

FUNCTIONALIZATION OF POROUS INORGANIC MATERIALS AND THEIR APPLICATIONS IN CATALYSIS



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*DEDICATED
TO MY BELOVED
PARENTS, WIFE and SONS*



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DECLARATION CERTIFICATE

This is to certify that the dissertation entitled “FUNCTIONALIZATION OF POROUS INORGANIC MATERIALS AND THEIR APPLICATIONS IN CATALYSIS” to Department of Chemistry, University of Rajshahi, is a record of bonafide thesis work under our supervision in Polymer Colloids & Nanomaterials (PCN) research laboratory, Department of Chemistry, and is worthy for the partial fulfillment of the degree of Doctor of Philosophy (Ph.D.) in Chemistry of the University. The candidate has fulfilled all prescribed requirements and the thesis, which is based on the candidate’s own work, has not been submitted elsewhere.

We have gone through the final draft of the thesis and wholeheartedly recommend its submission for the degree of **Doctor of Philosophy** in Chemistry.

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DECLARATION

I, hereby, declare that the thesis entitled '**FUNCTIONALIZATION OF POROUS INORGANIC MATERIALS AND THEIR APPLICATIONS IN CATALYSIS**' is a genuine record of research work carried out by me under the guidance and supervision of Professor **Dr. Hasan Ahmad** and co-supervisors Professor **Dr. Md. Mahbubor Rahman**, Department of Chemistry, University of Rajshahi, Rajshahi-6205. The thesis contains no materials which have been accepted for the award of any other degree or diploma elsewhere, and to the best of my knowledge, the thesis contains no material previously published or written by another person, except where due reference is made in the text.

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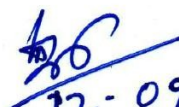
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I wish him every success in life.


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ABSTRACT

This work aims at preparing highly efficient robust monometallic as well as bimetallic supported transition metal based nanocatalysts. The unsupported nanocatalysts derived from metal and/ metal oxide tend to aggregate in the native state, prone to oxidation and thereby affect the stability and reusability following drastic fall in catalytic activity. It is also known that precious metals like Au, Pt, Pd and Ru possess comparatively better catalytic activity, but they are expensive, requiring expensive precursor salts. In order to achieve comparable catalytic performance like precious metal based nanocatalysts, three different nanocatalytic systems derived from transition metals (Cu, Cu-Ni and Cu-Ag) supported on magnetic or nonmagnetic mesoporous SiO₂ support are synthesized, characterized, evaluated and finally compared. For simplification and clear understanding this thesis has been divided into Seven chapters.

Chapter 1 is focused on general introduction covering importance of catalysis, catalysis types, classification of catalysts, monometallic and bimetallic catalysts and the role of metal nanoparticles (NPs) as catalysts in chemical reactions. This chapter also introduced the use of supporting materials like silica, metal oxide and graphite, the modification of supporting materials, and the mechanism of the formation of mesoporous silica. A brief objective of the present investigation is discussed towards the end of this chapter.

Chapter 2 described the preparation of stable suspension of copper nanoparticles (CuNPs). Mesoporous amine functionalized silica (SiO₂-NH₂) particles have been used as platform to house CuNPs for preventing their agglomeration. Mesoporous SiO₂-NH₂ particles are first prepared in one pot by diethyl amine, DEA catalyzed hydrolysis and condensation of tetraethyl orthosilicate, TEOS precursor in presence of hexamethylene diamine, HMDA and cetyltrimethylammonium bromide, CTAB. In the second step, sequential adsorption and chemical reduction of Cu ions are carried out to obtain SiO₂-NH₂/Cu nanocatalyst. The morphology and structural composition of SiO₂-NH₂/Cu nanocatalyst confirmed the fixation of evenly distributed ~ 28 nm sized Cu particles. The catalytic activity of nanocomposite particles for reductive degradation of Congo Red, CR and Eriochrome Black-T, EBT showed maximum degradation at pH values of 7 and 4, respectively. The degradation efficiency increased with the increase in catalyst dose and a

maximum degradation of $\sim 92\%$ is achieved for CR when 2 mg of catalyst nanocomposite particles is used. Comparatively, the degradation percent for EBT is low ($\sim 83\%$). Degradation kinetics of CR preferably followed a pseudo-first-order rate model, but for EBT degradation, hardly any particular kinetic rate model could be preferentially ascertained. The improved stability and increased surface-to-volume ratio of anchored CuNPs enhanced the degradation efficiency of catalyst nanocomposite particles.

In **Chapter 3**, preparation and application of $\text{SiO}_2\text{-NH}_2$ supported bimetallic Cu-Ni nanocatalyst are discussed. Cu-Ni nanoparticles (NPs) are doped on the $\text{SiO}_2\text{-NH}_2$ support via in situ simultaneous reduction of Cu and Ni ions. The X-ray diffraction, XRD pattern revealed the face-centered-cubic (fcc) crystalline alloy structure of Cu-Ni NPs in the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. X-ray photoelectron spectroscopy, XPS analyses showed that anchored Cu-Ni NPs contained Cu^0 and Cu^{2+} species, while Ni is present at its bivalent state (Ni^{2+}). In comparison to the unsupported Cu-Ni bimetal NPs, the supported $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst showed superior catalytic activity in chemical reduction of 4-nitrophenol, 4-NP to 4-aminophenol, 4-AP giving 98.5% conversion at pH 6 within 15 min. The kinetics preferably followed the pseudo-first-order rate model. The $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is recoverable magnetically from the reaction media and can be recycled up to six cycles without much loss in catalytic activity.

Chapter 4 is dealing with the preparation of magnetically recyclable supported Cu-Ni nanocatalyst to see any improvement in catalytic property for anchored bimetallic Cu-Ni alloy NPs (NPs). For this, inclusion of iron oxide (Fe_3O_4) in $\text{SiO}_2\text{-NH}_2$ support is attempted. The $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ support is first prepared by one-step solvothermal route. Secondly, bimetallic Cu-Ni alloy NPs are generated on the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ support via in-situ simultaneous sorption and reduction of Cu and Ni ions. The resulting product, named as $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst, contained face-centered-cubic (fcc) bimetallic Cu-Ni alloy with average crystallite size of 4.76 nm and possessed strong paramagnetic character (27.76 emu g^{-1}). The $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst showed faster reduction kinetics for the conversion of 4-NP to 4-AP compared to both unsupported Cu-Ni and supported $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalysts. The $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is recoverable magnetically and reused up to 6th cycle without any drop in activity, producing 100% conversion at pH 6. The reduction reaction preferably followed the pseudo-first-order kinetic rate model. Overall, the catalytic

activity and recycle stability of bimetallic Cu-Ni nanocatalyst enhanced dramatically following the use of magnetic $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support. Additionally, the prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst possessed good application potential as antibacterial agent due to the presence of Cu-Ni.

In **Chapter 5**, core-shell type magnetic functional $\text{SiO}_2\text{/Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support is used to anchor bimetallic Cu-Ag alloy NPs using glucose as a green reducing agent. $\text{SiO}_2\text{/Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support is prepared in one-pot via simultaneous co-precipitation of iron salts and alkaline hydrolysis-condensation reaction of TEOS in presence of SiO_2 sphere. HMDA and CTAB are used as functional agent and structure directing agent, respectively. Finally, Cu-Ag NPs are formed on the functional nanocomposite support via in-situ green reduction protocol to obtain $\text{SiO}_2\text{/Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ag}$ nanocatalyst. A comparative study of catalytic reduction of 4-NP to 4-AP showed that calcined $\text{SiO}_2\text{/Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ag}$ nanocatalyst possessed higher reduction kinetics compared to corresponding non-calcined nanocatalyst. Similar enhancement in catalytic property for unsupported bimetallic Cu-Ag NPs is noticed after calcination. The incorporation of magnetic Fe_3O_4 in the $\text{SiO}_2\text{/SiO}_2\text{-NH}_2$ support material also considerably enhanced the catalytic property of the nanocatalyst. The reduction reaction favorably followed pseudo-first-order kinetic rate model and the rate constants of non-calcined and calcined $\text{SiO}_2\text{/Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ag}$ nanocatalysts are 0.0517 and 0.0998 min^{-1} , respectively. The magnetically separable non-calcined $\text{SiO}_2\text{/Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ag}$ nanocatalyst is recyclable up to five cycles with fairly acceptable conversion.

Chapter 6 provides a general comparison among various supported and unsupported prepared bimetallic and monometallic nanocatalysts. The role of different support materials on catalysis are also taken into account for drawing an overall hypothesis. The reduction rate of 4-NP to 4-AP, recycle stability as well as recoverability have been used as the basis for such comparison. It is evident that $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support enhanced the recycle stability and long-term durability over the other support ($\text{SiO}_2\text{-NH}_2\text{/Cu-Ni}$) due to the inclusion of magnetic (Fe_3O_4) particles. Comparative study also shows that bimetallic Cu-Ni NPs supported on $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite possessed better catalytic activity.

Chapter 7 gives a short conclusion, and proposed a hypothesis model. Overall, it is found that incorporation of magnetic Fe_3O_4 in mesoporous amine functional SiO_2 support improved the catalytic activity and stability of anchored metal nanocatalyst. Amine functionality in SiO_2 support also played a positive role in enhancing the overall catalytic performance of the anchored NPs. However, for generalizing this hypothesis, a study of few other catalyst systems is necessary.

ABBREVIATIONS

Abbreviations	Details
NPs	Nanoparticles
IUPAC	International union of pure and applied chemistry
MCM	Mobil Composition of Matter
SBA	Santa Barbara Amorphous
MRI	Magnetic resonance imaging
CTAB	Cetyltrimethylammonium bromide
TEOS	Tetraethyl orthosilicate
DEA	Diethyl amine
HMDA	Hexamethylene diamine
APTES	3-Aminopropyltriethoxysilane
EG	Ethylene glycol
EtOAc	Ethylacetate
TLC	Thin layer chromatography
CR	Congo red
EBT	Eriochrome black-T
4-NP	4-Nitrophenol
4-AP	4-Aminophenol
CV	Coefficient of variation
mg	Milligram
fcc	Face-centered-cubic
MB	Methylene blue
RhB	Rhodamine B
MO	Methyl orange
SNM	Silica nanofibrous membranes
CPM	Carbon porous materials
DWCNTs	Double-walled carbon nanotubes
CAF	Cellulose acetate filter paper
SCJC	Sub-micrometer crystalline jute cellulose
QPOSS	Quaternized polyhedral oligomeric silsesquioxane
g-C ₃ N ₄	Graphitic carbon nitride

usGO	Ultrasmall graphene oxide
PDC	Plastic-derived carbon
SMt	Spherical montmorillonite
MMO	Mg–Al mixed metal oxide
ZOI	Zone of inhibition
Cal.	Calcination
Non-cal.	Non-calcination
TON	Turn over number
TOF	Turn over frequency
UV-Vis	UV-Visible Spectroscopy
FTIR	Fourier Transform Infra-Red Spectroscopy
VSM	Vibrational Sample Magnetometer
XRD	X-Ray Powder Diffraction
XPS	X-ray Photoelectron Spectroscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
EDS	Energy Dispersive X-ray Spectroscopy
BET	Brunauer–Emmett–Teller
BJH	Barrett-Joyner-Halenda

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Chapter-1

General Introduction

1. Introduction

1.1. Catalysis

In our society, catalysis plays a prominent character in many manufacturing processes and significantly contributes to constructing a sustainable future. Catalysis is used to initiate chemical reactions and allows access to novel chemical reactivity. In 1836, a Swedish scientist J. J. Berzelius introduced the term ‘catalysis’ for the first time. The Greek word ‘catalysis’ originated from the prefix, ‘cata’ meaning down and the verb ‘lysis’ meaning to split or break [1]. A catalyst is a matter that enhances the reaction rate without being used up or formed in the process. A more precise definition of a catalyst and catalysis is given by IUPAC as ‘*A substance that speeds up the reaction without changing the reaction total standard Gibbs energy change; this method is known as catalysis*’ [2]. A catalyst reduces the activation energy of a reaction and this reduction is occurred by lowering the energy of the transition state of the rate-limiting step, or by changing the reaction mechanism (Fig. 1.1). The reaction kinetics is affected by the catalysis but thermodynamics is retained.

A catalyst is a good tool for the transformations of reactions. About 90% of the chemical production on the earth has occurred using catalysts. Catalysis-based research has a wide range in applied science including different branches of chemistry, especially organometallic chemistry and materials science. This method is also related to various features of environmental science like the degradation of toxic contaminants, catalytic converter in automobiles, etc. Nowadays catalytic science is considered a promising research background of chemistry and reaction engineering and thus, the new catalyst is required for newer transformation [3, 4]. Since the twentieth century, catalysts show great significance in occurring chemical reactions. Recently catalyst has been used vastly in every sphere of the industry to prepare various chemicals where the multi-step reaction has been completed with at least one catalytic step. In summary, catalysis is a significant parameter in the manufacture of chemicals and ingredients [4].

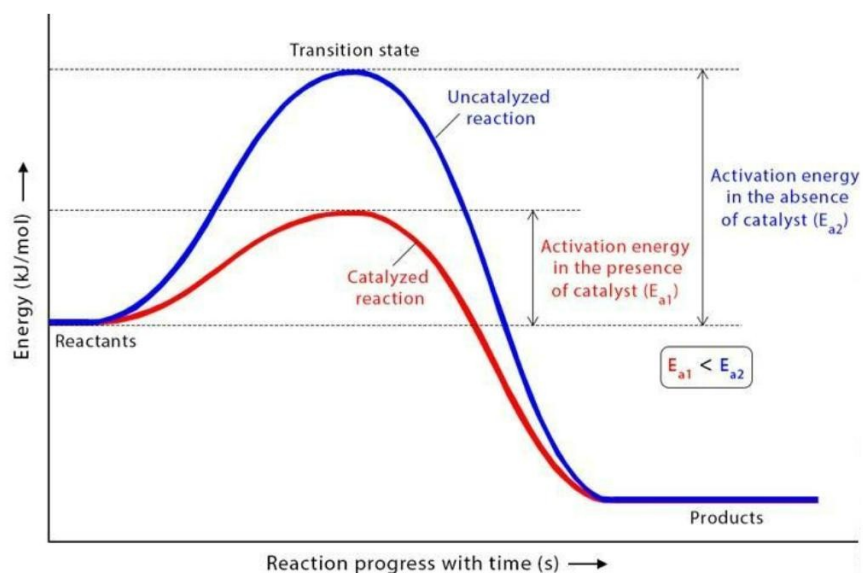


Fig. 1.1. A comparative study of the potential energy related to uncatalyzed and catalyzed reactions [5].

Bare metal nanoparticles (NPs) have been intensively used instead of bulk materials due to their vast specific surface area and huge free energy. Some demerits like aggregation, oxidation and deactivation appear in bare metal NPs; thus, supporting materials like SiO_2 , Al_2O_3 , graphite, and activated carbon are used to overcome these limitations. Because, supporting materials provide a large surface area, porosity, easy functionalization, high mechanical and chemical strength. Supporting materials also helped to reduce the aggregation or deactivation of metal NPs and thus increase stability. Metallic NPs are deposited on the supporting materials to form composite materials showing tremendous properties like both inorganic characters for the inorganic portion and organic characters for organic species. Moreover, the interaction between the catalyst and supporting materials also affects the catalytic path [6]. Therefore, supported metal catalysts have been successfully applied in different industrial sectors over the years.

1.2. Types of catalysis

There are three types of catalysis: (i) bio-catalysis; (ii) homogeneous catalysis; and (iii) heterogeneous catalysis. Normally, bio-catalysts like enzymes are found in nature. They are highly sensitive and selective, and thus the reaction takes place rapidly under mild conditions. Here homogeneous and heterogeneous catalysts are discussed in the subsequent sections.

1.2.1. Homogeneous catalysis

Homogeneous catalysis is defined as a catalytic system in which the catalyst, the reactant and the product are present in the same phase (solid, liquid, or gas), generally in a liquid phase. For example, the starch is decomposed into glucose in boiling water in the presence of H_2SO_4 . Another instance of homogeneous catalysts is organometallic catalysts [7]. The homogeneous catalyst shows greater activity due to the availability of all active sites of the catalyst to the reactant. It is also a highly selective catalyst. The drawbacks of homogeneous catalysts are separation difficulty, recovery, regeneration and reuse, corrosions, toxicity, expensive, large wastage, etc. which make it untenable for application in industrial sectors [7]. Even, some homogeneous catalytic processes are commercially inappropriate. Though, homogeneous catalysis has been used in many industrial applications.

They have several advantages over the heterogeneous catalyst:

- i. Catalyst has active sites due to the solubility in the same phase
- ii. In homogeneous catalysis, the reaction is conducted under gentle conditions
- iii. No diffusion problems in homogeneous catalysis
- iv. The reaction mechanism can be defined easily
- v. Catalysts show low sensitivity to impurities.

1.2.2. Heterogeneous catalysis

Heterogeneous catalysis is a catalytic system in which the substrate and the catalyst state are quite different. In heterogeneous catalysis, the catalysts are solid and the substrates in most cases are liquids or gases [8]. The reaction mechanisms of heterogeneous catalytic systems are known, depending on how the adsorption takes place. The total surface area of the catalyst is important for achieving maximum active



catalytic sites. As a result, researchers are making efforts for preparing smaller nano-sized particles to replace homogeneous catalysts with heterogeneous ones in organic synthesis. Nowadays, heterogeneous catalysts are achieving more importance in chemical reactions due to their supreme catalytic activity, good thermal stability, effectiveness and being economically beneficial.

In heterogeneous catalysis the product separation or the recovery of the catalyst from the reaction mixture becomes easy. Moreover, the versatile applications of heterogeneous catalysts led to the preparations of numerous inorganic chemicals, and compounds from petrochemicals, and very recently, innovative ‘environmentally friendly’ applications are noticed in fuel cells [9, 10] and biotechnology [11, 12].

The following steps generally occur in heterogeneous catalysis (Fig. 1.2).

- i. Diffusion of the reactants to the surface
- ii. Adsorption of the reactant molecules onto the surface
- iii. Surface reactions
- iv. Desorption of products.

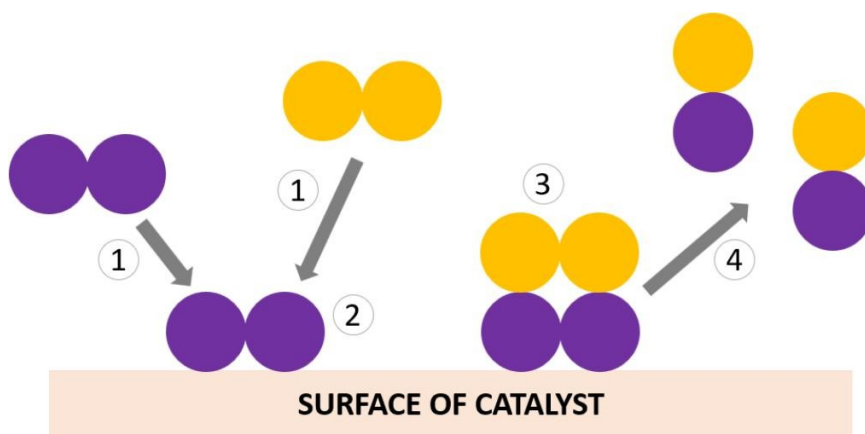


Fig. 1.2. Heterogeneous catalyzed reaction [98].

1.2.3. Advantages of heterogeneous catalyst

The effectiveness of a catalyst is dependent on various factors like surface area, porosity, acidity-basicity, as well as the crystalline or amorphous nature. Heterogeneous catalysis offers certain advantages and the following points play great role during heterogeneous catalysis.

Surface area

The reaction rate is increased by the increased surface area of the catalyst. That is, the number of collisions of reactants on the surface of the catalyst increases with increasing active sites for the reaction. A number of methods are available for increasing surface area but simply, it can be achieved by dispersing the catalyst over a high surface area material.

Easy work-up

In heterogeneous catalysis, the chemical reaction should be completed in a simple work-up. The product is to be isolated easily from the reaction mixture and catalyst by centrifugation or filtration. In addition, it should be possible to switch off reaction according to the requirements and an excess of catalyst must increase the reaction kinetics to drive the reaction towards completion. Any unwanted side reactions should be the minimum. The regeneration, reactivation and reuse of catalysts are preferable from the context of economic sustainability.

Environmental viability

In a heterogeneous catalytic system, the wastages or unwanted side products are minimum as the reaction generally proceeds at lower temperatures and pressure. Acid or base catalysts have fewer ecological problems than their soluble analogues. Therefore, it is very much favorable for the green chemistry protocol.

Increase local concentration on the surface

The reactant molecules adsorbed on the surface of the catalyst increased the possibility of the reactive encounter. Therefore, the reaction rate is increased and reaction kinetics becomes faster. Due to the columbic interaction, there is an increased

concentration (or activity) in the proximity of the surface in the case of the polyelectrolytic solid catalyst.

New or better selectivity

Heterogeneous catalysis is considered advantageous over the dissatisfactory performance of the soluble catalyst i.e., homogeneous catalysis. The heterogeneous catalysts show higher selectivity. Spectacular sensitivities can be obtained with the traditional, acid-treated, ion exchanges and columned variants of clays, similarly as zeolites. This catalyst gives the guest reactants extremely structured microreactors that favor the formation of a single product.

1.3. Metal NPs as heterogeneous catalyst

Metal NPs in the nanometer scale (1-100 nm) show great importance for their promising properties like large surface area to volume ratio, high chemical activity, selectivity and specificity relative to their bulk counterparts. Thus, they are very useful as catalysts. Metal NPs additionally possess different special characteristics in areas of chemical, electronic, optical, magnetic, thermal and mechanical properties owing to the high surface-to-volume ratio along with the size effects (quantum effects) [13-16]. Hence, researchers are focusing their attention in nanomaterials because of their vast application potential in conductors, electronics, sensors, photovoltaic devices, drug delivery, catalysis, fuel cells, light-emitting diodes, industrial lithography, quantum dots, quantum wires, quantum devices, optical and biological devices [17-32] etc.

1.3.1. Synthesis of Metal NPs

The synthesis of the NPs is well discussed in the literature. The preparation of NPs is done by two generic approaches, one is ‘top down’ and another is ‘bottom-up’ processes (Fig. 1.3). In the top-down approach, bulk material converts into small fragments with multiple layers by applying the energy and then, NPs are formed by the monolayers. The main feature of this process is the large production of synthesized material from the bulk material precursor with irregular shape and size. Some of the popular methods of top-down processes are mechanical methods, melt mixing, methods based on evaporation and lithographic methods. Though top-down approach is used largely for generating nanomaterials, it is expensive and their available utility has been



limited to certain industries [33]. Introducing imperfections on the surface of metal NPs produced by the top-down approach is a great problem. Because the surface structure of NPs dominates the surface chemistry and other physical features [34].

In bottom-up synthesis, the small entities of metallic particles are joined each other to generate NPs [35]. The morphology and properties of materials with certain ‘chemical’ versatility are controlled by the liquid-solid transformations. A bottom-up process is an approach that produces makeup of a material from the bottom, i.e., atom-by-atom, molecule-by-molecule or cluster-by-cluster. A good example of bottom-up approach is the colloidal dispersion in the synthesis of NPs. Other examples are techniques of nanolithography and nanomanipulation, which have been extensively used in the fabrication of structural composite nanomaterials. Though, NPs can be synthesized either by top-down or bottom-up approach; but bottom-up approach is mostly favorable in optoelectronics and catalysis because it provides more benefits over top-down approach. However, both methods exhibit promising roles in the electronics industry and nanotechnology as well.



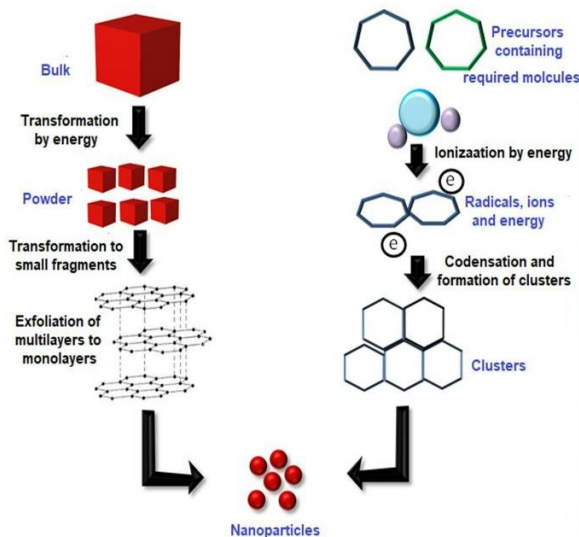


Fig. 1.3. Top-down and bottom-up approaches for the synthesis of NPs [36].

In our investigation, a bottom-up approach has been used for the preparation of NPs. So, a brief discussion is given on how this process is carried out by different methods.

Bottom-up Approach

In this approach, nanosized materials are formed by the combination of materials at the atom or molecular level. The atoms or groups of atoms are involved in NPs formation in this method. In bottom-up approach, various methods are involved which allow good control of scale dimension, even from an atomic or molecular level. They are

simple and low-cost as compared to top-down approaches. The most prominent methods of the bottom-up approach are shortly introduced here.

Wet chemical methods

This method involves the precipitation of chemical compounds in solution. Five major classifications in this method are available in the literature.

Colloidal methods

The different ions in solution are mixed well under controlled temperature and pressure and the insoluble precipitates are formed in solution.

Sol-gel processing

The chemical transformation of a liquid (the sol) into a gel state is first appeared in the sol-gel process and then subsequent post treatment and transition into solid oxide material occurred. The obtained products from this method are highly pure and uniform at nanoscale at low temperature.

Water-oil microemulsion method

This is a popular method for the preparation of NPs and the biocompatibility and biodegradability of prepared materials are the main advantages of this method.

Hydrothermal and solvothermal syntheses

The main role of solvothermal and hydrothermal approaches is played by the solvent and carried out under elevated pressure and temperature above or below the solvent critical point. As a result, the solubility of solid and rate of reaction between precursors are both increased.

Chemical precipitation route

The chemical precipitation method is very common for the preparation of NPs. In this method, huge number of small particles is produced and thus, nucleation is the main step during the process of precipitation. There are many parameters involved in this process like nucleation, growth, coarsening and agglomeration. Therefore, the reaction conditions are to be carefully controlled to obtain uniform-sized NPs. For this, the choice

of surfactants and their concentration, pH, temperature, solvent and precursor concentration is important to bring nucleation with just only one burst formation of nuclei during the whole precipitation reaction [37].

1.3.2. Monometallic nanocatalysts

Monometallic NPs consist of a unique metal species, which has shown extensive catalytic properties. Monometallic NPs are of different types depending on the metallic character like magnetic, mechanical, noble or transition metals and they can be generated by employing various processes.

Metal or metal oxide NPs have potential applications in nanocatalysis, nanomedicines, drug delivery, chemotherapeutic, photoelectronic devices and biosensor. Particularly in catalysis applications, noble metals (Au, Ag, Pt, Pd) are very much attractive due to their high catalysis power but recently, due to their high price, insufficiency, leaching and toxicity, researchers are searching for alternatives in transition metal-based catalysis [38, 39]. Therefore, transition metal-based catalysts (Cu, Ni, Fe, Co) are cultivated as alternative due to their secondary valency, availability, low cost, short reaction time and good yield. Since our investigation is focused on the preparation of transition metal based nanocatalyst, so, the following section briefly introduced their chemistry to understand the mechanism of catalysis.

Transition metals show great catalytic activity due to their distinctive electronic and structural properties. Due to partially filled d-orbitals and a very small energy difference between (n-1)d and ns orbitals, they have variable oxidation states. Thus, transition metals to readily accept or donate electrons during chemical reactions. The d-orbitals of the transition metal act as electron sinks, allowing the catalyst to adsorb reactant molecules by accepting or donating electrons [40]. This adsorption process weakens the bonds within the reactant molecules and lowers the activation energy required for the reaction to occur. Transition metals can easily undergo changes in their oxidation states, which is critical for catalytic reactions involving electron transfer. This electron transfer enables redox reactions, where oxidation and reduction occur simultaneously on the catalyst surface. Transition metal catalysts often interact with ligands, which are molecules or ions that bind to the metal center [41]. These ligands can

modify the electronic properties of the metal catalyst and influence its reactivity. Ligands can alter the charge distribution, electron density, and coordination geometry of the transition metal, thereby affecting the adsorption and activation of reactant molecules. Overall, the electronic properties of transition metal particles as catalysts stem from their partially filled d-orbitals, surface reactivity, ability to adsorb and activate reactant molecules, undergo redox reactions, and interact with ligands. These characteristics allow transition metal catalysts to facilitate a wide range of chemical transformations efficiently.

1.3.3. Bimetallic nanocatalysts

In recent years, researchers are showing interest in bimetallic NPs owing to their developed physicochemical properties. Bimetallic NPs are composed of two different types of metals that are superior to the monometallic assemblies due to the modification of surface geometry, synergistic effect and electronic configuration. In a bimetallic system, the disadvantage of one metal is compensated by the presence of the other metal beside it and the total system exhibits the properties of both the metals in one system. Therefore, the bimetallic NPs show improved catalytic properties, specificity, selectivity, recyclability, durability, long-term stability and so on [42, 43]. Bimetallic catalysts are widely used for various catalytic applications and are found to possess comparable catalytic efficiency as the precious metals [44]. Fig. 1.4 demonstrates the bimetallic catalytic characters influenced by different factors.

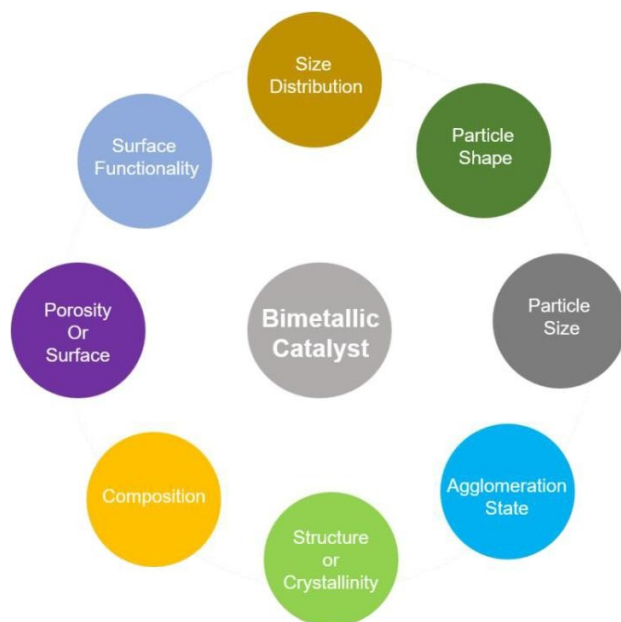


Fig. 1.4. Various aspects of bimetallic catalysts for diverse applications.

Bimetallic NPs have three types of morphology; cluster in cluster, core-shell and random alloy (Fig. 1.5) [45]. Particles are randomly spread throughout the random alloy NPs. Each metal is distributed among in clustered NPs. Core-shell NPs are made up of a core made of one metal species and an outer shell comprising a different metal [46].

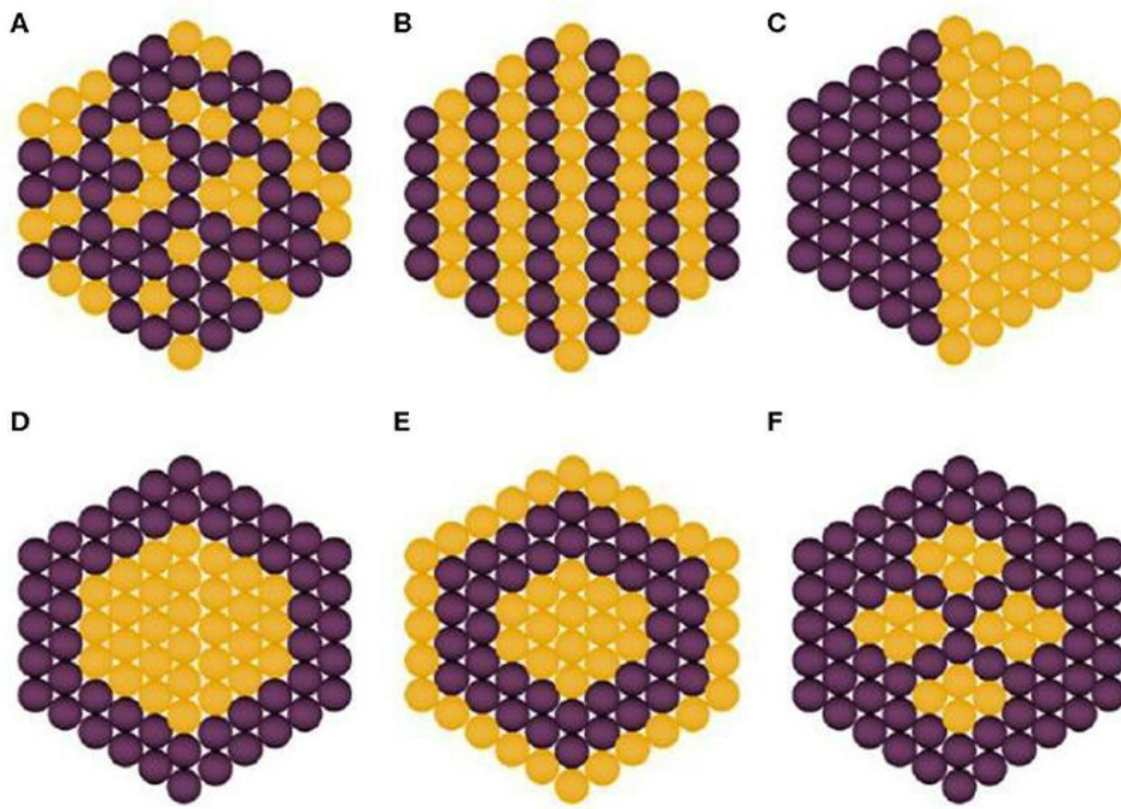


Fig. 1.5. Types of bimetallic NPs: (A) alloyed, (B) intermetallic, (C) subclusters, (D) core-shell, (E) multishell core-shell, and (F) multiple core materials coated by a single shell [45].

1.4. Importance of supported metal NPs in catalysis

Metal NPs in various applications, like catalysts, photonics, biosensor, medical devices, and drug delivery vehicles, are showing limitations due to agglomeration, oxidation, instability, separation, recovery difficulties, and short lifetime. One way to overcome these limitations is anchoring metal NPs onto solid supports. The supported metal NPs show overriding benefits over unsupported metal NPs due to increased active sites, mechanical strength to the catalyst, good accessibility, selectivity, and stability for longer versions. Different types of supporting materials are in use now that include carbon, graphene, SiO_2 and metal oxides [44]. In fact, the activity of supported metal nanocatalysts basically depends on metal loading, the distribution of metal NPs on the support, and their sizes. The supporting materials add the following advantages to nanocatalysts.

- i. Supporting materials act as a spacer between the metals and the supports to form metal-support interactions
- ii. Supporting materials make the active component highly active and highly stable
- iii. The embedded active component on the support exposes a big effective surface area
- iv. The support prevents the sintering of active components
- v. The supports provide better catalytic activity and selectivity than bare catalysts through a new complex formation between the interaction of support and metal NPs
- vi. The physical and chemical properties of metals are affected by the supporting materials to generate the special characteristics of supported metal NPs
- vii. Supports functioned as a stabilizer and prevented the agglomeration of immobilized metal NPs.

Among various support materials mentioned above, here in this thesis, functional mesoporous SiO_2 has been used for anchoring metal NPs. So, in the following sections the properties, composition, structure and suitability of SiO_2 as a support material are introduced briefly.

1.5. Mesoporous SiO_2 particles

SiO_2 has some special characteristics like nontoxicity, large surface area, simple surface modification, chemical inertness, chemical and thermal stability, and low cost. It has a large surface area of about 700-800 m^2/g and it consists of an internal network of interconnecting channels and pores. IUPAC prescribed that porous materials are classified into three categories based on their pore dimensions [47].

- i. Microporous materials: 0.2-2 nm.
- ii. Mesoporous materials: 2-50 nm.
- iii. Macroporous materials: > 50 nm.

The unique property of a high surface area to volume ratio results in extensive applications like chromatographic techniques, catalysis, drug delivery, diagnostics, and sensors, etc. The mesoporous SiO_2 , named as M41S phase, was first introduced by the

Mobil Oil Company in 1992. The pore diameter of the M41S family is around 2 to 10 nm. Some of the most known and studied components are MCM-41 (MCM-41 stands for Mobil Composition of Matter no. 41) (with a regular hexagonal mesopore arrangement, space group $p6mm$), MCM-48 (with a cubic arrangement of the mesopore, space group $Ia3d$) and MCM-50 (with a lamellar structure, space group $p2$) as illustrated in Fig. 1.6 [48]. In 1998 Stucky *et al.* developed another material, SBA-15 (SBA stands for Santa Barbara Amorphous) which is 2D-hexagonally ordered mesoporous silicas with a uniform pore size as high as 10 nm or more by using triblock-co-polymer, poly (ethylene oxide)–poly (propylene oxide)–poly (ethylene oxide) (PEO–PPO–PEO) as a structure directing agents under acidic pH conditions [49].

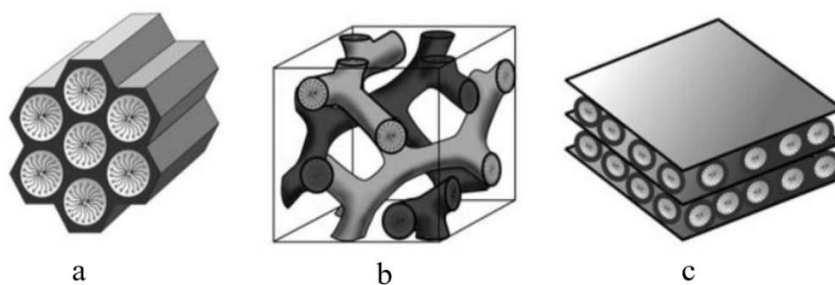


Fig. 1.6. Structure of M41S materials: (a) MCM-41 (2D hexagonal), (b) MCM-48 (cubic), and (c) MCM-50 (lamellar) [50].

1.5.1. Synthesis of mesoporous SiO_2 materials

A typical sol-gel process under hydrothermal conditions synthesizes mesoporous SiO_2 Materials. The SiO_2 precursors (e.g., sodium silicate, tetraethyl orthosilicate, TEOS and tetramethyl orthosilicate, TMOS) are hydrolyzed and converted into sol of silicate oligomers after the completion of continuous condensation reactions in the presence of structure directing agent called porogen. The oligomers interact with surfactant micelles followed by cooperative assembly and agglomeration. As a result, the precipitates are transferred into a gel [51]. Then the solution is exposed to hydrothermal treatment at an elevated temperature for a few hours. Lastly, after the purification step the solvent extraction method is employed for removing cetyl trimethylammonium bromide, CTAB

and the resultant product is mesoporous SiO_2 . Fig. 1.7 presents the scheme of the formation of mesoporous SiO_2 .

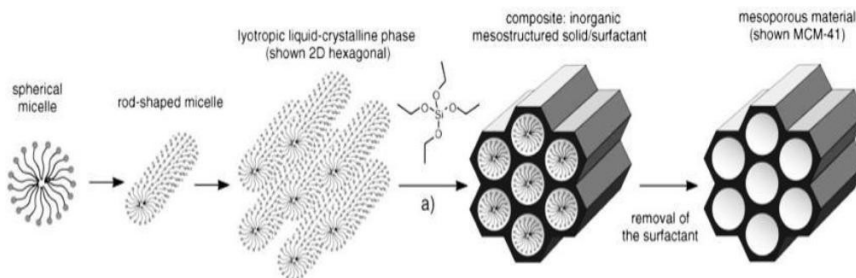


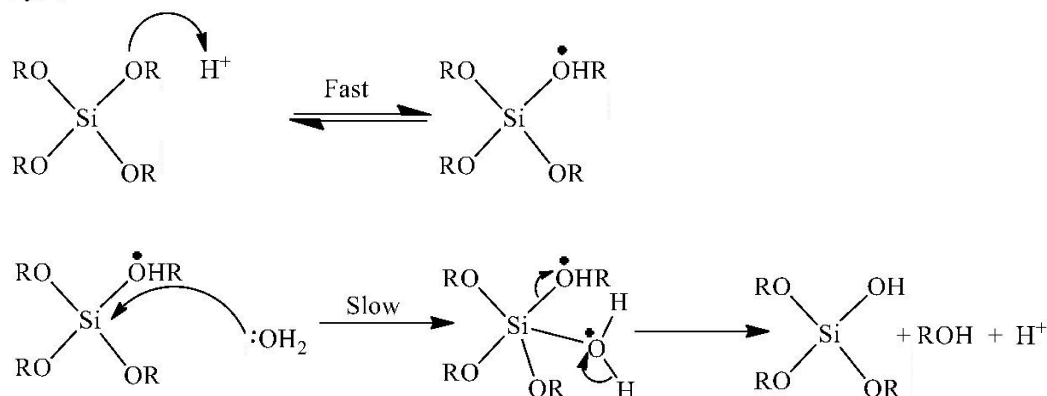
Fig. 1.7. Schematic representation of the formation of ordered mesoporous silica materials [52].

1.5.2. Mechanism for the formation of mesoporous SiO_2 materials

The mechanism of the formation of mesoporous SiO_2 is proposed by several models to provide a rational basis for all the synthetic routes. There are three main phases in all mechanisms: (i) molecular level interaction of the organic molecule (CTAB) with the inorganic SiO_2 precursor to form the composite molecule and continuation of the SiO_2 polymerization; (ii) the micellar structure and the long-range order developed at the mesoscopic scale; and finally (iii) the morphology of the final material is related to the macroscale. Initially, the silicate ions are adsorbed on the micellar interface and thus, the ordered phase is formed. Fig. 1.8 presents the probable reaction mechanism of the formation of mesoporous SiO_2 particles in presence of acid or base.

Acid catalyzed reaction

Hydrolysis



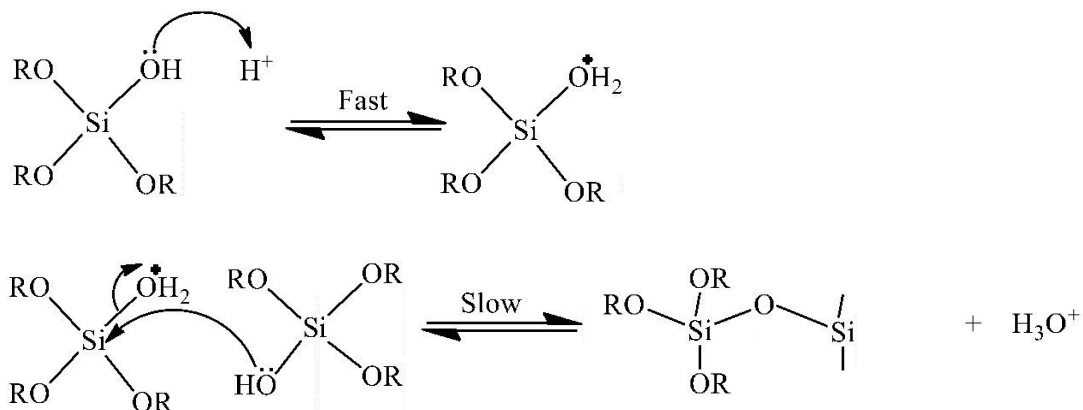
Condensation**Base catalyzed reaction**

Fig. 1.8. The probable reaction mechanism of the formation of mesoporous SiO_2 particles.

The liquid-crystal template (LCT) mechanism is first proposed by Mobil's scientists for the formation of mesoporous SiO_2 , known as the M41S phase, and liquid

crystals of surfactants act as a template for the fabrication of mesostructure [52]. Two main pathways, that is, cooperative self-assembly and the “true” liquid-crystal templating process seem to be effective in the synthesis of ordered silicate mesostructures, as shown in Fig. 1.9.

Fig. 1.9. Liquid-crystal templating (LCT) mechanism for self-assembly [50].

In the first pathway (1), the surfactants are self-aggregated to form micelles and then, micelles accumulated to form rod micelles. The hexagonal liquid crystals are formed with the assemblies of rod micelles. Silicate anions derived from SiO_2 precursor interact with the head of a cationic surfactant followed by hydrolysis and then, condensation of the silicate species initiates the fabrication of SiO_2 materials. Mesoporous SiO_2 is produced after the removal of the organic surfactant.

According to the second pathway (2), silicate species interact with randomly arranged rod-like micelles through coulombic interactions in the reaction mixture to form roughly two or three monolayers of silicate around the micelles' external surfaces. Together with silicate condensation, these randomly ordered composite species spontaneously pack into a highly ordered mesoporous phase with an energetically advantageous hexagonal layout [53, 54]. Since during the synthesis, the surfactant is used less amount than critical micelle concentration (CMC) for the liquid crystal (LC) phase, therefore it was determined that pathway 2 (Fig. 1.9) may be used to create MCM-41 phase rather than pathway 1.

1.5.3. Surface modification of mesoporous SiO₂ materials

Mesoporous SiO₂ has an enormous negative charge due to huge silanol groups and thus, the surface of mesoporous SiO₂ can be modified easily by the various organic functional moieties. The incorporation of organic functional groups on the surface of mesoporous SiO₂ could change their physical and chemical characteristics (hydrophilicity, hydrophobicity, acidity, basicity and coordinating ability between host and guest molecules). Various organic functional groups such as amines [55, 56], thiols [57], carboxylic acid [58], sulfonic acid [59] and vinyl [60] have been used for the surface modification of mesoporous SiO₂. Therefore, functionalized mesoporous materials are prepared by two different synthetic approaches. These are post-synthesis modification (also known as grafting method) and one pot synthesis or co-condensation method.

Grafting method (post-synthetic functionalization of SiO₂)

The grafting method is a method in which pre-manufactured mesoporous SiO₂ has been modified by organic groups. The silanol groups in mesoporous SiO₂ act as a target point for the grafting reaction. The surface of mesoporous materials is modified by various organosilane coupling agents known as silylation. Usually, it is carried out by condensation of organosilanes of the type (R'O)₃SiR, or chlorosilanes ClSiR₃ or silazanes HN(SiR₃)₃ with the free silanol groups of the silica surfaces (Fig. 1.10) [61]. In this methodology, the organic residue R in (R'O)₃SiR is covalently bonded with the silanol groups of mesoporous SiO₂. The dried host materials should be used for the incorporation of a functional agent in the post-synthesis method. Because the precursors are condensed repeatedly in the presence of water [62, 63].

Fig. 1.10. Functionalization of mesoporous materials by grafting method [63].

The particle morphology and pore structure after incorporation of organic reactive groups are retained under the synthesis procedure and conditions in this method. The main drawback of this method is that the functional groups are distributed non-uniformly over the entire mesoporous materials. However, it should be noted that silanol groups found on the outer surface and at the mesopores' apertures are more kinetically accessible than those found on the inner pore walls [64, 65]. As a result, the organic functional groups are concentrated near the mesopore entrance or on the outer surface. Thus, the organic groups are not uniformly distributed throughout the whole substance. This method is used for the selective functionalization of the outer surface of silica. The pores, however, become fully blocked when grafting with very bulky species.

Co-condensation method (one-pot synthesis)

There is a concurrence of the SiO_2 precursors (tetraalkoxysilanes $(\text{RO})_4\text{Si}$ such as TEOS, TMOS) and organosilane coupling agent (3-aminopropyltrimethoxysilane, APTMS, 3-aminopropyltriethoxysilane, APTES, 3-methacryloxypropyltrimethoxysilane,

MPS) or functional agent (amino acid, hexamethylenediamine, HMDA) in the presence of surfactant and auxiliary chemicals in one pot known as co-condensation method (one pot synthesis). Thus, organic functionalized mesoporous SiO_2 materials are produced directly in one step and during the formation of mesostructured, organic functional moieties are bonded covalently with the silanol groups of SiO_2 (Fig. 1.11) [62, 63]. In this method, prepared materials are more uniform than the materials prepared by grafting method. However, the disadvantage of this method is that the final material can be disordered mesostructured due to increasing concentration of $(\text{R}'\text{O})_3\text{SiR}$. Moreover, the pore volume and specific surface area are reduced with increased organic functional groups. At last, during the removal of surfactant, attention should be given for preserving the organic functionality. Solvent extraction is a common route for the elimination of surfactants. There is an opportunity to interfere with the periodicity of mesoporous structure in the presence of organosilane in the co-condensation method. The functionalizing agent is to be added to the reaction mixture before the hydrothermal treatment to stay away from the annihilation of the mesoporous structure. This is known as semi-direct synthesis which provides good periodicity to the structure of the functionalized mesoporous SiO_2 and probably an effective exposure of the organic functionality [66, 67].

Fig. 1.11. Functionalization of mesoporous materials by co-condensation method [63].

1.6. Methodologies for the preparation of supported metal nanocatalysts

Traditional methods typically used for the preparation of supported metal nanocatalysts are impregnation and precipitation techniques, but the chemical reduction method is superior because it is possible to fine-tune catalyst characteristics. The mechanism of different preparation methods is described below.

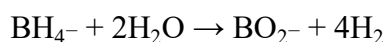
1.6.1. Chemical reduction method

Metal is obtained from the corresponding metallic ions by the reduction process using various reducing agents known as the chemical reduction method. For the preparation of various metallic particles, chemical precursor will consist of metal salt, reducing agent, surfactant with acidic/basic/neutral solvent. Thus, the process is accomplished at room temperature and carried out in an environmentally benign aqueous solution. The several reducing agents are NaBH_4 , $\text{H}_2\text{N-NH}_2$, ascorbic acid, glucose, citrate, alcohol, etc. involved in reducing metallic ions to metals like Cu, Co, Ni, Ag, Au,

and their alloy [68]. Therefore, there are several reduction methods like borohydride reduction, citrate reduction, and alcohol reduction as reducing agents which are applied for reducing metal salt solution.

Borohydride reduction

In this reduction reaction, hydrogen gas produced by the hydrolysis of borohydride reduces the metal precursor. The borohydride reduction process has been used to produce NPs of several metals. The drawbacks of this approach are the incorporation of boron in the final product and the irreproducibility of NPs in the aqueous medium [69].



Citrate reduction

In this procedure, metallic particles are formed by transferring acidified metal precursors to a boiled citrate solution [70]. The particle size can be controlled by varying the molar ratio of metal precursor and citrate.

Alcohol reduction

It has long been recognized in organic chemistry that tiny metal particles can catalyze the conversion of alcohols to aldehydes or acids. These reactions' fine metal catalysts undergo reduction during the process and are deposited as spongy precipitates [71].

Hydrazine reduction

Hydrazine adsorbs the water from the environment and thus, OH^- ions liberate from hydrazine hydrate to generate highly reactive hydrazinium ions (N_2H_5^+). Thus, the pH of the reaction mixture can be efficiently improved by adding huge reducing agents. Hydrazinium ions (N_2H_5^+) dissociate easily to produce nitrogen gas (N_2) during the course of the reaction and thus, the environment of the reaction converts inert atm. [72]. In this reduction method, N_2 gas did not pass through the reaction.

1.6.2. Solvothermal method

Solvothermal synthesis is the name given to chemical reactions that take place in a closed vessel or autoclave with precursors, organic solvents, a temperature that is higher than the solvent boiling point, and above ambient pressure. Various reaction parameters like reactant pH, temperature, concentration, and reaction duration are tightly controlled and various non-aqueous solvents, such as methanol, ethylene glycol, 1,4-butanediol, and amine are used in this method [75 - 77]. The operating temperature and pressure ranges for solvothermal procedures are 100 to 1000 °C and 1 to 10000 bars [73]. Due to the high pressure and temperature, reactants interact more readily, resulting in single-crystalline products with good shape. With no impurities, this environmentally benign method produces very fine grain-size particles. Due to its controllable, affordable, reproducible deposition strategy and improved nucleation, it is regarded as an appealing technology for the creation of NPs with highly monodisperse and even shaped particles [74].

1.6.3. Co-precipitation method

The co-precipitation method has been extensively used for the production of mixed-oxide catalysts. This technique typically entails precipitating the analyte in an aqueous medium from the chemical precursor of the required metal salts. Herein, inorganic salts like chlorides, sulfates, nitrates, etc. are dissolved into the water or other proper solvents to precipitate the oxo-hydroxide form by the addition of an alkaline solution such as NaOH, Na₂CO₃, K₂CO₃ or NH₃ solution. Generally, a vigorous interaction is found between the metal and the supporting medium in this approach. The metal precursor must be added to an aqueous suspension of the support medium before the hydroxide is precipitated out by raising the pH in a similar but alternative process known as deposition-precipitation [78]. The support particles' surfaces operate as nucleating agents to strengthen the link between the active precursor and the support. Then, the obtained hydroxide materials are under washing, filtration, drying and calcination process and reduced to produce the desired product [79]. Fig. 1.12 presents a schematic diagram of the co-precipitation method.

Fig. 1.12. Schematic diagram of the co-precipitation method for the formation of metal-supported NPs.

1.7. The objective of the current research

In the present investigation, attempt is made to prepare a robust recyclable nanocatalyst. It is already mentioned that transition metal NPs are useful as catalyst in different chemical syntheses [80, 81]. But their utility in the native state suffered drawback due to limited stability that led to rapid agglomeration, oxidation, poisoning and deactivation during recycle. The catalytic power of transition metal based nanocatalysts is also relatively poor compared to noble metals like Pt, Au, Pd and Ru. [82]. So, large scale industrial use of bare transition metal derived NPs is remained a challenge despite their low cost and easy availability. One way to overcome these drawbacks is fixation / immobilization of transition metal NPs onto stable solid supports. Various solid supports such as cellulose [83 - 85], graphene [86, 87], zeolite [88], activated carbon [89, 90] and SiO₂ [91- 93] have popularly been applied to stabilize metal NPs. Among these, SiO₂ as support material offer certain advantages over others as they are easy to functionalize, possess high thermal and chemical stability as well as they are low cost and available with a wide variety of fabrication technologies. Despite these recognizable advantages of SiO₂ as support material, little efforts have been made to use them. Only, some researches are available on the encapsulation of Zn, Cu, Fe, Co and Ti based metal oxide within mesoporous SiO₂ layer [93 - 97]. In these above reports, the researchers mainly used a two-step process: first surfactant stabilized metal NPs are

prepared and then encapsulation is carried out. In such cases it is predictably difficult to prepare metal NPs with homogeneous distribution and uniform morphology.

Here, organo-functional mesoporous SiO₂ particles have been used as support material for anchoring various monometallic and bimetallic metal NPs via electrostatic interaction and coordination. The support materials are prepared mostly by a one-step process and it is believed that fixation via functional groups would improve the uniformity and homogeneous distribution of metal NPs and hence the catalytic activity as well as recycle stability. This thesis described the preparation of four different supported nanocatalysts, characterizations and subsequent application performance in catalytic transformation reactions in four different chapters (**Chapter 2 to 5**). Each chapter is followed by a brief introduction detailing the background of investigation, current literature review, originality and objective.

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Chapter-2

**Mesoporous Amine Functionalized SiO₂
Supported Cu Nanocatalyst and a Kinetic-
mechanistic Degradation Study of Azo Dyes**

2.1. Introduction

In the last two decades, metal nanoparticles (NPs), particularly transition metals have generated great interest as heterogeneous catalysts in many organic transformations [1, 2], because of their unparalleled physicochemical properties, which are different from bulk materials [3]. The transition metals that have been studied most for their catalytic properties are Ti, Cr, Mn, Fe, Ni, Cu, Ru, Pd and Ag. Among these metals, a considerable volume of research is available on the preparation of metallic Cu and Cu based NPs (Cu_2O , CuO and their blends) due to their significant catalytic as well as antimicrobial, optical, low band-gap energy and electrical conducting properties [4–8]. Additionally, Cu is considered as economic alternative to many of precious metals like Au, Pt, Pd and Ru [9]. Various methods have so far been employed to synthesize CuNPs, which include chemical reduction [10, 11], sonochemical reduction [12], laser ablation [13], thermal decomposition [14], polyol method [15], and microemulsion technique [16]. Despite the wide variation in the aforementioned methods, the obtained CuNPs are generally poor in colloidal stability due to stronger surface energy, larger surface area and inter particle dipolar force compared to bulk counterparts and hence, compromising the potential for long time application and preservation. Another limitation is unstable nature of metallic Cu in air as it readily oxidizes. So, the large-scale production of CuNPs is becoming difficult due to easy aggregation, deactivation and poisoning [17].

The use of inert and effective solid support either to anchor or encapsulate metal or metal oxide NPs is now gaining popularity, so that NPs can retain their morphology and nano-size distribution to maintain the activity and facilitate reuse. Various solid supports such as graphene [18, 19], zeolite [20], cellulose [21–23], activated coke/carbon [24, 25], Sepiolite [26], bentonite [27] and SiO_2 [7, 28, 29] have popularly been used to stabilize metal or metal oxide NPs. Among these, SiO_2 support provides certain advantages like chemical inertness, mechanical and thermal stability, low cytotoxicity, easy functionalization and low cost [30, 31]. The numerous hydroxyl groups on the SiO_2 surface also make them highly stable in aqueous dispersion. So far, researchers have mostly used mesoporous SiO_2 layer to encapsulate Cu, Zn, Fe, Co and Ti based oxide materials [7, 29, 32–34] to facilitate easy passage of the reactant substrate through the porous channel and allow catalytic reaction. Few reports are also available on the

encapsulation of metallic Cu based nanohybrids (like Cu-Ni and graphene-Cu) by mesoporous SiO₂ coating [35–37]. In case of encapsulation, stabilizing agent is essential for preparing stable NPs and it is also difficult to control the composition and size distribution of individual metal NPs. However, such stabilizing agent is not essential during the surface mineralization of SiO₂ with metal NPs. The surface functionalization of mesoporous SiO₂ particles with organic functionality can offer additional advantages for its use as adsorption materials. For example, organo-functionalized mesoporous SiO₂ particles enhanced the catalytic activity and stability of immobilized enzymes [38, 39]. A wide range of organic functionality on mesoporous SiO₂ particles also had improved the adsorption of heavy and noble metal ions [40–42]. Therefore, it is expected that the anchoring or fixation of CuNPs on the functional mesoporous SiO₂ particles would effectively reduce aggregation and leaching during application in heterogeneous catalysis. Overall, only few reports are available on the anchoring of CuNPs to the SiO₂ surface. In an early investigation, Kim et al. deposited antibacterial CuNPs on the surface of SiO₂ NPs via deprotonation of hydroxy groups followed by electrophilic attack and subsequent growth in presence of ammonia solution [43]. Ghos et al. loaded different amounts of CuNPs on mesoporous SiO₂, SBA-15, via in situ chemical reduction of precursor salt and studied the reduction of dyes [44]. The synthesis process was simple but the stability and recyclability of the catalyst could not be ascertained. Zhao and his group prepared mesoporous SiO₂ particles by solvothermal method and used them as support for Cu catalyst [45]. Ammonia evaporation followed by calcination was carried out to form Cu particles. The catalyst was found good for hydrogenation of dimethyl oxalate but the synthesis of catalyst required long time, which is economically unfavorable. In a recent work, mesoporous SiO₂, SBA-15 was prepared by hydrothermal method and then functionalized with mono-, di- and tri-amines to form amine-Cu²⁺ complex and measured the catalytic performance for Aza Michael addition [46]. The syntheses routes used for above amino-functional SiO₂ particles were pretty complex and required multi-steps. Moreover, the kind of interaction, fixation and purity of adhered Cu phase were hardly assessed. Therefore, a further effort for the preparation of new, efficient, low cost and stable Cu nanocatalysts is necessary for durable applications in organic synthesis and environmental remediation. It is evident from above literature that

limited effort is given so far on the use of mesoporous functional SiO_2 support for Cu nanocatalyst.

The objective of the present investigation is to propose a simple cost-effective way for the synthesis of stable Cu nanocatalyst that would exhibit good catalytic activity. In this paper, sub-micrometer sized mesoporous amine functionalized SiO_2 ($\text{SiO}_2\text{-NH}_2$) particles have been used as support to anchor CuNPs. The use of mesoporous $\text{SiO}_2\text{-NH}_2$ particles would offer multiple advantages such as increased surface area due to porous structure, the coordination of CuNPs and high Cu ion affinity through the nitrogen rich functionalities along with controlled growth of NPs within the confined mesopores of SiO_2 surface [47–49]. It is believed that the above approach would produce excellent heterogeneous Cu nanocatalyst and the proposed idea can be extended to produce other transition metal based nanocatalysts.

Herein, the $\text{SiO}_2\text{-NH}_2$ particles were first prepared in one pot by diethyl amine, DEA catalyzed hydrolysis and condensation of tetraethyl orthosilicate, TEOS using hexamethylene diamine, HMDA and cetyltrimethylammonium bromide, CTAB for generating amine functionality and porosity, respectively. In the second step, $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles were prepared by sequential adsorption and chemical reduction of anchored Cu ions using NaBH_4 reducing agent and ascorbic acid was used as capping agent. The synthesis of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles is depicted in Fig. 2.1. The structural composition and morphology were confirmed by Fourier Transform infrared, FTIR, electron microscopic images, Brunauer–Emmett–Teller, BET surface analysis, X-ray diffraction, XRD and X-ray photoelectron spectroscopy, XPS. The catalytic performance of prepared catalyst nanocomposite particles was explored for the reductive degradation of two synthetic azo dyes, Congo red, CR and Eriochrome black-T, EBT. The degradation reaction was carried out in presence of BH_4^- electron donor and the performance of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst was compared with that of prepared CuNPs and commercial CuO powder, respectively. The degradation of synthetic dyes was selected as a model reaction because widespread use of these non-degradable dyes in various industries such as plastics, paper, leather, textile and printing are discharging large volume of effluents in soil and aquatic system and is thus causing serious ecological and health problems [50].

Fig. 2.1. Preparation scheme of SiO₂-NH₂/Cu nanocatalyst particles

2.2. Experimental

2.2.1. Materials

Tetraethyl orthosilicate, TEOS (Sigma Chemical Company, USA), cetyltrimethylammonium bromide, CTAB (Fluka, Biochemica, Switzerland) and hexamethylene diamine, HMDA (Fluka, Biochemica, Switzerland) were used as received. Copper sulphate pentahydrate, CuSO₄·5H₂O (Merck, India), and sodium borohydride, NaBH₄ (Smart Lab, Indonesia) were used as precursor of CuNPs and reducing agent, respectively. L-Ascorbic acid (E-Merck, Germany) was used as both capping agent and antioxidant. Congo red, CR (Matheson Coleman and bell, USA) and Eriochrome black-T, EBT (Matheson Coleman and bell, USA) were used for catalytic study. Among the substances used as reagents were ethanol, copper oxide (CuO), DEA, NH₄OH (25%) and HCl (37%). Reverse osmosis and UV

light were used to obtain deionized water from Puricom (Taiwan). Deionized water was used to prepare each solution.

2.2.2. Preparation of SiO₂-NH₂ particles

The synthesis procedure of SiO₂-NH₂ particles were slightly revised as prescribed literatures [51, 52]. SiO₂-NH₂ particles were synthesized in a three-necked round bottom flask equipped with a magnetic stirrer at 250 rpm and a reflux condenser under an inert N₂ atmosphere. Briefly, a reaction flask containing 25% CTAB solution (3.12 g of CTAB in 9.36 g of water), DEA (0.24 g), and 98.4 g of 27% (v/v) aqueous ethanol was dipped in a thermostat water bath kept at 60°C. Confirming the basicity of the reaction mixture, TEOS (8.76 g) was added slowly in drip, and 30 min later 0.88 g of HMDA was added. The reaction was continued for another 3.5 h. The resulting concoction gradually turned milky white. Centrifugation was used to separate the final product, which was then subjected to three ethanol washes. For the elimination of CTAB, the reflux was carried out at 78°C for 48 h while SiO₂-NH₂ particles were dispersed in ethanol (636.0 mL) containing 37% by mass HCl (18.2 mL). Then, the resulting deposits were collected by centrifugation and washed with deionized H₂O three times. The resulting particles were placed in a vacuum desiccator and allowed to dry overnight at ambient temperature.

2.2.3. Preparation of SiO₂-NH₂/Cu nanocatalyst

The SiO₂-NH₂ dispersion (16.27 g, solid 1.0 g) and Cu solution (CuSO₄·5H₂O) (1.34 g/30.0 mL H₂O) were taken into the reaction flask with magnetic stirring at 500 rpm, and instantly nitrogen gas was passed into the reaction mixture through for 30 min to dispel any dissolved oxygen. L-Ascorbic acid (9.46 g/82.0 mL H₂O) with pH adjusted to ~ 10 was added and nitrogen bubbling was continued for an additional 30 min. NaBH₄ (0.51g/7.5 mL H₂O) was finally added in a drop-wise manner and after complete addition, the dispersion turned brown indicating the formation of SiO₂-NH₂/Cu nanocatalyst. The prepared particles were separated by decantation and centrifugation and washed three times with deionized water and ethanol. Finally, the nanocatalyst was obtained followed by drying overnight under a vacuum.

2.2.4. Preparation of CuNPs

The aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.18 M/100 mL) was poured into a three-necked round-bottomed flask equipped with a condenser, magnetically stirred at 500 rpm and N_2 gas was bubbled through the solution for 30 min at room temperature to remove any dissolved oxygen. L-Ascorbic acid solution (0.66 M/275 mL) with pH adjusted to around 10 by NaOH (0.1 M) solution was added and stirred for 30 min more under a nitrogen flow. NaBH_4 solution (1.8 M/25 mL) was added slowly, and the reaction was allowed to proceed for another 30 min. The solution instantly turned dark brown from deep blue, indicating the formation of CuNPs. Ultimately, the dispersion of CuNPs was washed three times with water and ethanol to wash off any of the remaining reactants and finally dried under a vacuum.

2.2.5. Characterization

In all analyses, the samples were cleaned and dried as required. Each powdered sample's Fourier transform infrared, FTIR, spectra was captured by an FTIR spectrophotometer (Perkin Elmer, FTIR-100, USA) in KBr pellets using the deflection mode and a scanning range of $4000\text{--}200\text{ cm}^{-1}$. X-ray diffraction, XRD patterns of powdered samples were obtained by scanning XRD (Bruker D8 Advance, Germany) using monochromatic $\text{Cu K}\alpha$ radiation ($\lambda \approx 1.5418\text{ \AA}$), tube voltage of 40 kV, and tube current of 40 mA at room temperature. Diffraction analysis was conducted at 2θ values from $2\text{ \AA}$ to $80\text{ \AA}$ at a continuous scan rate of $10\text{ \AA min}^{-1}$ with a position-sensitive detector aperture at $3\text{ \AA}$. X-ray photoelectron spectroscopy, XPS (ESCA-3400, Shimadzu, Kyoto, Japan), which uses monochromatic Al K radiation (1486.6 eV) at 4 W and 15 kV and an X-ray current of 20 mA, was used to establish the elemental composition of dried particles put on carbon tape. The pressure in the measurement chamber was set at $8.0 \times 10^{-7}\text{ Pa}$, while the acquisition area and take-off angle were held constant at 14 m and 45° , respectively. The step size for the survey and high-resolution spectra (pass energy 280 eV) was 0.25 eV. Transmission electron microscope, TEM images of $\text{SiO}_2\text{-NH}_2$ particles, CuNPs and $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles were observed to check the internal morphology and size distribution, whereas, scanning electron microscope, SEM images were taken to analyze the surface morphology and size distribution. For TEM (JEM-

1230, JEOL, Japan) observation, each dispersion was diluted to roughly 0.01% solid by deionized water; a drop was placed on a carbon-coated copper grid and dried in at ambient atmosphere. TEM was operated at an accelerating voltage of 100 kV. The diluted dispersion (0.01% solid) was applied on a mica sheet and dried in a vacuum desiccator overnight for SEM (JSM-6510, JEOL, Japan) observation. The dried SEM samples were gold coated prior to observation to guard against sample damage from an electron beam. The specific surface area (S_{BET}), average pore diameter and pore volume of the dried samples were measured by Barrett-Joyner-Halenda (BJH) technique using a BET (NOVA3000e, USA) apparatus at 77 K. Before analysis, each sample was dried in an oven at 70°C. Visible spectrophotometer (OPTIMA, SP 300, Japan) was used for recording the color change during continuous reductive degradation of respective azo dye. The pH value was adjusted using a pH meter from the Mettler Toledo Company (MP 220, Switzerland), and the continuous phase was decanted and removed using a high-speed centrifuge (TG16-WS, China).

2.2.6. Catalytic activity

2.2.6.1. Degradation of Azo dyes

For investigating the catalytic performance of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst, the reductive degradation of CR in the presence of NaBH_4 as a reducing agent was monitored using a visible spectrophotometer at 25°C. The pH value was first optimized by running degradation experiment at various pH values (6 – 10). In a typical experiment, 50 mL of CR aqueous solution (40 mg L^{-1}) adjusted at the respective pH value was mixed with NaBH_4 (6 mg) and nanocatalyst (2 mg) under gentle stirring (500 rpm). Sample aliquots of around 5 mL were collected at a regular time intervals and the progress of the degradation reaction was monitored at the wavelength (493 nm) of maximum absorbance by a visible spectrophotometer. The same procedure was repeated to see effects of different variables like initial CR concentration, catalyst dose and contact time at the optimized pH value. The degradation percentage i.e., the degree of decoloration, (D %), as a function of time was estimated by using Eq. (2.1) :

$$D (\%) = [(C_0 - C_t)/C_0]100 = [(A_0 - A_t)/A_0]100 \quad (2.1)$$

The initial concentration and absorbance of CR are C_0 and A_0 , respectively, whereas the concentration and absorbance at time t are C_t and A_t .

The reductive degradation kinetic data were fitted with pseudo-first-order (Eq. (2.2)) and pseudo-second-order (Eq. (2.3)) models:

$$\ln (C_t/C_0) = \ln (A_t/A_0) = -k_1 t \quad (2.2)$$

$$1/C_t = 1/C_0 + k_2 t \quad (2.3)$$

Where k_1 (min^{-1}) and k_2 ($\text{L mg}^{-1} \text{min}^{-1}$) are the pseudo-first-order and pseudo-second-order rate constants, respectively.

A blank experiment was studied in presence of either nanocatalyst or NaBH_4 for the reductive degradation under similar conditions to study any variation in degradation percent (D %) with time. For comparison, degradation experiments in presence of prepared CuNPs and commercial CuO powder were carried out by keeping all other parameters such as pH (7), dye concentration (40 mg L^{-1}) and catalyst dose (2 mg) as identical.

Additionally, the effects of parameters like pH, initial dye concentration, catalyst dose and contact time were tested for the degradation of another anionic and comparatively low molecular weight azo dye, EBT by following the same procedure as described above. The calibration curve used for estimating the residual CR and EBT concentration after the degradation is shown in Fig. 2.2.

Fig. 2.2. Calibration curves of (A) CR and (B) EBT constructed by visible spectrophotometer. CR: wavelength, 493 nm and pH 7; EBT: wavelength, 530 nm and pH 4.

2.2.7. Recycling test

In a typical recycling experiment, a mixture of CR (40 mg L^{-1} , 200 mL) and NaBH_4 (24 mg) was taken in a beaker under mild stirring at 500 rpm. The nanocatalyst (8 mg) was added to the reaction mixture. The color intensity of the reaction mixture diminished gradually, and the reaction progress was monitored at a definite interval by a visible spectrophotometer with a maximum wavelength of 493 nm. The nanocatalyst was isolated from the reaction mixture by decantation and centrifugation, the recovered catalyst was washed with deionized water and ethanol and reused again.

2.3. Results and Discussion

2.3.1. Characterization of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst

$\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles were prepared by sequential adsorption and chemical reduction of anchored Cu ions using NaBH_4 reducing agent and ascorbic acid was used as a capping agent. $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst was characterized by different characterization techniques like FTIR, XRD, XPS, electron microscopy and BET and BJH measurements.

Organic functionality on the surface of hybrid particles is identified by FTIR spectra [54, 55]. Fig. 2.3a-c represents FTIR spectra of CuNPs, $\text{SiO}_2\text{-NH}_2$ particles, and $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalysts. In the spectrum of $\text{SiO}_2\text{-NH}_2$ particles (Fig. 2.3b), the presence of functional amine groups on the surface is confirmed by the presence of N-H bending at 1635 cm^{-1} and the weak signal of symmetrical -NH_3^+ bending at 1510 cm^{-1} [56]. The characteristic asymmetric vibrations of Si-O, Si-OH and Si-O-Si groups appear at 1092 , 969 and 798 cm^{-1} respectively [51]. The bands at 2929 and 2904 cm^{-1} in Fig. 2.3b represent the asymmetric and symmetric stretching vibrations due to aliphatic C-H groups, while the broad band at $3000\text{--}3650 \text{ cm}^{-1}$ corresponds to the cumulative asymmetric and symmetric stretching vibrations of NH_2 and O-H groups. The aliphatic C-H groups came from the bonded HMDA and residual CTAB (if any). The band of the C-H bending vibration in $\text{SiO}_2\text{-NH}_2$ particles (Fig. 2.3b) is visible at 1385 cm^{-1} but the band of C-N stretching vibration generally appears at 1155 cm^{-1} , is possibly buried inside the large signal of asymmetric Si-O vibration. Hence, the result suggested the grafting of HMDA to SiO_2 surface in one pot synthesis. The spectrum of CuNPs (Fig. 2.3a) shows a

fairly strong absorption band for bridging Cu-O-Cu vibration at 1110 cm^{-1} . This indicates that CuNPs contained a fraction of Cu⁺/Cu²⁺ species either due to incomplete in situ chemical reduction of Cu precursor salt or due to post-oxidation of metallic Cu during storage and handling. The vibration band at $400\text{--}600\text{ cm}^{-1}$ due to Cu-O bond is also visible in the spectrum of CuNPs [57]. Both these vibration bands are hardly visible in the spectrum of nanocatalyst particles (Fig. 2.3c) because of the overlapping vibrations from SiO₂ matrix. However, a change in the overall shape of these overlapping vibration bands from SiO₂ matrix along with the disappearance of Si-OH band can be observed after anchoring CuNPs. Fig. 2.3c also shows a little broadening effect and slight blue shifting of N-H bending to 1632 cm^{-1} after anchoring CuNPs. These differences indirectly confirm the fixation of CuNPs with functional SiO₂ (Fig. 2.1) and the formation of SiO₂-NH₂/Cu nanocatalyst particles. It is to be mentioned that a broad and diffuse signal at 1623 cm^{-1} in the spectrum of CuNPs (Fig. 2.3a) represents the O-H bending vibration of free and hydrogen bonded water.

Fig. 2.3. FTIR spectra of (a) CuNPs, (b) SiO₂-NH₂ particles and (c) SiO₂-NH₂/Cu nanocatalyst recorded in KBr pellets.

To evaluate the crystalline structure and oxidation states of metallic particles XRD patterns, shown in Fig. 2.4a-c, have been conducted. The diffraction pattern of amorphous $\text{SiO}_2\text{-NH}_2$ (Fig. 2.4a) shows only a single broad diffraction signal centered at about 23° in the range of $2\theta = 18\text{--}30^\circ$. The same broad amorphous signal also appears in the diffraction profile of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst (Fig. 2.4c). The XRD pattern of synthesized CuNPs (Fig. 2.4b) exhibits three distinct peaks at the 2θ positions of 44.46° , 51.32° and 75.24° and they are attributed to the (111), (200), and (220) crystallographic planes (JCPDS 4-0836) of the face-centered cubic structure of metallic Cu [58, 59]. The additional minor peaks at 37.38° and 62.28° (Fig. 2.4b) are assignable to copper(I) oxide (Cu_2O), in accordance with those described in the literature (ASTM card no. 34-1354) [59]. The average crystallite size of CuNPs estimated from Debye–Scherrer equation is about 20.6 nm. Comparatively, the XRD profile of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst (Fig. 2.4c) exhibits a weak signal at $2\theta = 43.42^\circ$ due to Cu (111) reflection and intense signals at 37.64° and 63.06° due to Cu_2O . The percentage of zero-valent Cu in CuNPs is estimated to be around 64% and this reduces to $\sim 35\%$ in nanocatalyst. The strong interaction between Cu ions and $\text{SiO}_2\text{-NH}_2$ particles possibly hindered the complete reduction [45]. The above findings suggest that anchored CuNPs on the surface of $\text{SiO}_2\text{-NH}_2$ consisted of both metallic and ionic species.

Fig. 2.4. XRD patterns of (a) SiO₂-NH₂ particles, (b) CuNPs and (c) SiO₂-NH₂/Cu nanocatalyst.

XPS is analyzed to evaluate the chemical composition and valence state of the metallic particles in Fig. 2.5Aa-c illustrates the comparative XPS survey spectra of SiO₂-NH₂ particles, CuNPs and SiO₂-NH₂/Cu nanocatalyst particles. The survey spectrum of functional SiO₂-NH₂ particles (Fig. 2.5Aa) shows the presence of Si2p signal at about 104 eV. However, the presence of N1s signal could not be confirmed. Hardly, any literature is available that confirmed the presence of N1s signal on SiO₂-NH₂ surface by XPS. Since, XPS can read the surface composition at a depth of only few angstrom (10–20 Å), it is likely that porous structure hindered such detection. The signal intensities of Si2p, C1s and O1s in SiO₂-NH₂ particles (Fig. 2.5Aa) are 25, 8 and 66 atom%, respectively. Comparatively, the spectrum of SiO₂-NH₂/Cu nanocatalyst particles (Fig. 2.5Ac) shows an additional Cu2p signal in the (924–974) eV range. Correspondingly, after anchoring CuNPs the intensities of Si2p and O1s signals decrease to 14 and 44 atom%, while that of C1s signal increases to 23 atom%. The increase in C1s signal is possibly due to the addition of L-ascorbic acid as an antioxidant and capping agent. Similarly, high C1s signal intensity (48 atom%) is also observed for bare CuNPs (Fig. 2.5Ab). The Cu2p signal in CuNPs can be resolved into two satellite peaks, assignable to

Cu2p_{3/2} and Cu2p_{1/2} at ~ 933 and 953 eV, respectively, as shown in Fig. 2.5Bd [60]. These satellite signals indicated the presence of Cu⁺ and/or Cu⁰ species in the prepared CuNPs. Whereas, in the case of SiO₂-NH₂/Cu nanocatalyst (Fig. 2.5Be), Cu2p signal can be resolved into two additional minor satellite peaks of Cu2p_{3/2} and Cu2p_{1/2} at ~ 945 and 963 eV, respectively, indicated the existence of Cu²⁺ species as well [60]. Moreover, compared to bare CuNPs (Fig. 2.5Bd), a slight shifting of satellite signals to higher binding energy is visible in nanocatalyst (Fig. 2.5Be). This might have resulted from the grafting reaction on SiO₂-NH₂ particles [61]. The above analysis also confirms that anchored CuNPs contained zero-valent Cu as well as ionic Cu (Cu⁺/Cu²⁺) species. One probable reason is an incomplete reduction of strongly interacted Cu²⁺ with ≡ SiO- species as predicted in the formation mechanism of SiO₂-NH₂/Cu nanocatalyst (Fig. 2.09).

Fig. 2.5. (A) XPS survey spectra of a) SiO₂-NH₂ particles, b) CuNPs and c) SiO₂-NH₂/Cu nanocatalyst. (B) Cu2p core-line spectra of d) CuNPs and e) SiO₂-NH₂/Cu nanocatalyst.

SEM images, given in Fig. 2.6a-c have been used to analyze the surface morphology and size distribution of synthesized CuNPs, SiO₂-NH₂ particles and SiO₂-NH₂/Cu nanocatalysts. CuNPs (Fig. 2.6a) are mostly aggregated into spherical as well as some non-spherical clusters. The shape of individual CuNPs embedded within the cluster is irregular and size distribution is not uniform, lying in the 10–180 nm range. The partial oxidation of colloidal CuNPs in water might have caused the agglomeration of individual CuNPs [63]. SiO₂-NH₂ particles (Fig. 2.6b) are almost spherical and exhibit broad particle size distribution. The average size and coefficient of variation (CV) of SiO₂-NH₂ particles are 468.6 nm and 32%, respectively. The broad particle size distribution of SiO₂-

NH₂ particles is possibly associated with noninstantaneous nucleation i.e., prolonged nucleation [64]. The colloidal stability of SiO₂-NH₂ suspension was good and the SEM image supports the observation as no big cluster is found. Comparatively, the SEM image of SiO₂-NH₂/Cu nanocatalyst (Fig. 2.6c) indicates a slightly different morphology as many small particles can be observed in the same domain. These small particles are possibly CuNPs, anchored on the surface of SiO₂-NH₂ particles. The average size of SiO₂-NH₂/Cu nanocatalyst also noticeably increased to 516.50 nm. It is reasonable to assume that the fixation of Cu ions to the functional SiO₂ surface hindered the particle growth, which ultimately helped to control the size distribution in the nano range.

Fig. 2.6. SEM images of (a) CuNPs, (b) SiO₂-NH₂ particles and (c) SiO₂-NH₂/Cu nanocatalyst. The scale bar represents 1 μ m and the inset image in (c) shows magnified particles.

TEM has been used to further analyze the particle morphology and size distribution as shown in Fig. 2.7a-d. Interestingly, the TEM image of CuNPs (Fig. 2.7a) demonstrates some spherical shape entities with an average diameter of 672.5 nm. A similar observation was also found in the SEM image (Fig. 2.6a). The spherical-shaped individual entity is possibly the dense agglomerate of many smaller Cu particles. These were possibly formed during nucleation process and rearranged into spherical shapes to become thermodynamically stable in the suspension. SiO₂-NH₂ particles possess (Fig. 2.7b) clear spherical shape, having an average diameter of 327 nm, lower than that measured from the SEM image. High polydispersity index might have affected the accuracy of measurement. The aggregation of SiO₂-NH₂ particles might have occurred during sample preparation for TEM observation as no such aggregation was observed in

colloidal suspension. The surface porosity of $\text{SiO}_2\text{-NH}_2$ particles can be confirmed from the TEM image (Fig. 2.7c) as well. On the contrary, the TEM image of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles (Fig. 2.7d) clearly shows the presence of firmly attached CuNPs on the functional SiO_2 surface. This is to be mentioned that all the images were taken after repeated washings. The CuNPs of average diameter ~ 28 nm is evenly distributed on the SiO_2 support. The SEM and TEM images thus confirmed the successful formation of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles.

Fig. 2.7. TEM images of (a) CuNPs, (b, c) $\text{SiO}_2\text{-NH}_2$ particles and (d) $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst.

The pore size distributions of $\text{SiO}_2\text{-NH}_2$ particles, $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalysts and CuNPs are shown in Fig. 2.8A. It is evident that $\text{SiO}_2\text{-NH}_2$ particles have mesoporous surface as the average pore diameter (4.3 nm) is in the 2–50 nm range [32] and BJH pore distribution suggests fairly narrow (bimodal) pore size distribution. The specific surface area (S_{BET}) is found to be large ($403 \text{ m}^2 \text{ g}^{-1}$) and average pore volume is 0.047 cc g^{-1} . After fixation of CuNPs, the average pore diameter slightly increases to 5.6 nm in $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalysts and interestingly, the pore size distribution becomes more uniform, exhibits a monomodal type distribution. However, the BET surface area and average pore volume of nanocatalysts are reduced to $248 \text{ m}^2 \text{ g}^{-1}$ and 0.038 cc g^{-1} , respectively. The

agglomeration and formation of CuNPs on and within the pores of functional SiO₂ has most likely reduced the BET surface area and pore volume. The prepared CuNPs also exhibit mesoporous structure with average pore diameter of 3.1 nm and the BJH pore distribution is bimodal. The BET surface area of CuNPs is found very low (13.5 m² g⁻¹) due to agglomeration of NPs as already mentioned in the discussion of electron microscopic images. Fig. 2.8B shows nitrogen adsorption-desorption isotherms of SiO₂-NH₂ particles and SiO₂-NH₂/Cu nanocatalysts. The isotherm types generally depend on the nature of the adsorbent-adsorbate interactions and porosity of adsorbent. In either case, the adsorption followed mesoporous type IV isotherm [65, 66] and the sharp upward transition at the relative pressure of 0.29 in SiO₂-NH₂ particles indicated the presence of porous structure and is accompanied with the progressive filling of mesopores by the capillary condensation process. The initial part of the isotherm ($P/P_0 < 0.29$) in SiO₂-NH₂ particles is associated with mono- and multi-layer adsorptions, generally observed for both porous and nonporous adsorbents. Comparatively, the adsorption-desorption isotherm of SiO₂-NH₂/Cu nanocatalysts is little flattening, indicating decrease in porosity following fixation of CuNPs at both inside and outside the pores.

Fig. 2.8. (A) BJH pore distribution of CuNPs (circle), SiO₂-NH₂ particles (triangle) and SiO₂-NH₂/Cu nanocatalyst particles (cube). (B) Nitrogen adsorption-desorption isotherms of SiO₂-NH₂ particles (triangle) and SiO₂-NH₂/Cu nanocatalyst particles (cube).

2.3.2. Formation mechanism of nanocatalyst

The formation of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles is associated with the co-ordination of Cu^{2+} and subsequent reduction. All the probable co-ordination pathways are shown in Fig. 2.09. The terminal NH_2 groups of HMDA at the SiO_2 surface can function as both mono- and bi-dentate ligands. These ligands would favor the formation of primary, secondary and quaternary Cu - amine complexes. Additionally, the generation of negatively charged $\equiv \text{SiO}^-$ species in presence of Cu^{2+} is possible, which can promote strong interaction of Cu^{2+} with the surface of $\text{SiO}_2\text{-NH}_2$. The $\equiv \text{SiO}^-$ species can also be formed through the reaction of the OH^- from the basic medium with weakly acidic silanol groups before strong interaction with Cu^{2+} in association with amino groups [62]. These strong interactions might inhibit the complete reduction of Cu^{2+} and the successive formation of metallic Cu. The less stable primary and secondary Cu^{2+} - amine complexes are more favorable to form zero-valent copper (Cu^0) by borohydride reduction. In contrast, the quaternary Cu^{2+} - amine complex is considered more stable as it is formed due to coordination with four electron-donating atoms (N/O). Post-oxidation of metallic Cu to $\text{CuO}/\text{Cu}_2\text{O}$ is also probable as metallic Cu is unstable in air and the presence of water in the reaction media can also induce such oxidation during handling and storage.

Fig. 2.9. Formation mechanism of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst via co-ordination and subsequent reduction of copper ions.

2.3.3. Catalytic activity of nanocatalyst

The heterogeneous reductive degradation catalyzed by metal/metal ions usually depends on number of variables like nature of the surface-active center, concentration, surface charge, electronic structure, crystalline structure, method of synthesis, pH and temperature [67]. In the following section, the catalytic performance of prepared $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles has been discussed for the reductive degradation of two model azo dyes, CR and EBT in presence of borohydride reducing agents under ambient conditions.

The surface charge property of any catalyst, influenced by the pH of the solution, plays a vital role during the absorption and/or adsorption of reactant molecules. In case of our prepared mesoporous functional SiO_2 particles, the use of the term ‘sorption’ would be more appropriate and has been used to explain catalysis phenomena. Fig. 2.10A, B shows the effect of initial pH value on the degradation percent of respective 50 mL CR

(40 mg L⁻¹) and EBT (20 mg L⁻¹) dye solution. It is expected that the sorption capacity of anionic CR and EBT on SiO₂-NH₂/Cu nanocatalysts would increase in the acidic pH range and decrease in the basic pH range. The degradation percent of CR (Fig. 2.10A) remains almost identical (~ 92%) in the pH range 6–7, gradually decreases to ~ 50% up to pH 9 and then increases to ~ 90% at pH 10. The degradation study of hydrophobic CR below pH 6 was avoided due to its aggregation feature and formation of tautomers in an acidic aqueous solution [68]. It is probable that in the pH range of 6–7 there is almost no electrostatic interaction between the particles surface and anionic CR molecules. In the pH range 8–9, the decrease in degradation percent is possibly associated with lower sorption of anionic CR due to electrostatic repulsion with R-SO₃⁻ ions and negatively charged Si-O⁻ surface formed by deprotonation of Si-OH groups [69]. With a further increase of pH value to 10 the increase in degradation percent of CR is quite unexpected.

However, one research group found that an increase in alkalinity can improve degradation via the generation of •OH radicals, primary oxidizing species, from excess hydroxyl anions [67]. On the contrary, the degradation percent of EBT studied in the pH range 4–10 (Fig. 2.10B) shows almost a steady decrease from ~ 83% to ~ 48%. EBT is a comparatively hydrophilic low molecular weight azo dye and has no tendency to aggregate in solution. The lower pH value in the acidic pH range favored the sorption of EBT due to electrostatic attraction, which possibly contributed to the high degradation percentage. The protonation of azo nitrogen in EBT at pH 4 might also promote decolorization [70]. Whereas, in the alkaline range, the catalyst surface is expected to be anionically charged due to deprotonation of Si-OH functionality as mentioned above. This reduces the degree of sorption of anionic EBT and hence the degradation percent. The lower sorption of EBT in the alkaline pH range might also result from the presence of excess OH⁻ ions in the solution, which can hinder the access of anionic EBT to the active catalyst site. Moreover, semiconductor materials like Cu/Cu₂O/CuO bearing hydroxyl groups are also amphoteric in nature and can associate or dissociate protons with changing pH values. This behavior might also influence the sorption of anionic dye on the catalyst [67]. Nevertheless, the above study suggests that the initial pH value of the dye solution has a significant effect on the degradation percentage. The maximum degradation percents for CR (~ 92%) and EBT (~ 83%) obtained at pH values of 7 and 4,

respectively, were considered as optimized pH values for carrying out the rest of the degradation experiments.

Fig. 2.10. Effect of pH on degradation of (A) CR and (B) EBT in presence of 2 mg of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst. Conditions: temperature, 25°C , dye concentration, CR: 40 mg L^{-1} and EBT: 20 mg L^{-1} ; total volume, 50 mL.

The effects of initial concentrations of both CR and EBT on their reductive degradation in presence of fixed dose (2 mg) of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles were studied at optimized pH values and the results are presented in Fig. 2.11A, B. Irrespective of dye, the concentration decreases sharply at the beginning and then only slowly. This decreasing trend is more pronounced at higher dye concentration. The initial rapid decrease in dye concentration is the result of combined effect of sorption and degradation. On the contrary, gradual and slow decrease in dye concentration towards the end of reaction is associated with catalytic degradation only. The degradation rate and overall degradation percent are little low for comparatively low molecular weight EBT. The magnitude of sorption, determined by molecular weight and solubility, possibly played a role in slowing the degradation of EBT. Comparatively, in the control experiment carried out in presence of either NaBH_4 or $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles, almost no degradation is observed (Fig. 2.12). These results confirm the catalytic property of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles in presence of a reducing agent. The degradation percent (inset of Fig. 2.11A, B) decreases with an increase in dye concentration in solution and observed maximum when the respective dye concentration

was the lowest i.e., 40 and 20 mg L⁻¹ for CR and EBT. There are two probable hypotheses for this behavior. One hypothesis is the high surface coverage of the catalyst with dye molecules at higher initial dye concentrations and the reduction of active catalyst sites for the transfer of electrons from BH₄⁻ to the acceptor dye molecules required for initiating degradation [71]. Another hypothesis is reduced sorption of dye molecules on the catalyst surface at higher initial dye concentration [72]. The competition for sorption on the catalyst surface from an increasing amount of intermediate degradation products generally accounted for this reduced sorption of dye molecules. The catalytic performance of our prepared SiO₂-NH₂/Cu nanocatalyst particles is found reasonably good and even, comparable with some already reported precious metals in terms of degradation percent (Table 2.1). It is to be mentioned that the nature of dyes and the content of active catalysts are not always identical and might have some effects on the kinetics of dye degradation.

Fig. 2.11. Time dependent change in (A) CR and (B) EBT concentration during reductive degradation in presence of 2 mg of SiO₂-NH₂/Cu nanocatalyst. Inset Figures represent the change in degradation percent against different initial concentrations of CR and EBT. Conditions: pH, CR: 7 and EBT: 4; temperature 25°C; total volume, 50 mL.

Fig. 2.12. Degradation of CR in presence of NaBH_4 (triangle), $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst (diamond) and both NaBH_4 and $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst (circle). Conditions: dye concentration, 40 mg L^{-1} ; pH, 7; temperature 25°C ; total volume, 50 mL.

Table 2.1. Nanocomposites catalyzed degradation/reduction reactions of organic pollutants.

Catalysts	Organic pollutant	Degradation conditions	Catalyst dose (mg) / Time (min)	Degradation / reduction (%)	References
Cu@SBA-15	CR	9×10^{-2} mM, 12.5 mL H ₂ O, NaBH ₄ , $30 \pm 1^\circ\text{C}$	1 / 7	~ 100	[44]
Cu-Mn/SiO ₂	MB	7.8×10^{-2} mM, 250 mL H ₂ O, H ₂ O ₂ , pH 7, 25°C	100 / 300	~ 85 - 97	[75]
SiO ₂ /Cu(II) complex	MO	1×10^{-2} mmol, 100 mL H ₂ O, room temp.	50 / 360	100	[76]
Cu/CuO-Ag	MB	1.6×10^{-1} mM, 10 mL, H ₂ O ₂ , room temp 4.7×10^{-2} mM, 10 mL	10 / 36	>96	[77]
CuFe ₂ O ₄ @SNM	MB	H ₂ O, H ₂ O ₂ , pH 6, room temp. 1.4×10^{-2} mM, 25 mL	5 / 20	93	[78]
Cu/ZnO NPs	CR	H ₂ O, NaBH ₄ , room temp.	7 / 9	100	[79]
CuO nanosheets	Allura Red AC	2.0×10^{-3} mM, 10 mL, NaBH ₄ , room temp.	5 / 6	96.99	[80]
Cu/Pd	MO	10 mM, 0.05 mL H ₂ O, NaBH ₄ , room temp.	0.05 / 5	100	[81]
Cu ₂ O-Cu	MB	3.1×10^{-2} mM, 30 mL H ₂ O, H ₂ O ₂ , 25°C	9 / 10	90.10	[82]
Fe ₂ O ₃ /Cu ₂ O	RhB	1×10^{-2} mM, 200 mL H ₂ O	10 / 120	100	[83]
Au@NiAg	MO	1×10^{-1} mM, 2 mL, NaBH ₄ , room temp. 3.0×10^{-2} mM, 5 mL	0.0084 / 1.5	~ 100	[84]
Ni/CPM	MB	H ₂ O, NaBH ₄ , room temp.	2 / 13	100	[85]
Fe/DWCNTs-MMO	MB	1.5×10^{-1} mM, 45 mL, H ₂ O ₂ , 25°C	25 / 360	~ 100	[86]
Fe ₃ O ₄ @SiO ₂ -Ag	4-NP	1.2×10^{-1} mM, ~ 60	1 / 8	~100	[28]

		mL H ₂ O, NaBH ₄ , 25°C			
		5 × 10 ⁻² mM, 3 mL			
Ag@CAF	MO	H ₂ O, NaBH ₄ , room temp.	10 / 10	94.7	[87]
Dendritic-mSiO ₂ -NH ₂ -Ag	4-NP	1.2 × 10 ⁻¹ mM, 2.5 mL H ₂ O, NaBH ₄ , 25°C	0.005 / 8	~ 100	[88]
SCJC/Ag	CR	1.0 × 10 ⁻¹ mM, 20 mL H ₂ O, NaBH ₄ , 25°C	0.1 / 14	100	[89]
8 % Ag-TiO ₂	MB	3.1 × 10 ⁻¹ mM, 50 mL H ₂ O, 40°C	100 / 120	78	[90]
TiO ₂ /SiO ₂	MB	6.2 × 10 ⁻² mM, 500 mL H ₂ O, H ₂ O ₂ , room temp.	200 / 40	99	[91]
		1.4 × 10 ⁻² mM, 25 mL			
GO/Pd	CR	H ₂ O, NaBH ₄ , room temp.	5 / 10	100	[92]
		1.4 × 10 ¹ mM, 2 mL			
PdNPs@QPOSS	CR	H ₂ O, NaBH ₄ , room temp.	0.00025 / 3	100	[93]
		2.0 × 10 ⁻² mM, 0.2 mL			
Pd/g-C ₃ N ₄	MB	H ₂ O, NaBH ₄ , room temp.	0.02 / 1.33	~ 100	[94]
Fe ₃ O ₄ /usGO	MB	1.5 × 10 ⁻² mM, 50 mL, H ₂ O ₂ , pH 3, room temp.	0.5 mL / 90	100	[95]
Si@p-RuNP	CR	10 mM, 0.01 mL, NaBH ₄ , 25°C	20 μL / 5	100	[96]
Ru@PDC	New fuchsin	5 mM, 3 mL H ₂ O, NaBH ₄ , room temp.	3 / 9	98	[97]
		3.6 × 10 ⁻² mM, 100 mL			
SMt@GO@Au	CR	H ₂ O, NaBH ₄ , room temp.	10 / 12	~ 100	[98]
		5.7 × 10 ⁻² mM, 50 mL H ₂ O, NaBH ₄ , 25°C	2 / 15	92.2	This work

Abbreviations: CR, congo red; MB, methylene blue; MO, methyl orange; RhB, rhodamine B; 4 -NP, 4-nitro phenol; SNM, silica nanofibrous membranes; CPM, carbon porous materials; DWCNTs, double walled carbon nanotubes; MMO, Mg–Al mixed metal oxide; CAF, cellulose acetate filter paper; SCJC, sub-micrometer crystalline jute cellulose; QPOSS, quaternized polyhedral oligomeric silsesquioxane; g-C₃N₄, graphitic carbon nitride; usGO, ultrasmall graphene oxide; PDC, plastic-derived carbon; SMt, spherical montmorillonite

The catalyst dose effect was also studied for the degradation of 50 mL CR dye solution as presented in Fig. 2.13. It is generally expected that an increase of catalyst amount would increase the availability of active sites for transferring electrons to the reactant dye molecules. This is the common feature of any successful catalyst. Fig. 2.13 shows that an increase of catalyst dose increases the degradation percent of CR molecules and reaches nearly the saturation point at the dose of 2 mg. It can be said that the increased addition of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst into dye solution improved the electron storage capacity and hence the electron availability for the reductive degradation of dye.

Fig. 2.13. The amount of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst affects degradation percent of CR. Conditions: pH, 7; temperature, 25°C , dye concentration, 40 mg L^{-1} ; total volume, 50 mL.

The time dependent change in concentration of CR and EBT during degradation, shown in Fig. 2.11A, B was analyzed using pseudo-first-order and pseudo-second-order kinetic equations (Eqs. (2.2) and (2.3)) to understand the kinetic mechanism. Both pseudo-first-order and pseudo-second-order kinetic plots for respective dye molecules were linearized (Figs. 2.14 and 2.15). The rate constants (k_1 and k_2) and correlation coefficients (R_1^2 and R_2^2) estimated from the linearized plots are presented in Table 2.2.

Irrespective of dye concentration, the relatively higher value of R_1^2 indicates that reductive degradation of CR followed favorably pseudo-first-order reaction kinetics. This result is in agreement with the theoretical expectation [74]. However, in the degradation of EBT, the correlation coefficients (R_1^2 and R_2^2) for pseudo-first-order and pseudo-second-order rate equations are very close to each other, hardly favoring any particular kinetic mechanism. Independent of dye concentration, the rate constant (k_1) for the degradation of CR is comparatively high, indicating faster degradation kinetics. Even, the maximum degradation percent of CR in presence of nanocatalyst is higher than that of EBT. The higher molecular weight, linearity of CR molecules and poor solubility possibly contributed to better sorption at pH 7 on mesoporous $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles than the lower molecular weight nonlinear EBT molecules, though in the latter degradation was carried out at the acidic pH 4.

Fig. 2.14. Linearized pseudo-first-order kinetic plots for degradations of (A) CR and (B) EBT in presence of 2 mg of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst. Conditions: pH, CR: 7 and EBT: 4; temperature 25°C ; total volume, 50 mL.

Fig. 2.15. Linearized pseudo-second-order kinetic plots for degradations of (A) CR and (B) EBT in presence of 2 mg of SiO₂-NH₂/Cu nanocatalyst. Conditions: pH, CR: 7 and EBT: 4; temperature 25°C; total volume, 50 mL.

Table 2.2. Kinetic parameters of degradation of azo dyes in aqueous solution at different initial dye concentrations.

Initial dye conc. (mg L ⁻¹)		CR					EBT				
CR	EBT	Pseudo-first-order			Pseudo-second-order		Pseudo-first-order			Pseudo-second-order	
		D (%)	k ₁ (min ⁻¹)	R ₁ ²	k ₂ (L mg ⁻¹ min ⁻¹)	R ₂ ²	D (%)	k ₁ (min ⁻¹)	R ₁ ²	k ₂ (L mg ⁻¹ min ⁻¹)	R ₂ ²
40	20	92.2	0.1177	0.9635	0.0135	0.9175	82.5	0.0286	0.9451	0.0031	0.9795
50	30	91.0	0.1073	0.9713	0.0095	0.9048	63.8	0.0135	0.9829	0.0007	0.911
60	40	85.0	0.0896	0.9948	0.0036	0.6166	70.0	0.0183	0.9623	0.0007	0.9646
70	50	65.0	0.0281	0.9145	0.0007	0.8615	64.6	0.0152	0.8899	0.0004	0.9266
80	60	62.9	0.0259	0.9208	0.0004	0.8901	50.8	0.0104	0.8805	0.0002	0.9146

The catalytic activity of SiO₂-NH₂/Cu nanocatalyst particles was compared with that of prepared CuNPs and commercial CuO powder, respectively. In this experiment, the catalyst dose was fixed with respect to the amount of Cu in the sample and other conditions were kept identical. Comparative plots of degradation behavior and maximum degradation percent are shown in Fig. 2.16. Despite the presence of fair amount of Cu⁺/Cu²⁺, the catalytic degradation efficiency of SiO₂-NH₂/Cu nanocatalyst is found

maximum followed by CuNPs and then commercial CuO powder (Fig. 2.16A). The improved stability of CuNPs due to fixation with functional SiO₂, well dispersed nature, large surface-to-volume ratio and mesoporous structure, all contributed positively for improving the catalytic efficiency of nanocomposite particles. While, the least degradation efficiency possessed by CuO powder is attributed to its low electron density that normally defines the structure of active site and also the poor interaction with the reactant dye molecules [73]. Fig. 2.16B also shows that CuNPs as well as CuO powder degrades smaller EBT more efficiently, whereas, SiO₂-NH₂/Cu nanocatalyst degrades the larger CR more efficiently. This behavior is possibly based on differences in surface property, chemical nature and mode of interaction between dye molecules and the catalyst surface. The overall results suggest that the prepared catalyst nanocomposite particles functioned efficiently, even at the neutral pH value of 7.

Fig. 2.16. (A) Degradation of CR in presence of commercial CuO powder (circle), CuNPs (triangle) and SiO₂-NH₂/Cu nanocatalyst (square). (B) Maximum degradation percent of CR and EBT in presence of different catalysts. Conditions: pH, CR: 7 and EBT: 4; temperature, 25°C, dye concentration, CR: 40 mg L⁻¹ and EBT: 20 mg L⁻¹; total volume, 50 mL.

2.3.4. Recovery and recycle

The recycle and reuse of any catalyst is a burning demand in industrial applications. To monitor the long-term durability of the synthesized SiO₂-NH₂/Cu nanocatalyst, a recycle experiment was carried out for the degradation of CR. For this, a series of

repeated degradation experiments was carried out with the same recovered catalyst under identical conditions. The catalyst, recovered from the reaction medium by centrifugation and decantation, was first cleaned with deionized water and then with ethanol to wash off any remaining adhered dye molecules. The degradation percent of CR up to third cycles (Fig. 2.17) shows that the catalytic activity of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst decreases regularly with increasing number of recycle and reuse. However, the degradation percent after the third cycle (66 %) indicates that the recovered catalyst retained sufficient catalytic property and remained active as much as CuNPs (65%) in the first cycle. The catalytic performance of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst is encouraging but the sustainability during reuse still needed to be improved. The regular decrease in degradation percent might result from the loss of catalyst during recovery and/or loss of catalytic property of recovered catalyst. The loss of catalytic property can occur through several probable routes such as aggregation of catalyst support, leaching of CuNPs from solid support and oxidation of active Cu/Cu^+ species to mostly inactive Cu^{2+} . Among these, the third probability is pretty high as metallic Cu is prone to oxidation. In this case, the use of proper capping agent for CuNPs during fabrication of nanocomposite particles along with reducing atmosphere during catalytic degradation reaction could improve the sustainability.

Fig. 2.17. Degradation percent of CR aqueous solution in presence of 2 mg of SiO₂-NH₂/Cu nanocatalyst during repeated recycle. Conditions: pH, 7; temperature, 25°C; dye concentration, 40 mg L⁻¹; total volume, 50 mL.

2.3.5. Degradation mechanism

The possible reaction mechanisms occurred during the degradation of anionic CR and EBT are shown in Fig. 2.18. These are both azo dyes containing azo group along with chromophores and auxochromes which are responsible for color. In the reaction system NaBH₄, dye molecules and catalyst were set to function as electron donor, acceptor and electro transfer mediator, respectively. Since, CuNPs are deposited on mesoporous SiO₂ particles containing -OH and -NH₂ groups, it can be assumed that the degradation reaction is followed dominantly by the sorption of dye molecules through hydrophobic interaction, hydrogen bonding and electrostatic interaction. The presence of SiO₂-NH₂/Cu nanocatalyst with potential between those of the donor and acceptor makes the electron transfer easy to dye molecules. BH₄⁻ ions produced from the dissociation of NaBH₄ in aqueous solution involves in reaction with Cu based NPs to create the highly active surface-hydrogen (Cu-H) [23]. Instantly, active surface hydrogen transfers to the azo group of dye molecules with the electron being supplied from BH₄⁻ to initiate

reduction and degradation. The degraded products are ultimately desorbed from the catalyst surface.

Fig. 2.18. The probable degradation mechanism of anionic CR and EBT in the presence of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst.

2.4. Conclusion

CuNPs are doped on mesoporous $\text{SiO}_2\text{-NH}_2$ particles, and it was preferable in the presence of mesoporous surface structure of SiO_2 and amine functionality. Thus, anchored Cu particles show good catalytic activity for the sorption of reactant molecules. First, $\text{SiO}_2\text{-NH}_2$ particles are prepared via a one-pot simple sol-gel approach in presence of HMDA as an amine-generating precursor. Finally, $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalysts are prepared by in situ coordination with Cu^{2+} and subsequent reduction by borohydride reducing agent. XRD and XPS analyses suggested that anchored CuNPs contained zerovalent Cu ($\sim 35\%$) with the rest being ionic Cu ($\text{Cu}^+/\text{Cu}^{2+}$) species. A formation mechanism of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalysts is proposed and it is predicted that strong interaction of negatively charged $\equiv \text{SiO}^-$ groups with Cu^{2+} probably hindered the complete reduction to zero-valent Cu^0 . Post-oxidation of metallic Cu during storage is also another possibility. TEM image and BJH pore distribution confirmed that the mesoporous surface structure is maintained even after fixation of around 28 nm sized CuNPs. The catalytic activity of $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalysts is evaluated for the degradation of two model azo dyes, CR and EBT in the presence of a reducing agent. The maximum degradation percent of CR and EBT is $\sim 92\%$ and $\sim 83\%$ at pH 7 and 4 respectively. The $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalysts exhibited superior degradation properties compared to bare CuNPs despite the latter containing more ($\sim 64\%$) metallic Cu. The high stability and large surface-to-volume ratio of anchored CuNPs are accounted for improving catalytic performance. The reusability experiment suggested that $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalysts can be reused for at least three cycles with fair efficiency (about 66%). In this respect, the use of a proper capping agent for CuNPs, organic reaction media and finally chemical reduction at higher temperatures can be tried to effectively reduce Cu(I) and Cu(II) contents in the prepared $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst particles.

2.5. References

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Chapter-3

Amine Functional Silica-supported Bimetallic Cu-Ni Nanocatalyst and Investigation of Some Typical Reductions of Aromatic Nitro- substituents

3.1. Introduction

Metal nanoparticles (NPs) having large surface area, huge porosity, and chemical tenability at the nanoscale show promising catalytic activity corresponding to bulk counterparts. Researchers focused their attention on precious metal NPs like Au, Pt, Pd, Rh, and Ru as catalysts due to their enlarged stability, proficiency and high selectivity [1–3]. Despite the higher catalytic activity, the large-scale usage of precious metals is disfavored because of their high cost and rare abundance on the planet. So, non-precious metal-based nanocatalysts are developed day by day because of their high activity, long lifetime and obviously economic feasibility. In this regard, non-precious metals such as Fe, Co, Cu, and Ni have been extensively used to develop bimetallic nanocatalysts and they could be good alternatives to precious metals as these are proven beneficial for improving the catalytic activity and selectivity [4–6] compared to corresponding monometallic analogue and found sometimes even comparable with those of individual precious metal nanocatalysts [7]. The strong synergistic interaction between metals improves the physicochemical properties, such as high specific surface area, functionality, and stability [8]. These bimetallic NPs also showed prospective application potential in electronics, photonics, sensing, labeling, and imaging [9–11]. So far, many researchers have focused their attention on the preparation of cost-effective bimetallic Cu-Ni alloy nanocatalysts as they have high strength, low melting temperatures, corrosion resistance, and thermal and electrical conductivity. Magnetic behavior is another vital property that can enable the magnetic Cu-Ni nanoalloy more attractive for applications ranging from catalysis to optoelectronic, magnetic, metallurgical, and even medical applications [12–14]. However, the efficient use of any unsupported bimetal nanocatalysts is believed to suffer major drawbacks due to tendency to aggregation, low recyclability, and recovering difficulty. One way to overcome these drawbacks is to embed or anchor bimetal nanocatalysts onto solid supports [15–17]. The supporting material provides mechanical strength to the catalyst, reduces the amount of metal nanocatalyst, improves exposure of active sites to the reactants, and also enhances the selectivity through altering molecular interaction with the loaded nanocatalyst [6]. In the majority of cases, four different groups of support materials such as carbon [7, 18], graphene [12, 18–23], SiO₂ [24–27], and metal oxides [7, 28–32] have been used for

stabilizing bimetallic Cu-Ni nanocatalysts. Among the support materials, SiO₂, a natural biomaterial which can be easily synthesized, offered promising advantages as support materials because of chemical inertness, low cytotoxicity, mechanical and thermal stability, low cost, and easy functionalization [33, 34]. Besides, the surface hydroxyl functional groups on SiO₂ made them highly stable in the aqueous reaction medium. Further functionalization of SiO₂ surface with organic reactive groups is also possible to facilitate the anchoring of metal ions/metals through chelation [35–38]. Few related literatures are available on the utilization of SiO₂ support for bimetallic Cu-Ni nanocatalyst. Wu et al. had stabilized Cu-Ni alloy NPs via encapsulation with SiO₂ shell through a two-step microemulsion and polymerization of tetraethyl orthosilicate, TEOS and observed superior catalytic performance to pure Ni nanocomposite catalyst [24]. The same group had used hydrothermal technique to embed Cu-Ni alloy NPs in nanosheets of hierarchical SiO₂ hollow spheres [25]. However, encapsulation by SiO₂ shell and use of large amount of surfactant can reduce the catalytic efficiency. Rad et al. used cationic–anionic Cu-Ni precursor to prepare SiO₂-supported bimetallic catalyst via wetness impregnation followed by drying and finally calcination at 600°C [26]. Chirieac et al. had used similar incipient wetness impregnation method followed by mild drying and calcination (550°C) to prepare Cu-rich CuNi/SBA-15 catalysts [39]. In a similar type of investigation, CuNi/SiO₂ catalysts were prepared from CuNi phytosilicates by treatment in autoclave and finally calcined at 400°C [40]. Yoshida had used citric acid–assisted impregnation followed by drying and calcination to prepare Cu-Ni/SiO₂ catalysts and tested the hydrogenation reaction [41]. All these preparations required extra effort like separate calcination step and chemicals as well. Ang et al. had used two-step in situ reduction and calcination to prepare xNi_yCu/SiO₂ catalyst and studied the promotional effect of oleic acid for activating SiO₂ particles [27]. Physical blending was also used to obtain CuNi/SiO₂ and observed the size effect of SiO₂ spheres on the hydrolysis of ammonia borane but the interaction among SiO₂ spheres and CuNi NPs was hardly addressed [42, 43].

The present investigation is aimed at developing a simple one-pot in situ co-reduction of Cu and Ni precursor salts in presence of amine functionalized SiO₂ (SiO₂-NH₂) spheres for preparing SiO₂-NH₂/Cu-Ni nanocatalyst (Fig. 3.1). The amine

functionality was favored to improve Cu^{2+} and Ni^{2+} affinity, coordination of Cu and Ni NPs through the nitrogen-rich functionalities and controlled growth of NPs. The composition and morphology of the supported nanocatalyst were confirmed by Fourier-transform IR, FTIR, electron microscopy, Brunauer–Emmett–Teller, BET surface analysis, X-ray diffraction, XRD and X-ray photoelectron spectroscopy, XPS. The catalytic activity of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was then tested for chemical reduction of some aromatic nitro compounds, the common organic pollutants widely used in the manufacturing of dyes, plasticizers, pesticides, fungicides, and explosives [19]. These pollutants caused deleterious effects on aquatic photosynthesis, biochemical oxygen demand, and chemical oxygen demand, and are poisonous to aquatic environment, which ultimately resulted in serious health problems for human life. The positive aspects of this investigation are simple and scalable one-pot production of cost-effective SiO_2 -supported bimetallic Cu-Ni nanocatalyst, enhanced catalytic power compared to pure Cu-Ni NPs, rapid and easy recovery of used nanocatalyst, and finally good recycle stability.

Fig. 3.1. Preparation scheme of SiO₂-NH₂/Cu-Ni nanocatalysts

3.2. Experimental

3.2.1. Materials

Tetraethyl orthosilicate, TEOS (Sigma-Aldrich Chemie GmbH, USA), cetyltrimethylammonium bromide, CTAB (Fluka, Biochemica, Switzerland) and 3-aminopropyltriethoxysilane, APTES (TCI, Japan) were used as received. Copper sulfate pentahydrate, CuSO₄·5H₂O (Merck, India), nickel sulfate hexahydrate, NiSO₄·6H₂O (E-Merck, Germany), 4-nitrophenol, 4-NP (Loba Chemie, India), ethylene glycol (Loba Chemie, India), hydrazine hydrate, H₂N-NH₂·H₂O (Merck, India), and sodium borohydride, NaBH₄ (Smart Lab, Indonesia) were used as precursor of Cu and Ni bimetal NPs, solvent and reducing agent, respectively. L-Ascorbic acid (E-Merck, Germany) was used as capping agent and antioxidant. Nitrobenzene, 4-nitrotoluene, 4-bromonitrobenzene, 3-nitroaniline, diethyl amine (DEA), NH₄OH (25%), HCl (37%), ethanol, and other chemicals were of either reagent or analytical grade. Deionized water

was obtained from Puricom (Taiwan) by reverse osmosis and UV radiation. All the experimental samples were prepared in deionized water.

3.2.2. Preparation of SiO₂-NH₂ particles

SiO₂-NH₂ particles were synthesized according to the slightly modified procedure as discussed in the 2nd Chapter. Herein, APTES is used as a functional agent instead of HMDA and the molar ratio of APTES/TEOS is 0.15. Table 3.1 presents the required amounts of different reagents for the preparation of SiO₂-NH₂ particles.

Table 3.1. Preparation of SiO₂-NH₂ particles by one-pot synthesis.

Ingredients	Amount (g)
25% CTAB	3.12
DEA	0.45
27% (v/v) EtOH (aq.)	22.5
TEOS	8.76
APTES	1.39

Conditions: N₂, magnetically stirring 250 rpm, reaction duration 4h, temperature 60°C.

3.2.3. Preparation of SiO₂-NH₂/Cu-Ni nanocatalyst

The supported SiO₂-NH₂/Cu-Ni nanocatalyst was prepared from the Cu and Ni ions by in situ co-reduction via the solvothermal method [40, 44]. The apparent solution of equimolar amount (0.05 M) of CuSO₄·5H₂O (0.5940 g) and NiSO₄·6H₂O (0.6258 g) in 50 mL of ethylene glycol was poured slowly into the suspension of SiO₂-NH₂ particles at 70°C and the pH was adjusted to around 11 by adding NaOH solution. After that 5 mL of H₂N-NH₂·H₂O as a reducing agent dropped quickly into the solution. The solution twisted black immediately with the evolution of gases. After stirring for 30 min, the black colloidal suspension was transferred into a Teflon-coated stainless-steel autoclave followed by degassing process and then heated at 200°C for 3 h. Afterward, the particles were magnetically isolated followed by washing three times with distill ethanol under ambient conditions and overnight dried at 60°C.

The bare bimetal Cu-Ni NPs as reference nanocatalysts were synthesized without functional SiO₂-NH₂ support. Before adding H₂N-NH₂·H₂O reducing agent, L-ascorbic

acid was used as a capping agent and antioxidant. Otherwise, the procedure and molar ratio of Cu to Ni were maintained as discussed above.

3.2.4. Characterization

For all characterization techniques, cleaned samples were used as required. FTIR spectra of powdered samples were taken by an FTIR spectrophotometer (Perkin Elmer, FTIR 100, USA) in KBr pellets over the scanning range of 4000–200 cm^{-1} in the deflection mode. The morphology and size distribution of the prepared nanocatalysts were measured by Scanning electron microscope, SEM (JSM 6510, JEOL, Japan). The diluted dispersion (0.01% solid) was placed on a mica sheet and dried in a vacuum desiccator overnight before observation. Though there is little scope of sample damage under electron beam, the dried SEM samples were gold coated before observation. The specific surface area (S_{BET}), average pore diameter, and pore volume (if any) of the respective dried nanocatalyst were checked by Barrett–Joyner–Halenda (BJH) technique using a BET (NOVA3000e, USA) apparatus at 77 K. Before employing BET analysis, the nanocatalyst sample was dried in an oven at 70°C. X-ray diffraction, XRD data of powdered nanocatalyst samples were recorded by X-ray diffractometer (Bruker D8 Advance, Germany) using monochromatic Cu $K\alpha$ radiation ($\lambda \approx 1.5418 \text{ \AA}$), tube voltage of 40 kV, and tube current of 40 mA at room temperature. The diffraction scanning was conducted at a continuous scan rate of 10 $\text{\AA min}^{-1}$ with a position sensitive detector aperture at 3 $\text{\AA}$ between 2θ values from 20 $\text{\AA}$ to 80 $\text{\AA}$. The surface elemental composition of the dried sample mounted on a carbon tape was detected by XPS (PHI X-tool, ULVAC-PHI, Inc., Japan), equipped with a monochromatic Al $K\alpha$ radiation (1486.6 eV) at 4 W and 15 kV, and an X-ray current of 20 mA. The acquisition area and take-off angle were kept fixed at $1.4 \times 0.1 \text{ mm}$ and 45° respectively. The pressure in the measurement chamber was $8.0 \times 10^{-7} \text{ Pa}$. The step size was 1.5 eV for the both survey and high-resolution spectra (pass energy 280 eV). The magnetic property was analyzed by a vibrating sample magnetometer, VSM (Micro Sense, EV9, USA). Visible spectrophotometer (OPTIMA, SP 300, Japan) was used for recording the color change during continuous reductive conversion of the 4-NP. A pH meter from Mettler Toledo Company (MP 220, Switzerland) was used for adjusting the pH value, and a high-speed

centrifuge machine (TG16-WS, China) was used for decantation and washing of nanocatalyst samples.

3.2.5. Catalytic activity

3.2.5.1. Reductive conversion of 4-NP

The catalytic activity of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was evaluated by studying the reductive conversion of 4-NP in the presence of NaBH_4 as a reducing agent at constant temperature of 25°C . A visible spectrophotometer was used to monitor the changes in the 4-NP reduction reaction. The pH value was first optimized at different pH values for this experiment. In a typical reaction procedure, 4-NP (10 mg L^{-1}) was dissolved in deionized water to prepare 25 mL aqueous solution and the pH was adjusted at the respective pH value. NaBH_4 (8 mg) and $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst (5 mg) were added by gentle stirring at 350 rpm. The color intensity of the reaction mixture changed gradually, indicating the conversion of 4-NP to 4-aminophenol, 4-AP. The change in the absorbance value of 4-NP at 400 nm was recorded by a visible spectrophotometer at definite intervals. The same procedure was repeated to see effects of different variables like initial concentration and catalyst dose at the optimized pH value. A calibration curve shown in Fig. 3.2 was used for calculating the residual 4-NP concentration after the conversion. The respective conversion (D %) at different time intervals was estimated by using the Eq. (2.1) and the conversion data were fitted with the pseudo-first-order (Eq. (2.2)) and pseudo-second-order (Eq. (2.3)) models.

A blank experiment was studied in presence of either nanocatalyst or NaBH_4 or functional SiO_2 support with added NaBH_4 for the reductive conversion under similar conditions to study any variation in conversion percent (D %) with time. For comparison, the reduction of 4-NP in presence of pure Cu-Ni NPs was also carried out by keeping all other parameters, such as pH 6, 4-NP concentration (10 mg L^{-1}), and reaction time as identical. The doses of Cu-Ni NPs and functional SiO_2 support were ~ 2 and ~ 3 mg, equivalent to 5 mg of the nanocatalyst on the basis of metal and SiO_2 contents, respectively.

The catalytic activity of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst in the reduction reaction of little series of aromatic nitro compounds (nitrobenzene, 4-nitrotoluene, 4-bromonitrobenzene and 3-nitroaniline) were also investigated as reported in the literature [45]. A mixture of aromatic nitro compounds (1 mmol), $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst (5 mg) and water (10 mL) was added into a three-necked round-bottomed flask with stirring for about 5 min. Next, NaBH_4 (2 mmol) was added and the reaction mixture was stirred magnetically for 3 min under oil bath conditions (60–70°C) followed by thin layer chromatography, TLC monitoring (eluent, n-hexane/ethylacetate (EtOAc): 5/2) to monitor the reaction progress. After the completion of the reduction reaction, the mixture was cooled to room temperature. EtOAc (8 mL) was then added, stirring the resulting mixture for 10 min. The magnetic nanocatalyst was separated by an external magnet followed by extraction with EtOAc (2×5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 . The purity of the reduced product was confirmed by TLC monitoring and qualitative analysis performed to detect the primary amino group. The following equation was used to calculate the yield of the respective product.

$$\text{Yields (\%)} = \frac{\text{Moles of the product formed}}{\text{Initial mole of aromatic nitro compound}} \times 100 \quad (3.1)$$

Fig. 3.2. Calibration curves of 4-NP constructed by visible spectrophotometer. 4-NP: wavelength, 400 nm and pH 6.

3.2.6. Recycling test

In a typical recycling experiment, a mixture of 4-NP (10 mg L^{-1} , 50 mL) and NaBH_4 (16 mg) was taken in a beaker under mild stirring at 350 rpm. The nanocatalyst (10 mg) was added to the reaction mixture. The yellow color of the reaction mixture diminished gradually, and the reaction progress was monitored at a definite interval by a visible spectrophotometer with a maximum wavelength of 400 nm. The nanocatalyst was isolated magnetically from the reaction mixture, the recovered catalyst was repeatedly washed with deionized water and ethanol and reused again.

3.3. Results and Discussion

3.3.1. Characterization of nanocatalyst

The supported $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst prepared by in situ co-reduction of Cu and Ni salts in presence of functional SiO_2 particles was characterized by using different techniques like FTIR, XRD, XPS, electron microscopy, and BET analyses.

FTIR spectra (Fig. 3.3) of $\text{SiO}_2\text{-NH}_2$ particles, pure Cu-Ni NPs, and $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst were analyzed to identify the surface functionality. The spectrum of $\text{SiO}_2\text{-NH}_2$ particles (Fig. 3.3a) shows the characteristic asymmetric vibrations of Si-O, Si-OH, and Si-O-Si groups at 1087, 969, and 796 cm^{-1} [46]. The intense signal at 467 cm^{-1} in $\text{SiO}_2\text{-NH}_2$ particles is for the bending mode of Si-O group. The N-H bending vibration in primary amino group at 1640 cm^{-1} demonstrates functionalization of SiO_2 particles following one pot synthesis via sol-gel method. Another sharp peak at 1554 cm^{-1} corresponds to N-H bending vibration due to amino group being also visible [47]. The bands at 2985 and 2902 cm^{-1} in Fig. 3.3a describe the asymmetric and symmetric stretching vibrations for aliphatic C-H groups, originating from 3- APTES and residual CTAB. The C-N stretching vibration that normally appears at 1155 cm^{-1} could not be distinguished because of the presence of intense signal of asymmetric Si-O vibration in the same region. The spectrum of $\text{NH}_2\text{-SiO}_2$ particles also shows the characteristic broad absorption signal at 3000–3650 cm^{-1} due to amine N-H and O-H stretching vibrations. The spectrum of Cu-Ni NPs (Fig. 3.3b) exhibits absorption bands at 470 and 517 cm^{-1} , possibly attributed to the bending vibrations of Ni-O and/or Cu-O bond, while a sharp band at 624 cm^{-1} can be due to Ni-O-H stretching bond [48, 49]. This result indicates that surface atoms of Cu-Ni NPs might contain a fraction of Cu and Ni ions either due to partial oxidation in air during preservation and handling or due to incomplete in situ chemical co-reduction of precursor salts. The remaining bands may have come from the absorbed ascorbic acid and ethylene glycol. In the spectrum of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst (Fig. 3.3c), again the sharp stretching vibrations in the 467–618 cm^{-1} region may represent the Cu-Ni band [50, 51]. The intense asymmetric vibrations of Si-O (Fig. 3.3c) are visible at 1103 and 781 cm^{-1} with no signal of Si-OH band. Figure 3.3c also shows a little broadening effect and slight shifting of N-H bending to 1640 cm^{-1} and 1561 cm^{-1} after anchoring Cu-Ni NPs. The disappearance of Si-OH band and a

little shift of different bands in the spectrum of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst from the corresponding spectrum of $\text{SiO}_2\text{-NH}_2$ particles indicate the interaction of Cu-Ni NPs with functional SiO_2 particles. The comparative analyses suggest that functional SiO_2 particles have been anchored with Cu-Ni NPs.

Fig. 3.3. FTIR spectra of (a) $\text{SiO}_2\text{-NH}_2$ particles, (b) Cu-Ni NPs and (c) $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst recorded in KBr pellets.

The crystalline structure and oxidation states of the metallic phase were identified from XRD diffraction data. Fig. 3.4a–c illustrates the XRD patterns of the $\text{SiO}_2\text{-NH}_2$ particles, pure Cu-Ni NPs, and $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalysts, respectively. The diffraction pattern of amorphous $\text{SiO}_2\text{-NH}_2$ (Fig. 3.4a) shows only a single broad diffraction signal centered at about 23° in the $2\theta = 18\text{--}30^\circ$ range. The XRD pattern of synthesized pure Cu-Ni NPs (Fig. 3.4b) shows the sharp diffraction signals at 2θ values of 43.36° , 44.61° , 50.58° , 51.94° , 74.25° , and 76.6° . The signals at 43.36° , 50.58° , and 74.25° indicate the presence of Cu corresponding to the (111), (200), and (220) planes of the face-centered-cubic (fcc) metallic Cu (PDF standard cards, JCPDS 04–0836, space

group Fm3m) respectively [52, 53], whereas the peaks at 2θ values of 44.61° , 51.94° , and 76.6° can be assigned to (111), (200), and (220) fcc Ni crystals, consistent with the reported value (PDF standard cards, JCPDS 04–0850, space group Fm3m) [54]. The experimental lattice parameters for Cu and Ni were found to be 3.6046 Å and 3.5162 Å, respectively. These values are in good agreement with the lattice parameter for pure Cu (3.614 Å, PDF# 00–004-0836) and pure Ni (3.524 Å, PDF# 00–004-0850), respectively [55]. Therefore, it can be said that bimetal Cu-Ni NPs contained Cu and Ni in different metallic phases, with no signals for other species or oxides. However, the formation of trace amounts of metallic oxide cannot be ruled out under the existing preparation condition and the oxide layer might be too thin to be detected by XRD. The percentages of zero-valent Cu and Ni in pure Cu-Ni NPs, based on the (111) crystal plane, are about 51.77 and 48.23%, respectively, which are close to the preparation recipe. In Fig. 3.4c, the broad peak centered at around 24° in the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst indicates the presence of amorphous functional SiO_2 . The intense but little broadened diffraction peaks at 2θ values of 43.3° , 50.4° , and 74.3° respectively correspond to (111), (200), and (220) planes, indicating the formation of fcc structured metallic Cu-Ni NPs over the functional SiO_2 particles. A minor peak at 35.6° in the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst may indicate CuO indexed to (111) plane [12, 19, 44, 56, 57]. Interestingly, the absence of distinct peaks corresponding to individual lattice planes for neat elemental Cu and Ni metals and the slight broadening of signals indicated the homogeneity in the metallic phase and synthesis of alloy NPs [57]. Further, the slight difference in peak positions between Cu-Ni NPs (Fig. 3.4b) and $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst (Fig. 3.4c) is an indication of Cu-Ni alloying effect [58]. The average crystallite sizes of Cu and Ni, using the Debye–Scherrer equation, in pure Cu-Ni NPs are 57.81 and 14.36 nm and that of Cu-Ni alloy in the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is only 5.52 nm. The smaller crystallite size of bimetallic nanoalloy particles in the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst indicates the homogeneous nucleation and growth due to complexation reaction among metallic ions and functional $-\text{NH}_2$ groups on SiO_2 particles. Finally, it can be said that the prepared $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is successfully obtained by in situ co-reduction of Cu and Ni ions.

Fig. 3.4. XRD patterns of (a) SiO₂-NH₂ particles, (b) Cu-Ni NPs, and (c) SiO₂-NH₂/Cu-Ni nanocatalyst.

XPS was used to identify the surface elemental composition and oxidation states of Cu and Ni. A comparative plot of XPS survey spectrum of SiO₂-NH₂ particles, pure Cu-Ni NPs, and SiO₂-NH₂/Cu-Ni nanocatalyst is depicted in Fig. 3.5. For comparative perception, the relative atom% of different elements and binding energy of synthesized NPs are summarized in Table 3.2. The spectrum for SiO₂-NH₂ particles (Fig. 3.5Aa) shows the presence of Si2p signal at about 104 eV. A reasonably weak signal due to N1s appears at about ~ 399 eV in SiO₂-NH₂ particles, confirming the functionalization with amine groups. The relative signal intensities of Si2p, C1s, N1s, and O1s in SiO₂-NH₂ particles are around 19, 25, 3, and 52 atom%, respectively. The XPS spectrum of the SiO₂-NH₂/Cu-Ni nanocatalyst (Fig. 3.5Ac) expectedly shows the existence of Cu, Ni, Si, O, and C elements. Correspondingly, after anchoring Cu-Ni alloy NPs, the signal intensities of Si2p and O1s decrease to around 1 and 30 atom%, respectively, while that of C1s signal increases to ~ 65 atom%. The increase in C1s signal intensity may have originated from the fractions of adsorbed ethylene glycol solvent. This is to mention that in Cu-Ni NPs (Fig. 3.5Ab), the C1s signal intensity is also high (~ 58 atom%) and N1s signal derived from the reducing agent, H₂N-NH₂, is present at around 400 eV. The core line spectrum of Cu2p (Fig. 3.5Bd) in pure Cu-Ni NPs is differentiable into four distinct

satellite peaks, two peaks corresponding to $\text{Cu}2p_{3/2}$ at 933.5 and 942.5 eV and two peaks corresponding to $\text{Cu}2p_{1/2}$ at 953.5 and 961.25 eV, respectively. The intensity of these satellite signals is attributable to the presence of major amount of metallic Cu and/or Cu^+ with minor amount of Cu^{2+} species [38, 59], whereas, in the case of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst (Fig. 3.5Be), $\text{Cu}2p$ core line signal can be differentiated into three clear peaks, two peaks at ~ 932.5 and ~ 941.5 eV for $\text{Cu}2p_{3/2}$ and one peak at ~ 952.25 eV for $\text{Cu}2p_{1/2}$, respectively. The nanocatalyst contained hardly detectable second signal due to $\text{Cu}2p_{1/2}$ for Cu^{2+} . From this result, it may be reasonable to say that the nanocatalyst contained less amount of Cu^{2+} than the pure Cu-Ni NPs. The $\text{Ni}2p$ core line signal in either Cu-Ni NPs or composite nanocatalyst (Fig. 3.5C) is distinguishable into two characteristic doublets of $\text{Ni}2p_{3/2}$ and $\text{Ni}2p_{1/2}$. The binding energy difference of ~ 18 eV between the two spin states indicates the presence of Ni^{2+} oxidation state in both Cu-Ni NPs and $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst [59]. The multiplet structure of $\text{Ni}2p_{3/2}$ shows that the main asymmetric signal appears at around 6.5 eV above the shake-up satellite peak. Thus, the $\text{Ni}2p_{3/2}$ signal position again matches with the presence of surface NiO rather than with metallic Ni and Ni(OH)_2 [54]. Since the XRD spectra of neither pure NPs nor nanocatalyst showed diffraction signal due to metallic oxide and XPS can read elemental composition up to a depth of only few angstroms from the surface, it is reasonable to conclude that oxide layer is formed only at the surface in contact with air. The binding energy of $\text{Cu}2p_{3/2}$ and $\text{Ni}2p_{3/2}$ shifted only marginally in nanocatalyst from that in unsupported Cu-Ni NPs. However, the shifting is found opposite; i.e., $\text{Cu}2p$ core line signal shifted to lower binding energy and $\text{Ni}2p$ core line shifted to higher binding energy, which exposes the balancing regulation of near-surface electronic structure of the anchored Cu-Ni NPs due to alloying effect [60]. In addition to the above, some literature concluded that the shifting of binding energy of $\text{Cu}2p_{3/2}$ and $\text{Ni}2p_{3/2}$ indirectly confirms the formation of alloy NPs between Cu and Ni along with interaction between metallic alloy and $\text{SiO}_2\text{-NH}_2$ surface [19, 42, 61, 62]. Besides the interaction between alloy NPs and functional $-\text{NH}_2$ groups, the synergetic interaction between Cu and Ni induced the formation of alloy Cu-Ni structure in nanocatalyst.

Fig. 3.5. (A) XPS survey spectra of (a) SiO₂-NH₂ particles, (b) Cu-Ni NPs, and (c) SiO₂-NH₂/Cu-Ni nanocatalyst particles. Core-line spectra of (B) Cu2p and (C) Ni2p in (d, f) Cu-Ni NPs and (e, g) SiO₂-NH₂/Cu-Ni nanocatalyst.

Table 3.2. Relative atom% of different elements and binding energy of respective Cu2p and Ni2p main and satellite peaks.

Particles	Atom (%)						Binding energy (eV)			
	C1s	N1s	O1s	Si2p	Cu 2p _{3/2}	Ni 2p _{3/2}	Cu2p		Ni2p	
							Cu 2p _{3/2}	Cu 2p _{1/2}	Ni 2p _{3/2}	Ni 2p _{1/2}
SiO ₂ -NH ₂	25.29	2.54	52.07	19.13	-	-	-	-	-	-
Cu-Ni	58.36	5.78	27.56	-	3.93	4.39	934.50	954.00	854.75	873.50
							943.00	962.75	861.25	880.00
SiO ₂ -NH ₂ /Cu-Ni	64.88	-	29.97	1.45	0.46	3.24	932.50	~953.50	855.00	873.75
							942.25	-	861.50	880.25

The surface morphology, particle size distribution (measured by the ImageJ software) and agglomeration state of SiO₂-NH₂ particles, Cu-Ni NPs, and SiO₂-NH₂/Cu-Ni nanocatalyst were examined by SEM images as illustrated in Fig. 3.6a–c. The average size and coefficient of variation (CV) of SiO₂-NH₂ particles (Fig. 3.6a), prepared by one-step modified sol–gel technique, are 384.28 nm and 33.73%, respectively. Both spherical and oval-shaped SiO₂-NH₂ particles are formed and the polydispersity index is pretty high. The non-instantaneous nucleation, i.e., prolonged nucleation following hydrolysis and condensation of TEOS, is possibly accounted for broad distribution of SiO₂-NH₂ particles [46]. The functional SiO₂ particles possessed good colloidal stability. Comparatively, the SEM image of SiO₂-NH₂/Cu-Ni nanocatalyst (Fig. 3.6b) shows some big irregular-shaped cluster particles comprising many tiny individual particles. These tiny individual particles appear almost spherical and uniform-sized (~ 268 nm), and clusters formed look very compact. Moreover, SiO₂-NH₂ particles with identical shape and size are not visible in the image of SiO₂-NH₂/Cu-Ni nanocatalyst (Fig. 3.6b). Thus, it can be said that SiO₂-NH₂ particles are buried inside the cluster and the detectable tiny individual particles belong to Cu-Ni alloy NPs. Interestingly, some very uniform-sized spheres (arrow marked) of 1653.27 nm average size, obviously greater than the functional SiO₂ particles, are also evident. The magnified image of such uniform sphere (inset image of Fig. 3.6b) shows the difference in contrast due to individual Cu-Ni NPs doped on the

functional SiO_2 surface. On the contrary, from the SEM image of Cu-Ni NPs (Fig. 3.6c), it is apparent that many tiny spherical Cu-Ni NPs of average size ~ 218 nm are agglomerated into loosely bound irregular-shaped cluster. The agglomeration of metal particles definitely influenced the measurement of average size from SEM images and as they differed widely from the respective average crystallite size measured from the XRD data. Previously, we noticed the same agglomeration phenomena for both pure Cu [38] and Ni [54] NPs into large and perfectly spherical as well as anomalous-shaped particles of around $1\ \mu\text{m}$, due to Van-der Waals interaction and partial oxidation in air. In the background of SEM image of Cu-Ni NPs (Fig. 3.6c), some bigger particles doped with smaller Ni particles are discernable (arrow marked). The bigger particle possibly represented the clusters of CuNPs as nucleation is comparatively faster compared to Ni particles. It is obvious that there is a striking difference in morphology between Cu-Ni NPs and $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalysts. It is also worth mentioning that $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst on treatment with concentrated HCl produced soluble metal chloride in the supernatant and insoluble white SiO_2 particles were obtained as residue. From the above comparative analysis, it can be said that $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is obtained via in situ co-reduction of Cu and Ni salt in presence of functional SiO_2 particles.

Fig. 3.6. SEM images of (a) SiO₂-NH₂ particles, (b) SiO₂-NH₂/Cu-Ni nanocatalyst, and (c) Cu-Ni NPs

The experimental data of Cu-Ni NPs, SiO₂-NH₂ particles and SiO₂-NH₂/Cu-Ni nanocatalysts from BJH and BET method are shown in Table 3.3. Their average pore diameter and pore volume are 3.8, 30.85, 34.37 nm and 0.017, 0.064 and 0.036 cc g⁻¹ respectively. The surface area of SiO₂-NH₂ particles is 61.65 m² g⁻¹ and after doping with Cu-Ni NPs, the surface area decreased to 14.85 m² g⁻¹. The decrease in specific surface area is due to the increase in particle size following doping with NPs. Comparatively, the specific surface area of pure Cu-Ni NPs is much less (6.62 m² g⁻¹) attributable to the agglomeration effect.

Table 3.3. The data of BET and BJH method

Materials	BJH			BET surface
	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume (cc g^{-1})	Pore radius (nm)	area ($\text{m}^2 \text{g}^{-1}$)
Cu-Ni	6.62	0.017	1.906	7.156
$\text{SiO}_2\text{-NH}_2$	61.653	0.064	15.425	430.922
$\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$	14.484	0.036	17.188	16.012

The magnetic properties of synthesized particles Cu-Ni NPs and $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalysts are evaluated using a vibrating sample magnetometer, VSM at room temperature. As shown in Fig. 3.7, the curves show no obvious remanence or coercivity at room temperature, expressing that they are paramagnetic. The magnetic hysteresis curves indicated that the saturation magnetization (M_s) of Cu-Ni particles is 23.38 emu g^{-1} . The magnetization value of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalysts decreases to 5.04 emu g^{-1} . The lower value of magnetization determined the resultant force of total magnetic materials and increases nonmagnetic components. The classic “S” shape reversible magnetization curve also suggested that the paramagnetic property of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalysts is maintained after surface modification of Cu-Ni alloy NPs. Nevertheless, all the particles show moderate magnetic properties to ensure the microspheres are easily isolated in presence of an external magnetic field within a few seconds (Fig. 3.7 inset), which is more useful to the applications.

Fig. 3.7. VSM curves of (a) Cu-Ni NPs, and (b) SiO₂-NH₂/Cu-Ni nanocatalyst. Inset Fig. indicates the magnetic separation.

3.3.2. Mechanism of the formation of nanocatalyst

The formation of SiO₂-NH₂/Cu-Ni nanocatalyst proceeds via the interaction of Cu²⁺ and Ni²⁺ ions with functional SiO₂ surface and subsequent reduction by H₂N-NH₂·H₂O at 200°C. Fig. 3.8 shows all the probable interaction pathways for metal ions. The terminal -NH₂ groups, silanol groups ($\equiv\text{Si}-\text{OH}$), and siloxane groups with oxygen-silicone (Si-O-Si) backbone present on the functional SiO₂ surface act as ligands for metal ions. These ligands would allow the formation of primary, secondary, and quaternary aminated Cu and Ni complexes. Additionally, Ni²⁺ can also form an octahedral complex. The primary and secondary complexes of Cu or Ni are less stable than the quaternary complex, and these complexes are reduced easily by reducing agents to favor the formation of metallic particles [38]. In the alkaline medium, the $\equiv\text{SiO}^-$ species can also be generated through the reaction of OH⁻ with weakly acidic silanol groups before strong interaction with metallic ions in association with amino groups [43]. In such cases, the negatively charged $\equiv\text{SiO}^-$ species can be electrostatically attracted toward metal ions which ultimately may inhibit the complete reduction of Cu²⁺/Ni²⁺.

Since the metal ion reduction was carried out in presence of reducing agents like $\text{H}_2\text{N}-\text{NH}_2 \cdot \text{H}_2\text{O}$ at 200°C in ethylene glycol medium, it is expected that in situ simultaneous reduction of both metal precursors proceeded smoothly resulting in the formation of nanocatalyst with CuNPs anchored to amine functional SiO_2 particles. The formation of an intermetallic Cu-Ni compound is followed by the synergetic interaction between Ni and Cu through electronic transfer.

Fig. 3.8. Proposed formation mechanism of the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst during in situ co-reduction of precursor metal salts.

3.3.3. Catalytic activity

$\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst showed good catalytic activity evaluated by the reduction of some aromatic nitro-substituents in presence of NaBH_4 reducing agent. In this heterogeneous catalysis, reactant molecules are generally sorbed (adsorption and/or absorption) on the surface of the catalyst and the product is formed by transferring electrons from the added reducing agent via metal NPs doped on the support. In the following section, the catalytic activity of prepared $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalysts has been studied for the reduction of nitro groups in various substrates specially 4-NP using sodium borohydride as reducing agent at room temperature under aerobic conditions.

In the control experiment, the pH-dependent study carried out in the pH range of 3–10 (Fig. 3.9) shows that a maximum conversion of 98.5% is achieved after 15 min of reaction at pH 6. It is reasonable to believe that at pH 6 there is no ionic interaction between the nanocatalyst surface and phenolate ions as well as with electron-rich 4-NP because the nanocatalyst surface is almost neutral. It is clear that catalytic conversion over the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst significantly reduces to 74% at pH 3 after 25 min. In the acidic pH range, the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst oxide surface in water attained a positive charge due to the specific adsorption of H^+ ions. So, there should be increased $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst activity at pH 3 due to enhanced interaction of both phenolate ions and electron-rich 4-NP with the positively charged nanocatalyst surface. However, contrary to this, a diminished nanocatalyst activity at pH 3 is observed. Two probable reasons can be accounted for this. One is, some free electrons of 4-NP in the acidic conditions might undergo protonation that increased the repulsion between protonated oxygen and positive nanocatalyst and thereby prevented a fraction of 4-NP molecules to come close to the nanocatalyst surface [63, 64]. The other reason might be the leaching or dissolution of active Cu-Ni catalyst in acidic solution that could reduce the nanocatalyst performance, as well [63]. In the alkaline region, the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst activity is poor, as 72.7 and 86% conversions to 4-AP are obtained at pH 8 and 10, respectively. The point of zero charges for CuO and NiO are reportedly 7.4 and 8.45, respectively [65, 66]. Therefore, the expected repulsion between negatively charged nanocatalyst and electron-rich 4-NP/phenolate ions weakened their sorption, which might have reduced the conversion of 4-NP. The lower sorption of reactant in the alkaline pH

range might also come from the increased competition with OH^- anions in solution. The slight increase in conversion at pH 10 is a bit surprising. It is known that presence of increased OH^- ion concentration under strong basic conditions can produce hydroxyl radical, which can attack 4-NP molecules to initiate partial mineralization through conversion to CO_2 and H_2O [67]. Hence, partial oxidative degradation might have proceeded under the conditions. Nonetheless, it is evident that initial pH value of the reaction medium produced significant effect on the conversion of 4-NP with the maximum conversion being obtained at pH 6.

Fig. 3.9. Effect of initial pH value on the conversion of 4-NP in presence of the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. Conditions: 4-NP, 10 mg L^{-1} ; nanocatalyst, 5 mg; NaBH_4 , 8 mg; total volume, 25 mL; temperature, 25°C .

Following the pH optimization experiment, the effect of initial concentration of 4-NP on its conversion was evaluated in the presence of fixed dose (5 mg) of the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst at pH 6. Fig. 3.10 shown the decrease in concentration following conversion to 4-aminophenol, 4-AP. Fig. 3.10 states that in the presence of the nanocatalyst, the concentration of 4-NP decreases acutely at the initial stage and then it goes down only slowly. This slow decreasing tendency towards the end of the reduction

process is relatively catchy at the highest concentration (30 mg L^{-1}). The initial rapid decrease in 4-NP concentration occurred due to both sorption as well as due to catalyst-assisted reduction reaction. The initial sorption of nitrophenolate ions and/or 4-NP molecules is the culmination of synergistic effect of hydrogen bonding and π - π interactions with the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst surface which acted as a relay center for electrons. The slow conversion of 4-NP at the finishing end represents the catalytic reduction only. Almost complete conversion (98.5%) to 4-AP is possible at a lower initial concentration (10 mg L^{-1}) of 4-NP, and the percent conversion is reduced as the initial concentration of 4-NP is increased (inset of Fig. 3.10). Since the nanocatalyst dose was kept constant during the experiment, the available vacant space was not enough for complete sorption of increasing amount of added 4-NP and intermediate ionic products [68]. In other words, the decrease of active catalyst sites due to increased addition of 4-NP hindered the smooth transfer of electrons from BH_4^- to the acceptor 4-NP molecules [69, 70].

Fig. 3.10. Time-dependent change in 4-NP concentration during catalytic reduction over the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. Inset figure shows the final conversions at different initial concentrations of 4-NP. Conditions: nanocatalyst, 5 mg; Cu-Ni NPs, 2 mg; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; temperature, 25°C .

The effect of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst dose in the range of 4–5 mg was studied in the reduction of 4-NP (10 mg L^{-1}) at pH 6, and the conversions are shown in a time-conversion plot (Fig. 3.11). The final conversion of 4-NP to 4-AP increases with increase in the nanocatalyst weight. It is also noticeable that the reduction rate enhanced with the increase in catalyst weight. The introduction of more nanocatalysts means more active catalyst centers are available for transferring electrons to the reactant 4-NP molecules. In another sense, the increased addition of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst for identical amounts of reactant 4-NP increases the availability of electrons for reduction reaction. The increase in catalytic power for increased amount of nanocatalyst dose is recognized as obvious outcome for a good catalyst.

Fig. 3.11. The effect of the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst dose on the time-dependent change in conversion of 4-NP during catalytic reduction. Inset figure shows the final conversions obtained at different nanocatalyst doses. Conditions: 4-NP, 10 mg L^{-1} ; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; temperature, 25°C .

A comparative study of catalytic activity, illustrated in Fig. 3.12, shows that Cu-Ni NPs exhibit pretty good activity for the reduction of 4-NP under identical reaction conditions. It is also evident that the use of functional SiO_2 support for Cu-Ni NPs further

improved the catalytic power in terms of both conversion and reaction rate. The catalysis power of pure and functional SiO₂-supported Cu-Ni NPs was further compared by using the parameter turnover frequency (TOF). The TOF was simply obtained from turnover number (TON)/reaction time, where TON represents the number of 4-NP molecules converted into 4-AP over 1 g of nanocatalyst [71]. The TOFs of Cu-Ni NPs and SiO₂-NH₂/Cu-Ni nanocatalyst are estimated to be 0.1993×10^{19} and 0.1423×10^{20} molecules min⁻¹ g⁻¹, respectively, which indicated a tenfold increase in catalyst efficiency for supported nanocatalyst. The SiO₂ support employed in nanocatalyst development increases the active surface area favoring the sorption of reactant molecules and reducing agents. In addition to this, the improved stability of anchored Cu-Ni NPs also helped to enhance the catalytic power of the SiO₂-NH₂/Cu-Ni nanocatalyst. The reduction reaction of 4-NP in the presence of either NaBH₄ or SiO₂-NH₂/Cu-Ni nanocatalyst produced only 6 to 16% conversion to 4-AP (Fig. 3.13). Figure 3.12 also illustrates that use of SiO₂-NH₂ support along with NaBH₄ sharply increased the conversion of 4-NP to around 23%, understandably through sorption rather than via reduction, and then reaches almost a static value. Comparatively, in presence of SiO₂-NH₂/Cu-Ni nanocatalyst, the conversion of 4-NP is much high (98.5%). The overall comparative analysis suggests that the prepared SiO₂-NH₂/Cu-Ni nanocatalyst functioned efficiently at the pH value of 6, which is near the pH of most supplied water.

Fig. 3.12. Change in conversion of 10 mg L^{-1} of 4-NP at different time intervals in presence of pure Cu-Ni NPs and the nanocatalyst. Conditions: nanocatalyst, 5 mg; Cu-Ni NPs, 2 mg; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; temperature, 25°C .

Fig. 3.13. Change in conversion of 4-NP in presence of (circle) NaBH_4 , (triangle) $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$, (diamond) $\text{SiO}_2\text{-NH}_2 + \text{NaBH}_4$ and (square) $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni} + \text{NaBH}_4$. Conditions: 4-NP, 10 mg L^{-1} ; total volume, 25 mL; pH, 6; temperature, 25°C .

The 4-NP reduction reaction was found dependent on different parameters like reactant pH, concentration, catalyst weight, and catalyst composition. The reduction reaction proceeds by the formation of intermediate products, nitrophenolate ion and borohydride ion derived from 4-NP and NaBH_4 respectively. Since the reduction reaction did not progress in absence of nanocatalyst, even using the reducing agent (Fig. 3.13), it is predictable that reduction of 4-NP followed pseudo-first-order kinetic rate model [58]. In order to reaffirm, the time-dependent and pH-dependent variations in concentration of 4-NP were analyzed by pseudo-first-order and pseudo-second-order kinetic equations (Eqs. 2.2 and 2.3). Both pseudo-first-order and pseudo-second-order kinetic plots for 4-NP were linearized and shown in Figs. 3.14 and 3.15. The rate constants (k_1 and k_2) and correlation coefficients (R_1^2 and R_2^2) obtained from the linearized plots are presented in Table 3.4. The relatively higher values of R_1^2 in both cases of concentration and pH-dependent study indicated that the reduction of 4-NP preferentially followed pseudo-first-order reaction kinetics, which is in agreement with the theoretical prediction. The higher values of rate constant k_1 (min^{-1}) indicated the faster reduction kinetics for the pseudo-first-order rate model. It can also be validated from the rate constant k_1 values for different solution pH (Table 3.4) that at pH 6 the reaction proceeds faster than at other pH values. The performance of our prepared $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst has been compared with the catalytic power of some other catalysts (including precious metals) in terms of pseudo-first-order rate constant, k_1 (min^{-1}) (Table 3.5). The activity of the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is comparable and sometimes even better. It is to be mentioned that reduction conditions are not always the same and the catalyst composition is also different, so they may have substantial effect on the value of rate constant.

Fig. 3.14. Linearized (a) pseudo-first-order and (b) pseudo-second-order kinetic plots obtained from time-dependent change in 4-NP concentration during catalytic reduction over the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. Conditions: nanocatalyst, 5 mg; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; temperature, 25°C

Fig. 3.15. Linearized (a) pseudo-first-order and (b) pseudo-second-order kinetic plots obtained from pH-dependent change in 4-NP concentration during catalytic reduction over the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. Conditions: 4-NP, 10 mg L^{-1} ; nanocatalyst, 5 mg; NaBH_4 , 8 mg; total volume, 25 mL; temperature, 25°C .

Table 3.4. Kinetic parameters of reductive conversion of 4-NP in aqueous solution as a function of initial dye concentration and pH

4-nitrophenol											
Experimental parameters		Pseudo-first-order		Pseudo-second-order		Expt. parameters		Pseudo-first-order		Pseudo-second-order	
Initial conc. of 4-NP (mg L ⁻¹)	E (%)	k ₁ (min ⁻¹)	R ₁ ²	k ₂ (L mg ⁻¹ min ⁻¹)	R ₂ ²	pH	E (%)	k ₁ (min ⁻¹)	R ₁ ²	k ₂ (L mg ⁻¹ min ⁻¹)	R ₂ ²
10	98.5	0.2898	0.9215	0.3795	0.7418	3	73	0.0602	0.9264	0.0395	0.9764
20	95.75	0.1131	0.9656	0.0407	0.7554	6	98.5	0.2898	0.9215	0.3795	0.7418
30	91.67	0.1196	0.9941	0.0177	0.8617	8	72.7	0.0487	0.9875	0.0101	0.9699
						10	86	0.0698	0.9892	0.0202	0.9647
Average			0.9604		0.7863				0.9562		0.9132

Table 3.5. Pseudo-first-order rate constants of some already reported nanocatalysts for reduction of 4-NP.

Catalysts	[4-NP] (M)	[NaBH ₄] (M)	K ₁ (min ⁻¹)	References
AuAg-G	1.0×10^{-4}	1.5×10^{-1}	0.534	[73]
RGO-Ni ₂₅ Co ₇₅	5.0×10^{-3}	15×10^{-1}	0.093	[13]
Fe ₃ O ₄ @C-Pt-Pd	3×10^{-2}	3×10^{-1}	1.212	[74]
SBA-Au _{0.25} Pd _{0.75}	4-NP : NaBH ₄	10 : 500	0.7326	[75]
Ag ₅₀ Ni ₅₀ /RGO	2.5×10^{-4}	1×10^{-1}	2.904	[76]
Cu/Ag	1.0×10^{-4}	3×10^{-1}	0.237	[77]
Pd/Fe ₃ O ₄ @SiO ₂ @m-SiO ₂	1×10^{-2}	5×10^{-1}	0.0348	[78]
Cu-Ni-AAPTMS@GO	5.0×10^{-3}	5.29×10^{-2}	361.08	[19]
CoMn ₂ O ₄	1×10^{-3}	1×10^{-1}	0.897	[79]
Cu ₇₅ Ni ₂₅	5×10^{-4}	5×10^{-3}	1.3512	[53]
Cu ₅₀ Ni ₅₀	5×10^{-4}	5×10^{-3}	0.126	
CuNi/EDA-SBA-15	5×10^{-3}	5×10^{-2}	0.354	[56]
Cu ₇₅ Ni ₂₅ -400	5×10^{-4}	5×10^{-3}	0.2934	[58]
Co-Ni	2×10^{-4}	2×10^{-3}	0.15	[59]
CuNi/Co ₃ O ₄	2×10^{-4}	2×10^{-3}	0.912	[80]
Au-Pd/CeO ₂	1.2×10^{-2}	5×10^{-1}	0.009	[81]
Ni/SiO ₂	1×10^{-4}	2×10^{-1}	0.066	[69]
CuNi@CP NPs	1×10^{-4}	1×10^{-3}	0.00018	[82]
SiO ₂ -NH ₂ /Cu	7.19×10^{-5}	8.5×10^{-3}	0.0874	[38]
NH ₂ -SiO ₂ /Cu-Ni	7.19×10^{-5}	8.5×10^{-3}	0.2898	This work
Cu-Ni NPs	7.19×10^{-5}	8.5×10^{-3}	0.1182	

3.3.4. Reduction of other aromatic nitro compounds

Considering the potentiality of the SiO₂-NH₂/Cu-Ni nanocatalyst in the catalytic reduction of 4-NP molecules, the reduction reaction was extended to few other aromatic nitrosubstituents under identical conditions and the experimental results are displayed in Table 3.6. The progress of the reactions was validated by thin layer chromatography, TLC and a single spot found on the TLC plate confirmed the desirable reduced amino product without impurities. It can be concluded from the table that major substrates are converted into the expected amino products. In the case of 4-bromonitrobenzene (entry 3), the low

yield is due to the relatively strong resonance effect in respect to 4 (*para*) position of bromo group (-Br). On the other, the steric hindrance might have affected the electrophilicity of 3-nitroaniline (entry 4). On the basis of above findings, it can be said that the prepared SiO₂-NH₂/Cu-Ni nanocatalyst has good potential for application in catalyzing organic reactions.

Table 3.6. Catalytic reduction of various nitroaromatic compounds over SiO₂-NH₂/Cu-Ni particles.

Entry	Substrate	Product	Molar ratio (Substrates/NaBH ₄)	Catalyst (g)	Time (min)	Yield (%)	Ref.
1			1:2	0.005	5	83	[57]
2			1:2	0.005	5	81	[57]
3			1:2	0.005	8	38	[57]
4			1:2	0.005	12	57	[57]

3.3.5. Recovery and recycle

The recovery and recyclability of the catalyst are important from the viewpoint of catalyst durability. In order to measure the stability and long-term durability, the recycle experiment of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was carried out for the reduction reaction of 4-NP in presence of NaBH_4 . For this, six consecutive reaction cycles were carried out with the recovered catalyst under identical reaction conditions and the results are presented in Fig. 3.16 and Table 3.7. The plot of $\ln(C_t/C_0)$ against reaction time, t (min), fitted well with the pseudo-first-order kinetics (Fig. 3.16a). From Fig. 3.16b, it is observed that 98.5% conversion in the first cycle decreases gradually to 90.5% in the sixth cycle but still high enough for industrial use. The reaction kinetics slightly slowed down as the reaction time increased from 15 min in the first cycle to 30 min in the sixth cycle. Frequently, it is apparent from the literature that the efficacy of any catalyst in catalytic reaction is reduced in successive experiments [72]. It is probable that small decrease in conversion percent during recycle experiment has originated from small loss of nanocatalyst during the magnetic separation, washing, and reuse of catalyst. Partial leaching and transition of valence state of active metal part during handling are the other probable reasons, which generally influenced the performance of supported nanocatalyst. Despite the slight decrease in reaction kinetics during recycle experiment, we can say that the prepared $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is good enough for application up to 6 cycles as the conversion percent (90%) remained considerably high.

Fig. 3.16. (a) Linearized pseudo-first-order kinetic plots for reduction of 4-NP in presence of the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. (b) Percent conversions of 4-NP during repeated recycle experiment. Conditions: 4-NP, 10 mg L^{-1} ; nanocatalyst, 5 mg; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; temperature, 25°C .

Table 3.7. Recyclability and reusability test over 10 mg of the catalyst.

Entry	Time (min)	Conversion (%)	k (min^{-1})	R ²
1	15	98.5	0.2898	0.9215
2	20	97	0.1452	0.9415
3	20	97.6	0.1719	0.7346
4	20	95	0.1644	0.9842
5	25	95	0.1195	0.9993
6	30	90.5	0.0879	0.9862

3.3.6. Reaction mechanism of 4-NP

The proposed mechanism of the reduction reaction of 4-NP on the surface of the nanocatalyst is demonstrated in Fig. 3.17. Initially, the color of the 4-NP solution is light yellow and in the presence of NaBH_4 , the color of 4-NP changed to yellowish green indicating the deprotonation of 4-NP. 4-NP reacts with NaBH_4 to form nitrosophenol [$\text{C}_6\text{H}_4\text{NO}(\text{OH})$] which rapidly changes to 4-hydroxylaminophenol ($\text{C}_6\text{H}_4(\text{NHOH})\text{OH}$) by further reduction due to its instability [82]. In the reduction process, 4-NP, NaBH_4 and

catalyst act as an electron acceptor, donor and electron transfer mediator, respectively. BH_4^- ions release electrons and hydride ions upon the surface of the catalyst. As a result, active hydrogen species are generated via electron transfer get readily abstracted by phenolate ions to produce 4-AP [12]. The sorption ability of the amino groups is very weak than that of the nitro groups facilitating the product 4-AP was desorbed readily from the catalyst surface once generated [70]. It is concluded that the conversion of 4-NP to 4-AP occurs in three steps: (i) the adsorption of reactants into the external surface of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst, (ii) transfer of electrons from donor, BH_4^- to acceptor, 4-NP and (iii) the desorption of 4-AP.

Fig. 3.17. The proposed mechanism of 4-NP reduction conversion in presence of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst.

3.4. Conclusion

In conclusion, $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ were successfully synthesized through electrostatic-adsorption and in situ simultaneous reduction process via solvothermal method. Various characterization techniques for example FTIR, XRD, XPS, BET and SEM images were used for the confirmation of the chemical composition and morphology of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. Cu-Ni NPs attached on $\text{SiO}_2\text{-NH}_2$ particles are fcc alloy structures confirmed by both XPS and XRD patterns and their average crystallite size is 5.52 nm. But the SEM image indicated the formation of some clustered particles comprising smaller spherical metal particles. XPS demonstrated that Cu^0 , Cu^+ and Ni^{2+} species are present in bimetallic Cu-Ni alloy NPs. The reduction of 4-NP as a model compound has been used for the evaluation of catalytic activity and $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst showed great catalytic activity compared to unsupported Cu-Ni NPs. The conversion of 4-NP to 4-AP in presence of nanocatalyst is attained about 98.5% within 15 min at pH 6. Comparatively, the conversion of 4-NP (92%) and reaction rate over unsupported Cu-Ni NPs are both lower than the supported nanocatalyst. In respect of the initial pH and concentration (reactant) dependent kinetic study, the reduction of 4-NP preferably followed a pseudo-first-order rate kinetic model. $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst also employed the reduction of few other aromatic nitro compounds and got a fair conversion. The recycle experiment of $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst showed good results and the conversion of 4-NP is obtained more than 90% up to sixth cycle. It is concluded that the synthesized $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst exhibits high catalytic activity and can be potentially used as an efficient and sustainable catalyst for various chemical transformations due to easy recovery and long-term durability.

3.5. References

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Chapter-4

**Magnetite Incorporated Amine-Functional
SiO₂ Support for Bimetallic Cu-Ni Alloy
Nanoparticles Produced Highly Effective
Nanocatalyst**

4.1. Introduction

Noble metal nanoparticles (NPs) like Pt, Au, Pd, Rh and Ru have received much attention as catalysts due to their unique features like stability, selectivity, catalysis power and better efficiency [1-6]. However, noble metals are high price and limited availability; thus, researchers are focusing their view on trying alternative catalysts based on transition metals. Researchers are surprised to see that transition metal-based bimetallic nanocatalysts exhibit better activity and selectivity than individual noble metals [7-9]. Their physicochemical properties like specific surface area, electron density, electron storage capacity, functionality and stability enhanced greatly due to synergistic interaction and alloying effect created by metal-to-metal interaction [10-12]. Additionally, these bimetallic particles have large applications such as electronics, photonics, sensing, labeling, imaging and antibacterial agents [13–16].

The present investigation is focused on the preparation of durable and effective bimetallic Cu-Ni alloy nanocatalysts as they are both cheap and available. The magnetic property of Cu-Ni alloy also contributes to applications in electronics, magnetic, metallurgical and medical fields [17–20]. In a previous article, amine functionalized silica ($\text{SiO}_2\text{-NH}_2$) supported bimetallic Cu-Ni alloy (named as $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$) nanocatalyst was fabricated via one-pot in-situ co-reduction of Cu and Ni precursor salts [21]. The amine functionalized SiO_2 support was preferred to facilitate anchoring and fixation of metal atoms, thus enabling improvement in air stability, recyclability and dispersibility during application. Though the $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was stable, but from the industrial perspective the stability seems to be not enough as the recycle experiment for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) indicated a drop in conversion from 98.5% to 90.5% in the 6th cycle. The present investigation is aimed at further improving the stability of $\text{SiO}_2\text{-NH}_2$ supported bimetallic Cu-Ni nanocatalysts during recycling and thus minimize the cost and environment pollution through leakage or washing. As such, magnetic iron oxide (Fe_3O_4) is included in $\text{SiO}_2\text{-NH}_2$ support before modification with Cu-Ni nanoalloy. The addition of Fe_3O_4 in support materials would facilitate the incorporation of Cu and Ni due to the presence of subsurface cation vacancy structure in the Fe_3O_4 (011) surface [22, 23]. Like SiO_2 , Fe_3O_4 as support material offer advantages of high surface area to volume ratio, chemical

inertness, low toxicity and stability [24, 25]. Izgi et al. synthesized $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$, a core-shell type amine functional support by a two-step process and then decorated with Ru via in-situ chemical reduction of RuCl_3 [26]. The objective was to impart magnetic core for effecting efficient recovery of catalyst without using filtration or centrifugation. Veisi et al. had used chitosan-coated core-shell $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$ NPs (NPs) to anchor Pd NPs via in-situ green reduction protocol [27]. In both the above cases, the catalysts were magnetically retrievable and recycled. There are also reports to employ core-shell type $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-NH}_2$ spheres for the removal of Pb^{2+} ions and alkaloids [28, 29]. So far, to our knowledge, no investigation is available on the use of dual $\text{Fe}_3\text{O}_4\text{-SiO}_2$ composite matrix as support for bimetallic catalyst, but a core-shell type $\text{Fe}_3\text{O}_4@\text{SiO}_2$ morphology prepared via a two-step process is tried [26, 27].

Herein, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support is evaluated for bimetallic Cu-Ni alloy NPs. In the previous works [26, 27], the magnetic core inside the SiO_2 layer rather added magnetic property but reasonably failed to improve interaction with metal NPs due to core-shell type morphology. On the contrary, the use of dual $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite matrix as support could directly improve the synergistic interaction of metal NPs with exposed Fe_3O_4 and SiO_2 surfaces. Hence, we can expect an ultimate improvement in catalytic performance and recycle stability. The $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support is prepared via a one-step solvothermal procedure (Fig. 4.1) from a mixture of FeCl_3 , tetraethyl orthosilicate, TEOS, 3-aminopropyl triethoxysilane, APTES and a structure directing agent, cetyltrimethyl ammonium bromide, CTAB. Under the condition, a composite structure comprising Fe_3O_4 and $\text{SiO}_2\text{-NH}_2$ should be formed rather than a core-shell type structure. Hence, it was assumed that simultaneous formation and aggregation of Fe_3O_4 and SiO_2 as well as amine functionalization occurred in alkaline medium under solvothermal condition. Finally, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst particles are obtained by in-situ sorption and chemical co-reduction of Cu^{2+} and Ni^{2+} ions using hydrazine hydrate ($\text{H}_2\text{N-NH}_2\cdot\text{H}_2\text{O}$) as a reducing agent (Fig. 4.1). Structure and morphology of the supported nanocatalyst are confirmed by Fourier Transform infrared, FTIR, electron microscopy, Brunauer–Emmett–Teller, BET surface analysis, X-ray diffraction, XRD and X-ray photoelectron spectroscopy, XPS. The catalytic activity and reusability of the prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst are evaluated for

chemical reduction of 4-nitrophenol, 4-NP a common organic chemical used in the manufacturing of dyes, plasticizers, pesticides, fungicides, and explosives [30].

Fig. 4.1. Preparation scheme of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst.

4.2. Experimental

4.2.1. Materials

Ferric chloride, FeCl_3 , copper sulphate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, nickel sulphate hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and hydrazine hydrate, $\text{H}_2\text{N}-\text{NH}_2 \cdot \text{H}_2\text{O}$ were purchased from Merck, India. Ethylene glycol, EG (Loba Chemie, India), *n*-heptanol (Fisher Scientific, UK), L- ascorbic acid (E-Merck, Germany) and anhydrous sodium acetate, CH_3COONa were used as solvent, reducing agent, capping agent and nucleating agent respectively. Tetraethyl orthosilicate, TEOS from Sigma-Aldrich Chemie GmbH, USA was used as a SiO_2 source. Cetyltrimethylammonium bromide, CTAB from Fluka, Biochemica, Switzerland and 3-aminopropyl triethoxysilane, APTES from TCI, Japan were used as cationic template and $-\text{NH}_2$ functionalizing agent, respectively. Sodium borohydride, NaBH_4 from Smart Lab, Indonesia was used during reductive degradation. 4-Nitrophenol, 4-NP (Loba Chemie, India), nitrobenzene, 4-nitrotoluene, 4-bromonitrobenzene, 3-nitroaniline, diethyl amine, DEA, NaOH, HCl (37%), ethanol, and other chemicals were of analytical grade. Deionized water was obtained from Puricom (Taiwan) by reverse osmosis and UV radiation. All the solutions were prepared in deionized water.

4.2.2. One-step solvothermal synthesis of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites

The one-step solvothermal method was employed for the preparation of magnetic $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support. Briefly, anhydrous FeCl_3 (0.5 g), CTAB (0.3 g) and CH_3COONa (1.5 g) were taken in 20 mL of ethylene glycol followed by the sonication for ~10 min at ambient temperature. Under a constant N_2 flow, the solution was transported into a three-necked round-bottomed flask mechanically stirring at 250 rpm for 30 min. The reaction mixture was then given *n*-heptanol (30 g) and DEA (0.15 g). TEOS (0.3 g) was added dropwise after confirmation of pH at around 10 under mechanical stirring for an additional 30 min. The reaction mixture was shifted into a Teflon-coated stainless-steel autoclave after adding APTES (0.03 g) and then, heated at 200°C for 8 h. The produced composite was washed three times using magnetic separation and decantation to remove any excess CTAB and nonmagnetic by-products before collecting in deionized water.

4.2.3. Synthesis of Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst

A slightly modified method of simultaneous in-situ co-reduction of metal precursor salts was used to create the supported Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst [21]. At first Fe₃O₄-SiO₂-NH₂ (0.3286 g) support spheres were added in 30 mL of distilled water and then sonicated for about 15 min. Equimolar (0.075 M) mixture of CuSO₄.5H₂O (0.5857 g) and NiSO₄.6H₂O (0.6169 g) was taken in 30 mL of distilled water and then the mixture was added slowly into the suspension of support spheres followed by transferring in a round-bottom flask with constant mechanical stirring at 70°C under continuous N₂ flow. During the progress of the reaction, pH was kept at 11 by NaOH. After that, hydrazine hydrate (10 g) was added to the reaction mixture and the reaction lasted for another 2 h. The produced composites were purified by washing three times with deionized water and ethanol to remove any unreacted entities and finally, the nanocatalysts were dispersed in ethanol.

The unsupported Cu-Ni bimetallic NPs were also prepared as reference nanocatalyst material without the Fe₃O₄-SiO₂-NH₂ support. The process and molar ratio of Cu to Ni were kept identical as discussed above. In addition, L-ascorbic acid was used as capping agent and antioxidant before adding the reducing agent.

4.2.4. Characterizations

Cleaned samples were used for all characterizations. FTIR spectrum of each powdered sample was recorded by a FTIR spectrophotometer (Perkin Elmer, FTIR-100, USA) in KBr pellets over the scanning range of 4000–200 cm⁻¹ in the deflection mode. X-ray diffraction patterns by scanning XRD (Bruker D8 Advance, Germany) was obtained by using monochromatic Cu K α radiation ($\lambda \approx 1.5418$ Å), tube voltage of 40 kV, and tube current of 40 mA at room temperature. Diffraction experiment was conducted between 2 θ values of 10°–80° at a continuous scan rate of 10° min⁻¹. The surface elemental composition of dried sample mounted on a carbon tape was measured by XPS (PHI X-tool, ULVAC-PHI, Inc., Japan), equipped with a monochromatic Al K α radiation (1486.6 eV) at 4 W and 15 kV and an X-ray current of 20 mA. The acquisition area and take-off angle were fixed at 14 μ m and 45° respectively and the pressure in the measurement chamber was 8.0×10^{-7} Pa. The step size was 0.25 eV for both survey and

high-resolution spectra (pass energy 280 eV). SEM images were taken to analyze the surface morphology and size distribution. Before SEM (JSM- 6510, JEOL, Japan) observation, the diluted suspension (0.01% solid) was dried on a mica sheet in a vacuum desiccator overnight. To prevent sample damage under electron beam, the dried SEM samples were gold coated before observation. The specific surface area (S_{BET}), average pore diameter and pore volume of the dried samples were estimated by Barrett-Joyner-Halenda, BJH technique using a Brunauer–Emmett–Teller, BET (NOVA3000e, USA) apparatus at 77 K. The magnetic property was analyzed by a vibrating sample magnetometer, VSM (Micro Sense, EV9, USA). Visible spectrophotometer (OPTIMA, SP 300, Japan) was used for recording the color change during catalysis experiment and a pH meter from Mettler Toledo Company (MP 220, Switzerland) was used for adjusting the pH value.

4.2.5. Catalytic activity

The reduction of 4-NP to 4-AP as a model reaction was tested for the catalytic performance of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst followed by the typical reaction procedures with a little change as discussed in subsection 3.2.5.1 in 3rd Chapter. Here, the dose of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was 3 mg.

A few other aromatic nitro compounds were catalytically reduced in presence of the nanocatalysts. The typical reaction procedures as discussed in 3rd Chapters was directly followed.

The recycling test of the nanocatalysts was also performed according to the procedure as discussed in 3rd Chapters.

4.3. Results and Discussion

4.3.1. Characterizations

$\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was synthesized by a two-step process. First, amine functional magnetic $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites were prepared via a modified one-step solvothermal method. Finally, in-situ co-reduction of electrostatically interacted Cu^{2+} and Ni^{2+} ions was carried out in presence of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites using $\text{H}_2\text{N-NH}_2\cdot\text{H}_2\text{O}$ as a reducing agent.

FTIR spectra analysis primarily gives an idea about the change in functional groups on the surface during different stages of nanocatalyst fabrication. Fig. 4.2 shows the FTIR spectra of Cu-Ni NPs, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. The FTIR spectrum of Fe_3O_4 generally shows absorption bands for Fe-O bond at 399.62, 591.26 and 1633.51 cm^{-1} and an intense broad stretching vibration band of O-H for Fe-OH groups at 3399.26 cm^{-1} [31, 32]. In addition to these absorption signals of Fe-O bonds the spectrum of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites (Fig. 4.2b) exhibits characteristic asymmetric stretching vibrations of Si-O-Fe, Si-OH and Si-O-Si at 1027, 900 and 792 cm^{-1} respectively [31, 33]. Two more signals at 1369 and 1557 cm^{-1} represent the C-H stretching and -NH bending vibrations, which implies the successful incorporation of propylamino group from organosilane coupling agent, APTES, on the surface of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites [34]. The bands at 2863 and 2930 cm^{-1} (Fig. 4.2b) correspond to the asymmetric and symmetric stretching vibrations of aliphatic C-H originated from APTES and residual CTAB. In the spectrum of Cu-Ni NPs (Fig. 4.2a), the absorption peaks at 470 and 517 cm^{-1} are attribute to bending vibrations of Ni-O and/or Cu-O bond, while a sharp band at 624 cm^{-1} represents Ni-O-H stretching vibration [35, 36]. The other bands are probably derived from ascorbic acid or ethylene glycol. This result indicates that Cu-Ni surface atoms are partially oxidized in air either during preservation or due to incomplete in-situ co-reduction of precursor ions. In the spectrum of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst (Fig. 4.2c) the absorption peaks in the 373–631 cm^{-1} region can be allocated to the lattice vibration modes of M-O, M-OH bonds [37, 38]. The appearance of aforementioned bands of Fe-O bonds appeared in the spectrum of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites changed following inclusion of Cu-Ni NPs. The interaction of Cu-Ni NPs with functional SiO_2 also results in significant suppression and slight

shifting of N-H bending signal to 1553 cm^{-1} along with relatively larger impacts on Si-O-Fe asymmetric vibrations at 1001 cm^{-1} (Fig. 4.2c). Moreover, the C-H band in the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is hardly visible. Therefore, the overall analyses confirm the decoration of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites with Cu-Ni NPs.

Fig. 4.2. FTIR spectra of (a) Cu-Ni NPs, (b) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and (c) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst in KBr pellets.

The different crystalline phases were identified by XRD patterns as shown in Fig. 4.3. Diffraction pattern of Cu-Ni NPs (Fig. 4.3a) shows the existence of sharp peaks at 2θ values of 43.46° , 44.61° , 50.58° , 51.94° , 74.25° and 76.6° . The characteristic diffraction peaks at 43.46° , 50.58° , and 74.25° represent the (111), (200), and (220) planes of the face-centered-cubic (fcc) metallic Cu (PDF standard cards, JCPDS 04-0836, space group Fm3m) [39]. Whereas, the peaks at 44.61° , 51.94° and 76.6° can be indexed to (111), (200) and (220) fcc structure of Ni metal, matched with the reported value (PDF standard cards, JCPDS 04-0850, space group Fm3m) [40]. The experimental lattice parameters for Cu ($3.6046\text{ \AA}$) and Ni ($3.5162\text{ \AA}$) are in good agreement with the lattice parameter for pure Cu ($3.614\text{ \AA}$, PDF# 00-004-0836) and pure Ni ($3.524\text{ \AA}$, PDF# 00-004-0850) [41]. Additionally, the slightly lower experimental lattice parameter for Cu compared to

standard lattice parameter ($3.614 \text{ \AA}$) is attributed to the incorporation of Ni metal. These results indicate that in Cu-Ni NPs, Cu and Ni are present in different metallic phases with no sign of other species or oxides. Despite this above finding, formation of negligible amount of metallic oxide, not detectable by XRD, is still possible under the existing preparation condition. The percentages of Cu^0 and Ni^0 in bimetallic Cu-Ni NPs based on the (111) crystal plane is estimated as $\sim 51.77\%$ and $\sim 48.23\%$, respectively. These calculated values matched well with the Cu-Ni molar ratio (1:1) in the recipe. The average crystallite sizes of Cu and Ni NPs in bare Cu-Ni NPs are 57.81 and 14.36 nm respectively. The diffraction pattern of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites (Fig. 4.3b) display signals at 2θ values of 30.28° , 35.72° , 43.33° , 53.78° , 57.28° and 62.97° which are assignable to (220), (311), (400), (422), (511) and (440) planes of cubic inverse spinel Fe_3O_4 (JCPDS 03-0863) respectively [42, 43]. The average crystallite size of Fe_3O_4 in $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite calculated from Debye–Scherrer formula, is 23.56 nm. Comparatively, the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst (Fig. 4.3c) shows almost all diffraction signals of Fe_3O_4 with three new intense but broad diffraction signals at 43.64° , 50.78° and 74.46° . These signals are corresponding to (111), (200) and (220) planes of fcc structure of pure bimetallic Cu-Ni (1:1) alloy as no distinct signal due to individual neat Cu and Ni metals can be identified. The average crystallite size of Cu-Ni alloy in the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst is only 6.3 nm. The smaller crystallite size of bimetallic Cu-Ni alloy particles indicates that amine functionality in magnetic SiO_2 support favored homogeneous nucleation and growth. This above comparative interpretation of XRD diffractions indicates that $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst is successfully prepared via co-reduction of Cu and Ni precursor salts.

Fig. 4.3. XRD spectra of (a) Cu-Ni NPs, (b) Fe₃O₄-SiO₂-NH₂ composites and (c) Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst.

The elemental composition by XPS survey spectrum in Fig. 4.4A exhibits the presence of C1s, O1s, Si2p, Fe2p3, Cu2p and Ni2p signals in the Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst. The atomic concentrations (%) and binding energy of synthesized particles in XPS results are shown in Table 4.1. Additionally, the core-line spectrum of each Cu2p and Ni2p (Fig. 4.4B, C) can be differentiated into four distinct satellite signals which ultimately show the existence of Cu⁰, Cu⁺, Cu²⁺ and Ni²⁺ in the prepared nanocatalyst [44, 45]. It is therefore reasonable to conclude from XRD and XPS results that metal oxide is formed only at the nanocatalyst surface in contact with air.

Fig. 4.4. (A) XPS survey spectra of (a) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites, (b) Cu-Ni NPs and (c) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst. Core-line spectra of (B) Cu 2p and (C) Ni 2p in (d, f) Cu-Ni NPs and (e, g) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst.

Table 4.1. Atomic concentrations and binding energy in XPS results of synthesized particles.

Particles	Atomic concentrations (%)							Binding energy (eV)			
	C1s	N1s	O1s	Si2p	Cu2p3	Ni2p3	Fe2p3	Cu2p		Ni2p	
								Cu2p _{3/2}	Cu2p _{1/2}	Ni2p _{3/2}	Ni2p _{1/2}
Cu-Ni	58.36	5.78	27.56	-	3.93	4.39	-	933.5 942.5	953.5 961.25	854.5 860.25	872.5 879
$\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$	28.28	-	52.36	9.94	-	-	9.04	-	-	-	-
$\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$	40.77	-	45.12	1.58	3.05	4.99	4.48	933.5 942.5	952.75 961.25	854.5 860.25	873 878.5

The surface morphology, size distribution and physical state of aggregation of the nanocatalyst and associated particles were analyzed by SEM images as illustrated in Fig. 4.5. The unmodified Cu-Ni NPs shown in Fig. 4.5a are composed of many tiny (137 nm) spherical particles, which are visibly aggregated into cluster. This cluster formation was affected by the metal-metal interaction and magnetic property [2]. $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites prepared by one-step solvothermal process are mostly spherical (Fig. 4.5b), dispersity index is apparently high and the surface is heterogeneous. Most likely, the heterogeneous surface structure is derived from the Fe_3O_4 NPs formed near the surface of amine functional SiO_2 surface. Under the preparation conditions some free iron oxide NPs might have also been produced. The average size of incorporated Fe_3O_4 NPs is roughly 4.3 nm. In case of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst, a clear boundary layer among particles can be observed. Smaller Cu-Ni alloy NPs with sizes between 12 and 22 nm are tightly packed into larger particles. The overall morphology of the nanocatalyst is noticeably different from the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support. Particles similar to composite support is rarely visible in the SEM image of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. The size distribution could not be compared as they are very much polydispersed. It is clear that there is a distinct dissimilarity in morphology between support materials and supported nanocatalyst.

Fig. 4.5. SEM images of (a) Cu-Ni NPs, (b) Fe₃O₄-SiO₂-NH₂ composites, and (c) Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst.

The N₂ adsorption-desorption isotherms of Fe₃O₄-SiO₂-NH₂ composites and Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst are shown in Fig. 4.6. In both cases, the adsorption follows mesoporous type IV isotherms [46, 47]. The sharp increase in adsorption at the relative pressure of 0.3 in Fe₃O₄-SiO₂-NH₂ composites indicates the presence of porous structure, which may also arise from surface heterogeneity. On the other, the adsorption-desorption isotherm of the Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst flattens sharply, reflecting a decrease in porosity or surface heterogeneity, which is ascribed to the anchoring of Cu-Ni NPs. The BET specific surface areas of Fe₃O₄-SiO₂-NH₂ composite support and Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst also revealed a decrease from 280.5 to 108.9 m² g⁻¹ (Table 4.2) due to surface coverage of some pores by Cu-Ni alloy NPs [46, 47]. This is to mention that average diameter (12–22 nm) of Cu-Ni alloy NPs is larger

than the average pore diameter (3.4 nm) in $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ support materials. On the contrary, the average pore diameter in $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst increases to 6.57 nm.

Fig. 4.6. N_2 adsorption-desorption isotherms of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites (blue line) and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst (red line).

Table 4.2. BET and BJH physicochemical parameters.

Materials	BJH			BET surface area ($\text{m}^2 \text{g}^{-1}$)
	Surface area	Pore volume	Pore radius	
	($\text{m}^2 \text{g}^{-1}$)	(cc g^{-1})	(nm)	
Cu-Ni	6.62	0.017	1.906	7.156
$\text{NH}_2\text{-SiO}_2\text{-Fe}_3\text{O}_4$	90.638	0.086	1.724	280.489
$\text{NH}_2\text{-SiO}_2\text{-Fe}_3\text{O}_4/\text{Cu-Ni}$	118.906	0.280	3.286	108.86

The magnetic hysteresis loops of Cu-Ni NPs, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst measured by VSM at room temperature are shown in Fig. 4.7. Independent of nature, the hysteresis loops of particles show almost zero coercivity and remanence. The saturation magnetization of neat Cu-Ni NPs is 23.38 emu g^{-1} (Fig. 4.7a). Whereas, the saturation magnetization values of iron oxide containing magnetic $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst are 31.45 and 27.76 emu g^{-1} respectively (Fig. 4.7b, c). The classic “S” shape reversible magnetization curve confirms the paramagnetic character of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst. The relatively strong paramagnetic property obviously ensured the magnetic separation and recovery of the nanocatalyst.

Fig. 4.7. VSM curves of (a) Cu-Ni NPs, (b) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and (c) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst.

4.3.2. Formation mechanism of the nanocatalyst

The $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst was synthesized by in situ co-reduction Cu and Ni precursor salts in presence of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites. In the first step, a one-step solvothermal route comprising simultaneous co-precipitation of Fe^{2+} and Fe^{3+} and hydrolysis of TEOS was employed for preparing the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites.

$\text{Fe}(\text{OH})_3$ produced from Fe^{3+} precursor salts was reduced to $\text{Fe}(\text{OH})_2$ in presence of ethylene glycol, a mild reducing agent, at 200°C [48, 49]. The formation of Fe_3O_4 particle nuclei was then followed by the combination of Fe^{3+} and Fe^{2+} hydroxides. The reactions are:

It is speculated that almost simultaneously, TEOS started to hydrolyze with the aid of DEA around the Fe_3O_4 particle nuclei forming $\text{Fe}_3\text{O}_4\text{-SiO}_2$ and grafted with APTES to form $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites. Since simultaneous co-precipitation of Fe salts was continued, there is an extreme possibility of further nucleation and coordination of Fe_3O_4 nuclei via -NH_2 functional group on the surface of already formed $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and subsequent surface modification with aminated SiO_2 . Thus, the ultimate $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites are expected to be composed of Fe_3O_4 particles in SiO_2 matrix. The hydrolysis reactions and grafting of APTES can be symbolically written as.

In the second step, the formation of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was affected by adding the precursors of Cu^{2+} and Ni^{2+} in presence of $\text{H}_2\text{N-NH}_2$, a reducing agent. During the process, Cu^{2+} ions and Ni^{2+} ions interacted with the surface of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites via amino (-NH_2), silanol ($\equiv \text{Si-OH}$), and siloxane groups (Si-O-Si). All probable coordination paths of metal ions are shown in Fig. 4.8. Co-

reduction of metal ions was followed immediately producing the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst.

Fig. 4.8. Probable interactions between $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and M^{2+} ions (Cu^{2+} / Ni^{2+}) during in-situ co-reduction of Cu and Ni precursor salts.

4.3.3. Catalytic activity

The performance of prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was tested for the reductive reduction of 4-nitrophenol (4-NP), a model aromatic nitro compound. 4-NP is a highly toxic organic compound that causes skin and eye irritation, shortness of breath, rapid heartbeat and weakness. Comparatively, the reduced product, 4-AP is less toxic and more biodegradable in air.

The pH-dependent study in the pH range of 3–10 (Fig. 4.9) shows that a maximum conversion of 99.5% is achievable at pH 6 within 10 min in presence of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. A comparative study with $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst [21] indicates that inclusion of iron oxide in support materials improves the

reduction rate and conversion to 4-aminophenol (4-AP). Hence, it can be said that Fe_3O_4 in support materials assisted the sorption of 4-NP on the nanocatalyst surface, enhanced electron density and storage capacity and thus favored the smooth electron-transfer from the reducing agent, NaBH_4 , to the reactant 4-NP.

Fig. 4.9. Effect of initial pH value on the conversion of 4-NP in presence of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst. Conditions: 4-NP, 10 mg L^{-1} ; nanocatalyst, 3 mg; NaBH_4 , 8 mg; total volume, 25 mL; and temperature, 25°C .

The impact of initial concentration of reactant, 4-NP, in presence of identical amount of nanocatalyst (3 mg) was then studied at pH 6 and results are presented in Fig. 4.10. Independent of initial concentration, the concentration of 4-NP decreases rapidly up to 2 min and then goes down slowly. The initial rapid decrease in 4-NP concentration up to 2 min is associated with sorption and the comparatively slower decrease in 4-NP concentration towards the end of the reaction is due to the catalytic conversion to 4-AP. Maximum conversion to 4-AP is obtained at the initial concentration of 10 mg L^{-1} , because, the catalyst dose was kept identical in all experiments. Hence, the active catalyst site is not enough when the initial concentration of 4-NP exceeds 10 mg L^{-1} . This is to mention that in all cases a higher conversion of 4-NP is obtained in presence of $\text{Fe}_3\text{O}_4\text{-}$

SiO₂-NH₂/Cu-Ni nanocatalyst than that in presence of SiO₂-NH₂/Cu-Ni nanocatalyst [21].

Fig. 4.10. Time-dependent change in 4-NP concentration during catalytic reduction over the Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst. Inset figure shows the final conversions at different initial concentrations of 4-NP. Conditions: nanocatalyst, 3 mg; NaBH₄, 8 mg; total volume, 25 mL; pH, 6; and temperature, 25°C.

The variation of nanocatalyst dose in the range of 1–4 mg shows that 3 mg loading is enough to achieve maximum reduction capacity for 25 mL of 10 mg L⁻¹ 4-NP aqueous solution (Fig. 4.11). Here, metal catalyst functioned as a relay center for smooth transfer of electrons from BH₄⁻ to 4-NP molecules. Hence, more catalyst should provide more active sites for electron transfer and sorption of reactant molecules. However, an increase in nanocatalyst amount to 4 mg reduces reduction capacity to 95%. Increasing amount of nanocatalyst (4 mg) possibly reduces the total surface area through coagulation.

Fig. 4.11. Effect of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst dose on the time-dependent variation in conversion of 4-NP during catalytic reduction. Inset figure shows the final conversions obtained at different nanocatalyst doses. Conditions: 4-NP, 10 mg L^{-1} ; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; and temperature, 25°C .

Comparative study of catalytic activity shown in Fig. 4.12a, suggests that use of magnetic amine functional SiO_2 support for Cu-Ni NPs enhances the performance of nanocatalyst for the reduction of 4-NP under the same reaction conditions. It is obvious that use of magnetic SiO_2 support improved the active surface area for the sorption of 4-NP molecules and borohydrate reducing agent, a prerequisite condition for efficient catalysis. It is also reasonable to assume that supported Cu-Ni NPs are less aggregated compared to neat Cu-NPs due to linkage with the functional support. Thus, the interaction of metal to metal and metal to supporting materials along with higher stability all helped to improve the catalytic efficiency [50]. It is also interesting to see that $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support themselves possessed significant sorption and catalytic property, produced around 53% conversion of 4-NP after 50 min. Turn over frequency (TOF), defined by turn over number (TON)/reaction time, was also used to compare the catalytic power. The TOFs of Cu-Ni NPs, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst are obtained as 5.11×10^{18} , 8.56×10^{17} and 3.59×10^{19}

molecule's $\text{min}^{-1} \text{g}^{-1}$ respectively. These results again confirmed the increase in catalytic activity for the supported nanocatalyst. These findings are based on alloying effect, higher stability as well as metal to metal and metal to support interactions. Thus, the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst can function as a potential reductive catalyst. It is noteworthy to mention that neither $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nor NaBH_4 alone possesses catalytic activity as the conversion curves almost flattens after 10 min (Fig. 4.12b). The initial sharp increase in conversion possibly results from the sorption of 4-NP.

Fig. 4.12. (a) Change in conversion of 10 mg L^{-1} of 4-NP at different time intervals in presence of pure Cu-Ni NPs (diamond), $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites (triangle) and the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst (cube). Conditions: Cu-Ni NPs, 1.1 mg; $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$, 1.9 mg; $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst, 3 mg; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; and temperature, 25°C . (b) Change in conversion of 4-NP in presence of NaBH_4 (triangle), $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ (diamond), and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni} + \text{NaBH}_4$ (cube). Conditions: 4-NP, 10 mg L^{-1} ; total volume, 25 mL; pH, 6; temperature, 25°C .

Temperature effect on conversion percent was also measured by running catalysis at 10, 25 and 40°C respectively (Fig. 4.13). It is observable that maximum conversion of 100% can be attained within 8 min at 40°C . The increase in catalysis power is a general property of any good catalyst. It is apparent that increase of temperature increased the energy of reactant molecules and hence reduces the energy barrier for successful conversion of reactant into product.

Fig. 4.13. Effect of reaction temperature on the conversion of 4-NP in presence of 3 mg of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. Conditions: 4- NP, 10 mg L^{-1} ; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; and temperature, 25°C .

The above experiments suggested that chemical reduction of 4-NP proceeds well with the fabricated $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst in presence of NaBH_4 reducing agent. Hence, theoretically it can be anticipated that the reduction reaction followed pseudo-first-order kinetic model. In order to reassess the findings, the time-dependent and pH-dependent changes in concentration of 4-NP following catalysis reactions were applied to pseudo-first-order and pseudo-second-order kinetic models. The linear forms of pseudo-first-order and pseudo-second-order kinetic plots are shown in Figs. 4.14 and 4.15. The estimated values of correlation coefficients obtained from linearized plots (Table 4.3) shows that reduction of 4-NP enthusiastically followed pseudo-first-order reaction as values of R_1^2 are comparatively higher in both concentration and pH-dependent experiments. The relatively higher value of first-order rate constant, k_1 (min^{-1}), indicated the faster reduction kinetics for the pseudo-first-order rate model. It is also clear that reaction goes faster at pH 6 as the corresponding rate constant (k_1) is the highest. A comparative performance of our prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$

nanocatalyst with already available nanocatalyst (including unsupported metals) in terms of pseudo-first-order rate constant, k_1 (min^{-1}) is presented in Table 4.4. The important point is the improvement in reaction rate following incorporation of iron oxide in amine functional SiO_2 support. This improvement in performance is based on synergistic effects of interaction of metal to iron oxide and SiO_2 , as well as substantial catalytic property of iron oxide itself. In comparison with other catalytic systems, the activity of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is proportionately good and sometimes even observed better. Thus, the simple and easily prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst can be a good replacement for unsupported metal nanocatalyst in the catalytic hydrogenation of 4-NP.

Fig. 4.14. Linearized (a) pseudo-first-order and (b) pseudo-second-order kinetic plots obtained from time-dependent change in 4-NP concentration during catalytic reduction over the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. Conditions: nanocatalyst, 3 mg; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; and temperature, 25°C .

Fig. 4.15. Linearized (a) pseudo-first-order and (b) pseudo-second-order kinetic plots obtained from pH-dependent change in 4-NP concentration during catalytic reduction over the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. Conditions: 4-NP, 10 mg L^{-1} ; nanocatalyst, 3 mg; NaBH_4 , 8 mg; total volume, 25 mL; and temperature, 25°C .

Table 4.3. Kinetic parameters of reductive conversion of 4-NP in aqueous solution at different initial reactant concentrations and pH values.

Experimental parameters	Initial concentration					pH			
	10 (mg L^{-1})	15 (mg L^{-1})	20 (mg L^{-1})	25 (mg L^{-1})	30 (mg L^{-1})	3	6	8	10
Reduction Efficiency (%)	99.5	97.3	98	96.4	93.83	96	99.5	95	92.5
$k_1 (\text{min}^{-1})$	0.5388	0.3697	0.3807	0.3262	0.3183	0.3197	0.5388	0.3796	0.255 1
R^2_1	0.9805	0.9804	0.9685	0.9906	0.9704	0.9993	0.9805	0.8931	0.989
$k_2 (\text{L mg}^{-1} \text{min}^{-1})$	0.4983	0.2167	0.1351	0.0802	0.0519	0.19	0.4983	0.2265	0.127 7
R^2_2	0.8262	0.7706	0.9678	0.9148	0.9275	0.9064	0.8262	0.8399	0.936 8

Table 4.4. Pseudo-first-order rate constants of some reported nanocatalysts for reduction of 4- NP.

Catalysts	[4-NP] (M)	[NaBH ₄] (M)	k ₁ (min ⁻¹)	References
Fe ₃ O ₄ @COF-Au	1.8 × 10 ⁻³	0.99	0.222	32
PCA/PDA/SFNPs-3	1 × 10 ⁻⁴	0.1	0.3504	43
Fe ₃ O ₄ @C-Pt-Pd	3 × 10 ⁻²	3 × 10 ⁻¹	1.212	52
PCP@Au-Ag	2.0×10 ⁻⁴	1.5×10 ⁻²	0.1722	53
Cu NPs	1.2 × 10 ⁻⁴	0.02	0.09529	54
Fe ₃ O ₄ @SiO ₂ -Au@mSiO ₂	5 × 10 ⁻³	0.2	0.42	55
AuPt@BGNs/Fe ₃ O ₄	1 × 10 ⁻²	3	9.9096	56
GO@Fe ₃ O ₄ -Au	1 × 10 ⁻²	0.1	1.932	57
CoMn ₂ O ₄	1 × 10 ⁻³	0.1	0.897	58
Fe ₃ O ₄ /SiO ₂ -H ₂ @CS/Pd	2.5 × 10 ⁻³	2.5×10 ⁻⁴	0.72	27
Fe ₃ O ₄ @PANI@Au	1 × 10 ⁻²	0.1	0.5178	59
Fe ₃ O ₄ @Cu	1.499 × 10 ⁻³	1.316 × 10 ⁻³	2.744	60
Fe ₃ O ₄ @SiO ₂ @C-Ni-500	1 × 10 ⁻⁴	5 mg	0.339	61
Fe ₃ O ₄ /SiO ₂ /HPG-Pt	0.01	0.1	4.14 × 10 ⁻¹	62
AuNC@BNNSs	2.0×10 ⁻⁴	0.02	0.581	63
NH ₂ -SiO ₂ /Cu-Ni	7.19 × 10 ⁻⁵	8.5 × 10 ⁻³	0.2898	21
Au/SiO ₂ /Fe ₃ O ₄	5 × 10 ⁻³	0.2	0.468	46
Fe ₃ O ₄ -SiO ₂ -NH ₂ /Cu-Ni	7.19 × 10 ⁻⁵	8.5 × 10 ⁻³	0.5888	This work

4.3.4. Reduction of other aromatic nitro compounds

The usefulness of the Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst was further examined by carrying out reduction of a few other aromatic nitro-compounds. All reactions were carried out under identical reaction conditions at 70°C in presence of 5 mg of

nanocatalyst. The reaction progress was monitored by thin layer chromatography, TLC and purity of the respective amino product was confirmed by a single spot on the TLC plate. The results depicted in Table 4.5 indicates fairly good yield for almost all products. The lowest yield from *m*-amino-nitrobenzene (entry 4) is possibly due to the relatively strong resonance or hindrance effect that might have affected the electrophilicity. Therefore, the prepared Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst has good prospect for application in reduction reactions. The proposed mechanism of 4-NP reduction reaction was explained in 3rd chapter. Overall, the conversion of 4-NP to 4-AP occurs in three steps: (i) the adsorption of reactants and reducing agents onto the surface of the Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst, (ii) transfer of electrons from donor, BH₄⁻ to acceptor, 4-NP and (iii) the desorption of product 4-AP.

Table 4.5. Catalytic reduction of various nitroaromatic compounds over Fe₃O₄-SiO₂-NH₂/Cu-Ni particles

Entry	Substrate	Product	Molar ratio (Substrates/NaBH ₄)	Catalyst (g)	Time (min)	Yield (%)
1			1:2	0.005	5	93
2			1:2	0.005	5	82.68
3			1:2	0.005	8	80.76
4			1:2	0.005	12	66

4.3.5. Recovery and recycle

The recovery and recyclability of the Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst was evaluated to measure the sustainable use for practical applications. The reduction reactions of 4-NP over six consecutive cycles were carried out in presence of recovered Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst under ambient conditions using borohydride reducing agent. After each cycle of 4-NP reduction, the nanocatalyst was recovered magnetically, washed several times with water and ethanol before reuse. The obtained results shown in Fig. 4.16a indicates 100% retention of initial catalytic activity as the conversion of 4-NP to 4-AP remained 100%. The slight fall in conversion during the initial three runs can be considered within the measurement error. However, the interesting finding is the almost 5-fold increase in reaction kinetics (Fig. 4.16b, Table 4.6) during 6th reaction cycle. This result is quite surprising. The phase structure of the

recovered nanocatalyst after the 6th run was investigated by recording XRD pattern. It can be seen from Fig. 4.17 that all diffraction signals due to (111), (200) and (220) planes of pure fcc Cu-Ni alloy at 2θ values of 43.64° , 50.78° and 74.46° are retained in the reused and washed nanocatalyst (after 6th run) without any distortion or deviation. But the diffraction signals corresponding to both Fe_3O_4 and Cu-Ni alloy NPs became more intense after reuse. The average crystallite size of Cu-Ni nanoalloy in the reused washed nanocatalyst is estimated as 10.8 nm, slightly increased from that initial (6.3 nm) used in the first run. Hence, the repeated use and washing of nanocatalyst during recycle experiment did not produce agglomeration or reduction in overall active surface area. The increased reaction kinetics of the reused nanocatalyst is somehow promoted by better sorption of reactant molecules and smooth transfer of electrons. Nonetheless, it is important to conclude that the prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst has improved catalytic activities and higher stability compared to the previously prepared $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst [21]. Thus, the synergistic interactions of Cu-Ni nanoalloy with iron oxide and amine functional groups on the SiO_2 support, enhanced electron density and storage capacity significantly promoted the catalytic activity [51]. Moreover, the whole preparation of comparatively stable as well as highly effective $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was possible by a simple two-step process.

Fig. 4.16. (a) Percent conversions of 4-NP during recycle experiment, and (b) linearized pseudo-first order kinetic plots during catalytic recycle of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{CuNi}$ nanocatalyst for the reduction of 4-NP. Conditions: 4-NP, 10 mg L^{-1} ; nanocatalyst, 10 mg ; NaBH_4 , 16 mg ; total volume, 50 mL ; pH, 6; and temperature, 25°C .

Fig. 4.17. XRD diffraction patterns of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst (a) before catalysis and (b) after 6th cycle of catalysis.

Table 4.6. Pseudo-first-order rate constants and conversions during recycle experiment of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst in the reduction reaction of 4-NP.

Cycle No.	Time (min)	Conversion (%)	k_1 (min^{-1})	R_1^2
1	10	99.5	0.4887	0.96
2	10	97.5	0.9156	0.9184
3	10	98	0.4286	0.9749
4	10	100	0.5716	0.6203
5	5	100	1.3562	0.6607
6	5	100	2.7854	0.5906

4.4. Conclusion

In this protocol, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites are fabricated using a simple and scalable one-step solvothermal method to support bimetallic Cu-Ni alloy NPs. XRD patterns indicate the formation of metallic fcc Cu-Ni alloy without any ionic phase but FTIR and XPS analyses show the existence of oxide particles, possibly resulting from surface oxidation of metals during handling and storage. The average crystallite sizes of Fe_3O_4 and Cu-Ni NPs in the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst are 23.6 and 6.3 nm, respectively. SEM images reveal that both $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalysts possess a heterogeneous non-smooth surface. The nanocatalyst exhibits a strong paramagnetic character and is separable from the media magnetically. The reductive catalytic reduction of 4-NP to 4-AP in the presence of nanocatalyst shows conversion up to 99.5% within 10 min at pH 6. Both, the reaction kinetics and recycle stability of the nanocatalyst remarkably improve following the inclusion of magnetic iron oxide in the SiO_2 matrix. The phase structure of supported fcc Cu-Ni alloy NPs did not change after the 6th reaction cycle and interestingly, a five-fold increase in reaction rate is observed during the recycle experiment. Overall, the direct interaction of Cu-Ni alloy NPs with iron oxide and functional SiO_2 is possible due to the use of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support, which finally enhances the catalytic performance. Hence, this work allows a facile and efficient synthetic approach for the preparation of highly effective and stable $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst.

4.5. References

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Chapter-5

A potential Recyclable Catalyst: In Situ Growth of Bimetallic Cu-Ag Nanoalloy on the Magnetic $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ Nanocomposite Support Using a Green Approach

5.1. Introduction

Transition metal based bimetallic NPs (NPs), formed by the integration of different metals, are attracting much attention from researchers as they show many interesting and improved properties [1–3]. According to the mixing patterns, these bimetallic NPs are normally of three categories like core@shell nanostructures, heterostructures, and alloy structures [4–6]. In many cases, due to strong synergistic interaction and alloying effects, bimetallic NPs have shown intriguing properties like high stability, selectivity, functionality, specific surface area, electron storage capacity, and electron density [4, 7, 8]. As such these transition metal based bimetallic NPs are used with huge potentiality in catalysis, electronics, photonics, sensing, labeling, data storage, imaging, antibacterial agents and in many instances their performance proved comparable to monometallic precious metals (e.g., Pt, Au, Pd, Rh and Ru) [8, 9]. Numerous methodologies such as polyol, chemical co-reduction, solvothermal, thermal decomposition, ion implantation, sonochemical, electrochemical deposition etc. have been used for synthesizing bimetallic Au-Pt, Cu-Ag, Pd-Ir, Au-Ag, Ag-Pd, Fe-Pt, Co-Ni, Cu-Ni, Au-Pd and Cu-Pd materials [8, 10–17].

The present research is centered on the fabrication of effective and durable bimetallic Cu-Ag alloy nanocatalyst. Individually, Cu and Ag metals possess promising catalytic, biological and optical properties [18, 19]. They also exhibit good antimicrobial property and have been recommended for relevant use in wound dressings, health care appliances, personal care products, military protective clothing and apparel, food packaging, water filters etc. [20, 21]. However, in many of these applications, recovery and reuse of spent bimetallic Cu-Ag NPs are often hampered due to aggregation, oxidation and leaching, and thus ultimately reduces the performance [22–25]. The use of supporting materials such as SiO₂ [26, 27], cellulose [28], carbon [29, 30], graphene [31, 32] and zeolites [33] has been proved beneficial for preventing aggregation and thus improved mechanical strength, stability and selectivity. In previous investigations, we observed a dramatic improvement in catalytic activity for both monometallic Cu as well as bimetallic Cu-Ni alloy NPs after immobilization on mesoporous SiO₂-NH₂ support [18, 24]. Following these works, in another recent groundbreaking work we found that

inclusion of magnetic Fe_3O_4 NPs in mesoporous $\text{SiO}_2\text{-NH}_2$ support sharply improve the reaction rate, stability and recyclability of immobilized Cu-Ni NPs [8]. The subsurface cation vacancy structure in Fe_3O_4 (111) surface promoted the incorporation of Cu and Ni [34, 35]. In order to reaffirm the findings, here we immobilized catalytically less active Cu and Ag on magnetic mesoporous $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support. So far, core-shell type magnetic SiO_2 microspheres have been evaluated for potential applications in biological and environmental areas [36–38], but little is known about it as support material for bimetallic Cu-Ag alloy NPs. However, support materials like graphene [39–41], SiO_2 [42, 43], metal oxides [44, 45] and cellulose acetate [46] have been employed for decoration with Cu-Ag alloy NPs.

Here, magnetic mesoporous $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support is first prepared in one-pot by simultaneous co-precipitation of iron salts (Fe^{2+} and Fe^{3+}) and alkaline hydrolysis-condensation reaction of tetraethyl orthosilicate, TEOS in presence of solid SiO_2 sphere using hexamethylene diamine, HMDA and cetyltrimethylammonium bromide, CTAB as functional agent and porogen, respectively. Finally, the nanocatalyst named as $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ is prepared by in-situ adsorption and co-reduction of Cu and Ag salts using D-glucose as a green reducing agent. The preparation scheme is shown in Fig. 5.1. It is believed that the dual magnetic and amine functionality present near the surface of core-shell type $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite would enhance the synergistic interaction and fixation of Cu-Ag NPs [8]. On the other, the mesoporous SiO_2 layer would improve the contact area, desirable for improved catalytic activity. The step-wise preparation of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst is confirmed by Fourier Transform infrared, FTIR, electron micrographs, X-ray diffraction, XRD, Brunauer–Emmett–Teller, BET surface analysis and X-ray photoelectron spectroscopy, XPS. Finally, the catalytic activity of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst for the reduction of 4-nitrophenol, 4-NP to 4-aminophenol, 4-AP is evaluated and compared with those of reference materials like $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$, $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$, $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$, $\text{SiO}_2/\text{Fe}_3\text{O}_4/\text{Cu-Ag}$ and Cu-Ag. The role of magnetic $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ support as well as influence of each individual component (e.g., Fe_3O_4 , mesoporous SiO_2 layer) in support material is discussed. The

effect of calcination at 400°C on the catalytic property of respective $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ /Cu-Ag nanocatalyst and unsupported bimetallic Cu-Ag NPs is also studied.

Fig. 5.1. Preparation scheme of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ /Cu-Ag nanocatalyst

5.2. Experimental

5.2.1. Materials

Ferric chloride, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ferrous sulfate hexahydrate, $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, copper sulfate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and silver nitrate, AgNO_3 were purchased from Merck, India. D-glucose, $\text{C}_6\text{H}_{12}\text{O}_6$ and trisodium citrate, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ from Merck, India was used as reducing agents, and stabilizer/capping agents, respectively. SiO_2 suspension in water donated by Nippon Shokubai Co. Ltd. Japan, was used after centrifugal washing. Cetyltrimethylammonium bromide, CTAB and hexamethylene diamine, HMDA both purchased from Fluka, Biochemica, Switzerland, were used as a porogen and $-\text{NH}_2$ functionalizing agent, respectively. Sodium borohydride, NaBH_4 from Smart Lab, Indonesia was used during catalytic reduction of 4-NP. n-Hexane (E Merck, Germany), 4-NP (Loba Chemie, India), nitrobenzene (Thomas Baker, India), 4-nitrotoluene (BDH, UK), 4-bromonitrobenzene and 3-nitroaniline (Thomas Baker, India), NH_4OH (25%), NaOH , HCl (37%), ethyl acetate, ethanol, and other chemicals used during the investigation were of either analytical or reagent grade. Deionized water was obtained from Puricom (Taiwan) by reverse osmosis and UV radiation.

5.2.2. Preparation of magnetic mesoporous $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite particles

The magnetic mesoporous $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite particles were synthesized as reported in the literature [8]. First, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.070 g) and $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ (0.060 g) were taken in a beaker containing 20 mL of deionized water. Another beaker was used for the dispersion of supplied SiO_2 (1.0 g solid) and cetyltrimethylammonium bromide, CTAB (0.3 g) in 40 mL of water-ethanol (50:50) mixture. Under a constant N_2 flow, both of these solutions were added into a three-necked round-bottomed flask and mechanically stirred at 250 rpm. The pH of the reaction mixture was maintained at about 10 by adding 10 mL of 25% NH_4OH solution. After the addition of TEOS (0.63 g) dropwise, HMDA (0.063 g) was poured after 30 min and then, the reaction mixture was run with mechanical stirring at 70°C for a further 3.5 h. The resultant yield was recovered magnetically and washed with water/ethanol before being collected in acetone. The

refluxation of produced materials was maintained for 48 h at 65°C to eliminate the template and the nanocomposites were once again purified with ethanol and then with deionized water.

The non-magnetic mesoporous ($\text{SiO}_2/\text{SiO}_2\text{-NH}_2$) composite particles were also prepared as reference material.

5.2.3. Preparation of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst

The $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst was synthesized by a little revised procedure of simultaneous adsorption and co-reduction of metal salts [24]. To start, 30 mL of deionized water with 1.0 g of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite was sonicated into a round-bottomed flask. In 40 mL of distilled water, an equimolar (0.03 M) mixture of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (0.3177 g) and AgNO_3 (0.2187 g) was transferred gently to the suspension of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite particles. The mixture was heated in a thermostat hot water bath at 80°C under a nitrogen atmosphere while the mixture was continuously stirred. 1.9706 g of sodium citrate solution (0.3 M) was added and stirred for about 30 min under nitrogen flow. The pH was immediately adjusted at 10.0 by NaOH and an inert atmosphere was maintained. After adding the green reducing agent, glucose (1.0669 g), the reaction mixture was then carried out for 2 h. The nanocatalyst was magnetically isolated and then, washed with water and ethanol to remove any impurities as well as dried at about 50°C. The nanocatalyst was separated into two batches and one batch was subjected to calcination at 400°C for 4 h. The non-calcined and calcined nanocatalysts were named non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ and cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ respectively. The identical procedure was employed to prepare the non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ and non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4/\text{Cu-Ag}$ nanocatalysts.

As reference materials, the bare bimetallic non-cal: Cu-Ag NPs and cal: Cu-Ag were also produced. The method and the molar ratio of Cu to Ag remained constant.

5.2.4. Characterizations

All respective characterization was carried for purified samples. Fourier transform infrared, FTIR spectra of dried samples pressed in KBr pellets were recorded by an FTIR spectrophotometer (Perkin Elmer, FTIR-100, USA) over the scanning range of 4000–200

cm^{-1} in the deflection mode. X-ray diffraction patterns of powdered samples were obtained by scanning XRD (Bruker D8 Advance, Germany) using monochromatic Cu K α radiation ($\lambda \approx 1.5418 \text{ \AA}$), tube voltage of 40 kV, and tube current of 40 mA at a room temperature. Diffraction analysis was performed between 2θ values of $10\text{--}90^\circ$ at a scan rate of $10^\circ \text{ min}^{-1}$. The surface element composition of dried samples mobilized on carbon tapes were measured by X-ray photoelectron spectroscopy, XPS (ESCA-3400, Shimadzu, Kyoto, Japan), equipped with a monochromatic Al K α radiation (1486.6 eV) at 100 W and 20 kV and an X-ray current of 20 μA . The acquisition area and take-off angle were kept fixed at 14 μm and 45° respectively and the pressure in the measurement chamber was $8.0 \times 10^{-7} \text{ Pa}$. The step size was 0.25 eV for both the survey and high-resolution spectra (pass energy 280 eV). The size distribution and morphology were analyzed by transmission electron microscope, TEM (JEM-1230, JEOL, Japan) and Scanning electron microscope, SEM (JSM-6510, JEOL, Japan). For TEM measurement, a drop of diluted suspension ($\sim 0.01\%$ solid) was dried on a carbon-coated copper grid at an ambient condition. TEM was operated at an accelerating voltage of 100 kV. While, for SEM observation, the diluted suspension was taken on mica sheet and dried in a vacuum desiccator overnight. Prior to the SEM observation, the dried SEM samples were gold coated to prevent any sample degradation. BET (NOVA 3000e, USA) instrument was employed to determine specific surface area (S_{BET}). Average diameter and pore volume of the respective powdered sample were measured using Barrett-Joyner-Halenda (BJH) technique at 77 K. Magnetic properties at ambient temperature were analyzed by a vibrating sample magnetometer, VSM, (Micro Sense, EV9, USA). Energy Dispersive X-ray Spectroscopy (EDS) spectra were taken by an energy dispersive X-ray analyzer coupled with the SEM. A visible spectrophotometer (OPTIMA, SP 300, Japan) was used for monitoring the color change during continuous reduction reaction of 4-NP. A pH meter from Mettler Toledo Company (MP 220 Switzerland) and a high-speed centrifuge machine (TG16-WS, China) were used during the investigation.

5.2.5. Catalytic activity

The catalytic activity of the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst was evaluated for the reduction reaction of 4-NP to 4-AP. The others respective materials like SiO₂/SiO₂-NH₂, SiO₂/Fe₃O₄-SiO₂-NH₂, non-cal:SiO₂/SiO₂-NH₂/Cu-Ag, non-cal:SiO₂/Fe₃O₄/Cu-Ag, cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag, non-cal:Cu-Ag and cal:Cu-Ag nanocatalyst were tested for the reduction of 4-NP to 4-AP to show the catalytic efficiency. This typical reaction procedure has been discussed in 3rd Chapter and based on the calibration curve of the 4-NP standard solution, as mentioned in the 3rd Chapter. .

Moreover, a few aromatic nitro compounds like nitrobenzene, nitrotoluene, were used to perform for the reduction reaction of 4-NP by the noncal: SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst. This procedure is also described in the 3rd Chapter. The recycle experiment of noncal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag and cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalysts was carried out following the described procedure in 3rd Chapter.

5.3. Results and discussion

5.3.1. Characterizations of SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst

The SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst was prepared by a two-step process. First, the mesoporous SiO₂/Fe₃O₄-SiO₂-NH₂ nanocomposite support was prepared by concurrent co-precipitation of Fe²⁺ and Fe³⁺ and hydrolysis-condensation of tetraethyl orthosilicate, TEOS in alkaline media in presence of SiO₂ particles. Finally, in-situ green co-reduction of Cu²⁺ and Ag⁺ salts in presence of SiO₂/Fe₃O₄-SiO₂-NH₂ nanocomposite should lead to the anchorage of Cu-Ag alloy NPs on the surface. In the following section, the characterizations of non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag and cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalysts and some related reference materials are briefly discussed.

The step-wise formation of the SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst is analyzed by following the change in surface functionality through FTIR spectra as illustrated in Fig. 5.2A. The IR spectrum of SiO₂/Fe₃O₄-SiO₂-NH₂ nanocomposite support (Fig. 5.2Aa) shows the characteristic absorption signals at 472, 782, 960 and 1107 cm⁻¹ for Si-O bending, Si-O-Si symmetric stretching, Si-OH and Si-O-Fe asymmetric stretching vibrations, respectively [24, 47]. Two moderate signals for N-H and C-H bands at 1569 and 1329 cm⁻¹ confirm the incorporation of amine functionality from HMDA [8, 48]. The absorption signal at 1643 cm⁻¹ corresponds to cumulative vibrations for Fe-O and N-H bending [47, 49]. Amine functionality is also evident from the broad intense absorption signal in the region of 3000–3650 cm⁻¹ emanate from the superimposition of amine N-H and O-H stretching vibrations [47]. The stretching vibrations for Fe-O bond generally appear at 460 and 620 cm⁻¹ are hardly visible in the spectrum of SiO₂/Fe₃O₄-SiO₂-NH₂ nanocomposite support (Fig. 5.2Aa) due to overlapping with Si-O vibration [49–51]. Comparatively, the spectrum of magnetic non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst (Fig. 5.2Ab) resemble mostly to the spectrum of nanocomposite support (Fig. 5.2Aa). But, after calcination at 400°C, the intense signal at 960 cm⁻¹ due to Si-OH band disappears in the spectrum of cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst (Fig. 5.2Ac). Similarly, the aliphatic C-H band intensity at 2853 and 2922 cm⁻¹ in cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag becomes almost negligible because of burning off of

organic Na-citrate, glucose and cetyltrimethylammonium bromide, CTAB. Interestingly, the band derived from N-H band remains almost identical due to improved thermal stability following complexation of Cu-Ag alloy NPs with amine functionality. Traces of M-O and M-OH bonds (here, M stands for metallic Cu and Ag) derived from partial oxidation of Cu-Ag alloy NPs could not be assigned in the spectrum of neither calcined nor non-calcined nanocatalyst (Fig. 5.2Ab, c) because of conjoining with broad bending Si-O and symmetric stretching Si-O-Si vibrations in the 472–782 cm^{-1} range [8]. However, the identical shape of these vibrations in magnetic support (Fig. 5.2Aa) and supported magnetic nanocatalyst (Figs. 2Ab, c) is an indication of the formation of mostly zero-valent metallic Cu-Ag alloy NPs, favored by complexation with amine functional magnetic mesoporous SiO_2 support. The spectrum of non-cal:Cu-Ag bimetallic nanocatalyst (Fig. 5.2Ad) shows the vibration band for M-O bond in the 400–630 cm^{-1} range [8, 52, 53]. Thus, the non-cal:Cu-Ag bimetallic nanocatalyst contains a fraction of Cu and Ag ions due to either partial oxidation in air or incomplete reduction of precursor salts. In contrast, the calcination of bimetallic Cu-Ag nanocatalyst (Fig. 5.2Ae) produces relatively intense and broad M-O signal in the same region. This increasing amount of MO in the cal:Cu-Ag nanocatalyst might have resulted from increased oxidation of metal atoms during calcination in presence of air. The other peaks in bimetallic nanocatalyst, independent of calcination, are derived from the absorbed organic molecules (Na-citrate and glucose). Fig. 5.2B shows the FTIR spectra of $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ support and corresponding non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst. Likewise, the spectrum of $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ particles (Fig. 5.2Bf) shows the absorption signals of Si-O, Si-OH, Si-O-Si bands at 1095, 960 and 800 cm^{-1} respectively [18]. The N-H bending vibrations from primary amino group (-NH_2) are also available in the spectrum of $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ particles at 1563 and 1641 cm^{-1} , respectively. In the spectrum of non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst (Fig. 5.2Bg), the absorption signals identical to $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ particles can be assigned and the bands due to M-O and M-OH are not visible, possibly buried under the broad and intense signal of Si-O bending vibration. Overall, relative study shows that interaction of iron oxide with SiO_2 in $\text{SiO}_2/\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$ nanocomposite support (Fig. 5.2Aa) shifted asymmetric vibration of Si-O to higher wavenumber (1107 cm^{-1}). The slight decrease in intensity and distortion in shape of Si-O

and Si-O-Si vibrations indirectly imply the incorporation of Cu-Ag NPs. The above FTIR spectra analyses suggest that relative to unsupported Cu-Ag NPs, supported nanocatalysts contained mostly zero-valent Cu-Ag metals. However, in supported nanocatalysts formation of trace amount of surface M-O cannot be ruled out following contact with air. Since FTIR spectral study is not suitable for mapping the valence states of Cu-Ag, so, XRD and XPS measurements are performed as discussed below.

Fig. 5.2. (A) FTIR spectra of (a) $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$, (b) non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (c) cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (d) non-cal:Cu-Ag and (e) cal:Cu-Ag particles. (B) FTIR spectra of (f) $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ and (g) non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ particles. Spectra are taken in KBr pellets.

The crystallinity and the oxidation states of the metallic phase of different composites were analyzed by studying the XRD patterns. The diffraction pattern of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support (Fig. 5.3a) shows one broad signal at 2θ position of 23.39° for amorphous SiO_2 . The other comparatively sharp but weak signals at 31.95° , 35.52° , 43.58° , 57.13° and 62.82° are ascribable to the Bragg reflections (220), (311), (400), (511) and (440) of cubic inverse spinel structure (JCPDS 03–0863) of Fe_3O_4 [54, 55]. The average crystallite size of Fe_3O_4 in $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite, calculated by the Debye-Scherrer formula, is 10.39 nm. The non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst (Fig. 5.3b) exhibit identical but feeble diffraction signals for Fe_3O_4 . The remaining signals at 37.96° , 43.93° , 64.39° and 77.32° in Fig. 5.3b appear to

be diffused and primarily correspond to the lattice planes (111), (200), (220), and (311) of the metallic fcc structured Ag metal (JCPDS card no. 03–0931). Signal due to neat metallic Cu or Cu₂O/CuO could not be assigned. However, the wide signal at 43.93° is coincided well with Cu, Ag and Fe₃O₄ phases [44]. It is reported that when Cu and Ag NPs are prepared together, the added Ag ions generates much more amount of Ag with the help of reducing agent and Cu, this ultimately reduces the yield of Cu [39]. The above findings suggest that Cu-Ag alloy NPs have been formed in the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst (Fig. 5.3b) with less loading of Cu along the dominant Ag lattice [56, 57] and Cu-Ag alloy NPs possessed the crystal structure almost similar to pure Ag [11, 58]. Diffraction signal due to silver oxide is not visible. The average crystallite size of bimetallic Cu-Ag alloy NPs in the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst is 7.19 nm. The calcination at 400°C improved the signal intensity and also sharpened the overall signals of bimetallic Cu-Ag alloy NPs in the cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst (Fig. 5.3c). The reduction of amorphous SiO₂ signal following calcination is also noticed. These results indicate improvement in crystallinity for the cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst. The degrees of crystallinity in non-calcined and calcined nanocatalysts are 23.19% and 32.08% based on the (111) crystal plane. The average crystallite size of Cu-Ag alloy NPs in the cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst is slightly increased to 20.55 nm. The increase in size is affected by the removal of irregularities, edges and defects during calcination and hence produces explicit crystalline phase [59, 60]. On the other, the diffraction pattern of non-cal:Cu-Ag (1:1) bimetallic NPs depicted in Fig. 5.3d shows distinct signals at 36.33°, 42.23°, 61.39°, and 73.49° for (111), (200), (220), and (111) crystal planes of the fcc structured Cu₂O phase [42, 56, 61, 62]. Besides, fcc structured metallic Ag reflections appear at 37.94°, 44.07°, 64.32°, and 77.26° corresponding to the (111), (200), (220) and (311) crystal planes [41, 56, 63] show marginal shifting of (111), (220) and (311) crystal planes to lower angles from the corresponding non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst. This behavior is attributable to alloy formation in the supported nanocatalyst. The independent signals for Cu and Ag in non-cal:Cu-Ag NPs prove the existence of two different phases. Between the two phases, Ag phase dominates because of higher atomic size (Cu = 140 pm, Ag = 172 pm), larger reduction potential (Cu = 0.34

V, Ag = 0.80 V) for Ag [56] and reduction of Ag ions by Cu [39]. Based on the (111) crystal plane, the calculated percentages of Cu⁺ and Ag⁰ in non-cal:Cu-Ag bimetallic NPs are about 40.33 and 43.88 respectively. These results agreed well with the molar ratio of Cu-Ag (1:1) used in the recipe for synthesis. The average crystallite sizes of Cu and Ag in non-cal:Cu-Ag NPs calculated from the Debye-Scherrer formula are 27.61 and 10.61 nm respectively. However, calcination at 400°C produced altogether twelve diffraction different signals in cal:Cu-Ag NPs (Fig. 5.3e) at 2θ positions of 35.67°, 38.23°, 38.86°, 44.41°, 48.89°, 58.38°, 61.64°, 64.54°, 66.34°, 68.27°, 77.49° and 81.63°. These signals can be indexed to fcc structures of Ag metal and Cu₂O/CuO [43, 64–67]. Obviously, calcination in presence of air favored more oxidation of Cu. The diffraction pattern of the non-cal:SiO₂/SiO₂-NH₂/Cu-Ag nanocatalyst (Fig. 5.3f) shows identical signal behavior as observed for the non-cal: SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst (Fig. 5.3b). The average crystallite size of Cu-Ag alloy NPs in the non-cal:SiO₂/SiO₂-NH₂/Cu-Ag nanocatalyst is 6.1 nm. The above discussion shows that both support materials favored the formation of alloy NPs via co-reduction of Cu and Ag salts with the aid of glucose reducing agent.

Fig. 5.3. XRD patterns of (a) $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$, (b) non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (c) cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (d) non-cal: Cu-Ag , (e) cal: Cu-Ag and (f) non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ particles.

The elemental compositions of magnetic support material and nanocatalysts as well as the valence states of Cu and Ag were analyzed by XPS as shown in both Fig. 5.4 and Fig. 5.5. The survey spectrum of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support (Fig. 5.4a) shows signals for C1s, O1s and Si2p but signals for Fe2p3 and N1s could not be detected. It is likely that heterogeneous mesoporous surface and less amounts of both iron oxide and -NH_2 hindered the smooth detection. XPS instrument has also limitation as it can read the elemental composition up to a depth of only few angstroms (10–20 Å) from the surface [23, 68, 69]. The spectrum of the non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst (Fig. 5.4b) exhibits one additional peak for Ag3d. The core-level of Ag3d (Fig. 5.5Ag) fragmented into two binding energies of 367 and 373 eV are assignable to $3d_{5/2}$ and $3d_{3/2}$ spin states respectively. An energy gap of 6.0 eV between two spin states ultimately confirms the presence of Ag in the prepared nanocatalyst [70]. The narrow and sharp signal of Ag3d can be assigned to mostly zero-valence Ag as a major component [70, 71]. Unfortunately, no Cu2p3 signal appears in the survey spectrum of non-

cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst (Fig. 5.4b). The interstitial distribution of small amount of Cu embedded within the Ag lattice, as hypothesized from XRD patterns, is possibly the reason [56]. It was assumed that loading of Cu is massively reduced at the expense of Ag during simultaneous co-reduction of bimetallic Cu-Ag alloy NPs. The survey spectra of both cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag (Figs. 5.4c) and non-cal:SiO₂/SiO₂-NH₂/Cu-Ag (Fig. 5.4f) nanocatalysts exhibit similar signals for C1s, O1s, Si2p and Ag3d as observed in the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst. Following calcination, the signal intensities of C1s is slightly reduced from 71 to 69 atom% and that of O1s is slightly increased to 26 from 25 atom%, indicating higher oxidation of metal and degradation of smaller organic molecules derived from organic additives. Alternatively, the survey spectra of both non-calcined (Fig. 5.4d) and calcined (Fig. 5.4e) unsupported bimetallic Cu-Ag NPs exhibit signals due to both Cu2p and Ag3d. The core-level of Cu2p in non-cal:Cu-Ag NPs (Fig. 5.5Bn) can be resolved into two distinct satellite signals at 933.5 and 953.5 eV which correspond to Cu2p_{3/2} and Cu2p_{1/2}, confirming the existence of Cu⁰ and Cu⁺ (Cu₂O) species. Whereas, in cal:Cu-Ag NPs the core-level of Cu2p (Fig. 5.5Bo) can be separated into three distinct satellite signals, two peaks at 933.5 and 942.5 eV are corresponding to Cu2p_{3/2} and the remaining one at 954.5 eV is corresponding to Cu2p_{1/2}. The intensity of these satellite signals indicates that calcination in presence of air enhanced oxidation of Cu to Cu (II) in bimetallic Cu-Ag NPs. On the contrary, both non-cal: and cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalysts contained very low level of Cu2p (Fig. 5.5Bl, m). The incorporation of small amount of Cu in nanocatalysts as predicted in XRD study, interstitial distribution of Cu in Ag lattice, porous network of amine functional magnetic SiO₂ surface, and limitation of XPS instrument might have all hampered the smooth measurement of Cu. Overall comparison of core-line spectra, especially for Ag3d (Fig. 5.5A), show shifting of satellite signals towards lower binding energy in supported nanocatalysts. This is due to change in environment and grafting reaction with amine functionality of support materials [18]. Above all, the above interpretation of XPS results suggest that supported nanocatalysts contained small amount of Cu/Cu⁺ (Fig. 5.5Bl, m) along with larger amount of Ag⁰ (Fig. 5.5A) in identical homogeneous phase, while, in unsupported

bimetallic Cu-Ag NPs two separate phases of Cu/Cu⁺/Cu²⁺ (Fig. 5.5Bn,o) and Ag⁰ (Fig. 5.5A) exist.

Fig. 5.4. XPS survey spectra of (a) SiO₂/Fe₃O₄-SiO₂-NH₂, (b) non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag, (c) cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag, (d) non-cal:Cu-Ag, (e) cal:Cu-Ag and (f) non-cal:SiO₂/SiO₂-NH₂/Cu-Ag particles.

Fig. 5.5. (A) Ag3d core line spectra of (g) non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag, (h) cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag, (i) non-cal:Cu-Ag, (j) cal:Cu-Ag and (k) non-cal:SiO₂/SiO₂-NH₂/Cu-Ag particles; (B) Cu2p core line spectra of (l) non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag, (m) cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag, (n) non-cal:Cu-Ag, (o) cal:Cu-Ag and (p) non-cal:SiO₂/SiO₂-NH₂/Cu-Ag particles.

SEM images illustrate in Fig. 5.6 give information on the surface morphology and particle size distribution. The image of SiO₂/Fe₃O₄-SiO₂-NH₂ nanocomposite support (Fig. 5.6a) shows some tiny spherical Fe₃O₄ particles adhered to the amine functional SiO₂ particles. It is also apparent that some tiny Fe₃O₄ particles are buried inside the mesoporous functional SiO₂ layer. Since the nanocomposite particles were recovered magnetically, it is reasonable to say that some free magnetite particles were produced during one pot synthesis of SiO₂/Fe₃O₄-SiO₂-NH₂ nanocomposite particles. The average diameter and coefficient of variation (CV) of SiO₂/Fe₃O₄-SiO₂-NH₂ nanocomposite particles are 523 nm and 13.53% respectively. On the other, the average size of Fe₃O₄ particles is around 50.4 nm. The average diameters and CVs of non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag (Fig. 5.6b) and cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag (Fig. 5.6c) nanocatalysts are 545.8 nm, 20.96% and 549.67 nm, 5.64% respectively. The in-situ co-reduction of Cu and Ag salts in presence of SiO₂/Fe₃O₄-SiO₂-NH₂ nanocomposite noticeably increases the average size of produced nanocatalysts. In either case, numerous tiny Cu-Ag alloy NPs are attached firmly on the surface of mesoporous SiO₂ support via -NH₂ and/or -OH groups. The nanocatalyst surfaces are increasingly heterogeneous compared to SiO₂/Fe₃O₄-SiO₂-NH₂ nanocomposite core particles and shapes are spherical in

compliance with SiO_2 core particles. It is perceived that prepared nanocatalysts are highly stable as repeated washing after preparation did not remove the adhered alloy NPs. Even, the calcination of nanocatalyst at 400°C did not impart any recognizable change in overall morphology for cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst. The smaller particles observed in Fig. 5.6b, c probably constitutes $\text{Fe}_3\text{O}_4/\text{Cu-Ag}$ NPs as morphology and size are visibly different from Fe_3O_4 alone. However, the increasing number of smaller particles found in the image of cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst (Fig. 5.6c) might have originated from desorption of some loosely bonded Cu-Ag alloy NPs. Similarly, the reference non-magnetic $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ particles (Fig. 5.6d) possessed smooth homogeneous surface, and the corresponding non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst (Fig. 5.6e) possessed heterogeneous surface following decoration with Cu-Ag alloy NPs. The average sizes and coefficient of variation (CVs) of $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ particles and non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst are 576 nm, 9.49% and 557 nm, 9.06% respectively. The high polydispersity index might have affected the measurement. Comparatively, the unsupported bimetallic Cu-Ag NPs are .5.6irregular shaped and partially aggregated as shown in Fig.5.6f, g. The mean diameters of non-calcined and calcined Cu-Ag NPs are 49 nm and 850 nm respectively. The calcination at 400°C for 4 h caused sharp increase in average size due to sintering [72]. The overall surface morphology indicates that whether support material is non-magnetic or magnetic, both have improved the dispersibility and produced perfectly homogeneous distribution of uniform Cu-Ag alloy NPs.

Fig. 5.6. SEM photographs of (a) $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$, (b) non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (c) cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (d) $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$, (e) non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (f) non-cal: Cu-Ag and (g) cal: Cu-Ag particles. The scales represent 1.0 and 0.5 μm (inset image).

TEM images, used to reconfirm the morphologies and particle size distributions of as-synthesized materials, are shown in Fig. 5.7. In the TEM image of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support (Fig. 5.7a), the particle morphology and shape remained the same as observed by the SEM. Many smaller Fe_3O_4 particles are present near particles surface and some of them are remained attached to the particles surface. The average diameter and CV are 587 nm and 7.24%, slightly larger than that measured from the SEM image (Fig. 5.6a). The higher polydispersity index possibly makes the difference. The in-situ co-reduction of Cu and Ag salts in presence of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite appreciably increases the surface heterogeneity of both non-calcined

and calcined $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalysts as illustrated in Fig. 5.7b, c. In contrast to $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite, the surface of the respective nanocatalyst becomes a bit hairy. It is also apparent from high magnification TEM images (Fig. 5.8) that many tiny Cu-Ag alloy NPs are distributed near the surface of supported nanocatalysts. Free Cu-Ag NPs are produced hardly during the process. The effect of calcination on the morphology of the as-prepared nanocatalyst could not be ascertained except some probable desorption of Cu-Ag alloy NPs as speculated from the SEM image (Fig. 5.6c). The average diameters and CVs of non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ and cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalysts are 669 nm, 12.98% and 645 nm, 7.12% respectively. As reference materials, TEM images of $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ particles and non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst are also shown in Fig. 5.7d, e. The smooth surface of $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ particles turned heterogeneous following decoration with alloy NPs. The average sizes of $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ particles and non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalysts are 643 and 649 nm respectively. All these analyses of morphology by electron micrographs suggest the formation of stable bimetallic nanocatalysts via in-situ growth of Cu-Ag alloy NPs on the respective mesoporous magnetic and non-magnetic amine functional SiO_2 support.

Fig. 5.7. TEM photographs of (a) $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$, (b) non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (c) cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (d) $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ and (e) noncal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ particles. Scale represents 0.5 μm

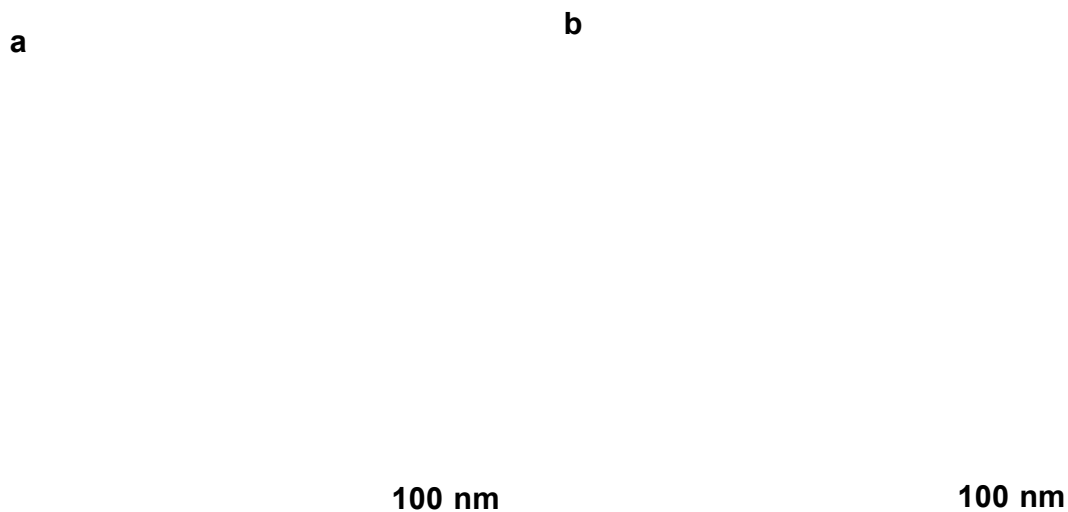


Fig. 5.8. TEM images of (a) non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ and (b) cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalysts.

The BJH pore size distributions of both $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ and $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ support materials are narrow as shown in Fig. 5.9. The average pore diameters of

$\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ and $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ are 3.8 and 4.3 nm, lying below the upper limit (50 nm) of mesoporous particles [73, 74]. After in-situ co-reduction of metal salts, the average pore diameters of as-prepared non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ and non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalysts are obviously reduced to 3.0 and 3.4 nm respectively and the pore size distributions became remarkably flattened and broad. This indicates formation of Cu-Ag alloy NPs on or within the pore space. As such the average pore volumes have also been reduced as shown in Table 5.1. Independent of nature of support materials, the average BET specific surface areas of as-prepared nanocatalysts are also decreased, owing to the slight aggregation, reduction in pore volume and surface heterogeneity. However, an abrupt increase in average pore diameter, pore volume and BET specific surface area are observed for cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst (Table 5.1). The BJH pore size distribution also turned narrow after calcination. This behavior can be resulted from the partial desorption of some of loosely anchored Cu-Ag alloy NPs from the surface, removal of irregularities and edges following calcination at 400°C. It is also likely that some organic template molecules trapped inside the pores are removed during calcination and thus increased the average pore diameter and hence the pore volume. The N_2 adsorption-desorption isotherms of prepared materials (Fig. 5.10) indicate that all materials exhibit identical type IV curves with an H2 hysteresis loop in the relative pressure range of 0.01 – 0.5, reflecting characteristics of a mesoporous structure [75, 76]. Comparatively, $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ particles possessed large mesoporous surface structure possibly with cylindrical and parallel pores as ascertained by the large adsorption of N_2 gas at higher relative pressure [47]. After decoration with Cu-Ag alloy NPs the adsorption-desorption isotherms for non-calcined nanocatalysts (Fig. 5.10g, j) expectedly flattened, suggesting reduction of pore volume and heterogeneity. However, the appearance of isotherm for cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst (Fig. 5.10h) is reversed due to increase in pore volume.

Fig. 5.9. Pore size distributions of (a) $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$, (b) non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (c) cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (d) $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ and (e) non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ particles measured by BJH method.

Fig. 5.10. Nitrogen adsorption-desorption isotherms of (f) $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$, (g) non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (h) cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$, (i) $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ and (j) non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ particles.

Table 5.1. BET and BJH physicochemical parameters.

Materials	Surface area ($\text{m}^2 \text{g}^{-1}$)	BJH		BET surface area ($\text{m}^2 \text{g}^{-1}$)
		Pore volume (cc g^{-1})	Pore diameter (nm)	
$\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$	12.886	0.028	3.8	17.477
Non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$	8.159	0.021	3.0	10.384
Cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$	16.791	0.032	3.8	18.788
$\text{SiO}_2/\text{SiO}_2\text{-NH}_2$	69.043	0.092	4.3	84.402
Non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$	8.085	0.023	3.4	10.883

The magnetic hysteresis loops of magnetic materials obtained by VSM at room temperature are presented in Fig. 5.11. All curves exhibit nearly zero coercivity and no-remanence. The saturation magnetization values of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite, non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ and cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalysts are 58.87, 47.45 and 69.79 emu g^{-1} respectively. The magnetization value of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support reasonably decreases after inclusion of non-magnetic Cu-Ag alloy NPs. But unexpectedly, the magnetization value reaches maximum for calcined supported nanocatalyst. The reason is pretty unclear. However, it is reasonable to say that the removal of trapped organic template [77], increase in porosity index and partial desorption of loosely bonded Cu-Ag NPs increased the access of magnetic Fe_3O_4 to the surface. The increase in crystallinity index following calcination might also have role in improving the magnetic property [78, 79]. The classic ‘S’ shaped magnetic hysteresis loops indicate the paramagnetic character of prepared nanocomposite support and nanocatalysts, respectively. In either case, the prepared magnetic particles moved under the influence of external magnet and separated easily from the suspension.

Fig. 5.11. Magnetic hysteresis loops of (a) $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite, (b) non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ and (c) cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalysts.

5.3.2. Formation mechanism of nanocatalyst

For comparing the catalytic property among different nanocatalysts, surface area is important. As such in this investigation fairly monodispersed SiO_2 seed particles have been used to prepare magnetic as well as non-magnetic mesoporous SiO_2 layered amine functional support. In both syntheses one-pot method is used. In this section, the formation mechanism of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst is discussed. $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support was prepared in alkaline solutions by concurrent in situ co-precipitation of Fe^{2+} and Fe^{3+} salts, the hydrolysis-condensation reaction of tetraethyl orthosilicate, TEOS and amine functionalization with hexamethylene diamine, HMDA in presence of SiO_2 seed particles. It is assumed that coprecipitation and nucleation of Fe_3O_4 and SiO_2 as well as functionalization occurred at the same time on the SiO_2 seed particles as they are all compatible to each other. The possible reactions taken place in one pot synthesis are:

In the final step, the formation of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst proceeded via sequential addition of precursor salts and green reducing agent (glucose). The adsorption of Cu^{2+} and Ag^+ on the surface of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support led to the formation of metal complexes through ligands like -NH_2 groups, silanol groups ($\equiv\text{Si-OH}$) and siloxane groups (Si-O-Si). Primarily, the less stable primary and secondary aminated Cu and Ag complexes thus formed should undergo co-reduction under mild condition. Simultaneously, the quaternary metal complex of Cu^{2+} could also be generated, is supposed to be more stable. The higher stability can limit complete reduction of Cu^{2+} due to the weak reducing action of glucose. Moreover, under the alkaline preparation condition deprotonation of silanol groups and strong electrostatic interaction of resultant electronegative species ($\equiv\text{SiO}^-$) with metal ions can inhibit the complete reduction of Cu^{2+} [24]. Fig. 5.12 shows all possible co-ordination routes of metal ions (Cu^{2+} and Ag^+) with the $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support material.

Fig. 5.12. Possible routes of interactions between $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support and metal precursor salts (Cu^{2+} and Ag^+).

5.3.3. Catalytic activity

The catalytic activity of different types of nanocatalysts and support materials have been measured for the reduction reaction of 4-NP as a model reaction. The objective is to see whether the incorporation of mesoporous SiO_2 and magnetic Fe_3O_4 in support materials had any positive effect on the catalytic property of bimetallic Cu-Ag NPs. Nitrophenols in general possess adverse effects on aquatic and non-aquatic bodies due to their high natural stability and possess poisonous, hazardous and carcinogenic effects on life [24]. The reduced products are often less toxic, more biodegradable and conform to green chemistry demands.

In the pH optimization experiment, non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ was employed as a typical nanocatalyst. The catalytic reduction in presence of the

nanocatalyst (5 mg) using NaBH_4 (8 mg) reducing agent (Fig. 5.13) shows the maximum conversion of 91% at pH 6 within 40 min. Any reductive catalysis is generally followed by sorption of reactants and subsequent transfer of electrons from reducing agent in solution to the reactant site via metal catalyst. Hence, the catalytic activity is largely influenced by the degree of sorption and electron storage capacity of a particular catalyst. It is therefore evident that despite the non-existence of electrostatic attraction between nanocatalyst surface and electron rich phenolate ions/4-NP at pH 6, sorption of 4-NP occurred preferably due to the presence of mesoporous SiO_2 [80] and magnetic Fe_3O_4 component [8, 80]. In the alkaline pH range, the catalytic property of the nanocatalyst decreases because sorption capacity is reduced following repulsion between negatively charged (Si-O^-) catalyst surface and electron-rich 4-NP/phenolate ions [81]. On the other, in the acidic pH range the degree of sorption should have increased via electrostatic attraction between protonated primary amine ($-\text{NH}_3^+$)/hydroxyl ($-\text{OH}_2^+$) group [18] on the catalyst surface and 4-nitrophenolate ions/4-NP molecules. But this was not the case and reduced activity is noticed. The probable reason is that some free electrons of 4-NP might have accepted H^+ to produce protonated oxygen and electrostatic repulsion thus occurred [24, 82]. A comparative study with our previously prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst [8] revealed that both reaction rate and percent conversion reduced in presence of the non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst. The anchored Cu-Ag alloy NPs in the non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ are believed to have lower electron density compared to Cu-Ni alloy NPs in the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. As the maximum conversion of 4-NP to 4-AP was achieved at pH 6, the rest of the experiments were performed at pH 6.

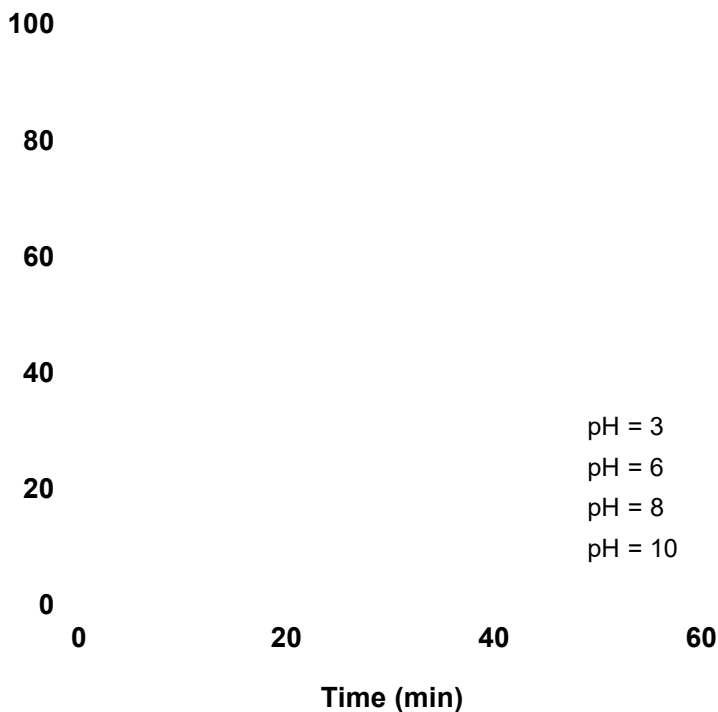


Fig. 5.13. Effect of initial pH value on the conversion of 4-NP in presence of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst. Conditions: 4-NP, 10 mg L^{-1} ; nanocatalyst, 5 mg; NaBH_4 , 8 mg; total volume, 25 mL; temperature, 25°C .

The effect of the initial 4-NP concentration in presence of fixed amount of non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ (5 mg) nanocatalyst was studied while other reaction parameters were kept constant. The results presented in Fig. 5.14a demonstrate that reduction reaction reduces the initial concentration of 4-NP with time. The initial rapid decrease of 4-NP is related to both sorption and catalyzed conversion to 4-AP. While, the slower decrease towards the end represents the catalytic conversion. This decreasing trend is more visible at higher concentration of 4-NP (30 mg L^{-1}). It is also evident that the higher is the initial concentration (30 mg L^{-1}) of 4-NP, the minimum is the final conversion (82.5%) to 4-AP (see inset of Fig. 5.14a). This behavior is common and attributable to limited surface area of the nanocatalyst which is not enough for sorption of larger number of 4-NP molecules [8]. Hence, the surface of the non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst became saturated at higher initial concentration and no vacant active site is available for further sorption. The highest conversion efficiency is observed at the initial concentration of 10 mg L^{-1} . The reductive catalytic efficiency of non-

cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst at all initial concentrations of 4-NP are less than that of the previously prepared Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst [8]. The probable reason is the difference in preparation method, reduction in surface area following use of SiO₂ solid as seed particles, and use of Cu-Ag instead of Cu-Ni. The effects of reducing agent (NaBH₄) and nanocatalyst alone on the reductive reaction are shown in Fig. 5.14b. This Figure indicates that individually NaBH₄ or nanocatalyst possesses little or no catalytic property. Hence, a combination of nanocatalyst and reducing agent is necessary to achieve higher conversion of 4-NP.

Fig. 5.14. (a) Time-dependent change in 4-NP concentration during catalytic reduction over the SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst. Inset figure shows the final conversions at different initial concentrations of 4-NP. (b) Change in the conversion of 4-NP in presence of (circle) NaBH₄, (cube) SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag, and (triangle) SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag + NaBH₄. Conditions: 4-NP, 10 mg L⁻¹; total volume, 25 mL; pH, 6; temperature, 25°C.

Though the supported cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst possessed the best catalytic performance, the following analyses are carried out over the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag as a model for all alternative supported nanocatalysts. The nanocatalyst dosing effect in the range of 2–6 mg (Fig. 5.15) shows that conversion of 4-NP to 4-AP increases from 37% to 91% after 40 min of reaction. Beyond 91% conversion the solution became colorless and no change in color as well as absorbance

value could be detected. Here, the nanocatalyst acted as a relay center that provided the electron from BH_4^- to 4-NP. More nanocatalyst obviously provided more active sites for smooth electron transfer and enhanced the sorption of reactant molecules. However, in presence of 6 mg of nanocatalyst, the effect on conversion is less evident. Optimum catalyst dose is always necessary as excess amount of nanocatalyst sometimes causes aggregation and thereby reduces the active surface area.

Fig. 5.15. The effect of the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst dose on the time-dependent change in conversion of 4-NP. The inset figure shows the final conversions obtained at different nanocatalyst doses. Conditions: 4-NP, 10 mg L⁻¹; NaBH₄, 8 mg; total volume, 25 mL; pH, 6; temperature, 25°C.

In order to test the effects of the nature of support materials and heat treatment (e.g., calcination) on nanocatalysts, the catalytic reductions of 4-NP were carried out in the presence of identical amounts of different support materials, supported and unsupported nanocatalysts. A comparative conversion plot against time is shown in Fig. 5.16. Based on the conversion data, the catalytic activity increases in the order: SiO₂/SiO₂-NH₂ < SiO₂/Fe₃O₄-SiO₂-NH₂ < non-cal:SiO₂/SiO₂-NH₂/Cu-Ag < non-cal:Cu-Ag < non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag < cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag < cal:Cu-

Ag. The non-magnetic $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ support produces the minimum conversion (17.5%) after 40 min as they contain no Cu-Ag alloy NPs and Fe_3O_4 . The conversion reaches the highest point (17.5%) within 10 min and then almost leveled off, indicates that small change in initial concentration of 4-NP is mainly affected by its sorption rather than by catalytic reduction. Incorporation of Fe_3O_4 in $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ support material improved the conversion to 25.5% and the conversion gradually increases showing the characteristics of catalytic reaction. Similarly, comparison between non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ and non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalysts clearly demonstrates that the inclusion of Fe_3O_4 in support material improves both rate and conversion of 4-NP to 4-AP. This is to mention that non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst possessed slightly higher pore volume and pore diameter (Table 5.1) than non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst. But the above advantages have been neutralized by the incorporation of Fe_3O_4 in the $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$ support material. Hence, Fe_3O_4 added extra impetus through enhanced sorption of reactant molecules, electron density, storage capacity and smooth transfer of electron from the reducing agent, NaBH_4 , to the reactant 4-NP [8]. Interestingly, relative to non-calcined one, calcination of either nanocatalyst improves the ultimate conversion. The increased crystallinity, composite effects, pore volume, BET surface area, size effects, and heterogeneous structure accounted for this increase in catalytic conversion [83]. It is also evident that in case of non-calcined nanocatalyst, the use of $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ support material considerably improves both conversion and reaction rate. Comparatively, for calcined nanocatalyst this effect is less discernible on conversion, but improved the reaction rate appreciably. The catalytic performances of different nanocatalysts are also compared by the turn over frequency (TOF) which is obtained from turn over number (TON)/reaction time. The TOFs of $\text{SiO}_2/\text{SiO}_2\text{-NH}_2$, $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$, non-cal: $\text{SiO}_2/\text{SiO}_2\text{-NH}_2/\text{Cu-Ag}$, non-cal: Cu-Ag , Cal: Cu-Ag , non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ and cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ are 6.32×10^{17} , 9.63×10^{17} , 5.5×10^{18} , 5.71×10^{18} , 7.03×10^{18} , 6.5×10^{18} and 9.75×10^{18} molecules $\text{min}^{-1} \text{g}^{-1}$ respectively. These results confirmed the superior catalytic activity for the calcined supported nanocatalyst. In addition to larger BET surface area and pore volume (Table 5.1), cumulative effect of uniform size distribution of Cu-Ag alloy NPs on support, strong metal-metal and metal-support interactions, alloying effect,

surface heterogeneity and increased crystallinity contributed positive role in improving catalytic property of cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst. In contrast, non-cal:SiO₂/Fe₃O₄/Cu-Ag nanocatalyst shows abnormal increase in absorbance value of the reaction mixture after 20 min (Fig. 5.17) and could not be used for comparison. The increase of pH to ~ 9.0 following addition of NaBH₄ might have initiated the partial deprotonation of surface hydroxyl groups of iron oxide to -FeO⁻ as the point of zero charge for iron oxide lies in the pH range of 5.5–9.0 [84]. The possible electrostatic repulsion and ultimate desorption of electron rich phenolate ions/4-NP from the nanocatalyst surface might have increased the residual 4-NP concentration and thereby reduces the catalyst activity. Whatever the reason, it is clear that combination of Fe₃O₄ and mesoporous SiO₂-NH₂ in the support material as well as calcination is crucial for obtaining increased catalytic activity of anchored Cu-Ag alloy NPs.

Fig. 5.16. Changes in the conversion of 4-NP at different time intervals in presence of support and nanocatalyst materials. Conditions: 4-NP, 10 mg L⁻¹; non-cal:Cu-Ag NPs, 1.4286 mg; SiO₂/Fe₃O₄-SiO₂-NH₂, 3.5714 mg; supported nanocatalysts, 5 mg (equivalent amount); NaBH₄, 8 mg; total volume, 25 mL; pH, 6; temperature, 25°C.

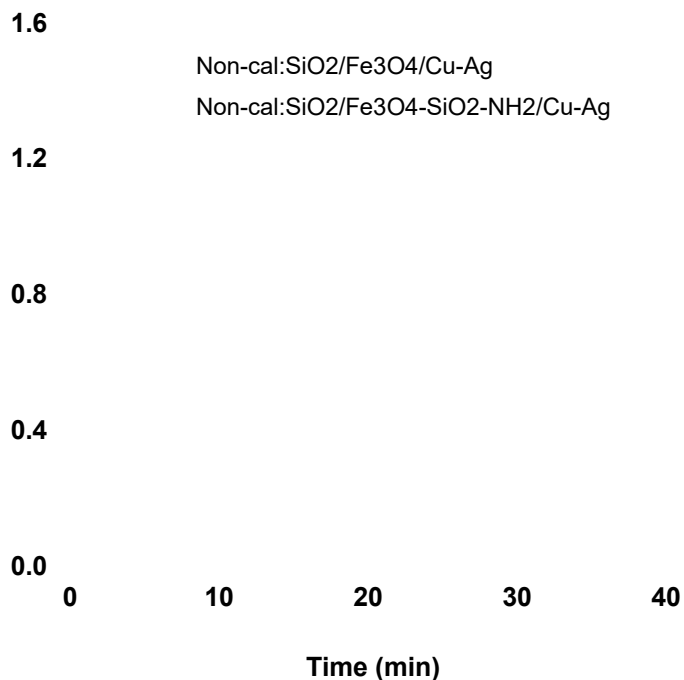


Fig. 5.17. Change in absorbance value during catalyzed conversion of 4-NP in presence of different nanocatalysts. Conditions: 4-NP, 10 mg L⁻¹; nanocatalyst, 5 mg; NaBH₄, 8 mg; total volume, 25 mL; temperature, 25°C.

The above discussion shows that both percent conversion and reaction rate are dependent on parameters like initial concentration of 4-NP, pH, nanocatalyst dose and type. The smooth progress of reduction reaction requires the presence of both nanocatalyst and reducing agent (NaBH₄) (Fig. 5.14b). Hence, the reduction kinetics of 4-NP presumably followed pseudo-first-order kinetic rate model [85]. The time and pH dependent variations in concentrations of 4-NP in presence of non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst were further evaluated by pseudo-first-order and pseudo-second-order kinetic rate equations (Eqs. (2.2) and (2.3)). The linearized kinetic plots are shown in Figs. 5.18 and 5.19. The values of correlation coefficients (R_1^2 and R_2^2) estimated from linearized plots presented in Table 5.2 show that reduction reaction of 4-NP can be best explained by pseudo-first-order kinetic model as the value of R_1^2 is comparatively higher and approaches unity. The first-order rate constant, k_1 (min⁻¹) is comparatively higher relative to the second-order rate constant k_2 (L mg⁻¹ min⁻¹), indicating faster reduction kinetics for the pseudo-first-order rate model. It is evident

(Table 5.2) that at optimized initial concentration of 4-NP (10 mg L^{-1}) and solution pH (pH 6) the reduction reaction proceeds at a faster rate.

Table 5.2. Kinetic parameters of reductive conversion of 4-NP in aqueous solution at different initial reactant concentrations and pH values

Experimental parameters	Initial concentration			pH			
	10 (mg L^{-1})	20 (mg L^{-1})	30 (mg L^{-1})	3	6	8	10
Reduction Efficiency (%)	90	85	83	65	90	68	60
$k_1 (\text{min}^{-1})$	0.0584	0.0493	0.0273	0.0247	0.0517	0.0391	0.0176
R_1^2	0.9785	0.9679	0.9847	0.9841	0.9834	0.9382	0.9894
$k_2 (\text{L mg}^{-1} \text{min}^{-1})$	0.0203	0.0084	0.0023	0.0067	0.0203	0.0062	0.0046
R_2^2	0.7905	0.9243	0.9913	0.9676	0.7905	0.8258	0.9736

Fig. 5.18. Linearized (a) pseudo-first-order and (b) pseudo-second-order kinetic plots obtained from time-dependent change in 4-NP concentration during catalytic reduction over the non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst. Conditions: 4-NP, variable mg L^{-1} ; nanocatalyst, 5 mg; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; temperature, 25°C .

Fig. 5.19. Linearized (a) pseudo-first-order and (b) pseudo-second-order kinetic plots obtained from time-dependent change in 4-NP concentration during catalytic reduction over the non-cal: SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst. Conditions: 4-NP, 10 mg L⁻¹; nanocatalyst, 5 mg; NaBH₄, 8 mg; total volume, 25 mL; pH, variable; temperature, 25°C.

5.3.4. Reduction of other aromatic nitro-compounds

The catalytic activity of the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst was investigated by carrying out the reduction of a few other aromatic nitro-compounds under similar conditions and the experimental results are depicted in Table 5.3. The progress of the reaction was monitored by thin layer chromatography, TLC and the pure product of each reduced amino compound was confirmed by the presence of a single spot on the TLC plate. A fairly good yield was obtained except for *p*-bromo nitrobenzene (entry 3) and *m*-aminobenzene (entry 4). Finally, it can be said that noncal: SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst has moderate activity for application in catalyzing organic reactions. The mechanisms of catalyzed reduction of aromatic nitro-compounds are well established. This mechanism illustrated in Fig. 3.16 as discussed in 3rd Chapter is used to take place through the sorption of nitro-compounds and reducing agent on the active part of nanocatalyst surface. Nitrophenol in aqueous solution releases proton to generate nitrophenolate ions and undergo sorption on the nanocatalyst surface. Nitrophenolate ions capture active hydrogen generates from adsorbed BH₄⁻ ions and electrons from the nanocatalyst-hydride complex [86]. Eventually, NP/nitrophenolate ions convert into

aminophenol as the final product through hydrodeoxygenation multistep reactions via interfacial electron transfer [46]. Amino products get released from the nanocatalyst surface as sorption affinity of the amino products is very weak.

Table 5.3. Catalytic reduction of various nitroaromatic compounds over SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag particles

Entry	Substrate	Product	Molar ratio (Substrates/NaBH ₄)	Catalyst (g)	Time (min)	Yield (%)
1			1:2	0.005	5	83
2			1:2	0.005	5	74
3			1:2	0.005	8	56
4			1:2	0.005	12	59

5.3.5. Recovery and recycle

The reusability and stability of a catalyst have great significance for industrial applications. The recycle experiment of the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst was carried out for the reduction of 4-NP using a reducing agent, NaBH₄, under identical conditions. For this, five successive reactions were performed with the same recovered nanocatalyst under similar conditions. The nanocatalyst was recovered from the reaction medium by magnetic separation and washed repeatedly with water and ethanol. The percent conversion data shown in Fig. 5.20a indicates a decrease in conversion from 95% in the 1st cycle to 80% in the fifth cycle. In the first three cycles the change in conversion is negligible, indicating high stability of the recovered nanocatalyst. But after the third cycle a sharp drop in conversion is observed. Despite the drop in conversion, it is still high enough for industrial applications. The plot of $\ln(C_t/C_0)$ against reaction time, t (min) (Fig. 5.20b) indicates that reaction kinetics goes down slowly with cycle number (Table 5.4) and the reaction time increased from 10 min in the first cycle to 50 min in the fifth cycle. This finding is quite in match with literature as the catalytic efficiency of any catalyst often reduces with increase in cycle number. The stability of the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst was evaluated by measuring any change in crystal structure after 5 cycles of catalysis experiment. Fig. 5.22 shows the comparative XRD plot of used and unused non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalysts. Since the crystal structure of Cu-Ag alloy NPs is dominated by Ag phase so the diffraction signals are labeled as Ag. The lattice planes (111), (200), (220), and (311) of the metallic fcc structured Ag can be observed for recovered non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst without much deviation from the unused nanocatalyst. The average crystallite size of Cu-Ag alloy NPs in the recycled non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst is 6.93 nm, agreed well with that of unused nanocatalyst (7.19 nm). EDS elemental mapping and spectra of unused and used (after five times recycle) non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalysts are also followed as illustrated in Fig. 5.23. Elemental mapping shows that after 5 times recycling of nanocatalyst, the distribution of Cu and Ag in the anchored Cu-Ag alloy NPs on the support materials remained almost identical without agglomeration. The atom percentages of Cu and Ag after recycle experiment are almost remained same (1.98 and

2.04) as those present before recycle (2.55 and 1.85). The atom percentages of other elements like O, Si and Fe varied slightly after recycle (61.43, 14.77 and 0.75) from those before recycle (60.74, 17.27, and 0.34). The slight variation in composition is possibly ascribed to variation in sampling conditions as one element is decreased but the other is increased. So, it is sensible to say that the gradual loss in catalytic power during recycle is hardly due to leaching of anchored metals but rather mostly due to weight loss of nanocatalyst during repeated recovery, and probable minor oxidation of active metal species [18, 24]. Overall, it can be said that the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst retained enough activity and stability for at least five cycles. For comparison, the recycle stability of cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst is also tested and the bar diagram is presented in Fig. 5.21. The conversion of 4-NP to 4-AP gradually reduces from 90% to 80% after the fifth cycle. The decreasing trend is almost identical to the non-calcined nanocatalyst. The kinetics was bit faster initially as observed in Fig. 5.16 but reduced gradually during recycle experiment. This is to mention that slight lowering of catalytic efficiency from Fig. 5.16 is ascribed to aging of the cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst as this recycle experiment is carried out after about six months of nanocatalyst preparation. The ultimate catalytic activities of our non-calcined and calcined supported nanocatalysts have been compared with some supported as well as un-supported Cu and Ag based bimetallic nanocatalysts (Table 5.5). The catalytic performance is obviously dependent on the total surface area. This is to mention that the average size of our magnetic SiO₂/Fe₃O₄-SiO₂-NH₂ support is 523 nm, which reduces the total surface area of loaded Cu-Ag alloy NPs. The activity factors of prepared nanocatalysts are thus reasonably low. However, in terms of percent conversion the catalytic activity of synthesized nanocatalyst is pretty good. This table clearly demonstrates improvement in catalysis power following Fe₃O₄ inclusion in support materials and calcination. This idea can be extended to develop more effective supported bimetallic nanocatalysts.

Fig. 5.20. (a) Percent conversion of 4-NP during recycle experiment for catalytic reduction over the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst, (b) Linearized pseudo-first-order kinetic plots obtained from time-dependent change in percent conversion of 4-NP. Conditions: 4-NP, 10 mg L⁻¹; nanocatalyst, 10 mg; NaBH₄, 16 mg; total volume, 50 mL; pH, 6; temperature, 25°C.

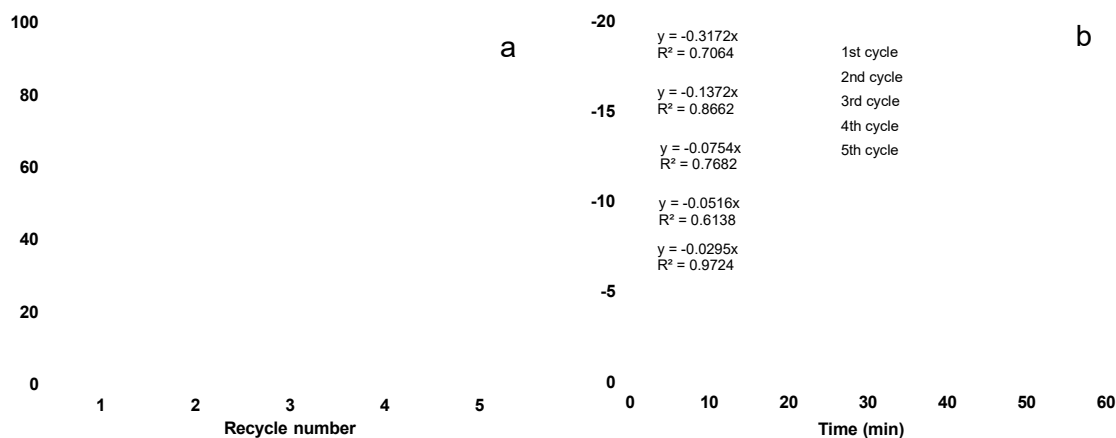


Fig. 5.21. (a) Percent conversion of 4-NP during recycle experiment for catalytic reduction over the cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst, (b) Linearized pseudo-first-order kinetic plots obtained from time-dependent change in percent conversion of 4-NP. Conditions: 4-NP, 10 mg L⁻¹; nanocatalyst, 10 mg; NaBH₄, 16 mg; total volume, 50 mL; pH, 6; temperature, 25°C.

Fig. 5.22. XRD diffraction patterns of the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst (a) before catalysis and (b) after 5th cycle of catalysis.

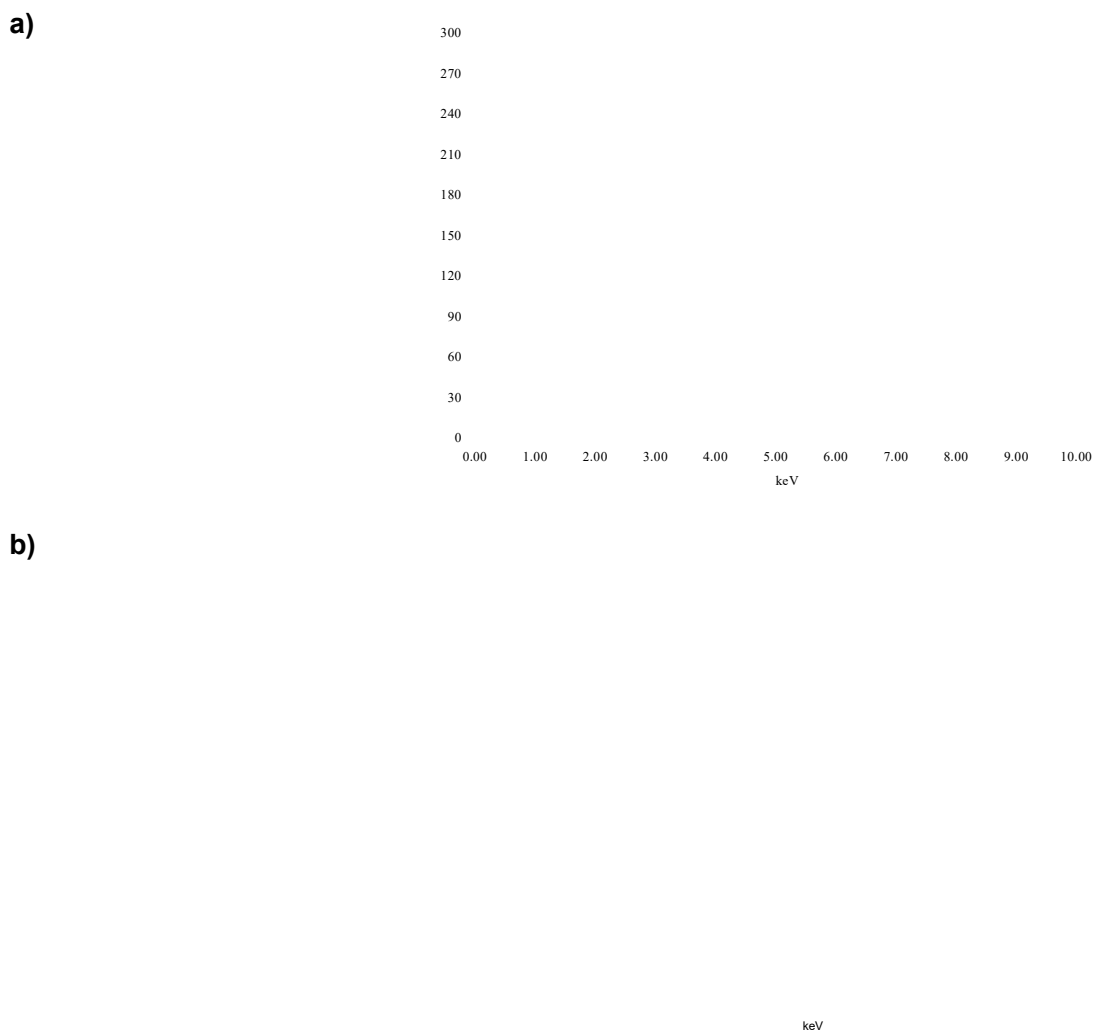


Fig. 5.23. EDS elemental mapping and spectra of the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst (a) before catalysis and (b) after 5th cycle of catalysis.

Table 5.4. Pseudo-first-order rate constants and conversions during recycle experiment over the non-cal:SiO₂/Fe₃O₄-SiO₂-NH₂/Cu-Ag nanocatalyst in the reduction reaction of 4-NP.

Cycle No.	Time (min)	Conversion (%)	k_1 (min ⁻¹)	R_1^2
1	10	95	0.3535	0.923
2	10	90	0.2865	0.9359
3	30	92	0.094	0.9335
4	40	81	0.0497	0.9384
5	50	80	0.030	0.9799

Table 5.5. A comparison of catalyst performance with literature.

Catalyst	Temp (K)	Mean size of metal NPs (nm)	Oxidant/Conc. (mM)	Catalyst Conc. (mg)	Time (min)	Conversion (%)	Activity factor (K) (min ⁻¹ mg ⁻¹)	Ref.
CuNW-Ag	298	160	4NP/1.0	0.091	7	~ 100	4.418	[87]
Cu-Ag	---	40.3	4NP/0.1	2.0	4	~ 60	0.1185	[9]
Cu-Ag/GP	---	---	4NP/1.0	10.0	10	96	0.0243	[88]
Cu-Ni/GP	---	---	4NP/1.0	10	7	97	0.0365	[88]
Cu	---	5.6	4NP/0.12	12.5	50	~ 100	0.0076	[89]
AgNPs@MP TMS-TiO ₂	---	7.0	4NP/2.0	1	0.2	~ 100	23.64	[90]
Fe ₃ O ₄ -CuAg	---	18	4NP/10.0	0.07	3	99	17.306	[44]
Ag _{0.7} -Cu _{0.3} NPs@PZS	---	10-15	4NP/0.1	0.1	5	~100	5.358	[7]
NH ₂ - SiO ₂ /Cu-Ni	298	---	4NP/0.0018	5.0	5	98.5	4.729	[24]
Non-cal: SiO ₂ /SiO ₂ - NH ₂ /Cu-Ag	298	---	4NP/0.0018	5.0	30	80	0.012	This Work
Non-cal: SiO ₂ /Fe ₃ O ₄ - SiO ₂ - NH ₂ /Cu-Ag	298	---	4NP/0.0018	5.0	40	91	0.012	This Work
Cal:SiO ₂ /Fe ₃ O ₄ -SiO ₂ - NH ₂ /Cu-Ag	298	---	4NP/0.0018	5.0	20	90	0.023	This Work

5.4. Conclusion

The core-shell type magnetic $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalysts are prepared by the interaction of Cu and Ag ions with magnetic $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support. The pore diameter, pore volume and BET-specific surface area of the $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst are developed by the calcination due to the removal of organic part and accelerate the oxidation of Cu, though Ag metal is retained. XPS results indicate that supported nanocatalysts contained a little quantity of Cu/Cu^+ and a higher amount of Ag^0 in a homogenous phase. Electron micrographs suggested that particles are heterogeneous with high polydispersity. The reduction of 4-NP to 4-AP as a model reaction is evaluated for the catalyst performance of supported and unsupported catalysts as well as reference supporting materials. A comparative study showed that $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ support played a great role in developing the catalytic performance of decorated Cu-Ag alloy NPs. However, Fe_3O_4 alone in the support material is not beneficial for the reduction of 4-NP at pH 6. The catalytic power of supported nanocatalyst and unsupported bimetallic NPs under calcination show a positive effect on the catalysis due to the increase in overall crystallinity, composite effects, pore volume, BET surface area, size effects, and heterogeneous structure. Non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ as a model nanocatalyst used for the reaction kinetics. The reduction reaction of 4-NP is preferable to follow the pseudo-first-order kinetic model. The recyclability experiment has been carried out for both non-calcined and calcined $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalysts and both exhibited moderate stability as 80% conversion of 4-NP to 4-AP was accomplished after 5 cycles. The overall assessment suggested that synthesized non-calcined and calcined $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalysts showed good potentiality in various organic transformations.

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Chapter-6

A Comparative Study Among Different Prepared Nanocatalysts for Chemical Reduction of 4-Nitrophenol

6.1. Comparative Study

In this Chapter, a comparative study is made among different prepared supported and unsupported nanocatalysts discussed in Chapters 2 to 5. The reduction of 4-NP conducted under ambient conditions at 25°C and atmospheric pressure was considered as a model reaction for catalysis. This reaction did not proceed in the absence of catalyst, even in presence of excess reducing agent (Fig. 3.12). This behavior confirmed that the reduction reaction followed the pseudo-first-order rate model [1]. The probable explanation is that the activation energy between the BH_4^- and 4-nitrophenolate ions is so high that it is unreachable for any reaction without any catalyst. Therefore, this reaction has been preferred for explaining the catalytic performance of the prepared nanocatalysts [2, 3].

The catalytic activities of prepared $\text{SiO}_2\text{-NH}_2/\text{Cu}$, $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ and $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalysts for the reduction of 4-NP under optimized conditions (nanocatalyst 5/3 mg, pH 6, temperature 25°C, 4-NP 10 mg L^{-1}) are summarized in Table 6.1.

Table 6.1. A summary of the conversion and kinetics of monometallic and bimetallic supported catalysts on the reduction of 4-NP by NaBH_4 .

catalysts	Catalyst dose (mg)	Time (min.)	Conversion of 4-NP (%)	Kinetics, k (min^{-1})	TOF ($\text{mol. min}^{-1} \text{g}^{-1}$)
$\text{SiO}_2\text{-NH}_2/\text{Cu}$	5	30	88	0.0874	0.635×10^{19}
$\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$	5	15	98.5	0.2898	1.423×10^{19}
$\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$	3	10	99.5	0.5388	3.59×10^{19}
Non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$	5	40	91	0.0584	0.65×10^{19}

The reduction of 4-NP in the presence of supported bimetallic $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst reached maximum conversion of 98.5% within 15 min while supported monometallic $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst showed lower conversion (88%) and taken longer time (30 min). The reaction kinetics is also slower for monometallic $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst. It is obvious that integration of Ni in $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalyst enhanced the catalytic performance. The cumulative electronic effect of bimetallic Cu-Ni systems

increases the catalytic effect. The geometric effect is another factor where atoms are rearranged on the supporting materials that can increase the catalytic activity [4]. It is also found that incorporation of iron oxide (Fe_3O_4) in amine functional silica ($\text{SiO}_2\text{-NH}_2$) support improved the catalytic activity as the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst showed the best catalytic activity, even at lower catalyst dose (3 mg). This improvement in catalytic activity for $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is accountable to the synergistic effects of the interaction of metal to iron oxide and SiO_2 , as well as the substantial catalytic property of iron oxide itself [5]. On the other, the non-cal: $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ag}$ nanocatalyst had less catalytic activity compared to both $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalysts in terms of conversion and chemical kinetics. This behavior is attributable to less electron density and storage capacity of Cu-Ag NPs relative to Cu-Ni NPs. Turnover frequency (TOF) is another promising factor to estimate catalytic performance. Correspondingly, the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst exhibited the highest value of TOF compared to other prepared nanocatalysts.

Relative to respective supported nanocatalyst, the unsupported monometallic and bimetallic NPs e.g., Cu, Cu-Ni and Cu-Ag had lower catalytic activity as observed from Tables 6.1 and 6.2. This is to mention that catalyst dose of unsupported nanocatalyst is fixed on the basis of metal content present in supported nanocatalyst. The improvement in colloidal stability, homogeneous distribution of metal NPs and increase in active surface area following anchorage on amine functional SiO_2 support obviously increased the catalytic activity of supported nanocatalysts. The trend in catalytic activity is similar to those of supported nanocatalyst i.e., bimetallic Cu-Ni NPs possessed the highest catalytic activity.

Table 6.2. A summary of the conversion and kinetics of monometallic and bimetallic unsupported catalysts on the reduction of 4-NP by NaBH₄.

Unsupported catalysts	Catalyst dose (mg)	Time (min.)	Conversion of 4-NP (%)	Kinetics, k (min ⁻¹)
Cu	1.527	70	65.2	0.017
Cu-Ni	2	20	92	0.1182
Cu-Ag	1.4286	60	85	0.0332

The overall trend of conversion during recycle experiment for different supported nanocatalysts, shown in Table 6.3, is also analyzed to understand the effect of composition. It is evident that nature of support materials as well as metal composition of nanocatalyst played a crucial role in maintaining the catalytic efficiency during recovery and recycle. Fe₃O₄ in support materials not only favored easy recovery but also improved the stability of the nanocatalyst through synergistic interaction, high electron density, functional support with proper dispersion, to prevent the aggregation, large surface area, and more active sites [6].

Table 6.3. A summary of the recyclability of supported catalysts on the reduction of 4-NP by NaBH₄.

Catalysts	Recycle number	Maximum conversion (%)	Minimum conversion (%)
SiO ₂ -NH ₂ /Cu	3	95	66
SiO ₂ -NH ₂ /Cu-Ni	6	98.5	90
Fe ₃ O ₄ -SiO ₂ -NH ₂ /Cu-Ni	6	100	100
Non-cal: SiO ₂ /Fe ₃ O ₄ -SiO ₂ -NH ₂ /Cu-Ag	5	95	80

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Chapter-7

Conclusions

The use of transition metal NPs as catalyst is limited due to poor dispersion stability and this led to aggregation, oxidation, low recyclability and poor recoverability. Therefore, the anchoring of metal NPs to inert and effective solid support is considered useful. For this, mesoporous SiO_2 has been used as primary supporting material for fixing transition metal NPs. To maximize the catalytic activity, comparable to precious metals (Au, Pt, Ru, Rh, and Pd), various modifications of SiO_2 solid support have been carried out. Additionally, the anchoring feasibility of both monometal and bimetal NPs on support materials have been studied. For better understanding, the overall research done in this work is discussed in four different chapters, Chapter 2 to 5.

In chapter 2, mesoporous $\text{SiO}_2\text{-NH}_2$ particles are decorated with CuNPs. Mesoporous surface structure and -NH_2 functional groups have favored the fixation of CuNPs. Due to this, compared to bare CuNPs, the resulting supported $\text{SiO}_2\text{-NH}_2/\text{Cu}$ nanocatalysts showed better catalytic activity. In chapter 3, Ni atom is integrated and prepared bimetallic $\text{SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. The prepared nanocatalyst exhibited improvement in catalytic power due to the synergistic effect, increased electron density and alloying effect. Following the above work, in Chapter 4, magnetic property is introduced in support materials and prepared magnetic mesoporous silica ($\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$) supported Cu-Ni alloy NPs. The resultant nanocatalyst showed substantial improvement in both catalysis property and stability during recycle. This finding has been extended in Chapter 5 and prepared a core-shell type $\text{SiO}_2/\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite support for immobilizing Cu-Ag bimetallic NPs. The finding is similar to Chapter 4, i.e., improvement in catalysis power is observed following inclusion of iron oxide in support materials. It is also observed that calcination had positive effect on the catalytic efficiency of supported nanocatalyst.

The following hypotheses can be drawn from the overall findings of this investigation:

- i. Use of support materials for metal NPs is beneficial for improving catalytic efficiency of nanocatalyst.
- ii. As support materials, mesoporous functional SiO_2 support is a good choice for metal NPs as it helps to improve the anchoring as well as

distribution of metal NPs and thus enhances both catalytic conversion and kinetics.

- iii. Amine group in support materials provides good anchoring ability for metal NPs.
- iv. Introduction of magnetic property through introduction of Fe_3O_4 NPs in mesoporous functional SiO_2 support not only assist magnetic recovery but also improve catalytic power and stability through higher synergistic effect, electron density and sorption capacity.
- v. Introduction of bimetals on support materials is effective for enhancing catalytic power of the prepared nanocatalyst. With this finding, attempt can be made to introduce trimetal for further improvement in catalytic efficiency.
- vi. Selection of proper transition metal is important for maximizing the catalytic power of supported nanocatalyst.
- vii. Calcination of supported nanocatalyst enhances the catalytic power.
- viii. Above all, the two-step process applied for the preparation of amine functional SiO_2 supported nanocatalyst is simple and economically viable.

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1. M. Z. Sarker, M. M. Rahman, H. Minami, T. Suzuki, M. K. Hossain, H. Ahmad, Mesoporous amine functionalized SiO₂ supported Cu nanocatalyst and a kinetic-mechanistic degradation study of azo dyes, Colloids and surfaces A: Physicochemical and Engineering Aspects 617 (2021) 126403. <https://doi.org/10.1016/j.colsurfa.2021.126403>
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Amine functional silica–supported bimetallic Cu-Ni nanocatalyst and investigation of some typical reductions of aromatic nitro-substituents

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Abstract

Herein, preparation and application of amine functionalized silica ($\text{NH}_2\text{-SiO}_2$)–supported Cu-Ni nanocatalyst are reported. Cu-Ni nanoparticles (NPs) are doped on the $\text{NH}_2\text{-SiO}_2$ support via in situ simultaneous reduction of Cu and Ni ions. The X-ray diffraction (XRD) pattern revealed the face-centered-cubic (fcc) crystalline alloy structure of Cu-Ni NPs in the $\text{NH}_2\text{-SiO}_2\text{/Cu-Ni}$ nanocatalyst. X-ray photoelectron spectroscopy (XPS) analyses showed that anchored Cu-Ni NPs contained Cu^0 and Cu^{2+} species, while Ni was present at its bivalent state (Ni^{2+}). In comparison to the unsupported Cu-Ni bimetal NPs, the supported $\text{NH}_2\text{-SiO}_2\text{/Cu-Ni}$ nanocatalyst showed superior catalytic activity in chemical reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP), giving 98.5% conversion at pH 6 within 15 min. The kinetics preferably followed the pseudo-first-order rate model. The $\text{NH}_2\text{-SiO}_2\text{/Cu-Ni}$ nanocatalyst is recoverable magnetically from the reaction media and can be recycled up to six cycles without much loss in catalytic activity.

Keywords Supported Cu-Ni nanocatalyst · Catalytic reductions · Aromatic nitro-substituents · Kinetics

Introduction

Metal nanoparticles (NPs) show promising catalytic activity corresponding to bulk counterparts because of their unique features such as huge surface area, high porosity, and chemical tenability at the nanoscale. Precious metal NPs like Au, Pt, Pd, Rh, and Ru have been extensively employed as catalyst materials because of their superior stability, selectivity, and efficiency [1–3]. But, the large-scale usage of precious metals is often discouraged because of their high cost and rare abundance on the earth. Thus, nowadays efforts are made to develop non-precious metal–based nanocatalysts with good activity and extended durability and these are undoubtedly being relatively economical. In this regard,

the bimetallic nanocatalysts based on non-precious metals such as Fe, Co, Cu, and Ni could be good alternatives to precious metals as these are proved beneficial for improving the catalytic activity and selectivity [4–6] compared to corresponding monometallic analogue, and found sometimes even comparable with those of individual precious metal nanocatalysts [7]. The strong synergistic interaction between metals improves the physicochemical properties, such as high specific surface area, functionality, and stability [8]. These bimetallic NPs also showed prospective application potential in electronics, photonics, sensing, labeling, and imaging [9–11]. So far, many researchers have focused their attention on the preparation of cost-effective bimetallic Cu-Ni alloy nanocatalysts as they have high strength, low melting temperatures, corrosion resistance, and thermal and electrical conductivity. Magnetic behavior is another vital property that can enable the magnetic Cu-Ni nanoalloy more attractive for applications ranging from catalysis to optoelectronic, magnetic, metallurgical, and even medical applications [12–14].

However, the efficient use of any unsupported bimetal nanocatalysts is believed to suffer major drawbacks due to tendency to aggregation, low recyclability, and recovering

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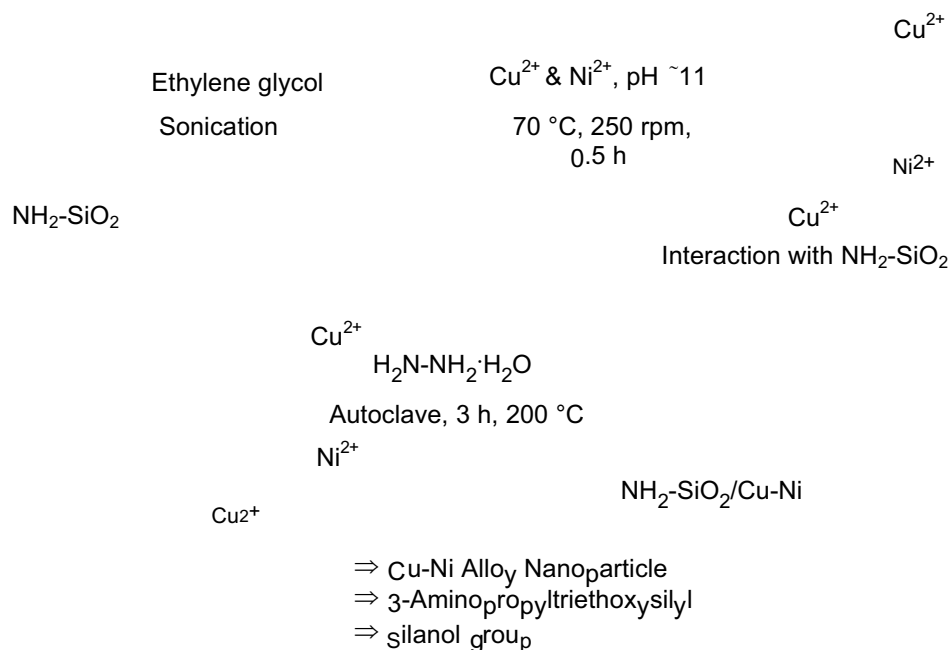
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difficulty. One way to overcome these drawbacks is to embed or anchor bimetal nanocatalysts onto solid supports [15–17]. The supporting material provides mechanical strength to the catalyst, reduces the amount of metal nanocatalyst, improves exposure of active sites to the reactants, and also enhances the selectivity through altering molecular interaction with the loaded nanocatalyst [6]. In majority cases, four different groups of support materials such as carbon [7, 18], graphene [12, 18–23], SiO_2 [24–27], and metal oxides [7, 28–32] have been used for stabilizing bimetallic Cu-Ni nanocatalysts. Among the support materials, SiO_2 , a natural biomaterial which can be easily synthesized, offered promising advantages as support materials because of chemical inertness, low cytotoxicity, mechanical and thermal stability, low cost, and easy functionalization [33, 34]. Besides, the surface hydroxyl functional groups on SiO_2 made them highly stable in the aqueous reaction medium. Further functionalization of SiO_2 surface with organic reactive groups is also possible to facilitate the anchoring of metal ions/metals through chelation [35–38]. Few related literatures are available on the utilization of SiO_2 support for bimetallic Cu-Ni nanocatalyst. Wu et al. had stabilized Cu-Ni alloy NPs via encapsulation with SiO_2 shell through a two-step microemulsion and polymerization of tetraethyl orthosilicate (TEOS) and observed superior catalytic performance to pure Ni nanocomposite catalyst [24]. The same group had used hydrothermal technique to embed Cu-Ni alloy NPs in nanosheets of hierarchical SiO_2 hollow spheres [25]. However, encapsulation by SiO_2 shell and use of large amount of surfactant can reduce the catalytic efficiency. Rad

et al. had used cationic–anionic Cu-Ni precursor to prepare SiO_2 -supported bimetallic catalyst via wetness impregnation followed by drying and finally calcination at 600 °C [26]. Chirieac et al. had used similar incipient wetness impregnation method followed by mild drying and calcination (550 °C) to prepare Cu-rich CuNi/SBA-15 catalysts [39]. In a similar type investigation, CuNi/ SiO_2 catalysts were prepared from CuNi phytosilicates by treatment in autoclave and finally calcined at 400 °C [40]. Yoshida had used citric acid-assisted impregnation followed by drying and calcination to prepare Cu-Ni/ SiO_2 catalysts and tested the hydrogenation reaction [41]. All these preparations required extra effort like separate calcination step and chemicals as well. Ang et al. had used two-step in situ reduction and calcination to prepare $\text{xNi}_y\text{Cu}/\text{SiO}_2$ catalyst and studied the promotional effect of oleic acid for activating SiO_2 particles [27]. Physical blending was also used to obtain CuNi/ SiO_2 and observed the size effect of SiO_2 spheres on the hydrolysis of ammonia borane but the interaction among SiO_2 spheres and CuNi NPs was hardly addressed [42].

The present investigation is aimed at developing a simple one-pot in situ co-reduction of Cu and Ni precursor salts in presence of amine functionalized SiO_2 ($\text{NH}_2\text{-SiO}_2$) spheres for preparing $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocomposite catalyst (Fig. 1). The amine functionality was favored to improve Cu^{2+} and Ni^{2+} affinity, coordination of Cu and Ni NPs through the nitrogen-rich functionalities and controlled growth of NPs. The composition and morphology of the supported nanocatalyst were confirmed by Fourier-transform IR (FTIR), electron microscopy, Brunauer–Emmett–Teller

Fig. 1 Preparation scheme of the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst



(BET) surface analysis, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The catalytic activity of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst was then tested for chemical reduction of some aromatic nitro compounds, the common organic pollutants widely used in the manufacturing of dyes, plasticizers, pesticides, fungicides, and explosives [19]. These pollutants caused deleterious effect on aquatic photosynthesis, biochemical oxygen demand, and chemical oxygen demand, and are poisonous to aquatic environment, which ultimately resulted in serious health problems for human life. The positive aspects of this investigation are simple and scalable one-pot production of cost-effective SiO_2 -supported bimetallic Cu-Ni nanocatalyst, enhanced catalytic power compared to pure Cu-Ni NPs, rapid and easy recovery of used nanocatalyst, and finally good recycle stability.

Materials and methods

Materials

Tetraethyl orthosilicate (TEOS, Sigma-Aldrich Chemie GmbH, USA), cetyltrimethylammonium bromide (CTAB, Fluka, Biochemica, Switzerland), and 3-aminopropyltriethoxysilane (APTES, TCI, Japan) were used as received. Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Merck, India), nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, E-Merck, Germany), 4-nitrophenol, 4-NP (Loba Chemie, India), ethylene glycol (Loba Chemie, India), hydrazine hydrate ($\text{H}_2\text{N-NH}_2 \cdot \text{H}_2\text{O}$, Merck, India), and sodium borohydride (NaBH_4 , Smart Lab, Indonesia) were used as precursor of Cu and Ni bimetal nanoparticles, solvent and reducing agent, respectively. L-Ascorbic acid (E-Merck, Germany) was used as capping agent and antioxidant. Nitrobenzene, 4-nitrotoluene, 4-bromonitrobenzene, 3-nitroaniline, diethyl amine (DEA), NH_4OH (25%), HCl (37%), ethanol, and other chemicals were of either reagent or analytical grade. Deionized water was obtained from Puricom (Taiwan) by reverse osmosis and UV radiation. All the experimental samples were prepared in deionized water.

Preparation of $\text{NH}_2\text{-SiO}_2$ particles

$\text{NH}_2\text{-SiO}_2$ particles were synthesized according to slightly modified procedure as reported in the literature [38, 43]. 25% CTAB solution (3.12 g of CTAB in 9.36 g of water) as structure-directing agent, and ethanol (22.5 g) were taken in a three necked round bottom flask, placed in a thermostat water bath at 60 °C and stirred (250 rpm) magnetically under a N_2 atmosphere. DEA (0.45 g) was added and allowed stirring for another 30 min. Then, TEOS (8.76 g) was added drop-wise into the reaction mixture and prehydrolyzed for 2 h in the basic condition before adding 1.3980 g of APTES

with APTES/TEOS molar ratio at 0.15. The reaction was progressed further for 2 h and finally the solution was cooled to room temperature. The resulting mixture turned into white milky dispersion. The final product was collected through centrifugation and washed three times with ethanol.

To ensure the complete removal of CTAB, the obtained $\text{NH}_2\text{-SiO}_2$ particles were dispersed in ethanol (637.0 mL) containing 37% HCl (17.5 mL) and refluxed at 78 °C for 48 h. The recovered $\text{NH}_2\text{-SiO}_2$ particles were subjected to repeated washing with deionized H_2O using a desk-top centrifuge machine. After that the product was left for drying overnight at room temperature under vacuum.

Preparation of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst

The supported $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst was synthesized by in situ co-reduction of precursor metal salts [40, 44]. Briefly, equimolar amounts (0.05 M) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.5940 g) and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.6258 g) were mixed in 50 mL of ethylene glycol and the apparent homogeneous solution was poured slowly into the suspension of $\text{NH}_2\text{-SiO}_2$ particles maintained at 70 °C and the pH was immediately adjusted at around 11 by adding NaOH. The reducing agent $\text{H}_2\text{N-NH}_2 \cdot \text{H}_2\text{O}$ (5 mL) was added at once into the solution and immediately the suspension twisted black with evolution of gases. After stirring for 30 min, the black colloidal suspension was transferred into a Teflon-coated stainless steel autoclave, and degassed and then heated at 200 °C for 3 h. Afterwards, the particles were magnetically isolated, washed three times with distilled ethanol under ambient conditions, and dried at 60 °C overnight.

The unsupported bimetal Cu-Ni NPs were prepared as reference nanocatalyst material without functional $\text{NH}_2\text{-SiO}_2$ support. Here, L-ascorbic acid was used as capping agent and antioxidant before adding $\text{H}_2\text{N-NH}_2 \cdot \text{H}_2\text{O}$ reducing agent. Otherwise, the process and molar ratio of Cu to Ni were kept identical as discussed above.

Characterization

For all characterization techniques, cleaned samples were used as required. FTIR spectra of powdered samples were taken by a FTIR spectrophotometer (Perkin Elmer, FTIR-100, USA) in KBr pellets over the scanning range of 4000–200 cm^{-1} in the deflection mode. The morphology and size distribution of the prepared nanocatalysts were measured by scanning electron microscope, SEM (JSM-6510, JEOL, Japan). The diluted dispersion (0.01% solid) was placed on a mica sheet and dried in a vacuum desiccator overnight before observation. Though there is little scope of sample damage under electron beam, the dried SEM

samples were gold coated before observation. The specific surface area (S_{BET}), average pore diameter, and pore volume (if any) of the respective dried nanocatalyst were checked by Barrett–Joyner–Halenda (BJH) technique using a BET (NOVA3000e, USA) apparatus at 77 K. Before employing BET analysis, the nanocatalyst sample was dried in an oven at 70 °C. X-ray diffraction (XRD) data of powdered nanocatalyst samples were recorded by a X-ray diffractometer (Bruker D8 Advance, Germany) using monochromatic Cu K α radiation ($\lambda \approx 1.5418 \text{ \AA}$), tube voltage of 40 kV, and tube current of 40 mA at room temperature. The diffraction scanning was conducted at a continuous scan rate of $10 \text{ \AA min}^{-1}$ with a position sensitive detector aperture at $3 \text{ \AA}$ between 2θ values from $20 \text{ \AA}$ to $80 \text{ \AA}$. The surface elemental composition of the dried sample mounted on a carbon tape was detected by XPS (PHI X-tool, ULVAC-PHI, Inc., Japan), equipped with a monochromatic Al K α radiation (1486.6 eV) at 4 W and 15 kV, and an X-ray current of 20 mA. The acquisition area and take-off angle were kept fixed at $1.4 \times 0.1 \text{ mm}$ and 45° respectively. The pressure in the measurement chamber was $8.0 \times 10^{-7} \text{ Pa}$. The step size was 1.5 eV for the both survey and high-resolution spectra (pass energy 280 eV). Visible spectrophotometer (OPTIMA, SP 300, Japan) was used for recording the color change during continuous reductive conversion of the 4-NP. A pH meter from Mettler Toledo Company (MP 220, Switzerland) was used for adjusting the pH value, and a high-speed centrifuge machine (TG16-WS, China) was used for decantation and washing of nanocatalyst samples.

Catalytic activity

The changes in the reduction of 4-NP were monitored by a visible spectrophotometer at a constant temperature of 25 °C. The initial pH value was first optimized by running out reduction reaction at different pH values. In a typical reaction procedure, 4-NP (10 mg L^{-1}) was dissolved in deionized water to prepare 25 mL aqueous solution and the pH was adjusted at a specific pH value. NaBH_4 (8 mg) and $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst (5 mg) were added and the contents were gently stirred at 350 rpm. The color intensity of the reaction mixture changed gradually, indicating the conversion of 4-NP to 4-aminophenol (4-AP). The change in the absorbance value at 400 nm was measured by a visible spectrophotometer. The same procedure was repeated to see effects of different variables like initial concentration and catalyst dose at the optimized pH value. A calibration curve was used for calculating the residual 4-NP concentration after the conversion. The respective conversion (D %) at different time intervals was estimated by using the Eq. (1):

$$D(\%) = [(C_0 - C_t)/C_0]100 = [(A_0 - A_t)/A_t]100 \quad (1)$$

where C_0 and A_0 are the initial concentration and absorbance of 4-NP and C_t and A_t are the concentration and absorbance at time t , respectively.

The conversion data were fitted with the pseudo-first-order (Eq. 2) and pseudo-second-order (Eq. 3) rate models:

$$\ln(C_t/C_0) = \ln(A_t/A_0) = -k_1 t \quad (2)$$

$$1/C_t = 1/C_0 + k_2 t \quad (3)$$

where k_1 (min^{-1}) and k_2 ($\text{L mg}^{-1} \text{ min}^{-1}$) are the pseudo-first-order and pseudo-second order rate constants, respectively.

The catalytic activities of either $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst or NaBH_4 and functional SiO_2 support with added NaBH_4 were evaluated by measuring change in conversion percent (D %) with time. For comparison, the reduction of 4-NP in presence of pure Cu-Ni NPs was also carried out by keeping all other parameters, such as pH 6, 4-NP concentration (10 mg L^{-1}), and reaction time as identical. The doses of Cu-Ni NPs and functional SiO_2 support were ~ 2 and $\sim 3 \text{ mg}$, equivalent to 5 mg of the nanocatalyst on the basis of metal and SiO_2 contents, respectively. The recyclability of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst was also tested after repeated washing of recovered nanocatalyst with deionized water and ethanol.

The reduction reaction in presence of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst was extended to few other aromatic nitro-substituents such as nitrobenzene, 4-nitrotoluene, 4-bromonitrobenzene, and 3-nitroaniline, and the yields of the corresponding amino compound were measured [45]. A mixture of aromatic nitro-compound (1 mmol), $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ (5 mg) nanocatalyst, and water (10 mL) was added into a three-necked round bottomed flask and stirred for about 5 min. Next, NaBH_4 (2 mmol) was added and the reaction mixture was stirred magnetically for 3 min under oil bath conditions ($60\text{--}70 \text{ }^\circ\text{C}$) and the reaction progress was monitored by TLC (eluent, n -hexane/ethylacetate (EtOAc): 5/2). After complete reduction reaction, the mixture was cooled to $\sim 25 \text{ }^\circ\text{C}$. EtOAc (8 mL) was added and the resulting mixture was stirred for 10 min. The magnetic nanocatalyst was recovered by an external magnet followed by repeated (two times) extraction with EtOAc (5 mL). The organic solution was evaporated trailed by drying over anhydrous Na_2SO_4 to afford almost pure product. TLC was used to ensure the purity of the reduced product, and the primary amino group was also qualitatively confirmed. The following equation was used to calculate the yield of the respective product.

$$\text{Yields (\%)} = \frac{\text{Moles of the product formed}}{\text{Initial mole of aromatic nitro compound}} \times 100 \quad (4)$$

Fig. 2 FTIR spectra of (a) $\text{NH}_2\text{-SiO}_2$ particles, (b) Cu-Ni NPs, and (c) $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst recorded in KBr pellets

Results and discussion

Characterization of nanocatalyst

The supported $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst prepared by in situ co-reduction of Cu and Ni salts in presence of functional SiO_2 particles was characterized by using different techniques like FTIR, XRD, XPS, electron microscopy, and BET analyses.

FTIR spectra (Fig. 2) of $\text{NH}_2\text{-SiO}_2$ particles, pure Cu-Ni NPs, and $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst were analyzed to identify the surface functionality. The spectrum of $\text{NH}_2\text{-SiO}_2$ particles (Fig. 2a) shows the characteristic asymmetric vibrations of Si–O, Si–OH, and Si–O–Si groups at 1087, 969, and 796 cm^{-1} [46]. The intense signal at 467 cm^{-1} in $\text{NH}_2\text{-SiO}_2$ particles is for the bending mode of Si–O group. The N–H bending vibration in primary amino group at 1640 cm^{-1} demonstrates functionalization of SiO_2 particles following one pot synthesis via sol–gel method. Another sharp peak at 1554 cm^{-1} corresponds to N–H bending vibration due to amino group being also visible [47]. The bands at 2985 and 2902 cm^{-1} in Fig. 2a describe the asymmetric and symmetric stretching vibrations for aliphatic C–H groups, originating from APTES and residual CTAB. The C–N stretching vibration that normally appears at 1155 cm^{-1} could not be distinguished because of the presence of intense signal of asymmetric Si–O vibration in the same region. The spectrum of $\text{NH}_2\text{-SiO}_2$ particles also shows the characteristic broad

absorption signal at $3000\text{--}3650\text{ cm}^{-1}$ due to amine N–H and O–H stretching vibrations. The spectrum of Cu-Ni NPs (Fig. 2b) exhibits absorption bands at 470 and 517 cm^{-1} , possibly attributed to the bending vibrations of Ni–O and/or Cu–O bond, while a sharp band at 624 cm^{-1} can be due to Ni–O–H stretching bond [48, 49]. This result indicates that surface atoms of Cu-Ni NPs might contain a fraction of Cu and Ni ions either due to partial oxidation in air during preservation and handling or due to incomplete in situ chemical co-reduction of precursor salts. The remaining bands may have come from the absorbed ascorbic acid and ethylene glycol. In the spectrum of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst (Fig. 2c), again the sharp stretching vibrations in the $467\text{--}618\text{ cm}^{-1}$ region may represent the Cu-Ni band [50, 51]. The intense asymmetric vibrations of Si–O (Fig. 2c) are visible at 1103 and 781 cm^{-1} with no signal of Si–OH band. Figure 2c also shows a little broadening effect and slight shifting of N–H bending to 1640 cm^{-1} and 1561 cm^{-1} after anchoring Cu-Ni nanoparticles. The disappearance of Si–OH band and a little shift of different bands in the spectrum of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst from the corresponding spectrum of $\text{NH}_2\text{-SiO}_2$ particles indicate the interaction of Cu-Ni NPs with functional SiO_2 particles. The comparative analyses suggest that functional SiO_2 particles have been anchored with Cu-Ni NPs.

The crystalline structure and oxidation states of the metallic phase were identified from XRD diffraction data. Figure 3a–c illustrate the XRD patterns of the $\text{NH}_2\text{-SiO}_2$ particles, pure Cu-Ni NPs, and $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst, respectively. The diffraction pattern of amorphous $\text{NH}_2\text{-SiO}_2$

Fig. 3 XRD patterns of (a) $\text{NH}_2\text{-SiO}_2$ particles, (b) Cu-Ni NPs, and (c) $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst

(Fig. 3a) shows only a single broad diffraction signal centered at about 23° in the $2\theta = 18\text{--}30^\circ$ range. The XRD pattern of as synthesized pure Cu-Ni NPs (Fig. 3b) shows the sharp diffraction signals at 2θ values of 43.46° , 44.61° , 50.58° , 51.94° , 74.25° , and 76.6° . The signals at 43.46° , 50.58° , and 74.25° indicate the presence of Cu corresponding to the (111), (200), and (220) planes of the face-centered-cubic (fcc) metallic Cu (PDF standard cards, JCPDS 04–0836, space group Fm3m) respectively [52, 53], whereas the peaks at 2θ values of 44.61° , 51.94° , and 76.6° can be assigned to (111), (200), and (220) fcc Ni crystals, consistent with the reported value (PDF standard cards, JCPDS 04–0850, space group Fm3m) [54]. The experimental lattice parameters for Cu and Ni were found to be $3.6046 \text{ \AA}$ and $3.5162 \text{ \AA}$, respectively. These values are in good agreement with the lattice parameter for pure Cu ($3.614 \text{ \AA}$, PDF# 00–004-0836) and pure Ni ($3.524 \text{ \AA}$, PDF# 00–004-0850), respectively [55]. Therefore, it can be said that bimetal Cu-Ni NPs contained Cu and Ni in different metallic phases, with no signals for other species or oxides. However, formation of trace amount of metallic oxide cannot be ruled out under the existing preparation condition and the oxide layer might be too thin to be detected by XRD. The percentages of zero valent Cu and Ni in pure Cu-Ni NPs, based on the (111) crystal plane, are about 51.77 and 48.23%, respectively, which are close to the preparation recipe. In Fig. 3c, the broad peak centered at around 24° in the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst indicates the presence of amorphous functional SiO_2 . The intense but little broadened diffraction peaks at 2θ values of 43.3° , 50.4° ,

and 74.3° respectively correspond to (111), (200), and (220) planes, indicating the formation of fcc structured metallic Cu-Ni NPs over the functional SiO_2 particles. A minor peak at 35.6° in the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst may indicate CuO indexed to (111) plane [12, 19, 44, 56, 57]. Interestingly, the absence of distinct peaks corresponding to individual lattice planes for neat elemental Cu and Ni metals and slight broadening of signals indicated the homogeneity in the metallic phase and synthesis of alloy NPs [57]. Further, the slight difference in peak positions between Cu-Ni NPs (Fig. 3b) and $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst (Fig. 3c) is the indication of Cu-Ni alloying effect [58]. The average crystallite sizes of Cu and Ni, using the Debye–Scherrer equation, in pure Cu-Ni NPs are 57.81 and 14.36 nm and that of Cu-Ni alloy in the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst is only 5.52 nm. The smaller crystallite size of bimetallic nanoalloy particles in the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst indicates the homogeneous nucleation and growth due to complexation reaction among metallic ions and functional $-\text{NH}_2$ groups on SiO_2 particles. Finally, it can be said that the prepared $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst is successfully obtained by in situ co-reduction of Cu and Ni ions.

XPS was used to identify the surface elemental composition and oxidation states of Cu and Ni. A comparative plot of XPS survey spectrum of $\text{NH}_2\text{-SiO}_2$ particles, pure Cu-Ni NPs, and $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst is depicted in Fig. 4. The spectrum for $\text{NH}_2\text{-SiO}_2$ particles (Fig. 4Aa) shows the presence of Si2p signal at about 104 eV. A reasonably weak signal due to N1s appears at about $\sim 399 \text{ eV}$

Fig. 4 (A) XPS survey spectra of (a) $\text{NH}_2\text{-SiO}_2$, (b) Cu-Ni NPs, and (c) $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ catalyst nanocomposite particles. Core-line spectra of (B) Cu2p and (C) Ni2p in (d, f) Cu-Ni NPs and (e, g) $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst

in $\text{NH}_2\text{-SiO}_2$ particles, confirming the functionalization with amine groups. The amplified N1s core-line spectrum of $\text{NH}_2\text{-SiO}_2$ particles is further illustrated in Fig. S1. The relative signal intensities of Si2p, C1s, N1s, and O1s in $\text{NH}_2\text{-SiO}_2$ particles are around 19, 25, 3, and 52 atom %, respectively. The XPS spectrum of the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst (Fig. 4Ac) expectedly shows the existence of Cu, Ni, Si, O, and C elements. Correspondingly, after anchoring Cu-Ni alloy NPs, the signal intensities of Si2p and O1s decrease to around 1 and 30 atom %, respectively, while that of C1s signal increases to ~ 65 atom %. The increase in C1s signal intensity may have originated from the fractions of adsorbed ethylene glycol solvent. This is to mention that in Cu-Ni NPs (Fig. 4Ab), the C1s signal intensity is also high (~ 58 atom %) and N1s signal derived from the reducing agent, $\text{H}_2\text{N-NH}_2$, is present at around 400 eV. The core

line spectrum of Cu 2p (Fig. 4Bd) in pure Cu-Ni NPs is differentiable into four distinct satellite peaks, two peaks corresponding to Cu 2p_{3/2} at 933.5 and 942.5 eV and two peaks corresponding to Cu 2p_{1/2} at 953.5 and 961.25 eV, respectively. The intensity of these satellite signals is attributable to the presence of major amount of metallic Cu and/or Cu⁺ with minor amount of Cu²⁺ species [38, 59], whereas, in the case of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst (Fig. 4Be), Cu2p core line signal can be differentiated into three clear peaks, two peaks at ~ 932.5 and ~ 941.5 eV for Cu2p_{3/2} and one peak at ~ 952.25 eV for Cu 2p_{1/2}, respectively. The composite nanocatalyst contained hardly detectable second signal due to Cu 2p_{1/2} for Cu²⁺. From this result, it may be reasonable to say that the composite nanocatalyst contained less amount of Cu²⁺ than the pure Cu-Ni NPs. The Ni2p core line signal in either Cu-Ni NPs or composite nanocatalyst (Fig. 4C) is

Fig. 5 SEM images of (a) $\text{NH}_2\text{-SiO}_2$ particles, (b) $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst, and (c) Cu-Ni NPs

distinguishable into two characteristic doublets of $\text{Ni}2\text{p}_{3/2}$ and $\text{Ni}2\text{p}_{1/2}$. The binding energy difference of ~ 18 eV between the two spin states indicates the presence of Ni^{2+} oxidation state in both Cu-Ni NPs and $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst [59]. The multiplet structure of $\text{Ni}2\text{p}_{3/2}$ shows that the main asymmetric signal appears at around 6.5 eV above the shake-up satellite peak. Thus, the $\text{Ni}2\text{p}_{3/2}$ signal position again matches with the presence of surface NiO rather than with metallic Ni and $\text{Ni}(\text{OH})_2$ [54]. For comparative perception, the relative atom% of different elements and binding energy of respective main and satellite peak due to Cu2p and Ni2p are summarized in Table S1. Since the XRD spectra of neither pure NPs nor composite nanocatalyst showed diffraction signal due to metallic oxide and XPS can read elemental composition up to a depth of only few angstroms from the surface, it is reasonable to conclude that oxide layer is formed only at the surface in contact with air. The binding energy of Cu $2\text{p}_{3/2}$ and Ni $2\text{p}_{3/2}$ shifted only marginally in composite nanocatalyst from that in unsupported Cu-Ni NPs. However, the shifting is found opposite;

i.e., Cu2p core line signal shifted to lower binding energy and Ni2p core line shifted to higher binding energy, which exposes the balancing regulation of near-surface electronic structure of the anchored Cu-Ni NPs due to alloying effect [60]. In addition to the above, some literature concluded that the shifting of binding energy of Cu $2\text{p}_{3/2}$ and Ni2p indirectly confirms the formation of alloy NPs between Cu and Ni along with interaction between metallic alloy and $\text{NH}_2\text{-SiO}_2$ surface [19, 42, 61]. Besides the interaction between alloy NPs and functional $-\text{NH}_2$ groups, the synergistic interaction between Cu and Ni induced the formation of alloy Cu-Ni structure in composite nanocatalyst.

The surface morphology, particle size distribution (measured by the ImageJ software), and agglomeration state of $\text{NH}_2\text{-SiO}_2$ particles, Cu-Ni NPs, and $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst were examined by SEM images as illustrated in Fig. 5a–c. The average size and coefficient of variation (CV) of $\text{NH}_2\text{-SiO}_2$ particles (Fig. 5a), prepared by one-step modified sol–gel technique, are 384.28 nm and 33.73%, respectively. Both spherical and oval-shaped $\text{NH}_2\text{-SiO}_2$

particles are formed and polydispersity index is pretty high. The non-instantaneous nucleation, i.e., prolonged nucleation following hydrolysis and condensation of TEOS, is possibly accounted for broad distribution of $\text{NH}_2\text{-SiO}_2$ particles [46]. The functional SiO_2 particles possessed good colloidal stability. Comparatively, the SEM image of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst (Fig. 5b) shows some big irregular-shaped cluster particles comprising many tiny individual particles. These tiny individual particles appear almost spherical and uniform-sized (~ 268 nm), and clusters formed look very compact. Moreover, $\text{NH}_2\text{-SiO}_2$ particles with identical shape and size are not visible in the image of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst (Fig. 5b). Thus, it can be said that $\text{NH}_2\text{-SiO}_2$ particles are buried inside the cluster and the detectable tiny individual particles belong to Cu-Ni alloy NPs. Interestingly, some very uniform-sized spheres (arrow marked) of 1653.27 nm average size, obviously greater than the functional SiO_2 particles, are also evident. The magnified image of such uniform sphere (inset image of Fig. 5b) shows the difference in contrast due to individual Cu-Ni NPs doped on the functional SiO_2 surface. On the contrary, from the SEM image of Cu-Ni NPs (Fig. 5c), it is apparent that many tiny spherical Cu-Ni NPs of average size ~ 218 nm are agglomerated into loosely bound irregular-shaped cluster. The agglomeration of metal particles definitely influenced the measurement of average size from SEM images and as they differed widely from the respective average crystallite size measured from the XRD data. Previously, we noticed the same agglomeration phenomena for both pure Cu [38] and Ni [54] NPs into large and perfectly spherical as well as anomalous-shaped particles of around 1 μm , due to Van der Waals interaction and partial oxidation in air. In the background of SEM image of Cu-Ni NPs (Fig. 5c), some bigger particles doped with smaller Ni particles are discernable (arrow marked). The bigger particle possibly represented the clusters of CuNPs as nucleation is comparatively faster compared to Ni particles. It is obvious that there is striking difference in morphology between Cu-Ni NPs and $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst. It is also worthy to mention that $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst on treatment with concentrated HCl produced soluble metal chloride in the supernatant and insoluble white SiO_2 particles were obtained as residue. The specific surface area (S_{BET}) of $\text{NH}_2\text{-SiO}_2$ particles, measured by BJH method, is $61.65 \text{ m}^2 \text{ g}^{-1}$, and after doping with Cu-Ni NPs, the surface area decreased to $14.85 \text{ m}^2 \text{ g}^{-1}$. The decrease in specific surface area is due to the increase in particle size following doping with NPs. Comparatively, the specific surface area of pure Cu-Ni NPs is much less ($6.62 \text{ m}^2 \text{ g}^{-1}$), attributable to the agglomeration effect. Both Cu-Ni NPs and $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst possessed magnetic property and can be separated magnetically (Fig. S2). From the above comparative analysis, it can be said that $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst is obtained via

in situ co-reduction of Cu and Ni salt in presence of functional SiO_2 particles.

The formation of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst proceeds via the interaction of Cu^{2+} and Ni^{2+} ions with functional SiO_2 surface and subsequent reduction by $\text{H}_2\text{N-NH}_2\cdot\text{H}_2\text{O}$ at 200°C . Figure S3 shows all the probable interaction pathways for metal ions. The terminal $-\text{NH}_2$ groups, silanol groups ($\equiv\text{Si-OH}$), and siloxane groups with oxygen-silicone (Si-O-Si) backbone present on the functional SiO_2 surface act as ligands for metal ions. These ligands would allow the formation of primary, secondary, and quaternary aminated Cu and Ni complexes. Additionally, Ni^{2+} can also form octahedral complex. The primary and secondary complexes of Cu or Ni are less stable than the quaternary complex, and these complexes reduced easily by reducing agent to favor the formation of metallic particles [38]. In the alkaline medium, the $\equiv\text{SiO}^-$ species can also be generated through reaction of OH^- with weakly acidic silanol groups before strong interaction with metallic ions in association with amino groups [43]. In such case, the negatively charged $\equiv\text{SiO}^-$ species can electrostatically attract towards metal ions which ultimately may inhibit the complete reduction of $\text{Cu}^{2+}/\text{Ni}^{2+}$. Since the metal ion reduction was carried out in presence of reducing agents like $\text{H}_2\text{N-NH}_2\cdot\text{H}_2\text{O}$ at 200°C in ethylene glycol medium, it is expected that in situ simultaneous reduction of both metal precursors proceeded smoothly resulting in the formation of nanocatalyst with Cu-NPs anchored to amine functional SiO_2 particles. The formation of intermetallic Cu-Ni compound is followed by the synergetic interaction between Ni and Cu through electronic transfer.

Catalytic activity

The catalytic activity of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst was studied for the reduction of some aromatic nitro-substituents in presence of NaBH_4 reducing agent. First, toxic 4-NP was used as model nitro-aromatic compound for the detail kinetic reduction study. This compound is toxic and widely used to manufacture drugs, fungicides, insecticides, and dyes and to brighten leather, which on inhalation or ingestion causes health hazards. The reduced product, 4-AP, is considered less toxic to human and aquatic species and potentially being more biodegradable in air. The heterogeneous catalysis by the nanocatalyst is generally followed by adsorption and/or absorption of reactant molecules on the catalyst surface and transfer of electron from the added reducing agent via metal NPs doped on the support to form product. Hence, the catalytic power of any catalyst is generally influenced by the nature of surface-active center, concentration, surface charge, electronic structure, crystalline structure, method of synthesis, pH, and temperature [38]. The pH-dependent

Fig. 6 Effect of initial pH value on the conversion of 4-NP in presence of the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst. Conditions: 4-NP, 10 mg L^{-1} ; nanocatalyst, 5 mg; NaBH_4 , 8 mg; total volume, 25 mL; temperature, 25°C

variations in surface charge property of the catalyst as well as of reactant molecules always play a crucial role during adsorption and/or absorption of reactant molecules.

In the reduction process, 4-NP, NaBH_4 , and catalyst act as electron acceptor, donor, and electron transfer mediator, respectively. Specifically, in the NaBH_4 -assisted reduction process of 4-NP, 4-nitrophenolate ions produced by the removal of proton in solution are sorbed on the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst surface and active hydrogen species produced on the nanocatalyst surface via electron transfer get readily abstracted by phenolate ions to produce mostly non-toxic 4-AP [12]. Before adding the nanocatalyst, deprotonation of 4-NP in presence of NaBH_4 was detected by the change in color from light yellow to yellowish green. However, in the reduction process, possibility of some direct sorption of 4-NP and borohydride ions on the nanocatalyst surface, subsequent formation of phenolate ions, and reduction are also there [62]. For better visualization, the reduction mechanism of 4-NP over the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst surface assisted by NaBH_4 is schematically depicted in Fig. S4. It is worthy to say that in the case of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst both absorption and adsorption of reactant molecules/ions may have occurred simultaneously due to the inclusion of functional SiO_2 carrier, so the term “sorption” has been used to explain the catalysis. In the control experiment, the pH-dependent study (Fig. 6)

in the pH range of 3–10 shows that a maximum conversion of 98.5% is achieved after 15 min of reaction at pH 6. It is reasonable to believe that at pH 6 there is no ionic interaction between nanocatalyst surface and phenolate ions as well as with electron-rich 4-NP because the nanocatalyst surface is almost neutral. It is clear that catalytic conversion over the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst significantly reduces to 74% at pH 3 after 25 min. In the acidic pH range, the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst oxide surface in water attained positive charge due to the specific adsorption of H^+ ions. So, there should be increased $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst activity at pH 3 due to enhanced interaction of both phenolate ions and electron-rich 4-NP with the positively charged nanocatalyst surface. However, contrary to this, a diminished nanocatalyst activity at pH 3 is observed. Two probable reasons can be accounted for this. One is, some free electrons of 4-NP in the acidic conditions might undergo protonation that increased the repulsion between protonated oxygen and positive nanocatalyst and thereby prevented a fraction of 4-NP molecules to come close to the nanocatalyst surface [63, 64]. The other reason might be the leaching or dissolution of active Cu-Ni catalyst in acidic solution that could reduce the nanocatalyst performance, as well [63]. In the alkaline region, the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst activity is poor, as 72.7 and 86% conversions to 4-AP are obtained at pH 8 and 10, respectively. The point of zero charges for CuO and NiO

Fig. 7 (a) Time-dependent change in 4-NP concentration during catalytic reduction over the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst. Inset figure shows the final conversions at different initial concentrations of 4-NP. (b) Change in conversion of 10 mg L^{-1} of 4-NP at different time

are reportedly 7.4 and 8.45, respectively [65, 66]. So, the expected repulsion between negatively charged nanocatalyst and electron-rich 4-NP/phenolate ions weakened their sorption, which might have reduced the conversion of 4-NP. The lower sorption of reactant in the alkaline pH range might also come from the increased competition with OH^- anions in solution. The slight increase in conversion at pH 10 is a bit surprising. It is known that presence of increased OH^- ion concentration under strong basic conditions can produce hydroxyl radical, which can attack 4-NP molecules to initiate partial mineralization through conversion to CO_2 and H_2O [67]. Hence, partial oxidative degradation might have proceeded under the conditions. Nonetheless, it is evident that initial pH value of the reaction medium produced significant effect on the conversion of 4-NP with the maximum conversion being obtained at pH 6.

Following the pH optimization experiment, the effect of initial concentration of 4-NP on its conversion was evaluated in the presence of fixed dose (5 mg) of the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst at pH 6. The decrease in concentration following conversion to 4-AP is shown in Fig. 7. Figure 7a states that in the presence of the nanocatalyst, the concentration of 4-NP decreases acutely at the initial stage and then it goes down only slowly. This slow decreasing tendency towards the end of the reduction process is relatively catchy at the highest concentration (30 mg mL^{-1}). The initial rapid decrease in 4-NP concentration occurred due to both sorption as well as due to catalyst-assisted reduction reaction. The initial sorption of nitrophenolate ions and/or 4-NP molecules is the culmination of synergistic effect of

intervals in presence of pure Cu-Ni NPs and the nanocatalyst. Conditions: nanocatalyst, 5 mg; Cu-Ni NPs, 2 mg; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; temperature, 25°C

hydrogen bonding and $\pi\text{-}\pi$ interactions with the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst surface which acted as a relay center for electrons. The slow conversion of 4-NP at the finishing end represents the catalytic reduction only. Almost complete conversion (98.5%) to 4-AP is possible at a lower initial concentration (10 mg L^{-1}) of 4-NP, and the percent conversion is reduced as the initial concentration of 4-NP is increased (inset of Fig. 7a). Since the nanocatalyst dose was kept constant during the experiment, the available vacant space was not enough for complete sorption of increasing amount of added 4-NP and intermediate ionic products [68]. In other words, the decrease of active catalyst sites due to increased addition of 4-NP hindered the smooth transfer of electrons from BH_4^- to the acceptor 4-NP molecules [69, 70].

A comparative study of catalytic activity, illustrated in Fig. 7b, shows that Cu-Ni NPs exhibit pretty good activity for the reduction of 4-NP under identical reaction conditions. It is also evident that the use of functional SiO_2 support for Cu-Ni NPs further improved the catalytic power in terms of both conversion and reaction rate. The catalysis power of pure and functional SiO_2 -supported Cu-Ni NPs was further compared by using the parameter turnover frequency (TOF). The TOF was simply obtained from $\text{TON}/\text{reaction time}$, where TON represents the number of 4-NP molecules converted into 4-AP over 1 g of nanocatalyst [71]. The TOFs of Cu-Ni NPs and $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst are estimated to be 0.1993×10^{19} and $0.1423 \times 10^{20} \text{ molecules min}^{-1} \text{ g}^{-1}$, respectively, which indicated a tenfold increase in catalyst efficiency for supported nanocatalyst. The SiO_2 support employed in nanocatalyst development

Fig. 8 The effect of the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst dose on the time-dependent change in conversion of 4-NP during catalytic reduction. Inset figure shows the final conversions obtained at different nanocatalyst doses. Conditions: 4-NP, 10 mg L^{-1} ; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; temperature, 25°C

increases the active surface area favoring the sorption of reactant molecules and reducing agent. In addition to this, the improved stability of anchored Cu-Ni NPs also helped to enhance the catalytic power of the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst. The reduction reaction of 4-NP in the presence of either NaBH_4 or $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst produced only 6 to 16% conversion to 4-AP (Fig. S5). Figure S5 also illustrates that use of $\text{NH}_2\text{-SiO}_2$ support along with NaBH_4 sharply increased the conversion of 4-NP to around 23%, understandably through sorption rather than via reduction, and then reaches almost a static value. Comparatively, in presence of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst, the conversion of 4-NP is much high (98.5%). The catalytic efficiency of non-functional $\text{SiO}_2/\text{Cu-Ni}$ nanocatalyst was not evaluated and compared, as the preparation of SiO_2 support in absence of amine functional silane, APTES, would obviously affect the

size distribution and, hence, the loading of metal nanocatalyst. The overall comparative analysis suggests that the prepared $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst functioned efficiently at the pH value of 6, which is near the pH of most supplied water.

The effect of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst dose in the range of 4–5 mg was studied in the reduction of 4-NP (10 mg L^{-1}) at pH 6, and the conversions are shown in a time-conversion plot (Fig. 8). The final conversion of 4-NP to 4-AP increases with increase in the nanocatalyst weight. It is also noticeable that reduction rate enhanced with the increase in catalyst weight. The introduction of more nanocatalyst means more active catalyst centers are available for transferring electrons to the reactant 4-NP molecules. In other sense, the increased addition of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst for identical amount of reactant 4-NP increases the availability of electrons for reduction

Table 1 Kinetic parameters of reductive conversion of 4-NP in aqueous solution at different initial reactant concentrations and pH values

Experimental parameters	Initial concentration			Initial pH			
	10 (mg L^{-1})	20 (mg L^{-1})	30 (mg L^{-1})	3	6	8	10
Reduction efficiency (%)	98.5	95.75	91.67	74	98.5	72.7	86
k_1 (min^{-1})	0.2898	0.1131	0.1196	0.0602	0.2898	0.0487	0.0698
R_1^2	0.9215	0.9656	0.9941	0.9264	0.9215	0.9875	0.9892
k_2 ($\text{L mg}^{-1} \text{min}^{-1}$)	0.3795	0.0407	0.0177	0.0099	0.3795	0.0101	0.0202
R_2^2	0.7418	0.7554	0.8617	0.9764	0.7418	0.9699	0.9647

Fig. 9 Linearized (a) pseudo-first-order and (b) pseudo-second-order kinetic plots obtained from time-dependent change in 4-NP concentration during catalytic reduction over the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst. Conditions: nanocatalyst, 5 mg; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; temperature, 25 °C

reaction. The increase in catalytic power for increased amount of nanocatalyst dose is recognized as obvious outcome for a good catalyst.

The 4-NP reduction reaction was found dependent on different parameters like reactant pH, concentration, catalyst weight, and catalyst composition. The reduction reaction proceeds by the formation of intermediate products, nitrophenolate ion and borohydride ion derived from 4-NP and NaBH_4 respectively. Since the reduction reaction did not progress in absence of nanocatalyst, even using the reducing agent (Fig. S5), it is predictable that reduction of 4-NP followed pseudo-first-order kinetic rate model [58]. In order to reaffirm, the time-dependent and pH-dependent variations in concentration of 4-NP were analyzed by pseudo-first-order and pseudo-second-order kinetic equations (Eqs. 2 and 3). Both pseudo-first-order and pseudo-second-order kinetic plots for 4-NP were linearized and shown in Figs. 9 and 10.

The rate constants (k_1 and k_2) and correlation coefficients (R_1^2 and R_2^2) obtained from the linearized plots are presented in Table 1. The relatively higher values of R_1^2 in both cases of concentration and pH-dependent study indicated that the reduction of 4-NP preferentially followed pseudo-first-order reaction kinetics, which is in agreement with the theoretical prediction. The higher values of rate constant k_1 (min^{-1}) indicated the faster reduction kinetics for the pseudo-first-order rate model. It can also be validated from the rate constant k_1 values for different solution pH (Table 1) that at pH 6 the reaction proceeds faster than at other pH values. The performance of our prepared $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst has been compared with the catalytic power of some other catalysts (including precious metals) in terms of pseudo-first-order rate constant, k_1 (min^{-1}) (Table S2). The activity of the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst is comparable and sometimes even better. It is to be mentioned that

Fig. 10 Linearized (a) pseudo-second-order and (b) pseudo-second-order kinetic plots obtained from pH-dependent change in 4-NP concentration during catalytic reduction over the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nano-

catalyst. Conditions: 4-NP, 10 mg L^{-1} ; nanocatalyst, 5 mg; NaBH_4 , 8 mg; total volume, 25 mL; temperature, 25 °C

Table 2 Evaluation of the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst for reduction of various aromatic nitro-substituents.

Entry	Substrate	Product	Molar ratio (Substrates/ NaBH_4)	Catalyst (g)	Time (min)	Yield (%)
1	NO_2	NH_2	1:2	0.005	5	83
2	NO_2	NH_2	1:2	0.005	5	81
3	CH_3NO_2	CH_3NH_2	1:2	0.005	8	38
4	BrNO_2	BrNH_2	1:2	0.005	12	57
	NH_2	NH_2				

reduction conditions are not always the same and the catalyst composition is also different, so they may have substantial effect on the value of rate constant.

Reduction of other aromatic nitro-substituents

Considering the potentiality of the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst in the catalytic reduction of 4-NP molecules, the reduction reaction was extended to few other aromatic nitro-substituents under identical conditions and the experimental results are displayed in Table 2. The progress of the reactions was validated by TLC and a single spot found on the TLC plate confirmed the desirable reduced amino product without impurities. It can be concluded from the table that major substrates are converted into the expected amino products. In the case of 4-bromonitrobenzene (entry 3), the low yield is due to the relatively strong resonance effect in respect to 4 (*para*) position of bromo group (-Br). On the other, the steric hindrance might have affected the electrophilicity of 3-nitroaniline (entry 4). On the basis of above findings, it can be said that the prepared $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$

nanocatalyst has good potential for application in catalyzing organic reactions.

Recovery and recycle

The recovery and recyclability of the catalyst are important from the view point of catalyst durability. In order to measure the stability and long-term durability, the recycle experiment of $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst was carried out for the reduction reaction of 4-NP in presence of NaBH_4 . For this, six consecutive reaction cycles were carried out with the recovered catalyst under identical reaction conditions and the results are presented in Fig. 11 and Table S3. The plot of $\ln(C/C_0)$ against reaction time, t (min), fitted well with the pseudo-first-order kinetics (Fig. 11a). From Fig. 11b, it is observed that 98.5% conversion in the first cycle decreases gradually to 90.5% in the sixth cycle but still high enough for industrial use. The reaction kinetics slightly slowed down as the reaction time increased from 15 min in the first cycle to 30 min in the sixth cycle. Frequently, it is apparent from the literature that the efficacy of any catalyst

Fig. 11 (a) Linearized pseudo-first-order kinetic plots for reduction of 4-NP in presence of the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst. (b) Percent conversions of 4-NP during repeated recycle experiment. Conditions:

4-NP, 10 mg L^{-1} ; nanocatalyst, 5 mg; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; temperature, 25 °C

in catalytic reaction is reduced in successive experiments [72]. It is probable that small decrease in conversion percent during recycle experiment has originated from small loss of nanocatalyst during the magnetic separation, washing, and reuse of catalyst. Partial leaching and transition of valence state of active metal part during handling are the other probable reasons, which generally influenced the performance of supported nanocatalyst. Despite the slight decrease in reaction kinetics during recycle experiment, we can say that the prepared $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst is good enough for application up to 6 cycles as the conversion percent (90%) remained considerably high.

Conclusion

Cu-Ni bimetallic alloy NPs supported on amine functional SiO_2 particles, named as $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst, are prepared through interaction of metal ions with amine groups and subsequent in situ simultaneous reduction via solvothermal method. The chemical composition and morphology of the nanocatalyst are confirmed by FTIR, XRD, XPS, and SEM images. The average crystallite size of Cu-Ni NPs anchored on functional SiO_2 particles is 5.52 nm, but the SEM image indicated the formation of some clustered particles comprising smaller spherical metal particles. Both XPS and XRD confirmed the formation of fcc alloy structure in anchored Cu-Ni NPs. The bimetallic alloy structure contained major amounts of Cu^0 , Cu^+ , and

Ni^{2+} species. The catalytic activity of the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst is evaluated for the reduction of 4-NP as a model aromatic nitro compound and compared the performance with unsupported bimetallic Cu-Ni NPs. A maximum conversion of about 98.5% to 4-AP is achieved over the nanocatalyst within 15 min at pH 6. The reduction reaction preferably followed the pseudo-first-order kinetic model in the respective initial pH and concentration (reactant) dependent kinetic study. Comparatively, over unsupported NPs, the conversion (92%) and reaction rate are both inferior to the supported nanocatalyst. The reduction reaction over the nanocatalyst was further extended to few other aromatic nitro substituents and obtained fairly good conversion. The durability of the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst is pretty good as the recycle experiment showed more than 90% conversion up to sixth cycle. In summary, it can be said that the as prepared $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst shows good potential for application in catalysis due to easy recovery and reusability along with negligible loss in catalytic power.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00396-021-04910-w>.

Data availability Supporting information is available.

Declarations

Conflict of interest The authors declare no competing interests.

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journal homepage: www.elsevier.com/locate/colsurfaMagnetite incorporated amine-functional SiO₂ support for bimetallic Cu-Ni alloy nanoparticles produced highly effective nanocatalyst

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HIGHLIGHTS

- Fe₃O₄-SiO₂-NH₂ composite supports are prepared by one-step solvothermal method.
- Simultaneous co-reduction of metal salts produced Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst.
- The prepared nanocatalyst is paramagnetic in nature.
- The catalytic activity of the nanocatalyst is superior to NH₂-SiO₂/Cu-Ni.
- The prepared nanocatalyst is magnetically separable after catalysis reaction.

GRAPHICAL ABSTRACT

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ABSTRACT

In this article, inclusion of iron oxide (Fe₃O₄) in amine functional silica (SiO₂-NH₂) support is attempted to see any improvement in catalytic property for anchored bimetallic Cu-Ni alloy nanoparticles. The Fe₃O₄-SiO₂-NH₂ support is first prepared by one-step solvothermal route. Secondly, bimetallic Cu-Ni alloy nanoparticles are generated on the Fe₃O₄-SiO₂-NH₂ support via in-situ simultaneous sorption and reduction of Cu and Ni ions. The resulting product, named as Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst, contained face-centered-cubic (fcc) bimetallic Cu-Ni alloy with average crystallite size of 4.76 nm and possessed strong paramagnetic character (27.76 emu g⁻¹). The Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst showed faster reduction kinetics for the conversion of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) compared to both unsupported Cu-Ni and supported SiO₂-NH₂/Cu-Ni nanocatalysts. The Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst is recoverable magnetically and reused up to 6th cycle without any drop in activity, producing 100% conversion at pH 6. The reduction reaction preferably followed the pseudo-first-order kinetic rate model. Overall, the catalytic activity and recycle stability of bimetallic Cu-Ni nanocatalyst enhanced dramatically following the use of magnetic Fe₃O₄-SiO₂-NH₂ composite support. Additionally, the prepared Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst possessed good application potential as antibacterial agent due to the presence of Cu-Ni.

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1. Introduction

Precious metal nanoparticles say Pt, Au, Pd, Rh and Ru are being widely investigated as catalyst materials for their better stability, selectivity, efficiency and catalysis power [1–6]. But, due to high cost and limited abundance of precious metals, researchers are now trying to develop transition metal based nanocatalysts as alternative. As a result, transition metal based bimetallic nanocatalysts are attracting increasing interest from the researchers since they show improved activity and selectivity, which in many instances, are comparable to individual precious metals [7–9]. The metal to metal synergistic interaction, as well as alloying effect largely enhance physicochemical properties like specific surface area, electron density, electron storage capacity, functionality and stability [10–12]. Moreover, these bimetallic materials have the potential for applications in fields like electronics, photonics, sensing, labeling, imaging and antibacterial agents [13–16]. The present investigation is focused on the preparation of durable and effective bimetallic Cu-Ni alloy nanocatalyst as they are both cheap and available. The magnetic property of Cu-Ni alloy also contributes to applications in electronics, magnetic, metallurgical and medical fields [17–20].

In a previous article, amine functionalized silica ($\text{NH}_2\text{-SiO}_2$) supported bimetallic Cu-Ni alloy (named as $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$) nanocatalyst was fabricated via one-pot in-situ co-reduction of Cu and Ni precursor salts [21]. The amine functionalized SiO_2 support was preferred to facilitate anchoring and fixation of metal atoms, thus enabling improvement in air stability, recyclability and dispersibility during application. Though the $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst was fairly stable, but from industrial perspective the stability seems to be not enough as the recycle experiment for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) indicated a drop in conversion from 98.5% to 90.5% in the 6th cycle. The present investigation is aimed at further improving the stability of $\text{NH}_2\text{-SiO}_2$ supported bimetallic Cu-Ni nanocatalysts during recycle and thus minimize the cost and environment pollution through leakage or washing. As such, magnetic iron oxide (Fe_3O_4) is included in $\text{NH}_2\text{-SiO}_2$ support before modification with Cu-Ni nanoalloy. The addition of Fe_3O_4 in support materials would facilitate the incorporation of Cu and Ni due to the presence of subsurface cation

vacancy structure in the Fe_3O_4 (011) surface [22,23]. Like SiO_2 , Fe_3O_4 as support material offer advantages of high surface area to volume ratio, chemical inertness, low toxicity and stability [24,25].

Izgi et al. synthesized $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$, a core-shell type amine functional support by a two-step process and then decorated with Ru via in-situ chemical reduction of RuCl_3 [26]. The objective was to impart magnetic core for effecting efficient recovery of catalyst without using filtration or centrifugation. Veisi et al. had used chitosan-coated core-shell $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$ nanoparticles (NPs) to anchor Pd NPs via in-situ green reduction protocol [27]. In both the above cases the catalysts were magnetically retrievable and recycled. There are also reports to employ core-shell type $\text{Fe}_3\text{O}_4/\text{SiO}_2\text{-NH}_2$ spheres for the removal of Pb^{2+} ions and alkaloids [28,29].

So far, to our knowledge, no investigation is available on the use of dual $\text{Fe}_3\text{O}_4\text{-SiO}_2$ composite matrix as support for bimetallic catalyst, but a core-shell type $\text{Fe}_3\text{O}_4/\text{SiO}_2$ morphology prepared via a two-step process is tried [26,27]. Herein, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support is evaluated for bimetallic Cu-Ni alloy nanoparticles. In the previous works [26,27], the magnetic core inside the SiO_2 layer rather added magnetic property but reasonably failed to improve interaction with metal NPs due to core-shell type morphology. On the contrary, the use of dual $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite matrix as support could directly improve synergistic interaction of metal NPs with exposed Fe_3O_4 and SiO_2 surfaces. Hence, we can expect an ultimate improvement in catalytic performance and recycle stability. The $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support is prepared via a one-step solvothermal procedure (Fig. 1) from a mixture of FeCl_3 , tetraethyl orthosilicate (TEOS), 3-aminopropyl triethoxysilane (APTES) and a structure directing agent, cetyltrimethyl ammonium bromide (CTAB). Under the condition, a composite structure comprising Fe_3O_4 and $\text{SiO}_2\text{-NH}_2$ should be formed rather than a core-shell type structure. Hence, it was assumed that simultaneous formation and aggregation of Fe_3O_4 and SiO_2 as well as amine functionalization occurred in alkaline medium under solvothermal condition. Finally, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst particles are obtained by in-situ sorption and chemical co-reduction of Cu^{2+} and Ni^{2+} ions using hydrazine hydrate ($\text{H}_2\text{N-NH}_2\cdot\text{H}_2\text{O}$) as a reducing agent (Fig. 1). Structure and morphology of the supported nanocatalyst are confirmed by

Fig. 1. Preparation scheme of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst.

Fourier Transform IR (FTIR), electron microscopy, Brunauer–Emmett–Teller (BET) surface analysis, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The catalytic activity and reusability of the prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst are evaluated for chemical reduction of 4-nitrophenol (4-NP), a common organic chemical used in the manufacturing of dyes, plasticizers, pesticides, fungicides, and explosives [30].

2. Experimental

2.1. Materials

Ferric chloride (FeCl_3), copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) and hydrazine hydrate ($\text{H}_2\text{N-NH}_2 \cdot \text{H}_2\text{O}$) were purchased from Merck, India. Ethylene glycol, EG, (Loba Chemie, India), *n*-heptanol (Fisher Scientific, UK), L-ascorbic acid (E-Merck, Germany) and anhydrous sodium acetate (CH_3COONa) were used as solvent, reducing agent, capping agent and nucleating agent respectively. TEOS from Sigma-Aldrich Chemie GmbH, USA was used as a SiO_2 source. CTAB from Fluka, Biochemica, Switzerland and APTES from TCI, Japan were used as cationic template and -NH_2 functionalizing agent, respectively. Sodium borohydride (NaBH_4) from Smart Lab, Indonesia was used during reductive degradation. 4-NP (Loba Chemie, India), nitrobenzene, 4-nitrotoluene, 4-bromonitrobenzene, 3-nitroaniline, diethyl amine (DEA), NaOH, HCl (37%), ethanol, and other chemicals were of analytical grade. Deionized water was obtained from Puricom (Taiwan) by reverse osmosis and UV radiation. All the solutions were prepared in deionized water.

2.2. One-step solvothermal synthesis of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites

Magnetic $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ support spheres were prepared by a one-step solvothermal method. Briefly, 0.5 g of anhydrous FeCl_3 and 0.3 g of CTAB were taken in 20 mL of ethylene glycol followed by 1.5 g of CH_3COONa and then sonicated for ~10 min at ambient temperature. The solution was transferred into a three necked round bottomed flask under a continuous N_2 flow and mechanically stirred at a speed of 250 rpm for 30 min. Subsequently, 30 g of *n*-heptanol and 0.15 g of DEA were added to the reaction mixture. After confirming the pH at around 10.0, TEOS (0.3 g) was added drop by drop and the stirring was continued for another 30 min. Finally, APTES (0.03 g) was added to the reaction flask, transferred the reactant mixture into a Teflon coated stainless steel autoclave and heated at 200°C for 8 h. The produced composite was washed three times using magnetic separation and decantation to remove any excess CTAB and nonmagnetic by-product before collecting in deionized water.

2.3. Synthesis of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst

The supported $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was prepared by following a slightly modified process of simultaneous in-situ co-reduction of metal precursor salts [21]. At first, 0.3286 g of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ support spheres were taken in 30 mL of distilled water and dispersed via sonication for about 15 min. Equimolar (0.075 M) mixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.5857 g) and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.6169 g) in 30 mL of distilled water was poured slowly into the suspension of support spheres taken in a round-bottom flask, maintaining at 70°C under constant mechanical stirring. The pH was immediately adjusted at 11.0 by NaOH and an inert atmosphere was maintained. The reducing agent, $\text{H}_2\text{N-NH}_2 \cdot \text{H}_2\text{O}$, (10 g) was added at once and the reduction reaction was continued for another 2 h. The nanocatalyst composite was purified by washing three times with deionized water and ethanol to remove any unreacted entities and finally collected in ethanol.

The unsupported Cu-Ni bimetallic NPs were also prepared as reference nanocatalyst material without the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ support. The process and molar ratio of Cu to Ni were kept identical as discussed

above. In addition, L-ascorbic acid was used as capping agent and antioxidant before adding the reducing agent.

2.4. Characterizations

Cleaned samples were used for all characterizations. FTIR spectrum of each powdered sample was recorded by a FTIR spectrophotometer (Perkin Elmer, FTIR-100, USA) in KBr pellets over the scanning range of $4000\text{--}200\text{ cm}^{-1}$ in the deflection mode. X-ray diffraction patterns by scanning XRD (Bruker D8 Advance, Germany) was obtained by using monochromatic $\text{Cu K}\alpha$ radiation ($\lambda \approx 1.5418\text{ \AA}$), tube voltage of 40 kV, and tube current of 40 mA at room temperature. Diffraction experiment was conducted between 2θ values of $10^\circ\text{--}80^\circ$ at a continuous scan rate of 10° min^{-1} . The surface elemental composition of dried sample mounted on a carbon tape was measured by XPS (PHI X-tool, ULVAC-PHI, Inc., Japan), equipped with a monochromatic $\text{Al K}\alpha$ radiation (1486.6 eV) at 4 W and 15 kV and an X-ray current of 20 mA. The acquisition area and take-off angle were fixed at $14\text{ }\mu\text{m}$ and 45° respectively and the pressure in the measurement chamber was $8.0 \times 10^{-7}\text{ Pa}$. The step size was 0.25 eV for both survey and high-resolution spectra (pass energy 280 eV). Scanning electron microscopic (SEM) images were taken to analyze the surface morphology and size distribution. Before SEM (JSM-6510, JEOL, Japan) observation, the diluted suspension (0.01% solid) was dried on a mica sheet in a vacuum desiccator overnight. To prevent sample damage under electron beam, the dried SEM samples were gold coated before observation. The specific surface area (S_{BET}), average pore diameter and pore volume of the dried samples were estimated by Barrett-Joyner-Halenda (BJH) technique using a BET (NOVA3000e, USA) apparatus at 77 K. The magnetic property was analyzed by a vibrating sample magnetometer, VSM (Micro Sense, EV9, USA). Visible spectrophotometer (OPTIMA, SP 300, Japan) was used for recording the color change during catalysis experiment and a pH meter from Mettler Toledo Company (MP 220, Switzerland) was used for adjusting the pH value.

2.5. Catalytic activity

The catalytic performance of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was measured by following the reduction of 4-NP to 4-AP. In a typical procedure, 10 mg L^{-1} of 4-NP was dissolved in 25 mL deionized water and the pH was adjusted at the respective pH value. NaBH_4 (8 mg) and 3 mg of nanocatalyst were added to the 4-NP solution and the contents were gently mixed (350 rpm) at 25°C . The change in color intensity of the reaction mixture was monitored by measuring the absorbance value at 400 nm via a visible spectrophotometer at specific time interval. The same procedure was employed to study effects of other variables like initial 4-NP concentration, temperature, catalyst dose at the optimized pH value. A calibration curve was drawn for calculating the residual 4-NP concentration. The percentage of conversion (C %), as a function of time was estimated by using Eq. (1):

$$C(\%) = [(C_0 - C_t) / C_0] \times 100 = [(A_0 - A_t) / A_t] \times 100 \quad (1)$$

Where, C_0 and A_0 are the initial concentration and absorbance of 4-NP. C_t and A_t are the concentration and absorbance at time t , respectively.

The reductive conversion kinetic data were fitted with the following pseudo-first-order [Eq. (2)] and pseudo-second-order [Eq. (3)] models:

$$\ln(C_t / C_0) = \ln(A_t / A_0) = -k_1 t \quad (2)$$

$$1 / C_t = 1 / C_0 + k_2 t \quad (3)$$

Where k_1 (min^{-1}) and k_2 ($\text{L mg}^{-1} \text{ min}^{-1}$) are the pseudo-first-order and pseudo-second order rate constants, respectively.

A blank experiment in presence of either nanocatalyst or NaBH_4 was carried out to see any change in color removal percent (D %) with time.

Fig. 2. FTIR spectra of (a) Cu-Ni NPs, (b) Fe₃O₄-SiO₂-NH₂ composites and (c) Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst in KBr pellets.

For comparison, the reductive reaction of 4-NP in presence of equivalent amount of either Cu-Ni NPs or Fe₃O₄-SiO₂-NH₂ composites was carried out by keeping all other parameters such as pH, 4-NP concentration (10 mg L⁻¹) and catalyst dose as identical.

Besides, the catalytic activities of the Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst were further tested in the reduction reactions of few other nitro aromatic compounds. A 10 mL aqueous solution containing respective nitro aromatic compound (1 mmol) and Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst (5 mg) was taken in a three-necked round bottom flask and stirred for about 5 min. Then NaBH₄ (w/w ratio 2/1 with respect to nitro compound) was added, and the reaction mixture was stirred for 3 min at 70 °C. The progress of the reaction was followed by thin layer chromatography (TLC) monitoring (eluent, *n*-hexane/ethyl acetate (Teac): 5/2). After complete reduction, the mixture was cooled to 25 °C. Then, Teac (8 mL) was added and the mixture was again stirred for 10 min. The magnetic nanocatalyst was taken out magnetically followed by repeated (two times) extraction with Teac (5 mL). The organic solution was evaporated trailed by drying over anhydrous Na₂SO₄ to get almost pure product. The purity of the reduced product was confirmed by TLC and qualitative analysis. The following equation was used to calculate the yield of the respective product.

$$\text{Yields(\%)} = \frac{\text{Moles of the product}}{\text{Initial moles of aromatic nitro compound}} \times 100 \quad (4)$$

2.6. Recycling experiment

In a typical recycling experiment, a mixture of 4-NP (10 mg L⁻¹, 50 mL) and NaBH₄ (16 mg) was taken in a beaker under mild stirring at 350 rpm. The nanocatalyst (10 mg) was added and the color change of the reaction mixture was monitored at different time intervals. The nanocatalyst was isolated magnetically, washed with water and ethanol and reused again.

3. Results and discussion

3.1. Characterizations

Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst was synthesized by a two-step process. First, amine functional magnetic Fe₃O₄-SiO₂-NH₂ composites

were prepared via a modified one-step solvothermal method. Finally, in-situ co-reduction of electrostatically interacted Cu²⁺ and Ni²⁺ ions was carried out in presence of Fe₃O₄-SiO₂-NH₂ composites using H₂N-NH₂-H₂O as a reducing agent. FTIR spectra analysis primarily gives idea about the change in functional groups on the surface during different stages of nanocatalyst fabrication. Fig. 2 shows the FTIR spectra of Cu-Ni NPs, Fe₃O₄-SiO₂-NH₂ composites and Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst. The FTIR spectrum of Fig. 2a is generally show absorption bands for Fe-O bond at 399.62, 591.26 and 1633.51 cm⁻¹ and an intense broad stretching vibration band of O-H for Fe-OH groups at 3399.26 cm⁻¹ [31, 32]. In addition to these absorption signals of Fe-O bonds the spectrum of Fe₃O₄-SiO₂-NH₂ composites (Fig. 2b) exhibits characteristic asymmetric stretching vibrations of Si-O-Fe, Si-OH and Si-O-Si at 1027, 900 and 792 cm⁻¹ respectively [31,33]. Two more signals at 1369 and 1557 cm⁻¹ represent the C-H stretching and -NH bending vibrations, which implies the successful incorporation of propylamino group from organosilane coupling agent, APTES, on the surface of Fe₃O₄-SiO₂-NH₂ composites [34]. The bands at 2863 and 2930 cm⁻¹ (Fig. 2b) correspond to the asymmetric and symmetric stretching vibrations of aliphatic C-H are originated from APTES and residual CTAB. In the spectrum of Cu-Ni NPs (Fig. 2a), the absorption peaks at 470 and 517 cm⁻¹ attribute to bending vibrations of Ni-O and/or Cu-O bond, while a sharp band at 624 cm⁻¹ represents Ni-O-H stretching vibration [35,36]. The other bands are probably derived from ascorbic acid or ethylene glycol. This result indicates that Cu-Ni surface atoms are partially oxidized in air either during preservation or due to incomplete in-situ co-reduction of precursor ions. In the spectrum of Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst (Fig. 2c) the absorption peaks in the 373–631 cm⁻¹ region can be allocated to the lattice vibration modes of M-O, M-OH bonds [37,38]. The appearance of aforementioned bands of Fe-O bonds appeared in the spectrum of NH₂-SiO₂-Fe₃O₄ composites changed following inclusion of Cu-Ni NPs. The interaction of Cu-Ni NPs with functional SiO₂ also results in significant suppression and slight shifting of N-H bending signal to 1553 cm⁻¹ along with relatively larger impacts on Si-O-Fe asymmetric vibrations at 1001 cm⁻¹ (Fig. 2c). Moreover, the C-H band in the Fe₃O₄-SiO₂-NH₂/Cu-Ni nanocatalyst is hardly visible. Therefore, the overall analyses confirm the decoration of Fe₃O₄-SiO₂-NH₂ composites with Cu-Ni NPs.

The different crystalline phases were identified by XRD diffraction

Fig. 3. XRD spectra of (a) Cu-Ni NPs, (b) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and (c) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst.

patterns as shown in Fig. 3. Diffraction pattern of Cu-Ni NPs (Fig. 3a) shows the existence of sharp peaks at 2θ values of 43.46° , 44.61° , 50.58° , 51.94° , 74.25° and 76.6° . The characteristic diffraction peaks at

43.46° , 50.58° , and 74.25° represent the (111), (200), and (220) planes of the face-centered-cubic (fcc) metallic Cu (PDF standard cards, JCPDS 04-0836, space group Fm3m) [39]. Whereas, the peaks at 44.61° , 51.94° and 76.6° can be indexed to (111), (200) and (220) fcc structure of Ni metal, matched with the reported value (PDF standard cards, JCPDS 04-0850, space group Fm3m) [40]. The experimental lattice parameters for Cu ($3.6046 \text{ \AA}$) and Ni ($3.5162 \text{ \AA}$) are in good agreement with the lattice parameter for pure Cu ($3.614 \text{ \AA}$, PDF# 00-004-0836) and pure Ni ($3.524 \text{ \AA}$, PDF# 00-004-0850) [41]. Additionally, the slightly lower experimental lattice parameter for Cu compared to standard lattice parameter ($3.614 \text{ \AA}$) is attributed to the incorporation of Ni metal. These results indicate that in Cu-Ni NPs, Cu and Ni are present in different metallic phases with no sign of other species or oxides. Despite this above finding, formation of negligible amount of metallic oxide, not detectable by XRD, is still possible under the existing preparation condition. The percentages of Cu^0 and Ni^0 in bimetallic Cu-Ni NPs based on the (111) crystal plane are estimated as $\sim 51.77\%$ and $\sim 48.23\%$, respectively. These calculated values matched well with the Cu-Ni molar ratio (1:1) in the recipe. The average crystallite sizes of Cu and Ni NPs in bare Cu-Ni NPs are 57.81 and 14.36 nm respectively. The diffraction pattern of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites (Fig. 3b) display signals at 2θ values of 30.28° , 35.72° , 43.33° , 53.78° , 57.28° and 62.97° , which are assignable to (220), (311), (400), (422), (511) and (440) planes of cubic inverse spinel Fe_3O_4 (JCPDS 03-0863) respectively [42,43]. The average crystallite size of Fe_3O_4 in $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ nanocomposite, calculated from Debye-Scherrer formula, is 23.56 nm. Comparatively, the

Fig. 4. SEM images of (a) Cu-Ni NPs, (b) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites, and (c) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst.

$\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst (Fig. 3c) shows almost all diffraction signals of Fe_3O_4 with three new intense but broad diffraction signals at 43.64° , 50.78° and 74.46° . These signals are corresponding to (111), (200) and (220) planes of fcc structure of pure bimetallic Cu-Ni (1:1) alloy as no distinct signal due to individual neat Cu and Ni metals can be identified. The average crystallite size of Cu-Ni alloy in the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is only 6.3 nm. The smaller crystallite size of bimetallic Cu-Ni alloy particles indicates that amine functionality in magnetic SiO_2 support favored homogeneous nucleation and growth. This above comparative interpretation of XRD diffractions indicates that $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is successfully prepared via co-reduction of Cu and Ni precursor salts.

The elemental composition by XPS survey spectrum in Fig. S1A exhibits the presence of C1s, O1s, Si2p, Fe2p3, Cu2p and Ni2p signals in the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. Additionally, the core-line spectrum of each Cu2p and Ni2p (Fig. S1B,C) can be differentiated into four distinct satellite signals which ultimately show the existence of Cu^0 , Cu^+ , Cu^{2+} and Ni^{2+} in the prepared nanocatalyst [44,45]. It is therefore reasonable to conclude from XRD and XPS results that metal oxide is formed only at the nanocatalyst surface in contact with air.

The surface morphology, size distribution and physical state of aggregation of the nanocatalyst and associated particles were analyzed by SEM images as illustrated in Fig. 4. The unmodified Cu-Ni NPs shown in Fig. 4a are composed of many tiny (137 nm) spherical particles, which are visibly aggregated into cluster. This cluster formation was effected by the metal-metal interaction and magnetic property [2]. $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites prepared by one-step solvothermal process are mostly spherical (Fig. 4b), dispersity index is apparently high and the surface is heterogeneous. Most likely, the heterogeneous surface structure is derived from the Fe_3O_4 NPs formed near the surface of amine functional SiO_2 surface. Under the preparation conditions some free iron oxide NPs might have also been produced. The average size of incorporated Fe_3O_4 NPs is roughly 4.3 nm. In case of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst, a clear boundary layer among particles can be observed. Smaller Cu-Ni alloy NPs with sizes between 12 and 22 nm are tightly packed into larger particles. The overall morphology of the nanocatalyst is noticeably different from the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support. Particles similar to composite support is rarely visible in the SEM image of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. The size distribution could not be compared as they are very much polydispersed. It is clear that there is a distinct dissimilarity in morphology between support materials and supported nanocatalyst.

The N_2 adsorption-desorption isotherms of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst are shown in Fig. S2. In both cases, the adsorption follows mesoporous type IV isotherms [46, 47]. The sharp increase in adsorption at the relative pressure of 0.3 in $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites indicates the presence of porous structure, which may also arise from surface heterogeneity. On the other, the adsorption-desorption isotherm of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst flattens sharply, reflecting a decrease in porosity or surface heterogeneity, which is ascribed to anchoring of Cu-Ni NPs. The BET specific surface areas of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst also revealed a decrease from 280.5 to 108.9 $\text{m}^2 \text{g}^{-1}$ due to surface coverage of some pores by Cu-Ni

Fig. 5. VSM curves of (a) Cu-Ni NPs, (b) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and (c) $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst.

alloy NPs [46,47]. This is to mention that average diameter (12–22 nm) of Cu-Ni alloy NPs is larger than the average pore diameter (3.4 nm) in $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ support materials. On the contrary, the average pore diameter in $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst increases to 6.57 nm.

The magnetic hysteresis loops of Cu-Ni NPs, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst measured by VSM at room temperature are shown in Fig. 5. Independent of nature, the hysteresis loops of particles show almost zero coercivity and remanence. The saturation magnetization of neat Cu-Ni NPs is 23.38 emu g^{-1} (Fig. 5a). Whereas, the saturation magnetization values of iron oxide containing magnetic $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst are 31.45 and 27.76 emu g^{-1} , respectively (Fig. 5b, c). The classic “S” shape reversible magnetization curve confirms the paramagnetic character of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. The relatively strong paramagnetic property obviously ensured the magnetic separation and recovery of the nanocatalyst.

3.2. Nanocatalyst formation mechanism

The $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was synthesized by in situ co-reduction Cu and Ni precursor salts in presence of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites. In the first step, a one-step solvothermal route comprising simultaneous co-precipitation of Fe^{2+} and Fe^{3+} and hydrolysis of TEOS was employed for preparing the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites. $\text{Fe}(\text{OH})_3$ produced from Fe^{3+} precursor salts was reduced to $\text{Fe}(\text{OH})_2$ in presence of ethylene glycol, a mild reducing agent, at 200°C [48,49]. Formation of Fe_3O_4 particle nuclei was then followed by the combination of Fe^{3+} and Fe^{2+} hydroxides. The reactions are:

It is speculated that almost simultaneously, TEOS started to hydrolyze with the aid of DEA around the Fe_3O_4 particle nuclei forming $\text{Fe}_3\text{O}_4\text{-SiO}_2$ and grafted with APTES to form $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites. Since simultaneous co-precipitation of Fe salts was continued, there is extreme possibility of further nucleation and coordination of Fe_3O_4 nuclei via -NH_2 functional group on the surface of already formed $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and subsequent surface modification with aminated SiO_2 . Thus the ultimate $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites are expected to be composed of Fe_3O_4 particles in SiO_2 matrix. The hydrolysis reactions and grafting of APTES can be symbolically written as.

In the second step, the formation of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst was effected by adding the precursors of Cu^{2+} and Ni^{2+} in presence of $\text{H}_2\text{N-NH}_2\cdot\text{H}_2\text{O}$, a reducing agent. During the process, Cu^{2+} ions and Ni^{2+} ions were interacted with the surface of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites via amino (-NH_2), silanol (Si-OH), and siloxane groups (Si-O-Si). All probable coordination paths of metal ions are shown in Fig. S3. Co-reduction of metal ions was followed immediately producing the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst.

3.3. Catalytic activity

The performance of prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst was tested for the reductive reduction of 4-NP, a model aromatic nitro compound. 4-NP is a highly toxic organic compound that causes skin and eye irritation, shortness of breath, rapid heartbeat and weakness. Comparatively, the reduced product, 4-AP is less toxic and more biodegradable in air.

The pH-dependent study in the pH range of 3–10 (Fig. S4) shows that a maximum conversion of 99.5% is achievable at pH 6 within 10 min in presence of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst. A comparative study with $\text{SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst [21] indicates that inclusion of iron oxide in support materials improves the reduction rate and conversion to 4-aminophenol (4-AP). Hence, it can be said that Fe_3O_4 in support materials assisted the sorption of 4-NP on the nanocatalyst surface, enhanced electron density and storage capacity and thus favored the smooth electron-transfer from the reducing agent, NaBH_4 , to the reactant 4-NP.

The impact of initial concentration of reactant, 4-NP, in presence of identical amount of nanocatalyst (3 mg) was then studied at pH 6 and results are presented in Fig. 6a. Independent of initial concentration, the concentration of 4-NP decreases rapidly up to 2 min and then goes down slowly. The initial rapid decrease in 4-NP concentration up to 2 min is associated with sorption and the comparatively slower decrease in 4-NP concentration towards the end of the reaction is due to the catalytic conversion to 4-AP. Maximum conversion to 4-AP is obtained at the initial concentration of 10 mg L^{-1} , because, the catalyst dose was kept identical in all experiments. Hence, the active catalyst site is not enough when the initial concentration of 4-NP exceeds 10 mg L^{-1} . This is to mention that in all cases a higher conversion of 4-NP is obtained in presence of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst than that in presence of

$\text{SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst [21].

Comparative study of catalytic activity shown in Fig. 6b, suggests that use of magnetic amine functional SiO_2 support for Cu-Ni NPs enhances the performance of nanocatalyst for the reduction of 4-NP under the same reaction conditions. It is obvious that use of magnetic SiO_2 support improved the active surface area for the sorption of 4-NP molecules and borohydrate reducing agent, a prerequisite condition for efficient catalysis. It is also reasonable to assume that supported Cu-Ni NPs are less aggregated compared to neat Cu-NPs due to linkage with the functional support. Thus, the interaction of metal to metal and metal to supporting materials along with higher stability all helped to improve the catalytic efficiency [50]. It is also interesting to see that $\text{Fe}_3\text{O}_4\text{-}$

$\text{SiO}_2\text{-NH}_2$ composite support themselves possessed significant sorption and catalytic property, produced around 53% conversion of 4-NP after 50 min. Turn over frequency (TOF), defined by turn over number (TON)/reaction time, was also used to compare the catalytic power. The TOFs of Cu-Ni NPs, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst are obtained as 5.11×10^{18} , 8.56×10^{17} and $3.59 \times 10^{19}\text{ molecule}^{-1}\text{g}^{-1}$ respectively. These results again confirmed the increase in catalytic activity for the supported nanocatalyst. These findings are based on alloying effect, higher stability as well as metal to metal and metal to support interactions. Thus, the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst can function as a potential reductive catalyst. It is noteworthy to mention that neither $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nor NaBH_4 alone possesses catalytic activity as the conversion curves almost flattens after 10 min (Fig. S5). The initial sharp increase in conversion possibly results from the sorption of 4-NP.

The variation of nanocatalyst dose in the range of 1–4 mg shows that 3 mg loading is enough to achieve maximum reduction capacity for 25 mL of 10 mg L^{-1} 4-NP aqueous solution (Fig. S6a). Here, metal catalyst functioned as a relay center for smooth transfer of electrons from BH_4^- to 4-NP molecules. Hence, more catalyst should provide more active sites for electron transfer and sorption of reactant molecules. But, an increase in nanocatalyst amount to 4 mg reduces reduction capacity to 95%. Increasing amount of nanocatalyst (4 mg) possibly reduces the total surface area through coagulation. Temperature effect on conversion percent was also measured by running catalysis at 10, 25 and 40 °C respectively (Fig. S6b). It is observable that maximum conversion of 100% can be attained within 8 min at 40 °C. The increase in catalysis power is a general property of any good catalyst. It is apparent that increase of temperature increased the energy of reactant molecules and hence reduces the energy barrier for successful conversion of reactant into product.

The above experiments suggested that chemical reduction of 4-NP proceeds well with the fabricated $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2\text{/Cu-Ni}$ nanocatalyst in presence of NaBH_4 reducing agent. Hence, theoretically it can be anticipated that the reduction reaction followed pseudo-first-order kinetic model. In order to reassess the findings, the time-dependent and pH-dependent changes in concentration of 4-NP following catalysis reactions were applied to pseudo-first-order and pseudo-second-order kinetic models. The linear forms of pseudo-first-order and pseudo-second-order kinetic plots are shown in Figs. 7 and 8. The estimated values of

Fig. 6. (a) Time-dependent change in 4-NP concentration during catalytic reduction over the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. Inset figure shows the final conversions at different initial concentrations of 4-NP. (b) Change in conversion of 10 mg L^{-1} of 4-NP at different time intervals in presence of pure Cu-Ni NPs (diamond), $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites (triangle) and the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst (cube). Conditions: Cu-Ni NPs, 1.1 mg; $\text{NH}_2\text{-SiO}_2\text{-Fe}_3\text{O}_4$, 1.9 mg; $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst, 3 mg; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; and temperature, 25°C .

Fig. 7. Linearized (a) pseudo-first-order and (b) pseudo-second-order kinetic plots obtained from time-dependent change in 4-NP concentration during catalytic reduction over the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. Conditions: nanocatalyst, 3 mg; NaBH_4 , 8 mg; total volume, 25 mL; pH, 6; and temperature, 25°C .

correlation coefficients obtained from linearized plots (Table S1) shows that reduction of 4-NP enthusiastically followed pseudo-first-order reaction as values of R_1^2 are comparatively higher in both concentration and pH-dependent experiments. The relatively higher value of first-order rate constant, k_1 (min^{-1}), indicated the faster reduction kinetics for the pseudo-first-order rate model. It is also clear that reaction goes faster at pH 6 as the corresponding rate constant (k_1) is the highest. A comparative performance of our prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst with already available nanocatalyst (including unsupported metals) in terms of pseudo-first-order rate constant, k_1 (min^{-1}) is presented in Table S2. The important point is the improvement in reaction rate following incorporation of iron oxide in amine functional SiO_2 support. This improvement in performance is based on synergistic effects of interaction of metal to iron oxide and SiO_2 , as well as substantial catalytic property of iron oxide itself. In comparison with other catalytic systems, the activity of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst is proportionately good and sometimes even observed better. Thus, the simple and easily prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst can be a

good replacement for unsupported metal nanocatalyst in the catalytic hydrogenation of 4-NP.

3.4. Reduction of other aromatic nitro-compounds

The usefulness of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was further examined by carrying out reduction of few other aromatic nitro-compounds. All reactions were carried out under identical reaction conditions at 70°C in presence of 5 mg of nanocatalyst. The reaction progress was monitored by TLC and purity of the respective amino product was confirmed by a single spot on the TLC plate. The results depicted in Table 1 indicates fairly good yield for almost all products. The lowest yield from *m*-amino-nitrobenzene (entry 4) is possibly due to the relatively strong resonance or hindrance effect that might have affected the electrophilicity. Therefore, the prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst has good prospect for application in reduction reactions. This is to mention that mechanism of catalytic reduction of nitrobenzene and derivatives is already known. The mechanism of

Fig. 8. Linearized (a) pseudo-second-order and (b) pseudo-second-order kinetic plots obtained from pH-dependent change in 4-NP concentration during catalytic reduction over the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst. Conditions: 4-NP, 10 mg L^{-1} ; nanocatalyst, 3 mg; NaBH_4 , 8 mg; total volume, 25 mL; and temperature, 25°C .

reduction is schematically represented in Fig. S7. Overall, the conversion of 4-NP to 4-AP occurs in three steps: (i) the adsorption of reactants and reducing agents onto the surface of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst, (ii) transfer of electrons from donor, BH_4^- to acceptor, 4-NP and (iii) the desorption of product 4-AP.

3.5. Recovery and reuse

The recovery and recyclability of the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was evaluated to measure the sustainable use for practical applications. The reduction reactions of 4-NP over six consecutive cycles were carried out in presence of recovered $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst under ambient conditions using borohydride reducing agent. After each cycle of 4-NP reduction, the nanocatalyst was recovered magnetically, washed several times with water and ethanol before reuse. The obtained results shown in Fig. 9a indicates 100% retention of initial catalytic activity as the conversion of 4-NP to 4-AP remained 100%. The slight fall in conversion during the initial three runs can be considered within the measurement error. However, the interesting finding is the almost 5 fold increase in reaction kinetics (Fig. 9b, Table S3) during 6th reaction cycle. This result is quite surprising. The phase structure of the recovered nanocatalyst after the 6th run was investigated by recording XRD pattern. It can be seen from Fig. S8, that

Table 1

Catalytic reduction of various nitro aromatic compounds over $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst.

Entry	Substrate	Product	Molar ratio (Substrates/ NaBH_4)	Catalyst (g)	Time (min)	Yield (%)
1			1:2	0.005	5	93
2			1:2	0.005	5	83
3			1:2	0.005	8	81
4			1:2	0.005	12	66

Fig. 9. (a) Percent conversions of 4-NP during recycle experiment, and (b) linearized pseudo-first order kinetic plots during catalytic recycle of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst for the reduction of 4-NP. Conditions: 4-NP, 10 mg L^{-1} ; nanocatalyst, 10 mg; NaBH_4 , 16 mg; total volume, 50 mL; pH, 6; and temperature, 25°C .

all diffraction signals due to (111), (200) and (220) planes of pure fcc Cu-Ni alloy at 2θ values of 43.64° , 50.78° and 74.46° are retained in the reused and washed nanocatalyst (after 6th run) without any distortion or deviation. But, the diffraction signals corresponding to both Fe_3O_4 and Cu-Ni alloy NPs became more intense after reuse. The average crystallite size of Cu-Ni nanoalloy in the reused washed nanocatalyst is estimated as 10.8 nm, slightly increased from that initial (6.3 nm) used in the first run. Hence, the repeated use and washing of nanocatalyst during recycle experiment did not produce agglomeration or reduction in overall active surface area. The increased reaction kinetics of the reused nanocatalyst is somehow promoted by better sorption of reactant molecules and smooth transfer of electrons. Nonetheless, it is important to conclude that the prepared $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst has improved catalytic activities and higher stability compared to the previously prepared $\text{NH}_2\text{-SiO}_2/\text{Cu-Ni}$ nanocatalyst [21]. Thus, the synergistic interactions of Cu-Ni nanoalloy with iron oxide and amine functional groups on the SiO_2 support, enhanced electron density and storage capacity significantly promoted the catalytic activity [51]. And, the whole preparation of comparatively stable as well as highly effective $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst was possible by a simple two-step process.

4. Conclusion

In this protocol, $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites are fabricated using a simple and scalable one-step solvothermal method to support bimetallic Cu-Ni alloy NPs. XRD patterns indicates the formation of metallic fcc Cu-Ni alloy without any ionic phase but FTIR and XPS analyses show the existence of oxide particles, possibly resulted from surface oxidation of metals during handling and storage. The average crystallite sizes of Fe_3O_4 and Cu-Ni NPs in the $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst are 23.6 and 6.3 nm, respectively. SEM images reveal that both $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composites and $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst possess a heterogeneous non-smooth surface. The nanocatalyst exhibits fairly strong paramagnetic character and is separable from the media magnetically. The reductive catalytic reduction of 4-NP to 4-AP in presence of nanocatalyst shows conversion up to 99.5% within 10 min at pH 6. Both, reaction kinetics and recycle stability of the nanocatalyst remarkably improve following the inclusion of magnetic iron oxide in SiO_2 matrix. The phase structure of supported fcc Cu-Ni alloy NPs did not change after the 6th reaction cycle and interestingly, a five-fold increase in reaction rate is observed during the recycle experiment. Overall, the direct interaction of Cu-Ni alloy NPs with iron oxide and

functional SiO_2 is possible due to the use of $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2$ composite support, which finally enhances the catalytic performance. Hence, this work allows a facile and efficient synthetic approach for the preparation of highly effective and stable $\text{Fe}_3\text{O}_4\text{-SiO}_2\text{-NH}_2/\text{Cu-Ni}$ nanocatalyst.

CRediT authorship contribution statement

Mohammad Z. Sarker: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft. **Mohammad M. Rahman:** Conceptualization, Validation, Resources, Writing – review & editing, Supervision. **Hideto Minami:** Methodology, Investigation, Resources, Data curation. **Toyoko Suzuki:** Methodology, Investigation, Data curation. **Mohammad A. Rahman:** Formal analysis, Visualization. **Alam Khan:** Methodology, Investigation. **Sheikh M. Hoque:** Investigation. **Hasan Ahmad:** Conceptualization, Methodology, Formal analysis, Resources, Data curation, Writing – review & editing, Visualization, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.colsurfa.2022.129044](https://doi.org/10.1016/j.colsurfa.2022.129044).

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