Synthesis of Colloidal CuO/ γ -Al₂O₃ by Microemulsion and Its Catalytic Reduction of Aromatic Nitro Compounds

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Abstract: Monodispersed colloidal copper oxide nanoparticles were synthesized by water-in-oil microemulsion using CuCl₂·H₂O and NaOH. The effect on CuO particle size was studied by varying the water-to-surfactant molar ratio, precursor concentration and molar ratio of NaOH to CuCl₂. The morphology, size and size distribution of the particles were studied by transmission electron microscopy and dynamic light scattering. Dispersion destabilization of the colloidal copper oxide nanoparticles was detected by a Turbiscan apparatus. CuO/ γ -Al₂O₃ catalysts were prepared by dispersing highly stable CuO nanoparticles on γ -alumina by mechanical stirring. The catalysts were analyzed by scanning electron microscopy, transmission electron microscopy, X-ray photoelectron, and X-ray diffraction, which confirmed the uniform dispersion of CuO on the support. The reduction of the nitro aromatic compounds, 4-nitrophenol, 3-nitrophenol, and 2-nitrophenol, were studied. The CuO/ γ -Al₂O₃ catalysts were active for the reduction of these nitro aromatic compounds.

Key words: microemulsion; copper oxide; alumina; nanocatalyst; catalytic reduction; nitro aromatic compound

CLC number: O643

Document code: A

Received 10 April 2012. Accepted 3 July 2012.

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This work was supported by the Sardar Vallabhbhai National Institute of Technology, Surat, India.

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

The preparation and characterization of transition metal nanoparticles have received much attention due to their use in magnetic recording substrates, and as semiconductors, ceramics, and metallic catalysts for their novel electronic, magnetic, mechanical and optical properties that can be different from those of conventional bulk materials [1]. A copper oxide (CuO) nanoparticle is a p-type semiconductor, which has been used in various applications as gas sensor, glucose sensor, field emission emitter, thermoelectric material, and solid catalyst [2–6]. Various supports like TiO₂, SnO₂, ZnO, BiVO₄, SiO₂, γ -Al₂O₃, and zeolite are used to support CuO catalysts [7], on which the metal catalysts are highly dispersed as fine particles on the surface of the support. Gamma alumina is one of the most widely used catalyst supports for commercial catalytic applications. In addition to factors such as low cost and mechanical strength, the features responsible for the wide application of gamma alumina are its high surface area and open mesoporosity, which allows molecules to penetrate rapidly to catalytic sites. Many methods have been used to synthesize CuO nanomaterials, such as electrochemical deposition [8], thermal oxidation [9], simple hydrolysis [10], template-based sol-gel [11], hydrothermal [12] microwave-hydrothermal [13], solvothermal [14], and microemulsion [1,15,16,17] synthesis.

Microemulsions are clear and thermodynamically stable

liquid mixtures of oil, water, and a surfactant, which is frequently used in combination with a cosurfactant. Microemulsions are of two types: (1) oil-in-water (oil dispersed in water, o/w) and (2) water-in-oil (water dispersed in oil, w/o), where the second compound is the dispersion medium or solvent [18]. A water-in-oil (w/o) microemulsion is visible and attractive because it gives nanoparticles that have a narrow size distribution and also the particle size can be easily controlled by the microemulsion composition [19]. Generally, microemulsions consist of nanosized water droplets containing metal salts dispersed in a continuous oil medium and stabilized by surfactant molecules present at the oil-water interface. These highly dispersed water pools have been shown to be an ideal nanostructured microreactor for the synthesis of monodispersed nanoparticles.

The microemulsion method has been considered an ideal liquid-phase method to synthesize inorganic nanoparticles. Han et al. [1] prepared CuO nanoparticles from the Triton X-100 based water-in-oil reverse micelle system. The nanoparticles were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Their study showed that the grain size, morphology, and distribution were highly dependent on the ratio of water to surfactant. Li et al. [15] prepared one-dimensional (1D) Cu(OH)₂ nanowires by coupling the routes of microemulsion with homogenous precipitation using CuSO₄ and NH₃·H₂O as

raw materials. Copper oxide nanoparticles were synthesized by Nassar et al. [16] from CuCl₂ as a precursor in a single microemulsion by the direct addition of NaOH using sodium bis(2-ethylhexyl) sulfosuccinate (AOT) as surfactant and cyclohexane as the oil phase. The size of the particle was found to increase with increasing surfactant concentration, concentration of the precursor salt, and water to surfactant molar ratio, while the nanoparticle yield increased linearly with the surfactant concentration, and displayed an optimum with water-to-surfactant molar ratio (ω) and was a power function of the concentration of the precursor salt. Vahidshad et al. [17] synthesized CuO-ZrO₂ nanoparticles by the microemulsion technique by varying different process parameters and using different surfactants like cationic (CTAB), anionic (AOT), and nonionic (Brij56) to control the size and size distribution of the particles.

The aromatic amino compound, 4-aminophenol (4-AP), is used for the production of analgesic and antipyretic drugs like paracetamol, acetanilide, and phenacetin. It is also a very important ingredient in the production of industrial dyes, it is marketed as a photographic developer and its oxalate salt is used as a corrosion inhibitor [20]. 4-AP is obtained by the hydrogenation of nitrobenzene using the molecular rearrangement of the phenylhydroxylamine intermediate by an iron acid [21]. It is also synthesized by the catalytic amination of hydroquinone [22] and electrochemical reduction [23].

Various transition metal nanoparticles have been used as catalyst for the reduction of nitro aromatic compound to produce amino compounds. Oh et al. [24] prepared PVP stabilized Pd-M (M = Ag, Au, Cu, Ni, and Pt) colloids by γ -irradiation in aqueous solution. The catalytic activity of this bimetallic catalyst was characterized for the reduction of 4-nitrophenol in aqueous solution at room temperature. Palladium nanoparticle was incorporated in a poly-(3,4) ethylenedioxythiophene (PEDOT) matrix in aqueous medium and its catalytic performance was studied by the reduction of 4-nitrophenol [25]. In the literature, it has been reported that silver metal nanoparticles and NaBH₄ smoothly reduced aromatic nitro compounds to amines in aqueous medium [26–28]. Recently, Solanki and Murthy [29] used a Ag/Al₂O₃ catalyst for the reduction of nitro aromatic compounds such as 4-nitrophenol (4-NP) and 4-nitroaniline. Gold nanocatalysts were also used for the reduction of nitro aromatic compounds in the liquid phase at room temperature [30–33]. CuO is an active and comparatively cheap catalyst for the reduction of aromatic compounds. Recently, Mandlimath et al. [34] reported that the first row transition metal oxides (CuO, Co₃O₄, Fe₂O₃, and NiO) were also active catalysts for the conversion of *p*-nitrophenol to *p*-aminophenol at room temperature using sodium borohydride as reducing agent.

Nitrophenols and their derivatives, which result from the production of pesticides, insecticides, synthetic dyes, and herbicides, are some of the most refractory pollutants in industrial waste waters. Due to this, the study of the catalytic reduction of 4-NP is also useful for pollution abatement. Aromatic nitro compounds are reduced by various reducing agents such as sodium borohydride, hydrazine hydrates, and hydrogen. Hydrazine hydrate and hydrogen are the cheapest reducing agents. Hydrazine is a neurotoxin, which produces carcinogenic and mutagenic effects that cause damage to lungs, kidneys, and livers, and causes respiratory tract infection and has long-term effects on the central nervous system. Sodium borohydride (NaBH₄) is the most popular reducing agent for the reduction of amino nitro compounds for its many advantages over hydrazine. It is a much milder reducing agent, safe to handle, has no pressure apparatus requirement, gives rapid reduction, is easy to work at the experimental condition, and gives good selectivity in the reduction of nitro compounds.

Various metal catalysts (silver, gold, and palladium) are used for the reduction of aromatic nitro compound. All these catalysts are very expensive for industrial use in bulk quantity. To reduce the cost of the catalyst, a highly active CuO/ γ -Al₂O₃ nanocatalyst was developed. This is a new solid catalyst synthesized by the microemulsion method for the reduction of 4-NP. The aim of the present study is to prepare highly monodispersed colloidal copper oxide nanoparticle in a water-in-oil microemulsion system at room temperature (30 $\pm$ 2 °C). The size, size distribution, and morphology of the CuO nanoparticles were controlled by the ω , concentration of the precursor, and molar ratio of NaOH to CuCl₂ (R). The nanoparticles were characterized by dynamic light scattering (DLS) and transmission electron microscopy (TEM). A Turbiscan apparatus was used to monitor the back scattering profiles of the colloidal copper oxide nanoparticles to characterize their dispersions for the kinetic study of their stability. The CuO/ γ -Al₂O₃ nanocatalyst was characterized by TEM, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) to confirm the presence of CuO on the alumina support. The reduction of a nitro aromatic compound was carried out with the CuO/ γ -Al₂O₃ catalyst in a continuously stirred batch reactor. Absorbance spectra were recorded versus time to characterize the reduction of 4-NP, 3-nitrophenol (3-NP), and 2-nitrophenol (2-NP).

1 Experimental

1.1 Materials

Copper chloride (CuCl₂, 99%) and sodium borohydride (NaBH₄, 95%) were purchased from Merck, India. Cyclo-

hexane, ammonium hydroxide, and sodium hydroxide were purchased from Finar Chemicals, India. The nonionic surfactant polyoxyethylene octyl phenyl ether (Triton X-100), 4-NP, 3-NP, and 2-NP were purchased from S.D. Fine Chemicals, India. γ - Al_2O_3 of 98% purity and 100 mesh size was purchased from National Chemicals, India. All the chemicals were used without further purification. Distilled water of $\text{pH} = 5.9 \pm 0.2$, conductivity $1.0 \mu\text{S}/\text{cm}$ (Millipore, Elix, India) was used for preparing the aqueous solutions.

1.2 Synthesis of copper oxide nanoparticles

The copper oxide nanoparticles were synthesized in a water-in-oil microemulsion. A fixed amount of copper chloride was dissolved in distilled water to obtain a 0.1 mol/L stock solution. The precursor concentration was varied by the salt amount in the stock solution. To first prepare the microemulsion, the required amount of nonionic surfactant (Triton X-100, 0.2 mol/L) was dissolved in cyclohexane and a fixed volume of the above stock solution was added to keep the ω value at 4. A higher ω was achieved by adding an additional amount of aqueous solution as required. The mixture was vigorously stirred by a high speed mechanical stirrer (Ultraturax T25 basic, IKA®-WERKE, GmbH & Co. KG) at 6500 r/min for 5 min at room temperature until it became transparent. Similarly, a second microemulsion of the same ω value was prepared by replacing the solution of CuCl_2 with that of a NaOH (0.3 mol/L) solution. The two microemulsions were mixed to produce a third microemulsion, and the system was left to mix for 3 h at room temperature. The mixture was washed with methanol and destabilized by acetone. Finally, metal nanoparticles were separated by high speed centrifugation to get concentrated CuO colloidal nanoparticles.

1.3 Preparation of $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst

To synthesize a uniformly distributed $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst, it is necessary to maintain the homogeneous distribution when transferring the nanoparticles onto the support. The concentrated colloidal CuO nanoparticle (accumulated by repeated syntheses) was re-dispersed in methanol and the required amount of the $\gamma\text{-Al}_2\text{O}_3$ support was added under vigorous stirring. The mixture was mechanically stirred (6500 r/min) for 24 h at room temperature to form a homogeneous suspension. After that, the mixture was washed with acetone to remove the organic material and dried at 60°C for 6 h. The powder (metal and supporting agent) was stored in a moisture-free atmosphere.

1.4 Characterization of colloidal CuO nanoparticles and $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst

TEM images were obtained with a Tecnai-20 apparatus (Philips, Holland) operated at 200 kV , which provided 0.27 nm resolution for determining the size and shape of the CuO nanoparticles. TEM images were prepared by putting a droplet of the nanoparticle sample on a copper grid with 300 mesh size and 3 nm diameter. This was covered with perforated carbon followed by evaporating off the solvent under the atmosphere. The particle size distribution of the nanoparticles was measured by dynamic light scattering (DLS, Malvern Zetasizer, Nano ZS90, UK). In addition, the average particle size (hydrodynamic diameter, Z-average size) was calculated by the DLS apparatus with its supplied function (by means of the diffusion constant of the particles calculated with the Stokes-Einstein equation). Nanoparticle stability was analyzed using transmission and back scattering profiles by scanning the colloidal sample with light rays of 880 nm wavelength using a Turbiscan Classic MA 2000 apparatus (Formulation, France).

XPS spectra were performed using a Multilab-2000 (Thermo-Scientific UK) spectrometer using a monochromic Mg K_α X-ray source (1256 eV) with K_α analyzer pass energy of 10 eV . The XRD measurement of supported $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ was carried out using a Philips X'Pert-MPD diffractometer employing Ni-filtered $\text{Cu } K_\alpha$ radiation with 40 kV and 30 mA at a scanning rate of $5^\circ/\text{min}$. Reaction progress was studied systematically by recording absorption spectra at various time intervals and observing the variation in absorption maxima and the corresponding wavelength with time.

1.5 Catalytic performance of $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst

The catalyst was used for the reduction of aromatic nitro compounds, namely, 4-NP, 3-NP, and 2-NP. A standard aqueous solution of 4-NP was prepared (20 ml of $4.3 \times 10^{-5} \text{ mol/L}$) and a freshly prepared aqueous solution of NaBH_4 (0.05 mol/L , 10 ml) was used for the reaction. The absorbance spectra of 4-NP after and before the addition of NaBH_4 (reducing agent) was recorded by a UV-Vis spectrophotometer (Hach, USA). To the mixture, 0.05 g of the $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst was added into a continuously stirred batch reactor at 300 r/min at room temperature. This caused a gradual fading of the characteristic yellow color of 4-NP. The reaction was studied versus time by the UV-Vis spectra. Similar experiments were performed at the same concentration for aqueous solutions of 3-NP and 2-NP.

2 Results and discussion

2.1 Effect of different papermaters

2.1.1 Water-to-surfactant molar ratio

To produce CuO nanoparticles, the microemulsion droplets acted as nanoreactors. The size of the nanoreactor, which provided a confined environment for the growth of the nanoparticle, depended on the rigidity of the interfacial film in the microemulsion [35]. With a lower water content in the microemulsion, the interfacial film was more closely surrounded by surfactant molecule, and thus was more rigid, which induced a relatively smaller particle size and narrower size distribution of the resulting crystals. With increased water content, there were more free water molecules in the microemulsion and the interfacial flexibility was improved, which caused an increase in the size of the nanoreactor and produced larger particles with a broader size distribution [1].

To study the effect on the size of the CuO nanoparticles, the ω was varied from 2 to 6, keeping the precursor and surfactant concentrations at 0.1 and 0.2 mol/L, respectively. It was observed that at $\omega = 2$, the smallest CuO nanoparticles (Z-average = 13.28 nm) were obtained. The size of the particles increased with an increase in water-to-surfactant molar ratio. Figures 1 and 2 show the morphology, size, and size distribution of CuO nanoparticles prepared at $\omega = 2, 4,$

Fig. 1. TEM images of copper oxide nanoparticles prepared at different ω values. (a) $\omega = 2$; (b) $\omega = 4$; (c) $\omega = 6$.

Fig. 2. Particle size distributions of copper oxide nanoparticles obtained at different ω values.

and 6.

The UV-Vis absorption spectra of the copper oxide nanoparticles were recorded at different ω values by keeping the other parameters constant. Increasing the ω value from 2 to 6, a red shift towards higher wavelength was observed, indicating an increase in particle size (Fig. 3). Larger particles were formed inside the micellar water core due to the

Fig. 3. UV-Vis spectra of colloidal copper oxide nanoparticles obtained at different ω values.

increase of the water core size with increasing ω , and these showed a red shift in the absorption spectra [36].

2.1.2 Precursor concentration

In this experiment, while keeping $\omega = 4$, the copper chloride (precursor) concentration was varied in the range of 0.05–0.25 mol/L. At lower concentrations of copper chloride (0.05 mol/L), the average particle size was found to be 19.55 nm. Figure 4 shows that with the increase in the concentration of copper chloride from 0.05 to 0.2 mol/L, the average particle size decreased from 19.55 to 14.07 nm. The presence of a higher concentration of precursor in otherwise identical systems resulted in a larger number of smaller particles in the droplets of the microemulsion [37]. With the further increase in concentration from 0.2–0.25 mol/L, the average particle size increased as the collision frequency of the particles formed increased, and also the protection from the adsorption of surfactant molecules on the particle surface was weakened due to a lower surfactant concentration compared with the precursor concentration. Thus, the tiny particles agglomerated to form larger particles [38].

Fig. 4. Effect of precursor concentration on particle size and stability.

To check the stability of the well dispersed colloidal CuO nanoparticles (prepared with different CuCl₂ concentration ranging from 0.05–0.25 mol/L), they were scanned from the bottom to the top of the vial for a period of 20 min and the scanning was performed at different time intervals for up to 4 d. It was observed that there were changes in the back scattering profile at different time intervals. This indicated that the structure and average size of the nanoparticles changed with time. It was found that after 4 d, the back scattering profiles of all samples remained the same, which suggested that the particles remained stable after 4 d. From Fig. 4, it was found that the back scattering profile of the colloidal CuO nanoparticles decreased with increasing precursor concentration (from 0.05 to 0.2 mol/L) due to the

formation of smaller nanoparticles with a higher population density. This then slightly increased with the further increase of concentration up to 0.25 mol/L because of the formation of larger particles with a lower population density.

2.1.3 Molar ratio of NaOH to CuCl₂ (R)

The molar ratio of precipitating agent NaOH to precursor CuCl₂ is an important parameter that controls the nanoparticle size. Figure 5 shows the particle size distributions of the CuO nanoparticles synthesized in the range of $R = 1$ –10. At the lower value ($R = 1$), the average particle size of the copper oxide nanoparticles obtained was 19.5 nm. When increasing the R value from 3 to 10, the particle size was found to be in the range of 17.51–14.85 nm. It was found from Fig. 5 that the particle size of copper oxide decreased with increasing R value. It was observed that at a higher concentration of precipitating agent, intramicelle nucleation and growth were promoted, which resulted in a faster rate of reduction and formation of smaller particles. The available and sufficient concentration of surfactant (0.2 mol/L in this study) attached on the surface of the particles would help stabilize and protect the synthesized nanoparticles.

Fig. 5. Particle size distributions of copper oxide nanoparticles synthesized with different R values. Reaction conditions: $\omega = 4$; $c(\text{CuCl}_2) = 0.1$ mol/L, $c(\text{TX-100}) = 0.2$ mol/L.

2.2 Characterization of CuO/ γ -Al₂O₃ catalyst

2.2.1 SEM and TEM results

From the SEM image (Fig. 6) of the CuO/ γ -Al₂O₃ (1 wt% loading) catalyst prepared by mechanical stirring, it was found that CuO nanoparticles were well dispersed on γ -Al₂O₃ and completely covered the whole surface of the support. The uniform dispersion of CuO nanoparticles on the γ -Al₂O₃ support was also confirmed by TEM image. From Fig. 7, the sizes of the particles were in the range of

Fig. 6. SEM image of CuO/ γ -Al₂O₃. Fig. 7. TEM image of CuO/ γ -Al₂O₃.

6.54–15.91 nm.

2.2.2 XRD results

The XRD pattern of the CuO/ γ -Al₂O₃ catalyst (Fig. 8) showed two major characteristic peaks for the CuO particles. The peaks at $2\theta = 38.4^\circ$ and 48.4° represented the (111) and (202) crystal faces of monoclinic CuO (JCPDS 5-0661). The presence of alumina was confirmed by the peak at $2\theta = 66.7^\circ$, which was a reflection from the γ -alumina support. The size of the CuO particles (15.1 nm) calculated by the Scherrer formula was close to the average diameter (13.7 nm) obtained by TEM analysis.

Fig. 8. XRD pattern of CuO/ γ -Al₂O₃ catalyst.

2.2.3 XPS results

The XPS analysis of the CuO/ γ -Al₂O₃ catalyst is shown in Fig. 9. The chemical composition of the CuO catalyst was found by the XPS measurement. Alumina data have been partly removed from Fig. 9. All the other peaks were corrected accordingly. Elements C, Cu, and O were found in the catalyst. The Cu 2p_{3/2} and Cu 2p_{1/2} peaks were found at 933.6 and 953.6 eV, respectively. The peak at 530.6 eV was assigned to O 1s. No impurity was found in the sample by XPS.

Fig. 9. XPS spectrum of the CuO/ γ -Al₂O₃ catalyst.

2.3 Reduction of aromatic nitro compounds

In the literature, it was observed that 4-NP was reduced by NaBH₄ solution within 15 and 6 min in the presence of Pd or Ag catalysts [24,29]. 3-NP and 2NP was reduced by NaBH₄ within 9 and 20 min in the presence of Au particles [30]. Thus, the catalytic performance of CuO/ γ -Al₂O₃ for the reduction of 4-NP to 4-AP was studied in a continuously stirred batch reactor by the addition of freshly prepared NaBH₄ solution. The rate of reduction can be regarded as being independent of the NaBH₄ concentration as an excess amount of NaBH₄ solution was added. The progress of the reaction was studied versus time by UV-Vis. Figure 10 shows the absorbance peak at 317 nm for 4-NP before adding the NaBH₄ reducing agent. After the addition of freshly prepared NaBH₄ solution into the aqueous 4-NP solution, a red shift in the absorption peak from 317 to 404 nm was observed, and the light yellow color of the solution became dark yellow due to the formation of 4-nitrophenolate ion. This peak remained unchanged even up to 24 h in the absence of a catalyst, which showed that no reaction occurred without a catalyst.

Then, a weighed amount (0.05 g) of CuO/ γ -Al₂O₃ catalyst was added into the reaction mixture, which caused a gradual fading of the characteristic yellow color due to the

Fig. 10. UV-Vis spectra of the 4-NP before (1) and after (2) the addition of NaBH_4 .

formation of 4-AP. The time taken for complete conversion was noted by the disappearance of the peak at ~ 404 nm, which was attributed to the reduction of 4-nitrophenolate ions to 4-AP (Fig. 11). This took 12 min. Simultaneously the appearance of a new peak at 295–300 nm was observed, which confirmed the formation of 4-AP. Under the same reaction conditions, other reducing agents (hydrazine hydrate and molecular hydrogen) were also used but no reduction took place.

Fig. 11. UV-Vis spectra of the reduction of 4-NP by NaBH_4 in the presence of the $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst.

After the completion of the reduction, the reaction mixture was filtered or centrifuged to recover the $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst. The residue was extracted by 15 ml chloroform. The extract was washed twice with 15 ml saturated sodium chloride solution and then 10 ml distilled water. The organic layer was dried over sodium sulphate and then concentrated to get the desired amino derivative. The amino product was obtained without any impurity.

Because the initial concentration of sodium borohydride

Fig. 12. Absorbance versus time for the reduction of 4-NP by NaBH_4 in the presence of the $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst. Reaction conditions: $c(4\text{-NP}) = 4.3 \times 10^{-5}$ mol/L, $c(\text{NaBH}_4) = 0.05$ mol/L, 0.05 g catalyst, 30°C .

was very high in comparison with that of 4-NP, it was reasonable to assume that the concentration of BH_4^- remained constant during the reaction. The reaction can be considered a pseudo-first order reaction with respect to the nitro compound with the pseudo-first order rate equation,

$$c_A = c_{A0} \cdot e^{-kt} \quad (1)$$

where c_A is the absorbance at time t , which represents the concentration of the reactant, c_{A0} is the absorbance at the initial stage or initial concentration of the reactant, and k is pseudo-first order rate constant. Figure 12 shows the absorbance versus time plot for the reduction of 4-NP.

Generally, an electron transfer mechanism from the donor BH_4^- ion is involved in the reduction of 4-NP to 4-AP. Actually two steps are involved in this reaction: (a) chemisorption of BH_4^- on the surface of the metal oxide [39] and (b) discharge of electrons from BH_4^- through the metal oxide to the acceptor. Water is a polar protic solvent, and it supplies the required H^+ ion for the completion of the reduction reaction [34]. The adsorption plays an important role in catalysis. Here, the $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst provided the adsorption sites for BH_4^- ions as well as for the nitro aromatic compounds and also assisted in the transfer of electrons from the donor BH_4^- ions to the nitro aromatic compound (acceptor).

2.3.1 Effect of temperature on the reduction of 4-NP

The reaction temperature plays a very important role in the reduction of 4-NP. The reaction temperatures were varied from 10 to 50°C while keeping the other parameters constant. The pseudo-first-order rate constant (k) was calculated and given in Table 1. An increase of reaction temperature gave an increase in the rate constant. From the kinetic data and Arrhenius equation, the activation energy was found to be 27.41 kJ/mol (Fig. 13). Jana et al. [40] found that the activation energy was 24.08 kJ/mol using silver

Fig. 13. Rate constant vs temperature for the reduction of 4-NP. Conditions: $c(4\text{-NP}) = 4.3 \times 10^{-5} \text{ mol/L}$, $c(\text{NaBH}_4) = 0.05 \text{ mol/L}$.

Fig. 14. Rate constant versus amount of catalyst for the reduction of 4-NP. Reaction conditions: $c(4\text{-NP}) = 4.3 \times 10^{-5} \text{ mol/L}$, $c(\text{NaBH}_4) = 0.05 \text{ mol/L}$, 30°C .

Table 1. Temperature dependent rate of reduction of 4-NP by NaBH₄ catalyzed by CuO/ γ -Al₂O₃ nanoparticles

Entry	Temperature ($^\circ\text{C}$)	Rate constant (10^{-2} min^{-1})
1	10	11.91
2	20	17.37
3	30	29.92
4	40	37.46
5	50	49.01

nanoshell-coated resin beads for the 4-NP reduction reaction [40]. Our calculated data was in agreement with the reported data.

2.3.2 Effect of catalyst amount on the reduction of 4-NP

In catalysis, the rate of reaction generally increases linearly with the amount of the catalyst, e.g., as reported by Spiro et al. [41]. The rate of reaction was determined by varying the amount of catalyst from 0.01 to 0.05 g while keeping the other parameters constant. Using the smaller amount of catalyst of 0.01 g, the rate of reduction of 4-NP was found to be $7.81 \times 10^{-2} \text{ min}^{-1}$. With increasing amount of catalyst, the rate of reaction increased. The rate constant values for 4-NP are plotted against the amounts of catalyst in Fig. 14.

2.3.3 Effect of size of CuO nanoparticles

The size of the CuO nanoparticles plays a very important role in the reduction 4-NP. Figure 15 shows the effect of CuO nanoparticle size on the reduction of 4-NP. The CuO/ γ -Al₂O₃ catalyst having a smaller diameter ($d = 13.28 \text{ nm}$) showed a slightly higher reduction rate of 4-NP than the catalyst having the particle size of 18.54 nm. Because no

Fig. 15. Effect of CuO nanoparticles size on the reduction rate of 4-NP.

large change was observed in the reduction rate with particle size, the CuO/ γ -Al₂O₃ catalyst having 18.54 nm CuO particle size was used in all other experiments.

2.3.4 Reduction of 2-NP and 3-NP

The reduction of the other nitro aromatic compounds, 2-NP and 3-NP, was also studied in the continuous batch reactor in the presence of NaBH₄ solution. For 2-NP, initially an absorbance peak was observed at 351 nm. After the addition of the reducing agent NaBH₄, a red shift in the absorbance peak from 351 to 417 nm was observed and the light yellowish solution was turned into a dark yellow colored solution. After the addition of a small amount (0.05 g) of CuO/ γ -Al₂O₃ catalyst into the reaction mixture, a decrease in the absorbance peak at 417 nm and the appearance of a new absorbance peak at 330 nm (due to the formation of 2-AP) were observed within 15 min (Fig. 16(a)) of reaction time. In the case of aqueous 3-NP, absorbance peaks at

Fig. 16. UV-Vis spectra of the reduction of 2-NP (a) and 3-NP (b) by NaBH_4 in the presence of $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst.

332 and 400 nm before and after addition of NaBH_4 into solution and the appearance of a new peak at 400 nm (after addition of 0.05 g of $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst) were observed within 20 min of reaction time (Fig. 16(b)). Thus, the three isomers of nitrophenol showed the relative rates for catalytic reduction in the sequence of 4-NP > 2-NP > 3-NP.

3 Conclusions

Colloidal CuO nanoparticles were synthesized using a water-in-oil microemulsion. The experimental conditions included the varying of the different parameters of water-to-surfactant molar ratio, precursor concentration, and molar ratio of NaOH to CuCl_2 . $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalysts were synthesized by dispersing CuO nanoparticles onto a γ -alumina support by mechanical stirring. The CuO nanoparticles and $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ were characterized using DLS, TEM, UV-Vis, SEM, XPS, and XRD. The $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalysts were active for the reduction of nitro aromatic compounds. The reduction rate was a little slower than with other transition metal catalysts (e.g. Pd, Ag, and Au) but since the catalysts in this work are comparatively cheaper and easily available, they have a good potential for

use in this process.

References

- Han D, Yang H, Zhu C, Wang F. *Powder Technol*, 2008, **185**: 286
- Frietsch M, Zudock M F, Goschnick J, Bruns M. *Sens Actuators B*, 2000, **65**: 379
- Zhang X J, Gu A X, Wang G F, Wei Y, Wang W, Wu H Q, Fang B. *CrystEngComm*, 2010, **12**: 1120
- Hsieh C T, Chen J M, Lin H H, Shih H C. *Appl Phys Lett*, 2003, **83**: 3383
- Koumoto K, Koduka H, Seo W S. *J Mater Chem*, 2001, **11**: 251
- Reddy V P, Kumar A V, Swapna K, Rao K R. *Org Lett*, 2009, **11**: 951
- Li J, Sun F, Gu K, Wu T, Zhai W, Li W, Huang S. *Appl Catal A*, 2011, **406**: 51
- Dierstein A, Natter H, Meyer F, Stephan H-O, Kropf Ch, Hempelmann R. *Scr Mater*, 2001, **44**: 2209
- Chen J T, Zhang F, Wang J, Zhang G A, Miao B B, Fan X Y, Yan D, Yan P X. *J Alloys Compd*, 2008, **454**: 268
- Zhu J, Bi H, Wang Y, Wang X, Yang X, Lu L. *Mater Lett*, 2007, **61**: 5236
- Su Y-K, Shen C-M, Yang H-T, Li H-L, Gao H-J. *Trans Non-ferrous Met Soc China*, 2007, **17**: 783
- Zhang H, Li S, Ma X, Yang D. *Mater Res Bull*, 2008, **43**: 1291
- Keyson D, Volanti D P, Cavalcante L S, Simoes A Z, Varela J A, Longo E. *Mater Res Bull*, 2008, **43**: 771
- Song X, Yu H, Sun S. *J Colloid Interface Sci*, 2005, **289**: 588
- Li C, Yin Y, Hou H, Fan N, Yuan F, Shi Y, Meng Q. *Solid State Commun*, 2010, **150**: 585
- Nassar N N, Husein M M. *J Colloid Interface Sci*, 2007, **316**: 442
- Vahidshad Y, Abdizadeh H, Akbari Baseri M, Baharvandi H R. *J Sol-Gel Sci Technol*, 2010, **53**: 263
- Stubenrauch C, Wielputz T, Sottmann T, Roychowdhury C, DiSalvo F J. *Colloids Surf A*, 2008, **317**: 328
- Kumar A R, Hota G, Mehra A, Khilar K C. *AIChE J*, 2004, **50**: 1556
- Kkroschwitz J I, Kirk-Othmer. 4th Ed. Wiley Interscience, 1995
- Polat K, Aksu M L, Pekel A T. *J Appl Electrochem*, 2002, **32**: 217
- Bean F R, Donovan S. US 2 376 112. 1945
- Abbar A H, Sulaymon A H, Jalhoom M G. *Electrochim Acta*, 2007, **53**: 1671
- Oh S-D, Kim M-R, Choi S-H, Chun J-H, Lee K-P, Gopalan A, Hwang C-G, Kim S-H, Hoon O J. *J Ind Eng Chem*, 2008, **14**: 687
- Harish S, Mathiyarasu J, Phani K L N, Yegnaraman V. *Catal Lett*, 2009, **128**: 197
- Pradhan N, Pal A, Pal T. *Colloids Surf A*, 2002, **196**: 247
- Shin K S, Choi J-Y, Park C S, Jang H J, Kim K. *Catal Lett*, 2009, **133**: 1

- 28 Liu P, Zhao M. *Appl Surf Sci*, 2009, **255**: 3989
- 29 Solanki J N, Murthy Z V P. *Ind Eng Chem Res*, 2011, **50**: 7338
- 30 Yao Y, Sun Y, Han Y, Yan C. *Chin J Chem*, 2010, **28**: 705
- 31 Kuroda K, Ishida T, Haruta M. *J Mol Catal A*, 2009, **298**: 7
- 32 Chang Y-C, Chen D-H. *J Hazard Mater*, 2009, **165**: 664
- 33 Koga H, Kitaoka T. *Chem Eng J*, 2011, **168**: 420
- 34 Mandlimath T R, Gopal B. *J Mol Catal A*, 2011, **350**: 9
- 35 Quintillan S, Tojo S C, Blanco M C, Lopez-Quintela M A. *Langmuir*, 2001, **17**: 7251
- 36 Towey T F, Khan-Lodhi A, Robinson B H. *J Chem Soc, Faraday Trans*, 1990, **86**: 3757
- 37 Nagy K, Dekany I. *Colloids Surf A*, 2009, **345**: 31
- 38 Nandanwar S U, Chakraborty M, Murthy Z V P. *Ind Eng Chem Res*, 2011, **50**: 11445
- 39 Fernandes R, Patel N, Miotello A, Filippi M. *J Mol Catal A*, 2009, **298**: 1
- 40 Jana S, Ghosh S K, Nath S, Pande S, Praharaj S, Panigrahi S, Basu S, Endo T, Pal T. *Appl Catal A*, 2006, **313**: 41
- 41 Spiro M, Bradley J N, Gillard R D, Hudson R F eds. *Essay in Chemistry*. London: Academic Press, 1973. 63