

Facile synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2\cdot\text{Cu}_2\text{O}$ system and enhanced catalytic reduction of 4-nitrophenol

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ABSTRACT

Herein, we describe a facile method to synthesize $\text{Fe}_3\text{O}_4@\text{SiO}_2\cdot\text{Cu}_2\text{O}$ catalyst. The as-prepared $\text{Fe}_3\text{O}_4@\text{SiO}_2\cdot\text{Cu}_2\text{O}$ structure was characterized by powdered X-ray diffraction (*p*-XRD), infrared spectroscopy (IR), field emission scanned electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The as-prepared catalyst were successfully used to reduce 4-nitrophenol to 4-aminophenol at ambient temperature in 5 minutes. The recycling experiments confirmed the stability and superior catalytic efficiency of as synthesized catalyst.

Keywords: *Copper oxide nanoparticles, catalysis, 4-nitrophenol, heterogeneous catalysis, magnetic nano particles.*

1. INTRODUCTION

Nitroarenes and their halide derivatives have gained considerable interest in last decade due to their use in synthesis of drugs, dyes, herbicides and insecticides [1-3]. However, by-products of these reactions particularly, 4-nitrophenol (4-NP) and studies have shown that 4-NP pose major threats on vital organs kidney, liver and central nervous system of humans [4-10]. Furthermore, 4-NP and their derivatives are soluble in aqueous media and do not degrade themselves. Therefore, there is a need to reduce the 4-NP into 4-aminophenol (4-AP) a less toxic compound and important intermediate [11, 12] in the synthesis of corrosion inhibitors, anticorrosion lubricants, hair-dyeing agents, photo developers, analgesic and antipyretic drugs [11, 13, 14]. Many methods have been reported to reduce 4-NP to 4-AP such as metal-acid reduction, catalytic hydrogenation, electrolytic reduction, homogeneous catalytic transfer hydrogenation and heterogeneous catalytic transfer hydrogenation [12, 15-19].

Direct reduction of 4-NP to 4-AP have been attempted in the presence of bulk metal catalyst using sodium borohydride (NaBH_4) as reductant [20]. The use of metal nanoparticles to carry

out the transformation of 4-NP to 4-AP have been reported extensively [14, 21] like Au [12], Ag [22], Pt [23], Pd [24], and Ni [25] etc. These metal nanoparticles need special methods to recover at the end of reaction. In addition, the nanoparticles can aggregate to bulk material with reduce catalytic activity [26].

Magnetic nanoparticles are promising candidates as heterogeneous supports in the catalytic transformations because of enhance efficiency and magnetic recoverability [11, 12, 27]. Silica coating prevent from agglomeration of particles as well as impart the biocompatibility and hydrophobicity. The surface of the silica coating is compatible with different materials which make $\text{Fe}_3\text{O}_4@\text{SiO}_2$, a favorable system for different metal catalysis [28, 29]. In present study, we report the synthesis of magnetically supported cuprous oxide ($\text{Fe}_3\text{O}_4@\text{SiO}_2\cdot\text{Cu}_2\text{O}$) catalyst for the direction reduction of 4-nitrophenol using NaBH_4 as reductant. The results have shown the superior catalytic ability for the reduction of 4-NP to 4-AP in five minutes. The catalytic ability was not much affected during reusability experiments.

2. EXPERIMENTAL SECTION

2.1. Chemicals and measurements.

Ferric chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$), ferrous sulphate tetrahydrate ($\text{FeSO}_4\cdot 4\text{H}_2\text{O}$), ammonium hydroxide (NH_4OH), Tetraethyl orthosilicate (TOES), fehling solution were purchased from sigma-aldrich and used without further purification. Phase purity of synthesized material was determined by powdered X-ray diffraction using *X'Pert PRO PANalytical* equipment with Cu K α radiation ($K=1.54178$). UV-Visible (UV-Vis.) spectra were measured by using shimadzu UV-1700 spectrophotometer at room temperature.

2.2.Synthesis of Iron oxide Nanoparticles.

The synthesis of Fe_3O_4 was carried out by mixing 11.7g of ferric chloride hexahydrate ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$) and 6g of ferrous sulphate tetrahydrate ($\text{FeSO}_4\cdot 4\text{H}_2\text{O}$) in 500 ml of deionized water. The reaction mixture was then stirred vigorously at 70°C under inert atmosphere for one hour. Followed by, 50 ml of ammonium hydroxide (NH_4OH) was immediately introduced into the reaction mixture. The color of the solution instantly turned black. The stirring continued for one hour under inert atmosphere. After that reaction was stopped, cool the reaction mixture to room temperature. The black precipitates obtained were separated with

the help of magnet, washed with hot water for five times and then dried in oven at 50°C overnight.

2.3. Synthesis of Silica coated Fe₃O₄ nanoparticles.

The synthesis of silica coated Fe₃O₄ nanoparticles were carried out by taking 1g of iron oxide nanoparticles dispersed by sonication in 400ml of ethanol, 100 ml of water and 12 ml of ammonium hydroxide solution for one hour. Afterward 3.5 ml of tetraethyl orthosilicate (TOES) was added drop wise and then the mixture was stirred for two hours under inert atmosphere. The precipitate was separated by magnet, washed three times with deionized water and then dried under vacuum at 60°C.

2.4. Synthesis of Fe₃O₄@SiO₂-supported copper (I) oxide (Fe₃O₄@SiO₂-Cu₂O).

After being taken 5 g of Fe₃O₄@SiO₂ in round bottom flask, the fehling solution was added and the reaction mixture was stirred at 100°C. After every interval of 30 min, 2 ml of glucose solution (0.25 g in 45 mL of water) was added up to 12 h. Then

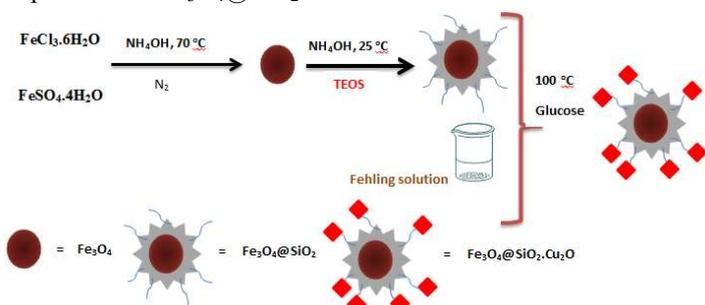
the catalyst was filtered off, washed with water until the washings were colorless, and dried in an oven at 110 °C. To remove excess glucose, the catalyst was refluxed in water at 120°C for 6 h (3 × 2 h). Then the catalyst was dried at 110°C for 5 h in an oven.

2.5. Catalytic reduction reaction.

To investigate the catalytic reduction of 4-nitrophenol, 10 cm³ of 5 ppm solution of 4-nitrophenol was taken in the beaker. Then calculated amount of sodium borohydride (NaBH₄) was added in the 4-nitrophenol solution. Afterwards 1mg/ml of Fe₃O₄@SiO₂.Cu₂O catalyst was added in the reaction at room temperature, the bright yellow color of 4-nitrophenol start fading. The concentration of 4-nitrophenolate was determined by UV-Vis spectroscopy. The recycling experiment was performed by applying an external magnetic field to collect the Fe₃O₄@SiO₂.Cu₂O catalyst. The separated catalyst was washed two times with distilled water, dried at 50°C for 30 minutes and then reused.

3. RESULTS SECTION

Scheme 1 shows the systematic for the synthesis of Fe₃O₄@SiO₂.Cu₂O magnetic catalyst in which commercially inexpensive precursors were used. First of all Fe₃O₄ nanoparticles were synthesized by co-precipitation in basic media. The well dispersed Fe₃O₄ in ethanol/water were coated with SiO₂ by the hydrolysis of the TEOS in basic media and separated by a magnet. Then Cu₂O were obtained by the reduction of Fehling solution in the presence of Fe₃O₄@SiO₂.



Scheme 1. Schematic diagram shows the preparation of Fe₃O₄@SiO₂.Cu₂O catalyst.

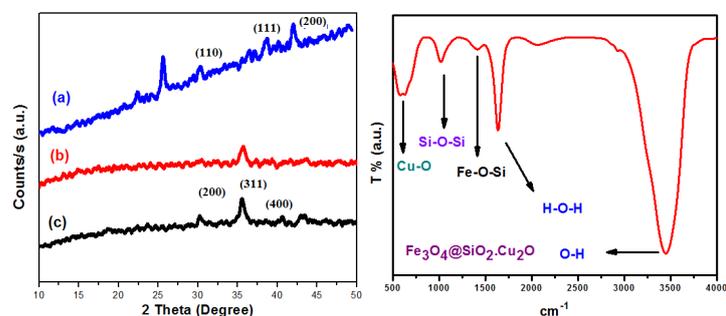


Figure 1. (A) The *p*-XRD spectra of the as-synthesized (a) Fe₃O₄@SiO₂.Cu₂O (b) Fe₃O₄@SiO₂ and (c) Fe₃O₄ (JCPDS card no. 05-0667), (B) FT-IR spectra of as-synthesized catalyst Fe₃O₄@SiO₂.Cu₂O showing the major peaks.

Figure 1 (a-c) shows the *p*-XRD pattern of as-prepared Fe₃O₄@SiO₂.Cu₂O catalyst. The diffraction peaks at 29.3 (110),

36.4 (111) and 42.8 (200) indicating the rhombic dodecahedral crystals in the cubic phase of the Cu₂O coated on the Fe₃O₄@SiO₂ (JCPDS card no. 05-0667). Similar, results are also reported in the literature [30, 31].

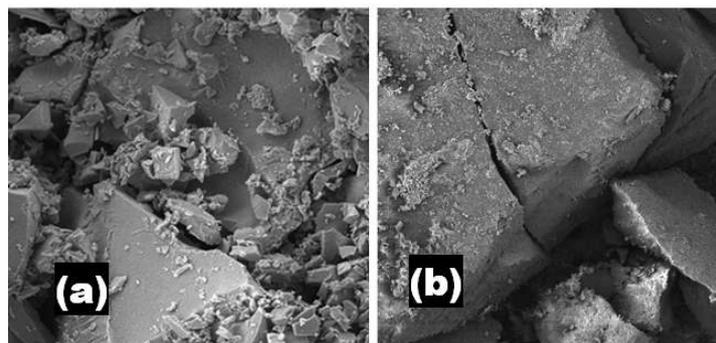


Figure 2. Top view field emission scanned electron microscopic image of as-synthesized (a) Fe₃O₄ and (b) Fe₃O₄@SiO₂-Cu₂O catalyst.

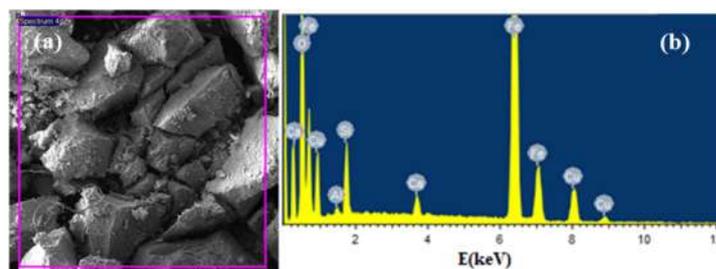


Figure 3. Energy dispersive X-ray spectra showing the elemental analysis of as-synthesized Fe₃O₄@SiO₂.Cu₂O catalyst.

The FTIR spectrum of as-synthesized Fe₃O₄@SiO₂.Cu₂O catalyst has shown the important characterizing bands in the range of 500-4000 cm⁻¹ (Figure2).

The vibrational bands at 1100, 1400 and 3400 cm⁻¹ corresponds to Si-O-Si, Fe-O-Si and OH respectively indicating the existence of Fe₃O₄, SiO₂. The Cu-O vibrations show a characterizing peak at ~ 580 cm⁻¹. The H-O-H bending vibrations at 1628 cm⁻¹ demonstrate the presence of several OH groups at

surface. The morphology and texture of as synthesized Fe_3O_4 , SiO_2 and $\text{Fe}_3\text{O}_4@/\text{SiO}_2\cdot\text{Cu}_2\text{O}$ catalyst were observed by the SEM analysis shown in the Figure 3 (a-b). The images shows that the Fe_3O_4 have flakes like structure as compare to $\text{Fe}_3\text{O}_4@/\text{SiO}_2\cdot\text{Cu}_2\text{O}$ which exists in mat like structure. Energy Dispersion X-ray spectroscopy gave the relative composition of as synthesized $\text{Fe}_3\text{O}_4@/\text{SiO}_2\cdot\text{Cu}_2\text{O}$ catalysis by showing 31.2% Fe, 59.1% oxygen, 3.5% silicon, 4.8% copper (Figure 4 (a-b)).

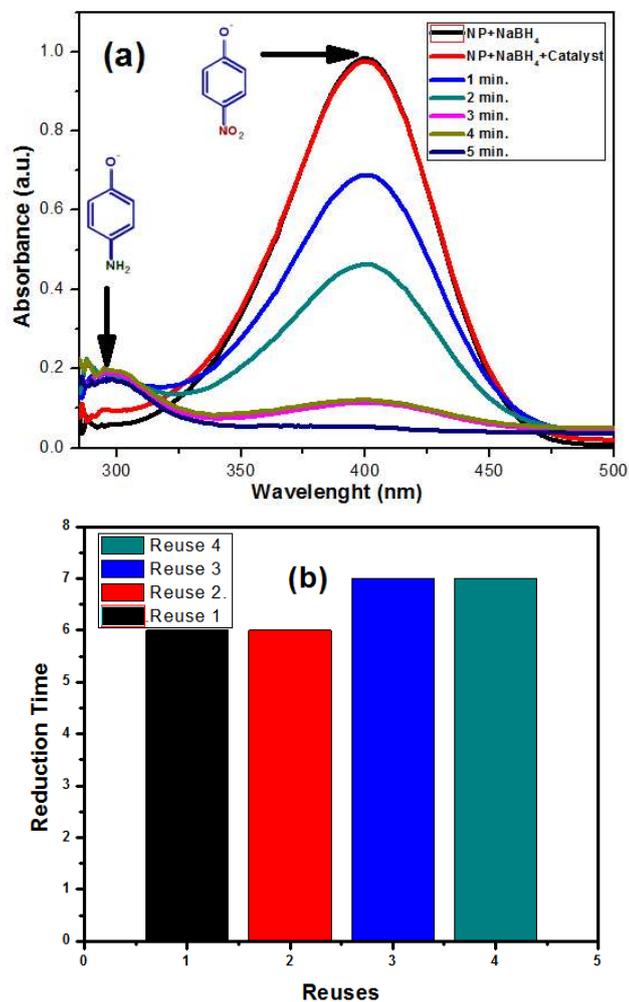


Figure 4. (a) UV-Vis. absorption spectra of 4-nitrophenol reduction by NaBH_4 catalyzed by $\text{Fe}_3\text{O}_4@/\text{SiO}_2\cdot\text{Cu}_2\text{O}$, (b) graph showing recycled catalyst with varying reduction time.

4. CONCLUSIONS

In summary, the $\text{Fe}_3\text{O}_4@/\text{SiO}_2\cdot\text{Cu}_2\text{O}$ catalyst was prepared by the Cu_2O on the magnetic carries $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ using Fehling solution. The catalyst can be easily separated by applying external magnetic field. The comparative p-XRD demonstrates the formation of $\text{Fe}_3\text{O}_4@/\text{SiO}_2\cdot\text{Cu}_2\text{O}$ catalyst with the appearance of some characterizing peaks around 40° region which appears due to

5. REFERENCES

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Figure 5 (a) shows the reduction of 4-nitrophenol to 4-aminophenol by NaBH_4 with time. The solution becomes deep yellow indicating the formation of 4-nitrophenolate ion in alkaline condition by the sodium borohydride. The absorption maxima of 4-nitrophenolate at 400 nm remains same indicating that there is no reduction reaction in the absence of catalyst. However, in the presence of as-synthesized catalyst, the concentration of 4-nitrophenol start decreasing gradually with the development of fresh peak at 295nm which directs the formation of 4-aminophenol. After 5 minutes the 5ppm solution of 4-nitrophenol is completely reduced to 4-aminophenol by NaBH_4 which demonstrate the excellent catalytic ability of catalyst.

It has been observed that the rate of reduction remains almost same throughout the reaction with gradually decrease in concentration of 4-NP till the reaction completed (figure 5 (a-b)). Figure 5(b) shows the reusability of $\text{Fe}_3\text{O}_4@/\text{SiO}_2\cdot\text{Cu}_2\text{O}$ catalyst for the reduction of 4-nitrophenol. It has been observed that the recycled catalyst remain active with slight increase in reduction time. The catalytic experiment was executed for 4 times. The reuse of catalyst shows no sign of deactivation or poisoning after successive recycles which indicates the stability of the as-synthesized catalyst.

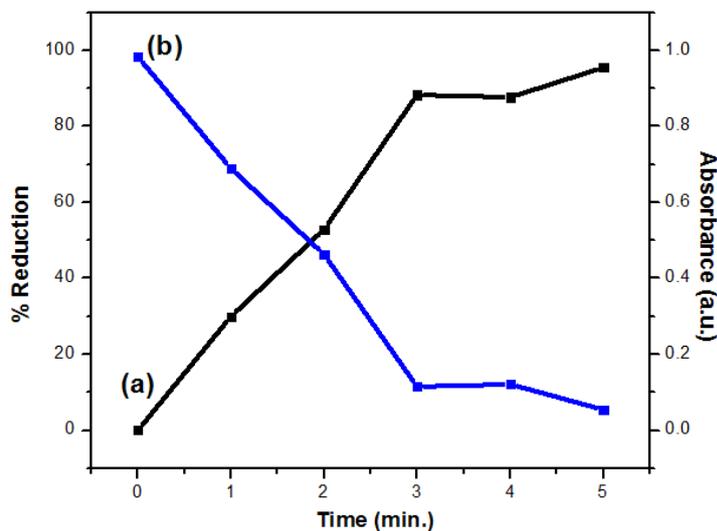


Figure 5. (a) Graph showing the % reduction/degradation of 4-NP and (b) relative decrease of absorbance of 4-NP with time.

fabricated Cu_2O . The $\text{Fe}_3\text{O}_4@/\text{SiO}_2\cdot\text{Cu}_2\text{O}$ catalyst was also confirmed by IR spectrometry and SEM-EDX. The as-synthesized catalyst has shown a superior catalytic ability by reducing the 4-nitrophenol with NaBH_4 in 5 minutes.

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6. ACKNOWLEDGEMENTS

JA thanks and acknowledge the financial assistance received from HEC and COMSATS start-up grants.

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