



# Catalytic activity of first row transition metal oxides in the conversion of p-nitrophenol to p-aminophenol

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## ABSTRACT

The catalytic activities of first row transition metal oxides in the conversion of p-nitrophenol to p-aminophenol were investigated. The conversion was carried out at room temperature (30°C) using aqueous sodium borohydride. The reduction process was accelerated by CuO, Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and NiO. The oxides such as TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, Cr<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub> and ZnO were found to be inactive towards the conversion of the nitrophenol. The active catalysts were analyzed before and after the reaction by XRD and the reduction reaction was monitored and confirmed by UV–vis, HPLC, <sup>1</sup>H NMR and FT-IR techniques.

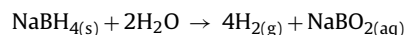
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## 1. Introduction

Catalysis has revolutionized the field of manufacturing of chemicals. One such manufacturing process is reduction of organic molecules by catalytic hydrogenation. p-Aminophenol (PAP) is an important intermediate in the synthesis of various analgesic and antipyretic drugs such as paracetamol, acetanilide, and phenacetin. It is also a main ingredient in the synthesis of industrial dyes, marketed as a photographic developer and its oxalate salt is used as a corrosion inhibitor [1]. It is noted that p-aminophenol could be obtained by methods such as hydrogenation of nitrobenzene involving molecular rearrangement of phenylhydroxylamine intermediate in the presence of iron–acid [2], catalytic amination of hydroquinone [3], electrochemical reduction [4], etc. The disadvantages of such methods include formation of aniline as a side product, longer duration, extensive methodology involving usage of hydrogen gas etc. An alternative approach is hydrogenation of p-nitrophenol (PNP). Conventional methods of hydrogenation of p-nitrophenol employ reagents such as iron/acid and tin/acid [5,6]. Such methods are associated with serious pollution problem due to the formation of large amounts of metal oxide sludge, corrosion of the equipment, expensive nature, etc. Methods for the catalytic hydrogenation of p-nitrophenol in solvents such as ethanol at rel-

atively high temperature and high hydrogen pressure have been reported [7,8]. Other approaches involving direct hydrogenation of p-nitrophenol using hydrogen in the presence of metal catalysts such as Pt, Pd, Ru, and Ni [7,8], supported metal catalysts [9,10] are available. Such methods involve hydrogen pressure, elevated temperature, usage of autoclaves, etc.

In recent times, based on the requirements such as greener route and safer operation, environmentally friendly direct catalytic conversion routes have been developed for the conversion of p-nitrophenol to p-aminophenol in aqueous medium under mild conditions. One such route by which p-aminophenol is obtained involves direct hydrogenation of p-nitrophenol using sodium borohydride which is a milder agent and the reaction can be carried out in aqueous medium [11]. This method is relatively simple and clean against the above-mentioned methods. But, the sluggish self-hydrolysis of NaBH<sub>4</sub> [12] affects the rate of hydrogenation of the nitro compound:



Studies reported that the presence of suitable catalysts accelerated the hydrolysis [13]. Transition metal based compounds have been used as catalysts for the hydrolysis of NaBH<sub>4</sub> [14].

Many reports are available on the application of metal nanoparticles as catalysts for the hydrogenation of PNP in the presence of NaBH<sub>4</sub> [11,15–17]. Metal oxide supported metal nanoparticles have been tested as catalysts for the p-nitrophenol to p-aminophenol conversion. Pd nanoparticles dispersed alumina has been reported [18] in the presence of NaBH<sub>4</sub>. Taekyung et al. used PVP-stabilized

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Pt nanoparticles and CeO<sub>2</sub> supported Pt nanoparticles [19]. In the conversion, even though PVP-stabilized Pt nanoparticles showed high activity than Pt/CeO<sub>2</sub> hybrid, it lost its catalytic activity over a course of reusability. Yuangpeng et al. used gold coated Fe<sub>3</sub>O<sub>4</sub> as a catalyst [16]. In such approach, although nanomaterials have their own advantages the protocol is time consuming due to multi-step nanoparticle preparation procedure [11,15–17].

The search for the utilization of metal oxides as catalysts for PNP to PAP conversion showed very limited reports. Works on application of TiO<sub>2</sub> as a photocatalyst are considerable [20–23]. Oxides such as TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> have been used as supports [9,24]. Recently, cuprous oxide in its nanoform is tested for its activity towards hydrogenation of p-nitrophenol using NaBH<sub>4</sub> [25]. Perovskite oxide, LaFeO<sub>3</sub> has been tested for the same reaction under microwave irradiation in the presence of alcohol and potassium hydroxide [26]. Complex systems such as M<sub>1x</sub>Cr<sub>1-x</sub>Mo<sub>x</sub>P<sub>1-x</sub>O<sub>4</sub> have been tested for the catalytic activity [27]. Swati and Buvaneshwari reported on the application of spinel oxide NiCo<sub>2</sub>O<sub>4</sub> as a catalyst [28]. Metal oxides with higher reactivity along with other advantages such as thermal stability, chemical stability, easy recovery and reusability may become promising cost effective catalysts. The apparent lesser reports on the metal oxides as catalysts for the conversion prompted the authors to attempt a systematic investigation of the first row transition metal oxides. Conversion of p-nitrophenol to p-aminophenol is carried out using sodium borohydride in aqueous medium at room temperature in the presence of first row transition metal oxides. In this report, the difference in the catalytic activity among the first row transition metal oxides in the reduction process is documented.

## 2. Experimental

### 2.1. Materials

CuO (99%, S.D. Fine), Co<sub>3</sub>O<sub>4</sub> (99%, SRL), Fe<sub>2</sub>O<sub>3</sub> (95%, S.D. Fine), Ni(COOCH<sub>3</sub>)<sub>2</sub> (98%, CDH), TiO<sub>2</sub> (98%, Thomas Baker), V<sub>2</sub>O<sub>5</sub> (99%, S.D. Fine), Cr<sub>2</sub>O<sub>3</sub> (98%, Thomas Baker), MnO<sub>2</sub> (80%, S.D. Fine), ZnO (99.5%, NICE Chemicals), p-nitrophenol (99%, S.D. Fine) and NaBH<sub>4</sub> (98%, S.D. Fine). Nickel oxide was prepared by thermal decomposition of nickel acetate at 600 °C.

### 2.2. Catalytic test

In a typical test, to 20 ml of 0.1 mmol L<sup>-1</sup> aqueous solution of p-nitrophenol, freshly prepared aqueous solution of NaBH<sub>4</sub> (0.5 M, 12.5 mL) was introduced. To the mixture, 0.1 g of the transition metal oxide was added and stirred at room temperature (30 °C). The stirring rate is kept constant at 180 rpm for all the experiments. The conversion of p-nitrophenol was monitored by UV–vis spectroscopy (Hitachi Model U-2800, spectrophotometer). The experiments have been carried out using various catalyst amounts in the range 0.1 g to 0.8 mg: 0.1 g, 0.05 g, 0.025 g, 0.0125 g, 0.0063 g, 0.0032 g, 0.0016 g and 0.0008 g. Similar experiment was performed in the absence of the metal oxide for comparison. Reusability was tested for CuO and Co<sub>3</sub>O<sub>4</sub>. The used catalysts were separated from the solution by centrifuge and washed, dried and used for the next cycle.

### 2.3. Characterization

The metal oxides were characterized by powder X-ray diffraction method (Cu K $\alpha$ , D8 Advance, Bruker) before and after the reaction. Surface area of the metal oxides was determined by BET method using Micromeritics ASAP 2020 porosimeter. The selective formation of p-aminophenol was confirmed by HPLC (HPLC-200

**Table 1**  
Effect of the amount of active metal oxides on the reaction duration.

Metal oxide	Decolorization time	
	0.1 g of the catalyst Time (s)	0.0008 g of the catalyst Time (s)
CuO	40	960
Co <sub>3</sub> O <sub>4</sub>	120	960
Fe <sub>2</sub> O <sub>3</sub>	130	1200
NiO	1080	14,520

series), <sup>1</sup>H NMR (Bruker – 500 MHz) and FT-IR (ThermoNicolate Company Avatar 330) spectroscopic techniques.

## 3. Results and discussion

The mechanism of the hydrogenation of the nitro compound indicates that the process is influenced by the factors such as electron transfer to the nitro compound and proton availability [17]. The experiment is carried out in the presence of oxides such as TiO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, Cr<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, NiO, CuO and ZnO. The results obtained in the present study classify the oxides into active (group A) and inactive (group B) and thus indicating the electron transfer is enhanced in the presence of former.

The experiments in the presence and absence of the oxides are performed under similar conditions. The reaction is monitored by observing the disappearance of yellow color of p-nitrophenol and further determination of the absorbance by UV–vis spectrophotometry. In the absence of the transition metal oxide, the decolorization of the yellow color of p-nitrophenol solution indicating the conversion to p-aminophenol required 4½ to 5 h. It is observed that in the presence of group A oxides the conversion completes within a span of few seconds to minutes (Table 1). However, in the case of group B oxides the duration required for the conversion in the presence of the oxides of vanadium, chromium and manganese matches with the control experiment. No decolorization of the yellow color even after the duration of more than two days in the presence of TiO<sub>2</sub> and ZnO suggests a possible retardation of hydrogen evolution from the aqueous solution of sodium borohydride.

After immediate addition of freshly prepared NaBH<sub>4</sub> solution the color of the nitrophenol solution has become intense yellow. This is reflected in the UV–vis spectrum where, the peak due to p-nitrophenol observed at 317 nm is red shifted to 404 nm in the UV–vis spectrum. This peak is due to the formation of p-nitrophenolate ion in alkaline condition caused by the addition of NaBH<sub>4</sub>. Addition of calculated quantity (0.1 g) of group A oxides leads to decrease in the absorbance of the characteristic peak at ~404 nm and the simultaneous appearance of a new peak around 295–300 nm confirm the formation of p-aminophenol. The time taken for the completion of the conversion is noted based on the disappearance of the peak at ~404 nm. It is observed that for the fixed amount of NaBH<sub>4</sub> and p-nitrophenol (Section 2.2) the duration for the completion of the conversion of p-nitrophenol to p-aminophenol is dependent on the chemical nature and the amount of the oxides taken. Fig. 1 displays the activity of group A metal oxides and the variation of decolorization time with respect to the amount of the catalyst.

The time consumed for the completion of the reaction for the higher and lower limit (0.1 g and 0.0008 g) of the amount of the group A metal oxides is given in Table 1. For the higher limit of 0.1 g of the catalyst, the reaction time is found to vary with respect to the metal oxides, viz., CuO, Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and NiO. The duration is between 40 s and 2 min in the case of first three metal oxides and ~18 min in the case of NiO. Hence, it is understood that the less effective electron and hydrogen transfer from BH<sub>4</sub><sup>-</sup> species to the

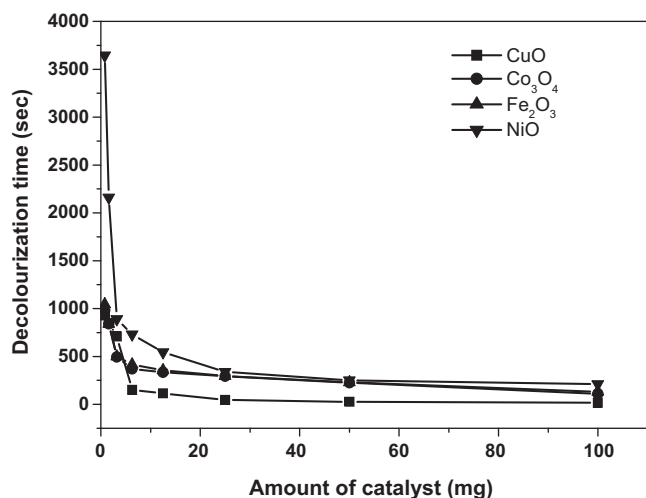


Fig. 1. Reaction duration vs. the amount of the transition metal oxides.

aromatic nitro compound taking place in the absence of the catalyst is dramatically enhanced in the presence of group A oxides. An overall increase in the reaction duration is noticed with a decrease in the quantity of the catalyst to 0.0008 g for all the four oxides. No significant change in time is observed with respect to copper, cobalt and iron oxides for the conversion (16–20 min). Whereas, nickel oxide requires 4 h 20 min. In the case of highly reactive CuO, though 0.1 g of the oxide leads to the decolorization within few seconds its activity becomes feeble when it is added in trace amount. The values of surface area of the oxides are determined to be CuO –  $0.63 \text{ m}^2/\text{g}$ ,  $\text{Co}_3\text{O}_4$  –  $4.27 \text{ m}^2/\text{g}$ ,  $\text{Fe}_2\text{O}_3$  –  $25.7 \text{ m}^2/\text{g}$  and NiO –  $1.54 \text{ m}^2/\text{g}$ . The current study finds out the difference in the activity of the metal oxides based on their electronic structure. The effect of surface area of the oxides on the activity is not focused.

The progress of the conversion of p-nitrophenol to p-aminophenol is monitored at various intervals and the UV–vis spectra are compiled in Fig. 2. Examination of the plots in the case of the reaction catalyzed by ‘CuO’ (for 0.1 g) reveals a sudden decrease in the absorbance at  $\sim 404 \text{ nm}$  along with subsequent growth of the peak at  $\sim 300 \text{ nm}$ . This illustrates the spontaneous activity of ‘CuO’. However, inspecting the UV–vis spectra (Fig. 2b–d) representing

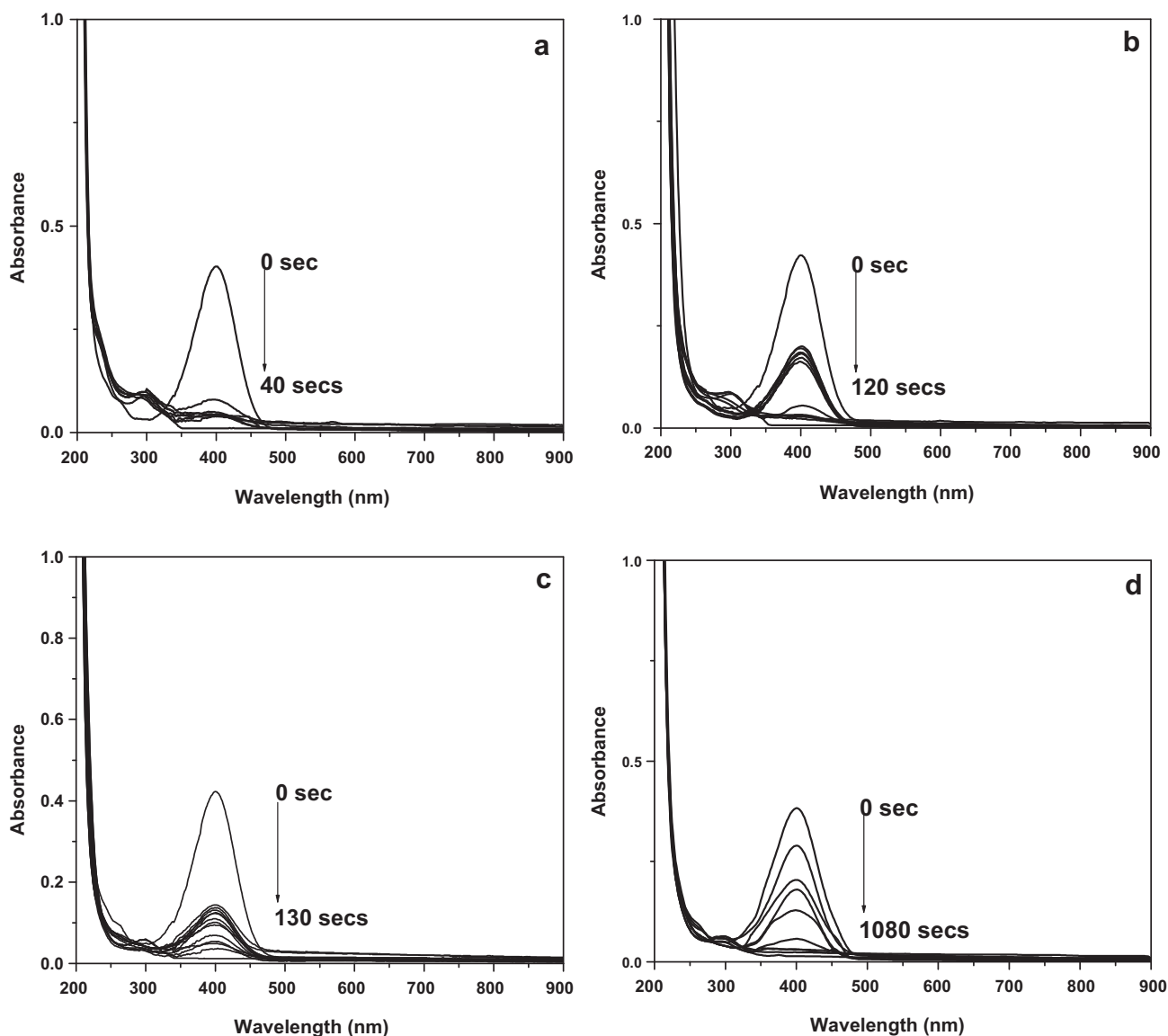
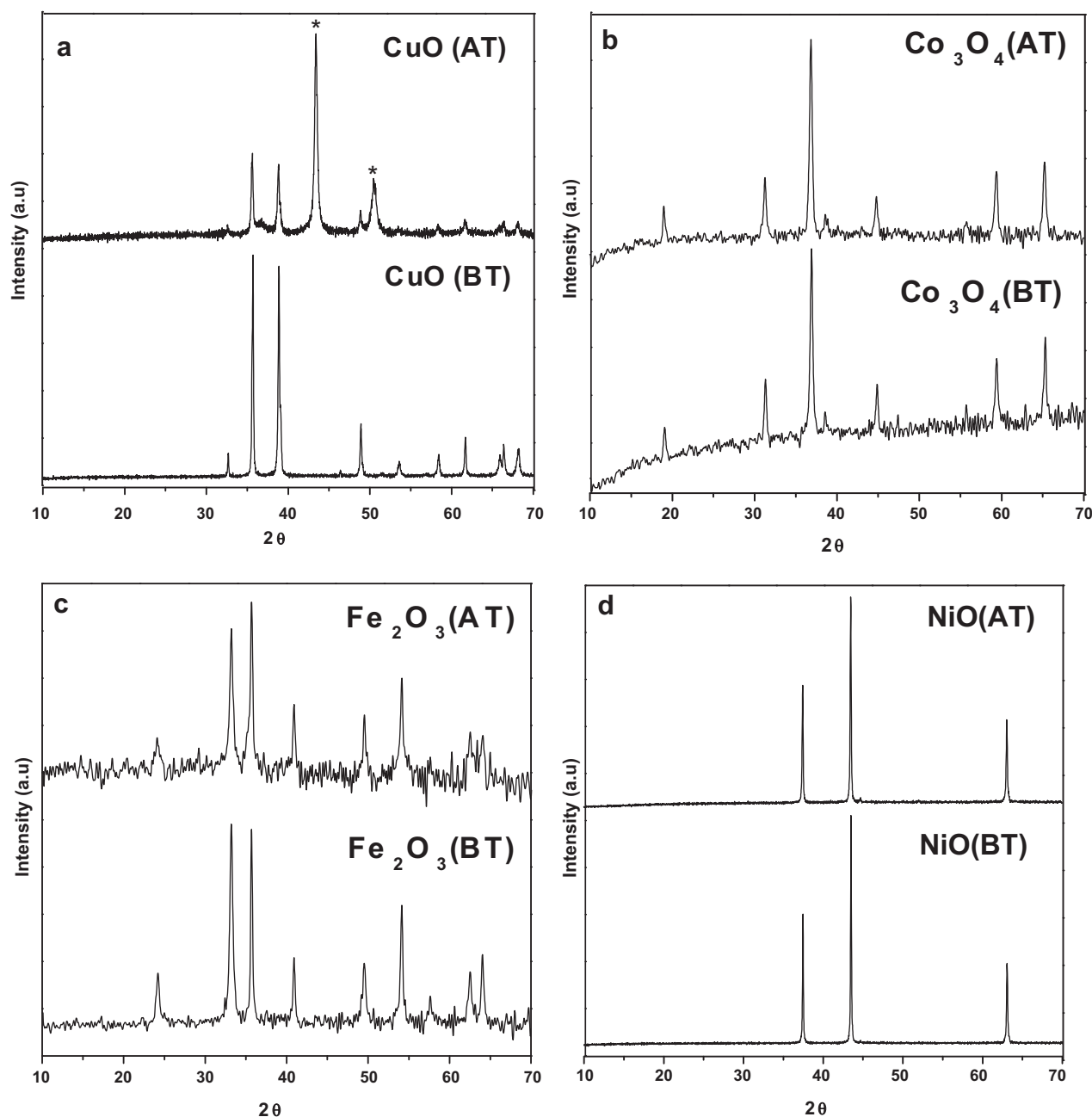


Fig. 2. Successive UV–vis spectra showing the reduction of p-nitrophenol catalyzed by 0.1 g of (a) CuO, (b)  $\text{Co}_3\text{O}_4$ , (c)  $\text{Fe}_2\text{O}_3$  and (d) NiO.



**Fig. 3.** Powder X-ray diffraction patterns of the oxides before (BT) and after (AT) treatment: (a) CuO (\*Cu), (b)  $\text{Co}_3\text{O}_4$ , (c)  $\text{Fe}_2\text{O}_3$  and (d) NiO.

the reduction process in the presence of 0.1 g of  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and NiO reveals that there is a gradual decrease in the absorbance at  $\sim 404$  nm.

No impurity peak is observed in the HPLC analysis of the products obtained in reactions catalyzed by CuO,  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and NiO. The percentage conversion of p-nitrophenol to p-aminophenol is determined as 99.4, 99, 98.3 and 98.3 in the presence of CuO,  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and NiO respectively (20 ml of 0.1  $\text{mmol L}^{-1}$  of p-nitrophenol, 12.5 mL of 0.5 M  $\text{NaBH}_4$  and 0.1 g of metal oxide). The selective formation of p-aminophenol is further confirmed by FT-IR and NMR spectroscopic analysis.

FT-IR data:  $\nu$  ( $\text{cm}^{-1}$ ): 3181 (OH), 3341 and 3281 ( $\text{NH}_2$ ), 3031 (aromatic C–H), 1615 (aromatic C–C).

$^1\text{H}$  NMR data  $\text{DMSO-}d_6$ ,  $\Delta$  (ppm): 8.38 (s, 1H, –OH); 6.50 (d, 2H, ArH); 6.40 (d, 2H, ArH), 4.79 (s, 2H,  $\text{NH}_2$ ) [29].

The metal oxide residues collected after the completion of the reduction process are analyzed by powder X-ray diffraction method and the diffraction patterns are given in Fig. 3. The analysis specifies that the oxides  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and NiO do not undergo any chemical and structural changes (Fig. 3b–d) thus proving their surface catalytic activity towards the reduction of p-nitrophenol to p-aminophenol. On the other hand, presence of peaks due to metallic copper is noted in the powder XRD pattern of the residue in the case of 'CuO' (Fig. 3a). The powder XRD patterns of CuO,  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and NiO are indexed based on the JCPDS files 48-1548, 65-3103, 39-1346 and 89-5881, respectively. The formation of copper is identified based on the reported data using the JCPDS file

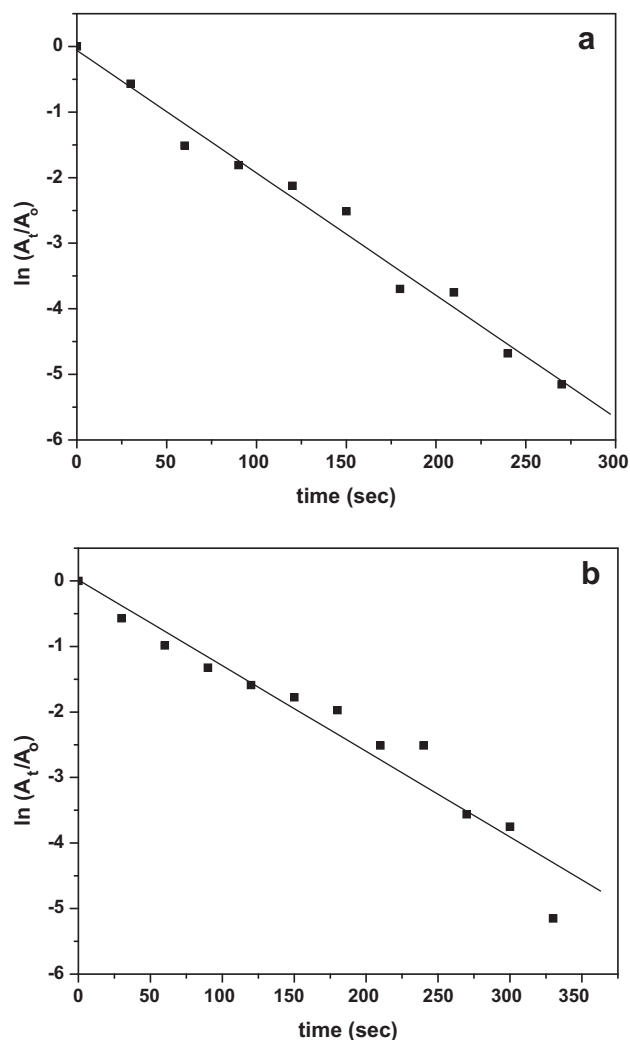


Fig. 4. Plots of  $\ln(A_t/A_0)$  vs. time for the reduction of p-nitrophenol in the presence of (a) CuO and (b)  $\text{Co}_3\text{O}_4$ . Reaction conditions: p-nitrophenol =  $5 \text{ mmol L}^{-1}$ ,  $\text{NaBH}_4 = 0.05 \text{ M}$ , CuO,  $\text{Co}_3\text{O}_4 = 0.1 \text{ g}$ ,  $T = 303 \text{ K}$ .

85–1326. Simultaneous formation of metallic copper does not hinder the process of reduction of p-nitrophenol. Rather, the accumulation of freshly formed metallic copper enriches the surface reactivity which leads to spontaneous reduction of p-nitrophenol. The activity of metallic copper is cross checked by carrying out the reaction using copper powder (0.1 g, 99.5% pure) under similar experimental conditions. Observations indicate that complete conversion of p-nitrophenol to p-aminophenol takes place with in 30 s.

The active metal oxides have been tested by varying the amounts of p-nitrophenol and sodium borohydride. The concentrations of p-nitrophenol tested are  $1 \text{ mmol L}^{-1}$ ,  $5 \text{ mmol L}^{-1}$  and  $10 \text{ mmol L}^{-1}$  and that of sodium borohydride are 0.05 M and 0.005 M. The amount of the metal oxide is kept as 0.1 g. For the combinations of  $[\text{PNP}] = 1 \text{ mmol L}^{-1}$ ,  $5 \text{ mmol L}^{-1}$  and  $[\text{NaBH}_4] = 0.05 \text{ M}$ , the metal oxides CuO and  $\text{Co}_3\text{O}_4$  showed activity, iron oxide and nickel oxide are found to be inactive. However, for combination of PNP and  $\text{NaBH}_4$  concentrations such as  $10 \text{ mmol L}^{-1}$  and 0.05 M, respectively, 0.1 g of copper oxide and cobalt oxide is found to be insufficient to convert the nitro compound. Plots of  $\ln(A_t/A_0)$  versus time for the reduction of p-nitrophenol with the reaction conditions:  $[\text{PNP}] = 5 \text{ mmol L}^{-1}$ ,  $[\text{NaBH}_4] = 0.05 \text{ M}$ , CuO,  $\text{Co}_3\text{O}_4 = 0.1 \text{ g}$ ,  $T = 303 \text{ K}$  shown in Fig. 4a and b indicate linear correlation. The pseudo-first order rate constant values for both CuO

and  $\text{Co}_3\text{O}_4$  catalyzed reactions are determined to be  $1.9 \times 10^{-2} \text{ s}^{-1}$  and  $1.3 \times 10^{-2} \text{ s}^{-1}$ , respectively.

The reusability of the copper oxide and cobalt oxide is tested using  $[\text{PNP}] = 1 \text{ mmol L}^{-1}$  and  $[\text{NaBH}_4] = 0.05 \text{ M}$ , respectively. The duration required for the conversion against the number of cycles is plotted in Fig. 5 for both CuO and  $\text{Co}_3\text{O}_4$ . It is noted that after the first cycle the time required for the conversion decreases in the case of CuO. This is due to the formation of metallic copper which is also actively catalyzing the p-nitrophenol conversion. The retention of the same duration through the cycles demonstrates that the metallic copper catalyst is highly active even for the tenth cycle. In the case of  $\text{Co}_3\text{O}_4$ , the conversion time slightly increases but no drastic change in the duration is observed. Powder X-ray analysis on these catalysts after the tenth cycle is performed and the results are given in Fig. 6.

As evidenced from the steps involved in the mechanism, the reduction reaction [30] requires electron transfer from the donor,  $\text{BH}_4^-$  ion. Under the current experimental conditions in the presence of the active metal oxides it is understood that the steps involved to be (i) chemisorption of  $\text{BH}_4^-$  on the surface of the metal oxide [12,31] followed by (ii) discharge of electrons from  $\text{BH}_4^-$  through metal oxide to the acceptor. The medium water which is a polar protic solvent, offers the required  $\text{H}^+$  ions for the completion of the reduction reaction. An experiment has been performed using DMSO, a polar aprotic solvent instead of water as a medium under similar conditions. It is noted that the reduction reaction is not taking place. This confirms the role of  $\text{NaBH}_4$  as an electron donor.

The metal oxides possessing 'd $n$ ' ( $n = 5-9$ ) electronic configuration are active whereas, the oxides with 'd $0$ ', d $3$  and 'd $10$ ' configurations are found to be inactive. The oxides with 'd $n$ ' configuration induce the catalytic reduction by relaying electrons from the donor  $\text{BH}_4^-$  ions to the acceptor once they get adsorbed on the metal oxide surface. It is envisaged that the surface positive charge of the group A oxides that are of p-type semiconductors facilitated the interaction between the metal oxide surface and the donor species  $\text{BH}_4^-$ . The main reason for the inactivity of group B oxides could be due to the absence of electron relay which is decided by the electronic structure of the oxides. Though  $\text{TiO}_2$  does not enhance such electron relay under the current experimental conditions, under light illumination the conduction band of the oxide gets populated and the electron transfer is thus facilitated. Hence,  $\text{TiO}_2$  is reported as a photocatalyst for the reduction of p-nitrophenol [30].

The results are compared with the other catalytic systems reported for the reaction such as arginine modified  $\text{TiO}_2$  [21], combination of KI and N-doped  $\text{TiO}_2$  [22] in the case of oxide systems and metal [7], metal supported catalysts [9,10],  $\text{Fe}_3\text{O}_4$ -Au nanoparticles [16], supported Ni catalysts [9] in the category of metal based catalysts and nanomaterials. Such systems are associated with photocatalytic conditions in the former and hydrogen pressure, elevated temperature, usage of autoclaves, tedious procedure for the preparation of nanomaterials, etc, in the later. The estimated rate constant values ( $1.9 \times 10^{-2} \text{ s}^{-1}$  in the presence of CuO and  $1.3 \times 10^{-2} \text{ s}^{-1}$  in the presence of  $\text{Co}_3\text{O}_4$ ) are highly comparable with that of other nanoparticles catalyzed p-nitrophenol reduction reaction using aqueous  $\text{NaBH}_4$ . The closest systems in terms of  $[\text{NaBH}_4]/[\text{PNP}]$  ratio and reaction temperature to be compared are  $\text{Cu}_2\text{O}$  nanoparticles [25], copper nanorods and nanospheres [32], Ag nanoparticles supported on oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  [33], gold nanoparticles [34] and cobalt nanoparticles [35]. The current rate constant values are found to be higher compared to many of these systems and are of the same order to that of silver supported  $\text{TiO}_2$  [33]. Thus, the observations made in the current study entail that both the oxides CuO and  $\text{Co}_3\text{O}_4$  in their normal

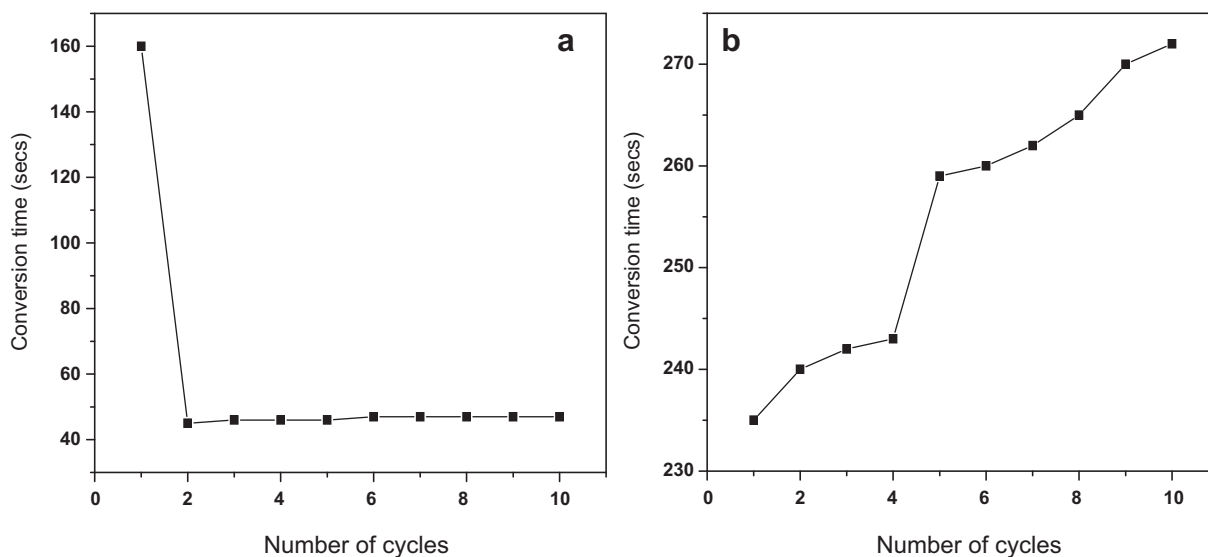


Fig. 5. Conversion time against number of cycles for (a) CuO and (b) Co<sub>3</sub>O<sub>4</sub>.

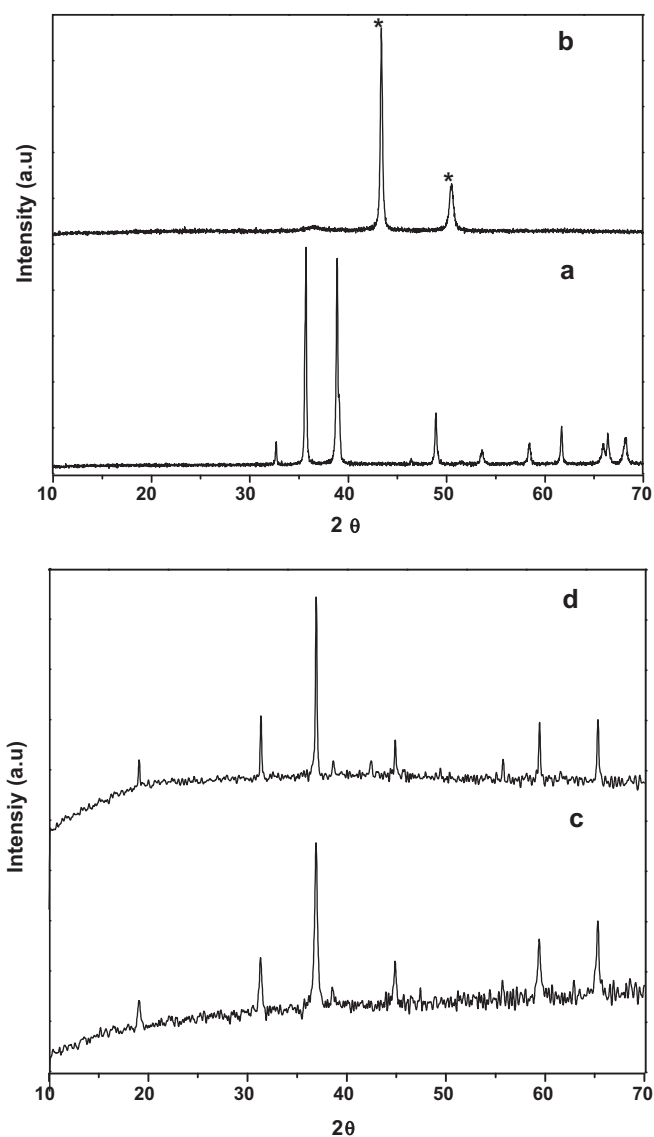


Fig. 6. Powder X-ray diffraction patterns of (a) CuO before treatment, (b) CuO after 10 cycles, (c) Co<sub>3</sub>O<sub>4</sub> before treatment and (d) Co<sub>3</sub>O<sub>4</sub> after 10 cycles (\*Cu).

bulk form could be employed as catalysts for faster reduction of p-nitrophenol.

The duration required for the conversion of p-nitrophenol to p-aminophenol in the presence of 0.1 g of the group A oxides follows the trend: CuO < Co<sub>3</sub>O<sub>4</sub> ≈ Fe<sub>2</sub>O<sub>3</sub> « NiO (Table 1). This suggests a possible correlation between the activity of these semiconducting oxides and their respective band gap energy values. Fig. 7 shows the relationship between the duration of the reaction and the reported band gap values 1.7, 2.07, 2.2 and 3.8 eV for CuO, Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and NiO, respectively [36–38]. This behavior implies that lower band gap in the case of the oxides such as CuO, Co<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> facilitates faster electron transfer. In the case of CuO, the surface is enriched with metallic copper (as confirmed by powder X-ray diffraction pattern) which in turn facilitates the relaying of electrons to the substrate (p-nitrophenol) from borohydride ion. The more positive reduction potential (+0.34 V) for Cu<sup>2+</sup>/Cu couple in comparison with other metal ions, viz., Co<sup>2+</sup>, Fe<sup>3+</sup> and Ni<sup>2+</sup> (Co<sup>2+</sup>/Co = −0.277 V, Fe<sup>3+</sup>/Fe = −0.036 V and Ni<sup>2+</sup>/Ni = −0.250 V) designates the feasible reduction of Cu<sup>2+</sup> [23]. In addition to the lower band gap of CuO, the freshly formed

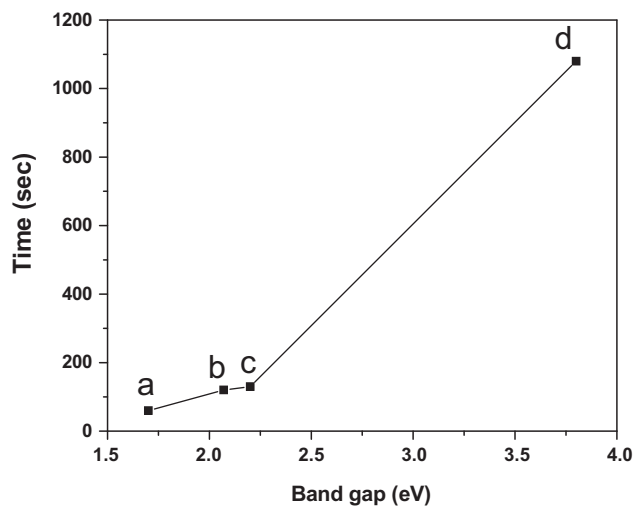


Fig. 7. Correlation of the band gap energies of the metal oxides with the time taken for the conversion of PNP: (a) CuO, (b) Co<sub>3</sub>O<sub>4</sub>, (c) Fe<sub>2</sub>O<sub>3</sub>, and (d) NiO [amount of the metal oxide = 0.1 g].

metallic 'Cu' together could be the reason for the spontaneous reaction of copper oxide compared to other group A oxides. The influence of varying the parameters such as the particle size of the active metal oxide, stirring rate, temperature etc. on the conversion will be studied in the future.

#### 4. Conclusions

The rapid conversion of p-nitrophenol to p-aminophenol in the presence of the oxides CuO, Co<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and NiO specifies the faster electron relay. In the testing using higher concentration of p-nitrophenol and lesser concentration of sodium borohydride, the oxides CuO and Co<sub>3</sub>O<sub>4</sub> are found to be highly active with the PNP and NaBH<sub>4</sub> concentrations up to 5 mmol L<sup>-1</sup> and 0.05 M, respectively. Thus, it is noted that both the oxides CuO and Co<sub>3</sub>O<sub>4</sub> in their normal bulk form could be employed as better catalysts. By modifying these oxides into porous form or nanoform or supported catalysts both copper oxide and cobalt oxide will evolve as suitable catalysts for the aforesaid conversion with the consumption of minimal amount of sodium borohydride. Work in this direction is in progress in our laboratory.

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