

Short communication

Nitro compounds reduction via hydride transfer using mesoporous mixed oxide catalyst

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Abstract

The catalysts NiCo_2O_4 were prepared by co-precipitation and surfactant approach. These catalysts were characterized by crystal size, BET surface area, pore volume, average pore size, XRD and SEM. The catalytic activity of co-precipitated NiO, CoO, NiCo_2O_4 and surfactant-assisted NiCo_2O_4 was tested for the reduction of 4-Chloro-nitrobenzene using variety of hydrogen donor and basic promoters. The reaction was carried out at different temperatures and catalysts concentrations. Reusability, recyclability of the catalyst and reductions of variety of nitro arenes was also studied.

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Keywords: NiCo_2O_4 ; Co-precipitation; Surfactant; Reduction

1. Introduction

Reduction of nitro compounds is carried industrially to obtain hydroxylamine, azo-, azoxycompounds and amines, which find applications in dyes, agrochemicals, pharmaceuticals and photographic chemicals. Extensive reduction methodologies are being practiced using metal/HCl system, H_2 gas, sulfides and polysulfides. Due to the stringent environmental concerns constant efforts are being made to find safer alternative to the above-mentioned processes. Catalytic hydride transfer reduction (CHTR) has received continuous recognition as an alternative for the clean production of variety of chemicals [1]. CHTR is facilitated by hydride transfer from the readily available hydrogen sources such as hydrocarbons [2], primary or secondary alcohols [3], formic acid and its salts [4].

Nitro compounds CHTR is an important reaction for the synthesis of amines which are used as bulk chemical as well as an intermediate in pharmaceuticals, dye stuff industries, etc. [5]. CHTR have been demonstrated by various greener processes, namely reduction in super critical water [6], ultrasound promoted reduction [7], use of ionic liquid [8]. These processes are efficient to laboratory scale but lack commercial viability and

also require sophisticated techniques and sometime hazardous chemicals. Activity and selectivity of CHTR of nitrobenzene and substituted nitrobenzene using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}/\text{In}$ [9], Ni [10], $\text{Ru}_3(\text{CO})_{12}$ /chelating diimines [11], Te [12] have been studied but the regio- and stereoselectivity suffers. Selvam and co-workers [13] have made good attempt to enhance the selectivity of amines by incorporating Co in hexagonal molecular sieves (HMS) but the synthesis of the catalyst by hydrothermal treatment and incorporation of Co inside the cavity of the HMS increases the cost of the catalyst. Further as Co is supported inside the cavity of HMS, subsequent recycling can leach the Co.

In order to improve regio-, stereoselectivity and prevent catalyst leaching we have synthesized mesoporous NiCo_2O_4 using novel sugar based surfactant (alkyl polyglucoside, C_{10}) act as a template.

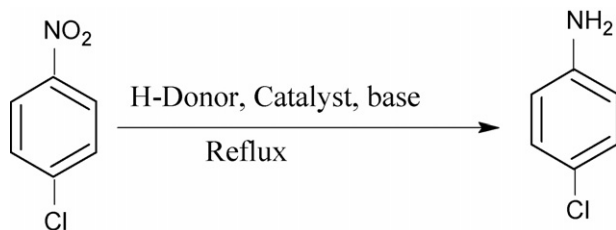
2. Experimental

2.1. Chemicals

Nickel chloride, cobalt chloride, sodium hydroxide, ethanol, 1&2-propanol, 1-butanol, formic acid, acetic acid, glucose, Vitamin C, pyridine, liquid ammonia, triethyl amine, trimethyl amine, calcium and magnesium nitrates, for the preparation of

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Scheme 1. Probable reaction mechanism on the surface of the catalyst containing electron rich and electron deficient sites \ominus is electron rich site and \oplus is electron deficient site on the surface of the catalyst.

their hydroxides by co-precipitation method, were obtained from m/s S.D. Fine Chemicals Ltd., Mumbai. Cognis, Germany, is acknowledged for alkyl polyglycoside (C_{10}).

2.2. Choice of catalyst

Cobalt and nickel based catalysts are attracting much attention in the recent years. They are used in various industrially important reactions such as hydrodesulphurization [14], reduction of nitriles [15] and azocompounds [16]. Literature for hydride transfer reduction over cobalt and nickel based catalysts shows lack of stereo- as well as regioselectivity due to their non-porous nature; if porosity of these catalysts increases, these catalysts can be used to selectively reduce a particular functional group as well as bulky moieties can be reduced effectively with good yields. Hence we have extended the amphiphilic template approach to cobalt nickel mixed oxide catalyst to improve the mesoporosity and to enhance the surface area, so that the bulky moieties will be reduced selectively with high yields. Individual cobalt and nickel were used for the hydrogenation; no attempt has been made to study the synergism in the activity of the mixed cobalt and nickel catalyst in the reaction. So we have thought it desirable to study the effect of mixed cobalt and nickel oxide catalyst in the transfer hydrogenation with an aim to obtain maximum selectivity and high yield for the reduced products (Scheme 1).

2.3. Catalyst preparation

2.3.1. Co-precipitation [17]

Ni and Co nitrates were taken in the 1:2 molar ratio, respectively. Ten percent NaOH solution was added as a precipitating agent under vigorous stirring until pH of 9.0–9.5 was achieved. The solution was kept on a water bath maintained at 80°C for 3 h and then oxidized by adding requisite amount of 30% H_2O_2 drop wise with constant stirring and aged for 24 h. The resultant precipitate was filtered and washed with distilled water to remove excess of precipitating agent and nitrate ions. The precipitate was dried at 110°C for 3 h and calcined at 300°C for 10 h. Similar procedure was applied for preparation of NiO and CoO. H_2O_2 addition gives single-phase catalyst.

2.3.2. Templated route [18]

In a typical preparation, Co and Ni nitrates were taken in stoichiometric amounts (2:1) and were dissolved in 10 ml of

methanol; to this 50% of decylpolyglycoside aqueous solution was added with vigorous stirring for 1 h. The resulting solution was gelled at 50°C for 20 h (catalyst preparation is optimized). This as made bulk samples were calcined at 300°C for 6 h in air to remove the surfactant.

2.4. Catalyst characterization

All the catalysts were characterized by XRD and BET surface area measurements. %Composition of each element in the catalysts was done by ICP-AES. SEM and FT-IR of NiCo_2O_4 (a) and (b) are reported.

From the XRD, NiO, CoO and NiCo_2O_4 (a) were crystalline with the sharp peaks in wide angle whereas NiCo_2O_4 (b) gave no peaks. Small angle XRD of NiCo_2O_4 (b) gave a peak at $2\theta = 2.0^\circ$, thus the catalyst NiCo_2O_4 (b) prepared by surfactant templated approach is mesoporous in nature. Crystallite size is calculated by Scherrer formula (Fig. 1; Table 1). The nitrogen adsorption–desorption isotherm shown in Fig. 2 is a type-IV isotherm, as defined by the IUPAC, with a sharp step at intermediate relative pressures with an H2 hysteresis loop [19] due to capillary condensation. The isotherm, shows three well-defined stages can be identified: (a) a slow increase in nitrogen uptake at 0.0–0.2 relative pressures, corresponding

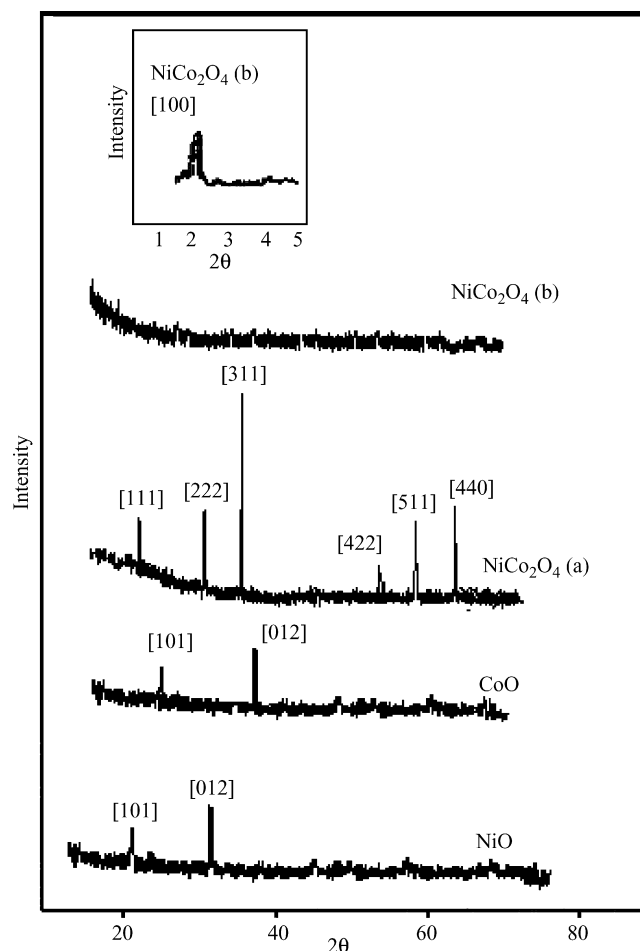


Fig. 1. XRD of all the catalysts.

Table 1
Elemental analysis of the catalysts NiCo₂O₄ (b)

Compound	%Co		%Ni	
	ICP-AES	Theoretical	ICP-AES	Theoretical
NiCo ₂ O ₄ (b) (fresh)	28	28	14.7	14
NiCo ₂ O ₄ (b) (used)	28	–	14.7	–

to monolayer–multilayer adsorption on the pore walls, (b) a sharp step at 0.2–0.6 relative pressures indicative of capillary condensation in mesopores and (c) a plateau at 0.6–0.9 relative pressures associated with multilayer adsorption on the external surface. Characteristic nitrogen BET surface area is 202.9 m²/g. As observed from BJH adsorption pore size distribution, a major part of the surface area is contributed by pores with a diameter characteristic of pores ranging from 35 to 65 Å. There is also a significant part due to mesopores ranging from 65.0 to 100.0 Å, as shown the pore size distribution (Fig. 3). The catalyst is essentially mesoporous.

This narrow (PSD) shows the particles are uniform. Theoretical and observed percentage of Co and Ni by ICP-AES are given in Table 1. From the results obtained from elemental analysis we can say that catalyst is stable under the given reaction condition.

Three SEM photographs of (a) and (b) are shown in Figs. 4 and 5, respectively. SEM of (a) shows the aggregation of the particles due to which not many active sites are being exposed to the substrate and reaction yield is low. SEM of sample b shows the rod-like morphology of the particles with two lobes at one end suggesting the increasing surface area with large exposure of active sites for the substrate to react on the surface.

(a) and (b) correspond to the co-precipitated catalyst and templated catalyst. Sharp peaks in the region 1600–1700 cm⁻¹ indicate the presence of Bronsted acidity and in the region 1400–1500 cm⁻¹ indicate the presence of Lewis acidity the catalyst (see Fig. 6).

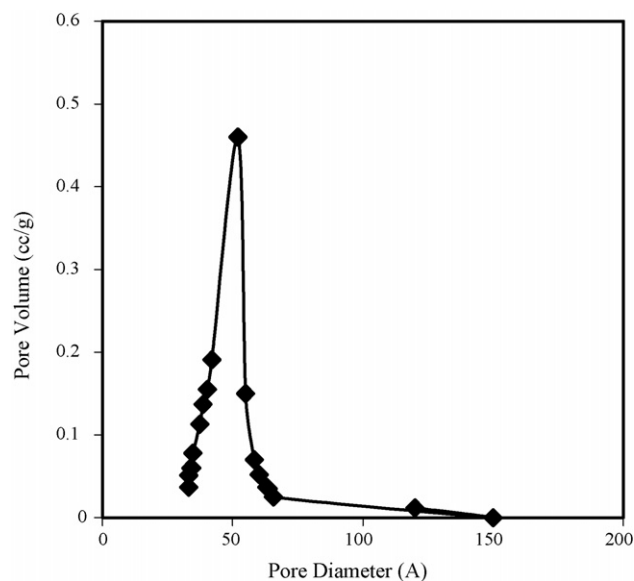


Fig. 3. Pore size distribution.

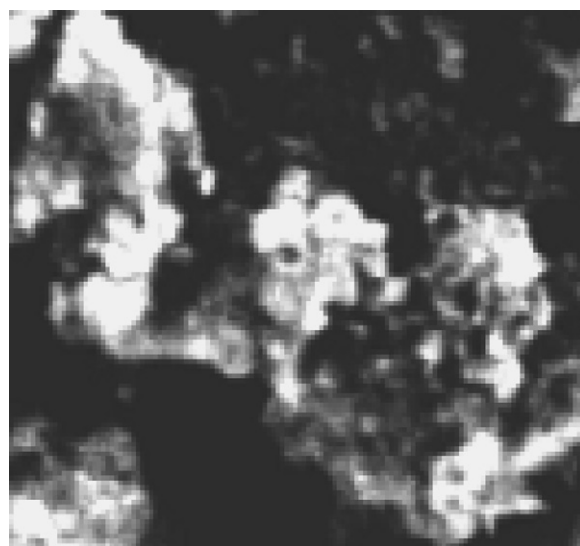


Fig. 4. SEM of NiCo₂O₄ (a).

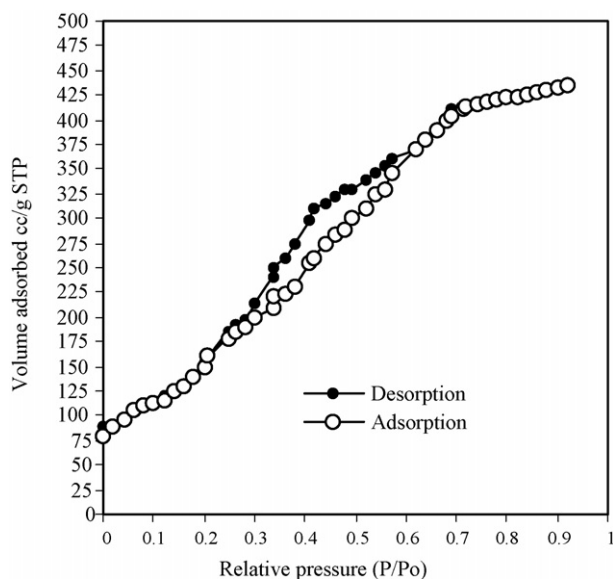


Fig. 2. N₂ adsorption–desorption isotherms.

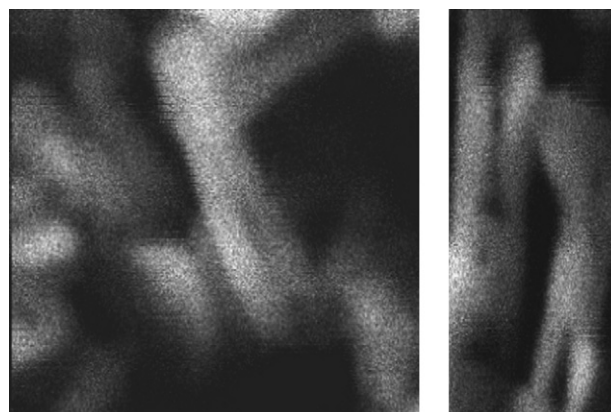


Fig. 5. SEMs of NiCo₂O₄ (b).

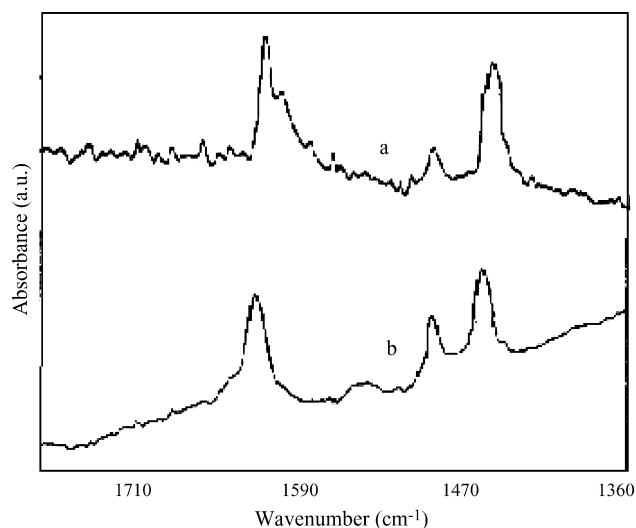


Fig. 6. IR spectra of NiCo₂O₄ (a) co-precipitated catalyst and (b) templated catalyst.

2.5. Experimental procedure

The reactor consisted of a standard flat bottom cylindrical vessel of 6 cm internal diameter of 100 ml capacity equipped with four equi-spaced baffles, a pitched bladed turbine impeller and a condenser. The assembly was kept in an isothermal oil bath at a known temperature and mechanically agitated with an electric motor. In a typical experiment, the reaction mixture consisted of 15 mmol 4-Chloro1-nitrobenzene and 15 mmol sodium hydroxide. The total volume of the reaction mixture was made up to 15 ml with 2-propanol which acts as a hydrogen donor as well as a solvent. The reaction was carried out at 82 °C at a speed of 700 rpm with 0.05 g/cm³ as the standard catalyst loading. Samples of the reaction mixture were withdrawn periodically for analysis.

3. Results and discussions

The main objective of the work was to investigate the activity of NiCo₂O₄ and probable mechanism of hydrogen transfer reduction of 4-Chloro1-nitrobenzene. The reaction is given in Scheme 2.

Table 2

Transfer hydrogenation of 4-Chloro1-nitrobenzene to amine with 2-propanol over different catalysts

Catalyst	BET surface area (m ² /g)	Crystallite ^a size (Å)	Unit cell parameter (<i>a</i>) (Å)	Porosity ^b	Pore size ^c (Å)	Unreacted 4-Chloro1-nitrobenzene (mass%)	Yield ^d of amine (mass%)
No catalysts/no NaOH	–	–	–	–	–	100	00.0
CoO (a)	13.3	0.4	4.012	0.15	12	34.2	65.8
NiO (a)	15	0.59	4.23	0.2	20	33.1	66.9
NiCo ₂ O ₄ (a)	20.1	10	8.111	0.25	22	10.1	89.9
NiCo ₂ O ₄ (b)	202.9	35	8.056	0.46	65	4.0	94.0

(a) Prepared by co-precipitation method and (b) prepared by templated approach. Reaction conditions: 4-Chloro1-nitrobenzene (15 mmol), NaOH pellets (15 mmol) refluxed in 15 ml of 2-propanol and catalyst (0.05 g/cm³).

^a Determined by Scherrer equation, *a* is determined by XRD.

^b The porosity is estimated from the pore volume determined using the adsorption branch of the N₂ isotherm curve at the *P/P*₀ = 0.986 single point.

^c Average pore size by BET.

^d All yields are isolated, purified by column chromatography and analyzed by IR spectroscopy.

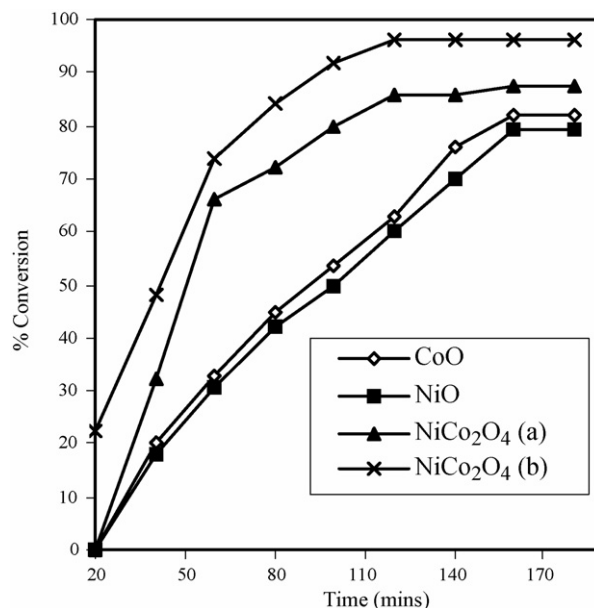
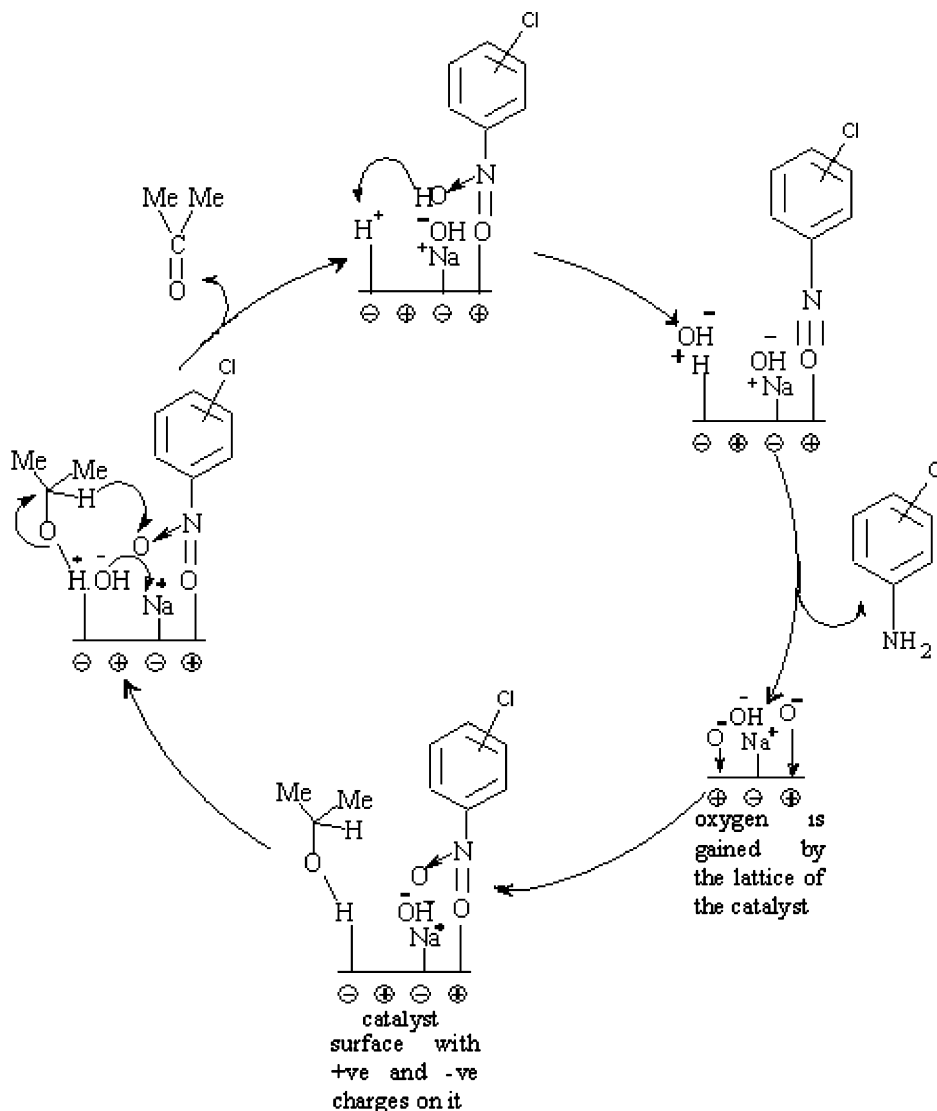


Fig. 7. Effect of various catalysts.

3.1. Effect of various catalysts

The effect of various catalysts on transfer hydrogenations was studied over CoO, NiO, NiCo₂O₄ (a) and NiCo₂O₄ (b) keeping other reaction parameters constant (Fig. 7; Table 2). NiCo₂O₄ (a) was prepared by co-precipitation method whereas NiCo₂O₄ (b) was prepared in the presence of the alkyl polyglucoside (C₁₀) template. A trend dependent on surface area was seen from the result, as the surface area increases yield of amines goes on increasing. Thus NiCo₂O₄ (a) was selected to optimize other parameters of the hydrogenations. In absence of either catalyst or base no reaction occurred as reported.

A standard experiment was done wherein the reaction was started with 4-Chloro1-nitrobenzene and 2-propanol under alkaline conditions at refluxing temperature without NiCo₂O₄. After 1.5 h no conversion of 4-Chloro1-nitrobenzene was observed due to absence of catalyst. Same reaction was repeated without base in the presence of the catalyst. It was found that the catalyst alone was unable to reduce 4-Chloro1-nitrobenzene via hydride transfer from the H-donor. Hence both catalyst as well as base



Scheme 2. Reduction of nitrobenzene by catalyst transfer hydrogenation.

was necessary for promoting hydride ion from alcohol to nitro moiety to obtain the reduced product.

3.2. Effect of various hydrogen donors and bases

The entries in Table 3 report the effect of different hydrogen donors and bases used; under otherwise similar conditions it was concluded that 2-propanol/NaOH was the efficient pair for transfer hydrogenation of 4-Chloro-1-nitrobenzene to 4-Chloro-1-aminobenzene. Amongst alcohols 2-propanol was the most suited hydrogen donor as primary alcohols dehydrogenate to aldehyde which acts as a catalysts poison. HCOOH and CH₃COOH fail to produce aniline with Et₃N/Me₃N/NH₃ or with NaOH. D-Glucose and Vitamin C were unsuccessful with pyridine as a promoter, but with NaOH yield of azoxy benzene was more as compared to aniline. 2-Propanol with Ca(OH)₂ and Mg(OH)₂ yielded less amount of 4-Chloro-1-aminobenzene due to their lower basicity than NaOH. With Et₃N, Me₃N or NH₃ 2-propanol did not give any product. Hence all further reactions were carried with 2-propanol/NaOH system.

3.3. Effect of pH, [base], [4-Chloro-1-nitrobenzene] and [2-propanol]

It was observed that in the absence of base reaction did not proceeded. The pH of the system was varied to study its effect on the reduction. As the pH of the reaction system was increased, the selectivity towards amines increased. At lower pH formation of hydroxybenzene was favored. At acidic pH no reduction was observed. The best results were obtained above pH 9.0. Concentration of the base was varied to study the dependence of the reaction. From Fig. 8, it can be said that as the concentration of the base increases conversion of 4-Chloro-1-nitrobenzene to 4-Chloro-1-aminobenzene increases. At lower concentration the partially reduced compounds are obtained. We can conclude that the rate of reaction is dependent on the concentration of the base till the optimum concentration (15 mmol) beyond that the rate of reaction was independent of the concentration of base. Change in the concentration of either nitrobenzene or 2-propanol do not affect the reduction reaction, i.e. rate of reaction is independent of the concentration of 4-Chloro-1-nitrobenzene and 2-propanol.

Table 3

Effect of different hydrogen donors and different bases on transfer hydrogenation of 4-Chloro1-nitrobenzene to amine

H-donor	Promoter	Yield ^c (mass%)		
		Amine	Azoxycompound ^a /azocompound ^b	4-Chloro1-nitrobenzene
CH ₃ CH ₂ OH	NaOH	72.8	–	27.0
CH ₃ CHOHCH ₃	NaOH	96.0	–	3.8
CH ₃ CHOHCH ₃	Ca(OH) ₂	17.0	40.0 ^a	42.0
CH ₃ CHOHCH ₃	Mg(OH) ₂	15.0	36.0 ^a	48.1
CH ₃ CHOHCH ₃	Et ₃ N	–	–	100.0
CH ₃ CHOHCH ₃	Me ₃ N	–	–	100.0
CH ₃ CHOHCH ₃	NH ₃	–	–	99.8
CH ₃ CHOHCH ₂ CH ₃	NaOH	45.0	–	54.0
HCOOH	NaOH	–	–	100.0
HCOOH	Et ₃ N	–	–	100.0
HCOOH	Me ₃ N	–	–	99.0
HCOOH	NH ₃	–	–	99.0
CH ₃ COOH	NaOH	–	–	100.0
CH ₃ COOH	Et ₃ N	–	–	100.0
CH ₃ COOH	Me ₃ N	–	–	99.6
CH ₃ COOH	NH ₃	–	–	98.7
D-Glucose	NaOH	4.0	34.0 ^a	61.2
D-Glucose	Pyridine	–	–	99.0
Vitamin C	NaOH	10.0	28.0 ^a	61.0
Vitamin C	Pyridine	–	–	99.9

Reaction conditions: 4-Chloro1-nitrobenzene (15 mmol), promoter (15 mmol) refluxed at 80 °C in 15 ml of 2-propanol and catalyst (0.05 g/cm³).

^a Azoxy compound.

^b azo compound.

^c All yields are isolated, purified by column chromatography and analyzed by IR spectroscopy.

The ratio of base and 4-Chloro1-nitrobenzene should be maintained at 1, below that partially reduced compound are obtained predominantly and above which the reduction is independent.

3.4. Effect of [catalyst]

Rate of reaction is directly proportional to [catalyst] base on the entire liquid phase volume. The catalyst concentration was varied from 0.01 to 0.06 g/cm³ on the basis of total volume of the reaction mixture keeping all other conditions similar.

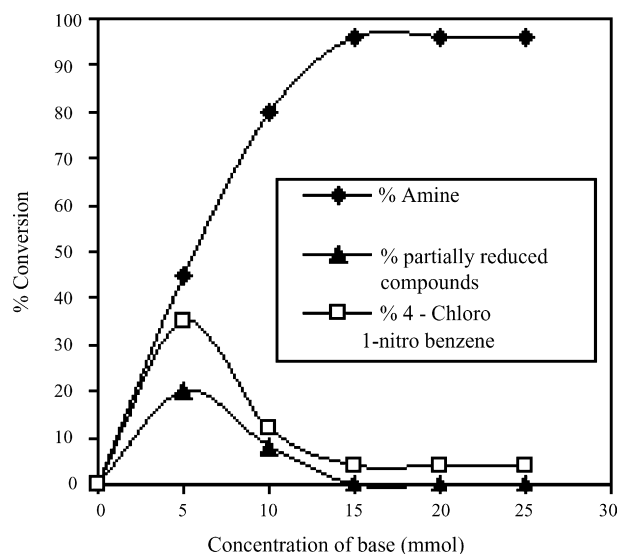


Fig. 8. Effect of [base].

Fig. 9 shows the effect of [catalyst] on the conversion of 4-Chloro1-nitrobenzene. The conversion increased with increase in [catalyst], which is due to the proportional increase in the number of active sites. However, beyond of 0.05 g/cm³ [catalyst], there was no significant increase in the conversion and hence all further experiments were carried out at this catalyst loading. At

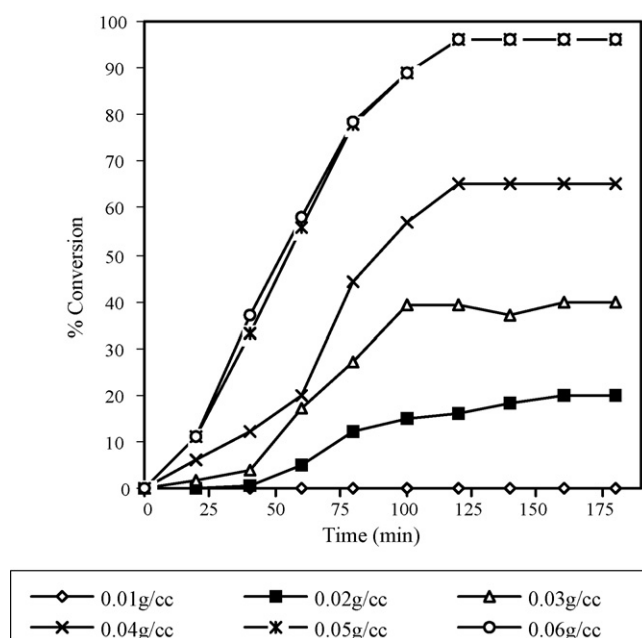


Fig. 9. Effect of [catalyst].

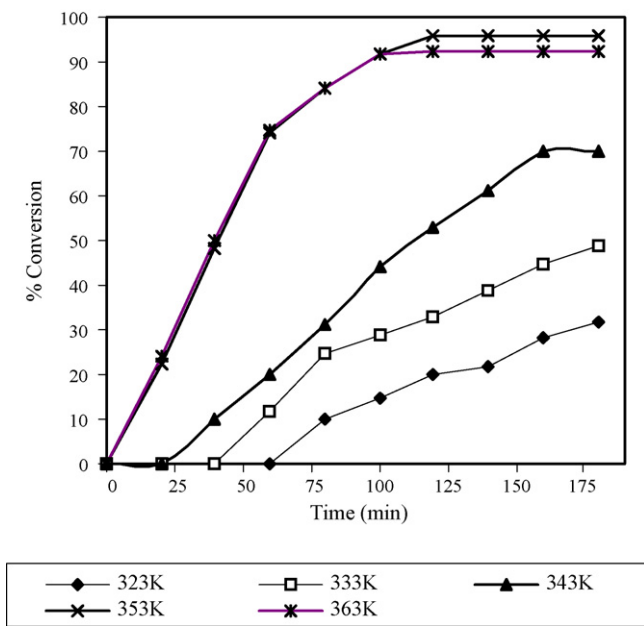


Fig. 10. Effect of temperature.

lower catalyst concentration partially hydrogenated product was also obtained along with amine. From the results obtained we can say that as the concentration of catalyst increases, the conversion of 4-Chloro1-nitrobenzene to 4-Chloro1-aminobenzene with 100% selectivity.

3.5. Effect of temperature

Catalytic transfer hydrogenation is highly temperature dependant. The reaction did not proceed at room temperature and at lower temperature partially hydrogenated product was obtained, thus the effect of temperature was studied from 323 to 363 K under otherwise similar conditions (Fig. 10). The conversion of 4-Chloro1-nitrobenzene increased with increase in the temperature of the reaction. Beyond 353 K there was no increase in the conversion of nitrobenzene.

3.6. Reusability and activity of the catalyst

The reusability of the catalyst was studied by recycling the filtered and acetone washed catalyst under otherwise similar conditions. Fig. 11 shows the conversion of nitrobenzene against time, and that the conversion has been decreased from 96 to 76% from the fresh to the third reuse of the catalyst. There was attrition of the catalyst; hence some catalyst was lost during filtration. There was a loss of ~5% catalyst during filtration. Thus in the next experiment, the volume of the reaction mixture was adjusted to make the catalyst loading 0.05 g/cm^3 , the standard value. It was found that the conversion were practically the same as in the previous run, thereby suggesting that there was no loss in activity. Thus it can be concluded that there was little decrease in the catalyst activity with reuse.

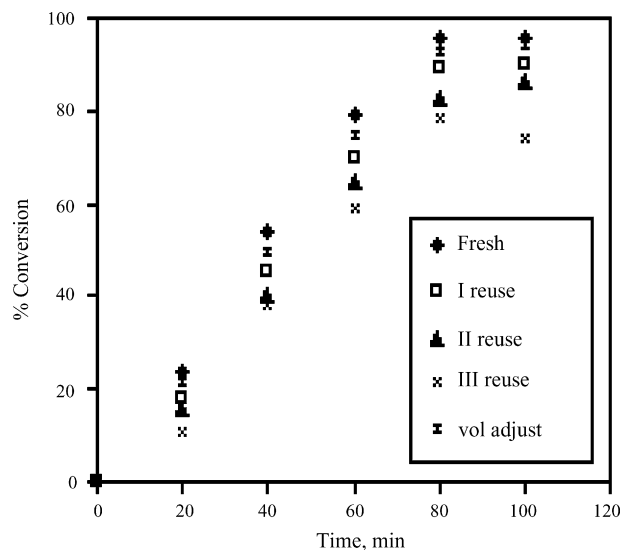


Fig. 11. Reusability of the catalyst.

3.7. Catalytic hydrogen transfer reduction of substituted nitro compounds

The selective and rapid reduction of nitro compounds is an interesting area of research, particularly when other potentially reducible moieties are present in the molecule (see Table 4). Nitro group attached to the aromatic ring can withdraw more strongly from benzene as compared to other reducible groups. Hence, can be easily adsorbed on the catalyst as soon as the product is formed, it is desorbed, the reaction is chemo selective. The catalyst also promises regioselectivity as can be seen from the dinitro compounds. It was found that the activity was significantly influenced by the position of the substituents on the aromatic ring. Halo nitro aryls has the tendency of hydrogenolysis of C–X bond (Cl, Br, I), but no hydrogenolysis was observed in the case of 4-Chloro1-nitrobenzene. It was also observed that presence of electron releasing group reduces the reduction of nitro compounds thus electron releasing group at para position enhanced the reduction. Hence it is possible that rate of reduction is decided by initial adsorption of the substrate which is rate determining.

Aliphatic nitro were totally reluctant for reduction may be due to structural similarity between substrate, 2-propanol and acetone formed in the reaction, thus this method cannot be used for obtaining aliphatic amines.

4. Plausible reaction mechanism on the surface of the catalyst

On the surface NiCo_2O_4 we have two types of sites electron rich (electrons provided by lattice oxygen) and electron deficient (holes as nature of NiCo_2O_4 is P-type semiconductor).

Step 1. An electron deficient site forms weak adsorption bond with nitro compound through the oxygen of nitro compound due to presence of electron pair on it. An electron rich site on the surface of the catalyst forms

Table 4
Catalytic hydride transfer reduction of substituted nitro benzenes

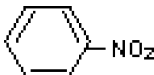
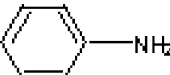

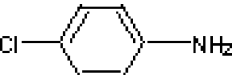








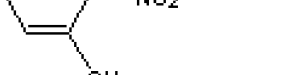
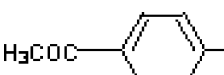
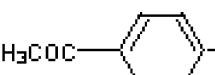

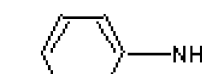


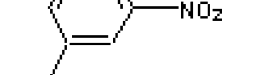
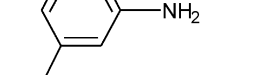
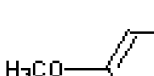

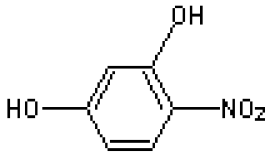
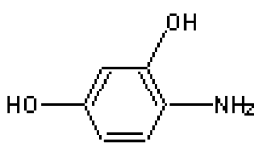
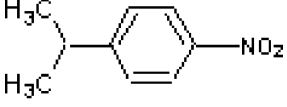
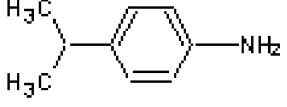


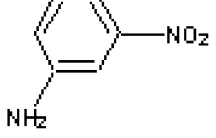
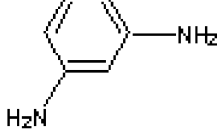
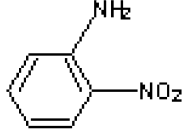
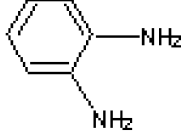
Substrate (15 mmol)	Product (15 mmol)	Time (min)	Yield (mass%)
		35	97.0
		50	96.0
		120	70.0
		90	90.0
		90	89.0
		90	85.0
		150	78.0
		120	92.0
		90	87.0
		270	92.0
		210	91.0
		300	69.8

Table 4 (Continued)

Substrate (15 mmol)	Product (15 mmol)	Time (min)	Yield (mass%)
		100	81.0
		180	72.0
		150	85.5
		150	83.0
		150	86.0

Reaction conditions: 4-Chloro1-nitrobenzene (15 mmol), base (15 mmol) refluxed at 80 °C in 15 ml of 2-propanol and catalyst (0.05 g/cm³). All yields are isolated, purified by column chromatography and analyzed by IR spectroscopy.

weak adsorption bond with –OH group of 2-propanol. Na⁺OH⁻ is also adsorbed on electron deficient site.

- Step 2. Na⁺OH⁻ transfers OH⁻ to 2-propanol, which in turn transfers H to nitro group to form hydroxyl intermediate and acetone is given out as a side product.
- Step 3. OH⁻ is retransferred to Na⁺ to form Na⁺OH⁻. H from hydroxyl compound is also retransferred to an electron rich site to form H₂O and azoxy intermediate.
- Step 4. In this step azoxy intermediate is reduced completely to amine and desorbed from the surface and oxygen is gained back by the catalyst lattice. Again the surface is ready to adsorb new reactant molecules and the process continues till optimum conversion of nitro arenes to amines. Throughout the catalytic cycle NaOH promotes the transfer of hydrogen from 2-propanol.

5. Conclusions

Hydride transfer reaction of 4-Chloro1-nitrobenzene was studied over different catalysts with 2-propanol as a hydrogen donor and NaOH. NiCo₂O₄ prepared by the alkyl polyglucoside (C₁₀) template was the best catalyst that gave 100% selectivity towards amine. Templated assisted route increases the surface area compared to co-precipitated NiCo₂O₄. Enhancement in the surface area enhances the reaction. The effects of various parameters on rates and selectivities were discussed. The electronic characteristics of electron withdrawing (Cl, CH₃CO) or donating (CH₃, OCH₃) were relatively insensitive to the reduction.

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