

# LIQUID-PHASE CATALYTIC TRANSFER HYDROGENATION OF AROMATIC NITRO COMPOUNDS OVER NICKEL-DOPED CARBON CATALYSTS

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## Abstract

Ni-doped carbon aerogel catalysts were prepared through sol-gel polycondensation of furfural with resorcinol in the presence of nickel nitrate salts, followed by drying at ambient pressure and then carbonization in N<sub>2</sub>. The catalysts were used for catalytic transfer hydrogenation of aromatic nitro compounds with propan-2-ol as hydrogen donor and KOH as promoter, and have been found to exhibit excellent catalytic activity for transfer hydrogenation of nitrobenzene, chloronitrobenzene and nitrotoluene. The results show that the yield of the products could reach as high as 100% within 3 hours. The effect of nickel loading amount (ranging from 2.5 to 20 wt%) on the catalytic activity was also studied. It has been found that the nickel amount has little effect on the catalytic activity. The reusability of the catalysts was also addressed. It is interesting to note that the catalytic activity of the catalysts remain at the same level even after six cycles, which is evidenced by the excellent yield of the target products. The recycled catalyst can be easily recovered from the reaction medium by a magnetically separable approach.

## Introduction

Catalytic hydrogenation of aromatic nitro compounds to make the corresponding amino derivatives is one of the most important reactions for the synthesis of various fine chemicals such as dyes, urethanes, agro-chemicals, and pharmaceuticals. The oldest method and the industrially practiced one is the Bechamp reduction, which involves use of stoichiometric amounts of finely divided iron metal and water in the presence of small amounts of acid. But the distinct disadvantage of this method is the formation of iron sludges that are difficult to dispose. The sulfide reduction has a broader selectivity than Bechamp reduction. The major disadvantages are toxicity and odor of most reducing agents and sulfur containing organic side products. Selective hydrogenation of aromatic nitro compounds using molecular hydrogen is non-polluting, but providing considerable hazards due to the flammability of the hydrogen gas. Hydrogen transfer reduction is safe, highly selective and eco-friendly compared to the three above-mentioned methods. Many soluble metal complexes have been reported for the hydrogen transfer reduction of aromatic nitro compounds. However, the reduction rates are quite difficult to control with these highly active homogeneous catalysts. And the homogeneous catalysts are difficult to recover. Heterogeneous catalysts offer several advantages over homogeneous systems such as easy recovery, easy recycling of the catalysts, and minimization of undesired toxic wastes. Several metal oxide supported catalysts have been employed, whereas the activity of most of these catalysts decreases with subsequent recycling. Susanta K. et al. reported that mesoporous based heterogeneous catalyst, viz., Co(II) substituted hexagonal mesoporous aluminophosphate molecular sieves were very efficient and highly selective for the catalytic transfer hydrogenation (CTH).

Carbon aerogels are very porous materials with interesting properties such as: low density, high surface area, continuous open porosity and electrical conductivity. The incorporation of metal species into the carbon framework can modify the structure, conductivity and catalytic activity of the carbon aerogels. The mesoporous property of the metal-doped carbon aerogels can be used to carry out certain important organic transformations. High surface acidity of metal-doped carbon aerogels has been reported. Since the CTH process requires acidic sites, metal-doped carbon aerogels may be very well suited for this purpose. Hence, in this paper, we use nickel-doped carbon aerogels for CTH reactions. It has been found that the nickel-doped carbon aerogels exhibited excellent catalytic activity and stability for CTH of aromatic nitro compounds.

## Experimental

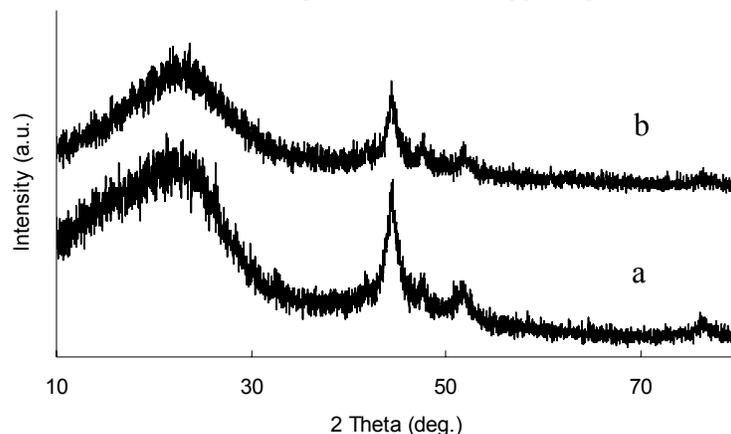
The preparation of Nickel-containing carbon aerogels reported is performed by sol-gel method which starts from a homogeneous solution containing nickel salt. This approach is not reliable for the homogeneous distribution of metal particles throughout carbon aerogels. Typically, 3.2 g resorcinol (R), 4.9 mL furfural, and 1.4 g nickel acetate tetrahydrate were dissolved by 32 mL ethanol, followed by curing for 7 days at 75 °C, drying at ambient pressure and room temperature for 4 days and then at 110 °C for about 5 h. Then the resulting dried sample was heated to 450 °C with a heating rate of 5 °C/min and kept at this temperature for 3 h in flowing N<sub>2</sub>. In order to investigate the effect of nickel content on the CTH catalytic activities, a series of nickel-doped carbon aerogels is obtained with nickel content from 2.5 wt% to 20 wt%. The obtained catalysts were named Ni-CAs.

The nickel loading was determined by an ICP apparatus (Optima 2000DV). X-ray diffraction (XRD) patterns were recorded on Rigaku D/MAX 2400 diffractometer equipped with a CuK $\alpha$  X-ray source operating at 40 kV and 50 mA. The as-made nickel-doped carbon aerogel catalysts were examined by scanning electron microscopy (SEM, KYKY-2800B)

All the reactions were carried out in a two-necked 50 mL round bottom flask under continuous stirring fitted with a reflux condenser. In a typical run, 100 mg of the catalyst was dispersed in a solution containing nitrobenzene (20 mmol), KOH pellets (20 mmol) and propan-2-ol (20 mL). The mixture was stirred and heated under reflux for 2-6 h in an oil bath. The products were analyzed at the regular intervals on the basis of their retention times using a Gas Chromatograph.

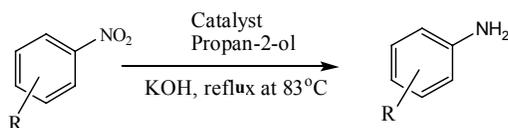
## Results and discussion

Figure 1a shows the XRD patterns of the 5% Ni-CAs. Two reflection signals at 44.6 (111) and 51° (200) are characteristic of metallic nickel with a fcc structure. The peaks are broad, suggesting a better metal dispersion.



**Figure 1.** XRD patterns of fresh 5% Ni-CAs catalyst (a) and the catalyst used for CTH of nitrobenzene after six cycles (b).

The catalysts were tested as catalysts for reduction of nitrobenzene to aniline with propan-2-ol. Scheme 1 depicts a typical catalytic transfer hydrogenation. During the reaction, the alcohol is oxidized to ketone and nitrobenzene is reduced to aniline. Aniline was the only product obtained under these conditions.



Scheme. 1

The effect of promoters is illustrated in table 1. KOH is better than NaOH because the dissociation of KOH in propan-2-ol is higher than that of NaOH. KOH can be act as a strong base. Therefore, the high yield of aniline is obtained when KOH is used as promoter.

**Table 1.** Effect of promoters on the reduction of nitrobenzene to aniline

Catalyst	Promoters	Substrate	Product	Time (h)	Yield (%)
20%Ni-CAs	NaOH	Nitrobenzene	Aniline	5	92
20%Ni CAs	KOH	Nitrobenzene	Aniline	3	98

Substrate (20 mmol), KOH pellets (20 mmol), propan-2-ol (20 ml) and catalyst (100 mg).

Table 2 summarizes the results of CTH of several aromatic nitro compounds over Ni-CAs with different nickel loading from 2.5 to 20 wt%. The compounds were reduced with excellent yields. It has been found that the nickel amount has little effect on the catalytic activity. Even when the nickel loading amount is low to 2.5%, the yield of aniline over the catalyst is still high. However, when the reduction of nitrobenzene was performed without a catalyst, the reaction failed completely. The observed high activity could be attributed to nickel and the acidic characteristics of the catalyst. Susanta et al. reported that the high activity of nitrobenzene CTH was accounted for by the presence of the Co (II) in the aluminophosphate framework

and by the acidic characteristics of the catalyst. Interestingly, we found that metal nickel can work for it. And the catalyst can be comparable with the references.

**Table 2.** Reduction of various nitro aromatics to anilines on Ni-CAs catalysts with different nickel loading amount.

Catalyst	Substrate	Product	Yield (%)	Time (h)
2.5%Ni-CAs	Nitrobenzene	Aniline	83	2
5%Ni-CAs	Nitrobenzene	Aniline	85	2
10%Ni-CAs	Nitrobenzene	Aniline	88	2
20%Ni-CAs	Nitrobenzene	Aniline	96	2
5%Ni-CAs	2-Chloronitrobenzene	2-Chloroaniline	89	2
10%Ni-CAs	2-Chloronitrobenzene	2-Chloroaniline	100	2
20%Ni-CAs	2-Chloronitrobenzene	2-Chloroaniline	96	2
5%Ni-CAs	4-Nitrotoluene	4-Toluidine	85	4
20%Ni-CAs	4-Nitrotoluene	4-Toluidine	83	4
La <sub>0.8</sub> Sr <sub>0.2</sub> FeO <sub>3</sub> <sup>[1]</sup>	Nitrobenzene	Aniline	92	3
La <sub>0.8</sub> Sr <sub>0.2</sub> FeO <sub>3</sub> <sup>[1]</sup>	2-Chloronitrobenzen	2-Chloroaniline	85	6
4.3%NiMCM-41 <sup>[2]</sup>	Nitrobenzene	Aniline	93	4
4.3%NiMCM-41 <sup>[2]</sup>	2-Chloronitrobenzen	2-Chloroaniline	85	5
4.3%NiMCM-41 <sup>[2]</sup>	4-Nitrotoluene	4-Toluidine	80	4.5

Substrate (20 mmol), KOH pellets (20 mmol), propan-2-ol (20 ml) and catalyst (100 mg), while La<sub>0.8</sub>Sr<sub>0.2</sub>FeO<sub>3</sub> is 150mg.

[1] Amrita S. Kulkarni, Radha V. Jayaram, 2003, *Applied Catalysis A: General*, 252: 225–230.

[2] Susanta K. Mohapatra, Sachin U. Sonavane, Radha V. Jayaram, Parasuraman Selvam, 2002, *Organic letters*, 4(24): 4297-4300.

The catalyst was also tested for its reusability. The results are listed in table 3. Interestingly, the yield was practically unaffected during up to six cycles. The XRD of the spent catalyst revealed no structural changes, as shown in Figure 1b. The catalyst can be conveniently separated by an applied magnet.

Table 3. The reusability of the catalyst.

Catalyst	Substrate	Product	Time (h)	Yield (%)	
				1st run	6st run
5%Ni-CAs	Nitrobenzene	Aniline	3	93	93
5%Ni-CAs	2-Chloronitrobenzene	2-Chloroaniline	3	91	91
4.3%NiMCM-41 <sup>[2]</sup>	Nitrobenzene	Aniline	4	93	92
La <sub>0.8</sub> Sr <sub>0.2</sub> FeO <sub>3</sub> <sup>[1]</sup>	Nitrobenzene	Aniline	3	92	92

Substrate (20 mmol), KOH pellets (20 mmol), propan-2-ol (20 ml) and catalyst (100 mg), while La<sub>0.8</sub>Sr<sub>0.2</sub>FeO<sub>3</sub> is 150mg.

### Conclusions

The Ni-CAs exhibits excellent catalytic activity for catalytic transfer hydrogenation in liquid phase. The catalyst was recyclable without any significant loss in activity.

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