Comparison of hydrogenation of nitrobenzene with chloronitrobenzenes on NiC composite catalyst

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Raney nickel was prepared by leaching out Al from a commercial Ni-Al (50/50) alloy by applying aqueous sodium hydroxide. Subsequently, methane was decomposed over Raney nickel in a tubular flow reactor at 395°C to deposit carbon and thereby NiC composite catalyst was obtained. The NiC catalyst was characterised by elemental analysis and scanning electron microscopy. Hydrogenation of nitrobenzene, *para*-chloronitrobenzene, and *ortho*-chloronitrobenzene was carried out on the NiC composite catalyst. Influence of solvent was also investigated. Methanol was found to be excellent medium for the reactions. Hydrogenation of nitrobenzene and *para*-chloronitrobenzene followed zero order kinetic pathways, but that of *ortho*-chloronitrobenzene followed first order kinetic pathway.

Keywords: Hydrogenation, NiC catalyst, chloronitrobenzene, solvent effect, kinetics.

Introduction

Aromatic amines and substituted aromatic amines receive great attention and find wide applications in chemical industries[1–6]. They are extensively used in the production of value added products in the industries like pigment, pesticide, herbicide, pharmaceutical sector, etc. They are also used as solvent and diluents in several industrial processes. The syntheses of aromatic amines and substituted aromatic amines are done by the hydrogenation of corresponding parent aromatic nitro compounds. Catalytic hydrogenation of aromatic nitro compounds to corresponding aromatic amines is always preferred process over the non-catalytic ones. This is because catalytic processes produce less amount of waste, and hence they are environmentally friendlier. Therefore, catalytic hydrogenation of nitrobenzene and substituted nitrobenzenes to corresponding anilines are of immense significance. Noble metal catalysts are highly active in effecting hydrogenation of organic substrates[1,2,7,8]. However, cost of catalyst may become critical. Hence, cheap metal catalyst like Ni may be a better choice provided the catalyst activity and product selectivity are acceptable[4,9,10]. Product selectivity is always a critical issue. Even though properties of catalysts play lead role in shaping reaction rate and product selectivity, reaction medium also significantly influences reaction route and thereby catalytic activity and product distribution. Extent of adsorption of substrate molecules on the catalytic surface, which likely varies with substrate, may define the reaction pathway and thereby reaction rate and product selectivity. Studies on direct comparison of hydrogenation of nitrobenzene and chloronitrobenzenes are rare. Also, studies on the influence of solvent on the said reaction are scanty[5,11]. Comparative studies on the hydrogenation of nitrobenzene, *para*-chloronitrobenzene, and *ortho*-chloronitrobenzene on NiC composite catalyst was assessed by employing methanol, ethanol, ethyl acetate, cyclohexane and toluene as solvents in the present study.

Experimental

Raney nickel (RNi) was prepared by leaching out Al from a commercial Ni-Al (50/50) alloy with concentrated NaOH solution at room temperature for 2 h and subsequent thorough washing with distilled water followed by ethanol. The RNi was placed in a tubular reactor and dried under N_2 at 85°C for 4 h. Methane was then decomposed over the RNi

at 395°C in order to deposit carbon[9,10]. Thus the NiC composite catalyst was synthesized. The reactor was subsequently cooled to room temperature under N_2. The catalyst was collected and stored in capped bottle under air.

Nickel content in the catalyst was determined by elemental analysis, atomic emission spectroscopy (AES). Scanning electron microscopy (SEM) analysis of the catalyst was carried out using an electron beam of 20 kV to assess the surface morphology.

Catalytic hydrogenation of nitrobenzene, *para*-chloronitrobenzene, and *ortho*-chloronitrobenzene was performed in a stainless steel batch reactor. Substrate/catalyst ratio was taken as 20. The reaction runs were executed under 1.5 MPa of H_2 at 120°C. Influence of solvent was assessed by employing five solvents – methanol, ethanol, ethyl acetate, cyclohexane, and toluene. In a typical experiment, calculated amount of catalyst, solvent, and substrate were put into the reactor and purged 4 times with H_2. The reactor was then heated to reaction temperature at a heating ramp of 25°C min^{-1} under 0.02 MPa H_2. Finally, the H_2 pressure was adjusted to reaction pressure and the reaction was commenced by initiating stirring. The progression of reaction was evaluated by collecting minute amount of liquid samples periodically and examining chromatographically; the gas chromatograph was equipped with flame ionization detector. Chromatographic peaks were identified and standardized by injecting known samples – nitrobenzene (NB), *para*-chloronitrobenzene (*p*-CNB), *ortho*-chloronitrobenzene (*o*-CNB), aniline (AN), *para*-chloroaniline (*p*-CAN), and *ortho*-chloroaniline (*o*-CAN).

Results and discussion

The catalyst was examined by AES to ordain the amount of nickel. The content of Ni (wt%) in the catalyst was found to be 79.6%. Morphology of the catalyst surface was assessed by scanning electron microscopy (SEM). Micrograph of the catalyst is shown in Fig. 1; micrograph of the parent RNi is also included for comparison.

It is clear from the micrographs that the NiC catalyst possess surface morphology that is quite different than the parent RNi. Carbon deposition is clearly visible on the surface of the NiC catalyst. Earlier XRD and XPS studies of similar
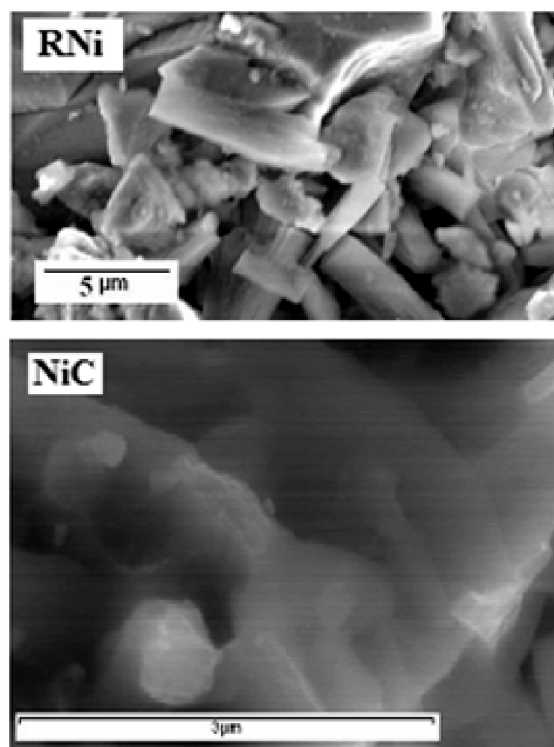

Fig. 1. SEM photographs of NiC and parent RNi catalyst.

NiC composite catalysts revealed that Ni remains in zero valent metallic form with a very thin superficial oxide layer[4,6,9,10]. Carbon perform the role of stabilizer and keep Ni in metallic form (zero valent).

Catalytic hydrogenation of nitrobenzene and chloronitrobenzenes are of immense importance. Hydrogenation of NB, *p*-CNB, and *o*-CNB on NiC composite catalyst was assessed in five solvents. Table 1 displays the results of hydrogenation of NB, *p*-CNB and *o*-CNB carried out in the five solvents – methanol, ethanol, ethyl acetate, cyclohexane and toluene. As can be seen in the table, AN is the main product of NB hydrogenation, whereas the CNBs have produced mainly the corresponding CANs[10,12]. NB has lead exclusively to AN (>99%). Hydrogenation of *p*-CNB resulted in the formation of *p*-CAN with very high selectivity (98 – >99%); only some insignificant amount of AN was detected. However, considerable amount of AN has formed along with the major product *o*-CAN as the result of hydrogenation of *o*-CNB. Production of AN during the hydrogenation of CNBs was due to the side reaction, hydrodechlorination. There are two possible

routes to the production of AN[13]. One route is – hydrodechlorination of CNB to NB, followed by hydrogenation of NB to AN. The other route is – hydrogenation of CNB to CAN, followed by hydrodechlorination of CAN to AN.

Table 1. Influence of solvent on the performance of the NiC catalyst in the hydrogenation of NB, p-CNB, and o-CNB

Solvent	NB		
	R_i [mol (mol Ni)$^{-1}$ min^{-1}]	C_{2h} (%)	S_{AN} (%)
Methanol	0.173	90	> 99
Ethanol	0.129	67	> 99
Ethyl acetate	0.083	43	> 99
Cyclohexane	0.087	45	> 99
Toluene	0.079	41	> 99
	p-CNB		
	R_i [mol (mol Ni)$^{-1}$ min^{-1}]	C_{2h} (%)	S_{p-CAN} (%) S_{AN} (%)
Methanol	0.120	50	> 99 —
Ethanol	0.089	37	> 99 —
Ethyl acetate	0.057	24	99 1
Cyclohexane	0.060	25	98 2
Toluene	0.055	23	99 1
	o-CNB		
	R_i [mol (mol Ni)$^{-1}$ min^{-1}]	C_{2h} (%)	S_{o-CAN} (%) S_{AN} (%)
Methanol	0.107	42	95 5
Ethanol	0.080	31	95 5
Ethyl acetate	0.051	20	94 6
Cyclohexane	0.054	21	93 7
Toluene	0.049	19	94 6

R_i: initial reaction rate, C_{2h}: conversion at 2 h, S_X: selectivity of X. Reaction conditions: 0.074 g catalyst (containing 1 mmol Ni), 20 mmol substrate (NB/p-CNB/o-CNB), 98 mL solvent (methanol), 120°C, 1.5 MPa H$_2$, 1200 rpm.

It is very clear from the results shown in Table 1 that NB is much more reactive catalytically than the CNBs towards hydrogenation. Catalytic reactivity follows the order: NB > p-CNB > o-CNB[10,13]. No doubt, the presence of Cl diminishes the hydrogenation reactivity of the -NO$_2$ group. Catalytic hydrogenation is preceded by the adsorption of the substrate molecule through the reducible group (in this case -NO$_2$ group). Adsorption of NB through -NO$_2$ group is hassle-free because of absence of any steric hindrance, and thus facile.

Similarly, adsorption of p-CNB also seems to be hassle-free and facile since the Cl is far from the -NO$_2$ group. In spite of that, catalytic reactivity of p-CNB is considerably less than NB. This clearly indicates that Cl inherently retard reactivity of CNB towards hydrogenation at the -NO$_2$ group, irrespective of adsorption. However, the situation with o-CNB is different. In o-CNB, proximity of Cl to the -NO$_2$ group renders steric hindrance towards the adsorption of o-CNB through the -NO$_2$ group. Consequently, extent of adsorption of o-CNB through the -NO$_2$ group diminishes; as a result, catalytic hydrogenation reactivity of o-CNB retarded further. Thus, hydrogenation reactivity of o-CNB is less than that of p-CNB. In addition, proximity of Cl of adsorbed o-CNB (through the -NO$_2$ group) to the catalytic surface and thus interaction of Cl with the catalyst surface induce hydrodechlorination to some extent; subsequent hydrogenation of -NO$_2$ group results in AN.

Among the solvents used, methanol offered best results. Catalytic reactivity of the substrates, even of o-CNB, in methanol medium is acceptably high. Product selectivity is also excellent. However, ethyl acetate, cyclohexane and toluene appears to be poor as solvent for the title reaction. Earlier studies also recommended short chain alcohols, particularly methanol as solvent for this type of catalytic hydrogenation[1–3,5,8,12].
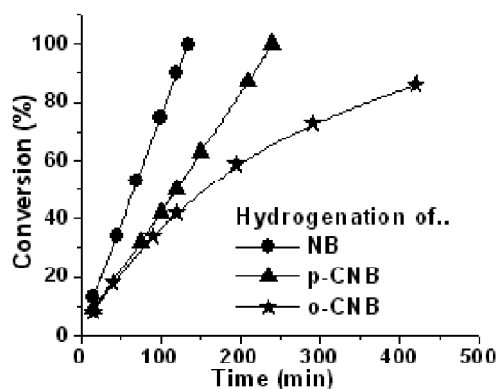
Fig. 2 shows the conversion profiles of NB, p-CNB, and

Fig. 2. Conversion profiles of hydrogenation of NB, p-CNB, and o-CNB with time on NiC catalyst. Reaction conditions: 0.074 g catalyst (containing 1 mmol Ni), 20 mmol substrate (NB/p-CNB/o-CNB), 98 mL solvent (methanol), 120°C, 1.5 MPa H$_2$, 1200 rpm.

o-CNB with time on the catalyst in methanol. NB rapidly converted completely in 135 min, followed by *p*-CNB (240 min). However, conversion of *o*-CNB was rather slow. 86% conversion was achieved in 420 min. Also, it can be seen that conversion of NB and *p*-CNB approach completion (100%) linearly; whereas conversion of *o*-CNB follows asymptotic path.

It seems that hydrogenation of NB and *p*-CNB follows zero order kinetic path, but hydrogenation of *o*-CNB follows first order kinetic path. To make the picture clearer, zero and first order kinetic plots were constructed for all the three substrates and shown in Fig. 3 and Fig. 4, respectively. If C_0 and C are concentrations of substrate at time t = 0 and t = t, then the zero order rate law can be given by

$$C = C_0 - kt \qquad (1)$$

And first order rate law can be given by

$$\ln C = \ln C_0 - kt \qquad (2)$$

Therefore, zero order kinetic plots were constructed by plotting C versus t (eq. (1)), and first order kinetic plots were constructed by plotting ln C vs. t (eq. (2)). Linearity of kinetic plots ascertains reactions with respective order.
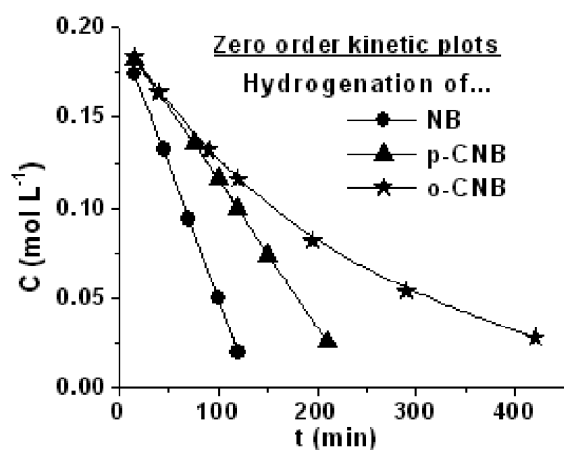

Fig. 3. Zero order kinetic plots of hydrogenation of NB, *p*-CNB, and *o*-CNB on NiC catalyst. Reaction conditions: same as given in Fig. 2.

Fig. 3 shows that the zero order kinetic plots of NB and *p*-CNB beautifully maintain linearity but that of *o*-CNB clearly deviates from linearity. The results admittedly establish that
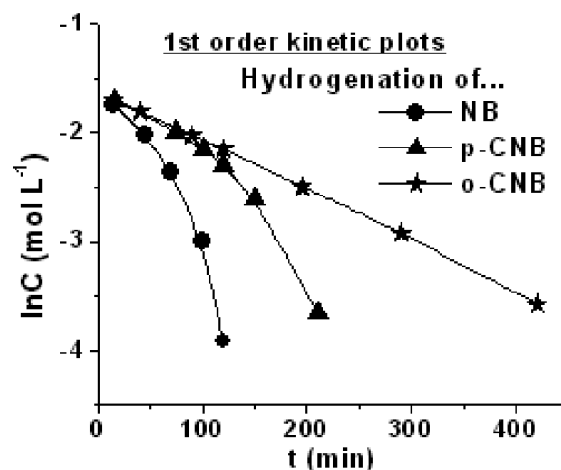

Fig. 4. First order kinetic plots of hydrogenation of NB, *p*-CNB, and *o*-CNB on NiC catalyst. Reaction conditions: same as given in Fig. 2.

hydrogenation of NB and *p*-CNB follows zero order kinetic pathways with respect to the substrates. On the other hand, Fig. 4 shows that first order kinetic plot of only *o*-CNB maintains linearity, but that of NB and *p*-CNB not. Hence, it is obvious that hydrogenation of *o*-CNB follows first order kinetic pathway with respect to the substrate.

Adsorption of NB and *p*-CNB on the catalyst surface is hassle-free and thus strong; consequently, the surface remains saturated with respect to the substrates. Hence, the reaction velocity becomes independent of substrate concentration in the solution; and the reaction becomes zero order with respect to the substrate. On the other hand, adsorption of *o*-CNB on the catalyst surface is disturbingly interfered by the Cl, positioned close to the $-NO_2$ group. Consequently, the adsorption of *o*-CNB becomes weak and thus the surface remains unsaturated with respect to *o*-CNB. Increase in concentration of *o*-CNB in the solution phase increases extent of adsorption of *o*-CNB on the surface; thereby increases the reaction velocity, and the reaction becomes first order with respect to the substrate.

Conclusions

Methanol was found to be the best among the five solvents (methanol, ethanol, ethyl acetate, cyclohexane and toluene) employed in the hydrogenation of NB, *p*-CNB and *o*-CNB on NiC catalyst. Hydrogenation of NB and *p*-CNB fol-

lowed zero order kinetic pathways; on the other hand hydrogenation of *o*-CNB followed first order kinetic pathway on the NiC catalyst. The three substrates exhibited reactivity order as: NB > *p*-CNB > *o*-CNB.

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