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Nickel–alumina prepared by constant and varying pH method: Evaluation by hydrogen–oxygen chemisorption and aniline hydrogenation

S. Narayanan *, R. Unnikrishnan, V. Vishwanathan

Catalysis Section, Indian Institute of Chemical Technology, Hyderabad, India

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Abstract

Ni/Al_2O_3 catalysts with different weight percentages of nickel (10–50 wt.-%) were prepared by a co-precipitation method under constant and varying pH conditions. Bulk density, pore volume and surface area of the catalysts were measured. The catalysts were characterized by X-ray diffraction. Hydrogen and oxygen chemisorptions were used to measure the metal area, percentage reducibility and metal dispersion. The crystallite size, as calculated from adsorption measurements, is very high. This is explained as being due to poor dispersion. Aniline hydrogenation under vapour phase conditions over these catalysts was studied. Catalysts prepared by the constant pH method show higher activity compared to those prepared by the varying pH method, especially at low metal content. *N*-phenylcyclohexylamine is the major product. The mechanism of product selectivity under different experimental conditions is explained.

Keywords: Nickel–alumina; Preparation; Hydrogen–oxygen chemisorption; Aniline hydrogenation; *N*-phenylcyclohexylamine

1. Introduction

Supported nickel has been widely used as a catalyst for various industrial reactions such as hydrogenation of aromatic compounds, methanation of carbon monoxide, steam reforming of hydrocarbons and for the reductive amination of alcohols. The activity and selectivity of supported catalysts vary considerably from those of unsupported metal catalysts. In the case of a supported nickel system extensive studies [1–14] have been carried out to understand the role of supports, nickel–alumina ratios on metal–support interactions and the dispersion of the metal. The

* Corresponding author. Fax. (+91-40) 673387/673757.

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preparative conditions such as the pH of precipitation and the method of metal incorporation onto the support will influence the availability of the nickel for catalysis.

Supported nickel catalysts containing low metal loadings are usually prepared by the impregnation method. However, high nickel content catalysts are prepared by co-precipitation and deposition–precipitation.

In a series of publications [7–14] we have earlier discussed the influence of the support and the additive effects on the reducibility and dispersion of supported nickel catalysts. We have concluded that metal–support interaction is an integral part of a supported nickel catalyst, especially if the support is interactive, such as alumina, titania and zirconia. The interactive property of the support can be modified by calcination [7] and by the addition of lithium [9], barium [11], copper [10] and lanthanum [11]. The interacting ability of the support was thus modified so as to make more metal available on the surface for the hydrogenation reaction. This type of study is possible mainly on impregnated catalysts with low nickel loading. It is believed that the chances of interaction between the metal and support are higher when they are co-precipitated from a homogeneous solution. The concentration of the solution, the temperature and the pH of precipitation of the hydroxides will affect the chemistry of the interaction between the metal and the support. In the present investigation, we will report the preparation of nickel–alumina catalysts of varying concentration. Two methods of preparation were followed: (i) under constant pH, where the pH is maintained constant at a desired value; and (ii) by varying or raising the pH during the precipitation process. The physico-chemical properties of these catalysts are characterized. Hydrogen and oxygen chemisorption properties are compared. Aniline hydrogenation has been studied under vapour phase conditions to evaluate the catalytic properties.

2. Experimental

2.1. Preparation

Constant pH method

A series of Ni/Al_2O_3 catalysts with varying concentration of nickel (10–50 wt.-%) was prepared by co-precipitation at a constant pH of 8. The required volumes of 0.5 molar solutions of nickel nitrate and aluminium nitrate were mixed. A stoichiometric quantity of the precipitating agent, a sodium hydroxide solution, was prepared. Both the nitrate solutions and the sodium hydroxide solution were added simultaneously to a beaker containing distilled water. The addition of the solutions was controlled in such a way as to maintain the pH at 8. The contents of the beaker were continuously stirred. A green hydroxide precipitate was formed. The supernatant liquid was tested for the completion of the precipitation. The precipitate was aged in the mother liquor overnight at 353 K. The precipitate was

filtered and washed thoroughly until free of nitrates. The hydroxide was dried in an oven at 373 K overnight. The dried catalyst was calcined in air at 723 K for 15 h, the temperature was raised to the final value at 4 K per minute. The calcined sample was then reduced in a hydrogen flow (0.3 mol h^{-1}) at 723 K for 24 h. The reduction temperature was first raised to 503 K [15] at a heating rate of 4 K per minute and maintained there for an hour. It was further raised to 723 K at the same heating rate. After reduction, the sample was cooled to room temperature in hydrogen and passivated in a stream of nitrogen for 2 h. The same pre-treatment conditions were followed for all the Ni/Al_2O_3 samples.

Varying pH method

In a similar way, a series of Ni/Al_2O_3 catalysts with varying nickel concentration (10 to 50 wt.-%) was prepared by varying the pH. In this case a stoichiometric equivalent of sodium hydroxide solution was added dropwise to a mixture of nickel and aluminium nitrate solutions in a beaker. The addition was continued till the final pH of the solution reached 8. The remaining procedure was the same as in the case of the constant pH method.

2.2. Characterization

Nickel content of the calcined sample was estimated gravimetrically by dimethyl glyoxime (DMG) method following the procedure described in Vogel [16]. Pore volume and apparent bulk density of the calcined samples were calculated by conventional methods. BET surface areas of the samples were determined by using the Micromeritics Pulse Chemisorption Unit (model 2700).

X-ray diffraction (XRD) measurements of the calcined samples were measured with a Philips PW 1140 diffractometer with nickel-filtered Cu Kα radiation ($\lambda = 1.54$ Å)

2.3. Adsorption

Hydrogen and oxygen chemisorption studies on Ni/Al_2O_3 samples were carried out in an all-glass constant volume adsorption system. Ca. 0.3 g of the passivated catalyst sample was reduced in hydrogen atmosphere at 723 K for 2 h and evacuated to a pressure of 10^{-6} Torr (1 Torr = 133.3 Pa). The catalyst sample was cooled to room temperature and a hydrogen adsorption isotherm was measured. The same sample was heated to 673 K, degassed to give a pressure of 10^{-6} Torr and oxygen adsorption at 673 K was then carried out. The details of the experimental procedure are described in our earlier publication [7]. Metal area, extent of reduction, dispersion and crystallite size were calculated from the hydrogen and oxygen chemisorption data following the procedure described earlier [7].

2.4. Catalysis

A vapour phase aniline hydrogenation reaction was carried out in a vertical down-flow reactor. Ca. 1.0 g of the catalyst, in the form of small pellets of size 1000–1400 μm, was packed in a tubular reactor. The catalyst was reduced at 723 K in hydrogen for 2 h before the start of the experiment. Aniline was fed over the catalyst from a motor driven syringe at a fixed rate. The reaction temperature was varied from 473 to 623 K. The liquid products were collected and analyzed by a gas chromatograph using a SE-30 column in a programme mode from 353 K to 483 K at a rate of 10 K per minute. The products identified were cyclohexane (CH), cyclohexylamine (CHA), dicyclohexylamine (DCHA) and *N*-phenylcyclohexylamine (N-PCHA). For details see earlier publications [17,18].

3. Results and discussion

3.1. Physical properties

The physical properties of Ni/Al_2O_3 catalysts with varying nickel contents are plotted in Fig. 1. Bulk densities of constant pH method catalysts are lower than for

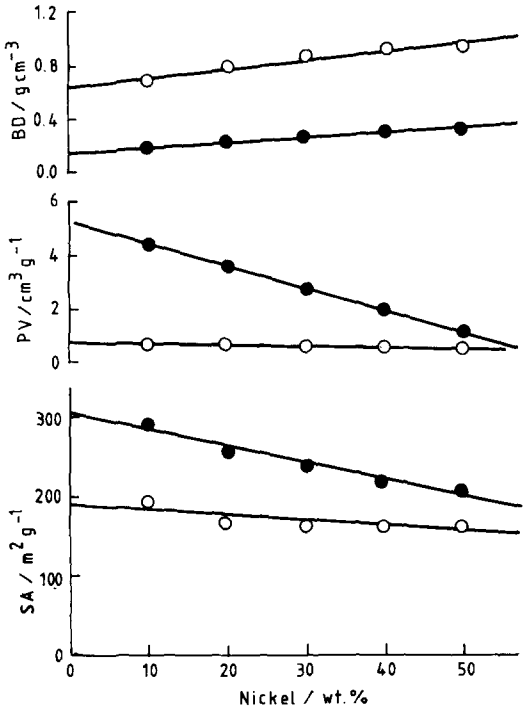

Fig. 1. Variation in surface area (SA), pore volume (PV) and bulk density (BD) with nickel content. (●) constant pH method, and (○) varying pH method.

the catalysts of the varying pH method. Pore volume and surface area of catalysts prepared by the constant pH method are higher than that for catalysts prepared by the varying pH method for all the metal content levels. The bulk density increases with metal content for both methods of preparation. Pore volume and surface area, on the other hand, decrease with metal content. The decrease is more significant for nickel alumina prepared by the constant pH method than for the varying pH method.

The X-ray diffraction patterns of the two catalysts show the presence of NiO. The NiO peak intensity increases with increase in nickel loading as expected. There is no evidence of bulk nickel aluminate formation.

3.2. Adsorption data

Hydrogen and oxygen adsorption data on Ni/Al_2O_3 samples are given in Table 1. Hydrogen adsorption per gram of catalyst increases with metal content. Oxygen uptake also increases with metal content. Metal surface areas calculated from hydrogen uptake show an increasing trend with increase in metal content. Even though the percentage of reduction is in the region of 60 to 90%, the percentage of dispersion is only between 5 and 8. In spite of the good reducibility, the dispersion of nickel is rather poor. Since dispersion is involved in the calculation of crystallite size, the calculated nickel crystallite size from hydrogen adsorption shows high values. Normally one would expect an increasing size of nickel crystallites with increasing metal content. In this case, the difference in the crystallite size with respect to metal content is not very significant. As a matter of fact, contrary to expectation, 10 wt.-% nickel shows a slightly higher crystallite size than 50 wt.-%. This anomaly arises probably out of poor dispersion and it may not really represent the metal crystallite size. Furthermore, the reasonable reducibility with poor dispersion indicates that nickel, though reduced, would be present in the bulk rather than on the surface and hence is not available for hydrogen chemisorption.

Hydrogen and oxygen uptake data as well as O/H ratio confirm the presence of bulk nickel rather than surface nickel. In spite of the co-precipitation technique

Table 1
Adsorption data on constant pH catalysts

Catalyst loading (wt.-%)	Weight of the catalyst W (g)	H_2 uptake X (μmol g_{cat}^{-1})	O_2 uptake (μmol g_{cat}^{-1})	MSA (m^2 g_{cat}^{-1})	Reduction f (%)	Dispersion D: 1.17 X/Wf	Crystallite size dnm = 101/%D	O_2/H_2
10	0.300	24	506	2	61	5	22	21
20	0.288	56	977	4.4	60	5	19	17
30	0.281	135	1843	11	78	7	15	14
40	0.250	188	2339	15	76	7	14	12
50	0.252	286	3250	22	87	8	13	11

MSA = metal surface area.

Table 2
Adsorption data on varying pH catalysts

Catalyst loading (wt.-%)	Weight of the catalyst (g)	H_2 uptake (μmol g_{cat}^{-1})	O_2 uptake (μmol g_{cat}^{-1})	MSA (m^2 g_{cat}^{-1})	Reduction (%)	Dispersion (%)	Crystallite size dnm	O_2/H_2
10	0.300	24	446	1.9	54	5	20	19
20	0.302	59	813	4.6	50	7	15	14
30	0.278	96	1429	7.5	60	6	17	15
40	0.250	179	2321	14.0	76	7	14	13
50	0.248	207	2976	16.2	79	6	17	14

used for the preparation of nickel–alumina catalyst, where one would expect an interaction between nickel and alumina resulting in nickel aluminate, the reducibility is reasonably good even for 10 wt.-% nickel. XRD does not indicate the presence of any bulk nickel aluminate. Only nickel oxide was identified in all the catalysts. The large crystallite size for these catalysts calculated from hydrogen adsorption may not actually reflect the size of the crystallite. The actual crystallite size may be much smaller than the calculated value. The differences in the crystallite size between the catalysts are attributed to the variation in dispersion between 5 and 8%.

For a comparison, the adsorption data of the catalyst made by the varying pH method are shown in Table 2. The variation in the percentage reduction, crystallite size and metal area are similar to the catalyst prepared by the constant pH method. The dispersion values are also not significantly different from the constant pH catalyst.

3.3. Catalysis

The influence of metal content on the vapour-phase aniline hydrogenation reaction is shown in Fig. 2. Aniline conversion generally increases with nickel content for the catalyst prepared by the constant pH method as well as by the varying pH method. It may also be noted that the catalyst prepared by the constant pH method gives conversion higher than the catalyst from the varying pH method at all metal loadings. However, the difference in the conversion between the two methods is larger at low nickel loadings than at high nickel loadings. For example, 10 wt.-% Ni/Al_2O_3 by the constant pH method gives conversion around 53% as compared to 10% on the catalyst prepared by the varying pH method having the same nickel loading. The difference in conversion between the two catalysts is 40% whereas the difference for the 50 wt.-% catalysts is only 15% (see Fig. 2). The constant pH method catalyst at low metal loading is more active than the catalyst from the varying pH method. This activity difference decreases as the metal content increases.

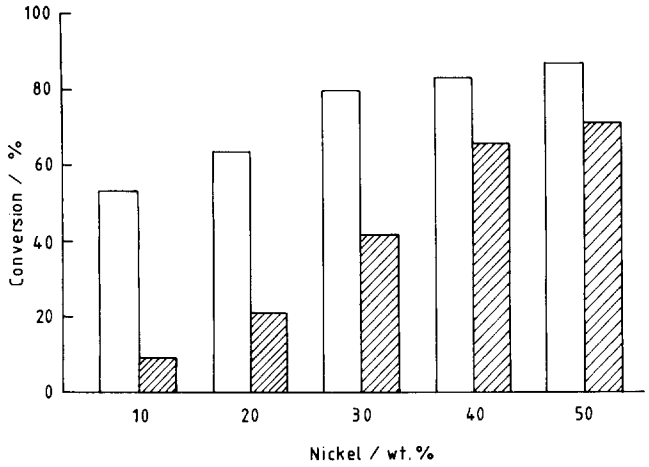

Fig. 2. Effect of nickel content on comparative aniline hydrogenation of catalysts by constant (open bar) and varying (hatched bar) pH methods. $T = 473$ K, H/aniline = 5.86 (mol/mol), 1/WHSW = 20.4 mol^{-1} g h.

In the case of supported nickel catalyst, we have observed that *N*-phenylcyclohexylamine (NPCHA) is a major product. Depending upon the conditions of the experiment and metal content, other products such as CHA, DCHA are also formed. Influence of metal loading (example 10 and 50 wt.-% Ni) on the product selectivity is shown in Fig. 3. At low nickel loading (10 wt.-%) both catalysts give primarily NPCHA. However, the constant pH method catalyst, in addition, gives some cyclohexylamine (CHA) and traces of dicyclohexylamine (DCHA). At 50 wt.-%, the

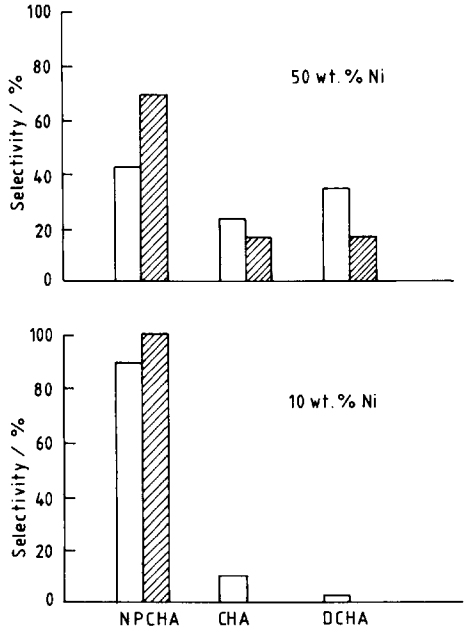

Fig. 3. Comparative product selectivity in aniline hydrogenation of catalysts by constant (open bar) and continuous (hatched bar) pH methods. Experimental conditions same as in Fig. 2.

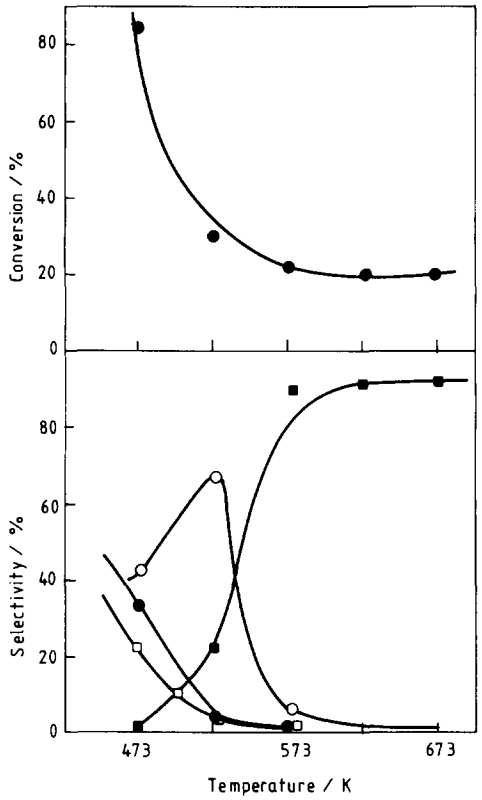

Fig. 4. Effect of temperature on aniline conversion and selectivity over 50 wt.-% nickel by the constant pH method. H/aniline = 5.86 (mol/mol); 1/WHSW = 20.4 mol^{-1} g h. (■) cyclohexane, (○) *N*-phenylcyclohexylamine, (●) dichyclohexylamine and (□) cyclohexylamine.

two catalysts show the formation of NPCHA, DCHA and CHA. Even though the constant pH method catalyst shows a higher conversion as compared to the varying pH method catalyst, there is not much difference as the selectivity of the products is concerned. The presence of all the three products at 50 wt.-% Ni and the absence of DCHA and CHA at 10 wt.-% in the case of the varying pH method catalysts suggests that with increase in metal concentration, the other two products viz., DCHA and CHA are formed at the expense of NPCHA. The observation on Ni/Al_2O_3 is in contrast to the Rh/Al_2O_3 system where CHA and DCHA are the two major products [17,18]. There was very little or no formation of NPCHA. This shows that the mechanism of aniline hydrogenation on the alumina supported nickel system seems to be different from that on Rh/Al_2O_3.

50 wt.-% nickel catalyst prepared by the constant pH method was chosen to study the effect of temperature and contact time (Fig. 4). The overall conversion decreases from 85 to 20% with increase of temperature from 473 to 673 K. The decrease in conversion is prominent between 473 and 573 K and then the conversion remains steady. This decrease in conversion with temperature may be due to the poisoning of the catalyst by ammonia which is formed by the deammoniation of

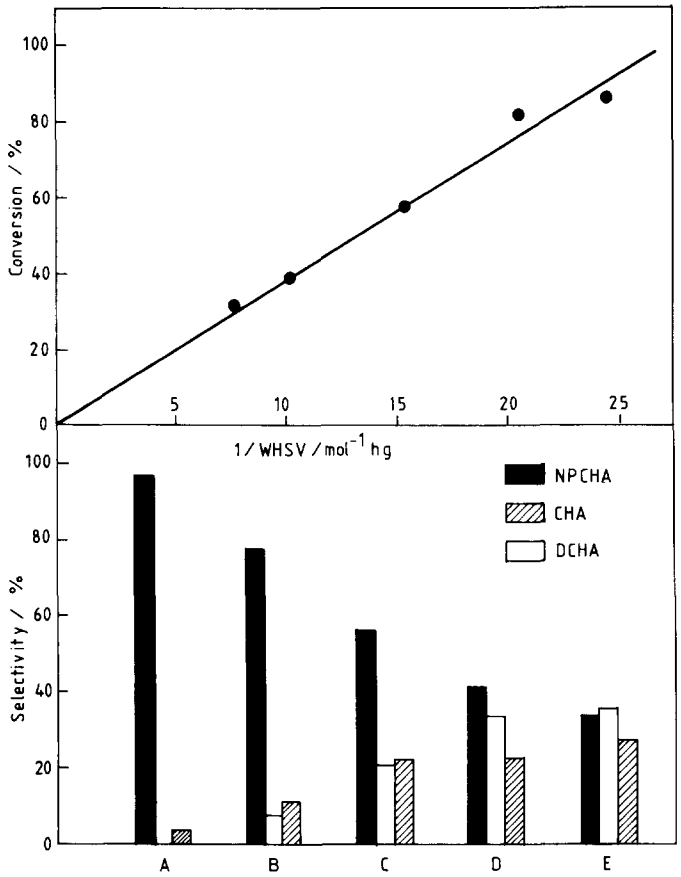

Fig. 5. Effect of contact time on aniline conversion and selectivity on 50 wt.-% nickel catalysts by the constant pH method. 1/WHSV (mol^{-1} g h): A = 7.6, B = 10.1, C = 15.2, D = 20.4, and E = 24.4; T = 473 K.

aniline at high temperature. The influence of temperature on product selectivity is also shown in Fig. 4. NPCHA goes through a maximum at 523 K. Cyclohexane (CH) formation increases sharply up to 573 K and then remains steady while the other two products viz., CHA and DCHA decrease with temperature up to 573 K and then disappear. The decrease of NPCHA and increase of cyclohexane at 523 K suggest the deammoniation of cyclohexylamine to give cyclohexane, which seems to be facile at high temperature.

The effect of contact time on product selectivity on 50 wt.-% nickel catalyst prepared by the constant pH method is shown in Fig. 5. As expected, the conversion increases with increase in contact time. At low contact time, NPCHA is the only major product formed. With increase in contact time, the DCHA and CHA are also formed. However, at high contact time, the selectivity for all the three products remains more or less the same. This suggests that the selectivity for *N*-phenylcyclohexylamine (NPCHA) is high at low contact time where the conversion is low. This may be explained by the fact that at conditions of low conversion, CHA that is formed as a primary product is easily converted into NPCHA by coupling with

the reactant aniline. This coupling reaction is feasible at temperatures above 443 K [19,20]. At high contact time, since the conversion is high, more CHA is formed as the primary product. However, not all of it could be converted into NPCHA due to the low availability of unreacted aniline at this condition. That is why we observe CHA also as a major product at high contact time of the feed.

From the foregoing studies, it may be presumed that aniline hydrogenation gives first cyclohexylamine (CHA) which can couple with aniline to form *N*-phenylcyclohexylamine (NPCHA) or the CHA formed can undergo dimerization to form DCHA. A high temperature favours deammoniation of cyclohexylamine to give cyclohexane. In the absence of cyclohexylamine, the secondary products viz., NPCHA and DCHA are not possible. Supported nickel catalyst seems to favour secondary amine formation more easily. On the other hand, Rh/Al_2O_3 catalyst favours cyclohexylamine formation.

4. Conclusion

Ni/Al_2O_3 catalysts have been prepared by two co-precipitation methods viz., (i) constant pH method and (ii) varying pH method. The former gives a catalyst with higher pore volume and surface area with low bulk density as compared to the latter at all metal levels. Hydrogen and oxygen adsorption data suggest that the catalysts are reasonably well reduced. However, the metal dispersion is very poor for both methods of preparation. Except for the morphological differences, there is hardly any difference in adsorption properties. The presence of nickel oxide is identified by XRD and it increases with increase in metal content. There is no evidence of bulk nickel aluminate. The crystallite size calculated by hydrogen chemisorption may not represent the real size of the nickel crystallites as the surface nickel availability for hydrogen adsorption is very low. Aniline hydrogenation gives predominantly *N*-phenylcyclohexylamine (NPCHA) on nickel catalysts. On low nickel content and low conversion levels, *N*-phenylcyclohexylamine is selectively formed. High temperature and high conversion favour the formation of other products like cyclohexylamine (CHA), dicyclohexylamine (DCHA), and cyclohexane (CH). The mechanism of product formation is discussed.

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