Liquid Phase Hydrogenation of Nitrobenzene over Nickel Supported on Titania

K. Joseph Antony RAJ¹, M. G. PRAKASH^{1,2}, R. MAHALAKSHMY², T. ELANGO VAN¹,
B. VISWANATHAN^{1,*}

¹National Centre for Catalysis Research, Indian Institute of Technology-Madras, Chennai 600036, India

²PG & Research Department of Chemistry, Thiagarajar College, Madurai 625009, India

Abstract: The catalytic hydrogenation of nitrobenzene to aniline employing nickel impregnated on rutile, anatase, and high surface area titania supports has been investigated. The nickel is present in elemental state as fcc phase on the catalyst as evidenced by X-ray diffraction results. The Ni crystallite size was found to be greater for Ni/anatase. The temperature-programmed reduction results suggest a greater metal-support interaction for Ni/rutile. The observed order of catalytic activity for the hydrogenation of nitrobenzene is Ni/rutile > Ni/anatase > Ni/TiO₂. A conversion of 99% was observed for Ni/rutile at 140 °C and hydrogen pressure of 1.96 MPa. Interestingly, aniline is the only product formed which demonstrates the catalytic hydrogenation of nitrobenzene proceeds with atom economy. Both Ni/rutile and Ni/anatase exhibited a better stability than Ni/TiO₂. The hydrogenation proceeds with the preferential adsorption of hydrogen on nickel present in the catalyst surface, possibly assisted by TiO_x species.

Key words: hydrogenation; nitrobenzene; nickel; titania; aniline

CLC number: O643

Document code: A

Received 2 March 2012. Accepted 25 April 2012.

*Corresponding author: Tel: +91-44-22574241; Fax: +91-44-22574202; E-mail: bvnathan@iitm.ac.in

This work was supported by Department of Science and Technology, Government of India.

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

Catalytic hydrogenation is a promising process as it does not generate acid effluents, and has little impact on environment. The Ni/Titania catalysts find wide applications in the hydrogenation of organic intermediates which are largely used in diverse industries. Titania offers itself as good catalyst support by virtue of strong metal support interaction (SMSI). The catalytic hydrogenation of nitrobenzene (NB) yields aniline (AN), a valuable intermediate for producing agricultural products, dyes, explosives, pharmaceuticals, and polyurethanes [1]. Conventional non-catalytic processes using either Bechamp reaction or sulphide reduction produce a large amount of waste [2]. Commercially, hydrogenation of NB is performed in the vapour phase over copper-based catalysts [3]. The metal supported catalysts such as Pd [4], Pt [5], Rh [6], and Re [7] have been studied for the reduction of nitro compounds. Holler et al. [8] showed a 100% yield of AN on Pd- and Pt-supported woven glass fibres at 50 °C and 7×10^5 Pa hydrogen pressure. Zhao et al. [9] reported a maximum NB conversion of 73% and 56% of AN selectivity on Pt/C at 35 °C and 4 MPa hydrogen pressure. However, their large-scale production has not materialized due to high costs. The other metals like Co [10], Zn [11], Sn [12], and Mo [13] have also been examined for the hydrogenation of nitroarenes. Junge et al. [14]

examined the iron-catalysed reduction of nitro compounds to the corresponding amines. The iron-based catalysts are more in the limelight of catalytic reduction of nitrobenzenes [15]. Li et al. [16] and Xu et al. [17] examined the hydrogenation of NB over the Ni based catalysts and showed a 100% of AN selectivity on mesoporous Ni-B at 90 °C and 1 MPa hydrogen pressure. Vilella et al. [18] reported the hydrogenation of NB over Pt/C catalysts with a lower selectivity for AN. Sun et al. [19] examined the NB reduction over the Pt-supported on multi-walled carbon nanotubes and showed a conversion and selectivity of 100% respectively for NB and AN at 60 °C and 4 MPa hydrogen pressure. Meng et al. [20] reported NB reduction over Ni/Al₂O₃ and showed a conversion of 13%–73% and 62%–99% of AN selectivity at 50 °C and 4 MPa hydrogen pressure. Due to the importance of selective reduction of aromatic nitro compounds, the study for improved methods remains an objective.

The present work aims to systematically study the liquid phase hydrogenation of NB into AN employing Ni-supported on various phases of titania namely, rutile, anatase, and high surface area. This paper also compares the activity of amorphous titania with the crystalline one in the NB hydrogenation. We have demonstrated the formation of AN

with atom economy. In addition, the catalyst stability is investigated.

1 Experimental

1.1 Chemicals

Rutile TiO_2 (Aldrich), anatase TiO_2 (Aldrich), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Qualigens), nitrobenzene (Qualigens), aniline (Qualigens), ethanol (Qualigens), and high surface area TiO_2 [21] were used without further purification. Water used as solvent in the study is doubly distilled.

1.2 Preparation of catalysts

The various forms of titania (anatase, rutile, and high surface area) support were impregnated with nickel by incipient wetness impregnation method using $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. In a typical synthesis, 2 g of anatase was mixed with 30 g of distilled water. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.48 g) was added to this mixture, and heated to 70–80 °C with stirring for 5–6 h. The slurry was filtered and dried at 100 °C for 12 h. The dried sample was calcined at 500 °C in flowing air for 2 h (Ni/anatase-500). Following the same procedure, nickel impregnated rutile support (Ni/rutile-500) and high surface area titania support (Ni/ TiO_2 -500) were prepared. The numbers in the abbreviations denote the temperature of calcination. The nickel contents of all the catalysts are 15 wt%, as determined by X-ray fluorescence (XRF) analysis. All the catalyst samples were reduced under hydrogen flow at 450 °C in a tubular reactor with a heating rate of 10 °C/min. The reduced samples were used in the NB hydrogenation study. A suffix of 450R is appended to the abbreviation to denote the reduced samples.

1.3 Characterization of Catalysts

Wide-angle X-ray diffraction (XRD) patterns for the calcined samples were obtained using a Rigaku Miniflex II, using $\text{Cu } K_\alpha$ radiation. The average crystallite size was calculated using Scherrer equation. The nickel contents of the catalysts were analyzed on Rigaku XRF spectrometer. Transmission electron microscopy (TEM) of the samples was performed on a CM 20 Phillips transmission electron microscope with an acceleration voltage of 200 KV. Sample preparation for TEM involved ultrasonic dispersion of the sample in methanol and placing a drop of the suspension on a carbon-coated copper grid and drying under room temperature in vacuum. Fourier transform infrared (FT-IR) spectra for the samples were recorded using a Bruker Tensor-27 instrument. The nitrogen adsorption-desorption isotherms were measured at –196 °C using a Micromeritics

ASAP 2020 surface area and porosity analyzer after the samples were degassed in vacuum at 300 °C for 3 h. Specific surface area was calculated from the BET plot. Pore volume was measured at the single point of $p/p_0 = 0.99$. Hydrogen temperature-programmed reduction (H_2 -TPR) was carried out in a quartz reactor using Micromeritics autochem II chemisorption analyzer.

1.4 Catalytic studies

Liquid phase NB hydrogenation was performed at 140 °C and 1.96 MPa of hydrogen pressure in a 100 ml Parr autoclave. Before the reaction, the autoclave was purged with nitrogen and thereafter pressurized with hydrogen. The autoclave was charged with 0.15 g of Ni-supported titania catalyst, 2 g of NB, and 40 ml of ethanol. The reaction was performed for 1 h while stirring the reaction mixture at 400 r/min. After each reaction, the autoclave was cooled to 30 °C. The reaction products were separated by filtration and analyzed on PerkinElmer Clarus-500 GC equipped with ZB-1 capillary column (30 m, stationary phase thickness 0.25 μm) and FID. A temperature programme of 10 °C/min from 50 to 250 °C was employed. The sample (0.1 μl) was injected with a split ratio set at 1:100. The reaction products were identified by GC-MS.

2 Results and discussion

2.1 XRD results

The XRD patterns of nickel impregnated on various phases of titania and calcined at 500 °C for 2 h are shown in Fig. 1. The Ni/ TiO_2 -500 sample showed reflections at 2θ of 25.3°, 38.3°, and 48.1° which are characteristic of anatase phase of titania. In addition, there is a reflection appearing

Fig. 1. XRD patterns of various phases of titania impregnated with nickel and calcined at 500 °C for 2 h. (1) Ni/ TiO_2 -500; (2) Ni/anatase-500; (3) Ni/rutile-500.

as a shoulder at 37.3° which is characteristic of NiO. This reflection becomes prominent in case of Ni/anatase-500 and Ni/rutile-500, with an additional reflection at 43.3° . The other reflections for Ni/anatase-500 at 25.3° , 37° , 37.8° , 38.6° , and 48.2° are due to anatase phase of titania. The reflections observed for Ni/rutile-500 at 27.5° , 36.2° , 39.4° , 41.3° , and 44.1° are characteristic of rutile phase of titania. The characteristic reflections due to nickel titanate at 2θ of 24.5° , 33.4° , and 49.7° were not observed in the samples, which shows that nickel titanate is not formed when calcined at 500°C .

Figure 2 displays the XRD patterns of nickel impregnated on various phases of titania and calcined at 500°C for 2 h and thereafter reduced at 450°C under flowing hydrogen for 4 h. The XRD patterns of all the samples showed a broad reflection at $2\theta = 44.5^\circ$, which is characteristic of *fcc* phase of Ni. The *hcp* phase of Ni was not formed for these samples because its characteristic reflection was not observed at $2\theta = 41.7^\circ$. The Ni/anatase-500 and Ni/rutile-500 samples exhibit reflections at 2θ of 37.3° and 43.3° for samples that are only calcined (Fig. 1), which are characteristic of *fcc* phase of NiO species (JCPDS 89-5881). These reflections are not seen in the reduced samples, which show the com-

plete reduction of NiO. The crystallite sizes for the reduced samples were calculated using Scherrer equation (Table 1). An evaluation of crystallite sizes of Ni shows nearly same crystallite sizes for Ni/TiO₂-500 (15.4 nm) and Ni/rutile-500 (16.4 nm), while it was greater for Ni/anatase-500 (23.3 nm). It is anticipated that anatase and rutile show similar crystallite sizes for Ni, however, the smaller crystallite size of Ni on rutile than anatase may be due to the overlapping of 2θ reflections at 44.5° for Ni and 44.2° for rutile.

The evaluation of XRD patterns of the reduced samples which are calcined at 500°C showed a decrease in crystallinity of 28% and 61% for anatase and rutile, respectively, while an enhancement in crystallinity (45%) was observed for high surface area titania. The XRD patterns suggest that all the Ni atoms on the surface of the three samples are in their elemental state, as discerned from the disappearance of NiO reflections and emergence of Ni⁰ reflection. The samples which are only calcined at 500°C (i.e. not reduced) did not show any change in crystallinity. However, the reduction of the samples showed a twofold decrease in crystallinity for Ni/rutile-500 than Ni/anatase-500. This demonstrates a greater interaction of Ni with rutile than with anatase.

2.2 DRIFT results

The DRIFT spectra obtained for the nickel supported titania samples are presented in Fig. 3. The DRIFT spectra of TiO₂ and NiO are also given for purpose of reference. In case of Ni/TiO₂-100 absorptions are observed in the region of $1250\text{--}1750\text{ cm}^{-1}$ which is essentially due to the presence of bulk NiO in the sample, as the spectrum is comparable with NiO (Fig. 3(4)). Similarly, Ni/TiO₂-500 also showed absorptions at 1354 and 1607 cm^{-1} characteristic of NiO. On the other hand, the XRD pattern obtained for Ni/TiO₂-500 did not have reflections due to NiO, which may be due to

Fig. 2. XRD patterns of nickel impregnated on various phases of titania and calcined at 500°C for 2 h and reduced at 450°C for 4 h. (1) Ni/TiO₂-500-450R; (2) Ni/anatase-500-450R; (3) Ni/rutile-500-450R.

Table 1 Specific surface area, pore volume, and crystallite size of Ni and titania

Sample	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Crystallite size	
			Ni	TiO ₂
Ni/TiO ₂ -500	44	0.13	—	10.0
Ni/TiO ₂ -500-450R	32	0.11	15.4	22.5
Ni/anatase-500	10	0.07	—	47.5
Ni/anatase-500-450R	13	0.08	23.3	46.0
Ni/rutile-500	10	0.06	—	49.3
Ni/rutile-500-450R	16	0.08	16.4	36.7

Fig. 3. DRIFT spectra of the nickel supported on high surface area TiO₂ calcined at various temperatures. (1) TiO₂; (2) Ni/TiO₂-100; (3) Ni/TiO₂-500; (4) NiO.

greater dispersion of NiO or the absence of NiO species on the surface of the sample. The DRIFT spectral profiles obtained for Ni/anatase and Ni/rutile samples were found to be similar to Ni/TiO₂ in the region of 1250–1750 cm⁻¹. It may be noted that, Ni/rutile showed a greater decrease in intensity than Ni/anatase when calcined at 500 °C suggesting an enhanced interaction of NiO.

2.3 TPD results

The TPD profiles of Ni/TiO₂, Ni/anatase, and Ni/rutile calcined at 500 °C are shown in Fig. 4. It was found that Ni/TiO₂-500 could be reduced at lower temperature than Ni/anatase-500 and Ni/rutile-500, and Ni/rutile displayed a broader TPR profile than Ni/TiO₂ and Ni/anatase. The Ni modified anatase and rutile showed three stage reduction with a peak reduction at 380 and 351 °C, respectively. A lower peak reduction temperature exhibited by rutile suggests a greater reducible activity of rutile than anatase. The observation of multiple stages of reduction for the Ni present in anatase and rutile is essentially attributed to the formation of nickel titanate. The TPR profiles of nickel supported on various phases of titania showed that Ni/TiO₂ could be fully reduced at 382 °C while Ni/anatase and Ni/rutile are fully reduced at 437 and 464 °C, respectively. A higher complete reduction temperature observed for Ni/rutile suggests a stronger metal-support interaction than Ni/anatase and Ni/TiO₂. It may be noted that the XRD patterns obtained for the samples calcined at 500 °C did not suggest the formation of nickel titanate. Nevertheless, the TPR profiles showed reduction in multiple stages for the Ni/anatase and Ni/rutile, suggesting the formation of nickel titanate.

Fig. 4. TPR profiles of Ni impregnated on various phases of titania calcined at 500 °C for 2 h. (1) Ni/TiO₂-500; (2) Ni/anatase-500; (3) Ni/rutile-500.

2.4 TEM results

Figure 5 shows TEM images with different magnifica-

Fig. 5. TEM images of Ni/TiO₂-500-450R with different magnifications.

tions for reduced Ni/TiO₂-500 sample. The sample is composed of many small particles which are nearly monodisperse with average particle diameters of 40 and 50 nm. This particle size is measured only for the titania support and particle size of Ni could not be measured because of the greater dispersion of Ni in the support. The sharp boundaries of the particles demonstrate crystalline characteristics of the sample. The images show spherical morphology for Ni/TiO₂ particles.

2.5 Specific surface area and pore volume

The specific surface area and pore volume of the nickel supported on TiO₂, anatase, and rutile calcined at 500 °C and thereafter reduced at 450 °C under flowing hydrogen are shown in Table 1. The specific surface area of the unmodified supports of TiO₂, anatase, and rutile were, respectively, 275, 12, and 11 m²/g. An inspection of the table reveals that the surface area of unmodified TiO₂ is greatly reduced on impregnation with Ni. In case of Ni/TiO₂-500, the specific surface area was found to decrease on reducing the sample. The decrease in the surface area could be due to aggregation of particles leading to lowering of porosity of the samples. On the other hand, there was a marginal increase in specific surface area for Ni/anatase and Ni/rutile on reduction. The specific surface area of the reduced samples follow the order Ni/TiO₂ > Ni/rutile > Ni/anatase. There was a decrease in pore volume with reduction for Ni/TiO₂ while it remains more or less the same with Ni/anatase and Ni/rutile. The Ni crystallite size, measured for the reduced samples, follows the order of Ni/anatase >

Ni/rutile > Ni/TiO₂. The crystallite size of TiO₂ particles of Ni/TiO₂-500 increased on reduction. The crystallite size of TiO₂ follows the order of Ni/rutile-500 > Ni/anatase-500 > Ni/TiO₂-500.

2.6 Effect of temperature

The effect of temperature on the conversion of NB has been examined on Ni impregnated on various phases of titania at 120–150 °C and at hydrogen pressure of 1.96 MPa (Fig. 6). Interestingly, the conversion of NB proceeded with atom economy to the exclusive formation of AN. An increase in conversion of NB with increasing temperature was observed. At 120 °C, the conversion was lower than 10% for all the samples. The conversion increased with temperature until 140 °C and the increase in conversion was steeper at 130 than at 140 °C. The conversion almost remained unchanged at 150 °C in comparison with 140 °C. The highest conversion of 99% was exhibited by Ni/rutile catalyst. As the conversion at 140 and 150 °C are comparable, further investigation was carried out only at 140 °C. The observed trend for NB conversion at the temperatures studied is Ni/rutile > Ni/anatase > Ni/TiO₂. The enhanced synergistic effect between rutile and Ni has a stronger influence on the catalytic activity of Ni/rutile than the other samples. The Ni/TiO₂ catalyst sample was found to possess lower activity than Ni/anatase and Ni/rutile. This could be due to the formation of Ti₂O₃ moieties in a facile manner in Ni/TiO₂ which may physically block the active nickel sites thereby altering the adsorptive properties of the Ni sites. Although the crystallite size of Ni supported on TiO₂ is smaller (15.4 nm) than on rutile (16.4 nm) and anatase (23.3 nm), Ni/anatase-500 and Ni/rutile-500 showed higher conversion than Ni/TiO₂-500. This could be due to higher concentration

Fig. 6. Effect of temperature on the conversion of nitrobenzene on Ni supported on various phases of titania. Reaction conditions: 15% Ni loading, 0.15 g catalyst, 1.96 MPa H₂ pressure, 400 r/min.

of nickel on the surface of anatase and rutile than on TiO₂ suggesting that they serve as effective supports for the preparation of reduction catalysts.

2.7 Effect of pressure

In the liquid phase hydrogenation, hydrogen pressure is a significantly important parameter, as hydrogen serves as one of the reactants. The effect of hydrogen pressure on the conversion of NB on Ni supported on various phases of titania at 140 °C is shown in Fig. 7. The conversion was found to increase with H₂ pressure up to 1.96 MPa and remains almost unchanged at 2.45 MPa. The observed order for the conversion of NB, irrespective of H₂ pressure, is Ni/rutile > Ni/anatase > Ni/TiO₂. A maximum conversion of 99% was exhibited by Ni/rutile at 1.96 MPa. As the conversion of NB tends to stabilize at 1.96 MPa, further experiments were performed at this hydrogen pressure only. The selectivity for AN is 100% at all hydrogen pressures for all the catalysts. The remarkable enhancement in conversion of NB with H₂ pressure illustrates the preferential adsorption of hydrogen on the surface of the catalyst over NB. Thus the adsorption of hydrogen on the catalyst surface seems to be a key first step in the hydrogenation of NB and thereby the rate of hydrogenation appears to depend only on the adsorption of hydrogen on the catalyst surface. The presence of NB in the solvent phase seems to lend support to this point.

Fig. 7. Effect of pressure on the conversion of nitrobenzene on Ni supported on various phases of titania. Reaction conditions: 15% Ni loading, 0.15 g catalyst, 140 °C, 400 r/min.

2.8 Effect of Ni loading

Nickel was supported on TiO₂, anatase, and rutile by conventional impregnation using an aqueous solution of Ni(NO₃)₂·6H₂O. The Ni content was varied from 5 to 20 wt%. Catalysts, after drying at 100 °C, were subjected to calcination at 500 °C in air and thereafter to reduction at 450 °C for 4 h in flowing hydrogen. Figure 8 shows the effect of

Fig. 8. Effect of nickel loading on the conversion of nitrobenzene on Ni supported on various phases of titania. Reaction conditions: 0.15 g catalyst, 140 °C, 1.96 MPa H₂ pressure, 400 r/min.

Ni loading on the conversion of NB. The experimental conditions used are: 140 °C, 1.96 MPa hydrogen pressure, and reaction duration of 1 h. The catalytic activity of the samples is found to increase with increasing Ni content for Ni/rutile and Ni/anatase up to 15% loading and levels off at 20% loading. Interestingly, Ni/TiO₂ displays an increase in the catalytic activity with Ni loading. The conversion was found to increase at 20% loading unlike Ni/rutile and Ni/anatase, and a conversion of about 80% could be achieved. The increase in conversion is attributed to the presence of more nickel active sites on the surface of the catalyst. The observed order for the conversion of NB for various Ni loading is Ni/rutile > Ni/anatase > Ni/TiO₂. The selectivity for AN was found to be 100% at all Ni loadings. As the highest possible conversion was reached at 15% Ni loading for Ni/rutile and Ni/anatase, all the experiments were carried out at 15% Ni loading.

2.9 Effect of catalyst amount

The amount of the catalyst was changed from 0.05 to 0.15 g in order to study its effect on the conversion of NB (Fig. 9). The experimental conditions employed were 140 °C, 1.96 MPa hydrogen pressure, 1 h. The conversion was

Fig. 9. Effect of quantity of catalyst on the conversion of nitrobenzene on Ni supported on various phases of titania. Reaction conditions: 15% Ni loading, 0.15 g catalyst, 140 °C, 1.96 MPa H₂ pressure, 400 r/min.

found to increase almost proportionately with increase in the catalyst amount for all the samples. The enhanced conversion with the amount of catalyst is attributed to improved the contact of the catalyst with reactants.

2.10 Catalyst stability

The conversion of NB with time was monitored by performing the reaction at 140 °C and 1.96 MPa hydrogen pressure (Fig. 10) with a view to measure the stability of the catalysts. The reaction was performed for 10 h. At every hour, the reaction effluent was decanted and analyzed on GC, while the autoclave containing spent catalyst was charged with fresh reactants and the reaction was continued. It was observed that the conversion decreased with time on stream by 3.4%, 5.8%, and 13.8%, respectively, for Ni/rutile-500, Ni/anatase-500 and Ni/TiO₂-500 at the end of 10 h. It may be noted that the drop in the conversion was not significant up to 5 h. The observed data shows that the activity is only marginally lost on Ni/rutile-500 and Ni/anatase-500 in comparison with Ni/TiO₂-500. The higher activity of Ni/rutile-500 could be due to the strong metal support interaction between Ni and rutile, arising from high surface enthalpy and unsatisfied charges on rutile. The electron density on Ni is altered as a result of electron transfer between Ni and rutile. The interaction between Ni and Ti³⁺ may generate negative charge on Ni atoms which may enhance the activity of Ni/rutile for the hydrogenation of NB. It is worth mentioning that AN was the exclusive product formed with time on stream for all the samples.

Fig. 10. Catalyst stability of nitrobenzene on Ni supported on various phases of titania. Reaction conditions: 15% Ni loading, 0.15 g catalyst, 140 °C, 1.96 MPa H₂ pressure, 400 r/min.

2.11 Hydrogenation of nitrobenzene

The hydrogenation of NB is anticipated to take place via the initial formation of nitrosobenzene, which subsequently reduced to phenylhydroxylamine. The phenylhydroxylamine is further reduced to form AN. The NB molecule possesses two reducible centers viz., N=O group and an aromatic ring

and in principle one could observe a mix of reduced products and the completely reduced product. The reduction of NB performed on Ni supported titania catalysts under different experimental conditions in this investigation clearly demonstrates the lone formation of AN. Interestingly, the selectivity for AN is 100% irrespective of the nature of titania phase and the extent of Ni loading. The hydrogenation of aromatic ring requires about 25 times higher energy (22.4 kJ/mol at 25 °C) than the hydrogenation of N=O group (−552.8 kJ/mol at 25 °C) in NB. Also, the hydrogenation of aromatic ring in NB requires the adsorption of benzene ring on the surface of the catalyst. It may be noted that on a polar support like TiO₂, the adsorption of C=C or benzene is less likely in comparison with the adsorption of N=O group.

The activity of various phases of titania is found to be different which shows that the strength of adsorption of N=O group or the concentration of nickel hydride on the surface is different on the various phases of titania. As described under effect of H₂ pressure section, hydrogen is adsorbed on the surface of the catalyst to form nickel hydrides. This activated H species may attack the N=O group of NB leading to AN formation. Alternatively, the partially reduced TiO_x species (with oxygen vacancies) present in interfaces are assumed to co-ordinate with the oxygen atom of the N=O group leading to the hydrogenation of the N=O bond.

The selectivity for AN is nearly same on all the catalysts. However the conversion of NB is halved on Ni/TiO₂ when compared with Ni/anatase and Ni/rutile. The dispersion of Ni supported on a high surface area titania is found to be greater than on anatase and rutile. It is worthy to note that the conversion of NB is increased with decreasing dispersion of Ni. The observed catalytic activity trend for these catalysts possibly suggests that a higher dispersion of Ni has detrimental effect. This explains the significance of surface concentration of Ni atoms in determining the conversion of NB on titania.

3 Conclusions

The catalytic activity of Ni impregnated on various phases of titania for the reduction of NB has been evaluated. The XRD profiles of the reduced catalyst samples show the presence of fcc phase Ni on the surface. A lower peak reduction temperature in TPR for Ni/rutile suggests its greater reducible property. A higher complete reduction temperature for Ni/rutile points out a strong metal-support interaction. It was observed that the surface area of unmodified titania is greatly reduced on impregnation with Ni and the surface area of the reduced catalyst samples follow the order of Ni/TiO₂ > Ni/rutile > Ni/anatase. The conversion was found to increase with temperature and reaches a plateau at higher temperatures. The observed order at all reaction temperatures was

Ni/rutile > Ni/anatase > Ni/TiO₂. Interestingly, AN is the only product formed which suggests the hydrogenation of NB proceeds with atom economy. The conversion was found to be optimum at 140 °C, 1.96 MPa H₂ pressure, and 15% Ni loading. A higher Ni dispersion seems to have a detrimental effect on the conversion. An increase in conversion with H₂ pressure suggests preferential adsorption of H₂ on Ni present on the catalytic surface, forming Ni-H species. The hydrogenation of nitrobenzene may also be facilitated by the oxygen-deficient TiO_x species present in the catalyst through interaction with N=O group. The conversion dropped only marginally when the experiment was run for 10 h in case of Ni/rutile and Ni/anatase suggesting a good catalytic stability.

References

- 1 Travis A S. In Rappoport Z ed. *The Chemistry of Functional Groups: The Chemistry of Anilines*. Weinheim: Wiley-VCH, 2007. 715
- 2 Blaser H U, Siegrist U, Studer M. In: Sheldon R A ed. *Fine Chemicals Through Heterogeneous Catalysis*. Weinheim: van Bakkum, Wiley-VCH, 2001. 389
- 3 Nishimura S ed. *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*. Weinheim: Wiley-VCH, 2001. 332
- 4 Rahaim R J, Maleczka R E. *Org Lett*, 2005, **7**: 5087
- 5 Motoyama Y, Kamo K, Nagashima H. *Org Lett*, 2009, **11**: 1345
- 6 Brinkman H R, Miles W H, Hilborn M D, Smith M C. *Synth Commun*, 1996, **26**: 973
- 7 de Noronha R G, Romao C C, Fernandes A C. *J Org Chem*, 2009, **74**: 6960
- 8 Holler V, Wegricht D, Yuranov I, Kiwi-Minsker L, Renken A. *Chem Eng Technol*, 2000, **23**: 251
- 9 Zhao F, Ikushima Y, Arai M. *J Catal*, 2004, **224**: 479
- 10 Lee H Y, An M. *Bull Korean Chem Soc*, 2004, **25**: 1717
- 11 Khan F A, Sudheer C. *Tetrahedron Lett*, 2009, **59**: 3394
- 12 Zhou Y, Li J, Liu H, Zhao L, Jiang H. *Tetrahedron Lett*, 2006, **47**: 8511
- 13 Iyer S, Kulkarni G M. *Synth Commun*, 2004, **34**: 721
- 14 Junge K, Wendt B, Shaikh N, Beller M. *Chem Commun*, 2010, **46**: 1769
- 15 Enthaler S, Junge K, Beller M. *Angew Chem, Int Ed*, 2008, **47**: 3317
- 16 Li H, Zhao Q, Wan Y, Dai W, Qiao M. *J Catal* 2006, **244**: 251
- 17 Xu R, Xie T, Zhao Y G, Li Y D. *Nanotechnology*, 2007, **18**: 55602
- 18 Vilella I M J, de Miguel S R, Scelza O A. *Chem Eng J*, 2005, **114**: 33
- 19 Sun Z, Zhao Y, Xie Y, Tao R, Zhang H, Huang C, Liu Z. *Green Chem*, 2010, **12**: 1007
- 20 Meng X, Cheng H, Akiyama Y, Hao Y, Qiao W, Yu Y, Zhao F, Fujita S, Arai M. *J Catal*, 2009, **264**: 1
- 21 Raj K J A, Ramaswamy A V, Viswanathan B. *J Phys Chem C*, 2009, **113**: 13750