# Reductive Amination of 2-Propanol to Monoisopropylamine Over $Ni/\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalysts

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Abstract Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with different nickel loadings (4–27 wt%) were used for the synthesis of monoisopropylamine by the reductive amination of 2-propanol in the presence of hydrogen and ammonia. H<sub>2</sub>chemisorption analysis indicated that the highly reduced nickel metal surface area could be correlated with the enhancement of the 2-propanol conversion. During the reaction, the catalyst was progressively deactivated in the absence of hydrogen but its initial activity was completely recovered by re-exposure to the feed containing hydrogen. The deactivation was due to the formation of surface nickel nitride and excess hydrogen hindered the phase transition of the nickel metal to the corresponding nitride, ultimately preventing deactivation.

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#### **1** Introduction

Alkyl amines are an important class of compounds, which find uses as intermediates in a variety of applications including the synthesis of herbicides, insecticides, pharmaceutical chemicals, corrosion inhibitors, plastics, and rubber chemicals. One of the most widely practiced routes is the reaction of alcohol with ammonia at relatively high operating temperature and pressure [1-3]. The reductive amination of aliphatic alcohols proceeds in the presence of hydrogenation-dehydrogenation catalysts such as nickel, cobalt, copper, and solid acids [4-7]. The metal-catalyzed synthesis of monoisopropylamine (MIPA) from 2-propanol includes the dehydrogenation of the alcohol to acetone; condensation with ammonia to form an imine, and hydrogenation to MIPA. Each intermediate and the product amine can take part in various side reactions such as condensation, decarbonylation, disproportionation, and hydrogenolysis. Proper reaction conditions for the amination reaction can result in a primary amine as the desired product in high yield [8, 9]. Other methods of reductive amination have also been developed, e.g., by Cho and Kang [10] and Johansson et al. [11], in which sodium borohydride and borane-dimethyl sulphide complex were used as reducing agents. However, these processes are only convenient on the laboratory scale due to the high cost of the reducing agents. Also, MIPA is industrially prepared by the amination of acetone with ammonia using heterogeneous catalysts [12].

Nickel-based catalysts have received extensive attention because they are more easily available and less expensive

than are noble metals; further, their properties are well suited for applications in reforming, hydrogenation, and hydrotreating reactions [13–16]. Nouwen et al. [12] claimed that the activity of supported nickel catalysts was very high in the amination of acetone to produce MIPA. However, the amination reaction of acetone was carried out at very high pressure (35-200 bar). In addition, Vedage et al. [17] demonstrated the reductive amination of 2-propanol over zeolite supported potassium-cobalt catalysts at high pressures ( $\sim 17$  bar) in an autoclave. However, in batch-type reductive amination, industrial separation and recycling of catalyst and by-product are difficult. The reductive amination of alcohols has been widely investigated. However, most of the studies focused on methanol, ethanol, and cyclohexanol [18-20]. There are few reports regarding the influence of reaction parameters on the reductive amination of 2-propanol. Here, we describe the catalytic properties of Ni/y-Al<sub>2</sub>O<sub>3</sub> catalysts for the reductive amination of 2-propanol in the presence of ammonia and hydrogen at atmospheric pressure. The effects of the reaction temperature, the partial pressures of ammonia and hydrogen, and space velocity were examined. 2-Propanol conversions and selectivities for MIPA, acetone, diisopropylamine (DIPA), and diisopropyl ether (DIPE) when using Ni/y-Al<sub>2</sub>O<sub>3</sub> catalysts with different nickel loadings were compared. The calcined and reduced catalysts were extensively characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), H<sub>2</sub>-temperatureprogrammed reduction (H<sub>2</sub>-TPR), N<sub>2</sub>-sorption, and H<sub>2</sub>chemisorption.

## 2 Experimental

#### 2.1 Catalyst Preparation

Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with different nickel loadings from 4 to 27 wt% were prepared by incipient wetness impregnation method with Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich) solution on a commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Procatalyse, 194 m<sup>2</sup> g<sup>-1</sup>). The impregnated catalyst samples were dried at 100 °C for 24 h and subsequently calcined at 500 °C for 2 h in a muffle furnace under flowing air (200 cm<sup>3</sup> min<sup>-1</sup>). The final catalysts are denoted as Ni(x)/Al<sub>2</sub>O<sub>3</sub>, where x (x = 4, 11, 17, 23 and 27) represents the weight percent of Ni metal.

#### 2.2 Catalyst Characterization

The surface area, pore volume, and pore size distribution were determined by N<sub>2</sub> physisorption at -196 °C using a Micromeritics ASAP 2020 apparatus. The samples were degassed at 250 °C for 6 h. The surface area was calculated in the relative pressure range of 0.05–0.2. The pore size

distribution was calculated from the desorption branch using the Barrett–Joyner–Halenda (BJH) formula. The XRD patterns were obtained on a Rigaku diffractometer using Cu K $\alpha$  radiation operating at 40 kV and 50 mA with a scanning rate of 2° min<sup>-1</sup> from 30 to 80°. The particle size of metallic Ni was determined from the broadening of the diffraction peak of the Ni (111) plane using Scherrer's equation. The Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were also characterized by TEM (TECNAI G2 instrument). The binding energies of nickel and nitrogen were determined by X-ray photoelectron spectroscopy (XPS) with a VG ESCALAB 210 spectrometer employing Mg K $\alpha$  X-ray source (1253.6 eV). All the binding energies are referenced to the C 1s from adventitious carbon.

Micromeritics AutoChem 2920 instrument was used to perform H<sub>2</sub>-TPR experiments in order to determine the reducibility of nickel oxides on NiO/y-Al<sub>2</sub>O<sub>3</sub> catalysts. Prior to the TPR studies, each catalyst was pretreated under flowing helium (50 cm<sup>3</sup> min<sup>-1</sup>) at 400 °C for 1 h. After pretreatment, the sample was cooled to ambient temperature. Then, the reducing gas containing 5 %  $H_2$  in argon as the diluent gas was passed over the samples at a flow rate of 50 cm<sup>3</sup> min<sup>-1</sup> with heating at the rate of 10 °C min<sup>-1</sup> up to 900 °C; the temperature was then kept constant for 0.5 h. The effluent gas was analyzed by a Balzers QMS200 quadrupole mass spectrometer (QMS). To identify the species adsorbed over the 17 wt% Ni/y-Al<sub>2</sub>O<sub>3</sub> catalyst and to investigate the deactivation phenomenon during the amination reaction, H2-TPR experiments were also carried out under flowing 5 % H<sub>2</sub>/Ar (50 cm<sup>3</sup> min<sup>-1</sup>) from 50 to 400 °C with 10 °C min<sup>-1</sup> heating. The evolution of  $NH_3$ (m/e = 17) and H<sub>2</sub> (m/e = 2) were recorded during H<sub>2</sub>-TPR. Prior to the H<sub>2</sub>-TPR experiment, the sample was reduced under flowing H<sub>2</sub> (50 cm<sup>3</sup> min<sup>-1</sup>) at 600 °C for 3 h; the reduced Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts were successively pretreated under flowing 20 % NH<sub>3</sub>/N<sub>2</sub> (50 cm<sup>3</sup> min<sup>-1</sup>) or 4 % NH<sub>3</sub>/16 % H<sub>2</sub>/N<sub>2</sub> (50 cm<sup>3</sup> min<sup>-1</sup>) at 170 °C for 12 h and then cooled to 50 °C.

The metal dispersion and surface area were measured by  $H_2$  chemisorption at 100 °C using a Micrometrics ASAP2020C instrument equipped with a high vacuum pump providing a vacuum of  $10^{-6}$  Torr. Prior to the adsorption experiments, the sample (0.3 g) was reduced at 600 °C for 3 h under flowing  $H_2$  (50 cm<sup>3</sup> min<sup>-1</sup>).  $H_2$ -chemisorption uptakes were separately determined as the difference between two successive measured isotherms. The metal dispersion and nickel metal surface area were calculated by assuming that H/Ni stoichiometry was one. The reduction degree was determined by the O<sub>2</sub> titration method and the particle size of the nickel metal was then corrected by considering the reduction degree. The reduction degree was determined by the following equation: [the amount of O<sub>2</sub> consumption]/[the theoretical amount of H<sub>2</sub> consumption]

with the assumption of fully reduced nickel oxides (mmol  $H_2$ ; NiO +  $H_2 \rightarrow Ni + 2H^+$ )] × 100 [21, 22].

## 2.3 Catalytic Activity Tests

All catalytic experiments were performed at atmospheric pressure under continuous flow in a fixed-bed microreactor. To establish a standard operating procedure, prior to testing, the catalysts were activated at 600 °C for 3 h under flowing  $H_2$  (50 cm<sup>3</sup> min<sup>-1</sup>) and kept at the desired temperature, allowing time for the product distribution to stabilize. Weight hourly space velocity (WHSV) was defined as the weight ratio of catalyst (g) to the 2-propanol feed rate  $(g h^{-1})$ . Standard reaction conditions were as follows: catalyst = 0.1 g; T = 170 °C; WHSV = 4.29 h<sup>-1</sup>; and feed composition of 2-propanol/NH<sub>3</sub>/H<sub>2</sub>/N<sub>2</sub> = 1:4:6:22.8. The partial pressure of 2-propanol and the WHSV were constant at 3 kPa and 4.29  $h^{-1}$  (total flow rate = 90 cm<sup>3</sup> min<sup>-1</sup>), respectively. To investigate the effects of the experimental parameters, the molar ratios of H<sub>2</sub>/2-propanol and NH<sub>3</sub>/ 2-propanol were varied in the ranges 2-12 and 2-16, respectively, and the reaction temperatures were varied between 140 and 200 °C. The effect of WHSV was also examined in the range 1.43-4.29 h<sup>-1</sup> (total flow rate =  $30-90 \text{ cm}^3 \text{ min}^{-1}$ ) at 170 °C with the feed composition of 2-propanol/NH<sub>3</sub>/H<sub>2</sub>/N<sub>2</sub> = 1:8:6:18.8. The reaction products were analyzed on-line with a Chrompack-CP-9001 gas chromatograph equipped with a CP-Volamine capillary column (60 m  $\times$  0.32 mm) and a flame ionization detector.

The conversion of 2-propanol and selectivity for MIPA was defined as follows:

Conversion (%)

$$=\frac{2\text{-propanol}_{fed} (mol) - 2\text{-propanol}_{unreacted} (mol)}{2\text{-propanol}_{fed} (mol)} \times 100$$

Selectivity (%)

$$=\frac{\text{MIPA}_{\text{produced}} \text{ (mol)}}{2\text{-propanol}_{\text{fed}} \text{ (mol)} - 2\text{-propanol}_{\text{unreacted}} \text{ (mol)}} \times 100$$

# **3** Results and Discussion

# 3.1 Characterization

The physical properties of the calcined Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts are summarized in Table 1. The BET surface areas, pore volumes, and pore sizes of the catalysts progressively decreased as the nickel loading increased. This may be due to the partial blockage of the Al<sub>2</sub>O<sub>3</sub> pores by the impregnation and successive calcination of the corresponding catalysts.

The XRD patterns of the various Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts calcined at 500 °C and reduced at 600 °C are shown in

Table 1 Physical properties of Ni/ $\gamma\text{-Al}_2O_3$  catalysts calcined at 500 °C for 2 h

Ni loading (wt%)	Surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Pore size (nm)	
4	177	0.627	14	
11	163	0.548	13	
17	154	0.461	12	
23	137	0.381	11	
27	123	0.352	11	



Fig. 1 XRD patterns of Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with various nickel loadings: **a** calcined at 500 °C for 2 h and **b** reduced at 600 °C for 3 h

Fig. 1. The diffraction peaks at  $2\theta = 37.6^{\circ}$ ,  $45.8^{\circ}$ , and  $66.8^{\circ}$  were attributed to crystalline  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JCPDS 29-0063). The XRD pattern of the calcined catalysts exhibited a characteristic reflection peak at  $2\theta = 43.2^{\circ}$  due to the presence of the NiO (JCPDS 47-1049) phase. The results suggested that there was no new compound formed by reaction between nickel oxide and alumina. The reduced Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts showed the characteristics peaks for metallic Ni (JCPDS 04-0850) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The sizes of the metallic Ni particles (Table 2) were determined from the broadening of the diffraction peaks, by using Scherrer's

Ni loading (wt%)	XRD		O <sub>2</sub> titration	H <sub>2</sub> chemisorption				H <sub>2</sub> -TPR peak temperature (°C)			
	Particle	Particle	Reduction degree (%) <sup>a</sup>	Uncorrected		Corrected		Metallic	Peak 1	Peak 2	Peak 3
	size of NiO (nm)	size of Ni (nm)		Dispersion (%)	Particle size (nm)	Dispersion (%) <sup>b</sup>	Particle size (nm) <sup>c</sup>	surface area $(m^2 g_{cat}^{-1})$	(Area, %)	(Area, %)	(Area, %)
4	_	9.5	34.6	3.5	28.9	10.1	10.0	0.9	-	670 (77)	788 (23)
11	8.1	8.2	47.6	5.3	19.2	11.0	9.2	3.9	441 (3)	617 (88)	787 (9)
17	8.8	9.9	49.1	4.4	22.8	9.0	11.2	5.0	434 (12)	604 (71)	742 (17)
23	14.8	16.1	51.4	3.0	33.3	5.9	17.1	4.7	414 (11)	591 (75)	758 (14)
27	15.2	18.4	51.6	2.8	35.7	5.7	17.4	5.1	411 (10)	575 (80)	745 (10)

Table 2 Physico-chemical properties of Ni/γ-Al<sub>2</sub>O<sub>3</sub> catalysts calcined at 500 °C for 2 h and successive reduction at 600 °C for 3 h

<sup>a</sup> Calculated from O<sub>2</sub> uptake

<sup>b</sup> Corrected dispersion (D) = surface Ni<sup>0</sup> atom/total reduced Ni<sup>0</sup> atom  $\times$  100 = surface Ni<sup>0</sup> atom/(total Ni atom  $\times$  reduced fraction)  $\times$  100

<sup>c</sup> Corrected Ni diameter = uncorrected Ni diameter  $\times$  reduced Ni fraction

equation. The calcined NiO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed NiO particles that increased in size from 8 to 15 nm as the Ni loading increased. High-temperature reduction at 600 °C resulted in metallic Ni particle sizes between 8 and 18 nm. The size of the metallic Ni particles increased with higher Ni loading in the Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Among the catalysts examined, the Ni(11)/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited the smallest Ni particle size of 8.2 nm, whereas the Ni(27)/Al<sub>2</sub>O<sub>3</sub> catalyst had the largest Ni particle size of 18.4 nm. The Ni species were more likely to be sintered to form larger Ni particles as the nickel loading increased. This result appears to be in good agreement with the data on the degree of metal dispersion (Table 2).

Figure 2 shows the TPR profiles of calcined Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. The TPR profiles of the Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 500 °C revealed three main reduction peaks in the temperature ranges of 300-450, 450-650, and 650-750 °C, with broad reduction profiles. The first peak at ca. 430 °C was generally attributed to the reduction of bulk NiO or of NiO weakly interacting with the support. The broad hightemperature reduction peak at ca. 600 °C could be ascribed to the reduction of NiO species strongly interacting with the support. The peak at ca. 760 °C was attributed to the reduction of surface nickel aluminate, which was not observed by XRD analysis [23]. In the case of the aluminasupported nickel catalyst, it has been reported that nickel aluminate may form, which hinders the complete reduction of the nickel species [24]. Thus, the peak at ca. 760 °C can be associated with the nickel oxide layer that contacts the alumina surface [25]. As the nickel loading in the Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst increased, the intensities and areas of both the first and second reduction peaks also increased, and the peaks shifted to lower temperatures (Table 2). This indicates that the interaction between NiO and the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support decreased as the nickel loading increased. However, Monti and Baiker observed that TPR peaks of pure nickel oxide



Fig. 2  $\,H_2\text{-}TPR$  profiles of Ni/ $\gamma\text{-}Al_2O_3$  catalysts calcined at 500 °C for 2 h

shift to higher temperature when the loading of the reducible component increases [26]. In addition, the higher peak intensity means more favorable reduction for the bigger particles of the Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst within the size range of 8.1–15.2 nm determined by XRD analysis. It is therefore appropriate to suggest that different particle sizes and nickel loadings lead to different degrees of reduction due to the differences in their interaction with alumina.

The H<sub>2</sub> chemisorption on Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts provides valuable and quantitative information such as the number of nickel metal sites, nickel dispersion, and the average nickel particle size. The results of the H<sub>2</sub> chemisorption, corrected by the reduction degree measured by O<sub>2</sub> titration, are presented in Table 2. The smallest nickel particle size, when corrected by considering the degree of reduction, was in Ni(11)/Al<sub>2</sub>O<sub>3</sub> (ca. 9.2 nm). The particle size increased from 9.2 to 17.4 nm as the nickel loading increased. The nickel particle sizes were in good agreement with the results of the XRD analysis, which showed that the minimum Ni particle size was in Ni(11)/Al<sub>2</sub>O<sub>3</sub> (8.2 nm), and the maximum was in Ni(27)/Al<sub>2</sub>O<sub>3</sub> (18.4 nm). By comparing the O<sub>2</sub> titration of nickel oxide on alumina support for different nickel loadings, it can be seen that the reduction degree increased with increasing nickel loading. This was in agreement with the H2-TPR results obtained with increased nickel loading, which showed shifts in the first and second peaks, corresponding to the reduction of the nickel oxide, towards lower temperatures. The low reduction degree of the Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst can be attributed to the small nickel oxide particles that can easily form nickel aluminate during calcination or the reduction process [27]. Furthermore, reduction of the nickel aluminate is difficult and impractical at the adopted experimental temperature, and therefore, it remains inactive during the reductive amination. Excluding the Ni(27)/Al<sub>2</sub>O<sub>3</sub> catalyst, the



Fig. 3 TEM images of a Ni(17)/Al\_2O\_3 and b Ni(27)/Al\_2O\_3 catalysts reduced at 600 °C for 3 h

reduced metal surface area of nickel was largest in the case of the Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst (around 5.0 m<sup>2</sup> g<sup>-1</sup><sub>catalyst</sub>). A highly reduced nickel metal surface area corresponds to the enhancement in the 2-propanol conversion. The reduced metal surface area of nickel was largest in the case of the Ni(27)/Al<sub>2</sub>O<sub>3</sub> catalyst (around 5.1 m<sup>2</sup> g<sup>-1</sup><sub>catalyst</sub>), but its surface area was not correlated with the conversion of 2-propanol (Fig. 4). This is probably because this catalyst shows the lowest dispersion and has large nickel particles.

Figure 3 shows the TEM images of Ni(17)/Al<sub>2</sub>O<sub>3</sub> and Ni(27)/Al<sub>2</sub>O<sub>3</sub> catalysts reduced at 600 °C for 3 h. As opposed to the Ni(27)/Al<sub>2</sub>O<sub>3</sub> catalyst, the Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst had finely dispersed metallic species on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which was consistent with the H<sub>2</sub>-chemisorption results of the reduced catalysts. In contrast, the nickel particles of the Ni(27)/Al<sub>2</sub>O<sub>3</sub> catalyst had irregular shapes and were not uniform.

## 3.2 Reductive Amination of 2-propanol

Figure 4 shows the effect of nickel loading in the reductive amination of 2-propanol over Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. The conversions and selectivities obtained after 30 min on stream were considered as intrinsic activities; the catalysts did not show deactivation during this time. A maximum yield of MIPA was obtained over 17 wt% Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Although the conversion was not directly proportional to the metallic surface area of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, the observed variation in the conversion could be correlated to the difference in the reduced metallic surface area of the catalysts. Despite the highest metallic surface area in Ni(27)/Al<sub>2</sub>O<sub>3</sub> catalyst, the conversion was rather



**Fig. 4** Influence of nickel loading on the reductive amination of 2-propanol over Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts. Reaction conditions: T = 170 °C; WHSV = 4.29 h<sup>-1</sup>; feed composition of 2-propanol/NH<sub>3</sub>/H<sub>2</sub> (mol%) = 1:4:6

less than that of catalysts having the lower loadings of nickel (11–23 wt% Ni). This may be due to the variation in the reducibility and nickel metal dispersion accompanying the various levels of nickel loading, which can be shown from H<sub>2</sub> chemisorption (Table 2). The sums of the selectivities to MIPA, acetone, and DIPA were almost constant at ca. 99 % under the tested operating conditions. Various by-products formed by condensation, decarbonylation, disproportionation, and hydrogenolysis of 2-propanol under these operating conditions, which could possibly be  $C_1-C_3$  compounds and di-isoprophyether, were negligible in the reductive amination of 2-propanol.

Acetone is first formed by the dehydrogenation of 2-propanol, small quantities of DIPA may be formed by the consecutive reaction of MIPA with 2-propanol, and DIPE could result from the condensation/dehydration of 2-propanol. The MIPA selectivity slightly decreased with increased nickel loading, accompanied by an increase of DIPA selectivity. The pattern of selectivity was found to be similar to reductive amination over Co/SiO<sub>2</sub> catalysts [28].

Effects of reaction parameters on the reductive amination of 2-propanol over  $Ni(17)/Al_2O_3$  catalyst were examined in Supporting Information as a function of hydrogen partial pressure, ammonia partial pressure, space velocity, and reaction temperature (see Fig. S1).

#### 3.3 Deactivation Behavior of Ni/Al<sub>2</sub>O<sub>3</sub> Catalyst

To gain more insight into the effect of catalyst deactivation, the evolution of 2-propanol conversion and selectivities for MIPA, DIPA, and acetone products were investigated as functions of time on stream in the presence or absence of  $H_2$ , for the reductive amination of 2-propanol over Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst. Figure 5 shows the deactivation behavior of the  $Ni(17)/Al_2O_3$  catalyst as observed during the reductive amination of 2-propanol. During the reaction, the flow of  $H_2$ was stopped and then the initial flow composition was restored. When the amination reaction was performed with the initial feed composition of 2-propanol/NH<sub>3</sub>/H<sub>2</sub>/N<sub>2</sub> (mol ratio) = 1:8:6:18.8, the 2-propanol conversion and selectivities for MIPA, DIPA, and acetone were 97, 78, 15.5, and 6.5 %, respectively. After the  $H_2$  flow in the reactant stream was stopped, the catalyst rapidly deactivated. The 97 % conversion of 2-propanol in the presence of hydrogen decreased to 25 % conversion within 5 h on stream. The selectivities for MIPA and acetone showed contrasting trends. The selectivity for MIPA decreased from 79 to 60%and that for acetone increased from 7 to 35 %. After reexposure to the initial feed compositions of hydrogen, the initial conversion and selectivities were obtained within 1 h on stream. Verhaak et al. [29] observed the rapid deactivation of a supported nickel catalyst in the disproportionation of *n*-propylamine when hydrogen in the feed was replaced by



**Fig. 5** Evolution of 2-propanol conversion and MIPA selectivity as a function of time on stream in the presence or absence of hydrogen for the reductive amination of 2-propanol over Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst. During the reaction, the composition of the N<sub>2</sub> + H<sub>2</sub> mixture was changed to pure N<sub>2</sub> and then the initial composition was restored. Reaction conditions: T = 170 °C; WHSV = 2.38 h<sup>-1</sup>; feed compositions of 2-propanol/NH<sub>3</sub>/H<sub>2</sub>/N<sub>2</sub> (mol%) = 1:8:6:18.8 and 1:8:0/24.8

nitrogen. They ascribed this deactivation is due to the formation of metal nitride during the amination reaction and concluded that the formation of metal nitride was a main factor in the deactivation of metallic catalysts for reductive amination [30]. The feed of excess hydrogen could efficiently hinder the phase transition of metallic catalyst to form nitride during the reaction, and therefore, prevent catalyst deactivation.

To evaluate the nature of the adsorbed species during the amination reaction and to evaluate the origin of deactivation, NH<sub>3</sub>-TPD and simultaneous NH<sub>3</sub>-TPD and H<sub>2</sub>-TPR experiments were conducted using a quadrupole mass spectrometer and argon gas or a hydrogen/argon mixture. Prior to each experiment, the sample was reduced under H<sub>2</sub> flow at 600 °C for 3 h at a heating rate of 10 °C  $\cdot$  min<sup>-1</sup>. Figure 6 shows the evolution of NH<sub>3</sub> and H<sub>2</sub> during TPD/ TPR using Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst under H<sub>2</sub>/Ar and Ar flows. The reduced samples were pretreated under flowing 20 % NH<sub>3</sub>/N<sub>2</sub> or 4 % NH<sub>3</sub>/16 % H<sub>2</sub>/N<sub>2</sub> at 170 °C for 12 h, and subsequently, pure Ar was passed through the reactor for 30 min. NH<sub>3</sub> desorption and H<sub>2</sub> consumption were recorded under flowing 5 % H<sub>2</sub>/Ar for the sample pretreated with 20 % NH<sub>3</sub>/N<sub>2</sub> (Fig. 6 A(a), (b). H<sub>2</sub>-TPR profiles of the sample pretreated with 20 % NH<sub>3</sub>/Ar revealed two main peaks at 100 °C and 145 °C, and broad peaks up to 400 °C. The first peak corresponded to the desorption of weakly adsorbed ammonia on the surface of the metal phase and the alumina support, and the second peak corresponded to the desorption of the ammonia strongly adsorbed on the nickel, which may be due to the formation of surface nickel nitride [31, 32]. In addition, the hydrogen

consumption peak was detected at 145 °C, and it indicated the removal of strongly adsorbed nitrogen-containing surface species in the presence of hydrogen. This means that the simple removal of strongly adsorbed nitrogen-containing surface species was possible in the presence of hydrogen. Figure 6 A(a), (b) show  $NH_3$  desorption and  $H_2$ consumption for the sample pretreated with 4 % NH<sub>3</sub>/16 % H<sub>2</sub>/N<sub>2</sub>. H<sub>2</sub> evolution was not detected during H<sub>2</sub>-TPR (Fig. 6 A(c), (d). Evolutions of NH<sub>3</sub> and H<sub>2</sub> were not observed over the sample pretreated with 4 % NH<sub>3</sub>/16 %  $H_2/N_2$  (Fig. 6 A(c), (d). The deactivation of metallic catalysts as copper, cobalt and nickel during the amination reaction of alcohols have been widely studied [29–36]. The main factor of deactivation could be concluded due to the formation of corresponding metal nitride. Baiker et al. [32-34] reported that the deactivation of metallic nickel and copper catalysts by nitride formation originating from ammonia can be suppressed by hydrogen. To investigate



the role of hydrogen in the amination of 2-propanol, NH<sub>3</sub>-TPD was performed under flowing Ar in the absence of hydrogen (Fig. 6B). Under these conditions, the result showed the typical NH<sub>3</sub>-TPD profile, indicating only the acid sites of the catalyst.

To investigate the changes in the surface of the Ni(17)/ $Al_2O_3$  catalyst during the amination of 2-propanol, XPS experiments were performed on samples retrieved at different reaction stages (Fig. 7). The presence of N was not detected in the spectrum for the H<sub>2</sub>-treated catalyst, but the sample treated under deactivation conditions showed a peak corresponding to a binding energy of 398.8 eV. This peak is due to the nitrogen trapped in the metal lattice [37, 38]. Also, N 1s peak from physically adsorbed NH<sub>3</sub> was seen at ca. 402–404 eV [37]. In addition, Soares et al. [39]



**Fig. 6** Evolution of NH<sub>3</sub> and H<sub>2</sub> during TPR/TPD for Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst under flowing **a** 5 % H<sub>2</sub>/Ar and **b** Ar. The samples reduced were pretreated under flowing **a** (*a*), (*b*) 20 % NH<sub>3</sub>/N<sub>2</sub> and (*c*), (*d*) 4 % NH<sub>3</sub>/16 % H<sub>2</sub>/N<sub>2</sub> at 170 °C for 12 h, **b** (*a*), (*b*) 20 % NH<sub>3</sub>/N<sub>2</sub> at 170 °C for 12 h

**Fig.** 7 XPS spectra of Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst at different reaction stages: *a* catalyst pretreated at 600 °C for 3 h in H<sub>2</sub> (50 cm<sup>3</sup> min<sup>-1</sup>); *b* catalyst after reaction under the deactivation conditions of T = 170 °C, WHSV = 2.38 h<sup>-1</sup>, feed composition of 2-propanol/ NH<sub>3</sub>/H<sub>2</sub>/N<sub>2</sub> (mol %) = 1:8:0:24.8; *c* catalyst after reaction under the deactivation conditions and re-exposed to H<sub>2</sub> (50 cm<sup>3</sup> min<sup>-1</sup>) at 170 °C for 1 h

reported that the binding energy of N 1s in N-O-metal bonding was ca. 402 eV. The absence of peaks around 402 and 404 eV indicated that the peak corresponding to 398.8 eV was consistent with nitride formation [37, 38, 40]. In many investigations [29], metal nitride formation was observed under similar reaction conditions as the major route for catalyst deactivation. In addition, after reaction under the deactivation condition re-exposed the H<sub>2</sub>  $(50 \text{ cm}^3 \text{ min}^{-1})$  catalyst was not detected the presence of N. In the absence of hydrogen, a reversible deactivation phenomenon that can be ascribed to ammonia-nickel interactions resulting from the strong chemisorption of ammonia is observed. In addition, Fig. 8 shows the Ni 2p spectra of the Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst measured at different reaction stages. After treatment under deactivation conditions, the Ni 2p peak position of the Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst shifted slightly to a higher binding energy. Vega and Cruz [41] suggested that the binding energy shifts could be interpreted as the result of charge transfer between metal and nitrogen atoms. In addition, the slight changes in intensity were due to modifications of the relative atomic concentrations between Ni and N [42]. The XPS spectra of N 1s and Ni 2p were exhibited due to nickel nitride formation caused by strong adsorption of ammonia on the surface of the nickel metal phase. We speculated that a feed of excess hydrogen could efficiently hinder the phase transition of catalyst to metal nitride formation during the reaction and prevent catalyst deactivation.

3.4 Long-Term Stability of Ni/Al<sub>2</sub>O<sub>3</sub> Catalyst on the Amination Reaction

The long-term stability of the  $Ni(17)/Al_2O_3$  catalyst during the reductive amination of 2-propanol is shown in Fig. 8.



Fig. 8 Long-term stability of Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst for the reductive amination of 2-propanol to MIPA at 170 °C. Reaction conditions: WHSV =  $2.38 \text{ h}^{-1}$ ; feed composition of 2-propanol/NH<sub>3</sub>/H<sub>2</sub>/N<sub>2</sub> (mol%) = 1:8:6:18.8

The reductive amination of 2-propanol was performed for 100 h using the optimum reaction conditions. The conversion of 2-propanol was 94.1 % at 170 °C and the selectivities to MIPA, DIPA, and acetone were 80.6, 12.0, and 7.4 %, respectively. The Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst showed high activity and stability, and its excellent performance make it economically viable.

# 4 Conclusions

Ni/y-Al<sub>2</sub>O<sub>3</sub> catalysts with different nickel loadings (4-27 wt%) were prepared by the incipient wetness impregnation method. Particle size increased with the increase in the nickel loading on Ni/y-Al<sub>2</sub>O<sub>3</sub>, from 8 to 15 nm. Larger nickel oxide particles could be reduced easily due to weak interaction with the support. With the exception of the Ni(27)/Al<sub>2</sub>O<sub>3</sub> catalyst, the reduced metal surface area of nickel was largest for the Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst at ca. 5.0 m<sup>2</sup>  $g_{catalyst}^{-1}$ . The highly reduced nickel metal surface area could be correlated with the enhancement of the 2-propanol conversion. Excess ammonia was effective in promoting the 2-propanol conversion and MIPA selectivity. Excess hydrogen could efficiently hinder the phase transition of the catalyst to form the metal nitride during the reaction, and ultimately, could prevent catalyst deactivation. The Ni(17)/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited not only the highest catalytic performance but also the greatest longterm stability of up to 100 h on stream.

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