高载量、高活性 Ni/Al₂O₃ 催化剂的制备及其芳环加氢催化反应

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摘要: 使用共沉淀法制备了负载量很高的 Ni/Al₂O₃ 催化剂, 通过正丁醇干燥处理, 提高了催化剂的表面积和负载镍的分散度. 实验发现, 镍的负载量和干燥过程对催化剂的表面积、孔结构及金属镍的还原度和分散度影响很大. 经过正丁醇处理的 80%Ni/Al₂O₃-B 催化剂具有较高的表面积, 而负载镍的还原度和分散度也显著提高, 使得催化剂具有很高的活性金属镍表面积 (90 m²/g-催化剂), 该催化剂对甲苯有较强的吸附作用, 在甲苯和苯酚的芳环加氢反应中表现出了很高的催化活性.

关键词: 镍; 氧化铝; 正丁醇干燥; 活性金属表面积; 微量吸附量热; 甲苯加氢; 苯酚加氢

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Preparation of Highly Loaded and Active Ni/Al₂O₃ Catalysts for the Hydrogenation of Aromatic Rings

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Abstract: Highly loaded and dispersed Ni/Al₂O₃-B catalysts were prepared by the co-precipitation method with an *n*-butanol drying process. The loading of nickel and drying process were found to be the two key factors in determining the surface area and pore structures of catalysts as well as the reducibility and dispersion of supported nickel. The 80%Ni/Al₂O₃-B treated with *n*-butanol during the drying process exhibited the high surface area and high reducibility and dispersion of supported nickel, leading to the high active nickel surface area (90 m²/g-catalyst). It adsorbed toluene strongly and thus exhibited high activity for the hydrogenation of aromatic rings in toluene and phenol.

Key words: Ni/Al₂O₃ catalyst; drying with *n*-butanol; active metal surface area; microcalorimetric adsorption; hydrogenation of toluene; hydrogenation of phenol.

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Since γ -Al₂O₃ exhibits the high surface area and thermal stability while nickel is of low cost and highly active for hydrogenation reactions, Ni/Al₂O₃ catalysts have been widely used in a variety of catalytic processes in fine chemical synthesis and petrochemical industries [1–14]. The hydrogenation of aromatics is important in the refineries for reducing the content of aromatics in diesel and gasoline

fuels. Thus, the hydrogenation of benzene or toluene, as a model reaction, on the Ni/Al₂O₃, Ni/SiO₂-TiO₂, Ni/ZSM-5, and Ni/MCM-41 has been investigated [7,10,15–17]. In addition, the hydrogenations of benzene and toluene are frequently used as probe reactions to characterize metal catalysts since they are taken as the insensitive reactions with respect to the surface structures of metals [18–20]. Due

to the low cost and high activity of nickel, the hydrogenation of phenol over supported nickel catalysts was studied as an alternative way to replace the thermal or catalytic incinerations for the treatment of wastes containing phenols [21,22].

Different factors have been investigated in order to prepare the Ni/Al₂O₃ catalysts with high activities. The factors studied include the precursor [7,12], loading [5,6,7,10,14,23], preparation method [10,24], pretreatment (drying and calcination) [7,13,14,25,26], and reduction condition (temperature, heating rate, hydrogen flow and reduction time) [7,13]. The reducibility and dispersion of the Ni/Al₂O₃ catalysts are significantly affected by these factors. The reducibility and dispersion are usually two contradictory factors that are difficult to improve simultaneously. They must be carefully balanced in order to optimize the active surface areas of nickel in the Ni/Al₂O₃ catalysts.

Loading of nickel is an important factor since it affects the number of surface active nickel sites and acidity of the Ni/Al₂O₃ catalysts, which in turn affect the hydrogenation activity of the catalysts. Supported nickel catalysts with high loadings beyond 50% are usually used for industrial hydrogenation processes [27,28]. However, the catalysts with loading of nickel less than 20% were reported in the majority literature. With the increase of loading of nickel (especially beyond 15%), the interaction between NiO and Al₂O₃ usually becomes weaker, leading to the improved reducibility but decreased dispersion of nickel in Ni/Al₂O₃ [14,23]. It was found that the reducibility of nickel was increased while the dispersion of nickel was hardly affected with the increase of nickel loading for the 10%–50%Ni/Al₂O₃ catalysts. Accordingly, the activity for the hydrogenation of aniline and acetone on the catalysts was increased owing to the increased surface active nickel sites. In addition, the product selectivity was varied, probably due to the change of surface acidity with loading [5,6].

The techniques used to prepare the Ni/Al₂O₃ catalysts include impregnation [4,7,10–14,23,24,26], sol-gel [1–3,10], and co-precipitation [5,6,10,11,23–25]. The supported nickel catalysts with high dispersion and loading of nickel are more easily obtained by the co-precipitation and sol-gel methods than by the conventional impregnation method. The co-precipitation is simple and economical, as compared to the sol-gel method. In order to obtain superfine or high surface area materials, the precipitate and gel could be dried by using a variety of methods, which were systematically reviewed by Wang et al. [29]. Among these methods, solvent replacement drying (usually an organic solvent with low surface tension) has the advantages of simplicity and low cost. It has been reported that the pore shrinkage and the agglomeration of particles could be reduced to a large extent for the preparation of ZrO₂/Al₂O₃ [30], TiO₂ [31],

and Ni/MgO [32] from gel or precipitation treated with *n*-butanol.

In this work, a series of highly loaded Ni/Al₂O₃ catalysts were prepared by the co-precipitation method with an *n*-butanol drying process. It was found that the treatment with *n*-butanol significantly improved the active surface area of nickel and thus activity of the Ni/Al₂O₃ catalysts for the hydrogenation reactions.

1 Experimental

1.1 Preparation of catalysts

The 60%–90% Ni/Al₂O₃ catalysts (weight percent) were prepared by the co-precipitation method. Specifically, desired amount of metal nitrates (Ni(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O, both in AR grade) were dissolved in 100 ml distilled water to form a solution (I). Desired amount of Na₂CO₃ (AR) was dissolved in 100 ml distilled water to form another solution (II). The two solutions were simultaneously dropwise added into a beaker containing 250 ml distilled water at 353 K under vigorous stirring. The precipitate formed was filtered and washed thoroughly with distilled water until pH of the filtrate was 7. *N*-butanol (about 200 ml, AR) was then added into the precipitate and heated at 353 K overnight during which water and *n*-butanol were evaporated. The precipitate was then dried in an oven at 393 K for 12 h. The catalysts were denoted as 60Ni/Al₂O₃-B and 60Ni/Al₂O₃ with and without the treatment with *n*-butanol, respectively, in which 60 stands for the weight percentage of nickel.

1.2 Characterization of catalysts

The nitrogen adsorption-desorption isotherms were determined at 77 K using a Micromeritics Gemini V 2380 autosorption analyzer. All the catalysts were out-gassed in flowing nitrogen at 673 K for 3 h prior to the measurements. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method, and the pore size distributions were obtained according to the desorption branches by the Barrett-Joyner-Halenda (BJH) method.

Powder X-ray diffraction (XRD) patterns were collected on a Philips X'Pert Pro diffractometer using Ni-filtered Cu K_α radiation ($\lambda = 0.15418$ nm), operated at 40 kV and 40 mA at a scanning rate of 25°/min.

Temperature-programmed reduction (TPR) measurements were performed by using a quartz U-tube reactor loaded with about 50 mg of a sample calcined at 573 K in 5.03% H₂/N₂ (v/v) at a flow rate of 40 ml/min. The hydrogen consumption was monitored by a thermal conductivity detector (TCD). The reducing gas was first passed through

the reference arm of the TCD before entering the reactor. The exiting gas passed through a trap filled with soda lime to remove water and possibly CO₂ and then reached the second arm of the TCD. The temperature was linearly raised from 303 to 1173 K with a rate of 10 K/min.

Microcalorimetric adsorption measurements were performed using a Tian-Calvet type C-80 microcalorimeter (Setaram, France), which was connected to a glass vacuum-dosing system, equipped with a Baratron capacitance manometer (USA) for the pressure measurement and gas handling. About 0.1 g of a catalyst was loaded, reduced for 2 h in flowing H₂ at 723 K, and then evacuated for 1 h prior to a measurement. Adsorption of toluene on 60Ni/Al₂O₃-B and 80Ni/Al₂O₃-B directly evacuated for 3 h were also determined in order to compare with that on the reduced ones.

The adsorption of H₂ and O₂ was carried out in a home-made volumetric apparatus. The catalyst was reduced in H₂ at the desired temperature for 2 h and evacuated at the same temperature for 1 h before the measurements. The adsorption of H₂ was performed at room temperature. After the adsorption of H₂, the sample was heated to 673 K at a rate of 10 K/min and evacuated at the temperature for 1 h. Then the adsorption of O₂ was performed at 673 K. The uptakes of H₂ and O₂ were obtained by extrapolating the coverage of corresponding isotherms to P=0. The degree of reduction (reducibility), dispersion, active surface area, and average particle size of supported nickel were calculated based on the amount of H₂ and O₂ adsorbed and the loading of nickel. The surface area of metallic nickel was calculated by the uptake of H₂ assuming the molar ratio of H/Ni_{surf}=1 and a surface area of 6.5×10^{-20} m² for a Ni atom [33, 34]. The amount of metallic nickel atoms in the catalyst were calculated according to the uptake of O₂ and the molar ratio of O/Ni=1 [35]. The reduction degree was then calculated by the number of nickel atoms titrated by O₂ adsorption divided by the number of nickel atoms present in the sample. Finally, the dispersion of nickel (*D*) could be calculated according to the following equation: *D* (%) = uptake of H₂/uptake of O₂ × 100, while the average Ni particle size *d* (nm) could be derived from the equation (*d* (nm) = 101/*D* (%)) suggested by Smith et al. [36] assuming the spherical shape of metal particles.

Transmission electron microscopy (TEM) images were recorded on a JEOL electron microscope (JEM-2100) with an accelerating voltage of 200 kV. The reduced sample was put into ethanol and ultrasonically dispersed to make a suspension. A drop of the suspension was placed on a copper grid.

1.3 Catalytic hydrogenation

The catalytic hydrogenation experiments were performed

at atmospheric pressure in a continuous down-flow fixed-bed microreactor (a vertical glass tube with i.d. = 8 mm). 20–50 mg of a powered catalyst (80–100 mesh) was mixed with about 3 g quartz sand, and placed on the glass frit of the glass reactor. The catalyst was reduced in flowing H₂ at 723 K for 2 h prior to the hydrogenation. An *n*-hexane solution containing toluene (toluene:*n*-hexane = 1:2, w/w) or a cyclohexane solution containing phenol (phenol:cyclohexane = 1:2, w/w) with H₂ was fed into the reactor for the hydrogenation reactions. The liquid feeds were delivered into the reactor using a 2ZB-1L10 dual-plunger infinitesimal quality metering pump. The reaction temperature was 423 K for hydrogenation of toluene and phenol. The weight hourly space velocity (WHSV) of toluene changed from 28 to 106 h⁻¹ while the WHSV of phenol varied from 70 to 411 h⁻¹. The WHSV was adjusted by changing the flow rates of liquids while keeping the H₂/reactant ratios. The products were collected using a trap in ice bath. The products were analyzed by a gas chromatograph (GC-122, Shanghai precision & scientific instrument Co., LTD) with an FID equipped with an HP-FFAP capillary column.

2 Results and discussion

2.1 Textural and structural properties of catalysts

The specific surface areas and pore structural parameters of the Ni/Al₂O₃ catalysts are summarized in Table 1. With the increase of loading of nickel from 60% to 90%, the surface areas decreased from 304 to 102 m²/g, while the pore volumes decreased from 1.17 to 0.29 cm³/g, for the Ni/Al₂O₃-B catalysts. The most probable pore diameters increased first, and then decreased with the increase of nickel loading, varying in the range of 5.7–14.3 nm for the Ni/Al₂O₃-B catalysts. Comparing to the series of Ni/Al₂O₃-B catalysts, the Ni/Al₂O₃ catalysts with the same loadings of nickel without the *n*-butanol drying process exhibited significantly lower surface areas, pore sizes, and pore volumes. Thus, a treatment with *n*-butanol increased the surface areas and porosities of the catalysts, which were the two factors favoring the dispersion of supported nickel.

Table 1 Surface areas and pore structures of the Ni/Al₂O₃ catalysts reduced at 723 K

Catalyst	Surface area (m ² /g)	Most probable pore size (nm)	Pore volume (cm ³ /g)
60Ni/Al ₂ O ₃ -B	304	7.2	1.17
60Ni/Al ₂ O ₃	258	4.3	0.66
80Ni/Al ₂ O ₃ -B	207	14.3	1.01
80Ni/Al ₂ O ₃	150	8.2	0.36
90Ni/Al ₂ O ₃ -B	102	5.7	0.29

N_2 adsorption-desorption isotherms and pore size distributions for the $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts reduced at 723 K are shown in Fig. 1. The isotherms (Fig. 1 (a)) for all the catalysts belonged to type IV with H3 hysteresis loops, typical of mesopores. The pore size distributions (Fig. 1 (b)) for all the catalysts exhibited only one peak with pore sizes ranging from 3 to 30 nm. The 80Ni/ Al_2O_3 -B exhibited the largest pores in the catalysts studied in this work with the most probable pore diameter of about 14.3 nm. The most probable pore diameters of 60Ni/ Al_2O_3 and 80Ni/ Al_2O_3 were much smaller than those of the corresponding catalysts treated with *n*-butanol.

Fig. 1. N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of the $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts reduced at 723 K.

Figure 2 shows the XRD patterns of the $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts reduced at 723 K. All the catalysts exhibited two broad and weak peaks around 37° and 63° , belonging to $\gamma\text{-Al}_2\text{O}_3$ [10]. No nickel aluminate spinel phases were detected, indicating the small crystallites of such phases in the $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts. The XRD peaks characteristic of metallic nickel are around 44° , 52° , and 76° , but these peaks were broad and weak in all the $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts. The XRD peaks of nickel in the 60Ni/ Al_2O_3 -B, 80Ni/ Al_2O_3 -B, and 90Ni/ Al_2O_3 -B

were gradually intensified with increasing the content of nickel. It can be seen that the peak around 52° in the 80Ni/ Al_2O_3 -B was weaker than in the 80Ni/ Al_2O_3 , indicating that *n*-butanol treatment enhanced the dispersion of nickel on $\gamma\text{-Al}_2\text{O}_3$.

Fig. 2. XRD patterns of the $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts reduced at 723 K.

Fig. 3. TPR profiles of $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts calcined at 573 K.

2.2 Reducibility and dispersion of supported nickel

TPR measurements were performed in order to investigate the effects of loading and *n*-butanol treatment on the $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts. Prior to the measurements, the catalysts were calcined at 573 K for 2 h. The results are shown in Fig. 3. All the catalysts displayed two reduction peaks. One with the reduction temperature below 600 K was small, and might be ascribed to the reduction of NiO not strongly interacted with Al_2O_3 [17,37]. Another one was broad with the reduction temperatures in the range of 600–1040 K, and might be assigned to the reduction of NiO highly dispersed in Al_2O_3 . With the increase of nickel loading from 60 to 80%, the temperature of the second reduction peak did not seem to change. The temperature was lowered only when the loading of nickel was increased to 90%. No difference

Table 2 Effect of reduction temperature on the chemisorption of H₂ and O₂ on 80Ni/Al₂O₃-B

Temperature (K)	H ₂ uptake (mol/g _{cat.})	O ₂ uptake (mol/g _{cat.})	S _{Ni} (m ² /g _{cat.})	Reducibility (%)	Ni dispersion (%)	Diameter (nm)
673	999	3736	78	66.8	26.7	3.8
723	1160	4588	90	82.0	25.3	4.0
773	1038	4763	81	85.1	21.8	4.6

was observed for the TPR profiles of Ni/Al₂O₃-B and Ni/Al₂O₃ with the same loading of nickel. Thus, the treatment with *n*-butanol did not seem to affect the interaction between NiO and Al₂O₃ in the Ni/Al₂O₃ catalysts.

The active surface area of nickel, reducibility, dispersion and average particle size of reduced nickel in the catalysts could be calculated from the uptakes of H₂ and O₂, as described in the experimental section. The data of H₂ and O₂ adsorption on the 80Ni/Al₂O₃-B reduced at different temperatures are given in Table 2. The H₂ and O₂ uptakes were 999 and 3736 μmol/g, respectively, for the catalyst reduced at 673 K, corresponding to the reducibility and dispersion of about 66.8% and 26.7%, respectively. With the increase of reduction temperature from 673 to 773 K, the reducibility of nickel was increased while the dispersion of nickel was decreased for the catalyst. The product of loading, reducibility and dispersion of nickel determines the number of surface active nickel sites. It was found that the 80Ni/Al₂O₃-B reduced at 723 K exhibited the highest active nickel surface area (90 m²/g). Therefore, 723 K was selected as the reduction temperature for all the catalysts in the hydrogenations of toluene and phenol.

The data of H₂ and O₂ adsorption for the Ni/Al₂O₃ catalysts reduced at 723 K are presented in Table 3. According to the H₂ and O₂ uptakes, the reducibility and dispersion were found to be 63.3% and 33.8% for the 60Ni/Al₂O₃-B, respectively, as compared to 67.9% and 22.9%, respectively, for the 60Ni/Al₂O₃. Thus, a treatment with *n*-butanol almost maintained the reducibility (in consistence with the TPR results) but increased the dispersion of nickel significantly for the 60Ni/Al₂O₃. As a result, the active surface area of nickel was significantly increased from 53 (for 60Ni/Al₂O₃) to 73 m²/g (for 60Ni/Al₂O₃-B). When the loading of nickel was increased from 60% to 80%, the reducibility of nickel was increased from 63.3% to 82.0% while the dispersion of

nickel was decreased from 33.8% to 25.3% for the Ni/Al₂O₃-B catalysts. Although the dispersion of nickel was decreased for the 80Ni/Al₂O₃-B as compared to the 60Ni/Al₂O₃-B, the increase of loading of nickel and reducibility resulted in the significantly increased active surface area of nickel from 73 (for 60Ni/Al₂O₃-B) to 90 m²/g (for 80Ni/Al₂O₃-B). Further increase of loading of nickel to 90% decreased greatly the dispersion of nickel (to 12%), leading to the greatly decreased active surface area of nickel (to 52 m²/g). As compared to the Ni/Al₂O₃ with the same loadings of nickel, the Ni/Al₂O₃-B treated with *n*-butanol exhibited the significantly higher dispersion of nickel and thus the significantly higher active surface areas of nickel since the reducibility of supported nickel was hardly affected by the *n*-butanol treatment. The data in Table 3 showed that the nickel particles were smaller in the Ni/Al₂O₃-B than in the corresponding Ni/Al₂O₃. The average sizes of nickel particles were calculated to be about 4.4 and 5.8 nm for the 60Ni/Al₂O₃ and 80Ni/Al₂O₃, respectively, while they were found to be about 3.0 and 4.0 nm for the 60Ni/Al₂O₃-B and 80Ni/Al₂O₃-B, respectively.

Representative TEM images and particle size distributions of 80Ni/Al₂O₃, 80Ni/Al₂O₃-B, and 90Ni/Al₂O₃-B are shown in Fig. 4. It can be seen that metallic nickel in the catalysts was uniformly dispersed in the form of aggregates of small crystallites on Al₂O₃, and the nickel particle sizes were affected by nickel loading and drying process. According to the TEM images, the average sizes of nickel particles in the 80Ni/Al₂O₃-B and 90Ni/Al₂O₃-B were estimated to be about 4.4 and 8.7 nm, respectively. Thus, the nickel particle size increased quickly with the increase of loading from 80% to 90%. On the other hand, the 80Ni/Al₂O₃ possessed the larger average size of nickel particles (6.2 nm) than the 80Ni/Al₂O₃-B. Thus, the treatment with *n*-butanol favored the dispersion of nickel particles on

Table 3 Chemisorption of H₂ and O₂ on Ni/Al₂O₃ catalysts reduced at 723 K

Catalyst	H ₂ uptake (mmol/g _{cat.})	O ₂ uptake (mmol/g _{cat.})	S _{Ni} (m ² /g _{cat.})	Reducibility (%)	Dispersion (%)	Diameter (nm)
60Ni/Al ₂ O ₃ -B	938	2779	73	63.3	33.8	3.0
60Ni/Al ₂ O ₃	683	2984	53	67.9	22.9	4.4
80Ni/Al ₂ O ₃ -B	1160	4588	90	82.0	25.3	4.0
80Ni/Al ₂ O ₃	765	4392	59	78.5	17.4	5.8
90Ni/Al ₂ O ₃ -B	672	5531	52	90.7	12.1	8.3

Fig. 4. TEM images and particle size distributions of 80Ni/Al₂O₃-B (a), 80Ni/Al₂O₃ (b), and 90Ni/Al₂O₃-B (c) catalysts reduced at 723 K.

Al₂O₃, agreeing with the results of chemisorptions of H₂ and O₂.

2.3 Microcalorimetric adsorption

The results of microcalorimetric adsorption of NH₃ at 423 K on the Ni/Al₂O₃ catalysts reduced and evacuated at 723 K are shown in Fig. 5. The initial heat was measured to be about 138 kJ/mol for NH₃ adsorption on the 90Ni/Al₂O₃-B while those were found to be about 180 kJ/mol on the other catalysts. The heats of NH₃ adsorption on the 60Ni/Al₂O₃-B were higher than on the 80Ni/Al₂O₃-B except for the initial heat in the whole coverage. Thus, the surface acidities on the Ni/Al₂O₃-B decreased with the increase of loading of

nickel. The Ni/Al₂O₃-B catalysts had slightly higher coverage of NH₃ than their Ni/Al₂O₃ counterparts. However, the heats of NH₃ adsorption on the Ni/Al₂O₃-B were almost the same as on Ni/Al₂O₃ at the same coverage of NH₃. Thus, the treatment with *n*-butanol had little effect on the surface acidity of Ni/Al₂O₃.

Figure 6 shows the results of microcalorimetric adsorption of toluene at 308 K on the Ni/Al₂O₃-B catalysts with and without the reduction at 723 K. The initial heats for the adsorption of toluene on the 60Ni/Al₂O₃-B and 80Ni/Al₂O₃-B evacuated directly at 723 K (without the reduction) were 116 and 80 kJ/mol, respectively. The initial heats were significantly higher (about 179 kJ/mol) on the 60Ni/Al₂O₃-B and 80Ni/Al₂O₃-B reduced at 723 K. How-

ever, the adsorption heats of toluene were decreased sharply to about 80 kJ/mol with the increase of toluene coverage. Thus, only small amount of toluene molecules were adsorbed on metallic nickel sites and most toluene molecules seemed to adsorb on acidic sites of the reduced Ni/Al₂O₃ catalysts.

Fig. 5. Differential heat vs. coverage for NH₃ adsorption at 423 K on the Ni/Al₂O₃ catalysts reduced and evacuated at 723 K.

Fig. 6. Differential heat vs. coverage for toluene adsorption at 308 K on the Ni/Al₂O₃ catalysts. Suffix (E) denotes the catalysts evacuated at 723 K without the reduction while suffix (R) denotes the catalysts reduced and then evacuated at 723 K.

Figure 7 shows the results of microcalorimetric adsorption of toluene at 308 K on the Ni/Al₂O₃ catalysts reduced and then evacuated at 723 K. The initial heats were about 179, 179, and 150 kJ/mol for the adsorption of toluene on the reduced 60Ni/Al₂O₃-B, 80Ni/Al₂O₃-B, and 90Ni/Al₂O₃-B, respectively, corresponding to the adsorption of toluene on metallic nickel atoms. The adsorption heats decreased sharply to lower than 80 kJ/mol with the increase of coverage of toluene, indicating the beginning of adsorption of toluene on acidic sites. Interestingly, the initial heats of toluene adsorption on metallic nickel seemed to be re-

lated to the surface acidity of the catalysts. High initial heat was generated when toluene was adsorbed on metallic nickel in the Ni/Al₂O₃ catalysts with higher surface acidity. Since the initial heat was lower than 120 kJ/mol for the adsorption of toluene on acidic sites, the higher heat generated by the adsorption of toluene on metallic nickel sites might be due to the effect of adjacent acidic sites. In fact, the acidic sites might attract electron charges from adjacent nickel atoms, leading to the electron-deficient nickel sites, which favored the donation of electron charges from the aromatic rings of toluene to the electron-deficient d orbitals of surface nickel atoms. Thus, the adsorption of toluene on metallic nickel could be enhanced by the presence of adjacent acidic sites.

Although the treatment with *n*-butanol had little effect on the surface acidity of Ni/Al₂O₃ catalysts, the initial heats of toluene adsorption on the 60Ni/Al₂O₃ (158 kJ/mol) and 80Ni/Al₂O₃ (145 kJ/mol) were significantly lower than that (179 kJ/mol) on the 60Ni/Al₂O₃-B and 80Ni/Al₂O₃-B. Thus, the density of surface metallic nickel sites seemed to be another factor affecting the adsorption of toluene. The Ni/Al₂O₃-B catalysts with higher density of nickel sites exhibited higher heats for the adsorption of toluene.

Fig. 7. Differential heat vs. coverage for toluene adsorption at 308 K on the Ni/Al₂O₃ catalysts reduced and evacuated at 723 K.

2.4 Catalytic hydrogenation

Figure 8 presents the results for the hydrogenation of toluene at 423 K over the Ni/Al₂O₃ catalysts reduced at 723 K. Methyl cyclohexane was found to be the only product and the conversion of toluene decreased with the WHSV of toluene for the reaction on the catalysts. The conversion of toluene was 50% and 45% over the 60Ni/Al₂O₃-B and 80Ni/Al₂O₃-B, respectively, while it was only 8% over the 90Ni/Al₂O₃-B, at the WHSV of toluene of 106 h⁻¹. At the same WHSV of toluene, the conversion of toluene was 39% and 11% over the 60Ni/Al₂O₃ and 80Ni/Al₂O₃, respectively.

These results showed that the 60Ni/Al₂O₃-B and 80Ni/Al₂O₃-B exhibited higher conversions of toluene than the 60Ni/Al₂O₃ and 80Ni/Al₂O₃, indicating that the treatment with *n*-butanol improved the activity of the Ni/Al₂O₃ catalysts for the hydrogenation of toluene.

Fig. 8. Conversion of toluene vs. WHSV (toluene) on the Ni/Al₂O₃ catalysts reduced at 723 K. Reaction conditions: $p = 1$ atm, $T = 423$ K, and H_2 /toluene = 5.

Fig. 9. Conversion of phenol vs. WHSV (phenol) on the Ni/Al₂O₃ catalysts reduced at 723 K. Reaction conditions: $p = 1$ atm, $T = 423$ K, and H_2 /phenol = 5.

Figure 9 shows the results for the hydrogenation of phenol at 423 K over the Ni/Al₂O₃ catalysts reduced at 723 K. Cyclohexanol was found to be the main product over the catalysts, with a small amount of cyclohexanone, especially over the 90Ni/Al₂O₃-B at the higher WHSV of phenol (data not presented). No other byproducts were observed. Fig. 9 shows that the conversion of phenol decreased with WHSV for the hydrogenation of phenol on the catalysts. The 80Ni/Al₂O₃-B and 60Ni/Al₂O₃-B exhibited the similar high activity for the conversion of phenol with the different WHSV of phenol from 70 to 411 h⁻¹. In contrast, the

90Ni/Al₂O₃-B showed the low activity for the reaction. At 411 h⁻¹, the conversion of phenol was 45%, 42%, and 7% over the 60Ni/Al₂O₃-B, 80Ni/Al₂O₃-B, and 90Ni/Al₂O₃-B, respectively. At the same WHSV of phenol, the conversion of phenol was 13% and 7% over the 60Ni/Al₂O₃ and 80Ni/Al₂O₃, respectively. Therefore, the treatment with *n*-butanol improved significantly the activity of Ni/Al₂O₃ catalysts for the hydrogenation of phenol.

The 90Ni/Al₂O₃-B with highest loading of nickel possessed the lowest active surface area of nickel and surface acidity in the series of Ni/Al₂O₃-B catalysts. Thus, it adsorbed toluene with the relatively lower initial heat and coverage as compared to other catalysts in the series. Accordingly, it exhibited relatively low activities for the hydrogenation of toluene and phenol. The activity of supported metal catalysts for the hydrogenation of aromatic rings depended not only on the accessible active sites of surface metals, but also on the surface acid-base properties [38]. Although the 80Ni/Al₂O₃-B possessed more active sites of surface nickel than the 60Ni/Al₂O₃-B, the two catalysts exhibited the similar activities for the hydrogenation of toluene and phenol. The 60Ni/Al₂O₃-B was even slightly more active than the 80Ni/Al₂O₃-B for the hydrogenation of toluene and phenol at the higher WHSV of reactants. These results might be due to that the 60Ni/Al₂O₃-B possessed stronger surface acidity than the 80Ni/Al₂O₃-B [39], as measured by the microcalorimetric adsorption of ammonia. The surface Lewis acidity dominated on the Ni/Al₂O₃ catalysts [40]. Apparently, the surface acidity played a key role for the hydrogenation of aromatic rings, besides the number of active sites of surface nickel. Toluene can be taken as a Lewis base due to its enriched electron density on the aromatic ring with a π -bond. Thus, the surface acidity favored the adsorption and activation of aromatic rings, even for the acidic phenol [39]. The activities for the hydrogenation of toluene and phenol were higher on the Ni/Al₂O₃-B than on the Ni/Al₂O₃, since the treatment with *n*-butanol increased the number of active sites of surface nickel on the Ni/Al₂O₃-B catalysts.

3 Conclusions

Ni/Al₂O₃ catalysts with high loadings of nickel (60%–90% weight percent) were prepared by the co-precipitation method. It was found that the loading and drying process were the two important factors in determining the number of active surface nickel atoms in the catalysts. The increase of loading of nickel increased the reducibility but decreased the dispersion of supported nickel. The 80%Ni/Al₂O₃ exhibited relatively high loading and high dispersion of nickel. In addition, use of *n*-butanol during the drying process significantly increased the surface

area of catalysts and the dispersion of nickel, leading to the significantly increased number of active surface nickel sites. Characterizations showed that the reduced nickel particles on the Al₂O₃ support could be as small as 4 nm, even at the high loading of 80wt%. Such catalysts with the high loading and dispersion possessed high active nickel surface areas and thus were highly active for the hydrogenation of aromatic rings in toluene and phenol. It was also found that the adsorption of toluene on nickel surface generated high initial heats, which seemed to increase with the increase of number of surface active nickel atoms and surface acidity of the Ni/Al₂O₃ catalysts. Thus, the catalysts treated with *n*-butanol adsorbed toluene more strongly and therefore exhibited higher activity for the hydrogenation of toluene and phenol, probably due to the more surface active nickel atoms and stronger surface acidity of the catalysts.

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