

Effect of Nickel Particle Size on Alumina Supported Nickel Catalysts for *p*-Nitrophenol Hydrogenation

Y. Du and R. Chen^{*,+}

College of Urban Construction and Safety & Environmental Engineering,
Nanjing University of Technology, Nanjing 210009, PR China

^{*}College of Chemistry and Chemical Engineering,
Nanjing University of Technology, Nanjing 210009, PR China

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The catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol was investigated over alumina supported nickel catalysts prepared by impregnation reduction method and mechanical mixing method. The catalysts were characterized by XRD and FESEM. The results show that the nickel particle diameter of alumina supported nickel prepared by impregnation reduction method (denoted as Ni/Al₂O₃) is slightly smaller than that of alumina supported nickel prepared by mechanical mixing method (denoted as Ni+Al₂O₃), and the catalytic activity of Ni/Al₂O₃ is higher. The nickel particle size of Ni/Al₂O₃ would increase as Ni/Al₂O₃ is reduced in hydrogen for 2 h at 270 °C and 600 °C, respectively, and its catalytic activity correspondingly decreases. These imply that the reaction is structure sensitive and the smaller nickel particle diameter is beneficial to obtain a higher catalytic activity. However, the nickel particle diameter almost has no influence on the catalytic selectivity of the *p*-nitrophenol hydrogenation to *p*-aminophenol

Key words:

p-nitrophenol, catalytic hydrogenation, alumina supported nickel, nano-sized nickel

Introduction

p-Aminophenol is an important intermediate in the preparations of analgesic and antipyretic drugs.^{1–5} Various methods have been reported to synthesize *p*-aminophenol, such as iron-acid reduction of *p*-nitrochlorobenzene or *p*-nitrophenol,¹ catalytic hydrogenation of nitrobenzene,^{1–3} and an electrochemical synthesizing method.⁴ The major disadvantage of the iron-acid reduction is the generation of large amounts of Fe-FeO sludge, which cannot be reused and causes severe disposal problems.^{1,2} The catalytic hydrogenation of nitrobenzene in a strong acid aqueous medium is an important commercial method, but it also has two major drawbacks: (1) the formation of side products such as aniline; and (2) the use of highly corrosive mineral acid.

In order to meet the growing demand of *p*-aminophenol, the direct catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol is becoming important, because this could be an efficient and greener route.⁵ Raney nickel,⁶ nano-sized nickel⁶ and several noble metals such as Pt/C⁵ have been used as catalysts for this reaction. Due to lower price and higher catalytic activity, supported nickel catalysts, such as Ni/Al₂O₃ catalysts, is widely used

in various hydrogenation reactions.^{7–9} Moreover, compared with nano-sized nickel catalysts, the supported nickel catalysts are easy to be recovered by membrane separation process. There have been few reports of the catalytic hydrogenation of *p*-nitrophenol over supported nickel catalysts.

In this paper, we have attempted to perform the catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol over alumina supported nickel catalysts prepared by impregnation reduction method and mechanical mixing method. The samples were characterized by different techniques in order to correlate the catalytic activity with the characteristics of the catalysts. The effects of nickel particle diameter on catalytic properties of alumina supported nickel catalysts were studied.

Experimental

Catalyst preparation

Nonporous Al₂O₃ with a mean particle diameter of $d_p = 22.8 \mu\text{m}$, supplied by Zhengzhou Fuwei New Materials Co. Ltd., PR China, was used as a support. Alumina supported nickel catalyst prepared by the impregnation reduction method is marked as Ni/Al₂O₃. The preparation procedure is as follows. First, 10 g Al₂O₃ calcined in stagnant air at 500 °C for 4 h was impregnated with 45 ml

⁺Corresponding author. Tel.: +86-25-83587502; Fax: +86-25-83300345; E-mail address: rizhichen@163.com.

NiSO₄ aqueous solution ($c = 0.44 \text{ mol L}^{-1}$) for 8 h under low magnetic stirring. Then it was dried at 110 °C with gentle stirring overnight to exclude residual water. 5 g precursor was reduced by adding 8 ml hydrazine hydrate (N₂H₄ · H₂O) alkaline solution, during which the mole ratio of N₂H₄ · H₂O to Ni²⁺ was controlled at 2 : 1, the solution temperature was controlled at 85 °C, and the mixture was vigorously stirred. The resulting Ni/Al₂O₃ catalyst was washed with deionized water, followed by ethanol, and then dried in oven at 80 °C. The nickel content was analyzed by inductively coupled plasma (ICP, Optima 2000DV) after extraction with nitric acid. In addition, some Ni/Al₂O₃ samples were reduced in a H₂/He mixture ($\varphi = 10 \% \text{ H}_2$) for 2 h at 270 °C and 600 °C, respectively.

Alumina supported nickel catalyst prepared by mechanical mixing of the nano-sized nickel and Al₂O₃ is designated as Ni+Al₂O₃. The used nano-sized nickel was prepared according to the literature.⁶

Catalyst characterization

X-ray powder diffraction (XRD) patterns were obtained on a Bruker D8 instrument with Ni-filtered Cu K α radiation ($\lambda = 0.154 \text{ nm}$) at 40 kV and 30 mA, employing a scanning rate of $0.05^\circ \cdot \text{s}^{-1}$ in the 2θ range from 42° to 55°.

The morphology and particle diameter of the supported nickel were observed by field emission scanning electron microscopy (FESEM, LEO1530VP).

Hydrogenation experiments

The catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol was carried out in a 300 ml stainless steel autoclave equipped with a magnetically driven impeller. After definite amounts of catalysts and $m = 14 \text{ g}$ *p*-nitrophenol in 163 ml ethanol solution were introduced into the autoclave, it was sealed and purged with hydrogen for five times to remove air. The reactor was then heated under low stirring ($n = 80 \text{ min}^{-1}$). When the temperature reached $T = 102 \text{ }^\circ\text{C}$, the stirring speed was increased to $n = 320 \text{ min}^{-1}$, and at the same time hydrogen was fed to the predetermined pressure ($p = 1.7 \text{ MPa}$). As the pressure decreased to $p = 1.6 \text{ MPa}$, the hydrogen was fed to $p = 1.7 \text{ MPa}$ again. When the pressure kept constant, we considered that the hydrogenation reaction had been over. The products were analyzed by a HPLC system (Agilent 1100 Series, USA) equipped with a diode array detector (DAD) and an auto-sampler. Chromatographic separations were performed at 35 °C using a ZORBAX Eclipse XDB-C18, 5 μm , 4.6 mm · 250 mm column. A mobile phase composed of $\Psi_{\text{H}_3\text{COH/H}_2\text{O}} = 0.8 : 0.2$ at a flow rate of $Q = 1 \text{ ml} \cdot \text{min}^{-1}$ was used.

Results and discussion

Catalyst characterization

The nickel loadings Ni+Al₂O₃ and Ni/Al₂O₃ are analyzed by ICP, and both are $w = 10.3 \%$. The XRD patterns of Al₂O₃, Ni+Al₂O₃ and Ni/Al₂O₃ are shown in Fig. 1. For the Ni+Al₂O₃ and Ni/Al₂O₃ samples, the characteristic peak of crystalline Ni (typically with $2\theta = 44.5^\circ$) marked by Miller index (1 1 1) is observed,¹⁰ respectively, as shown in Fig. 1(b) and (c). Fig. 2 shows the XRD patterns of Ni/Al₂O₃ reduced in hydrogen for 2 h at 270 °C and 600 °C, respectively. It is found from Fig. 2 and Fig. 1(c), when the Ni/Al₂O₃ sample is reduced in hydrogen the diffraction peak of crystalline Ni becomes sharp, and the trend is more obvious at a higher reduction temperature. The results show that the grain size of nickel becomes larger as the Ni/Al₂O₃ is reduced in hydrogen at a higher temperature. It is also found that, with respect to the Ni/Al₂O₃ reduced in hydrogen at 600 °C for 2 h, the characteristic peak of crystalline Ni (typically with $2\theta = 52.1^\circ$) marked by Miller index (2 0 0) can be observed.¹⁰ What is more, the color of the Ni/Al₂O₃ sample becomes gray from black when it is reduced in hydrogen at 600 °C for 2 h.

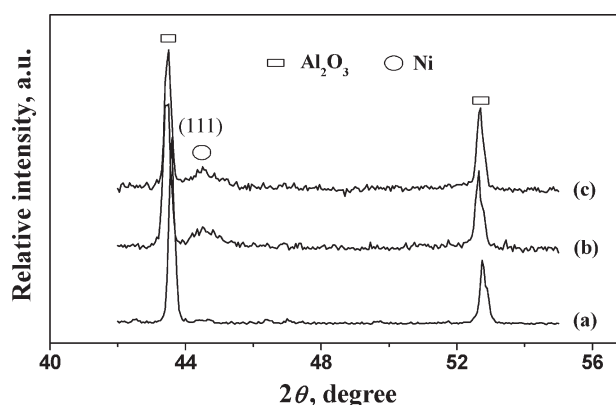


Fig. 1 – XRD patterns of samples: (a) Al₂O₃; (b) Ni + Al₂O₃; (c) Ni/Al₂O₃

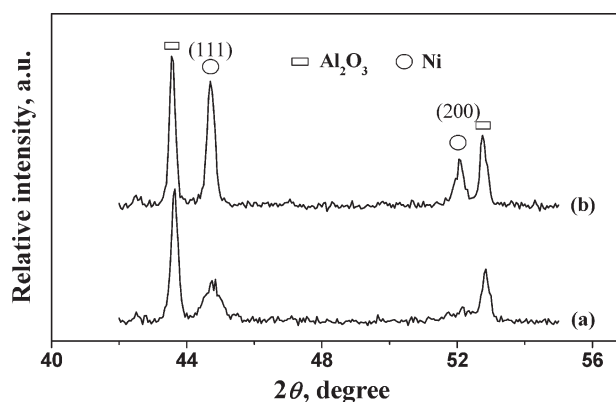


Fig. 2 – XRD patterns of samples: (a) Ni/Al₂O₃ reduced in hydrogen at 270 °C for 2 h; (b) Ni/Al₂O₃ reduced in hydrogen at 600 °C for 2 h

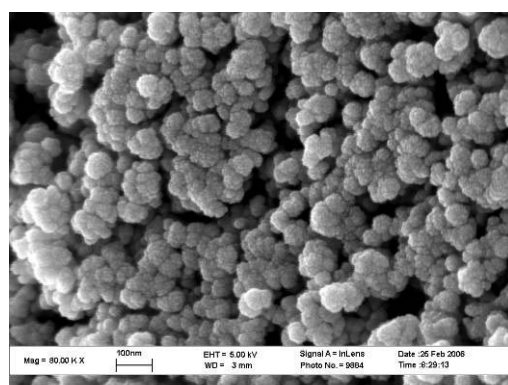
The FESEM micrographs of Ni+Al₂O₃ and Ni/Al₂O₃ are shown in Fig. 3. It can be found that the agglomeration of the nano-sized nickel particles for Ni+Al₂O₃ is more serious than that for Ni/Al₂O₃. With respect to Ni/Al₂O₃, the average diameter of nickel is about 40 nm and smaller than that of Ni+Al₂O₃ (the average diameter: $d_p = 50$ nm). Fig. 4 shows the FESEM micrographs of Ni/Al₂O₃ reduced in hydrogen for 2 h at 270 °C and 600 °C, respectively. In addition, the average diameter of the corresponding nickel is severally 47 nm and 65 nm. Compared with the fresh Ni/Al₂O₃ sample, the nickel particle diameter of Ni/Al₂O₃ reduced in hydrogen at 270 °C for 2 h is slightly larger. However, for the Ni/Al₂O₃ reduced in hydrogen at 600 °C for 2 h, the nickel particle diameter is clearly larger, as shown in Fig. 4(b), and the particle diameter of some nickel particles has been larger than 100 nm. The results show that the nickel particle diameter of Ni/Al₂O₃ will obviously increase as it is reduced in hydrogen at a higher temperature. These results are also indicated by the XRD characterization.

Catalytic properties

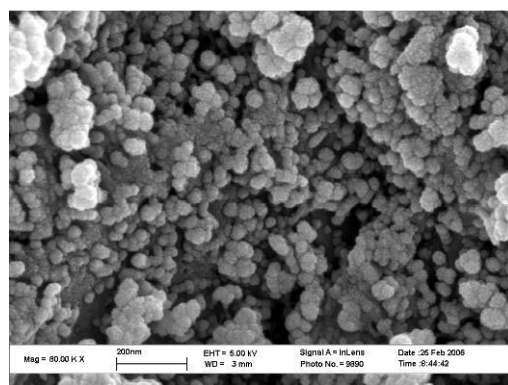
The preliminary experiments on the hydrogenation of *p*-nitrophenol indicate that no hydrogenation

reaction occurs in the absence of the catalyst, which confirms the absence of any non-catalytic reaction. Moreover, at a fixed temperature, the partial pressure of solvent ethanol-water also remains constant. So, the decrease of pressure in the reactor with time is caused only by catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol. Therefore, in this paper catalytic activity could be expressed by reaction rate defined as the amount of hydrogen consumed per minute and per gram nickel.⁶

The catalytic activities (expressed as the reaction rates at 20 min) of Ni+Al₂O₃ and Ni/Al₂O₃ in the hydrogenation of *p*-nitrophenol to *p*-aminophenol are shown in Fig. 5. It can be found, compared with Ni+Al₂O₃, the catalytic activity of Ni/Al₂O₃ is obviously higher. Combined with the foregoing results from XRD and FESEM, as shown in Fig. 1 and Fig. 3, it can be concluded that the smaller nickel particle diameter is responsible for the higher catalytic activity of Ni/Al₂O₃. In order to further study the effect of nickel particle diameter on the catalytic activity of alumina supported nickel, the Ni/Al₂O₃ sample was reduced in hydrogen for 2 h at 270 °C and 600 °C, respectively, and then their catalytic activities were investigated in

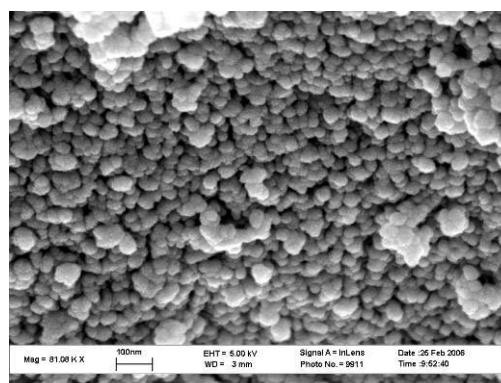


(a)

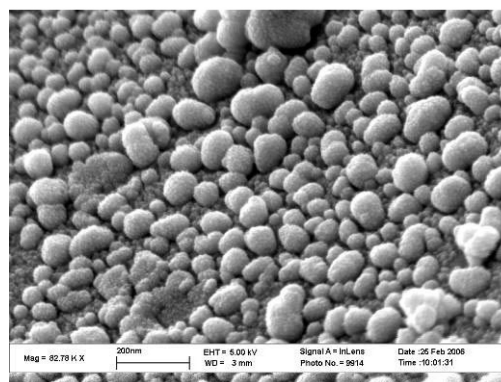


(b)

Fig. 3 – FESEM micrographs of samples: (a) Ni + Al₂O₃; (b) Ni/Al₂O₃



(a)



(b)

Fig. 4 – FESEM micrographs of samples: (a) Ni/Al₂O₃ reduced in hydrogen at 270 °C for 2 h; (b) Ni/Al₂O₃ reduced in hydrogen at 600 °C for 2 h

the *p*-nitrophenol hydrogenation reaction. The results are shown in Fig. 5, and for the sake of comparison, the result of Raney nickel (provided by Anhui Bayi Chemical Co. Ltd., PR China) is also presented. It is obvious that the catalytic activity of Ni/Al₂O₃ decreases when it is reduced in hydrogen at different temperatures and the attenuation ratio becomes more obvious at a higher reduction temperature of 600 °C. The catalytic activity of Ni/Al₂O₃ reduced in hydrogen at 600 °C for 2 h is only 11.6 % of that of the fresh Ni/Al₂O₃ sample and closed to that of Raney nickel. Combined with the XRD and FESEM results of Ni/Al₂O₃ samples, we can find that there is a comparatively good correlation between the nickel particle diameter and the catalytic activity of Ni/Al₂O₃; the smaller the nickel particle diameter, the higher the catalytic activity. These results clearly announce that the hydrogenation of *p*-nitrophenol to *p*-aminophenol is structure sensitive, the nickel particle diameter has a great influence on the catalytic activity of alumina-supported nickel and the smaller nickel particle diameter is beneficial to obtain a higher catalytic activity. Ermakova et al.¹¹ also found that the hydrogenation rate increased with decreasing average size of loaded nickel with respect to the reaction of benzene hydrogenation. However, if the behaviour of Ni+Al₂O₃ was put together for comparison, it seems to conflict the above conclusion: compared with Ni+Al₂O₃, the nickel particle diameter (47 nm) of Ni/Al₂O₃ reduced at 270 °C is slightly smaller, as shown in Fig. 3(a) and Fig. 4(a), but the catalytic activity of that is slightly lower. The possi-

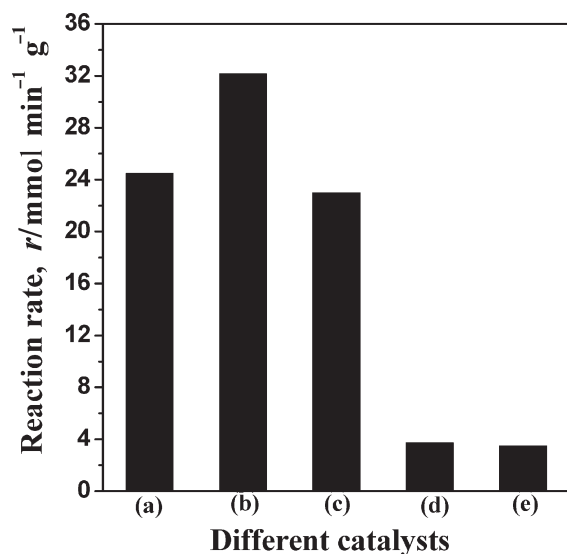


Fig. 5 – Reaction rate of *p*-nitrophenol hydrogenation over various catalysts: (a) Ni+Al₂O₃ (catalyst, 1.5 g); (b) Ni/Al₂O₃ (catalyst, 1.5 g); (c) Ni/Al₂O₃ reduced in hydrogen at 270 °C for 2 h (catalyst, 1.5 g); (d) Ni/Al₂O₃ reduced in hydrogen at 600 °C for 2 h (catalyst, 1.5 g); (e) Raney nickel (catalyst, 0.155 g)

ble reason is owed to the decrease of the defect sites on the nickel particle surface due to the high-temperature reduction of Ni/Al₂O₃.

HPLC analysis results show that the content of *p*-aminophenol in the products is all more than 98 % for the hydrogenation reactions catalyzed by Ni+Al₂O₃, Ni/Al₂O₃ and Ni/Al₂O₃ reduced in hydrogen at different temperatures, which indicate that the nickel particle diameter has no influence on the catalytic selectivity of alumina supported nickel in the *p*-nitrophenol hydrogenation reaction.

Conclusions

Alumina supported nickel catalysts were prepared by impregnation reduction method and mechanical mixing method, and characterized by XRD and FESEM. Catalyst characterization results show that the nickel particle diameter of alumina supported nickel Ni/Al₂O₃ prepared by impregnation reduction method is smaller than that of alumina supported nickel Ni+Al₂O₃ prepared by mechanical mixing method and the nickel particle diameter of Ni/Al₂O₃ will obviously increase as it is reduced in hydrogen at a higher temperature. The catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol was investigated over alumina supported nickel catalysts in a laboratory-scale batch-slurry reactor. It is found that the nickel particle diameter has a great influence on the catalytic activity of Ni/Al₂O₃ and the smaller nickel particle diameter is beneficial to obtain a higher catalytic activity. HPLC analysis results show that the nickel particle diameter has no influence on the catalytic selectivity of alumina-supported nickel in the hydrogenation reaction of *p*-nitrophenol to *p*-aminophenol.

List of symbol

- c – concentration, mol L⁻¹
- d_p – particle diameter, nm, μm
- m – mass, g
- n – stirring speed, min⁻¹
- p – pressure, MPa
- Q – volume flow rate, mL min⁻¹
- r – reaction rate, mmol min⁻¹ g⁻¹
- T – temperature, °C
- Θ – Bragg angle, °
- V – volume, ml
- φ – volume fraction, 1
- Ψ – volume ratio $V_{\text{H}_3\text{COH}}/V_{\text{H}_2\text{O}}$

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