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Effect of Alumina Particle Size on Ni/Al_2O_3 Catalysts for *p*-Nitrophenol Hydrogenation*

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Abstract The catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol was investigated over Ni/Al_2O_3 catalyst on alumina support with different particle size. It is found that support particle size has significant influences on physiochemical properties and catalytic activity of the resulting Ni/Al_2O_3 catalyst, but little influence on the selectivity. At a comparable amount of Ni loading, the catalytic activity of Ni/Al_2O_3 prepared with alumina support of smaller particle size is lower. The reduction behavior of the catalyst is a key factor in determining the catalytic activity of Ni/Al_2O_3 catalyst. The supported nickel catalyst $10.3Ni/Al_2O_3$-3 improves the life span of the membrane by reducing fouling on the membrane surface compared to nano-sized nickel.
Keywords *p*-nitrophenol, catalytic hydrogenation, *p*-aminophenol, Ni/Al_2O_3 catalysts, ceramic membrane filtration

1 INTRODUCTION

p-Aminophenol is of great commercial importance as an intermediate for the preparation of analgesic and antipyretic drugs[1—4]. In view of the growing demand for *p*-aminophenol, direct catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol becomes important, because this could be an efficient and greener route[5]. Up to now, some works have been reported on the liquid phase *p*-nitrophenol hydrogenation over Raney nickel[6], nano-sized nickel[7,8] and several noble metal catalysts such as Pt/C[5]. Our previous works have shown that the catalytic properties of nano-sized nickel have been proved to be superior to those of Raney nickel[8]. However, during the application of nano-sized nickel to membrane-based catalyst separation, it was found that nano-sized nickel particles would easily adsorb on the surface of pipeline, tank and membrane, which caused the decrease of catalyst concentration in reaction slurry and led to consequent decline in reaction rate and permeate flux of the membrane[9]. Due to their low cost and high catalytic activity, supported nickel catalysts are widely used in various reactions[10—13]. Moreover, compared to nano-sized nickel catalysts, the supported nickel catalysts are easy to be recovered by membrane separation process. More significantly, it is efficient to maintain high flux of membrane. So it is desired to find a supported nickel catalyst with better membrane filtration performance and comparable catalytic activity to replace nano-sized nickel. There are few reports on the catalytic hydrogenation of *p*-nitrophenol over supported nickel catalysts[14].

Therefore, this work is attempted to perform the catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol over Ni/Al_2O_3 catalysts. The catalysts were prepared by liquid-phase chemical reduction method, and were characterized by inductively coupled plasma (ICP), X-ray powder diffraction (XRD), X-ray photoelectron spectra (XPS) and temperature-programmed reduction (TPR) in order to correlate the catalytic activity with the characteristics of the catalysts. The effect of alumina support particle size on the physiochemical and catalytic properties of Ni/Al_2O_3 catalysts was studied. At the same time, the membrane filtration performance of Ni/Al_2O_3 suspension and nano-sized nickel suspension was compared.

2 EXPERIMENTAL

2.1 Catalyst preparation

A series of Ni/Al_2O_3 samples were prepared by a liquid-phase chemical reduction method. Nonporous Al_2O_3 supports of three different mean particle sizes, *i.e.*, 1.3μm, 11.2μm, 22.8μm, measured by Mastersizer 2000 (Malvern, UK), were supplied by Zhengzhou Fuwei New Materials Co., China and designated as Al_2O_3-1, Al_2O_3-2, Al_2O_3-3, respectively. 10g of Al_2O_3 calcined at 500℃ for 4h in stagnant air was impregnated with 45ml of $0.42mol\cdot L^{-1}$ aqueous $NiSO_4$ solution for 8h under low magnetic stirring, was dried at 110℃ under gentle stirring overnight to exclude residual water. 5g precursor was reduced by adding 8ml of hydrazine hydrate ($N_2H_4\cdot H_2O$) alkaline solution, during which the mole ratio of $N_2H_4\cdot H_2O$ to Ni^{2+} was controlled at 2∶1 and the mixture was vigorously stirred. The resulting Ni/Al_2O_3 catalyst was washed with deionized water at first, then by ethanol, and finally dried at 80℃ in oven to get the black powders of supported nickel. The nickel content in all samples was analyzed by inductively coupled plasma (ICP, Optima 2000DV, PerkinElmer, USA) after extraction with nitric acid. The resulting catalysts were denoted as *x*Ni/support, where *x* is the actual nickel loading.

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2.2 Catalyst characterization

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

X-ray photoelectron spectra (XPS) were obtained on an ESCALAB MK II system with a base pressure of 1×10^{-4}Pa. Mg K_α radiation source ($h\nu$=1253.6eV) was used in the XPS measurements. The C_{1s} signal (285eV) was taken as the reference to calculate the binding energies.

Temperature-programmed reduction (TPR) was carried out in a quartz U-tube reactor, and 100mg sample was used for each measurement. Prior to the reduction, the sample was pretreated in a N_2 stream at 100℃ for 30min and then cooled down to room temperature. After that, the H_2/Ar mixture (10% H_2 by volume) was switched on and the temperature was raised from 30℃ to 800℃ at a rate of $10℃\cdot min^{-1}$. The consumption of H_2 in the reactant stream was detected by a thermal conductivity cell.

2.3 Hydrogenation experiment

The catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol was carried out in a 300ml stainless steel autoclave equipped with a magnetically driven impeller. After given amounts of one catalyst and 14g of *p*-nitrophenol in 163ml ethanol were introduced, the autoclave was sealed and purged with hydrogen five times to remove air; then, the reactor was heated to a desired temperature under low stirring ($80r\cdot min^{-1}$), hydrogen gas was introduced into the reactor to a preset level, and the slurry were stirred at $320r\cdot min^{-1}$. The preliminary experiments proved that the hydrogenation reaction conducted at a stirring speed above $300r\cdot min^{-1}$ is not influenced by external diffusion. Finally, the hydrogenation reaction was performed at 102℃ and 1.65MPa. After the hydrogenation reaction was finished, 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℃ using a ZORBAX Eclipse XDB-C18, 5μm, 4.6mm×250mm column. A mobile phase composed of 80% methanol and 20% water at a flow rate of $1ml\cdot min^{-1}$ was used.

2.4 Membrane filtration experiment

In order to determine the membrane filtration behavior of the supported nickel catalyst, especially the effect of its presence on the permeate flux, the filtration performance of a nano-sized nickel catalyst suspension and a 10.3Ni/Al_2O_3-3 catalyst suspension with the same nickel concentration were performed. An asymmetric tubular ceramic membrane with 12mm outer diameter and 8mm inner diameter was used for the filtration experiments. The membrane was made up of a fine layer of α-Al_2O_3 with nominal pore size of 0.5μm on the outwall of a tubular α-Al_2O_3 porous support, and was provided by Nanjing Jiusi High-Tech Co., China. Nano-sized nickel particles with a mean size of 60nm were provided by Nanjing Jiusi High-Tech Co., China. During the filtration experiments the catalyst particles were suspended in deionized water by stirring. The filtration was continuously obtained by using a suction pump at a transmembrane pressure of 0.08MPa and a temperature of 25℃. After each run of experiments the membrane was cleaned with 10% (by volume) nitric acid and then rinsed with deionized water.

3 RESULTS AND DISCUSSION

3.1 Catalyst characterization

The XRD patterns of 10.3Ni/Al_2O_3-1, 9.8Ni/Al_2O_3-2, 10.3Ni/Al_2O_3-3 are shown in Fig.1. When alumina with small particle size is used as the support, no characteristic peaks of crystalline Ni can be observed, as shown in pattern (a). The result indicates that Ni is highly dispersed on the surface of Al_2O_3-1. For the samples that use Al_2O_3-2 and Al_2O_3-3 as supports and have a comparable Ni loading, however, the characteristic peak of crystalline Ni [2θ= 44.5°, corresponding to the Miller index (111)] is observed, respectively, as shown in patterns (b) and (c) in Fig.1. Compared to 9.8Ni/Al_2O_3-2, 10.3Ni/Al_2O_3-3 shows a slightly sharper characteristic peak of crystalline Ni. These results show that alumina support particle size can greatly influence the dispersion of Ni loaded, and with catalysts using alumina of smaller size having the higher Ni dispersion. This is because alumina support of smaller size has higher specific surface area and thus provides more space for Ni deposition, resulting in better Ni dispersion.

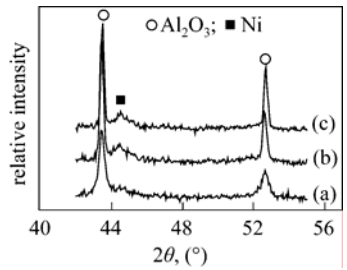

Figure 1 XRD patterns of the samples
(a) 10.3Ni/Al_2O_3-1; (b) 9.8Ni/Al_2O_3-2; (c) 10.3Ni/Al_2O_3-3

The XPS results of 10.3Ni/Al_2O_3-1, 9.8Ni/Al_2O_3-2, 10.3Ni/Al_2O_3-3 are shown in Fig.2 and Table 1. The Ni_{2p} spectra and the binding energies of $Ni_{2p3/2}$ show that nickel on the surfaces of the three samples is oxidized completely[15], and no obvious difference exists in their Ni_{2p} spectra. It is obvious from Table 1 that the surface Ni/Al atomic ratio increases with the increasing particle size of alumina support. This can be explained as follows: the ratio of alumina surface covered by Ni increases with increasing alumina support particle size, hence, the Ni atoms detected by XPS at certain surface area of alumina support increases with the increasing alumina support particle size, *viz.*, the surface Ni/Al atomic ratio for the sample using alumina of larger particle size as support is

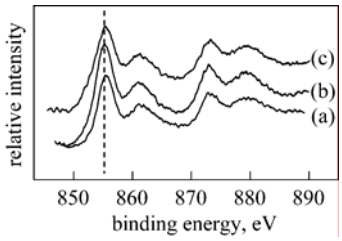

Figure 2 XPS spectra of Ni_{2p} for the samples
(a) 10.3Ni/Al_2O_3-1; (b) 9.8Ni/Al_2O_3-2; (c) 10.3Ni/Al_2O_3-3

Table 1 XPS results of surface elements of catalysts

Catalysts	Binding energy of $Ni_{2p3/2}$, eV	Surface Ni/Al atomic ratio
10.3Ni/Al_2O_3-1	855.4	0.6
9.8Ni/Al_2O_3-2	855.3	1.3
10.3Ni/Al_2O_3-3	855.3	1.5

higher.

Figure 3 shows the TPR profiles of the samples. For the Al_2O_3-3, Al_2O_3-2 and Al_2O_3-1 samples, no obvious H_2 consumption can be observed at temperatures lower than 800℃, as shown in profiles (a), (b) and (c) in Fig.3. The reduction profile of 10.3Ni/Al_2O_3-3 shows a broad hydrogen consumption band between 110℃ and 600℃. The reduction at low temperature from 110℃ to 260℃ may be ascribed to the reduction of Ni_2O_3, which was also found by Hardiman *et al*.[16]. The reduction at high temperature is probably due to the reductions of bulk NiO and NiO with stronger interaction with the support[17]. The reduction peaks of 9.8Ni/Al_2O_3-2 and 10.3Ni/Al_2O_3-1 have profiles basically similar to those of 10.3Ni/Al_2O_3-3. However, it is interesting to note that the onset temperature and the temperature of maximum reduction (T_M) obviously increase with the decreasing alumina support particle size. The results indicate that a stronger interaction between Ni and alumina support of smaller particle size exists, possibly due to the lower stacking height of nickel[18,19]. Comparing the profiles (d), (e) and (f), it is noted that the reduction peak areas are significantly different, and follow the order of 10.3Ni/Al_2O_3-1 > 9.8Ni/Al_2O_3-2 > 10.3Ni/Al_2O_3-3, signifying that the oxidation degree of Ni supported on alumina support of smaller particle size is comparatively higher. These results indicate that the reduction of nickel oxide to metallic nickel for the sample using alumina of smaller particle size as support is more difficult. Such discrepancies are also reflected in catalytic activities of these catalysts. The TPR results show the existence of nickel oxide on the surface of nickel, as also revealed by the XPS characterization.

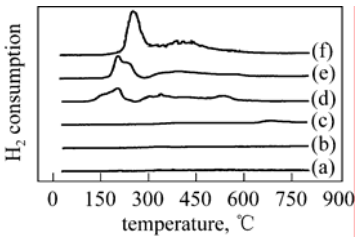

Figure 3 TPR profiles of the samples
(a) Al_2O_3-3; (b) Al_2O_3-2; (c) Al_2O_3-1; (d) 10.3Ni/Al_2O_3-3; (e) 9.8Ni/Al_2O_3-2; (f) 10.3Ni/Al_2O_3-1

3.2 Catalytic properties

The preliminary experiments on the hydrogenation of *p*-nitrophenol indicate that no hydrogenation reaction occurs in the absence of the catalyst, confirming the absence of any noncatalytic reaction. Moreover, at a fixed temperature, the partial pressure of solvent ethanol-water also remains constant. So, the decrease in the pressure in the reactor with time is caused only by catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol. Therefore, the catalytic activity could be expressed by the reaction rate defined as the amount of hydrogen consumed per minute and per gram nickel.

Figure 4 shows the catalytic activity (expressed as the reaction rates at 20min) of 10.3Ni/Al_2O_3-1, 9.8Ni/Al_2O_3-2, 10.3Ni/Al_2O_3-3 in the hydrogenation of *p*-nitrophenol to *p*-aminophenol, and for comparison purpose, the result of the nano-sized nickel catalyst with a mean particle size of 60nm is also presented. It can be found that compared to the nano-sized nickel catalyst, 10.3Ni/Al_2O_3-3 has higher catalytic activity, but the other two as-prepared Ni/Al_2O_3 catalysts have lower ones. It is worth noting that the catalytic activities of the three alumina supported nickel catalysts are significantly different at a comparable Ni loading, and the catalytic activity order is as follows: 10.3Ni/Al_2O_3-1 < 9.8Ni/Al_2O_3-2 < 10.3Ni/Al_2O_3-3. The result clearly shows that the alumina support particle size has great influence on the catalytic activity of Ni/Al_2O_3. Together with the XRD characterization results mentioned above, it is interesting to find that the catalytic activity order of Ni/Al_2O_3 is opposite to that of the nickel dispersion: the higher the nickel dispersion, the lower the catalytic activity. Combining these results with those of the TPR measurements as shown in Fig.3, it can be found

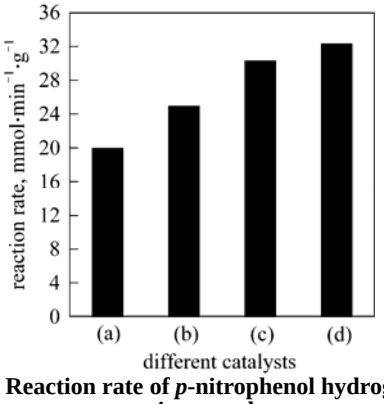

Figure 4 Reaction rate of *p*-nitrophenol hydrogenation over various catalysts
(a) 10.3Ni/Al_2O_3-1 (catalyst, 1.5g); (b) 9.8Ni/Al_2O_3-2 (catalyst, 1.5g); (c) nano-sized nickel (catalyst, 0.155g); (d) 10.3Ni/Al_2O_3-3 (catalyst, 1.5g)

that there is a very good correlation between the TPR data and the catalytic activity of Ni/Al_2O_3: the more difficult the reduction of nickel oxide to metallic nickel, the lower the catalytic activity. Therefore, one reasonable conclusion is that for the Ni/Al_2O_3 using alumina of smaller particle size as support the reduction of nickel oxide to metallic nickel is more difficult under the similar reaction conditions, and as a result, the amounts of metallic nickel for this catalyst are few at a comparable Ni loading, and the corresponding catalytic activity is lower. Rode *et al*.[20] also found that the catalytic activity was higher for the supported nickel catalyst having a smaller degree of nickel dispersion in the gas-phase hydrogenation of benzonitrile and acetonitrile. They suggested that the surface geometry of nickel particles was of importance for the catalytic activity. According to these results, it is concluded that the reduction behavior of alumina supported nickel catalyst is a key factor in determining the catalytic activity of Ni/Al_2O_3 in the hydrogenation of *p*-nitrophenol to *p*-aminophenol, and the catalytic activity is higher for the alumina supported nickel catalyst with an easier reduction of nickel oxide to metallic nickel.

The HPLC analysis results show that the contents of *p*-aminophenol in the products are all higher than 98% for the hydrogenation reactions catalyzed by Ni/Al_2O_3 catalysts with three different particle size alumina supports, indicating that alumina support particle size has no influences on the catalytic selectivity of Ni/Al_2O_3 in the hydrogenation reaction of *p*-nitrophenol.

3.3 Membrane filtration performance

Figure 5 shows the comparative results obtained with nano-sized nickel at $2.06g\cdot L^{-1}$ and $10.3Ni/Al_2O_3$-3 at $20g\cdot L^{-1}$ during membrane filtration process. It is evident from the membrane performance that when $10.3Ni/Al_2O_3$-3 is mixed with deionized water, the permeate flux is improved. For the nano-sized nickel suspension, the permeate flux is $527L\cdot m^{-2}\cdot h^{-1}$ at the filtration duration time of 200min while the permeate flux is $615L\cdot m^{-2}\cdot h^{-1}$ for the $10.3Ni/Al_2O_3$-3 suspension. Clearly, the supported nickel catalyst $10.3Ni/Al_2O_3$-3 improves the life span of the membrane by reducing fouling on the membrane surface. Moreover, unlike nano-sized nickel the supported nickel particles will not easily deposit internally, which will not eventually cause membrane pores closure.

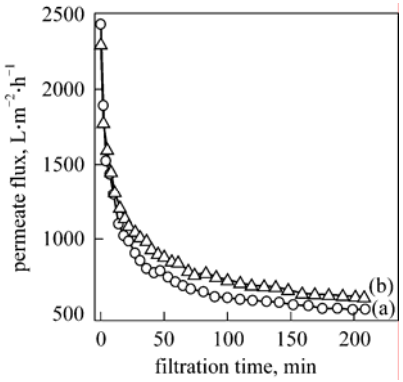

Figure 5 Change of permeate flux with filtration time
○ nano-sized nickel (catalyst, $2.06g\cdot L^{-1}$);
△ $10.3Ni/Al_2O_3$-3 (catalyst, $20g\cdot L^{-1}$)

4 CONCLUSIONS

A series of Ni/Al_2O_3 catalysts were prepared by a liquid-phase chemical reduction method, and characterized by ICP, XRD, XPS and TPR. The catalyst characterization results show that alumina support particle size has significant influences on the dispersion and reduction behavior of alumina supported nickel catalysts. The catalytic hydrogenation of *p*-nitrophenol to *p*-aminophenol was investigated over Ni/Al_2O_3 catalysts in a laboratory-scale batch-slurry reactor. At a comparable amount of Ni loading, the catalytic activity of Ni/Al_2O_3 using alumina of smaller particle size as support is lower under the similar reaction conditions. The reduction behavior of alumina supported nickel catalyst plays a key role in determining the catalytic activity of Ni/Al_2O_3 in the hydrogenation of *p*-nitrophenol to *p*-aminophenol, and the catalytic activity is higher for the alumina supported nickel catalyst with an easier reduction of nickel oxide to metallic nickel. The high performance liquid chromatography (HPLC) analysis results show that alumina support particle size almost has no influences on the catalytic selectivity of Ni/Al_2O_3 in the hydrogenation reaction of *p*-nitrophenol. According to the membrane filtration experiments, the permeate flux of membrane is improved and thus the membrane fouling phenomenon is reduced with the use of supported nickel catalyst $10.3Ni/Al_2O_3$-3. Therefore, the $10.3Ni/Al_2O_3$-3 catalyst can be potentially applied in the hydrogenation of *p*-nitrophenol to *p*-aminophenol.

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