Synthesis of m-phenylenediamine from m-dinitrobenzene over silica-supported nickel catalyst

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Abstract–The liquid-phase hydrogenation of m-dinitrobenzene to m-phenylenediamine was studied over silica-supported nickel catalyst. The effects of Ni loading, calcination temperature, and reduction temperature on the physicochemical characteristics and activity of the catalyst were investigated by XRD, TEM, TPR, and activity tests. The results show that the silica-supported nickel catalysts exhibited high catalytic property, which depended on the particle size of Ni and the reduction degree of NiO. The optimal Ni loading, calcination temperature and reduction temperature of the catalyst for m-dinitrobenzene hydrogenation were found to be 20 wt%, 773 K in air and 723 K, respectively. Under this condition, 97.2% conversion of m-dinitrobenzene and 88.9% yield of m-phenylenediamine were obtained at 373 K and 2.6 MPa hydrogen pressure. The particle size of nickel species increased with the increase in Ni loading or calcination temperature. In addition, it was found that the catalyst could not be completely reduced at low reduction temperature, whereas high reduction temperature led to the sintering of Ni.

Key words: Ni/SiO$_2$ Catalyst, Hydrogenation, m-Phenylenediamine, m-Dinitrobenzene

INTRODUCTION

m-Phenylenediamine (MPD) is an important raw material for both chemicals and intermediates. Traditionally, MPD is prepared by iron-powder reduction reaction in which the mixture of iron powder and hydrochloric acid are used to reduce m-dinitrobenzene (1,3-DNB) to m-phenylenediamine. However, this process is of high cost, lower yield and serious environmental pollution. Therefore, the commercialization of the process is restricted in many countries. Recently, much attention has been focused on the liquid-phase catalytic hydrogenation of m-dinitrobenzene due to its high product yield, mild reaction conditions and a reduced pollution to environment [Bird and Thompson, 1980]. Usually, the hydrogenation is carried out over Raney Ni catalyst [Shimazu et al., 1997]. Although Raney Ni has a high catalytic activity, a large amount of the catalyst is needed in the course of the reaction because it is easily crushed under intense agitation. Moreover, noticeable environmental pollution can be caused during the preparation of the catalyst. Besides Raney Ni catalyst, some supported noble metal catalysts such as Pd/C have been used for this reaction, and they also exhibit high activity and selectivity [Yu et al., 1997; Mizuta et al., 1993, 1994]. However, supported noble metal catalysts are expensive. From the industrial point of view, there is an urgency to look for a new catalyst that meets the need in terms of activity and cost. Supported nickel catalysts have been successfully used in a number of hydrogenation processes for years. Compared with supported noble metal catalysts,

these catalysts are less expensive and more environmentally benign [Song et al., 1992; Pawelec et al., 1996; Takahashi et al., 1997; Sato et al., 2000; Suh et al., 2001; Mäki-Arvela et al., 2002; Tobicík and Cerveny, 2003]. Therefore, it is expected that this kind of catalyst could be a promising substitute in the hydrogenation of m-dinitrobenzene to m-phenylenediamine. So far, however, few researches on the hydrogenation of m-dinitrobenzene over supported nickel catalyst have been reported in the literatures.

In this work, silica supported nickel catalysts have been examined for the liquid-phase hydrogenation of m-dinitrobenzene. The effects of Ni loading, calcination temperature and reduction temperature on the catalytic performance were intensively investigated. The catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and temperature-programmed reduction (TPR).

EXPERIMENTAL

1. Catalyst Preparation

Ni/SiO$_2$ catalysts with Ni loadings of 10, 20, 25, and 30 wt% were prepared by incipient wetness impregnation. SiO$_2$ (surface area=432 m^2/g) was purchased from Tianjin Research and Design Institute of Chemical Industry. After impregnating with an appropriate amount of aqueous solution of nickel nitrate at room temperature, the precursor was dried at 383 K overnight and calcined for 4 h in air at various temperatures, ranging from 673 to 973 K. Then the samples were crushed. The resulting powder had an average diameter of about 160 μm. Prior to the activity evaluation, the samples were reduced for 2 h in hydrogen stream at different tempera-

tures of 573, 673, 723 and 873 K, and then cooled to room temperature and stored in nitrogen atmosphere.

Raney Ni catalyst used was prepared by alkali leaching of the commercially available Ni-Al alloy (50 wt% Ni, 160 μm), as described by Li et al. [2000], and then stored in ethanol until time of use.

2. Catalyst Characterization

X-ray diffraction (XRD) pattern of the catalysts was measured with a Rigaku D/MAX-2308 instrument by using Cu K_α radiation. The diffraction patterns were recorded by varying 2θ from 10 to 84° at a scanning speed of 4°·min^{-1}.

Transmission electron microscopy (TEM) images were obtained with a JEM-CX-II microscope. Catalysts were pestled in an agate mortar and then dispersed in ethanol via ultrasonication. One or two drops of the dispersion were dripped onto a thin copper film to make the TEM samples.

Temperature-programmed reduction (TPR) of the catalyst was carried out in a quartz reactor. 100 mg catalyst was filled into the reactor, heated from 298 to 1,173 K at the rate of 10 K·min^{-1}, and swept with 90% nitrogen-10% hydrogen (vol) stream at flow rate of 50 ml·min^{-1}. The effluent hydrogen concentration was detected with a thermal conductivity detector (TCD). The cooling trap placed between the sample and the detector retained the water formed during the reduction process.

3. Catalytic Activity

The liquid-phase hydrogenation of m-dinitrobenzene was carried out in a 250 ml stainless steel autoclave at 373 K and 2.6 MPa hydrogen pressure. 2.72 g m-dinitrobenzene was dissolved in 100 ml ethanol. And 0.272 g catalyst prepared above was loaded into the autoclave vessel. The stirring rate was above 1,200 rpm. The solution was withdrawn at appropriate intervals and analyzed by gas chromatograph, which was equipped with a flame ionization detector (FID). The temperature of column oven was controlled at 493 K.

RESULTS AND DISCUSSION

1. Effect of Ni Loading

The catalytic properties of Ni/SiO$_2$ catalysts with various Ni loadings (10-30 wt% Ni) for the hydrogenation of m-dinitrobenzene are shown in Table 1. All the catalysts were calcined at 823 K in air and reduced at 723 K under hydrogen stream before the reac-

Table 1. Effect of Ni loading on NiO particle size^a and the activity of Ni/SiO$_2$ catalyst for hydrogenation of m-dinitrobenzene^b

Catalyst	Size (nm)	Activity (mol min^{-1}g$_{Ni}^{-1}$)^c $\times 10^4$
10 wt%Ni/SiO$_2$	14.5	14.87
20 wt%Ni/SiO$_2$	18.4	16.98
25 wt%Ni/SiO$_2$	19.4	11.83
30 wt%Ni/SiO$_2$	21.1	9.608
Raney Ni	-	1.629

^{a}Obtained from XRD analysis according to the Scherrer equation.
^{b}Reaction conditions: catalyst, 0.272 g; P=2.6 MPa; T=373 K; m-dinitrobenzene, 2.72 g; ethanol, 100 ml.
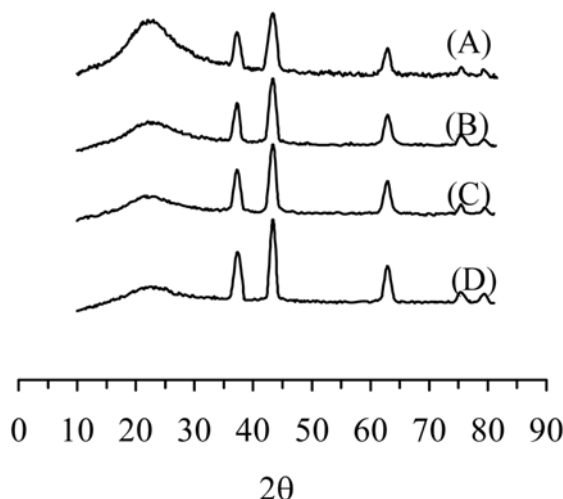^{c}Obtained based on measuring mol of reacted m-dinitrobenzene within the first 2 h.

Fig. 1. XRD patterns of Ni/SiO$_2$ catalyst precursors with different Ni loadings: (A) 10 wt%; (B) 20 wt%; (C) 25 wt%; (D) 30 wt%.

tion. The activity of Raney Ni catalyst is also listed for comparison. It can be clearly seen that Ni/SiO$_2$ catalysts exhibited higher activity for hydrogenation of m-dinitrobenzene to m-phenylenediamine than the Raney Ni catalyst. In addition, the Ni loading had a great effect on the catalytic properties. In general, the catalyst with lower Ni loading and smaller particle size of metal was more efficient. The catalyst with 10 wt% Ni loading, however, was not so active even though it had the smallest particle size, because it is not sufficient to provide enough active sites for molecular adsorption, as measured by H$_2$ chemisorption. With an increase in the content of Ni loading up to 20 wt%, the activity of the catalyst markedly increased, possibly owing to the increase of the surface active Ni sites, as determined by H$_2$ chemisorption. However, when the loading of Ni was higher than 20 wt%, the catalytic activity decreased with the increase of Ni loading.

XRD characterizations of the Ni/SiO$_2$ catalyst precursors with different Ni loadings are given in Fig. 1. Each of the spectra showed a wide diffraction peak corresponding to SiO$_2$ (2θ=22°) and three distinct peaks corresponding to NiO (2θ=37.3, 43.3 and 62.9°). No peaks were detected for new phases, suggesting that the interaction between Ni and SiO$_2$ was weak, and NiO was mainly dispersed in a "free" state on the surface of the support [Xu et al., 2001]. Fig. 1 also shows that the peak intensities of NiO increased with the increase in the Ni loading. It is well known that diffraction intensity is directly related to crystallite size. Therefore, it can be concluded that the crystallite sizes of NiO increased with the increase in the Ni loading, which would further lead to decrease in the dispersion of Ni. Using the peak width at 43.3°, the crystallite sizes of NiO were estimated according to the Scherrer equation. The results are listed in Table 1. It shows that the crystallite size of NiO increases from 14.5 to 21.1 nm when the Ni loading increases from 10 to 30 wt%.

TEM picture of reduced Ni/SiO$_2$ catalyst with 10 wt% Ni loading is shown in Fig. 2(A). The reduced catalyst contained small Ni particles dispersed homogenously on the support, with size distribution between 4 and 20 nm. For the reduced catalyst with 20 wt% Ni loading (Fig. 2(B)), however, only a few of the particles had sizes
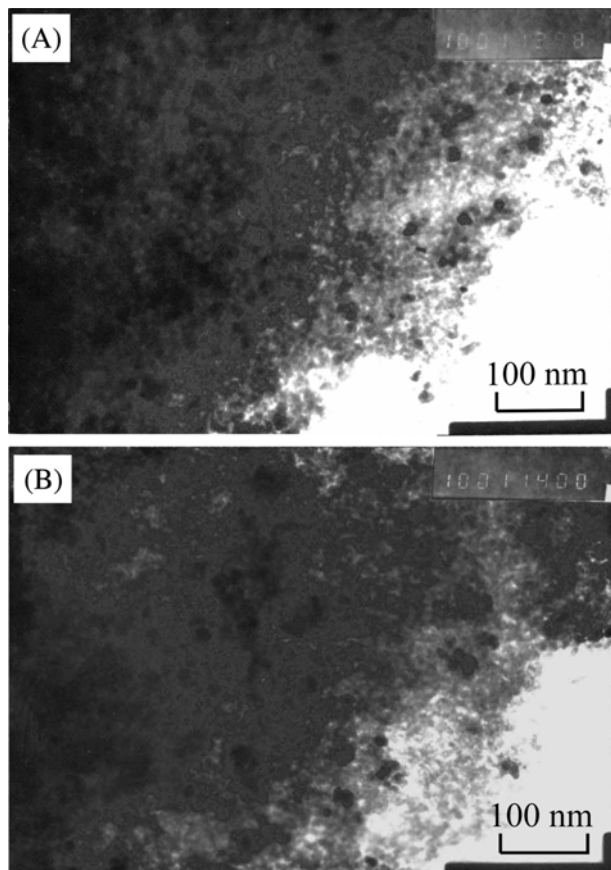
Fig. 2. TEM images of Ni/SiO₂ catalyst samples with different Ni loadings after reduction at 723 K for 2 h: (A) 10 wt%; (B) 20 wt%.
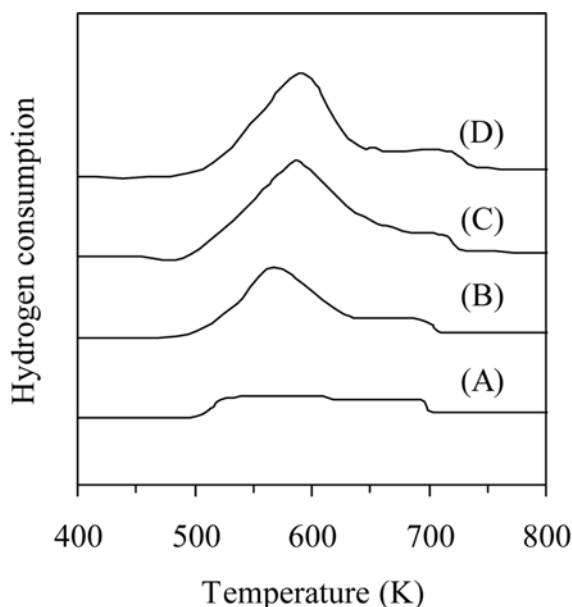

Fig. 3. TPR profiles of Ni/SiO₂ catalysts with different Ni loadings: (A) 10 wt%; (B) 20 wt%; (C) 25 wt%; (D) 30 wt%.

less than 10 nm and the size of most of them was between 20 and 30 nm. It can be seen that the particle size of Ni⁰ clearly increased

with the Ni loading increasing.

Fig. 3 shows the TPR profiles of Ni/SiO₂ catalysts with Ni loadings of 10, 20, 25, and 30 wt%. Two reduction peaks are observed between 550 and 750 K in all the profiles. The low temperature reduction peaks are ascribed to the reduction of NiO particles that were similar in nature to bulk NiO, whereas the high temperature peaks are attributed to the reduction of NiO in intimate contact with SiO₂ support [van de Loosdrecht et al., 1997; Diskin et al., 1998]. It is clear that the temperatures of both the low and the high temperature reduction peaks increased with the increase in the Ni loading. Diskin et al. [1998] reported that the increase in the temperature of the lower temperature peak, attributed to bulk NiO reduction, could be explained by the increase in the NiO particle size, which is in good agreement with the XRD and TEM results mentioned above. On the other hand, temperature increase of the higher temperature peak could be related to the increase in metal support interaction, which is responsible for the decrease of reducibility of the catalysts. In addition, it can be seen from Fig. 3 that the fraction of bulk NiO species and NiO strongly contacting with SiO₂ increases with the increase in Ni loading. These phenomena also suggest that the NiO dispersion decreased with increasing Ni loading [Chang et al., 2003].

2. Effect of Calcination Temperature

Many authors have reported that the preparation procedure of supported nickel catalysts has an important effect on their catalytic properties [Choi and Lee, 2000; Chang et al., 2004]. Therefore, it is necessary to study the effect of calcination temperature on the performance of the Ni/SiO₂ catalysts for the hydrogenation of m-dinitrobenzene. The catalytic activity of 20 wt% Ni/SiO₂ catalysts calcined at different temperatures ranging from 673 to 973 K and reduced at 723 K are shown in Fig. 4. The catalyst calcined at low temperature (673 K) showed less catalytic performance. With the increase in the calcination temperature, the catalytic activity increased. It is worthy of notice that the catalyst calcined at 773 K exhibited optimal catalytic activity, over which the conversion of m-dinitrobenzene and the yield of m-phenylenediamine were up to 97.2% and
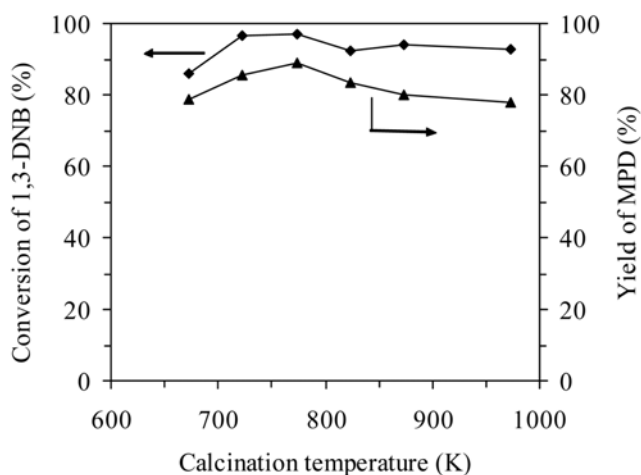

Fig. 4. Effect of the calcination temperature on the hydrogenation of m-dinitrobenzene over 20 wt% Ni/SiO₂ catalysts. Reaction conditions: catalyst, 0.272 g; H₂ pressure, 2.6 MPa; temperature, 373 K; 1,3-DNB, 2.72 g; ethanol, 100 ml; reaction time, 4 h.
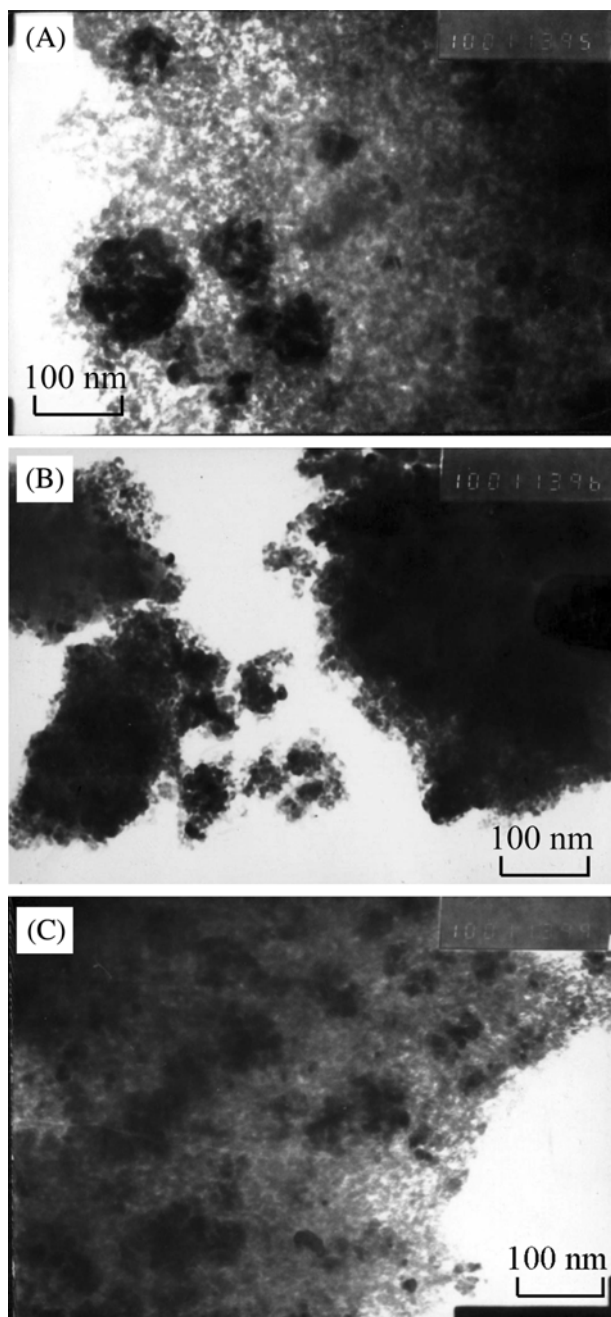
Fig. 5. TEM images of the 20 wt% Ni/SiO₂ catalysts calcined at different temperatures after reduction at 723 K for 2 h: (A) 673 K; (B) 773 K; (C) 973 K.
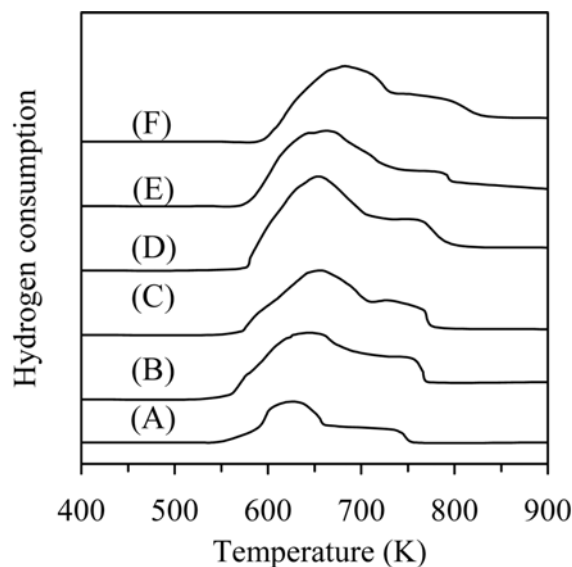

Fig. 6. TPR profiles of the 20 wt% Ni/SiO₂ catalysts calcined at different temperatures: (A) 673 K; (B) 723 K; (C) 773 K; (D) 823 K; (E) 873 K; (F) 973 K.

88.9%, respectively, after reaction for 4 h. However, a further increase in the calcination temperature resulted in a significant reduction in the activity.

Fig. 5 shows the TEM images of the 20 wt% Ni/SiO₂ catalysts calcined at 673, 773 and 973 K, respectively. Prior to the study, the samples were reduced for 2 h in hydrogen gas at 723 K. It can be seen that the shape and density of Ni crystallites changed with different calcination temperatures. The active Ni particles of the catalyst calcined at 673 K (Fig. 5(A)) were present in an aggregated state on the silica support. As the temperature increased to 773 K (Fig. 5(B)), the active metals appeared to be spherical and were ho-

mogeneously dispersed on the surface of the support, with a mean size of about 12 nm. However, when the calcination temperature was further increased, the Ni particle sizes increased obviously due to sintering, (Fig. 5(C)) with the size larger than 20 nm. This would directly lead to the decrease of the active surface area, further decreasing the activity of the catalyst.

Fig. 6 shows the TPR profiles of the 20 wt% Ni/SiO₂ catalyst precursors obtained after calcinations at different temperatures. All the catalysts exhibited two reduction peaks, namely two NiO species (species I and species II). It can be seen from Fig. 6 that both the low temperature peaks and the high temperature peaks shifted toward higher temperatures with the increase in the calcination temperature. The temperature of the low temperature peaks increased from 625 to 684 K, and that of the high temperature peaks increased from 729 to 801 K with the calcination temperature increasing from 673 to 973 K. This indicated that increasing calcination temperature made the reduction more difficult, which would result in a decrease of the reduction degree of the catalyst, further leading to a decrease of the amount of active Ni species. In addition, the relative proportions of the two NiO species decreased with the increase in the calcination temperature, indicating the progressive transformation of species I into species II.

3. Effect of Reduction Temperature

The effect of reduction temperature on the catalytic performance of 20 wt% Ni/SiO₂ catalyst calcined at 773 K for m-dinitrobenzene hydrogenation was investigated (Fig. 7). It can be obviously seen that the reduction temperature had a notable influence on the performance of the catalyst. In the range of 573-723 K, both the m-dinitrobenzene conversion and the m-phenylenediamine yield evidently increased with increasing the reduction temperature. However, the activity of the catalyst decreased a great deal as the reduction temperature was above 723 K. The 20 wt% Ni/SiO₂ catalyst reduced at 723 K exhibited the highest activity.

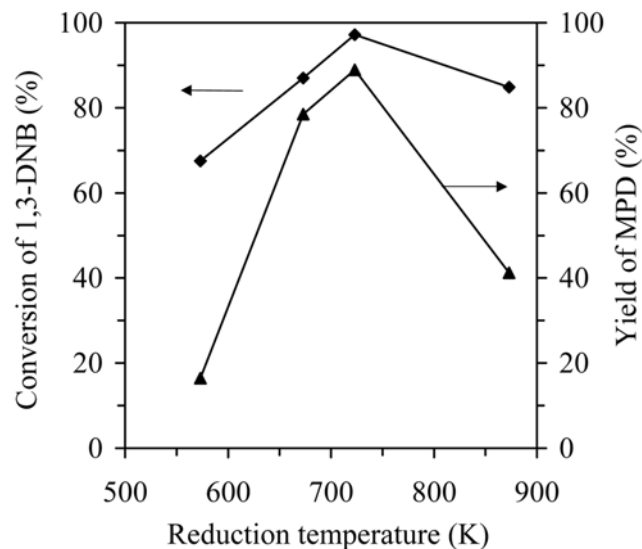Fig. 8 shows the XRD patterns of 20 wt% Ni/SiO₂ catalysts re-

Fig. 7. Effect of reduction temperature on the hydrogenation of m-dinitrobenzene over 20 wt% Ni/SiO₂ catalysts calcined at 773 K. Reaction conditions: catalyst, 0.272 g; H₂ pressure, 2.6 MPa; temperature, 373 K; 1,3-DNB, 2.72 g; ethanol, 100 ml; reaction time, 4 h.
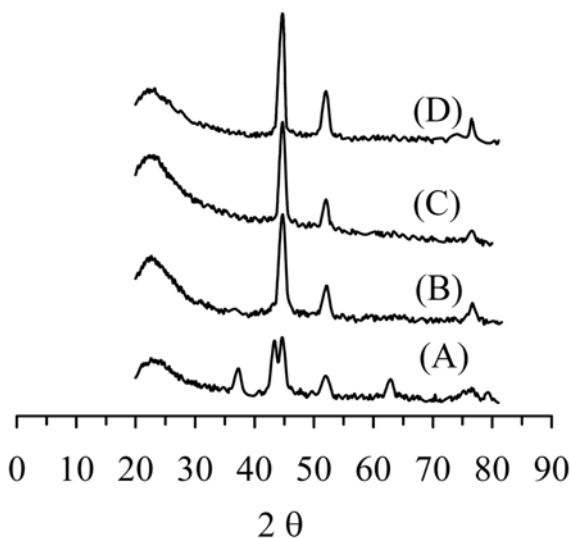

Fig. 8. XRD patterns of 20 wt% Ni/SiO₂ catalysts reduced at different temperatures, which were calcined at 773 K before reduction: (A) 573 K; (B) 673 K.

duced at different temperatures, which were calcined at 773 K before reduction. For the sample reduced at 573 K, the peaks at 37.3, 43.4 and 62.9° attributed to NiO coexist clearly with the peaks for metallic Ni. This suggests that the catalyst was only reduced partially at this temperature. In the case of the samples reduced at temperature above 673 K, the diffraction peaks corresponding to NiO disappeared and only those attributed to metallic Ni were observed, which meant that NiO were completely reduced to metallic Ni. However, when the catalyst was reduced at higher temperature (such as 873 K), the peaks for metallic Ni became obviously sharp, and the intensities of the peaks increased. This implies that high reduction temperature could result in an increase in the Ni particle size. Indeed, the crystal-

lite size of Ni for 20 wt% Ni/SiO₂ increased from 11.8 to 24.7 nm as the reduction temperature increased from 773 to 873 K. The XRD results were in agreement with the TPR result of the 20 wt% Ni/SiO₂ catalyst calcined at 773 K (Fig. 6), where it can be seen that the catalyst precursor started to be reduced at 571 K and was completely reduced at approximately 780 K.

CONCLUSIONS

The silica-supported nickel catalysts exhibited very high catalytic activity for the hydrogenation of m-dinitrobenzene to m-phenylenediamine. The Ni loading and the preparation conditions had obvious influences on the particle size of nickel and the degree of NiO reduction, and hence the catalytic behavior. The optimal Ni loading, calcination temperature and reduction temperature of Ni/SiO₂ catalysts were 20 wt%, 773 and 723 K, respectively. Under such conditions, the conversion of m-dinitrobenzene reached 97.2% and the yield of m-phenylenediamine was 88.9% after reaction for 4 h.

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