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RESEARCH ARTICLE

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Preparation and catalytic performance of monolayer-dispersed Pd/Ni bimetallic catalysts for hydrogenation

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Abstract Pd/Ni bimetallic catalysts were prepared by replacement reactions, characterized by X-ray diffraction, CO chemisorption and H_2 temperature-programmed desorption, and evaluated for hydrogenation of cyclohexene, styrene and acetone. The results show that Pd atoms are monolayer-dispersed on the Ni surface in these Pd/Ni catalysts. Consequently, Pd/Ni catalysts are much more active than Pd/Ni and Pd/γ-Al_2O_3 with the same Pd loading prepared by the conventional impregnation method.

Keywords palladium, nickel, monolayer dispersion, bimetallic catalyst, replacement reaction, hydrogenation

1 Introduction

Bimetallic catalysts have been widely used in many industrial processes [1–3], and many of the corresponding model catalysts have been investigated extensively in surface science studies. It has been found that depositing one metal onto the single crystal surface of another metal can often introduce unique physical and chemical properties that are not seen in either pure metal alone due to the electronic and structural interactions at the metal-metal interface [4,5]. For example, it has been reported that monolayer Pt bimetallic surfaces, in the form of either Ni/Pt(111) or Pt-Ni(111), bind with hydrogen much more weakly than clean Pt(111) or Ni(111) which in turn leads to a novel low-temperature reaction pathway for the self-hydrogenation and hydrogenation of cyclohexene [6–13]. Similar behavior has been recently observed on other bimetallic surfaces with monolayer-dispersed Pt and Pd, including Pt/Co (111), Pd/Ni (111), and Pd/Co (111) surfaces [14]. These results suggest the possibility of obtaining novel catalytic properties from monolayer-dispersed Pt and Pd bimetallic surfaces. However, the challenge is to extend the single crystal studies to the synthesis of monolayer-dispersed bimetallic catalysts in the more practical powder form.

In our previous work [15], we have prepared powder Pt/Ni bimetallic catalysts by replacement reactions. The as-synthesized catalysts showed higher hydrogenation activity for C=C and C=O bonds than Pt/Ni-im and Pt/γ-Al_2O_3 catalysts with the same Pt loading but prepared by the impregnation method. In the present paper, we have synthesized Pd/Ni bimetallic catalysts using the replacement reaction method. The catalysts were characterized by X-ray diffraction, CO chemisorption and H_2 temperature-programmed desorption, and evaluated for hydrogenation of cyclohexene, styrene and acetone.

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2 Experimental

2.1 Preparation of catalysts

Oxide powders of NiO were prepared by dropping aqueous ammonia into $Ni(NO_3)_2$ (A.R.) solution until the pH of the solution reached 7 and the deposit was then calcined at 673 K for 10 h after filtration. The metallic Ni was obtained by reducing NiO at 573 K, which was then placed into a $Pd(NO_3)_2$ (A.R., Strem Chemicals) solution. After the replacement reaction, the system was treated with H_2 at 393K to obtain the Pd/Ni bimetallic catalysts.

For comparison, 0.050 g Pd/g Ni-im and 0.050 g Pd/γ-Al_2O_3 catalysts were prepared by impregnation of NiO or γ-Al_2O_3 with aqueous solution of $Pd(NO_3)_2$, followed by reduction with H_2 at 573 K and 393 K, respectively.

2.2 Characterization of catalysts

X-ray diffraction (XRD) was carried out in a Rigaku D/MAX-200 X-ray powder diffractometer with Ni-filtered Cu Kα radiation at 40 kV and 100 mA. The CO chemisorption was measured on a Micromeritics ASAP 2010 volumetric adsorption system. Before CO adsorption, the catalysts were reduced by H_2 at 393 K for120 min and evacuated for 30 min, then cooled to 308 K and evacuated for 60 min. The CO adsorption isotherms were then measured to determine the CO uptake by various catalysts. In addition, the Brunauer–Emmett–Teller (BET) surface areas were calculated from the adsorption isotherms of N_2 at 77 K on the same adsorption system. The temperature programmed desorption of H_2 (H_2-TPD) was carried out in a quartz reactor coupled to a mass spectrometer (AVI GmbH Omnistar™). The catalyst samples (0.100 g) were reduced by H_2 at 393 K (573 K for pure Ni), cooled to room temperature and exposed for 30 min in hydrogen flow. The samples were then flushed by N_2 flow for 180 min. The TPD experiments were performed using N_2 as carrier gas at a flow rate of 50 mL/min and a heating rate of 5 K/min up to 873 K.

2.3 Catalytic evaluation

The hydrogenation of cyclohexene was carried out in a quartz glass reactor at 273 K and atmospheric pressure. 0.050 g of Pd/Ni catalysts were used for the catalytic evaluation. Cyclohexene was injected by a micro-syringe pump at a flow rate of 0.30 mL cyclohexene per hour and was carried by N_2 with a gas flow rate of 50 mL/min and H_2 with a gas flow rate of 1.0 mL/min. The products were analyzed by online gas chromatography using a FID detector. Hydrogenation of styrene was performed on the same equipment at 308 K and atmospheric pressure. 0.050 g catalysts were used and styrene was injected by a micro-syringe pump at a flow rate of 0.30 mL per hour and was carried by N_2 with a gas flow rate of 60 mL/min and H_2 with a gas flow rate of 1.5 mL/min. Hydrogenation of acetone was performed on the same equipment at 333 K and atmospheric pressure. 0.050 g catalysts were used and acetone was injected by a micro-syringe pump at a flow rate of 0.80 mL per hour and was carried by N_2 with a gas flow rate of 40 mL/min and H_2 with a gas flow rate of 10 mL/min.

3 Results and discussion

3.1 XRD characterization

Figure 1 shows the XRD patterns of Pd/Ni catalysts with different Pd loadings. For reference, the XRD pattern of a mixture of metallic Pd and Ni with the weight ratio of Pd:Ni = 0.010:1 is also included. We can see that the characteristic diffraction peaks of metallic Pd are detected in the Pd–Ni mixture, but absent in the sample with the same composition prepared through the replacement reaction. This suggests that there is no crystalline Pd in the 0.010 g Pd/g Ni sample prepared by the replacement reaction. When Pd content increases, the diffraction peaks of Pd start to appear and their intensities increase with increasing Pd loadings.

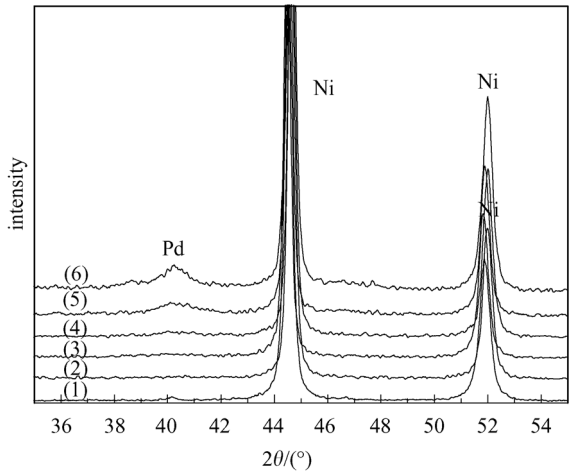

Fig. 1 XRD patterns of Pd/Ni catalysts with different Pd/Ni mass ratios prepared by replacement reaction
(1) 0.01 (mechanical mixture); (2) 0.01; (3) 0.03; (4) 0.05; (5) 0.07; (6) 0.1

The intensity ratio of diffraction peaks of Pd to Ni, I_{Pd}/I_{Ni}, reasonably assumed to be proportional to the ratio of the content of crystalline Pd to that of Ni, is plotted as a function of Pd loading, as shown in Fig. 2. The extrapolation of this ratio reveals that there is a critical dispersion capacity of Pd on the surface of Ni, about 0.022 g Pd/g Ni. This suggests that when the Pd content is lower than 0.022 g Pd/g Ni, Pd atoms are dispersed on the surface of substrate Ni. At higher loadings Pd forms crystalline particles that give rise to the XRD pattern.

Furthermore, it is interesting to point out that if Pd atoms with an atomic radius of 137.6 pm disperse in a close-packed monolayer on the surface of Ni with a BET surface area of 7.6 m^2g^{-1}, the monolayer coverage corresponds to 0.020 g Pd/g Ni, which is very close to the

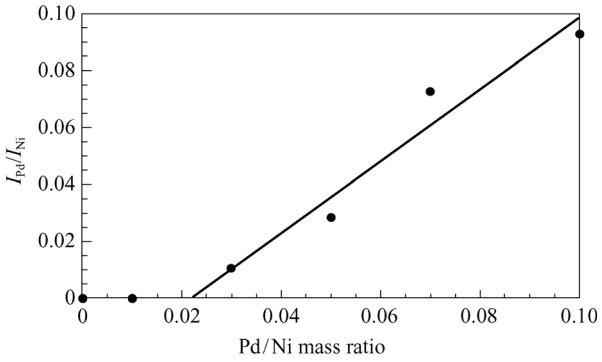

Fig. 2 Dispersion threshold of Pd on Ni measured by XRD

value of 0.022 g Pd/g Ni obtained from the extrapolation in Fig. 2. The excellent match of these two values is consistent with the hypothesis that Pd atoms are monolayer-dispersed on the Ni surface.

3.2 CO chemisorption

CO chemisorption was performed for the Pd/Ni catalysts with different Pd loadings, as shown in Fig. 3. The volume of adsorbed CO on the Pd/Ni catalysts increases with Pd loading up to 0.020 g Pd/g Ni, which is consistent with the monolayer-dispersion capacity of 0.022 g Pd/g Ni from XRD results.

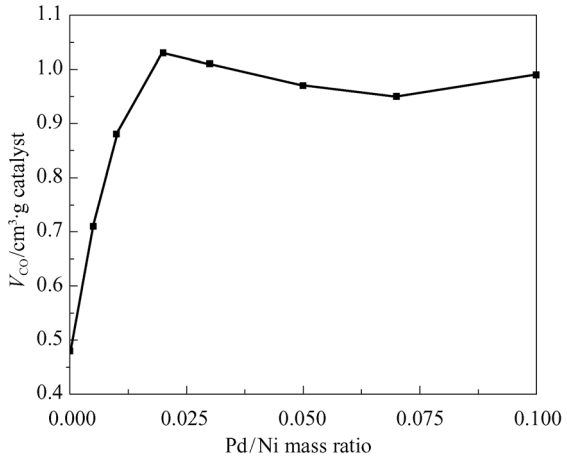

Fig. 3 The volume of CO adsorbed on Pd/Ni catalysts with different Pd loadings

3.3 H_2-TPD

The temperature of hydrogen desorption on the metal surface can be used to characterize the hydrogenation activity of catalysts. Figure 4 shows the results of the H_2-TPD spectra of different Pd/Ni catalysts. The hydrogen desorption peaks for Ni and Pd are both centered at about 503 K, while for the Pd/Ni samples prepared by replacement reactions, the hydrogen desorption peaks move to lower temperatures. The lower desorption temperature indicates that the M–H bond is weaker on Pd/Ni than on Ni or Pd. Therefore, it can be expected that the Pd/Ni bimetallic catalysts should show higher hydrogenation activity, as discussed below.

3.4 Catalytic activity for hydrogenation

Figure 5 shows the hydrogenation activity of cyclohexene for Pd/Ni catalysts with different Pd loadings. Cyclohexane is the only reaction product for the hydrogenation of cyclohexene under the experimental conditions. The results show that the hydrogenation rate increases rapidly with increasing Pd loading up to

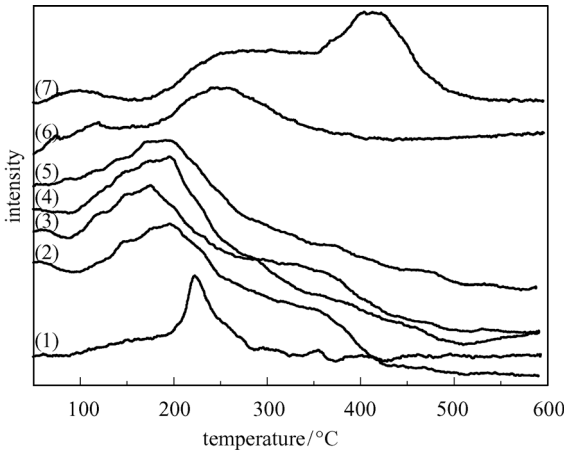

Fig. 4 H_2-TPD profiles of different catalysts
(1) Ni; Pd/Ni catalysts (replacement) with Pd/Ni mass ratios; (2) 0.005; (3) 0.01; (4) 0.03; (5) 0.05; (6) Pd; (7) Pd/Al_2O_3 (Pd/Al_2O_3 mass ratio of 0.01, impregnation)

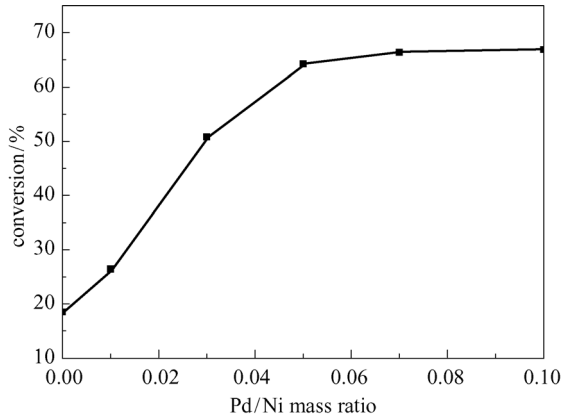

Fig. 5 Conversion of cyclohexene on Pd/Ni catalysts with different Pt loadings
Reaction conditions: 0°C; N_2, 50 mL/min; H_2, 1.0 mL/min; C_6H_{10}, 0.3 mL/h

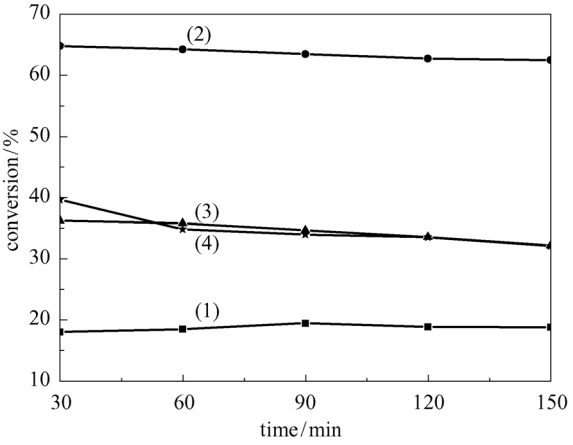

Fig. 6 Conversion of cyclohexene hydrogenation on Pd catalysts prepared by different methods
(1) Ni; (2) 0.050 g Pd/g Ni; (3) 0.050 g Pd/g Ni-im; (4) 0.050 g Pd/g Al_2O_3;
Reaction conditions: 0°C, N_2, 50 mL/min; H_2, 1.0 mL/min; C_6H_{10}, 0.3 mL/h

0.050 g Pd/g Ni, and then increases only slightly at higher Pd loadings. From previous CO chemisorption results, when Pd/Ni mass ratio reaches 0.02, the amount of CO adsorbed on the catalysts keeps constant. One possible explanation is that different types of active sites are involved for CO adsorption and for cyclohexene reaction; another explanation is that the reaction with cyclohexene may alter the surface structure of the Pd/Ni catalysts, generating additional active sites for the hydrogenation of cyclohexene.

For reference, the conversion of cyclohexene on catalysts with the same Pd loading but prepared by the impregnation method was also evaluated. Fig. 6 shows that the conversion for the Pd/Ni catalyst (64%–62%) prepared by the replacement reaction remains higher than those of the Pd/g Ni-im (36%–34%) and Pd-34%) catalysts prepared by the impregnation method. XRD measurements show that Pd and Ni formed solid solution in Pd/Ni-im (Fig. 7a) and Pd takes the form of crystallite in Pd/Al_2O_3 catalyst (Fig. 7b). A possible reason for the higher activity of the Pd/Ni catalyst is due to the monolayer-dispersion of Pd on the Ni surface.

Hydrogenations of styrene and acetone were also performed over the different Pd/Ni catalysts. As shown in Fig. 8, similar to the results of cyclohexene hydrogenation, Pd/Ni catalysts prepared by replacement reaction exhibited higher activity than Pd/Ni-im and Pd/Al_2O_3 catalysts prepared by conventional impregnation method.

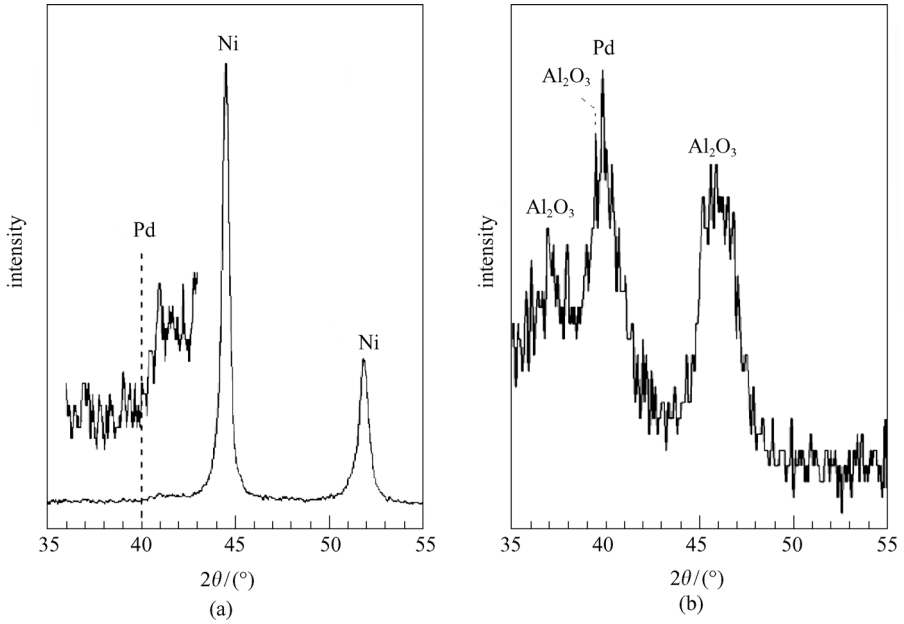

Fig. 7 XRD patterns of Pd/Ni-im (a) and Pd/Al_2O_3 (b) catalysts prepared by impregnation

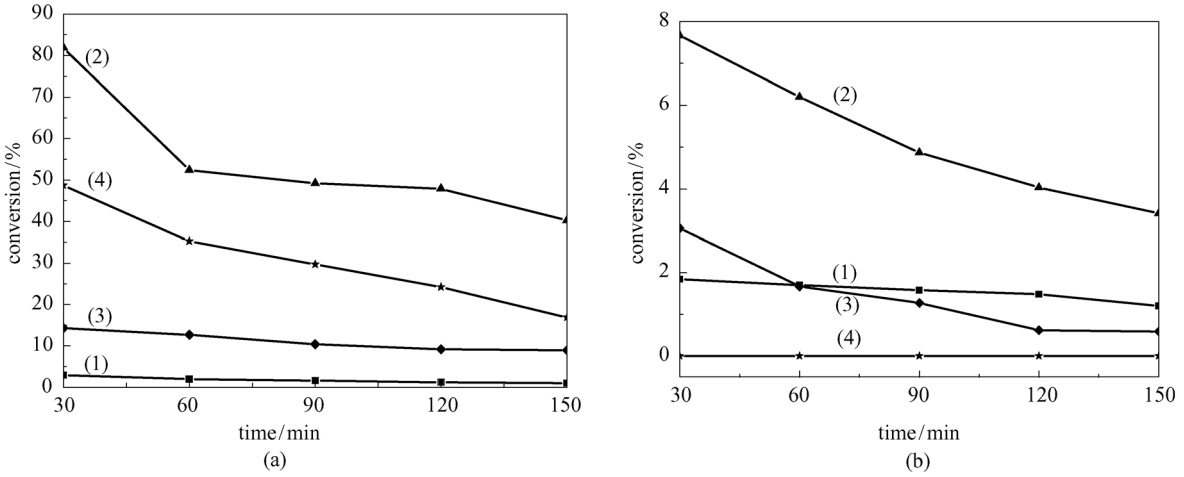

Fig. 8 Conversion of styrene (a) and acetone (b) hydrogenation on Pd catalysts prepared by different methods. (1) Ni; (2) Pd/Ni; (3) Pd/Ni-im; (4) Pd/g Al_2O_3
Reaction conditions: 35°C; N_2, 60 mL/min; H_2, 1.5 mL/min; C_8H_8, 0.3 mL/h for styrene and 60°C; N_2, 40 mL/min; H_2, 10 mL/min; C_3H_6O, 0.8 mL/h for acetone

Compared with the Pt/Ni catalyst [15], which was also prepared by replacement reaction, the Pd/Ni catalyst has higher activity for C=C bond hydrogenation, especially for styrene hydrogenation, while the activity is lower for C=O bond (acetone) hydrogenation.

4 Conclusions

In this present paper Pd/Ni bimetallic catalysts were prepared and the results of XRD, CO chemisorption and H_2-TPD proved that Pd atoms monolayer-dispersed on the Ni surface in the Pd/Ni catalysts with a dispersion threshold of 0.022 g Pd/g Ni. Catalytic hydrogenation tests showed that the monolayer-dispersed Pd/Ni catalysts exhibited higher activities than Pd/Ni-im and Pd/γ-Al_2O_3 prepared by the conventional impregnation method. Overall, the monolayer-dispersion of one metal on the surface of another metal provides a way to acquire new bimetallic catalysts with unique properties.

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References

1. Ponec V. Alloy catalysts: the concepts. Applied Catalysis, A: General, 2001, 222(1–2): 31–45
2. Li Z X, Chen X R. Influence of Pt on naphthalene conversion over nickel-based catalysts. Chinese Journal of Catalysis, 2003, 24(4): 253–258 (in Chinese)
3. Wang J, Yu Y B, Xie S X, He H. Catalytic activity of novel noble metal modified Ag/Al_2O_3 for selective catalytic reduction of NO and reaction mechanism. Chinese Journal of Catalysis, 2004, 25(10): 824–828 (in Chinese)
4. Hammer B, Norskov J K. Theoretical surface science and catalysis–calculations and concepts. Advances in Catalysis, 2000, 45: 71–129
5. Rodriguez J A. Physical and chemical properties of bimetallic surfaces. Surface Science Reports, 1996, 24(7–8): 223–287
6. Castellani N J, Legare P, Demangeat C, Pick S. Hydrogen molecule dissociation on Pt/Ni(111) systems. Surface Science, 1996, 352–354: 148–154
7. Hwu H H, Eng, J Jr, Chen J G. Ni/Pt(111) bimetallic surfaces: unique chemistry at monolayer Ni coverage. Journal of the American Chemical Society, 2002, 124(4): 702–709
8. Khan N A, Hwu H H, Chen J G. Low-temperature hydrodesulfurization of thiophene on Ni/Pt(111) bimetallic surfaces with monolayer Ni coverage. Journal of Catalysis, 2002, 205(2): 259–265
9. Kitchin J R, Khan N A, Barteau M A, Chen J G, Yakshinskiy B, Madey T E. Elucidation of the active surface and origin of the weak metal-hydrogen bond on Ni/P(111) bimetallic surfaces: a surface science and density functional theory study. Surface Science, 2003, 544(2–3): 295–308
10. Kitchin J R, Norskov J K, Barteau M A, Chen J G. Role of strain and ligand effects in the modification of the electronic and chemical properties of bimetallic surfaces. Physical review letters, 2004, 93(15): 156801
11. Khan N A, Zellner M B, Chen J G. Cyclohexene as a chemical probe of the low-temperature hydrogenation activity of Pt/Ni(111) bimetallic surfaces. Surface Science, 2004, 556(2–3): 87–100
12. Khan N A, Zellner M B, Murillo L E, Chen J G. A comparison of similarities and differences in the activities of Pt/Ni(111) and Ni/Pt(111) surfaces. Catalysis Letters, 2004, 95(1–2): 1–6
13. Humbert M D, Murillo L E, Chen J G. in preparation
14. Wang S R, Lin W, Zhu Y X, Xie Y C, Chen J G. Preparation and catalytic activity of monolayer-dispersed Pt/Ni bimetallic catalyst for C=C and C=O hydrogenation. Chinese Journal of Catalysis, 2006, 27(4): 301–330