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Pd-based bimetallic catalysts prepared by replacement reactions

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Several Pd-based bimetallic catalysts, Pd/Co, Pd/Ni and Pd/Cu, were synthesized by replacement reactions. The catalysts were characterized by XRD and CO chemisorption and their catalytic properties were evaluated using cyclohexene self-hydrogenation. The results suggest that the high catalytic activity of Pd/Ni is most likely due to the monolayer-dispersion of Pd on the Ni surface. The results also suggest that Pd is monolayer-dispersed on the Co surface in Pd/Co, whereas Pd forms surface alloy or solid solution with Cu in Pd/Cu.

KEY WORDS: Pd/Co; Pd/Ni; Pd/Cu; bimetallic catalysts; cyclohexene self-hydrogenation; monolayer-dispersed catalysts; CO chemisorption.

1. Introduction

Bimetallic catalysts have been widely used in many industrial processes [1–4], and many of the corresponding model catalysts have been investigated extensively in surface science studies [5–17]. 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. For example, it was reported that monolayer Pt bimetallic surfaces, in the form of either Pt–Ni–Pt(111) or Pt–Ni(111) [11–16], bound atomic hydrogen and cyclohexene much more weakly than clean Pt(111) or Ni(111), which in turn led to a novel low-temperature reaction pathway for the self-hydrogenation and hydrogenation of cyclohexene. Similarly behavior has been recently observed experimentally on monolayer-dispersed Pt on other bimetallic surfaces [17]. The results from these previous surface science studies suggested the possibility to obtain novel catalytic properties from monolayer-dispersed 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.

It is well known that many metal oxides or salts can be spontaneously dispersed on the surface of oxide supports to form a monolayer due to the formation of interfacial chemical bonds between them [18, 19]. For example, when MoO_3 was mixed with γ-Al_2O_3 and heated at 773 K, the X-ray diffraction peaks of MoO_3 disappeared if the content of MoO_3 was lower than its monolayer dispersion capacity. The corresponding catalytic studies of these systems also suggested the monolayer-dispersion of the MoO_3 active component [19]. In contrast, metals cannot be easily dispersed on the surface of γ-Al_2O_3 to form a monolayer. It was reported that the XRD patterns of metal/support mixture did not change even after the mixture was heated at a temperature higher than the melting point of the metal [18]. On the other hand, in principle a metal can potentially disperse on the surface of another metal to form monolayer-dispersed bimetallic systems due to the formation of bonds between the two metals.

In our previous work [20], we have prepared powder Pt/Ni bimetallic catalysts by replacement reactions, which involved the exchange reactions of controlled amounts of Pt^{2+} ions with bulk Ni catalysts. The as-synthesized catalysts showed higher hydrogenation activity for C = C and C = O bonds than catalysts with the same Pt loading but prepared by the impregnation method. In the present paper, we have utilized the replacement reactions to synthesize Pd/Co, Pd/Ni and Pd/Cu powder bimetallic catalysts. Results from catalytic evaluation and characterization reveal that the Pd/Ni catalysts prepared by replacement reactions show higher activity for cyclohexene self-hydrogenation than Pd/Ni and Pd/Al_2O_3 with the same Pd loading but prepared by the impregnation method, most likely due to the monolayer-dispersion of Pd on the Ni surface. In addition, Pd also appears to be monolayer-dispersed on

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the Co surface whereas it forms surface solid solution with Cu.

2. Experimental

2.1. Catalyst preparation

Oxide powders of Co_3O_4, NiO and CuO were prepared by dropping aqueous ammonia into $Co(NO_3)_2$, $Ni(NO_3)_2$ and $Cu(NO_3)_2$ solution, respectively, until the pH of the solution reached 7 and the deposit was calcined at 573 K after filtration. The metallic Co, Ni and Cu were obtained by reducing Co_3O_4 with H_2 at 623 K, and NiO and CuO at 573 K. The metallic Co (Ni or Cu) powder was then placed into $Pd(NO_3)_2$ solution. In principle, Pd would deposit on the surface of Co (Ni or Cu) due to the replacement reactions between Co (Ni or Cu) and Pd^{2+}, because the reduction potential of Co^{2+}/Co (−0.28 eV), (Ni^{2+}/Ni (−0.25 eV), Cu^{2+}/Cu (+0.34 eV)) is lower than Pd^{2+}/Pd (+0.83 eV). The completion of the replacement reaction was indicated by the disappearance of the characteristic color of the Pd^{2+} ions. After the replacement reaction, the system was treated with H_2 at 393 K to obtain the Pd/Co (Pd/Ni, Pd/Cu) bimetallic catalysts.

For comparison, 0.070 g Pd/g Ni-im and 0.070 g Pd/g 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. Catalyst characterization

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.

2.3. Catalyst evaluation

The self-hydrogenation of cyclohexene was carried out in a quartz glass reactor under atmospheric pressure. 0.050 g of Pd/Ni catalysts or 0.10 g of Pd/Co (Pd/Cu) catalysts were used for the catalytic evaluation. Cyclohexene was injected by a micro-syringe pump at a flow rate of 0.80 ml cyclohexene per hour and was carried by N_2 with a gas flow rate of 50 ml/min. The products were analyzed by online gas chromatography using a FID detector.

3. Results and discussion

3.1. XRD characterization

The structures of the Pd/Ni, Pd/Co and Pd/Cu catalysts were characterized by using powder XRD. Figure 1 shows the XRD patterns of Pd/Ni catalysts with different Pd loading. For reference, the XRD pattern of a mixture of metallic Pt and Ni with the weight ratio of Pd: Ni = 0.010:1 is also shown in figure 1 in the bottom spectrum, designated as a'. As compared in the upper-left figure in figure 1, the diffraction peaks characteristic of metallic Pd is 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 loading. The trend observed in figure 1 is similar to previous studies of monolayer-dispersed oxides [18]. 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 the upper-right figure in figure 1. 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. It should be pointed out that if crystalline Pd were formed at all Pd loadings, the extrapolation in figure 1 should cross the origin instead of at a Pd loading of 0.022 g Pd/g Ni.

Furthermore, it is interesting to point out that if Pd atoms with an atomic radius of 137.6 pm disperse in a

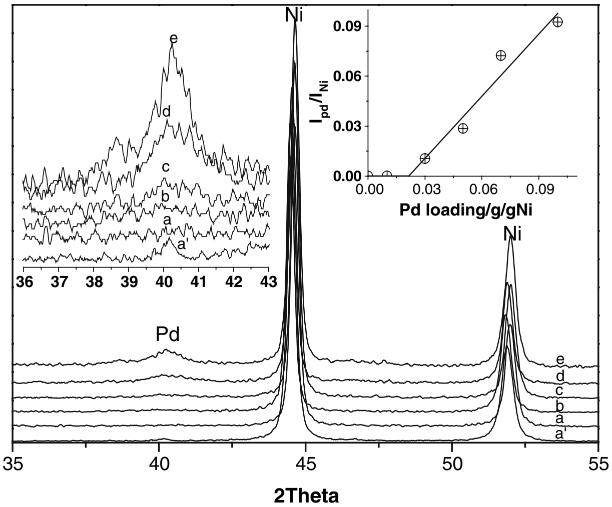

Figure 1. XRD patterns of Pd/Ni catalysts with different Pd loading, a', 0.010 (mix); (a) 0.010; (b) 0.030; (c) 0.050; (d) 0.070; (e) 0.100 g Pd/g Ni.

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 value of 0.022 g Pd/g Ni obtained from the extrapolation in figure 1. The excellent match of these two values is consistent with the hypothesis that Pd atoms are monolayer-dispersed on the Ni surface.

The XRD patterns of Pd/Co catalysts are shown in the upper-panel in figure 2. Similar to the Pd/Ni catalysts, the diffraction peaks characteristic of Pd are absent in the 0.010 g Pd/g Co catalyst but appear in samples with 0.030 g Pd/g Co or higher Pd loadings, suggesting that the growth mechanism of Pd on the Co surface should be similar to that on the Ni surface. The BET surface area of Co is 7.0 m^2g^{-1}, leading to a monolayer Pd coverage of 0.018 g Pd/g Co. However, because there are two kinds of Co crystals and that Co adsorbs the Cu K_α radiation, the intensities of the diffraction peaks are very weak, making it difficult to quantify the intensity ratio of diffraction peaks of Pd to Co, I_{Pd}/I_{Co}. Therefore it is not possible to determine the dispersion capacity of Pd on the surface of Co using the similar extrapolation method as in Pd/Ni.

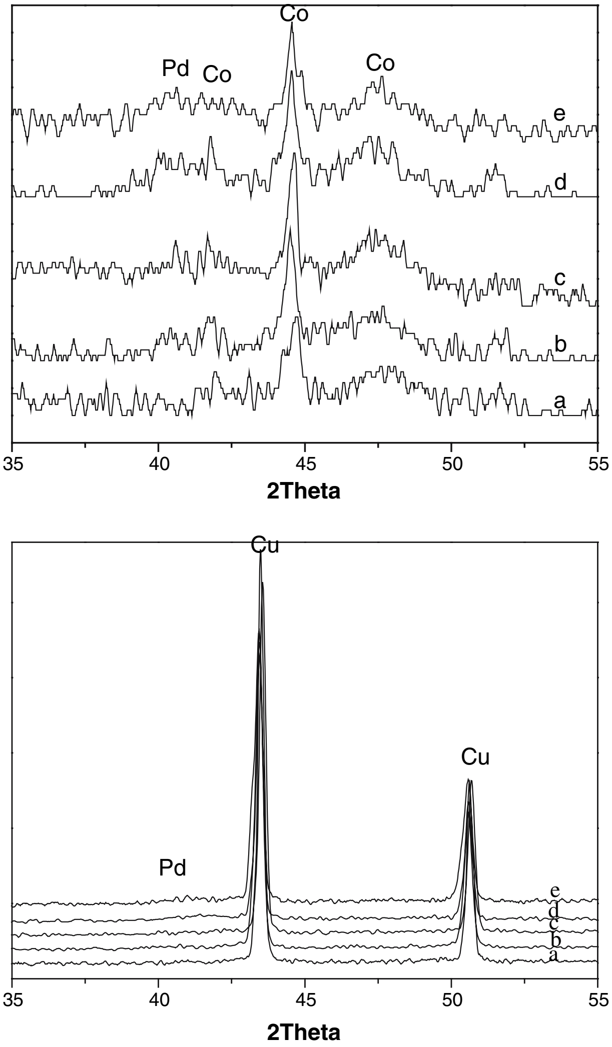

Figure 2. Upper-panel: XRD patterns of Pd/Co catalysts with different Pd loading, (a) 0.010; (b) 0.030; (c) 0.050; (d) 0.070; (e) 0.100 g Pd/g Co. Lower-panel: XRD patterns of Pd/Cu catalysts with different Pd loading, (a) 0.010; (b) 0.030; (c) 0.050; (d) 0.070; (e) 0.100 g Pd/g Cu.

The lower-panel in figure 2 shows the XRD patterns of the Pd/Cu system. The BET surface area of Cu is 5.2 m^2g^{-1}, leading to a monolayer Pd coverage of 0.014 g Pd/g Cu. Different from the Pd/Ni and Pd/Co catalysts, there is no crystalline Pd in Pd/Cu catalysts at all Pd loadings investigated. The absence of the diffraction peaks characteristic of Pd suggests that Pd atoms most likely form a surface alloy or solid solution with Cu that cannot be detected by XRD.

3.2. *CO chemisorption*

The CO chemisorption was performed to compare the surface properties of the Pd–M (M = Co, Ni, Cu) catalysts at different Pd loadings, as shown in figure 3. The volume of adsorbed CO on the Pd/Ni catalysts increases with Pd loading until up to 0.030 g Pd/g Ni, consistent with the monolayer-dispersion capacity of 0.022 g Pd/g Ni derived from the extrapolation from the XRD results. The volume of adsorbed CO on Pd/Co catalysts increases rapidly with Pd loading up to 0.030 g Pd/g Co, but relatively slowly when the Pd loading increases to 0.50 g Pd/g Co, which again suggests the possibility of monolayer-dispersion of Pd on Co.

In contrast, the Pd/Cu catalysts with low Pd loadings do not adsorb CO at all, indicating that the state of Pd on Cu is different from that on either Ni or Co. When the Pd loading reaches 0.050 g Pd/g Cu, very small amount of CO, about 2–3% of that of Pd/Ni and Pd/Co catalysts, is adsorbed. The CO chemisorption property of Pd/Cu system agrees well with the results of XRD

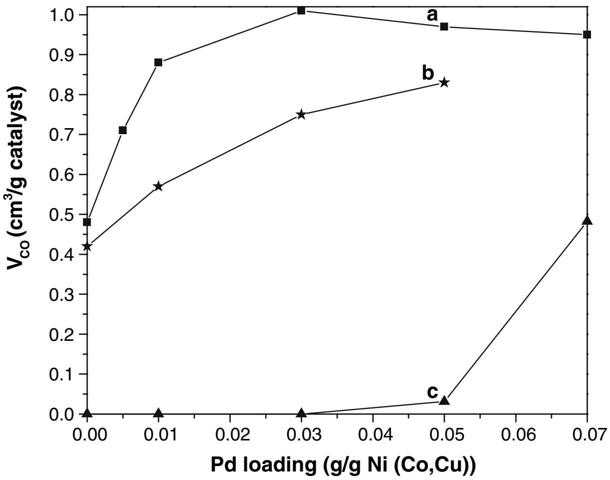

Figure 3. The volume of adsorbed CO on (a) Pd/Ni, (b) Pd/Co and (c) Pd/Cu catalysts with different Pd loading.

characterization. In Pd/Cu catalysts with low Pd loading, all Pd atoms are most likely embedded in Cu to form either surface alloy or bulk solution, resulting in the absence of CO adsorption. At higher Pd loadings, such as 0.050 g Pd/g Cu, some Pd atoms might be present on the catalyst surface, leading to the small amount of CO adsorption. Significant amount of CO adsorption occurs at a Pd loading of 0.070 g Pd/g Cu, although the corresponding XRD measurement (figure 2) does not show the diffraction peaks of Pd crystallites. The discrepancy between the CO chemisorption and XRD results might be explained by the formation of very small Pd particles on Cu at high Pd loadings (> 0.050 g Pd/g Cu).

3.3. Cyclohexene self-hydrogenation

The self-hydrogenation of cyclohexene is used as a probe reaction to compare the catalytic properties of Pd on Co, Ni and Cu. Figure 4 shows the conversion of cyclohexene on Pd/M (M = Co, Ni, Cu) catalysts with different Pd loadings. The conversion increases with Pd loading on both Pd/Ni and Pd/Co catalysts at low Pd loadings. At higher Pd loadings the conversion only increases slightly between 0.070 and 0.10 Pd/g Ni for Pd/Ni catalysts, and between 0.030 and 0.050 g Pd/g Co for Pd/Co catalysts. However, the catalytic behavior of Pd/Cu system is quite different from that of Pd/Ni or Pd/Co catalysts. The conversion of cyclohexene is negligible until the Pd loading increases to 0.050 g Pd/g Cu.

On both Pd/Co and Pd/Cu catalysts, the results of CO chemisorption (figure 3) are quite consistent with the conversion of cyclohexene (figure 4). However, for Pd/Ni catalysts, the volume of adsorbed CO increases with Pd loading up to 0.030 g Pd/g Ni, whereas the conversion of cyclohexene continues to increases with Pd loading up to 0.070 g Pd/g Ni. At present we do not understand the origin of this difference. 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 self-hydrogenation of cyclohexene. More detailed studies, such as Extended X-ray Absorption Fine Structure (EXAFS) measurements under *in-situ* conditions, will be performed to detect the formation of the Pd–Ni bond and the Pd–Ni coordination number to further understand the structure-property relationship in the Pd/Ni bimetallic catalysts.

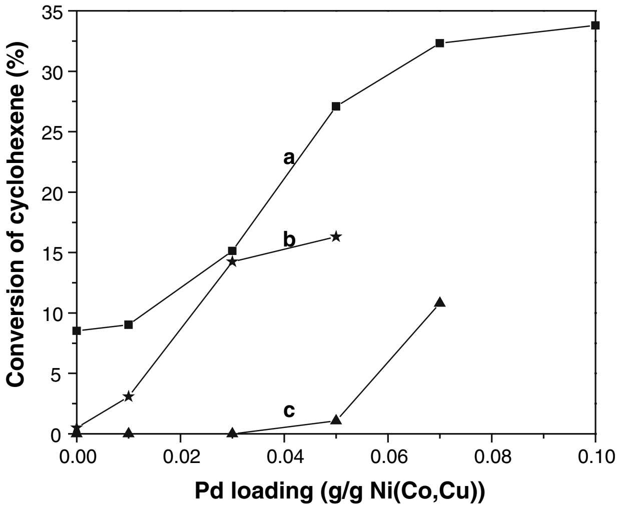

Figure 4. Conversion of cyclohexene self-hydrogenation on (a) Pd/Ni, (b) Pd/Co and (c) Pd/Cu catalysts with different Pd loading at (a,) 318 K and (b,c) 313 K.

Despite the uncertainty in the surface structure of the Pd/Ni catalysts under reaction conditions, our results demonstrate the advantage of the replacement reactions over the impregnation synthesis method. Figure 5 compares the catalytic activity of Pd/Ni catalysts prepared by different methods for the self-hydrogenation of cyclohexene. At all temperatures the product ratio of cyclohexane to benzene is approximately 2:1, confirming the self-hydrogenation pathway for all the catalysts. The comparison in figure 5 shows that, at all temperatures, the activity of the 0.070 g Pd/g Ni catalyst prepared by the replacement reaction remains higher than that of the 0.070 g Pd/g Ni-im and 0.070 g Pd/g Al_2O_3 catalysts prepared by the impregnation method. A possible reason for the higher activity of the 0.070 g Pd/g Ni catalyst is due to the monolayer-dispersion of Pd on the Ni surface, similar to that in the Pt/Ni catalysts prepared using replacement reactions [20].

Finally, the results in figures 4 and 5 demonstrate that the catalytic properties are different for Pd/Co, Pd/Ni, and Pd/Cu. Such differences can be related to their different electronic structures (Co $3d^7 4s^2$, VIII group; Ni $3d^8 4s^2$, VIII group; Cu $3d^{10} 4s^1$, IB group). Density functional theory (DFT) modeling and parallel single crystal surface science studies are underway to further understand the correlation between the catalytic, electronic and structural properties in Pd–M bimetallic alloys.

4. Conclusions

Based on the results presented above, the following conclusions can be made regarding the properties of Pd–M bimetallic catalysts prepared by the replacement reactions:

1. The 0.070 g Pd/g Ni catalyst prepared by the replacement reaction shows higher activity for cyclohexene self-hydrogenation than 0.070 g Pd/g Ni-im and 0.070 g Pd/g Al_2O_3 catalysts prepared by the impregnation method.

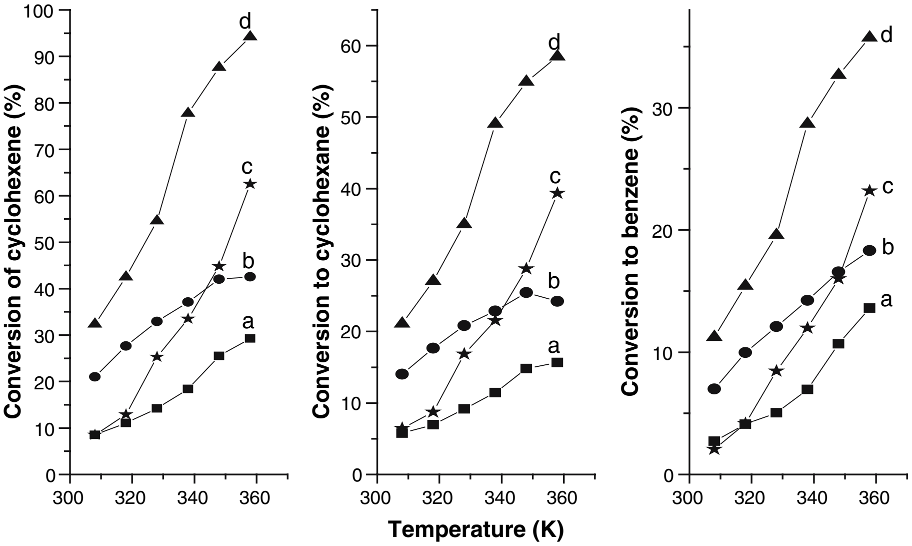

Figure 5. Conversion of cyclohexene(left), to cyclohexane (middle) and benzene(right) in cyclohexene self-hydrogenation on catalysts prepared by different methods: (a) Ni; (b) 0.070 g Pd/g Ni-im; (c) 0.070 g Pd/g Al_2O_3; and (d) 0.070 g Pd/g Ni by replacement reaction. The CO uptake volumes (cm^3 CO/g catalyst) for the four catalysts are 0.48, 2.41, 1.02, and 0.95, respectively.

2. A possible explanation for the enhanced activity is the monolayer-dispersion of Pd from the synthesis using replacement reactions. The monolayer-dispersion of Pd on Ni is supported by the XRD and CO chemisorption measurements. Pd is also likely monolayer-dispersed on the Co surface in the Pd/Co bimetallic catalysts.
3. A discrepancy is observed between the cyclohexene self-hydrogenation activity, which reaches to a plateau value at 0.07 g Pd/g Ni, and the CO chemisorption capacity, which reaches to a plateau value at 0.03 g Pd/g Ni. Further studies are needed to determine the origin of such difference.

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