

Characterization of Pd-Ni/SiO₂ Catalysts Prepared from Organometallic Cluster Precursor

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ABSTRACT

The Pd-Ni/SiO₂ catalysts were prepared by impregnation of two precursors on silica: an acetonitrile solution of [PPh₄]₄[Pd₁₃Ni₁₃(CO)₃₄] (1) and a mixture of palladium and nickel salts. Both catalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), BET surface area analysis, and temperature-programmed reduction (TPR). In addition, the metal loading was determined by ICP and the number of active sites was measured by hydrogen adsorption experiment. The cluster's carbonyl ligands were removed by heating at the 80°C for 10 minutes while the counter cations, [PPh₄]⁺ on were removed by heating at 400°C. XRD peaks of Pd-Ni/SiO₂ prepared from the cluster shifted slightly possibly due to Pd-Ni alloy formation. From TPR experiment, it was found that the reduction temperature of Ni in the Pd-Ni/SiO₂ catalysts prepared from cluster was significantly lowered than that of the Ni/SiO₂ reference indicating that Pd and Ni were still intact. When the two metals formed Pd-Ni alloy, some Pd coordination sites were taken by Ni and lowered the hydrogen adsorption sites. As a result, Pd-Ni/SiO₂ catalysts prepared from salt solution adsorbed hydrogen better than that from cluster.

INTRODUCTION

Metal clusters are complexes containing at least three metal-metal bonds that form triangular or larger metal-core structure.¹ They may be considered as intermediates between molecular compounds and solid-state materials. Large clusters like [Rh₁₃(CO)₂₄H₃]²⁻ and [Os₂₀(CO)₄₀]²⁻ have metal-core geometries that resemble close-packed metal atoms in small naked metal crystallites.² The metal-core atoms of each of these large metal carbonyl clusters can be thought of as a metal aggregate that is stabilized by CO ligands on its metal surface. Such clusters can be used as precursors for preparing heterogeneous catalysts.³

In general, heterogeneous catalysts are usually obtained by using inorganic metal salts adsorbed on supporting materials by techniques such as impregnation followed by calcination which is an oxidation at high temperatures. The resulting metal oxide crystals are then reduced into metal particles by a reductant such as hydrogen. However, catalysts prepared by this general method do not provide good control of particle size distribution and metal composition.⁴ Metal clusters have been used instead of metal salts to impregnate a support in order to prepare heterogeneous catalysts and such clusters possess attractive features such as solubility in organic solvents. Milder conditions can be used to activate the catalysts prepared from metal clusters because metal atoms in the clusters are in low oxidation states and can be reduced more easily than conventional metal salt precursors. Clusters of Pt, Rh, Ir, Ru can be synthesized in the cavity of zeolites by a procedure called "ship-in-bottle" which includes carbonylation of ion-exchanged

metals in zeolites. After decarbonylation, removal of carbonyl ligands, the metal atoms are still intact and are active catalysts.⁵

One method to modify the activity and selectivity of supported metal catalysts is to form alloy with another element. There are several reports that bimetallic catalysts show better catalytic performance than monometallic catalysts of the same metals. Bimetallic catalysts can be prepared by several methods such as coimpregnation of two metal salts on inorganic support, or ion-exchange.⁶

Our interest is on supported bimetallic Pd-Ni catalysts. Both Pd and Ni are active for several catalytic reactions but there are only a few examples of bimetallic Pd-Ni catalysts. Bimetallic PdNi_x/zeolite NaY was prepared by simultaneous exchange of the two metal ions and washed with either dilute nitric acid (pH = 6) to give loading 10.3Pd + 8.6Ni or with dilute sodium hydroxide (pH = 10.5) to give loading 10.0Pd + 9.2Ni. The evidence from TPR and TPD indicated that Pd and Ni in the same zeolite formed bi-metallic particles and enhanced each other's reducibility in which both Ni and Pd reduction temperature decreased.⁷ The bimetallic alloy catalysts were reported to have significantly higher selectivity for methane formation from CO hydrogenation.⁸ Polymer-supported PVP-PdCl₂-4NiCl₂-PPh₃ bimetallic catalyst [PVP=poly(*N*-vinyl-2-pyrrolidone)] was an efficient catalyst for the hydroesterification of styrene.⁹ The high activity and selectivity of the catalyst are achieved by the synergic effect of Pd-Ni bimetallic system and the effect of polymer protection.¹⁰ However, it is difficult to keep two metals intact and to control metal particle size. To solve this problem, bimetallic cluster precursors should be considered because they already contain metal-metal bond. In addition, shape and size of metal particles of catalysts prepared from clusters are not much different to that of the cluster precursor.

Recently, [PPh₄]₄[Pd₁₃Ni₁₃(CO)₃₄] (**1**) was successfully separated in high yield (> 90%) from reduction of Pd(OAc)₂ by [NMe₄]₂[Ni₆(CO)₁₂] in DMF.¹¹ The cluster metal core consists of 26 metal polyhedron with close-packed arrangement. Since the preparation procedure was simple, cluster **1** was selected a precursor for Pd-Ni/SiO₂ catalyst preparation in which an acetonitrile solution of cluster **1** was impregnated over silica support. After being dried under nitrogen, heated to remove CO ligands, and calcined to removed [PPh₄]⁺, the PdNi/SiO₂ catalysts were characterized by powder X-ray diffraction, scanning electron microscopy, BET surface area analysis, and temperature-programmed reduction. The metal loading on each catalyst was determined by ICP and the amount of active site was calculated from hydrogen adsorption experiment. All results will be compared with catalysts prepared from mixtures of palladium and nickel salt solution.

EXPERIMENTAL PROCEDURES

A. Synthesis of [PPh₄]₄[Ni₁₃Pd₁₃(CO)₃₄] (**1**)

Cluster **1** was used as a catalyst precursor. It was prepared and separated in high yields under nitrogen atmosphere by small modifications of the procedure, described by Tran et al. in reference 11. A solution of Pd(OAc)₂ in DMF was added dropwise via a stainless steel canula into a stirred DMF solution of [NMe₄]₂[Ni₆(CO)₁₂] over approximately 20 minutes. The solution color changed quickly from cherry red to dark brown. After being stirred at room temperature for six hours, a solution of PPh₄Br in methanol was added quickly. Then it was cooled in an ice bath after which the slow addition of deoxygenated water gave rise to a dark brown precipitate. This precipitate was separated by filtration, washed several times with methanol, and the remaining solid was extracted with of acetonitrile. The IR absorption bands of the acetonitrile

solution were at 2024(s), 2000(sh), 1883(s), and 1860(s) cm^{-1} in accordance with those reported by Tran et al. for **1**.

B. Preparation of Pd-Ni/SiO₂ by Impregnation of **1 on Silica**

The amount of acetonitrile required to wet the silica support (incipient wetness) was determined prior to the impregnation. An acetonitrile solution of **1** was dropped slowly onto oven-dried silica under nitrogen atmosphere. The samples were then dried under dry nitrogen flow at room temperature, heated at 80°C for 10 minutes to remove carbonyl ligands, and then calcined at 400°C for 3 hours to remove $[\text{PPh}_4]^+$. The removal of carbonyl ligands were confirmed by infrared spectroscopy. The metal loading in each catalyst was confirmed by ICP analysis while the surface area was measured by BET method. The number of active sites was determined by hydrogen adsorption experiments. The metallic phase and morphology were evaluated by XRD and SEM, respectively. In addition, metal reduction temperature was studied by temperature-programmed reduction (TPR).

C. Preparation of Pd-Ni/SiO₂, Pd/SiO₂, and Ni/SiO₂ from Metal Salts

Pd-Ni/SiO₂ catalysts were also prepared by impregnation silica with a mixture of Pd(OAc)₂ and Ni(OAc)₂ with the Pd:Ni mole ratio and loading similar to those of catalysts from cluster precursors. The metal salt solution was slowly dropped onto oven-dried silica, dried at 110°C and calcined at 400°C for 3 hours. Similarly, Pd/SiO₂ and Ni/SiO₂ reference catalysts were prepared by impregnation of Pd(OAc)₂ and Ni(OAc)₂ solution to silica, respectively.

D. Hydrogen Adsorption Experiment

A known amount of Pd-Ni/SiO₂ catalyst was placed in a U-tube reactor connected to a thermal conductivity detector (TCD) and gases. Catalyst was heated from room temperature to 450°C at a 5°C/min rate under hydrogen atmosphere and held for one hour in order to complete catalyst reduction. Then the temperature was lowered to 400°C, held for 30 minutes and cooled down to 50°C and hydrogen injection was detected by the TCD. The catalysts were then cooled down to room temperature in nitrogen.

E. Temperature-Programmed Reduction (TPR)

TPR studied was done in a thermogravimetric analyzer (TGA). Each catalyst sample was loaded into a sample pan, heated under nitrogen flow at 110°C to remove moisture and air in the pores, and cooled down to room temperature. Then flow gas was then switched to hydrogen as the temperature was raised to 900°C at the rate 10°C/min and held for 30 minutes. Each sample weight loss as well as its derivative from reduction was recorded.

F. Preparation of Pd-Ni/SiO₂ by Impregnation of **1 on Silica**

The amount of solvent required to wet the silica support (incipient wetness) was determined prior to the impregnation. An acetonitrile solution of **1** was dropped slowly onto oven-dried silica under nitrogen atmosphere. The samples were then dried under nitrogen flow at room temperature and calcined at 400°C for 1, 2, and 3 hours to remove carbonyl ligands and $[\text{PPh}_4]^+$ cation. Metal phase, morphology, and surface area of all catalysts were evaluated by XRD, SEM, and BET, respectively. Metal loading was also confirmed ICP.

RESULTS AND DISCUSSION

An amount of Pd and Ni was determined by ICP technique and the results are shown in Table 1. The catalysts prepared from cluster were labeled CC1, CC2, and CC3, which had total loading of

1.468, 1.858, and 1.594, respectively. According to their weight percent of Pd and Ni, the mole ratio of Pd/Ni were 0.31, 0.39, 0.37 which were not 1 as expected from the cluster precursor, $[\text{Pd}_{13}\text{Ni}_{13}(\text{CO})_{34}]^{4+}$. The possible explanation for this ratio might be from crystallographic disorder in which palladium atomic positions were substituted by nickel. As reported by Tran [11], the Pd/Ni ratios of occupancy at some positions were 0.23/0.77, 0.22/0.78 and 0/1.00.

Upon heating at 80°C for 10 minutes, carbonyl ligands on the cluster were removed and the carbonyl peaks were no longer observed. Further calcination at 400°C for 3 hours removed successfully $[\text{PPh}_4]^+$ from the cluster as phosphorus was not detected.

The catalysts prepared from salts were labeled SC1, SC2, and SC3 for loading of 1.634, 5.114, and 8.364%, respectively. However, the only catalyst with comparable loading to catalysts from cluster was SC1. Hydrogen adsorption experiment revealed that SC1 had higher hydrogen adsorption and higher H/Pd ratio than CC1, CC2, and CC3. Because Pd is known to adsorb hydrogen better than Ni, it is possible that Pd and Ni in catalysts prepared from cluster were still intact resulting in lower hydrogen adsorption of Pd. When compare the SC series, the ratio H/Pd of SC3 was lower than others due to higher loading in which larger metal particle (i. e., lower surface area) was expected. Surface areas of all catalysts from BET analyses were in the same range indicating that preparation from either cluster or salt at our conditions did not cause obvious pore clogging from metal sintering.

Table 1 Metal loading on PdNi/SiO₂ catalysts prepared from cluster and metal salts determined by ICP analysis, results from hydrogen adsorption experiment, and BET surface area (CC = catalyst prepared from cluster, SC = catalyst prepared from salt)

Cat.	Total	Pd	Ni	H atom/g cat	H/Pd	H/M	BET surface area (m ² /g)
CC1	1.468	0.685	0.782	1.20665E-06	0.0187	0.0061	282.02
CC2	1.858	0.928	0.931	2.8640E-06	0.0328	0.0117	277.50
CC3	1.594	0.781	0.813	0.0000E+00	0.0000	0.0000	275.31
SC1	1.634	0.523	1.111	3.0559E-06	0.0621	0.0128	277.12
SC2	5.113	1.857	3.256	1.1267E-05	0.0645	0.0154	277.45
SC3	8.364	4.590	3.774	1.9870E-05	0.0461	0.0185	262.19

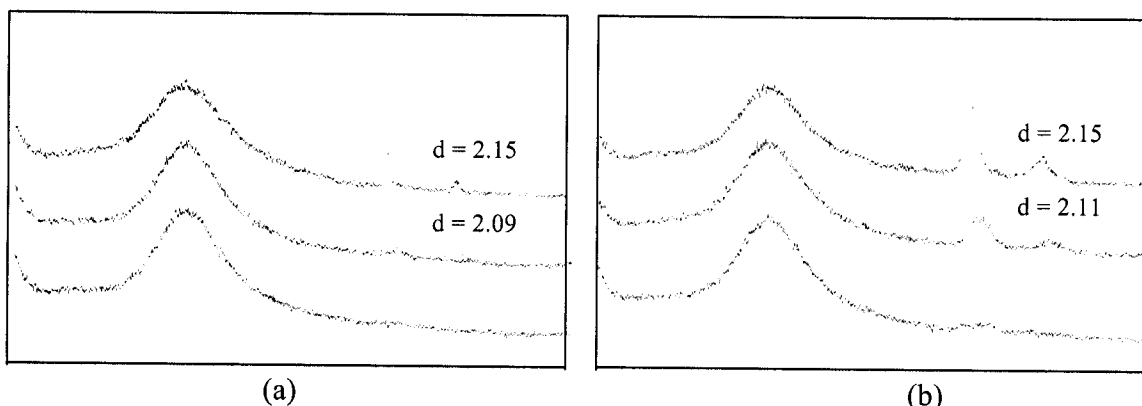


Figure 1 XRD spectrum of (a) PdNi/SiO₂ cluster-catalysts reduced at 450 °C for 1 hour, from top to bottom, CC3, CC2, and CC1. (b) PdNi/SiO₂ salt-catalysts reduced at 450 °C for 1 hour, from top to bottom, SC3, SC2, and SC1. Note the d of pure Pd and pure Ni are 2.25 and 2.03, respectively.

XRD spectrum of catalysts prepared from both cluster and salt mixture are shown in Figure 2. There was a slight shift of peaks in Figure 2a compared to Figure 2b which might cause by alloy formation. From the shape of the peaks, the metal particle size increased in the order $CC3 > CC2 > CC1$. Thus, it agreed well with hydrogen adsorption experiment of CC3 which was unable to detect.

Similarly, metal particle size of catalysts prepared from salts were in the order $SC3 > SC2 > SC1$. Even though the total hydrogen adsorption increased with loading, the H/Pd ratio was smallest for SC3.

Morphology of all catalysts was studied by scanning electron microscopy and the surface images taken with 20,000 magnification are displayed in Figure 2 and 3. In Figure 2 there was no distinction among catalysts prepared from clusters. It was hard to conclude the existence of metal particle. When an electron beam was directed at random areas for EDX measurements, at what seemed to be metal particles or smooth areas, both Pd and Ni were detected in all areas. Thus, the only conclusion to be made is that those catalysts contain good metal dispersion.

Similar EDX results were obtained from catalysts from salt mixtures despite the more messy appearance of the surface (Figure 3).

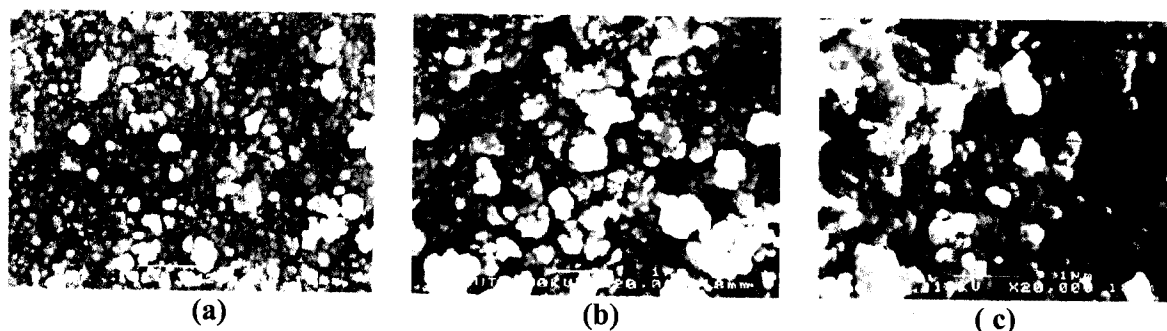


Figure 2 SEM picture (x 20,000) of PdNi/SiO₂ prepared by impregnation of 1 on silica. (a) 1.468%PdNi/SiO₂ (Pd = 0.685%, Ni = 0.782%), (b) 1.858 %PdNi/SiO₂ (Pd = 0.928%, Ni = 0.931 %), and (c) 1.594 %PdNi/SiO₂ (Pd = 0.7818%, Ni = 813%)

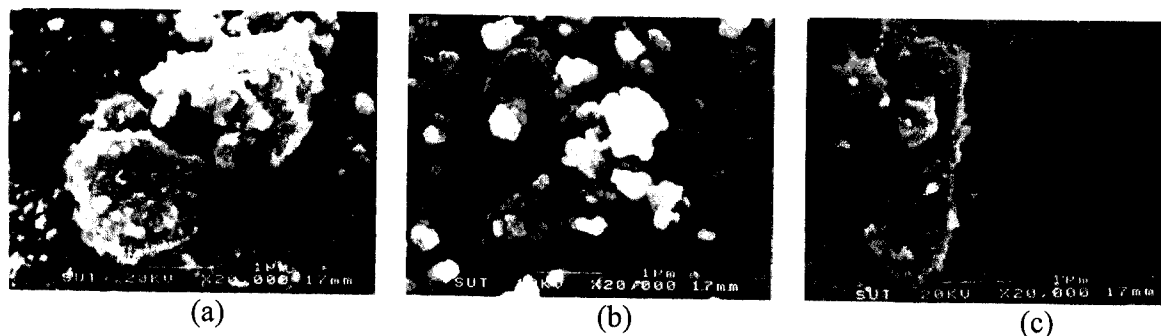


Figure 3 SEM picture (x 20,000) of PdNi/SiO₂ prepared by impregnation of 1 on silica. (a) 1.634%PdNi/SiO₂ (Pd = 0.523%, Ni = 1.111%), (b) 5.113 %PdNi/SiO₂ (Pd = 1.857%, Ni = 3.256%), and (c) 8.364 %PdNi/SiO₂ (Pd = 4.590%, Ni = 3.774%)

Temperature-programmed reduction of PdNi/SiO₂ was investigated on a TGA compared to Pd/SiO₂ and Ni/SiO₂ and the results are listed in Table 2. The peak of weight loss was obtained from derivative TG curve. The weight loss of Pd/SiO₂ was between 30-80°C which could be a contribution from loss of surface water as well as reduction. The weight loss over Ni/SiO₂ took place at two temperature ranges: 30-80 and 275-350°C. The loss during first range caused by elimination of surface water while that during the second range was caused by reduction. This result agreed with the fact that palladium oxide is reduced easier than nickel oxide.

The weight loss of PdNi/SiO₂ took place at the 30-160°C range with two peaks which were between that of Pd/SiO₂ and Ni/SiO₂. This result indicated that Pd and Ni in PdNi/SiO₂ were still intact. Hydrogen first dissociatively adsorbed on palladium oxide and reduced it to palladium metal which was active site for further hydrogen adsorption. Hydrogen on palladium then migrated to reduce nickel oxide next to palladium on the same particle. Thus, the reduction temperature of nickel was decreased.

Table 2 Ranges and peaks of weight loss and of Pd/SiO₂, Ni/SiO₂, and PdNi/SiO₂ from TPR experiment

Catalyst	Weight loss Temperature (°C)	Peak of weight loss (°C)
Pd/SiO ₂	30-80	43
Ni/SiO ₂	30-80 and 275-350	43 and 307
PdNi/SiO ₂ from cluster	30-160	52 and 103

CONCLUSIONS

The Pd-Ni/SiO₂ catalysts were prepared by impregnation of two precursors on silica: an acetonitrile solution of [PPh₄]₄[Pd₁₃Ni₁₃(CO)₃₄] (1) and a mixture of palladium and nickel salts. The cluster's carbonyl ligands were removed by heating at the 80°C while the counter cations, [PPh₄]⁺ on were removed by heating at 400°C. XRD peaks of Pd-Ni/SiO₂ prepared from the cluster shifted slightly possibly due to Pd-Ni alloy formation. TPR experiment revealed that the reduction temperature of Ni in the Pd-Ni/SiO₂ prepared from cluster was lowered than that of the Ni/SiO₂ reference indicating that Pd and Ni were still intact. When the two metals formed Pd-Ni alloy, some Pd coordination sites were taken by Ni and lowered the hydrogen adsorption sites. As a result, Pd-Ni/SiO₂ catalysts prepared from salt solution adsorbed hydrogen better than that from cluster.

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