

Direct Hydrothermal Synthesis of Palladium-Incorporated Silicate-Structured Mesoporous Catalysts

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Pd-Si-structured novel mesoporous nanocomposite catalytic materials, having quite high Pd/Si ratios, were synthesized by an acidic direct hydrothermal synthesis route. The nanocomposite catalytic materials were then characterized by XRD, XPS, EDS, nitrogen adsorption, and SEM techniques. Unlike MCM-41, the XRD patterns indicated a rather wide $d_{(100)}$ band at a 2θ value of about 1.9. The materials, with very high Pd/Si wt ratios between 1.43 and 2.66, were synthesized and had BJH surface area values between 600 and 200 m²/g. The pore size distributions of these materials were also quite narrow, indicating pores between 2 and 7 nm.

Key Words: Mesoporous catalysts, MCM-41, Pd, hydrothermal synthesis, reforming.

Introduction

Development of novel catalysts for hydrogen production by reforming alcohols has attracted the attention of researchers in recent decades.^{1–3} In a recent article,⁴ it was reported that Pd showed very high activity in steam reforming of ethanol. Pd-based supported catalysts also show very high activity in dry reforming of methane⁵ and in a number of hydrogenation reactions.^{6,7} Pd also has applications in the purification and storage of hydrogen.^{8,9}

Discovery of MCM-41-like mesoporous materials with narrow pore size distributions and high surface areas^{10,11} opened a new pathway in catalysis research. Catalytic performance of these materials was shown to be significantly improved by the incorporation of metals or metal oxides into their structure.¹² Synthesis of Pd-incorporated mesoporous catalysts, and nanocomposite materials composed of Pd nanoballs and nanowires within the pores of mesoporous materials has recently attracted the attention of researchers.^{13–15} In one of our previous reports,¹⁶ the effects of synthesis conditions on the structure of Pd-incorporated MCM-41-type catalytic materials were discussed. In the present study, Pd-Si mesoporous nanocomposite sponge-like materials with very high Pd/Si ratios were synthesized by an acidic hydrothermal route, for potential applications in hydrogen storage and in reforming methane and alcohols.

Experimental

A hydrothermal procedure used in MCM-41 synthesis is described in our recent publications.^{16–18} Conventionally, hydrothermal synthesis of MCM-41 is carried out in a basic medium at a pH of about 11. In the present study, Pd-Si mesoporous nanocomposite catalytic materials were synthesized by an acidic direct hydrothermal synthesis route. In this procedure, an acidic solution of PdCl₂ was first mixed with a hexadecyltrimethylammonium bromide (surfactant) solution. Then, sodium silicate solution (containing 27 wt% SiO₂ or a solution of TEOS (tetraethylortosilicate)) was slowly added to this mixture under continuous mixing.¹⁸ The pH of the solution was adjusted to 1.6 and the produced gel was transferred into a Teflon-lined autoclave for hydrothermal synthesis at 120 °C, for 96 h. The solid product was filtered and washed until the pH of the wash liquid was almost neutral. The solid material was then dried in a vacuum and calcined in a flow of dry air. During calcination, the furnace temperature was increased at a rate of 1 °C/min until 550 °C and then calcination was continued at this temperature for 6 h. Our previous TPR results¹⁶ indicated completion of the reduction of PdO by the hydrogen gas before 200 °C. Therefore, calcined samples were reduced in a flow of hydrogen gas at 200 °C. The synthesized nanocomposite materials were then characterized by XRD (Rigaku D/MAX2200), XPS (SPECS SAGE 150), EDS (JEOL JSM-6400), nitrogen adsorption (Micrometrics ASAP 2000), SEM, and atomic absorption spectroscopy (AAS) techniques.

Results and Discussion

Composite novel mesoporous materials with very high Pd/Si atomic ratios (as high as 0.7) were synthesized in this study. Typical XRD patterns of the calcined and the reduced materials with a Pd/Si atomic ratio of 0.38 (which corresponds to a Pd/Si weight ratio of 1.43 for the calcined material) are given in Figure 1a. The size of Pd clusters within the synthesized materials was estimated (from the Scherrer equation) to be about 16 and 31 nm for the calcined and reduced samples, respectively. For this sample, the Pd/Si molar ratio in the solution was adjusted to 0.26. Chemical analysis showed that the Pd/Si ratio in the solid product was higher than the corresponding value in the solution, indicating the loss of some Si during the hydrothermal synthesis and washing steps. As seen in the Table, for all the materials synthesized using sodium silicate as the Si source, Pd/Si ratios of the solid materials were higher than the corresponding values in the synthesis solution. However, when TEOS was used as the silica source, the Pd/Si ratio in the solid product was lower than the corresponding value in the solution. These results indicated that sodium silicate was a better silica source for the mesoporous materials synthesized in this work.

Table. Physical properties and chemical composition of the synthesized materials.

SAMPLE r: reduced c: calcined	Si source	Pd/Si atomic ratio (solution)	Pd/Si atomic ratio (EDS)	BET area m ² /g	BJH area m ² /g	Pore volume cm ³ /g	BJH average pore diameter nm
Pd-Si-Sp6r	Sodium silicate	0.50	0.70	168	221	0.24	4.3
Pd-Si-Sp4r	TEOS	0.50	0.31	397	511	0.62	4.8
Pd-Si-Sp1r	Sodium silicate	0.26	0.34	514	659	0.57	3.5
Pd-Si-Sp1c	Sodium silicate	0.26	0.38	480	604	0.52	3.4

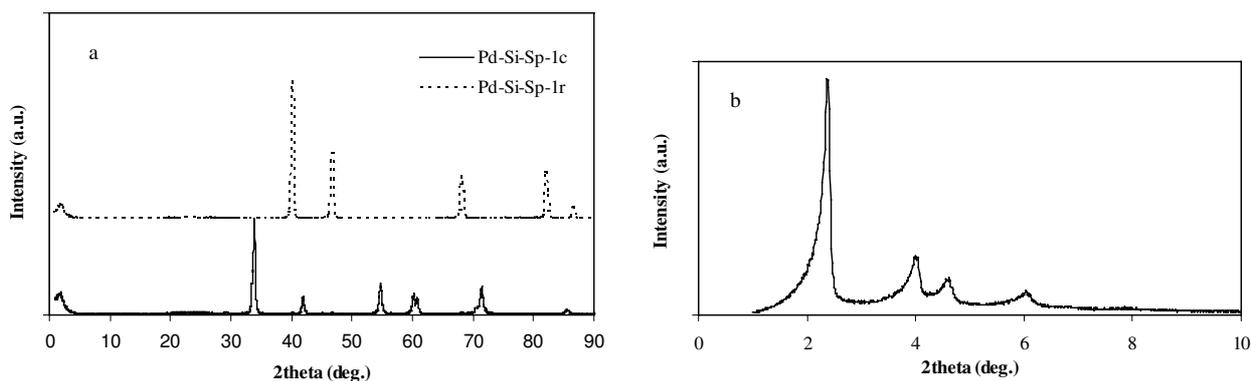


Figure 1. XRD patterns of (a) Pd-Si-Sp1 and (b) MCM-41.

A typical XRD of pure MCM-41, which was synthesized by the basic route, is given in Figure 1b. For the Pd-incorporated MCM-41-like mesoporous catalytic material synthesized in our previous study¹⁶ by the basic route and having a Pd/Si atomic ratio of 0.056, a very sharp Bragg peak, which was observed at a 2θ value of about 2.3 with 3 reflections, indicated the formation of the characteristic MCM-41 structure. Pd-incorporated novel sponge-like mesoporous Pd-Si materials synthesized in the present work were named Pd-Si-Spic or Pd-Si-Spir, for the calcined and reduced materials, respectively. Here, i corresponds to the sample number synthesized in our studies. The XRD patterns of the mesoporous sponge-like materials (calcined, Pd-Si-Sp1c and reduced, Pd-Si-Sp1r) synthesized by the acidic route gave rather wide $d_{(100)}$ bands at a 2θ value of about 1.87 (which corresponds to $d_{(100)} = 4.7$ nm) (Figure 1a). Such behavior was observed for all the samples synthesized by the acidic route having Pd/Si atomic ratios between 0.05 and 0.70. These materials cannot be considered MCM-41; however, they are new mesoporous sponge-like nanocomposite materials.

The SEM photograph of Pd-Si-Sp1r indicated the presence of agglomerated particles 0.5-3.0 μm in diameter (Figure 2). These materials were also found to be highly mesoporous, having pores between 2 and 10 nm in diameter and different Pd/Si ratios. Typical pore size distribution curves of the calcined and reduced materials (Pd-Si-Sp1c and Pd-Si-Sp1r) are given in Figure 3. Although the Pd/Si ratios of Pd-Si-Sp1r and Pd-Si-Sp4r were quite similar to each other (Table), Pd-Si-Sp4r had a wider pore size distribution. Moreover, the pore size distribution of Pd-Si-Sp4r shifted to the larger pores. Pd-Si-Sp4r was prepared by using TEOS as the silica source, whereas Pd-Si-Sp1r was synthesized from a sodium silicate solution. These results also indicated the importance of the silica source to the structure of the final product. The material containing the highest amount of Pd/Si (Pd-Si-Sp6r) had a much wider pore size distribution. The sponge-like mesoporous Pd-incorporated materials also had relatively high surface area values. The BJH surface area values of the reduced materials decreased from 659 to 221 m^2/g as the Pd/Si atomic ratio of the material increased from 0.34 to 0.70 (Table). However, our previous work¹⁶ indicated that Pd-MCM-41 materials synthesized by the basic route with lower Pd/Si atomic ratios (< 0.05) had much higher surface area values (over 1000 m^2/g). Although an increase in the Pd/Si ratio caused a decrease in surface area, the surface area values were still quite high for catalytic applications. The results reported in the Table also indicate that, among the mesoporous materials containing similar Pd/Si ratios (Pd-Si-Sp4r and Pd-Si-Sp1r), the material synthesized using sodium silicate as the silica source gave higher surface area. This is another advantage of sodium silicate over TEOS in the acidic synthesis route of such mesoporous materials.

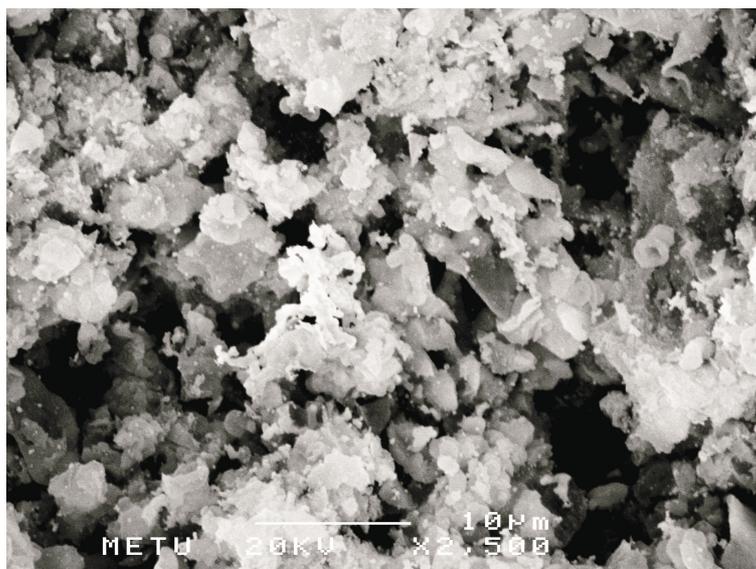


Figure 2. SEM image of Pd-Si-Sp1r.

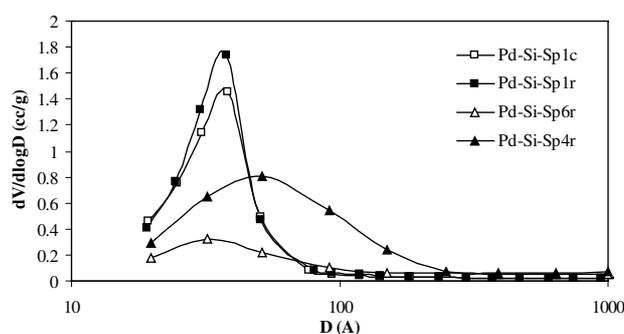


Figure 3. Adsorption pore size distribution of the calcined and reduced forms of Pd-Si-Sp.

Even the mesoporous sponge-like material containing the highest amount of Pd (Pd/Si atomic ratio of 0.70, which corresponds to a weight ratio of 2.66) had a BJH surface area value over 200 m²/g. This is quite advantageous for a material that can be used in hydrogen storage. Hydrogen is known to be chemisorbed within the Pd lattice, forming hydrides.⁹ This sponge-like material containing such a high Pd/Si ratio and relatively high surface area may have applications in hydrogen storage.

Some physical properties of the Pd-incorporated mesoporous materials synthesized in this work are summarized in the Table. The average pore diameters (d_{pore}) of the synthesized materials were all in the range of 4-5 nm, and pore volumes decreased from 0.57 to 0.24 cm³/g with an increase in the Pd/Si atomic ratio from 0.34 to 0.70 in the reduced materials. An average value for the lattice parameter of these mesoporous materials may be estimated from¹⁶ $a = \frac{2}{\sqrt{3}}d_{(100)}$. The lattice parameter and the average pore wall thickness (as estimated from $\delta = a - d_{pore}$) values for Pd-Si-Sp1r were estimated as 5.45 nm and 1.25 nm, respectively. For materials having higher Pd/Si ratios, XRD patterns and pore size distributions were much wider, although pore wall thickness was not estimated. The nitrogen adsorption isotherms of the synthesized materials showed typical type IV isotherms (Figure 4), also indicating that the mesoporous structure capillary condensation of nitrogen was observed at relative pressures over 0.4. For the calcined and reduced samples, nitrogen adsorption isotherms were quite similar, indicating similar pore structures.

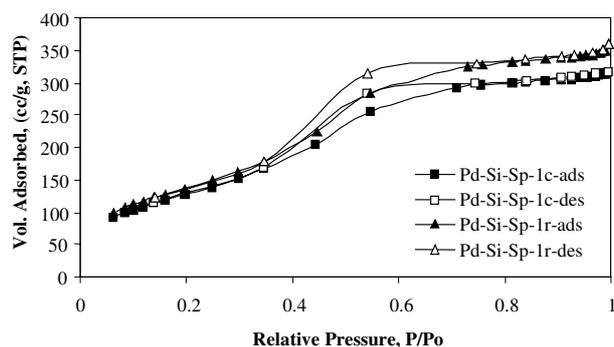


Figure 4. Nitrogen adsorption-desorption isotherms of Pd-Si-Sp1.

XPS analysis of the calcined material (Pd-Si-Sp1c) gave a wide $3d_5$ band, and 2 peaks at 336.7 and 337.5 eV (Figure 5a)¹⁸. These peaks corresponded to PdO_2 and PdO, respectively. For PdO_2 , PdO, and Pd, XPS bands were expected at 337.9, 336.3, and 335.1 eV, respectively.¹⁶ For the hydrogen treated material (Pd-Si-Sp1r), the XPS band was observed at 335.1 eV (Figure 5b), indicating that most of the Pd was reduced to the Pd^0 state.

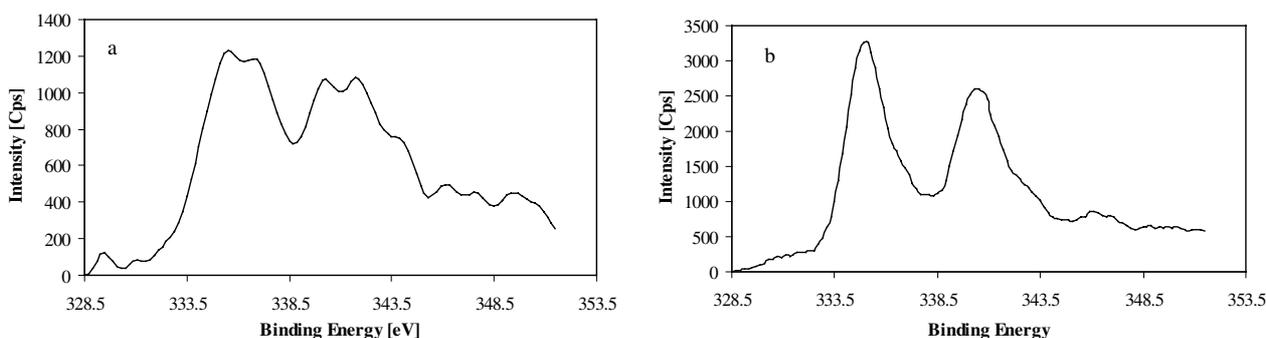


Figure 5. XPS of Pd-Si-Sp-1. (a) Calcined; (b) Reduced.

Conclusions

Mesostructured Pd-Si composite materials with very high Pd/Si atomic ratios, as high as 0.7, were synthesized by a direct acidic hydrothermal synthesis route. These materials were shown to have rather narrow pore size distributions and high surface areas, with average pore diameters between 4 and 5 nm. The surface area values of these Pd sponge-like materials decreased when the Pd/Si ratio increased. For the materials containing a Pd/Si atomic ratio of 0.38, Pd was estimated to be distributed within the lattice of the synthesized materials as Pd clusters of about 16 nm, for the calcined material. For the reduced material, cluster size increased to about 31 nm. The synthesized materials have attractive properties for potential use in hydrogen storage, as well as in hydrogen production by steam and dry reforming of alcohols and methane.

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