

Synthesis, Characterization, and Photoactivity of Nanosized Palladium Clusters Deposited on Titania-Modified Mesoporous MCM-41

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Nanoparticles of Pd supported in the mesopores of titania-modified MCM-41 have been synthesized by the photodeposition method for the first time and characterized by XPS spectroscopy, N₂ sorption isotherms, XRD, TEM, SEM, diffusion reflectance UV–vis absorption spectra, and Raman spectra. The metallic Pd clusters were dispersed uniformly in the mesopores of titania-modified MCM-41. The photocatalytic activity of Pd-deposited titania-modified MCM-41 has been investigated. For the photoreduction of Cr(VI) to Cr(III), Pd-deposited titania-modified MCM-41 exhibited much higher photocatalytic activity than the supports did. © 2001 Academic Press

INTRODUCTION

Nanoscale noble metal clusters on supports as a distinct state of matter are of interest due to their structure and reactivity (1, 2). Recently, supported metal catalysts have attracted much attention because of their high catalytic activity for NO reduction, CO oxidation, CO hydrogenation, and CH₃OH synthesis. Palladium catalysts are well known for high activity in hydrogenation and oxidation (3). Palladium nanoparticles dispersed on porous supports could be prepared via the sonochemical reduction method (4, 5) and vapor grafting, and Pd-grafted mesoporous materials showed remarkable activity in Heck carbon–carbon coupling reactions (6). In addition, deposition of metal nanoparticles on the surface of titania powder could efficiently enhance the photocatalytic activity of titania (7, 8).

In the present work, we synthesized Pd clusters deposited in the mesopores of titania-modified MCM-41 by UV irradiation of an aqueous solution of tetrachloropalladate(II) and found that the photoactivity of the Pd clusters deposited materials in the photoreduction of Cr(VI) to Cr(III) was enhanced significantly.

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EXPERIMENTAL SECTION

Synthesis of Pd-Deposited Titania-Modified MCM-41

The titania-modified MCM-41 (MCM–TiO₂) was prepared through a postsynthesis procedure reported previously (9). A 1.0-g amount of PdCl₂ was dissolved in 5 M HCl solution and diluted to 2 wt% H₂PdCl₄ aqueous solution with distilled water. The slurry of 1.0 g of calcined MCM–TiO₂ dispersed in 400 mL of aqueous solution was stirred while an appropriate amount of H₂PdCl₄ was added dropwise, and then the pH was adjusted to ca. 3 with dilute HCl solution. The suspension was stirred at room temperature for at least 8 h in order that more PdCl₄²⁻ could be adsorbed on the inner surface of MCM–TiO₂. The dissolved O₂ in the solution was then removed by argon bubbling at a flow rate of 100 mL/min for 0.5 h. The slurry was irradiated with UV light (300-W high-pressure mercury vapor lamp) for about 4 h until PdCl₄²⁻ was completely reduced to Pd⁰. The strong UV absorption bands of PdCl₄²⁻ disappeared after the irradiation, indicating that the photoreduction of Pd(II) readily proceeded. After being washed repeatedly with distilled water, the gray powder was collected by filtration and dried at 323 K in a vacuum oven overnight. Two samples with Pd loading of 0.5 wt% and 1.0 wt% (determined by X-ray fluorescence spectroscopy) were used as photocatalysts for the following reaction.

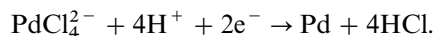
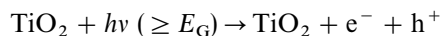
Photocatalytic Testing of Cr(VI) to Cr(III)

Na₂Cr₂O₇ was used as the source of Cr(VI). A typical reaction mixture consisted of 400 mL of 100 ppm Na₂Cr₂O₇ aqueous solution and 2.0 g/L of photocatalyst. The system was stirred at room temperature. A 300-W high-pressure mercury vapor lamp was used as the light source and placed in a water-cooled cylindrical jacket in the center of the reactor. Experiments were conducted in the presence of N₂ flow (100 mL/min) to remove dissolved O₂ in the solution. A 4-mL sample of the suspension was withdrawn

at regular intervals (0.5 or 1 h) and was diluted to 20 mL. After high-speed centrifugation, the supernatant was analyzed quantitatively for the remaining Cr(VI) concentration at a wavelength of 370 nm using UV-vis spectroscopy. The photocatalytic activity was evaluated by the decrease of Cr(VI) concentration after irradiation.

RESULTS AND DISCUSSION

As we previously found titania modified the inner surface of MCM-41 and existed as a thin layer on the mesopore walls (9). Under UV light irradiation with a wavelength less than 400 nm, titania generated photoexcited electrons and positive holes. The reduction of PdCl_4^{2-} took place on the surface of a tiny "TiO₂ nanoelectrode" in the solution. The "electrode" reaction was believed to occur in the following steps:



The PdCl_4^{2-} ions adsorbed over the surface of titania could trap the electrons, and were reduced to metallic clusters. Increasing the content of PdCl_4^{2-} in the solution during the photoreduction considerably raised the Pd loading content in MCM-TiO₂. However, if the Pd loading was more than 3 wt%, there would be excess nanosized Pd clusters outside the mesopores.

The direct evidence for the metallic palladium deposition on the surface of titania was the Pd 3d X-ray photoelectron spectroscopy (Fig. 1). Although the amount of loaded Pd was not enough to give a resolved spectrum, two specific peaks with binding energies of 335.1 and 340.3 eV were observed as $3d_{5/2}$ and $3d_{3/2}$ electrons of Pd⁰ (10), respectively. These peaks suggested that the photocatalytic deposition procedure effectively reduced Pd²⁺ (H₂PdCl₄) to metallic palladium.

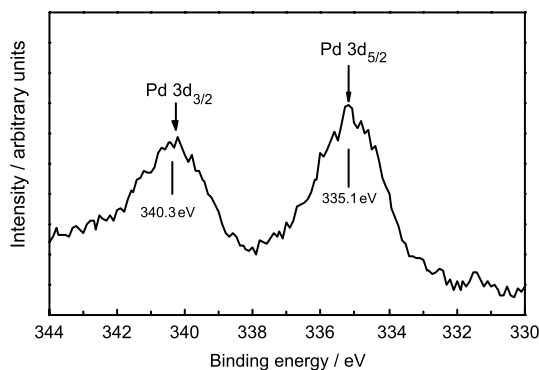


FIG. 1. XPS spectrum of Pd/MCM-TiO₂ (1%).

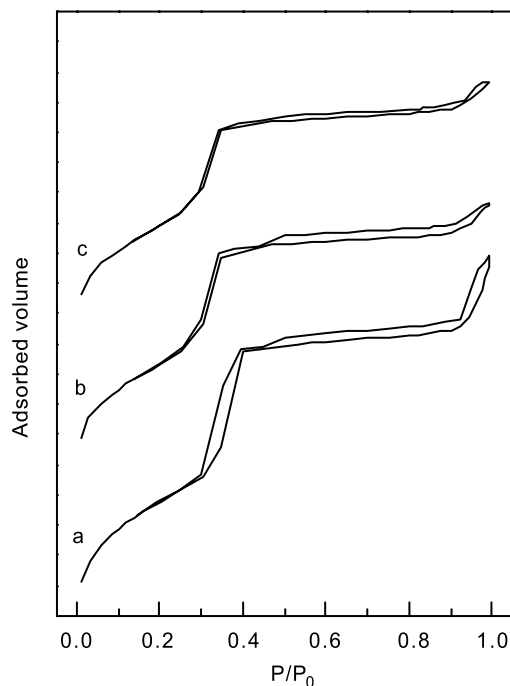


FIG. 2. Nitrogen adsorption/desorption isotherms of (a) MCM-41, (b) MCM-TiO₂, and (c) Pd/MCM-TiO₂ (1%).

Figure 2 shows the N₂ sorption isotherms of samples. Almost no difference could be observed between the N₂ sorption curves of mesoporous MCM-41 and the Pd/MCM-TiO₂, which suggested that the introduced titania and palladium nanoclusters did not affect the mesoporous structure of MCM-41. Importantly, in the isotherms of MCM-TiO₂ and Pd/MCM-TiO₂ (1%) samples, there was no broad loop indicative of a type H2 hysteresis loop. It confirmed that the titania and palladium clusters diffused throughout the channels in MCM-41, rather than agglomerating at the opening of the mesopores associated with "ink bottle"-shaped pores. Accordingly, the BET surface areas and pore volume decreased after the introduction of palladium nanoclusters (Table 1).

The prepared composite material, Pd/MCM-TiO₂, retained its hexagonally packed mesoporous structure as

TABLE 1
BET Surface Areas, Pore Volumes, and Average Pore Diameters of the Samples

Sample	A_{BET} (m ² /g)	V_{BJH} (cm ³ /g)	D_{BJH} (nm)
MCM-41	1048	1.15	3.18
MCM-TiO ₂	972	0.91	2.83
Pd/MCM-TiO ₂ (1%)	893	0.73	2.82

shown in XRD patterns. Although the diffraction patterns of Pd/MCM-TiO₂ and pristine MCM-41 were almost identical, the peak intensity for Pd/MCM-TiO₂ was reduced, attributed to the grafted titania and palladium. TEM (Fig. 3a) showed long and straight one-dimensional channels of Pd/MCM-TiO₂, with no free palladium clusters, which indicated that palladium was uniformly dispersed over the entire mesopore surface of the MCM-TiO₂ support. A similar conclusion could be drawn from the SEM image (Fig. 3b).

Figure 4 illustrates the solid state UV-vis spectra of MCM-TiO₂ and Pd/MCM-TiO₂. Unmodified MCM-41 was transparent in the UV-vis spectrum. For titania-modified MCM-41, there was a broad band from 200 to 300 nm centered at 233 nm in the absorption spectrum. This band was assigned to a charge-transfer transition between the oxygen ligands and a central Ti⁴⁺ ion with tetrahedral coordination (*T_d*) (11, 12). In the UV-vis absorption spectrum of Pd/MCM-TiO₂ (1%), two specific peaks at ca. 233 nm and 304 nm could be observed clearly, which showed behavior more characteristic of partially crystallized anatase (13). It was explained that this part of the titanium species, which modified the inner pore surface of MCM-41, transformed from amorphous into anatase par-

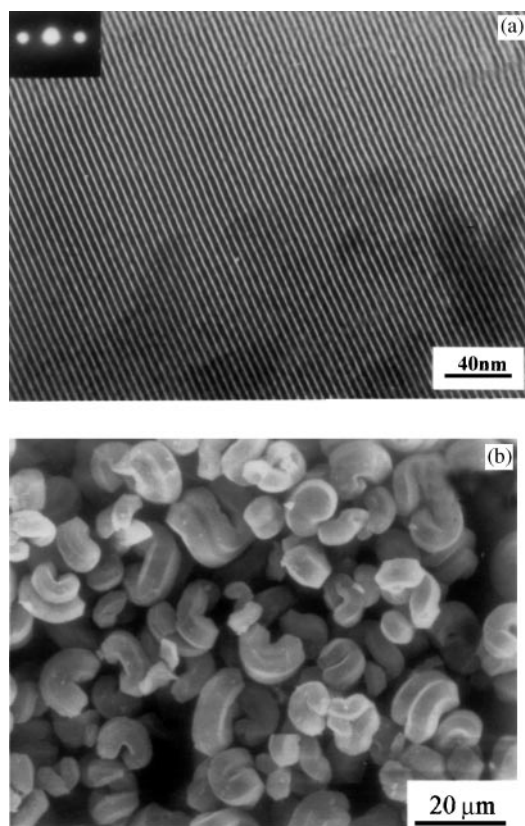


FIG. 3. (a) TEM and (b) SEM of Pd/MCM-TiO₂ (1%).

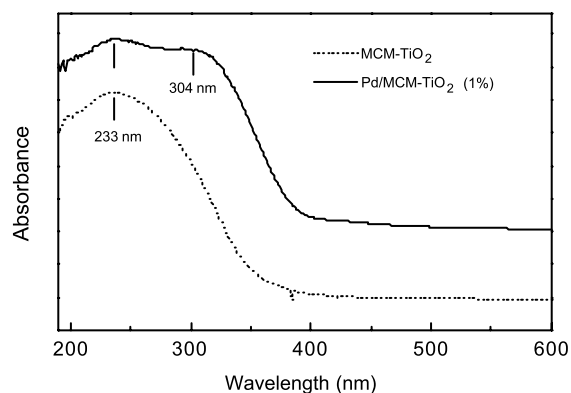


FIG. 4. Solid state UV-vis spectra of samples.

tially (14). Because of the interaction between the metallic Pd clusters and titania, part of the titanium species was in octahedral coordination (*O_h*) rather than in tetrahedral coordination (*T_d*).

The Raman spectra for the as-synthesized Pd/MCM-TiO₂ and MCM-TiO₂ are compared in Fig. 5. A well-resolved Raman band was seen at 179 cm⁻¹ in the spectrum of Pd/MCM-TiO₂, which could be assigned to TiO₂ anatase phase (15). Therefore, it was evident that amorphous TiO₂ on the inner surface of mesoporous MCM-41 transformed into anatase phase during the Pd deposition process.

Cr(VI) is a frequent contaminant in wastewater arising from industrial processes, while Cr(III) is less toxic to the environment than Cr(VI) and can be precipitated in neutral or alkaline solutions as Cr(OH)₃. When titania is excited under irradiation with a wavelength less than 400 nm (16, 17), it generates excess photoelectrons and positive holes, and Cr(VI) could be photoreduced by photo-generated electrons to Cr(III). Table 2 shows the photoactivities in reduction of Cr(VI) to Cr(III) with various photocatalysts. It is notable that in the case of Pd-deposited

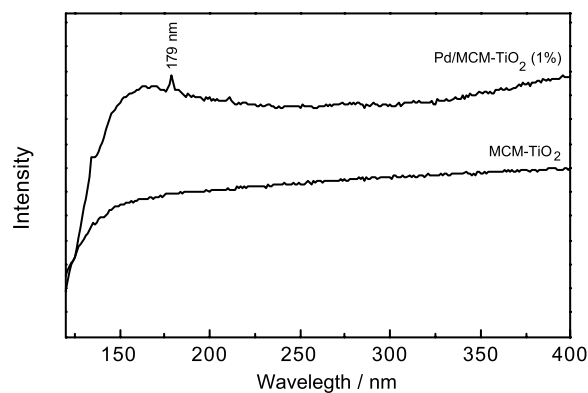


FIG. 5. Raman spectra of samples.

TABLE 2
Photoactivities of Pd/MCM-TiO₂ and Other Photocatalysts
for Cr(VI) Reduction after 2 h Reaction

Sample	Conversion (%)
MCM-TiO ₂	30.0
TiO ₂ -SiO ₂ (25 wt% TiO ₂)	8.6
Pd/MCM-TiO ₂ (0.5%)	84.5
Pd/MCM-TiO ₂ (1%)	93.7

MCM-TiO₂ as photocatalyst, the reduction rate was increased significantly. Palladium deposits are believed to cause better separation of photogenerated charge carriers, with electrons being collected in palladium islands. Owing to this enhanced charge separation, more photoelectrons are available to reduce Cr(VI) before the recombination. When the metallic Pd deposited on the surface of titania, the photoelectrons were apt to flow to the metal clusters, which could separate the photoelectrons and the positive holes efficiently and prevent the recombination. Thus, more photoelectrons took part in the photoreduction, and the photocatalytic activity improved remarkably after Pd deposited on MCM-TiO₂. Additionally, for most photocatalytic reactions, the photocatalytic activity of amorphous TiO₂ is negligible due to the fast recombination of photo-generated electrons and holes (18). Therefore, the crystallization of amorphous TiO₂ on the inner surface of mesoporous MCM-41 during the Pd deposition process also played an important role in the significant enhancement of photocatalytic activity.

CONCLUSIONS

In summary, we have demonstrated the synthesis, structure characterization, and optical properties of pallad-

ium-deposited titania-modified MCM-41 prepared by the photodeposition method. Metallic Pd clusters were efficiently photoreduced on the surface titania in the mesopores from the metal ion solution. Moreover, the crystallization of amorphous TiO₂ of titania-modified MCM-41 to anatase phase took place during the photodepositing process. The photoactivity of the titania-modified MCM-41 was enhanced remarkably in the photoreduction of Cr(VI) after the nanosized Pd clusters were deposited on it.

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