Preparation and characterization of nanosized Pt/Au particles on TiO₂-nanotubes

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Abstract

TiO₂-nanotubes were prepared by hydrothermal treatment of TiO₂ powders in concentrated NaOH solution at 110°C for 90 hours. The immobilization of Pt and Au was carried out by photochemical deposition method with TiO₂-nanotubes suspending in an aqueous solution containing H₂PtCl₆·6H₂O or HAuCl₄·3H₂O. Transmission electron micrographs revealed that the diameter of the as-made TiO₂-nanotube is about 10 nm with an inner diameter around 6 nm. The nanotube shows layered structures similar to the carbon nanotubes. The layer spacing is about 0.88 nm. Nanosized Pt (~2 nm) and Au (~10 nm) particles were dispersed uniformly on the surface of the nanotubes. The BET surface area of the nanotube is ~200 m²/g as estimated by N₂ adsorption isotherm, that was not significantly affected after the immobilization of Pt or Au. In-situ IR spectroscopic studies revealed that the Pt/TiO₂-nanotube is highly active for CO₂ hydrogenation, while Au/TiO₂-nanotube exhibits pronounced activity for CO oxidation at room temperature. In general, Pt/TiO₂-nanotubes presents a relatively higher activity than Au/TiO₂-nanotubes, and the catalytic activities of TiO₂ supported Pt and Au catalysts are significantly enhanced by the high surface area of TiO₂-nanotube.

Keywords: TiO₂-nanotubes; Pt, Au nanocatalysts; In-situ IR; CO₂ hydrogenation, CO oxidation

1. Introduction

Nanoscale materials have attracted great interest because of their novel properties, which are different from those of bulk materials. The materials with nanosized tubular structure include carbon, metal sulfides and metal oxides have been developed [1]. Among the nanostructured oxides, titania has been a focus of extensive research due to its chemical stability, large surface area, non-toxicity, and low production cost [2]. Titania nanotubes have been shown their potentials in many fields such as of photocatalysis [3], hydrogen sensing [4] and solar cells [5].

The methods to prepare titania nanotubes are mainly template synthesis [6,7] and hydrothermal method [8,9]. Titania nanotubes with diameters of 20–40 nm and inner diameters of 2.5–5 nm were made using anodic alumina as a template [7]. Smaller TiO₂ nanotubes with diameters of about 9 nm and inner diameters of about 5 nm were reported using hydrothermal method via reaction of TiO₂ and NaOH aqueous solution [9].

Titania is a well-known n-type semiconductor with high photocatalytic activity and widely used as a catalyst or catalyst supports [10]. Group VIII metals deposited titania are known to induce strong metal-support interactions (SMSI) which significantly affect on the chemisorptive

properties and the catalytic reactions involving hydrogen and carbon monoxide [11]. The semiconductor-metal system could produce the Schottky barrier at the interface, which can serve as an efficient electron trap preventing electron recombination [12]. Bamwenda and coworkers [13] have reported a comparison of the photoassisted hydrogen production from a water-ethanol solution between Au/TiO₂ and Pt/TiO₂. The overall activity of Au samples was generally about 30% lower than that of Pt samples. Besides, titania supported metal catalysts prepared by photochemical deposition showed higher activities than those prepared by deposition-precipitation and impregnation [13,14].

In our previous study [14,15], nanosized Pt particles immobilized on TiO₂ nanoparticle have been prepared by photochemical deposition and possess remarkably high catalytic activities for CO hydrogenation, NO reduction and NO/CO reactions. We have prepared TiO₂-nanotubes with high surface area following the hydrothermal method. Immobilized nanosized Pt particles on the surface of the nanotubes seem to result a potential catalyst for methane formation from CO₂ [16]. In the present study, we converted the commercial TiO₂ powders into TiO₂-nanotubes and immobilized Pt and Au particles on the nanotubes. The characterization of the as-made TiO₂-nanotubes and the supported Pt and Au catalysts were

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Fig. 1. TEM micrographs of (a) Pt/Tnt and (b) Au/Tnt.

carried out by TEM, XRD, EDS, XPS, N_2 adsorption isotherm and H_2 /CO chemisorption. The catalytic activities for CO_2 hydrogenation and CO oxidation were investigated by in-situ IR spectroscopy, or performed on a steady state flow-mode microreactor system.

2. Experimental

TiO_2 -nanotubes were prepared by hydrothermal method. In a typical procedure, 5 g of TiO_2 powders, obtained from Merck (Art. 808) were dispersed in an aqueous solution of 10 M NaOH (180 ml) and then loaded into a Teflon-lined stainless steel autoclave. The autoclave was statically heated at $110^\circ C$ for 90 hours. After the hydrothermal treatment, the resultant precipitate was separated by centrifugation and washing with diluted HCl solution, and repeated washing until $pH < 7$. The sample was then dried in an oven at $110^\circ C$. After carefully grinding, TiO_2 -nanotubes were obtained.

The immobilization of 2 wt% of Pt and Au onto TiO_2 -nanotubes was carried out by photochemical deposition [14]. The TiO_2 -nanotubes (2 g) was dispersed in 200 ml of deionized distilled water and then an appropriate amount of $H_2PtCl_6 \cdot 6H_2O$ or $HAuCl_4 \cdot 3H_2O$ aqueous solution was added. The suspension was irradiated in a Rayonet Photochemical Reactor (model RPR-100) with wavelength of 3500 Å lamps under stirring. After irradiation for 4 hr, the sample was washed twice with water and dried at $110^\circ C$. Pt and Au supported on TiO_2 powders were also prepared for comparison with those supported on TiO_2 -nanotubes.

The morphology of the prepared catalyst was investigated by transmission electron microscopy (TEM). For getting better pictures, the sample specimens for TEM experiment were prepared by dispersing the powders in ethanol by ultrasonic treatment for several minutes, dropping onto a holey carbon film supported by a copper grid. The structural characterizations of the prepared TiO_2 -nanotubes and Pt/Au-immobilized catalysts were carried out by X-ray diffraction (XRD). The surface area and pore size distribution were obtained from nitrogen adsorption

and desorption isotherm. H_2 and CO chemisorption was employed to determine the metal dispersion of platinum and gold, respectively. In-situ infrared spectroscopic studies of catalytic properties were performed on a Bomem DA-8 FT-IR spectrometer.

The measurements of the catalytic activity for CO_2 hydrogenation were carried out on a steady state flow-mode microreactor system operating at atmospheric pressure. 25 mg of the prepared catalyst was activated in hydrogen with a flow rate of 25 ml/min at $300^\circ C$ for 2 hours. The mixed gas stream contained 25% CO_2 in H_2 was introduced through the catalyst bed with a flow rate of 10 ml/min. The exit gases were analyzed by an on-line Varian 3700 gas chromatograph with a GS-Q column (J&W) heated at $40^\circ C$ and a thermal conductivity detector (TCD). The TCD peak area was determined by Hewlett Packward 3395 integrator and calibrated with Matheson standard calibration gases.

3. Results and Discussion

TiO_2 powders with particle size in the range of 200–500 nm have been hydrothermally transformed into TiO_2 -nanotubes at $110^\circ C$ for 90 hours. The resultant TiO_2 -nanotube, denoted as “Tnt” hereafter, was washed with diluted HCl solution. The results of EDS and XPS indicated that appreciable amount of sodium was still retained in the as-made TiO_2 -nanotubes after washing with HCl. TEM micrographs reveal an open end of the nanotube, which is typical for the TiO_2 nanotubes. The diameter is about 9–10 nm with the inner diameter of around 5–6 nm. The tubular structure is similar to the carbon nanotube. The layer spacing is about 0.7 nm. The wall of the nanotube consists of two to five layers. The number of layers on each side is usually not the same, indicating the nanotube is possibly scrolled [9]. Fig. 1 (a) and (b) show the TEM micrographs of Pt/Tnt and Au/Tnt samples. The tubular structure of TiO_2 nanotube was sustained after the deposition of platinum and gold. The platinum and gold particles were found to be uniformly dispersed on the TiO_2 -nanotubes with the diameters of around 2 nm and 10 nm, respectively

Fig. 2. XRD patterns of (a) TiO_2 , (b) Tnt, (c) Pt/Tnt and (d) Au/Tnt.

Fig. 2 shows the XRD patterns of the raw TiO_2 powders, the as-prepared TiO_2 -nanotubes (Tnt), and Pt and Au immobilized Tnt. The raw TiO_2 consists of major anatase phase and a trace of rutile phase. The characteristic peaks of the raw material were decreased with hydrothermal time and completely absent after 90 hours [16]. The results were consistent with the corresponding Raman and EPR spectra. XRD pattern of the Tnt sample shows new and weak diffraction peaks appeared at $2\theta = 9.9^\circ$, 24.5° , 28.0° and 48.5° , that are neither anatase nor rutile phase of TiO_2 . The tubular spacing of 0.88 nm was obtained from the corresponding d spacing at $2\theta = 9.9^\circ$ by the Bragg's law. The XRD patterns of nanotubes were still retained after the immobilization of Pt and Au. The XRD peak of Pt was not found due to the peak broadening caused by the smaller Pt particles. The strongest peak (111) of Au was observed at 38.2° on the pattern of Au/Tnt (Fig. 2 (d)). The average particle size estimated from Scherrer equation is comparable to the TEM observation.

The N_2 adsorption and desorption isotherm at 77K of the TiO_2 -nanotubes is typically the type IV isotherm. The BET surface area of $\sim 200 \text{ m}^2/\text{g}$ was obtained, which is about 40 times greater than that of the raw TiO_2 ($\sim 5 \text{ m}^2/\text{g}$). The average pore size of 0.87 nm derived from the Horvath-Kawazoe plot is similar to the tubular spacing obtained in XRD results. The surface areas of Pt/Tnt and Au/Tnt are similar to that of Tnt, which indicates the deposition of nanosize Pt and Au particles do not cause significant variation in the surface area of nanotubes.

H_2 chemisorption was employed to determine the metal dispersion of platinum on TiO_2 -nanotubes. The catalyst was activated in H_2 flow at 200°C for 1 hour. The Pt dispersion (H/Pt) on Tnt and TiO_2 particle are 0.63 and 0.41, respectively. The corresponding particle size of

Fig. 3. In-situ FT-IR spectra of CO oxidation over Au/Tnt catalyst: (a) admission of 1 torr CO, (b) admission of 10 torr CO and 40 torr O_2 , (c) static aging overnight, and then heating to (d) 50°C , (e) 75°C , (f) 100°C , (g) 110°C , (h) 125°C , (i) 150°C and (j) 150°C for 10 min.

platinum is 1.8 and 2.8 nm, respectively, which is consistent with the TEM results. The Au dispersion (CO/Au) on TiO_2 -nanotubes was measured by CO chemisorption. The catalyst was pretreated at 300°C in O_2 flow for 1 hour and then in H_2 flow for another hour. The Au dispersion is 0.11, and the corresponding particle size of Au is 10.6 nm.

As shown in our previous studies [16], Pt/ TiO_2 catalyst seemed to be a capable catalyst of absorbing CO_2 and catalyzing the methane formation from CO_2 through the intermediate CO. The Pt/Tnt catalyst directly converted CO_2 to CH_4 at a relatively low temperature of 100°C . For Au/Tnt and Au/ TiO_2 catalysts, no methane or hydrocarbon products were found during heating in 60 torr H_2 .

Fig. 3 shows the in-situ IR spectra of Au/Tnt catalyst. The catalyst was activated in H_2 flow at 200°C . After introduction of 1 torr CO, besides the IR peaks of gaseous CO appeared at 2143 cm^{-1} , the adsorbed carbonate species at 1634 and 1568 cm^{-1} were recorded. The admission of 10 torr CO and 40 torr O_2 enhanced the intensity of gaseous CO. After static aging overnight, the peak intensities of CO and the carbonate species were significantly decreased. CO_2 at 2349 cm^{-1} was increased in the peak intensity. The IR cell was then heated at a constant rate of $2^\circ\text{C}/\text{min}$. The CO_2 peak was increased with temperature as the digesting CO and carbonate species. The IR peak of gaseous CO was vanished at 150°C for 10 min. The result indicated that the prepared Au/Tnt catalyst is a capable catalyst for CO oxidation. Again, the TiO_2 or Tnt supported Pt catalysts exhibit high catalytic activity for CO oxidation.

The CO_2 hydrogenation over Pt and Au supported on TiO_2 -nanotubes and TiO_2 particles were also performed in

Fig. 4. Catalytic activity of CO₂ hydrogenation over (a) Pt/Tnt and (b) Pt/TiO₂.

Fig. 5. Catalytic activity of CO₂ hydrogenation over (a) Au/Tnt and (b) Au/TiO₂.

a steady state flow-mode microreactor system. For all experiment, the prepared catalyst was activated in hydrogen at 300°C for 2 hours and then the mixed gas stream contained 25% CO₂ in H₂ was introduced through the catalyst bed. Fig. 4 shows the CO₂ conversion over Pt/Tnt and Pt/TiO₂. It is noticeable that the catalytic activity of nanotubes-supported Pt catalyst is much higher than that of the Pt/TiO₂. CO₂ conversion increased with temperature and the primary product was CH₃OH with a trace amount of CH₄. The results of CO₂ hydrogenation over Au/Tnt and Au/TiO₂ catalysts, as can be seen in Fig. 5, also indicated that nanosized Au particles supported on TiO₂-nanotubes presents a much higher catalytic activity than that supported on TiO₂. TiO₂-nanotubes supported Pt and Au catalysts possess much higher surface areas than the conventional TiO₂ support and lead to higher catalytic activities. Pt/Tnt catalyst presents a relatively higher activity than Au/Tnt catalyst. It was found that methane became to be the main product when the H₂/CO₂ ratio of the reactant stream was increased.

4. Conclusions

We have successfully prepared TiO₂-nanotubes by hydrothermal conversion from the commercial TiO₂ powders. Nanosized Pt (~2 nm) and Au (~10 nm) particles uniformly dispersed on the surface of TiO₂-nanotubes by photochemical deposition. The TiO₂-nanotubes revealed the diameter of ~10 nm and the inner diameter of ~6 nm. It showed a layered structure similar to a carbon nanotube with a layer spacing of about 0.88 nm. The Pt and Au immobilized TiO₂-nanotubes have a large surface of ~200 m²/g. In-situ IR spectroscopic studies revealed that the Pt/TiO₂-nanotubes is highly active for CO₂ hydrogenation. Although TiO₂-nanotube-supported Au catalyst exhibits no activity for methane formation; it is active for CO oxidation at room temperature. Pt/Tnt catalyst presents a relatively higher activity than Au/Tnt catalyst. The catalytic activities of TiO₂ supported Pt and Au catalysts were significantly enhanced by high surface area of TiO₂-nanotubes.

Acknowledgments

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References

- [1] Y. Zhu, H. Li, Y. Koltypin, Y.R. Hachon, A. Gedanken, *Chem. Commun.* (2001) 2616.
- [2] V.V. Ivanovskaya, A.N. Enyashin, A.L. Ivanovskii, *Mendelev Commun.* 1 (2003) 1.
- [3] M. Adachi, Y. Murata, M. Harada, S. Yoshikawa, *Chem. Lett.* 8 (2000) 942.
- [4] O.K. Varghese, D. Gong, M. Paulose, K.G. Ong, C.A. Grimes, *Sens. Actuators B* 93 (2003) 338.
- [5] S. Uchida, R. Chiba, M. Tomiha, N. Masaki, M. Shirai, *Electrochemistry* 70 (2002) 418.
- [6] P. Hoyer, *Langmuir* 12 (1996) 1411.
- [7] S.M. Liu, L.M. Gan, L.H. Liu, W.D. Zhang, H.C. Zeng, *Chem. Mater.* 14 (2002) 1391.
- [8] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Nihara, *Langmuir* 14 (1998) 3160.
- [9] Y.Q. Wang, G.Q. Hu, X.F. Duan, H.L. Sun, Q.K. Xue, *Chem. Phys. Lett.* 365 (2002) 427.
- [10] A. Fujishima, K. Honda, *Nature* 238 (1972) 37.
- [11] J. M. Herrmann, *J. Catal.* 89 (1984) 404.
- [12] A.L. Linsebigler, G. Lu, J.T. Yates, Jr. *Chem. Rev.* 95 (1995) 735.
- [13] G.R. Bamwenda, S. Tsubota, T. Nakamura, M. Haruta, *J. Photochem. Photobiol. A: Chem.* 89 (1995) 177.
- [14] S.H. Chien, K.N. Lu, C.T. Chen, *Bull. Inst. Chem., Acad. Sin.* 40 (1993) 37.
- [15] S.H. Chien, M.C. Kuo, C.H. Lu, K.N. Lu, *Catal. Today*, 97 (2004) 121.
- [16] S.H. Chien, M.C. Kuo, Y.C. Liou, *Chem. Mater.* submitted.