Applied Catalysis B: Environmental 84 (2008) 112–118

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Pt/titania-nanotube: A potential catalyst for CO_2 adsorption and hydrogenation

Kuo-Pin Yu [a], Wen-Yueh Yu [a], Ming-Chih Kuo [a], Yuh-Cherng Liou [a,b], Shu-Hua Chien [a,b,*]

[a] Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan
[b] Department of Chemistry, National Taiwan University, Taipei 10617, Taiwan

ARTICLE INFO

Article history:
Received 25 December 2007
Received in revised form 26 February 2008
Accepted 17 March 2008
Available online 22 March 2008

Keywords:
Titania-nanotube
Pt catalyst
CO_2-TPD/MS
CO_2 hydrogenation

ABSTRACT

The titania-nanotube-supported Pt (Pt/Tnt) catalyst was prepared by the photochemical deposition of Pt complex on the titania-nanotube (Tnt) synthesized by the alkaline hydrothermal method. The physicochemical properties of Pt/Tnt catalyst were investigated by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, N_2 adsorption and desorption isotherms, temperature-programmed reduction and X-ray photoelectron spectroscopy. The Pt/Tnt catalyst exhibited mixed-valence Pt nanoparticles (1–3 nm) dispersed uniformly on the surface of Tnt with a Brunauer–Emmett–Teller surface area of 187 m^2/g. The results of the temperature-programmed desorption of CO_2 indicated the CO_2 adsorption capacity of Tnt was highly enhanced by the supported Pt nanoparticles. *In situ* Fourier-transform infrared spectroscopy demonstrated that the Pt/Tnt catalyst was highly active for the CO_2 hydrogenation toward methane production at relatively low temperature of 100 °C.

1. Introduction

Titania (TiO_2) has received considerable attention in heterogeneous catalysis due to its high chemical stability, high photoactivity, nontoxicity and low cost, and is used in many applications such as environmental remediation, chemical synthesis and energy production and storage [1–10]. Hydrogenation of CO_2 [11–14] and CO [14–17] over TiO_2-supported noble metal catalysts have been intensively studied. Since Iijima [18] discovered carbon nanotubes in 1991, one-dimensional nanomaterials, including oxide nanotubes, have attracted extensive attention due to their nanotubular morphologies and high surface areas. Many synthesis methods for titania-nanotube have been reported, including the electrodeposition (replicated) process using porous anodic-alumina as a template [19,20], the sol–gel template process using self-assembled organic surfactant as a template [21–23], anodization of Ti foil [24,25] and the alkaline hydrothermal method [26,27]. Among them, the alkaline hydrothermal method reported by Kasuga et al. [26,27] is relatively simple and can convert several grams of TiO_2 powder to titania-nanotube. Several research groups [12,28–44] have reported the synthesis of titania-nanotubes by modifying Kasuga's process. Due to the unique morphology and high surface area of titania-nanotube, it exhibited promising applications such as gas adsorbent [38,39] and catalyst supports [12,40–44].

In our preliminary study, we converted the commercial TiO_2 particles to titania-nanotubes (Tnts) by modifying Kasuga's method and then uniformly immobilized Pt nanoparticles on the titania-nanotubes by photochemical deposition (PCD) method [12]. Herein, we will report the detailed physicochemical properties of the Pt/Tnt catalyst. Since methane signals were accidentally detected in the activation process of the Pt/Tnt in hydrogen, we also systematically investigated the adsorption capability and the hydrogenation of CO_2 over Pt/Tnt using temperature-programmed desorption/mass spectrometry (TPD/MS) as well as *in situ* Fourier-transform infrared spectroscopy (*in situ* FT-IR). The Pt/Tnt is a potential catalyst for application in the CO_2 recycling and methane production.

2. Experimental methods

2.1. Preparation of titania-nanotube and Pt/titania-nanotube

Titania-nanotube was prepared by the hydrothermal method. Briefly, 5 g of anatase TiO_2 powder (Merck, Art. 808) was added into a perfluoroalkoxy (PFA) bottle containing 180 mL of 10 M NaOH and stirred for 30 min to form a suspension. The suspension was placed in a Teflon-lined stainless steel autoclave and heated at 110 °C for 90 h. The resultant precipitate was retrieved by centrifugation and rinsed with 0.1 M HCl until the pH value of the eluate reached around 7. Then the collected precipitate was

---

[*] Corresponding author at: Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan. Tel.: +886 2 2789 8528; fax: +886 2 2783 1237.
E-mail address: chiensh@gate.sinica.edu.tw (S.-H. Chien).

0926-3373/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2008.03.009

dried in an oven at 110 °C overnight. 2 wt% Pt/Tnt was prepared by the PCD method [12,17]. Appropriate amounts of hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) and Tnt were mixed in deionized distilled water (resistance $> 18\ M\Omega$) in a pyrex beaker. After deaerating by flowing argon (30 mL/min), the sample was irradiated by 350-nm UV lamps for 4 h ($(1.5–5) \times 10^{16}$ photons/(cm^3 s)) in a Rayonet Photochemical Reactor (model RPR-100). The resulted catalyst was collected by centrifugation, rinsed with deionized distilled water, and dried in an oven at 110 °C overnight. 2 wt% Pt/TiO_2 was also prepared by the same procedure using TiO_2 powders (Merck, Art. 808) as the supporting material for a comparative study.

2.2. Sample characterization

The field-emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HRTEM) and field-emission transmission electron microscopy (FE-TEM) images of the prepared samples were recorded by a LEO 1530 microscope, a JEOL 2011 microscope and a JEOL JEM-2100 microscope, respectively. The energy dispersive X-ray (EDX) analysis facility in conjunction with the LEO 1530 field-emission scanning electron microscope was used to analyze the chemical composition of the sample. The nitrogen adsorption and desorption isotherms of the catalysts were carried out at −196 °C using a Micromeritics ASAP 2010 Analyzer for the determination of Brunauer–Emmett–Teller (BET) surface area and pore size distribution. The Barrett–Joyner–Halenda (BJH) pore size distribution was obtained according to the desorption isotherm. The Horvath–Kawazoe (HK) method was used to determine the micropore size distribution. The X-ray diffraction (XRD) patterns were recorded by a Siemens D5000 diffractometer equipped with a Cu Kα X-ray source ($\lambda = 1.5405$ Å), operating under a voltage of 40 kV and a current of 30 mA. X-ray photoelectron spectroscopy (XPS) was investigated on an Omicron ESCA spectrometer with a monochromatic Al Kα X-ray source. All spectra were calibrated by the C 1s spectrum at 284.5 eV.

2.3. Temperature-programmed techniques

The reducibility of the catalysts was investigated by the temperature-programmed reduction (TPR). In the TPR experiments, 25 mg of the as-prepared catalyst was heated in a flow of 10% H_2/Ar gas mixture (25 mL/min). The heating rate of 10 °C/min was controlled by a WEST 2500 temperature programmer. The amount of H_2 consumption in the reduction of the catalyst was recorded with a thermal conductivity detector built in an Agilent model 6890 N gas chromatograph.

The gas-desorption properties of the catalysts were investigated by a temperature-programmed desorption (TPD) system. In the TPD experiments, 25 mg of catalyst sample was placed in a pyrex tube, which was evacuated to 2×10^{-4} Torr at room

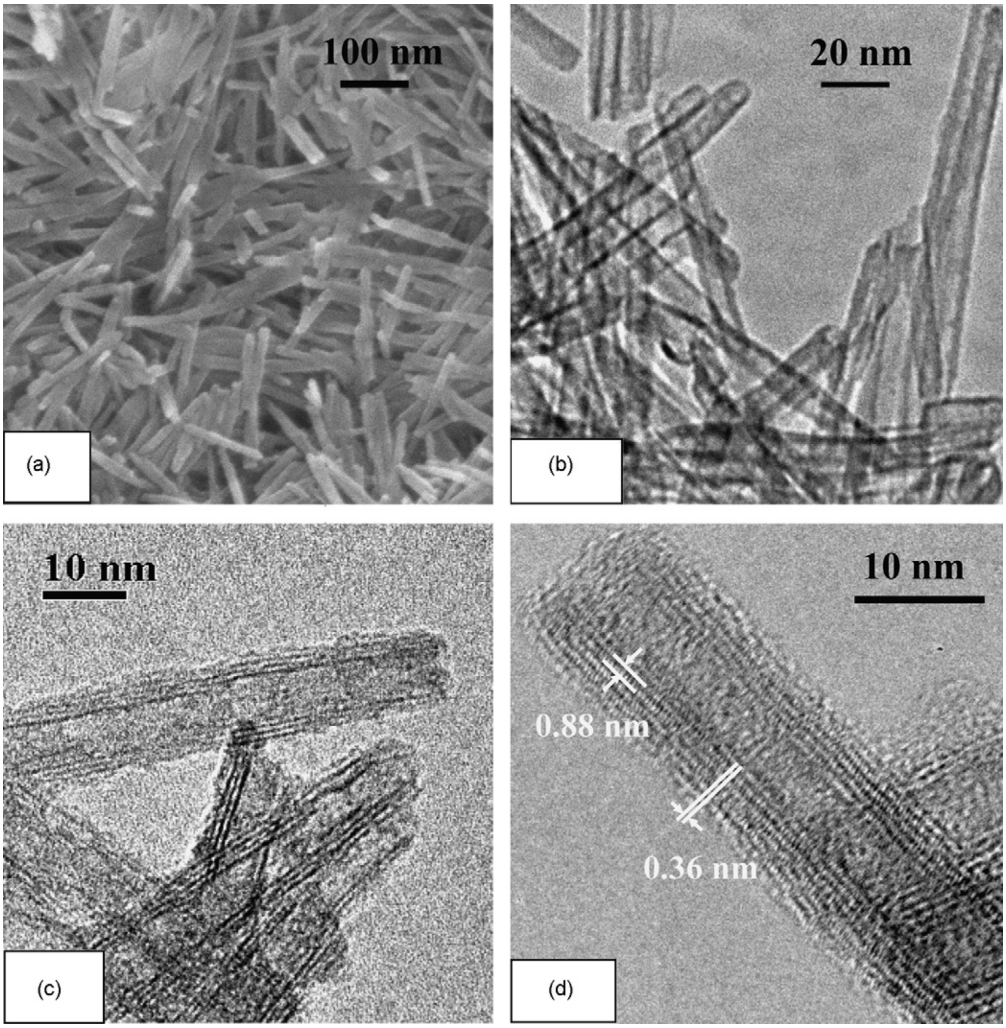

Fig. 1. Electron microscopy images of titania-nanotube (Tnt). (a) FE-SEM, (b) TEM (c) HR-TEM and (d) FE-TEM.