Catalysis Communications 10 (2009) 1689–1692

Contents lists available at ScienceDirect

Catalysis Communications

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

Total oxidation of toluene over Pt–MCM-41 synthesized in a one-step process

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ARTICLE INFO

Article history:
Received 7 April 2009
Received in revised form 28 April 2009
Accepted 13 May 2009
Available online 20 May 2009

Keywords:
Pt–MCM-41
Toluene
Total oxidation

ABSTRACT

Pt–MCM-41 materials were synthesized by a simple method via simultaneous self-assembling and Pt incorporation, using cetyltrimethylammonium chloride (CTAC) as a structure directing agent. Sample characterization was performed by N_2 sorption, XRD, TEM and high-resolution TEM (HRTEM) measurements. The highly ordered structure of MCM-41 was not appreciably affected by the formation of the Pt particles well dispersed in the MCM-41 as cubic nano-crystallite of ca. 10 nm. The Pt–MCM-41 sample was tested as a highly active catalyst towards complete oxidation of toluene. High surface area, well dispersed Pt, and appropriate Pt crystallite size may answer for the excellent catalytic performance.

1. Introduction

The MCM-41 material, a member of the M41S ordered mesoporous silicate and aluminosilicate family discovered in 1992 by Kresge et al. [1], has been widely studied as supports for catalysts [2,3] or as a matrix for the preparation of nanosized, high surface area materials [4–7]. MCM-41 has not only a high surface area (up to 1400 $m^2 g^{-1}$), but also a narrow pore size distribution (2–6 nm). The advantage of metal particles confined inside M41S materials lies in the high dispersion of the metal itself, an increased resistance against sintering [8,9], and a longer lifetime of the catalyst at high temperatures as well.

Pt nanoparticles used as catalysts are well known for many chemical reactions [10–15]. Several methods have been disclosed in literatures for the incorporation of Pt nanoparticles in MCM-41, including incipient wetness impregnation and ion exchange [10–12]. Toshima et al. reported a systematic study on the stabilization of Pt nanoparticles by cationic surfactants, which prevented aggregation of the metal clusters [13]. Mastalir et al. synthesized Pt nanoparticles in MCM-41 by applying a cationic surfactant [14].

Volatile organic compounds (VOCs) in industrial gas represent a serious environmental problem. Catalytic oxidation is considered to be an effective way in reducing the emissions of volatile organic compounds (VOCs) [16–19]. Supported noble metals are very active catalysts for VOCs total oxidation. Toluene has been chosen as VOC probe molecule because aromatics are present in the industrial and automotive emissions, and toluene possesses an important photochemical ozone creativity potential (POCP) [20,21] as well.

In this study, we prepared MCM-41 with Pt nanoparticles (Pt–MCM-41) by a simple one-step method using tetradecyltrimethylammonium chloride (CTAC) as the structure directing agent of MCM-41. The catalytic performance of Pt–MCM-41 was investigated for total oxidation of toluene.

2. Experimental

2.1. Materials

The precursor $H_2PtCl_6{\cdot}6H_2O$ (>99.9%), tetraethyl orthosilicate (TEOS, 98%), the cationic surfactant cetyltrimethylammonium chloride (CTAC, 98%) were from Beijing Chemicals Co.

2.2. Preparation of Pt–MCM-41

0.08 g of $H_2PtCl_6{\cdot}6H_2O$ was dissolved in 120 mL of distilled water before 9.5 g of aqueous ammonia (25 wt%, 0.14 mol) was added with stirring. After 10 min, 2.103 g of CTAC was added to the mixture. Afterwards, 10 g of TEOS was added dropwise over a period of 10 min. The resulting gel had the molar composition TEOS:CTAC:NH_3:H_2O:$H_2PtCl_6{\cdot}6H_2O$ = 1:0.152:2.8:141.2:0.0032. The mixture was subject to magnetic stirring for 1 h and the precipitate was subsequently filtered and washed with 150 mL of distilled water in three times. After drying at ambient conditions for 24 h, a careful calcination was conducted by heating from room temperature to 540 °C at 2 °C min^{-1} and holding at 540 °C for 6 h to remove CTAC. Reduction of the precursor was accomplished under hydrogen

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doi:10.1016/j.catcom.2009.05.008

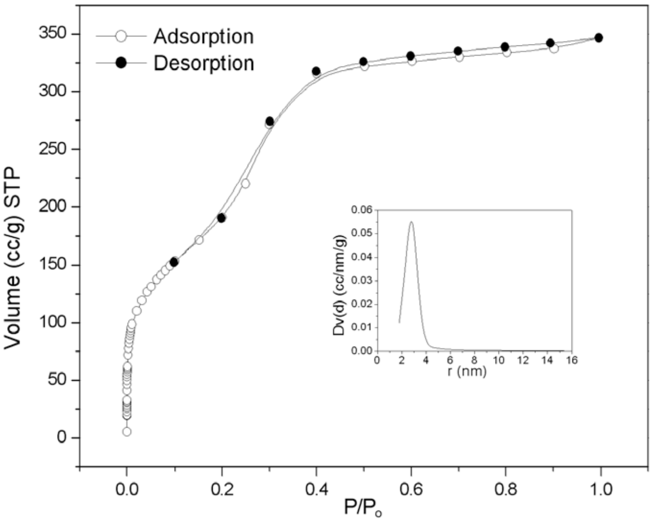

Fig. 1. N_2 adsorption–desorption isotherm of Pt–MCM-41.

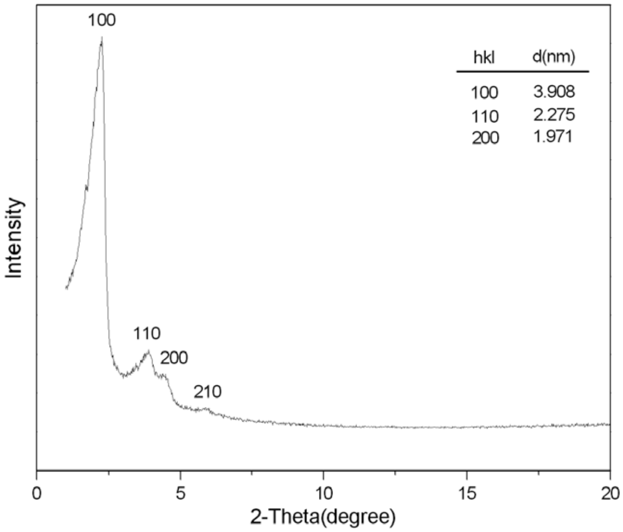

Fig. 2. X-ray diffraction pattern of Pt–MCM-41.

atmosphere (100 mL min^{-1}) at 200 °C for 2 h (heating rate 1 °C min^{-1}).

2.3. Characterization

The Pt content of the sample was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Jobin Yvon 24 sequential ICPAES. The Pt loading of Pt–MCM-41 was 0.94% as obtained from the emission intensity by means of a calibration curve.

N_2 sorption measurements were performed after degassing the samples at 13 Pa and 120 °C for 12 h using a Micromeritics 2375 BET apparatus at −196 °C. The specific surface areas were calculated from the BET equation and the total pore volume was obtained from the amount adsorbed at the relative pressure of 0.99. Powder X-ray diffraction (XRD) was performed on a Rich Siefert 3000 diffractometer using Cu Kα_1 radiation (λ = 0.15405 nm). Transmission electron microscopy (TEM) was carried out in a JEOL 2000FX microscope working at 200 kV. High-resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL 2010 TEM. The samples were deposited from ethanol suspensions of the products onto amorphous carbon coated copper grids.

2.4. Toluene oxidation

Toluene oxidation was carried out in a conventional fixed bed microreactor and studied between 80 and 300 °C (1 °C min^{-1}) with 0.1 g of catalyst loaded. The catalysts were freshly prepared Pt–MCM-41 with 0.94 or 0.48 wt% of Pt loadings. The reactants flow was composed of air and 1000 ppm of gaseous toluene. The flow rate through the reactor was set at 100 mL min^{-1}. The combustion products were analyzed on-line by gas chromatography equipped with TCD and FID. Before the catalytic test, the catalyst was calcined under a flow of hydrogen flow (2 L h^{-1}) at 200 °C (1 °C min^{-1}).

3. Results and discussion

The N_2 adsorption–desorption isotherms of as-synthesized sample (Fig. 1) is characteristic of MCM-41 materials with small mesopores and corresponds to type IV according to the IUPAC classification [22]. The fairly linear increment of the adsorbed volume at low pressures is followed by a steep growth in the nitrogen uptake at p/p_0 = 0.2–0.35 due to capillary condensation inside the mesopores [5]. Both isotherms exhibit narrow hysteresis loops, being indicative of reversible filling and emptying of the pores

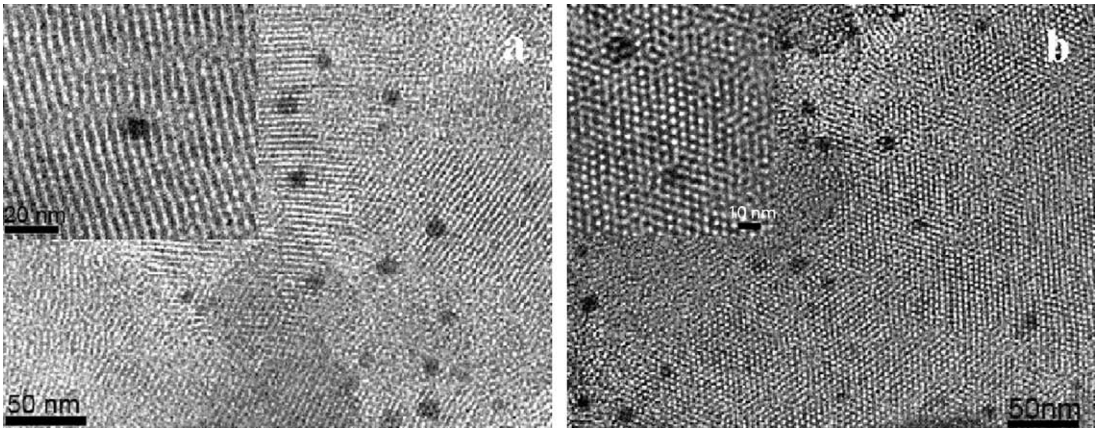

Fig. 3. TEM images of Pt–MCM-41: (a) images taken with the electronic beam vertical to the axis of channels and (b) images taken with the electronic beam parallel with the axis of channels.