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Applied Catalysis A: General 329 (2007) 148–155

APPLIED CATALYSIS A: GENERAL

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Preparation and characterization of P–Mo–V mixed oxide-incorporating mesoporous silica catalysts for selective oxidation of methane to formaldehyde

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Received 27 March 2007; received in revised form 4 July 2007; accepted 5 July 2007
Available online 10 July 2007

Abstract

P–Mo–V mixed oxide-incorporating mesoporous silica catalysts with different contents were prepared by a template method with Keggin-type heteropoly acid (HPA), $H_5PMo_{10}V_2O_{40}$, under acidic conditions, followed by calcination at 873 K for 5 h. During the preparation, the HPA used as a precursor of the oxide acted as a co-acid of HCl that controlled the acidity of the starting mixture. The catalysts were characterized by thermal analysis, X-ray diffraction, X-ray fluorescence spectroscopy, N_2 adsorption, transmission electron microscopy, and Raman spectroscopy. The results indicated that the framework of P–Mo–V incorporated mesoporous silicas was similar to that of MCM-48. The molar ratio of P:Mo:V (1:10:2) in the catalysts showed no significant change from the HPA precursor and the mixed oxides were highly dispersed below 6.68 wt% content. The catalysts showed good activity in the selective oxidation of methane to formaldehyde with oxygen.

Keywords: Mesoporous silica; Heteropoly acid; Co-synthesis; Methane; Formaldehyde

1. Introduction

The direct utilization of natural gas (consisting mainly of C_1–C_4 alkanes) has received extensive attention due to the increasing shortage of crude oil [1]. The catalytic conversion of light alkane feedstock is one of the promising routes to prepare valuable chemical products [2–5]. Although many catalysts have been studied for functionalization of C_2–C_5 alkanes, the efficient catalysts for methane selective oxidation to CH_3OH or HCHO are far below expectations due to the chemical inertness of methane [6–8]. Among different catalytic systems for the methane-selective oxidation reaction, silica-supported molybdenum and vanadium oxide have been extensively studied [9–10]. Generally, the selectivity to formaldehyde reaches *ca.* 70% at low conversion of methane (*ca.* 0.5–1%) whereas at the high methane conversion the selectivity to formaldehyde decreases rapidly due to the over-oxidation of formaldehyde to carbon monoxide and carbon dioxide. Meanwhile, other supporters such as Al_2O_3 [11] and TiO_2 [12] have also been applied in the methane selective oxidation but yield to formaldehyde is very low.

Since the discovery of ordered mesoporous silicas, much attention has been centered on these materials because of their mesoporous structure, large surface area and high thermal stability [13–15]. Recently, some investigations indicated that MoO_3 or V_2O_5 supported on MCM-41 [16], SBA-1 [17] and SBA-15 [18], prepared by the impregnation method, showed better catalytic activities than that supported on commercial amorphous silica. They also showed that the supported phosphorus-assisted vanadium or molybdenum oxide exhibited better activity due to the formation of active dispersed oxide species or molybdophosphoric acid-like fragments on the support [19]. However, the impregnation method may result in a low number of active sites and sometime causes the blockage of the pore system of mesoporous supports [20]; thus it is necessary to apply other catalyst preparation methods. It is believed that the highly dispersed metal oxide-incorporating

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doi:10.1016/j.apcata.2007.07.008

mesoporous silica catalysts can be acquired through the co-synthesis method [21]. On the other hand, in the synthesis of mesoporous silica materials, the acidity of the precursor mixture is an important factor that influences the self-assembly of mesoporous silica. The acidity is normally controlled by adjusting the amount of inorganic acid such as HCl or HNO_3 [22]. In this work, Keggin-type heteropoly acid (HPA), $H_5PMo_{10}V_2O_{40}$, was used as a precursor of P–Mo–V mixed oxide and a co-acid of HCl in the co-synthesis of highly dispersed mixed oxide-incorporating mesoporous silicas. The catalytic activity of these materials in methane selective oxidation reaction was also investigated.

2. Experimental

2.1. Catalyst preparation

$H_5PMo_{10}V_2O_{40}$ was prepared according to the literature [23]. The P–Mo–V mixed oxide-incorporating mesoporous silica catalysts were prepared by a procedure described below: five portions of solution containing 5.0 g of triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$) and 25.0 g of anhydrous ethanol were obtained by stirring the mixture for 10 min. Then, 10.0, 8.27, 5.68, 1.37 or 0 mL of dilute hydrochloric acid (0.10 mol L^{-1}) and 10.4 g of tetraethylorthosilicate (TEOS) were added to one of the above five solutions. After stirring for 2 h at ambient temperature, 0, 0.06, 0.15, 0.30 and 0.60 g of $H_5PMo_{10}V_2O_{40}$ were added in order, and the solutions were continuously stirred for another 10 min. The mixtures were kept at ambient temperature for 5 days and subsequently at 313 K in oven for 2 days to obtain gels. The gel samples were finally calcined in air at 873 K for 5 h. The samples were denoted as mesoSiO_2, 1.35PMoV–mesoSiO_2, 3.40PMoV–mesoSiO_2, 6.68PMoV–mesoSiO_2, and 14.1PMoV–mesoSiO_2 for the mixtures containing 10.0, 8.27, 5.68, 1.37 and 0.00 mL of HCl, respectively, where the numbers are the weight percentage of the P–Mo–V mixed oxide in the final samples calculated from the X-ray fluorescence spectroscopic (XRF) results. It should be pointed out that the total amount of H^+ contributed from hydrochloric acid and heteropoly acid was *ca.* 1.0×10^{-3} mol in the preparation of all the samples except 14.1PMoV–mesoSiO_2. In the preparation of 14.1PMoV–mesoSiO_2, the amount of H^+ in the solution is 1.7×10^{-3} mol, which is solely from HPA.

In order to compare the catalytic performance of the above catalysts with that of the catalyst prepared by the conventional impregnation method, a catalyst containing 3.53 wt% P–Mo–V mixed oxide in mesoSiO_2 was prepared by the impregnation method using $H_5PMo_{10}V_2O_{40}$ as a precursor and finally calcined in air at 873 K for 5 h. The sample was denoted as 3.53PMoV(im)–mesoSiO_2.

2.2. Characterization

Thermalgravimetric (TG) analysis and differential thermal analysis (DTA) were performed on a Perkin-Elmer TGA7/DTA7 thermal analyzer from 300 to 1000 K with a heating rate of 10 K min^{-1} in air atmosphere. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance X-ray diffractometer equipped with nickel filtered Cu-Kα radiation (40 kV, 40 mA). The composition of catalysts was determined by X-ray fluorescence spectroscopy (XRF) on a Bruker AXS S4 Explorer spectrometer. N_2 adsorption was measured using a Micromeritics Tristar 3000 automatic physisorption instrument at 77 K. The specific surface area was determined by the BET method. The BJH model was used to determine the pore size distribution. The transmission electron microscopic (TEM) images were taken on a JEOL JEM2010 transmission electron microscope operating at 200 kV with an Oxford energy dispersive X-ray detector for elemental analysis. Raman spectroscopic measurements were carried out with a Dilor LABRAM-1B spectrometer using an excitation line at 632.81 nm.

2.3. Catalytic test

The selective oxidation of CH_4 was performed on a fixed bed quartz reactor with inner diameter of 3 mm operated at atmospheric pressure and 873–933 K using catalyst loading of 100 mg. All the gas lines and valves between the reactor exit and the gas chromatograph were heated to 383 K to prevent the condensation of products. A reaction gas containing CH_4:O_2:N_2 in a molar ratio of 2:1:7 was used. The products were analyzed with an on-line gas chromatograph equipped with a thermal conductivity detector and two packed columns (Porapak N and TDX-01).

3. Results and discussion

3.1. Characterization of the catalysts

The typical TG-DTA curves of 3.40PMoV–mesoSiO_2 before calcination in the region of 300–1000 K are shown in Fig. 1. A gradual weight loss below 480 K is attributed to the loss of water. A consecutive sharp weight loss in the range of 480–550 K with an acute exothermic peak is ascribed to the decomposition of P123 template. The small weight loss in the region of 550–800 K can be assigned to the decomposition of

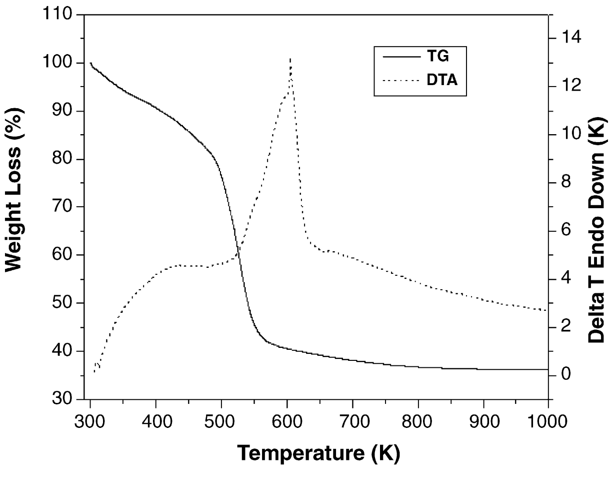

Fig. 1. TG-DTA curves of 3.40PMoV–mesoSiO_2 before calcination.