A VO$_x$/meso-TiO$_2$ catalyst for methanol oxidation to dimethoxymethane

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ABSTRACT

Mesoporous TiO$_2$ was prepared by simply controlling the hydrolysis of Ti(OBu)$_4$ with the help of acetic acid. The mesoporous TiO$_2$ had a well-crystallized anatase phase and a high surface area of 290 m^2 g^{-1} with a pore size of about 4 nm. The anatase phase and the mesoporous structure were maintained in the VO$_x$/TiO$_2$ catalyst with a monolayer dispersion of V$_2$O$_5$, however, the surface area decreased to 126 m^2 g^{-1}. The catalyst was highly active and selective for methanol oxidation, giving about 55% conversion of methanol and 85% selectivity to dimethoxymethane at 423 K.

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1. Introduction

TiO$_2$ is one of the most important metal oxides in heterogeneous catalysis. In addition to be used as a typical photocatalyst, it is also an essential component in oxidation catalysts [1]. For example, the reaction rate of methanol oxidation over a VO$_x$/TiO$_2$ catalyst is at least one order of magnitude larger than those on VO$_x$/SiO$_2$ and VO$_x$/Al$_2$O$_3$ catalysts at near monolayer coverage of V$_2$O$_5$ [2]. However, the surface area of the currently used TiO$_2$ material is usually less than 100 m^2 g^{-1}, hindering the preferred monolayer dispersion of vanadia, particularly at higher loading (>10% V$_2$O$_5$). Mesoporous TiO$_2$ materials synthesized using structure-directing agents have high surface area up to 1000 m^2 g^{-1}, but they are usually amorphous or semi-crystalline [3–5]. As a result, the mesoporous structure tends to collapse due to crystal growth upon thermal treatment at relatively higher temperatures (723–823 K) [4,5]. Hydrolysis of titanium alkoxide in the presence of mineral acids (HNO$_3$ or H$_3$PO$_4$) produced mesoporous TiO$_2$ of anatase crystalline with a surface area of 106–294 m^2 g^{-1} after calcination above 723 K [6,7], but the mineral acids are difficult to be removed completely. Deshpande et al. [8] have recently reported that hydrolysis of Ti(OBu)$_4$ in the presence of acetic acid produced anatase mesoporous TiO$_2$ with a surface area of 125 m^2 g^{-1} after calcination at 673 K. However, the process proceeded very slowly and the synthetic period was up to 120 days for obtaining the mesoporous structure. Therefore, a simple and effective method for preparing crystalline mesoporous TiO$_2$ material with a high surface area is of high importance.

In this work, we synthesized mesoporous TiO$_2$ with anatase crystalline by simply controlling the hydrolysis process of Ti(OBu)$_4$. The TiO$_2$ material was used to support VO$_x$ species as a catalyst for the selective oxidation of methanol to dimethoxymethane (DMM).

2. Experimental

2.1. Materials preparation

The mesoporous TiO$_2$ was prepared by hydrolysis of Ti(OBu)$_4$. About 50 g Ti(OBu)$_4$ and 10 ml acetic acid were dissolved into 200 ml ethanol at 273 K, and added to 700 ml ethanol aqueous solution (90%) at the same temperature under stirring. The mixture was kept at 298 K for 2 h and 323 K for 2 h, respectively. 45 ml deionized water was then added at 323 K and the mixture was kept at this temperature for 13 h. The precipitate was filtered, washed with deionized water and ethanol, and dried at 383 K for 12 h under vacuum.

The VO$_x$/TiO$_2$ catalyst with the initial V$_2$O$_5$ loading of 14.6% was prepared by an impregnation method. The 3.5 g as-prepared TiO$_2$ powder was mixed with 3 ml aqueous solution containing 0.77 g NH$_4$VO$_3$ and 1.67 g oxalic acid at room temperature and kept for 12 h. After dried at 383 K for 12 h, the resultant solid was calcined at 673 K for 4 h in air. The final loading of V$_2$O$_5$ was 16.0%.

2.2. Characterization

The N$_2$ adsorption–desorption isotherms were recorded on a Quantachrome Autosorb-1 instrument at 77 K. Before the measurement, the sample was degassed at 573 K for 6 h. The specific

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surface area (S_{BET}) was estimated by a multipoint Braunauer–Emmett–Teller (BET) method, and the pore size distribution was calculated by the BJH method.

The X-ray powder diffraction (XRD) patterns were recorded on a D/MAX 2500/PC powder diffractometer (Rigaku) operated at 40 kV and 200 mA using Cu Kα radiation. The crystallite size of TiO_2 was estimated from the (1 0 1) diffraction peak by using the Scherrer equation.

The transmission electron microscope (TEM) images of the samples were recorded on a Philips Tecnai G^2 Spirit microscope operated at 120 kV. The high-resolution TEM images were recorded on a Philips Tecnai G^2-F30 S-Twin microscope operated at 300 kV. The specimen was prepared by ultrasonically dispersing the sample powder into ethanol, and drops of the suspension were deposited on a copper grid and then dried in air.

The X-ray photoelectron spectroscopy (XPS) was recorded on a VG ESCALAB MK-II spectrometer using Al Kα (1486.6 eV) radiation operated at an accelerating voltage of 11 kV (current 20 mA). The powder sample was pressed into thin disc and mounted on a sample rod placed in the analysis chamber, where the spectra of V 2p, Ti 2p, and O1s were recorded. Charging effect was corrected by adjusting the binding energy of C1s to 284.6 eV.

The temperature programmed reduction (TPR) of H_2 was performed over a U-shape quartz reactor connected to a thermal conductivity detector (TCD). About 25 mg sample was loaded and pretreated with a 20 vol.% O_2/N_2 mixture (30 ml min^{-1}) at 673 K for 1 h. After cooled to room temperature and purged with N_2 (30 ml min^{-1}) for 30 min, a 5 vol.% H_2/N_2 mixture (30 ml min^{-1}) was introduced and the temperature was risen to 1273 K at a rate of 10 K min^{-1}.

2.3. Methanol oxidation

Methanol oxidation was performed with a continuous-flow fixed-bed quartz reactor at atmospheric pressure. About 200 mg VO_x/TiO_2 catalyst (40–60 mesh) was diluted with 800 mg of quartz powder and loaded into the reactor. The catalyst was pretreated with a 20 vol.% O_2/N_2 mixture (30 ml min^{-1}) at 673 K for 1 h. After cooled to the reaction temperature, a mixture of methanol and O_2 (methanol/O_2 = 44/56 mole ratio) generated by bubbling O_2 through liquid methanol in a flask kept at 318 K was introduced to the catalyst bed with a flow rate of 12.5 ml min^{-1}. The effluent was analyzed by an on-line GC (Agilent 6890 N) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID).

3. Results and discussion

3.1. Mesoporous TiO_2

Fig. 1 shows the XRD pattern of the as-prepared TiO_2 material. It exhibited typical diffraction peaks of crystalline anatase structure (JCPDS #86-1157). The crystalline size estimated from the (1 0 1) diffraction peak was about 7 nm. Fig. 2 shows the N_2 adsorption–desorption isotherms and the pore size distribution (inset) of the as-prepared TiO_2 material. It displayed type IV adsorption isotherm with H_2 hysteresis loop, characteristics of mesoporous structure. This kind of pore structure may be a result of agglomerates or aggregates of the TiO_2 particles [9]. The specific surface area was 290 m^2 g^{-1} with an average pore size of about 4 nm. Fig. 3 shows the TEM images of the as-prepared TiO_2 material. The particles are spindle-like unconsolidated agglomerates with the particle size around 10–30 nm. This further confirms that the mesoporous structure is generated by the agglomeration of TiO_2 particles.
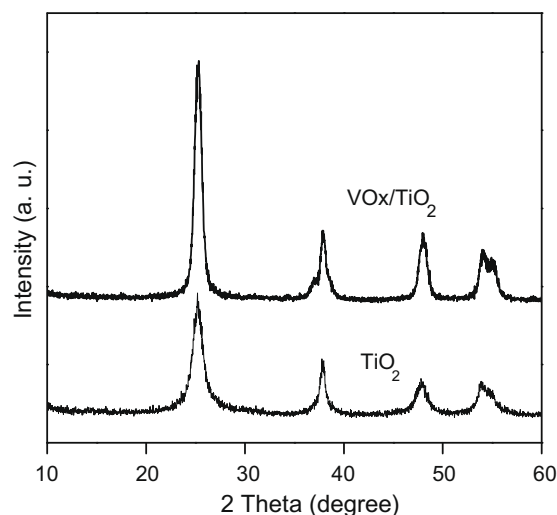

Fig. 1. XRD patterns of the as-prepared TiO_2 and the VO_x/TiO_2 catalyst.
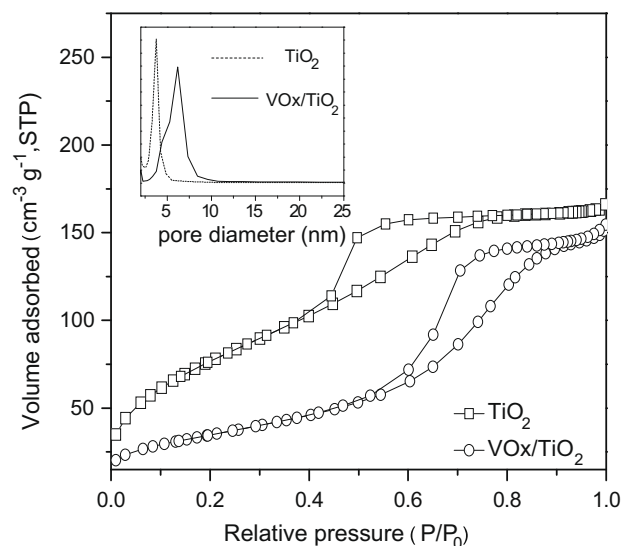

Fig. 2. N_2 adsorption–desorption isotherms and pore size distributions of the as-prepared TiO_2 and the VO_x/TiO_2 catalyst.

Hydrolysis of Ti(OBu)$_4$ initially produces Ti(OH)$_4$ which further condenses to form TiO_2 particles [10]. Usually, slow condensation process favors the formation of mesoporous structure through the reaction-limited aggregation process [11]. Here, acetic acid may play an important role in the formation of the mesoporous structure and the crystallization of TiO_2. The proton generated from acetic acid may adsorb onto the primary particles, and induces electrostatic repulsion between the positively charged particles, causing a slow condensation rate [10]. Meanwhile, acetic acid itself may also adsorb onto the surface of the primary TiO_2 particles and act as a steric barrier [8]. This syngenetic effect of acetic acid decreases the condensation rate and facilitates the formation of mesoporous structure. Moreover, the well anatase crystalline of the as-prepared TiO_2 further implies that the proton generated from acetic acid accelerates the crystallization of TiO_2, in good agreement with previous observations [10,12]. Compared to the procedure reported by Deshpande et al. [8], a higher concentration of acetic acid and a proper variation in crystallization temperature were adopted, through which the role of acetic acid was enhanced significantly. As a result, the formation of anatase