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Photo-assisted synthesis of V and Ti-containing MCM-41 under UV light irradiation and their reactivity for the photooxidation of propane

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Abstract

V and Ti-containing mesoporous molecular sieves MCM-41 were prepared using a photo-assisted synthesis method with UV light irradiation of the starting solutions at room temperature within a short synthesis time. The prepared V-MCM-41 showed high reactivity for the photocatalytic partial oxidation of propane into acetone. This reaction was enhanced on the V–Ti-MCM-41 catalyst with a higher acetone yield and selectivity than for V-MCM-41. After quenching, the recovery of the photoluminescence of V–Ti-MCM-41 proceeded more efficiently than that of V-MCM-41 by evacuation at 295 K. These results suggest that the excited state of the V-oxide moieties in V–Ti-MCM-41 interacts more weakly with the O_2 molecules, leading to the suppression of further oxidation of the photo-formed acetone into CO_2.

Keywords: Photo-assisted synthesis; Photocatalytic oxidation of propane; V-MCM-41; V–Ti-MCM-41

1. Introduction

Silica as well as zeolites and mesoporous molecular sieves supported vanadium and titanium oxide catalysts are known to be active and selective in various catalytic and photocatalytic reactions, e.g., in the selective oxidation of methane to methanol and formaldehyde [1–3], ethanol to acetaldehyde [4] and the selective catalytic reduction (SCR) of NO_x [5,6]. In line with such work, MCM-41 has attracted much attention as a catalyst support since its discovery in 1992, due to its regularly oriented pore systems, large pore spaces and high surface area [7,8]. However, conventional methods of synthesizing MCM-41 require hydrothermal conditions and an extended reaction time as well as careful control of the reaction temperature and pH, although a temperature-controlled microwave-assisted synthesis method for MCM-41 which could shorten the crystallization time compared to conventional autoclave heating has been reported [9].

Recently, we have reported on a novel photo-assisted synthesis method for MCM-41 under UV light irradiation of the starting solutions at 295 K, which has exhibited significant advantages such as a shortening of the synthesis reaction time while achieving a highly ordered mesoporous structure under ambient atmospheric conditions [10]. The selective conversion of light alkanes into more valuable compounds is also of great interest from both a scientific and industrial viewpoint [11–13].

In the present work, we have reported on the photo-assisted synthesis of V, Ti and V–Ti-containing MCM-41 under UV light irradiation of the starting solutions at 295 K along with an investigation of their photocatalytic reactivities for the partial oxidation of propane in the presence of O_2 at 295 K.

2. Experimental

2.1. Preparation of the catalysts

V-MCM-41 gels were synthesized under both acidic and basic conditions. Under both pathways, cetyltrimethylammonium bromide (CTMABr) served as the template. For the acidic pathway, tetraethyl orthosilicate (TEOS) and NH_4VO_3 were used as the silicon source and the vanadium ion precursor,

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respectively. The molar composition of the reaction mixture was 1.0 Si:0.0125 V:0.2 [$C_{16}H_{33}N(CH_3)_3$]Br:160 H_2O. The pH of the solution was adjusted to 1.0 by HCl solution. For the basic condition pathway, silica as well as sodium silicate and vanadyl sulfate trihydrate solution were used as the Si and the V ion source, respectively, and the pH of the reaction mixture was adjusted to 11.0 with dilute sulfuric acid. The molar composition of the gel was 1.0 Si:0.0125 V:0.27 CTMABr:0.13 Na_2O:0.26 tetramethylammonium hydroxide:60 H_2O. Ti-MCM-41 and V–Ti-MCM-41 were synthesized through a basic pathway and tetraisopropyl orthotitanate was used as the Ti source. For both pathways, the reaction mixtures were stirred under UV light irradiation. A 100 W high-pressure Hg lamp was used as the UV light source and a water bath was used to keep the synthesis system at room temperature. The crystalline products were filtered, washed with deionised water, dried overnight at 373 K and calcined in air at 773 K for 8 h.

Prior to photocatalytic reactions and spectroscopic measurements, the catalysts were degassed at 773 K for 1 h, heated in O_2 at the same temperature for 2 h, and finally degassed at 473 K for 2 h.

2.2. Catalyst characterizations

The metal content of these materials were determined with a Shimadzu atomic absorption flame emission spectrophotometer, model AA-6400F. The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Shimadzu XRD-6100 with Cu Kα radiation (λ = 1.5417 Å). Transmission electron microscope (TEM) measurements were performed with a JEOL 2000 instruments. Diffuse reflectance UV–vis spectroscopic measurements were carried out on a Shimadzu UV–vis recording spectrophotometer, model UV-2200A. The photoluminescence was measured at 295 K with a Spex Fluorog-3 spectrophotometer.

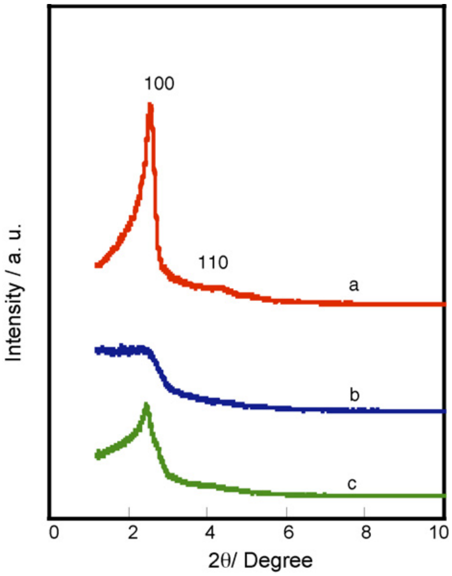

Fig. 1. XRD patterns of V-MCM-41 (2 wt.%) prepared in acidic solutions: (a) under UV light irradiation for 24 h; (b) in the dark for 24 h; (c) for 5 days.

2.3. Photocatalytic reactions

The photocatalytic partial oxidation of propane with O_2 was carried out in a closed reaction system. The catalyst (80 mg) was loaded in a quartz cell with a flat bottom connected to a vacuum system. After pretreatment, propane and O_2 (180 μmol g cat^{-1}) were introduced into the quartz cell. UV irradiation was carried out using a 100 W mercury lamp through a UV cut filter ($\lambda > 270$ nm) at 295 K and a water bath was employed to keep the flat bottom at a constant temperature. After each run, the catalyst bed was heated up to 573 K to collect the products that were adsorbed tightly onto the catalyst at room temperature. The products were analyzed with an on-line gas chromatographer equipped with a flame ionization detector (FID) for analysis of such hydrocarbons as CH_4, C_2H_4, C_3H_6, CH_3CHO, acetone, etc., and a thermal conductivity detector (TCD) for analysis of CO and CO_2, etc.

3. Results and discussions

The XRD patterns of the calcined V-MCM-41 prepared under pH 1.0 conditions are shown in Fig. 1. The sample prepared under UV irradiation for 24 h (Fig. 1a) shows a typical MCM-41 pattern with a hexagonal arrangement of pores having a unit cell size (a_0) of 4.0 nm. Moreover, this sample shows a sharper 1 0 0 plane peak than that prepared under dark conditions for 5 days, indicating that the former sample has a higher ordered mesopore structure and crystallinity. However, for the sample synthesized without UV light for 24 h, the (1 0 0) peak is very broad. It is, thus, clear that UV light irradiation of the starting solution can shorten the crystallization time.

Fig. 2 shows the XRD patterns of V-MCM-41 prepared in basic solutions. Compared to the broad (1 0 0) peak pattern of the sample prepared in the absence of UV light, a sharp (1 0 0) peak and small (1 1 0), (2 0 0) peaks were observed on V-MCM-41 prepared under UV light irradiation. The TEM images confirmed that this catalyst has a higher ordered hexagonal pore structure than that prepared without UV

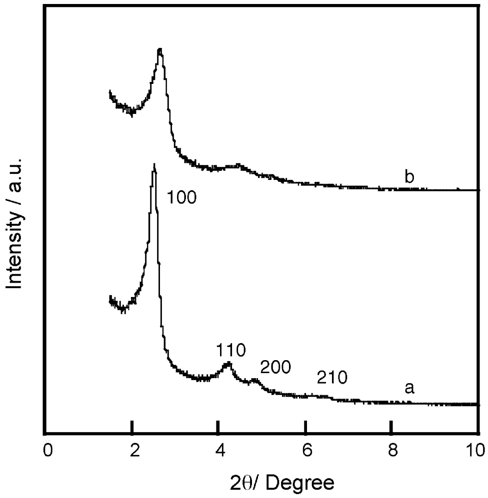

Fig. 2. XRD patterns of V-MCM-41 prepared for 24 h in basic solutions: (a) under UV light irradiation; (b) under dark conditions.