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Effective VTeO/SBA-15 Catalyst Prepared by Precursor Method for the Selective Oxidation of Propane to Acrolein

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Abstract Precursor decomposition was used for the preparation of VTeO/SBA-15 catalyst for the selective oxidation of propane to acrolein. The catalyst shows a better performance compared with those prepared by conventional impregnant method. A yield of 9.3% of acrolein was achieved with 2% V loadings at 500 °C. XRD, N_2-adsorption, H_2-TPR, Py-IR and XPS measurements were used to unclose the relationship between the structure and performance of the catalyst.

Keywords Acrolein; Propane; Vanadium catalyst; Precursor decomposition

1 Introduction

In our previous communication[1], VTeO/SiO_2 catalyst was used for the oxidation of propane to acrolein with a maximal yield of 6.6% at 520 °C. It has been proposed that V^{5+} is responsible for the activation of propane as usual, and Te^{4+} can eliminate the α-H of propene and further insert oxygen in the ally. A catalyst with a high density of vanadium clusters showed a decrease in the acrolein selectivity and an increase in deep oxidation products. It is desirable to synthesize an effective catalyst with maximum density of isolated vanadium species. It has been noted that precursor method like molecular designed dispersion is used to produce highly evenly dispersed metal oxide[2,3]. There are also many publications contributed to the synthesis and characterization of SBA-15 with high thermal stabilities and large surface areas[4—6], while the use of VO_x-SBA/15 as catalyst for the selective oxidation of propane is relatively scarce. In this study, we used VTeO/SBA-15 catalyst prepared by the decomposition of vanadyl acetylacetonate for the selective oxidation of propane to acrolein. The catalytic performances were compared with those of the catalysts prepared by co-impregnation and step-impregnation methods. A detailed characterization of the catalyst was performed.

2 Experimental

2.1 Sample Preparations and Treatments

2.1.1 Preparation of SBA-15

As the method of ref. [7], Plutonic P123 triblock copolymer surfactant EO_{20}-PO_{70}-EO_{20}(9.0 g) from Aldrich was dissolved in 300 mL of 2 mol/L hydrochloric acid. Tetraethyl orthosilicate(TEOS, 20.4 g, 141 mmol) was then added to the above solution. The resulting mixture was stirred for 24 h at 40 °C, and aged for another 24 h at 100 °C. A white solid was filtered, washed and dried. The product was then calcined at 600 °C for 10 h with a heating rate of 1 °C/min to obtain 5.5 g SBA-15(91 mmol, yield 65%).

2.1.2 Deposition of Vanadyl Acetylacetonate VO(acac)$_2$ on the Ordered Mesoporous Material SBA-15

SBA-15(1.0 g, 17 mmol) was impregnated with 8 mL of tellurium acid(19 mg, 83 μmol) for 4 h. The product was dried and calcined at 600 °C for 4 h with a heating rate of 1 °C/min. Vanadyl acetylacetonate

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saturated in toluene(50 mL) was added to the solid of TeO_x/SBA-15 and stirred for 1 h. The product was filtered and washed repeatedly with toluene until the filtrate was colorless, and then calcined in air at 600 °C for 4 h with a heating rate of 1 °C/min. The catalyst was named VTeO/SBA-15^M(Molecular designed deposition method).

Co-impregnation method was performed by impregnating SBA-15(1.0 g, 17 mmol) with 8 mL of a solution of tellurium acid(19 mg, 83 μmol) and ammonium metavanadate(39 mg, 333 μmol) for 4 h. The product was calcined in air at 600 °C for 4 h, and named VTeO/SBA-15^C(Co-impregnation method). In a similar way, step-impregnation method was performed by impregnating SBA-15(1.0 g, 17 mmol) with 8 mL of tellurium acid(19 mg, 83 μmol) for 4 h, and the product was calcined at 600 °C for 4 h. The solid was re-impregnated with a solution of ammonium metavanadate(39 mg, 333 μmol) for 4 h, followed by calcining in air at 600 °C for 4 h. The obtained catalyst was named VTeO/SBA-15^S(Step-impregnation method).

2.2 Characterization of Catalyst

The contents of V in the samples were determined by ICP on a Perkin-Elmer OPTIMA 3000 instrument. The above catalysts were dissolved in a solution of nitric, hydrochloric and hydrofluoric acids. The mixture was evaporated at 180 °C to remove Si. The solid was then redissolved in 5 mL of nitric acid, and the solution was diluted to a V concentration less than 30 μL/L. The molar ratios of V, Te and SBA-15 in the catalysts were about 2:0.5:100 by the ICP measurements.

X-Ray diffraction patterns(XRD) were collected on a Rigaku Rotflex D/Max-C powder diffractometer with C-filtered Cu $K\alpha$ radiation(λ=0.15064 nm). Py-IR was measured on a Nicolet Nexus-XT spectrometer. 32 scans were taken with a resolution of 4 cm^{-1}. The catalysts were heated at 500 °C for 1 h, followed by vacuuming and cooling. When the temperature was cooled to 150 °C, a spectrum was collected. The temperature was further down to 100 °C, pyridine was adsorbed for 15 min. After vacuum-pumping, the temperature was raised to 150 °C and IR spectrum was re-collected. N_2 adsorption was performed on a Tristar 3000 autosorb instrument.

The H_2-TPR measurement was carried out using a flow quartz reactor. The catalyst(20 mg) were pretreated at 400 °C for 3 h in a flow of argon(20 mL/min), which was cooled to room temperature, and contacted with a dilute hydrogen gas in argon(1%, volume fraction). The heating rate was 10 °C/min from room temperature to 800 °C. The hydrogen consumption was monitored by a TCD detector after removing the water formed.

X-Ray photoelectron spectra(XPS) were taken on VG ESCLABMK-II(Al $K\alpha$, 10.1 kV). Spectra were recorded for $V_{2p3/2}$, $Te_{3d5/2}$ regions. The binding energies were referred to 284.8 eV for C_{1s}. Transmission electron microscopy was performed on a Phillips FEI Tecnai 30 high resolution analytical electron microscope operated at 300 kV.

3 Results and Discussion

3.1 Characterization of Precursors

Fig.1 shows the XRD patterns of VTeO/SBA-15 samples. The peaks of (100), (110) and (200) indexed to hexagonal regularity of SBA-15 were clearly observed for the four samples. However, the shifts of the diffraction peaks to higher 2θ values were found for the V grafted SBA-15 catalysts, which was possibly caused by the contraction of their frameworks with vanadium and tellurium loading during the calcination procedure. Furthermore, the peak of d(100) was reduced with vanadium loading compared with that of pure SBA-15 supporter. This is possibly due to a degradation of the hexagonal arrangement of SBA-15 pores[8,9]. However, the detail forms of the vanadium and tellurium oxides remain unresolved. The XRD shows no peak related to vanadium and tellurium oxides, which may be caused by the very low contents of the catalysts. Fig.2 shows the X-ray diffraction peaks in high 2θ region, which also indicates highly dispersed VTeO species on SBA-15 or the contents or

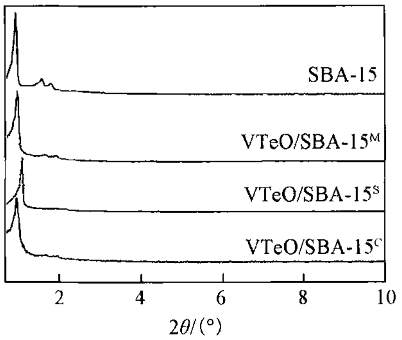

Fig.1 **Low-angle X-ray diffraction patterns of VTeO catalysts prepared by different methods**