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Selective oxidation of isobutane to methacrolein over MoVTe mixed oxide supported on SBA-3 and SiO_2

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ABSTRACT

SBA-3 and SiO_2-supported MoVTe mixed oxide catalysts have been prepared by impregnation and/or direct synthesis methods and tested for selective oxidation of isobutane to methacrolein (MAL). It was found that the supported catalysts showed much higher activity than the bulk MoVTe mixed oxide for the reaction. Among the supported catalysts, better isobutane conversion and MAL yield were achieved on the 3% $MoV_{0.8}Te_{0.23}O_x$/SBA-3 catalyst prepared by the impregnation method. The catalysts were characterized with BET, XRD, Raman, H_2-TPR, XPS and FT-IR of pyridine adsorption. The good performance of the SiO_2 and SBA-3 supported $MoV_{0.8}Te_{0.23}O_x$ catalysts was attributed to a combination of different properties: (i) formation of well dispersed active phases on large surface areas of SiO_2 and SBA-3 supports, which is beneficial for the isolation of active site and preventing the further oxidation of unstable reaction intermediate as well as product; (ii) improved activity for hydrogen abstraction of C–H bond of isobutane due to the formation of isolated pseudotetrahedral VO_4 species.

1. Introduction

Methacrolein (MAL) is an important industrial chemical used as an intermediate to produce methyl methacrylate (MMA). The one-step oxidation of isobutane to MAL is an interesting alternative to the well-developed isobutene oxidation process because isobutane is an abundant product in refinery or from natural gas and is considered as cheap raw material for petrochemical catalytic process. Many studies on selective oxidation of isobutane to MAL have been reported [1–13]. The catalysts employed for the reaction are mainly unsupported multi component oxides and supported single or binary components based on vanadium and/or molybdenum [8–13]. Among them, bulk $MoVTeO_x$ and $MoVTeSbO_x$ catalysts showed high catalytic activity at relatively low temperature for the selective oxidation of isobutane to MAL in the presence of water vapor [10–12]. However, in our case, bulk MoVTe based mixed oxide prepared by a solution method exhibited poor catalytic performance for the selective oxidation of isobutane to MAL under the condition without water added to the feed. Moreover, MoVTe(Sb) mixed oxides have low surface area, which may limit their potential industrial applications. On the other hand, metal oxides supported on silica based supports (e.g. SiO_2, MCM-41) [8,13–19] as catalysts, have been widely studied for the selective oxidation of light alkanes. By spreading the oxide onto a support, the supply of the active oxygen species able to activate C–H bonds of alkanes on the catalyst surface can be controlled which will be helpful to prevent the further oxidation of desired products. Our previous study also indicated that MoVTe(Nb) mixed oxide highly dispersed on MCM-41 and/or silica supports demonstrated much higher selectivity and yield to the acrolein formation than that of the bulk samples for the direct oxidation of propane to acrolein [14–17]. Potentially, supported $MoVTeO_x$ catalysts may also have the advantages over the unsupported ones for direct oxidation of isobutane to MAL, especially when using the water free reaction feed. However, to the best of our knowledge, there were very few reports in the literature on the aspects of supported MoVTe mixed oxide catalysts for the reaction.

The objective of this study is to determine the role of a silica support either amorphous or organized in specific arrays as in SBA-3 on the catalytic properties of MoVTe mixed oxide for oxidation of isobutane to MAL. The physicochemical properties of the catalysts were systematically investigated by means of BET, XRD, Raman, H_2-TPR, XPS and FT-IR of pyridine adsorption. The structure-performance relationships were discussed.

2. Experimental

2.1. Catalyst preparation

The micro-spherical silica was commercially available from Aldrich Chemical Company (Silica gel, Davisil, Grade 636, 35–60

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mesh) and was pretreated with 20 wt.% of nitric acid. SBA-3 was synthesized according to the method reported originally by Stucky et al. [20]. Cetyltrimethylammonium bromide (CTAB) and tetraethylorthosilicate (TEOS) were used as a surfactant and silica source, respectively. The surfactant was mixed with water and hydrochloric acid (37%). TEOS was then added dropwise to the acidic CTAB solution with stirring to form a mixture with a molar ratio of: 1 SiO_2:0.12 CTAB:9.2 HCl:130 H_2O. The mixture was stirred at room temperature for 24 h. The solid component was recovered by filtration, washed with a copious amount of water and dried at 200 °C for 3 h. After calcination at 550 °C for 8 h in air, the mesoporous SBA-3 was finally obtained.

SiO_2 and SBA-3 supported MoVTe mixed oxide catalysts were prepared by impregnation method using an aqueous solution of ammonium heptamolybdate (Sinopharm Chemical Reagent Co., Ltd., Analytical reagent), ammonium metavanadate (Guangdong Xilong Chemical Co., Ltd., Analytical reagent) and tellurium acid (Tianjin Beilian Chemical Co., Chemically pure) mixture. After water was evaporated at 80 °C, the precursors were calcined in air at 600 °C for 4 h. In order to optimize the atomic ratios of Mo/V/Te/Si in the catalyst, a series of SiO_2 supported catalysts with different Mo/V/Te and $(Mo_k+V_y+Te_z)/Si$ ratios were prepared and tested for the isobutane oxidation reaction (Supporting Information Table S1–S4). According to the experimental results, optimal Mo/V/Te atomic ratio of 1/0.8/0.23 with $(Mo_k+V_y+Te_z)/Si=3\%$ were obtained. This ratio was followed in the preparation of SBA-3 supported catalysts. In addition, SiO_2 supported single oxide samples (MoO_x/SiO_2, VO_x/SiO_2 and TeO_x/SiO_2) with the MoO_x, VO_x and TeO_x loadings same as those in the optimized composition of 3% $MoV_{0.8}Te_{0.23}O_x/SiO_2$ catalyst were also prepared by the same method. According to the optimized composition of 3% $MoV_{0.8}Te_{0.23}O_x$, the weight percents of MoO_x/SiO_2, VO_x/SiO_2 and TeO_x/SiO_2 are 2.3 wt.%, 1.0 wt.% and 0.7 wt.%, respectively. The catalysts are denoted as 1.5% MoO_x/SiO_2, 1.2% VO_x/SiO_2 and 0.3% TeO_x/SiO_2, where 1.5%, 1.2% and 0.3% are the atomic ratios of Mo/Si, V/Si and Te/Si, respectively.

A SBA-3 supported $MoV_{0.8}Te_{0.23}O_x$ catalyst was also prepared by direct synthesis method (denoted as 3% $MoV_{0.8}Te_{0.23}O_x$/SBA-3-ds). In this case, ammonium heptamolybdate, ammonium metavanadate and tellurium acid with desired Mo/V/Te atomic ratio were dissolved in hydrochloric acid (37%) with stirring. Then CTAB was added to the mixture. TEOS was then added dropwise to the above solution to form a mixture with a color of brick red. The mixture was stirred at room temperature for 24 h. The solid component was recovered by filtration, washed with a great deal of water and dried at 200 °C for 3 h. After calcination at 550 °C for 8 h in air, the 3% $MoV_{0.8}Te_{0.23}O_x$/SBA-3-ds catalyst was finally obtained.

For comparison, bulk $MoV_{0.8}Te_{0.23}O_x$ catalyst was prepared by a solution method. Ammonium metavanadate was dissolved in 80 ml distilled water at 80 °C to give a yellow solution. Telluric acid and ammonium heptamolybdate with desired molar ratio were then added with stirring to obtain an orange solution. After water in the solution was evaporated at 80 °C, the solid component was calcined at 600 °C for 4 h in air.

2.2. Catalyst characterization

The BET surface area and pore volume of the catalysts were determined by nitrogen adsorption at −196 °C on a Micromeritics Tristar 3000 instrument. Before adsorption, the samples were pretreated at 300 °C for 3 h in vacuum. The pore volume and pore diameter of the catalysts were calculated by BJH method based on the desorption curve.

X-ray powder diffraction (XRD) analysis was carried out by a Panalytical X'pert PRO diffractometer scanning 2θ from 0.5 to 90°. Cu Kα radiation obtained at 40 kV and 30 mA was used as the X-ray source. JCPDS file database was used for peak identification.

Raman spectra were recorded at room temperature with a Renishaw inVia Raman System equipped with a CCD detector. The excitation wavelength was a 532 nm diode laser with power of ~5 mW measured at the analysis spot. The microscope attachment for the Renishaw inVia system is based on a Leica DMLM system using a PL Fluotar 50× objective. The Raman spectra were measured with 2 cm^{-1} spectral resolution.

The H_2-temperature-programmed reduction (H_2-TPR) experiments were performed with a GC-TPR apparatus. The samples (50 mg) were treated in a flow of O_2/Ar (20 ml/min, 5% O_2) at 500 °C for 30 min and then cooled to 50 °C. After that, the samples were switched to a flow of H_2/Ar mixture (20 ml/min, 5% H_2) and heated from 50 to 800 °C at a rate of 10 °C/min. The effluent gas mixture was passed through a cold trap (−30 °C) to remove water. Hydrogen consumption was monitored by an on-line gas chromatograph equipped with a TCD.

XPS spectra were taken by a VG ESCLAB MK-II system with Al Kα (1486.6 eV) as the X-ray source. The binding energy of the element was reference to the C1s peak at 284.6 eV.

IR spectra of pyridine adsorption were recorded using a Thermo Nicolet Nexus FT-IR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. The samples were pressed into self-supporting wafers and treated at 400 °C in an in situ IR cell for 0.5 h followed by evacuation at 300, 200, 150 and 100 °C for 5 min to record the background spectra respectively. After cooling to 100 °C, the samples were exposed to pyridine vapor for 10 min. The spectra were recorded after evacuation at high temperatures (100, 150, 200 and 300 °C). The IR spectra were recorded in the spectral range 1700 to 1400 cm^{-1} with 32 scans and at a resolution of 4 cm^{-1}.

2.3. Catalytic testing

The catalytic performance tests were carried out in a fixed bed flow reactor (quartz tube, 8 mm i.d.) at atmospheric pressure and at 440 °C. 200 mg of the catalyst was used in each experiment. Void volume of the reactor was filled with quartz chips to eliminate the gas phase reaction. The reaction gas mixture with a molar composition of $i\text{-}C_4H_{10}:O_2:N_2=1:1:4$ was passed through the catalyst bed at a space velocity of 3000 ml g_{cat}^{-1} h^{-1}. Reactants and reaction products were analyzed on-line by two gas chromatographs (a FID-GC with RT-PLOT Q column and a TCD-GC with squalane/Al_2O_3 and carbon molecular sieve columns). The data were collected after 0.5 h on stream.

3. Results and discussion

3.1. Catalytic activity evaluation

Catalytic performance of the samples for isobutane oxidation at 440 °C is shown in Table 1. The reactor filled with quartz chips shows no activity for the oxidation of isobutane at 440 °C (Table S5). Among the three silica supported Mo, V and Te single oxides catalysts, 1.2% VO_x/SiO_2 shows the highest isobutane conversion, but the selectivity toward MAL is poor. The isobutane conversions on other two single oxide catalysts are very low, but 1.5% MoO_x/SiO_2 and 0.3% TeO_x/SiO_2 show good selectivities toward isobutene and MAL, respectively. Under the experimental condition, the bulk $MoV_{0.8}Te_{0.23}O_x$ catalyst shows poor isobutane conversion. Compared to the bulk catalyst, the supported $MoV_{0.8}Te_{0.23}O_x$ catalysts exhibit much higher activity and better selectivity for the oxidation of isobutane to MAL. The 3% $MoV_{0.8}Te_{0.23}O_x$/SBA-3 shows the highest conversion and yield to MAL among the three supported catalysts for isobutane oxidation. It is also noteworthy that highest selectivity of isobutene with lowest selectivity to carbon oxides is obtained on 3% $MoV_{0.8}Te_{0.23}O_x$/SBA-3-ds catalyst. This indicates that over-oxidation of reaction intermediate (such as isobutene) and target products are restrained on the 3% $MoV_{0.8}Te_{0.23}O_x$/SBA-3-ds catalyst, resulting in improving the selectivity of the catalyst.

The reaction results of supported $MoV_{0.8}Te_{0.23}O_x$ catalysts for isobutane oxidation at different temperatures are shown in Fig. 1. It