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Feature Article

Controlled silylation of MoVTeNb mixed oxide catalyst for the selective oxidation of propane to acrylic acid

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ABSTRACT

Acrylic acid is an important industrial chemical, and efficient catalysts for its direct preparation by propane oxidation are highly desirable. For this purpose, neutral silica networks were introduced on the surface of MoVTeNb mixed oxide catalysts by controlled silylation using a methyl silicate oligomer (MS-51). The modified catalysts gave ~56.5% yield of acrylic acid with a selectivity of 77.1% in the oxidation of propane at 380 °C. The catalysts were characterized by X-ray fluorescence, Fourier-transform infrared spectroscopy, Brunauer–Emmett–Teller specific surface area, X-ray diffraction (Rietveld analysis), pyridine desorption, and scanning electron microscopy. MoVTeNb mixed oxide was found to be composed of 90.9% M1 phase and 2.3% M2 phase, and upon silylation, the surface was uniformly covered by a thin SiO_2 layer with 0.14 molar ratio with respect to Mo and an estimated thickness of 2.4 nm. The amount of acid sites decreased after the first three silylation cycles, but was not affected by repeated cycles. The results of the kinetic study based on the comparison of the simulated contribution of each side reaction were consistent with those of the model reactions using acrylic acid and other reactants: the controlled silylation effectively suppressed acrylic acid oxidation, especially after repeated silylation cycles, which is responsible for the superior performance of the silylated catalysts. Considering the relatively large size of acrylic acid compared to propane and the efficient propane activation by silica-covered catalysts, the controlled silylation was proposed to have two roles, by which further consecutive oxidation is prevented effectively to exhibit excellent performance in oxidation of propane: i) to block the unfavorable acidic sides, ii) to generate a silica layer with pore mouth openings on the surface of MoVTeNb mixed oxide, which allow the entrance of propane but inhibit re-entrance of the produced acrylic acid.

1. Introduction

Acrylic acid is an important industrial chemical with world annual production capacity of about 4.8 million metric tons in 2014, which ranks it among the top 100 chemicals produced worldwide. Currently, acrylic acid is produced by a two-step process from propylene via acrolein; propylene is, in turn, obtained from the naphtha cracking process. However, the naphtha cracking reaction requires large amounts of energy, because it is under thermodynamic control, and is hazardous to the ecosystem and human health. Thus, the direct oxidation of propane is advantageous because it decreases the environmental impact by 20%, as estimated by a life cycle assessment [1]. To date, the most promising catalytic system for the selective oxidation of propane to acrylic acid is MoVTe(Sb)Nb mixed oxide, discovered by Mitsubishi Chemicals [2,3] and Toagosei [4]. Much attention has been focused on both the improvement of the performance and the elucidation of the mechanism of action of this catalyst. Over the past twenty years, significant progress has been made toward a better understanding of the crystalline of MoVTe(Sb)Nb mixed oxide catalysts and their complex catalytic mechanism [2–51]. The MoVTe(Sb)Nb mixed oxide catalysts are mainly composed of two crystalline phases, the so-called M1 and M2 phases [5,6].

The M1 phase with space group Pba2 is constructed from center-occupied pentagonal rings linked together by corner-sharing MO_6 octahedrons (M = Mo, V), which are assembled in the (001) plane to form hexagonal and heptagonal rings hosting Te–O units. Niobium is preferentially located in a pentagonal bipyramidal environment. The M2 phase has a hexagonal bronze-like network with space group

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Abbreviations: SEM, scanning electron microscopy; XRD, X ray diffraction; BET, Brunauer–Emmett–Teller; XRF, X-ray fluorescence; GHSV, gas hourly space velocity; PP, propylene; AA, acrylic acid; ACA, acetic acid; CO_x, sum of CO and CO_2; r, reaction rate; FTIR, fourier transform infrared; rpm, revolution per minute

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P6 mm, where octahedra form a framework with the hexagonal channels that contain tellurium atoms [31]. The M1 phase is crucial for the selective oxidation of propane to acrylic acid, whereas the M2 phase poorly activates propane but selectively converts propylene to acrylic acid [30,32,33].

Many efforts have also been made to improve the catalyst performance, including modifications of the preparation method [7–21], replacement of components [22], and doping with other elements such as P, B, Pd, and W [23–27]. MoVTeNb mixed oxide catalysts were more efficient than MoVSbNb mixed oxides, probably because of the excellent activity of tellurium. Moreover, the catalyst performance was improved by a suitable modification, while excessive modifications led to an opposite effect on the selectivity [26,27] because of over-oxidation or pore filling of the active site. When additives were added in a molar ratio of 0.01 with respect to Mo, a negative effect on either the selectivity or the activity of the catalyst was observed. To overcome these difficulties, MoVTeNb mixed oxide catalysts have been modified by the introduction of a neutral silica network based on a bulky alkoxide, such as tetraethyl silicate, which resulted in reduced pore filling and remarkably improved catalyst performance [16]. In this study, the catalytic behavior of silylated MoVTeNb mixed oxide was investigated, and the role of the silica layer in the catalytic activity and its mechanism of action were explored using kinetic and model reaction studies.

2. Experiments

2.1. Preparation of the catalysts

MoVTeNb mixed oxide, rich in the M1 phase with a Mo/V/Te/Nb molar ratio of 1/0.28/0.14/0.18, was prepared by a slurry method reported previously [14,15]. A typical preparation procedure includes the following steps. (1) Preparation of the tellurium source: fine metallic tellurium was synthesized by heat-treatment of an aqueous slurry containing 4.7 g of TeO_2 (Mitsuwa Pure Chemicals, Osaka, Japan, 99.9%), 3.6 g of hydrazine hydrate (Wako Pure Chemicals Industry, Osaka, Japan, 80 wt%), and 77.0 g of distilled water at 80 °C while stirring for 6 h, followed by rinsing of the remaining hydrazine hydrate with distilled water. (2) Preparation of the slurry: an aqueous solution of 37.1 g of ammonium heptamolybdate (Wako Pure Chemicals Industry, Osaka, Japan, 99%) and 6.5 g of ammonium metavanadate (Wako Pure Chemicals Industry, Osaka, Japan, 99%) was mixed with the prepared aqueous suspension of tellurium source (diluted with 20 g of distilled water) at 70 °C. A blue slurry was formed indicating slight oxidation and reduction of the Te, Mo, and V sources. An aqueous solution of niobium oxalate, prepared by heating an aqueous slurry of 5.5 g of $Nb_2O_5 \cdot xH_2O$ (CBMM, assay 80%), 16.4 g of oxalic acid dihydrate (Wako Pure Chemicals Industry, Osaka, Japan, 99.9 wt%), and 19.9 g of distilled water at 80 °C for 4 h, was added promptly to the blue slurry at 40 °C under stirring with a semilunar-shaped blade rotating at 400 rpm. Before mixing, 57.0 g of 2% aqueous ammonia was added, and after mixing for 5 min, 9.6 g of ammonium nitrate was added. Coprecipitation occurred, probably due to the reaction of oxalate ligand of the niobium complex with the ammonium counterions of the Mo and V oxoanions, generating a viscous slurry. (3) Drying of the slurry: the slurry was dried in a tray with Teflon sheets at 120 °C within a laboratory Constant Temperature Ovens (Yamato Scientific Co. Ltd., KDN-302), and crushed into granules of size < 1.0 mm. (4) Pre-calcination and calcination of the granules for crystallization to M1 phase: the granules were placed into a crucible preheated at 340 °C and the temperature was adjusted to 300 °C and kept for 1.5 h under atmospheric condition; Insert the granules into a stainless steel tube (10 mm diameter), semi-close the two sides with a small amount of active carbon, quartz wool and nuts, then heat the stainless steel tube in an oven under 590 °C for 1.5 h. (5) Ball-milling of the granules: 10 g of catalyst granules, 5 g of methanol, and 0.5 g of oxalic acid dihydrate were placed in a pot, which was rotated for 24 h at 120 rpm, followed by solvent removal by filter paper and drying at 120 °C for 1 h.

The silylation of MoVTeNb mixed oxide was carried out as follows. (1) Crushing the ball-milled granules with a high-speed rotation crusher (Osaka Chemical, Osaka, Japan, Wonder Crusher WC-3) twice at 28000 rpm for 30 s. (2) Drying the granules at 120 °C for 1 h. (3) Mixing 10 g of granules with an equal amount of a 2.7% solution of oligomers of methyl silicate (MKC silicate MS-51, Mitsubishi Chemical, Tokyo, Japan) in hexane (Wako Pure Chemicals Industry, Osaka, Japan, 96 + % GC) under stirring for 3 min. (4) Washing the slurry with 20 g of hexane and decanting the solution twice. (5) Stirring of the slurry in 10 g of hexane for 30 min, followed by decanting and drying at 120 °C for 30 min. (6) Repeating steps (1)–(5) six times. For convenience, the MoVTeNb mixed oxide catalysts were named S_0–S_6, where the footnote indicates the number of silylation cycles. B_1–B_6 represent the samples contained crushing procedure in sequence of S_1, B_1, S_2, B_2, S_3, B_3, S_4, B_4, S_5, B_5 and S_6 of all procedures.

2.2. Catalyst characterization

Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 field emission SEM. Powder X-ray diffraction (XRD) patterns of silylated and non-silylated catalysts were recorded on a Bruker AXS KK D8 Advance (Lynxeye XE) diffractometer operating at 40 kV, 40 mA, using CuKα radiation with a wavelength of 0.1542 nm. The unit cell parameters of the M1, M2, $TeMo_5O_{16}$, and $Mo(V)_5O_{14}$ phases were refined according to the Rietveld method using a TOPAS software (version 4.2, Bruker AXS KK) and the M1 and M2 crystallographic information reported by DeSanto et al. [31] Infrared spectra were recorded at room temperature with an accumulation of 32 scans and a resolution of 4 cm^{-1} in the 400–4000 cm^{-1} region on a Nicolet iS50 spectrometer (Thermo Fisher Scientific) equipped with a DTGS (deuterated triglycine sulfate) detector. The pellets were prepared with 20 mg of sample mixed with 100 mg of dry KBr. The Brunauer–-Emmett–Teller (BET) surface area was determined with an Autosorb-1 adsorption analyzer (Quantachrome Instruments), and elemental analysis was performed by wavelength dispersive X-ray fluorescence (XRF) using a Rigaku ZSX Primus II spectrometer. Pyridine desorption was measured with a FID gas chromatograph equipped with a TC-1 capillary column (30 m, i.d. 0.32 mm) in the temperature range from 180 °C to 450 °C after sample pretreatment for 30 min, injection of pyridine, and holding at 180 °C for 30 min in a helium flow.

2.3. Catalyst evaluation

The catalytic activities of the samples were measured in a fixed-bed quartz tubular reactor (i.d. 8 mm). The catalyst granules were prepared by mixing 10 g of catalyst powder and 0.4 g of a 5 wt% starch solution in distilled water, drying at 120 °C, and sieving into 0.3–0.5 mm particle sizes. The reactions were carried out at 380 °C, using a feed gas with a propane:air:steam:nitrogen molar ratio of 1.0:11.0:4.5:4.5, a gas hourly space velocity (GHSV) of 900–32940 h^{-1}, and 1.6 g of catalyst in a 25-mm-long catalyst bed packed with alumina balls. Catalyst evaluation data were taken after 2 h of time-on-stream. To localize the point of maximum temperature, a one-end closed stainless tube (o.d. 2 mm) containing a movable thermocouple was placed in the center of the catalyst bed. To investigate extended reactions (SV $<$ 1300 h^{-1}), a second reactor operating at the same temperature was connected to the outlet of the first reactor with a Teflon tube kept at 120 °C. The reactants and products were analyzed using a gas chromatograph equipped with three packed columns: (i) Gaskuropack 56 for acetic acid and acrylic acid; (ii) Gaskuropack 54 for CO_2, water, propylene, and propane; and (iii) molecular sieve MS-5A column for nitrogen, oxygen, and CO. The conversion of propane, selectivity and yield of acrylic acid expressed in molar percentage form were calculated on a propane base, as follows: