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Catalytic oxidation of methacrolein to methacrylic acid over silica-supported 11-molybdo-1-vanadophosphoric acid with different heteropolyacid loadings

Mitsuru Kanno [a], Toshiya Yasukawa [b], Wataru Ninomiya [b], Ken Ooyachi [b], Yuichi Kamiya [c,*]

[a] *Graduate School of Environmental Science, Hokkaido University, Kita 10 Nishi 5, Sapporo 060-0810, Japan*
[b] *Corporate Research Laboratories, Mitsubishi Rayon Co., Ltd., 20-1, Miyuki-cho, Otake, Hiroshima 739-0693, Japan*
[c] *Research Faculty of Environmental Earth Science, Hokkaido University, Kita 10 Nishi 5, Sapporo 060-0810, Japan*

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ABSTRACT

Catalytic oxidation of methacrolein (MAL) to methacrylic acid (MAA) over SiO_2-supported $H_4PMo_{11}VO_{40}$ with different $H_4PMo_{11}VO_{40}$ loadings was investigated. $H_4PMo_{11}VO_{40}/SiO_2$ showed high activity in comparison with unsupported $H_4PMo_{11}VO_{40}$, and 3.3 mol% $H_4PMo_{11}VO_{40}/SiO_2$ (50 wt.% $H_4PMo_{11}VO_{40}$) had the highest activity, which was five-times larger than that of unsupported $H_4PMo_{11}VO_{40}$ due to high dispersion of $H_4PMo_{11}VO_{40}$ on SiO_2, as determined by temperature-programmed desorption of benzonitrile. On the other hand, the supported catalysts were less selective toward the formation of MAA. From X-ray diffraction and Raman spectroscopy, it was determined that $H_4PMo_{11}VO_{40}$ decomposed to form MoO_3 on SiO_2 during the catalytic reaction. Since SiO_2-supported MoO_3 and unsupported MoO_3 had only very low selectivity toward the formation of MAA in the oxidation of MAL, it was concluded that the formation of MoO_3 caused the decrease in the catalytic performance of the supported catalysts.

1. Introduction

Methacrylic acid (MAA) is an important intermediate in the production of methyl methacrylate and other derivatives, including polymers. Selective oxidation to produce MAA via methacrolein (MAL) is a two-stage process involving the oxidation of isobutene to MAL, followed by MAL to MAA. The first step of the reaction is conducted in the presence of a Mo–Bi-oxide catalyst, and the second step involves Keggin-type heteropoly compounds containing Mo, V, and P as catalysts [1,2]. The oxidation of MAL to MAA has some issues, and in order to improve the yield of MAA, a highly active and selective catalyst is needed.

Selective oxidation of MAL over heteropoly compounds composed of P and Mo has been studied extensively [3–14]. It has been shown that substituting some Mo atoms with V atoms improves the catalytic activity and selectivity for the formation of MAA [13]. In addition, substituting H^+ with Cs^+ retards the oxidation of MAA to CO and CO_2 [13,14].

Solid heteropolyacids, that is to say, unsupported heteropolyacids, can be used as heterogeneous catalysts. However, they have low surface area and consequently have only a small number of active sites available. Thus, solid heterpolyacids frequently show only low catalytic activity. Increasing the surface area of heteropolyacids by supporting them on a carrier with a high surface area could afford highly active catalysts. Supporting $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ on SiO_2, TiO_2, and active carbon shows a great success in solid acid catalysts [15–20]. As for oxidation catalysts, supported $H_{3+x}PMo_{12-x}V_xO_{40}$ (x = 0–2) have been investigated for gas-phase oxidations of methanol [21–24], ethanol [25,26], ethene [27], propene [28], ethane [29], isobutane [30], ammoxidation of 2-methyl pyrazine [31], and liquid-phase oxidations of tetrahydrothiophene [32,33], cycloalkenes [34], toluene [35], benzyl alcohol [36] and stylene [37,38]. Nowińska et al. have demonstrated that SiO_2-supported $H_5PMo_{10}V_2O_{40}$ is highly active than unsupported one for the oxidation of ethane [27]. Liu and Iglesia have reported that supporting $H_{3+n}PMo_{12-n}V_nO_{40}$ on SiO_2 enhances the catalytic activity and decreases the CO_x selectivity in a one-step synthesis of dimethoxymethane via the oxidation of dimethyl ether or methanol [21]. Kim et al. have reported that $H_3PMo_{12}O_{40}$ supported on a mesostructured cellular SiO_2 foam, in which the support has been modified with 3-aminopropyl triethoxysilane, shows high activity for the oxidation of ethanol to acetaldehyde at 503 K [25]. However, there are only a few reports on supported heteropolyacid catalysts being used in the selective oxidation of MAL. Kim et al. [39,40] have demonstrated that $H_5PMo_{10}V_2O_{40}$ supported on nitrogen-containing mesoporous carbon and $H_3PMo_{12}O_{40}$ supported on polystyrene have higher activity for the oxidation of MAL and selectivity toward the formation of MAA compared with the corresponding unsupported catalysts.

In this study, we investigated the catalytic performance of SiO_2-supported $H_4PMo_{11}VO_{40}$ for the selective oxidation of MAL to MAA

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* Corresponding author. Fax: +81 11 706 2217.
E-mail address: kamiya@ees.hokudai.ac.jp (Y. Kamiya).

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and compared its catalytic performance with unsupported $H_4PMo_{11}VO_{40}$. The effects of the loading amount of $H_4PMo_{11}VO_{40}$ on the activity and selectivity were investigated. Changes in the catalytic performance, especially selectivity against the loading amounts, are discussed in conjunction with the chemical and physical properties of the catalysts before and after the catalytic reaction.

2. Experimental

2.1. Preparation of catalysts

MoO_3, V_2O_5, and 85% H_3PO_4, which were used to prepare $H_4PMo_{11}VO_{40}$, were purchased from Wako Pure Chemical Co., Ltd. MoO_3 (31.7 g), V_2O_5 (1.82 g), and water (1.5 dm^3) were added to a roundbottom flask. After the addition of 85% H_3PO_4 (2.3 g) into the resulting suspension, it was heated and vigorously stirred at 358 K for 3 h. After the solution was cooled to room temperature, the insoluble matter was filtered off to obtain a clear orange solution. Then the solvent was evaporated to obtain $H_4PMo_{11}VO_{40}$, which was dried in air at 333 K overnight.

SiO_2-supported $H_4PMo_{11}VO_{40}$ with different $H_4PMo_{11}VO_{40}$ loadings were prepared by using an incipient-wetness method with an aqueous solution of $H_4PMo_{11}VO_{40}$ (0.08 mol dm^{-3}) and SiO_2 (Aerosil 300: 295 $m^2\,g^{-1}$, Nippon Aerosil Co., Ltd.). $H_4PMo_{11}VO_{40}/SiO_2$ with 0.37, 1.4, and 3.3 mol% loadings, which correspond to 10, 30, and 50 wt.%, respectively, were prepared by changing the amount of the aqueous $H_4PMo_{11}VO_{40}$ solution added. The resulting wet solid was dried in air at 333 K overnight and was then calcined in air at 523 K for 4 h. Since each Keggin cluster (KU) occupies about 1.44 nm^2 [41], a theoretical monolayer of KU with 0.69 KU nm^{-2} formed. Thus, the catalysts with loadings of 0.37, 1.4, and 3.3 mol% correspond to monolayer coverages of 0.18, 0.71, and 1.65, respectively, if Keggin clusters are ideally dispersed on SiO_2.

As a reference, 3.96 mol% MoO_3/SiO_2 (9.0 wt.% MoO_3) was prepared by using an impregnation method involving SiO_2 and an aqueous solution of MoO_3, which was prepared by adding aqueous ammonia (25%, Wako Pure Chemical Co., Ltd.) to an aqueous suspension of MoO_3.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) was performed using an X-ray diffractometer (Rigaku Mini Flex) with Cu Kα radiation (λ = 0.154 nm). Raman spectroscopy was performed using a laser Raman spectrometer (JASCO, RMP 200) with a 100-mW laser with a wavelength of 532 nm and a CCD detector. Temperature-programmed desorption of benzonitrile (BN-TPD) was carried out using a custom-built TPD system equipped with a mass spectrometer (ANELVA, M-QA100S) as a detector. After the catalyst was pretreated in a N_2 flow at 523 K for 1 h, it was exposed to 0.122 μmol h^{-1} of BN in a He flow at 373 K for 2 h. The weakly adsorbed or physisorbed BN was removed in a He flow at 373 K for 2 h and then at 393 K. The temperature was then increased at a rate of 10 K min^{-1} to 873 K under a He flow while monitoring the mass signals (m/e = 18, 28, 44, and 103 for H_2O, CO, CO_2, and BN, respectively) in the exit gas.

2.3. Catalytic reaction

Catalytic oxidation of MAL was performed in a continuous flow reactor at 573 K and atmospheric pressure. Before the reaction, the catalyst was pretreated under a flow of a gas mixture consisting of O_2 (10.7 vol.%), H_2O (17.9 vol.%), and N_2 (balance) at a total flow rate of 28 $cm^3\,min^{-1}$ and a temperature of 593 K for 1 h. After the temperature was decreased to 573 K, a reactant gas mixture of MAL (3 vol.%), O_2 (6 vol.%), H_2O (15 vol.%), and N_2 (balance) was fed into the reactor to start the catalytic reaction. The amount of the catalyst and total flow rate were adjusted to control the conversion. The reaction products were analyzed by using on-line gas chromatographs (GCs) connected at the outlet of the reactor. For acetic acid (AcOH), MAL, and MAA, a GC (Shimadzu GC-14B) equipped with a flame ionization detector and a capillary column (TC-FFAP, 0.25 mm × 50 m) was utilized. For CO and CO_2, a GC (Shimadzu GC-8A) equipped with a thermal conductivity detector (TCD) and two packed columns (Molecular Sieve 5A, 2.85 mm × 3 m and Activated Carbon, 2.85 mm × 2 m) was used. In order to prevent interference from organic compounds, prior to the GC–TCD analysis, the gas was passed through a dry-ice trap to remove them. As an internal standard for GC analysis, CH_4 (31%) diluted with He was mixed at the outlet of the reactor.

3. Results and discussion

3.1. Catalytic oxidation of MAL over unsupported and SiO_2-supported $H_4PMo_{11}VO_{40}$

Fig. 1 shows time courses of the catalytic oxidation of MAL over unsupported $H_4PMo_{11}VO_{40}$ and 1.4 mol% $H_4PMo_{11}VO_{40}/SiO_2$, in which WF^{-1} were 101 and 17 $g_{-cat}\,h\,mol^{-1}_{-MAL}$, respectively, where W is the weight of the catalyst (g) and F is the flow rate of MAL (mol h^{-1}). In the initial stage of the reaction, selectivity of unsupported $H_4PMo_{11}VO_{40}$ toward the formation of MAA slightly increased and then reached nearly constant values after 50 min. On the other hand, the conversion of MAL and the selectivity toward AcOH and CO_x decreased with time in the initial stage of the reaction and reached nearly constant values after 50 min. For 1.4 mol% $H_4PMo_{11}VO_{40}/SiO_2$, although the selectivity changed in the initial stage of the reaction, constant selectivities were obtained within

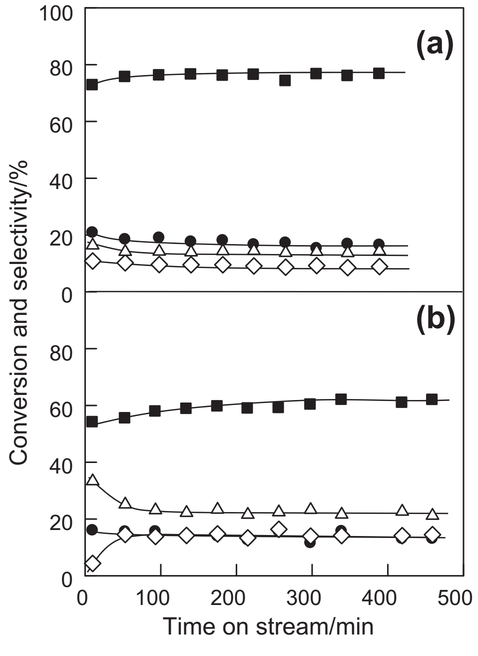

Fig. 1. Time courses of oxidation of MAL over (a) unsupported $H_4PMo_{11}VO_{40}$ and (b) 1.4 mol% $H_4PMo_{11}VO_{40}/SiO_2$. (●) Conversion of MAL and selectivities for (■) methacrylic acid, (◇) acetic acid, and (△) CO_x. Reaction conditions: MAL:O_2:H_2O:N_2 = 3:6:15:76, temperature = 573 K, total pressure = 0.1 MPa, and WF^{-1} = 101 and 17 $g_{-cat}\,h\,mol^{-1}_{-MAL}$ for unsupported $H_4PMo_{11}VO_{40}$ and 1.4 mol% $H_4PMo_{11}VO_{40}/SiO_2$, respectively.