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**11-Molybdo-1-vanadophosphoricacid $H_4PMo_{11}VO_{40}$ supported on ammonia-modified
silica as highly active and selective catalyst for oxidation of methacrolein**

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ABSTRACT

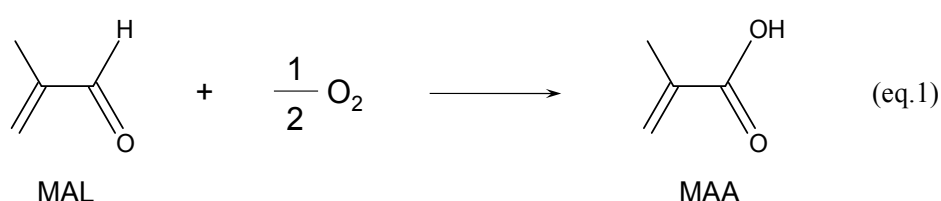
Gas-phase oxidation of methacrolein to methacrylic acid has been carried out over various unsupported and supported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ catalysts. While SiO_2 -supported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ showed low selectivity to methacrylic acid, $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ supported on NH_3 -modified SiO_2 , which was prepared by using an impregnation method with acetone as the solvent, exhibited high selectivity (~90%) and high activity for the formation of methacrylic acid. The activity of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}/\text{NH}_3$ -modified SiO_2 was more than five times higher than that of the corresponding unsupported catalysts.

Keywords:

Supported heteropolyacid; Ammonia-modified silica; Methacrylic acid; Selective oxidation

1. Introduction

Methacrylic acid (MAA), which is an important basic chemical, is prepared by gas-phase catalytic oxidation of methacrolein (MAL) (eq. 1).



Heteropolyacids with a Keggin structure composed of P, Mo, and V have been utilized as industrial catalysts [1,2]. However, the catalytic performance, including activity and selectivity, must be improved.

Solid heteropolyacids, that is, unsupported heteropolyacids, often show low catalytic activities because of their low surface area. Supporting the heteropolyacids on oxide supports with high surface areas, especially SiO₂, increases the amount of the heteropolyacids exposed on the surface, leading to an enhancement in the catalytic activity [3]. In fact, several acid catalyzed reactions [4-14], as well as oxidation reactions [15-25] over supported heteropolyacid catalysts, have been reported so far. However, there are only a few reports on supported heteropolyacid catalysts being used for the gas-phase oxidation of MAL [26,27].

We have previously reported the gas-phase oxidation of MAL over SiO₂-supported H₄PMo₁₁VO₄₀ catalysts (H₄PMo₁₁VO₄₀/SiO₂) [28]. In fact, H₄PMo₁₁VO₄₀/SiO₂ shows much higher activity than unsupported H₄PMo₁₁VO₄₀ due to the high dispersion of H₄PMo₁₁VO₄₀ on SiO₂. However, H₄PMo₁₁VO₄₀ on SiO₂ undergoes thermal decomposition to form MoO₃ below a reaction temperature of 573 K. Since MoO₃ formed on SiO₂ accelerates the formation of CO₂ and acetic acid, H₄PMo₁₁VO₄₀/SiO₂ shows only low selectivity toward the formation of MAA [28].

Here we report that H₄PMo₁₁VO₄₀ supported on ammonia-modified SiO₂ (designated as NH₃-SiO₂) is a highly active and selective catalyst for the gas-phase oxidation of MAL to MAA. On NH₃-SiO₂, H₄PMo₁₁VO₄₀ did not decompose during the catalytic oxidation reaction due to the formation of a thermally stable crystalline NH₄⁺ salt of H₄PMo₁₁VO₄₀. The stabilization and high dispersion of H₄PMo₁₁VO₄₀ led to not only high activity but also high selectivity for the formation of MAA in the gas-phase oxidation of MAL.

2. Experimental

2.1. Preparation of catalysts

H₄PMo₁₁VO₄₀ was prepared from MoO₃, V₂O₅, and 85% H₃PO₄ [28], which 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 round-bottom 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 $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ (designated as HPA), which was dried in air at 333 K overnight.

$\text{NH}_3\text{-SiO}_2$ was prepared according to a published method with some modifications [29]. SiO_2 (CARIACT Q-10 : $258 \text{ m}^2 \text{ g}^{-1}$, Fuji Silysia Chemical Ltd.) was treated in an N_2 flow at 1073 K for 1 h and then in an NH_3 flow ($50 \text{ cm}^3 \text{ min}^{-1}$) at 1073 K for 4 h. The treated SiO_2 was then cooled to room temperature in an N_2 flow to obtain $\text{NH}_3\text{-SiO}_2$.

$\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ supported on $\text{NH}_3\text{-SiO}_2$ was prepared by using an impregnation method with acetone as the impregnation solvent. After impregnation, the resulting wet solid was dried in air at 333 K overnight, followed by calcination in air at 523 K for 4 h. The obtained catalyst was designated as $\text{HPA}[\textit{acetone}]/\text{NH}_3\text{-SiO}_2$. The loading amount of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ was 43 wt%. For comparison, $\text{HPA}[\textit{water}]/\text{NH}_3\text{-SiO}_2$ was prepared in a similar manner to $\text{HPA}[\textit{acetone}]/\text{NH}_3\text{-SiO}_2$, except that water was used instead of acetone.

As a reference, one unsupported and two supported catalysts were prepared.

Unsupported $(\text{NH}_4)_3\text{PMo}_{11}\text{VO}_{40}$ (designated as NH_4^+ -HPA) was prepared by a titration method. An aqueous solution of NH_4NO_3 (0.1 mol dm^{-3}) was added to an aqueous solution of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ (0.08 mol dm^{-3}), which was vigorously stirred, until the $\text{NH}_4^+/\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ ratio reached unity. The resulting suspension was dried up, and then the resulting solid was dried in air at 333 K overnight.

$\text{H}_4\text{PMo}_{11}\text{VO}_{40}/\text{SiO}_2$ (designated as HPA/ SiO_2) was prepared by impregnating SiO_2 with an acetone solution of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ (0.08 mol dm^{-3}) in a similar manner to that for HPA[*acetone*]/ NH_3 - SiO_2 . $(\text{NH}_4)_3\text{PMo}_{11}\text{VO}_{40}/\text{SiO}_2$ (designated as [NH_4^+ -HPA]/ SiO_2) was prepared by adding an aqueous suspension of NH_4^+ -HPA to SiO_2 . The loading amount of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ for all of the supported catalysts was 43 wt%.

All of the catalysts were calcined in air at 523 K for 4 h before use.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) was performed using an X-ray diffractometer (Rigaku Mini Flex) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). 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. ^{31}P MAS-NMR spectra were recorded using a JEOL ECA-400

spectrometer with a spinning frequency of 7 kHz. All the measurements were carried out at room temperature. The chemical shifts are expressed relative to external 85% H₃PO₄.

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 O₂ (10.7 vol.%), H₂O (17.9 vol.%), and N₂ (balance) at a total flow rate of 28 cm³ 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.%), O₂ (6 vol.%), H₂O (15 vol.%), and N₂ (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 CO₂, 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, CH₄ (31%) diluted with He was mixed at the outlet of the reactor.

The conversion of MAL was calculated by eq. 1.

$$\text{Conversion(\%)} = \frac{[\text{MAL}]_{\text{in}} - [\text{MAL}]_{\text{out}}}{[\text{MAL}]_{\text{in}}} \times 100 \quad \text{eq. 1}$$

Here [MAL]_{in} and [MAL]_{out} are the concentrations of MAL at the inlet and outlet of the reactor, respectively.

3. Results and discussion

The catalytic data for the unsupported and supported catalysts for the gas-phase oxidation of MAL are summarized in Table 1. The activity and selectivity toward the formation of MAA of the unsupported HPA catalysts were 13 μmol g⁻¹ min⁻¹ and 75%, respectively (entry 1). Unsupported NH₄⁺-HPA (entry 2), in which 25% of the H⁺ of HPA was substituted with NH₄⁺, was more selective for the formation of MAA (91% selectivity). However, the catalytic activity was similar to that of the unsupported HPA, indicating that the substitution of H⁺ with NH₄⁺ did not affect the activity. On the other hand, further

substitution of H^+ with NH_4^+ dramatically lowered the activity and selectivity for MAA (Fig. A1 in Supplementary data).

In the case of the supported catalysts (entries 3–6), the activities were more than 5 times higher than those for the unsupported HPA catalyst. However, the selectivity varied significantly depending on the support (SiO_2 or NH_3-SiO_2), impregnation solvent (acetone or water), and preparation method. HPA/ SiO_2 exhibited the highest activity, although the selectivity for MAA was low (entry 3). The unsupported NH_4^+ -HPA showed high selectivity to MAA (entry 2), whereas it was low for supported NH_4^+ -HPA on SiO_2 (entry 4). On the other hand, HPA[*acetone*]/ NH_3-SiO_2 showed the highest selectivity for MAA among the supported catalysts examined (entry 5). The catalyst was highly selective for MAA with a high conversion in comparison with that of [NH_4^+ -HPA]/ SiO_2 (Fig. 1). In addition, the catalytic performance of HPA[*acetone*]/ NH_3-SiO_2 barely changed over at least 4 h (Fig. 2). However, HPA[*water*]/ NH_3-SiO_2 , which was prepared using water as the impregnation solvent, showed only low selectivity for MAA (entry 6). These results demonstrate that HPA[*acetone*]/ NH_3-SiO_2 has potential for practical use.

It has been reported that substituting H^+ in unsupported $H_{3+x}PMo_{12-x}V_xO_{40}$ with Cs^+ ions is effective for suppressing the formation of byproducts, including acetic acid and CO_x , in the

gas-phase oxidation of MAL [30]. In fact, unsupported NH_4^+ -HPA showed the highest selectivity for MAA (entry 2) among the catalysts examined, probably because of the lower number the acid sites due to the substitution of H^+ with NH_4^+ similar to unsupported $\text{H}_{3+x-y}\text{Cs}_y\text{PMo}_{12-x}\text{V}_x\text{O}_{40}$. However, $[\text{NH}_4^+\text{-HPA}]/\text{SiO}_2$ exhibited only limited selectivity for MAA (entry 4). In contrast, $\text{HPA}[\textit{acetone}]/\text{NH}_3\text{-SiO}_2$ showed both high activity and high selectivity for MAA. To understand the differences in the selectivities among the supported catalysts, their structures were investigated before and after the reaction.

$\text{HPA}[\textit{acetone}]/\text{NH}_3\text{-SiO}_2$ showed an XRD pattern identical to a crystalline NH_4^+ salt of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ (cubic $(\text{NH}_4)_x\text{H}_{4-x}\text{PMo}_{11}\text{VO}_{40}$) [31] (Fig. A2(a) in Supplementary data), although the catalyst was prepared by supporting $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ on $\text{NH}_3\text{-SiO}_2$. The crystallite size of the NH_4^+ salt estimated from Scherrer's equation was 39 nm. In the ^{31}P MAS-NMR spectrum (Fig. A3(a) in Supplementary data), $\text{HPA}[\textit{acetone}]/\text{NH}_3\text{-SiO}_2$ gave a intense peak at -4.4 ppm and relatively weak one at -3.6 ppm, which were assignable to the NH_4^+ salt of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ and $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$, respectively. The ^{31}P MAS-NMR spectrum indicated that the main species of the heteropolyacid formed on $\text{HPA}[\textit{acetone}]/\text{NH}_3\text{-SiO}_2$ was $(\text{NH}_4)_x\text{H}_{4-x}\text{PMo}_{11}\text{VO}_{40}$. On the other hand, HPA/SiO_2 before the reaction showed an XRD pattern due to $\text{H}_4\text{PMo}_{11}\text{VO}_{40}\cdot 14\text{H}_2\text{O}$ microcrystallites (Fig. A2(b)) [32]. For

$[\text{NH}_4^+\text{-HPA}]/\text{SiO}_2$, strong and sharp diffraction lines attributed to cubic $(\text{NH}_4)_x\text{H}_{4-x}\text{PMo}_{11}\text{VO}_{40}$ and broad and weak ones due to $\text{H}_4\text{PMo}_{11}\text{VO}_{40}\cdot 14\text{H}_2\text{O}$ microcrystallites were observed (Fig. A2(c)), suggesting that relatively large-size $(\text{NH}_4)_x\text{H}_{4-x}\text{PMo}_{11}\text{VO}_{40}$ crystallites and dispersed $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ microcrystallites were present. In fact, the peak at -3.6 ppm due to $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ was strong comparing with the peak at -4.4 ppm due to $(\text{NH}_4)_x\text{H}_{4-x}\text{PMo}_{11}\text{VO}_{40}$ in the ^{31}P MAS-NMR spectrum for $[\text{NH}_4^+\text{-HPA}]/\text{SiO}_2$ (Fig. A3(c)). In a separate experiment (Supplementary data), the aqueous suspension of $\text{NH}_4^+\text{-HPA}$ used for the preparation of $[\text{NH}_4^+\text{-HPA}]/\text{SiO}_2$ was separated using a centrifuge, affording a yellow solid and a clear orange solution. Elemental analysis and powder XRD indicated that the yellow solid was $(\text{NH}_4)_2\text{H}_2\text{PMo}_{11}\text{VO}_{40}$ crystallites and that the orange solution was an aqueous solution of the acid-form $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$. Since $[\text{NH}_4^+\text{-HPA}]/\text{SiO}_2$ was prepared by adding such a suspension to SiO_2 , large-size $(\text{NH}_4)_x\text{H}_{4-x}\text{PMo}_{11}\text{VO}_{40}$ crystallites and dispersed $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ microcrystallites coexist on the support. The structure of the heteropolyacid compounds in $\text{HPA}[\text{water}]/\text{NH}_3\text{-SiO}_2$ before the reaction was similar to that in $[\text{NH}_4^+\text{-HPA}]/\text{SiO}_2$ as evidenced by XRD pattern (Fig. A2(d)), and ^{31}P MAS-NMR spectrum (Fig. A3(d)).

After gas-phase oxidation of MAL, the structures of the supported catalysts were different. For HPA/SiO_2 , the XRD lines due to $\text{H}_4\text{PMo}_{11}\text{VO}_{40}\cdot 14\text{H}_2\text{O}$ microcrystallites were

significantly less intense (Fig. 3b), and the Raman spectrum indicated the formation of molybdenum oxides (Fig. 4b) because the bands for molybdenum oxide phases (α -MoO₃ and β -MoO₃) were observed at 849, 820, 772, and 660 cm⁻¹, resulting in the low selectivity for MAA [28]. In the case of [NH₄⁺-HPA]/SiO₂, the XRD pattern of H₄PMo₁₁VO₄₀·14H₂O microcrystallites disappeared after the reaction (Fig. 3c), although it was clearly observed before the reaction. In addition, Raman bands attributed to MoO₃ were observed in the spectrum for NH₄⁺-HPA/SiO₂ after the reaction (Fig. 4c). For HPA[*water*]/NH₃-SiO₂ after the reaction, Raman bands due to α -MoO₃ were present at 820 cm⁻¹. Thus, it is thought that some of the H₄PMo₁₁VO₄₀ microcrystallites on SiO₂ decompose to MoO₃ during the reaction in the cases of [NH₄⁺-HPA]/SiO₂ and HPA[*water*]/NH₃-SiO₂. In contrast to these, HPA[*acetone*]/NH₃-SiO₂ showed only the XRD pattern (Fig. 3a) due to the cubic (NH₄)_xH_{4-x}PMo₁₁VO₄₀ even after the gas-phase oxidation of MAL. In addition, there were no Raman bands for MoO₃ after the reaction in the case of HPA[*acetone*]/NH₃-SiO₂ (Fig. 4a). Since there were a less amount of H₄PMo₁₁VO₄₀ crystallites in HPA[*acetone*]/NH₃-SiO₂, i.e., cubic (NH₄)_xH_{4-x}PMo₁₁VO₄₀ crystallites were mainly present, before the reaction, the heteropolyacid was hard to decompose to MoO₃ during the reaction. Thus, we concluded that the high dispersion of H₄PMo₁₁VO₄₀ on the support and the formation of the crystalline

NH_4^+ salt resulted in the high catalytic performance of $\text{HPA}[\text{acetone}]/\text{NH}_3\text{-SiO}_2$ for the gas-phase oxidation of MAL.

4. Conclusion

$\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ supported on ammonia-modified SiO_2 , which was prepared by using an impregnation method with acetone as the impregnation solvent, exhibited high selectivity (~90%) for the formation of methacrylic acid in the gas-phase oxidation of methacrolein. On the ammonia-modified SiO_2 , $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ did not decompose to molybdenum oxide phases during the catalytic reaction due to the formation of thermally stable crystalline NH_4^+ salt of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$. The high dispersion of $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ on the support and the formation of the crystalline NH_4^+ salt lead to the high catalytic performance of the catalyst.

Appendix A. Supplementary data

Supplementary data to this article can be found online at [doi:10.1016/j.petech.2019.04.011](https://doi.org/10.1016/j.petech.2019.04.011).

References

- [1] M. Wada, *Petrotech* 15 (1992) 452–458.

- [2] M. Misono, N. Nojiri, *Appl. Catal.* 64 (1990) 1–30.
- [3] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113–252.
- [4] J. Kaur, K. Griffin, B. Harrison, I.V. Kozhevnikov, *J. Catal.* 208 (2002) 448–455.
- [5] J.X. Mao, Y. Kamiya, T. Okuhara, *Appl. Catal. A* 255 (2003) 337–344.
- [6] L.A.M. Cardoso, W. Alves, A.R.E. Gonzaga, L.M.G. Aguiar, H.M.C. Andrade, *J. Mol. Catal. A* 209 (2004) 189–197.
- [7] B.C. Gagea, Y. Lorgouilloux, Y. Altintas, P.A. Jacobs, J.A. Martens, *J. Catal.* 265 (2009) 99–108.
- [8] K.A.D. Rocha, P.A. Robles-Dutenhefner, I.V. Kozhevnikov, E.V. Gusevskaya, *Appl. Catal. A* 252 (2009) 188–192.
- [9] Y.D. Xu, Y.X. Qi, G.X. Lu, S.B. Li, *Catal. Lett.* 125 (2008) 83–89.
- [10] A. Miyaji, R. Ohnishi, T. Okuhara, *Appl. Catal. A* 262 (2004) 143–148.
- [11] H. Liu, N.H. Xue, L.M. Peng, X.F. Guo, W.P. Ding, Y. Chen, *Catal. Commun.* 10 (2009) 1734–1737.
- [12] J.C. Juan, J.C. Zhang, M.A. Yarmo, *J. Mol. Catal. A* 267 (2007) 265–271.
- [13] M.M.M.A. El-Wahab, A.A. Said, *J. Mol. Catal. A* 240 (2005) 109–118.
- [14] K.A. da Silva, I.V. Kozhevnikov, E.V. Gusevskaya, *J. Mol. Catal. A* 192 (2003)

- 129–134.
- [15] H. Liu, E. Iglesia, *J. Phys. Chem. B* 107 (2003) 10840–10847.
- [16] L.M. Gomez Sainero, S. Damyanova, J.L.G. Fierro, *Appl. Catal. A* 208 (2001) 63–75.
- [17] H. Kim, J.C. Jung, P. Kim, S.H. Yeom, K.-Y. Lee, I.K. Song, *J. Mol. Catal. A* 259 (2006) 150–155.
- [18] Y. Liu, K. Murata, M. Inaba, N. Mimura, *Catal. Commun.* 4 (2003) 281–285.
- [19] M. Sopa, A. Wąclaw-Held, M. Grossy, J. Pijanka, K. Nowińska, *Appl. Catal. A* 285 (2005) 119–125.
- [20] N. Lingaiah, K.M. Reddy, P. Nagaraju, P.S. Prasad, I.E. Wachs, *J. Phys. Chem. C* 112 (2008) 8294–8300.
- [21] R.D. Gall, C.L. Hill, J.E. Walker, *Chem. Mater.* 8 (1996) 2523–2527.
- [22] Z. Karimi, A.R. Mahjoub, F.D. Aghdam, *Inorg. Chim. Acta* 363 (2009) 3725–3730.
- [23] K.T. Venkateswara Rao, P.S.N. Rao, P. Nagaraju, P.S. Sai Prasad, N. Lingaiah, *J. Mol. Catal. A* 303 (2009) 84–89.
- [24] P. Sharma, A. Patel, *J. Mol. Catal. A* 299 (2009) 37–43.
- [25] Y. Kamiya, T. Okuhara, A. Miyaji, K. Tsuji, T. Nakajo, *Catal. Surv. Asia* 12 (2008)

- 101–113.
- [26] H. Kim, J.C. Jung, D.R. Park, S.-H. Baeck, I.K. Song, *Appl. Catal. A* 320 (2007) 159–165.
- [27] H. Kim, J.C. Jung, S.H. Yeom, K.-Y. Lee, I.K. Song, *J. Mol. Catal. A* 248 (2006) 21–25.
- [28] M. Kanno, T. Yasukawa, W. Ninomiya, K. Ooyachi, Y. Kamiya, *J. Catal.* 273 (2010) 1–8.
- [29] Y. Inaki, Y. Kajita, H. Yoshida, K. Ito, T. Hattori, *Chem. Commun.* (2001) 2358–2359.
- [30] L.M. Deusser, J.C. Petzoldt, J.W. Gaube, H. Hibst, *Ind. Eng. Chem. Res.* 37 (1998) 3230–3236.
- [31] N. Laronze, C. Marchal-Roch, N. Guillou, F.X. Liu, G. Hervé, *J. Catal.* 220 (2003) 172–181.
- [32] T. Ilkenhans, B. Herzog, T. Braun, R. Schlögel, *J. Catal.* 153 (1995) 275–292.

Table 1

Catalytic data for gas-phase oxidation of methacrolein (MAL) over unsupported and supported $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ catalysts.

Entry	Type	Catalyst	Activity $/\mu\text{mol g}^{-1} \text{min}^{-1}$	Selectivity ^a /%				(Conv. ^b)
				MAA	AcOH	CO_x	others	/%
1	Un-supported	HPA	13	75	5	16	4	8
2		NH_4^+ -HPA	15	91	5	4	n.d. ^c	5
3	Supported	HPA/ SiO_2	175	72	12	13	3	14
4		$[\text{NH}_4^+\text{-HPA}]/\text{SiO}_2$	71	65	14	17	4	6
5		HPA[<i>acetone</i>]/ $\text{NH}_3\text{-SiO}_2$	76	89	4	7	n.d. ^c	9
6		HPA[<i>water</i>]/ $\text{NH}_3\text{-SiO}_2$	113	75	8	9	8	9

Reaction conditions: $\text{MAL}:\text{O}_2:\text{H}_2\text{O}:\text{N}_2 = 3:6:15:76$; temperature = 573 K, and total pressure = 0.1 MPa.

The activity and selectivity were estimated from the data obtained below 14% conversion.

^aMAA: methacrylic acid, AcOH: acetic acid, and others: acetone, acetaldehyde, acrolein and acrylic acid.^bConversions at which activity and selectivity were evaluated.^cNot detected.

Figure captions

Fig. 1. Relationship between selectivity and conversion for HPA[*acetone*]/NH₃-SiO₂ (closed symbols) and [NH₄⁺-HPA]/SiO₂ (open symbols). (■, □) MAA, (◆, ◇) acetic acid and (▲, △) COx. Reaction conditions: MAL:O₂:H₂O:N₂=3:6:15:76; temperature = 573 K, and total pressure = 0.1 MPa

Fig. 2. Time courses for the gas-phase oxidation of MAL over HPA[*acetone*]/NH₃-SiO₂. (●) Conversion of MAL and selectivities for (■) methacrylic acid, (◇) acetic acid, and (△) COx. Reaction conditions: MAL:O₂:H₂O:N₂ = 3:6:15:76, temperature = 573 K, total pressure = 0.1 MPa, and $W F^{-1} = 20 \text{ g}_{\text{-cat}} \text{ h mol}_{\text{-MAL}}^{-1}$

Fig. 3. XRD patterns for the supported H₄PMo₁₁VO₄₀ catalysts after gas-phase oxidation of MAL. (□) cubic (NH₄)_xH_{4-x}PMo₁₁VO₄₀ and (▲) H₄PMo₁₁VO₄₀·14H₂O. (a) HPA[*acetone*]/NH₃-SiO₂, (b) HPA/SiO₂, (c) [NH₄⁺-HPA]/SiO₂, and (d) HPA[*water*]/NH₃-SiO₂. Reaction conditions: MAL:O₂:H₂O:N₂ = 3:6:15:76, temperature = 573 K, total pressure = 0.1 MPa, and 4 h.

Fig. 4. Raman spectra of the supported catalysts after the gas-phase oxidation of MAL.

(●) MoO₃ phases (α -MoO₃ and β -MoO₃). (a) HPA[*acetone*]/NH₃-SiO₂, (b)

HPA/SiO₂, (c) [NH₄⁺-HPA]/SiO₂, and (d) HPA[*water*]/NH₃-SiO₂.

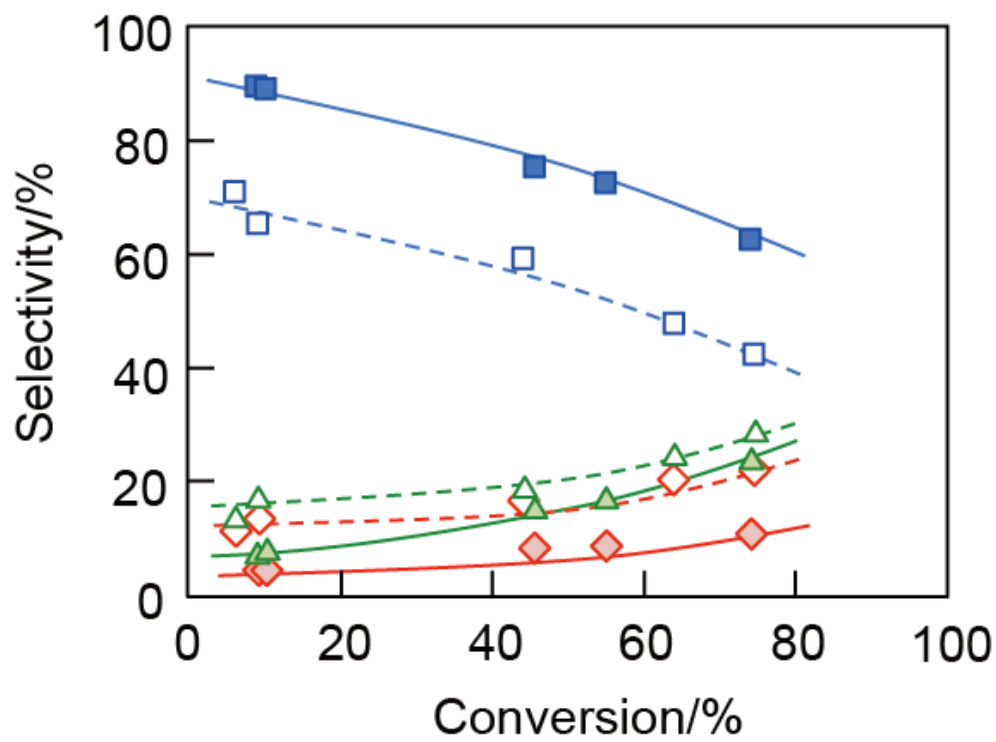


Fig. 1

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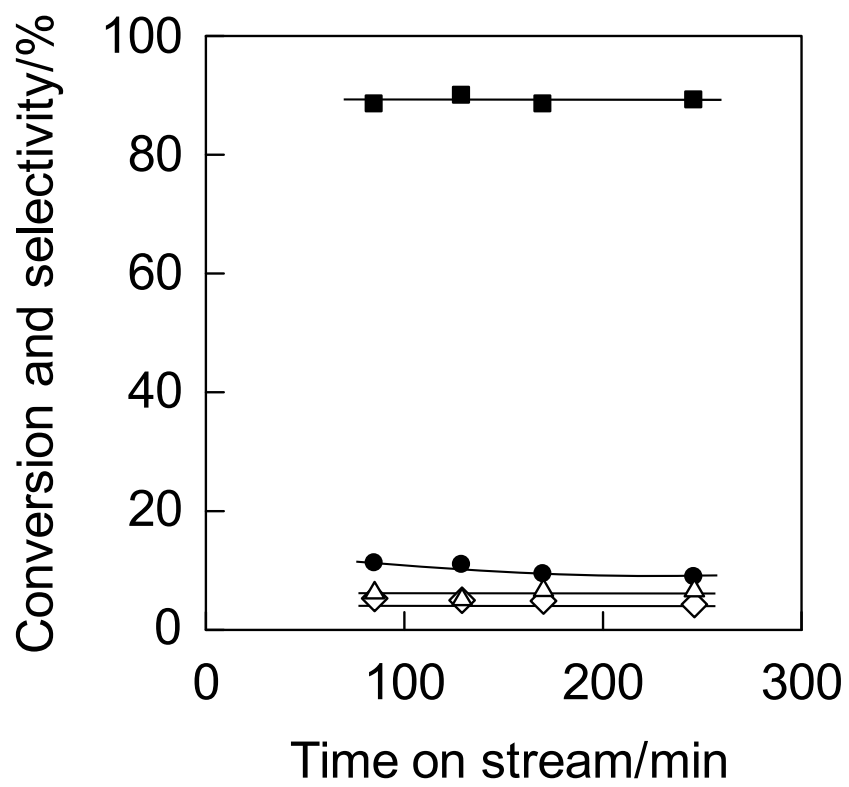


Fig. 2

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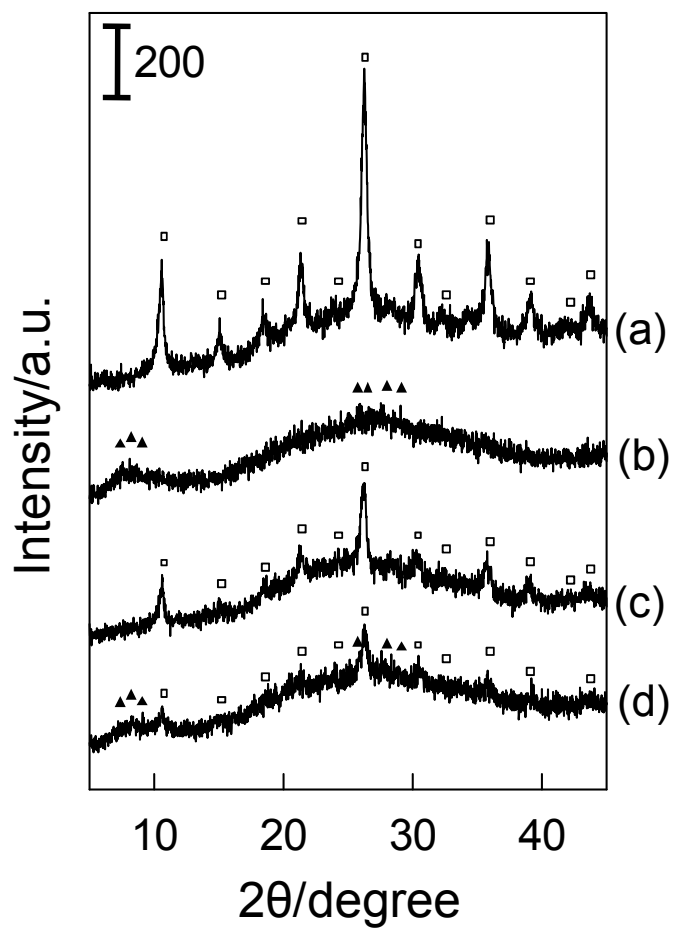


Fig. 3

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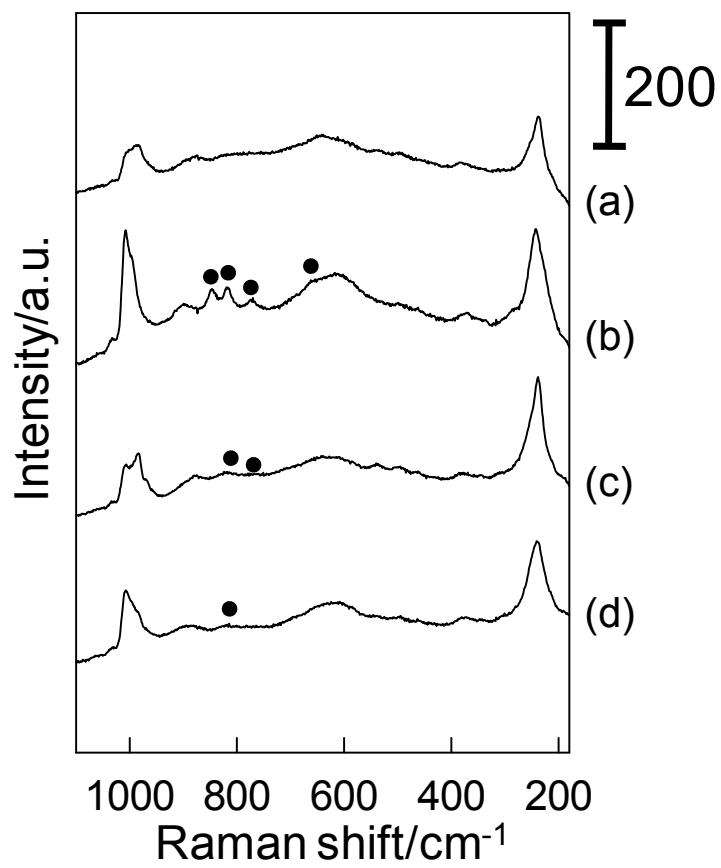


Fig. 4

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