

Preparation of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ catalyst immobilized on polystyrene support and its application to the methacrolein oxidation

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Received 3 November 2005; received in revised form 12 December 2005; accepted 12 December 2005

Available online 18 January 2006

Abstract

$\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo) catalyst was immobilized on the aminated polystyrene (PS) support as a charge compensating component, by taking advantage of the overall negative charge of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$. It was revealed that PMo catalyst was finely and molecularly dispersed on the PS support via chemical immobilization. The supported $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -polystyrene (PMo-PS) catalyst was applied to the vapor-phase oxidation of methacrolein into methacrylic acid, a typical surface-type reaction. The PMo-PS catalyst exhibited higher conversion of methacrolein and higher selectivity for methacrylic acid than the unsupported PMo catalyst. It is concluded that $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ species were chemically and finely immobilized on the PS support as charge matching species, and thus, the PMo-PS catalyst showed an excellent oxidation activity in the model surface-type reaction.

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Keywords: Heteropolyacid catalyst; Chemical immobilization; Polystyrene support; Methacrolein; Oxidation

1. Introduction

Heteropolyacids (HPAs) have been widely employed as oxidation catalysts in various homogeneous and heterogeneous reactions [1–5]. Vapor-phase oxidation of methacrolein into methacrylic acid is a typical commercialized process using HPAs as heterogeneous catalysts [6–8]. One of the great advantages of HPA catalysts is that their oxidation catalytic properties can be controlled in a systematic way by changing the identity of charge compensating counter-cations, heteroatoms, and framework polyatoms [1–4,9,10]. Another advantage that makes HPAs promising catalysts is their great thermal stability [11].

One of the disadvantages of HPA catalysts is that their surface area is very low [4]. To overcome the low surface area, HPAs have been supported on inorganic materials by a conventional impregnation method. For example, a number of mesoporous materials have been extensively investigated as supporting materials [12–15]. Another promising approach to enlarge the surface

area of HPA catalysts is to utilize polymer materials. By taking advantage of the overall negative charge of heteropolyanions, HPAs have been immobilized on ion-exchanged resins such as poly-4-vinylpyridine [16] or conjugated conducting polymers such as polyaniline and polypyrrole [17–23] to obtain molecularly dispersed HPA catalysts. The HPA catalysts immobilized on conjugated conducting polymers have found successful applications as heterogeneous oxidation catalysts in some vapor-phase reactions such as ethanol and 2-propanol conversions. For example, it was reported that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ -polyaniline [19] and $\text{H}_3\text{PW}_{11}\text{Mo}_1\text{O}_{40}$ -polyaniline [23] catalysts exhibited higher oxidation activities but lower acid-catalytic activities in the 2-propanol conversion than the corresponding solid bulk catalysts. The above examples imply that polymer materials can be utilized as excellent supports for HPA catalyst if they can be modified to have the positive charge for the immobilization of heteropolyanions.

Polystyrene bead has found successful applications in catalysis as a support [24,25]. It is expected that polystyrene can serve as an excellent support for HPA immobilization due to its feasible nature of surface modification. In this work, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo) catalyst was immobilized on the aminated polystyrene

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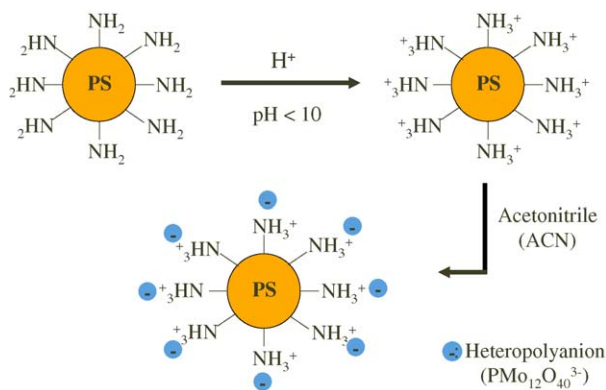


Fig. 1. Scheme for immobilization of PMo catalyst on PS support.

(PS) bead, by taking advantage of the overall negative charge of heteropolyanion. The supported catalyst was applied to the vapor-phase oxidation of methacrolein. It is known that the catalytic oxidation of methacrolein into methacrylic acid over HPA catalysts is a typical surface-type reaction [1,4,6–8], where the enhanced oxidation catalytic performance can be expected over the highly dispersed HPA catalysts.

2. Experimental

2.1. Preparation of $H_3PMo_{12}O_{40}$ catalyst immobilized on polystyrene support

$H_3PMo_{12}O_{40}$ (PMo) catalyst and aminated PS bead (2.0 mmole NH_2/g) were purchased from Aldrich Chemical Co. PMo was thermally treated at $300^\circ C$ for precise quantification prior to use. PMo catalyst immobilized on the aminated PS bead was prepared according to the similar method reported in literatures [19–23,26]. In short, PMo was immobilized on the PS bead as charge matching components in an acetonitrile medium, as presented in Fig. 1. Immobilization of PMo was done by the reaction of PS bead (1.0 g) with PMo (1.2 g) dissolved in acetonitrile (50 ml). The solid product was repeatedly washed several times with water until the washing solvent became colorless, and then it was dried overnight at $80^\circ C$ to yield the final form (PMo–PS). The loading of PMo in the PMo–PS catalyst was 23.1 wt.%.

2.2. Characterization

Infrared spectra of support (PS) and supported catalyst (PMo–PS) were obtained with an FT-IR spectrometer (Nicolet, Impact 410). Support and supported catalyst were further characterized by SEM-EDX (Jeol, JSM-6700F) and XRD (Mac Science, M18XHF) measurements. Thermal stability of PS support and PMo–PS catalyst was confirmed by TGA analyses (Pheometric Scientific, TGA-1000).

2.3. Oxidation of methacrolein

Vapor-phase oxidation of methacrolein into methacrylic acid was carried out in a continuous flow fixed-bed reactor at an

atmospheric pressure. Each catalyst (115 mg on PMo basis) was charged into a tubular quartz reactor, and the catalyst was pre-treated with a mixed stream of nitrogen (10 ml/min) and oxygen (10 ml/min) at $300^\circ C$ for 1 h. The reaction temperature was maintained at $280^\circ C$. Methacrolein (2.4×10^{-3} mole/h) was sufficiently vaporized by passing a pre-heating zone and fed into the reactor continuously together with oxygen, water vapor, and nitrogen carrier. Feed composition (mole ratio) was oxygen (1.0):nitrogen (1.0):water vapor (1.48):methacrolein (0.21). The catalytic reaction was carried out for 5 h. Reaction products were periodically sampled, and analyzed with a gas chromatography (HP 5890 II). Conversion of methacrolein and selectivity for methacrylic acid were calculated on the basis of carbon balance.

3. Results and discussion

3.1. Immobilization of PMo on PS support

Immobilization of PMo catalyst on the PS support was confirmed by FT-IR analyses, as shown in Fig. 2. The primary structure [27] of PMo can be identified by the four characteristic IR bands appearing within the range $700\text{--}1200\text{ cm}^{-1}$. Characteristic IR bands of the unsupported PMo catalyst appeared at 1064 (P–O band), 964 (Mo=O band), 868, and 789 cm^{-1} (Mo–O–Mo bands). It is noteworthy that the four characteristic IR bands of PMo in the PMo–PS catalyst were observed at slightly shifted positions compared to those of the unsupported PMo, indicating the strong interaction between PMo catalyst and PS support.

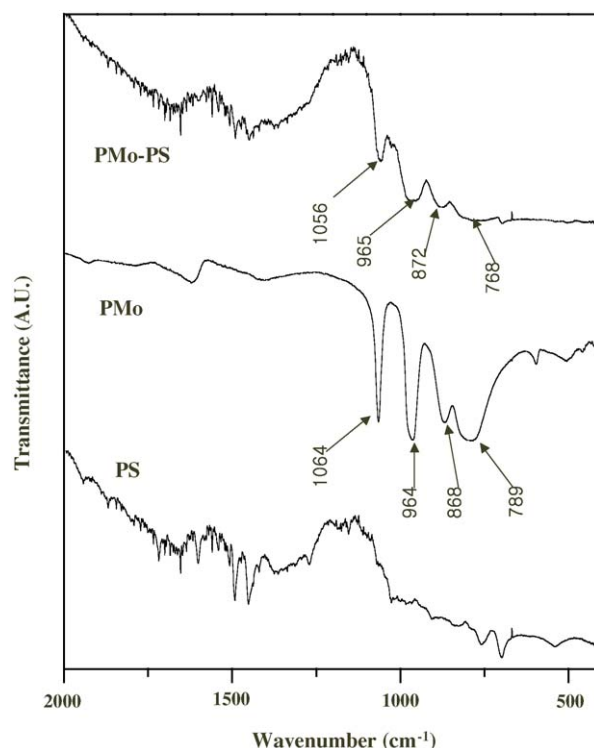


Fig. 2. FT-IR spectra of PS support, PMo catalyst, and PMo–PS catalyst.

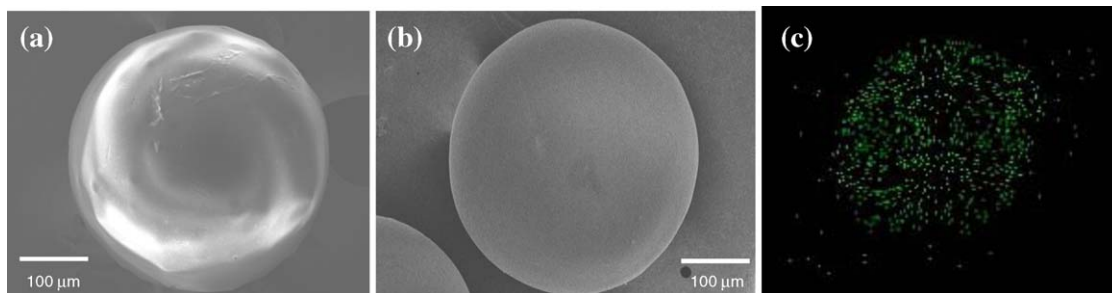


Fig. 3. (a) SEM image of PS bead, (b) SEM image of PMo-PS catalyst, and (c) EDX image of PMo-PS catalyst obtained by mapping on molybdenum.

3.2. Fine dispersion of PMo catalyst via chemical immobilization

Fig. 3 shows the SEM images of PS support and PMo-PS catalyst. The surface of PMo-PS catalyst was very clean, and no visible evidence representing PMo agglomerates was found in the PMo-PS catalyst. This indicates that PMo species were finely dispersed on the surface of PS bead. Fine dispersion of PMo catalyst on the PS support was also confirmed by EDX analysis, as shown in Fig. 3(c). N_2 adsorption isotherm analysis revealed that PS bead had no pore-like feature.

Fig. 4 shows the XRD patterns of PS bead, unsupported PMo, and PMo-PS samples. PS bead showed no characteristic XRD pattern due to its amorphous nature. Unsupported PMo catalyst showed the characteristic XRD pattern of the HPA catalyst. On the other hand, however, PMo-PS catalyst showed no characteristic XRD pattern of PMo. This indicates that PMo species were not in a crystal state but in an amorphous-like state, demonstrating that PMo species were finely and molecularly dispersed on the PS support via chemical interaction. As attempted in this work, it is believed that heteropolyanions ($PMo_{12}O_{40}^{3-}$) were strongly immobilized on the cationic sites of the PS bead as charge compensating components.

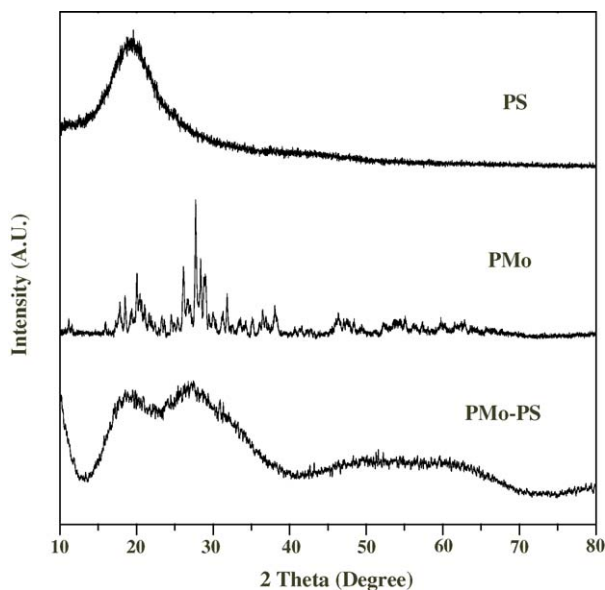


Fig. 4. XRD patterns of PS support, PMo catalyst, and PMo-PS catalyst.

3.3. Thermal stability of PS and PMo-PS

Fig. 5 shows the TGA profiles of PS support and PMo-PS catalyst. Thermal scanning was done at temperatures ranging from 30 to 500 °C in an air stream. According to the conventional definition, the temperature at which 5% loss of the initial weight was detected was taken as the decomposition temperature of polymer material. The decomposition temperatures of PS and PMo-PS samples were found to be 307 and 394 °C, respectively. Importantly, PMo-PS catalyst was more thermally stable than the PS support, representing that the thermal stability of PS support was much enhanced via chemical immobilization with PMo catalyst. This result also indicates that the PMo species did not serve as an impurity for PS, and furthermore, the binding of PMo with PS support was chemical rather than physical. The sudden weight loss observed in the PMo-PS at around 400 °C may be due to the thermal decomposition of PMo species [4].

Fig. 6(a) shows the SEM image of PMo-PS catalyst obtained after 5 h catalytic oxidation of methacrolein. Compared to the SEM image of bare PMo-PS catalyst (Fig. 3(b)), no difference in catalyst morphology and particle size was observed between the two catalysts. Furthermore, EDX images of PMo-PS catalyst obtained before and after the reaction were almost identical (Figs. 3(c) and 6(b)). Low magnification SEM and EDX images of PMo-PS catalyst shown in Fig. 6(c) and (d) clearly support that PMo-PS bead catalysts are thermally and morphologically stable even after the 5 h catalytic reaction. TGA and SEM results

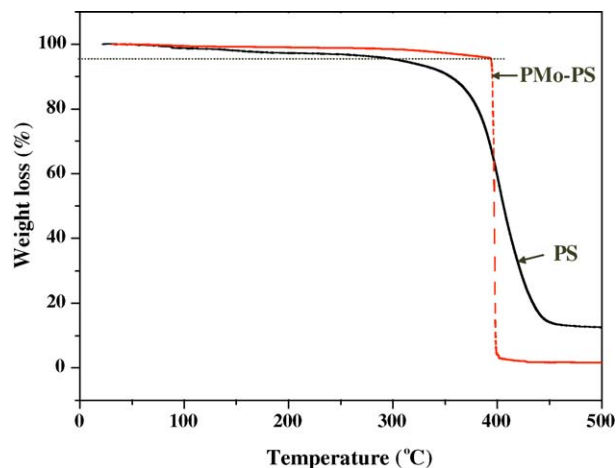


Fig. 5. TGA profiles of PS support and PMo-PS catalyst (heating rate = 10 °C/min).

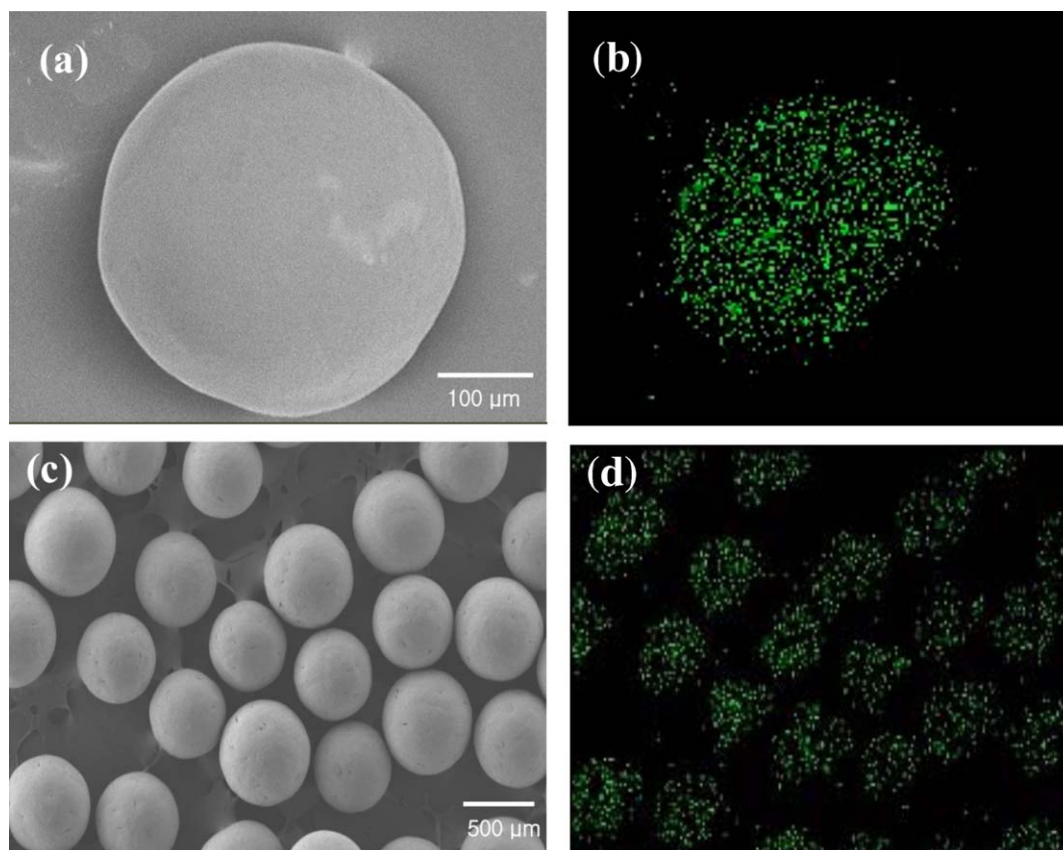


Fig. 6. (a) SEM image of PMo–PS catalyst (high magnification), (b) EDX image of PMo–PS catalyst obtained by mapping on molybdenum in (a), (c) SEM image of PMo–PS catalyst (low magnification), and (d) EDX image of PMo–PS catalyst obtained by mapping on molybdenum in (c). All the images were obtained after 5 h catalytic oxidation of methacrolein.

imply that PMo–PS catalyst was thermally stable during the catalytic oxidation of methacrolein performed at 280 °C.

3.4. Performance of PMo–PS catalyst

Fig. 7 shows the catalytic performance of unsupported PMo and PMo–PS catalysts in the vapor-phase oxidation of methacrolein at 280 °C. Conversions of methacrolein and

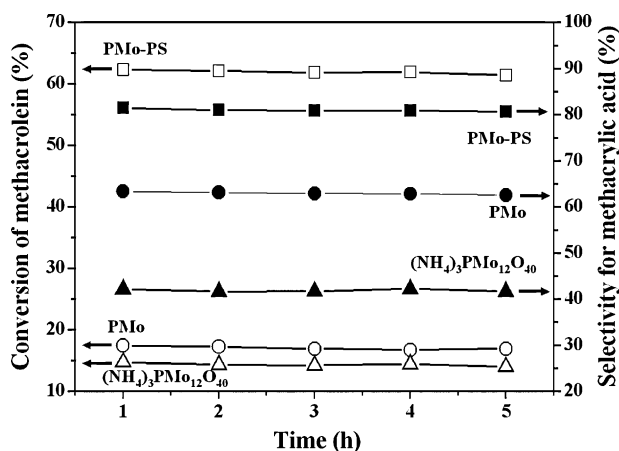


Fig. 7. Catalytic performance of PMo, PMo–PS, and (NH₄)₃PMo₁₂O₄₀ catalysts in the vapor-phase oxidation of methacrolein at 280 °C.

selectivities for methacrylic acid over the PMo–PS catalyst were much higher than those over the unsupported catalyst. The enhanced catalytic performance of PMo–PS catalyst was attributed to the finely and molecularly dispersed PMo species on the surface of PS bead via chemical immobilization. As mentioned earlier, the catalytic oxidation of methacrolein into methacrylic acid is a typical surface-type reaction [1,4,6–8]. As attempted in this work, highly dispersed PMo catalyst on the PS bead formed via chemical immobilization eventually led to the enhanced catalytic performance of PMo–PS catalyst in the surface-type oxidation reaction. The catalytic performance of (NH₄)₃PMo₁₂O₄₀ was also tested for comparison purpose. The catalytic performance of bulk (NH₄)₃PMo₁₂O₄₀ was inferior to that of bulk PMo catalyst. This is attributed to the lack of acid sites and the low oxidizing power of (NH₄)₃PMo₁₂O₄₀ catalyst [4]. It is inferred that the role and effect of aminated group in the PMo–PS catalyst may differ from that of ammonium cation in the (NH₄)₃PMo₁₂O₄₀ catalyst.

4. Conclusions

PMo catalyst was immobilized on the PS support as a charge compensating component, by taking advantage of the overall negative charge of [PMo₁₂O₄₀]³⁻. It was observed that PMo catalyst was finely and molecularly dispersed on the PS support via chemical immobilization. Thermal analyses revealed that the

binding of PS with PMo was chemical rather than physical. In the vapor-phase oxidation of methacrolein into methacrylic acid, the PMo–PS catalyst showed an enhanced oxidation catalytic performance than the unsupported PMo catalyst. It was concluded that $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ species were chemically and finely immobilized on the PS support as charge matching species, and thus, the PMo–PS catalyst showed an excellent oxidation activity in the model surface-type reaction.

Acknowledgement

The authors acknowledge the support from Korea Science and Engineering Foundation (KOSEF R01-2004-000-10502-0).

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