Heterogeneous liquid-phase hydration of isobutene by heteropoly acid–polymer composite film catalyst

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$H_3PMo_{12}O_{40}$–polymer composite film catalysts were prepared by blending these two materials using a methanol–chloroform mixture by a membrane preparation technique. Polyphenylene oxide (PPO), polyethersulfone (PES) and polysulfone (PSF) were used as blending polymers. A $H_3PMo_{12}O_{40}$–PPO composite catalyst coated on Al_2O_3 was also prepared. These catalysts were used as heterogeneous catalysts for the liquid-phase *tert*-butanol (TBA) synthesis from isobutene and water. It was found that all the composite film catalysts showed higher catalytic activities than homogeneous $H_3PMo_{12}O_{40}$ in the TBA synthesis. Among the composite film catalysts, $H_3PMo_{12}O_{40}$–PPO showed the best catalytic performance. Not only high absorption capability of $H_3PMo_{12}O_{40}$–PPO for isobutene but also stability of $H_3PMo_{12}O_{40}$–PPO in the reaction medium was responsible for such a catalytic performance. The $H_3PMo_{12}O_{40}$–PPO/Al_2O_3 also showed a higher activity than a homogeneous solution of $H_3PMo_{12}O_{40}$.

Keywords: heteropoly acid, polymer, hydration, isobutene, *tert*-butanol

1. Introduction

Solid heteropoly acids (HPAs) such as $H_3PMo_{12}O_{40}$ are inorganic acids and at the same time strong oxidizing agents [1–4]. The acid and redox catalytic properties of HPAs have been conventionally modified by replacing the protons with metal cations and/or by changing the heteroatom or the framework polyatoms [5–8]. Other unique features that make solid HPAs be commercial catalysts are their characteristic absorption property and pseudo-liquid phase behavior [9]. HPAs have been also used as homogeneous catalysts in a few commercial processes such as hydration of propylene to 2-propanol [10] and isobutene to *tert*-butanol (TBA) [11]. Taking advantage of a solubility property that HPAs are highly soluble in some polar solvents such as water and amines, TBA was successfully synthesized by reacting isobutene with concentrated aqueous solution of HPA [12]. It was reported that the homogeneous HPA catalyst was more active than the conventional mineral acids in the TBA synthesis [13].

Polymer materials have been used in chemical reactions as supports or catalysts [14–19]. Although application of polymer materials to chemical reactions has been restricted due to their thermal and mechanical instability at high temperatures, much attention has also been paid to polymer materials because of their flexible applicability [20]. HPAs have been combined with ion-exchange resins [21] or conjugated conducting polymers [22–24] such as polyaniline and polypyrrole for the modified catalysis of HPAs. A new attempt utilizing polymer materials for the modification of novel catalysis of HPAs reported by this group [25–29] is to blend HPAs with polymers using a solvent to form a membrane-like film catalyst by a membrane preparation technique. Highly dispersed HPA catalyst supported on polymer matrix has been designed by this method to show an enhanced oxidation catalytic activity in the heterogeneous vapor-phase ethanol conversion [27] and 2-propanol conversion [28]. It was observed that the characteristics and oxidation catalysis of HPA–polymer composite film catalysts were strongly affected by the nature of solvents and polymer materials used. The pore characteristics of the composite catalysts also affected their catalytic activities in a model reaction [30]. However, not much progress has been made on the modified acid catalysis of HPA–polymer composite film catalysts.

In this work, membrane-like $H_3PMo_{12}O_{40}$–polymer composite film catalysts were prepared by a membrane preparation technique and they were used as heterogeneous catalysts for the liquid-phase hydration of isobutene to TBA in a semi-batch reactor. A $H_3PMo_{12}O_{40}$–polymer composite film catalyst coated on Al_2O_3 was also prepared and tested under the same reaction conditions. The catalytic activities of the composite catalysts were compared to those of the homogeneous aqueous solution of $H_3PMo_{12}O_{40}$.

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2. Experimental

2.1. Preparation of $H_3PMo_{12}O_{40}$–polymer composite film catalysts

$H_3PMo_{12}O_{40}$ (PMo, from Aldrich Chem. Co.) was used as an active catalyst for the reaction. Polysulfone (PSF, Udel 1700, from UCC), polyethersulfone (PES, Victrex 5200P, from ICI), and polyphenylene oxide (PPO, poly-2,6-dimethyl-1,4-phenylene oxide, from Aldrich Chem. Co.) were used as blending polymers for their excellent thermal and mechanical stability. It was found that PMo was highly soluble in methanol (M), whereas polymers were soluble in chloroform (C). Although PMo was not soluble in chloroform and polymers were not soluble in methanol, PMo and polymers could be blended using methanol (M)–chloroform (C) mixture because both solvents were highly miscible. It is noteworthy that there are so many choices in selecting a pair of solvents for the blending of HPA with the above-mentioned polymers.

A homogeneous PMo (1.22 wt%)–PPO (6.9 wt%)–methanol (4.41 wt%)–chloroform (87.47 wt%) solution was obtained at room temperature to prepare the membrane-like PMo–PPO composite catalyst by a membrane preparation technique. The homogeneous PMo–PPO–MC solution was casted on a glass plate with uniform thickness and was subsequently dried in ambient condition (56% relative humidity) to obtain PMo–PPO. PMo–PSF and PMo–PES composite film catalysts were also prepared with the same preparation conditions. The thickness of composite film catalysts was 17 μm. PMo-free polymer films were also prepared under the same conditions for reference and comparison.

A PMo–PPO composite catalyst coated on Al_2O_3 beads (γ-Al_2O_3, from Grace Korea, Ltd., surface area $= 220$ m^2/g, bulk density $= 0.43$ g/cm^3, pore volume $= 1.05$ cm^3/g, average particle diameter $= 1.65$ mm) was also prepared for the practical application of PMo–PPO composite catalyst to the liquid-phase TBA synthesis. Here, Al_2O_3 was simply used as a matrix for the coating of PMo–PPO, not as an active support for PMo. Al_2O_3 was thermally treated at 300 °C for 1 h for the precise quantification before the coating. Al_2O_3 beads were soaked in the homogeneous solution of PMo (1.22 wt%)–PPO (6.9 wt%)–methanol (4.41 wt%)–chloroform (87.47 wt%) at room temperature, and then allowed to remain for 10 min for sufficient wetting. After eliminating the residual solution, it was evacuated at 25 mTorr for 30 min to dry up. The whole coating process was repeated twice for the complete coating. The final composite catalyst was denoted as PMo–PPO/Al_2O_3. All the composite catalysts were thermally treated at 170 °C before reaction and characterization.

2.2. Characterization

DSC measurements (TA Instruments TA200) were carried out in order to confirm the thermal behavior and the blending pattern of the composite film catalysts. SEM analyses (Jeol JMS-35, LEO-420) were also carried out to investigate the surface morphology of the composite film catalyst. Absorption amounts of isobutene into the composite film catalysts were measured at room temperature. Amounts of PMo extracted from the composite film catalysts in the reaction medium were also measured by UV spectroscopy (Kontron Instruments Uvikon 930).

2.3. Reaction

Heterogeneous liquid-phase hydration of isobutene to TBA was carried out in a semi-batch reactor. Film catalysts were cut into small pieces (2 mm × 2 mm) and were treated at 170 °C for 1 h by flowing air before introducing them into the reactor. Bulk PMo was also pretreated at 300 °C with air before the reaction. Small pieces of the composite film catalyst or beads of PMo–PPO/Al_2O_3 were dispersed in water (50 cm^3) of the semi-batch reactor. The reactor was heated up to 70 °C and was stirred vigorously. The reaction was initiated by introducing isobutene into the reactor. Reaction temperature and isobutene pressure were maintained at a constant level during the reaction. Reaction products were analyzed periodically with a gas chromatograph (Yanaco G180). Hydration of isobutene by a homogeneous aqueous catalyst of PMo was also carried out at the same reaction conditions for comparison.

3. Results and discussion

3.1. Thermal analysis of the composite film catalysts

Table 1 shows the glass transition temperatures of PMo–polymer composite films and PMo-free polymer films. The glass transition temperature was measured at the second scan after most of the moisture in the film was removed. It was found that the glass transition temperature of PSF and PES decreased after blending with PMo, whereas that of PPO increased after blending with PMo. This result shows that there was neither interaction nor bonding between PMo and PSF (or PES), and that PMo only served as an impurity for PSF (or PES). It also means that there was a certain interaction or bonding between PPO and PMo, and that PMo was no longer an impurity for PPO. It can be summarized that the blending of PMo with PSF (or PES) was physical while that with PPO was physicochemical.

Table 1
Glass transition temperatures of PMo–polymer composite film catalysts.[a]

Film catalyst	Glass transition temperature (°C)
PSF	185
PMo–PSF	<180
PES	236
PMo–PES	219
PPO	211
PMo–PPO	221

[a] Heating rate = 15 °C/min.

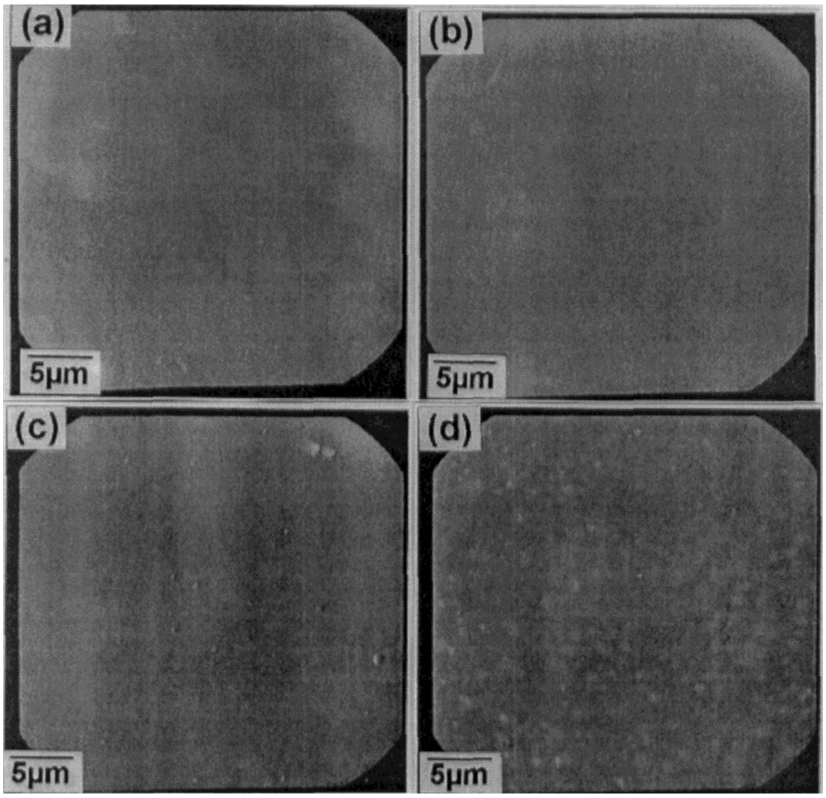

Figure 1. SEM images of (a) PSF, (b) PMo–PSF, (c) PPO and (d) PMo–PPO.

3.2. Morphology of the composite film catalysts

Figure 1 shows the SEM images of PSF, PMo–PSF, PPO and PMo–PPO. There was no distinctive difference in surface morphology between PSF and PMo–PSF. No visible evidence representing PMo was found in PMo–PSF. These two films had no pore-like feature and their surfaces were dense and clean. It was also observed that PES and PMo–PES showed similar surface morphology with PSF and PMo–PSF in SEM images. These results mean that PMo was not recrystallized into large particles but instead was dispersed as fine particles throughout PMo–PSF and PMo–PES. Although PPO was a dense film with no pore-like feature, there was a distinctive difference in surface morphology between PPO and PMo–PPO. PMo was dispersed as large particles having diameters of less than 1 μm throughout PMo–PPO. This may be due to the different blending pattern of PMo–PPO from PMo–PSF (or PES), as observed by the thermal analysis.

3.3. Catalytic activity of the composite film catalysts

Figure 2 shows the catalytic activities of the composite film catalysts for the liquid-phase TBA synthesis with respect to reaction time. All the composite film catalysts showed higher TBA yields than the homogeneous aqueous solution of mother acid. Among the composite film catalysts, PMo–PPO showed the best catalytic performance. The catalytic activities of the composite film catalysts were in the following order: PMo–PPO > PMo–PES > PMo–PSF > PMo.

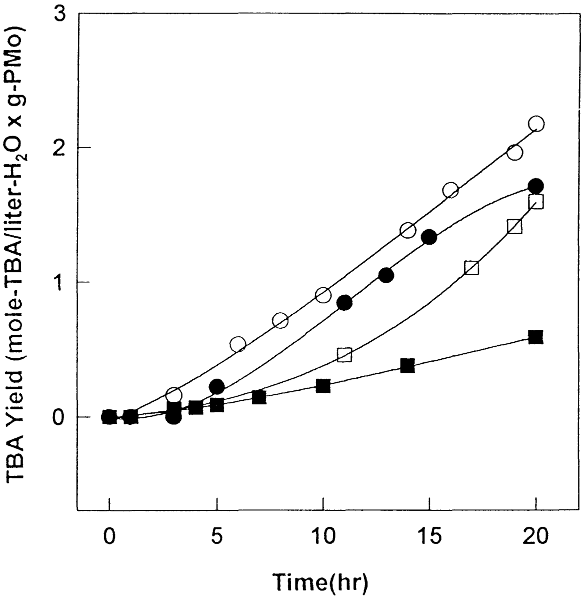

Figure 2. TBA yields with respect to reaction time; isobutene pressure = 2.0 kg_f/cm^2, temperature = 70 °C, (○) PMo–PPO, (□) PMo–PSF, (●) PMo–PES and (■) homogeneous PMo.

In order to confirm such a catalytic behavior of the composite film catalysts in the liquid-phase hydration of isobutene, the absorption amounts of isobutene in/on the composite film catalysts were measured at room temperature, as shown in figure 3. All the film catalysts were treated at 170 °C before the absorption measurements were taken. PMo–PPO showed the highest absorption amounts of isobutene among three composite film catalysts. It was also observed that PMo-free PPO film showed the highest absorption amounts of isobutene among three PMo-free polymer films. These results imply that the absorption capability of polymer material for isobutene was one of the important factors affecting the catalytic activities in the TBA synthesis, although these absorption characteristics measured at gaseous phase were not directly correlated with the catalytic activities in the liquid-phase reaction. It is believed that the high absorption capability of PMo–PPO for isobutene played an important role in enhancing isobutene concentration in/on the PMo–PPO composite catalyst in the reaction medium, although the fundamental reason for the enhanced absorption capability was not fully understood yet. And the absorption capability of PMo–PPO was high enough to overcome the low solubility of isobutene in water, which was encountered in a normal liquid-phase TBA synthesis. A previous NH_3 adsorption experiment in/on solid-state PMo and PMo–polymer composite film catalyst revealed that the bulk adsorption characteristics of PMo was not greatly changed by the blending with polymer material [31].

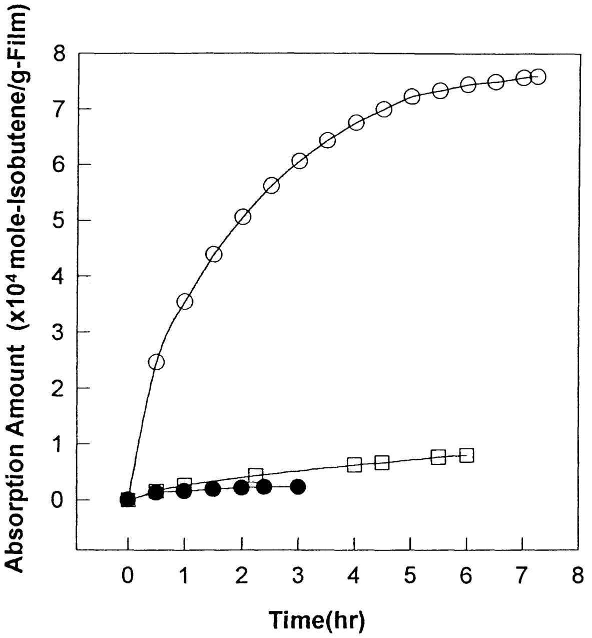

Figure 3. Absorption amounts of isobutene in/on the composite film catalysts at room temperature: (○) PMo–PPO, (□) PMo–PSF and (●) PMo–PES.

3.4. Stability of the composite film catalysts

Stability of the composite film catalysts in the water medium was examined in order to confirm the above-mentioned catalytic performance of the composite catalysts in the TBA synthesis. Table 2 shows the amounts of PMo extracted from composite film catalysts with reaction time. The amounts were in the following order: PMo–PPO < PMo–PES < PMo–PSF. It is noticeable that this trend is well matched with TBA yields shown in figure 2. PMo–PPO showed the smallest amounts of PMo extraction and the highest TBA yield. This is because PPO was physicochemically blended with PMo unlike PSF and PES. This result implies that PMo in PMo–PPO was more stable than that in PMo–PSF and PMo–PES during the reaction. The stability of PMo–PPO was also confirmed by observing the surface morphology of the composite film catalyst after

Table 2
Amounts of PMo extracted from composite film catalysts with reaction time.

Composite catalyst	Reaction time (h)	Amounts of PMo extracted/ PMo in composite catalyst (wt%)
PMo–PSF	10	7.5
	20	8.6
	30	9.1
PMo–PES	10	5.0
	20	5.3
	30	5.5
PMo–PPO	10	2.5
	20	2.5
	30	2.7

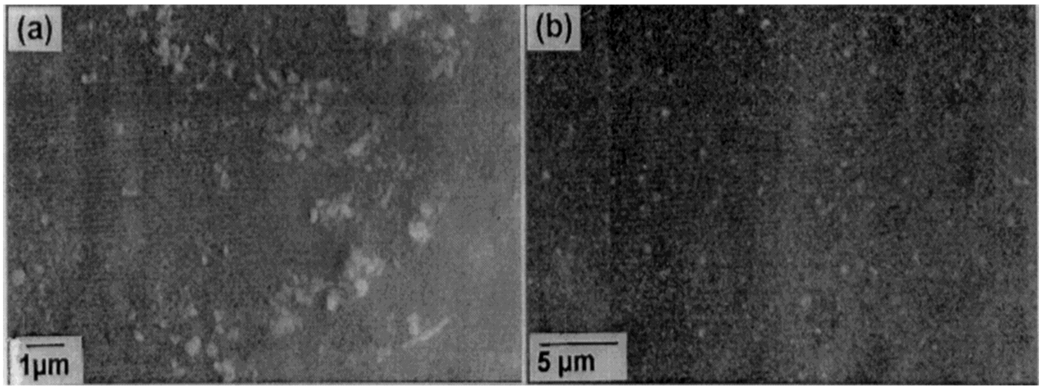

Figure 4. SEM images of (a) PMo–PSF and (b) PMo–PPO after 20 h TBA synthesis.

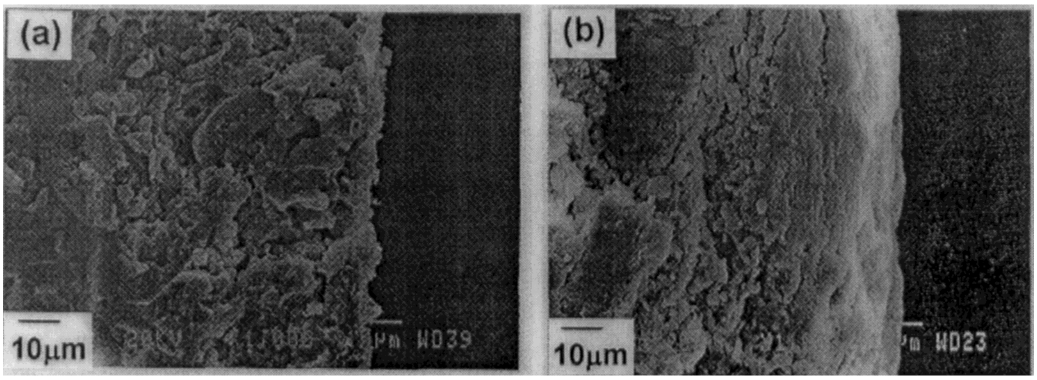

Figure 5. SEM images of (a) bare Al_2O_3 and (b) PMo–PPO/Al_2O_3.

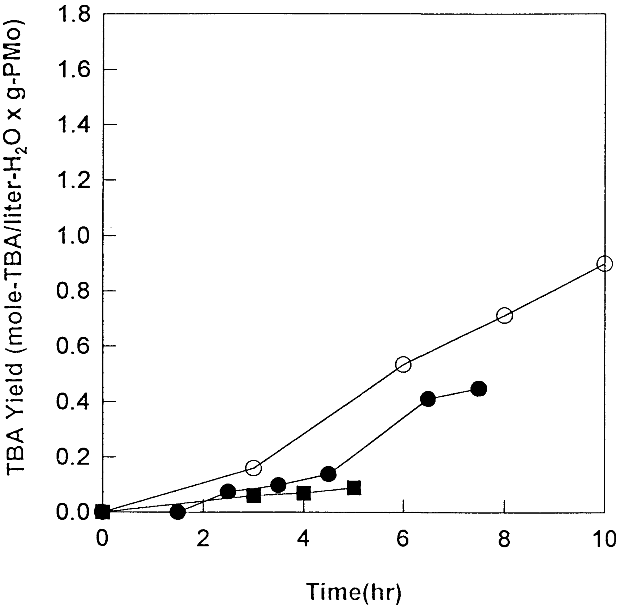

Figure 6. TBA yields with respect to reaction time: isobutene pressure = 1.5 kg_f/cm^2, temperature = 70 °C, (○) PMo–PPO, (●) PMo–PPO/Al_2O_3 and (■) homogeneous PMo.

20 h reaction, as shown in figure 4. No great difference in surface morphology was found in PMo–PPO before and after TBA synthesis, as shown in figures 1 and 4. However, a great difference in surface morphology was observed in PMo–PSF before and after TBA synthesis.

It is concluded that the high catalytic activity of PMo–PPO in the liquid-phase TBA synthesis was attributed to its high absorption capability for isobutene as well as its stability in the reaction medium. It is expected that PMo–PPO composite film can be used as an energy-saving catalyst for the TBA synthesis because of its high catalytic activity and easy recovery.

3.5. *Catalytic activity of PMo–PPO/Al_2O_3*

PMo–PPO/Al_2O_3 was designed for the practical use of the PMo–PPO composite catalyst. Al_2O_3 was used as a matrix for the coating of the PMo–PPO composite catalyst, not as an active support for PMo. Figure 5 shows the cross-sectional SEM images of bare Al_2O_3 and PMo–PPO/Al_2O_3. It was observed that the PMo–PPO film was well coated on the surface of Al_2O_3. Figure 6 shows the catalytic activities of the PMo–PPO and PMo–PPO/Al_2O_3 composite catalysts for the liquid-phase TBA synthesis with reaction time. The catalytic activities were in the following order: PMo–PPO $>$ PMo–PPO/Al_2O_3 $>$ PMo. Both heterogeneous composite catalysts showed higher TBA yields than the homogeneous catalyst. The catalytic performance of PMo–PPO/Al_2O_3 was lower than that of the PMo–PPO composite film catalyst. It is inferred that high mass transfer resistance of reaction species through PMo–PPO/Al_2O_3 was responsible for such a catalytic behavior. However, the PMo–PPO/Al_2O_3 composite catalyst has many advantages over the PMo–PPO composite film in terms of handling and recovery.

4. Conclusions

PMo–polymer composite film catalysts were prepared by a membrane preparation technique in this work. The composite catalysts were used as heterogeneous catalysts for the liquid-phase TBA synthesis. All the composite film catalysts showed higher catalytic activities than a homogeneous aqueous solution of PMo. Among the composite catalysts, PMo–PPO showed the best performance. Not only high absorption capability of PMo–PPO for isobutene but also stability of PMo–PPO in the reaction medium was responsible for the enhanced catalytic activity of PMo–PPO. Although the PMo–PPO/Al_2O_3 catalyst showed a lower activity than the PMo–PPO film catalyst, it showed a higher performance than the homogeneous PMo catalyst.

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