Heteropolyacid (HPA)-polymer composite films as catalytic materials for heterogeneous reactions

Seong Soo Lim[a], Gyo Ik Park[a], In Kyu Song[a,b], Wha Young Lee[a,*]

[a] *School of Chemical Engineering, Seoul National University, Shinlim-dong, Kwanak-ku, Seoul 151-742, South Korea*
[b] *Department of Industrial Chemistry, Kangnung National University, Kangnung, Kangwondo 210-702, South Korea*

Abstract

In this work, $H_3PMo_{12}O_{40}$-polymer composite film catalysts were prepared by a membrane preparation technique by blending $H_3PMo_{12}O_{40}$ with polymers using a mixed solvent of methanol(M)–chloroform(C) or ethanol(E)–chloroform(C). Polyphenylene oxide (PPO) and polysulfone (PSF) were used as blending polymers because of their excellent thermal and mechanical stability. The composite film catalysts were cut into small pieces, and applied as heterogeneous catalysts to the liquid-phase TBA(*tert*-butyl alcohol) synthesis and to the vapor-phase ETBE (ethyl *tert*-butyl ether) synthesis. It was observed that $H_3PMo_{12}O_{40}$ was finely dispersed throughout the polymer supports, and the blending patterns of the composite film catalysts were different depending on the identity of polymer material used. In the liquid-phase TBA synthesis, catalytic activities were in the following order; $H_3PMo_{12}O_{40}$-PPO-MC > $H_3PMo_{12}O_{40}$-PSF-MC > homogeneous $H_3PMo_{12}O_{40}$. Not only high absorption capability of $H_3PMo_{12}O_{40}$-PPO-MC for isobutene but also high stability of $H_3PMo_{12}O_{40}$-PPO-MC during the reaction was responsible for its enhanced catalytic performance. In the vapor-phase ETBE synthesis, catalytic activities were in the following order; $H_3PMo_{12}O_{40}$-PPO-EC > $H_3PMo_{12}O_{40}$-PSF-EC > bulk $H_3PMo_{12}O_{40}$. It was revealed that the residual ethanol in the composite film catalysts played an important role to improve and maintain the catalytic activities of the composite film catalysts. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *Tert*-butyl alcohol; Ethyl *tert*-butyl ether; Isobutene; Heteropolyacid; Film catalyst

1. Introduction

Heteropolyacids (HPAs) have both acid and redox catalytic properties [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 commercial catalysts are their characteristic adsorption property and pseudo-liquid phase behavior [9] depending on adsorbates. HPAs have been successfully utilized in some commercial processes such as vapor-phase oxidation of methacrolein [10–12] and liquid-phase hydration of isobutene [13–15].

Although application of polymer materials to chemical reactions at high temperatures has been restricted due to their thermal and mechanical instability, much attention has been paid to the polymer materials because of their flexible applicability. As one of the promising approaches to the modification

* Correspoding author. Tel.: +82-2-880-7404;
fax: +82-2-888-7295.
E-mail address: wyl@snu.ac.kr (W.Y. Lee).

of novel catalysis of HPAs, polymer materials have been utilized as supporting materials. Taking advantage of the overall negative charge of heteropolyanion, e.g., HPAs have been combined with polymer materials such as ion-exchange resins [16] or conjugated conducting polymers [17–20]. It was previously reported that $H_3PMo_{12}O_{40}$-doped polyacetylene film catalyst exhibited higher oxidation and acid-catalytic activities in the vapor-phase ethanol conversion than the bulk $H_3PMo_{12}O_{40}$ [17]. On the other hand, $H_3PW_{12}O_{40}$-dispersed polyaniline [18] and $H_3PW_{11}Mo_1O_{40}$-dispersed polyaniline [19] catalysts were reported to show a higher oxidation activity but a lower acid-catalytic activity in the 2-propanol conversion than the corresponding bulk catalyst.

Another typical examples utilizing polymer materials for the modified catalysis of HPAs can be found in the HPA-polymer composite film catalysts [21–25]. HPAs have been successfully blended with polymer materials using a common or a mixed solvent to prepare the membrane-like HPA-polymer composite film catalysts. As catalytic materials, the HPA-polymer composite films have the following advantages: (i) preparation procedures are quite simple [21], (ii) highly dispersed HPA catalysts in/on polymer supports can be obtained, and HPA dispersion can be easily controlled [22], (iii) acid and redox properties of HPAs can be modified by the properties of solvents and polymer materials used [23], (iv) pore characteristics of the polymer matrix can be modulated by a membrane preparation technique [24], and (v) they have potential applications as catalytic membranes [25]. Up to date, however, not much progress has been made on the acid catalysis of HPA-polymer composite film catalysts because of their complicated blending characteristics depending on the kind of solvent, HPA, and polymer material used.

In this work, $H_3PMo_{12}O_{40}$-polymer composite film catalysts were prepared by a membrane preparation technique by blending $H_3PMo_{12}O_{40}$ with polymers using a mixed solvent, and they were applied as heterogeneous catalysts to the liquid-phase TBA (*tert*-butyl alcohol) synthesis and to the vapor-phase ETBE (ethyl *tert*-butyl ether) synthesis. TBA is commercially produced by reacting isobutene with concentrated aqueous solution of HPA [13–15]. As one of fuel ethers, ETBE is growing in importance along with MTBE

(methyl *tert*-butyl ether) and TAME (*tert*-amyl methyl ether) [26,27]. Together with the MTBE synthesis from methanol and isobutene [28,29], much attention has also been paid to the liquid-phase [30] and vapor-phase [31] ETBE synthesis from ethanol and isobutene over acid catalysts. One mole of ETBE is formed from the equimolar amounts of ethanol and isobutene. As reported in the MTBE synthesis [32–34], HPAs are expected to be active in the ETBE synthesis.

2. Experimental

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

PMo ($H_3PMo_{12}O_{40}$ from Aldrich Chem.) was used as an active catalyst for the reactions. PSF (polysulfone, Udel-1700 from UCC) and PPO (polyphenylene oxide, poly-2,6-dimethyl-1,4-phenylene oxide from Aldrich Chem.) were used as blending polymers because of 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 and polymers were not soluble in chloroform and methanol, respectively, PMo could be blended with polymers using a mixed solvent of methanol (M)–chloroform (C) because these two solvents were highly miscible. A homogeneous solution of PMo(1.22 wt.%)–PPO(6.9 wt.%)–methanol (4.41 wt.%)–chloroform (87.47 wt.%) was obtained at room temperature. The homogeneous solution was then cast on a glass plate with uniform thickness, and subsequently it was dried in ambient condition to obtain PMo-PPO-MC composite film catalyst. PMo-PSF-MC composite film catalyst was also prepared with the same procedures. The thickness of the composite film catalysts was 17 μm. PMo-free polymer films, PPO-MC and PSF-MC, were also prepared for reference and comparison. It is noteworthy that there are many choices in selecting a pair of solvents for the blending of HPA with above polymers. For example, PMo-polymer composite film catalysts could be prepared using a mixed solvent of ethanol(E)–chloroform(C) with the same procedures described above. These composite film catalysts were abbreviated as PMo-PPO-EC and PMo-PSF-EC.

2.2. Characterization

DSC measurements were carried out in order to measure the glass transition temperatures and to confirm the blending patterns of the composite film catalysts. SEM analyses were conducted to examine the morphologies of the composite film catalysts before and after reactions. The composite film catalysts were further characterized by XRD and ^{31}P MAS NMR. Absorption amounts of isobutene in/on the composite film catalysts were measured at room temperature in order to understand their catalytic performance.

2.3. Catalytic reactions

Heterogeneous liquid-phase hydration of isobutene to TBA was carried out in a semi-batch reactor. Either PMo-PPO-MC or PMo-PSF-MC was cut into small pieces (2 mm × 2 mm) to be used as a heterogeneous catalyst. They were treated at 170 °C for 1 h by flowing air before introducing them into the reactor. Small pieces of the composite film catalyst were dispersed in water (50 cm^3) of the semi-batch reactor. The reactor was then heated up to 70 °C with stirring. 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 GC. Hydration of isobutene by homogeneous aqueous solution of PMo was also carried out under the same reaction conditions for comparison.

Vapor-phase ETBE synthesis was carried out in a continuous flow fixed-bed reactor. The membrane-like composite film catalyst, PMo-PPO-EC or PMo-PSF-EC, was also cut into small pieces (2 mm × 2 mm) to be used as a fixed-bed catalyst. Prior to the reaction, all the composite catalysts were treated at 170 °C for 1 h with an air stream. Ethanol was continuously vaporized and supplied with N$_2$ carrier (20 cm^3/min). Equal amounts of ethanol and isobutene were introduced into a mixing chamber at the same time, and the mixed reactants were continuously fed into the reactor for the gas–solid reaction. The reacted stream was periodically sampled and analyzed with a GC. For comparison and reference, ETBE synthesis over the unsupported PMo catalyst was also carried out under the same reaction conditions.

3. Results and discussion

3.1. Blending pattern of the composite film catalysts

Fig. 1 shows the DSC results of the composite film catalysts and their corresponding PMo-free polymer films. After most of the moisture in the film was removed during the first scan from room temperature to 300 °C, the glass transition temperature (T_g) was measured at the second scan. T_g of PSF-MC was found to be 185 °C, while that of PMo-PSF-MC was not clearly detected from room temperature to 350 °C. However, PMo-PSF-MC was deformed morphologically and became fragile after the thermal treatment at 185 °C, suggesting that T_g of PMo-PSF-MC would be less than 185 °C. The decreased thermal stability of PSF after the blending with PMo represents that there was neither interaction nor bonding between PMo and PSF, and that PMo only served as an impurity for PSF in the PMo-PSF-MC composite film catalyst. This result can also be deduced from a previous study [23] investigating a PMo-PSF-dimethylformamide (DMF) composite film. In that work [23], it was experimentally determined that T_g of PSF-DMF was 187 °C while that of PMo-PSF-DMF was found to be 174 °C, demonstrating that T_g of PSF decreased after the
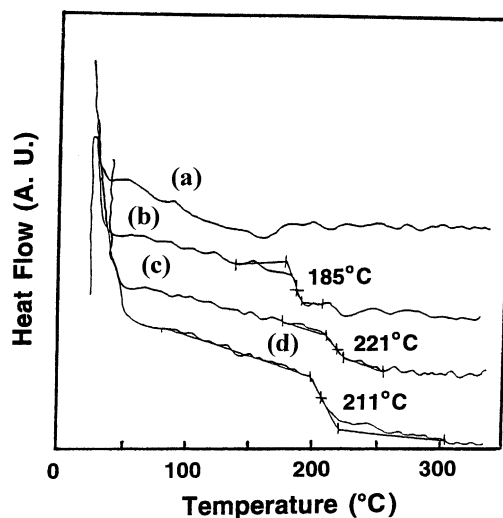

Fig. 1. DSC results of: (a) PMo-PSF-MC, (b) PSF-MC, (c) PMo-PPO-MC, and (d) PPO-MC; heating rate = 15 °C/min.

blending with PMo. Similarly, it was also observed that T_g of PMo-polyethersulfone-MC (219 °C) was lower than that of polyethersulfone-MC film (236 °C) [35]. In the case of PPO-based samples, however, T_g of PPO was increased after the blending with PMo from 211 to 221 °C. This indicates that there was a certain interaction or bonding between PMo and PPO, and that PMo was no longer an impurity for PPO. In fact, there is no special reason to expect any chemical interaction between PMo and PPO in this catalytic material system. Therefore, it is prudent to conclude that the interaction between PMo and PPO is physicochemical rather than chemical. It can be summarized from the DSC results that the blending of PMo with PSF is physical while that with PPO is physicochemical.

The physicochemical interaction of PMo with PPO was further confirmed by the solid-state ^{31}P MAS NMR analyses. As shown in Fig. 2, bulk PMo and PMo-PSF-MC samples showed the singlet while PMo-PPO-MC showed the doublet. The ^{31}P chemical shift observed for bulk PMo was −3.9 ppm, in good agreement with the reported value [1]. The ^{31}P chemical shifts for bulk PMo and PMo-PSF-MC were slightly different from each other, although both samples exhibited the singlet. It is known that the ^{31}P chemical shift for HPA in the solid-state NMR strongly depends on the identity and the number of coordi-

nated organic molecule [1]. Therefore, the different chemical shift of PMo-PSF-MC from bulk PMo was believed to be due to the effect of solvent and polymer contributed in the course of composite film fabrication. On the other hand, the doublet observed for PMo-PPO-MC strongly indicates the existence of two types of P compounds. Although the chemical species showing a shift at −0.6 ppm has not been identified yet, it is believed that this peak may be attributed to the PMo ingredient physicochemically interacted with PPO. Above results support that the blending of PMo with PSF is physical while that with PPO is physicochemical.

3.2. PMo dispersion throughout the composite film catalysts

Fig. 3 shows the SEM images of the composite film catalysts and their corresponding PMo-free polymer films. There was no distinctive difference in surface morphology between PSF-MC and PMo-PSF-MC samples. These two samples had no pore-like feature, and their surfaces were dense and clean. No visible evidence representing PMo was observed in the PMo-PSF-MC composite film catalyst, suggesting that PMo was not recrystallized into large particles, but instead was highly dispersed as fine particles throughout the PSF matrix. Similar to the PSF-based samples, PPO-MC was also a dense film with no pores. However, there was a distinctive difference in surface morphology between PPO-MC and PMo-PPO-MC. Unlike PMo in the PMo-PSF-MC, PMo was partly dispersed as large particles on/near the surface of PMo-PPO-MC. The difference in PMo dispersion between PMo-PSF-MC and PMo-PPO-MC may be attributed to different blending patterns, as evidenced by DSC and NMR analyses.

In fact, the non-porous feature of the composite film catalysts is not quite surprising [36]. To modulate pore formation and its characteristics, three components are generally considered in a membrane preparation technique; polymer, solvent, and non-solvent [37]. Here, the miscibility between solvent and non-solvent for polymer plays a key role for the pore formation through the polymer membrane [36]. The non-porosity of the composite film catalysts shown in Fig. 3 was attributed to the immiscible nature of chloroform (a solvent for polymers, and a major component of the
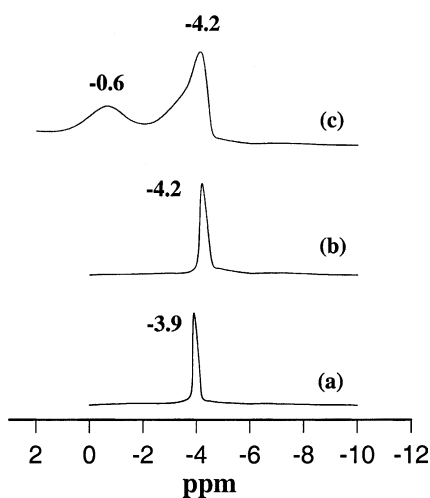

Fig. 2. ^{31}P MAS NMR spectra of: (a) PMo, (b) PMo-PSF-MC, and (c) PMo-PPO-MC with respect to H_3PO_4.
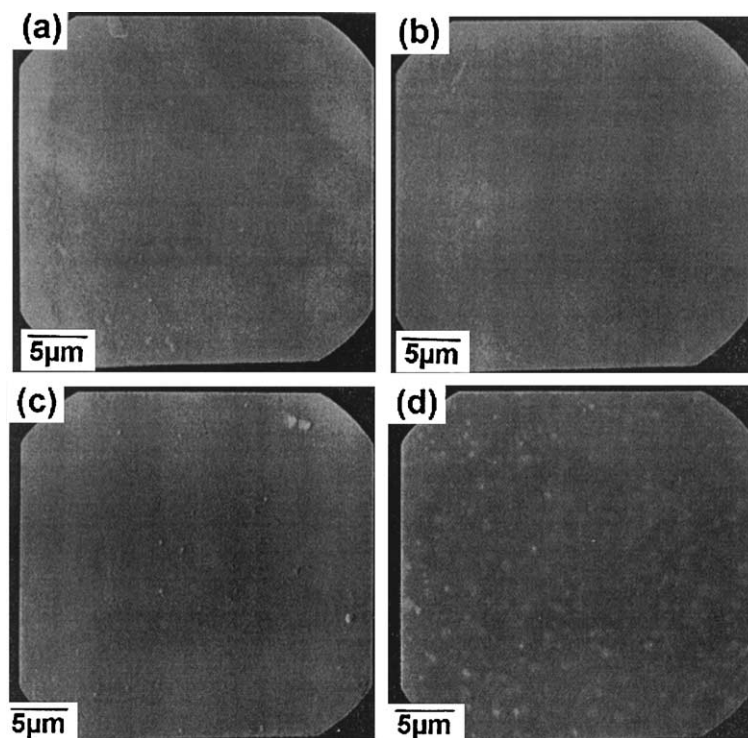
Fig. 3. SEM images of: (a) PSF-MC, (b) PMo-PSF-MC, (c) PPO-MC, and (d) PMo-PPO-MC.

mixed solvent) with water vapor (a non-solvent for polymers) in the air.

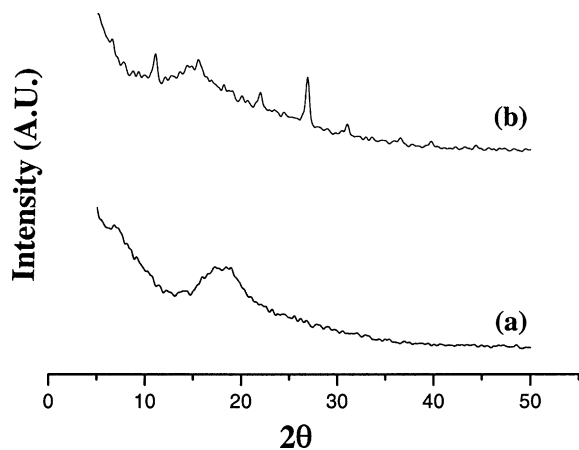Fig. 4 shows the XRD patterns of the composite film catalysts. The composite film catalysts were

Fig. 4. XRD patterns of: (a) PMo-PSF-MC and (b) PMo-PPO-MC.

thermally treated at $170\,^{\circ}$C under the air stream before XRD measurements were taken. Both PSF-MC and PPO-MC films showed almost the same diffractogram as that observed for PMo-PSF-MC in Fig. 4(a). They exhibited no characteristic XDR peaks because of the amorphous nature of polymers, and only showed a broad peak-like feature at around $2\theta = 20^{\circ}$, as generally observed for amorphous polymers such as polyemeraldine base [18]. Therefore, the broad peak-like feature observed for PMo-PSF-MC was not due to PMo in the composite film. The fact that PMo-PSF-MC film catalyst showed no characteristic XRD patterns indicates that PMo in the PMo-PSF-MC composite catalyst did not exist as a crystal form but as an amorphous state. In other words, PMo was dispersed as very fine particles throughout the PSF matrix, as observed in the SEM image of Fig. 3(b). On the other hand, however, PMo-PPO-MC film catalyst exhibited a certain crystal form of PMo, which may originate from PMo agglomerations shown in Fig. 3(d). It is believed that the differences in XRD

patterns between these two film catalysts also arose from their different blending patterns. Undoubtedly, there might be some different and complex interactions between blending components depending on the kind of polymer material used. However, fundamental reasons for these different characteristics of the composite film catalysts have not been fully elucidated yet. The characteristics of the PMo-polymer-EC samples were almost the same as those of the corresponding PMo-polymer-MC catalysts.

3.3. Liquid-phase TBA synthesis

The PMo-polymer-MC catalysts were applied as heterogeneous catalysts to the liquid-phase TBA synthesis from isobutene and water in a semi-batch reactor. As shown in Fig. 5, the composite film catalysts showed the higher TBA yields than the homogeneous PMo. The catalytic activities were in the following order: PMo-PPO-MC > PMo-PSF-MC > homogeneous solution of PMo. In order to understand such a catalytic performance of the composite film catalysts, the absorption amounts of isobutene in/on the composite film catalysts were measured at room temperature, as shown in Fig. 6. The PMo-PPO-MC
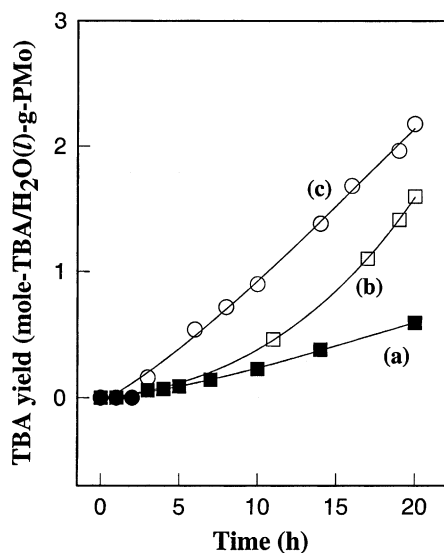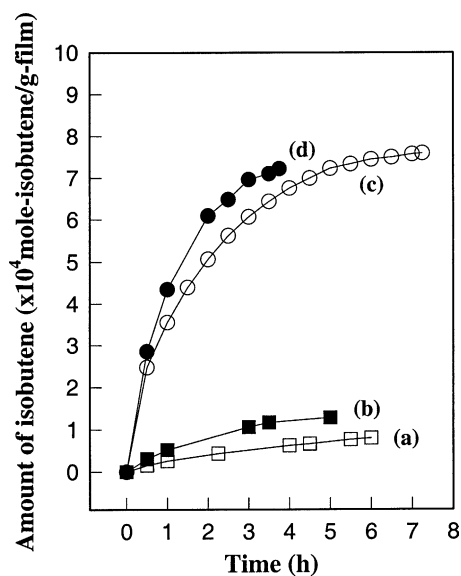

Fig. 6. Absorption amounts of isobutene in/on: (a) PMo-PSF-MC, (b) PSF-MC, (c) PMo-PPO-MC, and (d) PPO-MC at room temperature.

uptakes much amounts of isobutene than the PMo-PSF-MC, and furthermore, the PPO-MC film absorbs much amounts of isobutene than the PSF-MC film. Fig. 6 also shows that the amounts of isobutene uptake per gram of PMo-free film samples are slightly higher than those measured for the corresponding composite catalysts, which is because PMo catalyst itself has very poor absorption capability for olefins. Above results represent that the absorption capability of polymer material for isobutene is one of the important factors affecting the catalytic performance of the composite films in the TBA synthesis, although these absorption characteristics measured at gaseous phase are not directly correlated with the catalytic performance in the liquid-phase reaction. It is clear from the above result that polymer matrix is not a simple support for PMo but serves as an efficient reservoir for isobutene. It is believed that the high absorption capability of PMo-PPO-MC for isobutene played an important role in enhancing the isobutene concentration in/on PMo-PPO-MC composite catalyst in the catalytic reaction. This is very important in overcoming the low solubility of isobutene in water, which is encountered in a normal liquid-phase TBA synthesis [13–15]. In fact, a single component

Fig. 5. TBA yields by: (a) homogeneous PMo, (b) PMo-PSF-MC, and (c) PMo-PPO-MC; isobutene pressure = $2.0 \, kg_f/cm^2$, reaction temperature = $70\,°C$, $H_2O = 50 \, cm^3$.
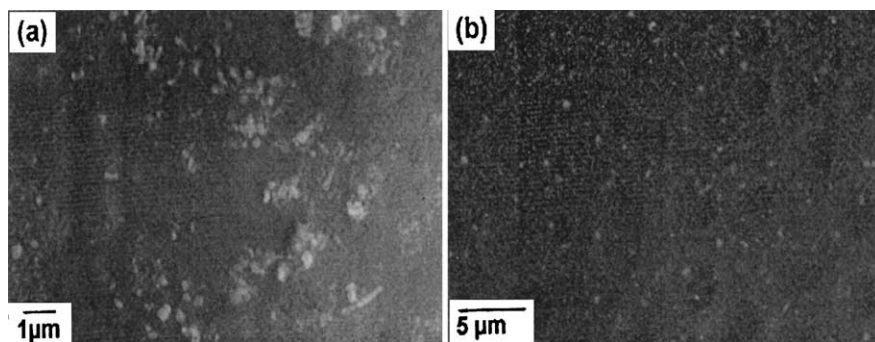
Fig. 7. SEM images of: (a) PMo-PSF-MC and (b) PMo-PPO-MC after 20 h TBA synthesis.

of isobutene absorbed in/on solid acid catalysts can be oligomerized into heavier products such as di-isobutylene [31,38]. Vaughan et al. [39] also reported appreciable oligomerization of propene over HPA catalysts at much higher pressures of 5 MPa and at 220–230 °C. However, isobutene oligomers would not be considerable amounts under our gas–solid absorption conditions, because the composite film catalysts themselves retained certain amounts of residual solvents. Moreover, the amounts of isobutene oligomers were not in a detectable range in our liquid-phase TBA synthesis.

Stability of PMo-PPO-MC was well confirmed by observing the surface morphology of the composite film catalyst after 20 h reaction, as shown in Fig. 7. No great difference in surface morphology was observed in the PMo-PPO-MC before and after TBA synthesis, as shown in Figs. 3 and 7. However, a great difference in surface morphology was observed in the PMo-PSF-MC before and after TBA synthesis. The amounts of PMo loss from the PMo-PPO-MC composite film catalyst measured after 10 h reaction were 2.5 wt.% of the initial amounts, but no more loss were observed even after 20 h reaction. In the case of PMo-PSF-MC catalyst, however, these amounts were found to be 7.5 and 8.6 wt.% after 10 and 20 h reaction, respectively. These results show that the stability of PMo-PPO-MC catalyst was superior to the PMo-PSF-MC catalyst during the reaction, which is believed to be due to the physicochemical blending nature of the former. At the second run of the reaction with the used PMo-PPO-MC catalyst, moreover, it was also observed that the catalyst exhibited performance of more than 95% of the first run activity.

It is concluded that the high catalytic activity of PMo-PPO-MC in the liquid-phase TBA synthesis was attributed to its high absorption capability for isobutene as well as its stability during the reaction. Thus, high catalytic performance of PMo-PPO-MC and easiness of catalyst recovery in the liquid-phase reaction make it a good candidate as a heterogeneous catalyst for an energy-saving TBA synthesis.

3.4. Vapor-phase ETBE synthesis

The PMo-polymer-EC catalysts were applied to the vapor-phase ETBE synthesis from isobutene and ethanol. In a previous work on the vapor-phase ETBE synthesis over H-mordenite catalyst [31], it was reported that a single feed of isobutene without ethanol deactivated the catalyst due to oligomerization of isobutene. In our reaction experiments, ethanol and isobutene were fed simultaneously as a mixture in order to prevent possible formation of isobutene oligomers. In the reaction, the catalysts experienced a slight deactivation at the initial stage of the reaction, but a stable state was attained after ca. 30 min from the start-up. By-products such as diisobutylene were not in a detectable range under the steady-state operation. Fig. 8 shows the steady-state catalytic activities of the unsupported PMo and composite film catalysts in the vapor-phase ETBE synthesis with respect to reaction temperature. Maximum ETBE yields over the composite film catalysts were observed at 60 °C. The ETBE yields decreased at high temperatures, and the yields for three catalysts became closer at high temperatures, possibly due to the equilibrium limitation. The composite film catalysts
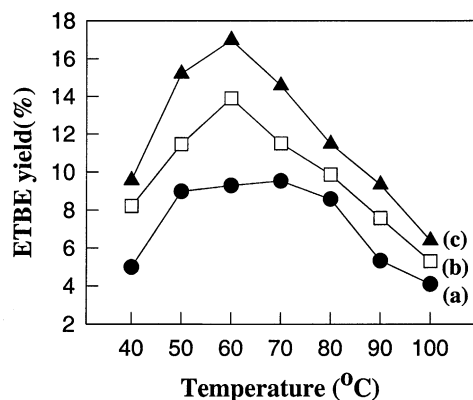
Fig. 8. Catalytic activities of: (a) unsupported PMo, (b) PMo-PSF-EC, and (c) PMo-PPO-EC in the vapor-phase ETBE synthesis; feed mole ratio of ethanol/isobutene $= 1/1$, N_2 carrier $= 20 \, cm^3/min$, $W/F = 11.8 \, g \, PMo \, h$ per feed mole.

Fig. 9. ETBE yields over PMo-PPO-EC composite film catalyst in the absence or presence of ethanol feed; reaction temperature $= 60 \, °C$, N_2 carrier $= 20 \, cm^3/min$, $W/F = 11.8 \, g \, PMo \, h$ per feed mole (in the presence of ethanol feed).

showed the higher ETBE yields than the mother catalyst, and the catalytic performance was in the order of PMo-PPO-EC > PMo-PSF-EC > unsupported PMo. The enhanced performance of the composite film catalysts is believed to be due to fine dispersion of PMo catalyst throughout the polymer matrix. The enhanced activity of the PMo-PPO-EC compared to the PMo-PSF-MC may also be attributed to the high absorption capability of PPO ingredient for isobutene.

In order to elucidate the effect of remaining ethanol in the composite film catalysts on the catalytic performance, a PMo-PPO-EC composite film catalyst was prepared with vacuum drying intentionally to minimize the residual ethanol in the composite catalyst. The PMo-PPO-EC catalyst prepared without vacuum drying, a composite catalyst prepared in a normal way as described earlier, showed the higher catalytic performance than that prepared with vacuum drying. The effect of residual ethanol in the composite film catalysts was further confirmed by performing the ETBE synthesis over the PMo-PPO-EC catalyst with/without ethanol feed, as shown in Fig. 9. When ethanol feed was stopped, the ETBE yield decreased gradually instead of a sudden drop to zero yield, with the evolution of small amounts of diisobutylene. Inversely, the ETBE yield increased gradually up to the normal value when ethanol was supplied again. It can be inferred that the absorbed isobutene reacts with the residual ethanol in the composite film catalyst as a first step, and then the resultant vacant ethanol sites in the com-
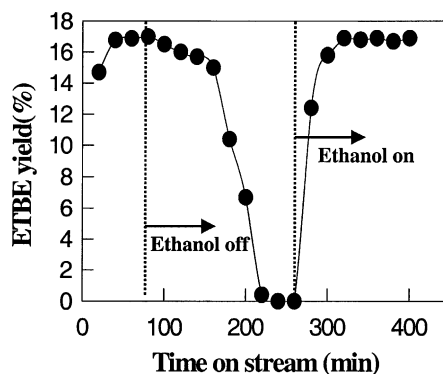
posite film catalyst are filled with ethanol supplied from the vapor-phase. Above results support that the residual ethanol in the composite film catalysts played an important role in maintaining the high catalytic activities of the composite film catalysts.

4. Conclusions

In this work, membrane-like HPA-polymer composite film catalysts were prepared by a membrane preparation technique. The composite film catalysts were cut into small pieces, and they were applied as heterogeneous catalysts to the liquid-phase TBA synthesis and to the vapor-phase ETBE synthesis. It was observed that PMo was finely dispersed throughout the composite film catalysts. The blending patterns of the composite film catalysts varied depending on the kind of polymer material used; the blending of PMo with PSF was physical while that with PPO was physicochemical. In the liquid-phase TBA synthesis, the composite film catalysts showed higher catalytic activities than the homogeneous solution of PMo, and PMo-PPO-MC exhibited a higher catalytic performance than PMo-PSF-MC. Not only high absorption capability of PMo-PPO-MC for isobutene but also high stability of PMo-PPO-MC during the reaction was responsible for its enhanced catalytic performance. In the vapor-phase ETBE synthesis, the catalytic activities were in the following

order: PMo-PPO-EC > PMo-PSF-EC > bulk PMo. The high absorption capability of PMo-PPO-EC for isobutene was also responsible for such a high catalytic performance. The residual ethanol in the composite film catalysts played an important role to improve and maintain the catalytic performance of the composite film catalysts.

Acknowledgements

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