

Design of novel catalyst imbedding heteropoly acids in polymer films: Catalytic activity for ethanol conversion

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Abstract

Membrane-like $H_3PMo_{12}O_{40}$ or $H_5PMo_{10}V_2O_{40}$ -imbedded polymer films were prepared by blending these materials using a chloroform–methanol mixture as solvent, and they were tested as catalysts for the ethanol conversion reaction in a continuous flow fixed-bed reactor. It was found that the chloroform–methanol mixture itself gave no influence on the catalytic activity of bulk $H_3PMo_{12}O_{40}$ and $H_5PMo_{10}V_2O_{40}$. Polysulfone, polyethersulfone and polyphenylene oxide were used as blending polymers in this study. $H_3PMo_{12}O_{40}$ -imbedded polymer films showed a higher catalytic activity than $H_3PMo_{12}O_{40}$ itself due to uniform and fine dispersion of $H_3PMo_{12}O_{40}$ through polymer films, but the extent of activity and selectivity was varied according to a kind of polymer materials. It was revealed that $H_3PMo_{12}O_{40}$ or $H_5PMo_{10}V_2O_{40}$ -imbedded polyphenylene oxide film showed much higher oxidation catalytic activity than the corresponding bulk heteropoly acids. This may be due to the interaction (or bonding) of proton of heteropoly acid with polyphenylene oxide, judging from the fact that glass transition temperature of polyphenylene oxide was increased after blending with heteropoly acid. The catalytic activity of the heteropoly acid imbedded in the same polymer was greatly affected by the composite of heteropoly acid. The permeabilities of reactants through polymer films also affected the product selectivity.

Keywords: Ethanol; Heteropoly acid; Polymer; HPA-imbedded polymer film catalyst

1. Introduction

Heteropoly acids (HPAs) such as $H_3PMo_{12}O_{40}$ are inorganic acids, but at the same time can act as oxidizing agents [1–6]. They are mostly soluble in polar solvents such as water, alcohols, and amines, but some acids are insoluble in non-polar chemicals such as

benzene and olefins [7]. The solubility of these acids and their compounds in turn is closely connected to their ability to adsorb various reactants. Non-polar chemicals are adsorbed on the surface of bulk HPAs, while most polar molecules are mainly adsorbed in the bulk, forming a pseudo-liquid phase [8]. This characteristics leads to two typical catalytic reaction types for HPAs; namely, surface-type reaction and bulk-type reaction [7].

It is well known [9–14] that the acid and redox properties of HPAs can be controlled in a systematic way by replacing the protons with

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metal cations and/or by changing the heteroatom or the polyatoms (transition metals). Novel catalysis of HPAs can be also modified by combining HPAs with ion-exchange resins [15,16] or conjugated polymers [17–20] because of the overall negative charge of heteropoly anions. Although acidic properties of HPAs are prohibited because protons of HPAs are replaced by the molecules of ion-exchange resins or conjugated polymers, redox properties of HPAs can be enhanced because uniform and fine dispersion of HPAs leads to the enlarged surface area of HPAs. Another way toward the modification of novel catalysis of HPAs reported by this group [21–23] is to blend HPAs with polymers using a common solvent for these materials and then to make membrane-like films. The surface area and acidic property of HPAs can be controlled by this method to meet the need for desirable reactions. This method strongly depends on the properties of common solvent and polymer material, because acidic/basic properties of solvent affect the acidic function of HPAs and permeabilities of reaction components through polymer films affect the product yield and selectivity.

A new method for the preparation of HPA-embedded polymer films using mixed solvents is developed in this work toward the modification of novel catalysis of HPAs. The novelty of this work is to use mixed solvents comprising methanol and chloroform in order to prepare various HPA-embedded polymer films. Even in the case of the absence of a common solvent for HPA and polymer, they can be easily blended using mixed solvents if the solvents are miscible each other. It is also expected that the effect of mixed solvents on the catalysis of HPA-embedded polymer film can be minimized or maximized to meet the need for desirable reaction. Ethanol conversion reaction was tested as a model reaction in a continuous flow reactor using HPA-embedded polymer films as a fixed bed catalyst. Ethylene and diethylether are formed via dehydration of ethanol (acid-catalyzed reaction) while acetaldehyde is formed via

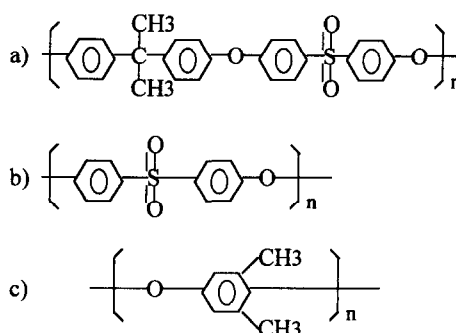
oxidative dehydrogenation of ethanol (oxidation reaction) [24].

2. Experimental

2.1. Preparation of HPA-embedded polymer films

$\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (PMo) was obtained from Aldrich Chemical Co. and $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ (PMoV) was prepared according to the method in a literature [25]. These HPAs were recrystallized and calcined at 300°C for the precise quantification. Polysulfone (PSF, Udel 1700 from Union Carbide), polyethersulfone (PES, Victrex 5200P from ICI) and polyphenylene oxide (PPO, poly-2,6-dimethyl-1,4-phenylene oxide from Aldrich Co.) were used as blending polymers. Their chemical formula were shown in Scheme 1.

HPAs and polymer can be easily blended if both materials can be dissolved in the same solvent like dimethylformamide (DMF) [21–23]. Though HPAs and polymer are not soluble in the same solvent, if a solvent dissolving HPA and another solvent dissolving polymer are miscible, the HPA and polymer can be blended using the solvent mixture. In this study, methanol was used as a solvent dissolving HPA and chloroform was used as a solvent dissolving polymer.



Scheme 1. Chemical formula of (a) PSF (Udel 1700), (b) PES (Victrex 5200P) and (c) PPO (poly-2,6-dimethyl-1,4-phenylene oxide).

1.76 g of HPA (PMo or PMoV) was completely dissolved in 133 g of methanol (4.8 wt%)-chloroform (95.2 wt%) mixture and then 10 g of each polymer was added into this homogeneous solution. The solution was stirred with a magnetic stirrer until the polymer was completely dissolved. The HPA-blended polymer solution was casted on a glass plate with uniform thickness and allowed to dry for ca. 10 min at room temperature to form a membrane-like HPA-imbedded polymer film. Then it was soaked in water to separate the films from the glass plate. The HPA-imbedded polymer film was further dried to remove remaining solvent and water in the atmosphere. The HPA loading of the film catalyst was 14.9 wt%/polymer and the film thickness was 0.017 mm. HPA-free polymer films were also prepared by using same mixed solvent for reference and characterization. The HPA-imbedded polymer film was denoted as follows: for example, PMo-imbedded PSF film was denoted as PMo-PSF.

2.2. Characterization and reaction procedure

Keggin structure (primary structure) of HPA in HPA-PSF, HPA-PES and HPA-PPO was confirmed by FT-IR (Midac Co. M2000) analyses and the glass transition temperature (T_g) of HPA-free or -imbedded polymer film was obtained by DSC (differential scanning calorimetry; TA Instruments TA200) measurements. The surface of HPA-imbedded polymer film was observed by SEM (Jeol JSM-35). The ethanol conversion reaction was examined in a continuous flow fixed bed reactor in order to confirm the modified catalytic behavior of HPA-imbedded polymer film. The HPA-imbedded polymer film was cut into small pieces (2 mm \times 2 mm) to be used as a fixed-bed catalyst. Net amounts of HPA in the reactor were 50 mg in each run. All the catalysts were pretreated at 160°C in air stream (5 cc/min) for 30 min before the reaction, and then ethanol was preheated for vaporization and fed to the reactor together with air (5 cc/min) as a carrier gas and

an oxygen source. The reaction temperature was at the range from 160°C to 210°C. The reaction products were analyzed periodically to confirm the steady state reaction. The thermal decomposition temperature of HPA and T_g of other polymers except PSF are higher than 210°C. Therefore, all the tested film catalysts except PMo-PSF were thermally stable during the reaction. The products under the steady state condition were analyzed with on-line GC (HP 5890II) using a column packed with Porapak Q. Conversion and selectivity were calculated on the basis of carbon balance.

2.3. Permeability measurement

In order to see the effect of polymer materials on the product yield and selectivity, permselectivities of O₂/ethanol through HPA-imbedded polymer films were measured at 80°C using a conventional permeation unit [26]. Vapor-phase ethanol–O₂ mixture with constant composition was introduced to the permeation cell at 80°C. The permeation area was 17.65 cm² and the concentration polarization was avoided by the rejected stream. The permeated and the rejected stream were analyzed with GC.

3. Results and discussion

3.1. FT-IR analyses

FT-IR analysis for PMo-PPO is shown in Fig. 1. Fig. 1(a) and (c) show IR bands of PMo and PPO respectively, and (b) represents IR bands of PMo-PPO film. The primary structure of HPAs can be identified by the four characteristic bands ranging from 700 to 1400 cm⁻¹. The four characteristic bands of PMo appear at 788, 863, 965 and 1064 cm⁻¹. Bands at 788 and 863 cm⁻¹ represent Mo–O–Mo. Bands at 965 and 1064 cm⁻¹ are the Mo=O and P–O band respectively. Among these four characteristic bands, bands at 788 cm⁻¹ and 1064 cm⁻¹ which are not seen in PPO appear in PMo-PPO

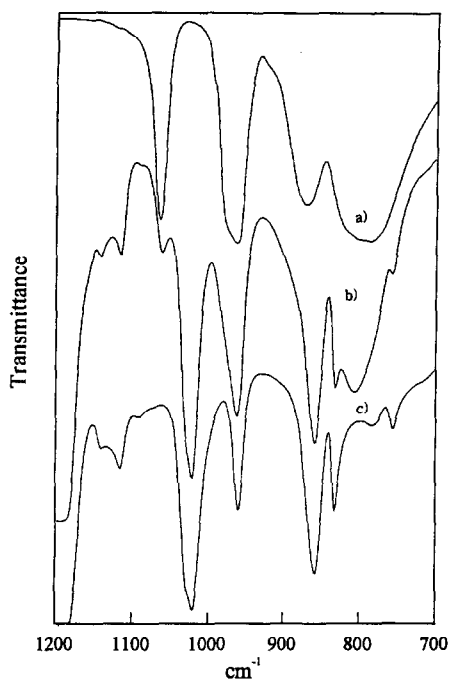


Fig. 1. IR spectra of (a) PMo, (b) PMo-PPO and (c) PPO.

film and the other two bands coincide with the bands of PPO itself. It is clear that PMo-PPO kept Keggin structure (primary structure) and it might retain catalytic activity. PMo-PSF and PMo-PES also showed the characteristic bands of PMo. These results mean that HPA keeps its unique structure of heteropoly anion even after the blending with polymer.

3.2. SEM analyses

Fig. 2 shows SEM images of PMo, HPA-free polymer films, and PMo-polymer films. The PMo was seen as large clusters having diameters of 10–100 μm . The HPA-free polymer films are transparent, and their surfaces are dense and clean as evidenced by SEM. The PMo-imbedded polymer films retain greenish color implying fine distribution of PMo through polymer films. No visible evidence representing PMo was found in PMo-PSF and PMo-PES in the SEM images. This means that PMo is dispersed as very fine particles through polymer films. On the other hand, PMo in PMo-PPO

exists as agglomerations having diameters of less than 1 μm . Above results imply that the surface area of PMo must be increased upon blending.

3.3. Thermal behavior

The results of DSC measurements are shown in Fig. 3. The T_g of PES is 236°C whereas that of PMo-PES is 219°C. The T_g of PSF before blending is 185°C, but that of PMo-PSF was not detected by DSC measurement from room temperature to 350°C. However, the fact that the physical state of PMo-PSF after reaction above 170°C was changed and became fragile indicates that the T_g of PSF was lowered after blending with PMo.

The decreased T_g of PSF and PES after blending with PMo means that there is no interaction or no bonding between two materials in PMo-PSF and PMo-PES, and PMo only serves as impurity for each polymer upon blending. However, T_g of PPO changes from 211°C to 221°C after blending with PMo. The increased T_g of PPO after blending with PMo means that there is a certain interaction or bonding between the two materials and PMo is not impurity for PPO any more. The different trend of thermal behavior between PMo-PES (or PSF) and PMo-PPO implies that they might show a different catalytic activity pattern for the model reaction. The thermal decomposition temperature of bulk PMo crystal is 430°C and it is thermally stable during the reaction.

3.4. Effect of HPA-imbedded polymer film

The ethanol conversion reaction was carried out to investigate the difference in the catalytic characteristics of PMo-imbedded polymer films. Ethanol conversion and product selectivity for these catalysts at 170°C are presented in Table 1. All HPA-imbedded polymer films showed a higher conversion than the bulk HPA crystal. The enhanced conversion of HPA-imbedded

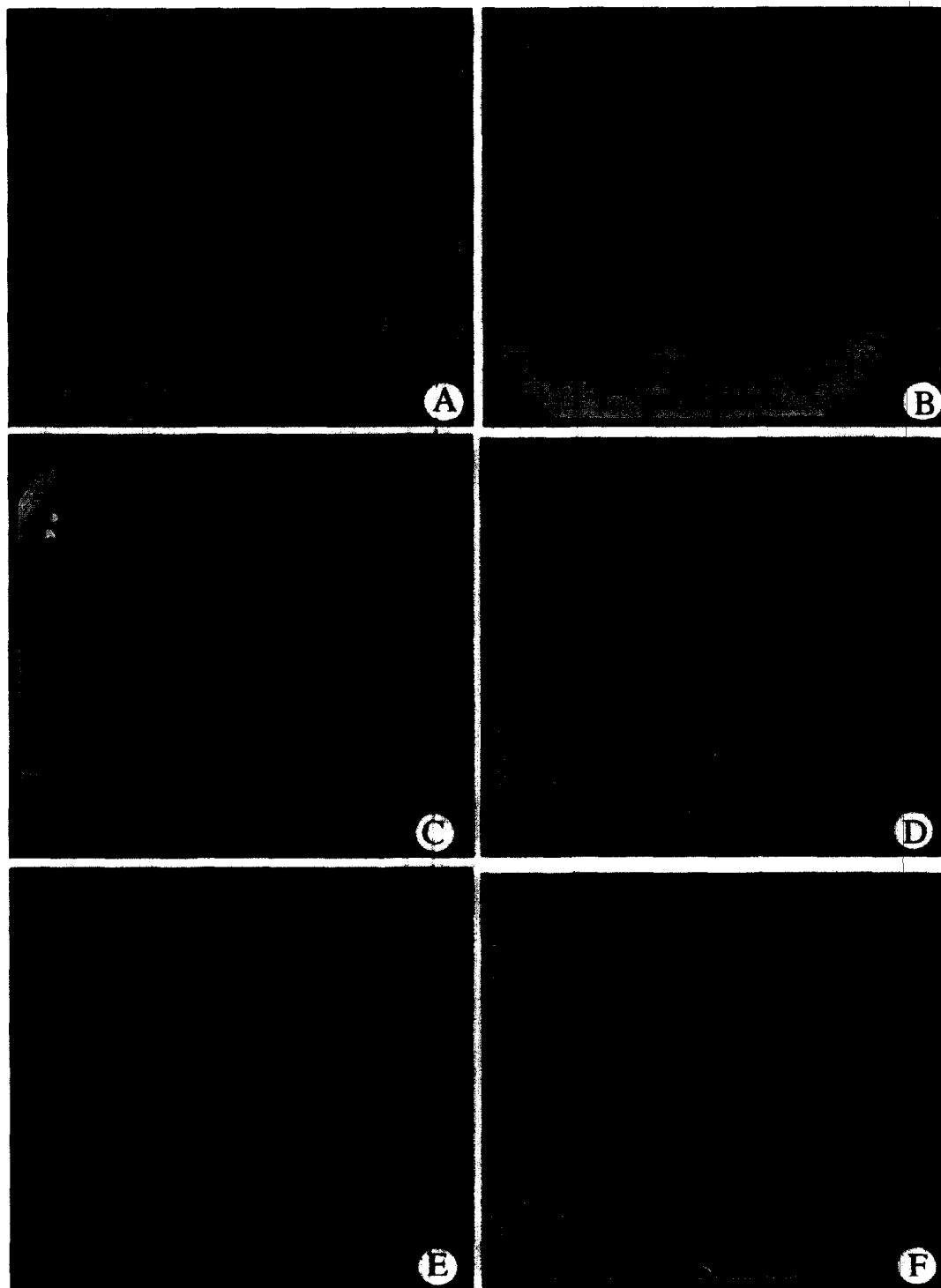


Fig. 2. SEM images of (a) PMo ($\times 480$), (b) PSF ($\times 3,000$), (c) PPO ($\times 3,000$), (d) PMo-PSF ($\times 3,000$), (e) PMo-PPO ($\times 3,000$) and (f) PMo-PES ($\times 3,000$).

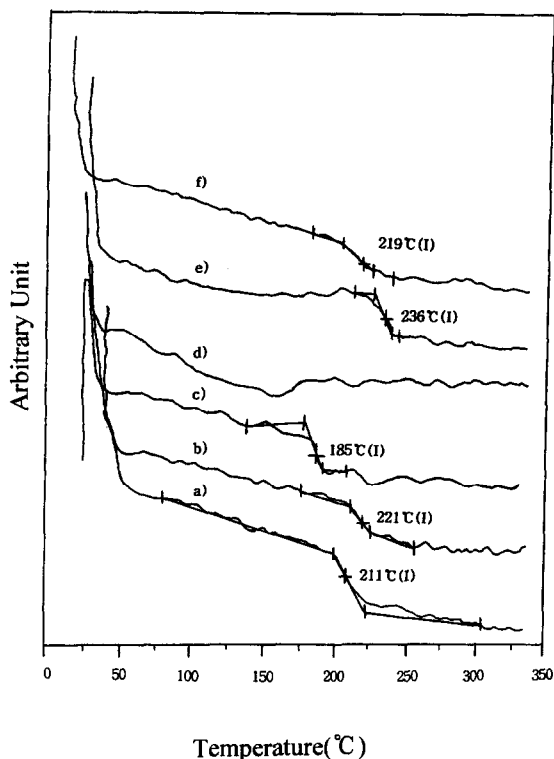


Fig. 3. Differential scanning calorimetry analyses of (a) PPO, (b) PMo-PPO, (c) PSF, (d) PMo-PSF, (e) PES and (f) PMo-PES.

polymer films may be caused by the enhanced surface area of PMo through polymer films. The conversion over the HPA-imbedded polymer film is in the following order; PMo-PSF > PMo-PES > PMo-PPO. As expected by SEM

Table 1

Conversion and product selectivity over heteropolyacid and heteropolyacid-imbedded polymer film catalysts at 170°C for ethanol conversion reaction

Run	Catalyst	Conversion (%)	Selectivity(%)		
			CH ₃ CHO	C ₂ H ₄	C ₂ H ₅ OC ₂ H ₅
1	PMo	6.9	12.8	8.4	78.8
2	PMo-C ^a	7.4	10.5	8.6	80.9
3	PMo-PSF	39.5	20.0	16.1	63.9
4	PMo-PES	33.7	9.0	32.4	58.6
5	PMo-PPO	13.4	59.4	9.8	30.8
6	PMoV	2.5	26.6	8.5	64.9
7	PMoV-C ^a	3.0	25.8	8.4	65.8
8	PMoV-PPO	4.0	91.6	—	8.4

W/F = 169.1 g cat h/EtOH mol, air = 5 cc/min.

^a HPA recrystallized from methanol–chloroform mixture.

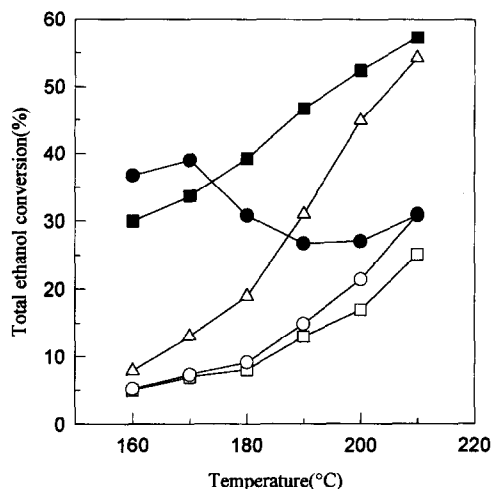


Fig. 4. Total ethanol conversion over HPA and film catalysts with respect to reaction temperature: W/F = 161.9 g cat h/EtOH mol, air = 5 cc/min: (□) PMo, (○) PMo-C, (△) PMo-PPO, (●) PMo-PSF, (■) PMo-PES.

analyses, PMo-PPO shows the smallest conversion among three catalysts. This may be partly resulted from partial agglomeration of PMo through PPO film. The fact that both bulk HPA and recrystallized HPA from methanol–chloroform show similar ethanol conversion and product selectivity means that the mixed solvent has no influence on the catalytic activity of HPAs.

The steady state ethanol conversion with respect to reaction temperatures is shown in Fig. 4. The amounts of ethanol converted to ethylene and diethylether by an acidic function of PMo are shown in Fig. 5, and the amounts of ethanol converted to acetaldehyde by an oxidation function of PMo are shown in Fig. 6. In order to test the solvent effect on the catalytic activity of PMo, PMo was recrystallized at 150°C after dissolving PMo in the chloroform–methanol mixture (this was noted as PMo-C). According to the previous works [22,23] examining PMo-PSF film which was prepared using DMF as a common solvent, it was reported that acidic function of PMo-PSF was decreased due to the strong adsorption of DMF on the acid sites of PMo while redox activity of PMo-PSF was remarkably enhanced due to the fine dispersion

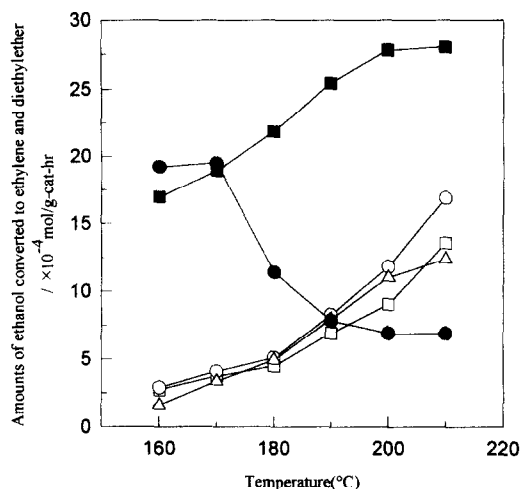


Fig. 5. Amounts of ethanol converted to ethylene and diethylether by the acidic function of heteropoly acid with respect to reaction temperature: W/F = 161.9 g cat h/EtOH mol, air = 5 cc/min: (□) PMo, (○) PMo-C, (△) PMo-PPO, (●) PMo-PSF, (■) PMo-PES.

of PMo through PSF film. This effect of DMF on the acidic property of PMo was also confirmed by the DMF-TPD experiment. Unlike PMo recrystallized from DMF, PMo and PMo-C showed almost the same acidic and oxidation function along with the reaction temperature. It suggests again that chloroform–methanol mixture gives no effect on the catalytic activity of PMo. Catalytic activities of HPA-imbedded polymer films are remarkably enhanced comparing with the bulk and recrystallized HPAs. The main reason for the enhanced activity of PMo-imbedded polymers is not the effect of mixed solvent but the enhanced dispersion of PMo upon blending. The ethanol conversion of PMo-PES and PMo-PPO increases with the increase of reaction temperature while PMo-PSF shows entirely different trend. T_g of PSF was 185°C and that of PMo-PSF might be lower than 185°C upon blending. This low T_g of PMo-PSF might be responsible for the sharp decrease of catalytic activity at the temperature above 170°C. In other words, PMo-PSF is thermally deformed

at the reaction temperature above 170°C and this might have affected the catalytic activity.

According to the previous work [27] examining vapor-phase ethanol dehydration reaction over solid HPAs, it was reported that ethylene was mainly formed from ethanol adsorbed in the bulk of HPA while diethylether was formed from ethanol adsorbed on the surface. The diethylether formation is dominant over solid HPA at low reaction temperatures. Diethylether can be easily converted to ethylene thermodynamically over 170°C. It can be inferred that the enhanced dispersion of HPA through polymer film offers more adsorption sites for the surface reaction yielding diethylether. The produced diethylether reacts more to form ethylene over the dispersed HPA. Polymer properties such as porosity, pore area and permeability can affect adsorption sites and reaction pathway, although this is not clearly understood yet. It is also believed that the enhanced ethanol conversion over HPA-imbedded polymer film is partly attributed to the enhanced acetaldehyde yield via

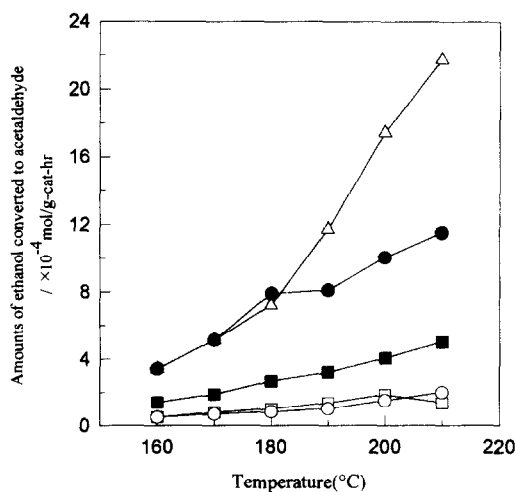


Fig. 6. Amounts of ethanol converted to acetaldehyde by the oxidation function of heteropoly acid with respect to reaction temperature: W/F = 161.9 g cat h/EtOH mol, air = 5 cc/min: (□) PMo, (○) PMo-C, (△) PMo-PPO, (●) PMo-PSF, (■) PMo-PES.

oxidation reaction over highly dispersed HPA through polymer film.

3.5. Effect of polymers

Because of the enhanced surface area of PMo after imbedding through polymer films, both acidic and oxidation activity for ethanol conversion reaction might be more or less increased. The ratio of an oxidation activity (selectivity to acetaldehyde) to an acidic activity was dependable on a kind of polymer materials. Examining Run 3–5 in Table 1, PMo modified by polymers exhibited different behaviors along with the polymers. PMo-PSF and PMo-PES showed similar conversion, but PMo-PPO showed different selectivity from those two catalysts and much lower activity. The selectivity to oxidation reaction over PMo-PPO is 3 times or more to other two catalysts and that to dehydration reaction is 50% or less. Lower surface area of PMo-PPO may be responsible for the lower activity but different selectivity can not be explained by the different surface area of PMo-PPO. We can find another factor affecting this behavior of PMo-PPO in DSC measurement. The T_g of PMo-PSF and PMo-PES was somewhat decreased while that of PMo-PPO was increased by 10°C upon blending. These results suggest that PMo acts as impurities in PMo-PSF and PMo-PES (physical mixing) while there is some interaction (like chemical bonding) between PMo and PPO. It can be deduced that interaction between two materials of PMo-PPO is attributed to the inhibition of acidic activity of PMo after blending with PPO.

Acetaldehyde is formed via oxidative dehydrogenation of ethanol in the presence of oxygen. Acetaldehyde selectivity over PMo-PES shows the smallest value. We should consider another factors for this catalytic behavior; namely, the properties of polymer materials. Most of PMo in polymer films locates in the bulk phase of polymer films with fine dispersion. Ethanol and oxygen should permeate through the film in order for the reaction to take

Table 2
Permeability ratio of O₂/ethanol through PMo-imbedded polymer films at 80°C

Film catalyst	Pressure (atm)	Permeability ratio of O ₂ /ethanol	
		feed side	permeation side
PMo-PSF	0.9	1.04	0.57
PMo-PPO	1.1	1.04	0.85
PMo-PES	0.9	1.04	0.11

place. In order words, the permeabilities of ethanol and oxygen through the films can affect the ethanol conversion and product selectivity. In order to confirm the individual effect of polymer materials on the product yield and selectivity, the permselectivities of O₂/ethanol through HPA-imbedded polymer films were measured at 80°C. The ethanol conversion during permeability measurement was negligible at this temperature. At high temperatures, it was difficult to see the individual effect of polymer materials because of the reaction during permeability measurement. Although it was difficult to correlate directly the permselectivities at 80°C with catalytic activities over 170°C, we could observe their trends.

As shown in Table 2, the ratio of O₂/ethanol in permeation side is smaller than that in feed side. This indicates that the permeability of O₂ is smaller than that of ethanol and the permeation rate of O₂ is rate-determining step for oxidation reaction. The ratio in permeation side through PMo-PES is the smallest among three HPA-imbedded polymer films. It is believed that this low O₂/ethanol ratio through PMo-PES is partly responsible for the low acetaldehyde selectivity of PMo-PES. O₂/ethanol ratio in permeation side and acetaldehyde selectivity showed the same trend in the following order as shown in Tables 1 and 2; PMo-PPO > PMo-PSF > PMo-PES.

3.6. Effect of composite of heteropoly acid

A series reaction (Run 6–8) using PMoV was examined as shown in Table 1. It is well known

that PMoV shows a stronger oxidation activity and a weaker acidic activity than PMo. It is supported by the results of Run 1 and Run 6. PMoV and PMoV-C shows almost same conversion and selectivity as in the case of PMo and PMo-C, meaning that methanol–chloroform has no influence on their catalytic behaviors. Although PMoV and PMoV-PPO shows almost same ethanol conversion, PMoV-PPO shows much higher acetaldehyde selectivity of 91.6% and a lower diethylether selectivity of 8.4% than PMoV. This value is also much higher acetaldehyde selectivity than PMo-PPO. This means that acidic activity of PMoV is almost inhibited by blending with PPO. Assuming that the blending pattern of PMo-PPO and PMoV-PPO is almost same, the interaction of PMo and PMoV with PPO may be chemical bonding of protons on acids with PPO. It is noticeable that the activity trend between PMo and PMoV is the same as the trend between PMo-PPO and PMoV-PPO. This suggests that one of the bi-functional catalytic activities of heteropoly acids can be suppressed by choosing a proper heteropoly acid and a proper polymer.

4. Conclusions

Membrane-like $H_3PMo_{12}O_{40}$ or $H_5PMo_{10}V_2O_{40}$ -imbedded polymer films were prepared by blending these materials using chloroform–methanol mixture as a solvent, and they were tested as catalysts for ethanol conversion reaction. The chloroform–methanol mixture gave no influence on the catalytic activity of HPAs. All the HPA-imbedded polymer films showed a higher catalytic activity than bulk HPA owing to the increased surface areas. It was found that the acidic and oxidation catalytic activities of HPA could be controlled by blending HPA with polymer using a mixed solvent. The interaction of HPA and PPO suppressed the acidic activity of HPA. The permeability ratio of O_2 /ethanol through HPA-imbedded polymer films was partly responsible for the oxidation

activity. It is revealed that the novel catalysts of HPAs can be designed by blending with polymers. Selecting the solvent, polymer material, and HPA is the key step for the modification of novel catalysis of HPA in this method.

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References

- [1] Y. Konishi, K. Sakata, M. Misono and Y. Yoneda, *J. Catal.* 77 (1982) 169.
- [2] M. Akimoto, Y. Tsuchida and K. Sato, *J. Catal.* 72 (1981) 83.
- [3] M. Ai, *J. Catal.* 71 (1981) 88.
- [4] T. Komaya and M. Misono, *Chem. Lett.* (1983) 1177.
- [5] N. Mizuno, K. Katamura, Y. Yoneda and M. Misono, *J. Catal.* 83 (1983) 384.
- [6] N. Muzuno and M. Misono, *Chem. Lett.* (1984) 669.
- [7] M. Misono, *Catal. Rev. Sci. Eng.* 29 (1987) 269.
- [8] M. Misono, K. Sakata, Y. Yoneda and W.Y. Lee, in T. Seiyama and K. Tanabe (Editors), *Inter. Congr. Catal., Tokyo, 30 June–4 July 1980, Studies in Surface Science and Catalysis, Vol. 7B* (Kodansha/Elsevier, 1980) p. 1047.
- [9] G.M. Brown, M.R. Neo Spiret, W.R. Bushing and H.A. Levy, *Acta. Cryst. B* 33 (1977) 1038.
- [10] Y. Saito, P.N. Cook, H. Niiyama and E. Echigoya, *J. Catal.* 95 (1985) 49.
- [11] T. Baba, H. Watanabe and Y. Ono, *J. Phys. Chem.* 87 (1983) 2406.
- [12] I. Mochida, K. Yata, H. Fujitsu and Y. Komatsubara, *Bull. Chem. Soc. Jpn.* 58 (1985) 900.
- [13] Y. Izumi, M. Ogawa, W. Nohara and K. Urabe, *Chem. Lett.* (1992) 1987.
- [14] T. Okuhara, M. Yamashita, K. Na and M. Misono, *Chem. Lett.* (1994) 1451.
- [15] S.S. Saidkhanov, A.I. Kokorin, E.N. Sainov, A.I. Vokov and V.N. Parmon, *J. Mol. Catal.* 21 (1983) 365.
- [16] K. Nomiya, H. Murasaki and M. Miwa, *Polyhedron* 5 (1986) 1031.
- [17] J. Pozniczek, I. Kulszewicz-Bajer, M. Zagorska, K. Kruczala, K. Dyrek, A. Bielanski and A. Pron, *J. Catal.* 132 (1991) 311.
- [18] M. Hasik, W. Turek, E. Stochmal, M. Lapkowski and A. Pron, *J. Catal.* 147 (1994) 544.
- [19] M. Hasik, A. Pron, I. Kulszewicz-Bajer, J. Pozniczek, A. Bielanski, Z. Piwowska and R. Dziembaj, *Synth. Metals* 55 (1993) 972.
- [20] A. Pron, *Synth. Metals* 46 (1992) 277.
- [21] I.K. Song, S.K. Shin and W.Y. Lee, *J. Catal.* 144 (1993) 348.

- [22] I.K. Song, J.K. Lee and W.Y. Lee, *Appl. Catal.* 119 (1994) 107.
- [23] J.K. Lee, I.K. Song and W.Y. Lee, *J. Mol. Catal.* 104 (1996) 311.
- [24] H. Niiyama and E. Echigoya, *Bull. Chem. Soc. Jpn.* 44 (1971) 1739.
- [25] D.P. Smith and M.T. Pope, *Inorg. Chem.* 12 (1973) 331.
- [26] I.K. Song, W.Y. Lee and J.J. Kim, *Appl. Catal.* 96 (1993) 53.
- [27] T. Okuhara, A. Kasai, N. Hayakawa, Y. Yoneda and M. Misono, *J. Catal.* 83 (1983) 121.