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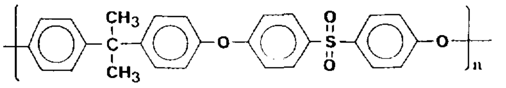
NOTES

Catalytic Activity of $H_3PMo_{12}O_{40}$-Blended Polysulfone Film in the Oxidation of Ethanol to Acetaldehyde

A heteropoly compound has acidic and redox catalytic properties (*1*). It also shows a characteristic sorption behavior (*2*) depending on the properties of the adsorbates. Most nonpolar substances such as olefins are adsorbed only on the surface (surface area is less than 10 m^2/g), while polar compounds such as alcohols, water, pyridines, and ethers mostly penetrate into the bulk to form a pseudo-liquid phase (*3*). Thus, some reactions occur only on the surface, whereas others occur in the bulk of the heteropoly acid.

A heteropoly compound is highly soluble in some organic solvents. Taking advantage of this property, heteropoly acid can be blended with a polymer to form a porous film by using a common solvent which dissolves both the heteropoly compound and the polymer. Since polymer materials are thermally unstable at high temperatures, their utilization has been restricted within the lower temperature ranges. Therefore, if the heteropoly acid and blended polymer film is used as a catalyst, it must be applied in low-temperature reactions. However, if the heteropoly acid catalyst is well dispersed in the bulk of the film, a high catalytic activity can be expected for certain reactions even at low reaction temperatures. In this study $H_3PMo_{12}O_{40}$-blended polysulfone (abbreviated as PMo–PSF hereafter) film was prepared and its catalytic activity for the ethanol conversion reaction was investigated.

PMo was prepared according to the method described by Tsigdinos (*4*). PSF (Udel 1700 from Union Carbide Co.), for which the chemical structure is given below,



was used as the blending polymer. Various solvents were examined in order to find a common solvent dissolving both PMo and PSF. It was found that they were highly soluble in dimethylformamide, dimethylacetamide and dimethylsulfoxide. Among the solvents tested, dimethylformamide (abbreviated as DMF hereafter) was chosen. PMo–PSF film was prepared by casting the PMo (4.76 wt.%)–PSF (23.81 wt.%)–DMF (71.43 wt.%) solution on a glass plate, before it was dried in air for 4–5 h and subsequently in vacuum for 2 h. The thickness of the PMo–PSF film was 0.1 mm.

The reaction was carried out in a conventional flow fixed-bed reactor. Air (5 ml/min), as an oxygen source, was supplied together with ethanol vapor. The small pieces (2 mm × 2 mm) of the PMo–PSF film were used as catalyst in a fixed-bed reactor. The products were analyzed with an on-line GC (Yanaco G1800) using a column packed with Porapak Q. The amount of each product was calculated on the basis of carbon balance. Thermal analysis showed that the glass transition temperature of PSF was 176°C and the thermal decomposition temperature of PMo was 430°C. The prepared PMo–PSF film was calcined at 150°C, before the reaction was carried out at 170°C.

Figure 1 shows the IR spectra of PMo, PSF, and PMo–PSF film. The primary structure (Keggin structure) of PMo can be identified by the four characteristic bands ranging from 700 to 1200 cm^{-1}. Bands at

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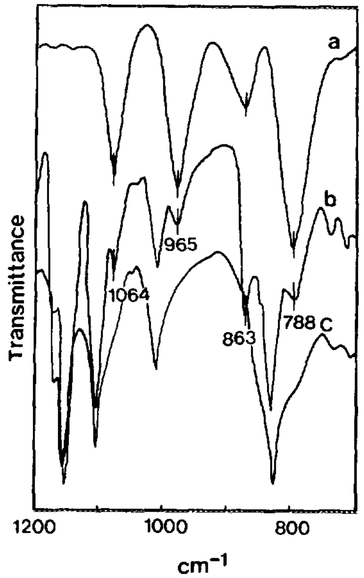

FIG. 1. IR spectra of (a) PMo, (b) PMo–PSF film, and (c) PSF film.

788 and 863 cm^{-1} represent Mo–O–Mo bonding. Bands at 965 and 1064 cm^{-1} signify Mo═O and P–O bonds, respectively. As shown in Fig. 1, the four characteristic bands of PMo are shown at each wavenumber in the PMo–PSF film. IR bands other than those due to PMo in the PMo–PSF film are due to PSF film. This fact suggests that the PMo in the PMo–PSF film keeps the primary structure of PMo.

In order to investigate any interaction between PMo and PSF, the oxidation state of molybdenum in PMo and in PMo–PSF film was measured by XPS. The spectrum could be fitted with only one doublet due to Mo $3d_{3/2}$ and Mo $3d_{5/2}$. The binding energies of Mo $3d_{3/2}$ and Mo $3d_{5/2}$ in both catalysts were 235.3 and 232.1 eV, respectively. It was confirmed that there is only one type of molybdenum (VI) in both PMo and PMo–PSF film, in good agreement with that of a previous report (*5*).

A TPD experiment of DMF adsorbed on the PMo catalyst (powder) revealed that DMF desorption was initiated at 150°C and reached maximum points at 270 and 337°C. This fact suggests that the chemically adsorbed DMF (organic base) on the Brønsted acid site of PMo in the PMo–PSF film can remain at a reaction temperature of 170°C.

SEM micrographs of PSF film and PMo–PSF film in Fig. 2 show that there is no distinctive difference between the two, although the magnification in Fig. 2b is twice that in Fig. 2a. No visible evidence representing PMo was found in the PMo–PSF film. This may indicate that PMo was not recrystallized into large particles but was finely distributed as fine particles invisible in the SEM in the PMo–PSF film. The pores in both films may be due to the shrinking of polymer film when they have been dried. They are very large and hence have practically no importance from the catalytic point of view. To confirm the uniform distribution of PMo in the PMo–PSF film, EDX analysis

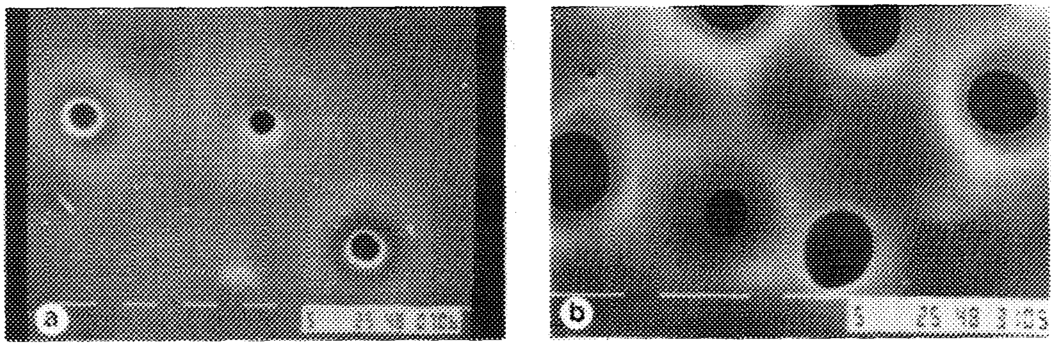

FIG. 2. SEM micrographs of (a) PSF film (×680) and (b) PMo–PSF film (×1360).

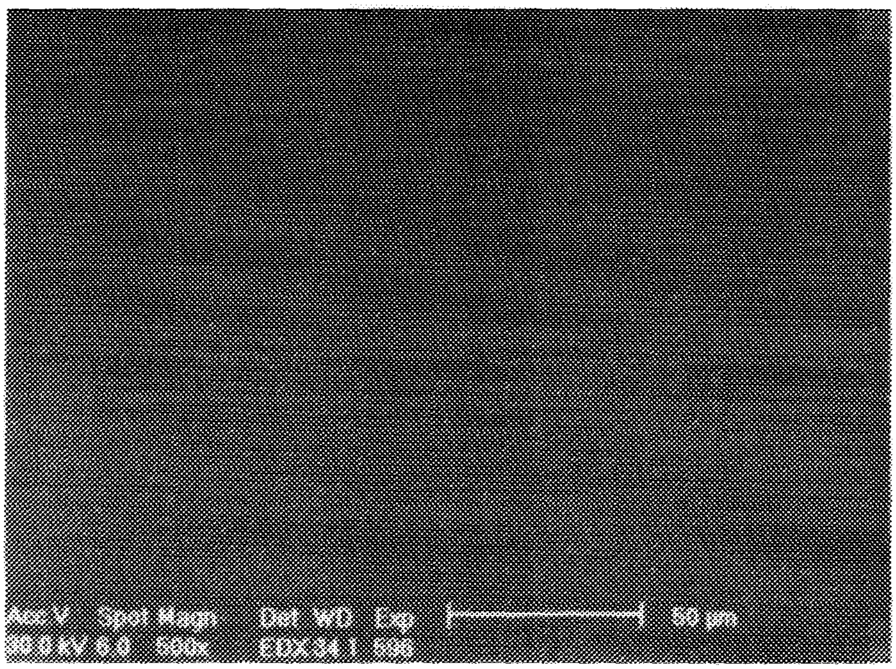

FIG. 3. EDX image of PMo–PSF film by mapping on only molybdenum.

was performed. The EDX image of Mo in Fig. 3 reveals that PMo is uniformly distributed in the PMo–PSF film.

Catalytic activities of PMo and PMo–PSF film are shown in Table 1. When PMo acts as an acid catalyst, ethanol is dehydrated into diethylether and ethylene. When PMo acts as an oxidation catalyst, on the other hand, acetaldehyde (as a main product), CO, and CO_2 are formed. At 170°C, the formation of ethylene, CO, and CO_2 over both the PMo and PMo–PSF film was negligible. The amount of diethylether over the PMo–PSF film was less than that over the

TABLE 1

Catalytic Activities of PMo and PMo–PSF Film at 170°C

Catalyst	Amount of ethanol consumed to produce each product (mol/g-cat h)		Sum of products (mol/g-cat h)	Ethanol conversion (%)
	$C_2H_5OC_2H_5$	CH_3CHO		
PMo[a]	5.965×10^{-5}	4.193×10^{-5}	1.016×10^{-4}	2.5
PMo–PSF[b]	3.176×10^{-5}	4.913×10^{-5}	5.231×10^{-4}	12.6
Ratio *b*/*a*	0.53	11.72	5.15	

Note. $F/W = 4.141 \times 10^{-3}$ EtOH mol/g-cat h, air carrier flow rate = 5 ml/min. (F, flow rate of ethanol in reactant stream; W, weight of PMo).

[a] Dehydrated PMo calcined at 300°C.

[b] PMo–PSF film calcined at 150°C.

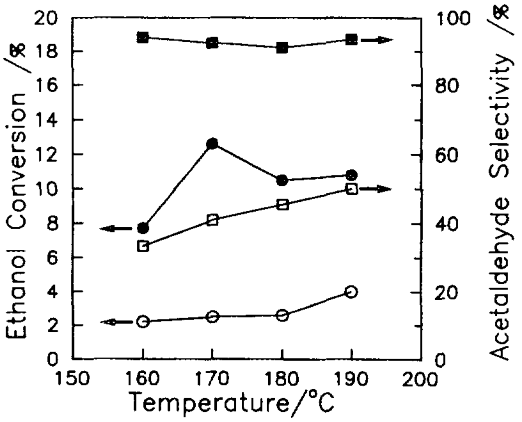

FIG. 4. Ethanol conversion and acetaldehyde selectivity over PMo and PMo–PSF film with respect to reaction temperature: open symbols, PMo; closed symbols, PMo–PSF.

PMo, while the amount of acetaldehyde over the PMo–PSF film was about 10 times higher than that over the PMo. In other words, the PMo–PSF film showed a higher activity for the oxidation reaction and a lower activity for the acid-catalyzed reaction than did PMo. The decrease of an acidic activity of the PMo–PSF film is mainly due to DMF adsorbed on its acid sites and the remarkable increase of an oxidation activity may be due to the uniformly dispersed PMo in a fine particle form through the PSF film.

Ethanol conversion and the selectivity for acetaldehyde over PMo and PMo–PSF film are represented with respect to the reaction temperature in Fig. 4. The catalytic activity of PMo–PSF film was about 10 times than that of PMo in the temperature range tested. A slight decrease of the catalytic activity over PMo–PSF film at higher temperatures than 170°C may have resulted from the thermal deformation of the PSF film above the glass transition temperature of 176°C.

In conclusion, the catalytic activity of heteropoly acid can be remarkably enhanced even in a low reaction temperature by blending it with polymer materials to form a porous film where the heteropoly acid is uniformly and finely dispersed. A highly active catalyst at a low temperature has the advantage of enhancing the selectivity for a desirable product by suppressing side reactions. In this study, it was found that the oxidation rate of ethanol was remarkably increased by using the PMo–PSF film and the selectivity for acetaldehyde was high since the side reactions forming CO and CO_2 were suppressed at low temperatures.

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