JOURNAL OF CATALYSIS **178,** 378–381 (1998)
ARTICLE NO. CA982166

RESEARCH NOTE

Modification of Pore Characteristics and Catalytic Activities of Heteropolyacid-Polymer Composite Catalysts by Membrane Technology

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Received November 4, 1997; revised May 13, 1998; accepted May 16, 1998

$H_3PMo_{12}O_{40}$-polysulfone composite film catalysts were prepared with a membrane preparation technique by blending these two materials using dimethylformamide or methanol–chloroform mixture. They were used as fixed-bed catalysts for the vapor-phase ethanol conversion in a continuous flow reactor. It was observed that $H_3PMo_{12}O_{40}$ was finely dispersed throughout a polysulfone matrix. The composite catalysts showed the modified catalysis compared to the bulk acid. The effects of solvent on the pore characteristics and catalytic activities of these composite film catalysts were investigated. © 1998 Academic Press

Key Words: **heteropolyacid; polysulfone; ethanol; catalysis; pore characteristics.**

The acid and oxidation catalytic properties of heteropolyacids (HPAs) have been conventionally modified by replacing the protons with metal cations and/or by changing the heteroatom or the polyatoms for the new catalyst design (1–4). Novel catalysis of HPAs has been also modified by introducing them into polymer materials. Taking advantage of the overall negative charge of heteropolyanions, HPAs have been combined with ion-exchange resins (5) or conducting polymers (6–8) such as polyacetylene, polyaniline, and polypyrrole. Another work of utilizing polymer materials was on the membrane-like HPA-polymer composite catalysts (9, 10). HPAs have been blended with polymer materials using a common solvent or a mixed solvent to prepare the membrane-like film catalysts by a membrane preparation technique. The following advantages are expected in HPA-polymer composite film catalysts: (a) preparation of the thin composite film catalyst having highly dispersed HPA is quite simple; (b) HPA dispersion throughout polymer matrix can be easily controlled; (c) acid and redox properties of HPAs can be modified by the nature of solvent and polymer used; and (d) they have versatile applicability at low temperature reactions. Another promising advantage of HPA-polymer film catalysts is that their pore characteristics can be easily controlled by the membrane preparation technique for the modification of novel catalysis of HPA. In this study, $H_3PMo_{12}O_{40}$-blended polysulfone (denoted as PMo-PSF hereafter) solutions were prepared using dimethylformamide as a common solvent or using methanol–chloroform mixture to form membrane-like film catalysts by the phase inversion method. These film catalysts were tested as fixed-bed catalysts for the vapor-phase ethanol conversion in a continuous flow reactor. The effects of solvent on the pore characteristics and catalytic activities of PMo-PSF film catalysts were investigated.

PMo (Aldrich Chem. Co.) was calcined at 300°C for precise quantification. PSF (Udel 1700 from Union Carbide Co.) was selected as a blending polymer for its excellent thermal and chemical stability. PSF was pretreated at 150°C to remove water molecules before blending. Dimethylformamide (DMF) dissolving both PMo and PSF was used as a common solvent. A homogeneous PMo (4.76 wt%)–PSF (23.81 wt%)–DMF (71.43 wt%) solution was obtained at room temperature. The PMo–PSF–DMF solution was cast on a glass plate with constant thickness at 56% relative humidity to form a membrane-like film, and subsequently, it was dried at 56% relative humidity (denoted as PMo-PSF-DMF-1). The PMo-PSF-DMF solution was also cast and dried at 85% relative humidity (denoted as PMo-PSF-DMF-2). Although both PMo and PSF were not soluble in methanol or chloroform, PMo could be also blended with PSF using a methanol(M)–chloroform(C) mixture because methanol dissolving PMo and chloroform dissolving PSF were miscible. A homogeneous PMo (1.22 wt%)–PSF (6.9 wt%)–methanol (4.41 wt%)–chloroform (87.47 wt%) solution was obtained at room temperature. The PMo–PSF–MC solution was cast and dried at 56% relative

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0021-9517/98 $25.00

humidity (denoted as PMo-PSF-MC-1) or at 85% relative saturation of methanol vapor (denoted as PMo-PSF-MC-2) to form a membrane-like film catalyst. PMo-free PSF-DMF film and PSF-MC film were also prepared and dried at 56% relative humidity for reference and comparison. The thickness of the film catalyst was 17 μm.

Vapor-phase ethanol conversion was carried out in a continuous flow fixed-bed reactor. The membrane-like film catalyst was cut into small pieces (2 mm × 2 mm) to be used as a fixed-bed catalyst. All film catalysts were pretreated at 170°C for 1 h by passing air (30 cc/min) before the reaction. Bulk PMo was pretreated at 300°C with air before the reaction. *Ethanol was continuously supplied to the reactor by using a micro-feeder. Air (5 cc/min) was used as both a carrier gas and an oxygen source. The reactants were sufficiently vaporized for the reaction by passing a preheating zone*. The steady-state reaction was carried out at 170°C. The products were analyzed periodically with an on-line GC (Yanaco G180). Ethanol conversions and product yields were calculated on the basis of carbon balance. *Formation of CO and CO_2 was negligible*. The film catalysts were characterized by DSC (TA Instruments TA200), XRD (Jeol JDX-5P), SEM (Jeol JMS-35), and mercury porosimeter (Autopore 9220).

The blending pattern of PMo with PSF was confirmed by the thermal analysis. The glass transition temperature of PSF-DMF and PMo-PSF-DMF-1 were found to be 187°C and 174°C, respectively. The glass transition temperature of PSF-MC was 185°C, but that of PMo-PSF-MC-1 was hardly detected by DSC measurement. However, the physical state of PMo-PSF-MC-1 was changed and became fragile after the reaction above 180°C. This means that the glass transition temperature of PMo-PSF-MC-1 was less than 180°C. The above results indicate that PMo in PMo-PSF-DMF-1 and PMo-PSF-MC-1 film catalysts acted as an impurity for PSF and that the blending between PMo and PSF was physical, regardless of the kind of solvent used. The film catalysts were thermally stable at the reaction temperature of 170°C.

Figure 1 shows the cross-sectional SEM images of PMo-PSF-DMF and PMo-PSF-MC film catalysts which were prepared at different conditions. Distinctive differences were found in morphologies of the film catalysts. Both

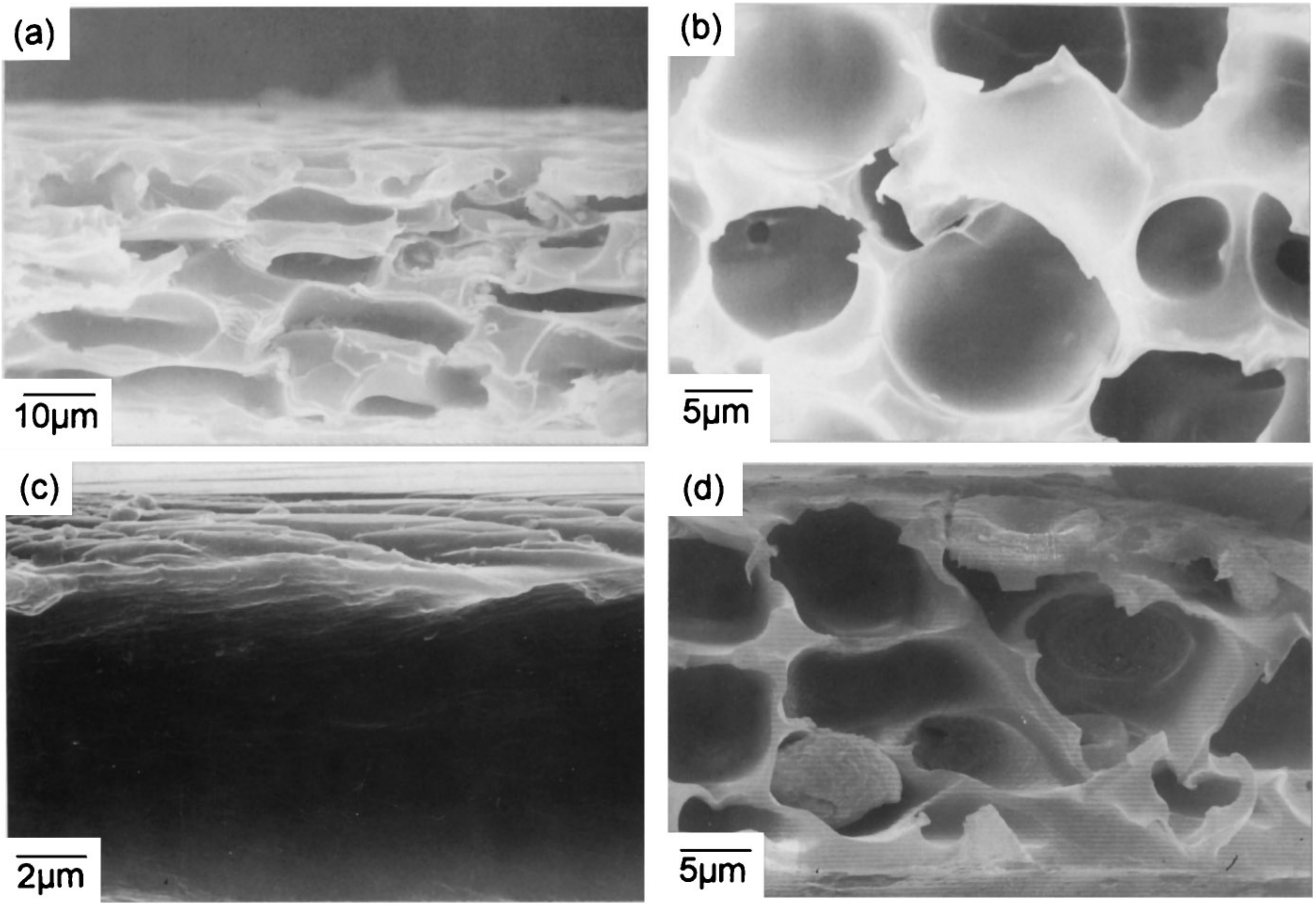

FIG. 1. Cross-sectional SEM images of (a) PMo-PSF-DMF-1, (b) PMo-PSF-DMF-2, (c) PMo-PSF-MC-1, and (d) PMo-PSF-MC-2.

PMo-PSF-DMF-1 and PMo-PSF-DMF-2 showed well-developed macropores. PMo-PSF-MC-1 had no pore-like feature while PMo-PSF-MC-2 had well-developed macropores. However, any visible evidence representing PMo was found in all the film catalysts. This means that PMo was not recrystallized into large particles but was highly dispersed as fine particles throughout the PSF matrix. Fine dispersion of PMo was also confirmed by observing the uniform greenish color of the film catalysts. The different pore characteristics of the film catalysts were intentionally controlled in this work by a membrane preparation technique called a phase inversion method (11–14). The miscibility of solvent with nonsolvent for PSF was found to be a very important factor for the pore formation through film catalysts. It was revealed that pores of PMo-PSF-DMF film catalysts were formed due to the miscible nature of DMF (solvent for PSF) with water vapor (nonsolvent for PSF) in the air. The nonporous nature of PMo-PSF-MC-1 was due to the immiscibility of water vapor with chloroform (a major component of the mixed solvent). The miscibility of chloroform with methanol vapor also led to the pore formation through PMo-PSF-MC-2 film catalyst. PMo-PSF-DMF-2 had enhanced pore characteristics compared to PMo-PSF-DMF-1, as expected in Fig. 1. Pore characteristics of the film catalysts were described in Table 1.

The XRD measurements were taken after the film catalysts were treated at 170°C under the air stream for 1 h. Two PMo-PSF-DMF catalysts exhibited characteristic XRD peaks. The XRD peaks of PMo-PSF-DMF-1 and PMo-PSF-DMF-2 were attributed to PMo with the action of residual DMF and water because PSF was an amorphous polymer. The above result means that PMo in the PMo-PSF-DMF film catalysts existed as a crystal form. On the other hand, however, PMo-PSF-MC-1 showed no characteristic XRD peaks. This means that PMo in the PMo-PSF-MC-1 film catalyst did not exist as a crystal structure but as an amorphous phase. It is clear that PMo in the PMo-PSF-MC-1 had structural flexibility which was provided by forming a pseudo-liquid phase (15, 16). It was found that PMo in the PMo-PSF-MC-2 formed a crystal structure.

TABLE 1

Pore Characteristics of PMo-PSF Composite Film Catalysts

Catalyst	Porosity (%)	Average pore diameter (μm)	Total pore area (m^2/g)
PMo-PSF-DMF-1[a]	14.0	2.78	26.5
PMo-PSF-DMF-2[b]	56.0	4.26	29.7
PMo-PSF-MC-1[c]	-	-	-
PMo-PSF-MC-2[d]	81.5	5.48	14.9

[a] It was prepared in ambient condition (at 56% relative humidity).
[b] It was prepared at 85% relative humidity.
[c] It was prepared in ambient condition (at 56% relative humidity).
[d] It was prepared at 85% relative saturation of methanol vapor.

TABLE 2

Catalytic Activities of PMo-PSF-DMF Film Catalysts at 170°C

Catalyst	EtOH conversion (%)	Amounts of EtOH converted to product ($\times 10^4$ moles/g-PMo-hr)		
		CH_3CHO	C_2H_4	$C_2H_5OC_2H_5$
Bulk PMo[a]	2.7	0.69	0.42	3.0
PMo-DMF[b]	1.5	1.50	0.19	0.50
PMo-PSF-DMF-1	6.2	7.44	0.49	1.39
PMo-PSF-DMF-2	9.6	11.50	0.63	2.23

Note. W/F = 66.73 g-PMo-hr/EtOH-mole; air = 5 cc/min; film thickness = 17 μm.
[a] Bulk PMo was treated at 300°C.
[b] PMo was recrystallized from dimethylformamide and then treated at 170°C.

Typical catalytic activities for the vapor-phase ethanol conversion over bulk PMo and PMo-PSF-DMF film catalysts are summarized in Table 2. Ethylene and diethylether are formed by acid-catalyzed reaction, whereas acetaldehyde is formed by oxidation. PMo-PSF-DMF film catalysts showed higher ethanol conversions than bulk PMo. PMo-PSF-DMF films showed remarkably enhanced yields for acetaldehyde, but they showed drastically decreased yields for ethylene and diethylether compared to bulk PMo. The PMo-PSF-DMF-2 showed a higher conversion than PMo-PSF-DMF-1. This may be attributed to the reduced mass transfer resistance of reaction species through the well-developed macropores. The enhanced ethanol conversions over PMo-PSF-DMF film catalysts were attributed to the enhanced surface oxidation reaction over highly dispersed PMo throughout PSF matrix. The suppressed activity for the acid-catalyzed reaction over PMo-PSF-DMF was due to strongly adsorbed DMF (organic base) on PMo in the course of blending. This was well confirmed by a DMF-TPD experiment over the bulk acid (17). The DMF effect was also confirmed by observing the catalytic activity of PMo-DMF in Table 2. It is concluded that PMo could be modified by the membrane preparation technique to show a selective oxidation activity.

Catalytic activities for ethanol conversion reaction over bulk PMo and PMo-PSF-MC film catalysts are listed in Table 3. PMo-PSF-MC film catalysts showed higher ethanol conversions than bulk PMo. They also showed enhanced product yields for both acid-catalyzed and oxidation reactions, compared to the bulk acid. The fact that bulk PMo and PMo-MC showed a similar activity pattern means that the mixed MC had no great effect on the catalytic activity of PMo. The enhanced catalytic activity of the nonporous PMo-PSF-MC-1 may be understood in terms of PMo dispersion and the amorphous behavior of PMo in the film catalyst. The enhanced activity of the PMo-PSF-MC-2 film catalyst was believed to be due to the enhanced pore characteristics, as in the case of PMo-PSF-DMF film catalysts.

TABLE 3

Catalytic Activities of PMo-PSF-MC Film Catalysts at 170°C

Catalyst	EtOH conversion (%)	Amounts of EtOH converted to product ($\times 10^4$ moles/g-PMo-hr)		
		CH_3CHO	C_2H_4	$C_2H_5OC_2H_5$
Bulk PMo[a]	6.9	0.52	0.34	3.22
PMo-MC[b]	7.4	0.46	0.38	3.54
PMo-PSF-MC-1	39.5	4.67	3.76	14.93
PMo-PSF-MC-2	46.0	2.95	9.67	14.60

Note. W/F = 169.1 g-PMo-hr/EtOH-mole; air = 5 cc/min; film thickness = 17 μm.

[a] Bulk PMo was treated at 300°C.

[b] PMo was recrystallized from methanol–chloroform and then treated at 170°C.

It is concluded that pore characteristics of HPA-PSF composite film catalysts could be controlled by the phase inversion method which was frequently used in the membrane science. The pore characteristics and catalytic activities were strongly affected by the preparation condition and by the nature of the solvent. All the film catalysts showed enhanced catalysis in oxidation and/or an acid-catalyzed reaction. It is expected that this preparation technique can be directly applied to the preparation of HPA-polymer composite catalytic membranes for the membrane reactor.

ACKNOWLEDGMENT

The authors acknowledge the financial support from Daelim Industry Co. for this work.

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