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Short Communication

SEPARATION OF H_2/CO BY THE SELECTIVE SORPTION PROPERTY OF $H_3PMo_{12}O_{40}$ EMBEDDED IN POLYVINYLALCOHOL MEMBRANE

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Abstract—H_2 and CO permeabilities through $H_3PMo_{12}O_{40}$-blended polyvinylalcohol membrane and catalyst-free polyvinylalcohol membrane were measured. The blended membrane showed better selectivity and higher permeation flux of H_2 than the catalyst-free polyvinylalcohol membrane. Its enhanced H_2 separation ability was mainly due to the selective sorption property of PMo embedded in the polyvinylalcohol membrane.

Key words: *PVA, 12-Molybdophosphoric Acid, Blending, H_2-CO Separation*

INTRODUCTION

A heteropoly acid has acidic and redox catalytic properties [Mizuno et al., 1985; Song et al., 1991; Song et al., 1994; Song et al., 1991]. It also shows a characteristic adsorption behavior [Misono, 1987; Okuhara et al., 1983; Song et al., 1993; Lee et al., 1994] depending on the properties of adsorbates. Most nonpolar chemicals are adsorbed only on its surface, while polar compounds like water, alcohols, pyridines and ethers mostly penetrate into its bulk to form a pseudo-liquid phase [Okuhara et al., 1983]. In other words, heteropoly compounds are highly soluble in polar solvents. Taking advantage of this property, a heteropoly acid can be blended with a polymer by using a common solvent dissolving both a heteropoly acid and a polymer [Song et al., 1993, 1994a, 1992, 1994b]. In this study, the $H_3PMo_{12}O_{40}$ (denoted as PMo)-blended polyvinylalcohol (denoted as PVA) membrane was prepared and its separation ability of H_2/CO was examined at room temperature.

EXPERIMENTAL

PMo was prepared according to the method in a literature [Tsigdinos, 1974]. PMo was recrystallized after dissolving the prepared catalyst in water to eliminate the insoluble components. PMo was calcined at 300℃, before it was used for blending with PVA (Elvanol 71-30 from Du Pont, 99% hydrolyzed PVA, M=52,000). In order to prepare the PMo-blended PVA (denoted as PMo-PVA) membrane, various solvents were tested to find a common solvent dissolving both PMo and PVA. It was found that they were highly soluble in water. Viscous PVA-water solution was made after slight heating at 50℃ for 4 hours. The opaque solution was changed into a transparent solution. PMo-free PVA membrane was prepared by casting the transparent PVA(4 g)-water(36 g) solution on a PMMA plate and by drying it in air for 4 hours and subsequently under vacuum for 2 hours. PMo-PVA membrane was also prepared by casting greenish transparent PMo(1 g)-PVA(4 g)-water(36 g) solution on a PMMA plate like the procedure of the PVA membrane preparation.

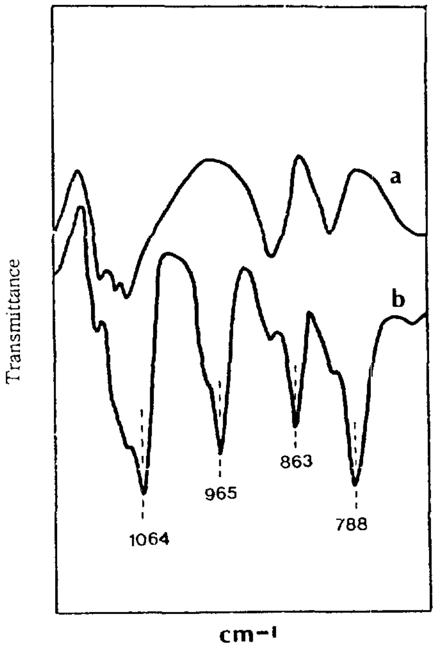

Fig. 1. IR Spectra of (a) PVA membrane and (b) PMo-PVA membrane.

Pure H_2 and CO permeabilities were measured using a conventional apparatus [Nakagawa, 1994] equipped with a bubble flow meter. The thickness of PVA and PMo-PVA membrane were 8 μm and 22 μm, respectively. The cross-sectional permeation area was 17.65 cm^2. The permselectivity between H_2 and CO was defined as the permeability ratio of the two pure gases. In order to confirm the role of PMo in the PVA membrane, the amounts of H_2 and CO adsorption in/on PMo were also measured.

RESULTS AND DISCUSSION

Fig. 1 showed the IR spectra of PVA and PMo-PVA membrane. The primary structure of PMo can be identified by the four characteristic bands ranging from 700-1200 cm^{-1}. Bands at 788 cm^{-1}

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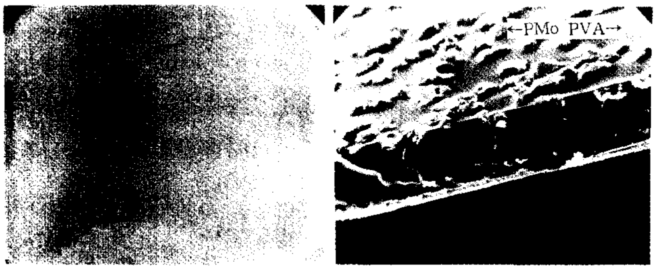

(a) (b)

Fig. 2. SEMs of (a) PVA (×2,000) and (b) PMo-PVA (cross-section, ×1,000).

Table 1. Permeabilities of H_2 and CO through PVA and PMo-PVA membrane at 25°C

Membrane	Gas	Permeability cm³-cm/cm²-sec-cmHg	Permselectivity H_2/CO
PVA	H_2	9.76×10^{-9}	1.24
	CO	7.88×10^{-9}	
PMo-PVA	H_2	3.31×10^{-7}	2.96
	CO	1.12×10^{-7}	
H_2 permeability ratio (PMo-PVA/PVA)			33.91
CO permeability ratio (PMo-PVA/PVA)			14.21

and 863 cm^{-1} represent Mo-O-Mo bondings. Bands at 965 cm^{-1} and 1064 cm^{-1} signify Mo=O and P-O bonds, respectively. The four characteristic bands of PMo are shown at each wave number in the PMo-PVA membrane. IR bands other than due to PMo in the PMo-PVA membrane are due to the PVA membrane. This fact means that the blending is physical.

Fig. 2 showed the SEMs of PVA and PMo-PVA membrane. PVA and PMo-PVA membrane were nonporous membranes. However, visible evidence representing PMo was found in the PMo-PVA membrane. This indicates that PMo exists as a recrystallized form in the blended membrane. It can be inferred from the fact that the catalytic action of PMo embedded in the PVA membrane may play a distinct role in determining the separation ability of the membrane. In other words, not only gas permeation through the PVA part but also catalytic action of PMo, presumed to be the adsorption property, determines the separation ability of the PMo-PVA membrane.

Table 1 showed gas permeabilities through two membranes. H_2 and CO permeability through the PVA membrane are small and have an order of 10^{-9}. Permselectivity of H_2/CO through the PVA membrane is 1.24. However, the PMo-PVA membrane shows large H_2 and CO permeability of order 10^{-7}, and permselectivity of H_2/CO through it is 2.96. This result means that selective gas separation mainly occurs not through the PVA part but through the PMo part in the PMo-PVA membrane. The H_2 permeability through the PMo-PVA membrane is about 34 times higher than that through the PVA membrane. From these results, it can be summarized that the PMo-PVA membrane shows better selectivity and higher permeation flux of H_2 than the PVA membrane. In order words, the selective and high flux H_2 separation through the modified PVA membrane was possible by blending PMo with PVA.

In order to confirm the role of PMo embedded in the PVA membrane, an adsorption measurement was carried out. PVA membrane itself shows no adsorbing property of H_2 and CO. As shown in Table 2, adsorption amounts of H_2 and CO in/on PMo are 0.06 and 0.02 molecules/Keggin Unit, respectively. Much more amounts of H_2 are adsorbed on PMo than CO. Considering the fact that gas separation in the PMo-PVA membrane mainly occurs through the PMo part, it may be concluded that the adsorbing property of PMo plays a major role in the selective and high flux separation of H_2 in the PMo-PVA membrane. Although its performance is somewhat lower than the commercialized membranes, it is recommended that the commercialized membrane can be modified by this method for better performance.

Table 2. Adsorption amounts of H_2 and CO on PMo at 25°C

Gas	Molecules/PMo-Keggin unit
H_2	0.06
CO	0.02

CONCLUSIONS

It is concluded that PMo-PVA membrane was easily prepared by blending PMo and PVA using water as a common solvent. The PMo-PVA membrane showed better selectivity and higher permeation flux of H_2 than the PVA membrane. Its enhanced H_2 separation ability was mainly due to the selective sorption property of PMo embedded in the PVA membrane.

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