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APPLICATION OF HETEROPOLY ACID CATALYST IN AN INERT POLYMER MEMBRANE CATALYTIC REACTOR IN ETHANOL DEHYDRATION

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The ethanol dehydration reaction was carried out in an inert membrane catalytic reactor. 12-Tungstophosporic acid as a catalyst and polysulfone as an inert membrane were used in this study. Ethanol conversion and ethylene selectivity were remarkably enhanced in comparison with those in a fixed-bed reactor under the same reaction condition.

Keywords: Heteropoly acid, polysulfone, ethanol dehydration, inert membrane catalytic reactor

1. Introduction

A two-fold advantage Is expected from membrane reactors: (1) chemical reaction and (2) genuine separation. The higher is the permeability of a specific component through a membrane in a reversible reaction, the better is the selectivity of that component [1–3]. Two types of the membrane catalytic reactor have been used in chemical reactions. The inorganic membrane reactors have been mainly applied to decomposition reactions such as dehydrogenation reaction [4–6]. The polymer membranes have more versatile applicability in separation processes than inorganic membranes because the polymer membranes show better diffusivity and solubility. However, few polymer membranes have been used due to their thermal instability at high temperatures.

The inert membrane catalytic reactor is different from the single-phase membrane reactor. It is composed of two parts, one for reaction and the other for separation. The reaction part of the membrane reactor is located in front of the inert membrane and completely isolated from it. This type of reactor has been widely used in enzymatic reaction systems [7,8].

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Heteropoly acid has acidic and redox catalytic properties [9–11]. It also shows a characteristic adsorption behavior [12–15] depending on the properties of adsorbates. Most nonpolar chemicals like olefins are adsorbed only on its surface, while polar compounds like alcohols, water, pyridines, and ethers are mostly penetrated into its bulk to form pseudo-liquid phases [16]. Thus some reactions occur only on the surface, whereas others occur in the bulk of the heteropoly acid.

The main products of ethanol dehydration reaction are ethylene and diethylether. According to a previous report [17], diethylether is formed on the surface of the heteropoly acid, while ethylene is mainly formed in the bulk of the heteropoly acid. The polysulfone membrane has the higher permeability for ethylene than for diethylether and it is thermally stable (T_g: 190°C) during a reaction.

With reference to the above-mentioned behaviors of the heteropoly acid and the polysulfone membrane, ethanol dehydration has been carried out, as a model reaction, in an inert membrane catalytic reactor which consists of the heteropoly acid as the reaction part and a polysulfone membrane as the separation part.

2. Experimental

At the beginning of this study, our effort was focused on finding out the single-phase membrane composed of heteropoly acid and polysulfone. For this purpose, various solvents were examined in order to find a common solvent dissolving both heteropoly acid and polysulfone (Udel 1700 from Union Carbide Co.). Among the solvents, dimethyl formamide (denoted as DMF hereafter) was chosen. Polysulfone (denoted as PSF hereafter) membrane was prepared by casting the 25–30 wt% PSF solution on a glass plate and drying in the air. After dissolving 12-tungstophosphoric acid (designated as PW_{12} hereafter) and PSF in DMF, this viscous solution was casted on a glass plate. Finally, the PW_{12}/PSF blended single phase catalytic membrane was prepared. However, since it was not a chemically bonded membrane but a physically blended one, the permselectivity of H_2 and N_2 through the membrane was less than that through the PW_{12}-free PSF membrane. Moreover, our experimental results showed that DMF was adsorbed on the Bronsted acid sites to cause catalyst deactivation. For these reasons, we abandoned the single-phase membrane reactor and as a substitute, our effort was focused on an inert membrane catalytic reactor.

Fig. 1 illustrates the structure of the inert membrane catalytic reactor in detail. To prevent local overheating of membrane, the top and bottom of the membrane were sealed with O-ring and Teflon. The thickness and cross-sectional area of PSF membrane were 0.266 mm and 17.65 cm^2, respectively. Thermocouples were inserted into the catalyst bed and located on the membrane surface. A schematic diagram of the experimental unit is shown in fig. 2. Ethanol was sufficiently preheated for vaporization and fed with He to the reactor at 3 ml/min. The effluent stream from fixed bed passed through the buffer zone and was continu-

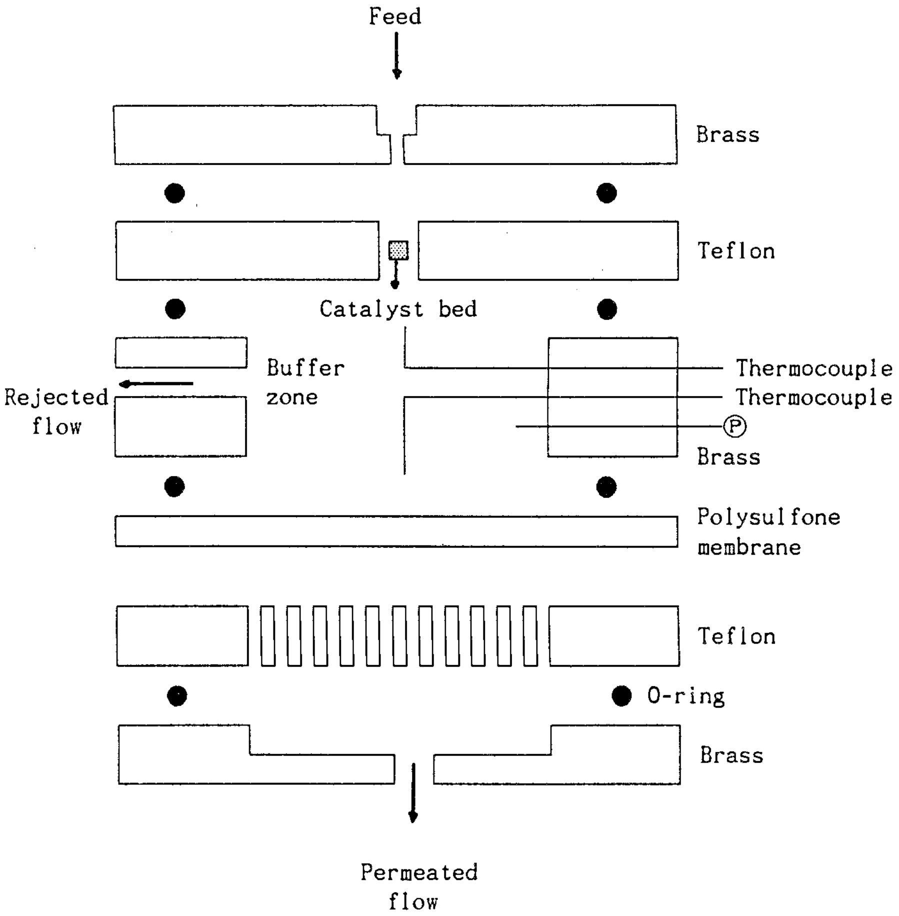

Fig. 1. Inert polymer membrane catalytic reactor.

ously splitted into two streams, permeated flow and rejected flow. The rejected flow was necessary to reduce the concentration polarization, that is, to keep the concentration of less permeable diethylether at constant level. In this work, the ratio of the permeated flow to the flow fed to the membrane was controlled at 0.8.

For comparison of the reactor performance, the conventional fixed bed reactor and the membrane reactor were operated under the same reaction condition. The products were analyzed with GC using a column packed with porapak Q. The selectivity for each product was calculated on the basis of carbon balance.

3. Results and discussion

Fig. 3 shows ethanol conversion and product selectivity with respect to the reaction temperatures in the fixed-bed reactor and in the inert membrane catalytic reactor under the same reaction condition. The total product distribution

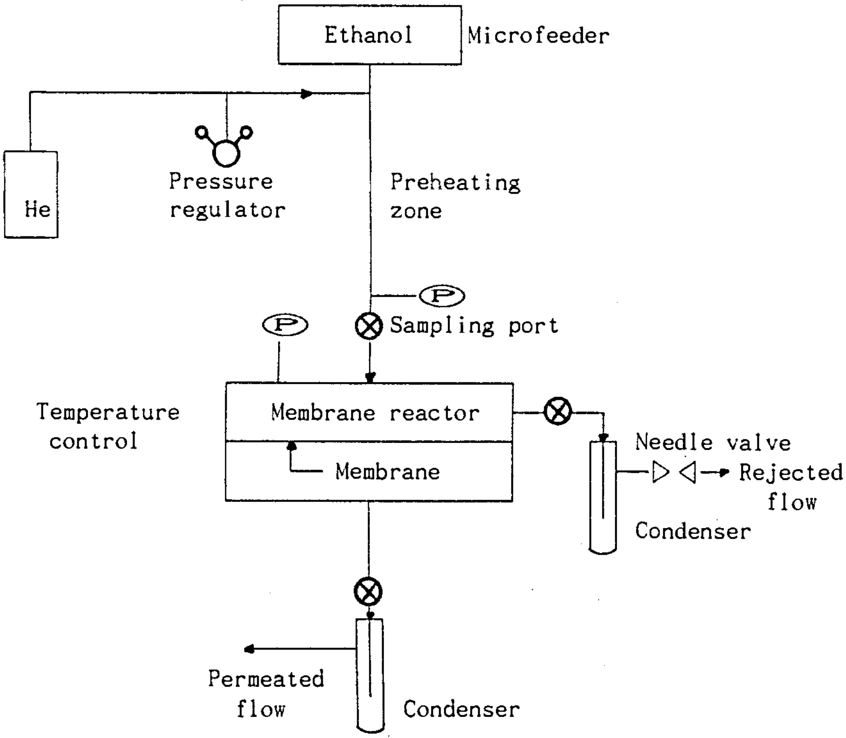

Fig. 2. Schematic flow diagram of inert polymer membrane catalytic reaction unit for ethanol dehydration.

determined at 150 °C on the basis of 100 mole of ethanol feed is presented for both reactors in table 1. The selectivity for ethylene in the permeated stream is 66.5%, about sevenfold of that from the fixed-bed reactor. It is noted that production of ethylene from the membrane reactor is much higher than that from

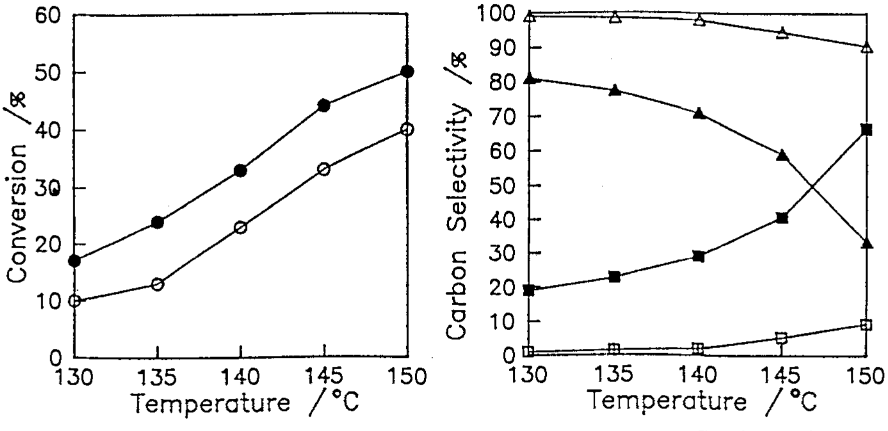

Fig. 3. Conversion and selectivity with respect to reaction temperature. Catalyst: 12-tungstophosphoric acid; W/F: 37-g-cat-hr/EtOH mole; Open symbol: fixed bed reactor; Closed symbol: permeated flow of inert membrane reactor; (□, ■) Ethylene; (△, ▲) Diethylether.

Table 1
Carbon balance in the effluent streams at 150 °C (basis: 100 mole of ethanol)

Fixed bed reactor			Inert membrane catalytic reactor					
			Permeated flow			Rejected flow		
EtOH	$C_2^=$	DEE	EtOH	$C_2^=$	DEE	EtOH	$C_2^=$	DEE
60	3.7	36.3	37.6	25	12.6	11.3	4.8	8.7

EtOH: Ethanol, $C_2^=$: Ethylene, DEE: Diethylether.

the fixed-bed reactor. This means that 11.1 moles of ethanol and 15 moles of diethylether was additionally converted to ethylene in the inert membrane reactor compared to the case of the fixed-bed reactor. It is believed that the high selectivity for ethylene results from the characteristic adsorption behavior of the heteropoly acid as well as from the selective permeation property of the PSF membrane.

The permeability of ethanol, ethylene, and diethylether through the PSF membrane has been measured in this laboratory. As shown in table 2, the permeability of ethylene is greater than those of ethanol and diethylether. However, the big difference in ethanol conversion and ethylene selectivity between two reactors cannot be explained only by the permeability difference of the reaction products. The result suggests that the less permeable ethanol and diethylether retained at the buffer zone are reabsorbed into the bulk of the heteropoly acid and converted into ethylene. Should the reaction take place only on the catalyst surface, which is less than 10 m^2/g-cat., the high conversion of ethanol and diethylether into ethylene can not be obtained.

In fig. 4, ethanol conversion and product selectivity in both reactors are plotted against the contact time. As expected, the selectivity for ethylene increases with the contact time.

4. Conclusions

It is concluded that in the inert membrane catalytic reactor composed of 12-tungstophosphoric acid and PSF membrane, the selective permeation of

Table 2
Permeability of pure components through polysulfone membrane at various temperatures

		130 °C	140 °C	150 °C
Permeability (cm^3-cm/cm^2-sec-cm Hg)	Ethylene	2.043E-8	2.129E-8	2.702E-8
	Ethanol	5.987E-9	6.084E-9	7.302E-9
	Diethylether	3.207E-9	3.703E-9	3.945E-9
Selectivity	$\alpha_{c2}=/\mathrm{EtOH}$	3.42	3.50	3.70
	$\alpha_{\mathrm{EtOH}}/\mathrm{DEE}$	1.87	1.64	1.85

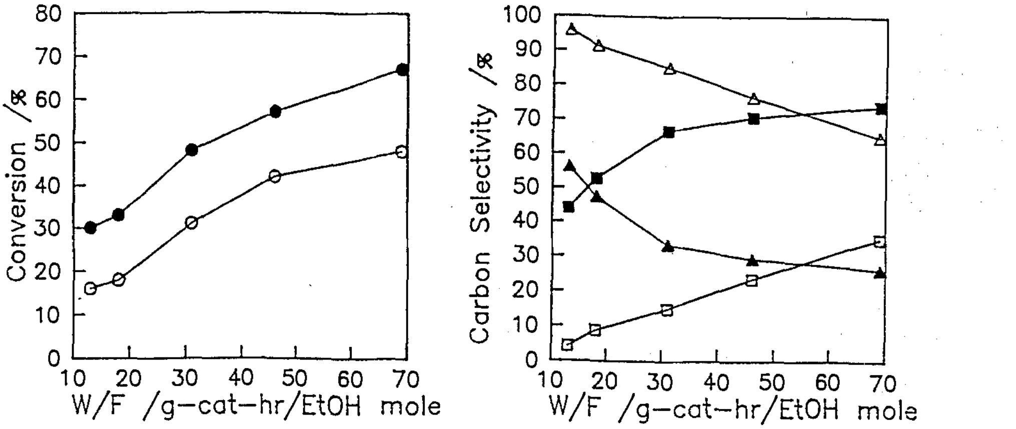

Fig. 4. Conversion and selectivity with respect to contact time. Catalyst: 12-tungstophosphoric acid; Reaction temp.: 150 ° C; Open symbol: fixed bed reactor; Closed symbol: permeated flow of inert membrane reactor; (□, ■): Ethylene; (△, ▲): Diethylether.

ethylene through the membrane and the reabsorption of diethylether into the bulk of the heteropoly acid yield the higher conversion of ethanol and the higher selectivity for ethylene than in the fixed-bed catalytic reactor.

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