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Methyl tert-butyl ether decomposition over heteropoly acid catalyst in a cellulose acetate membrane reactor

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In this study the methyl tert-butyl ether (MTBE) decomposition over $H_3PW_{12}O_{40}$ was carried out in a cellulose acetate membrane reactor. The permeability of methanol through the cellulose acetate membrane was about 30 and 300 times higher than that of either isobutene or MTBE, respectively. The isobutene selectivity in the fixed bed reactor was only slightly higher than the methanol selectivity due to the side reaction. In the cellulose acetate membrane reactor, however, the isobutene selectivity in the rejected stream was 68% and the methanol selectivity in the permeated stream was up to 97%. The MTBE conversion in the membrane reactor was about 7% higher than that in the membrane-free fixed bed reactor under the same reaction conditions. The enhanced performance of the membrane reactor in this reversible reaction was mainly due to the selective permeation of methanol which resulted in a methanol-deficient condition suppressing MTBE synthesis reaction.

Keywords: MTBE decomposition; isobutene; heteropoly acid; cellulose acetate; membrane reactor

1. Introduction

A membrane reactor is a unit which consists of a membrane and a reactor. Recently, the membrane reactor has been spotlighted due to its simultaneous function of chemical reaction and separation. By removing products selectively and continuously through a membrane from the reactor, the total reaction conversion may be improved markedly for equilibrium limited reversible reactions [1–3]. An inert membrane reactor consists of a catalyst on the feed side and a membrane [4]. Here the membrane is inert and serves as a barrier to the reactants and some of the products. Because of the thermal instability of the polymer membranes, the majority of investigations has been concentrated on the application of inorganic membrane reactors. Although inorganic membrane reactors have been mainly applied

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to decomposition reactions such as dehydrogenation [5–7], polymer membranes have more versatile applicabilities than inorganic membranes because polymer membranes show better diffusivity and solubility. However, not much progress has been made in the application of polymer membrane reactors due to thermal instability at high temperatures.

A heteropoly acid has acidic and redox catalytic properties [8]. It also shows a characteristic adsorption behavior [9] depending on the properties of adsorbates. Most non-polar chemicals are adsorbed only on its surface (surface area is less than 10 m^2/g) whereas polar compounds mostly penetrate into its bulk. Therefore, some reactions occur only on the surface while others mainly occur in the bulk of heteropoly acids. It is known [10] that methyl tert-butyl ether (MTBE) decomposition mainly occurs in the bulk phase of heteropoly acids because MTBE adsorption mainly occurs in the bulk.

MTBE synthesis and decomposition have been used to yield high purity isobutene from C_4 raffinates. When methanol reacts with C_4 fractions, only isobutene is reacted to yield MTBE [11] and subsequently the MTBE is cracked to obtain equimolar isobutene and methanol [12]. Although MTBE synthesis is an important process due to the increasing demand for MTBE, MTBE decomposition is also an attractive reaction due to the potential demand for pure isobutene. It is well known that the MTBE synthesis and the decomposition are a reversible and acid-catalyzed reaction.

In this study the MTBE decomposition was carried out in a polymer membrane reactor composed of a heteropoly acid catalyst and a polymer membrane. Among the heteropoly acids, 12-tungstophosphoric acid catalyst was used due to its strong acidic function. Cellulose acetate membrane was used as a constituent membrane of the membrane reactor.

2. Experimental

2.1. CATALYST PREPARATION

The 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) was prepared according to the method proposed by Tsigdinous [13]. It was prepared by using $Na_2WO_4\cdot 2H_2O$, $Na_2HPO_4\cdot 12H_2O$, water and HCl as the starting materials. An IR observation showed that the prepared catalyst kept the "Keggin structure", the characteristic structure of heteropoly acids. $H_3PW_{12}O_{40}$ was calcined at 300°C to remove the remaining water, before it was used in the membrane reactor. The catalyst was thermally stable during the reaction.

2.2. MEMBRANE PREPARATION

Cellulose acetate (denoted as CA hereafter) was purchased from Eastman Kodak Co. To prepare the CA membrane, various solvents were tested to find a solvent dissolving a CA. It was found that CA was highly soluble in acetone. The CA membrane was prepared by casting the CA (15 wt%)–acetone (85 wt%) solution on a glass plate and by drying it in air for 5–6 h and subsequently under vacuum for 2 h. It was soaked in water to separate the CA membrane from the glass plate. Finally, the CA membrane was dried in air for 10 h and under vacuum for 2 h. The thickness of the CA membrane was 16 μm. The glass transition temperature of CA was 125°C, and it was thermally stable during the reaction.

2.3. REACTION UNIT

Fig. 1 illustrates the detailed structure of the membrane reactor. The membrane reactor was composed of three brass bodies, catalyst support (teflon), CA membrane, and porous membrane support. A thermocouple was inserted to the catalyst bed to control the reaction temperature. In order to prevent leakage, the constituent bodies were sealed with O-rings and tightened up with bolts-nuts. The rejected flow was controlled by a needle valve. 1.22 cm^3/min of helium was introduced into the membrane reactor as a carrier gas. The permeated and the rejected helium flow rate were 0.52 and 0.7 cm^3/min, respectively. At this steady flow of helium, MTBE was sufficiently preheated for vaporization and fed into the reactor at the rate of $W/F = 178.3$ g-cat h/MTBE mole. The total reaction pressure was 1.3 atm (gauge pressure). The reacted stream from the catalyst bed passed through the buffer zone and continuously split into two streams, a rejected stream and a permeated stream. Another catalyst bed was also installed in the rejection side of the

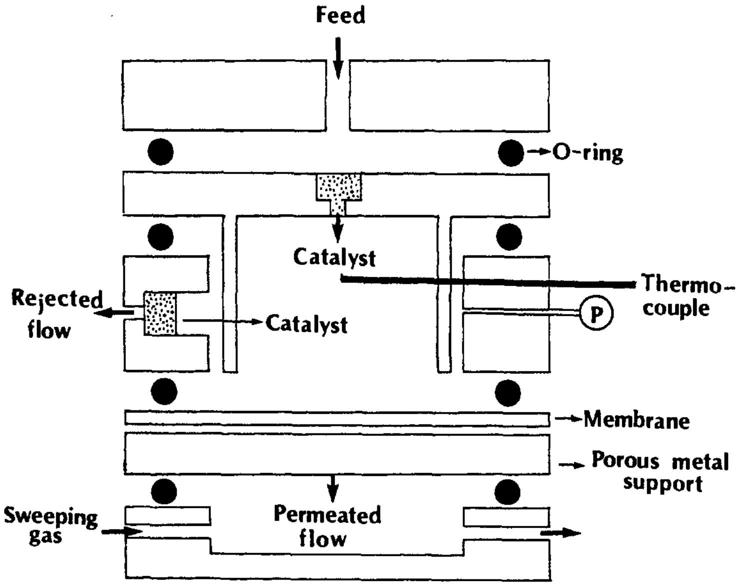

Fig. 1. The detailed structure of the inert membrane reactor.

membrane reactor for further reaction of the rejected stream like a shell plus tube type membrane reactor. The permeated stream was swept continuously by 3 cm^3/min of helium at 1 atm (absolute pressure). Helium did not permeate from the sweeping gas phase into the reactor and this did not affect the gas composition of the membrane reactor. The cross-sectional permeation area was 17.65 cm^2. The conventional fixed bed reactor and the membrane reactor were compared under the same reaction conditions to investigate the performance of the two reactors. After eliminating the membrane and blocking the permeated stream of the membrane reactor, it was used as a fixed bed reactor.

In order to confirm the reversibility of the reaction and to know the extent of reduction of product inhibition, a closed loop recycling reaction was carried out. The recycling reaction was accomplished by manipulating the valves of the continuous flow reactor. The steady state W/F was 36.38 g-cat h/MTBE mole before the recycling. The closed loop recycling membrane reactor means that there is no feed stream and only a rejected flow is recycled. For the comparison with the membrane reactor, the outward flow of the fixed bed reactor was also recycled. The reaction temperature and pressure were 100°C and 0.4 atm (gauge pressure), respectively. The compositions of the recycled flow were measured with time on stream.

The products were analyzed with GC using a column packed with Porapak Q. The MTBE conversion and product selectivity (methanol or isobutene/methanol + isobutene) were calculated on the basis of mole balance.

3. Results and discussion

In order to confirm the applicability of the CA membrane to the catalytic decomposition of MTBE, the permeabilities of MTBE, methanol and isobutene were measured with respect to reaction temperature as shown in table 1. It is essential that more products should permeate than the reactants in order for the membrane

Table 1
Permeability of reaction component through a cellulose acetate membrane

		Temperature (°C)			
		80	90	100	110
permeability[a]	methanol	79.26	75.54	65.92	71.67
	isobutene	2.96	2.74	2.32	2.18
	MTBE	0.212	0.207	0.147	0.224
selectivity (permeability ratio)	methanol/isobutene	26.7	27.5	28.4	32.8
	isobutene/MTBE	13.96	13.24	15.48	9.73
	methanol/MTBE	369.1	364.8	447.6	320.1

[a] (cm^3 cm/cm^2 s cmHg) × 10^9.

reactor to show better performance than the fixed bed reactor. In this reaction system, higher permeability of methanol or isobutene than of MTBE is favorable. As shown in table 1, the permeability of methanol is greater than that of either isobutene or MTBE. The reactant MTBE is the least permeable component. The permeability of methanol through the CA membrane is about 30 and 300 times higher than that of either isobutene or MTBE, respectively. This fact means that the selective permeation of methanol through the membrane may shift the chemical equilibrium or may cause the reduction of product inhibition towards further MTBE decomposition by making a methanol-deficient condition in this reversible reaction. It also means that the permeated stream is a methanol-rich flow and the rejected stream is an isobutene-rich flow.

It is generally believed that the permeability through a polymer membrane is controlled by both diffusivity and solubility. Solubility decreases but diffusivity increases with the increase of temperature. Permeability, defined as the product of diffusivity and solubility, increases with the increase of temperature because the increasing rate of diffusivity is generally greater than the decreasing rate of solubility [14]. However, it was found that the permeabilities of reaction components through the CA membrane decrease with an increase in temperature. It can be inferred from the result that the decreasing rate of the solubility of reaction components through the CA membrane is greater than the increasing rate of the diffusivity of reaction components through the membrane.

Fig. 2 shows the steady state MTBE conversions with respect to reaction temperature in two reactors, the fixed bed reactor and the CA membrane reactor. As expected from the permeability data, the MTBE conversion over $H_3PW_{12}O_{40}$ in the CA membrane reactor was about 7% higher than that in the membrane-free fixed

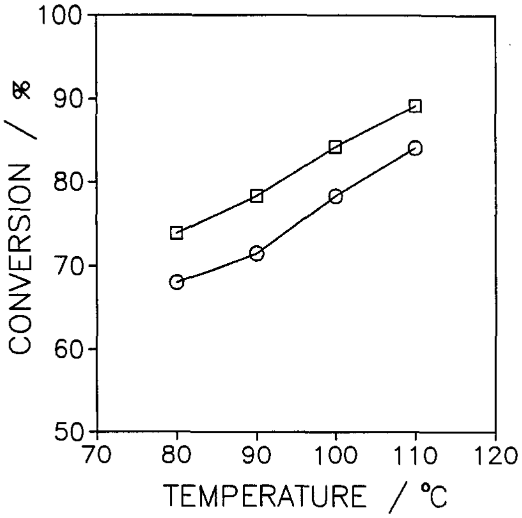

Fig. 2. MTBE conversion with respect to reaction temperature, $W/F = 178.3$ g-cat h/MTBE mole, $P = 1.3$ atm. (□) Membrane reactor, (○) fixed bed reactor.

bed reactor. In other words, we can reduce the reaction temperature by 10°C in the membrane reactor to achieve the same MTBE conversion as in the fixed bed reactor. In both cases, the reaction pressure was kept at 1.3 atm (gauge pressure) and W/F was 178.3 g-cat h/MTBE mole. The total helium flow rate was 1.22 cm^3/min and the permeated helium flow rate in the membrane reactor was 0.52 cm^3/min. Because the sweeping helium (1 atm in absolute pressure) did not permeate from the sweeping gas phase into the membrane reactor, the enhanced performance of the membrane reactor was not due to dilution effect. In general, the enhanced performance of a membrane reactor is due to a shift in equilibrium or a reduction of product inhibition. Because the reaction conditions in this experiment were not equilibrium conditions at that temperature and pressure, the conversions in fig. 2 were not equilibrium conversions but steady state conversions. Therefore, the enhanced performance of the CA membrane reactor is mainly due to the selective permeation of methanol and the rejection of MTBE through the CA membrane causing the reduction of product inhibition rather than the shift in equilibrium.

The performance of a membrane reactor depends on not only permselectivity but also permeation amounts. The permeation amounts are affected by permeability and the surface area of the membrane per unit volume of the membrane. Considering the relatively small permeation area of the tested CA membrane reactor, it is expected that the performance of the CA membrane reactor can be enhanced by changing the membrane module to the direction of increasing membrane area per unit volume of the membrane.

Fig. 3 shows isobutene selectivities in two reactors with respect to reaction temperature. Isobutene selectivities in the permeated flow and in the rejected flow are

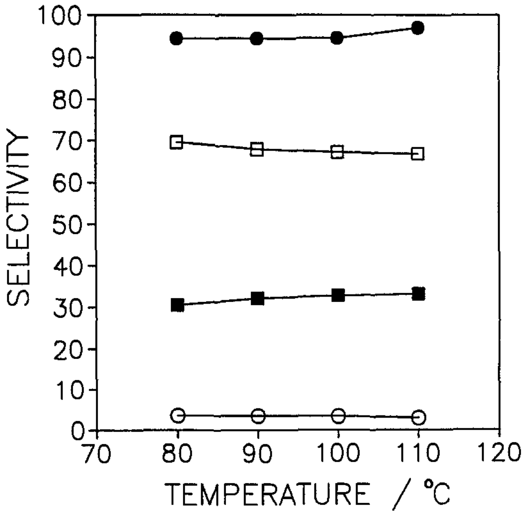

Fig. 3. Isobutene and methanol selectivity of the inert membrane reactor with respect to reaction temperature, $W/F = 178.3$ g-cat h/MTBE mole, $P = 1.3$ atm. Open symbols: isobutene, closed symbols: methanol. (○, ●) Permeated stream, (□, ■) rejected stream.

about 3 and 68%, respectively. The isobutene selectivity in the rejected stream is smaller than the methanol selectivity in the permeated stream. This is due to the following two factors. One is the small permeation area of the membrane resulting in small amount of methanol permeation, the other is that additional equimolar amounts of methanol and isobutene were produced due to further decomposition of MTBE when the rejected stream flowed through another catalyst bed installed in the rejection part.

Fig. 4 shows isobutene selectivities in two closed recycle reactors. In the closed recycle membrane reactor, the rejected flow was continuously recycled to the reactor inlet. Since the decomposition of one mole MTBE yields equimolar amounts of isobutene and methanol, ideal selectivity of isobutene is 50%. Isobutene selectivity in the fixed bed reactor slightly increased due to the side reaction, methanol dehydration to dimethylether, as the recycle reaction continued. The isobutene selectivity in the membrane reactor, however, increased continuously as the recycle continued. These results mean that the most rejected MTBE by the CA membrane in the membrane reactor was continuously decomposed into isobutene and methanol. The decomposed methanol permeates rapidly through the membrane, whereas isobutene retains by the membrane. Moreover, the rapid permeation of methanol in the membrane reactor has a merit such that the dehydration of methanol to dimethylether can be prevented.

4. Conclusions

In this work the MTBE decomposition reaction was carried out in a CA membrane reactor. The permeability of methanol through a CA membrane was about

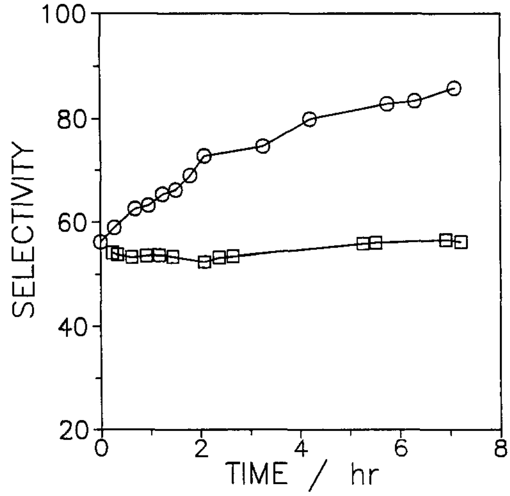

Fig. 4. The variation of isobutene selectivity in two closed recycle reactors at 100°C, $W/F = 36.38$ g-cat h/MTBE mole, $P = 0.4$ atm. (○) Membrane reactor, (□) fixed bed reactor.

30 and 300 times higher than that of either isobutene or MTBE, respectively. It was revealed that the MTBE conversion over $H_3PW_{12}O_{40}$ in the CA membrane reactor was about 7% higher than that in the membrane-free fixed bed reactor. In other words, the reaction temperature in the membrane reactor can be reduced by 10°C to achieve the same MTBE conversion as in the fixed bed reactor. The good performance of the membrane reactor is mainly due to the selective permeation of methanol which made a methanol-deficient phase suppressing MTBE synthesis.

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