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An experimental study on the application of polymer membranes to the catalytic decomposition of MTBE (methyl *tert.*-butyl ether)

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Abstract

In this experimental study, the methyl *tert.*-butyl ether (MTBE) decomposition was carried out in various inert membrane reactors composed of $H_3PW_{12}O_{40}$ and a polymer membrane. Polycarbonate (PC), polyarylate (PA) and cellulose acetate (CA) membranes were used in the membrane reactor. It was revealed that all the tested polymer membranes showed larger permeability of methanol than that of either MTBE or isobutene, and the membrane reactor showed better performance than the corresponding fixed bed reactor. The perm-selectivity of methanol/MTBE was in the order of CA > PC > PA, and the permeation ratio of product/MTBE was in the order of CA > PA > PC. Among the membrane reactors tested, CA membrane reactor showed the best performance. The enhanced performance of the membrane reactor was mainly due to the selective permeation of methanol that made a methanol-deficient phase suppressing MTBE synthesis reaction in the reversible reaction.

1. Introduction

Recently, membrane technology occupies an important position in various chemical processes. One of the frontier applications utilizing membranes is a membrane reactor. A membrane reactor is a unit that acts as a separator and a reactor simultaneously. By removing products selectively and continuously through a membrane from the reactor, the total conversion of reaction may be improved markedly for equilibrium limited reversible reactions [1-3]. Although most investigations are concentrated on the inorganic membrane reactors for their good thermal stability, their applications have been confined to the reactions concerned with small molecules or decomposition reactions such as dehydrogenation reactions [4-7]. The organic membrane reactors have more versatile applicabilities than inorganic membrane reactors because the organic membranes separate substances by both diffusivity and solubility [8-11]. However, not much progress has been made in the polymer membrane reactors due to the thermal instability of the organic membranes.

MTBE (methyl *tert.*-butyl ether) 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 [12] and subsequently MTBE is cracked to obtain equimolar amounts of isobutene and methanol [13]. Although MTBE synthesis is an important process because MTBE demand as an octane booster increases, MTBE decomposition reaction is also an attractive reaction due to the potential demand for pure isobutene. It is well

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known that the MTBE synthesis and decomposition are reversible and acid-catalyzed reactions.

In this experimental study, the MTBE decomposition was carried out in various inert polymer membrane reactors. 12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$) catalyst was used due to its strong acidic function. PC, PA and CA membranes were prepared and tested for the MTBE decomposition reaction in order to investigate the performances of the membrane reactors.

2. Experimental

2.1. Catalyst and membrane preparation

$H_3PW_{12}O_{40}$ (PW) was prepared according to the method proposed by Tsigdinos [14] by using Na_2WO_4 $42H_2O$, Na_2HPO_4 $12H_2O$, water and HCl as starting materials.

It was found that PC and PA were highly soluble in chloroform and CA was dissolved in acetone. After a polymer was fully dissolved in a solvent, the solution was casted on a glass plate with constant thickness and it was dried for 5–6 h in air. Subsequently, it was immersed into water to separate a membrane from the glass plate. Finally, the prepared membrane was further dried in air for 10 h and under vacuum for 2 h to evaporate the remaining solvent. The glass transition temperatures (T_g) of PC, PA and CA are 141, 194 and 125°C, respectively. The compositions of polymer solution for each membrane are shown in Table 1.

Table 1
Permeability of reaction component through each polymer membrane at 100°C

		Membranes		
		PC	PA	CA
Permeability (cm^3 cm/cm^2 sec cm Hg) $\times 10^9$	Methanol	1.66	15.08	65.92
	Isobutene	0.12	5.87	2.32
	MTBE	0.32	3.65	0.15
Selectivity (permeability ratio)	Methanol/isobutene	13.83	2.57	28.41
	Isobutene/MTBE	0.38	1.61	15.47
	Methanol/MTBE	5.19	4.13	439.47
Permeation ratio of product/MTBE		5.56	5.74	454.93
Polymer contents in solution (wt.-%)		7	5	15

2.2. Reaction unit

Fig. 1 illustrates the detailed structure of a disc type membrane reactor. This reactor was partly modified from the previous one [15]. The disc type membrane reactor was composed of three brass bodies, catalyst support (teflon), membrane, and porous support for membrane. All constituent bodies were sealed with o-rings and tightened up with bolt-nuts. The MTBE was sufficiently preheated for vaporization and fed into a reactor with helium as a carrier gas. The exit stream from the catalyst (A) bed positioned at the inlet of the reactor passed a buffer zone and was split into two streams by the membrane, a rejected stream and a permeated stream. The permeated stream was continuously swept by helium (3 cm^3/min). The rejected stream passed through the catalyst (B) bed located at the rejection part to increase the conversion of unreacted MTBE. The rejected and the permeated stream were analyzed by on-line G.C. using a column packed with Porapak Q. In order to compare the performance of the membrane and fixed bed reactors, a membrane reactor was modified to a fixed bed reactor by removing the membrane parts and plugging the inlet and outlet for the sweeping gas flow. The reaction conditions such as temperature and pressure of two type reactors were controlled to be equal. For a closed loop recycling reaction, only a rejected stream in the membrane reactor was recycled to the feed inlet by manipulating valves in the steady-state continuous flow membrane

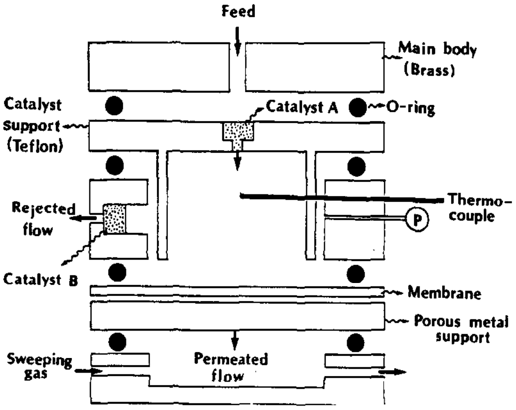

Fig. 1. The detailed structure of a disc type membrane reactor.

Table 2
Performance of various disc type polymer membrane reactors at 100°C (W/F = 178.3 g cat h/MTBE mol; membrane area = 17.65 cm^2)

Polymer	Membrane thickness (mm)	Reaction pressure (atm)	Carrier helium (cm^3/min)	MTBE conversion		Selectivity	
				Membrane reactor	Fixed bed reactor	Isobutene in rejected stream	Methanol in permeated stream
PC	0.017	1.3	1.35	82.6	79.8	60.6	93.2
PA	0.017	1.45	0.75	78.6	75.5	63.2	83.5
CA	0.016	1.3	1.22	84.2	78.3	67.2	96.6

reactor. The closed loop recycle reactor means that there is no feed [9]. In the fixed bed reactor, the recycle was accomplished by recycling the exit flow to the inlet. The MTBE conversion and the product selectivity (isobutene or methanol/isobutene + methanol) were calculated on the basis of mole balance. The effective membrane area was 17.65 cm^2. The specific reaction conditions and the membrane conditions were illustrated in Table 2 and in each figure.

A shell and tube type (tubular type) reaction unit [16] was also used. The CA membrane was rolled on the outside of a perforated inner glass tube and was sealed with an epoxy resin. A Pyrex tube was used as an outer shell. The inner tube and the outer shell were isolated by o-rings and connected with a joint made of aluminum. The catalysts were placed in the shell side. The reaction was carried out in the shell side and the product permeated through the membrane to the tube side. The permeated flow in the tube side was continuously swept by sweeping gas. The effective membrane area was 123 cm^2. The carrier helium flow rate and the sweeping helium flow rate was 5.1 and 12 cm^3/min, respectively. The reaction procedure was similar to the disc type membrane reaction.

3. Results and discussion

3.1. Permeability and perm-selectivity

It is essential that products permeate more rapidly than the reactant through the membrane in order for the membrane reactor to show an enhanced performance. In this point of view, the lower permeability for MTBE and higher permeability for isobutene and methanol are favorable in this reaction system. In order to find the applicability of each membrane to the MTBE decomposition reaction, the permeabilities of methanol, isobutene and MTBE were measured at 100°C and the results were given in Table 1. All membranes showed higher permeability for methanol than for MTBE or isobutene. The selective permeation of methanol through the membrane means that the permeated stream is methanol rich and the rejected stream is isobutene rich. It also means that further MTBE decomposition may take place because the backward reaction, the MTBE synthesis, would be suppressed when the methanol-deficient rejected flow passes the catalyst (B) bed at the rejection part. The perm-selectivity of methanol/MTBE was in the order of CA > PC > PA, and the permeation ratio of product/MTBE was in the order of CA > PA > PC. Especially, the CA membrane shows about 30 and 440 times higher permeability of methanol than that of isobutene and MTBE, respectively. It can be inferred from this that the CA membrane reactor would show the best performance.

3.2. Performance of the disc type membrane reactor

Table 2 shows the steady-state MTBE conversion in two reactors and the selectivities for isobutene and methanol in the membrane reactor. MTBE conversion in the membrane reactor involves conversions in both rejected stream and permeated stream. As shown in Table 2, however, each membrane reactor exhibited higher conversion than the corresponding fixed bed reactor, even though the rejected stream only passed the catalyst (B) in the membrane reactor while the whole stream passed both catalyst (A) and catalyst (B) in the fixed bed reactor. This enhanced performance of the membrane reactor is mainly due to the selective permeation of methanol through the membranes that causes the reverse reaction to be suppressed.

In actual experiments, it was very difficult to maintain the same reaction conditions for all membrane reactors due to the different permeation properties of the membranes. However, we tried to maintain the experimental reaction conditions as similar as possible. Since one mole of MTBE decomposes into equimolar amounts of methanol and isobutene, the ideal selectivity of isobutene is 50% in a fixed bed reactor. As presented in Fig. 2, however, the isobutene selectivity in the fixed bed reactor was slightly higher than 50% because a small amount of dimethylether was formed by methanol dehydration. The isobutene selectivities in the rejection side of the membrane reactor ranged from 60 to 67% depending on the membrane materials. The isobutene selectivity in the rejected stream is smaller than the methanol selectivity in the permeated stream. This is mainly because additional equimolar amounts of methanol and isobutene were produced by the decomposition of MTBE in the rejected stream when it passed through the catalyst (B) bed in the rejection part.

3.3. *Performance of the tubular type CA membrane reactor*

Generally, the performance of a membrane reactor depends not only on perm-selectivity but also on the amount of permeation. The permeation amounts are affected by permeability and the effective permeation area of the membrane. Fig. 2 shows the steady-state MTBE conversion and isobutene selectivity in the rejected stream from a tubular type CA membrane reactor. The MTBE conversion in the membrane reactor was about 10% higher than that in the fixed bed reactor at 100°C. In other words, the reaction temperature for the tubular type reactor can be lowered by 20°C to achieve the same MTBE conversion in the fixed type one.

It is believed that better performance of this reactor in comparison with the disc type membrane reactor is mainly due to the large permeation area in the membrane. Another noticeable feature is that conversion ratio of the membrane reactor to the fixed bed reactor is higher at low temperatures than at high temperatures. In the exit stream from the catalyst (A) bed, there are larger amounts of undecomposed MTBE at lower reaction temperatures. Therefore, when the methanol-deficient flow rejected by the membrane passes the catalyst (B) bed, the opportunity of further MTBE decomposition is greater at a lower temperature.

The isobutene selectivity in the rejected stream of the tubular type CA membrane reactor increases with the reaction temperature. This is mainly because a large amount of isobutene was rejected at high temperature and, as expected from conversion curves in Fig. 2, equimolar isobutene and methanol were comparatively more formed by the additional MTBE decomposition in the catalyst (B) bed at low temperature. It was also found that the isobutene selectivity in the rejected flow increased to some extent as the sweeping gas

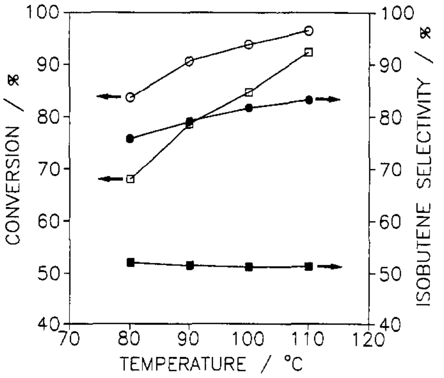

Fig. 2. MTBE conversion and isobutene selectivity in two reactors with reaction temperatures, where the isobutene selectivity of the membrane reactor represents the selectivity in the rejection side, $W/F = 475.4$ g cat h/MTBE mole, $P = 0.53$ atm, carrier helium flow rate = 5.1 cm^3/min. (○,●), shell and tube type CA membrane reactor (permeation area = 123 cm^2); (□,■), fixed bed reactor.

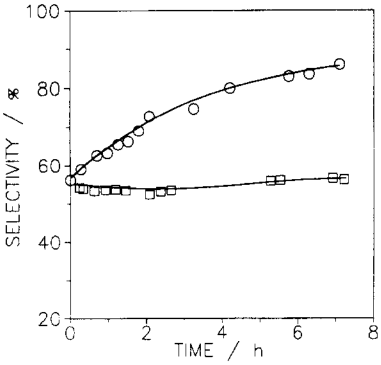

Fig. 3. The variation of isobutene selectivity in two closed recycle reactors at 100°C, where the isobutene selectivity of the membrane reactor represents the selectivity in the recycled stream, $W/F = 36.38$ g cat h/MTBE mole, $P = 0.4$ atm. (○), disc type CA membrane reactor (permeation area = 17.65 cm^2); (□), fixed bed reactor.

flow rate increased, because methanol removal by the sweeping gas accelerated the permeation of methanol through the membrane.

3.4. Reduction of MTBE production

Fig. 3 shows the isobutene selectivity in two closed recycle reactors [9], a disc type CA membrane reactor and a fixed bed recycle reactor. In the closed loop recycling membrane reactor, only the rejected flow was continuously recycled to the reactor inlet. As the recycle continued, the isobutene selectivity in the fixed bed reactor slightly increased due to the side reaction, methanol dehydration to dimethylether. However, MTBE conversion and isobutene selectivity in the membrane reactor increased continuously. This is a typical advantage of the membrane reactor over the conventional reactors. It indicates that the unreacted MTBE in the membrane reactor could be continuously decomposed by suppressing the backward reaction, the MTBE synthesis, due to the selective removal of methanol.

4. Conclusions

In this experimental study, the MTBE decomposition was carried out in various inert membrane reactors composed of PW and a polymer membrane. CA, PA and PC membranes were used in the membrane reactor. It was revealed that all membranes showed higher permeability for methanol than for MTBE or isobutene. All membrane reactors showed higher MTBE conversion than the fixed bed reactor. The CA membrane reactor showed the best performance. The enhanced performance of the membrane reactor was mainly due to the selective permeation of methanol which made a methanol-deficient phase suppressing the MTBE synthesis reaction in the reversible reaction.

Acknowledgements

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