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Performance of shell and tube-type membrane reactors equipped with heteropolyacid-polymer composite catalytic membranes

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Abstract

Experimental studies on the performance of shell and tube-type membrane reactors equipped with heteropolyacid-polymer composite catalytic membranes were carried out for the vapor-phase decomposition of MTBE (methyl *tert*-butyl ether). Three types of catalytic membranes comprised of 12-tungstophosphoricacid ($H_3PW_{12}O_{40}$, PW) and polyphenylene oxide (PPO) were designed in this work. The PW-PPO/Al_2O_3 (type-1), PW-PPO/PPO/Al_2O_3 (type-2) and PW/PPO/Al_2O_3 (type-3) catalytic membranes not only showed catalytic reactivity for the reaction, but also were perm-selective for the reaction species. The selective removal of methanol through the catalytic membrane led to an equilibrium shift in a direction favorable to MTBE decomposition. Among three types of catalytic membrane reactor, the PW-PPO/PPO/Al_2O_3 (type-2) catalytic membrane reactor showed the best performance. The enhanced performance of the PW-PPO/PPO/Al_2O_3 (type-2) catalytic membrane reactor can be attributed to the intrinsic perm-selective capabilities of the PW-PPO catalytic membrane and the sub-layered PPO membrane.

Keywords: Heteropolyacid catalyst; Polyphenylene oxide membrane; Blending; Composite catalytic membrane; Methyl *tert*-butyl ether decomposition

1. Introduction

Catalytic membrane reactor (CMR) technology represents a currently challenging research topic in the fields of membrane science and catalytic reaction engineering. A membrane reactor is composed of a membrane and a catalytic reactor. As a result, a membrane reactor allows for significant improvements in total reaction conversion and product yield, for the case of equilibrium limited reversible reactions, by continuously removing reaction products from the reactor through a permeable membrane [1–3]. Most investigations of catalytic membrane reactors have focused on the use of inorganic membranes because of their excellent thermal stability at high reaction temperatures [4,5]. Although applications of inorganic membrane reactors have been made on the reactions concerned with small molecules or decomposition reactions at high temperature [6], polymer membrane reactors can be applied to low-temperature reactions with versatile applicability. However, only a few studies on polymer membrane reactors have been reported [7–9]. In their works, polysulfone and cellulose acetate membranes were utilized for the decomposition of organic material on the gas phase in the packed bed membrane reactor (PBMR).

Heteropolyacid (HPA) catalysts have both acid and redox catalytic properties. They also show

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characteristic adsorption behaviors depending on the properties of the adsorbates [10,11]. One of the distinctive features of HPAs is that they are highly soluble in polar solvents such as water, alcohols and amines, but have generally poor solubility in non-polar chemicals such as benzene and olefins [12]. By taking advantage of these solubility properties, HPAs can be blended with polymer materials using a common or a mixed solvent to form a membrane-like film [13]. Highly dispersed HPA catalysts can be prepared by this technique [14,15]. It has been reported that HPA-polymer composite films, when used as fixed-bed solid catalysts, showed an enhanced catalytic activity for ethanol conversion reaction compared to the mother catalyst [16,17]. It is well known that HPAs are active for MTBE (methyl *tert*-butyl ether) synthesis and decomposition [18]. Although MTBE synthesis is an important chemical process, its decomposition is also an attractive chemical process, because of the potential demand for pure isobutene. The synthesis and decomposition of MTBE represents a reversible and acid-catalyzed reaction [19–21]. Theoretically, 1 mol of MTBE decomposes into equimolar amounts of methanol and isobutene.

This study reports on a method for preparing HPA-polymer composite membranes and their successful use in catalytic membrane reactors as catalytic membranes. A shell and tube-type membrane reactor was designed in order to evaluate the performance of HPA-polymer composite catalytic membranes. The vapor-phase decomposition of MTBE was examined in the membrane reactors as a model reaction.

2. Experimental

2.1. Materials

12-Tungstophosphoricacid (PW, $H_3PW_{12}O_{40}$ from Aldrich Chem. Co.) was used as an active catalyst for the vapor-phase decomposition of MTBE. Polyphenylene oxide (PPO, poly-2,6-dimethyl-1,4-phenylene oxide from Aldrich Chem. Co.) was used as a membrane material. Chloroform was used as a solvent for PPO while methanol was used as a solvent for PW. A porous double-layered alumina tube (I.D.: 0.74 cm, O.D.: 1.0 cm, inside pore diameter: 0.02 μm, outside pore diameter: 13 μm) was used as a support for the catalytic membrane.

2.2. Design of catalytic membrane and membrane reactor

Fig. 1 shows the detailed structure of the shell and tube-type catalytic membrane reactor. Three types of HPA-polymer composite catalytic membranes were designed for use in the membrane reactor. A porous α-Al_2O_3 tube was used as both an

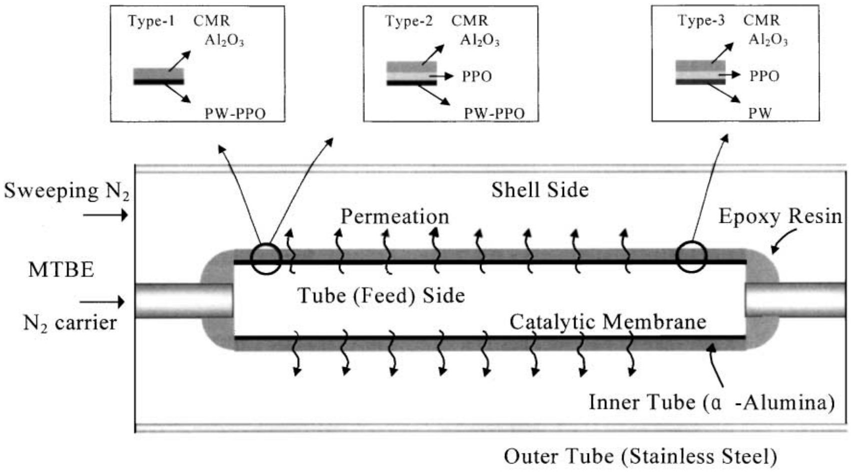

Fig. 1. Detailed structure of the shell and tube-type membrane reactor equipped with heteropolyacid-polymer composite catalytic membrane.

inner tube of the membrane reactor and as a support for the catalytic membrane. A homogeneous solution of PPO-chloroform was coated by a dip coating method on the tube side of the Al_2O_3 to form PPO/Al_2O_3, which was subsequently dried at 100°C for 1 h. A second homogeneous solution of PW-PPO-methanol-chloroform was prepared at room temperature, and coated onto the Al_2O_3 to give PW-PPO/Al_2O_3 (type-1) or onto the PPO/Al_2O_3 to give PW-PPO/PPO/Al_2O_3 (type-2). PW/PPO/Al_2O_3 (type-3) was prepared by coating a homogeneous solution of PW-methanol-chloroform onto the PPO/Al_2O_3. The effective length of the catalytic membrane reactor was ca. 4.5 cm. All the end portions of the Al_2O_3 tube were sealed with epoxy resin. A stainless steel tube was used as an outer tube. No leakage was detected prior to the reaction.

2.3. Reaction

The catalytic membrane reactor was conditioned at the indicated reaction temperatures for 12 h by passing a stream of N_2 through the system prior to the reaction. MTBE was sufficiently vaporized and continuously fed into the catalytic membrane reactor, along with the N_2 carrier (3.5–10.5 cm^3/min). The contact time (W/F_{MTBE}) was varied by controlling the amounts of MTBE. The performance of catalytic membrane reactor was examined at temperatures ranging from 80 to 100°C and at the tube side total pressures ranging from 1.0 to 2.3 atm. The permeated stream was continuously removed by sweeping with N_2 gas (4.0 cm^3/min). The permeated (shell side) and reacted (tube or feed side) streams were periodically sampled and analyzed by gas chromatography. MTBE conversion and isobutene selectivity in the feed (tube) side were calculated as follows: A represents the amount of MTBE in the feed flow, and B, D and E are the amounts of MTBE, isobutene and methanol, respectively, in the effluent flow of the tube side, while C indicates the amounts of MTBE in the permeation (shell) side of the reactor.

$$\text{MTBE conversion (\%)} = \left[\frac{1-(B+C)}{A}\right] \times 100 \quad (1)$$

$$\text{Isobutene selectivity (\%) in the feed side} = \left[\frac{D}{(D+E)}\right] \times 100 \quad (2)$$

3. Results and discussion

3.1. SEM images of the catalytic membrane

Fig. 2 shows the cross-sectional SEM images of Al_2O_3, PW-PPO/Al_2O_3 (type-1), PW-PPO/PPO/Al_2O_3 (type-2), and PW/PPO/Al_2O_3 (type-3) catalytic membranes. It is clear that PPO or PW-PPO was coated well on the Al_2O_3 tube, and that the pores of the Al_2O_3 tube were filled with PPO or PW-PPO. The coating thickness was not entirely uniform along the tube. The PW-PPO layer was clearly distinguishable from PPO/Al_2O_3 layer, as shown in Fig. 2(c). No visible evidence for the presence of the PW catalyst was found in the SEM images of the type-1 and type-2 catalytic membranes. This indicates that PW was highly dispersed as fine particles throughout these catalytic membranes. However, solid agglomerations of PW catalyst were formed in the type-3 catalytic membrane, as shown in Fig. 2(d).

3.2. Performance of catalytic membrane reactor

The performance of membrane reactors equipped with three types of composite catalytic membrane was examined. Fig. 3 shows the conversion of MTBE in the three reactors with respect to contact time. It is noteworthy that all the catalytic membranes showed catalytic activities in the decomposition of MTBE. The MTBE conversions were increased with increasing reaction temperature and contact time. However, the conversions of MTBE in the three reactors were not directly comparable because of differences in the amounts of PW loaded.

In order to verify differences in the performance of the composite catalytic membranes, isobutene selectivities in the tube and shell side of the catalytic membrane reactor were measured, as shown in Fig. 4. If the catalytic membranes were not perm-selective for the reaction species, the isobutene selectivity in the feed side should be 50%. According to our recent report [22], the permeabilities through a pure PPO membrane were in the following order: methanol $\gg$ isobutene $\approx$ MTBE. This means that the permeated stream is a methanol-rich flow while the reacted (rejected) flow is an isobutene-rich flow. It can be seen from Fig. 4 that all the catalytic membranes have perm-selective

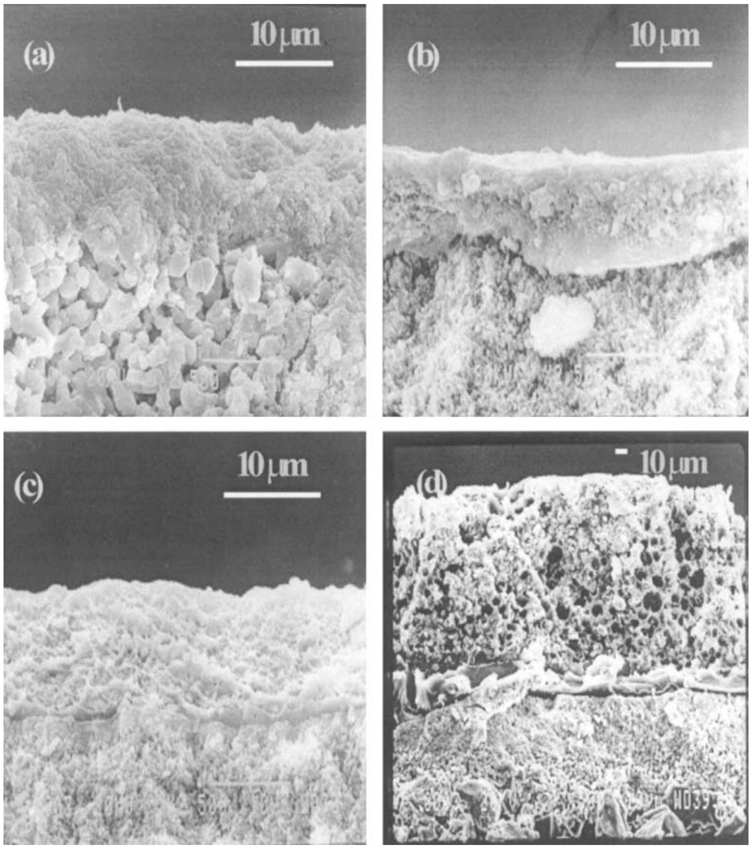

Fig. 2. Cross-sectional SEM images of (a) Al_2O_3; (b) PW-PPO/Al_2O_3 (type-1); (c) PW-PPO/PPO/Al_2O_3 (type-2); and (d) PW/PPO/Al_2O_3 (type-3).

capabilities for the reaction species, although different trends are observed in the three reactors. The selectivities for isobutene attained in the type-1 and type-3 catalytic membrane reactors remained constant at values of ca. 59 and 56%, as shown in Fig. 4(a) and (c), respectively. These values were higher than the theoretical value of 50%, which could be attained in a normal catalytic reactor. This indicates that PW-PPO (active phase of the type-1 catalytic membrane) and PW/PPO (active phase of the type-3 catalytic membrane) clearly have intrinsic perm-selectivity for the reaction species.

On the other hand, however, isobutene selectivities in the type-2 catalytic membrane reactor were increased with increasing contact time, as shown in Fig. 4(b). Isobutene selectivities in the type-2 catalytic membrane reactor were higher than those in the type-1 and type-3 catalytic membrane reactors, for contact times higher than ca. 8 g-PW-h/mol. Because the permeabilities of the reacted species were different through the catalytic membrane or pure membrane, the different behaviors between the type-1, type-3, and type-2 CMR were raised. Type-1 and type-3 catalytic membranes were not as efficient as the type-2 catalytic membrane. We conclude that the enhanced performance of the type-2 catalytic membrane reactor can be attributed to the intrinsic perm-selective capabilities of the PW-PPO catalytic membrane and the sub-layered PPO membrane. Differences in the separation capabilities of three types of catalytic membrane were also confirmed by measuring the isobutene selectivities in the feed and shell side as a function of cut-off, as shown in Fig. 5. Cut-off was defined as the ratio of permeation moles/feed moles. Isobutene

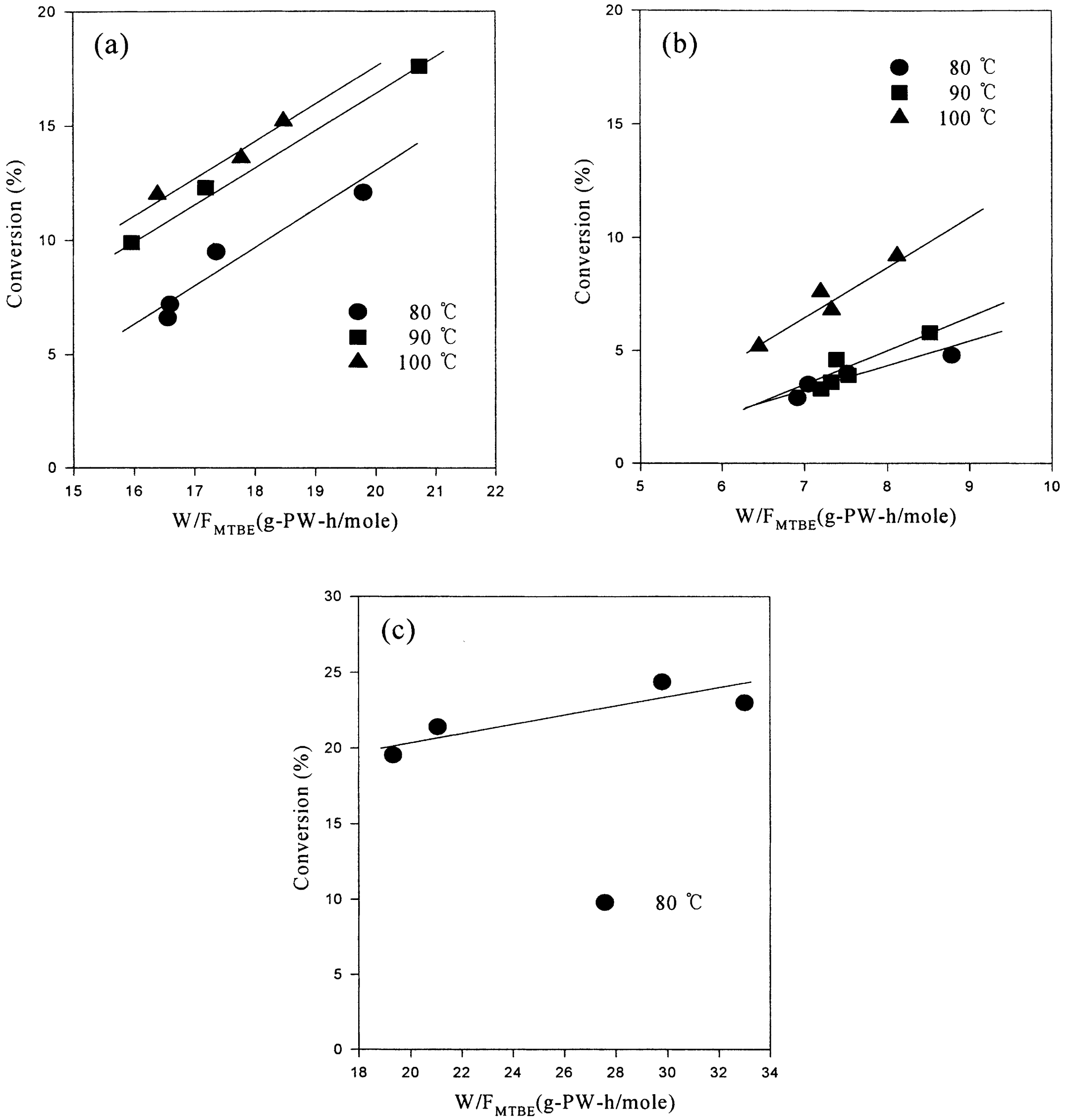

Fig. 3. MTBE conversions in the feed side of the catalytic membrane reactor with respect to contact time: (a) PW-PPO/Al_2O_3 (type-1, PW = 0.023 g); (b) PW-PPO/PPO/Al_2O_3 (type-2, PW = 0.01 g); and (c) PW/PPO/Al_2O_3 (type-3, PW = 0.066 g).

selectivities in the feed side of the type-1 and type-3 catalytic membrane reactors remained constant regardless of the cut-off variation. However, the isobutene selectivities in the type-2 catalytic membrane reactor increased in a linear manner with increasing cut-off. As shown in Fig. 5, isobutene selectivities of the type-2 catalytic membrane reactor was superior to the type-1 and type-3 catalytic membrane reactors in the range of cut-off higher than 0.01.

It can be inferred that the separation capability of PW-PPO/Al_2O_3 (type-1) catalytic membrane is determined by the PW-PPO layer alone. Reaction and separation occur simultaneously in this layer, and MTBE would be expected to permeate through the

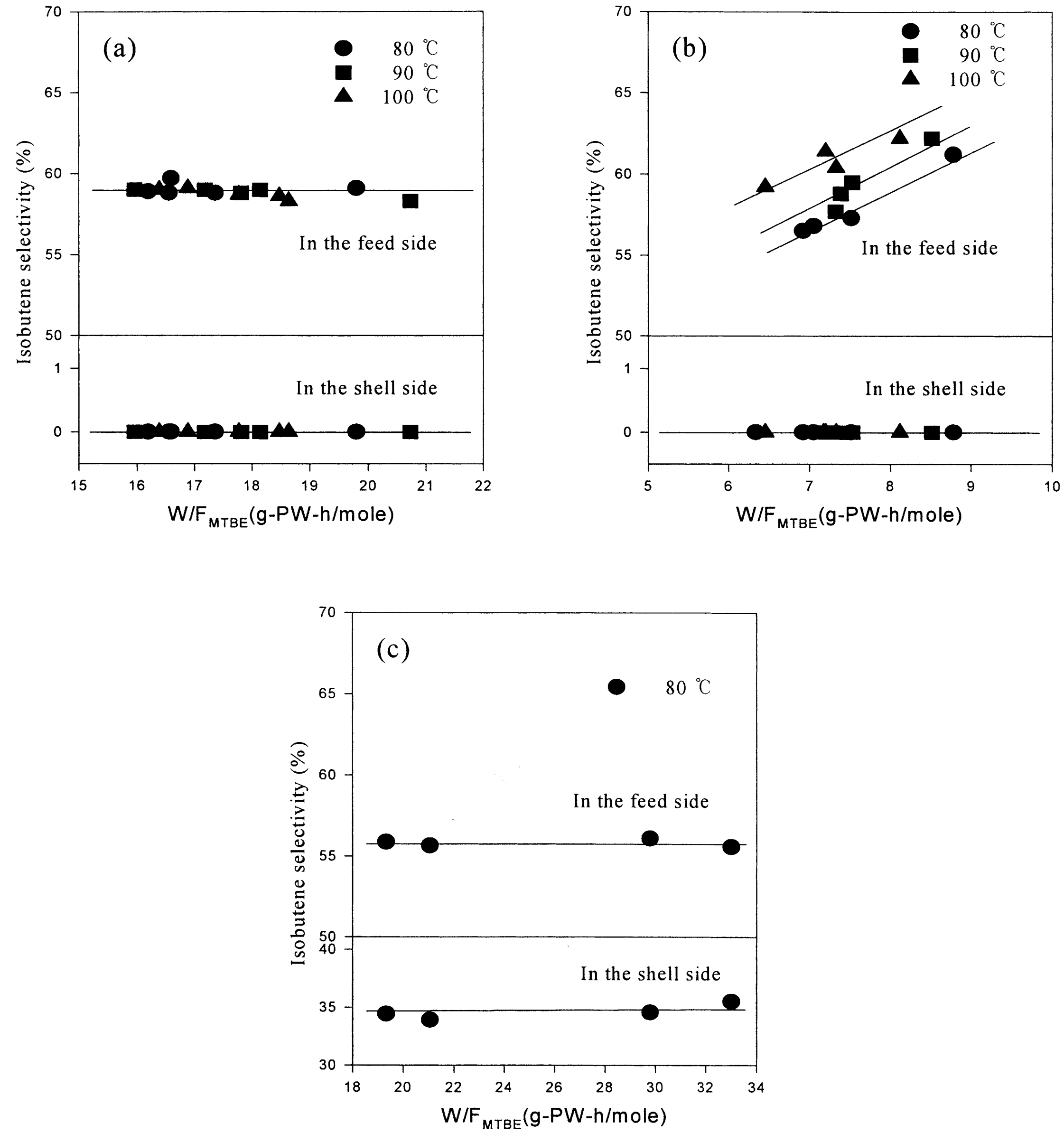

Fig. 4. Isobutene selectivities in the feed and shell side of the catalytic membrane reactor with respect to contact time: (a) PW-PPO/Al_2O_3 (type-1, PW = 0.023 g); (b) PW-PPO/PPO/Al_2O_3 (type-2, PW = 0.01 g); and (c) PW/PPO/Al_2O_3 (type-3, PW = 0.066 g).

catalytic membrane prior to reaction and separation. Therefore, the isobutene selectivity in the type-1 membrane reactor may be independent of W/F and cut-off, although permeation amounts of reaction species may differ. Also the separation capability of PW/PPO/Al_2O_3 (type-3) catalytic membrane is determined by PW/PPO layer. In this case, isobutene selectivity in the feed side was not economically affected by PPO membrane, because the reaction rate of MTBE was faster than the permeation rate of reaction species. In case of PW-PPO/PPO/Al_2O_3 (type-2) catalytic membrane, however, it has an

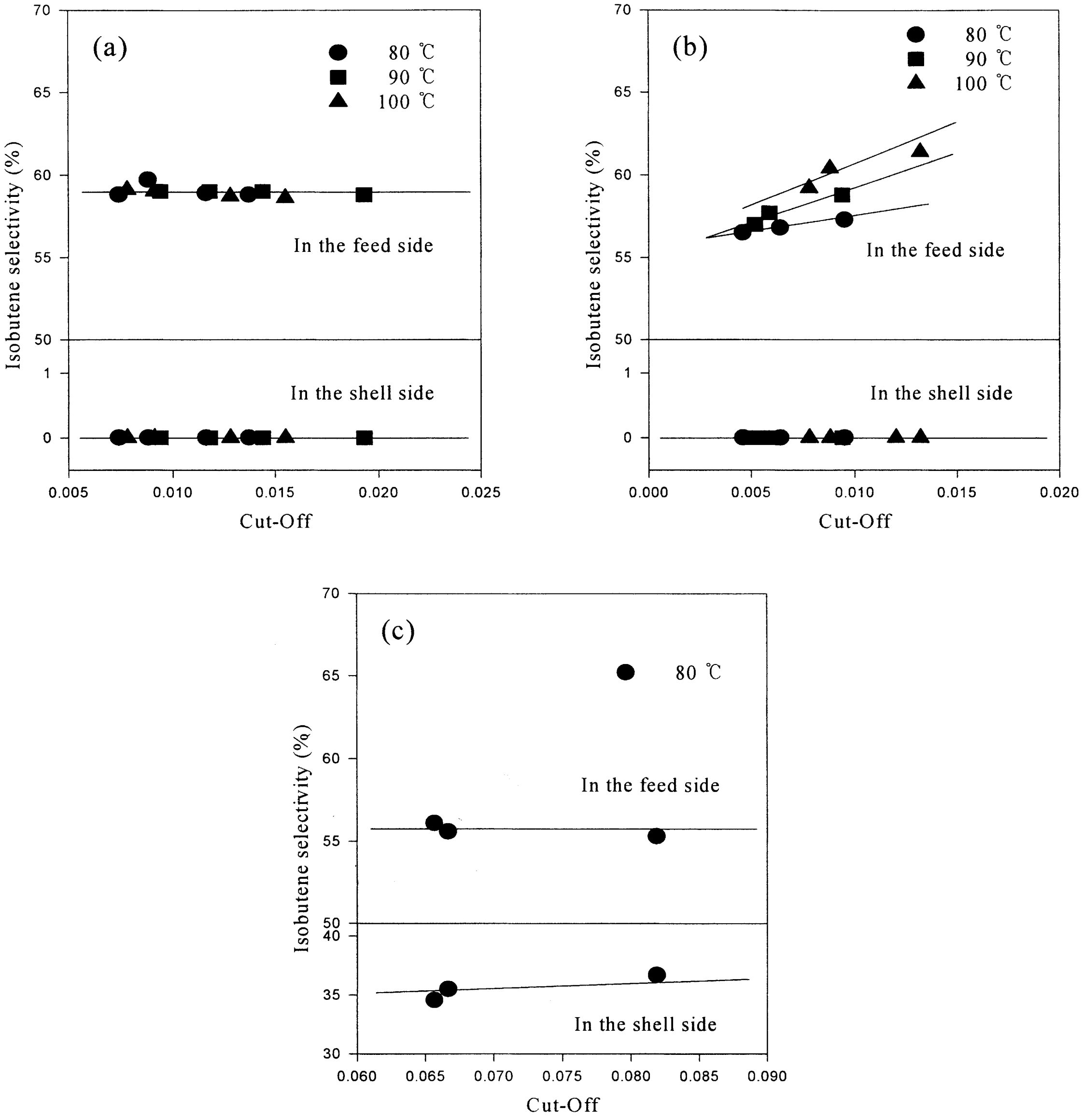

Fig. 5. Isobutene selectivities in the feed and shell side of the catalytic membrane reactor with respect to cut-off: (a) PW-PPO/Al_2O_3 (type-1, PW = 0.023 g, W/F_{MTBE} ≈ 17 g-PW-h/mol, cut-off = 0.005–0.02); (b) PW-PPO/PPO/Al_2O_3 (type-2, PW = 0.01 g, W/F_{MTBE} ≈ 7 g-PW-h/mol, cut-off = 0.005–0.015); and (c) PW/PPO/Al_2O_3 (type-3, PW = 0.066 g, W/F_{MTBE} ≈ 30 g-PW-h/mol, cut-off = 0.06–0.085).

additional sub-layered PPO membrane. Therefore, the PW-PPO/PPO/Al_2O_3 (type-2) shows a typical behavior of the conventional membrane.

The above results indicate that the selective removal of methanol through catalytic membranes may shift the chemical equilibrium in the case of MTBE decomposition. In order to verify the selective removal of methanol through the catalytic membrane, a closed-loop recycling reaction was carried out in the type-2 catalytic membrane reactor. As shown in Fig. 6, MTBE conversions and isobutene selectivities in the tube side were increased with increasing

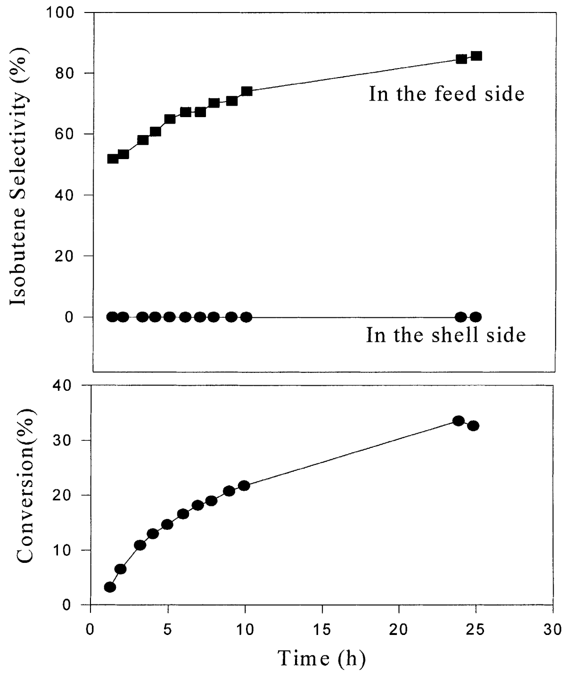

Fig. 6. MTBE conversions and isobutene selectivities in the closed-loop recycling membrane reactor at 90°C: PW-PPO/PPO/Al_2O_3 (type-2, PW = 0.01 g).

circulation time. This result strongly indicates that an equilibrium shift can be attained in the membrane reactor which is favorable for MTBE decomposition.

3.3. Comparison between PW-PPO/PPO/Al_2O_3 catalytic membrane and bulk PW

Fig. 7 shows the typical catalytic performance of the PW-PPO/PPO/Al_2O_3 (type-2) catalytic membrane in a membrane reactor and that of bulk PW in a continuous flow fixed-bed reactor. The experimental data, which was acquired at conditions of low cut-off, showed that the performance of the catalytic membrane was lower than that of the bulk catalyst. Ideally, the reactant in the PW-PPO/PPO/Al_2O_3 catalytic membrane reactor would be predicted to permeate through the PW-PPO layer by a solution mechanism in order for the reaction to take place, and the reacted species then permeate through the sub-layered PPO membrane. In other words, reaction species in the catalytic membrane reactor have higher mass transfer resistance than those in a fixed bed reactor. However, the conversion of MTBE in the catalytic membrane reactor surpassed the equilibrium conversion by means of an enhanced equilibrium shift when the cut-off was higher than ca. 0.064. Thus, the performance of the catalytic membrane reactor can be considerably improved by the operation at as high a cut-off as possible.

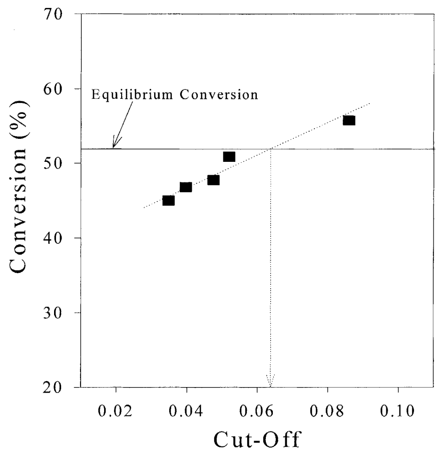

Fig. 7. Comparison between MTBE conversions in the PW-PPO/PPO/Al_2O_3 (type-2) and the equilibrium conversions obtained from the reaction kinetics on the bulk PW catalyst at 90°C and 2.3 atm of total pressure: $P_{MTBE} \approx 1.65$ atm, PW = 0.043 g, $W/F_{MTBE} \approx 17$ g-PW-h/mol; (■) experimental (PW-PPO/PPO/Al_2O_3); (—) equilibrium (bulk PW).

4. Conclusions

Experimental studies on the performance of shell and tube-type membrane reactors equipped with heteropolyacid-polymer composite catalytic membranes were carried out for the vapor-phase decomposition of MTBE. Three types of catalytic membranes comprising PW and PPO were designed in this work. The results showed that PW-PPO/Al_2O_3 (type-1), PW-PPO/PPO/Al_2O_3 (type-2) and PW/PPO/Al_2O_3 (type-3) catalytic membranes not only showed catalytic reactivity for the reaction, but also were perm-selective for the reaction species. Among three types of catalytic membrane reactors, the PW-PPO/ PPO/Al_2O_3 (type-2) catalytic membrane reactor (CMR) showed the best performance. The enhanced performance of PW-PPO/PPO/Al_2O_3 (type-2) catalytic membrane reactor can be attributed to the intrinsic perm-selective capabilities of the PW-PPO catalytic membrane and the sub-layered PPO membrane. The performance of the type-2 catalytic membrane reactor was considerably improved by operation at an elevated cut-off. The selective removal of methanol through the catalytic membrane led to an equilibrium shift to the favorable direction in the decomposition of MTBE.

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