

## A Composite Catalytic Polymer Membrane Reactor Using Heteropolyacid-Blended Polymer Membrane

Jun Seon Choi, In Kyu Song\* and Wha Young Lee†

Department of Chemical Engineering, Seoul National University, Shinlim-dong,  
Kwanak-ku, Seoul 151-742, Korea

\*Department of Industrial Chemistry, Kangnung National University, Kangnung,  
Kangwondo 210-702, Korea

(Received 27 September 1999 • accepted 15 January 2000)

**Abstract**—The vapor-phase MTBE decomposition was examined in a shell and tube-type catalytic membrane reactor (CMR). 12-Tungstophosphoric acid (PW) was used as a catalyst and poly-2,6-dimethyl-1,4-phenylene oxide (PPO) was used as a polymer material. A single-phase CMR (PW-PPO/Al<sub>2</sub>O<sub>3</sub>, type-1) and a composite CMR (PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub>, type-2) were successfully designed and characterized. It was revealed that the single-phase PW-PPO/Al<sub>2</sub>O<sub>3</sub> showed perm-selectivities for reaction products. The selective removal of methanol through the catalytic membrane shifted the chemical equilibrium toward the favorable direction in the MTBE decomposition. The PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> showed the better performance than PW-PPO/Al<sub>2</sub>O<sub>3</sub>. The enhanced performance of PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> CMR was due to the intrinsic perm-selectivity of PW-PPO and the additional separation capability of sub-layered PPO membrane.

Key words: MTBE, Membrane Reactor, Heteropolyacid, Polymer Membrane

### INTRODUCTION

In recent years, membrane technology has been an important issue in various chemical processes. One of the challenging membrane technologies is a catalytic membrane reactor (CMR). The membrane reactor is a unit comprising a membrane and a catalytic reactor. The total reaction conversion and product yield in the membrane reactor can be improved for the equilibrium limited reversible reactions by removing reaction products continuously from the reactor through a membrane. The membrane reactor has many advantages over the conventional chemical reactor because of its simultaneous function of chemical reaction and genuine separation [Govind and Itoh, 1989].

Up to now, most of investigations on the membrane reactors have been concentrated on the application of inorganic membranes because of their excellent thermal stability at high reaction temperatures [Amor, 1989; Zaman and Chakma, 1994]. The inorganic membrane reactors have been mainly applied to the reactions concerned with small molecules or decomposition reactions such as dehydrogenation reaction [Itoh et al., 1984; Gokhale et al., 1993]. Polymer membrane reactors, on the other hand, have versatile applicability because separation capability of polymer membranes depends on both diffusivity and solubility. However, only a few studies on the polymer membrane reactors have been reported in literatures [Song et al., 1991; Gao et al., 1993; Lee et al., 1994, 1995].

A heteropolyacid (HPA) catalyst has both acidic and redox catalytic properties. It also shows characteristic adsorption behaviors depending on the properties of adsorbates [Okuhara et

al., 1996]. It is known that HPA is an active catalyst for the MTBE (methyl tert-butyl ether) synthesis and decomposition [Makssimov and Kozhenikov, 1987]. The MTBE synthesis and decomposition have been used for the separation of isobutene from C<sub>4</sub> fractions. When methanol reacts with C<sub>4</sub> fractions, only isobutene reacts with methanol selectively to form MTBE. And subsequently, the synthesized MTBE is cracked under the favorable conditions to obtain methanol and isobutene. Although MTBE synthesis is an important chemical process, MTBE decomposition is also an attractive chemical reaction due to the potential demand for pure isobutene. MTBE synthesis and decomposition are a reversible and acid-catalyzed reaction.

HPAs are highly soluble in polar solvents such as water, alcohols and amines, but some are insoluble in non-polar chemicals such as benzene and olefins [Kozhevnikov and Mateev, 1983]. Novel catalysis of HPAs has been modified by combining HPAs with conjugated conducting polymers [Nomiya et al., 1986]. Some examples for the application of HPA-polymer system to the chemical reactions can be found in literatures [Hasik et al., 1994; Lee et al., 1995]. Another method for the modification of novel catalysis of HPA reported by this research group [Song et al., 1993; Lee et al., 1997] is to blend HPA with polymer material to form a membrane-like film catalyst.

Taking advantage of a property that HPAs are highly soluble in some solvents, HPA-blended polymer membranes can be prepared by blending these two materials using suitable solvents. In this work, a shell and tube-type catalytic membrane reactor using HPA-blended polymer membrane was designed for the vapor-phase MTBE decomposition. Experimental studies on the reactor performance of HPA-blended polymer membrane reactor were carried out.

†To whom correspondence should be addressed.

E-mail: wyl@snu.ac.kr

### EXPERIMENTAL

## 1. Materials

$H_3PW_{12}O_{40}$  (PW, Aldrich Chem. Co.) was used as an active catalyst for the reaction, and poly-2,6-dimethyl-1,4-phenylene oxide (PPO, Aldrich Chem. Co.) was used as a membrane material or blending polymer. A mixed solvent of methanol and chloroform was used to form a homogeneous solution of PW and PPO (PW-PPO).

## 2. Design of Catalytic Membrane Reactor

A porous double-layered alumina tube ( $\alpha$ - $Al_2O_3$  from Dong-suh Ind. Co.) was used as a support for catalytic membrane. A homogeneous solution of PPO-chloroform was coated on the tube side of  $Al_2O_3$  to form PPO/ $Al_2O_3$ , and subsequently, it was dried completely at 100 °C for 1 hr. A composite catalytic membrane was finally prepared by coating the homogeneous solution of PW-PPO onto the PPO/ $Al_2O_3$  to form PW-PPO/PPO/ $Al_2O_3$ .

Two types of catalytic membrane reactor (CMR) were examined to evaluate the performance of PW-PPO catalytic membrane. Type-1 was a single-phase catalytic membrane reactor equipped with PW-PPO/ $Al_2O_3$ , and type-2 was a composite catalytic membrane reactor equipped with PW-PPO/PPO/ $Al_2O_3$ . The length of membrane reactor was about 4.5 cm. All the end parts of the alumina tube were sealed with epoxy resin. No leakage was confirmed before the reaction. A stainless steel tube was used as an outer tube of the catalytic membrane reactor.

## 3. Reaction and Characterization

Fig. 1 shows the details of the shell and tube-type CMR. The catalytic membrane reactor was treated at 80-100 °C for 12 hrs by passing nitrogen before the reaction. MTBE was sufficiently vaporized and fed into the CMR continuously together with  $N_2$  carrier (3.5-10.5 cm<sup>3</sup>/min). Contact time (W/F<sub>MTBE</sub>) was varied by controlling the amounts of MTBE. The performance of CMR was examined at temperatures ranging from 80 to 100 °C and at tube side pressures ranging from 1.0 to 2.3 atm. The permeated stream was continuously removed by  $N_2$  sweeping gas (4.0 cm<sup>3</sup>/min). The permeated and reacted stream were periodically sampled and analyzed with a GC (Yanaco, G180) using a column packed with Porapak Q. The catalytic membranes were characterized by SEM (Jeol, JMS-35) and FT-IR (Bomem, MB100).

The MTBE conversion and isobutene selectivity in the feed (tube) side were calculated as follows. Here, A represents the amounts of MTBE in the feed flow. B, D and E are the amounts of MTBE, isobutene and methanol in the effluent flow of the tube side, respectively. And C represents the amounts of MTBE

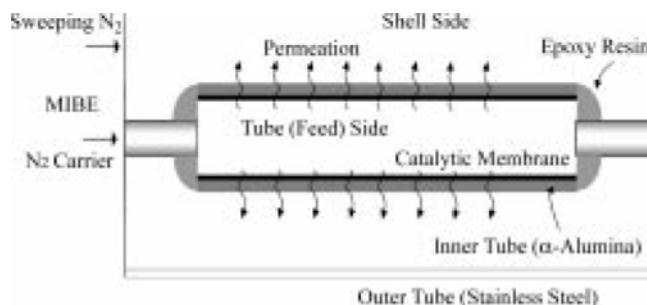


Fig. 1. A shell and tube-type membrane reactor.

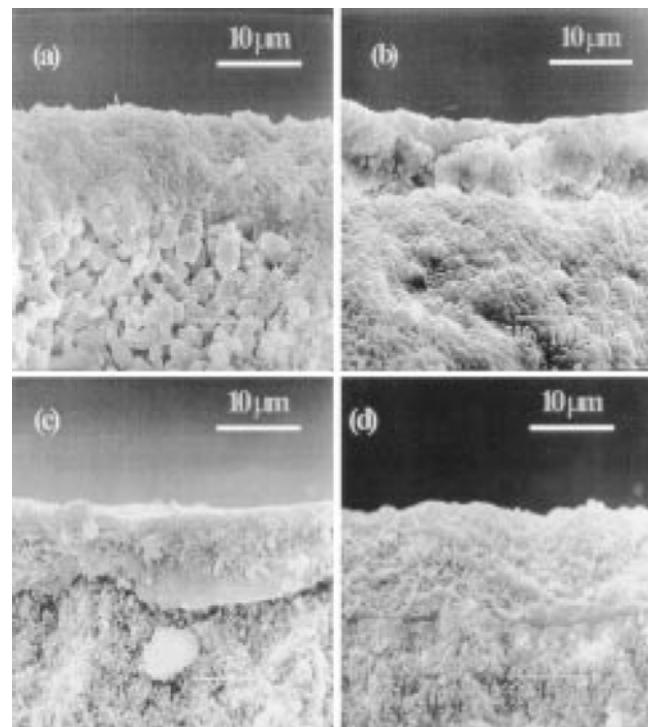


Fig. 2. SEM images of (a)  $Al_2O_3$ , (b) PPO/ $Al_2O_3$ , (c) PW-PPO/ $Al_2O_3$  and (d) PW-PPO/PPO/ $Al_2O_3$ .

in the permeation (shell) side of the membrane reactor.

$$\text{Conversion (\%)} = [1 - (B + C)/A] \times 100$$

$$\text{Isobutene selectivity (\%)} \text{ in the feed side} = [D/(D+E)] \times 100$$

## RESULTS AND DISCUSSION

### 1. Characteristics of Catalytic Membrane

Fig. 2 shows the cross-sectional SEM images of bare  $Al_2O_3$ , PPO/ $Al_2O_3$ , PW-PPO/ $Al_2O_3$  (type-1), and PW-PPO/PPO/ $Al_2O_3$  (type-2). Both PPO and PW-PPO were well coated on  $Al_2O_3$  tube. It was observed that the pores of the alumina tube were filled with PPO or PW-PPO. The coating thickness was not perfectly uniform throughout the tube. PW-PPO layer was clearly distinguished from PPO/ $Al_2O_3$  layer, as shown in Fig. 2(d). There was no visible evidence representing PW in PW-PPO/ $Al_2O_3$  and PW-PPO/PPO/ $Al_2O_3$ . This indicates that PW was dispersed as fine particles throughout the catalytic membranes.

The IR spectra for PW, PPO and PW-PPO catalytic membrane are shown in Fig. 3. Four characteristic bands indicating the Keggin structure of PW appeared at 1,081, 982, 889 and 802 cm<sup>-1</sup>. The bands at 889 and 802 cm<sup>-1</sup> can be assigned to W-O-W bands. The bands appearing at 1,081 and 982 cm<sup>-1</sup> represent P-O band and W=O band, respectively. The four prominent bands appeared at 1,020, 960, 857 and 831 cm<sup>-1</sup> for PPO membrane material. It is noteworthy that the four characteristic IR bands of PW were observed in the PW-PPO catalytic membrane.

### 2. Performance of Catalytic Membrane Reactor

Vapor-phase MTBE decomposition was carried out in PW-PPO/ $Al_2O_3$  (type-1) and PW-PPO/PPO/ $Al_2O_3$  (type-2) catalytic membrane reactors for the comparison of reactor performance.

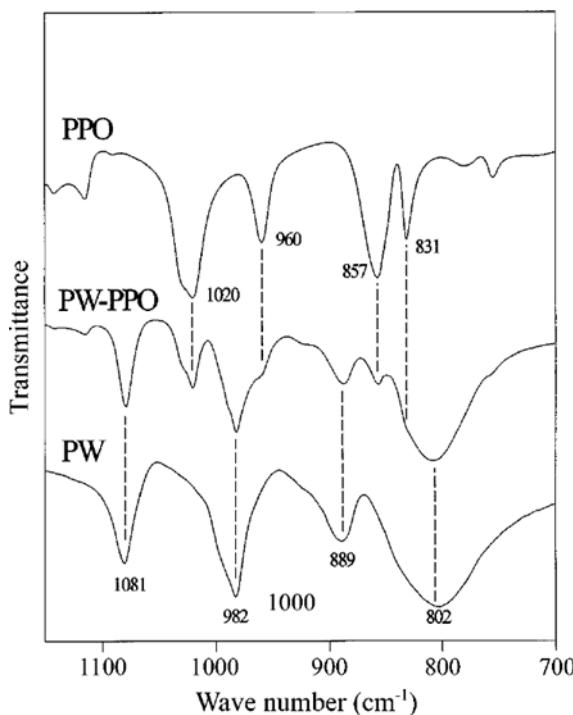


Fig. 3. IR spectra of PW, PPO and PW-PPO.

Fig. 4 shows the MTBE conversions with respect to  $W/F_{MTBE}$ . As shown in this figure, both PW-PPO/Al<sub>2</sub>O<sub>3</sub> and PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> catalytic membranes were active for the MTBE decomposition. The MTBE conversions were increased with the increase of reaction temperature and with the decrease of reaction pressure, as inferred from the thermodynamic equilibrium. MTBE conversions were also increased with the increase of  $W/F_{MTBE}$ . However, only a little difference in MTBE conversions between two membrane reactors was observed under the actual experimental conditions because of the short reactor length.

Fig. 5 shows the isobutene selectivities in the tube side of the catalytic membrane reactors. Contrary to MTBE conversions, there was a great difference in isobutene selectivities between

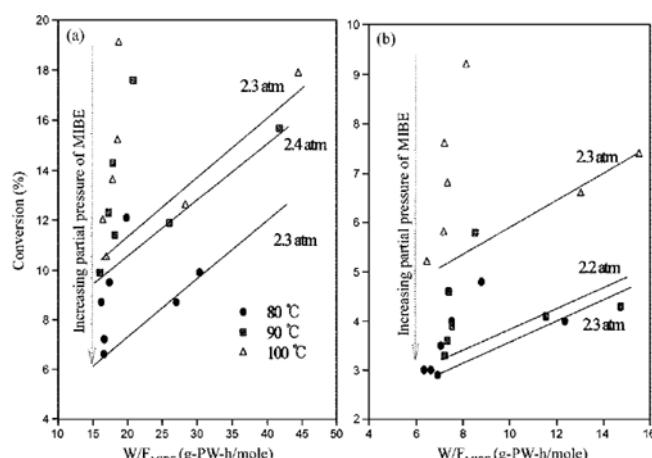


Fig. 4. MTBE conversion in the tube side of CMR with respect to  $W/F_{MTBE}$ ; (a) PW-PPO/Al<sub>2</sub>O<sub>3</sub> (type-1, PW=0.023 g) and (b) PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> (type-2, PW=0.01 g).

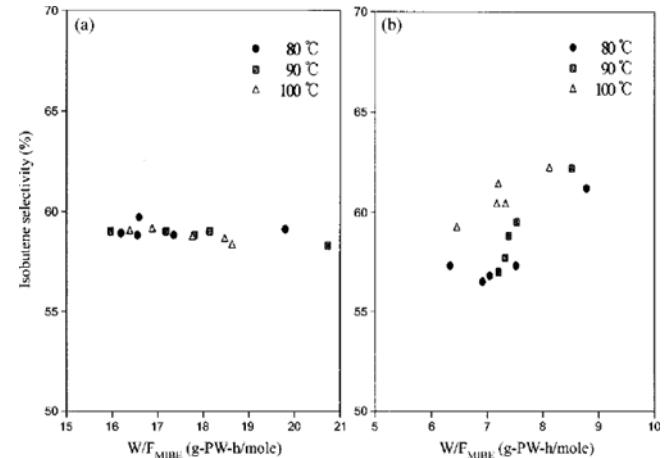


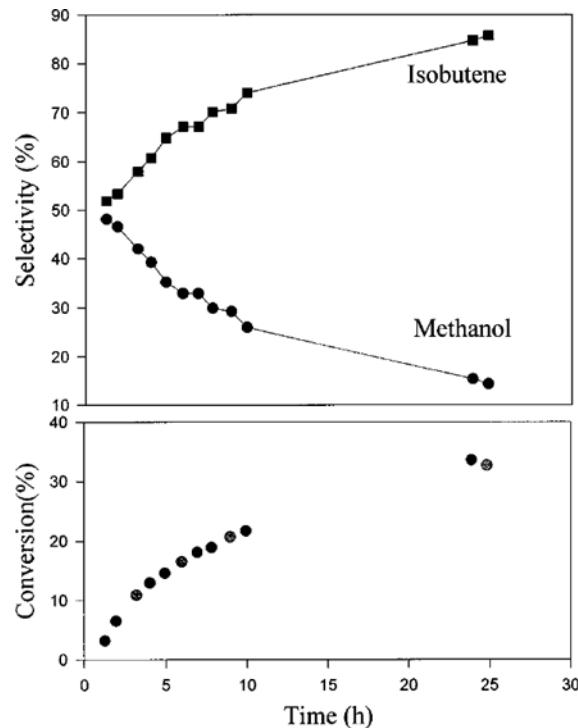
Fig. 5. Isobutene selectivity in the tube side of CMR with respect to  $W/F_{MTBE}$ ; (a) PW-PPO/Al<sub>2</sub>O<sub>3</sub> (type-1, PW=0.023 g) and (b) PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> (type-2, PW=0.01 g).

two catalytic membrane reactors. The isobutene selectivities in PW-PPO/Al<sub>2</sub>O<sub>3</sub> (type-1) catalytic membrane reactor kept the almost constant value of ca. 59% with  $W/F_{MTBE}$ . It is noticeable that this value is higher than the theoretical value of 50% which can be attainable in a normal catalytic reactor. This means that the single-phase PW-PPO catalytic membrane has its own perm-selectivity. On the other hand, however, isobutene selectivities in PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> (type-2) catalytic membrane reactor were increased with the increase of  $W/F_{MTBE}$ . The isobutene selectivities in PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> (type-2) catalytic membrane reactor were much higher than those in PW-PPO/Al<sub>2</sub>O<sub>3</sub> (type-1) catalytic membrane reactor. In other words, this represents that the perm-selectivity of methanol/isobutene of PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> (type-2) catalytic membrane reactor was much higher than that of PW-PPO/Al<sub>2</sub>O<sub>3</sub> (type-1) catalytic membrane reactor. Therefore, the enhanced performance of PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> (type-2) catalytic membrane reactor can be understood in terms of the intrinsic perm-selectivity of PW-PPO and the additional separation capability of sub-layered PPO membrane. It is inferred that the selective removal of methanol through the catalytic membrane may shift the chemical equilibrium toward the favorable direction.

### 3. Reactor Performance in a Closed Recycling Loop

When PW-PPO was used as a simple solid catalyst in a conventional flow reactor for the MTBE decomposition, it showed the lower catalytic activity than the bulk solid PW catalyst. However, the catalytic membrane reactor with PW-PPO as a catalytic membrane showed the better performance than the conventional flow reactor with solid PW in a certain range of pressure and temperature.

In order to ensure and to evaluate the performance of PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> catalytic membrane reactor, the partially reacted reaction product was circulated in a closed recycling loop. As shown in Fig. 6, MTBE conversions and isobutene selectivities were increased with the circulation time. Once again, this result indicates that PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> catalytic membrane has a selective permeation property for methanol, and the selective removal of methanol through the membrane in turn results in the increase of MTBE conversions in this reversible reaction.



**Fig. 6. Reactor performance of PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> (type-2) CMR in a closed recycling loop.**

The MTBE conversion and isobutene selectivity in the catalytic membrane reactors were much higher than the equilibrium conversion and isobutene selectivity in the feed side, respectively.

## CONCLUSIONS

Experimental studies on the PW-PPO catalytic membrane reactors were carried out for the vapor-phase MTBE decomposition. A single-phase catalytic membrane reactor (PW-PPO/Al<sub>2</sub>O<sub>3</sub>, type-1) and a composite catalytic membrane reactor (PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub>, type-2) were successfully designed in this work. It was revealed that the single-phase PW-PPO/Al<sub>2</sub>O<sub>3</sub> showed perm-selectivities for reaction products. The selective removal of methanol through the catalytic membrane shifted the chemical equilibrium toward the favorable direction in the MTBE decomposition. The PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> showed the better performance than PW-PPO/Al<sub>2</sub>O<sub>3</sub>. The enhanced performance of PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> catalytic membrane reactor was due to the intrinsic perm-selectivity of PW-PPO and the additional separation capability of sub-layered PPO membrane. A closed loop recycling experiment performed in the PW-PPO/PPO/Al<sub>2</sub>O<sub>3</sub> catalytic membrane reactor revealed that the MTBE conversion and isobutene selectivity in the catalytic membrane reactor were much higher than the equilibrium conversion and isobutene selectivity in the feed side, respectively.

## ACKNOWLEDGEMENT

The authors acknowledge the support from Daelim Industry

Co. and Seoul National University.

## REFERENCES

Amor, J. N., "Catalysis with Permselective Inorganic Membrane," *Appl. Catal.*, **49**, 1 (1989).

Gao, H., Xu, Y., Liao, S., Liu, R., Liu, J. and Yu, D., "Catalytic Hydrogenation and Gas Permeation Properties of Metal-Containing Poly(phenylene oxide) and Polysulfone," *J. Appl. Polym. Sci.*, **55**, 1035 (1993).

Gokhale, Y. V., Noble, R. D. and Falconer, J. L., "Analysis of a Membrane Enclosed Catalytic Reactor for Butane Dehydrogenation," *J. Membrane Sci.*, **77**, 197 (1993).

Govind, R. and Itoh, N., "Membrane Reactor Technology," *AICHE Symp. Ser.*, **85**, 268 (1989).

Hasik, M., Turek, W., Stochmal, E., Lapkowski, M. and Pron, A., "Conjugated Polymer-Supported Catalysts-Polyaniline Protonated with 12-Tungstophosphoric Acid," *J. Catal.*, **147**, 544 (1994).

Itoh, N., Shundo, Y., Haraya, K., Obata, K. and Hakuda, T., "Enhanced Catalytic Decomposition of HI by Using a Microporous Membrane," *Int. J. Hydro. Ener.*, **9**, 835 (1984).

Kozhevnikov, I. V. and Matveev, K. I., "Homogeneous Catalysts Based on Heteropoly Acids," *Appl. Catal.*, **5**, 135 (1983).

Lee, J. K., Song, I. K. and Lee, W. Y., "An Experimental Study on the Application of Polymer Membranes to the Catalytic Decomposition of MTBE (Methyl Tert-Butyl Ether)," *Catal. Today*, **25**, 345 (1995).

Lee, J. K., Song, I. K. and Lee, W. Y., "Methyl Tert-Butyl Ether Decomposition over Heteropoly Acid Catalyst in a Cellulose Acetate Membrane Reactor," *Catal. Lett.*, **29**, 241 (1994).

Lee, J. K., Song, I. K. and Lee, W. Y., "Separation of H<sub>2</sub>/CO by the Selective Sorption Property of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> Embedded in PVA Membrane," *Korean J. Chem. Eng.*, **12**, 384 (1995).

Lee, W. Y., Song, I. K., Lee, J. K., Park, G. I. and Lim, S. S., "Design of Heteropoly Compound-Imbedded Polymer Film Catalyst and Their Application," *Korean J. Chem. Eng.*, **14**, 432 (1997).

Maksimov, G. M. and Kozhenikov, I. V., "Heteropoly Acids as Catalysts for Synthesis of Methyl Tert-Butyl Ether," *React. Kinet. Katal. Lett.*, **39**, 317 (1987).

Nomiya, K., Murasaki, H. and Miwa, M., "Catalysis by Heteropolyacids-VIII. Immobilization of Keggin-Type Heteropolyacids on Poly(4-vinylpyridine)," *Polyhedrons*, **5**, 1031 (1986).

Okuhara, T., Mizuno, N. and Misono, M., "Catalytic Chemistry of Heteropoly Compound," *Adv. Catal.*, **41**, 113 (1996).

Song, I. K., Lee, W. Y. and Kim, J. J., "Application of Heteropolyacid Catalyst in an Inert Polymer Membrane Catalytic Reactor in Ethanol Dehydrogenation," *Catal. Lett.*, **9**, 339 (1991).

Song, I. K., Shin, S. K. and Lee, W. Y., "Catalytic Activity of H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>-Blended Polysulfone Film in the Oxidation of Ethanol to Acetaldehyde," *J. Catal.*, **144**, 348 (1993).

Zaman, J. and Chakma, A., "Inorganic Membrane Reactors," *J. Membrane Sci.*, **92**, 1 (1994).