

## Aromatization of Propane Assisted by Palladium Membrane Reactor

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A palladium membrane reactor was successfully applied to aromatization of propane. Conversion of propane to aromatics was apparently enhanced by use of a membrane reactor because hydrocracking, dealkylation, and hydrogen transfer were suppressed as a result of the rapid separation of produced hydrogen.

Recently, dehydrocyclization of alkanes has been recognized as a new route to produce aromatics. Considerable studies have been done on the conversion of propane to BTX on ZSM-5 modified with gallium,<sup>1-4)</sup> zinc,<sup>5)</sup> or platinum.<sup>6)</sup> The yield of aromatics, however, has been found to be limited due to hydrocracking, dealkylation, and hydrogen transfer, which lead to the formation of methane and ethane. In order to suppress these reactions, Clayson et al.<sup>7)</sup> have proposed the application of hydrogen-permeating membrane reactor and have reported that the yield of aromatics increases from 32.5 to 37.9 wt% by use of the membrane reactor constructed with a palladium-silver alloy membrane having 0.1 mm thickness.

We have reported in a previous paper<sup>8)</sup> that palladium membrane supported as a thin film on a porous supporting cylinder exhibits higher rate of hydrogen permeation than commercially obtainable palladium-alloy membranes, due to thinness of the film. We have further ascertained that promoting effect of the membrane reactor increases with decreasing thickness of palladium film.<sup>9)</sup> We wish to report in the present communication that the applicability of membrane reactor with the supported thin palladium membrane to aromatization of propane.

A double-tubular type membrane reactor, as shown previously,<sup>9)</sup> was used in this study. The palladium membrane, which was used as the inner tube, was prepared in the same manner as shown in the previous paper.<sup>8)</sup> A porous alumina cylinder supplied by Toshiba Ceramics Co. was used as the supporting material. Deposition of palladium on the outer surface of the cylinder was carried out by a technique of electroless-plating. The palladium membrane used in this study had a film thickness of 8.6  $\mu\text{m}$ .

Sodium type ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio, 49.8), supplied by Tosoh Corporation, was converted to ammonium type by exhaustive exchange with  $1 \text{ mol dm}^{-3}$  solution of ammonium chloride. Gallium was loaded onto the ZSM-5 by ion exchange method using a solution of gallium nitrate. Gallium type ZSM-5 thus obtained was calcined at 873 K for 2 h. The amount of gallium loaded was 1.25% by weight as oxide.

Ga/H-ZSM-5 (2.0 g) diluted with silica sand (5.9 g) was packed at the central section of the reactor. Prior to reaction, the catalyst was calcined at 813 K for 1 h, followed by hydrogen reduction at 773 K for 0.5 h to activate the palladium membrane. Reactions were carried out at 773 K. The pressure of reaction side (outside the membrane) was atmospheric and the permeation side (inside the membrane) was evacuated by use of a vacuum pump. A mixture of propane and nitrogen in a equi-molar ratio was supplied to the reaction side in a down-flow manner. Reaction products were analyzed by means of gas chromatography. In order to investigate the promoting effect of membrane reactor, comparative studies were also carried out using a nonporous Pyrex glass tube instead of the hydrogen-permeating membrane. The level of conversion, yields, and selectivities, which were expressed on a basis of mole of carbon, were compared using data taken in the initial 15 min of run.

Figure 1 shows the level of propane conversion and the yield of aromatics as a function of time factor  $W/F$ , which was defined by the weight of Ga/H-ZSM-5  $W(\text{g})$  and the feed rate of propane  $F(\text{mol min}^{-1})$ . By use of membrane reactor, conversion of propane to aromatics was apparently enhanced. The membrane reactor used in this study gave high yield of aromatics compared with the results of Clayson et al.<sup>7)</sup> Note that the thickness of palladium was 8.6 and 100  $\mu\text{m}$  for this study and for the study by Clayson et al., respectively. These results lead us to conclude that the yield of aromatics depends on hydrogen permeability of membrane.

Figure 2 illustrates the product distribution. Without the membrane, the selectivities for methane and ethane increased with increasing  $W/F$ , and those for toluene and xylenes decreased, indicating the occurrence of hydrocracking, dealkylation and hydrogen

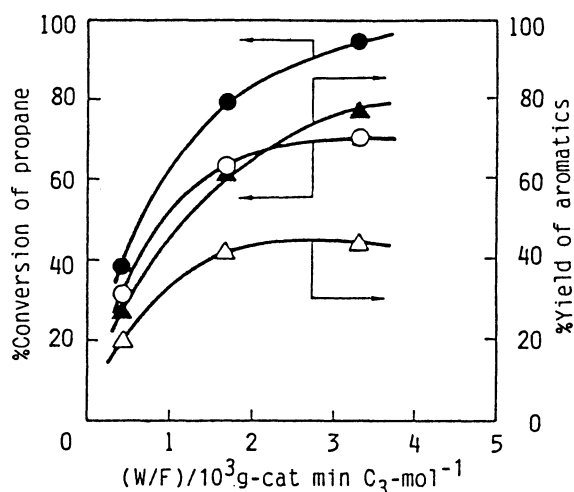


Fig. 1. Conversion of propane (O, ●) and yield of aromatics (Δ, ▲) as a function of time factor ( $W/F$ ). (O, Δ), conventional reactor; (●, ▲), membrane reactor.

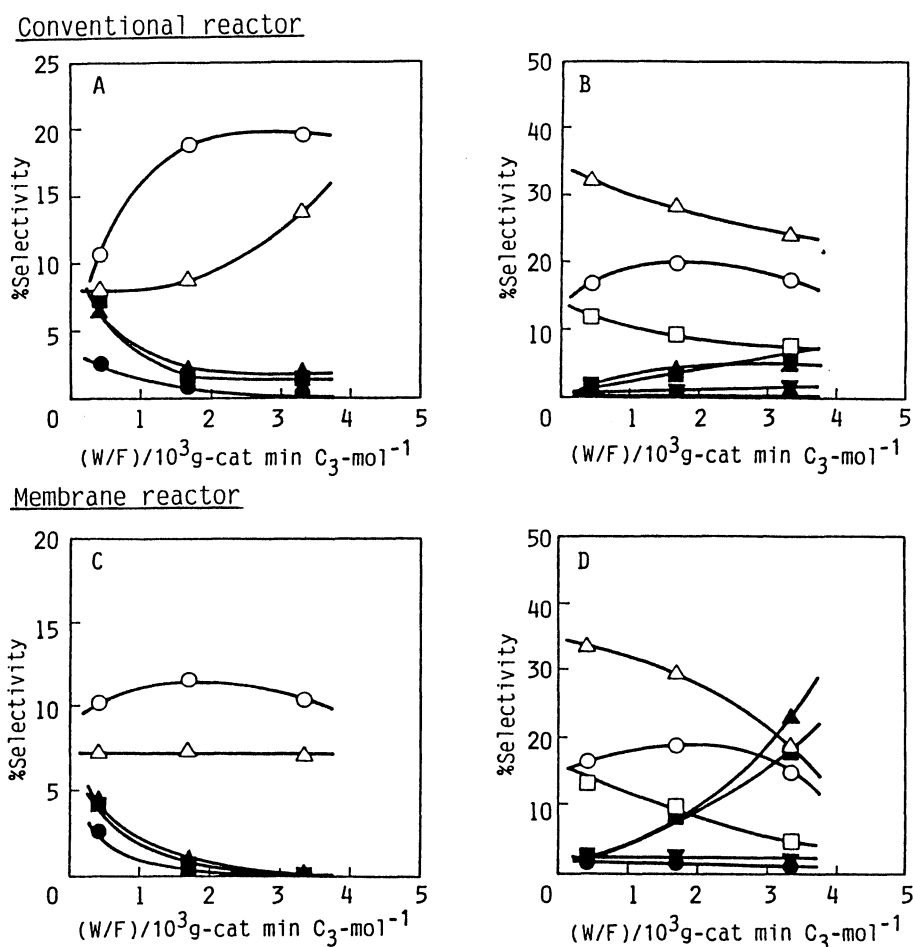


Fig. 2. Product distribution as a function of time factor (W/F).  
 (A,C): ○, methane; △, ethane; ▲, ethylene; ■, propene;  
 ●,  $\text{C}_{4+}$  aliphatics.  
 (B,D): ○, benzene; △, toluene; □,  $\text{C}_8$  aromatics; ●,  $\text{C}_9$  aromatics;  
 ▲,  $\text{C}_{10}$  aromatics; ■,  $\text{C}_{11}$  aromatics; ▼,  $\text{C}_{12+}$  aromatics.

transfer. On the other hand, the selectivities for methane and ethane scarcely changed with W/F in the case of palladium membrane reactor, while those for BTX decreased with increasing W/F, due to increased formation of naphthalene and methyl naphthalene. Shibata and co-workers<sup>10)</sup> reported that a considerable amount of naphthalene was formed in the conversion of propene on gallium type ZSM-5. Thus, formation of naphthalene and methyl naphthalene in membrane reactor would be ascribed to the high concentration of propene. We, thus, conclude that high yield of aromatics obtained in the membrane reactor is attributed to suppression of hydrocracking, dealkylation, and hydrogen transfer, and also to enhancement of dehydrogenation of propane to propene.

The partial pressure of hydrogen remaining in the reaction side is shown in Fig. 3. Since formation of aromatics was accompanied by hydrogen,

the partial pressure of hydrogen increased with W/F in the conventional reactor and then hydrocracking, dealkylation, and hydrogen transfer caused high selectivities for methane and ethane. In the membrane reactor, however, the partial pressure of hydrogen decreased with increasing W/F, due to the removal of produced hydrogen from the reaction system.

Gallium species loaded on ZSM-5 was reported to function as the active sites for dehydrogenation of either oligomers (higher olefins) as the intermediate to aromatics, or propane.<sup>1-4)</sup> Fujimoto and co-workers<sup>11)</sup> reported that gallium species acted as a port of reverse spillover of produced hydrogen: desorption of hydrogen from zeolite surface to gas phase was promoted by the presence of gallium. Although the role of membrane reactor is not well-established at present, we consider that it promotes the dehydrogenation of oligomers and propane, and desorption of produced hydrogen from the surface of zeolite.

#### References

- 1) H. Kitagawa, Y. Sendoda, and Y. Ono, *J. Catal.*, **101**, 12 (1986).
- 2) T. Inui, Y. Makino, F. Okazumi, S. Nagano, and A. Miyamoto, *Ind. Eng. Chem. Res.*, **26**, 647 (1987).
- 3) T. Yashima, T. Sasaki, K. Takahashi, S. Watanabe, and S. Namba, *Sekiyu Gakkai Shi*, **31**, 154 (1988).
- 4) N.S. Gnep, J.Y. Doyemet, and M. Guisnet, *J. Molecular Catal.*, **45**, 281 (1988).
- 5) T. Mole, J.R. Anderson, and G. Creer, *Appl. Catal.*, **17**, 141 (1985).
- 6) T. Inui and F. Okazumi, *J. Catal.*, **90**, 366 (1984).
- 7) D.M. Clayson and P. Howard, UK Patent Application, GB 2190397A (1987).
- 8) S. Uemiya, Y. Kude, K. Sugino, N. Sato, T. Matsuda, and E. Kikuchi, *Chem. Lett.*, **1988**, 1687.
- 9) S. Uemiya, N. Sato, H. Ando, T. Matsuda, and E. Kikuchi, *Sekiyu Gakkai Shi*, submitted for publication.
- 10) M. Shibata, H. Kitagawa, Y. Sendoda, and Y. Ono, *Stud. Surf. Sci. Catal.*, **28**, 717 (1986).
- 11) K. Fujimoto, I. Nakamura, and K. Yokota, *Chem. Lett.*, **1989**, 681.

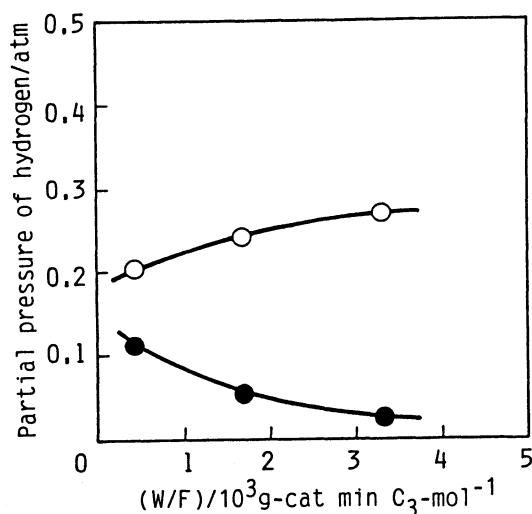


Fig. 3. Partial pressure of hydrogen remaining in the reaction side as a function of time factor (W/F).

○, conventional reactor;  
●, membrane reactor.

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