

## [Regular Paper]

## High Propylene Selectivity in Methanol-to-olefin Reaction over H-ZSM-5 Catalyst Treated with Phosphoric Acid

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H-ZSM-5 zeolite was treated with phosphorus acid by impregnating H-ZSM-5 with aqueous solutions of phosphoric acid at various concentrations. H-ZSM-5 (P-HZSM-5) modified with phosphoric acid was used as a catalyst for the methanol-to-olefin reaction. The molar ratios of P/Si and Si/Al in H-ZSM-5 and P-HZSM-5 were measured by EDX analysis. The Si/Al molar ratios of P-HZSM-5 increased with higher concentration of  $H_3PO_4$  in the solution, which might be caused by partial dealumination of H-ZSM-5 by the  $H_3PO_4$  treatment. The P/Si molar ratio of P-HZSM-5 after washing was proportional to the  $H_3PO_4$  concentrations in the aqueous solutions. The remaining phosphorus species after the washing must be strongly adsorbed by interaction with the pore surface of H-ZSM-5 zeolite. The P-HZSM-5 catalyst showed very high propylene selectivity up to 57% with methanol conversion of 100%. Furthermore, catalyst stability was significantly improved for the P-HZSM-5 catalysts. Ammonia TPD spectra showed that the strong acid sites of H-ZSM-5 disappeared after the phosphoric acid treatment. Consequently, the formation of aromatics and coke was inhibited, resulting in higher light olefin selectivity and catalyst stability.

**Keywords**

ZSM-5, Methanol-to-olefin, Light olefin, Phosphoric acid, Propylene production, MFI

**1. Introduction**

Light olefins, especially propylene, are important starting materials for many chemical processes, so demand continues to rise every year. Light olefins provide very versatile building blocks for synthesis and are the feedstocks for a wide range of important monomers, polymers, intermediates and chemicals. Primary production of *light olefins* is based on either steam cracking or recovery from refinery processes. However, methanol can be easily obtained from the huge reserves of natural gas, so the methanol-to-olefin (MTO) reaction has gaining interest recently.

Many researchers have concentrated on converting methanol to hydrocarbons such as methanol to gasoline (MTG), methanol to hydrocarbons (MTH) and MTO using zeolitic catalysts such as ZSM-5<sup>1)~3)</sup>, zeolite Beta<sup>4),5)</sup>, and SAPO-34<sup>6)~8)</sup>, and the reaction paths of MTO and MTG processes over zeolitic catalysts have been reported<sup>9)</sup>. Silicoaluminophosphate SAPO-34 (pore size *ca.* 0.43 nm) is an excellent catalyst for the selective production of light olefins (ethylene and propylene) in the MTO reaction. However, this catalyst is

rapidly deactivated by coke accumulation in the internal narrow channels of SAPO-34 crystals<sup>10),11)</sup>.

ZSM-5 has medium pore size (*ca.* 0.55 nm), so may be stable in the MTO reaction. However, the strong acid sites of the catalyst result in large fractions of by-products formed through oligomerization reactions<sup>12)</sup>, especially aromatic compounds. Several techniques have been proposed to improve the catalytic specificity of ZSM-5 catalyst for the selective formation of light olefins<sup>13)~16)</sup>. Recently, phosphorus modified H-ZSM-5 catalysts were proposed for cracking butene and C<sub>4</sub>-alkanes to produce light olefins<sup>17),18)</sup>. A high fraction of light olefins could be obtained over the modified H-ZSM-5 because the acid strength of the H-ZSM-5 catalyst was weakened by phosphorus addition.

In the present study, we used phosphoric acid-modified H-ZSM-5 catalysts to take advantage of the stability for the production of propylene in the MTO reaction. The effect of the treatment with phosphoric acid on the light olefin selectivity and catalyst stability was evaluated.

**2. Experimental****2.1. Catalyst Preparation and Characterization**

H-ZSM-5 (Tosoh Corp., crystal size = *ca.* 3  $\mu$ m, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 310 (EDX analysis)) was used as the cat-

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Table 1 Sample Preparation

Sample name		1P-Z	2P-Z	3P-Z	4.5P-Z	5.5P-Z
H-ZSM-5 added	[g]	1.00	1.00	1.00	1.00	1.00
Water added	[g]	5.00	5.00	5.00	5.00	5.00
85 wt% H <sub>3</sub> PO <sub>4</sub> added	[g]	0.037	0.074	0.112	0.167	0.205
Final concentration of H <sub>3</sub> PO <sub>4</sub>	[wt%]	0.74	1.47	2.18	3.24	3.93
Mass ratio of P/H-ZSM-5	[g/g]	0.01	0.02	0.03	0.045	0.055

alyst. H-ZSM-5 was impregnated with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) aqueous solutions of various concentrations. First, 1.00 g H-ZSM-5 was mixed with 5.00 g of deionized water, then the appropriate amount of 85 wt% H<sub>3</sub>PO<sub>4</sub> was added. The amounts of 85 wt% H<sub>3</sub>PO<sub>4</sub> added and the concentrations of the H<sub>3</sub>PO<sub>4</sub> aqueous solutions are listed in **Table 1**. The solvents were completely evaporated by heating. Therefore, all H<sub>3</sub>PO<sub>4</sub> molecules in the solutions were loaded on the H-ZSM-5. The mass ratios of phosphorus (P) in the solutions to H-ZSM-5 were 0.01, 0.02, 0.03, 0.045 and 0.055. The H-ZSM-5 samples modified with H<sub>3</sub>PO<sub>4</sub> (P-HZSM-5) were designated as: 1P-Z, 2P-Z, 3P-Z, 4.5P-Z and 5.5P-Z, respectively. The P-HZSM-5 catalysts were dried again at 383 K for 5 h and then calcined in air at 873 K for 5 h with a heating rate of 1 K·min<sup>-1</sup>. After calcination, the samples of 1P-Z, 2P-Z, 3P-Z, 4.5P-Z and 5.5P-Z were washed with deionized water to remove excess H<sub>3</sub>PO<sub>4</sub> on the catalysts. Here, the P-HZSM-5 samples were immersed in deionized water for 3 h at room temperature with stirring, then dried at 383 K and calcined again at 873 K for 5 h. After washing, the samples were renamed W1P-Z, W2P-Z, W3P-Z, W4.5P-Z and W5.5P-Z.

The products were characterized by X-ray diffraction (XRD) using a Rigaku Miniflex with Cu-K $\alpha$  radiation. The chemical compositions of the samples were analyzed by Energy Dispersive X-ray Spectrometry (EDX). The acidic strength of the samples was analyzed by temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) using an Autosorb-1-Chemi (Quantachrome Instruments) in the temperature range from 373 to 973 K. A 0.2 g sample was pretreated in helium at 773 K for 1 h, then cooled to 373 K for 1 h. After NH<sub>3</sub> was adsorbed on the samples for 2 h, temperature-programmed desorption was started at 10 K·min<sup>-1</sup> from 373 to 973 K using a Quantachrome TPRWin v2.0.

## 2.2. Catalytic Test

MTO reactions over H-ZSM-5 and P-HZSM-5 catalysts were performed using a fixed bed reactor made of quartz glass (i.d. 4 mm) with a continuous flow system under atmospheric pressure. The temperature and *W/F* (mass of the catalyst [kg] divided by the feed rate of methanol [mol/h]) were systematically varied for comparison. The reaction products were analyzed by a GC-14B (Shimadzu Corp.) gas chromatograph equipped with a flame ionization detector (FID) using

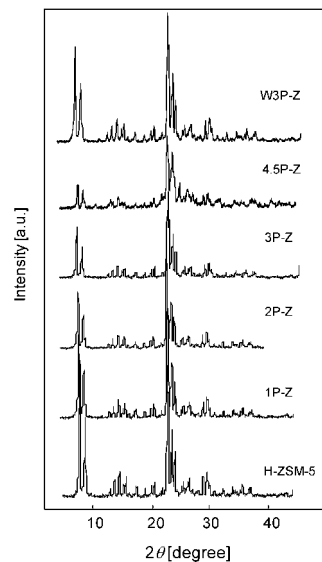


Fig. 1 XRD Patterns of H-ZSM-5 and P-HZSM-5

an SM-6 column (6 m, 3 mm) and a gas chromatograph GC-2014 (Shimadzu Corp.) equipped with a flame ionization detector (FID) using a Xylene Master column PRC 7791 (50 m, 0.32 mm).

## 3. Results and Discussion

### 3.1. Catalyst Characterization

**Figure 1** shows the XRD patterns of the H-ZSM-5 and P-HZSM-5 catalysts. The MFI structure of H-ZSM-5 was retained after the treatment with H<sub>3</sub>PO<sub>4</sub>. The XRD patterns of P-HZSM-5 did not contain a broad peak indicating an amorphous phase. However, the peak intensity of the XRD patterns decreased after the H<sub>3</sub>PO<sub>4</sub> treatment, possibly due to partial blockage of HZSM-5 pores by excess H<sub>3</sub>PO<sub>4</sub> molecules because the XRD peak intensity of P-HZSM-5 decreased with higher contents of H<sub>3</sub>PO<sub>4</sub> and recovered after removal of the excess H<sub>3</sub>PO<sub>4</sub> by washing.

The molar ratios of P/Si and Si/Al in H-ZSM-5 and P-HZSM-5 were measured by EDX analysis as shown in **Fig. 2**. The molar ratio of P/Si was greatly decreased after washing. The H<sub>3</sub>PO<sub>4</sub> molecules deposited on the external surface and on the entrances of the pores of H-ZSM-5 would be easily removed. The P/Si molar ratio was directly proportional to the H<sub>3</sub>PO<sub>4</sub> concentra-

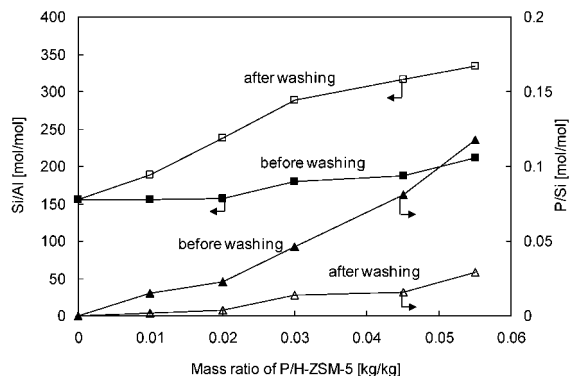


Fig. 2 Molar Ratios of P/Si and Si/Al Measured by EDX Analysis

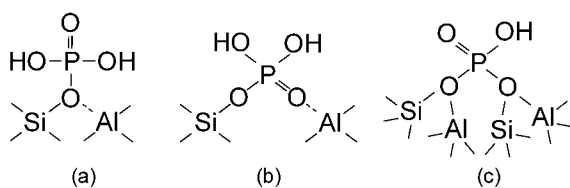


Fig. 3 Models for the Interaction of Phosphorus with the Brønsted Acid Sites of H-ZSM-5 (a) Proposed by Keading *et al.*<sup>21)</sup> (b) Proposed by Lercher *et al.*<sup>22)</sup> and (c) Proposed by Xue *et al.*<sup>17)</sup>

tions in the aqueous solutions. The remaining phosphorus species after the washing must be strongly adsorbed by interacting with the pore surface of H-ZSM-5 zeolite.

The Si/Al ratios were increased after washing. The Si/Al molar ratios increased with higher concentration of H<sub>3</sub>PO<sub>4</sub> in the solution, which might be caused by partial dealumination over H-ZSM-5 by the H<sub>3</sub>PO<sub>4</sub> treatment. For the 5.5P-Z samples, more than half of the Al was dissolved from the H-ZSM-5 framework.

The models for H<sub>3</sub>PO<sub>4</sub> deposited on the external surface and inside the pore before and after calcination were previously described<sup>19)</sup>. Various interactions of phosphorus with the Brønsted acid sites of H-ZSM-5 prepared by impregnation with H<sub>3</sub>PO<sub>4</sub> and calcinations have been proposed by some researchers<sup>20)–23)</sup>. The models proposed by Keading *et al.*<sup>21)</sup> and Lercher *et al.*<sup>22)</sup> are illustrated in **Figs. 3(a)** and **(b)**, respectively. Recently, a schematic mechanism for the phosphorus interaction with H-ZSM-5 was suggested as shown in **Fig. 3(c)**<sup>17)</sup>. Two zeolitic hydroxyls are condensed with one phosphate molecule after calcination in air leading to a decrease in the number of OH groups on P modification. This mechanism has been convincingly supported by D<sub>2</sub>/OH measurements.

**Figure 4** shows the NH<sub>3</sub>-TPD profiles of H-ZSM-5 and P-HZSM-5. There are two desorption peaks for H-ZSM-5, one in the range of 373–473 K and the other from 523 to 723 K, corresponding to the weak acid sites

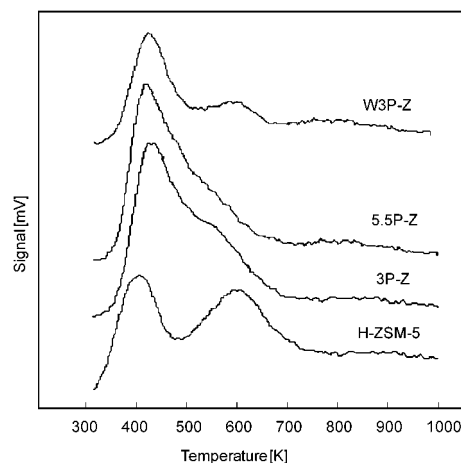


Fig. 4 NH<sub>3</sub>-TPD Profiles of the H-ZSM-5 and P-HZSM-5 Catalysts

and strong acid sites, respectively. The peak intensity for the strong acid sites decreased with higher H<sub>3</sub>PO<sub>4</sub> content whereas the desorption peak for weak acid sites was not changed so much. After washing with deionized water, the peak for strong acid sites slightly reappeared. These new acid sites might be caused by the interaction of phosphorus with the Brønsted acid sites of H-ZSM-5 as shown in **Fig. 3**.

### 3.2. MTO Reactions over H-ZSM-5 and P-HZSM-5

The methanol conversions and product selectivities over various catalysts are listed in **Table 2**. The product selectivities were calculated based on the total amount of the products, including aromatic compounds. With increasing H<sub>3</sub>PO<sub>4</sub> content, the selectivities for ethylene and aromatics were decreased and the propylene selectivity was increased. The highest propylene selectivity obtained in this study was about 57%, which is very high compared to the reported values. Ethylene was formed predominantly *via* aromatics such as xylenes and/or trimethylbenzenes<sup>12)</sup>. The hydrogen transfer reactions take place on strong acid sites. Apparently, the formation of aromatics and ethylene was inhibited by the decrease in the numbers of strong acid sites after the H<sub>3</sub>PO<sub>4</sub> treatment.

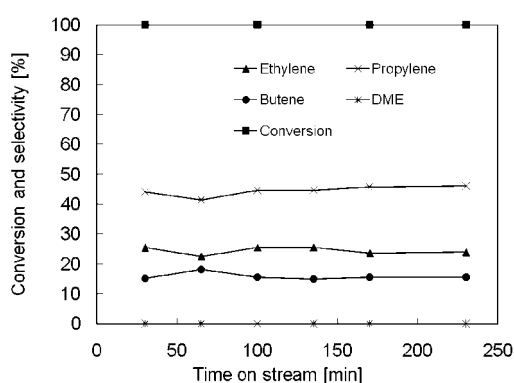
The selectivity for propylene reached 54.9% over 3P-Z catalyst. However, by increasing the H<sub>3</sub>PO<sub>4</sub> content further, the methanol conversion over 5.5P-Z decreased to 71.1% and light olefin selectivity was about 3%. Instead, dimethylether (DME) was a main product. After the removal of excess H<sub>3</sub>PO<sub>4</sub> by washing, the selectivity for ethylene and aromatics as well as propylene was increased again due to the partial recovery of strong acid sites. However, the acidity of the strong acid sites was still lower than that on the untreated H-ZSM-5 due to the partial dealumination.

**Figures 5–10** show the changes in methanol conversions and product selectivities with reaction time. The

Table 2 Methanol Conversion and Product Selectivity over H-ZSM-5 and P-HZSM-5 Catalysts

Catalyst	Conversion [%]	Selectivity [%]								
		C <sub>1</sub>	C <sub>2</sub> <sup>=</sup>	C <sub>3</sub>	C <sub>3</sub> <sup>=</sup>	C <sub>4</sub>	C <sub>4</sub> <sup>=</sup>	C <sub>5</sub> -	DME	Aromatics
H-ZSM-5	100	1.5	22.5	3.1	39.0	3.7	13.4	5.8	0	11.0
1P-Z	100	1.7	19.9	2.4	44.1	3.3	16.4	7.9	0	4.3
2P-Z	100	1.9	17.4	1.3	48.4	2.1	18.0	8.2	0	2.9
3P-Z	100	1.9	8.9	0.7	54.9	1.6	17.10	13.9	0	1.3
4.5P-Z	86.8	4.8	6.8	0.4	52.6	0.7	18.3	14.7	0.6	1.1
5.5P-Z	71.1	1.3	2.3	0.4	0.5	0.4	0.3	0.3	94.5	0
W1P-Z	100	2.1	22.0	3.8	37.3	5.2	14.7	7.6	0	7.4
W2P-Z	100	2.6	22.6	3.3	40.7	4.3	15.1	7.0	0	4.4
W3P-Z	100	1.5	19.9	2.4	45.7	2.8	16.7	8.1	0	3.0
W4.5P-Z	100	1.2	9.6	0.6	57.0	1.0	18.8	10.7	0	1.1
W5.5P-Z	97.4	2.6	11.4	0.4	52.9	0.9	16.2	14.4	0	1.1

$W/F = 0.065 \text{ kg} \cdot \text{h} \cdot \text{mol}^{-1}$ , reaction temperature = 723 K, reaction time = 30 min.

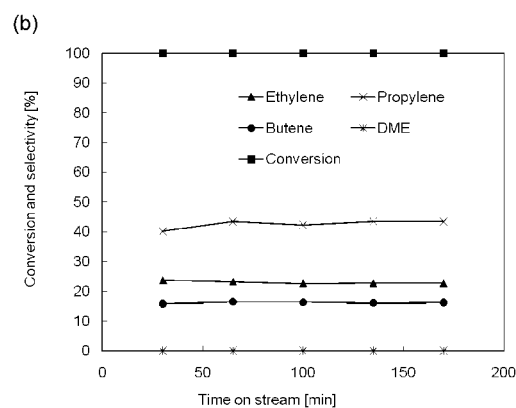
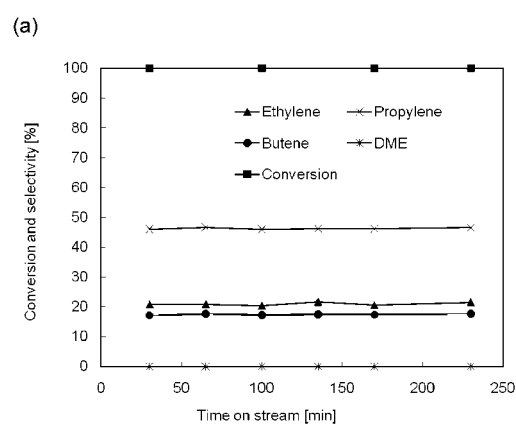


$W/F = 0.065 \text{ kg} \cdot \text{h} \cdot \text{mol}^{-1}$ .

Fig. 5 Methanol Conversion and Product Selectivities over H-ZSM-5 at 723 K

selectivities for hydrocarbons were calculated from the product amounts excluding aromatic compounds. The selectivity for propylene over the 3P-Z catalyst was slightly decreased after several hours with the presence of DME. The selectivity for DME was slightly increased after 200 min, indicating that catalytic deactivation by coke formation occurred over the catalyst with high phosphorus contents. Catalytic deactivation was obviously observed over the 4.5P-Z and 5.5P-Z catalysts (Figs. 9 and 10). After the deactivation, DME was mainly produced. DME is formed by methanol dehydration, which is the first step of the MTO reactions. The strong acid sites must have been covered with excess  $\text{H}_3\text{PO}_4$  molecules which inhibited the conversion of DME into other hydrocarbons. In addition, for the samples before washing (4.5P-Z and 5.5P-Z), octahedral aluminum species must have remained inside the pores as a result of dealumination in the  $\text{H}_3\text{PO}_4$  solutions with high concentrations. These aluminum species would reduce the durability in the MTO reaction.

The methanol conversions and propylene selectivities

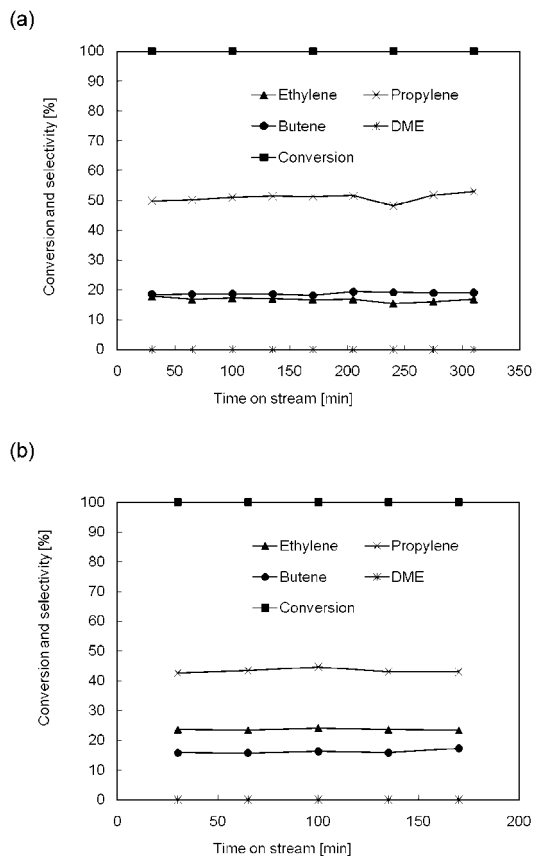


$W/F = 0.065 \text{ kg} \cdot \text{h} \cdot \text{mol}^{-1}$ .

Fig. 6 Methanol Conversion and Product Selectivities over (a): 1P-Z; (b): W1P-Z at 723 K

over the P-HZSM-5 catalysts were much improved after washing. The catalyst performance of W4.5P-Z and W5.5P-Z was very stable with very high propylene selectivities because the acidity of the strong acid sites of H-ZSM-5 after dealumination was lower than that of untreated H-ZSM-5.

The effect of  $W/F$  on the product selectivities is shown in Fig. 11. The reactions were performed over

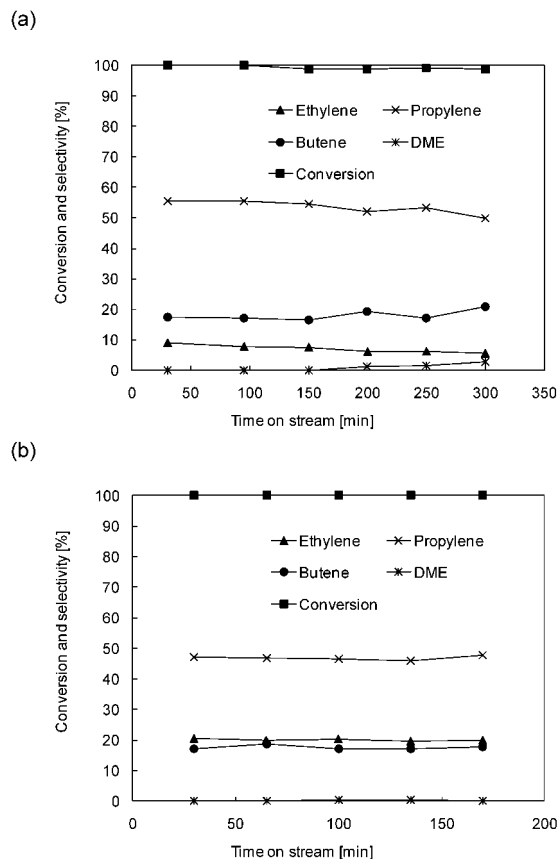


$$W/F = 0.065 \text{ kg} \cdot \text{h} \cdot \text{mol}^{-1}$$

Fig. 7 Methanol Conversion and Product Selectivities over (a): 2P-Z; (b): W2P-Z at 723 K

the 3P-Z catalyst at 723 K. The data were collected after reaction for 30 min. The selectivities for hydrocarbons were calculated based on the amount of products excluding aromatic compounds. The conversion of methanol was 100% for each  $W/F$ . However, a small fraction of DME was formed at a low  $W/F$  of  $0.024 \text{ kg} \cdot \text{h} \cdot \text{mol}^{-1}$ , indicating that the contact time was not sufficient to convert all DME to olefins. The highest selectivities for propylene were obtained at  $W/F$  from 0.033 to  $0.065 \text{ kg} \cdot \text{h} \cdot \text{mol}^{-1}$ .

The effects of reaction temperature on methanol conversion and product selectivity are shown in Fig. 12. The reactions were carried out at  $W/F = 0.065 \text{ kg} \cdot \text{h} \cdot \text{mol}^{-1}$  over the 3P-Z catalyst. The methanol conversion was nearly 80% at 573 K, whereas the main product was DME with other hydrocarbons as minor products. On the other hand, MTO reaction over untreated H-ZSM-5 showed nearly 100% methanol conversion with a small amount of DME at 573 K. These results indicate that the acidity was weakened by the  $\text{H}_3\text{PO}_4$  treatment, suggesting that higher temperatures are required for MTO reactions over P-HZSM-5 catalysts. The highest selectivity for propylene (nearly 57%) was



$$W/F = 0.065 \text{ kg} \cdot \text{h} \cdot \text{mol}^{-1}$$

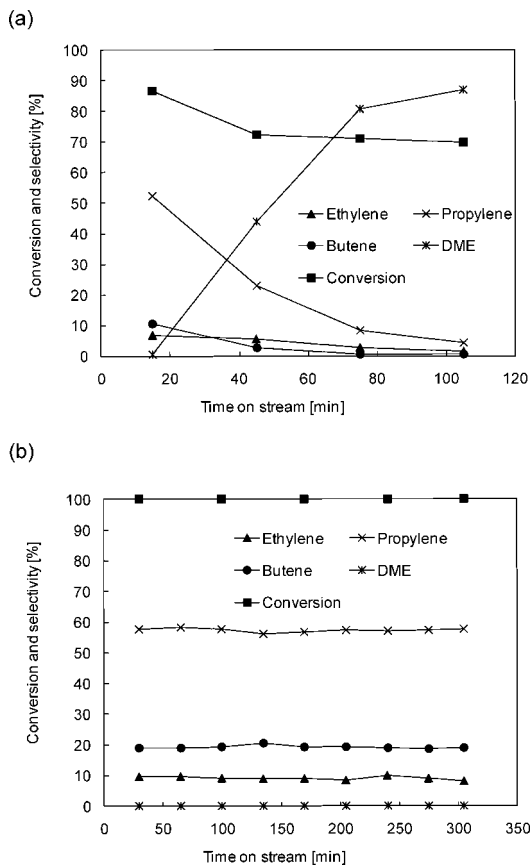
Fig. 8 Methanol Conversion and Product Selectivities over (a): 3P-Z; (b): W3P-Z at 723 K

obtained at 723 K, although the selectivity for aromatics was not significantly increased at other temperatures.

#### 4. Conclusions

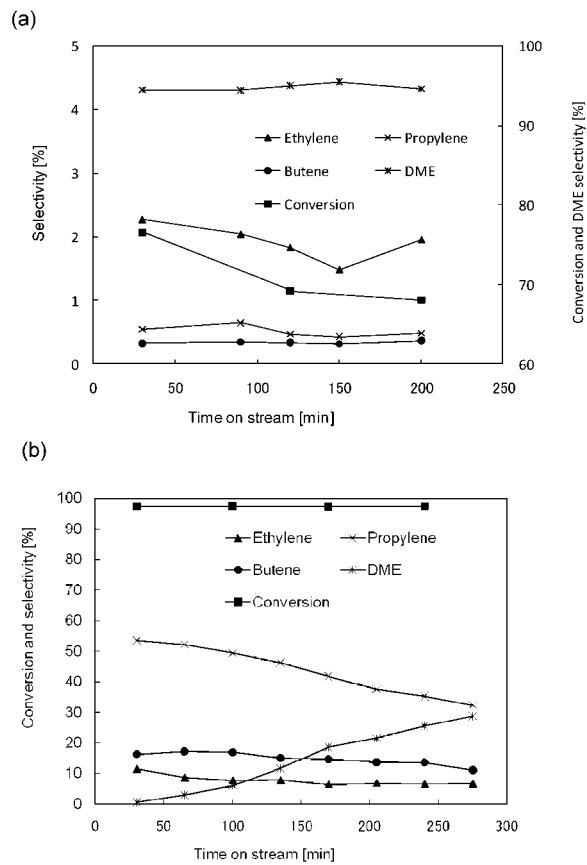
H-ZSM-5 catalyst was treated with  $\text{H}_3\text{PO}_4$  solutions of various concentrations. The selectivities for olefins over P-ZSM-5 in the MTO reactions were significantly improved by the  $\text{H}_3\text{PO}_4$  treatment. Higher phosphorus content in P-HZSM-5 significantly decreased the selectivity for ethylene and aromatics due to lower acidity of the strong acid sites of H-ZSM-5 caused by dealumination. The highest selectivity for propylene over modified P-HZSM-5 reached 57% with small amounts of aromatic by-products. The removal of excess  $\text{H}_3\text{PO}_4$  after washing resulted in partial recovery of the strong acid sites. The catalyst performance of washed P-HZSM-5 was very stable with very high propylene selectivities.

The significant increase in propylene selectivity over P-HZSM-5 catalysts has important practical applications in current petroleum chemistry.



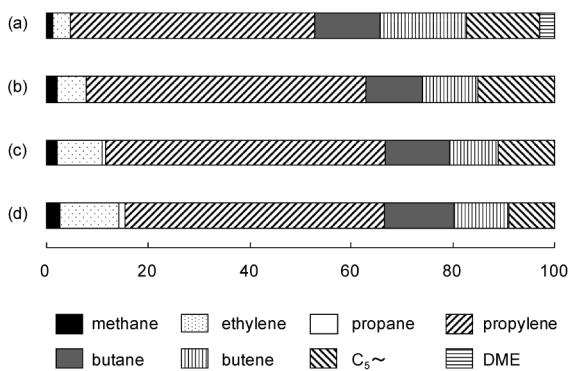
$W/F = 0.065 \text{ kg} \cdot \text{h} \cdot \text{mol}^{-1}$ .

Fig. 9 Methanol Conversion and Product Selectivities over (a): 4.5P-Z; (b): W4.5P-Z at 723 K



$W/F = 0.065 \text{ kg} \cdot \text{h} \cdot \text{mol}^{-1}$ .

Fig. 10 Methanol Conversion and Product Selectivities over (a): 5.5P-Z; (b): W5.5P-Z at 723 K

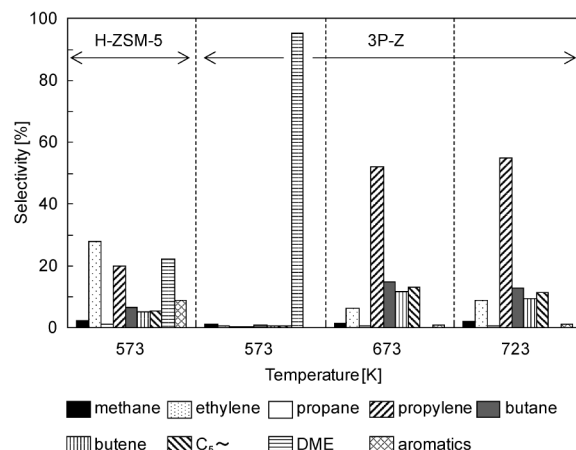


$W/F$ : (a) 0.024; (b) 0.033; (c) 0.065; (d) 0.200  $\text{kg} \cdot \text{h} \cdot \text{mol}^{-1}$ .  
Reaction time of 30 min.

Fig. 11 Product Selectivities over 3P-Z Catalyst at 723 K

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Reaction time of 30 min. Methanol conversions are 100% (H-ZSM-5, 573 K), 79.1% (3P-Z, 573 K), 100% (3P-Z, 673 K) and 100% (3P-Z, 773 K).

Fig. 12 Effect of Temperature on Methanol Conversion and Product Selectivities over H-ZSM-5 and 3P-Z Catalysts in MTO Reaction at  $W/F$  of  $0.065 \text{ kg} \cdot \text{h} \cdot \text{mol}^{-1}$

## References

- 1) Haw, J. F., Nicholas, J. B., Song, W., Deng, F., Wang, Z., Xu, T., Heneghan, C. S., *J. Am. Chem. Soc.*, **122**, 4763 (2000).
- 2) Valle, B., Alonso, A., Atutxa, A., Gayubo, A. G., Bilbao, J., *Catal. Today*, **106**, 118 (2005).
- 3) Tago, T., Iwakai, K., Morita, K., Tanaka, K., Masuda, T., *Catal. Today*, **105**, 662 (2005).
- 4) Bjørgen, M., Olsbye, U., Petersen, D., Kolboe, S., *J. Catal.*, **221**, 1 (2004).
- 5) Sassi, A., Wildman, M. A., Haw, J. F., *J. Phys. Chem. B*, **106**, 8768 (2002).
- 6) Wei, Y., Zhang, D., He, Y., Xu, L., Yang, Y., Su, B.-L., Liu, Z., *Catal. Lett.*, **114**, 30 (2007).
- 7) Chen, J. Q., Bozzano, A., Glover, B., Fuglerud, T., Kvisle, S., *Catal. Today*, **106**, 103 (2005).
- 8) Park, J. W., Lee, J. Y., Kim, K. S., Hong, S. B., Seo, G., *Appl. Catal. A: General*, **339**, 36 (2008).
- 9) Dahl, I. M., Kolboe, S., *J. Catal.*, **149**, 458 (1994).
- 10) Chen, D., Moljord, K., Fluglerud, T., Holmen, A., *Micropor. Mesopor. Mater.*, **29**, 191 (1999).
- 11) van Heyden, H., Mintova, S., Bein, T., *Chem. Mater.*, **20**, 2956 (2008).
- 12) Bjørgen, M., Svelle, S., Joensen, F., Nerlov, J., Kolboe, S., Bonino, F., Palumbo, L., Bordiga, S., Olsbye, U., *J. Catal.*, **249**, 195 (2007).
- 13) Mei, C., Wen, P., Liu, Z., Liu, H., Wang, Y., Yang, W., Xie, Z., Hua, W., Gao, Z., *J. Catal.*, **258**, 243 (2008).
- 14) Bjørgen, M., Joensen, F., Holm, M. S., Olsbye, U., Lillerud, K.-P., Svelle, S., *Appl. Catal., A: General*, **345**, 43 (2008).
- 15) Kaarsholm, M., Joensen, F., Nerlov, J., Cenni, R., Chaouki, J., Patience, G. S., *Chem. Eng. Sci.*, **62**, 5527 (2007).
- 16) Li, J., Qi, Y., Xu, L., Liu, G., Meng, S., Li, B., Li, M., Liu, Z., *Catal. Commun.*, **9**, 2515 (2008).
- 17) Xue, N., Chen, X., Nie, L., Guo, X., Ding, W., Chen, Y., Gu, M., Xie, Z., *J. Catal.*, **248**, 20 (2007).
- 18) Jiang, G., Zhang, L., Zhao, Z., Zhou, X., Duan, A., Xu, C., Gao, J., *Appl. Catal. A: General*, **340**, 176 (2008).
- 19) Kalbasi, R. J., Ghiaci, M., Massah, A. R., *Appl. Catal. A: General*, **353**, 1 (2009).
- 20) Blasco, T., Corma, A., Martínez-Triguero, J., *J. Catal.*, **237**, 267 (2006).
- 21) Keating, W. W., Butter, S. A., *J. Catal.*, **61**, 155 (1980).
- 22) Lercher, J. A., Rimplmayr, G., *Appl. Catal. A: General*, **25**, 215 (1986).
- 23) Zhao, T.-S., Takemoto, T., Tsubaki, N., *Catal. Commun.*, **7**, 647 (2006).

## 要 旨

## リン酸処理した H-ZSM-5 触媒を用いたプロピレン高選択性による Methanol-to-olefin 反応

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H-ZSM-5ゼオライトを種々の濃度のリン酸水溶液に浸漬し乾燥させたリン酸修飾 H-ZSM-5 (P-HZSM-5), およびこれを水で洗浄した触媒を調製した。生成物の P/Si および Si/Al を EDX にて測定した。水で洗浄した P-HZSM-5 の Si/Al 比は、リン酸水溶液の濃度の増加とともに増加したことから、リン酸処理による脱アルミが起こったものと考えられる。洗浄後もリン種はゼオライト内に残存し、P/Si 比はリン酸水溶液の濃度の増加とともに増加した。リン酸種は ZSM-5 細孔表面に強い相互

作用で結合しているものと思われる。本触媒を methanol-to-olefin 反応に用いたところ、メタノールの転化率 100% の条件で、57% 以上の高いプロピレン選択性を示した。同時に、触媒の安定性も向上した。アンモニア TPD 測定により、H-ZSM-5 の強酸点の酸量がリン酸処理によって減少することが分かった。その結果、芳香族炭化水素およびコークの生成が抑制され、高い低級オレフィン選択性および触媒の優れた安定性が得られたものと思われる。