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Phosphorus-modified ZSM-5 for conversion of ethanol to propylene

Zhaoxia Song^{a,b}, Atsushi Takahashi^a, Isao Nakamura^a, Tadahiro Fujitani^{a,*}

^a Research Institute for Innovation in Sustainable Chemistry, National Institute of Advanced Industrial Science and Technology (AIST) 16-1, Onogawa, Tsukuba, Ibaraki 305-8569, Japan

^b College of Life Science, Dalian Nationalities University, Dalian 116600, China

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1. Introduction

The petroleum crisis has driven many researchers to seek new routes for converting coal or natural gas into gasoline and other chemicals. In particular, methanol-to-hydrocarbon, methanol-togasoline (MTG), and methanol-to-olefins (MTO) reactions have been regarded as especially attractive reactions for this purpose. Many papers and reviews about MTO processes have been published [1–7]. However, in view of decreasing fossil fuel resources and increasing CO₂ emissions, the production of olefins from ethanol has attracted much attention in recent years [8-13], since ethanol can be obtained from renewable biomass sources. At the same time, the demand for propylene is increasing, and new processes to yield large quantities of propylene are being sought.

Recently, we reported the conversion of ethanol to propylene on H-ZSM-5 and ZSM-5 zeolites modified with various metals [14]. Our results suggested that moderate surface acidity was optimum for the production of propylene. Furthermore, the catalytic stability of the zeolites was improved by modification of the zirconium with Zr/Al = 0.4. However, the zeolites poor hydrothermal stability and resistance to coke formation render this process unviable for industrial applications.

Many researchers have reported that phosphorus-modified ZSM-5 shows improved catalytic performance and hydrothermal stability relative to unmodified zeolites [2,15-29]. However,

ABSTRACT

In this work, phosphorus-modified ZSM-5 zeolites were used to transform ethanol to propylene. The selectivity of propylene formation depended strongly on the phosphorus content in the zeolites; the highest propylene yield (32%) was observed over H-ZSM-5(80) modified with phosphorus at a P/Al molar ratio of 0.5. The enhancement of propylene selectivity with increasing phosphorus content was attributed to reduction of strong acid sites on the H-ZSM-5. Modification of the zeolite with phosphorous also improved the material's catalytic stability.

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to the best of our knowledge, the conversion of ethanol to propylene over phosphorus-modified ZSM-5 has not been studied extensively to date. In this study, phosphorus-modified ZSM-5 catalysts were prepared and were used in the conversion of ethanol to propylene. The results show that phosphorusmodified ZSM-5 exhibited enhanced catalytic stability relative to unmodified zeolites and also effectively produced propylene from ethanol.

2. Experimental

2.1. Catalyst preparation

H-ZSM-5(80) and H-ZSM-5(30) were obtained by calcination of as-received zeolites (Zeolyst, CBV3024E and CBV8014 with Si/Al₂ molar ratios of 30 and 80, respectively) at 873 K in air for 4 h. The phosphorus-modified ZSM-5 samples were prepared by an impregnation method. NH₄-ZSM-5(80) powder (3g) was suspended in a 40 ml solution of $1 \text{ M} (\text{NH}_4)_2 \text{HPO}_4$, and the solvent was slowly evaporated from the suspension in a rotary vacuum evaporator at 323 K. Then, the residue was dried at 373 K for 5 h and calcined at 873 K in air for 4 h. The molar ratios of P to Al were 0.25, 0.5, 0.7, and 1.0 (corresponding to P contents of 0.3, 0.6, 0.9, and 1.3 wt%, respectively). The obtained samples were designated as PZ(80)-x, where x is the molar ratio of P/Al. Phosphorous-modified ZSM-5(30) samples were prepared by means of the same method described above, and these samples were designated as PZ(30)-x, where x = 0.5 or 0.7 (corresponding to P contents of 1.7 and 2.3 wt%, respectively).

^{*} Corresponding author. Tel.: +81 298 61 8454; fax: +81 298 61 8172. E-mail address: t-fujitani@aist.go.jp (T. Fujitani).

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Fig. 1. XRD patterns of unmodified and phosphorus-modified ZSM-5 samples.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of the samples were obtained with a diffractometer (Rigaku, RINT2000) operated at 40 kV and 40 mA with Cu K α monochromatized radiation (λ = 0.154178 nm).

NH₃-temperature-programmed desorption (TPD) was performed in a flow system (BEL-CAT-32). The catalyst sample (0.1 g) was placed in a small quartz tube and heated at 773 K in a He flow (30 ml min^{-1}) for 1 h. The sample was cooled to 373 K, and NH₃ adsorption was performed under a flow of 5 vol% NH₃/He (30 ml min^{-1}) for 1 h. The sample was flushed with He gas at a rate of 30 ml min^{-1} for 1 h to remove NH₃ that was physically adsorbed on the sample surface. The desorption of NH₃ species was measured from 373 to 873 K at a constant heating rate of 10 K min^{-1} . A thermal conductivity detector was used to monitor NH₃ desorption.

2.3. Catalytic testing

Catalytic reactions were carried out at atmospheric pressure in a fixed-bed, continuous-flow reactor equipped with a quartz tube (inner diameter 12 mm). The samples were pelletized, crushed, and then sieved to 14–22 mesh. In a typical run, 0.3 g of catalyst was placed in the central zone of the reactor. A thermocouple reaching into the center of the catalyst bed was used to measure the temperature during the reaction. The catalyst was activated at 873 K for 1 h in flowing N₂ before each reaction. Ethanol (Wako, purity >99.5%) was pumped into the vaporizer and mixed with N₂ at a total flow rate of 30 ml min⁻¹ ($P_{C_2H_5OH}$ = 50 kPa). The products were analyzed on-line with gas chromatographs (Shimadzu GC-14A) equipped with a flame ionization detector and thermal conductivity detectors. An Rt[®]-Alumina capillary column (0.32 mm × 60 m) was used to detect ethanol and C₁–C₄ hydrocarbons. A MS-5A packed column (3 mm × 2 m) was used to detect N₂ and H₂.

3. Results and discussion

3.1. Characterization

The XRD patterns of all the samples are shown in Fig. 1. Phosphorus-modified ZSM-5 samples exhibited diffraction patterns that were similar to those of the unmodified samples, showing



Fig. 2. NH₃-TPD profiles of unmodified and phosphorus-modified ZSM-5 samples.

the typical MFI structure and no additional phases. It has been reported previously that the XRD crystallinity of zeolites decreases after phosphorus modification owing to the framework defects caused by dealumination [25,29]. Compared to H-ZSM-5(80), the phosphorus-modified ZSM-5(80) samples showed decreased crystallinity. In contrast, for phosphorus-modified ZSM-5(30), no observable reduction in crystallinity was seen.

The NH₃-TPD profiles of the unmodified and phosphorusmodified samples are shown in Fig. 2. All the samples showed two desorption peaks: one centered at 473 K and the other at 673 K, corresponding to weak and strong acid sites, respectively. With increasing phosphorus loading, the intensity of the strong acid desorption peak decreased markedly, while the intensity of the weak acid desorption peak increased. Furthermore, the desorption peaks shifted slightly toward lower temperatures as the phosphorus content increased. These results clearly indicate that impregnation of phosphorus in H-ZSM-5 not only decreased the concentration of strong acid sites but also increased the concentration of weak acid sites on the zeolite.

3.2. Catalytic activity

H-ZSM-5 and the phosphorus-modified ZSM-5 samples showed 100% conversion of ethanol at temperatures above 673 K. Fig. 3 shows the product distribution for the initial reaction over phosphorus-modified ZSM-5(80) and ZSM-5(30) samples compared with their unmodified counterparts at 823 K. The product distribution depended strongly on the phosphorus content. For H-ZSM-5(80) and phosphorus-modified ZSM-5(80) samples, when the phosphorus content increased, C_{1-4} paraffins as well as C_{5+} aliphatic and aromatic compounds were significantly suppressed, and the ethylene yield increased. The propylene yield increased with increasing phosphorus loading to a maximum value of 32% at P/Al = 0.5; further increase in the phosphorus loading resulted in a decrease in the propylene yield. Samples with high phosphorus content, such as PZ(80)-1, exhibited marked decreases in propylene yield, with ethylene becoming the predominant product. Therefore we concluded that the optimum molar ratio of P to Al was around 0.5. Compared with H-ZSM-5(80) samples, H-ZSM-5(30) samples, which had a higher Si/Al₂ ratio, produced more paraffins, C_{5+}



Fig. 3. Initial product distribution over ZSM-5 samples at 823 K. *Reaction conditions*: 0.3 g catalyst; 0.1 MPa pressure; total flow rate 30 ml min⁻¹, $P_{C_2H_5OH} = 50$ kPa; time-on-stream, 30 min. The category "Others" includes C_{5+} aliphatics and C_{5+} aromatics.

aliphatics, and C₅₊ aromatics. After H-ZSM-5(30) was modified with phosphorus, the catalyst's selectivity for light olefins increased, and the selectivity for C₁₋₄ paraffins, C₅₊ aliphatics, and C₅₊ aromatics decreased. The propylene yield was 26% for PZ(30)-0.5, which was lower than that obtained for PZ(80)-0.5. Under identical reaction conditions, unmodified and phosphorus-modified ZSM-5 exhibited a different product distribution: A higher selectivity toward propylene was observed for the phosphorus-modified samples. As noted above in the NH₃-TPD experiments, the phosphorus-modified samples featured reduced acidity relative to the unmodified samples. The strong acid sites on the zeolites are responsible for hydrogen transfer reactions, and thus the presence of reduced acidity in turn decreased the conversion of olefins to paraffins. In addition to lower amounts of aromatics and long-chain hydrocarbons, less coke formation was observed over the phosphorus-modified samples, along with higher selectivity toward light olefins. However, excessive loading of phosphorus on the samples resulted in greatly reduced acidity, which decreased the catalysts' selectivity toward propylene. These results demonstrate that acidity played an important role in the product distribution over these catalysts, with high selectivity toward propylene being associated with moderate surface acidity.

Fig. 4 shows the effect of reaction temperature on product yield over PZ(80)-0.5. The yield of ethylene increased with increasing temperature, whereas the yields of C_{1-4} paraffins, C_{5+} aliphatics, and aromatics gradually decreased. The propylene yield increased with temperature to a maximum value at 823 K; further increases in the reaction temperature decreased the propylene yield. These results indicate that the conversion of ethanol to propylene is a complicated process involving oligomerization, hydrogen transfer, isomerization, aromatization, and cracking reactions. Of these reactions, oligomerization and the conversion of ethylene to longer-chain hydrocarbons were favored at lower temperature (673 K); at a higher temperature (873 K) thermal cracking was favored, resulting in an increase in ethylene production. In other words, at low temperatures ethylene was primarily produced by dehydration of ethanol, whereas at higher temperatures ethylene was a product of secondary cracking. These observed trends were in agreement with the thermal equilibrium calculation. Therefore, the distribution of products should have been limited by the thermodynamic calculation.

Fig. 5 shows the effect of reaction contact time on the yield of products over PZ(80)-0.5 at 823 K. At low W/F, the dehydration of ethanol to ethylene was predominant owing to the short contact time, whereas at higher W/F, the long contact time led to the subsequent conversion of ethylene to products including propylene, butene, paraffins, C_{5+} aliphatics, and C_{5+} aromatics. On



Fig. 4. Effect of reaction temperature on product yields over PZ(80)-0.5. *Reaction conditions*: 0.3 g catalyst; 0.1 MPa pressure; total flow rate 30 ml min⁻¹, $P_{C_2H_5OH} = 50$ kPa. The category "Others" includes C_{5+} aliphatics and C_{5+} aromatics.

the basis of the above results, we concluded that a W/F of ca. $0.01-0.02 \text{ g ml}^{-1}$ min at 823 K was most favorable for propylene production.

Fig. 6 shows the time course of ethanol conversion over H-ZSM-5(80) and over phosphorus-modified ZSM-5(80) samples at 823 K. Under these reaction conditions, the propylene yield over H-ZSM-5(80) was 23.4% at 30 min; however, after 6 h, the propylene yield dropped to 4.6%, and the yield of ethylene increased rapidly from 24.5 to 90.8%. These results show that H-ZSM-5(80) was greatly deactivated over time, showing very poor catalytic stability. Compared with H-ZSM-5(80), the phosphorus-modified sample (P/Al = 0.25) exhibited improved catalytic stability. Phosphorus-modified samples containing even greater P content, that is, PZ(80)-0.5 and PZ(80)-0.7, showed excellent catalytic stability with no deactivation during this reaction period. During ethanol-to-propylene (ETP) conversion, the observed deactivation of H-ZSM-5 could have been caused by two mechanisms: (1) the deposition



Fig. 5. Effect of reaction contact time on the yield of products over PZ(80)-0.5. *Reaction conditions*: T = 823 K; 0.1 MPa pressure; $P_{C_2H_5OH} = 50$ kPa. The category "Others" includes C_{5+} aliphatics and C_{5+} aromatics.



Fig. 6. Time course of ethanol conversion over H-ZSM-5(80) phosphorus-modified ZSM-5 samples. *Reaction conditions*: 0.3 g catalyst; T = 823 K; 0.1 MPa pressure; total flow rate 30 ml min⁻¹, $P_{C_2H_2OH} = 50$ kPa.

of carbonaceous residue (coke) on H-ZSM-5 or (2) an irreversible loss of activity due to dealumination of the zeolite structure. The strong acidity of H-ZSM-5 encourages the dehydration of ethanol to form oligomers responsible for coke formation. Coke would already have been formed in the early stages of the ethanol conversion reaction and would have covered the strong acid sites, thus reducing the conversion of ethylene to propylene. However, when the H-ZSM-5 was modified with phosphorus, the number of these sites as well as their acidic strength decreased as discussed above. This decrease in acidity can successfully suppress the oligomerization and cyclization reactions that lead to coke formation. For regeneration of deactivated H-ZSM-5(80), the coke in the zeolite was burned off under a mixed flow of O_2 (15 ml min⁻¹) and N_2 (60 ml min^{-1}) at 823 K for 1 h. The regenerated H-ZSM-5(80) was then used for another reaction cycle, for which the yield of propylene increased from 4.6% (for the deactivated zeolite) to 10.9%; the yield of ethylene decreased from 90.8% to 79.6%. Compared to the catalysts' initial activity in the first reaction cycle (propylene and ethylene yields of 23.4% and 24.6%, respectively), the activity of the regenerated H-ZSM-5(80) was not recovered completely. Since the catalytic activity was not fully recovered by coke combustion alone, these results suggest that, in addition to coke deposition, dealumination in water vapor was another major cause of H-ZSM-5(80) deactivation. To investigate the hydrothermal stability of unmodified and phosphorus-modified ZSM-5, we treated H-ZSM-5(80) and PZ(80)-0.5 samples with a flow of 33% steam with N₂ at 873 K before reaction with ethanol. Table 1 shows the catalytic performance of H-ZSM-5(80) and PZ(80)-0.5 after steam treatment. For H-ZSM-5(80), the yield of propylene decreased from 23.4 to 0% when the catalyst was treated with steam for 10 h. In contrast, for PZ(80)-

Table 1

The catalytic performance of H-ZSM-5(80) and PZ(80)-0.5 for conversion of ethanol to propylene after steam treatment.

Steaming time/h ^a	Yield of propylene/% ^b	
	H-ZSM-5(80)	PZ(80)-0.5
0	23.4	32.4
2	6.4	32.3
4	1.9	32.2
10	0.0	32.2

^a Steam treatment in H_2O/N_2 (mol/mol = 1/2) flow at 873 K.

 b The data were obtained at 30 min on stream. Reaction conditions: T=823 K, C₂H₅OH/N₂ (mol/mol)=1/1, W/F=0.01 g ml^{-1} min.

0.5, the yield to propylene remained nearly constant (near 32%) after the stream treatment. The results indicate that aluminum was easily released from the framework of the unmodified ZSM-5 at high temperature and in aqueous environments, but the presence of phosphorus protected the catalyst from dealumination. In fact, modification with phosphorus is a widely used method for improving the hydrothermal stability of ZSM-5 [2,15-29]. The structures of aluminum and phosphorus in phosphorus-modified ZSM-5 have been extensively identified by solid-state magic angle spinning nuclear magnetic resonance (NMR). The results of NMR showed that the enhancement of structure stability by phosphorous modification is due to the suppression of dealumination [17,19,22,25–29]. However, controversy exists as to how phosphorus interacts with the zeolite and whether phosphorus occupies framework positions within the zeolite. Some researchers have proposed that Si-O-Al bonds are broken under hydrothermal conditions while phosphorus atoms simultaneously occupy framework silicon positions to form $(SiO)_x Al(PO)_{4-x}$ species [25]. Others have proposed that phosphorus interacts with tetrahedral-framework aluminum to form aluminum phosphates external to the framework [19,22,26-29]. In other words, modification of zeolites with phosphorus results in the formation of new species that appears as distorted tetrahedral aluminum atoms. These distorted species exhibit higher hydrothermal resistance than that of the original framework species. Thus, the phosphorus modification effectively stabilizes zeolite-framework aluminum.

4. Conclusions

Impregnation of phosphorus in H-ZSM-5 decreased the number of strong acid sites in the zeolite. Acidity played an important role on the product distribution for ethanol conversion over unmodified and phosphorus-modified ZSM-5; the catalyst's high selectivity toward propylene was associated with the moderate surface acidity observed on the phosphorus-modified catalysts. The optimal propylene yield was 32%, which was observed on H-ZSM-5(80) modified with phosphorus (P/AI=0.5) at 823 K.

Unmodified ZSM-5 was deactivated rapidly owing to both dealumination and, to a lesser extent, coke formation. In contrast, both coke deposition and dealumination were inhibited in the presence of phosphorus. Thus, both propylene selectivity and catalytic stability were greatly improved by phosphorus modification of ZSM-5 zeolites.

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