

Increase in the number of acid sites of a H-ZSM5 zeolite during the dehydration of ethanol

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The activity of a H-ZSM5-90 for the dehydration of ethanol at 473 K increased with an increase in time on stream. The results of NH₃-TPD and Ar adsorption showed that the number of acid sites of the H-ZSM5-90 increased during the dehydration. On the other hand, the activity and the number of acid sites of H-mordenite-90 were almost unchanged during the dehydration. Since the pre-treatment of the H-ZSM5-90 with ethylene at 473 K largely increased its activity for the dehydration of ethanol, it is suggested that a large number of new acid sites could be formed inside the pores of H-ZSM5-90 via the polymerization of ethylene produced by the dehydration of ethanol.

KEY WORDS: H-ZSM5; acid site; dehydration; ethanol.

1. Introduction

In recent times, the reduction of CO₂ emission has become a crucial problem in the chemical industry. The utilization of ethanol from biomass fermentation instead of petroleum as chemical feedstock may facilitate the reduction of CO₂ emission. Therefore, the authors have focused attention on the catalytic conversion of ethanol into ethylene at low temperatures such as 473 K. The authors reported that H-mordenites and H-ZSM5 zeolites were active for the dehydration of ethanol into ethylene and suggested that the catalyst activity could be correlated with the number of strong Brønsted acid sites of the catalyst [1]. Therefore, it is important to prepare a catalyst with a large number of strong acid sites for this reaction.

In the present study, the dehydration of ethanol into ethylene was investigated over a H-ZSM5-90 and a H-mordenite-90 at 473 K. It was newly found out that the activity increased during the dehydration of ethanol due to the increase of the number of acid sites on H-ZSM5-90.

2. Experimental

In the present study, a H-ZSM5-90 zeolite (JRC-Z5-90H(1)) and a H-mordenite (JRC-Z-HM90(1)), which were the reference catalysts supplied by Catalysis Society

of Japan, were used as the catalysts for the dehydration of ethanol. In the present paper, the symbols HZ5-90 and HM90 represent JRC-Z5-90H(1) and JRC-Z-HM90(1), respectively. The molar ratios of SiO₂ to Al₂O₃ in HZ5-90 and HM90 were 90. Those catalysts were used as received for the dehydration of ethanol.

The dehydration was carried out in a fixed-bed flow reactor at 473 K under atmospheric pressure. Pure ethanol (99.5%) obtained from Nacalai Tesque Inc. was used as received. The temperature of the catalyst placed in the reactor was raised to the reaction temperature in a flow of He. Ethanol or a mixture of ethanol and water was then fed into the reactor along with He. The reaction products were analyzed by FID gas chromatographs directly connected to the reactor. The products detected were ethylene, diethyl ether and small amounts of ethane, acetaldehyde, propene, and butenes. The yield of each product was defined as the conversion of ethanol to the products.

In order to characterize the acidity of the fresh and used catalysts, NH₃-TPD and Ar adsorption measurements were carried out.

The NH₃-TPD measurement was carried out under atmospheric pressure using a TPD apparatus connected to a mass spectrometer (Microvision from Leda-Mass Ltd).

Approximately 150 mg of the catalyst sample was treated in a sample tube at 773 K for 1 h in a flow of He. The temperature was reduced to 373 K, and the sample was placed in a flow of a gas mixture of NH₃(10)/He(90) for 1 h and then in the flow of He (30 mL/min) for

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1.5 h. The effluent gas at the outlet of the sample tube was analyzed with the mass spectrometer while the sample was heated to 1073 K at a rate of 10 K/min. The signals of $m/e = 16$ and 18 were simultaneously monitored. Since the signal of $m/e = 17$ might originate from both NH_3 and H_2O , the signal of $m/e = 16$ was considered to indicate the presence of NH_3 in the effluent gas.

The argon adsorption measurement was carried out using a conventional BET system. The sample (0.3 g) was placed in a glass tube and pre-treated in a vacuum at 773 K for 2 h. The argon adsorption isotherms were measured employing a volumetric technique at 213–243 K, as described in a previous paper presented by one of the authors [2]. The saturated adsorption amount of Ar on the catalyst acid sites (number of acid sites) and the heat of Ar adsorption of the catalyst were determined in the same way as described in the previous paper [2].

3. Results and discussion

Figure 1 shows the change of ethylene yield as a function of time on stream during the dehydration of ethanol with or without of water over the HZ5-90 or the HM90. The yield of ethylene increased with an increase in time on stream during the reaction over the HZ5-90 in both conditions. In the presence of water in gas phase, the yield of ethylene increased more slowly than in the condition without water. On the other hand, the increase of ethylene yield was not observed on HM90. The yield of ethylene was almost constant during the tested reaction time over the HM90. The increase of the yield was the characteristic observation on HZ5-90.

Figures 2 and 3 show the NH_3 -TPD profiles of the fresh catalyst or the catalysts used for the dehydration. The amount of NH_3 desorbed from the HZ5-90 used for the dehydration of ethanol or ethanol/water was much larger than that of the fresh HZ5-90, suggesting that the number of acid sites of the HZ5-90 increased during the dehydration. The increase of dehydration activity of HZ5-90 can be attributed to the increase of the number of active sites. On the other hand, the amount of NH_3 desorbed from the HM90 used for the dehydration was almost the same as that of the fresh HM90, suggesting that the number of acid sites of HM90 should be unchanged.

Figures 4 and 5 show the argon adsorption isotherms of the fresh catalyst and the catalyst used for the dehydration. The adsorption amount of Ar at monolayer coverage of the acid sites is determined as follows. An adsorption isotherm is composed of several Langmuir-type adsorption isotherms when the measurement is carried out at an elevated temperature. In lower adsorption amount part, the slope of log–log plot of the adsorption isotherm is 1, because the Henry's Law can

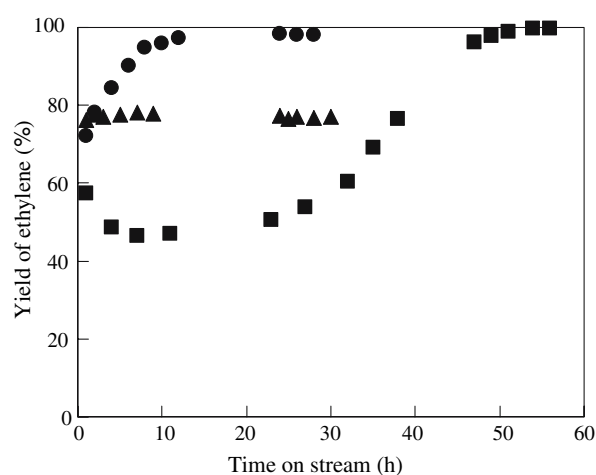


Figure 1. The yield of ethylene as a function of time on stream during the dehydration over HZ5-90 (●, ■), or HM90 (▲). Reaction conditions: 473 K; atmospheric pressure; feed = $\text{C}_2\text{H}_5\text{OH}$ (3.4%)/He (●, ▲), or $\text{C}_2\text{H}_5\text{OH}$ (3.4%)/ H_2O (2.2%)/He (■); $W/F = 6.9$ (g-cat min/mmol- $\text{C}_2\text{H}_5\text{OH}$).

be applied. Afterward, the adsorption on acid sites becomes to be saturated and the slope is decreased gradually. Therefore, the log–log plot of adsorption isotherm is approximated by two straight tangential lines at low and high pressure regions. The intersection of these two lines gives the number of acid sites.

The argon adsorption on acid sites was saturated around 10 kPa and 2 kPa on HZ5-90 and HM90, respectively. The number of acid sites of the fresh HZ5-90 or the fresh HM90 was almost the same as that of Al^{3+} surface ion. The adsorption amount of Ar at monolayer coverage of acid sites on the used HZ5-90 was about 2.3 times as large as that on the fresh HZ5-90, as shown in figure 4. The heat of adsorption of the

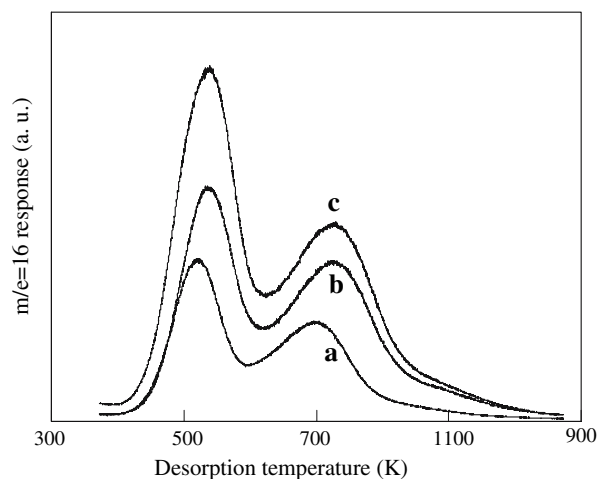


Figure 2. NH_3 -TPD profile of a fresh HZ5-90 (a) or a HZ5-90 used for the dehydrogenation of ethanol (b) or of a mixture of ethanol and water (c). Operating conditions for NH_3 -TPD measurements: 0.1 MPa; flow rate of He = 60 mL/min; heating rate = 10 K/min. Reaction conditions are shown in figure 1.

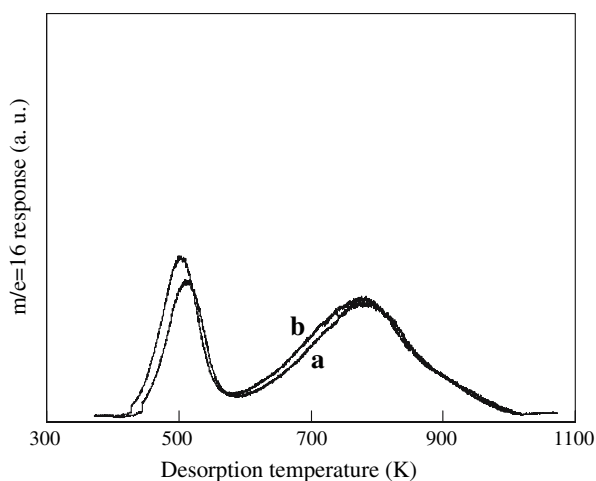


Figure 3. NH_3 -TPD profile of a fresh HM90 (a) or a HM90 used for the dehydrogenation of ethanol (b). Operating conditions: 0.1 MPa; flow rate of He = 60 mL/min; heating rate = 10 K/min. Reaction conditions are shown in figure 1.

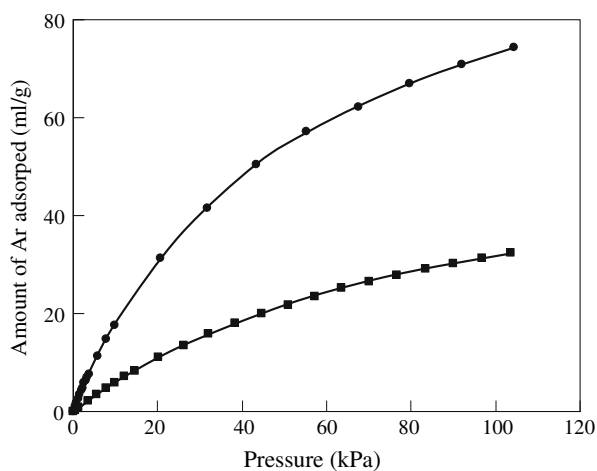


Figure 4. Ar adsorption isotherm at 213 K on a fresh HZ5-90 (■) or a HZ5-90 used for the dehydration of a mixture of ethanol and water (●). Reaction conditions are shown in figure 1.

used HZ5-90 was 19 KJ/mol and almost the same as that of the fresh HZ5-90. On the other hand, the adsorption amount of Ar at monolayer coverage on the used HM90 was the same as that on the fresh HM90, as shown in figure 5. The heat of adsorption of the fresh HM90 or the used HM90 was 21 KJ/mol and higher than that of the HZ5-90. The findings shown in the figures 4 and 5 are in harmony with the findings shown in figures 2 and 3. Accordingly, it is strongly suggested that the number of acid sites of the HZ5-90 increased during the dehydration of ethanol, whereas that of the HM-90 should be almost unchanged. Furthermore, it is also suggested that the catalytic activity of the HZ5-90 or the HM90 for the dehydration of ethanol could be correlated with the number of strong acid sites of the catalyst, as previously suggested [1].

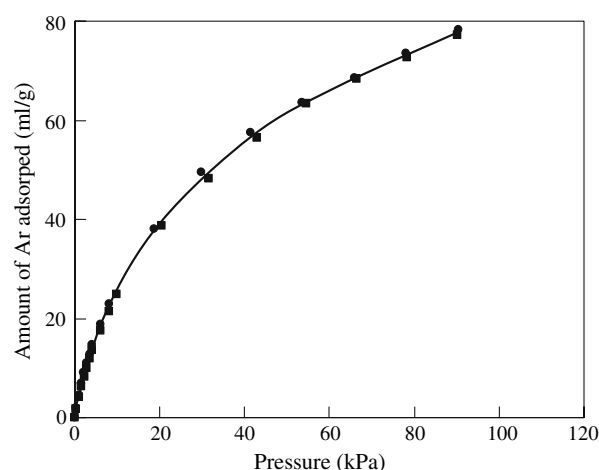


Figure 5. Ar adsorption isotherm at 213 K on a fresh HM90 (■) or a HM90 used for the dehydration of ethanol (●). Reaction conditions are shown in figure 1.

In order to find out the cause of the increase in the number of acid sites of HZ5-90 during the dehydration of ethanol, the activity of the HZ5-90 pre-treated with water or ethylene at 473 K was examined in the dehydration at 473 K. The activity of the HZ5-90 pre-treated with water at 473 K for 4 h was almost the same as that of the fresh HZ5-90. Then, the activity of the HZ5-90 pre-treated with ethylene was examined in the dehydration. Figure 6 shows the yield of ethylene as a function of time on stream during the dehydration of ethanol over the HZ5-90 or the HZ5-90 pre-treated by passing ethylene/He (3% C_2H_4 in He) to the catalyst bed at 473 K for 4 h. The yield of ethylene during the dehydration over the pre-treated HZ5-90 was much higher than that during the dehydration over the HZ5-90 not pre-treated, and hardly increased with an increase

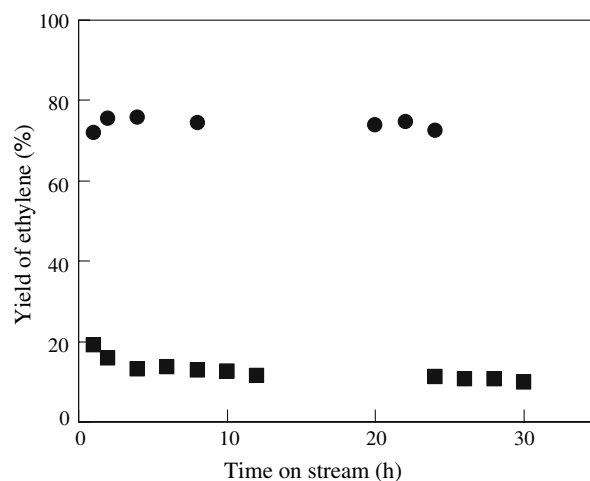


Figure 6. The yield of ethylene as a function of time on stream during the dehydration over a HZ5-90 pre-treated with C_2H_4 (●) or a HZ5-90 not pre-treated (■). Reaction conditions: 473 K; atmospheric pressure; feed = $\text{C}_2\text{H}_5\text{OH}$ (3.4%)/He; W/F = 3.0 (g-cat min/ mmol - $\text{C}_2\text{H}_5\text{OH}$).

in time on stream. This finding suggests that a large number of new acid sites might be formed inside the pores of the HZ5-90 via the polymerization of ethylene produced by the dehydration of ethanol. The time on stream at which the yield of ethylene started to increase during the dehydration of ethanol/water was much longer than that during the dehydration of ethanol, as shown in figure 1. And the yield of ethylene during the dehydration over a small amount of the HZ5-90 loaded was very low and did not increase for 30 h, as shown in figure 6. These findings might suggest that a certain amount of polymer should be accumulated inside the pores of HZ5-90 for the formation of the new acid sites. In addition, the HZ5-90 pre-treated in He at 773 K for 2 h and then pre-treated with ethylene at 473 K for 4 h was found to be much more active for the dehydration than the HZ5-90 pre-treated in He at 773 K for 2 h but not pre-treated with ethylene. This finding suggests that the pre-treatment of the HZ5-90 in He at 773 K would hardly affect its catalytic behavior in the dehydration of ethanol.

Although the findings observed in the present study are greatly interesting, further investigation is necessary for clarifying the more detailed mechanism for the

formation of the new acid sites inside the pores of HZ5-90 and the positions of the new acid sites formed.

4. Conclusions

The activity of a H-ZSM5-90 for the dehydration of ethanol at 473 K increased with an increase in time on stream, and the number of acid sites of the H-ZSM5-90 also increased during the dehydration. On the other hand, the activity and the number of acid sites of a H-mordenite-90 were almost unchanged during the dehydration. Since the pre-treatment of the H-ZSM5-90 with ethylene at 473 K largely increased its activity for the dehydration of ethanol, it is suggested that a large number of new acid sites could be formed inside the pores of H-ZSM5-90 via the polymerization of ethylene produced during the dehydration of ethanol.

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