

# Catalytic Application of Hydrophobic Properties of High-Silica Zeolites

## I. Hydrolysis of Ethyl Acetate in Aqueous Solution

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The hydrolysis of ethyl acetate in aqueous solution over various solid acid catalysts was investigated. The activity of high-silica zeolites (H-ZSM-5, dealuminated H-mordenite) was moderate, while that of silica-alumina, nondealuminated H-mordenite, and H-Y zeolite was very small. Notably, the activity of H-ZSM-5 (Si/Al = 47) was high and about 40% of that of the cation exchange resin. The H-ZSM-5 had acid sites whose strength was  $-5.6 < H_0 \leq -3.0$  in water. The higher Si/Al atomic ratio provided a more hydrophobic property on the catalytic surface, which, therefore, showed better affinity for organic materials than water. However, too high a Si/Al atomic ratio resulted in the decrease in the activity, because the acid sites decreased in number.

### INTRODUCTION

Common solid acid catalysts, such as silica-alumina and H-Y zeolite, which are insoluble in water, are generally considered to be inactive in aqueous solutions at relatively low temperatures. Because these catalysts are hydrophilic, water covers the surface of the catalysts and prevents the adsorption of organic materials. On the other hand, cation exchange resins are active as solid acid catalysts in aqueous solutions (1), probably because they have good affinity for organic materials. However, the cation exchange resins do not have high thermal and mechanical stability.

High-silica zeolites, such as dealuminated mordenite (2) and ZSM-5 (3), are known to be hydrophobic. These zeolites are expected to have a high activity as solid acid catalysts in aqueous solution.

As a typical reaction in an aqueous solution we have chosen the hydrolysis of ethyl acetate, because this reaction is simple and well known in the homogeneous system.

### EXPERIMENTAL

*Reactants.* Methyl acetate was obtained from a commercial source with a purity of 99.5%. The other reactant was pure water.

*Catalysts.* H-Mordenite (H-M) was prepared by a conventional cation exchange procedure using 1 N NH<sub>4</sub>Cl and Na-mordenite (supplied by Nihon Kagaku Kogyo Co.) having a Si/Al atomic ratio of 5.5, followed by calcination in air at 500°C. The degree of cation exchange was 96%.

Dealuminated H-M was prepared by repeated alternate treatment in 1 N HCl solution at 70°C or refluxing in 6 N HCl solution for 0.5-8.0 h. The Si/Al atomic ratio was varied from 5.5 to 11.4.

ZSM-5 zeolites with various Si/Al ratios were synthesized by a method similar to that described in Mobil's patent (4) using tetrapropylammonium bromide, sodium silicate, aluminum sulfate, sulfuric acid, sodium chloride, and water at 160°C. The synthesized zeolites were calcined in air at 500°C to remove organic materials. Then, sodium cation in ZSM-5 was exchanged for proton using 1 N HCl solution at 60°C. The degree of cation exchange was more than

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99.5%. The Si/Al atomic ratio of the H-ZSM-5 was varied from 29 to 92.

One of the H-Y zeolites was prepared by a conventional cation exchange procedure using 0.5 N  $\text{NH}_4\text{Cl}$  solution and Na-Y (SK 40) at 60°C followed by calcination in air at 450°C. Its degree of cation exchange was 80%. The other H-Y zeolites, whose Si/Al ratios and degrees of cation exchange were 2.4, 3.1, and 3.8 and 96, 99, and 93%, respectively, were prepared by the calcination of  $\text{NH}_4\text{-Y}$  (supplied by Catalyst & Chemicals Industries Co.) in air at 450°C.

The degree of cation exchange and the Si/Al atomic ratio of the zeolites were determined by flame photometry and atomic absorption photometry.

The other catalysts were cation exchange resin Amberlite 200C (sulfonic acid type) and silica-aluminas with Si/Al atomic ratios of 5.7 and 2.6 supplied by Nikkaseiko Company.

*Apparatus and procedure.* The hydrolysis of ethyl acetate was carried out in a flask using a 5.0% aqueous solution of ethyl acetate mainly at 60°C. The extent of hydrolysis of ethyl acetate was determined by conventional titrimetry with 0.1 N NaOH solution and phenolphthalein to measure the concentration of acetic acid in the reaction batch.

*Measurement of acid strength.* The

strength of the catalysts in water was qualitatively measured as follows: 20 mg of the catalyst and 10 ml of water were put in a test tube, 2 drops of 2% ethanol solution of Hammett indicator ( $H_0 = +3.3, +1.5, +0.8, -3.0, \text{ or } -5.6$ ) was added to the water; the mixture was allowed to stand for 12 h at room temperature. From the color of the indicator, all of which was adsorbed on the catalyst, the acid strength was determined visually.

#### RESULTS AND DISCUSSION

The qualitative determination of the acid strength of the various solid acid catalysts, except the cation exchange resin, was carried out in water and results are shown in Table 1. Although these solid acid catalysts activated by dehydration have the acid strength of  $H_0 \leq -5.6$  in nonpolar solvent (5), they do not have such strong acid sites in water. Especially, the acid strength of silica-alumina (SA) or H-Y was weak. However, in all types of zeolites the Si/Al ratio affected the acid strength, that is, the higher Si/Al ratio provided the stronger acid sites. In the case of H-ZSM-5, whose Si/Al ratio was 47, the existence of strong acid sites ( $-5.6 < H_0 \leq -3.0$ ) was observed. Even in amorphous SA, the Si/Al ratio seemed to affect the acid strength.

Kinetic studies were made of the hydroly-

TABLE 1  
Acid Strength of Various Catalysts in Water

Catalyst	Cation exchange degree (%)	Si/Al atomic ratio	$H_0$				
			+3.3	+1.5	+0.8	-3.0	-5.6
H-ZSM-5	100	47	+	+	+	+	-
H-M	96	5.5	+	+	+	-	-
H-M	98	7.2	+	+	+	±	-
H-Y	80	2.4	+	±	-	-	-
H-Y	96	2.4	+	±	-	-	-
H-Y	99	3.1	+	+	±	-	-
H-Y	93	3.8	+	+	±	-	-
SA	—	5.7	+	±	-	-	-
SA	—	2.6	+	-	-	-	-

Note. +, Acidic color; ±, slightly acidic color; -, basic color.

TABLE 2

The First-Order Rate Constants, Activation Energies, and Acidities of Various Catalysts

Catalyst	Si/Al atomic ratio	Rate constant $10^3 \times k$ ( $\text{min}^{-1} \cdot \text{g}^{-1}$ )	Activation energy $E$ ( $\text{kJ} \cdot \text{mol}^{-1}$ )	Acidity ( $\text{meq} \cdot \text{g}^{-1}$ )
0.0236 N HCl	—	—	63	—
200C	—	4.44	58	1.17
H-ZSM-5	47	1.75	68	0.47
H-M	5.5	0.03	—	0.01
H-M	7.4	0.49	67	0.13
H-M	8.7	0.77	—	0.20
H-Y	2.4	0.04	—	0.01
SA	5.7	0.04	—	0.01
SA	2.6	0.04	—	0.01

ysis of ethyl acetate in aqueous solution over various catalysts and in hydrochloric acid solution. In every case, the hydrolysis rate obeyed good first-order kinetics with respect to the concentration of ethyl acetate up to a conversion of 30%. The representative plots of the first-order kinetics over several catalysts are shown in Fig. 1. During the hydrolysis in various concentrations of HCl solution ( $0.0236 N \cong C_{\text{HCl}} \cong 0.0976 N$ ), the first-order rate constant [ $k_{\text{HCl}}$  ( $\text{min}^{-1}$ )] was proportional to the concentration of HCl and was expressed as

$$k_{\text{HCl}} = 3.72 \times 10^{-2} C_{\text{HCl}}$$

In Table 2 are listed the first-order rate constants ( $k$ ) measured at  $60^\circ\text{C}$ , the activation energies, and the acidities expressed as the amount of HCl required to attain the same reaction rates over the solid acid catalysts. The activation energies on various catalysts were almost the same as that in HCl solution. The rate constants of SA, H-Y, and nondealuminated H-M were very small. However, the dealumination of H-M raised the rate constant remarkably. H-ZSM-5 (Si/Al = 47) had high activity, which was about 40% of that of the cation exchange resin (Amberlite 200C). The acidity of H-ZSM-5 (Si/Al = 47) was 0.47 meq/g and this value was a little higher than the amount of aluminum H-ZSM-5. The cation exchange resin exhibited the

highest activity of all the solid acid catalysts examined here; its acidity was about 70% of the cation exchangeable capacity.

The activities of SA, H-Y, and nondealuminated H-M were extremely small, while those of H-ZSM-5 and dealuminated H-M were very high. This suggested a good correlation between Si/Al atomic ratio and the activity. The effect of Si/Al ratio on the activity was examined and the results on H-M, H-ZSM-5, and H-Y are shown in Figs. 2, 3, and 4, respectively. In the case of H-M, a notable increase in activity on dealumination and a decrease in activity on overdealumination were observed. The ac-

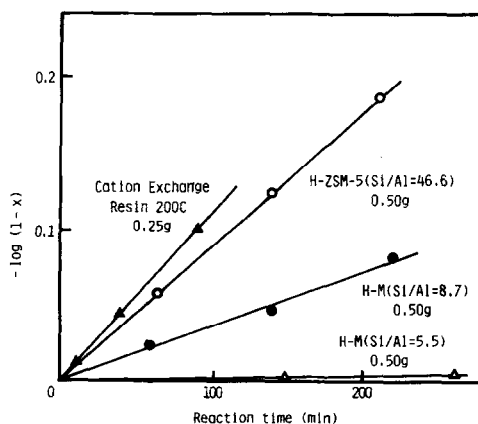


FIG. 1. Representative plots of the first-order kinetics over various catalysts.  $x$ : Conversion of ethyl acetate (reaction temperature:  $60^\circ\text{C}$ ).

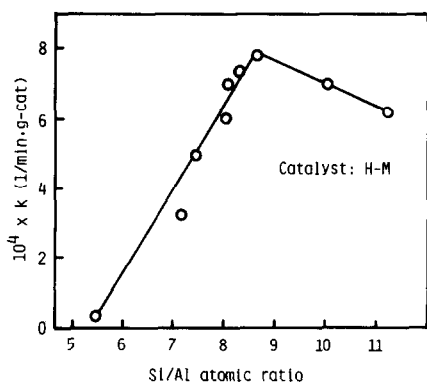


FIG. 2. The effect of the Si/Al atomic ratio on the activity of H-M (reaction temperature: 60°C).

tivity was maximized at Si/Al = 8.7. This maximum value was higher than the activity of the parent H-M by a factor of about 27. In the case of H-ZSM-5, the maximum activity was also observed at Si/Al = 47. Even in the case of H-Y, which exhibited very low activity, the activity was maximized around Si/Al = 3. At Si/Al = 2.4 the activities of the two different H-Y zeolites, whose degrees of cation exchange were 80 and 96%, were almost the same. These facts indicate that the activity was influenced less by the degree of cation exchange (probably in the region of high exchange degree) than by the Si/Al atomic ratio. It has been reported by Kerr that H-Y loses about 25% of the Brønsted acidity

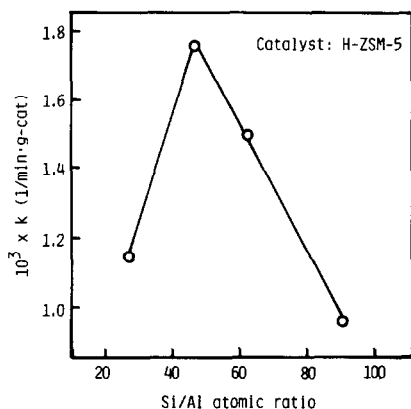


FIG. 3. The effect of the Si/Al atomic ratio on the activity of H-ZSM-5 (reaction temperature: 60°C).

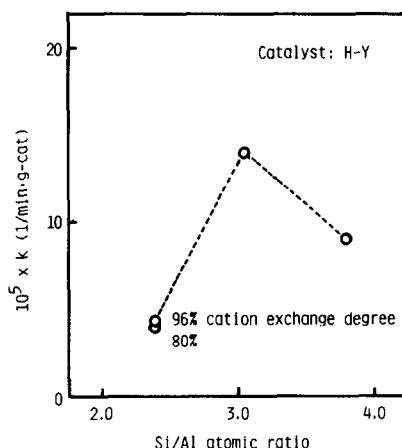


FIG. 4. The effect of the Si/Al atomic ratio on the activity of H-Y (reaction temperature: 60°C).

simply by slurring it in water for 10–15 min (6). The loss of the Brønsted acidity of H-Y by addition of water should affect the catalytic activities shown in Fig. 4 and may be one of the main reasons why H-Y has the low activity.

For three kinds of zeolites (H-M, H-ZSM-5, and H-Y), the activity in every case changed with the Si/Al ratio and was maximized at the optimum ratio. This was because the surface of the zeolite became more hydrophobic and, therefore, had better affinity for methyl acetate with increasing Si/Al ratio, while the number of acid sites decreased with increasing Si/Al ratio. The optimum Si/Al ratios were 8.7, 47, and 3 for H-M, H-ZSM-5, and H-Y, respectively. These optimum ratios were significantly different from each other. At the present time, these differences can not be clearly explained. However, they might be due to the difference in the skeletal structure of the zeolite or to the nonuniformity of the distribution of the aluminum atoms in the zeolite crystallite induced by the dealumination.

In conclusion, the activities of high-silica zeolites, such as H-ZSM-5 and dealuminated H-M, are moderate, while those of silica-alumina and H-Y are slight for the hydrolysis of ethyl acetate in aqueous solu-

tion. Especially, the activity of H-ZSM-5, whose Si/Al ratio is 47 is high and about 40% of that of the cation exchange resin Amberlite 200C. The H-ZSM-5 has the acid sites whose strength is  $-5.6 < H_0 \leq -3.0$  in water. The higher Si/Al atomic ratio provides a more hydrophobic environment on the catalytic surface; the surface, therefore, acquires better affinity for organic materials than for water. However, too high Si/Al ratios result in the decrease in the activity, because the acid sites decrease in number.

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