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Cumene-Cracking Activity of Zeolite Catalysts.

I. Effects of Ion Exchange and Silica-to-Alumina Mole Ratio

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The effects of the degree of ion exchange and the silica-to-alumina mole ratio on the cumene-cracking activity of faujasite-type zeolite were examined.

When sodium ions in Na-form zeolite are replaced with polyvalent metal ions or NH_4 ions, protons are produced by the increase in the electrostatic field strength or by the liberation of NH_3, and these protons exert a great influence by forming solid acid sites on the catalytic activity in cumene cracking. The order of activity is :La > NH_4 > Ca > Na:, where the activity would be determined by both the acidity and the acid strength.

The higher the silica/alumina mole ratio is, the larger the catalytic activity is; this is attributable to the stability of the cations inside the structure. Though a difference in the pretreatment temperatures influences the solid acidity of the catalyst, the effects vary according to the silica/alumina mole ratio. The transition from the Brönsted to the Lewis acid on the zeolite surface is reversible in the presence of water, when the silica/alumina mole ratio is higher.

INTRODUCTION

The crystalline aluminosilicate, such as zeolite, has pores and channels with the molecular dimensions throughout the structure. Due to the high regularity of the lattice, its pore structure is so uniform that zeolite exhibits unique sorption characteristics. The sorption studies were prompted by the elegant works of Barrer, who investigated in great detail the correlation between the size and shape of molecules adsorbed and the diameter of pores of zeolites (*1*). Among a wide variety of zeolite, faujasite and mordenite with comparatively large pores show a catalytic activity like some other porous materials do.

Since 1960, when Rabo, Pickert, Weisz, Frilette, and others reported the high catalytic activity of zeolite for the cracking, dehydration, and isomerization of hydrocarbons (*2*, *3*), the zeolite catalysts have been utilized for many reactions (*4*). Furthermore, zeolite has aroused the attention of many investigators, since it is so highly crystalline that its theoretical study seems easier than that of many other catalysts. The exact definition on its active sites, however, has not yet been done. This is because of the abundance of factors which affect the catalytic activity, that is, the type of zeolite (the type of crystal structure), the kind and the quantity of cations, the silica/alumina mole ratio, etc.

Many authors reported already the influence of the degree of ion exchange and the pretreatment temperature on the activity of zeolite catalysts. The effect of the silica/alumina mole ratio, however, has scarcely been investigated (*27*). Since these factors would not independently affect the catalytic activity, it is interesting to make a summary of the various factors affecting the activity of zeolite catalysts.

This paper will report the result of studies mainly on the effect of the silica-to-alumina mole ratio, with correlation to the other factors mentioned above, by using five different faujasite-type zeolites with silica-to-alumina mole ratios from 2.5 to 5.0.

EXPERIMENTAL

The original Na-form zeolites were as follows: Na–$X_{2.5}$* and Na–$Y_{5.0}$, which are Linde Molecular Sieve 13X and SK-40, respectively, and Na–$Y_{3.25}$, Na–$Y_{3.85}$, and Na–$Y_{4.6}$, which were synthesized from silica–alumina gel and caustic soda. Their silica/alumina mole ratio was determined by chemical analysis and the unit-cell dimensions measured by X-ray diffraction analysis. The diffraction pattern and water sorption capacity were similar to those of binder-free Linde 13X. The ion-exchange was performed at about 90°C by immersing the Na-form zeolite in an aqueous solution of metal and ammonium chloride. The treatment was repeated several times in order to obtain a high degree of exchange. The samples were then collected by filtration, washed until no chloride ion was detected by silver nitrate treatment, and finally dried. The extent of ion exchange was determined by chemical analysis and flame photometry, and designated by the molar percent of the sodium ions replaced.

Cumene was a guaranteed-grade sample of Wako Pure Chemical Industries, Ltd.; it was dehydrated with a Molecular Sieve 4A.

For studying the catalytic activity, a pulse microreactor was used. This apparatus was a small catalytic reactor connected to a conventional gas-chromatography assembly with a product trap between the reactor and the analytical column. The vapor pressure of cumene was extremely low at room temperature; therefore, the piping tube of the apparatus was maintained at about 100°C. The helium carrier gas was passed through a column of Molecular Sieve 4A in order to dehydrate before it entered the system. The helium flow was measured accurately with a soap-bubble-flow meter.

The catalytic reactor was made of a stainless-steel or Pyrex glass tube. Sixty milligrams of the dehydrated sample were packed in this tube (4mm i.d.) and held by small plugs of quartz glass wool. The catalyst was pretreated for 2 hr at the specified temperatures between 350 and 850°C by using helium gas as a carrier. The reactant, cumene, was injected into the carrier gas flow by means of a microsyringe. The reactant volume was 8 μl (liquid), that is, 5.74×10^{-5} mole. The reaction temperature was varied between 350 and 650°C. The products were trapped by liquid nitrogen, by-passed, and analyzed by gas chromatography. The helium flow rate during the pretreatment and the reaction was 60 cm^3/min in the case of pellet (28/60 mesh) catalysts and 30 cm^3/min in the case of powdery ones. The gas-chromatographic separation of the products was effected with a column of 20 wt % DOP on 30/60 mesh Kacelite-B at 140°C.

After the first pulse reaction had been carried out, the temperature of the reactor was again adjusted to the temperature used for pretreating in order to remove adsorbed substances. The catalytic activity was given in terms of the conversion of cumene to propylene and benzene during the first pulse reaction.

RESULTS

Effects of Degree of Ion Exchange

The main products of the cumene-cracking reaction are benzene and propylene; the others can be neglected in a reaction below 500°C. The Na–$Y_{3.25}$ zeolite showed no catalytic activity below 450°C. Figure 1 shows the correlation between the catalytic activity and the extent of ion exchange on Ca–Na–$Y_{3.25}$ and NH_4–Na–$Y_{3.25}$ preheated at 450°C; these samples were prepared by the exchange of Na–$Y_{3.25}$ with Ca or NH_4 ions, respectively. NH_4–Na–$Y_{3.25}$, however, changed into H–Na–$Y_{3.25}$, with liberation of NH_3 during the pretreatment at 450°C (*5*). Both samples begin to show catalytic activity when the extent of exchange exceeds 25% and, upon further exchange, H–Na–$Y_{3.25}$ exhibits a larger activity than Ca–Na–$Y_{3.25}$. Even if it is taken into account that Ca–Na–$Y_{3.25}$ is powdery, while H–Na–$Y_{3.25}$ is in a pellet form, in ad-

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* This refers to the faujasite-type zeolite X with sodium cation, for which the silica-to-alumina mole ratio is 2.5.

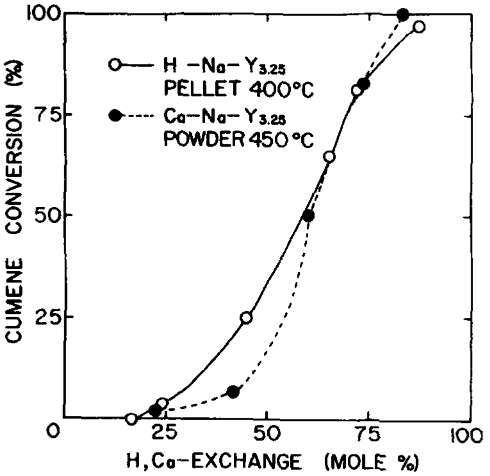

FIG. 1. Change of catalytic activity with degree of ion exchange. The indicated temperature represents the reaction temperature.

dition to the differences in the reaction temperatures and the flow rate of the carrier gas, it is apparent that H–Na–$Y_{3.25}$ is more active as a catalyst than Ca–Na–$Y_{3.25}$.

The catalytic activity of La–Na–$Y_{3.25}$ pretreated at 450°C is given in Fig. 2. The increase in catalytic activity, which becomes notable after the cation exchange exceeds 50%, is more rapid than that of H–Na–$Y_{3.25}$ or of Ca–Na–$Y_{3.25}$.

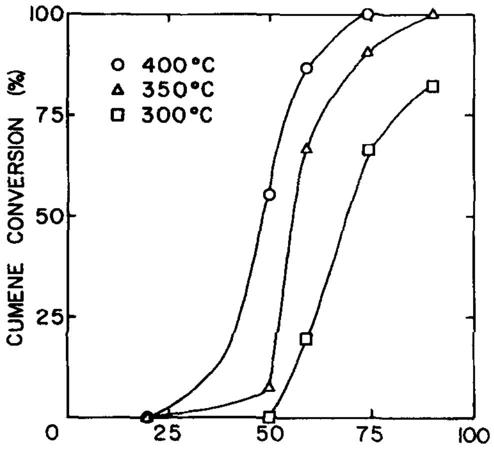

FIG. 2. Change of catalytic activity with degree of ion exchange of La–Na–$Y_{3.25}$. The indicated temperature represents the reaction temperature.

Effects of the Silica-to-Alumina Mole Ratio

Figure 3 shows the relationship between the silica/alumina mole ratio and the cumene conversion on the Ca–zeolite* pretreated at 450°C. The catalytic activity increases with the increasing silica/alumina mole ratio, and Ca–$Y_{4.6}$ is the most active. The results on the NH_4–zeolite (substantially the H–zeolite) pretreated at 450°C are shown in Fig. 4. The catalytic activity of the H-form zeolite exhibits a similar behavior as that of the Ca-form and the H-form is more active on the whole.

In order to compare the zeolite and the silica–alumina catalyst in terms of the silica/alumina mole ratio, the activities of the silica–alumina catalysts treated under the same conditions are listed in Table 1. It is clear from these data that zeolite has an extremely high catalytic activity in comparison with silica–alumina, despite a lower silica/alumina mole ratio.

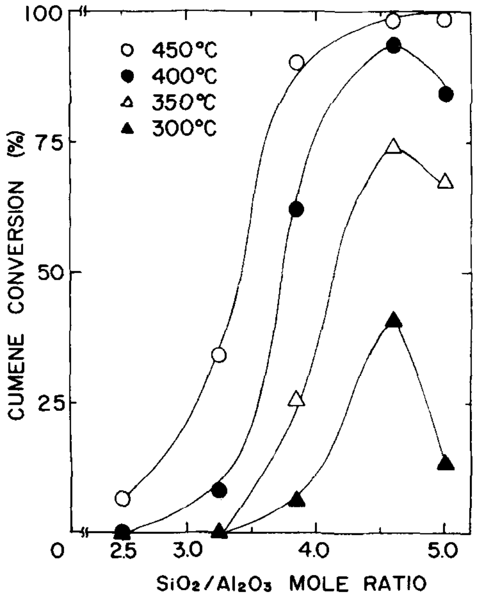

FIG. 3. Correlation between catalytic activity and silica/alumina mole ratio of Ca-form zeolite. The degrees of Ca-exchange of Ca–$X_{2.5}$, Ca–$Y_{3.25}$, Ca–$Y_{3.85}$, Ca–$Y_{4.6}$, Ca–$Y_{5.0}$ are 98.9, 95.7, 94.3, 92.6, 92.9 mole %, respectively. The indicated temperature represents the reaction temperature.

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* This contains a small amount of residual sodium ions.

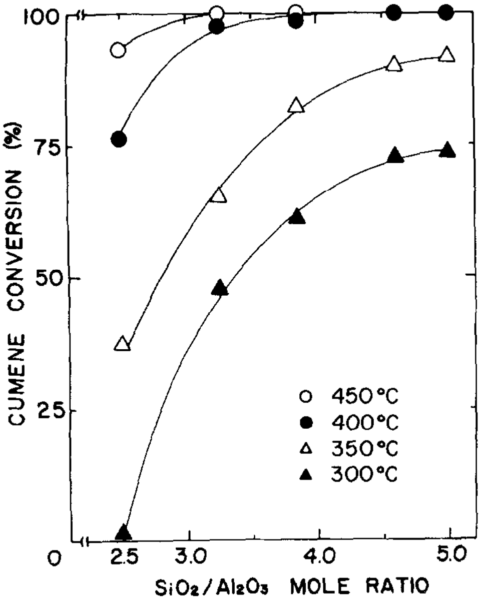

FIG. 4. Correlation between catalytic activity and silica/alumina mole ratio of H-form zeolite. The degrees of H-exchange of $H\text{-}X_{2.5}$, $H\text{-}Y_{3.25}$, $H\text{-}Y_{3.85}$, $H\text{-}Y_{4.6}$, $H\text{-}Y_{5.0}$ are 93.7, 94.3, 92.6, 92.0, 94.4 mole %, respectively. The indicated temperature represents the reaction temperature.

Effects of the Pretreatment Temperature

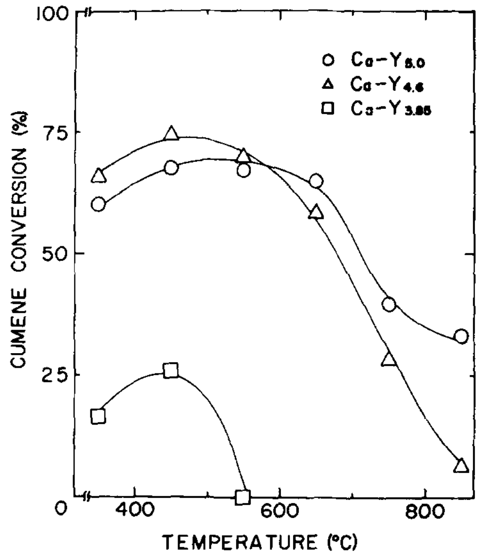

FIG. 5. Dependence of catalytic activity on pretreatment temperature over Ca-form zeolite. The degrees of Ca-exchange are the same as the samples in Fig. 3.

Figures 5 and 6 show the dependence of the catalytic activity on the pretreatment temperature for some Ca-form zeolites and H-form zeolites at the reaction temperature of 350°C. The activities of $Ca\text{-}Y_{3.85}$ and $Ca\text{-}Y_{4.6}$ show the maximum values upon the pretreatment at 450 and 550°C, respectively. $Ca\text{-}Y_{5.0}$ is rather active even by the pretreatment at 850°C. The maximum of activity appears upon the pretreatment at 350°C for both $H\text{-}X_{2.5}$ and $H\text{-}Y_{3.25}$. When the silica/alumina mole ratio is larger than 3.85, the activity is almost unchanged between 350 and 450°C, but decreases rapidly above 450°C.

TABLE 1
CUMENE CONVERSION OF SILICA–ALUMINA CATALYST PREHEATED AT 450°C

Catalyst	Silica/ alumina mole ratio	Cumene conversion (mole %)			
		300°C	350°C	400°C	450°C
High alumina	5.1	0.5	10.8	35.2	62.5
Low alumina	11.2	13.1	49.8	72.8	90.8

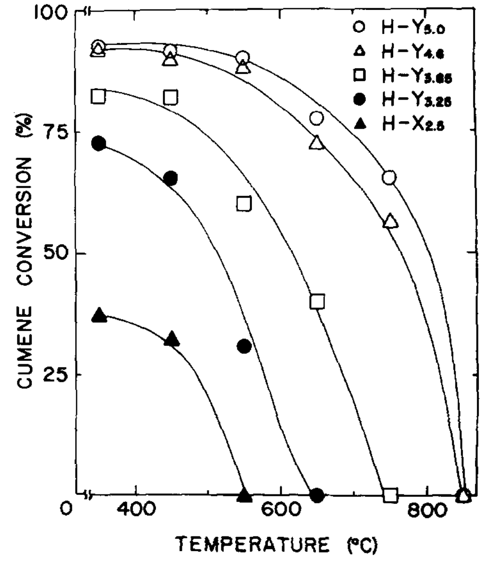

FIG. 6. Dependence of catalytic activity on pretreatment temperature over H-form zeolite. The degrees of H-exchange are the same as the samples in Fig. 4.

DISCUSSION

It is evident from the results presented in the preceding section that the Na-form zeolite, which is originally inactive, evolves catalytic activity upon the replacement of Na ions with Ca, NH_4, or La ions as cations. It is considered that the cumene-cracking reaction occurs through the formation of a carbonium-ion intermediate with the Brönsted acid catalyst (*6*). It was also proved from investigations by the base titration (*7*) and the ir spectroscopy (*8–15*), that zeolite has both Brönsted and Lewis acid sites on its surface. Since Na–$Y_{3.25}$, which has only a few weak acid sites (0.6 meq/g, $H_0 \geq +3.3$) (*7*), does not show any activity, only the strong acid sites would be effective for the cumene cracking. Since, upon the heat treatment, the NH_4–zeolite liberates NH_3 to form H–zeolite, in which protons are mobile (*16*), the solid acidity of the decationated zeolite naturally increases. The strong acidity of the Ca-form is the result of the polarization of water molecules, which is caused by the electrostatic field formed near the surface (*17*). With the La-form, stronger or more acid sites appear since the electrostatic field of the La ions is stronger.*

It is to be noted here that, when the extent of ion exchange is adequately low, the activity does not appear. This can be explained as follows: the faujasite zeolite has several kinds of cation sites (*19*), of which the most stable site, S_I, is remote from the large cavity by a pore of about 2 Å in diam composed of a six-oxygen ring. The divalent metal ions strongly prefer this site (*19*), and while the extent of ion exchange remains low, they occupy selectively the S_I site. There is no interaction between the divalent cations at S_I and the adsorbed molecules since the molecules in the cavity cannot pass the pore. As has been reported elsewhere (*17*), when the extent of ion exchange was below 43.8%, the electrostatic field strength of Ca–Na–$Y_{3.25}$ was almost the same as that of the Na-form; this agrees with the result of the catalytic activity change. These behaviors resemble the results observed for the hexane cracking and isomerization on Ca–Y catalysts reported by Tung and McIninch (*20*). The La-form zeolite shows similar results. Taking the fact into consideration that La ions move into the sodalite cage cavity upon dehydration (*21*), the La–Na–$Y_{3.25}$ is still inactive when the La exchange is low. Also in the case of the NH_4-form zeolite, the protons would enter into hexagonal prisms of the structure at a low extent of exchange.

As ascertained by the measurement on the heat of immersion (*22*), results from the increase in the electrostatic field strength show that the activity of the Ca-form zeolite becomes higher with an increase in the silica/alumina mole ratio. Though a decrease in the amount of alumina induces a decrease in the number of cations, at the same time it lowers the electrostatic shielding of the cations. The low activity of Ca–$Y_{5.0}$ is probably due to the decrease in the number of Ca ions.

The NH_4-zeolite turns into the H-form zeolite upon heat treatment by liberating NH_3, and the proton thus produced forms the active site. The higher the silica/alumina ratio is, the fewer is the number of anions in the zeolite structure, so the protons, with weaker electrostatic shielding, become mobile and form strong acid sites (*7*).

The variation in the activity of Ca–zeolite caused by the difference in the pretreatment temperatures can be explained as follows. The pretreatment at high temperatures makes the polarization of the adsorbed water molecules so easy that the formation of the protons is prompted. Accordingly, the number of the Brönsted acid sites increases on the surface and the activity becomes higher. The pretreatment at higher temperatures, however, brings about the elimination of one water molecule from the two hydroxyls to form electron-

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* The electronic spectra of adsorbed *p*-nitrotoluene and dinitrotoluene show that the La-form zeolite has strong acid sites ($H_0 < -10$) when the extent of ion exchange exceeds 50%, but that the H-form, and silica-alumina have no such sites (*18*).

pair acceptors. Lewis acid sites (*23, 24*). It was already confirmed from the adsorption experiment that the decomposition of the crystalline structure does not occur until 850°C in the case of Ca–$Y_{4.6}$, and until 950°C in the case of Ca–$Y_{5.0}$ (*25*) and, therefore, the decrease in activity with the pretreatment would be due to the transition of the acid type. As the silica/alumina mole ratio increases, the temperature where the activity begins to decrease becomes higher. This seems to be not only because the crystalline structure is more stable, but also because the lower density of each Brönsted acid site restricts the chance for dehydroxylation. The activity decrease at higher pretreatment temperatures for the NH_4–zeolite is probably the result of the decomposition of the zeolite structure itself. In the adsorption experiment, the gradual structural decomposition of the NH_4–zeolite was observed above 300°C (*25*). When the silica/alumina mole ratio is large, the activity remains even at high temperatures. This seems to be because the crystalline structure is more stable, and also because the transition temperature from the Brönsted acid to the Lewis acid becomes higher.

TABLE 2

EFFECT OF H_2O ADDITION ON CUMENE CONVERSION OVER ZEOLITE CATALYST

Catalyst	Pretreatment	Conversion (mole %) (reaction temperature)
Ca–$Y_{3.85}$ (Ca^{2+}, 89.5%)	I. 450°C	85.9 (450°C)
	II. 750°C	12.7 (450°C)
	II + H_2O at 300°C & heat treatment at 450°C	31.8 (450°C)
	II + H_2O at 40°C & heat treatment at 450°C	59.1 (450°C)
Ca–$Y_{5.0}$ (Ca^{2+}, 84.6%)	I. 450°C	64.2 (350°C)
	II. 750°C	36.9 (350°C)
	II + H_2O at 40°C & heat treatment at 450°C	67.3 (350°C)
H–$Y_{5.0}$ (H^+, 94.4%)	I. 450°C	72.9 (300°C)
	III. 650°C	46.0 (300°C)
	I + H_2O at 40°C & heat treatment at 450°C	72.7 (300°C)

The catalytic activity of zeolites for the cumene cracking decreases with the formation of Lewis acid, and it is expected that, if water is added, the Lewis acid may return to the Brönsted acid. Table 2 shows the change in activity by addition of water to zeolites with various silica/alumina mole ratios. The recovery of the activity of Ca–$Y_{3.85}$ is slight when the addition was made at 300°C, because the adsorbed amount of water was small; moreover, a structural decomposition would be caused by the water molecules (*5*). In the case of water addition at 40°C, the recovery was incomplete even though an adequate amount of water was adsorbed. This is probably either because part of the structure was decomposed or because the dehydroxylated sites (Lewis acid sites) were stabilized, like the siloxane structure in silica (*26*), so that they did not return to the Brönsted sites, by rehydration. As the activities of Ca–$Y_{5.0}$ and H–$Y_{5.0}$ recover completely with the addition of 40°C, it is known that the Lewis acid sites return to the Brönsted acid sites when the silica/alumina mole ratio is high.

The silicious zeolites pretreated at high temperatures show a remarkable activity change with time. As indicated in Table 3,

TABLE 3

AGING OF CUMENE CONVERSION OVER Ca–$Y_{5.0}$ CATALYST (Ca^{2+}, 84.6%) AT 330°C

Pretreatment	Pulse number	Conversion (mole %)
Preheat treatment at 650°C	I	56.3
	II	51.9
	III	49.7
	IV	44.2
Further heat treatment at 650°C		54.9
Preheat treatment at 650°C	I	58.9
	IV	46.0
O_2 Addition (5×10^{-4} mole)		61.4

their activity decreases with every addition of cumene. Some treatments, however, can recover it again—for example, the treatments at higher temperatures, or the addition of oxygen. The cause of the aging, therefore, seems to be either that the oily polymers fill up the cavity or that coke produced during the hydrocarbon-cracking process was strongly adsorbed.

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