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Cumene-Cracking Activity of Zeolite Catalysts.
II. Transition-Metal-Exchanged Zeolites

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The catalytic properties for cumene-cracking reaction of nickel-form zeolite Y were examined. The activity of nickel-form zeolite gradually increases with each slug of cumene and attains a maximum value. At the same time nickel ions are reduced to nickel metal by cumene. The hydroxyl groups generated upon reduction contribute to the activity increase. Magnetic data and X-ray diffraction analysis confirm this mechanism. By the addition of oxygen, after nickel metal was formed in the zeolite, the activity of zeolite was depressed, and the decomposition of the zeolite structure was observed.

The catalytic behaviors of iron-, cobalt-, chrome-, or cadmium-form zeolite were also examined.

INTRODUCTION

Faujasite-type zeolites, when they include polyvalent cations such as alkaline-earth metal and rare-earth metal or ammonium ion, exhibit catalytic activity for various reactions (*1*). In the case of metal cation-form, the strong electrostatic field, formed on the zeolite surface, polarizes the hydrocarbon to form carbonium ion, which acts as a reaction intermediate (*2–4*). Furthermore, this field polarizes the water to form a proton and a hydroxyl group, and this proton acts as the catalytic active site (*5*). In the case of ammonium-form zeolite, ammonia is released by calcination and proton-form zeolite is formed (*6, 7*). This type of zeolite has similar active sites to those of the silica–alumina solid acid, but the behaviors of these two catalysts are fairly different from each other.

Among the metal catalysts, some transition metals have been known to show outstanding properties in catalytic reactions. In zeolite catalyst, transition-metal ion-exchanged zeolites are expected to have different catalytic active sites and mechanism compared with alkaline-earth- or rare-earth-exchanged zeolite, so it appears desirable to elucidate effects of metal on the catalytic action of zeolite. Furthermore, such an investigation could possibly yield some insight into the nature of catalytic process with zeolite.

In this paper, catalytic activities for cumene-cracking reaction of transition-metal zeolites such as nickel, iron, cobalt, chrome, and cadmium were investigated from a viewpoint of the aging behavior of catalysts. The conversion during each cumene pulse was measured, and the effect of oxygen addition to the zeolite was also studied.

EXPERIMENTAL

The starting material was synthetic sodium faujasite (Na–$Y_{4.6}$, $Na_2O \cdot Al_2O_3 \cdot 4.6 SiO_2 \cdot nH_2O$) prepared from silica–alumina gel and caustic soda. The diffraction pattern and water sorption capacity were similar to those of binder-free Linde 13X.

The ion exchange of sodium ions for other metal ions was performed by stirring an aqueous suspension of Na–$Y_{4.6}$ zeolite in the presence of a proper amount of metal chloride or metal nitrate for several hours at 90°C. High-exchange species were obtained by repeating the treatment several times with concentrated salt solutions. The pH of the suspension was maintained above 5. After the exchange, the products were collected by filtration and washed with water, and the free ions were removed. The degree of ion exchange was determined from chemical analysis and flame photometry.

The catalytic activity for the cumene-cracking reaction was estimated from reactions in a microreactor. The apparatus were described in detail in the previous paper (*5*). Sixty milligrams of 28–60 mesh dehydrated zeolite was packed in the reactor. The catalyst was activated for 2 hr in a helium gas carrier. The reactant, cumene, was injected by a microsyringe and fed to the catalyst with a flow of helium. The helium flow rate was 60 cm³/min. The reactant volume was 8 μl in liquid, that is 5.74×10^{-5} mole. Oxygen was introduced to the catalyst at 450°C in the normal case, and the volume of oxygen was 10 cm³. The products were trapped and analyzed by gas chromatography. The catalytic activity was recorded in terms of cumene conversion.

The static magnetic susceptibility was measured with a Faraday-type microbalance (*8*).

The X-ray powder diagrams were recorded by the X-ray diffractometer. Experimental conditions were as follows: Copper radiation was used; scanning speed was 1° or ¼°2θ/min; the time constant was 4 sec; receiving slit was 0.2 or 0.1 mm; angular aperture was 1°. Silicon was used as an internal standard for the measurement of crystallite size.

Results

In the microcatalytic experiments, successive slugs of cumene were passed over the catalyst sample. In Fig. 1, the cumene-cracking activities of H(70%)-Na-$Y_{4.6}$ and Ni(9.2%)-Na-Y were plotted against the pulse number, and the effect of oxygen addition was also shown. The cracking activity of H-Na-$Y_{4.6}$ gradually decreases by every addition of cumene and is restored by the oxygen addition. Therefore, the decrease in activity seems to be due to the formation of coke and oily polymers in the zeolite cavity. The cracking activity of

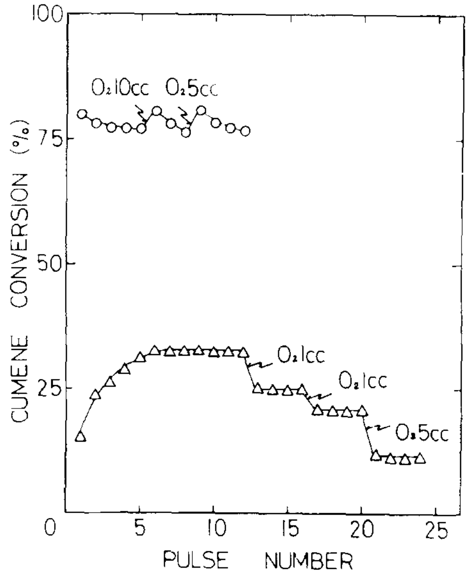

Fig. 1. Conversion of cumene over H(70.0%)-Na-$Y_{4.6}$ and Ni(9.2%)-Na-$Y_{4.6}$ as a function of cumene pulse number and effect of oxygen addition. —○—, H-Na-$Y_{4.6}$; Pretreatment, 450°C; Reaction, 400°C. —△—, Ni-Na-$Y_{4.6}$; Pretreatment, 450°C; Reaction, 400°C.

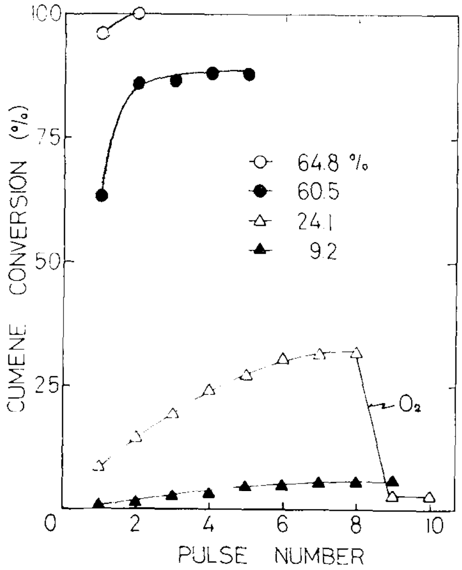

Fig. 2. Conversion of cumene over Ni-Na-$Y_{4.6}$ having various Ni^{2+} ion exchange as a function of cumene pulse number. Pretreatment, 450°C; Reaction, 350°C.

$Ni–Na–Y_{4.6}$, on the other hand, increases with the respective cumene additions to a saturated value. With oxygen addition, the activity decreases sharply with formation of water, and it is not able to be restored even with the addition of an excess amount of cumene.

In Fig. 2, the change in activities of $Ni–Na–Y_{4.6}$ with increasing Ni^{2+} exchange were shown in relation to the pulse number of added cumene. The amount of added cumene which was required to saturate the activity depends upon the degree of ion exchange. This amount depends also upon the reaction temperature as shown in Fig. 3; the higher the temperature is, the less the amount is. Therefore, the converted cumene seems to affect the activity.

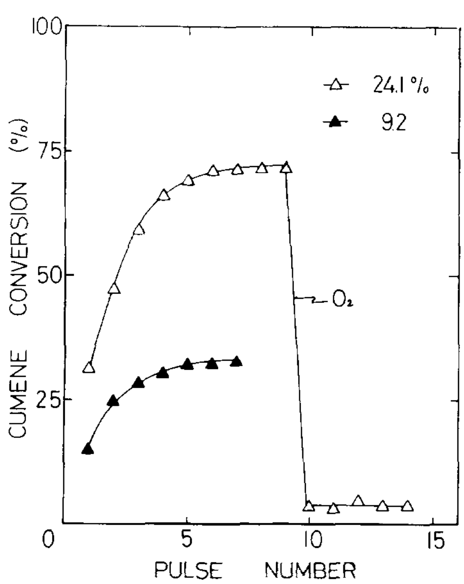

FIG. 3. Conversion of cumene over $Ni–Na–Y_{4.6}$ having various Ni^{2+} ion exchange as a function of cumene pulse number. Pretreatment 450°C; Reaction 400°C.

In Fig. 4, the saturated activity which was obtained from Fig. 2 was plotted against the increasing Ni^{2+} exchange of $Ni–Na–Y_{4.6}$. In the case of Ca-exchange, the activities of the low exchange species are negligibly small; this follows from the mechanism that the Ca ions enter preferably into S_I site (*5*). Accordingly, if Na ions in S_I site are first exchanged for Ni ions, no interaction would be expected between the Ni ions and the hydrocarbon molecules and the activity would not appear up to about 55% ion exchange for zeolite with a silica/alumina ratio of 4.6. The $Ni–Na–Y_{4.6}$ of low Ni^{2+} exchange, however, shows the catalytic activity, so that Ni ions must enter into the zeolite cavity with some ligand molecules.* The size of a Ni ion accompanied with a ligand is too large to enter into the S_I site, so the exchange would rather occur at the S_{II} site.

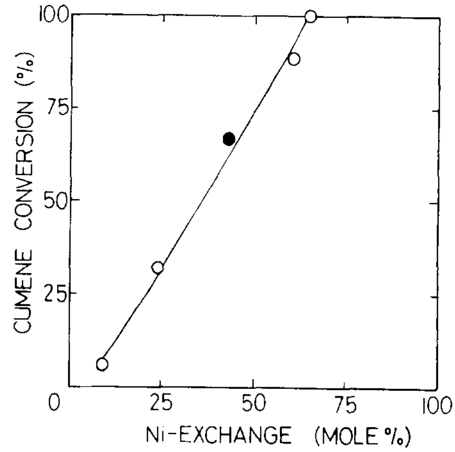

FIG. 4. Change of maximum catalytic activity with degree of Ni^{2+} ion exchange. Closed symbol represents the sample prepared from nickel-nitrate solution. Pretreatment, 450°C; Reaction 350°C.

Figure 5 illustrates the dependence of catalytic activity of $Ni(24.1\%)–Na–Y_{4.6}$ at 400°C upon the pretreatment temperature. Though the initial activity decreases as the pretreatment temperature increases, the maximum activities are similar in all cases. Therefore, the activity increase with multiple cumene addition would be caused not by residual water but by Ni ion. The catalytic activities of the decationated zeolite and the alkaline-earth metal-exchanged zeolites are greatly influenced by the pretreatment temperature, and the maximum activity is obtained for the pretreatment at about 450°C. When the temperature is over 450°C, the activity decreases owing to the destruction of zeolite structure and the dehydroxylation from two Brönsted acid sites

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* Probably water molecules are held as the ligand.

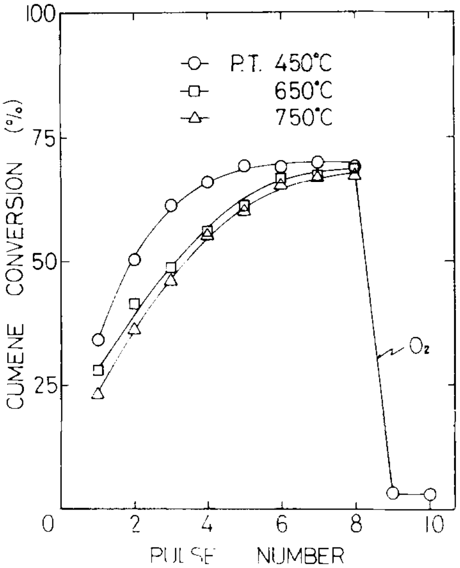


FIG. 5. Conversion of cumene over Ni(24.1%)-Na-$Y_{4.6}$ pretreated at various temperatures as a function of cumene pulse number. Reaction, 400°C.

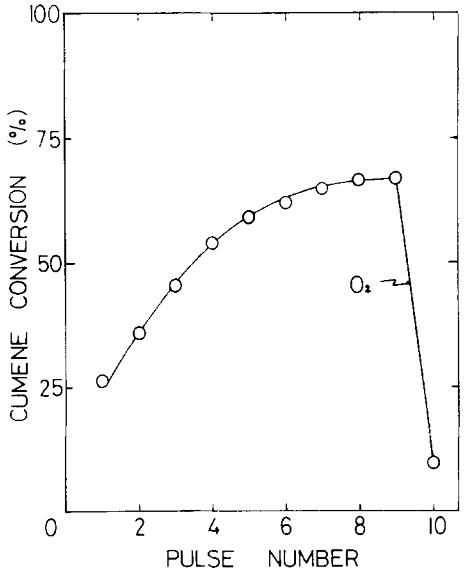


FIG. 6. Conversion of cumene over Ni(43.1%)-Na-$Y_{4.6}$ exchanged from nickel-nitrate solution as a function of cumene pulse number. Pretreatment, 400°C; Reaction, 350°C.

(*5*). In the case of Ni-Na-$Y_{4.6}$, the effect of pretreatment temperature could be interpreted from neither the destruction nor the dehydroxylation.

The existence of a ligand influences remarkably the catalytic properties of the Cu-form zeolite, as will be reported in another paper; then the catalytic behaviors of the two Ni-form zeolites (one was prepared in a nickel-chloride solution and the other from a nickel-nitrate solution) were investigated. The Ni-form zeolite, prepared in an $Ni(NO_3)_2$ solution, also shows the activity increase by cumene additions as shown in Fig. 6, and attains the maximum activity similar to that of the Ni-form prepared in an $NiCl_2$ solution. Also, the activity is affected by the oxygen addition.

The cumene-conversion rate observed on the Ni(24.1%)-Na-$Y_{4.6}$ (pretreated at 450°C) with added hydrogen of 10 cm^3 was 45.6% at 400°C; this value is higher than that for Ni-Na-$Y_{4.6}$ without added hydrogen, 31.3%.

The cumene-conversion rates over Fe(46.4%)-Na-$Y_{4.6}$ and Co(56.4%)-Na-$Y_{4.6}$ are shown in Fig. 7. The pretreatment temperatures are both 450°C, and the reaction temperatures are 330 and 300°C, respectively. In both cases, the activities increase gradually to the maximum value and are depressed by oxygen addition. As

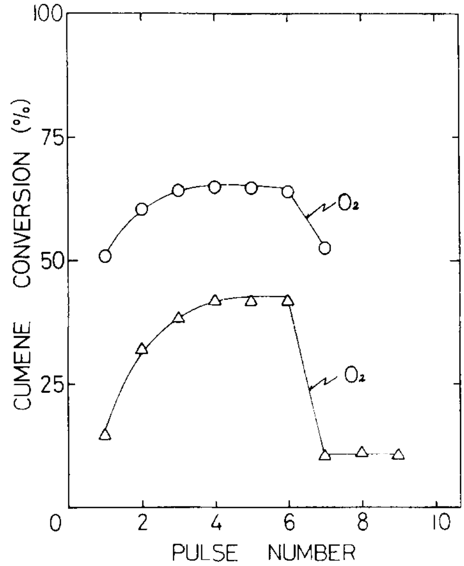


FIG. 7. Conversion of cumene over Fe(46.4%)-Na-$Y_{4.6}$ and Co(56.4%)-Na-$Y_{4.6}$ as a function of cumene pulse number and effect of oxygen addition. —○—, Co-Na-$Y_{4.6}$; Pretreatment, 450°C; Reaction, 300°C; —△—, Fe-Na-$Y_{4.6}$. Pretreatment, 450°C; Reaction, 330°C.

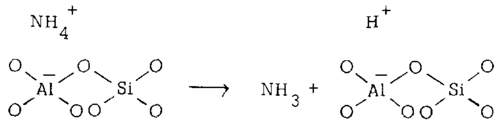
in the case of Ni-form zeolite, water is generated by oxygen addition and the activity cannot be restored in these catalytic systems.

In Fig. 8, the changes in activities of Cr(73.3%)-Na-$Y_{4.6}$ and Cd(68.4%)-Na-$Y_{4.6}$ are plotted against the cumene pulse number. The pretreatment was carried out at 450°C, and the reaction temperatures were 300 and 400°C, respectively. All the trends are the same as cases of the other transition-metal-form zeolites described already.

The Mn- and the Zn-form zeolite do not show such a behavior in cracking activities. The activities are depressed gradually with the increasing addition of cumene and restored by oxygen addition.

Discussions

It is generally accepted that the cumene-cracking reaction occurs through the formation of carbonium ion intermediate of cumene together with the Brönsted acid site on the solid acid. For the ammonium zeolite, it was shown from ir spectroscopy, tga and dta, that, after loss of physically adsorbed water, ammonia is evolved from the lattice to yield the decationated zeolite (*6*, *7*).



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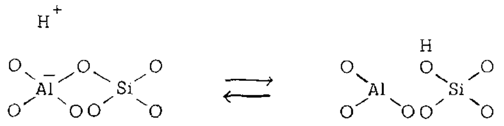

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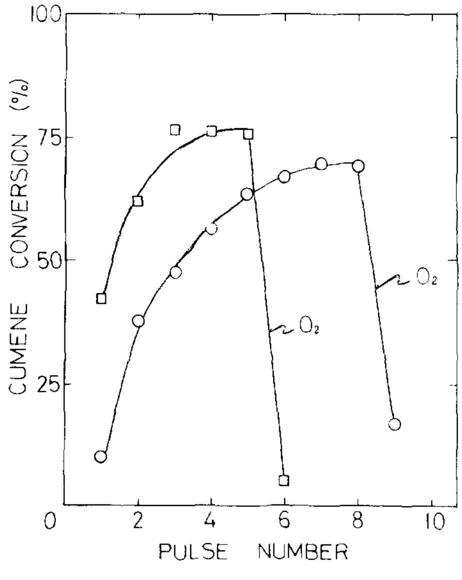

Fig. 8. Conversion of cumene over Cr(73.3%)-Na-$Y_{4.6}$ and Cd(68.4%)-Na-$Y_{4.6}$ as a function of cumene pulse number and effect of oxygen addition. —○—, Cd-Na-$Y_{4.6}$; Pretreatment, 450°C; Reaction, 400°C; —□—, Cr-Na-$Y_{4.6}$; Pretreatment, 450°C; Reaction, 300°C.

The group in the left-hand side of Eq. (2) serves as a Brönsted acid site. For the alkaline-earth metal and the rare-earth metal-exchanged zeolite, both the electrostatic field and the Brönsted acid act as active sites, that is, hydrocarbon and water are polarized by the electrostatic field. Therefore, the cracking activity of such zeolites depends also upon the electrostatic field strength.

Transition-metal ions have various oxidation states, so the catalytic behaviors are expected to vary according to the oxidation state in the zeolite. As nickel, iron, and cobalt, investigated in this study, are liable to be reduced, the zero-valency state rather than the ionic states is used for the catalyst in most cases. Normally, metal salt supported on kieselguhr, silica, alumina, etc., is reduced by hydrogen, and the metal dispersed in such supporters is used for catalysts.

In the present investigation, transition metal was incorporated into zeolite as bivalent or trivalent ions by replacing the

Na ion. Ni–Na–$Y_{4.6}$ has increasing activity with the addition of cumene; this fact suggests that a proton is produced with the reduction of Ni^{2+} to Ni^0 as in Eq. (3).

$$Ni^{2+} \xrightarrow{RH} Ni^0 + 2\,H^+ \qquad (3)$$

The reduction agent, RH, is to be cumene. At all events, it is obvious that Ni^{2+} is reduced together with the abstraction of hydrogen from cumene. This agrees with the result that the activity increases with the addition of hydrogen. If the reduction as shown by Eq. (3) proceeds completely, the zeolite thus formed would have the same quantity of Brönsted acid sites as that of the decationated zeolite. The activity increases necessarily with the formation of Brönsted acid site by cumene addition. When the reduction does occur no longer, the activity becomes maximum. From Eq. (3), a relation may be expected between the converted cumene and the quantity of Ni^{2+} ions. Table 1 listed the difference between the maximum activity value (Ms) and the value extrapolated to pulse number zero (Mo), and the quantity of Ni^{2+} ions.*

TABLE 1

RELATIONSHIP BETWEEN QUANTITIES OF Ni IONS CONTAINED IN Ni–Na–$Y_{4.6}$ AND AMOUNTS OF CONVERTED CUMENE ON THE NEWLY FORMED ACTIVE SITE

Ni on exchange (mol %)	Ni ion contained ($\times 10^5$ mole/ 60 mg-zeolite)	Ms − Mo ($\times 10^5$ mole-cumene)
9.2	1.2	0.3
24.1	3.2	2.2
60.5	8.6	3.5

Yates reported that the reduction of Cd-, Hg-, Zn-, Ni-, and Ag-form zeolites occurs by addition of hydrogen after evacuation at 140–500°C (*9*). The reduced cadmium, mercury, and zinc sublimated, and the reduced nickel and silver were held loosely to the zeolite lattice because of their low vapor pressures. In such cases, the reduction does not occur by evacuation. Rabe *et al.* investigated by ESR the oxidation state of ions contained in the Ni–Na-form zeolite which was treated by either sodium vapor or by hydrogen (*10*). Gioia *et al.* reported recently the reduction of Ni^{2+}–X by hydrogen (*11*). In these studies, the reductions were performed by strong reducing agents such as hydrogen or sodium vapor.

If the proton is produced according to Eq. (3), the elimination of water results in the formation of Lewis acid site from two Brönsted acid sites by high-temperature treatment. Table 2 lists the result on the elimination of water from Ni(64.8%)–Na–$Y_{4.6}$ during various treatments. W_1 is the water formed from the structure I, and W_2 from the structure II. The value ($W_1 - W_2$) would be related to the amount of protons produced by cumene addition.

TABLE 2

ELIMINATION OF WATER FROM Ni(64.8%)–Na–$Y_{4.6}$ BY VARIOUS TREATMENTS

Treatment[a]	Water ($\times 10^5$ mole/ 60 mg-zeolite)
1	2.2
2	3.9
3	1.3

[a] 1. The zeolite was pretreated at 450°C, and then heated to 750°C. (W_1)
2. After the pretreatment at 450°C, the zeolite experienced cumene-cracking reaction at 300°C and then was heated to 750°C. (W_2)
3. After the treatment of 2, the zeolite experienced again cumene-cracking reaction at 300°C and then was heated to 750°C. (W_3)

The magnetic properties of Ni(64.8%)–Na–$Y_{4.6}$ treated in various ways are shown in Table 3. The original Ni–Na–$Y_{4.6}$ is paramagnetic and the susceptibility, χ, is 4.5×10^{-6} (emu/g); that is the molar susceptibility, χ_M, is 4014×10^{-6} (emu/mole-Ni^{2+}). After the diamagnetic correction, the paramagnetic susceptibility becomes probably ten-odd percentages greater. As the paramagnetic susceptibility of nickel chloride is 5798×10^{-6} (emu/

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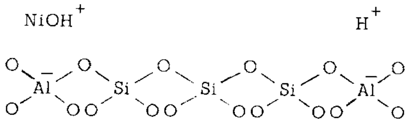
* Generally, the reaction occurs also on the active sites that resemble the alkaline-earth metal-form zeolite and the amount of these sites decreases by each cumene pulse. When the activity becomes maximum, the number of these sites is zero.



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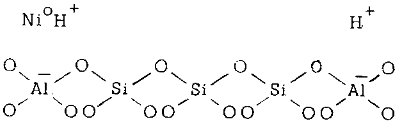


(II)

mole), nickel seems to exist as free ions in the original zeolite. Samples II, III, and IV show ferromagnetism, which indicates that nickel metal is formed in the zeolites. Ni–Na–$Y_{4.6}$ heated in helium flow or in air does not show ferromagnetism. The apparent magnetizations of these samples are in the order of II < III < IV. In sample II, both paramagnetic and ferromagnetic species coexist. It was estimated from the data of cumene-cracking activity that a portion of Ni^{2+} ions in sample II was reduced. Therefore, the coexistence of both species is evident. On the other hand, Ni^{2+} ions in sample III are completely converted to Ni^0, and this sample becomes ferromagnetic. The apparent magnetization of sample IV is double that of III; this fact is very interesting, because the mol wt of species in IV cannot be half that of III. The zeolite structure of IV is destroyed, as mentioned below, so the dispersion state of Ni^0 in the zeolite should be changed. This problem, however, is beyond this investigation.

TABLE 3

MAGNETIC PROPERTIES OF Ni(64.8%)-Na-$Y_{4.6}$ TREATED BY VARIOUS WAYS

Species	Magnetic property
I. Original	Paramagnetism $\chi = 4.53 \times 10^{-6}$ (emu/g) at 296°K
II. After addition of cumene (12 μl-cumene to 60 mg-zeolite)	Paramagnetism + Ferromagnetism
III. After addition of cumene (80 μl-cumene to 60 mg-zeolite)	Ferromagnetism
IV. Above + 40 cm^3-oxygen	Ferromagnetism

According to the magnetic data, it is certain that Ni^{2+} ion would be reduced to atomic Ni^0 by cumene addition and then aggregate to Ni metal. Atomic Ni^0 should be rather mobile in the zeolite cavity. When Ni^{2+} ions are converted to Ni metal, the Ni-form zeolite catalyst becomes the decationated one with highly dispersed Ni metal. However, Ni metal would not participate directly in the reaction, because no change is observed in the product distribution of cumene cracking catalyzed by this zeolite.

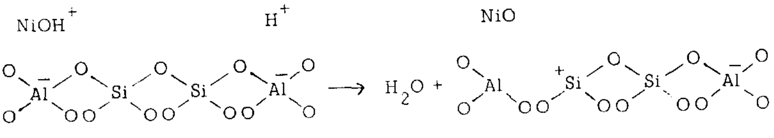
The studies of Yates showed the necessity of high-temperature treatment under hydrogen flow for the reduction. For example, the treatment at higher than 600°C is necessary to reduce the zinc ions in the faujasite. The temperature dependence of cumene conversion on the Ni(64.8%)–Na–$Y_{4.6}$ catalyst is shown in Table 4. At 250°C, the conversion rate is low and the activity change is scarcely observed at each pulse. On the other hand, the activity change at each pulse is remarkable and the conversion rate is high at 300°C. In comparison with Ni–Na–$Y_{4.6}$, the temperature effect for

TABLE 4

REACTION TEMPERATURE DEPENDENCE OF CUMENE CRACKING ACTIVITIES OF Ni(64.8%)-Na-$Y_{4.6}$ AND H(70.0%)-Na-$Y_{4.6}$ PRETREATED AT 450°C

Temperature (°C)	Cumene conversion rate (mol %)	
	Ni-Na-$Y_{4.6}$[a]	H-Na-$Y_{4.6}$
250	16.7	27.5
300	91.3	70.1
350	100	88.0

[a] Maximum activity.



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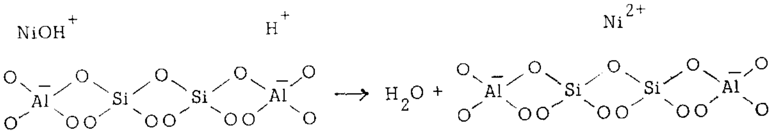
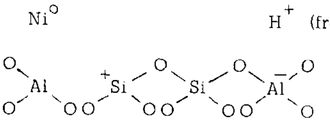


(5)

NH_4–Na–$Y_{4.6}$ is not large. This is not because the activation energy is so much different from Ni–Na–$Y_{4.6}$ to NH_4–Na–$Y_{4.6}$, but because the reduction rate of Ni^{2+} is small, below 300°C.

It would also be considered that the reduction of Ni^{2+} occurs in the zeolite treated at higher temperatures, since the maximum activities are similar in the zeolite treated at various temperatures as shown in Fig. 5. When the Ni-form zeolite is treated at higher temperatures, the following two reaction mechanisms are presumed. Whenever reaction (4) or (5) proceeds, Ni^{2+} ions are possibly reduced to Ni^0. These reaction mechanism are now investigated by the magnetic technique and the result will be published later. As the cation vacancy (Lewis base) of Eq. (4) seems to abstract a proton from a hydrocarbon, the activity change is also probable from this mechanism. The results on catalytic activity of Ni(64.8%)–Na–$Y_{4.6}$ treated at 750°C are shown in Fig. 9. When this zeolite was reheated at 750°C after this activity test, water was generated, as shown in Table 2. For the reheated zeolite, the activity still changed with each cumene pulse, but the maximum activity became lower. This would result from the formation of coke or oily polymers in the zeolite cavity. When the reduced Ni-form zeolite is retreated at 750°C, the initial activity becomes lower with change from Brönsted acid to Lewis acid. On the other hand, it seems that the activity increase of this catalyst is due to the change from Lewis acid to Brönsted acid. Since water is not added to the system during the reaction, protons would be transferred from reactants or products to the Lewis acid site. The amount of water removed from this zeolite, W_3, is half of W_2, shown in Table 2; this would be reasonable, considering structures II and III.



(III)

In addition to the activity experiments, some work has been done on Ni(64.8%)–Na–$Y_{4.6}$ by using X-ray analysis. Portions

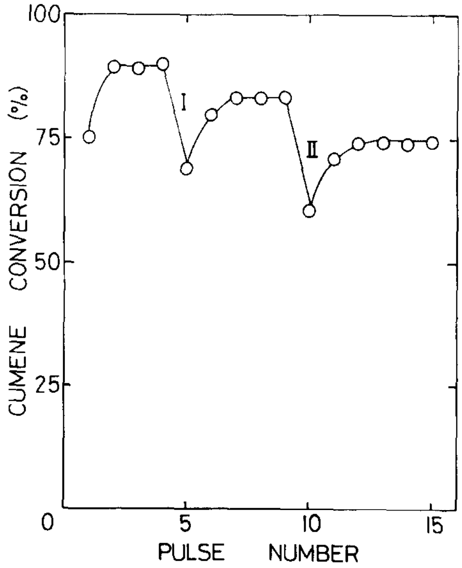


FIG. 9. Conversion of cumene over Ni(64.8%)–Na–$Y_{4.6}$ treated by various ways as a function of cumene pulse number. Pretreatment, 750°C, 2 hr; Treatment I, 750°C, 1 hr; Treatment II, 750°C, 1 hr.

of the spectrum of this sample treated in various ways are shown in Fig. 10. No structural decomposition was observed on the sample with added cumene, but a prominent peak was seen at about $2\theta = 44.5°$. The zeolite becomes partially amorphous after the treatment with cumene and oxygen, and the intensity of the new peak increases. Since this peak corresponds to (111) reflection of crystalline nickel, it is clear that Ni^{2+} ions are reduced to Ni^0, which aggregates to metal. The crystallite sizes of nickel metals in the zeolites treated with cumene only and cumene–oxygen were estimated to be 140 and 200 Å, respectively, from the half-width of (111) reflection. It is reasonable that these species show ferromagnetism.

When oxygen was added to Ni(64.8%)–Na–$Y_{4.6}$ before the activity test, no water was generated and the cumene-cracking activity at 300°C increased by each cumene pulse to the maximum value, which was 89.3 mol % conversion comparable to that without oxygen addition. However, by oxygen addition after these activity tests, the cumene-conversion rate decreased to 3.9% and the water generation was observed. This indicates that the dissociation of oxygen molecules and the attack to the structure do not occur in absence of metallic nickel.

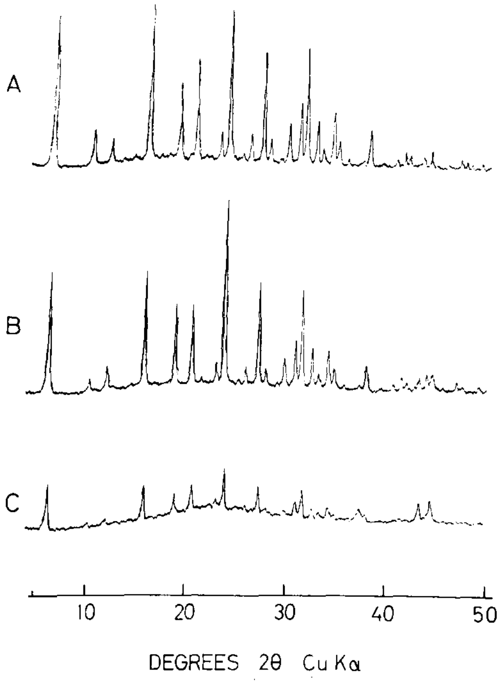


Fig. 10. X-Ray diffraction patterns of Ni(64.8%)-Na-$Y_{4.6}$: A: original; B: after addition of cumene; C: after addition of cumene and oxygen.

The amount of water removed from Ni(24.1%)–Na–$Y_{4.6}$, which was treated with cumene to the maximum activity of conversion and then with addition of oxygen, is 4.0×10^{-5} mole/60 mg-zeolite; this is compared with 3.2×10^{-5} mole/60 mg-zeolite of Ni^{2+}-form. The dependence of activity upon the temperature of oxygen addition is shown in Table 5. It is observed that the oxygen effect occurs when the temperature of oxygen addition is higher than 350°C.

TABLE 5

Temperature Dependence of Addition of Oxygen on the Activity Change of Ni(24.1%)-Na-$Y_{4.6}$

Pretreatment 450°C
Reaction 400°C

Temperature (°C)	Cumene conversion rate (mol %)
Without addition	68.9
300	71.5
350	23.8
400	21.9

The zeolites containing iron, cobalt, cadmium, or chrome ions show the catalytic behaviors similar to that of the nickel-form zeolite. The iron- and cobalt-form zeolites become ferromagnetic after the activity experiment. Therefore, it is clear that iron and cobalt ions are reduced to metals. Also, in the case of cadmium- or chrome-form zeolite, metals are probably formed. It is certain that such metals influence the oxygen effect.

As to the behavior of the activity increase and the degree of the oxygen effect, the electronegativity of cations and the *d*-character of transition metals should be concerned, but the relations among them are not clear in this study.

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