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Cumene Cracking Activity of Zeolite Catalysts

III. Effect of Copper(II) Ion Exchange on the Faujasite-Type Synthetic Zeolites

KAZUO TSUTSUMI, SHIGEO FUJI, AND HIROSHI TAKAHASHI

Institute of Industrial Science, The University of Tokyo, 7-22-1 Roppongi,
Minato-ku, Tokyo, Japan

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The characteristics of the cumene cracking activity of the Cu-form synthetic faujasite-type zeolites was examined.

The extent of the activity increases resulting from the exchange of sodium by copper ions depends upon whether the exchange is performed in a chloride solution or in a nitrate solution. The zeolite exchanged in a chloride solution is more active than that in a nitrate solution; this would be because the exchange in a chloride solution occurs in the form of the $CuCl^+$ ion. Since the residual chlorine content in the zeolite is correlated with the activity, the strong acid sites formed according to the following equations affect the activity:

$$CuCl^+ + H_2O \rightarrow Cu(OH)^+ + HCl,$$
$$CuCl^+ + Cu(OH)^+ \rightarrow Cu^{2+} + CuO + HCl.$$

INTRODUCTION

Regarding the active sites of the zeolite catalyst, the solid acid theory and the electrostatic-field theory have been proposed. The former is based on the idea which has been applied to the silica-alumina catalyst; that is, the protons are formed from hydroxyl groups on the zeolite surface. The hydroxyl groups on the surface of the faujasite-type zeolite have, therefore, been studied in detail by means of infrared spectroscopy (*1–10*). Generally speaking, the stretching vibrations of OH groups are observed around 3550, 3650, and 3750 cm^{-1}; with the zeolite exchanged by rare earth metal cations, the absorption occurs also in the 3470–3520 cm^{-1} region. Among these OH groups, the effective solid acids are those responsible for the 3550, 3650, and 3470–3520 cm^{-1} bands. For the study of the OH group, the active hydrogen has also been determined by using organometallic reagents (*11, 12*). The solid acids have been investigated by amine titration (*13–15*) and by electron spin resonance (*16–20*).

The latter theory was first proposed by Rabo *et al.* (*21, 23*) and Pickert *et al.* (*22*). The C–H bond is polarized by the strong electrostatic field formed between anion sites of the zeolite framework and cations, and the carbonium ions thus produced facilitate the reaction. The field strength has also been measured by Huang *et al.* (*24*), and by the present authors (*25*). The activity of the decationated zeolite, which is prepared by the ammonium ion exchange and then the liberation of ammonia, is explained by the former theory, whereas the activity of metal-ion-exchanged zeolite is responsible for the latter theory, as well as for the protons generated by the polarizing effect of the electrostatic field (*26*).

For the zeolites which are replaced by alkaline earth metals such as Ca, the above idea is useful, while for the zeolites containing transition metal ions, more complicated factors seem to contribute to the active site owing to the influence of the ligand. On the samples that were replaced part of the alkaline or alkaline earth metal ions by Cu^{2+} in synthetic faujasite, Richardson (*27*) measured the crystal-field effect on Cu^{2+} by means of electron spin resonance and reported on the effect of coordinated water. Metal ions of a 1 B group like Cu^{2+} have a d^9 outer-shell electron and form an *spd* hybrid orbit; this orbital makes it easy for those metal ions to form stable monodentate complex ions with hallogen ions, CN^- ions, NH_3, H_2O, etc., as ligands. Thus, with regard to the activity of the zeolites containing these metal cations, the effect of the ligand is important.

In the present investigation, the catalytic activity for cumene cracking was measured on Cu^{2+}–$Y_{4.6}$ zeolite, which had been prepared by the ion exchange of Na–$Y_{4.6}$ in $CuCl_2$ or $Cu(NO_3)_2$ aqueous solution.

EXPERIMENTAL METHODS

The starting material was synthetic sodium faujasite Na–$Y_{4.6}$, $Na_2O \cdot Al_2O_3 \cdot 4.6SiO_2 \cdot nH_2O$, synthesized from silica–alumina gel and caustic soda. The X-ray diffraction pattern and water adsorption capacity of this species were the same as those of Linde Na–X and SK–40.

The ion exchange with Cu^{2+} was performed by immersing Na–$Y_{4.6}$ in $CuCl_2$ or $Cu(NO_3)_2$ aqueous solution. The aqueous solutions at the exchange were fixed above pH 5. After the exchange, the products were collected by filtration and washed to remove the free ions. The degree of ion exchange was determined by chemical analysis and flame photometry. The chlorine in the zeolite was determined by the Mohr method after the zeolite had been dissolved in nitric acid and the pH of the solution had been fixed as 7 by adding an NaOH aqueous solution. The catalytic activity for cumene cracking was measured by means of a microreactor. The apparatus used was described in detail in a previous paper (*26*).

RESULTS

Usually, the ion exchange of zeolite is performed in an aqueous solution of chloride, but, for the ion exchange of sodium with cupric ions, a great difference is observed in the activity of the samples depending on whether the exchange is performed in a chloride or in a nitrate solution. For example, if we compare two zeolites, one prepared by ion exchange with a $CuCl_2$ solution and having a Cu^{2+} exchange of 71.0 mole % and the other prepared by exchange with a $Cu(NO_3)_2$ solution and having a Cu^{2+} exchange of 73.5 mole %, when both of them were pretreated at 450°C and used at 350°C, the cumene conversion activity with the former is 91.6%, while with the latter is only 64.5%. Therefore, the catalytic activity of the former, which was ion exchanged with the $CuCl_2$ aqueous solution, seems to be affected by the residual chlorine. Its catalytic activity was, then, investigated by determining the extent of ion exchange and the amount of chlorine. Table 1 shows the extent of ion exchange and the amount of chlorine of Cu–Na–$Y_{4.6}$. Generally, the amount of chlorine increases as the pH of the aqueous cupric chloride solution is lowered at the exchange and as the exchange is repeated. Accordingly, it is possible to increase to some extent the amount of chlorine inside the zeolite at low ion exchange by controlling the concentration of the salt and the number of the exchange. As is shown in Table 1, the zeolite with the largest amount of chlorine has 1 chlorine/5 cupric ions, whereas the zeolite with the smallest chlorine content has 1 chlorine/100 cupric ions.

Figure 1 plots the amount of chlorine contained in zeolite versus the catalytic activity. The catalytic activity here is the value for the first pulse, since it changes with time. Generally, the catalytic activity increases with an increase in the amount of chlorine, though it is also influenced by the extent of exchange. For the zeolites replaced by Ca^{2+}, NH_4^+, or La^{3+} ions, the activity increases with an increase in the extent of ion exchange (*26*); whereas the

TABLE 1
Relation Between the Degree of Ion Exchange and Amount of Chlorine of Cu-Na-$Y_{4.6}$

Cu exchange (mole %)	Cu content (mole/g × 10^3)	Cl content (mole/g × 10^4)	Cl/Cu ratio
17.7	0.40	0.04	0.01_0
29.5	0.68	0.09	0.01_3
47.7	1.06	0.36	0.03_4
71.0	1.59	2.83	0.18_1
75.9	1.67	1.59	0.09_5
76.7	1.69	1.16	0.06_9

activity decreases for copper-form zeolites of 71.0 and 76.7% exchange. This confirms the remarkable effect of chlorine on the activity.

Figure 2 shows the correlation between the pretreatment temperature and the activity of the zeolites ion exchanged in an aqueous $CuCl_2$ solution or an aqueous $Cu(NO_3)_2$ solution. Both samples have nearly the same extent of ion exchange. Clearly, the zeolite ion exchanged with $CuCl_2$ shows a higher activity than that exchanged with $Cu(NO_3)_2$; besides, its change with the pretreatment temperature is slow compared with those of Ca- and H-form zeolites (*26*). The zeolite ion exchanged with $Cu(NO_3)_2$ decreases in activity because of the transition from Brönsted to Lewis acid and because of the decomposition of the zeolite structure by sintering when it was pretreated at a higher temperature. On the other band, the activity of the zeolite prepared with $CuCl_2$ decreases only above 800°C. It seems, as described below, that this is a result of structural decomposition caused by the generated HCl.

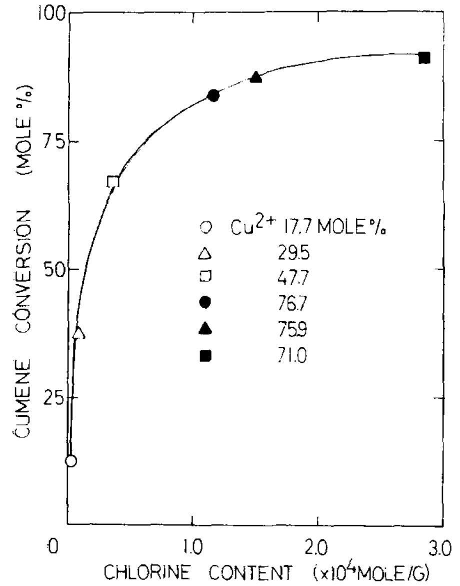

Fig. 1. Change of catalytic activity with amount of chlorine: The degree of Cu^{2+} exchange is shown; pretreatment, 450°C; reaction, 350°C.

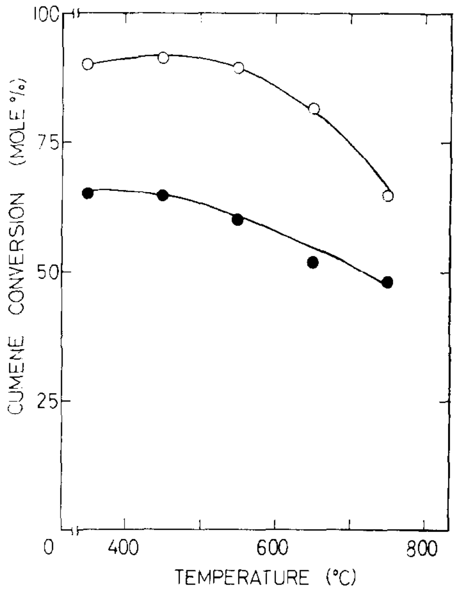

Fig. 2. Change of catalytic activity with pretreatment temperature: reaction, 350°C; (○) The catalyst is prepared by ion exchange with a $CuCl_2$ aqueous solution. The degree of ion exchange is 71.0% and the amount of chlorine is 2.83×10^{-4} mole/g-cat. (●) The catalyst is prepared by ion exchange with a $Cu(NO_3)_2$ aqueous solution. The degree of ion exchange is 73.5%.

Discussion

After the ion exchange with chloride solution, the zeolite was washed free of chloride. It was confirmed by the use of $AgNO_3$ that the free chloride ions inside the framework were removed completely. Nevertheless, the fact that chlorine was contained in the zeolite suggests that the copper is combined with the anion site of the framework as a complex ion containing chlorine. Cupric chloride hydrolyzes in the aqueous solution according to the following equation (the concentration of $CuCl^+$ becomes higher as the pH is smaller):

$$CuCl_2 + mH_2O \rightarrow CuCl^+ + H^+ + Cl^- + OH^- + (m - 1)H_2O. \quad (1)$$

However, it is known that when the pH becomes still smaller, $CuCl_4^{2-}$ ions are formed, and that when the pH is raised up to around 7, $Cu(OH)_2$ precipitates. Therefore, the pH must be around 5 for the ion exchange. The aqueous solution at about pH 5 used for the ion exchange contains $CuCl^+$ and H^+ ions, so that chloride ion is combined with an anion of the zeolite framework as a $CuCl^+$ ion and so that even after washing it remains inside the zeolite. On the other hand, Ca–Na–$Y_{4.6}$ does not contain any chloride, so no such a phenomenon occurs.

The Cu^{2+} ion has the electrons of the d^9 orbit, and the coordination is in square-planar. Four ligands are placed on the same plane, and sometimes two more ligands coordinate above and below the plane at a slightly longer bonding distance. The distance between Cu and Cl of $CuCl_2 \cdot 2H_2O$ is 2.3 Å and the distance between Cu and O is 2.01 Å. Therefore, it is impossible for the chloride to enter into the S_I cation site of the faujasite-type zeolite framework when the exchange proceeds in the form of $CuCl^+$. The exchange occurs at the S_{II} and S_{III} cation sites, so that the $CuCl^+$ interacts with the adsorbed molecules even at a fairly low extent of exchange. This behavior is very different from that of Ca^{2+}- or La^{3+}-exchanged zeolites. When the zeolite with a 4.6 silica-to-alumina mole ratio is ion exchanged by usual divalent ions, its activity does not increase until the cation exchange exceeds 50 mole %.

As Cu^{2+} has a very large heat of hydration (499 kcal/mole), the hydrated Cu ions are stable. Hence, it is considered that Cu^{2+} has coordinated water during and after the exchange. Though Cu–Na–$Y_{4.6}$ is light blue at room temperature, it turns light green with heating up to 100°C, then green with further heating, and finally becomes brown at 500°C. However, it returns to light blue when rehydrated at room temperature. These facts indicate that copper exists as a hydrated complex ion at room temperature and that it returns to the same hydrated ion when it is placed in an atmosphere containing of water vapor after dehydration with heating, if the structure would not been decomposed.

Furthermore, when the extent of ion exchange of the zeolite prepared by the exchange with an aqueous $CuCl_2$ solution is high, sometimes acidic vapor is generated with heating. For example, Cu–Na–$Y_{4.6}$, which has an ion exchange of 71.0% and contains 2.83×10^{-4} mole/g of chlorine, generates acidic vapor when being heated above 400°C. The gradual generation continues until 900°C. Above 900°C, the generated amount increases remarkably, and the zeolite structure is decomposed. It seems that HCl is formed according to Eqs. (2) and (3):

$$CuCl^+ + H_2O \rightarrow Cu(OH)^+ + HCl, \quad (2)$$

$$CuCl^+ + Cu(OH)^+ \rightarrow Cu^{2+} + CuO + HCl. \quad (3)$$

The brown color mentioned above results from the formation of CuO. As the HCl formed thus acts as a proton donor on the zeolite surface, there appears a strong active site of the solid acid catalyst. Morita *et al.* (*28*) reported that the Na–Y zeolite, which was originally inactive, became active remarkably for the alkylation of benzene when it adsorbed HCl. However, HCl sometimes facilitates the decomposition of the zeolite structure. When Na–$Y_{3.25}$ is changed to Cu–Na–$Y_{3.25}$, at a Cu-exchange ratio of 99%, the zeolite structure is considerably decomposed by the exchange. Besides, it turns brown black with heating at 300°C. The complete decomposition of the structure was proved by X-ray diffraction analysis. Further, by evacuation with heating, a yellow-brown substance is sublimated, and, since this substance turns green with hydration, it is obviously $CuCl_2$ formed according to Eq. (4):

$$CuCl^+ + CuCl^+ \rightarrow CuCl_2 + Cu^{2+}. \quad (4)$$

The chlorine content of Cu–Na–$Y_{4.6}$ treated at various temperatures changes as is shown in Table 2. With the zeolite which originally contained only a little chlorine, the amount of chlorine changed almost not at all until 650°C, while with the zeolite that had a large amount of chlorine content, the amount of chlorine decreases rather remarkably. Therefore, it is evident that some chlorine is combined fairly strongly with the zeolite, so the change of activity due to the preparation temperature must be comparatively slow.

TABLE 2

Relation Between Amount of Chlorine and Calcination Temperature of Cu–Na–$Y_{4.6}$

Calcination (°C)	Amount of chlorine (mole/g × 10^4) Cu-Na-$Y_{4.6}$ (Cu^{2+}, 71.0 mole %)	 Cu-Na-$Y_{4.6}$ (Cu^{2+}, 75.9 mole %)
Room T.	3.29	1.60
350	3.22	1.58
450	2.83	1.59
650	2.74	1.50
750	2.20	1.04

Thus, the catalytic activity of the zeolite ion exchanged with an aqueous $CuCl_2$ solution is more evidently influenced by the coordinated chloride ions than by the electrostatic field on the surface. This behavior is different from that of the zeolite ion exchanged with an alkaline earth metal or a rare earth metal. A similar phenomenon probably occurs with the zeolites containing other halogen ions, CN^- ion, and others.

Such a contribution of chloride to the activity is also shown by the dependence of the activity on the temperature of the reaction. Figure 3 illustrates the dependence of the activity on the reaction temperature when Cu–Na–$Y_{4.6}$ is pretreated at 450°C. The activity of the zeolite containing chlorine increases suddenly when the reaction temperature exceeds 350°C. The activities upon samples subjected to pretreatments at other temperatures behave similarly. This is a phenomenon never observed with alkaline earth metal- or rare earth metal-form zeolites. It also never occurs even with the zeolite ion exchanged in the aqueous $Cu(NO_3)_2$ solution. Such an effect of temperature also supports the idea that chlorine forms a solid acid site according to Eqs. (2) and (3).

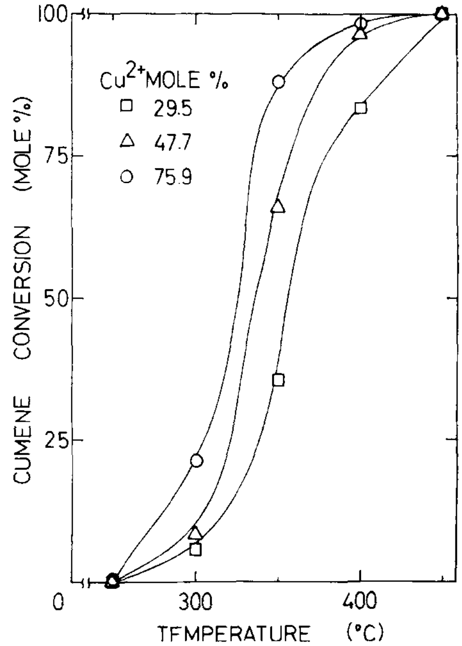

Fig. 3. Change of catalytic activity with reaction temperature: The degree of Cu^{2+} exchange is shown. Pretreatment, 450°C.

When the ion exchange is performed with an aqueous solution that hydrolyzes as in Eq. (1), H^+ also acts as an exchangeable cations. Accordingly, the Na^+ inside the zeolite is exchanged not only with the cations including Cu^{2+}, but also with protons. Here, the ratio of Cu^{2+} plus Na^+ to $(AlO_4)^-$ was measured over the Cu–Na–$Y_{4.6}$ zeolites with the cation exchanges of 17.7, 29.5, and 47.9 mole %; the values are 88.7, 90.8, and 90.5% respectively. Meanwhile, the ratios of chlorine:Cu in these samples are between 1:100 and 1:30, so that, if it would be supposed that Cu is combined with $(AlO_4)^-$ as a form of $CuCl^+$, evidently some 10% of the $(AlO_4)^-$ must combine with protons as a cation. Thus, Cu–Na–$Y_{4.6}$ is partially in the form of the decationated zeolite, so that the activity characteristic of the decationated zeolite would also appear.

On the other hand, when the zeolite was prepared by ion exchange with the aqueous $Cu(NO_3)_2$ solution, the exchange proceeds by means of $Cu(H_2O)_{1-4}^{2+}$ formed according to Eq. (5) since the coordination of NO_3^{2-} is weak,

$$Cu(NO_3)_2 + mH_2O \rightarrow Cu(H_2O)_{1-4}^{2+} + 2NO_3^- + [(m-1) - (m-4)]H_2O. \quad (5)$$

Heating does not generate acidic vapor, and the change in color shows the presence of hydrated cupric ions. With regard to the temperature where the structural decomposition takes place, no behavior which differs from that of usual metal-ion-exchanged zeolite was observed. Thus, the activity of the Cu–Na–$Y_{4.6}$ zeolite in this case seems to be influenced by both the electrostatic field and the protons formed by the polarization of water by the field, as in the cases of alkaline earth metal and rare earth metal zeolites. Cu–Na–$Y_{4.6}$ and Cu–Na–$Y_{3.25}$, which were prepared by $Cu(NO_3)_2$ treatment and which have almost the same extent of ion exchange as the corresponding Ca-form zeolite, show far higher activities than Ca-form zeolite; their activities are similar to that of the decationated zeolite. Of course, this is because Cu can easily enter into the site; however, it seems also to be owing to a strong electrostatic field on the surface, since Cu^{2+} has a fairly large polarizing capacity. If we express the polarizing capacity by the charge/ion radius (Å^{-1}), the capacity of Ca^{2+} is 2.0, while that of Cu^{2+} is 2.8.

The zeolite ion exchanged with the aqueous $CuCl_2$ solution shows a remarkable change in the catalytic activity with the passing of time. The activity of Cu–Na–$Y_{4.6}$ (71.0 mole % cation exchange) pretreated at 450°C and reacted at 300°C shows the change illustrated in Fig. 4. The activity repeatedly increases and decreases; in addition, a decrease is caused by oxygen. This phenomenon is also different from the cases of transition metal-form zeolites like Ni, Fe, Co, and Cr, which were reported on previously (*29*). Perhaps the reduction of Cu^{2+} and the oxidation of Cu^+ and Cu^0 are caused by the reactant or the products, namely, hydrocarbons. Hydrocarbons become carbonium ions with reduction and carbonions with oxidation. It seems that Cu^+ and Cu^0 formed by the reduction of Cu^{2+} play an effective part in the above reaction with oxygen.

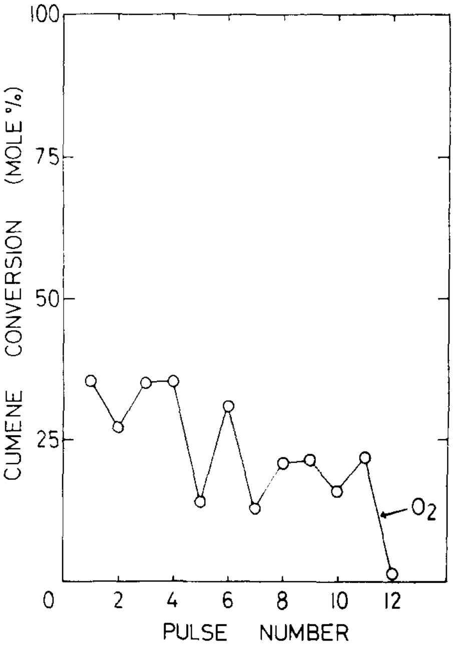

FIG. 4. Conversion rate of cumene over Cu (71.0%)-Na-$Y_{4.6}$ as a function of cumene pulse number: pretreatment, 450°C; reaction, 300°C.

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