Dehydration of Alcohol over CuY Zeolites

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    Catalytic activities and IR spectra of CuY zeolites have been investigated. The activity in de-
hydration of alcohol increased with the increase of copper content. IR spectra and poisoning effects
by pyridine shows that the active centers are weak Broensted acid sites. There is a large difference
in activity between CuY of 0.354 mmol/g-cat and CuY of 0.581 mmol/g-cat. The difference can be
explained as a part of copper ions are located in inner sites of sodalite units and ineffective to the re-
action. Amount of the ineffective copper ions is estimated from conversion of alcohol and lethal
doses of pyridine. About 70% of copper ions are supposed to be ineffective when copper content is
less than 0.384 mmol/g-cat.

I. INTRODUCTION

    Synthetic zeolites contain sodium ions as cations to neutralize the negative charge
produced by AlO_4 tetrahedra. The sodium ions can be exchanged with various kinds
of cations including ammonium ions. It is known that the zeolites exchanged with
alkaline earth and rare earth ions are effective catalysts in reactions such as polymeriza-
tion, alkylation, cracking and isomerization. The nature of active site in these catalysts
is well established as acid site and correlated to physical parameters of the cations.[1]
    Transition metal ion-exchanged zeolites (MeT) are also found to act as catalysts for
some reactions, but the systematic investigations have not been carried out in so many
cases. In this paper, the catalytic activity of CuY zeolites for dehydration of alcohol
are reported.
    It is well known that dehydration of alcohol is catalyzed by solid acid, especially by
alumina. The catalytic actions of zeolite for this reaction have also been reported. Bryant
and Kranich found that the activities of zeolites for the reaction decreased in the order
of decationated zeolite>alkaline earth cation zeolite>alkaline cation zeolite.[2] Cataly-
sis by transition metal ion-exchanged zeolite is also reported, but the reports did not clarify
the nature of active site in catalysis. Stone and Agudo reported that MnY was more
active than CaY in dehydration of iso-propanol, when the degree of exchange is low
($\simeq 30\%$).[3] Ward investigated IR spectra of transition metal ion-exchanged zeolite and
concluded that only Broensted acid existed on the surface.[4] But he did not investigate
the catalytic activity. Recently, Kazanskii *et al.* reported an interesting paper which
stated that dehydrogenation of ethanol was catalyzed by CuY zeolites and they attributed
the active sites to copper ions themselves.[5]
    This paper is concerned with the nature of active site of CuY zeolite in connection
with the location of copper ions.

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II. EXPERIMENTAL

1. Samples

Na ions in Linde Y zeolite (SK-40, NaY) were exchanged with Cu^{2+} ions in a given concentration of copper nitrate solution according to the procedure as described previously.[6] X-ray diffraction showed that the zeolite frame work was not altered by the exchange procedure. The content of Cu^{2+} ions were determined from difference of Cu^{2+} concentration of the solution before and after the exchange operation. The analysis was carried by EDTA titration. Table I shows degree of exchange of the catalysts. G.P. grade ethanol was purified by vacuum distillation after dehydration by anhydrous calcium sulphate.

Table I. CuY Zeolite Catalysts

Catalyst	Cu exchanged (%)	Cu content (mmol/g)
NaY	0.0	0.0
CuY-10	9.9	0.197
CuY-18	17.8	0.354
CuY-29	29.2	0.581
CuY-36	36.3	0.722
CuY-58	57.8	1.150

2. Apparatus and Procedure

Pulse technique using a micro reactor.—Catalytic activity of the catalyst was investigated by so-called "pulse technique". A micro reactor made by a U-type glass tube of 5 mm I.D. was attached to a Shimadzu GC-2B gas chromatograph. The one end of the reactor was connected to the sample inlet of the gas chromatograph and the other end to the separation column (porapack Q, 2 m). Carrier gas (helium) flows through sample inlet→micro reactor→separation column. 12.5 or 12.6 mg of the catalyst was placed in the reactor, the thickness of which was less than 1 mm and preheated at 400°C for 1.5~2 hr in the He stream. A 3 μl of ethanol was supplied to the carrier gas stream from the sample inlet as the usual mannar of analysis, thus a pulse of ethanol was fed to the catalyst bed. The reaction mixture leaving the catalyst bed was directly carried to the separation column and analyzed. The flow rate of He carrier was 30 ml/min and GHSV was about 9200 hr^{-1}. Reaction temperature was changed from 200° to 325°C by using an electric furnace. IR spectra and Acidity.—Measurements of IR spectra and acidity of catalysts were carried out as described previously.[6]

III. RESULTS

1. Products

Ether, ethylene and water were the products detected in gas chromatograms. Acetaldehyde was not detected in products resulted from reaction over all CuY zeolites at the reaction temperatures from 200 to 325°C. Kazanskii et al. reported the formation
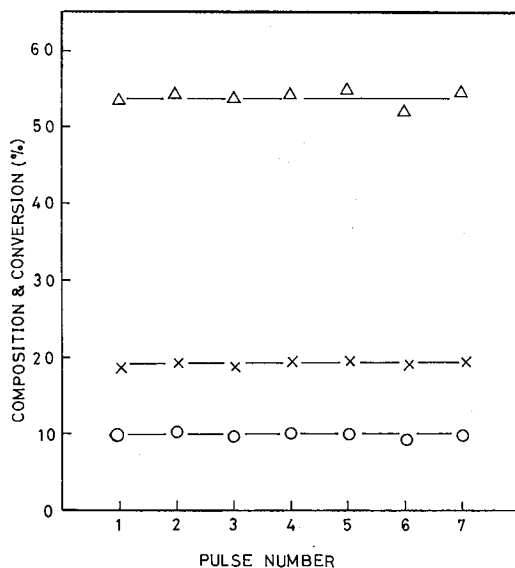
Fig. 1. Catalytic activity of CuY-36 at 250°C in successive feeds of alcohol pulse.

△ stands for conversion of alcohol.

× and ○ stand for compositions of ether and ethylene in product, respectively.

of acetaldehyde from alcohol over CuY zeolites.[5] They carried out the reaction by a flow method with LHSV$=0.4$ hr^{-1}. At 250°C, GHSV is calculated as about 300 hr^{-1}. Hence, the feed rate is about 30 times slower than that of our case. We obtained IR spectra of acetaldehyde adsorbed on CuY, when alcohol was adsorbed at room temperature and heated for 30 min at higher temperature than 170°C. Absorption bands due to adsorbed ether was not obtained in this case as degradation of ether was very fast. Hence, the dehydrogenation is a very slow side reaction of dehydration of alcohol. Present paper is concerned with catalytic activity of CuY zeolite in the dehydration reaction. The results of a research on the dehydrogenation of alcohol followed by IR spectra will appear in the near future.

In the pulse technique, reactants pass through the catalyst bed as pulses, the catalyst do not necessarily reveal a steady state activity and could show different activity at each pulse. In the present work the catalytic activity was very stable as shown in Fig. 1. Time interval between each pulse feed was 40 minutes. Conversion is calculated from corrected peak area $S_{C_2H_4}$, $S_{ethanol}$, S_{ether} in a chromatogram as

$$\text{conversion} = \frac{S_{C_2H_4} + 2 \times S_{ether}}{S_{C_2H_4} + 2 \times S_{ether} + S_{ethanol}}$$

The figure shows that alcohol and reaction products did not affect catalysis in the following pulse. This means that compounds concerned in the reaction were not adsorbed tightly on active sites and desorbed at 250°C within 40 minutes.

2. Temperature Effects on Catalytic Activity

Catalytic activities of CuY zeolites depend highly on both reaction temperature
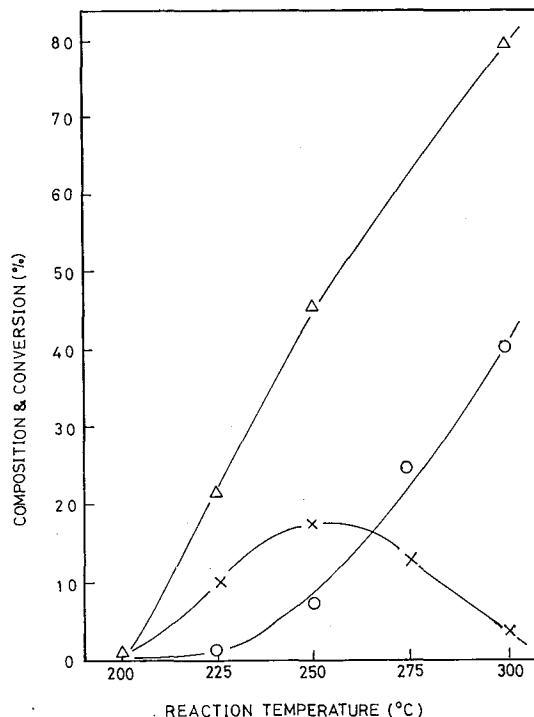
Fig. 2. Temperature dependence of activity of CuY-29. Marks have the same meaning as that in Fig. 1.

and Cu content (degree of exchange). At 200°C, dehydration of alcohol did not occur over CuY-10 and CuY-18 catalysts. CuY-18 revealed the catalytic activity at temperatures higher than 225°C. All CuY zeolites prepared in this work revealed the catalytic activity at 250°C, but original NaY zeolite did not at 300°C.

As an example, Fig. 2 shows the temperature dependence of the catalytic activity of CuY-29. At lower temperatures, a main product was ether. By increase of the temperature, the main product changed from ether to ethylene, together with the increase of conversion. Figure 2 is a typical pattern of a consecutive reaction and a main reaction scheme will be

$$C_2H_5OH \longrightarrow C_2H_5OC_2H_5 \longrightarrow C_2H_4$$
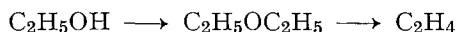
in the dehydration of alcohol.

High reactivity of ether was confirmed over CuY-58 catalyst. As shown in Fig. 3, ether decomposed easily at temperatures higher than 225°C. Products were mostly composed of ethylene and a small amount of alcohol. Hence, ethylene should be mostly formed via ether in the dehydration of alcohol.

3. Variation of Activity with Cu Content (Degree of Exchange)

An effect of Cu content in CuY zeolite was examined to the catalytic activity at 225° and 250°C. As shown in Fig. 4, the activity increased with the increase of degree of exchange of Na to Cu. It should be noticed that there is a large change in the activity
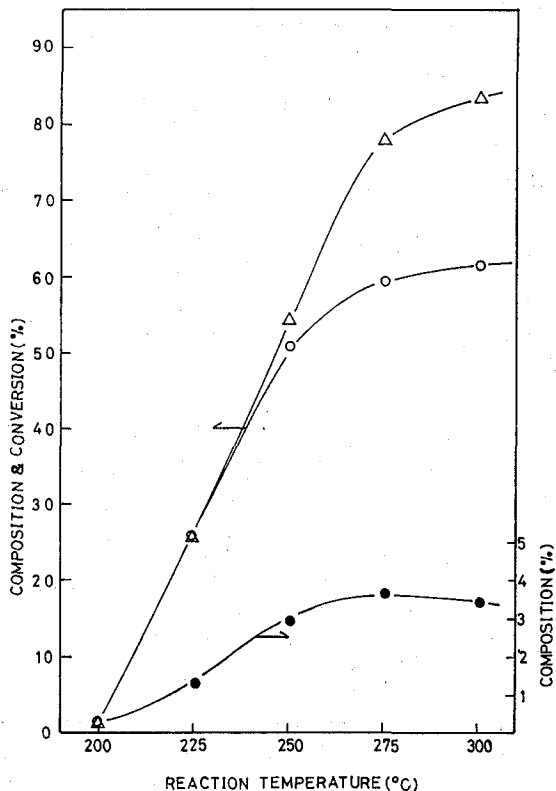
Fig. 3. Reaction of ether over CuY-58. A dose of ether was 3 μl. △ stands for conversion. ● and ○ stand for compositions of ethylene and alcohol in product, respectively.

between CuY-18 and CuY-29. The result is very similar to that in butene isomerization over CuX catalysts,[7] and in contrast to an activity pattern of CoY zeolites in butene isomerization.[6] Figure 5 shows acidity dependence of CuY zeolites on degree of exchange. By comparison with Fig. 4 and Fig. 5, it is expected that the catalytic activity will correlate with acidity resulted from an exchange of Na to Cu in Y zeolites.

4. Effects on Pretreatments

Generally, acidity of solid catalyst is influenced by a thermal treatment. As the catalytic activity of CuY zeolite would correlate with acidity, the thermal treatments can influence the activity. Changes of activities of CuY-18 and CuY-36 by preheating at 250, 350, and 450°C were investigated. The activities were tested at 250°C after keeping the catalysts at a given temperature for 2 hr in a stream of He and adjusting the temperature at 250°C in situ. In the case of CuY-18, the catalytic activity decreased with the increase of temperatures of pretreatment and ratio of ethylene to ether in products was also decreased as shown in Table II. On the other hand, there was no change in the activity and the ratio by the pretreatments in the case of CuY-36.

A 3 μl pulse of water was admitted at 250°C to the catalyst which had been kept at 450°C for 2 hr. The catalytic activity after 1 hr was tested. Both catalysts were not
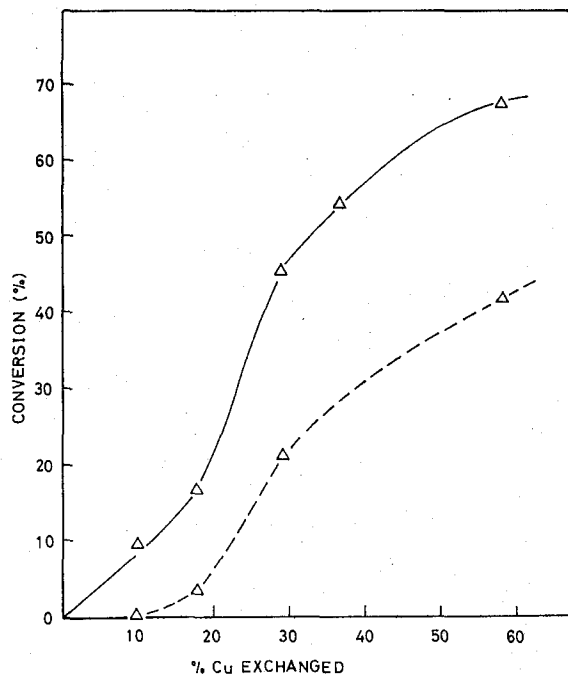
Fig. 4.   Change of activities by Cu contents in Y zeolite.   Solid line shows
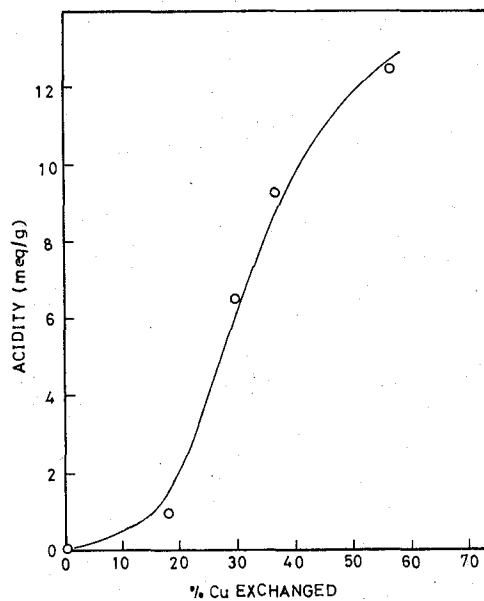conversion at 250°C and broken line shows conversion at 225°C.

Fig. 5.   Change of acidity by Cu contents in Y zeolite.   Butter yellow
(pKa=+3.3) was used as an indicator.

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Table II. Effects of Temperature of Preheating[a]

temperature (°C)	CuY-18				CuY-36			
	conv. (%)	composition in product (%)		$\dfrac{\text{ethylene}}{\text{ether}}$	conv. (%)	composition in product (%)		$\dfrac{\text{ethylene}}{\text{ether}}$
		ethylene	ether			ethylene	ether	
250	25.9	1.8	11.8	0.16	50.6	9.3	18.3	0.50
350	21.6	1.6	9.8	0.16	47.0	8.3	17.4	0.48
450	12.1	0.7	5.6	0.13	51.6	9.1	18.9	0.48
450[b]	12.7	0.7	5.9	0.13	50.2	9.0	18.4	0.49

[a] Reaction temperature was 250°C.
[b] 1 hr before supplying alcohol pulse, a 3 μl water pulse was supplied at 250°C to the catalyst which had been preheated at 450°C.

influenced by the feed of water as shown in Table II. This means that water adsorbed on the surface was desorbed easily at 250°C or water was adsorbed on sites independent of catalysis. IR spectra showed that water adsorbed was not removed completely by evacuation at 250°C, hence some parts of water would be adsorbed on inactive sites. The change of activity of CuY-18 by thermal treatments should not be resulted from
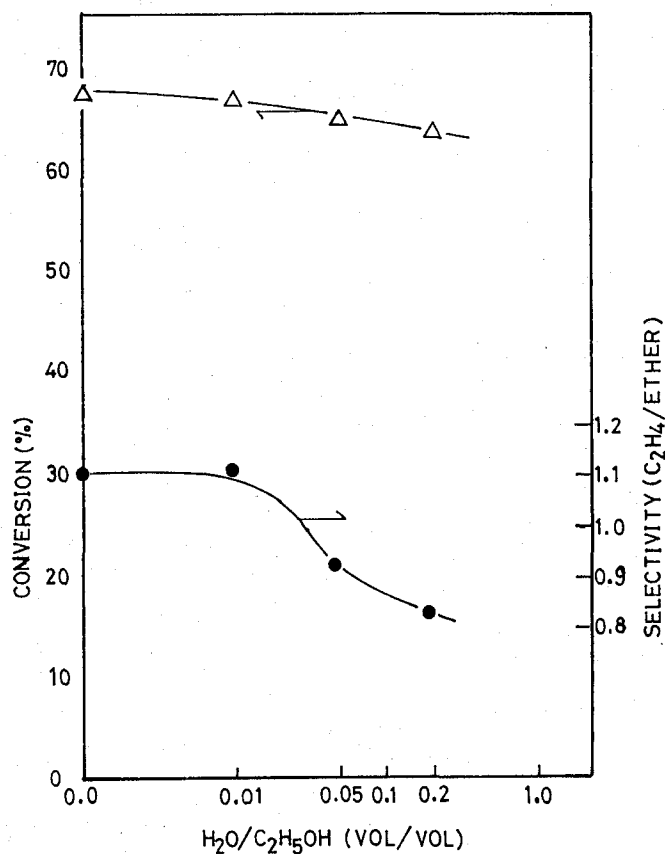

Fig. 6. Effects of addition of water to alcohol. Δ stands for conversion at 250°C and ● stands for selectivity (ratio of ethylene to ether in product).

the influence of water fixed on the surface but from another reason. This point will be discussed later.

5. Effect of Addition of Water in Alcohol

As mentioned above, a feed of water prior to supplying a pulse of alcohol do not influence dehydration of alcohol. However, it was found that alcohol was formed from ether even if a small amount (Fig. 3). It is possible that the reaction is influenced by water, when water is mixed to alcohol and a mixture of water and alcohol is supplied as a pulse. Figure 6 shows the activity and selectivity (ratio of $C_2H_4/(Et)_2O$) of the reaction over CuY-58, when small amounts of water was mixed to alcohol. The activity decreased slightly by addition of water, while selectivity changed considerably. As ether will be the first product in the dehydration and it decomposed mostly to ethylene over a highly active catalyst, the decrease of activity will cause the decrease of formation of ethylene as a result. However, the change of selectivity in Fig. 6 is too higher extent than the expected one from the decrease of activity and thus suggest that nature of active site is influenced by water involved in the reaction mixture. The slight decrease of a activity would be resulted from a possible reverse reaction of ether and water to form alcohol.

6. Pyridine Poisoning

As mentioned previously, the active sites for dehydration of alcohol are considerd to be acid points. To obtain a clear evidence of acid points as active sites, we investigate an effect of pyridine adsorption. Pyridine is a strong stable base and can poison acid
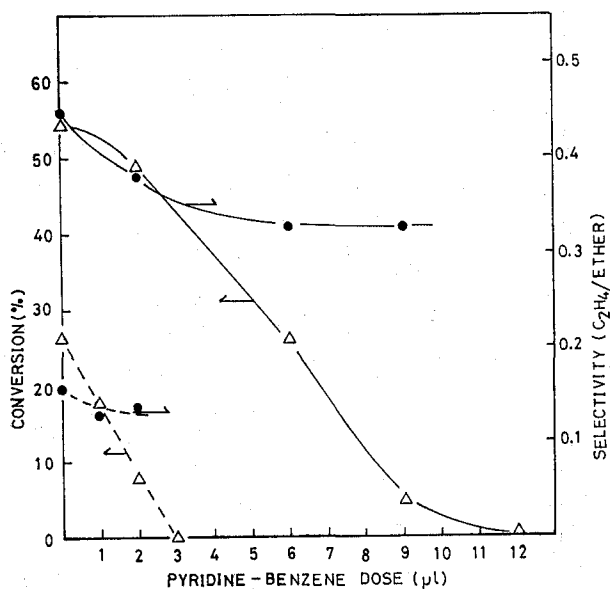

Fig. 7. Effects of poisoning by pyridine. Pyridine solution was composed of pyridine 1 vol. and benzene 5 vol. Marks have the same meaning as that in Fig. 6.

Solid line; CuY-36.   Broken line; CuY-18.

sites which have acid strength stronger than pKa=5.13. A small amount of pyridine-benzene solution (pyridine : benzene=1 vol. : 4 vol.) was supplied from the sample inlet successively and catalytic activity was examined after each pyridine feed. Preliminary experiments revealed that benzene did not poison the catalysts under the conditions adopted here. Figure 7 shows changes of activity and selectivity of CuY-18 and CuY-36 by dose of pyridine. Catalytic activity decreased with increase of total dose of pyridine as is expected. From the figure, lethal doses of pyridine-benzene solution can be estimated as 3 μl and 12 μl for CuY-18 and CuY-36, respectively. Amount of pyridine corresponding to these values are 7.4×10^{-6} mol and 29.6×10^{-6} mol. As weight of the catalysts was 12.6 mg in both cases, effective acidities are estimated as 0.59 and 2.32 mmol/g-cat. 0.354 mmol and 0.722 mmol of Cu^{2+} ions are contained in one gram of CuY-18 and CuY-36, respectively and hence ratios of effective acidity to amounts of Cu ions are 1.7 and 3.2. The selectivity decreased also by pyridine poisoning.

IV. DISCUSSION

1. Active Sites in Dehydration of Alcohol

There is no doubt that active site for dehydration of alcohol is acid site as an intimate correlation was observed between acidity and activity (Fig. 4 and Fig. 5) and also poisoning effect by pyridine was clear (Fig. 7). The nature of the acid site will be discussed below.

Possible acid sites on surface of CuY zeolite are Broensted acid sites induced by copper ions, Lewis acid sites revealed by copper ions themselves and also Lewis acid sites revealed by trigonally coordinated aluminum ions. The last one is confirmed in NH_4Y zeolites evacuated at high temperature by IR spectra.[8] In our case, copper ions themselves can not considered active sites, because acidities measured by amine titration were much higher than amounts of copper ions involved in catalysts and also lethal doses of pyridine corresponded to 1.7 (CuY-18) and 3 (CuY-36) times the amounts of copper ions. Ward reported absence of trigonally coordinated aluminum ions in CuY zeolites evacuated at 400°C by IR measurements of adsorbed pyridine.[4] This has been confirmed by our investigation, too. Figure 8 shows an IR spectra of pyridine adsorbed on CuY-58 which was preevacuated at 480°C for 5 hr. There is not a adsorption band at 1451 cm^{-1} which indicates the presence of trigonally coordinated aluminum ions. Hence, Lewis acids associated by aluminum ions are also excluded. From these facts, it can be concluded that active sites in dehydration of alcohol are Broensted acids induced by exchange of sodium to copper ions. In Fig. 8, a weak band can be observed at 1542 cm^{-1} which is an indicator of pyridinium cations. The band due to pyridinium cations is very weak comparing to bands due to pyridine coordinating to copper ions (1443 cm^{-1}, 1604 cm^{-1}). This would indicate that the most Broensted acids are very weak acid in CuY zeolites. If we assume the Broensted acid as being weak, the results shown in Fig. 1 can be easily explained. In the experiment, the time interval between successive alcohol pulse was 40 min and water formed in a pulse did not affect the reactions following to the pulse. As water can act as a weak base (pKa=−1.74), it will be adsorbed on a strong acid site such as acid site on silica-alumina surface and affect the reactions catalyzed by strong acids. But ours is not the case, as one might expect when a reaction is catalyzed by weak acid. The active site is considered to be as weak as it release water to helium stream within 40 min at 250°C.

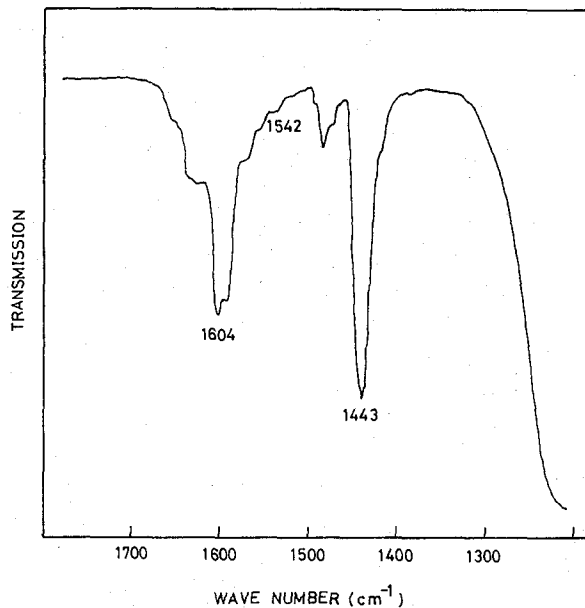S. YOSHIDA, K. AKIMOTO, Y. KOSHIMIDZU, and K. TARAMA

Fig. 8. IR spectrum of pyridine adsorbed on CuY-58 evacuated at 480°C for 5 hr. Pyridine was adsorbed at room temperature for 30 min and evacuated at room temperature for 15 min.

However, the result shown in Fig. 6 indicates that water is not completely independent of the reaction. The effect of addition of water in alcohol manifested itself mainly as decrease of selectivity to ethylene. As the extent of decrease in activity is small, the change of selectivity would be resulted from the change of distribution of acid strength by adsorption of water. Our samples are colored and the distribution of acid strength can not be measured, hence the assumption mentioned above was not able to be directly examined, but was supported by the results of poisoning by pyridine. Figure 7 shows ethylene formation was depressed to more extent than that of ether formation. It is natural to expect that pyridine adsorption beings at strong acid sites and alive acid sites are weak acids. As a result, the distribution of acid strength will change. This might affect the selectivity.

2. Effects of Degree of Exchange

As mentioned above, copper ions themselves can not be believed as active (acid) sites. However, active sites should be created by exchange of sodium to copper ions as original NaY showed no activity even at 300°C. Ward has explained the acidity of transition metal Y zeolites from results of IR spectra.[4] He attributed the Broensted acidity to protons released from adsorbed water on divalent ions as following.

$$M^{2+} + H_2O \longrightarrow MOH^+ + H^+ \tag{1}$$

The driving force to dissociate water is believed to be the electrostatic field of cation as firstly proposed by Rabo.[9] The results obtained in this work support this explanation as a whole. As the acid formed by Eq. (1) is weak, equilibrium constant will be con-

Table III. Activities and Effective Acidities

Catalyst	Cu content (mmol/g)	Activity (% conv.)	Effective acidity (meq/g)
CuY-10	0.197	9.8	
CuY-18	0.354	16.6	0.54
CuY-29	0.581	45.5	
CuY-36	0.722	54.0	2.32

sidered to be considerably small. The fact that ratios of effective acid sites to copper ions are larger than 1 and depend on the degree of exchange shows that one copper ion can adsorb waters more than one molecule and the accesibility of water changes with the degree of exchange.

There are three kinds of location sites of cation, S_I, S_{II}, and S_{III} sites in Y zeolite as discussed in the previous paper.[6] S_I sites are located far inner part of sodalite unit and cations accommodated in the site can not adsorb water. Hence, acidity can not be created by copper ion on S_I site. Figure 5 and difference of the lethal dose of pyridine between CuY-18 and CuY-36 suggest that considerable amounts of copper ions are located at S_I or $S_{I'}$ sites when the degree of exchange is 18%. From the data of activity and the effective acid sites, one can estimate the amount of copper ions in S_I sites on the basis on following assumption.

1. Conversion of alcohol is proportional to number of acid sites in the case of CuY-10, CuY-18, and CuY-29. The activity of CuY-36 was very high and there is a possibility that reverse reaction occurred. The proportional constant will be designated as A.

2. Enhanced acid sites by one copper ions in an effective site are constant (designated as B).

3. Maximum number of copper ions accommodated in S_I site is limited (designated as M).

4. There is equilibrium between copper ions in S_I sites (Cu_I) and those in effective sites (Cu_e)

$$Cu_e \xrightleftharpoons{K} Cu_I \tag{2}$$

untill amount of Cu_I reaches to M.
Available data are listed in Table III.

Figure 4 shows a large increase in activity at CuY-29 and hence we expect that Eq. (2) does not hold in this catalyst. Then following equations are derived using the data for CuY-18, -29, -36. Concerning activity

$$45.5 = AB(0.581 - M)$$
$$16.6 = 0.354 \times AB/(1+K) \tag{3}$$

Concerning effective acid sites

$$0.59 = 0.354 \times B/(1+K)$$
$$2.32 = B(0.722 - M). \tag{4}$$

From Eqs. (3) and (4), following values are obtained.

$A = 28.1$ $B = 4.97$(acid sites/Cu_e) $M = 0.255$ mmolCu/g–cat
$K = 1.98$

Using the values of A, B, and K, one can calculate the activity of CuY-10.

$$0.197 \times AB/(1+K) = 9.2$$

The calculated activity agrees well with experimental value of 9.8. Therefore, the assumptions mentioned above are considered to be reasonable. The maximum content of copper Cu_m to which Eq. (2) holds is calculated as

$$[Cu_m] = [M] \times (1+K)/K = 0.255 \times 2.98/1.98 = 0.384 \quad \text{(mmol Cu/g-cat)}$$

The value supports the assumption that Eq. (2) does not hold in CuY-29. When the copper content is less than 0.384, ratio of $[Cu_I]$ to total amount of copper ions is given by

$$K/(1+K) = 0.66$$

hence, about 70% of copper ions would be located in S_I site.

On preheating of Cu-18, the activity decreased with the increase of temperatures of the treatment. This would be caused by movement of copper ions from S_{II} (or $S_{II'}$) site to S_I sites at high temperature. ESR and UV spectra shows that coordination state of copper ions change with thermal treatment.[10] This means the movement of copper ions in zeolite. A feed of water at 250°C to the CuY preheated at 450°C did not affect the activity. It is known that ESR and UV spectra change reversibly by hydration-dehydration cycles.[10] However, it is observed that the reversible change is very slow. As water was supplied to a stream of helium as a pulse, contact time is very short. So, the copper ions in S_I site would not be pulled up to catalytically effective sites by the water.

Over CuY-36, there was no effect of preheating. CuY-36 contains 0.722 mmol/g-cat of copper ions which is far beyond the value of $[Cu_m] = 0.384$. Of course, value of K should depend on temperature and the value of $[Cu_m]$ is obtained on catalysts preheated at 400°C. However, it is conceivable that CuY-36 contains so much amount of copper ions that $[Cu_I]$ is saturated even at 250°C.

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