

Oxidizing and Acidic Properties of Copper-Exchange Y Zeolite

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Copper Y zeolites have been studied by ESR and ir spectroscopy. At low activation temperatures, the zeolite exhibits Brønsted acidity. Pyridine is coordinatively adsorbed on cupric ions and gives rise to an ir band at 1451 cm^{-1} . No true Lewis acid sites are detected. However, CO-reduced samples acquire Lewis acid centers and cupric ions are reduced to cuprous ions. Hydrogen reduction results in the formation of metallic copper, and the solid acquires acidic hydroxyl groups which are more stable than those held on HY zeolites. The oxidizing properties of the cupric Y zeolite are attributed to the cupric ions while those of reduced samples are due to true Lewis acid sites.

INTRODUCTION

Metal-exchanged Y zeolites have been exhaustively studied by several workers (1-7) using different techniques. Richardson was interested in the oxidizing properties (8) and in the catalytic activities (9) of a series of CuY and NiY zeolites. The oxidizing power was related to the electron affinity of the cation, and the influence of the cation on the activity of the catalyst was demonstrated in the cumene dealkylation reaction. A model of the acidic sites in faujasite was suggested (9).

The acidic character of zeolites cation-exchanged with transition metal ions has been studied by pyridine adsorption. Hall *et al.* (1) and Ward (4) provided strong evidence of the existence of pyridine coordinated with the cation. Both of them related the frequency of the Py:M^{n+} characteristic band at about $1440\text{--}1460\text{ cm}^{-1}$ to the electron affinity of the cation. Recently Ward (10) carried out an important study on the nature of the active sites on X zeolites. Mn, Co, Cu, Zn, Ag, and Cd zeolites were investigated, but no simple relationship between the acidity of the transition metal form and the physical parameters was found, and hence it appeared useful to

study the properties of the solid as related to the nature of the cation itself.

Rabo *et al.* (3) have studied an $\text{Ni}^{(II)}\text{Y}$ which was partially reduced to $\text{Ni}^{(I)}\text{Y}$ and Ni^0Y by sodium vapor; the $\text{Ni}^{(I)}\text{Y}$ species and some nonstoichiometric compounds such as Na_6^{5+} , Na_4^{3+} were detected. The two latter species provided some useful data for the $\text{Ni}^{(II)}$ location as a function of the exchange level. Carbon monoxide and hydrogen were adsorbed on this solid but the reduction of Ni^{2+} by either CO or H_2 was not attempted. Recently Dimitrov and Leach (11) studied the isomerization of *n*-butene on a series of CuX zeolites. In order to account for an induction period they were led to postulate a reduction of the Cu^{2+} to Cu^+ either by hydrogen or some other species, but no reduction study was carried out.

It appeared necessary, therefore, to investigate the nature of the surface sites of copper zeolite and to study the effect of various pretreatments (such as reduction by CO or H_2) on the acidic and oxidizing properties of the solid since these last parameters appeared to be of great importance in the catalytic processes. Moreover, many catalytic reactions (hydrocracking,

oxidation, alkylation, isomerization, etc.) provide and/or need appreciable amounts of hydrogen or carbon monoxide. In addition, many gas-liquid chromatography studies use H_2 as carrier which may modify the zeolite properties.

EXPERIMENTAL SECTION

(a) Materials

All the samples came from the same NaY zeolite supplied by Linde Division, Union Carbide. The starting material was treated by conventional ion-exchange methods with a $Cu(NO_3)_2$ solution, the concentration of which was calculated to obtain the required exchange level. The solids were then washed in distilled water ten times at least and dried at $110^\circ C$ in an oven.

The degree of ion exchange was determined by flame spectrometric analysis of the residual sodium. Analytical results for these samples are given in Table 1.

TABLE I
CHEMICAL ANALYSIS OF SAMPLES EXCHANGED
WITH COPPER IONS

Samples	Cu ²⁺ Y			H ₂ re-	CO re-
	I	II	III	duced II at 500°C	duced II at 450°C
% Cu ²⁺	8.5	6.5	0.5	2.26	1.81
% Cu ⁺	—	—	—	0	4.83
% Cu ⁰	—	—	—	4.18	0

The NH_4Y sample was prepared by the same method using a NH_4NO_3 solution. Pyridine was dried over 5A molecular sieve; the polynuclear aromatic solutions were dried and then outgassed by a freeze-pump-thaw procedure. Hydrogen and carbon monoxide were dried over 5A molecular sieve cooled to liquid nitrogen temperature.

(b) Techniques

Infrared measurements were conducted in a cell described previously (12). The samples were compressed into thin wafers weighing 30–40 mg. The diameter of the disc was 18 mm. The spectra were recorded,

after cooling the sample to room temperature, on a Perkin-Elmer model 125 spectrophotometer using a spectral slit width of 3 cm^{-1} between 4000 and 1200 cm^{-1} . The cell permitted evacuation of the sample over a temperature range $25\text{--}1000^\circ C$ or equilibration of the sample with pyridine vapor under a pressure of 1 Torr.

ESR measurements were carried out in a special cell which allowed the adsorption of aromatics in the absence of moisture and/or oxygen. The spectra of positive radicals were continuously recorded before and after anthracene adsorption. After equilibrium had been reached the spin concentration was determined by comparing the radical ESR spectrum with that of a DPPH solution of known concentration.

RESULTS

ESR Measurements

The oxidizing power of the exchanged $Cu^{2+}Y$ was sufficient to ionize anthracene. As suggested by Richardson (8) electron transfer appears to occur at the cupric ion. Richardson provided no direct evidence to account for such an hypothesis. In our case the spectra of several CuY samples were recorded before anthracene adsorption. Typical spectra are shown in Fig. 1. The hyperfine structure in the spectrum of the dehydrated solid depends largely on the degree of ion exchange. When anthracene (A_0) was adsorbed on the catalyst the intensity of the Cu^{2+} signal decreased regularly while a sharper single line at $g = 2.002$ due to the (A_0^+) species appeared and increased regularly. After a longer time (at least 2 weeks) the broad Cu^{2+} signal decreased in such a way that all the hyperfine components became distinct and the signal eventually disappeared. It is interesting to notice that the signal due to (A_0^+) species increased at the expense of the Cu^{2+} signal. This suggests strongly that electron transfer occurred at the cupric ions. On the other hand no hyperfine structure was observed for the (A_0^+) (Fig. 2b); this may be explained by dipolar interaction in the presence of a large concentra-

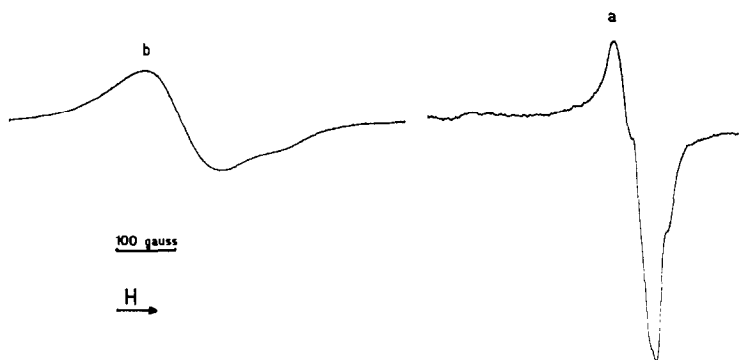


FIG. 1. ESR spectra of Cu^{2+}Y zeolite, (a) 0.5% Cu^{2+} , (b) 8.5% Cu^{2+} .

tion of paramagnetic species. Moreover, the Cu^{2+} broad signal disappeared completely. This suggests that all the Cu^{2+} ions are accessible to the anthracene molecules.

The dependence of the (A_0^+) concentration on the treatment temperature was investigated, and it appeared that between 150 and 600°C no variation of the (A_0^+) concentration was observed. In Table 2 the spin concentrations are given against the pretreatment temperature. No effect of oxygen on the oxidizing properties was observed. Reduction of the Cu^{2+}Y provided interesting information on the role of the Cu^{2+} ions in radical-ion formation. When

the cupric ions were reduced by H_2 at 500°C, the solid turned from grey-blue to red-pink, the color change being attributed to the formation of copper metal crystals as confirmed by chemical analysis and X-ray diffraction. Since no signal of Cu^{2+} was observed after reduction, it appears that Cu^{2+} ions are reduced to Cu^0 species.

The reduced solid when dehydrated at 500°C showed no oxidizing properties, but on further dehydration (dehydroxylation) at 600–700°C, the solid acquired oxidizing properties and a well resolved (A_0^+) signal appeared when anthracene was added. The signal was similar to that obtained by an-

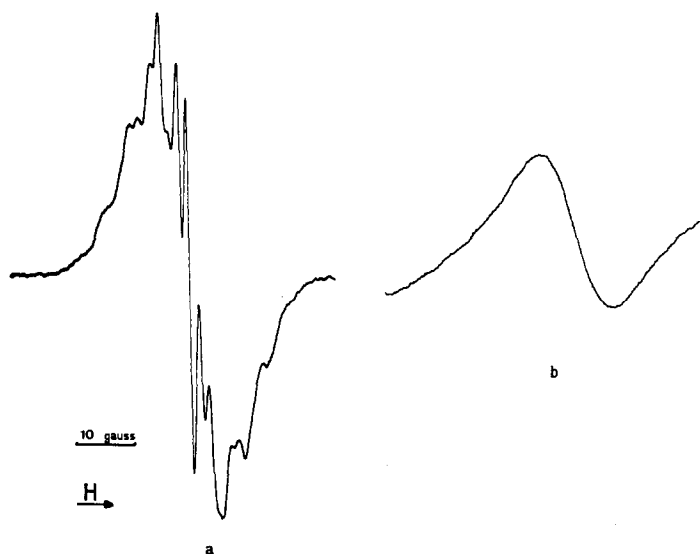


FIG. 2. ESR spectra of anthracene positive radical on (a) dehydroxylated NH_4Y and/or on a Cu^+Y zeolite or on a dehydroxylated zeolite Cu^+Y , and (b) on a Cu^{2+}Y zeolite 8.5% Cu^{2+} .

TABLE 2
EFFECT OF THE ACTIVATION TEMPERATURE ON
THE FORMATION OF POSITIVE ANTHRACENE
RADICAL ON CuY(I) ZEOLITE
The estimated error is 0.5×10^{18} spins/g.

Temperature °C	170	200	300	400	550	600
Spin number/g 10^{-18}	5.5	5.9	4.9	5.4	5.6	6.0

thracene adsorption on dehydroxylated NH_4Y zeolite (Fig. 2a); however, the Cu^0Y solid required to be evacuated at higher temperature than the NH_4Y in order to acquire appreciable oxidizing power (13, 25). A similar effect of oxygen on the anthracene signal intensity was observed; the higher the evacuation temperature the stronger was the oxygen effect (13). The effect was the same whether oxygen was added before or after anthracene adsorption on the catalyst. These results showed that the oxidizing centers of Cu^0Y are different from those of Cu^{2+}Y and that the oxidizing properties of the latter are related to the presence of Cu^{2+} ions.

Another experiment was carried out in order to confirm the direct role of the cupric ions in the oxidation process of the aromatic hydrocarbon. After preliminary evacuation, a Cu^{2+}Y sample was reduced by CO at 500°C for 48 hr, during which time the solid turned from blue-grey to white. The ESR spectrum of this reduced solid showed no Cu^{2+} signal, and chemical analysis demonstrated the existence of copper as Cu^+ ions. On the other hand, when an anthracene solution was added, a well-resolved signal was observed indicating positive radical formation. The recorded signal was identical to that shown in Fig. 2a. The oxygen effect was similar to that observed previously in the case of the NH_4Y zeolite (14). Moreover, in the same way, the rehydration of a CO-reduced sample inhibited the generation of positive radicals. On the other hand, the spin concentration remained constant in the same reduction conditions regardless of the subsequent evacuation temperature.

INFRARED STUDIES

Hydroxyl Groups

The spectra in the hydroxyl stretching region of Cu^{2+}Y , Cu^+Y , and Cu^0Y forms are shown in Fig. 3. All the samples were first heated under 160 Torr oxygen for 12 hr and evacuated overnight at 500°C . After reduction either by carbon monoxide or hydrogen, they were once more heated in vacuum at a series of temperatures to a residual pressure of 10^{-5} Torr; the disks were then cooled to room temperature and spectra recorded. The absence of the 1640 cm^{-1} vibration showed that all molecular water was removed. Figure 3 compares spectra of Cu^{2+}Y and Cu^+Y obtained by reduction with either dried or slightly moist carbon monoxide and dried hydrogen. These latter samples were given final evacuation at 500°C also. All the spectra showed OH bands at 3745 and 3680 cm^{-1} . The intensity of the latter increased when small amounts of water were added to a pretreated sample and then removed at 500°C . It is significant that while the two OH bands of Cu^{2+}Y are rather weak, the H_2 -reduced samples acquire more surface hydroxyl groups and especially silanol groups with stretching

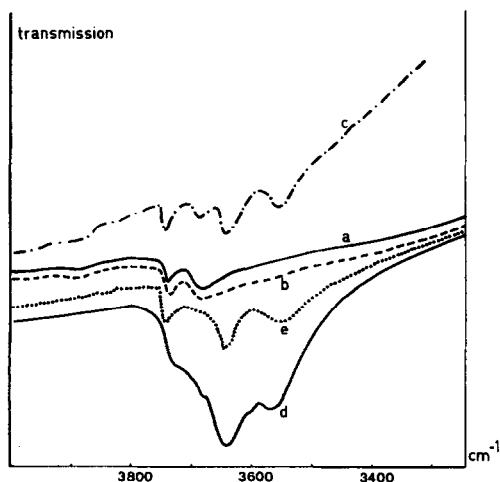


FIG. 3. Infrared spectra, OH region, (a) of Cu^{2+}Y dehydrated at 500°C , (b) Cu^{2+}Y reduced by CO at 500°C , (c) reduced by CO at 500°C in the presence of small amount of water, (d) reduced by H_2 at 500°C and (e) dehydroxylated NH_4Y at 495°C .

frequencies at 3640 and 3550 cm^{-1} similar to those of HY zeolite, in addition to the preexisting OH groups responsible for the 3745 and 3680 cm^{-1} bands. On the other hand, the CO-reduced samples gave a spectrum identical with the Cu^{2+}Y one, provided the carbon monoxide was carefully dried. When a small amount of moisture remained in the CO, the reduced solid gave rise to a spectrum comparable to that obtained for the H_2 -reduced catalyst. In particular, the bands at 3640 and 3550 cm^{-1} were not removed by an overnight evacuation at 500°C.

The intensities of the OH bands of the hydroxyl groups of Cu^0Y depended markedly on the evacuation temperature, and Fig. 4 shows the changes in these bands when the evacuation temperature was raised from 500 to 700°C. At 700°C, the OH bands at 3640 and 3550 had disappeared while those at 3745 and 3680 cm^{-1} remained unchanged. It appears, therefore, that the 3640 and 3550 cm^{-1} OH bands observed in H_2 -reduced Cu^{2+}Y zeolite have a higher thermal stability than those of the HY zeolite. In the case of HY, in the same vacuum condition, the 3640 and 3550 cm^{-1} bands are almost completely removed at 500°C (Fig. 3e) in agreement with the thermogravimetric results (25).

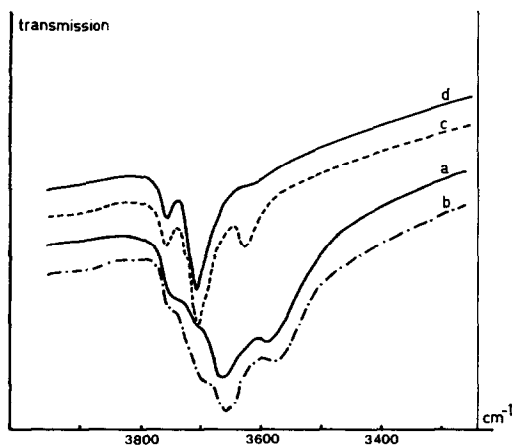


FIG. 4. Infrared spectra; OH region, of hydrogen reduced Cu^0Y , after calcination at various temperatures: (a) 500°C, (b) 600°C, (c) 650°C, and (d) 700°C.

Pyridine Adsorption

Characterization of the acidity of zeolites by infrared spectra of adsorbed pyridine has been reported by several workers (1, 4). Three principal bands are used to distinguish the different surface sites:

The band at 1540–1545 cm^{-1} , specific for pyridinium ions, is indicative of Brönsted acid sites; the band at 1451–1455 cm^{-1} due to the same 19-b vibration mode characterizes tricoordinated aluminum atoms while a band whose frequency varies between 1438 and 1454 cm^{-1} indicates pyridine-cation coordination complexes (1, 4).

However, the frequencies of other ring vibrations can provide interesting information concerning the nature of acid sites. The bands at 1630, 1620, and 1610 cm^{-1} are of particular interest. Figure 5 shows the spectra of pyridine adsorbed on a Cu^{2+}Y sample after preliminary activation at 200 and 500°C. Excess pyridine was removed

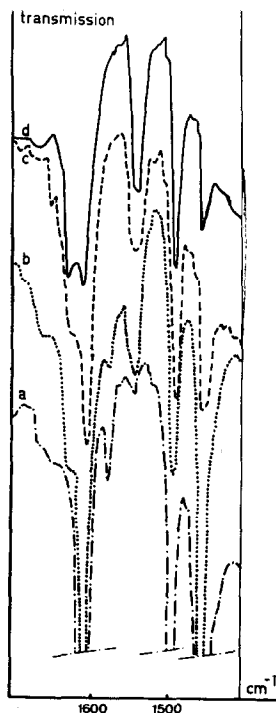


FIG. 5. Effect of reduction on pyridine adsorption, infrared spectra (a) Cu^{2+}Y calcined at 500°C, (b) Cu^{2+}Y calcined at 200°C, (c) Cu^{2+} reduced by H_2 at 400°C, and (d) Cu^{2+}Y reduced by H_2 at 500°C.

at 150°C. The main bands of these spectra are those at 1608, 1488, and 1451 cm^{-1} , and there is a very weak band at 1540 cm^{-1} . When appreciable amounts of water are added, no increase of the weak band at 1540 cm^{-1} is observed. The same figure shows the changes in the adsorbed pyridine spectra produced by a change in the copper valence state. Reduction of Cu^{2+}Y zeolite by dry hydrogen at 400 and 500°C, respectively, removes the bands at 1451 and 1608 cm^{-1} , while that at 1540 cm^{-1} increases in intensity and a shoulder at 1630 cm^{-1} appears. On further reduction, the 1608 and 1451 cm^{-1} bands vanished, but the pellet became opaque and the recorded spectra were not so satisfactory. The effect of activation temperature on the H_2 -prereduced Cu^{2+}Y zeolite, with adsorbed pyridine, is shown in Fig. 6. The samples were reduced at 500°C by hydrogen and then evacuated at 500–600, and 650°C, respectively. Excess pyridine was equilibrated with the sample

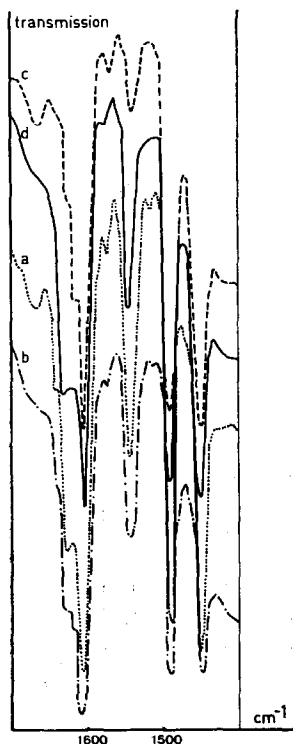


FIG. 6. Effect of calcination at various temperature on spectra of pyridine chemisorbed on H_2 -reduced Cu^{2+}Y : (a) 500°C, (b) 600°C, (c) 650°C, and (d) after water adsorption on sample 650°C.

for 2 hr and then removed at 150°C. All the spectra showed weak bands at 1608 and 1451 cm^{-1} compared with those obtained in the Cu^{2+}Y sample. The intensities of these bands were unaffected by the activation temperature of the prereduced sample. As pointed out previously, the 500°C activated sample gives rise to a strong band at 1540 cm^{-1} and to a shoulder at 1630 cm^{-1} indicative of Brönsted acid sites. When the activation temperature of the prereduced solids has increased, the intensity of these bands decreased and a shoulder appeared at 1620 cm^{-1} .

When water was added to a prereduced sample which had been activated at 650°C, the spectrum of adsorbed pyridine was modified as follows: The 1608 cm^{-1} band was unaffected, that at 1451 cm^{-1} sharpened to lower frequencies; the bands at 1488 and 1540 cm^{-1} increased markedly, and at the same time, the shoulder at 1620 cm^{-1} vanished, while that at 1630 cm^{-1} increased in intensity.

When the cupric ions were reduced by wet carbon monoxide, addition of excess pyridine and further evacuation at 150°C gave rise to strong bands at 1608, 1540, 1488, and 1451 cm^{-1} (Fig. 7). Shoulders at 1630 and 1620 cm^{-1} became noticeable. On the other hand when the CO was carefully dried, the spectrum showed a rather weak band at 1540, strong bands at 1608, 1488, 1451, and an appreciable shoulder at 1620 cm^{-1} . Rehydration gave rise to a shoulder at 1630 cm^{-1} and a strong band at 1540 cm^{-1} appeared in the spectrum.

Hydrogen Reduction Kinetics

Samples were heated under 160 Torr oxygen at 500°C and then evacuated overnight at the same temperature. Reduction at different temperatures was conducted in an excess of dry hydrogen. The reduction was monitored by recording the Cu^{2+} ESR signal after various intervals of time. At each temperature, the decay in the Cu^{2+} signal intensity was obtained by double integration of the ESR first derivative spectrum. At each temperature a linear relation was obtained by plotting the reciprocal of the Cu^{2+} concentration against the time in-



FIG. 7. Spectra of pyridine chemisorbed on CO-reduced Cu^{2+}Y : (a) pyridine evacuated at 150°C , (b) exposed to water and re-evacuated at 150°C , and (c) sample reduced by CO in the presence of small amount of water.

dicating that the reduction obeys a second order law.

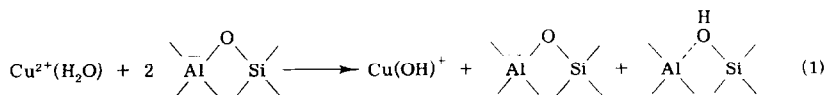
DISCUSSION

Oxidative and Acidic Properties of the Cu^{2+}Y Form

As indicated above, the Cu^{2+} ions appear to be directly involved in the anthracene oxidation process. The experiments on hydrogen-reduced samples confirm this interpretation. Reduction with hydrogen of the Cu^{2+}Y zeolite results in the reduction of Cu^{2+} ions to metallic copper. As the metal has no oxidizing properties, a decrease in the oxidizing power of the CuY zeolite is expected if the Cu^{2+} ions are the acceptor sites. This is what is actually found.

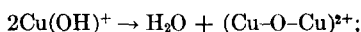
Several workers (14-16) attributed the oxidative properties of the dehydroxylated Y zeolites or polyvalent cations-exchanged Y zeolites to tricoordinated aluminum atoms. In a previous work (16) on the LaY zeolites, we reached the same conclusion. One might expect, therefore, that for Cu^{2+}Y some tricoordinated aluminum atoms may be involved in the electron transfer process. Moreover the ir spectra of adsorbed pyridine on evacuated Cu^{2+}Y at a series of temperatures showed that the exchanged zeolites acquire acidic hydroxyl groups, and hence the formation of tricoordinated aluminium atoms by a conventional dehydroxylation process is to be expected. Furthermore, the specific infrared band at 1451 cm^{-1} which characterizes pyridine coordinated with trigonal aluminium is also present. Although Lewis acid sites seem to be present, several results militate against this hypothesis. Thus, (i) there is an absence of a band at 1620 cm^{-1} characteristic of pyridine adsorbed on dehydroxylated Y zeolite; (ii) addition of water to adsorbed pyridine does not affect the initial infrared spectrum, in contrast with the behavior of the Lewis acid sites which are converted into Brönsted acid sites; (iii) the number of anthracene positive radical ions is independent on the pretreatment temperature over the range $150\text{--}600^\circ\text{C}$, while the number of Lewis sites increases (14-16); (iv) the number of paramagnetic species obtained by anthracene adsorption on Lewis acid catalysts (17) or on dehydroxylated Y zeolite increases in the presence of molecular oxygen, while the concentration of anthracene radicals on the copper zeolite is not affected by the addition of oxygen.

It is possible, therefore, that different sites are formed on Cu^{2+}Y in the following way. Because of the strong electrostatic fields in the cavities, water molecules adsorbed near cupric ions are easily ionized, as has been postulated by several authors (18, 19), and Brönsted acidity results according to the following equation:



Dehydroxylation by condensation of two silanol groups is unlikely since it would generate tricoordinated aluminium atoms. However dehydration may occur in two different ways.

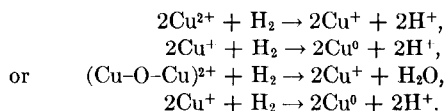
(a) Between two $\text{Cu}(\text{OH})^+$ groups so as to bridge two cupric ions,



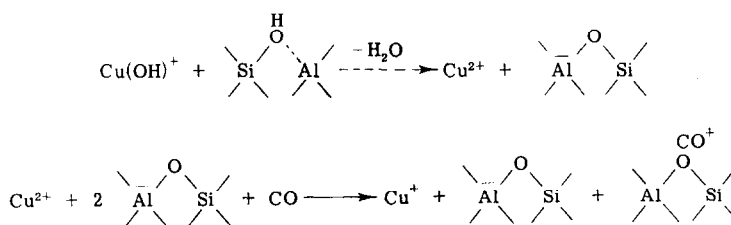
a similar dehydration scheme has been reported by Rabo for CeY zeolites (18) and by Uytterhoeven (20);

(b) Between a $\text{Cu}(\text{OH})^+$ species and a silanol group:

irreversible chemical transformation occurs. The kinetic data show a second order dependence on copper concentration which suggests the following scheme for the reduction:



It is noticeable that the hydroxyl groups generated by hydrogen reduction are thermally more stable than those of HY. We think that the presence of cations, in the case of partially reduced samples, helps to



Properties of Cu^0Y Form

The structural hydroxyl groups of a Cu^{2+}Y zeolite have been studied previously (21). The bands at 3745, 3640, and 3550 cm^{-1} were assigned, respectively, to siliceous impurities and acidic silanol groups, while the band at 3680 cm^{-1} was attributed to Al-OH in agreement with several workers (2, 21, 22). Activation of the solid at 500°C under vacuum releases the acidic hydroxyl groups (3640 and 3550 cm^{-1}) without any formation of Lewis acidity. Strong evidence for the formation of acidic hydroxyl groups, similar to those of HY, on the hydrogen-reduced sample is given by the presence of the two bands at 3640 and 3550 cm^{-1} and their interaction with pyridine to give the characteristic pyridinium bands at 1630, 1540, and 1488 cm^{-1} . The data presented so far have demonstrated that the reduced CuY zeolite behaves as a protonic solid. Since no Cu^{2+} ESR signal could be observed from the reduced sample, and since reduction by hydrogen followed by oxidation in oxygen or air at 400°C results in CuO formation, it can be concluded that an

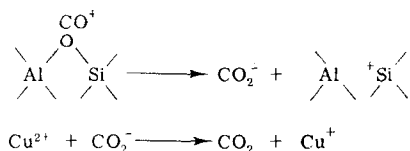
stabilize the hydroxyl groups. Such a phenomenon has already been reported by Ward (23) in his study of MgHY zeolite. Kerr has shown that HY zeolites combine with water at high temperature to produce materials referred to as ultrastable zeolite (26). As water molecules can be produced during the H_2 -reduction process, the formation of such an ultrastable zeolite (26) could also explain the high thermal stability of the hydroxyl groups. Whatever the reason for the thermal stability of the hydroxyl groups, heat treatment at temperatures higher than 650°C is necessary to remove all these OH groups. The behavior of the reduced samples is similar to that of HY zeolite as revealed by the infrared and ESR results. The decrease in the intensity of the bands at 3640 and 3550 cm^{-1} and the simultaneous decrease in the bands at 1630 and 1540 cm^{-1} obtained by pyridine adsorption, when the reduced samples were evacuated at 500, 600, and 650°C, is indicative of a dehydroxylation process. The simultaneous increase of the band at 1620 cm^{-1} indicates formation of Lewis acidity

at the expense of Brönsted acidity. Conversely, rehydration of Cu^0Y activated at 650°C restores the original spectrum, Lewis acidity being converted into protonic acidity. Studies of anthracene ionization provide convincing proof that the reduced copper zeolites acquire the same properties as those of HY. Cu^0Y acts as an electron acceptor when the samples are evacuated at 600 or 700°C . Precisely this occurs in the same temperature range where pyridine is adsorbed on the surface by coordination. Since the Cu^0 cannot be involved, and since oxygen produces an increase in the positive radical-cation concentration as reported for Lewis acid solids like silica-alumina (17) and decaordinated zeolites (14), formation of tricoordinated aluminium atoms can account for our results.

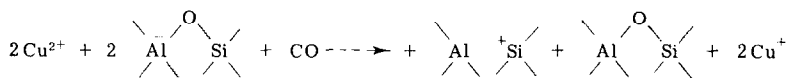
Cu⁺Y Forms

Carbon monoxide reduced samples are white, give no ESR signal, and by chemical analysis Cu^+ ions are detected. As the degree of reduction increases the amplitude of the broad unresolved ESR signal of the Cu^{2+} ions recorded for the 70% exchanged zeolite decreases and the spectra are better resolved. The good resolution of the hyperfine structure of the spectra is related to the decrease in the concentration of cupric ions suggesting that the latter are better dispersed.

into Brönsted acid sites as reported for dehydroxylated HY zeolites (23, 24). The presence of strong bands at 1630 and 1540 cm^{-1} by pyridine adsorption on CO-reduced samples in the presence of small amounts of moisture shows an increase in Brönsted acidity probably due either to rehydration of some pairs of vacancies generated by CO reduction, or to treatment by hydrogen, resulting from the reaction $\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + \text{H}_2$. Strong evidence for the existence of such anion vacancies is provided by the formation of positive radicals when anthracene is adsorbed at the surface of a Cu^+Y sample evacuated at 500°C . The effect of oxygen is similar to that observed for LaY (14) and silica-alumina (17), and indicates that the electron affinity of the tricoordinated aluminium atoms formed by the reduction process is increased by the chemisorbed oxygen. Moreover, rehydration of the solid rendered it inactive for anthracene ionization. This is expected since small amounts of water poison the Lewis acid sites. The reduction of the zeolite may occur as follows:



In summary



Since no new band appears in the hydroxyl stretching region, in contrast to the results for hydrogen reduced samples, it seems that the reduction proceeds in a different way. The lack of the pyridinium ir bands at 1540 and 1630 cm^{-1} confirms that the solid has no Brönsted acid sites. However, in addition to the bands at 1608 , 1488 , and 1451 cm^{-1} , the strong shoulder observed at 1620 cm^{-1} suggested that some Lewis acid centers are formed during the CO-reduction process. If this is the case, water adsorption would convert Lewis acid sites

In conclusion, it should be noted that Cu^{2+}Y zeolites have strong oxidizing properties, the active sites at which electron transfer occurs being identified, as suggested by Richardson, as dehydrated Cu^{2+} ions. At the same time the introduction of copper ions provides acidic hydroxyl groups which react with pyridine to give pyridinium ions. Interaction of pyridine with the cation is supported by the band at 1451 cm^{-1} which is not affected by adsorption of a small amount of water. A true Lewis acid site formed by a dehydroxylation process

would, in contrast, be converted into a Brönsted acid site. The results of pyridine adsorption on Cu^{2+}Y zeolite exchanged at different levels (4–20 copper ions/unit cell) have shown that at least several of these ions are able to coordinate with pyridine. Several authors have used the position of the cations in the zeolite framework to explain the nonlinear change in the catalytic activity with cation content, and concluded that for low exchange levels, these cations occupy internal sites in the zeolite which are not exposed to the reactant molecules. The present study suggests that these interpretations must be considered with care, at least for copper-exchanged zeolites. For example, if Cu^{2+} occupies preferentially internal site I (hexagonal prisms), adsorption of water, pyridine, or reactant molecules might produce a partial cation migration to external sites. Reduction of Cu^{2+}Y zeolite either by hydrogen or by carbon monoxide produces Brönsted or Lewis acid sites depending strongly on the nature of the reducing gas and on the outgassing conditions. Reduction by hydrogen at 500°C followed by a desorption at the same temperature generates acidic hydroxyl groups more stable than those obtained by decomposition of NH_4Y form. On further outgassing at higher temperatures, the dehydroxylation converts Brönsted into Lewis acid sites. During the reduction, metallic copper is obtained. Copper ions in the monovalent state are formed by CO reduction, and by this means tricoordinated aluminium atoms are generated; these latter can be converted into Brönsted acid sites by water adsorption.

Recently Dimitrov and Leach (11) have reported several interesting results on *n*-butene isomerization over copper X zeolites. According to our results it appears that some of their interpretations must be reconsidered. They have suggested that the CuX zeolite exhibited a radical-type mechanism for low Cu^{2+} content and for high level exchange a typical carbonium ion mechanism. However, we have shown that for all copper contents, the samples have both Brönsted acidity and oxidizing

properties and both must be taken into account. Dimitrov and Leach have suggested that the Cu^+ ions formed by reduction with hydrogen are the active sites. Our results, however, show that the cupric ions are reduced preferentially to metallic copper. The formation of Brönsted acid sites in these conditions might well explain the results of Dimitrov and Leach.

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