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A Kinetic Study of the Reduction of Divalent Copper-Exchanged Faujasite with Butadiene and Ammonia

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ESR and phosphorescence spectroscopic studies have shown that in the presence of butadiene or ammonia, divalent copper-exchanged zeolites X and Y are reduced to the monovalent form. Kinetic measurements show that in all these cases the rate of reduction is second order in the divalent-copper concentration. Furthermore, the rate of reduction is found to be markedly dependent on the dehydration temperature adopted prior to reduction.

A mechanism involving formation of Brønsted and Lewis acid sites is proposed to explain these observations.

INTRODUCTION

Divalent-copper-exchanged zeolites such as faujasite are of interest as catalysts for oxidation, cracking, and isomerization reactions. Recently it has been shown (*1–5*) that the divalent-copper ion can be readily reduced to what has been assumed to be the monovalent form in the presence of mild reducing agents such as olefins, carbon monoxide, and ammonia. It has been suggested (*3*) that the monovalent species may play an important role as an intermediate in some of the above catalytic reactions.

However, when an exchangeable metal ion is reduced on the surface of a support, in order to maintain charge balance there must also be some reaction with the support itself. The present study was undertaken to obtain direct evidence of the formation of Cu^+ and to determine the reaction mechanism. The paramagnetic properties of Cu^{2+} enabled the kinetics of the reduction to be followed by means of ESR spectroscopy. The reducing agents used were butadiene and ammonia.

EXPERIMENTAL

Samples of zeolites X (13X, Union Carbide) and Y (SK40, Union Carbide), commercially available as powders without binder, were initially washed to pH 9. These samples (10 g) were then exchanged with 200 ml of 0.01 *N* copper(II) acetate solution for 1 hr. Chemical analysis showed that the exchange corresponded to approximately three and four Cu^{2+} ions per unit cell for X and Y zeolites, respectively. These relatively low concentrations of Cu^{2+} were used to avoid exchange narrowing effects in the ESR spectra. The samples were finally washed with distilled water, dried at 100°C, and allowed to equilibrate over a saturated ammonium chloride solution.[1]

Dehydration and gas adsorption experiments were carried out on a vacuum line ($\sim 10^{-5}$ Torr) using specially designed quartz sample tubes which could be melted off for subsequent ESR and/or phosphor-

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[1] All the samples approximately followed the Curie law.

escence measurements. ESR measurements were made at −196°C on an *X*-band Varian spectrometer and phosphorescence measurements were carried out on a Becquerel-type phosphoroscope (*6*) also at −196°C.

For the kinetic experiments the zeolite samples were first dehydrated for 16 hr at a particular temperature under vacuum. During the adsorption of butadiene or ammonia the dehydrated zeolite was cooled to −80°C in order to prevent immediate reduction due to the temperature rise resulting from the highly exothermic adsorption.

Weakly adsorbed gas was then pumped off at room temperature; the remaining adsorbate still corresponded to a large molar excess (~20-fold) relative to the Cu^{2+} concentration. During the kinetic runs, the samples were heated in sealed quartz ESR tubes in an oil bath at 100°C. After heating at various time intervals the samples were quenched in liquid nitrogen and then the ESR spectra were measured. The Cu^{2+} concentration was assumed to be proportional to the peak heights of the ESR signals and measurements were therefore made using the maximum height of the $g_\perp$ derivative peak from the base line. This approximation is reasonable because all spectra were measured at a constant temperature (−196°C), and the peak linewidths remained invariant. The experimental error in each signal intensity measurement was in all cases <5%; thus, the scatter of data in Figs. 4 and 7 is largely due to small differences in sample packing density. Since the ammonia or butadiene was always present in a rather large excess, the change in reducing agent concentration during the reaction could be neglected.

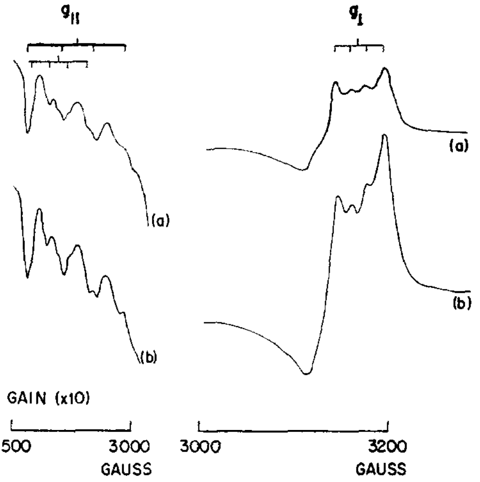


FIG. 1. ESR spectra of Cu^{2+},Na^{+}-X after (a) dehydration at 200°C, (b) followed by adsorption of butadiene at −80°C and then slowly warmed to room temperature (20°C).

RESULTS

Reduction with Butadiene

Typical ESR spectra of Cu^{2+},Na^{+}-X and Cu^{2+},Na^{+}-Y zeolites after dehydration and adsorption of butadiene, and after heating at 100°C for various periods of time, are shown in Figs. 1–3. In agreement with previous findings (*3*, *7*), the spectra of zeolites X and Y before as well as after adsorption of butadiene could be analyzed in terms of at least two magnetically nonequivalent Cu^{2+} ions, each having axial symmetry. The two different Cu^{2+} ions which correspond to different cation sites

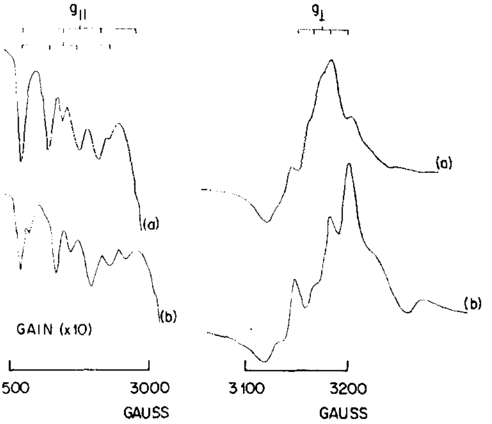


FIG. 2. ESR spectra of Cu^{2+},Na^{+}-Y (a) after dehydration at 200°C, (b) followed by adsorption of butadiene at −80°C and then slowly warmed to room temperature (20°C).

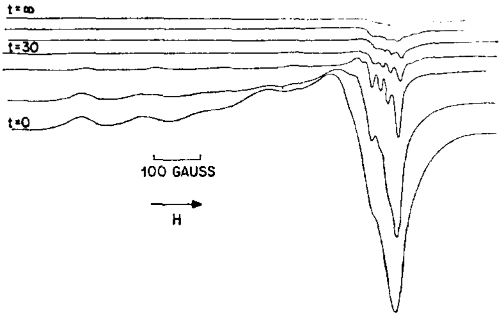


FIG. 3. ESRs pectra of Cu^{2+},Na-X after adsorption of butadiene and heating for various periods of time.

in the zeolites have been arbitrarily labeled Cu^{2+}(1) and Cu^{2+}(2). The calculated g values in the parallel and perpendicular directions for each of the Cu^{2+} ions in the two zeolites after the adsorption of butadiene are given in Table 1. The hyperfine interaction with the Cu nuclei (^{63}Cu, I = $\frac{3}{2}$, 69.1% natural abundance and ^{65}Cu, I = $\frac{3}{2}$, 30.9% natural abundance) for each of the two Cu^{2+} ions could be identified in the $g_{\parallel}$ direction; the measured hyperfine splitting constants, $A_{\parallel}$, are also given in Table 1. In the $g_{\perp}$ direction the ESR signals of the two Cu^{2+} ions were not resolved and hence only an average hyperfine splitting constant, $A_{\perp}$, could be determined.

It should be noted that although this analysis accounts for all the major features of the ESR spectra, a number of small peaks and shoulders in the $g_{\parallel}$ direction could not be accounted for. This implies that there is a small amount of a third magnetically nonequivalent type of Cu^{2+} ion. A careful analysis using Q-band spectra would be necessary to resolve these extra peaks. This, however, was not the purpose of the present investigation.

As shown in Figs. 1 and 2, after the adsorption of butadiene there is a marked redistribution of the Cu^{2+} cations and on heating at 100°C there is a gradual decrease in intensity of the ESR signals. The rates of reduction with butadiene at 100°C were measured for various dehydration temperatures (16 hr, $\sim 10^{-5}$ Torr) and the results are shown in Fig. 4. Plots of the reciprocal of the divalent-copper-ion concentration at time t, $[\mathrm{Cu}^{2+}]_t$, minus the copper concentration at the completion of the reaction, $[\mathrm{Cu}^{2+}]_{\infty}$, i.e., $\{[\mathrm{Cu}^{2+}]_t - [\mathrm{Cu}^{2+}]_{\infty}\}^{-1}$, versus time are linear, indicating that the rate of reduction is second order in the Cu^{2+} concentration. Powell plots also confirmed the second-order kinetics. Furthermore, the rate of reduction was found to be markedly dependent on the dehydration temperature.

In the literature (*1–5*) it has been assumed that under mild conditions with reducing agents such as olefins, NH_3 and CO, Cu^{2+}-exchanged zeolites are reduced to the Cu^{+} oxidation state. Monovalent Cu^{+} is known to phosphoresce (*8*, *9*) and we have made use of this property to determine directly whether Cu^{+} is indeed formed. Phosphorescence spectra in the excitation mode are shown in Fig. 5. On heating at 100°C for 3 hr, a sample of Cu^{2+}, Na^{+}-Y containing adsorbed butadiene gives a peak at 390 nm. For comparison, the figure also shows the spectrum of a sample of Cu^{+},Na^{+}-Y, also containing absorbed

TABLE 1

ESR Parameters for Cu^{2+}-Exchanged Zeolites X and Y

(a) After adsorption of butadiene

	Cu^{2+},Na^{+}-X		Cu^{2+},Na^{+}-Y	
	Cu(1)$^{2+}$	Cu(2)$^{2+}$	Cu(1)$^{2+}$	Cu(2)$^{2+}$
$g_{\perp}$	2.05	2.05	2.06	2.06
$A_{\perp}$^{a}	14	14	13	13
$g_{\parallel}$	2.42	2.35	2.31	2.38
$A_{\parallel}$^{a}	77	137	153	130

(b) After adsorption of Ammonia

	Cu^{2+},Na^{+}-X	Cu^{2+},Na^{+}-Y
$g_{\perp}$	2.04	2.02
$g_{\parallel}$	2.29	2.25
$A_{\parallel}$^{a}	160	180

[a] Hyperfine splitting constants given in gauss.

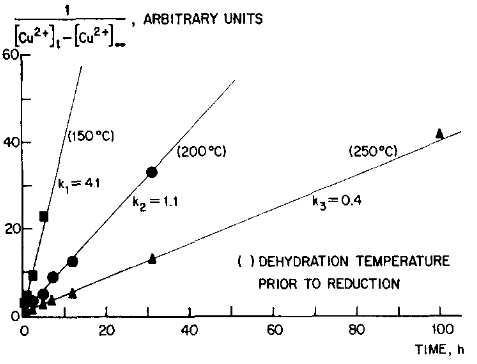


FIG. 4. Reaction kinetics of the reduction of Cu^{2+}-exchanged zeolite X with butadiene at 100°C. Second-order rate constants are given in units of $conc^{-1} \cdot h^{-1}$, where the concentration units are arbitrary.

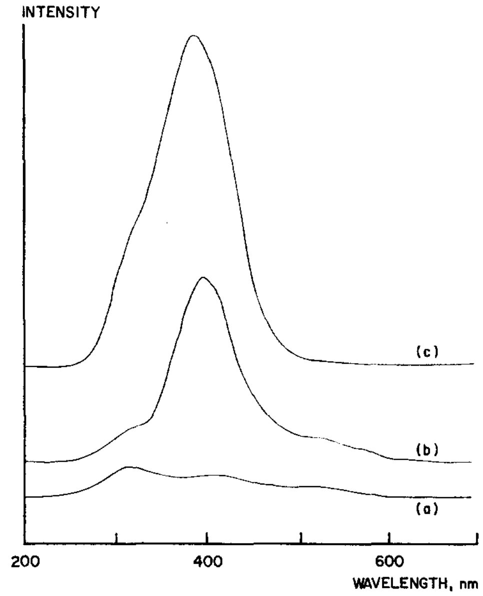


FIG. 5. Excitation spectra of various zeolite Y samples, measured at −196°C with 4-mm slit-widths, WI_2 source, and Philips 6199 photomultiplier. (a)Cu^{2+}, Na^+-Y after dehydration at 300°C for 16 hr and adsorption of butadiene. (b) Above sample after heating for 3 hr at 100°C. (c) Cu^+, Na^+-Y (made by direct exchange of Cu^+ in liquid ammonia) after adsorption of butadiene and heating overnight at 100°C.

butadiene (similar copper concentration), which was prepared by direct exchange of Cu^+ in liquid NH_3 in the absence of air. Clearly, a similar peak is observed at 387 nm. No such excitation peak was found for the Cu^{2+},Na^+-Y (see Fig. 4) or Na^+-Y samples, and it is therefore concluded that the excitation peaks at approximately 390 nm correspond to Cu^+ ions. Phosphorescence spectra were also measured in the emission mode for the Cu^+,Na^+-Y sample and a single peak was observed at 530 nm. This is in reasonable agreement with the value of 530 nm reported in the literature (*8*, *9*) for emission maxima due to Cu^+. The weak peak at 310 nm in all the spectra shown in Fig. 5 is due to some unidentified luminescent impurity in the original zeolite Y sample.

Thus the luminescence measurements have provided direct evidence that Cu^+ is indeed formed after reduction of Cu^{2+}, Na^+-Y with butadiene. Although the technique is not quantitative, there are several indications that no further reduction to the metal has occurred under the present conditions. On reduction of Cu^{2+},Na^+-Y with butadiene (or ammonia) the initially green-blue samples turned white, similar to those obtained by direct Cu^+ exchange. In a separate series of experiments Cu^+, Na^+-Y samples were treated at high temperatures (~400°C) where reduction to Cu^0 occurs. The formation of metallic copper even in very low concentrations is immediately evidenced by a marked change in colour from white to a reddish brown. No

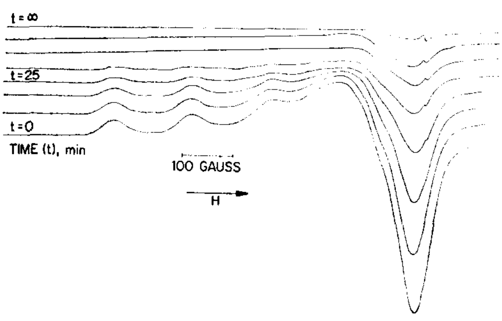


FIG. 6. ESR spectra of Cu^{2+}, Na-X after adsorption of ammonia and heating for various periods of time.

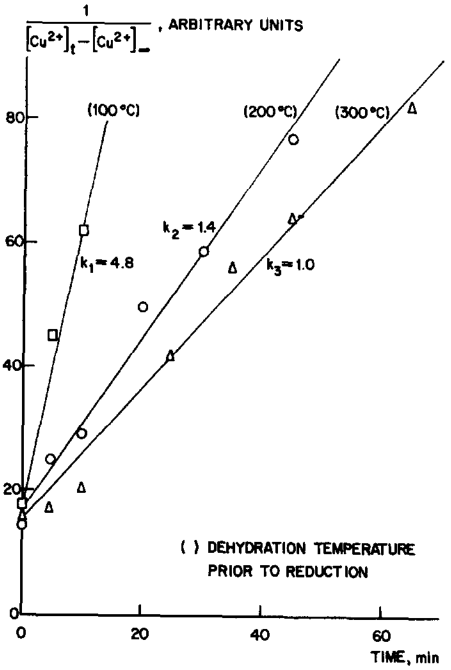


FIG. 7. Reaction kinetics of the reduction of Cu^{2+}-exchanged zeolite Y with ammonia at 100°C. Second-order rate constants are given in units of $conc^{-1} \cdot min^{-1}$, where the concentration units are arbitrary.

such colour change was observed for Cu^{2+}, Na^{+}-Y samples after reduction with butadiene or ammonia.

Reduction with Ammonia

Typical ESR spectra of Cu^{2+},Na^{+}-X samples after dehydration and adsorption of ammonia, followed by heating at 100°C are shown in Fig. 6. After the adsorption of ammonia the ESR spectra are considerably simplified and can be analyzed in terms of a single Cu^{2+} species. Similar results were obtained for Cu^{2+},Na^{+}-Y and the ESR parameters for both zeolites, after the adsorption of ammonia, are given in Table 1. In no case was the hyperfine splitting in the $g_\perp$ direction resolved.

In an analogous way to the butadiene reduction, the reaction of Cu^{2+},Na^{+}-Y with ammonia was followed as a function of time. Plots of $\{[Cu^{2+}]_t - [Cu^{2+}]_\infty\}^{-1}$ against time, for different dehydration temperatures prior to reduction, are shown in Fig. 7. Clearly, reduction with ammonia is considerably faster than with butadiene. Although a similar increasing rate of reduction with decreasing dehydration temperature is observed, the effect is less marked than with butadiene.

The second-order rate constants, expressed in arbitrary concentration units, for the reduction of Cu^{2+},Na^{+}-X, and Y zeolites with butadiene and ammonia are shown in Figs. 4 and 7.

DISCUSSION

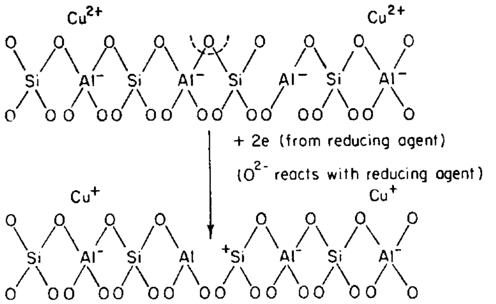
Mechanism of Reduction

By means of ESR and phosphorescence spectroscopy it has been shown that at 100°C, Cu^{2+}-exchanged zeolites X and Y are readily reduced to the Cu^{+} form by both butadiene and ammonia. Furthermore, in both cases the following rate law

$$-d[Cu^{2+}]/dt = k[Cu^{2+}]^2, \qquad (1)$$

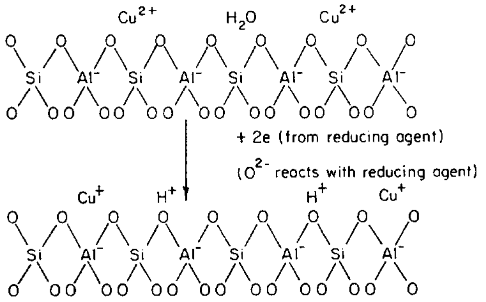
is observed, where $[Cu^{2+}]$ is the concentration of reactive Cu^{2+} (the reducing agent being present in a large excess). The rates of reduction are also shown to be markedly dependent on the dehydration temperature prior to reduction. This indicates that the reduction is more facile in the presence of small quantities of residual zeolite water.

These results can be explained in the following manner. If we consider a subunit of the zeolite framework consisting of four aluminum ions, two Cu^{2+} ions will be required to maintain charge balance. However, when these two Cu^{2+} ions are reduced to the monovalent Cu^{+} species, by a reducing agent, this charge balance is no longer satisfied. For a completely dehydrated zeolite the most obvious way of restoring the necessary charge balance is to remove an oxide ion from the lattice, which can then react with the reducing agent.



The site formed by the removal of an oxide ion is identical with the Lewis acid sites formed during dehydroxylation of the hydrogen form of zeolites at high temperatures (*10*). Clearly, the removal of a single oxide ion involves the participation of two Cu^{2+} ions, thus accounting for the observed second-order kinetics.

If, however, residual zeolitic water is present during reduction, an alternative mechanism is possible. Instead of removing an oxide ion from the framework, charge balance can be maintained by dissociation of a water molecule.



The two protons so generated can react with the zeolitic framework to form two Brønsted acid sites and the oxide ion reacts with the reducing agent. The zeolitic water may already be partially dissociated into a proton (Brønsted acid site) and a $CuOH^+$ species, as has been shown to occur for divalent-metal ions exchanged into zeolites (*10*). This, however, makes no difference to the overall reaction, which remains the same, although one might expect dissociated water to be more reactive. Thus in the presence of residual zeolitic water we would also expect the reaction to be second order in the Cu^{2+} concentration with the rate law

$$-d[Cu^{2+}]/dt = k_2[Cu^{2+}]^2[H_2O]. \quad (2)$$

The rate equations (1) and (2) represent two extremes and one can imagine that more often an intermediate situation prevails. This can be represented by simply combining these two equations:

$$-d[Cu^{2+}]/dt = \{k_1 + k_2[H_2O]\}[Cu^{2+}]^2.$$
$$\text{(excess reducing agent)}$$

Thus a single second-order rate law would be expected, as is observed. Moreover, the dissociation of a water molecule (particularly if it is already partially dissociated) might be expected to be a more facile process than the removal of an oxide ion from the lattice. This would then account for the enhanced rate of reduction in the presence of residual zeolitic water. A large excess of zeolitic water would be expected to block the Cu^{2+} sites from reaction with the reducing agent, and this is indeed found to be the case. Clearly, somewhere there is presumably an optimum residual water content which maximizes the rate of reaction.

The proposed mechanism requires that two Cu^{2+} ions must come into relatively close proximity before reaction can occur. Considering the low Cu^{2+} loadings used for the present experiments and assuming a random distribution, one would expect the Cu^{2+} ions to be relatively far apart. Indeed, ESR provided no evidence of an interaction between the Cu^{2+} ions or pair formation, as was observed by Chao and Lunsford (*11*) at much higher Cu^{2+} concentrations. Thus there must be considerable cation mobility before the reduction reaction can take place. This could provide an alternative explanation for the enhanced rate of reduction in the presence of residual water. Small amounts of water in zeolites have a very marked effect on ionic mobility, as is evidenced by ionic conductivity measurements (*12*).

In all cases there remains a small proportion (<5%) of Cu^{2+} ions, i.e. $[Cu^{2+}]_\infty$, which cannot be reduced with butadiene or ammonia at 100°C. These could be either the Cu^{2+} ions located in the dense cage structure, where they are inaccessible to reducing agent, or widely separated Cu^{2+} species. However, in the case of ammonia all the Cu^{2+} ions appear to be at one site and bound to NH_3.

Naccache and Ben Taarit (*1*) also observed a second-order dependence on the Cu^{2+} concentration for the hydrogen reduction of Cu^{2+}-exchanged zeolites Y to the zero-valent form, Cu^0. To explain these observations the reduction to an intermediate Cu^+ species was proposed:

$$2Cu^{2+} + H_2 \rightarrow 2Cu^+ + 2H^+,$$

$$2Cu^+ + H_2 \rightarrow 2Cu^0 + 2H^+.$$

This scheme is indeed consistent with the present results.

Interpretation of ESR spectra

Cation siting in zeolites with the faujasite structure has been extensively investigated (*13*). Partially exchanged Cu^{2+}-Y was studied by Gallezot *et al.* (*14*) using powder X-ray diffraction techniques. Copper ions were found to show a preference for site I′[2] and were observed to migrate toward the supercage under the influence of adsorbed molecules. More recently an accurate single-crystal X-ray analysis has been carried out on natural faujasite crystals completely exchanged with Cu^{2+} ions (*15*). In addition to site I′ (14.2), Cu^{2+} ions were also located at sites I (1.5), II (5.3), II′ (0.8), and III (3.3) (figures in parentheses indicate the number of cations per unit cell) in the dehydrated form. Sites II and III are in the supercage and are therefore accessible to adsorbed molecules.

At least two magnetically nonequivalent Cu^{2+} ions could be distinguished in the ESR spectra of Cu^{2+}-exchanged forms of zeolites X and Y (see Figs. 1 and 2). Clearly, these correspond to cations at different sites in the structure. Moreover, after the adsorption of butadiene there is a marked charge in the relative intensities of the ESR signals, which can be interpreted in terms of migration of cations toward the adsorbate molecules in the supercage. Similar results were obtained by Leith and Leach (*3*) on the adsorption of 1-butene into Cu^{2+}, Na^+-X.

For example, in the case of Cu^{2+},Na^{2+}-X the ESR signal characterized by $g_\perp = 2.05$, $g_\parallel = 2.35$, $A_\parallel = 137g$, increases in intensity relative to the signal characterized by $g_\perp = 2.05$, $g_\parallel = 2.42$, $A_\parallel = 77g$, on adsorption of butadiene. Furthermore, the former signal decreases in intensity more rapidly during the reduction reaction with butadiene than the latter signal.[3]

The more reactive Cu^{2+} ions are presumably located at sites II or III in the zeolite structure. Site III-type cations are located at the pore entrances to the supercage (*15*) and are coordinatively unsaturated, and would thus be expected to be the more reactive species.

In agreement with other workers (*5*, *7*), in the case of ammonia adsorption a single Cu^{2+} species is observed by ESR (see Fig. 6). This presumably corresponds to a $Cu(NH_3)_4^{2+}$ complex located inside the supercage, as recently demonstrated by Flentge *et al.* (*16*). This implies that most, if not all, of the Cu^{2+} ions migrate to the supercage on adsorption of NH_3 and that this is also the site for the reduction reaction. After reduction, conceivably a new

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[2] The site nomenclature is as follows: site I, center of hexagonal prism; site II, six-membered ring face of sodalite cage on the super-cage side; sites I′ and II′ lie on the other sides of the six-membered rings, opposite sites I and II, respectively, inside the sodalite cage.

[3] The rate data shown in Fig. 4 were determined from the $g_\perp$ component of the spectra. Owing to overlap of different Cu^{2+} signals, this clearly corresponds to an average rate of the two Cu^{2+} ions.

monovalent copper complex, e.g., $Cu(NH_3)_2^+$, is formed in the supercages.

CONCLUSIONS

(1) Cu^{2+} cations exchanged into zeolites X and Y can be readily reduced to Cu^+ at 100°C by butadiene and ammonia.

(2) The rate of reduction is considerably higher with ammonia than with butadiene.

(3) The rate of reduction is markedly affected by the dehydration temperature (and thus by the residual water content of the zeolites) prior to reduction.

(4) The rate of reduction with both butadiene and ammonia is second order in the Cu^{2+} concentration.

(5) A mechanism is proposed whereby, in order to maintain charge balance, either an oxide ion is extracted from the zeolite framework or, when residual zeolitic water is present, a water molecule is dissociated. In the former case Lewis acid sites are formed and in the latter case Brønsted acid sites. In either event the mechanism involves the participation of two Cu^{2+} ions in the transition state.

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