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On the preparation and properties of CuZSM-5 catalysts for NO decomposition

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Equilibrium exchange isotherms were determined for the exchange of Cu^{2+} with NaZSM-5 at varying $Cu(Ac)_2$ concentrations in solutions of constant volume and zeolite weight. At low Cu^{2+} levels the solid scavenged all the copper ions. When copper could be detected in the equilibrated solutions, "overexchange" was observed. The extent of "overexchange" was higher at pH $\approx$ 6 than at pH $\approx$ 4. These results were analyzed in relation to catalytic activity.

Keywords: NO decomposition-sites; Cu^{2+}/Na^+ exchange equilibria; effects of pH on catalytic properties; overexchange in CuZSM-5

1. Introduction

The CuZSM-5 catalysts are more active in NO decomposition and reduction than the CuY zeolites [1–3]. The reason for this is not understood. An obvious difference between the two systems is that, beside the structural and compositional differences that would tend to favor the latter, the ZSM-5 zeolites easily become overexchanged, while under comparable conditions the exchange level tends to remain below 100% for Y zeolites. (The exchange level is taken as 100% (and considered "stoichiometric") when Cu/Al = 0.5, i.e., when one Cu^{2+} ion has replaced two Na^+ ions.) It was also found that the best catalysts were those containing excess copper [1–3]. The maintenance of charge balance in these cases requires the incorporation of extralattice anionic ligands. For catalysts calcined in an oxidizing atmosphere the extralattice ligand is undoubtedly an oxygen atom or a hydroxyl group. Thus, extralattice oxygen is introduced into the zeolite. This has been studied in detail and discussed elsewhere [4]. The formation of ELO does not necessa-

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rily lead to the observation of overexchange, i.e., Cu/Al ratios >0.5. The presence of such species in Y zeolites has been conjectured for many years [5–11]. It has been shown that CuY zeolites containing ELO are more active for CO oxidation than those without ELO [12,4].

Recent MAS NMR and IR results [13,14] have led to the conclusions that the ELO is carried into the zeolite during the Cu-exchange process and that lattice oxygen is not removed as Cu^{2+} is converted to Cu^{+}. The existence of the ELO species explains how the reversible redox couple, Cu^{2+}/Cu^{+}, can be established without effecting dealumination. In essence the catalyst, as prepared, is already an oxygen carrier which can be reduced by CO, by hydrocarbons, or by spontaneous desorption of O_2 above 623 K [2,15,16]. Correlations established between the rate or the amount of O_2 desorption and the NO decomposition activity emphasize the importance of the ELO carrying species in this reaction [2,3,17]. Recently overexchanged Cu-mordenites have been reported [18,19]. While the introduction of ELO with Cu^{2+} is not unusual, the overexchange phenomenon seems to be a characteristic of high-silica zeolites.

Contradictory ideas concerning the reaction mechanism of the NO decomposition reaction and the nature of the active sites have been advanced [20–22]. The kinetics of this reaction have been determined [2,3] and were shown to be consistent with a redox mechanism. Most of the evidence favors this idea [21], but an alternative mechanism involving an ELO species as the active site has recently been shown [22] also to be consistent with the kinetics. In the redox process the ELO species may be reversibly removed and replaced; in the alternative mechanism it plays a key role, acting as an active center and as the precursor of the active intermediate. An objective of the present work was to learn more about this ELO and its role in the reaction mechanism.

The exchange equilibria of Cu^{2+} for Na^{+} in ZSM-5 zeolites have not previously been studied in detail. The existing data for Y-zeolites do not suggest any deviation from the expected stoichiometry. No overexchange in other systems has been reported [23–25]. The present work is a preliminary investigation of this phenomenon. The analytical data obtained have been correlated with the NO decomposition activities of the preparations. The NO reduction and decomposition reactions have also been compared.

2. Experimental

2.1. BASE-EXCHANGE PROCEDURES

The preparations were made using dilute aqueous solutions of copper(II) acetate (Fisher Scientific, ACS Grade). The *parent* ZSM-5 sample (NaZ-14), was provided by Air Products and Chemicals Company; it was a template free preparation made in the sodium form with an Si/Al ratio of 14.6. The sodium content of the sample was higher than the stoichiometric amount (Na/Al = 1.2).

Aliquots (100 mg) of the parent ZSM-5 were added to 100 cm^3 solution at room temperature in plastic bottles, and placed on a mechanical shaker. The solid was removed by filtration, washed with 20 cm^3 deionized H_2O and dried at 350 K. The filtrates were analyzed by AAS for Cu and AES for Na. The Cu-content of the zeolites was determined by XRF. Identification of the catalysts is given in table 1 together with the results of these experiments. The pH of the several solutions was measured before adding the zeolite (initial pH) and was not adjusted in experiments 1–10; after equilibration final pH values were determined. Another set of samples (Nos. 11–18) was studied after adjusting the starting solutions with acetic acid to pH = 4.0 ± 0.01.

Table 1
Catalyst preparation [a] and characterization

No.	Preparation identification	Cu conc. [b] (meq/ℓ)	Initial pH	Equil. pH	Equilibrium data		
					Cu_z/Na_s [c]	Cu_z/Al [d]	$Cu_z/g \times 10^{-20}$
1	CuZ-14 175 [e]	8.8	6.08	6.00	0.76	0.88	5.50
2	CuZ-14-153	4.5	6.11	6.06	0.68	0.76	4.76
3	CuZ-14-149	2.3	6.10	6.13	0.72	0.74	4.63
4	CuZ-14-151 [f,g]	2.4	6.19	6.14	0.72	0.75	4.69
5	CuZ-14-135	1.4	6.10	6.39	0.68	0.67	4.19
6	CuZ-14-133 [f,g]	1.7	6.20	6.45	0.67	0.66	4.13
7	CuZ-14-76	0.83	6.02	7.05	0.51	0.38	2.37
8	CuZ-14-36	0.38	6.51	7.17	0.39	0.18	1.13
9	CuZ-14-19 [f]	0.18	6.62	7.22	0.28	0.09	0.56
10	CuZ-14-8 [f]	0.08	6.50	7.41	0.15	0.04	0.25
11	CuZ-14-116	8.6	4.01	3.99	0.55	0.58	3.62
12	CuZ-14-108	4.2	4.01	4.01	0.53	0.54	3.38
13	CuZ-14-106	2.2	4.01	4.03	0.54	0.53	3.31
14	CuZ-14-105	1.18	4.01	4.05	0.56	0.52	3.25
15	CuZ-14-86	0.96	4.01	4.30	0.53	0.43	2.69
16	CuZ-14-35 [f]	0.34	3.99	4.33	0.28	0.17	1.06
17	CuZ-14-27	0.26	4.00	4.23	0.24	0.13	0.81
18	CuZ-14-16 [f]	0.17	4.01	4.14	0.15	0.08	0.50

[a] 100 mg zeolite was equilibrated with 100 cm^3 solution of given concentration at room temperature.

[b] Initial concentration before exchange.

[c] The amount of Cu in the zeolite (Cu_z) ratioed to the amount of Na in the solution (Na_s) at equilibrium. Ideally this would be 0.5.

[d] This catalyst contains 6.25×10^{20} Al/g.

[e] Z represents ZSM-5. The Si/Al ratio of the sample was 14. The last number of the ID is 200 (Cu/Al); this assumes Cu^{2+} replaced two Na^+.

[f] These zeolites were equilibrated with the solutions for one week while the rest were agitated in a shaker for 24 h.

[g] NO decomposition activity was not tested.

Catalyst CuZ-14-114 was also included in the catalytic results. It was prepared by the Air Products and Chemicals Co. using Cu-acetate and has been used in earlier studies [9,22].

2.2. CATALYTIC MEASUREMENTS

The atmospheric microcatalytic steady state flow reactor and the conditions of the gas-chromatographic analyses have been described elsewhere [26]. The standard catalyst pretreatment was drying in flowing, carefully dried He as the temperature was raised from 293 to 773 K over a 2 h period where the treatment was continued for an additional hour. The NO decomposition activity of the catalysts was tested in the steady state flow mode using 4% NO/He. The conversion to N_2 was also measured in the presence of propylene, CO and O_2. In order to study the effect of these gases, pure He, 1% O_2/He, 1% propylene/He and 4% CO/He mixtures were mixed with the 4% NO/He flow in such a way that the composition was varied, but the total flow rate (90 cm^3/min) and the partial pressure of NO were kept constant. To accomplish this three streams, each flowing at 30 cm^3/min were mixed to provide the gas compositions listed in the legend of fig. 4.

Catalyst samples weighing 20–80 mg were used. The W/F and the conversion to N_2 were 1×10^5 g s/mol and <20%, respectively. The differential reaction rates so determined were expressed as turnover frequencies (TOF), i.e., as NO molecules converted to N_2 per Cu ion per second.

3. Results

Data relating to exchange equilibria in the CuZSM-5 system are listed in table 1. The pH of the dilute cupric acetate solutions was in the 6.0–6.5 region and typically increased upon equilibration with the NaZ-14 parent zeolite. A similar increase was observed using solutions with pH = 4.0. Interestingly, the most significant changes were obtained with the most diluted solutions (table 1, rows 7–10 and 15–18). For these samples the Cu_z/Na_s ratios were smaller than 0.5, indicating that more than two sodium ions appeared in the solution for each cupric ion exchanged into the zeolite. Evidently some hydrolysis of the NaZ-14 occurred in these cases increasing the pH. (To maintain the charge balance, the exchange of protons in the solution with some of the Na^+ is required.)

The Cu_z/Na_s ratio was usually higher than 0.5 (table 1, rows 1–6 and 11–15). The values were around 0.7 at the higher and 0.55 at the lower pH. This ratio would be ideally 0.50 if one Cu^{2+} replaced $2Na^+$ during the exchange.

In accordance with the Cu_z/Na_s balance, the Cu/Al atom ratio in the zeolite also increased above 0.5, i.e., the exchange level relative to the stoichiometric exchange was more than 100% (table 1, last number of catalyst ID). The phenomenon of "overexchange" has been noted previously [27,28]. The degree of overexchange was more significant in the 6.0–6.5 pH region than at lower pH.

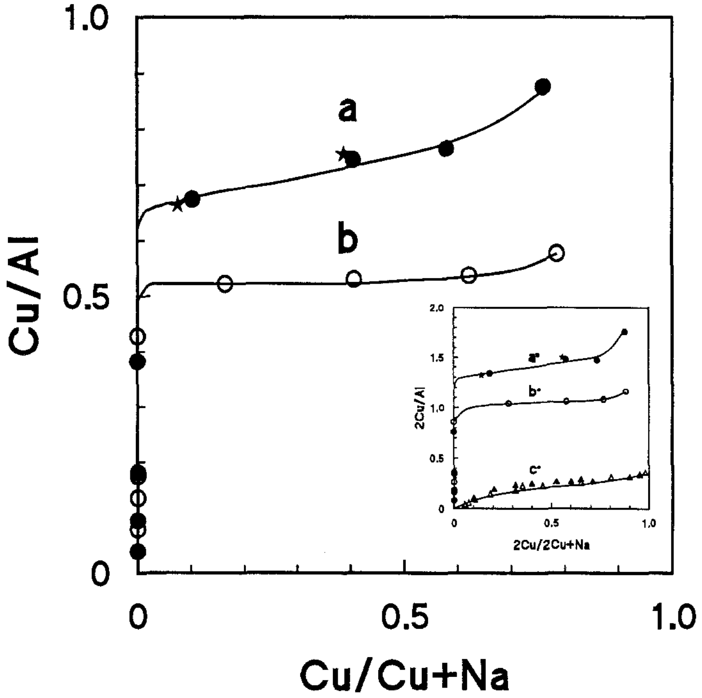

Fig. 1. Cu^{2+}/Na^+ ion exchange isotherms of Z-14 at 298 K. The pH of the Cu acetate solutions was (a) 6.0–7.4 and (b) 4.0–4.3. The time allowed to reach equilibrium was 24 h (●, ○) and 1 week (★). The Cu/Al *atom* fraction in the solid is plotted against the *atom* fraction of Cu in the solution (abscissa). Curve (a) shows extensive overexchange of the zeolite while curve (b) depicts more nearly ideal behavior at the lower pH. The inset shows the same data (a′ and b′) plotted according to Sherry [26] (equivalents of Cu^{2+}/Al versus the normality of Cu^{2+} in solution at equilibrium). Data for the related exchange of Ca^{2+} with NaZSM-5 are shown (c′) for comparison (data taken from ref. [25]).

Equilibrium Cu^{2+} for Na^+ ion exchange isotherms are shown in fig. 1. Because of the unusual exchange properties, an unusual representation of the data was employed. Copper concentrations in the zeolite phase and in the solution are expressed as atom fractions. On this basis values of the ordinate should approach 0.5 for stoichiometric exchange as the Cu^{2+} concentration in the equilibrated solution phase increases. The ZSM-5 zeolite is highly selective for cupric ions. In every case whenever cupric ion became detectable in the solution at equilibrium, the preparation was already overexchanged (and much more so at the higher pH). This behavior may be contrasted with that of other divalent ions. The same data are replotted in the inset of fig. 1 (a′ and b′) according to the formalism of Sherry [25] [#1], and data for exchange of Ca^{2+} into NaZSM-5 taken from ref. [24] are plotted (c′) for comparison. These data were included to emphasize the atypical behavior of Cu^{2+} in the exchange process.

[#1] This formalism expresses the data in much the same way as ours, but the point of stoichiometry is 1.0 on the ordinate instead of 0.5. See ref. [25] for details.

The turnover frequencies for the NO decomposition reaction are plotted versus temperature in fig. 2 for preparations of various degrees of exchange. The activity increased with the degree of exchange and with the pH at which the preparation was made. The two overexchanged catalysts had the highest activities and the underexchanged ones the lowest, confirming the findings of Ione et al. [12] for the $CO + O_2$ reaction. The data suggest that catalysts of higher activity can be made by increasing the pH (compare curves (b) and (d)). As usual the TOF passed through a maximum as a function of the reaction temperature. Interestingly, this maximum moved to higher temperatures as the activity, the exchange level, and the extent of the overexchange increased.

Interesting features concerned with the effects of exchange level and the onset of overexchange are expressed in two different ways in fig. 3 where the activity (TOF) is plotted as a function of the Cu/Al ratio in the zeolite (fig. 3A) and the ratio of Cu_z/Na_s (fig. 3B). These figures demonstrate that the turnover frequency increases with increasing exchange level up to about the point of stoichiometry and then becomes constant at higher loadings. The TOF would be a constant as these ratios increase if all that was occurring was an increase in the number of identical sites (as shown above the point of stoichiometry).

As shown in fig. 4, the activity of the CuZ-14-114 catalyst for the several reactions in the low temperature region below 773 K was not as different as might be expected. Above 773 K, the NO decomposition activity passed through a maximum and decreased with increasing temperature while the activity in the CO reduc-

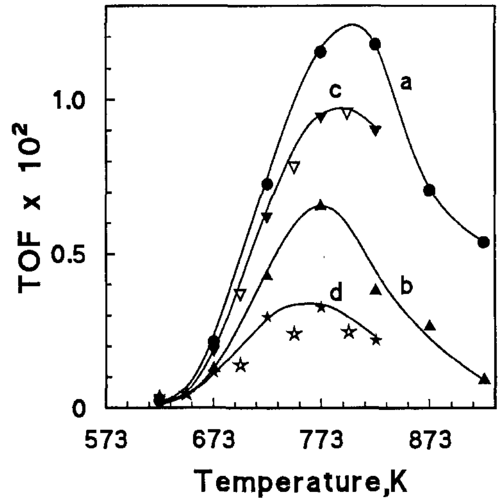

Fig. 2. The effect of exchange level and temperature on the catalytic activity per Cu ion (TOF) for NO decomposition: (a) CuZ-14-153, ●; (b) CuZ-14-76, ▲; (c) CuZ-14-108, ▽, ▼; (d) CuZ-14-86, ☆, ★. Preparations (a) and (b) were made at pH $\approx$ 4. The solid and open symbols represent increasing and decreasing temperature respectively. The turnover frequency (TOF) is defined as the number of NO molecule converted to N_2 per second per Cu ion in the zeolite.

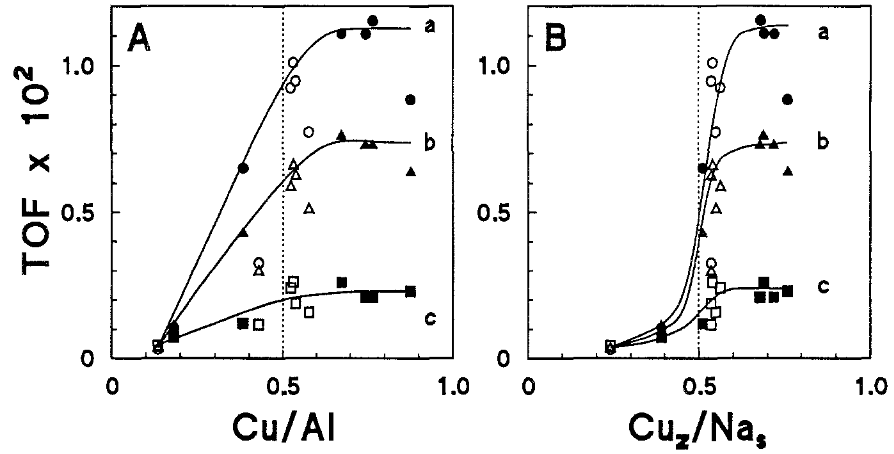

Fig. 3. The turnover frequency for NO decomposition at (a) 773 K, (b) 723 K, and (c) 673 K as a function of exchange conditions: (A). Cu/Al is the ratio of Cu ions in the zeolite to the number of Al-T sites; the point of stoichiometry for satisfying the base-exchange capacity with Cu^{2+} is 0.5; (B) Cu_z/Na_s is the ratio of the number of Cu atoms introduced into the zeolite to the number of Na^+ ions that appeared in the solution at ion-exchange equilibrium. For stoichiometric exchange this value is 0.5. Open symbols represent samples made at lower (4.0–4.3), and solid symbols those made at higher (6.0–7.4) pH.

tion continued to increase before leveling off. The NO/CO reaction showed a similar response to the addition of O_2 as the decomposition. In the presence of excess oxygen, propylene proved to be the best reducing agent. The activity in the reduction of NO to N_2 was the highest for this reaction. It increased up to 823 K and remained practically unchanged up to 923 K (fig. 4a). With the exception of the NO/O_2 system, the addition of a reducing, or a reducing plus oxidizing agent to the NO, had a strong effect on the activity only above 773 K.

4. Discussion

As is well known, the FeY zeolites are oxygen carriers. When properly prepared, the $Fe^{2+}Y$ nay be oxidized to $Fe^{3+}Y$ with O_2, NO or N_2O and in the process pick up an atom of ELO for each two Fe ions. This is reversible; the catalyst may be reduced with CO or H_2 back to its initial condition; Fe^0 is not formed at temperatures up to at least 1023 K. The way a similar oxygen carrying capacity is developed in the Cu zeolites has posed a problem. Cu^{2+} ions are exchanged into the zeolite and, seemingly, must be reduced to Cu^+ before the Cu^+/Cu^{2+} couple can be established. Jacobs and Beyer [10] proposed that this was accomplished by removing a lattice oxygen in the first reduction step, this being followed by a lattice reconstruction accompanied by dealumination. This way the lattice would become charge compensated by equal amounts of Cu^+ and AlO^+. Recent work [9,22] has

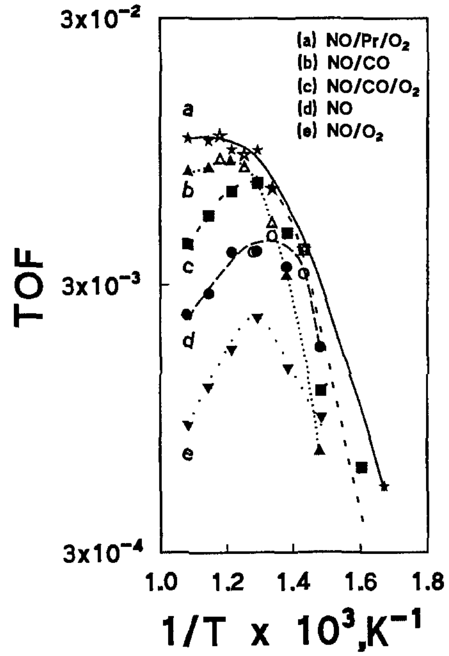

Fig. 4. The turnover frequencies (TOF) of NO conversion to nitrogen (CuZ-14-114) from different gas mixtures: (a) 1.29% NO/0.11% propylene/0.55%O_2/He, ☆, ★, (b) 1.29%NO/1.37% CO/He △, ▲, (c) 1.29% NO/1.37% CO/0.33% O_2/He ■, (d) 1.29% NO/He, ○, ●; and (e) 1.29% NO/0.33% O_2/He, ▽. The total flow rate and the NO space velocity were kept constant ($W/F = 0.24 \times 10^5$ g s/mol NO) and the reaction temperature was increased step by step from 623 K to 923 K (full symbols) then decreased (open symbols).

shown that CuY and, presumably CuZSM-5 also, is not dealuminated in this way. Where then does the ELO originate and how is it held on the catalyst so that it may participate in the NO decomposition and/or reduction reactions? A likely answer to this question [9] is that it is introduced during the preparation of the catalyst and is closely associated with the Cu^{2+} ions introduced by base exchange. Moreover, it is probable that the overexchange that is frequently encountered with these silica-rich materials is in some way associated with this process. In view of the importance of these questions, the present study of the solution chemistry was initiated and the catalytic properties of some of the resulting catalysts were determined.

The data in table 1 relate to the zeolites at equilibrium in aqueous media. Clearly, lowering the pH results in lower loadings, i.e., only slightly above the stoichiometric composition (fig. 1). The large extents of overloading required to obtain the maximum catalytic activities were only achieved at higher values of the pH. Moreover, in these latter cases (pH $\approx$ 6) more Cu^{2+} entered the catalyst than could be balanced by the Na^+ appearing in the solution. Invariably, in these cases, the Cu^{2+}/Al ratios exceeded the stoichiometric value 0.50 (overexchange). Raising the pH will of course enhance adsorption of cations by a more negatively charged lattice, but neutrality must be restored as the catalyst is dried. Thus auxiliary anions must be carried along as previously reported [11], and they may be directly involved in the deposition of the ELO as well as the overexchange. In effect a portion of the Cu^{2+} is exchanged into the zeolite as $[CuOH]^+$, i.e., Cu^{2+} bearing an OH^-. This could happen by cleavage of a H_2O molecule in the hydration sphere of the Cu^{2+}. The driving force for this hydrolysis is that it is energetically more favorable to charge balance the lattice with two monovalent entities than one divalent cation, especially in silica-rich zeolites where the negatively charged Al-T sites are widely separated from each other. Note, however, that if the ejected proton became a Brønsted site, overexchange would not result unless this site could in turn be replaced by another $CuOH^+$. Another possibility exists, however, and this is that it combines with and Ac^- anion forming HAc. In this case the pH would remain nearly constant on exchange as observed (table 1, lines 1–6). The probable reason that overexchange is pH dependent is that the hydrolysis of H_2O molecules in the hydration sphere of Cu^{2+} is promoted by higher concentrations of OH^- ions in the aqueous exchange media.

Fig. 2 shows that the pH at which the catalyst is made can materially affect its catalytic efficiency (compare curves b and d). Thus the data suggest that the development of the active catalytic sites is dependent on the solution chemistry. This is reemphasized by Chu and Dwyer's report [23] that the exchange of Cu^{2+} with Na^+ was stoichiometric when $CuCl_2$ was used with ZSM-5 of higher Si/Al ratio.

These same points are reemphasized in fig. 3 where the turnover frequencies increase with the Cu/Al ratio (A) up to Cu/Al >0.5 and then become constant. The same TON plotted against Cu_z/Na_s (B) are consistent. The steep increase below the point of stoichiometry suggests that the Cu ions are being deposited in two ways, one forming active sites (or more active sites) and the other inactive (or much less active) ones. One way this could happen would be if the inactive sites were isolated from each other or inaccessible to the gas phase and if the active ones were in close proximity and bearing an ELO.

The Russian workers [12,4] have pointed out that two different exchange mechanisms may occur depending upon the pH of the exchange medium. At pHs much less than the value corresponding to the start of hydrolysis of the salt, isolated base exchange cations will result; at higher values of the pH partial hydrolysis of the starting salt may occur with the association of cations as dimeric oxycations or even as polynuclear cations. They state that for cobalt and nickel the association of cations begins in suspensions of a zeolite in the solution of the chlorides or nitrates at a pH = 6–8. The intensity of the ESR signal from Cu preparations fell rapidly between pH 4 and 8. In the range $4<pH<6$, the spin intensity fell to roughly 20% of its initial value and this was attributed to "formation of copper cation clusters" resulting from hydrolysis of the original salt. These ideas are sufficiently flexible to afford a satisfactory explanation for our results. In passing from pH = 4 to pH = 6 hydrolysis has started, carrying into the zeolite anions which become ELO after calcining. The possibility that $Cu(OH)_2$ is precipitated in the pore system cannot be overlooked. This possibility leaves other questions, more difficult to answer, e.g., why ZSM-5 is overexchanged with Na^+; why it is overexchanged with Cu^{2+}, while the Y zeolite is not; and why are the NO decomposition properties of the overexchanged catalyst different from those of CuO, etc?

Schoonheydt et al. [11], in studies with copper or nickel acetate, observed that both cations and anions were disappearing from the solution during equilibration. They concluded that no polyvalent cations or clusters were formed in solution. Presumably then, cluster formation, if it occurs, must take place within the catalyst, but before it is completely dried. Kuroda et al., in a recent study [18,19], proposed an analogous model. This envisaged hydrated cations diffusing into the zeolite pores as the Na^+ ions diffuse out. In the pore system, either before or as H_2O is removed, H_2O molecules of the hydration sphere dissociate, forming a proton and an entity of reduced positive charge. We expressed similar ideas many years ago [5].

The Cu_z/Na_s values listed in column five show that at a pH near 6 more Cu^{2+} enters the catalyst than its equivalent of Na^+ appearing in the solution. Thus, in agreement with earlier ideas [11], acetate ions are entering the zeolite together with their associated cations, and regardless of the subsequent chemistry, oxygen carrying species are deposited in the zeolite. At pH = 4, cation hydrolysis is not expected and here the results approach ideality. As shown in fig. 1, the underexchanged values obtained at low initial solution concentrations result from removal of most of the Cu ions from the solution.

Ancillary questions remain concerning the nature of ELO and the catalytic sites. How can a divalent ion like Cu^{2+}or Ca^{2+} neutralize the two negatively charged Al-T sites which are remote from each other in high silica materials? In the Y-zeolites a partial answer is found by placing a divalent ion in the hexagonal prism between two 6-rings where it is exposed to several such sites on both sides. With the ZSM-5 zeolites, on the other hand, the cation siting is entirely in the straight or zigzag side channels. How can the lattice charge be balanced by a single divalent ion when the distance between two negatively charged sites becomes large, i.e., how can Cu^{2+} neutralize two AlO_2^- high silica materials? In solution this problem is at least partially mitigated by the presence of H_2O or associated anions, i.e., as a dissociated two-dimensional salt. Indeed, studies of other divalent ions of similar size invariably show underexchange rather than overexchange. This is indicated by the inset in fig. 1 which is a re-plot of the data of McAleer et al. [25] for Ca^{2+} in ZSM-5. If the ELO is held bridged between two Cu^{2+} ions as the data suggests, how do these two oxygen atoms, which are still more remote from each other, get together to recombine and spontaneously eliminate O_2? Answers to these important questions are urgently needed.

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