

## X-Ray Diffraction Study of Cupric Ion Migrations in Two Y-Type Zeolites Containing Adsorbed Reagents

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Received May 12, 1971; revised January 31, 1972

X-Ray diffraction study of two copper-exchanged Y zeolites ( $\text{Cu}_{16}\text{Na}_{24}\text{Y}$  and  $\text{Cu}_{12}\text{Na}_5\text{H}_{27}\text{Y}$ ) in the dehydrated state showed that the cupric ions strongly prefer  $\text{S}_I$  sites in the sodalite cages where they are firmly bonded to three framework oxygen atoms. The effect of sorbed molecules on the cation distribution was studied by adding ammonia, pyridine, naphthalene and butene to the dehydrated zeolite. Adsorption of a small amount of ammonia which can enter the sodalite cages produced slight but significant changes in the copper position. Addition of pyridine, naphthalene or butene induced an important migration of copper ions from  $\text{S}_I$  and  $\text{S}_I'$  sites to the supercages where they can interact with sorbed molecules. The nature of the cation-organic molecule associations was investigated; infrared measurements and X-ray results provided evidence of a proton transfer from the organometallic complexes to the framework oxygen atoms.

### INTRODUCTION

The zeolite catalysts appear to be so active in a wide range of chemical reactions that Venuto (1) compared their potentialities with that of enzymes. However, due to the versatility of these solids and the multiplicity of possible active sites the mechanism of action of these catalysts is still under discussion. The reactant molecules entering the porous dehydrated zeolite framework may chemisorb on the Lewis or Brønsted acid sites, or alternatively they may react directly with the cations. Reference to this latter hypothesis has been made to explain some results dealing with dehydrogenation (2), oxidation (3) and isomerization (4) carried out on type X and Y zeolites exchanged with transition metal cations. However, it is known that for dehydrated zeolites the cations are often located in hidden sites (hexagonal prisms and sodalite cages). It is then necessary to consider the possibility for cations to migrate towards the supercages where reagent molecules can interact with them.

Cation migrations have already been reported in comparative studies of hydrated

and dehydrated zeolites (5-9); but as far as we know, only Simpson and Steinfink (10, 11) provide evidence for the formation of complexes in the supercages between cations and adsorbed organic molecules in the case of a Ni-faujasite.

The purpose of this study is to show the probable migrations of the cupric ions occurring on chemisorption of various reagents and to try to elucidate the nature of the resulting complexes. In this paper the results of an X-ray study concerning the copper-sodium Y zeolite,  $\text{Cu}_{16}\text{Na}_{24}\text{Y}$ , are discussed; crystal structures of the dehydrated sample were determined before and after adsorption of ammonia, pyridine and naphthalene. Preliminary results concerning this zeolite have been published in a short communication (12).

In order to corroborate the results obtained with  $\text{Cu}_{16}\text{Na}_{24}\text{Y}$  a similar study was undertaken with a copper-hydrogen Y zeolite,  $\text{Cu}_{12}\text{Na}_5\text{H}_{27}\text{Y}$ . This low sodium content sample was selected because the attribution of the calculated electronic densities is much easier. Crystal structures of the dehydrated sample were determined

before and after naphthalene and butene adsorptions.

### METHODS

The starting material, Linde NaY sieve, was ion exchanged with a  $\text{CuSO}_4$  solution in the conventional way to obtain the CuNaY zeolite. Chemical analysis for both sodium and copper showed the composition of the unit cell to be  $\text{Cu}_{16}\text{Na}_{24}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}$ .

Sample Ia ( $\text{Cu}_{16}\text{Na}_{24}\text{Y}$ ) was dehydrated as follows: the zeolite was first heated in oxygen at  $500^\circ\text{C}$  in order to oxidize adsorbed organic molecules and then evacuated at the same temperature under vacuum ( $10^{-5}$  Torr) for 12 hr.

Sample Ib ( $\text{Cu}_{16}\text{Na}_{24}\text{Y}, x\text{NH}_3$ ) was obtained by equilibrating sample Ia with ammonia; excess ammonia was evacuated at room temperature.

Sample Ic ( $\text{Cu}_{16}\text{Na}_{24}\text{Y}, x\text{C}_5\text{H}_5\text{N}$ ) was prepared by chemisorbing pyridine; excess pyridine was evacuated at  $150^\circ\text{C}$  for 3 hr.

Sample Id ( $\text{Cu}_{16}\text{Na}_{24}\text{Y}, x\text{C}_{10}\text{H}_8$ ) was obtained by adsorbing naphthalene vapor on sample Ia.

The CuHY zeolite was prepared as follows: the Linde NaY sieve was first exchanged to 90% extent with a  $\text{NH}_4\text{NO}_3$  solution and then exchanged with a  $\text{CuSO}_4$  solution. The unit cell composition determined by chemical analysis was  $\text{Cu}_{12}\text{Na}_5(\text{NH}_4)_{27}\text{Al}_{56}\text{Si}_{136}\text{O}_{384}$ . This sample was then heated in oxygen and finally treated under vacuum ( $10^{-5}$  Torr) for 12 hr at  $300^\circ\text{C}$ . This mild treatment was chosen to prevent dehydroxylation of the zeolite framework. The resulting sample had a composition  $\text{Cu}_{12}\text{Na}_5\text{H}_{27}\text{Y}$  and is designated IIa.

Samples IIB ( $\text{Cu}_{12}\text{Na}_5\text{H}_{27}\text{Y}, x\text{C}_{10}\text{H}_8$ ) and IIc ( $\text{Cu}_{12}\text{Na}_5\text{H}_{27}\text{Y}, x\text{C}_4\text{H}_8$ ) were obtained by adsorption of naphthalene and *n*-butene, respectively, on sample IIa.

X-Ray powder diffraction patterns were taken at room temperature using a large diameter Debye-Scherrer camera and a narrow, collimated X-ray beam to assure optimum resolution of lines. A multiple-film technique was used to collect line intensities which were photometered and then planimetered; unresolved lines at high Bragg angles were estimated with a curve ana-

lyzer. Crystal structures of all the samples were determined by usual difference Fourier syntheses and least squares procedures. The ORFLS program (13) was modified in order to calculate line intensity corrections (absorption, Lorentz-polarization and multiplicity factors) and, in each case where more than one plane contributed to a line, to apportion at each iteration the observed intensity among the contributing planes in accordance with  $MF_c^2$  (multiplicity times the square of the calculated structure factor) for the respective planes.

Atomic parameters of framework and extra-framework atoms were refined using 232 structure factors corresponding to all lines with  $h^2 + k^2 + l^2 \leq 395$ , except the 111 line. No attempt has been made to locate adsorbed organic molecules.

A listing of observed and calculated structure factors for all the structures discussed in this paper can be supplied upon request to the authors.

### RESULTS

Cubic unit cell constants and unweighted  $R$  indexes ( $R = \sum |F_o - KF_c| / \sum |F_o|$ ) after final refinements of atomic coordinates, isotropic temperature factors and occupation factors are given in Table 1.

Atomic parameters and interatomic distances calculated with the ORFFE program (14) are given in Table 2. Conventional nomenclature (15) has been used for extra-framework sites.

**1. Sample Ia ( $\text{Cu}_{16}\text{Na}_{24}\text{Y}$ ).** Fourier synthesis showed three main electron-density peaks corresponding to  $S_I$ ,  $S_{I'}$  and  $S_{II}$  sites; the first two were assigned to copper and the last to sodium. After structure refinement 3.2 and 11.1  $\text{Cu}^{2+}$  ions were found in sites  $S_I$  and  $S_{I'}$ , respectively, and 20.5  $\text{Na}^+$  in sites  $S_{II}$ . The difference Fourier map showed a peak in the sodalite cage near  $x = y = z = 0.1$ . This scattering matter (not taken into account in the last refinement) may be tentatively assigned to about five extra-framework oxygen atoms.

**2. Sample Ib ( $\text{Cu}_{16}\text{Na}_{24}\text{Y}, x\text{NH}_3$ ).** In this structure 2.1 and 12.1 cupric ions were found to occupy  $S_I$  and  $S_{I'}$  sites, whereas 17.8 sodium ions occupy  $S_{II}$  sites. Thus

TABLE 1  
 ATOMIC PARAMETERS

Sample	Atom	Population	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Ia ( <i>R</i> = 0.075 <i>a</i> = 24.66 Å)	T	192	0.1244(1)	-0.0530(1)	0.0353(1)	1.2(1)
	O(1)	96	0.1061(2)	-0.1061	0.0	1.5(3)
	O(2)	96	-0.0039(4)	-0.0039	0.1406(5)	4.2(3)
	O(3)	96	0.1798(3)	0.1798	-0.0283(5)	3.5(3)
	O(4)	96	0.1755(3)	0.1755	0.3162(5)	3.9(3)
	Cu(I)	3.2(2)	0.0	0.0	0.0	3.0
	Cu(I')	11.1(2)	0.0439(3)	0.0439	0.0439	3.0
	Na(II)	20.5(1.1)	0.2310(4)	0.2310	0.2310	2.2(7)
Ib ( <i>R</i> = 0.094 <i>a</i> = 24.63 Å)	T	192	0.1248(2)	-0.0530(2)	0.0361(2)	0.7(1)
	O(1)	96	0.1038(4)	-0.1038	0.0	1.8(4)
	O(2)	96	-0.0040(5)	-0.0040	0.1408(6)	3.3(4)
	O(3)	96	0.1807(4)	0.1807	-0.0307(6)	2.4(4)
	O(4)	96	0.1734(4)	0.1734	0.3158(6)	3.2(4)
	Cu(I)	2.1(2)	0.0	0.0	0.0	3.0
	Cu(I')	12.1(4)	0.0500(4)	0.0500	0.0500	3.0
	NH <sub>3</sub> (II')	9.4(1.5)	0.161(2)	0.161	0.161	3.0
	Na(II)	17.8(1.6)	0.2315(7)	0.2315	0.2315	3.1(1.2)
Ic ( <i>R</i> = 0.126 <i>a</i> = 24.66 Å)	T	192	0.1269(2)	-0.0536(2)	0.0351(2)	1.5(2)
	O(1)	96	0.1069(4)	-0.1069	0.0	0.6(4)
	O(2)	96	-0.0047(6)	-0.0047	0.1452(7)	3.0(5)
	O(3)	96	0.1817(6)	0.1817	-0.0337(9)	4.2(6)
	O(4)	96	0.1752(5)	0.1752	0.3183(8)	2.9(6)
	Cu(I)	1.9(3)	0.0	0.0	0.0	3.0
	Cu(I')	2.3(4)	0.043(2)	0.043	0.043	3.0
	Na(II)	26.0(1.5)	0.233(1)	0.233	0.233	5.0
Id ( <i>R</i> = 0.098 <i>a</i> = 24.70 Å)	T	192	0.1254(2)	-0.0527(2)	-0.0352(2)	1.1(2)
	O(1)	96	0.1051(4)	-0.1051	0.0	0.8(4)
	O(2)	96	-0.0048(5)	-0.0048	0.1417(6)	1.9(4)
	O(3)	96	0.1809(5)	0.1809	-0.0306(6)	2.1(5)
	O(4)	96	0.1756(4)	0.1756(4)	0.3183(6)	1.8(4)
	Cu(I)	2.3(2)	0.0	0.0	0.0	3.0
	Cu(I')	3.5(4)	0.046(2)	0.046	0.046	3.0
	Na(II)	22(2)	0.236(1)	0.236	0.236	5.1(1.3)
IIa ( <i>R</i> = 0.082 <i>a</i> = 24.61 Å)	T	192	0.1240(1)	-0.0529(1)	0.0346(1)	1.5(1)
	O(1)	96	0.1063(3)	-0.1063	0.0	2.2(3)
	O(2)	96	-0.0042(4)	-0.0042	0.1378(5)	5.3(4)
	O(3)	96	0.1793(4)	0.1793	-0.0284(6)	5.7(4)
	O(4)	96	0.1757(4)	0.1757	0.3156(6)	5.4(4)
	Cu(I)	1.7(3)	0.0	0.0	0.0	3.0
	Cu(I')	9.9(3)	0.0444(4)	0.0444	0.0444	3.0
	Na(II)	8.0(1.0)	0.232(1)	0.232	0.232	5.0
IIb ( <i>R</i> = 0.101 <i>a</i> = 24.69 Å)	T	192	0.1244(2)	-0.0525(2)	0.0352(2)	1.3(2)
	O(1)	96	0.1047(4)	-0.1047	0.0	0.7(3)
	O(2)	96	-0.0050(4)	-0.0050	0.1396(6)	1.5(4)
	O(3)	96	0.1805(5)	0.1805	-0.0296(7)	2.9(5)
	O(4)	96	0.1761(5)	0.1761	0.3176(7)	2.3(4)
	Cu(I)	2.1(3)	0.0	0.0	0.0	3.0
	Cu(I')	3.2(4)	0.0413(2)	0.0413	0.0413	3.0
	Na(II)	6.8(1.2)	0.231(2)	0.231	0.231	5.0

TABLE 1 (Continued)

Sample	Atom	Population	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
IIc ( $R = 0.089$ $a = 24.69$ Å)	T	192	0.1244(2)	-0.0535(2)	0.0354(2)	1.2(2)
	O(1)	96	0.1054(3)	-0.1054	0.0	0.8(3)
	O(2)	96	-0.0037(4)	-0.0037	0.1413(6)	2.9(4)
	O(3)	96	0.1786(4)	0.1786	-0.0305(6)	2.8(4)
	O(4)	96	0.1731(4)	0.1731	0.3200(6)	1.7(4)
	Cu(I)	1.9(2)	0.0	0.0	0.0	3.0
	Cu(I')	2.7(3)	0.050(2)	0.050	0.050	3.0
	Na(II)	5.8(1.0)	0.238(2)	0.238	0.238	5.0

after adsorption of ammonia a displacement of 1.1 cupric ions from  $S_I$  to  $S_{I'}$  is observed; this last type of site is occupied by 85% of the localized cupric ions. The Cu(I') are probably not uniformly coordinated since too much ammonia was released on thermodesorption; only 25% of these ions are located in a distorted octahedron built up by 3 O(3) and 3 NH<sub>3</sub> molecules.

**3. Sample Ic (Cu<sub>16</sub>Na<sub>24</sub>Y<sub>x</sub>C<sub>5</sub>H<sub>8</sub>N).** After the adsorption of pyridine on sample Ia only 1.9 and 2.3 Cu<sup>2+</sup> ions are left in  $S_I$  and  $S_{I'}$  sites, respectively. Thus about 10 cupric ions are withdrawn mainly from the sodalite cage. No attempt has been made to locate these ions and the pyridine molecules within the supercages, although some electron-density peaks on the difference Fourier map were observed at  $x = y = z = 0.28$  and  $x = y = z = 0.375$ . An X-ray investigation by Simpson and Steinfink (10) of a Ni-faujasite containing adsorbed *m*-dichlorobenzene emphasizes the difficulty of locating the organometallic complexes in the supercages; these authors suggest that both nickel and organic molecules are uniformly distributed in a sphere of 5.8 Å radius throughout each supercage.

**4. Sample Id (Cu<sub>16</sub>Na<sub>24</sub>Y<sub>x</sub>C<sub>10</sub>H<sub>8</sub>).** Naphthalene adsorption on the dehydrated CuNaY sample induces an important migration of cupric ions similar to that observed on pyridine adsorption: 2.3 and 3.5 cupric ions occupy  $S_I$  and  $S_{I'}$  positions, while 8.5 cations are shifted towards the supercages.

**5. Sample IIa (Cu<sub>12</sub>Na<sub>5</sub>H<sub>27</sub>Y).** Almost all cupric ions were located: 1.7 and 9.9 Cu<sup>2+</sup> ions occupy  $S_I$  and  $S_{I'}$  sites, respec-

tively, while  $S_{II}$  sites are filled with 8 Na<sup>+</sup> ions.

**6. Sample IIb (Cu<sub>12</sub>Na<sub>5</sub>H<sub>27</sub>Y<sub>x</sub>C<sub>10</sub>H<sub>8</sub>).** In this sample, 2.1 and 3.2 cupric ions are localized on  $S_I$  and  $S_{I'}$  sites, respectively, while 6.8 Na<sup>+</sup> ions occupy  $S_{II}$  positions. Hence, addition of naphthalene results in a displacement of 6.3 Cu<sup>2+</sup> ions towards the supercages.

**7. Sample IIc (Cu<sub>12</sub>Na<sub>5</sub>H<sub>27</sub>Y<sub>x</sub>C<sub>4</sub>H<sub>8</sub>).** The cation distribution for sample IIc was similar to that found on naphthalene adsorption.

## DISCUSSION

Cation distribution and cation coordination are quite similar in the two dehydrated samples Ia and IIa. The cupric ions exhibit a great affinity for  $S_{I'}$  sites, since they have the opportunity to be firmly bonded to 3 O(3) of the zeolite framework. The Cu(I')-O(3) distance (2.00 and 2.01 Å in samples Ia and IIa, respectively) suggests a partial covalency in the Cu(I')-O(3) bond. The strong interaction between Cu(I') and O(3) atoms induces an important lengthening of T-O(3) bonds with distortion of the TO<sub>4</sub> tetrahedra (1.703 and 1.695 Å in sample Ia and IIa, respectively). The observed coordination for cupric ions in site  $S_{I'}$  is in good agreement with the results obtained by Barry and Lay (16) for metal ions such as Zn<sup>2+</sup> and Co<sup>2+</sup>; these cations prefer sites of specific symmetry rather than those of higher coordination number such as sites  $S_I$ .

Adsorption of ammonia molecules which can enter the sodalite cages increases the number of the  $S_{I'}$  copper ions. However, after elimination of excess ammonia only

TABLE 2  
INTERATOMIC DISTANCES AND ANGLES

Distances (Å)	Sample Ia	Sample Ib	Sample Ic	Sample Id	Sample IIa	Sample IIb	Sample IIc
T-O(1)	1.636(5)	1.618(6)	1.649(8)	1.638(7)	1.626(5)	1.628(7)	1.620(6)
T-O(2)	1.600(5)	1.609(6)	1.619(8)	1.595(7)	1.569(5)	1.582(7)	1.617(6)
T-O(3)	1.703(6)	1.686(8)	1.731(11)	1.713(9)	1.695(7)	1.696(9)	1.683(8)
T-O(4)	1.621(5)	1.591(6)	1.583(8)	1.618(7)	1.634(5)	1.636(7)	1.631(6)
M	1.640	1.626	1.645	1.641	1.631	1.635	1.635
O(1)-O(2)	2.662(10)	2.623(12)	2.604(16)	2.639(13)	2.631(11)	2.610(13)	2.666(12)
O(1)-O(3)	2.732(10)	2.622(14)	2.644(19)	2.663(15)	2.733(13)	2.671(16)	2.691(14)
O(1)-O(4)	2.697(5)	2.715(6)	2.673(8)	2.689(6)	2.695(5)	2.698(6)	2.676(5)
O(2)-O(3)	2.591(9)	2.606(11)	2.710(15)	2.638(11)	2.546(10)	2.598(11)	2.618(11)
O(2)-O(4)	2.615(8)	2.627(11)	2.618(14)	2.644(11)	2.624(10)	2.645(11)	2.694(10)
O(3)-O(4)	2.762(12)	2.714(16)	2.775(23)	2.795(17)	2.742(15)	2.796(12)	2.697(16)
M	2.676	2.651	2.685	2.678			
Cu(I)-O(1)	3.701(9)	3.615(13)	3.727(15)	3.672(13)	3.699(10)	3.655(13)	3.681(12)
Cu(I)-O(2)	3.469(11)	3.471(15)	3.586(18)	3.505(14)	3.395(13)	3.451(14)	3.492(14)
Cu(I)-O(3)	2.545(11)	2.528(14)	2.521(21)	2.529(15)	2.558(14)	2.534(17)	2.604(15)
Cu(I')-O(2)	2.909(11)	2.922(15)	3.019(19)	2.958(15)	2.855(13)	2.917(15)	2.933(16)
Cu(I')-O(3)	2.002(11)	2.098(11)	2.088(28)	2.059(20)	2.012(14)	2.008(20)	2.124(25)
Cu(I')-NH <sub>2</sub> (II')	3.05(4)						
Na(II)-O(2)	2.369(12)	2.368(17)	2.296(21)	2.416(18)	2.445(22)	2.405(31)	2.456(45)
Na(II)-O(4)	2.857(11)	2.899(15)	2.916(19)	2.928(16)	2.843(16)	2.870(20)	3.044(29)
Angles (°)							
O(3)-Cu(I)-O(3)	84.9(4)	87.0(5)	89.7(7)	87.0(5)	84.8(5)	86.1(6)	86.1(5)
O(3)-Cu(I')-O(3)	115.9(2)	111.1(4)	115.0(1.5)	114(1)	115.9(2)	116.7(6)	112(1)
O(2)-Na(II)-O(2)	111.9(3)	111.6(5)	111.3(8)	108.9(7)	111(1)	112(2)	105(2)

small amounts of  $\text{NH}_3$  are still attached to the cations, so that only 25% of the  $\text{Cu}(\text{I}')$  can be bonded to 3 O(3) ions and to 3  $\text{NH}_3$  molecules simultaneously. The remainder should be coordinated as in sample Ia. The interaction between the available ammonia and  $\text{Cu}(\text{I}')$  ions produces a slight shift of the cations towards the inside of the sodalite cages and, simultaneously, a slight decrease of the interaction between the framework oxygen atoms and the copper cations. However, it is expected that adsorption of large amounts of ammonia would probably induce migration of cupric ions towards the supercages to form  $\text{Cu}(\text{NH}_3)_6^{2+}$  complexes.

Addition of pyridine or naphthalene to the dehydrated zeolite provided different results because the size limitation of the sodalite cage openings prevents any organic molecule to enter the cavities. In samples Ic and Id, the cupric ions essentially deposited from  $\text{S}_{\text{I}'}$  sites are displaced towards the supercages in order to form organometallic complexes. The number of the migrating ions per unit cell fits that of the supercages and hence each large cavity would contain a complexed cupric ion. In the same way, on naphthalene or butene addition to sample IIa, cupric ions are displaced from their initial location towards the supercages in about the same amount as that noticed for sample Ic and Id.

Before discussing the nature and the structure of the organometallic species, the consequences of the formation of such species have to be examined. One can think that complexed copper ions are no longer available in order to balance the net negative charges, especially those distributed on the two six-membered rings of the hexagonal prisms. Therefore, proton transfer from the aromatic hydrocarbon towards the six-membered rings is needed in order to restore the charge equilibrium. This should be possible if the aromatic species are ionized. This hypothesis is supported by the following observations.

The T-O(3) bonds were noticed to be considerably lengthened as far as sample Ia is concerned, because of the strong interaction between the  $\text{Cu}(\text{I}')$  and the O(3)

atoms. Then one could expect, since the number of copper ions in sites  $\text{S}_{\text{I}'}$  is greatly reduced in samples Ic and Id, that the T-O(3) distance should be similar to the other T-O distances; however, this does not occur. Consequently, the elongation of the T-O(3) bonds, in the absence of important amounts of cupric ions in the  $\text{S}_{\text{I}'}$  positions, should be explained by means of proton transfers from the ionized organic species to the O(3) lattice oxygen atoms where they generate silanol groups  $\text{Si-O(3)-H}$ . This interpretation has been fully corroborated by infrared measurements discussed below. Except for two weak bands at 3745 and 3680  $\text{cm}^{-1}$  the infrared spectrum of sample Ia showed no other band in the hydroxyl stretching region. However, upon addition of carefully dehydrated naphthalene to this solid a strong band appeared at 3550  $\text{cm}^{-1}$ , whereas no band appeared in the  $\text{H}_2\text{O}$  bending region at 1640  $\text{cm}^{-1}$ . The appearance of this band is of interest since it was assigned to O(3)-H groups by many authors studying deca-cationated zeolites (17, 18). Thus, this result fits well with the explanation suggested above.

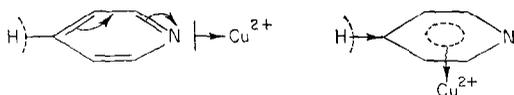
On the other hand, adsorption of pyridine on the dehydrated sample did not give rise to a band at 3550  $\text{cm}^{-1}$ ; however, addition of deuterated pyridine ( $\text{C}_5\text{D}_5\text{N}$ ) gave rise to several characteristic bands. It is not our purpose to discuss here the attributions of all these bands; however, one which appeared at 1366  $\text{cm}^{-1}$  is assigned in agreement with Pichat *et al.* (19) to  $\text{C}_5\text{D}_5\text{ND}^+$  ions. The formation of these species necessarily requires a preliminary ionization of the pyridine and subsequent formation of acidic OD groups which can transfer their deuterium to the N atom of the organic base.

The possibility for electrostatic fields associated with bivalent cations to polarize or even fracture sorbed organic molecules has already been suggested by Pickert *et al.* (20). Richardson (21) postulated that high electron affinity cations such as  $\text{Cu}^{2+}$  ionize aromatic molecules and an electron transfer probably occurs from the aromatic nucleus to the orbitals of the cations. More-

over, ESR studies in this laboratory showed that the CuNaY zeolite ionizes pyridine molecules providing charge transfer complexes.

According to the results obtained in this study, the following models are suggested. Stable associations are formed at room temperature throughout the supercages between the migrating  $\text{Cu}^{2+}$  ions and the sorbed molecules, the electron cloud of the aromatic nuclei being shifted towards the  $d$  orbitals of  $\text{Cu}^{2+}$  ions. Thus protons are released from the electron deficient molecules and they may react with framework oxygen atoms O(3) in order to form hydroxyl groups. Although no suitable data are available in order to describe precisely the structure of the organometallic complexes, some suggestions may be made. Concerning sample Id the only possible bonds are those which occur by the transfer of  $\pi$  electrons to the  $d$  orbitals of the cupric ions. The oxidation of aromatic molecules provides positive naphthalene radicals which have been actually detected by ESR spectroscopy and such positive radicals may release protons. A reasonable assumption about the steric conformation of copper-naphthalene complexes may be that copper is sandwiched between two naphthalene molecules.

In sample Ic, copper ions are either associated with pyridine molecules in ferrocene-like species or bonded to pyridine molecules via nitrogen atoms. In any case the mobility of  $p$ -hydrogen should be increased:



In sample IIc, the double bond  $\pi$  electrons of  $n$ -butene molecules may provide electron transfer to the copper  $d$ -orbitals. Interaction between cupric ions and naphthalene or butene in samples IIb and IIc probably releases protons from the organic molecules as reported for sample Ic and Id. These protons are expected to react with the framework oxygen atoms and hence formation of new O(3)-H hydroxyl groups is probable; however, since hydroxyl groups

are present in this copper-hydrogen zeolite, the formation of additional groups will be difficult to show experimentally.

### CONCLUSION

This study has clearly shown that the cupric ions when introduced in the zeolite porous framework are in no case uniquely located. It has been demonstrated that their mobility and their final location depends essentially on the nature of the sorbed reagent. Thus adsorption of reagents which can penetrate into the sodalite cages (ammonia) does not produce important displacements of cations when introduced in small amounts, whereas for large reagent molecules which cannot enter the sodalite cages (pyridine, naphthalene, butene) an important migration of the cupric ions from the initial hidden sites to surface sites is observed.

Interaction between cupric ions and pyridine or naphthalene molecules provides ionized species and may result in a proton transfer from these species to oxygen atoms of the zeolite framework. This proton transfer is necessary to neutralize the net negative charges, particularly those of the six-membered oxygen rings of the hexagonal prisms. Transferred protons react with O(3) oxygen atoms allowing the formation of O(3)-H hydroxyl groups and these are detected both by infrared techniques (sample Id) and X-ray diffraction as suggested by the unusual lengthening of the T-O(3) bonds (samples Ic and Id). These results contribute to a better understanding of the role of cations in catalytic reactions carried out on Y-type zeolites. The displaced cations may be directly involved in the ionization or the dissociation of reagent molecules and the species generated can then act in two ways: they may react directly with other molecules or they may release protons which are involved in many catalytic reactions as Brønsted sites.

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