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Comparison of cupric ion location and adsorbate interactions in Cu(II)-exchanged H-SAPO-5 and H-SAPO-11 molecular sieves determined by electron spin resonance and electron spin echo modulation spectroscopies

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The locations and interactions of cupric ion exchanged into H-SAPO-11 and H-SAPO-5 molecular sieves with water, methanol, ethanol, ammonia, ethylene and pyridine have been compared by electron spin resonance and electron spin echo modulation spectroscopies. After dehydration, equilibration with ethylene and pyridine adsorbates was slower compared with that for more polar adsorbates. One major difference between these two molecular sieves in cupric ion coordination to adsorbates is that two waters are coordinated in CuH-SAPO-11 while three waters are coordinated to cupric ion in CuH-SAPO-5. This indicates different coordination sites for the cupric ion in these two molecular sieves of rather similar structure. By considering a particular location of the cupric ion, these coordination numbers can be understood, however. Another major difference involves coordination to ammonia; four ammonias are coordinated to cupric ion in CuH-SAPO-11 consistent with the cupric ion being located in the center of a 10-ring channel, while only three ammonias are coordinated in cupric ion to CuH-SAPO-5. This indicates a different coordination site for cupric ion between these two molecular sieves also with ammonia adsorbate. The coordination site in the SAPO-5 material for cupric ion is suggested to be the same for ammonia coordination and water coordination and is different from the site for water coordination in the SAPO-11 material.

Keywords: Aluminosilicate zeolites; SAPO molecular sieve structures; aqueous solution ion exchange; cupric ion; SAPO-5 structures; SAPO-11 structures; electron spin resonance (ESR) spectroscopy; electron spin echo modulation (ESEM) spectroscopy; catalytic activity

1. Introduction

The efficacy of the aluminosilicate zeolite molecular sieves is well known in catalysis. Microporous aluminophosphate molecular sieves or $AlPO_4$ materials have been synthesized since 1982 [1]. These materials have a neutral framework

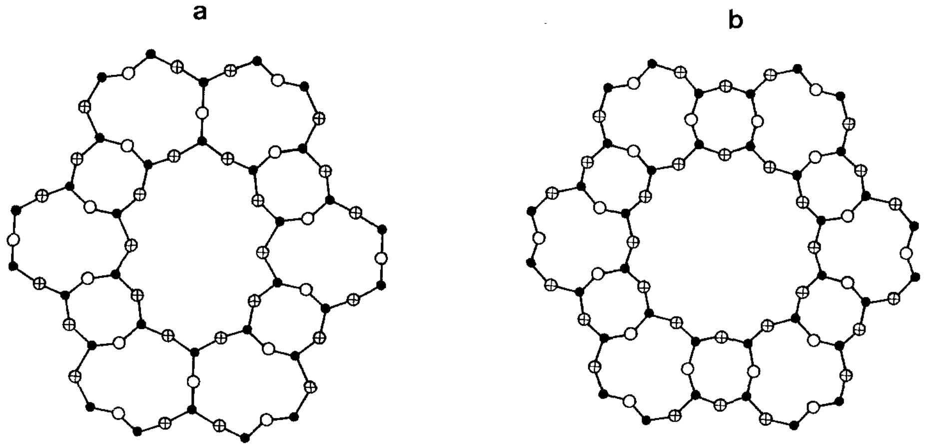

Fig. 1. View along the large central ring channel axis of SAPO-11 (a) and SAPO-5 (b) where the solid circles are Al, P or Si (T atoms) and the open circles (with or without a plus sign) are O; the open circles correspond to oxygens below the plane of the T atoms in a given ring and the circles containing pluses correspond to oxygens above this plane. The smallest and next smallest rings are called 4-rings and 6-rings respectively, while the large ring is an elliptical 10-ring in SAPO-11 and a circular 12-ring in SAPO-5.

and no ion exchange capacity. However, the addition of silica into the aluminophosphate structure introduces both ion exchange capacity and catalytic activity [2]. More silicon substitutes for phosphorous than for aluminum so there is a net negative charge for the SAPO framework. Thus, SAPO materials show some cation exchange capacity although the amount is much less than for comparable zeolite materials. The SAPO molecular sieve structures that have been determined include some that are also found in zeolite materials and some that are unique to the $AlPO_4$ and SAPO systems.

Here we compare the incorporation by aqueous solution ion exchange of cupric ion into the SAPO-5 and SAPO-11 structures which do not have analogs in zeolite structures. These structures are shown in fig. 1 in which it can be seen that SAPO-5 consists of 4-, 6- and 12-rings while SAPO-11 consists of 4-, 6- and 10-rings. The local environment of cupric ion exchanged into these two materials is compared by electron spin resonance (ESR) and electron spin echo modulation (ESEM) spectroscopies. ESEM is particularly useful in determining the distances to deuterium in specifically deuterated adsorbate molecules which leads to the coordination geometry of the cupric ion [3]. In this work we focus on the differences in coordination of cupric ion between these two SAPO molecular sieve structures which can have relevance for their possible differential catalytic activity.

2. Experimental

The molecular sieves H-SAPO-11 and H-SAPO-5 were synthesized according to the Union Carbide patent [4] with modification made in our laboratory [5,6]. Cupric ion was exchanged into these materials with an aqueous solution of cupric nitrate to the extent of less than one cupric ion per three unit cells. After drying, the exchanged SAPO materials were loaded into 3 mm o.d. × 2 mm i.d. Suprasil quartz ESR tubes and dehydrated under vacuum for 12 h at 480°C to achieve complete dehydration as monitored by ESEM. The samples were then heated at 480°C under 500 Torr of dry oxygen for 6 h to reoxidize any reduced cupric ions. After removal of the oxygen, adsorbates including water, methanol, ethanol, ammonia, ethylene and pyridine from Stohler Isotopes and Aldrich Chemicals with complete and partial deuteration were adsorbed at room temperature at ambient vapor pressure or at 200–300 Torr for gases.

The ESR spectra were measured at 77 K on a Varian E-4 spectrometer. ESEM spectra were recorded at 4 K on a home-built spectrometer described elsewhere [7]. Typically three-pulse echoes are reported and the simulation of the echo modulation pattern has been described [3].

3. Results and discussion

The ESR spectra of the hydrated SAPO materials show a major cupric ion species with $g_{\parallel} \approx 2.37$ and other parameters characteristic of distorted octahedral symmetry [4,5]. After dehydration the $g_{\parallel}$ value decreases to ≈ 2.30 and the parallel hyperfine splitting constant increases. Thus the $g_{\parallel}$ value can be used to monitor the degree of dehydration and the subsequent adsorbate interaction when the dehydrated sample is exposed to various adsorbates. After exposure to polar adsorbates such as water, methanol and ethanol the $g_{\parallel}$ value changes to ≈ 2.37 in less than 1 h. However, for less polar adsorbates such as pyridine and ethylene the development of the $g_{\parallel}$ value to ≈ 2.37 takes more than 10 h, and ethylene takes longer than pyridine in SAPO-11. These kinetics have not been studied in detail, but it seems clear that cupric ion migrates to a new site in the process of dehydration and to another site after exposure to these various adsorbates. Subsequent ESEM analysis after coordination with various adsorbates gives the results in table 1. Major parameters are the number and the distance from the cupric ion of interacting adsorbate deuteriums. For example, if there are four interacting deuteriums from deuterated water one concludes that two molecules of water are coordinated to the cupric ion. Also, the distance tells whether or not the coordination is direct. For example a distance from copper to deuterium of water of 0.27–0.28 nm indicates direct coordination to a cation consistent with a cupric ion to oxygen(D_2O) distance of 0.21–0.22 nm which corresponds to the sum of the crystallographic ionic radii of cupric ion

Table 1
Simulated ESEM parameters for cupric ion with various adsorbates in CuH-SAPO-5 and CuH-SAPO-11

Adsorbate	N [a]	R [b] (nm)	No. of molecules	Site
CuH-SAPO-5				
D_2O	6	0.29	3	II_2^*
CH_3OD	2	0.28	2 [c]	II_2^*
C_2H_5OD	2	0.28	2	II_2^*
NH_3	–	–	3 [d]	II_2^*
CuH-SAPO-11				
D_2O	4	0.28	2	II_1^*
CH_3OD	2	0.28	2 [c]	II_1^*
C_2H_5OD	2	0.27	2	II_1^*
NH_3	–	–	4 [d]	U

[a] Number of deuteriums.
[b] Distance between Cu(II) and deuterium (±0.01 nm).
[c] There is a third nondirectly coordinated molecule observed in an adjacent large ring.
[d] This was determined by resolved ^{15}N hyperfine in the ESR spectrum.

and oxygen in D_2O. It can be seen from table 1 that the coordination of cupric ion in SAPO-5 versus SAPO-11 molecular sieve is the same for methanol and ethanol but are different for water and ammonia adsorbates.

In the case of ammonia adsorbate, resolution of the nitrogen coupling in the ESR spectrum is found. This was more clearly determined by using $^{15}NH_3$ to detect the number of interacting nitrogens because the ^{15}N has a nuclear spin of 1/2.

Fig. 2 shows the structure of SAPO-11. Fig. 2a shows a view looking down the c-axis into the 10-ring and the dashed lines at the borders of the 10-ring represent 6-ring edges in the faces of the 10-ring channel which are probable positions for cation location by analogy to cation locations in zeolites. The 6-ring locations are denoted as site II by analogy to the 6-ring locations in zeolites. Notice that there are two different II positions in the SAPO-11 materials which are denoted as II_1 and II_2. The II position corresponds to a position in the plane of three oxygens in the 6-ring window whereas II^* corresponds to displacement from that position out towards the 10-ring and II' corresponds to displacement of that position back into the 6-ring. This is shown more clearly in fig. 2b. Also note that site I is in the center of a double 6-ring and site U is in the center of a 10-ring.

In SAPO-5 the structure is somewhat different in that only one type of site II exists which corresponds to the II_2 position in SAPO-11. We conclude that sites II_1^* and II_2^* are not both populated after incorporation of the cupric ion by ion exchange. Note that site II_1 is in a more constrained environment than site II_2. Because of the differences between the results in SAPO-5 and SAPO-11, we

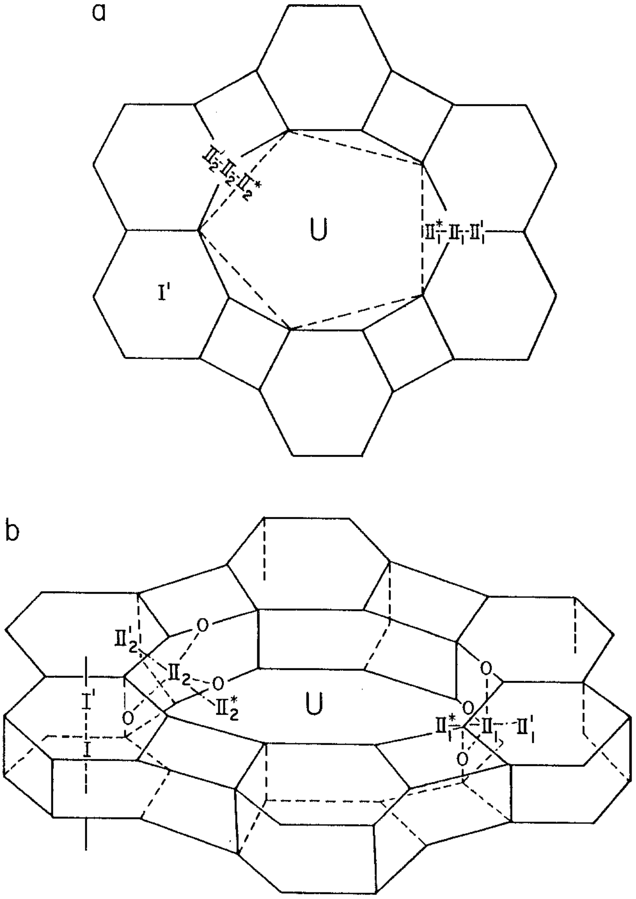

Fig. 2. (a) View along the elliptical 10-ring channel axis of SAPO-11 where the dashed lines show edges of 6-ring windows that form the surfaces of a 10-ring channel. (b) A simplified structure of SAPO-11 showing possible cation positions. See text for description of the cation positions.

conclude that the cupric ion must be in different locations in these two SAPO materials. Thus, since the II_1 site is unique to SAPO-11, we suggest that it is the site preferably occupied by cupric ion in SAPO-11. In SAPO-5 there is only one type of II site which corresponds to the II_2 site in SAPO-11.

After this discussion of the structural differences between SAPO-5 and SAPO-11 we can now interpret the data given in table 1. In CuH-SAPO-5 the cupric ion is initially exchanged into site II* and on dehydration the cupric ion moves into a double 6-ring in site I or site I′ which is displaced from the center of the double 6-ring. This corresponds to the change in the $g_{\parallel}$ value of the cupric ion as observed experimentally. After subsequent exposure to a polar adsorbate [5] such as water, alcohol or ammonia the cupric ion moves from the double 6-ring to site II* (which is equivalent to II_2^* in the SAPO-11 structure) and interacts with three oxygens of the 6-ring and three water molecules or three ammonia molecules to give a distorted octahedral environment for the cupric ion.

In CuH-SAPO-11 the copper is initially exchanged into site II_1^* and on dehydration it moves into the 6-ring in sites I or I′. Then after subsequent exposure to water it moves back into site II_1^* where because of the more constrained environment it coordinates to only two water molecules in addition to three oxygens of the 6-ring.

In the case of ammonia adsorbate the copper moves all the way to site U where it coordinates to four ammonia molecules. The size of the 10-ring is such that the nitrogens of the four ammonia molecules can coordinate to copper with the hydrogens of the ammonia molecules being able to interact favorably, perhaps through a type of hydrogen bonding interaction, with the oxygens of the 6-ring faces of the 10-ring channels. Site U is not a good coordination site for cupric ion interacting with ammonia in the 12-ring of SAPO-5 since the 12-ring is larger than the 10-ring of SAPO-11. In SAPO-5 site U is therefore not as easily stabilized by hydrogen bonding with oxygens from the 6-ring faces of the 12-ring channel.

4. Conclusions

These results show that ESEM spectroscopy can be used effectively to determine cupric ion–adsorbate structures and interactions in SAPO molecular sieve materials. It is particularly interesting that the cupric ion–water and the cupric ion–ammonia coordinations differ between the SAPO-11 and SAPO-5 structures. However, an evaluation of the framework structural differences of these two SAPO molecular sieves appears to give a reasonable explanation for these coordination differences. The determination of the cupric ion location and adsorbate geometry in these SAPO structures is potentially useful for understanding and controlling transition metal ion catalysis in SAPO molecular sieves.

Acknowledgement

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