



## Cupric Ion Species in Cu(II)-Exchanged Mesoporous MCM-41 Gallosilicate Determined by Electron Spin Resonance Studies

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**Abstract:** Mesoporous MCM-41 gallosilicate material was synthesized through shifting gallosilicate polymer equilibrium towards a MCM-41 phase by addition of acid. The location of Cu(II) exchanged into MCM-41 and its interaction with various adsorbate molecules were investigated by electron spin resonance and electron spin echo modulation spectroscopies. It was found that in the fresh hydrated material, Cu(II) is octahedrally coordinated to six water molecules. This species is located in a cylindrical channel and rotates rapidly at room temperature. Evacuation at room temperature removes three of these water molecules, leaving the Cu (II) coordinated to three water molecules and anchored to oxygens in the channel wall. Dehydration at 450 °C produces one Cu (II) species located in the inner surface of a channel as evidenced by broadening of its ESR lines by oxygen. Adsorption of polar molecules such as water, methanol and ammonia on dehydrated CuNa-MCM-41 gallosilicate material causes changes in the ESR spectrum of Cu (II), indicating the complex formation with these adsorbates. Cu(II) forms a complex with six molecules of methanol as evidenced by an isotropic room temperature ESR signal and ESEM data like upon water adsorption. Cu(II) also forms a complex containing four molecules of ammonia based on resolved nitrogen superhyperfine interaction.

### INTRODUCTION

Recently, a new family of mesoporous materials, designated as M41S, with pore diameters in the range between 2 nm and 10 nm has been reported by Mobil scientists.<sup>1,2</sup> An exciting property of these M41S materials is the possibility to control the pore size by using surfactants with different molecular sizes and auxiliary organic species during crystallization process. One member of these M41S family is MCM-41 which consists of a hexagonal array of parallel one dimensional channels with an internal diameter of about 3 nm and 1 nm wall thickness.<sup>3,4</sup> The novelty in synthesis of the MCM-41 is the use of surfactant micelles, around which silicates polymerize hydrothermally to form the matrix structure. The large channel diameter and its tailorability provide new opportunity as

supports for catalysts, hosts for the inclusion of compounds and nanosize clusters, and molecular sieves for large molecules.<sup>3-5</sup>

The incorporation of gallium into a pure silica MCM-41 framework causes a negative charge of the framework that is compensated by sodium cations introduced during synthesis procedure.<sup>6,7</sup> Therefore, we expect that gallium containing MCM-41 will possess an ion-exchange capacity of sodium ion by paramagnetic transition metal ions as found in zeolite and SAPO-n materials. As in zeolite, such transition metal ion species may offer potential for specially tailored catalytic applications of the MCM-41 gallosilicate materials.

In this work, we report for the first time the synthesis of mesoporous MCM-41 gallosilicate materials with uniform hexagonal array of cylindrical pores through shifting gallosilicate polymerization equilibrium by addition of acid during the conversion of gallosilicate and  $N(\text{Me})_3(\text{C}_{16}\text{H}_{33})\text{Cl}$  to an MCM-41 phase. The location of Cu(II) in Cu-MCM-41 gallosilicate and its interaction with adsorbates are explored by electron spin resonance (ESR) and electron spin echo modulation (ESEM) spectroscopies.

## EXPERIMENTAL SECTION

### *Synthesis and Ion Exchange*

A typical mesoporous MCM-41 gallosilicate material has been synthesized based on modification of the procedure described by Ryoo et. al.<sup>8</sup> A surfactant source was obtained by dissolving 1.20 g of dodecyltrimethylammonium (DTA) bromide (from Aldrich) and 1.04 g of tetrapropylammonium (TPA) bromide (from Aldrich) in a mixture of 20.00 g of 25 wt% aqueous solution of hexadecyltrimethylammonium chloride (HTACl), 0.29 g of 28 wt% aqueous  $\text{NH}_3$  solution, and 10.00 g of doubly distilled water. A clear solution of sodium silicate with a Na/Si ratio of 0.5 was prepared by combining 46.90 g of 1.00 M aqueous NaOH solution with 14.30 g of a colloidal silica, Ludox HS40 (39.5 wt%  $\text{SiO}_2$ , 0.4 wt%  $\text{Na}_2\text{O}$  and 60.1 wt%  $\text{H}_2\text{O}$ , from Aldrich) and heating the resulting gel mixture with stirring for 2 h at 353 K. Gallium source was a solution of 0.22 g of  $\text{Ga}_2\text{O}_3$  (from Aldrich) added in a mixture solution prepared by dissolving 0.18 g of NaOH in 10.00 g of doubly distilled water. The resulting sodium gallate solution was heated to boiling with stirring for about 2 h to form a clear solution, and then cooled to 313 K.

The silicate solution was dropwise added to the surfactant source with vigorous stirring at room temperature. After the resulting surfactant-silicate gel mixture was stirred for 1 h at room temperature, the sodium gallate solution was dropwise added with vigorous stirring. The resulting surfactant - gallosilicate gel mixture had a bulk molar composition of 6.00  $\text{SiO}_2$ : 0.075  $\text{Ga}_2\text{O}_3$ : 1.00 HTACl: 0.25 DTABr: 0.25 TPABr: 0.16  $(\text{NH}_4)_2\text{O}$ : 1.70  $\text{Na}_2\text{O}$ : 315  $\text{H}_2\text{O}$ . The gel mixture was stirred for 30 min more to form a homogeneous mixture before heating in oven at 373 K for 1 day. The HTA-gallosilicate mixture was then cooled

to room temperature. Subsequently, pH of the reaction mixture was adjusted to 10.2 by dropwise addition of 30 wt% acetic acid with vigorous stirring. The reaction mixture after the pH adjustment was heated again to 373 K for 1 day. This procedure for pH adjustment to 10.2 and subsequent heating for 1 day was repeated twice more. The precipitated product, MCM-41 with HTA template, was filtered, washed with doubly distilled water, and dried at room temperature. The dried MCM-41 gallosilicate product was stirred in an ethanol-hydrochloric acid mixture (0.1 mol of HCl/ L of ethanol) for 1 h under reflux conditions. Subsequently, the product was washed with ethanol at room temperature and dried at room temperature. Calcination of the product was carried out in O<sub>2</sub> flow while the sample was heated to 813 K over 10 h and maintained at this temperature for 10 h. Elemental analysis for the Si/Ga ratio was performed with inductively coupled plasma(ICP) emission spectroscopy. The Si/Ga ratio was determined to be 40.0.

This surfactant-free mesoporous MCM-41 gallosilicate was then exchanged at room temperature for 12 h by dropwise addition of a 10 mM solution of cupric nitrate (Alfa Products) according to the procedure described earlier.<sup>9</sup> Copper exchange was 2.2 % by weight of calcined MCM-41 gallosilicate, assuming complete exchange.

### ***Sample Treatment***

The gallosilicate sample was loaded directly into a Suprasil quartz ESR tube (2 mm i.d. by 3 mm o.d.) reactor which could be connected to a vacuum and gas handling line. Dehydration of the sample was carried out by first evacuating the sample at room temperature followed by heating to 200 °C over an 8 h period in a static reactor. In general, gallosilicate is known to have a lower thermal stability than the corresponding aluminosilicate.<sup>6,7</sup> Thus no evacuation was usually made at temperatures higher than 210 °C in this work. Following this evacuation the sample was exposed to 200 ~ 400 Torr of static high-purity dry oxygen for 5 ~ 10 h at 450 °C in order to oxidize any copper species that had been reduced during the heating period. Finally, the oxygen was pumped off at room temperature under a 10<sup>-5</sup> Torr vacuum. This heat treated sample with oxygen is termed as a dehydrated sample.

After dehydration, adsorbates as gases were admitted at room temperature to the sample tubes and left to equilibrate. Deuterated adsorbates such as D<sub>2</sub>O and CH<sub>3</sub>OD, and other isotope substituted adsorbate, <sup>15</sup>NH<sub>3</sub>, were obtained from Aldrich and used after repeated freeze-pump-thaw cycles.

### ***Spectroscopic Measurements***

Mesoporous MCM-41 gallosilicate samples after synthesis, calcination and Cu(II) exchange are examined by powder x-ray diffraction (XRD) with a Philips PW 1840 diffractometer. ESR spectra were measured both at room temperature and 77 K on an ESP 300 Bruker spectrometer. ESEM spectra were recorded with a Bruker ESP 380 pulsed ESR spectrometer at 4.5 K. Three-pulse echoes were measured by using a  $90^\circ$ -t- $90^\circ$ -T- $90^\circ$  pulse sequence with the echo measured as a function of T. The time domain deuterium ESEM patterns were simulated using the spherical averaging approximation. In this procedure the modulation function is simulated and fitted to the experimental data by a least-squares procedure. The parameters are the number of interacting nuclei N, the distance R between the paramagnetic center and the interacting nuclei, and their isotropic hyperfine interaction  $A_{\text{iso}}$ .<sup>10</sup>

## **RESULTS**

### ***X-Ray Diffraction***

Powder XRD measurements were performed before and after calcination of as-synthesized MCM-41 gallosilicate to confirm that the synthesis product has an MCM-41 structure. The XRD patterns show high crystallinity with at least four signals shown in Fig. 1. The spectrum shows an intense peak at  $2q = 2.1^\circ$ , indicating the existence of the hexagonal MCM-41 phase with a spacing about  $d_{100} = 4.2$  nm. Upon calcination, the intense peak slightly shifts to a higher angle  $2q = 2.3^\circ$ , corresponding to a spacing of  $d_{100} = 3.9$  nm. The intensity of the signals upon calcination increases to more than twice that in as-synthesized MCM-41 gallosilicate

### ***Electron Spin Resonance***

The Cu(II) ESR spectral measurements at 77 K and at room temperature of fresh, hydrated Cu-MCM-41 gallosilicates are illustrated in Fig. 2. The fresh, hydrated sample measured at 77 K before evacuation produces an anisotropic ESR signal, denoted as species A characteristic of an axial powder spectrum of Cu(II) as shown in Fig. 2b. Species A has ESR parameters of  $g_{\parallel} = 2.407$ ,  $A_{\parallel} = 144 \times 10^{-4} \text{ cm}^{-1}$ . The hyperfine lines of the perpendicular component are not resolved. A value of  $g_{\perp} = 2.08$  was estimated for the perpendicular component of the g tensor. The ESR spectrum measured at room temperature of fresh hydrated Cu-MCM-41 gallosilicate, however, shows an almost isotropic signal at  $g_{\text{iso}} = 2.186$  with  $\Delta \text{pp} = 144$  G as shown in Fig. 2a. Evacuation at room temperature decreases the isotropic ESR signal of the fresh, hydrated Cu-MCM-41 gallosilicate sample. After about 1 ~ 2 h evacuation at room temperature, the isotropic signal is no longer

observed in the room temperature ESR spectrum. The ESR spectrum measured at 77 K shows development of another new species, denoted as B which has  $g_{\parallel} = 2.385$ ,  $A_{\parallel} = 152 \times 10^{-4} \text{ cm}^{-1}$  and  $g_{\perp} = 2.08$  as shown in Fig. 2c.

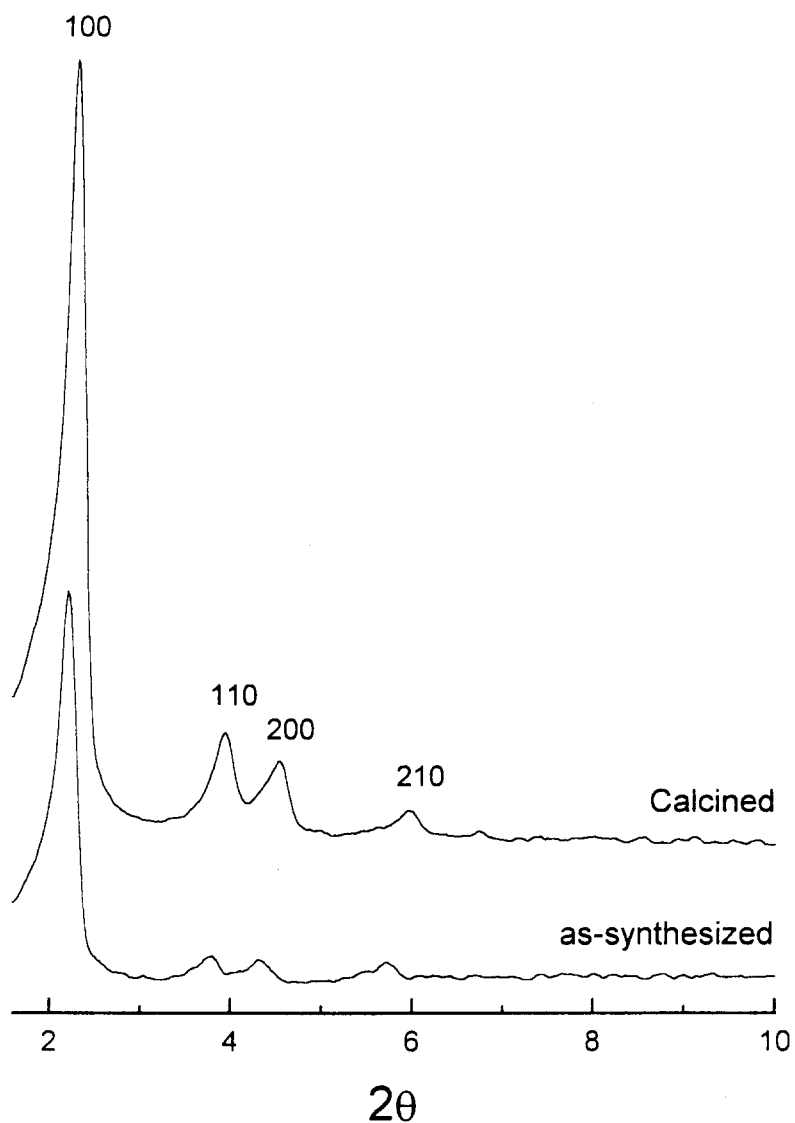


Fig. 1. X-ray powder diffraction patterns of MCM-41 gallosilicate as synthesized sample and as calcined sample.

Evacuation was continued at higher temperatures to 200 °C. Oxygen is then added to the evacuated sample in order to reoxidize any reduced copper species formed during evacuation. Fig. 3a illustrate the development of a new Cu(II) species with  $g_{\parallel} = 2.327$ ,  $A_{\parallel} = 174 \times 10^{-4} \text{ cm}^{-1}$  and  $g_{\perp} = 2.08$  after dehydration. Upon adsorption of 150 Torr of oxygen at room temperature upon dehydrated Cu-MCM-41 sample, the ESR intensity of the Cu(II) species was broadened. After the dehydration treatment, complete rehydration of the

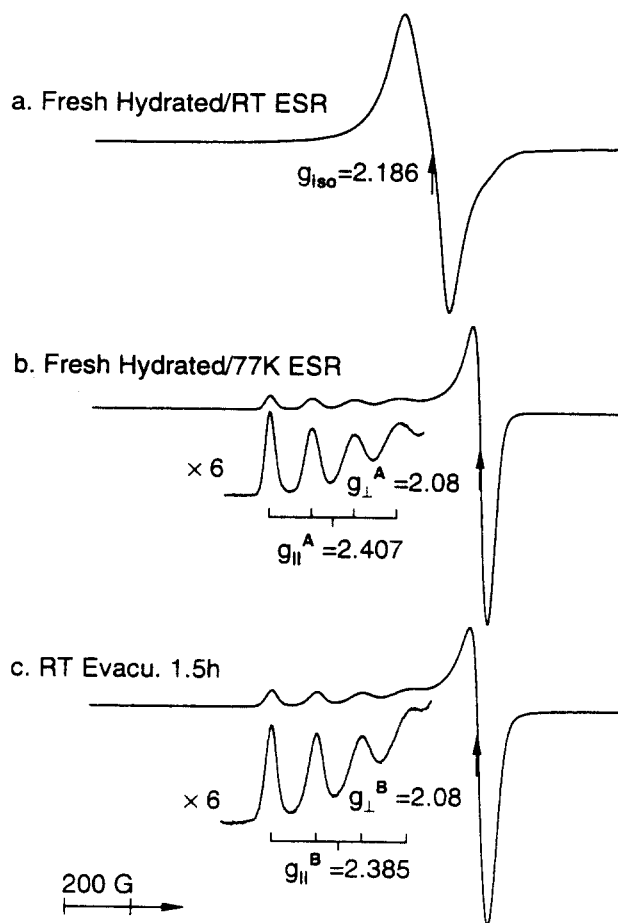


Fig. 2. ESR spectra of fresh hydrated Cu-MCM-41 gallosilicate recorded (a) at room temperature, (b) at 77 K and (c) at 77 K after room temperature evacuation for 1.5 h.

dehydrated sample by exposure to the saturation vapor pressure of water at room temperature regenerates the original species A seen in fresh, hydrated Cu-MCM-41 gallosilicate (see Fig. 2a) which shows a room temperature isotropic ESR signal.

Fig. 3b and 3c show the ESR spectra at 77 K and room temperature observed after adsorption of methanol on dehydrated Cu-MCM-41 gallosilicate. Adsorption of methanol produces an ESR spectrum at 77 K with  $g_{\parallel} = 2.417$ ,  $A_{\parallel} = 137 \times 10^{-4} \text{ cm}^{-1}$  and  $g_{\perp} = 2.08$  as

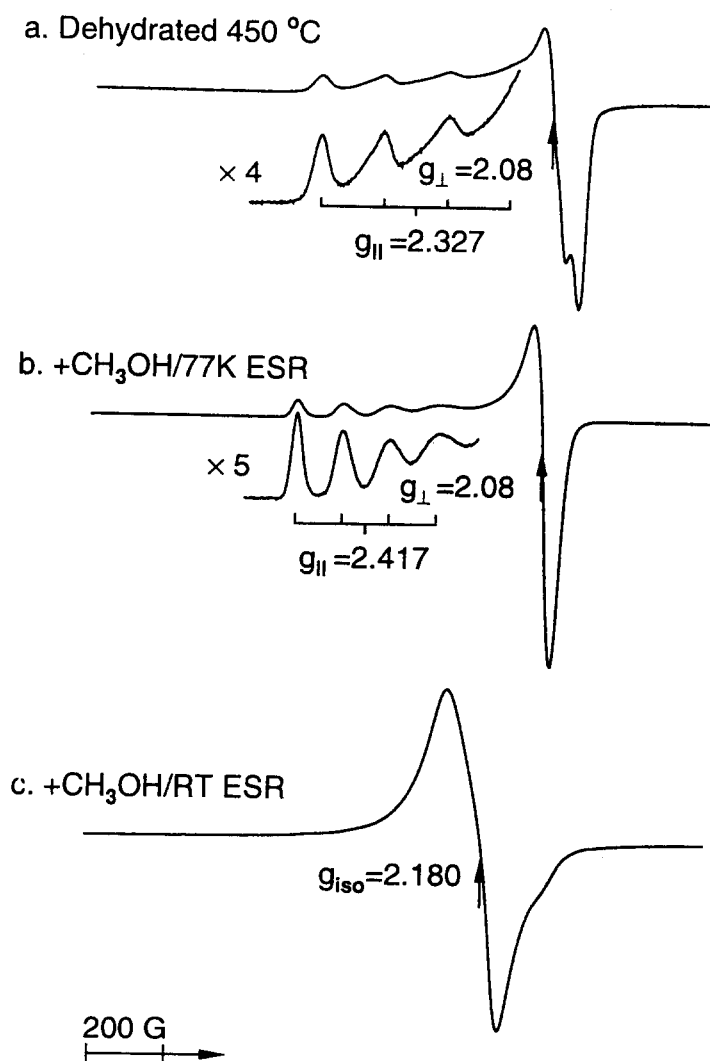


Fig. 3. ESR spectra of Cu-MCM-41 gallosilicate measured (a) at 77 K after dehydration (b) at 77 K and (c) at room temperature after equilibration with methanol at room temperature following dehydration as in (a)

shown in Fig. 3b. However, almost an isotropic signal at  $g_{\text{iso}} = 2.180$  with  $D_{\text{pp}} = 146$  G was observed in the ESR spectrum measured at room temperature almost like upon water adsorption (Fig. 3c).

Fig. 4 shows the ESR spectra at 77 K after adsorption of 30 Torr ammonia gas. The color of the sample turns from pale blue to blue after adsorption. A new cupric ion species due to complex formation with ammonia is observed with ESR parameters of  $g_{\parallel} = 2.279$  and

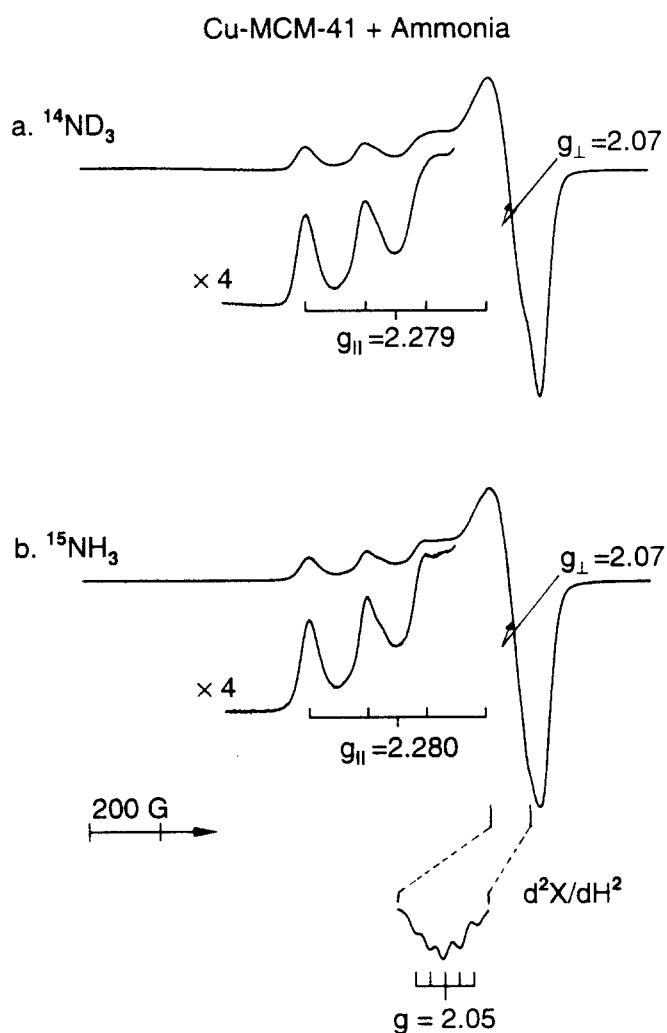


Fig. 4. ESR spectra at 77 K of dehydrated Cu-MCM-41 gallosilicate (a) after adsorption of 30 Torr  $^{14}\text{NH}_3$  and (b) after adsorption of 30 Torr  $^{15}\text{NH}_3$  at room temperature.



Table 1. ESR Parameters at 77 K of Cu(II) in Cu-MCM-41 Gallosilicate After Various Sample treatments

treatment <sup>a</sup>	species	$g_{\parallel}$ <sup>b</sup>	$A_{\parallel}$ <sup>c</sup>	$g_{\perp}$ <sup>b</sup>
fresh/RT ESR		2.186 <sup>d</sup>		
Fresh	A	2.407	144	2.08
evac <sup>a</sup> RT/1.5 h	B	2.385	152	2.08
Dehydrated		2.327	174	2.08
+H <sub>2</sub> O	A	2.406	145	2.08
+CH <sub>3</sub> OH/RT ESR		2.180 <sup>d</sup>		
+CH <sub>3</sub> OH		2.417	137	2.08
+NH <sub>3</sub>		2.279	177	2.07

<sup>a</sup> RT = room temperature.

<sup>b</sup> Estimated uncertainty is  $\pm 0.006$ .

<sup>c</sup> The unit of  $A_{\parallel}$  is  $1 \times 10^{-4} \text{ cm}^{-1}$ . The estimated uncertainty is  $\pm 6 \times 10^{-4} \text{ cm}^{-1}$ .

<sup>d</sup>  $g_{\text{iso}}$  value.

$A_{\parallel} = 177 \times 10^{-4} \text{ cm}^{-1}$ . Cu-MCM-41 gallosilicate with adsorbed  $^{15}\text{NH}_3$  ( $^{15}\text{N}$  has a nuclear spin of 1/2) shows five  $^{15}\text{N}$  hyperfine lines centered at  $g = 2.050$  and split by  $19 \times 10^{-4} \text{ cm}^{-1}$  which are shown in the expanded seconded derivative spectrum. With  $^{14}\text{NH}_3$  ( $^{14}\text{N}$  has a nuclear spin of 1), the ESR spectrum shows more hyperfine lines in the  $g_{\perp}$  region, but they are not clearly resolved. Table 1 summarizes the ESR parameters of Cu(II) in Cu-MCM-41 gallosilicate after various sample treatments.

### Electron Spin Echo Modulation

Three-pulse ESEM spectra and simulation parameters for Cu(II) in dehydrated Cu-MCM-41 gallosilicate interacting with various deuterated adsorbates are shown in Fig. 5 and 6. Fig. 5a shows an ESEM spectrum of dehydrated Cu-MCM-41 gallosilicate fully hydrated with D<sub>2</sub>O which shows an isotropic ESR signal at room temperature. The simulation shown indicates that Cu(II) is interacting with twelve neighboring deuterium nuclei, i.e. six water molecules, with a Cu(II)-D distance of 0.28 nm, which indicates direct coordination. Fig. 5b shows an ESE spectrum of dehydrated Cu-MCM-41 gallosilicate after adsorption of D<sub>2</sub>O followed by evacuation at room temperature for 1 h. The spectrum is

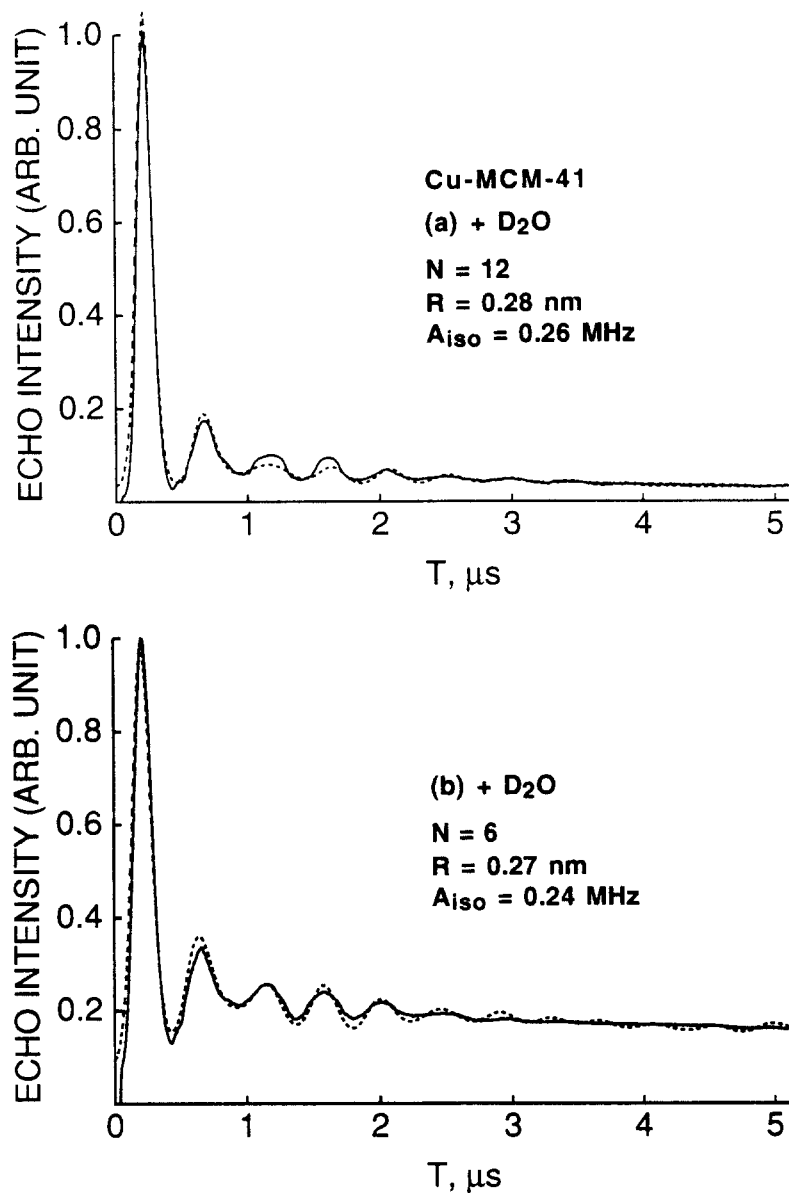


Fig. 5. Experimental (—) and simulated (- - -) three-pulse ESEM spectra recorded at 4.5 K of dehydrated Cu-MCM-41 gallosilicate (a) with adsorbed D<sub>2</sub>O and (b) with adsorbed D<sub>2</sub>O followed by evacuation at room temperature for 1.5 h.

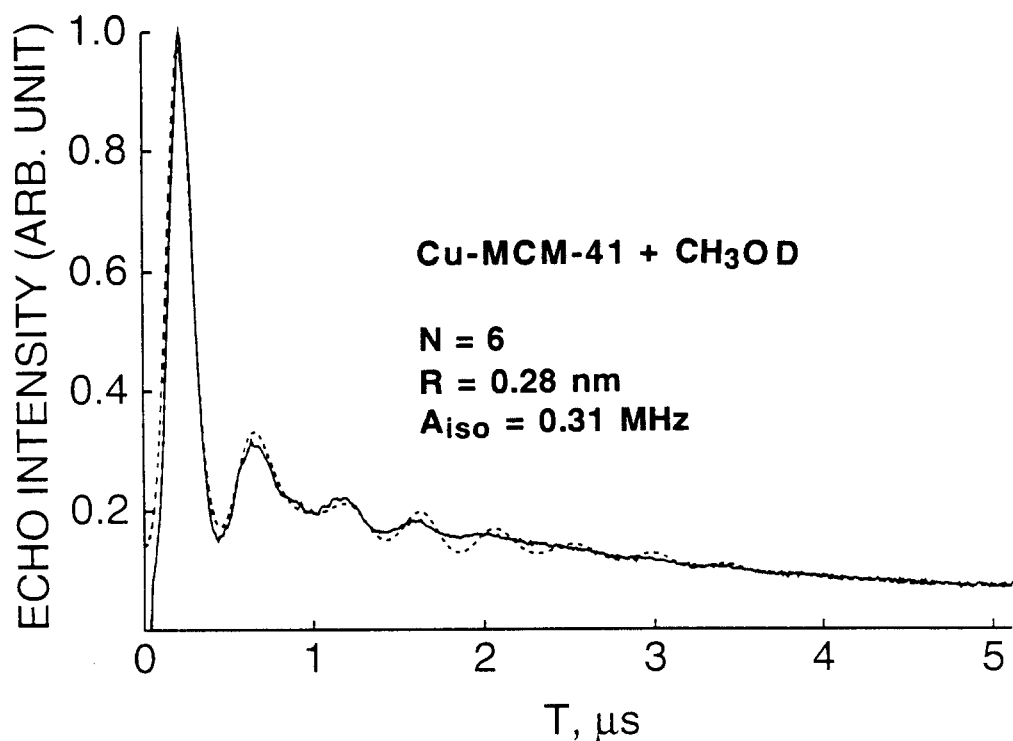


Fig. 6. Experimental (—) and simulated (- - -) three-pulse ESEM spectrum recorded at 4.5 K of dehydrated Cu-MCM-41 gallosilicate with adsorbed CH<sub>3</sub>OD.

best simulated by six deuteriums at 0.27 nm. This indicates that Cu(II) is directly coordinated to only three water molecules after evacuation.

Fig. 6 shows a three-pulse ESEM spectrum of dehydrated Cu-MCM-41 gallosilicate with adsorbed CH<sub>3</sub>OD. The simulation for CH<sub>3</sub>OD indicates interaction with six deuterium nuclei, i.e. six methanol molecules, with a Cu(II)-D distance of 0.28 nm.

## DISCUSSION

ESR and pulsed ESR known as ESEM are powerful tools for the exploration of the location of exchanged paramagnetic transition metal ions and their adsorbate interactions in

microporous materials such as zeolites.<sup>11,12</sup> The specific ion exchange sites are determined by the symmetry of the transition metal site, its accessibility to different adsorbates, and the number of coordinated adsorbate molecules in such crystalline microporous structures with well-defined nonframework sites. However, the determination of the location of ion-exchanged transition metal ions in more amorphous materials such as MCM-41 is more complicated since nonframework sites are poorly determined. The changes in the ESR parameters of dehydrated Cu-MCM-41 gallosilicate after adsorption of various adsorbate molecules indicate that the adsorbates interact with the Cu(II) ion. The Cu(II) spin Hamiltonian parameters usually provide some guide to the overall coordination symmetry of the metal ion site based on extensive studies of known Cu(II) crystalline compounds. In general,  $A_{\parallel}$  increases from  $\sim 0.007 \text{ cm}^{-1}$  for tetrahedral symmetry, through distorted octahedral and square pyramidal symmetry, to  $\sim 0.017 \text{ cm}^{-1}$  for square-planar symmetry, whereas  $g_{\parallel}$  decreases from 2.516 to 2.245 for this sequence of coordination symmetries.<sup>13,14</sup> Together with the number of adsorbed molecules determined by ESEM and a comparison with known Cu(II) locations in zeolites, the Cu(II) ESR parameters provide information about the coordination and location of Cu(II) ions exchanged into MCM-41 gallosilicate.

The fresh hydrated Cu-MCM-41 gallosilicate gives an ESR spectrum predominantly consisting of a broad isotropic line at ambient temperature (Fig 2a). Such an isotropic ESR signal at room temperature is indicative of a rotating species. Analysis of the three-pulse ESEM spectrum (Fig. 5a) of dehydrated gallosilicate rehydrated with D<sub>2</sub>O indicates twelve nearest deuteriums corresponding to a water solvation number of six around Cu(II), i.e.  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . A similar broad isotropic ESR signal has been observed at room temperature for Cu(II) in L zeolite<sup>15</sup> and in other zeolites<sup>16,17</sup> and was assigned to  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  from ESR and ESEM analyses. At 77 K this  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  complex becomes immobilized and gives rise to an asymmetric spectrum as shown in Fig. 2b. Mesoporous MCM-41 molecular sieve consists of hexagonal array of cylindrical mesopore channels whose diameter is about 3.0 nm. The internal area of the channel is large enough to accommodate a hexaaquo complex with a diameter of about 0.67 nm.

When the hydrated sample is evacuated at room temperature, the isotropic ESR component decreases. After 1 ~ 2 h of evacuation, the ESR signal shows another species B. This is indicative of the copper losing some water ligands and becoming immobilized by coordination to several lattice oxygens. Three-pulse ESEM (Fig. 5b) indicates that Cu(II) species B is now coordinated to three water molecules. Cu(II) species B is presumably also coordinated to several oxygens in the inner surface of a channel.

Upon dehydration, the ESR spectrum shows the formation of a new Cu(II) species ( $g_{\parallel} = 2.327$  and  $A_{\parallel} = 174 \times 10^{-4} \text{ cm}^{-1}$ ) (Fig. 3a). Based on the spin Hamiltonian parameters, the Cu(II) species is likely to have distorted octahedral or square pyramidal symmetry. Since compared to those of the octahedral Cu(II) species A,  $g_{\parallel}$  value decreases and  $A_{\parallel}$  value

increases more close to the parameters of square planar symmetry, the Cu(II) species in dehydrated sample is more likely to have square pyramidal symmetry with five oxygen atoms in the lattice surface of a mesopore than to have distorted octahedral symmetry. After such dehydration, the Cu(II) species shows broadening of its ESR lines upon oxygen adsorption at room temperature. Thus Cu(II) species in dehydrated MCM-41 gallosilicate is likely to be located near the inner surface of the mesopore which can be exposed to oxygen. After dehydration, the samples were examined by powder X-ray diffraction and there was no loss of crystallinity.

Adsorption of methanol on dehydrated Cu-MCM-41 gallosilicate produces an anisotropic Cu(II) species (Fig. 3b) in 77 K ESR spectrum. The ESR parameters are consistent with octahedral symmetry.<sup>13,14</sup> However, almost an isotropic signal was observed in room temperature ESR spectrum like upon water adsorption. This also indicates a mobile

Table 2. ESR Parameters at 77 K of Cu(II)-Ammonia Complexes in Various Molecular Sieves.

matrix	complex	$g_{\parallel}^a$	$A_{\parallel}^b$	ref
MCM -41 gallosilicate	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	2.279	177	this work
K-L gallosilicate	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	2.254	175	19
K-L aluminosilicate	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	2.255	177	20
H-mordenite	$[\text{Cu}(\text{NH}_3)_3]^{2+}$	2.249	179	21
Na,K-mordenite	$[\text{Cu}(\text{NH}_3)_2]^{2+}$	2.245	179	21
ZSM-5 zeolite	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	2.246	183	11,17,22
SAPO-5 <sup>c</sup>	$[\text{Cu}(\text{NH}_3)_3]^{2+}$	2.245	204	23
SAPO-11 <sup>c</sup>	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	2.226	190	24
X zeolite	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	2.228	178	25
Y zeolite	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	2.235	175	26
rho zeolite	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	2.239	175	27

<sup>a</sup> Estimated uncertainty is  $\pm 0.008$ .

<sup>b</sup> The unit of  $A_{\parallel}$  is  $1 \times 10^{-4} \text{ cm}^{-1}$ . The estimated uncertainty is  $\pm 6 \times 10^{-4} \text{ cm}^{-1}$ .

<sup>c</sup> SAPO-n represents silicoaluminophosphate molecular sieves.

Cu(II) species, i.e. Cu(II) species octahedrally coordinated with methanol. ESEM analysis also indicates a complex involving six molecules of methanol (Fig. 6) and supports the assignment of the species to a  $[\text{Cu}(\text{CH}_3\text{OH})_6]^{2+}$ .

Adsorption of  $\text{NH}_3$  on dehydrated Cu-MCM-41 gallosilicate results in complex formation with  $\text{NH}_3$  as shown by the changes in its ESR parameters. Since  $^{15}\text{N}$  has a nuclear spin of  $1/2$ , the five hyperfine lines on the second-derivative spectrum indicate four ammonia molecules coordinated to the Cu(II) (Fig. 4b). Tetracoordinated cupric complexes such as  $\text{CuX}_4$  ( $\text{X} = \text{Cl}, \text{NH}_3$ , etc) generally prefer a square-planar configuration.<sup>18</sup> The ESR parameters of this species are consistent with those of other tetraammonia complexes of Cu(II).<sup>19,20,24-27</sup> Thus, in this case the Cu(II) species is suggested to be located in a mesopore channel, coordinating to four ammonias in a square planar geometry. The ESR parameters of complexes formed between Cu(II) and ammonia in various zeolites and molecular sieves are tabulated in Table 2 for comparison.

## CONCLUSIONS

The combination of ESR and ESEM spectroscopic measurements has provided fairly good information on probable locations and ligand coordination of Cu(II) ions distributed in amorphous surface of Cu-MCM-41 gallosilicate. The main Cu(II) species in fresh hydrated MCM-41 gallosilicate is an octahedrally coordinated hexaaqua species  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  which resides in the mesopore channel with rotational freedom at room temperature. Upon partial dehydration at room temperature, the fully hydrated cupric ion loses some of its coordinated water and becomes anchored to the inner surface of the channel by partial coordination to channel surface oxygens. When completely dehydrated, the cupric ions are still located in somewhat exposed sites on the inner surface of the mesopores. Cu(II) also forms a hexagonally coordinated hexamethanol species,  $[\text{Cu}(\text{CH}_3\text{OH})_6]^{2+}$  inside a large mesopore channel. Cu(II) forms a complex with four molecules of ammonia

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