



ESR Analysis of Cupric Ion Species Exchanged into NaH-ZSM-5 Gallosilicate

Jeong Yeon Kim and Jong-Sung Yu*

Department of Chemistry, Hannam University, Taejon, 306-791, Korea

Received March 22, 2001

Abstract: ZSM-5 gallosilicate molecular sieves was synthesized and cupric ion was ion-exchanged into the gallosilicate. The locations of Cu(II) species in the framework and their interactions with various adsorbates were characterized by combined electron spin resonance (ESR) and electron spin echo modulation (ESEM) methods. It was found that in a fresh hydrated material, Cu(II) is octahedrally coordinated to six water molecules. This species is located in the channel intersections of two sinusoidal channels and rotates rapidly at room temperature. Evacuation removes some of these water molecules, leaving the Cu(II) coordinated to less water molecules and anchored to oxygens in the channel wall. Dehydration produces two Cu(II) species, both of which are located in sites inaccessible to oxygen as evidenced by non-broadening of its ESR lines by oxygen. Adsorption of adsorbate molecules such as water, alcohols, ammonia, acetonitrile and ethylene on dehydrated CuNaH-ZSM-5 gallosilicate materials causes changes in the ESR spectrum of Cu(II), indicating the migration of Cu(II) into main channels to form complexes with these adsorbates there. Cu(II) forms a complex with two molecules of methanol, ethanol and propanol, respectively as evidenced by ESR parameters and ESEM data. Cu(II) also forms a square planar complex with four molecules of ammonia, based on the resolved nitrogen superhyperfine interactions and their ESEM parameters. Cu(II) forms a complex with two molecules of acetonitrile based on the ESR parameters and ESEM data. Interestingly, however, only part of Cu(II) interacts indirectly with one molecule of nonpolar ethylene based on ESR and ESEM analyses.

INTRODUCTION

Zeolites are composed of three-dimensionally interconnected SiO_2 and AlO_2 tetrahedra and thus can be used as important catalysts for a wide variety of chemical reactions.¹ Isomorphous substitution of Si or Al in the zeolite structure by other elements with tetrahedral coordination is a route to modify the framework characteristics and geometries. Gallium can incorporate into framework composition instead of aluminum to form gallosilicates. The gallium analogs of zeolites usually possess physical and chemical properties different from their aluminum analogs.²⁻⁴ ZSM-5 is a pentasil zeolite that is

*To whom : jsyu@eve.hannam.ac.kr

industrially important in the catalytic conversion of methanol to gasoline⁵ and in paraffin dewaxing.⁶ The structure of ZSM-5 is unique in that it consists of a three-dimensional channel systems.⁷ One set of channels run parallel to the [010] axis with 10-ring oxygens of 0.54 x 0.56 nm. These channels are intersected by a second set of sinusoidal channels, the entrances to which also have 10-rings with openings of 0.51 x 0.55 nm. Recently it has been reported that zeolite ZSM-5 exchanged with Cu(II) is highly active for the continuous decomposition of nitrogen monoxide.⁸ ZSM-5 zeolites doped with cupric ions have been examined by electron spin resonance(ESR)^{9,10} and electron spin echo modulation(ESEM)¹¹ studies. There is an increase in free space at the channel intersections of two sinusoidal channels, and it is here that Cu(II) is thought to form complexes with adsorbates.^{10,11} In the present work, the interaction of paramagnetic Cu(II) with various adsorbates in Cu(II)-exchanged ZSM-5 gallosilicate is studied by ESR and ESEM spectroscopies in order to deduce the locations and coordination geometries of Cu(II) with adsorbates in this material.

EXPERIMENTAL SECTION

A gallium analog of ZSM-5 zeolite was synthesized according to the procedure described by Price et al.¹² The synthesis mixture consisted of 26.5 g of Ga₂O₃; 14.8 g of NaOH; 62.7 g of 40 % aqueous solution of Tetrapropylammonium hydroxide; 206.0 g of diethanolamine; 264.5 g of silica gel and 480 g of H₂O. The as-synthesized samples were calcined with flowing oxygen at 450 °C for 10 h to remove templating agents and examined by powder X-ray diffraction (XRD) before and after calcination. The resulting template-free NaH-ZSM-5 gallosilicates was exchanged at room temperature for 12 h by addition of 10 mmol/L solution of Cu(II) nitrate according to the procedure described earlier.¹³⁻¹⁷ Copper exchange was 1.8 by weight of the calcined materials, assuming complete exchange. Sample prepared in this manner is termed as a fresh, hydrated

Sample Treatment: The samples were 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 was carried out by 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.^{2,3} 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 210 °C and then heated to 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 10⁻⁵ 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 D₂O,

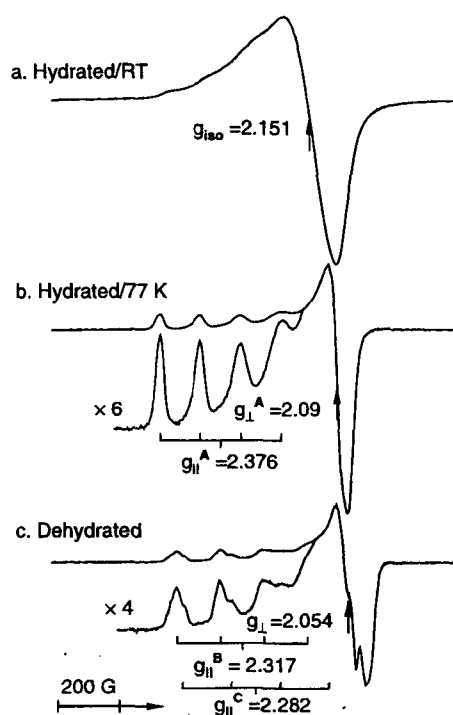


Fig. 1. ESR spectra recorded (a) at room temperature in fresh hydrated state, (b) at 77 K in fresh hydrated state and (c) at 77 K after dehydration of CuNaH-ZSM-5 gallosilicate.

CH_3OD , CD_3OH , $\text{CH}_3\text{CH}_2\text{OD}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OD}$, C_2D_4 , ND_3 and CD_3CN and other isotope substituted adsorbate, $^{15}\text{NH}_3$, were obtained from Aldrich and used after repeated freeze-pump-thaw cycles.

Spectroscopic Measurements: ESR spectra were measured both at room temperature and at 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° - t - 90° - T - 90° pulse sequence with the echo measured as a function of T . The parameters are the number of interacting nuclei N , the distance R between the paramagnetic center Cu(II) and the interacting nuclei and their isotropic hyperfine interaction A_{iso} .¹⁸

RESULTS

ESR spectra: Fig. 1 shows the ESR spectra of CuNaH-ZSM-5 gallosilicate before and after dehydration. The fresh hydrated sample measured at 77 K produces an anisotropic ESR signal, denoted as species A characteristic of an axial powder spectrum of Cu(II) as shown

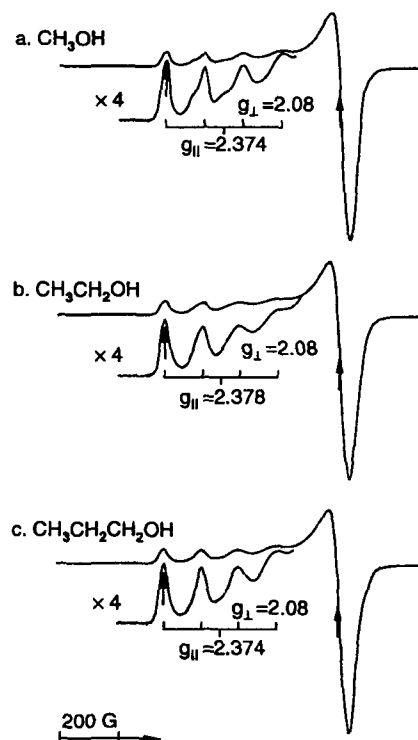


Fig. 2. ESR spectra at 77 K of dehydrated CuNaH-ZSM-5 gallosilicate (a) after adsorption of methanol, (b) after adsorption of ethanol, and (c) after adsorption of propanol for 1h at room temperature vapor pressure.

in Fig. 1b. Species A has ESR parameters of $g_{\parallel} = 2.376$, $A_{\parallel} = 146 \times 10^{-4} \text{ cm}^{-1}$ and $g_{\perp} = 2.09$. The ESR spectrum measured at room temperature, however, shows an almost isotropic signal at $g_{\text{iso}} = 2.15$ as shown in Fig. 1a. Evacuation for 1h at room temperature did not change significantly the ESR spectra at 77 K. However, the isotropic ESR signal $g_{\text{iso}} = 2.15$ is not observed any more at room temperature after evacuation at room temperature.

Fig. 1c shows the ESR spectrum mainly consisting of two species, denoted as B and C with better resolved perpendicular components after dehydration. Species B has the ESR parameters of $g_{\parallel} = 2.317$, $A_{\parallel} = 157 \times 10^{-4} \text{ cm}^{-1}$, $g_{\perp} = 2.054$ and $A_{\perp} = 20 \times 10^{-4} \text{ cm}^{-1}$. Species C is developed weakly on the shoulder of species B as a minor with the ESR parameter of $g_{\parallel} = 2.282$, $A_{\parallel} = 170 \times 10^{-4} \text{ cm}^{-1}$, $g_{\perp} = 2.054$ and $A_{\perp} = 20 \times 10^{-4} \text{ cm}^{-1}$. Upon adsorption of 200 Torr of oxygen at room temperature, the ESR lines of both species B and C are clearly observed. However, the relative intensity of species B compared to that of species C increases more.

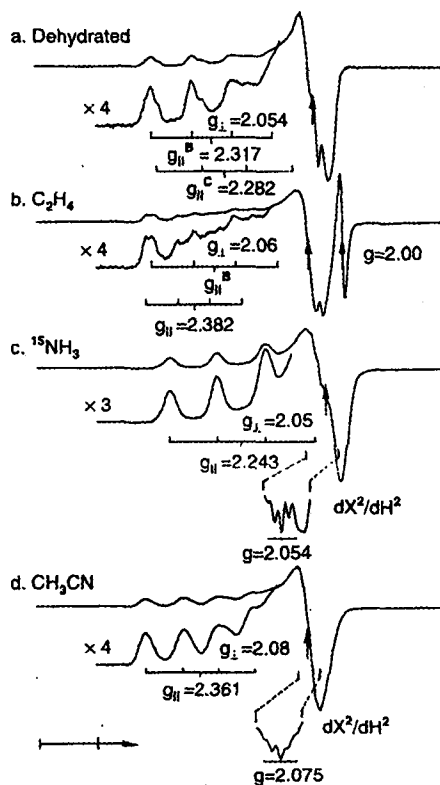


Fig. 3. ESR spectra at 77 K of (a) a dehydrated CuNaH-ZSM-5 gallosilicate (b) a dehydrated sample after adsorption of 100 Torr ethylene, (c) a dehydrated sample after adsorption of 45 Torr $^{15}\text{NH}_3$ and (d) a dehydrated sample after equilibration with acetonitrile at room temperature.

Fig. 2 and 3 show the ESR spectra at 77 K observed after adsorption of different adsorbates on dehydrated CuNaH-ZSM-5 gallosilicate samples. Adsorption of methanol produces a new Cu(II) species with $g_{\parallel} = 2.374$, $A_{\parallel} = 144 \times 10^{-4} \text{ cm}^{-1}$, and $g_{\perp} = 2.08$ as shown in Fig. 2a. The new species is generated probably due to a complex formation between Cu(II) and methanol. Adsorption of ethanol and propanol also gives very similar ESR parameters as adsorption of methanol as shown in Fig. 2b and 2c.

Upon ethylene adsorption, a new Cu(II) species is observed with $g_{\parallel} = 2.382$, $A_{\parallel} = 126 \times 10^{-4} \text{ cm}^{-1}$ and $g_{\perp} = 2.06$ while species C almost disappears and species B is still predominantly observed as shown in Fig. 3b.

Fig. 3c shows ESR spectrum after adsorption of $^{15}\text{NH}_3$ onto a dehydrated CuNaH-ZSM-5 gallosilicate. A new cupric ion species is observed with ESR parameters of $g_{\parallel} = 2.243$ and $A_{\parallel} = 177 \times 10^{-4} \text{ cm}^{-1}$. The ESR spectrum also shows five ^{15}N superhyperfine lines

Table 1. ESR parameters at 77 K of Cu(II) in CuNaH-ZSM-5 gallosilicate observed after various sample treatments

Treatment	species	g_{\parallel} ^a	A_{\parallel} ^b	g_{\perp} ^c
fresh/RT ESR ^d	Cu(H ₂ O) ₆	2.151 ^e		
fresh	Cu(H ₂ O) ₆	2.376	146	2.09
dehydrated	B	2.317	157	2.054
	C	2.282	170	2.054
+CH ₃ OH	Cu(CH ₃ OH) ₂	2.374	144	2.08
+CH ₃ CH ₂ OH	Cu(CH ₃ CH ₂ OH) ₂	2.378	140	2.08
+CH ₃ CH ₂ CH ₂ OH	Cu(CH ₃ CH ₂ CH ₂ OH) ₂	2.374	140	2.08
+C ₂ H ₄	Cu(C ₂ H ₄) ₁	2.382	126	2.06
+NH ₃	Cu(NH ₃) ₄	2.243	177	2.05
+CH ₃ CN	Cu(CH ₃ CN) ₂	2.361	141	2.08

^aEstimated uncertainty is ± 0.005 . ^bThe unit of A_{\parallel} is 10^{-4} cm^{-1} and the estimated uncertainty is $\pm 5 \times 10^{-4} \text{ cm}^{-1}$. ^cEstimated uncertainty is ± 0.01 . ^dESR measured at room temperature ^e g_{iso} value.

Table 2. ESEM simulation parameters for Cu(II) in CuNaH-ZSM-5 gallosilicate including the number of deuterium nuclei(N), Cu(II) to distance(R), and isotropic hyperfine coupling(A_{iso}).

Treatment	N ^a	R, nm ^b	A_{iso} , MHz ^a
+D ₂ O	12	0.28	0.33
+CD ₃ OH	6	0.36	0.16
+CH ₃ OD	2	0.26	0.25
+CH ₃ CH ₂ OD	2	0.27	0.26
+CH ₃ CH ₂ CH ₂ OD	2	0.26	0.12
+ND ₃	12	0.28	0.35
+CD ₃ CN	6	0.47	0.05
+C ₂ D ₄	4	0.42	0.12

^aEstimated uncertainty is 10 %. ^bEstimated uncertainty is 0.01 nm.

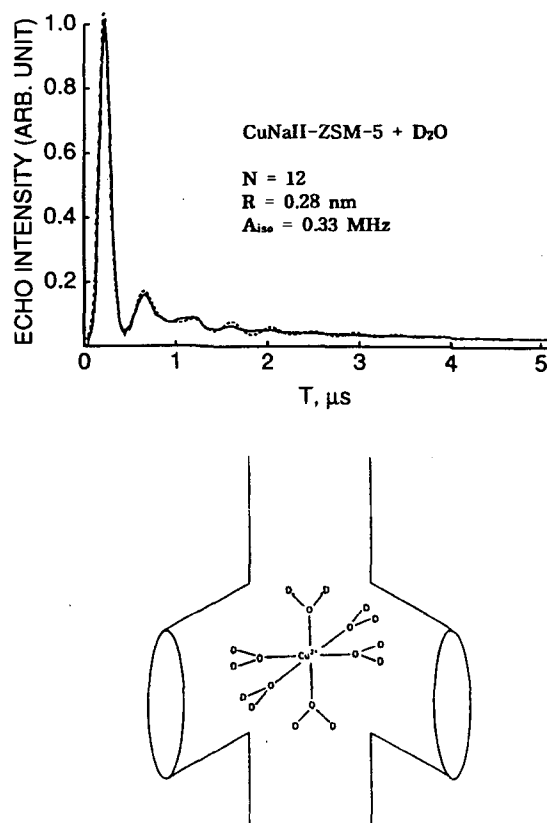


Fig. 4. Experimental (—) and simulated(---) three-pulse ESEM spectrum recorded at 4.5 K of dehydrated CuNaH-ZSM-5 gallosilicate (a) with adsorbed D₂O.

centered at $g = 2.054$ and split by $18 \times 10^{-4} \text{ cm}^{-1}$ which is shown in the expanded second derivative spectrum in the bottom of Fig. 3c. When acetonitrile is equilibrated with a dehydrated CuNaH-ZSM-5 gallosilicate, a new cupric ion species develops with ESR parameters of $g_{\parallel} = 2.361$, $A_{\parallel} = 141 \times 10^{-4} \text{ cm}^{-1}$ and $g_{\perp} = 2.08$ as shown in Fig. 3d. The new species shows interaction with acetonitrile by five nitrogen hyperfine lines centered at $g = 2.075$ and split by $13 \times 10^{-4} \text{ cm}^{-1}$ as shown in the expanded second derivative spectrum. Table 1 summarizes the ESR parameters of Cu(II) in CuNaH-ZSM-5 gallosilicate before and after various sample treatments

ESEM spectra: Fig. 4-6 show ESEM spectra and simulated data of the dehydrated CuNaH-ZSM-5 gallosilicate samples treated with various deuterated adsorbates. Deuterium modulations with period of about 500 ns are clearly observed due to interactions of Cu(II) with deuterium nuclei. Table 2 summarizes their ESEM parameters.

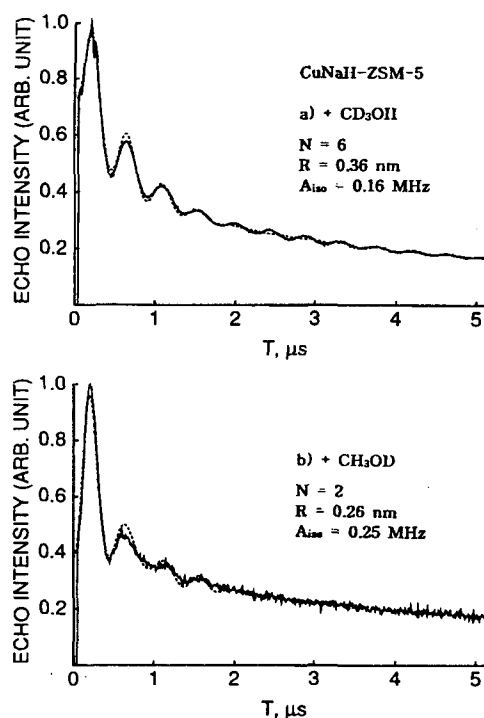


Fig. 5. Experimental (—) and simulated(----) three-pulse ESEM spectra recorded at 4.5 K of dehydrated CuNaH-ZSM-5 gallosilicate (a) with adsorbed CD₃OH and (b) with adsorbed CH₃OD.

DISCUSSION

A schematic representation of the structure of zeolite ZSM-5 is shown in Fig. 7. The structure consists mainly of five-membered rings which are linked together to give a system of channels. Running parallel to the crystallographic [010] direction are straight channels with an ten-membered elliptical close section of 0.54 x 0.56 nm diameter. Perpendicular to these channels run cross-linking zigzag ten-membered elliptical channels with diameter 0.51 x 0.55 nm. Possible cation sites lie close to the walls of these channels adjacent to 4-rings, 5-rings or 6-rings.

Species A shows an almost isotropic signal at $g_{iso} = 2.15$ in room temperature ESR spectrum. Such an isotropic signal at room temperature is indicative of a rotating specie which is rotationally unrestricted on the ESR timescale.^{15,17} Analysis of the three-pulse ESEM spectrum of dehydrated gallosilicate which has been rehydrated with D₂O indicates twelve nearest deuterium nuclei corresponding to a water solvation number of six around Cu(II), i.e. [Cu(H₂O)₆]²⁺ (Fig. 4). At 77 K this [Cu(H₂O)₆]²⁺ complex becomes immobilizes

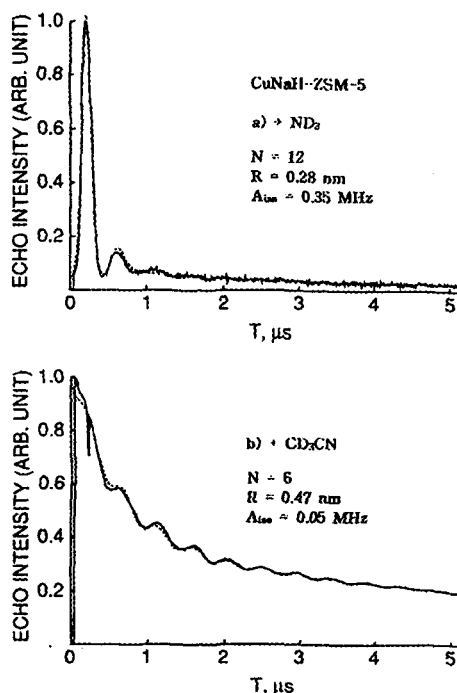


Fig. 6. Experimental (—) and simulated(---) three-pulse ESEM spectra recorded at 4.5 K of dehydrated CuNaH-ZSM-5 gallosilicate (a) with adsorbed ND_3 and (b) with adsorbed CD_3CN .

and gives rise to an asymmetric spectrum as shown in Fig. 1b. ZSM-5 structure consists of set of channels with 10-ring oxygens which are intersected by a second set of sinusoidal channels with 10-ring. There is an increase in free space at the channel interactions. These are the only locations large enough to accommodate a hexaquo complex as shown in schematic figure in the bottom of Fig 4.

Dehydrated sample showed the two new species B and C. Upon adsorption of 200 Torr of oxygen at room temperature, the ESR lines of both species B and C are clearly observed. This indicates that both species B and C are located in the recessed sites from a main 10-ring channel.^{14,16} However, the relative intensity of species B compared to that of species C increases more, suggesting that species B is located in more recessed sites from a main channel than species C.

Adsorption of adsorbates into dehydrated samples produced new ESR signals due to migration of Cu(II) and their coordination to the adsorbates. The three-pulse ESEM spectrum of dehydrated CuNaH-ZSM-5 gallosilicate with adsorbed CD_3OH and its simulation indicate interaction with six- deuterium nuclei, i.e. two methanol molecules with a Cu(II)-D distance of 0.36 nm, The simulation for CH_3OD indicates interaction with two

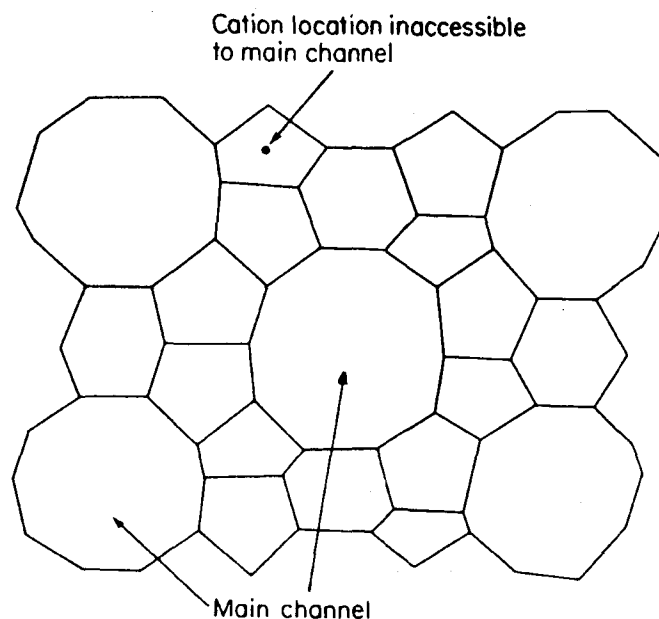


Fig. 7. Schematic representation of the (100) face of ZSM-5 showing the ten-membered ring main channels that are accessible to adsorbates and the smaller five-membered units that are inaccessible to adsorbates.

deuterium nuclei, i.e. two molecules of methanol, with a Cu(II)-D distance of 0.26 nm (Fig. 5). It is apparent that the methanol is complexed to Cu(II) through its hydroxy oxygen. The ESEM spectra also indicate that Cu(II) is coordinated to two molecules of ethanol and propanol, respectively. However, since these alcohols are too bulky to enter the recessed sites near a 5-rings, Cu(II) is believed to migrate from the recessed sites probably to the channel intersection of the main channels to coordinate to the alcohols.

The ESR spectrum also shows five ^{15}N superhyperfine lines upon equilibration with $^{15}\text{NH}_3$. Since ^{15}N has a nuclear spin of 1/2, the five hyperfine lines indicates four ammonias coordinated to the Cu(II). Tetracoordinated cupric complexes such as CuX_4 (X = Cl and NH_3) generally prefer a square-planar configuration.^{16,19} Thus in this case the Cu(II) species is suggested to be located in the center of the channel intersection, coordinating to four ammonias in a square planar geometry. With a nuclear spin of 1 for ^{14}N in acetonitrile, five lines indicate two molecules of acetonitrile directly coordinated to Cu(II) by Cu(II)-N bonds

In this case, Cu(II) is also suggested to migrate to the main channel to coordinate with acetonitrile. These ESR results are further supported by ESEM simulation parameters obtained from the dehydrated CuNaH-ZSM-5 gallosilicates with adsorbed ND₃ and CD₃CN, respectively as shown in Fig. 6.

The relative locations of species B and C in dehydrated sample are further supported by observations of Cu(II) signals upon ethylene adsorption onto dehydrated sample. The ESR intensity of species C decreased since species C mainly reacted with ethylene to form a new Cu(II) species upon ethylene adsorption, while species B, located in more recessed sites, remained almost intact. Thus relative ratio of species B to species C increased upon ethylene adsorption. The new species upon ethylene adsorption is ascribed to Cu(II) interaction with ethylene. The simulation of ESEM spectrum indicates that only part of Cu(II) species interacts with one molecule of ethylene.

In summary, Cu(II) ions are initially coordinated to six water molecules in channel interactions of two sinusoidal channels and then migrate into recessed or inaccessible sites from main channels upon dehydration. Upon adsorption of polar adsorbate molecules, Cu(II) ions migrate back to the main channel where they can form coordination complexes with adsorbates.

Acknowledgment

This work was supported by the research fund of Hannam University(1999). The authors are also grateful to Prof. Larry Kevan at the Department of Chemistry in University of Houston for ESEM measurements.

REFERENCES

1. D. W. Breck, *Zeolite, Molecular Sieves*; Wiley-Interscience: New York, 1974.
2. J. M. Mewsam, D. E. W. Vaughan, *Stud. Surf. Sci. Catal.*, **28**, 457 (1986).
3. (a) R. M Barrer, *Hydrothermal Chemistry of Zeolite*, 251, Academic Press, London, 1982. (b) R. Szostak, *Molecular Sieves, Principles of Synthesis and Identification*, Chap. 4, Van Nostrand Reinhold: New York, 1989.
4. A. V. Kucherov, A. A. Slinkin, H. K. Beyer, and G. Borbely, *Kinet. Katal.*, **30**, 429 (1989).
5. C. D. Chang, *Catal. Rev.-Sci. Eng.*, **25**, 1 (1983).
6. N. Y. Chen, R. L. Goring, H. R. Ireland, and T. R. Stain, *Oil Gas J.*, **75**, 165 (1977).
7. D. H. Olson, G. T. Kokotailo, S. L. Lawton, and W. M. Meier, *J. Phys. Chem.*, **85**, 2238 (1981).
8. M. Iwamoto, H. Furukawa, Y. Mine, F. Uemura, S. Mikuriya, and S. Kagawa, *J. Chem. Soc., Chem. Commun.*, 1272 (1986).
9. A. V. Kucherov, and A. A. Slinkin, *Zeolites*, **6**, 175 (1986).
10. Y. Sendoda, and Y. Ono, *Zeolites*, **6**, 209 (1986).

11. M. W. Anderson, and L. Kevan, *J. Phys. Chem.*, **91**, 4147 (1987).
12. G. L. Price, V. I. Kanazirev, and K. M. Dooley, *Zeolites*, **15**, 725 (1995).
13. J. S. Yu, and L. Kevan, *J. Phys. Chem.*, **94**, 7620 (1990).
14. J. S. Yu, and L. Kevan, *J. Phys. Chem.*, **95**, 3262 (1991).
15. J. S. Yu, J. M. Comets, and L. Kevan, *J. Phys. Chem.*, **97**, 11047 (1993).
16. J. S. Yu, and L. Kevan, *J. Phys. Chem.*, **98**, 12436 (1994).
17. J. S. Yu, S. J. Kim, S. B. Hong, and L. Kevan, *J. Chem. Soc., Faraday Trans.*, **92**, 855 (1996).
18. L. Kevan, In *Modern Pulsed and Continuous-Wave Electron Spin Resonance*; L. Kevan and M. K. Bowman Eds., Chapter 5, Wiley-Interscience, New York, 1990.
19. R. D. Willett, *J. Chem. Phys.*, **41**, 2243 (1964).