Copper Sites in Copper-Exchanged ZSM-5 for CO Activation and Methanol Synthesis: XPS and FTIR Studies

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Received February 2, 1996⊗

Cu−ZSM-5 samples with various Cu^+/Cu^{2+} ratios have been successfully prepared in three different methods and studied by XPS and FTIR. Cu^+ ions are found, by XPS, to mainly exist in the samples prepared by solution ion exchange and microwave solid-state reaction exchange. On the basis of the chemical shift of the Al 2p core level to a higher binding energy [Al(species II)], with the atomic ratio of Cu^+/Al(species II) being approximately one, and the vanishing of the IR band at 3640 cm^{-1} due to copper exchange, it is suggested that Cu^+ ions locate in the open channels of the ZSM-5 framework and bind to mixed (Si- and Al-) bridged oxide ion. From the ZSM-5 pore structure consideration, as well as from the observed decrease in the IR intensity ratio of bands 550/450 cm^{-1} with enhanced Cu^{2+} loading, it is also suggested that Cu^{2+} ions are a predominant Cu species in solid-state reaction exchanged Cu−ZSM-5 samples and exist as a CuO cluster in small cages as well as in open channels. The IR bands at 907 and 964 cm^{-1} are identified as zeolite asymmetric internal vibration perturbed by exchanged Cu^{2+} and Cu^+ ions, respectively. Cu ions in Cu−ZSM-5 samples can be reduced to Cu^0 by CO adsorption at room temperature. The IR bands at 2128, 2158, and 2176 cm^{-1} are observable and ascribed to the CO adsorbed on Cu^0, Cu^+, and Cu^{2+} sites, respectively. Methanol formation from syngas over Cu−ZSM-5 is observed at 250 °C and 2 MPa.

1. Introduction

Increasing interest has been attracted to the study of Cu-exchanged ZSM-5 zeolites because of its high activity in NO catalytic decomposition and selective reduction.[1−4] Recently it has been found in our laboratory that Cu-exchanged ZSM-5 can also catalyze methanol synthesis from syngas. The microporous structure of the aluminosilicate lattice of ZSM-5 has been well defined by X-ray and neutron diffraction in earlier literature. However a unified conclusion on the location and oxidation state of the Cu sites in Cu-exchanged ZSM-5 has yet to be established. Many previous studies used analytical methods such as electron spin resonance (ESR),[5−9] Fourier transform infrared spectroscopy (FTIR),[10,11] and photoluminescence emission spectroscopy,[12,13] which are basically bulk techniques. In particular ESR is only sensitive to Cu^{2+}, and not to Cu^0 and Cu^+, both of which are of d^{10} configuration. In this paper we prepare Cu−ZSM-5 catalysts in three different ways, conventional solution ion exchange, solid-state reaction, and microwave solid-state exchange, and study them by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR). XRD is used to ensure a well-defined aluminosilicate framework for all the samples after Cu exchange. XPS study focuses on the characterization of surface copper species and its microenvironment. FTIR is useful in determining the Cu locations; in particular, diffuse reflectance infrared Fourier transform (DRIFT) enables in-situ CO adsorption study and thus provides a useful probe to active sites in Cu−ZSM-5. Furthermore, the microreactor evaluation of Cu−ZSM-5 catalyst for methanol synthesis from syngas ($CO + H_2$) is reported in this paper. TPD and detailed kinetic study have also been performed, but the results will be presented later in a separate paper.

2. Experimental Section

2.1. Catalysts Preparation. All chemicals used in the experiment were of research grade made by Merck company. The NaZSM-5 was used as a starting material, exchanged with NH_4^+ in 0.5 M NH_4NO_3 solution and then heated at 550 °C for 2.5 h to form HZSM-5. The ratio of Si/Al in this precursor zeolite was 21.3 as measured by XPS. Three different methods, i.e. solution ion exchange, solid-state reaction exchange, and microwave solid-state reaction exchange, were employed for Cu exchange.

2.1.1. Cu-Exchange in Solutions. A 15 g amount of HZSM-5 thus prepared was immersed in 1 dm^3 of 0.01−0.08 M Cu(II) acetate solution at temperature of 40−60 °C for 24 h while stirring. The Cu-exchanged samples thus prepared were washed with distilled water for three times and kept at 120 °C overnight to dry.

2.1.2. Cu-Exchange by Solid-State Reaction. These samples were prepared by mechanically grinding a mixture of 1 g of HZSM-5 and 0.2 g of $CuCl_2$ followed by heating to 400 °C or above for 2 h.

⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1997.

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S0020-1669(96)00122-X CCC: $14.00

2.1.3. Cu-Exchange by Microwave Interaction. Following the procedure as suggested by Xiao et al.,[14] 1 g of HZSM-5 was mixed with a certain amount of $CuCl_2$ (0.1, 0.2, or 0.3 g, respectively); the mixture was then perfectly ground and heated in a microwave oven for 2 h.

The samples prepared by three methods mentioned above were kept in a vacuum desiccator. They were then characterized, without pretreatment, by XRD, XPS, and FTIR.

2.2. XRD, XPS, and FTIR Studies. XRD experiments were performed on a Philips PW 1710 diffractometer equipped with a Cu Kα X-ray generator under ambient condition.

XPS measurements were undertaken with a VG ESCALAB MK II with a Mg Kα (1253.6 eV) excitation source. The analyzer pass energy was set at 20 eV to achieve a good energy resolution.

Infrared spectra were obtained with a Perkin-Elmer FTIR 2000 system equipped with a diffuse reflectance accessory and a reaction cell, which allowed in-situ study at temperatures between −190 and 600 °C. In transmission mode the pellet technique was used, involving mixing the finely ground sample with KBr powder and pressing in an evacuable die to produce a transparent disk. In the DRIFT mode the zeolite sample was located in the reaction cup inside the reaction cell and was purged with Ar before contact with CO. Pure carbon monoxide or 10% CO in argon was used in CO adsorption studies.

2.3. Microreactor. Methanol synthesis was carried out in a stainless-steel microreactor with 1 mL of catalyst loading. Before the reaction started, the catalysts were reduced by 10% H_2 in N_2 at temperatures around 250 °C for 8 h. A mixture of 21 vol % CO in hydrogen was then used as the feedgas, and a reaction pressure of 2 MPa was achieved in the system. The feedgas flow rate was normally controlled at 3600 mL/h. The reaction temperature was governed by a heating controller and set at a fixed temperature between 200 and 300 °C. On-line gas chromatography (GC) with a Porapak-Q column and mass spectrometry (MS) (Balzers QMG 064) were employed to detect the products in the outlet gas and to evaluate the activity and selectivity of methanol synthesis.

3. Results and Discussion

3.1. XRD Results. The existence of Cu in Cu−ZSM-5 samples prepared as described in section 2.1 was confirmed by inductively coupled plasma−atomic emission spectroscopy (ICP-AES) analysis.

As shown in Figure 1, XRD patterns from the selected Cu-exchanged samples are identical to that of HZSM-5,[15] with no signals from $CuCl_2$, $Cu(CH_3COO)_2$, or other precursor compounds, indicating that Cu has been well exchanged and distributed over the ZSM-5 framework.

3.2. Microreactor Study of Methanol Synthesis. Methanol synthesis from CO + H_2 using Cu−ZSM-5 as catalyst was carried out under the conditions of temperatures between 200 and 300 °C and pressure of 2 MPa. On-line GC and MS both show that the methanol and dimethyl ether are the main products in the outlet gas. Although the CO conversion to methanol is not as high as that of commercial industrial catalysts, it is evident that CO + H_2 reaction can be catalyzed by all three different types of Cu−ZSM-5, forming methanol and dimethyl ether. The methanol yield is found to be related to the Cu loading, with Cu-free ZSM-5 samples showing no catalytic activity. Figure 2 gives the products yield against reaction temperature. It is seen that the production of methanol decreases at temperatures below 240 °C and above 260 °C. At temperatures near 250 °C methanol is the main product from syngas. The methanol yield is estimated to reach the maximum of 0.8 mol/(L of catalyst·h) with the molecular ratio of CH_3OH/CH_3OCH_3 being approximately 2:1 at 250 °C and 2 MPa.

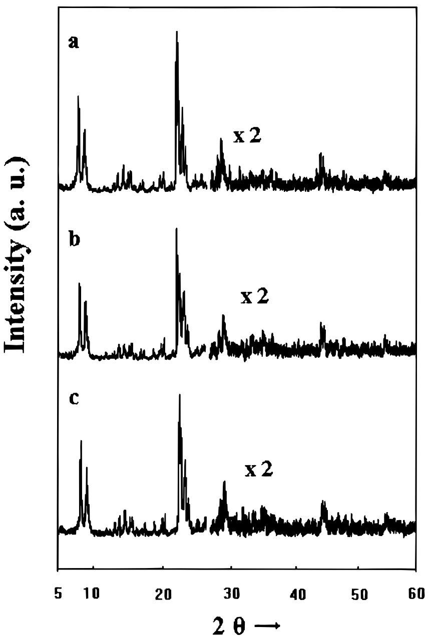

Figure 1. X-ray diffraction spectra taken from samples of (a) solution ion exchange, (b) solid reaction exchange, and (c) microwave-exchanged Cu−ZSM-5 samples.

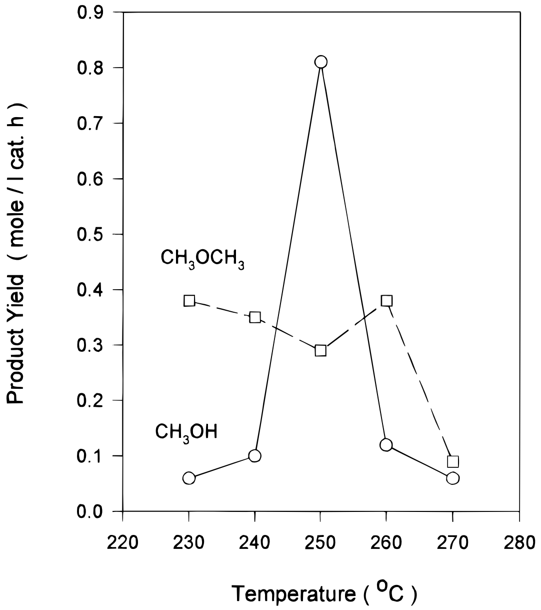

Figure 2. Products yield as a function of the temperature for the Cu−ZSM-5 catalyst prepared by the solid-state reaction between 0.2 g of $CuCl_2$ and 1 g of HZSM-5.

3.3. XPS Studies. 3.3.1. Cu−ZSM-5 by Solution Exchange. XPS wide-scan shows that, apart from carbon, the surface of all Cu−ZSM-5 samples consists mainly of Cu, Si, Al, and O. The O 1s and Si 2p peaks obtained from different samples are always observed at binding energy (BE) 531.4 and 102.1 eV, respectively, identical to those of the ZSM-5 samples without Cu exchange. However different Cu−ZSM-5 samples have shown some changes in their Cu 2p and Al 2p spectra, depending on the Cu loading or preparation methods.

Figure 3 shows the Cu $2p_{3/2}$ spectra for the Cu-exchanged ZSM-5 samples prepared from copper acetate solutions at concentrations of 0.01, 0.04, and 0.08 M. For the sample of low Cu concentration the Cu $2p_{3/2}$ peak is observed at BE 932.4 eV with no shake-up satellite at higher binding energy (see Figure 3a), and for the samples of higher Cu concentration of acetate solutions two peaks denoted by I and II (at 932.4 and

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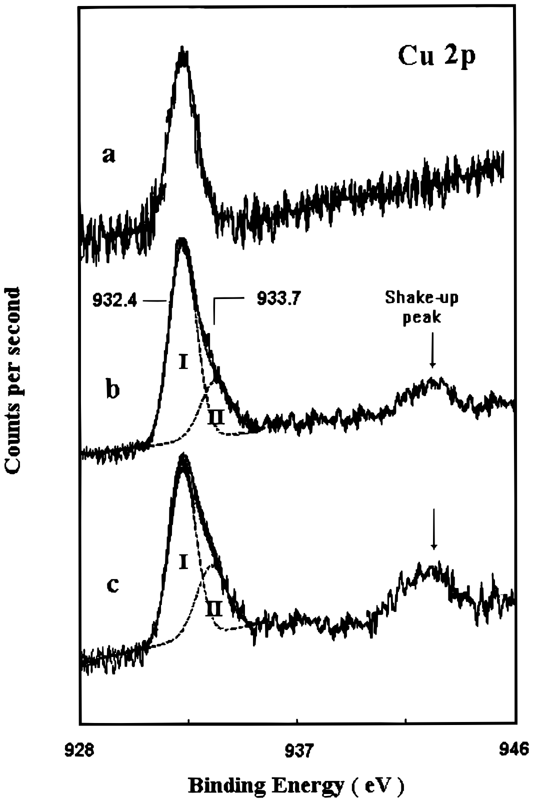

Figure 3. Cu $2p_{3/2}$ core-level spectra of Cu-exchanged ZSM-5 samples prepared from copper acetate solutions of (a) 0.01 M, (b) 0.04 M, and (c) 0.08 M. Dashed lines are produced by a curve-fitting procedure in which the peak width is fixed while the peak height varies to obtain a best fit.

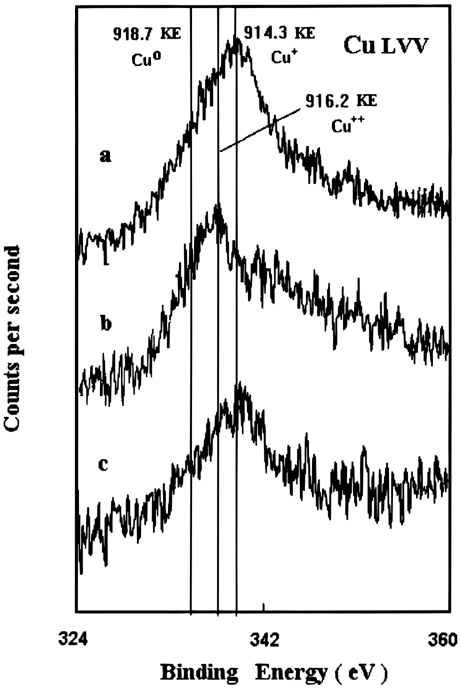

Figure 4. X-ray-induced Auger Cu LVV lines obtained from the samples prepared in different methods: (a) solution exchange; (b) solid-state reaction exchange; (c) microwave solid-state reaction exchange.

Table 1. Surface Atomic Concentrations of Cu Loaded in ZSM-5 with Different Exchange Methods with Surface Concentrations Derived From XPS Data (Atomic Ratio %)

sample no.	O	Si	Al	Cu	Cu/Al	Cu^+/Al(II)
101[a]	68.4	29.2	1.8	0.6	0.33	1.05
102[a]	65.6	27.1	4.9	2.4	0.49	1.08
103[a]	64.6	27.3	5.0	3.1	0.62	1.03
201[b]	68.4	28.0	2.4	1.2	0.50	
202[b]	68.0	28.8	2.1	1.1	0.52	
301[c]	69.2	27.1	3.0	0.7	0.22	0.97
302[c]	67.4	25.8	3.0	0.8	0.27	0.96
303[c]	68.1	28.0	3.3	0.7	0.21	0.90

[a] 101−103: Samples are prepared by solution ion exchange with copper acetate solutions of 0.01, 0.04, and 0.08 M, respectively. [b] 201 and 202: Samples are prepared by solid-state reaction of 0.2 g of $CuCl_2$ with 1 g of HZSM-5 under the temperatures of 427 and 600 °C. [c] 301−303: Samples are prepared by microwave exchange of 0.1, 0.2, and 0.3 g of $CuCl_2$ with 1 g of HZSM-5 separately.

933.7 eV, respectively) can be resolved, by using a curve-fitting procedure, with a shake-up satellite at 8.9 eV higher in BE than that of peak II. It is obvious that peak II is due to Cu^{2+} loaded in ZSM-5. Peak I may be attributable to either Cu^+ or Cu^0, both of which are known to have the same BE of 932.4 eV for Cu $2p_{3/2}$. In order to distinguish Cu^+ from Cu^0, X-ray-induced Auger spectra were taken for these samples and are shown in Figure 4. The peak has maximum intensity at kinetic energy (KE) 914.3 (see Figure 4a), indicating the peak I in Figure 3 is due to Cu^+ rather than Cu^0.[16]

Obviously, as shown in Figure 3, Cu^+ is the main species of copper in solution-exchanged Cu−ZSM-5 samples. The ratio of Cu^{2+}/Cu^+ in different samples is 0, 0.32, and 0.45 corresponding to the Cu precursor concentrations of 0.01, 0.04, and 0.08 M, respectively. Table 1 lists the surface atomic concentrations derived from XPS data according to the quantitative analysis calculation shown in ref 16. It appears that the total Cu loading increases from 0.6 to 3.1% with increasing concentration of copper acetate from 0.01 to 0.08 M. From the same table, it is interesting to note that surface Al concentration is also enhanced from 1.8 to 5.0%. The phenomenon of Al migration from bulk to surface has been reported.[17]

As shown in Figure 5, Al 2p core-level spectra are significantly broadened after Cu ions are incorporated into ZSM-5. In Figure 5, spectrum a is obtained from HZSM-5 before Cu exchange while spectrum b is from Cu-exchanged ZSM-5, with two Al 2p peaks (I and II) being resolved. Peak I at a lower energy of 73.5 eV is attributed to Al atoms in the ZSM-5 framework, where Al atoms are connected to the bridged O atom in the −Si−O−Al− chains. Peak II at a higher BE of 74.9 eV does not appear in the ZSM-5 samples without Cu loading. The area of peak II is found to be closely related to the Cu signals, giving an approximately 1:1 ratio for Cu^+/Al(species II). This appears to give a hint that Cu^+ ions are bound in the vicinity of Al. Electron density is transferred from Al atoms to Cu ions, leading to the reduction of Cu^{2+} ions and partial oxidation of Al atoms and resulting in the chemical shift toward higher BE of Al 2p.

3.3.2. Cu−ZSM-5 by Solid-State Reaction Exchange. Figure 6a,b shows Cu $2p_{3/2}$ spectra for samples prepared by the solid reaction between HZSM-5 and $CuCl_2$ at 427 and 600 °C, respectively. The peaks are strong and broaden, with significant shake-up satellites. The main component peak at higher BE (~933.7 eV) is assigned to Cu^{2+} ions in Cu−ZSM-5. As supplemented by X-ray-induced Auger spectra (see Figure 4b), the peak at lower BE is due to Cu^+. By comparison of spectrum 6a with 6b, it is observed that with increasing solid-state reaction temperature the amount of Cu^+ decreases whereas Cu^{2+} increases.

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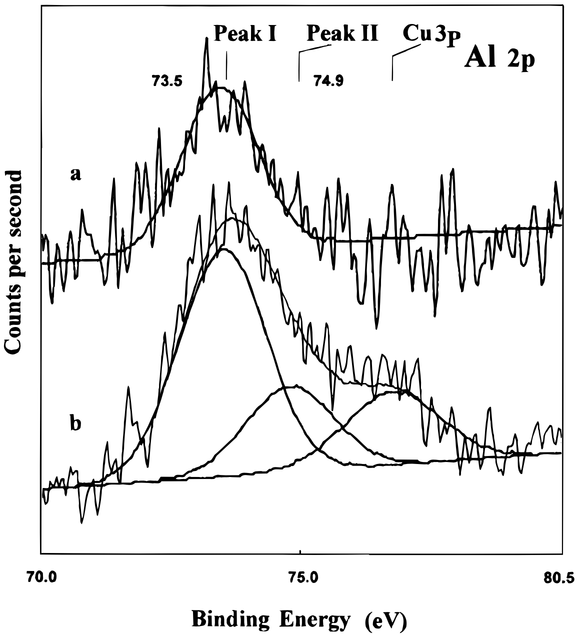

Figure 5. Al $2p_{3/2}$ core-level spectra of (a) blank HZSM-5 and (b) a Cu-exchanged ZSM-5 sample by solution exchange. Curve fitting is performed using the same procedure as in Figure 3.

Compared with solution-exchanged samples, in which Cu^+ is the main Cu species, more Cu^{2+} than Cu^+ ions are observed in the solid-state reaction exchanged Cu−ZSM-5 samples. The main differences in preparing these two types of Cu−ZSM-5 samples are that the former one is prepared in solution at lower temperatures and the latter is in solid state and heated to higher temperatures. We have increased the preparation temperatures for the solution-exchanged samples and see little change in their XPS results. Therefore the main difference must arise from the matter state where the exchange process occurs. In the solid state Cu^{2+} is of small size with its diameter less than 2 Å, whereas in solution Cu ions are hydrated ions having a large size, which is estimated to range between 4 and 5 Å. ZSM-5 is well-known for its constrained transition state and is composed of 5-, 6-, and 10-membered oxygen rings. The small cages with 5- or 6-membered oxygen rings have apertures smaller than 3 Å in diameter and would not allow hydrated Cu ions to enter. On the other hand the channels consisting of 10-membered oxygen rings (5.5 Å in diameter) should be accessible to hydrated Cu ions. From the above pore structure consideration it seems that Cu^+ is mainly located in open channels while Cu^{2+} in found in small cages as well as in channels.

This consideration can find support from the electron spin resonance studies reported by Anderson and Kevan,[7] where the Cu^{2+} ion in hydrated Cu-exchanged ZSM-5 was found to be coordinated to six water molecules and located in the channels of the zeolite. The water-coordinated Cu^{2+} had considerable freedom of movement at room temperature within the channel. It might lose some (not all) water ligands at 60−100 °C and became anchored to the zeolite lattice by partial coordination to the framework oxygen atoms. Complete dehydration is found to be effected at 400 °C. Since the solution exchange in our experiments was conducted below 120 °C, it is expected that in the sample prepared by this method copper ions reside mainly in the channels.

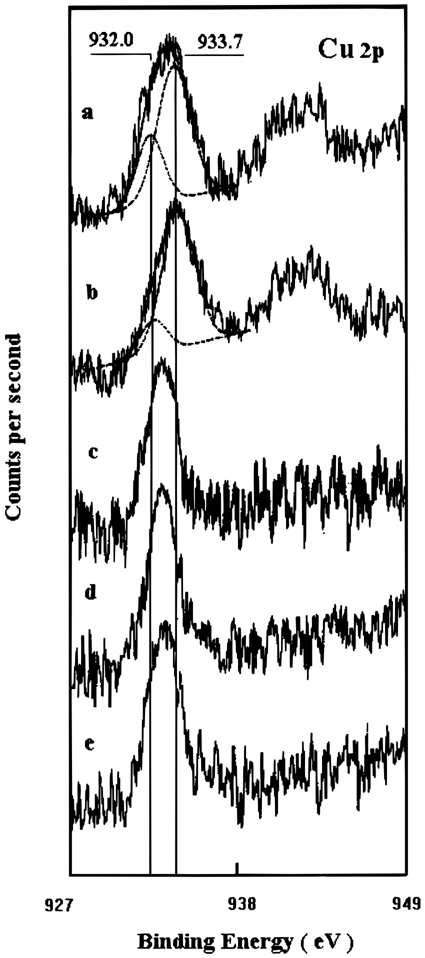

Figure 6. Cu $2p_{3/2}$ core-level spectra taken from samples prepared by the solid-state reaction or microwave solid-state reaction exchange: (a) solid reaction between 0.1 g of $CuCl_2$ and 1 g of HZSM-5 at 427 °C; (b) solid-state reaction between 0.1 g of $CuCl_2$ and 1 g of HZSM-5 at 600 °C; (c) microwave solid-state reaction between 0.1 g of $CuCl_2$ and 1 g of HZSM-5; (d) microwave solid-state reaction between 0.2 g of $CuCl_2$ and 1 g of HZSM-5; (e) microwave solid-state reaction between 0.3 g of $CuCl_2$ and 1 g of HZSM-5.

In small cages of the ZSM-5 sample with high Si/Al ratio, which is about 21 in our case (see section 2.1), the chance for Cu^{2+} ions to locate in the vicinity of Al is low, so that Cu^{2+} retains its higher oxidation state. In channels, if Cu^{2+} is exchanged with the acidic proton and bound to the Al- and Si-bridged oxygen, Cu^{2+} can be easily reduced to Cu^+ as shown in section 3.4.1. This also explains the XPS results shown in Figure 6a,b; i.e., with increasing solid-state reaction temperature, the intensity ratio of peak I (Cu^+) to peak II (Cu^{2+}) decreases, meaning more Cu^{2+} ions driven by higher temperatures migrate into small cages. Further support can be found by FTIR studies shown below (in section 3.4).

3.3.3. Cu−ZSM-5 by Microwave Solid-State Reaction Exchange. For the samples prepared from microwave solid-state reaction exchange, XPS spectra shown in Figure 6c,d,e are different from those of samples prepared by the other two methods. The Cu $2p_{3/2}$ peaks are sharp, located at BE 932.8 eV with little shake-up satellite in the higher binding energy region. Referred to the Auger spectrum shown in Figure 4c, the Cu species on the surface of these samples is entirely Cu^+, without Cu^{2+} or Cu. Increasing the amount of copper precursor does not affect the Cu surface concentration in Cu−ZSM-5. Further study is required to ascertain the reason for the absence of Cu^{2+} species.

3.4. FTIR Studies. In this section attention is focused mainly on the IR signals in three special energy regions: 400−600, 900−1000, and 3000−3700 cm^{-1}. As a useful probe, CO adsorption data are also included to assist the identification of copper active sites and their locations.

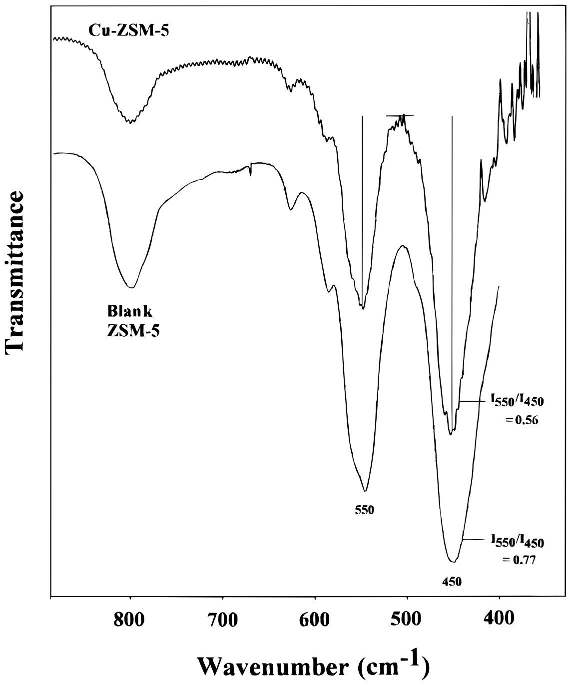

Figure 7. FTIR spectra of blank HZSM-5 and a Cu−ZSM-5 sample.

3.4.1. The 400−600 cm^{-1} Region. In this region, there are two strong absorbances located at 450 and 550 cm^{-1} (see Figure 7). These two bands are characteristic of ZSM-5[18] and may serve as an indication whether the sample is keeping the structure of the ZSM-5 framework when copper is loaded. The band at 450 cm^{-1} is assigned to the internal five-membered ring O−T−O asymmetric vibration correlated to the TO_4 (SiO_4 or AlO_4) tetrahedral bending vibration according to Flanigen−Khatami−Szymanski,[19] while the band at 550 cm^{-1} is due to external double ring vibration of ZSM-5. The intensity ratio of band 550 cm^{-1} versus 450 cm^{-1} has been reported as a measurement of the crystallinity of ZSM-5 samples.[20]

In this work the value of 0.77 for the intensity ratio 550/450 cm^{-1} is obtained from microwave-exchanged Cu−ZSM-5 samples as well as the HZSM-5 sample without Cu exchange (see Figure 7a), in good agreement with the known value.[20] The ratio is found to decrease linearly when the copper loading of Cu−ZSM-5 increases with increasing solution concentration or solid-state reaction temperature (see Figures 7 and 8). Since little Cu^{2+} is found in microwave-exchanged samples whereas in solution or solid-state reaction exchanged samples Cu^{2+} concentration increases with enchanced precursor concentration or solid-state reaction temperature, the deviation of the the intensity ratio from 0.77 seems to imply that Cu^{2+} ions may exist as a CuO cluster[20] inside the zeolite pore structures and reduce the crystallinity and, therefore, the 550/450 cm^{-1} intensity ratio in IR spectra.

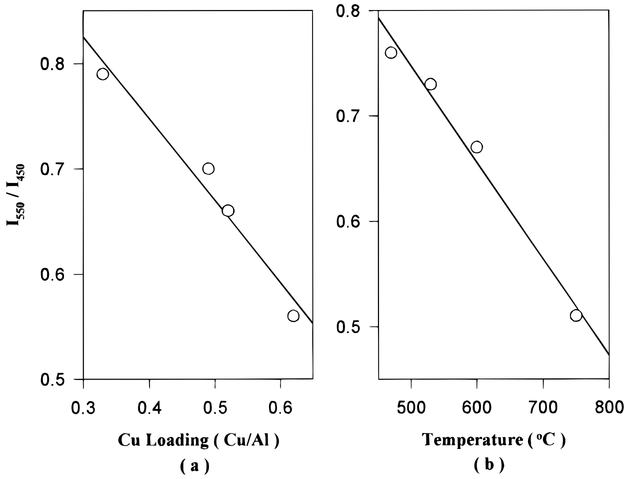

Figure 8. Intensity ratio of a band at 550 cm^{-1} versus 450 cm^{-1} as a function of (a) relative copper loading in Cu−ZSM-5 samples by solution exchange and (b) reaction temperatures in Cu−ZSM-5 samples by solid-state reaction exchange.

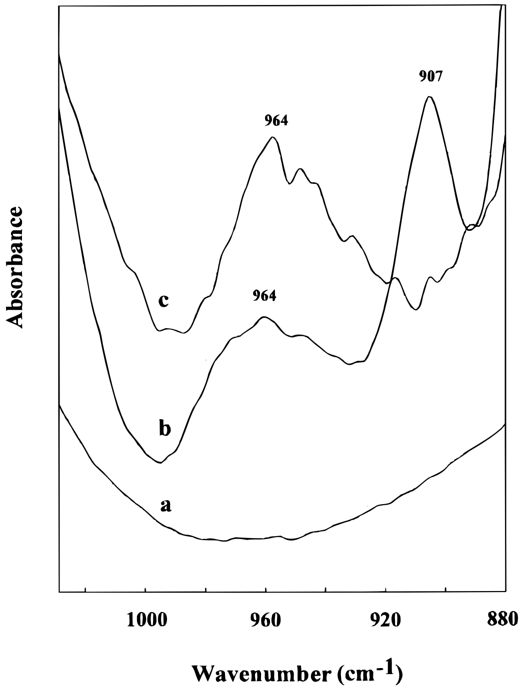

Figure 9. FTIR spectra in the region between 900 and 1000 cm^{-1} for a (a) blank HZSM-5 sample, (b) Cu−ZSM-5 sample by solid-state reaction exchange, and (c) Cu−ZSM-5 sample by solution ion exchange.

3.4.2. The 900−1000 cm^{-1} Region. IR spectra in this region are of particular interest because the band near 964 cm^{-1} has been shown to originate from the disturbance of the zeolite framework by exchanged ions.[21−23] Indeed there is no band detectable in this region for the ZSM-5 sample without Cu exchange (see Figure 9a). For the Cu−ZSM-5 samples with only Cu^{+} as observed from the XPS study, the band at 964 cm^{-1} is very evident (see Figure 9c). On the other hand, we have recorded an extra band at 907 cm^{-1}, in addition to that at 964 cm^{-1}, for the Cu−ZSM-5 samples with Cu^{2+} and Cu^{+} both observed by XPS. Obviously, in analogue to the band around 964 cm^{-1}, which is assigned to the zeolite asymmetric internal T−O stretching vibration perturbed by Cu^{+} located in the zeolite framework, the band at 907 cm^{-1} is due to the perturbation by Cu^{2+} in the zeolite structure (Figure 9b). This region may show some changes upon CO adsorption and will be further discussed below.

3.4.3. The 3000−4000 cm^{-1} Region. The infrared absorption in the region between 3000 and 4000 cm^{-1} is characteristic of different types of hydroxyl groups. They are not contributed from adsorbed water since the rotation−vibrational IR signals

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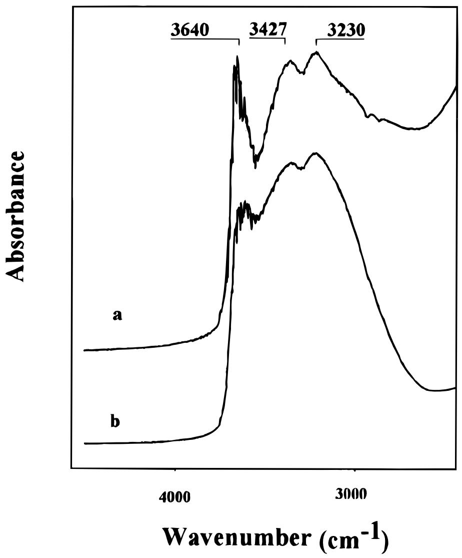

Figure 10. FTIR spectra in the region 2500−4000 cm^{-1}, taken from (a) the HZSM-5 sample before copper exchange and (b) Cu−ZSM-5 sample after copper exchange.

characteristic of water in the region 1300−1800 cm^{-1} are not simultaneously observed. Three bands located at 3230, 3427, and 3640 cm^{-1} are observed from ZSM-5 prior to Cu exchange, as shown in Figure 10a. The bands at 3230 and 3427 cm^{-1} may be attributed to germinal groups, Si(OH)$_2$, terminal OH, SiOH, and vicinal hydrogen-bonded OH groups, SiOH−OHSi.[24] They both undergo little change after Cu exchange. The band of 3640 cm^{-1} is due to a structural (or acidic) Al- and Si-bridged hydroxyl group, −Si−(OH)−Al−. After Cu exchange the intensity of the band is evidently reduced as shown in Figure 10b, indicating that this mixed bridged OH group is destructured, probably through replacing H by a Cu ion. The disappearance of the 3640 cm^{-1} band due to Cu exchange is observed from all three different types of Cu−ZSM-5. Combined with the XPS results it can be concluded that Cu$^+$ ions are prevalently bound to the oxygen atoms bridged to Al and Si atoms.

3.5. CO Adsorption as a Probe to Cu Sites. CO adsorption on a variety of Cu sites has been extensively studied and well understood. Therefore it can be used as a probe to understand the nature of Cu sites in Cu−ZSM-5.

Prior to Cu exchange, HZSM-5 has shown no activity in CO adsorption at room temperature in our experiment. But CO adsorption can be easily observed by FTIR to occur on a variety of Cu−ZSM-5 samples, indicating the active sites are Cu species.

As mentioned in section 3.4.2, IR bands at 964 and 907 cm^{-1} are derived from the perturbation of a zeolite framework vibration by Cu exchange and are characteristic of Cu$^+$ and Cu^{2+}, respectively. Thus in Figure 11 the CO absorbance bands (in the 2000−2200 cm^{-1} region) obtained from various CO/Cu−ZSM-5 systems are presented together with the corresponding Cu perturbation absorbances between 900 and 1000 cm^{-1}, in order to confirm our assignments.

Figure 11a is the IR spectrum of a solution-exchanged Cu−ZSM-5 sample prior to CO adsorption. There is no band in the CO absorbance region between 2000 and 2200 cm^{-1} but an evident band at 964 cm^{-1} due to the Cu$^+$ perturbation. After the sample is exposed to pure CO at room temperature, the CO band appears at 2128 cm^{-1} while the Cu$^+$ perturbation band disappears (see Figure 11b). The decay of the 964 cm^{-1} band may be indicative of the reduction of Cu$^+$ to Cu^0 by pure CO. As a result, the ionic bonding between Cu$^+$ and bridged oxide (Al−O$^-$−Si) diminishes and so does the perturbation of framework vibration by this bonding. The existence of Cu^0 has been confirmed by XPS and X-ray-induced AES results. The band at 2128 cm^{-1} is therefore assigned to the stretching vibration of CO adsorbed at Cu^0 sites.

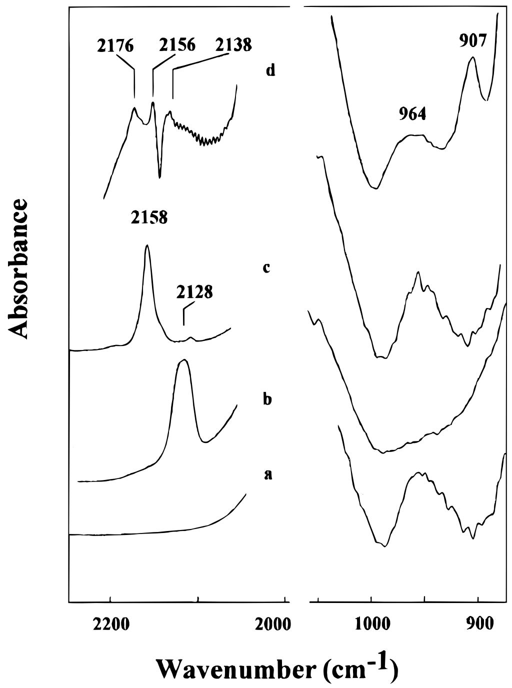

Figure 11. IR spectra in the CO absorbance region 2000−2200 cm^{-1} and the Cu perturbation absorbance region 900−1000 cm^{-1}, taken from (a) a Cu−ZSM-5 sample prepared by solution ionn exchange, prior to CO adsorption, (b) the sample in (a) but exposed to pure CO at room temperature, (c) the same sample in (a) but exposed to 10% CO balanced with Ar at room temperature, and (d) the Cu−ZSM-5 sample by solid-state exchange, exposed to 10% CO at room temperature.

If this sample is exposed to 10% CO balanced by Ar at 200 °C, the 964 cm^{-1} band remains and the CO absorbance band is observable at 2158 cm^{-1} (see Figure 11c). Obviously the 2158 cm^{-1} IR absorbance is due to the CO adsorbed at Cu$^+$ sites, as those reported for the form of Cu$^+$−CO.[25]

Figure 11d is obtained from the Cu−ZSM-5 sample, which was prepared from solid-state reaction exchange and exposed to 10% CO at room temperature. In this figure there are basically three bands at 2138, 2156, and 2176 cm^{-1} in the CO absorbance region and two bands at 907 and 964 cm^{-1} in the Cu ion perturbation region. Since the bands at 2138 and 2156 cm^{-1} are due to Cu^0 and Cu$^+$ as discussed above, the band at 2176 cm^{-1} is therefore assigned to the CO adsorbed at Cu^{2+} ions having a characteristic perturbation vibration band at 907 cm^{-1}.

The above assignments can be understood in terms of molecular orbital (MO) theory.[26] When CO is bonded to metal sites such as Cu in zeolite, the σ-bond is formed by donating the 5σ electrons of CO to the empty σ orbital of Cu. This tends to raise the C−O stretching vibration, ν(CO), since the CO 5σ orbital is slightly antibonding. Simultaneously, the π-bond can be formed by back-donating the dπ-electrons of the Cu site to the lowest unoccupied antibonding orbital, the 2π* orbital of

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[25] Spoto, G.; Zecchina, A.; Bordiga, S.; Ricchiardi, G.; Martra, G. *Appl. Catal. B* **1994,** *3,* 151. Chajar, Z.; Primet, M.; Praliaud, H.; Chevrier, M.; Gauthier, C.; Mathis, F. *Appl. Catal. B* **1994,** *4,* 199.

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CO; this results in lowering ν(CO). Although these two components of bonding are synergetic, the net result is a drift of electron density from copper to CO when the copper site is in a low oxidation state. If CO adsorbs at Cu sites in higher oxidation state, such as Cu^{2+}, the electron donation from CO 5σ to Cu^{2+} would prevail, with little π back-bonding. The net result is the decrease in the antibonding component of the C−O bond, shortening the length of the C−O bond, and increasing the ν(CO) vibration which should correspond to the 2176 cm^{-1} absorption band. Without reinforcement by π back-bonding CO bonding to Cu^{2+} would be weak. Indeed upon Ar purge it is the 2176 cm^{-1} band which is observed to diminish at first. By an increase of the back-donation (due to the lower oxidation state and its higher electron density) of Cu^{+}, the CO bonded to the $Cu^{+}-O-Al^{-}-$ site should have its stretching vibration at lower wavenumber than that of $CO-Cu^{2+}$. This is the 2158 cm^{-1} band, which is dominant in Figure 11 curve b. On Cu^{0} atoms, the back-donation of electronic charge from Cu to the CO $2\pi^{*}$ orbital would be the strongest as compared with Cu^{2+} and Cu^{+} and prevails over σ-donation. As such, the bands at frequencies lower than that of gaseous CO (2143 cm^{-1}) would correspond to those CO adsorbed on Cu^{0}. Note that ν(CO) decreases with increasing coordination number of Cu sites in various Cu single-crystal surfaces.[27]

4. Conclusions

Cu-exchanged ZSM-5 samples with different Cu^{2+}/Cu^{+} ratios are prepared using different methods. Cu^{+} mainly exists in the samples prepared by solution ion exchange and microwave solid-state reaction exchange. Cu^{2+} is found mainly in the samples prepared by solid-state reaction exchange.

Cu^{+} in Cu-exchanged ZSM-5 is suggested to be located in the open channels of the ZSM-5 framework. This is based on the XPS results that Cu exchange causes chemical shift of the Al 2p core level to a higher binding energy [Al(speciesII)], with the quantitative atomic ratio of Cu^{+}/Al(species II) being approximately one. The conclusion is also supported by the IR observation that Cu exchange results in the vanishing of the IR band at 3640 cm^{-1}, characteristic of a mixed (Si- and Al-) bridged OH group.

Cu^{2+} is thought to exist as a CuO cluster in small cages as well as in open channels. This suggestion is derived from the pore structure consideration that the small cages with five- or six-membered ring apertures are accessible to Cu^{2+} ions but inaccessible to hydrated Cu ions. The IR study has found that the intensity ratio of 550/450 cm^{-1} decreases with increasing Cu^{2+} exchange. The IR observation indicates the reduction of the crystallinity due to the existence of Cu^{2+} in the zeolite, giving support to the above suggestion.

IR bands at 450 and 550 cm^{-1} are assigned to internal five-membered ring O−T−O asymmetric vibration and external double ring vibration, and their intensity ratio is a measurement of the crystallinity of ZSM-5 structures. The IR bands at 907 and 964 cm^{-1} are found to be characteristic of exchanged Cu^{2+} and Cu^{+} and assigned to the zeolite asymmetric internal vibration perturbed by Cu^{2+} and Cu^{+}, respectively.

Cu−ZSM-5 is found to adsorb CO readily at room temperature and can catalyze methanol synthesis from CO + H_2 at 250 °C and 2 MPa. The infrared absorption bands at 2128, 2158, and 2176 cm^{-1} are assigned to the stretching vibration of the CO adsorbed on Cu^{0}, Cu^{+}, and Cu^{2+}, respectively, according to the correlation between the CO absorbance and Cu perturbation absorbance.

Acknowledgment. The authors thank Dr. Y. Xu for the preparation of some Cu-exchanged ZSM-5 samples.

IC960122L

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