Copper Sites in Cu-ZSM-5 Zeolites. Part II. An Identification of Defective AlOCu$^+$ Sites by FTIR

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By in-situ FTIR study using CO as a probe molecule, a new type of Cu$^+$ site, identified as defective (AlO$^{\delta-}$)Cu$^+$, was found to exist mainly in activated solution-exchanged Cu-ZSM-5, and was thought to derive from mixed oxo-bridged Cu$^+$ ions, (SiAlO)Cu$^+$, due to high-temperature (400 °C) calcination. At room temperature the CO adsorption on this sample produced three infrared carbonyl bands at 2176, 2156, and 2138 cm^{-1}. The first two bands, previously ascribed to the CO adsorbed at Cu^{2+} sites and mixed oxo-bridged (SiAlO)Cu$^+$ ions, respectively, vanished upon Ar purge at room temperature whereas the last band remained unaffected. The 2138 cm^{-1} band was assigned to the CO adsorbed at defective (AlO$^{\delta-}$)Cu$^+$ site, and its desorption energy was higher than those at oxo-bridged Cu$^+$ and Cu^{2+} sites. The stronger Cu$^+$−CO bonding and weaker C−O stretching are explained by a stronger π back-donation due to the defective structure. The 2138 cm^{-1} band was found to convert to the 2156 cm^{-1} band during heating between 100 and 280 °C, with an estimated activation energy of the transition approximately equal to 4.8 kcal/mol. A reaction scheme is proposed to depict the mechanism of this transition.

1. Introduction

Recently copper-exchanged ZSM-5 zeolites have attracted increasing interest due to their catalytic activities for NO decomposition,[1−5] CO hydrogenation,[6] and N$_2$ storage.[7] Much effort has been devoted to elucidating the nature of the active sites in this system. Using electron spin resonance (ESR) Kevan et al.[8] have found that in dehydrated Cu-ZSM-5 samples Cu^{2+} ions are coordinated to lattice oxygen atoms in the positions recessed from or inaccessible to the main channels and can rapidly migrate into main channels due to the adsorption of polar molecules. Similar results on the location and mobility of Cu ions have been reported by Woo et al.[9,10] Two kinds of cuprous ions corresponding to C−O vibration of 2157 and 2138 cm^{-1} have been suggested to exist inside the oxygen five-membered ring and in the intersection of main channels, respectively. They can migrate from one kind of location to the other upon gas adsorption. Two types of oxocationic Cu^{2+} ions in calcined Cu-ZSM-5, [Cu^{2+}-O-Cu^{2+}] and Cu-O, were also identified by Sachtler et al.[11] and by Joyner et al.[12] As for Cu$^+$ ions, luminescence spectroscopy has been used to determine the location of two types of Cu$^+$ sites,[13] with one in close proximity to the two Al framework atoms and the second adjacent to one Al framework atom. According to the results of local spin density functional theoretical calculation, Bell and co-workers suggested that Cu$^+$ was asymmetrically coordinated to two lattice oxygen atoms and Cu^{2+} was coordinated to two lattice oxygen atoms and one extra-lattice oxygen.[14,15] In our preceding paper on the Cu sites in Cu-ZSM-5,[6] we found that Cu in Cu-ZSM-5 could exist in both +2 and +1 oxidation states, with Cu$^+$ ions being bonded to mixed (Si and Al) bridged oxide ions and located in the open channels as (AlOSi)Cu$^+$, while Cu^{2+} was mainly located in small cages as a CuO cluster.

In this work we report the detection of another type of Cu$^+$ site, linear defective (AlO$^{\delta-}$)Cu$^+$, by using CO as a probe molecule diagnostic for Cu sites. At room temperature the CO adsorption on a dehydrated Cu-ZSM-5 sample was found to produce infrared absorption bands at 2176, 2156, and 2138 cm^{-1}. The carbonyl bands at 2176 and 2156 cm^{-1} were previously identified as the C−O stretching vibration over Cu^{2+} and Cu$^+$, i.e., Cu^{2+}CO and (AlOSi)Cu$^+$CO, respectively,[6,16−18] whereas the assignment of the 2138 cm^{-1} band is still controversial at present. To better understand the nature of the Cu site related to the carbonyl band at 2138 cm^{-1}, the CO adsorption on the dehydrated Cu-ZSM-5 sample is studied by in-situ IR measurement as a function of Ar purge and heating. As will be shown in the Results and Discussion section, while

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the bands at 2176 and 2156 cm^{-1} eventually disappear by Ar purge, the 2138 cm^{-1} band is unaffected at room temperature. However, it is converted by heating at 100−280 °C to a 2156 cm^{-1} band, with simultaneous intensity increase of hydroxyl band at 3740 cm^{-1}. These findings enable us to relate, less ambiguously, the 2138 cm^{-1} band to the CO adsorbed at linear defective cuprous site, $(AlO^{\delta-})Cu^+$. On account of the defective structural effect, molecular orbital theory is able to explain the stronger Cu−CO bonding and weaker C−O stretching observed for linear $(AlO^{\delta-})Cu^+CO$ as compared with oxo-bridged $(AlOSi)Cu^+CO$ and $Cu^{2+}CO$. A reaction scheme is proposed to illustrate the transition between (AlOSi)Cu and $(AlO^{\delta-})Cu$.

2. Experimental Section

The Cu-exchanged ZSM-5 samples were prepared by the conventional solution ion exchange method. As described previously,[6] Na-type ZSM-5 was exchanged with NH_4^+ and decomposed at 550 °C to form H-ZSM-5, which was then stirred for 12 h in 0.01, 0.04, 0.08, or 0.12M aqueous solution of Cu(II) acetate, respectively, for preparing samples with different copper contents. This solution-exchange process was repeated for three times. The Cu-exchanged ZSM-5 was washed by deionized water, filtered, and dried at 120 °C overnight. The ratio of Si/Al determined by XPS[19] was 23. The Cu-exchange percentage was measured by ICP-AES, showing no Cu overloading. The crystallinity of Cu-ZSM-5 was well defined by powder X-ray diffraction without any observable Cu oxide texture contribution.

FTIR spectra were acquired in Perkin-Elmer System 2000, equipped with a reaction cell and a diffuse reflectance accessory (Harrick CHA-CH), which allowed the CO adsorption to be studied in-situ at temperatures between −180 and 600 °C. CO gas was introduced into the reaction cell after the sample was pretreated by Ar purge at elevated temperatures. All IR spectra were obtained in ratio mode to subtract the background spectrum, with resolution of 4 cm^{-1}.

3. Results and Discussion

CO adsorption on a variety of Cu sites has been extensively studied and well understood.[20] Therefore it can be used as a probe molecule to investigate the nature of Cu sites in Cu-ZSM-5.

Prior to Cu exchange, Cu-free H-ZSM-5 has shown no activity in CO adsorption at room or higher temperatures (see Figure 1a), indicating that the activity of CO adsorption, shown by Cu-exchanged samples in the same figure, is due to Cu sites. Figure 1b shows the carbonyl IR spectrum obtained from the activated Cu-ZSM-5 which was pretreated by Ar purge at 400 °C for 15 min and then exposed to 10% CO at room temperature for 10 min. Three CO bands are clearly observed at 2176, 2156, and 2138 cm^{-1}. According to our preceding paper,[6] Cu^+ and Cu^{2+} ions both exist in this sample, with the former being predominant, and the IR bands at 2176 and 2156 cm^{-1} were assigned to the CO adsorbed at Cu^{2+} and $(SiAlO)Cu^+$ sites, respectively. CO is not strongly held at these two Cu sites and can be removed simply by Ar purge at room temperature. Figure 1c−e demonstrates a rapid intensity decrease of the 2176 cm^{-1} band and a less significant but continuous decrease of the 2156 cm^{-1} band with increasing purging time. In contrast, the 2138 cm^{-1} band remains strong after 25 min of purge, while the 2176 cm^{-1} band almost vanishes and the 2156 cm^{-1} band diminishes in intensity greatly, appearing as a shoulder of the 2138 cm^{-1} band (Figure 1e). CO is well-known to be bound to transition metal sites through a σ bonding and π back-donation scheme. In this synergetic scheme the C−O stretching frequency depends on the relative extent of σ donation from CO to the metal site, which would increase the C−O bonding and its frequency, versus the π back-bonding from the metal site to CO, which has the opposite effect.[20] High-frequency CO (>2170 cm^{-1}) is generally related to those transition metal ions with high oxidation states (>2). These metal ions such as Zn^{2+}, Ni^{2+}, and Cu^{2+} are of small ionic size and high electron affinity and thus interact with CO through weak π back-donation coupled with σ bonding, which would result in high C−O frequencies.[17,18,20] In an early paper about the CO adsorption on CuO,[17] the 2173 cm^{-1} band was assigned to the CO vibration at Cu^{2+} site and the number of valence electrons of the adsorbed CO molecule was estimated, based on an empirical formula, to be 9.35 as compared with 10 for gaseous CO (2143 cm^{-1}), 9.76 for the CO adsorbed at Cu^+ (2156 cm^{-1}), and 9.0 for CO^+ (2183.9 cm^{-1}). This indicates obviously a rather weak π-back-donation from Cu^{2+} to CO, weaker than that from Cu^+ to CO. Conventionally CO is considered as a strong π-acceptor and the metal-to-CO π back-donation to be responsible for the thermal stability of many classical transition-metal carbonyl complexes.[21] It is therefore understandable that the bonding between CO and Cu^{2+} is weaker than that between CO and Cu^+ due to weaker π back-donation so that the 2176 cm^{-1} band is more easily removed than the 2156 cm^{-1} band upon the Ar purge at room temperature. This agrees well with previous observations that CO is adsorbed exceptionally strongly on Cu^+ sites, but only weakly on Cu^{2+} at room temperature.[22]

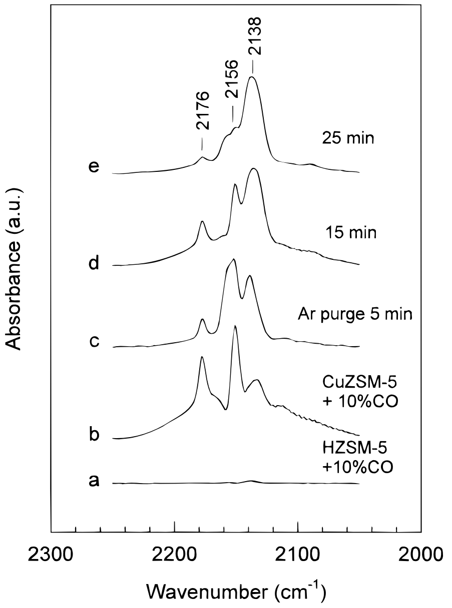

Figure 1. In situ FTIR spectra of ZSM-5 samples in the carbonyl region: CO adsorption for 10 min on (a) Cu-free HZSM-5 and on (b) the activated (400 °C) solution-exchanged Cu-ZSM-5; (c) Ar purge for 5 min after CO adsorption on Cu-ZSM-5; (d) Ar purge for 15 min after CO adsorption; (e) Ar purge for 25 min after CO adsorption. Adsorption gas consists of 10% CO and 90% Ar.

It was noted that upon the Ar purge the IR band at 907 cm^{-1}, which was assigned to zeolite asymmetric internal T−O stretching vibration perturbed by Cu^{2+} and had been significantly attenuated due to the CO adsorption,[6] was observed to recover

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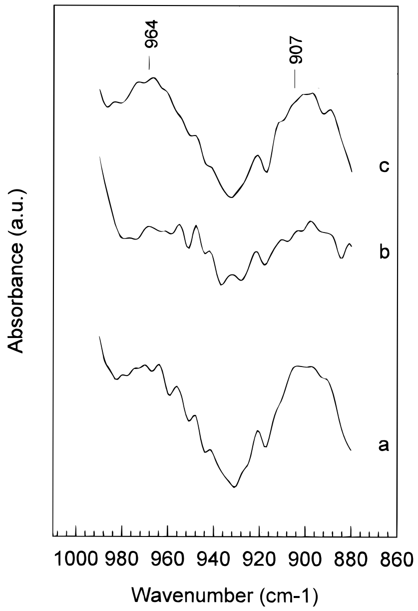

Figure 2. FTIR spectra in the region between 900 and 1000 cm^{-1} for the activated Cu-ZSM-5 sample (a) before the CO adsorption; (b) after CO adsorption for 10 min; and (c) after 5 min of Ar purge following the CO adsorption.

and increases its intensity evidently after a five-minute Ar purge (see Figure 2). This happened at the same time when the decay of the 2176 cm^{-1} band was already significantly observed (see Figures 1c and 2c), which may confirm our assignment of the 2176 cm^{-1} band to the CO adsorbed at Cu^{2+} sites.

As shown in Figure 1e, upon 25 min of Ar purging, the CO adsorption corresponding to the 2138 cm^{-1} band is even stronger than that corresponding to the 2156 cm^{-1} band. Previously the 2138 cm^{-1} band was assigned to liquidlike CO adsorbed in the zeolite channels[23] or to the CO adsorbed at the intersection of the channels[9,24] at high CO coverage, both of which contradict our above observation at low CO coverage. To understand the nature of the adsorbed CO corresponding to the 2138 cm^{-1} band, further test was performed at elevated temperatures as described below.

After 45 min of Ar purge at room temperature, the system was heated gradually up to 280 °C. As shown in Figure 3 the band at 2138 cm^{-1} shrinks with increasing sample temperature up to 280 °C while the band at 2156 cm^{-1} increases accordingly. At 280 °C, there remains only the 2156 cm^{-1} band. This observation appears to indicate the transformation from the adsorbed CO corresponding to 2138 cm^{-1} to mixed bridged (AlSiO)Cu^{+}CO corresponding to 2156 cm^{-1}. Again previous assignments[9,23,24] of the 2138 cm^{-1} cannot explain this transformation at higher temperatures. On the other hand Kuroda et al. attributed the 2159 cm^{-1} band to the CO adsorbed at Cu sites having two-coordinated lattice oxygens and the 2136 cm^{-1} band to a Cu species which took a transferring state from hydroxy-bridged copper species to form $Cu(O)_{2-3}$ on the specific sites.[25] Similarly we may assume that the observed 2138 to 2156 cm^{-1} transition involves certain kind of transferring state. It is found in our IR study that accompanying the transition from 2138 to 2156 cm^{-1}, i.e., the attenuation of the 2138 cm^{-1} band and the simultaneous enhancement of the 2156 cm^{-1} band, the growth of the 3740 cm^{-1} band was evident at temperatures between 100 and 280 °C (see Figure 4). Note that the 3740 cm^{-1} band is due to the OH stretching mode of isolated and terminal silanols, SiO−H.[23] These IR spectral changes upon heating can then be best explained in the following reaction schemes:

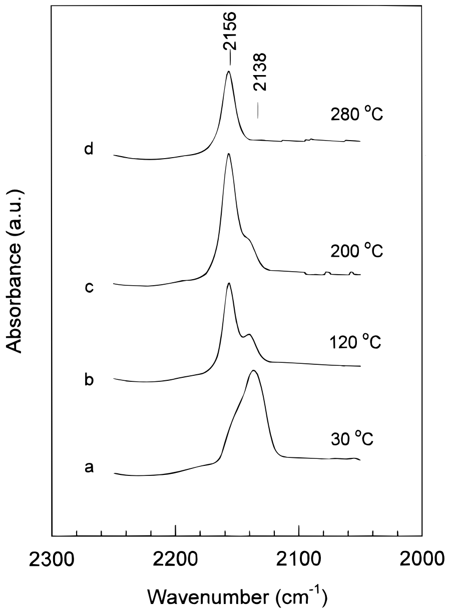

Figure 3. FTIR spectra of CO/Cu-ZSM-5 after Ar purge for 45 min and heated to (a) 30, (b) 120, (c) 200, and (d) 280 °C.

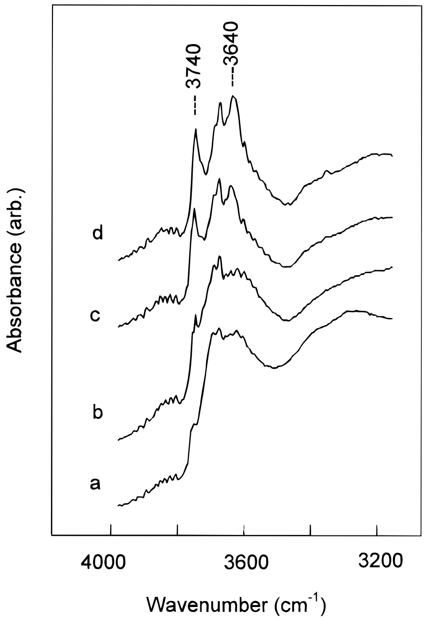

Figure 4. FTIR spectra of hydroxyl stretching vibration obtained from the same sample in Figure 2, i.e., CO/Cu-ZSM-5 after Ar purge for 45 min and heated to (a) 30, (b) 120, (c) 200, and (d) 280 °C.

Scheme 1a represents the CO adsorption on (SiOAl)Cu^{+} which is made by solution Cu exchange. Scheme 1b illustrates the formation of a defective (AlO$^{\delta-}$)Cu^{+} site from a mixed Al- and Si-bridged OH group, which is subjected to a dehydration at activation temperatures around 400 °C and to a subsequent Cu exchange. Note that the negative charge of the defective AlO ion is compensated by the positive charge of neighboring

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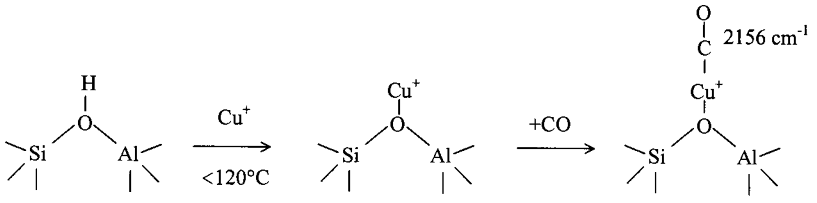
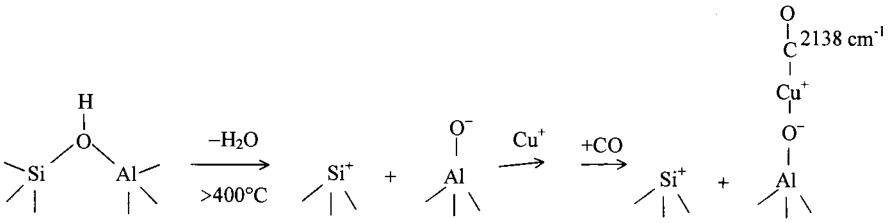
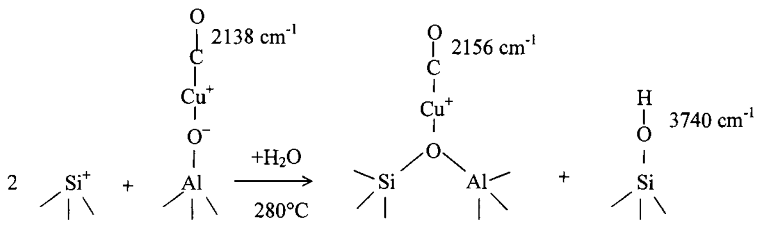
Scheme 1



(a) CO adsorption on Cu$^+$(SiOAl)



(b) CO adsorption on Cu$^+$(O$^{\delta-}$Al)



(c) $\mathrm{CO}\,[\mathrm{Cu^+(O^{\delta-}Al)}] \xrightarrow[280\,°\mathrm{C}]{+\mathrm{H_2O}} \mathrm{CO}[\mathrm{Cu^+(SiOAl)}]$

unsaturated Si sites as previously reported in the reference.[23] The negatively charged defective (AlO$^{\delta-}$)Cu$^+$ site can back-donate more electron density to the CO adsorbed on it due to the extra negative charge. As a result, stronger Cu–CO bonding and lower C–O bond strength (2138 vs 2156 cm^{-1} for mixed-bridged CO) are observable. Therefore upon the Ar purge at room temperature, the 2138 cm^{-1} band remains whereas the 2156 cm^{-1} band vanishes. Scheme 1c is devoted to the transition from the linear-defective to oxo-bridged Cu$^+$ at elevated temperatures. During heating between 100 and 280 °C water molecules, derived from the decomposition of hydroxyl groups or from the movable caged water,[8] may help the transition as shown in Scheme 1c to take place, leading to the regeneration of oxo-bridged (AlSiO)Cu$^+$ and the formation of terminal or isolated sinanol.[23] This can explain the simultaneous rise of the 3740 cm^{-1} band during the transition of the IR band from 2138 to 2156 cm^{-1}. The linear-defective Cu ion model is strongly supported by the fact that the above experimental observations are not found in the identical tests performed on unactivated (without pretreatment at 400 °C) Cu-ZSM-5 samples, for which the 2138 cm^{-1} band is not the predominant band upon Ar purge at room temperature and no transition from 2138 to 2156 cm^{-1} is observed upon heating.

The activation energy for the transformation from the linear-defective (AlO$^{\delta-}$)Cu$^+$ to mixed oxo-bridged (AlSiO)Cu$^+$ can be estimated to be about 4.8 kcal/mol from the plot of the IR band intensity versus inverse temperature as illustrated in Figure 5.

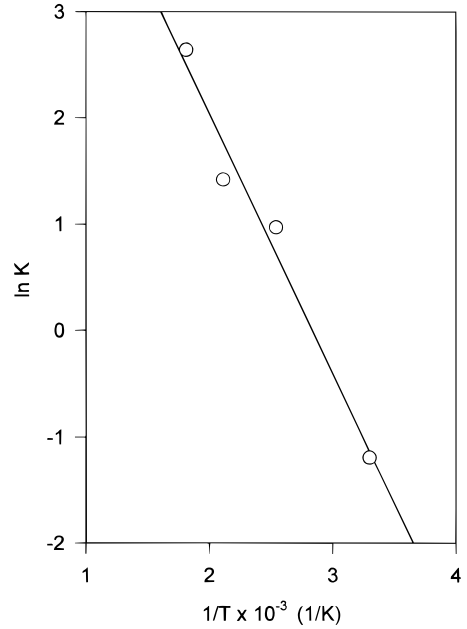


Figure 5. A plot of ln K versus $1/T$ for the transition of CO adsorption from defective (–AlO$^{\delta-}$)Cu$^+$ to mixed bridged (AlSiO)Cu$^+$ sites. K denotes the band intensity ratio of 2156 vs 2138 cm^{-1}, as measured from Figure 3.

4. Conclusions

A new type of Cu$^+$ site, identified as linear-defective (AlO$^{\delta-}$)Cu$^+$, is found to exist mainly in activated Cu-ZSM-5 and is thought to derive from mixed oxo-bridged (SiAlO)Cu^+ due to defective dehydration at 400 °C calcination.

The CO adsorbed at this site produces characteristic CO stretching vibration at 2138 cm^{-1}. It has stronger Cu^+-CO bonding than that for the CO adsorbed at other Cu sites in Cu-ZSM-5 and therefore remains unaffected upon Ar purge at room temperature while CO on other types of Cu sites is removed. The stronger Cu−CO binding and the lower CO stretching vibration are attributed to the stronger π back-bonding due to the defective structure.

The CO adsorbed at linear-defective Cu^+ site can be converted to the CO adsorbed at mixed oxo-bridged (SiAlO)-Cu^+, as manifested in the gradual drop of the 2138 cm^{-1} band and simultaneous growth of the bands at 2156 and 3740 cm^{-1} upon heating at temperatures between 100 and 280 °C. The activation energy of this transition is estimated to be about 4.8 kcal/mol. A scheme has been proposed for this reaction.

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