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Articles

Assignment of Nonclassical $[Cu(CO)_n]^+$ ($n = 1, 2$) Complex Ions in Zeolite Cages

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A time-resolved FT-IR technique combined with an isotopic tracer method has been applied to study CO adsorbates on Cu^+ ions in copper ion-exchanged zeolites. Three kinds of monocarbonyl species were found to adsorb strongly on Cu−zeolite samples after admission and subsequent evacuation of gas phase CO at room temperature. Their absorption bands were observed at 2146−2160, 2128−2150, and 2097−2129 cm^{-1}, respectively, dependent on the zeolite structures. In the presence of gaseous CO, the monocarbonyl species at 2146−2160 cm^{-1} (so called nonclassical $[Cu(CO)]^+$ complexes) could react with a CO molecule to form a dicarbonyl species $[Cu(CO)_2]^+$ with ν_{sym} bands at 2169−2180 cm^{-1}. The reactivity of the nonclassical $[Cu(CO)]^+$ complexes was dependent on the zeolite structures, ferrierite > mordenite > ZSM-5 > X-type $\leftrightharpoons$ offretite/erionite $\leftrightharpoons$ Y-type > L-type. The remaining two types of monocarbonyl species have little been affected by gas phase CO.

Introduction

Copper ion-exchanged zeolites are promising materials for the catalytic decomposition[1] and selective catalytic reduction[2] of nitrogen monoxide and the decomposition of dinitrogen oxide.[3] It has been suggested that the oxidation−reduction process of copper ions in the zeolites plays an important role in determining catalytic activity. For example, Iwamoto et al.,[4] Hall et al.,[5] and Liu and Robota[6] have suggested that Cu^+ cations are active for the decomposition of NO, though Shelef has claimed that only the Cu^{2+} cations would be involved.[7] It should be very significant to characterize the Cu^+ cations in zeolite framework.

Carbon monoxide is widely used as a useful probe to investigate the state of Cu^+ ions in zeolite since the reports of Huang,[8,9] in which formation of a $[Cu(CO)]^+$ complex was confirmed by an intense IR absorption band at 2160 cm^{-1}. The Cu^{2+} ions or the metallic Cu atoms can much more weakly adsorb CO than the Cu^+ ions. However, the assignment of the absorption bands, particularly that of the band at around 2177 cm^{-1} appearing in the presence of gaseous CO, is still one of the controversial problems. For example, Howard and Nicol[10] have reported that an additional band at 2178 cm^{-1} was dependent on the pressure of CO and could be assigned to CO interacting with a Lewis acid site. Sarkany et al.[11] have claimed the appearance of the band at 2177 cm^{-1} to be due to a migration of $[Cu(CO)]^+$ induced by a weak CO adsorption. Spoto et al.[12] have suggested that the band at 2178 cm^{-1} made a pair with a 2151-cm^{-1} band and was attributable to $[Cu(CO)_2]^+$, though they could not confirm the assignment by experiments with $^{12}CO/^{13}CO$ (1/1) isotopic mixtures. In addition, the formation of $Cu^{2+}-CO$ species[13] or polycarbonylic species $Cu(CO)_x$ ($x \geq 2$)[14] has also been reported.

In homogeneous solution a number of cationic metal carbonyl complexes with average ν(CO) values higher than 2143 cm^{-1}, the value of free CO, have been isolated and studied. The so-called nonclassical metal carbonyls have well been investigated on Cu^+ ions[15] and Ag^+ ions by Strauss and his co-workers. Carbon−oxygen stretching frequency is 2164 cm^{-1} for $[Cu(CO)_2][AsF_6]$, which is consistent with a two-coordinate linear ($D_{\infty h}$) structure for the $[Cu(CO)_2]^+$ ion.[15] The comparison of the results of Cu^+-CO complexes on zeolites with those in solution or solid will allow us meaningful discussion of the structure of the surface carbonyl species on Cu−zeolites and of the characterization of the Cu^+ ions.

Experimental Section

All parent zeolites were supplied by Tosoh Corp. Copper ion-exchanged zeolites were prepared as follows. Approximately 20 g of each zeolite was washed in 2 dm^3 of dilute $NaNO_3$ solution and then ion-exchanged in 1 dm^3 of an aqueous copper acetate solution overnight. After filtration, the resulting cake was washed and dried at 383 K for 12 h. The amounts of cations in the ion-exchanged zeolites were determined by a inductive coupled plasma analysis (ICP, Perkin Elmer

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Table 1. Properties of Copper Ion-Exchanged Zeolites and Absorption Bands of Carbonyl Species[a]

zeolite				wavenumber of carbonyl species/cm^{-1}			
				ν of monocarbonyl			
structure	Si/Al ratio	exchange level/%	Cu/Al ratio	α	β	γ	ν_{sym} of dicarbonyl[b]
FAU	1.3	60	0.3	2154	2144	2126[c]	2176
FAU	2.8	76	0.38	2160	2145	2109[c]	2180
LTL	3.0	34	0.17	2150	2140	2122[c]	2176
OFF/ERI	3.9	81	0.41	2146	2128	2097[c]	2169
MOR	5.3	76	0.38	2157	2147	2129[c]	2176
FER	6.2	66	0.33	2156	2140	2122	2175
MFI	11.7	110	0.55	2158	2150	2108[c]	2177

[a] CO was introduced at 13 Torr for 120 min and then removed by evacuation for 30 min at ambient temperature. [b] In the presence of gaseous CO of 13 Torr. [c] Very weak.

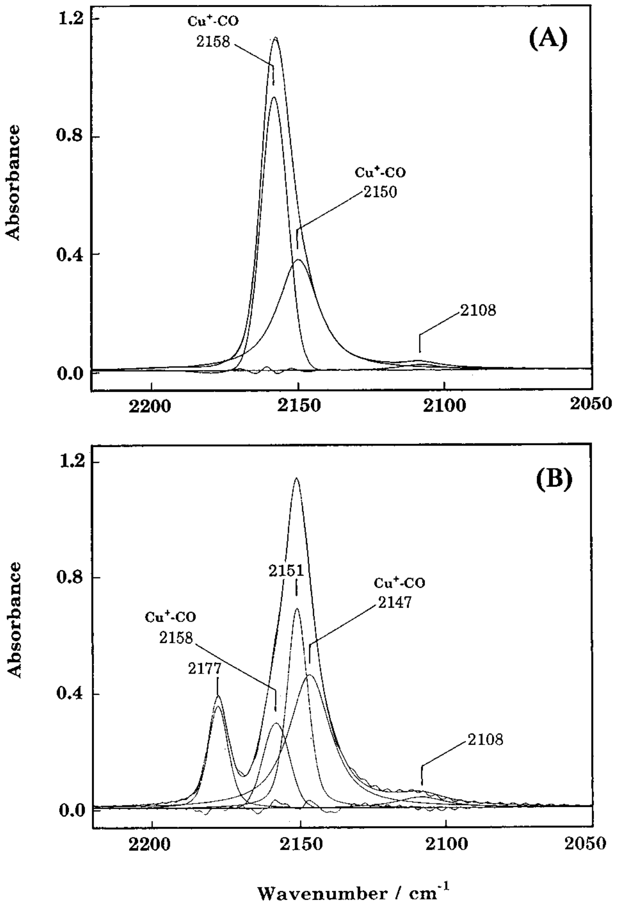

Figure 1. IR spectra and their deconvolution of CO adsorbed on the Cu–MFI–zeolite after adsorption of CO of 13 Torr for 120 min at ambient temperature (B) and subsequent evacuation for 30 min (A).

Optima 3000) after the samples obtained were dissolved in HF solution. The Si/Al molar ratios of parent zeolites used and the ion exchange levels are summarized in Table 1, where the latter values were calculated by 2(amount of Cu)/(amount of Al). IR absorption spectra were recorded at room temperature by using a Perkin-Elmer System 2000 spectrometer. A quartz IR cell with KBr windows was used. A self-supporting wafer (ca. 4 mg cm^{-2}) of the Cu–zeolite was heated in the cell at 773 K for 2 h under a vacuum ($<10^{-2}$ Torr, 1 Torr = 133Pa), oxidized in O_2 of 100 Torr at the same temperature for 2 h, evacuated for 1 h, and then cooled down to ambient temperature in a vacuum as a pretreatment. The IR spectra of adsorbed species were obtained by subtracting the spectrum of wafer.

Results and Discussion

Monocarbonyl Adsorbates on Cu$^+$ Ions. Figure 1 shows the IR spectra of CO adsorbed on Cu–MFI in the region 2200–2050 cm^{-1}. Figure 1A was measured after introduction of CO of 13 Torr into the cell for 2 h and subsequent evacuation of the gas-phase CO for 30 min at ambient temperature. The absorption band at 2158 cm^{-1} can be assigned to the C–O stretching mode of a monocarbonyl adsorbate, $[Cu(CO)]^+$, on the basis of the literature reported.[8–15] Although Sarkany et al.[11] and Spoto et al.[12] have reported that the band consists of a single absorption peak, its shape is not symmetrical as shown in Figure 1A. A numerical deconvolution technique was applied here to decompose the peak and two absorption peaks were obtained at 2158 and 2150 cm^{-1}. This suggests the existence of two kinds of monocarbonyl species on the Cu$^+$ ions exchanged into the MFI structure.

With FAU zeolites of a Si/Al ratio of 2.4–2.5 (so called Y-type zeolite), Borgard et al.[17] and Borovkov and Karge[14] have clearly observed two kinds of monocoarbonyl species at 2160 and 2145 cm^{-1} on the Cu$^+$ ions. In the present study the effect of zeolite structure on absorption bands of CO adsorbates has been independently measured and summarized in Table 1. It is clear that there are three kinds of peak positions on all Cu-zeolites used: 2146–2160, 2128–2150, and 2097–2129 cm^{-1}. The table strongly supports the deconvolution in Figure 1A to be quite reasonable. The C–O stretching frequency is a useful indicator of the magnitude of metal–ligand σ- and π-bonding in metal carbonyls. The C-O bond is strengthened by donation of electrons from the slightly antibonding 5σ orbital of CO to Cu. In contrast to the σ-bonding, the π-back-bonding lowers ν(CO) by the transfer of metal d_π electron density to the CO_{π^*} orbitals. The blue shift in the IR band to 2146–2160 cm^{-1} from the gas phase value of 2143 cm^{-1} indicates that there is little or no π-back-bonding in the $[Cu(CO)]^+$ complexes. Similar ν(CO) values have been observed at 2165 cm^{-1} for BH_3-CO,[18] 2184 cm^{-1} for HCO^+,[19] 2178 cm^{-1} for $[Cu(CO)]^+$ in solid,[15] and 2208 cm^{-1} for $[Ag(CO)]^+$ in solid.[16] In addition, *ab initio* calculation of Bates and Dwyer[20] concludes that the σ-bonding between CO and Al^{3+} ions in zeolites results in a blue shift of the CO band.

On the other hand, there are species with CO stretching frequencies lower than free CO, which indicates that the effect of π-back-bonding on ν(CO) is larger than that of σ-bonding. This type of carbonyl species is widely known on various metal ions as has been summarized by Nakamoto.[21] The observation of three bands on Cu–zeolites suggests the presence of three kinds of Cu$^+$ centers with different adsorption properties in the zeolite lattice. At the present it is unknown what factors decide the degree of contribution of the σ-bonding and the π-back-bonding. On the basis of reactivity of the respective species to gaseous CO, which will be described in the next section, the monocarbonyl adsorbates corresponding to 2146–2160, 2128–2150, and 2097–2129 cm^{-1} are here referred to as α, β, and γ species, respectively. The α species correspond to the nonclassical metal carbonyls, the β species give similar IR wavenumbers to that of free CO, and the γ species are the classic ones.

Dicarbonyl Adsorbates on Cu$^+$ Ions. The time-resolved FT-IR spectra during adsorption of CO onto the Cu–MFI and during removing the gaseous CO by evacuation are shown in parts A and B of Figure 2, respectively. Figure 2A reveals that

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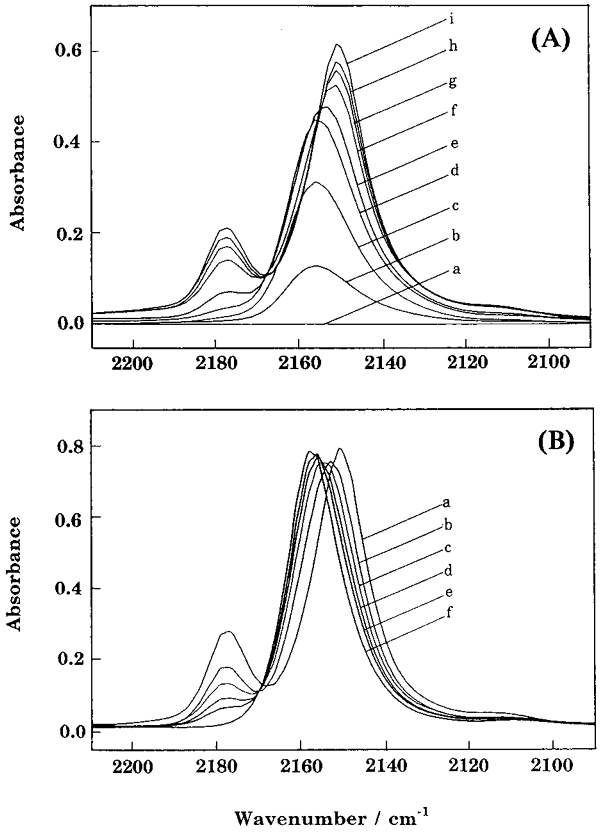

Figure 2. Change in IR spectra during adsorption treatment of CO of 13 Torr on the Cu−MFI−zeolite at ambient temperature (A) and during evacuation treatment of gaseous CO after admission of CO of 13 Torr for 120 min (B). (A) (a) before the introduction of CO, (b) after 0.1 s from admission of CO, (c) 0.2 s, (d) 0.3 s, (e) 0.5 s, (f) 1.0 s, (g) 2.0 s, (h) 5.0 s, (i) 60 s. (B) (a) before the evacuation, (b) after 3.0 s, (c) 6.0 s, (d) 12.0 s, (e) 18.0 s, (f) 180 s.

the absorption peak monotonically increased at 2158 cm^{-1} up to 0.3 s after the introduction of CO, and then the peak gradually increased in intensity with shifting its position to 2151 cm^{-1}. The additional peak at 2177 cm^{-1} appeared simultaneously with the shift of the 2158-cm^{-1} peak. The evacuation of gaseous CO resulted in shift of the 2151 cm^{-1} peak to 2158 cm^{-1} and disappearance of the 2177 cm^{-1} peak. The change between the initial and final spectra depicted in Figure 2B was completely reversible at room temperature. It was also confirmed in a separate experiment that the intensity of the 2177-cm^{-1} peak was dependent on the partial pressure of CO in the gas phase.

To assign the absorption bands in the presence of CO, the spectrum was deconvoluted by using a computor simulation, and typical results were shown in Figure 1B. There are four kinds of bands at 2177, 2158, 2151, and 2147 cm^{-1}. All spectra shown in Figure 2A were also deconvoluted to clarify correlation among these four peaks. Peak areas of the respective absorption bands were plotted against the adsorption time in Figure 3. The 2158 and 2150 cm^{-1} bands appeared first. The former decreased with the adsorption time after reaching a maximum at 0.3 s, while the latter monotonically increased and leveled off around 1.0 s. The position of the latter peak was slightly shifted from 2150 to 2147 cm^{-1}. It should be noted that the intensity of the 2177-cm^{-1} band is in proportion to that of the new 2151-cm^{-1} band, and both of them increased along with the disappearance of the 2158-cm^{-1} band. The change of the spectra during the evacuation of gaseous CO (Figure 2B) was also examined by the deconvolution technique. The [Cu(CO)]$^+$-(α) at 2158 cm^{-1} increased with the disappearance of 2177- and 2151-cm^{-1} bands, while the 2147-cm^{-1} band did not change in intensity with the evacuation but the peak position was shifted back to 2150 cm^{-1}. The findings conclude mutual change between the species corresponding to the 2177 and 2151 cm^{-1} and the [Cu(CO)]$^+$(α) complex.

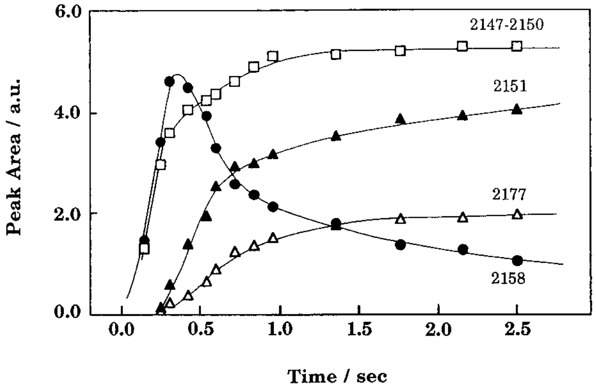

Figure 3. Peak areas of the four absorption bands as a function of the adsorption time. The experimental conditions are the same as those in Figure 2A.

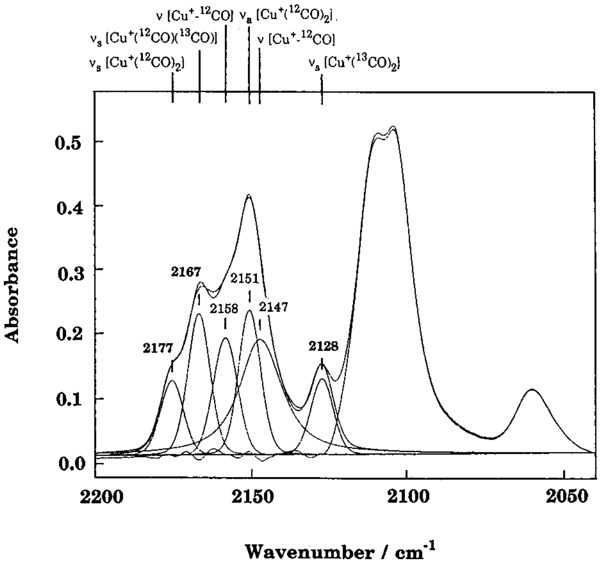

Figure 4. IR spectrum and its deconvolution after introduction of an equimolar mixture of ^{12}CO and ^{13}CO at ambient temperature on the Cu−MFI−zeolite. Both partial pressures of ^{12}CO and ^{13}CO were 7 Torr.

An equimolar mixture of ^{12}CO and ^{13}CO was introduced onto the Cu−MFI sample to determine the adsorbed species in the presence of gas phase CO. The results are shown in Figure 4. In the present experiments the purchased ^{13}CO gas contained 10 vol% $^{13}C^{18}O$ other than $^{13}C^{16}O$, and thus $^{13}C^{18}O$ gave additional peaks around 2060 cm^{-1}. The introduction of the ^{12}CO and ^{13}CO mixture resulted in the appearance of 2167 and 2110 cm^{-1} peaks which were not observed upon the admission of ^{12}CO or ^{13}CO alone. The intensity ratio of the peaks at 2177, 2167, and 2128 cm^{-1} was roughly 1:2:1 as shown in Figure 4. The conclusive assignment of each band is described in Figure 4 on the basis of the calculation of isotopic effect. The results in Figures 2−4 conclude the formation of dicarbonyl species on Cu$^+$ ions through the reaction of the α-type monocarbonyl species with a gaseous CO molecule. The dicarbonyl species reversibly decompose to give the original monocarbonyl species and a free CO molecule by evacuation. The bond angle, 2θ, between two carbonyl ligands can be calculated by the following equation.[22]

$$2\theta = 2\ [\mathrm{arccotan}(A_{\mathrm{sym}}/A_{\mathrm{asym}})]^{0.5}$$

In the equation A_{sym} and A_{asym} are peak areas of the symmetric and asymmetric bands, respectively. The bond angle of dicarbonyl species on Cu−MFI was 110° independent of the partial pressure of CO or the adsorption time. This is very different from the value of 180° in solution or in solid and close to the value of 106° for Rh^+ ions[23] in the FAU zeolite.

The same experiments as those in Figure 2 have been carried out on all zeolites. The α species were all in equilibrium with corresponding dicarbonyl species in the presence of gaseous CO. The ν_{sym} values have been listed in Table 1. The ratio of peak area of ν_{sym} of the dicarbonyl species (A_{di}) to that of the remaining α species (A_{mono}) in gaseous CO of 13 Torr is a good indication of reactivity of the α-type monocarbonyl species. The order was FER(3.9) > MOR(2.1) > MFI(1.1) > FAU(X)(0.9) $\simeq$ OFF/ERI(0.8) $\simeq$ FAU(Y)(0.7) > LTL(0.1), where the numerical values are the ratios of $A_{\mathrm{di}}/A_{\mathrm{mono}}$. It is clear that the order does not agree the order of peak positions of α-type monocarbonyl species, indicating that the degrees of σ-bonding and π-back-bonding are not the significant factor controlling the reactivity of α species to gaseous CO. In addition no correlation between the order of the above reactivity and that of the catalytic activity of Cu−zeolites for NO decomposition and reduction[1−7] can be recognized. The CO-adsorption is a good method to characterize the Cu^+ ions in zeolites, but the catalytic activity of the Cu−zeolites would be determined not only by the characteristics of the copper ions but also by the cage structure, the Si/Al ratio, and the ion exchange level. On the other hand, β and γ species were less reactive with Co in gas phase. It follows that the α carbonyl species have little reception of electrons from the Cu^+ ion through the π-back-bonding and show great ability to form the dicarbonyl species in the presence of gaseous CO, while the β species show the similar peak positions to that of free CO and their reactivity to the gaseous CO are quite low. The intensity of γ adsorbates were very weak in the present experimental conditions, and therefore detailed investigation has not been carried out.

In homogeneous phase Rack et al. reported that the $[Cu(CO)][AsF_6]$ complex was dark brown in color and the $[Cu(CO)_2][AsF_6]$ complex was colorless.[15] The color of Cu−MFI was whitish blue after the pretreatment and did not change during the adsorption−desorption treatment of CO. It has already been reported that half or more of the copper ions loaded on the MFI zeolite lattice exist as Cu^{2+} and 20−50% of the copper is in the form of Cu^+ after the oxidation in O_2 at 673−873 K and subsequent evacuation at the same temperatures.[4−6,11] The formation of Cu^+ ions upon evacuation of Cu−MFI at elevated temperatures has also been revealed by a Cu^+ photoluminescence study.[24] The presence of a significant amount of Cu^+ is thus without doubt in the present Cu−MFI. No color change in the present study might indicate a very small change of the Cu^+ color. The redox behavior of copper ions in the other zeolites has not been studied in detail; the reason for no color change of the Cu−zeolites should be solved in the future. Rack et al. have also reported a Raman absorption band at 2177 cm^{-1} for $[Cu(CO)_2][AsF_6]$ in the solid state,[15] but we could not observe a corresponding Raman band probably because of the low concentration of the adsorbates compared to the sensitivity of the Raman spectrometer (Perkin-Elmer System 2000 R).

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