# Assignment of the 2177 cm$^{-1}$ Absorption Band Appearing upon Admission of CO on a Copper Ion-exchanged MFI Zeolite

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The titled absorption band was attributable to $\nu_{sym}$ of a dicarbonyl species adsorbed on a Cu$^+$ ion. The monocarbonyl species at 2158 cm$^{-1}$ and the dicarbonyl species at 2177 and 2151 cm$^{-1}$ have reversibly changed each other dependent on the partial pressure of CO.

Copper ion-exchanged zeolites are active for the catalytic decomposition[1] and selective catalytic reduction[2] of nitrogen monoxide and the decomposition of dinitrogen oxide.[3] It has widely been suggested that Cu$^+$ cations are active for the decomposition of NO,[4-6] though Shelef has claimed that only Cu$^{2+}$ cations would be involved.[7] It is very significant to characterize the Cu$^+$ cations in zeolite framework.

Carbon monoxide is used as a useful probe to investigate the state of Cu$^+$ ions in zeolite since the reports of Huang.[8,9] However, the assignment of the absorption band at 2177 cm$^{-1}$ appearing in the presence of gaseous CO is still a controversial problem. Howard and Nicol[10] have reported that the band at 2178 cm$^{-1}$ could be assigned to CO interacting with a Lewis acid site on zeolite lattice. Sarkany et al.[11] have claimed that the appearance of the band at 2177 cm$^{-1}$ was due to migration of [Cu(CO)]$^+$ induced by weak CO adsorption. On the other hand, it has been suggested by Spoto et al.[12] 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 isotopic mixtures. The other adsorbates suggested were Cu$^{2+}$-CO species[13] and polycarbonylic species Cu(CO)$_x$ ($x \geqq 2$).[14]

A time-resolved FT-IR technique combined with an isotopic tracer method has been applied here to study CO adsorbates on Cu$^+$ ions in copper ion-exchanged MFI zeolites.

Copper ion-exchanged MFI zeolites were prepared by a conventional method.[4] The Si/Al molar ratio and the ion exchange level were 11.7 and 110%. IR absorption spectra were recorded at room temperature by using Parkin 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-MFI was heated in the cell at 773 K for 2 h under a vacuum (<10$^{-2}$ Torr, 1 Torr=133 Pa), 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 substracting the spectrum of wafer.

Introduction of CO at 13 Torr onto Cu-MFI for 2 h and subsequent evacuation of the gas-phase CO for 30 min at ambient temperature gave an intense absorption band at 2158 cm$^{-1}$ and a very weak band at 2108 cm$^{-1}$. The former can be assigned to the C-O stretching mode of a monocarbonyl adsorbate on the basis of the literature.[8-15] Although several workers[11,12] have reported that the 2158 cm$^{-1}$ band consists of a single peak, its peak shape was not symmetrical. A numerical deconvolution technique was applied here to decompose the peak and two absorption peaks were obtained at 2158 and 2150 cm$^{-1}$. With FAU zeolites, Borgard et al.[15] and Borovkov and Karge[14] have clearly observed two kinds of monocarbonyl species at 2160 and 2145 cm$^{-1}$ on the Cu$^+$ ions. It follows that there are three kinds of peaks at 2158, 2150, and 2108 cm$^{-1}$ on Cu-MFI after evacuation of gaseous CO. Three bands suggest the presence of three kinds of Cu$^+$ centers with different adsorption properties in the zeolite lattice. At the present it is unknown what factors control the degree of contribution of the σ-bonding and the π-backbonding.

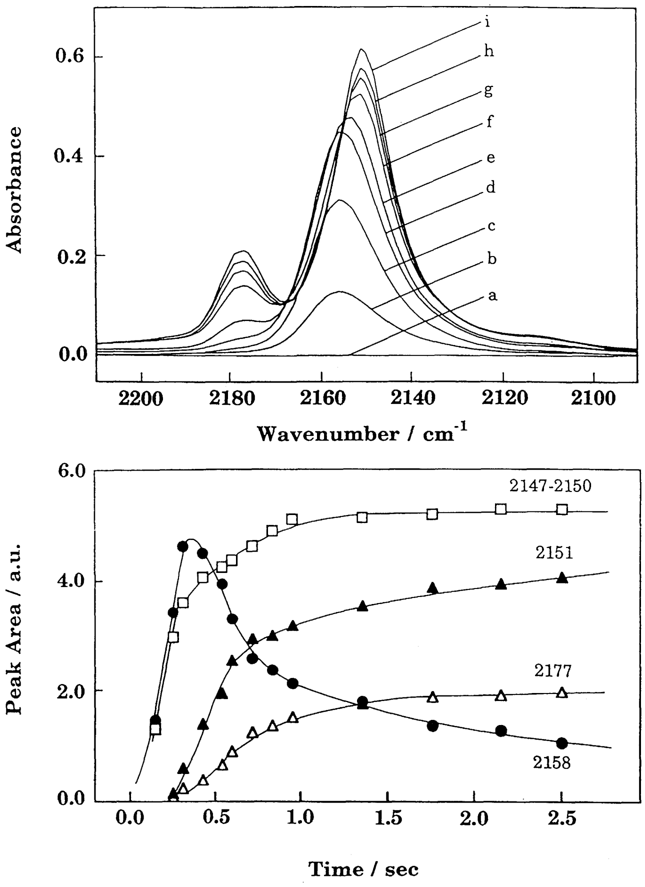

**Figure 1.** Change in IR spectra during adsorption treatment of CO of 13 Torr on Cu-MFI at ambient temperature (A) and peak areas of four absorption bands as a function of the adsorption time (B). (A) (a) before the introduction of CO, (b) after 0.1, (c) 0.2, (d) 0.3, (e) 0.5, (f) 1.0, (g) 2.0, (h) 5.0, and (i) 60 sec from admission of CO.

The time-resolved FT-IR spectra during adsorption of CO on the Cu-MFI are shown in Figure 1a. It reveals that the absorption peak monotonically increased at 2158 cm$^{-1}$ up to 0.3 sec after the introduction of CO and then the peak

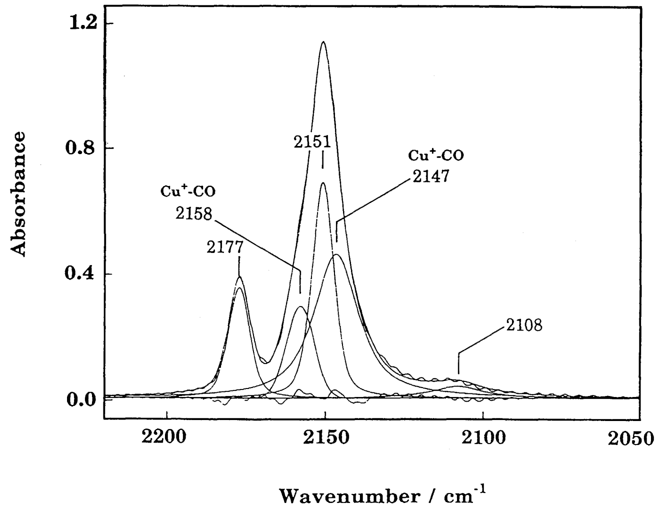

**Figure 2.** An IR spectrum and its deconvolution of CO adsorbates on the Cu-MFI zeolite after adsorption of CO of 13 Torr for 120 min at ambient temperature.

gradually increased in intensity with shifting its position to 2151 cm$^{-1}$. A new peak at 2177 cm$^{-1}$ appeared simultaneously with the shift of the 2158 cm$^{-1}$ peak and increased with time. 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. It was also confirmed that the intensity of the 2177 cm$^{-1}$ peak was dependent on the partial pressure of CO in the gas phase.

The spectra were deconvoluted and a typical result was shown in Figure 2. There are four kinds of strong bands at 2177, 2158, 2151, and 2147 cm$^{-1}$. Peak areas of the respective absorption bands were plotted against the adsorption time in Figure 1b. The 2158 and 2150 cm$^{-1}$ bands appeared first. The former decreased with the adsorption time after reaching a maximum at 0.3 sec, while the latter monotonically increased and leveled off around 1.0 sec. The position of the latter peak was slightly shifted from 2150 to 2147 cm$^{-1}$. The intensity of the 2177 cm$^{-1}$ band is in proportion to that of newly recognized 2151 cm$^{-1}$ band, and both of them increased along with the disappearance of 2158 cm$^{-1}$ band. The findings conclude mutual change between the species corresponding to the 2177 and 2151 cm$^{-1}$ and the $[Cu(CO)]^+$ complex at 2158 cm$^{-1}$.

An equimolar mixture of $^{12}CO$ and $^{13}CO$ was introduced onto the Cu-MFI sample to determine the adsorbed species. The results are shown in Figure 3. 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. The conclusive assignment of each band is described in Figure 3 on the basis of the calculation of isotopic effect. In the pairs of the IR absorption bands, the peaks at higher wavenumbers are attributable to the respective symmetric stretching vibration modes.

Figures 1 and 3 conclude the formation of dicarbonyl species on Cu$^+$ ions through the reaction of the monocarbonyl species with a gaseous CO molecule. It follows that the only

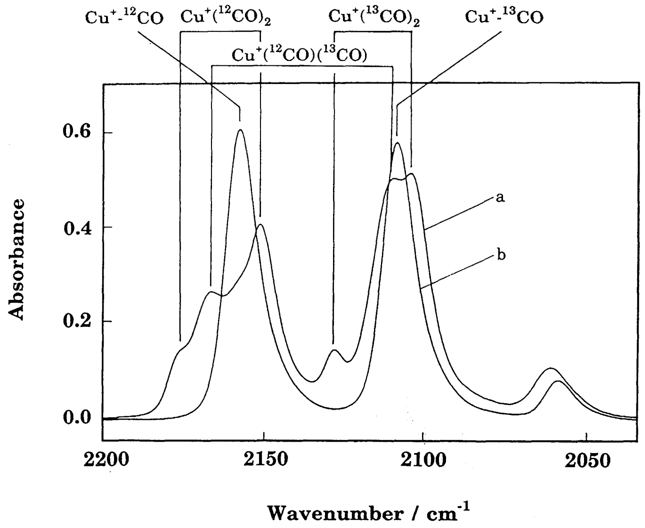

**Figure 3.** IR spectra after introduction of an equimolar mixture of $^{12}CO$ and $^{13}CO$ on the Cu-MFI zeolite (a) and subsequent evacuation (b). Both partial pressures of $^{12}CO$ and $^{13}CO$ were 7 Torr.

monocarbonyl species at 2158 cm$^{-1}$ show great ability to form the dicarbonyl species in a CO atmosphere, which gave the bands at 2177 and 2151 cm$^{-1}$. The detection of the inert 2147-2150 cm$^{-1}$ band in the absence of gaseous CO and the dynamic change in IR spectra during CO adsorption have also been clarified here.

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