RESEARCH NOTE

FTIR Study of Low-Temperature CO Adsorption on Cu-ZSM-5: Evidence of the Formation of $Cu^{2+}(CO)_2$ Species

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CO adsorption at ambient temperature leads to formation of the well-known Cu^+–CO species (2158 cm^{-1}) and $Cu^+(CO)_2$ dicarbonyls (2177 and 2150 cm^{-1}). In addition, Cu^{2+}–CO complexes (2179 cm^{-1}) appear under equilibrium CO pressure and are very easily destroyed by evacuation. The CO stretching frequency almost coincides in position with ν_s of the $Cu^+(CO)_2$ species. Lowering the temperature in the presence of gas-phase CO leads to formation of $Cu^{2+}(CO)_2$ geminal dicarbonyls (2170 cm^{-1}) and a small amount of $Cu^+(CO)_3$ tricarbonyls (evidenced by a band at 2191 cm^{-1}). The results demonstrate the high coordinative unsaturation of both Cu^+ and Cu^{2+} ions in Cu-ZSM-5. ©️ 2000 Academic Press

1. INTRODUCTION

The discoveries that Cu-ZSM-5 catalyzes both NO decomposition (1) and selective catalytic reduction of NO_x by hydrocarbons (2, 3) have roused immense interest in this catalyst (4–22). Many studies deal with IR characterization of Cu-ZSM-5 by adsorption of probe molecules, in particular CO (4–21). Usually, CO adsorption at ambient temperature on oxide-supported copper ions leads to formation of linear Cu^+–CO species observed in the IR spectra at about 2130 cm^{-1} (7, 23–30). These species are relatively stable because of the cooperative effect of the σ and π bonds. In fact, they are partly destroyed but do not disappear during evacuation at ambient temperature. Cu^+–CO complexes with a higher frequency, at 2160–2156 cm^{-1}, have been observed with Cu^+ ions exchanged in some zeolites, such as CuY (31–35), Cu-mordenite (12, 36), and Cu-ZSM-5 (4–21). It was reported, in 1994 (4), that under CO equilibrium pressure the monocarbonyls on Cu-ZSM-5 are converted to $Cu^+(CO)_2$ geminal species characterized by $\nu_s(CO)$ at 2178 cm^{-1} and $\nu_{as}(CO)$ at 2151 cm^{-1}. Moreover, at low temperatures up to three CO molecules can be bound to one Cu^+ site, the respective $Cu^+(CO)_3$ species being characterized by a set

of bands at 2192, 2167, and 2140 cm^{-1} (5, 6). Similar conclusions have also been drawn concerning CuY (34) and Cu-mordenite (36) samples. All this suggests a low coordination of Cu^+ in zeolites, in particular Cu-ZSM-5, which allows bonding of more than one adsorbate molecule. In agreement with this, it has been reported that Cu^+ ions from Cu-ZSM-5 can form $Cu^+(H_2O)$–CO (7, 8), $Cu^+(NH_3)$–CO (9), $Cu^+(NH_3)(CO)_2$ (9), and $Cu^+(NO)_2$ (22) complexes.

Multicarbonyls are typical of some cations, such as Rh^+ (37), Ir^+ (38), Ru^{n+} (39), and Os^{3+} (40). In all these cases, however, the support effect is negligible and the species formed are very stable. As multicarbonyls of Cu^+ are reported with Cu in zeolite matrix only, in these cases a site-specified formation of those complexes occurs. Recent investigations revealed similar properties with other cations exchanged in zeolites. Thus, at low temperatures, more than one CO and/or one N_2 molecule can be bound to Ag^+ in Ag-ZSM5 (41), to Na^+ in NaY (42), Na-ZSM-5 (43), Na-EMT (44), and Na-ETS-10 (45), and to K^+, Rb^+, and Cs^+ in EMT (44). These observations imply that the process is rather typical of cations in some positions in the zeolites but is not limited by the nature of the cation.

Many data suggest that the active sites for the SCR of nitrogen oxides by hydrocarbons on Cu-ZSM-5 are Cu^{2+} cations (8, 22). For this reason, it is of great importance to characterize these cations. In the light of the above discussion, one could expect the formation, under appropriate conditions, of multicarbonyls of Cu^{2+}. However, no data are available in the literature in this respect, since low-temperature measurements of CO adsorption have been performed on Cu^+-ZSM-5 samples (5, 6).

In principle, the Cu^{2+}–CO complexes are unstable and are detected at about 2175 cm^{-1} at low temperatures only (20, 23, 29, 46, 47). There are some reports on the detection of Cu^{2+}–CO species at ambient temperature, but under equilibrium CO pressure alone (7, 11, 14, 12, 24, 28, 30). In these cases the C–O stretching frequencies have been reported in the region 2225–2180 cm^{-1}. For Cu-ZSM-5, there

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is again disagreement in the interpretation of the IR spectra of adsorbed CO. Most authors assign the 2178 cm^{-1} band, observed under equilibrium CO pressure, to $\nu_s(CO)$ of $Cu^+(CO)_2$ species (4–10, 17–20), whereas according to others (11, 14) this band is produced by Cu^{2+}–CO complexes. Indeed, taking into account the low coordination number of Cu^{2+} in Cu-ZSM-5, one can suppose that this is the ideal system for observation of Cu^{2+}–CO species at ambient temperature.

The aim of this investigation was to characterize the carbonyls of Cu^{2+} formed on Cu-ZSM-5. For this purpose we studied CO adsorption on Cu-ZSM-5 at different temperatures. For better interpretation of the spectra we also performed some ^{12}CO–^{13}CO coadsorption experiments. The results obtained revealed the formation of Cu^{2+}–CO species at ambient temperature and $Cu^{2+}(CO)_2$ species at low temperature. Additional information about the $Cu^+(CO)_x$ species was also obtained.

2. EXPERIMENTAL

IR spectroscopy studies were carried out with a Bruker IFS 66 apparatus at a spectral resolution of 1 cm^{-1} accumulating 128 scans. Self-supporting wafers (ca. 10 mg cm^{-2}) were prepared by pressing the sample powders at 10^4 kPa. The samples were heated directly in the IR cell. The latter was connected to a vacuum/sorption system with a base pressure of less than 10^{-3} Pa. Prior to the adsorption measurements the sample was activated by calcination at 400°C for 1 h and evacuation at 500°C for 1 h. A specially constructed cell allowed the IR measurements to be performed at different temperatures down to 85 K.

The Cu-ZSM-5 sample was prepared by ion exchange of H-ZSM-5 (Si : Al ratio = 40) with a $Cu(NO_3)_2$ solution according to the procedure described by Iwamoto *et al.* (48). Chemical analysis showed 1.9 wt% Cu, which corresponded to 150% exchange.

Carbon monoxide (>99.997) and nitrogen monoxide (>99.5) were supplied by Linde AG, and the ^{13}C-labeled CO, by Aldrich Chemical Company Inc. Its isotopic purity toward ^{13}C was 99 at.% but it contained about 10 at.% $^{13}C^{18}O$.

3. RESULTS AND DISCUSSION

3.1. Sample Characterization

The IR Spectrum of the activated sample is typical of Cu-ZSM-5. In particular we note the lack of bands around 3610 cm^{-1} where the acidic zeolite hydroxyls are observed. This is consistent with the high-exchange degree of the sample.

Although CO is the most appropriate probe molecule for characterization of Cu^+ cations, the state of Cu^{2+} cations is better monitored by NO (17, 22, 49–53). Adsorption of NO

(1-kPa equilibrium pressure) on the sample results in the appearance of an intense band at 1986 cm^{-1} and a weaker band at 1811 cm^{-1}. In addition, three more low-intensity bands have also been detected, their maxima being at 1965, 1825, and 1733 cm^{-1}. According to data from the literature (17, 49, 50), the principal band at 1986 cm^{-1} is due to Cu^{2+}–NO complexes formed with the participation of isolated copper ions in a square-planar configuration. It is also believed that these cations have an adjacent O^- anion; i.e., the structure of the adsorption site is Cu^{2+}–O^- (50–52). The weak band at 1965 cm^{-1} is considered to be due to nitrosyls on associated Cu^{2+} cations (53). The band at 1811 cm^{-1} characterizes Cu^+–NO species, whereas the corresponding dinitrosyls, $Cu^+(NO)_2$, produce the set of bands at 1825 and 1733 cm^{-1} (17, 22, 51). Thus, the NO adsorption experiments evidence that the major part of copper on our activated Cu-ZSM-5 sample is in the form of isolated Cu^{2+} cations. In addition, small fractions of Cu^+ ions and associated Cu^{2+} sites are also present.

3.2. Adsorption of CO at Ambient Temperature

Introduction of CO (1-kPa equilibrium pressure) at ambient temperature to the activated Cu-ZSM-5 sample leads to the appearance of three bands with maxima at 2177, 2157.5, and 2150.5 cm^{-1}, which is consistent with literature data (4–9). The band at 2157.5 cm^{-1} is due to Cu^+–CO species, whereas the bands at 2177 and 2150.5 cm^{-1} have been assigned to $Cu^+(CO)_2$ dicarbonyls (4–10, 17–20). Some authors assign the 2177 cm^{-1} band to Cu^{2+}–CO species (11, 14). Simultaneously, a band at 2357 cm^{-1} with a shoulder at 2363 cm^{-1} appears and grows with time. The latter is assigned to adsorbed CO_2. Evacuation leads to disappearance of the CO_2 bands as well as of the bands at 2177 and 2150 cm^{-1}. Simultaneously, the band at 2157.5 cm^{-1} grows in intensity. A second CO admission restores the spectrum in the C–O stretching region (with a slightly higher intensity of the bands) and only a very small amount of CO_2 is produced. Evacuation and introduction of a third CO portion result in no CO_2 bands. The results suggest that CO reduces some Cu^{2+} cations to Cu^+ at ambient temperature. To prevent the eventual effects of CO_2 on the spectra, we studied samples repeatedly exposed to CO.

Figure 1 shows the variations of the CO bands as a function of equilibrium pressure. It is evident that the 2177 cm^{-1} band is more sensitive to equilibrium pressure than the band at 2150.5 cm^{-1}. In addition, an isosbestic point at 2153.5 cm^{-1} is found for the 2157.5 and 2150.5 cm^{-1} bands, whereas no such point exists with the two bands at 2157.5 and 2177 cm^{-1}. This indicates that the latter bands are not (totally) due to interconverted species. Computer deconvolution of the spectra suggests that the 2177 cm^{-1} band at high coverages consists of at least three components with maxima at 2179, 2177, and 2175 cm^{-1}.
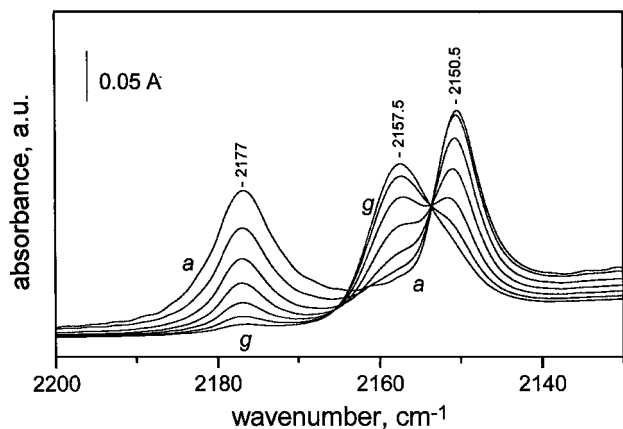
FIG. 1. FTIR spectra of CO adsorbed on Cu-ZSM-5 at ambient temperature and equilibrium pressures of 7200 (a), 3000 (b), 1500 (c), 600 (d), 250 (e), 110 (f), and 50 (g) Pa of CO.

FIG. 3. FTIR spectra of CO (150 Pa equilibrium pressure) adsorbed on Cu-ZSM-5 at different temperatures: 283 (a), 253 (b), 223 (c), 193 (d), 173 (e), 153 (f), 133 (g), 113 (h), and 85 (i) K.

The Cu-ZSM-5 wafer has been prereduced in CO at different temperatures. Adsorption of CO on the sample prereduced at 523 K results in the appearance of two principal bands at 2177 and 2150.5 cm^{-1} with an intensity ratio of 0.61 (Fig. 2, spectrum a). In addition, a small Cu$^+$–CO band is detected at 2158 cm^{-1}, whereas the weak absorbance at ca. 2130 cm^{-1} is assigned to CO adsorbed on associated Cu$^+$ ions. With the increase in the prereduction temperature up to 723 K (Fig. 2, spectra b–e), the intensity ratio of the 2177 and 2150.5 cm^{-1} bands decreases to 0.23. Simultaneously the FWHM of the 2177 cm^{-1} band decreases from 4.2 cm^{-1} (spectrum a) to 3.5 cm^{-1} (spectrum e) (see the inset to Fig. 2) and its maximum is slightly redshifted. All this supports the hypothesis that at least part of the band at 2177 cm^{-1} is due to Cu^{2+}–CO species. However, the absolute intensity of this band increases with the prereduction temperature, which indicates that it is partly due to carbonyls of Cu$^+$.

3.3. Low-Temperature Adsorption of CO

An activated Cu-ZSM-5 sample was placed in an atmosphere of 150 Pa CO and the temperature was gradually decreased. Lowering the temperature to 223 K resulted in the rapid disappearance of the Cu$^+$–CO monocarbonyl band at 2157 cm^{-1} and an increase in intensity of the bands at 2178 and 2150.5 cm^{-1} (Fig. 3, spectra a–c). Further decrease in the temperature down to 193 K (Fig. 3, spectrum d) did not affect the 2150 cm^{-1} band but resulted in a significant enhancement in intensity of the band at 2177 cm^{-1} (shifted to 2178 cm^{-1}). Computer deconvolution (using Lorentzian functions) revealed the complex character of this band which consisted of three components at 2179, 2177, and 2170 cm^{-1} (Fig. 4, spectrum d). The band at
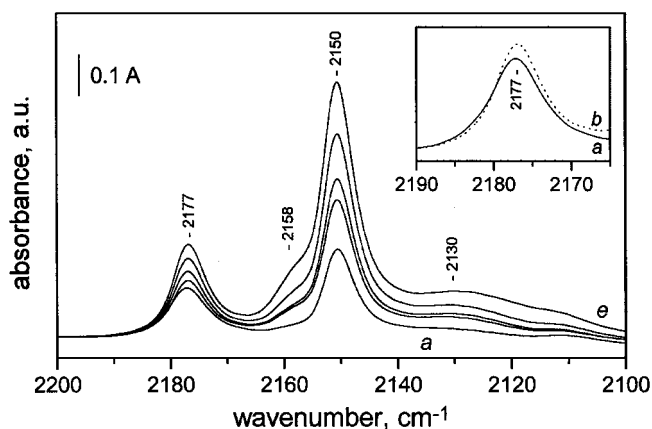

FIG. 2. FTIR spectra of CO (3 kPa equilibrium pressure) adsorbed at ambient temperature on Cu-ZSM-5 pre-reduced at 523 (a), 573 (b), 623 (c), 673 (d), and 723 (e) K.
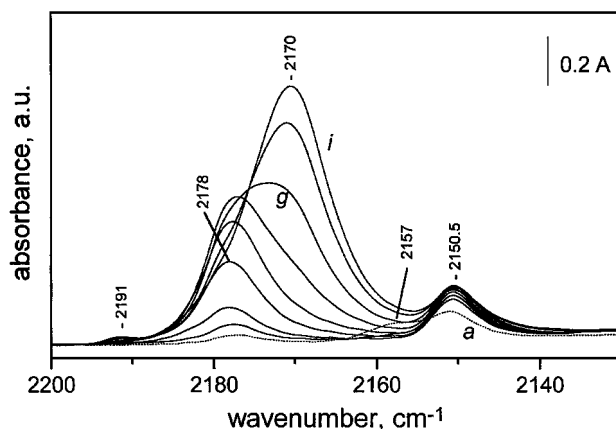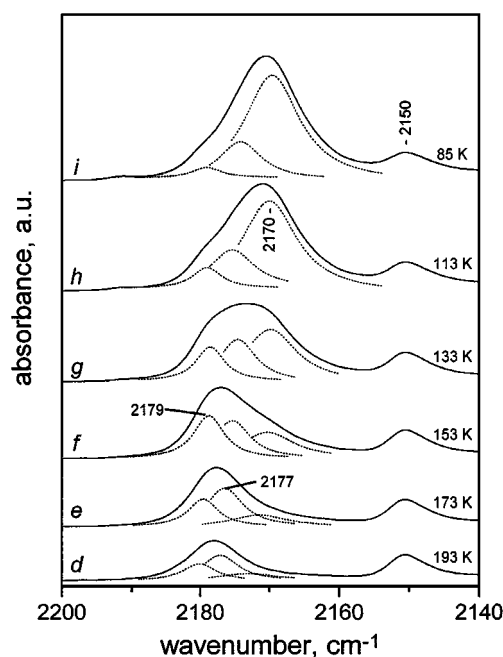

FIG. 4. Computer deconvolution of some spectra presented in Fig. 3.

TABLE 1

C–O Stretching Frequencies of the Carbonyls Formed on Cu-ZSM-5

Species	Formation conditions	$\nu(^{12}CO)$ (cm^{-1})	Ref.
Cu^+–CO	Ambient temperature; resistant toward evacuation	2157.5	4–21
$Cu^+(CO)_2$	Ambient temperature and equilibrium CO pressure; resistant toward evacuation at 85 K	2177 2151	(4–10, 17–20)
$Cu^+(^{12}CO)(^{13}CO)$	As above, after adsorption of isotopic mixtures	2169	This work
$Cu^+(CO)_3$	Observed only at low temperatures and under equilibrium CO pressure	2192 2167 2138^a	(5, 6)
Cu^{2+}–CO	Ambient temperature, high equilibrium CO pressures; slowly decomposed during evacuation at 85 K	2179	This work
$Cu^{2+}(CO)_2$	Observed only at low temperatures and under equilibrium CO pressure; more stable than the $Cu^+(CO)_3$ species	2170	This work

^{a} Not detected in this work.

$2179\ cm^{-1}$ reached maximum intensity at 153 K and than started to decline, almost disappearing at 85 K (Fig. 4, spectrum i). The band at $2177\ cm^{-1}$ was close to saturation even at 173 K and its intensity slightly depended on temperature. The band at $2170\ cm^{-1}$ showed a pronounced rise with the decrease in temperature. In addition, the band at $2150\ cm^{-1}$ slightly decreased in intensity below 133 K and a new band at $2191\ cm^{-1}$ developed.

The above results suggest that low-temperature CO adsorption on Cu-ZSM-5 leads to the formation of some species in addition to those already reported in the literature. The known complexes are listed in the upper part of Table 1. Evidently, the $2177\ cm^{-1}$ band is partly due to $Cu^+(CO)_2$ species. However, its relatively high intensity (as compared with the intensity of the $2150.5\ cm^{-1}$ band) suggests the contribution of another vibration to this absorbance. This is most probably due to quazi-free CO molecules in the zeolite channels; however, formation of CO complexes with residual Na^+ cations is not excluded (43).

The new species are characterized by bands at 2179 and $2170\ cm^{-1}$. The behavior of the band at $2179\ cm^{-1}$ is typical of monocarbonyls that are converted into dicarbonyls. Considering the frequency of the band and the results on CO adsorption at ambient temperature, as well as the results on NO adsorption, we assign the band at $2179\ cm^{-1}$ to Cu^{2+}–CO species formed on isolated Cu^{2+} ions (see Table 1). The only band that is developed at the expense of the band at $2179\ cm^{-1}$ is that at $2170\ cm^{-1}$. For this reason it is assigned to the vibrations of $Cu^{2+}(CO)_2$ species. In this case no split of the C–O modes into symmetric and antisymmetric stretching modes has been observed because the adsorption is very weak and no coupling between the adsorbed molecules is expected. Although formation of some tricarbonyls is not excluded, we have no direct evidence of it. Note that the Cu^{2+}–CO band almost coincides in position with the $\nu_s(CO)$ of the $Cu^+(CO)_2$ species.

The $2191\ cm^{-1}$ band has already been observed after low-temperature CO adsorption on Cu^+-ZSM-5 (5, 6). It has been established that this band, together with two bands at 2167 and $2140\ cm^{-1}$, characterizes $Cu^+(CO)_3$ species. Our results are in agreement with this interpretation, since the $Cu^+(CO)_2$ band at $2150\ cm^{-1}$ decreases with the development of the band at $2191\ cm^{-1}$. The results question, however, the assignment of a band at $2140\ cm^{-1}$ to tricarbonyls since we have not observed such a band. Unfortunately, we cannot draw any conclusions about the band at $2167\ cm^{-1}$, since it is masked by the strong band at $2170\ cm^{-1}$.

To obtain information on the vibrational interaction between the geminal CO molecules, we performed a study of ^{12}CO–^{13}CO coadsorption. This would also confirm the assignment of part of the $2177\ cm^{-1}$ band to $Cu^+(CO)_2$ species, which was somewhat questioned by the above results.

Adsorption of a ^{12}CO–^{13}CO isotopic mixture (molar ratio of ca. $1:1$) on the sample results in the appearance of three intense bands, assigned to $\nu(^{12}CO)$ ($2170\ cm^{-1}$), $\nu(^{13}CO)$ ($2121\ cm^{-1}$), and $\nu(^{13}C^{18}O)$ ($2062\ cm^{-1}$) of dicarbonyls of Cu^{2+} (spectra not shown). Progressive evacuation results in a decrease in intensity of the bands and the appearance, at their expense, of bands due to Cu^{2+}–CO monocarbonyls: $2179\ cm^{-1}$ (^{12}CO), $2131\ cm^{-1}$ (^{13}CO), and $2080\ cm^{-1}$ ($^{13}C^{18}O$). At low pressures the different bands of Cu^+ dicarbonyl species are clearly visible (Fig. 5, spectra a–d). First are the bands observed after adsorption of ^{12}CO or ^{13}CO only: $\nu_s(^{12}CO)$ at $2177\ cm^{-1}$; $\nu_{as}(^{12}CO)$ at $2150.5\ cm^{-1}$; $\nu_s(^{13}CO)$ at $2130\ cm^{-1}$; and $\nu_{as}(^{13}CO)$ at $2103\ cm^{-1}$ (the $^{13}C^{18}O$ species are considered later). In addition, two new bands, not observed after adsorption of pure isotopes, have been detected, their maxima being at 2169 and $2112\ cm^{-1}$. These bands are assigned to $\nu(^{12}CO)$ and $\nu(^{13}CO)$, respectively, of mixed $Cu^+(^{12}CO)(^{13}CO)$ species (see Table 1). The positions of both bands are intermediate between the frequencies of the symmetric and
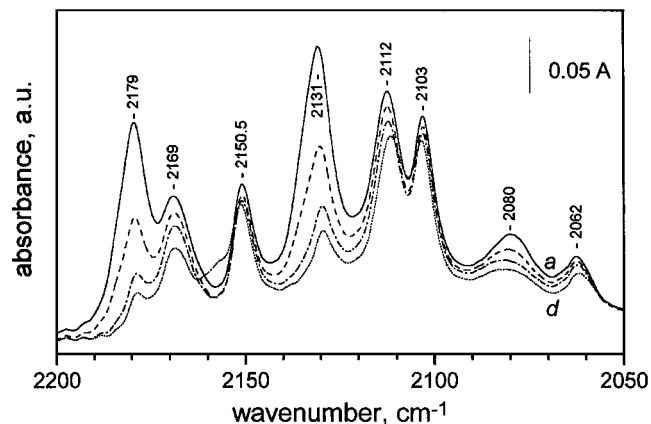
FIG. 5. FTIR spectra of ^{12}CO–^{13}CO isotopic mixtures adsorbed on Cu-ZSM-5 at 85 K, then evacuated at different temperatures: 103 (a), 123 (b), 153 (c), and 173 (d) K.

antisymmetric modes of pure isotopic species. Since the concentration of $^{13}C^{18}O$ is negligible (see Experimental), no $Cu^+(^{13}C^{18}O)_2$ species in a measurable concentration are expected. In agreement with this, only a band for mixed $Cu^+(^{13}C^{18}O)(^{13}C^{16}O)$ and $Cu^+(^{13}C^{18}O)(^{12}C^{16}O)$ complexes was observed at 2062 cm^{-1}.

Thus, the results on adsorption of ^{12}CO–^{13}CO isotopic mixtures indicate that: (i) the vibrational interaction between the two CO molecules in $Cu^{2+}(CO)_2$ complexes is negligible and (ii) the $\nu_s(^{12}CO)$ mode of geminal $Cu^+(^{12}CO)_2$ species is observed around 2177 cm^{-1} and the band almost coincides in position with the Cu^{2+}–CO band (2179 cm^{-1}).

4. CONCLUSIONS

Both Cu^+ and Cu^{2+} ions in Cu-ZSM-5 are low-coordinated. This allows simultaneous coordination of more than one CO molecule to one cation.

Due to the cooperative effect of the σ and π bonds, the Cu^+–CO complexes in Cu-ZSM-5 are stable at ambient temperature. Consequently, $Cu^+(CO)_2$ species are formed at ambient temperature in the presence of CO. However, $Cu^+(CO)_3$ species are stable only at low temperature and under equilibrium CO pressure.

Adsorption of CO on Cu^{2+} ions from Cu-ZSM-5 is weak and occurs via formation of a σ bond and/or polarization. As a result, the Cu^{2+}–CO species are unstable and are destroyed by evacuation even at low temperature. The geminal $Cu^{2+}(CO)_2$ species are stable only at low temperatures and under equilibrium CO pressure.

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