



Editor's Choice paper

FTIR study of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ coadsorption on Cu–ZSM-5Nicola Drenchev^a, Peter A. Georgiev^b, Konstantin Hadjiivanov^{a,*}^a Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria^b Department of Structural Chemistry, University of Milan, 21 Via G. Venezian, I-20133 Milan, Italy

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ABSTRACT

Adsorption of $^{12}\text{C}^{16}\text{O}$ – $^{13}\text{C}^{18}\text{O}$ isotopic mixtures was used to establish polycarbonyl structures formed with Cu^+ ions in Cu–ZSM-5. The principal $\text{Cu}^+(\text{C}^{16}\text{O})_2$ dicarbonyls are characterized by ν_s at 2178 cm^{-1} and ν_{as} at 2151 cm^{-1} . In excellent agreement with theory, $\text{Cu}^+(\text{C}^{16}\text{O})(\text{C}^{18}\text{O})$ mixed-ligand species were found to absorb at 2168 and 2065 cm^{-1} . Another kind of dicarbonyls, characterized by ν_s at 2183 cm^{-1} , was also unambiguously detected. Tricarbonyls are characterized by two IR modes, at 2191 and 2166 cm^{-1} . Different bands of $\text{Cu}^+(\text{C}^{16}\text{O})_x(\text{C}^{18}\text{O})_y$ ($x+y=3$) species were established. The use of isotopic mixtures also helped in the assignment of a shoulder at 2194 cm^{-1} to Cu^{2+} –CO adducts.

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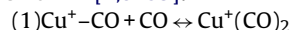
1. Introduction

Cu–ZSM-5 is one of the most studied solids in the field of catalysis. This is the classic catalyst for selective catalytic reduction of NO_x with hydrocarbons (HC-SCR) [1,2] and is also reported to be very active in NO decomposition [3]. Because of these valuable properties, many research groups have focused efforts on detailed characterization of Cu–ZSM-5 [4–45]. One of the most informative techniques for that purpose is IR spectroscopy of probe-molecules, especially of adsorbed CO. Note that CO is very convenient probe for detection of Cu^+ sites [46]. The Cu^+ –CO bond is relatively strong, due to the synergism between the σ - and π -components. In addition, the π -bond enhances the C–O extinction coefficient which allows detection of small amounts of Cu^+ sites. An important point is that the C–O stretching frequencies are very sensitive to the coordination state of Cu^+ [4].

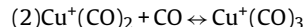
There is no consensus in the literature about the possibility of detection of Cu^{2+} sites by CO [46]. In any case, the Cu^{2+} –CO bond is much weaker as compared to the Cu^+ –CO bond. For that reason, Cu^{2+} sites are expected to be detected with CO only at low temperatures [46].

It was reported that Cu^+ –CO species in Cu–ZSM-5 are characterized by an unusual high frequency (2158 cm^{-1}) [4–39] as compared to carbonyls formed with oxide-supported copper (2130 – 2120 cm^{-1}) [4,47–50] and this is attributed to the low coordination of Cu^+ and the enhanced σ -component of the Cu^+ –CO bond

[4]. Some authors have reported heterogeneity of the exchanged Cu^+ ions [5–9]. It was also found that, at r.t. and in the presence of CO in the gas phase, the monocarbonyls are converted into dicarbonyl species characterized by $\nu_s(\text{CO})$ at 2178 cm^{-1} and $\nu_{as}(\text{CO})$ at 2151 cm^{-1} [4,8–35]:



Zecchina et al. [10] also reported that at low temperature conversion of fraction of the dicarbonyl species to tricarbonyls took place:



The authors concluded that two bands, at 2191 and 2167 cm^{-1} , characterized the tricarbonyls. In more recent works [11–14] the same team proposed a band at 2137 cm^{-1} , coinciding in position with the band characterizing physically adsorbed CO, to be due to the complex. However, other authors [15] questioned the belonging of the 2137 cm^{-1} band to tricarbonyl structures.

The polycarbonyl structures are normally established by adsorption of CO isotopic mixtures [46]. However, irrespective of the fact that there are too many studies of CO adsorption on Cu–ZSM-5, only few papers deal with CO isotopic mixtures [5,15] and some of them are not related to polycarbonyl structures [5]. Sárkány et al. [16] concluded, on the basis of analysis of weak bands arising from ^{13}CO natural abundance, that $\text{Cu}^+(\text{CO})(^{13}\text{CO})$ species were characterized by a band at 2111 cm^{-1} . Analyzing the spectra of a 1:1 $\text{CO} + ^{13}\text{CO}$ isotopic mixture, Hadjiivanov and Knözinger [15] reported frequencies of mixed-ligand $\text{Cu}^+(\text{CO})(^{13}\text{CO})$ species at 2169 and 2112 cm^{-1} . Similar bands were reported for Cu/DAY [51]. However, to the best of our knowledge there are no reports for the spectral behavior of copper tricarbonyl species having mixed ligands. Schay et al. [18] have studied low-temperature co-adsorption

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of CO and ^{13}CO but they have not published the spectra and have only noted their complexity. Indeed, the superimposition of too many bands makes the assignment very difficult.

In this study we report on the carbonyls formed in two different Cu–ZSM-5 samples differing in copper concentration. To confirm the polycarbonyl structures we utilized isotopic mixtures of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$. We have shown that these mixtures are advantageous as compared to the usually used $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ mixtures because the isotopic shift of the CO modes is ca. twice higher and is about 100 cm^{-1} [52–56] which results in a better resolution of the different bands.

2. Experimental

2.1. Materials

The ammonium form of ZSM-5 zeolite with a Si/Al ratio of 25 was purchased from Zeolyst. It has been converted into the corresponding protonated form by calcinations at 823 K for 2 h. Copper ion-exchange has been performed in aqueous solutions of copper acetate with concentrations of 0.004 and 0.006 mol L^{-1} , respectively, in a single step process. The exchanged materials were filtered out, washed and dried at 393 K for 16 h. The total copper content in the samples has been determined by atomic absorption spectroscopy. The samples contained 0.77 and 1.01 wt % of Cu, respectively. They will be further on denoted as Cu–ZSM-5(A) (low copper concentration) and Cu–ZSM-5(B) (high copper concentration).

2.2. Techniques

The IR investigations were carried out using a Nicolet Avatar 360 spectrometer with a spectral resolution of 2 cm^{-1} and accumulating 64 scans. Self-supporting pellets ($\approx 10\text{ mg cm}^{-2}$) were prepared by pressing the sample at 10^4 kPa and were directly treated in the IR cell. The latter was connected to a vacuum apparatus with a residual pressure of about 10^{-3} Pa . Prior to the adsorption measurements, the samples were activated by heating for 1 h at 723 K under oxygen and evacuation for 1 h at the same temperature.

Carbon monoxide (>99.5% purity) was supplied by Merck. $^{13}\text{C}^{18}\text{O}$ (^{13}C isotopic purity of 99% and ^{18}O isotopic purity of 95%) was provided by Cambridge Isotope Laboratories, Inc. Before adsorption, CO and the CO isotopic mixtures were passed through a liquid nitrogen trap.

3. Results

3.1. Background spectra

The background IR spectra of the activated parent zeolite and the two Cu–ZSM-5 samples in the OH region are presented in Fig. 1. The spectrum of H–ZSM-5 contains three main bands at 3744, 3665 and 3612 cm^{-1} (Fig. 1, spectrum a). A shoulder around 3730 cm^{-1} is also visible. In addition, a broad absorbance centered on 3500 cm^{-1} can be distinguished.

The band at 3744 cm^{-1} is assigned to external silanol groups [57] and that at 3730 cm^{-1} , to internal silanols [58]. The band at 3612 cm^{-1} corresponds to zeolite acidic hydroxyls [57]. The band at 3665 cm^{-1} is associated with Al–OH species [57] and evidences the existence of EFAL species. Finally, the broad band around 3500 cm^{-1} is due to H-bonded hydroxyls [57].

The spectrum of Cu–ZSM-5(A) is similar. In this case, however, the band at 3612 cm^{-1} appeared with a reduced intensity. This is consistent with the fact that some protons have been exchanged with copper ions. Also, the band at 3665 cm^{-1} is slightly more

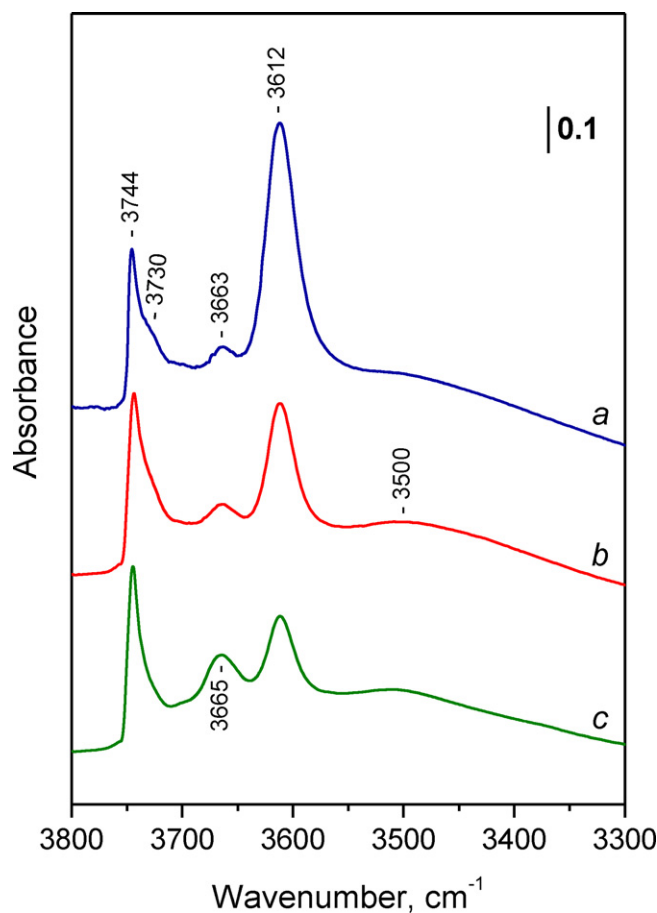


Fig. 1. FTIR spectra (OH region) of activated H–ZSM-5 (a), Cu–ZSM-5(A) (b) and Cu–ZSM-5(B) (c).

intense as compared to the parent sample which suggests increase of the concentration of the EFAL species.

With Cu–ZSM-5(B) we detected additional reduction of the intensity of the 3612 cm^{-1} band which is consistent with the higher copper content. The band at 3665 cm^{-1} appeared with strongly enhanced intensity. With this sample the band assigned to internal silanols (3730 cm^{-1}) was hardly observable. This suggests that these hydroxyls have also reacted with copper species. Finally, the bands due to H-bonded hydroxyls are more pronounced with the Cu-exchanged samples, which indicates that some defects have been created during copper deposition.

3.2. Adsorption of CO on Cu–ZSM-5(A)

Adsorption of CO (600 Pa equilibrium pressure) at 100 K on the activated sample leads to appearance of carbonyl bands located at 2191, 2174, 2170, 2166, 2151 and 2138 cm^{-1} (Fig. 2, spectrum a). This spectrum is similar to the already reported [10–15]. The band at 2138 cm^{-1} has two shoulders, around 2142 and 2135 cm^{-1} and, upon evacuation, the triplet quickly loses intensity to ultimately disappear (Fig. 2, spectra b–d). These bands are assigned to physically adsorbed CO [46]. The band at 2191 cm^{-1} also loses intensity during the initial stages of evacuation. Second derivatives (inset in Fig. 2) and difference spectra indicate this band changes in concert with a band at 2167 cm^{-1} . Note that no band around 2140 cm^{-1} was found to follow these changes.

In agreement with literature data [10] we assign the two bands at 2191 and 2166 cm^{-1} to the A_1 and E modes, respectively, of $\text{Cu}^+(\text{CO})_3$ species. The fact that only two bands are observed

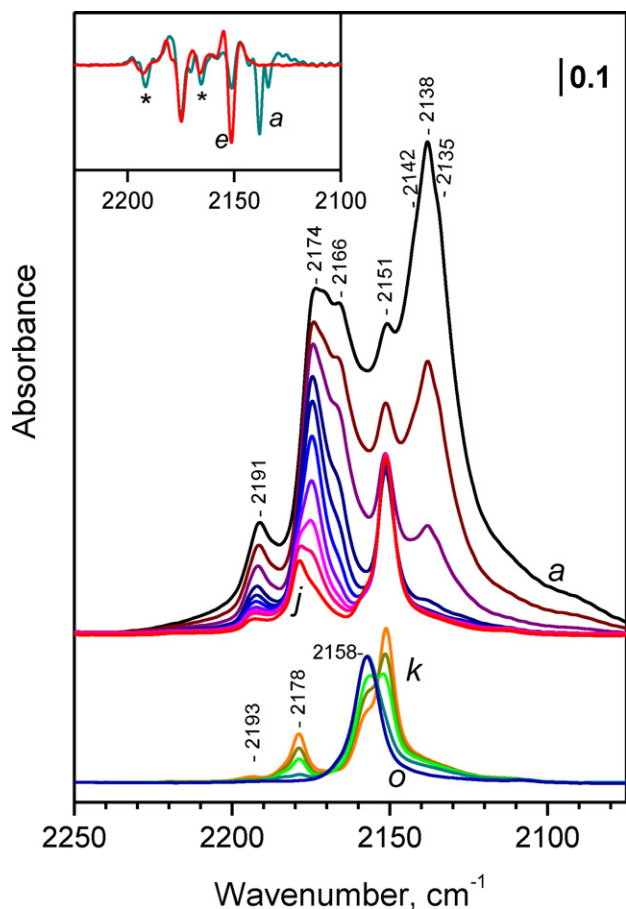


Fig. 2. FTIR spectra of CO adsorbed at 100 K on Cu-ZSM-5(A). Equilibrium CO pressure of 600 Pa and evolution of the spectra during evacuation (b–o). The spectra are background corrected. The second derivatives of spectra “a” and “e” are shown in the inset.

indicates these tricarbonyls have a C_{3v} symmetry. This is somewhat unexpected because most of the known tricarbonyls species observed in zeolites, e.g. $Ni^+(CO)_3$ [59], $Co^+(CO)_3$ [60] and $Rh^+(CO)_3$ [61] are characterized by a distorted C_{3v} symmetry. A careful inspection of the spectra indicates that the only possibility the copper tricarbonyls to be characterized by three C–O stretching modes is one of them to coincide with the dicarbonyl band at 2151 cm^{-1} . However, we have not found any support of this hypothesis.

Another band that is characterized by a low stability is that at 2170 cm^{-1} . It changes in concert with a red shift of the Al–OH band at $3665\text{--}3480\text{ cm}^{-1}$ ($\Delta\nu = -185\text{ cm}^{-1}$) and is attributed to CO polarized by Al–OH groups [46]. The band at 2175 cm^{-1} is more stable and is assigned to CO attached to the 3612 cm^{-1} zeolite acidic hydroxyls. In this case a larger shift of about 300 cm^{-1} was detected which is consistent with the higher acidity of these hydroxyls.

In parallel with the decrease in intensity of the bands at 2191 and 2167 cm^{-1} , bands at 2178 and 2151 cm^{-1} develop. This fact is explained by conversion of tricarbonyls of Cu^+ to dicarbonyl species (reverse of reaction (2)).

Further evacuation (see Fig. 2) leads to decrease in intensity of the bands at 2178 and 2151 cm^{-1} and appearance, at their expense, of a band at 2158 cm^{-1} due to Cu^+-CO species. These results indicate decomposition of the dicarbonylic species to monocarbonyls. In addition, a feature around 2135 cm^{-1} is observed. This band is due to Cu^+-CO complexes formed with copper ions that are not in exchanged positions [4]. A weak band at 2183 cm^{-1} is also discernible at low coverages. It is slightly more resistant towards evacuation than the band at 2178 cm^{-1} . The 2183 cm^{-1} band could be due to (i) the symmetric modes of another kind of dicarbonyls

or (ii) to $Cu^{2+}-CO$ species. It is practically impossible to choose between these two possibilities on the basis of the CO adsorption experiments. However, the experiments involving adsorption of isotopic mixtures (see below) clearly demonstrated that the band arises from dicarbonyls. The respective monocarbonyls species are expected around 2160 cm^{-1} and are masked by the intense band at 2158 cm^{-1} . Note that the behavior of the monocarbonyls observed around 2134 cm^{-1} excludes they to correspond to the 2183 cm^{-1} dicarbonyls.

Also, at low coverages, a band at 2194 cm^{-1} is seen. In principle the maxima of the bands due to polycarbonyls are coverage independent. In addition, the band at 2194 cm^{-1} starts to appear without concomitant formation of a band at 2166 cm^{-1} . For these reasons we suggest that a component of the band around 2191 (located around 2194 cm^{-1}) is due to $Cu^{2+}-CO$ species. Additional arguments in support of this assignment will be provided below.

It can also be seen from Fig. 2 that even at very high CO coverages (spectrum a) a residual band at 2151 cm^{-1} is observed. This confirms the conclusion [4] that not all Cu^+ sites can form tricarbonyls.

In summary, our results confirm formation of Cu^+-CO species on Cu-ZSM-5 that are able to be converted into dicarbonyls, and part of them, to tricarbonyls. The results suggest that tricarbonyls are characterized by a C_{2v} symmetry and are characterized by two IR modes, at 2191 and 2167 cm^{-1} . Some Cu^{2+} species were also detected at low temperature by a carbonyl band at 2194 cm^{-1} .

3.3. Adsorption of CO on Cu-ZSM-5(B)

In order to support the above assignments and check for the effect of copper loading, we have studied CO adsorption on a sample with a higher copper concentration. The carbonyl spectra registered after CO adsorption on the Cu-ZSM-5(B) sample (Fig. 3) are similar to those already described for sample Cu-ZSM-5(A). However, there are some noticeable differences. All bands assigned to copper carbonyls and polycarbonyls are more intense in line with the higher concentration of copper. The same accounts for the band at 2170 cm^{-1} which is in agreement with the more important concentration of Al–OH species in this sample. On the contrary, the relative intensity of the band at 2175 cm^{-1} is lower, which is consistent with the lower concentration of bridged hydroxyls on the sample. It is also clear that the fraction of the dicarbonyl species that cannot be converted into tricarbonyls is more important with the Cu-ZSM-5(B) sample: this is evidenced by the high intensity, at high CO coverages, of the band at 2151 cm^{-1} due to ν_{as} of dicarbonyls. Finally, the sample is characterized by a higher content of Cu^+ ions that are not in exchange positions, as indicated by the band at 2134 cm^{-1} .

3.4. Co-adsorption of $^{12}C^{16}O$ and $^{13}C^{18}O$ on Cu-ZSM-5(A)

To prove polycarbonyl structure, it is necessary to study adsorption of CO isotopic mixtures. Available literature data show that usually $^{12}C^{16}O$ – $^{13}C^{16}O$ mixtures are utilized for that purpose [46]. The isotopic shift factor of 0.9777 ensures a red shift of about 50 cm^{-1} of the individual carbonyl bands. However, when the carbonyl spectra are complex and different bands are situated in a region exceeding 50 cm^{-1} (as in our case) overlapping can occur which complicates spectral analysis.

Here we report results on co-adsorption of two $^{12}C^{16}O$ – $^{13}C^{18}O$ isotopic mixtures. In this case the isotopic shift factor is 0.9531 and the shift of the individual carbonyl modes is about 100 cm^{-1} . This allows a much better separation of the carbonyl bands as compared to the case of $^{12}C^{16}O$ – $^{13}C^{16}O$ isotopic mixtures. Note that, irrespective of this advantage, there are only few adsorption studies

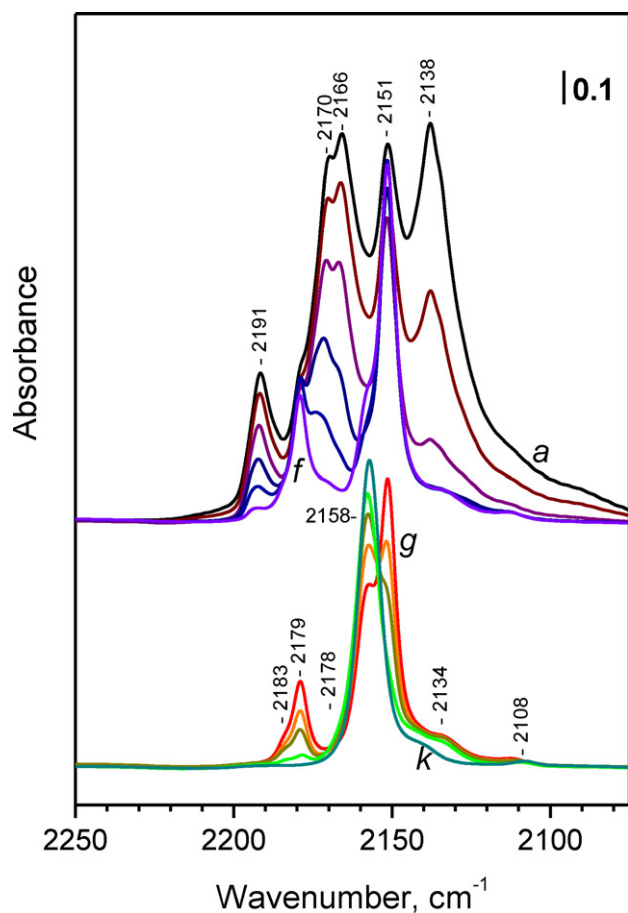


Fig. 3. FTIR spectra of CO adsorbed at 100 K on Cu-ZSM-5(B). Equilibrium CO pressure of 600 Pa and evolution of the spectra during evacuation (b-k). The spectra are background corrected.

involving $^{12}\text{C}^{16}\text{O}$ – $^{13}\text{C}^{18}\text{O}$ isotopic mixtures [52–57] (one dealing with Cu-ZSM-5 [53]) and, except our recent reports [52,53], none of them was aimed at establishing the structure of polycarbonyls.

Let us now briefly recall how adsorption of CO isotopic mixtures can reveal dicarbonylic structures. Dicarbonyls are normally characterized by symmetric and antisymmetric CO modes. Adsorption of isotopic mixtures, $\text{CO} + \text{CO}^*$ (where CO^* stands for an isotopically labelled molecule), will result in six bands: (i) two bands (ν_s and ν_{as}) of dicarbonyls with CO ligands; (ii) two bands of the dicarbonyls with CO^* ligands and (iii) two bands (ν_{CO} and ν_{CO^*}) characterizing $\text{M}(\text{CO})(\text{CO}^*)$ mixed ligand species. With equimolar $\text{CO} + \text{CO}^*$ mixtures the ratio between $\text{M}(\text{CO})_2:\text{M}(\text{CO})(\text{CO}^*):\text{M}(\text{CO}^*)_2$ species should be 1:2:1. Therefore, the bands due to mixed-ligand species should be the most intense ones. Note also that the approximate force field model [62,63] predicts very well the wavenumbers of the different bands. If the species formed are tricarbonyls, the spectra of isotopic mixtures are more complicated and up to 16 bands could be detected after adsorption of isotopic mixtures.

Based on the frequencies of 2178 and 2151 cm^{-1} observed for the $\text{Cu}^+(\text{CO})_2$ dicarbonyls, approximate force field model [62,63] predicts IR modes at 2166 and 2061 cm^{-1} for $\text{Cu}^+(\text{CO})(\text{CO}^*)$ species and at 2076 and 2050 cm^{-1} for $\text{Cu}^+(\text{CO}^*)_2$ dicarbonyls. In fact, due to anharmonicity, the ^{13}C – ^{18}O modes are observed at somewhat higher (by ca 2 cm^{-1}) frequencies.

Because of the more homogeneous distribution of Cu^+ sites in the Cu-ZSM-5(A) sample and the higher degree of conversion of di- to tricarbonyls, we have used this material for adsorption of isotopic mixtures. Selected spectra at low coverage, obtained

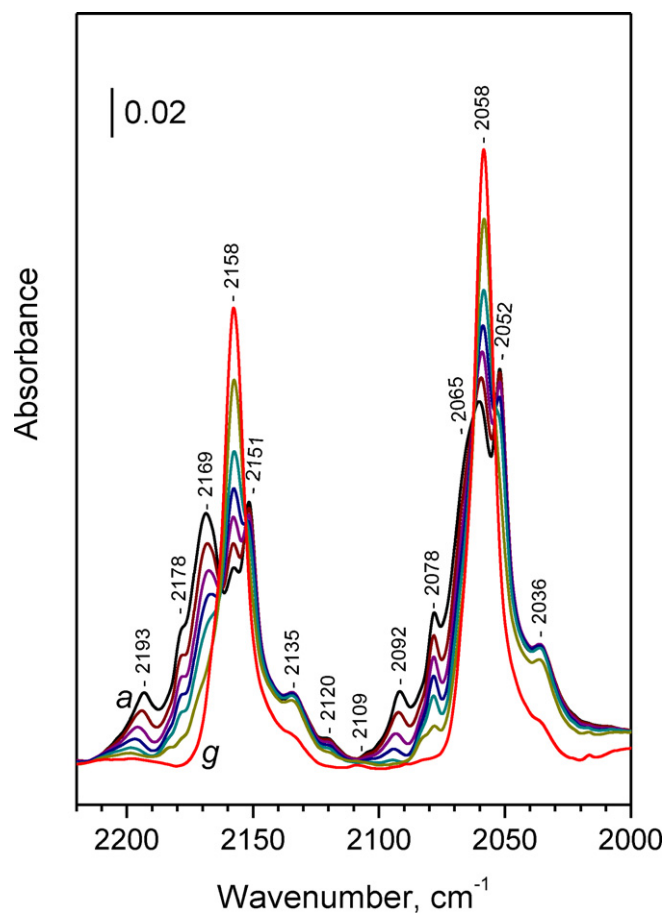


Fig. 4. FTIR spectra of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ isotopic mixture (1:1) adsorbed at 100 K on Cu-ZSM-5(A). Initial equilibrium pressure of 600 Pa, followed by evacuation (a-g). The spectra are background corrected.

after adsorption of a ca. 1:1 $^{12}\text{C}^{16}\text{O}$ – $^{13}\text{C}^{18}\text{O}$ isotopic mixture on the Cu-ZSM-5(A) sample, are presented in Fig. 4. For convenience, we shall consider our spectra starting from low coverage, although this is opposite to their chronological detection. Note that, due to the fact that $^{13}\text{C}^{18}\text{O}$ is more difficult to evacuate, at low coverages the system was slightly enriched to $^{13}\text{C}^{18}\text{O}$.

After prolonged evacuation mainly two bands due to individual monocarbonyl species ($\text{Cu}^+ \text{--}^{12}\text{C}^{16}\text{O}$ at 2158 cm^{-1} and $\text{Cu}^+ \text{--}^{13}\text{C}^{18}\text{O}$ at 2058 cm^{-1}) are detected (Fig. 4, spectrum g). Two other monocarbonyls (formed with Cu^+ cations not in exchange position) produce the bands at 2135 and 2036 cm^{-1} . A band of very weak intensity at 2109 cm^{-1} is assigned to $\text{Cu}^+ \text{--}^{13}\text{C}^{16}\text{O}$ traces. At higher coverages (Fig. 4, spectra a–f) the bands at 2158 and 2058 cm^{-1} decline and bands at 2194, 2183, 2178, 2169, 2151, 2135, 2120, 2092, 2078, 2065, 2052 and 2038 cm^{-1} are formed.

The set of bands at 2178 and 2151 cm^{-1} were already assigned to the symmetric and antisymmetric modes of $\text{Cu}^+(\text{CO})_2$ dicarbonylic species. The respective bands of $\text{Cu}^+(\text{CO}^*)_2$ species are at 2078 and 2052 cm^{-1} . In agreement with the calculations, we assign the bands at 2168 and 2065 cm^{-1} to $\text{Cu}^+(\text{CO})(\text{CO}^*)$ mixed-ligand species (see Table 1).

Let us now discuss the band at 2183 cm^{-1} . It could be due Cu^{2+} –CO species or to the symmetric C–O modes of a second type of dicarbonyl species. In the latter case the antisymmetric modes are expected around 2150 cm^{-1} , but, due to superimposition, the exact value cannot be determined. Analyzing of the ^{12}C – ^{16}O modes of the respective $\text{Cu}^+(\text{CO})(\text{CO}^*)$ mixed-ligand species (expected around 2170 cm^{-1}) is inutile because they are masked by the strong band at 2168 cm^{-1} of the principal mixed-ligand dicarbonyls. In

Table 1
Bands of mono- and di-carbonyl species of Cu^{II} in Cu-ZSM-5 formed with ¹²C¹⁶O and ¹³C¹⁸O.

Species	$\nu(^{12}\text{C}^{16}\text{O}), \text{cm}^{-1}$	$\nu(^{13}\text{C}^{18}\text{O}), \text{cm}^{-1}$	Note
Monocarbonyls			
Cu ⁺ - ¹² C ¹⁶ O	2158	–	Principal monocarbonyls
Cu ⁺ - ¹³ C ¹⁸ O	–	2058	
Cu ²⁺ - ¹² C ¹⁶ O	2194	–	–
Cu ²⁺ - ¹³ C ¹⁸ O	–	2093	
Dicarbonyls			
Cu ⁺ (¹² C ¹⁶ O) ₂	2178 (ν_s)	–	Principal dicarbonyls
	2151 (ν_{as})	–	
Cu ⁺ (¹² C ¹⁶ O)(¹³ C ¹⁸ O)	2168	2065	–
Cu ⁺ (¹³ C ¹⁸ O) ₂	–	2078 (ν_s)	
	–	2052 (ν_{as})	
Cu ⁺ (¹² C ¹⁶ O) ₂	2183 (ν_s)	–	Low concentration, monocarbonyls masked
Tricarbonyls			
Cu ⁺ (¹² C ¹⁶ O) ₃	2191	–	–
	2167	–	
Cu ⁺ (¹² C ¹⁶ O) ₂ (¹³ C ¹⁸ O)	2187	2097	(2088)
Cu ⁺ (¹² C ¹⁶ O)(¹³ C ¹⁸ O) ₂	2204	2091	
Cu ⁺ (¹³ C ¹⁸ O) ₃	–	2066	

order to establish whether the band at 2183 cm⁻¹ belongs to dicarbonyls, we studied adsorption of a 3:1 ¹²C¹⁶O + ¹³C¹⁸O isotopic mixture. In this case the bands due to monocarbonyls should appear with proportional intensities in the ¹²C¹⁶O and ¹³C¹⁸O regions. However, concerning dicarbonyls, the concentration of Cu⁺(¹³C¹⁸O)₂ species should be very small and mainly bands due to mixed-ligand species should be observed in the ¹³C¹⁸O region.

Fig. 5 presents a spectrum registered after adsorption of a 3:1 ¹²C¹⁶O + ¹³C¹⁸O isotopic mixture on the sample, followed by a pro-

longed evacuation (spectrum a). The spectrum is selected in order the band at 2183 cm⁻¹ to be clearly observed. Spectrum “b” is the same spectrum expanded along the Y-axis in order the monocarbonyl Cu-¹³C¹⁸O band at 2058 cm⁻¹ to reach the intensity of the band at 2158 cm⁻¹. It is clearly seen that the band at 2083 cm⁻¹ is much less intense in spectrum “b” as compared to the band at 2183 cm⁻¹ in spectrum “a”. Note that the same accounts for the set of bands at 2178 and 2078 cm⁻¹. Therefore, the results unambiguously demonstrate that the 2183 cm⁻¹ band is due to dicarbonyl

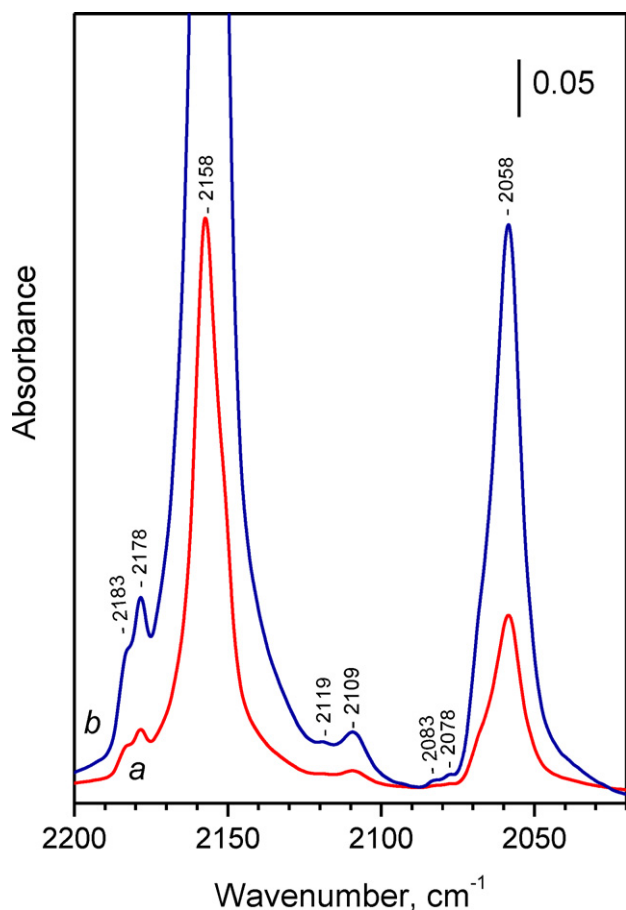


Fig. 5. FTIR spectrum of ¹²C¹⁶O and ¹³C¹⁸O isotopic mixture (3:1) adsorbed at 100 K on Cu-ZSM-5(A), followed by a prolonged evacuation. The spectrum is background corrected. Spectrum b represents spectrum “a” multiplied by a factor of 3.3.

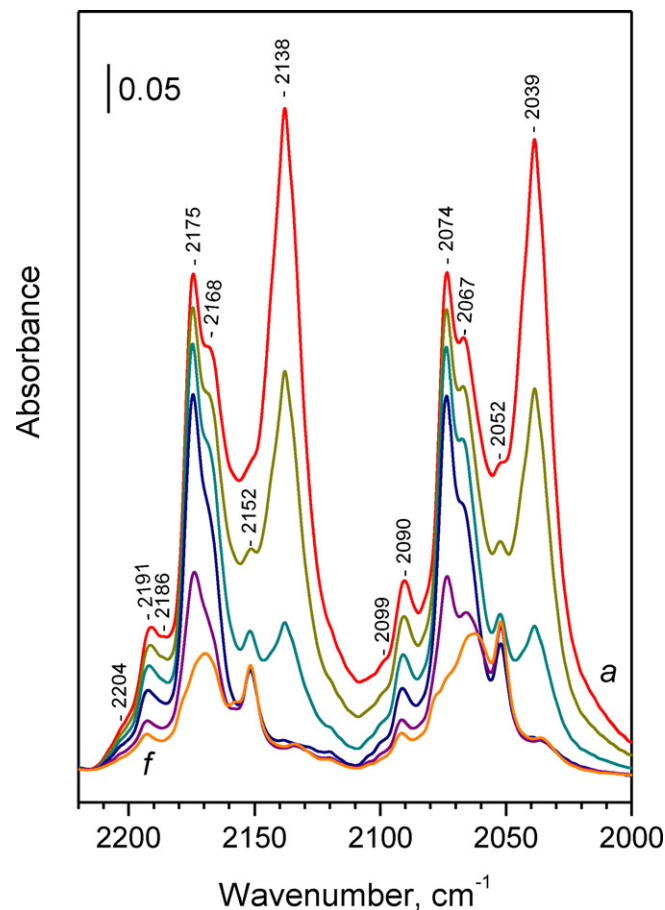


Fig. 6. FTIR spectra of ¹²C¹⁶O and ¹³C¹⁸O isotopic mixture (1:1) adsorbed at 100 K on Cu-ZSM-5(A). Initial equilibrium pressure of 600 Pa (a), followed by evacuation (b-f). The spectra are background corrected.

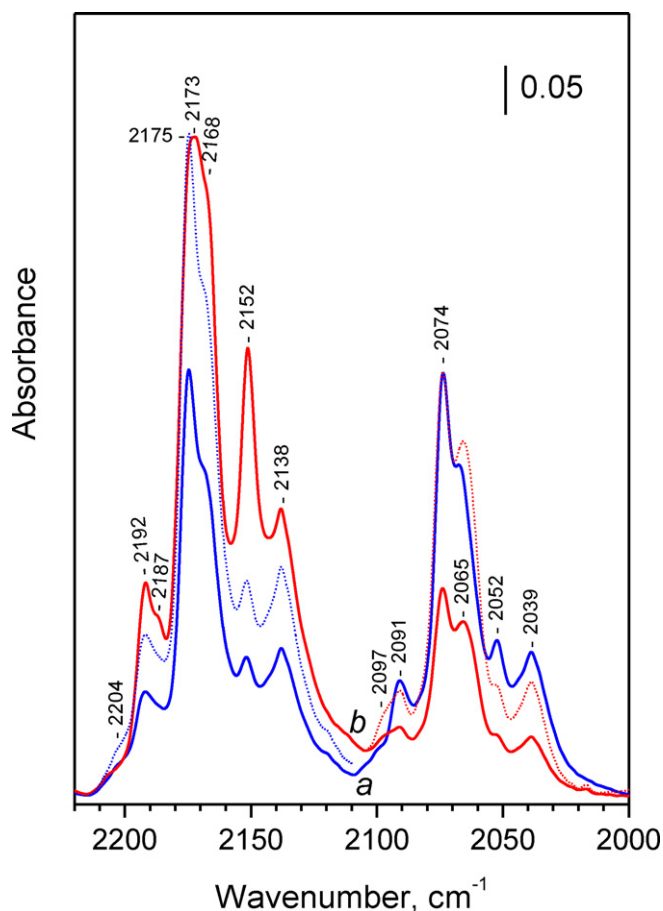


Fig. 7. FTIR spectra of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ coadsorbed at 100 K on Cu-ZSM-5(A). Initial equilibrium pressure of 600 Pa, followed by brief evacuation. Molar $^{12}\text{C}^{16}\text{O}$ to $^{13}\text{C}^{18}\text{O}$ ratio of 1:1 (a) and 3:1 (b). The spectra are background corrected. Dotted lines represent spectra normalized according to the most intense band in the region.

species. Note that this conclusion was possible owing to the use of a $^{12}\text{C}^{16}\text{O} + ^{13}\text{C}^{18}\text{O}$ isotopic mixture.

Although the band at 2194 cm^{-1} (and the satellite at 2093 cm^{-1}) almost coincides in position with a band characteristic tricarbonyls, it is detected at relatively low coverages, when no tricarbonyls are expected. This confirms the above made proposition that the band corresponds to $\text{Cu}^{2+}\text{-CO}$ species. This conclusion was also supported by analysis of the spectra registered after adsorption of a 3:1 $^{12}\text{C}^{16}\text{O} + ^{13}\text{C}^{18}\text{O}$ isotopic mixture (details not reported).

Finally, the weak band at 2120 cm^{-1} is attributed to dicarbonyls involving one $^{13}\text{C}^{16}\text{O}$ molecule.

Consider now the spectra registered at high coverages (Fig. 6) where significant concentration of tricarbonyls is expected. With a 1:1 molar ratio between $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$, one should expect a ratio of 1:3:3:1 between the $\text{Cu}^+(\text{C}^{16}\text{O})_3$, $\text{Cu}^+(\text{C}^{16}\text{O})_2(^{13}\text{C}^{18}\text{O})$, $\text{Cu}^+(\text{C}^{16}\text{O})(^{13}\text{C}^{18}\text{O})_2$ and $\text{Cu}^+(\text{C}^{18}\text{O})_3$ species. Therefore, the intensities of the $\text{Cu}^+(\text{C}^{16}\text{O})_3$ bands should be 1/8 from those observed after $^{12}\text{C}^{16}\text{O}$ adsorption, i.e. hardly observable.

At high CO coverage the spectra are dominated by the bands due to physically adsorbed species (2138 and 2039 cm^{-1}). There is also a strong contribution of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}$ attached to different OH groups ($2175\text{--}2170$ and $2075\text{--}2070\text{ cm}^{-1}$). (Fig. 6, spectra a–c). Comparison with the spectra registered after CO adsorption (Fig. 2) shows appearance of some additional bands located at 2204 and 2186 cm^{-1} . These bands should be attributed to mixed-ligand species of the $\text{Cu}^+(\text{C}^{16}\text{O})_2(^{13}\text{C}^{18}\text{O})$ and $\text{Cu}^+(\text{C}^{16}\text{O})(^{13}\text{C}^{18}\text{O})_2$ type.

To obtain more information on the spectral behavior of the tricarbonyl species we studied adsorption of isotopic mixture with different compositions (see Fig. 7). The detailed analysis of the spectra is hindered because of the superimposition of too many bands. However, the spectra of adsorbed 3:1 $^{12}\text{C}^{16}\text{O}\text{--}^{13}\text{C}^{18}\text{O}$ mixture contain, in addition to the features observed after $^{12}\text{C}^{16}\text{O}$ adsorption, a band at 2187 cm^{-1} which thus appears to be characteristic of $\text{Cu}^+(\text{C}^{16}\text{O})_2(^{13}\text{C}^{18}\text{O})$ species (Fig. 6, spectrum b). This band is hardly observable when a 1:1 $^{12}\text{C}^{16}\text{O}\text{--}^{13}\text{C}^{18}\text{O}$ mixture was adsorbed (Fig. 7, spectrum a). The same accounts for the band at 2097 cm^{-1} in the $^{13}\text{C}\text{--}^{18}\text{O}$ region. On the contrary, the band at 2204 cm^{-1} is hardly observed when the 3:1 isotopic mixture was adsorbed. Therefore, this band is associated with $\text{Cu}^+(\text{C}^{16}\text{O})(^{13}\text{C}^{18}\text{O})_2$ species. Due to superimposition, we cannot determine the other bands due to mixed-ligand tricarbonyls.

4. Conclusions

Adsorption of $^{12}\text{C}^{16}\text{O}\text{--}^{13}\text{C}^{18}\text{O}$ isotopic mixtures with different molar ratios is useful for establishing of polycarbonyl structures.

Two types of dicarbonyls are established for Cu^+ ions in Cu-ZSM-5; (i) the well known dicarbonyls with ν_s at 2178 cm^{-1} and ν_{as} at 2151 cm^{-1} and (ii) dicarbonyls with ν_s at 2183 cm^{-1} and ν_{as} around 2150 cm^{-1} . The latter are in a low concentration.

A fraction of the dicarbonyls can be converted into tricarbonyl species (2191 and 2166 cm^{-1}) and this fraction is more important at low copper loading. Bands at 2204 and 2187 cm^{-1} characterize tricarbonyls with two and one $^{13}\text{C}^{18}\text{O}$ ligands, respectively.

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