Investigation of Copper Carbonyl Species Formed upon CO Adsorption on Copper-Exchanged Zeolites by Diffuse Reflectance FTIR

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Diffuse reflectance FTIR spectroscopy was applied to the study of the fundamental C−O bond stretching vibrations and their first overtones and combination modes of copper carbonyl species formed upon CO adsorption on aqueous ion-exchanged CuZSM-5, CuM, CuY, and CuL zeolites autoreduced at 673 K in vacuo and on Cu(I)Y (sse) zeolite prepared by solid-state ion exchange of NH_4Y with CuCl. At low CO pressures, different kinds of Cu(I)(CO) monocarbonyl species are formed depending upon the types of the zeolites. With increasing the CO pressure, $Cu(I)(CO)_2$ dicarbonyl species are formed on CuZSM-5, CuM, and CuY. After an evacuation of the preadsorbed CO at room temperature, the dicarbonyl species are transformed into monocarbonyl species. Such a transformation is reversible upon a change of the CO pressure. On the CuL zeolite, however, only one type of monocarbonyl is observed, no dicarbonyl species being detected even at high CO pressures. The frequency of the stretching vibration of the metal cation−carbon bond, i.e., Cu(I)−C bond, in the monocarbonyl species, which is difficult to detect directly by infrared measurements, can be calculated using the corresponding frequencies of the fundamental C−O bond stretching vibration and combination mode. It has been found that this frequency is much more sensitive to the electron donor−acceptor ability of the Cu(I) cation in the monocarbonyl species than that of the fundamental C−O stretching vibration alone. On all of the zeolites except CuL, the monocarbonyl species characterized by the frequencies of fundamental C−O and Cu(I)−C bond stretching vibrations of 2157 and ∼440 cm^{-1} is observed. Another type of monocarbonyl species with its frequencies of fundamental C−O and Cu(I)−C bond stretching vibrations of about 2143 and 500 cm^{-1} is only formed on the high silica containing zeolites, CuZSM-5 and CuM. The Cu(I) cation in this type of monocarbonyl species possesses a very high electron donor−acceptor ability. On CuY, CuL, and CuZSM-5 (with a low copper loading) one more type of Cu(I) cations with a low electron donor−acceptor ability is detected by the CO probe. Those cations are able to form monocarbonyl species characterized by the lowest frequency of Cu(I)−C bond stretching vibration ranging within 390∼420 cm^{-1}.

Introduction

Copper-exchanged zeolites have been extensively investigated because of their excellent performance in the decomposition and selective catalytic reduction of nitric oxide that is considered as one of the causes of air pollution.[1−5] It has also been found that copper-exchanged zeolites (e.g., CuZSM-5 and CuM) have a unique capability to adsorb N_2 at ambient temperature.[6−8] Since N_2 is adsorbed on a solid surface only under conditions of low temperatures and/or high pressures, copper-exchanged zeolites may become a novel type of catalysts for adsorption, separation, fixation, and activation of nitrogen at ambient conditions. From a considerable number of studies concerning copper-exchanged zeolites over the past few years, the conclusion has been drawn, though still in debate, that the active sites for NO elimination and CO and N_2 adsorption are Cu(I), instead of Cu(II) cations, in zeolites.[4,6−14]

Cu(I) cations in zeolites can be produced either by thermal activation in vacuo or in an inert gas, i.e., autoreduction,[15,16] of Cu(II) zeolites prepared by aqueous ion exchange of alkali forms of zeolites with solutions of Cu(II) salts, such as copper acetate

and chloride, or by reactions of a hydrogen form of zeolites with CuCl in the solid state[17,18] or in gas phase.[19−21] The first method results in copper-exchanged zeolite samples containing both Cu(II) and Cu(I) cations, whereas the second one produces the samples containing Cu(I) cations only. In some cases, to avoid ambiguity in understanding catalytic and adsorption properties of Cu(I) cations in copper-exchange zeolites, the latter method is preferably employed.

A wealth of studies can be found in the literature concerning the use of NO and CO molecules as probes for exploration of the nature of copper cations in zeolites by employing a variety of techniques such as infrared spectroscopy,[8,19−22] electron spin resonance,[23] photoluminescence,[13,14,24,25] and X-ray absorption fine structure.[8,21] It has been established that NO is able to interact with a Cu(I) cation in CuZSM-5 zeolites to form a Cu(I)(NO) mononitrosyl adduct at a low NO pressure and/or low temperature.[23] With increasing the pressure or adsorption time, a second NO molecule can coordinate to the Cu(I) cation and a dinitrosyl species is formed accompanied by a simultaneous oxidation of the Cu(I) cation to Cu(II).[26] The formation of the Cu(I) nitrosyl species is observed not only for CuZSM-5 but also for CuY and CuL.[27−30] Cu(I) nitrosyl species are thought to be, e.g., in the case of CuZSM-5, the intermediates in the dissociation of nitric oxide toward the formation of N_2

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molecules.[31,32] However, the bond of NO with Cu(I) cation in mononitrosyl species is bent and rather weak.[33] No substantial charge transfer between the metal cation and ligand can be inferred. Therefore, even if more than one type of Cu(I) mononitrosyl species are formed on zeolites, they have nearly the same structure and neither electronic paramagnetic resonance nor infrared spectroscopy can distinguish them.[6,20,21]

In the investigation of Cu(I) cation sites in zeolites, the CO molecule is a more stable probe than NO and able to form a carbonyl species with Cu(I) without oxidation of the cation. Because of the strong coordination of CO to Cu(I) cations, Cu(I) carbonyl species of different natures can be discriminated by their infrared spectra. Similar to the case of NO adsorption on copper-exchanged zeolites, upon CO adsorption, Cu(I) carbonyl species with different numbers of CO ligands, i.e., Cu(I)-$(CO)_x$ (x = 1, 2, 3), can be formed depending on the type of zeolites, CO pressure, and adsorption temperature.[20,21] Elucidation of the type and nature of Cu(I) cations in different zeolites probed by CO molecules is still not very clear and controversial results can be found in the literature.

It is worthwhile to point out that in the majority of publications the interpretations of spectroscopic data on different types of Cu(I) cation sites in copper-exchanged zeolites probed by CO molecules were performed on the basis of deconvolutions of infrared spectra of CO adsorbed on the zeolites. Direct spectroscopic evidences seem not to be available because of the significant overlap of the bands of fundamental C−O bond stretching vibrations corresponding to different Cu(I) carbonyl species. We have employed diffuse reflectance FTIR spectroscopy to the study of Cu(I) carbonyl species formed upon CO adsorption on a reduced CuY zeolite measured over a wide spectral range including the fundamental C−O bond stretching vibrations and their first overtones and combination modes of copper carbonyl species.[34] It was established that this approach is effective for the determination of direct information on the nature of Cu(I) cations in the zeolite. In comparison with the spectra measured merely in the region of fundamental C−O bond stretching vibrations, the infrared bands of copper carbonyl species are better resolved in the regions of combination modes and overtones of C−O vibrations.

In the present work, the diffuse reflectance FTIR spectroscopy is applied to the study of copper carbonyl species formed upon CO adsorption on copper-exchanged zeolites, CuZSM-5, CuY, CuM, and CuL. The influence of the structures and chemical compositions of the zeolites on the nature of the Cu(I) carbonyl species formed upon CO adsorption is examined. The properties of Cu(I) cations in different zeolites are analyzed using spectral characteristics of copper carbonyls including frequencies of Cu(I)−C metal−carbon bond stretching vibrations.

Experimental Section

NaZSM-5 zeolite (Si/Al atomic ratio 25) was supplied by the Manufactures of Catalysts of Nankai University of China and additionally washed with a $NaNO_3$ solution. CuZSM-5 zeolites were prepared by one- and fourfold ion exchanges of NaZSM-5 in aqueous $Cu(NO_3)_2$ solutions of 0.01 mol dm^{-3} at 303 K for 24 h. The resulting samples were repeatedly washed with distilled water to remove the residual NO_3^- anions in the zeolites and then dried at 373 K for 12 h. On the basis of atomic absorption analyses, the exchange degrees of the one- and fourfold ion-exchanged CuZSM-5 zeolites were 30 and 100%, and the zeolites were denoted as CuZSM-5(30) and CuZSM-5(100), respectively. CuY, CuM (mordenite) and CuL zeolites were prepared by twofold aqueous ion exchanges of NaY

(Degussa, Si/Al: 2.5), NaM (Degussa, Si/Al: 6.25), and KL (LTL, Tosoh, TSZ-500KOA, Si/Al: 3.1) in $CuCl_2$ solutions of 0.1 mol dm^{-3} at 333 K for 10 h. The obtained samples were washed and dried at 373 K for 12 h. According to the atomic absorption analyses, the exchange degrees of the zeolites were 85, 78, and 55%, respectively.

CuY zeolite that contained Cu(I) cations only was obtained by a solid-state ion exchange of NH_4Y with CuCl (Cu/Al atomic ratio: 1.0) in vacuo at 673 K for 12 h and denoted as Cu(I)Y (sse). The NH_4Y zeolite (exchange degree: 99%) used for the solid-state exchange was prepared by 10-fold ion exchange of NaY in NH_4Cl solution.

Carbon monoxide with a purity of 99.99% was obtained from the Institute of Guang Ming Chemical Industry Research, the Ministry of Chemical Industry of China and used as supplied. The adsorption of CO on the powder zeolite samples placed in quartz cells was performed at room temperature. Prior to CO adsorption, the zeolite samples were activated at 673 K in vacuo for 12 h.

Diffuse reflectance FTIR spectra of CO adsorbed on the zeolite samples were measured at room temperature using a Nicolet 460 ESP FTIR spectrometer supplied with a diffuse reflectance attachment which was modified for the use of the present work. All of the spectra were recorded with a resolution of 4 cm^{-1} and accumulations of 250 and converted to Kubelka−Munk units after subtracting their backgrounds. The details of the procedure have been described elsewhere.[34]

Results

It is well-known that heat treatment of Cu(II) ion-exchanged zeolites at a high temperature in vacuo results in an autoreduction of the Cu(II) cations to Cu(I) as a result of the elimination of the extra-lattice oxygen atoms attached to the cupric species.[15,16] For the CuZSM-5, CuM, and CuL zeolites under study, this process is manifested by a change of the sample color from greenish to white during heating at 673 K in vacuo. In contrast, the color of the CuY zeolite, after such a treatment, is still slightly greenish, indicating that the extent of the autoreduction of CuY is lower and the state of certain quantity of the copper cations in the zeolite remains as cupric. Cu(I)Y (sse) prepared by the above-mentioned solid-state exchange gives a white sample, indicating that the copper cations in the zeolite are Cu(I).

Copper Carbonyl Species Formed on the CuZSM-5 Zeolites. The diffuse reflectance FTIR spectra of CO adsorbed on the autoreduced CuZSM-5(100) zeolite at different equilibrium CO pressures are shown in Figure 1. Prior to CO adsorption, the spectra do not show any absorption bands in the regions under study. At low CO pressures, the spectra in the fundamental region mainly consist of a single band at 2157 cm^{-1} (Figure 1A, spectra a and b), which can be assigned to Cu(I)(CO) monocarbonyl species.[10,11,20,21] The corresponding overtone of C−O stretching vibration is observed at 4288 cm^{-1} (Figure 1C, spectra a and b). These two bands are progressively eroded in a proportional way with increasing the CO pressure, while two new bands grow at 2175 and 4340 cm^{-1} (Figure 1A and C, spectra c and d). At a CO pressure of 25 000 Pa, the bands at 2157 and 4288 cm^{-1} are transformed into the doublets of the bands in the respective regions at 2175, 2150 cm^{-1} and 4340, 4300 cm^{-1} (Figure 1A and C, spectrum e). The bands at 2175 and 2150 cm^{-1} have been assigned to the symmetric and asymmetric stretching vibrations of $Cu(I)(CO)_2$ dicarbonyl species.[20,34] Obviously, the bands at 4340 and 4300 cm^{-1} can accordingly be ascribed to their first overtones. By carefully
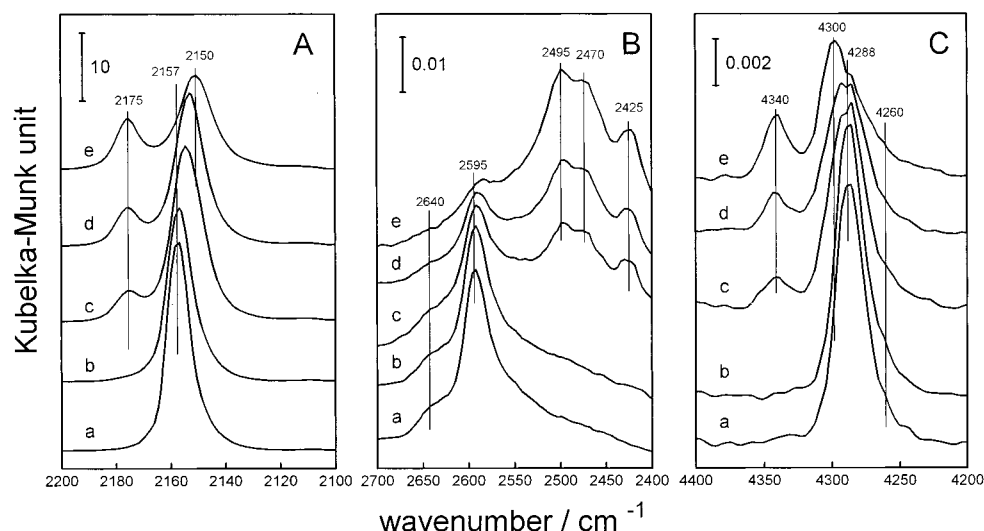
Figure 1. Diffuse reflectance FTIR spectra of CO adsorbed on the autoreduced CuZSM-5(100) zeolite in the regions of fundamental (A), combination (B), and overtone vibrations of copper carbonyl species (C) recorded at CO pressures of 10 Pa (a), 50 Pa (b), 500 Pa (c), 1000 Pa (d), and 25000 Pa (e).

increasing the CO pressure, it has been found that the transformation of Cu(I)(CO) into Cu(I)(CO)$_2$ species is progressively taking place and becomes nearly completed at about 1500 Pa. Further increase in CO pressure, e.g., up to 25000 Pa, cannot completely eliminate the band at 4288 cm^{-1} corresponding to the Cu(I)(CO) monocarbonyl species, though the band at 2157 cm^{-1} in the fundamental region seems to be totally removed. It definitely indicates that a part of the carbonyl species remains as monocarbonyl (Figure 1C, spectrum e). During the increase of the CO pressure, the spectra of combination vibrations of the carbonyl species are first represented by the bands at 2640 and 2595 cm^{-1} (Figure 1B, spectra a and b) and are gradually transformed into those consisting of three bands centered at 2495, 2470, and 2425 cm^{-1} (Figure 1B, spectra c–e). We have reported previously the assignments of combination bands that appeared upon CO adsorption on a CO-reduced CuY zeolite.[34] Similar assignments can be performed in the present case. At low CO pressures, the band at 2595 cm^{-1} can be ascribed to the combination of C–O and Cu(I)–C bond stretching vibrations of the Cu(I)(CO) species which are characterized by the corresponding fundamental and overtone bands at 2157 and 4288 cm^{-1}, respectively. The pair of high-frequency bands at 2495 and 2470 cm^{-1} that appeared at high CO pressures can be attributed to the combinations of symmetric and asymmetric stretching vibrations of the carbon–cation–carbon fragments in dicarbonyl species, i.e., C–Cu(I)–C, with their respective fundamentals of C–O stretching vibrations of corresponding symmetry. The low-frequency band at 2425 cm^{-1} may arise from the interaction of C–O stretching vibration with the bending mode due to the change in the ∠Cu(I)CO angle. Similar to the overtone band at 4288 cm^{-1}, the band at 2595 cm^{-1} cannot be completely eliminated even at a CO pressure of as high as 25 000 Pa (Figure 1B, spectrum e). The spectroscopic transformation between the Cu(I) mono- and dicarbonyl species is reversible upon the change of the CO pressure. When the CO pressure is decreased to ~10^2 Pa, the dicarbonyl species start to decompose into monocarbonyl species. With a further decrease of the CO pressure to less than 100 Pa, the initial spectra of monocarbonyl species in all the regions are restored.

The monocarbonyl species possess high thermal stability. As illustrated in Figure 2, after an evacuation of CO adsorbed on the CuZSM-5(100) zeolite at a temperature of as high as 573 K for long periods, the band at 4288 cm^{-1} cannot be thoroughly
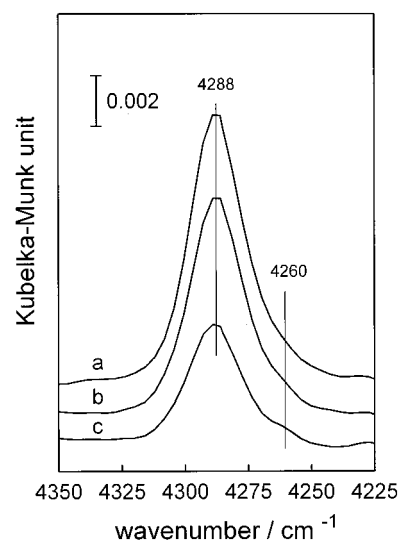

Figure 2. Diffuse reflectance FTIR spectra of CO adsorbed on the autoreduced CuZSM-5(100) zeolite in the region of overtone vibrations of copper carbonyl species recorded after evacuation of the preadsorbed CO at 573 K for 5 min (a), 30 min (b), and 90 min (c).

removed. Moreover, accompanied by the decrease in intensity of this band with increasing the duration of evacuation, a shoulder at 4260 cm^{-1} becomes clearly visible (Figure 2, spectra a–c). The difference in position of the two bands is about 28 cm^{-1}; that should be approximately twice the separation of their corresponding bands of fundamental C–O stretching vibrations. From this point of view, the band of fundamental C–O stretching vibration with its corresponding C–O overtone vibration at 4260 cm^{-1} should be centered at about 2143 cm^{-1} and is most likely hidden inside the band at 2157 cm^{-1} (see Figure 1A). The bands at about 2143 and 4260 cm^{-1} indicate the existence of one more type of Cu(I) monocarbonyl species in the zeolite. This type of monocarbonyl species is also characterized by the combination band at 2640 cm^{-1} (Figure 1B). With increasing the CO pressure, the intensity of the band at 2640 cm^{-1} decreases to some extent, indicating that this type of monocarbonyl species can also be transformed into dicarbonyl species.

To make a comparison with the spectra of CO adsorbed on the CuZSM-5(100) zeolite, the spectra of CO adsorbed on the
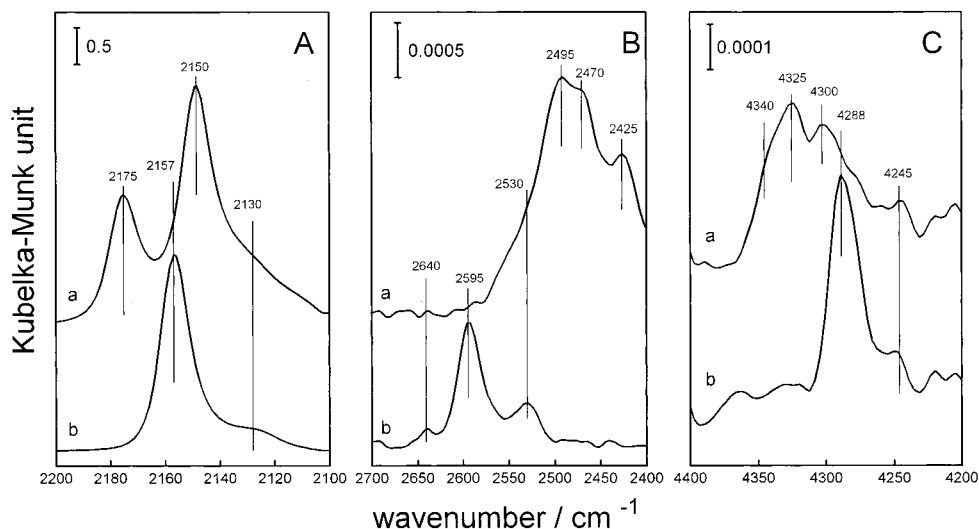
Figure 3. Diffuse reflectance FTIR spectra of CO adsorbed on the autoreduced CuZSM-5(30) zeolite in the regions of fundamental (A), combination (B), and overtone vibrations of copper carbonyl species (C) recorded at a CO pressure of 25 000 Pa (a) and after an evacuation of the preadsorbed CO at room temperature (b).

autoreduced CuZSM-5(30) zeolite with a lower degree of ion exchange measured at a high CO pressure of 25 000 Pa and after a subsequent evacuation of the preadsorbed CO at room temperature are presented in Figure 3. At the high CO pressure, a doublet of the bands at 2175 and 2150 cm^{-1} in the region of fundamental C$-$O stretching vibrations and a triplet of the bands at 2495, 2470 and 2425 cm^{-1} in that of carbonyl combination modes (Figure 3A and B, spectrum a) clearly demonstrate that a substantial amount of dicarbonyl species forms on the CuZSM-5(30) zeolite. The same assignments of these bands as those in the spectra shown in Figure 1 can be performed. Similar to the case of CO adsorption on the CuZSM-5(100) zeolite, with decreasing the CO pressure the formed dicarbonyl species are transformed into the monocarbonyl species as defined by the bands at 2157 and 2595 cm^{-1} (Figure 3A and B, spectrum b). Moreover, the band that appeared at 2640 cm^{-1} indicates that the monocarbonyl species with its C$-$O fundamental and overtone bands at about 2143 and 4260 cm^{-1} as depicted in Figure 2 are also present. Additionally, two bands at about 2130 and 2530 cm^{-1} can be detected in the respective regions of fundamentals and combinations of C$-$O vibrations (Figure 3A and B, spectrum a). After an evacuation of the adsorbed CO at room temperature, the two bands become more clearly visible (Figure 3A and B, spectrum b). The existence of the two bands suggests the formation of one more type of monocarbonyl species in CuZSM-5(30), which is absent in the case of CO adsorption on CuZSM-5(100). As indicated by the band intensities, it seems that this type of monocarbonyl species cannot be completely transformed into dicarbonyl species even at high CO pressures.

More information about the Cu(I) carbonyl species formed on the autoreduced CuZSM-5(30) zeolite can be obtained from a detailed analysis of the overtone spectra of C$-$O bond stretching vibrations (Figure 3C). At the high CO pressure, the spectrum of the C$-$O overtones consists of two relatively intense bands at 4325 and 4300 cm^{-1} together with a distinguishable shoulder at 4340 cm^{-1} and a weak band at 4245 cm^{-1} (Figure 3C, spectrum a). The weak band most likely corresponds to the monocarbonyl species with its corresponding C$-$O fundamental and combination bands at 2130 and 2530 cm^{-1}, respectively. As described above that the separation between the bands in the region of C$-$O overtones is approximately twice that in the region of C$-$O fundamentals, the position of the

fundamental C$-$O stretching vibration band with its corresponding overtone band at 4325 cm^{-1} can be determined by a calculation using the fundamental band at 2157 cm^{-1} and the overtone band at 4288 cm^{-1} as references (see spectrum b in Figure 3). The location of the band is thus determined to be at about 2175 cm^{-1}. It is important to note that this band is at the same position as one of the bands corresponding to the Cu(I) dicarbonyl species. According to the literature data,[3] it may arise from the species of the adsorbed CO molecules weakly interacting with the Cu(II) cations in the zeolite, i.e., Cu(II) monocarbonyl species. This kind of species, however, are not detected in the case of CO adsorption on CuZSM-5(100). It implies that the extent of the autoreduction of CuZSM-5(30) may be noticeably lower than that of CuZSM-5(100) and a certain number of copper cations in CuZSM-5(30) remain as Cu(II) which are accessible to the adsorbed CO molecules to form the Cu(II) monocarbonyl species. This is in agreement with the observation that the rate of the spontaneous oxygen desorption from a CuZSM-5 zeolite with a low copper loading is lower than that from a zeolite with a high copper loading.[35] Here, one can find that it is hardly possible to distinguish the Cu(II) and Cu(I) carbonyl species formed on the zeolite samples under study using only the spectra of the fundamental C$-$O stretching vibrations of the carbonyl species.

Copper Carbonyl Species Formed on the CuM Zeolite. The spectra of CO adsorbed on the autoreduced CuM zeolite are depicted in Figure 4. At low CO pressures, two kinds of Cu(I) monocarbonyl species are observed as identified by two groups of bands at 2157, 2590, 4288 cm^{-1} and 2142, 2640, 4268 cm^{-1} in the respective regions of fundamental, combination, and overtone vibrations of carbonyl species (Figure 4, spectrum a). With increasing the CO pressure, the monocarbonyl species are transformed into dicarbonyl species as indicated by the appearance of a doublet of the bands at 2177 and 2150 cm^{-1} in the region of C$-$O fundamentals, a triplet of the bands at 2495, 2470 and 2430 cm^{-1} in that of combination modes, and a doublet of bands at 4340 and 4297 cm^{-1} in that of C$-$O overtones (Figure 4, spectra b$-$f). In comparison with the spectra of CO adsorbed on CuZSM-5, the monocarbonyl species characterized by the bands at 2157, 2590, and 4288 cm^{-1} can almost be completely transformed at high CO pressures into dicarbonyl species as revealed by the absence of the corresponding bands at, e.g., 4288 cm^{-1} (compare spectra e and f in
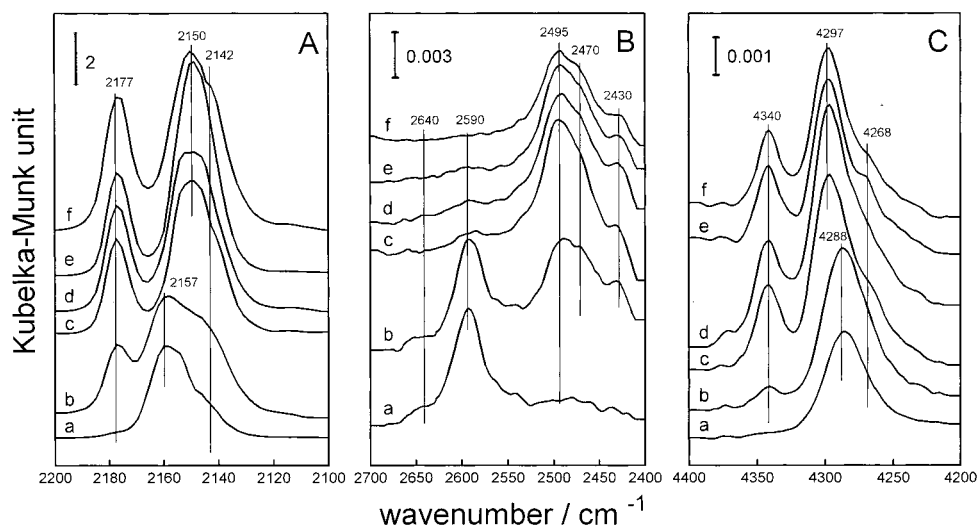
Figure 4. Diffuse reflectance FTIR spectra of CO adsorbed on the autoreduced CuM zeolite in the regions of fundamental (A), combination (B), and overtone vibrations of copper carbonyl species (C) recorded at CO pressures of 10 Pa (a), 50 Pa (b), 500 Pa (c), 1000 Pa (d), 5000 Pa (e), and 25000 Pa (f).
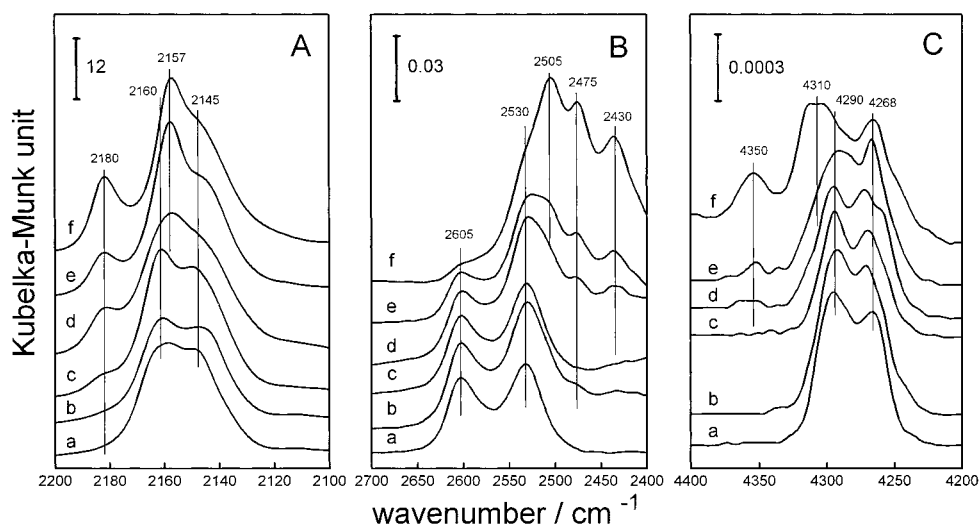

Figure 5. Diffuse reflectance FTIR spectra of CO adsorbed on the autoreduced CuY zeolite in the regions of fundamental (A), combination (B), and overtone vibrations of copper carbonyl species (C) recorded at CO pressures of approximately 0 Pa (a), 10 Pa (b), 50 Pa (c), 500 Pa (d), 1000 Pa (e), and 6000 Pa (f).

Figure 4C with spectrum e in Figure 1C). In contrast, the monocarbonyl species characterized by the bands at 2142, 2640, and 4268 cm^{-1} cannot be fully eliminated even at a high CO pressure of 25 000 Pa as indicated by the existence of the corresponding bands in the regions of C—O fundamentals and overtones (Figure 4A and C, spectrum f).

Copper Carbonyl Species Formed on the CuY and Cu(I)Y (sse) Zeolites. The spectra of CO adsorbed on the autoreduced CuY zeolite are presented in Figure 5. At low CO pressures, two kinds of Cu(I) monocarbonyl species can be identified by two groups of the bands at 2160, 2605, 4290 cm^{-1} and 2145, 2530, 4268 cm^{-1} (Figure 5, spectra a and b). With increasing the CO pressure, the formation of Cu(I) dicarbonyl species is clearly indicated by a doublet of the bands at 2180 and 2157 cm^{-1}, a triplet of the bands at 2505, 2475 and 2430 cm^{-1}, and a doublet of the bands at 4350 and 4310 cm^{-1} in the respective regions of C—O fundamentals, combination modes, and overtones (see, e.g., Figure 5, spectrum f). Upon an evacuation of the preadsorbed CO the dicarbonyl species can easily be transformed into monocarbonyl species (not shown in the figures). Detailed analysis of the spectra of fundamental and combination modes of C—O vibrations indicates that, similar

to the case of CO adsorbed on the CuM zeolite, the second type of Cu(I) monocarbonyl species characterized by the bands at 2145, 2530, and 4268 cm^{-1} cannot be completely transformed into dicarbonyl species at high CO pressures (Figure 5, spectrum f). It is necessary to point out that in the spectra of C—O overtones, the band at 4325 cm^{-1}, as indicated in Figure 3C (spectrum a), corresponding to the complexes of CO interacting with divalent Cu(II) cations is absent despite that the autoreduced CuY zeolite is of a light greenish color because of the presence of the unreduced Cu(II) cations in the zeolite. It can therefore be concluded that the unreduced Cu(II) cations in CuY are most likely located on the hidden cationic positions of, e.g., S$_I$ sites, which are not accessible to the adsorbed CO molecules even at high CO pressures.

For a comparison with the spectra of CO adsorbed on the autoreduced CuY, the spectra of CO adsorbed on the Cu(I)Y (sse) zeolite containing only Cu(I) cations prepared by the solid-state ion exchange of NH$_4$Y with CuCl were presented in Figure 6. Since there is a large amount of Cu(I) cations in the zeolites, the spectra in the region of fundamental C—O stretching vibrations are not well resolved in comparison with those of CO adsorbed the autoreduced CuY. At low CO pressures, two
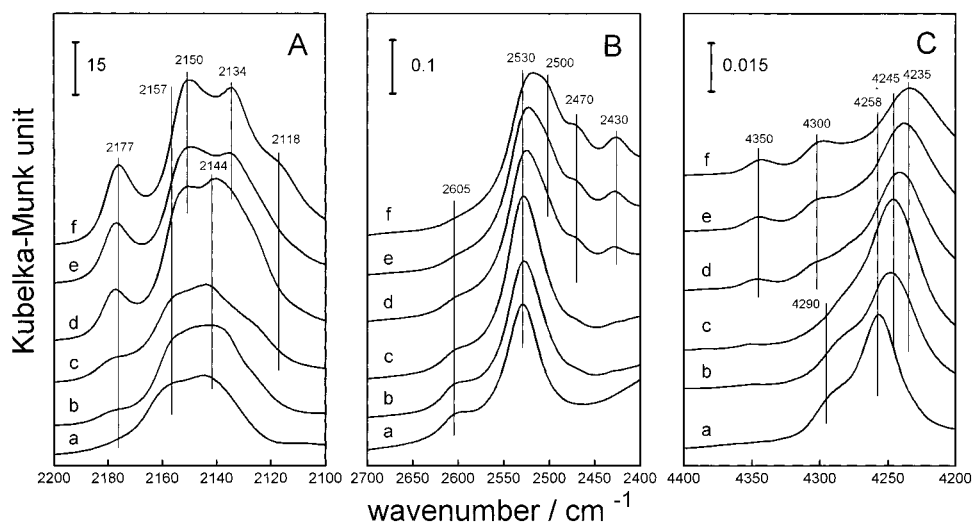
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Figure 6. Diffuse reflectance FTIR spectra of CO adsorbed on the solid-state ion-exchanged Cu(I)Y (sse) zeolite in the regions of fundamental (A), combination (B) and overtone vibrations of copper carbonyl species (C) recorded at CO pressures of 10 Pa (a), 50 Pa (b), 500 Pa (c), 1000 Pa (d), 5000 Pa (e), and 25000 Pa (f).
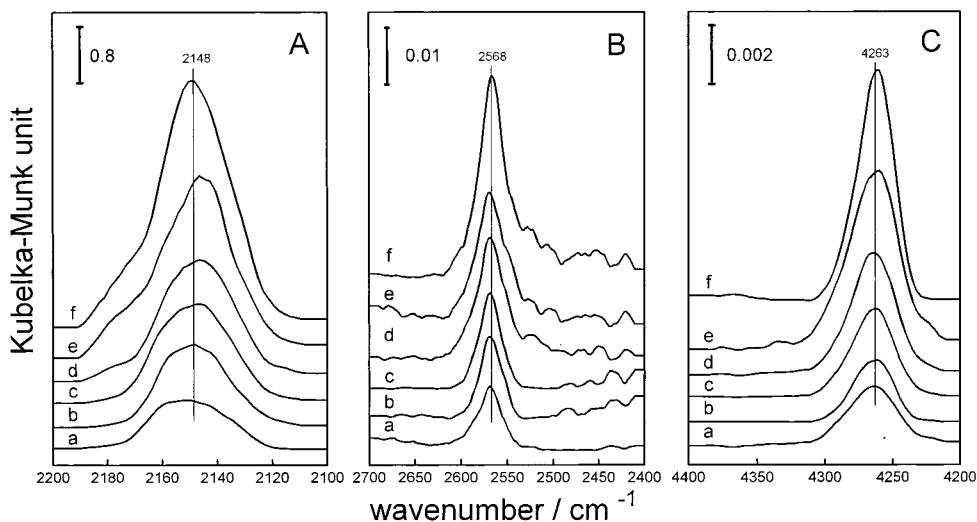

Figure 7. Diffuse reflectance FTIR spectra of CO adsorbed on the autoreduced CuL zeolite in the regions of fundamental (A), combination (B), and overtone vibrations of copper carbonyl species (C) recorded at CO pressures of 10 Pa (a), 50 Pa (b), 100 Pa (c), 500 Pa (d), 1000 Pa (e), and 25000 Pa (f).

kinds of Cu(I) monocarbonyl species present, which are characterized by two groups of bands at 2157, 2605, 4290 cm^{-1} and 2144, 2530, 4258 cm^{-1}, respectively. Unlike to the case with the autoreduced CuY, in Cu(I)Y (sse) zeolite the relative amount of the first type of Cu(I) monocarbonyl species is much less than that of the second one as revealed by the intensities of the corresponding bands, especially, in the region of combination modes. With the increase of the CO pressure, the dicarbonyl species gradually evolves and increases in concentration. This is manifested by the appearance and increase in intensity of the fundamental, combination, and overtone bands at 2177, 2150 cm^{-1}, at 2500, 2470, 2430 cm^{-1}, and at 4350, 4300 cm^{-1}, respectively. Consistent with the observation for the autoreduced CuY, a large amount of the second type of monocarbonyl species remains as Cu(CO) even at a high CO pressure of 25 000 Pa as demonstrated by the high intensity of the combination band at 2530 cm^{-1} and relatively low intensities of the overtone bands at 4350 and 4300 cm^{-1} (Figure 6B and C, spectrum f). With increasing CO pressure, the bands at 2144, 2530, and 4258 cm^{-1} are shifted to 2134, 2525, and 4235 cm^{-1}, respectively, The shift of the overtone band (~23 cm^{-1}) is approximately twice that of the fundamental band (~10 cm^{-1}).

At the high CO pressure of 25 000 Pa, a weak shoulder can be detected at 2118 cm^{-1} (Figure 6A, spectrum f). It may arise from CO adsorbed on Cu(0) sites which could be created because of the autoreduction in vacuo of a small amount of Cu(I) cations in CuY(I) (sse).

Copper Carbonyl Species Formed on the CuL Zeolite. The spectra of CO adsorbed on the autoreduced CuL zeolite recorded at different CO pressures are presented in Figure 7. They are very much different from those of CO adsorbed on the other copper-exchanged zeolites mentioned above. With changing the CO pressure, only single bands at 2148, 2568, and 4263 cm^{-1} can be observed in the respective regions of fundamental, combination, and overtone vibrations of carbonyl species. The formation of only one type of monocarbonyl species on the CuL zeolite likely results from the specific zeolitic structure.

The main results of the spectroscopic study of CO adsorbed on the different copper-exchanged zeolites are summarized in Table 1.

Discussion

From the above analyses of the spectra of CO adsorbed on the copper-exchanged zeolites, it is obvious that the types of

TABLE 1: Infrared Bands of the Copper Carbonyl Species Formed upon CO Adsorption on the Copper-Exchanged Zeolites and Their Assignments

zeolite	fundamentals	combinations	overtones	assignment
	2157	2595	4288	
	~2143	2640	4260	Cu(I)(CO)
CuZSM-5(100)				
	2175	2495	4340	
	2150	2470	4300	Cu(I)(CO)$_2$
		2425		
	2157	2595	4288	
	~2143	2640	4260	Cu(I)(CO)
	2130	2530	4245	
	2175		4325	Cu(II)(CO)
CuZSM-5(30)	2175	2495	4340	
	2150	2470	4300	Cu(I)(CO)$_2$
		2425		
	2157	2590	4288	
	2142	2640	4268	Cu(I)(CO)
CuM				
	2177	2495	4340	
	2150	2470	4297	Cu(I)(CO)$_2$
		2430		
	2160	2605	4290	
	2145	2530	4268	Cu(I)(CO)
CuY				
	2180	2505	4350	
	2157	2475	4310	Cu(I)(CO)$_2$
		2430		
	2157	2605	4290	
	2144	2530	4258	Cu(I)(CO)
Cu(I)Y (sse)				
	2177	2500	4350	
	2150	2475	4300	Cu(I)(CO)$_2$
		2430		
CuL	2148	2568	4263	Cu(I)(CO)

the Cu(I) cation sites accessible to CO probe cannot be correctly determined by the infrared spectra measured merely in the region of fundamental C–O stretching vibrations. For the CuZSM-5 zeolites, the typical Cu(I) monocarbonyl species formed upon CO adsorption is characterized by the band at 2157 cm^{-1} as observed by many authors.[10,11,20,21] Lamberti et al.[21] reported that at room temperature this type of monocarbonyl species can be quantitatively transformed into dicarbonyl species with increasing CO pressure based upon the analysis of infrared spectra of CO adsorbed on a Cu(I)ZSM-5 zeolite recorded in the region of fundamental C–O stretching vibrations. Spectroscopic studies of CO adsorption at a low temperature (110~120 K) reveal that about 50% of this species can further be transformed into tricarbonyl species. The authors thus concluded that this type of monocarbonyl species may be formed with the participation of two different kinds of Cu(I) cation sites in the zeolites. However, the study of CO adsorption at a lower temperature (80~90 K) indicates that in reality the dicarbonyl species can be completely transformed into tricarbonyl species (see ref 21, Note Added in Proof). In such a case, the derived conclusion that the band at 2157 cm^{-1} corresponds to two types of Cu(I) cation sites in the zeolites remains ambiguous. Actually, such an incomplete transformation can also be observed in the transformation of mono- to dicarbonyl species as shown by the infrared spectra of CO adsorbed on CuZSM-5 measured over the wide spectral range at room temperature. Indeed, as mentioned above, with increasing the CO pressure the fundamental band at 2157 cm^{-1} seems to disappear completely, whereas the corresponding combination and overtone bands at 2595 and 4288 cm^{-1} can still be detected with noticeable intensities. The incomplete transformation of mono- to dicarbonyl species cannot be a result of an insufficient amount of dosed CO molecules since further increase of the equilibrium

CO pressure does not modify the spectra. It is likely that because of the steric hindrance created by the specific structure of the zeolite the CO molecules adsorbed into the zeolites block the further approach of the incoming CO molecules to Cu(I) cations to form polycarbonyl species. By the measurements of photo-luminescence spectra of CuZSM-5 zeolites, several authors observed two emissions at about 480 and 540 nm and assigned them to two types of Cu(I) cation sites in the zeolites having slightly different environments. Most probably, they correspond, as proposed by Dedecek et al., to the Cu(I) cations adjacent to one or two aluminum framework atoms, respectively.[14] Lamberti et al.[21] also concluded that they may correspond to two types of Cu(I) cation sites surrounded by two and three equivalent nearest framework oxygen atoms, respectively. The two types of Cu(I) cation sites seem hardly possible to be discriminated by infrared spectroscopy using CO as a probe. One more type of Cu(I) cation site accessible to CO probe is characterized by the weak combination and overtone bands at about 2640 and 4260 cm^{-1}, respectively. Since there is a significant overlap of the band characteristic of this species (~2143 cm^{-1}) with the band at 2157 cm^{-1} in the fundamental region, this type of monocarbonyl species has not been described in the literature. Anpo et al.[25] reported that in an autoreduced CuZSM-5 zeolite there are three different photoluminescence emissions at 420, 470, and 515 nm. The low-energy emission has been ascribed to the Cu(I)–Cu(I) dimeric species. Since ZSM-5 is a silicon-rich zeolite having an MFI-type structure, in which randomly distributed aluminum atoms in the framework are essentially isolated, the presence of the dimeric species remains plausible. For over-exchanged zeolites with the exchange degree larger than 100% (calculated on the basis of an assumption of one cupric cation exchanging two monovalent alkali cations or protons in the zeolites), the presence of the dimeric species may not be ignored. However, in the present study, the infrared bands appeared at 2640 and 4260 cm^{-1} upon CO adsorption and are observed not only for CuZSM-5(100) but also for CuZSM-5(30), in which the Cu(I) cations should essentially be isolated. This means that the two bands indeed correspond to a certain type of monocarbonyl species formed on isolated Cu(I) cation sites instead of on dimeric Cu(I)–Cu(I) species. By CO adsorption-heat measurements, Kuroda et al.[22] also proved the presence of one more type of Cu(I) cation site in CuZSM-5 zeolites beside the sites characterized by the CO adsorption band at 2157 cm^{-1}.

In the autoreduced CuM zeolite, two types of Cu(I) cation sites are probed by CO adsorption (vide supra). As is known, two types of pores exist in mordenite-type zeolites; the large straight channel running along the c-axis connects with the small one elongated in the b-axis.[36] In these channels, the presence of some exchangeable sites has been revealed for calcium cation-exchanged mordenite by Mortier.[37] The cations located in the pores of smaller sizes are not accessible to the CO molecules in taking account of the relatively larger van der Waals radius of the probe molecule. In such a case, the sites for CO adsorption might correspond to the sites located in the large pores as suggested by Geobaldo et al.[38] Therefore, the two groups of the bands at 2157, 2590, 4288 cm^{-1} and at 2142, 2640, 4268 cm^{-1} may correspond to the CO molecules adsorbed on the two types of cation sites. Photoluminescence spectra also reveal two emissions of Cu(I) species in mordenite zeolites at about 470 and 530 nm.[8] However, whether the two emissions indeed correspond to the two types of the monocarbonyl species detected by infrared spectroscopy needs further clarification.

Adsorption of CO on the autoreduced CuY zeolite indicates the existence of two types of Cu(I) cation sites accessible to

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the probe molecules. The Cu(I) cation sites represented by the bands of monocarbonyl species at 2160, 2605, and 4290 cm^{-1} are situated in the supercages since the monocarbonyl species formed on those sites can fully be transformed into dicarbonyl species with increasing the CO pressure. Instead, the Cu(I) cation sites represented by the bands of monocarbonyl species at 2145, 2530, and 4268 cm^{-1} are located inside the sodalite cages adjacent to the centers of six-membered entrance windows. The probe molecules adsorbed into the supercages can likely interact with the Cu(I) cations on, e.g., S$_{I'}$ sites through those windows. At high CO pressures, the Cu(I) cations in the sodalite cages can even be pulled out by the probe from the sodalite cages into supercages.[10,11] However, such a migration of the Cu(I) cations is not very pronounced since the bands characteristic of the corresponding monocarbonyl species remain intense in the spectra measured at high CO pressure. This conclusion can further be confirmed by the infrared spectra of CO adsorbed on the Cu(I)Y (sse) zeolite which contains only Cu(I) cations. In comparison with the autoreduced CuY, a large number of Cu(I) cations in Cu(I)Y (sse) are located in the small cages. Therefore, even at high CO pressures, the bands corresponding to the adsorbed CO interacting with the Cu(I) cations located in the sodalite cages are much more intense than those of carbonyl species formed in the supercages.

The populated cation sites in zeolite L were proposed and verified by many authors.[39-42] The cations inside the hexagonal prisms and carcrinite cages and located midway between two of these cages are not accessible to the CO probe. The only accessible cations to the adsorbed CO molecules are those located on the wall of the main channel (see, e.g., ref 39). In comparison with the other zeolites used in the present work, the exchange degree of CuL is low although the same procedure was employed for the sample preparation. This is not unexpected, since L-type zeolite is well known to have a high affinity for potassium cations.[40-42] The cation sites accessible to the adsorbed CO molecules give rise to the formation of the monocarbonyl species characterized by the infrared bands at 2148, 2568, and 4263 cm^{-1}. Because of the spatial restriction, the monocarbonyl species cannot be transformed into dicarbonyl species even at high CO pressures. As revealed by Takaishi,[39] there are two types of cation sites in the main channel with three and one neighboring aluminum atoms, respectively. For KL, they can be discriminated by the infrared spectra of CO adsorbed on the zeolite measured at a low temperature (110~120 K).[43] In the case of CuL, however, the two types of cation sites, if any difference, are difficult to distinguish by the infrared spectra of CO adsorbed at room temperature.

The interaction of the adsorbed CO molecules with the Cu-(I) cations in the copper-exchanged zeolites is evidenced by the frequency shifts of the fundamental C–O stretching vibrations with respect to the frequency of 2143 cm^{-1} characteristic of CO molecules in gas phase. The formation of the bond between CO and a copper cation exchanged into zeolites consists of the so-called σ-donation, i.e., the donation of a pair of electrons from the CO 5σ orbital to the hybrid d–s orbital of the copper cation, and the π-back-donation, i.e., an electron transfer from the occupied d orbital of the copper cation to the antibonding 2π orbital of CO molecule. In the former case, the Cu(I) cation acts as an electron acceptor and in the latter as a donor. By studying photoemission and thermal desorption spectra of CO adsorbed on a Cu$_2$O(100) single crystal, Cox et al.[44] showed the importance of the σ-donation. In addition to the σ-donation there are also both experimental and theoretical evidences of π-back-donation.[45,46] The 5σ orbital of a CO

TABLE 2: Fundamental C–O and Cu(I)–C Stretching Vibration Frequencies of the Cu(I) Monocarbonyl Species Formed upon CO Adsorption on the Copper-Exchanged Zeolites

zeolite	frequency of C–O stretching vibration	frequency of Cu(I)–C stretching vibration
CuZSM-5(100)	2157	~440
	~2143	~500
CuZSM-5(30)	2157	~440
	~2143	~500
CuM	2130	~400
	2157	~430
	2142	~500
CuY	2160	~440
	2145	~390
Cu(I)Y (sse)	2157	~450
	2144	~390
CuL	2148	~420

molecule adsorbed on a charged metal cation is of weak antibonding character.[47,48] Therefore, the withdrawal of a pair of electrons from the 5σ orbital of a CO probe to the cation leads to the strengthening of the C–O bond. In such a case, the frequency of the C–O stretching vibration is shifted to a higher wavenumber relative to that of free gas CO molecules. On the other hand, the π-back-donation increases the electron density on the antibonding 2π orbital of CO and thus decreases the strength of the C–O bond. This results in a frequency shift of C–O bond stretching vibration to a lower value. The actual frequency of the stretching vibration of the CO molecule coordinating to the Cu(I) cation will be determined by the balance between the contributions of the σ- and π-back-donation. In contrast, both of the two contributions strengthen the bond between the Cu(I) cation and C atom of the coordinated CO molecule and, therefore, increase the frequency of the Cu(I)–C bond stretching vibration. One can expect that the frequency of Cu(I)–C stretching vibration should be more sensitive to the electron donor–acceptor ability of the Cu(I) cation than that of the C–O stretching vibration in the coordinated CO molecule.

However, the frequency of Cu(I)–C bond stretching vibration is normally ranged below 800 cm^{-1}.[49] This makes it difficult to obtain the information of the Cu(I)–C bonds of carbonyls in zeolites by a direct use of infrared spectroscopy because of strong light absorption by the vibrations of zeolite frameworks in this region. Nevertheless, with the frequency of the combination mode of the formed monocarbonyl molecule, the corresponding Cu(I)–C stretching vibration frequency can be derived indirectly. It is generally accepted that the structure of monocarbonyl species of transition metal atoms or cations is linear.[49] The combination mode of a monocarbonyl molecule formed upon CO adsorption on copper-exchanged zeolites may be represented as the superposition of the stretching vibrations of C–O and Cu(I)–C bonds. Thus, the Cu(I)–C stretching vibration frequency can be calculated as a frequency difference of the combination mode and fundamental C–O bond stretching vibration of the monocarbonyl molecule. On the basis of this assumption, the calculated frequencies of the Cu(I)-C stretching vibrations of the monocarbonyl species formed on the different copper-exchanged zeolites are listed in Table 2. For clarity, the corresponding frequencies of their fundamental C–O bond stretching vibrations are also presented in this table.

From Table 2 it obviously follows that the frequencies of the Cu(I)–C stretching vibrations are much more sensitive to the electron donor–acceptor abilities of the Cu(I) cations in the monocarbonyl species than the corresponding frequencies of C–O stretching vibrations. For instance, for two types of monocarbonyl species formed on the CuZSM-5, CuM, and CuY

zeolites with their fundamental C—O stretching vibration frequencies at about 2157 and 2143 cm^{-1} ($\Delta\nu \sim 14$ cm^{-1}) the difference of the respective Cu(I)—C stretching vibration frequencies is larger than 50 cm^{-1}.

One type of the monocarbonyl species with its corresponding C—O and Cu(I)—C stretching vibration bands at about 2157 and 430~450 cm^{-1} is observed on CuZSM-5, CuM, and CuY zeolites. This indicates that the properties of the Cu(I) cations participating in the formation of this type of monocarbonyl species seem to be similar despite that the pore structures and chemical compositions of the zeolites are different. At high CO pressures this type of monocarbonyl species can be transformed into dicarbonyl species. Another type of monocarbonyl species with a higher donor—acceptor ability of the Cu(I) cations characterized by the fundamental C—O stretching vibration frequency at about 2143 cm^{-1} and the noticeably higher Cu(I)—C stretching vibration frequency at about 500 cm^{-1} is present only on the autoreduced CuZSM-5 and CuM zeolites. This type of monocarbonyl species can also be transformed into dicarbonyl species at high CO pressures. One more type of monocarbonyl species, which cannot be completely transformed into dicarbonyl species at high CO pressures, appears on the CuZSM-5(30), CuY, and CuL zeolites. It is characterized by the low Cu(I)—C stretching vibration frequency of 390~420 cm^{-1}. The Cu(I) cations participating in the formation of this type of monocarbonyl species likely occupy the sites where there is not enough space for the formation of dicarbonyl species as described above.

The ability of the Cu(I) cations to form several types of monocarbonyl species on the copper-exchanged zeolites with noticeably different frequencies of the Cu(I)—C vibrations indicates that the environments of the cations located on different sites of zeolite frameworks strongly modify their electronic donor—acceptor ability. This can be a result of the electron density redistribution between the cations and neighboring oxygen anions and the number and basicity of the oxygen anions affecting the electronic properties of the cations.

To our mind, an important result of the present study is the detection on the autoreduced CuZSM-5 and CuM zeolites of the monocarbonyl species characterized by the very high Cu(I)—C stretching vibration frequency of about 500 cm^{-1}. By comparing the spectral characteristics of this species with those of the species in Cu(I)Y or Cu(I)Y (sse) with its fundamental C—O and Cu(I)—C vibration frequencies at about 2144 and 390 cm^{-1}, one can find that there is no straightforward relation between the C—O and Cu(I)—C vibration frequencies. The two types of the species have the same fundamental C—O vibration frequencies at about 2144 cm^{-1}, which are essentially the same as that for gaseous CO, indicating that the σ- and π-back-donations in the two types of the species are equally balanced. However, the large difference between their fundamental Cu(I)—C frequencies ($\Delta\nu \sim 110$ cm^{-1}) surely demonstrates that the σ- and π-back-donations in the species formed on CuZSM-5 or CuM are much stronger. From the point of view of the electron donor—acceptor, it is also quite understandable that, e.g., in the case of CO adsorption on CuZSM-5, the monocarbonyl species with a larger fundamental C—O frequency (ca. 2157 cm^{-1}) may correspond to a smaller fundamental Cu(I)—C one (ca. 440 cm^{-1}). Clearly, the knowledge of the Cu(I)—C vibration allows one to determine more efficiently the degree of electron density transfer between a CO molecule and a cation for forming carbonyls than that of C—O vibration.

Because of the strengthening of the Cu(I)—C bond by the electronic donation and acceptance, the thermal stability of the formed monocarbonyl species will be increased. This point may be manifested by the spectra of CO adsorbed on CuZSM-5. From the spectra recorded at room temperature (Figure 1, spectrum a and Figure 2, spectrum a), it seems that the monocarbonyl species with the higher fundamental Cu(I)—C vibration frequency (ca. 500 cm^{-1}) is no more, or even less, stable than that with the lower one (ca. 440 cm^{-1}). However, considering the noticeably lower number of sites for the formation of the former species, the bands corresponding to the latter would certainly be predominated. Nevertheless, it can be seen, from the spectra shown in Figure 2, that the ratio in intensity of the bands corresponding to the two types of the species increases with the evacuation of the adsorbed CO at an elevated temperature. This fact indicates that the former species is more thermally stable than the latter.

It is worthwhile to point out that in the case of CO adsorption on CuY and CuL, the species with such high donor—acceptor ability is not detected. At high CO pressures this type of species can be transformed to a great extent into dicarbonyl species. Most probably, these Cu(I) cations are also be able to form dinitrosyl complexes with adsorbed NO through a transformation of mononitrosyl species and, therefore, act as the active sites for the reactions of NO elimination which may not be attained with CuY zeolites. These active sites might also be related to the high activity of CuZSM-5 and CuM zeolites to N$_2$ adsorption as revealed by Kuroda et al.[8,22]

Conclusions

Analysis of the diffuse reflectance FTIR spectra of CO adsorbed on the aqueous ion-exchanged CuZSM-5, CuM, CuY, and CuL zeolites autoreduced in vacuo at 673 K and on the Cu(I)Y (sse) zeolite prepared by the solid-state ion exchange between CuCl and NH$_4$Y measured over a wide spectral range demonstrates that different kinds of Cu(I) monocarbonyl species are formed depending on the types of the zeolites. At high CO pressures, part of the monocarbonyl species can be reversibly transformed into dicarbonyl species. It has been found that the frequency of the Cu(I)—C stretching vibration is more sensitive to the structure of the Cu(I) monocarbonyl species than that of the fundamental C—O stretching vibration alone. The different types of monocarbonyl species formed on the copper-exchanged zeolites can be strongly discriminated by their Cu(I)—C stretching vibration frequencies, which likely reflect the electron donor—acceptor abilities of the Cu(I) cations in the carbonyl species. On the autoreduced CuZSM-5 and CuM zeolites, the monocarbonyl species with a very high Cu(I)—C stretching vibration frequency of about 500 cm^{-1} is observed. The existence of the Cu(I) cations participating in the formation of this type of monocarbonyl species might be an important clue in the interpretation of the high activity of CuZSM-5 and CuM zeolites in the reaction of NO elimination and N$_2$ adsorption.

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