JOURNAL OF CATALYSIS **173,** 540–542 (1998)
ARTICLE NO. CA971928

RESEARCH NOTE

Formation of Nonplanar $Cu^I(CO)_3$ Tricarbonyls on Cu^I–ZSM-5: An FTIR Study at 80 K

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Received May 29, 1997; revised September 16, 1997; accepted September 16, 1997

Because the production of undesired nitric oxide gas as a coproduct of several industrial and civil activities constitutes a great problem for modern society, copper-exchanged zeolites recently have attracted great interest as catalysts for the direct conversion of NO into N_2 and O_2 (1–4). Although full conversion is not easily obtained in practical application because the catalyst is not stable in the presence of H_2O vapor, the decomposition over Cu–ZSM-5 is intrinsically interesting because it is stoichiometric (without the formation of the undesirable N_2O side product (5)) and not poisoned by O_2, and because reducing agents are not required to sustain the catalytic activity (1–5). Therefore it is of considerable and fundamental interest to understand the physical basis of the outstanding activity of copper ions in ZSM-5 with respect to other copper-supported catalysts. It has been suggested that such activity is related mainly to the high coordinative unsaturation of copper counterions hosted in the MFI structure. In this brief note we explore this point by probing the coordination state of Cu^I with CO. We will show that, in a Cu^I–ZSM-5 sample prepared through a gas phase reaction with CuCl (6–12), *all* Cu^I ions interact, at 80 K, with CO with formation of $Cu^I(CO)_3$ complexes. This investigation completes a previous recent study (8), carried out at higher temperature ($\simeq$110–120 K), where it was found that only a fraction of Cu^I cations were forming tricarbonylic species.

As the details concerning the cation exchange procedure (in which a 1 : 1 substitution of the acidic protons with Cu^I cations has been obtained), the sample preparation, and the IR setup already have been reported elsewhere (8), in this brief note we shall describe only the new experimental procedure which has allowed us to further lower the temperature of the sample. The IR spectra reported in Ref. (8) were collected in transmission mode on the zeolite sample in the form of a self-supported pellet (typical thickness 100–150 μm) mounted on a sample holder cooled at 77 K. Due to the highly insulating character of the zeolite itself and the heating effect of the IR beam, the actual temperature at the center of the pellet was significantly higher than 77 K: $\simeq$110–120 K. This is an unavailable limit of the adopted configuration method, where only the external borders of the pellets are in contact with the sample holder, and are thus at about 77 K. In order to overcome this difficulty, an extremely thin layer of zeolite (5–10 μm) was deposited on a silicon wafer, and this wafer, instead of the pellet, was positioned in the sample holder inside the IR cell. Due to the higher heat conductivity of silicon than the siliceous zeolite and to the considerably lower thickness of the sample deposited on it, a temperature of $\simeq$80 K (i.e., about 30–40 K below the temperature reached in previous experiments (8)) was easily reached at the center of the sample.

In two recent contributions (7, 8), we have demonstrated by using XANES, UV–Vis (diffuse reflectance), and IR spectroscopy that copper-exchanged ZSM-5 prepared through a gas phase reaction of H–ZSM-5 with CuCl (6–12) contains Cu^I as predominant species and that the Cu^{II} content (determined by EPR) is less than 1%. Photoluminescence data also have evidenced that Cu^I ions are located in two nearly equipopulated families of sites, indicated as **I** and **II** characterized by a different coordinative unsaturation (7, 8). Computer graphic simulations have identified two different families of TO_4 tetrahedra in the MFI structure exhibiting three and two oxygens exposed on the channels. When the T center of these TO_4 tetrahedra is Al, the bridged oxygens are negatively charged and, for electrostatic reasons (13), they become the ideal sites for Cu^+ counterions which thus will be stabilized by maximizing their coordination to these oxygens (13) (three and two, respectively). We can consequently speak about two families of sites. In family **I**, the Cu^I ion is coordinated to three equivalent next-neighboring negatively charged framework oxygens, defining an equilateral triangle of the AlO_4 tetrahedra having a side of 2.6 Å and where the Cu^I–O distance is about 2 Å. In family **II**, the Cu^I ion is coordinated to two equivalent framework oxygens (against at about 2 Å) and to a

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0021-9517/98 $25.00

third, more internally located, at about 3 Å (see Fig. 15 in Ref. (8)). This situation is fully compatible with the EXAFS results (obtained at EXAFS1 beamline of the DCI storage ring at LURE, see Table I in Ref. (8)), which shows that, under *in vacuo* conditions, the coordination number of Cu^I is 2.5 ± 0.3 and the Cu^I–O distance is 2.00 ± 0.02 Å. The coordination number of 2.5 ± 0.3 probably results from Cu^I ions nearly equidistributed in families **I** and **II**. This picture explains why (at $\simeq$110–120 K) one family of sites coordinates up to three CO molecules and the other family only up to two CO molecules, and why both emission and excitation photoluminescence spectra exhibit two distinct components.

Evidence of the formation of mono-, di-, and tricarbonylic complexes first was observed in copper-exchanged zeolites only recently (6–8, 14–21). The ability of Cu^I to form polycarbonylic species has been confirmed by the direct synthesis and characterization of $Cu^I(CO)_n$ ($n = 1, 2, 3$) complexes under homogeneous conditions, which was only obtained in 1996 (22).

Turning now to the discussion of the new IR data, we see that Fig. 1 reports the comparison of the spectra of increasing doses of CO on Cu^I–ZSM-5 at $\simeq$110–120 K (part a) and $\simeq$80 K (part b). As already reported in Refs. (6–8), at the lowest CO coverages the typical band at 2157 cm^{-1} (part a)) is due to the $Cu^I(CO)$ complex, which reaches its maximum at about 7×10^{-3} Torr (1 Torr $\simeq$ 133.3 Pa). By increasing the amount of dosed CO this band is progressively eroded while two strong and distinct bands at 2178 and 2151 cm^{-1} grow in a parallel way (assigned to symmetric and asymmetric modes of dicarbonylic species (6–8)). Upon further CO dosage the transformation of $Cu^I(CO)$ into $Cu^I(CO)_2$ species is complete for $P_{CO} = 7 \times 10^{-2}$ Torr (see Fig. 1a). By further increasing the CO pressure the 2178 cm^{-1} band begins to decrease and two new distinct bands appear at 2192 and 2167 cm^{-1} together with a low-frequency shoulder of the 2151 cm^{-1} band: this has been interpreted in terms of the $Cu^I(CO)_2 \overset{CO}{\rightarrow} Cu^I(CO)_3$ transformation.

In Fig. 1b, the $Cu^I \overset{CO}{\rightarrow} Cu^I(CO)$ and $Cu^I(CO) \overset{CO}{\rightarrow} Cu^I(CO)_2$ steps are not evidenced because the process leading to the mono- and dicarbonylic structures is going to completion at this temperature (80 K), as demonstrated by the presence of the high-frequency band of $Cu^I(CO)_3$ even at the lowest equilibrium pressure: $P_{CO} \simeq 7 \times 10^{-3}$ Torr. It is worth mentioning that, in contrast to what is observed at $\simeq$110–120 K, the $Cu^I(CO)_2$ species are totally irreversible upon outgassing at 80 K. Our observation is in agreement with the recently reported data by Meyer *et al.* (23), who have determined by collision-induced dissociation measurements that the 0 K limit of the $(Cu^+(CO)_{n-1})$–CO ($n = 1$–4) bond energy is 1.54, 1.78, 0.78, and 0.55 eV for $n = 1$, 2, 3, and 4,

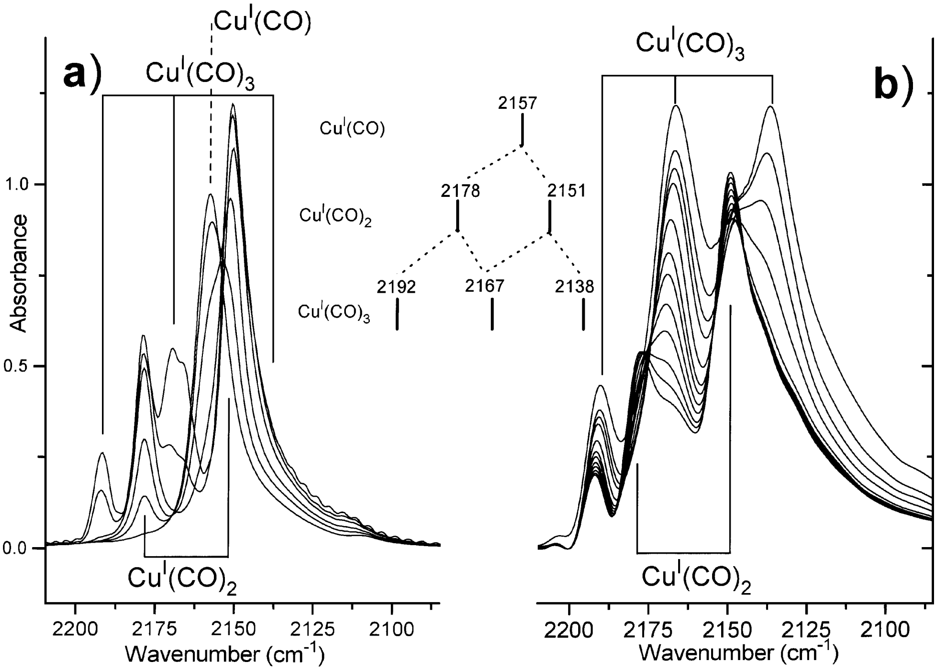

FIG. 1. IR spectra of CO dosed at increasing equilibrium pressures on Cu^I–ZSM-5 at (a) $\simeq$110–120 K (from $\simeq 7 \times 10^{-3}$ to 10 Torr: 1 Torr $\simeq$ 133.3 Pa) and (b) $\simeq$80 K (from $\simeq 7 \times 10^{-3}$ to 3 Torr). Vertical bars indicate the band(s) assigned to mono-, di-, and tricarbonyl adducts. The difference in the optical absorption of the spectra reported in (a) and (b) is remarkable and is indicative of a reduced sample thickness of more than one order of magnitude (see Experimental part). The scheme between (a) and (b) recalls the evolution of the C–O stretching frequencies of the $Cu^I(CO)_n$ adducts upon increasing the CO equilibrium pressure or upon lowering the zeolite temperature (from top to bottom).

respectively. Like in the gas phase, the higher stability at low temperature of the $Cu(CO)_2^+$ complex with respect to $Cu(CO)^+$ is now demonstrated to hold also for the zeolitic framework-hosted complexes.

By increasing the CO coverages, the decrease of the $Cu^I(CO)_2$ bands (2178 and 2151 cm^{-1}) starts and is complete at $P_{CO} \simeq 2$ Torr (see Fig. 1b). In the final spectrum of Fig. 1b ($P_{CO} = 3$ Torr) the three bands of the $Cu^I(CO)_3$ complex (at 2192, 2167, and 2138 cm^{-1}) are clearly dominating.

It is worth mentioning that, when CO is dosed at low temperature on any type of zeolite, a complex broad and asymmetric band centered at 2138 cm^{-1} often appears at high CO equilibrium pressures. This absorption has been attributed to CO molecules weakly interacting with the zeolite framework through Van der Waals forces and already indicated as "liquid like" contribution (24–28). However, the band at 2138 cm^{-1} observed in the spectra collected at lower temperature (see Fig. 1b) cannot be ascribed solely to liquid-like CO, since an evident isosbestic point at 2146 cm^{-1} indicates that the 2138 cm^{-1} band grows at the expense of the low-frequency band of dicarbonilic species (2151 cm^{-1}). Furthermore, because the absorption coefficient of carbonylic species is very high (certainly much higher than that of liquid-like CO) we can conclude that the contribution of liquid-like CO to the band at 2138 cm^{-1} is small or negligible.

The fact that the $Cu^I(CO)_3$ complex is associated with three different C–O stretching frequencies implies that the structure is not planar, that the three CO molecules are not equivalent (otherwise only two IR bands should be observed), and that the symmetry is less than C_{3v}. The formation of nonplanar structures instead of the planar ones (recently reported under homogeneous conditions (22)) is due to the steric constrains imposed by the channel walls which induce the loss of planarity and the lowering of symmetry with the $Cu^I(CO)_n$ ($n = 2, 3$) complexes. This consideration about the symmetry of the di- and tricarbonylic species formed inside Cu^I zeolites can explain why Iwamoto and Hoshino (15) have not observed any Raman signal of the $Cu^I(CO)_2$ complex formed at room temperature on Cu^I–ZSM-5 while under the same experimental conditions the corresponding IR bands are well visible.

In conclusion, the data reported in this note demonstrate that under the more drastic temperature conditions adopted here (80 K), family **I** of sites also can complete its coordination with 3 CO ligands. Consequently this means that both sites **I** and **II** display a very similar chemistry toward CO and that the difference between them lies in the ΔG of the carbonyl addition. In other words, both **I** and **II** sites are extremely accessible to reactants molecules although in different temperature domains.

The results obtained with CO together with those obtained with NO (where the initial formation of dinitrosylic $Cu^I(NO)_2$ complexes was rapidly followed by the formation of $Cu^{II}(NO_2)(NO)$ species (8)) show that the high coordinative unsaturation of all the Cu^I cations in ZSM-5 is indeed the key factor determining high catalytic activity of copper-exchanged ZSM-5.

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