FTIR spectroscopic study of CO adsorption on Cu/SiO_2: formation of new types of copper carbonyls

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Received 6 February 2001; accepted 4 June 2001

Adsorption of CO on a reduced Cu/SiO_2 catalyst (1 wt% Cu) results in formation of Cu^0–CO species characterized by an IR band at 2128 cm^{-1}. During the contact of the sample with CO two new species characterized by bands at 2045 and 2018 cm^{-1} appear. Experiments on ^{12}CO–^{13}CO co-adsorption prove that they are carbonyls. The 2045 cm^{-1} species are assigned to $Cu^0(CO)_2$ geminal complexes formed on copper atoms with a low coordination number. During evacuation the geminal species lose one CO ligand, thus being converted into linear carbonyls (band at 2018 cm^{-1}). Both species are not affected by hydrogen, but easily disappear in the presence of small amounts of oxygen.

KEY WORDS: adsorption; FTIR spectroscopy; carbon monoxide; copper; copper carbonyls

1. Introduction

IR spectroscopy of adsorbed CO is one of the most used methods for determination of oxidation states of supported metal cations. Because of the great importance of copper-containing systems in catalysis, there are many studies devoted to CO adsorption on copper-containing catalysts [1–23]. It is believed that the carbonyls of Cu^{2+} cations are unstable and that they are detected between 2236 and 2160 cm^{-1} at high equilibrium CO pressures [1–7] or at low temperatures [7–11]. The Cu^+ cations form both, σ- and π-back bonds with CO. As a result of the synergistic effect between the two bonds, the Cu^+–CO species are characterized by a high stability. Two groups of IR bands are usually observed with Cu^+–CO carbonyls, namely at a higher frequency (HF) of about 2160 cm^{-1} [1,12–14], and at a lower frequency (LF) of about 2130 cm^{-1} [1–8,10,11,15–18]. The HF bands are observed mainly with zeolites and characterize rather stable complexes which resist evacuation at ambient and higher temperatures [1,12–14]. The LF bands are typical for bulk CuO [18] and oxide-supported copper [1–8,10,11,15–17]. These bands decrease in intensity after evacuation at ambient temperature.

According to Lokhov *et al.* [19], CO forms mainly a π-bond with Cu^0 atoms and the resulting complexes are unstable [3,4,7,16,17] (in some cases they are not observed at room temperature [7]). According to Balkenende *et al.* [15], the Cu^0–CO bands keep only *ca.* 2% of their integral intensities after evacuation. De Jong *et al.* [16] have reported that the frequency of adsorbed CO depends on the surface roughness rather than on the copper particle size and that it is found in the 2145–2099 cm^{-1} spectral region. There are many other examples evidencing that the frequency of CO adsorbed on metallic copper can be as low as 2070 cm^{-1} [7,9,17]. On the basis of the studies performed with single crystals, it can be concluded that CO adsorbed on low-index planes absorbs at *ca.* 2080 cm^{-1}, whereas bands above 2100 cm^{-1} are typical for high-index planes [20]. Generally, carbonyls formed with highly dispersed supported copper are characterized by IR bands above 2120 cm^{-1} [16,20]. Since the spectral regions of Cu^0–CO and Cu^+–CO species overlap, the stability of the species is an important criterion for the discrimination between both kinds of complexes with Cu^0–CO species being easily decomposed during evacuation [3,4,7,16].

Bridged carbonyls are not typical for copper. They are only observed at low temperatures and at high CO coverages [20–22]. The spectral region where bridged carbonyls of copper are detected is 1835–1814 cm^{-1} [21,22]. However, Dandekar and Vannice [7] have reported that low-temperature CO adsorption on a reduced Cu/Al_2O_3 catalyst results in the appearance of a broad band at 2003 cm^{-1} tentatively assigned to bridged species.

In this study we report the formation of unusual mono- and dicarbonyls on reduced Cu/SiO_2 catalysts. They appear with time in CO atmosphere and are observed in the wavenumber region between 2252 and 2003 cm^{-1}.

2. Experimental

The CuO/SiO_2 sample was synthesized by incipient wetness impregnation of SiO_2 (Aerosil) with a 0.05 mol dm^{-3} $Cu(NH_3)_6(NO_3)_2$ solution, followed by calcination at 673 K. The sample contained nominally 1 wt% CuO.

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Carbon monoxide (>99.997%) was supplied by Linde AG. The ^{13}C-labelled CO was purchased from Aldrich Chemical Company Inc. Its isotopic purity was 99 at% ^{13}C but it contained about 10 at% $^{13}C^{18}O$.

IR spectroscopy studies were carried out with a Bruker IFS 66 apparatus at a spectral resolution of 2 cm^{-1} accumulating 128 scans. Self-supporting wafers (*ca.* 10 $mg\,cm^{-2}$) were prepared by pressing the sample powders at 10^4 kPa. The samples were heated directly in the IR cell. The latter was connected to a vacuum/adsorption system with a base pressure of less than 10^{-3} Pa. Prior to the adsorption measurements, the sample was activated by calcination at 673 K, evacuation at the same temperature, reduction in hydrogen (60 kPa) at 573 or 673 K and evacuation at the same temperature. For some experiments the reduction was performed in flowing hydrogen at 573 K. The duration of each individual treatment step was 1 h.

The TPR experiments were performed with 10 vol% hydrogen in argon (30 $ml\,min^{-1}$) at a heating rate of 10 $K\,min^{-1}$, the hydrogen consumption being measured by a thermal conductivity detector.

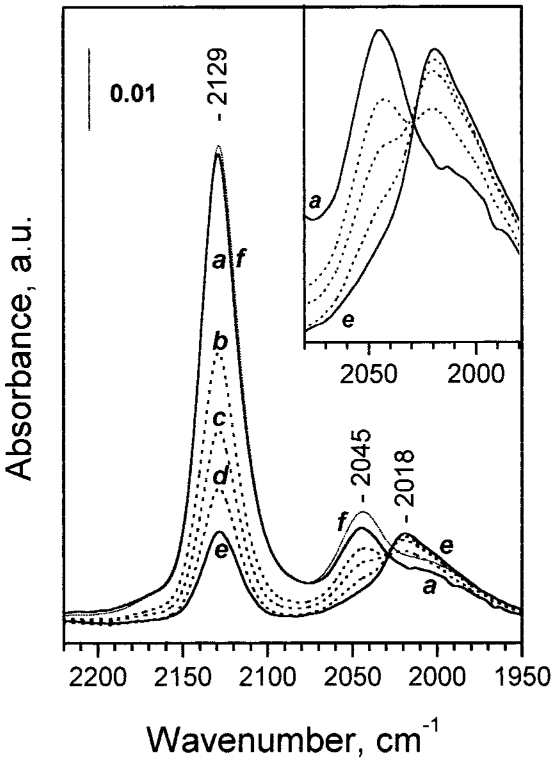

Figure 1. FTIR spectra of CO adsorbed on Cu/SiO_2 reduced at 573 K. Equilibrium pressure of 5000 (a), 100 (b), 30 (c), 10 (d) and 2.5 Pa CO (e) and again 5000 Pa CO (f). Spectrum (a) is recorded 20 min after the admission of CO.

3. Results

The Cu/SiO_2 sample was light blue in color suggesting that no separate CuO phase was formed during the calcination. This is in agreement with the low copper concentration as well as with the method of preparation. In fact, Cu^{2+} cations are strongly adsorbed on silica from alkali solutions, thus stabilizing an atomic dispersion.

The TPR profile of the sample contains one symmetric TPR peak with a maximum at 523 K which is assigned to the reduction of Cu^{2+} ions to metallic copper. The reduction is complete below 550 K. Thus, one can infer that a sample reduced at higher temperatures does not contain residual copper cations. After reduction, the sample turns brown. However, subsequent exposure to air restores the initial blue color. This suggests high dispersion of the metallic copper, which is consistent with the high dispersion of the copper cations before the reduction.

Adsorption of CO on a sample reduced at 573 K results in the appearance of one band at 2129 cm^{-1}. This band, which decreases in intensity with decreasing equilibrium CO pressure and disappears after evacuation, may be assigned, according to its position, to both, Cu^+–CO and Cu^0–CO species. Taking into account the low stability of the carbonyls we have detected as well as the results of the TPR experiments, we assign the 2129 cm^{-1} band to Cu^0–CO species. This band will not be discussed in any details in the following.

After allowing the sample to stand in a CO atmosphere (5 kPa), another band at 2045 cm^{-1} with a lower frequency shoulder slowly develops (figure 1, spectrum (a)). Further on, we shall denote the respective species as B species and their assignment will be proposed in section 4. With decreasing equilibrium CO pressure this band gradually decreases in intensity and a new band at 2018 cm^{-1} (A species) develops at its expense (figure 1, spectra (b)–(e)). A clear isosbestic point between the two bands is observed at 2029 cm^{-1}. This indicates direct conversion between the A and B species. The A species are resistant towards evacuation at ambient temperature and disappear after evacuation at 373 K.

Subsequent introduction of CO (5 kPa) to the sample almost restores the initial spectrum (figure 1, spectrum (f)). However, the intensity of all carbonyl bands slightly increases. This is more pronounced with the bands characterizing the A and B species and is in agreement with the observation that the latter species are formed in a CO atmosphere. In addition, the results evidence that the conversion of B to A species is a reversible process.

The effect of temperature on the formation of the A and B species was also studied. Heating the sample for 5 min at 573 K in CO atmosphere, followed by cooling down to room temperature, resulted in a pronounced increase in intensity of the bands due to the A and B species and slight erosion of the principal Cu^0–CO band at 2129 cm^{-1} band. These results confirm the assumption that the A and B species are formed as a result of interaction of CO with metallic copper.

Since the A species are converted into B species in a CO atmosphere, one could expect that further conversion could occur at lower temperatures and under a certain CO equilibrium pressure. To check this, we adsorbed CO at an equilibrium pressure of 2 kPa. At this pressure almost all low frequency species were in the B form (figure 2, spectrum (a)).

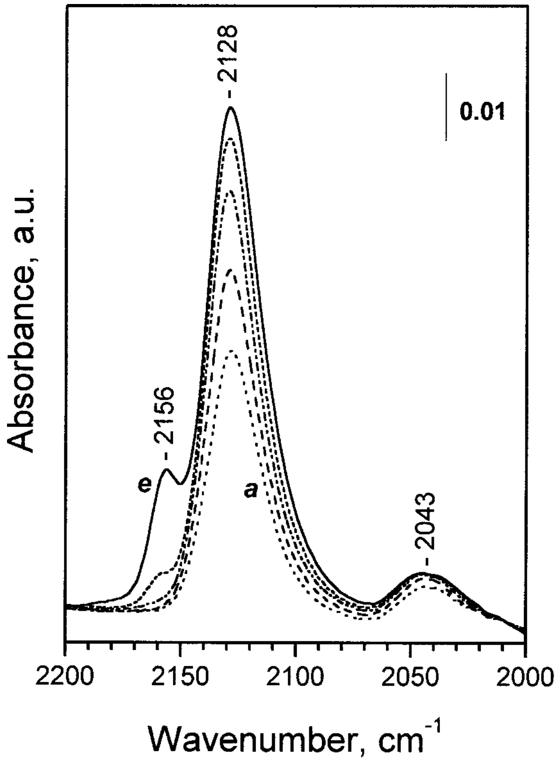

Figure 2. FTIR spectra of CO (2 kPa equilibrium pressure) adsorbed on Cu/SiO$_2$ reduced at 573 K. Sample temperature: 283 (a), 243 (b), 203 (c), 163 (d) and 133 K (e).

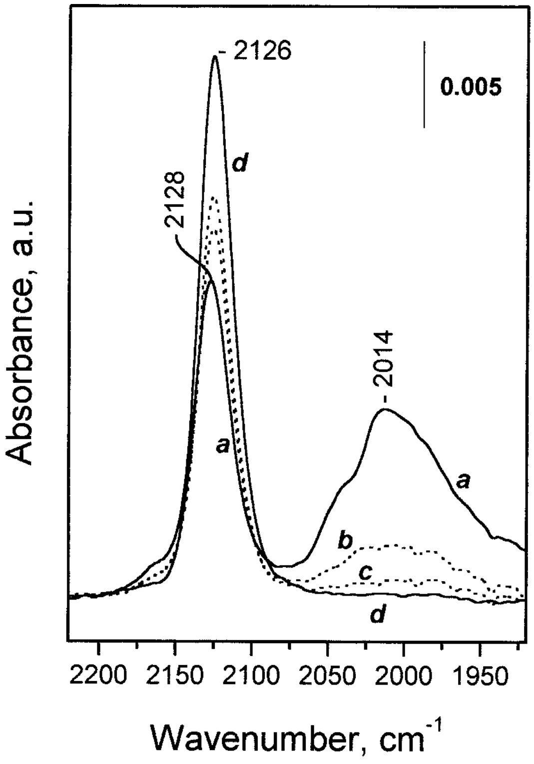

Figure 3. FTIR spectra of CO adsorbed on Cu/SiO$_2$ reduced at 573 K. Equilibrium CO pressure of 20 Pa CO (a), and subsequent short exposure to *ca.* 1 Pa O$_2$ (b), after 5 min exposure at 1 Pa O$_2$ (c), and after exposure to 20 Pa O$_2$ (d).

Then the temperature was gradually lowered. As a result, the 2043 cm^{-1} band remained almost unchanged (figure 2, spectra (b)–(e)). Only the Cu^0–CO band at 2128 cm^{-1} strongly increased in intensity. At 163 K a weak band at 2156 cm^{-1} appeared and increased in intensity as the temperature decreased (figure 3, spectra (d) and (e)). This band is assigned to CO H-bonded to the surface Si–OH groups of the support [24]. The results obtained evidence that the B species are not able to coordinate an additional CO molecule even at low temperature.

The reactivity of the A and B species towards reducing and oxidizing agents was also tested. It was found that hydrogen does not affect the spectra of the A and B species. The interaction of the A and B species with O$_2$ is illustrated on figure 3. In the presence of 20 Pa CO the A and B species are mainly in the A form, which is evidenced by the band at 2014 cm^{-1} (figure 3, spectrum (a)). Exposure to a small amount of oxygen (*ca.* 1 Pa partial pressure) results in a drop in intensity of the 2014 cm^{-1} band and an increase in intensity of the band at 2128 cm^{-1} (figure 3, spectrum (b)). These changes become more pronounced with time (figure 3, spectrum (c)). Admission of more O$_2$ (20 Pa) leads to the complete disappearance of the 2014 cm^{-1} band and to a strong increase of the intensity of the band at 2128 cm^{-1}, its maximum being shifted to 2126 cm^{-1} (figure 3, spectrum (d)). The latter band does not disappear after evacuation, which indicates that it characterizes (at least partly) Cu$^+$–CO species. The above results suggest that the copper sites responsible for the formation of A and B species are easily oxidized.

Some experiments were performed to check how the reduction conditions affect the A and B species. CO was adsorbed on a sample reduced at 673 K. In this case the Cu^0–CO species were found at the same frequency as with the sample reduced at 573 K, namely at 2129 cm^{-1}. The band responsible for the B species was also detected at 2046 cm^{-1}. A remarkable difference was noted with the band due to A species. It was registered at 2003 cm^{-1}, *i.e.*, at a frequency lower by 11–15 cm^{-1} than that observed with the sample reduced at 573 K.

A fresh sample was reduced in flowing hydrogen. Thus, the water evolved during the reduction was permanently removed and one could expect a restricted sintering of the metal particles. CO adsorption on the sample thus reduced induced the appearance of a band at 2135 cm^{-1}, which suggested a higher copper dispersion (or particle roughness). After contact of the sample with CO, A and B species were formed. In this case their characteristic bands were detected at 2052 and 2028 cm^{-1}, respectively.

To obtain more information on the nature of the A and B species, co-adsorption of ^{12}CO and ^{13}CO was performed. First, CO was adsorbed at a pressure of 20 Pa (figure 4, spectrum (a)). Addition of *ca.* 60 Pa ^{13}CO (figure 4, spectra (b) and (c)) resulted in a decrease in intensity of the ^{12}CO bands at 2134 cm^{-1} and appearance of new bands at 2086, 2037, 2005 and 1982 cm^{-1}. Taking into account the isotopic fac-

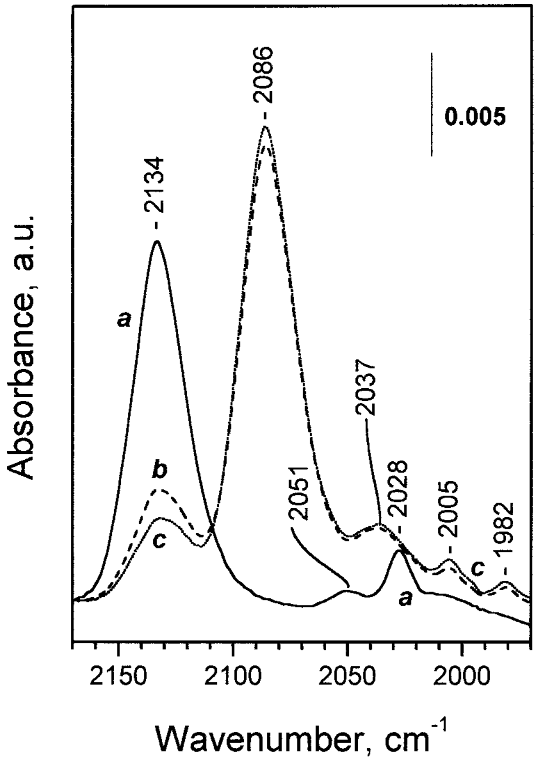

Figure 4. FTIR spectra of ^{12}CO and ^{13}CO co-adsorbed on Cu/SiO$_2$ reduced at 573 K. Equilibrium ^{12}CO pressure of 20 Pa (a), addition of 60 Pa ^{13}CO (b) and after 5 min exposure (c).

tors, it is easy to assign the band at 2086 and 2037 cm^{-1} to Cu^0–^{13}CO and Cu^0–$^{13}C^{18}O$ species, respectively. The calculated shifts of the bands characterizing A and B species (assuming they are due to carbonyls) are: 2051 → 2005.5 and 2028 → 1983 cm^{-1}. This is in good agreement with the experimentally obtained values of 2005 and 1982 cm^{-1}.

4. Discussion

To the best of our knowledge, no copper carbonyls comparable to those observed in this study have been reported in the literature. There are some papers describing carbonyls of metallic copper absorbing below 2050 cm^{-1}. Thus, Amara *et al.* [2] reported that when CO is adsorbed on a Cu^+/SiO$_2$ sample evacuated at 773 K, a Cu^0–CO band arises at 2050 cm^{-1} after CO adsorption (1.7 kPa equilibrium pressure). However, in this study no data on the stability of the species were provided. Thus, we can only suppose that we have observed the species found by Amara *et al.* [2]. Recently, Dandekar and Vannice [7] reported carbonyl bands at 2099 and 2003 cm^{-1} arising from CO adsorption on a reduced Cu/Al$_2$O$_3$ sample. The band at 2003 cm^{-1} was assigned to bridged carbonyls. However, it was detected at low temperature only and showed no conversion to another band. This suggests that despite the close stretching frequency, the species observed by these authors were different from those detected here. Rochester *et al.* [23] reported a band at 2014–2008 cm^{-1} to appear after acetic acid decomposition at 473 K on Cu/Al$_2$O$_3$ and Cu/SiO$_2$. It seems very probable that the respective species should be the same as the A species observed by us.

An interesting study concerning supported gold catalysts was reported recently [25]. The authors observed bands similar to those detected by us as well as an interconversion between the species. The bands were assigned to carbonyls on small negatively charged Au clusters, namely linear carbonyls and bridged carbonyls characterized by bands at 2055 and 1990 cm^{-1}, respectively.

Our results clearly show that the sites responsible for the formation of the A and B species are created in CO atmosphere. This is not unexpected, taking into account the known phenomenon of transport of metallic copper in a CO atmosphere [26]. The results also demonstrate that the A and B species can be interconverted according to the reaction:

$$S\text{–}(CO) + CO \rightarrow S\text{–}(CO)_2 \qquad (1)$$

where S denotes part of the copper surface.

There are two possible explanations for this reaction: first, the A species could be bridged carbonyls that are converted into linear B species in the presence of CO as proposed for gold catalysts [25]. However, there are some details contradicting this hypothesis:

- The bridged carbonyls of copper are observed around 1820 cm^{-1} and only at low temperatures and high CO coverages [21,22].
- Formation of bridged carbonyls involves rehybridization of CO. Thus, the extinction coefficients of bridged and linear carbonyls are generally expected to be very different. However, assuming reaction (1), we estimated the extinction coefficient of the B species to be *ca.* 64% of the extinction coefficient of the A species.

Another possibility to explain reaction (1) is the conversion between mono- and dicarbonyls. At low CO pressures the B species are predominant. Supposing they are linear carbonyls and taking into account their high stability, the copper sites should be characterized by a very low coordination number. Thus, CO would form a strong bond with these copper atoms where the π-back-donation could also be sterically facilitated. The high coordinative unsaturation is a factor allowing a second CO molecule to be coordinated to the same site. Because of the simultaneous action of both CO molecules as electron acceptors, the strength of the π-bond between the copper site and the CO molecules will decrease and, as a result, the stretching frequency will be blue-shifted. It is known that the formation of a π-bond strongly enhances the extinction coefficient of adsorbed CO. Thus, the above hypothesis explains the small decrease of the CO extinction coefficient when the monocarbonyls are converted into dicarbonyls.

In many cases dicarbonyls exhibit symmetric and antisymmetric CO stretching modes. The symmetric vibrations are less intense and are observed at higher frequencies. In our case these modes may be masked by the strong Cu^0–CO band at 2129 cm^{-1}. No evidence of splitting of the CO stretching modes was found in the ^{12}CO–^{13}CO co-adsorption experiments but in this case masking of bands is also possible. However, we infer that no splitting of the CO stretching modes occurs. Many recent investigations indicate that when the adsorption is weak and the formation of geminal species is caused by the low coordination number of the adsorption site, both ligands behave as independent oscillators. This is, for instance, the case of CO adsorption on Na$^+$ cations in zeolites [27–29] as well as Ag$^+$ cations in Ag-ZSM-5 [30]. There are also similar examples concerning coordination of two N$_2$ molecules to one site [31,32] which have been confirmed by DF studies [33].

It is of interest to speculate as to whether the copper sites responsible for the formation of the mono- and dicarbonyls (A and B species) are isolated on the silica surface or are created on the surface of the copper particles formed during the initial reduction of the sample with hydrogen. Let us consider the monocarbonyls. On the sample reduced at 573 K, the CO stretching frequency of the monocarbonyls was found at 2018 cm^{-1}. On the sample reduced at 673 K (where bigger copper particles are expected) the respective frequency was 2003 cm^{-1}. This fact could be explained by the participation of the whole copper particle in the electron donation to the π-orbitals of CO. Greater particles could donate more electron density and the resulting CO stretching modes will shift to a lower frequency. Thus, the results suggest that the sites are located on the copper particles. This assumption is also supported by the fact that the creation of the sites where mono- and dicarbonyls are formed is accompanied by a decrease in intensity of the principal Cu^0–CO band. Note that no correlation between the frequency of the dicarbonyl species and the copper dispersion was observed. This fact remains unexplained, although the dicarbonyl bands are expected to be less sensitive to the copper particle size.

The above considerations are consistent with the experiments with the sample reduced in flowing hydrogen, where the highest copper dispersion is expected. In this case the monocarbonyls were detected at 2028 cm^{-1}.

Finally, we should like to note that the new mono- and dicarbonyls described here could be important intermediates in some CO conversion reactions occurring under anaerobic conditions.

Acknowledgement

This work was financially supported by the Deutsche Forschunggemeinshaft (SFB 338) and by the Fonds der Chemischen Industrie. KH acknowledges the award of an Alexander-von-Humboldt Fellowship.

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