Low-Temperature CO Adsorption on Ag$^+$/SiO$_2$ and Ag−ZSM-5: An FTIR Study

Konstantin Hadjiivanov*,† and Helmut Knözinger

Institut für physikalishe Chemie, Univeristät München, Sophienstr. 11, 80333 München, Germany

Received: August 13, 1998; In Final Form: October 28, 1998

Carbon monoxide is adsorbed on Ag$^+$ cations of Ag$^+$/SiO$_2$ and Ag−ZSM-5 samples via coordination bonds having predominantly σ-character, with the π-character being weak. The support strongly affects the strength of the Ag−CO bond. Thus, the carbonyls on Ag$^+$/SiO$_2$ are characterized by ν(CO) at 2169 cm^{-1} and are easily decomposed by evacuation even at low temperature, which reveals weak σ-bonding. On the contrary, the Ag$^+$−CO species formed on Ag−ZSM-5 absorb at 2192 cm^{-1} and are highly resistant toward evacuation even at ambient temperature, indicating a relatively strong σ-bond. The Ag$^+$ cations in Ag−ZSM-5 are able to coordinate a second CO molecule, thus forming dicarbonyls at low temperature. The angle between both CO ligands is near 180°, and as a result, the dicarbonyl species gives rise to a single C−O stretching mode at 2186 cm^{-1}. These conclusions are confirmed by adsorption of ^{12}CO−^{13}CO isotopic mixtures.

1. Introduction

Supported silver ions show good catalytic properties for several reactions, such as ethanol oxidation to acetaldehyde[1] and aromatization of alkanes, alkenes, and methanol.[2] Very promising is the use of silver-containing catalysts in different DeNO$_x$ processes, such as photocatalytic decomposition of NO[3] and selective catalytic reduction of NO$_x$ by hydrocarbons.[4] However, the activity and selectivity of the catalysts depend on many factors, one of the most important being the kind of the support, which usually determines the electronic and coordination state of the cation. In many cases, the existence of cations with a high electron deficiency favors the catalytic processes.

The Brønsted acid sites of the H−ZSM-5 zeolite are among the most acidic surface OH groups that are known at present.[5] This suggests a high electron deficiency of cations exchanged in ZSM-5. Accordingly, we reported that the Cu$^+$ ions in Cu−ZSM-5 possess more coordinative vacancies than do Cu$^+$ ions supported on oxides, e.g., silica.[6] As a result, monocarbonyls only are produced after CO adsorption on Cu/SiO$_2$, whereas Cu$^+$(CO)$_x$ ($x = 1−3$) species are formed on Cu−ZSM-5.[6,7] A high electron deficiency of Na$^+$ cations in Na−ZSM-5 (compared to other Na$^+$-containing systems) was reported by Bordiga et al.[8] It may be expected that Ag$^+$ ions in Ag−ZSM-5 would also be characterized by a high electron deficiency and could form Ag$^+$(CO)$_x$ species upon CO adsorption.

The adsorption of CO on different Ag$^+$-containing samples has been studied by several research groups,[9−11] and the frequency of the Ag$^+$−CO surface species has been observed within the 2200−2150 cm^{-1} spectral region.

Pestryakov et al.[9] have reported that the ν(CO) stretching vibration of Ag$^+$−CO complexes depends on the type of the support. They observed the highest frequency (2195 cm^{-1}) with a Ag/SiO$_2$−Al$_2$O$_3$ sample, whereas the lowest frequency (2170 cm^{-1}) was found with Ag/Al$_2$O$_3$ catalysts. The frequency of CO adsorbed on different Ag-exchanged zeolites also differs.

Thus, ν(CO) at 2174−2170 cm^{-1} has been observed after CO adsorption on AgY, whereas the respective band for AgX was found at 2195 cm^{-1}.[10] It was reported that adsorption of CO on a Ag/SiO$_2$ sample produced a band at 2180−75 cm^{-1}.[9] In general, the CO adsorption species are moderately unstable. In various cases, the ν(CO) bands disappear after evacuation at ambient temperature (Ag/SiO$_2$, Ag/Al$_2$O$_3$[9,10f]) or show only a decrease in intensity (Ag-exchanged zeolites[11a−d] and Ag/TiO$_2$[11e]).

No surface silver dicarbonyls have been evidenced so far. However, spectra of Ag$^+$(CO)$_2$ bulk species have been reported recently.[12] A single IR band has been observed, with its maximum ranging from 2207 to 2186 cm^{-1} in the different cases.

Only a weak bond with a predominant π-character is formed between Ag^0 and CO. As a result, bulk Ag^0(CO)$_n$ species are unknown and surface Ag^0−CO complexes are observed at about 2060 cm^{-1} only when the CO adsorption is performed at low temperature.[13]

The aim of the present work is a detailed comparative study of formation of silver(I) carbonyls on Ag−ZSM-5 and Ag$^+$/SiO$_2$ samples. For this purpose, we investigated, by means of IR spectroscopy, the adsorption of CO on both samples at ambient and at low temperature. For better interpretation of the spectra obtained, we also used ^{12}CO−^{13}CO isotopic mixtures.

2. Experimental Section

2.1. Sample Preparation. Ag−ZSM-5 was prepared by ion exchange of Na−ZSM-5 (Si/Al molar ratio = 22) with 0.01 mol dm^{-3} AgNO$_3$ solution in excess. The exchange procedure was performed at ambient temperature for 24 h and repeated 3 times. Then, the sample was filtered, washed thoroughly with distilled water, and dried at 105 °C. The sample obtained had a light-pink color. The silver content, according to the chemical analysis, was 4.82 wt %, which corresponded to an exchange degree of 65%.

Ag$^+$/SiO$_2$ was prepared as described elsewhere[14] by adsorption of silver ions on silica (aerosil, 223 m^2 g^{-1}) from a 0.1 mol dm^{-3} Ag$^+$ solution, which was obtained by adding NH$_4$-OH to AgNO$_3$ (final ammonia concentration of 12 wt %). The

* Corresponding author.
† On leave from the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria.
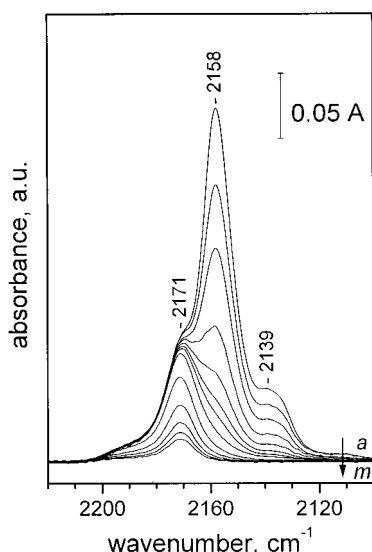
CO Adsorption on Ag$^+$/SiO$_2$ and Ag–ZSM-5

J. Phys. Chem. B, Vol. 102, No. 52, 1998 **10937**

Figure 1. FTIR spectra of CO adsorbed on Ag$^+$/SiO$_2$ at 85 K. The spectra are recorded at gradually decreasing equilibrium pressure from 0.2 kPa (a) to 1.3×10^{-3} Pa (m).

adsorption procedure was carried out for 1 h, and then the sample was washed with distilled water and dried at 105 °C. This preparation technique ensures a high dispersion of the deposited cations,[14] which allows comparison with the silver ions in the Ag–ZSM-5 sample. The Ag$^+$/SiO$_2$ sample has a gray color, and its silver concentration was 1.83 wt %.

2.2. Methods. IR spectroscopy studies were carried out with a Bruker IFS 66 apparatus. Self-supporting pellets (ca. 10 mg cm^{-2}) were prepared from the samples by pressing at a pressure of 10^4 kPa and heated directly in the IR cells. The latter were connected with a vacuum/sorption apparatus with a residual pressure of less than 10^{-3} Pa. Prior to the adsorption measurements, the samples were activated by calcination at 400 °C for 1 h and 1 h of evacuation at the same temperature. A specially constructed cell allowed the IR measurements to be performed at both ambient temperature and 85 K.

The chemical analysis of silver was performed by flame atomic absorption spectrophotometry using a PYE-UNICAM SP-1950 apparatus.

3. Results

3.1. CO Adsorption at Ambient Temperature on Ag$^+$/SiO$_2$. Introduction of CO (1.6 kPa) to the activated Ag$^+$/SiO$_2$ sample results in the appearance of one main band with a maximum at 2169 cm^{-1} with a high-frequency shoulder at 2186 cm^{-1} (Figure 1S of the Supporting Information). Both bands decrease in intensity with the decrease in equilibrium pressure and disappear completely after evacuation. However, it is the high-frequency component that is less sensitive to the pressure changes. According to literature data,[9–11] both bands are assigned to Ag$^+$–CO species. Deconvolution of the spectra shows that the position of the 2169 cm^{-1} band is coverage independent, which implies that the respective Ag$^+$ adsorption sites are isolated cations. The 2186 cm^{-1} band is slightly blue shifted with decreasing coverage, which proves a slight interaction between the adsorbed molecules and suggests that the band corresponds to CO located on associated Ag$^+$ cations.

3.2. Low-Temperature CO Adsorption on Ag$^+$/SiO$_2$. Three main bands have developed in the ν(CO) stretching region after adsorption of CO (0.2 kPa equilibrium pressure) at 85 K on the Ag$^+$/SiO$_2$ sample (Figure 1). Their maxima are located at 2171, 2158, and 2139 cm^{-1}. In addition, a weak feature at about

2185 cm^{-1} is also visible. The band at 2139 cm^{-1} is typical for physically adsorbed CO and disappears quickly with decreasing equilibrium pressure. The band at 2158 cm^{-1} is more stable but also disappears at low equilibrium pressures. This band is assigned to CO H-bonded to surface Si–OH groups[5] since it changes in intensity simultaneously with the shift of the Si–O–H modes from 3745 to 3655 cm^{-1}. The bands at 2171 and 2185 cm^{-1}, although decreasing in intensity with the CO pressure, do not disappear after evacuation. These bands are caused by the same Ag$^+$–CO species that were already detected at ambient temperature. The intensities of the bands are higher at low temperature, which is due to the fact that at 85 K and under sufficiently high equilibrium pressure all Ag$^+$ sites are occupied by CO molecules.

3.3. CO Adsorption at Ambient Temperature on Ag–ZSM-5. CO adsorption (0.8 kPa equilibrium pressure) on the activated Ag–ZSM-5 sample leads to the appearance of an intense and slightly asymmetric band with a maximum at 2191 cm^{-1} (Figure 2S of the Supporting Information). This band is assigned to Ag$^+$–CO carbonyls.[9–11] The band negligibly decreases in intensity with decreasing equilibrium CO pressure. A difference spectrum (inset in Figure 3S of the Supporting Information) indicates that this decrease is mainly caused by the disappearance of a low-frequency component of the band. Simultaneously, it gains some intensity in the higher frequency region. Even after a prolonged evacuation at ambient temperature, the band maintains most of its integral absorbance. Evacuation at 100 °C leads to a strong decrease of the band intensity, but it only disappears from the spectrum after evacuation at 150 °C. The higher frequency and stability of the 2191 cm^{-1} band, relative to that observed for the Ag$^+$/SiO$_2$ sample, suggests significantly stronger σ-bonding between CO and the Ag$^+$ cation. Thus, the results imply that the Ag$^+$–CO species on Ag–ZSM-5 are much more stable than on the Ag$^+$/SiO$_2$ sample.

3.4. Low-Temperature CO Adsorption on Ag–ZSM-5. Adsorption is favored at low temperatures, and some carbonyls that are not stable at ambient temperature can thus be detected. Carbon monoxide adsorption on the Ag–ZSM-5 sample at 85 K (0.01 kPa equilibrium pressure) causes the appearance of a set of IR bands (Figure 3S of the Supporting Information), their maxima being located at 2185, 2175, 2161, and 2138 cm^{-1}. Two shoulders are also clearly observed: a high-frequency shoulder of the 2185 cm^{-1} band and a low-frequency shoulder of the 2138 cm^{-1} band. The bands in the 2138–33 cm^{-1} region are typical for CO physically adsorbed inside the zeolite channels.[15] According to data from the literature,[15] the complex contour of this feature is due to hindered rotation modes. The band at 2161 cm^{-1} can be attributed to CO attached to delocalized protons,[16] since it changes in intensity simultaneously with the shift of a broad OH band at ca. 3200 cm^{-1} to ca. 2800 cm^{-1}. The band at 2175 cm^{-1} coincides in position with the bands reported for CO on Na$^+$ cations on different systems, in particular Na–ZSM-5.[8,15,17] We assign it to CO polarized by residual Na$^+$ cations.

Evacuation results in successive disappearance from the spectrum of the bands at 2138, 2162, and 2175 cm^{-1}, and at about 4×10^{-2} Pa, they are poorly observable (spectrum a in Figure 2). This is in agreement with the expected low stability of the physically adsorbed molecules and of both, Na$^+$- and H-bonded CO. In addition, a small decrease in intensity of the band at 2185 cm^{-1} as well as a shift to 2186 cm^{-1} was detected.

At a pressure of about 10^{-5} kPa, only the band at 2186 cm^{-1} and its high-frequency shoulder are visible (spectrum b in Figure
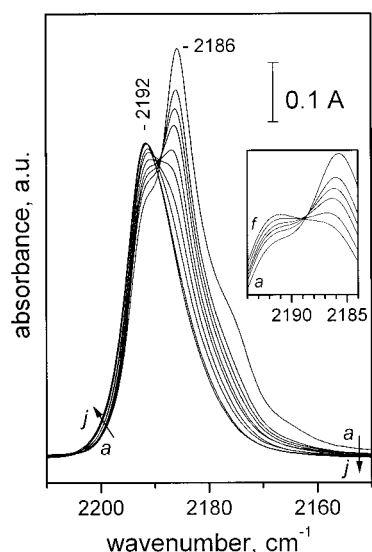
Figure 2. FTIR spectra of CO adsorbed on Ag−ZSM-5 at 85 K and an equilibrium pressure of 4×10^{-2} Pa (a) and evolution of the spectra (e−j) under dynamic vacuum down to 2.5×10^{-3} Pa (j).

Figure 3. FTIR spectra of ^{12}CO−^{13}CO isotopic mixtures adsorbed on Ag−ZSM-5 at 85 K, ^{12}CO/^{13}CO ratio of ca. 1/2, 0.1 Pa total equilibrium pressure (a) and after introduction of small amount of ^{12}CO into the IR cell (b).

2). Further evacuation causes a decrease of the 2186 cm^{-1} band intensity and a simultaneous rise in intensity of the shoulder (developed as a band) at 2192 cm^{-1}. An isosbestic point at 2189 cm^{-1} suggests the interconversion of two corresponding surface species (this point was observed for a series of spectra, except for very low pressures, since then the 2192 cm^{-1} band also starts to decrease). After prolonged evacuation, a slightly asymmetric band at 2192 cm^{-1} is the only one left in the ν(CO) spectral region. Both the position and the intensity of the band indicate that it is the same band that was observed upon CO adsorption at ambient temperature.

Heating the sample to ambient temperature in the presence of 10^{-4} kPa CO (no physically adsorbed CO was detected at this pressure) leads to changes similar to those observed during the CO evacuation at 85 K. First, the bands at 2162 and 2175 cm^{-1} vanish and disappear completely at about 200 K. Second, the 2186 cm^{-1} band gradually decreases in intensity with temperature rise and the band at 2192 cm^{-1} develops at its expense. At ambient temperature, the 2185 cm^{-1} band is no longer observed.

As in the case of the Ag$^+$/SiO$_2$ sample, no metallic silver (expected band at ca. 2060 cm^{-1})^{13} was detected on the surface.

3.5. Coadsorption of ^{12}CO and ^{13}CO on Ag−ZSM-5. To obtain more information about the structure of the complexes characterized by the bands at 2192 and 2186 cm^{-1}, we studied the coadsorption of ^{12}CO and ^{13}CO. A mixture of ^{12}CO−^{13}CO (ca. 2:1 ratio, 0.1 kPa total pressure) was introduced into the IR cell at ambient temperature. In addition to the band at 2192 cm^{-1}, two more bands at 2143 and 2090 cm^{-1} were detected (Figure 4S of the Supporting Information). Taking into account the values of the isotopic shifts, the 2143 and 2090 cm^{-1} bands are assigned to the Ag$^+$−^{13}CO and Ag$^+$−^{13}C^{18}O species, respectively (the latter species originating from ^{13}C^{18}O isotopic impurities in ^{13}C^{16}O). Introduction of ^{13}CO (0.1 kPa) results in a fast increase of the bands due to ^{13}C-containing carbonyls at the expense of the ^{12}C-species.

As expected, cooling the sample down to 85 K (in an atmosphere of 0.1 Pa ^{12}CO−^{13}CO mixture) leads to the appearance of bands characteristic of CO coordinated to Na$^+$ ions (2175 cm^{-1}) and OH groups (2161 cm^{-1}) as well as their respective ^{13}CO analogues (at 2127 and 2113 cm^{-1}) (Figure 3). The silver carbonyls are now detected at 2186 and 2137
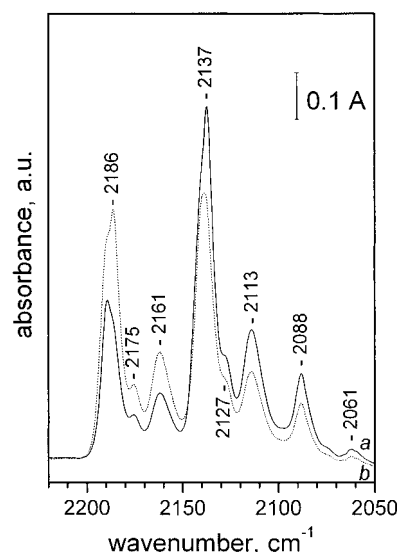
cm^{-1}. A medium-intensity band at 2088 cm^{-1} is due to ^{13}C^{18}O bonded to Ag$^+$ ions. The other ^{13}C^{18}O species are of weak intensity but still discernible: ^{13}C^{18}O polarized by Na$^+$ cations at 2076 cm^{-1}, H-bonded ^{13}C^{18}O at 2061 cm^{-1}, and physically adsorbed ^{13}C^{18}O at 2037 cm^{-1}.

Introduction of a small amount of ^{12}CO leads to a fast change of the intensity ratio of the different bands; the ^{12}CO carbonyl bands rise at the expense of the bands due to the ^{13}C^{16}O and ^{13}C^{18}O adspecies (Figure 3).

Contrary to the case of pure ^{12}CO adsorption, two bands are now clearly visible in place of the 2186 cm^{-1} band, namely one with a maximum at 2186 and one at 2189 cm^{-1}, with their intensity ratio depending on the concentration of the two different isotopes. The band at 2186 cm^{-1} rises with the ^{12}CO concentration, whereas the 2189 cm^{-1} band intensity is proportional to the concentration of ^{13}CO (Figure 3). The situation is similar in the ν(^{13}CO) stretching region (see also Figure 5S of the Supporting Information); the respective shifted bands are observed at 2137 and 2140 cm^{-1}. When the percentage of ^{13}CO in the isotopic mixture is higher, the band at 2137 cm^{-1} is more intense. With a higher amount of ^{12}CO, the intensity ratio reverses. Because of the participation of the physically adsorbed ^{12}CO in this region, both bands are not so clearly distinguished at high equilibrium pressures.

During the evacuation, the effects already observed with ^{12}CO are again detected. First, the bands due to physically adsorbed CO as well as to CO attached to OH groups and to Na$^+$ cations decrease fast in intensity with decreasing equilibrium pressure. Second, the 2189 and 2186 cm^{-1} bands (and their respective ^{13}CO satellites) disappear and a band at 2192 cm^{-1} grows in their place (Figure 4). The band at 2186 cm^{-1} disappears a little faster than that at 2189 cm^{-1}. In the ν(^{13}C−O) region, however, the bands at 2140 and 2137 cm^{-1} change in intensity almost in parallel (inset in Figure 5S of the Supporting Information). After a prolonged evacuation, only three bands remain in the 2300−2000 cm^{-1} spectral region, namely one Ag$^+$−^{12}CO band at 2192 cm^{-1} and its Ag$^+$−^{13}CO and Ag$^+$−^{13}C^{18}O satellites at 2143 and 2090 cm^{-1}, respectively. These bands are not affected by further evacuation at elevated temperatures up to about 200 K. Above this temperature, the bands begin to decrease in intensity but are not fully removed
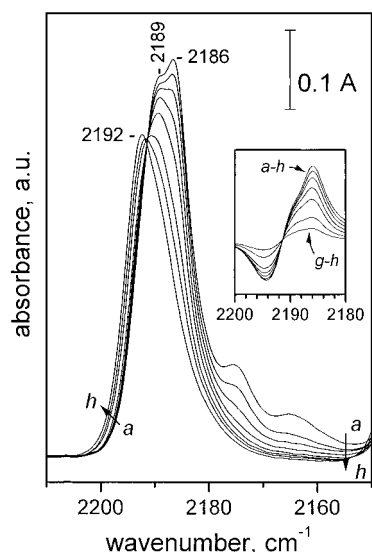
CO Adsorption on Ag$^+$/SiO$_2$ and Ag−ZSM-5

J. Phys. Chem. B, Vol. 102, No. 52, 1998 **10939**

Figure 4. FTIR spectra of ^{12}CO−^{13}CO isotopic mixtures adsorbed on Ag−ZSM-5 at 85 K. Equilibrium pressure of 8×10^{-2} Pa (a) and evolution of the spectra (b−h) under dynamic vacuum down to 2.5×10^{-3} Pa (h).

even at ambient temperature (Figure 6S of the Supporting Information).

4. Discussion

4.1. Nature of the Ag$^+$−CO Bond. Two types of Lewis acid sites may be distinguished by the preferred bonding nature to ligands, namely electrostatic and covalent.[18] Silver cations are considered to be covalent acids; that is, they form a covalent bond with the ligands.[18] Compared to other related cations (Cu$^+$ and Au$^+$), Ag$^+$ cations are weak Lewis acids.

In general, carbon monoxide can be bonded to covalent Lewis acid sites by both σ-donation and π-back-donation. Many data suggest that the π-back-donation in Ag$^+$−CO complexes is negligible and a σ-donor bond is predominantly formed.[12]

Our results confirm this general view. The frequency of CO adsorbed on Ag$^+$/SiO$_2$ (2170 cm^{-1}) is higher than the respective frequency measured for CO on Cu$^+$/SiO$_2$ (ca. 2130 cm^{-1}). At the same time, the adsorption is weaker in the former case since the carbonyl complexes are decomposed upon evacuation at ambient temperature. This means that the π-back-bonding in the Ag$^+$−CO complexes is much smaller than that in the case of Cu$^+$−CO. The same conclusions can be drawn when one compares the carbonyls formed on the ZSM-5 samples. The Ag$^+$−CO species are characterized by a lower stability and higher frequency (2192 cm^{-1}) as compared to Cu$^+$−CO species (2158 cm^{-1}). It should be noted that, although strongly reduced, there is π-back-donation in the Ag$^+$−CO bond. This is evident from the following considerations.

(a) When only a σ-bond is formed between CO and a metal cation, the respective complexes are easily decomposed during evacuation,[19] which is not the case with the Ag−ZSM-5 sample.

(b) A reliable criterion for the estimation of the strength of the σ- and π-bonds of coordinated CO is its extinction coefficient.[6,20] It is known that the extinction coefficient practically does not depend on the formation of a σ-bond but is strongly enhanced by π-back-bonding.[21] The extinction coefficient of CO attached to Ag$^+$ sites is, according to literature data,[21a] 12.8×10^{19} cm^2 mol^{-1} (measured for the band at 2170 cm^{-1} observed on Ag$_2$O/Al$_2$O$_3$). This value is 1 order of magnitude lower than the extinction coefficient of Cu$^+$−CO carbonyls (152.0×10^{19} cm^2 mol^{-1}, band at 2140 cm^{-1} on CuO/

Al$_2$O$_3$),[21a] which suggests a weak π-back-donation in the Ag−CO bond. At the same time, the extinction coefficient for Ag$^+$ carbonyls is higher than that measured for typical σ-bound CO species (for instance 1.4×10^{19} cm^2 mol^{-1} for the Ti^{4+}−CO band at 2190 cm^{-1} on TiO$_2$),[21a] which indicates, though weak, some π-back-bonding in the Ag$^+$−CO species.

4.2. Low-Temperature CO Adsorption on Ag−ZSM-5. It is evident from the spectra presented in Figure 2, that the Ag$^+$−CO species on Ag−ZSM-5 (2192 cm^{-1} band) are converted, at low temperature and in the presence of CO in the gas phase, into a second type of species (2186 cm^{-1} band). Moreover, this transformation is reversible. The 2186 cm^{-1} band developed at low temperature was about 2 times more intense than the band assigned to monocarbonyl species. Assuming the same extinction coefficient for both bands (on the basis of the close wavenumber), one can propose the following scheme, involving complexes containing two equal CO molecules:

$$(Z-Ag^+) - CO + CO \rightarrow (Z-Ag^+) - (CO)_2$$
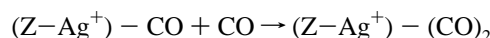
where Z represents the zeolite framework.

The formation of similar species is also supported by the fast isotopic exchange between ^{12}CO and ^{13}CO, even at low temperature.

There are two possibilities for the nature of the proposed species. The first one is that they are formed with the participation of isolated pairs of silver cations. However, this is unlikely for Ag−ZSM-5, where single isolated silver cations are expected. The other possibility is formation of Ag$^+$(CO)$_2$ dicarbonyls. This is in agreement with the existence of isolated Ag$^+$ cations in Ag−ZSM-5. A dicarbonyl structure is also supported by the following facts: (i) a comparison with the spectral performance of bulk silver dicarbonyls;[12] (ii) the higher Lewis acidity of Ag$^+$ in Ag−ZSM-5 than in Ag/SiO$_2$; (iii) an analogy with the Cu−ZSM-5, where dicarbonyls are formed even at ambient temperature.[6,7]

Usually, dicarbonyls develop two IR modes symmetric and antisymmetric C−O stretchings.[22] Both modes have to be shifted in two steps when the ^{12}CO molecules are gradually substituted by ^{13}CO. However, we detected no intermediate band. There are two possible explanations for this fact.

(1) The angle between both CO molecules in the Ag$^+$(CO)$_2$ complexes is near 90° or 180°. In this case only one new peak should be observed after partial or total exchange.[23] This hypothesis is in agreement with the reported angle of 180° for bulk silver dicarbonyls.[12] A similar structural arrangement seems to be possible for Ag−ZSM-5.

(2) The interaction between both CO molecules is not strong enough to produce ν_s and ν_{as} bands. This hypothesis is supported by the small shift of the Ag$^+$−CO band when dicarbonyls are formed. Indeed, the known cases where ν_s and ν_{as} modes of ionic multicarbonyls are detected always concern strongly bonded CO ligands, e.g., Ru^{n+} and Rh$^+$ di- and tricarbonyls.[24] In contrast, some authors[8,17,25] have proposed dicarbonyls on d^0 cations (weak adsorption) that are characterized only by one ν(CO) band.

Although the silver dicarbonyls are typical for low-temperature CO adsorption on Ag−ZSM-5, it seems that at high equilibrium CO pressures a small part of the Ag$^+$−CO species are converted into Ag$^+$(CO)$_2$ even at ambient temperature (see inset in Figure 2S of the Supporting Information).

The frequencies of the adsorbed molecules are summarized in Table 1. An interesting phenomenon that we have observed is the splitting of the ν(CO) bands of the dicarbonyls when ^{12}CO and ^{13}CO were coadsorbed. Usually, the dilution of ^{12}CO

TABLE 1: C−O Stretching Frequencies of the Carbonyls Formed on Ag−ZSM-5 at 85 K

compound	$\nu(^{12}CO)$, cm^{-1}	$\nu(^{13}CO)$, cm^{-1}
Ag$^+$−^{12}CO	2192	
Ag$^+$(^{12}CO)$_2$	2186	
Ag$^+$(^{12}CO)(^{13}CO)	2189	2140
Ag$^+$(^{13}CO)$_2$		2137
Ag$^+$−^{13}CO		2143

with ^{13}CO leads to hindering of the dynamic coupling[26] between the ^{12}CO dipoles. As a result, the $\nu(^{12}CO)$ stretching frequency, measured after adsorption of isotopic mixtures, is detected at lower frequencies. However, we have observed the reverse trend. It is evident that an effect just opposite to the dynamic coupling takes place. A possible explanation for this phenomenon is that the bond angle between the CO molecules in the dicarbonyls is near 180° and thus the dipoles are oriented in opposite directions. As a result, the interaction between them should lead to a decrease in their stretching frequency.

Another interesting phenomenon was that, during evacuation, the ^{12}CO band at 2186 cm^{-1} decreased faster than the band at 2189 cm^{-1}, whereas the respective ^{13}CO bands (at 2140 and 2137 cm^{-1}) diminished almost in parallel. This effect is evidently due to the different properties of the ^{12}CO and ^{13}CO molecules; during the evacuation it is ^{13}CO that is more difficult to desorb. However, if this is the only reason for the discussed phenomenon, one should expect a faster disappearance of the 2140 cm^{-1} band of ^{13}CO during evacuation, which was not observed in the experiments. Evidently, another effect also contributes to the phenomenon. We infer that the above-discussed "dynamic anticoupling" is a reason for a somewhat lower stability of the Ag$^+$(^{12}CO)$_2$ and Ag$^+$(^{13}CO)$_2$ complexes compared to mixed Ag$^+$(^{12}CO)(^{13}CO) species.

Finally, the results of the present study reveal a drastic effect of the support on the properties of deposited silver cations; Ag$^+$−CO species on the Ag$^+$/SiO$_2$ sample are formed in a CO atmosphere and are easily decomposed after evacuation even at low temperature. In contrast, the carbonyls on Ag−ZSM-5 are highly resistant toward evacuation even at ambient temperature. These results confirm the hypothesis about the high electron deficiency of various cations exchanged in ZSM-5 zeolites.

Supporting Information Available: Infrared spectra (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Lai, D.; Li, J.; Huang, P.; Wang, D. *J. Mater. Gas. Chem.* **1994**, *3*, 211.

(2) (a) Ono, Y.; Osako, K.; Kim, G.-J.; Inoue, Y. *Stud. Surf. Sci. Catal.* **1994**, *84*, 1773. (b) Inoue, Y.; Nakashiro, K.; Ono, Y. *Microporous Mater.* **1995**, *4*, 379.

(3) (a) Matsuoka, M.; Matsuda, E.; Tsuji, K.; Yamashita, H.; Anpo, M. *J. Mol. Catal., A.* **1996**, *107*, 399. (b) Matsuoka, M.; Matsuda, E.; Tsuji, K.; Yamashita, H.; Anpo, M. *Chem. Lett.* **1995**, 375.

(4) (a) Sato, S.; Yu-u, Y.; Yahiro, K.; Mizuno, N.; Iwamoto, M. *Appl. Catal.* **1991**, *70*, L1. (b) Miyadera, T. *Appl. Catal., B* **1998**, *16*, 155. (c) Jen, H. W. *Catal. Today* **1998**, *42*, 37. (d) Haneda, M.; Kintaichi, Y.; Inaba, M.; Hamada, H. *Catal. Today* **1998**, *42*, 127. (e) Kintaichi, Y.; Haneda, M.; Inaba, M.; Hamada, H. *Catal. Lett.* **1997**, *48*, 121.

(5) Zecchina, A.; Lamberti, C.; Bordiga, S. *Catal. Today* **1998**, *41*, 169.

(6) Hadjiivanov, K.; Kantcheva, M.; Klissurski, D. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4595.

(7) (a) Pieplu, T.; Poignant, F.; Vallet, A.; Saussey, J.; Lavalley, J.-C. *Stud. Surf. Sci. Catal.* **1995**, *96*, 619. (b) Lamberti, C.; Bordiga, S.; Salvalaggio, M.; Spoto, G.; Zecchina, A.; Geobaldo, F.; Vlaic, G.; Bellatreccia, M. *J. Phys. Chem.* **1997**, *101*, 344.

(8) Bordiga, S.; Escalona Platero, E.; Otero Arean, C.; Lamberti, C.; Zecchina, A. *J. Catal.* **1992**, *137*, 179.

(9) Pestryakov, A.; Davydov, A.; Kurina, A. *Russ. J. Phys. Chem.* **1988**, *62*, 1813.

(10) Huang, Y. Y. *J. Catal.* 1974, *32*, 482.

(11) (a) Baumann, J.; Beer, R.; Calzaferri, B.; Waldeck, B. *J. Phys. Chem.* **1989**, *93*, 2292. (b) Baba, T.; Akinaka, N.; Nomura, M.; Ono, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 339. (c) Beyer, H. K.; Jacobs, P. A.; Uytterhoeven, J. B. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 674. (d) Jacobs, P. A.; Uytterhoeven, J. B.; Beyer, H. K. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1755. (e) Hadjiivanov, K.; Vassileva, E.; Kantcheva, M.; Klissurski, D. *Mater. Chem. Phys.* **1991**, *28*, 367. (f) Keulks, G. W.; Ravi, A. *J. Phys. Chem.* **1970**, *74*, 783.

(12) (a) Hurlburt, P.; Rack, J.; Dec, S.; Anderson, O.; Strauss, S. *Inorg. Chem.* **1993**, *32*, 373. (b) Xu, Q.; Souma, Y. *Top. Catal.* **1998**, *6*, 17.

(13) Wang, X. D.; Greeneer, R. D. *Surf. Sci.* **1990**, *226*, L51.

(14) Hadjiivanov, K.; Abadjieva, N.; Mintchev, L.; Kantcheva, M.; Pesheva, Y.; Stefanov, P.; Vassileva, E.; Karadjova, I.; Klissurski, D. *Proceedings of the 8th International Symposium on Hetergeneous Catalysis*; 1996; Part 1, p 667.

(15) Zecchina, A.; Bordiga, S.; Lamberti, C.; Spoto, G.; Carnelli, L.; Otero-Arean, C. *J. Phys. Chem.* **1994**, *98*, 9577.

(16) Zaki, M.; Knözinger, H. *Mater. Chem. Phys.* **1987**, *17*, 281.

(17) Katoh, M.; Yamazaki, T.; Ozawa, S. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1246.

(18) Zhang, Y. *Inorg. Chem.* **1982**, *21*, 3886.

(19) Busca, G. *Catal. Today* **1998**, *41*, 191.

(20) Hadjiivanov, K. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1901.

(21) (a) Davydov, A. *IR Spectroscopy Applied to Surface Chemistry of Oxides*; Nauka: Novosibirsk, 1984. (b) Angel, C.; Schaffer, P. *J. Phys. Chem.* **1966**, *70*, 1413.

(22) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

(23) Saur, O.; Bensitel, M.; Mohammed Saad, A.; Lavalley, J. C.; Tripp, C.; Morrow, B. *J. Catal.* **1986**, *99*, 104.

(24) (a) Hadjiivanov, K.; Lavalley, J. C.; Lamotte, J.; Mauge, F.; Saint-Just, J.; Che, M. *J. Catal.* **1998**, *176*, 415. (b) Bazu, P.; Panayotov, D.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 2074.

(25) Paukshtis, E.; Soltanov, R.; Yurchenko, E. *React. Kinet. Catal. Lett.* **1983**, *22*, 147.

(26) Dynamic coupling between adsorbed CO molecules is observed when they have the same intrinsic frequency, the same orientation, and are parallel each other.