Two Coordination Modes of CO in Zeolites: A Temperature-Dependent Equilibrium

Carlos Otero Areán,* Alexey A. Tsyganenko,
Estrella Escalona Platero, Edoardo Garrone,
and Adriano Zecchina

Besides their wide application as solid acid catalysts in the petrochemical industry, zeolites are currently being investigated as catalysts for the manufacture of fine chemicals. New directions include the incorporation of redox metals and chiral centers either in the zeolite framework or as encaged extraframework species, which can lead to highly selective biomimetic solid catalysts.[1] Intrazeolite (catalytic) chemical processes are mediated, inter alia, by strong electrostatic fields acting inside the zeolite channels and by spatial restrictions imposed by the dimensions and topology of the intracrystalline void space. Electrostatic fields, created mainly by extraframework (exchangeable) cations, contribute to the formation of internal adducts with adsorbed molecules. The electron distributions of these molecules are thereby significantly modified, and this can lead ultimately to new reactivity patterns. Precise characterization of such intrazeolite species is a prime requirement to understanding chemical reactivity. Detailed knowledge of the interaction of CO with zeolites is also of considerable interest with regard to zeolite characterization, since CO is the most widely used probe molecule for IR spectroscopic investigations,[2] including determination of acidity and intrazeolite electrostatic fields. We report here on a variable-temperature (77 to 303 K) FT-IR study of CO adsorbed on Na-ZSM-5, which is a medium-pore zeolite having the MFI-type structure.[3] It is shown that CO can coordinate to Na^+ ions in two different modes: either through the C end or through the O end. Both adducts are in a temperature-dependent equilibrium which follows the van't Hoff relationship with a $\Delta H^{\ominus}$ value of 3.8 kJ mol^{-1}; the C-bonded adduct is the more stable species.

Interaction of CO at 77 K with extraframework alkali metal cations in zeolites is known to give rise to a main IR absorption band that is shifted to higher wavenumber with respect to the band for free CO (2143 cm^{-1}). In the case of M^+-ZSM-5 (M = Li, Na, K, Rb, Cs) this cation-specific high-frequency (HF) band appears at wavenumbers from 2188 cm^{-1} for Li^+ to 2157 cm^{-1} for Cs^+, and corresponds to the fundamental C–O stretching mode of CO perturbed by the electrostatic field created by cations in $M^+\cdots CO$ species.[2, 4] A minor low-frequency (LF) band is also observed at 2108, 2113, 2117, 2119, and 2122 cm^{-1} for Li^+, Na^+, K^+, Rb^+, and Cs^+, respectively.[4, 5] Several authors have pointed out that this LF band could be assigned to the C–O stretching mode of $M^+\cdots OC$ adducts.[6] It is clear that formation of such species would lead to a bathochromic shift of the C–O stretching frequency,[6, 7] but direct experimental proof of the correlation between HF and LF bands for adducts formed on the same cation was lacking so far. The question thus arises as to whether they reflect an isomerization equilibrium between C-bonded and O-bonded cation–CO adducts or whether they correspond to species formed on different sites. We show here that the first situation applies.

With an IR cell suitable for variable-temperature measurements, IR spectra of CO adsorbed on Na-ZSM-5 were taken between 77 K and room temperature; the IR cell was closed after dosing with CO. A selection of these spectra is depicted in Figure 1 a, b. All spectra show absorption bands at 2178 (strong) and 2112 cm^{-1} (weak), which correspond to the aforementioned HF and LF bands, respectively. The small shoulder on the low-frequency side of the HF band is due mainly to a weak interaction of CO with silanol groups (and other spurious effects); its contribution was excluded when the integrated intensity was computed. A weaker feature centered at 2130 cm^{-1} is also observed in Figure 1 a, which corresponds to the ^{13}CO counterpart of the main band at 2178 cm^{-1}.

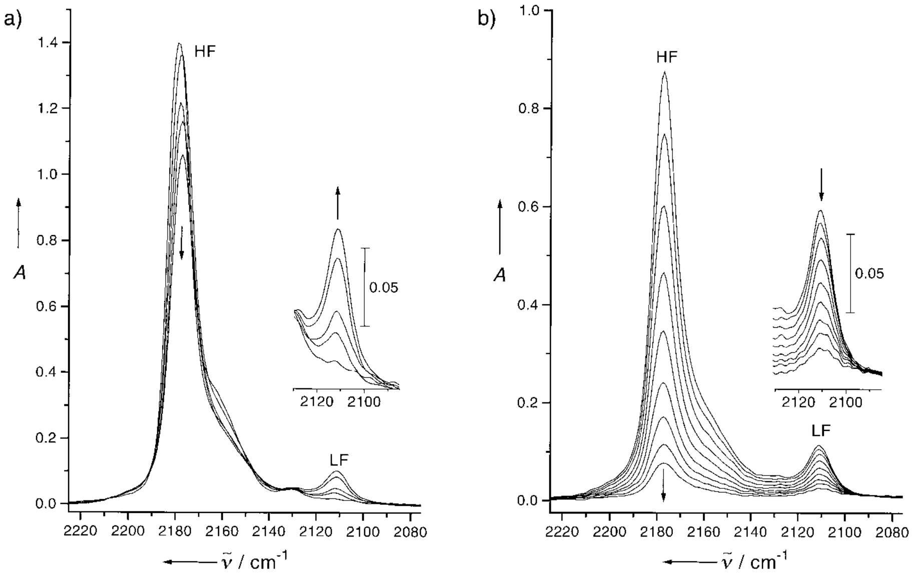

Figure 1. FTIR spectra of CO (ca. 0.8 Torr) adsorbed on Na-ZSM-5 at variable temperature. a) From top to bottom: 83, 133, 153, 183, and 203 K. b) From top to bottom: 223, 233, 243, 253, 263, 273, 283, 293, and 303 K. The inset shows an expanded view of the low-frequency bands.

Correlation between the HF and LF bands is clearly shown in Figure 1 a: When the temperature is increased from 83 to

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[*] Prof. C. Otero Areán, Dr. E. Escalona Platero
Departamento de Química
Universidad de las Islas Baleares
07071 Palma de Mallorca (Spain)
Fax: (+34) 971-173426
E-mail: dqueep0@ps.uib.es

Prof. A. A. Tsyganenko
Institute of Physics, St. Petersburg University (Russia)

Prof. E. Garrone, Prof. A. Zecchina
Dipartimento di Chimica Inorganica
Chimica Fisica e Chimica dei Materiali
Università di Torino (Italy)

203 K the intensity of the HF band decreases, whereas that of the LF band increases. At higher temperatures (Figure 1 b) both bands decrease in intensity (because the net amount of adsorbed CO decreases), but the ratio of integrated intensities A_{LF}/A_{HF} increases over the whole temperature range. This behavior can only be explained in terms of an equilibrium between C-bonded and O-bonded species, as described by Equation (1); Z represents the zeolite framework. The intensity ratio A_{LF}/A_{HF} should be proportional to the equilibrium constant K through the corresponding ratio of extinction coefficients $\varepsilon_{LF}/\varepsilon_{HF}$. When the van't Hoff Equation (2) is applied for constant values of $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$[8] over the whole temperature range (83–303 K), an almost perfect linear plot of $\ln(A_{LF}/A_{HF})$ versus $1/T$ is obtained (Figure 2).

$$\text{Z–Na}^{+}\cdots\text{CO} \rightleftharpoons \text{Z–Na}^{+}\cdots\text{OC} \qquad (1)$$

$$\ln K = -\Delta H^{\ominus}/RT + \Delta S^{\ominus}/R \qquad (2)$$

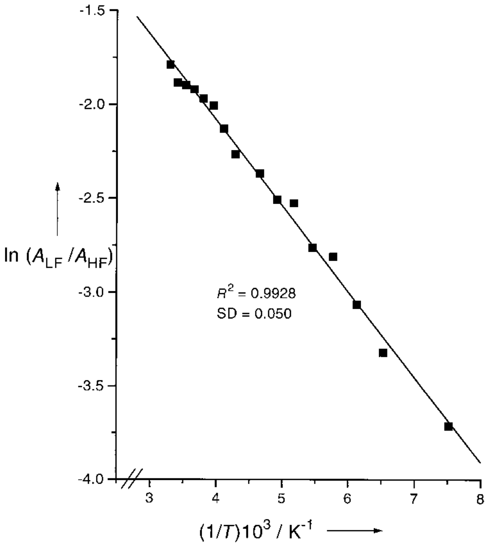

Figure 2. The van't Hoff plot of the natural logarithm of the intensity ratio of LF and HF bands versus the reciprocal of the temperature between 133 and 303 K.

From this linear plot, the resulting enthalpy change $\Delta H^{\ominus}$ for the process in Equation (1) is 3.8 kJ mol^{-1}. The enthalpy difference at 0 K between C-bonded and O-bonded species has been evaluated by means of quantum chemical calculations for adducts of CO containing both the bare Na^{+} cation and the $[HAl(OH)_3]^{-}Na^{+}$ cluster;[6c, e] the values are 10.9 and 5.6 kJ mol^{-1}, respectively (the C-bonded species always shows the higher interaction energy). The experimental value reported here (3.8 kJ mol^{-1}) is even lower than that for the model cluster, thus showing that the zeolite framework reduces the difference in stability between C-bonded and O-bonded adducts.

The hypsochromic frequency shift of adsorbed CO with respect to the value for the free molecule (2143 cm^{-1}) gives a measure of the effective electric field near the Na^{+} ion. If this shift is assigned to the vibrational Stark effect, a simple electrostatic model leads to $\Delta\tilde{\nu} = k_{ST}E$, where k_{ST} is the vibrational Stark constant for the CO molecule and E the electric field strength.[9] With $k_{ST} = 4.29 \times 10^{-9}$ cm^{-1}V^{-1}m,[10] the observed value $\Delta\tilde{\nu} = 35$ cm^{-1} (for the C-bonded adduct) yields $E = 8.2$ V nm^{-1}. More refined quantum chemical calculations lead to $E = 6.3$ V nm^{-1} for the same value of $\Delta\tilde{\nu}$.[6c, 11] In such a field, the estimated energy difference between the two orientations of the CO dipole (0.1098 D) is 2.8 to 3.6 kJ mol^{-1}, which is in fair agreement with the measured value of 3.8 kJ mol^{-1}.

Hydrogen-bonded OC···HF and CO···HF complexes similar to those described here have been obtained by UV photofragmentation of matrix-isolated formyl fluoride;[12] they showed C–O stretching bands at 2162 and 2129 cm^{-1}. The enthalpy difference at 20 K between these hydrogen-bonded isomers was estimated to be $\Delta H^{\ominus} = 0.3$ kJ mol^{-1}.[12] In a recent theoretical analysis, Lupinetti et al.[13] found a shortening of the C–O bond length (relative to that in free CO) in HCO^{+} and a lengthening in COH^{+}. They ascribed these effects to a change in the polarization of the CO bonding orbitals induced by the positive charge of the proton. These variations in C–O bond length give rise to changes in vibration frequency.

The intercept of the straight line in Figure 2 with the vertical axis (at $1/T = 0$) is at -0.26. Since the computational estimate for $\Delta S^{\ominus}$ (in units of R) is two orders of magnitude smaller,[6c, e] we assume that $\Delta S^{\ominus}$ for the process in Equation (1) is negligible and ascribe the above intercept to the different values of ε_{LF} and ε_{HF}; it follows that $\varepsilon_{LF}/\varepsilon_{HF} = 0.8$. This is at variance with computational estimates, which suggest that coordination through the oxygen atom intensifies the fundamental C–O stretching mode, while the opposite applies to coordination through the carbon atom.[5]

Similar experiments carried out on other zeolite/CO systems have shown that equilibrium between C-bonded and O-bonded species occurs in all cases. For instance, in the case of CO adsorbed on faujasite-type Na-Y the HF and LF bands were found at 2170 and 2122 cm^{-1}, respectively, while for Ca-Y the corresponding values are 2198 and 2094 cm^{-1}. The different wavenumber values for Na-ZSM-5 and Na-Y show the influence of the zeolite framework. The full set of results (which is currently being analyzed) will be published shortly. Note that equilibrium between C-bonded and O-bonded species may have notable consequences on (catalytic) processes occurring in zeolites and involving CO, and it might also apply to other adsorbed species which could have their electron distribution modified in different ways depending on their interaction mode with cationic centers. We hope this work will encourage the investigation of similar amphipathic behavior of other heteroatomic molecules adsorbed (or encaged) in zeolites.

Experimental Section

The Na-ZSM-5 zeolite (Si/Al = 17) was synthesized following standard hydrothermal methods.[14] Powder X-ray diffraction showed good crystallinity and absence of any diffraction lines not assignable to the MFI-type structure. For IR studies, a thin self-supported wafer was prepared and activated in a dynamic vacuum (residual pressure less than 10^{-4} Torr) for 2 h at 680 K inside an IR cell which allowed in situ high-temperature activation, gas dosage, and variable-temperature measurements to be carried out. Details on the design and performance of this home-made IR cell are given elsewhere.[15] For better thermal contact between the zeolite wafer and the cooled environment, helium (about 0.5 Torr) was admitted into the sample compartment before the background spectrum was recorded at 77 K (liquid nitrogen). Then CO was dosed to an equilibrium pressure of about 0.8 Torr, and IR spectra were measured at 77 K and on gradual heating of the IR cell after evaporation of liquid nitrogen. Reversibility of the IR spectra was checked by cooling again after the spectrum at 303 K was taken, thus proving that the observed spectral changes are due solely to temperature variation and not to any (unexpected) alteration of the system upon heating. The temperature was measured by means of a platinum resistance thermometer; the accuracy was about ±5 K. Transmission IR spectra were recorded at a resolution of 3 cm^{-1} with a Bruker IFS66 FTIR spectrometer. The spectrum of zeolite taken before dosage with CO was used as a background; this background spectrum was subtracted from all spectra shown in this work.

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Long-Range N → Si Interactions in Organosilicon Compounds with Hepta- and Octacoordinate Silicon Centers

Hans Bock,* Zdenek Havlas, and Volker Krenzel

Dedicated to Professor Corriu

Si centers in organosilicon compounds exhibit coordination numbers between 1 and 10,[1] and the resulting distances vary over wide ranges as exemplified by the interaction N → Si in 1-amino-8-silylnaphthalene derivatives[2, 3] (Figure 1). The Cambridge Structural Database contains a total of 574 entries for d_{Si-N} distances greater than 200 pm (Figure 1 a). The range of shorter interactions are assigned to so-called "SiN single bonds" such as in sitrol (Figure 1 b). The compounds with SiN distances between 220 and 260 pm (Figure 1 c and d)[3c,d] have repeatedly been defined as intramolecular donor–acceptor complexes. What type of interaction is, however, represented by the numerous distances Si ⋯ N exceeding 275 pm? Two selected structures with Si coordination numbers of 7[4] and 8[5]

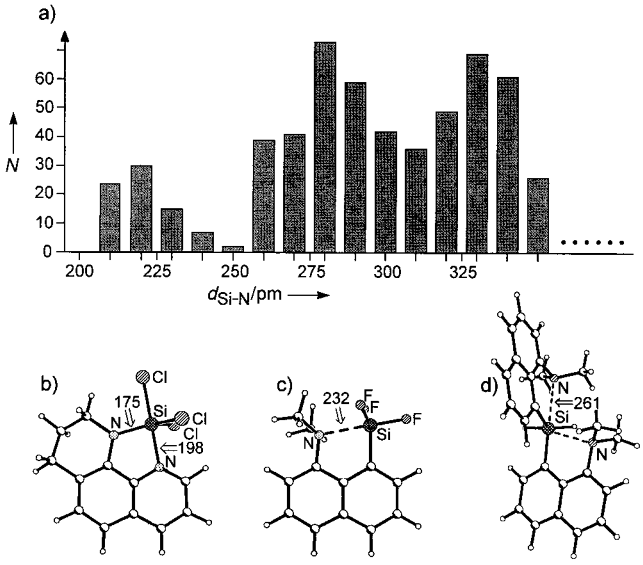

Figure 1. Differences in various Si–N bond lengths: a) histogram for the range between 200 and 350 pm, as revealed by a search in the Cambridge Structural Database, in which *N* is the number of hits within 10 pm ranges, and selected examples of Si–N interactions in 1-amino-8-silylnaphthalene derivatives (b, c), in which N ⋯ Si distances longer than 275 pm are also observed (d).

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[*] Prof. Dr. H. Bock, Dipl.-Chem. V. Krenzel
Institut für Anorganische Chemie der Universität
Marie-Curie-Straße 11, D-60439 Frankfurt am Main (Germany)
Fax: (+49) 69-798-29188

Dr. Z. Havlas,
Institute of Organic Chemistry and Biochemistry of the
Czech Academy of Sciences
Flemingovo nam 2, CZ-11610 Prague (Czech Republic)

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