Amphipathic hydrogen bonding of CO in protonic zeolites

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CO interacts with Brønsted acid sites of protonic zeolites to form both ZH···CO and ZH···OC hydrogen bonds (Z = zeolite framework); by means of variable-temperature FTIR spectroscopy, these hydrogen-bonded species were found to be in a temperature-dependent equilibrium which, for the faujasite-type H-Y zeolite, involves an enthalpy change of 4.3 kJ mol^{-1}.

Studies on hydrogen bonding are relevant to a number of biological and chemical fields, including theoretical chemistry,[1] molecular recognition,[2] crystal engineering[3] and catalysis. Regarding the field of heterogeneous catalysis, interaction of CO with acidic hydroxy groups (Brønsted acid sites) of metal oxides and zeolites is well known[4,5] to give rise to OH··CO adducts which can easily be observed by low-temperature IR spectroscopy. In fact, the corresponding shift of the O–H stretching frequency is often used to quantify zeolite Brønsted acidity.[6,7] There is some evidence[8] that CO can also form OH··OC hydrogen bonds when adsorbed on acid (protonic) zeolites, but detailed experimental studies on this interaction mode are not available.

The aim of this work was to analyse variable-temperature FTIR spectra of CO adsorbed on the faujasite-type zeolite H-Y, which show not only that both OH··CO and OH··OC hydrogen-bonded species are formed upon interaction of CO with the zeolite Brønsted acid sites, but also that these hydrogen-bonded adducts are in a temperature-dependent equilibrium; the C-bonded adduct showing the higher interaction energy. These findings extend recent work on cation-exchanged zeolites, where a similar behaviour of adsorbed CO was found.[9] They are also in consonance with the known ability of CO to form hydrogen bonded OC··HF and CO··HF adducts with hydrogen fluoride.[10]

The H-Y zeolite used was prepared following standard methods. For IR studies, a thin self-supported wafer was outgassed (activated) for 2 h at 700 K inside an infrared cell, described elsewhere,[11] which allowed *in situ* high-temperature activation, gas dosage, and variable-temperature spectroscopy to be carried out. After running the blank spectrum of the zeolite, *ca.* 0.3 Torr of helium (to secure good thermal equilibrium)† and 3 Torr of CO (at room temperature) were dosed. The cell was then closed and a series of spectra were taken at *ca.* 10 K intervals from 77 K to room temperature.

As shown in Fig. 1, the blank spectrum of H-Y displays characteristic bands at 3545 and 3648 cm^{-1} arising, respectively, from bridged Si(OH)Al hydroxy groups inside the sodalite cages and in the supercage.[4] A minor silanol band at 3748 cm^{-1} is also observed. After dosing with CO (at 77 K) the band at 3648 cm^{-1} is reduced, and there is a simultaneous growth of a new band at 3353 cm^{-1} which proves hydrogen bonding between CO and the acidic OH groups at the supercage. The band at 3545 cm^{-1} is not affected, which is consistent with the known fact that the sodalite cages are not accessible to CO.

Fig. 2 shows selected variable-temperature spectra in the C–O stretching region. The major band seen at 2173 cm^{-1} (HF band) corresponds to the fundamental C–O stretching mode of OH··CO adducts,[4] while the minor band at 2124 cm^{-1} (LF band), downward shifted with respect to the 2143 cm^{-1} value

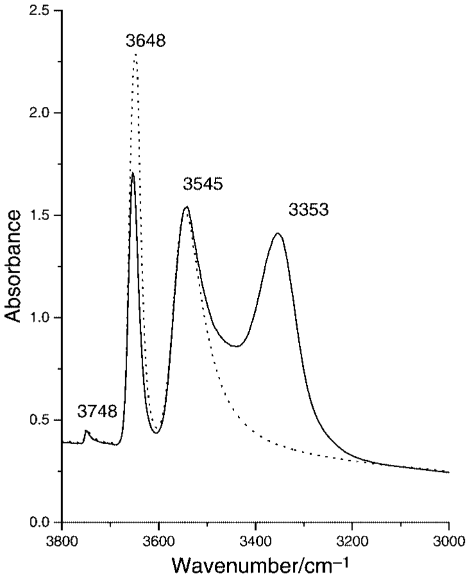

Fig. 1 IR spectra in the O–H stretching region of CO adsorbed, at 77 K, on H-Y. The dotted line is the zeolite blank spectrum while the continuous line is the spectrum obtained after dosing with CO.

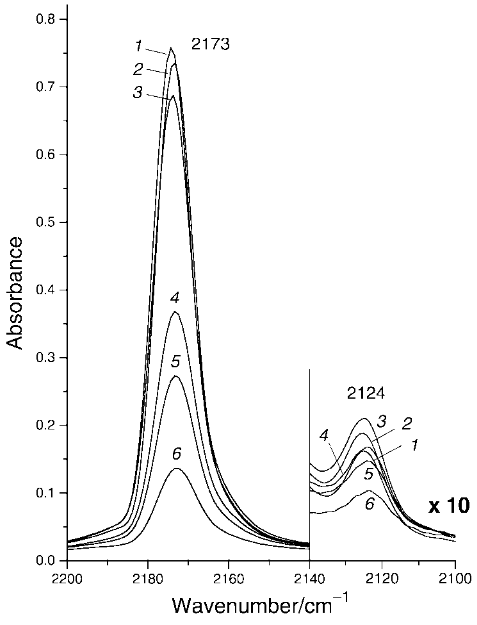

Fig. 2 Selected FTIR spectra of CO (*ca.* 3 Torr) adsorbed on H-Y at variable temperatures: 1, 119; 2, 138; 3, 153; 4, 173; 5, 179; 6, 191 K.

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for free CO, is due to OH··OC adducts[9,10,12] in which the CO molecule interacts with a positively charged centre through the oxygen atom. A distinctive feature of the spectra in Fig. 2 is the temperature dependence of the intensity of the HF and LF bands. When temperature is raised from 119 to 153 K, the intensity of the HF band (A_{HF}) decreases, whereas that of the LF band (A_{LF}) increases. At higher temperatures both bands decrease, since the net amount of adsorbed CO decreases, but the ratio of integrated intensities, A_{LF}/A_{HF}, was found to increase over the whole temperature range. It should be noted that the ^{13}CO counterpart of the HF band occurs in the same frequency region as the LF band. For this reason, integrated A_{LF} values were corrected by subtracting 1% of the corresponding A_{HF} values (1% is approximately the natural abundance of the ^{13}CO isotope). A variable contribution from C-bonded ^{13}CO explains the slight variations observed in the peak position of the LF band.

The temperature dependence of the intensity of the HF and LF bands can be explained in terms of a temperature-dependent equilibrium between C- and O-bonded species: [eqn. (1)] (Z = zeolite framework):‡

$$\mathrm{ZH\cdot\cdot CO} \rightleftarrows \mathrm{ZH\cdot\cdot OC} \qquad (1)$$

The equilibrium constant, K, for this process should be equal to the ratio of fractional coverages of O- and C-bonded species. If ε_{LF} and ε_{HF} are the corresponding molar absorption coefficients, the well known van't Hoff relationship [eqn. (2)] leads to eqn. (3):

$$\ln K = -(\Delta H°/RT) + (\Delta S°/R) \qquad (2)$$

$$\ln(A_{LF}/A_{HF}) = -(\Delta H°/RT) + (\Delta S°/R) + \ln(\varepsilon_{LF}/\varepsilon_{HF}) \qquad (3)$$

Fig. 3 shows that the above equation is obeyed for the whole temperature range studied, therefore proving that hydrogen-bonded OH··CO and OH··OC species are in a temperature-dependent equilibrium. The enthalpy change was found to be $\Delta H° = 4.3$ kJ mol^{-1}, as derived from the linear plot in Fig. 3.§ Knowledge of this enthalpy value is relevant to theoretical studies on weak hydrogen bonding. On the other hand, the amphipathic behaviour shown by carbon monoxide could also be manifested by other heteroatomic molecules adsorbed on zeolites, and this would have important consequences for zeolite mediated catalytic processes. This is a field deserving further studies.

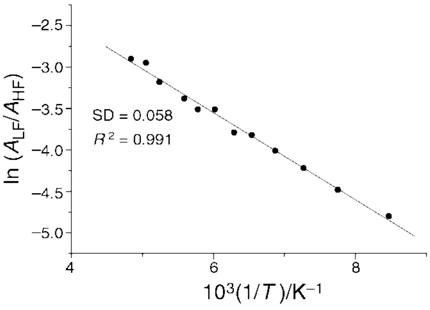

Fig. 3 van't Hoff plot of the natural logarithm of the intensity ratio of the LF and HF bands *vs.* reciprocal temperature.

Finally, it can be stated that preliminary results on the CO/H-ZSM-5 system have shown a similar equilibrium between hydrogen-bonded species as that found for CO/H-Y. It is also relevant to add, that for the CO/Na-Y system,[13] the corresponding enthalpy change for the isomerization equilibrium between C- and O-bonded adducts of CO with Na$^+$ ions was found to be $\Delta H° = 2.4$ kJ mol^{-1}. It is clear that the value of $\Delta H°$ depends upon the nature of the active centre interacting with adsorbed CO, and on the nature of such an interaction. However, more experimental work is needed before general trends can be established.

Notes and references

† Liquid nitrogen was used for refrigeration, and its gradual removal allowed variable-temperature spectra to be taken. The actual temperature was measured with a platinum resistance thermometer inserted close to the sample wafer.

‡ A similar equilibrium was recently documented[9] for CO adsorbed on Na-ZSM-5, but data for hydrogen-bonded species are reported here for the first time.

§ Correct application of the van't Hoff relationship for equilibrium data obtained over a large temperature range implies constant values of $\Delta H°$ and $\Delta S°$. Theoretical calculations[8,14] have shown that the difference in specific heat, $\Delta C_p°$, between C- and O-bonded adducts of CO with alkali-metal cations is negligible. It seems safe to assume that the same applies to hydrogen-bonded species.

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