Thermodynamics of Hydrogen Bonding between CO and the Supercage Brønsted Acid Sites of the H-Y Zeolite − Studies from Variable Temperature IR Spectrometry

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A procedure was developed for studying the thermodynamics involved in the interaction of carbon monoxide with Brønsted acid sites in zeolites, without the need for microcalorimetric measurements. The observables are the integrated infrared intensity of the C–O stretching mode of the OH···CO adducts, temperature, and equilibrium pressure. These quantities were measured by means of variable-temperature IR spectroscopy, using a home made IR cell equipped with a capacitance pressure gauge. Interaction of CO with Brønsted acid sites at the supercage of the faujasite-type H-Y zeolite involves a standard enthalpy change, $\Delta H°$ of -25.6 kJ mol^{-1}, and a standard entropy change, $\Delta S°$ of -161 J mol^{-1} K^{-1}. These values were compared with the corresponding figures obtained from the calorimetric determination of CO adsorption on a number of metal oxides and zeolites.

Introduction

Carbon monoxide is by far the most extensively used probe molecule for IR spectroscopic studies in surface chemistry, involving both metal oxides[1−5] and zeolites.[5−10] For a detailed characterisation of active solids, which is relevant to the general field of surface chemistry and (in particular) to the more specialised field of heterogeneous catalysis, it is desirable to have a detailed knowledge of the energy involved in the adsorbent-adsorbate interaction, and not only of the spectroscopic changes involving the probe molecule. Relatively strong interactions between CO and strongly adsorbing surface centres, such as coordinatively unsaturated transition metal ions, are readily studied by performing the spectroscopic measurements at room temperature. Interactions with weaker centres, such as alkali metal ions or protons, usually require IR measurements at a lower temperature, typically around the boiling point of nitrogen.[8−12] The same applies to calorimetric studies,[13] although measurements at room temperature are sometimes possible.[14]

Recent infrared spectroscopic[15−18] and quantum chemical[16,19] studies have shown that carbon monoxide can interact with extra-framework alkali[15−17] and alkaline earth[18] metal cations in zeolites forming both, C-bonded and O-bonded adducts; there is strong evidence[16,20] that suggests hydrogen-bonding between CO and Brønsted acid OH groups, however, protonic zeolites have been less studied in this context. The two linkage isomers are characterised by C−O stretching frequencies, which are both higher (C-bonded adduct) and lower (O-bonded adduct) than the 2143 cm^{-1} value corresponding to free CO. Variable temperature FTIR studies[15,17] on Na-ZSM-5 and Na-Y zeolites have shown that the population of the two isomers is a function of temperature, the O-bonded adducts are always a minority, but their relative population grows as the temperature increases.

The only observables needed for the above mentioned studies are the integrated areas of the IR absorption peaks corresponding to the C-bonded and O-bonded CO measured over a large temperature range, and the corresponding temperature values. However, if the equilibrium pressure could be measured simultaneously,[21] a more detailed thermodynamic study of the CO/zeolite system could, in principle, be carried out. The variable temperature IR cell used in our previous studies[15,17] has now been equipped with suitable pressure gauges, and here we report on the results obtained on the CO/H-Y system. It is shown that the whole set of experimental data, which includes temperature, pressure, and integrated IR intensity, allows a full thermodynamic description of the system to be obtained without resorting to microcalorimetric studies. To the best of our knowledge this experimental approach has never been reported before. It opens up a new strategy for the thermodynamic study of weakly interacting adsorbate-adsorbent systems, for which direct calorimetric studies are very cumbersome and very difficult to carry out due to the small energies involved.

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Results and Discussion

Data analysed in this paper correspond to two independent sets of measurements. In one of them (series I), 3 Torr of carbon monoxide was admitted into the IR cell which contained a self-supported H-Y zeolite wafer. The cell was then closed and IR spectra were obtained at different temperatures (starting from 77 K), simultaneously recording the equilibrium CO pressure inside the cell (see Experimental Section). After completing this series of measurements, the cell was outgassed and a second run (series II) was started after dosing with 13 Torr of CO.

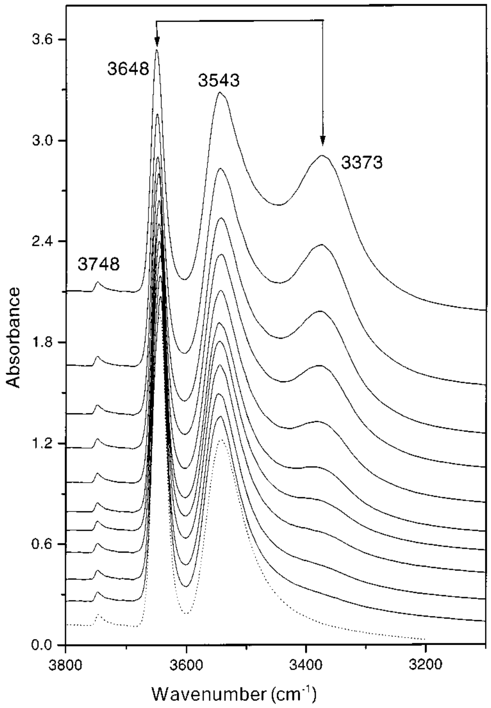

Figure 1. IR spectra, in the O−H stretching region, of CO adsorbed on H-Y. The dotted line is the zeolite blank spectrum at 77 K. Continuous line spectra correspond (from top to bottom) to I1 to I10 in Table 1. For clarity, the spectra have been offset on the vertical scale

Figure 1 reports the IR spectra (in the O−H stretching region) of the blank zeolite sample at 77 K, and at several different temperatures after admitting a dose of CO into the IR cell; corresponding values of temperature and equilibrium pressure are given in Table 1. Note that, although the total amount of CO inside the cell remains fixed, the fraction adsorbed diminishes when the temperature is raised, and this contributes to the increase in pressure. The zeolite blank spectrum shows a sharp band at 3648 cm^{-1}, which corresponds to bridged Si(OH)Al hydroxy groups (Brønsted acid sites) located in the supercage of the faujasite-type structure, and another band at 3543 cm^{-1} which is due to the Si(OH)Al species situated inside sodalite cages.[8] The weak band seen at 3748 cm^{-1} is readily assigned to silanols.[8,9]

Table 1. Numerical data corresponding to two independent runs

Spectra	Temp. (K)	Pressure (Torr)	Absorbance (cm^{-1})	Coverage
Small CO dose				
I1	145	0.14	9.04	0.430
I2	153	0.33	8.39	0.399
I3	159	0.63	7.31	0.348
I4	166	1.03	6.00	0.286
I5	173	1.48	4.54	0.216
I6	179	1.86	3.33	0.158
I7	185	2.20	2.31	0.110
I8	191	2.44	1.61	0.077
I9	197	2.62	1.09	0.052
I10	207	2.82	0.58	0.028
Large CO dose				
II1	155	5.38	18.63	0.887
II2	161	6.04	16.98	0.809
II3	167	6.77	15.00	0.714
II4	173	7.56	12.63	0.601
II5	178	8.36	10.21	0.486
II6	184	9.12	7.94	0.378
II7	190	9.79	5.96	0.284

The band due to the Brønsted acid sites in the supercages decreases upon interaction with the adsorbed CO molecule, and a new broad band (from the hydrogen-bonded OH···CO species[8,22]) develops at 3373 cm^{-1}. This is in accordance with the accessibility of the Brønsted acid sites to the adsorbed CO. In contrast, the band at 3543 cm^{-1} was not affected by the CO. This was expected due to the inaccessibility of the sodalite cages. The shift of the O−H stretching mode (from 3648 down to 3373 cm^{-1}) can be considered to be a measure of the acidity of the Si(OH)Al species available for interaction with the adsorbed (basic) CO molecule.[8,23−25] Although Brønsted acid sites are perhaps not completely homogeneous, the shift observed is quite the same for all coverage values, thus indicating that heterogeneity is in fact very limited. This has implications for the treatment of data given below, where all Si(OH)Al acid centres located in the zeolite supercages are considered to be equivalent and noninteracting, i.e. they constitute an ideal ensemble in the thermodynamic sense.

Figure 2 depicts the same spectra as in Figure 1 in the C−O stretching region. The spectra are dominated by a strong band at 2173 cm^{-1} which corresponds to the fundamental C−O stretching mode of hydrogen-bonded OH···CO adducts.[8,9] A weak band is also observed at 2124 cm^{-1}, which is mainly due to carbon monoxide interacting with the acidic Si(OH)Al species via the oxygen atom of the CO molecule;[15,16] it also contains the ^{13}CO counterpart (natural abundance about 1%) of the band at 2173 cm^{-1}. For the purposes of the present paper the weak band at 2124 cm^{-1} constitutes a minor feature, which shall not be considered any further.

With increasing temperature, the intensity of the 2173 cm^{-1} band decreases, the concomitant increase in pressure notwithstanding. Table 1 reports the integrated intensity

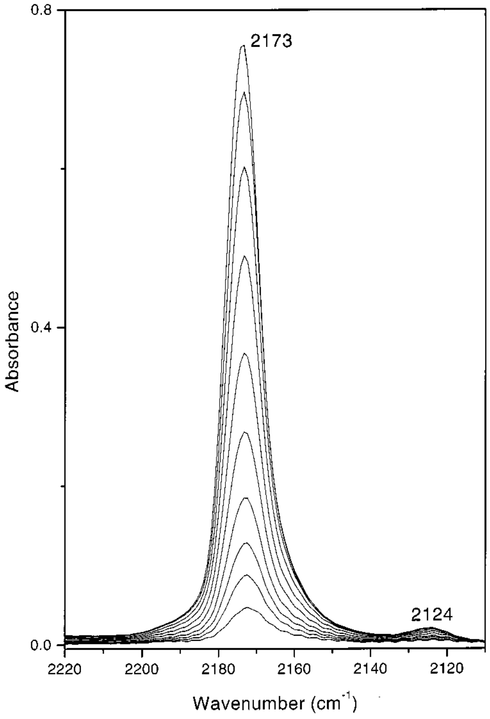

Figure 2. C−O stretching region of the same IR spectra as reported in Figure 1, increasing temperature from top to bottom. The zeolite blank was subtracted from all spectra shown

(A) of the peak at 2173 cm^{-1} (absorbance), and the temperature and pressure for all spectra considered for further treatment. They correspond to the two different CO doses (I and II) in separate experiments. The number of adsorbed molecules should be proportional to the integrated intensity of the 2173 cm^{-1} band, according to the Beer−Lambert law.

At temperatures lower than those reported in Table 1, small shifts (to higher frequency) in the peak position were observed. The corresponding spectra have been consequently discarded from the present treatment, as a small change in the molar absorption coefficient could have taken place and the intensities are not necessarily related to the coverage.

The observables, band intensity (A), temperature (T), and pressure (p), are interrelated by an equation of state. On the basis of the assumption of ideality made above, this equation of state is proposed to be according to Equation (1) which corresponds to the Langmuir isotherm at constant temperature.

$$A/A_M = \theta = K(T)p/[1 + K(T)p] \tag{1}$$

A_M is the highest integrated intensity, corresponding to full coverage, and θ is the fractional coverage. Note that pressure and temperature are not really independent, even for each individual set of measurements, but this is not important in the present context. The equilibrium constant, K, may be written as in Equation (2).

$$K(T) = \exp[\Delta S°(T)/R]\exp[-\Delta H°(T)/RT] \tag{2}$$

As is normally the case, the standard changes in both enthalpy and entropy may be assumed to be constant, in the first instance. This is equivalent to neglecting any role of the standard change in specific heat in the adsorption process. Under this assumption, the equation of state becomes as shown in Equation (3).

$$\theta = \exp(\Delta S°/R)\exp(-\Delta H°/RT)\cdot p/[1 + \exp(\Delta S°/R)\exp(-\Delta H°/RT)\cdot p] \tag{3}$$

It can be linearised as in Equation (4).

$$\ln\{p[(1/\theta) - 1]\} = -\Delta S°/R + \Delta H°/RT \tag{4}$$

For the highest coverage (temperatures close to 77 K in series II), the measured values of the integrated intensity were found to be in the range 20 to 23 cm^{-1}. Transforming the set of intensity data in Table 1 into a corresponding set of θ values, and assuming that $A_M = 21.0$ cm^{-1} for the present set of data (see below), the validity of Equation (4) can be examined as shown in Figure 3, where the left hand side of the equation is plotted against the inverse of the temperature. The two sets of experimental data are seen to line up in a very satisfactory manner, which allowed the determination of $\Delta S°$ and $\Delta H°$. The values obtained are $\Delta S° = -161$ J mol^{-1}K^{-1} and $\Delta H° = -25.6$ kJ mol^{-1}.

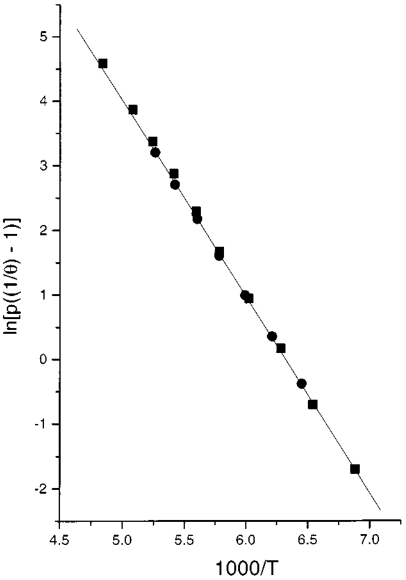

Figure 3. Check of the validity of an ideal model for adsorption; dose I: squares, dose II: circles

Note that the linear plot in Figure 3 was obtained by selecting a value of 21.0 cm^{-1} for the highest intensity, A_M. The selection of an A_M value differing from 21.0 cm^{-1} by as little as ±0.5 cm^{-1}, resulted in a loss of linearity of the plot in Figure 3. Therefore, the accuracy with which A_M can be determined is 0.5 cm^{-1}.

The feasibility of assuming constant $\Delta H°$ and $\Delta S°$ values over a rather wide temperature range (ca. 60 K, i.e. some 30% of the highest temperature used) has been verified as follows. If the opposite assumption is made, i.e. that the standard change in specific heat, $\Delta c_p°$, is not negligible, we can write [Equation (5)].

$$\Delta c_p° = -\gamma R \qquad (5)$$

where R is the gas constant and γ is a positive number. Note that $\Delta c_p°$ is expected to be negative for an adsorption process, since translational degrees of freedom are lost, and rotational degrees of freedom are substituted by intermolecular modes. From Equation (5) the following expressions can be derived [Equation (6) and Equation (7)].

$$\Delta S°(T) = \Delta S^* - \gamma R \ln(T/T^*) \qquad (6)$$

$$\Delta H°(T) = \Delta H^* - \gamma R (T - T^*) \qquad (7)$$

T^* is a reference temperature, e.g. the ambient one, and ΔH^* and ΔS^* are the standard changes in enthalpy and entropy at that temperature. Accordingly, Equation (4) should be written as Equation (8).

$$\ln \{p[(1/\theta) - 1)]\} - \gamma [\ln(T/T^*) - (1 - T^*/T)] = -\Delta S^*/R + \Delta H^*/RT \qquad (8)$$

The choice of different γ values in Equation (8), up to 3/2 (corresponding to complete loss of translational freedom), does not significantly alter the values calculated for the standard enthalpy and entropy changes. As a result the standard enthalpy and entropy changes are considered to be temperature independent.

The values obtained for $\Delta S°$ and $\Delta H°$ can be directly checked against independent experimental evidence. Concerning the standard enthalpy change, the present value of $\Delta H° = -25.6$ kJ mol^{-1} for the CO/H-Y system compares well with the calorimetrically determined heat of interaction of CO with the protonic form of ZSM-5, which was found to be[13] $\Delta H° = -27$ kJ mol^{-1}. It is well-known[26–28] that the H-Y zeolite is slightly less acidic than H-ZSM-5. Therefore, a slightly smaller value of $\Delta H°$ for the CO/H-Y system relative to that of the CO/H-ZSM-5 system was expected.

With respect to the standard change in entropy, the present value of $\Delta S° = -161$ J mol^{-1}K^{-1} can be compared with a set of calorimetrically determined values for the adsorption of CO performed under nearly ideal conditions on different metal oxides and on the zeolite Na-ZSM-5, reported in the literature[14,29,30]. This comparison is made in Figure 4, which shows a linear correlation between log $(-\Delta S°)$ and log $(-\Delta H°)$ for several CO/adsorbent systems. The discussion of such a linear correlation, usually called the *compensation effect*,[31,32] is outside the scope of this paper. However, it should be noted that the $\Delta S°$ value found for the CO/H-Y system satisfactorily fits into the correlation, thereby supporting the overall validity of the thermodynamic treatment developed here. Note that a general criticism can be raised against many correlation diagrams similar to that in Figure 4, because correlation can be an artefact when $\Delta S°$ and $\Delta H°$ values are simultaneously determined from the variation of an equilibrium constant experimentally measured within a narrow temperature range. However, data in Figure 4 are not biased in this sense, since $\Delta H°$ values taken from the cited literature were determined calorimetrically, and the $\Delta S°$ and $\Delta H°$ values corresponding to the CO/H-Y system were obtained from measurements covering a fairly large temperature range.

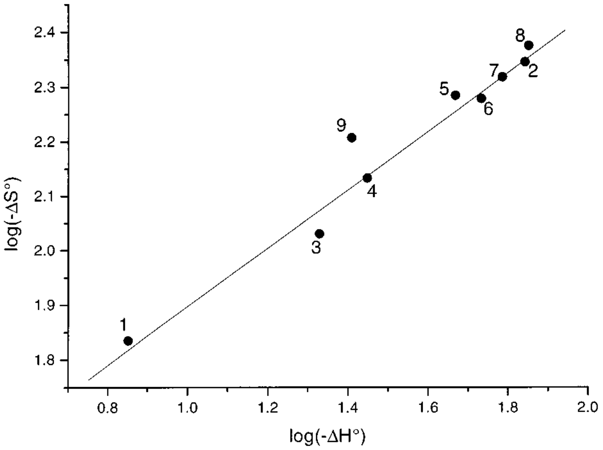

Figure 4. Correlation between $\Delta S°$ and $\Delta H°$ for CO adsorbed on: 1) alumina (weak Lewis site); 2) alumina (strong Lewis site); 3) silica-supported (reduced) chromia; 4) Na-ZSM-5; 5) zinc oxide; 6) titania (weak Lewis site); 7) titania (intermediate site); 8) titania (strong Lewis site); 9) H-Y. References: metal oxides [29, 30], Na-ZSM-5 [14], H-Y: present work

Conclusions

The integrated intensities observed for the 2173 cm^{-1} band, corresponding to the stretching mode of CO interacting via the carbon atom with Si(OH)Al hydroxy groups inside the supercage of the H-Y zeolite, satisfy a model for ideal adsorption. The derived value of $\Delta H° = -25.6$ kJ mol^{-1} is close to that of $\Delta H° = -27$ kJ mol^{-1} determined calorimetrically for the analogous CO/H-ZSM-5 system. Remarkably also, the value of $\Delta S° = -161$ J mol^{-1}K^{-1} obtained for CO/H-Y fits a correlation diagram applicable to a number of systems involving CO adsorbed on metal oxides and on the zeolite Na-ZSM-5. These facts provide strong evidence that the experimental strategy used in this work yields reliable equilibrium data for thermodynamic studies. Both the experimental and calculation procedures described here should have a general validity for other systems. Furthermore, they can advantageously be used in cases where the weakness of adsorbate-adsorbent interactions precludes the use of calorimetric methods.

Experimental Section

The H-Y zeolite used was synthesized following standard methods;[33] it had a nominal Si/Al ratio of 5.6. Powder X-ray diffraction showed good crystallinity and the absence of any diffraction lines not assignable to the corresponding structure type.

Figure 5 depicts a scheme of the home-made variable temperature IR cell used. It was equipped with a platinum resistance thermo-

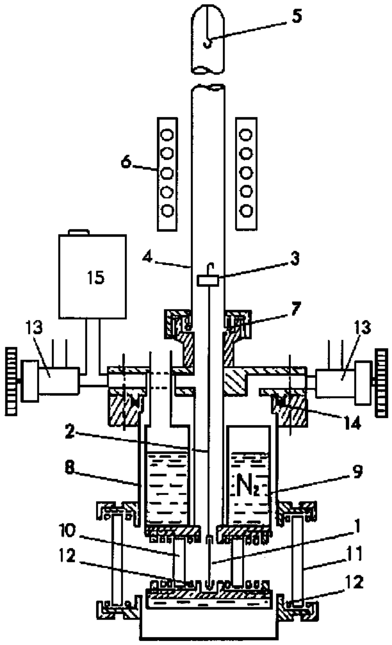

Figure 5. Scheme of the home-made (stainless-steel) variable-temperatur IR cell: 1) sample wafer, 2) sample holder, 3) magnetically driven anchoring piece, 4) quartz tube, 5) hook for fixing the sample wafer inside the furnace, 6) furnace, 7) Viton O-ring, 8) cell body, 9) refrigerated region, 10) BaF_2 windows, 11) NaCl windows, 12) indium gaskets, 13) valve, 14) Teflon gasket, 15) pressure gauge

meter and a capacitance pressure gauge (Edwards, 600). The accuracy of pressure measurements was ± 0.02 Torr. For IR measurements, a thin self-supported wafer of the zeolite was prepared and activated (outgassed) in a dynamic vacuum (residual pressure $<10^{-4}$ Torr) for 2 h at 680 K, inside the IR cell. For variable temperature infrared spectroscopy, liquid nitrogen was used for refrigeration. For better thermal contact between the zeolite wafer and the cooled environment, 0.5 Torr of helium was admitted into the sample compartment before recording the background spectrum at liquid-nitrogen temperature. CO was then dosed to an equilibrium pressure of 3 or 13 Torr (at room temperature), in two different sets of measurements. After dosing with CO, the cell was closed and IR spectra were recorded at 77 K and on gradual warming up of the IR cell following the removal of liquid nitrogen. Transmission IR spectra were recorded, at 2 cm^{-1} resolution, by means of a Bruker IFS66 FTIR spectrometer.

In order to allow for the pressure due to the helium inside the IR cell, a blank experiment was conducted in which a fixed amount of helium was dosed into the cell and the corresponding pressure was measured at different temperatures. These measurements gave a calibration plot from which the pressure correction was deduced.

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