Variable-temperature IR spectroscopic studies of CO adsorbed on Na-ZSM-5 and Na-Y zeolites

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CO interacts with extra-framework alkali metal cations (M^+) of zeolites to form both $M^+\cdots CO$ and $M^+\cdots OC$ species. By using variable-temperature FTIR spectroscopy, these C-bonded and O-bonded species were found to be in a temperature-dependent equilibrium. For the same cation, the difference in interaction energy depends upon the zeolite framework. Thus, for the equilibrium process $ZNa^+\cdots CO \rightleftharpoons ZNa^+\cdots OC$, where Z represents the zeolite framework, ΔH^0 was found to take the values 3.8 and 2.4 kJ mol^{-1} for CO/Na-ZSM-5 and CO/Na-Y, respectively. The C-bonded species show always the highest cation–CO interaction energy.

Keywords: carbon monoxide adsorption, heterogeneous catalysis, IR spectroscopy, zeolites

1. Introduction

Interaction of adsorbed molecules with extra-framework cations in cation-exchanged zeolites is a key factor controlling intrazeolite (catalytic) chemical processes [1–5]. Electrostatic fields created by these cations and surrounding framework anions contribute to polarization of adsorbed molecules, which thus find their electron distribution significantly modified. Precise characterization of the physicochemical processes occurring upon interaction of zeolites with guest molecules is a prime requirement to understand chemical reactivity. Complete understanding of the interaction between CO and zeolites is also of considerable interest in regard to zeolite characterization, since carbon monoxide is the most widely used probe molecule for IR spectroscopic studies of metal oxides [6] and zeolites [7–11].

Low-temperature IR spectra of CO adsorbed on alkali-metal-exchanged zeolites show a main absorption band upward shifted with respect to the 2143 cm^{-1} value for free CO. The magnitude of the shift depends on the alkali metal cation and on the number of surrounding framework anions. Thus, for the series of M^+-ZSM-5 zeolites (M = Li, Na, K, Rb, Cs) this cation-specific high-frequency (HF) band was observed at wavenumbers which decrease from 2188 cm^{-1} for Li^+, and 2178 cm^{-1} for Na^+, down to 2157 cm^{-1} for Cs^+ [12], while for Na^+-Y the corresponding band shows a maximum at about 2172 cm^{-1} [11,13]. Both, experimental results and theoretical calculations show that this HF band corresponds to the fundamental C–O stretching mode of carbon monoxide perturbed by the electrostatic field created by cations (and surrounding framework anions) in $M^+\cdots CO$ adducts [12,14–16].

Besides the HF band, a minor low-frequency (LF) band was also noted in the IR spectra of zeolites containing adsorbed CO [12,17–20]. This LF band, which appears below 2143 cm^{-1}, is also cation-specific; thus, for the above series of M^+-ZSM-5 zeolites it was observed at wavenumbers gradually increasing from 2108 cm^{-1} for Li^+ up to 2122 cm^{-1} for Cs^+ [12,21]. Several authors have pointed out that the LF band should correspond to the C–O stretching mode of $M^+\cdots OC$ adducts [15,18–21]. Indeed, formation of such species would lead to a bathochromic shift of the C–O stretching frequency [22,23], and the ability of CO to form hydrogen-bonded $OC\cdots HF$ and $CO\cdots HF$ complexes with hydrogen fluoride is well established both in the gas phase [24] and in matrix-isolated systems [25]. However, concerning CO adsorbed on zeolites, the question arises as to whether the HF and LF bands reflect an isomerization equilibrium between C-bonded and O-bonded adducts of CO with the same cation or whether they correspond to CO adsorbed on different sites.

The aim of this paper is to analyse temperature-dependent IR spectra of CO adsorbed on Na-ZSM-5 and Na-Y zeolites, so as to study the correlation which might exist between the corresponding HF and LF bands and to infer the right answer to the above question. A brief account of the results on the CO/Na-ZSM-5 system was recently published [26]. However, they are included here in order to facilitate comparison with the CO/Na-Y system and to draw more general conclusions.

2. Materials and methods

Zeolites Na-ZSM-5 and Na-Y were synthesized following standard methods [27]; they had nominal Si/Al ratios of 17 and 2.5, respectively. Powder X-ray diffraction showed

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good crystallinity in both cases, and absence of any diffraction lines not assignable to the corresponding structure types. For IR studies, thin self-supported wafers were prepared and activated in a dynamic vacuum (residual pressure $<10^{-4}$ 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 [28]. Liquid nitrogen was used for refrigeration and temperature was measured by means of a platinum resistance thermometer; accuracy of sample temperature measurements was likely to be about ±5 K. For better thermal contact between the zeolite wafer and the cooled environment, about 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 about 0.8 Torr, the cell was closed and IR spectra were registered at 77 K and on gradual warming up of the IR cell following gradual removal of liquid nitrogen. For both systems, CO/Na-ZSM-5 and CO/Na-Y, series of spectra were taken at about 10 K intervals in the temperature range going from 77 to 303 K.

Transmission IR spectra were recorded, at 3 cm^{-1} resolution, by means of a Bruker IFS66 FTIR spectrometer. The zeolite blank spectrum, taken at 77 K before dosage with CO gas, was used as a background; all the spectra shown in this work are background subtracted.

3. Results

Figure 1 shows some selected spectra for CO adsorbed on Na-ZSM-5. The HF band, corresponding to $\text{Na}^+\cdots\text{CO}$ adducts, is observed at 2178 cm^{-1}. The LF band, assigned to $\text{Na}^+\cdots\text{OC}$ species, appears at 2112 cm^{-1}. At 77 K the intensity of this band is extremely low. However, on raising the temperature, when the HF band starts to decrease the LF band first increases (spectra (1)–(3) in figure 1) and then, at higher temperatures, both bands decrease rapidly (spectra (4)–(6)) because the net amount of adsorbed CO decreases. However, the ratio of integrated intensities $A_{\text{LF}}/A_{\text{HF}}$ was found to increase over the whole temperature range, from 77 to 303 K.

A weaker band centred at 2130 cm^{-1} is also observed in spectra (1)–(3) of figure 1. Unlike the above LF band, its intensity gradually decreases, showing the same temperature dependence as the HF band. This weaker band displays a bathochromic shift of 48 cm^{-1}, referred to the HF band, which is exactly the value of the isotopic shift expected from the reduced mass increase on substituting ^{12}C by ^{13}C; thus, the 2130 cm^{-1} band clearly corresponds to the ^{13}CO counterpart of the main band at 2178 cm^{-1}.

The silanol band, at 3744 cm^{-1} (not shown in the spectra) was found to be only very slightly eroded by adsorbed CO, and the same applies to the Na-Y zeolite. For both zeolites, the IR spectra did not show any trace of residual water, thus proving that dehydration was complete during thermal activation at 680 K.

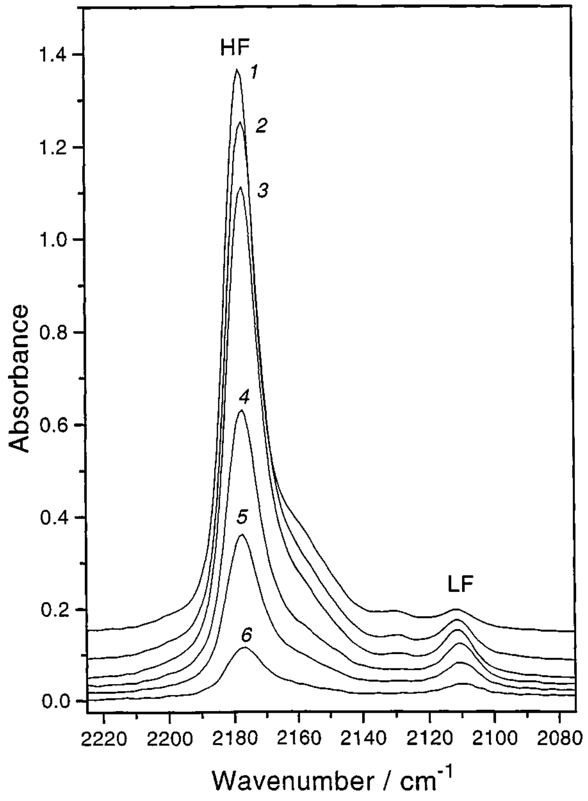

Figure 1. FTIR spectra of CO (ca. 0.8 Torr) adsorbed on Na-ZSM-5 at variable temperature as follows: (1) 123, (2) 143, (3) 163, (4) 243, (5) 263 and (6) 293 K.

Selected spectra of CO adsorbed on Na-Y are shown in figure 2. The LF band, which exhibits the same temperature dependence as in the case of Na-ZSM-5, appears at 2122 cm^{-1}, while the HF band has its maximum at 2171 cm^{-1} and distinct shoulders at 2156 and 2183 cm^{-1}. The complex nature of this band suggests that Na^+ ions (accessible to adsorbed CO) occupy different positions in regard to the zeolite framework. Some of the spectra in figure 2 show that the LF band also has a complex nature. This should be expected, because each component of the HF band should have its own LF counterpart. Moreover, three corresponding ^{13}CO counterparts of the HF band have to occur in this frequency region, the most intense of which should overlap with the LF band because the separation between HF and LF peaks practically coincides with the ^{13}C isotopic shift. For this reason, measured values of A_{LF} were corrected by subtracting 1% of the corresponding A_{HF} values (1% is approximately the natural abundance of the ^{13}CO isotope).

Figure 3 shows the van't Hoff plot of $\ln(A_{\text{LF}}/A_{\text{HF}})$ versus $1/T$ for both systems studied: CO/Na-ZSM-5 and CO/Na-Y. This plot covers a wide temperature range which goes from 133 up to 303 K. Spectra taken at temperatures lower than 133 K were excluded, because the corresponding values of A_{LF} were very low and did not allow precise measurements to be taken. From the slope of the straight lines in figure 3, corresponding values of ΔH^0 were derived. These were found to be $\Delta H^0 = 3.8\ \text{kJ}\,\text{mol}^{-1}$ for

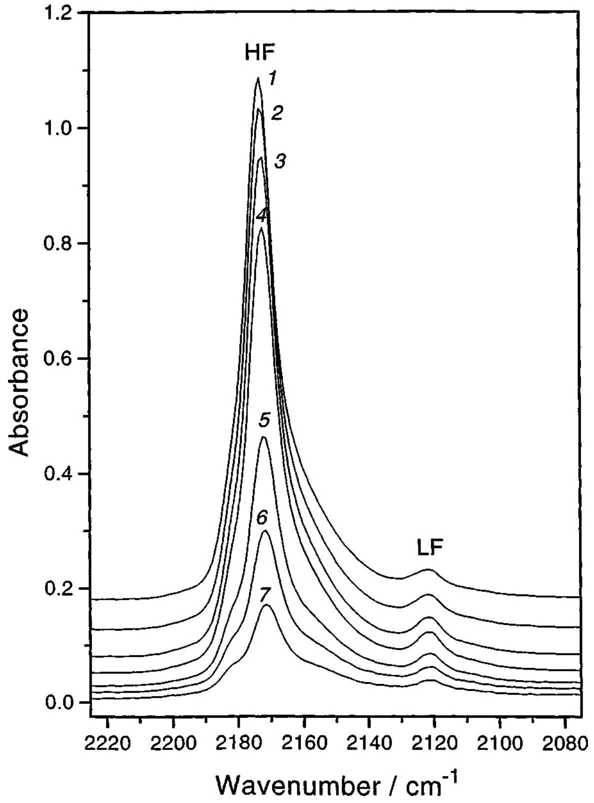

Figure 2. FTIR spectra of CO (ca. 0.8 Torr) adsorbed on Na-Y at variable temperature as follows: (1) 167, (2) 177, (3) 187, (4) 197, (5) 215, (6) 225 and (7) 233 K.

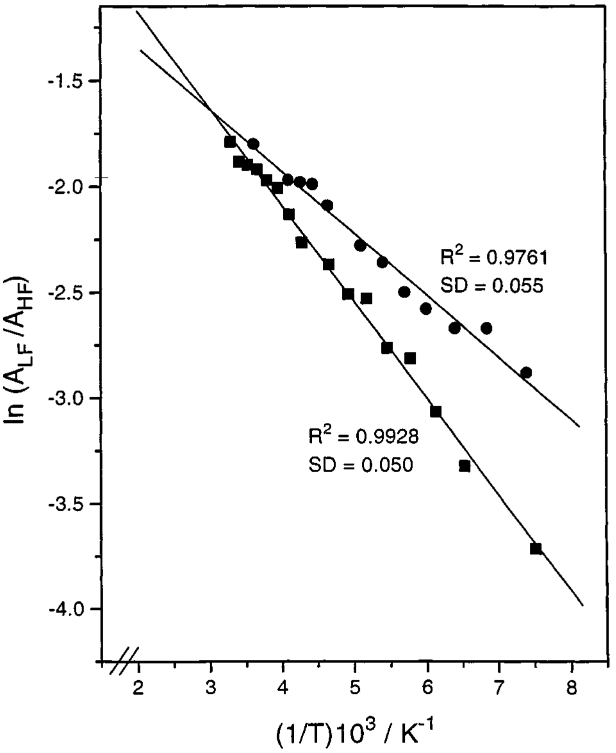

Figure 3. The van't Hoff plots of the natural logarithm of the intensity ratio of LF and HF bands versus the reciprocal of the temperature. Circles correspond to the CO/Na-Y system, and squares to CO/Na-ZSM-5.

the CO/Na-ZSM-5 system, and $\Delta H^0 = 2.4\ \mathrm{kJ\,mol^{-1}}$ for CO/Na-Y. The straight lines intercept the vertical axis (at $1/T = 0$) at -0.26 for CO/Na-ZSM-5 and at -0.75 for CO/Na-Y.

4. Discussion

The presence of a main peak (at 2171 $\mathrm{cm^{-1}}$) and two distinct shoulders (at 2156 and 2183 $\mathrm{cm^{-1}}$) in the HF band of CO adsorbed on Na-Y (figure 2) is in agreement with known structural data concerning faujasite-type zeolites. It is known from X-ray and neutron diffraction [29–31] and from ^{23}Na NMR [32] that in dehydrated Na-Y sodium cations occupy only sites SI, SI′ and SII. Sites SI and SI′ lie inside the hexagonal prism and the sodalite cage, respectively, where they are inaccessible to CO. The only accessible site is SII which is located in the supercage, facing the 6-ring window of the sodalite cage. In agreement with Knözinger and Huber [11], who also noted the complex nature of the HF band, the observed multiplicity can be explained in terms of an ordering of silicon and aluminium in the zeolite framework, i.e., the 6-ring windows may contain varying numbers of aluminium atoms, as suggested also by ^{29}Si MAS-NMR [33]. Since the negative charge density (due to framework oxygens) increases with increasing number of aluminium atoms in the 6-ring, the net (positive) electric field at $\mathrm{Na^+}$ sites could take different values thus explaining the observed multiplicity of the HF band. Note also that the high concentration of $\mathrm{Na^+}$ ions present in the supercages of faujasite-type zeolites could result in perturbation of adsorbed CO by more than one positively charged centre, which would also contribute to a complex nature of the corresponding IR absorption band. The same arguments apply also to the LF band, which, in addition, is expected to have components due to ^{13}CO counterparts of the HF band, as already stated. It should be noted that even in Na-ZSM-5 the $\mathrm{Na^+}$ sites are not completely homogeneously dispersed [34,35]. Differences are smaller than in Na-Y, but they are reflected in the broadening of the HF band and in the shoulder at about 2156 $\mathrm{cm^{-1}}$ (figure 1). At the lower temperatures this shoulder could also have a small contribution from CO interacting with silanols.

For both systems studied CO/Na-ZSM-5 and CO/Na-Y, the observed linear dependence (figure 3) of the natural logarithm of the intensity ratio, $A_{\mathrm{LF}}/A_{\mathrm{HF}}$, versus $1/T$ is precisely the behaviour to be expected for an equilibrium process between C-bonded and O-bonded species, as described by equation (1), where Z stands for the zeolite framework:

$$\mathrm{ZNa^+\cdots CO} \overset{K}{\rightleftharpoons} \mathrm{ZNa^+\cdots OC} \tag{1}$$

The equilibrium constant, K, of equation (1) should be equal to the ratio $\theta_{\mathrm{OC}}/\theta_{\mathrm{CO}}$, where θ_{OC} and θ_{CO} are the fractional coverages of O-bonded and C-bonded adducts, respectively. Consequently, if $\varepsilon_{\mathrm{HF}}/\varepsilon_{\mathrm{LF}}$ is the ratio of molar absorption coefficients of the corresponding IR bands, we have

$$K = (A_{\mathrm{LF}}/A_{\mathrm{HF}})(\varepsilon_{\mathrm{HF}}/\varepsilon_{\mathrm{LF}}). \qquad (2)$$

The temperature dependence of K is given by the van't Hoff and Kirchhoff relationships, equations (3) and (4), respectively:

$$\mathrm{d}\ln K/\mathrm{d}T = \Delta H^0(T)/RT^2, \qquad (3)$$

$$\mathrm{d}\Delta H^0/\mathrm{d}T = \Delta C_p^0(T). \qquad (4)$$

Note also that

$$\mathrm{d}\Delta S^0/\mathrm{d}T = \Delta C_p^0(T)/T. \qquad (5)$$

For a small temperature range, ΔH^0 is usually assumed to be constant, which corresponds to a negligible value of ΔC_p^0. Therefore, ΔS^0 may also be considered as a constant. Under these assumptions, the integrated form of the van't Hoff relationship becomes

$$\ln K = -\Delta H^0/RT + \Delta S^0/R. \qquad (6)$$

In our work, a large temperature range (from 133 up to 303 K) was covered, and indiscriminate use of equation (6) would not be justified. However, computational results on model systems [15,21] have shown that ΔC_p^0 for the equilibrium process described in equation (1) is negligible. Therefore, equation (6) can be used with full confidence.

By combining equations (2) and (6) we have

$$\ln(A_{\mathrm{LF}}/A_{\mathrm{HF}}) = -\Delta H^0/RT + \Delta S^0/R + \ln(\varepsilon_{\mathrm{LF}}/\varepsilon_{\mathrm{HF}}). \qquad (7)$$

The observed linear plots of $\ln(A_{\mathrm{LF}}/A_{\mathrm{HF}})$ versus $1/T$ (figure 3) prove that $\mathrm{Na}^+\cdots\mathrm{CO}$ and $\mathrm{Na}^+\cdots\mathrm{OC}$ species are in a temperature-dependent equilibrium. The enthalpy difference corresponding to the isomerization process described by equation (1) takes the value $\Delta H^0 = 3.8\ \mathrm{kJ\,mol^{-1}}$ for the CO/Na-ZSM-5 system and $\Delta H^0 = 2.4\ \mathrm{kJ\,mol^{-1}}$ for CO/Na-Y, as derived from the slope of the corresponding van't Hoff plots in figure 3. Note, however, that for CO/Na-Y the value of ΔH^0 corresponds to an average over the different SII cation sites. Heterogeneity of these sites is probably the main cause why the experimental points in the corresponding van't Hoff plot are more scattered than in the case of CO/Na-ZSM-5; note the higher value of the standard deviation (SD = 0.055) on the least-squares linear regression (figure 3) for the CO/Na-Y system.

The enthalpy difference, at absolute zero, between C-bonded and O-bonded species has also been evaluated by means of quantum chemical calculations on the interaction of CO with both the bare Na^+ cation and the model cluster $[\mathrm{HAl(OH)_3}]^-\mathrm{Na}^+$, which was used to mimic cation sites in zeolites. The reported results are $\Delta H^0 = 10.9\ \mathrm{kJ\,mol^{-1}}$ for the bare cation [15] and $\Delta H^0 = 5.6\ \mathrm{kJ\,mol^{-1}}$ for the cluster [16]. In both cases C-bonded CO showed the higher interaction energy, in agreement with the experimental results. However, the experimentally determined values of ΔH^0 (3.8 and 2.4 $\mathrm{kJ\,mol^{-1}}$) are even lower than that corresponding to the model cluster, thus showing that the contribution of the zeolite framework leads to a smaller difference in stability between C-bonded and O-bonded adducts.

Comparing the results obtained for the CO/Na-Y system with those corresponding to CO/Na-ZSM-5, the influence of the zeolite framework is clearly seen. It has the effect of lowering ΔH^0 (for the equilibrium process in equation (1)) from 3.8 $\mathrm{kJ\,mol^{-1}}$ in Na-ZSM-5 to 2.4 $\mathrm{kJ\,mol^{-1}}$ in Na-Y. This effect may be associated to a higher coordination of Na^+ cations in Na-Y, as compared to Na-ZSM-5. This higher coordination number results in a lower value of the net (positive) electric field surrounding the extra-framework cations in Na-Y, as reflected in the lower wavenumber at which the HF band appears: 2171 $\mathrm{cm^{-1}}$ (for the main peak) in CO/Na-Y as compared to 2178 $\mathrm{cm^{-1}}$ for CO/Na-ZSM-5. It is known from X-ray and neutron diffraction studies [30,31] that at site SII of Na-Y the Na^+ ion has six nearest framework oxygens. No precise studies appear to be available for Na-ZSM-5. However, for Ag(I)-ZSM-5 and Cu(I)-ZSM-5 recent EXAFS results suggest an average coordination number of about 2.5 for both extra-framework cations [36].

Referring to the HF band in both the CO/Na-ZSM-5 and the CO/Na-Y systems, the hypsochromic frequency shift of adsorbed CO with respect to the free molecule value (2143 $\mathrm{cm^{-1}}$) gives a measure of the (positive) electric field in the neighbourhood of extra-framework Na^+ ions [9,14,22]. For a weak interaction, a simple electrostatic model can be used [37,38] where the frequency shift can be considered to arise from the vibrational Stark effect. The electric field strength, E, can thus be obtained from the expression

$$\Delta\nu = k_{\mathrm{ST}}E, \qquad (8)$$

where k_{ST} is the vibrational Stark constant for CO, which according to Lambert [39] takes the value $k_{\mathrm{ST}} = 4.29 \times 10^{-9}\ \mathrm{m\,cm^{-1}\,V^{-1}}$. For the CO/Na-ZSM-5 system, where $\Delta\nu = 35\ \mathrm{cm^{-1}}$, equation (8) leads to $E = 8.2\ \mathrm{V\,nm^{-1}}$. In such a field, the energy difference between the two orientations of the CO dipole (0.1098 D) amounts to 3.6 $\mathrm{kJ\,mol^{-1}}$ [38], which is in very good agreement with the measured value of 3.8 $\mathrm{kJ\,mol^{-1}}$. Corresponding values for the most intense peak of the HF band in the CO/Na-Y system are $\Delta\nu = 28\ \mathrm{cm^{-1}}$ and $E = 6.5\ \mathrm{V\,nm^{-1}}$. This electric field leads to a value of 2.6 $\mathrm{kJ\,mol^{-1}}$ for the energy difference between the two orientations of the CO dipole, which should be compared with the experimental value of 2.4 $\mathrm{kJ\,mol^{-1}}$; a good agreement is also found in this case.

Although no detailed studies on variable-temperature IR spectra seem to be available for other CO/zeolite systems, cation specific HF and LF bands (of adsorbed CO) similar to those described in the present work were previously reported for a number of cases [12,17,19,21,26]. A summary is given in table 1. Within the scope of the foregoing electrostatic model, interaction of carbon monoxide with cations

Table 1
Wavenumber values (cm^{-1}) for HF and LF bands of CO adsorbed on different zeolites, and corresponding shifts ($\Delta\nu$) from the value of 2143 cm^{-1} for free CO.

System	ν(HF)	ν(LF)	$\Delta\nu$(HF)	$\Delta\nu$(LF)	Ref.
CO/Li-ZSM-5	2188	2108	+45	−35	[12,21]
CO/Na-ZSM-5	2178	2112	+35	−31	[present work]
CO/K-ZSM-5	2166	2117	+23	−26	[12,21]
CO/Rb-ZSM-5	2162	2119	+19	−24	[12,21]
CO/Cs-ZSM-5	2157	2122	+14	−21	[12,21]
CO/H-ZSM-5	2172	2115	+29	−28	[21]
CO/Na-Y	2171	2122	+28	−21	[present work]
CO/Ca-Y	2198	2094	+55	−49	[26]

via the carbon or the oxygen atom corresponds to opposite orientations of the CO dipole in the same electric field. Therefore, the same absolute values (although with a different sign) should in principle be obtained for $\Delta\nu$(HF) and $\Delta\nu$(LF) for each CO/zeolite system. Table 1 shows that this is not strictly the case. However, deviations are small, particularly when experimental errors are taken into account, and one could hardly expect better precision from such an oversimplified electrostatic model. Note that the carbon and oxygen atoms do not both have the same van der Waals radius, and thus the distance from the centre of the CO molecule to the cation centre in Na$^+\cdots$CO adducts could be different from that corresponding to the Na$^+\cdots$OC species. On the other hand, it is debatable whether the reference value for calculating frequency shifts should be 2143 cm^{-1}, corresponding to free CO, or 2138 cm^{-1} which corresponds to carbon monoxide physisorbed on zeolites [34,40].

The straight lines in figure 3 intercept the vertical axis (at $1/T = 0$) at -0.26 for CO/Na-ZSM-5 and at -0.75 for CO/Na-Y. Since the computational estimate for ΔS^0 (in units of R) is two orders of magnitude smaller [15,16], it can be assumed that ΔS^0 for the temperature-dependent equilibrium described in equation (1) is negligible, and the above intercepts should be ascribed to different values of the extinction coefficients $\varepsilon_{\mathrm{LF}}$ and $\varepsilon_{\mathrm{HF}}$ of the LF and HF bands, respectively. It follows that, for the CO/Na-ZSM-5 system, $\varepsilon_{\mathrm{LF}}/\varepsilon_{\mathrm{HF}} = 0.8$, while for CO/Na-Y the corresponding ratio is $\varepsilon_{\mathrm{LF}}/\varepsilon_{\mathrm{HF}} = 0.5$. These results are somewhat surprising, since the electrostatic model predicts that no large differences in extinction coefficient should be found by reversing the orientation of the CO molecule in the cationic electric field. Moreover, more refined computational estimates [15,21] suggest that coordination of CO to a cationic centre through the oxygen atom should intensify the C–O stretching vibration, while the opposite applies to coordination through the carbon atom. While the reason for this discrepancy has yet to be elucidated, we remark that (according to the experimental results described here) the $\varepsilon_{\mathrm{LF}}/\varepsilon_{\mathrm{HF}}$ ratio seems to be critically dependent on the nature of the adsorbent: Na-ZSM-5 or Na-Y. This is in line with recent measurements [41] which suggest that values of the extinction coefficient for CO adsorbed on different zeolites change significantly from one adsorbent to another, even for zeolites having the same extra-framework cations.

5. Conclusions

By using variable-temperature FTIR spectroscopy, two coordination modes of carbon monoxide in Na-ZSM-5 and Na-Y zeolites were found which correspond, respectively, to formation of Na$^+\cdots$CO and Na$^+\cdots$OC adducts between adsorbed CO and extra-framework Na$^+$ ions. These two coordination modes are in a temperature-dependent equilibrium. At room temperature (300 K) the proportion of CO molecules coordinated through the oxygen atom to Na$^+$ ions amounts to about 20% for CO/Na-ZSM-5 and 35% for CO/Na-Y, as deduced from the corresponding $A_{\mathrm{LF}}/A_{\mathrm{HF}}$ and $\varepsilon_{\mathrm{LF}}/\varepsilon_{\mathrm{HF}}$ ratios.

Frequency shifts for the C–O stretching mode in Na$^+\cdots$CO and Na$^+\cdots$OC adducts, and the energy difference between both coordination modes could be accounted for by using a simple electrostatic model which assigns such frequency shifts to the vibrational Stark effect for CO in the cation electric field. However, this electrostatic model was found to be unable to predict the correct ratio of extinction coefficients.

Equilibrium between C-bonded and O-bonded species could have relevant consequences on (catalytic) processes taking place in zeolites and involving adsorbed CO. Note that distribution of electron density and consequent activation of the adsorbed molecule would be dependent on its coordination mode to extra-framework cations.

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