Spectroscopic and Thermodynamic Characterization of Strontium Carbonyls Formed upon Carbon Monoxide Adsorption on the Zeolite Sr−Y

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The adsorption of CO on the faujasite-type zeolite Sr−Y generates four types of carbonyls: the $Sr(CO)^{2+}$ species, which has a characteristic IR absorption band at 2191 cm^{-1}; the $Sr(OC)^{2+}$ species at 2095 cm^{-1}; $Sr(CO)_2^{2+}$, which has a single mode at 2187 cm^{-1}; and $Sr(CO, OC)^{2+}$, which has a mode at 2098 cm^{-1}. The use of a variable-temperature IR cell allowing the simultaneous measurements of temperature, pressure, and coverages (intensities) of CO species to be made has allowed the determination of the standard enthalpy and entropy of formation of each species, so obtaining a fairly thorough thermodynamic characterization of the CO/Sr−Y system. C- and O-bonded carbonyl species were found to be in a temperature-dependent isomerization equilibrium, which was also studied by means of variable-temperature IR spectroscopy.

Introduction

Carbon monoxide adsorbed, usually at a low temperature, on alkali metal (M^+) and alkali earth metal (M^{2+})-exchanged zeolites interacts with cations, forming $M(CO)^+$ and $M(CO)^{2+}$ adducts, respectively, which have been recently termed[1] non-classical metal carbonyls. The study of these carbonyls constitutes an active research field that is relevant to both theoretical coordination chemistry and the practical usage of zeolites. Besides monocarbonyls, dicarbonyl $Na(CO)_2^+$ and $Li(CO)_2^+$ species have recently been documented for CO adsorbed on Na−Y[2] and Li−ZSM-5 zeolites[3] as well as $Ca(CO)_n^{2+}$ ($n = 1$−3) species[4−6] for CO adsorbed on Ca−Y. Variable-temperature FTIR spectroscopic studies[7−10] have shown that, for the case of the alkali metal cations, C-bonded $M(CO)^+$ carbonyls are in thermal equilibrium with O-bonded $M(OC)^+$ species. This finding is in agreement with quantum chemical calculations[11,12] for CO adsorption on both bare alkali metal cations and the model cluster $[AlH(OH)_3]^-M^+$, which was used to simulate extraframework monovalent cations in zeolites.[13] Such quantum chemical studies show, in agreement with experimental results, that both $M(CO)^+$ and $M(OC)^+$ species have a smaller energy than the corresponding unbound systems and that C-bonded carbonyls show a higher cation−CO interaction energy than O-bonded species. The enthalpy change, $\Delta H_{is}°$, involved in the isomerization between $M(CO)^+$ and $M(OC)^+$ alkali metal carbonyls in M^+−ZSM-5 zeolites has been experimentally determined for all cations except Cs^+. It was found[14,15] to decrease continuously from $\Delta H_{iso}° = 7.8$ kJ mol^{-1} for M = Li^+ to $\Delta H_{iso}° = 1.8$ kJ mol^{-1} for M = Rb^+, and this trend was correlated[14] with the decreasing electric field created by the extraframework cation (and nearby framework oxygens) that goes[16] from 9.5 V nm^{-1} in Li−ZSM-5 down to 3.4 V nm^{-1} in Rb−ZSM-5. However, to study this correlation between the isomerization enthalpy and the electric field further, and also

to put it on a more quantitative basis, other cation-exchanged zeolites have to be explored.

Studies on the above field are also relevant to applications of zeolites as catalysts. For instance, alkali and alkaline earth-exchanged faujasite-type zeolites have been used[17−20] for the selective photooxidation of hydrocarbons, and it was suggested[18,21] that the electric field generated by the extraframework cation facilitates the stabilization of the hydrocarbon−dioxygen charge-transfer complex. However, the magnitude and geometry of intrazeolite electric fields and the behavior of exchangeable cations toward adsorbed molecules are important factors in the design of zeolite-based nanostructured materials.[22]

The aim of this work was to carry out a detailed FTIR spectroscopic study of the adsorption of CO, at a variable temperature, on the faujasite-type zeolite Sr−Y. It is shown how the whole set of experimental data, which includes the temperature, pressure, and integrated intensity of infrared absorption bands, allowed the following information to be obtained: (i) formation of strontium mono- and dicarbonyl species, (ii) determination of the isomerization enthalpy (between C- and O-bonded species) for both mono- and dicarbonyls, and (iii) determination of the enthalpy and entropy of formation of both mono- and dicarbonyls, so establishing a fairly complete thermodynamic description of the CO/Sr−Y system.

Experimental Section

The Sr−Y zeolite sample used was prepared from a commercial NH$_4$−Y zeolite (nominal Si/Al ratio of 5.6) by ionic exchange with an aqueous solution of strontium nitrate. After ion exchange, X-ray powder diffraction showed good crystallinity and the absence of any diffraction lines not assignable to the faujasite structure type. Infrared spectroscopy (see later) revealed that exchange of NH$_4^+$ by Sr^{2+} ions was not complete, but it will be shown that this fact did not affect experimental measurements.

For infrared spectroscopic studies, a thin self-supported wafer of the zeolite sample was prepared and outgassed (activated) in a dynamic vacuum (residual pressure < 10^{-4} Torr) for 3 h

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at 700 K inside an infrared cell that allowed in situ high-temperature activation, gas dosage, and variable-temperature measurements to be carried out. Details of the design and performance of this homemade infrared cell were given elsewhere.[23] It was equipped with a platinum resistance thermometer (inserted close to the sample wafer) and a capacitance pressure gauge. The accuracy of the temperature and pressure measurements was about ±0.5 K and ±0.02 Torr, respectively.

For variable-temperature infrared spectroscopy, liquid nitrogen was used for refrigeration. For better thermal contact between the zeolite wafer and the cooled environment, 0.3 Torr of helium was admitted into the sample compartment before recording the background spectrum at liquid-nitrogen temperature. Carbon monoxide was then dosed to the desired amount, the cell was closed, and IR spectra were recorded at 77 K and also on gradual warming of the IR cell following the removal of liquid nitrogen. Transmission IR spectra were recorded, at 3-cm^{-1} resolution, by means of a Bruker IF66 FTIR spectrometer.

To allow for the residual pressure due to the helium inside the IR cell, a blank series of measurements were 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 corresponding pressure correction was deduced.

Results and Discussion

Preliminary Measurements. Before running the variable-temperature measurements, an experiment was conducted in which the sample wafer was exposed, at the fixed temperature of 77 K, to increasing pressure of CO from about 0.5 up to 5 Torr. The corresponding IR spectra are reported in Figure 1. At the lowest CO dose, the main IR absorption band is seen at 2191 cm^{-1}, with a shoulder at about 2183 cm^{-1}. Upon increasing CO dosage, the band at 2191 cm^{-1} gradually shifts to lower wavenumber values without showing any discontinuous steps. In agreement with the available literature on CO adsorbed on alkali- and alkaline earth-exchanged zeolites,[2−7] this band is assigned to the fundamental C−O stretching mode of carbon monoxide in C-bonded $Sr(CO)_n^{2+}$ carbonyls, where the number of CO ligands increases (as the frequency of the band decreases) from 1 to 2 and possibly 3. Indeed, for the case of CO adsorbed at 77 K on Ca−Y, the formation of mono-, di-, and tricarbonlys has been reported.[5,6] For weakly bound CO, each ligand in a polycarbonyl behaves as an independent oscillator,[2,15] and only a single C−O stretching band is expected, regardless of the corresponding geometry; this band, however, shifts to lower frequency when the same Sr^{2+} ion is shared by an increasing number of CO ligands. The formation of $Sr(CO)_n^{2+}$ carbonyls at 77 K occurs at relatively low pressures, as shown by the presence of a shoulder at 2183 cm^{-1} in the first spectrum, corresponding to a CO equilibrium pressure of ca. 0.5 Torr.

For the sake of completeness, it should be pointed out that the very weak IR absorption band observed in the range of 2144−2135 cm^{-1} (Figure 1, inset a) is the ^{13}CO counterpart (natural abundance about 1%) of the main band. This band shifts with coverage from 2144 to 2135 cm^{-1}. A constant isotopic ratio of 0.9785 is found, in agreement with the theoretical value of 0.9777 given by the relation $\nu^{13}CO/\nu^{12}CO = (\mu^{13}CO/\mu^{12}CO)^{1/2}$, where μ is the reduced mass. For the formation of $Sr(^{13}CO)_n^{2+}$ carbonyls with $n > 1$ being statistically forbidden, the ^{13}CO bands originate from a single carbonyl ligand: its shift with coverage is ascribed to the formation of polycarbonyls in which only one ligand is a ^{13}CO molecule. A contribution from
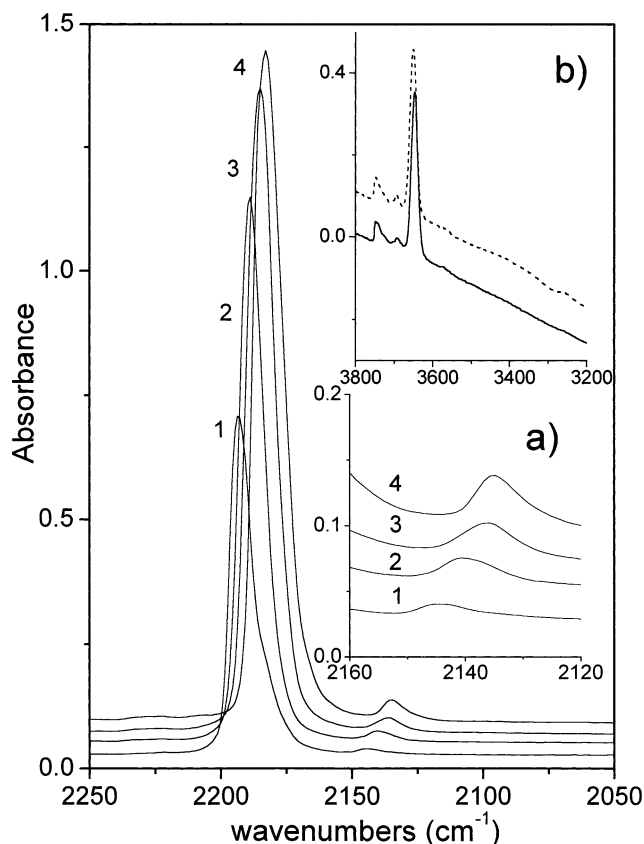

Figure 1. Infrared spectra in the C−O stretching region of carbon monoxide adsorbed on Sr−Y at 77 K at increasing dosage: (1) 0.5, (2) 2, (3) 4, (4) 5 Torr. The zeolite blank spectrum was subtracted. Inset a shows a magnification of the ^{13}C−O stretching region. Inset b shows the O−H stretching region of the zeolite blank (—), and after the adsorption of the largest CO dose (- -), the dashed-line spectrum was offset on the vertical scale for clarity.

physisorbed CO (which could also give IR absorption around 2138 cm^{-1}) is unlikely to exist at the small CO dosage used in the experiments.

Inset b in Figure 1 shows the zeolite blank spectrum in the O−H stretching region (continuous line). The peak at 3748 cm^{-1} corresponds to the expected silanol band, whereas the weaker feature at about 3695 cm^{-1} can be assigned[24,25] to hydroxyl groups in extraframework (aluminum oxohydroxide) species. A sharp band is also observed at 3648 cm^{-1}. This band corresponds to the O−H stretching of Brønsted acid Si(OH)Al groups,[24,26] which come from the thermolysis (during the thermal activation of the zeolite wafer) of a fraction of NH_4^+ ions that were not exchanged by Sr^{2+}. However, at the low CO dosage used in our measurements, the presence of some acidic protons does not complicate the interpretation of the IR spectra. The dashed-line spectrum in inset b of Figure 1 shows that, at the highest CO dose used, the ν(OH) spectral pattern is not significantly modified. Clearly, Sr^{2+} ions, being stronger adsorbing centers, prevent CO from interacting with protons.

Variable-Temperature IR Spectroscopy. For variable-temperature spectroscopy, the IR cell containing the activated zeolite wafer was dosed with ca. 4 Torr of CO and 0.3 Torr of helium at room temperature. The cell was then closed and cooled, and a series of spectra were taken (at about 5 K intervals) from 77 K up to room temperature.

Spectra covering the temperature range from 184 up to 205 K are shown in Figure 2a, whereas Figure 2b shows spectra taken from 259 to 299 K. In both of these temperature ranges, the maximum of the main IR absorption band kept a nearly
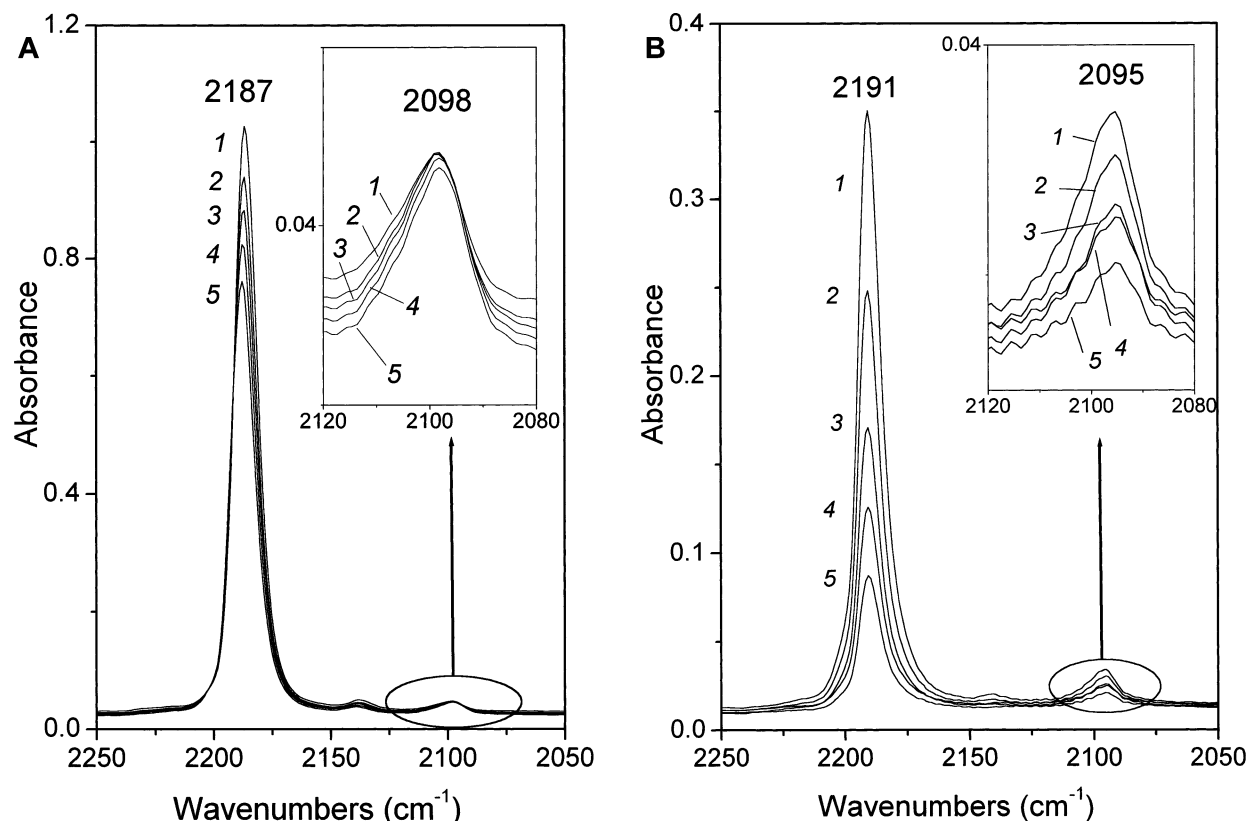
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Figure 2. (a) Infrared spectra of CO (ca. 4 Torr) adsorbed on Sr−Y at variable temperature: (1) 184.4, (2) 189.4, (3) 194.4, (4) 199.4, (5) 204.8 K. Inset shows an expanded view of the low-frequency band. (b) As in part a: (1) 259.3, (2) 269.3, (3) 279.7, (4) 289.8, (5) 298.8 K.
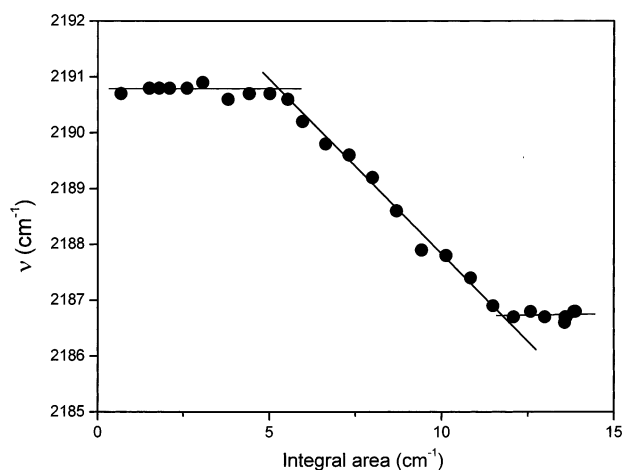

Figure 3. Wavenumber of peak maxima versus integrated intensity for the main C−O stretching band in variable-temperature IR spectra upon dosage of ca. 4 Torr of CO on Sr−Y.
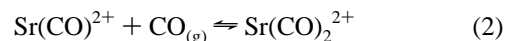
constant position: 2187 cm^{-1} in Figure 2a and 2191 cm^{-1} in Figure 2b. The band at 2187 cm^{-1} is assigned to the C−O stretching mode of the dicarbonyl species Sr(CO)$_2$$^{2+}$, whereas that at 2191 cm^{-1} should correspond to the C−O stretching of the monocarbonyl Sr(CO)$^{2+}$.

For temperature values intermediate between those covered by Figure 2a and b, the main IR absorption band (which gradually lost intensity as the temperature was raised) was observed to shift in a continuous mode from 2187 up to 2191 cm^{-1}. For brevity, the corresponding spectra are not shown, but Figure 3 reports the peak position versus integral area for the main IR absorption band in all of the recorded spectra. Two plateaus are observed in this Figure, which correspond respectively to the regions where monocarbonyl (left-hand side) and

dicarbonyl (right-hand side) species predominate. The sloping portion in Figure 3 corresponds to spectra that have a substantial contribution from both mono- and dicarbonyl species. We have chosen the region up to 5 cm^{-1} of the integrated band intensity (Figure 3) as being representative of the formation of the monocarbonyl from empty Sr^{2+} sites and adsorbed CO, following the process

$$Sr^{2+} + CO_{(g)} \leftrightharpoons Sr(CO)^{2+} \tag{1}$$

and the region having an integrated intensity larger than 12 cm^{-1} as representing the formation of dicarbonyls from monocarbonyls in the absence of empty Sr^{2+} sites:

$$Sr(CO)^{2+} + CO_{(g)} \leftrightharpoons Sr(CO)_2{}^{2+} \tag{2}$$

Let θ_0, θ_1, and θ_2 be the coverages of bare cations, monocarbonyl, and dicarbonyl species, respectively. The spectra in Figure 2a correspond to the situation $\theta_0 \approx 0$, $\theta_1 < \theta_2$, and those in Figure 2b, to the situation $\theta_2 \approx 0$.

Besides the main band, the spectra in Figures 2a,b also show the weak ^{13}CO band (2134−2144 cm^{-1}) already commented upon, and a weak infrared absorption which peaks at 2095 cm^{-1} in Figure 2b and at 2098 cm^{-1} in Figure 2a. In agreement with recent reports on IR spectroscopy of CO adsorbed on Ca−Y[4] and on alkali metal-exchanged zeolites,[7−10] these minor bands are assigned to the C−O stretching mode of the O-bonded monocarbonyl Sr(OC)$^{2+}$ (band at 2095 cm^{-1}, Figure 2b) and to the C−O stretching of the O-bonded ligand in the dicarbonyl species Sr(OC,CO)$^{2+}$ (band at 2098 cm^{-1}, Figure 2a). Coordination of two CO molecules through the oxygen atom to the same Sr^{2+} ion is unlikely to occur, because of the much higher probability of C-bonding.[7,12] Further discussion on these bands will be given after the next section.

TABLE 1: Numerical Data Corresponding to the Dicarbonyl[a] and Monocarbonyl Regions[b]

T (K)	p (Torr)	absorbance (cm^{-1})	coverage (θ)
184.4	0.19	13.50	0.722
189.4	0.25	13.30	0.700
194.4	0.33	12.99	0.666
199.4	0.45	12.58	0.620
204.8	0.59	12.09	0.566
259.3	2.44	5.02	0.716
269.3	2.79	3.80	0.543
279.7	3.14	2.61	0.372
289.8	3.39	1.79	0.256
298.8	3.58	1.25	0.178

[a] Upper section. [b] Lower section.

Adsorption Thermodynamics. The thermodynamic characterization of the adsorption process of CO on Sr−Y (i.e., the determination of the standard adsorption enthalpy (ΔH°_{ads}) and entropy (ΔS°_{ads}) for both C-bonded and O-bonded carbonyl species) is done in two steps because the formation of O-bonded species affects only a very small fraction of the adsorbed molecules. First, we examine the set of data concerning C-bonded carbonyls, namely, the temperature, pressure, and integrated intensity of the IR bands, by applying the van't Hoff relationship, and then we study the equilibrium between C-bonded and O-bonded species. This procedure allows a fairly complete thermodynamic description of the system to be obtained without making use of microcalorimetric data.

Table 1 reports the relevant numerical data for both the monocarbonyl region (lower part of the Table) and the dicarbonyl region (upper part). In the monocarbonyl region, Figure 2b and Table 1 show that the IR absorption band at 2191 cm^{-1} gradually loses intensity as the temperature is raised because the temperature increase drives the equilibrium described by eq 1 to the left, the corresponding increase in pressure notwithstanding. The dependence of the integrated IR absorption of the 2191 cm^{-1} band (A_{2191}) on the temperature and pressure can be described by the Langmuir-type equation

$$\theta_1/[(1 - \theta_1)p] = \exp(\Delta S^\circ_m/R) \exp(-\Delta H^\circ_m/RT)$$
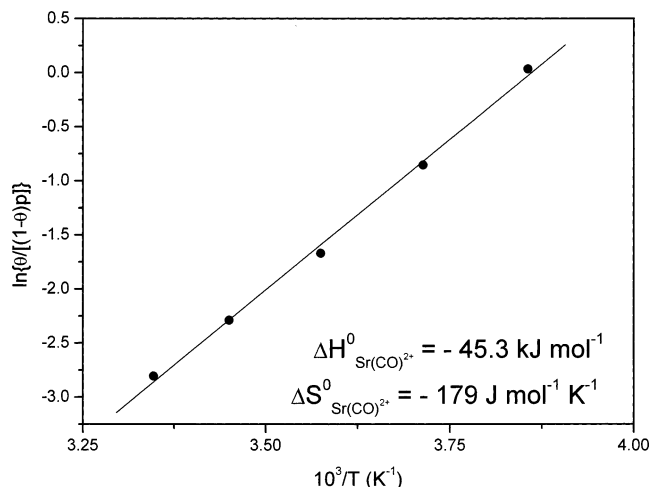$$\text{with } \theta_1 = A_{2191}/A^M_{2191} \quad (3)$$

where p is the equilibrium pressure, T is the temperature, A^M_{2191} is the integrated intensity corresponding to full coverage of monocarbonyls ($\theta_1 = 1$), and ΔH°_m and ΔS°_m refer to the formation of monocarbonyl species (eq 1).

Equation 3 can be linearized as

$$\ln\{\theta_1/[(1 - \theta_1)p]\} = (\Delta S^\circ_m/R) - (\Delta H^\circ_m/RT) \quad (4)$$

The actual value of A^M_{2191} that is needed to apply eq 4 is not known from experimental measurements. The maximum absorbance value that appears in Table 1 for the monocarbonyl is 5.02 cm^{-1}. However, this value does not correspond to full coverage ($\theta_1 = 1$) since that coverage cannot be obtained before dicarbonyl species start to form. We arrived at a value of A^M_{2191} = 7.0 cm^{-1} by a trial-and-error fit of the experimentally determined points to a Langmuir equation: the value of A^M has been varied between 6.5 and 8 cm^{-1}, corresponding to the sloping portion of Figure 3; when good linear fits were obtained, the actual value of A^M was that yielding the best fit. The result of this fit is shown in Figure 4, where the left-hand side of eq 4 is plotted against the inverse of the temperature. From this plot, the corresponding values of standard enthalpy and entropy corresponding to the formation of the monocarbonyl were found

Figure 4. Check of the validity of the Langmuir equation (see text) for monocarbonyl formation.

to be $\Delta H^\circ_m = -45.3 \pm 1$ kJ mol^{-1} and $\Delta S^\circ_m = -179 \pm 5$ J mol^{-1} K^{-1}, respectively.

Calorimetric measurements concerning CO adsorption on the Sr−Y zeolite have not been carried out, so the standard enthalpy of formation of the Sr(CO)$^{2+}$ carbonyl determined here from IR spectroscopy cannot be compared with direct measurements. This value, however, appears to be quite reasonable on the following bases. First, the standard enthalpy of formation of Ca(CO)$^{2+}$ in the Ca−Y zeolite was found to be -50 kJ mol^{-1} by adsorption microcalorimetry.[27] The value for Sr^{2+} is expected to be somewhat lower because of the weaker polarizing power of the Sr^{2+} cation with respect to that of the Ca^{2+} cation. Second, if reference is made to the empirical relationship proposed by Bolis and Morterra[28] between the heat of adsorption of CO and the corresponding stretching frequency for a set of non-d cations ($\Delta H^0 = (2191 - 2143)/1.02$ kJ mol^{-1}), then the observed frequency of 2191 cm^{-1} for the Sr(CO)$^{2+}$ species would correspond to a ΔH°_m value of -48 kJ mol^{-1}, in agreement (within experimental error) with the value of -45.3 kJ mol^{-1} reported here.

The thermodynamic parameters related to eq 2, which describes the formation of Sr(CO)$_2^{2+}$ from the corresponding monocarbonyl and CO, can be obtained by following a procedure similar to the one above. The relationship between θ_2 and the measured integrated intensity of the band at 2187 cm^{-1}, A_{2187}, is more complex because both mono- and dicarbonyl species contribute to such integrated intensity. It can be shown[29] that the corresponding value of θ is given by

$$\theta_2 = (A_{2187} - A^M_{2191})/(A^M_{2187} - A^M_{2191}) \quad (5)$$

where A^M_{2187} is the intensity corresponding to $\theta_2 = 1$, a situation again not actually reached experimentally. The needed value, which has to be higher than the highest value of absorbance reported in Table 1 (13.5 cm^{-1}), was again obtained by a best-fit criterion. $A^M_{2187} = 15.0$ cm^{-1} gave a very satisfactory straight line for the corresponding Langmuir plot, shown in Figure 5. From this plot, the enthalpy and entropy changes involved in the formation of the dicarbonyl from the monocarbonyl and adsorbed CO (eq 2) were found to be $\Delta H^\circ_d = -30.2 \pm 1$ kJ mol^{-1} and $\Delta S^\circ_d = -138 \pm 6$ J mol^{-1} K^{-1}, respectively.

Again, the enthalpy of formation of the dicarbonyl species cannot be compared with any direct experimental measurement, which is lacking. The value determined here, however, appears
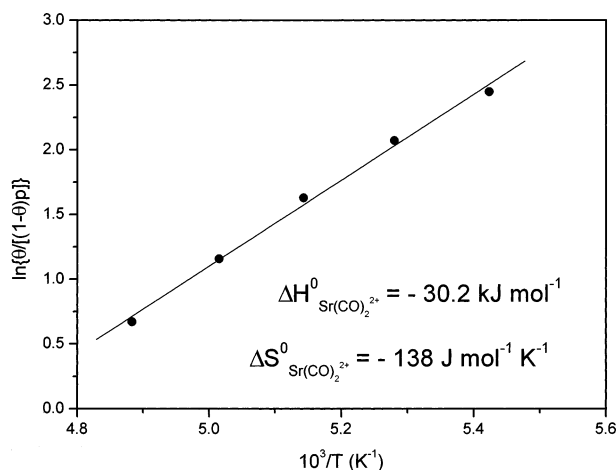
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Figure 5. As in Figure 4, the formation of the dicarbonyl.
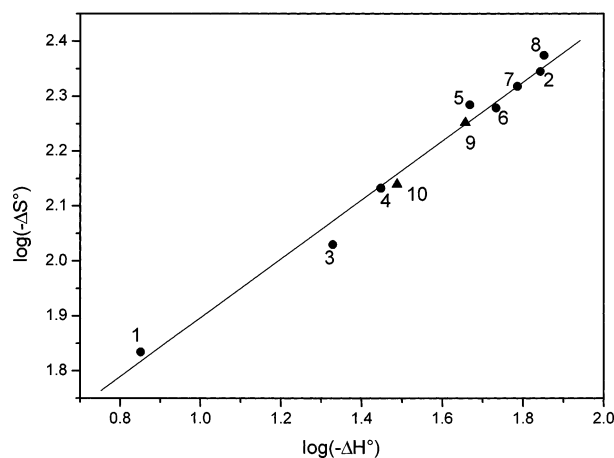

Figure 6. Correlation between $\Delta S°$ and $\Delta H°$ for CO adsorbed on (1) alumina (weak Lewis site); (2) alumina (strong Lewis site); (3) silica-supported (reduced) chromia; (4) Na–ZSM-5; (5) zinc oxide; (6) titania (weak Lewis site); (7) titania (intermediate site); (8) titania (strong Lewis site); (9) Sr–Y (monocarbonyl); and (10) Sr–Y (dicarbonyl). References: metal oxides (30, 31), Na–ZSM-5 (32), Sr–Y, present work.

to be reasonable since it should be expected to be significantly lower than that corresponding to the formation of the mono-carbonyl.

The above values of the standard enthalpy and entropy change for the CO/Sr–Y system can be compared with a set of reported data,[30–32] calorimetrically determined, for the adsorption of CO on several metal oxides and on the zeolite Na–ZSM-5. This comparison is made in Figure 6, which shows a linear correlation between $\log(-\Delta S°)$ and $\log(-\Delta H°)$ for several CO/adsorbent systems. A discussion of such a linear correlation, usually called the compensation effect,[33–35] is outside the scope of this paper. However, the values of the thermodynamic parameters derived here for the CO/Sr–Y system satisfactorily fit into the correlation, which lends further support to the present work.

Isomerization between C- and O-Bonded Carbonyls. The temperature dependence of the relative intensities of the IR absorption bands at 2187 and 2098 cm^{-1} in Figure 2a and those at 2191 and 2095 cm^{-1} in Figure 2b will now be discussed. Qualitatively, it can be seen in those Figures that when temperature is increased the relative intensity of the low-frequency bands (as compared to that of the corresponding high-frequency bands) increases. For quantitative analysis, the natural logarithm of the intensity ratios A_{2095}/A_{2191} and A_{2098}/A_{2187} was plotted as a function of reciprocal temperature, and straight lines were obtained in both cases, as shown in Figure 7. These straight lines constitute the van't Hoff plots corresponding to the
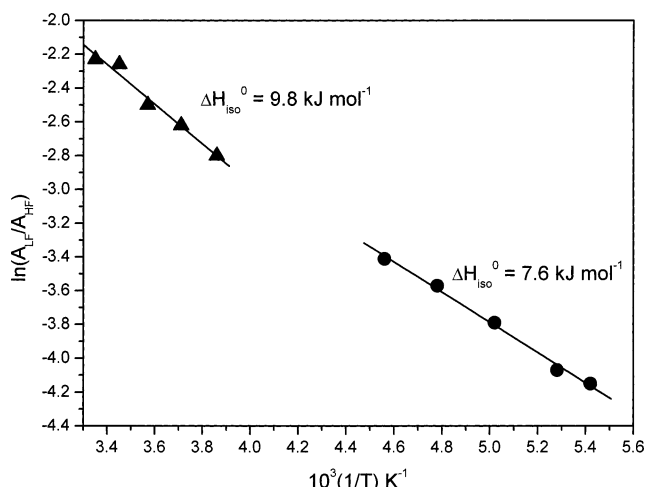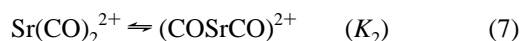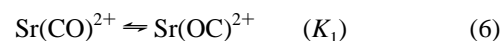

Figure 7. van't Hoff plot of the natural logarithm of the intensity ratio of LF and HF bands versus reciprocal temperature.

isomerization equilibria between C- and O-bonded carbonyls, as described by eqs 6 and 7 below:

$$Sr(CO)^{2+} \rightleftharpoons Sr(OC)^{2+} \qquad (K_1) \qquad (6)$$

$$Sr(CO)_2^{2+} \rightleftharpoons (COSrCO)^{2+} \qquad (K_2) \qquad (7)$$

The corresponding equilibrium constant, K, should be equal to the ratio θ_{OC}/θ_{CO} of the fractional coverages of O- and C-bonded species. Hence, if ϵ_{HF} and ϵ_{LF} are the molar absorption coefficients of the corresponding IR absorption bands, then we have

$$K = (A_{LF}/A_{HF})(\epsilon_{HF}/\epsilon_{LF}) \qquad (8)$$

where the suffixes LF and HF stand for low-frequency and high-frequency bands, respectively.

Combining eq 8 with the well-known van't Hoff equation (eq 9) for the temperature dependence of K yields eq 10:

$$\ln K = -(\Delta H°/RT) + (\Delta S°/R) \qquad (9)$$

$$\ln(A_{LF}/A_{HF}) = -(\Delta H°/RT) + (\Delta S°/R) + \ln(\epsilon_{HF}/\epsilon_{LF}) \qquad (10)$$

Figure 7 shows that eq 10 is obeyed for the isomerization processes of both mono- and dicarbonyl species.[36] From the van't Hoff plots, the corresponding isomerization enthalpy values $\Delta H°_{iso}$ were found to be equal to 9.8 kJ mol^{-1} for the monocarbonyl (eq 6) and 7.6 kJ mol^{-1} for the dicarbonyl (eq 7).

Regarding monocarbonyls, values of the isomerization enthalpy are known for most alkali metal cations, as stated in the Introduction; they were found to increase with increasing electric field,[14] which in turn correlates with the increasing wavenumber of the corresponding HF infrared absorption band.[22,24] The present value of $\Delta H°_{iso} = 9.8$ kJ mol^{-1} for the isomerization of the Sr^{2+} monocarbonyl is to be compared with that of $\Delta H°_{iso} = 7.8$ kJ mol^{-1} for the Li$^+$ monocarbonyl[15] since the Li(CO)$^+$ species was found to give the characteristic IR absorption band at 2195 cm^{-1}, which is close to the 2191-cm^{-1} value for Sr-(CO)$^{2+}$. This comparison shows that the isomerization enthalpy found for Sr(CO)$^{2+}$ is significantly higher that what could be expected from previous studies on the carbonyls formed by alkali metal cations. It would seem that besides the electric field other factors, probably related to the detailed nature of the chemical bond and to cation–CO equilibrium distances, sig-
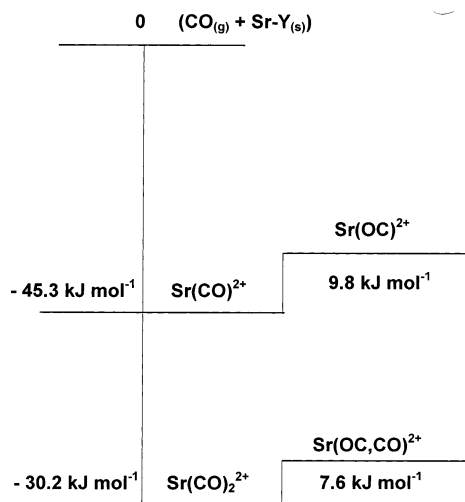
Figure 8. Standard enthalpies of formation of the four types of Sr^{2+} carbonyls occurring in the CO/Sr$-$Y system (i.e., $Sr(CO)^{2+}$, $Sr(OC)^{2+}$, $Sr(CO)_2^{2+}$, and $Sr(CO, OC)^{2+}$).

nificantly affect the isomerization enthalpy. An analysis of such factors has to await both detailed quantum chemical calculations and experimental measurements on other alkaline earth carbonyls.

A recent report[37] on CO adsorption, at room temperature, on Sr^{2+}-exchanged zeolite beta gives the characteristic C$-$O stretching band at 2190 cm^{-1}, which coincides (within experimental error) with the value of 2191 cm^{-1} found in the present work for the monocarbonyl species $Sr(CO)^{2+}$. By using the computational results of Pacchioni et al.,[38] which correlate the electric field with the vibrational frequency of adsorbed CO, the value of $\nu(CO) = 2191$ cm^{-1} leads to the value of $E = 8.6$ V nm^{-1} for the intrazeolite electric field created by the Sr^{2+} ion. As already commented upon in the Introduction, a knowledge of this value is relevant to both theoretical studies on intrazeolite chemical processes and practical applications of zeolites.

Finally, some spectroscopic considerations are pertinent. The independence of the two CO oscillators in $Sr(CO)_2^{2+}$, assumed so far on the basis of the literature, can be supported by the following observations. The bandwidth of the $Sr(CO)_2^{2+}$ band at 2187 is 15 cm^{-1} and basically coincides with that of the 2191-cm^{-1} band of the monocarbonyl species. The A^M_{2187} value is about twice the value of A^M_{2191}, showing that the molar absorption coefficient of CO is nearly the same in the mono-carbonyl and dicarbonyl species. The $Sr(CO, OC)^{2+}$ species exhibits a mode at 2098 cm^{-1} due to the OC ligand; the CO mode due to the C-bonded ligand is expected (on the basis of the independence between oscillators) to be at 2187 cm^{-1}, where the CO ligand in the $Sr(CO)_2^{2+}$ species absorbs.

Conclusions

The use of a variable-temperature IR cell that allows the simultaneous measurement of the temperature, pressure, and coverage (intensity) of CO species has enabled, through a systematic application of the van't Hoff relationship, the determination of the standard enthalpy of formation of four types of Sr^{2+} carbonyls occurring in the CO/Sr$-$Y system (i.e., Sr-$(CO)^{2+}$, $Sr(OC)^{2+}$, $Sr(CO)_2^{2+}$, and $Sr(CO,OC)^{2+}$). The obtained values are summarized in the chart shown in Figure 8. Standard entropies of C-bonded species have also been determined, and they were observed to conform to a linear correlation between $\log(-\Delta S°)$ and $\log(-\Delta H°)$ values that have already been established for other CO/adsorbent systems. Standard entropies

of O-bonded species are expected to be close to those of C-bonded species. A fairly thorough thermodynamic characterization of the CO/Sr$-$Y system has been achieved by using a novel technique that appears to have a wide potential for studying adsorbate/adsorbent systems where the weak interaction energy that is involved renders adsorption microcalorimetry more difficult to carry out.

References and Notes

(1) Lupinetti, A. J.; Strauss, S. H.; Frenking, G. *Prog. Inorg. Chem.* **2001**, *49*, 1.

(2) Hadjiivanov, K.; Knözinger, H. *Chem. Phys. Lett.* **1999**, *303*, 513.

(3) Otero Areán, C.; Manoilova, O. V.; Rodríguez Delgado, M.; Tsyganenko, A. A.; Garrone, E. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4187.

(4) Tsyganenko, A. A.; Otero Areán, C.; Escalona Platero, E. *Stud. Surf. Sci. Catal.* **2000**, *130*, 3143.

(5) Hadjiivanov, K.; Knözinger, H.; Ivanova, E.; Dimitrov, L. *Phys. Chem. Phys.* **2001**, *3*, 2531.

(6) Hadjiivanov, K.; Knözinger, H. *J. Phys. Chem. B* **2001**, *105*, 4531.

(7) Otero Areán, C.; Tsyganenko, A. A.; Escalona Platero, E.; Garrone, E.; Zecchina, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 3161.

(8) Tsyganenko, A. A.; Escalona Platero, E.; Otero Areán, C.; Garrone, E.; Zecchina, A. *Catal. Lett.* **1999**, *61*, 187.

(9) Manoilova, O. V.; Peñarroya Mentruit, M.; Turnes Palomino, G.; Tsyganenko, A. A.; Otero Areán, C. *Vib. Spectrosc.* **2001**, *26*, 107.

(10) Otero Areán, C.; Peñarroya Mentruit, M.; Rodríguez Delgado, M.; Turnes Palomino, G.; Manoilova, O. V.; Tsyganenko, A. A.; Garrone, E. *Stud. Surf. Sci. Catal.* **2002**, *142*, 207.

(11) Ferrari, A. M.; Ugliengo, P.; Garrone, E. *J. Chem. Phys.* **1996**, *105*, 4129.

(12) Ugliengo, P.; Garrone, E.; Ferrari, A. M.; Zecchina, A.; Otero Areán, C. *J. Phys. Chem. B* **1999**, *103*, 4839.

(13) Ferrari, A. M.; Neyman, K. M.; Rösch, N. *J. Phys. Chem. B* **1997**, *101*, 9292.

(14) Otero Areán, C.; Turnes Palomino, G.; Tsyganenko, A. A.; Garrone, E. *Int. J. Mol. Sci.* **2002**, *3*, 764.

(15) Otero Areán, C.; Rodríguez Delgado, M.; Manoilova, O. V.; Turnes Palomino, G.; Tsyganenko, A. A.; Garrone, E. *Chem. Phys. Lett.* **2002**, *362*, 109.

(16) Garrone, E.; Rodríguez Delgado, M.; Otero Areán, C. *Trends Inorg. Chem.* **2001**, *7*, 119.

(17) Blatter, F.; Moreau, F.; Frei, H. *J. Phys. Chem.* **1994**, *98*, 13403.

(18) Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1994**, *116*, 1812.

(19) Sun, H.; Blatter, F.; Frei, H. *Catal. Lett.* **1997**, *44*, 247.

(20) Myli, K. B.; Larsen, S. C.; Grassian, V. H. *Catal. Lett.* **1997**, *48*, 199.

(21) Blatter, F.; Frei, H. *J. Am. Chem. Soc.* **1993**, *115*, 7501.

(22) Otero Areán, C. *Comments Inorg. Chem.* **2000**, *22*, 241.

(23) Otero Areán, C.; Manoilova, O. V.; Tsyganenko, A. A.; Turnes Palomino, G.; Peñarroya Mentruit, M.; Geobaldo, F.; Garrone, E. *Eur. J. Inorg. Chem.* **2001**, 1739.

(24) Zecchina, A.; Otero Areán, C. *Chem. Soc. Rev.* **1996**, *25*, 187.

(25) Lavalley, J. C. *Catal. Today* **1996**, *27*, 377.

(26) Knözinger, H.; Huber, S. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2047.

(27) Bolis, V.; Fubini, B.; Garrone, E.; Giamello, E.; Morterra, C. *Stud. Surf. Sci. Catal.* **1989**, *48*, 159.

(28) Bolis, V.; Magnacca, G.; Morterra, C. *Res. Chem. Intermed.* **1999**, *25*, 25.

(29) The overall intensity A_{2187} of the band at 2187 cm^{-1} is $A_{2187} = A^M_{2191}\,\theta_1 + A^M_{2187}\,\theta_2$, with $\theta_1 \approx 1 - \theta_2$ because ($\theta_0 \approx 0$), from which eq 5 follows.

(30) Garrone, E.; Ghiotti, G.; Giamello, E.; Fubini, B. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2613.

(31) Bolis, V.; Fubini, B.; Garrone, E.; Morterra, C. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 1383.

(32) Garrone, E.; Fubini, B.; Bonelli, B.; Onida, B.; Otero Areán, C. *Phys. Chem. Chem. Phys.* **1999**, *1*, 513.

(33) Galway, A. K. *Adv. Catal.* **1977**, *26*, 247.

(34) Cremer, E. *Adv. Catal.* **1955**, *7*, 75.

(35) Kral, H. *Chem. Eng. Technol.* **1988**, *11*, 113.

(36) The application of the van't Hoff equation to equilibrium data covering a fairly large temperature range implies constant values of $\Delta H°$ and $\Delta S°$. Theoretical calculations[11,12] have shown that the difference in specific heat, ΔC_p^0, between C- and O-bonded adducts of CO with alkali metal cations is negligible; it seems safe to assume that the same applies to alkaline earth cations.

(37) Li, P.; Xiang, Y.; Grassian, V. H.; Larsen, S. C. *J. Phys. Chem. B* **1999**, *103*, 5058.

(38) Pacchioni, G.; Cogliandro, G.; Bagus, P. *Int. J. Quantum Chem.* **1992**, *42*, 1115.