Computational and Fourier Transform Infrared Spectroscopic Studies on Carbon Monoxide Adsorption on the Zeolites Na-ZSM-5 and K-ZSM-5: Evidence of Dual-Cation Sites

7 AUTHORS, INCLUDING:

Montserrat Rodríguez Delgado
University of the Balearic Islands
64 PUBLICATIONS   1,315 CITATIONS

SEE PROFILE

Karel Frolich
University of Pardubice
16 PUBLICATIONS   212 CITATIONS

SEE PROFILE

Angeles Pulido
University of Southampton
24 PUBLICATIONS   451 CITATIONS

SEE PROFILE

Petr Nachtigall
Charles University in Prague
141 PUBLICATIONS   3,562 CITATIONS

SEE PROFILE

Computational and Fourier Transform Infrared Spectroscopic Studies on Carbon Monoxide Adsorption on the Zeolites Na-ZSM-5 and K-ZSM-5: Evidence of Dual-Cation Sites

**C. Otero Areán,[†] M. Rodríguez Delgado,[†] K. Frolich,[‡] R. Bulánek,[‡] A. Pulido,[§]
G. Fiol Bibiloni,[†] and P. Nachtigall*,[§]**

*Departamento de Química, Universidad de las Islas Baleares, E-07122 Palma de Mallorca, Spain,
Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice,
Nám. Čs. Legií 565, 53010 Pardubice, Czech Republic, and Institute of Organic Chemistry and Biochemistry,
Academy of Sciences of the Czech Republic and Center for Biomolecules and Complex Molecular Systems,
Flemingovo n. 2, CZ-16610 Prague, Czech Republic*

A combination of variable-temperature Fourier transform infrared (FTIR) spectroscopy with calculations performed at the periodic density functional theory (DFT) level was used in the investigation of carbon monoxide adsorption on zeolites Na-ZSM-5 and K-ZSM-5. On the basis of a very good agreement between experimental and calculated frequencies and adsorption enthalpies, it is shown that the IR absorption band appearing in the intermediate frequency range for adsorbed CO (2155 and 2150 cm^{-1} for Na-ZSM-5 and K-ZSM-5, respectively) is due to the formation of linearly bridged CO adsorption complexes on dual-cation sites (M$^+$···CO···M$^+$, M = Na, K). The population of such adsorption complexes increases with increasing cation radius and with decreasing Si/Al ratio. Bridged adsorption complexes are slightly more stable than carbonyl complexes formed on isolated extraframework metal cations. Adsorption enthalpies and CO stretching frequencies of carbonyl complexes formed on isolated extraframework metal cations were found to depend on the metal cation coordination with the zeolite framework. This dependence is particularly apparent for Na-ZSM-5, where cations located on the intersection sites are coordinated to only two framework oxygen atoms and CO adsorption on these sites is up to 8 kJ/mol more stable than adsorption on the channel wall sites; CO stretching frequencies of carbonyls formed on intersection sites are up to 7 cm^{-1} higher than frequencies of carbonyls formed on channel wall sites.

1. Introduction

Carbon monoxide is frequently used as a probe molecule for zeolite characterization by means of infrared spectroscopy. When adsorbed (at a low temperature) on alkali-metal-exchanged zeolites having a high Si/Al ratio, carbon monoxide is well-known to form mainly C-down adducts with the metal cation, which show a blue-shifted C−O stretching frequency. However, a minor proportion of O-down adducts, having a red-shifted C−O stretching frequency, are also frequently observed in the IR spectra, as well as dicarbonyl species having two CO molecules coordinated to a single metal cation.[1−5] These common features appearing in IR spectra of CO adsorbed on high-silica zeolites are already well understood, and that knowledge allows IR characterization of a range of cation sites. However, it often happens that the spectra also show bands (or shoulders) within a frequency range intermediate between the value for free CO (2143 cm^{-1}) and that shown by the blue-shifted M$^+$···CO species (where M$^+$ stands for the alkali metal cation). These latter spectroscopically observed features have not hitherto been well understood, and yet they might contain valuable information about zeolite cation sites.

Recently, combined IR spectroscopic and computational studies on carbon monoxide adsorption on the zeolites Na-FER and K-FER have shown that, besides M$^+$···CO (monocarbonyl) and M$^+$···OC (isocarbonyl) species, bridged M$^+$···CO···M$^+$ complexes are also formed.[6,7] These bridged species appear whenever two alkali metal cations happen to be at the right distance apart from each other, and such a pair of metal cations was termed a dual-cation site. The bridged M$^+$···CO···M$^+$ complex in ferrierite does show a characteristic C−O stretching frequency lower than that of the M$^+$···CO carbonyl but higher than that of free CO. Note that in the bridged CO complex polarization of the molecule through the carbon atom is partially counterbalanced by polarization through the oxygen atom. The finding of M$^+$···CO···M$^+$ species for CO adsorbed on alkali-metal-exchanged FER prompted the question of whether similar dual-cation sites would also occur in other high-silica zeolites having a topology widely different from that of ferrierite, and whether or not that information was actually contained in the above-mentioned (not well understood) IR absorption bands falling between the characteristic frequency of M$^+$···CO mono-carbonyls and that of free CO. The existence of dual-cation sites was also recently proposed by Busca and co-workers[8−10] on the basis of IR investigation; several possible structures of adsorption complexes were proposed. Aiming at answering those questions, we report on a combined theoretical and Fourier transform infrared (FTIR) spectroscopic study of (low-temperature) CO adsorption on the MFI-type zeolites Na-ZSM-5 and K-ZSM-5.

---

* Corresponding author: phone +420-220410324; fax +420-220410320; e-mail petr.nachtigall@uochb.cas.cz.
† Universidad de las Islas Baleares.
‡ University of Pardubice.
§ Academy of Sciences of the Czech Republic and Center for Biomolecules and Complex Molecular Systems.

CO Adsorption on Zeolites Na-ZSM-5 and K-ZSM-5

J. Phys. Chem. C, Vol. 112, No. 12, 2008 **4659**

2. Materials and Methods

2.1. Experimental Procedures. The parent ZSM-5 samples used were supplied (in the ammonium form) by Sud-Chemie (sample with nominal Si:Al ratio of 13.5:1) and Zeolyst (Si:Al ratio 30:1 and 75:1). From the parent zeolite, sodium and potassium-exchanged forms were obtained by repeated ion exchange with a 0.5 M solution of the corresponding alkali metal nitrate. Powder X-ray diffraction of the exchanged samples showed good crystallinity in both cases, and all diffraction lines appearing in the diffractograms corresponded to the MFI structure type.[11] Complete ion exchange was checked by the absence of IR absorption bands corresponding to either the ammonium ion or the (Brønsted acid) Si(OH)Al group, which would be generated during thermal activation of the zeolite wafer for IR spectroscopy (see below) if total exchange of Na^+ or K^+ for the ammonium ion did not take place in the parent NH_4-ZSM-5 zeolite.

For IR spectroscopy, a thin self-supported wafer of the zeolite sample was prepared and activated (outgassed) in a dynamic vacuum (residual pressure $<10^{-4}$ Torr) for 3 h at 700 K inside an IR cell,[12] which allowed on-line sample activation, gas dosage, and variable-temperature IR spectroscopy to be carried out. Liquid nitrogen was used for cooling, and to facilitate thermal contact between the zeolite wafer and the cooled cell, 0.2 Torr of helium was admitted into the sample compartment before the background spectrum was recorded at 77 K. The cell was then dosed with CO and closed, and IR spectra were recorded at several temperature values (within the range of 170–280 K) upon gradual warming of the IR cell. Simultaneously, temperature and equilibrium pressure inside the cell were registered. A platinum resistance thermometer (Tinsley) and a capacitance pressure gauge (MKS, Baratron) were used for that purpose. The precision of these measurements was better than ±2 K and ±10^{-2} Torr, respectively. Pressure correction (for helium) was determined from a calibration plot, as described elsewhere.[13] Transmission FTIR spectra were recorded at 3 cm^{-1} resolution on a Bruker IFS66 instrument; 64 scans were accumulated for each spectrum.

2.2. Models and Computational Methods. The interaction of CO with Na-FER and K-FER zeolites was investigated recently.[6,7] Rather similar computational strategy was adopted here for the description of Na-ZSM-5; therefore, only a brief description of the method is provided below, and only the differences in computational strategy are described in detail. In the case of Na-FER and K-FER zeolites, the CO adsorption complexes formed on all stable alkali metal cation sites in the vicinity of framework AlO_4 units in all four distinguishable positions in FER were investigated. On the contrary, only a subset of possible Na^+ sites in Na-ZSM-5, representing individual Na^+ site types in MFI reported previously,[14] was considered in the present study. This limitation is due to the following reasons: (i) MFI has a relatively large unit cell (UC) and it is computationally rather demanding to describe the large zeolite UC at the periodic DFT level, and (ii) there are 12 distinguishable framework T sites when the orthorhombic symmetry of MFI UC is considered, and for many of them there is more than one stable Na^+ site in their vicinity;[14] therefore, investigation of CO adsorption complexes on all possible Na^+ sites would be extremely demanding on computational resources. For the same reasons, calculations were performed only for zeolite Na-ZSM-5. One geometry optimization of CO/Na-ZSM-5 takes about 2 days on 64 (IBM Power PC 970MP/2.3 GHz) processors at Marenostrum supercomputer in Barcelona.
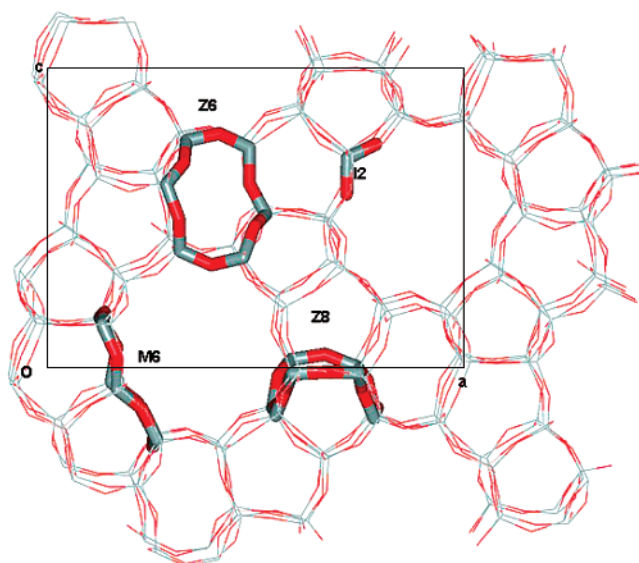

Figure 1. Definition and location of the individual types of extraframework cation sites in ZSM-5. View along the [010] direction; the 10-MR (membered rings) represent the main channels of ZSM-5. The Z6 and Z8 sites are located on the wall of the zigzag channel, and M6 is located on the wall of the main channel. The I2 (intersection) sites are on the edge of both channels. Framework oxygen and T-atoms are depicted in red and gray, respectively.

2.2.1. Models. Calculations were performed by use of a periodic model of the orthorhombic UC of ZSM-5 with the composition $Si_{96-n}Al_nO_{192}Na_n(CO)_m$ where $n = 1$ and 2 and $m = 0$, 1, and 2. The equilibrium volume was obtained by constrained optimization of the all-silica form of MFI via periodic DFT (details in section 2.2.2) and Birch's equation of state.[15] Optimized UC dimensions ($a = 20.241$ Å, $b = 20.001$ Å, $c = 13.514$ Å, $V = 5471.0$ Å^3) are in good agreement with experimental data[16] ($a = 20.092$ Å, $b = 19.952$ Å, $c = 13.414$ Å, $V = 5377.3$ Å^3).

The following set of Na^+ sites in Na-ZSM-5 was considered in the DFT investigation: (i) type II sites on the channel intersection, I2/T12, I2/T6, and I2/T10; (ii) type I sites on the main (M) or zigzag (Z) channel walls, M6/T11, Z8/T12, M6/T12, M5/T12, and Z6/T4; and (iii) the dual-cation site consisting of a pair of I2/T10 and Z8/T12 sites. The notation introduced originally in ref 17 and adopted also for alkali-metal-exchanged MFI[14] is used: I2 denotes a site located on the intersection of two channels (the cation is coordinated to two framework O atoms of a single AlO_4 tetrahedron) and Mx and Zx ($x = 5$ or 6) denotes sites located on top of the x-member ring on the wall of M and Z channels, respectively (see Figure 1). The site "Z8" was originally denoted "Z10" in ref 14; it is the same as site "nest2" described in ref 18.

CO adsorption complexes were computationally investigated only for energetically favorable Na^+ sites in the vicinity of a particular framework aluminum. Both C-down and O-down adsorption complexes were investigated and also the formation of dicarbonyl species was considered for several Na^+ sites. Formation of bridged CO adsorption complex on the dual-cation site was also investigated. The following nomenclature, introduced in ref 6 for K-FER, is used: Na^+ sites not having a nearby cation (within 7.5 Å distance) are termed "isolated sites". A site constituted by a pair of Na^+ cations (at a distance smaller than 7.5 Å) is termed a "dual site". The term "monocarbonyl" is used for CO interacting with only a single Na^+ ion, via either the carbon or the oxygen atom (carbonyl and isocarbonyl

TABLE 1: Parameters of the ω_{CO}/r_{CO} Correlation for the CO/Na$^+$-ZSM-5 System[a]

complex	method basis set[a]	a (Å^{-1} cm^{-1})	b (cm^{-1})	$\Delta\omega$ (cm^{-1})
C-down	PBE/400 eV	−6650.6	9780.0	−2.5
O-down	PBE/400 eV	−7099.1	10 284.0	−0.8

[a] For details see Section 2.2.

complexes, respectively). The term "dicarbonyl" is used for complexes where two CO molecules interact with a single Na$^+$ ion. The term "bridged CO complex" is used for CO interacting with a pair of Na$^+$ ions constituting a dual site; in such a site, CO interacts via the C atom with one Na$^+$ cation and via the O atom with the second Na$^+$ cation.

2.2.2. Computational Methods. Periodic DFT calculations were performed by use of the VASP program;[19−21] the Perdew−Burke−Ernzerhof (PBE) exchange−correlation functional,[22] the projector augmented wave approximation (PAW) of Blöchl,[23,24] and the plane wave basis set with a kinetic energy cutoff of 400 eV were used; Brillouin-zone sampling was restricted to the Γ-point. Zero-point energy (ZPE) corrections were calculated within the harmonic approximation by use of six degrees of freedom for every CO molecule in the model system; ZPE was calculated for each of the complexes reported here. The sum of the electronic interaction energy and ZPE gives the internal energy change at 0 K, $\Delta U°(0)$. Experimental determination of standard adsorption enthalpy, $\Delta H°$, was carried out at temperatures around 250 K; therefore, $\Delta H°(250)$ was evaluated from the ideal gas model, $\Delta H°(T) = \Delta U°(0) + {}^{7}\!/_{2}RT$.

A recently introduced ω/r correlation method[25] was used for CO frequency calculations. By correlating the $r(CO)$ bond lengths obtained at the DFT level with CO stretching frequencies calculated at the coupled cluster level, this method gives the CO stretching frequency with near spectroscopic accuracy for metal carbonyl species at various environments. Aside from the fact that the ω/r correlation method gives much more reliable results than the standard methodology for calculating frequencies (DFT and harmonic approximation), the ω/r correlation method does not require construction of the Hessian matrix of the CO/ M$^+$-zeolite system. Instead, only the $r(CO)$ bond length needs to be determined at the DFT level.

Within the concept of the ω/r correlation method, the CO stretching frequencies ν_{CO} (in reciprocal centimeters) are calculated from

$$\nu_{CO} = ar_{CO} + b + \Delta\nu + \Delta\omega \qquad (1)$$

where a and b were obtained from CCSD(T) calculations on the set of testing molecules, Na$^+$CO, H$_2$O···Na$^+$CO, (H$_2$O)$_2$···Na$^+$CO, F$^-$···Na$^+$CO, and (F$^-$)$_2$···Na$^+$CO (for details see ref 7). A constant anharmonicity correction for C−O stretching, $\Delta\nu = -29$ cm^{-1}, was adopted.[26] A $\Delta\omega$ correction was obtained as the difference between the C−O stretching frequency calculated from eq 1 and those explicitly calculated at the CCSD(T) level for the Al(OH)$_4$Na−CO (1-T) cluster model, under the C_{2v} symmetry constraints. The same type of ω/r correlation was also obtained for O-down adducts. The results obtained for the MFI unit cell are shown in Table 1. More details about the method can be found in ref 7, where the same computational strategy was adopted for the CO/Na-FER system. It should be pointed out that using the parameters a and b previously obtained for the ferrierite UC in the CO/Na-ZSM-5 system leads to only very small changes in calculated vibrational frequencies (within 1 cm^{-1}). Since the plane-wave basis set depends on the UC size, we used the parameters a and b obtained for UC of MFI (Table 1).

Equation 1 derived for the monocarbonyl species can be also used for the dicarbonyl complexes. In the case of alkali metal cations there is only negligible coupling of CO stretching modes; calculations performed for dicarbonyl formed on 1-TNa (Al-(OH)$_4$Na) cluster model showed that CO stretching frequencies differ only by 1.3 cm^{-1}.[1] A similar conclusion has been drawn recently for CO interacting with the Li-ZSM-5 system.[27] Note, however, that this is not the case for the dicarbonyls formed on transition metal cations.[28,29]

3. Results

3.1. Calculations. Calculated properties (summarized in Table 2) clearly depend on the structural details of Na$^+$ adsorption sites; therefore, Na$^+$ sites in Na-ZSM-5 are described first. Results obtained at the periodic DFT level are in good agreement with the previous theoretical investigation of alkali metal cation sites in MFI, where two site types[14] of alkali metal cations were reported: type I sites (channel wall sites), located on top of six- or five-membered rings on the zeolite channel wall, and type II sites (intersection sites), located at the edge of two intersecting channels. For a detailed comparison of the previous results (calculations using a combined quantum mechanics/ interatomic potential function, QM-pot, model[30] employing B3LYP exchange−correlation functional) with the results of the periodic DFT model (PBE functional), the Na$^+$ sites in the vicinity of framework Al atom at T12 position were investigated in detail. The Z8/T12 and I2/T12 sites were found to be the most stable Na$^+$ sites in the vicinity of Al at T12 at the QM-pot level, followed by the M6/T12 site, which was 8 kJ/mol less stable. Very similar results are found with the periodic DFT model, with the Z8/T12 site being the most stable one, followed by I2/T12 (9 kJ/mol above) and M6/T12 (15 kJ/mol above) sites; the Na$^+$ site on top of the 5-membered ring (M5/T12 site) is 23 kJ/mol less stable than that at the Z8/T12 site.

In agreement with the results of a previous study,[14] the Na$^+$ cation at the intersection site is coordinated to only two framework oxygen atoms of a single AlO$_4$ tetrahedron; due to the fact that the optimized geometries are very similar for all three I2 sites investigated here, only the details of the I2/T6 site are reported in Figure 2a. At the M6/T11 and Z6/T4 channel wall sites, the Na$^+$ cation is located on top of the six-membered ring (R6) on the wall of main and zigzag channels, respectively. In addition to coordination to two oxygen atoms of AlO$_4$ tetrahedron, the Na$^+$ cation is close to another two framework oxygen atoms of the R6 ring (see Figure 2b,c for details). A similar Na$^+$ coordination was found for the Z8/T12 site located on the wall of a zigzag channel (Figure 2d).

Calculated vibrational frequencies of adsorbed CO, structural parameters of adsorption complexes, electronic interaction energies (ΔE^{el}), and adsorption enthalpies at 250 K ($\Delta H°(250)$) are summarized in Table 2. Calculations showed that several types of stable carbonyl complexes could be formed on Na-ZSM-5 zeolite. A monocarbonyl complex can be formed on any of the Na$^+$ sites in Na-ZSM-5 investigated here. The calculated adsorption enthalpy ranges from −29 kJ/mol (Z6/T4 site) to −37 kJ/mol (I2/T6 site). The monocarbonyl complexes formed on the intersection sites are 4−8 kJ/mol more stable than those formed on the channel wall sites. The vibrational frequencies calculated for monocarbonyl complexes formed on intersection and channel wall sites are 2184 and 2177−2181 cm^{-1}, respectively. Formation of dicarbonyl complexes can be expected on the intersection Na$^+$ sites. The calculated adsorption enthalpy for the second CO adsorption is −29 and −32 kJ/mol for I2/T6 and I2/T12 sites, respectively.

TABLE 2: CO Vibrational Frequencies, Electronic Interaction Energies, and Adsorption Enthalpies of Mono- and Dicarbonyl Complexes on Single and Dual Na⁺ Sites in Na-ZSM-5

Na⁺ site[a]	CO complex[b]	$r(NaC),^c\ r(NaO)^c$	$r(CO)$ (Å)	ν_{CO} (cm⁻¹)	ΔE^{el} (kJ/mol)	$\Delta H°(250)$ (kJ/mol)
I2/T6	CO	2.61	1.1374	2184	−31.7	−36.6
I2/T6	2×CO	2.64	1.1381	2180	−24.0	−28.8
I2/T6		2.62	1.1382	2179		
I2/T12	CO	2.62	1.1374	2184	−30.3	−35.2
I2/T12	2×CO	2.65	1.1382	2179	−27.1	−32.0
I2/T12		2.65	1.1378	2182		
I2/T12	*OC*	*2.42*	*1.1482*	*2103*	*−20.5*	*−26.4*
I2/T10	CO	2.61	1.1376	2183	−31.4	−36.2
M6/T11	CO	2.64	1.1383	2178	−26.5	−31.5
Z8/T12	CO	2.65	1.1379	2181	−25.9	−30.7
Z8/T12	2×CO	2.70	1.1396	2169	−17.5	−22.5
Z8/T12		2.68	1.1385	2177		
Z8/T12	*OC*	*2.45*	*1.1479*	*2105*	*−18.4*	*−24.3*
Z6/T4	CO	2.63	1.1385	2177	−24.1	−28.9
Z8/T12−I2/T10	CO	2.75, 2.58	1.1422	2152	−30.6	−35.2
I2/T10−Z8/T12	CO	2.71, 2.71	1.1407	2162	−31.6	−36.2

[a] Na⁺ site type and framework Al position. For details see Figure 1. [b] Results for O-bonded complexes are shown in italic type. [c] Distance (in angstroms) between Na⁺ and C or O atom of CO for C-down and O-down complexes, respectively.
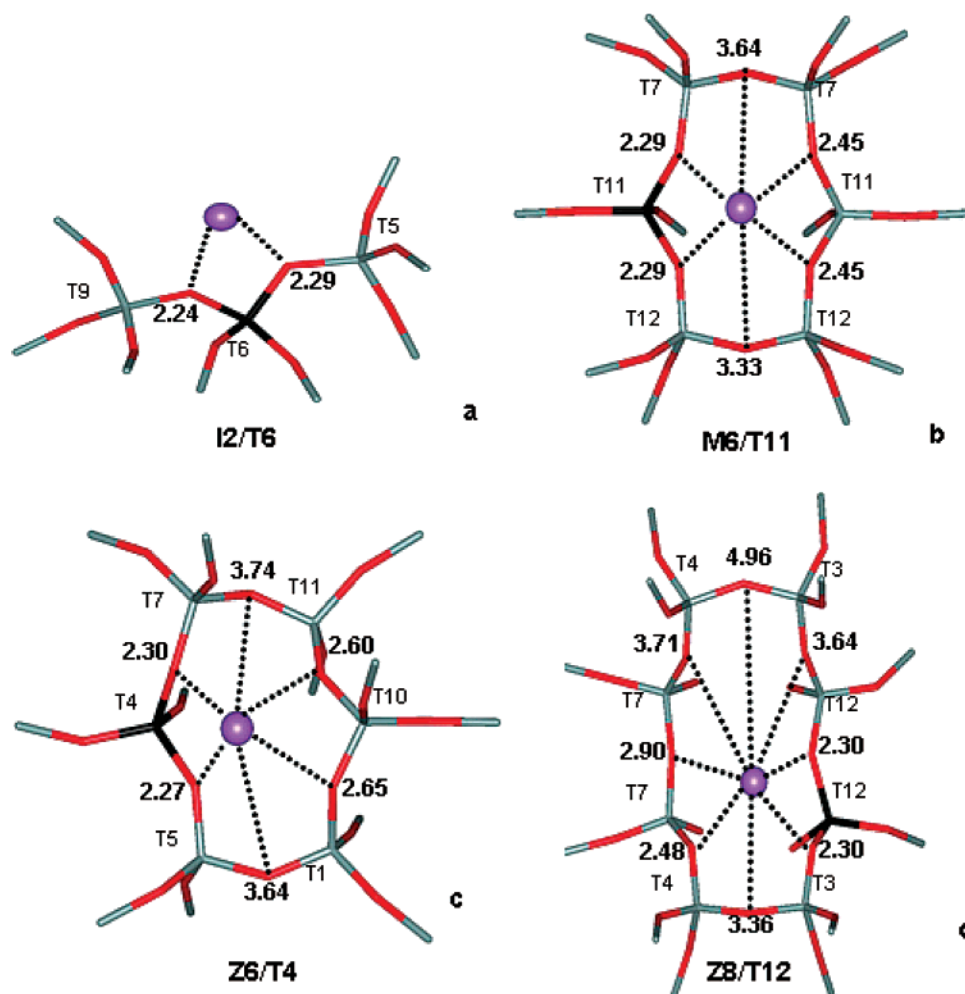

Figure 2. Structural details of several Na⁺ sites in ZSM-5: (a) I2/T6 site located on the intersection of main and zigzag channels in the vicinity of framework Al atom in T6 position, (b) M6/T11 site on the wall of main channel, (c) Z6/T4 site on the wall of zigzag channel, and (d) Z8/T12 site on the wall of zigzag channel. Framework O, Si, and Al atoms depicted in red, gray, and black, respectively, and Na⁺ is depicted as a violet ball. Distances between Na⁺ and close-framework oxygen atoms are given in angstroms; numbering of T-sites (assuming orthorhombic symmetry[41]) is also given.

Vibrational frequencies of dicarbonyl species are 2−5 cm⁻¹ lower compared to corresponding monocarbonyl complexes. Note that both adsorption enthalpy of the second CO and ν_{CO} of dicarbonyls formed on the intersection sites are very close to those calculated for monocarbonyl complexes formed on the channel wall sites. On the contrary, formation of dicarbonyl
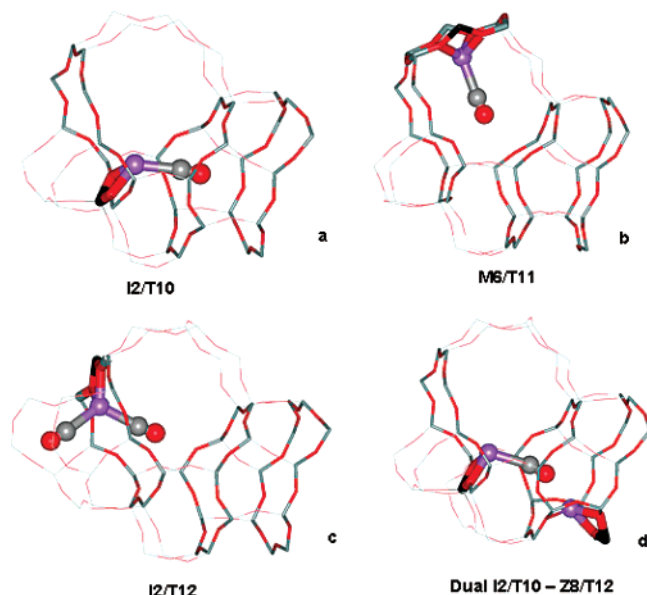
Figure 3. Carbonyl complexes formed in Na-ZSM-5: (a) monocarbonyl complex on I2/T10 Na$^+$ site, (b) monocarbonyl complex on M6/T11 site, (c) dicarbonyl formed on I2/T12, and (d) linearly bridged carbonyl complex on a dual-cation site constituted by I2/T10 and Z8/T12 Na$^+$ sites (I2/T10···CO···Z8/T12). Na, C, and O atoms are denoted as violet, gray, and red balls. Si, Al, and O framework atoms are depicted as gray, black, and red sticks, respectively. The view is along the main channel where 10-MR windows of zigzag channel are highlighted (thin tube mode).

Figure 4. Variable-temperature FTIR spectra (zeolite blank subtracted) of CO adsorbed on Na-ZSM-5 (Si:Al = 13.5:1). Temperature (in kelvins) and equilibrium pressure (Torr, in parentheses) were as follows: *1*, 233 (2.72); *2*, 243 (3.24); *3*, 253 (3.63); *4*, 263 (3.92); *5*, 272 (4.14); *6*, 278 (4.26). (Inset) An example of band resolution; note that the very weak band seen at about 2130 cm^{-1} is the ^{13}CO counterpart of the main band at 2179 cm^{-1}.

species on the channel wall site is less favorable; the adsorption enthalpy of the second CO on the channel wall site (Z8/T12) is about 10 kJ/mol smaller than for the intersection sites (Table 2). Calculations on isocarbonyl complexes were performed for one intersection site (I2/T12) and one channel wall site (Z8/T12); calculated ν_{CO} is in the range 2103−2105 cm^{-1} and calculated adsorption enthalpies are 9 and 6 kJ/mol smaller (I2/T12 and Z8/T12 sites, respectively) than those found for the corresponding carbonyl complexes. The structure of several mono- and dicarbonyl complexes is depicted in Figure 3.

The calculations performed previously for Na-FER zeolite show that stable and spectroscopically (IR) detectable bridged CO complexes can be found for dual-cation sites where two Na$^+$ ions are about 6.5 Å apart from each other. The Na$^+$ cations at I2/T10 and Z8/T12 sites (6.26 Å apart) thus constitute a dual-cation site suitable for formation of bridged CO complexes. Bridged CO complexes formed at this dual-cation site were investigated; both C-end to Z8/T12 and C-end to I2/T10 complexes were considered (Table 2). In the Z8/T12···CO···I2/T10 adsorption complex (CO interacts with Na$^+$ at Z8/T12 via C-end), the calculated adsorption enthalpy (−35 kJ/mol) is 4 kJ/mol larger than that found for the corresponding monocarbonyl on isolated Z8/T12 site. The I2/T10···CO···Z8/T12 adsorption complex (CO interacts with Na$^+$ at I2/T10 via C-end) is slightly more stable than the Z8/T12···CO···I2/T10 adsorption complex. However, the stability of the I2/T10···CO···Z8/T12 adsorption complex is only 0.2 kJ/mol larger than that found for the corresponding isolated monocarbonyl formed on Na$^+$ at I2/T10 site. The reason for only a small stabilizing effect of the secondary cation is the too-close proximity of two Na$^+$ ions (6.26 Å). As a result, the CO molecule is slightly displaced from its ideal position for the isolated I2/T10 site due to the presence of the secondary Na$^+$ cation; this displacement is apparent from the Al−Na−C angle that goes from 86° on an isolated site to 108° on a dual site (Figure 3). Note that the optimum Na−Na distance found for the formation of linearly
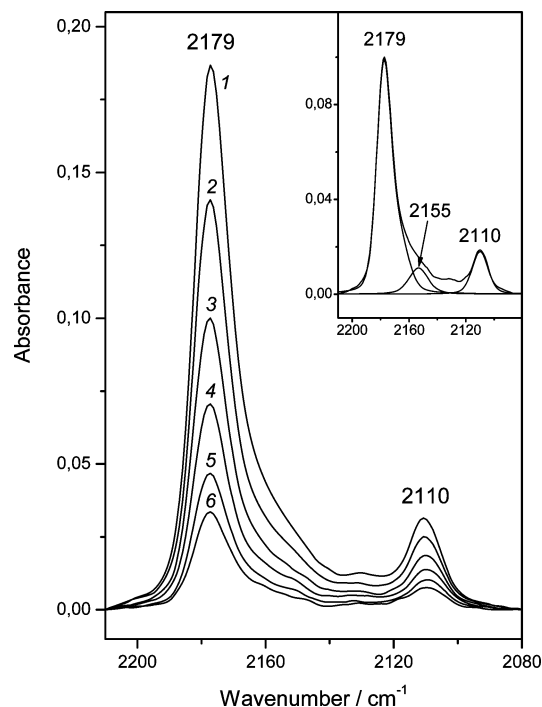
bridged CO complex in Na-FER was found to be 6.5−6.75 Å. Vibrational frequencies of bridged CO complexes were calculated by use of ω_{CO}/r_{CO} correlation obtained for C-down species; using the correlation obtained for O-down species leads to 6 cm^{-1} decrease of CO stretching frequencies.

3.2. Infrared Spectroscopy: *3.2.1. CO Adsorption on Na-ZSM-5.* Variable-temperature FTIR spectra (in the C−O stretching region) of carbon monoxide adsorbed on Na-ZSM-5 are shown in Figure 4. Main IR absorption bands are seen at 2179 and 2110 cm^{-1}, together with a shoulder at about 2155 cm^{-1}. According to the foregoing calculation and also to previous reports[3,31] on CO adsorbed on Na-ZSM-5, the band at 2179 cm^{-1} should correspond to the C−O stretching mode of monocarbonyl species having the CO molecule interacting through the carbon atom with a single Na$^+$ cation. For the same reasons, the band at 2110 cm^{-1} is assigned to isocarbonyl species, in which the adsorbed CO molecule interacts through the oxygen atom with a single Na$^+$ cation. Since all spectra shown in Figure 4 correspond to a low coverage (see below), both carbonyl and isocarbonyl species should be forming only (or at least mainly) on the most coordinatively unsaturated Na$^+$ cations, that is, type II (intersection sites) located at the edge of two intersecting channels.

The shoulder at about 2155 cm^{-1} is assigned to the C−O stretching mode of CO molecules bridging two Na$^+$ ions (i.e., to CO molecules located in dual-cation sites). Two main reasons support this assignment. First, calculations described above have shown that dual-cation sites capable of bridging the CO molecule (forming a Na$^+$···CO···Na$^+$ complex) are likely to be present in Na-ZSM-5. Second, it is well-known[32,33] that the blue shift of the C−O stretching frequency of CO interacting through the carbon atom with an alkali metal cation arises mainly from electrostatic polarization. A second cation facing the oxygen atom of CO partially cancels polarization;[34] hence,
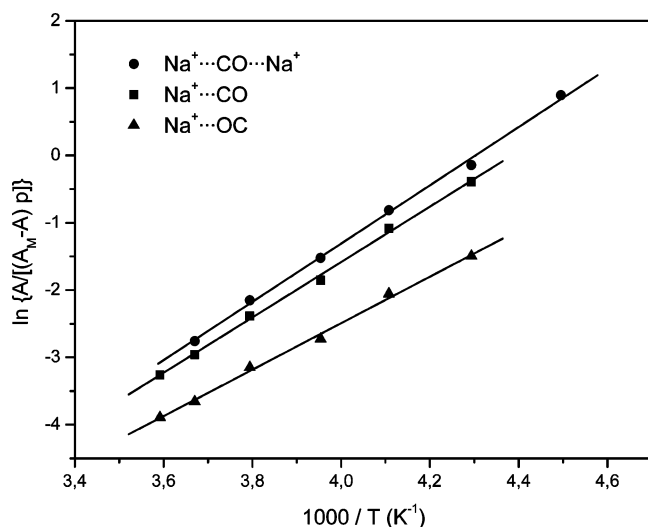
Figure 5. Plot of the left-hand side of eq 4 against the reciprocal of temperature for the IR absorption bands (Figure 4) at 2155 (●, Na$^+$···CO···Na$^+$), 2179 (■, Na$^+$···CO), and 2110 cm^{-1} (▲, Na$^+$···OC).

a smaller blue shift should be expected for CO in a dual-cation site, as experimentally observed.

As described in detail elsewhere,[35] a set of IR spectra recorded (for a fixed CO dose) over a temperature range can be used to determine the standard adsorption enthalpy corresponding to each adsorption complex. Briefly, under adsorption equilibrium at any given temperature, the integrated intensity of a characteristic IR absorption band should be proportional to the fractional coverage, θ, of the adsorbed CO species giving rise to that band. Hence, integrated band intensity A, temperature T, and CO equilibrium pressure p can be considered to be interrelated by the Langmuir-type equation:

$$\theta = A/A_M = K(T)p/[1 + K(T)p] \qquad (2)$$

where A_M stands for the integrated band intensity corresponding to full coverage ($\theta = 1$) and K is the adsorption equilibrium constant. Combination of eq 2 with the well-known van't Hoff equation (eq 3) leads to eq 4:

$$K(T) = \exp(-\Delta H^\circ/RT) \exp(\Delta S^\circ/R) \qquad (3)$$

$$\ln \{A/[(A_M - A)p]\} = (-\Delta H^\circ/RT) + (\Delta S^\circ/R) \qquad (4)$$

When the left-hand side of eq 4 is plotted against the reciprocal of the temperature, the standard adsorption enthalpy, ΔH°, and entropy, ΔS°, can be derived.

Values of integrated band intensity obtained after computer resolution of the variable-temperature IR spectra depicted in Figure 4 were used to obtain the linear plots shown in Figure 5. Note that the needed values of A_M, for which only an approximation was experimentally known, were chosen as those giving the best linear fit of eq 4 for the whole set of experimental data, following the procedure described elsewhere.[35] From the linear plots in Figure 5, the standard adsorption enthalpy obtained for the monocarbonyl species giving rise to the IR absorption band at 2179 cm^{-1} was $\Delta H^\circ = -33.5$ kJ/mol, while for the isocarbonyl species (band at 2110 cm^{-1}) the value of $\Delta H^\circ = -28.5$ kJ/mol was obtained. The bridged Na$^+$···CO···Na$^+$ species (formed on dual-cation sites) showed $\Delta H^\circ = -35.8$ kJ/mol. The estimated error limits in the experimentally determined ΔH° values are about ± 2 kJ/mol. The linear plots in Figure 5 were also used to obtain the corresponding values of standard adsorption entropy. ΔS° was found to be -154 and
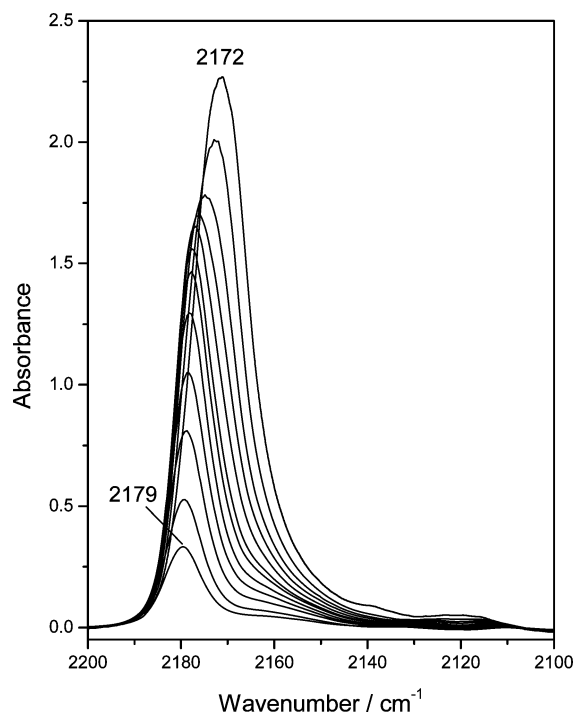

Figure 6. Red shift of the main IR absorption band, in the CO/Na-ZSM-5 system upon increasing CO dose at 77 K.

-136 J/(mol·K) for (C-down) monocarbonyls and (O-down) isocarbonyls, respectively, and -156 J/(mol·K) for the bridged CO complex. The estimated error limits for these ΔS° values are about ± 10 J/(mol·K).

To conclude this section, it should be added that (according to calculations) formation of dicarbonyls, and also monocarbonyls having a smaller interaction energy (and C−O stretching frequency) than those giving rise to the band at 2179 cm^{-1}, should be expected for increasing CO coverage. Figure 6 depicts a series of spectra obtained for successive CO doses at 77 K, clearly showing that the band initially appearing at 2179 cm^{-1} gradually shifts to lower wavenumbers (down to 2172 cm^{-1}) upon increasing CO dose. However, since this shift is likely to involve formation of both less stable monocarbonyls and dicarbonyls, it was not possible to make (from the experimental side) a quantitative assessment of the enthalpy change involved on each of those processes. In fact, for the variable-temperature IR spectra shown in Figure 4, surface coverage was deliberately kept small ($\theta < 0.35$) in order to avoid complications due to formation of dicarbonyl species.

3.2.2. CO Adsorption on K-ZSM-5. Figure 7 shows variable-temperature FTIR spectra of CO adsorbed (at a low coverage) on K-ZSM-5. Distinctive IR absorption bands are seen at 2164, 2150, and 2117 cm^{-1}. By analogy with the CO/Na-ZSM-5 system, and also following literature reports,[36] the band at 2164 cm^{-1} is assigned to the C−O stretching mode of (C-down) monocarbonyl species formed on single K$^+$ ions, while that at 2117 cm^{-1} corresponds to the same mode of (O-down) isocarbonyl species. The band at 2150 cm^{-1} should be assigned to the C−O stretching mode of bridged K$^+$···CO···K$^+$ complexes formed on dual-cation sites. When a large dose of CO was adsorbed on K-ZSM-5, a red shift (by about 3 cm^{-1}) of the band at 2164 cm^{-1} was observed (spectra not shown in Figure 7). Such a shift would be expected from formation of dicarbonyl species, as already pointed out for the CO/Na-ZSM-5 system.

After computer resolution of the variable-temperature spectra shown in Figure 7 and determination of the corresponding
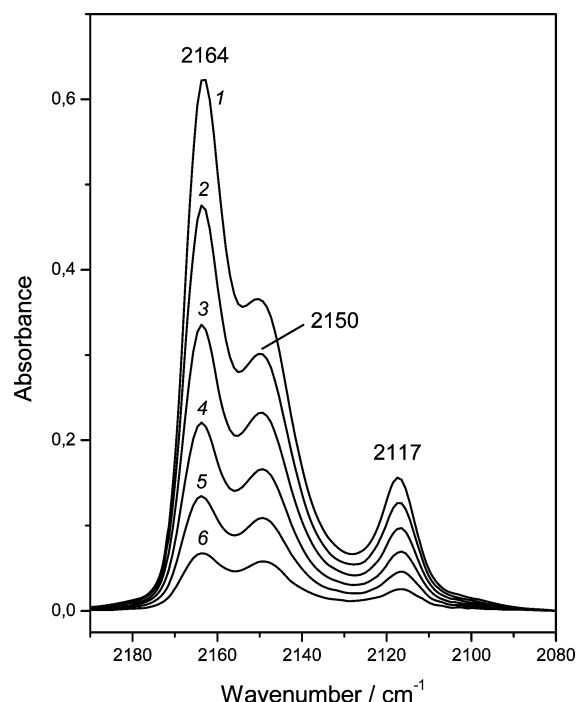
Figure 7. Variable-temperature FTIR spectra (zeolite blank subtracted) of CO adsorbed on K-ZSM-5 (Si:Al = 13.5:1). Temperature (in kelvins) and equilibrium pressure (Torr, in parentheses) were as follows: *1*, 187 (3.46); *2*, 197 (4.34); *3*, 207 (5.18); *4*, 217 (5.91); *5*, 227 (6.51); *6*, 242 (7.07).
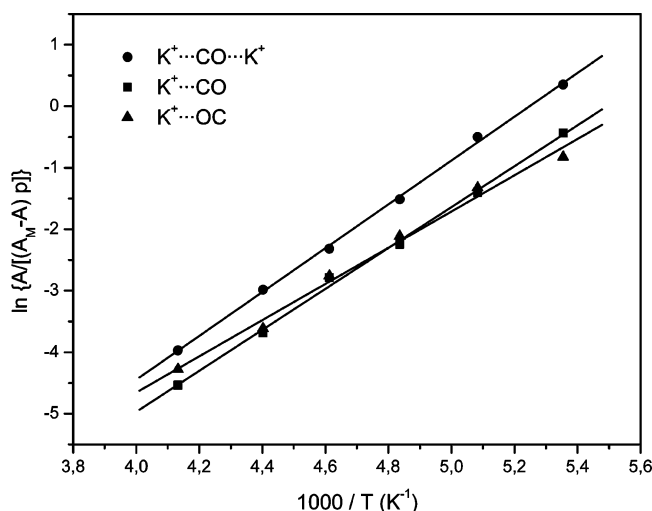

Figure 8. Plot of the left-hand side of eq 4 against the reciprocal of temperature for the IR absorption bands (Figure 7) at 2150 (●, $K^+ \cdots CO \cdots K^+$), 2164 (■, $K^+ \cdots CO$), and 2117 cm^{-1} (▲, $K^+ \cdots OC$).

integrated intensity for each band, the linear plots depicted in Figure 8 were obtained. It should be noted that (in this case) the ^{13}CO counterpart of the band at 2163 cm^{-1} (A_{2163}) occurs in the same frequency region covered by the band at 2117 cm^{-1}. For this reason the integrated intensity of this latter band was corrected by subtracting 1% of the corresponding A_{2163} value.

From the linear plots in Figure 8, the standard adsorption enthalpy obtained for the monocarbonyl species (band at 2164 cm^{-1}) was $\Delta H° = -28.2(\pm2)$ kJ/mol, while for the isocarbonyl species (band at 2117 cm^{-1}) a value of $\Delta H° = -24.5(\pm2)$ kJ/mol was obtained. For the bridged CO species (dual-site band at 2150 cm^{-1}) the corresponding value is $\Delta H° = -31.6(\pm2)$ kJ/mol. Standard adsorption entropy, $\Delta S°$, was found to be $-153(\pm10)$ and $-137(\pm10)$ J/(mol·K) for (C-down) monocarbonyls and (O-down) isocarbonyls, respectively, and $-162(\pm10)$

J/(mol·K) for the bridged CO complex. It should be noted that, for each of the adsorbed CO species, adsorption enthalpy is significantly smaller for K-ZSM-5 as compared to Na-ZSM-5. This fact, which reflects the smaller polarizing power of the K^+ ion, was also observed in previous studies of CO adsorption on Na-FER[7] and K-FER.[6]

4. Discussion

Calculated and experimental results for CO on Na-ZSM-5 are in good agreement regarding both C−O stretching frequencies and adsorption enthalpies. For the monocarbonyl the observed frequency (at the low coverage range) is 2179 cm^{-1}, to be compared with 2184 cm^{-1} calculated for intersection sites and 2177−2181 cm^{-1} calculated for channel-wall sites. Experimentally determined adsorption enthalpy for this species (-33.5 kJ/mol) falls in the range of calculated values (starting at -29 kJ/mol for channel wall sites and going up to -37 kJ/mol for intersection sites). For CO adsorption complexes on dual-cation sites, calculations give ν_{CO} in the range 2152−2162 cm^{-1} and adsorption enthalpies -36 kJ/mol; these values are very close to the corresponding experimentally derived results of 2155 cm^{-1} and -36 kJ/mol. Hence, this band can be confidently assigned to the bridged CO complex. Further support comes from the spectra shown in Figure 9A, which were obtained (at 77 K) for CO adsorbed on two Na-ZSM-5 samples having widely different Si/Al ratios. It is clearly seen that the sample having Si/Al = 13.5 shows a significantly more pronounced shoulder in the region of bridged CO complex than the sample having Si/Al = 30, as expected. For the isocarbonyl complexes, calculations give the adsorption enthalpies -26 and -24 kJ/mol for intersection and channel-wall sites, respectively, and ν_{CO} 2104 cm^{-1}. This is, again, in good agreement with the experimentally determined adsorption enthalpy of -28.5 (±1) kJ/mol, and CO stretching frequency (for low coverage) of 2110 cm^{-1}.

In contrast to Na-ZSM-5, where the IR absorption band corresponding to the bridged CO complexes appears only as a shoulder at the low-frequency side of the main absorption band, in the case of K-ZSM-5 the band corresponding to the bridged CO complex (dual sites) is well developed and shows a distinct maximum at 2150 cm^{-1}, as seen in Figure 7. Corresponding frequency values for monocarbonyl and isocarbonyl species are 2164 and 2115 cm^{-1}, respectively. From variable-temperature IR spectra adsorption enthalpy was found to be -28, -32, and -24 (±1) kJ/mol for the monocarbonyl, the bridged CO species, and the isocarbonyl, respectively. Note that, as observed for Na-ZSM-5, the intensity of the band at 2150 cm^{-1} (bridged CO complexes) markedly increases with decreasing Si/Al ratio (Figure 9B).

For the three types of CO adsorption complexes (monocarbonyl, bridged CO, and isocarbonyl), the experimental adsorption enthalpies are found to be systematically smaller for K-ZSM-5 than for Na-ZSM-5, as expected. The same trend was also found for CO adsorbed on K-FER as compared to CO adsorbed on Na-FER.[6,7] The results shown here for Na-ZSM-5 and K-ZSM-5, together with those obtained previously (using the same level of theory and experiments) for Na-FER[7] and K-FER,[6] can be understood in terms of the recently proposed concept of vibrational dynamics of adsorbed molecules in zeolites.[34] According to this concept, the observed vibrational frequency of adsorbed CO results from a combination of the effect from bottom and the effect from top.

"Effect from bottom" reflects the coordination environment of the metal cation (cation coordination with the framework
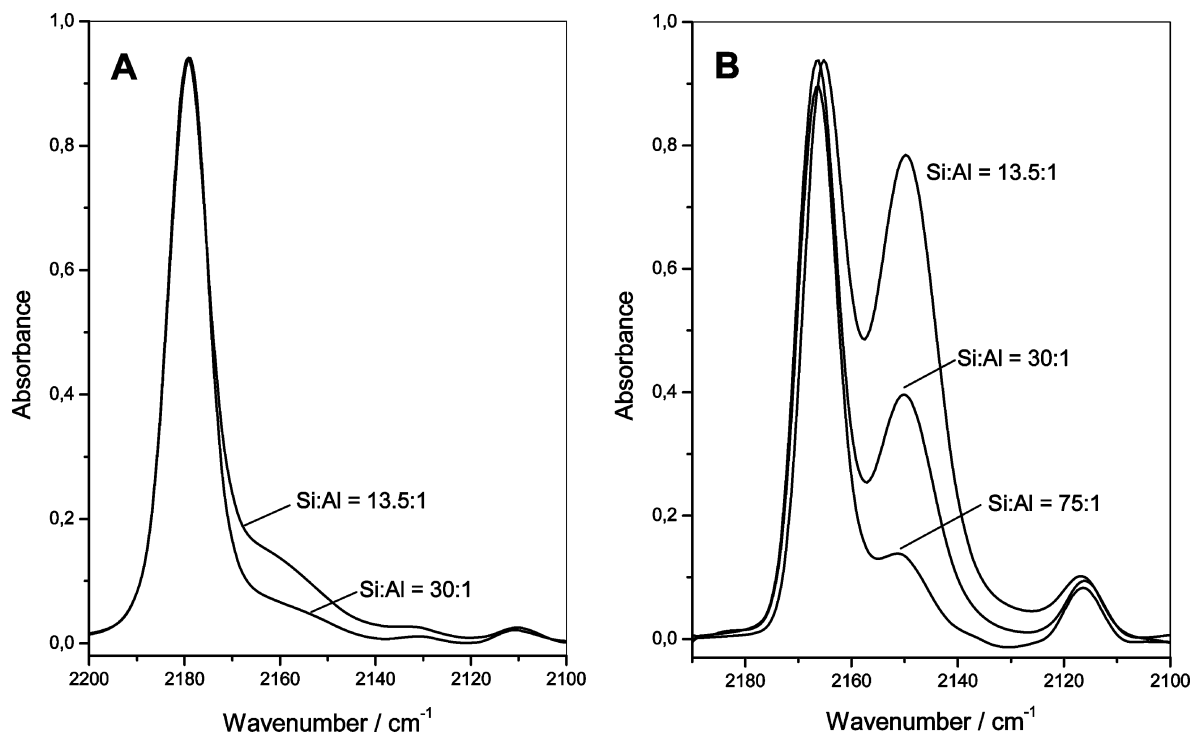
CO Adsorption on Zeolites Na-ZSM-5 and K-ZSM-5

J. Phys. Chem. C, Vol. 112, No. 12, 2008 **4665**

Figure 9. IR spectra of CO adsorbed, at 77 K, on (A) Na-ZSM-5 and (B) K-ZSM-5 samples having different Si:Al ratios.

and accessibility of the site). With increasing cation−framework coordination, the interaction with CO becomes weaker and ν_{CO} becomes lower; this effect is expected to be larger for smaller cations. The data reported in Table 2 for the CO/Na-ZSM-5 system show that carbonyl complexes formed on the intersection sites have up to 7 cm^{-1} higher frequency and they are up to 8 kJ/mol more stable than complexes formed on the channel wall sites. These computational results are consistent with the experimental spectra obtained for increasing CO coverage (Figure 6) showing a shift of the main CO stretching band from 2179 to 2172 cm^{-1} upon increasing CO dosis at 77 K; this band shift is due to the population of less stable sites on the channel wall and also due to the formation of dicarbonyl complexes. Note that such a large shift of main-band maximum upon increased CO coverage was not observed for other Na- and K-zeolites. The IR spectra of CO on K-ZSM-5 recorded at 77 K showed only 4−5 cm^{-1} shift upon increasing CO coverage; a shift smaller than 5 cm^{-1} was also observed for CO adsorbed on Na-FER and K-FER, in agreement with frequencies calculated for intersection and channel wall sites in these zeolites.[6,7] All these effects can be consistently understood in terms of differences in M$^+$ coordination. The Na$^+$ cation at the intersection site is coordinated to only two oxygen atoms of the framework (Figure 2), while the cation at the channel wall site is coordinated to at least three framework oxygens. In addition, cations at the intersection sites are located at the open space of the channel crossing (and thus easily accessible), while cations on the channel wall sites are located closer to the zeolite channel wall; and these differences in coordination explain the difference in corresponding CO stretching frequencies and interaction energies. Note that in Na-FER[7] the experimentally determined ν_{CO} was 2175 cm^{-1}, 4 cm^{-1} less than that found for Na-ZSM-5. Calculated frequencies for the monocarbonyl in Na-FER were found to be in the range of 2174−2178 cm^{-1}, to be compared with the frequency range 2177−2184 cm^{-1} for monocarbonyls in Na-ZSM-5 (Table 2). Differences in ν_{CO} observed upon comparison of Na-ZSM-5 with Na-FER are also due to the different coordination of the Na$^+$ cation with framework oxygen

atoms; in Na-FER there are no cation sites where the Na$^+$ cation is coordinated to only two framework oxygen atoms.[7] For the same reasons, the calculated and experimental adsorption enthalpies (for monocarbonyls) are lower in Na-FER than in Na-ZSM-5 (−30.5 and −33.5 kJ/mol, respectively, for the experimental values). Similar differences were found when Li-FER and Li-ZSM-5 zeolites were compared.[37] Calculations show that, for intersection sites in Na-ZSM-5, the adsorption enthalpy (−36 kJ/mol) is larger than that for the channel-wall sites (about −30 kJ/mol). The experimentally determined value (−33.5 kJ/mol) should correspond mainly to CO adsorption on the intersection sites, since it was derived from spectra corresponding to a coverage range up to 0.35 of a monolayer only. Similarly, for intersection sites, calculations predict higher ν_{CO} (2184 cm^{-1}) than for channel wall sites (2177−2181 cm^{-1}).

The differences between intersection and channel wall sites are less pronounced in K-zeolites than in Na-zeolites. This is due to the fact that site-specificity of the effect from bottom decreases with increasing cation size;[34] in addition, the larger K$^+$ cation is located further above the channel wall than Na$^+$,[38] which makes differences of accessibility to intersection and to channel wall sites smaller.

"Effect from top" reflects the interaction of CO either with the channel wall (resulting in a blue shift of ν_{CO} that usually is not site-specific; for details see refs 6 and 34) or with the secondary extraframework cation. Interaction with the secondary M$^+$ cation—resulting in a decrease of ν_{CO}—is behind the IR band centered at 2155 and 2150 in CO/Na-ZSM-5 and CO/K-ZSM-5, respectively. A remarkable difference between Na-ZSM-5 and K-ZSM-5 is that for the same Si/Al ratio the band due to bridged CO complexes is much more intense in the case of K-ZSM-5. One of the reasons for this difference is that the optimum cation−cation distance in a dual-cation site is larger in the case of potassium than for sodium (7.5 and 6.5 Å, respectively).[34] This larger optimum distance for the K$^+$ dual site would (statistically) make available more dual sites in K-ZSM-5 than in Na-ZSM-5. In addition, due to their larger size, the K$^+$ cations are more exposed to the free space in the

channel system than Na$^+$ cations;[39] also, K$^+$ cations were shown to have a larger preference for intersection sites than Na$^+$ cations.[14] For these reasons, formation of the bridged CO complex would be expected to be more favorable in the case of K-ZSM-5.

5. Conclusions

Carbon monoxide adsorption on the zeolites Na-ZSM-5 and K-ZSM-5 was investigated by combining variable-temperature FTIR spectroscopy with calculations performed at the periodic DFT level. The IR spectra of CO adsorbed on both Na- and K-ZSM-5 show three distinct features: a high-frequency (HF) band (2179 and 2164 cm^{-1} for Na- and K-ZSM-5, respectively), a low-frequency (LF) band (2110 and 2117 cm^{-1} for Na- and K-ZSM-5, respectively), and a band or shoulder at an intermediate frequency range (MF, 2155 and 2150 cm^{-1} for Na- and K-ZSM-5, respectively). While the first two bands (HF and LF) were already well understood for most alkali-metal-exchanged zeolites,[2] the origin of the band at intermediate frequency range (MF band) was not hitherto fully understood. On the basis of a combination of experimental and theoretical investigations, we assign this MF band to linearly bridged CO adsorption complexes (Figure 3d) formed on dual-cation sites. The following arguments support this assignment: (i) For linearly bridged CO adsorption complexes, calculations show lower ν_{CO} and slightly higher adsorption enthalpy than for carbonyl complexes on isolated sites, in agreement with experimental data (MF vs HF bands). (ii) Intensity of MF band increases with decreasing Si/Al ratio. (iii) Intensity of MF band is higher for K-ZSM-5 than for Na-ZSM-5 zeolite samples having the same Si/Al ratio.

Linearly bridged CO adsorption complexes were recently identified in Na-FER and K-FER zeolites,[6,7] and it is shown here that such complexes also form when CO is adsorbed on Na-ZSM-5 and K-ZSM-5. Thus, it is likely that formation of such bridged complexes (where CO interacts with a metal cation via the C-end and with another metal cation via the O-end) could well be a rather general phenomenon in alkali-metal-exchanged zeolites. The probability of formation of the bridged CO adsorption complexes depends on the Si/Al ratio of the zeolite, on the cation radius, and on the zeolite topology. In the case of aluminum-rich zeolites, formation of bridged CO adsorption complexes on dual-cation sites (or even on multiple-cation sites) is expected to be more predominant than formation of carbonyl species on isolated cation sites. In fact, the predominant role of dual- and multiple-cation sites was recently shown for the (Al-rich) zeolite 4A.[40]

References and Notes

(1) Zecchina, A.; Arean, C. O. *Chem. Soc. Rev.* **1996**, *25*, 187.
(2) Hadjiivanov, K. I.; Vayssilov, G. N. *Adv. Catal.* **2002**, *47*, 307.
(3) Tsyganenko, A. A.; Platero, E. E.; Arean, C. O.; Garrone, E.; Zecchina, A. *Catal. Lett.* **1999**, *61*, 187.
(4) Knozinger, H.; Huber, S. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2047.
(5) Arean, C. O.; Manoilova, O. V.; Delgado, M. R.; Tsyganenko, A. A.; Garrone, E. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4187.
(6) Garrone, E.; Bulanek, R.; Frolich, K.; Arean, C. O.; Delgado, M. R.; Palomino, G. T.; Nachtigallova, D.; Nachtigall, P. *J. Phys. Chem. B* **2006**, *110*, 22542.
(7) Nachtigall, P.; Rodriguez Delgado, M.; Frolich, K.; Bulanek, R.; Turnes Palomino, G.; Lopez Bauca, C.; Otero Arean, C. *Microporous Mesoporous Mater.* **2007**, *106*, 162.
(8) Salla, I.; Montanari, T.; Salagre, P.; Cesteros, Y.; Busca, G. *J. Phys. Chem. B* **2005**, *109*, 915.
(9) Salla, I.; Montanari, T.; Salagre, P.; Cesteros, Y.; Busca, G. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2526.
(10) Montanari, T.; Kozyra, P.; Salla, I.; Datka, J.; Salagre, P.; Busca, G. *J. Mater. Chem.* **2006**, *16*, 995.
(11) Treacy, M. M. J.; Higgins, F. M. *Collection of Simulated XRD Powder Patterns for Zeolites*; Elsevier: Amsterdam, 2001.
(12) Tsyganenko, A. A.; Storozhev, P. Y.; Arean, C. O. *Kinet. Catal.* **2004**, *45*, 530.
(13) Arean, C. O.; Manoilova, O. V.; Tsyganenko, A. A.; Palomino, G. T.; Mentruit, M. P.; Geobaldo, F.; Garrone, E. *Eur. J. Inorg. Chem.* **2001**, 1739.
(14) Kucera, J.; Nachtigall, P. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3311.
(15) Birch, F. *Phys. Rev.* **1947**, *71*, 809.
(16) Lermer, H.; Draeger, M.; Steffen, J.; Unger, K. K. *Zeolites* **1985**, *5*, 131.
(17) Nachtigallova, D.; Nachtigall, P.; Sierka, M.; Sauer, J. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2019.
(18) Spuhler, P.; Holthausen, M. C.; Nachtigallova, D.; Nachtigall, D.; Sauer, J. *Chem.—Eur. J.* **2002**, *8*, 2099.
(19) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *48*, 13115.
(20) Kresse, G.; Hafner, J. *Phys. Rev. B* **1994**, *49*, 14251.
(21) Kresse, G.; Furthmuller, J. *Phys. Rev. B* **1996**, *54*, 11169.
(22) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
(23) Blochl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.
(24) Kresse, G.; Joubert, D. *Phys. Rev. B* **1999**, *59*, 1758.
(25) Bludsky, O.; Silhan, M.; Nachtigallova, D.; Nachtigall, P. *J. Phys. Chem. A* **2003**, *107*, 10381.
(26) Bludsky, O.; Silhan, M.; Nachtigall, P. *J. Chem. Phys.* **2002**, *117*, 9298.
(27) Nachtigallova, D.; Nachtigall, P.; Bludsky, O. *Phys. Chem. Chem. Phys.* **2004**, *6*, 5580.
(28) Bulanek, R.; Drobna, H.; Nachtigall, P.; Rubes, M.; Bludsky, O. *Phys. Chem. Chem. Phys.* **2006**, *8*, 5535.
(29) Loffreda, D.; Simon, D.; Sautet, P. *Surf. Sci.* **1999**, *425*, 68.
(30) Sauer, J.; Sierka, M. *J. Comput. Chem.* **2000**, *21*, 1470.
(31) Arean, C. O.; Tsyganenko, A. A.; Platero, E. E.; Garrone, E.; Zecchina, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 3161.
(32) Lupinetti, A. J.; Fau, S.; Frenking, G.; Strauss, S. H. *J. Phys. Chem. A* **1997**, *101*, 9551.
(33) Goldman, A. S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1996**, *118*, 12159.
(34) Nachtigallova, D.; Bludsky, O.; Arean, C. O.; Bulanek, R.; Nachtigall, P. *Phys. Chem. Chem. Phys.* **2006**, *8*, 4849.
(35) Garrone, E.; Arean, C. O. *Chem. Soc. Rev.* **2005**, *34*, 846.
(36) Manoilova, O. V.; Mentruit, M. P.; Palomino, G. T.; Tsyganenko, A. A.; Arean, C. O. *Vibr. Spectrosc.* **2001**, *26*, 107.
(37) Nachtigall, P.; Frolich, K.; Drobna, H.; Bludsky, O.; Nachtigallova, D.; Bulanek, R. *J. Phys. Chem. C* **2007**, *111*, 11353.
(38) Arean, C. O.; Nachtigallova, D.; Nachtigall, P.; Garrone, E.; Delgado, M. R. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1421.
(39) Kucera, P.; Nachtigall, P. *Collect. Czech. Chem. Commun.* **2003**, *68*, 1848.
(40) Arean, C. O.; Delgado, M. R.; Bauca, C. L.; Vrbka, L.; Nachtigall, P. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4657.
(41) Koningsveld, H. v.; Jansen, J. C.; Bekkum, H. v. *Acta Crystallogr.* **1987**, *7*, 564.