

Density Functional Studies of Alkali-Exchanged Zeolites. Cation Location at Six-Rings of Different Aluminum Content

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The interaction of a sodium cation and six-rings of a zeolite framework with different numbers of aluminum atoms was studied with the aid of a density functional method and cluster models. The cation preferentially interacts with the oxygen atoms connected to aluminum at shortest distances of about 220 pm. For six-rings with two or three aluminum atoms, sodium positions on each side of the rings were identified. At both locations Na^+ interacts mainly with the oxygen atoms directed toward the inside of the six-ring. From a comparison of calculated Na–O distances with crystallographic data and vibrational frequencies with the IR spectra of CO on NaY zeolite, it is deduced that the crystallographic SII site in faujasites may actually consist of two cation positions. The sodium location in a ring with one aluminum atom differs from that in the other clusters; it is almost in the plane of the T atoms. The sodium cation was calculated to experience a very low-energy barrier for crossing the six-ring (ca. 10 kJ/mol), which allows easy displacement perpendicular to the ring upon interaction with guest molecules. The vibrational frequency of adsorbed carbon monoxide was calculated as a measure for the polarizing power of the sodium cation. Both the calculated binding energies of CO and vibrational frequency shifts are in agreement with the experimental values. According to our results, the aluminum content of the six-rings can be the reason for the asymmetric broadening of the stretching mode region in the IR spectra of CO adsorbed on NaY zeolite at low pressure. The calculations indicate that a discrimination of six-rings of different aluminum content via IR spectroscopy is difficult.

1. Introduction

Owing to their specific balance of acidic and basic functions, alkali-exchanged zeolites are successfully applied as catalysts or selective sorbents in separation technologies.^{1–6} For both catalytic and sorption processes a concerted action of polarizing alkali cations and basic oxygen atoms is discussed.^{7,8} Therefore, it is important to establish the strength of active centers and their relative positions in the zeolite structure. Various experimental methods and simulation techniques have been applied to study the positions of alkali cations relative to the zeolite framework and the interaction of alkali ions with guest molecules. In the present work we shall focus on faujasites (X and Y zeolites). X-ray and neutron diffraction supply precise information for different alkali cation positions in zeolite structures and their occupancies.^{9–14} However, diffraction techniques are unable to distinguish Si and Al centers in tetrahedral framework positions and they provide only averaged values over the whole sample. Since the geometry of the zeolite rings depends on the number of aluminum centers of a ring, the exact cation location at each window will also be affected by the aluminum content of a ring.

Since the acid–basic properties as well as the local arrangement at individual zeolite rings depend strongly on the aluminum

content of the ring, it is necessary to establish the actual distribution of rings with different numbers of aluminum atoms in a given zeolite sample. This is a problem for zeolites with high Al content, e.g., faujasites, while zeolites with high Si content contain at most one Al center per ring. However, there is still no certified method to measure this distribution. It is not even clear yet whether the ordering in the zeolite ring is governed by thermodynamics or whether it depends on kinetic factors during preparation. Thus, it remains open whether the zeolite samples of equivalent structure and Al/Si ratio have the same ordering or not. Serious attempts have been made to estimate the ordering of T atoms (Si or Al) in the faujasite framework of NaX and NaY zeolites^{15,16} using ²⁹Si NMR. This spectroscopy yields information about the ratio of the silicon tetrahedra surrounded by different numbers (0–4) to aluminum tetrahedra. Various possible ordering schemes satisfying some additional requirements (such as the Loewenstein rule,¹⁷ minimal electrostatic repulsion, etc.) have been simulated^{15,16} to gain insight into the ordering of T atoms in faujasites. However, the large number of possible structures does not allow a determination of the fractions of the various rings with different number of aluminum atoms.

A promising technique for elucidating the location and properties of metal cations in oxides and zeolites is IR spectroscopy of adsorbed probe molecules. Usually weakly interacting diatomic molecules are employed as probes—carbon monoxide, molecular nitrogen, or hydrogen.^{2,3,5,18} Since the vibrational frequency shift of these adsorbed molecules is essentially due to their polarization in the field of the metal

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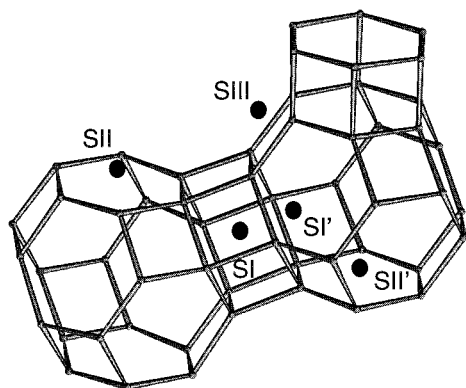


Figure 1. Structure of faujasite with crystallographic cation sites.

cation, the stretching frequency peak position provides information about the location of the cation and its local environment. Both the stretching modes of adsorbed CO and N₂ increase with the polarizing power of the alkali metal cation, i.e., with decreasing radius of the ion.^{2,3,5} Recently, Knözinger and Huber^{2,19} established that the CO vibrational band splits after adsorption on NaY zeolite at low temperature and pressure. It is suggestive to assign the four observed bands to various locations of the sodium cation at zeolite rings that contain different numbers of aluminum atoms. This would provide an experimental method for discriminating rings of different aluminum content in Y zeolites. As shown previously,²⁰ density functional (DF) calculations with basis sets of good quality are able to accurately reproduce experimental frequency shifts obtained for CO adsorbed on a series of alkali metal ions in zeolite cavities.

Here, we report a DF study on the interaction of a sodium cation close to zeolite six-rings (of faujasite structure), which contain different numbers of aluminum atoms (one to three, distributed according to the Loewenstein rule). The goal of the present work was to elucidate the effect of the aluminum content of the ring on the cation position and its Lewis acidity as measured by the vibrational frequency of adsorbed CO. We studied whether CO adsorption is really a tool that allows experimental determination of the distribution of six-rings of different aluminum content in zeolite samples. In the following section we present details about choice and justification of the model clusters. In the third section we report the results for the optimized geometries of different clusters and the corresponding sodium positions. Adsorption energies and calculated frequency shifts of CO adsorbed at the metal cation centers are also discussed. In the fourth part, the calculated Na⁺ positions are compared with crystallographic cation sites of NaX and NaY zeolites. Finally, the assignment of the experimentally observed CO vibrational shifts is discussed in connection with the calculated data. In a companion work²¹ we have studied the basicity of oxygen centers in six-rings of different aluminum content and we demonstrated that calculated O 1s core level shifts provide a reliable measure for the base strength of such centers.

2. Models and Method

2.1. Zeolite Clusters. The zeolites X and Y have a faujasite structure that is composed of sodalite cages (Figure 1). These cages consist of rings with four or six T atoms (four- or six-rings, respectively) connected by oxygen atoms. In a faujasite framework, two neighboring sodalite cages are linked by hexagonal prisms. Crystallographic data show that the T atoms both in the four- and six-rings lie in one plane, while the oxygen

atoms are positioned above or below this plane, oriented inside or outside the ring. This is important for our considerations because this alternation determines variations in the cation–oxygen distances and in the properties of the oxygen atoms. The main feature of the faujasite structure are the so-called “supercages” with a diameter of about 1.3 nm, which are connected by windows of a diameter of 0.74 nm. These cavities and windows are interesting for catalytic or adsorption processes in faujasites because they are large enough to accommodate small or medium-size molecules, while the opening of the largest (six-ring) windows of the sodalite cage allows only hydrogen molecules to enter at low temperature; it is too narrow even for molecules such as nitrogen or carbon monoxide.^{2,5}

Owing to the presence of three-valent aluminum in tetrahedral framework positions instead of tetravalent silicon, the zeolite framework is negatively charged and its charge is compensated by different cations. Since these cations are outside the lattice, they are easy exchangeable, which allows a wide variation of zeolite properties. In H forms of zeolites, the charge-compensating cations are protons that are attached to framework oxygen atoms, thus forming bridging hydroxyl groups (Al–OH–Si). In alkali forms of zeolites (as well other zeolites, which contain metal cations) the metal ions are located near Al positions of the lattice because of the local negative charge there. According to crystallographic results, five different types of cationic sites exist in a faujasite structure (Figure 1).²² Site SI is in the hexagonal prism, where the cation is surrounded by six oxygen atoms (three from both six-rings; the other oxygen atoms of each six-ring are directed toward the outside of the prism). Site SII is located at the six-ring of the sodalite cage from the side of the supercage. In this position the cation is near three oxygen atoms directed toward the inside of the ring but further away from those oxygen centers directed outside. Site SIII is also on the wall of the supercage but in front of the four-rings of a sodalite cage or a hexagonal prism. Owing to the local geometry of the framework, a cation at this position has a lower number of nearest-neighbor oxygen centers and thus is coordinatively less saturated compared to other sites. For this reason such positions are not occupied in the Y zeolite, but only in the X zeolite, where the cation concentration is higher. There are two more positions SI' and SII' situated in the sodalite cage in front of the SI and SII positions, respectively. Both sites are at six-rings, similar to SII, but at different M⁺–O distances. (Actually, for pure alkali forms of X and Y zeolites, site SII' is not occupied by cations.^{9–11,13,14}) As mentioned above, at low temperature guest molecules can access only cations in the supercage. Thus, in Y zeolites probe molecules can interact only with cations at SII positions; for X zeolite they can interact with cations at both SII and SIII positions.

In the present work we studied the interaction of a sodium cation with six-rings of sodalite cages where the six-rings contain one (Al-1), two (Al-2), or three (Al-3) aluminum atoms (Figures 2–5). For a cluster Al-2, both possible relative positions of the two aluminum atoms in the rings as allowed by the Loewenstein rule¹⁷ are considered, *para*-(Al-2p) and *meta*-(Al-2m) (Figures 3 and 4). The free valencies of silicon and aluminum atoms in the ring are saturated by hydrogen atoms. The initial positions of the T atoms and oxygen centers in the ring were taken from mean crystallographic values;^{10,11} the structures of the cluster models were partially optimized keeping the T atoms fixed. This approach is similar to the real situation in the zeolite framework, where the motion of the T atoms is restricted because of the two additional bonds outside the ring, while the positions of the oxygen atoms are much more flexible.

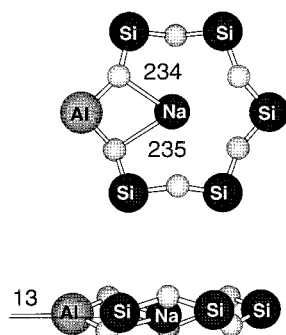


Figure 2. Sodium cation location at the six-ring with one aluminum center (Al-1). Only Na–O distances shorter than 250 pm are given.

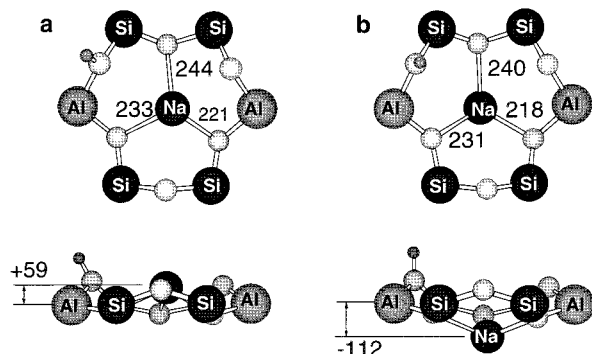


Figure 3. Sodium cation location at the cluster Al-2p. Only Na–O distances shorter than 250 pm are given. Na⁺ in (a) anti and (b) syn positions with respect to the centers O_{in}.

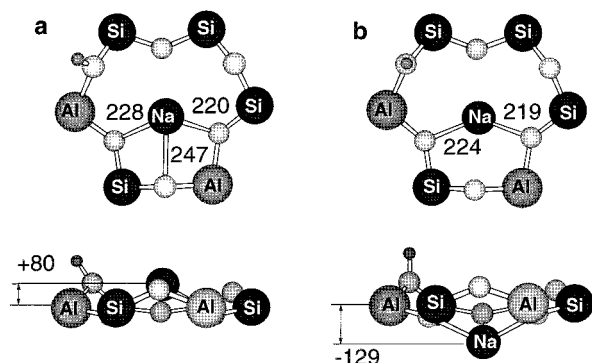


Figure 4. Sodium cation location at the Al-2m cluster. Only Na–O distances shorter than 250 pm are given. Na⁺ in (a) anti and (b) syn positions with respect to the centers O_{in}.

The number of Al atoms in the ring determines the negative charge of the model cluster. The negative charge of a ring with only one Al center is simply compensated by the sodium cation inside the ring. However, for clusters with two or three Al atoms the problem arises of how to correctly compensate the negative charge of the cluster, since it is not possible to have more than one Na⁺ in a six-ring. In the real faujasite framework each aluminum atom participates in four rings, which contain four or six T atoms. If in one of these rings there is more than one aluminum atom, the negative charge of the framework is compensated by a sodium (or other) cation at one of the neighboring rings. In our models this implies that other compensating cations have to be put somewhere outside the ring. We tested charge compensation by two cations, H⁺ and Na⁺, connected to an oxygen center from the Al–O–Si bridge that is directed outside the ring in order to reduce the direct effect of the compensating cation on the central Na⁺ ion. We checked the effect of charge compensation on the properties of

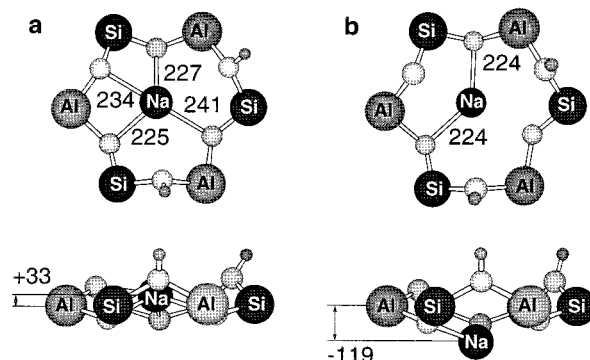


Figure 5. Sodium cation location at the cluster with three aluminum atoms (Al-3). Only the Na–O distances shorter than 250 pm are given. Na⁺ in (a) anti and (b) syn positions with respect to the centers O_{in}.

the oxygen nearest the compensating ion. A good reference for this purpose is an oxygen atom of the cluster Al-1 with Na⁺ in the center, since in this case no further charge compensation is required.

We used two criteria for comparison of oxygen centers in different charge-compensated models: the Kohn–Sham (KS) O 1s core level energy and the vibrational frequency of an acidic “probe” molecule (HCl) coordinated to the oxygen atom considered. The probe molecule was placed opposite the compensating cation with the H end oriented to the framework oxygen center at the distance optimized for the cluster with one aluminum atom. For the two variants of charge compensation, the vibrational frequencies changed by less than 2% (16 cm^{−1} for H⁺ compensation and 35 cm^{−1} for Na⁺ compensation). The core level energy increased by less than 0.5% (0.2 eV for H⁺ compensated cluster and 0.03 eV for Na⁺ compensated one) compared to the reference oxygen center of the six-ring with one Al atom. Thus, both charge compensation strategies seem to be reliable, with the compensation by protons being computationally more economic.

Comparison of the charge-compensated model with the charged cluster (without a compensating proton) showed a strong overestimation of the Na⁺ bonding to the charged cluster and correspondingly very weak interaction of the central sodium cation with a carbon monoxide probe molecule. The C–O distance increased by 0.2 pm relative to the calculated bond length of the free molecule and the vibrational frequency decreased by 28 cm^{−1}, opposite the experimental trend. Thus, charged models can entail computational artifacts due to the excess negative charge of the cluster. We therefore refrained from using them in our study.

After optimization of the initial six-rings, a Na⁺ ion was added near the center of the ring, and the position of oxygen atoms of the ring, of the sodium ion, and of the charge-compensating cations (where present) were optimized. Since in most clusters two possible locations of the sodium ion were found, it is convenient to use the plane of T atoms as reference. In this convention the oxygen atoms (O_{out}) that are outside the ring are considered to be above the ring and those directed inward the ring (O_{in}) to be below the ring (Figures 3–5).

For the sake of comparison with the SIII cationic site in NaX zeolite, the sodium location at a four-ring with one or two aluminum atoms was also considered.

Adsorption of carbon monoxide on the cationic site of zeolite is modeled by coordination of a CO molecule to Na⁺ via the carbon end (Figure 6).

2.2. Computational Details. Density functional calculations were performed using the ParaGauss code for parallel calcula-

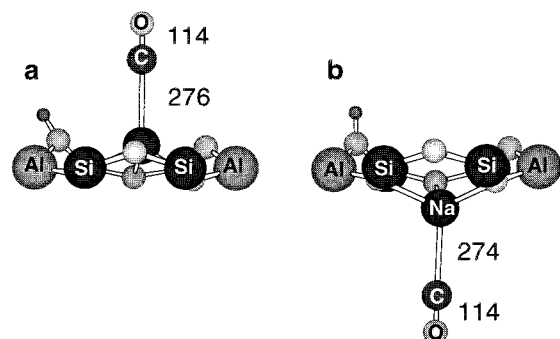


Figure 6. Adsorption of carbon monoxide on a sodium cation at the ring Al-2p with Na⁺ in (a) anti and syn (b) positions.

tion.²³ Contracted Gaussian-type basis sets were taken from a previous study:²⁰ (6s1p) → [3s1p] for H, (9s5p1d) → [5s4p1d] for O and C, (12s9p1d) → [6s4p1d] for Al and Si, and (12s8p1d) → [6s5p1d] for Na. The basis sets of all non-hydrogen atoms have one d-type polarization exponent. All contractions are of generalized form. The auxiliary fitting basis sets employed to represent the electron charge density are constructed in a standard fashion by properly scaling the s and p exponents of the orbital basis sets.²⁴ The fitting functions are used to calculate the classic Coulomb contribution to the electron–electron interaction. The exchange–correlation energy and the matrix elements of the exchange–correlation potential are evaluated by numerical integration.^{25,26} The geometric structures were automatically optimized using analytical energy gradients.²⁷

After optimization of the complete cluster model, a constrained frequency analysis was carried out where the C–O and Na–C stretching modes and the Na–C–O bending vibrational mode were taken into account. Normal harmonic vibrational frequencies were calculated by diagonalizing the mass-weighted force constant matrix in internal coordinates. The force constants were obtained numerically by finite differences of analytical energy gradients.

Two strategies for the geometry optimization were tested for the clusters Al-1 and Al-2p. In the first one all calculations of the clusters described in the previous section were performed with a gradient-corrected functional based on Becke’s exchange and Perdew’s correlation functional²⁸ (BP level). The second procedure started with a geometry optimization at the LDA level (local density approximation)²⁹ followed by a single-point calculation at the optimized geometry with the BP functional. The later method often works well and allows substantial time savings. Unfortunately, for present models we obtained unrealistically low binding energies for the adsorption of carbon monoxide (4.1 and 0.5 kJ/mol for the clusters with one and two aluminum atoms, respectively) as well as low or even slightly negative values for the frequency shift of the CO stretching mode (Table 1). These results are probably due to an overestimation of the interaction of Na⁺ with oxygen atoms of the ring during the geometry optimization at the LDA level. Indeed, in this latter approach sodium is found almost in the center of the ring with a mean Na⁺–O_{in} distance of 225 pm (for Al-2p), while the corresponding distances of the BP optimization are 230–233 pm, closer to the crystallographic structure (distances of 233–239 pm are expected), as discussed in section 4.1. Therefore, only results obtained by the first strategy, i.e., consistent calculations at the BP level of theory, will be reported in the following.

In this work, interatomic distances are given in pm, vibrational frequencies in cm^{−1}, binding energies (BE) in kJ/mol, and Mulliken charges in e.

TABLE 1: Comparison of the Levels of Geometry Optimization for CO Adsorbed on Na⁺ at Al-1 and Al-2p Rings

	method ^a	$\Delta\nu^b$	Δr^c	BE ^d
Al-1	LDA	+11	−0.2	4.1
	BP	+24	−0.3	13.2
Al-2p	LDA	−5	−0.0	0.5
	BP	+38	−0.4	17.4

^a Geometry optimization and evaluation of the C–O vibrational frequency at the LDA or BP levels of theory. ^b C–O vibrational frequency shift $\Delta\nu$ (in cm^{−1}) with respect to the frequency of free CO, 2165 cm^{−1} (LDA) and 2111 cm^{−1} (BP). ^c Difference Δr in C–O bond length (in pm) with respect to value of the free molecule, 113.6 pm (LDA) and 114.5 pm (BP). ^d Binding energy BE of CO (in kJ/mol) evaluated at the BP level for the distance optimized at the LDA (single-point BP calculation) or BP levels of theory.

TABLE 2: Binding Energies^a (in kJ/mol) of a Sodium Cation at Six- and Four-Rings with Different Numbers of Aluminum Centers

	cluster	anti	syn
six-rings	Al-1	519	
	Al-2m	515	515
	Al-2p	515	513
	Al-3	493	505
four-rings	Al-1	461	
	Al-2	477	

^a Calculated at the BP level of theory.

3. Results

3.1. Location of the Sodium Cation. The optimized sodium cation positions in the six-rings studied are shown in Figures 2–5. In these schemes short Na–O distances and the deviation of the cation from the plane of the ring are given. As expected, for all structures considered Na⁺ prefers positions near oxygen centers bonded to Al atoms rather than those of Si–O–Si bridges. Also, the cation is far from oxygen centers that are connected to compensating cations.

The mean T–O distances in the rings increase from 169.5 pm in the cluster Al-1 to 175.5 pm in the cluster Al-3 mainly because of the larger number of the longer Al–O bonds. Mean Al–O and Si–O distances elongate only by about 1 pm from the cluster with one Al atom to the cluster with three Al centers. The mean Na–O distances of the rings with two or three aluminum atoms are close to the value obtained for the simpler model Al(H)(OSiH₃)₃.²⁰ When Na⁺ is present in the ring, the oxygen centers move slightly inward toward the ring.

Binding Energy of Na⁺ to the Ring. The calculated BE of a sodium ion at six-rings with one or two aluminum atoms are 513–519 kJ/mol (Table 2), while for the cluster Al-3 the BE is 493–505 kJ/mol. The binding energies of the cation at six-rings are calculated to be larger than those at the four-rings. For instance, the Na⁺ BE at the four-ring with two aluminum atoms is 40 kJ/mol lower than at the six-rings with two Al centers. This is in agreement with the experimental observation that in faujasites sodium cations prefer locations at six-rings (SII and SI’ sites) over SIII sites. An additional reason for the absence of sodium cations in SIII sites of NaY zeolites is that in these materials four-rings with one aluminum center dominate because of the low Al content. This reduces the BE of sodium in the SIII position even further, by 16 kJ/mol. The binding energy of Na⁺ at the SIII position is probably underestimated to some extent in our model calculations because we did not account for the cation interaction with neighboring four-rings. However, considering the local geometry around SIII sites,^{10,13} this contribution should not be crucial.

It is interesting to compare the relative energies of the two

isomeric clusters with two aluminum atoms, Al-2p and Al-2m, both for the initial negatively charged cluster and the clusters with Na^+ . The ring with aluminum atoms in the para position is more stable by 21–23 kJ/mol. This agrees with Dempsey's rule³⁰ applied to six-rings of faujasites.

Six-Ring with One Aluminum Atom. The sodium cation in the cluster Al-1 is located almost in the plane of the ring, only 13 pm above, near the aluminum atom, at 234 and 235 pm from the oxygen atoms of the Al–O–Si bridges. After carbon monoxide coordination, the sodium ion shifts slightly higher, along the axis perpendicular to the ring. This could indicate that the potential energy surface for Na^+ motion perpendicular to the ring is flat, since even such a weak interaction as that with CO can shift the sodium ion position. After CO adsorption the sodium cation is 47 pm above the plane of T atoms and the BE is reduced only by 1 kJ/mol compared to the optimized position. The energy gain from carbon monoxide adsorption (13 kJ/mol) easily compensates this loss of binding energy.

Six-Rings with Two Aluminum Atoms. The geometry optimizations of the two clusters containing two aluminum atoms were performed for rings whose negative charge excess is compensated by a proton. For both structures two possible positions of the sodium ion were found, one at each side of the ring. The positions are denoted by reference to the oxygen atoms directed inward toward the ring (O_{in}), syn or anti. The anti cation position is located almost in the plane of the oxygen atoms O_{out} , which are directed toward the outside of the ring; it lies 59 pm above the plane of T atoms for Al-2p and 80 pm above the reference plane for Al-2m (Figures 3a and 4a). Despite the fact that Na^+ is on the side of the oxygen atoms O_{out} , it is closer to the oxygen atoms O_{in} because they are directed inward toward the ring. The position of the O_{in} centers with respect to the ring is important not only because they are near the center of the ring but also because their nonbonding lone pair orbitals are directed inward toward the ring. The lone-pair density of the O_{out} centers is mainly directed toward the outside of the six-rings studied. Therefore, the centers O_{out} can take part in the coordination of cations outside the ring or they can play a role of basic centers (on the walls of the supercage) in catalytic reactions or adsorption. Indeed, the sites with the highest proton affinity in the clusters studied correspond to oxygen centers directed outward from the ring.²¹

The sodium position syn is on the side of the centers O_{in} (Figures 3b and 4b), at 112 pm below the plane of T atoms for the cluster Al-2p or 129 pm for Al-2m. This is 60–70 pm beyond the plane of the oxygen atoms at the same side of the ring. In the syn configuration, Na^+ is by more than 40 pm farther from the O_{out} atoms at the other side of the ring, compared to the anti position. The distances Na– O_{in} to the closer oxygen centers are by 1–5 pm shorter. The two sodium positions have almost the same energy for both clusters (Table 2). This also suggests that the interaction of a sodium cation with O_{out} oxygen atoms, directed outside the ring, is weak in both positions.

A comparison between T–O distances in the zeolite ring for the two locations of the cation shows small changes of individual bond lengths (by less than 2 pm); the mean values are the same, 172 pm.

Six-Ring with Three Aluminum Atoms. The positions of a sodium cation at the cluster containing three aluminum atoms are similar to that with two Al centers. The first one (anti) is 33 pm above the ring, and the second one (syn) is 119 pm below the plane of T atoms (Figure 5). In this ring all oxygen atoms participate in Al–O–Si bridges, but owing to the charge compensation two of them have each a proton attached. In the

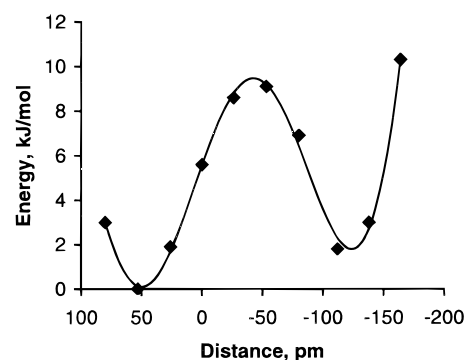


Figure 7. Potential energy barrier for Na^+ motion perpendicular the Al-2p ring.

anti position, Na^+ is closer to the plane of T atoms than in clusters with two aluminum centers, and the cation interacts not only with two of the O_{in} atoms (at distances of 225–227 pm) but also with one of the O_{out} oxygen centers (at 234 pm), which in this cluster model, is also oriented inward the ring. Although the third O_{in} center is also involved in a Al–O–Si bridge, it is far from the central cation (241 pm) because it is between the oxygen atoms connected to the charge-compensating cations. In the syn position, Na^+ is almost at the same distance to the O_{in} atoms but much farther from the others (the mean Na– O_{out} distance increases by 40 pm). This position is 12 kJ/mol more stable than the corresponding anti configuration (Table 2).

Four-Rings. Similar to the six-ring, the four-ring with one aluminum atom has only two oxygen atoms connected to Al. The four-ring is smaller, Na^+ is located farther from the ring, and its interaction with both oxygen atoms of the Al–O–Si bridges is weaker. For this reason the binding energy of Na^+ is the lowest of all clusters investigated. In the four-ring with two Al centers, the sodium cation is at 233–235 pm from two of the oxygen atoms. The position is shifted in the direction opposite the charge-compensating cation.

Energy Barrier for Crossing a Six-Ring. To gain information on the potential energy barrier for the transfer of a sodium cation between the two local minima observed for three of the six-rings, several intermediate sodium positions at the cluster Al-2p were partially optimized. For each structure the Na^+ position was fixed relative to the ring and the positions of the oxygen centers and the charge compensation proton were optimized. As seen in Figure 7, there is a clear energy barrier for crossing the ring, which however, is only about 10 kJ/mol. The barrier occurs when Na^+ is in the plane of the oxygen atoms directed inside the ring (at about –50 pm) because of the short Na–O distances. During the transfer of the cation across the ring, the O_{in} centers shift slightly outward to keep optimal distances. A similar energy check for the sodium motion perpendicular to the ring with one aluminum center did not reveal other stationary points except the (global) minimum described earlier.

3.2. Adsorption of CO. Binding Energy of CO. Carbon monoxide is adsorbed on a sodium cation via the carbon end as shown in Figure 6 for the cluster Al-2p. The calculated distances, CO binding energies, and vibrational C–O frequencies for different clusters are collected in Table 3. For comparison also the parameters of CO adsorbed on bare Na^+ are given. The calculated parameters for the bare cation (BE, C–O and Na–CO distances, CO frequency shift) are similar to those calculated by other DF or conventional quantum chemical methods.⁶ Our values are closest to the results of the quadratic configuration interaction procedure, QCISD. However, as shown earlier,²⁰ bare cation models can be used only for

TABLE 3: Calculated Properties of CO Adsorbed on a Sodium Cation at Six- and Four-Rings with Different Numbers of Aluminum Centers^a

cluster	r (C—O) ^b	r (Na—C)	BE	$\Delta\nu$	$\Delta\nu$ (exptl) ^c	ν (Na—CO) ^d	q (Na)
Na ⁺ —CO six-rings ^e	113.6	260.6	31	73		175	
Al-1	114.2	277.8	13	24	14	112	0.51
Al-3, anti	114.2	277.5	14	28	23	111	0.51
Al-2p, anti	114.1	276.0	16	32	29	118	0.53
Al-2m, anti	114.1	276.0	18	33	29	122	0.54
Al-3, syn	114.1	273.3	19	37	40	126	0.61
Al-2p, syn	114.1	273.8	19	38	40	125	0.62
Al-2m, syn	114.1	272.5	20	38	40	130	0.61
four-ring							
Al-2	114.0	269.6	23	43			0.62

^a Distances r (in pm), binding energy BE of CO (in kJ/mol), frequency shift $\Delta\nu$ (in cm⁻¹) of the CO stretching vibration with respect to the free molecule, and cation charge q of the cluster without adsorbate (in e) calculated at the BP level of theory. ^b r (C—O) of free CO is calculated to be 114.5 pm. ^c Proposed assignment of measured vibrational frequency shifts (ref 2). ^d Frequency of the Na—CO stretching mode (in cm⁻¹). ^e For the cluster models, see Figures 2–5.

qualitative estimates while a quantitative study requires a realistic representation of the zeolite framework. The present cluster model calculations are not the exception (Table 3).

The calculated BE values for CO adsorption on the extended model clusters are close to the experimentally observed heats of adsorption of CO on NaY zeolite,³¹ 21–24 kJ/mol. The probe molecule is found to be closer to the sodium cations in their syn positions for clusters Al-2 and Al-3 than in the anti positions. The BE in the former positions are also slightly higher. This is due to the higher positive charge of Na⁺ in the syn position (+0.61 to 0.62 e) compared to the anti configuration (+0.51 to 0.54 e) and the weaker repulsion between CO and the O_{out} centers. For the anti position of Na⁺, the O_{out} centers are inside the supercage, while for the syn position those centers are directed to the sodalite cage and their repulsion with the probe molecule is reduced. When the cation is located in the anti position, the BEs of carbon monoxide are lower but still on the order of the experimental values. As expected, at all the clusters the C—O bond is slightly shorter than in the free CO molecule (by 0.3–0.4 pm). The interaction of CO with Na⁺ at the four-ring with two aluminum atoms is stronger than at the six-rings, as judged by both the Na—CO distances and the BE.

As mentioned in the previous section, the potential energy surface of the sodium motion perpendicular to the ring is relatively flat. Since the BE of carbon monoxide is higher than the estimated energy barrier, the cation is expected to move after CO adsorption in order to find a deeper energy minimum. Such a displacement of Na⁺ out of the ring was observed for all clusters studied. For the six-rings with two aluminum atoms, the new position of sodium is only about 10 pm farther from the ring. Stronger displacements are observed for the clusters Al-1 (32 pm) and anti-Al-3 (26 pm). In both cases, the initial sodium position is closer to the plane of T atoms (compared to the corresponding location in the clusters with two aluminum centers) where it is more strongly screened by the oxygen atoms of the ring. When Na⁺ is farther from the plane of the ring, the repulsion between CO and the framework oxygen atoms is reduced. As a result of the sodium displacement, the mean Na—O distances increase in all clusters by 3–6 pm.

After carbon monoxide adsorption, the positive charge on sodium cation decreases by 0.1 e because of transfer of electron density from the probe molecule.

C—O and Na—CO Stretching Frequencies. As pointed out in the Introduction, one of the goals of our study was to

distinguish the effect of the number of Al atoms in the six-ring on the C—O vibrational frequency shift after adsorption on a sodium cation located at this ring. For all six-rings the calculated frequencies shift in the expected direction, i.e., to higher values, by a reasonable amount, 24–38 cm⁻¹ (Table 3). There is a clear correlation between the BE of CO to the model clusters and the calculated frequency shift of the probe molecule (Table 3).

The calculated frequency shift of CO on Na⁺ at the ring with one aluminum center (24 cm⁻¹) is smaller than those of other rings. Intuitively one might expect the opposite trend for this cluster because it has the lowest number of basic oxygen atoms (directly connected to aluminum). By this reason, the sodium ion should be less screened by the ring and thus should interact more strongly with the probe molecule. However, the most favorable position of sodium at this cluster is closer to the plane of the ring than at the other clusters; therefore, the effective screening of the cation is higher and the distance between the probe molecule and the oxygen atoms of the ring is shorter.

The calculated vibrational frequencies of CO on Na⁺ at the clusters with two aluminum atoms, Al-2p and Al-2m, coincide for the both sodium positions; the shifts are 32–33 cm⁻¹ for the anti position and 38 cm⁻¹ for the syn position. Therefore, these two isomeric rings can hardly be distinguished by the stretching frequency of adsorbed CO. However, a distinction can be made between the two sodium locations observed (syn and anti) because of their difference of 6 cm⁻¹.

The frequency shift for carbon monoxide adsorbed on Na⁺ at the syn position of the cluster Al-3 (37 cm⁻¹) is almost the same as the shift for the syn position of the clusters Al-2. The calculated frequency of CO on sodium in the anti position at this ring (28 cm⁻¹) falls between the frequencies of clusters with one and two aluminum atoms.

From a combinational band in the IR spectra of CO adsorbed on Na—ETS-10, a value of 122 cm⁻¹ was very recently derived for the Na—CO vibrational mode.³² The frequencies, 111–130 cm⁻¹ (Table 3), calculated for this mode from different cluster models agree well with this experimental value.

4. Discussion

4.1. Comparison of the Calculated Cationic Positions with Crystallographic Data. *Comparison with SII Site.* Since we aim at modeling the location of the sodium cation at the SII site of faujasite, we have to compare the averaged calculated Na—O distances with the corresponding crystallographic values that are also averaged (Table 4). At this crystallographic position, the cation interacts with two groups of oxygen atoms from the nearest six-ring: O(2) atoms, directed inside the ring at Na—O distances of 233–239 pm, and O(4) oxygen atoms, directed outside the ring at a distance of 286–291 pm. For the clusters with two or three aluminum atoms, the mean calculated distances between sodium and the centers O_{in} (whose location corresponds to the O(2) crystallographic position when Na⁺ is at a SII site) are 230–236 pm. This value is close to the crystallographic values of both NaY and NaX zeolites, 233–239 pm (Table 4). The calculated mean distances to O_{out} centers are substantially different for the two possible Na⁺ positions with respect to the ring, as calculated for the clusters with two and three aluminum centers. When the sodium cation is close to the plane of the ring (anti structures in Figures 3–5), the mean Na—O_{out} distances are 272–288 pm. These distances increase to 313–350 pm when Na⁺ is on the other side of the ring. A comparison of these two sets of values with the crystallographic data, 286–291 pm (O_{out} corresponds to the crystallographic position O(4)), shows that the anti positions of sodium fit better to Na⁺ in the cationic site SII of faujasites.

TABLE 4: Comparison of Mean Na–O Distances (in pm) between Crystallographic Values for SI' and SII Positions and Calculated Cluster Results for Six-Rings

zeolites ^a	Na(SI')-O		Na(SII)-O		f_{ring}^b				$\langle \text{Na-O} \rangle^c$	
	O(3)	O(2)	O(2)	O(4)	Al-1	Al-2m	Al-2p	Al-3	O _{in}	O _{out}
NaY (2.4) ^d	244	310	233	289	25	37.5	37.5		237	275
NaY (2.4) ^e	224	293	239	286						
NaY (2.6) ^f	232	298	234	289						
NaX (1.2) ^g	224	294	234	289		25		75	232	276
NaX (1.2) ^h	224	294	236	291						
cluster ⁱ	anti position		syn position							
Al-1	249	252								
Al-2m	236	288	234	350						
Al-2p	233	279	230	334						
Al-3	231	272	233	313						

^a Si/Al ratio of the samples given in parentheses. ^b Fraction of rings estimated for models with Si/Al ratios of 2.42 for NaY and 1.18 for NaX; ref 15. ^c Average of cluster results based on the values for the anti position of the sodium cation. ^d Reference 9. ^e Reference 11. ^f Reference 14. ^g Reference 10. ^h Reference 13. ⁱ For the cluster models see Figures 2–5.

Since the crystallographic values are averaged over rings of different aluminum content, the corresponding calculated values are also presented in Table 4 (based on the anti positions of sodium). The relative contribution of different six-rings was taken from the estimates of ref 15.³³ For the distances to the crystallographic centers O(2), the averaged calculated distances Na–O_{in} (232 pm for NaX, 237 pm for NaY) agree well with the experimental values, 234–236 pm for NaX and 233–239 pm for NaY.^{9–13} However, the calculated distances to the farther lying oxygen centers O_{out} are 11–15 pm shorter than the corresponding crystallographic values (Table 4). This indicates that the other sodium position (syn) may also exist in the actual zeolite structure and that it may indeed contribute to an elongation of the measured distances Na–O(4). Such a contribution does not change the distance to the nearest oxygen atoms O(2) because these distances are almost the same at both calculated sodium locations (Table 4). The existence of two cation subsites at the SII crystallographic site, which correspond to the two structures presented in Figures 3–5, is supported by a comparable binding energy of Na⁺ at these pairs of clusters for the Al-2 and Al-3 rings (Table 2). As will be discussed in the next section, IR spectra of CO on NaY zeolite show some amount of adsorbed probe molecules with a frequency shift higher than that of the main peak; thus, in these samples a small fraction of less saturated sodium cations exists. The experimental frequency shift of this band is very close to the shift calculated for Na⁺ in the syn position at the six-rings. Indeed, in the syn position the inner oxygen centers O_{in} of the six-ring are directed toward the supercage, and therefore, the sodium cations are located deeper in the supercage. According to the comparison with the crystallographic data the anti position of sodium is more populated in real zeolites than the syn position.

Since the SII site is at the six-ring window of the sodalite cage that faces the supercage, the exact location of the sodium cation at this site depends on the orientation of the oxygen atoms of each individual ring with respect to the supercage. If the centers O_{in} are directed inside the sodalite cage, sodium at a SII site will be located at the other side of the ring, in the anti position. If these oxygen atoms are pointing to the supercage, then the cation (also in this cage) will be in the syn position with respect to them and correspondingly will be located further into the supercage.

Comparison with Other Crystallographic Sites. There are three more cationic positions in faujasites in front of the six-ring windows: SI, SI', and SII'. SI sites in the hexagonal prism present a rather specific case because there cations interact also with a second six-ring. For the cations in the sodalite cage (SI'

and SII') the influence of the surrounding cage walls is stronger than that of the walls of the supercage on Na⁺ in the SII site. Probably this effect causes somewhat larger deviations of the mean calculated distances from the crystallographic data for sodium at the SI' site (Table 4). The experimental distances to the nearest oxygen atoms (O(3) for SI' site) are in general 5–10 pm shorter than those for the SII site, while the distances to the farther oxygen atoms (O(2) for the SI' site) are 3–21 pm longer (Table 4). These distance changes can be related to increased contributions of the syn position of Na⁺ when the cation is at the SI' site (compared to the SII site).

As mentioned in the description of the faujasite structure in section 2.1, it is well-known that sodium cations do not occupy SII' sites, despite this position being expected to be energetically equivalent to the SI' and SII sites. An explanation of this phenomenon can be based on the low calculated energy barrier of the Na⁺ ring crossing. In the presence of water or even when the sample is exposed to air, guest molecules enter mainly into the supercage and interact with the cations there. If there are some sodium cations in the SII' site in the sodalite cage, but near the supercage wall, the guest molecules can interact also with these cations through the six-ring window. Since the distance between the guest molecule and Na⁺ in this case is longer than the optimal one, the guest molecules abstract the cation from the sodalite cage into the supercage (to the SII site) where the molecule–cation interaction is stronger. The energy gain from the interaction is probably high enough for barrier crossing (estimated to 10 kJ/mol) because even such a weakly interacting molecule as CO has a BE of at least 13 kJ/mol (see above). After removal of the guest molecules, there is no driving force for the sodium cations to move back into the sodalite cage and they remain at the SII sites. Note also that crystallographic studies on molecular adsorption^{11–13} show a displacement of Na⁺ along the axis perpendicular to the ring (in the direction of the supercage).

4.2. Assignment of the Experimental C–O Frequency Shifts. The experimentally observed values for the stretching vibrational shift of CO on NaY zeolites at low temperature are about +30 cm^{−1},³ but a recent more accurate spectral study at low CO pressure furnished a more detailed picture of this frequency range.^{2,19} Deconvolution of the spectrum yields four bands at 2183, 2172, 2166, and 2157 cm^{−1} with shifts of 40, 29, 23, and 14 cm^{−1}, respectively, relative to free CO (Figure 8). The strongest peak features a shift of 29 cm^{−1}. Since six-rings with two aluminum atoms are expected to dominate in Y zeolites,^{15,16} this band can be considered as the frequency of carbon monoxide adsorbed on sodium at a SII position of such

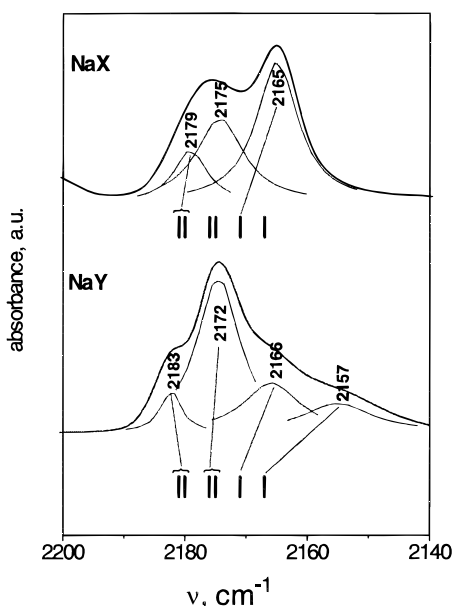


Figure 8. Positions of the calculated frequency shifts of CO (bars) with respect to the measured IR bands of CO on NaY and NaX zeolites (refs 2 and 34).

a ring. The experimental shift fits well the calculated value of the clusters Al-2p and Al-2m with Na⁺ in the anti position, 32–33 cm^{−1} (Table 3).

As seen in Table 3 and Figure 8, the calculated shifts vary less than the experimental values. However, this is not unexpected, since the vibrational shifts result from a delicate balance of various interactions in the zeolite environment. Nevertheless, our calculations suggest that rings of different aluminum content may give rise to the splitting of the CO frequency upon adsorption at Na⁺ in the SII positions. The calculated vibrational frequency shifts are rather small. Therefore, we are only able to propose a tentative assignment of the experimental spectrum, based on the assumption that our calculations represent the proper cause of this inhomogeneous line broadening.

As can be seen from Table 3, the calculated frequency shifts for the six-rings fall into four groups: (i) 37–38 cm^{−1} for the clusters Al-2m, Al-2p, and Al-3 with Na⁺ in the syn position; (ii) 32–33 cm^{−1} for the clusters Al-2m and Al-2p with Na⁺ in the anti position; (iii) 28 cm^{−1} for the cluster Al-3 with Na⁺ in the anti position; (iv) 24 cm^{−1} for the cluster Al-1. The size of the CO vibrational frequency shift of these groups roughly correlates with the CO binding energy at the cluster. Following the order of the shifts, the highest frequency band with a shift of 40 cm^{−1} in the experimental spectrum of CO on NaY is assigned to adsorption at Na⁺ in the syn position at six-rings of the type Al-2m, Al-2p, or Al-3, with a calculated shift of 37–38 cm^{−1}. As discussed above, this sodium position corresponds to a fraction of Na⁺ cations attributed to the crystallographic SII site but located deeper in the supercage (because of the structures of the various syn positions). The principal band in the IR spectrum, with a shift of 29 cm^{−1}, is characteristic for Na⁺ cations in the anti position at the six-rings with two aluminum atoms. The high intensity of this band correlates with the high concentration of Al-2 six-rings in NaY zeolite^{15,16} and with the conclusion that most Na⁺ cations in the SII position of actual zeolite samples are located in an anti configuration (see section 4.1). Extending the present line of argument, the two lower frequency bands with experimental shifts of 23 and 14 cm^{−1} are assigned to Na⁺ in the anti position at six-rings with three and one aluminum centers, respectively. Figure 9

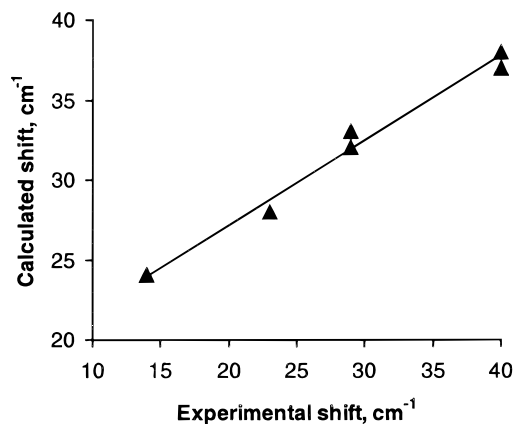


Figure 9. Correlation between calculated and experimental vibrational frequency shifts of CO on NaY zeolite corresponding to the proposed assignment.

displays the linear relationship between the calculated and experimental frequency shifts according to the proposed assignment. The correlation is quite good although the calculated values, as mentioned above, appear somewhat scaled compared to the experimental shifts.

An argument for the assignment of the IR peak of CO on NaY zeolite with the shift of 23 cm^{−1} to Na⁺ at a six-ring containing three Al centers can be brought from the IR spectra of CO on NaX zeolite. In this zeolite about 70% of the six-rings have three Al atoms.^{15,16} In the experimental IR spectra of CO on this zeolite, two main bands of almost equal intensity are observed at 2175 and 2165 cm^{−1} with shifts of 32 and 22 cm^{−1}.³⁴ In the NaX zeolite, sodium cations are accessible for CO not only in SII sites (in front of six-rings) but also in SIII sites (near four-rings). The sodium populations in these sites are almost equal,¹⁰ and the two bands of adsorbed CO can be simply assigned to them. Since at position SIII the sodium cation is bound more weakly to the zeolite framework (as discussed in section 3.1), it interacts more strongly with CO, and correspondingly, the CO vibrational frequency should be higher. Thus, one should expect a higher frequency shift for CO adsorbed on Na⁺ at the SIII site than at the SII site. Therefore, the higher frequency band with a shift of 32 cm^{−1} should be assigned to sodium at position SIII, and the band with a shift of 22 cm^{−1} to Na⁺ in position SII at the six-ring that contains three aluminum atoms. Indeed, the calculated frequency shift of CO on sodium at the four-ring with two Al is higher than that for both clusters of Al-3, syn and anti (Table 3).

Let us briefly discuss an alternative assignment of the two lower frequency bands that is based on the similarity of calculated and experimental values of shifts. Under this assumption, the IR band with a shift of 23 cm^{−1} is assigned to CO adsorption on Na⁺ at rings with one aluminum center (24 cm^{−1} calculated for cluster Al-1). CO adsorption on sodium in anti position at rings with three aluminum centers (shift of 28 cm^{−1} for calculated cluster Al-3) would then be assigned to the most intensive peak of the IR spectrum with a shift of 29 cm^{−1}, together with adsorption at rings of two aluminum centers in the anti position. However, in this alternative assignment the origin of the lowest frequency band with a shift of 14 cm^{−1} in the experimental spectrum remains unclear. Also, in this case experimental and calculated frequency shifts do not exhibit a clear linear correlation.

The model cluster calculations demonstrate convincingly that different numbers of aluminum atoms in six-rings can cause an inhomogeneous line broadening of the stretching vibrational

mode of CO adsorbed on NaY zeolite at low pressure. However, the cluster models do not support a one-to-one correspondence between vibrational shifts and the numbers of aluminum centers in a six-ring (see both assignments of the experimental band with a shift of 40 cm⁻¹). Therefore, IR spectra of adsorbed CO can be hardly used to estimate the fractions of six-rings with different numbers of aluminum atoms.

5. Conclusions

Our model cluster study showed that the sodium cation location at the six-rings of faujasites depends on the aluminum content of the ring. The cation preferentially interacts with oxygen atoms connected to aluminum centers at distances down to 218–234 pm (for rings with different numbers of Al atoms). For six-rings with two or three aluminum atoms, sodium positions on each side of the ring were established. At both locations Na⁺ interacts mainly with the oxygen atom directed inward toward the six-ring (corresponding to the crystallographic O(2) oxygen atoms when Na⁺ is at a SII cation position). The sodium configuration at the ring with one aluminum atom differs from the other clusters, since this cluster has only two oxygen atoms involved in Al–O–Si bridges and Na⁺ is situated near both of them, almost in the plane of the T atoms.

The binding energies of a sodium cation at six-rings with one and two aluminum atoms are calculated to be very similar, about 515 kJ/mol. The binding of Na⁺ to the four-rings is weaker than to all six-rings, in agreement with experimental data. The six-ring with two aluminum atoms in the para position is 21–23 kJ/mol more stable than the corresponding meta configuration, in agreement with Dempsey's rule.

A low potential energy barrier for Na⁺ crossing the plane of the six-ring (about 10 kJ/mol) allows easy motion of the sodium cations perpendicular to the ring upon interaction with guest molecules. This finding is supported by the experimentally observed mobility of sodium cations at SII sites and has been related to the absence of alkali cations at SII' sites.

On the basis of a comparison of calculated Na–O distances with crystallographic data as well as of vibrational frequencies with IR spectra of CO on NaY zeolite, we proposed that the crystallographic SII site of faujasites actually comprises two cation locations. The mean Na–O distances of the anti position of Na⁺ are closer to the crystallographic values. From this finding we deduced that most of the cations found in the SII site in actual zeolite samples are located in such a configuration.

The calculated CO adsorption energies and vibrational frequency shifts were found to agree with experimental values. Carbon monoxide is bound more strongly to sodium cations at four-rings and at the syn position of six-rings. The calculated CO frequency shifts for different zeolite model clusters can be separated into four groups, similar to the experimental IR spectra of CO on NaY zeolite. However, rather close frequency shifts have been calculated for six-rings of different aluminum content. Therefore, it does not seem feasible to estimate fractions of different six-rings in a sample on the basis of the IR spectra of CO. Thus, the present results show that the original model for the interpretation of the experimental CO spectra^{2,19} was somewhat oversimplified. As a consequence, the earlier band

assignments have to be reconsidered on the basis of the theoretical treatment of the NaY/CO interaction.

Calculated sodium charges and vibrational frequency shifts of CO adsorbed at six-rings show that Na⁺ features a higher polarizing power in the syn configuration (when this configuration exists). For the anti position of sodium, the highest cation charges and the largest CO frequency shifts were found for rings with two aluminum centers.

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References and Notes

- (1) Barthomeuf, D. *Catal. Rev.* **1996**, *38*, 521.
- (2) Knözinger, H.; Huber, S. J. *Chem. Soc., Faraday Trans.* **1998**, *94*, 2047.
- (3) Zecchina, A.; Otero Arean, C. *Chem. Soc. Rev.* **1996**, *25*, 187.
- (4) Bezoukhanova, C.; Kalvachev, Yu. *Catal. Rev.* **1994**, *36*, 125.
- (5) Zecchina, A.; Bordiga, S.; Lamberti, C.; Spoto, G.; Carneli, L.; Otero Arean, C. *J. Phys. Chem.* **1994**, *98*, 9577.
- (6) Ferrari, A. M.; Ugliengo, P.; Garone, E. J. *Chem. Phys.* **1996**, *105*, 4129.
- (7) Corma, A.; Fornes, V.; Martin-Aranda, R. M.; Garcia, H.; Primo, J. *Appl. Catal.* **1990**, *59*, 237. Corma, A.; Martin-Aranda, R. M.; Sanchez, F. J. *Catal.* **1990**, *126*, 192.
- (8) Itoh, H.; Miyamoto, A.; Murakami, Y. *J. Catal.* **1980**, *64*, 284.
- (9) Eulenberger, G. R.; Shoemaker, D. P.; Keil, J. G. *J. Phys. Chem.* **1967**, *71*, 1812.
- (10) Olson, D. H. *Zeolites* **1995**, *15*, 439.
- (11) Fitch, A. N.; Jobic, H.; Renouprez, A. *J. Phys. Chem.* **1986**, *90*, 1311.
- (12) Czjzek, M.; Fuess, H.; Vogt, T. *J. Phys. Chem.* **1991**, *95*, 5255.
- (13) Vitale, G.; Mellot, C. F.; Bull, L. M.; Cheetham, A. K. *J. Phys. Chem. B* **1997**, *101*, 4559. Auerbach, S. M.; Bull, L.; Henson, N. J.; Metiu, H. I.; Cheetham, A. K. *J. Phys. Chem.* **1996**, *100*, 5923.
- (14) Grey, C. P.; Poshni, F. I.; Gualtieri, A. F.; Norby, P.; Hanson, J. C.; Corbin, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 1981.
- (15) Klinowski, J.; Ramdas, S.; Thomas, J. M. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1025.
- (16) Melchior, M. T.; Vaughan, D. E. W.; Jacobson, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4859.
- (17) Loewenstein, W. *Am. Mineral.* **1954**, *39*, 92.
- (18) Hadjiivanov, K.; Lamotte, J.; Lavalley, J.-C. *Langmuir* **1997**, *13*, 3374. Hadjiivanov, K. *Appl. Surf. Sci.* **1998**, *135*, 331.
- (19) Huber, S.; Knözinger, H. *Appl. Catal. A* **1999**, *181*, 239.
- (20) Ferrari, A. M.; Neyman, K. M.; Rösch, N. *J. Phys. Chem. B* **1997**, *101*, 9292.
- (21) Vayssilov, G. N.; Rösch, N. *J. Catal.*, in press.
- (22) Smith, J. V. *Adv. Chem. Ser.* **1971**, *101*, 171.
- (23) Belling, T.; Grauschopf, T.; Krüger, S.; Nörtemann, F.; Stauffer, M.; Mayer, M.; Nasluzov, V. A.; Birkenheuer, U.; Rösch, N. *ParaGauss*, version 1.9; Technische Universität München: München, 1998.
- (24) Dunlap, B. I.; Rösch, N. *Adv. Quantum Chem.* **1990**, *21*, 317.
- (25) Pople, J. A.; Gill, P. M. W.; Johnson, B. G. *Chem. Phys. Lett.* **1992**, *199*, 557.
- (26) Gill, P. M. W.; Johnson, B. G.; Pople, J. A. *Chem. Phys. Lett.* **1993**, *209*, 506.
- (27) Nasluzov, V. A.; Rösch, N. *Chem. Phys.* **1996**, *210*, 413.
- (28) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822; **1986**, *34*, 7406.
- (29) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
- (30) Dempsey, E.; Köhl, G. H.; Olson, D. H. *J. Phys. Chem.* **1969**, *73*, 387.
- (31) Egerton, T. A.; Stone, F. S. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 22. Soltanov, R. I.; Paukshtis, E. A.; Yurchenko, E. N. *Kinet. Katal.* **1980**, *23*, 164.
- (32) Zecchina, A.; Otero Arean, C.; Turnes Palomino, G.; Geobaldo, F.; Lamberti, C.; Spoto, G.; Bordiga, S. *Phys. Chem. Chem. Phys.* **1999**, *1*, 1649.
- (33) The percentage corresponds to the simulated lowest energy ordering for samples with a Si/Al ratio closest to the one used in the diffraction studies.
- (34) Hadjiivanov, K.; Knözinger, H. *Chem. Phys. Lett.* **1999**, *303*, 513.