A density functional study of the electronic structure of sodalite

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We have conducted a first principles density functional theory (DFT) calculation to explore the electronic structure of sodalite at various stages of Al-substitution. By calculating the electronic structure of both substituted and unsubstituted frameworks, with and without the presence of extra-framework atoms, we show that Al-substitution and cation compensation essentially affect the electronic structure only at the upper valence band edge (i.e., the frontier orbitals of reactivity theory). In addition, we show that the equilibrium positions of the extra-framework cations are located in the vicinity of the frontier orbitals which are preferentially localized near aluminum.

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I. INTRODUCTION

Zeolites have become the subject of an increasing number of first principles studies due to their abundant and diverse applications in industry. They consist of corner sharing SiO4 and AlO4 tetrahedra linked in three-dimensional networks. These networks arrange in a number of configurations containing open pores offering unique environments for guest molecules. Zeolites have been used traditionally as heterogeneous catalysts,1–4 commercial adsorbents, molecular sieves5–7 and in liquid and gas separations.8,9 More recently, the application of zeolites has broadened with the suggestion of new materials utilizing the diversity of pore structure in zeolites to control optical and electronic properties.10,11

Much of the early first principles work in zeolites has been restricted to calculations on clusters of molecules carefully controlled to mimic a given crystal geometry. These calculations, however, only approximate the true crystalline structure of zeolites and often prohibitively large clusters are required to ensure macroscopic properties are sufficiently converged.12 However, improvements in algorithms for calculating electronic structure now enable one to conduct computations of fully periodic zeolite crystals,13–17 making it possible to predict the complete electronic structure of zeolites in the solid state. In the future, predictions of adsorption behavior using clusters18–21 may be extended to fully periodic lattices.

To explore the nature of Al-substitution and to better understand bonding and interactions within zeolites, we have conducted a fully periodic, first principles investigation of the electronic structure of various forms of the sodalite framework. We are ultimately concerned with the effect of Al substitution on the electronic states compared to the unsubstituted (siliceous) compound in connection with catalysis and aluminum ordering. We have therefore examined sodalite structures with differing amounts of Al and extra-framework ions. We present a comparison of the resulting density of states (DOS) and relate these properties to the characteristics of bonding.

II. SODALITE STRUCTURES

We studied three frameworks of sodalite with differing amounts of Al and extra-framework ions. These are (1) silica sodalite [Si12O24], (2) cation-free sodalite [Al6Si6O24], (3) anhydrous sodalite [Na6Al6Si6O24], and (4) natural sodalite [(NaCl)2(NaAlSi)6O24].

Silica sodalite (hereafter referred to as S1) is the Al-free (and thus extra-framework ion-free) form of sodalite. Its unit cell (Fig. 1-A) is cubic and consists of an interconnecting network of SiO4 tetrahedra joined at each vertex (O atom). In S1 all tetrahedra are equivalent. The S1 framework has been synthesized in the presence of organic templates22 where the tetrahedra were observed to be aligned along vectors with components parallel to the lattice vectors—forming a highly symmetric framework. The unit cell of S1 is commonly referred to as the β-cage; it resembles a truncated octahedron (Fig. 2) with each vertex corresponding to a Si atom (or equivalently the center of an SiO4 tetrahedron).

Cation-free sodalite (hereafter referred to as S2) can be conceptualized by replacing every other Si atom in S1 with an Al atom. Its unit cell (Fig. 1-B) consists of alternating SiO4 and AlO4 tetrahedra and is similar to the S1 framework except that the tetrahedra are rotated with respect to the lattice boundary (and each other). The structural properties of this framework have been described in a previous paper.23 The S2 framework has not been observed experimentally and is not believed to exist naturally without the presence of extra-framework atoms. We included this purely hypothetical structure as a conceptual tool in order to isolate the effects of aluminum substitution without extra-framework ions.

Anhydrous sodalite (hereafter referred to as S3) is obtained by adding six Na atoms to the cation-free framework (Fig. 1-C). The six accompanying valence electrons fill the holes (electron vacancies) left by the substitution of Al atoms for Si in S2. The Na atoms are located in the special positions described below for S4. The S3 framework can be synthesized through the dehydration of hydro-sodalite.24

Natural sodalite (hereafter referred to as S4) is the natu-
rally occurring form of sodalite. Its unit cell is similar to that of \( \text{S}_2 \), but with the addition of 10 Na and 2 Cl atoms (extra-framework ions). The Cl atoms are situated at the corner and the center of the unit cell in \( \text{S}_3 \), coinciding with the centers of each \( \beta \)-cage in the fully periodic structure. The Na\( ^{1+} \) ions occupy four of the eight positions situated on the interior of the \( \beta \)-cage near the center of the Si/Al sixfold rings. Each Na\( ^{1+} \) is therefore tetrahedrally coordinated with three oxygen and one Cl\( ^{-} \). The other four Na\( ^{1+} \) atoms are situated on the exterior of the \( \beta \)-cage near the remaining sixfold rings. Each Cl\( ^{-} \) ion is tetrahedrally coordinated with four Na\( ^{1+} \) ions. In \( \text{S}_3 \), the Na atoms occupy three of the four interior sites and likewise for the exterior sites.

III. COMPUTATIONAL METHOD

We used a variable cell molecular dynamics scheme and the local density approximation (LDA) to density functional theory (DFT). This strategy allows us to calculate ground state structural and electronic properties of periodic systems. The damped variable-cell molecular dynamics scheme allows us to simultaneously relax atomic positions and lattice parameters through self-consistent calculations of crystal energy, forces and stress. The efficiency of this method has been demonstrated in previous calculations of silica, silicates, alumina and alumina-silicates.

Norm-conserving pseudopotentials were used with a chosen planewave cut-off energy of \( E_{\text{pw}} = 64 \) Ry. Cut-off radii of \( r_s = r_p = 1.45 \) au and \( r_s = r_p = r_d = 2.00 \) au were used for oxygen and aluminum, respectively, and were thoroughly tested in a previous study of \( \text{Al}_2\text{O}_3 \). Cut-off radii of \( r_s = r_p = r_d = 2.00 \) au., \( r_s = r_p = r_d = 2.72 \) au., and \( r_s = r_p = r_d = 1.27 \) au were used for Si, Na, and Cl, respectively. The self-consistent calculation was achieved with one k-point generated in the irreducible Brillouin zone by a \( 2\times2\times2 \) Monkhorst-Pack grid for frameworks \( \text{S}_1, \text{S}_2, \) and \( \text{S}_4 \), and at the \( \Gamma \) point for framework \( \text{S}_3 \). The Perdew-Zunger parameterization of the Ceperley-Alder exchange-correlation potential was used for all calculations. Density of states were calculated using the tetrahedral method with 10 k-points calculated in the irreducible wedge.

Optimized structural parameters are given in Table I along with experimental data from Richardson and from

FIG. 1. Unit cells of sodalite structures: (A) silica sodalite (\( \text{S}_1 \)), (B) cation-free sodalite (\( \text{S}_2 \)), (C) anhydrous sodalite (\( \text{S}_3 \)), and (D) natural sodalite (\( \text{S}_4 \)). \( \text{S}_1 \) is cubic with space group \( \text{Im} \overline{3} \text{m} \). \( \text{S}_2, \text{S}_3, \) and \( \text{S}_4 \) have space group \( \text{P} \overline{4} \text{3n} \). AlO\(_4\) and SiO\(_4\) coordination tetrahedra are represented by dark and light tetrahedra respectively. Na (dark spheres) and Cl (light spheres) are located in special positions (8\( e \)) and (2\( a \)) respectively.

FIG. 2. (A) Model representation of the sodalite \( \beta \)-cage. Vertices correspond to Si (Al) positions and edges (roughly) represent Si–O–Si (Si–O–Al) bonds. (B) The periodic structure of solid sodalite.

FIG. 3. Valence density of states (DOS) for the four sodalite frameworks: (A) silica sodalite (\( \text{S}_1 \)), (B) cation-free sodalite (\( \text{S}_2 \)), (C) anhydrous sodalite (\( \text{S}_3 \)), and (D) natural sodalite (\( \text{S}_4 \)).
Hassen and Grundy\textsuperscript{33} for \textbf{S1} and \textbf{S4} respectively. Our calculated parameters show good agreement—bond lengths and angles within 1%—with available x-ray data for both of these structures—typical of LDA-based calculations of oxides. A full discussion of the structural properties of these sodalite frameworks has been given in a previous paper.\textsuperscript{23}

### IV. VALENCE DENSITY OF STATES

In Fig. 3 we show the complete valence density of states (DOS) for the four sodalite frameworks. The valence bands can be grouped into three distinct band regions separated by gaps (labeled I, II, and III in Fig. 3-A). Decomposing the electronic states into specific angular momentum contributions for each atom, we found that the majority of the DOS contribution comes from oxygen states.\textsuperscript{34} We further examined the characteristics of these states by plotting the charge density distribution associated with each band region. Figure 4 shows the charge densities for band regions I, II, and III of \textbf{S1} along a plane slicing a four-fold ring. It clearly shows that band regions I, II, and III are characteristic of oxygen 2s, bonding 2p, and non-bonding 2p orbitals respectively. The total charge densities calculated for \textbf{S1} and \textbf{S4} are provided in Fig. 5 for comparison.

Comparison of the \textbf{S1} and \textbf{S2} DOS shows that, aside from slight differences in the definition of peaks, there is little qualitative difference between the two eigenvalue spectra. When Al was substituted, there was a slight widening of the gap between groups I and II and a reduction of the gap between groups II and III. The widths of all three band regions decreased and, particularly in band region III, the peaks were more sharply resolved. This trend continued with \textbf{S3} and \textbf{S4}, though there are additional peaks in \textbf{S4} at around \textapprox 12 eV due to the Cl 3s states, and in band region III due to Cl 3p states.

The narrowing of band regions, widening of gaps, and higher peak resolution are all characteristic of the longer Al–O and O–O bond-lengths observed in \textbf{S2} as compared to the Si–O bond length in \textbf{S1}. In order to rationalize the gap reduction between regions II and III, we observe that when Al was substituted in silica sodalite, there was a substantial

| TABLE I. Structural parameters for all four sodalite frameworks. Bond lengths are reported in Å and bond angles in degrees. Experimental values are reported in parentheses for \textbf{S1} and \textbf{S4} as given by references (22) and (33) respectively. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | \textbf{S1}     | \textbf{S2}     | \textbf{S3}     | \textbf{S4}     |
| \text{Si-O}    | 8.91 (8.827)    | 8.86            | 8.83            | 8.79 (8.88)     |
| \text{Al-O}    | 1.60 (1.593)    | 1.60            | 1.62            | 1.62 (1.62)     |
| \text{Si-O-T}  | 160.5° (159.7)  | 139.2°          | 138.4°          | 137.2° (138.2)  |
| \text{O-Si-O}  | 109.5(x6) (109.5)| 110.8(x4) (4)  | 110.8(x4) (113.8) | 113.8(x2) (113.0) |
| \text{O-Al-O}  | 111.8(x4) (109.5)| 112.0(x4) (1)  | 112.1(x2) (111.0)|                  |
| \text{O-AI-O}  | 104.9(x2) (1)   | 105.4(x2) (2)  | 108.2(x4) (108.7)|                  |

FIG. 4. Charge density distributions along the fourfold ring of the sodalite frameworks. The \textbf{S1} charge distribution of states corresponding to band group I (A), band group II (B), and band group III (C) are designated as oxygen 2s, bonding 2p, and non-bonding 2p regions respectively. (D) shows the charge distribution corresponding to the lowest three unoccupied states of \textbf{S2}. (E) and (F) show the charge distributions corresponding to the states occupied in band region III, and the lowest unoccupied states, respectively, of a sodalite framework containing only one Al atom. Light (dark) spheres represent Si (Al) positions in the fourfold ring.
reduction in the Al–O–Si bond angle. This is due to the larger Al tetrahedra; all tetrahedra rotate in order to compensate for the disparity in Al/Si tetrahedra size (a direct result of the difference in the Al–O and Si–O bond lengths). We expect increasing overlap between the bonding and non-bonding states as the bond angle closes, similar to what occurs in α-quartz under pressure. In quartz, the Si–O–Si bond angle decreases in response to increased pressure, and the gap between the bonding and non-bonding band regions closes—finally merging at approximately 35 GPa. The band structure of quartz reportedly develops anticrossing and repulsion features between these band regions, evidencing increased hybridization between the bonding and non-bonding orbitals.

V. FRONTIER ORBITALS

The substitution of Al atoms for Si (S1→S2) was accompanied by a reduction in the number of valence electrons. Examining the DOS for S1 and S2 we observe that the Al-substitution resulted in a mostly rigid shift of the Fermi level through the top of the valence band. The eigenvalue spectrum adjusted to changes in the self-consistent potential—through Al-substitution directly (external potential and reduced number of electrons) and indirectly (structural relaxation)—however, it appears that the rigid shift is a good approximation near the valence band edge. In anhydrous and natural sodalite (S3 and S4) these vacancies were filled by the inclusion of the extra-framework atoms (Na and Cl). The creation of holes at the valence band edge during Al-substitution is consistent with reactivity theory where, as a first order approximation, the frontier orbitals are assumed to be solely involved with charge transfer processes. Accordingly, we show in Fig. 4-D the charge density distribution associated with the three lowest unoccupied bands in the S2 eigenvalue spectrum. It is these three bands that were vacated by the substitution of six Al for six Si in S1. Here we note that the charge density was distributed preferentially towards the Al atoms in the fourfold rings (away from Si).

As a first order approximation, with the addition of extra-framework atoms, the accompanying electrons fill these three bands—as was first predicted by Filippone et al.17 We would then expect the extra-framework Na+ ions to be situated near the O atoms neighboring Al—as indeed they are—due to their strong coulombic interaction with electrons transferred to these orbitals.

The Na atoms in S3 and S4 are located near the center of the sixfold rings of the β-cage—slightly above and below the planes of the rings—and are thus equidistant to Al and Si alike. It is therefore useful to analyze the effect of Al-substitution in a system with only one Al atom in the local vicinity. We conducted a self-consistent calculation on the S1 framework with the replacement of one Si with one Al atom. In Figs. 4-E and 4-F we show the resulting charge density distributions corresponding to the occupied bands in band region III, and the lowest unoccupied band (hole density), respectively. The occupied bands were decidedly characteristic of non-bonding p-orbitals, however, they exhibited a slight deficiency of charge near the Al atom in the four-fold ring. In contrast, the unoccupied band again showed a charge distribution aligned preferentially towards the Al atom—directed somewhat along the Al–O bond direction. That is to say the hole-states correspond to oxygen 2p non-bonding orbitals partially hybridized with Al.

The emerging picture therefore is as follows: With the presence of extra-framework atoms, these vacant bands (hole-states) are filled and consequently we would expect the equilibrium positions of the corresponding ions to be located near the framework Al atoms. In fact, previous calculations of alumina-silicate clusters confirm this, predicting that H+ (or other ions) reside near O atoms adjoined by Al—preferentially orientated towards these Al atoms. These observations are consistent with reaction theory in that the hole-states play the most significant role in charge transfer processes. Of course, it remains to be seen what direct effect the Na+ potential has on these states. The addition of only one Na atom might for instance localize the hole state on the nearest neighboring oxygen. Furthermore, it would be interesting to explore the response of these states to changes in the Na+ (or H+) position. This would be useful in analyzing the initial stages of catalytic processes.

VI. SUMMARY

We have shown that the DOS of purely siliceous and Al–substituted frameworks resemble that of quartz in the sense that specific band regions corresponding to oxygen 2s, 2p bonding, and 2p non-bonding orbitals can be identified. Furthermore, the substitution of Al (without extra-framework atoms) results in a nearly rigid shift of the Fermi level through the edge of the valence band, producing hole-states corresponding to empty non-bonding 2p oxygen orbitals. These hole bands (highest energy) involve orbitals preferentially localized near Al (evident of hybridization with Al orbitals) with the rest of the non-bonding band region involving oxygen p-orbitals slightly localized near Si. This is plausible since the Al atomic states are less bound than the Si atomic states.

With the addition of extra-framework atoms, electrons are transferred to the hole states in the valence band. We then expect the charge compensating ions to be localized near the filled hole states due to strong coulombic interactions (ionic bonding). This rationalization explains, for instance, the apparent bonding of H+ ions to oxygens neighboring Al. It is also consistent with reaction theory which suggests such charge transfer processes are largely accomplished via the frontier states.
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