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Chemisorption of sodium on a six-membered ring, $\text{Si}_3\text{Al}_3\text{O}_6$

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Abstract. The chemisorptions of a sodium atom and a Na_3 cluster on a six-membered ring of zeolite are studied by using the extended Hückel method and cluster model. The six-membered ring of zeolite consists of $\text{Si}_3\text{Al}_3\text{O}_6$, which is one of the basic structure units of zeolite. The site preference and the density of states are determined for both cases.

1. Introduction

Zeolites are of interest because of their exceptional catalytic properties, attributed in part to the presence of intracrystalline cavities and channels [1]. The chemical formula of a zeolite containing alkali metal cations M^+ is $\text{M}_x[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot z\text{H}_2\text{O}$, and the structure is composed of corner-sharing SiO_4 and AlO_4 tetrahedra with exchangeable cations which balance the negative charge of the aluminosilicate framework located within the cavities. The silicon-to-aluminium ratio is an important parameter which determines the number of exchangeable cations. The water molecules which normally occupy the cavities can be removed by heating, and varieties of molecules and small clusters can be adsorbed provided that their dimensions are smaller than those of the channels.

Recently, several experiments [2–4] have been performed to investigate optical and magnetic properties of alkali metal in zeolite by Goto *et al.* When alkaline-metal clusters are incorporated into zeolite LTA, the clusters will be periodically arranged because of the confinement of the frameworks of zeolite. Goto *et al.* found that the periodically arranged alkaline clusters in zeolite have some interesting optical and magnetic properties which are not only different from those of isolated clusters but are also different from those of the original bulk material [5–7, 9, 10]. However, all of the above-mentioned investigations are mainly experimental. In this paper, by using the extended Hückel method we have studied the chemisorption of sodium on a six-membered ring (6MR) which consists of $\text{Si}_3\text{Al}_3\text{O}_6$. The 6MR is one of the basic structure units of zeolite. Using the cluster model, the site preference of the Na adatom is determined, and the electronic structures for both adsorbed systems, $\text{Na}/\text{Si}_3\text{Al}_3\text{O}_6$ and $\text{Na}_3/\text{Si}_3\text{Al}_3\text{O}_6$, are investigated.

The paper is organized as follows. First, the extended Hückel theory and parameters adopted are presented in section 2. Then, in section 3, the calculated results are discussed, and a summary is given in section 4.

2. Computational method

The charge self-consistent extended Hückel method has been described in detail elsewhere [11]; here only a brief description of the method will be given.

Table 1. Parameters used in the calculation: atomic orbital exponent (ξ), orbital ionization potential (I_j^0), constant of interaction (K) and modified ionization potential parameter (β).

| Atom | Orbital | ξ | I_j^0 (au) | K | β |
|------|---------|--------|--------------|-----|---------|
| Na | 3s | 0.8356 | 0.1889 | 1.1 | 0.53 |
| | 3p | 0.6432 | 0.1128 | 1.0 | 0.53 |
| O | 2s | 2.2458 | 1.0471 | 2.4 | |
| | 2p | 2.2266 | 0.5007 | 2.2 | |
| Al | 3s | 1.3724 | 0.3904 | 1.4 | |
| | 3p | 1.3552 | 0.2201 | 1.2 | |
| Si | 3s | 1.6344 | 0.4947 | 1.6 | |
| | 3p | 1.4284 | 0.2997 | 1.4 | |

In the framework of the linear combination of atomic orbitals (LCAO) method, the wave function of the system is expanded as

$$\Psi_i = \sum_{\mu j} C_{ij}(\mu) \phi_j(\mu) \quad (1)$$

where Ψ_i is the wave function of the system and $\phi_j(\mu)$ is the j th orbital of the μ th atom. The atomic orbitals used are of the Slater type [11]:

$$\phi_j(\mu) = \frac{(2\xi)^{n+1/2}}{\sqrt{(2n!)}} r^n e^{-\xi r} Y_{lm} \quad (2)$$

where ξ is the orbital exponent. The energy levels are determined by solving the secular equations

$$\sum_{\mu j} [H_{jk}(\mu\nu) - E_i S_{jk}(\mu\nu)] C_{ij}(\mu) = 0 \quad (3)$$

where H_{jk} and S_{jk} are the Hamiltonian and the overlap matrix element of the j th and k th orbitals:

$$H_{jk}(\mu\nu) = \langle \phi_j(\mu) | H | \phi_k(\nu) \rangle = \begin{cases} -I_j & j = k \\ -0.5K_{jk}(I_j + I_k)S_{jk}(\mu\nu) & j \neq k \end{cases} \quad (4)$$

$$S_{jk}(\mu\nu) = \langle \phi_j(\mu) | \phi_k(\nu) \rangle \quad (5)$$

$$I_j = I_j^0 - \alpha(Q^0 - Q) \quad (6)$$

$$K_{jk} = 0.5(K_j + K_k). \quad (7)$$

In the above expressions, I_j^0 is the ionization energy of the j th orbital of a free atom, and I_j is the modified ionization energy of the j th orbital due to the charge transfer, while Q is the Mulliken charge population of the atom obtained in the process of self-consistent calculation. α [11] is the modification factor of the ionization energy and K_j is the orbital interaction constant. For atoms with large charge transfer, an empirical modified ionization energy can be used:

$$I_j = I_j^0 \left(1 + \frac{2\beta}{n\xi} + \frac{\beta^2}{n^2\xi^2} \right) \quad (8)$$

where n is the main quantum number, and β is a parameter related to the transferred charge. The parameters ξ and I_j^0 are taken from [8] and [12], respectively. The parameters used in the present calculation are listed in table 1.

The total density of states (TDOS), $\rho(E)$, is defined as

$$\rho(E) = \sum_{\mu j} \rho_{\mu j}(E) = \sum_{\mu j} \left[\sum_i \sum_{\nu k} C_{ij}^*(\mu) C_{ik}(\nu) S_{jk}(\mu\nu) \delta(E - E_i) \right] \quad (9)$$

where $\rho_{\mu j}(E)$ is the local density of states for the j th orbital of the μ th atom. The adsorption energy can be calculated from

$$\Delta E = E_{\text{Na}/6\text{MR}} - E_{\text{Na}} - E_{6\text{MR}}. \quad (10)$$

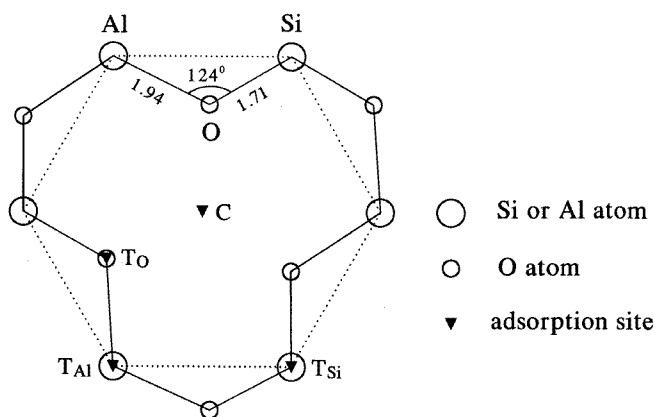


Figure 1. A schematic plot of the 6MR cluster and the adsorption positions.

3. Results and discussion

Figure 1 shows a schematic plot of the 6MR cluster, in which the saturation atoms for Si and Al at the boundary are not shown, for simplicity. The bond lengths of O–Si and O–Al (in ångströms), and the bond angle between O–Si and O–Al used in our calculation are listed in figure 1. The sites considered for Na adsorption on the 6MR are C, T_O , T_{Si} and T_{Al} . The site C is the centre site of the 6MR, and T_O , T_{Si} and T_{Al} are the top sites of O, Si and Al atoms, respectively.

Table 2. The calculated chemisorption energy ΔE , charge transfer Δq , equilibrium bond length R and optimal distance d of the adatom for the sites C considered: T_O , T_{Si} and T_{Al} . The distance d is the vertical distance of the adatom from the plane of the 6MR.

| Site | ΔE (eV) | Δq (e) | Bond length R (Å) | Distance d (Å) |
|----------|-----------------|----------------|---------------------|------------------|
| C | -4.27 | 0.96 | 2.27 (Na–O) | 1.10 |
| T_O | -3.05 | 0.64 | 2.20 (Na–O) | 2.20 |
| T_{Si} | -1.74 | 0.39 | 2.80 (Na–Si) | 2.80 |
| T_{Al} | -1.63 | 0.37 | 2.80 (Na–Al) | 2.80 |

The calculation is carried out in the following way. Firstly, four adsorption sites are chosen, and the optimal position of the adatom adsorption on the 6MR plane is found. Meanwhile, the electronic structures are calculated for the system with the adatom at its

optimal position. The calculated chemisorption energy ΔE , charge transfer Δq , equilibrium bond length R and the distance d of the Na atom from the plane of the 6MR are listed in table 2 for the four sites considered (C, T_O, T_{Si}, and T_{Al} in figure 1). From table 2, it can be seen that, among the four sites considered, the Na atom prefers to be adsorbed at site C, which is above the centre of a triangle formed by three oxygen atoms. The chemisorption energy ΔE of a Na atom at site C is calculated to be -4.27 eV when Na is situated at the height of 1.1 Å above the 6MR plane. Almost $1e$ charge is transferred from Na to the 6MR substrate and the Na atom becomes a Na¹⁺ cation. The equilibrium bond length R between Na and O is 2.22 Å, which is slightly smaller than the sum of ionic radii of these two atoms (2.30 Å). The reason for the reduction of the Na–O bond length and the lowering of the chemisorption energy might be the attraction exerted by the three oxygen anions lying below the Na cation.

In table 2, when a Na atom is situated at site T_O, the chemisorbed system is the next most stable one among the four cases. The chemisorption energy ΔE is -3.05 eV, and the equilibrium bond length is 2.20 Å. The charge transfer from Na to the 6MR plane is $0.64e$. When the Na atom is situated at the T_{Si} or T_{Al} site, the chemisorption energies ΔE of the two cases are almost equal (1.74 eV, 1.63 eV).

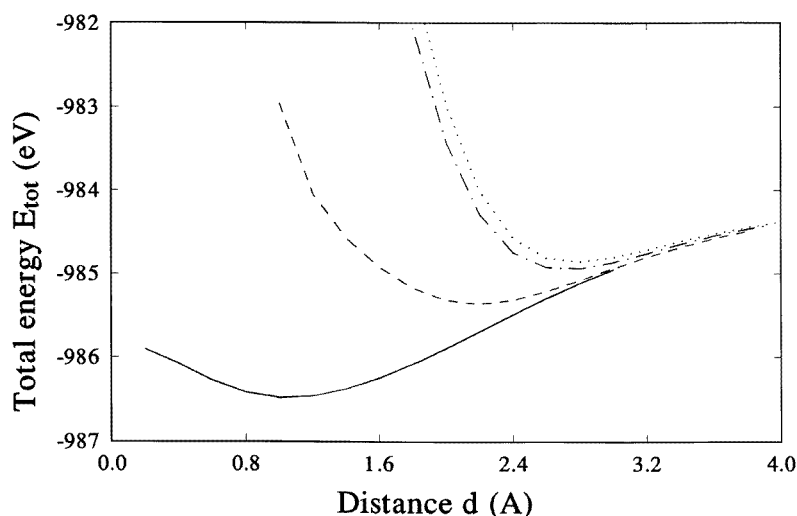


Figure 2. The total energy (E_{tot}) curves of the adsorption system Na/Si₃Al₃O₆ with respect to the vertical distance d of the Na atom from the 6MR plane are presented as the solid line, dashed line, chain line and dotted line along the direction for the chemisorption sites C, T_O, T_{Si} and T_{Al}, respectively.

The total energy (E_{tot}) curves of the adsorption system Na/Si₃Al₃O₆ with respect to the distance d of the Na atom from the 6MR plane are presented in figure 2 as the solid line, dashed line, chain line and dotted line along the directions for the chemisorption sites C, T_O, T_{Si} and T_{Al}, respectively. In comparing the minima of the total energy curves for the four cases, it can be readily seen that site C gives the lowest total energy of the system.

Our theoretical results are qualitatively consistent with those obtained in x-ray scattering [13], which is used to identify the position of the cation in zeolite. According to [14], in LTA (Na₁₂[(AlO₂)₁₂(SiO₂)₁₂]) zeolite eight Na ions occupy the six-membered-ring centre site and the O–Na bond length is 2.32 Å.

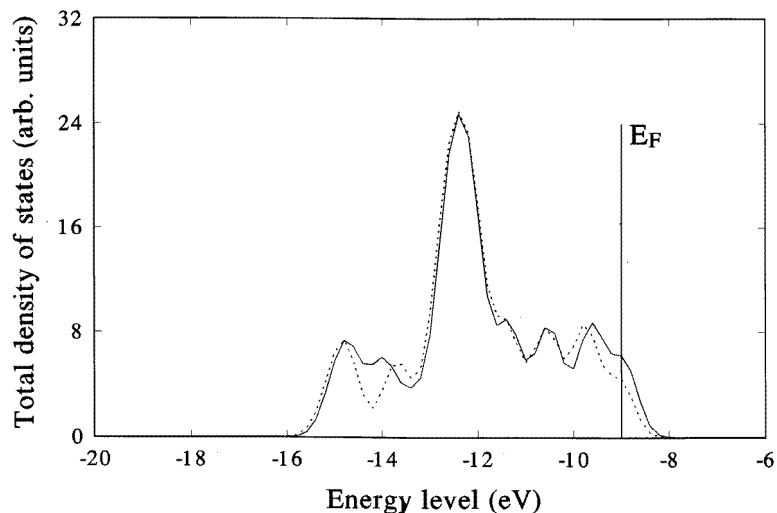


Figure 3. The density of states (DOS) for the adsorption system with a Na atom at site C (the solid line); the DOS for the 6MR is plotted as a dotted line for comparison.

The density of states (DOS) for the adsorption system with a Na atom at site C is plotted as a solid line in figure 3, while the DOS for the 6MR is given as the dotted line. The curves were obtained by Gaussian broadening. Comparing the DOS of the adsorbed system with that of the 6MR, it can be seen that the densities of states near the Fermi energy (E_F) are increased after the chemisorption of a Na atom.

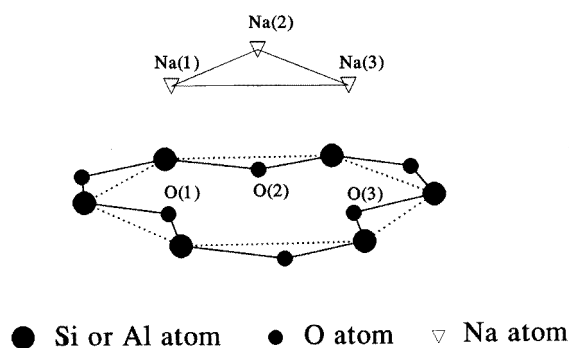


Figure 4. A schematic representation of three Na atoms adsorbed on the 6MR.

In order to achieve a further understanding of the effect of Na adatoms on the properties of zeolite, the system with three Na atoms adsorbed on the 6MR is investigated. Figure 4 gives a schematic representation of a stable configuration of the Na_3 cluster chemisorbed on the 6MR. The stable configuration is obtained by minimizing the total energy of the adsorption system in the following way. Firstly, each Na atom (denoted by Na(1), Na(2) and Na(3), respectively) is located at the top site of an O atom (denoted by O(1), O(2) and O(3), respectively), which is just like the case of one Na adatom adsorbed at the top site of an O atom discussed above. The three Na atoms form an equilateral triangle. By shrinking

the triangle, and reducing the distance of Na atoms from the 6MR plane, the total energy of the system can be minimized. A stable geometric configuration of the Na₃ cluster can be determined relative to the 6MR and is shown in figure 4. In the stable configuration, the adsorbed Na₃ cluster forms an equilateral triangle; the distance between two Na atoms is 3.17 Å. The calculated bond lengths Na(1)–O(1), Na(2)–O(2) and Na(3)–O(3) are 2.10 Å, which is slightly smaller than the bond length between Na and O (2.20 Å) in the case of one Na atom adsorbed at the top site of O. The charge transfer of each Na atom is 0.76e, and the average chemisorption energy of each Na atom is –3.27 eV. Compared with the charge transfer (0.64e) and the chemisorption energy (–3.05 eV) for the case of one Na atom adsorbed on the top site of O, the case for the Na₃ cluster adsorbed on the 6MR gives more charge transfer (0.76e) and lower chemisorption energy (–3.27 eV). This indicates that the highly ionized Na₃ cluster can be easily formed on the 6MR plane. In the present case, the ionized Na₃^{2.2+} cluster is obtained. This agrees quite well with experimental electron spin-resonance (ESR) results where Na₃²⁺ is found in zeolite [15].

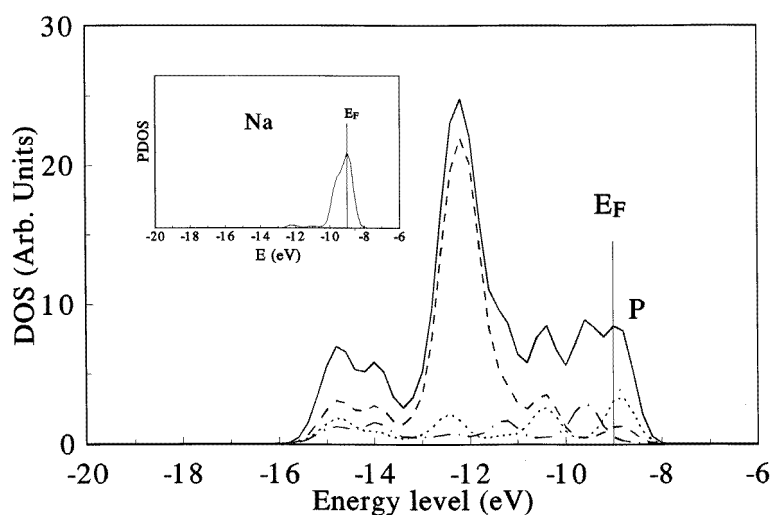


Figure 5. The DOS of the adsorption system Na₃/Si₃Al₃O₆ (solid line), and the partial density of states (PDOS) for O (dashed line), Al (chain line) and Si (dotted line). In the inset of this figure, the PDOS for Na adatoms in the adsorption system is also shown. P represents a new peak which is mainly contributed by the chemisorbed Na atoms on the 6MR.

The DOS for the adsorption system Na₃/Si₃Al₃O₆ is shown in figure 5 (solid line), while the partial density of states (PDOS) for O, Al and Si are also shown as the dashed line, chain line and dotted line respectively. For the purpose of achieving a clearer understanding of the contribution of Na adatoms to the DOS of the adsorption system, the PDOS of Na adatoms in the adsorption system has been obtained and is illustrated in the inset of figure 5. From the PDOS of the Na adatom in the inset of figure 5, it can be seen that the energy levels due to the interaction between the Na atoms and the 6MR atoms are mainly distributed in the vicinity of the Fermi energy. If we make a comparison between the DOS of the 6MR and the adsorption system Na₃/Si₃Al₃O₆, it can be found that the DOS peak near the Fermi level, labelled P in figure 5, increases obviously after the Na₃ are adsorbed on the 6MR. From the distribution of the PDOS for Na, O, Al and Si atoms in figure 5, it can be seen that the PDOS of Na adatoms makes the most significant contribution to the peak. The obvious

variation of the DOS near the Fermi energy is due to the interaction between the 3s orbital of Na and the 2p orbitals of O. It is well known that the physical and chemical properties of a system are mainly determined by the electronic structures near the Fermi energy; the calculated results indicate that when a sodium cluster is incorporated into zeolite, some new interesting properties might appear.

4. Conclusions

The chemisorption of sodium on the 6MR of zeolite is investigated by using the extended Hückel method and a cluster model. The site preference for a Na adatom is determined, and a stable configuration of a Na_3 cluster on the 6MR is obtained by minimizing the total energy of the adsorbed systems. The electronic structures for both adsorbed systems, $\text{Na}/\text{Si}_3\text{Al}_3\text{O}_6$ and $\text{Na}_3/\text{Si}_3\text{Al}_3\text{O}_6$, are investigated. It is found that the adsorbed Na adatom prefers the centre site C of the 6MR and a stable highly ionized equilateral triangle cluster $\text{Na}_3^{2.2+}$ can be formed on the 6MR. These results are in good agreement with experimental results. When a Na atom is adsorbed on the 6MR, the total density of states of the 6MR increases somewhat near the Fermi level, whereas a new peak P near the Fermi level appears when three Na atoms are chemisorbed on the 6MR.

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