

Zeolite adsorption site location and shape shown by simulated isodensity surfaces

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The graphics software package Ribbons¹ is used to display isodensity surfaces of Xe atoms adsorbed in the alpha cage of zeolite NaA. The location, size, and shape of the adsorption sites are highly dependent on the loading and the crystal cation content. When the zeolite has a high number of cations, ellipsoidal sites arrange in a cuboctahedron. When the zeolite has fewer cations, cone-shaped sites arrange in an octahedron at low loading, but at high loading the sites become ellipsoidal and new sites form at cuboctahedral positions. The effect of the nature of the adsorption site on the development of a universal adsorption model is discussed.

Keywords: zeolite, NaA, adsorption, Xe, Monte Carlo, molecular simulation, isosurface

INTRODUCTION

Zeolites are a family of aluminosilicates whose crystal structure exhibits a regular network of interconnecting, molecularly sized pores.² This unique feature makes zeolites ideally suited for many industrial applications. Catalysis, separations, and ion-exchange each rely on the adsorption of molecules into these micropores, so a fundamental understanding of the adsorption process is clearly needed.

Molecular simulation has lent significant insight into zeolite adsorption.³⁻¹¹ Many studies^{3-8,10} use the grand canonical ensemble Monte Carlo method (i.e., a simulation at constant chemical potential, volume, and temperature) to examine the equilibrium between adsorbed and bulk phases. Although the adsorption isotherm and other thermodynamic properties may be obtained in this way, the location of adsorbed molecules is obscured because this ensemble produces a density profile which is an average of several discrete cage loadings. To examine the locations of adsorption

sites at specified loadings, we have recently reported the results of canonical ensemble Monte Carlo studies^{9,11} (i.e., at constant number of particles, volume, and temperature) of Xe adsorbed in an alpha cage of zeolite NaA.

Three-dimensional (3D) isodensity surfaces provide a greatly detailed map of the adsorption sites. The graphics software package Ribbons¹ allows us to view the adsorbate isodensity contours and a ball and stick model of the zeolite cage simultaneously. Viewing these contour maps *together* with the zeolite framework has helped us to see the influence of the zeolite structure on the adsorbed phase structure. In this paper, we present a series of images produced using Ribbons of Xe isodensity surfaces in zeolite NaA. From these images, we will draw conclusions regarding adsorption site size and morphology.

SIMULATION MODEL AND METHOD

The Xe/NaA system has the advantage that Xe atoms will neither leave the alpha cage nor interact chemically with the zeolite, so we can examine only the *physics* of site arrangement. The alpha cage (Figure 1) consists of a negatively charged framework of silicon or aluminum atoms which are connected by bridging oxygen atoms. Charge balancing sodium cations occupy positions within the framework; thus the cage is neutral. Atomic coordinates have been obtained from X-ray diffraction analysis.¹² We will consider two cases: one in which sodium cations are located in the centers of both the 6- and 8-membered rings (cation-rich alpha cage) and another in which sodium ions are present only in the 6-membered rings (cation-poor alpha cage).

The classical interactions between the Xe atoms and the zeolite alpha cage are calculated atomistically¹³ and follow the form

$$\Phi = \Phi_R + \Phi_D + \Phi_P + \Phi_{Xe-Xe} \quad (1)$$

where Φ_R accounts for the short range repulsion between Xe and the zeolite atoms, Φ_D accounts for the long range attraction due to the interaction of the induced dipole of the Xe atoms with the induced dipole of the framework atoms, Φ_P accounts for the interaction between the Xe induced dipole and the zeolite framework static electric field, and Φ_{Xe-Xe} accounts for the induced dipole-induced dipole interaction

Color Plates for this article are on page 188.

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Received 20 August 1992; accepted 17 December 1992

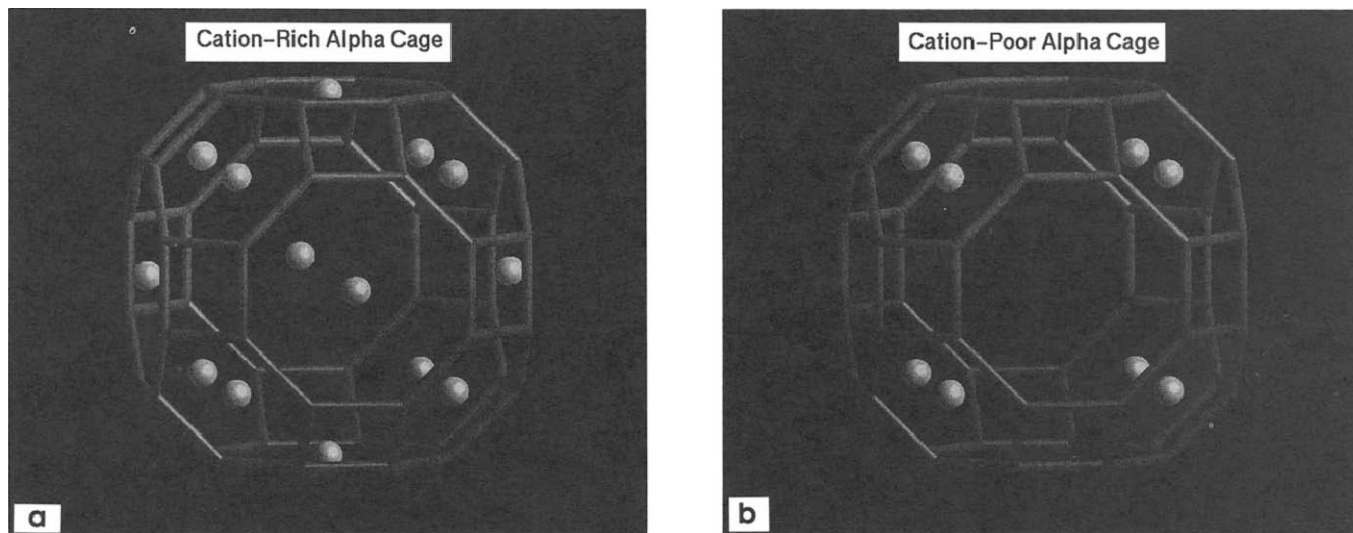


Figure 1. NaA alpha cage. The framework vertices represent either silicon or aluminum atoms which are connected by bridging oxygen atoms (not shown) located near to, but not at, the centers of the line segments. Sodium ions appear as spheres. The cation-rich cage (a) has sodium ions in the 6- and 8-member rings, while the cation-poor cage (b) has sodium ions only in the 6-member rings.

between Xe atoms. The calculation of these terms is described elsewhere.^{9,13}

We use the canonical ensemble Monte Carlo algorithm of Metropolis¹⁴ to generate the equilibrium Xe density distribution in the alpha cage. The simulation algorithm involves the initial, random placement of N Xe atoms in the alpha cage. Successive states, which correspond to different arrangements of the N atoms, are generated by random translations of single Xe atoms. Newly generated configurations are accepted to a Markov chain of states with probability

$$P_{\text{acc}} = \min(1, \exp(-\Delta\Phi/kT)) \quad (2)$$

where $\Delta\Phi$ is the change in potential energy upon going to a new state, k is the Boltzmann constant, and T is the absolute temperature. Physical properties of interest may be calculated as arithmetic averages over all accepted states in the Markov chain. The density distribution is obtained by placing a $48 \times 48 \times 48$ grid inside of the alpha cage and counting the total number of Xe atoms that occupy each grid space during the course of the simulation. Further details of the simulation appear elsewhere.⁹

The length of each simulation is 200,000 steps, which follow 50,000 to 150,000 discarded steps (to assure equilibration). The simulations are performed on the Cray X-MP supercomputer at the Minnesota Supercomputer Institute.

GRAPHICS SOFTWARE

Ribbons is a molecular modeling software package written by M. Carson of the University of Alabama at Birmingham for use on the Silicon Graphic's Iris 24-bit color graphics workstation. Although originally designed for use with proteins, Ribbons has all of the features necessary for visualization of many systems. Additionally, Ribbons may be used to visualize a function in three dimensions by rendering a closed surface representing the locations of constant value of this function. These isodensity surfaces may be displayed

together with a molecular model. Real-time rotation and animation capabilities allow for an enhanced 3D effect and for cycling through isosurfaces of varying densities. We use Ribbons here to display isodensity surfaces of the simulated Xe density distribution inside the zeolite alpha cage.

Shell scripts and minor program modifications have been developed by one of the authors. The modifications use the isosurface generation methods developed by others.¹⁵

RESULTS

Monte Carlo simulations of Xe atoms adsorbed in a zeolite NaA alpha cage were presented previously¹¹ and the canonical ensemble adsorbate density distribution is presented here. Figure 2a shows the adsorbate isodensity surface for a loading of one Xe atom in the cation-rich alpha cage at 300 K. The density of the surface in this and all subsequent figures is ten times the average cage density (N/V). Twelve "clouds" appear, each surrounding a local maximum in the density distribution. We refer to this region of space as an adsorption site. The sites are positioned directly in front of the 4-membered rings of the cage. Their arrangement is that of a cuboctahedron (a 12-vertex polyhedron, each vertex 4-connected as shown in Figure 3a). Since 12 separate sites appear, the Xe atom must move about over the course of the simulation to sample each site. The lack of significant density between the sites indicates that this motion is characterized as "hopping" rather than "continuous diffusion." The sites are ellipsoidal in shape. Figure 2b shows a view from inside the cavity.

The cuboctahedral arrangement of adsorption sites is retained as the loading of the cage is increased (Color Plate 1), but the volume of each site decreases. In other words, the adsorbates become more localized as crowding increases. At a loading of 12 Xe, each of the cuboctahedral sites is occupied. A loading of 13 Xe differs only in the placement of an additional adsorbate at the cage center. Finally, a

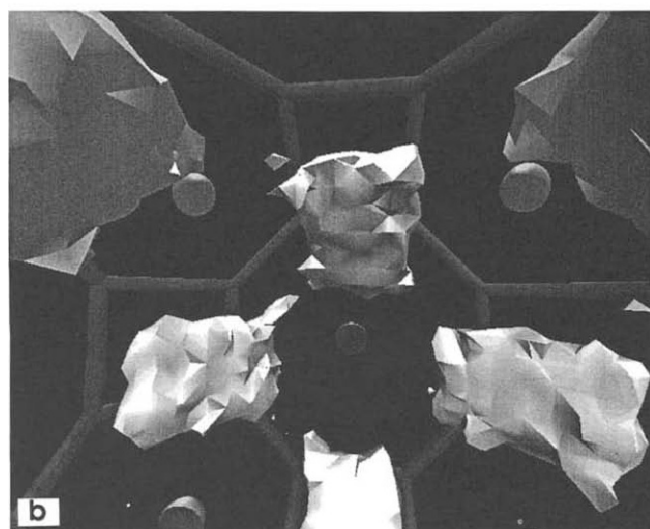
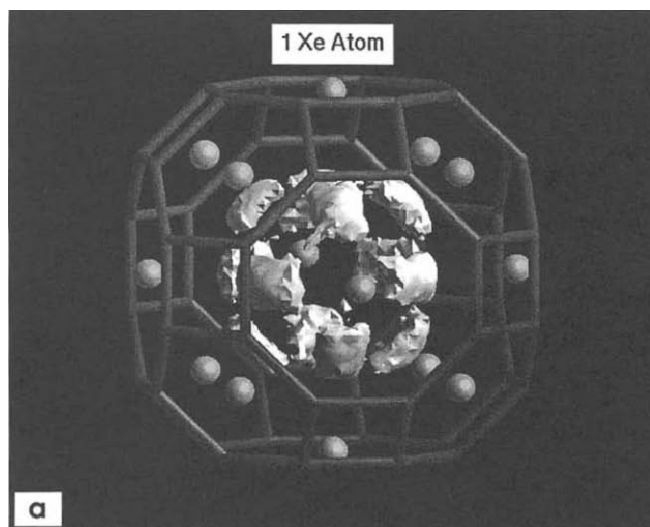


Figure 2. (a) Cation-rich alpha cage and isodensity surface for a loading of 1 Xe atom at 300 K viewed from outside of the cage. The isodensity surface represents a density of 10 times the average cage density in this and subsequent figures. (b) View from inside the cage.

loading of 14 Xe breaks the symmetry of the cuboctahedron and we see a delocalization of the sites.

The adsorbate isodensity surface for one Xe atom in the cation-poor alpha cage at 300 K is shown in Figures 4a and 4b. The removal of the sodium cations from the 8-membered rings now allows the adsorption sites to be established in front of these rings. The arrangement of the sites are now that of an octahedron (Figure 3b). The individual sites are now shaped like a cone and retain their shape and location even as the loading exceeds the number of primary adsorption sites (Color Plate 2). Beyond a loading of 6, some Xe atoms must reside outside of the octahedral sites. The change in the isodensity surface upon a loading of 7 Xe atoms is due to the additional Xe atom which is completely delocalized in the space between the 6 sites. As the loading is increased further, the octahedral sites decrease in volume

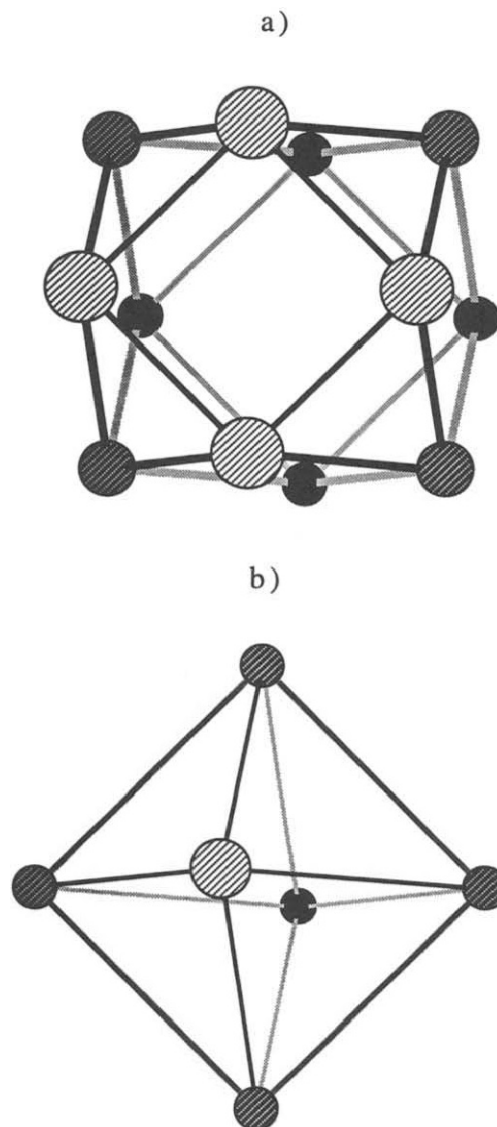


Figure 3. Cuboctahedral arrangement of Xe atoms (a) found in the cation-rich alpha cage and the octahedral arrangement of Xe atoms (b) found in the cation-poor alpha cage.

and additional sites form near the cuboctahedral positions seen in the cation-rich cage. Finally, at a loading of 19 Xe atoms, a highly symmetric arrangement of 6 octahedral sites, 12 cuboctahedral sites, and the center position are each occupied.

The change in the isodensity surface with loading is due to Xe-Xe crowding, which causes the range of motion of the Xe atoms to be reduced. A parameter describing the average distance between Xe atoms (i.e., a crowding parameter) has recently been introduced¹¹ and is shown in Figure 5 as a function of loading. In the cation-rich cage, the Xe-Xe separation decreases gradually as the cuboctahedral sites fill. In the cation-poor cage, a sharp decrease in the average distance is noted at loadings greater than 6 Xe (i.e., octahedral site saturation), the same loading at which the isodensity surface begins to change. Thus, gradual Xe-Xe

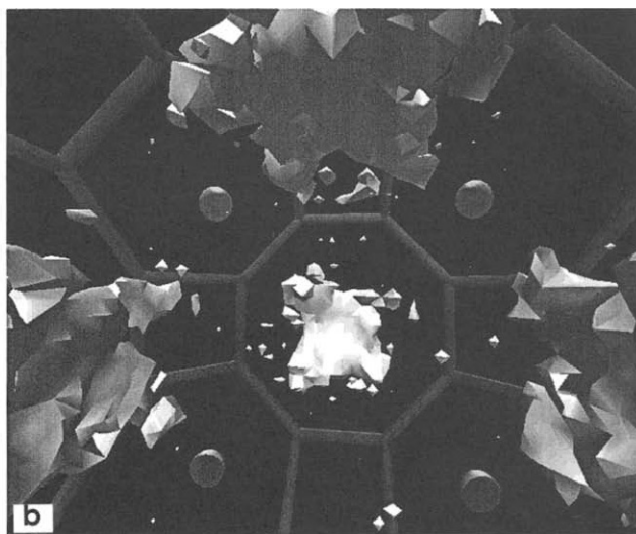
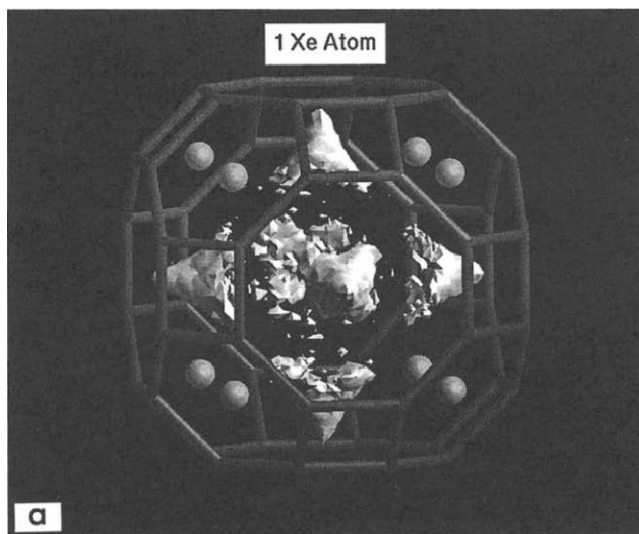


Figure 4. Cation-poor alpha cage and isodensity surface for a loading of 1 Xe atom at 300 K viewed from (a) outside and (b) inside of the cage.

crowding may cause a decrease in adsorption site volume, while abrupt crowding may signal a shift in adsorption site location.

DISCUSSION

The arrangement, size, and morphology of zeolite adsorption sites, determined computationally and visualized graphically, will play an important role in developing new theoretical models of adsorption in micropores. To date, though, little work has been done in this direction. Three-dimensional isosurfaces, when viewed along with the cage framework, provide us with necessary information on the number, shape, and position of the adsorption sites in the alpha cage.

Only with the aid of Ribbons are we now able to investigate the size and shape of the adsorption sites. The isosurfaces show that the volume of the sites decreases with loading and that the shape of the sites changes from ellipsoidal to conic when the cation content is altered. Also, the

shape of the sites in the cation-poor cage changes from conic to ellipsoidal as the primary sites become saturated. The isotherm must depend on the nature of the adsorption sites, and the sites themselves depend on the extra-framework cation positions. Therefore, an understanding of the effect of cation alteration on the adsorption sites will enhance our ability to design zeolites as selective adsorbents.

The adsorption site size and shape show the extent of translational freedom experienced by the adsorbates, which gives an indication of the translational entropy present. (The number of adsorption sites available contributes to the configurational entropy of the adsorbed phase.) As the adsorbed phase becomes less localized, the translational entropy will contribute heavily to the total entropy. For this reason, a thorough understanding of the adsorption site size as a function of loading may be crucial in understanding adsorption equilibrium.

Many adsorption models treat the sites as static entities, i.e., changes in position and size are not considered. Others neglect the notion of sites altogether in favor of pore filling arguments. Both of these approaches are flawed because, as seen by the isodensity surfaces, distinct adsorption sites do exist, but their properties depend heavily on the crystal structure and the loading. A more detailed treatment of the adsorption sites, based on the observations presented here, is needed in the development of a truly universal zeolite adsorption model. The ideas presented in this paper are currently being used in the development of a new model isotherm for zeolite NaA based on the statistical mechanics of finite lattice gases.¹⁶

ACKNOWLEDGMENTS

The authors wish to thank the Minnesota Supercomputer Institute (MSI) for access to the Cray X-MP supercomputer and the Silicon Graphic's Iris-4D workstations, P. Van Valkenberg for acquiring Ribbons for use at MSI, M.V. Hughes for graphical support, and the entire MSI staff for their technical support. This work was partially supported

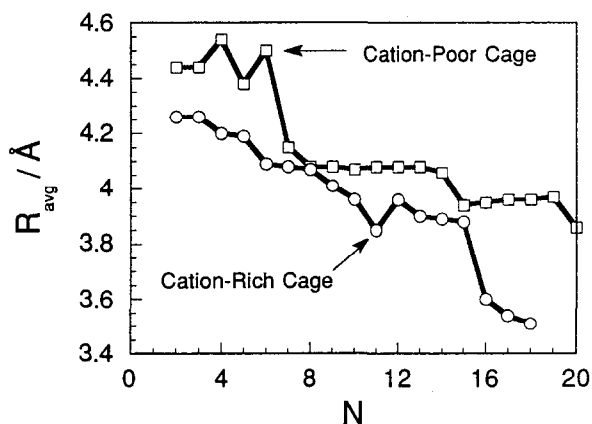


Figure 5. Characteristic Xe-Xe separation distance, R_{avg} ,¹¹ as a function of loading for the cation-rich and cation-poor alpha cages at 300 K.

by the ACS Petroleum Research Fund, the National Science Foundation, MSI, and the University of Minnesota Graduate School Doctoral Dissertation Fellowship Program.

The authors of the isosurface generation methods¹⁵ have requested that the following message be included in all derived work:

Portions developed at the National Center for Supercomputing Applications at the University of Illinois at Urbana-Champaign.

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