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Research Article

Rare Gas Adsorption to Silver-Exchanged Zeolites

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The adsorption of rare gas atoms to silver aluminosilicate has been investigated using density functional theory (DFT) with the local density approximation, generalized gradient approximation, and dispersion correction. The adsorption energies of rare gas atoms to the honeycomb lattice of silver aluminosilicate were calculated, and the results are discussed. The relationship between the electric charge density distribution and the adsorption energy is discussed. It indicates that the xenon atom has the most electrons to affect the van der Waals dispersion, so it has the highest minimum charge density, strongest polarization, most spacious spherical scope, and most favorable adsorption on silver zeolites.

1. Introduction

Rare gas adsorption technology is important to detect and prevent the leakage of radioactive isotopes, including radioactive xenon isotopes in the products of radio nuclides [1–3]. Zeolites are crystal in aluminosilicates containing micropores at the molecular level, and they are widely used as catalyst carriers and adsorbents with sieving effects [4–8].

The micropores of zeolites have a significant influence on the adsorption properties. Rare gases exhibit unique adsorption properties on silver-exchanged zeolite molecular sieves; in particular, the adsorption heat of xenon on silver-exchanged zeolite is significantly higher than that on the sodium zeolite molecular sieve [9]. It is important to study the adsorption of rare gas atoms on silver-exchanged zeolite molecular sieves for the development of rare gas collection, separation, and purification.

Kaolin is a major source of Si and Al in the preparation of zeolites and is rich in the mineral kaolinite [10]. Kaolinite has the formula $Al_4(Si_4O_{10})\cdot(OH)_8$ and is composed of silica-tetrahedron and alumina-octahedron sharing oxygen atoms. A tetrahedron is constructed with four oxygen atoms around a silicon atom, and an octahedron is constructed with six oxygen atoms around an aluminum atom. The layered structures composed of tetrahedron and octahedron have negative charges, and protons H^+ are distributed among the layers to ensure electrical neutrality. Zeolite molecular sieves prepared with kaolin as the raw material have the advantages of large size, good thermal stability, and low price.

In this study, a silver aluminosilicate ($AgSiAlO_4$) system is derived from the structure of kaolinite, and its symmetry and energy are optimized using density functional theory (DFT) with the local density approximation (LDA), general gradient approximation (GGA), and explicitly parameterized van der Waals correction [11, 12], with the ABINIT crystal structure code [13]. The adsorption energies of rare gases on the $AgSiAlO_4$ system are calculated, and the mechanics of the adsorption are analyzed.

2. Methods

To reasonably describe the structure of silver-exchanged zeolite, a silver aluminosilicate ($AgSiAlO_4$) system was derived from the kaolinite structure, in which the protons were replaced by silver ions, some of the water molecules were removed, and the alumina-octahedron changed to tetrahedron with four oxygen atoms around each aluminum atom (see Figure 1). Figure 1(a) shows the top view with four primitive cells, and Figure 1(b) shows the side view with two primitive cells. Every primitive cell includes two $AgSiAlO_4$ units. The lattice is layered with $a = b \neq c$ and space

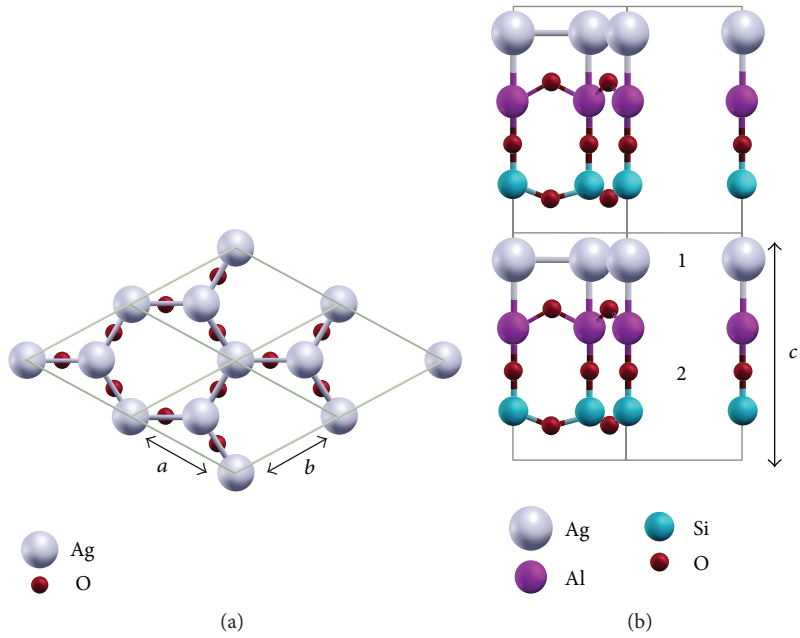

Figure 1: Silver aluminosilicate: (a) top view and (b) side view.

group *P6mm*. The negative $SiAlO_4^-$ ions form hexagonal honeycomb reticular pores. Si and Al atom are bridged by an oxygen atom to form a line group, which translates and is repeated along the *a*-axis and *b*-axis to form honeycomb reticular pores with $a/\sqrt{3}$ length sides. The oxygen atoms at both ends of the line of Si-O-Al groups form the "doorways" with side lengths $a/2$.

Along the direction of the *c*-axis shown in Figure 1(b), the atoms (numbers) in a primitive cell are in the order Ag(2), O(3), Al(2), O(2), Si(2), and O(3). Silicon and aluminum atoms are surrounded by oxygen atoms and form SiO_4 and AlO_4 tetrahedron, respectively. Because the aluminum atom has only three valence electrons, AlO_4 can accept an electron to form negatively charged AlO_4^- ions. Silver ions (Ag^+) attach to the tetrahedral AlO_4^- ions to maintain charge balance and form silver aluminosilicate salt.

The geometries and energies were optimized and calculated based on DFT using the ABINIT crystal structure code. The norm-conserving pseudopotential method was used in the calculations, and Troullier-Martins pseudopotentials files were downloaded from the ABINIT website [14–16]. The *k* points were sampled by a $5 \times 5 \times 3$ grid in the Brillouin zone. The kinetic energy cutoff was 40 Hartree for the plane waves. A smearing parameter of 0.5 Hartree was used for the energy cutoff to smooth the geometry optimization.

A general drawback of all common DFT formulations is that long-range electron correlations cannot be described, which are responsible for van der Waals forces (dispersion). The van der Waals interactions between atoms play an important role in the adsorption of rare gases. A semiempirical formulation of long-range dispersion correction, so-called DFT-D, was introduced in the calculations for the adsorption of rare gases in silver zeolites (silver aluminosilicate) as follows [12, 13]:

$$E_{\text{DFT-D}} = E_{\text{KST-DFT}} + E_{\text{disp}}, \tag{1}$$

where $E_{\text{KS-DFT}}$ is the usual self-consistent Kohn-Sham DFT energy and E_{disp} is an empirical dispersion correction given by

$$E_{\text{disp}} = -s_6 \sum_{i=1}^{N_{\text{at}}-1} \sum_{j=i+1}^{N_{\text{at}}} \frac{C_6^{ij}}{R_{ij}^6} f_{\text{dmp}}\left(R_{ij}\right). \tag{2}$$

Here, N_{at} is the number of atoms in the system, C_6^{ij} denotes the geometric mean of the dispersion coefficients for atom pairs *i* and *j*,

$$C_6^{ij} = \sqrt{C_6^i C_6^j}, \tag{3}$$

s_6 is a global scaling factor that only depends on the DF used, and $s_6 = 0.75$ was used in this work for the exchange correction formulation of Perdew et al. [17]. R_{ij} is the interatomic distance. To avoid near-singularities for small *R*, a damping function f_{dmp} must be used, which is given by

$$f_{\text{dmp}}\left(R_{ij}\right) = \frac{1}{1 + e^{-d(R_{ij}/R_r - 1)}}. \tag{4}$$

Here, the empirical parameter $d = 20$ was used. R_r is the sum of the atomic van der Waals radii:

$$R_r = R_0^i + R_0^j. \tag{5}$$

All of the atomic dispersion coefficients C_6 and van der Waals radii R_0 used in this work are listed in Table 1.

Table 1: Dispersion coefficients C_6 (J·nm^6/mol) and van der Waals radii R_0 (Å) [13].

	C_6	R_0
Si	9.23	1.716
Al	10.79	1.639
O	0.70	1.342
Ag	24.67	1.639
He	0.08	1.012
Ne	0.63	1.243
Ar	4.61	1.595
Kr	12.01	1.727
Xe	29.99	1.881

Table 2: Lattice parameters and bond lengths of silver aluminosilicate.

	LDA	GGA	GGA-D
$a = b$	5.390	5.396	5.383
c	8.945	8.979	8.992
Si-O	1.646	1.682	1.678
	1.587	1.563	1.563
Al-O	1.729	1.743	1.740
	1.698	1.703	1.698
Ag-Al	2.6895	2.766	2.757
Ag-Si	2.9700	2.947	2.974
Ag-O(Al)	2.4842	2.523	2.514
Ag-O(Si)	2.8894	2.788	2.810

Table 3: Relative coordinates of atoms along the c-axis.

	O (near Si)	Si	O (bridge)	Al	O (near Al)	Ag
LDA	0.0	0.0599	0.2373	0.4272	0.5114	0.7278
GGA	0.0	0.0707	0.2448	0.4344	0.5216	0.7425
DFT-D	0.0	0.0703	0.2442	0.4330	0.5199	0.7396

3. Results

Table 2 gives the lattice parameters and bond distances of silver aluminosilicate $AgSiAlO_4$, and Table 3 shows the relative coordinates of the atoms in the c direction. The results show that the effect of van der Waals forces on the geometry of silver aluminosilicate is very small. The lattice parameters calculated with the DFT-D method are $a = b = 5.383$ Å and $c = 8.992$ Å, which are within 0.5% of those calculated with the GGA and LDA methods. The differences between the interatomic distances are less than 3%, and those between the atomic coordinates are less than 1.4%.

The bond distances between Si and O atoms are 1.646 and 1.587 Å, which is 2.2% less than the S-O distance in kaolinite (1.61 Å). The bond distances between Al and O atoms are 1.698 and 1.729 Å, which is 10% less than the Al-O distance in kaolinite (1.90 Å) [18, 19]. It is reasonable that the Al-O bond lengths in the octahedron of kaolinite are longer than those in the tetrahedron of silver aluminosilicate. The ionic radii of Ag^+ and O^{-2} are 1.15 and 1.40 Å, respectively [20].

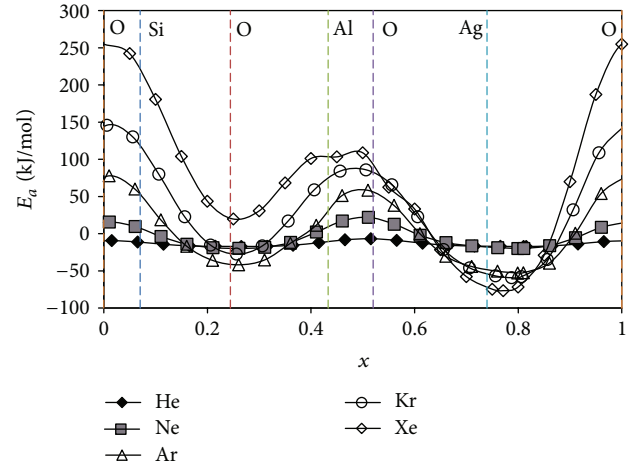

Figure 2: Relationship between adsorption energy (E_a) and the c-axis coordinate (x).

The distance between the silver atom and its nearest neighbor atoms (the doorway oxygen atom bonded to the aluminum atom) in silver aluminosilicate is 2.514 Å, which is 1.4% less than the sum of the ionic radii. Therefore, the calculated results are acceptable.

The distance between the silver atom and the doorway oxygen atom bonded to the silicon atom is 2.810 Å, which is 0.26 Å longer than the ionic bond length. This shows that the interactions between different honeycombs layers are van der Waals forces, which agrees with the fact that zeolite cannot form bulk crystals.

The geometries of the R-$(AgSiAlO_4)_2$ (R = He, Ne, Ar, Kr, or Xe) systems were optimized, where R was located on the hexagonal axis. The electron configurations of He, Ne, Ar, Kr, and Xe were $1s^2$, $2s^22p^6$, $3s^23p^6$, $4s^24p^6$, and $5s^25p^6$, respectively. The adsorption energy of R-$(AgSiAlO_4)_2$ is expressed as

$$E_a = E_{[\text{R-}(AgSiAlO_4)_2]} - E_{\text{R}} - E_{(AgSiO_4)_2}, \quad (6)$$

where E_a is the adsorption energy, $E_{[\text{R-}(AgSiAlO_4)_2]}$ is the calculated energy of the system after adsorption, $E_{(AgSiO_4)_2}$ is the system energy before adsorption, and E_{R} is the energy of the rare gas atom. A negative E_a value indicates that the adsorption process is exothermic, and a positive E_a value indicates endothermic adsorption. Figure 2 shows the adsorption energies of the rare gas atoms on the pore axis, where the unit cell parameters and the coordinates of all atoms are optimized.

When the He atom goes through the pore of silver aluminosilicate, the adsorption energy is negative (exothermic) and changes little. The energy peaks appear at the narrow doorways of the pore. The peak adsorption energy near the aluminum atom (−6.770 kJ/mol) is higher than that near the silicon atom (−9.374 kJ/mol). Near the oxygen bridge and the positively charged Ag^+ ions, there are energy minima of −17.126 and −17.282 kJ/mol, respectively. The difference of the two minima is small (0.156 kJ/mol), which indicates that the two sites are both favorable for the adsorption of He atoms, and it is easier for He to adsorb at the site near the Ag^+ ion.

Table 4: Adsorption energies of rare gas atoms on silver aluminosilicate (kJ/mol).

	He	Ne	Ar	Kr	Xe
LDA	−10.461	−23.807	−38.416	−40.546	−105.778
GGA	−7.639	6.721	−6.378	0.186	−5.242
DFT-D	−17.282	−19.858	−52.759	−59.165	−76.568

The adsorption energy of the Ne atom is positive at the two doorways of the pore and has energy peaks of 15.635 kJ/mol near the silicon atom and 22.009 kJ/mol near the aluminum atom. Near the oxygen bridge and the positively charged Ag^+ ions, there are energy minima of −19.810 and −19.858 kJ/mol, respectively. The difference 0.048 kJ/mol between the two minima is small. The repulsion of the oxygen atom at the doorway is not beneficial for the adsorption of the Ne atom. It is easier for the Ne atom to adsorb near the Ag^+ ion than inside the pore.

The two adsorption peaks for the Ar atom are 77.745 and 58.267 kJ/mol near the silicon and aluminum atoms, respectively, with a difference of 19.478 kJ/mol. The adsorption energy minimum of −41.836 kJ/mol near the Ag^+ ion is less energetically favorable than that of −52.759 kJ/mol inside the pore, with a difference of 10.922 kJ/mol. The rejection of the oxygen atoms at the doorway is very clear, and the Ar atom adsorbing to the Ag^+ ion is energetically favorable.

The two adsorption peaks for the Kr atom are 145.863 and 85.919 kJ/mol near the silicon and aluminum atoms, respectively, with a large difference of 59.944 kJ/mol. The adsorption energy of −59.165 kJ/mol near the Ag^+ ion is lower than that of −27.460 kJ/mol inside the pore. The limited space inside the pore of $AgSiAlO_4$ has an effect on the rejection of the relatively large Kr atoms. The site near the Ag^+ ion has no space limit and is able to accommodate the large Kr atom.

The two adsorption peaks for the Xe atom are very high (254.860 and 146.127 kJ/mol). The adsorption energy minimum (19.706 kJ/mol) inside the pore is positive, and that near the Ag^+ ion is negative (−76.568 kJ/mol). This indicates that the repulsion inside the pore is strong for the large Xe atom, but adsorption near the Ag^+ ion is very strong.

Table 4 gives the adsorption energies of the rare gas atoms to silver aluminosilicate calculated with the LDA, GGA, and DFT-D methods. The results calculated with the LDA and DFT-D methods show that, with increasing atomic number (Z) of the rare gases, the adsorption energy on silver aluminosilicate decreases; that is, the adsorption capacity increases. However, the energies (absolute values) of adsorption calculated with the GGA method are low and do not show a clear trend.

With increasing Z, the adsorption energy calculated with the LDA is significantly higher than that calculated with DFT-D. The adsorption energy of He calculated with the LDA is −10.461 kJ/mol, which is higher than that calculated with the DFT-D method of −17.639 kJ/mol (difference of 7.178 kJ/mol). However, the adsorption energy of Xe calculated with the LDA method of −105.778 kJ/mol is significantly lower than that calculated with the DFT-D method of −76.568 kJ/mol (a difference of 29.21 kJ/mol).

The adsorption energies (absolute value) calculated with the GGA without van der Waals dispersion correction are less than those calculated with the LDA, and they do not effectively describe the van der Waals forces between rare gas atoms and silver aluminosilicate. The adsorption values calculated with the GGA can be considered as the fluctuation of the numerical calculation of DFT method. With respect to the DFT-D method, the relative fluctuation of the He adsorption is quite large, about 44%; and that of the Xe adsorption is relative smaller, about 6.8%. Thus, the adsorption energy of Xe given by DFT-D is acceptable.

Because the adsorption of rare gas atoms mainly depends on van der Waals forces, the gas rare atoms do not affect the electronic bands of silver aluminosilicate. However, it is necessary to analyze and discuss the change of the electronic charge distribution of silver aluminosilicate because of the introduction of rare gas atoms to understand the mechanism of adsorption.

Figure 3 shows the charge density contours of R-$(AgSiAlO_4)_2$ in the plane of the rare gas atom. Because silver aluminosilicate has a hexagonal pore structure, the charge density around the rare gas atom changes from a spherical to a hexagonal distribution, because the electric polarization and the minimum value of the charge density appear in the transition zone. The three-dimensional minimum charge densities of the He, Ne, Ar, Kr, and Xe atoms in the transition zone are 0.0028, 0.0040, 0.0100, 0.0130, and 0.0180 a.u., respectively. Figure 4 shows that there is a linear relationship between the adsorption energy and the minimum charge density. The polarization of the rare gas atom by the positively charged Ag^+ ions plays an important role in the van der Waals dispersion, and the minimum charge density is a measure of the polarization. Xenon has the most of electrons to affect the van der Waals dispersion, so it has the highest minimum charge density and the most spacious spherical scope.

Among the five rare gases, Xe has the most number of electrons to affect the van der Waals dispersion, so it has the highest minimum charge density, strongest polarization, and most spacious atom spherical spatial scope. It is easy to understand why the adsorption of Xe to silver aluminosilicate is the most favorable.

4. Conclusion

The adsorption energies of rare gases (He, Ne, Ar, Kr, and Xe) to silver aluminosilicate were calculated using DFT with LDA, GGA, and DFT-D methods. The structure of silver aluminosilicate ($AgSiAlO_4$) was derived from the kaolinite structure. The optimized geometry was acceptable compared with the actual bond lengths and shows that van der Waals dispersion has little effect on the geometry of silver aluminosilicate. The adsorption energies of rare gas atoms were calculated at different sites in the honeycomb lattice of silver aluminosilicate, and the affect of van der Waals dispersion is discussed. The calculated adsorption energy of Xe with the DFT-D method is acceptable, with relative fluctuation of about 6.8%. This indicates that rare gas atoms have no effect on the electronic bands of silver aluminosilicate. However,

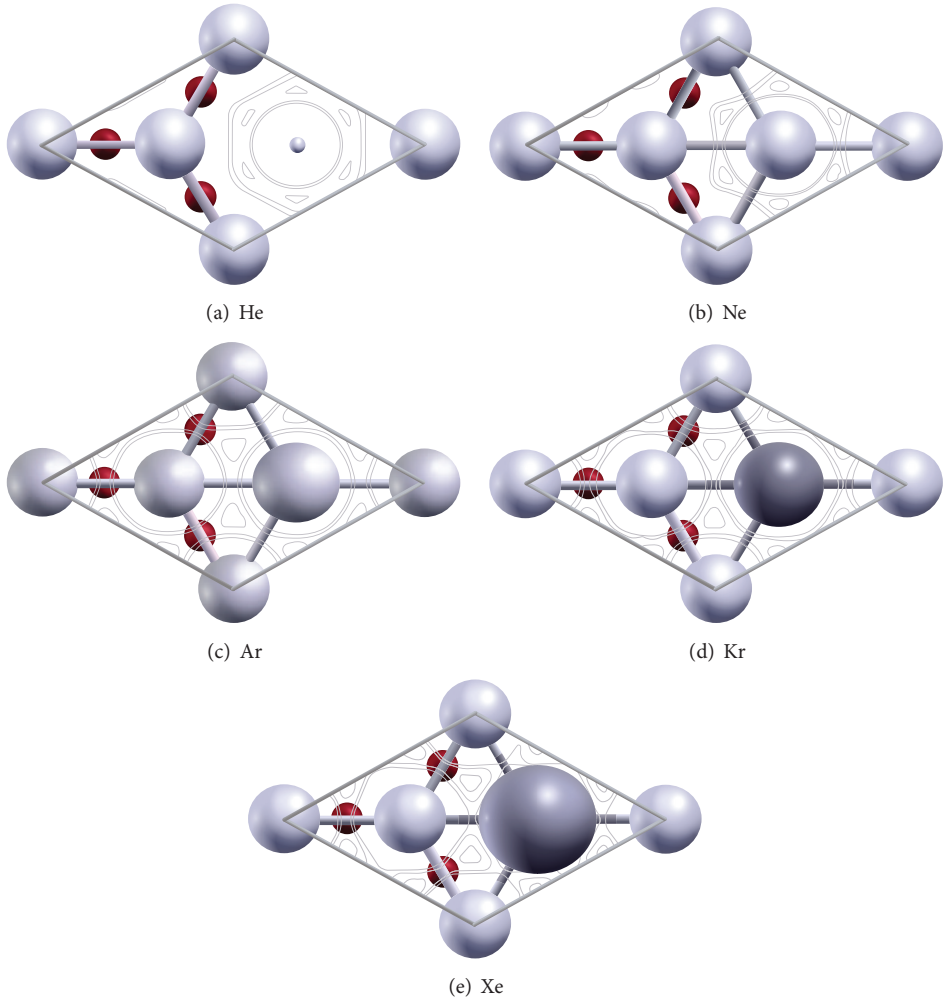

Figure 3: Electric charge density of rare gas atoms adsorbed on silver aluminosilicate.

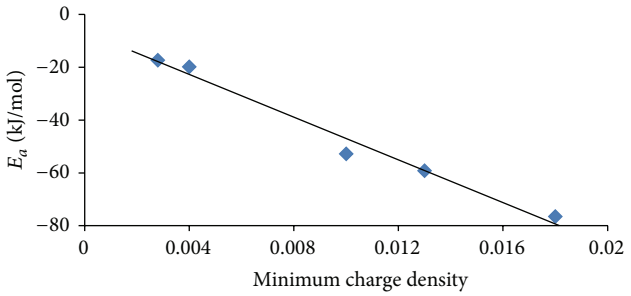

Figure 4: Relationship between the adsorption energy and the minimum charge density around the rare gas atoms.

because of the hexagonal lattice of silver aluminosilicate, the electronic charge density around the rare gas atoms changes from a spherical to hexagonal distribution, and the minimum values of the charge density appear in the transition zone. The linear relationship between the minimum charge density and the adsorption energy shows that polarization plays an important role in the van der Waals dispersions in the adsorption of rare gas atoms. The Xe atom has the most electrons of the rare gases for van der Waals dispersion, so it has the highest minimum charge density, strongest polarization, most spacious spherical scope, and strongest adsorption on silver zeolites.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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