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Adsorption of He gas on the Ag_n nanoclusters: A molecular dynamic study

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ABSTRACT

Using molecular dynamics simulations, the adsorption of He gas on the Ag nanoclusters were investigated as a function of pressure, temperature and diameter of nanoclusters. We have calculated the average interaction energy between the gas atoms and the Ag nanoclusters, adsorption constant and enthalpy of adsorption for all of the Ag nanoclusters. Results show that the adsorption constant, the value of average interaction energy and the enthalpy of adsorption decrease when cluster size increases.

1. Introduction

In recent years, metallic nanoclusters have attracted a large portion of research interest due to their different physical and chemical properties in comparison with macroscopic metals [1,2]. These differences in most cases are related to the large surface/volume ratio in nanoscale. Also, another important feature of nanoclusters is that their properties are usually size and shape-dependent [3]. As it has been known before, the intrinsic properties of metallic nanoclusters depend on their size, shape, composition, crystallinity, and structure, considerably [4–6]. Therefore, study on the effect of mentioned parameters on the chemical activity of metallic nanoclusters is a running and challenging area of computational chemistry. Ag nanoclusters are one of the important metallic clusters which have several applications such as in catalysis [6], electrocatalysis [7], nano optics [3,8], solar cells [9], molecular sieve membranes [10], and antibacterial activities [11–15] which can be produced by various methods [2,16–20].

One of the important factors that can affect the shape of metallic nanoclusters, is the influence of gas atmosphere around the cluster which usually leads to adsorption of gases on their surface. These adsorption phenomena can be chemical or physical which depends on the chemical activity of gas particles and clusters. Hansen et al. studied the effect of gas atmosphere on the shape of Cu nanocrystals dispersed on ZnO and silica supports using transmission electron microscopy (TEM) in H_2O/H_2 and CO/H_2 gas mixtures [21]. They observed considerable distortions in the cluster shape by changing the gas atmosphere. Lamas et al. performed a MD simulation to investigate the effect of inert gas adsorbates (Ar, Xe, and He) on the shape and structure of Pt nanoclusters supported on a graphite substrate. They found that the gas phase substantially alters the vacuum cluster structure, and the changes are mostly irreversible in the time frame of the simulations (2 ns), especially at temperatures well below the cluster melting point [22].

Also, some MD simulations have been performed for Ag clusters. Baletto et al. used MD simulations to study the growth of free silver nanoclusters [23]. They found that the final shape of the cluster depends on deposition flux and temperature. Also, they reported a reentrant morphology transition at intermediate values of temperature and deposition flux in which a decahedral window is formed and around it icosahedrals preferentially grow. In another work, Baletto et al. studied freezing of the Ag nanodroplets in time scales by MD according to experimental conditions [24]. Their calculations show that at small sizes (2–3 nm), both crystalline and non-crystalline clusters (icosahedral and decahedral) are created, while at large sizes silver droplets solidify preferentially as non-icosahedral clusters. Ao et al. used MD simulations based on Sutton–Chen many-body potentials to study the size dependency of melting point (T_m) and Kauzmann temperature (T_K) of Ag nanoclusters [25]. Their simulations indicate that as the size of Ag particles decreases, T_K and T_m functions reduce. However, the T_K

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and T_m ratio of Ag nanoparticles are size independent. Kuzmin et al. studied the behavior of Ag clusters with magic numbers of atoms in the 0–1300 K temperature range with embedded atom model by MD method [26]. Their work exhibits structural transitions of cubic octahedral clusters to the stable icosahedral structures. Luo et al. calculated the Gibbs free energy (G) of Ag nanoparticles from the bulk free energy and surface free energy of both solid and liquid phases using MD simulations based on the embedded atom model [27]. Their calculations indicate that thermodynamic properties of mentioned nanoparticles can be divided into two parts: bulk quantity and surface quantity; and thermodynamic properties of nanoparticles depends on the number of surface atoms. However, in despite of mentioned investigations, size dependence of adsorption properties of inert gaseous atmosphere on Ag nanoclusters has not been investigated clearly.

In this work, we have investigated adsorption of He atoms on the Ag nanoclusters of different sizes at some temperatures and pressures using MD simulations. The inert gas atmosphere was selected due to the fact that reactive gas atmosphere leads to chemisorption process. This process includes charge transfer between adsorbates and the cluster and it influences the structure and chemical activity of nanoparticles. It would be more complex if we had used reactive gases.

2. Calculation methods

Ag is a metal with a FCC structure. Spherical Ag nanoclusters were constructed from this large FCC structure, using various spherical cutoff radii [28]. The cluster cutoff radius is defined as

$$R_c = R_g\sqrt{\frac{5}{3}+R_i} \tag{1}$$

where R_i is the interatomic radius for the Ag cluster (R_i = 1.44 Å) and the radius of gyration R_g is given by

$$R_g^2 = \frac{1}{N}\sum_j \left(R_j - R_{\text{c.m.}}\right)^2 \tag{2}$$

where $(R_j - R_{\text{c.m.}})$ is the distance between j atom and the cluster center of mass. We constructed Ag nanoclusters ranging from 138 to 1057 atoms to take into account a variety of size ranges in the mesosclae region [28,29].

The spherical Ag nanoclusters were initially subjected to mild annealing in the 0–300 K intervals. The shape of Ag nanoclusters remained almost spherical after the annealing process.

The interactions between metal atoms were modeled by quantum Sutton–Chen potential (QSC) [30,31]:

$$U_{\text{tot}} = \varepsilon\left[\frac{1}{2}\sum_{\text{i}\neq\text{j}}\sum_{\text{j}}\left(\frac{a}{r_{ij}}\right)^n - c\sum_i \rho_i^{1/2}\right] \tag{3}$$

The first term is pair repulsion potential and the second term describes the cohesion associated with the local density ρ_i:

$$\rho_i = \sum_{j\neq i}\left(\frac{a}{r_{ij}}\right)^m \tag{4}$$

In Eq. (3), r_{ij} is the separation distance between atoms i and j, ε is the potential well-depthwith dimensions of energy, a is the lattice constant with the dimensions of length, c is a dimensionless parameter scaling the attractive terms, and m and n are positive integer values with $n > m$. For Ag–Ag interactions, the QSC parameters are ε = 0.033147 eV, a = 4.05 Å, n = 7, m = 6 and c = 16.399.

In these simulations, we considered two different force field models for the He gas:

Table 1
The Lennard–Jones 12–6 parameters for He–He and Ag–He interactions.

interaction	ε (eV)	σ (Å)
Ag–He	0.017613	2.597
He–He	0.000900	2.550

(1) The Lennard–Jones (LJ) 12–6 potential was employed for the He–He.
(2) The Feynman–Hibbs (FH) potential was applied for He–He interactions. The HF potential for He can be found in study of Tchouar et al. [32]

We compared the results obtained from the two models. There was no significant difference in results between the models. Therefore, the quantum effects are not important for He in these simulations. In this paper, we have reported the results obtained from the first model.

Also, the Lennard–Jones (LJ) 12–6 potential was employed for the Ag–He interactions [33,34] (see Table 1). The LJ parameters for Ag–He atoms were obtained by the Lorentz–Berthelot mixing rules (the Lennard–Jones parameters for Ag–Ag are ε = 0.3447 eV and σ = 2.644 Å [33]).

Constant temperature and constant volume MD simulations were carried out by using DLPOLY 2.20 [35,36]. To keep temperature constant, the Berendsen thermostat [37] with a relaxation time of 0.1 ps was applied. In these simulations Verlet's leapfrog algorithm [38] was used in conjunction with the multiple time step method to integrate Newton's equation of motion over time. In each simulation we considered a simulation box, which had periodic boundaries in three directions. The size of the box was chosen such that the interaction between the particle and its own image in the neighboring box is negligible. For all simulations a time step of 0.5 fs was used and statistical data were collected every 1000 time step. After an equilibration period of 500 ps, data production runs of 1 ns were conducted for all the simulations. A cutoff radius of 10.0 Å was applied to the nonbonding interactions. Simulations were performed under different isothermal conditions (150–350 K) and for pressures up to 500 kbar for different sizes of Ag nanoclusters.

MD simulations were carried out in a cubic box for a system including the annealed spherical Ag nanoclusters and He gas (He atoms were located randomly in the cell). Various gas pressures at constant volume and temperature were created by changing the number of gas atoms. So the pressure was reduced in several steps. At each step, gas atoms were removed, and after the end of each simulation, its output was used as the input for the next step. In these simulations, pressure was calculated by van der Waals (VDW) equation of state for He. Fig. 1 gives snapshots of a Ag_{457} nanocluster surrounded by He atoms at 150 K. This figure shows that He gas adsorption does not change the shape of the Ag nanocluster surface. Also, He atoms diffuse freely on the Ag nanocluster surface and do not form clusters on the surface. Also, He atoms do not prefer to be adsorbed on certain sites of the surface. The distance between Helium atoms is almost much. Therefore, He atoms are gas under the conditions of study.

3. Results and discussions

The adsorption constant represents the ratio of the number of gas atoms within the first layer and the surface area of the Ag nanoclusters. These gas atoms are located in the first layer and are directly adsorbed by the surface of Ag nanoclusters. For counting the number of adsorbed gas atoms, we used the Ag–He radial distribution function (RDF). The position of the first peak in RDF was applied as a criterion to locate the adsorbed gas atoms position.