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Hydrogen atom adsorption on aluminum icosahedral clusters: A DFT study

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ABSTRACT

Properties of hydrogenated, icosahedral aluminum clusters were investigated using density functional theory in comparison with those of aluminum bulk systems. The most stable site for H adsorption to Al_{13} was the hollow HCP site. The H binding energy suggests that the top and the bridge configurations are transition states. Results for $Al_{13}H$ were compared with those obtained for two surface models simulating f.c.c. and icosahedral (1 1 1) surfaces. Results show that the H atom interacts weakly with surface of clusters when the cluster size is increased. The migration energy of H atom between neighboring T and O sites becomes smaller for icosahedral subsurface than for either bulk material or the f.c.c. subsurface. A similar relation between the two surface models was found for the migration energy between surface and subsurface sites. These results indicate that the icosahedral surface lowers the migration barriers of H atom both within the subsurface and between the surface and the subsurface.

1. Introduction

Nanomaterials have attracted great interest in recent years because of their unusual mechanical, electrical, electronic, optical, magnetic and surface properties. The high surface/volume ratio of these materials presents important implications with respect to energy storage. Nanostructured materials are promising for hydrogen storage because of their unique features such as adsorption on the surface, intergrain and intragrain boundaries, and bulk absorption [1]. Nanostructured and nanoscale materials strongly influence the thermodynamics and kinetics of hydrogen absorption and dissociation by increasing the diffusion rate and by decreasing the required diffusion length.

Investigation of suitable materials for hydrogen storage has driven attention to different lightweight nanostructures. Among various hydrogen storage materials, hydrogen adsorption by aluminum clusters of different sizes, aluminum nanowires, and aluminum f.c.c. clusters can be considered as promising candidates for fuel cell hydrogen storage devices [2,3]. These findings are important because light metals such as aluminum are inexpensive and can store large amounts of hydrogen, which is crucial for fuel cell design [4]. Crane and Nuzzo [5] obtained evidence related to H adsorption on Al(1 1 1). Through careful examination of temperature-programmed desorption data, they suggested that chemisorbed H on Al(1 1 1) occupies both surface and subsurface sites. Using low-energy ion spectroscopy Bastasz and Whaley [6] showed that the occupied site of atomic hydrogen exists on the top layer of the surface. Based on both experimentation and simulation [7–11], hydrogen is known to adsorb strongly on the surface of aluminum clusters, thereby greatly changing the structure of the clusters.

It is important to understand the properties of aluminum clusters and their interaction with hydrogen at a fundamental level. In previous reports [12,13], we demonstrated the electronic properties of aluminum clusters from small clusters up to several hundreds of atoms. The stable structures of small-size clusters are known to have dense packing and high symmetry of icosahedra in geometrical structures. The icosahedral structure can be viewed as 20 nearly regular tetrahedra, each with an approximate f.c.c. structure, joined at a common corner [14,15]. The 20 tetrahedral parts have pseudo-(1 1 1) faces that become the 20 triangular surfaces of the icosahedral cluster. An atom on a (1 1 1) surface is the most highly coordinated of any f.c.c. surface atom, having 9 of its 12 nearest neighbors. Therefore, (1 1 1) surfaces have the lowest energy. Moreover, the icosahedral structure, being roughly spherical in shape, has a low surface-to-volume ratio.

In this study, energetic properties of aluminum clusters absorbed with hydrogen atoms were investigated for the "magic" clusters with icosahedral (I_h) symmetry based on the first-principles calculation. We investigate the hydrogen-site specific effects and how the hydrogen storage properties of aluminum clusters change with the cluster size. The hydrogen diffusion barriers are calculated for interstitial sites of aluminum clusters and compared to those of bulk aluminum system, which can provide us an interpretation of the stability of the hydrogenated clusters.

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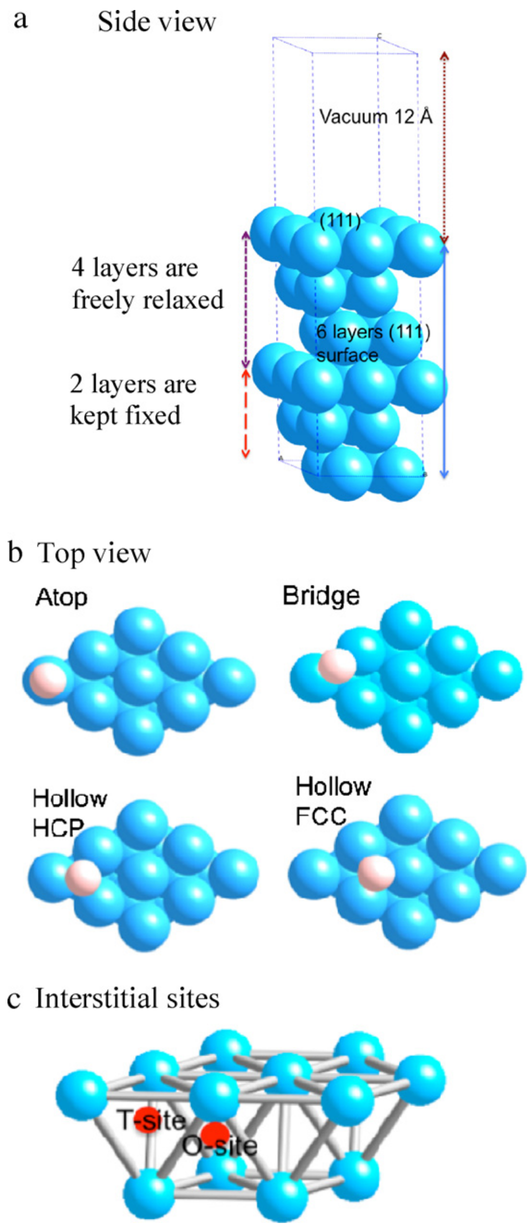

Fig. 1. (a) Side view of the slab model of clean Al(1 1 1) surface used in simulation. (b) Top views of the equilibrium geometry of four sites of the adsorption of hydrogen on the surface. (c) View of two interstitial sites on the subsurface of Al(1 1 1.).

2. Method and computational details

We used four structure models in this study. For the examination of H impurities in the f.c.c. bulk, we construct 2 × 2 × 2 supercells containing 32 Al atoms. For the surface calculation, we use two slab models with six (1 1 1) layers including 24 Al atoms, as presented in Fig. 1a. One slab model is constructed as the ideal f.c.c. case. The other slab model is for representing the surfaces of icosahedral clusters by deforming the f.c.c. model with 1.0261 times elongation parallel to the surface and 0.9498 times contraction perpendicular to the surface under the constant volume condition. For the cluster system, an isolated cluster is placed inside a very large cubic cell with size-length as 35 Å in the periodic boundary conditions, so the interaction between the clusters in neighboring cells can be negligible.

The density functional theory (DFT) [16,17] calculations in this study were performed using the Vienna Ab-initio Simulation Package (VASP) [18–21] with ultrasoft pseudopotentials [20,22] to describe the electron–ion interaction. The spin-polarized calculations were conducted to determine the magnetic ground state of the bare Al_n and hydrogenated Al_nH clusters within local density approximation (LDA). A cutoff energy of 350 eV was used in all calculations with plan-wave basis set to make energy convergence within 0.001 eV. For comparison with calculated results [23,24] for hydrogen in aluminum crystal system and to ensure the precision of energies and geometries, we conducted the bulk and Al(1 1 1) surface calculation with extensive tests of k-point sampling using Monkhorst–Pack [25] k-point meshes to demonstrate that total energies for all cells are converged to within 0.001 eV. In this study, k-point grids of 16 × 16 × 16 and 4 × 4 × 1 were used, respectively, for the bulk and slab models. Fermi smearing of the electronic occupancy with a fictitious electronic temperature of 0.025 eV was used.

The nudged elastic band (NEB) method [26] was used to find the minimum energy path (MEP) and the corresponding energy barriers for hydrogen diffusion process. In this approach, the reaction path is discretized between the initial and final configurations. All discrete configurations and images were optimized simultaneously along the reaction path until the forces acting on the atoms were smaller than 0.01 eV/Å.

3. Results and discussion

3.1. Hydrogenation of small icosahedral clusters

We first discuss the reactivity and bonding of the hydrogen atom to an Al_{13} cluster. The binding energy of hydrogen to the Al_n systems, E_B, has been calculated according to the following expression:

$$E_B = E_{Al_n} + E_H - E_{Al_nH}, \tag{1}$$

where E_{Al_nH} and E_{Al_n} respectively represent the total energy (eV) of a hydrogenated Al_n cluster and a pure Al_n system. We use n to represent the number of Al atoms in the cluster. The unit of E_B is eV/H atom.

In Fig. 2 we present four different geometries and their binding energies of $Al_{13}H$: (from left to right) tetrahedral (T), on top, bridge, and HCP hollow positions. In this model, $Al_{13}H$ has 40 valence electrons, which gives a structure of closed electronic shells. The geometrical structure of $Al_{13}H$ is obtained with a distorted icosahedron. The most stable site for hydrogen atoms is the hollow HCP site, the only hollow site on Al_{13} cluster located above the center of the triangle face, with the binding energy of 3.383 eV. Inside the Al_{13} cluster, only one kind of interstitial site exists: tetrahedral (T) sites which are more unstable than three surface sites. The results of H binding energy suggest that the top and the bridge configurations are the transition states, a small energy difference between the hollow site and other positions shows a high mobility of the H atoms over the cluster surface at room temperature.

We have also investigated the minimized energy structures of Al_{55} cluster. In this case, there are several adsorption positions: on top of the Al atom at vertex and at the edge, hollow FCC and hollow HCP, bridge site. In the Al_{55} subsurface, there are two kinds of interstitial sites, tetrahedral and octahedral (O) site positions, similar to those of subsurface Al(1 1 1) system. In static, unrelaxed calculations for Al_{55} cluster, the H atom energetically prefers the O site to the T site in the subsurface. The calculated migration energy of H between the tetrahedral and octahedral interstitial sites is 0.35 eV in subsurfaces of the Al_{55} cluster, which is lower than the migration barriers from surface to subsurface from 0.55 to 0.59 eV. It is not easy to discuss the optimized structures of large clusters because the hydrogenated clusters are strongly distorted. For this reason, we discuss the interaction of the H atoms and surface of

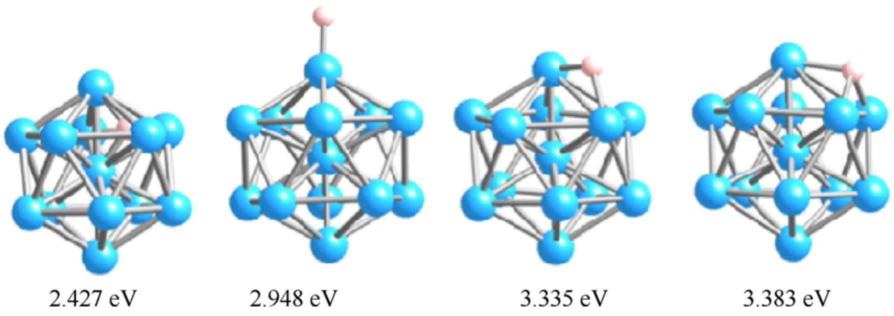

Fig. 2. Four different geometries of $Al_{13}H$: (from left to right) tetrahedral position, on top, bridge and hollow positions of the hydrogen atom. The numbers show calculated binding energies, in eV/H atom. The most stable structure is the hollow HCP geometry. Inside the Al_{13} cluster, there is only one kind of interstitial site, the tetrahedral site position, which is unstable.

the larger icosahedral clusters hereinafter using the pseudo-(1 1 1), icosahedral slab model.

Table 1
The binding energy of hydrogen to the aluminum systems with different hydrogen positions on the cluster surface and of the icosahedral, f.c.c. (1 1 1) surfaces. Energy unit is eV/H atom.

Sites	Distorted icosahedral Al_{13} cluster	Icosahedral surface	f.c.c. (1 1 1) surface
On top	2.948	2.369	2.070
Bridge	3.335	2.373	2.102
Hollow FCC	–	2.544	2.360
Hollow HCP	3.383	2.402	2.156
O-site	–	2.058	1.841
T-site	–	2.042	1.903

3.2. Comparison of icosahedral and f.c.c. (1 1 1) surfaces

To elucidate the H mobility mechanism, it is convenient to look at the hydrogen chemisorption on a solid aluminum surface and the site preference of H in Al bulk systems. We consider the adsorption of hydrogen atoms on the surface (Fig. 1b) and in subsurface (Fig. 1c) of both f.c.c. and icosahedral (1 1 1) slab models. The different sites of the hydrogen adsorption on the surface are presented in Fig. 1b. Results show that H energetically prefers the hollow FCC position for crystal surface. For the icosahedral surface, however, the preferred site of H atoms is the hollow FCC site. We find that the atomic relaxation effect plays an important role on the site preference of H at the tetrahedral versus octahedral interstitial sites in subsurface of the f.c.c. surface. Under the relaxed condition, H energetically prefers the larger O site in icosahedral subsurface, although the T site is the favored site for the f.c.c. subsurface.

The site preference of the H atom in a bulk system is also compared to those of DFT simulation results presented by Lu et al. [23] and Wolverton et al. [24]. As depicted in Fig. 3 and Table 1, tetrahedral sites are clearly favored over octahedral sites. Our results show good agreement with the result of Lu et al. [23] in the bulk f.c.c. case by LDA approach. Fig. 3 also shows the relative energy for migration of a H atom from tetrahedral to octahedral positions in the slab models. The energy barrier of 0.175 eV, which separates the T-site and O-site positions in the bulk system, compares well with the experimental value of 0.17 eV [27]. The O-site is also preferred in the case of f.c.c. subsurface. The smaller energy barrier of 0.1 eV separates the T-site and O-site positions between two Al(1 1 1) layers in f.c.c. surface; this energy value is reduced in the icosahedral surface to 0.088 eV. In contrast to bulk or crystal surface, the O site is favorable compared to T-site in icosahedral surface, although the energy difference between the two sites is quite small: 0.016 eV. These results suggest that the migration of H atom between interstitial sites becomes easier in the icosahedral subsurface.

As presented in Table 1, when the cluster size is small, the H atom interacts strongly with the cluster surface. The result also suggests that the H atom at each site in surface or subsurface of the icosahedral slab model is more stable than that in the f.c.c. slab model. To examine the possibility of the diffusion of a H atom between the surface and the subsurface, we estimated the energy barriers for H migrating between the surface and the subsurface. The results are portrayed in Fig. 4 as a comparison between crystal f.c.c. surface and icosahedral surfaces. Two possible paths of H migration from the interstitial sites in subsurface to the surface adsorption sites:

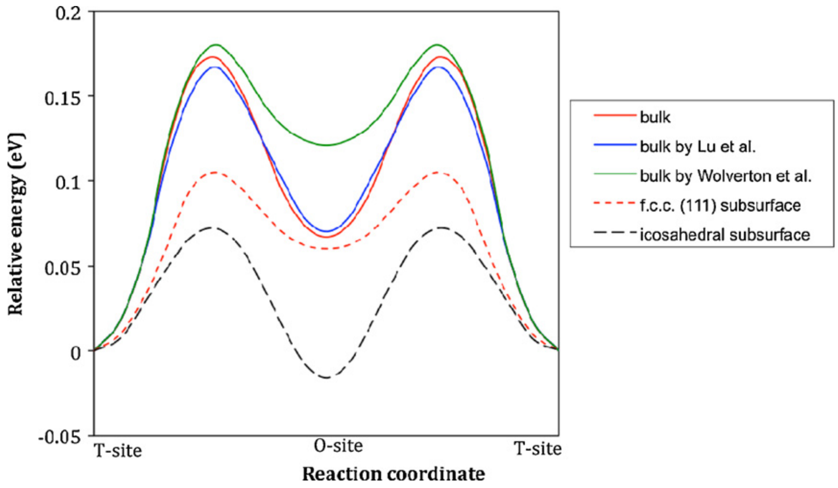

Fig. 3. Relative energy for motion of a H atom from the tetrahedral to octahedral positions in the bulk system, the f.c.c. surface and icosahedral surface models.

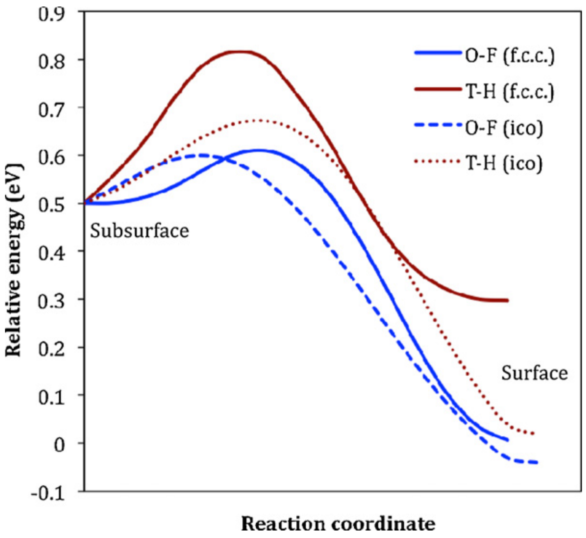

Fig. 4. Energy barriers for H atom migrating from the interstitial sites to surface adsorption sites for f.c.c. Al(1 1 1) surface and icosahedral surface. O–F denotes the migration of H atoms from octahedral (O) sites to hollow FCC sites; T–H denotes the migration of H atoms from tetrahedral (T) sites to hollow HCP sites.

from O-site to hollow FCC site and from T-site to the hollow HCP site. The hydrogen diffusion into the subsurface would occur at the cost of 0.5–0.7 eV. These results are consistent with the experimental data reported by Crane and Nuzzo [5]. The energy barriers are lower in the case of icosahedral surface, although the energy difference is rather small. The results indicate that the icosahedral surface lowers the migration barriers to H atoms between the surface and subsurface compared to the f.c.c. surface.

4. Summary

Using density functional theory calculations, we investigated the energetics and stability of icosahedral and f.c.c. aluminum systems. We confirmed that the most stable structure of $Al_{13}H$ is the hollow HCP position. For the icosahedral surface, however, H energetically prefers the hollow FCC site, which is the same as the f.c.c. (1 1 1) surface. In contrast to a bulk or f.c.c. surface, the O-site is the favored site compared to the T-site on the icosahedral surface, but the energy difference between the two sites is quite small. Our results suggest that the migration of H atoms between interstitial sites becomes easier for an icosahedral subsurface. Similar results were obtained on the H motion from subsurface to surface sites. In summary, to achieve the theoretical, high hydrogen storage capacities of Al, the use of icosahedral surface and subsurface might be valuable. Comprehensive studies of icosahedral clusters are anticipated for understanding and improving the hydrogen storage properties of aluminum.

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References

[1] R. Schulz, S. Boily, L. Zaluski, A. Zaluka, P. Tessier, J.O. Strom-Olsen, Innov. Met. Mater. (1995) 529–535.
[2] R. Ahlrichs, S.D. Elliott, Phys. Chem. Chem. Phys. 1 (1999) 13.
[3] J.A. Alonso, Chem. Rev. 100 (2000) 637.
[4] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, Chem. Lett. 16 (1987) 405–408;
C.T. Campbell, Science 306 (2004) 234–235;
M. Haruta, Chem. Rec. 3 (2003) 75–87;
M. Valden, X. Lai, D.W. Goodman, Science 281 (1998) 1647–1650.
[5] E.L. Crane, R.G. Nuzzo, J. Phys. Chem. B 105 (2001) 3052–3061.
[6] R. Bastasz, J.A. Whaley, Proc. International Conference on Hydrogen Effects on Material Behavior and Corrosion Deformation Interactions, 2003, pp. 919–926.
[7] S. Burkart, N. Blessing, B. Klipp, J. Muller, G. Gantefor, G. Seifert, Chem. Phys. Lett. 301 (1999) 546–550.
[8] H. Kawamura, V. Kumar, Q. Sun, Y. Kawazoe, Phys. Rev. B 65 (2001) 045406.
[9] A. Mananes, F. Duque, F. Mendez, M.J. Lopez, J.A. Alonso, J. Chem. Phys. 119 (2003) 5128–5141.
[10] L. Schlapbach, A. Züttel, Nature 414 (2001) 353–358.
[11] I. Yarovskya, A. Goldberg, Mol. Simul. 31 (2005) 475–481.
[12] T.V.B. Phung, K. Nishikawa, H. Nagao, AIP Proc. Int. Conf. on Computational Methods in Science and Engineering, 1046, 2008, pp. 64–67.
[13] T.V.B. Phung, T. Hashimoto, K. Nishikawa, H. Nagao, Int. J. Quantum Chem. 109 (2009) 3602–3612.
[14] A.L. MacKay, Acta Crystallogr. 15 (1962) 916.
[15] J. Farges, M.F. de Feruady, B. Raoult, G. Torchet, Acta Crystallogr. A38 (1982) 656.
[16] P. Hohenberg, W. Kohn, Phys. Rev. 136 (1964) B864.
[17] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133.
[18] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558.
[19] VASP code, http://cms.mpi.univie.ac.at/vasp.
[20] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251.
[21] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15.
[22] D. Vanderbilt, Phys. Rev. B 41 (1990) 7892.
[23] G. Lu, D. Orlikowski, I. Park, O. Politano, E. Kaxiras, Phys. Rev. B 65 (2002) 064102.
[24] C. Wolverton, V. Ozolins, M. Asta, Phys. Rev. B 69 (2004) 144109.
[25] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
[26] G. Henkelman, B.P. Uberuaga, H. Jonsson, J. Chem. Phys. 113 (2000) 9901.
[27] G.A. Young, J.R. Scully, Acta Mater. 46 (1998) 6337.