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Al クラスターの水素吸着に関する理論的研究

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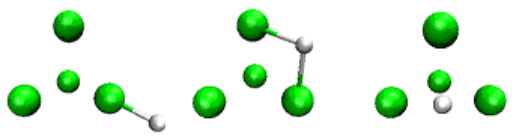
【Introduction】Recently, hydrogen gains attention as the new primary energy source because of the depletion of fossil fuels and environmental issues like global warming. Hydrogen is derived from fossil fuels like petroleum and natural liquid gas in a present technology. It is also derived from water if the method is established. Hydrogen is excellent in the point of not generating CO_2 at all in the process of combustion and chemical reactions in a fuel cell.

There are three basic research challenges — production, storage, application — for hydrogen economy. In this research, we study hydrogen storage systems because recent reports on basic research challenges for hydrogen storage tell us that effective hydrogen storage is a key factor in enabling the success of the hydrogen economy. Hydrogen storage system must have following properties: appropriate thermodynamics, fast kinetics, high storage capacity (more than 10wt%), effective heat transfer, high volumetric densities, long cycle lifetime, and safety under normal use. The materials with all the properties have not been found yet. For some of these properties, solid-state storage materials are useful. Metal hydrides, chemical storage, nanostructured materials are famous for being effective solid-state storage systems. We research about aluminum hydrides (one of the metal hydrides) using aluminum clusters. Especially, we study aluminum hydrides using Al_4 tetrahedral cages which was recently observed in experiment and confirmed to have enhanced stability[1]. In this research, we suggest new structures of aluminum hydrides. In addition, we evaluate and discuss about the chemical properties between aluminum clusters and hydrogen by using the data derived from quantum chemical calculation.

【Calculating method】Structures optimizations and energy calculations were performed with Gaussian03 program package. The 6-311G** basis set and the exchange-correlation functional PW91 were used. We also used MP2 method to calculate energies of structures. The quantum energy density calculations were done with MRDFT program package uniquely developed in our laboratory.

【Result & discussion】Al_4 cluster has three sites that can adsorb hydrogen shown in Fig.1. Table1 shows the binding energy of Al_4H. Terminal site has the lowest energy, so that hydrogen is adsorbed on terminal site first. After terminal sites are filled with hydrogen, hydrogen is adsorbed on bridge site which has the second lowest energy.



(a)Terminal (b)Bridge (c)Hollow

Fig.1 The structure of Al_4H.

Table1 Binding energy of Al_4H.

Site	Terminal	Bridge	Hollow
Binding energy (eV)	-2.444	-1.737	-1.704

We show the path way of hydrogen adsorption from Al_4 to Al_4H_{12} in Fig.2. Structures in Fig.2 have the lowest energy among all isomers. Fig.3 shows the tendency of binding energy of these structures to be lower as hydrogen is adsorbed on the clusters. This result shows clusters become more stable as hydrogen is adsorbed. Al_4H_{12} contains 10wt% hydrogen, so it has satisfactory capacity to be used in actual system.

Transition states of hydrogen adsorption reactions and energy of the intermediate states are shown on Fig.4. The activation barrier height of 1.73 eV for the first reaction step ($Al_4+4H_2 \rightarrow TS1+3H_2$) and of 1.98 eV for the second reaction step ($Al_4H_2+3H_2 \rightarrow TS2+2H_2$) were found. These are relatively higher than those of third reaction step ($Al_4H_4+2H_2 \rightarrow TS3+H_2$) 0.186 eV and fourth reaction step ($Al_4H_6+H_2 \rightarrow TS4$) 0.0953 eV. This results show that hydrogen is easily adsorbed on bridge sites. Barrier heights of hydrogen desorbtion reactions from bridge sites are also relatively low comparing to those from terminal sites. Concluding, bridge sites are suitable for hydrogen storage. These extremely low barrier heights suggest that Al_4 tetrahedral cluster has appropriate thermodynamics and fast kinetics to be hydrogen storage system.

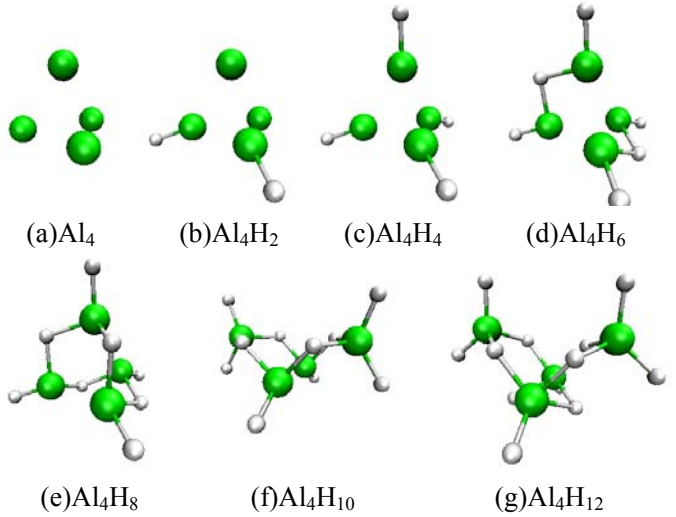


Fig.2 The path way of hydrogen absorption

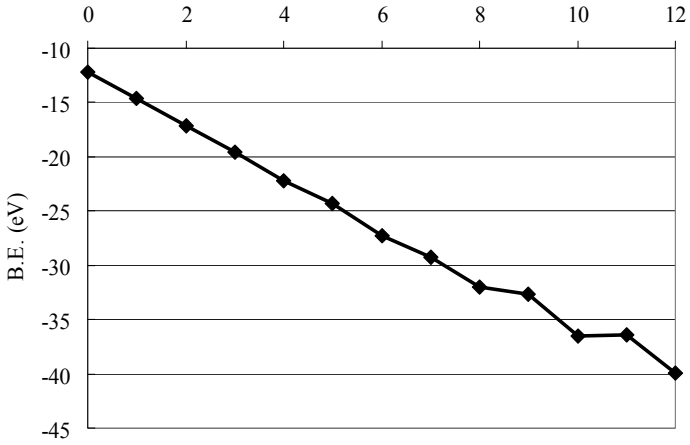


Fig.3 Binding energy of Al clusters. X-axis is the number of hydrogen.

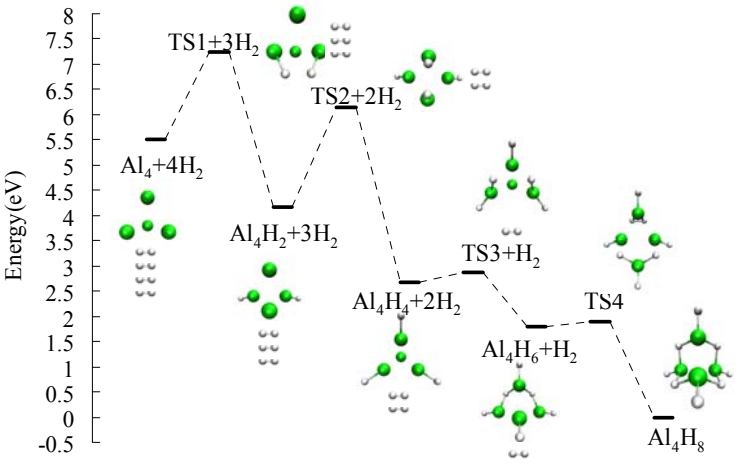


Fig.4 Transition state of hydrogen absorbing reaction and energy of the states

【Reference】

1. A. Grubisic, X. Li, S. T. Stokes, J. Cordes, G. F. Gantefor, K. H. Bowen, B. Kiran, P. Kena, R. Burgert, and H. Kchonockel, J. AM. CHEM. SOC. 2007, 129, 5969-5975.