NANOHy

Novel Nano Composites for Hydrogen Storage Applications

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Deliverable D 2.4

Report and recommendations for optimal material/size combinations (M 36)

Abstract

From systematic studies on selected 40 complex hydrides we found that most of the complex hydrides have critical particle size below 2nm. The particle size either stabilizes or de-stabilizes the system depending upon the nature of the system. Hence, we recommend synthesis of nanocomposite systems with particle size in the order of 2 nm or below if thermodynamic modification of the hydride shall be achieved.

In addition to the investigations of complex hydrides, the electronic structures based on parameterized HCTH functionals reveal that all polymorphs of AlH_3 are insulators with calculated band-gap varying between 2.53 and 4.41 eV. From our theoretical simulation we have found that the (0 1 0) in α-, (1 0 0) in α'-, (101) in α-, and (1 0 1) in γ-AlH_3 surfaces are the most stable surface in the corresponding polymorphs. We have predicted that the critical size for the AlH_3 nano-cluster is less than 1 nm. As opposite to complex hydrides we have investigated so far, the calculated formation energy as a function of particle size reveal that the nano particles of AlH_3 are relatively stable than the corresponding decomposed phases.

I) Stability enhancement by particle size reduction in AlH_3

a) Surface energy study

For the surface calculations the unrelaxed slabs have been cut from the optimized bulk crystal, where bulk structures have been fully relaxed with respect to stress and strain. All atoms in such created slabs have been allowed to relax using the minimization of forces acting on them. The thickness of a slab and the width of the vacuum layer can affect the surface energy of the surface model. Therefore, we first performed the effects of these variables on the surface energy to determine the model parameters. Calculations have been performed for slab thicknesses of 3-15 layers and a variety of different vacuum widths. The surface energy of a crystal can be calculated using the following equation

$$E_{surf}(n) = \{E_{tot}(n) - E_{bulk}(n)\}/2A \quad (1)$$

where E_{tot} and A are the total energy and total surface area, respectively. E_{bulk} refers to the energy of the bulk AlH_3 polymorph containing the same number of molecular units as the slab. Since the constructed supercell of slab has two surfaces, the energy difference is normalized by twice the area of each surface in Eq.1. In all the studied thin film geometries we have found that 8 to 10 Å layer thickness supercell (depending upon the surface) is sufficient to get the well converged surface energy. The calculated surface energies for all the possible low energy surfaces are given in Table 1 for AlH_3 polymorphs. The calculated surface energies for the α-AlH_3 are vary from 0.68 to 1.99 J/m^2 (depending upon the surface) and the surface energy is almost the similar for (010), (011), (100), (111) surfaces. The possible reason is that in α-AlH_3 (010), (011), (100), and (111) surfaces have almost a similar atomic arrangement. Similarly, in β- polymorph both (010)-(100), and (011)-(110) surfaces have almost similar surface energy. In γ- polymorph (010) and (010) have a similar surface energy. Among the considered surfaces the (010) in α-, (100) in α'-, (101) in β-, and (101)

in γ-AlH_3 surfaces has the lowest surface energy and hence it becomes the most stable surface in the corresponding polymorphs. The calculated stable surface energy for these polymorphs are in the following order $\gamma < \beta < \alpha' < \alpha$.

Table 1. Calculated surface energy (in J/m^2) for AlH_3 polymorphs in different possible lowenergy surfaces.

Direction	α	α'	β	γ
(001)	1.99	0.89	0.98	1.39
(010)	0.68	1.30	0.81	1.38
(011)	0.70	0.69	0.76	0.68
(100)	0.69	0.63	0.81	1.09
(101)	0.94	0.71	0.52	0.45
(110)	1.30	1.02	0.76	1.17
(111)	0.70	0.77	1.05	0.55

b) Nanoparticle modelling

From the variation in the interatomic distances compared with bulk materials it should be anticipated that nano-phase materials have different physical and chemical property than the bulk materials. Once we reduce the particle size beyond certain range (called critical particle size), most of the atoms will be exposed to the surface. It is at this region where the property of the material begins to differ drastically from that of the bulk materials. In order to identify the critical particle size we have calculated the total energy as a function of the cluster size for AlH_3 as shown in Fig.1. From Fig.1 it is evident that if the cluster size decreases the total energy becomes more positive. In particular there is a steep increase in the total energy when the size of the cluster is below 1nm for α-AlH_3. Further, the reduction in the total energy for the nanoparticles suggest the changes in thermodynamical properties and in particular the hydrogen sorption temperature is expected to reduce in nanophases compared with that in bulk materials. The reason is that the surface-to-volume ratio increases upon decreasing the cluster size. Since the surface atoms have lower coordination (generally found to occupy the less stable top and bridge sites) than that in bulk materials, the average number of bonds between constituents is lower for smaller clusters. This could explain why the decomposition temperature for nanoparticles are usually lower than that in bulk materials.

If one compare the variation in total energy with particle size for α-AlH_3 and that with the combination of nanoparticles of Al with H_2 molecule (see Fig.1), even the particle size below 1 nm the nanoparticle from α-AlH_3 is energetically stable compared with the corresponding decomposed phases (i.e. nanoparticles of Al with H_2 molecule). Especially, below the critical particle size i.e. ca. 1nm, the total energy get more positive (i.e. highly unstable) for the combination of nanoparticles of Al with H_2 molecule. This is opposite to the conclusion we have arrived on nanoparticles of MgH_2 and borohydrides, where, below the critical particle size these nanoparticles decompose and release hydrogen. So, the present result suggest that, unlike other hydrides we have investigated for their nanophase aspects, one can stabilize nanoparticles of AlH_3 even below 1 nm size. In order to substantiate this observation we have calculated the formation energy (ΔH) as a function of particle size using the following equation.

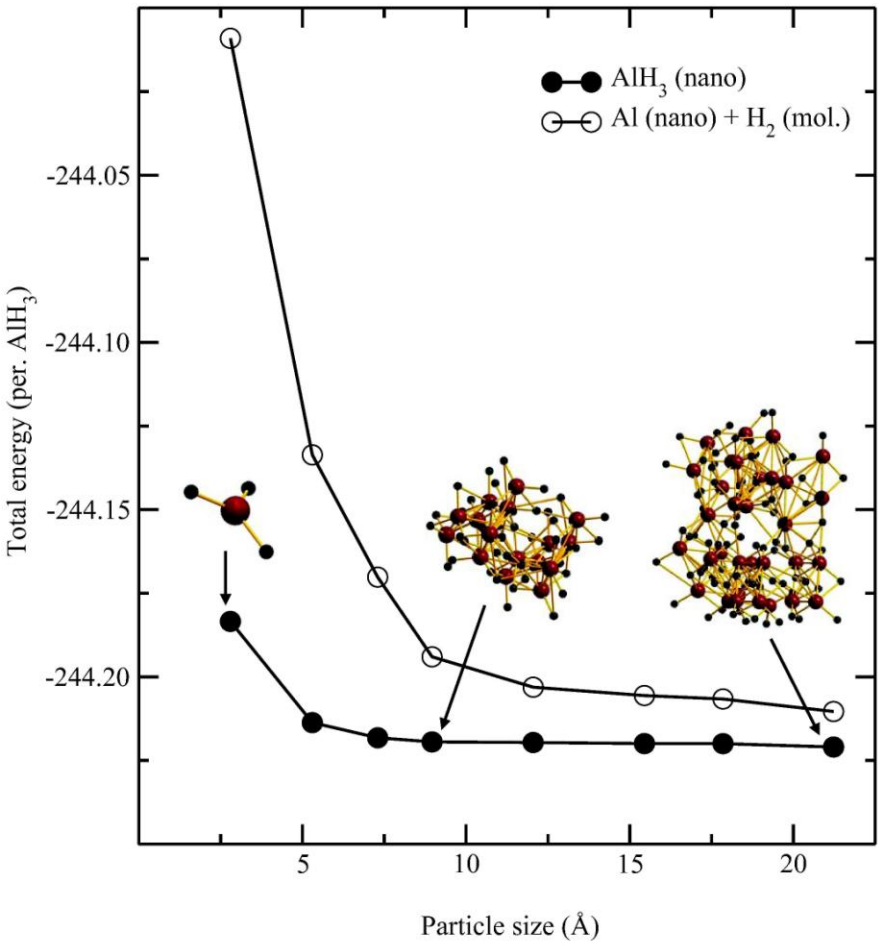

Fig.1 Calculated total energy as a function of particle size for the AlH_3 nano-clusters (in filled circle) and nano particles of Al with the H_2 molecule [i.e, E_{Al} (nano)+ $3/2E_{H2}$ (mol.)] (in open circle).

$$\Delta H = E_{AlH3}\,(nano)-[E_{Al}(nano)+ 3/2\ E_{H2}(mol.)] \qquad (2)$$

where E_{AlH3}(nano) and E_{Al}(nano) are the total energy of the AlH_3 and Al nano-clusters respectively. E_{H2} (mol.) refers to the total energy of the hydrogen molecule. The calculated ΔH value for the bulk α-AlH_3 phase is -5.99 kJ/mol. This result is in good agreement with the experimental (varies from -9.0 to -11.4 kJ/mol) [1-3] as well as other theoretical findings (-5.0 kJ/mol) [4]. In reality, due to the lower formation energy AlH_3 easily decomposes into Al and H_2 on elapse of time. It should be noted that the phase diagram study on Al-H system shows that AlH_3 is a metastable compound at ambient conditions and it become stable at high hydrogen pressure (~7 kbar at room temperature). The calculated ΔH as a function of the particle size is displayed in Fig.2. The critical particle size is found to be 1nm and the corresponding ΔH value is -5.8 kJ/mol, which is similar to that in the bulk phase (i.e, the system is unstable). From Fig.2 it is evident that when the particle size is smaller (below ~1nm) the formation energy of the system becomes much higher and the system can be more stable compared to Al+H_2). This clearly tells us that when the particle size is smaller and smaller the system becomes more stable. On the other hand, in MgH_2, the particle size reduction destabilizes the system [5, 6, 7]. The possible reason for such deviation may be due to the different chemical bonding present in these two materials. In MgH_2 the interaction between the Mg and H is almost pure ionic while in AlH_3 the interaction between Al and H is

mixed iono-covalent bonding. These findings clearly indicate that, depending upon the system, the reduction in the particle size may either stabilize or destabilize the system. It should be noted that, when we increase the cluster size above the critical size, these nano-objects will have core AlH_3 structural units which makes them behave like a bulk system. This is one of the reason why the calculated total energy and formation energy are almost constant for above 1 nm particles and the formation energies are almost similar to that of the bulk system.

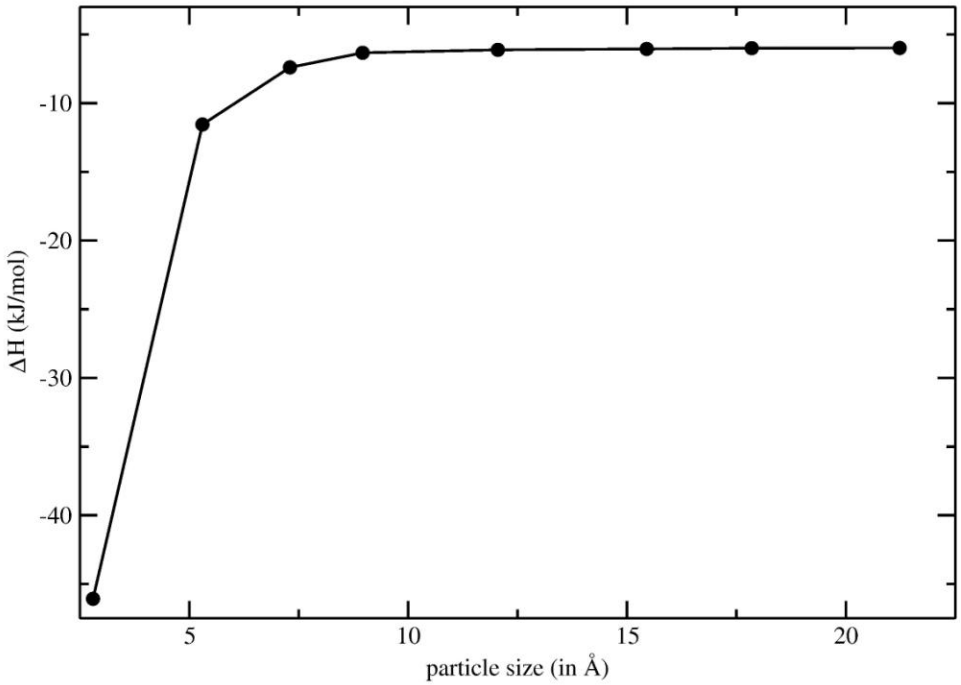

Fig. 2 Calculated formation energy as a function of particle size for the AlH_3 nano-clusters.

Though AlH_3 is one of the promising candidate for hydrogen storage application, it is not a stable compound and its property changes with time when store it in ambient condition and especially releases the hydrogen around 100^o C. In order to increase the stability of this system one must reduce the particle size beyond the critical particle size. The present study suggest that the particle size of α-AlH_3 clusters below 1~nm might have the required physical/chemical properties for the practical applications.

II) Critical particle size and optimal materials

If one reduces the particle size beyond certain range (called critical size), most of the atoms will be exposed to the surface. It is at this region where the properties of the material begin to differ drastically from that of the bulk materials. In order to identify the critical particle size we have calculated the total energy as a function of the cluster size for selected 40 compounds in this project. Among the studied 40 compounds AlH_3 has lower and $Nb(AlH_4)_2$ has higher critical particle size. It should be noted that the critical particle size of the most of these hydrides are lesser than the 2 nm.

The relative energy difference (ΔE) between the ultra small (ex. AlH_3) nano clusters and sum of atomic energies of the constituent atoms are defined as follows:

$$\Delta E = [E_{Al}(nano) + 3/2\ E_{H2}(mol.)] - E_{AlH3}\ (nano) \quad (3)$$

where $E_{AlH3}(nano)$ and $E_{Al}(nano)$ are the total energy of the AlH_3 and Al nano-clusters respectively. E_{H2} (mol.) refers to the total energy of the hydrogen molecule. If the ΔE value is positive then the systems become stable while the negative value indicates the instability of the system. The calculated ΔE values for the selected 40 complex hydrides we found that most of the complex hydrides are highly stable when we reduce the particle size to ultra smaller size (i.e., only one f.u. in the clusters). Among the 40 compounds only 7 compounds destabilize during the particle size reduction and $Mg(BH_4)_2$ is a borderline compound that has very small ΔE value. It should be noted that in this present study we have treated the clusters in the vacuum space and do not have any contact/support with any surfaces. If one embedded this ultra small nano clusters into the carbon media this picture may change.[8]

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