A First-Principles Investigation of Magnesium-Hydrogen System: From Bulk to Nano

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Abstract : Bulk MgH_2 has drawn much attention for the purpose of hydrogen storage because of its high hydrogen storage capacity ($\sim$7.7 wt %) as well as low cost and abundant availability. However, its practical usage has been hindered because of its high hydrogen desorption enthalpy ($\sim$0.8 eV/H2 molecule), which results in an undesirable desorption temperature of 3000C at 1 bar H2 pressure. To surmount the limitations of bulk MgH_2 for the purpose of hydrogen storage, a detailed first-principles density functional theory (DFT) based study on the structure and stability of neutral (Mg_m) and positively charged (Mg_m+) Mg nanoclusters of different sizes (m = 2, 4, 8 and 12), as well as their interaction with molecular hydrogen (H2), is reported here. It has been found that due to the absence of d-electrons within the Mg atoms, hydrogen remained in molecular form even after its interaction with neutral and charged Mg nanoclusters. Interestingly, the H2 molecules do not enter into the interstitial positions of the nanoclusters. Rather, they remain on the surface by ornamenting these nanoclusters and forming new structures with a gravimetric density higher than 15 wt %. Our observation is that the inclusion of Grimme's DFT-D3 dispersion correction in this weakly interacting system has a significant effect on binding of the H2 molecules with these nanoclusters. The dispersion corrected interaction energy (IE) values (0.1-0.14 eV/H2 molecule) fall in the right energy window, that is ideal for hydrogen storage. These IE values are further verified by using high-level coupled-cluster calculations with non-iterative triples corrections i.e. CCSD(T), (which has been considered to be a highly accurate quantum chemical method) and thereby confirming the accuracy of our 'dispersion correction' incorporated DFT calculations. The significance of the polarization and dispersion energy in binding of the H2 molecules are confirmed by performing energy decomposition analysis (EDA). A total of 16, 24, 32 and 36 H2 molecules can be attached to the neutral and charged nanoclusters of size m = 2, 4, 8 and 12 respectively. Ab-initio molecular dynamics (AIMD) simulation shows that the outermost H2 molecules are desorbed at a rather low temperature viz. 150 K (-1230C) which is expected. However, complete dehydrogenation of these nanoclusters occur at around 1000C. Most importantly, the host nanoclusters remain stable up to $\sim$500 K (2270C). All these results on the adsorption and desorption of molecular hydrogen with neutral and charged Mg nanocluster systems indicate towards the possibility of reducing the dehydrogenation temperature of bulk MgH_2 by designing new Mg-based nano materials which will be able to adsorb molecular hydrogen via this weak Mg-H2 interaction, rather than the strong Mg-H bonding. Notwithstanding the fact that in practical applications, these interactions will be further complicated by the effect of substrates as well as interactions with other clusters, the present study has implications on our fundamental understanding to this problem.

Keywords : density functional theory, DFT, hydrogen storage, molecular dynamics, molecular hydrogen adsorption, nanoclusters, physisorption