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Effect of microsolvation on hydrogen trapping potential of metal ions

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ABSTRACT

A thorough analysis is carried out to understand how the microsolvation affects the hydrogen adsorbing capacity of metal ions in the presence as well as absence of the counter ions. Calculations are done at different levels of theory by using different functionals and basis sets and also by using the BSSE correction. The Be^{2+} ion doped systems exhibit stronger interaction with the hydrogen molecule than the other metal doped systems. The extent of interaction is less affected by the method of computation. The reaction free energy values imply that adsorption on alkaline earth metal doped systems is spontaneous at room temperature. Interaction energies are favorable for hydrogen adsorption on the systems containing alkaline earth metal ions and the gravimetric density of adsorbed hydrogen molecule is more in those containing the alkali metal ions.

1. Introduction

The utility of hydrogen in storage, transport, and energy is a topic of active research for both the experimentalists and theoreticians. Hydrogen is a colorless, odorless and tasteless gas which upon combustion evolves neither air pollutants nor greenhouse gasses as byproducts. In a fuel cell, the chemical energy of hydrogen is converted to heat energy and electrical energy with the production of water, a harmless and useful byproduct. Hydrogen has the maximum energy content per unit of weight of any known element. Hence hydrogen has got the potential to solve an upcoming energy crisis which may occur due to the uncontrolled use of coal, oil and other fossil fuel reserves. But, in order to be used as a fuel, the on-board storage of hydrogen is necessary. Hydrogen, requires enough precautions and cryogenic conditions to be liquefied and stored safely in manageable quantities in large cylinders. Moreover, a large-scale manufacture of such cylinders capable of sustaining such extreme conditions for hydrogen storage is still not at par with the demands as the entire process is quite cost-effective. Therefore, the need for the designing of suitable molecular motifs as potential sites for the binding and storage of gaseous hydrogen under ambient conditions is of top priority. The desirable properties of a molecular material to be employed as an efficient hydrogen binding template are (i) light weight and stability, (ii) cost-effectiveness and ease of availability, (iii) high volumetric and gravimetric density, (iv) fast reaction kinetics (with a low activation barrier) followed by chemical reversibility, (v) low temperature of dissociation or decomposition of hydrogen from mother moiety, (vi) appropriate thermodynamic properties. Several research groups in this regard are quite successful in designing novel molecular templates having the potential ability to bind hydrogen in both atomic and molecular forms under optimum conditions.

The potential usage of the metal organic frameworks (MOFs) as selective adsorbents for various gasses as well as effective storage media for hydrogen is well investigated [1–8]. The importance of metal-doping onto the surface of an MOF moiety shows that the metal atom/ion serves as the primary site for hydrogen binding for use of these porous organic molecules as hydrogen storage materials [9–11]. Densely interpenetrated metal–organic frameworks [12] consisting of a Zn atom coordinated with aromatic-rich di-carboxylic acids are found to behave as fairly good hydrogen storage materials. Recent studies also highlight the application of sophisticated theoretical techniques [13] towards designing novel 3D covalent organic frameworks (COFs) having high hydrogen storage capacity. The hydrogen storage in COFs is studied [14,15] and it is found that they serve as a better storage template than the MOFs. It is found that upon metal doping [16,17] the hydrogen loading in the 3D-COFs, like the MOFs is also enhanced. The hydrogen storage capacity in COFs and MOFs by spillover is also compared [18].

The utility of graphene as a plausible hydrogen storage material got attention owing to their low cost, non-toxic behavior and easy synthetic protocols. The decoration of these graphenes with suitable metal atoms/ions can remarkably enhance their hydrogen binding aptitude. The metal site, by virtue of possessing a formal positive charge functions as the active site towards binding molecular hydrogen through a dipole–induced dipole type of interaction. Recently, Srinivasu et al. [19] confirmed that the hexagonal carbon rings of a graphene segment or a carbon nanotube as such is not an efficient candidate for the hydrogen storage, but, an ionic surface

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with a significant degree of curvature created by doping alkali metal ions significantly improves its hydrogen adsorption capability. Liu et al. [20] have further established that the boron-doping onto a graphene sheet considerably improves the Li binding strength of graphene. Again, the probable usage of few-layer graphenes as a plausible chemical storage of hydrogen is recently demonstrated by Subrahmanyam et al. [21]. However, the goals set by U.S. Department of Energy (DOE) regarding the mass ratio and volume density are not achieved either experimentally or via theoretical calculations on reversible model graphene systems.

The complex metal hydrides and metal clusters composed of the alkali metals, alkaline earth metals and the transition metals serve as rich storage materials for hydrogen. Hydrogen trapped on the metals as a hydride (in a solid form) is secured than its storage in the gas or liquid forms, the latter requiring cryogenic conditions which is practically hard to maintain. Moreover, the metal hydrides render higher hydrogen storage density than that of the gas or liquid form [22]. The potential usage of the metal hydrides and complex hydrides as a rich hydrogen storage media is well elaborated elsewhere [23,24]. A new method involving the direct synthesis of the complex metal hydrides, $LiAlH_4$ and $NaAlH_4$, which consecutively can act as suitable hydrogen trapping materials is also proposed [25]. The efficacy of solid metallo-hydrides like $NaAlH_4$ and $NaBH_4$ as high-density hydrogen storage materials [26] is also studied. The hydrogenation and dehydrogenation kinetics associated with sodium alanate, $NaAlH_4$ system is found to be catalyzed by various nanomaterials [27,28]. In recent times Srinivasu et al. [29] explored the hydrogen binding ability of different class of bimetallic clusters, viz. Be_3M_2, Mg_3M_2, and Al_4M_2 (M = Li, Na, and K). Recently group I and II metal amidoboranes are acknowledged as promising H_2 storage materials. The mechanisms and kinetics of H_2 release in metal amidoboranes are theoretically studied by Kim et al. [30,31] by means of high level ab initio calculations and kinetic simulations.

Among the alkaline earths, Mg clusters [32] have got a wide utility in this aspect. Moreover, its binary hydride can hold ample quantitative amounts of hydrogen and is also cost-efficient. The incorporation of a H_2 molecule onto Mg_n ($n = 8–10$) cage clusters have been studied theoretically by McNelles and Naumkin [33]. A study [34] however also point out some practical disadvantages like slow desorption kinetics and very high dehydrogenation temperatures for the metal hydrides in spite of the latter being a fairly capable medium for hydrogen storage. The applicability of the transition metal titanium, Ti, as an active site for hydrogen binding upon many template moieties is quite noteworthy. Yildirim and co-workers [35–37] in some articles have shown the significant effect of doping a titanium atom on the surface of carbon nanotubes and C_{60} cages whereby the Ti-center binds as many as four hydrogen molecules. The nature of the interaction between the incoming H_2 molecules and the active Ti-site on the given template is somewhat in between physisorption and chemisorption which can be explained by the well known Kubas interaction [38]. The doping of other transition metals and light metals like lithium with the C_2H_4 moiety to form stable metal–ethylene complexes is also reported [39]. Again the efficacy of transition metal supported C_5H_5 system [40], C_4H_4–Ti and $(C_4H_4)_2$–Ti complexes [41], M_n – (C_2H_4) (M = Sc, Ti, Fe, Ni; $n = 1, 2$) [42] and multi-decker $TiC_3B_2H_5$ complex [43] as effective hydrogen storage materials is also acknowledged. Some small to medium all-metal Ti_n ($n = 2–15$) clusters [44], especially Ti_{13} cluster as well as a couple of other M_{13} (M = Sc, Ti, Zr) clusters [45] are also capable of binding hydrogen molecules. Recently, the neutral and multiply charged titanium–H_2 systems ($Ti–H_2$, $Ti^+–H_2$, $Ti^{2+}–H_2$, $Ti^{3+}–H_2$, and $Ti^{4+}–H_2$) are studied theoretically [46] as precursors for hydrogen storage materials.

A number of experimental and theoretical investigations [47–59] showed that the charged species get stabilized by the polar solvent molecule through microsolvation method due to distribution of charge. The term, microsolvation is used to study the solvation process at molecular level. The system having a fixed number of solvent molecules and the solute is recognized as molecular cluster or microsolvated species. Recently, it has become possible to prepare and determine the structure and photoelectron spectral properties of both cationic and anionic clusters with the introduction of nozzle beam experiment. Previously Sing et al. [60] investigated the local structure around the ion and its importance to hydration and dissociation occurrence. The effect of counter ion on the modulation of structure of local hydration is also studied by Sing et al. In a theoretical study, Olleta et al. [61] investigated the dissociation phenomenon of NaX (X = halides) by water molecules as well as structural and energetic characteristics of the $NaX(H_2O)_{1–6}$ clusters. In our present work we consider some alkali metal ions (Li^+, Na^+) and alkaline earth metal ions (Be^{2+}, Mg^{2+}) microsolvated by a single solvent molecule like $H_2O/NH_3/HF$ molecule. Based on studies, we expect that these charged systems can be used for hydrogen adsorption and due to their light weight the gravimetric wt.% of adsorbed hydrogen will be quite high. Here we carried out systematic study on the interaction of molecular hydrogen with these microsolvated ions. The effect of counter ion on the geometry, the interaction energy and the gravimetric wt.% of adsorbed hydrogen are also studied.

2. Computational details

All DFT calculations are performed using the GAUSSIAN09 package [62]. The hybrid DFT method B3LYP is employed in conjugation with 6-311G(d, p), 6-311+G(d, p) and polarized valence double-ζ(cc-pVDZ) set of Dunning [63] basis sets for geometry optimization as well as frequency calculation. In order to build the general idea about the consequence of basis sets and methods of computation on the interaction energy of hydrogen molecule with parent moiety optimization is carried out with different basis sets and methods. The newly developed hybrid meta-GGA functionals of Truhlar and co-workers [64,65] M052X is used for optimization. It is already established [66] that for non-covalent interaction M052X works well and hence it is important in interaction energy calculation. The M052X method is used in combination with 6-311+G(d, p). The single point calculation is carried out with 6-311++G(2d, 2p) and 6-311++G(3d, 3p) basis sets. For comparison all the structures are optimized by applying the second-order Moller–Plesset (MP2) perturbation method. The optimization is carried out using 6-311+G(d, p) basis set. The single point MP2 calculation is carried out with 6-311++G(2d, 2p) and 6-311++G(3d, 3p) basis sets. For reference, interaction energy of hydrogen with main moiety is also calculated at CCSD(T)/6-311+G(d, p) level of theory. In order to take account of dispersion energy in a better way wB97XD method and B3LYP functional is applied along with its DFT-D counterpart (B3LYP-D) as implemented in GAUSSIAN09 package. The B3LYP-D method is applied in combination with polarized valence double-ζ(cc-pVDZ) type Dunning [63] basis set for geometry optimization as well as frequency calculation. For comparison, the latest functional from Head-Gordon and coworkers, wB97XD, which includes empirical dispersion as well as long range corrections, is applied for geometry optimization and frequency calculation in combination with polarized valence double-ζ(cc-pVDZ) set of Dunning [63] basis set. The basis set superposition error (BSSE) correction using the counterpoise (CP) procedure suggested by Boys and Bernardi [67] is made to the interaction energy of all hydrogen bound systems calculated by applying B3LYP methods using 6-311+G(d, p) and cc-pvdz basis sets. In order to analyze the effect of counter-ion the microsolvated alkali metal ion (Li^+, Na^+) systems are optimized in presence of counter ions (F^-/Cl^-) applying the