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Hydrogen adsorption on Ce-ethylene complex using quantum chemical methods

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ABSTRACT

Hydrogen storage capacity of Ce-ethylene complex is studied at MP2/SDD level. We have suggested suitable temperature and pressure range over which H₂ adsorption on this complex is energetically favorable. The kinetic stability of H₂ adsorbed complexes is verified by means of a gap between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). Six H₂ molecules can be adsorbed on Ce-ethylene complex thereby showing the H₂ uptake capacity of 6.71 wt % and satisfying the target set by US Department of Energy for vehicular application. Adsorption of all the six H₂ is in molecular form so we expect faster adsorption and desorption kinetics for this complex. Temperature dependent study of H₂ adsorption energy with Gibbs free energy correction has shown that H₂ adsorption on Ce-ethylene complex is energetically favorable below 190 K. Interaction of Ce:C₂H₄ with adsorbed H₂ molecules is found to be attractive in nature. The vibrational frequencies for H₂ and D₂ adsorbed complexes viz. Ce:C₂H₄(6H₂) and Ce:C₂H₄(6D₂) have been used to calculate the Equilibrium Isotope Effect (EIE) which is found to be 0.67.

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Introduction

For hydrogen economy to be a reality a material is required which can adsorb multiple H₂ molecules at room temperature with faster adsorption/desorption kinetics. Several classes of materials have been suggested for hydrogen storage both,

theoretically as well as experimentally. Recently small organic compound decorated with early transition metal atom have attracted attention from H₂ storage point of view since early transition metal atoms have almost empty *d* orbitals. It has been observed that these small organometallic (OM) complexes show high hydrogen storage capacity. Ma et al. have used density functional theory to investigate hydrogen absorption/

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desorption performances of $Zr-\eta^2-(C_2H_2)$ and predicted H_2 storage capacity 9.35 wt% [1]. Tavhare et al. have shown that hydrogen adsorption on alkali metal-doped acetylene complexes is energetically unfavorable whereas it is favorable on Ti-acetylene complex [2]. There is an excellent agreement between theory and experiment for the H_2 uptake capacity of $Ti:C_2H_4$ complex [3]. Zhou et al. have predicted the H_2 uptake capacity of $C_2H_4Li_2$ as 16 wt% [4]. Guo et al. have shown that CoC_mH_m and NiC_mH_m complexes can store up to 3.49 wt% hydrogen with an average binding energy of about 1.3 eV [5].

Kalamse et al. found that C_2H_2Ti complex favors over C_2H_2Li complex as a possible H_2 storage media [6]. Durgun et al. through first-principles calculations have obtained the H_2 uptake capacity of $Ti_2C_2H_4$ complex as 14 wt% and discussed its dimerization and polymerizations [7]. Liu et al. have shown that ionization of $Li_2C_2H_4$ and TiC_5H_5 enhances the H_2 uptake and also increases the number of nondissociative molecules attached [8]. Chakraborty et al. observed Kubas type interaction between the metal and H_2 molecules and an electrostatic interaction between the metal and the atomic hydrogens for metal-ethylene complex [9]. Yasuharu elucidated dependence of H_2 adsorption energy on the computational method and clarified the importance of Gibbs free energy correction on the adsorption energy for H_2 adsorbed $Ti_2C_2H_4$ complex [10]. H_2 uptake capacity of V-capped and V-inserted VC_3H_3 OM complexes was reported to be 10.07 and 6.66 wt% respectively [11]. The H_2 storage capacity of C_2H_4V and its cation was reported as 11.32 and 13.28 wt %, respectively by Kalamse et al. [12]. Ma et al. have shown that H_2 uptake capacity of both $Ti-\eta^2-C_2H_2$ and $HC\equiv C-TiH$ complexes is 14.06 wt% with binding energy of 0.20–0.42 eV/ H_2 [13]. They also predicted the H_2 uptake capacity of $Sc-\eta^2-C_2H_2$ and $HC\equiv C-SCH$ as 14.56 wt% [14]. It has been observed that cation of C_2H_4Sc shows higher H_2 uptake capacity by about 2 and 4 wt % than the neutral and anion, respectively [15]. A difference of about 2 wt% in H_2 uptake capacity of C_2H_4Ti complex and its cation is also observed [18].

Molecular dynamic simulations have been used to confirm the H_2 uptake capacity of VC_3H_3 complex predicted by electronic structure calculations [16]. Mavrandonakis and Klopfer have studied H_2 interactions with C_6H_5Li , C_6H_5OLi and C_6H_5COOLi complexes [17]. Weck et al. have shown that the H_2 storage capacity of Sc, Ti, and V transition metal atoms bound to C_mH_m rings is limited by the 18-electron rule [19]. Wadnerkar et al. observed that the Sc-capped and Sc-inserted ScC_3H_3 adsorb same number of H_2 molecules whereas Ti-inserted TiC_3H_3 complex adsorbs less number of H_2 molecules than that of Ti-capped TiC_3H_3 complex [20]. The H_2 uptake capacity of C_2H_2Ni and C_2H_4Ni complexes is found to be 4.54 and 4.44 wt% respectively and dimerization of C_2H_2Ni reduces the H_2 uptake capacity [21]. Dong et al. also observed lowering of H_2 uptake capacity after dimerization and oligomerization of Sc-methylidyne complex [22]. Chen et al. have studied interaction of H_2 , NH_3 and O_2 gas molecules with Ti benzene complexes using first-principles calculations [23]. Kiran et al. using 18 electron rule have shown that Ti containing C_nH_n organic molecules can store H_2 up to 9 wt% [24]. Kandalam et al. have studied H_2 adsorption on $TiC_3B_2H_5$ multidecker complexes and predicted its storage capacity as 5.1 wt% [25]. On experimental side Phillips and Shivaram have reported hydrogen storage on

transition metal-ethylene and transition metal-benzene complexes [26–28]. Theoretically calculated hydrogen uptake capacity of $Ti:C_2H_4$ OM complex is found to be in excellent agreement with the experimental determinations [3,18].

Most of the above mentioned studies are found to be focused on hydrogen storage capacity of either transition metal doped or alkali metal doped organic substrates. To our knowledge Ce doped small complexes have not been considered yet from hydrogen storage point of view. The aim of this work is to study hydrogen uptake capacity of $Ce:C_2H_4$ complex using second order Møller Plesset method. Using H_2 adsorption energies with Gibbs free energy correction we have predicted suitable temperature and pressure range over which H_2 adsorption on this complex is energetically favorable so that it can be used in different environment and applications. The vibrational frequencies are also obtained for these complexes to confirm their stability. We have also studied D_2 adsorbed $Ce:C_2H_4$ complex and the vibrational frequencies for H_2 and D_2 adsorbed $Ce:C_2H_4$ complex have been used to calculate the equilibrium isotope effect. The kinetic stability of these complexes is studied by means of HOMO-LUMO gap.

Computational details

The geometries of $Ce:C_2H_4(nH_2)$ and $Ce:C_2H_4(nD_2)$ ($n = 1-6$) are optimized using second order Møller Plesset method (MP2) with SDD pseudopotential. The vibrational frequencies are also obtained at the same level of theory and used to calculate equilibrium isotope effect (EIE). The EIE depends on the three terms namely MMI, EXC and ZPE and is given by Ref. [29–32].

$$EIE = MMI \times EXC \times ZPE \quad (1)$$

The MMI factor which is close to unity in many cases accounts for the molecular masses and moments of inertia of the isotopic species. It is close to unity since masses and moments of inertia do not change significantly between isotopes. The presence of vibrational levels beyond the zero point level results in arising of the second factor EXC. This factor plays an important role in EIE calculation when low frequency modes sensitive to isotope are present. The ZPE factor which is the dominant contributor to the EIE arises due to the zero point energy. The MMI, EXC and ZPE factors required for EIE calculation are obtained as follows:

$$MMI = \frac{\nu_{D_2}^{\nu_{H_2}}}{\prod_i^{3N-6} \frac{\nu_{iD_2}^*}{\nu_{iH_2}}} \quad (2)$$

$$EXC = \frac{\prod_i^{3N-6} \frac{1 - \exp(-\mu_i)}{1 - \exp(\mu_i^*)}}{\prod_j^{3N-6} \frac{1 - \exp(-\mu_j)}{1 - \exp(\mu_j^*)}} \quad (3)$$

$$ZPE = \frac{\prod_i^{3N-6} \frac{\exp(\mu_i/2)}{\exp(\mu_i^*/2)}}{\prod_j^{3N-6} \frac{\exp(\mu_j/2)}{\exp(\mu_j^*/2)}} \quad (4)$$

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