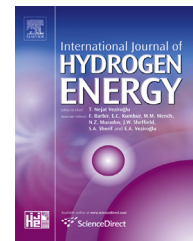




ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ijhydene

“Capping” out oxygen interference: An approach to achieve efficient hydrogen storage via Kubas binding

Rafia Ahmad¹, Pankaj Lochan Bora¹, Abhishek Kumar Singh*

Materials Research Centre, Indian Institute of Science, Bangalore 560012, India

ARTICLE INFO

Article history:

Received 1 September 2015

Received in revised form

12 February 2016

Accepted 20 February 2016

Available online 18 March 2016

Keywords:

Hydrogen storage

Oxygen interference

Density functional theory

Open metal sites

ABSTRACT

Hydrogen bound via Kubas interaction on metal decorated light weight materials forebodes a much efficient alternative for the fast depleting fossil fuels. However, oxygen interference in hydrogen storage on metal decorated carbonaceous systems obstructs the successful realization of the theoretically promised high storage of Kubas bound H₂. The interference is a consequence of preferred O₂ binding at the metal site, thereby blocking it for H₂ adsorption. Here, we report that arene capping of a Sc-metallacarborane (MCB) efficiently reverses the preferential adsorption of O₂ over H₂. The capped MCB completely repels O₂ off the Sc-site allowing purely Kubas binding of H₂. This is enabled by the down-shift of the *d*-band center of Sc below the Fermi-level from 1.29 eV in the uncapped to 5.67 eV in the capped MCB, respectively. The optimised *d*-band center position enables the empty Sc antibonding states to only be available for hydrogen adsorption via Kubas interaction, thereby, to completely avoid oxygen binding. This novel approach tunes a cluster electronically to enhance gas adsorption selectivity, which can be efficiently utilized in various catalytic, sensing and gas storage systems.

Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Excessive reliance on petroleum-based polluting fuel can be alleviated by employing hydrogen-powered fuel cells [1,2]. Hydrogen has been recognized as a non-polluting, energy efficient fuel that is abundant and relies on renewable resources [3]. The success of hydrogen economy primarily depends on finding inexpensive light-weight materials that can store hydrogen molecules with high gravimetric capacity [4–6]. According to the U.S. Department of Energy (DOE), the

target of gravimetric storage density is 9 wt% for vehicles that use hydrogen as a fuel. The stored hydrogen is useful as a fuel, when H₂ binding is neither weak as in physisorption nor high as in chemisorption [7,8]. Therefore, the major challenge in achieving high and retrievable H₂ storage is having binding energies lying between physisorption and chemisorption [9,10]. This is realised essentially by the non-classical Kubas type of binding (–0.2 to –0.4 eV/H), at ambient conditions [11]. Kubas interaction involves a charge transfer from the σ orbital of H₂ molecule to an empty *d*-orbital of metal [12]. Subsequently there is a back-donation from the metal *d*-orbital into

* Corresponding author. Tel.: +91 80 2293 2784.

E-mail address: abhishek@mrc.iisc.ernet.in (A.K. Singh).

¹ Tel.: +91 80 2293 2784.

<http://dx.doi.org/10.1016/j.ijhydene.2016.02.081>

0360-3199/Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

the σ^* antibonding orbital of the H_2 molecule resulting in an 8–9% [13] increase of H–H bond length.

Transition metal decorated carbonaceous systems [14–18] have been widely reported in the literature as a promising Kubas hydrogen storage media due to the presence of large number of empty d -orbitals and large surface area [19–22]. However, considering the experimental environment, hydrogen adsorption process is easily influenced by other competitive gas molecules present in the atmosphere, among which oxygen has been recognized as the main interferent [23,24]. As a consequence of strong oxygen-binding on transition metals, none of the experiments, so far have been successful in reaching the theoretical H_2 storage limit [25,26]. The hydrogen storage capacity of Ti-doped graphene has been reported to reduce significantly, when exposed to air, since the Ti atoms have high probabilities of getting oxidized to titanium dioxide [15]. Rojas et al. further predict that for transition metal-doped graphene, hydrogen coverage does not attain a useful amount even at ultra high vacuum conditions of oxygen partial pressures ($\sim 10^{-15}$ bar) [24]. Therefore, the bottleneck in hydrogen storage on transition metal-decorated porous materials is the irreversible chemisorption of oxygen on metal atoms. The given problem despite being grave has evoked few concerns and the solution remains elusive to the scientific community.

Here, we propose a solution to this critical challenge by introducing a concept of capping the metal atoms to enhance hydrogen adsorption selectivity over oxygen. The arene capping of MCB completely avoids the oxygen adsorption allowing exclusive adsorption of hydrogen via Kubas binding. The modification of the position of d -band center of Sc, induced by arene capping, optimizes empty antibonding states such that their availability is purely restricted to H_2 . To establish this complete elimination of oxygen interference at room temperature, a statistical analysis reveals that degree of hydrogen coverage (θ_{H_2}) to be 100%, at realistic oxygen partial pressures and hydrogen partial pressure (p_{H_2}) of 200 bar. The capped MCB also demonstrates a high reversible hydrogen storage capacity of seven Kubas bound hydrogen. The capping strategy is generalized on other hydrogen storage systems to successfully avoid oxygen binding on open metal sites. This concept can further be utilized on various catalytic and gas sensing systems requiring selective adsorption.

Computational method

The calculations were performed using *ab-initio* density-functional theory with pseudo potential plane wave method as implemented in Vienna Ab initio Simulation Package (VASP) [27]. All electron projector-augmented wave (PAW) potentials [28,29] were used to treat the ion-electron interaction with spin-polarized generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) [30] for electronic exchange and correlation. The Brillouin zone was sampled at Γ point. The conjugate gradient scheme was applied to relax the structure until the forces on every atom were ≤ 0.005 eV/Å. To minimize any spurious cell–cell interaction, large vacuum spaces (15 Å) were used in the supercell structures. The

binding energies of H_2 and O_2 are calculated according to the given equation:

$$E_b = E_{\text{MCB-A/AB/BA/B}} - E_{\text{MCB/MCB-A/MCB-B}} - E_{\text{A/B}} \quad (1)$$

where A, AB, BA, and B respectively, are representing the systems, where H_2 adsorbs independently, O_2 adsorbs in the presence of H_2 , H_2 adsorbs in the presence of O_2 , and O_2 adsorbs independently. $E_{\text{MCB-A/AB/BA/B}}$ and $E_{\text{MCB/MCB-A/MCB-B}}$ are the corresponding total energies of these systems with and without the corresponding adsorbates, respectively. The minimization of the reaction pathways and the search of the transition states (TS) have been performed with the steepest-descent Nudged Elastic Band method (NEB) [31,32]. The hydrogen dissociation reaction pathway and barrier was then calculated by NEB method through the identified TS.

Results and discussion

We study the hydrogen storage on tetra decker sandwiched type of MCB, $[\text{Cp}^*(\text{RR}'\text{C}_2\text{B}_3\text{H}_2\text{X})_2\text{Sc}]$, where R, R', and X = H. This MCB has been synthesized experimentally by Greiwe et al. [33] via metal-stacking reactions involving *nido*- $[\text{Cp}^*(\text{RR}'\text{C}_2\text{B}_3\text{H}_2\text{X})]^-$ anion and transition metal at room temperature. These double decker $[\text{Cp}^*(\text{RR}'\text{C}_2\text{B}_3\text{H}_2\text{X})]$, MCBs can be easily prepared and derivatized via substitution on the carborane ring and such transition metal sandwiches incorporating C_2B_3 carborane rings form an extensive family of thermally stable, well-characterized organometallic complexes. The Sc based tetra decker complexes are employed for this study as Sc($3d^1 4s^2$) has been previously reported to have better hydrogen storage capacity than other transition metals, owing to its light weight and maximum number of available d -orbitals [12].

We initiate the study by analysing adsorption strength of both oxygen and hydrogen on the uncapped and capped MCB, respectively. The completely optimized structures of uncapped and capped MCB are shown in Fig. 1(a) and (b). Oxygen chemisorbs on the Sc atom by an adsorption energy of $E_{ad} = -3.35$ eV (inset of Fig. 2(c)). This is a very strong binding that blocks the site, hence hindering the hydrogen storage. In the absence of oxygen, hydrogen adsorbs with $E_{ad} = -1.04$ eV, which is futile for reversible hydrogen storage (inset of Fig. 2(d)). The second oxygen molecule, in the presence of the first has $E_{ad} = -3.14$ eV, showing that the uncapped MCB always prioritises oxygen binding over hydrogen. The second hydrogen molecule adsorbs via $E_{ad} = -0.58$ eV, in the presence of only the first hydrogen. Hydrogen binds to the uncapped Sc site, in the presence of an oxygen molecule by an adsorption energy as low as $E_{ad} = -0.16$ eV. On the other hand, in the case of capped MCB, O_2 molecule is observed to be completely repelled by the cluster, as seen in the inset of Fig. 2(e). On this capped MCB, the first hydrogen binds in the Kubas range of -0.69 eV/ H_2 and is shown in the inset of Fig. 2(f). This comes off as a rather striking feature of the given arene capped MCB, where hydrogen adsorption is completely unhampered by oxygen interference. Therefore, the adsorption energy analysis establishes that it is the capping of the MCB which brings about the drastic reversal of preferential adsorption of O_2 over

Download English Version:

<https://daneshyari.com/en/article/1273601>

Download Persian Version:

<https://daneshyari.com/article/1273601>

[Daneshyari.com](https://daneshyari.com)