



Theory-guided metal-decoration of nanoporous carbon for hydrogen storage applications



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ABSTRACT

The current paper presents a combined ab initio and experimental study of H₂ adsorption on carbon. Adsorption energetics of a H₂ molecule on pristine graphene were obtained for various molecule orientations, showing that the perpendicular-to-surface orientation is energetically more preferable ($E_{\text{ads}} = -0.076\text{eV}/\text{H}_2$) than the parallel orientations ($E_{\text{ads}} \approx -0.071\text{eV}/\text{H}_2$). Subsequently, B, Co, Ni, Pd, Pt and Ru substituents of a C atom in graphene were considered, leading to the conclusion that Pt and Ru promote the H₂ adsorption by $\approx -0.012\text{eV}/\text{H}_2$. Pt promotes adsorption in all its neighbouring hexagons, while Ru impact is localised to the position directly above the dopant. Pure, Pt and Ru-doped ordered mesoporous carbon samples were evaluated experimentally for their H₂ adsorption performance under a low-pressure regime (up to 1 bar) at cryogenic and room temperatures (*i.e.*, 77 and 298 K, respectively). These experimental measurements indicated that, while the specific area of the metal-decorated carbons is lower than that of the pristine carbon material, the presence of Pt and Ru nanoparticles leads to a slight improvement of the H₂ uptake performance at room temperature.

1. Introduction

The efficient, practical and safe storage of molecular hydrogen (H₂) still remains one of the last frontiers towards the transition to a worldwide H₂-fuelled community with drastically reduced greenhouse emissions. The physical adsorption (physisorption) of H₂ gas in porous materials has been identified as one of the most promising alternatives to currently available technologies such as H₂ compression in high-pressure cylinders up to 700 bar and H₂ liquefaction in cryogenic tanks at $\approx 20\text{ K}$ [1]. Molecular integrity, complete reversibility, fast kinetics and low applied pressures between H₂ adsorption and desorption processes are the key features of this solid-based storage method [2]. However, pure H₂ physisorption in solid surfaces via weak van der Waals forces is favoured only under cryogenic temperatures ($< 100\text{ K}$) due to the low polarizability and weak quadrupole moment of the H₂ molecule [3] and usually the equivalent adsorption performance drops significantly by increasing the operating temperatures up to ambient ones. For example, a reduction by $\approx 95\%$ in the gravimetric H₂ storage capacity at $\approx 20\text{ bar}$ was reported for a nanoporous CO₂-activated carbon cloth material by increasing the operating temperature from 77

up to 298 K [4]. Therefore, the potential enhancement of the gaseous H₂-solid surface interactions, especially at ambient temperatures, is considered a major technical challenge towards an increased H₂ uptake performance.

Even though a large majority of porous materials have been already investigated as H₂ adsorbents and reported in the literature, carbon-based materials, such as amorphous activated carbons, ordered mesoporous carbons and more recently graphene-based architectures, still attract significant attention mainly due to their lightweight structures, high specific surface areas and pore volumes, plethora of manufacturing methods and low production costs [5]. However, the low isosteric adsorption enthalpies (Q_{st}) between carbon and H₂, which are usually scattered between 5 and 8 kJ/mol (or $\approx 0.05\text{--}0.08\text{ eV}/\text{H}_2$) [6], cannot facilitate the efficient H₂ storage under non-cryogenic conditions ($> 100\text{ K}$). Based on theoretical calculations, the optimum average Q_{st} value for efficient and still reversible H₂ adsorption at ambient temperatures and moderate pressures (*i.e.*, up to 30 bar) corresponds to 15 kJ/mol (or $\approx 0.15\text{eV}/\text{H}_2$) [7]. Therefore, the development of nanostructured composite/hybrid systems has been proposed as a potential route towards increasing the H₂ adsorption energy and further

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improving their H₂ storage performance [8, 9]. More specifically, it has been stated that the incorporation of transition metals onto a carbon surface could potentially improve the interaction with H₂ by modifying the energetic landscape and introducing also weak chemical adsorption (chemisorption) mechanisms [10,11]. These may include the formation of complexes between molecular H₂ (non-dissociated) and transition metal atoms supported within the carbon surface (*i.e.*, known as Kubas-type interactions) [12] or the catalytic dissociation of molecular H₂ onto the transition metals followed by migration and diffusion of the atomic hydrogen onto the carbon surface (*i.e.*, known as spillover effect) [13].

In the current work, first principles calculations were performed by means of Density Functional Theory (DFT) to investigate the influence of a series of metals on the H₂ adsorption behaviour of metal-substituted graphene surfaces. The selected dopants include mainly transition metals, such as platinum (Pt), palladium (Pd), ruthenium (Ru), cobalt (Co) and nickel (Ni), which substitute carbon (C) atoms within the 2D graphene lattice. These metals are very well-known for their superior catalytic activity and thus are widely used as catalysts in various industrial procedures (*i.e.*, reforming of hydrocarbons, hydrogenation of aromatic compounds, H₂ production) as well as technological applications (*i.e.*, automotive catalytic converters, batteries and supercapacitors, fuel cells) [14,15]. However, their high cohesivity usually leads to the formation of metallic clusters instead of single/individual metal atoms (as the ones examined herein) upon metal-decoration of a carbon surface via physical and/or chemical means [16]. The H₂ adsorption energy maps for pristine and metal-substituted graphene surfaces were calculated and the favourable binding sites for H₂ were determined. Subsequently, experimental H₂ adsorption data for metal-decorated carbon materials are presented with the aim to investigate the influence of the most effective dopants, as predicted from the DFT studies, in real carbon–H₂ interaction systems.

2. Methodology

2.1. Computational methods

The quantum-mechanical calculations of adsorption energetics were performed using the Vienna Ab initio Simulation Package (VASP) [17,18], a plane-wave pseudopotential implementation of the Density Functional Theory [19,20]. The electron-electron exchange-correlation (xc) interactions were treated with a generalised gradient approximation (GGA) as parametrized by Perdew, Burke and Ernzerhof (PBE) [21]. The non-local van der Waals interactions were included using the method of Grimme [22], which has been shown to provide reliable structural and energy predictions in combination with the GGA-PBE xc potential [23]. The electron-ion interactions were evaluated using projector-augmented wave method-enabled pseudopotentials [24]. Plane-wave cut-off energy was set to 900 eV and the reciprocal cell corresponding to the 3 × 3(×1) supercell (containing 18 atoms) of the substrate was sampled with a 23 × 23 × 1 Monkhorst-Pack gamma-centred mesh [25]. These relatively high values were necessary in order to obtain reliable energies with accuracy below meV/at. All structural relaxations were performed until the total energy was converged to below 0.1 meV (*i.e.*, ≈ 0.005 meV/at.). A 15 Å vacuum in the direction perpendicular to the substrate plane was considered enough to eliminate undesirable interactions with its periodic images. These parameters yield an H₂ binding energy of 6.74 eV, which agrees well with previously reported values of 6.8 eV using the same methodology [26]. When spin-polarisation is included, the binding energy decreases to 4.58 eV [27], which is very close to experimental as well as accurate chemical calculated values 4.75 eV [28]. Another systematic error is related to the omission of a self-interaction correction, which is around 0.2 eV in the case of H₂ and GGA-PBE functional [28].

The full structural relaxation of pure graphene resulted in a C–C–bond-length of 1.424 Å, which agrees well with the experimental value of 1.42 Å [29]. After this, the supercell size was kept fixed. When a metal atom replaced a C atom (hence leading to an effective doping of $x_{\text{metal}} = 1/18$), the substrate structure was again re-optimised. For the subsequent potential energy surface (PES) calculations, all substrate atoms were fixed. A single H₂ molecule was placed above the substrate into a desired position and its lateral coordinates were fixed followed by an optimisation of its distance from the substrate in order to obtain the lowest energy configuration. Three orientations of the H₂ molecule rotational axis were considered along the ⟨2110⟩, ⟨0110⟩ and ⟨0001⟩ directions. In all cases, the ‘vertical’ configuration with H₂ molecule axis perpendicular to the substrate yielded the lowest energy. It should be also noted that in all the calculations (corresponding to 0 K) no dissociation of the H₂ molecule was predicted, therefore suggesting that the Kubas-type interactions are more significant than the spillover effect at 0 K for the present set of dopants.

The calculated adsorption energy, E_{ads} , is defined as

$$E_{\text{ads}} = E_{\text{tot}}(\text{substrate with H}_2) - E_{\text{tot}}(\text{substrate}) - E_{\text{tot}}(\text{H}_2), \quad (1)$$

where $E_{\text{tot}}(\text{substrate with H}_2)$, $E_{\text{tot}}(\text{substrate})$ and $E_{\text{tot}}(\text{H}_2)$ are the total energies of a (doped) substrate with an adsorbed H₂ molecule, a (doped) substrate alone and a free (non-absorbed) H₂ molecule, respectively. The substrate is either a pristine graphene, or a ‘doped’ graphene with one C atom replaced by a dopant (*i.e.*, B, Co, Pd, Pt, Ni or Ru).

2.2. Experimental details

Pure, Pt-, Ru- and mixed Pt/Ru-decorated ordered mesoporous carbon materials (denoted hereafter as OMC, Pt-OMC, Ru-OMC and Pt-Ru-OMC, respectively) were synthesized in powder form via an evaporation-induced self-assembly method under acidic conditions as presented elsewhere [30,31]. The synthesis procedure includes surfactant organization, reduction, polymerization and pyrolysis steps using resorcinol as a carbon precursor as well as chloroplatinic acid hydrate and ruthenium chloride hydrate as Pt and Ru sources, respectively. The Pt-OMC, Ru-OMC and Pt-Ru-OMC samples exhibited elemental compositions of 0.03 at.% Pt, 0.03 at.% Ru and 0.01 at.% Pt/0.02 at.% Ru respectively, (dominantly ≈ 95 at.% carbon and the rest ≈ 5 at.% oxygen), on the basis of X-ray photoelectron spectroscopy (XPS) studies using a ThermoFisher Scientific Theta Probe spectrometer equipped with a monochromated Al K α X-ray source at 300 eV pass energy. No other impurities were detected from the synthesis precursors (*e.g.* chlorine). The morphological structure of the OMC samples was studied using a Philips CM-20 transmission electron microscope (TEM) equipped with a LaB₆ filament at 200 kV acceleration voltage.

The total specific area (multi-point Brunauer-Emmet-Teller/BET method [32]) and pore size/width distribution (Quenched Solid Density Functional Theory/QSDFT method for slit-/cylinder-shaped pores [33]) of the OMC materials were extracted from nitrogen gas (N₂) adsorption/desorption data recorded at 77 K using a Quantachrome Autosorb MP-1 volumetric gas sorption analyzer equipped with a liquid N₂ bath and ultra-pure (99.999%) N₂ gas. Samples of ≈ 50 mg were degassed under vacuum (10^{−6} mbar) at 250 °C for 12 h with the aim to remove any adsorbed species from the porous surface. The H₂ adsorption behaviour was investigated by recording low-pressure (0–1 bar) adsorption isotherms at 77 and 298 K using the same instrument employed for the porosity studies and ultra-pure (99.9999%) H₂ gas. Once again samples of ≈ 50 mg were degassed by following the same protocol.

3. Results and discussion

3.1. H₂ adsorption on pure graphene based on DFT

The adsorption energy, E_{ads} , was calculated for a mesh of 27

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