

DFT Study of Hydrogen Storage by Spillover on Graphite with Oxygen Surface Groups

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Several studies^{1–4} have shown that the hydrogen storage capacity of a variety of adsorbents, such as graphite nanofibers, activated carbons, carbon nanotubes, and metal–organic frameworks, can be enhanced by doping them with small amounts of transition metals (Pt, Pd) or by mixing them with supported transition metal catalysts, such as Pt/C or Pd/C. Hydrogen storage on metal-doped carbon materials, through the so-called “spillover” mechanism,^{5,6} involves a series of elementary steps: molecular H₂ dissociates on the metal nanoparticles, and atomic H migrates to the carbon support and diffuses on the carbon surface. Recent DFT calculations⁶ have shown that the migration of atomic hydrogen from the metal nanoparticle to a graphitic substrate is kinetically and thermodynamically inefficient and limits the rate of H spillover.

Recent experimental studies have shown that a further enhancement of the storage capacity of metal-doped activated carbons^{7,8} can be achieved by chemically modifying the carbon substrate through introducing oxygen functionalities. Furthermore, it was observed⁸ that Pd-doped graphite oxide (GO) exhibited 3.8 times the capacity of Pd-doped superactivated carbon AX-21, when the uptake was normalized by the surface area of the materials. The role of oxygen functional groups in enhancing the hydrogen uptake by spillover may also be operative in the work of Yang’s group,^{3,9} where the materials were functionalized by mixing them with “carbon bridges” that are composed of carbonized sugar molecules, and may contain O left over from the carbonization.

The structure of graphite oxide is still being debated.^{10,11} Recently, however, there was very clear evidence¹¹ via solid-state NMR that graphite oxide contains atomic oxygen in the form of the epoxide group (C–O–C) as well as the hydroxyl group (C–OH). Strong cross peaks indicated that the C–O–C group and the C–OH groups are bonded to each other. The structure of the chemically modified activated carbons of ref 7 and 8 presumably has the same functionalities on the surface as graphite oxide, despite at a lower coverage. Elemental analysis of the materials in ref 8 showed that the O content of O-modified AX-21 and GO (O/(C+O)) was 13 and 21 wt %, respectively. Despite the weight increase of the material, the gravimetric capacity increased in both cases.

In the present work we used a simple model to probe the kinetics of a plausible mechanism for the spillover of H atoms on GO and O-modified materials. A Pt₄ cluster was used to model the nanoparticle. The graphite surface was modeled using either the coronene molecule C₂₄H₁₂ (Figure 1a) or a larger polycyclic C₄₂H₁₆ planar molecule (Figure 1b, 1c). DFT calculations were performed with the program Turbomole, using the B-P86 functional and the def2-TZVP basis sets for all atom types. The computational setup and benchmark calculations have been described elsewhere.⁶ Electronic energy scans were produced by constrained optimizations, where, for each data point, one bond length was fixed and all other degrees of freedom were allowed to optimize. We have shown in previous work⁶ that this model system can predict with

sufficient accuracy key experimental quantities that are pertinent to real spillover materials. For example,⁶ the calculated binding strength and normal vibrational frequency of atomic H on coronene (0.63 eV and 2655 cm⁻¹) are very close to the experimental values on highly ordered pyrolytic graphite (0.61 eV and 2650 cm⁻¹), and the binding strength of hydrogen on a fully saturated Pt₄ cluster (0.85 eV with respect to molecular H₂) lies within the range of available experimental data for H on a Pt(111) surface at full coverage (0.7–0.88 eV). These comparisons suggest that the model is sufficient for an approximate analysis of the energetics of spillover.

Migration of H Atoms from Pt to Surface O. The left-most structure of Figure 1a shows the minimum-energy structure for a Pt₄ cluster and an O atom chemisorbed on coronene adjacent to the cluster. The optimum structure of the O atom is in the epoxide form, having a calculated binding strength of 1.93 eV. The Pt₄ cluster, when adsorbed on the surface, can hold a maximum of 10 H atoms. Our DFT calculations showed that the dissociation of five H₂ molecules is barrierless on the adsorbed Pt₄ cluster. The average binding strength of H atoms on a fully saturated Pt₄ cluster was calculated to be 2.85 eV.

Figure 1a also shows the final-state structure and the energy scan for the migration of a H atom from the Pt₄ cluster to the O atom in the vicinity of the cluster that eventually produced a hydroxyl group (OH). The calculations indicated that the migration event is exothermic by 0.67 eV. A 0.4 eV energy barrier has to be crossed for the migration to take place. The small barrier indicates that the process is facile at intermediate temperatures. This value should be compared with the energy barrier that was previously⁶ calculated for the migration of H atoms from the Pt cluster to a C atom of the graphite surface to form a chemisorbed surface H, 2.6 eV, a prohibitive barrier for normal conditions.

Diffusion of H on O-Modified Graphite and GO. Figure 1b shows the initial and final state structures and the corresponding energy scan for the migration of a H atom from the hydroxyl group to an adjacent O (epoxide) atom on graphite. The energy barrier for this step is only 0.33 eV. In comparison, the energy barrier for the migration of a chemisorbed H atom on graphite is⁶ 0.81 eV. Thus, the diffusion process of H atoms on graphite oxide should be expected to happen extensively, in a similar manner to the H spillover mechanism on metal oxide surfaces.¹² The proximity of O groups of GO, previously determined by NMR¹¹ facilitates the diffusion of H on O-modified graphite.

Equilibrium between OH and CH Bonds. Figure 1c shows the initial and final state structures and the corresponding energy scan for the dissociation of OH to form O and H chemisorbed on adjacent carbon sites on graphite. This elementary reaction has a very high energy barrier, 2.75 eV, and OH is more stable than the two fragments on graphite by 1.85 eV. Thus, the equilibrium is such that, on O-covered carbon surfaces, the concentration of H atoms directly adsorbed on graphite would be very low compared

to the concentration of OH. The result indicates that the main adsorption and diffusion channel for H on GO and O-modified carbons is via the hydroxyl H. In other words, we expect that at room temperature H atoms are hopping on the epoxide O atoms, forming OH. Wang et al.⁸ explained their high capacity results for Pd-doped GO by performing calculations that show an increase in the chemisorption strength of H on carbon, when O is present in the vicinity. We show here, however, that H atoms would mainly be bonded to O, covering the surface with OH groups.

Formation of H₂O from OH Groups. Figure 1d shows the initial and final states for the formation of water from two interacting OH groups adsorbed on the same graphitic ring. It was verified first that the minimum energy structure had the OH groups in the para configuration. The corresponding reaction energy scan for the formation of physisorbed H₂O as a function of the O–H bond length is shown in Figure 1d. The results indicate that the formation of water is exothermic by 0.45 eV

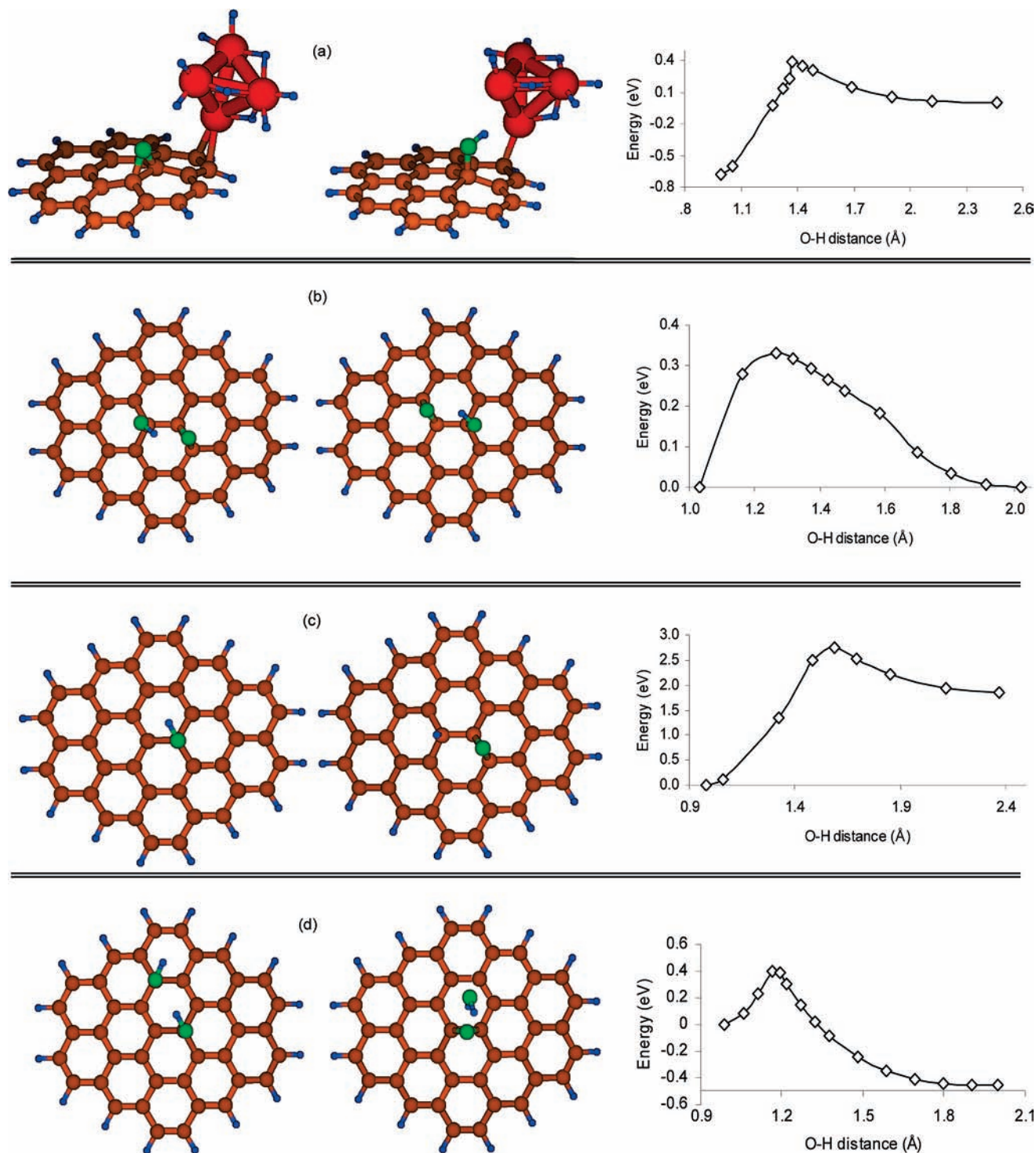


Figure 1. Optimized structures of the initial and final states and DFT-calculated reaction coordinate scans for the migration of H (a) from a Pt₄ cluster to epoxide O on a model graphite surface; (b) from the OH group to an epoxide O, both adsorbed on graphite (H diffusion); (c) from the OH group to the graphite surface; (d) from an OH group to another OH group (water formation). The lines in the energy scans are guides to the eyes.

and the energy barrier is 0.41 eV. The identified elementary reaction has a thermodynamic propensity for water formation, and a small energy barrier suggests that it can happen at high enough rates during the spillover process.

Formation of H₂ from OH Groups. An additional calculation was performed to quantify the energy change for the formation of gaseous H₂ from two surface OH groups. The initial structure was as shown in Figure 1d (left-most structure). The final structure consisted of two epoxide groups on the surface and physisorbed molecular H₂. It was found that the formation of H₂ is endothermic by 2.2 eV and thus energetically unfavorable. Another possible mechanism for the formation of H₂ is via the reverse-spillover process whereby H atoms migrate back to the metal cluster and desorb associatively. However, as shown in Figure 1a the migration of atomic H from a surface OH group to the Pt cluster is endothermic and has a 1.1 eV barrier. We therefore conclude that H₂O formation is thermodynamically and kinetically much easier than H₂ formation, when the surface is populated with OH groups.

The limited molecular-level understanding of hydrogen storage by spillover has long been inhibiting the bottom-up design of effective spillover adsorbents. In this work, we showed that when a graphitic surface is populated with atomic O, the spillover mechanism is operative without significant energy barriers. The mechanistic analysis shows that H can migrate from a Pt cluster to epoxide O groups on the surface and can easily diffuse on the O atoms by a hopping mechanism whereby hydroxyl OH groups are continuously created and dissociated. Through this mechanism, H is stored on the surface in the form of OH groups. We can then expect that greater surface coverage with O atoms would give a higher uptake of hydrogen. This explains the higher gravimetric capacity of GO, compared to O-modified AX-21, in the experiments of Wang et al.,⁸ when both are normalized by the pore surface area. High surface area carbons modified with a large quantity of surface oxygen should be ideal. According to this picture, an upper limit to the spillover H uptake with the present mechanism should be set to approximately one H atom per O atom on the surface. However, smaller quantities of physisorbed H₂ might also be held, as well as atomic H that spills and bonds to the carbon surface, when the surface O becomes saturated with H. Furthermore, since all barriers to H migration and diffusion are reduced in this mechanism, compared to a carbon surface without any functional groups, the charge/discharge kinetics of H₂ on the adsorbent would be correspondingly faster than that of pure carbon.

The results also indicate that O-modified carbon should also be a good catalyst substrate for H diffusion to secondary spillover materials, such as metal–organic frameworks. In the experiments^{3,9} of Yang's group, utilization of secondary spillover through the formation of 'carbon bridges' that can contain oxygen functionalities

was found to enhance the spillover capacity. Based on the present results, the possible role of the 'bridge' material is to serve as a medium of migration for the dissociated H atoms, from the metal nanoparticles to the secondary spillover sorbent. This role is achieved through the existence of oxygen functionalities on the material.

On the other hand, we identified a possible mechanism for water formation from interacting surface-bound OH groups. Formation of water would have obvious negative consequences for the total capacity and the reversibility of hydrogen storage in oxygen-modified graphitic materials. The experiments of refs 7 and 8 do not report any release of water during the spillover process. Further experimental work would thus be indispensable to confirm the presence or absence of the identified mechanism for the spillover of hydrogen and the possibility and necessary conditions for water formation on these materials.

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