

Mechanisms for permeation of chemisorbed hydrogen atoms through graphene

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Recent experiments have shown that protons¹ and hydrogen atoms² can permeate through defect-free graphene, with associated activation energies of the order of 1 eV. These findings are opposed to previous theoretical studies³ which indicated that these species need to surmount energy barriers of about 2 or 3 eV to pass through the middle of a carbon ring. If H⁺ or H are initially chemisorbed to graphene, even larger energy barriers (3.4 or 4.5, respectively) were estimated for the flipping of the atoms from one side to the other of the graphene layer³. By means of density functional theory computations^{4,5} we have found that these energy barriers can significantly decrease (to become in the range of 1-1.5 eV) if protons or hydrogen atoms are initially chemisorbed at high local coverage. The main flipping mechanism involves the insertion of the chemisorbed H⁺ or H into the middle of an effectively broken C-C bond, a linkage that is restored once the process is completed. The permeation barrier is reduced (with respect to the case of just one chemisorbed atom) due to a sp^2 rehybridization of the C atoms at the transition state as well as an enlargement of the ring area in the initial state (see Fig. 1 for the case of a 5-times protonated carbon ring). In the talk we will present the details of these calculations and mechanisms, accompanied by a discussion about the role of other competing processes (diffusion, desorption, etc.) as well as charge doping and isotopic (deuterium) substitution effects. We believe that these studies will help to rationalize the above mentioned experiments as well as to provide some clues about properties of hydrogenated graphene.

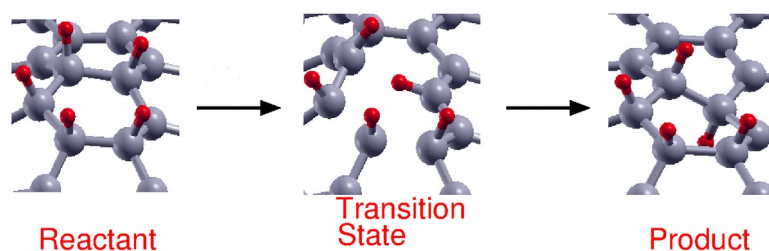


Fig. 1: Stationary point geometries of the reactant, transition and product states for a hydrogen atom flipping through a five- times hydrogenated carbon ring. The activation energy is about 1.5 eV.

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References

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