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Assessment of H-abstraction Reactions in Graphene Growth

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Highlights
- Activation energy increases linearly with the stability of the abstracting carbon
- Same trend is found on monolayer and multilayer graphene
- A correction factor is proposed to extend investigation to gas phase reactions

1. Introduction

Graphene growth is of relevance in the production of carbon fibers and composite carbon-based materials. The first step of graphene growth in Chemical Vapor Infiltration (CVI) or Chemical Vapor Deposition (CVD) process is the H-abstraction from graphene armchair and zigzag edges to form a carbon active site [1-4]. To the best of our knowledge, theoretical studies describing details of reactions in CVI or CVD processes on graphene edges are not available in the literature. Indeed, the kinetic studies presented so far are mostly based on empirical corrections to parameters typical of gas phase kinetics [5-7]. In this work, to gain insights in microkinetics of graphene growth, ab initio calculations using density functional theory (DFT) are employed to investigate H-abstraction reactions and to evaluate the effect of abstracting radicals, surface dimensions, and edges type. Following the standard approach to gas phase kinetics of combustion and pyrolysis [8], this work also aims to provide rate rules for H-abstraction reactions and theoretically based corrections to derive heterogeneous kinetic parameters from gas phase kinetics. Hence, this work allows developing a methodology of general application to gas-solid phases interactions, not only for pyrocarbon deposition, but also for other heterogeneous processes such as thermal conversion of biomass, coke formation in cracking furnaces and soot growth kinetics.

2. Methods

DFT calculations were performed by Quantum ESPRESSO code with ultrasoft pseudo-potentials approaches. Exchange and correlation energies were described by the GGA-PBE functional with plane-waves whose kinetic energy cutoff is 30Ry as basis sets. Van der Waals forces were accounted using the Grimme-D2 correction method. Dipole correction was also applied along the vacuum direction in gas-surface reactions. Spin-polarized calculations were employed both on gas-surface reactions on graphene edges and on analogous gas phase reactions. Transition States (TSs) were searched with the Climbing Image – Nudged Elastic Band (CI-NEB) method with the threshold of the forces on the images equal to 0.05 eV/Å and then were confirmed by checking their vibrational frequencies using Atomic Simulation Environment (ASE).

3. Results and discussion

Reaction barriers were calculated for H-abstraction reactions by H, alkyl radicals (CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, 2-C_4H_9, i-C_4H_9), resonance-stabilized radicals (*CH_2-CH=CH_2, 3-C_4H_7). Our results for monolayer graphene, shown in Figure 1, clearly highlight a trend for the activation energies with respect to the nature of the abstracting radical. On one hand, as shown in Figure 1a, a linear relationship between the activation energy and the degree of carbon is observed for the alkyl radicals, and the same activation energy is obtained for abstracting radicals with the same degree of carbon. On the other hand, the difference in the structure of the armchair and zigzag edges does not significantly affect the reaction barrier and the linear relationship with respect to the degree of carbon. By digging into the structural details, we find that all the TSs are all late and share almost the same H-graphene distance on each edge, indicating that the nature of the abstracting

radical is the only factor affecting the reaction barrier. Then, we extend the investigation to the reactions on multilayer graphene with different types of alkyl radicals (CH_3, C_2H_5, n-C_3H_7, i-C_3H_7), including H, and discovered a similar correlation between the activation energies and the degree of abstracting carbons. A comparison with monolayer graphene results shows a negligible difference (~1 kcal/mol), i.e. within the accuracy of DFT methods for activation barrier calculations. This implicates the possibility to use monolayer for theoretical modeling the growth of both the single layer graphene and the multilayer graphene, resulting in a reduction of computational efforts. The assessments of the correlation between gas phase and monolayer results are reported in Figure 1b, showing a linear correlation between the activation energy of them. This again indicates that the barrier change of H abstraction is only determined by the stability of the radical that accepting the H, and approved the usage of the activation energy in the gas phase to estimate the activation energy of the corresponding reactions on graphene surfaces.
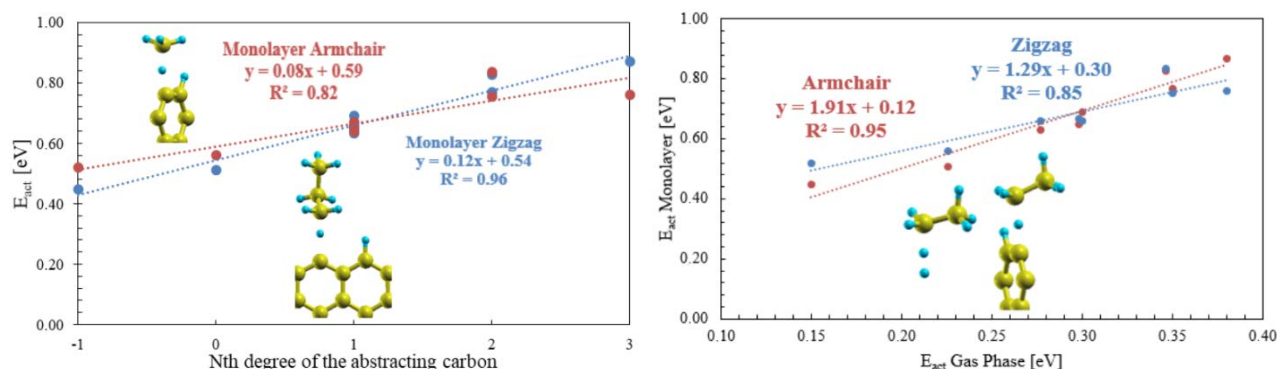

Figure 1. a. Linear correlation between the activation energy and the stability of the abstracting carbon radical. To be systematic, we denote H as -1st degree of the abstracting carbon, and the CH_3 as the 0th degree. The primary carbons (C_2H_5, n-C_3H_7, n-C_4H_9), secondary carbons (i-C_3H_7, 2-C_4H_9), and tertiary carbon (i-C_4H_9) carbons are denoted as the first, the second and the third degree of carbon, respectively. b. Correction factor for using gas phase calculation to estimate the activation energies of the corresponding gas-surface reactions on armchair and zigzag edges.

4. Conclusions

In this work we calculated the activation barriers for H-abstraction reactions on graphene edges as the first step of investigating graphene growth kinetics, and found a linear correlation between the degree of carbon and the activation barrier for H-abstraction by alkyl radicals. This suggests the stability of the hydrocarbon radicals as the main factor that determines the reaction barrier. Furthermore, a correlation has also been found between gas phase and monolayer graphene results, encouraging the application of correction factors to obtain heterogeneous kinetic parameters from theoretical estimations of gas phase rate constants.

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Keywords
Graphene; DFT; CVI; H-abstraction reactions.