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## Graphene nucleation on Si(100): a DFT study on toluene decomposition steps and condensation reactions

The direct chemical vapor deposition (CVD) of graphene on industrially preferred semiconductor (like Si wafers) or dielectric substrates has been considered a valid alternative to directly incorporate graphene into electronic devices, thus preventing the common transfer process of the as-grown film which inevitably induce residual contamination and mechanical defects [1]. Usually, the thermal CVD synthesis of graphene on Si substrates is realized with methane at high temperature ( $>900^{\circ}\text{C}$ ), although the low diffusivity of carbon species and the strong carbon solubility on Si which induce unavoidable formation of SiC buffer layers severely hamper an efficient growth [2]. Though several strategies have been adopted to overcome such limitations, few studies are focused on aromatic hydrocarbons as possible carbon precursors [3].

In this work, we investigate at the molecular-level the first decomposition steps of toluene and possible recombination pathways of as-formed active species onto the reconstructed Si(100)-c(4x2) surface through density functional theory (DFT) calculations with van der Waals corrections (DFT-D3). First, toluene molecules can chemisorb with several configurations onto the Si surface by addition reactions [4]. We found the most stable configuration (the aromatic ring forming four sigma bonds with two adjacent Si dimers) with adsorption energy of  $-1.39$  eV which is higher than the value reported in [4], mainly due to the inclusion of the DFT-D3 corrections in this work. Then, the minimum energy pathway (MEP) and transition state (TS) of chemical reactions (decomposition and recombination steps) were investigated through the climbing-image nudged elastic band (CI-NEB) method. The dehydrogenation of the methyl group of toluene were found the most likely early decomposition path with an energy barrier of  $1.4$  eV. However, the formation of  $\text{CH}_3$  radicals is strongly hampered by the much higher energy required for demethylation. Finally, we investigated the formation of anthracene (three connected phenyl rings) as one of the possible stable graphene nuclei for which we found a strong adsorption energy of  $-2.43$  eV. Such carbon structure was achieved by a recombination of two  $\text{C}_7\text{H}_5$  radicals and described by a two-step reaction, as shown in Fig.1. However, the cost to produce anthracene through this pathway is rather high with an energy barrier of at least  $2.6$  eV which is not beneficial for the low-temperature CVD synthesis of graphene on Si(100).

**Figure 1.** Condensation reaction of two  $\text{C}_7\text{H}_5$  producing anthracene, described as a two-step process.

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