

A DFT study of early decomposition steps of aromatic hydrocarbon precursors on Cu(111): pathways to low-temperature CVD of graphene

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The chemical vapor deposition (CVD) of graphene on copper substrates using methane (CH₄) requires processing temperatures in the range 800-1000°C. However, lowering the growth temperatures down to 300°C, while preserving the high quality of graphene layers is highly desirable for economic and technological reasons. Among various strategies, alternative carbon precursors, especially liquid aromatic hydrocarbons like benzene [1] and toluene [2], have been proposed to lower the growth temperatures. However, the actual role and effectiveness of these precursors in the CVD synthesis is still debated [3].

In this work, we investigated the molecular-level decomposition steps of such aromatic molecules adsorbed onto the Cu(111) surface through density functional theory (DFT) calculations with van der Waals corrections (DFT-D3). Geometries and energies of adsorbates in various structural configurations were first analysed to identify the most stable adsorption sites. It was found that benzene and toluene adsorb preferentially on the Cu *hcp* site with binding energies of 0.88 eV and 0.97 eV, respectively. The higher value for toluene could be attributed to the electron donor character of the methyl group that enhances toluene adsorption. In both cases the calculated adsorption energies are much higher than that found for CH₄ (0.20 eV). Then, early decomposition reactions were studied through the investigation of the minimum energy pathway (MEP) and the transition state (TS). The energy barriers for the C-H bond dissociation in the phenyl group of adsorbed benzene and toluene were found to be almost the same (~1.7 eV), while demethylation of toluene requires a much higher energy (2.51 eV). In comparison, methane dehydrogenation requires ~1.6 eV. However, a lower activation energy (1.20 eV) was found for hydrogen removal from the methyl group of toluene (reaction pathway shown in Figure 1). This reaction may constitute the main low-temperature decomposition step of toluene, leading to a rich formation of benzyl radicals onto the Cu surface as primary active carbon species. Possible reaction paths among benzyl radicals leading to graphene nucleation are finally discussed. Present findings suggest that toluene (and related aromatic molecules, such as xylene and trimethylbenzene) are preferable to benzene for the low-temperature synthesis of graphene.

References

- [1] Jang et al., Sci. Reports 2015, 5, 1.
- [2] Zhang et al., ACS Nano 2012, 6, 2471.
- [3] Khan et al., Carbon 2019, 153, 458.

Figures

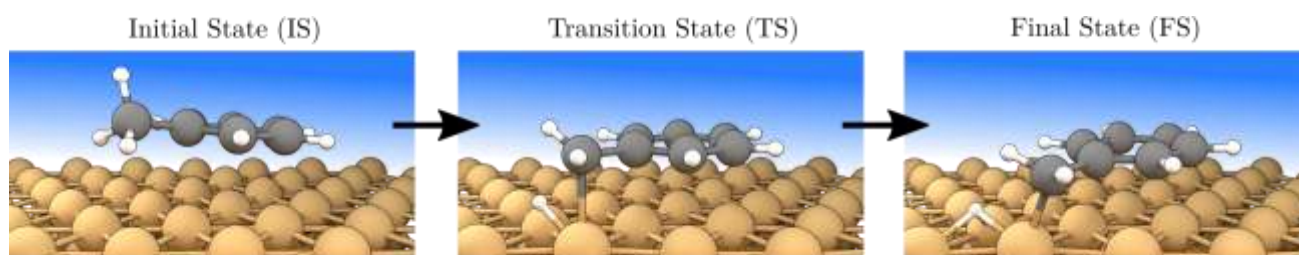


Figure 1: Reaction pathway of toluene dehydrogenation on the methyl group.