

DFT investigation of active carbon species and early nucleation of graphene on Cu(111) using toluene as CVD carbon precursor

Onofrio Tau ^a, Nico Lovergine ^{a,*}, Riccardo Rurali ^b, Paola Prete ^a

^a Department of Innovation Engineering, University of Salento, Via Monteroni, I-73100 Lecce, Italy

^b Institut de Ciència de Materials de Barcelona, ICMAB-CSIC, Campus UAB, 08193 Bellaterra, Spain

ARTICLE INFO

Keywords:

Graphene
Chemical vapor deposition
Aromatic hydrocarbon precursors
DFT calculations
Cu-catalyzed surface decomposition
Graphene nucleation mechanisms

ABSTRACT

Liquid aromatic hydrocarbons may be used as alternative precursors in the chemical vapor deposition of graphene, leading to reduced growth temperatures with respect to those required by methane. We study by density functional theory the dehydrogenation steps of toluene precursor adsorbed on Cu(111). Dehydrogenations of toluene - at the methyl or ortho positions - are characterized by low activation energies and result in the formation of multiple active species, leading to the abundant production (among others) of adsorbed C₇H₅ fragments. We extend our analysis to provide a molecular-level description of anthracene (C₁₄H₁₀) formation - as early graphene nuclei - by recombination reactions between two C₇H₅ fragments. In particular, the formation of zig-zag or armchair anthracene is facilitated by the almost inexpensive energetic cost for the creation of a C=C double bond between the C₇H₅ fragments; however, its formation could be hindered for specific relative orientations of the two adsorbed species, for which steric hindrance effects strongly impede internal rotations of the reaction intermediate. Finally, the dehydrogenation of anthracene elucidates that vertically chemisorbed configurations make them more prone to lose their hydrogens. This may lead to further condensation reactions and the formation of larger graphene nuclei. These results open the way to a better understanding of surface adsorption, decomposition and recombination phenomena for clear control of the nucleation of high-quality graphene layers by CVD.

1. Introduction

Graphene, a one-atom-thin layer of sp²-bonded carbon atoms organized in a honeycomb lattice, has gathered significant attention after its discovery in 2004 [1] due to its peculiar electronic properties [2–4] that make it an exceptional material for novel high-performance low-dimensional electronic devices [5–10] and sensors [11–14]. Chemical vapor deposition (CVD) is a well-established synthesis technique to produce high-quality wafer-scale single-layer graphene with relatively low defect density [15–21]. To this purpose, methane (CH₄) is widely used as carbon precursor [22,23], although its thermal stability requires very high temperatures (900–1100 °C), making the CVD growth of graphene energy consuming and risky. Furthermore, such temperatures forbid the use of conventional semiconductor substrates, which is a considerable practical limitation. A metal substrate, usually polycrystalline Cu chosen for its low carbon solubility [24], is employed to induce the surface-catalyzed pyrolytic decomposition of the carbon precursor, leading to active hydrocarbon species that can trigger the

formation of sp²-hybridized graphene nuclei. The latter then grow and merge until a single graphene layer is obtained. However, the metal substrate requires the transfer of as-grown graphene layers on appropriate substrates (e.g., a semiconductor or dielectric material) for the fabrication of the final graphene-based electronic devices/sensors and most transfer methods [25–27] may introduce mechanical and chemical defects within the graphene structure and contamination at its surface, thus degrading the device performances.

The synthesis of high-quality graphene on Cu or semiconductor/dielectric substrates by a low-temperature CVD (LT-CVD) process would be technologically advantageous [28–32]. To this purpose, alternative carbon precursors [31,33,34], especially liquid aromatic hydrocarbons - e.g. benzene (C₆H₆) [35–37] and toluene (C₇H₈) [38] - have been proposed: in particular C₆H₆, due to its weaker C–H bond with respect to CH₄, would allow its decomposition at lower temperatures; C₇H₈ can be a valid alternative to C₆H₆ since the C–H bond energy in its methyl group (357 kJ/mol) is lower than that of C–H bonds in the molecule C-ring (444 kJ/mol [39]). The hexagonal C-rings of aromatic precursors

* Corresponding author.

E-mail address: nico.lovergine@unisalento.it (N. Lovergine).

<https://doi.org/10.1016/j.surfin.2026.110139>

Received 20 January 2026; Received in revised form 6 June 2026; Accepted 14 July 2026

Available online 15 July 2026

2468-0230/© 2026 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

would further act as building blocks during graphene synthesis.

Atmospheric pressure LT-CVD growth of graphene was reported on Cu using C_6H_6 [35]; full substrate surface coverage was reported in this case at 300 °C, though only partial coverage was achieved when growing at temperatures down to 100 °C. However, Khan et al. [40] claimed the impossibility to grow graphene on Cu from C_6H_6 below 700 °C, attributing previous reports on the LT-CVD of graphene to the effect of unintentional decomposition of C_6H_6 residues formed within the CVD reactor from previous high-temperature growth runs or during pre-annealing steps (~1000 °C) of Cu immediately before graphene growth. They reported instead, monolayer graphene synthesis above 825 °C using C_6H_6 . Temperatures around 600 °C were required in the case of C_7H_8 to produce large-area single-layer graphene on electro-polished Cu foils [38]. To date the actual role and effectiveness of these precursors in the CVD synthesis of graphene is still debated, their decomposition steps and as-formed intermediate active species being not known in detail.

To provide more insights into the CVD of graphene using aromatic precursors, *ab initio* studies and multiscale models can offer a complementary approach to investigate the complex transformation of C precursor molecules into graphene [41–44]. Density functional theory (DFT) calculations reported that the surface-catalyzed dehydrogenations of CH_4 , C_6H_6 and p-Terphenyl ($C_{18}H_{14}$) on Cu(111) have similar activation energy values (~1.5 eV) [45], although only the latter aromatic molecules exhibit strong London dispersion forces with the metal catalyst surface, thereby favoring their surface adsorption. We demonstrated for the first time [46] the higher stability (with respect to C_6H_6) of Cu(111)-adsorbed C_7H_8 and other methyl-substituted C_6H_6 derivatives, like o-xylene and 1,2,3-trimethylbenzene, as result of the electron donor character of the methyl group(s). Moreover, we have also shown that, among all possible decomposition routes of C_7H_8 , o-xylene and 1,2,3-trimethylbenzene, C–H bond scission within their methyl group is energetically more favored (as low as 1.20 eV for toluene) than the C–H scission in CH_4 (1.52 eV) or in the aromatic C-rings of C_6H_6 and C_7H_8 (1.67 eV and 1.72 eV, respectively), while demethylation of C_7H_8 remains negligible due to its prohibitive energy barrier (2.49 eV) [46, 47]. When using C_6H_6 and C_7H_8 the combination of strong surface adsorption and relatively reduced energy barriers to their dehydrogenation, would thus lead to the formation of adsorbed phenyl and benzyl radicals onto Cu at low temperatures.

Molecular dynamics simulations using a hybrid force field [48] reported on the splicing behavior of fully dehydrogenated C_6H_6 intermediates (C_6) on Cu(111), which promotes graphene domain agglomeration. Nevertheless, we believe that nucleation reactions may easily occur well before such fully dehydrogenated aromatic species could be obtained. However, little has been said about the subsequent dehydrogenation steps of phenyl and benzyl radicals, the nature of active hydrocarbon species and their possible recombination reactions.

In this work we study by DFT simulations the multiple dehydrogenation of C_7H_8 on Cu(111) and related reaction activation energies, and identify most probable active hydrocarbon species produced during the LT-CVD of graphene. Finally, we extend our analysis to provide a detailed description of possible recombination reactions between such active species, leading to the formation of anthracene ($C_{14}H_{10}$) as early graphene nuclei.

2. Computational methods

DFT calculations were performed using the Quantum ESPRESSO (QE) v.6.7 code [49–51]. The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) flavor was used as the exchange-correlation functional [52] with ultrasoft (US) pseudopotentials. To account for van der Waals (vdW) interactions, we used the semi-empirical DFT-D3 correction scheme introduced by Grimme *et al.* [53]. The reason behind the choice of the semi-empirical DFT-D3 method, already discussed in our previous work [46], is the compromise

between good accuracy and moderate computational cost.

For the Cu(111) surface, $p(4 \times 4)$ supercells containing four-layer slabs (64 Cu atoms each) were sufficient for investigating the dehydrogenation of small molecules like toluene. Larger supercells with the $p(8 \times 5)$ scheme containing three-layer slabs (120 Cu atoms) were used to study the recombination mechanisms of as-formed active hydrocarbon species leading to early graphene nuclei (i.e., anthracene) including their dehydrogenation reactions. A vacuum region of 15 Å was inserted in all the supercells. Active species of the toluene molecule were positioned only on one side of the slab. The supercell lateral dimension and the vacuum thickness were chosen to be large enough to avoid spurious interactions among periodic images since periodic boundary conditions were applied. During structural optimization, the bottom layer was kept fixed to mimic bulk behavior, while the upper layers and the adsorbate were fully relaxed. Importantly, under typical LT-CVD conditions (300–600 °C), Cu surfaces are expected to exhibit thermally activated processes such as surface diffusion and local structural rearrangements. While these effects are not explicitly included in the present model, they are likely to enhance the mobility of reactive intermediates and increase the reactivity of low-coordinated surface sites. Therefore, the ideal Cu (111) surface adopted in this work provides a reliable and conservative description of the intrinsic reaction energetics, while preserving the validity of the identified atomistic mechanisms governing precursor decomposition and early-stage nucleation. Future studies should explicitly account for the role of step edges, defects, and dynamic surface restructuring to further refine the quantitative description of reaction kinetics under realistic growth conditions. All computational parameters used in the present *ab initio* simulations follow exactly the protocol established in our previous work [46]. Specifically, the choice of plane-wave and charge density cutoff energies, the electronic smearing scheme, the Monkhorst–Pack k -point sampling of the Brillouin zone (the Γ point sampling is used only for the $p(8 \times 5)$ supercell), and all the self-consistent field (SCF) and structural relaxation convergence thresholds are identical to those reported in our earlier study. For consistency, the procedure employed to compute the adsorption energy (E_{ads}) of hydrocarbon molecules is the same as described in our prior publication, in which the full definition of energy parameters and methodological details are provided.

The transition state (TS) configuration and minimum energy path (MEP) of decomposition and recombination reactions were computed using the climbing image nudged elastic band (CI-NEB) method [54] using a convergence force threshold of 0.05 eV/Å for optimization and a sufficient number of images to guarantee an inter-image distance <1.0 Å. The initial and final states were deduced from single geometry optimization calculations. The adopted force convergence threshold represents a commonly used compromise between computational accuracy and cost in CI-NEB calculations of complex surface reactions involving large supercells. Since all reaction pathways were treated consistently within the same computational framework, the relative energetic trends and mechanistic comparisons discussed in this work are expected to remain robust against small residual numerical uncertainties in the absolute activation barrier values.

To establish a quantitative connection between computed activation barriers and LT-CVD experimental conditions in the 300–600 °C range, reaction rates were estimated using transition state theory (TST), according to

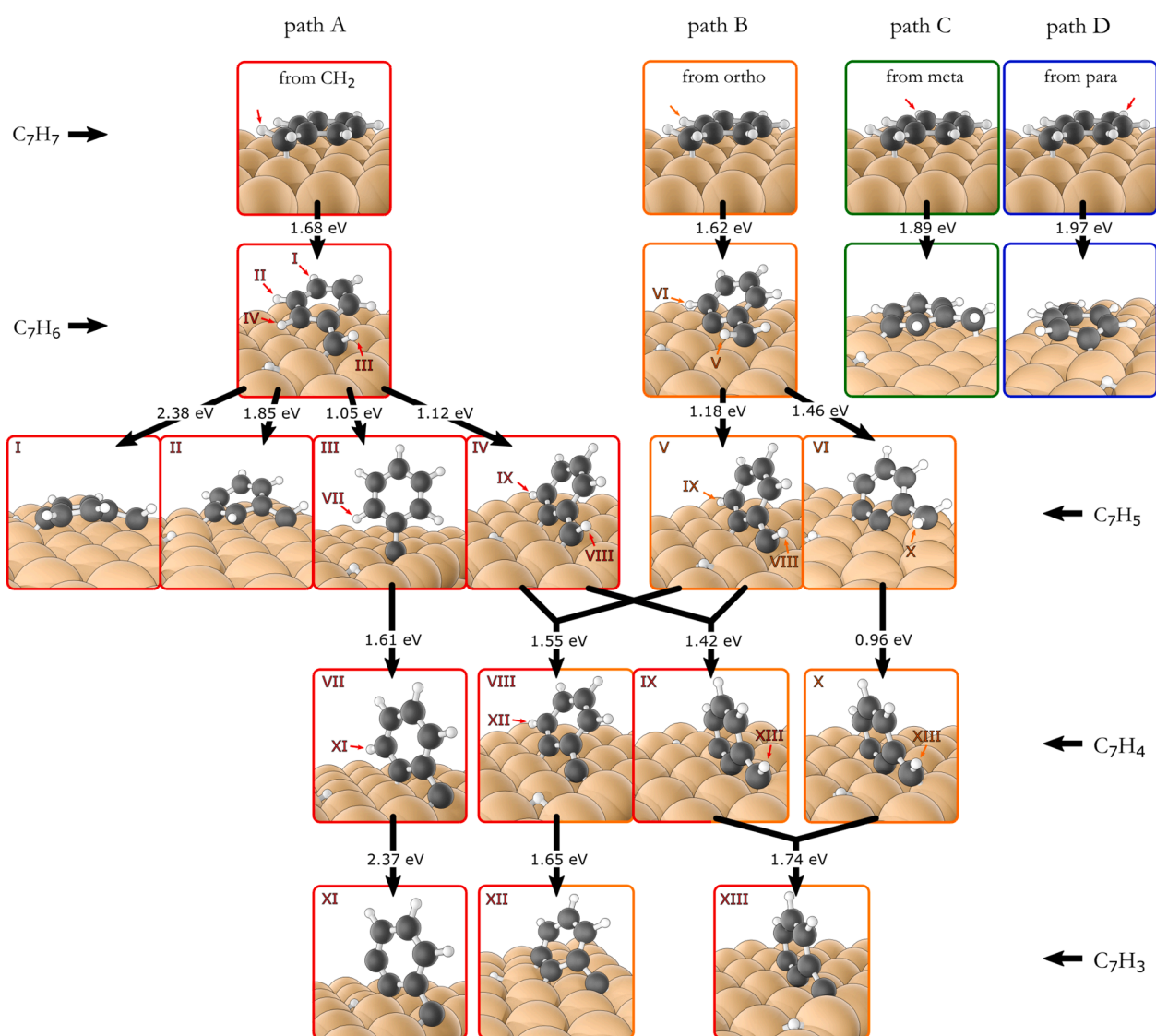
$$k(T) = \nu e^{-\frac{E_b}{k_B T}}$$

where E_b is the activation energy, k_B is the Boltzmann constant and T the temperature. A typical pre-exponential frequency factor $\nu = 10^{13} s^{-1}$ was assumed for surface reactions. Relative pathway probabilities were then evaluated from normalized rate constants according to $P_i = k_i / \sum_j k_j$, allowing for a quantitative comparison of competing reaction channels.

3.1. Multiple dehydrogenation reactions of benzyl (C_7H_7) active species

To identify the most-probable dehydrogenation pathways that produce such active species, we investigated subsequent dehydrogenation reactions of the benzyl radical, as schematically shown in Fig. 1. Since the C_7H_7 radical arranges in a parallel-to-surface configuration with the methylene ($-CH_2-$) group attached to the underlying surface, four distinct main dehydrogenation steps leading to the C_7H_6 species can be uniquely identified, representing the H abstraction from the $-CH_2-$ group (path A), or from the ortho (path B), meta (path C) or para (path D)

The dehydrogenation reactions in paths A and B (highlighted by the red- and orange-contoured panels in Fig. 1, respectively) are characterized by approximately the same E_b (1.6–1.7 eV), i.e. comparable to the energetic cost required for the dehydrogenation of toluene and benzene on the C-ring [46]. When the H abstraction occurs in the methylene group (path A), the resulting C_7H_6 fragment arranges with a tilted geometry on the surface with the C_7H_6 head, i.e. the methine ($=CH-$) group, positioned above the hollow site. The same applies to the final state obtained upon dehydrogenation in the ortho position, but with the C_7H_6 body (i.e., the aromatic C-ring) now anchored to the surface by the C atom involved with the C–H bond cleavage.



3

The subsequent dehydrogenation step of the as-formed C_7H_6 radicals was then studied for the cost-effective paths A and B. Along path A, four distinct dehydrogenation reactions were evaluated involving the C–H bond cleavage in the para (red-contoured panel ‘I’), meta (red-contoured panel ‘II’) or ortho (red-contoured panel ‘IV’) position of the aromatic C-ring, as well as in the methine group (red-contoured panel ‘III’). The H abstraction in the ortho position ($E_b = 1.12$ eV) and in the methine group ($E_b = 1.05$ eV), is energetically favored over the dehydrogenation in the meta and para positions ($E_b = 1.85$ and 2.38 eV, respectively) with energy barriers even slightly lower than that of the toluene methyl dehydrogenation (1.20 eV). The higher activation energies for the meta and para pathways arise from the buckling of the aromatic C-ring (see panels I and II), as observed for paths C and D, whereas ortho and methine dehydrogenation preserve ring planarity. In the latter case, the resulting C_7H_5 radical adopts a vertical configuration due to the strong interaction of the fully dehydrogenated methyl carbon with the Cu(111) surface (see panel III). Along path B, two distinct dehydrogenation reactions of the C_7H_6 species were evaluated, involving the C–H bond cleavage in the methylene group (orange-contoured panel ‘V’) or in the meta position (orange-contoured panel ‘VI’) of the aromatic C-ring. More interestingly, the former exhibits a lower activation barrier ($E_b = 1.18$ eV) leading to a final radical configuration that is identical to that obtained via ortho dehydrogenation, as shown in the red-contoured panel IV of path A. This indicates that two consecutive dehydrogenations of the benzyl radicals, one on the methylene and the other on the ortho position, converge to the same C_7H_5 structure (see panels IV and V), irrespective of reaction sequence. In contrast, the C–H bond cleavage in the meta position of the C_7H_6 radical along path B requires 1.46 eV to overcome the activation barrier. The final C_7H_5 state (panel VI), in which the radical retains the aromatic C-ring planarity, exhibits reduced mobility due to anchoring to the surface through three distinct radical centers (one on the methylene, and two on the ortho and para positions). Noteworthy, we did not consider dehydrogenation in the para position, as it is expected to involve prohibitively high activation energies associated with substantial structural distortions of the resulting radical for the same reasons explained previously.

The dehydrogenation leading to C_7H_4 radicals was mainly investigated for the C_7H_5 active species with the highest likelihood of formation, namely those with configurations shown in panels III and IV (or equivalently V). For these species, dehydrogenation in the meta (panel VIII) and methine (panel IX) positions is associated with relatively lower activation barriers ($E_b = 1.42$ and 1.45 eV, respectively) with respect to that in the ortho site (panel VII) which involves a higher barrier (1.66 eV). In contrast, for the C_7H_5 configuration shown in panel VI, characterized by three distinct radical centers, there is a significant probability for dehydrogenation to occur at the methylene group. This reaction exhibits an activation barrier of only 0.96 eV, the lowest among all dehydrogenation processes considered. The resulting C_7H_4 fragment (panel X) adopts an almost vertical orientation with respect to the surface and is structurally equivalent to that shown in panel IX. Similarly, the configurations in panels VII and VIII are equivalent in terms of bonding, with the only difference being their chemisorption geometry: although the ortho radical center in both cases interacts with a Cu top site, the C-ring in panel VII lies perfectly vertical on the surface, whereas it is tilted in panel VIII. Notably, despite the generally higher activation barriers associated with the C_7H_5 dehydrogenation, C_7H_4 radicals are expected to co-exist with C_7H_5 species during the LT-CVD process.

Finally, the dehydrogenation analysis was also extended to the formation of C_7H_3 radicals. Starting from the configurations in panels VIII and IX (or equivalently X), C–H bond cleavage in the meta and methine positions involves comparable activation barriers in the range of 1.65–1.74 eV. In contrast, meta dehydrogenation of the configuration in panel VII becomes significantly less favorable, requiring an activation barrier of 2.37 eV. This increase reflects the greater structural rigidity of the C_7H_4 radicals, which hampers further H abstraction. In this case, the meta radical center (panel XI) is not stabilized by interaction with the Cu

surface, accounting for the prohibitively high barrier. Depending on the chemisorption site, the resulting C_7H_3 radicals adopt either vertically-oriented (panels XI and XIII) or tilted (panel XII) configurations. Further dehydrogenation steps were not explored, as they are expected to involve prohibitively high activation barriers due to the substantial structural distortions induced upon additional H removal. More, importantly, dehydrogenation reactions must be evaluated in competition with desorption. For toluene, the comparable magnitude of the methyl dehydrogenation barrier (~ 1.2 eV) and desorption energy (~ 0.97 eV) suggests that both processes may occur concurrently [46]. In contrast, strongly bound species such as chemisorbed intermediates typically exhibit much higher desorption energies, making further reaction pathways (i.e., dehydrogenation steps) significantly more probable.

Noteworthy, under realistic CVD conditions the presence of highly reactive hydrogen species ($H^\bullet$) may enable alternative $H^\bullet$ -assisted dehydrogenation pathways, in which H abstraction occurs via the formation of molecular H_2 , especially at high H^* coverage. Indeed, the formation of a strong H–H bond may stabilize the transition state, potentially lowering the effective activation barriers compared to direct C–H bond cleavage. While not explicitly considered in this work, such mechanisms may further enhance the formation of reactive intermediates.

Among the possible pathways in which benzyl radicals undergo stepwise dehydrogenations to yield C_7H_6 , C_7H_5 , C_7H_4 and C_7H_3 active species, C–H bond cleavage at the methylene and ortho positions is energetically favored, while meta and para pathways are typically hindered by higher barriers due to aromatic ring buckling. Successive methylene and ortho dehydrogenation steps most probably converge to C_7H_5 configurations shown in panels III, IV and V of Fig. 1, whose radicals would constitute the main building blocks leading to subsequent condensation reactions of early graphene nuclei like anthracene ($C_{14}H_{10}$) during the LT-CVD of graphene. For clarity, the energy pathways leading to the formation of such dehydrogenated active species onto Cu(111) are summarized in Fig. 2, starting from gas-phase toluene taken as the reference state (0 eV).

At representative LT-CVD temperatures (300–600 °C), the calculated rates show a strong dependence on the activation barrier. For example, at 600 °C (873 K), methylene and ortho dehydrogenation steps with barriers of ~ 1.0 – 1.2 eV yield rate constants on the order of 10^6 – 10^7 s $^{-1}$, indicating rapid kinetics, whereas barriers of ~ 1.6 – 1.8 eV reduce the rates to $\sim 10^2$ – 10^3 s $^{-1}$. Processes exceeding ~ 2.0 eV become comparatively slow (~ 10 s $^{-1}$ or lower), leading to strong suppression of meta and para pathways. Although the initial benzyl dehydrogenation steps at the methylene and ortho positions ($E_b \approx 1.6$ eV) constitute the kinetic bottleneck toward the formation of the most probable C_7H_5 active species (see Fig. 2), they remain the dominant reactive channels for chemisorbed benzyl radicals under LT-CVD conditions. Competing processes such as radical desorption are expected to be less favorable due to the strong benzyl–Cu(111) interaction, while extensive fragmentation or C–C bond dissociation is unlikely at the relatively low growth temperatures considered here. Consequently, these dehydrogenation events are expected to govern the formation of reactive C_7H_5 intermediates on the Cu surface at 600 °C. However, such kinetic bottleneck becomes significantly more critical at 300 °C since activation barriers of ~ 1.6 – 1.7 eV yield rate constants as low as $\sim 10^2$ – 10^1 s $^{-1}$, suggesting that the formation of reactive C_7H_5 species may become considerably slower and potentially rate-limiting for graphene nucleation.

For the initial $C_7H_7 \rightarrow C_7H_6$ conversion, a relative pathway probability analysis within the 300–600 °C temperature range indicates that ortho dehydrogenation (path B in Fig. 1) contributes approximately 70% of the total reaction flux, while methylene dehydrogenation (path A) accounts for about 25–30%, despite the small barrier difference of only 0.06 eV. In contrast, meta and para pathways contribute only marginally due to their substantially higher activation barriers (less than a few

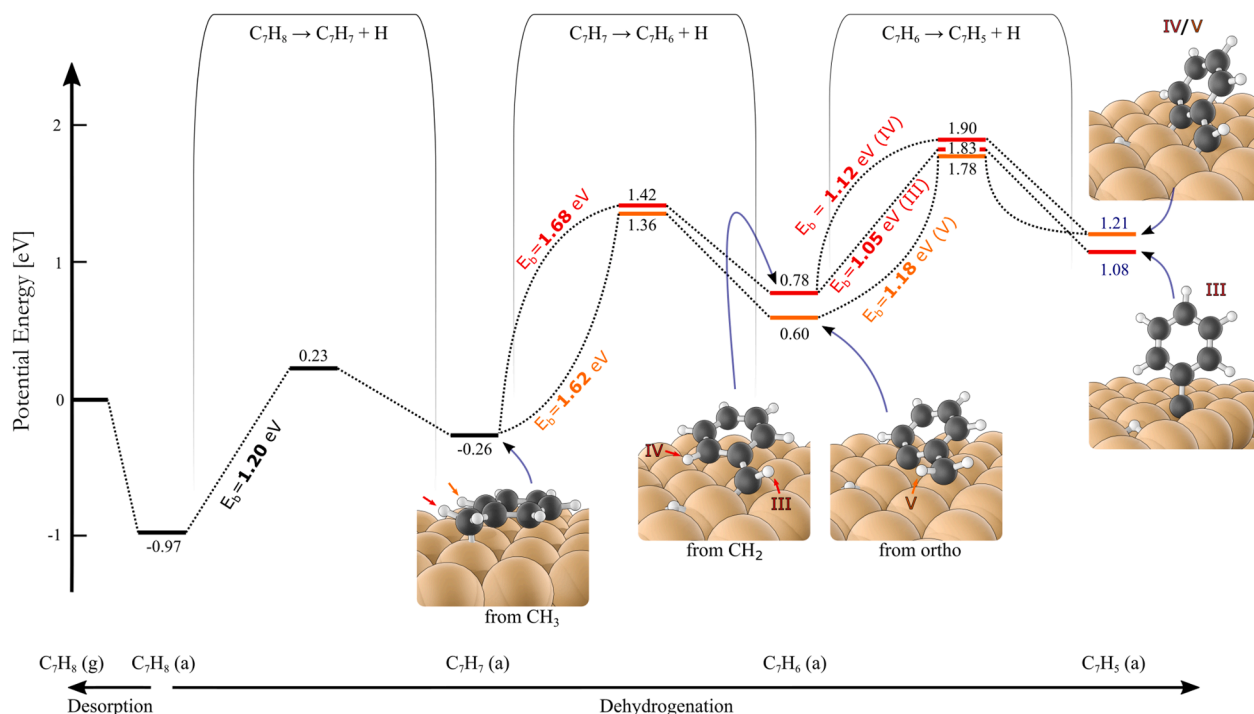


Fig. 2. Potential energy diagram of the most favourable dehydrogenation pathways of toluene on Cu(111) leading to the formation of the dominant chemisorbed C_7H_5 active species. Gas-phase toluene on Cu(111) is taken as the reference state at 0 eV. The activation barrier associated with the first dehydrogenation step of toluene to benzyl (C_7H_7) was taken from [46], while the remaining barriers were calculated in the present work. The reported activation energies correspond to the elementary dehydrogenation reactions occurring along the kinetically preferred methyl/methylene and ortho pathways. Atomic configurations of the relevant intermediates adsorbed on Cu(111) are also shown.

percent overall). In the subsequent $C_7H_6 \rightarrow C_7H_5$ step, the reaction network exhibits strong kinetic convergence: along path A, methine and ortho dehydrogenation dominate with branching probabilities of ~ 70 – 80% and ~ 20 – 30% , respectively, whereas along path B, methylene dehydrogenation overwhelmingly prevails ($>95\%$), leading to the same C_7H_5 configuration obtained via path A. Further dehydrogenation toward C_7H_4 and C_7H_3 becomes progressively less favorable because of the higher activation barriers, suggesting that recombination reactions of C_7H_5 species may compete effectively before further dehydrogenation occurs.

In conclusion, the kinetic analysis reveals that benzyl dehydrogenation on Cu(111) follows a highly selective reaction network characterized by an initial competition between ortho and methylene activation, followed by rapid convergence toward the dominant C_7H_5 intermediates shown in panels III–V. These species therefore represent the most probable reactive building blocks governing the early nucleation stages under LT-CVD conditions.

3.2. Condensation reactions leading to the formation of anthracene

The expected plentiful presence of distinct radical species on Cu(111), from singly dehydrogenated toluene (i.e., the C_7H_7 benzyl radical) to C_7H_4 , can trigger the nucleation of small sp^2 -hybridized carbon clusters during the early stages of the LT-CVD of graphene. As opposed to the dissociation stage, the cluster nucleation involves almost exclusively recombination reactions between active species. Due to the multitude of complex reaction mechanisms for a given set of involved radicals, the study of such nucleation turns out challenging. One of the most appealing and simplest carbon clusters that could be found in the early nucleation stage of graphene is anthracene ($C_{14}H_{10}$). Its molecular structure is characterized by three connected phenyl rings that could be formed, for example, from the reaction of two toluene molecules. To make possible the formation of anthracene from two interacting toluene molecules, six H atoms must detach from the carbon backbone to favor

the chemical bonding between the two molecules. The ideal case would correspond to the condensation of two C_7H_5 radicals (labeled with ‘ α ’ and ‘ β ’ in the ‘Initial State’ of Fig. 3) on Cu(111), each one formed as a result of three consecutive dehydrogenation reactions of toluene, one on the ortho position and two on the methyl group. Such dehydrogenation mechanism giving C_7H_5 radicals follows the most likely reaction pathways identified in Section 3.1, and shown in the panel ‘IV’ of Fig. 1. Recombination reactions involving radicals like C_7H_7 and C_7H_6 are also possible but, in this case, the excess hydrogens would detach upon radical recombination.

The condensation reaction of two C_7H_5 radicals can result into two different anthracene stereoisomers, namely, the *zig-zag* and the *armchair* anthracene as shown in the ‘Final State’ of Fig. 3. Indeed, the presence of two distinguishable centers in the C_7H_5 radical structure, one on the C atom in the ortho position belonging to the aromatic C-ring (labeled ‘C_B’ in Fig. 3, where the subscript ‘B’ stems from ‘Body’) and one on the C atom belonging to the methine group (labeled ‘C_H’ in Fig. 3, where the subscript ‘H’ stems from ‘Head’), leads to the creation of three possible C=C double bonds represented as (i) $C_B=C_H$, (ii) $C_H=C_H$ and (iii) $C_B=C_B$. Zig-zag anthracene is thus produced when two indistinguishable $C_B=C_H$ double bonds are formed upon recombination, while one $C_H=C_H$ and one $C_B=C_B$ formed for armchair anthracene.

For a proper investigation of the overall condensation mechanism starting from a reactant state represented by the two unconnected C_7H_5 radicals chemisorbed onto the Cu(111) to the product state in which anthracene is produced, we systematically explored various initial spatial arrangements of the two interacting C_7H_5 species and accounted for the bond formation ordering by examining which type of chemical bond among $C_B=C_H$, $C_H=C_H$ and $C_B=C_B$ is first established. Three main recombination pathways were identified for each anthracene stereoisomer as schematically represented in Figs. 4 and 5 for the zig-zag and armchair anthracene, respectively. In the former case, the two $C_B=C_H$ double bonds, namely, $C_{B\alpha}=C_{H\beta}$ and $C_{B\beta}=C_{H\alpha}$, are indistinguishable due to molecular symmetry and because they share the same chemical

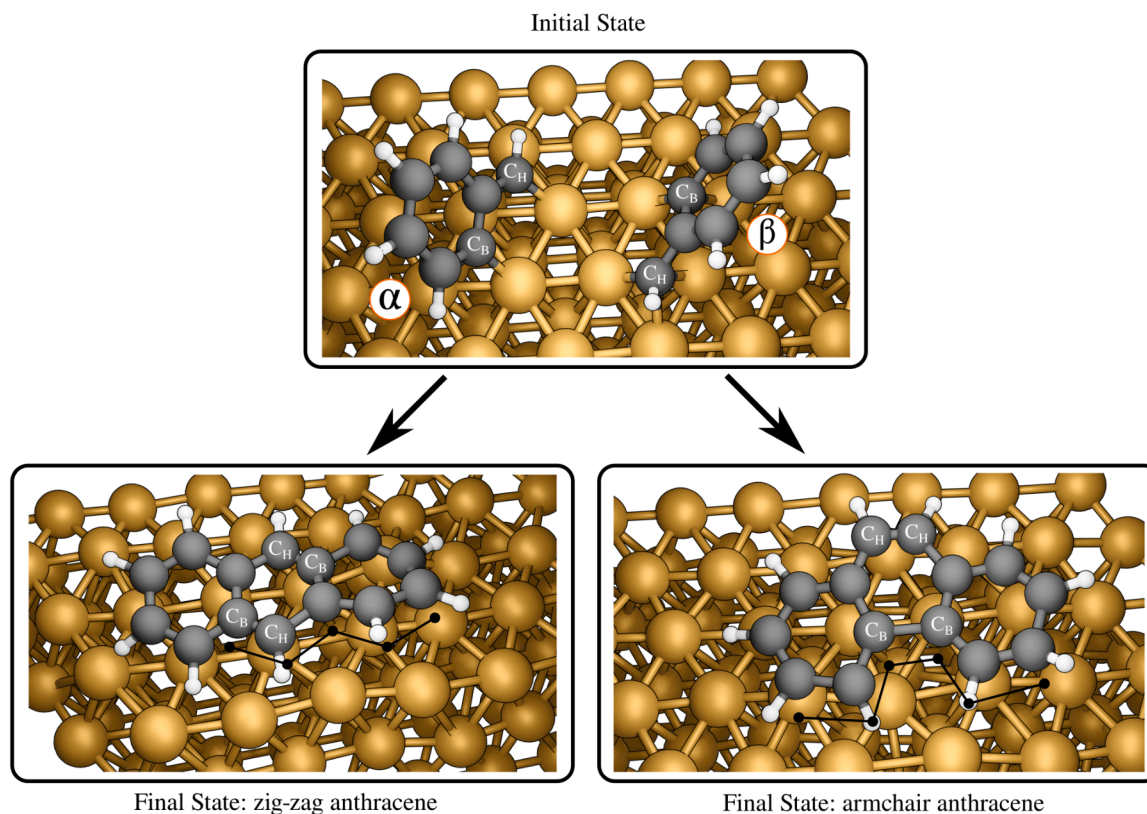


Fig. 3. Condensation reactions between two C_7H_5 radicals on Cu(111) forming the anthracene molecule. Atomic geometries of the initial and final states are given. Radical C atoms that belong to aromatic C-rings are identified by the ' C_B ' label (where the subscript 'B' stems from 'Body'), while those that belong to the methyl groups are identified by the ' C_H ' label (where the subscript 'H' stems from 'Head'). The presence of two different radical centers (' C_B ' and ' C_H ') can lead to the creation of three types of C=C double bonds: the $C_B=C_H$, $C_B=C_B$ and $C_H=C_H$ bonds. As a result, the zig-zag or armchair anthracenes can be produced.

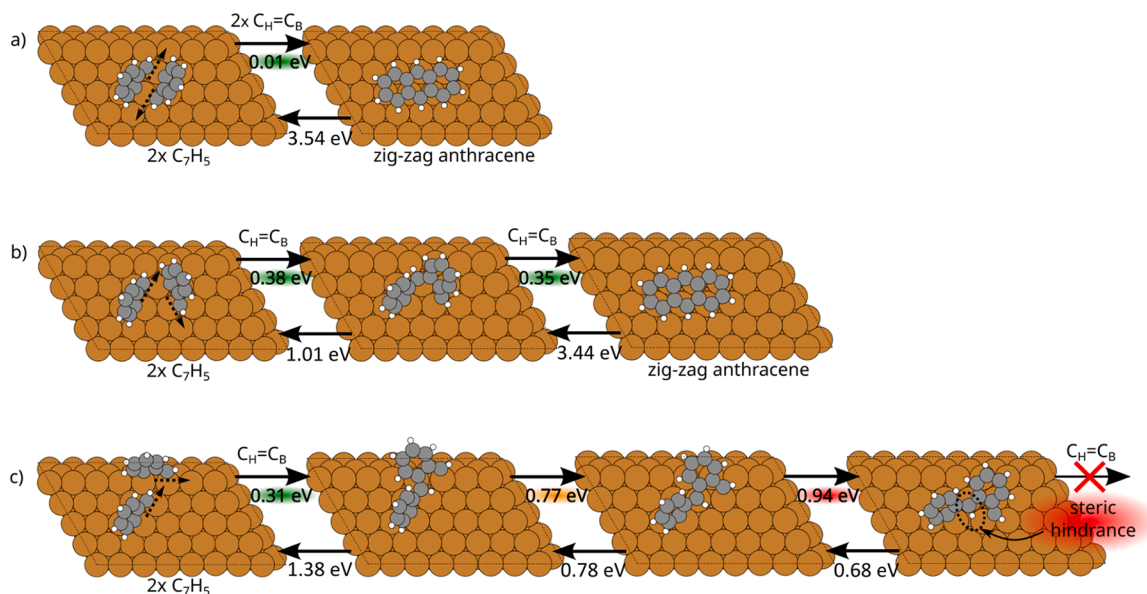


Fig. 4. Recombination pathways of two C_7H_5 radicals on Cu(111) leading to zig-zag anthracene. For each pathway, the atomic geometries of the initial, intermediate and final states are given. The three distinct pathways in (a), (b) and (c) differ by the relative alignment between radicals in the initial state. Dashed black arrows show the initial radical orientation on the copper surface.

environment, meaning that investigating the bond formation ordering effect on the recombination mechanism is irrelevant. When the $C_{B\alpha}$ and $C_{H\beta}$ (or equivalently $C_{B\beta}$ and $C_{H\alpha}$) radical centers of the two C_7H_5 radicals get sufficiently closer to each other, the zig-zag anthracene can be

produced by one of the three recombination pathways shown in Fig. 4, in which the two radicals in the initial state can either (a) share two surface Cu atoms with antiparallel alignment (the two C_7H_5 are arranged almost parallel to each other but they have opposite orientations, as

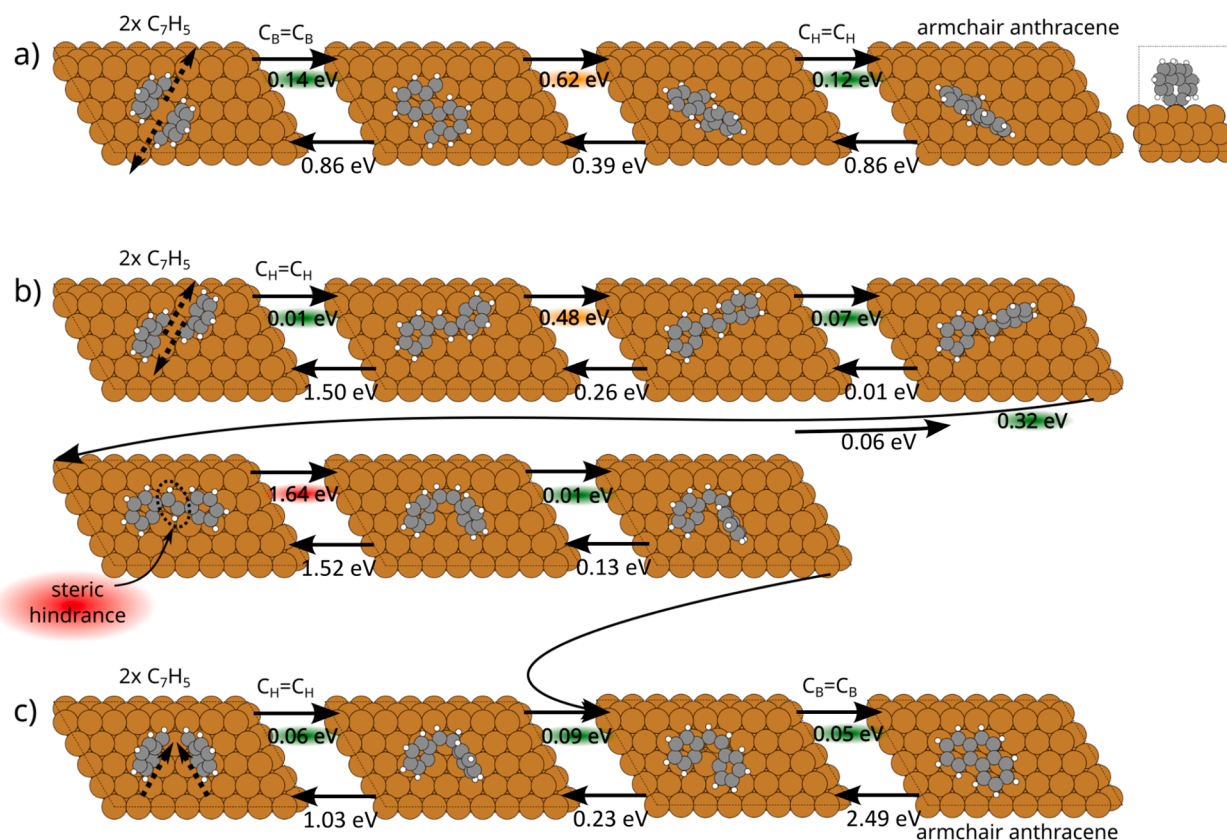


Fig. 5. Recombination mechanisms of two C_7H_5 radicals on Cu(111) leading to armchair anthracene. Atomic geometries of the initial, intermediate and final states are given. Three distinct pathways were identified depending on the relative alignment between radicals in the initial state and the bond formation sequence. Dashed black arrows show the radical orientation on the copper surface.

indicated in Fig. 4.a), or have one $C_{H\alpha}/C_{B\beta}$ radical pair on the same surface Cu atom but with (b) 120° or (c) 60° alignment of the reactive C_7H_5 radicals (see the dashed black arrows in Figs. 4.b and c). Noteworthy, if the parallel alignment was considered in case (a), the recombination reaction would have led to the armchair anthracene formation. In path (a), only one activated event could be observed, since the two $C_B=C_H$ double bonds form almost simultaneously with negligible energetic cost (0.01 eV). The near-zero activation barrier observed in this case originates from the strong interaction between radical centers already in close proximity, which promotes orbital overlap and enables spontaneous bond formation without requiring significant structural rearrangement. In path (b), the anthracene formation mechanism proceeds instead through two distinct elementary steps, each one related to the $C_B=C_H$ double bond creation, whose E_b are within 0.35–0.38 eV. Here, the mutual interaction between the two radicals is weaker with respect to the case (a), since only one C_B/C_H radical centers pair shares the same surface Cu atom with a minimum pair distance of 2.76 Å in the initial state, which increases to 4.80 Å for the other C_B/C_H pair. This discussion also applies to path (c) for which we obtained a similar E_b value of 0.31 eV for the first $C_B=C_H$ bond creation relative to the C_B/C_H radical centers pair, having a relative short distance of 3.20 Å. Afterwards, part of the as-formed intermediate must rotate relative to the rest of such radical in order to facilitate the second $C_B=C_H$ formation by approaching the remaining two C_B/C_H radical centers together. This overall internal rotation can be thought of as a series of rotational transitions typically hindered by potential energy barriers that arise from steric hindrance effects. In the intermediate structure of path (c) one methine bridge chemically connects two C-rings: one vertically oriented aromatic ring binds with the underneath surface by its C_B radical center, while the other one aligns horizontally and binds to the surface by one more methine group. The internal rotation around the

methine bridge (identified by the dashed black circle in the final state of Fig. 4.c) would require expensive energetic costs that are typically higher than those of the $C_B=C_H$ formation, which further increase along the reaction coordinate. At a critical internal rotation angle, the molecular motion will be totally hindered by the steric hindrance manifested when the two methine groups are in proximity and, thus, their steric bulk will create strong repulsive interactions (see Fig. S1.a in Supplementary Information for further details). These findings suggest that zig-zag anthracene cannot be produced through path (c) since the second $C_B=C_H$ double bond formation is prevented by the steric hindrance arisen during the internal rotational stage; while <0.4 eV are required for the recombination mechanism through path (a) or (b).

As a result, the initial relative orientation of the two C_7H_5 fragments plays a crucial role in determining which pathway to follow and, thus, the reaction outcome. Moreover, the intermediate in path (c) may be further attached by other radicals forming larger intermediates leading to other graphene nuclei, before other decomposition reactions could occur.

For the armchair anthracene case, the bond formation sequence becomes as relevant as the spatial arrangement of the radicals. Depending on the radical centers, i.e., the C_B/C_B or C_H/C_H pair that combine to construct the first $C=C$ double bond, the recombination mechanism can follow three main different pathways as shown in Fig. 5. For example, the $C_B=C_B$ bond is first produced if the two C_B radical centers recombine as occur in path (a). Here, the two radicals share one surface Cu atom and dispose in the antiparallel alignment (see the dashed black arrows in Fig. 5.a). A similar configuration is observed in the initial state of Fig. 4.a, but in this case one of the radicals is shifted to the next Cu atom along the Cu [010] direction. Once the $C_B=C_B$ is formed, the bond requires an E_b of 0.14 eV. After the $C_B=C_B$ is established the intermediate will arrange in a bridge-like molecular structure

with the two methine groups anchored to the Cu surface. The methine groups are both located at the opposite ends of the two C-rings and they are 5.52 Å far apart. To facilitate the second $C_H=C_H$ creation, internal rotation must occur to let the two C_H radical centers get closer to each other. The internal rotational step was identified with a computed E_b of 0.62 eV, whose motion occurs around the C—C bond connecting the two C-rings that rotate in opposite directions, until the two C_H radical centers are 2.96 Å far apart. The two methine groups are then sufficiently close to combine and form the second $C_H=C_H$ which requires an E_b 0.12 eV. The as-formed armchair anthracene chemisorbs vertically by its two C_H on top of one surface Cu atom with average bond distance of 2.08 Å, with the two C_H-H bonds pointing out-of-plane of the C-ring. Such strong interaction leads to changes in the molecule's shape and behavior since the inner C-ring facing the metallic surface puckers: the C_H-C_H turns single bond with distance of 1.49 Å and the molecule will partially lose its aromaticity, as will be discussed in detail below in Section 3.3. If one of the two C_7H_5 radicals in path (a) moves along the Cu [010] direction preserving its antiparallel alignment, such that the two C_H radical centers will be found close to each other (2.71 Å far apart) and about to combine on top of the same surface Cu atom, the recombination mechanism follows the path (b) of Fig. 5.b as opposed to path (c) in which the two C_7H_5 have a 60° alignment (see the dashed black arrows in Fig. 5.c). Notice that path (c) shows lower activation energies that do not overcome 0.1 eV. Here, the $C_H=C_H$ formation event is followed by a single internal rotation step of one C-ring around the two connected methine groups. Once the two C_B radical centers are 2.80 Å apart on the same surface Cu atom, the mechanism proceeds forward to the second $C_B=C_B$ bond formation, leading to the armchair anthracene molecule that lays horizontally on the Cu surface. Path (b) is slightly more complex since it includes more internal rotational steps. The first $C_H=C_H$ formation was found inexpensive ($E_b = 0.01$ eV) leading to an intermediate structure composed of two connected methine bridges (see the dashed black circle in Fig. 5.b) that link the two C-rings. It should be noted that similar structural features were also observed for the intermediate produced in path (c) of Fig. 4.c, although it holds only one methine bridge in the middle of the two C-rings. The steric hindrance effect is more pronounced in path (b) and introduce significant energy barriers to rotation with respect to path (c). Indeed, E_b can reach 0.5 eV in the first rotation stage, which easily increases along the reaction coordinate as the two C-rings approach each other, giving rise to strong repulsive interactions with the methine bridge, whose H atom lies in close proximity to the two C_B radical centers. For this specific methine, we therefore investigated a methine rotation mechanism analogous to path (c) in Fig. 4, yielding a 180° rotation with a calculated energy barrier of 1.64 eV (see Fig. S1.b in Supplementary Information). Supported by the new (optimal) intermediate conformation, the recombination mechanism will then proceed forward to the second $C_B=C_B$ bond formation through the last stage of path (c).

To further elucidate the competition among the different recombination mechanisms, we evaluated the relative probability of each pathway by comparing their estimated reaction rates over the LT-CVD temperature range (300–600 °C). A quantitative comparison of activation barriers, estimated reaction rates and branching probabilities for the rate-determining steps of each studied recombination pathway is

summarized in Table 1.

For the zig-zag anthracene formation the nearly barrierless formation of the two $C_B=C_H$ bonds ($E_b = 0.01$ eV) - pathway (a) - yields extremely high constant rates (on the order of 10^{12} – 10^{13} s⁻¹), indicating a spontaneous recombination process once the antiparallel alignment of the radicals is achieved. In contrast, pathway (b), involving two sequential $C_B=C_H$ bond formations with activation barriers of 0.35–0.38 eV, exhibits significantly lower but still accessible rates, ranging from $\sim 10^8$ – 10^9 s⁻¹ at 300 °C to $\sim 10^{10}$ s⁻¹ at 600 °C. The pathway probability analysis indicates that pathway (a) accounts for >99% of the total zig-zag formation flux at low temperature and remains dominant even at 600 °C, while pathway (b) contributes only marginally. Although the first $C_B=C_H$ formation in pathway (c) is characterized by a moderate barrier (0.31 eV), the subsequent internal rotation becomes progressively hindered by steric repulsion between adjacent methine groups. Consequently, the overall probability of successfully completing pathway (c) becomes negligible.

A more complex kinetic competition emerges for armchair anthracene formation, where the reaction outcome depends not only on the initial radical arrangement but also on the sequence of $C_B=C_B$ and $C_H=C_H$ bond formation. Among the identified mechanisms, pathway (c) is the most kinetically favourable: since all elementary steps exhibit activation barriers below 0.1 eV, the corresponding rate constants remain extremely high ($\sim 10^{11}$ – 10^{13} s⁻¹) throughout the investigated temperature range. In contrast, pathway (a) is limited by the internal rotational step characterized by $E_b = 0.62$ eV. While the initial $C_B=C_B$ formation is rapid, the rotational rearrangement reduces the effective overall rates to $\sim 10^7$ s⁻¹ at 300 °C and $\sim 10^9$ s⁻¹ at 600 °C. The transition-state-theory probability analysis indicates that pathway (c) contributes >99% of the total armchair formation flux at both temperatures, whereas pathway (a) becomes only marginally accessible. Conversely, pathway (b) appears strongly suppressed by steric hindrance (E_b up to 1.64 eV), despite the first $C_H=C_H$ bond formation is almost barrierlessly ($E_b = 0.01$ eV). Such large energetic costs reduce the effective rate constants to values below $\sim 10^{-2}$ s⁻¹ at 300 °C, making this mechanism kinetically irrelevant.

Comparison between the two anthracene stereoisomers reveals that both products can form efficiently under LT-CVD conditions, but through markedly different kinetic scenarios. Zig-zag anthracene formation is dominated by a single highly selective near-barrierless pathway requiring an optimal antiparallel radical configuration of Fig. 4(a), whereas armchair anthracene formation involves a broader competition among multiple pathways, although strongly biased toward the low-barrier mechanism of Fig. 5(c). Overall, the kinetic analysis indicates that the condensation process is governed more by steric accessibility and geometrical alignment of the radical centres than thermodynamic stability alone. The strong exponential dependence of the reaction rates on the activation barriers leads to highly selective branching, so that only a limited subset of radical configurations effectively contributes to anthracene nucleation on Cu(111). Nevertheless, it should be emphasized that the present kinetic analysis is based exclusively on the computed activation barriers and does not explicitly account for additional statistical and dynamical factors, such as surface diffusion kinetics or geometrical accessibility of the reactive

Table 1

Kinetic parameters and reaction path probabilities in the 300–600 °C temperature range for zig-zag and armchair anthracene formation from two C_7H_5 radicals adsorbed on Cu(111).

Anthracene type	Rate-determining reaction pathway	E_b (eV)	k (300 °C) (s ⁻¹)	k (600 °C) (s ⁻¹)	P (300 °C)	P (600 °C)
Zig-zag	(a): $C_B=C_H$ formation	~0.01	$\sim 10^{12}$ – 10^{13}	$\sim 10^{13}$	>99%	>99%
	(b): $C_B=C_H$ formation	0.35–0.38	$\sim 10^8$ – 10^9	$\sim 10^{10}$	<1%	<1%
	(c): internal rotation	Sterically blocked	/	/	0%	0%
Armchair	(a): internal rotation	0.62	$\sim 10^7$	$\sim 10^9$	<1%	<1%
	(b): internal rotation	1.64	$\sim 10^{-2}$	$\sim 10^3$	~0%	~0%
	(c): $C_H=C_H + C_B=C_B$	<0.1	$\sim 10^{11}$ – 10^{12}	$\sim 10^{12}$ – 10^{13}	>99%	>99%

configurations on Cu(111). These effects may alter the effective branching ratios under realistic LT-CVD conditions by modifying the probability that radicals encounter each other in favorable arrangements prior to recombination.

3.3. Dehydrogenation reactions of anthracene

Once anthracene is produced onto the Cu(111) surface, the LT-CVD can eventually proceed forward through more complex nucleation mechanisms. New active species generated from the dehydrogenation of anthracene become indispensable to trigger the condensation of larger graphene nuclei. To gain information on the dehydrogenation energy barriers of anthracene, we investigated its C–H bond scission. Fig. 6 reports the computed E_b values along with the energetics of the adsorption/initial state (AS/IS), referring to the anthracene molecule adsorbed onto the Cu(111) surface, the transition and final states (TS and FS, respectively). All energies are reported with respect to a 0 eV reference gas state (GS) which represents the isolated molecule in the gas phase. The adsorbed molecule in the AS can either desorb and return to the gas phase (in GS) or undergo a surface-catalyzed dehydrogenation forming active species (FS). The outcome of this scenario is driven by the energetic competition between these two events. Moreover, the desorption barriers are calculated considering barrierless adsorption (i.e., E_b of desorption equals E_{ads}).

It should be first noted that the recombination mechanism of two C_7H_5 studied in Section 3.2 usually leads to anthracene in horizontally

adsorbed configurations (see Figs. 4 and 5), while a perpendicular-to-surface structure originates only in the final state of path (a) in Fig. 4, a for the armchair anthracene case. When physisorption occurs, the E_{ads} of zig-zag anthracene is -1.64 eV (red line in AS), which we expect to be similar in magnitude for the equivalent physisorbed armchair stereoisomer; instead, it increases (in absolute value) to -2.51 eV for the abovementioned vertically chemisorbed armchair anthracene (blue line in AS). In the latter structure, shown in the shaded blue panel of Fig. 6, the inner C-ring forms two chemical σ -bonds with the same surface Cu atom by its only two C (labelled with C_σ) that bear the two H atoms (labelled with H_σ). C_σ becomes sp^3 hybridized since it establishes four σ -bonds and no C_σ electrons left will be available for the delocalized molecular p orbitals. Consequently, the stabilizing effect of the overlapping p orbitals is locally absent, thus leaving the planar conformation of the C-ring unsupported. Moreover, the steric interactions of the two H_σ atoms, whose C_σ - H_σ bonds point towards the ring out-of-plane, result in torsional strain being exerted on that C_σ - C_σ bond which finally leads to the characteristic puckered conformation of cyclohexane, the nonaromatic counterpart of benzene, observed in that C_σ - C_σ backbone of the inner C-ring. Indeed, the two C_σ locate at alternating positions above and below the mean plane of the inner C-ring. The stabilization of this apparently unusual molecular structure leads to new bonding patterns at the surface interface at the expense of a partial loss of aromaticity. Despite the inner C-ring aromaticity reduction, the high configuration stability originates in the energy gain due to the formation of the two C_σ -Cu σ -bonds having average length of 2.08 Å. Dehydrogenation of physisorbed zig-zag anthracene requires an E_b of 1.87 eV, obtained by averaging over all possible dehydrogenation paths. Such large energy values could hinder the dehydrogenation of anthracene during the LT-CVD synthesis of graphene. Very interestingly, the H_σ abstraction on the inner C-ring of the vertically chemisorbed armchair anthracene has instead a much lower activation energy (0.30 eV) which makes it by far more energetically convenient with respect to the previous case. Moreover, the proclivity to dehydrogenate is further assisted by the stronger surface-molecule interaction since the molecule would require 2.51 eV to desorb. All dehydrogenated anthracene molecules, both zig-zag and armchair types, interact with the Cu surface in a tilted configuration. For example, vertically-oriented armchair anthracene tilts by approximately 40° upon dehydrogenation, as shown in the FS of Fig. 6, where the inner C-ring fully restores its aromatic structure.

4. Conclusions

We presented a comprehensive DFT investigation to elucidate the surface-catalyzed dehydrogenation of toluene precursor onto the Cu (111) surface up to the formation of C_7H_3 active species, and the nucleation mechanism of anthracene ($C_{14}H_{10}$) as an early graphene nuclei produced through recombination reactions between two C_7H_5 fragments, respectively. We first demonstrated that C–H bond scission preferentially occurs at the methyl group and ortho positions of adsorbed toluene, leading (through kinetically-accessible elementary steps) to the abundant formation of chemisorbed C_7H_5 radicals, a most probable active hydrocarbon species on the Cu(111) surface under low-temperature CVD conditions. The kinetic analysis further revealed that the initial benzyl dehydrogenation on methylene/ortho positions constitutes the key rate-controlling stage governing the generation of the C_7H_5 reactive intermediates. We further showed that the C_7H_5 radicals may readily recombine to form both zig-zag and armchair anthracene via multiple competing pathways, whose feasibility is governed by the relative alignment of the radicals, the sequence of C=C bond formation, and steric effects arising during internal rotational steps. While the formation of individual C=C bonds generally involve low activation barriers, internal rotations of reaction intermediates may become rate-limiting and, in some configurations, sterically hinder the completion of anthracene formation. Zig-zag anthracene formation is dominated by the nearly barrierless antiparallel recombination pathway, whereas

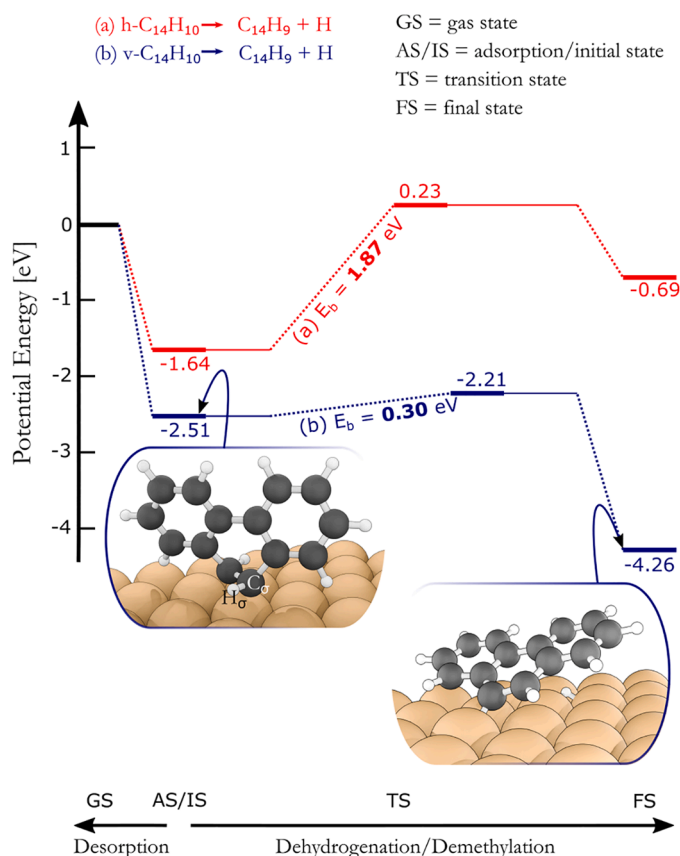


Fig. 6. List of dehydrogenation reactions of (a) horizontally adsorbed zig-zag anthracene and (b) vertically chemisorbed armchair anthracene on Cu(111). The reference state (GS) represents the molecule in the gas phase, while the adsorbed state (AS) refers to the molecule adsorbed onto the Cu(111) surface. IS, TS and FS indicate the reaction initial, transition and final adsorption states, respectively. The decomposition barrier E_b is indicated in the diagram for each of the reactions. The shaded blue panel shows the atomic coordinates of the vertically chemisorbed armchair anthracene.

armchair anthracene formation preferentially proceeds through the low-barrier 60° configuration. This implies that the decisive factor controlling early nucleation in low-temperature CVD is not the formation of C–C bonds themselves, but the accessibility of specific radical configurations enabling recombination without sterically hindered rearrangements. We also demonstrated that the anthracene reactivity on dehydrogenation strongly depends on its adsorption geometry on Cu (111): horizontally-adsorbed configurations exhibit higher activation barriers, whereas vertically-chemisorbed armchair anthracene undergoes energetically cost-effective C–H bond cleavage, yielding highly reactive carbon nuclei that can readily evolve into larger sp²-hybridized carbon networks through subsequent recombination steps. This finding suggests that surface-induced geometrical distortions and local loss of aromaticity may critically enhance the reactivity of early graphene precursors.

In conclusion, present results provide atomistic insight into the early stages of graphene nucleation from aromatic toluene precursor, and highlight the critical role of surface-mediated radical chemistry and sterically controlled recombination pathways, establishing a robust framework for extending first-principles modeling to larger polycyclic intermediates, cooperative radical reactions, and multiscale simulations of graphene growth. Nevertheless, it should be emphasized that the kinetic analysis performed here is based exclusively on activation barriers derived from static DFT calculations within a transition-state-theory framework. Additional statistical and dynamical effects — including surface diffusion, configurational populations of radicals, local surface restructuring, and the probability of achieving favorable mutual orientations prior to recombination — were not explicitly considered and may influence the effective branching ratios under realistic low-temperature CVD conditions. Future investigations combining first-principles calculations with dynamical and multiscale approaches will therefore be essential to achieve a more complete quantitative description of graphene nucleation kinetics.

CRedit authorship contribution statement

Onofrio Tau: Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis, Data curation, Conceptualization. **Nico Lovergine:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. **Riccardo Rurali:** Writing – review & editing, Validation, Resources, Methodology. **Paola Prete:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We acknowledge the Severo Ochoa Centres of Excellence Program under grant CEX2023-001263-S. We thank the Centro de Supercomputación de Galicia (CESGA) for the use of their computational resources.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.surfin.2026.110139](https://doi.org/10.1016/j.surfin.2026.110139).

Data availability

Data will be made available on request.

References

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I. V. Grigorieva, A.A. Firsov, Electric field in atomically thin carbon films, *Science* 306 (2004) 666–669, <https://doi.org/10.1126/science.1102896>.
- [2] A.H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, A.K. Geim, The electronic properties of graphene, *Rev. Mod. Phys.* 81 (2009) 109–162, <https://doi.org/10.1103/RevModPhys.81.109>.
- [3] M.F. Craciun, S. Russo, M. Yamamoto, S. Tarucha, Tuneable electronic properties in graphene, *Nano Today* 6 (1) (2011) 42–60, <https://doi.org/10.1016/j.nantod.2010.12.001>. Iss.
- [4] F. Molitor, J. Güttinger, C. Stampfer, S. Dröschner, A. Jacobsen, T. Ihn, K. Ensslin, Electronic properties of graphene nanostructures, *J. Phys. Cond. Matter* 23 (24) (2011) 243201, <https://doi.org/10.1088/0953-8984/23/24/243201>. Iss.
- [5] F. Schwierz, Graphene transistors: status, prospects, and problems, *IEEE Proc.* 101 (7) (2013) 1567–1584, <https://doi.org/10.1109/JPROC.2013.2257633>. Iss.
- [6] N.O. Weiss, H. Zhou, L. Liao, Y. Liu, S. Jiang, Y. Huang, X. Duan, Graphene: an emerging electronic material, *Adv. Mater.* 24 (2012) 5782–5825, <https://doi.org/10.1002/adma.201201482>.
- [7] K. Kim, J.Y. Choi, T. Kim, S.H. Cho, H.J. Chung, A role for graphene in silicon-based semiconductor devices, *Nature* 479 (2011) 338–344, <https://doi.org/10.1038/nature10680>.
- [8] R.H. Kim, M.H. Bae, D.G. Kim, H. Cheng, B.H. Kim, D.H. Kim, M. Li, J. Wu, F. Du, H.S. Kim, S. Kim, D. Estrada, S.W. Hong, Y. Huang, E. Pop, J.A. Rogers, Stretchable, transparent graphene interconnects for arrays of microscale inorganic light emitting diodes on rubber substrates, *Nano Lett* 11 (9) (2011) 3881–3886, <https://doi.org/10.1021/nl202000u>. Iss.
- [9] G.V. Bianco, M. Losurdo, M.M. Giangregorio, A. Sacchetti, P. Prete, N. Lovergine, P. Capezzuto, G. Bruno, Direct epitaxial CVD synthesis of tungsten disulfide on epitaxial and CVD graphene, *RSC Adv* 5 (2015) 98700–98708, <https://doi.org/10.1039/C5RA19698A>.
- [10] P. De Padova, B. Olivieri, C. Ottaviani, A. Generosi, P. Prete, M. Krawiec, Silicene, multilayer silicene and single layer blue phosphorus on different templates, *Nanomater. Nanotechnol.* 16 (2026) 18479804261419160, <https://doi.org/10.1177/18479804261419160>.
- [11] M. Kang, J. Kim, B. Jang, Y. Chae, J. Kim, J. Aun, Graphene-based three-dimensional capacitive touch sensor for wearable electronics, *ACS Nano* 11 (2017) 7950–7957, <https://doi.org/10.1021/acsnano.7b02474>.
- [12] P.A. Hu, J. Zhang, L. Li, Z. Wang, P. Estrela, Carbon nanostructure-based field-effect transistors for label-free chemical/biological sensors, *Sensors* 10 (2010) 5133–5159, <https://doi.org/10.3390/s100505133>.
- [13] K.R. Ratinaç, W. Yang, S.P. Ringer, F. Braet, Toward ubiquitous environmental gas sensors – capitalizing on the promise of graphene, *Environ. Sci. Technol.* 44 (2010) 1167–1176, <https://doi.org/10.1021/es902659d>.
- [14] J. Liu, S. Bao, X. Wang, Applications of graphene-based materials in sensors: a review, *Micromachines* (Basel) 13 (2022) 184, <https://doi.org/10.3390/mi13020184>.
- [15] Z.C. Huang, W.L. Liu, J. Li, Y. Jiang, G.W. Yuan, L.B. Gao, Current status and prospect of graphene growth by chemical vapor deposition, *New Carbon Mater* 40 (2025) 457–476, [https://doi.org/10.1016/S1872-5805\(25\)60991-7](https://doi.org/10.1016/S1872-5805(25)60991-7).
- [16] M. Choi, J. Baek, H. Zeng, S. Jin, S. Jeon, Toward high-quality graphene film growth by chemical vapor deposition system, *Curr. Opin. Sol. State Mater. Sci.* 31 (2024) 101176, <https://doi.org/10.1016/j.cossms.2024.101176>.
- [17] M. Bahri, S.H. Gebre, M.A. Elaguech, F.T. Dajan, M.G. Sendeku, C. Thili, D. Wang, Recent advances in chemical vapour deposition techniques for graphene-based nanoarchitectures: from synthesis to contemporary applications, *Coord. Chem. Rev.* 475 (2023) 214910, <https://doi.org/10.1016/j.ccr.2022.214910>.
- [18] F. Liu, P. Li, H. An, P. Peng, B. McLean, F. Ding, Achievements and challenges of graphene chemical vapor deposition growth, *Adv. Funct. Mater.* 32 (2022) 1–20, <https://doi.org/10.1002/adfm.202203191>.
- [19] K. Jia, J. Zhang, Y. Zhu, L. Sun, L. Lin, Z. Liu, Toward the commercialization of chemical vapor deposition graphene films, *Appl. Phys. Rev.* 8 (2021) 041306, <https://doi.org/10.1063/5.0056413>.
- [20] K. Yi, D. Liu, X. Chen, J. Yang, D. Wei, Y. Liu, D. Wei, Plasma-enhanced chemical vapor deposition of two-dimensional materials for applications, *Acc. Chem. Res.* 54 (2021) 1011–1022, <https://doi.org/10.1021/acs.accounts.0c00757>.
- [21] B. Sun, J. Pang, Q. Cheng, S. Zhang, Y. Li, C. Zhang, D. Sun, B. Ibarlucea, Y. Li, D. Chen, H. Fan, Q. Han, M. Chao, H. Liu, J. Wang, G. Cuniberti, L. Han, W. Zhou, Synthesis of wafer-scale graphene with chemical vapor deposition for electronic device applications, *Adv. Mater. Technol.* 6 (2021) 2000744, <https://doi.org/10.1002/admt.202000744>.
- [22] H. Yan, H. Yang, S. Lin, J. He, L. Kiss, S. Kunsági-Máté, M. Zhang, H. Li, Effect of staged methane flow on morphology and growth rate of graphene monolayer domains by low-pressure chemical vapor deposition, *Thin Solid Films* 736 (2021) 138921, <https://doi.org/10.1016/j.tsf.2021.138921>.
- [23] J.K. Wassei, M. Mecklenburg, J.A. Torres, J.D. Fowler, B.C. Regan, R.B. Kaner, B. H. Weiller, Chemical vapor deposition of graphene on copper from methane, ethane and propane: evidence for bilayer selectivity, *Small* 8 (2012) 1415–1422, <https://doi.org/10.1002/sml.201102276>.
- [24] R.S. Weatherup, A.J. Shahani, Z.J. Wang, K. Mingard, A.J. Pollard, M.G. Willinger, R. Schloegl, P.W. Voorhees, S. Hofmann, Situ graphene growth dynamics on polycrystalline catalyst foils, *Nano Lett.* 16 (2016) 6196–6206, <https://doi.org/10.1021/acs.nanolett.6b02459>.
- [25] H. Liu, J. Zhao, T.H. Ly, Clean transfer of two-dimensional materials: a comprehensive review, *ACS Nano* 18 (2024) 11573–11597, <https://doi.org/10.1021/acsnano.4c01000>.

- [26] Y. Song, W. Zou, Q. Lu, L. Lin, Z. Liu, Graphene transfer: paving the road for applications of chemical vapor deposition graphene, *Small* 17 (2021) 2007600, <https://doi.org/10.1002/smll.202007600>.
- [27] L.P. Ma, W. Ren, H.M. Cheng, Transfer methods of graphene from metal substrates: a review, *Small Methods* 3 (2019) 1900049, <https://doi.org/10.1002/smt.201900049>.
- [28] Š. Meskinis, A. Lazauskas, Š. Jankauskas, A. Guobienė, R. Gudaitis, Advancing graphene synthesis: low-temperature growth and hydrogenation mechanisms using plasma-enhanced chemical vapor deposition, *Molecules* 30 (2025) 33, <https://doi.org/10.3390/molecules30010033>.
- [29] M. Lei, P. Wang, X. Ke, J. Xie, M. Yue, M. Zhao, K. Zhang, Y. Dong, Q. Xu, C. Zou, S. Wang, L. Zhang, Low-temperature chemical vapor deposition growth of 2D materials, *Electron* 3 (2025) e43, <https://doi.org/10.1002/elt.2.43>.
- [30] M.J. Josline, E.T. Kim, J.H. Lee, Recent advances in the low-temperature chemical vapor deposition growth of graphene, *Appl. Sci. Conver. Technol.* 31 (2022) 63–70, <https://doi.org/10.5757/ASCT.2022.31.3.63>.
- [31] N.H. Shudin, M.A.R. Mukri, M. Aziz, M.H.D. Othman, M. Tanemura, M.Z. Mohd Yusop, The role of solid, liquid and gaseous hydrocarbon precursors on chemical vapor deposition grown carbon nanomaterials' growth temperature, *Synth. Met.* 274 (2021) 116735, <https://doi.org/10.1016/j.synthmet.2021.116735>.
- [32] J.B. Wang, Z. Ren, Y. Hou, X.L. Yan, P.Z. Liu, H. Zhang, H.X. Zhang, J.J. Guo, A review of graphene synthesis at low temperatures by CVD methods, *New Carbon Mater* 35 (3) (2020) 193–208, [https://doi.org/10.1016/S1872-5805\(20\)60484-X](https://doi.org/10.1016/S1872-5805(20)60484-X).
- [33] Z. Li, P. Wu, C. Wang, X. Fan, W. Zhang, X. Zhai, C. Zeng, Z. Li, J. Yang, J. Hou, Low-temperature growth of graphene by chemical vapor deposition using solid and liquid carbon sources, *ACS Nano* 5 (2011) 3385–3390, <https://doi.org/10.1021/nn200854p>.
- [34] X. Sun, L. Lin, L. Sun, J. Zhang, D. Rui, J. Li, M. Wang, C. Tan, N. Kang, D. Wei, H. Q. Xu, H. Peng, Z. Liu, Low-temperature and rapid growth of large single-crystalline graphene with ethane, *Small* 14 (2018) 1702916, <https://doi.org/10.1002/smll.201702916>.
- [35] J. Jang, M. Son, S. Chung, K. Kim, C. Cho, B.H. Lee, M.H. Ham, Low-temperature-grown continuous graphene films from benzene by chemical vapor deposition at ambient pressure, *Sci. Rep.* 5 (2015) 17955, <https://doi.org/10.1038/srep17955>.
- [36] C. Kang, D.H. Jung, J.S. Lee, Atmospheric pressure chemical vapor deposition of graphene using a liquid benzene precursor, *J. Nanosci. Nanotechnol.* 15 (2015) 9098–9103, <https://doi.org/10.1166/jnn.2015.11557>.
- [37] R. Sharma, E. Razia, D. Rathnayaka, P. Bhurtel, K. Upananda, B. Dahal, R. Poudel, U.K. Wijewardena, A. Kriisa, R. Samaraweera, R.G. Mani, Comparative study of CVD-grown graphene using methane and benzene as precursors, *J. Electr. Mater.* 55 (2026) 5033–5040, <https://doi.org/10.1007/s11664-026-12835-9>.
- [38] B. Zhang, W.H. Lee, R. Piner, I. Kholmanov, Y. Wu, H. Li, H. Ji, R.S. Ruoff, Low-temperature chemical vapor deposition growth of graphene from toluene on electropolished copper foils, *ACS Nano* 6 (2012) 2471–2476, <https://doi.org/10.1021/nn204827h>.
- [39] H. Fenglei, L. Mengyu, Z. Huangrong, L. Ting, L. Dandan, Z. Shuo, G. Wenwen, L. Fang, Product analysis and mechanism of toluene degradation by low temperature plasma with single dielectric barrier discharge, *J. Saudi Chem. Soc.* 24 (2020) 673–682, <https://doi.org/10.1016/j.jscs.2020.07.004>.
- [40] M.H. Khan, M. Moradi, M. Dakhoune, M. Rezaei, S. Huang, J. Zhao, K. V. Agrawal, Hydrogen sieving from intrinsic defects of benzene-derived single-layer graphene, *Carbon* 153 (2019) 458–466, <https://doi.org/10.1016/j.carbon.2019.07.045>.
- [41] Y. Xie, X. Tang, Y. Zhang, G. Yang, H. Yu, B. Yang, G. Xie, Multiscale simulation of graphene growth on Cu (111): insights from DFT, MD, KMC, and thermodynamic analyses, *Coatings* 15 (2025) 656, <https://doi.org/10.3390/coatings15060656>.
- [42] Q. Li, J. Luo, Z. Li, M.H. Rummeli, L. Liu, Density functional theory and molecular dynamics study on the growth of graphene by chemical vapor deposition on copper substrate, *J. Vac. Sci. Technol. A* 42 (2024) 042202, <https://doi.org/10.1116/6.0003667>.
- [43] J. Dong, L. Zhang, B. Wu, F. Ding, Y. Liu, Theoretical study of chemical vapor deposition synthesis of graphene and beyond: challenges and perspectives, *J. Phys. Chem. Lett.* 12 (2021) 7942–7963, <https://doi.org/10.1021/acs.jpclett.1c02316>.
- [44] Y. Tian, Z. Yan, L. Jiang, R. Liu, B. Liu, Y. Shao, X. Yang, M. Liu, Multiscale models of CVD process: review and prospective, *Materials* 17 (2024) 5131, <https://doi.org/10.3390/ma17205131>.
- [45] J.H. Choi, Z. Li, P. Cui, X. Fan, H. Zhang, C. Zeng, Z. Zhang, Drastic reduction in the growth temperature of graphene on copper via enhanced London dispersion force, *Sci. Rep.* 3 (2013) 1925, <https://doi.org/10.1038/srep01925>.
- [46] O. Tau, N. Lovergine, P. Prete, Adsorption and decomposition steps on Cu(111) of liquid aromatic hydrocarbon precursors for low-temperature CVD of graphene: a DFT study, *Carbon* 206 (2023) 142–149, <https://doi.org/10.1016/j.carbon.2023.02.011>.
- [47] O. Tau, N. Lovergine, P. Prete, Molecular decomposition reactions and early nucleation steps in CVD growth of graphene on Cu and Si substrates using toluene, in: *Proc. SPIE 13114, Low-Dimensional Materials and Devices 2024*, 2 Oct. 2024 1311409, <https://doi.org/10.1117/12.3029561>.
- [48] S. Zhao, Z. Luo, M. Fang, Q. Wang, J. Cen, Molecular simulation of graphene growth reactions at various temperatures derived from benzene in coal tar aromatic hydrocarbons, *Energies* 18 (2025) 392, <https://doi.org/10.3390/en18020392>.
- [49] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. De Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougousis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, R.M. Wentzcovitch, Quantum espresso: a modular and open-source software project for quantum simulations of materials, *J. Phys.: Condens. Matter* 21 (2009) 395502, <https://doi.org/10.1088/0953-8984/21/39/395502>.
- [50] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. Buongiorno Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. Dal Corso, S. De Gironcoli, P. Delugas, R.A. Distasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N.L. Nguyen, H.V. Nguyen, A. Otero-De-La-Roza, L. Paulatto, S. Poncè, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A.P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, S. Baroni, Advanced capabilities for materials modelling with Quantum ESPRESSO, *J. Phys.: Condens. Matter* 29 (2017) 465901, <https://doi.org/10.1088/1361-648X/aa8f79>.
- [51] P. Giannozzi, O. Baseggio, P. Bonfà, D. Brunato, R. Car, I. Carnimeo, C. Cavazzoni, S. De Gironcoli, P. Delugas, F. Ferrari Ruffino, A. Ferretti, N. Marzari, I. Timrov, A. Urru, S. Baroni, Quantum espresso toward the exascale, *J. Chem. Phys.* 152 (2020) 154105, <https://doi.org/10.1063/5.0005082>.
- [52] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.* 77 (1996) 3865–3868, <https://doi.org/10.1103/PhysRevLett.77.3865>.
- [53] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.* 132 (2010) 154104, <https://doi.org/10.1063/1.3382344>.
- [54] G. Henkelman, B.P. Uberuaga, H. Jónsson, Climbing image nudged elastic band method for finding saddle points and minimum energy paths, *J. Chem. Phys.* 113 (2000) 9901–9904, <https://doi.org/10.1063/1.1329672>.