The Site Effect on PAHs Formation in HACA-based Mass Growth Process

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Abstract Hydrogen-abstraction/acetylene-addition (HACA) pathway has long been postulated as the dominant pathway for the formation of polycyclic aromatic hydrocarbons (PAHs) and the surface growth of soot. In this study, the site effect on PAH formation following HACA pathway is systematically investigated using density functional theory, transition state theory and premixed flame kinetic modeling. The entire reaction network includes 186 elementary reactions, starting from benzene to pyrene. Analysis of the potential energy surface and kinetic parameters show that H abstraction and C₂H₂ addition reactions are greatly sensitive to the site position (ortho-, meta- and para-position) relative to the existing C₂H chain and surface site type (zig-zag, free-edge and armchair). Specifically, H abstraction and C₂H₂ addition reactions on the ortho-position and armchair surface site are kinetically unsupported due to the relatively high energy barrier and orientation hindrance effect compared with other site options. Therefore, the formation of a new benzene ring by the addition of the second C₂H₂ molecule on the ortho-position (e.g., 1-ethynylnaphthalene+C₂H₂→phenanthrene) or the first C₂H₂ molecule on the armchair surface site (e.g., phenanthrene+C₂H₂→pyrene) is unlikely, as demonstrated by PAH simulations in a premixed C₂H₄/O₂/N₂ sooting flame. The yield distribution of various reaction products has been investigated using a 0-D reactor, where the combustion conditions are taken from experimental data. The results show that the dominant products are di-substituted PAHs in benzene-naphthalene reaction system and PAHs with 5-membered ring structures in larger PAHs reaction systems. The existence of abundant PAHs with 5-membered rings contributes to clarifying the PAHs signal detected using laser induced fluorescence technology. Additionally, the observed sequence of mass peaks at intervals of mass number 26 in C₂H₂/C₂H₄ pyrolysis is reasonably explained by the HACA pathway with considering site effect.

Keywords: PAH, site effect, soot, kinetic, DFT.

1. Introduction

The science of polycyclic aromatic hydrocarbons (PAHs) plays a crucial role in our life. Evidence shows that PAH molecules attached to ultrafine particle surfaces can bond to critical targets in DNA molecules, and the PAH–DNA adducts increase the risk of cancer in humans, especially lung and skin cancers [1, 2]. In addition, studies on PAH formation are motivated by soot pollution in megacities, as PAHs are regarded as the precursors to soot formation in flames [3-11]. On the other hand, PAHs are widely used as modelling molecules of 2D graphene-type materials [12, 13], which present excellent optical, mechanical and electrical characteristic. Exploring the formation pathway of PAHs is also beneficial in developing chemically modified 2D graphene-type materials [14]. Furthermore, understanding the evolution of PAHs contributes to revealing the origin and evolution of our universe, especially the formation of galaxies as PAHs are major dust components in the interstellar medium [15, 16].

PAHs are mainly formed from the incomplete combustion of hydrocarbons, and the mass growth process is chemically driven by elementary reactions [7, 17-25]. In the past decades, the hydrogen-abstraction/acetylene-addition (HACA) pathways have been widely used to describe PAH evolution in flame, and are the framework of most PAH reaction mechanisms [7, 20, 26-30]. In the HACA framework, pyrene can be formed starting from phenyl radical via the reaction pathway of phenyl radical + acetylene $\rightarrow$ phenylacetylene (+acetylene) $\rightarrow$ naphthalene (+acetylene) $\rightarrow$ 1(2)-ethynylnaphthalene (+acetylene) $\rightarrow$ phenanthrene (+acetylene) $\rightarrow$ pyrene. Nowadays, these developed PAH sub-mechanisms are widely merged into reaction mechanisms of liquid transportation fuels for PAH and soot predictions in engines [31-38]. However, recent experimental evidence has raised questions regarding the predominance of PAHs constituted of benzene ring structures formed via HACA pathways [39-41]. Johansson et al. [39] investigated PAH growth and soot formation in Ar-diluted C_2H_2/O_2 counter-flow diffusion flames using photoionization mass spectrometry method. The results suggested that many PAHs with 5-membered rings may be the main contributors to some observed mass spectra peaks instead of PAHs with strong thermodynamic stability (like phenanthrene and pyrene). Furthermore, chemical structures with 5-membered ring were directly observed by Shulz et al. [40] using high-resolution atomic force microscopy in a premixed C_2H_4 -air flame. However, the only PAH with a 5-membered ring represented in the current HACA framework is acenaphthylene. The possibility of the formation of other PAHs with 5-membered rings within the HACA framework requires further discussion. With similar methods, Parker et al. [41] carefully examined the reaction of 1- and 2-naphthyl radical and acetylene at 1200 ± 100 K. They found that the main products were 1- and 2-ethynylnaphthalenes, acenaphthylene and diethynylnaphthalenes, neither anthracene nor phenanthrene was detected. Here, we postulate that the site effect of HACA growth pathways may account for the above experimental phenomenon. For example, the formation of new benzene rings is unlikely to happen if the ethynyl

substitution reactions are more likely to happen at the non-adjacent sites respective to the existing ethynyl chain. This is indirectly supported by recent theoretical studies that show reaction rates of H abstraction and PAH oxidation are greatly sensitive to the C-H site type [42-44].

In this study, we revisit the formation of PAHs within the HACA framework starting from benzene to pyrene, with a special focus on the site effects. The potential energy surface and elementary reaction rate coefficients are obtained using density functional theory (DFT) and transition state theory (TST). Subsequently, the yields of various products are evaluated using a closed homogeneous zero-dimensional batch reactor simulation with boundary conditions extracted from sooting $\text{C}_2\text{H}_4/\text{O}_2/\text{N}_2$ flame experiments. Then, correlation discussions are made between theoretical results in this study with PAH experimental results detected using laser induced fluorescence (LIF), vacuum ultraviolet single photon ionization time of flight mass spectrometry (TOFMS), and gas-chromatography-mass spectrometry (GC-MS) techniques.

2. Calculation details

The reaction network in this study includes 186 elementary reactions, which can be divided into benzene-naphthalene ($\text{A}_1\text{-A}_2$), naphthalene-acenaphthylene-phenanthrene ($\text{A}_2\text{-A}_2\text{R}_5\text{-A}_3$) and phenanthrene-pyrene ($\text{A}_3\text{-A}_4$) reaction systems. The structures of all local minima and transition states (TSs) were optimized at DFT with B3LYP hybrid functional 6-311+G(d,p) basis set [45]. The frequencies were obtained using the same method, then a factor of 0.967 was used for scaling [46]. It should be noted that this scaling factor is originally obtained for B3LYP hybrid functional and 6-311+G(3df,2p) basis set [47]. The sum of electronic and zero-point energies were firstly obtained at DFT B3LYP 6-311+G(d,p) level. To improve the energy accuracy, the CBS-QB3 [48] method was then employed to refine the energy in $\text{A}_1\text{-A}_2$ reaction system. The deviations of energy barriers between DFT B3LYP 6-311 +G(d,p) and CBS-QB3 levels in the $\text{A}_1\text{-A}_2$ reaction system were utilized to correct systematic errors in larger analogous reaction systems. Restricted wave function calculations were employed for close-shell structures, and unrestricted wave function calculations were employed for open-shell structure. Intrinsic reaction coordinate (IRC) calculations [49] were carried out to double-check that the TSs were connected with the corresponding reactant and product. The Gaussian 09 program package was selected for quantum chemistry calculation [50].

The biomolecular H abstraction and C_2H_2 addition reactions are essential to the HACA pathway. Their reaction rate coefficients are almost pressure-independent in the temperature range of 500-1700 K, especially for H abstraction reactions [42, 51]. Generally, the PAH adduct intermediate generated from H abstraction and C_2H_2 addition reaction leads to one product via the sole reaction channel. Few PAH adduct intermediates can split two different reaction channels, but the yield of the minor reaction products is negligible in this case. Therefore, it is

not necessary to explore the issue of pressure-dependent branching ratios starting from the single molecule PAH adduct intermediates. In this study, the rate coefficients of all elementary reactions were evaluated at the high-pressure limit using transition state theory (TST) [19]. Low frequency internal rotations were regarded as 1-D unsymmetrical hindered rotations. The torsional potential energy and rotation constant as function of dihedral angle were calculated at DFT B3LYP 6-31 G level [28]. Eckart tunneling correction and reaction pathway degeneration were considered [52].

To evaluate the yield of various PAHs produced by the HACA pathway in sooting flames, the concentrations of PAHs were predicted using PAH mechanisms that consider site effects in a premixed $C_2H_4/O_2/N_2$ flame using the premixed burner model in the Chemkin-Pro software. Here, the PAH mechanism consists of the USC II base mechanism and the investigated 186 elementary reactions. The Lennard-Jones transport parameters of new species are calculated using the method recommended by Wang et al. [53]. The thermodynamics parameters of new species are assumed to be equal to that of the corresponding PAH isomer considered in the ABF mechanism [26]. Generally, thermodynamics parameters determine the heat of reaction and reaction equilibrium constant in flame modeling. The former affects the flame temperature, and the latter can be utilized to get the reaction coefficients of reversible reactions. PAH reactions are unlikely to change the flame temperature due to the low concentrations of PAH found in a flame. On the other hand, rate coefficients of all reverse reactions are also calculated using TST method. Therefore, assumptions of thermodynamics parameters are acceptable in this study. The flame conditions including temperature, equivalence ratio, velocity of inlet-gas and pressure are based on experimental conditions in [54]. The mixture-averaged transport formulation is employed to calculate the species ordinary diffusion coefficients and fluxes. The maximum number of grid points allowed in simulation is set to 500. The maximum gradient and curvature allowed between grid points are given as 0.2 and 0.5, respectively.

3. Results and discussion

3.1. Potential energy surface

3.1.1 Benzene-naphthalene reaction system

The potential energy surface (PES) of benzene (A_1) - naphthalene (A_2) reaction system is shown in Fig.1. The first H abstraction and C_2H_2 addition lead to the unstable intermediate B-CS13 ($Benzene + H \rightarrow B-CS12 (+C_2H_2) \rightarrow B-CS13$). At flame temperatures, unstable species are likely to evolve into steady species. Once the B-CS13 structure is formed, the H elimination from the acetylene chain of B-CS13 may happen with the energy barrier of 38.4 kcal/mol ($B-CS13 \rightarrow B-CS14 + H$, 38.4 kcal/mol), and generate phenylacetylene (B-CS14) [18, 55]. It should be noted that B-CS14 is much more stable than B-CS13, although the H elimination reaction is an endothermic process. The reason why the energy of B-CS14+H is higher than that of B-CS13 in PES is because a radical on a hydrogen atom is less stable than a radical on B-CS13. The di-substituted species B-CS8, B-CS10

and B-CS11 can be formed through the second H abstraction, C₂H₂ addition and H elimination reactions. Specifically, the pathways of CS14 + H → B-CS1 (+C₂H₂) → B-CS4 (-H) → B-CS11+H, CS14 + H → B-CS2 (+C₂H₂) → B-CS7 (-H) → B-CS8+H and CS14 + H → B-CS3 (+C₂H₂) → B-CS9 (-H) → B-CS10+H lead to the formation of B-CS11, B-CS8 and B-CS10 respectively. Naphthyl radical can be isomerized from B-CS5, which is the conformer of B-CS4 and forms via the C-C rotation reaction (B-CS4 → B-CS5, 4.0 kcal/mol). Such conformation change is a low-barrier process, and can reach equilibrium quickly. The energy barrier of the cyclization reaction which generates naphthyl radical is 6.4 kcal/mol (B-CS5 → B-CS6). In terms of energy barriers, the cyclization rotation reaction (B-CS5 → B-CS6, 6.4 kcal/mol) is more likely to happen, as its energy barrier is lower than that of H elimination (B-CS5 → B-CS11+H, 38.6 kcal/mol) by 32.2 kcal/mol.

Alternatively, the intramolecular H transfer from the benzene ring to the acetylene chain is also a reaction possibility (B-CS13 → B-CS15, 26.7 kcal/mol), which generates B-CS15 with an active C site on the benzene ring. The active C site makes the second C₂H₂ addition feasible (B-CS15 + C₂H₂ → B-CS16, 3.3 kcal/mol), and the A₂ forms via the subsequent C-C rotation (B-CS16 → B-CS17, 3.4 kcal/mol), cyclization (B-CS17 → B-CS18, 1.8 kcal/mol), and H elimination (B-CS18 → A₂ + H, 28.6 kcal/mol) reactions. However, the subsequent kinetics result shows that the A₂ formation from the pathway of B-CS13 → B-CS15 → B-CS16 → B-CS17 → B-CS18 → A₂ + H (named as the Frenklach route in this study) can be ignored at flame temperatures, comparing with the pathway of B-CS13 → B-CS14 → B-CS1 → B-CS4 → B-CS5 → B-CS6 → A₂. Here, the Bittner–Howard route [56] where the second C₂H₂ attacks the acetylene chain of B-CS13 is not considered in this study, because the reaction probability is greatly limited by the instability of B-CS13 at flame temperature as discussed by Mebel et al. [51].

Fig.1. The potential energy surface of A₁-A₂ reaction system, energies are calculated at CBS-QB3 (labeled as green) and DFT B3LYP 6-311+g(d,p) (labeled as black) respectively.

Accurate energy barriers are necessary to obtain reliable reaction rate coefficients. However, the demand of computational resource increases rapidly with the molecule size in energy calculation using high-level methods. In this study, the energy barriers in A₁-A₂ reaction system are calculated at CBS-QB3 and DFT B3LYP 6-311+G(d,p) levels. The root-mean-square deviation of CBS-QB3 energy is 1.49 kcal/mol [48]. Based on the comparison results of energy barriers in A₁-A₂ reaction system, energy barrier corrections are introduced for the larger analogous reaction. As shown in Fig.1, the PAHs growth reactions within HACA frame can be classified into six types: 1) H abstraction, 2) C₂H₂ addition, 3) H transfer, 4) H elimination, 5) Cyclization, 6) C-C bond rotation. The energy barrier calculated at DFT level is reliable except for the H abstraction reaction type (PAH + H → PAH radical + H₂). As shown in Table 1, the deviations of energy barriers are within 0.1-2.2 kcal/mol for C₂H₂ addition, H transfer, H elimination, cyclization and C-C bond rotation reactions, but the value increases to 6.3-6.6 kcal/mol for H abstraction reactions and 4.3-4.7 kcal/mol for the reverse reactions (PAH radical + H₂ → PAH + H). Therefore, the energy corrections of 6.5 and 4.7 kcal/mol are taken for the H abstraction and H₂ addition reactions in the kinetic calculations, and the DFT B3LYP 6-311+G(d,p) energy is used for the rest of reactions. The similar treatment can be seen in ref [42, 57]. The reported energy barrier calculated at G3(MP2,CC) method is also taken for comparison. As shown in Table 1, the results obtained from CBS-QB3 method is highly close to that from G3(MP2,CC), indicating that the energy correction treatment from CBS-QB3 to DFT B3LYP 6-311+G(d,p) is reasonable.

Table1. Comparisons of the energy barriers (kcal/mol) obtained at CBS-QB3, G3(MP2,CC), and DFT methods.

Reaction	CBS-QB3	DFT	Difference	G3(MP2,CC)	Reaction type
Benzene+H→B-CS12+H ₂	17.3	10.8	6.5	17.0 [42]	H abstraction
B-CS14+H→B-CS1+H ₂	18.3	12.0	6.3		
B-CS14+H→B-CS2+H ₂	17.6	11.0	6.6		
B-CS14+H→B-CS3+H ₂	17.7	11.2	6.5		
B-CS12+H ₂ →Benzene+H	10.2	5.5	4.7	10.3 ^a [58]	H ₂ addition
B-CS1+H ₂ → B-CS14+H	9.8	5.5	4.3		
B-CS2+H ₂ → B-CS14+H	10.3	5.6	4.7		
B-CS3+H ₂ → B-CS14+H	10.2	5.5	4.7		
B-CS1+C ₂ H ₂ →B-CS4	2.7	3.5	0.8	3.1 [51]	C ₂ H ₂ addition
B-CS2+C ₂ H ₂ →B-CS7	2.3	4.2	1.9		
B-CS3+C ₂ H ₂ →B-CS9	4.8	4.1	0.7		
B-CS12+C ₂ H ₂ →B-CS13	4.9	4.4	0.5	3.6 [51]	
B-CS13→B-CS15	26.7	27.6	0.9	27.6 [51]	H transfer
B-CS7→B-CS8+H	37.8	38.4	0.6	38.8 [51] 27.8 [51]	H elimination
B-CS9→B-CS10+H	37.7	38.3	0.6		
B-CS4→B-CS11+H	40.0	40.1	0.1		
B-CS18→A2+H	28.6	28.5	0.1		
B-CS5→B-CS6	6.5	4.7	1.8		Cyclization

B-CS17→B-CS18	1.8	0.8	1.0	
B-CS4→B-CS5	4.0	4.9	0.9	C-C bond rotation
B-CS16→B-CS17	3.4	1.2	2.2	2.8 [51]

^athe energy barrier for 2-naphthyl radical + H₂ → naphthalene + H reaction at G3(MP2,CC) level [58].

3.1.2 Naphthalene-acenaphthylene-phenanthrene reaction system

Naphthalene is the simplest PAHs with zig-zag surface, which can lead to the formation of acenaphthylene and 1-naphthyl radical (N1-CS1) if the H atom near the zig-zag surface of A₂ is abstracted by the surrounding H atom (A₂+H→N1-CS1+H₂, 11.2 kcal/mol), as shown in Fig.2. Acenaphthylene (N1-CS4, A₂R₅) and 1-ethynylnaphthalene (N1-CS5) form via the pathways of N1-CS1+C₂H₂→N1-CS2→N1-CS3→N1-CS4+H and N1-CS1+C₂H₂→N1-CS2→N1-CS5+H. In this reaction network, phenanthrene (A₃) can be given by the Frenklach route shown as N1-CS2→N1-CS33→N1-CS34→N1-CS35→N1-CS35→N1-CS37→A₃+H in Fig.2, where the energy barrier of each reaction step is close to that of B-CS13→B-CS15→B-CS16→B-CS17→B-CS18→A₂+H. The formation of 2-ethynylnaphthalene (N2-CS3) and A₃ is feasible if the H atom near the free-edge surface of A₂ is abstracted, and the features of the formation pathways are almost the same with those of N1-CS5 and A₃ starting from N1-CS2. If the N2-CS38 proceeds with cyclization reaction (N1-CS38→N1-CS39, 12.5 kcal/mol), we would observe the formation of N2-CS39 with 5-membered ring, which can evolve to the plane structure N2-CS40 via the H elimination reaction (N2-CS39→N2-CS40+H). The N2-CS40 species may be the main product in this network in terms of energy barrier, as the energy barriers of A₂+H→N2-CS1+H₂, N2-CS2→N2-CS37 and N2-CS38→N2-CS39 are lower than the corresponding branch reaction A₂+H→N1-CS1+H₂, N2-CS2→N2-CS3 + H and N2-CS38→N2-CS41 by 0.3, 11.3 and 10.8 kcal/mol.

Fig.2. The potential energy surface of A₂-A₂R₅-A₃ reaction system, energies are calculated at DFT B3LYP 6-311+g(d,p) level.

To perfect the A₃ formation network, the further evolutions of 1-ethynylnaphthalene and 2-ethynylnaphthalene were investigated. The main formation pathway of A₃ radical in current PAH mechanisms consists of the H abstraction reaction (N1-CS5+H→N1-CS6+H₂ or N2-CS3+H→N2-CS10+H₂), and C₂H₂ addition to the adjacent C atom relative to the side chain of 1-ethynylnaphthalene and 2-ethynylnaphthalene (N1-CS6+C₂H₂→N1-CS13 or N2-CS10+C₂H₂→N2-CS17), C-C rotation (N1-CS13 →N1-CS27 or N2-CS17→N2-CS43) and cyclization reactions (N1-CS27 →N1-CS20 or N2-CS43→N2-CS44), as shown in Fig 3-4. In this study, all possible H abstraction reactions on 1-ethynylnaphthalene (N1-CS5) and 2-ethynylnaphthalene (N2-CS3) are explored. It was found that the energy barrier of H abstraction was sensitive to the existing acetylene chain. The energy barrier of H abstraction beside the acetylene chain of N1-CS5 (N1-CS5+H→N1-CS6+H₂ and N1-CS5+H→N1-CS12+H₂) and N2-CS3 (N2-CS3+H→N1-CS4+H₂ and N2-CS3+H→N2-CS10+H₂) are slightly higher than that of other site options. This means that the competitiveness of A₃ radical (N1-CS20 and N2-CS44) formation starting from N1-CS6 and N2-CS10 may be weaker than other channels. Within the HACA growth mode, di-substituted species including N1-CS22, N1-CS23, N1-CS26, N2-CS18, N2-CS19, N2-CS20, N2-CS21, N2-CS22, N2-CS23 and N2-CS24 and 5-membered ring species including N2-CS30 and N2-CS35 can be formed. We noted that the thermodynamic stability of the latter is stronger, and the highest energy barrier in its formation pathway is lower than that of the former. This means that the formation of 5-membered ring species is more favorable in this

reaction networks, which is confirmed by the following kinetic analysis. For brevity, the detail of their formation pathway is not discussed.

Fig.3. The potential energy surface of N1-CS5-A₃ reaction system, energies are calculated at DFT B3LYP 6-311+g(d,p) level.

Fig.4. The potential energy surface of N2-CS3-A₃ reaction system, energies are calculated at DFT B3LYP 6-311+g(d,p) level.

3.1.3 Phenanthrene-pyrene reaction system

The formation efficiency of new benzene rings in the HACA-based growth process peaks when the reaction happens on the armchair surface site, which make the cyclization reaction easier. In current PAH mechanisms, only H atoms located on armchair surface sites are allowed to be abstracted, producing the 1-phenanthrene radical and 4-phenanthrene radical (P1-CS1). The conversion rate between 1-phenanthrene radical and 4-phenanthrene radical reaches $3.4 \times 10^{11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at the presence of H atom at 1500 K. This treatment leads to that pyrene is the dominate product in phenanthrene reaction systems. However, it was found that the H abstraction and C₂H₂ addition were more likely to happen on other C atoms. As shown in Fig.5, the energy barrier of H abstraction reaction of A₃+H→P1-CS1+H₂ (11.5 kcal/mol) and C₂H₂ addition reaction of P1-CS1+C₂H₂→P1-CS2 (7.3 kcal/mol) is higher than other similar reactions by at least 0.3 (A₃+H→P(2-5)-CS1+H₂) and 2.7 (P(2-5)-CS1+C₂H₂→P(2-5)-CS2) kcal/mol. This means that A₄ may not be one of the main products in this reaction network, which is proved by the following kinetic analysis. Similar to the above reaction networks, the species with 5-membered ring structure P5-CS6 can be formed via the pathways of A₃+H→P4-CS1→P4-CS2→P4-CS4→P4-CS5→P5-CS6 and A₃+H→P5-CS1→P5-CS2→P5-CS4→P5-CS5→P5-CS6 if the C₂H₂ is attached to

the zig-zag surface site. The PAHs substituted with C_2H chain including P1-CS3, P2-CS3, P3-CS3, P4-CS3, P5-CS3 will form if the H elimination reaction happens immediately after the C_2H_2 addition reaction.

Fig.5. The potential energy surface of A_3 - A_4 reaction system, energies are calculated at DFT B3LYP 6-311+g(d,p) level.

3.2 Kinetical analysis

The rate coefficients of all elementary reactions are calculated in the temperature range of 500-2500 K using TST method, and the kinetic parameters are listed in Table 2. To examine the theoretical rate coefficients, our rate coefficients for $A_1 + H$ reaction are compared with the experimental data measured in shock-tubes by Giri et al. [59] and theoretical results evaluated at G3(MP2,CC) level by Semenikhin et al. [42]. A good agreement is obtained, and the deviation is within 1.5 times as shown in Fig. 6 (a). The deviation is likely due to slight differences in energy barriers calculated at CBS-QB3 and G3(MP2,CC) level. The comparison of our rate coefficients for $A_1 + C_2H_2$ with shock-tube experimental data by Heckmann et al. [60] and theoretical data by Mebel et al. [51] further confirm that the calculated rate coefficients in this study are reliable, as shown in Fig.6 (c). Here, our high-pressure rate values are closer to the experimental data in the temperature range of 1000-1500 K, where the rate coefficients of biomolecule $A_1 + C_2H_2$ reaction are expected to be pressure-independent. The deviation of the rate coefficient from theoretical value by Mebel et al [51] at 500 K is 5.1 times, mainly resulting

from the differences in energy barriers for $A_1^- + C_2H_2$ reaction. The energy barrier is evaluated as 3.6 kcal/mol at G3(MP2,CC) level in ref. [51] and 4.9 kcal at CBS-QB3 level in the study. A 1.3 kcal/mol deviation is within the error bars for our calculated energy barrier [48].

In addition, comparisons for H abstraction reaction and C_2H_2 addition reactions were also performed to estimate the accuracy of energy barrier in PAHs reaction systems. The calculated energy barriers of reaction naphthalene + H $\rightarrow$ 2-naphthyl radical + H_2 at G3(MP2,CC) level is 18.6 kcal/mol in forward direction and 10.3 kcal/mol in reverse direction [58]. With the energy correction, the corresponding energy barriers for forward and reverse reactions are 17.4 kcal/mol (10.9 kcal/mol with 6.5 kcal/mol correction) and 10.2 kcal/mol (5.5 kcal/mol with 4.7 kcal/mol correction), respectively. Therefore, our energy correction is reliable for the studied H abstraction reactions. For the addition reaction of C_2H_2 and PAH radical, the energy barrier calculated at DFT B3LYP 6-311+G(d,p) level is used in this study. The energy barrier calculated at DFT B3LYP 6-311+G(d,p) level is slightly higher than that obtained from G3(MP2,CC) level. For example, the energy barrier for the addition reaction of 2-naphthyl radical and C_2H_2 is 4.3 kcal/mol at DFT B3LYP 6-311+G(d,p) level, and the value is 2.6 kcal/mol at G3(MP2,CC) level [58]. The corresponding rate constant reported here is lower than that provided by Kislov et al [58] by a factor of 1.6 at 1500 K. The difference of energy barriers is still within the uncertainty of G3 based method (1-2 kcal/mol) [61, 62]. Better agreement is observed between the G3(MP2,CC) and DFT B3LYP 6-311+G(d,p) methods, in terms of the relative energy difference between two C_2H_2 addition reactions occurring at different position. The difference of energy barrier for the C_2H_2 addition on the armchair site and zig-zag site is 2.7-3 kcal/mol as shown in Fig.5, and is 2.4-3.3 kcal/mol as discussed by Frenklach et al [63] at G3(MP2,CC) level. The yield of products is mainly determined by the branching ratio of competing reactions, which highly relies on the difference of energy barriers between competing reactions. This adds more confidence to the following kinetic analysis, especially the yield analysis.

Fig.6. Rate coefficients for H abstraction on different positions (a) and different surface sites (b), C_2H_2 addition on different positions (c) and different surface sites (d).

As discussed in PES analysis, the various isomer products can be formed by considering site effects in the HACA framework. Among all elementary reaction types, the H abstraction from the close-shell PAH molecules and C_2H_2 addition to PAH radicals determine the yield of products. Here, the sensitivity of rate coefficients for H abstraction and C_2H_2 addition to the site position relative to the C_2H chain (ortho-, meta- and para-position) and surface site type (zig-zag, free-edge and armchair) is shown in Fig.6 (a)-(d). Fig.6 (a) shows that the environmental free H atom is inclined to attack the H atom on the carbon at the meta- and para-position relative to the C_2H chain on A_1C_2H molecule. The rate coefficient of H abstraction reaction on ortho-position is lower than that on meta- and para-position by a factor of 2.08 at 1500 K. According to the Arrhenius equation, the difference of rate coefficient can be introduced by the energy barrier and collision frequency. The energy barrier of A_1C_2H+H (ortho-position) is higher than the other two reactions by 0.6-0.7 kcal/mol as shown in Fig.1, resulting in a 1.22 times ($\exp(0.6 \times 4.1868 \times 1000 / 8.314 / 1500)$) of the rate deviation at 1500 K. This means that the other 0.86 times of the rate deviation come from the orientation hindrance introduced by the C_2H chain. The H abstraction reaction is also slightly sensitive to the type of surface site, as illustrated by Fig.6 (b). If one side of the H-C bond is the armchair surface site, the corresponding reaction rate coefficient is the lowest compared with that on free-edge and zig-zag surface site, which is in agreement with the study by Semenikhin et al. [42] Here, the rate coefficient of reaction $A_3+H \rightarrow P1-CS1+H_2$ is lower than other reactions by at least 1.42 time at 1500 K. It should be noted that the barrier height difference of 0.6-0.7 kcal/mol is less than half of the accuracy of CBS-QB3 method [48]. But similar conclusions are also obtained by the study of Semenikhin et al [42], where the rate constant of H abstraction reaction from zigzag site is 37-42% higher than that from armchair site based on the G3(MP2,CC) calculation.

Compared with H abstraction reactions, the C_2H_2 addition reaction is more sensitive to the site position and site type. If the active C atom is located at the ortho-position relative to the C_2H substituent, the rate coefficient of

C_2H_2 addition reactions ($N2-CS4+C_2H_2 \rightarrow N2-CS11$ and $N2-CS10+C_2H_2 \rightarrow N2-CS17$) are not competitive with other similar reactions, although the formed $N2-CS11$ and $N2-CS18$ species can lead to the formation of a new benzene ring (anthracene and phenanthrene). As shown in Fig.6 (c), the rate coefficients of $N2-CS10+C_2H_2 \rightarrow N2-CS17$ ($N2-CS4+C_2H_2 \rightarrow N2-CS11$) are lower than that of $N2-CS5+C_2H_2 \rightarrow N2-CS12$, $N2-CS6+C_2H_2 \rightarrow N2-CS13$, $N2-CS7+C_2H_2 \rightarrow N2-CS14$, $N2-CS8+C_2H_2 \rightarrow N2-CS15$, and $N2-CS9+C_2H_2 \rightarrow N2-CS16$ by a factor of 1.66 (1.18), 1.53 (1.09), 5.05 (3.60), 6.17 (4.39), and 1.76 (1.25), respectively. The C_2H_2 attack on the active C atom with two free-edge surface sites is preferred due to the relatively low energy barrier (4.3 kcal/mol). Examples of this include the reactions of $P2-CS1+C_2H_2 \rightarrow P2-CS2$ and $P3-CS1+C_2H_2 \rightarrow P3-CS2$ found in Fig.6 (d). The rate coefficient of the addition of C_2H_2 to $P1-CS1$ species is the lowest due to the relatively high energy barrier (7.3 kcal/mol) among all investigated C_2H_2 addition reactions. This means that PAHs that are fully constituted by benzene rings are not the preferred product in the HACA-based mass growth process, and the corresponding isomers with the 5-membered ring are more likely to form especially for large PAHs.

Table 2. Reaction rate parameters in the form of $AT^n \exp(-E/RT)$, the units are s^{-1} , $cm^3 mol^{-1} s^{-1}$ and kcal.

Reaction	A	n	E	Reaction	A	n	E
Benzene (A_1) $\rightarrow$ Naphthalene (A_2)							
Benzene+H $\rightarrow$ B-CS12+H ₂	6.75×10^8	1.9100	15.61	B-CS12+H ₂ $\rightarrow$ Benzene+H	1.22×10^4	2.6550	8.54
B-CS12+C ₂ H ₂ $\rightarrow$ B-CS13	8.75×10^4	2.5040	4.65	B-CS13 $\rightarrow$ B-CS12+C ₂ H ₂	8.36×10^{14}	0.3036	42.66
B-CS13 $\rightarrow$ B-CS14+H	7.63×10^{11}	0.8021	35.30	B-CS14+H $\rightarrow$ B-CS13	5.26×10^8	1.5610	5.73
B-CS13 $\rightarrow$ B-CS15	9.99×10^7	1.3140	21.44	B-CS15 $\rightarrow$ B-CS13	6.12×10^7	1.3980	18.90
B-CS15+C ₂ H ₂ $\rightarrow$ B-CS16	7.02×10^3	2.5630	2.92	B-CS16 $\rightarrow$ B-CS15+C ₂ H ₂	2.21×10^{14}	0.2209	40.52
B-CS16 $\rightarrow$ B-CS17	3.57×10^{11}	0.3574	0.39	B-CS17 $\rightarrow$ B-CS16	3.78×10^{12}	0.0149	2.19
B-CS17 $\rightarrow$ B-CS18	1.88×10^{11}	0.2239	0.25	B-CS18 $\rightarrow$ B-CS17	4.85×10^{12}	0.4702	51.08
B-CS18 $\rightarrow$ A ₂ +H	2.30×10^{11}	0.7058	25.00	A ₂ +H $\rightarrow$ B-CS18	9.08×10^8	1.5520	4.59
B-CS14+H $\rightarrow$ B-CS3+H ₂	6.57×10^7	1.9000	15.39	B-CS3+H ₂ $\rightarrow$ B-CS14+H	1.29×10^4	2.6620	7.88
B-CS3+C ₂ H ₂ $\rightarrow$ B-CS9	9.32×10^4	2.5860	3.72	B-CS9 $\rightarrow$ B-CS3+C ₂ H ₂	5.28×10^{14}	0.3253	40.78
B-CS9 $\rightarrow$ B-CS10+H	5.94×10^{11}	0.8054	33.64	B-CS10+H $\rightarrow$ B-CS9	1.11×10^9	1.5600	5.72
B-CS14+H $\rightarrow$ B-CS2+H ₂	6.06×10^7	1.9040	15.25	B-CS2+H ₂ $\rightarrow$ B-CS14+H	1.20×10^4	2.6620	7.97
B-CS2+C ₂ H ₂ $\rightarrow$ B-CS7	6.98×10^4	2.6340	1.83	B-CS7 $\rightarrow$ B-CS2+C ₂ H ₂	3.11×10^{14}	0.3803	41.04
B-CS7 $\rightarrow$ B-CS8+H	3.94×10^{11}	0.8174	33.76	B-CS8+H $\rightarrow$ B-CS7	4.76×10^8	1.5670	5.59
B-CS14+H $\rightarrow$ B-CS1+H ₂	7.55×10^7	1.8830	16.11	B-CS1+H ₂ $\rightarrow$ B-CS14+H	1.23×10^4	2.6600	7.52
B-CS1+C ₂ H ₂ $\rightarrow$ B-CS4	2.02×10^4	2.5720	3.13	B-CS4 $\rightarrow$ B-CS1+C ₂ H ₂	1.96×10^{14}	0.2971	41.48
B-CS4 $\rightarrow$ B-CS11+H	6.12×10^{11}	0.8095	36.04	B-CS11+H $\rightarrow$ B-CS4	4.62×10^8	1.5470	6.45
B-CS4 $\rightarrow$ B-CS5	1.34×10^{12}	0.1289	3.71	B-CS5 $\rightarrow$ B-CS4	2.74×10^{12}	0.0076	2.44
B-CS5 $\rightarrow$ B-CS11+H	4.82×10^{11}	0.8099	34.60	B-CS11+H $\rightarrow$ B-CS5	4.62×10^8	1.5470	6.45
B-CS5 $\rightarrow$ B-CS6	8.68×10^{11}	0.0285	4.55	B-CS6 $\rightarrow$ B-CS5	2.85×10^{13}	0.4022	57.24
B-CS6+H $\rightarrow$ A ₂	1.00×10^{14}	0	0				
Naphthalene (A_2) $\rightarrow$ Phenanthrene (A_3)							
A ₂ +H $\rightarrow$ N2-CS1+H ₂	8.16×10^9	1.5676	17.4	N2-CS1+H ₂ $\rightarrow$ A ₂ +H	1.57×10^7	1.8148	10.2
N2-CS1+C ₂ H ₂ $\rightarrow$ N2-CS2	1.04×10^5	2.5125	4.3	N2-CS2 $\rightarrow$ N2-CS1+C ₂ H ₂	2.23×10^{13}	0.5379	41.0
N2-CS2 $\rightarrow$ N2-CS37	2.30×10^{11}	0.2584	27.5	N2-CS37 $\rightarrow$ N2-CS2	2.55×10^{11}	0.3916	27.1
N2-CS2 $\rightarrow$ N2-CS3+H	2.75×10^{10}	0.9966	37.8	N2-CS3+H $\rightarrow$ N2-CS2	5.06×10^9	1.2681	4.7
N2-CS37+C ₂ H ₂ $\rightarrow$ N2-CS38	6.20×10^4	2.2527	7.2	N2-CS38 $\rightarrow$ N2-CS37+C ₂ H ₂	6.04×10^{13}	0.3680	37.0

N2-CS38→N2-CS41	2.63x10 ¹²	0.1161	1.7	N2-CS41→N2-CS38	2.76x10 ¹²	0.0646	1.1
N2-CS41→N2-CS42	1.23x10 ¹²	0.0235	0.3	N2-CS42→N2-CS41	2.20x10 ¹²	0.4947	54.0
N2-CS38→N2-CS39	6.69x10 ¹¹	0.1561	12.5	N2-CS39→N2-CS38	8.10x10 ¹¹	0.4987	35.0
N2-CS39→N2-CS40+H	3.01x10 ¹¹	0.7246	28.5	N2-CS40+H→N2-CS39	3.16x10 ⁷	2.2018	3.8
N2-CS42→A ₃ +H	2.31x10 ¹¹	0.6710	27.4	A ₃ +H→N2-CS42	6.38x10 ⁹	1.1534	3.5
N1-CS37→A ₃ +H	1.01x10 ¹¹	0.7809	28.5	A ₃ +H→N1-CS37	7.11x10 ⁹	1.1466	3.4
N1-CS36→N1-CS37	1.38x10 ¹²	0	0.2	N1-CS37→N1-CS36	1.80x10 ¹²	0.5197	53.9
N1-CS35→N1-CS36	7.90x10 ¹²	0	5.1	N1-CS36→N1-CS35	4.54x10 ⁹	0.8206	2.8
N1-CS34+C ₂ H ₂ →N1-CS35	8.06x10 ²	3.2433	5.4	N1-CS35→N1-CS34+C ₂ H ₂	9.18x10 ¹³	0.2837	40.2
N1-CS33→N1-CS34	5.61x10 ¹¹	0.2975	26.6	N1-CS34→N1-CS33	3.27x10 ⁹	1.3516	25.5
N1-CS2→N1-CS33	1.19x10 ¹²	0.1738	3.6	N1-CS33→N1-CS2	1.30x10 ¹²	0.1045	2.6
N1-CS2→N1-CS5+H	3.57x10 ¹¹	0.8706	38.2	N1-CS5+H→N1-CS2	8.99x10 ⁹	1.2034	5.2
N1-CS33→N1-CS5+H	3.34x10 ¹¹	0.8702	37.2	N1-CS5+H→N1-CS33	8.99x10 ⁹	1.2034	5.2
N1-CS3→N1-CS4 (A ₂ R ₅)+H	1.27x10 ¹¹	0.8322	27.9	N1-CS4(A ₂ R ₅)+H→ N1-CS3	2.58x10 ⁹	1.2534	4.5
N1-CS2→N1-CS3	3.54x10 ⁹	0.7858	16.1	N1-CS3→N1-CS2	1.53x10 ¹²	0.4175	32.3
N1-CS1+C ₂ H ₂ →N1-CS2	3.70x10 ⁴	2.5519	4.6	N1-CS2→N1-CS1+C ₂ H ₂	8.31x10 ¹¹	1.0246	41.0
A ₂ +H→N1-CS1+H ₂	9.12x10 ⁹	1.5489	17.7	N1-CS1+H ₂ →A ₂ +H	7.02x10 ⁶	1.9134	10.4
N1-CS32→N2-CS35+H	1.83x10 ¹¹	0.7991	31.3	N2-CS35+H→N1-CS32	3.81x10 ⁹	1.2164	4.2
N1-CS31→N1-CS32	6.22x10 ¹¹	0.1087	14.3	N1-CS32→N1-CS31	8.39x10 ¹¹	0.4962	35.2
N1-CS16→N1-CS31	9.43x10 ¹¹	0.1483	2.4	N1-CS31→N1-CS16	1.05x10 ¹²	0.1676	3.4
N1-CS16→N1-CS23+H	9.73x10 ¹⁰	0.9619	37.0	N1-CS23+H→N1-CS16	4.28x10 ⁹	1.2698	5.0
N1-CS9+C ₂ H ₂ →N1-CS16	4.72x10 ⁴	2.5230	4.5	N1-CS16→N1-CS9+C ₂ H ₂	6.28x10 ¹²	0.8018	39.8
N1-CS5+H→N1-CS9+H ₂	1.12x10 ⁹	1.5498	17.9	N1-CS9+H ₂ →N1-CS5+H	7.26x10 ⁶	1.9051	10.2
N1-CS5+H→N1-CS10+H ₂	1.13x10 ⁹	1.5603	17.6	N1-CS10+H ₂ →N1-CS5+H	7.90x10 ⁶	1.9110	10.2
N1-CS10+C ₂ H ₂ →N1-CS17	3.54x10 ⁵	2.4971	4.2	N1-CS17→N1-CS10+C ₂ H ₂	3.12x10 ¹⁴	0.4612	42.9
N1-CS17→N2-CS20+H	2.91x10 ¹¹	0.9823	39.6	N2-CS20+H→N1-CS17	9.91x10 ⁹	1.2793	4.5
N1-CS5+H→N1-CS11+H ₂	1.07x10 ⁹	1.5721	17.5	N1-CS11+H ₂ →N1-CS5+H	7.00x10 ⁶	1.9286	10.2
N1-CS11+C ₂ H ₂ →N1-CS18	1.12x10 ⁵	2.4893	4.3	N1-CS18→N1-CS11+C ₂ H ₂	5.37x10 ¹³	0.5104	41.8
N1-CS18→N2-CS23+H	2.16x10 ¹¹	1.0097	38.6	N2-CS23+H→N1-CS18	8.56x10 ⁹	1.3149	4.5
N1-CS5+H→N1-CS12+H ₂	9.41x10 ⁸	1.5466	19.5	N1-CS12+H ₂ →N1-CS5+H	5.88x10 ⁶	1.8890	11.8
N1-CS12+C ₂ H ₂ →N1-CS19	2.36x10 ⁴	2.4781	6.7	N1-CS19→N1-CS12+C ₂ H ₂	4.43x10 ¹¹	0.9366	33.8
N1-CS19→N1-CS26+H	9.03x10 ¹⁰	0.9797	35.0	N1-CS26+H→N1-CS19	3.02x10 ⁹	1.2456	4.8
N1-CS5+H→N1-CS6+H ₂	1.35x10 ⁹	1.5479	18.6	N1-CS6+H ₂ →N1-CS5+H	4.66x10 ⁶	1.9738	10.3
N1-CS6+C ₂ H ₂ →N1-CS13	1.76x10 ⁵	2.2917	3.4	N1-CS13→N1-CS6+C ₂ H ₂	1.38x10 ¹⁴	0.3088	42.4
N1-CS13→N2-CS24+H	1.11x10 ¹¹	1.0364	40.6	N2-CS24+H→N1-CS13	4.84x10 ⁹	1.2914	4.9
N1-CS13→N1-CS27	2.00x10 ¹²	0.1097	5.5	N1-CS27→N1-CS13	2.04x10 ¹²	0.1021	4.0
N1-CS27→N2-CS24+H	1.04x10 ¹¹	1.0355	39.1	N2-CS24+H→N1-CS27	4.82x10 ⁹	1.2914	4.9
N1-CS27→N1-CS20	1.23x10 ¹²	0	3.7	N1-CS20→N1-CS27	8.30x10 ¹¹	0.0432	61.2
N1-CS5+H→N1-CS8+H ₂	9.90x10 ⁵	2.0580	11.6	N1-CS8+H ₂ →N1-CS5+H	1.26x10 ⁴	2.9485	10.4
N1-CS8+C ₂ H ₂ →N1-CS15	5.55x10 ⁴	2.5188	4.3	N1-CS15→N1-CS8+C ₂ H ₂	4.07x10 ¹¹	1.4677	40.1
N1-CS15→N1-CS22+H	3.23x10 ⁹	1.8080	37.4	N1-CS22+H→N1-CS15	7.09x10 ⁹	1.2270	5.2
N1-CS15→N1-CS28	1.30x10 ¹⁰	1.0820	2.7	N1-CS28→N1-CS15	1.70x10 ¹²	0.1154	3.7
N1-CS28→N1-CS22+H	3.14x10 ⁹	1.8079	38.3	N1-CS22+H→N1-CS28	7.11x10 ⁹	1.2270	5.2
N1-CS28→N1-CS29	1.02x10 ¹²	0.0499	15.4	N1-CS29→N1-CS28	5.27x10 ¹²	0.2536	32.8
N1-CS29→N2-CS35+H	1.25x10 ¹¹	0.8359	28.4	N2-CS35+H→N1-CS29	2.86x10 ⁹	1.2418	4.5
N1-CS5+H→N1-CS7+H ₂	1.24x10 ⁹	1.5547	17.7	N1-CS7+H ₂ →N1-CS5+H	7.96x10 ⁶	1.9114	10.2
N1-CS7+C ₂ H ₂ →N1-CS14	3.91x10 ⁵	2.4569	4.1	N1-CS14→N1-CS7+C ₂ H ₂	2.19x10 ¹⁴	0.4591	41.5
N1-CS14→N2-CS19+H	4.35x10 ¹¹	0.9563	38.5	N2-CS19+H→N1-CS14	1.36x10 ¹⁰	1.2935	4.4
N2-CS32→N2-CS30+H	1.16x10 ¹¹	0.8386	27.6	N2-CS30+H→N2-CS32	2.80x10 ⁹	1.2400	4.8
N2-CS31→N2-CS32	6.33x10 ¹¹	0.1109	16.4	N2-CS32→N2-CS31	1.19x10 ¹²	0.4469	31.8
N2-CS13→N2-CS31	9.82x10 ¹¹	0.1388	2.5	N2-CS31→N2-CS13	1.22x10 ¹²	0.1629	3.5
N2-CS12→N2-CS28	1.05x10 ¹²	0.1354	2.4	N2-CS28→N2-CS12	9.59x10 ¹¹	0.1802	3.4

N2-CS28→N2-CS29	5.53x10 ¹¹	0.1168	16.0	N2-CS29→N2-CS28	2.13x10 ¹²	0.3739	32.3
N2-CS13→N2-CS20+H	1.00x10 ¹¹	0.9848	37.1	N2-CS20+H→N2-CS13	5.23x10 ⁹	1.2734	5.0
N2-CS31→N2-CS20+H	1.58x10 ¹¹	0.1002	36.1	N2-CS20+H→N2-CS31	5.23x10 ⁹	1.2734	5.0
N2-CS6+C ₂ H ₂ →N2-CS13	4.92x10 ⁴	2.5227	4.5	N2-CS13→N2-CS6+C ₂ H ₂	1.21x10 ¹³	0.6206	39.9
N2-CS3+H→N2-CS6+H ₂	1.01x10 ⁹	1.5640	17.8	N2-CS6+H ₂ →N2-CS3+H	7.42x10 ⁶	1.9073	10.4
N2-CS3+H→N2-CS5+H ₂	1.02x10 ⁹	1.5589	17.8	N2-CS5+H ₂ →N2-CS3+H	6.44x10 ⁶	1.9192	10.4
N2-CS5+C ₂ H ₂ →N2-CS12	5.64x10 ⁴	2.5102	4.4	N2-CS12→N2-CS5+C ₂ H ₂	1.12x10 ¹³	0.6524	39.6
N2-CS12→N2-CS19+H	2.46x10 ⁷	2.0707	37.3	N2-CS19+H→N2-CS12	4.44x10 ⁹	1.2671	5.0
N2-CS28→N2-CS19+H	2.32x10 ⁷	2.0645	38.4	N2-CS19+H→N2-CS28	4.43x10 ⁹	1.2672	5.0
N2-CS29→N2-CS30+H	1.37x10 ¹¹	0.8248	28.2	N2-CS30+H→N2-CS29	3.12x10 ⁹	1.2284	4.7
N2-CS3+H→N2-CS7+H ₂	9.93x10 ⁸	1.5737	17.5	N2-CS7+H ₂ →N2-CS3+H	7.94x10 ⁶	1.9069	10.2
N2-CS7+C ₂ H ₂ →N2-CS14	2.56x10 ⁵	2.4510	4.3	N2-CS14→N2-CS7+C ₂ H ₂	6.88x10 ¹³	0.5147	42.2
N2-CS14→N2-CS21+H	6.70x10 ¹⁰	1.0143	39.0	N2-CS21+H→N2-CS14	4.66x10 ⁹	1.2798	4.7
N2-CS3+H→N2-CS8+H ₂	9.24x10 ⁸	1.5842	17.5	N2-CS8+H ₂ →N2-CS3+H	5.10x10 ⁶	1.9619	10.2
N2-CS8+C ₂ H ₂ →N2-CS15	2.90x10 ⁵	2.4567	4.2	N2-CS15→N2-CS8+C ₂ H ₂	3.91x10 ¹³	0.4765	40.8
N2-CS15→N2-CS22+H	2.46x10 ¹⁰	1.0074	37.8	N2-CS22+H→N2-CS15	3.89x10 ⁹	1.3021	4.6
N2-CS3+H→N2-CS9+H ₂	1.05x10 ⁹	1.5548	17.9	N2-CS9+H ₂ →N2-CS3+H	6.84x10 ⁶	1.9134	10.4
N2-CS9+C ₂ H ₂ →N2-CS16	5.30x10 ⁴	2.5267	4.4	N2-CS16→N2-CS9+C ₂ H ₂	9.25x10 ¹²	0.6990	39.2
N2-CS16→N2-CS23+H	1.80x10 ¹¹	0.9365	36.6	N2-CS23+H→N2-CS16	7.53x10 ⁹	1.2305	5.1
N2-CS16→N2-CS33	1.37x10 ¹²	0.1278	1.8	N2-CS33→N2-CS16	1.37x10 ¹²	0.1278	3.4
N2-CS33→N2-CS23+H	1.16x10 ¹¹	0.9412	38.1	N2-CS23+H→N2-CS33	8.13x10 ⁹	1.2102	5.0
N2-CS33→N2-CS34	6.03x10 ¹¹	0.1068	14.3	N2-CS34→N2-CS33	9.31x10 ¹¹	0.4922	35.6
N2-CS34→N2-CS35+H	2.36x10 ¹¹	0.7638	31.7	N2-CS35+H→N2-CS34	3.58x10 ⁹	1.2191	3.8
N2-CS3+H→N2-CS10+H ₂	1.30x10 ⁹	1.5400	18.9	N2-CS10+H ₂ →N2-CS3+H	5.94x10 ⁶	1.9340	10.4
N2-CS10+C ₂ H ₂ →N2-CS17	2.98x10 ⁴	2.5282	4.4	N2-CS17→N2-CS10+C ₂ H ₂	9.50x10 ¹²	0.6691	38.5
N2-CS17→N2-CS36	1.68x10 ¹²	0	12.4	N2-CS36→N2-CS17	3.25x10 ⁻⁶	5.0727	12.0
N2-CS36→N2-CS35+H	1.62x10 ¹¹	0.8140	28.8	N2-CS35+H→N2-CS36	2.91x10 ⁹	1.2476	4.4
N2-CS17→N2-CS24+H	1.92x10 ¹¹	0.9906	35.9	N2-CS24+H→N2-CS17	6.89x10 ⁹	1.2688	5.1
N2-CS17→N2-CS43	4.04x10 ¹²	0	1.3	N2-CS43→N2-CS17	1.44x10 ¹²	0	2.0
N2-CS43→N2-CS24+H	1.69x10 ¹¹	0.9895	36.8	N2-CS24+H→N2-CS43	6.89x10 ⁹	1.2688	5.1
N2-CS43→N2-CS44	8.03x10 ¹¹	0	4.5	N2-CS44→N2-CS43	8.38x10 ¹¹	0.8597	62.3
N2-CS3+H→N2-CS4+H ₂	1.23x10 ⁹	1.5554	18.6	N2-CS4+H ₂ →N2-CS3+H	8.10x10 ⁶	1.9045	10.2
N2-CS4+C ₂ H ₂ →N2-CS11	1.14x10 ⁵	2.3544	3.6	N2-CS11→N2-CS4+C ₂ H ₂	2.81x10 ¹³	0.4462	40.5
N2-CS11→N2-CS25	2.68x10 ¹²	0	3.6	N2-CS25→N2-CS11	4.97x10 ¹²	0	4.5
N2-CS25→N2-CS26	1.16x10 ¹²	0	5.0	N2-CS26→N2-CS25	1.38x10 ¹¹	1.0160	55.1
N2-CS11→N2-CS18+H	2.76x10 ¹⁰	1.1079	38.7	N2-CS18+H→N2-CS11	5.00x10 ⁹	1.2478	5.0
N2-CS25→N2-CS18+H	2.91x10 ¹⁰	1.0998	39.4	N2-CS18+H→N2-CS25	6.21x10 ⁹	1.2341	4.8
N2-CS26+H→N2-CS27 ^a	1.00x10 ¹⁴	0	0	N2-CS44+H→A ₃ ^a	1.00x10 ¹⁴	0	0
N1-CS20+H→A ₃ ^a	1.00x10 ¹⁴	0	0				

Phenanthrene (A₃) → Pyrene (A₄)

A ₃ +H→P1-CS1+H ₂	7.33x10 ⁷	1.9090	16.66	P1-CS1+H ₂ →A ₃ +H	7.64x10 ³	2.6750	9.29
P-CS1+C ₂ H ₂ →P1-CS2	9.68x10 ³	2.5340	6.69	P1-CS2→P1-CS1+C ₂ H ₂	1.41x10 ¹⁴	0.2841	37.58
P1-CS2→P1-CS4	1.61x10 ¹²	0.1658	3.25	P1-CS4→P1-CS2	4.71x10 ¹²	0.0334	0.83
P1-CS4→P1-CS5	4.10x10 ¹¹	0.1168	2.52	P1-CS5→P1-CS4	7.57x10 ¹⁰	0.8813	38.72
P1-CS5→A ₄ +H	1.04x10 ¹¹	0.7490	18.65	A ₄ +H→P1-CS5	2.60x10 ⁸	1.6180	6.11
P1-CS2→P1-CS3+H	5.82x10 ¹¹	0.8635	38.04	P1-CS3+H→P1-CS2	1.51x10 ⁸	1.5800	3.73
P1-CS4→P1-CS3+H	5.06x10 ¹¹	0.8153	35.32	P1-CS3+H→P1-CS4	1.49x10 ⁸	1.5800	3.73
A ₃ +H→P2-CS1+H ₂	1.27x10 ⁸	1.9000	16.41	P2-CS1+H ₂ →A ₃ +H	1.37x10 ⁴	2.6440	7.28
P2-CS1+C ₂ H ₂ →P2-CS2	3.60x10 ⁴	2.5970	3.80	P2-CS2→P2-CS1+C ₂ H ₂	5.23x10 ¹⁴	0.3302	44.46
P2-CS2→P2-CS3+H	5.41x10 ¹²	0.7886	40.22	P2-CS3+H→P2-CS2	5.20x10 ⁸	1.5620	3.41
A ₃ +H→P3-CS1+H ₂	1.55x10 ⁸	1.8830	16.65	P3-CS1+H ₂ →A ₃ +H	1.47x10 ⁴	2.6410	7.23
P3-CS1+C ₂ H ₂ →P3-CS2	5.58x10 ⁴	2.5890	3.75	P3-CS2→P3-CS1+C ₂ H ₂	1.11x10 ¹⁵	0.3157	45.22
P3-CS2→P3-CS3+H	3.03x10 ¹²	0.8111	40.82	P3-CS3+H→P3-CS2	1.87x10 ⁹	1.5620	3.45

$A_3+H \rightarrow P4-CS1+H_2$	1.26×10^8	1.8860	16.73	$P4-CS1+H_2 \rightarrow A_3+H$	1.11×10^4	2.6560	7.48
$P4-CS1+C_2H_2 \rightarrow P4-CS2$	2.10×10^4	2.5860	4.06	$P4-CS2 \rightarrow P4-CS1+C_2H_2$	1.56×10^{14}	0.3543	41.06
$P4-CS2 \rightarrow P4-CS3+H$	3.71×10^{11}	0.8492	37.58	$P4-CS3+H \rightarrow P4-CS2$	3.16×10^8	1.5820	3.89
$P4-CS2 \rightarrow P4-CS4$	1.80×10^{12}	0.0887	1.93	$P4-CS4 \rightarrow P4-CS2$	2.66×10^{12}	0.0462	3.40
$P4-CS4 \rightarrow P4-CS3+H$	6.43×10^{11}	0.8150	39.18	$P4-CS3+H \rightarrow P4-CS4$	4.66×10^8	1.5610	4.05
$P4-CS4 \rightarrow P4-CS5$	3.57×10^{11}	0.1589	14.29	$P4-CS5 \rightarrow P4-CS4$	8.66×10^{12}	0.2254	33.90
$P4-CS5 \rightarrow P4-CS6+H$	2.44×10^{11}	0.7518	28.22	$P4-CS6+H \rightarrow P4-CS5$	1.28×10^8	1.5930	3.40
$A_3+H \rightarrow P5-CS1+H_2$	1.43×10^8	1.8750	16.67	$P5-CS1+H_2 \rightarrow A_3+H$	1.11×10^4	2.6560	7.48
$P5-CS1+C_2H_2 \rightarrow P5-CS2$	2.00×10^4	2.6060	3.98	$P5-CS2 \rightarrow P5-CS1+C_2H_2$	2.47×10^{14}	0.3188	41.20
$P5-CS2 \rightarrow P5-CS3+H$	3.79×10^{11}	0.8605	37.76	$P5-CS3+H \rightarrow P5-CS2$	3.06×10^8	1.5870	3.84
$P5-CS2 \rightarrow P5-CS4$	2.94×10^{12}	0.0421	2.20	$P5-CS4 \rightarrow P5-CS2$	3.93×10^{12}	0.0238	3.86
$P5-CS4 \rightarrow P5-CS3+H$	7.86×10^{11}	0.8104	39.56	$P5-CS3+H \rightarrow P5-CS4$	4.85×10^8	1.5530	3.99
$P5-CS4 \rightarrow P5-CS5$	3.75×10^{11}	0.1586	15.38	$P5-CS5 \rightarrow P5-CS4$	1.02×10^{13}	0.1896	32.86
$P5-CS5 \rightarrow P5-CS6+H$	2.56×10^{11}	0.7368	26.68	$P5-CS6+H \rightarrow P5-CS5$	1.22×10^8	1.5950	3.64

^aThe rate coefficients are assumed to be equal as that of $B-CS6+H \rightarrow A_2$ [26].

3.3 The yield of products in HACA-based mass growth process

Using the above PES and kinetic results, we investigated the yield distribution of various products within the HACA-based mass growth process. Here, the formation of various products are evaluated using a closed homogeneous zero-dimensional reactor for A_1 - A_2 , A_2 - A_2R_5 - A_3 , and A_3 - A_4 reaction systems respectively, using Chemkin Pro software. The species considered in the 0-D reactor include A_1 (A_2 or A_3), C_2H_2 , H_2 , H and N_2 in the A_1 - A_2 (A_2 - A_2R_5 - A_3 or A_3 - A_4) reaction system. The mole fraction of A_1 , A_2 , A_3 , C_2H_2 , H , and H_2 are fixed at 5×10^{-4} , 4×10^{-5} , 1×10^{-5} , 4×10^{-2} , 1×10^{-4} , 0.1, in accordance with experimental results [54, 64]. The mole fraction of N_2 is set to 0.8594, 0.85986, and 0.85989 in A_1 - A_2 , A_2 - A_3 , and A_3 - A_4 reaction systems respectively. The temperature is set to 1400 K, which is the peak temperature of the measured temperature profile [54].

The mole fractions of various products in A_1 - A_2 reaction system are shown in Fig.7 (a). The mole fraction of B-CS14 (phenylacetylene, A_1C_2H) is the highest, which is in agreement with the experimental results that A_1C_2H is the dominant product in the reaction of phenyl radical with C_2H_2 [65]. The concentration rank of secondary C_2H_2 addition products is in the following order: B-CS8 > A_2 > B-CS10 > B-CS11. It matches with the above PES and kinetic analysis that C_2H_2 is more likely to attach to the active C atom far from the C_2H chain. In the reaction system of A_2 - A_2R_5 - A_3 , the A_2R_5 is the dominant reaction product, and its mole fraction is higher than that of A_3 by at least 27.8 times as shown in Fig.7 (b). These results are in good agreement with the theoretical results by Kislov et al. [58], where A_3 is the minor product in the A_2 - C_2H_2 reaction system. In the A_3 - A_4 reaction system, the yield of products is mainly determined by the type of surface site as it makes reaction coefficients of H abstraction and C_2H_2 addition reactions different, as well as the thermal stability of product. In this study, the thermal stability rank of products is in the following order: PAHs with one or two C_2H chains (eg: P2-CS3 and P3-CS3) < PAHs with 5-membered rings (eg: P5-CS6) < PAHs containing only benzene rings (eg: A_4) as shown

in Fig.5. The formation of P2-CS3 and P3-CS3 is kinetically supported by the H abstraction and C₂H₂ addition reactions, as shown in Fig.6 (b) and (d). However, their concentration peaks around 0.5 ms, then decrease rapidly as shown in Fig.7 (c). It should be resulted from the low thermal stability of P2-CS3 and P3-CS3 molecules, which make the reaction highly reversible at flame temperature. Fig.7 (c) shows that the P5-CS6 with 5-membered rings with moderate thermal stability is the dominant product in this reaction system, and its mole fraction is higher than that of A₄ by 45.6 times. The A₄ formation is greatly limited by the rate coefficients of H abstraction and C₂H₂ addition reactions. Based on the yield distribution of products in A₂-A₂R₅-A₃ and A₃-A₄ reaction systems, we can deduce that the PAHs with 5-membered ring should be the dominant reaction products in HACA-based mass growth processes instead of PAHs containing only benzene rings, especially in large PAHs or soot surface growth processes. We also noted that the mole fraction of all intermediates are always lower than 1×10⁻¹⁰, which is lower than the main reaction products by at least three orders of magnitudes. This means the steady-state approximation, where the reaction intermediate consumed as quickly as it is generated and the concentration remains the same in a duration of the reaction, can be applied for HACA pathways to reduce the reaction number in mechanism simplification.

To discuss the importance of the Frenklach route where the active C atom generates through the intramolecular H transfer to the C₂H₂ chain (like routes N1-CS33→A₃+H and N2-CS37→A₃+H in Fig.2), the sensitivity of A₃ formation pathway is carried out. Considering the site effect, there are three A₃ formation pathways including Frenklach, N1-CS5→A₃ and N2-CS3→A₃ routes. The mole fraction of A₃ is calculated on the condition that each route is removed from A₃ formation network individually. The importance of each route can be evaluated by comparing the A₃ concentration calculated with and without the corresponding route. As shown in Fig.7 (d), only 4.96 % of A₃ is formed from the Frenklach route, and that most A₃ (90.5 %) is formed from the HACA route: A₂+C₂H₂→N2-CS3(C₂H₂)→A₃+H.

Fig.7. The yield of products in A₁-A₂ system (a), A₂-A₂R₅-A₃ system (b), A₃-A₄ system (c), and A₃ formation pathway analysis (d).

3.4 Connections to PAHs experiment

Generally, comparison between experimental observation and theoretical results updates our understanding of PAH formation. To this end, experimental results that detect PAHs using LIF [66-68], TOFMS [69] and GC-MS technique [54] are selected for discussions. The first two qualitatively describes the formation of PAHs, and the last one quantitatively describes the concentrations of PAHs up to pyrene. In LIF experiment, the detected fluorescence wavelength of PAHs ranges from 300 nm to 700 nm in premixed flames [66-68]. At a given flame height, the LIF signal intensity along fluorescence wavelength increases first, then decreases after reaching a peak value around 500 nm. Liu et al. [70] suggests that the signal in the UV region can be regarded as the fluorescence being emitted by the PAHs with two to three rings, and the fluorescence signals with the wavelength in the visible region are likely emitted by the PAHs with 5-membered rings. The above yield analysis indicates that concentrations of PAHs with 5-membered rings including A₂R₅, N2-CS30 and P5-CS6 are expected to be high in premixed sooting flame. The existence of abundant PAHs with 5-membered rings contributes to explaining that the PAH-LIF profile peaks in the visible region.

Shukla et al. [69] proposed that hydrogen abstraction and vinyl radical (C₂H₃) addition (HAVA) pathway is more promising compared with HACA pathway in C₂H₄ flame, as a remarkable sequence of mass peak at intervals of mass number 26 instead of 24 was observed in the case of C₂H₄ pyrolysis products using TOFMS technique. However, the mole fraction of C₂H₃ is lower than that of C₂H₂ by at least four orders of magnitude in C₂H₄ sooting flame. The simulated peak mole fraction of C₂H₃ is 2×10⁻⁶, and that of C₂H₂ is 4×10⁻² in premixed C₂H₄ flame with equivalence ratio of 3.06 using ABF mechanism [26]. This means that the contribution of PAHs formation

from HAVA pathway is expected to be small due to the low concentration of C_2H_3 . In this study, the formation of PAH isomers considering site effects is more attractive to explain the observed mass spectra results. The formation of 1,3-Diethynylbenzene (B-CS8), 1,4-Diethynylbenzene (B-CS10), N2-CS30 and N2-CS35 account for mass peaks at 126 and 176, which are not considered in any PAH mechanisms. In this way, the observed sequence of mass peaks at intervals of mass number 26 may result from the reaction pathways of $C_8H_6 \rightarrow C_{10}H_8$, $C_{10}H_6 \rightarrow C_{12}H_8 \rightarrow C_{14}H_{10}$ and $C_{14}H_8 \rightarrow C_{16}H_{10}$, and the corresponding attribution of the mass peaks are shown in Fig.8. It is notable that the mass peak at 178 ($C_{14}H_8$) is not observed in C_2H_2 pyrolysis, but observed with a weak signal intensity in C_2H_4 pyrolysis. It indicates that the formation of A_3 ($C_{14}H_8$) within HACA frame is greatly limited, which confirms the aforementioned conclusion. The formation of larger PAHs (e.g., $A_2 \rightarrow A_3$) via the reaction of PAH radical and vinylacetylene (C_4H_4) is also possible, as supported by experimental and theoretical evidence for the reaction of phenyl radical and C_4H_4 generating A_2 (like $A_1 \rightarrow A_2$) under different conditions [71-73]. In order to complement the HACA framework, future work should pay more attention to PAH radical + C_4H_4 reactions.

Fig.8. The mass spectra of acetylene and ethylene pyrolysis products observed at 1485 K [69].

To evaluate the site effect on the concentration of PAHs formed in the HACA route, PAH formation in premixed $C_2H_4/O_2/N_2$ flames [54] is simulated using the premixed flame model in Chemkin software. The USC II mechanism where benzene is the termination species is considered as the base-mechanism, and the investigated

186 elementary reactions listed in Table 2 are embedded into USC II mechanism. The new mechanism is named as “PAHs mechanism with site effects” in this study. If only the formation of A_2 , A_2R_5 , A_3 and A_4 is considered in the reaction networks, then the mechanism is labeled as “PAHs mechanism without site effect”. It is notable that this study only focus on the HACA route, so other pathway beyond HACA route is not considered. In this way, the relative contribution to PAHs formation from HACA route can be evaluated by comparing the experimentally detected PAHs concentration and predicted PAHs concentration using the PAHs mechanism here. Flame conditions including the temperature profile, equivalence ratio and velocity of inlet-gas are kept the same as experimental data [54]. As illustrated in Fig.9 (a)-(b), the mole fractions of A_1 and A_1C_2H are in accordance with the experimental data, and the deviation is generally within a factor of 3. In addition, the site effect on the mole fractions of A_1 and A_1C_2H is ignorable. The mole fraction of A_2 predicted by the PAH mechanism with site effects more closely agrees with the experimental profile, compared with the model without site effect as presented in Fig.9 (c). The comparison results mean that the formation of aromatic species up to A_2 can be accurately described by HACA route, at least for this flame case. The mole fraction of A_2 is determined by the competition between the formation and consumption rate. The main precursors of A_2 formation are A_1C_2H and C_2H_2 , and their concentration profiles are almost the same irrespective of the site effect. Therefore, it implies that the reduced consumption of A_2 in A_2R_5 and A_3 formation process should be the main reason for the better performance of the PAHs mechanism with site effect. Indeed, the mole fractions of larger PAHs including A_2R_5 , A_3 and A_4 simulated with site effect are much lower than that without site effect, as shown in Fig.9 (d)-(f). In addition, the predicted mole fractions of A_3 and A_4 with or without site effect in HACA frame are lower than that of experimental results by at least two orders of magnitudes. It agrees well with the mass spectra experiments for HACA-based reactions, where the mass peak at A_3 is not observed [65] or observed at a very weak signal intensity [69]. Therefore, reaction pathways beyond the HACA pathway should be investigated for accurate prediction of A_3 and A_4 .

Fig. 9 Comparison between experimental and calculated mole fraction of benzene and various PAHs in C_2H_4 premixed flame [54]. (1 atm, $C_2H_4/O_2/N_2 = 21.3/20.9/57.8$).

4. Conclusion

The site effect on PAH growth from benzene to pyrene within the HACA framework was systematically investigated by applying both DFT B3LYP 6-311+G(d,p) and TST methods. Also, the yield distribution of various products in A_1 - A_2 , A_2 - A_2R_5 - A_3 , and A_3 - A_4 reaction systems is calculated using a 0-D reactor simulation. Additionally, the correlation of theoretical results with LIF, TOFMS and GC-MS experimental results was discussed. The following conclusions can be drawn from this study.

The potential energy surface and kinetic analysis indicate that the H abstraction and C_2H_2 addition reactions are greatly sensitive to the site position (ortho-, meta- and para-position) relative to the C_2H chain and surface site type (zig-zag, free-edge and armchair). The H atoms located at the meta- and para positions are more likely to be abstracted from the PAHs. In addition, the active C atom on the free-edge of PAHs is the priority target of C_2H_2 molecule, compared with zig-zag and armchair surface site.

Considering the site effect, our results show that the di-substituted PAHs and PAHs with 5-membered ring can be formed in the HACA framework. The yield distribution results indicate that PAHs with 5-membered ring with

moderate thermal stability are the dominant reaction product in HACA-based mass growth processes, especially for larger PAH reactions. Furthermore, the formation of multi-ring PAHs fully constituted of benzene rings is kinetically unsupported in the HACA framework.

The sensitivity analysis of A_3 formation pathway indicates that the Frenklach route, wherein the active C atom is generated via the intramolecular H transfer to the C_2H_2 chain, can be ignored in PAHs mechanism for brevity.

The existence of abundant PAHs with 5-membered ring is indirectly confirmed by the dominant features of PAH-LIF signal profiles. The observed sequence of mass peak at intervals of mass number 26 in C_2H_2/C_2H_4 pyrolysis is reasonably explained by the theoretical results in this study. The comparison of the simulated PAH concentrations that consider site effects and detected PAH concentrations using GC-MS method reveals that the HACA pathway significantly underestimates the concentrations of phenanthrene and pyrene. The potential formation pathways for phenanthrene and pyrene should be explored in future.

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