Oxidative coupling assisted methane aromatization

— a simulation study

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ABSTRACT. This study simulates a high-temperature reaction in a plug-flow reactor (PFR) for the aromatization of methane via oxidative coupling of methane (OCM) using a state-of-the-art gas-phase chemical kinetic mechanism. Benzene is formed from a methane-oxygen ($\text{CH}_4\text{--O}_2$) feed via formation of ethylene through OCM followed by homogeneous gas-phase aromatization of C_2H_4 after O_2 depletion. Because both OCM and C_2H_4 aromatization are exothermic reactions, the process is advantageous over an endothermic non-oxidative methane aromatization reaction. For the OCM reaction, the previously reported mechanism in which the catalyst achieves the quasi-equilibrated formation of $\text{OH}\cdot$ from an $\text{H}_2\text{O--O}_2$ mixture was included in the combustion chemistry network. It was evident that $\text{OH}\cdot$ formation increased benzene yield as a consequence of enhanced C_2H_4 yield from the OCM. The influence of temperature, CH_4/O_2 ratio and contact time on benzene yield was elucidated, and reaction pathways leading to aromatic formation were analyzed. The maximum benzene yield on a carbon basis at a total pressure of 1 atm reached 10% at CH_4/O_2 ratios from 3 to 6 and temperatures of 800 to 900°C (isothermal). Our analysis on the differential rates of production suggest that benzene is formed from the benzyl radical via toluene and from the reaction between allyl and propargyl. Adiabatic operations were found to be beneficial for reducing external heat supply (i.e., inlet temperature) by utilizing the exothermic reactions.

1. Introduction

Natural gas is an important fossil fuel, and the global natural gas market would keep growing as a result of the shale gas revolution in the United States.¹ As stated in the World Energy Outlook 2018 from the International Energy Agency, the worldwide natural gas demand is predicted to increase from 3752 billion cubic meters in year 2017 to 5349 billion cubic meters in year 2040.¹ Therefore, it is highly desirable to enhance the conversion efficiency of natural gas into achievable energy and commodity products for both economic and environmental considerations. Many technologies have been developed for the conversion of CH₄ to value-added products, the process of which can be divided into two categories, namely direct and indirect routes.^{2,3} In the indirect CH₄ conversion routes, syngas (CO and H₂) is first produced by CH₄ reforming followed by various processes, such as the Fischer-Tropsch synthesis to produce liquid hydrocarbons.³ Although indirect conversion routes are well-established, there are several drawbacks; for instance, multiple chemical processes are required for products, and the high endothermicity of the reforming reaction is energy-intensive. Direct conversion routes into chemicals, on the other hand, reduce the number of reaction processes while potentially reducing energy consumption via selected exothermic reactions. For instance, a single reactor leads to production of C₂H₄ by the oxidative coupling of methane (OCM),⁴⁻⁷ or methanol and formaldehyde by selective oxidation,⁸ or aromatics by pyrolysis.⁹

OCM is a direct method for producing C₂H₄ from CH₄ with the combination of O₂ to decrease the thermodynamic barrier of the transformation relative to the non-oxidative counterpart,^{7,10,11} as shown in **reactions 1 and 2**.

The OCM reaction has been investigated extensively by both experiments^{12,13} and modeling.^{4,14,15} It is known that both heterogeneous surface and homogeneous gas-phase radical reactions contribute to the rate and C₂H₄ selectivity of the OCM process.^{16–18} Lunsford et al.^{19, 20} showed the existence of OH· during the reaction, and it was further demonstrated by Takanabe et al. that the generated OH· (described in **reaction 3**) actually plays an important role in increasing the conversion rate and C₂ selectivity of the OCM reaction with Na-based catalysts.^{21–24}

The improvement in C₂ selectivity by OH· could be explained based on two reasons: (1) C₂H₆ activation rate becomes relatively slower than that of CH₄ activation because the highly reactive OH· is less selective to the C–H bond energy during H-abstraction reaction (CH₄ 439 kJ mol^{−1} vs. C₂H₆ 423 kJ mol^{−1}).^{21,22} and (2) hydrocarbons are activated by OH· without surface adsorption. More precisely, C₂H₄ adsorption is more favored than CH₄ due to the π-electrons of the unsaturated bond; therefore, C₂H₄ combusts faster on the surface. In fact, an isotopic labeling study confirmed that the ratio of conversion rates for C₂H₄/CH₄ were significantly higher for the surface O* pathway than for the OH·-mediated pathway.^{22,25} With OH·, C₂H₄ reacts relatively slower than CH₄, which faithfully reflects the C–H bond strength (CH₄ 439 kJ mol^{−1} vs. C₂H₄ 463 kJ mol^{−1}).

Recently, we conducted a simulation study utilizing a state-of-the-art gas phase chemistry mechanism to theoretically elucidate the OH· effect in the OCM reaction on the reaction rate and the C₂ selectivity.²⁶ The contribution of the catalyst in generating OH· to the chemistry set was perturbed by adjusting the preexponential factor *A* in the Arrhenius rate constant equation for **reaction 3**. The simulation successfully reproduced the profiles of different species in the OCM process conducted with Na-based catalysts. It also demonstrated that the overall C₂ species

selectivity in the system involving OH· generation mechanism (**reaction 3**) was much higher due to the favored formation of C₂H₆ from CH₃·, while the selectivity ratio of C₂H₄/C₂H₆ is much higher in the absence of the OH· mediated mechanism.

Apart from the transformation of methane into a C₂ hydrocarbon, increasing attention has been given to its further transformation into aromatics, including C₆H₆ via homogeneous pyrolysis in one-pot. In a non-oxidative environment, pyrolysis can transform CH₄ into liquid fuels and chemicals, and the product yields can be fine-tuned by controlling the temperature and the residence time.^{27, 28} At temperatures lower than 800 K, CH₄ is comparatively more stable compared than other hydrocarbons based on the Gibbs free energy of formation (ΔG_f).^{29–31} This thermodynamic constraint necessitates high temperature operation in order to achieve efficient production of viable chemicals, including C₂H₂, C₂H₄, and C₆H₆ via CH₄ pyrolysis.³² Among the reactions considered for CH₄ conversion, the direct aromatization of CH₄ is an endothermic process as shown in **reaction 4**. Many studies have achieved high C₆H₆ selectivity via direct aromatization of CH₄ with molybdenum (Mo)-containing zeolite catalysts,^{33–35} which however suffered from catalyst deactivation due to coke deposition. Recently, Guo et al. achieved the formation of C₂H₄, benzene, and naphthalene in almost equimolar amount with total hydrocarbon selectivity exceeding 99% at a CH₄ conversion of 48.1% using single iron site catalysts at ~1050 °C in a non-oxidative environment.³⁶ Although the detailed reaction pathway remains elusive, free radical chemistry is likely involved at such high temperatures. The existing problem comes from the endothermicity of the direct conversion of CH₄ to C₆H₆ (**reaction 4**), which significantly increases the costs of the operation.

In contrast, C_2H_4 trimerization to benzene is an exothermic reaction (**reaction 5**) and can occur in the gas phase at high temperatures in a non-oxidative environment while coproducing H_2 . In practice, the products by non-catalytic high-temperature pyrolysis of C_2H_4 include CH_4 , H_2 , C_3 , C_4 , and various aromatics due to unavoidable free radical chemistry. If the OCM process is coupled with dehydroaromatization of C_2H_4 , the production of C_6H_6 and H_2 from CH_4 becomes achievable via exothermic reactions throughout, thus potentially reducing heat supply.

In the present study, we built an exothermic CH_4 aromatization process by combining two steps, namely C_2H_4 formation from OCM and the subsequent C_2H_4 aromatization. The research goal is to investigate how much benzene could be formed with a single Na-based catalyst through the further homogeneous aromatization of OCM product, C_2H_4 , by extending residence time. This study therefore investigates single plug-flow reactor (PFR) modeling that achieves generation of aromatics and H_2 from CH_4 via combining the OCM and C_2H_4 transformation using the state-of-the-art detailed gas-phase chemical kinetic model. This study is based on the catalytic contribution via $\text{OH}\cdot$ generation in **reaction 3** (i.e., adding catalytic contribution as a gas-phase reaction) is used to improve OCM selectivity, which was extensively studied in our previous study.^{21–24,26} Then, the OCM products are transformed only in the homogeneous gas-phase reactions in the latter part of the PFR. Therefore, this approach quantitatively identifies gas-phase contributions to the product distribution in this $\text{CH}_4\text{-O}_2$ scheme, which makes this study unique compared to the previously-reported studies for the heterogeneous catalytic aromatization. Detailed simulations were conducted in order to identify the effects of temperature and reactant CH_4/O_2 ratio on the rate and product selectivity, and the reaction pathways were elucidated in detail for the C_6H_6 formation. An adiabatic operation that utilizes the reaction heat was considered in addition to the isothermal conditions. The data reported in

this study provide a description of temperature profiles across the reactor and consequent reaction performances and present a new possibility for CH₄ conversion.

2. Simulation protocol

The simulations performed in this study investigated the formation of products other than C₂H₄ (such as C₆H₆ and H₂) from the gaseous CH₄/O₂ mixtures (surface reactions were not included). The reaction mechanism included the formation of C₂ and C₃ products in addition to the molecular growth pathway to higher hydrocarbons (such as C₆H₆ and polycyclic aromatic hydrocarbons [PAHs]). The model contained all relevant PAH consumption pathways except for the soot inception mechanism. However, adding this mechanism would not greatly change the PAH concentration profiles.³⁷ Simulations were performed with CHEMKIN software [ANSYS CHEMKIN-PRO v. 17.2, 2018.] using the PFR module under both isothermal and adiabatic conditions at 1 atm pressure with varying residence times, temperatures, and CH₄/O₂ mixture compositions. Typically, the volumetric flow rate was fixed at 30 sccm with different inlet CH₄/O₂ molar ratios. The cross-sectional area of the PFR was set to be 1 cm². The total residence time was set by adjusting the reactor length (the starting and ending axial positions of the PFR), to ensure that the simulation period covered the post-O₂ depletion regime. The gas phase chemical kinetic model employed here was KAUST-Aramco PAH Mech 1-GS, KAM1-GS. The following paragraphs describe the kinetic model and boundary conditions in detail.

The chemical kinetic model KAM-GS utilized here was developed using a hierarchical approach^{38–40} and consists of 574 species and 3379 reactions. The kinetic model includes only the high-temperature chemistry relevant for processes above 800°C. Oxidation of small hydrocarbons is modeled by AramcoMech 1.3^{38,39} and includes updated propene sub-chemistry³⁹

reactions for hydrocarbon oxidation up to benzene.⁴⁰ PAH formation and growth up to A7 coronene are also included and were modeled using KAUST PAH mechanisms (KM1, KM2).⁴¹⁻
⁴³ Full details on the KAM1-GS chemical kinetic model and validation according to fundamental experiments are available in the literature.^{37,44}

To represent the quasi-equilibrated nature of OH· produced from the catalytic reaction in the OCM simulation (**reaction 3**), the contribution was explicitly included in the ChemKin simulation with the forward rate constant of $k_f = 10^{18}$. The detailed discussion on the kinetic contribution of OH· for OCM rates and selectivities can be found in our previous report,²⁶ and this study includes only the sufficiently-large contribution of this OH· contribution (see also Supporting Information).

The conversion of CH₄, the selectivity, and the yield of carbon-containing products were calculated as cumulative integral values on a carbon basis, and the selectivity and yield for H₂ were obtained on a hydrogen basis with the total hydrogen as converted CH₄:

$$X_{\text{CH}_4} (\%) = \frac{\text{total moles of carbon in products}}{\text{total moles of carbon in products} + \text{residual CH}_4 \text{ moles}} \times 100 \quad (6)$$

$$S_{\text{C-products}} (\%) = \frac{\text{moles of carbon in the specific product}}{\text{total moles of carbon in products}} \times 100 \quad (7)$$

$$S_{\text{H}_2} (\%) = \frac{\text{moles of H}_2}{2 \times (\text{total moles of carbon in products})} \times 100 \quad (8)$$

$$Y_{\text{product}} (\%) = X_{\text{CH}_4} (\%) \times S_{\text{product}} (\%) / 100 \quad (9)$$

3. Results and Discussion:

This study investigated OCM-generated aromatization of CH₄ via C₂H₄ as an efficient and economical process for CH₄ utilization. The CHEMKIN simulations were conducted isothermally in a PFR module with a CH₄/O₂ ratio of 6 at 1000°C. As mentioned in the introduction, selective OCM process is considered via quasi-equilibrated OH· formation in **reaction 3**. Such OCM processes were investigated in more detail in our previous study with a particular focus on the OH· effect on the OCM process (see also the product profiles without OH· chemistry [**reaction 3**] in Supporting Information, **Figure S1** and **Table S1**).²⁶ The resulting conversion and selectivity profiles with quasi-equilibrated OH· formation as a function of residence time are shown in **Figure 1a** and **a'** with **a'** showing magnified profiles of the region before the O₂ depletion point. The reactant conversion and product distribution at the maximum C₂H₄ yield and the maximum C₆H₆ yield points are summarized in **Table 1**. In the region before O₂ depletion (**Figure 1 a'**), oxidative coupling of CH₄ proceeded, and CH₄ conversion monotonically increased and reached 39% at the O₂ depletion point of 3.8 ms. As a primary product, CH₄ was converted into a methyl radical (CH₃·), which predominantly underwent the subsequent coupling process and formed C₂H₆. C₂H₆ selectivity reached its maximum of 80% within 1 ms residence time and then started decreasing with dehydrogenation to C₂H₄. The C₂H₄ selectivity increased monotonically and reached 53% with C₂H₆ and C₂H₂ selectivity of 17% and 5%, respectively, at the O₂ depletion point. Before O₂ depletion, CH₄ and the C₂ products were oxidized to form CO with a selectivity of 13%. In the non-oxidative region after the O₂ depletion point (**Figure 1a**), CH₄ conversion did not significantly change and remained at ~39%. C₂H₆ and C₂H₄ dehydrogenations continued and were subsequently transformed predominantly to various aromatics, reaching a selectivity of 75% in total. While a maximum C₆H₆ selectivity of 24% was

observed at 3 s, other PAHs at this point were pyrene, acenaphthalene, and benze(ghi)fluoranthene (*vide infra*) in addition to C₂H₄ (8%) and CO (14%). The dehydrogenation reaction yielded H₂, reaching a selectivity of 54% on an H-basis at the maximum C₆H₆ selectivity point.

C₂H₄ aromatization occurred when O₂ was no longer present in the system, and the C₂H₄ yield from the OCM process proved to be a critical factor that would determine the yield of C₆H₆ from the non-oxidative region. The optimization of reaction conditions (temperature and CH₄/O₂ ratio) is therefore critical because these conditions will affect both the OCM and the homogeneous ethylene aromatization steps. We first investigated the effects of different temperatures (700–1200°C) at a constant CH₄/O₂ ratio of 6, and the resulting product distribution at the point of the maximum C₆H₆ yield is compared in **Figure 2a**. CH₄ conversion continued to increase with increasing temperature, while CO selectivity decreased from 53% at 700°C to 10% at 1200°C. In contrast, C₂H₄ selectivity increased with increasing temperature, which remained <10%, consistent with the previous equilibrium calculation.⁴⁵ C₂H₂ selectivity also monotonically increased with temperature, achieving 20% at 1200°C. The selectivity of total aromatics first increased from 43% at 700°C to 74% at 1000°C and then decreased to 61% at 1200°C. In accordance with aromatic formation, H₂ selectivity also increased as a consequence of dehydrogenation at high temperatures.

Figure 2a' shows the detailed distribution of aromatic products at the point of maximum C₆H₆ yield at different temperatures. In the intermediate temperature range, aromatic product distribution was mainly dominated by C₆H₆ and pyrene. C₆H₆ selectivity was approximately 40% in the temperature range of 700 to 900°C, which decreased with a further increase in temperature. The increase in pyrene selectivity coincided with a decrease in C₆H₆ selectivity and

reached its peak values in the intermediate temperature range of 900 to 1000°C. Above these temperatures, pyrene selectivity decreased, while the selectivity toward acenaphthalene and benzo(ghi)fluoranthene became comparable to those for C₆H₆ and pyrene at 1100 to 1200°C. It is apparent that the carbon ring number and C/H ratio of the products increased with increasing temperature, leading to high affinity toward coke at high temperatures since PAHs are coke precursors.⁹ Pyrene itself is a component of the tar that forms during the hydrocarbon pyrolysis process.² Taken together, these results demonstrate that the relatively lower temperature may lead to higher achievable C₆H₆ selectivity without the formation of tar or coke, while the required residence time is substantial. In other words, if C₂H₂ is the target product, high temperatures are required but present the risk of tar and coke coproduction.

We now turn to the other critical factor of the reactant ratio (CH₄/O₂). Simulations at CH₄/O₂ ratios of 2, 3, 6, and 12 (1 atm and 1000°C isothermal) were conducted, and the obtained product distribution is compiled in **Figure 2b and b'**. With the increase in the CH₄/O₂ ratio, CH₄ conversion decreased while C₂H₄ selectivity increased. At the higher CH₄/O₂ ratio corresponding to the lower amount of O₂ introduced, the selectivity of total aromatics apparently increased (45% at ratio 2 vs. 81% at ratio 12). Among the total aromatics, C₆H₆ and pyrene were the main products at the investigated temperature (1000°C). The selectivity of C₆H₆ increased from 13% to 27% with the increase in CH₄/O₂ ratio from 2 to 12.

Based on the resulting product distribution at a variety of temperatures and CH₄/O₂ ratios, we visualized the maximum C₆H₆ yields as contour plots in **Figure 3a** as a function of the temperature and CH₄/O₂ ratio. Similar contour plots for the corresponding total aromatic and H₂ yields at the point of maximum benzene yield are also presented in **Figure 3b and c**, respectively. As discussed previously, CH₄ conversion increased with increasing temperature.

Accordingly, the maximum C_6H_6 and corresponding total aromatic yield first increased and then decreased with the temperature increase from 700 to 1200 °C. A higher CH_4/O_2 ratio caused an increase in the selectivity toward C_6H_6 and total aromatics, which concurrently decreased with the CH_4 conversion. As a result, the C_6H_6 and total aromatic yield increased with the decrease in CH_4/O_2 ratio from 12 to 2 due to the contribution of enhanced CH_4 conversion at the expense of the selectivity. The extent of dehydrogenation leading to the H_2 formation was enhanced at high temperatures and low CH_4/O_2 ratios as can be seen from **Figure 3c**. Among the investigated simulations, the maximum C_6H_6 yield (10%) at 1 atm under isothermal conditions was achieved at the CH_4/O_2 ratios between 3 and 6 and temperatures between 800 and 900 °C.

Thus far, the product distribution at the maximum C_6H_6 yield was discussed in detail. Focusing on CH_4 conversion and selectivity of C_6H_6 and pyrene, the way in which these values evolve as a function of the residence time is compared in **Figure 4** at different temperatures and CH_4/O_2 ratios. At a total pressure of 1 atm and a CH_4/O_2 ratio 6 (**Figure 4a**), CH_4 conversion increased in the oxidative region via the OCM process with the residence time and then slightly decreased after O_2 depletion due to CH_4 formation as a product of C_2H_4 pyrolysis. C_6H_6 and pyrene began to form when CH_4 conversion reached the peak value at the O_2 depletion point, and their selectivity increased with the decrease in CH_4 conversion. However, for the systems at temperatures >1000 °C, CH_4 conversion increased again at the extended residence time due to CH_4 pyrolysis, which is only operational at such high temperatures.⁴⁶ Selectivity toward C_6H_6 and pyrene in systems at 1000 to 1200 °C decreased because of the formation of PAHs with higher C/H ratios. Higher temperatures cause acceleration of the whole process and cause the maximum C_6H_6 selectivity to be achieved at a shorter residence time.^{47,48} At 800 and 900 °C, C_6H_6 selectivity did not reach its maximum value within the 10 s residence time. On the

contrary, for systems at 1000, 1100, and 1200°C, the maximum C₆H₆ selectivity and yield were achieved simultaneously at 3, 0.4, and 0.06 s, respectively. These observations unambiguously demonstrate the significance of controlling the residence time to achieve the maximum C₆H₆ yield in a practical manner.

For processes at 1000°C but at different CH₄/O₂ ratios (**Figure 4b**), the CH₄ conversion reached its maximum almost at the same residence time, and the residence time required to reach the maximum C₆H₆ or pyrene selectivity was similar. With more initial O₂ as the reactant, higher CH₄ conversion was achieved, while C₆H₆ or pyrene selectivity decreased accordingly because of CO formation. Taking the practical operation into consideration, 800 and 900°C isothermal conditions are not realistic since the maximum C₆H₆ yield was reached at a residence time of longer than 10 s (1 atm and CH₄/O₂ ratio 6). The use of an effective catalyst for aromatization or operating temperatures >1000°C are therefore more reasonable for a practical system.

The process of C₆H₆ formation from CH₄ through the extended OCM could be regarded as a combination of two steps: (1) C₂H₄ formation from the OCM and (2) C₆H₆ formation from C₂H₄ aromatization. Since the detailed reaction mechanism of the first OCM part was investigated in detail in our previous study, in this study, we focus here on the second step, that of C₂H₄ pyrolysis to aromatics. To this end, a reaction pathway analysis under a condition of 1100°C (isothermal), 1 atm, CH₄/O₂ ratio 6 at a residence time of 0.04 s (marked with * in **Figure 4**) was conducted, and the resulting brief free radical mechanism is shown in **Figure 5**. The corresponding elementary reactions are listed in **Table 2**. In the reaction pathway plot, red numbers in parentheses are used to denote the corresponding elementary reaction. Initially C₂H₄ was activated, forming C₂H₃· through an H-abstraction reaction via H· or CH₃·. The generated C₂H₃· further decomposed to form C₂H₂ and H·. Carbon growth reactions include C₂H₂ reacting

with propargyl radical ($C_3H_3\cdot$) to form cyclopentadienyl radical ($C_5H_5\cdot$), which further reacts with another C_2H_2 to form benzyl radical ($C_6H_5CH_2\cdot$) via a norbornadienyl intermediate.^{49,50} The benzyl radical further formed C_6H_6 via toluene. The other pathway of C_6H_6 formation was found to be initiated by C_2H_4 methylation to form C_3H_6 . C_3H_6 then formed allyl radical ($C_3H_5\cdot$) by an H-abstraction reaction. Subsequently, the allyl reacted with propargyl radical ($C_3H_3\cdot$), leading to benzene formation.⁵¹ This reaction was actually reported to go through fulvene ($C_5H_4CH_2\cdot$), which then isomerizes to C_6H_6 ⁵¹ although the current kinetic mechanism does not particularly include this elementary step, and rather includes a lumped reaction leading directly to benzene. The recombination of two propargyl radicals was also found to lead to benzene. CH_4 is formed as the product of the H-abstraction reaction from C_2H_4 , C_3H_6 , and C_6H_6 by $CH_3\cdot$, which explains the CH_4 conversion decrease after O_2 depletion in **Fig. 4** (a). In the reaction pathway plot, the black value on each arrow is the relative rate of production. The CH_4 formation from C_2H_4 activation by $CH_3\cdot$ is relatively ~ 10 times larger than those of C_3H_6 and C_6H_6 , indicating that C_2H_4 reverse formation to CH_4 dominates the CH_4 formation in the non-oxidative region.

To improve the energy efficiency of the reactor system, utilization of the reaction exothermicity is effective, taking the advantage of reaction heat to support the thermal energy. Therefore, in this study, we considered adiabatic processes (inlet temperature $600^\circ C$, reactant CH_4/O_2 ratio 6 and total pressure 1 atm). The conversion and selectivity profiles are plotted in **Figure 6**. In the region before O_2 depletion (**Figure 6a'**), the OCM proceeded with C_2H_4 , C_2H_6 , and CO as the main products, similar to the observation under isothermal conditions (**Figure 1a'**). As the reaction proceeded (which is apparent with O_2 consumption), the system temperature in addition to CH_4 and O_2 conversions increased, which were boosted to reach 32% and 100%, respectively, at ~ 1.35 s. At this residence time, the temperature increased to $\sim 1075^\circ C$.

After the O₂ depletion point, C₂H₄ pyrolysis proceeded in a manner similar to the trend in the system at 1000 °C under isothermal conditions. C₆H₆ and other aromatics were formed with C₂H₄ consumption. The reactant conversion and product distribution at the maximum C₂H₄ yield and the maximum C₆H₆ yield points are summarized in **Table 3**. After comparison of the compositions between the 1000°C isothermal system (**Table 1**) and the 600°C adiabatic system (**Table 3**), it became apparent that the CH₄ conversion and the product distributions were almost identical between these two systems. It is therefore concluded that the optimal performance a system can achieve is determined by the final temperature in the system rather than the inlet temperature.

To determine optimal product selectivity and yield, it is important to not focus on inlet temperatures, but rather on the adiabatic temperature achieved as a consequence of the exothermic reaction. The performance of an adiabatic system can be estimated by referring to that of an isothermal system at the post-boost temperature. The change of the temperature in adiabatic reactors with different inlet temperatures (1 atm, CH₄/O₂ ratio 6) was investigated and the profiles are shown in **Figure 7**. The temperature increased after the induction period in all of the systems; however, the temperature increase (temperature difference between inlet and maximum C₆H₆ yield point) and induction period length (residence time of O₂ depletion point) were different between systems with different inlet temperatures. Specifically, the systems with lower inlet temperatures had longer induction periods and larger temperature increases. Based on the above discussion, it can be inferred that H₂O and OH· accumulated during the induction period and boosted the OCM reaction, leading to the temperature increase as a result of heat generation (see also **Figure S2** for H₂O pressure effects). Therefore, systems with lower inlet temperature need longer induction times. The non-oxidative conversion of CH₄ to C₆H₆ is an

endothermic process due to the stability of CH_4 molecules. The introduction of O_2 into the feed replaces endothermic CH_4 aromatization with a totally exothermic process, with the combination of OCM (**reaction 2**) and the subsequent C_2H_4 aromatization (**reaction 5**). The generated heat would provide the temperature needed for the reaction to proceed in a reasonable rate.

4. Conclusions

The current simulation study indicated that CH_4 aromatization assisted by an O_2 cofeeding process at high temperatures proceeds as a combination of two steps: (1) C_2H_4 production via OCM through $\text{OH}\cdot$ -mediated pathway and (2) subsequent C_6H_6 formation via C_2H_4 aromatization, all in gas-phase reactions. Compared to the purely non-oxidative aromatization of CH_4 in the gas-phase, the yields for the aromatics were improved with the OCM reaction as a consequence of the enhanced C_2H_4 production. Among the investigated simulation data, the maximum C_6H_6 yield of $\sim 10\%$ under a total pressure of 1 atm was achieved at CH_4/O_2 ratios from 3 to 6 in an isothermal operation at 800 to 900°C. The introduction of O_2 into the feed made the entire process exothermic throughout the reactor, which raises the temperature of a reactor from 600°C at the reactor inlet to $\sim 1000^\circ\text{C}$ inside the reactor (1 atm and CH_4/O_2 of 6). Although introduction of O_2 into the feed provides exotherm via the reaction itself, this OCM assisted CH_4 aromatization process exhibited relatively lower hydrocarbon selectivity due to the introduction of O_2 and CO_x formation. Desired hydrocarbon selectivity also suffered from formation of various PAHs in the unselective gas phase regime. However, many potential solutions can contribute to decrease such disadvantage, e.g., by utilizing membrane to control the O_2 input and the utilization of a second-stage aromatization catalyst to more selectively transform C_2H_4 to valuable benzene, leaving them to future work.

Figure 1. Conversion and selectivity of different species as a function of residence time at 1000°C isothermal, 1 atm, and CH_4/O_2 6, catalytic contribution occurred by involving reaction 3 in the simulation chemistry set (a' shows the beginning of the reaction of a).

Figure 2. Product distribution at the maximum C₆H₆ yield point in systems (a, a') 700–1200°C isothermal, 1 atm, and CH₄/O₂ 6; (b, b') 1000°C isothermal, 1 atm, and CH₄/O₂ 2–12, catalytic contribution occurred by involving reaction 3 in the simulation chemistry set.

Figure 3. (a) C_6H_6 yield, (b) total aromatic yield and (c) H_2 yield at the maximum C_6H_6 yield point. 700–1200 $^{\circ}\text{C}$ (isothermal), 1 atm, CH_4/O_2 2–12, catalytic contribution occurred by involving reaction 3 in the simulation chemistry set.

Figure 4. CH₄ conversion and selectivity of benzene and pyrene as a function of residence time at (a) 800–1200 °C (isothermal), 1 atm, CH₄/O₂ 6, and (b) 1000 °C (isothermal), 1 atm, CH₄/O₂ 2–12. (black star * indicates the point used for pathway analysis in Figure 5).

Figure 5. Rate of production analysis and reaction pathways of the systems. (1100 °C isothermal, 1 atm, and CH₄/O₂ 6, 0.04 s, as indicated by * in figure 4). The black value is the relative rate of production of the specific transformation, elementary steps are indicated by the red No. value in parentheses and corresponds to Table 2.

Figure 6. Conversion and selectivity of different species as a function of residence time under 600 °C adiabatic, 1 atm, and CH_4/O_2 6 with catalytic contribution involved by involving reaction 3 in the simulation chemistry set.

Figure 7. Adiabatic system temperature profiles as a function of residence time with different inlet temperatures 400–800 °C (1 atm, CH₄/O₂ ratio 6).

Table 1

Reactant conversions and product distributions under the maximum C_2H_4 and C_6H_6 yields (1000°C isothermal, 1 atm, CH_4/O_2 6, catalytic contribution occurred by involving reaction 3 in the simulation chemistry set).

		C_2H_2	C_2H_4	C_2H_6	C_6H_6	T.A. ^a	H_2	CO_x	CH_4	O_2
Max. C_2H_4 yield	Yield (%)	2	26	2	1	1	11	5	39	100
	Selectivity (%)	5	67	5	2	3	27	14		
Max. C_6H_6 yield	Yield (%)	1	3	0	9	29	21	6	39	100
	Selectivity (%)	3	8	0	24	74	54	15		

^a T.A.: total aromatics

Table 2

Detailed elementary reactions for the pathway analysis at 1100 °C isothermal, 1 atm, and CH₄/O₂ 6, 0.04 s (as indicated by * in figure 4). The number of the elementary step correspond to the red values in parentheses in figure 5.

No.	Elementary step	No.	Elementary step
1	$C_2H_4 + H\cdot \rightarrow C_2H_3\cdot + H_2$	2	$C_2H_4 + CH_3\cdot \rightarrow C_3H_6 + H\cdot$
3	$C_2H_4 + CH_3\cdot \rightarrow C_2H_3\cdot + CH_4$	4	$C_3H_6 + CH_3\cdot \rightarrow C_3H_5\cdot + CH_4$
5	$C_2H_3\cdot + M \rightarrow C_2H_2 + H\cdot + M$	6	$C_3H_5\cdot + C_3H_3\cdot \rightarrow C_6H_6 + H_2$
7	$C_2H_2 + C_5H_5\cdot \rightarrow C_6H_5CH_2\cdot$	8	$C_6H_5CH_2\cdot + CH_4 \rightarrow C_6H_5CH_3 + CH_3\cdot$
9	$C_6H_5CH_2\cdot + H_2 \rightarrow C_6H_5CH_3 + H\cdot$	10	$C_6H_5CH_3 + H\cdot \rightarrow C_6H_6 + CH_3\cdot$
11	$C_3H_6 + H\cdot \rightarrow C_3H_5\cdot + H_2$	12	$C_3H_6 + M \rightarrow C_3H_5\cdot + H\cdot + M$
13	$C_6H_6 + CH_3\cdot \rightarrow C_6H_5\cdot + CH_4$		

Table 3

Reactant conversions and product distributions under the maximum C₂H₄ yield point and the maximum C₆H₆ yield point (adiabatic reactor, 600°C inlet temperature, 1 atm, CH₄/O₂ 6 with the catalytic contribution occurred by involving reaction 3 in the simulation chemistry set).

		C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₆ H ₆	T.A. ^a	H ₂	CO _x	CH ₄	O ₂	T/°C
Max. C ₂ H ₄ yield	Yield (%)	2	22	2	1	1	10	6	36	100	1020
	Selectivity (%)	6	63	5	1	2	27	18			
Max. C ₆ H ₆ yield	Yield (%)	1	3	0	8	26	20	7	37	100	1006
	Selectivity (%)	3	7	0	22	71	54	19			

^a T.A.: total aromatics

ASSOCIATED CONTENT

Supporting Information. Reaction profiles without OH $\cdot$ contribution Figure S1, Table S1;

Water addition effects on adiabatic reactor temperature profiles Figure S2.

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