Impact of OH radical generator involvement in the gas-phase radical reaction network on the oxidative coupling of methane - A simulation study

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Keywords: OH radical, simulation, reaction mechanism, oxidative coupling of methane, radical

The impact of OH· generation during the oxidative coupling of methane (OCM) was simulated using state-of-the-art gas-phase chemistry and a comprehensive chemical kinetic model. The inclusion of the quasi-equilibrated formation of OH· from a H₂O-O₂ mixture into the combustion chemistry network enhanced the CH₄ conversion rate and C₂ selectivity, consistent with the previously proposed mechanism involving catalytically generated OH·. The OH-pathway increased the CH₃· concentration resulting in an enhanced transformation rate from CH₃· to C₂H₆ (second-order in CH₃·) more than to CO (first-order in CH₃·). Relative to other H-abstracting radical species, the OH· weakened the sensitivity of the H abstraction rate constant to C-H bond energy, or lower $k_{\text{C}_2\text{H}_6} / k_{\text{CH}_4}$, which comparatively slows the C₂H₆ conversion rate relative to CH₄, thus enhancing C₂ selectivity. Concurrent dehydrogenation of C₂H₆ to C₂H₄ may maximize the C₂H₄ selectivity even after O₂ depletion. With the involvement of the OH·-mediated pathway, this study addresses the effects of

temperature and CH_4/O_2 ratio on the achievable C_2 selectivity and C_2H_4 yield. The maximum C_2H_4 yield reached 32% at a CH_4/O_2 ratio of 3, temperature of 1100-1200 °C, and total pressure of 1 atm.

1. Introduction

As petroleum resources become limited, there is increased economic incentive for the conversion of abundant low-value light alkanes (e.g., CH_4 in natural gas) into value-added commodities (e.g., C_2H_4 for use as polymer precursors).^[1-3] Indirect processes of C_2H_4 production from CH_4 exist in the industry (e. g., methane $\rightarrow$ syngas $\rightarrow$ methanol $\rightarrow$ ethylene). In these indirect processes, syngas ($\text{H}_2 + \text{CO}$) is first produced by CH_4 steam reforming, followed by methanol synthesis, which is then transformed to olefins through methanol to olefin (MTO) processing. Oxidative coupling of methane (OCM) technology involves the direct conversion of CH_4 to C_2H_4 and has great potential to become competitive to indirect processes. OCM has attracted considerable interest in both academia and industry.^[1-6] The catalytically driven OCM process was first reported by Keller and Bhasin in 1982.^[7] Exotherms of the reaction ($2\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$, $\Delta H^\circ = -280 \text{ kJ mol}^{-1}$) have great potential to decrease operation costs when effectively utilized. The OCM process is economically feasible only when CH_4 conversion is greater than 20% and C_{2+} hydrocarbons selectivity greater than 80%.^[8] Alternatively, combining the sequential reactor/separator scheme has been considered, in which, for example, O_2 addition was distributed through a membrane reactor or product was removed from the mixture in a recycle reactor.^[9-11] In addition to the efforts toward engineering a novel reactor design, efforts should be collected to investigate the fundamental mechanism underlying the OCM reaction and, therefore, improve process performance intrinsically.

It is commonly accepted that OCM proceeds via a complex homogeneous-heterogeneous reaction network.^[12-16] Accordingly, there are a large number of reports that

combine the gas-phase radical reaction chains with surface catalyzed elementary reactions.^[12–14,17] As a commonly accepted reaction scheme, the first step is to generate active surface oxygen species (O^*) by the chemisorption of O_2 on the catalyst surface.^[18] CH_4 reacts with O^* to generate $CH_3\cdot$, which dimerizes homogeneously in the gas phase to form C_2H_6 .^[17,19,20] The reaction continues with C_2H_4 formation via dehydrogenation of C_2H_6 .^[21] The C_2 products inevitably react to be oxidized or to form higher hydrocarbons (C_3 – C_4) that are oxidized more rapidly.^[22,23] Such competitive reactions of oxygen species with C_2 products, relative to with CH_4 reactant, essentially determine the maximum C_2 yields.^[23] Other approaches include varying the contributions of rate constants to surface reaction pathways, yet the variation remains arbitrary and, therefore, introduces some ambiguity.

Elementary gas-phase reactions involving hydrocarbon activation and radical transformation are direct concerns of combustion chemistry.^[24,25] There are some reports that combine the radical chemistry with elementary surface reaction to estimate achievable C_2 product yields.^[23,26–31] Early work by Labinger and Ott demonstrated the importance of including C_3 product reaction to reasonably describe the loss of product yield at high conversions.^[26] Mims et al. established the methodology of combining a reaction network of 447 elementary gas-phase reactions together with some representative heterogeneous reactions to explain the measured distribution of the products.^[27] Their isotopic tracer study was effectively utilized for describing product distribution for C_2 and higher C_3 and C_4 hydrocarbons. Su et al. developed an approach to perturb some elementary reaction rates of the specific radical contribution, such as unselective $HO_2\cdot$ oxidant by selective quenching, where an upper bound for C_2 yield of 28% existed for the OCM process.^[28] Kechagiopoulos et al. developed a microkinetic model involving 39 gas phase and 26 catalytic elementary reactions. The effect of mass transfer phenomena inside the porous catalyst and catalyst textural properties on OCM performance were fully investigated, with the conclusion that the majority of molecule and radical conversions were contributed by catalysts.^[29] Karakaya et al.

demonstrated the simulation of the combined homogeneous-heterogeneous reaction network to reproduce experimental results obtained by Mn/Na₂WO₄/SiO₂ catalysts^[30] and La₂O₃/CeO₂ catalysts^[31] under non-isothermal conditions. Although the above-mentioned reaction simulations have had some success to describe to some degree, there still remains some ambiguity to account for the measured yield and selectivity.

Recently, several studies have proposed distinctive reaction mechanisms that may be able to predict the OCM reaction network: i.e., hydroxyl radicals (OH·) generated from O₂/H₂O mixture catalytically play a critical role in increasing both the OCM rate and the C₂H₄ selectivity.^[3,32–35] Since H₂O is one of the major products, a careful kinetic study was necessary to reveal this effect. Initially, using a Mn/Na₂WO₄/SiO₂ catalyst, the CH₄ conversion rate and C₂ selectivity increased with increasing H₂O partial pressure, according to the following simplified rate expression (**Equation 1**).^[32,33]

$$r = r_{O^*} + r_{OH\cdot} = k' P_{CH_4} P_{O_2}^{1/2} + k'' P_{CH_4} P_{O_2}^{1/4} P_{H_2O}^{1/2} \quad (1)$$

The first term corresponds to the CH₄ activation by surface active oxygen atoms (O*), which is in quasi-equilibrium with gas phase O₂. The second term corresponds to OH· induced CH₄ activation, in which OH· is in quasi-equilibrium with H₂O and O₂ (**Equation 2**).

This H₂O effect was further evident when the formed H₂O was continuously removed from the recirculating system during the OCM reaction, resulting in significant drops in the CH₄ conversion rate and C₂₊ selectivity.^[32] These results confirm that surface mediated pathways are unselective to OCM compared to the OH· mediated pathway at all conversion levels. The applicability of Equation 1 is only at the low conversion end; the kinetic regime switches to O₂ chemisorption limiting step (first order in O₂ partial pressure) at high conversion levels.^[33] Later, it was found that this H₂O effect was operational with alkali metals containing catalysts (Na and K), while Mn, W, or SiO₂ were not essential components for evidencing the OH·

pathway.^[34] Using *in situ* X-ray photoelectron spectroscopy, Na₂O₂ active species were identified under these reaction conditions.^[35] This peroxide species was deemed responsible for CH₄ activation^[36,37] but it actually catalyzes the selective activation of H₂O rather than CH₄, leading to the quasi-equilibrated nature of Equation 2.^[35] Maximizing the contribution from the OH· pathway relative to that from the surface O* pathway using Na₂WO₄/SiO₂, a 25% C₂₊ yield was experimentally achieved in a single reactor and 28% C₂₊ yield with successive reactors upon O₂ addition. In this context, C₂H₄ yields as high as 31% were experimentally achieved using NaCl addition to Mn/Na₂WO₄/SiO₂ catalysts but stability became an issue due to continuous loss of NaCl.^[10]

For the OH· mediated pathway, H₂O, rather than CH₄, is activated on the catalyst surface by O* (or peroxide) and forms OH·,^[35,38–40] which is released into the gas phase. In this way, the activation of hydrocarbon molecules happens in the gas phase, rather than on the catalyst surface, by the H-abstraction reaction of OH·. In the previous study, Lunsford et al. detected OH· in the gas phase from O₂/CH₄ or O₂/H₂O mixture over the basic metal oxide surfaces (e.g., La₂O₃ and Nd₂O₃, etc.) using laser-induced fluorescence spectroscopy.^[38–40] When O₂/H₂O were reactants, OH· was formed to reach equilibrium. It was stated that OH· played an important role in CH₄ combustion by generating more CH₃· but this beneficial effect was balanced by the formation of more CO_x via secondary reactions.^[39] More recently, OH· formation from H₂O/O₂ mixture was also evident over Na-based catalysts at high temperatures.^[35] Improvement of C₂ selectivity by OH· generation was explained multifold: here we focus on two main contributions. One reason for C₂ selectivity improvement is that the C₂H₆ conversion rate get slower relative to the CH₄ reaction rate because the highly reactive OH· compared to other H-abtractors weakens the effect of C-H bond energies on H-abstraction reaction rates (CH₄ 439 kJ mol⁻¹ vs. C₂H₆ 423 kJ mol⁻¹).^[2,32,33] The other important contribution of the OH· pathway is that the OCM reaction proceeds without the necessity of hydrocarbon adsorption: obviously, C₂H₄ adsorption is preferred over CH₄ due to

π -electrons of the unsaturated bond, thereby C_2H_4 combusts faster on the surface. The ratio of conversion rates for $\text{C}_2\text{H}_4/\text{CH}_4$ is indeed much higher for the surface O^* pathway than for the $\text{OH}\cdot$ mediated pathway, confirmed by an isotopic labeling study.^[22,33] In fact, C_2H_4 reacts relatively slower than CH_4 with $\text{OH}\cdot$ reflecting the C-H bond strength (CH_4 439 kJ mol^{-1} vs. C_2H_4 463 kJ mol^{-1}).

The current study explicitly elucidates the impact of $\text{OH}\cdot$ inclusion into the state-of-the-art gas phase chemistry on OCM rate and selectivity. In this study, an ideal situation is assumed where the catalytic generation of $\text{OH}\cdot$ is constantly at quasi-equilibrium: i.e., the catalyst works merely as an ideal $\text{OH}\cdot$ generator. The extent of $\text{OH}\cdot$ involvement was assessed by arbitrarily varying the rate constant of Reaction 2. Under such conditions, detailed simulations were conducted to identify the effects of different factors, such as CH_4/O_2 ratio and temperature on the OCM reaction network. The inclusion of $\text{OH}\cdot$ generation was found to improve OCM rate and selectivity, accounting for the previously reported beneficial effects of the $\text{OH}\cdot$ pathway. The reasons for its promoting capabilities are also discussed.

2. Results and Discussion

In the OCM simulation, the contribution of $\text{OH}\cdot$ produced from the catalytic reaction was explicitly included in the aforementioned gas-phase reaction mechanism used for CHEMKIN simulations. The Arrhenius-type expression was used to describe the reaction rate constant, k_f , as shown in **Equation 3**.

$$k_f = AT^m \exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

A , T , m , R and E_a represent the preexponential factor, temperature (K), temperature dependence factor, gas constant and activation energy (J), respectively. Although effective rate inclusion with appropriate kinetic parameters for OH radical generation is desired, there is no experimental data available to date. Instead, by changing the preexponential factor, the

contribution of the catalyst in generating $\text{OH}\cdot$ to the radical chemistry set was perturbed. For simplicity, m and E_a were both taken as zero. In this study, the preexponential factor A was varied from 10^{12} to 10^{18} to investigate the effect of $\text{OH}\cdot$ contribution on OCM performance.

The OCM processes were simulated utilizing an isothermal PFR reactor model at 800 °C and various $\text{OH}\cdot$ generation mechanism contributions. The system pressure was set at 1 atm with a CH_4/O_2 ratio 6. The achievable maximum CH_4 conversions as a function of preexponential factors, A , are shown in **Figure 1 (a)**. The CH_4 and O_2 conversion as a function of the residence time with various $\text{OH}\cdot$ generation contributions are presented in **Figure 1 (b)**. Without $\text{OH}\cdot$ generation mechanism involved ($A = 0$), i.e., pure homogeneous combustion reaction, the CH_4 reached a steady-state conversion of 19% at 10 seconds and the corresponding O_2 conversion was 98%. When the $\text{OH}\cdot$ generation mechanism was incorporated, the CH_4 and O_2 conversion rates improved drastically. With the $\text{OH}\cdot$ generation reaction preexponential factor set at 10^{12} , the CH_4 steady state conversion reached 24% at 1.4 s and O_2 was completely consumed. When the preexponential factor was further increased to 10^{16} and 10^{18} , the CH_4 and O_2 conversion rates were further enhanced. However, the beneficial effects of $\text{OH}\cdot$ generation mechanism on CH_4 and O_2 conversion rates did not change apparently with A increased from 10^{16} to 10^{18} , indicating that the $\text{OH}\cdot$ effect on CH_4 and O_2 conversion rates were approaching full saturation relative to other elementary reactions. The enhancement of OCM rate by the contribution of $\text{OH}\cdot$ has also been observed experimentally.^[3,32–34] In the kinetic analysis of OCM with alkali-metal-based catalysts ($\text{Na}_2\text{WO}_4/\text{SiO}_2$, $\text{Na}_2\text{MoO}_4/\text{SiO}_2$, $\text{K}_2\text{WO}_4/\text{SiO}_2$) by Liang et al.,^[34] the incremental rates of CH_4 conversion between H_2O -present and H_2O -absent fit well with the mechanism that CH_4 is activated by the quasi-equilibrated $\text{OH}\cdot$ from a $\text{H}_2\text{O}/\text{O}_2$ mixture (Equation 1). The highly active $\text{OH}\cdot$ propagates in the system and attacks the CH_4 molecules, which accelerates the CH_4 molecules activation and increases the OCM reaction rates.

The C_2 selectivity and yield ($C_2H_6 + C_2H_4$) from the same simulation are shown in **Figure 1 (c)**. In the low conversion range, C_2 selectivity reached its peak value and then decreased gradually. The C_2 selectivity (at all CH_4 conversions) improved with increasing $OH\cdot$ generation mechanism contribution. When $OH\cdot$ generation mechanism was excluded, the maximum C_2 selectivity was 57% with CH_4 conversion at 1.8%. With $OH\cdot$ generation mechanism involved, and A set at 10^{14} , the maximum C_2 selectivity increased to 77.8% with CH_4 conversion 3.5%. When the contribution of $OH\cdot$ was further increased with A set at 10^{16} to 10^{18} , the maximum C_2 selectivity were 87.1% (CH_4 conversion 0.76%) and 89.3% (CH_4 conversion 0.51%), respectively. For the yield of C_2 , it was enhanced apparently with A increased from 0 to 10^{13} . However, when A was further increased from 10^{13} to 10^{18} , the C_2 yield did not change significantly, due to the saturation of $OH\cdot$ quasi-concentrations at the steady state. With simulation conditions set as 800 °C isothermal, 1 atm and CH_4/O_2 6, the maximum C_2H_4 yield was 17.3% at CH_4 conversion 28.9%.

To understand the species concentration changes along the catalyst bed, CHEMKIN simulations were utilized. In the simulation, CH_4 and O_2 with ratio 6 was introduced as the reactant into a PFR, and the system was set as isothermal at 800 °C and total pressure of 1 atm. The simulated concentration profiles of major species for extreme A of 10^{18} are shown in **Figure 2 (a) and (a')**, with (a) as the enlarged view of the first 0.1 s resident time period. Oxygen was completely consumed within 0.079 s, which was the beginning of the OCM process. In the reaction period before O_2 depletion point, $OH\cdot$ generation from H_2O/O_2 mixture proceeds. In the practical OCM process, the main function of the catalyst is assumed to catalytically generate $OH\cdot$ from the H_2O/O_2 mixture according to Reaction 2. Therefore, the reaction period before O_2 is depleted is treated as catalytic region, while the region after O_2 depletion happens in gas phase regardless of the presence of catalyst, where $OH\cdot$ generation from H_2O/O_2 mixture does not occur. In the catalytic region, CH_4 was continuously converted and achieved 29% conversion at the O_2 depletion point. The $CH_3\cdot$

selectivity first increased to 50% as the product of CH_4 activation, and then dropped to almost 0 quickly, with the formation of C_2H_6 and CH_2O . The selectivity of CH_2O increased to 36% and then decreased. In practical experiment, $\text{CH}_3\cdot$ and CH_2O are deemed to quickly transform to either C_2H_6 or CO to be detected, due to their high reactivities. The concentration of C_2H_6 first increases because of the coupling of the $\text{CH}_3\cdot$ and then decreases with C_2H_4 concentration increasing simultaneously, due to the dehydrogenation of C_2H_6 to C_2H_4 . In the O_2 -depleted region (Figure 2 (a')), C_2H_6 selectivity decreased drastically to around 3%, while the C_2H_4 selectivity increased and reached its peak value (58%) at 4 s, and then decreased slowly. In this case, the maximum C_2H_4 selectivity was achieved after O_2 depletion, utilizing the non-oxidative portion of the reactor. However, at much greater residence time, the C_2H_4 would be further transformed to other hydrocarbons (e.g. C_2H_2 and aromatics), which would decrease C_2H_4 selectivity. The detailed information about further transformation of C_2H_4 is out of the scope of this article, but the simulation results in this work suggests that the OCM process should be carefully designed to provide optimum non-oxygen gas phase reaction range, which can maximize C_2H_4 yield. H_2 was formed and reached 20% selectivity at the maximum C_2H_4 yield point.

The selectivity of every major species as a function of residence time in the isothermal system in the absence of $\text{OH}\cdot$ generation mechanism is shown in **Figure 2 (b) and (b')** for comparison. The maximum C_2H_4 selectivity was achieved before the complete O_2 consumption point. It is apparent that within the same residence time, the system with $\text{OH}\cdot$ generation has a higher selectivity for C_2H_4 and H_2 compared to the system without $\text{OH}\cdot$ mechanism. Also, the selectivity of CO was relatively lower with the contribution of the $\text{OH}\cdot$. **Figure 2 (c) and (d)** show the species selectivity as a function of the CH_4 conversion under isothermal conditions with the presence and absence of $\text{OH}\cdot$ generation mechanism. In both cases, C_2 selectivity decreases with increasing CH_4 conversion. However, under the same CH_4 conversion, the system involving $\text{OH}\cdot$ generation mechanism has greater C_2 selectivity.

OCM at different temperatures from 700 °C to 1200 °C and different CH₄/O₂ ratios varied from 2 to 12 were simulated under isothermal conditions with the presence ($A = 10^{18}$) and the absence of OH· generation mechanism. As shown in **Figure 3 (a) and (b)**, in all cases, the maximum yield of C₂H₄ and its selectivity at this point were higher when OH· generation was included (solid lines) compared to when that reaction was absent (dash lines). In Figure 3 (a), with CH₄/O₂ 12, the C₂H₄ selectivity and yield were higher with the OH· mechanism, 69% and 13%, respectively, compared to without it, 40% and 4%, respectively. When the CH₄/O₂ ratio decreased, the performance enhancement contribution from OH· also decreased. As shown in Figure 3 (b), the C₂H₄ selectivity and yield increments by the OH· were 31% and 23%, respectively, under 1200 °C. At 800 °C, the C₂H₄ selectivity and yield enhancements were only 22% and 11%, respectively. The enhancement from the OH· generation mechanism was more apparent at higher reaction temperature.

In the same simulation, the result for maximum C₂H₄ yield is represented in **Figure 3 (c)** as a contour figure. C₂H₄ selectivity increased with increasing reaction temperature. As explained in the literature,^[23] the selectivity difference at high temperatures (higher thermal energy from the system and thus more vigorous molecule thermal movement) is because the selectivity to H-abstraction reaction from different hydrocarbons becomes less sensitive to difference in the reaction activation energy, E_a . As a result, the stable CH₄ molecules with large C-H bond energy would be relatively more favored for activation compared to C₂H₆ at higher temperatures. From 1000 °C to 1200 °C, the C₂H₄ selectivity decreased because of the successive transformation of C₂H₄ to C₂H₂ and C₃₊ products. The higher CH₄/O₂ ratio increased the C₂H₄ selectivity, yet naturally decreasing CH₄ conversion. Therefore, C₂H₄ yield increased with lowering the CH₄/O₂ ratio from 12 to 2 by increasing the CH₄ conversion at the sacrifice of the selectivity. Within the simulation range under total pressure 1 atm, the maximum C₂H₄ yield (32%) is achieved with CH₄/O₂ 3 and temperature 1100 °C (C₂H₄ selectivity 52%) to 1200 °C (C₂H₄ selectivity 48%) isothermal.

Reaction pathway analysis was conducted for both the reaction systems with the presence ($A=10^{18}$) and absence ($A=0$) of the $\text{OH}\cdot$ generation mechanism. The simulation conditions were 800 °C isothermal, 1 atm and CH_4/O_2 6. The reaction pathways at 50% O_2 conversion are presented in **Figure 4**. Generally, the reaction pathways were similar in both systems. CH_4 molecules were first activated and form $\text{CH}_3\cdot$, and the formed $\text{CH}_3\cdot$ recombined and formed C_2H_6 .^[41] C_2H_6 would further go through successive H-abstraction reactions and finally formed $\text{C}_2\text{H}_3\cdot$ through C_2H_4 , which is consistent with the C_2H_6 oxidation pathway concluded from previous experimental observation in heterogeneous case.^[22] CH_2O was also formed from the oxidation of $\text{C}_2\text{H}_3\cdot$ by O_2 , which eventually transformed to CO. However, for the activation of hydrocarbons (CH_4 , C_2H_6 , C_2H_4), the responsible radical species and their relative contributions were different (as shown in **Table 1**). For the activation of CH_4 , $\text{OH}\cdot$ and $\text{H}\cdot$ were the two main radical species. In the system that incorporated $\text{OH}\cdot$, the extent of $\text{OH}\cdot$ contribution was enhanced, which result in different product distribution. For C_2H_6 activation, the main responsible radical species were $\text{OH}\cdot$, $\text{CH}_3\cdot$ and $\text{H}\cdot$. In the system without $\text{OH}\cdot$ mechanism, $\text{CH}_3\cdot$ accounted for 77% with $\text{OH}\cdot$ at only 6%. However, the involvement of $\text{OH}\cdot$ generation mechanism increased the contribution of $\text{OH}\cdot$ in C_2H_6 activation to 36% and decreased $\text{CH}_3\cdot$ contribution to 40%. The situation for C_2H_4 activation was the same, in which $\text{OH}\cdot$ contributed 92% in the system incorporated with $\text{OH}\cdot$ generation mechanism but only 38% in the other system. Even though the involvement of $\text{OH}\cdot$ generation mechanism did not change the OCM reaction pathway, it did change the responsible radical species and their contributions as well as the magnitude of reaction flues, which would therefore influence the selectivity of C_2 products.

The initial step of CH_4 conversion was to generate $\text{CH}_3\cdot$, which then undergoes recombination to form C_2H_6 or oxidation to become CO. To analyze the initial selectivity, the $\text{C}_2\text{H}_6/\text{CO}$ ratio of rate of production (ROP; differential rate at each point) is plotted in **Figure**

5. During the initial stage of the OCM process, with dry CH_4 and O_2 as reactant feed, the analysis shows that CH_4 is activated by O_2 and form $\text{CH}_3\cdot$ and $\text{HO}_2\cdot$. The formed $\text{CH}_3\cdot$ would further react with O_2 and form CH_2O and $\text{OH}\cdot$. The $\text{OH}\cdot$ would proceed H-abstraction reaction with CH_4 and form H_2O . The formed H_2O would react with O_2 and produce $\text{OH}\cdot$ according to equation 2, which becomes the dominant pathway to activate hydrocarbons. After this common initial stage, it is apparent that the ROP ratio for $\text{C}_2\text{H}_6/\text{CO}$ with $\text{OH}\cdot$ generation mechanism was much higher than that without $\text{OH}\cdot$ generation mechanism, indicating that during the initial stage of OCM process (CH_4 conversion lower than 1%), the CH_4 was more converted to C_2H_6 rather than CO by the contribution of $\text{OH}\cdot$, which increases the selectivity of C_2 products in general. The recombination of $\text{CH}_3\cdot$ to C_2H_6 is the second order to $\text{CH}_3\cdot$ species, and the conversion of $\text{CH}_3\cdot$ to CO is first order to $\text{CH}_3\cdot$ species. CH_4 is activated more rapidly to increase steady-state $\text{CH}_3\cdot$ concentration, resulting in the increased ROP $\text{C}_2\text{H}_6/\text{CO}$ ratio.^[32–34] In the OCM study conducted by Labinger and Ott by both calculation and experiments, C_2H_6 and CO_2 were found to be main products under low CH_4 conversion ($< 5\%$). The C_2H_6 selectivity kept increasing with higher CH_4 pressure, which was also caused by the increased $\text{CH}_3\cdot$ concentration and the second order property of $\text{CH}_3\cdot$ recombination reaction.^[26]

The $\text{OH}\cdot$ induced H-abstraction reactions are exothermic owing to formation of stable H_2O product. According to the free energy relationship, these H-abstraction reactions by $\text{OH}\cdot$ are less sensitive to the difference of C-H bond energies in different hydrocarbons, compared with H-abstraction reactions using other general radicals.^[2,23,32,42] According to the DFT calculation by Deshlahra and Iglesia concerning the effect of hydrocarbon's C-H bond dissociation energy (BDE) and of abstractor's H association energy (HAE) on C-H bond activation energy for oxidative dehydrogenation in series of alkanes, stronger H-abstractor (more negative HAE) would decrease the C-H bond activation energy, which would

determine the rate constant ratio for activation of reactants and products in sequential oxidative dehydrogenation reactions.^[43] In this context, **Figure 6 (a)** shows the ratios of rate constants, $k_{\text{C}_2\text{H}_6} / k_{\text{CH}_4}$ and $k_{\text{C}_2\text{H}_4} / k_{\text{CH}_4}$, for H-abstraction reactions in gas phase with different H-atom abstractors ($\text{R}\cdot$) calculated at 800 °C.^[27] The value of $k_{\text{C}_2\text{H}_6} / k_{\text{CH}_4}$ was always greater than unity, and $k_{\text{C}_2\text{H}_4} / k_{\text{CH}_4}$ was always less than unity, which faithfully reflects the fact that stronger C-H bonds are harder to activate (CH_4 : 439 kJ mol⁻¹; C_2H_6 : 423 kJ mol⁻¹; C_2H_4 : 463 kJ mol⁻¹). However, $k_{\text{C}_2\text{H}_6} / k_{\text{CH}_4}$ decreases and $k_{\text{C}_2\text{H}_4} / k_{\text{CH}_4}$ increases (both change towards unity) as the H-abstraction reaction product, RH , becomes more stable, indicating the non-sensitivity of the reaction rates on C-H energies, which is the same as the competitive homogeneous oxidation of CH_4 and HCHO .^[44] The $\text{OH}\cdot$ leads to the lowest $k_{\text{C}_2\text{H}_6} / k_{\text{CH}_4}$ ratio and highest $k_{\text{C}_2\text{H}_4} / k_{\text{CH}_4}$. With the contribution of $\text{OH}\cdot$, C_2H_4 is activated much faster with a higher rate constant, while the activation rate of C_2H_6 decreases, leading to the simulation result that $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ selectivity ratio is lower in system with $\text{OH}\cdot$ generation mechanism (2.3) as shown in **Figure 6 (b)**. Labinger and Ott also simulated the OCM process by 12 elementary reactions on catalyst surface and in gas phase. The loss of C_2 products by $\text{CH}_3\cdot$ activation reactions were involved and $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ selectivity ratio 2.6 was calculated, which fits quite well with this simulation result.^[26] However, the overall C_2 selectivity was larger in the system with $\text{OH}\cdot$ generation mechanism due to the favored generation of C_2H_6 .

Finally, the obtained simulation results are compared with experimental data previously published. On the $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst at the low conversion level (<5%), the C_2 selectivity reaches ~90% (800 °C, 10 kPa CH_4 , $\text{CH}_4/\text{O}_2/\text{H}_2\text{O} = 6/1/0.7$),^[34] which is the similar value to the simulation presented in this study. This consistency suggests that the simulation well reproduces the experimental result when the products are not present at high pressures. The deviation from the experimental data however becomes apparent at high conversions. The reported highest C_2H_4 and C_2 yields were 17.7 % and 23.5 %, respectively

(880 °C, 10 kPa CH₄, CH₄/O₂/H₂O = 3/1/0.7).^[34] The current simulation at 900 °C gives ~25% C₂H₄ yield at total 101 kPa, CH₄/O₂ 3 (Figure 3). In the current simulation where ideal quasi-equilibrated OH radical generation is assumed, consumption of C₂ products is much slower than that of CH₄. This is apparent when the ratio, e.g., $k_{\text{C}_2\text{H}_4} / k_{\text{CH}_4}$, is compared between the simulation and measurement. The simulation gives the $k_{\text{C}_2\text{H}_4} / k_{\text{CH}_4}$ ratio lower than the unity regardless of counter radical species, reflecting the order of C-H bond strength, as discussed previously (Figure 6a). In practice, the surface pathway leads to combustion of C₂H₄ much faster than the gas-phase OH radical pathway, typically giving the $k_{\text{C}_2\text{H}_4} / k_{\text{CH}_4}$ ratio of >3.^[54] It is reasonable to consider that C₂H₄ reacts faster on the surface owing to the high sticking coefficient to the surface because of the presence of π -electrons, compared to saturated hydrocarbons. As conversion increases, this unavoidable surface transformation is appreciated, especially at higher temperatures (activation energy is larger for the surface pathway than for the gas-phase pathway)^[33] deviating from the simulation presented in this study. This surface combustion pathway is also applicable to higher hydrocarbon generated through transformation of C₂ products, which then combusts much faster.^[33] In this simulation study, the detailed analysis of C₃₊ products (propane, benzene, etc.) were not investigated, however, they are important commodities that influence the economy of the OCM process, which should be considered as a future study.

3. Conclusion

The involvement of OH· generation reaction in a CH₄/O₂ mixture improved both the CH₄ conversion rate and C₂ selectivity in the OCM reaction from the simulation of CHEMKIN with a state-of-the-art gas phase chemical kinetic model. The O₂ is completely consumed at the beginning of the process, and C₂H₄ selectivity reaches a maximum value after O₂ depletion. Within the simulation range under a total pressure of 1 atm, the maximum C₂H₄ selectivity,

which is 74%, is achieved with CH_4/O_2 12 and temperature 900 °C (CH_4 conversion 22%) to 1000 °C (CH_4 conversion 25%) isothermal. Under the conditions of CH_4/O_2 of 3 and fixed temperature of 1100 °C (C_2H_4 selectivity 52%) to 1200 °C (C_2H_4 selectivity 48%), the maximum C_2H_4 yield (32%) is achieved. With $\text{OH}\cdot$ mechanism included, CH_4 is more preferentially converted to C_2H_6 rather than CO , which in general enhances the C_2 selectivity of the OCM process. Since the $\text{OH}\cdot$ weakens the sensitivity of H-abstraction reaction rate on C-H bond energy, the C_2 product ratio $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ is much higher with the absence of $\text{OH}\cdot$ mechanism. However, the overall C_2 species selectivity in the system that incorporated the $\text{OH}\cdot$ generation mechanism is much higher due to the favored formation of C_2H_6 from $\text{CH}_3\cdot$.

4. Simulation protocol

The simulations performed in this study investigate the effect of gas-phase OH radical on the reactivity of gaseous CH_4/O_2 mixtures (i.e., surface reactions are not included). The primary discussion in this work focuses on the yield of CO_x and C_2 species but the reaction mechanism also includes the formation of C_3 and higher hydrocarbons (e.g., aromatics) for completeness. Simulations were performed in CHEMKIN [ANSYS CHEMKIN-PRO v. 17.2, 2018.] using the isothermal plug flow reactor (PFR) module. Simulations were conducted at 1 atm pressure with varying residence times, temperatures, and CH_4/O_2 mixture compositions. The gas-phase chemical kinetic model employed here is the (KAUST-Aramco PAH Mech 1-GS, KAM1-GS). The following paragraphs describe the kinetic model and boundary conditions in detail.

The chemical kinetic model KAM1-GS utilized here was developed using a hierarchical approach^[45] and consists of 574 species and 3379 reactions. The kinetic model includes only high-temperature chemistry relevant for processes above 800 °C. The oxidation of small hydrocarbons is modeled by AramcoMech 1.3^[46] including updated propene sub-

chemistry^[47] and reactions for hydrocarbon oxidation up to benzene^[48]. The formation and growth of polycyclic aromatic hydrocarbons (PAHs) is modeled using KAUST PAH mechanisms (KM1, KM2).^[49–51] Full details on the KAM1-GS chemical kinetic model and validation against fundamental experiments are available in the literature.^[52,53]

The CH₄ conversion, selectivity and yield of carbon-containing products are based on a carbon basis as cumulative integral values. The selectivity and yield of H₂ are based on a hydrogen basis utilizing the total hydrogen amount in converted CH₄ as the basis:

$$X_{\text{CH}_4} (\%) = \frac{\text{total moles of carbon in products}}{\text{total moles of carbon in products} + \text{residual CH}_4 \text{ mole}} \times 100 \quad (4)$$

$$S_{\text{C-products}} (\%) = \frac{\text{moles of carbon in the specific product}}{\text{total moles of carbon in products}} \times 100 \quad (5)$$

$$S_{\text{H}_2} (\%) = \frac{\text{moles of H}_2}{2 \times (\text{total moles of carbon in products})} \times 100 \quad (6)$$

$$Y_{\text{product}} (\%) = X_{\text{CH}_4} (\%) \times S_{\text{product}} (\%) / 100 \quad (7)$$

Acknowledgements

This work was partly supported by MHI Innovation Accelerator LLC. The authors are sincerely grateful for the valuable discussion with Drs. Tatsuya Shinagawa and Bhavin Siritanaratkul for fruitful discussion.

Received: ((will be filled in by the editorial staff))

Revised: ((will be filled in by the editorial staff))

Published online: ((will be filled in by the editorial staff))

References

- [1] A. Palermo, J. P. Holgado Vazquez, R. M. Lambert, *Catal. Lett.* **2000**, 68, 191–196.
- [2] J. A. Labinger, *J. Mol. Catal. A Chem.* **2004**, 220, 27–35.
- [3] K. Takanabe, *J. Japan Pet. Inst.* **2012**, 55, 1–12.
- [4] J. H. Lunsford, *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 970–980.

- [5] J. A. Labinger, K. C. Ott, S. Mehta, H. K. Rockstad, S. Zoumalan, *J. Chem. Soc., Chem. Commun.* **1987**, 543–545.
- [6] A. Galadima, O. Muraza, *J. Ind. Eng. Chem.* **2016**, 37, 1–13.
- [7] G. E. Keller, M. M. Bhasin, *J. Catal.* **1982**, 73, 9–19.
- [8] M. J. Gradassi, N. Wayne Green, *Fuel Process. Technol.* **1995**, 42, 65–83.
- [9] I. P. Androulakis, S. C. Reyes, *AIChE J.* **1999**, 45, 860–868.
- [10] E. M. Cordi, S. Pak, M. P. Rosynek, J. H. Lunsford, *Appl. Catal., A* **1997**, 155, L1–L7.
- [11] V. Fleischer, P. Littlewood, S. Parishan, R. Schomäcker, *Chem. Eng. J.* **2016**, 306, 646–654.
- [12] M. Y. Sinev, *J. Catal.* **2003**, 216, 468–476.
- [13] M. Y. Sinev, Z. T. Fattakhova, V. I. Lomonosov, Y. A. Gordienko, *J. Nat. Gas Chem.* **2009**, 18, 273–287.
- [14] M. Y. Sinev, *Catal. Today* **1992**, 13, 561–564.
- [15] B. Beck, V. Fleischer, S. Arndt, M. G. Hevia, A. Urakawa, P. Hugo, R. Schomäcker, *Catal. Today* **2014**, 228, 212–218.
- [16] V. I. Lomonosov, M. Y. Sinev, *Kinet. Catal.* **2016**, 57, 647–676.
- [17] K. D. Campbell, J. H. Lunsford, *J. Phys. Chem.* **1988**, 92, 5792–5796.
- [18] J. A. Labinger, K. C. Ott, *Catal. Lett.* **1990**, 4, 245–249.
- [19] M. Xu, T. H. Ballinger, J. H. Lunsford, *J. Phys. Chem.* **1995**, 99, 14494–14499.
- [20] Y. Tong, J. H. Lunsford, *J. Am. Chem. Soc.* **1991**, 113, 4741–4746.
- [21] P. F. Nelson, C. A. Lukey, N. W. Cant, *J. Phys. Chem.* **1988**, 92, 6176–6179.
- [22] V. T. Amorebieta, A. J. Colussi, *J. Am. Chem. Soc.* **1996**, 118, 10236–10241.
- [23] J. A. Labinger, *Catal. Lett.* **1988**, 1, 371–375.
- [24] D. J. C. Yates, N. E. Zlotin, *J. Catal.* **1988**, 111, 317–324.
- [25] M. Hatano, P. G. Hinson, K. Shay Vines, J. H. Lunsford, *J. Catal.* **1990**, 124, 557–561.

- [26] J. A. Labinger, K. C. Ott, *J. Phys. Chem.* **1987**, *91*, 2682–2684.
- [27] C. A. Mims, R. Mauti, A. M. Dean, K. D. Rose, *J. Phys. Chem.* **1994**, *98*, 13357–13372.
- [28] Y. S. Su, J. Y. Ying, W. H. Green, *J. Catal.* **2003**, *218*, 321–333.
- [29] P. N. Kechagiopoulos, J. W. Thybaut, G. B. Marin, *Ind. Eng. Chem. Res.* **2014**, *53*, 1825–1840.
- [30] C. Karakaya, H. Zhu, C. Loebick, J. G. Weissman, R. J. Kee, *Catal. Today* **2018**, *312*, 10–22.
- [31] C. Karakaya, H. Zhu, B. Zohour, S. Senkan, R. J. Kee, *ChemCatChem* **2017**, *9*, 4538–4551.
- [32] K. Takanabe, E. Iglesia, *Angew. Chem., Int. Ed.* **2008**, *47*, 7689–7693.
- [33] K. Takanabe, E. Iglesia, *J. Phys. Chem. C* **2009**, *113*, 10131–10145.
- [34] Y. Liang, Z. Li, M. Nourdine, S. Shahid, K. Takanabe, *ChemCatChem* **2014**, *6*, 1245–1251.
- [35] K. Takanabe, A. M. Khan, Y. Tang, L. Nguyen, A. Ziani, B. W. Jacobs, A. M. Elbaz, S. M. Sarathy, F. (Feng) Tao, *Angew. Chem., Int. Ed.* **2017**, *56*, 10403–10407.
- [36] H. Shimada, J. Galuszka, *Stud. Surf. Sci. Catal.* **1992**, *73*, 99–102.
- [37] K. Otsuka, Y. Murakami, Y. Wada, A. A. Said, A. Morikawa, *J. Catal.* **1990**, *121*, 122–130.
- [38] L. C. Anderson, M. Xu, C. E. Mooney, M. P. Rosynek, J. H. Lunsford, *J. Am. Chem. Soc.* **1993**, *115*, 6322–6326.
- [39] K. B. Hewett, L. C. Anderson, M. P. Rosynek, J. H. Lunsford, *J. Am. Chem. Soc.* **1996**, *118*, 6992–6997.
- [40] K. B. Hewett, M. P. Rosynek, J. H. Lunsford, *Catal. Lett.* **1997**, *45*, 125–128.
- [41] J. A. Sofranko, J. J. Leonard, C. A. Jones, A. M. Gaffney, H. P. Withers, *Catal. Today* **1988**, *3*, 127–135.

- [42] S. M. Sarathy, P. Oßwald, N. Hansen, K. Kohse-Höinghaus, *Prog. Energy Combust. Sci.* **2014**, *44*, 40–102.
- [43] P. Deshlahra, E. Iglesia, *J. Phys. Chem. C* **2016**, *120*, 16741–16760.
- [44] J. M. Zalc, W. H. Green, E. Iglesia, *Ind. Eng. Chem. Res.* **2006**, *45*, 2677–2688.
- [45] C. K. Westbrook, F. L. Dryer, *Symp. Combust.* **1981**, *18*, 749–767.
- [46] W. K. Metcalfe, S. M. Burke, S. S. Ahmed, H. J. Curran, *Int. J. Chem. Kinet.* **2013**, *45*, 638–675.
- [47] S. M. Burke, W. Metcalfe, O. Herbinet, F. Battin-Leclerc, F. M. Haas, J. Santner, F. L. Dryer, H. J. Curran, *Combust. Flame* **2014**, *161*, 2765–2784.
- [48] D. Darcy, H. Nakamura, C. J. Tobin, M. Mehl, W. K. Metcalfe, W. J. Pitz, C. K. Westbrook, H. J. Curran, *Combust. Flame* **2014**, *161*, 65–74.
- [49] A. Raj, I. D. C. Prada, A. A. Amer, S. H. Chung, *Combust. Flame* **2012**, *159*, 500–515.
- [50] Y. Wang, A. Raj, S. H. Chung, *Combust. Flame* **2013**, *160*, 1667–1676.
- [51] A. Raj, M. J. Al Rashidi, S. H. Chung, S. M. Sarathy, *J. Phys. Chem. A* **2014**, *118*, 2865–2885.
- [52] Y. Wang, S. Park, S. M. Sarathy, S. H. Chung, *Combust. Flame* **2018**, *192*, 71–85.
- [53] S. Park, Y. Wang, S. H. Chung, S. M. Sarathy, *Combust. Flame* **2017**, *178*, 46–60.
- [54] S. Wang, I. Agirrezabal-Telleria, A. Bhan, D. Simonetti, K. Takanabe, E. Iglesia, *Faraday Discuss.* **2017**, *197*, 9–39.

Figure 1. Effect of $\text{OH}\cdot$ generation reaction preexponential factor, A , on (a) the CH_4 conversion as a function of the preexponential factor, (b) the CH_4 and O_2 conversions as a function of the residence time, and (c) C_2 selectivity and yield ($\text{C}_2\text{H}_6 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$) as a function of the CH_4 conversion (800°C , isothermal, 1 atm, $\text{CH}_4/\text{O}_2 = 6$).

Figure 2. Conversion and selectivity of different species as a function of residence time under 800 °C isothermal, 1 atm and CH_4/O_2 6. (a) (a') A 10^{18} , (b) (b') OH· mechanism not involved; Selectivity of different species as a function of CH_4 conversion, (c) A 10^{18} , (d) OH· mechanism not involved.

Figure 3. OH· effect on C₂H₄ maximum selectivity and yield in isothermal systems under varied (a) CH₄/O₂ ratios (800 °C, 1 atm), (b) temperatures (1 atm, CH₄/O₂ 6). The C₂H₄ maximum yield (c) in systems with A 10¹⁸, 1 atm, 700-1200 °C and CH₄/O₂ 2-12.

Figure 4. The rate of production (ROP) analysis and reaction pathways of the systems (a) with ($A=10^{18}$) and (b) without ($A=0$) the $\text{OH}\cdot$ generation mechanism. (800°C isothermal, 1 atm and CH_4/O_2 6, at 50% O_2 conversion).

Figure 5. Ratio of the rate of production (ROP) of C₂H₆ to CO as a function of the CH₄ conversion under 800 °C, 1 atm and CH₄/O₂ 6 with the present (red solid line) and absent (black dash line) of OH· generation mechanism.

Figure 6. (a) Ratios of rate constants of H-abstraction reactions from C_2H_6 , C_2H_4 and CH_4 ($k_{C_2H_6}/k_{CH_4}$ and $k_{C_2H_4}/k_{CH_4}$) by different abstractors ($R\cdot$) as a function of ΔH of recombination reaction $R\cdot + H \rightarrow R-H$ (800 °C, 1 atm and CH_4/O_2 6);^[27,46] (b) C_2 selectivity and product ratio (C_2H_4/C_2H_6) as a function of CH_4 conversion, solid line: A 10^{18} , dash line: $OH\cdot$ mechanism not involved;

Table 1. The responsible radical species and their relative contributions (calculated based on the reaction rate) to the H-abstraction of CH₄, C₂H₆ and C₂H₄ in systems with the present ($A=10^{18}$) and absent ($A=0$) of the OH· generation mechanism.

		OH·	CH ₃ ·	H·
with OH· generation mechanism A^{18}	CH ₄	0.84		0.16
	C ₂ H ₆	0.36	0.40	0.23
	C ₂ H ₄	0.92		0.08
without OH· generation mechanism	CH ₄	0.81		0.19
	C ₂ H ₆	0.06	0.77	0.17
	C ₂ H ₄	0.38	0.46	0.15

Different extent of OH radicals generated from O₂-H₂O mixture is integrated to the state-of-the-art radical chemistry to simulate the performance of oxidative coupling of methane (OCM). Such simulation demonstrates the beneficial role of OH radical for OCM rates and selectivity, predicting the maximum C₂H₄ yield to be 32%.

OH• generator boosts C₂ yield

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Impact of OH radical generator involvement in the gas-phase radical reaction network on the oxidative coupling of methane - A simulation study