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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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 $k_{C_2H_6}/k_{CH_4}$, 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\textsubscript{4}/O\textsubscript{2} ratio on the achievable C\textsubscript{2} selectivity and C\textsubscript{2}H\textsubscript{4} yield. The maximum C\textsubscript{2}H\textsubscript{4} yield reached 32% at a CH\textsubscript{4}/O\textsubscript{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\textsubscript{4} in natural gas) into value-added commodities (e.g., C\textsubscript{2}H\textsubscript{4} for use as polymer precursors).\textsuperscript{[1–3]} Indirect processes of C\textsubscript{2}H\textsubscript{4} production from CH\textsubscript{4} exist in the industry (e.g., methane $\rightarrow$ syngas $\rightarrow$ methanol $\rightarrow$ ethylene). In these indirect processes, syngas (H\textsubscript{2}+CO) is first produced by CH\textsubscript{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\textsubscript{4} to C\textsubscript{2}H\textsubscript{4} and has great potential to become competitive to indirect processes. OCM has attracted considerable interest in both academia and industry.\textsuperscript{[1–6]} The catalytically driven OCM process was first reported by Keller and Bhasin in 1982.\textsuperscript{[7]} Exotherms of the reaction (2CH\textsubscript{4} + O\textsubscript{2} $ \rightarrow $ C\textsubscript{2}H\textsubscript{4} + 2H\textsubscript{2}O, $\Delta H^\circ = -280$ kJ mol$^{-1}$) have great potential to decrease operation costs when effectively utilized. The OCM process is economically feasible only when CH\textsubscript{4} conversion is greater than 20% and C\textsubscript{2+} hydrocarbons selectivity greater than 80%.\textsuperscript{[8]} Alternatively, combining the sequential reactor/separator scheme has been considered, in which, for example, O\textsubscript{2} addition was distributed through a membrane reactor or product was removed from the mixture in a recycle reactor.\textsuperscript{[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.\textsuperscript{[12–16]} Accordingly, there are a large number of reports that
combine the gas-phase radical reaction chains with surface catalyzed elementary reactions.\textsuperscript{[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\textsubscript{2} on the catalyst surface.\textsuperscript{[18]} CH\textsubscript{4} reacts with O* to generate CH\textsubscript{3}·, which dimerizes homogeneously in the gas phase to form C\textsubscript{2}H\textsubscript{6}.\textsuperscript{[17,19,20]} The reaction continues with C\textsubscript{2}H\textsubscript{4} formation via dehydrogenation of C\textsubscript{2}H\textsubscript{6}.\textsuperscript{[21]} The C\textsubscript{2} products inevitably react to be oxidized or to form higher hydrocarbons (C\textsubscript{3}-C\textsubscript{4}) that are oxidized more rapidly.\textsuperscript{[22,23]} Such competitive reactions of oxygen species with C\textsubscript{2} products, relative to with CH\textsubscript{4} reactant, essentially determine the maximum C\textsubscript{2} yields.\textsuperscript{[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.\textsuperscript{[24,25]} There are some reports that combine the radical chemistry with elementary surface reaction to estimate achievable C\textsubscript{2} product yields.\textsuperscript{[23,26–31]} Early work by Labinger and Ott demonstrated the importance of including C\textsubscript{3} product reaction to reasonably describe the loss of product yield at high conversions.\textsuperscript{[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.\textsuperscript{[27]} Their isotopic tracer study was effectively utilized for describing product distribution for C\textsubscript{2} and higher C\textsubscript{3} and C\textsubscript{4} hydrocarbons. Su et al. developed an approach to perturb some elementary reaction rates of the specific radical contribution, such as unselective HO\textsubscript{2}· oxidant by selective quenching, where an upper bound for C\textsubscript{2} yield of 28\% existed for the OCM process.\textsuperscript{[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.\textsuperscript{[29]} Karakaya et al.
demonstrated the simulation of the combined homogeneous-heterogeneous reaction network to reproduce experimental results obtained by Mn/Na$_2$WO$_4$/SiO$_2$ catalysts$^{[30]}$ and La$_2$O$_3$/CeO$_2$ 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 O$_2$/H$_2$O mixture catalytically play a critical role in increasing both the OCM rate and the C$_2$H$_4$ selectivity.$^{[3,32–35]}$ Since H$_2$O is one of the major products, a careful kinetic study was necessary to reveal this effect. Initially, using a Mn/Na$_2$WO$_4$/SiO$_2$ catalyst, the CH$_4$ conversion rate and C$_2$ selectivity increased with increasing H$_2$O partial pressure, according to the following simplified rate expression (Equation 1).$^{[32,33]}

\[ r = r_{\text{O}^*} + r_{\text{OH}^*} = k' P_{\text{CH}_4} P_{\text{O}_2}^{1/2} + k'' P_{\text{CH}_4} P_{\text{O}_2}^{1/4} P_{\text{H}_2\text{O}}^{1/2} \]  

(1)

The first term corresponds to the CH$_4$ activation by surface active oxygen atoms (O$^*$), which is in quasi-equilibrium with gas phase O$_2$. The second term corresponds to OH· induced CH$_4$ activation, in which OH· is in quasi-equilibrium with H$_2$O and O$_2$ (Equation 2).

\[ \text{O}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{K}} 4\text{OH·} \]  

(2)

This H$_2$O effect was further evident when the formed H$_2$O was continuously removed from the recirculating system during the OCM reaction, resulting in significant drops in the CH$_4$ conversion rate and C$_2$ 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 O$_2$ chemisorption limiting step (first order in O$_2$ partial pressure) at high conversion levels.$^{[33]}$

Later, it was found that this H$_2$O effect was operational with alkali metals containing catalysts (Na and K), while Mn, W, or SiO$_2$ were not essential components for evidencing the OH·
Using in situ X-ray photoelectron spectroscopy, Na$_2$O$_2$ active species were identified under these reaction conditions. This peroxide species was deemed responsible for CH$_4$ activation but it actually catalyzes the selective activation of H$_2$O rather than CH$_4$, leading to the quasi-equilibrated nature of Equation 2. Maximizing the contribution from the OH· pathway relative to that from the surface O* pathway using Na$_2$WO$_4$/SiO$_2$, a 25% C$_2$+ yield was experimentally achieved in a single reactor and 28% C$_2$+ yield with successive reactors upon O$_2$ addition. In this context, C$_2$H$_4$ yields as high as 31% were experimentally achieved using NaCl addition to Mn/Na$_2$WO$_4$/SiO$_2$ catalysts but stability became an issue due to continuous loss of NaCl.

For the OH· mediated pathway, H$_2$O, rather than CH$_4$, is activated on the catalyst surface by O* (or peroxide) and forms OH·, 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 O$_2$/CH$_4$ or O$_2$/H$_2$O mixture over the basic metal oxide surfaces (e.g., La$_2$O$_3$ and Nd$_2$O$_3$, etc.) using laser-induced fluorescence spectroscopy. When O$_2$/H$_2$O were reactants, OH· was formed to reach equilibrium. It was stated that OH· played an important role in CH$_4$ combustion by generating more CH$_3$· but this beneficial effect was balanced by the formation of more CO$_x$ via secondary reactions. More recently, OH· formation from H$_2$O/O$_2$ mixture was also evident over Na-based catalysts at high temperatures. Improvement of C$_2$ selectivity by OH· generation was explained multifold: here we focus on two main contributions. One reason for C$_2$ selectivity improvement is that the C$_2$H$_6$ conversion rate get slower relative to the CH$_4$ reaction rate because the highly reactive OH· compared to other H-abstractors weakens the effect of C-H bond energies on H-abstraction reaction rates (CH$_4$ 439 kJ mol$^{-1}$ vs. C$_2$H$_6$ 423 kJ mol$^{-1}$). The other important contribution of the OH· pathway is that the OCM reaction proceeds without the necessity of hydrocarbon adsorption: obviously, C$_2$H$_4$ adsorption is preferred over CH$_4$ due to
\( \pi \)-electrons of the unsaturated bond, thereby \( \text{C}_2\text{H}_4 \) 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 OH· mediated pathway, confirmed by an isotopic labeling study.\(^{[22,33]}\) In fact, \( \text{C}_2\text{H}_4 \) reacts relatively slower than \( \text{CH}_4 \) with \( \text{OH} \cdot \) reflecting the C-H bond strength (\( \text{CH}_4 \) 439 kJ mol\(^{-1} \) vs. \( \text{C}_2\text{H}_4 \) 463 kJ mol\(^{-1} \)).

The current study explicitly elucidates the impact of OH· 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 OH· is constantly at quasi-equilibrium: i.e., the catalyst works merely as an ideal OH· generator. The extent of OH· 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 \( \text{CH}_4/\text{O}_2 \) ratio and temperature on the OCM reaction network. The inclusion of OH· generation was found to improve OCM rate and selectivity, accounting for the previously reported beneficial effects of the OH· pathway. The reasons for its promoting capabilities are also discussed.

2. Results and Discussion

In the OCM simulation, the contribution of OH· 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, \( k_\text{f} \), as shown in Equation 3.

\[
 k_f = A T^m \exp\left(\frac{-E_a}{RT}\right)
\]  

(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 OH· 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 OH· contribution on OCM performance.

The OCM processes were simulated utilizing an isothermal PFR reactor model at 800 °C and various OH· 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 OH· generation contributions are presented in Figure 1 (b). Without OH· 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 OH· generation mechanism was incorporated, the CH$_4$ and O$_2$ conversion rates improved drastically. With the OH· 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 OH· 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 OH· 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 OH· has also been observed experimentally.$^{[3,32-34]}$ In the kinetic analysis of OCM with alkali-metal-based catalysts (Na$_2$WO$_4$/SiO$_2$, Na$_2$MoO$_4$/SiO$_2$, K$_2$WO$_4$/SiO$_2$) by Liang et al.,$^{[34]}$ the incremental rates of CH$_4$ conversion between H$_2$O-present and H$_2$O-absent fit well with the mechanism that CH$_4$ is activated by the quasi-equilibrated OH· from a H$_2$O/O$_2$ mixture (Equation 1). The highly active OH· propagates in the system and attacks the CH$_4$ molecules, which accelerates the CH$_4$ molecules activation and increases the OCM reaction rates.
The \( \text{C}_2 \) selectivity and yield \(( \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4 )\) from the same simulation are shown in Figure 1 (c). In the low conversion range, \( \text{C}_2 \) selectivity reached its peak value and then decreased gradually. The \( \text{C}_2 \) selectivity (at all \( \text{CH}_4 \) conversions) improved with increasing OH\(-\) generation mechanism contribution. When OH\(-\) generation mechanism was excluded, the maximum \( \text{C}_2 \) selectivity was 57\% with \( \text{CH}_4 \) conversion at 1.8\%. With OH\(-\) generation mechanism involved, and \( A \) set at \( 10^{14} \), the maximum \( \text{C}_2 \) selectivity increased to 77.8\% with \( \text{CH}_4 \) conversion 3.5\%. When the contribution of OH\(-\) was further increased with \( A \) set at \( 10^{16} \) to \( 10^{18} \), the maximum \( \text{C}_2 \) selectivity were 87.1\% (\( \text{CH}_4 \) conversion 0.76\%) and 89.3\% (\( \text{CH}_4 \) conversion 0.51\%), respectively. For the yield of \( \text{C}_2 \), 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 \( \text{C}_2 \) yield did not change significantly, due to the saturation of OH\(-\) quasi-concentrations at the steady state. With simulation conditions set as 800 °C isothermal, 1 atm and \( \text{CH}_4/\text{O}_2 \) 6, the maximum \( \text{C}_2\text{H}_4 \) yield was 17.3\% at \( \text{CH}_4 \) conversion 28.9\%.

To understand the species concentration changes along the catalyst bed, CHEMKIN simulations were utilized. In the simulation, \( \text{CH}_4 \) and \( \text{O}_2 \) 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 \( \text{O}_2 \) depletion point, OH\(-\) generation from \( \text{H}_2\text{O}/\text{O}_2 \) mixture proceeds. In the practical OCM process, the main function of the catalyst is assumed to catalytically generate OH\(-\) from the \( \text{H}_2\text{O}/\text{O}_2 \) mixture according to Reaction 2. Therefore, the reaction period before \( \text{O}_2 \) is depleted is treated as catalytic region, while the region after \( \text{O}_2 \) depletion happens in gas phase regardless of the presence of catalyst, where OH\(-\) generation from \( \text{H}_2\text{O}/\text{O}_2 \) mixture does not occur. In the catalytic region, \( \text{CH}_4 \) was continuously converted and achieved 29\% conversion at the \( \text{O}_2 \) depletion point. The \( \text{CH}_3\· \)
selectivity first increased to 50% as the product of CH₄ activation, and then dropped to almost 0 quickly, with the formation of C₂H₆ and CH₂O. The selectivity of CH₂O increased to 36% and then decreased. In practical experiment, CH₃· and CH₂O are deemed to quickly transform to either C₂H₆ or CO to be detected, due to their high reactivities. The concentration of C₂H₆ first increases because of the coupling of the CH₃· and then decreases with C₂H₄ concentration increasing simultaneously, due to the dehydrogenation of C₂H₆ to C₂H₄. In the O₂-depleted region (Figure 2 (a’)), C₂H₆ selectivity decreased drastically to around 3%, while the C₂H₄ selectivity increased and reached its peak value (58%) at 4 s, and then decreased slowly. In this case, the maximum C₂H₄ selectivity was achieved after O₂ depletion, utilizing the non-oxidative portion of the reactor. However, at much greater residence time, the C₂H₄ would be further transformed to other hydrocarbons (e.g. C₂H₂ and aromatics), which would decrease C₂H₄ selectivity. The detailed information about further transformation of C₂H₄ 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 C₂H₄ yield. H₂ was formed and reached 20% selectivity at the maximum C₂H₄ yield point.

The selectivity of every major species as a function of residence time in the isothermal system in the absence of OH· generation mechanism is shown in Figure 2 (b) and (b’) for comparison. The maximum C₂H₄ selectivity was achieved before the complete O₂ consumption point. It is apparent that within the same residence time, the system with OH· generation has a higher selectivity for C₂H₄ and H₂ compared to the system without OH· mechanism. Also, the selectivity of CO was relatively lower with the contribution of the OH·. Figure 2 (c) and (d) show the species selectivity as a function of the CH₄ conversion under isothermal conditions with the presence and absence of OH· generation mechanism. In both cases, C₂ selectivity decreases with increasing CH₄ conversion. However, under the same CH₄ conversion, the system involving OH· generation mechanism has greater C₂ selectivity.
OCM at different temperatures from 700 °C to 1200 °C and different CH\textsubscript{4}/O\textsubscript{2} ratios varied from 2 to 12 were simulated under isothermal conditions with the presence (A = 10\textsuperscript{18}) and the absence of OH- generation mechanism. As shown in Figure 3 (a) and (b), in all cases, the maximum yield of C\textsubscript{2}H\textsubscript{4} 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 CH\textsubscript{4}/O\textsubscript{2} 12, the C\textsubscript{2}H\textsubscript{4} selectivity and yield were higher with the OH- mechanism, 69% and 13%, respectively, compared to without it, 40% and 4%, respectively. When the CH\textsubscript{4}/O\textsubscript{2} ratio decreased, the performance enhancement contribution from OH- also decreased. As shown in Figure 3 (b), the C\textsubscript{2}H\textsubscript{4} selectivity and yield increments by the OH- were 31% and 23%, respectively, under 1200 °C. At 800 °C, the C\textsubscript{2}H\textsubscript{4} 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 C\textsubscript{2}H\textsubscript{4} yield is represented in Figure 3 (c) as a contour figure. C\textsubscript{2}H\textsubscript{4} 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 CH\textsubscript{4} molecules with large C-H bond energy would be relatively more favored for activation compared to C\textsubscript{2}H\textsubscript{6} at higher temperatures. From 1000 °C to 1200 °C, the C\textsubscript{2}H\textsubscript{4} selectivity decreased because of the successive transformation of C\textsubscript{2}H\textsubscript{4} to C\textsubscript{2}H\textsubscript{2} and C\textsubscript{3+} products. The higher CH\textsubscript{4}/O\textsubscript{2} ratio increased the C\textsubscript{2}H\textsubscript{4} selectivity, yet naturally decreasing CH\textsubscript{4} conversion. Therefore, C\textsubscript{2}H\textsubscript{4} yield increased with lowering the CH\textsubscript{4}/O\textsubscript{2} ratio from 12 to 2 by increasing the CH\textsubscript{4} conversion at the sacrifice of the selectivity. Within the simulation range under total pressure 1 atm, the maximum C\textsubscript{2}H\textsubscript{4} yield (32%) is achieved with CH\textsubscript{4}/O\textsubscript{2} 3 and temperature 1100 °C (C\textsubscript{2}H\textsubscript{4} selectivity 52%) to 1200 °C (C\textsubscript{2}H\textsubscript{4} 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 OH· 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 CH$_3$·, and the formed CH$_3$· recombined and formed C$_2$H$_6$. C$_2$H$_6$ would further go through successive H-abstraction reactions and finally formed C$_2$H$_3$· through C$_2$H$_4$, which is consistent with the C$_2$H$_6$ oxidation pathway concluded from previous experimental observation in heterogeneous case. CH$_2$O was also formed from the oxidation of C$_2$H$_3$· by O$_2$, which eventually transformed to CO. However, for the activation of hydrocarbons (CH$_4$, C$_2$H$_6$, C$_2$H$_4$), the responsible radical species and their relative contributions were different (as shown in Table 1). For the activation of CH$_4$, OH· and H· were the two main radical species. In the system that incorporated OH·, the extent of OH· contribution was enhanced, which result in different product distribution. For C$_2$H$_6$ activation, the main responsible radical species were OH·, CH$_3$· and H·. In the system without OH· mechanism, CH$_3$· accounted for 77% with OH· at only 6%. However, the involvement of OH· generation mechanism increased the contribution of OH· in C$_2$H$_6$ activation to 36% and decreased CH$_3$· contribution to 40%. The situation for C$_2$H$_4$ activation was the same, in which OH· contributed 92% in the system incorporated with OH· generation mechanism but only 38% in the other system. Even though the involvement of OH· 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 CH$_3$·, which then undergoes recombination to form C$_2$H$_6$ or oxidation to become CO. To analyze the initial selectivity, the C$_2$H$_6$/CO ratio of rate of production (ROP; differential rate at each point) is plotted in Figure 4.
During the initial stage of the OCM process, with dry CH\textsubscript{4} and O\textsubscript{2} as reactant feed, the analysis shows that CH\textsubscript{4} is activated by O\textsubscript{2} and form CH\textsubscript{3}\textperiodcentered and HO\textsubscript{2}\textperiodcentered. The formed CH\textsubscript{3}\textperiodcentered would further react with O\textsubscript{2} and form CH\textsubscript{2}O and OH\textperiodcentered. The OH\textperiodcentered would proceed H-abstraction reaction with CH\textsubscript{4} and form H\textsubscript{2}O. The formed H\textsubscript{2}O would react with O\textsubscript{2} and produce OH\textperiodcentered 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 C\textsubscript{2}H\textsubscript{6}/CO with OH\textperiodcentered generation mechanism was much higher than that without OH\textperiodcentered generation mechanism, indicating that during the initial stage of OCM process (CH\textsubscript{4} conversion lower than 1%), the CH\textsubscript{4} was more converted to C\textsubscript{2}H\textsubscript{6} rather than CO by the contribution of OH\textperiodcentered, which increases the selectivity of C\textsubscript{2} products in general. The recombination of CH\textsubscript{3}\textperiodcentered to C\textsubscript{2}H\textsubscript{6} is the second order to CH\textsubscript{3}\textperiodcentered species, and the conversion of CH\textsubscript{3}\textperiodcentered to CO is first order to CH\textsubscript{3}\textperiodcentered species. CH\textsubscript{4} is activated more rapidly to increase steady-state CH\textsubscript{3}\textperiodcentered concentration, resulting in the increased ROP C\textsubscript{2}H\textsubscript{6}/CO ratio\textsuperscript{32–34}. In the OCM study conducted by Labinger and Ott by both calculation and experiments, C\textsubscript{2}H\textsubscript{6} and CO\textsubscript{2} were found to be main products under low CH\textsubscript{4} conversion (< 5%). The C\textsubscript{2}H\textsubscript{6} selectivity kept increasing with higher CH\textsubscript{4} pressure, which was also caused by the increased CH\textsubscript{3}\textperiodcentered concentration and the second order property of CH\textsubscript{3}\textperiodcentered recombination reaction\textsuperscript{26}.

The OH\textperiodcentered induced H-abstraction reactions are exothermic owing to formation of stable H\textsubscript{2}O product. According to the free energy relationship, these H-abstraction reactions by OH\textperiodcentered are less sensitive to the difference of C-H bond energies in different hydrocarbons, compared with H-abstraction reactions using other general radicals\textsuperscript{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, \(k_{C_3H_6}/k_{CH_4}\) and \(k_{C_2H_4}/k_{CH_4}\), for H-abstraction reactions in gas phase with different H-atom abstractors (R·) calculated at 800 °C.\[^{[27]}\] The value of \(k_{C_3H_6}/k_{CH_4}\) was always greater than unity, and \(k_{C_2H_4}/k_{CH_4}\) was always less than unity, which faithfully reflects the fact that stronger C-H bonds are harder to activate (\(CH_4: 439 \text{ kJ mol}^{-1}; C_2H_6: 423 \text{ kJ mol}^{-1}; C_2H_4: 463 \text{ kJ mol}^{-1}\)). However, \(k_{C_3H_6}/k_{CH_4}\) decreases and \(k_{C_2H_4}/k_{CH_4}\) 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 OH· leads to the lowest \(k_{C_3H_6}/k_{CH_4}\) ratio and highest \(k_{C_2H_4}/k_{CH_4}\). With the contribution of OH·, \(C_2H_4\) is activated much faster with a higher rate constant, while the activation rate of \(C_2H_6\) decreases, leading to the simulation result that \(C_2H_4/C_2H_6\) selectivity ratio is lower in system with OH· 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 CH\(_3\)-activation reactions were involved and \(C_2H_4/C_2H_6\) 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 OH· 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 \(Na_2WO_4/SiO_2\) catalyst at the low conversion level (<5%), the \(C_2\) selectivity reaches \(~90\%\) (800 °C, 10 kPa \(CH_4\), \(CH_4/O_2/H_2O = 6/1/0.7\)),\[^{[34]}\] 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). 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., \( k_{C_2H_4} / k_{CH_4} \), is compared between the simulation and measurement. The simulation gives the \( k_{C_2H_4} / k_{CH_4} \) 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 \( k_{C_2H_4} / k_{CH_4} \) ratio of >3. 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 \( \pi \)-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) 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. 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\(_2\)H\(_4\) selectivity 52%) to 1200 °C (C\(_2\)H\(_4\) selectivity 48%), the maximum C\(_2\)H\(_4\) yield (32%) is achieved. With OH· mechanism included, CH\(_4\) is more preferentially converted to C\(_2\)H\(_6\) rather than CO, which in general enhances the C\(_2\) selectivity of the OCM process. Since the OH· weakens the sensitivity of H-abstraction reaction rate on C-H bond energy, the C\(_2\) product ratio C\(_2\)H\(_4\)/C\(_2\)H\(_6\) is much higher with the absence of OH· mechanism. However, the overall C\(_2\) species selectivity in the system that incorporated the OH· generation mechanism is much higher due to the favored formation of C\(_2\)H\(_6\) from CH\(_3\)·.

4. Simulation protocol

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

The CH\textsubscript{4} conversion, selectivity and yield of carbon-containing products are based on a carbon basis as cumulative integral values. The selectivity and yield of H\textsubscript{2} are based on a hydrogen basis utilizing the total hydrogen amount in converted CH\textsubscript{4} as the basis:

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

(4)

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

(5)

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

(6)

\[
Y_{\text{product}} (\%) = X_{\text{CH}_4} (\%) \times S_{\text{product}} (\%) / 100
\]  

(7)

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References


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Figure 1. Effect of OH· generation reaction preexponential factor, $A$, on (a) the CH₄ conversion as a function of the preexponential factor, (b) the CH₄ and O₂ conversions as a function of the residence time, and (c) C₂ selectivity and yield (C₂H₆+C₂H₄+C₂H₂) as a function of the CH₄ conversion (800 °C, isothermal, 1 atm, CH₄/O₂ 6).
Figure 2. Conversion and selectivity of different species as a function of residence time under 800 °C isothermal, 1 atm and CH₄/O₂ 6. (a) (a’) A 10⁻¹⁸, (b) (b’) OH⁻ mechanism not involved; Selectivity of different species as a function of CH₄ 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 10⁻¹⁸, 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 OH$^-$ 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 C$_2$H$_6$ to CO as a function of the CH$_4$ conversion under 800 °C, 1 atm and CH$_4$/O$_2$ 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\textsubscript{2}H\textsubscript{6}, C\textsubscript{2}H\textsubscript{4} and CH\textsubscript{4} ($k_{\text{C}_2\text{H}_6} / k_{\text{CH}_4}$ and $k_{\text{C}_2\text{H}_4} / k_{\text{CH}_4}$) by different abstractors (R·) as a function of $\Delta H$ of recombination reaction R· + H → R-H (800 °C, 1 atm and CH\textsubscript{4}/O\textsubscript{2} 6)\textsuperscript{[27,46]} (b) C\textsubscript{2} selectivity and product ratio (C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6}) as a function of CH\textsubscript{4} conversion, solid line: A $10^{18}$, dash line: OH· 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.

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Different extent of OH radicals generated from O$_2$-H$_2$O 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 C$_2$H$_4$ yield to be 32%.

**OH· generator boosts C$_2$ yield**

D. Li, W. S. Baslyman, S. M. Sarathy, K. Takanabe*

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