Abstract

A reliable dataset covering a parametric space of process conditions is essential for realizing catalyst informatics. A high-throughput screening (HTS) instrument was employed to obtain a parametric dataset
to develop a detailed reaction microkinetic model for the oxidative coupling of methane (OCM) over La$_2$O$_3$/CeO$_2$ catalyst. The model was combined with well-validated gas-phase kinetics to describe the interactions between homogeneous and heterogeneous reaction chemistry. Methane and oxygen conversions and selectivities of ethylene, ethane, carbon monoxide, and carbon dioxide were measured experimentally in the temperature range of 500-800 °C, CH$_4$/O$_2$ ratio between 3-13, and pressure between 1 to 10 bar. The proposed reaction network consists of 52 irreversible elementary steps describing catalytic reactions between 11 surface species and 123 reversible steps describing the contribution of gas-phase between 25 species. A packed-bed reactor model was developed based on dimensions of experimental setup and catalyst characterization results to account for homogeneous-heterogeneous interactions. The proposed mechanism was tested and validated over a wide range of operating conditions and showed a reasonable fit with an average difference of less than 5% compared to experimentally measured methane conversion and selectivities of ethylene and ethane. Rate-of-production (ROP) and sensitivity analysis were performed to identify main reaction pathways and highlight the important reactions in the OCM.

**Introduction**

For almost three decades, the OCM reaction has been widely accepted economically as a promising route for the single-stage conversion of natural gas to C$_2$ and higher hydrocarbons (Kee et al., 2017). The process started from the pioneering work of Keller and Bhasin in the early 80s and continues until today, attracting both industries and academia (Keller & Bhasin, 1982). The overall reaction, 2CH$_4$ + O$_2$ ↔ C$_2$H$_4$ + 2H$_2$O, occurs through a series of homogeneous and heterogeneous elementary reaction steps (Martin & Mirodatos, 1995; McCarty, 1992). As a catalytic process, significant efforts have been made in catalyst development to achieve the commercial yield requirements (Lunsford, 2000; Reyes et al., 1993). Catalysis can be improved by understanding reaction kinetics and how reactants convert to products. A method of combinational chemistry based on microkinetic studies was proposed by Boudart et al. (Boudart, 2000) to predict process’s conversion, yield, and heat development. Once the effects of surface chemistry on conversion and selectivity are understood, the catalyst composition and structure can be optimized to maximize performance (Thybaut et al., 2011).

Such a multi-step reaction network in OCM with parallel and serial homogeneous and heterogeneous reactions is difficult to predict without varying operating conditions due to high changes in product composition. Numerous catalysts have been investigated for OCM to overcome the conversion-selectivity trade-off arising from poor methane reactivity towards the desired products (Kondratenko et al., 2017; Sun et al., 2008). La$_2$O$_3$ is one of the suggested catalysts and its activity was found to be experimentally higher than other suggested OCM catalysts such as Li/MgO and Sn–Li/MgO due to the high stability of adsorbed hydroxyl, adsorbed oxygen, and the active catalyst density of La$_2$O$_3$ (Alexiadis et al., 2014). Doping La$_2$O$_3$ with other metals such as Sr, Mg, Ca, and Ce can enhance the catalytic activity and leads to higher C$_2$ selectivity (Choudhary et al., 1998). Doping La$_2$O$_3$ with cerium was investigated by Noon et al. in a packed bed reactor (Noon et al., 2013) and demonstrated improved performance for C$_2$ selectivity and less coke formation with a C$_2^+$ yield of 18%.

Despite extensive studies on La$_2$O$_3$ catalysts, there is no comprehensive kinetic model developed and validated under a wide range of operating conditions based on a process-consistent manner, which is necessary for high fidelity predictions (Daneshpayeh et al., 2009; Simon et al., 2007). It can be noted that the changes in pressures and temperatures in a reactor can result in various homogeneous and heterogeneous reactions (Daneshpayeh et al., 2009). Therefore, there is a need for a model to capture such effects in a wide range of operating conditions. An extension to previous work on the OCM homogeneous and heterogeneous kinetic models is presented in the current study (Karakaya et al., 2017). The aim is to provide an adequate description of a large number of experimental data collected over a broad range of operating conditions using high-throughput technology. The coupling of catalyst informatics with high-throughput experiments offers a means to achieve reliable results in a process-
consistent approach. The most relevant reaction network, rate equations, and kinetic parameters were optimized using the sensitivity analysis based (SAB) method (Davis et al., 2004), Rate-of-production (ROP), and species sensitivity analysis by direct comparison with the experimental measurements. Further, the developed model was integrated into a one-dimensional heterogeneous reactor model using CHEMKIN-PRO [ANSYS CHEMKIN-PRO 2021 R1] for validation with the given experimental boundary conditions. The reactor model explicitly accounted for interactions between gas-phase and catalytic reactions.

This study presents extensive high throughput experiments, which is different from the recently submitted paper (Haoyi Wang, 2022). The high throughput instrument generates more reliable experimental data in a process-consistent approach. Various of conditions were tested to generate large experimental data for more accurate optimization. The SAB methodology used for mechanism optimization was different compared to the submitted paper (Haoyi Wang, 2022). SAB is a method explicitly developed for optimizing gas/surface reaction rates directly from experimental data. For the gas-phase reduction and optimization, the smallest possible skeletal mechanism without compromising on the accuracy was achieved. The finally developed model has only 132 reactions between 25 species. So, the developed model had a much smaller number of reactions and species without interfering with the accuracy of the model.

**Previous studies on the OCM reaction kinetics**

**Previous studies on OCM Gas-phase kinetics.** Gas-phase reactions of C₁-C₄ hydrocarbons related to the OCM process have been studied since the early 1980s and understood at the elementary level (Chen et al., 1994; Reyes et al., 1993; Warnatz, 1984). AramcoMech3.0 (Zhou et al., 2018) and NUIGMech1.1 (Baigmohammadi et al., 2020) are detailed mechanisms developed for combustion applications and contain all the gas-phase reactions occurring during the OCM process. It was found that most of the OCM literature mechanisms are based on tuned gas-phase models, which is not a recommended practice. Regardless of the presence of a catalyst, the rates of gas-phase reactions should not be affected and should obey well-known homogeneous gas-phase processes (e.g., oxidation, pyrolysis, etc.). Consequently, the tuned gas-phase reactions negatively affect the surface kinetic rates optimization and accuracy. A comparison between different tuned and detailed gas-phase mechanisms against experimental performance was investigated by Wang et al. (Wang et al., 2021).

The gas-phase reactions are involved in forming all of the OCM products such as C₂, C₃, CO₂, and H₂O. Initially, methane converts to CH₃* radical in the Gas-phase by both oxidative and non-oxidative pathways, which are generally known from combustion research (Dooley et al., 2010; Reyes et al., 1993). Starting with oxidative reactions, methane reacts with O₂, O*, OH*, or HO₂* to form CH₃* radical as presented in reactions (1)(6) (Chen et al., 1994; Karakaya et al., 2017). The first set of reactions (1)(3) are important for the CH₃* radical formation at temperatures over the 700–850 °C (Reyes et al., 1993; Warnatz, 1984). Takanabe et al. (Takanabe & Iglesia, 2008) proposed that H₂O reacts with O₂ to form OH* radical and then CH₃* radical, as presented in reactions (5) and (6). Here, the O-H bond (497 kJ/mol) in H₂O is stronger compared to the C-H bond (439 kJ/mol) in CH₄, contributing to the formation of CH₃* radical (Chen et al., 1991; Warnatz, 1984). The non-oxidative CH₃* radical formation mainly happens through; thermal cracking via reaction (7) and H* radical attack via reaction (8). Both of these reactions are endothermic and require energy to proceed (Reyes et al., 1993).

\[
\begin{align*}
\text{CH}_4 + \text{O}_2 & \leftrightarrow \text{CH}_3^* + \text{HO}_2^* \\
\text{CH}_4 + \text{O}_2 & \leftrightarrow \text{CH}_3\text{O}^* + \text{OH}^* \\
\text{CH}_4 + \text{O}^* & \leftrightarrow \text{CH}_3^* + \text{OH}^*
\end{align*}
\]
\[
\begin{align*}
\text{CH}_4 + \text{HO}_2^* & \leftrightarrow \text{CH}_3^* + \text{H}_2\text{O}_2 \\
2\text{H}_2\text{O} + \text{O}_2 & \leftrightarrow 4\text{OH}^* \\
\text{CH}_4 + \text{OH}^* & \leftrightarrow \text{CH}_3^* + \text{H}_2\text{O} \\
\text{CH}_4 & \leftrightarrow \text{CH}_3^* + \text{H}^* \\
\text{CH}_4 + \text{H}^* & \leftrightarrow \text{CH}_3^* + \text{H}_2
\end{align*}
\] (4)-(8)

The \( \text{C}_2\text{H}_6 \) molecule is generated from the combination of two \( \text{CH}_3^* \) radicals, as presented in reaction (9). The formation of \( \text{C}_2\text{H}_6 \) requires less activation energy than \( \text{C}_2\text{H}_4 \) from a thermodynamic perspective (Quddus et al., 2010). Later, \( \text{C}_2\text{H}_6 \) reacts with \( \text{H}^*, \text{CH}_3^* \), or \( \text{OH}^* \) radicals to form \( \text{H}_2, \text{H}_2\text{O}, \) and \( \text{C}_2\text{H}_5^* \) radical, as shown in reactions (10)–(12) (Karakaya et al., 2017). The \( \text{C}_2\text{H}_5^* \) radical dehydrogenates further to form \( \text{C}_2\text{H}_4 \) in a later step. Alternatively, excess \( \text{O}_2 \) promotes \( \text{C}_2\text{H}_4 \) deep oxidation to generate \( \text{CO}_x \) and \( \text{H}_2\text{O} \). Both homogeneous and heterogeneous reactions propose direct and indirect pathways for \( \text{CO}_x \) generation. The oxidation of \( \text{CH}_3^* \) radicals forms \( \text{CO}_x \) via reactions (13) and (14) (Karakaya et al., 2018). The indirect pathways for \( \text{CO}_x \) generation occur via \( \text{C}_2\text{H}_4 \) reaction with \( \text{O}_2 \) (reaction (15)), \( \text{H}^* \) (reaction (16)), \( \text{OH}^* \) (reaction (17)), and \( \text{CH}_3^* \) (reaction (18)) to form \( \text{C}_2\text{H}_3^* \) (Karakaya et al., 2017). At low operating temperatures, the generation of \( \text{CO}_x \) is determined by the oxidation of formaldehyde (\( \text{CH}_2\text{O}^* \)) through reaction (19) (Karakaya et al., 2018). Hydrocarbons higher than \( \text{C}_2 \) are also generated but with mole fractions less than 1% (Kee et al., 2017).

\[
\begin{align*}
\text{CH}_3^* + \text{CH}_3^* + \text{M} & \leftrightarrow \text{C}_2\text{H}_6 + \text{M} \\
\text{C}_2\text{H}_6 + \text{H}^* & \leftrightarrow \text{C}_2\text{H}_5^* + \text{H}_2 \\
\text{C}_2\text{H}_6 + \text{OH}^* & \leftrightarrow \text{C}_2\text{H}_5^* + \text{H}_2\text{O} \\
\text{C}_2\text{H}_6 + \text{CH}_3^* & \leftrightarrow \text{C}_2\text{H}_5^* + \text{CH}_4 \\
\text{CH}_3^* + \text{O}_2 & \leftrightarrow \text{CH}_3\text{O}^* + \text{O}^* \\
\text{CH}_3^* + \text{O}_2 & \leftrightarrow \text{CH}_2\text{O}^* + \text{OH}^* \\
\text{C}_2\text{H}_4 + \text{O}_2 & \leftrightarrow \text{C}_2\text{H}_3^* + \text{HO}_2^* \\
\text{C}_2\text{H}_4 + \text{H}^* & \leftrightarrow \text{C}_2\text{H}_3^* + \text{H}_2 \\
\text{C}_2\text{H}_4 + \text{OH}^* & \leftrightarrow \text{C}_2\text{H}_3^* + \text{H}_2\text{O} \\
\text{C}_2\text{H}_4 + \text{CH}_3^* & \leftrightarrow \text{C}_2\text{H}_3^* + \text{CH}_4 \\
\text{CH}_2\text{O}^* + \text{HO}_2^* & \leftrightarrow \text{HCO}^* + \text{H}_2\text{O}_2
\end{align*}
\] (9)-(19)

**Previous studies on OCM surface kinetics.** The OCM catalytic mechanisms are less understood compared to the gas-phase owing to the complexity of understanding the nature of surface reactions and their interactions with the gas-phase (Karakaya et al., 2018). One of the first detailed OCM surface mechanisms was proposed by Sinev et al. (Sinev, 1992) in the early 1990s for Li/MgO catalyst and was extended recently (Sinev, 1995). Later, other detailed surface mechanisms were published (Simon et al., 2007; Sun et al., 2008). There is an agreement in the literature that the main contribution of the surface
reactions is the adsorption and desorption characteristics of surface-adsorbed oxygen O(s) (Karakaya & Kee, 2016; Thybaut et al., 2011). This contribution decreases at elevated temperatures, and gas-phase reactions become more effective. Methane reacts with surface-adsorbed oxygen O(s) to form CH$_3$* radical, as shown in reactions (20) and (21) (Sun et al., 2008; Thybaut et al., 2011). CH$_3$* radical generation increases the rate of C$_2$ formation in the gas-phase. On the other hand, catalytic reactions present direct and indirect pathways for CO$_x$ generation. O(s) can participate in nonselective oxidation by reacting with CH$_3$* to form CH$_3$O(s) (reaction (22)). Indirect CO$_x$ formation pathways are presented in reactions (23)–(25). C$_2$H$_4$ and C$_2$H$_6$ products react with O(s) to form C$_2$H$_5$* and C$_2$H$_3$*, acting as an intermediate for CO$_x$ generation in later steps (Karakaya et al., 2017).

\[
\begin{align*}
\text{CH}_4 + \text{O}(s) & \leftrightarrow \text{CH}_3^* + \text{OH}(s) \quad (20) \\
4\text{CH}_4 + \text{O}(s) & \leftrightarrow 4\text{CH}_3^* + 2\text{H}_2\text{O} \quad (21) \\
\text{CH}_3^* + \text{O}(s) & \leftrightarrow \text{CH}_3\text{O}(s) \quad (22) \\
4\text{C}_2\text{H}_6 + \text{O}(s) & \leftrightarrow 4\text{C}_2\text{H}_5^* + 2\text{H}_2\text{O} \quad (23) \\
\text{C}_2\text{H}_4 + \text{O}(s) & \leftrightarrow \text{C}_2\text{H}_3^* + \text{OH}(s) \quad (24) \\
\text{C}_2\text{H}_4 + \text{O}(s) & \leftrightarrow \text{C}_2\text{H}_4\text{O}(s) \quad (25)
\end{align*}
\]

**Experiments and methodology**

**High throughput experiments.** The experiments were performed on a HTS (Flowrence® from Avantium) setup consisting of 16 fixed-bed parallel reactors with operating conditions provided in **Table 1**. The HTS setup is connected to an Agilent 7890B gas chromatograph (GC)– flame ionization detector (FID)/ thermal conductivity detector (TCD). More than 200 data points were compiled by executing automated operations using the HTS system. The dimensions of the quartz reactor tubes were 2 mm (i.d.) × 3 mm (o.d.) × 30 cm (length). In view of the process exothermicity, the quartz reactors were selected to ensure the inertness of reactor walls at elevated temperatures. The reactors were symmetrically placed in an electric furnace for better temperature control. Radial temperature gradients were reduced by diluting the catalyst bed with SiO$_2$, a thermally conductive material. The catalyst powder was diluted in the mass ratio of 1/10 with SiO$_2$.

For uniform gas velocity distribution, the SiO$_2$ particles in the mixture had the same size as the catalyst. The reactors were pre-heated at 450 °C for 30 minutes under N$_2$ flow. Inlet gases were mixed and distributed equally between the 16 reactors by a gas distributor. Exit gases from the reactors passed through moisture traps to remove water vapor before entering the GC. The composition of products, including hydrocarbons from C$_1$ to C$_5$ was measured using a FID, whereas CO, CO$_2$, O$_2$, N$_2$, and H$_2$ were measured using TCD detectors. Three replications of each experiment were conducted to ensure the stability of the results. Experiments were randomly repeated, and no evidence of catalyst deactivation was observed within 72 hours of testing. An average carbon balance of all experiments was observed to be greater than 95%. Blank runs were conducted for internal standard calibration; they showed a minor gas-phase reaction of 0-7% methane conversion, indicating the need of a catalyst. The results from HTS experiments developed a database of methane conversion and selectivities of carbon monoxide, carbon dioxide, ethane, ethylene, propane, and propylene for the kinetic parameters' optimization.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total inlet flow at 298K (ml/min)</td>
<td>137</td>
</tr>
</tbody>
</table>
Table 1—Range of operating conditions for HTS experiments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet methane concentration (mol%)</td>
<td>0.7</td>
</tr>
<tr>
<td>Catalyst loading (mg)</td>
<td>5-20</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>1-10</td>
</tr>
<tr>
<td>CH₄/O₂</td>
<td>3-13</td>
</tr>
<tr>
<td>Inlet temperature (°C)</td>
<td>500-800</td>
</tr>
</tbody>
</table>

The catalyst was assumed to be coated on the honeycomb wall in this configuration, while the reactor cell density was reduced to neglect any unnecessary geometrical effects. Plug flow reactors were added before and after the catalyst bed to match the reactor configuration and define the location of the catalyst bed. Simulation input parameters were based on the experimental setup, as shown in Table 1 and Table 2. To evaluate and compare the results more effectively methane conversion ($X_{CH₄}$), oxygen conversion ($X_{O₂}$), and selectivities ($S_x$) were calculated based on Eq. (26)–(29), where $J_x$ represents molar flux in mole/sec in a specie $x$.

$$X_{CH₄} = \frac{J_{CH₄,in} - J_{CH₄,out}}{J_{CH₄,in}}$$  (26)

$$X_{O₂} = \frac{J_{O₂,in} - J_{O₂, out}}{J_{O₂,in}}$$  (27)

$$S_{C₂} = \frac{2 \times J_{C₂}}{J_{CH₄,in} - J_{CH₄,out}}$$  (28)

$$S_{COX} = \frac{J_{COX}}{J_{CH₄,in} - J_{CH₄,out}}$$  (29)
Results and discussion

**Proposed gas-phase reaction mechanism.** The gas-phase model used in this paper is a reduced version of AramcoMech3.0 (Zhou et al., 2018) that considers only the reactions pertaining to the OCM chemistry. The mechanism provides a detailed description of C₀–C₄ combustion kinetics and thermochemical properties of various fuel mixtures, including methane. The mechanism includes 3037 reactions and 581 species ranging from C₁ to C₁₀ and other important species for combustion applications. However, the OCM reaction is not a complete combustion process, and not all the reactions and species in the mechanism are observed. Therefore, AramcoMech3.0 has been reduced from 3037 reactions to 123 and from 581 species to 25 in order to minimize computational costs without compromising accuracy. The proposed model is given in the supplementary information, including all the species known to occur in the OCM reaction scheme, such as C₁ to C₃, CO, CO₂, OH*, O*, etc.

CHEMKIN-PRO Reaction Workbench, a powerful mechanism reduction tool, was used to reduce the mechanism by removing the irrelevant species and reactions. To achieve the smallest skeletal mechanism possible while preserving the target accuracy, a combination of different tools in an iterative process was implemented. Directed relation graph (DRG) (Lu & Law, 2005), directed relation graph with error propagation (DRGEP) (Liang et al., 2009; Pepiot-Desjardins & Petsch, 2008), directed relation graph with path flux analysis (DRGPFA) (Sun et al., 2010), the sensitivity analysis for DRG/DRGEP/DRGPFA, the optimization analysis for DRG/DRGEP/DRGPFA, and full species sensitivity analysis (FSSA) methods were applied. DRG (Lu & Law, 2005) is a method that determines unimportant species in a detailed mechanism by resolving species coupling without prior knowledge of the reaction system. DRGEP (Liang et al., 2009; Pepiot-Desjardins & Petsch, 2008) identifies direct species coupling using immediate error, while DRGPFA (Sun et al., 2010) uses a broader range of conditions for better accuracy. FSSA method calculates the induced error by removing each specie from the mechanism.

The reduced gas-phase mechanism includes oxidative and non-oxidative reactions for methane conversion to CH₃* radical. The oxidative pathways are reactions (3), (4), and (6), where methane reacts with O*, HO₂*, and OH*. The non-oxidative pathway that affected the mechanism reduction was reaction (8), where methane reacts with H* to form a CH₃* radical. The proposed model also describes the reactions forming C₂ and CO₂ products. It included reactions (9)–(12), representing C₂H₆ formation and its dehydrogenation to C₂H₄* radical. The model had the direct and indirect CO₂ formation pathways described in reactions (13)–(19). The description of the full effect of the gas-phase reaction, including C₂H₅* radical dehydrogenation and C₃ generation, is explained in section 4.3.

The developed model was validated against the original mechanism and jet stirred reactor (JSR) experiments. The details of the JSR experiments were reported in a different study (Wang et al., 2021). The study investigated the non-catalytic gas-phase chemistry in JSR experiments against literature mechanisms. The developed model was tested using CHEMKIN-PRO, while input parameters were corresponded to JSR experiments as (a) 1% CH₄, CH₄/O₂ = 2, (b) 1% CH₄, CH₄/O₂ = 2, (c) 2% CH₄, CH₄/O₂ = 3.5, (d) 5% CH₄, CH₄/O₂ = 3.5, N₂ as a balance in all the cases. Simulation results of the developed model showed a perfect agreement with the original mechanism and a reasonable fit with JSR experiments. Fig. 1 compares mole fraction profiles between JSR experiments and the developed model. Measured and predicted mole fractions for OCM main species CH₄, O₂, C₂H₄, C₃H₆, CO, and CO₂ were closely matched. Possible deviations were expected due to experimental and GC measurement errors due to the magnitude of the mole fractions studied. Generally, the developed model compared to AramcoMech3.0 (Zhou et al., 2018) and JSR experimental results demonstrated better accuracy in predicting the OCM gas-phase chemistry. Compared to tuned mechanisms, the model can be used as a reliable basis for heterogeneous mechanism optimization. Combining homogeneous and heterogeneous reactions will lead to an increase in modeling complexity and computational time. Therefore, it is
generally preferred to use reduced reaction mechanisms that describe most of the reaction chemistry using fewer reactions and species.

![Graphs showing mole fraction vs temperature for different fuel mixtures](image)

**Fig. 1**—Comparison between experimental (closed symbols) and simulated results (lines with corresponding color) of different fuel mixtures consumption and products generated (a) 1% CH₄, CH₄/O₂= 2, (b) 1% CH₄, CH₄/O₂= 2, (c) 2% CH₄, CH₄/O₂= 3.5, (d) 5% CH₄, CH₄/O₂= 3.5, N₂ as a balance in all cases. The experimental error is within 5%.

**Proposed surface reaction mechanism.** The heterogeneous reaction model used in this paper was initially suggested for Li/MgO and Sn/Li/MgO catalysts (Alexiades et al., 2014; Kechagiopoulos et al., 2014). The model was developed later by Karakaya et al. (Karakaya et al., 2017) for La₂O₃/CeO₂ catalysts based on a tuned gas-phase mechanism. An enhanced version of previous work is presented in this paper with using the proposed gas-phase mechanism in section 4.1 and high throughput catalytic experiments. The developed surface mechanism is provided in the supplementary information with rates modified compared to previous work (Karakaya et al., 2017). The model has 52 irreversible steps and 11 surface species representing reactions between gas-phase and surface-adsorbed species. The model can be classified into three reaction types: adsorption steps, Eley–Rideal reaction steps, and surface reaction steps, as shown in Table 3. The reaction mechanism was developed in the form of irreversible reaction pairs to avoid the need for thermodynamic properties of surface adsorbent species. The mechanism was written in the modified Arrhenius format or sticking probabilities.

The mechanism describes methane activation through oxygen dissociation (reaction 1, surface mechanism) and methane hydrogen abstraction (reaction 3, surface mechanism). Several possible heterogeneous reaction pathways and corresponding elementary steps were proposed in the literature for COₓ formation (Lunsford, 1995; Martin & Mirodatos, 1995). In the proposed model, there are three
catalytic reaction pathways to generate CO and CO$_2$ that are included. First, methyl radical scavenging and hydrogen removal from methoxy species (reactions 13–21, surface mechanism), considering these elementary steps: CH$_3^* \rightarrow$ CH$_3$O(s) $\rightarrow$ CH$_2$O(s) $\rightarrow$ HCO(s) $\rightarrow$ CO(s) $\rightarrow$ CO$_2$(s). Second, hydrogen abstraction from ethane and ethylene (reactions 5–7, surface mechanism), forming active radicals for CO$_x$ generation in the gas-phase. Although the C$_2$H$_4$ hydrogen bond is slightly stronger than CH$_4$, it is still possible that hydrogen can be extracted from C$_2$H$_4$. Third, the oxidation of ethylene through ethylene adsorption, hydrogen abstraction, and C–C bond cleavage (reactions 27–31, surface mechanism), following these elementary steps: C$_2$H$_4$ $\rightarrow$ C$_2$H$_3$O(s) $\rightarrow$ C$_2$H$_3$O(s) $\rightarrow$ CH$_2$O(s) $\rightarrow$ HCO(s) $\rightarrow$ CO(s) $\rightarrow$ CO$_2$(s). Sun et al. (Sun et al., 2008) suggested hydroperoxy radicals (HO$_2^*$) in reactions 43, surface mechanism) acting as a source of the deep oxidation pathways between catalytic and gas-phase reactions. Reaction 49–51 in the surface mechanism is responsible for quenching the hydroperoxy radicals on the catalyst surface. The regeneration of the active site is also included in the proposed model (reactions 9–11, surface mechanism).

<table>
<thead>
<tr>
<th>No</th>
<th>Adsorption steps</th>
<th>No</th>
<th>Eley–Rideal steps</th>
<th>No</th>
<th>Surface reaction steps</th>
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<tr>
<td>1</td>
<td>O$_2$+2La(s)$\rightarrow$2O(s)</td>
<td>3</td>
<td>CH$_3$O(s)$\rightarrow$CH$_3$+OH(s)</td>
<td>9</td>
<td>2OH(s)$\rightarrow$H$_2$O(s)+O(s)</td>
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<tr>
<td>2</td>
<td>2O(s)$\rightarrow$O$_2$+2La(s)</td>
<td>4</td>
<td>CH$_3$+OH(s)$\rightarrow$CH$_4$+O(s)</td>
<td>10</td>
<td>H$_2$O(s)+O(s)$\rightarrow$2OH(s)</td>
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<tr>
<td>11</td>
<td>H$_2$O(s)$\rightarrow$H$_2$O+La(s)</td>
<td>5</td>
<td>C$_2$H$_3$O(s)$\rightarrow$C$_2$H$_2$+OH(s)</td>
<td>15</td>
<td>CH$_3$O(s)+O(s)$\rightarrow$CH$_3$O(s)+OH(s)</td>
</tr>
<tr>
<td>12</td>
<td>H$_2$O+La(s)$\rightarrow$H$_2$O(s)</td>
<td>6</td>
<td>C$_2$H$_3$+OH(s)$\rightarrow$C$_2$H$_2$+O(s)</td>
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<td>C$_2$H$_5$+O(s)$\rightarrow$C$_2$H$_4$+OH(s)</td>
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<td>CH$_2$O(s)+O(s)$\rightarrow$HCO(s)+OH(s)</td>
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<td>C$_2$H$_5$+OH(s)$\rightarrow$C$_2$H$_4$+O(s)</td>
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<td>HCO(s)+OH(s)$\rightarrow$CH$_2$O(s)+O(s)</td>
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<td>19</td>
<td>HCO(s)+O(s)$\rightarrow$CO(s)+OH(s)</td>
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<td>24</td>
<td>CO(s)$\rightarrow$CO+La(s)</td>
<td>34</td>
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<td>20</td>
<td>CO(s)+OH(s)$\rightarrow$HCO(s)+O(s)</td>
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<td>26</td>
<td>CO$_2$(s)$\rightarrow$CO$_2$+La(s)</td>
<td>36</td>
<td>CH$_2$O+OH(s)$\rightarrow$CH$_3$O+O(s)</td>
<td>22</td>
<td>CO$_2$(s)+La(s)$\rightarrow$CO(s)+O(s)</td>
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<td>27</td>
<td>C$_2$H$_4$+O(s)$\rightarrow$C$_2$H$_3$O(s)</td>
<td>37</td>
<td>CH$_2$O+O(s)$\rightarrow$HCO+OH(s)</td>
<td>29</td>
<td>C$_2$H$_4$O(s)+O(s)$\rightarrow$C$_2$H$_3$O(s)+OH(s)</td>
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<td>38</td>
<td>HCO+OH(s)$\rightarrow$CH$_3$O+O(s)</td>
<td>30</td>
<td>C$_2$H$_3$O(s)+OH(s)$\rightarrow$C$_2$H$_2$O(s)+O(s)</td>
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<td>51</td>
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<td>39</td>
<td>HCO+O(s)$\rightarrow$CO+OH(s)</td>
<td>31</td>
<td>C$_2$H$_3$O(s)+O(s)$\rightarrow$CH$_2$O(s)+HCO(s)</td>
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<tr>
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<td>40</td>
<td>CO+OH(s)$\rightarrow$HCO+O(s)</td>
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<td>50</td>
<td>O$_2$+OH(s)$\rightarrow$HO$_2$+O(s)</td>
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</table>

Table 3—Catalytic elementary steps description (Alexiadis et al., 2014).

The rate coefficients were optimized first at low conversion levels, then at higher conversion levels to reduce parasitic phenomena. A diluted 5 mg catalyst was initially studied at low temperatures (500–650 °C) in order to decrease axial dispersion, velocity profiles, and radial temperature gradients,
thereby targeting intrinsic kinetic data and reactor ideality performance. Kinetic rates optimization was performed by a direct comparison between experimental measurements and the predicted mole fractions using the sensitivity analysis based (SAB) method (Davis et al., 2004), ROP, and species sensitivity analysis. The SAB method optimizes the rate of surface reactions by creating a kinetic response from experimental data. The technique was derived from a multivariate Taylor expansion and applied first-order sensitivity coefficients as a basis for kinetic optimization. A detailed description of the SAB method’s equations and parameters is available in the literature (Davis et al., 2004). The developed Python code for the SAB method is provided in the supplementary information. The ten most sensitive surface reactions were determined for CH₄, C₂H₄, C₂H₆, CO, and CO₂ for SAB optimization. The sensitive surface reactions were identified as 1, 2, 7, 11, 12, 13, 21, 23, 24, and 51 by CHEMKIN-PRO species sensitivity analysis.

The SAB method optimized the pre-exponential factors (A) of the sensitive surface reactions. The results showed an enhanced performance compared to the original mechanism; however, an additional improvement was required to match the experimental results. In contrast to gas-phase, surface species were difficult to identify or observe experimentally in order to calculate their activation energies. Therefore, the activation energies for some reactions had to be modified to replicate the experimental performance. The ROP and species sensitivity analysis were performed to identify the reaction paths followed for optimization. ROP was used to determine the reacting-flow path taken from the inlet feed to the final products. ROP measures each reaction's contribution to a specific specie’s net production or consumption rates. The sensitivity analysis identified the dependence of a specie on various surface reactions in a surface model. The identified reaction path was compared with the literature for confirmation and adjustment. Alexiadis et al. (Alexiadis et al., 2014) and Kechagiopoulos et al. (Kechagiopoulos et al., 2014) proposed an OCM reaction path similar to Fig. 5 and Fig. 6. The information obtained from ROP and species sensitivity analysis guided the increase or decrease of kinetic rate to match experimental performance. For example, surface reaction 3 represents methane activation to initiate CH₃* radical by one hydrogen abstraction through surface oxygen. The activation energy of this surface reaction [CH₄+O(s)=CH₃*+OH(s)] proposed by Karakaya et al. (Karakaya et al., 2017) was 174.4 kJ/mol, while Simon et al. (Simon et al., 2007) and Fleys et al. (Fleys et al., 2007) proposed it to be 37 kJ/mol. It was found in this study that the activation energy of 130 kJ/mol showed the optimized prediction of methane conversion. The kinetic rates of surface reactions 7-11 and 51 were optimized similarly for better predictions of mole fractions compared to experimental performance.

The developed homogeneous and heterogeneous mechanisms were implemented in a one-dimensional reactor module in CHEMKIN-PRO. The measured and predicted catalytic performance for feed mixtures of CH₄/O₂= 5 and 9 in the temperature range of 500-800 °C are shown in Fig. 2. The primary OCM gas-phase products C₂H₄, C₂H₆, C₃H₆, C₃H₈, CO, CO₂, and unreacted methane were compared with experimental data for validation. The proposed homogeneous and heterogenous models satisfactorily matched with experimental performance, and possible deviations can be attributed to errors in experiment and GC measurements. The catalytic activity did not initiate at low temperatures, and less than 5% methane conversion mainly to CO and CO₂, was observed. This indicated that direct methane oxidation was dominant at low temperatures. The model over-predicted oxygen consumption below 600 °C due to the conversion of oxygen into active oxygen species, such as O(s). As the temperature increased, the catalytic activity increased, and O₂ conversion reached 100% around 650 °C. The operating temperature played an important role in increasing CH₄ and O₂ conversions and the selectivities to C₂H₄, C₂H₆, and C₃, while decreasing selectivities to CO and CO₂. As compared to CH₄, O₂, and C₂H₆ profiles, C₂H₄ formed at a slower rate. This observation demonstrated that C₂H₄ formation proceeded by C₂H₆ dehydrogenation.
During OCM reaction, C₂ and COₓ formation occurred simultaneously and competitively. COₓ was formed by both gas-phase and surface reactions, and its formation depended on the local oxygen concentration and temperature. COₓ formation decreased with increasing temperature and CH₄/O₂ ratio, as shown in Fig. 2 and Fig. 3. The measured and predicted catalytic performance for CH₄/O₂ = 11 and 13 in the temperature range of 500-800 °C are depicted in Fig. 3. The conversion profiles of C₂, and COₓ products followed the same trend with higher oxygen feeds. As the temperature increased, the conversion rate of methane to methyl radical (CH₃*) increased, leading to more C₂ formation. Since less O₂ was supplied at higher CH₄/O₂ ratios, lower methane conversion and COₓ products were observed. As O₂ was the limiting reactant, O₂ availability decreased the rate of methane conversion through homogeneous and heterogeneous reaction steps. However, O₂-rich conditions led to total oxidation of COₓ products. Predicted selectivity to C₃ matched the experimental data, while COₓ selectivity was slightly under-estimated below 700 °C. Experimental results showed that increasing pressure to 5 and 10 bar negatively affected the process performance. Methane conversion and C₂ selectivity decreased with pressure, while COₓ increased.

Fig. 2—Comparison between experimental (closed symbols) and simulated results (lines with corresponding color) of different operating mixtures (a) CH₄/O₂ = 5, (b) CH₄/O₂ = 9. 20 mg catalyst diluted with SiO₂, 70.7kPa CH₄, 101kPa total pressure, N₂ as balance, inlet volumetric flow rate 137 cm³/min at 25 °C. The experimental error is within 5%.
The predictions of the homogeneous and heterogeneous models describe the experiments reasonably well. The results demonstrate good agreement with the experimental data over the investigated range of operating conditions is especially noteworthy. The accuracy of the developed kinetic models was evaluated by comparing the models’ prediction with the experimental data. Fig. 4 presents the parity plots of methane conversion and selectivities to C$_2$, CO$_x$, and yield of C$_2$, which demonstrate the validity of the model prediction. Data points were distributed almost symmetrically around the plot diagonal with some deviations. These deviations may be stemmed from the reactor’s ideality and expected experimental errors. The accuracy of the model prediction showed its reliability in describing the OCM reaction kinetics with high fidelity. The following presents the reaction network obtained from the simulation results and the effects of various parameters on the OCM process based on the developed kinetic model.

**Fig. 3**—Comparison between experimental (closed symbols) and simulated results (lines with corresponding color) of different operating mixtures (a) CH$_4$/O$_2$ = 11, (b) CH$_4$/O$_2$ = 13. 20 mg catalyst diluted with SiO$_2$, 70.7kPa CH$_4$, 101kPa total pressure, N$_2$ as balance, inlet volumetric flow rate 137 cm$^3$/min at 25 °C. The experimental error is within 5%.
Reaction network. The developed homogeneous and heterogeneous models’ reaction networks are presented in Fig. 5 and Fig. 6. They demonstrated methane activation as the first step in the OCM chemistry by breaking the C–H bond. The initiation process started with dissociative chemisorption of O₂ on the catalyst surface to form surface oxygen O(s) (reaction 1, surface mechanism). This was followed by hydrogen abstraction from methane using the available O(s) to form a CH₃* radical (reaction 3, surface mechanism). Here, the oxygen availability acted as the rate-determining step in the OCM reaction. Previous studies on the temporal analysis of products (Mallens et al., 1996) and steady-state isotope transient kinetic analysis (SSITKA) (Nibbelke et al., 1995) revealed the Eley–Rideal character of the hydrogen abstraction from methane (reaction 3, surface mechanism). Two CH₃* radicals combined in the gas-phase to produce C₂H₆ (reaction 73, gas-phase mechanism). Then, C₂H₆ dehydrogenated in the gas-phase to ethyl radical C₂H₅* (reactions 78, 79, 81, gas-phase mechanism). C₂H₅* dehydrogenated further in the gas-phase to C₂H₄ as the target product (reactions 83, 87, gas-phase mechanism).

In the presence of oxygen at elevated temperatures, complete oxidation of methane to COₓ is more favorable thermodynamically than the desired C₂ (Karakaya et al., 2017). Among the different pathways proposed earlier for COₓ generation, the dominant path found was CH₃* radical conversion to methoxy species followed by sequential hydrogen abstraction, considering these elementary steps: CH₃* → CH₃O* → CH₂O* → HCO* → CO → CO₂ (reactions 23, 24, 40, 57, 60, 62, 72, gas-phase mechanism). Several studies demonstrated strong interactions between catalyst performance and COₓ.

Fig. 4—Parity plots of (a) CH₄ conversion, (b) COₓ selectivity, (c) C₂ selectivity, and (d) C₂ yield. Operated conditions are based on Table 1.
formation. CO\textsubscript{3} adsorbed on the basic oxygen ions and caused inhibiting effect for methyl radical generation (Sun et al., 2008; Xu et al., 1992). This adsorption effect was investigated previously through SSITKA experiments (Nibbelke et al., 1995). Fourier transform infrared spectroscopy (FTIR) and temperature-programmed reduction (TPR) analyses showed the formation of carbonates species on the catalyst active sites due to CO\textsubscript{2} adsorption (Galuszka, 1994; Martin & Mirodatos, 1995). This unfavorable adsorption affected methane conversion, and therefore it was added to the proposed reaction network (reactions 23, 25, surface mechanism).

In a typically fixed bed reactor, the first part of the reactor operates under oxidative conditions, while the rest operates under non-oxidative conditions. Under non-oxidative conditions and high temperatures, carbon deposits on the catalyst surface can accumulate and contribute to catalyst fouling. (Noon et al., 2013; Zohour et al., 2014). Even though no significant coke was detected in the catalytic experiments performed within 72 hours of operation, gradual catalyst deactivation may occur over time. Regeneration of active sites is considered in reactions (9, 11, surface mechanism) through the formation and desorption of water and recombination of OH(s). Same regeneration steps were proposed previously (Aparicio et al., 1991; McCarty, 1992) and were observed by Electron paramagnetic resonance spectroscopy (Paganini et al., 2003).

**Effect of temperature.** The effect of temperature on the catalytic performance was investigated in the temperature range of 500-800 °C. After validating the proposed gas-phase and surface models, ROP analysis was performed to determine the primary reaction pathways and product distribution at low and high temperature regimes. Fig. 5 shows ROP analysis for 600 °C and 800 °C at CH\textsubscript{4}/O\textsubscript{2}= 13, representing catalytic performance in Fig. 3(b). The conversion of methane to CH\textsubscript{3}* radical increased with temperature via gas-phase reactions (28, 30, gas-phase mechanism) and catalytic reaction 3 [CH\textsubscript{4}+O(s)→CH\textsubscript{3}*+OH(s)]. The ROP results showed the contribution of gas-phase and surface reactions at each given temperature. For example, methane was converted homogeneously at 600 °C through reactions 28 and 30, whereas at 800 °C, reaction 28 was dominant. The fed oxygen was consumed initially via surface chemisorption [O\textsubscript{2}+2La(s)→2O(s)], then consumed completely by the gaseous phase reactions at higher temperatures.

Gaseous reactions were important to form the C\textsubscript{2}* products at low and high temperatures through reaction 73 [CH\textsubscript{3}*+CH\textsubscript{3}*→C\textsubscript{2}H\textsubscript{6}]. Ethane selectivity increased through homogeneous reaction 73 till 750 °C, then decreased due to its dehydrogenation rate (reaction 78,79,81, gas-phase mechanism). At elevated temperatures, the dehydrogenation rate of C\textsubscript{2}H\textsubscript{4} to C\textsubscript{2}H\textsubscript{5}* was greater than the production rate of C\textsubscript{2}H\textsubscript{6} from CH\textsubscript{3}*, which explains the reduction in selectivity to C\textsubscript{2}H\textsubscript{6} above 750 °C. These findings are in agreement with previous studies (Liu et al., 2018). Ethyl radicals dehydrogenated further in the gas-phase through reaction 87 [C\textsubscript{2}H\textsubscript{5}*+O\textsubscript{2}→C\textsubscript{2}H\textsubscript{4}+H\textsubscript{2}O*] at 600 °C and through reaction 83 [C\textsubscript{2}H\textsubscript{5}*(+M)→C\textsubscript{2}H\textsubscript{4}+H(+M)] at 800 °C. The difference in reaction pathways taken at 600 °C and 800 °C were explained by the oxygen availability at these temperature regimes and the activation energy difference in these reactions. Reaction 83 has higher activation energy than reaction 87 and requires higher temperatures to proceed.

In contrast to C\textsubscript{2}, CO\textsubscript{3} formation was favored at lower temperature regimes through surface reactions (13, 15, 17, 19, 21, 23, surface mechanism) and gas-phase reactions (23, 24, 25, 40, 45, 48, 49, 57, 59, 60, 62, 63, 72, gas-phase mechanism). The activation energies of CO and CO\textsubscript{2} are less than of C\textsubscript{2}H\textsubscript{6}, and this difference explains the increase in C\textsubscript{2} selectivity with temperature (Mleczko & Baerns, 1995). CO was mainly generated from the oxidation or dehydrogenation of HCO*, considering these elementary steps: CH\textsubscript{3}* → CH\textsubscript{2}O* → CH\textsubscript{2}O* → HCO* → CO. At 600 °C, HCO* dehydrogenated in the gas-phase mainly through reaction 63 [HCO*+O\textsubscript{2}→CO+H\textsubscript{2}O*], while at 800 °C, the dehydrogenation occurred through reaction 62 [HCO*+M→H+CO+M]. The different pathways adopted at 600 and 800 °C can be attributed to the difference in the activation energy and oxygen availability. C\textsubscript{3}H\textsubscript{6} was produced via gas-phase reaction 121 [C\textsubscript{2}H\textsubscript{4}+CH\textsubscript{3}*→C\textsubscript{3}H\textsubscript{6}+H], as shown in Fig. 5. Since C\textsubscript{3}
species were not included in the surface model, future work may be done to improve the product distribution by incorporating the surface oxidation of C₃ species into the surface model. It can be seen from the ROP analysis that the contribution of surface reactions was less than gas-phase reactions. This finding is in agreement with the literature (Karakaya et al., 2017). The main contribution of the surface reaction is to initiate the methane activation, then gas-phase reactions determine the end-product distribution.

Fig. 5—Reaction pathways for two operating temperatures as 600 °C in dark blue and 800 °C in bold purple font, percentages sum as 100%. Red arrows represent surface reactions and blue arrows represent gas-phase reactions. 20 mg catalyst diluted with SiO₂, 70.7kPa CH₄, 5.44kPa O₂, 101kPa total pressure, N₂ as balance, inlet volumetric flow rate 137 cm³/min at 25 °C.

Effect of CH₄/O₂. The effect of the CH₄/O₂ ratio on the catalytic performance was investigated by varying the inlet oxygen concentration at a constant space velocity and methane concentration (70%). ROP analysis for CH₄/O₂ = 3 & 13 at 800 °C identified the important reaction pathways and product distribution at each ratio, as shown in Fig. 6. The main reaction pathways were similar to Fig. 5, with minor differences discussed in this section. Oxygen availability was essential for forming methyl radicals in both homogeneous and heterogeneous reactions. Consequently, oxidative pathways for methane conversion were less active with increasing CH₄/O₂ ratio due to low oxygen concentration. However, oxygen availability favored CO formation through complete oxidation of hydrocarbons via surface reactions (13, 15, 17, 19, 23, 31, surface mechanism), gas-phase reactions (23, 24, 40, 57, 60, 62, 72, gas-phase mechanism) and ethylene surface oxidation via reaction 27 [C₂H₄+O(s)→C₂H₂O(s)]. Generally, as the inlet oxygen concentration increased, the methane conversion and selectivity to CO₂ increased, while selectivity to ethane decreased. Ethylene selectivity increased and then decreased due to the oxidation of hydrocarbons. Similar observations were found in the literature (Karakaya et al., 2017). It can be clearly observed that the relatively complex homogeneous and heterogeneous reaction pathways leading to the formation of C₂+ were significantly influenced by temperature and CH₄/O₂ ratio.
Fig. 6—Reaction pathways for two CH₄/O₂ ratios as 3 in dark blue and 13 in bold purple font, percentages sum as 100%. Red arrows represent surface reactions and blue arrows represent gas-phase reactions. 20 mg catalyst diluted with SiO₂, 70.7kPa CH₄, 101kPa total pressure, N₂ as balance, operating temperature 800 °C, inlet volumetric flow rate 137 cm³/min at 25 °C.

Sensitivity analysis

The steady-state species sensitivity analyses were conducted to demonstrate the influence of homogeneous and heterogeneous reactions on the reaction network proposed by the model. The sensitivity analyses were performed using CHEMKIN-PRO for C₂H₆ and CO at 800 °C and CH₄/O₂=13. Fig. 7 and Fig. 8 show the sensitivity coefficients on the x-axis, indicating the degree of promoting effect by the reactions having highest influence on the target specie. Fig. 7 highlights the important gas-phase reactions for C₂H₆ and CO production, while Fig. 8 highlights the important catalytic reactions. Fig. 7(a) shows the dimerization of methyl radicals [CH₃*+CH→C₂H₆] was the main source of ethane formation. This was followed by the formation of methyl radicals [CH₄+H→CH₃*+H₂]. It can be noted that an increase in the rate of formation of methyl radical increased the C₂ generation. In contrast, reactions consuming ethylene and methyl radical showed a negative effect. Ethane dehydrogenation to ethyl radical [C₂H₆+CH₃*→C₂H₅*+CH₄] was found to have the highest consumption of ethane, followed by ethyl radical dehydrogenation to ethylene [C₂H₅*+(+M)→C₂H₄+H(+M)]. The recombination of ethyl and methyl radicals [C₂H₅*(+M)+CH₃*↔C₃H₈(+M)] negatively affected ethylene formation.

Fig. 7(b) shows the sensitive gas-phase reactions for CO production. The dimerization of methyl radicals [CH₃*+CH₃*↔C₂H₆] had the most negative effect on CO production. There were three main routes for methyl radicals’ consumption to form CH₃O*, CH₃O(s), and C₂H₆. The first two led to the formation of CO, while the third led to C₂H₄ formation rather than CO. This explains the negative effect and can be seen in ROP Fig. 5 and Fig. 6. Generally, the reactions and species involved in the following elementary steps CH₃*→CH₃O*→CH₂O*→HCO*→CO had a positive sensitive coefficient (reactions 23, 24, 40, 57, 60, 62, 72, gas-phase mechanism). Gaseous reactions 81 and 83 that led to the formation of C₂H₅* and C₂H₄ were also found to have a positive sensitivity towards CO production. This can be attributed to CO formation through the hydrogen abstraction from ethylene (reactions 5, surface mechanism), forming active radicals for CO₂ generation, and the oxidation of ethylene via adsorption step (reactions 27–31, surface mechanism), following these elementary steps: C₂H₄→C₂H₄O(s)→C₂H₃O(s)→CH₂O(s)→HCO(s)→CO(s)→CO₂(s).
Fig. 7—Sensitivity analysis on (a) C$_2$H$_6$ and (b) CO over the proposed gas-phase kinetic model at steady state. 20 mg catalyst diluted with SiO$_2$, 70.7kPa CH$_4$, 5.44kPa O$_2$, 101kPa total pressure, N$_2$ as balance, operating temperature 800 °C, inlet volumetric flow rate 137 cm$^3$/min at 298K. Reactions with top ten sensitivity values are listed.

**Fig. 8(a) and (b) represent species sensitivity results for the most sensitive catalytic reactions involved in the production and consumption of C$_2$H$_6$ and CO, respectively. Oxygen adsorption and desorption on the catalyst surface and catalytic methane activation were essential steps in the OCM process. Therefore, they affected the C$_2$H$_6$ and CO sensitivity results. The formation of methyl radicals [CH$_4$+O(s)→CH$_3$+$^*$+OH(s)] had the highest positive sensitivity to ethane production. Regeneration of the active sites through water desorption [H$_2$O(s)+O(s)→2OH(s)] showed a positive effect and translated the stability of the catalyst reaction within 72 hours test. The methyl radicals surface oxidation to CH$_3$O(s) via [CH$_3$+$^*$+O(s)→CH$_3$O(s)] had the highest negative effect on the formation of C$_2$H$_6$. At the same time, it showed the highest positive impact on the formation of CO.**

The ROP results depicted in **Fig. 5 and Fig. 6** show that CH$_3$O(s) dehydrogenated to CO and resulted in reduced C$_2$ selectivity. **Fig. 8(b)** shows CO(s) desorption from the catalyst surface was the second-highest source of CO formation via reaction CO(s)→CO+La(s). Furthermore, C$_3$H$_4$ surface oxidation [C$_2$H$_4$+O(s)→C$_2$H$_4$O(s)] exhibited a positive effect on the formation of CO following reactions 27–31 from the surface mechanism.

Fig. 8—Sensitivity analysis on (a) C$_2$H$_6$ and (b) CO over the proposed surface kinetic model at steady state. 20 mg catalyst diluted with SiO$_2$, 70.7kPa CH$_4$, 5.44kPa O$_2$, 101kPa total pressure, N$_2$ as balance, operating temperature 800 °C, inlet volumetric flow rate 137 cm$^3$/min at 298K. Reactions with top ten sensitivity values are listed.
Conclusion

This study utilized a high-throughput screening instrument to collate an experimental dataset for OCM using La2O3/ CeO2 as a catalyst. For an adequate description of the complex chemistry involved in OCM, a wide range of operating conditions were defined and studied for the kinetic model development. The developed models accounted for the interactions between gas-phase and surface reactions in terms of elementary steps. A gas-phase model consisting of 123 elementary reactions and 25 species was developed. The model demonstrated satisfactory accuracy in predicting the OCM gas-phase chemistry and can be used as a reliable basis for surface mechanism optimizations. The developed surface model has 52 elementary steps between 11 surface species. The homogeneous and heterogeneous models were validated using packed-bed reactor simulations. The predictions of the models demonstrated acceptable agreement with the experimental data over the investigated range of operating conditions. The proposed mechanism showed a reasonable fit with an average difference of less than 5% compared to methane conversion and selectivities to ethylene and ethane experimental data. The models provided several advantages for accurate experimental predictions leading to save time and resources. Finally, the ROP and sensitivity analysis results revealed the important reactions driving the OCM process and can guide future catalyst development.

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