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Article

Optimizing Methane Oxidative Coupling Over La_2O_3 : Kinetic and Product Analysis

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Abstract: The Oxidative Coupling of Methane (OCM) is a promising process for converting methane directly into more valuable ethane and ethylene. In this work, high-time-resolution online mass spectrometry was employed to track the OCM reaction over a commercial La_2O_3 catalyst, focusing on the effects of methane to oxygen ratio, Gas Hourly Space Velocity (GHSV), and the presence of H_2O and CO in the feed gas on methane conversion and C_2 yield. The results demonstrated that an optimized GHSV (44640 to 93000 $\text{mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) and methane to oxygen ratio ($\text{CH}_4/\text{O}_2=3$) would achieve the highest methane conversion and C_2 yield at 740 °C. Furthermore, the introduction of 1% H_2O into the reaction mixture resulted in a twofold increase in C_2 yield at 650 °C, while the addition of 1% CO led to a threefold increase in C_2 yield at 550 °C. A model in which only the front-end catalyst is active was also developed to show excellent agreement with the experimental data. The relationship between catalytic performance and the effective catalyst position in the catalyst bed provides important insights into optimizing reactor design and operating conditions to maximize C_2 yield and selectivity in the OCM reaction.

Keywords: oxidative coupling of methane; La_2O_3 catalyst; online mass spectrometry; effect of operating parameters; kinetic study

1. Introduction

Methane, as the primary component of natural gas, holds substantial industrial value due to its abundance and versatility. It serves as a fundamental feedstock in the chemical industry, where it is converted into high-value products such as ethane and ethylene [1,2]. Among the various pathways for methane conversion, the oxidative coupling of methane (OCM) presents an effective and promising route for the direct transformation of methane into these valuable industrial compounds [3–6]. Due to its high activity in OCM and its high selectivity towards C_2 hydrocarbons at low temperature, La_2O_3 has been widely investigated and explored in research [7–10]. However, the C_2 yield achieved by the La_2O_3 catalyst falls short of meeting broadly accepted techno-economic targets of ~35% C_2 product yield and 90% C_2 selectivity [4,11]. To further enhance methane conversion and C_2 yield in La_2O_3 -based systems, thereby bringing the OCM process closer to achieving its desired industrial targets, an in-depth investigation of the reaction conditions is required.

Many researchers have extensively investigated the reaction conditions for the OCM process [12–16]. Yaghoobi et al. [12] conducted a parameter study on the GHSV and the methane to oxygen ratio in the OCM reaction. They found that, in the Sn/BaTiO_3 system, the optimal conditions for achieving the highest C_2 yield occur when the methane to oxygen ratio is 2 and the GHSV ranges from 8000 to 12000 $\text{mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. Ahari et al. [14] demonstrated that at higher GHSV ranges (12765–15790 $\text{mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), increasing GHSV significantly enhances C_2 selectivity. In contrast, Karimi et al. [13], investigating the same catalytic system at lower GHSV ranges (1300–2200 $\text{mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), reported that higher GHSV leads to a decrease in C_2 yield. This difference suggests that high GHSV and low GHSV may involve different reaction mechanisms. Therefore, a systematic analysis across a broader GHSV range is necessary to fully elucidate the impact of GHSV on both C_2 selectivity and yield. Achieving

a balance between selectivity and yield through a unified perspective is crucial for optimizing catalyst design and enhancing catalytic performance.

Another direction to change the operating parameters is to introduce H₂O into feed gas. Ni et al.[17] investigated the effect of H₂O on the Mn₂O₃-Na₂WO₄/TiO₂ catalyst (CH₄:O₂= 3:1, total GHSV of 7200 mL·g⁻¹·h⁻¹). Adding 20% H₂O increased methane conversion from 33.0% to 35.5% and improved C₂-C₃ selectivity from 62.1% to 66% at 700 °C, demonstrating that H₂O enhances catalytic performance. In addition, Aydin et al.[18] separately investigated the role of water in the OCM reaction (O₂-OCM) and the OCM reaction with N₂O (N₂O-OCM) systems. The results indicated that H₂O can enhance methane conversion and C₂ selectivity, with this positive promoting effect being more pronounced in the O₂-OCM system. Other researchers have also explained the promoting effect of water from the perspective of water-mediated enhancement of selective surface O species [19] or ·OH radicals [20]. However, studies on the promoting effect of water in the literature are primarily limited to the Mn₂O₃-Na₂WO₄ system, with very few investigations related to the La₂O₃ system. Considering the unique catalytic properties of La₂O₃, further research on its interaction with water could provide valuable insights into optimizing OCM performance.

The above literature has studied the effects of parameters such as GHSV, the methane to oxygen ratio, and the addition of H₂O into the feed gas on the catalytic performance of the OCM reaction. However, while valuable insights have been provided, the conclusions have shown some variation and may benefit from more systematic and comprehensive investigation to fully understand these influences. To gain a clearer understanding of how these parameters influence the catalytic performance of the La₂O₃ system, this work conducted a comprehensive experimental investigation of the operating parameters. The specific operating parameters include the methane to oxygen ratio, GHSV, and the addition of H₂O and CO to the feed gas. By tracking the reaction process by online mass spectrometry, we were able to directly observe the impact of these parameters on crucial catalytic performance indicators such as methane conversion, C₂ yield, and C₂ selectivity in the OCM reaction. Further analysis discusses the location of the active catalytic position within the reactor and establishes a model in which only the front-end catalyst remains active, while the rest gradually deactivates due to poisoning as the OCM reaction progresses. This model explains the observed effects of various experimental parameters on catalytic performance indicators.

2. Materials and Methods

2.1. Catalyst

Investigations are performed over a commercial La₂O₃ (L812319, ≥99.99%) catalyst supplied by Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). The BET surface area of commercial La₂O₃ is 3.4 m²·g⁻¹ (measured under Kr atmosphere) [21]. Samples with a mass of 6 mg to 25 mg are diluted with quartz powder (high-purity grade, 150Å pore size, 200-425 mesh), to a total loading is 100 mg. According to previous publication [21,22], the commercial La₂O₃ undergoes carbonation and hydroxylation upon exposure to air (contacting H₂O and CO₂), resulting in a decrease in the activity of the catalyst. Therefore, before using commercial La₂O₃ (hereinafter referred to as commercial La₂O₃) for OCM reaction, it is necessary to perform in situ pre-calcination to remove carbonates and hydroxides. The pretreatment steps are as follows: the La₂O₃ sample is placed in a microreactor, heated to 800 °C (heating rate: 10 °C/min) under argon atmosphere (argon flow rate: 20 mL·min⁻¹), and then cooled to room temperature for subsequent experiments. Previous XPS [22] and XRD [21] study show that when the sample is calcined to 800 °C under argon, a pure La₂O₃ phase can be obtained, and the catalyst surface is a clean surface.

2.2. Reactor

The kinetics experiments in this paper were conducted using our custom-designed microreactor, which is loaded with a ¼-inch quartz tube [23]. This microreactor is equipped with an efficient heat dissipation system, effectively preventing temperature runaway effect caused by the significant

exothermic nature of the OCM reaction. Additionally, the position of the microreactor where the catalyst is loaded is heated uniformly. The detailed temperature profiles of the microreactor were provided in previous publications [24].

2.3. Online MS and Reaction Conditions

The analysis of OCM products was achieved using a Pfeiffer Prisma quadrupole mass spectrometer. Detailed information on this equipment and the MS calibration procedure can be found in our previous publication [24].

Information on experimental settings such as sample mass, GHSV, and feed gas flow rate for the comparative experiments with varying operational parameters is listed in Table S1 in the Supporting Information. To unify standards, the GHSV in this study is calculated solely based on the flow rates of methane and oxygen. The La₂O₃ catalyst at a GHSV of X mL·g⁻¹·h⁻¹, with n% concentrations of H₂O/CO added to the reaction gas, is denoted as La₂O₃-XmL-nH₂O/CO. In all OCM experiments, 1.4 mL·min⁻¹ of Ar was added as an internal flow standard in the feed gas, and 147 mL·min⁻¹ of Ar was used as a diluent in the exhaust gas before MS analysis. The temperature ramping was programmed from RT to 740 °C with a heating rate of 10 °C/ min. The carbon balance for all OCM reactions discussed in this paper is shown in Figure S1-S4 in the Supporting Information. The carbon balance results indicate that for most OCM experiments, the carbon balance was below 100% at 600 °C, while at 740 °C, it reached approximately 110%, with a few cases exceeding this value. This discrepancy can be attributed to the partial adsorption of products on the catalyst surface at lower temperatures, followed by their desorption at elevated temperatures. The CH₄ conversion rate, C₂ selectivity, and yields of C₂ and CO₂ are calculated by the following equation:

$$\text{CH}_4 \text{ conversion}(\%) = \frac{[\text{CH}_4 \text{ input}] - [\text{CH}_4 \text{ output}]}{[\text{CH}_4 \text{ input}]} \times 100 \quad (1)$$

$$\text{Yield}(\%) = \frac{n * [\text{Product}]}{[\text{CH}_4 \text{ input}]} \times 100 \quad (2)$$

$$\text{Selectivity}(\%) = \frac{n * [\text{Product}]}{[\text{C}_{\text{total}} \text{ output}]} \times 100 \quad (3)$$

Where n in Equations (2) and (3) is the carbon number of the product molecules.

The mass activity is determined using the following equation:

$$\text{Mass activity}(\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}) = \frac{\text{Yield} * [\text{CH}_4 \text{ input}]}{m} \quad (4)$$

Where m is the loading quality of the sample; yield is calculated by Equation (2).

3. Results

3.1. Effect of Methane to Oxygen Ratio

The effect of the methane to oxygen ratio was investigated by comparing the CH₄ conversion, CO₂ yield, and C₂ yield in the OCM reaction over the La₂O₃ catalyst. Three distinct methane to oxygen ratios, namely 3:1, 5:1, and 10:1, were selected for the experimental investigations. As shown in Figure 1A, for GHSV= 44640 mL·g⁻¹·h⁻¹, the best results for methane conversion are achieved at CH₄:O₂= 3:1, indicating that a higher oxygen content improves the catalytic activity of La₂O₃ catalyst in OCM reaction. When CH₄:O₂= 3:1, the curve of methane conversion rises rapidly with increasing temperature, stabilizing only around 650 °C. The C₂ yield follows a similar trend. In contrast, under conditions with a higher methane to oxygen ratio, the rate of increase in methane conversion slows down around 520 °C. As shown in Figures 1B and 1C, this slowdown in methane conversion can be explained by the stabilization of CO₂ production after 520 °C, while C₂ products have not yet started

to form. This indicates that under low oxygen partial pressure conditions, methane activation is limited, hindering further conversion.

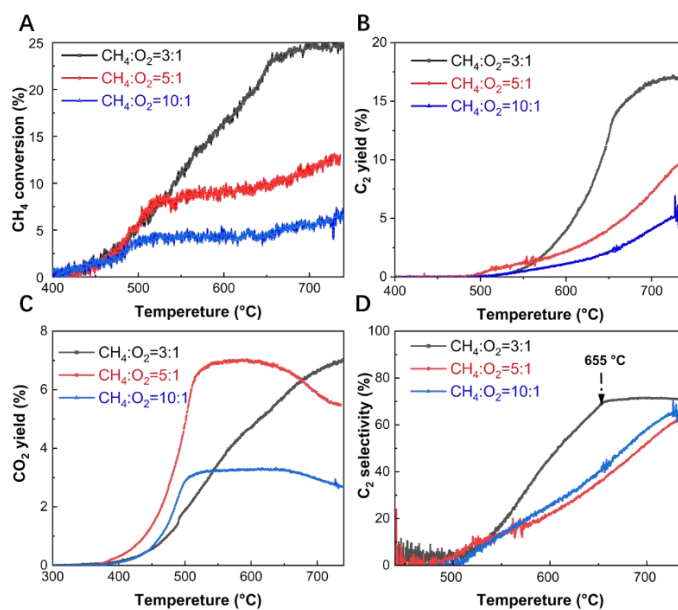


Figure 1. CH₄ conversion (A), CO₂ yield (B), C₂ yield (C) and C₂ selectivity (D) vs temperature of the OCM reaction over La₂O₃ catalyst by co-feeding 3:1 (black), 5:1 (red) and 10:1 (blue) CH₄ and O₂. OCM reaction conditions: 0.025 g of the catalysts under 20 mL·min⁻¹ CH₄: O₂: Ar=70:23:7, 77.5:15.5:7, 85:8.5:6.5 flow rate, GHSV= 44640 mL·g⁻¹·h⁻¹, heating rate:10 °C/min.

Figure 1D shows that the selectivity of C₂ products at different methane to oxygen ratios is similar at 740 °C. However, at 650 °C, significant differences in C₂ selectivity are observed. Specifically, for a methane to oxygen ratio of 3:1, the C₂ selectivity reaches 69%, while for ratios of 5:1 and 10:1, it is 38% and 43%, respectively. These indicate that a higher oxygen concentration (at a CH₄/O₂ ratio of 3:1) significantly enhances the C₂ selectivity at lower temperatures. To further investigate the impact of oxygen content, we examined the oxygen consumption under different methane to oxygen ratios. In Figure S5, under the conditions of a methane to oxygen ratio of 3:1, the higher oxygen concentration ensures that oxygen is fully consumed at 740 °C, even though the reaction rate is relatively slow. In contrast, at methane to oxygen ratios of 5:1 and 10:1, oxygen is consumed more rapidly initially but not fully depleted. The experimental observation can be explained by the role of a higher oxygen partial pressure in facilitating the formation of methyl radicals ($\cdot\text{CH}_3$). As reported in the literature [25], at lower CH₄/O₂ ratios, the formation of methyl radicals was improved by the high partial pressure of O₂ to achieve high CH₄ conversion. However, at higher CH₄/O₂ ratios, the excess methane may competitively occupy oxidative active sites on the catalyst surface, limiting the oxygen's ability to generate sufficient methyl radicals. As a result, the lower oxygen partial pressure under these conditions reduces the formation of methyl radicals, which in turn hinders methane activation and reduces methane conversion.

3.2. Effect of GHSV

In this work, the influence of GHSV is investigated by varying the sample mass and flow rate. The GHSV values range from 14880 to 186000 mL·g⁻¹·h⁻¹. The specific experimental settings are listed in Table S1. It should be noted that the methane to oxygen ratio in all experiments was optimized to 3:1. In these tests, methane conversion, C₂ yields, C₂ selectivity, and mass activity were all measured at a constant temperature of 740 °C. As shown in Figure 2A-C, both methane conversion, C₂ yields and C₂ selectivity first increase and then decrease with the rise in GHSV, reaching their optimal values

within the GHSV range of 44640-93000 mL·g⁻¹·h⁻¹. In this study, the trend in C₂ selectivity is consistent with that of methane conversion and C₂ yield. Moreover, within a specific range of GHSV (44640-93000 mL·g⁻¹·h⁻¹), both C₂ selectivity and yield remain at high levels. By enhancing C₂ selectivity without compromising C₂ yield, this study offers a new pathway for the industrial feasibility of direct methane conversion into high-value C₂ products.

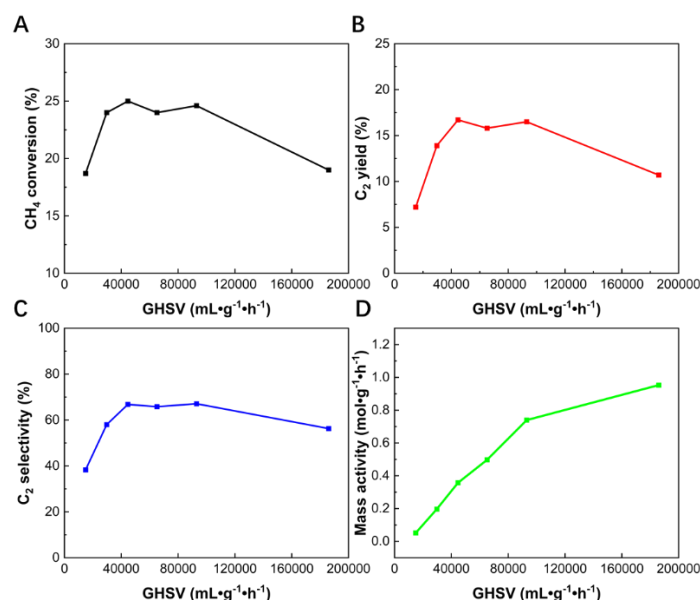


Figure 2. Comparison of CH₄ conversion (A), C₂ yield (B), C₂ selectivity (C) and mass activity (D) for catalysts at different GHSV, measured at 740 °C. The GHSV are varied from 14880 mL·g⁻¹·h⁻¹ to 186000 mL·g⁻¹·h⁻¹.

Figure 2D further illustrates the relationship between GHSV and mass activity (in mol·g⁻¹·h⁻¹). In a reactor with uniform temperature, the mass activity of the catalyst generally does not change with changes in GSHV. However, in this study, the mass activity increased with rising GHSV, suggesting that not all parts of the catalyst are equally active throughout the reactor. Even when the GHSV reaches 186000 mL·g⁻¹·h⁻¹, with a catalyst mass as low as 6 mg, the mass activity remains significant, with methane conversion still close to 19% and C₂ selectivity exceeding 56% (Table 1). This indicates that even a minimal amount of catalyst can exhibit considerable catalytic activity in a microreactor setup.

Table 1. Comparison of CH₄ conversion and C₂ selectivity for catalysts at different GHSV.

GHSV (mL·g ⁻¹ ·h ⁻¹)	CH ₄ conversion at 740 °C (%)	C ₂ selectivity at 740 °C (%)
14880	18.7	38.3
29760	24	58.1
44640	25	71
65100	24	70.3
93000	24.6	70.4
186000	19	56.3

3.3. Effect of H₂O in the Reaction Gas

To investigate the impact of adding water to the reaction gas on catalyst performance, two sets of OCM experiments were designed. Each set of experiments was conducted under two different GHSV conditions: 14880 mL·g⁻¹·h⁻¹ and 44640 mL·g⁻¹·h⁻¹, representing the lowest and the optimal GHSV values within the range explored in this study. For each GHSV condition, one group included

the addition of 1% water in the reaction gas, while the other served as a control group in the absence of water.

As shown in Figure 3A, at a GHSV of $14880 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, the addition of 1% water not only lowered the activation temperature for C_2 product formation by approximately $100 \text{ }^\circ\text{C}$ (from $540 \text{ }^\circ\text{C}$ to $440 \text{ }^\circ\text{C}$), but also nearly doubled the C_2 yield in both the low temperature ($650 \text{ }^\circ\text{C}$) and high temperature ($740 \text{ }^\circ\text{C}$) ranges. At the same time, it can be seen from Table 2 and Figure 3C that the methane conversion of the system with water added increased by 5% and the C_2 selectivity increased by 14.4%. These results suggest that the addition of water significantly enhances the performance of the La_2O_3 catalyst. As shown in Figure 3B and D, at $44640 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ (the optimized GHSV), the C_2 yield and C_2 selectivity curves for the water-added group (blue) and the non-water group (orange) completely overlap, indicating that the addition of water has no effect on catalytic performance. The effect of adding water to the reaction gas varies significantly under different GHSV conditions. This demonstrates that only at lower GHSV, where the contact time between the catalyst and water vapor is sufficiently long, can the catalytic activity be markedly improved.

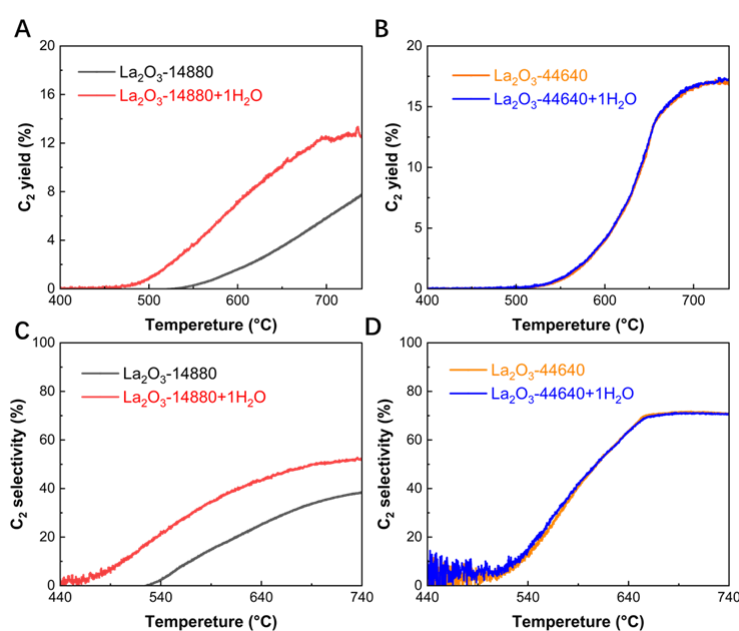


Figure 3. C_2 yield and selectivity vs temperature of the OCM reaction over La_2O_3 catalyst by co-feeding 3:1 CH_4 and O_2 with (orange) or without 1% vol H_2O (blue) at $\text{GHSV}=14880 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ (A and C) and $44640 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ (B and D). OCM reaction conditions: 0.025g of the catalysts under 6.7 (A and C) and $20 \text{ mL}\cdot\text{min}^{-1}$ (B and D) CH_4 ; O_2 : $\text{Ar}=70:23:7$ flow rate, heating rate: $10 \text{ }^\circ\text{C}/\text{min}$. The experiment represented by the orange line in Figure 3 correspond to the same experiment as those under the same conditions in Figure 2.

Table 2. Comparison of CH_4 conversion and C_2 selectivity for La_2O_3 with and without water at $14880 \text{ L}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. OCM reaction conditions: 0.025 g of the catalysts under $20 \text{ mL}\cdot\text{min}^{-1}$ CH_4 ; O_2 : $\text{Ar}=70:23:7$ flow rate, heating rate: $10 \text{ }^\circ\text{C}/\text{min}$.

Sample	CH_4 conversion at $740 \text{ }^\circ\text{C}$ (%)	C_2 selectivity at $740 \text{ }^\circ\text{C}$ (%)
$\text{La}_2\text{O}_3\text{-}14880\text{+}1\%\text{H}_2\text{O}$	25.3	52.7
$\text{La}_2\text{O}_3\text{-}14880$	18.7	38.3

It is noteworthy that water is also a product of the OCM reaction, accounting for approximately 10%. However, the introduction of just 1% H_2O into the reaction gas significantly enhances the catalytic activity. This suggests that the role of added water differs from that of the water produced during the OCM reaction. First, the interaction of added water with the catalyst involves unique chemical pathways, such as the formation of $\cdot\text{OH}$ radicals [20], which are absent or less pronounced

in the case of produced water. These radicals play a crucial role in enhancing the reaction kinetics and improving the overall efficiency of the OCM process. Secondly, added water directly participates in the reaction mechanism by promoting the formation of active oxygen species on the catalyst surface. These species facilitate the activation of methane and the subsequent formation of C₂ products [19]. In contrast, water produced during the reaction does not effectively interact with the catalyst due to its location downstream of the reaction zone. In light of the experimental observation that the addition of water shows no significant effect at high gas flow rates, the second explanation is more convincing. Under high flow conditions, the residence time of water on the catalyst surface is limited, which weakens its ability to promote the formation of active oxygen species. Therefore, the key to water's role is its effective interaction with the active part of the catalyst, where it contributes to the generation of active oxygen species by ensuring sufficient contact with the active catalytic sites.

3.4. Effect of CO in the Reaction Gas

The effect of CO was studied by adding 0%, 1%, and 5% CO into the reaction gas. All experiments were conducted under the optimized methane/oxygen ratio (3:1) and GHSV (44640 mL·g⁻¹·h⁻¹). As shown in Figure 4A and B, after the addition of 5% CO, both CH₄ conversion and C₂ yield are significantly lower compared to the control group in the absence of CO. This is attributed to the poisoning effect of CO₂[21], which is generated from the reaction between the added CO and oxygen. However, similar results were not observed in the experimental group with 1% CO addition. The C₂ yield with 1% CO addition is slightly lower than that of the control group without CO. At 550 °C, however, the C₂ yield is more than three times higher than the control group. This significant difference highlights the crucial role of CO in enhancing catalytic performance at lower temperatures. It is well known that low-temperature C₂ production in the OCM reaction holds substantial economic value, and this effect of CO underscores its important research potential.

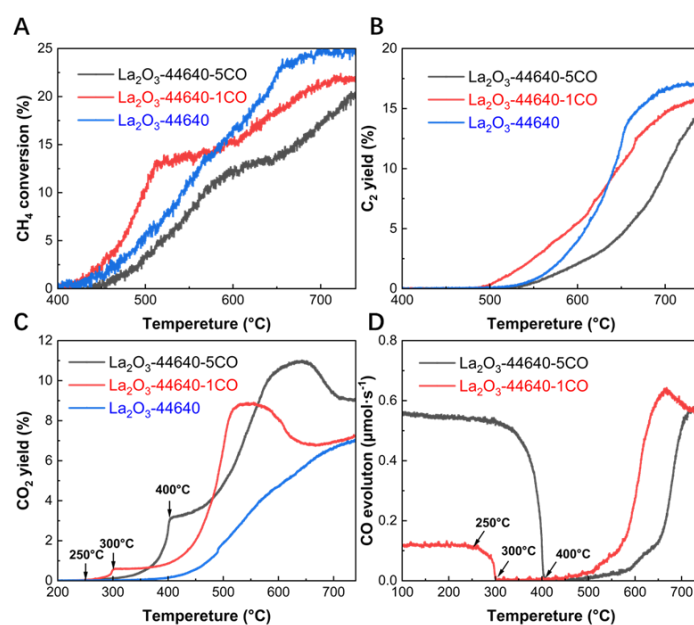


Figure 4. CH₄ conversion (A), C₂ yield (B) and CO₂ yield (C) vs temperature of the OCM reaction over La₂O₃ catalyst by adding 1% (black) and 5% (red) concentrations of CO to the reaction gas. The control group (blue) do not add CO. (D) The online MS results of the real time CO in exhaust outputs vs. temperature during the OCM reaction. OCM reaction conditions: 0.025 g of the catalysts under 20 mL·min⁻¹ CH₄: O₂: Ar: CO=70:23:6:1, 70:23:2:5, 70:23:7:0 flow rate, GHSV= 44640 mL·g⁻¹·h⁻¹, heating rate:10 °C /min.

Table 3. Comparison of C₂ yield for La₂O₃ with and without 1%, 5% concentrations of CO to the reaction gas at 44640 mL·g⁻¹·h⁻¹. OCM reaction conditions: 0.025 g of the catalysts under 20 mL·min⁻¹ CH₄: O₂: Ar: CO=70:23:6:1, 70:23:2:5, 70:23:7:0 flow rate, GHSV= 44640 mL·g⁻¹·h⁻¹, heating rate:10 °C /min.

Sample	C ₂ yield at 550 °C (%)	C ₂ yield at 740 °C (%)
La ₂ O ₃ -44640	0.77	17.0
La ₂ O ₃ -44640 +1%CO	2.5	15.6
La ₂ O ₃ -44640+5%CO	0.46	14.5

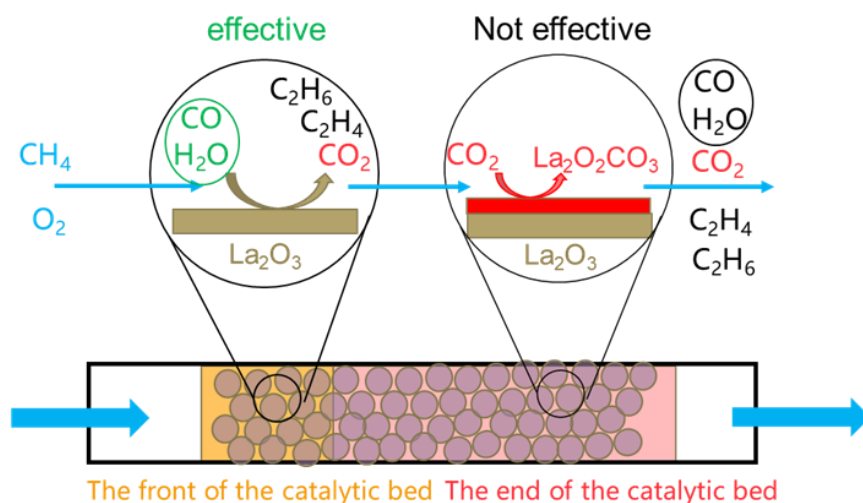
The distinctly different effects observed with varying concentrations of CO indicate that only low concentrations of CO can enhance catalytic performance. Figure 4C illustrates the dynamic changes in CO₂ production under different CO concentrations. With 1% CO added, a small amount of CO₂ begins to form when the reaction temperature reaches around 250 °C. However, with 5% CO, a large amount of CO₂ is generated in the temperature range between 300 °C and 400 °C. This suggests that at 1% CO concentrations, CO reacts with the oxygen in the system through CO oxidation around 250 °C. The La₂O₃ catalyst may have undergone structural changes during this reaction process, which would be a key factor in the subsequent improvement of catalytic activity. At higher CO concentrations, the poisoning effect of excessive CO₂ inhibits the promotional effect of this process, which explains why adding high concentrations of CO leads to a decrease in catalytic activity. Figure 4D shows the evolution of CO throughout the entire OCM process. The evolution in CO can be divided into two parts. First, as CO is introduced as a feed gas, 1% CO (0.11 μmol·s⁻¹) begins to decrease at 250 °C and is completely consumed by 300 °C, while 5% CO (0.55 μmol·s⁻¹) starts to decline at 300 °C and is depleted by 400 °C. This trend in CO corresponds precisely with the generation of CO₂ (Figure 4C), indicating that this portion of CO is fully converted to CO₂ within this temperature range. At temperatures above 500 °C, both the 1% and 5% CO experimental groups begin to gradually generate CO, with this portion of CO accounting for approximately 5% of the total products. This CO can be attributed to the CO generated by the OCM reaction. The impact of CO on catalyst activity occurs within the temperature range of 250–300 °C, during which the oxidation of CO to CO₂ ultimately leads to the early appearance of C₂ products and a significant increase in yield at lower temperatures.

4. Discussion

In the previous discussion, we suggested that the promotional effect of water originates from its role in facilitating the formation of active oxygen species. In prior research on the active sites of lanthanum oxide [22], XPS results indicate that the catalytic process of C₂ formation observed experimentally closely resembles the surface peroxide species predicted by the theoretical model, suggesting that peroxide is the active site. For this research, we infer that the use of H₂O as weak oxidants will promote the formation of peroxide sites, thereby increasing the C₂ yield and enhancing the OCM reaction. The promotional effect of a small amount of CO on low-temperature OCM reactions may be attributed to the generation of a small amount of CO₂, which acts as a weak oxidant similar to water, or to structural changes in the catalyst induced by oxidation reactions occurring at 250–300 °C.

In the OCM reaction, CO and H₂O are both products with yields exceeding 5%. In comparison, the addition of only 1% CO to the reaction feed significantly enhances catalytic activity, suggesting that H₂O and CO, as OCM products, do not play the same role as the 1% H₂O and CO added to the reaction feed. Notably, the low concentrations of H₂O and CO are added at the front-end of the catalyst in the reactor, while the H₂O and CO generated during the reaction are found at the rear end of the catalyst. The fact that smaller amounts have a greater effect suggests that H₂O and CO influence different active position of the catalyst. Tests related to GHSV also support this observation. Typically, when the temperature within the reactor is uniformly maintained and no significant catalyst deactivation or poisoning occurs, each part of the catalyst in the reactor is expected to contribute equally. However, the GHSV experiments show that over a significant range, the mass

activity of the catalyst increases as GHSV rises. Additionally, the fact that even a small amount of catalyst exhibits good OCM performance implies that only a small portion of the catalyst mass is actively contributing, and the catalyst's active position is limited to a small region. Based on these insights, we developed a new model to discuss and explain how various experimental parameters influence OCM performance, as shown in Scheme 1.



Scheme 1. Catalyst reaction activity at different positions in the bed.

In Scheme 1, we divided the catalyst bed into two positions: the front-end and the rear end. At around 400 °C, the La_2O_3 catalyst at the front starts to generate CO_2 after the OCM reaction. According to previous study on the poisoning effect of carbonate, the CO_2 generated during the OCM reaction gradually accumulates [21]. The $\text{La}_2\text{O}_2\text{CO}_3$ formed from the CO_2 poisons the catalyst surface, leading to a decline in catalyst activity. In this model, The CO_2 produced at the front-end of the catalytic bed during the OCM reaction is carried by the gas flow to the rear end of the bed. There, it interacts with La_2O_3 on the surface to form $\text{La}_2\text{O}_2\text{CO}_3$, which is identified as a poison for OCM [21]. Therefore, the active position of the catalyst is only present in the La_2O_3 at the front-end of the catalytic bed. Further studies on the distribution of $\text{La}_2\text{O}_2\text{CO}_3$ within the reactor based on this model are planned for future work.

The model on the active position of the catalyst explains well the experimental phenomena observed in OCM reaction kinetics. This model provides a comprehensive explanation of the experimental phenomena observed in the kinetics of the OCM reaction. In the GHSV experiments, even at the stage where the reaction rate begins to decline with increasing GHSV, the OCM reaction can still rely on the active portion at the front-end of the catalytic bed. This results in a continuous increase in the mass flow rate per unit of catalyst activity in the front position, thereby enhancing the catalyst's utilization efficiency per unit time. Consequently, while methane conversion and C_2 selectivity eventually decrease due to limited reaction time, the mass activity of the catalyst continues to increase with rising GHSV.

The model in which only the front-end catalyst is active explains water's varying effects at different GHSV levels. At low GHSV, the extended residence time in the catalyst's front position allows thorough contact between reactants and active sites. Under these conditions, 1% added water acts as a weak oxidant, promoting peroxide site formation and enhancing C_2 selectivity, thereby significantly boosting catalyst performance. However, at high GHSV, reduced residence time limits water's effect, diminishing its impact on enhancing activity. This model also explains the different effects of adding 1% versus 5% CO to the reaction gas on catalytic activity. With 1% CO_2 , the low concentration undergoes oxidation at 250–300 °C, altering the catalyst's redox state and significantly enhancing C_2 yield at low temperature. However, with 5% CO_2 the front-end concentration becomes

too high, leading to excess CO₂ that poisons the catalyst surface, preventing any improvement in catalytic activity. In the OCM reaction, the amounts of self-generated H₂O and CO typically exceed 5%, accumulating progressively in the middle-to-late stages, particularly in the rear position of the catalyst. However, according to this model, the rear portion of the catalyst is inactive, so the accumulated H₂O and CO in the later stages cannot promote catalysis at the onset as effectively as the 1% H₂O and CO added to the front.

5. Conclusions

The effects of operating parameters on OCM over commercial La₂O₃ catalyst have been studied by using online mass spectrometry. Experimental results show that an optimized GHSV (44640 to 93000 mL·g⁻¹·h⁻¹) and optimum methane to oxygen ratio (CH₄/O₂ = 3) would achieve the highest methane conversion and C₂ yield. Moreover, introducing a small amount of CO and H₂O into the reaction mixture can significantly improve the C₂ yield of OCM reaction at low temperature. The model we established explains the influence of the operating parameters on OCM performance. With only the front position active, the input of 1% CO and H₂O exhibits a distinct catalytic enhancement compared to the effects of self-generated H₂O and CO.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Figure S1: Carbon balance on La₂O₃ catalyst by cofeeding 3:1(black),5:1(red) and 10:1(blue) CH₄ and O₂. Figure S2: Carbon balance on La₂O₃ catalyst at different GHSV. The GHSV are varied from 14880 L·g⁻¹·h⁻¹ to 186000 mL·g⁻¹·h⁻¹. Figure S3: Carbon balance on La₂O₃ catalyst by cofeeding 3:1 CH₄ and O₂ with 1% vol H₂O at GHSV=14880 mL·g⁻¹·h⁻¹ and 44640 mL·g⁻¹·h⁻¹. Figure S4: Carbon balance on La₂O₃ catalyst by cofeeding 3:1 CH₄ and O₂ with 1% vol CO and 5% vol CO at GHSV=44640 mL·g⁻¹·h⁻¹. Figure S5: Oxygen consumption vs temperature of the OCM reaction over La₂O₃ catalyst by cofeeding 3:1, 5:1 and 10:1 CH₄ and O₂. Table S1. Experimental setup for catalysts at different operating parameters.

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