

Advances in Oxidative Coupling of Methane

Jinlin Deng ^{1,2,3}, Peili Chen ^{2,3}, Shengpeng Xia ^{2,3,*}, Min Zheng ⁴ , Da Song ^{2,3}, Yan Lin ^{2,3} , Anqi Liu ^{2,3}, Xiaobo Wang ^{2,3}, Kun Zhao ^{2,3,*} and Anqing Zheng ^{2,3}

¹ School of Mechanical and Power Engineering, Shenyang University of Chemical Technology, Shenyang 110142, China; dengjl@ms.giec.ac.cn

² Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China; chenpl@ms.giec.ac.cn (P.C.); sonda@glut.edu.cn (D.S.); linyan@ms.giec.ac.cn (Y.L.); liuaq@ms.giec.ac.cn (A.L.); wangxb@ms.giec.ac.cn (X.W.); zhengaq@ms.giec.ac.cn (A.Z.)

³ Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, China

⁴ State Key Laboratory of Complex Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650500, China; zhengmin1634@163.com

* Correspondence: xiasp@ms.giec.ac.cn (S.X.); zhaokun@ms.giec.ac.cn (K.Z.); Tel.: +86-020-8705-7716 (S.X. & K.Z.)

Abstract: C₂₊ hydrocarbons, especially C₂₊ olefins, as important basic chemical raw materials, mainly come from petroleum cracking. With the increasing scarcity of petroleum resources, the search for new olefins production routes has become the focus of research, and the production of olefins by the oxidative coupling of methane (OCM) process has attracted extensive attention. The OCM route is an important alternative to the production of olefins from petroleum resources and is also an important direction for the development of efficient and clean utilization of natural gas. In this paper, the mechanism, catalysts, and other key factors for the production of olefins by methane oxidative coupling are reviewed. The mechanism of OCM, including the reaction pathway and the formation of intermediate products, is introduced. Then, commonly used catalysts, such as alkali metal/alkaline earth metal oxides, rare earth metal oxides, composite metal oxides with special structures, and classical catalysts Mn/Na₂WO₄/SiO₂, and their mechanisms of action in the reaction are discussed. In addition, the application of chemical looping oxidative coupling of methane (CLOCM) in olefin production is also investigated, which is a promising alternative way due to the high selectivity of olefins and the low cost of catalysts owing to the excellent performance of the catalyst recycling. These studies will help to further understand the mechanism of OCM for olefin production and provide guidance and support for applications in related fields.

Keywords: oxidative coupling of methane; chemical looping; catalysts; reaction mechanism



Citation: Deng, J.; Chen, P.; Xia, S.; Zheng, M.; Song, D.; Lin, Y.; Liu, A.; Wang, X.; Zhao, K.; Zheng, A. Advances in Oxidative Coupling of Methane. *Atmosphere* **2023**, *14*, 1538. <https://doi.org/10.3390/atmos14101538>

Academic Editor: Patricia K. Quinn

Received: 14 August 2023

Revised: 28 September 2023

Accepted: 3 October 2023

Published: 8 October 2023



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1. Introduction

As important organic chemical raw materials and the core of the petrochemical industry, C₂₊ hydrocarbons are mainly used as intermediates in the production of various chemical products such as polyethylene, vinyl chloride, ethylene oxide, and ethylbenzene. As it is the most widely used basic organic chemical raw material, the production of ethylene is an important symbol to measure the production level of a country's petrochemical industry and the lifeblood of a country's basic chemical industry [1,2]. At present, ethylene used in industry is mainly separated from the gas produced by petroleum refining plants and petrochemical plants. Restricted by the production scale, raw material resources, and some other limitations, ethylene production capacity currently still has an enormous gap. Under the current pressure of carbon peaking and neutralization, the production of ethylene can no longer rely solely on petroleum resources, and the feedstock structure will once again change to a lighter one. The development of new routes to synthesize low-carbon olefins from non-petroleum resources such as natural gas is a strategic issue

of great academic significance and application value which can greatly contribute to the improvement of the energy use structure and environmental pollution problems [3].

Methane is the primary component of natural gas, combustible ice, and shale gas, accounting for approximately 70–90 percent of natural gas [4]. As a greenhouse gas, methane has approximately 25 times the greenhouse effect of carbon dioxide. In addition, direct emissions of methane still occur in oil extraction, coal mining, and animal husbandry. Furthermore, over 90% of the methane in natural gas is flared or combusted for energy generation instead of being used as an inexpensive carbon feedstock. With the development of modern industry, it is particularly important to develop a route to produce ethylene from clean, inexpensive raw materials such as methane, which has become a crucial topic for energy-efficient use [5–7].

The molecule of methane has a regular tetrahedron configuration with very stable chemical properties, such as the formation of four equivalent C–H bonds after the sp^3 hybridization of its central carbon atom, a H–C–H bond angle of 109.5° , a C–H bond length of $1.087 \text{ \AA}$ [8], a small molecular polarization rate ($2.84 \times 10^{-40} \text{ C}^2\text{m}^2\text{J}^{-1}$), etc. [9], which make it difficult for it to undergo intra-molecular polarization and chemical bond breaking in a conventional environment. At 298 K, the C–H bond dissociation energy of methane, which is the most stable energy molecule in nature, is $439.3 \text{ kJ} \cdot \text{mol}^{-1}$ [10,11]. Additionally, from the thermodynamic point of view, the Gibbs free energy $\Delta G > 0$ for direct conversion of methane to hydrocarbons is also a nonspontaneous reaction under standard conditions which needs reaction temperature to be higher than 1000°C . The realization of methane activation and selective conversion under mild conditions is an enormous challenge in catalysis and in chemistry [12]. The traditional conversion routes of methane can be divided into indirect and direct conversions, as shown in Figure 1. Direct conversion pathways include processes such as methane dehydrogenation, methane cracking, and methane oxidation. These methods directly convert methane into a variety of compounds, such as ethylene, propylene, formaldehyde, or formic acid, which can go on to be used in the production of plastics and chemicals. Indirect conversion pathways, on the other hand, convert methane first to syngas, and then undergo further conversions, including methane vapor reforming, hydrogen production from methane, and methanol synthesis from methane. Although these traditional methane conversion pathways have been widely used in industry, in recent years, there has been a growing interest in exploring greener, more sustainable ways to utilize methane. This shift is aimed at reducing greenhouse gas emissions and minimizing wasted resources.

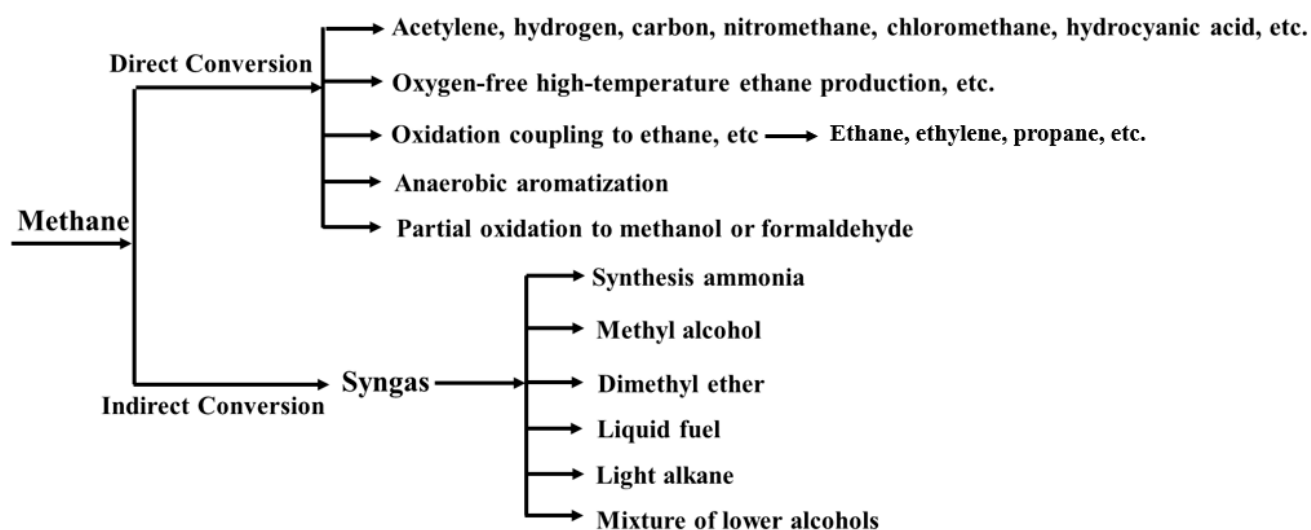


Figure 1. Methane conversion pathways.

Oxidative coupling of methane (OCM) refers to the process wherein methane is directly converted into carbon chain growth products such as ethylene, ethane, propylene,

propane, etc., in the presence of oxygen and under the action of catalyst with the formation of by-products such as carbon monoxide, carbon dioxide, and water [13,14]. OCM was originally proposed by Keller and Bhasin [15], who pioneered the preparation of ethylene by the oxidative coupling reaction of methane with oxygen. The OCM process overcomes the disadvantages of the high temperature required for oxygen-free dehydrogenation of methane to ethylene and the large amount of heat absorbed in the dehydrogenation reaction, making the process more attractive both in terms of thermodynamics and economic considerations [16]. However, the activation of methane with oxygen as oxidant is effective; the presence of oxygen tends to cause deep oxidation of methane to produce CO_x ($x = 0, 1, 2$) as a by-product, resulting in lower selectivity and yield of C_2 hydrocarbons [17]. To date, researchers have identified over two thousand kinds of catalysts, but no breakthroughs have been made in improving the selectivity and yield of C_2 , and industrial applications of OCM technology are still far away.

2. Catalysts for OCM

Currently, the development and design of catalysts, as well as the study of reaction mechanisms, are the focus of research on OCM technology. In order to realize further industrial applications, catalysts become the key in addition to the consideration of the reactor combined with the process design. So far, thousands of studies on OCM catalysts have been reported, and these studies have examined the reaction performance of catalysts in terms of metal screening, method of preparation, metal loading additives, and multi-type composites. Among them, several types of catalysts, such as alkali metal/alkali earth metal, rare earth metal oxide, transition metal oxide, and composite metal oxide, with special structure have the most potential for further investigations.

2.1. Alkali-Metal-Modified Alkaline Earth Metal Oxide

Alkali-metal-modified alkaline earth metal oxides were an early class of OCM catalysts, and researchers tried to improve the catalytic activity for OCM by adding various additives [18]. Among them, the effects of Li, Na, K, and Cs-modified MgO , CaO , SrO , and BaO on the performance of the OCM reaction were more widely studied. These catalysts typically feature highly basic active sites that adsorb and activate methane molecules, rendering them more amenable to oxidation reactions. Enhanced basicity is instrumental in promoting the activation and subsequent oxidation of methane, thereby augmenting the activity of the catalyst. Dorota Matras and her colleagues employed the sol-gel method to synthesize La-Sr/CaO catalysts for the oxidative coupling reaction of methane (OCM). Through the utilization of X-ray diffraction computed tomography, their study identified a pivotal factor contributing to the catalyst's performance—namely, the formation of Sr-doped CaO. This discovery holds promise for enhancing the catalyst's functionality by augmenting lattice oxygen diffusion and bolstering the catalyst's alkalinity, thereby optimizing its performance in the OCM reaction [19]. Gao et al. investigated the barium carbonate and magnesium oxide catalysts for OCM and found that the selectivity of C_2 stayed at 48–45% over barium carbonate catalysts, while H_2 selectivity reached about 18% at a CH_4/O_2 feed molar ratio of 4 in the temperature range of 780–820 °C [20]. Xu et al. conducted a systematic exploration of how various structural parameters affect catalytic performance. Their study revealed that both types of chalcogenides exhibit similar active sites in the OCM, with moderately and strongly basic sites proving to be favorable for OCM catalysis. Furthermore, the researchers observed a direct correlation between the surface alkalinity and the generation of reactive oxygen species, and they established an association between the presence of moderately basic sites and the concentration of oxygen vacancies which, in turn, plays a pivotal role in fostering the production of abundant reactive oxygen species [21]. Rane et al. studied the influence of alkali metal doping on the surface properties and catalytic activity/selectivity of CaO catalysts in the OCM reaction. The results showed that adding alkali metal promoters to CaO reduces the surface area but enhances the surface alkalinity (strong base sites) and the selectivity of C_2 . The research

team led by Lim et al. has successfully developed a novel catalyst that utilizes perovskite as a carrier and is loaded with alkaline earth metal oxides. Their primary objective was to achieve the highly selective production of C_{2+} compounds, even at relatively low reaction temperatures. The findings revealed the formation of intricate mixed oxides, which significantly contribute to C_{2+} yields. Furthermore, the basicity of the catalyst played a pivotal role in augmenting the activity of the OCM reaction [22]. The generation of mixed oxides, along with the catalyst's basicity, constitutes a pivotal determinant influencing the OCM process's efficiency. These combined factors contribute to enhanced yields of C_2 products and reduced reaction temperature prerequisites, consequently elevating the overall efficiency and selectivity of the OCM reaction. For example, Seoyeon Lim et al. [22] prepared a new catalyst for OCM by combining alkaline earth metal oxides with perovskite supports. Compared with pure perovskite, this new type of oxygen carrier exhibits better performance at lower reaction temperatures ($<700\text{ }^{\circ}\text{C}$) and can selectively generate C_2 compounds. In addition, as seen in Figure 2, they observed the formation of complex mixed oxides on the catalyst surface, such as Ba–Ca–Ti–Ox, Ba–Sr–Ti–Ox, and Ba_2TiO_4 . The presence of these mixed oxides helps to improve the yield of C_2 , and the catalyst itself has strong alkalinity, further enhancing the activity of OCM.

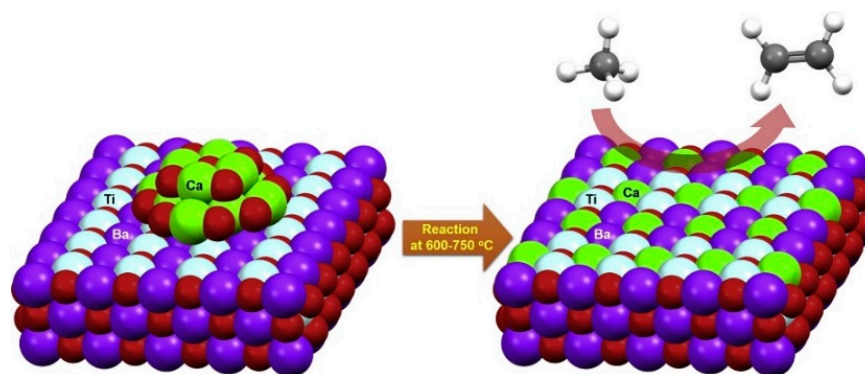


Figure 2. Schematic diagram of the mechanism of alkaline earth metal oxide and perovskite supported catalyst in methane oxidative coupling reaction [22].

Kun Qian et al. [23] reconstructed MgO by adding Li , which enhanced the surface density of the four coordinated Mg^{2+} sites on the MgO crystal plane. This ultimately resulted in the exposure of only Mg_{4c}^{2+} sites to the Li - MgO catalyst, which exhibited high efficiency in catalyzing the OCM reaction, as shown in Figure 3. In Figure 4A, it can be observed that with increasing Li loading, the CH_4 conversion rates of MgO , 1.3% Li - MgO , 5.6% Li - MgO , 11.2% Li - MgO , and 22.4% Li - MgO initially increased and then decreased at $750\text{ }^{\circ}\text{C}$, while the C_2 selectivity gradually increased. Figure 4B demonstrates that, under similar methane conversion rates, the C_2 selectivity also escalated. These results indicate that efficient single-site catalytic activity involving the Mg_{4c}^{2+} sites on the MgO crystal plane exists in the OCM reaction, particularly in Li - MgO catalysts with high Li content. Table 1 lists the characteristics of the catalysts.

Table 1. The OCM performance of some alkali-metal-modified alkaline earth metal oxide catalysts [2,4,6,10,24–29].

Catalyst	Temperature (K)	CH_4 Conversion (%)	C_{2+} Selectivity (%)	C_{2+} Yield (%)
CaO	1023	10.4	38.0	4.0
5% Na/CaO	1023	10.2	75.7	7.7
50% Ce/CaO	1023	10.6	73.8	4.8
10% La/CaO	1073	37.0	15.0	5.6
10% La –20% Sr/CaO	1073	43.0	20.0	8.6
7% wt Li/MgO	1073	22.6	72.5	12.8

Table 1. Cont.

Catalyst	Temperature (K)	CH ₄ Conversion (%)	C ₂₊ Selectivity (%)	C ₂₊ Yield (%)
3% wt Li/MgO	973	39.4	37.6	14.8
5.3% wt Li/MgO	803	23.0	54.0	12.4
Li/Mg/Zn (3/75/25, wt)	948	19	54.0	10.3
50% LiNiO ₂ -50% MgO	953	36.1	59.0	21.3
50% NaLnO ₂ -50% MgO	953	34.2	51.1	17.5
50 wt% LiCl-50 wt% Na ₂ MoO ₄	843	11.0	55.0	6.0
9 wt% K ₂ CO ₃ /7 wt% Bi ₂ O ₃ /Al ₂ O ₃	913	7.3	29.0	2.1

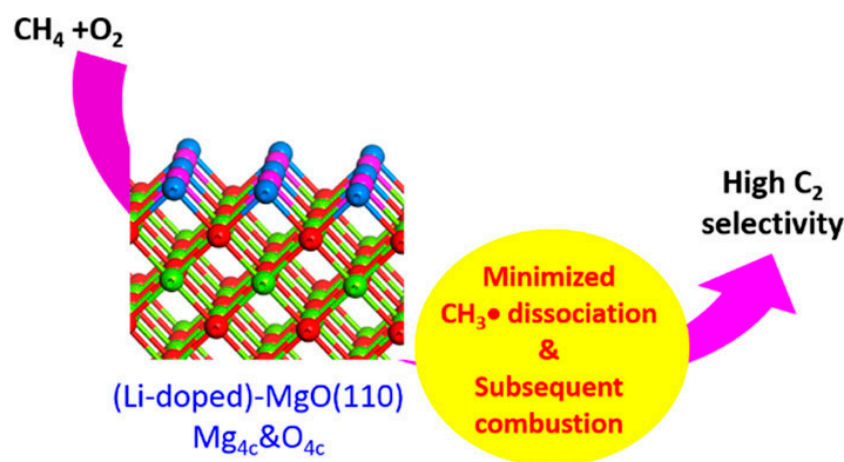


Figure 3. Li additives are used to modify MgO and enhance the surface density of four coordinated Mg²⁺ sites on the MgO crystal plane [23].

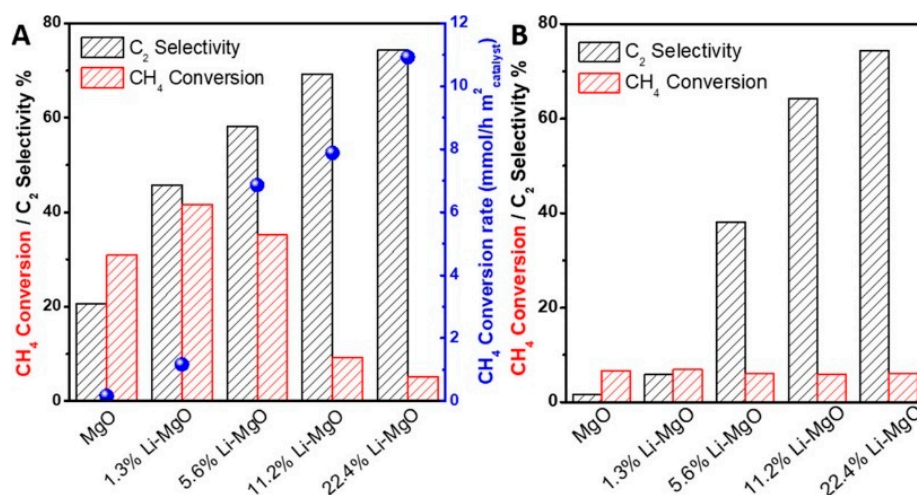


Figure 4. (A) Steady-state catalytic performance of Li-MgO catalysts in the OCM reaction at 750 °C and ambient pressure and (B) C₂ selectivity of various catalysts in the OCM reaction at similar CH₄ conversions. Reaction condition: 8% CH₄ and 4% O₂ balanced with Ar; flow rate: 150 mL/min [23].

2.2. Rare Earth Metal Oxides

Rare earth oxides are widely regarded as active and selective catalysts for OCM. They possess inherent basic sites that facilitate methane adsorption, thereby promoting C–H bond activation. In contrast to alkaline earth oxides, the alkalinity of rare earth oxides does not gradually decrease as the atomic number of the cation increases. As a consequence, distinct rare earth oxides exhibit varying degrees of alkalinity, which significantly impacts their performance in the OCM process.

Researches have demonstrated that rare earth oxides exhibit better activity and enhanced C_2 selectivity at lower temperatures compared to alkaline earth metal oxide catalysts. Achieving this can be accomplished through two primary strategies: tuning the shape of nanostructured materials or employing highly selective irreducible rare earth oxide catalysts. The morphology of nanostructures plays a pivotal role in facilitating low-temperature methane activation, as various oxidized surfaces exhibit varying degrees of reactivity [30,31]. Huang et al. [32] observed a substantial increase in C_2 selectivity which reached approximately 38% at 723 K with a slight drop to about 29% at 873 K. Notably, the C_2 selectivity of La_2O_3 nanorods outperformed that of La_2O_3 nanoparticles. This underscores the critical influence of operating temperature on the efficiency of low-temperature oxidative coupling of methane catalysts. Further investigations by Hou et al. [33] investigated the structure sensitivity of $La_2O_2CO_3$ and La_2O_3 catalysts, revealing that rod-shaped catalysts yield higher C_2 products. This phenomenon can be attributed to the relatively less dense atomic structure of rod-shaped catalysts, which promotes increased methane conversion and C_2 selectivity. Reducible rare earth oxides, such as CeO_2 , PrO_x , and TbO_y , exhibit high methane conversion rates but low selectivity. However, it is worth noting that the C_2 selectivity of these oxides can be enhanced through the introduction of alkali, alkaline earth, and other rare earth metal dopants. For instance, Ferreira et al. [34] demonstrated that doping CeO_2 with Ca^{2+} and Sr^{2+} cations increases the number of alkaline sites, thereby improving C_2 selectivity. Moreover, the choice of nanostructured materials can exert a substantial impact on the OCM reaction. Noon et al. [35] investigated nanofiber catalysts and observed heightened C_2 yields, potentially attributable to unique nanostructural properties. The efficacy of doping and preparation methods also varies, with recent studies showcasing the benefits of surface doping with Sr^{2+}/Ce^{4+} ions on La_2O_3 (001) for enhanced methane activation and sustained C_2 selectivity. Additionally, employing the nitrate combustion method for the synthesis of $La_2Ce_2O_7$ mixed-oxide catalysts prevents the formation of superoxide ions, thus contributing to improved C_2 selectivity [36]. The generation of C_2 products involves the direct coupling of CH_3 radicals in the gas phase. These CH_3 radicals are formed through the activation of CH_4 using oxygen sites on the catalyst surface [37]. Recent research has demonstrated that doped rare earth metal oxide catalysts, such as Sr/La_2O_3 , exhibit exceptional catalytic activity in OCM. However, La_2O_3 catalysts have shown relatively low C_2 yields, even at relatively low operating temperatures [38]. Jiang et al. reported that CH_4 conversion and C_2 selectivity could reach 32% and 46%, respectively, at a reaction temperature of 823 K [39]. Danusorn et al. employed a solution mixing technique to synthesize catalysts composed of rare earth oxide La_2O_3 promoted with alkaline earth metal oxides including Mg, Ca, Sr, and Ba. Extensive characterization techniques were applied to comprehensively investigate the influence of different alkaline earth metal oxides on catalyst performance, specifically focusing on C_{2+} yields, C_{2+} selectivities, and CH_4 conversion. Their findings reveal that La–Sr and La–Ba catalysts exhibit notable improvements in performance, signifying their efficacy as lanthanum-loaded alkaline earth metal oxide catalysts. Furthermore, it was observed that catalyst activity correlated closely with the presence of moderately basic sites and the adsorption of surface oxygen species in the form of O^{2-} [40]. Wang et al. successfully detected O^{2-} substances on the La_2O_3 catalyst surface using electron paramagnetic resonance (EPR) spectroscopy. Additionally, Louis et al. investigated the stability of O^{2-} substances on the La_2O_3 surface under OCM conditions. To gain deeper insights into the impact of oxygen sites on CH_4 activation, numerous studies have employed electronic structure calculations based on first principles [41]. Wang et al. proposed several strategies to enhance the reactivity of La_2O_3 catalysts. These strategies include constructing surfaces with a low coordination number of oxygen sites and doping with other elements [42]. It has also been demonstrated that on large clusters, O^{2-} sites can activate CH_4 by directly inserting an oxygen atom into the CH_3 –H bond [43]. Chrtien and Metiu investigated the dissociation of CH_4 on O^{2-} sites on the La_2O_3 surface through density functional theory (DFT) calculations [34], while

Schwach et al. suggested that gaseous O_2 may promote CH_3 radical formation, although the detailed mechanism is not yet fully understood [44].

The role and mechanism of catalysts in OCM are of great significance. The formation of C_2 products (e.g., C_2H_4 and C_2H_6) is crucial for efficiently converting unconventional natural gas, typically achieved through the direct coupling of CH_3 radicals in the gas phase. These radicals are generated by activating CH_4 at oxygen sites on the catalyst surface. However, due to the high C–H bonding energy in CH_4 , the OCM reaction demands a highly active catalyst, which may also lead to over-oxidation of C_2 products, resulting in the formation of CO and CO_2 by-products. To address this challenge, a wide range of catalysts has been explored, including alkali metal oxides, rare earth metal oxides, and mixed transition metal oxides, in pursuit of balanced reactivity and selectivity. La_2O_3 catalysts have exhibited good activity, especially at relatively low operating temperatures, but have yielded relatively low numbers of C_2 products. Experimental and theoretical calculations have elucidated the activation mechanisms of various surface oxygen sites, including lattice oxygen, peroxide, superoxide radicals, and oxygen radicals. Despite revealing different forms of catalyst surface oxygen, the precise catalytic mechanism of the OCM reaction remains a complex puzzle. These studies offer valuable insights into understanding OCM reactions and provide critical information for enhancing and optimizing catalyst performance.

In summary, optimizing nanostructures, incorporating dopant elements, and carefully controlling operating temperatures are crucial strategies for achieving heightened C_2 selectivity and superior reaction performance. These advancements hold significant promise for reducing operational costs, enhancing catalyst stability, and mitigating the formation of undesirable deep oxidation products, making them of paramount importance for the field of catalysis research.

Table 2 summarizes some kinds of rare-earth-based catalysts for OCM reactions, and C_{2+} yields are limited to lower than 16%.

Table 2. The OCM performance of some rare-earth-based catalysts [17,32,36,39,45–50].

Catalyst	Temperature(K)	CH_4 Conversion (%)	C_{2+} Selectivity (%)	C_{2+} Yield (%)
Sm_2O_3	1035	21.9	47.0	10.3
55 mol% Na/ Sm_2O_3	1035	21.2	61.0	12.1
30 mol% Ca/ Sm_2O_3	1035	22.6	50.0	11.3
ZnO/ Sm_2O_3	1048	21.7	41.9 a	9.1
MgO/ Sm_2O_3	1048	23.2	49.2 a	11.4
CaO/ Sm_2O_3	1048	25.0	57.2 a	14.3
SrO/ Sm_2O_3	1048	25.9	59.8 a	15.5
CaO	1058	13.3	49.3	6.6
La–CaO	1002	19.8	67.2	13.3
Ce–CaO	982	17.7	65.0	11.5
Sm–CaO	1013	18.7	62.5	11.7
Nd–CaO	973	19.5	70.8	13.8
Yb–CaO	999	20.1	66.4	13.3

2.3. Perovskite-Type Oxides

Perovskite-type oxides are a class of composite catalysts with potential for high OCM activity, characterized by the extremely easy formation of lattice defects on both their surface and bulk phases, with the formula of ABO_3 perovskite-type oxides and $A_2B_2O_7$ pyrochlore-type oxides [50]. Lu et al. synthesized a dense perovskite hybrid conductive membrane reactor comprising $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) to investigate the oxidative coupling reaction of methane (OCM) at elevated temperatures over an SrO/ La_2O_3 catalyst. They quantified the oxygen permeation flux of the BSCF functional membrane within the temperature range of 973 to 1123 K and scrutinized the membrane's surface morphology before and after the OCM-catalyzed reaction using scanning electron microscopy. The

findings indicated that, at 1123 K, the BSCF hybrid conductive membrane reactor exhibited remarkable selectivity for C_2 product formation, achieving a C_2 yield of 11.6%. Furthermore, the reactor displayed robust catalytic stability during the initial 30 h of operation. This investigation underscores the effectiveness of the BSCF hybrid conductive membrane reactor in catalyzing the high-temperature oxidative coupling of methane, resulting in the production of highly selective C_2 products with enduring stability. Such advances hold significant promise for applications in hydrocarbon chemical production and related industrial processes [51]. These lattice defects can act as oxygen vacancies to absorb the active oxygen species in the gas phase and to promote the migration and release of lattice oxygen stored within the catalyst, which is favorable for the OCM reaction [49,52,53]. The oxygen vacancies can be enhanced by doping with metal elements of different valence states, thus improving the performance of the OCM reaction [54]. Additionally, due to the high melting point, strong thermal stability, adjustable M–O bond, and positive surface alkalinity, they provide great potential for the enhancement of C_{2+} production [36,41,55,56]. The crystal structure of pyrochlore and defective fluorite is shown in Figure 5 [57].

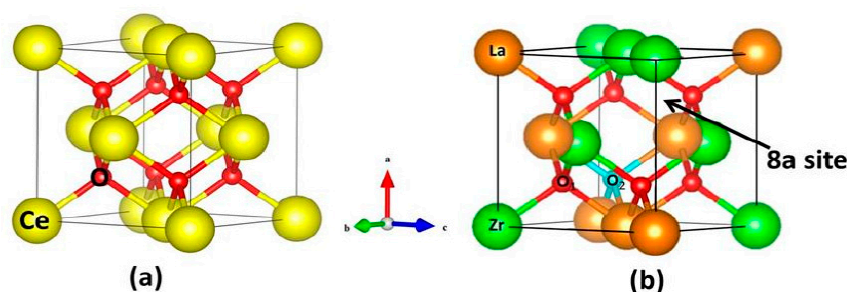


Figure 5. (a) Structure of pyrochlore (1/8 unit cell), (b) structure of defective fluorite [58].

The study conducted by Wang et al. investigated the utilization of perovskite oxides in the catalytic coupling of methane oxidation. In this study, $Ba_{0.5}Sr_{0.5}TiO_3$ perovskite was synthesized by partially substituting Sr sites with Ba. The researchers observed that this modified catalyst displayed significantly enhanced activity and stability. The reduction in grain size of $Ba_{0.5}Sr_{0.5}TiO_3$ resulted in an increased adsorption of surface oxygen, thereby facilitating the replenishment of active sites. Consequently, the researchers achieved a higher C_2 yield (18%) and C_2H_4/C_2H_6 ratio (1.7). Additionally, this nanoperovskite exhibited improved heat resistance and enhanced reaction stability. These findings offer valuable insights for enhancing catalyst performance, particularly in the realm of methane oxidation coupling reactions [59]. Sim et al. prepared ABO_3 -type perovskite catalysts with different structures and investigated the active site behavior of the catalysts. They found that the catalyst surface lattice oxygen plays an important role in the selective conversion of methane; especially, the surface lattice oxygen with moderate binding energy selectively catalyzes the formation of C_2 hydrocarbons from OCM. It was also found that the surface oxygen vacancies generated by the reaction between lattice oxygen and CH_4 were filled by adsorbed surface oxygen and bulk lattice oxygen, and this oxygen cycle was closely related to the oxygen ionic conductivity of chalcogenide. Therefore, the lattice oxygen nature and oxygen ion conductivity of perovskite catalysts are key factors in determining the catalytic activity [60].

Wang et al. [58] studied the Sr-modified $La_2Ce_2O_7$ catalyst for OCM. After Sr doping, a defective fluorite phase was formed, and the migration rate of lattice oxygen was improved. Among the three catalysts studied, $La_{1.5}Sr_{0.5}Ce_2O_7$ exhibited the highest lattice oxygen release, followed by 8% Sr/ $La_2Ce_2O_7$. The introduction of Sr increased the proportion of strong basic sites, which is usually beneficial for the production of C_2 products. As shown in Figure 6, at 800 °C, the selectivity and yield of the $La_{1.5}Sr_{0.5}Ce_2O_7$ catalyst reached 57% and 14%, respectively, and it demonstrated stable catalytic performance for up to 30 h without deactivation, as shown in Figure 7.

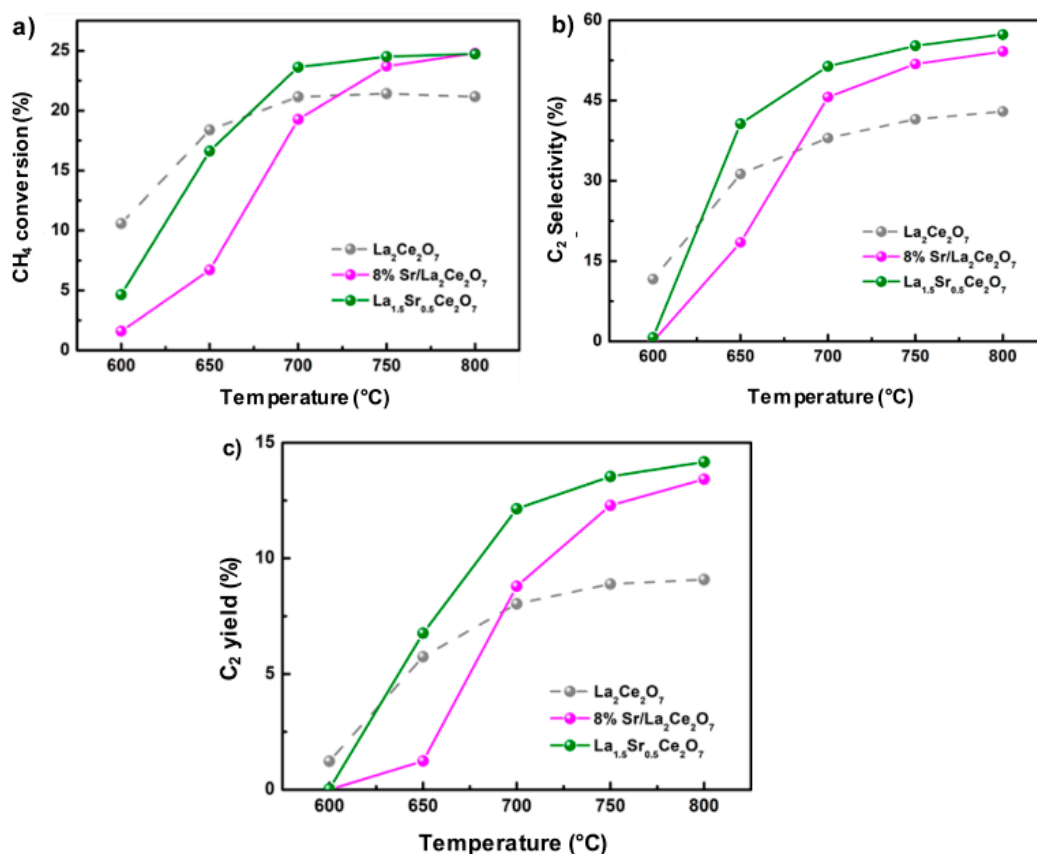


Figure 6. OCM reaction over the indicated catalysts: (a) CH_4 conversion, (b) C_2 selectivity, (c) C_2 yield. Reaction condition: $\text{CH}_4:\text{O}_2:\text{N}_2 = 4:1:5$, $\text{WHSV} = 72,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ [58].

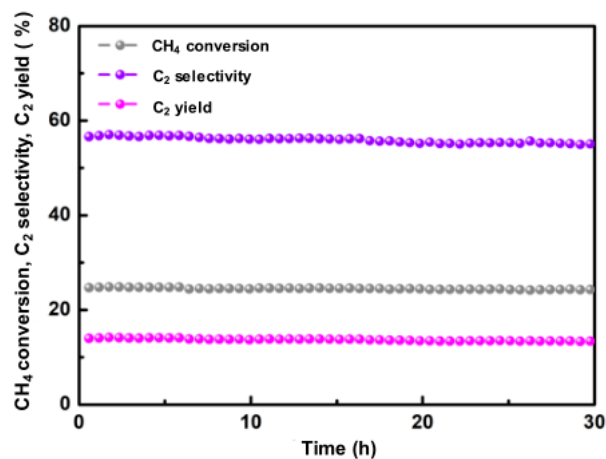


Figure 7. Stability test at 800 °C with the $\text{La}_{1.5}\text{Sr}_{0.5}\text{Ce}_2\text{O}_7$ catalyst. Reaction condition: $\text{CH}_4:\text{O}_2:\text{N}_2 = 4:1:5$, $\text{WHSV} = 72,000 \text{ mL}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ [58].

Gan et al. used X-ray photoelectron spectroscopy and $^{16}\text{O}/^{18}\text{O}$ isotope exchange reactions to investigate the effect of B-site elements in LaBO_3 ($\text{B} = \text{Al}, \text{Ga}, \text{In}, \text{Yb}, \text{Co}, \text{Mn}, \text{Fe}$) perovskite on the catalytic performance of OCM applications. It was found that LaAlO_3 , LaGaO_3 , LaInO_3 , and LaYbO_3 have higher activities for the generation of C_2 hydrocarbons in the OCM reaction. The kinetic study of the most and least active catalysts, LaAlO_3 and LaCoO_3 , revealed that the B-site element strongly affects the reaction of CH_4 with oxygen to form $\text{CH}_3\cdot$ as the first step of the OCM reaction and that the B-site element acts in LaBO_3 perovskite to produce a sufficient amount of surface oxygen [61]. Xu et al. employed various techniques to synthesize catalysts with different La/Ce molar ratios and

doped with Ca additives for the reaction performance of $\text{La}_2\text{Ce}_2\text{O}_7$ in OCM. The catalysts were characterized by altering the La/Ce ratio and doping with Ca additives to regulate the crystal structure and the number of active sites. They discovered that $\text{La}_2\text{Ce}_{1.5}\text{Ca}_{0.5}\text{O}_7$ exhibited the highest number of active sites, demonstrated superior reaction performance, and achieved higher C_2 yield at lower temperatures. Both active surface oxygen and basic sites were found to be crucial for OCM [62]. Wang et al. utilized perovskite compounds SrSnO_3 , Sr_2SnO_4 , and $\text{Sr}_3\text{Sn}_2\text{O}_7$ as catalysts and found that the fine crystal structure changes of these perovskite catalysts have a significant impact on their catalytic performance. Additionally, the $\text{O}^{2-}/\text{O}_2^{2-}$ electrochemical adsorption on the catalysts and the surface lattice O^{2-} play a crucial role in the production of C_2 products. Furthermore, medium and strong surface alkaline sites are important for the reaction. The study also revealed that the variation in Sn–O bond lengths among different perovskites is consistent with the changes in their catalytic performance. Finally, it was demonstrated that Sr_2SnO_4 possesses the highest number of active surface oxygen and alkaline sites, thus exhibiting the best performance in the methane oxidation reaction [63]. Petit et al. prepared a series of Sn-based perovskite ASnO_3 ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) by sol–gel method for the OCM reaction, and the results showed that different types of metal exhibit different activities. Among them, the catalysts synthesized with SnCl_4 as the tin-based precursor were superior to those synthesized with SnO in the OCM reaction, probably because the presence of Cl^- inhibited the deep oxidation of methyl radicals and thus improved C_2 hydrocarbon selectivity [64]. To investigate the role of Cl in OCM reactions, Fakhroueian et al. [65] de-modified BaSrTiO_3 catalysts with Li^+ , Na^+ , and Mg^{2+} chlorides for the OCM reaction and found that NaCl-modified catalysts exhibited the best OCM reaction performance, which was mainly because the doping of chlorides could increase the number of surface base centers of the catalysts.

2.4. Mn/ Na_2WO_4 / SiO_2 Catalysts

$\text{Mn}-\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts have attracted significant attention for their promising role in selective activation of methane. Researchers proposed three distinct activation mechanisms in their studies. As shown in Figure 8, Daniyal Kiani et al. [66] have collated an OCM mechanism of significance proposed by Lunsford and his team, known as the Lunsford Mechanism. The initial stage of the mechanism involves the activation of molecular O_2 in the gas phase through dissociative adsorption at the sodium (Na) site. This process leads to the generation of surface oxygen atoms on the catalytically active Na site. These oxygen atoms, in turn, facilitate the activation of the C–H bond within the methane molecule, resulting in the production of gas-phase CH_3 radicals. Subsequently, these CH_3 radicals undergo recombination to yield C_2H_6 .

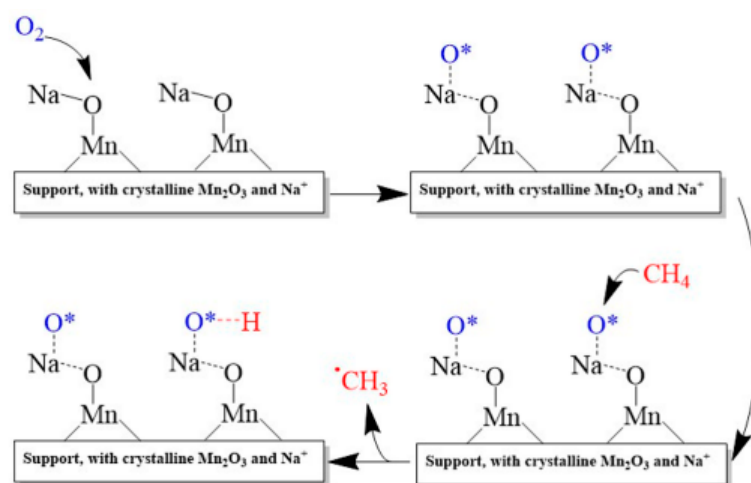


Figure 8. Catalytic OCM reaction mechanism proposed by Lunsford et al., where the active site is comprised of an Na–O–Mn bond, and WO_4 is only suggested as a stabilizer to prevent sintering/deactivation [67]. O^* represents the free ground state.

As shown in Figure 9, Daniyal Kiani and colleagues have compiled the second proposed reaction mechanism by Li [68] and Wang et al. [69], providing a comprehensive description of how two distinct active metal oxide sites within the catalyst synergistically facilitate the oxidative coupling of methane (OCM) reaction. Specifically, according to this mechanism, two different active metal oxide sites work together and play different roles in the reaction process. The CH_4 molecule is activated by the surface WO_4 (W^{6+}) site bounded with surface lattice oxygen, generating gaseous methyl radicals and reducing the surface WO_x site ($\text{W}^{6+} \rightarrow \text{W}^{5+}$). It is accompanied by electron transfer from W^{5+} to Mn^{3+} , which regenerates the W^{6+} site and reduces Mn^{3+} to Mn^{2+} . After that, Mn^{2+} continues to participate in the activation of gas-phase molecule O_2 , forming surface oxygen under the action of electron donors, which, once again, generates Mn^{3+} sites, and the OCM reaction involves multiple steps, including CH_4 molecule activation, redox reactions, and the involvement of various oxide sites, ultimately resulting in the conversion of methane into products, notably ethylene. It is crucial to note that the proposed mechanisms, despite their detailed elaboration, remain highly speculative due to the lack of experimental substantiation. Therefore, further experimental data are imperative to validate these hypotheses. Additionally, it is important to acknowledge that homogeneous gas-phase reactions become prominent at elevated temperatures. Under specific reaction conditions, such as temperature, CH_4/O_2 ratio, and reactor pressure, methane can undergo conversion to products such as ethylene and ethane even in the absence of a catalyst. In this catalytic process, lattice oxygen assumes a pivotal role characterized by two distinct forms: strongly adsorbed oxygen and weakly adsorbed oxygen. These two forms are associated with varying product selectivities, influencing the production of C_2 compounds or CO_2 . Recent experimental investigations have employed a range of techniques, including O_2 -TPD, H_2 -TPR, and TPSR, to scrutinize the role of oxygen within catalysts. The findings from these experiments lend support to the diverse functions of lattice oxygen in OCM reactions. Finally, it is noteworthy that an exchange between gas-phase O_2 and lattice oxygen occurs within the catalyst, with at least two distinct lattice oxygen species participating in the OCM reaction [70,71].

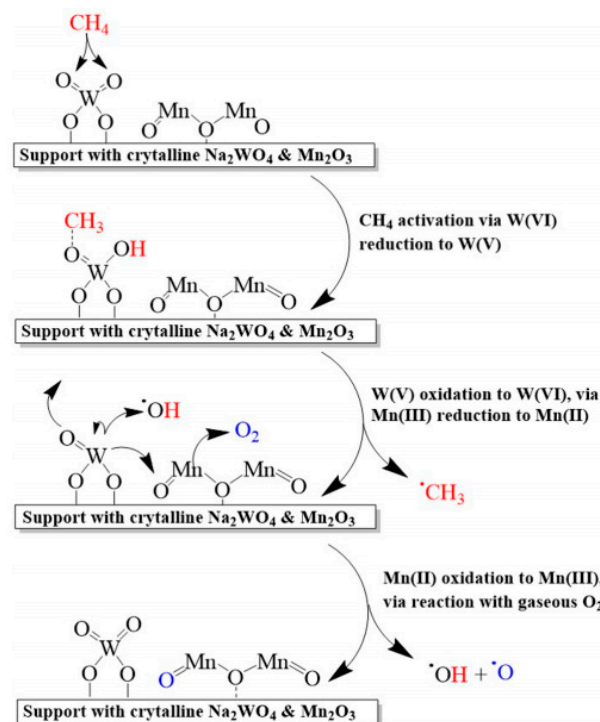


Figure 9. Catalytic OCM mechanism proposed by Li et al., where Na-coordinated WO_4 is the methyl-generating active site, while Mn_2O_3 in the neighborhood is responsible for gas phase activation. This mechanism and modified versions of it are widely accepted/discussed in the literature [66].

There is still no consensus on the type, role, and source of lattice oxygen in $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts. However, some studies have proposed hypotheses regarding the possible types, roles, and sources of lattice oxygen. For instance, the research conducted by Sagar Sourav et al. revealed the existence of two distinct oxygen species, dissolved O_2 and atomic O, in $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts at temperatures relevant to oxidative coupling of methane. Further investigations demonstrated that the incorporation of manganese oxides can enhance the total amount and release rate of dissolved O_2 , as well as improve the C_2 selectivity of dissolved O_2 and lattice atomic O. These findings suggest that the introduction of manganese oxides in supported catalysts can effectively modulate the oxygen species and promote enhanced C_2 selectivity [72]. Wang et al. [69] prepared a kind of TiO_2 -doped Mn_2O_3 $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst by solution combustion method consisting of 6 wt% titanium dioxide (TiO_2), 6 wt% manganese dioxide (Mn_2O_3), 10 wt% sodium tungstate dihydrate (Na_2WO_4), and silicon dioxide (SiO_2). Figure 10 shows the SEM, XRD, and Raman spectra of TiO_2 -doped Mn_2O_3 – $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst [73]. The TiO_2 -doped Mn_2O_3 – $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst exhibits special properties in terms of chemical composition and structure. Compared with the Raman bands of TiO_2 and Na_2WO_4 , as shown in Figure 10D, the calcined catalyst Mn_2O_3 exhibits significantly stronger Raman bands, and Mn_2O_3 exhibits weaker XRD peaks than TiO_2 and Na_2WO_4 . Therefore, it can be inferred that Mn_2O_3 dominates the surface of the catalyst.

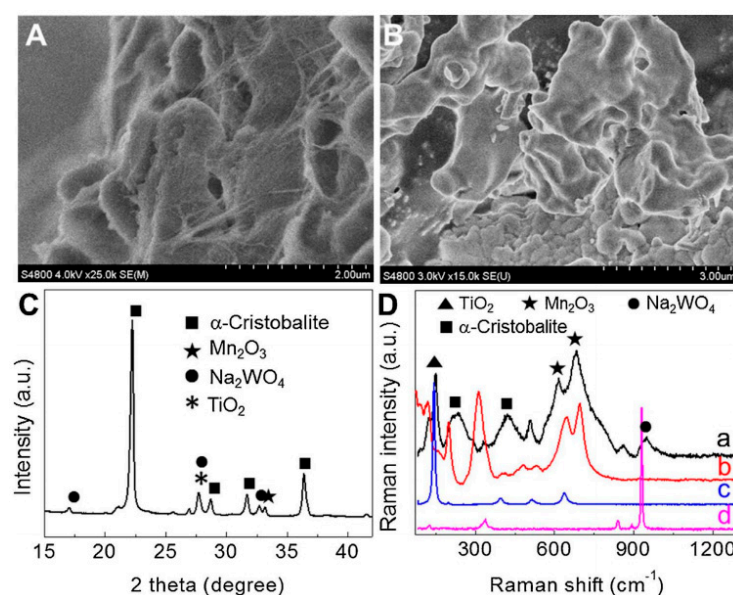


Figure 10. SEM images of typical SCS-synthesized TiO_2 -doped catalyst before (A) and after (B) calcining at 800 °C; (C) XRD pattern of calcined TiO_2 -doped catalyst; (D) Raman spectra: (a) the calcined TiO_2 -doped catalyst, (b) Mn_2O_3 , (c) TiO_2 , (d) Na_2WO_4 . Note of SCS preparation: titanium superoxide (Ti-I) as Ti precursor, ϕ of 2, and calcination temperature of 800 °C; 6 wt% TiO_2 , 6 wt% Mn_2O_3 , and 10 wt% Na_2WO_4 in catalyst [69].

As shown in Figure 11, Sagar Sourav and his research team [74] conducted a comprehensive study investigating the stability of crystalline Na_2WO_4 under the conditions of the oxidation coupling of methane (OCM) reaction. They employed in situ Raman spectroscopy and chemical probes to scrutinize the transformation of Na_2WO_4 and its impact on catalytic activity. Their findings unveiled a remarkable phenomenon: crystalline Na_2WO_4 experiences destabilization and partial conversion into thermally stable surface Na-WO_x sites when subjected to the OCM reaction conditions. Furthermore, the team conducted product time analysis and steady-state OCM reaction studies to elucidate the underlying reaction mechanism. Their investigations revealed a multifaceted process; the surface Na-WO_x sites exhibited selective catalytic activity, converting CH_4 to C_2H_x while over-oxidizing CH_y to CO. Concurrently, the molten Na_2WO_4 phase played a pivotal role in

the over-oxidation of CH_4 to CO_2 and facilitated the oxidative dehydrogenation of C_2H_6 to C_2H_4 . These insightful findings not only shed light on the nature of the catalytic active sites but also offer a comprehensive explanation for the OCM reaction mechanism over loaded $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts. Specifically, at lower loadings, no significant interaction occurred between the surface Na-WO_x sites and the three-dimensional Na_2WO_4 phase. However, at higher loadings, Na_2WO_4 diffused across the catalyst surface in the form of a molten salt. This diffusion hindered the easy access of CH_4 to the surface Na-WO_x sites, resulting in a complex structure and reaction network that posed challenges to the investigation of the OCM reaction mechanism on loaded $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts. In summary, the results underscore the catalytic activity of both surface Na-WO_x sites and the molten Na_2WO_4 phase in the OCM reaction. However, these active sites are engaged in distinct reaction steps, thus influencing the overall catalytic process.

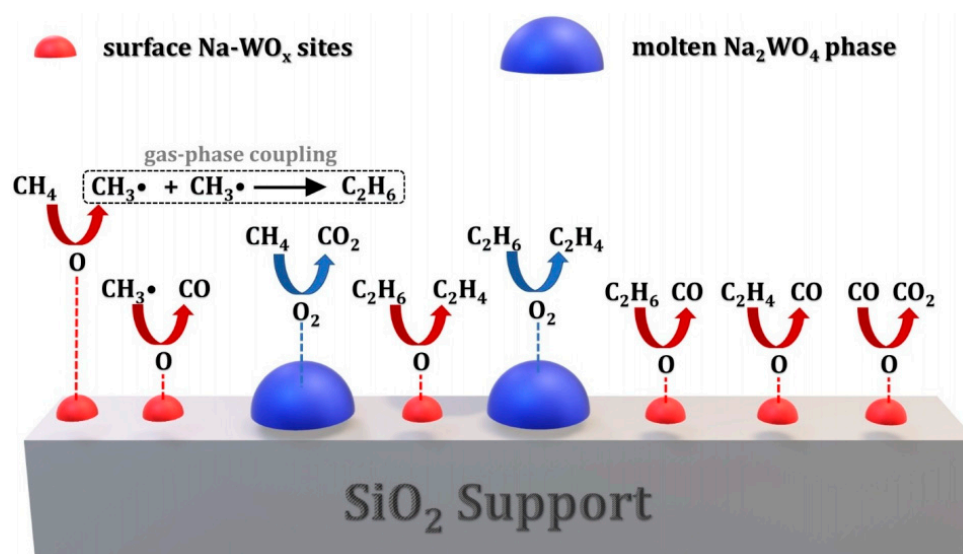


Figure 11. OCM reaction mechanism over supported $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst [74].

In a separate study conducted by Sagar Sourav and their research team [75], the role of manganese (Mn) in $\text{Mn-Na}_2\text{WO}_4/\text{SiO}_2$ catalysts for the oxidative coupling reaction (OCM) of methane has been elucidated. The investigation revealed that the catalyst undergoes significant structural modifications during the OCM process, with MnO_x playing a pivotal role as a promoter. The active sites responsible for catalysis consist of tungsten oxides (comprising both fused Na_2WO_4 and surface Na-WO_x sites). Notably, the promotional influence of MnO_x is highly sensitive to variations in temperature and the partial pressure of oxygen in the gas phase. These findings contribute substantially to our comprehension of the OCM reaction mechanism, offering valuable insights for the development of more efficient catalyst designs in line with the rigorous standards.

However, the understandings derived from the existing studies are limited to explaining the results within the experimental range, which are not extensible and generalizable. The problems faced so far are mainly because there is a seesaw effect between C_2 selectivity and methane conversion. The presence of oxygen tends to cause the deep oxidation reaction of methane to generate CO_x ($x = 0, 1, 2$) as a by-product, leading to a low selectivity of C_{2+} hydrocarbons, while the absence of oxygen makes methane activation difficult, resulting in low methane conversion. In view of this, the research on the methane coupling reaction using weakly oxidizing gas, such as CO_2 , N_2O , S, and other alternative oxidants, as an oxidant is gradually becoming active.

Catalysts based on $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ exhibit a key feature of high C_2 yield, which is currently the closest to meeting the minimum industrial yield requirement of 30%. However, achieving this yield typically requires high temperatures above 750°C . Therefore, further

study of the structure–activity relationship of $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts is necessary to improve their C_{2+} yield at lower temperatures.

3. Chemical Looping Oxidative Coupling of Methane

Significant progress has been made in OCM reaction studies in recent years, but improving reactivity and selectivity remains a challenge. Firstly, methane oxidation is a complex process involving high temperatures and pressures; hence, the stability of catalysts is a pivotal issue. Researchers need to design and synthesize catalysts with good thermal stability to improve catalyst lifetime and recoverability. Secondly, the mechanism of the methane oxidation reaction is not yet fully understood, and further exploration of the basic principles and key steps of the reaction is needed to guide the design and optimization of catalysts. Therefore, the team of Liang et al. proposed chemical looping oxidative coupling of methane (CLOCM) to olefins in 2016 [76], the core of which is the selective activation of methane to olefin by using the oxygen carrier's dual functions of oxygen carrying and catalysis in which lattice oxygen is involved in the oxidation and reduction reactions in the reaction, which not only provides reactive oxygen but also prevents over-oxidation of the reaction process and can improve the selectivity of C_{2+} hydrocarbons. As shown in Figure 12, the lattice oxygen in the oxygen carrier is used to provide reactive oxygen for methane activation, while the metal oxide acts as a catalyst for the coupling reaction to promote the growth of C–C coupling to produce olefins in the fuel reactor; the reduced oxygen carrier enters the air reactor to be oxidized by air to restore oxygen species and then to be re-circulated back to the fuel reactor [77,78]. CLOCM improves reaction selectivity and efficiency.

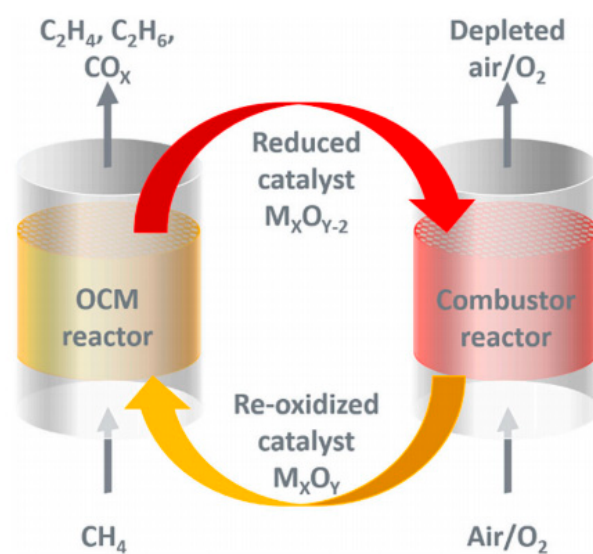


Figure 12. Schematic diagram of chemical looping oxidative coupling of methane [78].

Catalysts for CLOCM

Different research teams have conducted experiments on methane chemical looping oxidative coupling using various catalysts and reaction conditions and have discussed the reaction mechanism and product selectivity. These studies have shown that specific catalysts and reaction conditions can achieve high C_{2+} selectivity and yield, as well as the impact of catalyst doping on reaction performance. The design of catalysts remains a formidable challenge, with the imperative of enhancing both selectivity and yield necessitating a careful consideration of several pivotal criteria. Primarily, intrinsic attributes such as basicity and structural defects emerge as crucial factors for augmenting selectivity. Simultaneously, structural anomalies such as oxygen vacancies play a pivotal role in facilitating the activation of methane.

Mg–Mn-based catalysis is widely used in CLCOM due to its unique structure and composition, which gives it excellent catalytic activity and selectivity, and manganese oxides have excellent oxygen storage capacity [79]. A comprehensive investigation led by Elena Y. Chung and her research team centered on the utilization of doped Mg_6MnO_8 metal oxide as a catalyst in the CLOCM process. This study delved into several pivotal factors, including oxygen content, selectivity towards C_{2+} hydrocarbons, and the recuperation efficiency of the catalytic oxygen carrier. The research revealed that the catalytic carriers demonstrated a substantial oxygen capacity, registering at 4.40 wt%. This oxygen capacity could be bifurcated into two distinct categories: loosely bound oxygen and strongly bound oxygen. The study meticulously examined the performance trends in selectivity and conversion of C_{2+} products across various gas-phase air velocities. Furthermore, the research diligently ascertained the optimal operational parameters. Under these optimized conditions, an impressive C_{2+} selectivity of 63.2% and a commendable yield of 23.2% were achieved [77]. Huang et al. investigated the effect of heteroatom doping on the redox properties of Mg_6MnO_8 composite oxide carriers and the selective and stable production of C_{2+} hydrocarbons through methane CLOCM. By doping with Na, the content of O- and the species of $\text{Mn}^{2+}/\text{Mn}^{3+}$ on the surface of Mg_6MnO_8 were increased, resulting in improved selectivity and yield of C_{2+} . The results demonstrate that the key to achieving high C_{2+} selectivity and yield lies in the controlled formation of stable surface O^- and $\text{Mn}^{2+}/\text{Mn}^{3+}$ oxygen carriers through heteroatom doping [80]. Deven S. Baser et al. [81] investigated a new type of oxygen carrier, namely lithium–tungsten co-doped Mg–Mn-based oxygen carrier (Li, W)– Mg_6MnO_8 , for methane chemical looping oxidative coupling (CLOCM) technology. The researchers synthesized (Li, W)– Mg_6MnO_8 samples and studied the effect of co-doping on OCM activity. They tested two different compositions of dopants and determined the optimal composition that provided the highest C_{2+} yield of 2.65% Li and 4% W. Figure 13a shows the relationship between the optimized OCM activity of (Li, W) co-doped oxygen carrier and reaction temperature. At 850 °C, the total hydrocarbon yield of the co-doped sample was 28.6%. Experimental results indicated that as the reaction temperature increased, methane conversion rate increased but the selectivity towards C_{2+} and C_{3+} decreased. This was attributed to the increased tendency for over-oxidation at higher reaction temperatures. At high temperatures, the kinetics of the methane reaction with the catalytic oxygen carrier increased, enhancing the methane conversion rate. Figure 13b illustrates the synergistic effect of lithium and tungsten co-dopants, which not only enhanced the dimerization reaction of CH_3 but also suppressed the generation of CO_2 . This effect was attributed to the presence of co-dopants, which could inhibit the formation of non-selective oxygen vacancies, thereby improving the C_{2+} yield. Figure 13c demonstrates the synergistic effect between the two dopants. The total yield of the co-doped sample was 80% higher than that of samples doped with lithium or tungsten alone. Furthermore, the co-doping strategy increased the total yield of the undoped Mg_6MnO_8 from 6.7% to 28.6%, a 330% improvement. Mn–Mg catalysts have been extensively studied in this regard, as shown in Figure 13.

Jiang et al. conducted an investigation on the performance of a series of Na-doped LaMnO_3 catalysts in methane chemical epoxidation coupling reactions. They discovered that Na doping resulted in a higher molar ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ and led to an increase in oxygen vacancies. This enhancement improved the redox performance of the catalysts, resulting in higher methane conversion and C_2 yield. The most effective catalyst was the 018Na-doped sample, which exhibited a C_2 yield 7.44 times higher than that of undoped LaMnO_3 . Furthermore, the researchers demonstrated the catalyst's excellent renewability. This study presents a valuable strategy for identifying recyclable oxygen carriers [82].

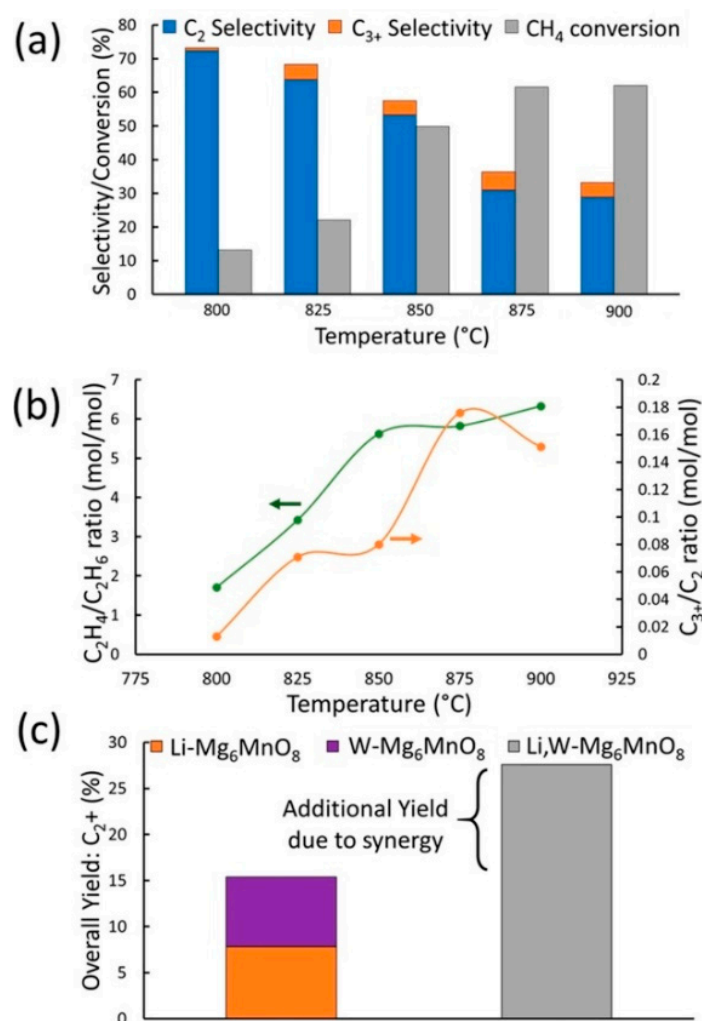


Figure 13. (a) C₂ selectivity, C₃₊ selectivity, and methane conversion versus temperature for (Li, W)–Mg₆MnO₈, (b) effect of temperature on the C₂H₄/C₂H₆ ratio, depicted by the green curve, and C₃₊/C₂ ratio of (Li, W)–Mg₆MnO₈, depicted by the orange curve, and (c) comparison of the combined overall yield of Li–Mg₆MnO₈ and WMg₆MnO₈ and the overall yield of (Li, W)–Mg₆MnO₈ at 850 °C and 1 atm at a GHSV of 2400 h^{−1}. The yields were calculated based on the average C₂₊ selectivity and CH₄ conversion over 15 s of Li[−] - and W-doped Mg₆MnO₈ samples.

Na₂WO₄/Mn/SiO₂ catalysts are highly active, selective, and stable in chemical looping oxidative coupling of methane, enabling efficient methane conversion. Qin et al. [83] and his research team have introduced an innovative reactor concept designed for methane oxidation coupling reactions utilizing Na₂WO₄/Mn/SiO₂ catalysts. Their work involves the utilization of chemical loops and simulated chemical loops to address various challenges in this process. Extensive experimentation was conducted to evaluate the performance of the catalyst materials, with a particular emphasis on mitigating the interference of gas-phase oxygen, resulting in enhanced stability. Furthermore, their findings indicate that the chemical looping mechanism exhibits superior efficiency in promoting methane conversion, especially when the methane conversion rate is below 0.3. Vinzenz Fleischer et al. [84] conducted a comprehensive study utilizing an Na₂WO₄/Mn/SiO₂ catalyst to evaluate its catalytic performance through chemical looping and repeated methane pulse experiments. The research revealed that the specific surface area of the catalyst plays a pivotal role in influencing its catalytic activity. Remarkably, the catalytic activity exhibited a noteworthy augmentation with an increase in the specific surface area, particularly when it was below 4 m²/g. However, intriguingly, in the context of chemical looping experiments, catalysts with a high specific surface area displayed reduced activity. Within this context, catalysts

containing 5 wt% Na_2WO_4 and 2 wt% Mn emerged as the most active, yet the C_2 yield did not surpass 0.25. This outcome underscores the intricate interplay of various factors affecting catalytic activity. Notably, the loading of manganese (Mn) proved to be a critical factor contributing to the oxygen storage capability of the $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$ catalysts. Furthermore, tungstate (Na_2WO_4) played a pivotal role in enhancing the selective activation of methane, a crucial aspect for the oxidative coupling of methane (OCM) reaction. In summary, this research sheds light on the multifaceted dynamics of catalytic activity in the $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$ catalyst system, emphasizing the significance of specific surface area, Mn loading, and the role of tungstate in facilitating selective methane activation, all of which are pivotal for advancing our understanding of the OCM reaction. Sun et al. [85] conducted a study on a promising and efficient $\text{Na}_2\text{WO}_4/\text{FeMnO}_3$ catalyst for the CLOCM process. By modifying FeMnO_3 , Na_2WO_4 can alleviate the evolution of lattice oxygen during the conversion of CH_4 stored in it, enabling the prepared catalyst to selectively convert CH_4 to $\text{C}_2\text{--C}_3$. FeMnO_3 , as an oxygen carrier, exhibits a high lattice oxygen capacity in CH_4 conversion but also promotes combustion. To mitigate the impact of lattice oxygen on the CH_4 conversion rate in FeMnO_3 , Na_2WO_4 modification is employed. This modified catalyst selectively converts CH_4 to $\text{C}_2\text{--C}_3$ products. The CL-OCM process using an $\text{Na}_2\text{WO}_4/\text{FeMnO}_3$ catalyst operates through the " $\text{FeMnO}_3 \leftrightarrow [\text{MnFe}_2\text{O}_4 + \text{MnO}]$ " redox cycle. At a temperature of 800 °C, the methane conversion rate can reach 20%, and the selectivity can reach 80%, as shown in Figure 14.

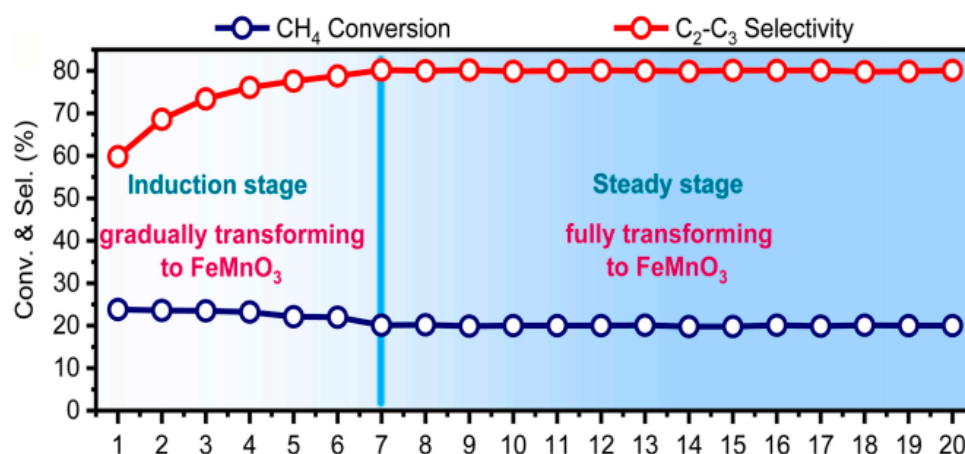


Figure 14. The CL-OCM performance and chemical evolution of $\text{Na}_2\text{WO}_4/\text{Mn}_2\text{O}_3\text{--Fe}_2\text{O}_3$ catalyst precursor. CH_4 conversion and $\text{C}_2\text{--C}_3$ selectivity over $\text{Na}_2\text{WO}_4/\text{Mn}_2\text{O}_3\text{--Fe}_2\text{O}_3$ precursor throughout 20 reaction-regeneration cycles [85].

Rare earth catalysts have shown numerous advantages in methane chemical looping oxidation coupling reactions, including exceptional activity, selectivity, stability, and tunability, rendering them highly intriguing catalysts in the field. In a study conducted by Jae Suk Sung et al. [86], the catalytic properties of $\text{Ag--La}_2\text{O}_3/\text{SiO}_2$ catalysts were investigated, revealing a significant synergistic effect between Ag and La_2O_3 in the oxidative coupling of methane (OCM). Specifically, at a composition of 3% Ag–10% $\text{La}_2\text{O}_3/\text{SiO}_2$, noteworthy results were obtained, with a remarkable 30% yield of C_2 hydrocarbons and a C_2 selectivity nearing 60%. Furthermore, the performance of La_2O_3 was found to be further augmented through silver (Ag) doping, which not only played a pivotal catalytic role in the process but also facilitated the efficient transport of oxygen from the metal oxide to the surface. Alexander A. Greish et al. [87] studied catalysts with 1% CeO_2 , 9% $\text{La}_2\text{O}_3/\text{SiO}_2$, 2% CeO_2 , and 8% $\text{La}_2\text{O}_3/\text{SiO}_2$, which showed reliable efficiency and high catalyst stability. Preliminary reduction of the catalyst using a small amount of hydrogen significantly improved the selectivity towards C_2 products. Zhuo Cheng et al. [88] studied the use of low concentrations of Li dopants to enhance the C_{2+} selectivity of Mg–Mn composite oxygen carriers. The results showed that the C_{2+} selectivity of Li-doped oxygen carriers was higher than

that of undoped Mg_6MnO_8 carriers, with a maximum increase of about 50%. Lithium in doping led to a reduction in oxygen vacancies, lowering the adsorption energy of methyl radicals and increasing the activation barrier of C–H bonds.

In recent years, there have been significant advancements in the research of CLOCM catalysts. Researchers have improved the synthesis methods of catalysts by controlling the synthesis conditions and catalyst composition, leading to the successful development of highly efficient catalysts. These catalysts exhibit high methane oxidation activity and stability, enabling efficient methane oxidation reactions at lower temperatures. Furthermore, researchers have conducted in-depth studies on the catalytic mechanisms of various catalysts. By characterizing the physicochemical properties of catalysts and the formation process of reaction intermediates, they have revealed the key steps and reaction pathways of methane oxidation reactions. These studies provide theoretical guidance for further optimizing the performance of catalysts. Additionally, researchers have explored the application of catalysts in other reactions. They have discovered that catalysts can not only catalyze methane oxidation reactions but also catalyze the oxidation of other organic chlorides. This opens up new possibilities for the multifunctional application of catalysts. However, despite the progress made in catalyst research, there are still challenges and unresolved issues. For example, the lifespan and stability of catalysts need further improvement to meet the requirements of practical applications. Moreover, the synthesis methods and catalytic mechanisms of catalysts require further research and optimization. Overall, catalyst research holds significant potential in methane chemistry and oxidation coupling reactions. With further research and optimization, catalysts are expected to play an important role in environmental protection and energy conversion.

4. Mechanism of OCM

The OCM reaction typically involves the extraction of hydrogen from methane by reactive oxygen species on the surface of the oxide catalyst to form methyl radicals ($\text{CH}_3\cdot$) which are then recombined and dehydrogenated to form C_{2+} products such as alkanes and alkenes [89].

4.1. Activation of Methane

Two pathways for the formation of free radicals during the catalytic oxidation of methane include the co-cracking of methane molecules and C–H key breakage. When methane molecules collide with strong oxidation sites with high hydrogen atom affinity, surface hydroxyl groups and free methyl groups are formed on the catalyst surface [90]. On the surface of the catalyst, the C–H bond in methane molecules is replaced by oxygen atoms at the oxidation site, forming a hydroxyl group and a methyl radical, as shown in Formula (1). Another pathway is that where the C–H bond on the methane molecule is attacked by an oxygen atom at the oxide site and forms a methyl radical, which is connected to the remaining CH_3O_2 radical, as shown in Formulas (2) and (3). Both mechanisms have been extensively discussed and studied in the literature.

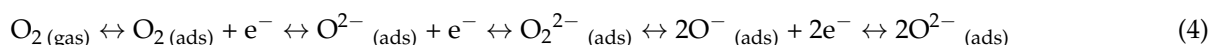


4.2. Gas-Phase Oxygen Activation

The active site nature in OCM (oxidative coupling of methane) reactions has garnered significant attention and is commonly attributed to the presence of reactive oxygen species on the surface of oxide catalysts. Nonetheless, there are varying opinions regarding the roles of different oxygen species, such as chemisorbed oxygen, dissociatively adsorbed oxygen, adsorbed oxygen ions, and lattice oxygen, in this reaction. These distinct oxygen

species could potentially influence reaction selectivity. Therefore, researchers have undertaken a series of experiments and conducted density functional theory (DFT) calculations to elucidate the distinct functions of these oxygen species [91]. Specifically, a study focused on the characterization of lattice oxygen on an NaWMn/SiO₂ catalyst and its impact on OCM reaction performance. The findings revealed that the catalyst exhibited both strong and weak oxygen binding, and alterations in reduction temperature resulted in varying trends in product selectivity. This suggests that different types of oxygen may induce distinct reaction pathways, with weakly bound oxygen playing a significant role in OCM activity and stability [71]. Additionally, another investigation systematically explored the influence of different oxygen species on OCM reactions employing lanthanide-based chalcogenide catalysts. It was observed that the nature of lattice oxygen on the catalyst predominantly determined the selectivity of OCM products, especially when gas-phase oxygen was absent. Different types of lattice oxygen were found to lead to varying product selectivities, primarily influenced by the metal X present in the catalyst [92]. Regarding methodology, one study mentioned the utilization of an infrared spectrometer as a detector, enabling temperature-programmed experiments for studying the nature of adsorbed oxygen and the formation of products with high resolution. This offers a promising avenue for investigating the characteristics of adsorbed oxygen and the catalytic behavior of different OCM catalysts [93].

In conclusion, the distinct roles of various oxygen species in OCM reactions, and particularly the characteristics of lattice oxygen, exert a significant influence on product selectivity [94]. Future research should also consider the impact of other factors, such as doped or rare earth metals, to gain further insights into the role of oxygen in OCM mechanisms. These studies contribute to the development of more efficient OCM catalysts, aiming to enhance C₂ product selectivity while minimizing the generation of CO_x (CO and CO₂), thus offering valuable insights for advancements in the field of energy conversion. Studies showed that different catalysts have different reactive oxygen species on them, and the reactive oxygen species are the key reactive species required for the activation of methane to generate methyl radicals during the OCM reaction [34]. As shown in Figure 15, it is reported that the electron-deficient electrophilic oxygen species, such as O^{2−}, O[−], and O₂^{2−}, adsorbed on the catalyst surface or activated by oxygen vacancies, as well as the lattice oxygen species O^{2−} on the catalyst surface, all have activation effects on methane. For alkaline metal, alkaline earth metal oxides, and rare earth oxide catalysts with stable equivalent states and irreducible metal oxides, the electrophilic oxygen species O^{2−}, O[−], and O₂^{2−} are conducive to the generation of C₂ hydrocarbons, while the surface lattice O^{2−} is prone to cause deep oxygenation of methane and coupling products [32,34,39]. For metal oxide catalysts with variable valence and reducibility, such as some transition metal oxides, Mn/Na₂WO₄/SiO₂, and some ABO₃ perovskite systems, surface lattice oxygen species O₂ is the active oxygen species for selective oxidation of CH₄ to C₂ hydrocarbons, while surface electrophilic oxygen species such as O^{2−}, O[−], and O₂^{2−} are prone to deep oxidation of methane and coupling products to CO_x. The generation of electrophilic oxygen species on the catalyst surface originates from two pathways, one of which is the conversion of gaseous oxygen on the catalyst surface, as shown in the following formula; the other way is that the gas-phase oxygen enters the surface of the catalyst or is activated by oxygen vacancy and migrates to the surface [95].



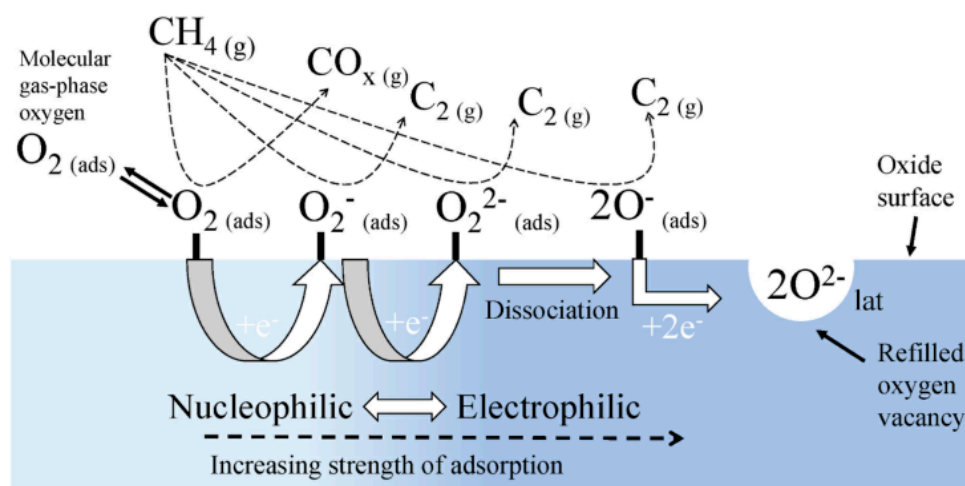


Figure 15. Schematic illustration of the gas-phase oxygen activation on the oxide catalyst surface [96].

Lunsford et al. [97] investigated the active oxygen species in the methane oxidation coupling reaction using the EPR technique with Li/MgO and Na/CaO series catalysts. The results showed that O^- species can be stably formed on the surface of MgO-based catalyst at 200 °C. The incorporation of Li^+ and Na^+ can generate $[Li^+O^-]$ and $[Na^+O^-]$ active sites on the surface of Li/MgO and Na/CaO catalysts and stabilize them on the surface of the catalyst. The subsequently generated O^- active oxygen species participate in the oxidative coupling reaction of methane to produce C_2 products [22]. They also investigated different metals, such as Ba supported by MgO, ZnO, Al_2O_3 , and other supports, for OCM reaction. It was found that the catalyst with high loading is prone to carbon dioxide poisoning during OCM reaction, and BaO can generate stable $BaCO_3$ to reduce the reaction activity. Researchers used EPR to detect the oxygen species on the surface of La_2O_3/CaO catalyst after O_2 adsorption at room temperature or 1053 K and found that the oxygen species on the catalyst surface was O^{2-} . After methane was introduced, there was a certain relationship between the amount of O^{2-} and the concentration of methane on the catalyst surface, indicating that the active oxygen species of the catalyst in the methane oxidative coupling reaction was O^{2-} [48]. Dubois and Gellings believe that there is a balance in the process of the methane oxidative coupling reaction, as shown in Formulas (5) and (6). Additionally, a certain amount of CO_2 can be generated during the OCM process, and carbonate can be subsequently generated due to the strong basicity center on the catalyst surface. Hence, O_2^{2-} species also can be produced after the contact of O_2 with the carbonate [98].



Ji et al. [84] studied Mn/ Na_2WO_4/SiO_2 catalysts with different contents of Na, W, and Mn for OCM, and O_2 -TPD and CH_4 pulse technology were used to explore the role of active oxygen species on the catalyst surface. They found that lattice oxygen species are active oxygen species in OCM. W and Mn play a role in activating lattice oxygen species O^{2-} in the catalyst system, and Na can improve the fluidity of lattice oxygen species in the reaction process and play a role in polarizing Mn–O and W–O bonds. A study conducted by Gordienko et al. [71] investigated the presence of lattice oxygen on NaWMn/ SiO_2 catalysts and its impact on the performance of the oxidative coupling of methane (OCM) reaction. The findings revealed that the catalysts synthesized exhibited both strong and weak oxygen binding, and the selectivity of the products was heavily influenced by the reduction temperature. This suggests that each type of oxygen species promotes the OCM reaction through distinct pathways upon activation. Although the exact contribution of strongly bound oxygen remains unclear, it was demonstrated that

weakly bound oxygen significantly contributes to the activity and stability of the OCM performance. It is widely accepted that the activation of the C–H bond in methane during the oxidative coupling of methane (OCM) reaction occurs at the active site, which is typically a reactive oxygen species located on the surface of the oxide catalyst. However, the presence of various types of oxygen species on the oxide surface suggests that each oxygen species may have distinct selective roles in the oxidation process [91]. These oxygen species encompass chemisorbed oxygen, dissociatively adsorbed oxygen, adsorbed oxygen ions, and lattice oxygen [70]. As for the active oxygen species of perovskite catalysts in the OCM, Kim et al. [92] systematically studied three perovskite-type LaXO_3 ($\text{X} = \text{Al, Fe, Ni}$) catalysts, where they fixed the A-site elements and changed the B-site elements. In the perovskite catalyst, the type of B-site element can affect the activity of lattice oxygen in the perovskite catalyst, thus showing a difference in the activity of methane [92]. The results showed that LaAlO_3 is a catalyst with oxidative coupling activity of methane. LaFeO_3 is a catalyst with catalytic activity of partial oxidation of methane to synthesis gas, and LaNiO_3 is a catalyst with catalytic activity of methane combustion. XPS, O_2 -TPD, and other technologies were used to explore the oxygen species on the surface of three catalysts, and results showed that the binding energy of the lattice oxygen species on the surface changed from high to low and from LaAlO_3 to LaNiO_3 by the XPS test, which is related to the transformation of lattice oxygen from electrophilic to nucleophilic. They used XPS to analyze the active oxygen species on the surface of the BaO/MgO catalyst with low loading and low support alkalinity and found that O_2^{2-} was the active oxygen species in the OCM reaction [99]. Under the OCM reaction conditions without oxygen participation, the reaction products were C_2 product (LaAlO_3), partial oxidation product CO (LaFeO_3), and deep oxidation product CO_2 (LaNiO_3). Additionally, it is considered that the surface-adsorbed oxygen species generated by oxygen vacancies are the oxygen species of modified methane deep oxidation [92]. Although a lot of related research works have been carried out so far, the mechanism of metal oxide oxygen carriers in the OCM process is still unclear. However, there is a consensus that the synergistic effects between the high oxygen storage, the formation of surface vacancies, and the impact of the supported materials contribute to OCM activity [100].

5. Conclusions

In summary, CLOCM presents a compelling array of advantages over the conventional OCM process, positioning it as a highly promising alternative to attain the elevated yield values requisite for industrial viability. This review highlights the key advantages of CLOCM, elucidating its potential as a transformative technology: Enhanced C_{2+} Product Selectivity: CLOCM distinguishes itself by achieving superior selectivity towards C_{2+} products through methane oxidation at the catalyst surface, obviating the necessity for molecular oxygen. This breakthrough allows for the generation of a broader spectrum of high-value compounds, thereby augmenting overall yield. Streamlined Product Separation: Unlike the co-feed OCM approach, CLOCM operates without the need for intricate product separation units. This streamlined process not only diminishes operational intricacies but also translates into substantial cost reductions, reinforcing its economic viability. Optimized Thermal Management: CLOCM employs an innovative recirculation strategy to proficiently manage heat within the reaction. This meticulous thermal control enhances catalyst performance and extends operational cycles, thereby minimizing downtime. Low-temperature Operation: operating at lower temperatures relative to OCM, CLOCM not only conserves energy but also mitigates potential heat losses, underlining its sustainability and efficiency. Mitigation of Parallel Reactions: CLOCM effectively circumvents parallel reactions in the gas phase by segregating oxidation and reduction steps. This strategic separation enhances reaction selectivity and overall efficiency. In summation, CLOCM stands out as an auspicious prospect, offering a suite of advantages encompassing elevated product selectivity, operational simplicity, superior thermal regulation, and reduced energy consumption. Nevertheless, the development of CLOCM catalysts does confront certain challenges. Various

catalyst types, including Mg–Mn oxides, rare earth oxides, ABO_3 chalcogenide-type oxides, and conventional Mn– Na_2WO_4 catalysts have been explored within the CLOCM domain. Addressing these challenges and optimizing catalyst performance entail tailored strategies for each catalyst category: Mg–Mn Oxides: Tailoring the Mg-to-Mn ratio, engineering carrier structures, surface modifications, and gaining a deeper comprehension of the catalytic mechanism stand as avenues for performance optimization. Rare Earth Oxides: Selecting appropriate rare earth elements, optimizing crystal structures, enhancing the formation of catalytic active sites, and delving into catalytic mechanisms are pivotal to augmenting their efficacy. ABO_3 Chalcogenide Oxides: Optimization involves selecting suitable ABO_3 components, modulating crystal structures, surface modifications, and in-depth investigations into catalytic mechanisms to bolster catalytic performance. Conventional Mn– Na_2WO_4 Catalysts: Improved catalyst synthesis methods, heightened stability and reproducibility, catalyst regeneration techniques, crystal structure enhancements, and in-depth catalytic mechanism studies collectively contribute to improved performance. In conclusion, the continuous refinement and optimization of diverse CLOCM catalysts, driven by a synergy of experimental and theoretical investigations, are indispensable for surmounting existing challenges and fostering the advancement of CLOCM catalysts. These endeavors hold the promise of revolutionizing methane conversion processes and enhancing their industrial applicability.

Author Contributions: Conceptualization, K.Z. and A.Z.; methodology, S.X.; software, P.C.; validation, analysis, X.W. and M.Z.; resources, data management, Y.L. and D.S.; writing—first draft preparation, J.D.; writing—review and editing, K.Z.; supervision, project management, A.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Key Research and Development Program of China (2021YFC1910401), National Natural Science Foundation of China (22279144.51866003), and Guangdong Natural Science Fund for Distinguished Young Scholars (grants 2023B1515020048).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Lunsford, J.H. Catalytic conversion of methane to more useful chemicals and fuels: A challenge for the 21st century. *Catal. Today* **2000**, *63*, 165–174.
2. Holmen, A. Direct conversion of methane to fuels and chemicals. *Catal. Today* **2009**, *142*, 2–8. [[CrossRef](#)]
3. Arinaga, A.M.; Ziegelski, M.C.; Marks, T.J. Alternative Oxidants for the Catalytic Oxidative Coupling of Methane. *Angew. Chem. Int. Ed.* **2021**, *60*, 10502–10515. [[CrossRef](#)]
4. Ming, T.; Richter, R.d.; Dietrich Oeste, F.; Tulip, R.; Caillol, S. A nature-based negative emissions technology able to remove atmospheric methane and other greenhouse gases. *Atmos. Pollut. Res.* **2021**, *12*, 101035. [[CrossRef](#)]
5. Jaworski, J.; Dudek, A. Study of the Effects of Changes in Gas Composition as Well as Ambient and Gas Temperature on Errors of Indications of Thermal Gas Meters. *Energies* **2020**, *13*, 5428. [[CrossRef](#)]
6. Sun, L.; Wang, Y.; Guan, N.; Li, L. Methane Activation and Utilization: Current Status and Future Challenges. *Energy Technol.* **2019**, *8*, 1900826. [[CrossRef](#)]
7. Horn, R.; Schlögl, R. Methane Activation by Heterogeneous Catalysis. *Catal. Lett.* **2015**, *145*, 23–39. [[CrossRef](#)]
8. Kolesnichenko, N.V.; Ezhova, N.N.; Snatenkova, Y.M. Single-atom catalysts in methane chemistry. *Russ. Chem. Rev.* **2023**, *92*, RCR5079. [[CrossRef](#)]
9. Chen, R.; Weng, G.M. Sustainable Energy Resources for Driving Methane Conversion. *Adv. Energy Mater.* **2023**, *13*, 2301734. [[CrossRef](#)]
10. Meng, X.; Cui, X.; Rajan, N.P.; Yu, L.; Deng, D.; Bao, X. Direct Methane Conversion under Mild Condition by Thermo-, Electro-, or Photocatalysis. *Chem* **2019**, *5*, 2296–2325. [[CrossRef](#)]
11. Schwach, P.; Pan, X.; Bao, X. Direct Conversion of Methane to Value-Added Chemicals over Heterogeneous Catalysts: Challenges and Prospects. *Chem. Rev.* **2017**, *117*, 8497–8520. [[CrossRef](#)]
12. Zhang, H.; Su, Y.; Kosinov, N.; Hensen, E.J.M. Non-oxidative coupling of methane over Mo-doped CeO_2 catalysts: Understanding surface and gas-phase processes. *Chin. J. Catal.* **2023**, *49*, 68–80. [[CrossRef](#)]

13. DeBoy, J.M.; Hicks, R.F. The oxidative coupling of methane over alkali, alkaline earth, and rare earth oxides. *Ind. Eng. Chem. Res.* **1988**, *27*, 1577–1582.
14. Hutchings, G.J.; Scurrall, M.S.; Woodhouse, J.R. Oxidative coupling of methane using oxide catalysts. *Chem. Soc. Rev.* **1988**, *18*, 251–283. [[CrossRef](#)]
15. Keller, G.E.; Bhasin, M.M. Synthesis of ethylene via oxidative coupling of methane: I. Determination of active catalysts. *J. Catal.* **1982**, *73*, 9–19.
16. Gao, Y.; Neal, L.; Ding, D.; Wu, W.; Baroi, C.; Gaffney, A.M.; Li, F. Recent Advances in Intensified Ethylene Production—A Review. *ACS Catal.* **2019**, *9*, 8592–8621. [[CrossRef](#)]
17. Zhang, Y.; Cho, Y.; Yamaguchi, A.; Peng, X.; Miyauchi, M.; Abe, H.; Fujita, T. CO(2) oxidative coupling of methane using an earth-abundant CaO-based catalyst. *Sci. Rep.* **2019**, *9*, 15454. [[CrossRef](#)] [[PubMed](#)]
18. Ampansang, S.; Srirangam, S.; Somchuea, P.; Witoon, T.; Wattanakit, C.; Chareonpanich, M.; Sohn, H.; Seubsai, A. Direct Conversion of Methane to Value-Added Hydrocarbons over Alumina-Supported Cobalt Modified by Alkaline Earth Catalysts. *Top. Catal.* **2023**, 1–15. [[CrossRef](#)]
19. Matras, D.; Jacques, S.D.M.; Poulston, S.; Grosjean, N.; Estruch Bosch, C.; Rollins, B.; Wright, J.; Di Michiel, M.; Vamvakeros, A.; Cernik, R.J.; et al. Operando and Postreaction Diffraction Imaging of the La–Sr/CaO Catalyst in the Oxidative Coupling of Methane Reaction. *J. Phys. Chem. C* **2019**, *123*, 1751–1760. [[CrossRef](#)]
20. Gao, Z.; Zhang, J.; Wang, R. Formation of hydrogen in oxidative coupling of methane over BaCO₃ and MgO catalysts. *J. Nat. Gas Chem.* **2008**, *17*, 238.
21. Xu, J.; Ouyang, R.; Zhong, X.; Fang, X.; Xu, X.; Wang, X. Alkali metal and alkaline earth metal perovskites for oxidative coupling of methane and oxidative dehydrogenation of ethane. *Mol. Catal.* **2023**, *547*, 113386. [[CrossRef](#)]
22. Lim, S.; Choi, J.-W.; Jin Suh, D.; Lee, U.; Song, K.H.; Ha, J.-M. Low-temperature oxidative coupling of methane using alkaline earth metal oxide-supported perovskites. *Catal. Today* **2020**, *352*, 127–133. [[CrossRef](#)]
23. Qian, K.; You, R.; Guan, Y.; Wen, W.; Tian, Y.; Pan, Y.; Huang, W. Single-Site Catalysis of Li–MgO Catalysts for Oxidative Coupling of Methane Reaction. *ACS Catal.* **2020**, *10*, 15142–15148. [[CrossRef](#)]
24. Ito, T.; Wang, J.; Lin, C.H.; Lunsford, J.H. Oxidative Dimerization of Methane over a Lithium-Promoted Magnesium Oxide Catalyst. *J. Am. Chem. Soc.* **1985**, *107*, 5062. [[CrossRef](#)]
25. Lanza, R.; Canu, P.; Järås, S.G. Methane partial oxidation over Pt–Ru catalyst: An investigation on the mechanism. *Appl. Catal. A Gen.* **2010**, *375*, 92–100. [[CrossRef](#)]
26. Pham, T.T.P.; Ro, K.S.; Chen, L.; Mahajan, D.; Siang, T.J.; Ashik, U.P.M.; Hayashi, J.-i.; Pham Minh, D.; Vo, D.-V.N. Microwave-assisted dry reforming of methane for syngas production: A review. *Environ. Chem. Lett.* **2020**, *18*, 1987–2019. [[CrossRef](#)]
27. Yang, K.; Gu, Z.; Long, Y.; Lin, S.; Lu, C.; Zhu, X.; Wang, H.; Li, K. Hydrogen production via chemical looping reforming of coke oven gas. *Green Energy Environ.* **2021**, *6*, 678–692. [[CrossRef](#)]
28. Elkins, T.W.; Roberts, S.J.; Hagelin-Weaver, H.E. Effects of alkali and alkaline-earth metal dopants on magnesium oxide supported rare-earth oxide catalysts in the oxidative coupling of methane. *Appl. Catal. A Gen.* **2016**, *528*, 175–190. [[CrossRef](#)]
29. Luo, L.; You, R.; Liu, Y.; Yang, J.; Zhu, Y.; Wen, W.; Pan, Y.; Qi, F.; Huang, W. Gas-Phase Reaction Network of Li/MgO-Catalyzed Oxidative Coupling of Methane and Oxidative Dehydrogenation of Ethane. *ACS Catal.* **2019**, *9*, 2514–2520. [[CrossRef](#)]
30. Luo, L.; Jin, Y.; Pan, H.; Zheng, X.; Wu, L.; You, R.; Huang, W. Distribution and role of Li in Li-doped MgO catalysts for oxidative coupling of methane. *J. Catal.* **2017**, *346*, 57–61. [[CrossRef](#)]
31. Ren, Y.; Liu, X.; Zhang, Z.; Shen, X. Methane activation on single-atom Ir-doped metal nanoparticles from first principles. *Phys. Chem. Chem. Phys.* **2021**, *23*, 15564–15573. [[CrossRef](#)] [[PubMed](#)]
32. Huang, P.; Zhao, Y.; Zhang, J.; Zhu, Y.; Sun, Y. Exploiting shape effects of La₂O₃ nanocatalysts for oxidative coupling of methane reaction. *Nanoscale* **2013**, *5*, 10844–10848. [[CrossRef](#)]
33. Hou, Y.-H.; Han, W.-C.; Xia, W.-S.; Wan, H.-L. Structure Sensitivity of La₂O₂CO₃ Catalysts in the Oxidative Coupling of Methane. *ACS Catal.* **2015**, *5*, 1663–1674. [[CrossRef](#)]
34. Ferreira, V.J.; Tavares, P.; Figueiredo, J.L.; Faria, J.L. Effect of Mg, Ca, and Sr on CeO₂ Based Catalysts for the Oxidative Coupling of Methane: Investigation on the Oxygen Species Responsible for Catalytic Performance. *Ind. Eng. Chem. Res.* **2012**, *51*, 10535–10541. [[CrossRef](#)]
35. Noon, D.; Seubsai, A.; Senkan, S. Oxidative Coupling of Methane by Nanofiber Catalysts. *ChemCatChem* **2013**, *5*, 146–149. [[CrossRef](#)]
36. Zhang, Y.; Xu, J.; Xu, X.; Xi, R.; Liu, Y.; Fang, X.; Wang, X. Tailoring La₂Ce₂O₇ catalysts for low temperature oxidative coupling of methane by optimizing the preparation methods. *Catal. Today* **2020**, *355*, 518–528. [[CrossRef](#)]
37. Alvarez-Galvan, M.C.; Mota, N.; Ojeda, M.; Rojas, S.; Navarro, R.M.; Fierro, J.L.G. Direct methane conversion routes to chemicals and fuels. *Catal. Today* **2011**, *171*, 15–23. [[CrossRef](#)]
38. Zohour, B.; Noon, D.; Senkan, S. New Insights into the Oxidative Coupling of Methane from Spatially Resolved Concentration and Temperature Profiles. *ChemCatChem* **2013**, *5*, 2729. [[CrossRef](#)]
39. Jiang, T.; Song, J.; Huo, M.; Yang, N.; Liu, J.; Zhang, J.; Sun, Y.; Zhu, Y. La₂O₃ catalysts with diverse spatial dimensionality for oxidative coupling of methane to produce ethylene and ethane. *RSC Adv.* **2016**, *6*, 34872–34876. [[CrossRef](#)]

40. Kiatsaengthong, D.; Jaroenpanon, K.; Somchuea, P.; Chuksaw, T.; Chareonpanich, M.; Faungnawakij, K.; Sohn, H.; Rupprechter, G.; Seubsai, A. Effects of Mg, Ca, Sr, and Ba Dopants on the Performance of La_2O_3 Catalysts for the Oxidative Coupling of Methane. *ACS Omega* **2022**, *7*, 1785–1793. [CrossRef] [PubMed]
41. Xu, J.; Zhang, Y.; Xu, X.; Fang, X.; Xi, R.; Liu, Y.; Zheng, R.; Wang, X. Constructing $\text{La}_2\text{B}_2\text{O}_7$ (B = Ti, Zr, Ce) Compounds with Three Typical Crystalline Phases for the Oxidative Coupling of Methane: The Effect of Phase Structures, Superoxide Anions, and Alkalinity on the Reactivity. *ACS Catal.* **2019**, *9*, 4030–4045. [CrossRef]
42. Wang, Z.-Q.; Wang, D.; Gong, X.-Q. Strategies To Improve the Activity While Maintaining the Selectivity of Oxidative Coupling of Methane at La_2O_3 : A Density Functional Theory Study. *ACS Catal.* **2019**, *10*, 586–594. [CrossRef]
43. Chrétien, S.; Metiu, H. Acid–Base Interaction and Its Role in Alkane Dissociative Chemisorption on Oxide Surfaces. *J. Phys. Chem. C* **2014**, *118*, 27336–27342. [CrossRef]
44. Chu, C.; Zhao, Y.; Li, S.; Sun, Y. Correlation between the acid–base properties of the La_2O_3 catalyst and its methane reactivity. *Phys. Chem. Chem. Phys.* **2016**, *18*, 16509–16517. [CrossRef]
45. Korf, S.; Roos, J.; Diphooorn, J.; Veehof, R.; van Ommen, J.; Ross, J. The selective oxidation of methane to ethane and ethylene over doped and un-doped rare earth oxides. *Catal. Today* **1989**, *4*, 279–292.
46. Rane, V.H.; Chaudhari, S.T.; Choudhary, V.R. Comparison of the surface and catalytic properties of rare earth-promoted CaO catalysts in the oxidative coupling of methane. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 208–215. [CrossRef]
47. Yu, C.; Weng, W.; Shu, Q.; Meng, X.; Zhang, B.; Chen, X.; Zhou, X. Additive effects of alkaline-earth metals and nickel on the performance of $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ in methane catalytic partial oxidation. *J. Nat. Gas Chem.* **2011**, *20*, 135–139. [CrossRef]
48. Ferreira, V.J.; Tavares, P.; Figueiredo, J.L.; Faria, J.L. Ce-Doped La_2O_3 based catalyst for the oxidative coupling of methane. *Catal. Commun.* **2013**, *42*, 50–53. [CrossRef]
49. Mefford, J.T.; Hardin, W.G.; Dai, S.; Johnston, K.P.; Stevenson, K.J. Anion charge storage through oxygen intercalation in LaMnO_3 perovskite pseudocapacitor electrodes. *Nat. Mater.* **2014**, *13*, 726–732. [CrossRef]
50. Nipan, G.D. Phase states of $\text{Li}/\text{W}/\text{Mn}/\text{SiO}_2$ composites in catalytic oxidative coupling of methane. *Inorg. Mater.* **2015**, *51*, 389–395. [CrossRef]
51. Lu, H.; Zhang, Q.; Liu, R.; Gui, J. Oxidative Coupling of Methane over $\text{SrO}/\text{La}_2\text{O}_3$ Catalyst in an Oxygen-Permeable Separation Membrane Reactor. *Catal. Lett.* **2020**, *151*, 1805–1809. [CrossRef]
52. Boivin, J.C.; Mairesse, G. Recent material developments in fast oxide ion conductors. *Chem. Mater.* **1998**, *10*, 2870–2888.
53. Chen, J.; Shen, M.; Wang, X.; Qi, G.; Wang, J.; Li, W. The influence of nonstoichiometry on LaMnO_3 perovskite for catalytic NO oxidation. *Appl. Catal. B Environ.* **2013**, *134–135*, 251–257. [CrossRef]
54. Wang, H.; Cong, Y.; Yang, W. Oxidative coupling of methane in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ tubular membrane reactors. *Catal. Today* **2005**, *104*, 160–167. [CrossRef]
55. Xu, J.; Xi, R.; Xu, X.; Zhang, Y.; Feng, X.; Fang, X.; Wang, X. $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore compounds: A category of potential materials for clean energy and environment protection catalysis. *J. Rare Earths* **2020**, *38*, 840–849. [CrossRef]
56. Zhang, F.X.; Tracy, C.L.; Lang, M.; Ewing, R.C. Stability of fluorite-type $\text{La}_2\text{Ce}_2\text{O}_7$ under extreme conditions. *J. Alloys Compd.* **2016**, *674*, 168–173. [CrossRef]
57. Xu, J.; Peng, L.; Fang, X.; Fu, Z.; Liu, W.; Xu, X.; Peng, H.; Zheng, R.; Wang, X. Developing reactive catalysts for low temperature oxidative coupling of methane: On the factors deciding the reaction performance of $\text{Ln}_2\text{Ce}_2\text{O}_7$ with different rare earth A sites. *Appl. Catal. A Gen.* **2018**, *552*, 117–128. [CrossRef]
58. Wang, Z.; Zhou, G.; Jiang, D.; Wang, S. Recent development of $\text{A}_2\text{B}_2\text{O}_7$ system transparent ceramics. *J. Adv. Ceram.* **2018**, *7*, 289–306. [CrossRef]
59. Wang, Y.; Yang, X.; Hou, C.; Yin, F.; Wang, G.; Zhu, X.; Jiang, G.; Li, C. Improved Catalytic Activity and Stability of Ba Substituted SrTiO_3 Perovskite for Oxidative Coupling of Methane. *ChemCatChem* **2021**, *13*, 4182–4191. [CrossRef]
60. Sim, Y.; Kwon, D.; An, S.; Ha, J.-M.; Oh, T.-S.; Jung, J.C. Catalytic behavior of ABO_3 perovskites in the oxidative coupling of methane. *Mol. Catal.* **2020**, *489*, 110925. [CrossRef]
61. Gan, R.; Nishida, Y.; Haneda, M. Effect of B Site Substitution on the Catalytic Activity of La—Based Perovskite for Oxidative Coupling of Methane. *Phys. Status Solidi B* **2022**, *259*, 2100544. [CrossRef]
62. Xu, J.; Zhang, Y.; Liu, Y.; Fang, X.; Xu, X.; Liu, W.; Zheng, R.; Wang, X. Optimizing the Reaction Performance of $\text{La}_2\text{Ce}_2\text{O}_7$ —Based Catalysts for Oxidative Coupling of Methane (OCM) at Lower Temperature by Lattice Doping with Ca Cations. *Eur. J. Inorg. Chem.* **2018**, *2019*, 183–194. [CrossRef]
63. Xu, J.; Xi, R.; Xiao, Q.; Xu, X.; Liu, L.; Li, S.; Gong, Y.; Zhang, Z.; Fang, X.; Wang, X. Design of strontium stannate perovskites with different fine structures for the oxidative coupling of methane (OCM): Interpreting the functions of surface oxygen anions, basic sites and the structure–reactivity relationship. *J. Catal.* **2022**, *408*, 465–477. [CrossRef]
64. Yu, C.Y.; Li, W.Z.; Martin, G.A.; Mirodatos, C. Studies of CaTiO_3 based catalysts for the oxidative coupling of methane. *Appl. Catal. A Gen.* **1997**, *158*, 201–214.
65. Katouzian, F.; Fakhroueian, Z.; Bidhendi, S.M. The Interesting of Antifungal Effects of Novel In Vitro Fabrics of Stabilized ZnO Nanofluids. *Adv. Nanopart.* **2016**, *5*, 206–223. [CrossRef]
66. Kiani, D.; Sourav, S.; Baltrusaitis, J.; Wachs, I.E. Oxidative Coupling of Methane (OCM) by SiO_2 -Supported Tungsten Oxide Catalysts Promoted with Mn and Na. *ACS Catal.* **2019**, *9*, 5912–5928. [CrossRef]

67. Pak, S.; Lunsford, J.H. Thermal effects during the oxidative coupling of methane over Mn/Na₂WO₄/SiO₂ and Mn/Na₂WO₄/MgO catalysts. *Appl. Catal. A Gen.* **1998**, *168*, 131–137. [\[CrossRef\]](#)
68. Wu, J.; Li, S. The Role of Distorted W04 in the Oxidative Coupling of Methane on Tungsten Oxide Supported Catalysts. *J. Phys. Chem.* **1995**, *99*, 4566–4568. [\[CrossRef\]](#)
69. Wang, P.; Zhao, G.; Liu, Y.; Lu, Y. TiO₂-doped Mn₂O₃-Na₂WO₄/SiO₂ catalyst for oxidative coupling of methane: Solution combustion synthesis and MnTiO₃-dependent low-temperature activity improvement. *Appl. Catal. A Gen.* **2017**, *544*, 77–83. [\[CrossRef\]](#)
70. Fleischer, V.; Steuer, R.; Parishan, S.; Schomäcker, R. Investigation of the surface reaction network of the oxidative coupling of methane over Na₂WO₄/Mn/SiO₂ catalyst by temperature programmed and dynamic experiments. *J. Catal.* **2016**, *341*, 91–103. [\[CrossRef\]](#)
71. Gordienko, Y.; Usmanov, T.; Bychkov, V.; Lomonosov, V.; Fattakhova, Z.; Tulenin, Y.; Shashkin, D.; Sinev, M. Oxygen availability and catalytic performance of NaWMn/SiO₂ mixed oxide and its components in oxidative coupling of methane. *Catal. Today* **2016**, *278*, 127–134. [\[CrossRef\]](#)
72. Sourav, S.; Wang, Y.X.; Kiani, D.; Baltrusaitis, J.; Fushimi, R.R.; Wachs, I.E. Resolving the Types and Origin of Active Oxygen Species Present in Supported Mn-Na₂WO₄/SiO₂ Catalysts for Oxidative Coupling of Methane. *ACS Catal.* **2021**, *11*, 10288–10293. [\[CrossRef\]](#)
73. Varma, A.; Mukasyan, A.S.; Rogachev, A.S.; Manukyan, K.V. Solution Combustion Synthesis of Nanoscale Materials. *Chem. Rev.* **2016**, *116*, 14493–14586. [\[CrossRef\]](#) [\[PubMed\]](#)
74. Sourav, S.; Wang, Y.; Kiani, D.; Baltrusaitis, J.; Fushimi, R.R.; Wachs, I.E. New Mechanistic and Reaction Pathway Insights for Oxidative Coupling of Methane (OCM) over Supported Na₂WO₄/SiO₂ Catalysts. *Angew. Chem. Int. Ed.* **2021**, *60*, 21502–21511. [\[CrossRef\]](#) [\[PubMed\]](#)
75. Sourav, S.; Kiani, D.; Wang, Y.; Baltrusaitis, J.; Fushimi, R.R.; Wachs, I.E. Molecular structure and catalytic promotional effect of Mn on supported Na₂WO₄/SiO₂ catalysts for oxidative coupling of methane (OCM) reaction. *Catal. Today* **2023**, *416*, 113837. [\[CrossRef\]](#)
76. Qin, L.; Cheng, Z.; Baser, D.; Goldenbaum, T.; Fan, J.A.; Fan, L.-S. Cyclic redox scheme towards shale gas reforming: A review and perspectives. *React. Chem. Eng.* **2020**, *5*, 2204–2220. [\[CrossRef\]](#)
77. Chung, E.Y.; Wang, W.K.; Nadgouda, S.G.; Baser, D.S.; Sofranko, J.A.; Fan, L.-S. Catalytic Oxygen Carriers and Process Systems for Oxidative Coupling of Methane Using the Chemical Looping Technology. *Ind. Eng. Chem. Res.* **2016**, *55*, 12750–12764. [\[CrossRef\]](#)
78. Damasceno, S.; Trindade, F.J.; Fonseca, F.C.; Florio, D.Z.d.; Ferlauto, A.S. Oxidative coupling of methane in chemical looping design. *Fuel Process. Technol.* **2022**, *231*, 107255. [\[CrossRef\]](#)
79. Li, D.; Xu, R.; Li, X.; Li, Z.; Zhu, X.; Li, K. Chemical Looping Conversion of Gaseous and Liquid Fuels for Chemical Production: A Review. *Energy Fuels* **2020**, *34*, 5381–5413. [\[CrossRef\]](#)
80. Huang, J.; Zhao, K.; Jiang, S.; Kang, S.; Lin, Y.; Huang, Z.; Zheng, A.; Zhao, Z. Heteroatom-doping regulated Mg₆MnO₈ for improving C₂+ hydrocarbons during chemical looping oxidative coupling of methane. *Fuel Process. Technol.* **2022**, *235*, 107352. [\[CrossRef\]](#)
81. Baser, D.S.; Cheng, Z.; Fan, J.A.; Fan, L.-S. Codoping Mg-Mn Based Oxygen Carrier with Lithium and Tungsten for Enhanced C₂ Yield in a Chemical Looping Oxidative Coupling of Methane System. *ACS Sustain. Chem. Eng.* **2021**, *9*, 2651–2660. [\[CrossRef\]](#)
82. Jiang, S.; Ding, W.; Zhao, K.; Huang, Z.; Wei, G.; Feng, Y.; Lv, Y.; He, F. Enhanced Chemical looping oxidative coupling of methane by Na-doped LaMnO₃ redox catalysts. *Fuel* **2021**, *299*, 120932. [\[CrossRef\]](#)
83. Fleischer, V.; Littlewood, P.; Parishan, S.; Schomäcker, R. Chemical looping as reactor concept for the oxidative coupling of methane over a Na₂WO₄/Mn/SiO₂ catalyst. *Chem. Eng. J.* **2016**, *306*, 646–654. [\[CrossRef\]](#)
84. Fleischer, V.; Simon, U.; Parishan, S.; Colmenares, M.G.; Görke, O.; Gurlo, A.; Riedel, W.; Thum, L.; Schmidt, J.; Risse, T.; et al. Investigation of the role of the Na₂WO₄/Mn/SiO₂ catalyst composition in the oxidative coupling of methane by chemical looping experiments. *J. Catal.* **2018**, *360*, 102–117. [\[CrossRef\]](#)
85. Sun, W.; Zhao, G.; Gao, Y.; Si, J.; Liu, Y.; Lu, Y. An oxygen carrier catalyst toward efficient chemical looping-oxidative coupling of methane. *Appl. Catal. B Environ.* **2022**, *304*, 120948. [\[CrossRef\]](#)
86. Sung, J.S.; Choo, K.Y.; Kim, T.H.; Greish, A.; Glukhov, L.; Finashina, E.; Kustov, L. Peculiarities of oxidative coupling of methane in redox cyclic mode over Ag-La₂O₃/SiO₂ catalysts. *Appl. Catal. A Gen.* **2010**, *380*, 28–32. [\[CrossRef\]](#)
87. Greish, A.A.; Glukhov, L.M.; Finashina, E.D.; Kustov, L.M.; Sung, J.-S.; Choo, K.-Y.; Kim, T.-H. Oxidative coupling of methane in the redox cyclic mode over the catalysts on the basis of CeO₂ and La₂O₃. *Mendeleev Commun.* **2010**, *20*, 28–30. [\[CrossRef\]](#)
88. Cheng, Z.; Baser, D.S.; Nadgouda, S.G.; Qin, L.; Fan, J.A.; Fan, L.-S. C₂ Selectivity Enhancement in Chemical Looping Oxidative Coupling of Methane over a Mg-Mn Composite Oxygen Carrier by Li-Doping-Induced Oxygen Vacancies. *ACS Energy Lett.* **2018**, *3*, 1730–1736. [\[CrossRef\]](#)
89. Noon, D.; Zohour, B.; Senkan, S. Oxidative coupling of methane with La₂O₃-CeO₂ nanofiber fabrics: A reaction engineering study. *J. Nat. Gas Sci. Eng.* **2014**, *18*, 406–411. [\[CrossRef\]](#)
90. Lomonosov, V.I.; Sinev, M.Y. Oxidative coupling of methane: Mechanism and kinetics. *Kinet. Catal.* **2016**, *57*, 647–676. [\[CrossRef\]](#)
91. Chen, S.; Ma, X. The role of oxygen species in the selective oxidation of methanol to dimethoxymethane over VOx/TS-1 catalyst. *J. Ind. Eng. Chem.* **2017**, *45*, 296–300. [\[CrossRef\]](#)

92. Kim, I.; Lee, G.; Na, H.B.; Ha, J.-M.; Jung, J.C. Selective oxygen species for the oxidative coupling of methane. *Mol. Catal.* **2017**, *435*, 13–23. [[CrossRef](#)]
93. Phung, T.K.; Garbarino, G. On the use of infrared spectrometer as detector for Temperature Programmed (TP) techniques in catalysts characterization. *J. Ind. Eng. Chem.* **2017**, *47*, 288–296. [[CrossRef](#)]
94. Gambo, Y.; Jalil, A.A.; Triwahyono, S.; Abdulrasheed, A.A. Recent advances and future prospect in catalysts for oxidative coupling of methane to ethylene: A review. *J. Ind. Eng. Chem.* **2018**, *59*, 218–229. [[CrossRef](#)]
95. Borchert, H.; Baerns, M. The effect of oxygen-anion conductivity of metal–oxide doped lanthanum oxide catalysts on hydrocarbon selectivity in the oxidative coupling of methane. *J. Catal.* **1997**, *168*, 315–320.
96. Ortiz-Bravo, C.A.; Chagas, C.A.; Toniolo, F.S. Oxidative coupling of methane (OCM): An overview of the challenges and opportunities for developing new technologies. *J. Nat. Gas Sci. Eng.* **2021**, *96*, 104254. [[CrossRef](#)]
97. Yoon, S.; Lim, S.; Choi, J.W.; Suh, D.J.; Song, K.H.; Ha, J.M. Study on the unsteady state oxidative coupling of methane: Effects of oxygen species from O(2), surface lattice oxygen, and CO₂ on the C₂₊ selectivity. *RSC Adv.* **2020**, *10*, 35889–35897. [[CrossRef](#)]
98. Vamvakeros, A.; Matras, D.; Jacques, S.D.M.; di Michiel, M.; Price, S.W.T.; Senecal, P.; Aran, M.A.; Middelkoop, V.; Stenning, G.B.G.; Mosselmans, J.F.W.; et al. Real-time multi-length scale chemical tomography of fixed bed reactors during the oxidative coupling of methane reaction. *J. Catal.* **2020**, *386*, 39–52. [[CrossRef](#)]
99. Dissanayake, D.; Lunsford, J.H.; Rosynek, M.P. Oxidative coupling of methane over oxide-supported barium catalysts. *J. Catal.* **1993**, *143*, 286–298.
100. Kondratenko, E.V.; Peppel, T.; Seeburg, D.; Kondratenko, V.A.; Kalevaru, N.; Martin, A.; Wohlrab, S. Methane conversion into different hydrocarbons or oxygenates: Current status and future perspectives in catalyst development and reactor operation. *Catal. Sci. Technol.* **2017**, *7*, 366–381. [[CrossRef](#)]

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