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Methane Activation

Alternative Oxidants for the Catalytic Oxidative Coupling of Methane

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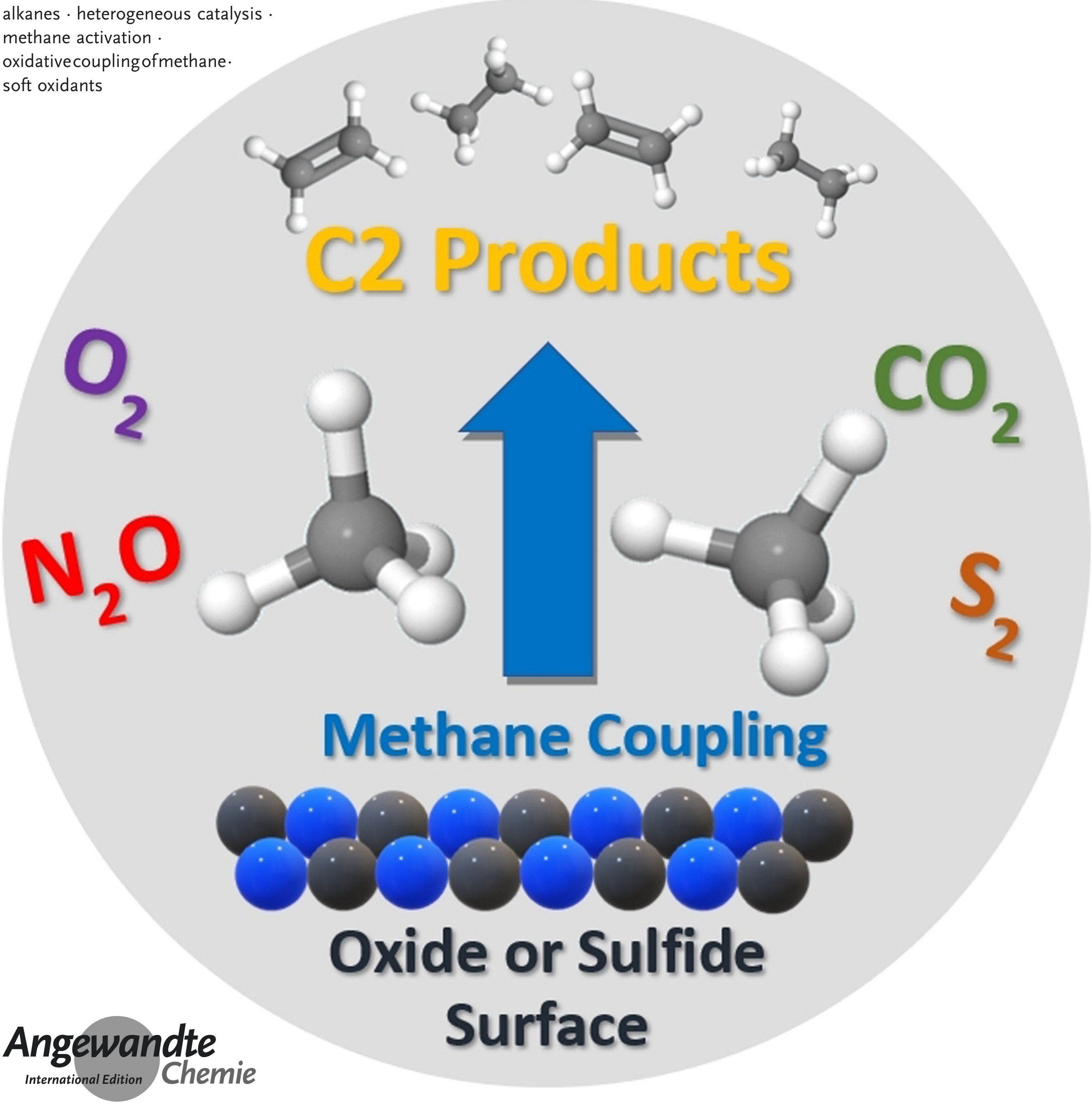
Keywords:
alkanes · heterogeneous catalysis · methane activation · oxidative coupling of methane · soft oxidants



The catalytic oxidative coupling of methane (OCM) to C_2 hydrocarbons with oxygen (O_2-OCM) has garnered renewed worldwide interest in the past decade due to the emergence of enormous new shale gas resources. However, the C_2 selectivity of typical OCM processes is significantly challenged by overoxidation to CO_x products. Other gaseous reagents such as N_2O, CO_2, and S_2 have been investigated to a far lesser extent as alternative, milder oxidants to replace O_2. Although several authoritative review articles have summarized OCM research progress in depth, recent oxidative coupling developments using alternative oxidants (X-OCM) have not been overviewed in detail. In this perspective, we review and analyze OCM research results reporting the implementation of N_2O, CO_2, S_2, and other non-O_2 oxidants, highlighting the unique chemistries of these systems and their advantages/challenges compared to O_2-OCM. Current outlook and potential areas for future study are also discussed.

From the Contents

1. Introduction

Methane is an abundant hydrocarbon and the principal component of natural gas. Currently, over 90% of the methane in natural gas is flared or combusted for energy generation instead of being used as an inexpensive carbon feedstock.[1] The rise of shale gas in the past decade has led to a renewed interest in upgrading methane to value-added chemicals. Methane reforming to syngas, CO and H_2, can serve as a source of methanol,[1] or followed by the Fischer–Tropsch oligomerization process, as a source of liquid hydrocarbons. These are the most widely utilized approaches to methane-derived chemicals on the industrial scale.[2] However, the direct catalytic conversion of methane into higher hydrocarbons such as ethylene would be highly desirable. Oxidative coupling of methane with O_2 (O_2-OCM), is one such approach in which methane molecules can be coupled to form C_2 products [Eqs. (1)–(2)].

$$2\,CH_4 + {}^1\!/_2\,O_2 \rightarrow C_2H_6 + H_2O \tag{1}$$

$$2\,CH_4 + O_2 \rightarrow C_2H_4 + 2\,H_2O \tag{2}$$

These OCM reactions are generally thought to involve the formation of methyl radicals ($CH_3^\bullet$) on the surface of metal oxide catalysts.[1,3] The radicals desorb and couple in the gas phase to form ethane, which can be further dehydrogenated to ethylene.[4] Unfortunately, in the presence of an oxidant, the ethane and ethylene also undergo facile oxidation to CO and CO_2, reflecting the pronounced thermodynamic stability of these over-oxidation products (Table 1). Mechanistically, CO_x may derive from a number of pathways. For example, C_2 products such as ethane and ethylene may be further activated on the catalyst surface.[5] Alternatively, surface or gas phase oxygen species may react with methyl radicals.[4,6] The high temperatures of O_2-OCM may also facilitate hydrocarbon combustion in the gas phase.[6]

Since the discovery of O_2-OCM by Keller and Bhasin in 1982,[7] there have been over 2000 publications on the topic.

Table 1: Gibbs free energies for methane coupling and overoxidation in OCM with O_2, N_2O, CO_2, and S_2.

Reactions	ΔG_{rxn} at 800 °C [kJ mol^{-1}]
Reactions with O_2	
$2\,CH_4 + O_2 \rightarrow C_2H_4 + 2\,H_2O$	−307
$2\,CH_4 + {}^1\!/_2\,O_2 \rightarrow C_2H_6 + H_2O$	−114
$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$	−792
$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$	−1294
Reactions with N_2O	
$2\,CH_4 + 2\,N_2O \rightarrow C_2H_4 + 2\,H_2O + 2\,N_2$	−622.7
$2\,CH_4 + N_2O \rightarrow C_2H_6 + H_2O + N_2$	−279
$CH_4 + 4\,N_2O \rightarrow CO_2 + 2\,H_2O + 4\,N_2$	−1432
$C_2H_4 + 6\,N_2O \rightarrow 2\,CO_2 + 2\,H_2O + 6\,N_2$	−2242
Reactions with CO_2	
$2\,CH_4 + 2\,CO_2 \rightarrow C_2H_4 + 2\,H_2O + 2\,CO$	+71
$2\,CH_4 + CO_2 \rightarrow C_2H_6 + H_2O + CO$	+72
$CH_4 + 3\,CO_2 \rightarrow 4\,CO + 2\,H_2O$	−44
$C_2H_4 + 4\,CO_2 \rightarrow 6\,CO + 2\,H_2O$	−1459
Reactions with S_2	
$2\,CH_4 + S_2 \rightarrow C_2H_4 + 2\,H_2S$	−4.90
$2\,CH_4 + {}^1\!/_2\,S_2 \rightarrow C_2H_6 + H_2S$	+33.9
$CH_4 + 2\,S_2 \rightarrow CS_2 + 2\,H_2S$	−124
$C_2H_4 + 3\,S_2 \rightarrow 2\,CS_2 + 2\,H_2S$	−236

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As shown in Figure 1, there was an initial surge in publications in the decade and a half following the original 1982 report. In the past several years, the hydrocarbon catalysis community has witnessed a second surge in OCM research due to the current shale gas revolution. However, despite the abundance of OCM research findings, achieving a high yield of C_2 products (ethane and ethylene) remains a major challenge. It has been estimated that a C_2 yield of at least 30% will be necessary for OCM commercialization, yet few catalytic systems are able to approach this benchmark.[8] The main limiting factor is the formation of the aforementioned CO_x byproducts. Thus, approaches that seek to suppress the formation of CO_2 and CO from methane or C_2 products will be necessary to achieve high yields of the desired products.

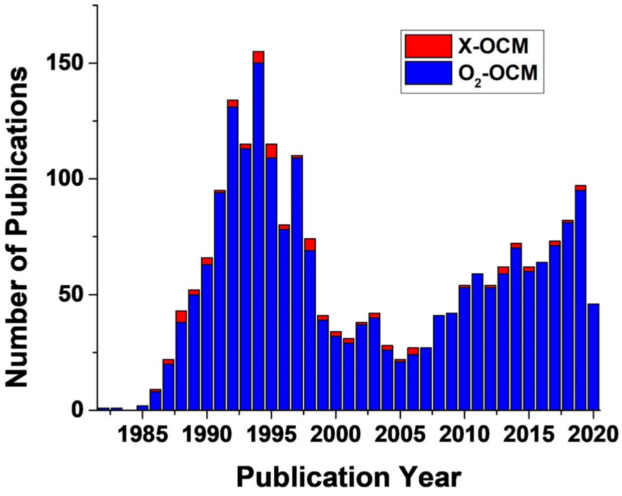

Figure 1. Number of OCM publications per year reported on Web of Science. The blue bars represent publications utilizing O_2 as the oxidant (O_2-OCM), while the red bars correspond to publications using other oxidants (X-OCM).

One conceivable strategy to enhance OCM selectivity is to control the types of active oxidizing species that are present under reaction conditions. The replacement of O_2 with other oxidants is one possible approach to achieve this goal. In fact, substituting O_2 with less aggressive, "softer" oxidants such as CO_2 or N_2O has been a frequent strategy for light alkane partial oxidations.[9] As shown in Figure 1, a small fraction (about 3%) of OCM publications have also pursued this strategy, making use of N_2O, CO_2, S_2, and other milder oxidants (X-OCM). Alternative oxidants may improve selectivity to desired products by decreasing the thermodynamic driving force for overoxidation processes, forming more selective active oxygen species, or a combination of these factors. Table 1 summarizes the Gibbs free energies of OCM coupling and overoxidation reactions for O_2, N_2O, CO_2, and S_2 oxidants. The unique thermodynamic characteristics of these various oxidants suggest innate differences in OCM activity and product distributions. Of course, catalyst- and reaction-dependent kinetic considerations relating to oxidant activation may also lead to differences in mechanistic pathways when alternative oxidants are employed.

Although there have been several recent reviews summarizing the OCM literature, many do not address research on alternative oxidants.[1,10] Those that do often only mention them briefly or only discuss one potential oxidant. However, X-OCM systems often exhibit unique, under-investigated chemistries and promising C_2 selectivities compared to traditional O_2-OCM. As such, this article will, for the first time, review recent developments in X-OCM research, focusing on the oxidants N_2O, CO_2, S_2, and others. We will compare and contrast the potential advantages and limitations of each oxidant, summarize the results that have been achieved to date, and critically assess current challenges and areas of interest for further study.

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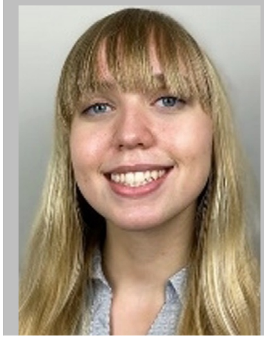

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2. N_2O as an Oxidant (N_2O-OCM)

2.1. Motivation

N_2O is one possible alternative oxidant for OCM and related partial oxidation reactions. Like CH_4, N_2O is a greenhouse gas, and its use in the production of value-added chemicals is desired.[11] It has been frequently investigated as an oxidant for methane partial oxidation to oxygenates such as methanol and formaldehyde over zeolite catalysts.[12] As such, N_2O can also act as the oxidant for OCM (N_2O-OCM) to form C_2 products via Equations (3) and (4).

$$2\,CH_4 + N_2O \rightarrow C_2H_6 + H_2O + N_2 \quad (3)$$

$$2\,CH_4 + 2\,N_2O \rightarrow C_2H_4 + 2\,H_2O + 2\,N_2 \quad (4)$$

$\Delta G°$ of the ethane-forming reaction is $-279\,kJ\,mol^{-1}$ at 800 °C, compared to $-114\,kJ\,mol^{-1}$ for the same coupling reaction with O_2 (Table 1).[13] Note that although N_2O-OCM is thermodynamically more “downhill” than O_2-OCM, the kinetic tendency of the catalyst to activate the oxidant is also an important parameter that influences reactivity.

Utilizing N_2O as an oxidant could conceivably lead to enhanced C_2 selectivity in OCM due to its relatively mild oxidizing tendency compared to O_2.[14] In particular, N_2O can only provide a monoatomic oxygen species, such as O^-.[15] Dioxygen, in contrast, can form peroxo species under OCM reaction conditions that are precursors to CO_2.[16] Furthermore, N_2O decomposes on the catalyst surface, leading to the release of N_2 gas and the formation of surface oxygen sites.[15] It has generally been observed in the OCM literature that monoatomic surface oxygen species (O*) are responsible for selective C_2 formation, whereas molecular or gas phase oxygen species facilitate overoxidation.[17] In fact, it has been estimated that there is an upper limit of 28 % single pass C_2 yield for OCM in the presence of gas phase O_2 under typical O_2/CH_4 cofeed conditions.[17a] Thus, if N_2O preferentially forms selective O* sites, with limited to no competing diatomic or gas phase oxygen formation, a high C_2 selectivity might be achieved. Additionally, the range of possible oxidant/CH_4 ratios is far wider when using N_2O, as there is no threat of explosion or runaway CH_4 combustion as with O_2.[18]

2.2. N_2O-OCM Scope and Mechanism

The literature reports for each different alternative oxidant for X-OCM systems tend to highlight very different aspects of the catalytic reaction. For example, studies of OCM with N_2O as the oxidant have focused primarily on comparing N_2O-OCM to O_2-OCM systems, activation of the oxidant, and mechanistic insights. As such, our discussion in this section will emphasize these aspects and end with a brief description of some nontraditional N_2O-OCM catalysts.

Catalysts for N_2O-OCM are frequently irreducible, basic, or rare earth metal oxides. For most of these catalysts, the use of N_2O leads to reduced methane conversions, but improved C_2 selectivities versus O_2 as the oxidant.[18,19] Even at approximately equal CH_4 conversion levels, the C_2 selectivity has been observed to be significantly higher using N_2O than O_2.[19f,20] For example, Hutchings et al. showed that the total C_2 selectivity over a Sm_2O_3-based catalyst was 75 % with N_2O compared to about 50 % using O_2 at similar CH_4 conversions. More recently, a 2012 publication from Schomäcker et al. compared the OCM performance of a series of literature catalysts and catalysts prepared via cellulose templating (CT) using both N_2O and O_2 as oxidants.[20b] The CT synthesis method had previously been applied to perovskite O_2-OCM catalysts in order to cheaply produce bulk materials with high surface area.[21] In the CH_4 conversion range of 25–35 %, the C_2 selectivity on average is 11 % higher when using N_2O compared to O_2. This trend can be visualized graphically in Figure 2.

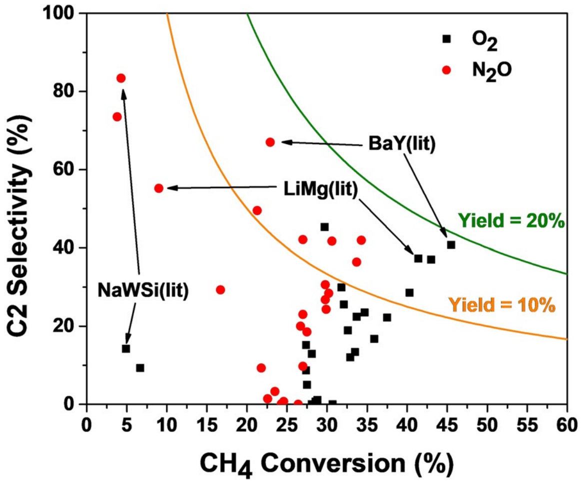

Figure 2. Selectivity versus conversion for optimized OCM catalysts at 1073 K using O_2 (black) and N_2O (red) as oxidants. Data taken from ref. [20b].

The observed higher C_2 selectivity with N_2O has been attributed to the preferential formation of surface O or O^- sites, which catalyze the formation of $^{\bullet}CH_3$ radicals.[18,20a,22] A series of publications investigated the nature of defects in Li/CaO catalysts following both O_2-OCM and N_2O-OCM.[23] The authors observed that N_2O-OCM leads to decreased CO production and greater yields of C_2 products. Electron paramagnetic resonance spectroscopy (EPR) was used to determine the concentrations of various defect centers, such as $O_3^{-\bullet}$, $CO_2^{-\bullet}$, $LiCO_3^{-\bullet}$, and $O^{-\bullet}$. In the presence of an O_2/CH_4 mixture, predominately $O_3^{-\bullet}$, $CO_2^{-\bullet}$, and $LiCO_3^{-\bullet}$ defects were detected. However, in an N_2O/CH_4 reaction medium, the concentration of $O^{-\bullet}$ increased significantly, providing evidence that $O^{-\bullet}$ species are derived from N_2O and lead to selective C_2 formation.[23a,b]

From the above discussion, the activation of N_2O on oxide catalysts to release N_2 and O* is presumably an important step in an N_2O-OCM process. The reduction of N_2O with CH_4 over Fe-exchanged zeolites may provide additional insight into this process.[11a,24] Such studies have reported the formation of adsorbed monoatomic oxygen species (O*) after N_2O treatment as assessed via techniques such as O_2-TPD and FT-IR spectroscopy. Additionally, results from pulse reactions of N_2O and CH_4 suggest that N_2O decomposition releases N_2 and creates O* species which then oxidize methane to CO, CO_2, or C_2 products.[24d,25]

Several reports using N_2O as an oxidant also investigated the mechanism of N_2O decomposition on the surface of metal oxide OCM catalysts.[25,26] Many of these studies attempted to differentiate between two possible N_2O decomposition pathways.[26] In Pathway 1 [Eqs. (5) and (6)], N_2O is activated at a coordinatively-unsaturated cation to form N_2 gas and an O* species. A second N_2O molecule then interacts with O* to regenerate the active center. In Pathway 2, N_2O decomposes into N_2 and O* over anion vacancies, and two O* species may come together to release molecular oxygen [Eqs. (7) and (8)].
Pathway 1:

$$N_2O + {}^* \rightarrow O^* + N_2 \tag{5}$$

$$N_2O + O^* \rightarrow O_2 + N_2 + {}^* \tag{6}$$

* = coordinately unsaturated cation

Pathway 2:

$$N_2O + {}^* \rightarrow O^* + N_2 \tag{7}$$

$$O^* + O^* \leftrightarrow O_2 + 2^* \tag{8}$$

* = anion vacancy

These pathways can be distinguished by measuring the effect of cofed O_2 during N_2O-OCM. Since Pathway 2 involves a reversible O_2 adsorption step, the addition of O_2 to the reactant stream should inhibit N_2O decomposition on catalysts that follow this route. In contrast, added O_2 should have no effect on the decomposition rate for catalysts that follow Pathway 1.[26a,c] In Pathway 1, the active centers for N_2O decomposition are suggested to be coordinately-unsaturated transition metal or redox active cations. Oxides such as undoped Bi_2O_3 or CaO catalysts with Fe impurities fall under this category.[26a–c] Contrarily, catalysts such as SrO and Li or Er-doped Bi_2O_3 proceed via Pathway 2. Here, the active sites for N_2O decomposition are anion vacancies, and O_2 addition inhibits the decomposition rate by competing for the same sites.[26a,27] In a comparative study of SrO (Pathway 2) and Na/CaO (Pathway 1), SrO exhibits significantly higher N_2O-OCM activity and selectivity.[26a] Thus, it can be argued that anion vacancies are the more desirable active sites for N_2O-OCM compared to redox sites such as under-coordinated cations.

Kinetic measurements on N_2O-OCM reactions have also provided insight into the role of N_2O. Lunsford measured the KIE and reaction rate orders of N_2O-OCM over Li/MgO and found that the kinetics depend on the N_2O concentration.[18] At low concentrations, the N_2O-OCM reaction is first order in oxidant and the measured KIE is near unity, suggesting that oxygen incorporation on the catalyst surface due to N_2O decomposition is rate determining. The CH_4 reaction order is zero under these conditions, consistent with previous studies by Otsuka that claimed the N_2O decomposition activation barrier was unchanged in the presence of CH_4.[22] However, under excess N_2O, the KIE increases to 1.9 and the reaction becomes first order in CH_4, suggesting that C–H activation becomes rate limiting. Kinetic analyses over Pb/MgO revealed an N_2O order that transitioned from 1 to 0 as the oxidant partial pressure was increased, although CH_4 remained first order across all N_2O/CH_4 ratios.[19d] In traditional O_2-OCM, C–H activation is typically the rate-limiting step, even at low O_2 concentrations.[28] However, N_2O decomposition is slow on oxide surfaces compared to that of O_2, plausibly accounting for the mechanistic differences.[19h]

Another important factor to consider is how the catalyst properties affect the activity of N_2O-OCM processes. Branco and co-workers studied a series of Ca/actinide oxide and Ca/lanthanide oxide catalysts for N_2O-OCM in order to determine how basicity and reducibility affected the product distribution.[29] They found that catalyst basicity, as measured by CO_2-TPD and probe reactions, correlated with high C_2 yields over lanthanide and actinide oxides. Furthermore, greater catalyst reducibility and more labile lattice oxygen species lead to increased activity but lower C_2 yields.[29b] These trends are depicted in Figure 3. Interestingly, the authors observed that the catalysts are more active under N_2O than under O_2, contrary to most other systems. They attributed this result to a cooperative effect between Ca and the f block elements.

In addition to traditional alkaline and rare earth-based oxides, a number of other catalyst systems have proven to be effective for N_2O-OCM. For example, Sugiyama examined hydroxyapatite catalysts for N_2O-OCM and observed that the selectivity displays little to no dependence on the N_2O partial pressure.[30] In contrast, O_2-OCM selectivity often falls significantly as more O_2 is added due to overoxidation reactions in the gas phase.[31] It was proposed that CH_4 is activated by surface O^- species, which are replenished by N_2O decomposition.[30a] The addition of tetrachloromethane (TCM) to the reactant mixture was observed to suppress total oxidation in N_2O-OCM by replacing surface OH groups with Cl.[30b]

Chlorine is also present in other effective N_2O-OCM catalysts, such as KCl–$LnCl_3$ molten salts.[20c] The La catalyst displays stable 75 % C_2 selectivity at about 10 % conversion for 48 hours, while the same catalyst only achieves 40 % C_2 selectivity with O_2 at isoconversion. After reaction, the presence of oxides and oxychlorides was confirmed via XPS and XRD, and catalysts with greater concentrations of these oxygen functionalities generally display increased activity but decreased C_2 yield. Chlorine has also been used as a dopant for perovskite catalysts.[32] The authors used O_2-TPD to show that Cl-doped $Ba_{0.5}Sr_{0.5}Fe_{0.2}Co_{0.8}O_{3-\delta}$ can attain a greater density of adsorbed O* species than the undoped structure, leading to higher activity and C_2 selectivity in N_2O-OCM. This catalyst achieved a remarkable 30.7 % C_2 yield (66.8 % CH_4 conversion, 46 % C_2 selectivity). Additionally, the major C_2 product was ethylene (ethylene/ethane = 2.6), whereas many OCM catalysts produce primarily ethane.[5a,33]

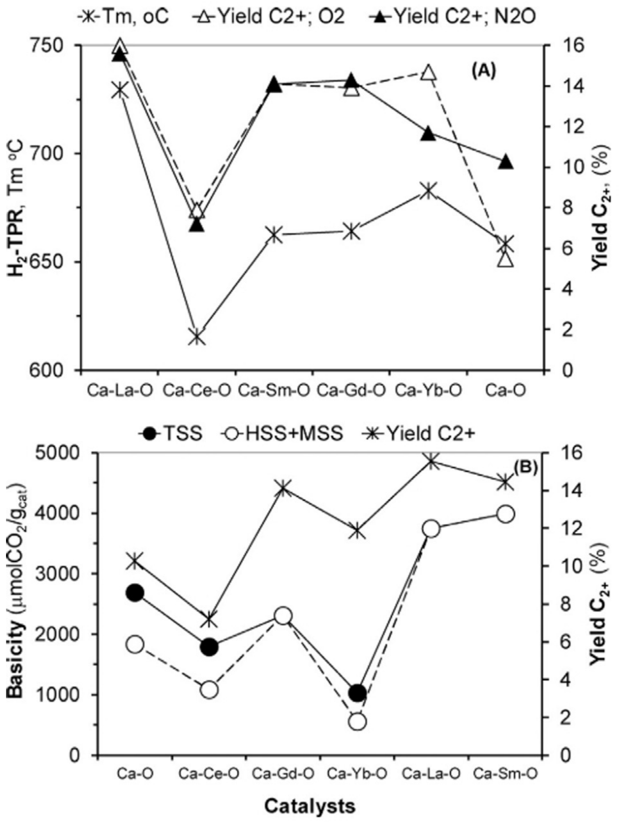

Figure 3. Top: Influence of catalyst reducibility/oxygen lability (as measured by maximum H_2-TPR temperature) on C_2 yield with O_2 and N_2O for various Ca-lanthanide catalysts. Bottom: Effect of catalyst basic properties (as measured by CO_2-TPD) on C_2 yield with N_2O over Ca-lanthanide catalysts. T_m = maximum temperature, TSS = total strength basic sites, HSS = high strength basic sites, MSS = medium strength basic sites. Reproduced from ref. [29b].

Many similarities can be drawn between O_2 and N_2O-OCM systems. Research on both oxidants has predominantly focused on basic, alkaline earth, or rare earth oxides. Surface basicity and oxygen content/lability are important factors affecting reactivity and selectivity for both systems.[10b,29] Furthermore, the role of both O_2 and N_2O in replenishing/forming active oxygen species on the surface has been emphasized.[27,34] However, the nature of these active species may differ. While O_2 can form peroxo species that act as CO_x precursors, N_2O can only initially form monoatomic O or O^- species and does not cause gas phase combustion reactions. These oxygen species can be formed via N_2O decomposition, releasing N_2. Figure 4 summarizes the mechanistic steps of N_2O-OCM that have been proposed by various authors.[18,19d,22,32] The higher C_2 selectivity with N_2O as an oxidant in turn has afforded promising yields. In fact, several catalysts achieve C_2 yields greater than 10%, which is greater than or on par with numerous O_2-OCM systems.[35] Figure 5 depicts the conversion and C_2 selectivity of the top-performing N_2O-OCM catalysts. These high C_2 yields highlight that N_2O-OCM is an approach that merits further study during this shale gas age.

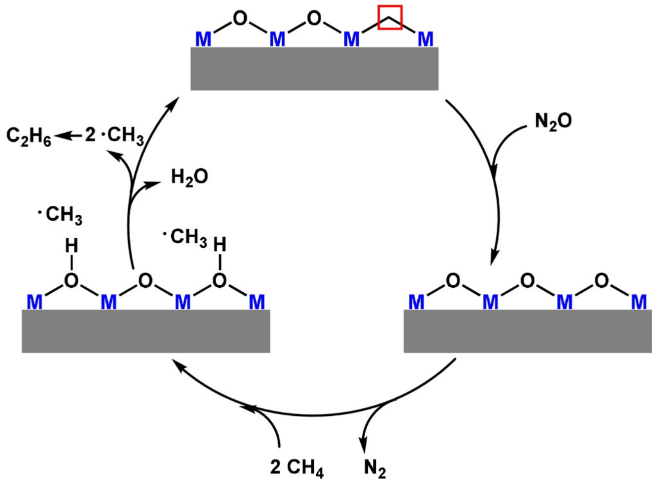

Figure 4. Generalized mechanism of N_2O-OCM, where N_2O dissociates over vacancy sites to form active oxygen surface species that in turn activate the methane molecule.

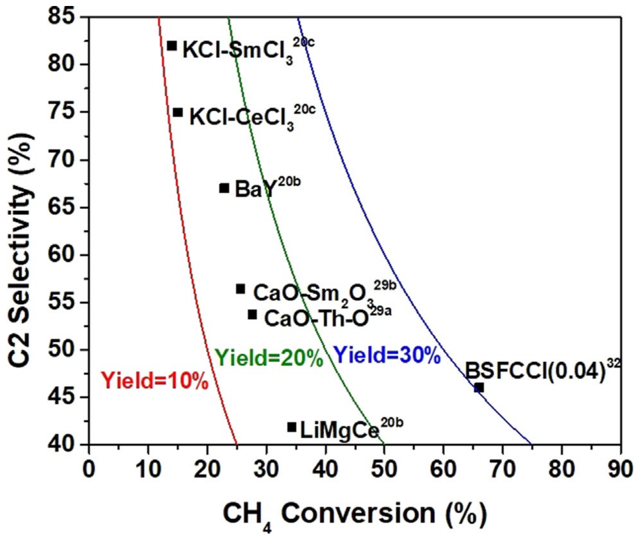

Figure 5. Conversion and C_2 selectivity of selected N_2O-OCM systems from the literature. The red, green, and blue lines represent C_2 yields of 10, 20, and 30%, respectively.

3. CO_2 as an Oxidant (N_2O-OCM)

3.1. Motivation

Carbon dioxide is another greenhouse gas that has been investigated frequently as a softer oxidant for light alkane partial oxidation reactions.[36] Its use as an oxygen source for light alkane activation is currently especially attractive due to the high content of CO_2 that is found in some shale gas reservoirs. For example, the New Albany Shale in Illinois and Kentucky contains up to 10% CO_2.[37] For OCM with CO_2 as an oxidant (CO_2-OCM), ethane and ethylene may be produced according to Equations (9) and (10).

$$2\,CH_4 + CO_2 \rightarrow C_2H_6 + H_2O + CO \qquad (9)$$

$$2\,CH_4 + 2\,CO_2 \rightarrow C_2H_4 + 2\,H_2O + 2\,CO \qquad (10)$$

$\Delta G°$ of the reaction in Equation (10) (ethylene) is $+71\,kJ\,mol^{-1}$ at 800 °C, compared to $-307\,kJ\,mol^{-1}$ with O_2 (Table 1).[38] The endergonic nature of CO_2-OCM, coupled with the inherent stability of the CO_2 molecule implies that CO_2-OCM is a more challenging reaction to drive forward than the O_2 variant. However, employing CO_2 as the oxidant alleviates heat management issues that challenge the highly exothermic O_2-OCM. Furthermore, ethylene forms via thermal dehydrogenation of ethane in the gas phase in many OCM systems according to Equation (11).[34,39]

$$C_2H_6 \rightarrow C_2H_4 + H_2 \tag{11}$$

The addition of CO_2 could help shift the equilibrium of this process towards the more valuable ethylene by consuming H_2 via the reverse water-gas shift reaction [Eq. (12)].

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{12}$$

Likewise, other side reactions between CH_4 and CO_2 to form CO [Eqs. (13) and (14)] such as dry reforming may occur, although they are less common over metal oxide catalysts compared to supported metallic catalysts.

$$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2 \tag{13}$$

$$CH_4 + 3\,CO_2 \rightarrow 4\,CO + 2\,H_2O \tag{14}$$

However, unlike O_2-OCM where both CO and CO_2 are formed, CO will be the only carbon-containing byproduct when CO_2 is the oxidant.

Furthermore, CO_2-OCM can plausibly improve the C_2 selectivity owing to the nature of active oxygen species. Like N_2O, CO_2 can only deliver monoatomic oxygen species to activate CH_4 on the catalyst surface, preventing the formation of surface peroxo and gas phase oxygen that lead to over-oxidation. Moreover, unlike O_2, CO_2 is unlikely to interact with $^{\bullet}CH_3$ radicals in the gas phase.[40] Thermodynamic analyses place equilibrium CH_4 conversions in the range of 10–30 % in the temperature range of 800–900 °C at atmospheric pressure and a 1:1 CH_4/CO_2 reactant ratio (Figure 6).[40,41] Thus, if a highly selective CO_2-OCM catalyst system can be developed, C_2 yields competitive with those of traditional OCM may be possible.

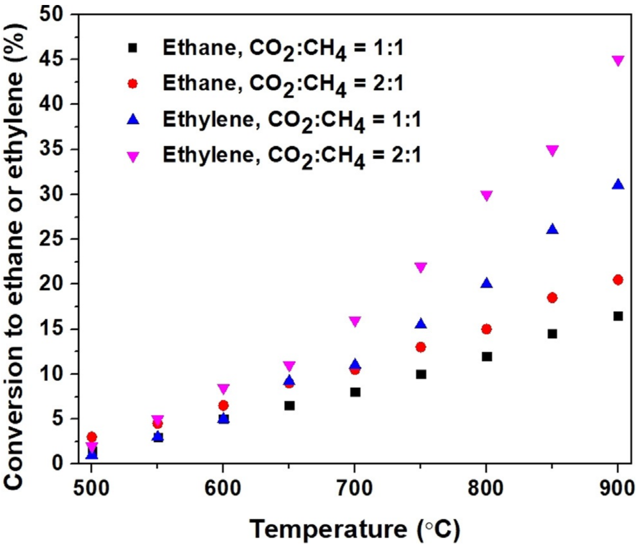

Figure 6. Calculated equilibrium conversion of methane to ethane (black and red) and ethylene (blue and purple) with a CO_2/CH_4 ratio of 1:1 (black and blue) or 2:1 (red and purple). Data taken from ref. [45].

3.2. CO_2-OCM Scope and Mechanism

Unlike the literature on N_2O-OCM, which focuses heavily on oxidant activation, prior discussions of CO_2-OCM tended to concentrate more on the development of active/selective catalysts and alternate reactor designs. This section will therefore examine the advancement of CO_2-OCM catalyst discovery, followed by a discussion of unconventional CO_2-OCM reactor concepts.

Because CO_2 is often a major (although undesired) product of O_2-OCM, several studies have cofed CO_2 along with CH_4 and O_2 in order to determine the effect on reactivity. For example, CO_2 was found to decrease OCM activity over Li/MgO due to the formation of carbonate species, but also to improve C_2 selectivity and stabilize the catalyst against deactivation.[42] In the early 1990s, researchers began to introduce significant concentrations of CO_2 as co-oxidants/reactive diluents in an attempt to manage heat production and make use of the oxygen in CO_2.[38,43] Aika and Nishiyama found that the addition of CO_2 increases the C_2 yield over PbO-based catalysts, although the reaction cannot be sustained without oxygen.[38] They also performed the reaction using isotopically labelled $^{13}CO_2$ and $^{12}CD_4$ with O_2 and found that only ^{13}CO and $^{12}C_2$ hydrocarbons are produced.[43a] Therefore, C_2 hydrocarbons form exclusively from methane, whereas CO is derived from CO_2, suggesting that CO_2 acts as an oxidant. A further study of Pb catalysts compared the reaction of CH_3I (a methyl radical precursor) under OCM conditions.[43c] With O_2 as an oxidant, only CO_2 is formed. However, when CO_2 is added, C_2 products are observed, implying that CO_2 inhibits the over-oxidation of methyl radicals. Suzuki also observed increased C_2 selectivity and yield in the presence of CO_2 over various basic oxides, although oxide catalysts that form highly stable carbonates such as SrO deactivated rapidly.[43b]

In the first example of CO_2-OCM without added O_2, Asami investigated 17 monometallic metal oxides for the reaction and found that rare earth oxides were most selective to C_2 products.[40] A follow-up study compared the CO_2-OCM reactivity of lanthanide oxides.[44] Pr and Tb oxides, in particular, afforded high C_2 yields. The authors suggested a mechanism in which CO_2 first oxidizes the catalyst surface, and these surface oxygen species activate the C−H bond in CH_4 to form methyl radicals. This mechanism was later supported by O_2-TPD experiments on the redox-active Pr_2O_3 catalyst.[45] The nature of the active oxygen species was also studied using the well-known Na_2WO_4-Mn/SiO_2 O_2-OCM catalyst.[46] Here O_2-TPD and CH_4 pulse experiments suggested that surface lattice oxygen is involved in methane activation. Furthermore, CO_2 pulse experiments showed that CO is formed over the catalyst in the absence of CH_4. This result suggests that CO_2 is activated to CO and O*, consistent with CO_2 producing oxygen species that can activate methane.

Several CO_2-OCM studies have also examined binary oxides.[41,47] The first of these systems utilized a La_2O_3/ZnO catalyst.[47a] The addition of La to ZnO led to a dramatic increase from 7.6% to above 90% C_2 selectivity, even at comparable conversions. The authors postulated a mechanism in which CO_2 dissociation leads to active O* formation according to Equations (15)–(17), where * represents an oxygen-deficient site. This mechanism bears strong resemblance to that of N_2O- and O_2-OCM, with the major difference being that CO_2 provides the active O* in this case.

$$O^* + 2\,CH_4 \rightarrow 2\,CH_3^{\bullet} + H_2O + {}^* \tag{15}$$

$$2\,CH_3^{\bullet} \rightarrow C_2H_6 \tag{16}$$

$${}^* + CO_2 \rightarrow O^* + CO \tag{17}$$

Later, a series of binary oxide systems was developed, consisting of basic oxide and redox-active oxide components. The idea here is that the basic component facilitates CO_2 chemisorption whereas the redox component enables dissociation into CO and O*. CaO-Cr_2O_3,[47b] CaO-CeO_2,[41,47c] CaO-ZnO,[47d] and Sr-Mn[47e,f] have all proven effective for CO_2-OCM. Ternary Ca-Mn/CeO_2 catalysts have also been explored.[47g–j] When tested alone under CO_2-OCM conditions, the redox-active oxide is typically highly active but poorly selective. Contrarily, the basic oxide displays negligible activity when used alone, presumably because it is unable to dissociate CO_2 and form active O*. However, the binary and ternary oxides display a cooperative effect in which high C_2 selectivity is sustained at reasonable conversions.[41,47b] Figure 7 depicts the proposed mechanism for CO_2-OCM over binary/ternary oxides such as CaO-CeO_2. This mechanism has been supported by CO_2-TPD and H_2-TPR experiments. Istadi[47g] and Wang[41] both showed that incorporating CaO into CeO_2 leads to the formation of basic sites, while CeO_2 alone displays little to no CO_2 sorption. TPR also revealed that catalysts with greater reducibility are more active for CO_2-OCM.[47g,h]

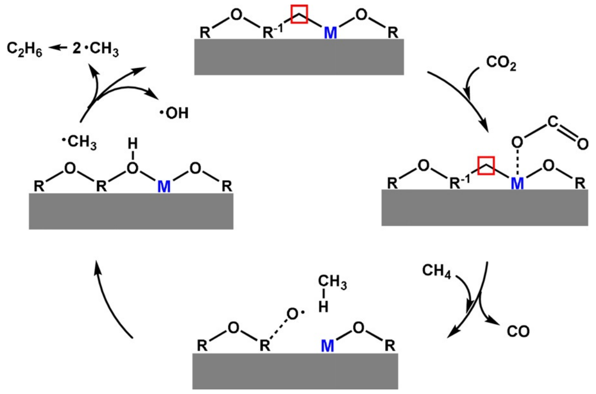

Figure 7. Proposed mechanism for C_2 hydrocarbon formation in CO_2-OCM over binary oxides, where R represents the redox active metal and M represents the basic metal.

Some research groups have also attempted to modify the synthetic method or morphology of CO_2-OCM catalysts in order to achieve enhanced performance. One group prepared CeO_2–ZnO nanocatalysts using a synthetic method combining homogeneous precipitation and micro-emulsions.[48] Although the C_2 selectivities were about the same, the nanocatalyst displayed significantly higher conversion and a 100°C lower light-off temperature than the traditionally prepared counterpart. An optimum C_2 yield of 4.8% was obtained. These researchers also found that the methane conversion rises with increasing fractal dimensions of the catalyst. Since fractal dimension is an indicator of surface defect density, this result suggests that more defects lead to greater active site density. Recent work by Zhang and co-workers also applied the polymerized complex (PC) synthesis method to NaCl/CaO catalysts for CO_2-OCM.[49] The catalyst synthesized by the PC method performed better than the same composition prepared by impregnation, with a maximum C_2 yield of 6.6% at 950°C.

To increase conversion and decrease reaction temperature, various non-traditional catalytic systems have also been proposed for CO_2-OCM. For example, Larkin and co-workers applied a plasma reactor system to achieve low-temperature CO_2-OCM in the absence of a catalyst.[50] Although, CH_4 conversions in excess of 20% were achieved, almost all the products were oxygenates such as formaldehyde. Another group achieved over 22% C_2 selectivity at a high 70.8% CH_4 conversion without a catalyst in a plasma reactor.[51] However, the reforming reaction still dominates, and the majority of the C_2 products are acetylene. Likewise, a catalytic system using a plasma reactor delivered 18.1% C_2 yield over La/Al_2O_3, but about 65% of the C_2 products were acetylene.[52]

CO_2-OCM reactor systems that use electric fields have also been studied. Oshima and co-workers examined Zr- and La-based catalysts for CO_2-OCM in the presence of an electric field.[53] The CH_4 conversion in the electric field at 423 K was significantly higher than in a conventional reactor at 1173 K. Nevertheless, the reaction heavily favored dry reforming to CO over the CH_4 coupling reaction. Another publication studied Ca-doped $LaAlO_3$ perovskites as CO_2-OCM catalysts in an electric field.[54] CH_4 conversions greater than 10% were achieved at low furnace temperatures of 348 K. The authors reported a maximum C_2 yield of 7.4%, the highest yield with CO_2 as an oxidant to date. However, the conversion, C_2 selectivity, and product breakdowns were unfortunately not provided under these conditions. A reaction rate order of 0.7 was also measured for CO_2, signifying that CO_2 may be involved in the rate-determining step.

Recently, photochemistry has also been explored as an unconventional method for CO_2-OCM catalysis. Although several publications have reported photocatalytic reactions between CH_4 and CO, most are focused on reforming and do not produce any C_2 products.[55] However, Li and co-workers reported significant ethylene yields over a 1 wt% Ag/TiO_2 catalyst at room temperature using a plasma-assisted photocatalytic system.[56] For example, under optimized conditions, the authors observed an ethylene yield rate of about

7 μmol g^{-1}/h × 10^2, compared to 12 μmol g^{-1}/h × 10^2 for CO. TPD experiments suggested that CO_2 adsorbs on TiO_2 while CH_4 adsorbs on the Ag sites. Additionally, isotope experiments using $^{13}CO_2$ showed that the produced CO derived from CO_2, while ethylene formed due to CH_4 coupling.

In summary, much like in O_2- or N_2O-OCM processes, oxygen species on the surface of the catalyst activate CH_4 to form methyl radicals when CO_2 is used as the oxidant. The CO_2 molecule provides one oxygen to form these sites via decomposition. Catalyst discovery has therefore focused on materials that are efficient at CO_2 adsorption and decomposition. Binary oxides with basic and redox components have been found to be most effective. In general, the addition of CO_2 in OCM has been shown to increase C_2 yield, which may reflect the formation of monatomic O* and/or reduced reaction exothermicity. However, far fewer comparative studies of O_2-OCM vis-a-vis CO_2-OCM have been performed than for N_2O-OCM, currently making a direct comparison between these oxidants difficult. The thermodynamic constraints on CO_2-OCM and competing dry reforming reaction have thus far limited the C_2 yield to mostly below 10% (see Table 2 for a summary of some of the best performing CO_2-OCM systems). Nevertheless, research into CO_2-OCM catalyst systems that are able to increase CH_4 conversion without sacrificing selectivity may provide valuable insight into how to effectively utilize these two greenhouse gases.

4. S_2 as an Oxidant (S_2-OCM)

4.1. Motivation

The elemental sulfur dimer (disulfur, S_2) was first investigated by Marks and Neurock as a soft oxidant for the OCM reaction in 2013.[57] S_2 is the primary sulfur allotrope above 700 °C and is isoelectronic with the O_2 molecule.[58] As such, an S_2-OCM process (SOCM; Table 1) could presumably proceed analogously to the O_2 system according to Equations (18)–(20), with total oxidation to CS_2 occurring via Equation (20).

$$2\,CH_4 + S_2 \rightarrow C_2H_4 + 2\,H_2S \tag{18}$$

$$2\,CH_4 + {}^{1}\!/_{2}\,S_2 \rightarrow C_2H_6 + H_2S \tag{19}$$

$$CH_4 + 2\,S_2 \rightarrow CS_2 + 2\,H_2S \tag{20}$$

Importantly, when O_2 is replaced with S_2, methane coupling remains thermodynamically feasible at 800 °C, and becomes more favorable at higher temperatures.[57] The feasibility of the reaction is also supported by studies of the partial oxidation of CH_4/H_2S mixtures with O_2 to produce ethylene, since H_2S and O_2 may react to produce S_2 at elevated temperatures.[59] Furthermore, as evident in Figure 8, the thermodynamic driving force for total oxidation is significantly reduced with S_2, suggesting that SOCM might afford higher ethylene selectivity.

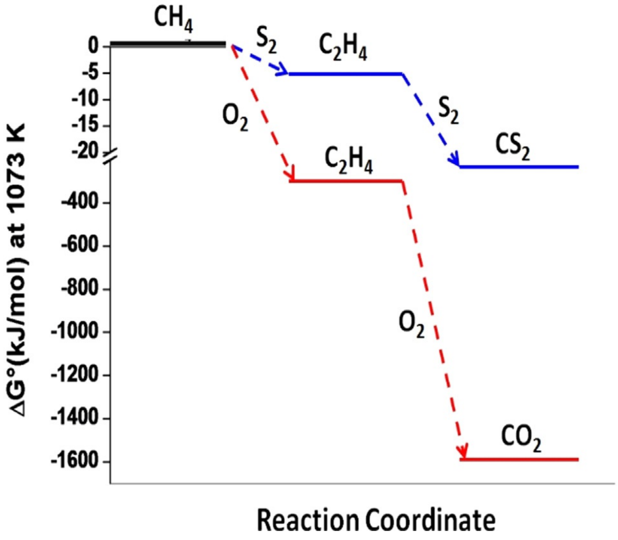

Figure 8. Reaction coordinate diagram comparing the thermodynamics of methane coupling to ethylene and total oxidation for S_2 (blue) and O_2 (red) at 1073 K (800 °C). Modified from ref. [57].

The reduced exothermicity may also alleviate heat management issues and local temperature hotspots that arise during the highly exothermic O_2-OCM process. Additionally, elemental sulfur is an abundant resource that is routinely processed at most plants that deal with hydrocarbons. For example, the H_2S byproduct of SOCM could be recycled back to elemental sulfur via the efficient, industrialized Claus process according to Equations (21) and (22).[60]

$$2\,H_2S + 3\,O_2 \rightarrow 2\,SO_2 + 2\,H_2O \tag{21}$$

$$2\,H_2S + SO_2 \rightarrow 3\,S + 2\,H_2O \tag{22}$$

Table 2: Reported CO_2-OCM catalyst systems with the highest C_2 yields to date.

Catalyst	Ref.	*T* [°C]	CH_4/CO_2 ratio	CH_4 Conversion [%]	C_2 Selectivity [%]	C_2 Yield [%]	$C_2H_4/C_2H_6/C_2H_2$
20% La_2O_3/ZnO	[47a]	850	2:1	3.1	90.6	2.8	0.7:1:0
CaO/Cr_2O_3	[45]	850	3:7	6.3	64	4.0	Not reported
Na_2WO_4Mn/SiO_2	[46]	820	1:.2	4.73	94.5	4.5	0.72:1:0
0.4 at% CaO/ZnO	[47d]	850	3:7	3.7	82	3.0	Not reported
Sr/MnO_2	[47e]	850	3:7	3.9	85	3.3	0.9:1:0
La_2O_3/Al_2O_3	[52]	Not reported—plasma	2:1	24.9	72.8	18.1	1:1:5.9
Mn-$SrCO_3$	[47f]	875	3:7	5.7	79.1	4.5	0.56:1:0
CeO_2/ZnO nano	[48]	825	1:2	5.73	83.6	4.8	Not reported
CaO-MnO/CeO_2	[47h]	850	1:2	5.1	75.6	3.9	0.79:1:0
CaO-NaCl/Na_2CO_3	[49]	950	1:1	18.9	34.9	6.6	1:0.34:0.15

4.2. SOCM Scope and Mechanism

Compared to N_2O- and CO_2-OCM, SOCM is relatively new, with the first report of the catalytic reaction appearing in 2013. The earliest two studies focused on catalyst discovery of the new reaction, with a more recent publication studying the mechanism in greater depth via both experiment and theory. This section will examine each of these literature reports chronologically.

In the original study of SOCM, four metal sulfide materials (PdS, MoS_2, TiS_2, RuS_2) displayed activity for the SOCM reaction.[57] Ethylene selectivities of up to 18% were achieved at a conversion of 15% over PdS, although the reaction temperature was quite high (1050 °C). Both conversion and selectivity could be improved by dispersing PdS onto a ZrO_2 support. DFT techniques were used to calculate the M−S bond energies of the various sulfide catalysts. A positive correlation was observed between methane C−H bond cleavage activation energy and the M−S bond strength, while the activation energy of :CH_2 methylene coupling to ethylene followed an opposite trend.

A follow-up study examined simple metal oxides as catalyst precursors for SOCM.[61] Since the oxides transform into the corresponding metal sulfides following pretreatment in an H_2S/S_2 mixture, the resulting metal sulfide was considered to be the active phase. Sulfided Fe_3O_4 achieves stable ethylene selectivity of about 30% at 950 °C and 5% conversion, a significant gain over the previous SOCM study at the same temperature ($<10\%$ ethylene over PdS at 950 °C). The addition of Pd to the Fe catalyst did not improve conversion or selectivity, signifying that precious metals are not required for high ethylene yields. Additionally, ethylene/ethane product ratios are notably higher than those reported for typical O_2-OCM.[5a,33]

Marks and Neurock more recently conducted a detailed mechanistic investigation of SOCM over sulfided Fe_3O_4 using combined theory and experiment.[62] Some key mechanistic differences are observed between the SOCM and OCM catalytic systems. For example, SOCM is found to be first order in both CH_4 and S_2, whereas O_2-OCM is first order in CH_4 and $^1/_2$ order in the oxidant over many catalysts, reflecting an O_2 dissociation step.[5a,63] DFT calculations on an FeS_2 surface corroborate the experimental results, and a complex reaction network (Figure 9) was proposed. Briefly, ethylene is suggested to form mainly over Fe−S surface sites via coupling of :CH_2 species (Figure 9, left). Dehydrogenation of ethane is also possible, although it is not the primary pathway (Figure 9, right). In contrast, adsorbed sulfur dimer (S_{dim}) sites catalyze the total oxidation of $CH_4 \rightarrow CS_2$ (Figure 9, center). Direct conversion of C_2 products to CS_2 is relatively minimal. These results stand in contrast to traditional OCM, where CO_x often arises from overoxidation of ethylene.[5]

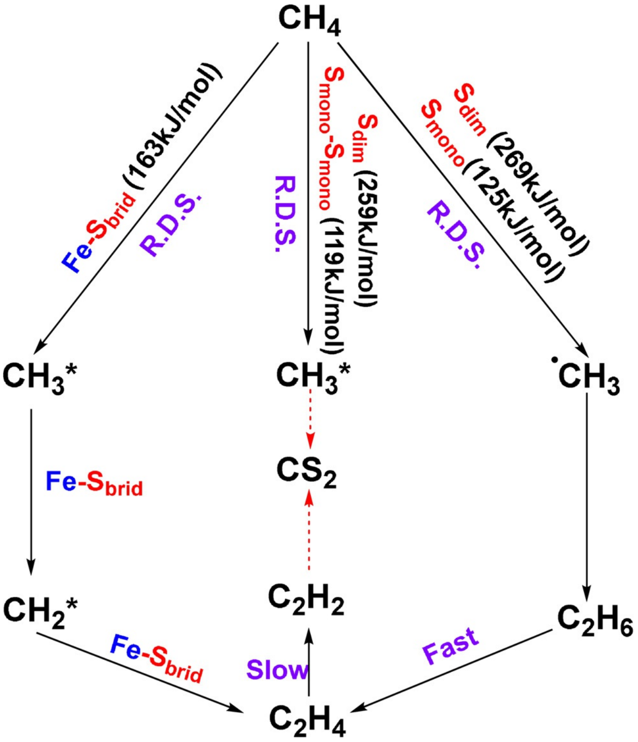

Figure 9. Reaction network of SOCM over a sulfided Fe_3O_4 catalyst surface at 865 °C. The numbers in brackets are the intrinsic activation barriers (kJ mol^{-1}) for C−H activation in methane over the respective surface sites. Modified from ref. [61].

To date, the C_2 yields obtained via SOCM remain below industrially attractive metrics. However, considering that only three investigations have been published on this reaction, there is a significant opportunity for future catalyst design and process engineering to improve upon the current metrics. Understandably, the SOCM mechanism over metal sulfides differs significantly from the OCM mechanism when O_2, N_2O, or CO_2 is the oxidant. Nevertheless, the unselective sulfur dimer sites that form CS_2 are reminiscent of peroxo species that are precursors to CO_x in O_2-OCM. The fact that monatomic sulfur species in Fe−S sites are selective for C_2 formation likewise mirrors the selectivity of O* sites in N_2O- and CO_2-OCM. These intriguing similarities highlight that far higher C_2 selectivities may be achievable in SOCM if the influence of the unselective sulfur dimer sites can be suppressed/modified. Additionally, the efficacy of S_2 as an oxidant has recently been expanded to the selective oxidative dehydrogenation of ethane and propane.[64] Future studies of these reactions may provide additional mechanistic understanding of SOCM.

5. Other Oxidants

While the oxidants that have been discussed in the previous sections represent the majority of publications in the field of alternative oxidants for OCM, it is conceivable that an oxidizing species could also be derived from a number of other gaseous species, such as NO, NO_2, SO_2, SO_3, O_3, or H_2O. A handful of studies in the 1980s and 1990s examined these potential oxidants. An early study by Asami and coworkers compared O_2, N_2O, and NO for gas-phase OCM in the absence of a catalyst.[65] The C_2 yield and selectivity were greater when using N_2O compared to O_2 under all the conditions tested. However, very little CH_4 conversion was observed when NO was employed, and carbon oxides were the primary products. The authors attributed these results to the known radical quenching nature of NO,[66] since the formation and coupling of methyl radicals is considered to be the route of C_2 formation.

The same group later studied OCM over a PbO/MgO catalyst using a variety of different oxidants.[13] Consistent with many of the reports discussed in Section 2, N_2O exhibited the best performance, with greater C_2 selectivity than O_2 at approximately equal CH_4 conversions. CO_2 as an oxidant also produced C_2 hydrocarbons, although the reaction rate was considerably slower. In contrast, NO and SO_2 formed CO_2 almost exclusively. Additionally, the PbO catalyst was sulfided to PbS under reaction conditions when SO_2 was employed, which led to catalyst deactivation with time on stream. Shepelev and co-workers also studied the effect of oxidant identity for OCM over zeolite catalysts.[67] Like the aforementioned Asami studies, N_2O-OCM displays promising activity and C_2 selectivity, while NO, NO_2, and SO_3 yield CO_2 as the only carbon-containing product.

Ozone (O_3) may potentially also act as an OCM oxidant. In particular, O_3 can activate methane at considerably lower temperatures (< 400 °C) than O_2 due to the capacity of O_3 to form radicals at these low temperatures.[68] Indeed, when O_3 was utilized as an oxidant for OCM over Li/MgO catalysts, methane conversion was observed at temperatures as low as 215 °C, whereas the same catalyst was inactive in methane conversion with O_2 until at least 400 °C.[19c,69] Although O_3 is a significantly more reactive oxidant than O_2 in the low temperature regime, the difference in activity becomes insignificant at higher temperatures. This effect likely reflects the fact that O_3 is unstable and decomposes to O_2 at elevated temperatures.[70] Furthermore, CO_2 and CO were the only carbon-containing products at low temperatures; C_2 products were not observed until the temperature reached 700 °C.

There has additionally been at least one publication using H_2O as an oxidant for OCM.[71] Unlike other systems, this oxidant is expected to produce H_2 as the main byproduct over metal oxide catalysts, according to Equations (23) and (24), where M is a metal site on the catalyst surface.

$$2\,CH_4 + MO \rightarrow C_2H_6 + H_2O + M \tag{23}$$

$$M + H_2O \rightarrow MO + 2\,H_2 \tag{24}$$

Steam reforming reactions of methane could also occur simultaneously, yielding CO and CO_2. A variety of Ti-containing perovskite oxide structures were examined for this reaction, and it was found that partially substituting Ti^{4+} with Mg^{2+} or Ca^{2+} shifts the product distribution from predominantely CO_x to C_2 products. However, the overall product yield remains very low (< 1 %). Nevertheless, various studies have reported improved activity and C_2 selectivity in O_2-OCM when H_2O is included as an additive, although the mechanism of such improvement is not agreed upon.[72] Thus, future research should address the mechanism of H_2O/O_2 cofeeding rather than H_2O as a sole oxidant.

OCM may also proceed in solid oxide membrane cells via electrochemically derived O^{2-} ions. The attraction of this approach is that by changing the electrode potential or current passing through the cell, the reaction rate and selectivity can also be influenced.[73] Early studies examined electrocatalytic OCM using yttria-stabilized zirconia (YSZ) as a catalyst and solid oxide oxygen source.[73,74] In general, electrochemically provided oxygen leads to higher C_2 yields compared to gas phase O_2, although the selectivity decreases with higher oxygen flux.[73,74b,c] More recently, Zhu and co-workers used perovskite anodes for electrocatalytic OCM and achieved a maximum C_2 selectivity of 82.2 %, a maximum CH_4 conversion of 40.5 %, and an C_2H_4/C_2H_6 ratio of 2.2:1.[75] Their system also coupled OCM with CO_2 electrolysis at the cathode. Thus, electrocatalytic OCM may be a promising method to produce C_2 compounds from methane while also utilizing greenhouse gases.

As can be inferred from the above discussion, although it is chemically feasible to use other oxygen-containing gases (NO, NO_2, SO_2, SO_3, O_3, and H_2O) as oxidants for OCM, these systems suffer from inherent low activity, preference for total oxidation, or catalyst deactivation. As such, most OCM research using alternative oxidants has focused on N_2O, CO_2, and S_2 oxidants that are able to provide appreciable C_2 yields and stable catalytic activity.

6. Summary and Outlook

To date, N_2O and CO_2 have received the most attention as alternative oxidants for OCM, with S_2 emerging as another contender in the recent decade. These oxidants are all milder compared to O_2, and as such are capable of yielding promising OCM selectivity to C_2 products. Additionally, for N_2O, CO_2, and S_2 OCM systems, the role of the oxidant in providing surface O or S species that activate CH_4 has been emphasized.

N_2O-OCM research has generally focused on basic alkaline earth and rare earth metal oxides. While these catalysts are also frequently employed for O_2-OCM, N_2O provides selective O* species that lead to enhanced C_2 selectivities compared to O_2, even over the same catalyst at isoconversion. Because N_2O-OCM is more selective, it may also facilitate heat management, since overoxidation is much more exothermic than the coupling reaction. However, the high cost of the oxidant challenges practical application, and the product stream also becomes diluted with N_2, which would likely necessitate additional separation steps. Nevertheless, N_2O-OCM is a useful process for studying the role of adsorbed oxygen species and highlights that high C_2 yields are possible if the presence of unselective oxygen species can be controlled. Moving forward, new process designs such as membrane reactors may also help mitigate some of the drawbacks of N_2O-OCM.

In contrast, many CO_2-OCM catalysts are binary oxides that contain a basic and a redox-active component. This combination permits both CO_2 adsorption onto the catalyst surface and activation to yield CO and O*. Compared to O_2-OCM, CO_2-OCM has generated lower C_2 yields, although the C_2 selectivities are comparable.[76] The main challenge is low CH_4 conversion due to the inherent thermodynamic stability of both reactants. Unconventional reactor setups such as plasma- or electric field-assisted CO_2-OCM may help miti-

Table 3: Summary of some important performance data of OCM with O_2, N_2O, CO_2, and S_2 oxidants.

Catalyst	Oxidant	Ref.	*T* [°C]	CH_4/oxidant ratio	CH_4 Conversion [%]	C_2 Selectivity [%]	C_2 Yield [%]
Na-W-Mn/SiO_2	O_2	[77a]	850	3:1	51.6	67.4	34.7
NaCl-MnNa_2WO_4/SiO_2	O_2	[77b]	750	5.7:3.5	55.0	56.8	31.2
La_2O_3-CeO_2 nano	O_2	[77c]	470	4:1	27.7	65	18.0
Li/MgO	O_2	[77d]	700	3:1	38.3	55	21.1
BSFCCl(0.04)	N_2O	[32]	850	2:5	66	46	30.4
CaO-Sm_2O_3	N_2O	[29b]	750	1:1	25.6	56.4	14.4
KCl-$SmCl_3$	N_2O	[20c]	750	1:2	14	82	11.5
CaO-NaCl/Na_2CO_3	CO_2	[49]	950	1:1	18.9	34.9	6.6
CeO_2/ZnO nano	CO_2	[48]	825	1:2	5.73	83.6	4.8
La_2O_3/Al_2O_3	CO_2	[52]	Not reported—plasma	2:1	24.9	72.8	18.1
FeS_x	S_2	[61]	950	7.5:1	5.4	32.9	2.0

gate this issue if more selective catalysts can be developed, although the industrial applicability of these unconventional processes may be limited. Another interesting possibility could be a combined process of O_2-OCM and CO_2-OCM, where both O_2 and CO_2 are cofed in order to achieve sufficient CH_4 conversion while also controlling the C_2 selectivity and reaction exothermicity.

In SOCM, transition metal sulfide surfaces have been shown to be the most promising catalysts, with both lattice sulfur and adsorbed sulfur acting as active sites. The use of sulfur may present unique challenges, such as the formation of CS_2. However, if the CS_2 formation can be suppressed, the principal sulfur byproduct, H_2S, could be recycled back to elemental sulfur via the efficient industrial Claus process. Additionally, the mechanistic studies of SOCM over sulfided Fe_3O_4 reveal that formation of CS_2 primarily occurs on different active sites than methane coupling reactions. As such, future research should focus on designing catalysts with fewer non-selective sulfur dimer sites and higher densities of M–S active sites. Alternate process designs such as chemical looping or site-specific poisoning may also be valuable in improving C_2 selectivity and provide more mechanistic insight on the role of the sulfide surface.

Thus far, replacing O_2 with alternative oxidants for OCM has proven to be an effective method for selectively producing C_2 hydrocarbons (ethane and ethylene). A summary of the key results for each oxidant, including O_2,[77] is provided in Table 3. The accomplished work has also provided valuable fundamental insight into how CH_4 interacts with various oxidants over oxide and sulfide catalyst surfaces. Moving forward, future research in X-OCM is needed to design catalysts and reactor systems that facilitate activation of the methane C–H bond without simultaneous CH_4 combustion or further activation of the weaker C–H bonds of C_2 products.

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Conflict of interest

The authors declare no conflict of interest.

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