



# Oxidative coupling of methane over mixed metal oxide catalysts: Steady state multiplicity and catalyst durability

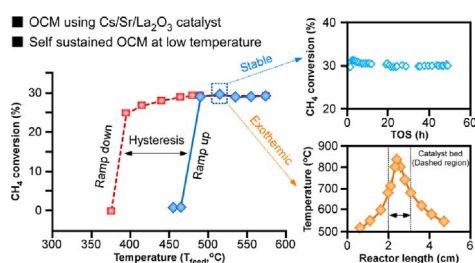


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## GRAPHICAL ABSTRACT



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## ABSTRACT

Exothermic heat effects are a crucial factor in determining the performance and stability of catalysts for the oxidative coupling of methane (OCM). Fixed bed temperature rise, steady state multiplicity, and catalyst durability are investigated over a range of feed conditions for the mixed metal oxides Cs/Sr/MgO, Cs/Ba/MgO, Cs/Sr/La<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>WO<sub>4</sub>-Mn/SiO<sub>2</sub>. A comparison with previous studies on doped metal oxides catalysts for OCM clearly indicates that doping not only improves the performance but also significantly improves the catalyst stability. We experimentally demonstrate for the first time hysteresis behavior for Cs/Sr/La<sub>2</sub>O<sub>3</sub> powder catalyst. Our results show that the catalyst stability depends on the magnitude of temperature rise in the catalyst bed. At a lower space velocity of 3,600 cc/h/g, the catalysts exhibit moderate temperature rise (< 50 °C) at complete O<sub>2</sub> conversion and sustained activity for extended time-on-stream (50–72 h). The performance of Cs/Sr/MgO and Cs/Ba/MgO are comparable to Na<sub>2</sub>WO<sub>4</sub>-Mn/SiO<sub>2</sub> (~19% C<sub>2+</sub> yield). While Cs/Sr/La<sub>2</sub>O<sub>3</sub> activates at lower temperature, its maximum C<sub>2+</sub> yield (~14%) is lower. At a higher space velocity of 14,400 cc/h/g, a significant temperature rise of ~300 °C and ignition-extinction behavior is encountered. Under these demanding conditions, improved OCM performance is observed for Na<sub>2</sub>WO<sub>4</sub>-Mn/SiO<sub>2</sub> (35% methane conversion, C<sub>2+</sub> selectivity 60%) but the catalyst deactivates due to the high bed temperature (930 °C). In comparison, methane conversion of ~25% and C<sub>2+</sub> selectivity of ~38% is observed for Cs/Sr/La<sub>2</sub>O<sub>3</sub> at a feed temperature of 395 °C. Despite a bed temperature of 830 °C, the Cs/Sr/La<sub>2</sub>O<sub>3</sub> catalyst is stable for 50 h. The findings show the importance of heat effects in both promoting OCM catalyst performance and leading to deleterious catalyst deactivation.

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## 1. Introduction

With the increased availability of recoverable natural gas (NG) reserves there is renewed interest in NG conversion to value-added chemicals. Oxidative coupling of methane (OCM), the main constituent of NG, provides an alternate route to the commodity chemical ethylene. Currently, ethylene is synthesized from steam cracking (dehydrogenation) of ethane, the second most abundant hydrocarbon in natural gas. In contrast to the thermodynamically-limited ethane cracking, OCM is highly exothermic and irreversible at moderate pressures. Very high temperatures are required to activate methane, which exacerbates its selective conversion to ethylene owing to high reactivity of the higher molecular weight product hydrocarbons. To date, a commercially-viable OCM process remains elusive.

Since the pioneering work of Keller and Bhasin [1], extensive research has been conducted on OCM to improve methane conversion and  $C_{2+}$  selectivity. A depiction of the global reaction network of the OCM reaction system is shown as Scheme 1. The coupling route to ethylene is particularly challenging because, as stated above, the desired products of coupling ( $C_{2+}$ ) are more reactive at the temperatures needed to activate methane. The reaction system involves a combination of heterogeneous and homogeneous reactions and is noted for significant parametric sensitivity, particularly of temperature. Carbon oxides may be formed directly from methane (in parallel with the desired reaction) as well as from  $C_2$  products (consecutive to the desired reaction). The complete and partial oxidation of methane are both exothermic reactions, with the former being a more thermodynamically favored reaction pathway. Finally, the desired product selectivity suffers from consecutive combustion of hydrocarbon products. Collectively, these factors highlight the challenges of the OCM reaction system.

Prior works in this field have explored the influence of catalyst composition [2–4], parametric sensitivity [5–7], and the optimization of reaction conditions [8]. OCM is primarily carried out in a packed bed reactor, although other types of reactors have been considered [9,10]. Most studies have focused on increasing the rate of OCM and the selectivity of  $C_{2+}$  hydrocarbons. The  $C_{2+}$  yields are generally low; to date under stable reaction conditions, the highest reported yield is 26% [11].

The most frequently studied OCM catalysts have been alkali-promoted alkaline earth metal oxides, transition metal oxides, and rare earth metal oxides. Basic oxides in pure or doped forms have been extensively studied for OCM [5,12–14]. A statistical analysis was conducted by Kondratenko et al. [15] of three-component catalysts for OCM comprising alkali, alkaline earth, and rare earth metal oxides in order to extract information relevant for design of potential catalytic materials with improved performance. Based on the synergistic effect of multicomponent materials it has been predicted that a high performance OCM catalyst should consist of a strongly basic oxide (Mg, La) with dopants having positive effects on both selectivity (Cs, Na, Sr, Ba) and catalyst activity (Mn, W, Cl).

It has been shown that the addition of certain alkali and alkaline earth metal oxides to MgO and  $La_2O_3$  catalysts can improve their activity and selectivity [16–19]. Basicity and high oxygen ion conductivity (electrical conductivity) are the main factors that promote OCM on these catalysts. Among the tested MgO-based catalysts doped with different alkali metals (Li, Na, Cs, Rb), Li/MgO is considered the most effective, but suffers from loss of metal ions at relevant temperatures [20]. For alkaline earth metal oxides several researchers have reported a direct relationship between basicity and  $C_2$  selectivity [21,22]. Notably,  $C_2$  selectivity increases with increasing basicity of the metal oxide; i.e.,  $BeO < MgO < CaO < SrO$ . Likewise, an increase in basicity also leads to an increased interaction of oxide with  $CO_2$  promoting the formation of more stable carbonates.

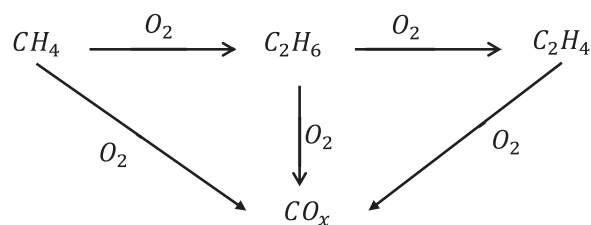
Rare earth oxides are relatively more active for OCM than other basic oxides, and allow  $C_{2+}$  hydrocarbons to be produced at much lower temperature [18]. Choudhary et al. [17] observed that among all strontium-promoted rare earth oxides,  $La_2O_3$  showed the best

performance for OCM owing to incorporation of  $Sr^{2+}$  in the bulk structure of lanthanum oxide. Cong et al. [16] suggested that Sr dopant provides a highly active oxygen-radical site and strengthens the basicity of non-radical acid-base pair sites which leads to lower  $CH_4$  activation energies and  $CH_3$  adsorption energies. As a result, nonselective surface reaction of methyl radicals and  $C_{2+}$  hydrocarbons with weakly adsorbed oxygen species is suppressed. Although several studies have shown improved performance with doped MgO and  $La_2O_3$  catalysts, there have only been few studies [23–25] conducted on long-term stability testing of these catalysts (except the extensively studied Li/MgO catalyst).

Exothermic reactions carried out in fixed-bed reactors lead to the formation of elevated temperature zones with the potential for hot spots that can lead to undesired reactor runaways and/or catalyst deactivation. The temperature rise depends on many factors, with the notable ones being the catalytic activity, limiting reactant feed concentration (usually  $O_2$ ),  $CH_4:O_2$  ratio, heat of reaction, feed rate, heat exchange with the surroundings, and extent of feed gas dilution. The temperature rise naturally affects catalyst performance (e.g., conversion and product distribution). With the adiabatic temperature rise for the OCM reaction system as high as several hundred °C (depending on reaction conditions), particular care must be taken to regulate the temperature of the reaction. Most of the reactor types reported in the literature for OCM are neither isothermal nor adiabatic; therefore, the hot spot temperature rise varies over a wide range (100–400 °C), as evidenced by the wide range of reported values listed in Table 1. Corresponding estimated values are much higher (i.e., 470–730 °C), underscoring the variable heat exchange features of bench flow reactors.

Several studies have examined various aspects of thermal effects during OCM. For instance, Kooh et al. [27] suggested that operating the reactor under reaction conditions where there is a large differential between the catalyst bed hot spot temperature and furnace temperature improves  $C_{2+}$  yield. Malekzadeh et al. [32] observed that hot spots can sustain reaction at lower feed temperatures (e.g., they reported  $C_{2+}$  yield of 14% at 370 °C for  $Na_2WO_4$ -Mn/SiO<sub>2</sub> catalyst). Wang et al. [26] observed that hot zones form due to the highly exothermic formation of  $CO_x$ , which provides heat for the ignition of OCM reactions. The thermal effect was believed to be responsible for OCM reaction taking place as low as 320 °C over  $BaCO_3/La_2O_3$  catalyst. Indeed, Wang et al. [29] reported that the  $SrCO_3/Sm_2O_3$  catalyst could sustain autothermal reaction at a furnace temperature as low as 200 °C for about 82 h before the catalyst began to deactivate. For a  $La_2O_3$ -CeO<sub>2</sub> nanofiber catalyst, Noon et al. [28] observed a hysteresis behavior and during reactor cool down the  $C_2$  selectivity was maintained at a feed temperature as low as 300 °C, albeit at the expense of reduced methane conversion. For  $Na_2WO_4$ -Mn/SiO<sub>2</sub>, Lee et al. [34] observed hysteresis behavior with ignition occurring at 780 °C and extinction at ~660 °C furnace temperature. In a recent study, Sarsani et al. [35] reported hysteresis for La-Ce oxide catalyst and noted that if the catalyst activity is high enough it is possible to operate OCM reactor autothermally at ambient feed temperature. In the same study they were not able to observe hysteresis behavior for  $Na_2WO_4$ -Mn/SiO<sub>2</sub> catalyst due to catalyst deactivation.

The main objective of this study is to characterize and understand hot zone formation and associated hysteresis over a range of conditions, and their effects on OCM catalyst performance including oxygen



Scheme 1. OCM reaction network.

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