

EXPLORING STRATEGIES TO IMPROVE YIELDS OF OXIDATIVE COUPLING OF METHANE IN A CHEMICAL LOOPING SYSTEM

PRIMARY AUTHOR

Deven Baser
baser.3@osu.edu

ADVISOR

Liang-Shih Fan, PhD
Distinguished University Professor
fan.1@osu.edu

Abstract

Since the shale gas boom, methane, a major component of shale gas, is an important source of energy in USA. Methane is largely viewed as a fuel, which is combusted in air to produce CO₂, H₂O, and energy. However, there exist several technologies that utilize methane as a hydrocarbon precursor to produce chemical products. One such technology is chemical looping oxidative coupling of methane (OCM), for directly converting methane into higher hydrocarbons such as ethylene. Traditionally, a catalytic OCM system is employed for this reaction, where methane and molecular oxygen are co-fed over a catalyst bed. The chemical looping method utilizes the lattice oxygen in a catalytic oxygen carrier (COC) for methane oxidation. This novel process eliminates the inefficiencies associated with molecular oxygen, theoretically improving the performance over the catalytic system. This study highlights the formation mechanism of oxygen vacancies on the COC and its role in chemical looping OCM.

Motivation

USA in the past decade experienced a ‘shale gas boom’ due to the improvement in fracking technologies.¹ Based on the natural gas reserves, it is estimated that USA will become a net exporter of natural gas before the year 2020.² Natural gas or shale gas is a major source of methane and has been known to be a relatively clean burning fuel.³ This abundance has inspired research in the direction of viewing methane as a chemical precursor instead of a fuel, for its value-addition to chemicals and fuels.⁴

Methane activation, however, is not trivial due to the high stability of this compound. Lack of a dipole moment due to its symmetry or a functional group that would provide a pathway for chemical reactions leads to this high stability. Thus, direct activation of methane has been a topic of research for several decades.^{5,6} Conventionally, this has been addressed by upgrading methane through indirect processes. These technologies convert methane to syngas which is then sent to a Fisher - Tropsch reactor to convert it to liquid fuels or petrochemicals. Alternatively, there exist direct processes for valorizing methane. These direct processes reduce the number of processing steps as compared to the indirect process and thus are economically more attractive.⁷ Of the several direct methane conversion techniques that have been investigated over the past decade, oxidative coupling of methane (OCM) has the highest estimated kinetic yield.⁸

Oxidative Coupling of Methane

OCM was first investigated by Keller and Bashin in 1982, where they coined the term oxidative dimerization of methane.⁹ A typical OCM reaction has two methane molecules reacting with an oxygen species to couple and form higher hydrocarbons such as ethane and ethylene with water as the co-product. Although, the coupling reaction is thermodynamically favorable, partial and

complete combustion of methane are thermodynamically more favorable. These combustion products (CO, CO₂) constitute the un-desired products which limit the yield of hydrocarbon products. These reactions are depicted in Figure 1, where the two modes of OCM operation are shown, viz. the catalytic system (co-feed mode) and the chemical looping system (redox mode). The co-feed mode has methane and molecular oxygen co-fed over a catalyst bed, whereas the redox mode has a metal oxide reacting with methane. The reduced metal oxide from this reaction is regenerated in a different reactor with air as depicted in Figure 1(b).

The chemical looping mode breaks the overall reactions into two steps, thus eliminating the contact between molecular oxygen and methane. There is a low energy barrier for molecular oxygen to react with methane and form combustion products. These gas phase reactions are believed to be the major reason for the unselective product formation for OCM in co-feed mode.¹⁰ Hence, theoretically the chemical looping system can achieve higher yields than the traditional co-feed method. As an example, sodium-tungsten-manganese-supported-silica catalyst (Na-W-Mn/SiO₂), is reported as one of the most active co-feed OCM catalyst with yields ranging from 16% to 30.4%.^{11,12} The higher yields are often reported with a degradation of stability in performance of the catalyst. Thus, regeneration of such catalysts becomes necessary, and may not be suitable for a commercial application. Chemical looping OCM over a proprietary metal oxide has shown yields of 23.2% with hydrocarbons up to C₇S on a Mg₆MnO₈ based metal oxide.¹³ The higher hydrocarbons seen are unusual and are never observed in the co-feed mode. The higher hydrocarbons are therefore attributed to the absence of molecular oxygen with the hydrocarbon products.

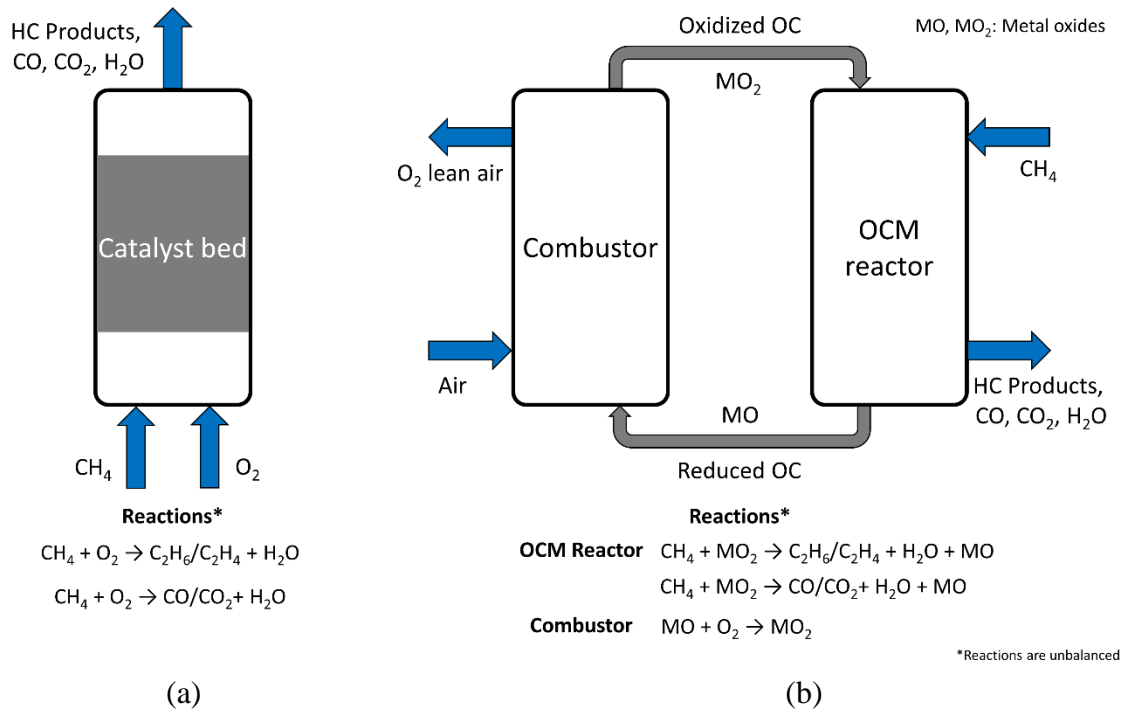


Figure 1. OCM reaction carried out in two separate modes (a) catalytic system (cofeed mode) (b) chemical looping OCM (redox mode)

It is projected that the industrial OCM process should have a C₂ yield between 25-40% and C₂ selectivity exceeding 80% in order to be profitable. These studies have been done in early 1990 over the co-feed system which involves the use of energy and cost intensive air separation unit (ASU). The ASU accounts for 14% of the capital cost of the plant for methane to olefins via OCM.^{14,15} A more recent co-feed study indicated that capital investment of the plant and the large requirement of electricity has the most significant effect on the final cost of ethylene.¹⁶

Importantly, the OCM reaction system has a challenging hurdle in the form of a trade-off relationship between achieving high methane conversion and high C₂ or higher hydrocarbon selectivity. This trade-off is seen in both the co-feed and the chemical looping mode of operation. During high methane conversion, partial oxidation of methane thermodynamically favors

undesirable and competing combustion products, which reduces the C₂ selectivity. The differences between co-feed and chemical looping modes are important to examine. The insights and understandings from the extensively studied co-feed mode can aid the chemical looping mode in achieving higher activity towards OCM. Additionally, the mechanisms of OCM over co-feed and chemical looping redox have significant differences. The co-feed mechanism has been thoroughly investigated, but the same is not true for chemical looping or redox mechanism. The co-feed mechanism involves reactions in the gas phase over an unchanging catalyst surface. The chemical looping reduction mechanism involves an additional parameter, where the metal oxide surface is constantly generating oxygen vacancies which interact in different ways with the gaseous species.¹⁷ These different facets of both the modes will help in rational metal oxide development so as to improve the yields of chemical looping OCM.

Chemical looping process

Chemical looping systems have been widely established for gas solid systems in both a fluidized bed and a moving bed scheme.^{7,18} Typically, a chemical looping system consists of at least two reactors with an intermediate carrier to transfer the reactive specie from one reactor to the other. For systems involving some form of oxidation, metal oxides are used as the intermediate carriers, where oxygen transfer between the two reactors takes place. The technology has been demonstrated for combustion and gasification applications with several different types of carbonaceous fuels. Figure 2 gives a general schematic for a catalytic system compared to a chemical looping system.

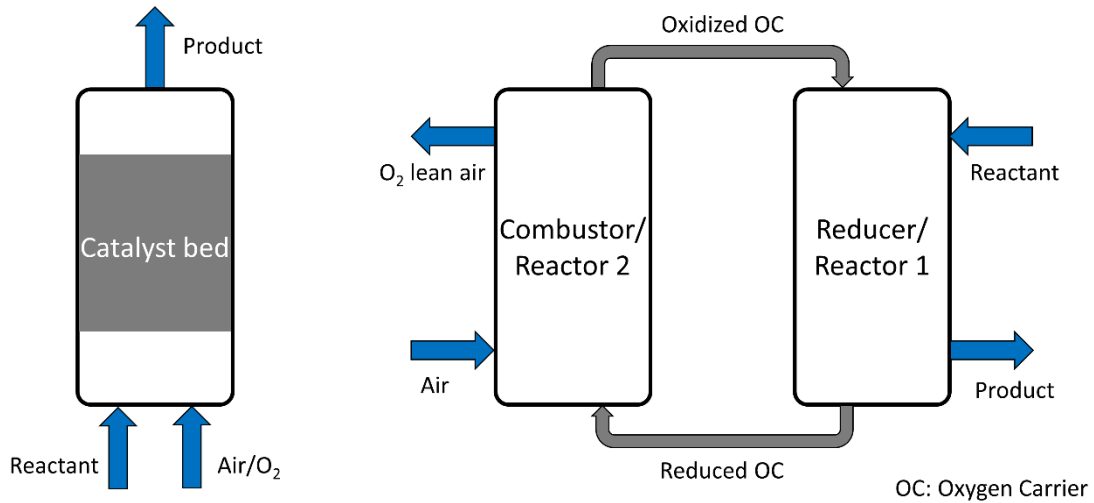


Figure 2. A generalized block diagram for a catalytic system versus the same system visualized in a chemical looping system for oxidation reactions.

The catalytic system is either operated in a fixed bed mode or a fluidized bed mode, with all the reactants fed into the reactor. The catalyst lowers the activation energy towards the desired reaction to maximize the selectivity towards the desired products. A big obstacle of a catalytic system is the deactivation of the catalyst over time. Fluid catalytic cracking (FCC) is one of the most important catalytic process to produce gasoline, olefinic gases etc.^{19,20} This process requires a constant regeneration cycle, essentially operating in a loop to burn off the carbon deposited on the catalyst. Catalysts in selective catalytic reduction (SCR) for NO_x removal from power plants also undergo deactivation due to SO₂ and SO₃.²¹ Another obstacle that catalytic fixed bed reactors encounter is heat management. Typically, a fluidized bed is used in that case, but such a system can lower the selectivity towards the desired products due to back mixing caused in the reactor. A chemical looping system could be a possible alternative technology, which could solve or control these issues.

Advantages of chemical looping system over a catalytic system

As depicted in Figure 2, the chemical looping process prevents the molecular oxygen from reacting directly with the gaseous reactant. This provides some additional degrees of freedom for operating a given oxidation reaction. These degrees of freedom correspond to the thermodynamics and kinetics of the metal oxide reacting with the precursor, temperatures of operation for both the reactors, inherent separation of the unreacted precursors. A moving bed chemical looping system has added advantage of tuning the residence times of the solid and gas reactants while running the system at the thermodynamic limits. A combination of these benefits become evident in partial oxidation of methane to syngas.

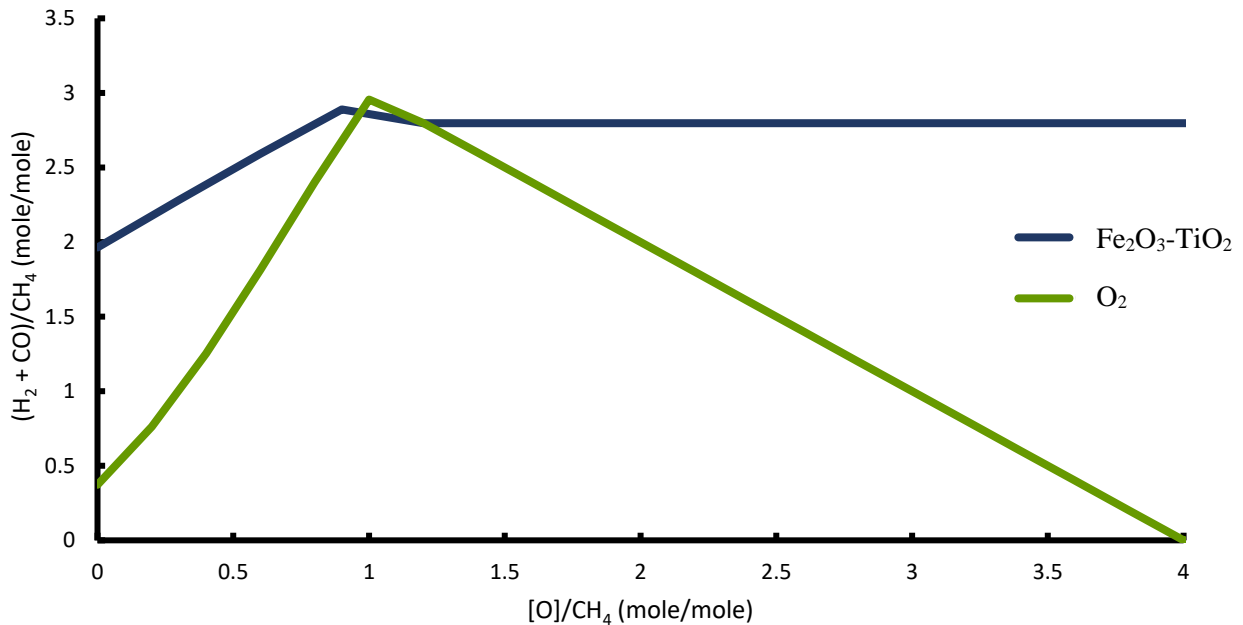


Figure 3. Comparison of molecular O_2 and iron titanium oxide particle syngas yields at 1000°C and 1 atm.

Figure 3 demonstrates the comparison between molecular oxygen partial oxidation of methane versus iron titanium chemical looping partial oxidation. For higher $[\text{O}]/\text{CH}_4$ ratios, it is

thermodynamically more favorable for the combustion products (CO_2 and H_2O) to form which are undesired. So, to get a high syngas yield, $[\text{O}]/\text{CH}_4$ ratio is a crucial parameter, as evident from Figure 3. For molecular oxygen, the maximum syngas yield is obtained at $[\text{O}]/\text{CH}_4$ ratio of 1, with a sharp peak at the optimum. The chemical looping mode however provides flexibility by widening the operating window to 1-4 for $[\text{O}]/\text{CH}_4$ ratio.

These additional degrees of freedom would theoretically improve selective oxidation reactions such as OCM. Thus, the chemical looping approach helps in tackling the issues with catalytic systems, by incorporating specific aspects of a catalyst into the reaction scheme and possibly achieving better performance than the traditional system.

Objectives

The chemical looping OCM process requires a selective metal oxide which limits the amount of oxygen donation, to prevent over-oxidation. The selective reactions being kinetically limited, the metal oxide needs to have catalytic sites, which aid the activity towards OCM. Such an oxygen carrier with catalytic sites have been termed as catalytic oxygen carriers (COC). The main goal of this study would be to synthesize a COC which would have the following characteristics:

1. A COC which gives a yield greater than 30% for C_2 and higher hydrocarbons, with selectivity towards C_2 and higher hydrocarbons greater than 70%.
2. A COC which shows consistent activity towards OCM with multiple redox cycles. In other words, a COC should not degrade over multiple redox cycles.

This was achieved through rational modification of the dopant induced oxygen vacancies in the COC. Experimental and computational tools have been applied to get a deeper understanding into the mechanism of the chemical looping OCM.

Experimental and computational setup

Mg₆MnO₈ was the base COC which was used for this study and was synthesized using physical mixing of MgO and MnO₂ in stoichiometric quantities and calcining it to 950°C under air. The performance of the base COC was compared against a Li doped Mg₆MnO₈, which was synthesized in a similar manner. The hydrocarbon selectivity and the methane conversion of the two COCs were investigated in a fixed bed reactor at 850°C and 1 atm.¹⁷ The reactions were also studied using density functional theory calculations using the Vienna Ab Initio Simulation Package (VASP). Details of the reactor and the computational parameters have been published elsewhere.^{13,17}

Results and Discussion

The synthesized undoped Mg₆MnO₈ and Li doped Mg₆MnO₈ were characterized using X-ray diffraction (XRD) and X-ray spectroscopy (XPS) to confirm the solid phase formation. The higher hydrocarbon selectivity, combustion product selectivity and methane conversion was investigated for both the samples in a fixed bed reactor.¹⁷ These were observed over the 25s reduction time with methane sent into the reactor over the oxidized COC. As evident from Figure 4, the C₂ selectivity of the Li-doped COC is higher than that of the undoped COC across the entire reaction time. The maximum improvement of the C₂ selectivity of 50.4% was seen at 22.5s prior to the advent of carbon deposition.

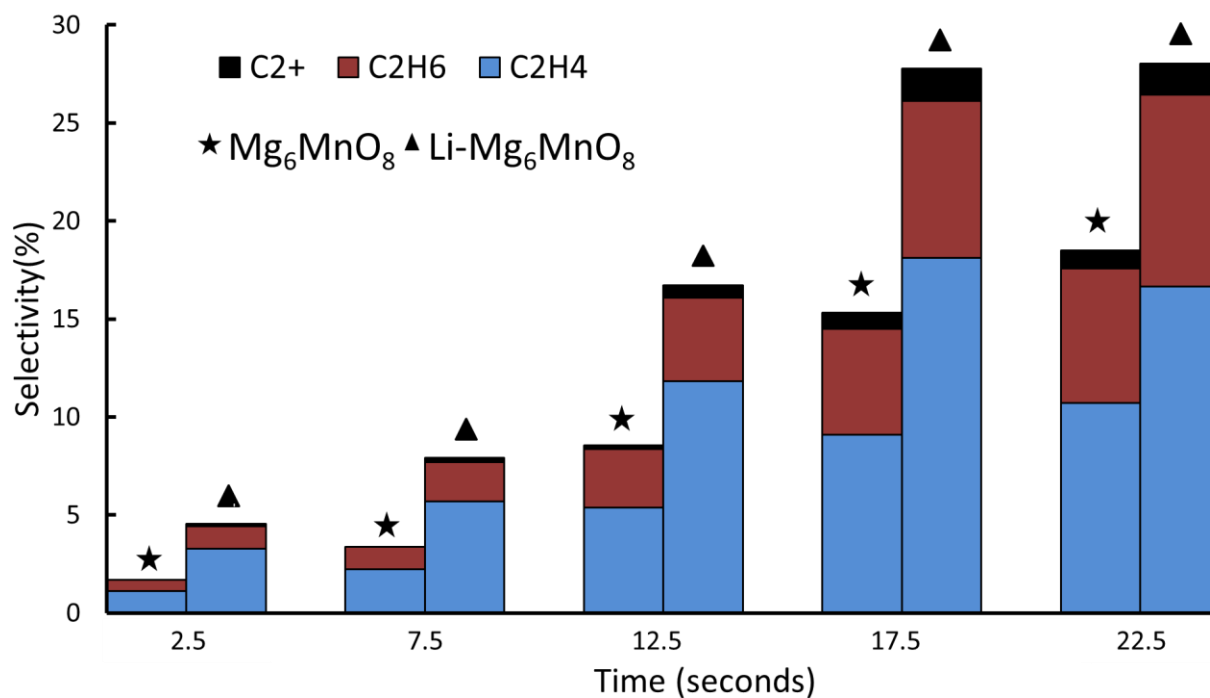


Figure 4. Selectivity of higher hydrocarbon products (C₂H₆, C₂H₄, C₂+) with reduction time over Mg₆MnO₈ and Li-Mg₆MnO₈ COCs.

With the help of the experimental and computational results, a mechanism was developed on a Mg₆MnO₈ system. An overview of this mechanism is outlined in Figure 5. As seen from the figure, methane first adsorbs on the surface after which the adsorbed molecule dissociates in a homolytic fashion to CH₃• and H•. This CH₃• can either desorb to the gas phase or can dissociate further into CH₂•. The desorption would be favored over the dissociation as two CH₃• would form C₂H₆, which is the desired product for OCM. The H-abstraction or dissociation would lead to eventual formation of CO_x products. The Li doping helps increase the activation energy barrier for this dissociation, thus giving a higher selectivity as compared to the undoped Mg₆MnO₈. It is important to note that CH₄ conversion is driven by the adsorbed methane activation to CH₃• (Step 2 to Step 3) as this elementary reaction has the highest activation barrier in the overall mechanism. The C₂ selectivity is determined by the binding energy for CH₃• to the dopant induced oxygen vacancy.

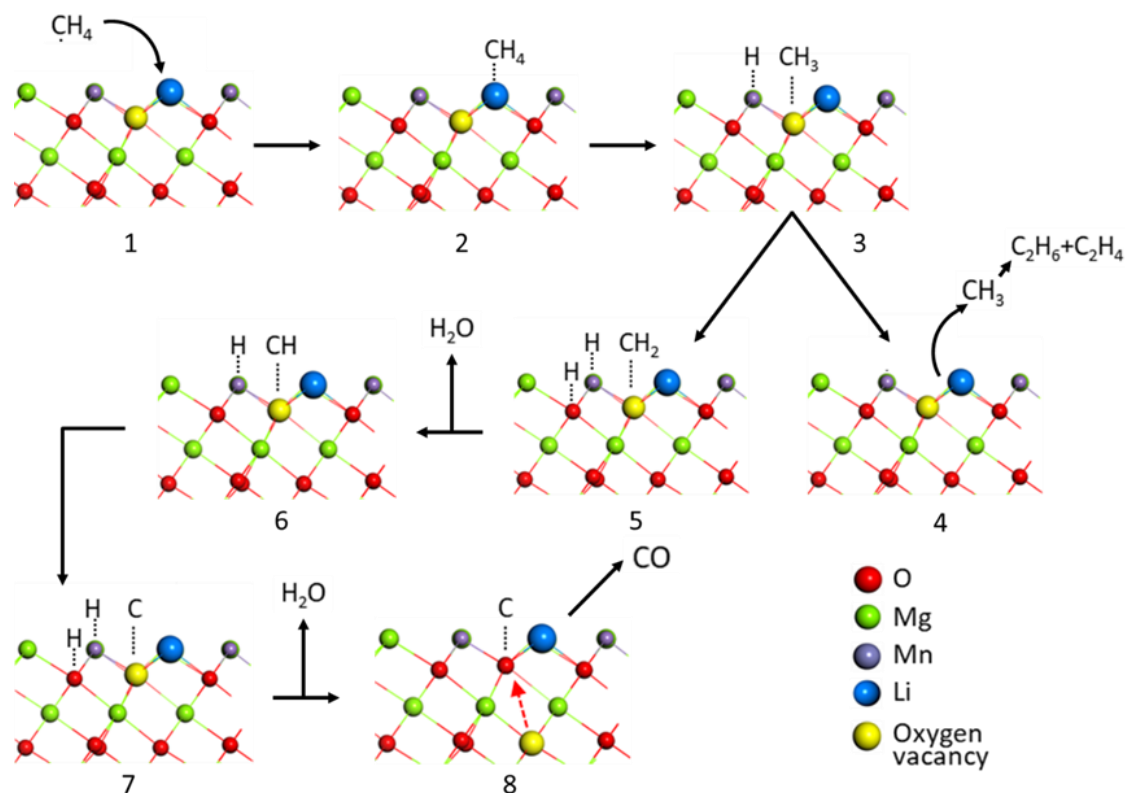


Figure 5. Proposed mechanism for CH₄ activation and dehydrogenation towards the formation C₂ hydrocarbon in chemical looping OCM

With the help of this guideline, several favourable dopants can be screened to get higher overall yield on the Mg₆MnO₈ COC.

Conclusions

Catalysis research focuses on understanding the mechanism of a particular process and reducing the activation energy of the rate determining step with the development of better catalysts. The chemical looping alternative provides a different approach, where it gives additional parameters or degrees of freedom to work with. To utilize these benefits, a chemical looping OCM system has been proposed and investigated. This study provides insight into key parameters that define the selectivity of higher hydrocarbons such as C₂H₄ and C₂H₆ in a chemical looping OCM system.

The dopant induced oxygen vacancy can modify the reaction pathway to favor the hydrocarbon products, thus ensuring higher hydrocarbon yields. Further understanding these oxygen vacancies can pave the way for the rational design of a highly active COC.

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