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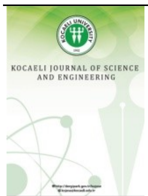

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Promising La_2O_3 Nanocatalysts for Low-Temperature Oxidative Coupling of Methane Reaction: A Short Review

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Abstract

This paper reviews the recent literature on La_2O_3 catalysts for the oxidative coupling of methane (OCM), which aims at ethylene production. The following subjects are discussed: (a) the main properties affecting the reaction mechanism such as oxygen vacancy, acid-base property, temperature, and morphology (b) prospects of nano-scale catalysts to improve the performance of the OCM process (c) the contribution of La_2O_3 nanocatalysts to the formation of ethane and ethylene (C_2 hydrocarbon) during the oxidative coupling of methane.

1. Introduction

Coal, then petroleum, and finally natural gas, have been utilized in energy generation and commodity chemical manufacture for the past two centuries. Due to strict environmental regulations and limited natural carbon reserves, the emergence of alternative processes based on renewable and/or "greener" technologies has been given priority for future industries [1]. With a continuous increase in natural gas resources (approximately 6×10^{12} cubic meters), chemical and fuel synthesis using methane as a feedstock has gotten a lot of attention from the petrochemical and energy industries throughout the world, in order to reduce our reliance on diminishing oil resources. Especially, the manufacturing of short-chain olefins, which are important building blocks in the modern chemical industry, immediately requires a synthesis method change from naphtha to methane. Due to the shortage of fossil fuel resources, attention has turned to alternate technologies that use more easily accessible feedstocks. Because methane is the primary component of natural gas, methane is a promising feedstock alternative for short-chain olefins. [2-7]. Ethylene is a large-scale manufactured chemical with yearly global sales above 140×10^6 tons and a 3.5% annual growth rate [2,7-8]. Nowadays, ethylene is produced by the steam cracking method, which cracks naphtha to olefins and other hydrocarbons [3-5]. In this process, methane is industrially converted to olefins in an indirect way, in which methane first decomposes into the syngas (i.e., CO and H_2) via the catalytic steam or auto thermal reforming at temperatures above 700 °C, then syngas is converted to methanol and finally to olefins. However, the syngas pathway is energy inefficient, and such an indirect method results in low atom usage efficiency. Therefore, the direct conversion of methane to olefins is a highly desirable method, and done many studies to reach this aim. [7,9]. OCM makes it possible for a direct route from feedstock such as natural gas, biogas, or shale gas into value-added chemicals, avoiding the intermediate production of syngas [7,10]. The design of catalysts with high activity and

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selectivity is vital for improving the performance of the OCM reaction [10]. Although much research has been done on OCM for over 30 years due to the opportunity to lower ethylene production costs, unfortunately, these studies have not resulted in a suitable catalyst with the required performance for commercialization. Although these catalysts had promising performance and selectivity, they were limited by their very high operating temperature, low activity, and short lifetime (a few hours to a few days).

The overall yield must be at least 30% for economic efficiency. The necessity to solve these issues has led to the creation of new systems and OCM catalyst designs. Because high temperatures lead to decreasing selectivities of C_2 products, the development of novel catalysts that can run at low temperatures is critical to the economic viability of OCM. Low-temperature oxidative coupling of methane (LT-OCM) allows producing ethylene with an alternative process that converts methane (natural gas) to ethylene in a one-step operation. Siluria Technologies Inc. (shortly Siluria) applied a combination of innovations in the catalyst area to develop unique catalysts. The Company began running a factory in 2015 to demonstrate the low-temperature OCM reaction's industrial application. The factory has been designed to produce at least 350 tons of ethylene per year. Unfortunately, no information about the catalyst utilized is available. Siluria employs nanowire catalysts that operate at lower temperatures than traditional materials, according to multiple patents [1]. Siluria's OCM catalysts work at much lower temperatures (several hundreds of degrees lower) and operating pressures (5-10 atmospheres), and under these conditions, they show high performance and standard lifetimes (years) [11,12].

Recently, developments have had in heterogeneous catalysts with controlled morphologies are expected to improve the activity/selectivity and stability of the OCM catalysts. This review covers topics interested in the La_2O_3 catalysts strategies adopted for enhancement of methane conversion, increasing ethylene selectivity, and decreasing the reaction temperatures.

2. Ethylene Formation Mechanism During Oxidative Coupling of Methane Reaction

CH_4 is transformed to ethane, ethylene, and higher hydrocarbons (C_{2+} hydrocarbons) in a single step under OCM conditions, usually in the presence of oxygen (O_2) and a suitable catalyst [12]. The OCM reaction generally involves the formation of methyl radicals ($CH_3{\cdot}$) via hydrogen extraction from methane by available active oxygen species on the surface of the oxide catalyst. The purpose of the OCM catalysts is to produce methyl radicals ($CH_3{\cdot}$) while avoiding deep oxidation (the formation of CO, CO_2, and H_2O) [7,9]. However, the oxidation of CH_4 to CO and CO_2 (CO_X) competes with the coupling of the CH_3 radical to C_{2+}, causing limitations on the selectivity of the desired hydrocarbon products. Furthermore, compared to CH_4, the over-oxidation of desirable hydrocarbon products such as ethane/ethylene is substantially more favorable [12]. Therefore, the most important performance of the OCM catalyst is to produce selective surface oxygen radicals that function as active sites for producing methyl radicals [7,9]. Then, the methyl radicals combine in the gas phase to form ethane (C_2H_6), which will be converted to ethylene (C_2H_4) by dehydrogenation as shown in Figure 1 [1,4,9]. However, OCM has long been limited to a low C_2 yield below economic feasibility, mainly due to the following reasons: (1) The catalyst capable of activating CH_4 also activate the generated C_2H_6 at a similar rate, resulting in the production of thermodynamically stable CO_X gases (2) Refilling generated vacant surface oxygen sites by gas-phase oxygen sometimes leads to adsorbed oxygen species, which promote CO_X formation as an undesirable scheme (3) Furthermore, diffusion of bulk lattice oxygen to the oxide surface is generally slow, leading to low overall activity, especially in the absence of oxygen flow in the gas phase (4) Because the OCM process requires high temperatures (over 800 °C), the probability of methane combustion is generally high [9].

It is generally believed that the OCM reaction consists of two typical steps, including the heterogeneous step of activating CH_4 molecules to $CH_3{\cdot}$ radicals in the gas phase at electrophilic oxygen sites on the active surface, followed by a homogeneous gas phase step to combine two $CH_3{\cdot}$ radicals to form C_2H_6 molecules, which are then dehydrogenated into C_2H_4 molecule. [13].

$$CH_4(g) \rightleftharpoons CH_4(a) \tag{1}$$

$$O_2(g) \rightleftharpoons O_2(a) \tag{2}$$

$$CH_4(a) + O_2(a) \rightarrow CH_3\cdot + HO_2\cdot \tag{3}$$

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6 \tag{4}$$

$$CH_3\cdot + O_2 \rightarrow CH_3O_2\cdot \rightarrow CO, CO_2 \tag{5}$$

where the gas phase and the adsorbed species are represented by [g] and [a], respectively.

The oxygen species involved in the initiation of the reaction is suggested to be O_2^- or O_2^{2-} on the surface [14,15]. The dissociative adsorption of O_2 on the catalyst surface first produces a peroxy-type species, which subsequently activates the C-H bond. The challenge in OCM is separating C_2H_4 and C_2H_6 products, which undergo additional oxidation and are ultimately prone to CO_X Eqs. (1-5) describe the general steps in the OCM that leads to production of C_2H_6 [16,17]. In equations (1) and (2), CH_4 and O_2 adsorptions occur on different active sites independently of one another. The abstraction of the hydrogen atom from CH_4 (equation (3)) appears to be the rate-determining step in the overall process. Because the C-H bond of CH_4 has a high dissociation energy (427 kJ/mol). The initation (equation (3)) is considered to be caused by an adsorbed diatomic oxygen rather than monoatomic oxygen. C_2H_6 is produced by combining two $CH_3^{\cdot}$ radicals (equation (4)). Two oxidation of $CH_3^{\cdot}$ radicals can result in deep oxidation according to equation (5).Competition between reactions (4) and (5) determines selectivity for C_2-compounds.

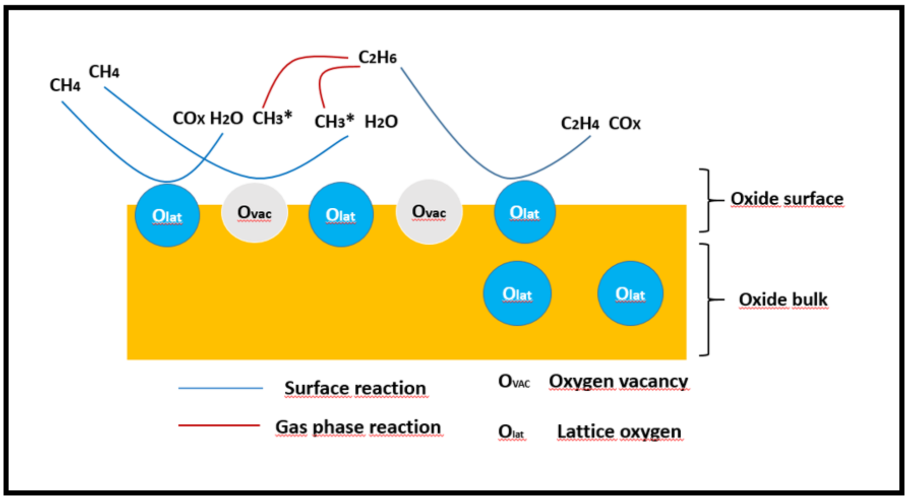

Figure 1. Schematic representation of OCM reaction over metal oxide catalyst surface [9].

2.1. Effect of Operating Temperature on Oxidative Coupling of Methane Reaction

The oxidative coupling of methane (OCM) is a direct way of converting methane into ethane or ethylene. Reaction 6 depicts the overall pathway. Since Keller and Bhasin's and Hinsen and Baerns's pioneer research, this reaction has gotten a lot of attention [18,19].

$$CH_4 + 0.5O_2 \rightarrow 0.5C_2H_4 + H_2O \qquad (6)$$

$$\Delta H_r\ (800\ {}^{\circ}C) = -139\ kJ/mol$$

$$\Delta G_r\ (800\ {}^{\circ}C) = -153\ kJ/mol$$

Methane coupling without an oxidizing agent is a strongly endothermic reaction, and due to thermodynamic constraints, the conversion is limited. By introducing an oxidant, the reaction becomes exothermic and the thermodynamic limitations can be overcome. However, partial oxidation (reaction (7)) and total oxidation (reaction (8)) are far more thermodynamically favorable than the oxidative coupling of methane.

$$CH_4 + 1.5O_2 \rightarrow CO\ + 2H_2O \qquad (7)$$

$$\Delta H_r\ (800\ {}^{\circ}C) = -519\ kJ/mol$$

$$\Delta G_r\ (800\ {}^{\circ}C) = -611\ kJ/mol$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (8)$$

$$\Delta H_r\ (800\ {}^{\circ}C) = -801\ kJ/mol$$

$$\Delta G_r\ (800\ {}^{\circ}C) = -801\ kJ/mol$$

To obtain optimum yields of C_2 hydrocarbons (C_2H_6 and C_2H_4) the reaction needs to be controlled kinetically. This requires appropriate catalysts.

It is reported that high temperatures and multistage processes are necessary in order to activate the C–H bond in CH_4. These cause unwanted reactions that inhibit the formation of hydrocarbons and enhance the deeper oxidation of methane, thereby producing products of combustion like CO and CO_2 [20]. According to Ma et al., maximum C_2H_6+C_2H_4 yields have been obtained at two optimum temperatures (500°C and 950°C). Since active catalysts working at low temperatures have not been developed commercially, most OCM studies have been performed at higher temperatures [21]. To decrease COx products and increase C_2 hydrocarbon yields, the OCM reaction should be performed at a low temperature. Researchers have attempted to lower reaction temperatures, however, spherical catalysts have not been able successfully to lower the temperature of OCM [20]. On the other hand, metal oxide nanocatalysts have recently been discovered to activate methane at lower temperatures. The advancement of OCM technology has been favored by the development of nanostructured catalysts. Siluria has recently developed the first commercial OCM process with a series of "nanowire catalysts" reported to work at temperatures below 600°C. The OCM catalysts are durable for long-run times at low process temperatures, according to Siluria's patent application, even though the single-pass C_2 yield did not reach the aim of 25%.

2.2. Catalysts for Oxidative Coupling of Methane

Oxide catalysts are the most often used catalysts in the OCM process. Transition metal oxides, either pure or modified, and mixed or promoted oxides of group IA and IIA elements, can be examples of these [22]. Some unmodified pure oxides of transition metals were investigated by Kus' et al [23]. Pure/unmodified La(III), Nd(III), Zr(IV), and Nb(V) oxides have catalytic efficiency in the OCM process in the following order: $La_2O_3 \geq Nd_2O_3 \gg ZrO_2 > Nb_2O_5$. Active oxide centers in modified transition metal oxide-based catalysts are thought to play a role in hydrogen abstraction, which has been identified as a key factor in the OCM process.

In this complex heterogeneous–homogeneous process, numerous catalysts have been examined and proven to be effective. Most of them are two-component or multi-component mixed or supported metal oxides, mainly containing components with basic properties like alkaline earth metal oxides, and rare earth metal oxides. The acid-base behavior of the oxide catalyst is largely determined by the kind and strength of the bond between the cationic and anionic species in the oxide. The acid-base characteristic of different oxide systems was discovered to be a critical factor determining their reactivity in the OCM process [9]. Metal oxides are the catalysts most often studied in terms of their acid-base properties, with surface metal cations are commonly referred to as acid centers and surface oxide anions as basic centers [24]. Zavyalova et al. used a statistical technique to examine a large amount of data on OCM catalysts. They showed that excellent C_2 selectivity requires a strong basic character increased by doping with alkaline (Cs, Na) and alkaline earth (Sr, Ba) metals. Inserting a suitable dopant metal in the crystalline structure of the host oxide often changes the lattice and electronic structure, transforming it into a multifunctional hybrid material [9,25].

The simple and complex oxides of alkaline, alkaline-earth and rare-earth elements have been used to create a catalyst formula with such qualities. Hundreds of catalysts, including the typical Li/MgO and La-based oxides catalysts, have been studied in order to promote ethane, ethylene, propane, propylene (C_2-C_3) selectivity and decrease over-oxidation [7]. One of the most commonly studied catalysts for the oxidative coupling of methane is Li/MgO. The Li element in the Li/MgO catalysts functions as a structural modifier to improve the OCM performance of the catalyst, but it suffers from loss of Li metal because of evaporation during long-term operation; La-based catalysts have relatively lower C_2-C_3 selectivity. Mn_2O_3-Na_2WO_4/SiO_2 catalyst is regarded as the most promising one with a methane conversion of 20-30%, 60-80% C_2-C_3 selectivity, and hundreds of hours of stability and, in particular, stability of several hundred hours [7,19]. According to Ji et al., the existence of WO_4 tetrahedron in the metals promoted by W-Mn/SiO_2 offers an opportunity for high OCM performance due to energy matching with methane and the suitable geometric structure for hydrogen extraction. [22]. But, this catalyst must be run at temperatures over 800 °C, and even a minor decrease in temperature below 800 °C can significantly reduce the activity of the catalyst itself and even stop the OCM process. However, none of them have yet reached the commercialization stage, as their C_2 performance is still relatively poor [7,19]. In Table 1, oxide catalysts reported recently has been presented [19,22,26-29].

Table 1. Recent studies on the metal oxides during OCM reaction [19,22,26-29].

Catalyst	CH_4/O_2	T(°C)	CH_4 Conversion (%)	C_2 Selectivity (%)	C_2 Yield (%)	References
$BaSrTiO_3$	2	800	47	29.5	14	[22,26]
4.49 wt.%Li/$BaSrTiO_3$	2	800	37	59.5	22	[22,26]
5.25 wt.%Mg/$BaSrTiO_3$	2	800	46.5	43	20	[22,26]

Table 1. (Cont.) Recent studies on the metal oxides during OCM reaction [19,22,26-29].

Catalyst	CH_4/O_2	T(°C)	CH_4 Conversion (%)	C_2 Selectivity (%)	C_2 Yield (%)	References
3.4 wt.%Mg/$BaSrTiO_3$	2	800	47	51	24	[22,26]
Sm_2O_3/MgO	4	700	24.3	52.3	11.1	[22]
Li-Sm_2O_3/MgO	4	700	24.4	62.5	13.2	[22]
Sm_2O_3	2,5	725	18	72	13	[27]
Na/W/Mn/SiO_2	7	850	43	71	30.4	[27]
Mn/Na_2WO_4/SiO_2	2.5	800	35	47	16.4	[27]
Ce/MgO	4	800	28	50	14	[28]
Li/MgO	2	750	37.8	50.3	19	[28]
CaO powder	4	800	40	50	20	[22,29]
30 wt.% CaO/silica	4	800	30	40	12	[22,29]
CaO fully-coated silica particles	4	800	40	70	28	[22,29]
Na_2WO_4/Mn/SiO_2	3.5	850	32	45	14.4	[22]
Na_2WO_4/Mn/SiO_2 modified with 3 wt.% Al_2O_3 (pellet)	2	850	41	47	19.3	[22]
Na_2WO_4/Mn/SiO_2 modified with 16.7 wt.% MgO (pellet)	2	850	50	38	19	[22]

3. La_2O_3 Catalysts

Many researches have shown that the activity of OCM catalysts is affected by the structural properties of the catalyst. In addition, basicity, surface oxgen and oxygen ion-conductivity, which has been identified as important factors for this reaction, are also impacted by the structural properties of the catalyst [18,26-27].

Zavyalova et al. demonstrated strong basicity as a critical factor for increasing the selectivity of C_2 products. Because CH_4 is a very weak acid, it's not unexpected that it requires a strong base to activate it. Rare earth oxides' basicity rises in the sequence Gd <Sn <Nd <Pr <La [14,24]. Since La_2O_3 is a strong base, it quickly reacts with CH_4. Lanthanum based materials have been studied widely in OCM. The La^{3+}-O^{2-} pair site can effectively activate CH_4, resulting in breaking of the CH_3–H bond and production of the CH_3^--La^{3+}-OH^- intermediate [24]. For surface reaction, the catalyst provides active oxygen and e^- vacancies via a mechanism $La_2O_3 \rightarrow 2La^{3+}O^{2-}e^{-}$ +[O] [30]. Metiu et al. recently performed periodic density functional theory (DFT) calculations and discovered that adsorption of CH_3^- at the La^{3+} site and H^+ at the O^{2-} site is the most stable dissociative adsorption configuration of CH_4 on the La_2O_3(001) surface [24].

La_2O_3 also prevents the formation of carbon on the metallic surface owing to basic characteristics and CO_2 absorption properties. La_2O_3 forms oxygen-containing species ($La_2O_2CO_3$) through the reaction and ultimately prevents the coke deposition on the catalyst surface. The reactions listed in Eqs. 9–10 are responsible for La_2O_3's excellent property of inhibiting coke deposition [31-32]:

$$La_2O_3 + CO_2 \rightarrow La_2O_2CO_3 \tag{9}$$

$$La_2O_2CO_3 + C \rightarrow La_2O_3 + 2 \tag{10}$$

Song et al. also showed that the basic strength of OCM oxide catalysts could be effectively adjusted by optimal doping. They found that strongly basic centers in Sr-doped La_2O_3 nanofibers are essential to enhancing the performance of the OCM, particularly at temperatures exceeding 600 °C. It should be noted that the basicity of catalysts has a strong impact on the oxidative coupling of methane. Moderately alkaline active centers are necessary for a high C_2 yield [9]. The catalytic performances of some La_2O_3 catalysts studied in literature for OCM are shown in Table 2 [27-28,33-34].

Table 2. Reactivity and performance of La_2O_3 catalyts [27-28,33-34].

Catalyst	CH_4/O_2	T(°C)	CH_4 Conversion (%)	C_2 Selectivity (%)	C_2 Yield (%)	References
La_2O_3/MgO	4	800	24	63	15.1	[27]
La_2O_3/CaO	3	900	31	51	15.8	[27]
La/CaO	4	800	28	56	16	[28]
Sr/La_2O_3	4	800	29	59	17	[28]
La_2O_3	5.4	800	24	65	15.6	[28]
$La_2O_3–CeO_2$	-	775	22.3	66	14.7	[33]
La_2O_3	4	740	-	-	13.5	[34]
$LaSrAlO_4$	4	720	-	-	13	[34]

The goal of the study in this area has been to improve catalytic performance in terms of C_2 selectivity and better methane conversion in OCM. Since the OCM reaction typically takes place at temperatures of 800 °C and above, it is very difficult to control the selective oxidation of methane to the desired products (ethylene and ethane). Even while OCM performance is more considerable at higher temperatures, exothermic thermal effects can cause poor catalyst stability and, as a result, increased CO_X production. [9]. This high-temperature necessity is in connection with the chemical inertness of methane (due to its strong C−H bond, low electron affinity, high ionization energy, poor polarity, and lack of dipole moment in the methane molecule). Therefore, it is very difficult to obtain kinetic control over the selective conversion of methane. Among several options to meet this challenge, lowering the reaction temperature appears to be the best strategy. The focus of research has recently turned to OCM catalysts that allow low-temperature performance. It has been found that as well as metal content, particle size and shape, affected catalyst activity. In particular, the use of nanostructured catalysts (nanoparticles, nanorods, nanowires, and nanofibers) allows methane to be activated at lower temperatures and to be achieved higher OCM performance compared to powder catalysts. [9,35].

Nano-scale catalysts with modified morphology have a lot of potential for improving the low-temperature OCM performance. Due to having a large surface-to-volume ratio, nanowire and nanofiber morphologies seem to be the most promising [9]. This is because selectively exposed crystallographic facets generally have high defect sites, low atomic density, and high oxygen vacancies that facilitate methane activation. DFT computations and experimental studies have shown that the performance of heterogeneous catalysts strongly depends on the nature of the exposed catalyst surfaces, particularly for structure-sensitive reactions such as OCM. This means that the design of OCM catalysts with an optimized surface structure will provide lower reaction temperatures. Therefore, Siluria Technologies Inc. showed great improvement in LT-OCM performance with nanowire-based catalysts [9,35].

More detailed research was carried out about facet-dependent catalysis of nanocrystal and nanowire catalysts, the effect of crystal facets of CeO_2 for OCM reaction is also investigated by Sun et al. They found out that CeO_2 (doped with 10 wt.% Ca) in nanowire or nanorod forms performed better in terms of LT-OCM performance than CeO_2 catalysts in the form of nanoparticles. Fast Fourier transform (FFT) analysis of their High-Resolution Transmission Electron Microscopy (HRTEM) images showed that nanoparticles and nanowires had some exposed planes in common. But, compared to nanoparticles, CeO_2 in the form of nanowire mostly had (110) exposed facets. To explain the cause of the observed difference in performance, the group performed a DFT calculation and found that methane activation on the peroxided surface (110) is highly preferred due to the existence of moderate alkaline active sites. Also, the addition of Ca on the exposed facet (110) enhanced the basic strength substantially [9]. In addition, Hou et al. [35] researched the structural sensitivity of $La_2O_2CO_3$ catalysts at the nanoscale have various morphology for OCM. The result showed that $La_2O_2CO_3$ and La_2O_3 catalyst in the forms of nanoparticle has only 2% methane activity with zero yields at 500°C, indicated that they are inadequate for the reaction. The morphological changes resulting from hydrothermal nanoscale synthesis caused exposure to various types of crystallographic facets on the surface of the resulting oxide catalysts. Surprisingly, the rod-shaped catalyst performed better in LT-OCM performance (methane conversion of 30% and C_2 selectivity of 50% at

420°C). Sun et al. also investigated La_2O_3 oxide and found that nanorod morphology catalysts showed superior performance at lower temperatures below 650 °C lower than nanoparticles. Also, Hou et al. found that the La_2O_3 catalyst with the rod-shaped morphology exhibited twice the OCM performance (27.4% methane conversion and 43.4% C2 selectivity) relative to its plate-shaped equivalent at temperatures 500 °C lower thanks to its higher surface area to volume ratio [20,35]. Table 3 presents the catalytic performances of nanostructured La_2O_3 catalysts for LT-OCM reaction [35-38].

Table 3. The potential of nanostructured La_2O_3 catalysts for low-temperature OCM [35-38].

Catalyst	Morphology	T(°C)	CH_4 Conversion (%)	C_2 Selectivity (%)	C_2 Yield (%)	References
$La_2O_2CO_3$	Nanorod	420	29.7	48.4	14	[35]
	Nanoplate		0	0	0	
La_2O_3	Nanorods	500	27.4	43.4	12	[35]
	Nanoplate		16.2	24.6	4	
La_2O_3	Nanosheets	550	32.3	45.9	15	[36]
	Nanorods		29	40.5	12	
	Nanoflower		28.9	41.6	12	
	Nanoparticle		9.9	6.4	6	
Sr-La_2O_3	Nanofiber	500	35	47	16	[37]
La_2O_3-CeO_2	Nanofiber	470	27.7	65	12	[38]
		520	28.6	70	4	

Nanostructured catalysts, containing La_2O_3-CeO_2 nanofibers and metal oxide nanowires, have been suggested as a way to enhance the amount of surface catalytic active sites and make better use of the catalytic materials. Although nanostructured materials can increase catalytic activity, the high reaction temperature of OCM quickly degrades structures with a large surface area, making high nanostructured catalysts ineffective [39].

The catalytic performances of La_2O_3 nanorod and nanoparticle catalysts for OCM are compared in Sun et al. study. In the study, the lower initial reaction temperature was achieved with La_2O_3 nanorods than La_2O_3 nanoparticles. Methane was initially converted on La_2O_3 nanorods at 450°C while it was found higher than 550°C on La_2O_3 nanoparticles. Besides, La_2O_3 nanorods showed higher selectivity towards C_2 hydrocarbons than La_2O_3 nanoparticles at low temperatures. To produce C_2 hydrocarbons over La_2O_3 nanoparticles requires higher temperatures than La_2O_3 nanorods. In this study, the reusability of the La_2O_3 nanorod catalyst is also investigated. The catalytic activity over the used catalyst is similar to the fresh catalyst. The shape-specific impact of La_2O_3 nanorods should contribute to the higher rate of CH_4 conversion at low temperatures. It is thought that electrophilic oxygen species O^- and O_2^- are the most important species, and their abundance on the catalyst surface has a positive effect on C_2 selectivity. However, lattice oxygen (O^{2-}) causes total oxidation. Sun et al. showed that the proportion of electrophilic oxygen species ($O^-$and O_2^-) to lattice oxygen (O^{2-}) determined using XPS analysis is much higher for the La_2O_3 nanorods than La_2O_3 nanoparticle catalysts. Thanks to La_2O_3 nanorods having a high surface area, strong basic surface centers, electron-deficient surface oxygen species, and well-defined surface structures can be obtained better activity and selectivity for OCM reaction than La_2O_3 nanoparticles at low temperature [20]. By optimizing the size and shape of La_2O_3 nanocrystals, high methane activity and high C_2 selectivity for low-temperature OCM reaction can be achieved.

4. Conclusions

To summarize, one of the most difficult problems confronting the catalysis community today is direct methane activation and conversion to other valuable compounds. In addition, the plenty of methane has raised interest in the development of methods for converting methane to higher hydrocarbons or chemicals. Because of the significant selectivity/conversion constraints associated with all studied catalysts, it has been concluded that traditional spherical catalysts have inadequate performance to obtain a desirable process economy. The catalysts studied in the literature for the oxidative coupling of methane are reviewed. It shows that nanoscale catalysts provide higher C_2 selectivity and methane conversion. Herein, we indicate the catalytic performance of La_2O_3 nanostructures for oxidative coupling of methane reaction. Catalytic properties of La_2O_3 nanocatalysts with different shapes have been compared and found that the activity and selectivity of the structure-sensitive OCM reaction are strongly related to the shape and size of La_2O_3 nanocatalysts. The ethylene yield at low temperature (<600°C) was increased with the invention of nanowire catalysts, and the commercialization of the OCM process was achieved by advanced nanowire catalysts.

Declaration of Ethical Standards

The authors of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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