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Oxidative coupling of methane in chemical looping design

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ABSTRACT

The search for alternative non-carbon-emitting uses of the huge reserves of natural gas has renewed the interest on direct conversion of methane to value added chemicals. Oxidative coupling of methane (OCM) is a key potential route to convert methane directly to ethylene and innumerous works have focused on the study and development of catalysis for such reaction. Despite these efforts, the limited yield and selectivity achieved still hinders the industrial deployment of such reactions. In this work, we provide a mini-review on studies that focus on OCM process based on the chemical looping (CL) concept, in which methane and oxygen are fed in two separated cyclic steps and a metal oxide catalyst is used as the oxygen source to activate the methane molecule. CL emerges as a promising design for viable methane conversion by improving selectivity due to the use lattice oxygen species for methane activation, avoiding undesired combustion gas phase reactions triggered by molecular oxygen. We review all classes of catalyst tested in this approach, including single oxides, doped and co-doped systems based on Mg-—Mn oxides, rare earths, Mn-Na_2WO_4, and perovskites, and most recent optimization of reactor operation conditions.

1. Introduction

The increase availability of natural gas due to the enormous reserves of shale gas and the increase in bio-gas sources have boosted the interest in the use of methane as a raw material for production of chemical compounds [1,2]. In this scenario, oxidative coupling of methane (OCM) has emerged as a suitable alternative for ethylene production since current industrial processes, steam reforming of naphtha and ethane, demand high energy inputs, release large amounts of CO_2, and involves complex products separation [3–5]. Such drawbacks added to the concerns about volatility in crude oil price and the finitude of oil reserves [6,7]. In addition, the development of industrial processes that directly convert methane to value added chemicals will provide alternatives for methane consumption that favor carbon assimilation, other than methane combustion, which is one of the drivers of climate changes [3].

Oxidative coupling of methane was proposed by Keller and Bhasin in the 1980's and since then many efforts have been devoted to make this process economically viable [8]. In this reaction, methane (CH_4) interacts with oxygen (O_2) with the aid of a catalyst, usually a metal oxide, under specific experimental conditions [9]. This reaction produces ethylene and ethane as main products, but it can also produce carbon monoxide (CO), carbon dioxide (CO_2), methanol (CH_3OH) and higher hydrocarbons depending on experimental conditions [10]. Usually, the process is carried in co-feed reactors whereas methane and oxygen are feed simultaneously at temperature ranging from 650 to 950 °C and pressures close to atmospheric one [8,11]. Despite of intense catalyst development to selectively convert methane to C_2 products, the yield requirement for industrial implementation of this process has not been achieved yet [3].

In this search, chemical looping (CL) OCM has emerged as an alternative to increase selectivity toward ethane and ethylene production [3,8,12]. In this reaction concept, methane and oxygen are fed in two separated steps in a loop and a metal oxide catalyst is reduced in one step of the loop and oxidized in the other one [13]. The main advantage of this approach is that methane oxidation takes place in absence of molecular oxygen, which avoids the undesired products of complete oxidation, CO and CO_2, increasing selectivity [14]. This concept provides several other advantages that will be discussed in this review, including for example, operation at lower temperatures compared to co-feed systems [8]. Nevertheless, the development of suitable catalysts remain as the main challenges to make CLOCM processes suitable for industrial scale. Several materials have been investigated as catalyst,

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from single oxides to doped and co-doped systems. Catalytic systems such as the ones based on Mg—Mn oxides [1,3,6,13–15], rare earths [4,12,16,17], Mn-Na_2WO_4 system [7,18–20], and most recently the perovskites, ABO_3 type [21,22], have been investigated.

In the coming sections, the most relevant works on CLOCM will be discussed in the following sequence. First, an overview of OCM reaction will be presented. The concept of CL reactor will be discussed with focus on its advantages over co-feed systems. The main catalyst families will be presented with discussion in terms of activity to selectively convert methane to C_2 products. In the final section, features of optimization of reactor operation conditions will be discussed, including insights for improving yields and for making this process auto sustainable from an energetic point of view.

2. Oxidative coupling of methane

The OCM reaction was first proposed by Keller and Bhasin, who were motivated by the search of a reaction that would require less energy input than dehydrogenation of methane [8]. They suggested the oxidative route to solve the problems related to thermodynamic barrier and high endothermic reactions to produce ethane and ethylene [6,8]. The general mechanism for C_2 products formation from methane is described by a two-step reaction presented in Eq. (1) and (2) [6].

$$2CH_4 + \frac{1}{2}O_2 \rightarrow C_2H_6 + H_2O \quad \Delta H^\circ = -176.6\ kJmol^{-1} \tag{1}$$

$$C_2H_6 + \frac{1}{2}O_2 \rightarrow C_2H_4 + H_2O \quad \Delta H^\circ = -105.5\ kJ\ mol^{-1} \tag{2}$$

In this reaction, which must be promoted by an oxygen carrier, usually a metal oxide catalyst, methyl radicals are initiated at catalyst surface and then couples in the gas phase to produce ethane. Thereafter, ethylene is produced by either oxidation in the catalyst surface or by dehydrogenation of ethane [11]. However, there are parallel and consecutive reactions in this process, among them, complete oxidation of methane that produces CO and CO_2, represented in Eq. (3) and (4) [9].

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + H_2 \quad \Delta H^\circ = -36\ kJ\ mol^{-1} \tag{3}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H^\circ = -802.6\ kJ\ mol^{-1} \tag{4}$$

The complete oxidation of methane is an undesired path that can decrease C_2 selectivity and increase products separation costs [9]. Besides, the primary products, ethane and ethylene, several other secondary chemicals can be formed from the primary, although in small quantities. In fact, due to multiple parallel reactions, several products have been identified by gas chromatography, such as acetylene, C_3 (most propylene), C_4 (mostly butadiene), C_5 (mostly diolefins, linear and branched dienes), and aromatics (toluene and benzene) [6,13,15]. A comprehensive review of numerous studies of OCM process is beyond the scope of this work and to the reader interested, some review articles are suggested that investigated in detail OCM process features [2,23–27].

3. Reactor concept and CLOCM

The co-feed OCM reactor concept has achieved interesting selectivity and yield results for methane conversion. However, there remain challenges for catalyst and reactor design development to make this process economically viable for industry. Benchmark performance parameters usually considered are yield values >30% and selectivity close to 80% [11,28,29]. In a pioneer work in 1982, Keller and Bhasin carried out a series of experiments to screen several metal oxide catalysts [8]. In order to minimize the effect of gas phase oxygen in parallel reactions, the authors reported a reactor operating in cyclic conditions, whereas methane and air were fed in separate steps. In this way, the yield of C_2 products increased one order of magnitude as compared to a co-feed system. An important finding was related to the capacity of the catalyst to supply oxygen for OCM reaction. By measuring the total surface area of the catalyst, they determined that oxygen molecules adsorbed on the catalysts surface could not account alone for the amount of converted methane. This result revealed that oxygen must diffuse from the bulk to the surface to oxidize the methane molecules, which thereafter is restored by cycling an air flow in the reactor [8].

One year later, the concept of CL was introduced by Richter and Knoche for a combustion reaction [30]. The general idea was similar and consisted of the separation of main chemical reactions in sub-reactions. Parallel reactions that occur in gas phase and gas-solid interfaces are separated into consecutive single steps reactions [19,30]. For methane conversion the CL concept has been extensively explored. For instance, in the CL combustion of methane (CLCM) metal oxide particles provide oxygen for the complete combustion generating power and CO_2 [31,32]. In addition to improvements in terms of power conversion efficiency, CL combustion also simplifies significantly the CO_2 capture process because it suppresses the need for the flue gas separation step. On the other hand, CL partial oxidation of methane (CLPOM) is used for production of high-quality syngas, whereas methane interacts with the catalyst to produce CO and H_2 [33,34]. In both CLCM and CLPOM processes, oxygen is replenished in an oxidation step whereby the oxygen carrier particles come in contact with air [34]. For that reason, the oxygen storage capacity of the carrier plays a key role. In CLCM, catalysts are based on an active compound (metal oxides of Ni, Cu, Fe, Mn, Co working as oxygen carriers) and a thermally stable substrate (TiO_2, SiO_2, MgO, Al_2O_3, ZrO_2, and CeO_2) [34]' whereas in the CLPOM oxides of Fe, Ni, Ce, mixed oxides, and perovskites-based oxides modified with small amounts of noble metal catalysts (Pt, Pd, Au, Rh, and Ru) are used. Besides the high-quality syngas production, the CLPOM, enables the separation of high endothermic reactions in separated steps and decrease the coke deposition over the catalyst [31,33,34].

The CL dry reforming of methane (CLDRM) and CL steam reforming of methane (CLSRM) are also used for syngas production from partial oxidation, but during the catalyst oxidation, CO_2 and steam are used, respectively [35,36]. In the CLDRM process, methane is first partially oxidized to produce syngas and the catalyst is reoxidized with CO_2 to replenish oxygen and consequently produce CO. For catalyst selection, besides the activity for methane activation and high oxygen storage capacity (OSC), the catalyst must provide sites for CO_2 reduction [34]. Therefore, for CLDRM iron- and ceria-based oxides modified with noble metals (Pt, Pd, Au, Rh, and Ru) have attracted significant attention for the catalyst development [31,35]. The advantages of CLDRM over the co-feed system is the usage of a high pollutant gas (CO_2) for oxygen replenishment, coke formation is avoided, and a better reactor thermal control can be achieved. For the CLSRM, process methane is first partially oxidized to produce syngas and the catalyst is reoxidized with steam to replenish oxygen and consequently produce H_2 [34,36]. The process for catalyst selection must consider the capability of water-splitting and moderate oxidizing ability, therefore metal oxides such as WO_3, SnO_2, Fe, Ni and Ce-based oxides, and perovskite oxides have been explored. In the CLSRM, the step of partial oxidation of methane is a mild exothermic reaction, and the splitting in two separated steps decreases the energy costs [34,36].

The reform methods described above are indirect methods that require subsequent Fischer-Tropsch reactions to transform syngas in liquid fuels [37]. Methods that direct convert methane to liquid fuels such as methanol or higher hydrocarbons would provide a simpler alternative to replace the use of oil and transfer the energetic matrix to natural gas sources [38]. The challenges in the co-feed system still being a suitable reactor design, an active catalyst to selectively convert methane and stability of catalytic systems at high temperatures. The CLOCM is schematically shown in Fig. 1. In this process, methane oxidation takes place on catalyst surface by use of lattice oxygen,

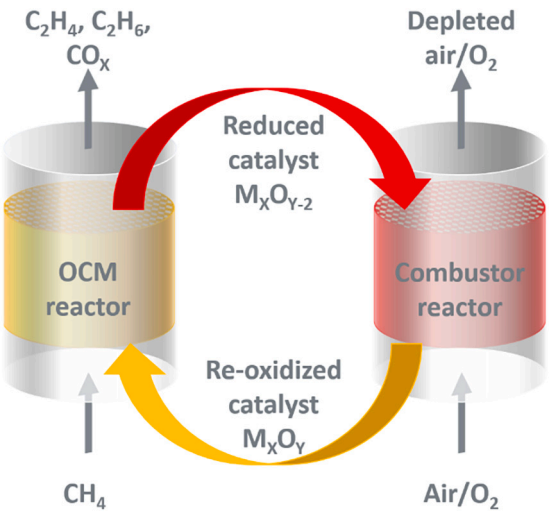

Fig. 1. Schematic representation of the chemical looping oxidative coupling of methane process.

different from co-feed system, in which methane oxidation occurs by both molecular oxygen in the reactor chamber and lattice oxygen supplied by the catalyst [39]. Besides the complex product separation unit demanded by co-feed, there are parallel gas phase reactions with molecular oxygen that completely oxidize methane and its products (CO_X), because they are thermodynamically more favorable, which decrease C_2 selectivity [6–8]. In the CLOCM processes, the metal oxide catalyst is regenerated by either air or oxygen flow in a subsequent re-oxidation step [1].

Chemical looping avoids another drawback of co-feed system, the direct mixture of methane and oxygen increases combustion risk and favors the formation of hot spots arising from parallel reactions that can accelerate methane complete oxidation and catalyst sintering or grain growth, leading to a decrease in the surface specific area of the catalyst. Such effect requires a large complexity in reactor design and operation, including strict temperature and pressure control [40]. In a CL reactor, separation units for products are minimized because the overall reaction is divided into consecutive sub-reactions, resulting in significant cost reduction. Coke formation can also be minimized because carbonaceous materials are consumed in the catalyst oxidation step [6,41].

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4. Catalysts for CLOCM

When the OCM reaction was proposed for ethane and ethylene production, one of the requirements pointed-out was the need of a catalyst to achieve high selectivity [8]. Since then, the design of catalysts to promote both selectivity and yield still remains the major challenge for OCM industrial application [8]. An analysis of catalytic data have shown that basicity (typically present in alkaline, alkaline earth, and rare earth metal oxides) is an important intrinsic characteristic to improve selectivity and that structural defects such as oxygen vacancies facilitate methane activation from charged oxygen species [11,42]. In addition, investigation of the active sites in methane conversion has demonstrated that the type of oxygen species define the selective and non-selective reaction routes: monoatomic oxygen species favor conversion to C_2 products, whereas molecular oxygen favors oxidation [1,6].

Considering the thermodynamics of OCM reaction, some requirements are critical for candidate oxides to be good catalysts. The equilibrium oxygen partial pressure of the oxide must be sufficient to provide an effective methane conversion, but the chemical potential of critical oxygen surface species must be tuned to guarantee C_2 selectivity [31]. Mn-oxides have been widely investigated because they can provide enough oxygen for fulfill, however they must be modified to reduce the equilibrium oxygen partial pressure, which is above the optimal required for OCM. Indeed, several works report the use of Mn-based oxides, by doping with Li [1,42], alkali earth metals such as Mg [31], and combination with Na_2WO_4 [27,43]. On the other hand, Fe-based oxides are not suitable for this reaction because they are not oxidative enough in the practical temperature range (650–950 °C) [31]. One important feature in co-feed systems is the ratio of CH_4/O_2 that must be tuned to achieve a maximum C_2 yield, a higher ratio increases selectivity, but decreases the conversion, whereas a lower ratio increases methane conversion but decreases selectivity [38].

Several catalytic systems have been investigated for co-feed reactor design, such as Mn-based catalysts and other transition metal combinations [1,3], Li-doped MgO [25,42], perovskites [21,22,44,45], Mn-Na_2WO_4 [5,24,27,43], and rare earth oxides [28,46,47]. With the later representing the most active catalyst, especially the lanthanides [42]. In addition, the doping, co-doping or impregnation has allowed the increase of selectivity. In this direction, doping with alkaline and alkaline earth, and some transition metals increase the basic sites and the redox capacity, respectively [26]. A more recent trend for both CL and co-feed processes is the use of perovskite-based oxides as catalysts. The composition flexibility of the perovskites, which has yet to be fully explored, will allow for improvements in both redox thermodynamic and kinetic parameters and a fine tuning of defect chemistry, surface oxygen species and basicity [22,44,48].

CLOCM allows for a flexibility in reactor design that facilitate the development of efficient oxygen carriers to improve OCM performance with the advantages reported above, and with some catalytic systems similar to the ones developed for Co-feed system [49]. Moreover, computational tools have allowed the screening, simulation, and optimization of several catalyst systems [50,51]. In fact, it is possible to evaluate the effects of dopants in the oxide electronic structures, to manipulate the active oxygen species, to determine energy parameters for methane adsorption and to investigate the role of oxygen vacancies, all this by the use of density functional theory (DFT) combined with experimental studies [1,3,50]. In addition, by using reported data, data-driven techniques and machine learning, it is possible to construct the reaction networks including the all possible chemical compounds participating in the reaction and to optimize the experimental design to improve OCM performance [51,52].

The first metal oxides applied as catalysts in OCM processes were prepared by wet-impregnation and supported on α-alumina [8]. Among the screened oxides, Mn, Cd, Sn, Sb, Tl, Pb, and Bi oxides showed selectivity toward C_2 products, whereas Li, Mg, B, Cr, Co oxides showed small activity; and others such as Ti, V, Fe, Ni, Cu, Zn, Sr, Ba, Zr, Mo, W, Ag, Pt, and Ce showed activity similar to a non-catalyzed OCM reaction [8]. After this initial screening, two concerns were pointed out by the authors, the volatility of some metals and metals oxides in the OCM temperature range, and the low abundance of some metal precursors. This pioneer work has provided the groundwork for the following catalyst development for CLOCM. The materials investigated are here grouped into four representative classes: Mg—Mn oxides [1,3,4,6,15], rare earth metal oxides [4,12,16,17,53], the $Na_2WO_4/Mn/SiO_2$ system [7,18–20], and recently the ABO_3 perovskite-type oxides [21,22]. The main results from the reported studies are summarized in Table 1.

As noticed in Table 1, reaction temperatures range from 700 to 850 °C. In general selectivity decreases with temperature similar to what is observed in co-feed processes. Higher temperatures result in higher oxygen mobility, generating an excess of surface O_2 molecular species that favor methane complete oxidation. To avoid that, several studies have focused on screening catalysts that are active at low temperatures [54]. Among the benefits of lowering the reaction temperature, reduction in energy costs, decreased catalyst sintering, and enhanced stability in long operation cycles are the most important ones. It is important to point out that, in the work of Parishan et al., the kinetics of methane conversion was investigated by using the main C_2 products of OCM,

Table 1
Summary of data and information about main CLOCM process reported in literature.

Catalyst	Particle size (μm)	Surface area (m^2 g^{-1})	Reactor temperature (°C)	Gas in the system	S_2[a] (%)	X[b] (%)	Y[c] (%)	Main Product	Reference
Mn/SiO_2	–	250–275	700–800	CH_4, O_2, Air, N2, C_2H_4, C_3H_6	50.0	34.0	17.0	C_2H_4, C_2H_6	[13]
$Na/Mn/SiO_2$	–	250	850	CH_4, Air, N_2, C_2H_6	77.0	22.0	17.0	C_2H_4, C_2H_6	[14]
Mg_6MnO_8	300–850	1.95	840	CH_4, Air, N_2	63.2	36.7	23.2	C_2H_4	[6]
Li-Mg_6MnO_8	1–2	–	850	CH_4, Air, N_2	16.77	68.97	11.57	C_2H_6, C_2H_4, C_{3+}	[1]
(Li,W)-Mg_6MnO_8	300–850	–	850	CH_4, Air, N_2	57.2	50.0	28.6	C_2H_6, C_2H_4	[3]
Na/Pr_6O_{11}	–	0.7–1.9	800	CH_4, Air, N_2	76	16	21	C_2H_4, C_2H_6, CO_2	[4]
$La_2O_3/CeO_2/SiO_2$	250–500	–	700–850	CH_4, Air, He	83.69	10.96	9.17	C_2H_6, C_2H_4	[16]
$Ag–La_2O_3/SiO_2$	250–500	–	700–800	CH_4, Air, O_2, He	60	50	30	C_2H_4, C_2H_6	[17]
$Ag–La_2O_3/SiO_2$	250–500 90–200	–	700–800	CH_4, Air, He	60	50	30	C_2H_6, C_2H_4	[12]
$Na_2WO_4/Mn/SiO_2$	–	3.5	700–850	CH_4, O_2, Ar	< 25	–	–	C_{2+} (mainly C_2H_6)	[18]
$Na_2WO_4/Mn/SiO_2$	200–300	1.86	775–800	CH_4, O_2, He	60	42	25	C_2H_6, C_2H_6	[5]
$Na_2WO_4/Mn/SiO_2$	200–300	3.2	–	C_2H_6, C_2H_6, O_2, He	–	–	–	–	[7]
$Na_2WO_4/Mn/SiO_2$	150–350	1.86	700–800	CH_4, O_2, He	29	67	22	C_2H_6, C_2H_4	[20]
Na-LaMnO3	–	1.273	825	CH_4, Air, N_2, Ar	55	30	20	C_2H_6, C_2H_4, C_{3+} (	[21]
$Na_2WO_4/FeMnO_3$	2.5	–	825	CH_4, O_2, He	80	20	16	C_2H_4	[22]

[a] S_{c2}: C_2 selectivity.
[b] X: CH_4 conversion.
[c] Y: C_2 yield.

ethane and ethylene, as reactants in order to understand the reaction network [7].

In the following sub-sections, each category of catalyst reported in Table 1 are discussed, with several features considered and reported by the authors. An important part of metal oxides characterization is the understanding of the role of oxygen species and OSC in methane activation. Therefore, some thermoanalytical techniques have been reported and extensively explored as tools in this process. These includes temperature programed reduction (TPR) to understand the catalyst reducibility [3,21,22,46], temperature programed desorption of oxygen (O_2-TPD) of oxygen to get insights on oxygens species present in the catalyst [22,55], and temperature programmed surface reaction (TPSR) to understand methane interaction with the catalyst [5,22]. In addition, thermogravimetric analysis (TGA) is reported as fundamental tool to obtain, for instance, the oxygen storage capacity for catalysts [6,13,14], redox stability along cycles [6], and the oxygen release rate during the catalyst reduction at specific temperatures [22]. The aforementioned techniques have supported the catalyst characterization presented in the following sub-sections.

4.1. Mg—Mn oxides

Magnesium and manganese oxides have shown promising performance for OCM and have been extensively explored in doped and undoped systems. They have yielded the best catalytic performance for conversion of methane to higher hydrocarbons in CL conditions. Manganese is present in most of catalysts that achieve yields above 25% [11]. This material have shown stability up to 100 cycles [6]. Moreover, it has the capability to store oxygen and to easily release oxygen at high temperatures (800–1200 °C), and low oxygen partial pressures [1,3,6,13–15]. The main results of selectivity, conversion, and yield are shown in Fig. 2.

It can be noticed from Fig. 2 that the best performance in a CLOCM experiment is achieved by Li-doped Mg—Mn oxides, which have yields close to 30%, a requirement for industrial viability. However, Li-doped catalyst has shown high instability over redox cycles, due to Li volatility

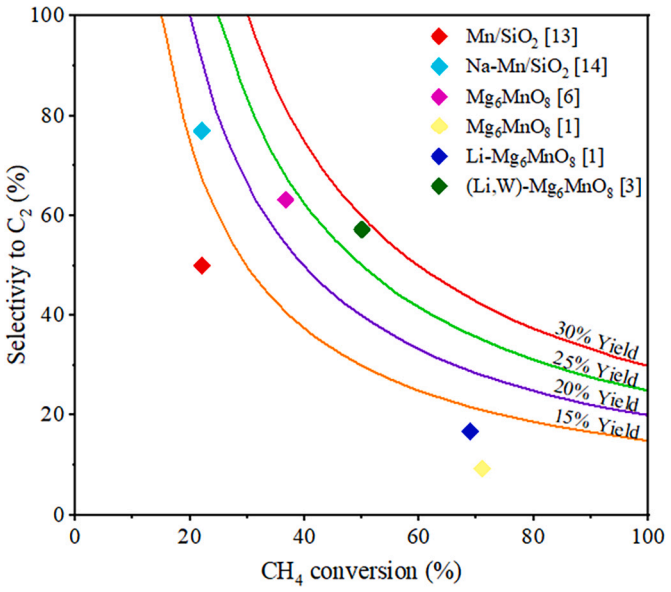

Fig. 2. Selectivity and conversion of Mg—Mn based catalysts applied to CLOCM reported in literature.

[2]. Despite this drawback, several features of this system are discussed below to offer further insights for CLOCM catalyst development.

In 1987, a report of CLOCM developed at ARCO Chemical Company, Sofranko et al. screened several transition metal oxides catalysts supported on silica and reported that Mn_2O_3/Mn_3O_4 had a relative higher stability and activity in the range of 700 to 800 °C [13]. On the other hand, In_2O_3, GeO_2, SnO_2, BiO_3, and Sb_2O_3, showed instability over redox cycles duo to their volatility. Besides the fundamental properties of this catalyst for OCM (activation of methane molecules, coupling of methyl and other transient species), the authors point out that Mn-based oxides can transfer its oxygen to oxidizes methane, with concomitant

regeneration from an air flow, a requirement for CL experiments. Moreover, they found an optimized load of 15 wt% of Mn over SiO_2, suggesting that there is a synergetic effect between catalyst and support to selectively convert methane. Methane activation for this system occurs via solid phase and higher carbons (C_{2+}) are built in gas phase. This was confirmed by carrying out surface reactions with ethane, whereas the rate of ethylene production from oxidative dehydrogenation is higher compared to thermal dehydrogenation, which indicates that ethane is formed near the surface [13].

The nature of the catalyst support and the effect of alkali and alkaline earth metals doping on Mn-oxides based catalysts were investigated by the same company [14]. The authors reported that silica as a substrate has a higher selectivity compared to alumina, due to the higher acidity of the later. Among the tested metal oxides, sodium promoted an increase in selectivity toward C_2 products and a decrease in coke deposition and products of complete oxidation. This was explained in terms of basicity increase promoted by sodium impregnation, interaction between sodium-manganese, observed by X-ray diffraction (XRD) experiments, which avoids overoxidation of hydrocarbons, and a decrease in surface area that is related to an oxygen supply control for methane oxidation. The authors found that for catalysts with higher surface area the activity is higher at the beginning but rapidly decreases due to a depletion of active oxygen species. On the other hand, catalysts with lower surface areas the activity is initially lower, but it remains constant along the entire operating cycle, resulting in an overall higher selectivity toward C_{2+} products [14].

Methane conversion using sodium promoted Mn/SiO_2 catalyst follows the same main reactions as reported above: methyl activation on the catalyst surface followed by coupling of methyl radicals in the gas phase [13]. This finding is confirmed by primary formation of propylene when ethylene and methane are injected in the reactor [14]. By studying co-feed and CLOCM for the same catalysts, the role of oxygen species is explained by a Mars-van Krevelen mechanism, whereas methyl radicals are formed on the metal oxide surface or by gas phase oxygen and then couples with other methyl radicals to products C_{2+} chemicals [15].

More recent works investigated doped Mn—Mg catalyst performance in CLOCM, with the best results also shown in Fig. 2 [1,3,6]. In this study, the oxygen releasing kinetics of commercial catalyst Mg_6MnO_8 was evaluated by performing TGA under CLOCM conditions [6]. Two independent oxygen species were identified, the loosely bound and the strongly bound. The former uncouples under inert atmosphere (N_2) and the latter is released under reducing atmosphere (H_2 or CH_4). In addition, the OSC was determined, 4.4 wt% of the catalyst weight, whereas 37.4% correspond to the loosely bound oxygen, and 62.6% correspond to the strongly bound. From the evaluation of the catalytic performance, it was observed that residence time plays an important role on selectivity trends. Higher residence times allow consecutive reactions however, as secondary products are more reactive, they are prone to deplete oxygen from catalyst, which decrease both methane conversion and C_2 products selectivity. On the other hand, lower residence times decrease secondary products formation, therefore the probability of primary products formation due to a higher availability of lattice oxygen is higher. It was observed that the particle size increased from 3 μm to 6 μm, which indicates that the catalyst undergoes sintering. However, despite of the decreased surface area with increasing number of thermochemical cycles, the catalyst maintained high levels of selectivity and conversion [6].

In the following studies the Mg_6MnO_8 catalyst was investigated with Li-doping and (Li, W)-codoping, in addition the role of oxygen vacancies formation was investigated [1,3]. Such doping was motivated by the known activity of Li in OCM and the similarity of ionic radii between Mg and Li, with doping restricted to less than 1 mol% to prevent changes in the crystalline structure [1]. As noticed in Fig. 2, the Li-doped Mg_6MnO_8 achieved a higher C_2 selectivity compared to the undoped system. As in the previous paper, they observed an increase in particle size after 15 cycles, duo to solid-state mass diffusion. Moreover, by using X-ray photoelectron spectroscopy (XPS), the formation of charged defects was observed as result of the Mg substitution by Li, that due to the difference in valences, an oxygen vacancy positively charged is created to keep the charge balance [2].

The co-doping of Mg_6MnO_8 with Li and W provided selective oxygen vacancies for methane activation, therefore, this system showed improved selectivity toward C_{2+} products (Fig. 2) [3]. The catalytic activity was even higher than the single doping, Li-Mg_6MnO_8 and W-Mg_6MnO_8, and the undoped system (Mg_6MnO_8). In order to understand the reducibility of this system, H_2 TPR was carried out in a TGA equipment. The effect of Li-doping is more pronounced in the co-doped catalyst, which indicates a higher tendency of the catalyst to convert CH_4. It is observed an increase in particle size and decrease in specific surface area after 50 cycles. However, the catalytic performance is almost constant along the cycles and the XPS analysis indicates insignificant changes in the spectra before and after the cycles [3].

By DFT computational modeling the oxygen vacancies were investigated for Li-doped system [1], it was observed that this defect has a short-range effect because the energy for vacancy formation is decreased only in sites close to the dopant. Moreover, methyl adsorption by oxygen vacancies is destabilized and the activation of CH* e CH_2* radicals is inhibited, which avoids methane complete oxidation. These findings are particularly important and reveals the relationship between oxygen vacancy induced by doping and C_2 selectivity, which is of pivotal importance in the search for an ideal catalyst for CLOCM [1]. For (Li,W)-Mg_6MnO_8 catalyst the theoretical DFT calculations indicates that (Li,W)-Mg_6MnO_8 has a synergetic effect caused by dopants. While for lower oxygen vacancies concentration the energy formation is similar to Li single doping, with smaller vacancy formation energy, at higher oxygen vacancies concentration the energy to form a vacancy is higher, similar to W single doping. This result corroborates the H_2 TPR experiments and indicates that co-doping induces the formation of active sites to selectively convert methane and avoid complete oxidation of methyl radicals by destabilizing these radicals, which is desorbed to gas phase [3].

4.2. Rare earth oxides

Rare-earth oxides were also a matter of study in chemical looping experiments at ARCO Chemical Company [4]. These catalysts showed promising catalytic activity in OCM, mainly because rare earth oxides have variable valence which can improve redox cycle performance [12]. Therefore, several oxides, such as La_2O_3, Nd_2O_3, Pr_6O_{11}, Tb_4O_7, and CeO_2, were investigated but only the three later showed relevant catalytic activity to convert methane to C_2 products. Moreover, the selectivity and conversion were tuned by promotion with alkali metals (Na, K, And Li). Pr_6O_{11} doped with Na at 4 to 8% showed the best yield (Fig. 3). For comparison, to achieve similar activity in co-feed experiments, the authors had to increase reactor temperature by 100 °C, however an increase in CO_2 production was observed and selectivity was almost 15% smaller than CLOCM [4]. The reaction mechanism proposed for CLOCM in the Na/Pr_6O_{11} system also follows the methyl activation in the solid interface and coupling to C_{2+} products in the gas phase. Furthermore, an oxygen active specie, namely superoxide (O_2^-) was attributed to be responsible for this activation. In the proposed mechanism, an alkali metal oxide (Na_2O_2) loses a superoxide specie that is replenished by an oxygen specie from Pr_6O_{11}. In the latter, oxygen has a high diffusive rate from the bulk to surface, and praseodymium is capable of a rapid change in oxidation states ($Pr^{3+} \leftrightarrow Pr^{4+}$). This idea is supported by XRD experiments which indicates the presence of sesquioxide Pr_2O_3, that has its oxygen species regenerated by an air flow, whereas samarium and lanthanum oxides have negligible catalytic activity [4].

The main difference between CL and co-feed OCM is the dynamic of oxidation. In CLOCM, it depends only on the catalyst capacity to supply oxygen for the reactions. Thus, CeO_2 and La_2O_3 supported on silica were tested as catalyst for CLOCM [16]. For these systems, it was also

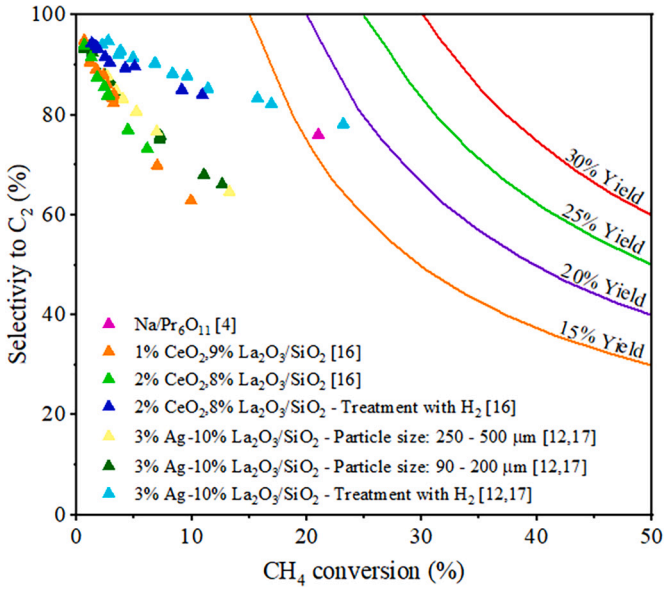

Fig. 3. Selectivity and conversion of rare earth oxides as catalysts applied to CLOCM reported in literature.

observed that single materials had a lower performance. On the other hand, ratios of 1:9 and 2:8 of CeO_2/La_2O_3 showed remarkable performance. Other factors that could influence C_2 selectivity, such as temperature and methane volume pulses, were also investigated. The main selectivity, conversion, and yield results for this system are shown in Fig. 3.

The data shown in Fig. 3 for the same catalyst indicates the increase of volume pulses of methane over $CeO_2/La_2O_3/SiO_2$ catalyst, from 0.1 to 6 cm^3 for each cycle. It can be observed that there is a decrease in selectivity and an increase in C_2 yield for higher methane pulses. Some features reported by the authors are related to recyclability, whereas the catalyst showed noteworthy stability and oxidative properties over many cycles, i.e., the catalyst recovered its activity after reoxidation process. Moreover, an increase in reaction temperature from 700 to 800 °C improved methane conversion, but the conversion was insensitive to an increase above 800 °C [16].

The role of oxygen species was studied in the same work [17]. According to the authors, a mobile lattice oxygen was responsible for interaction and activation of methane molecules to produce methyl radicals. A weakly bound oxygen specie was responsible for CO_2 production as non-selective specie that completely oxidize methane. Such oxidative species can be either an oxygen molecule adsorbed on the surface or oxygen atoms on the edges of the catalyst lattice [17]. On the other hand, the amount of strongly bound oxygen species responsible to increase ethylene and C_2 selectivity was found to be constant over the cycles. Further information about non-selective oxygen species was obtained by injecting hydrogen in the reactor before methane. In this way, C_2 selectivity was enhanced, as shown in Fig. 3, because hydrogen treatment depleted the loosely bound oxygen species [16].

Enhanced performance of La_2O_3 in CLOCM reactions was achieved by doping with Ag, which was previously reported as an OCM promoter [12,17]. Different loads of Ag in Ag-La_2O_3/SiO_2 were tested, and the best performance was achieved with ratios ranging from 3:10 to 6:10, as shown in Fig. 3. Higher loads of Ag result in surface blocking and decreased the selectivity. The increase in selectivity was attributed to a combined effect of Ag and La_2O_3 as active site and oxygen supplier, respectively. In this system reduced metal particles are responsible to keep methyl radicals at the surface, increasing its concentration and preventing complete oxidation. Moreover, silver nanocrystals could be responsible for buffering oxygen species from the metal oxide to the surface [12,16].

4.3. Mn-doped Na_2WO_4

The most employed OCM catalyst, $Na_2WO_4/Mn/SiO_2$, has been investigated in cyclic reactions [7,18–20]. This material has high oxygen storage capacity and good redox properties that are suitable for methane to C_2 conversion. Moreover, it has remarkable thermal and structural stability for long operation cycles. It is worth mentioning that for the synthesis of this catalyst the amorphous structure of silica as a precursor is of pivotal importance. It has been observed that, despite the transformation to α-cristobalite inert phase, there is a synergetic effect between the Na_2WO_4/Mn crystalline layers and the amorphous silica support that leads to increased selectivity. One reason is related to the decrease of the metal oxide layer thickness on the silica surface [18–20].

Salehoun et al. investigated $Na_2WO_4/Mn/SiO_2$ catalysts by XRD and identified the crystalline structures of the three main components: α-cristobalite SiO_2, Na_2WO_4, and Mn_2O_3 [18]. They showed that catalyst reduction (with Ar + CH_4) lead to formation of $MnWO_4$ and $Na_2WO_4.2H_2O$, which indicates that lattice oxygen was consumed. Additionally, they observed production of C_{2+} e CO_X in the absence of molecular oxygen, which indicates that lattice oxygen is responsible for methane conversion. By varying the reaction temperature, the contribution of two different oxygen species was proposed. At 800 °C, surface lattice oxygen is responsible for methane activation, and at 850 °C the bulk lattice oxygen has a major influence. The former is selective toward C_2 production, and the latter is selective toward CO [18].

The understanding of the reaction network that leads to the conversion of methane to C_2 products is one of the main challenges for the development of viable CLOCM processes by tuning catalyst properties and improving reactor design. The reaction network is rather complex due to concomitant gas phase and surface reactions, which are highly influenced by reactions on gas phase [56]. In the gas phase, several radical species are formed, whereas at the surface different oxygen intermediates can contribute to the selective or non-selective conversion of methane, as reported by Sung et al. and Greish et al. in their work with rare earth oxides catalysts [12,16]. Schomäcker's research group has extensively investigated the role of $Na_2WO_4/Mn/SiO_2$ catalyst for cofeed and CLOCM experiments for ethylene production [5,7,19,20,43,56]. By carrying out temporal analysis of products, both strongly and loosely bound oxygen species were identified. It was shown that in the $Na_2WO_4/Mn/SiO_2$ catalysts there is a higher ratio of selective species toward ethylene production [56]. Moreover, in a simulated experiment in absence of molecular oxygen, it was observed that theses oxygen species are differentiated by electrophilicity trend, nucleophilic and electrophilic species, that selectively activate methane molecules and are responsible for methane complete oxidation, respectively [5].

Some features of reaction network were investigated by TPSR using methane, ethane, and ethylene in absence of molecular oxygen [5]. Methane TPSR indicates that its activation in the catalyst surface is followed by a fast coupling of methyl radicals in the gas phase, due to initial production of C_2H_6, followed by a later increase in CO formation, which indicates that CO is formed preferentially by C_2 products oxidation. Ethane TPSR has ethylene as its major product and is activated mainly by oxidative dehydrogenation, which is limited by the catalyst capacity to supply oxygen, parallel thermal dehydrogenation occurs but at smaller rates. Ethylene TPSR confirms that complete oxidation occurs preferentially from C_2 products, whereas a non-selective highly reactive oxygen species activates C—H bond in ethylene. Moreover, by evaluation of the methane activation energy, the authors notice the influence of different oxygen species in this parameter that corroborates the simulated results: the electrophilic species are attributed to adsorbed oxygen, whereas the nucleophilic species can be either lattice oxygen or a dissociated oxygen that is strongly bound to the lattice [5].

In a CLOCM experiment carried out over $Na_2WO_4/Mn/SiO_2$ catalyst with variation of flow rate and temperature parameters, a maximum yield of 25% was obtained with a conversion of 42% and C_2 selectivity of 60%. This result, combined with other variation in this system is shown

in Fig. 4. It is related to the optimal operation parameters for methane conversion but indicates a limitation in the yield, which is attributed to competition among surface reactions in the catalyst, that leads to a decrease in selectivity. As previously mentioned, the complete oxidation of methane and its products is thermodynamically more favorable, compared to conversion to ethane and ethylene. Herein methane conversion is the rate determining step. For higher methane conversions there is an increase of ethane and ethylene partial pressures, followed by an increase of ethylene complete oxidation to CO_X. Therefore, the ethylene rate of deep oxidation is higher than the rate of ethane and ethylene formation. On the other hand, a lower conversion of methane leads to a lower partial pressure of ethane and ethylene, which avoids complete oxidation. Moreover, the different oxygen species play an important role in the interaction with ethane and ethylene and are responsible for complete oxidation of this products. A comparison between CLOCM with the co-feed system indicates that selectivity, yield, and methane conversion are remarkably improved in the looping system [19].

The role of OCM main products, ethane, and ethylene, was investigated in a chemical loop experiment [7]. Instead of methane, ethane and ethylene were injected, followed by catalyst oxidation in a subsequent step. By comparison with co-feed system, a lower conversion of ethylene is observed in CL conditions, as well as a lower CO_X selectivity. For ethane injection, the conversion in the co-feed system was similar to CL experiments, which is influenced by thermal dehydrogenation to produce ethylene. These results indicates that the CL reactor concept is an important tool to increase selectivity of the C_2 products. Moreover, the H_2 produced in the dehydrogenation of ethane competes with methane for the catalyst's oxygen sites limiting the conversion of methane. The production of methyl radicals has a lower activation energy than the dehydrogenation of ethane at low temperatures (<750 °C). Therefore, CLOCM should be carried out at lower temperatures that activate methane molecules and do not activate ethane. However, as the main product of such process is ethylene, the use of a second reactor is proposed to convert ethane to ethylene [7].

The optimization of catalytic properties of $Na_2WO_4/Mn/SiO_2$ was investigated in CLOCM by variation of specific surface area and precursors concentration [20]. Results for methane conversion and selectivity are shown in Fig. 4. Lower concentrations of Mn(II) resulted in a higher specific surface area. By carrying out CLOCM experiments, an optimum surface area of 3.2 $m^2\ g^{-1}$, corresponding to Mn(II) load of 2 wt%, was determined to result in maximum methane conversion. This condition coincides with the highest value of oxygen storage capacity. Higher loads of Mn result in a decrease in conversion. This is explained in terms of higher crystallinity of the manganese oxide at higher loads and to the presence of other oxidation states. The authors observed that manganese transits from Mn^{3+} to Mn^{2+} throughout the cycles confirming a Mars-van Krevelen type of mechanism. When evaluating the oxidation states of tungsten, they reported that there is a transition between $MnWO_4$ and Na_2WO_4 along redox cycles. Moreover, the results show that under OCM condition, the Na_2WO_4/Mn phase melts forming a homogeneous layer a few nanometers thick that strong adheres to the SiO_2 support. They found that the activity of the catalysts is dependent on the thickness of such layer and that there is an optimum layer thickness, theoretically calculated as 25 atomic layers of active compounds. If the layer is too thick (> 25 layers), part of its stored oxygen is not accessible and cannot be used in methane activation during a cycle, whereas thinner layers (< 25 layers) lacks structural flexibility to promote the redox reactions [20].

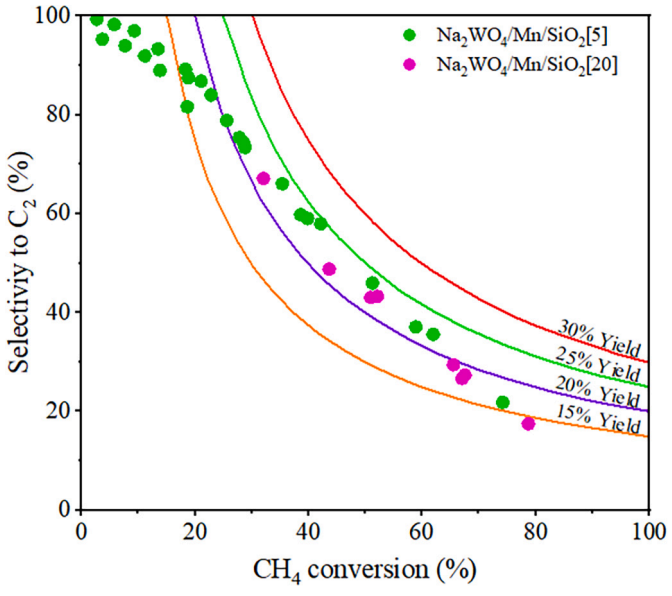

Fig. 4. Selectivity and conversion of $Na_2WO_4/Mn/SiO_2$ catalyst applied to CLOCM reported in literature. The different points comprise different experimental conditions, such as temperature (700 to 850 °C) and methane flow rate.

4.4. Perovskites

Perovskite-type ABO_3 oxides have also been investigated in CLOCM experiments due to several advantages [21,22]. Such systems have also been explored in co-feed OCM [44]. In the ABO_3 perovskite lattice, the A site is in the center of a dodecahedron structure and the B site coordinated with oxygens in an octahedral structure [21]. Depending on the elements that occupy the A and B sites, the electrophilicity of the lattice oxygen can be tuned to enhance C_2 selectivity of methane conversion [44]. Moreover, a moderate binding energy between oxygen species and the metal can favor the selective conversion of CH_4 [21].

$LaMnO_3$ perovskite was investigated as catalyst in CLOCM because it combines two elements that form the main oxides that are active for OCM, as reported in the previous sections [45]. The effect of Na doping in improving OCM selectivity was investigated in the work of Jiang et al. [21] The use of undoped $LaMnO_3$ result in a high conversion of methane but a very low C_2 selectivity (~2%). By adding Na, the selectivity was remarkably improved resulting in considerable C_2 yield of ~18%. The oxygen vacancies concentration was found to increases with increasing Na-doping level. Such effects can be attributed to the increase the activation barrier of C—H bond breaking and decrease the adsorption energy for methyl radicals [1]. The role of oxygen species was further investigated by O_2-TPD experiments. A surface lattice oxygen was identified as an active site for OCM reaction, and by doping with Na, a reduction in the temperature for this oxygen specie desorption was observed. Such reduction is explained in terms of an "un-fully reduced" oxygen specie from the lattice due to Na doping, similar to what has been observed in the works on the $Na_2WO_4/Mn/SiO_2$ catalysts [5]. In addition, TPR experiments have shown that Na doping leads to a shift of the $Mn^{4+} \rightarrow Mn^{3+}$ and $Mn^{3+} \rightarrow Mn^{2+}$ reduction pairs to lower temperatures and XPS results reveal an increase in the relative concentration of Mn^{4+} with respect to Mn^{3+} due to Na doping, which is also indicates that charge compensation and defect formation due to Na addition directly benefits selectivity [21]. Such recent result is another evidence of the good catalytic activity of Na-doped materials for OCM [4].

In the work Sun et al., the conventional OCM catalyst, Na_2WO_4, has been combined with $FeMnO_3$ [22]. A methane conversion of 20% was achieved, with a selectivity and yield toward C_2 products of 80% and 16%, respectively. Interestingly, the looping experiments reveal that during CH_4 oxidation the $FeMnO_3$ undergoes a reduction separating in two phases $MnFe_2O_4$ and MnO, as identified by XRD and Raman spectroscopy, respectively. In the subsequent catalyst oxidation step, it returns to the original perovskite structure. The decoration with Na_2WO_4 plays an important role in slowing the oxygen species release, thus reducing the overoxidation of methane, which results in high C_2 yields [22].

5. Features of reactor operation conditions

Several studies have focused on catalyst development; however, the design of the reactor has also been a matter of concern and must be considered to improve both the selectivity and yield for a viable process. A reactor design with optimal heat management toward auto-sustainable processes is essential. Greish et al. and Sung et al., reported that decreasing reactors diameter, for instance from 5.6 to 2.5 mm, resulted in higher selectivity and stability, due to a decrease of methane dilution [12,17]. Chung et al. reported that selectivity and yield can be tuned by variation of residence time in the reactor [6]. Increasing the residence time decreases the selectivity toward primary products, therefore a higher gas input favor C_2 products formation. Cruellas et al. [9], based on previous reports, simulated a system wherein the catalyst is diluted in inert particles, and consequently the reaction velocity is decreased by the heat management inside the reactor. Therefore, controlling residence time can improve the selectivity and provide tools to understand the complex reaction pathway of OCM reactions. The use of CL to understand the reaction network of OCM reaction and improve its selectivity was highlighted by Baser et al. [3]. They suggest that pure methane feeding can show the real capacity of the system to selectively convert methane to C_2 products, due to the split of oxidation and reduction in different steps. Therefore, the effect of catalytic activity (basic sites, oxygen vacancies, doping) and the oxygen species supplied by the catalyst is evidenced in each step. Moreover, parallel reactions with molecular oxygen in the gas phase are avoided.

Chung et al. have highlighted the importance of heat management for the process [6]. In their studies the heat of reactions is investigated in terms of catalyst interaction with both methane and ethane for its oxidation (catalyst reduction), and the process for catalyst regeneration with oxygen (catalyst oxidation). As the catalyst reduction and oxidation reactions have different enthalpies, the CL approach of splitting the conversion in two reactions steps enables a more efficient heat management in industrial operation. As the overall heat of reaction depends on the oxide, the authors take the example of several manganese oxides that are thermodynamically stable at 840 °C, and the respective redox pairs, such as Mn_2O_3–Mn_3O_4, Mn_3O_4–MnO, and Mn_2O_3–MnO. The catalyst reduction and oxidation reactions have heat of reaction of +198 kJ mol^{-1} and -522 kJ mol^{-1}, respectively Indeed, they observe a difference of almost 20 °C between each reaction step (oxidation/reduction). Therefore, splitting the reaction in two steps allows optimized heat management. In a co-feed system, which is carried out in a single step, the creation of hot spots can lead to catalyst sintering, that can directly influence the catalyst activity. Thus, the separation in CLOCM approach can improve the metal oxide catalyst stability over redox cycles.

Moreover, among several considerations, Chung et al. suggest that the exothermal reactions in the catalyst oxidation can be used to keep the reactor isothermally controlled [6]. The system can be auto sustainable from the energetic standpoint, i.e., the heating of air and CH_4 can be achieved by the heat generated in the oxidation step. On the other hand, by using internal tubes the heat can be exchanged and transported to produce steam from water and cogenerate electricity [6].

To make OCM economically viable, selectivity is a crucial factor. A high selectivity toward C_2 products decrease the capital investment and energy cost related to gas separation units for removal of CO_2 and other by-products [6]. A general conclusion from CLOCM research studies is that the chemical lopping concept clearly increases the selectivity toward C_{2+} products, despite the lower methane yield. Based on the this and the fact that the CLOCM system is more cost effective than traditional co-feed reactor, Fleischer et al. have proposed the use of several parallel fixed bed reactor operating as CLOCM systems having the gas feed being alternate among them [19]. As these systems operate at the same time scale a constant level of ethylene production can be achieved. Moreover, with the high levels of selectivity, the decrease of energy costs and methane separation from the products can significantly make CLOCM an viable process for industry [19].

6. Conclusion

In summary, CLOCM has great advantages over co-feed systems, and it is a promising alternative to achieve yield values of 30% or more that are needed for industrial viability. Co-feed OCM using molecular oxygen has limited C_2 selectivity due to partial or complete oxidation, whereas in CLOCM, methane oxidation takes place at catalyst surface in absence of molecular oxygen, offering the possibility of higher C_{2+} products selectivity, while complex units for product separation are avoided. The cyclic approach allows a better heat management, which can increase catalyst performance for longer operation cycles. Moreover, for some systems the temperature in CLOCM is lower as compared to co-feed OCM and parallel reactions in the gas phase are avoided by splitting the oxidation and reduction. In addition, there is a cost reduction for complex units for products separation, and a decrease of combustion risk by the mixture of oxygen and methane in co-feed reaction, the formation of hot spots is diminished due to separation of reduction and oxidation steps, and coke formation can be bypassed in the oxidation step by reaction with oxygen.

Despite these several advantages there remain challenges to be addressed for further catalyst development for CLOCM. Several catalysts have been reported, such as Mg—Mn oxides, rare earth oxides, recently the ABO_3 perovskite-type oxides, and the traditional Mn-Na_2WO_4 catalyst. The latter shows the highest activity, and the Li-Mg_6MnO_8 catalyst has the best performance. However, Li-doped catalysts have shown high instability over redox cycles. In this way some requirements for the design of catalysts must be considered: it must possess high oxygen storage capacity, and its redox properties must be optimized to exhibit high thermal and structural stability. Moreover, the catalyst must be selective for methane activation and avoid ethane and ethylene complete oxidation. Furthermore, despite all the work developed to date, the understanding of role of metal oxides catalysts in the OCM process is still not complete, but there is a consensus that there is a synergistic effect between high oxygen storage capacity, formation of surface vacancies, and influence of doping materials.

Declaration of Competing 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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