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Chapter 13

Syngas Production Using Natural Gas from the Environmental Point of View

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Additional information is available at the end of the chapter

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Abstract

The search for clean and low-cost fuels as alternative for petroleum is a popular research focus in the energy field. The demand of natural gas as an energy source has increased steadily. The high H:C ratio and the absence of heteroatoms make natural gas an attractive feedstock for synthetic fuels and chemicals that can replace those that are typically petroleum-derived. The search for efficient routes to convert methane to other higher added-value products is a challenge for the scientific community. In addition, new fields of oil and gas contain associated CO_2 (8–18%), and, in some specific fields, the associated gas encloses a higher CO_2 content (79%). In this context, the tri-reforming process combines two of the most problematic greenhouse gases (CH_4 and CO_2) to generate syngas for the synthesis of clean liquid fuels and valuable chemicals. Developments in tri-reforming processes, which include the new catalysts, are presented in this chapter.

Keywords: tri-reforming, syngas, catalysts, carbon dioxide, hydrogen production

1. Introduction

Significant efforts are being directed nowadays towards finding alternatives that could restrain the climate change. The consistent rise of CO_2 concentration in the atmosphere is known to be significantly detrimental to the environment. Thus, mitigating CO_2 is becoming an urgent need.

Current methods involving CO_2 mitigation can be broadly divided into two major categories, which involve (1) CO_2 capture and sequestration (CCS) and (2) CO_2 capture and utilization (CCU). Since the production of fuels/chemicals is an added feature along with mitigation in

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CO_2 valorization-based methods, they could be economically favorable. An energy-intensive CO_2 capture step is a common drawback of most CO_2 valorization methods that aim to mitigate CO_2 from major CO_2 emission sources (such as industrial flue gases).

Different methane-rich gas streams can be found, both of natural and of anthropogenic origin. A decrease in fossil fuels and environmental concerns across the globe enforced researchers to work on energy resources like methane, which is the most abundant natural gas on earth [1].

Therefore, it is of utmost importance to seek for technologies that could convert two of the main product gases responsible for the greenhouse effect, methane and carbon dioxide, avoiding their massive release into the atmosphere.

Reforming of methane is one of the most important industrial processes, which convert natural gas into synthesis gas. Syngas is an intermediate feedstock for the production of hydrocarbons and hydrogen for fuel cells. Synthesis gas is produced from natural gas via catalytic processes based on dry reforming of methane (DRM), steam reforming of methane (SRM) and partial oxidation of methane (POM) [2]. In fact, the available natural gas can be exploited for the production of chemicals and fuels.

The reforming processes are classified based on the energetic demand of the process and the type of reforming agent. Steam reforming of methane (SRM) produces a high ratio of syngas ($H_2/CO = 3$), suitable for the production of ammonia. This process is endothermic and requires high investments. The partial oxidation of methane, an exothermic reaction, is an alternative process with reduced capital and operation costs. However, the partial oxidation of methane (POM) needs oxygen, and the cost of its production is about 50% of the investment of the whole process. There is a high risk of explosion at an elevated temperature [3]. On the other hand, the dry reforming of methane (DRM) is a valuable reaction for biogas utilization and transformation of greenhouse gases (CH_4 and CO_2) in high-valued products. DRM produces a low syngas ratio ($H_2/CO = 1$), which is suitable for the syntheses of oxygenates [4–6].

Tri-reforming of methane (TRM) is nowadays of great interest, because it combines the steam and dry reforming and partial oxidation of methane ($CH_4 + O_2 + CO_2 + H_2O$) processes; however, it holds the main advantages and disadvantages of all processes, to some extent [7].

It is well known that the major limitation of methane-reforming processes is the rapid deactivation of the catalyst, which has been commonly attributed to coke deposition and catalyst sintering.

The tri-reforming of methane may drastically reduce the carbon deposition. Furthermore, the presence of O_2 in the feed allows the generation of energy in situ, due to the exothermal oxidation of methane, which increases the energy efficiency of the process. Besides, the possibility of changing the reactants' compositions, allows for a versatile synthesis of gas composition, which can be suitable for different applications of synthesis gas [8, 9].

2. Tri-reforming process

Energy is the most important issue to modern economies, and it is predicted that a fast-rising energy demand will require US $45 trillion for new infrastructure investment by 2030.

In particular, natural gas processes increase the options for the production of high added-value chemicals and energy demand. The Fischer-Tropsch (FT) technology is the main technology for the production of liquid fuels, named GTL process, but this technology is yet very expensive, due to the high costs of syngas production using steam reforming of methane (SRM) [7]. The tri-reforming process (TRM), introduced by Song et al. [10], allows to use flue gas and methane to produce syngas, which can be converted to methanol and higher hydrocarbons. This new process is a synergic combination of the endothermic CO_2 and steam-reforming reactions with the exothermic oxidation of methane, as shown in Eqs. (1)–(4) [11], which are carried out in a single reactor.

$$H_2O + CH_4 \rightarrow CO + 3H_2; \Delta H^0_{298K} = 206.3kJ.mol^{-1} \quad (1)$$

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2; \Delta H^0_{298K} = 247.3kJ.mol^{-1} \quad (2)$$

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2; \Delta H^0_{298K} = -35.6kJ.mol^{-1} \quad (3)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O; \Delta H^0_{298K} = -880kJ.mol^{-1} \quad (4)$$

In addition, during the tri-reforming process, methane cracking (Eq. (5)), CO disproportionation or Boudouard (Eq. (6)), water-gas shift (Eq. (7)) and complete oxidation of carbon reactions (Eq. (8)) occur simultaneously [12].

$$CH_4 \rightarrow C + 2H_2; \Delta H^0_{298K} = 75kJ.mol^{-1} \quad (5)$$

$$2CO \rightarrow C + CO_2; \Delta H^0_{298K} = -172kJ.mol^{-1} \quad (6)$$

$$CO + H_2O = CO_2 + H_2; \Delta H^0_{298K} = -41kJ.mol^{-1} \quad (7)$$

$$C + O_2 = CO_2; \Delta H^0_{298K} = -393.7kJ.mol^{-1} \quad (8)$$

The heat released during the POM reaction is used to supply the heat needed for the SRM and DRM reaction, and therefore the TRM reaction is energetically more efficient [13]. In addition, TRM offers several advantages for syngas production compared to the single reactions [14]. TRM does not require pure CO_2 supply in the reaction. This implies that the flue gas from the combustion processes of power plants or the coke oven gas (COG) from iron-making industries can be used directly as a CO_2 source for TRM process [15–17]. TRM can also be used to upgrade the syngas quality produced from biomass or coal gasification [18, 19]. The H_2/CO ratio in syngas produced from tri-reforming can be adjusted varying the amounts of reactants to satisfy the requirement for further processes, such as methanol and Fischer-Tropsch synthesis [20, 21]. In addition, integrating steam reforming and partial oxidation with CO_2 reforming could dramatically reduce or eliminate carbon formation on a reforming catalyst, thus increasing the catalyst life and process efficiency [14] due to the addition of O_2 in the feed, which also generates heat that increases the energy efficiency. Therefore, the tri-reforming has the advantage of using natural gas and flue gases from power plants. The syngas from tri-reforming is used for the production of chemicals (such as MeOH and dimethyl ether by oxo-synthesis), fuels (for the Fischer-Tropsch synthesis) and electricity in fuel cells, as shown in **Figure 1** [14].

Table 1 shows the advantages and disadvantages of tri-reforming compared to other reforming technologies [7, 18, 22].

However, due to the inherent problems of the reforming processes, there is a need to improve catalysts for optimizing the TRM process, improving the oxygen tolerance, resistance to coke formation and sintering of the metal-active sites at a high temperature.

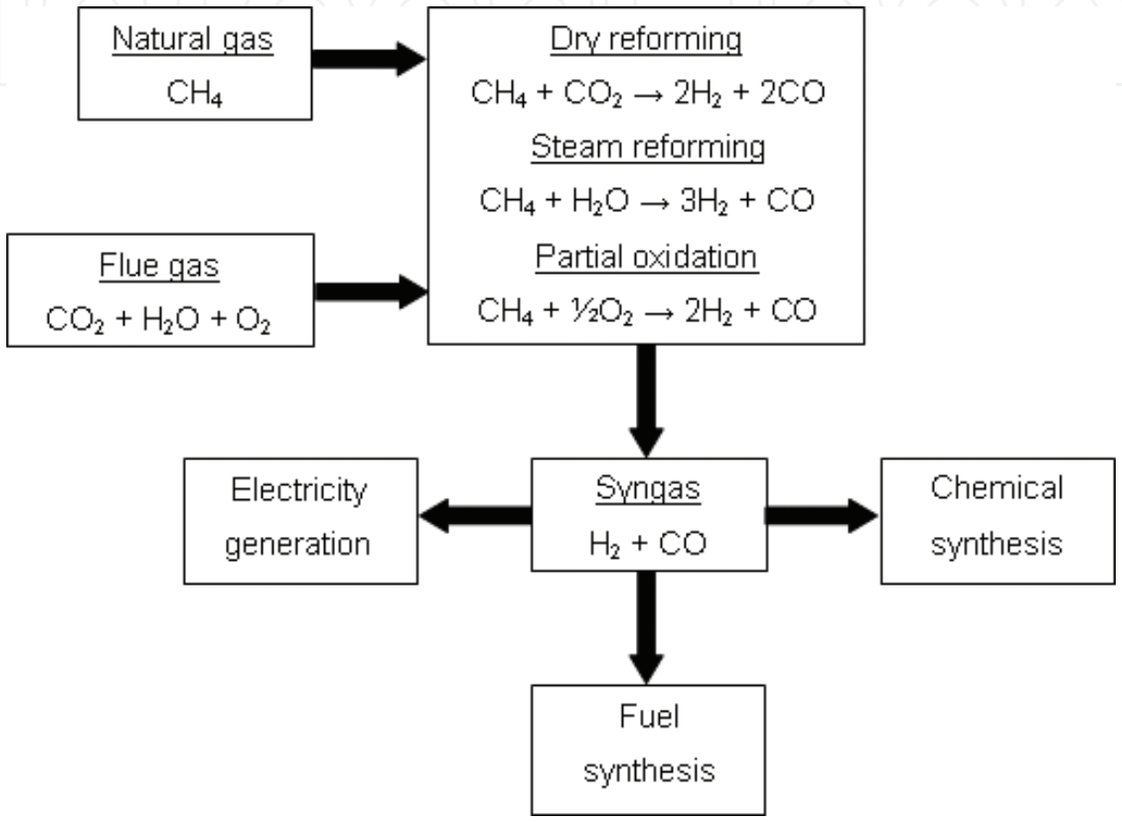


Figure 1. Tri-reforming of natural gas using flue gas from fossil fuel-based power plants.

Advantages	**Disadvantages**
Direct use of flue gases	Usually requires oxygen plant
High methane conversion	No existing industrial process
Elimination of CO_2 separation	No existing commercial catalysts
Different H_2/CO ratios	Would require high GHSV
Minimization of coke formation	Heat management
Use of waste H_2O/O_2	Mass management
Simplifying the processing system	

Table 1. Advantages and disadvantages of tri-reforming [7, 18, 22].

3. Catalysts for methane-reforming reactions

The drawback of methane-reforming processes is mainly the severe tendency to carbon formation that deactivates the catalysts [23–25]. Noble metal-based catalysts (Rh, Ru, Pt, Pd and Ir) presented a high activity and stability against coke formation [26, 27]. However, their costs are still highly prohibitive for feasible application in this process. In fact, nickel-based catalysts are more preferable in the CH_4 reforming, due to their availability and lower costs [28–30]. However, the stability of the nickel catalysts at elevated temperatures and the coke formation are the main obstacles for industrial applications [31, 32].

The addition of promoters to Ni-containing catalysts led to the reduction of coke deposition, better metal dispersion or smaller particle size, and the synergic effect between Ni and the promoter [33–36]. In fact, bimetallic catalyst exhibits a higher activity compared to noble metals but not totally eliminate the carbon deposition.

The metal dispersion influences the coke deposition, since this process is structure-sensitive. The build-up of carbon involves quite large active metal particles, which are usually formed at high reforming temperatures.

Alumina-based supports have been investigated mainly due to the high specific surface area, increasing the metal dispersion [37]. Nevertheless, the alumina supports easily deactivate due to the coke deposition and sintering. The formation of coke has been associated with the dehydration, cracking and polymerization reactions, occurring on the acid sites, while sintering is due to the transition of crystalline phase during reaction [37].

Additional improvement can be achieved using well-developed supports. An effort to overcome these problems is to search for basic additives or promoters, such as CeO_2, SiO_2, La_2O_3, BaO, CaO, SrO, MgO and ZrO_2 [37, 38].

Sintering of metal clusters can be prevented with supports having a strong interaction with the active component. In fact, ceria-based catalysts can minimize sintering and coke formation [39] compared to MgO, TiO_2, Al_2O_3, SiO_2 and ZrO_2 supports [40–46]. On the contrary, these supports facilitate sintering when submitted to higher temperatures. Moreover, ceria-based catalysts present good redox properties and high oxygen mobility, and as reported in the study, without noticeable oxygen mobility, the deactivation of the catalyst occurs very fast [47]. On the other hand, the thermal stability of pure ceria under the typical reforming conditions is quite poor.

3.1. Promising catalysts

Although tri-reforming has not yet been implemented commercially, similar to steam or to dry reforming, Ni catalysts supported on a wide range of different supported materials, such as Al_2O_3, ZrO_2, MgO, TiO_2, CeO_2, TiO_2, CeZrO and SiO_2, are the most popular catalysts for tri-reforming of methane [48].

Song et al. [14] suggested that the supports should have a high oxygen storage capacity that promotes CO_2 adsorption. They proposed a simplified mechanism for the CO_2 reforming

reaction. The first step occurs with the activation of methane, followed by the surface reaction and the adsorbed surface CO_2 species or adsorbed oxygen atoms (Eq. (9)); CO_2 is more acidic, and basic supports may preferentially interact with CO_2. Therefore, the CO_2 adsorption at the surface facilitates the reaction with CH_4 producing CO and H_2. Moreover, supports with a high oxygen storage capacity may also facilitate the dissociative adsorption of CO_2 into CO and adsorbed oxygen, according to Eq. (9) [14]

$$CO_2 + \square = CO + O^{\square} \tag{9}$$

where $^{\square}$ denotes an active site.

Perovskite-type oxides have attracted significant interest as promising catalytic materials with applications in a wide range of reactions, including total oxidation and partial oxidation of hydrocarbons, carbon monoxide oxidation, alkenes hydrogenation, alkanes hydrogenolysis, alcohol synthesis, dry reforming and water-gas shift reaction [49–51]. The perovskites contain metallic and non-metallic elements, with a well-defined crystal structure. In general, the molecular formula is represented by ABO_3, where A refers to an alkali metal, an alkaline earth metal or a lanthanide and B to a transition metal. These solids exhibit interesting properties such as superconductivity, ferromagnetism, appreciable thermal stability and conductivity and finally a high catalytic activity. The intrinsic properties of each perovskite are dependent on the type of inserted element and principally on the preparation method. In fact, perovskites as catalysts showed a reductive capacity under appropriate conditions. The metal particles are highly dispersed in the oxide matrix (AO_X), inhibiting sintering of metal particles and carbon deposition. In fact, the high thermal stability makes the perovskites promising catalysts for the reforming of methane. Therefore, they are attractive alternatives to classic catalysts traditionally used in these reactions such as supported nickel and noble metals.

Various perovskites, including $LaFeO_3$, $LaNi_xFe_{1-x}O_3$, $LaNiO_3$ or $La_{1-x}Ce_xFe_{0.7}Ni_{0.3}O_3$, have been found to exhibit a high activity in the steam reforming of methane with a minimal coke deposition under low steam-to-carbon ratios [52–67]. However, the need for high-operating temperatures (e.g. $T \geq 600^{\circ}C$) of methane-reforming reactions provokes irreversible structural changes, including structural collapse and dissolution of (reactive or inactive) metal particles from the perovskite lattice [57–60, 63, 64].

Choudhary et al. [63] verified that the oxygen from the $La_{1-x}Sr_xFeO_3$ perovskite-type oxides surface was responsible for the complete oxidation of CH_4–CO_2 and H_2O, while the bulk lattice oxygen was responsible for the deep reduction of Fe^{3+}–Fe^{2+}, and this was suitable for the partial oxidation of CH_4–H_2 and CO. The $La_{1-x}Sr_xFeO_3$ has had good repeatability in the catalytic performance, and no significant deactivation was observed over five redox cycles.

The $LaCrO_3$ and $LaFeO_3$ oxides doped with alkaline earth (AE = Ba, Ca, Mg and Sr) metals were prepared and studied on how the atomic oxygen influences the partial oxidation of methane to syngas [66]. A-site doping with AE metals generally increases the mobility of lattice oxygen ions and thus decreases the temperature for the hydrogen and CO production, when compared with the non-doped $LaCrO_3$ and $LaFeO_3$ oxides. There are minor structural changes during the partial oxidation of methane of $LaCrO_3$, which can be regenerated by

oxidation at 950°C. However, the $LaFeO_3$ presented negligible structural modifications. The stability of the perovskites occurs during repeated reaction cycles of generation-regeneration.

The $LaFeO_3$, $La_{0.8}Sr_{0.2}FeO_3$ and $La_{0.8}Sr_{0.2}Fe_{0.9}Co_{0.1}O_3$ perovskite-type oxides were investigated in a continuous flow and sequential redox reaction [67] for the partial oxidation of methane in the absence of gaseous oxygen. The authors observed that methane reacted with sub-surface oxygen species of perovskite oxides in the absence of gaseous oxygen. The sequential redox reaction revealed that the structural stability is attributed to the continuous oxygen supply in the redox reaction, which evidences an excellent structural stability of the perovskite materials.

Other perovskites were employed for the DRM, SRM and POM reactions [68–72]. The effect of replacing cobalt by iron in $LaCo_{1-x}Fe_xO_3$ (x = 0.0, 0.5 and 1.0) perovskite-type oxides over its physical properties and catalytic performance in the partial oxidation of methane (POM) was investigated. The product distribution varying with space time and with perovskite-type catalyst employed is found to be remarkable. For lower W/F values, the major product was H_2 for the $LaCoO_3$ (55.8%) and $LaCo_{0.5}Fe_{0.5}O_3$ (59.2%), with similar ratios H_2/CO (1.8–1.9) and a low CO_2 formation [73].

We studied the combined dry and partial oxidation reaction on $LaCrO_3$ and perovskites, fed with CH_4:CO_2:O_2 = 1:1:0.5 and using a GSVH 60,000 h^{-1} at 700°C for 4 h. The conversions were 17% CH_4 and 94% O_2, respectively, and no conversion of CO_2. Results showed an increasing formation of CO_2 and a H_2/CO ratio equal to 2.7, which suggests that the partial and total oxidation of methane initially takes place, producing CO, CO_2 and H_2O, and subsequently the steam and dry reforming occur to produce syngas. In fact, the water-gas shift reaction also takes place due to the high H_2:CO ratio.

3.2. Effect of O_2 and H_2O concentration

Steam reforming of methane is the only large-scale industrial process currently available for the production of synthesis gas, producing high-purity hydrogen with a H_2/CO ratio equal to 3. The partial oxidation of methane produces synthesis gas with a H_2/CO ratio of 2, as required for methanol synthesis. However, the POM reaction is exothermic, and the control of the temperature of this process is difficult. Tri-reforming of methane is energetically favorable compared to the steam reforming of methane and partial oxidation of methane. The process is energetically thermal neutral. Compared to the SRM and POM reactions, the tri-reforming process has the advantage to produce different H_2/CO ratios.

Singha et al. [74] found the optimum feed ratio and the effect of O_2 and H_2O concentration (mole ratio) conditions for the reaction, by monitoring the feed mixture and keeping the methane to CO_2 mole ratio constant. The addition of oxygen in the feed helps to attain a thermal-neutral balance and compensate the heat necessary for the endothermic reactions occurring during the whole process [75]. A high oxygen concentration in the reaction feed inhibits the CO_2 reforming and lowers the CO_2 conversion [13] because the reaction between oxygen and methane is thermodynamically favored over the reaction between methane and CO_2. The higher concentration of oxygen in the feed allows a maximum methane consumption, and the available methane for the dry and steam reforming is very low [76]. **Table 2** shows the effect of O_2 concentration

Catalyst	GHSV (ml.g^{-1}.h^{-1})	Feed ratio, O_2:CO_2:H_2O:CH_4:He	CH_4 conv. (%)	CO_2 conv. (%)	H_2O conv. (%)	H_2/CO ratio
4.8NiZrO_2	80,000	0.75:1:2.1:5:18	60	50	55	2.3
		1:1:2.1:5:18	83	81	82	2.0
		1.25:1:2.1:5:18	90	38	89	3.0

Table 2. The effect of O_2 concentration (mole ratio) on the reactant conversions verified by reference [74].

over methane, CO_2 and H_2O conversions and H_2/CO ratios [74]. The effect of concentration of O_2 over the reactant conversion was mainly due to the heat generated by the partial oxidation and complete oxidation of methane and the enhanced coke removal process [76, 77]. Increasing O_2 concentration, the total oxidation of methane also increases, due to the exothermic reaction, and the amount of energy is released. The heat generated is useful for the steam- and dry-reforming reactions, which are endothermic, minimizing the required temperature to obtain a higher CH_4 conversion [78] and external energy. On the opposite, lower O_2 concentrations led to lower conversion; however, increasing the temperature, H_2O and CO_2 react with methane to produce synthesis gas [77]. The higher H_2/CO ratio was attributed to the steam reforming of methane, producing a H_2/CO ratio of 3, attributed to the water-gas shift reaction, which produces only hydrogen, without the production of CO [79]. On the other hand, with increasing temperature, one observes that the RWGS (reverse water-gas shift) reaction outweighs other reactions [77].

3.3. Effect of space velocity and methane/oxygen ratio

The effect of replacing cobalt by iron in $LaCo_{1-x}Fe_xO_3$ (x = 0.0, 0.5 and 1.0) perovskite-type oxides on its catalytic performance in the partial oxidation of methane (POM) process was investigated, varying the space velocity and methane/oxygen ratio. The inlet methane to oxygen proportion was fixed at 2:1. The methane conversion increased with the space time and the maximum conversion was 31% at 0.67 kg.s.mol^{-1} for the LF perovskite. In terms of product selectivity, the catalysts produced mainly H_2 and CO, CO_2, C_2H_4 and/or C_2H_6, as shown in **Table 3**. The product distribution varying with space time and perovskite type catalyst is found to be remarkable. The H_2 production decreased by about a half and the CO decreased four times for both LC and LCF catalysts. However, the CO_2 formation increased by a factor of about 10, and the H_2/CO ratio also increased by a factor of 2. Different was the product distribution of the LF perovskite presenting low H_2 and CO formations and a high production of CO_2, but a significant higher formation of C_2 hydrocarbons compared to the other samples as W/F increases [73].

Catalytic tests with the LF and LCF perovskites were also performed with a methane/oxygen ratio of 4 (W/F = 0.67 kg.s.mol^{-1}). **Table 4** shows that increasing the CH_4/O_2 ratio to 4, the methane conversion was halved, compared to the previous condition at a CH_4/O_2 ratio of 2 [73].

The formations of ethane and ethylene are attributed to secondary reactions. In particular, the oxidative coupling of methane reaction takes place, which increased the C_2H_4 and C_2H_6 to C_2H_4 at high temperatures ($2CH_4 + 1/2O_2 \rightarrow H_2O + 1/2C_2H_6$). Parallel reactions of oxidative or non-oxidative dehydrogenation of ethane would occur, converting also C_2H_6 to C_2H_4 and then

W/F (kg.s.mol^{-1})	Catalysts	X CH_4 (%)	H_2/CO	Selectivity (%)			
				H_2	CO	C2	CO_2
0.16	LC	13.7	1.8	55.8	31.5	5.50	7.10
	LF	19.2	1.6	46.0	28.0	4.10	22.0
	LCF	17.1	1.9	59.2	30.9	3.80	6.10
0.40	LC	22.0	2.8	22.2	7.90	1.50	68.4
	LF	28.1	2.2	16.6	7.50	3.10	72.8
	LCF	27.7	3.2	20.5	6.50	0.90	70.2
0.67	LC	28.6	3.5	25.7	7.30	0.70	66.3
	LF	31.0	3.2	8.30	2.60	5.30	83.8
	LCF	28.7	4.4	22.2	5.10	0.80	72.0

Table 3. Conversions and selectivity results over perovskites. Experimental conditions: P = 1 atm, inlet molar CH_4/O_2 ratio = 2/1, space time of reactants = 0.16, 0.40 and 0.67 kg s mol^{-1} and temperature of 700°C [73].

CH_4:O_2	Catalysts	X CH_4 (%)	H_2/CO	Selectivity (%)			
				H_2	CO	C2	CO_2
2	LF	31.0	3.2	8.30	2.60	5.30	83.8
	LCF	28.7	4.4	22.2	5.10	0.80	72.0
4	LF	15.5	0.0	0	2.70	10.5	86.8
	LCF	15.5	2.0	5.00	3.60	0.80	90.6

Table 4. Conversions and selectivities over LF and LCF perovskites. Experimental conditions: P = 1 atm, inlet molar CH_4/O_2 ratio = 2/1 and 4/1, space time of reactants = 0.67 kg s mol^{-1}, and temperature of 700°C [73].

ethane could be oxidized to CO_2. This last hypothesis is reinforced due to the increasing CO_2 concentration at higher temperatures, most likely due to the oxidation of part of C_2H_6 (which leads to H_2O and CO_2), according to the following reactions, suggesting different reaction paths: $C_2H_6 + 1/2O_2 \rightarrow C_2H_4 + H_2O$ and $C_2H_6 \rightarrow C_2H_4 + H_2$.

4. Discussion

Different reactions may occur in the whole process; the formation of the desired product with maximum selectivity depends on the input feed mixture. Steam increases the methane reforming and the water-gas shift (Eq. (7)) (WGS) reaction. It also helps to reduce the carbon deposition, which occurs during the dry reforming of methane [75]. Therefore, the addition of H_2O is thermodynamically more favorable for the methane reforming than for the dry reforming [13]. For a lower H_2O concentration, the methane conversion was lower than the CO_2 conversion, which is assigned to the competition between H_2O and CO_2 molecules with methane. Increasing the H_2O concentration input, the CO_2 conversion decreases. Both WGS and steam reforming are equally important at a temperature below 650°C; however, with

increasing temperature, the H_2O conversion increases. Above 650°C, the RWGS reaction prevailed, producing less H_2 and decreasing the H_2/CO ratio [77, 80].

The reaction mechanisms are yet unknown for oxide catalysts and in particular for perovskite structures, which apparently are the most promising catalysts for the tri-reforming, based on the combined SRM, DRM and POM reactions. One explanation is that these materials present defects which promote the modification of electronic effects. Indeed, electronic effects may arise in the presence of ions with different charges of those belonging to the ions of the network, or as a consequence of the transition energy levels of electrons normally filled (usually the valence band) to empty levels (the conduction band). In all cases, when an electron is missing, that is, when there is an electron deficiency, this is usually called electronic holes. In the absence of an electric field, the ionic networks of the oxide structures tend to be electronically neutral, which requires that charge defects are compensated by the presence of other filler defects in order to obtain the condition of electro-neutrality, making the structure more stable. This means that charge defects are always present as a combination of two or more types of failures [55].

A reaction mechanism on mixed oxides can be suggested, assuming that CH_4 is activated by the metal at the surface, forming carbon and H_2. The carbon atoms adsorbed at the surface can react directly with oxygen, forming CO and H_2. These intermediate species may react with the adsorbed CO_2 species or dissociated steam. Song et al. [14] claim that the different extent of interaction between CO_2 and catalysts could be responsible for this mechanism. They assumed that the interaction between CO_2 and the catalyst could change the CH_4 conversion rate, based on a simplified Langmuir-Hinshelwood (L-H) mechanism (Eqs. (10)–(12)).

$$CH_4 + \square \rightarrow CH_4^{\square} \tag{10}$$

$$CO_2 + \square \rightarrow CO_2^{\square} \tag{11}$$

$$CH_4^{\square} + CO_2^{\square} \rightarrow 2CO + H_2 + 2^{\square} \tag{12}$$

where $^{\square}$ are the metallic surface sites.

They observed that the reaction order of CH_4 on Ni/MgO is strongly compared to the adsorption of CO_2 over Ni/MgO/CeZrO which is close to zero. This suggests that the CH_4 conversion rate almost does not change with the partial pressure of CO_2. However, it was found that Ni/MgO/CeZrO has even more stronger interaction with CO_2 than Ni/MgO. In fact, the sites for a strong CO_2 adsorption over Ni/MgO/CeZrO are probably not the same as for CH_4 adsorption. It is important to note that the metal is itself believed to be able to activate CH_4, as suggested by Rostrup-Nielsen [47], while the types of supports, like MgO, facilitate the adsorption of CO_2. Hence, the locations of the interfaces between Ni and supports are fundamental, where the adsorption and reaction take place.

5. Conclusion

The energy crisis is a problem which will get exacerbated with depleting crude oil reserves around the world. There is an urgent need for alternative fuels around the world. The conversion

of CO_2 to a high-valued product could provide the necessary economic incentive towards both CO_2 mitigation and fuel generation. The study reported new strategies of CO_2 valorization. The tri-reforming produces directly synthesis gas from flue gases using methane as a co-feed. The utilization of CO_2 without pre-separation from its sources saves energy, since a substantial energy input is required for CO_2 separation from its concentrated sources [81]. Tri-reforming of methane can be carried out by using CO_2, H_2O and O_2 as a co-feed with natural gas or methane, and flue gas can be a very good source of highly concentrated feed for the tri-reforming process. New catalysts have been suggested with suitable promoters, mixed oxides and different supports, resistant to coke formation and sintering of the metal-active sites and stable at an elevated temperature. Stable and active catalysts for industrial application are under development, and researches are expected to bridge the gaps in science and technology for the tri-reforming process, providing further improvements and economically feasible.

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