

Review Article

Syngas Generation from Methane Using a Chemical-Looping Concept: A Review of Oxygen Carriers

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Conversion of methane to syngas using a chemical-looping concept is a novel method for syngas generation. This process is based on the transfer of gaseous oxygen source to fuel (e.g., methane) by means of a cycling process using solid oxides as oxygen carriers to avoid direct contact between fuel and gaseous oxygen. Syngas is produced through the gas-solid reaction between methane and solid oxides (oxygen carriers), and then the reduced oxygen carriers can be regenerated by a gaseous oxidant, such as air or water. The oxygen carrier is recycled between the two steps, and the syngas with a ratio of $H_2/CO = 2.0$ can be obtained successively. Air is used instead of pure oxygen allowing considerable cost savings, and the separation of fuel from the gaseous oxidant avoids the risk of explosion and the dilution of product gas with nitrogen. The design and elaboration of suitable oxygen carriers is a key issue to optimize this method. As one of the most interesting oxygen storage materials, ceria-based and perovskite oxides were paid much attention for this process. This paper briefly introduced the recent research progresses on the oxygen carriers used in the chemical-looping selective oxidation of methane (CLSOM) to syngas.

1. Introduction

Methane, the principal constituent of natural gas and coal-bed gas, is an excellent raw material for production of fuels and chemicals [1]. Conversion of methane to value-added products can be achieved in two ways, either via syngas (a mixture of CO and H_2) as an intermediate or directly into C_2 and higher hydrocarbons. Since the direct catalytic conversion of methane is inefficient, almost all the commercial processes for large scale chemical utilization of methane such as Fischer-Tropsch synthesis, methanol, or dimethyl ether production involve syngas [2].

Syngas generation from methane can be achieved in three routes: water steam reforming (SMR), carbon dioxide reforming (CDR), and partial oxidation of methane (POM) [3]. The two reforming reactions are all highly endothermic and operated at high temperature and high pressure, termed as costly chemical processes. POM technology, by contrast,

is a mildly exothermic route, which makes the process less energy and capital cost than the reforming routes. In addition, it also allows excellent syngas yield in compact reactors due to the fast reaction rate and product selectivity [3–5]. However, this technology requires additional safety measures to avoid the risk of explosion due to the premixing of CH_4/O_2 mixture and pure oxygen supply to avoid the dilution of syngas by nitrogen and the formation of NO_x [6], which partly offset its advantages in the saving of energy and capital cost. To avoid such problems, a chemical-looping concept was proposed to use in the POM technology.

2. Chemical-Looping Concept

The term “chemical looping” is a new concept for fuels conversion, which is based on the transfer of oxygen from gaseous oxygen source to the fuel by means of a cycling process using solid oxides as oxygen carriers to avoid direct

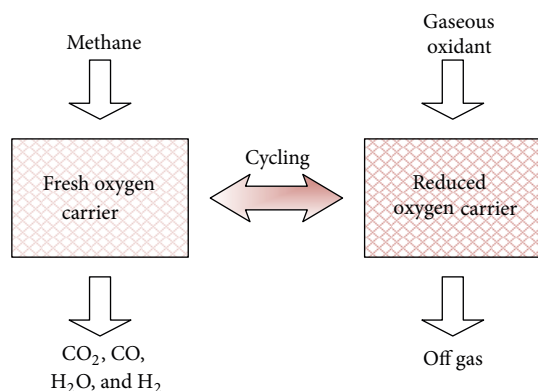


FIGURE 1: Schematic of chemical-looping concept for methane conversion.

contact between fuel and gaseous oxygen [7]. In the case of methane as fuel, the schematic of the chemical-looping process was shown in Figure 1. Lattice oxygen in oxygen carriers was used to oxidize methane, and then the reduced oxygen carriers can be reoxidized by gaseous oxidant to restore its initial state. Two interconnected reactors or fluidized-bed system are used in this technique to achieve the circulation of oxygen carrier between the oxidizing and reducing steps.

The first design using this concept was developed for power generation, which is known with the general term “chemical looping combustion” (CLC). For this process, the oxygen carrier can convert fuels to H_2O and CO_2 , and the reduced oxygen carriers must be reoxidized by air. Because of the separation of fuels from air, this technology is identified as owning inherent advantages for CO_2 separation with minimum energy losses [8]. Further designs of this concept were used in the syngas production from methane. After methane is oxidized to CO_2 and H_2O by oxygen carriers, the by-product gases (CO_2 and H_2O) were introduced into another reactor (reforming reactor) to reform with additional methane to produce syngas in the presence of a reforming catalyst (e.g., $\text{Ni}/\text{Al}_2\text{O}_3$) [9, 10]. Since the additional reforming process is a highly endothermic reaction needing large energy supply, this technology is less-than-ideal for syngas generation.

On the other hand, the direct generation of syngas by the reaction between oxygen carriers and methane is more acceptable, but this process needs an oxygen carrier owning ability to selectively oxidize methane. This vision was firstly realized over CeO_2 oxygen carrier, and the authors also proposed that the reduced oxygen carrier can be reoxidized by H_2O with obtaining H_2 simultaneously [11, 12]. In this case, the design and elaboration of suitable oxygen carriers with high activity, selectivity, and redox stability for methane selective oxidation is a key issue for this technology.

Comparing with the traditional POM process, the chemical-looping concept allows air instead of pure oxygen as oxygen source without the dilution of product gas with nitrogen, which brings about considerable cost saving. When using H_2O as an oxidant (two-step SRM process), it gives the possibility of coproduction of pure hydrogen without

separating equipments and syngas with a H_2/CO ratio of 2.0 which is ideal for the major downstream processes such as methanol production or Fischer-Tropsch synthesis. The present paper would mainly discuss the progresses on the oxygen carriers for this technology.

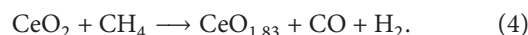
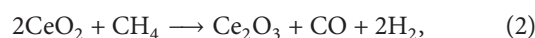
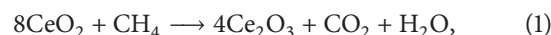
3. Oxygen Carriers for Chemical-Looping Selective Oxidation of Methane (CLSOM)

Chemical-looping concept involves the use of a redox cycle process of chosen oxygen carriers to implement the selective oxidation of methane to syngas. The yield of syngas depends on the activity and selectivity of the oxygen in oxygen carriers. In this case, selection of the oxygen carrier, which relies on the understanding of reaction mechanism of methane selective oxidation in the absence of the gaseous oxygen, is considered as one of the most essential components of the CLSOM process.

For the CLC process, it is proposed that the oxygen carriers must own the following properties in chemistry [7, 8]: (i) sufficient oxygen storage and transport capacity; (ii) high reactivity in both reduction and oxidation cycles; (iii) ability to completely combust a fuel; (iv) ability of resistant to agglomeration and carbon deposition. This list also applies to the CLSOM oxygen carriers except the third one (iii), which should be changed to “ability to selectively oxidize a fuel.”

Most of previous technical literatures on CLSOM focused on development of suitable oxygen carrier materials for methane selective oxidation. Ceria-based materials and perovskite-type oxides were paid the most attention due to their high lattice oxygen activity, excellent redox properties, and good thermal stability.

3.1. CeO_2 -Based Oxygen Carriers. The selective oxidation of methane to CO and H_2 (syngas) by gas-solid reaction was firstly achieved over CeO_2 oxygen carrier [11, 12]. The reaction between methane and CeO_2 may occur in four equations:



The thermodynamic considerations of the reactions in (1)–(4) were shown in Figure 2. It is clear that the complete oxidation of methane to CO_2 and H_2O by CeO_2 (reaction (1)) is thermodynamically unfeasible under 1000°C , and the syngas generation through selective oxidation of methane by CeO_2 is favorable with the reaction temperatures $\geq 700^\circ\text{C}$. The experimental results supported the thermodynamic analysis [12]. It shows that syngas with H_2/CO ratio of 2.0 was indeed produced via the gas-solid reaction between methane and CeO_2 at 700°C , and the reduction degree of CeO_2 reached 21% with platinum as a catalyst, suggesting that almost all the CeO_2 was reduced to Ce_2O_3 . This indicates that the oxidation of methane over CeO_2 may occur follow (2) in the presence of platinum.

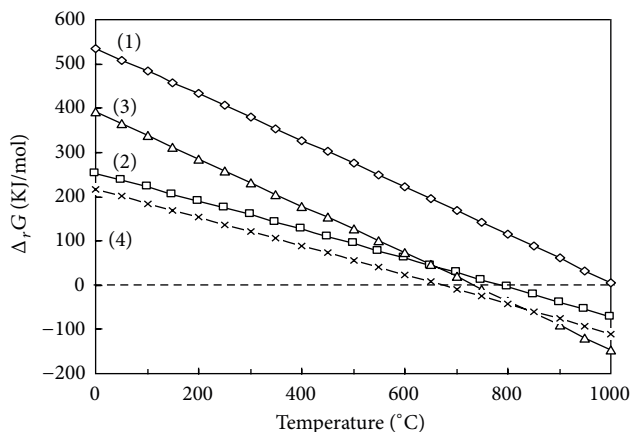


FIGURE 2: Thermodynamic calculations for the possible reactions between methane and CeO_2 [14].

Fathi et al. [13] also investigated the reaction between methane and CeO_2 with $\gamma\text{-Al}_2\text{O}_3$ as a support and Pt or Rh as a promoter. They observed that the selectivity to syngas depends on the reduction degree of CeO_2 . Numbers of CO_2 and H_2O were produce in the early stage of the reaction, and then the syngas selectivity increased quickly with the reduction degree of cerium oxide. Pt or Rh promoters could lower the temperature necessary to reduce the cerium oxide but also result in the formation of carbon deposition. Pantu et al. [6] found that the surface area of Pt/ CeO_2 sample affects the formation rate of syngas: methane conversion slightly increased, and syngas selectivity slightly decreased with increasing surface area. This indicates that ether high or low surface area of oxygen carrier will reduce the yield of syngas. They also observed that there was no significant effect of Pt loading on the activity of CeO_2 for methane oxidation, and the differences in metal dispersion on CeO_2 are not substantial.

Wei et al. [14] investigated the effects of CeO_2 loading on the reactivity of $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ oxygen carrier for methane selective oxidation in the absence of platinum catalyst. The results showed that higher CeO_2 loading will seriously decrease the selectivity of syngas. The other major innovation in this paper is the use of molten salt system as thermal carrier, which can avoid the agglomeration of circulating particles and improve the thermal efficiency of the whole reaction system.

It is generally accepted that the addition of Zr^{4+} could enhance the oxygen storage capacity by increasing the oxygen vacancies of ceria. Otsuka et al. [15] tested the reactivity of $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ for the direct conversion of methane to syngas by gas-solid reactions. The formation rates of H_2 and CO were increased, and the activation energy was remarkably decreased due to the incorporation of ZrO_2 into CeO_2 . The conversion of CH_4 to H_2 and CO could be achieved at a temperature as low as 500°C by using $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ in the presence of Pt, which is 200°C lower than CeO_2 sample. Pantu et al. [6] observed that addition of ZrO_2 to CeO_2 significantly increases the methane oxidation rate and the reducibility of the CeO_2 but decreases the selectivity to H_2

and CO . Wei et al. [16] also reported a similar observation on using $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ as oxygen carrier, but they found that the ZrO_2 -rich materials own better activity and stability.

Kang and Eyring [17, 18] investigated the activity of the Ce-Zr-Tb-O system for methane oxidation and found that the oxygen transfer capacity and the oxygen storage capacity are equally important for syngas generation. The reactivity of ceria-zirconia oxides doped by Pr, Gd, or La for methane conversion was also investigated by CH_4 -TPR technology and pulse reduction experiments, and it is proved that Pr-doped sample showed good activity for syngas generation [19]. The reaction between methane and Ce-Zr-Pr-O oxygen carrier with Pt as catalyst at high temperatures is controlled by the lattice oxygen diffusion, while the reactivity of weak bound surface oxygen determine the activity of the mixed oxides at the lowest temperature ($\sim 550^\circ\text{C}$).

Sadykov et al. [20] designed incorporating Sm^{3+} and Bi^{3+} cations into the ceria lattice to enhance the oxygen mobility while increasing the rate of methane dissociation by supporting Pt, and the results were also compared with the Pt/Ce-Zr-La-O mixed oxides. It showed that only the Ce-Sm-based oxide system is promising for methane selective oxidation by gas-solid reaction due to a high mobility and reactivity of the lattice oxygen, good selectivity for syngas generation, and high stability in redox cycles. The selective conversion of methane into syngas by lattice oxygen depends not only on the route of its primary activation (i.e., on supported Pt clusters) but on the features of activated fragments transformation on the support surface as well, provided the lattice oxygen mobility that is comparable.

Several reports showed that the oxidation activity and redox property of the ceria can be strongly enhanced by the addition of Fe^{3+} due to the formation of surface structural defects and Ce-Fe solid solution [21–25]. In addition, the modified iron oxides can also produce CO and H_2 through reduction with methane in an appropriate condition [26, 27], and that the iron species can strongly enhance the adsorption of methane [28]. Fe_2O_3 is possibly the most common and one of the cheapest metal oxides available in nature, and Fe^{3+} are very suitable as a dopant to improve the performance of ceria [29, 30]. Combination of CeO_2 and Fe_2O_3 gives people very high expectation to obtain attractive oxygen carriers for methane selective oxidation. Given the above, the investigation on the possibility of using $\text{CeO}_2\text{-Fe}_2\text{O}_3$ composite as oxygen carrier for methane selective oxidation attracted much attention [31–41].

It was reported that the $\text{CeO}_2\text{-Fe}_2\text{O}_3$ mixed oxides own good activity, selectivity, and stability for syngas generation through gas-solid reactions, as shown in Figure 3, and the interaction between exposed Fe_2O_3 and Ce-Fe solid solution in the oxygen carrier plays an important role on the syngas generation [36]. In addition, the dispersion of surface Fe_2O_3 and the formation of the Ce-Fe solid solution were enhanced by the redox treatment, which made the oxygen carrier very stable in the successive generation of syngas [36]. The selectivity of Ce-Fe mixed oxides for syngas production is strongly affected by the specific surface area of oxygen carriers, and high surface area would result in abundant

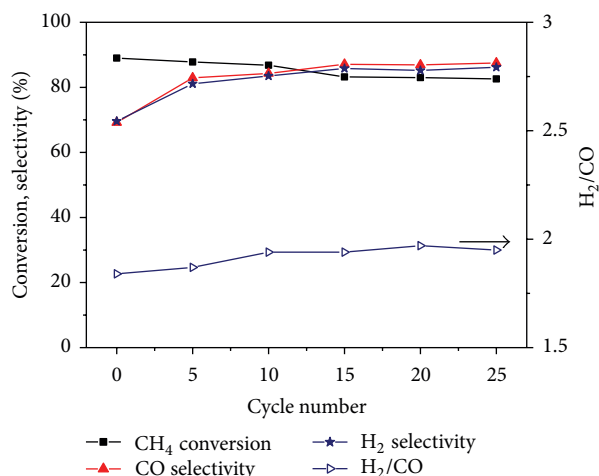


FIGURE 3: The effect of redox cycle number on the selective oxidation of methane using $\text{Ce}_{0.7}\text{Fe}_{0.3}\text{O}_2$ oxygen carrier at 850°C [36].

surface adsorbed oxygen, favoring the complete oxidation of methane to carbon dioxide and water [42].

For the reaction process between methane and Ce-Fe mixed oxides [36], methane was found to adsorb and activate on the reduced iron and cerium sites, and the subsequent oxidation of activated methane relied on the lattice oxygen mobility of the oxygen carrier. The dispersion of surface iron species and the consistence of oxygen vacancy in Ce-Fe mixed oxides in turn markedly affect the formation rate of syngas, and the strong interactions between dispersed Fe species and Ce-Fe solid solution have a distinct positive effect on the catalytic activity for methane selective oxidation.

Comparison of Ce-Zr and Ce-Fe mixed oxides demonstrated that the two samples showed similar activity for methane oxidation, but the Ce-Fe sample revealed higher selectivity of syngas, as shown in Figure 4 [33]. Addition of ZrO_2 into $\text{CeO}_2\text{-Fe}_2\text{O}_3$ system could enhance the interaction between iron and cerium oxides via increasing the oxygen vacancy concentration and improving the dispersion of free Fe_2O_3 , which improved the activity of Ce-Fe mixed oxides for methane selective oxidation. However, heavy loading of ZrO_2 would lead to a phase segregation of CeO_2 and Fe_2O_3 from the Ce-Fe solid solution, resulting in a decrease in syngas selectivity [34].

The effect of supports (Al_2O_3 , SiO_2 , and MgO) on the activity and selectivity of Ce-Fe-Zr mixed oxides for methane selective oxidation was also investigated [40]. Al_2O_3 support could result in the complete oxidation of methane, and SiO_2 obvious reduced the reactivity of Ce-Fe-Zr mixed oxides. On the other hand, MgO support strongly enhanced the activity and selectivity of Ce-Fe-Zr oxygen carriers for syngas generation.

Ce-Cu-O, Ce-Mn-O, and Ce-Nb-O and Ce-Ni-O were also considered as an oxygen carrier for methane oxidation [38, 43–45]. Compared with the Ce-Fe mixed oxides, Ce-Cu-O and Ce-Mn-O oxygen carriers are more favorable to completely oxidize methane [38], and the Ce-Ni-O would result in the decomposition of methane when the Ni loading

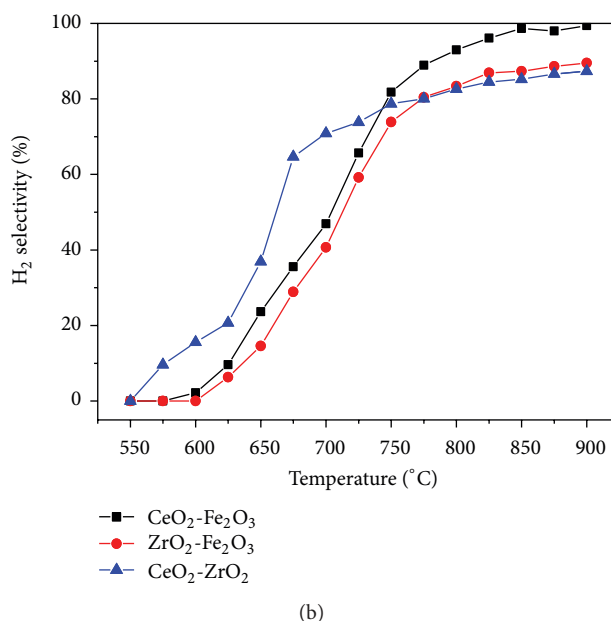
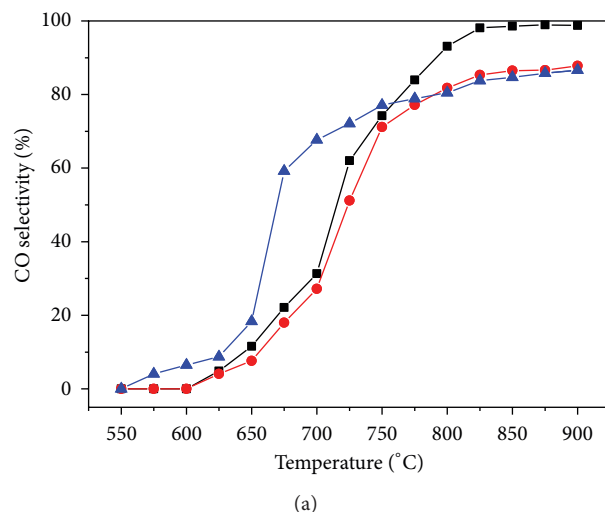


FIGURE 4: CO and H_2 selectivity as a function of reaction temperature over $\text{CeO}_2\text{-Fe}_2\text{O}_3$, $\text{CeO}_2\text{-ZrO}_2$, and $\text{ZrO}_2\text{-Fe}_2\text{O}_3$ oxygen carriers [33].

is too high [44]. For Ce-Nb-O system, the further oxidation of hydrogen to water was observed, and the CO and H_2O were the main production [45]. For all ceria-based oxygen carriers, the reoxidation process by air is very easy to accomplish.

3.2. Perovskite Oxygen Carriers. Perovskite oxides with an ABO_3 -type crystal structure usually exhibit excellent redox properties, high oxygen mobility, and thermal stability, which can be used in many reactions related to a redox process, such as catalytic purification of automotive exhaust and solid oxide fuel cell (SOFC) [46–50]. As a famous perovskite oxides, LaFeO_3 was firstly chosen to selectively oxidize methane by Dai et al. [51, 52], and its performance was compared with NdFeO_3 and EuFeO_3 . The oxygen storage and transport

ability of $AFeO_3$ ($A = La, Nd, \text{ and } Eu$) is related to its Fe–O bond distance and shorter distance given lower activity of oxygen. The reaction rate between methane $AFeO_3$ strongly depends on the reaction temperature, and high-temperature ($>800^\circ C$) is necessary for obtaining a high syngas yield. The $LaFeO_3$ oxide exhibits the best performance among these tested $AFeO_3$ oxides ($A = La, Nd, \text{ and } Eu$) for syngas production, and it also maintains high catalytic activity and structural stability in the redox experiment between methane and air at $900^\circ C$. It was also observed that the reduction of $LaFeO_3$ by methane was performed through a reduction of Fe^{3+} to Fe^{2+} , and further reduction is very difficult [53]. They also investigated the redox property of $LaFeO_3$ for successive generation of syngas in a circulating-fluidized bed (CFB) reactor [54]. It showed that methane could be oxidized to syngas by lattice oxygen with high selectivity, and the depleted oxygen species could be regenerated in a CFB condition. The methane conversion remains at 60%–70% with the CO selectivity of ca. 96% during the 30 redox cycles. However, this paper did not involve the mechanical performance of the oxygen carriers in the redox process, and it is proposed that the attrition resistance for CFB process should be paid much attention.

Li et al. [55, 56] added Sr into the $LaFeO_3$ system to partially substitute the sites of La and investigated that performance of the $La_{0.8}Sr_{0.2}FeO_3$ oxide for methane selective oxidation. They proposed that there are two kinds of oxygen species on the oxide: (i) the active oxygen species (weakly bound oxygen species) which are responsible for complete oxidation of methane and (ii) the weaker oxygen species (strongly bound oxygen species) which are responsible for partial oxidation of methane to syngas. This is similar with the observation by Greish et al. [57]. Methane reacts firstly with the active oxygen species to form CO_2 and H_2O , and then the weaker oxygen species can oxidize methane to CO and H_2 with high selectivity.

On the other hand, substituting La for Sr was found to increase the oxygen capacity of these materials but reduce the selectivity to syngas and the reactivity with CH_4 [58]. Addition of Cr, Ni, and Cu into the La–Sr–Fe–O perovskite system to partially replace the Fe sites could improve the reactivity for methane conversion [59], while incorporation of Co ions into La–Sr–Fe–O mixed oxides could enhance the activity of this material for methane combustion [58] and reduce the stability under redox testing [60]. The $La_{0.7}Sr_{0.3}Cr_{0.1}Fe_{0.9}O_3$ with physically mixed NiO as a catalyst showed good activity and stability in the redox testing [59]. The improvement on the syngas production and stability of material was also observed over the $NiO/La_{1-x}Sr_xFeO_3$ system due to the presence of exposed NiO particles, but the presence of NiO also improved the catalytic activity for methane decomposition, resulting in the formation of carbon deposition [61].

$La_{1-x}Sr_xMO_3$ ($M = Mn, Ni$) and $LaMnO_{3-\alpha}F_\beta$ perovskite oxides were also investigated as oxygen carriers for methane oxidation [62]. It is proposed that the reactivity and selectivity of lattice oxygen depend on (i) B-site element, (ii) degree of substitution of La with Sr, and (iii) fluorination of the perovskite oxide. The $La_{1-x}Sr_xMO_3$ with relatively low degree of Sr-substitution and the fluorinated $LaMnO_{3-\alpha}F$

are suitable oxygen carriers for syngas generation. The high substitution degree of La by Sr increases the reactivity of lattice oxygen but decreases the selectivity to syngas. Evdou et al. [61] observed that the reduction degree of $La_{1-x}Sr_xMO_3$ oxides by methane relies on the Sr content and the reaction temperature.

$BaTi_{1-x}In_xO_3$ perovskite oxides with nickel as a catalyst were also investigated for methane oxidation in the absence of gas phase oxygen [63]. Based on the temperature-programmed surface reaction of methane (TPSR- CH_4) and pulses reaction results, they found that the reducibility of B cation (ABO_3) and the anionic conductivity of the material strongly influence the activity and selectivity of $BaTi_{1-x}In_xO_3$ oxygen carriers. It is also observed that $Ni/BaTi_{0.3}In_{0.7}O_3$ oxygen carrier was more stable than $Ni/BaTiO_3$ due to the existence of Ni–In alloys which is relatively inert for catalyzing the cracking reaction.

3.3. Other Oxygen Carriers. Fe_2O_3 as oxygen carrier was proved to own the ability for methane combustion [7, 8], but addition of other suitable oxides can modify the selectivity of its lattice oxygen for selective oxidation of methane to syngas. Fe_2O_3 – Rh_2O_3/Y_2O_3 and Fe_2O_3 – Cr_2O_3 – MgO oxides were found to be active to produce syngas with a moderate methane conversion and selectivity [64]. It is also proved that combining CuO and Fe_2O_3 to form a Cu-ferrite could obtain a suitable oxygen carrier for methane selective oxidation. Cha et al. [65, 66] investigated the reactivity of $Cu_xFe_{3-x}O_4/Ce-ZrO_2$ ($x < 1$) for methane selective oxidation, and the results showed that the Cu-ferrite suppressed carbon deposition and promoted the reactivity with methane to produce syngas. On the other hand, since the lattice oxygen from Fe_2O_3 to Fe_3O_4 can completely oxidize methane to CO_2 and H_2O , the redox of FeO/Fe_3O_4 was proposed to convert methane to syngas by a chemical looping step [67].

NiO-based materials were also used for the methane selective oxidation, but significant amount of CO_2 and H_2O was observed in the products over NiO, $NiO/\gamma-Al_2O_3$, $NiO/\alpha-Al_2O_3$, and $NiO/Mg-ZrO_2$ oxygen carriers [68–73]. During the reaction between methane and NiO-based oxides, the syngas yield depends on the oxidation degree of the oxygen carriers: highly oxidized oxide particles resulted in the formation of CO_2 and H_2O , while reduced particles could produce CO and H_2 [70, 74]. Addition of Cr_2O_3 into NiO–MgO system could change reactivity of the lattice oxygen in the materials, and the fully oxidized NiO– Cr_2O_3 –MgO produced H_2 and CO with high selectivity during the reaction with CH_4 [64, 75]. The appearance of $NiAl_2O_4$ also could reduce the activity of oxygen in the material and promote the formation of H_2 and CO [76].

Based on the previous discussions, CeO_2 -based oxygen carrier could convert methane into syngas at relatively low temperatures (ca. $700^\circ C$) in the presence of Pt promoter, but the redox stability of the oxygen carriers needs to be improved. The perovskite-type oxygen carriers own high selectivity and redox stability for syngas generation, but they are only active at high temperatures (ca. $850^\circ C$). For the Fe_2O_3 - and NiO-based oxygen carriers, a large number of CO_2 and H_2O were produced during the gas-solid reaction

between oxygen carrier and methane. Although addition of suitable promoters could improve the selectivity of oxygen carriers for syngas generation, but it also reduced the reactivity for methane conversion. Among the different oxygen carriers, perovskite-type oxygen carriers are more competitive for the CLSOM process, if the activity could be enhanced by the structure modifications. On the other hand, the use of the various combinations of catalysts (e.g., combinations of perovskite-type or CeO_2 - ZrO_2 oxygen carriers with Ni or Fe species) may also achieve the greater efficiency for syngas generation.

4. Conclusions

Chemical-looping selective oxidation of methane (CLSOM) is a promising, energy-efficient, and low-cost route for syngas generation. However, at the present time, this technology is not fully established for large-scale implementation, and valuable researches need to be developed to address the important issues of this technology. Nowadays, numbers of works were performed on this technology, and most of previous technical literatures had been focused on the development of suitable oxygen carrier materials. After reviewing such references, it is found that a suitable oxygen carrier should own abundant active sites for methane activation, high oxygen storage capacity, and good oxygen mobility. This finding gives useful references for the further developing highly efficient oxygen carriers.

Due to the two-step redox process, the chemical engineering of whole process is actually a key factor for success in practical application, and the specific selected reactor design is very critical. The mechanical performance of the oxygen carriers should be paid much attention when a fluidized bed reactor is used. In addition, since the reaction between methane and oxygen carriers is endothermic, while the reoxidation of reduced oxygen carriers is an exothermic reaction, the energy efficiency of the whole process strongly depends on the transfer of the heat from the exothermic reaction to the endothermic reaction. This issue is also very important for the practical application of this technology.

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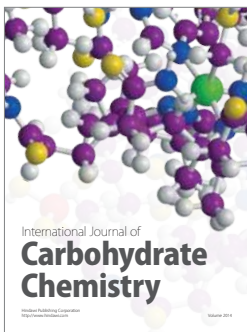
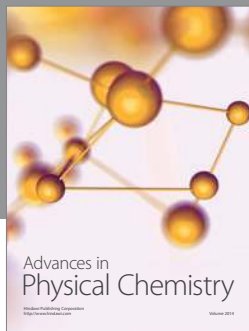
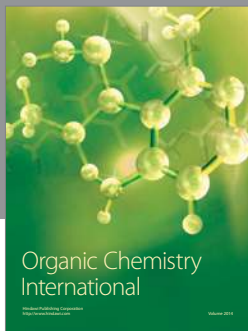
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