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Article

La_{1-x}Sr_xFeO₃ perovskites as oxygen carriers for the partial oxidation of methane to syngas

Kun Zhao ^{a,b}, Fang He ^{a,*}, Zhen Huang ^a, Anqing Zheng ^a, Haibin Li ^a, Zengli Zhao ^a^a Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, Guangdong, China^b University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

We prepared perovskite-type oxides La_{1-x}Sr_xFeO₃ ($x = 0, 0.3, 0.5, 0.9$) by a combustion method and used these as oxygen carriers for the partial oxidation of methane. X-ray diffraction, scanning electron microscopy and H₂ temperature-programmed reduction techniques were used to characterize the samples. Their reduction and oxidation activities were investigated using a thermogravimetric analysis reactor and fixed-bed reaction equipment, respectively. The results showed that the lattice oxygen in La_{1-x}Sr_xFeO₃ was suitable for the partial oxidation of methane to produce syngas. Their capacity to provide oxygen was enhanced by the partial substitution of La³⁺ by Sr²⁺ and the synthesized materials have good regenerability. The optimal degree of Sr substitution was found to be $x = 0.3-0.5$ for La_{1-x}Sr_xFeO₃ with regard to reactivity, selectivity, and oxygen-donating ability. CH₄ conversion was higher than 70%, and the $n(\text{H}_2)/n(\text{CO})$ ratio remained about 2:1 and no obvious decomposition of CH₄ occurred.

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1. Introduction

In China, the dependence on external petroleum is increasing with the rapid development of the economy. The demand for petrol will reach 190 to 200 million tons by 2015, accounting for 50% of the total consumption [1]. The search for clean and low-cost fuel to substitute petroleum is a popular research focus in the energy field. Natural gas is a clean and environmentally friendly source of energy, and its demand is increasing steadily. It will be a dominant energy source in the early-to-mid part of this century. The main component of natural gas is CH₄ and it is predominantly converted into syngas (H₂ + CO), which is used as a fuel directly or can be converted into liquid fuel or other chemicals through the Fischer-Tropsch synthesis

method.

Three methods can be used to convert CH₄ to syngas: the steam reforming of CH₄ (SRM) [2], the CO₂ reforming reaction (CDR) [3], and the partial oxidation of CH₄ (POM) [4]. Compared to SRM or CDR, several advantages are apparent for the POM: it is a moderate exothermic reaction requiring a small reactor, has low energy consumption and is highly efficient. The H₂/CO ratio is close to 2:1 during syngas production at 750 to 800 °C, and syngas can be used as a feed gas for direct methanol or Fischer-Tropsch synthesis [5]. However, this reaction has several disadvantages, including the expensiveness of the Pt or Pd catalysts. Ni-based catalysts are cheap and are widely used but they inactivate because of carbon deposition. Moreover, CH₄ is easily completely oxidized to CO₂ and H₂O because

* Corresponding author. Tel: +86-20-87057721; Fax: +86-20-87057737; E-mail: hefang@ms.giec.ac.cn

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pure oxygen is required for the reaction. This leads to reduced syngas productivity and the risk of explosion [6]. A novel technology has been introduced based on chemical looping combustion (CLC) [7], otherwise referred to as chemical looping reforming (CLR) [8,9]. In CLR technology, CH₄ is partially oxidized to synthesis gas (H₂/CO = 2) by the lattice oxygen in the oxygen carrier. The reaction process is shown in Fig. 1.

In the reforming reactor, CH₄ is partially oxidized by the oxygen carrier as shown in Eq. (1):

In the air reactor, the reduced oxygen carrier is re-oxidized to recover its lattice oxygen as shown in Eq. (2):

CLR technology is a popular research topic because it is novel, concise, and highly efficient. In this technology, the selection of oxygen carrier is crucial because the oxygen carrier must carry lattice oxygen between the reforming reactor and the air reactor. Additionally, it must also transmit heat energy from the air reactor to the reforming reactor. A Ni-based oxygen carrier was used by Ryden et al. [10] to validate the feasibility of CLR technology, and the conversion of natural gas to syngas ranged from 96% to 100%. De Diego et al. [11] also used a Ni-based oxygen carrier for CLR technology on a 900Wth CLR experimental platform, and achieved a CH₄ conversion of 98%. CeO₂-Fe₂O₃ was used by Zhu et al. [12] for steam methane reforming in two steps to obtain syngas and hydrogen. Perovskite-type metal oxides such as La_{0.8}Sr_{0.2}FeO₃ was used by Li et al. [13] in CLR technology, and their results show that CH₄ can be partially oxidized to CO and H₂ by the lattice oxygen in La_{0.8}Sr_{0.2}FeO₃. The reduced La_{0.8}Sr_{0.2}FeO_{3-δ} can then be re-oxidized by air to recover the lattice oxygen. Various additional perovskite-type metal oxides AFeO₃ (A = La, Nd, Sm, Eu) have also been used for CLR technology [14,15] by this research group. The perovskite-type metal oxides have good recycling capacity in terms of losing and regaining lattice oxygen.

In this work, La_{1-x}Sr_xFeO₃ perovskite-type metal oxides ($x = 0, 0.3, 0.5, 0.9$) were prepared by the combustion method. The properties of the oxides were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and H₂ temperature-programmed reduction (H₂-TPR) techniques. The reactivities of the La_{1-x}Sr_xFeO₃ were then investigated in a thermogravimetric analysis (TGA) reactor and in a fixed-bed reactor.

Fig. 1. Chemical looping reforming of CH₄.

2. Experimental

2.1. Synthesis of La_{1-x}Sr_xFeO₃

La_{1-x}Sr_xFeO₃ perovskite-type metal oxides ($x = 0, 0.3, 0.5, 0.9$) were prepared by a combustion method. First, the required amounts of La(NO₃)₃·6H₂O, Fe(NO₃)₃·9H₂O, and Sr(NO₃)₂ were weighed at the desired stoichiometric ratio and put into a beaker. A specific amount of deionized water was added to produce an aqueous solution of the mixed nitrates. A glycine (H₂NCH₂CO₂H) solution was added to the mixed nitrates solution to give a glycine/nitrates molar ratio of 1.05. The resulting solution was allowed to evaporate by stirring in a 100 mL beaker at 70 °C until a viscous brown gel was obtained. The gel was then put in a muffle furnace at 250–260 °C to combust, which generated an alveolate precursor. The powdered precursor was calcined at 750 °C for 1 h, and then at 900 °C for 6 h. The resulting product was then ground to obtain the fresh perovskite-type oxides: La_{1-x}Sr_xFeO₃.

2.2. Characterization

The crystal phases of the oxides were identified using an X'Pert PRO MPD (PW3040/60) diffractometer with Cu K α radiation at an operating voltage of 40 kV and a current of 40 mA. The diffraction angle (2 θ) scan range was from 5° to 80°. The morphology of the perovskite-type oxides was studied by SEM on a Hitachi S4800 instrument. H₂-TPR experiments were conducted on a full-automatic temperature programmed reduction analysis instrument.

2.3. TGA test

Reduction-oxidation (redox) multicycles of the oxides exposed to alternating methane and air conditions were conducted in a TGA reactor. A gas control system, temperature control system, mass recording system and a quartz tube were part of the TGA reactor. For each test, a certain amount of oxygen carrier was placed in the quartz pan. The control system was then turned on for heating under N₂ to 850 °C. When the temperature reached a desired value, CH₄ (40 vol% CH₄ in N₂) and air were alternately introduced into the reaction tube. The degree of oxidation X was calculated as follows:

$$X = (m - m_{\text{red}}) / (m_{\text{ox}} - m_{\text{red}}) \quad (3)$$

where m is the instantaneous mass of the sample, m_{ox} is the mass of the sample when fully oxidized, and m_{red} is the mass of the sample in the reduced form.

2.4. Fixed-bed test

The fixed-bed reactor was also a quartz tube with a baffle that only allows gas to get through. 1.0 g of the oxygen carrier was evaluated on the baffle under a N₂ atmosphere at 850 °C. A mixture of 40.0 vol% CH₄ balanced with N₂ was used as the feed gas (20 ml/min). The product gases from the reactor were collected using gas bags and analyzed by gas chromatography.

3. Results and discussion

3.1. Characterization of the oxygen carriers

3.1.1. XRD results

The structures of the perovskite-type oxides of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ were examined by XRD to identify the crystalline phases, as shown in Fig. 2. XRD patterns of the fresh $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ were compared with typical peaks of perovskite-type compounds using a standard card. We found that the samples consisted of a monophasic crystalline perovskite structure without other impurity crystalline phases. The 2θ gradually increased as x increased. The symmetric crystal form changed from orthogonal to rhombohedral and to cubic as substitution by Sr increased, as shown in Table 1. Additionally, the half-peak width of the maximum diffraction peak increased, which means that the grain size of the sample decreased. The reason is that the ionic radius of Sr^{2+} (0.144 nm) is larger than that of La^{3+} (0.136 nm), and the substitution of Sr caused the oxidation of a fraction of the Fe^{3+} ions to Fe^{4+} ions as well as the generation of oxygen vacancies. While the ionic radius of Fe^{4+} (0.0585 nm) is smaller than that of Fe^{3+} (0.0645 nm) that leads to the decrease of grain size [16].

The XRD patterns of the reduced perovskite-type oxides are shown in Fig. 3. It was found that the reduced samples retained the main perovskite structure although La_2O_3 , Fe_2O_3 , Fe_3O_4 and carbon deposition was detected. The presence of Fe_2O_3 and Fe_3O_4 may indicate the reduction of $\text{Fe}^{4+}/\text{Fe}^{3+}$ to Fe^{2+} , while carbon deposition comes from CH_4 decomposition. The XRD patterns of the regenerated oxides after five cyclic redox reactions indicate recovered perovskite structures, as shown in Fig. 4, which means that the perovskites have good regenerability.

Fig. 2. XRD patterns of fresh $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ samples.

Table 1

Strongest peak (2θ) in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$.

$\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$	$2\theta/(\circ)$	Crystal system
$x = 0$	32.20	orthogona
$x = 0.3$	32.50	rhombohedral
$x = 0.5$	32.53	cubic
$x = 0.9$	32.92	cubic

Fig. 3. XRD patterns of the reduced $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ samples.

Fig. 4. XRD patterns of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ after 5 cycles.

3.1.2. H_2 -TPR results

The reduction peak area in the H_2 -TPR profile is a reflection of the ease or complexity of metal ion reduction. As shown in Fig. 5, a broad reduction peak is present in the LaFeO_3 sample, and this was at 473 °C with a peak shoulder at 520 °C. This reduction peak comes from the reduction of Fe^{4+} to Fe^{3+} , while the presence of a peak shoulder may be because of a partial reduction of Fe^{4+} to Fe^{3+} and Fe^{3+} to Fe^{2+} [17]. H_2 consumption

Fig. 5. H_2 -TPR profiles of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ samples.

for this reduction peak was found to be 0.1898 mol per mol oxygen carrier by a quantitative calculation. The TPR profile for the sample with $x = 0.3$ shows an intense reduction peak at about 445 °C with H_2 consumption of 0.1681 mol, and two weaker peaks at 590 and 770 °C were also present. The two reduction peaks at high temperature with H_2 consumption of 0.3425 mol comes from the deep reduction of Fe^{3+} to Fe^{2+} [18], which indicates that H_2 consumption increased with Sr substitution. With a further increase in the degree of Sr substitution, a reduction peak appeared at 470 °C with H_2 consumption of 0.1292 mol and another at 805 °C with H_2 consumption of 0.0393 mol for $La_{0.5}Sr_{0.5}FeO_3$. Only one reduction peak was present at 475 °C with H_2 consumption of 0.0782 mol for $La_{0.1}Sr_{0.9}FeO_3$. Therefore, H_2 consumption over the whole reaction was 0.1898, 0.5106, 0.1685 and 0.0782 mol for the four samples, respectively. It has been reported that two types of perovskite oxygen species, α and β , may exist in perovskite-type oxides because of different metal ion reductions. The α peak is attributed to the complete oxidation of CH_4 to CO_2 and H_2O , and is usually observed at a lower temperature. This represents the desorption of oxygen adsorbed on the catalyst surface. The β peak is prone to the partial oxidation of CH_4 to CO and H_2 , and is characterized by a higher onset temperature [19,20]. Therefore, the reducibility of the oxygen carrier can be enhanced by the partial substitution of Sr^{2+} for La^{3+} , and H_2 consumption was the highest for $La_{0.7}Sr_{0.3}FeO_3$. The two reduction peaks that appeared at higher than 750 °C are beneficial for the partial oxidation of CH_4 to syngas. The H_2 consumptions for $La_{0.5}Sr_{0.5}FeO_3$ and $LaFeO_3$ are similar, but the reduction of $La_{0.5}Sr_{0.5}FeO_3$ appeared more easily than that of $LaFeO_3$, which means that the reducibility of $La_{0.5}Sr_{0.5}FeO_3$ is better. The worst reducibility was found for $La_{0.1}Sr_{0.9}FeO_3$.

3.1.3. SEM results

The fresh and regenerated perovskite-type oxides were characterized by SEM, as shown in Fig. 6. The fresh oxygen carrier existed as small granules and accumulated in space with a smooth surface. The grains of the $LaFeO_3$ and $La_{0.7}Sr_{0.3}FeO_3$ samples were dispersed and uniform with many holes, which is beneficial for the delivery of lattice oxygen. The holes in the $La_{0.5}Sr_{0.5}FeO_3$ sample were smaller and the microstructure developed into a stratiform. The grains in the $La_{0.1}Sr_{0.9}FeO_3$ sample were unequal. When the samples were exposed to five alternating reducing and oxidizing atmospheres, the oxygen carriers

Fig. 6. SEM images of different $La_{1-x}Sr_xFeO_3$ samples. (a) $LaFeO_3$ -fresh; (b) $La_{0.7}Sr_{0.3}FeO_3$ -fresh; (c) $La_{0.5}Sr_{0.5}FeO_3$ -fresh; (d) $La_{0.1}Sr_{0.9}FeO_3$ -fresh; (e) $LaFeO_3$ -after 5 cycles; (f) $La_{0.7}Sr_{0.3}FeO_3$ -after 5 cycles; (g) $La_{0.5}Sr_{0.5}FeO_3$ -after 5 cycles; (h) $La_{0.1}Sr_{0.9}FeO_3$ -after 5 cycles.

showed slight agglomeration behavior and larger grains formed giving a rough surface. However, the samples still existed as particles with a porous structure and with good reactivity.

3.2. TGA tests

The degree of oxidation as a function of time for the four kinds of $La_{1-x}Sr_xFeO_3$ with different Sr substitution is shown in Fig. 7. Using $LaFeO_3$ as an example, CH_4 reacted with the oxygen

Fig. 7. Degree of oxidation with reaction time for $La_{1-x}Sr_xFeO_3$ samples.

carrier immediately when the reaction started and the mass of the oxygen carrier reduced rapidly. The final degree of oxidation was 0.65 in the reduction stage, which means that 35% of the reactive oxygen was used as an oxidant when the oxygen carrier was exposed to CH_4 flow. When the reacting atmosphere was changed from CH_4 to air, the mass of the oxygen carrier increased immediately and thus its lattice oxygen was recovered. The oxygen delivery capacity did not obviously decline after five cycles, suggesting that the LaFeO_3 oxides have good regenerability. Detailed parameters of the degree of oxidation as a function of time for the four kinds of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ are listed in Table 2.

Table 2 shows that the final degree of oxidation was 0.5, 0.54 and 0.58 for the samples with $x = 0.3, 0.5$, and 0.9 , respectively. This indicates that a higher amount of Sr substitution leads to less lattice oxygen taking part in the reaction. However, the degree of oxidation for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0.3, 0.5, 0.9$) is still larger than that of LaFeO_3 ($X_{\text{red}} = 0.64$). Moreover, the reaction rate decreased with Sr substitution over the reaction time, which means that reduction became more difficult. Chen et al. [21] prepared $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ($x = 0.0\text{--}0.6$) by a glycine-nitrate process and determined the average valency and non-stoichiometry of oxygen by iodometry. Their results showed that the average valency of Fe increased with Sr substitution and the maximum value was obtained at $x = 0.4$. Zhong et al. [22] investigated $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ by Mössbauer spectroscopy. They found that the system energy and the reactivity of the lattice oxygen increased with an increase in Fe^{4+} . The oxidation activity increased within certain x value limits but decreased with a further increase in x . This is because the distribution of Fe^{4+} and the oxygen vacancies became ordered, which reduced the system energy. As above mentioned, Sr substitution may im-

prove the amount of adsorbed oxygen species in the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ perovskite-type oxides to some extent. The optimal range of Sr substitution is $x = 0.3\text{--}0.5$ for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$, and the degree of oxidation increased by 17% to 39%. These results also correspond with the H_2 -TPR results.

3.3. Fixed-bed reaction test

The reactivity of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ was evaluated using a fixed-bed reactor, as shown in Fig. 8. CH_4 conversion as a function of time is shown in Fig. 8(a). CH_4 conversion is high during the initial period of the reaction, but it decreases rapidly and reaches a minimum value at 4–6 min. CH_4 conversion then increases gradually as the reaction proceeds. This can be explained by the desorption of adsorbed oxygen from the catalyst surface, which takes part in the reaction and is depleted immediately. Lattice oxygen delivery is indicated by a hysteresis and thus an insufficient amount of oxygen reacted with CH_4 [23,24]. As the reaction proceeds, a good oxygen delivery capacity is apparent and lattice oxygen takes part in the reaction, which increases CH_4 conversion. CH_4 conversion by LaFeO_3 was found to be highest and this is due to CH_4 cracking, which is also shown in Fig. 8(b) where the $n(\text{H}_2)/n(\text{CO})$ ratio increased rapidly. CH_4 conversion remained around 70% for the $x = 0.3$ and $x = 0.5$ samples. CH_4 conversion of the sample with $x = 0.9$ was found to be the lowest with a maximum value of 55%. The $n(\text{H}_2)/n(\text{CO})$ ratio remained around 2:1 for the $x = 0.3, 0.5$, and 0.9 samples, indicating that there was no obvious CH_4 cracking.

The selectivity for CO and H_2 as a function of time is shown in Fig. 9. The selectivity for CO and H_2 in the initial stage was

Table 2

Redox performance of the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ oxides over five cycles.

$\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$	Time (s)	1st		2th		3th		4th		5th	
		X_{red}	X_{ox}	X_{red}	X_{ox}	X_{red}	X_{ox}	X_{red}	X_{ox}	X_{red}	X_{ox}
$x = 0$	14430	0.60	0.95	0.65	0.96	0.65	0.95	0.65	0.95	0.65	0.95
$x = 0.3$	17190	0.50	0.96	0.50	1.00	0.50	0.96	0.52	0.96	0.52	0.96
$x = 0.5$	16500	0.50	0.93	0.54	1.00	0.52	1.00	0.54	1.00	0.58	1.00
$x = 0.9$	19470	0.57	1.00	0.59	1.00	0.60	1.00	0.56	1.00	0.60	1.00

Fig. 8. Reactivity as a function of reaction time over $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ samples. (a) CH_4 conversion; (b) $n(\text{H}_2)/n(\text{CO})$.

Fig. 9. Selectivity toward CO and H_2 over $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ samples. (a) Selectivity for CO; (b) Selectivity for H_2 .

low because of complete oxidation by the desorbed oxygen. Upon the gradual release of lattice oxygen, selectivity for CO and H_2 began to increase. As the reaction proceeded, selectivity for CO decreased. Selectivity toward CO by LaFeO_3 decreased quickly while that by $\text{La}_{0.1}\text{Sr}_{0.9}\text{FeO}_3$ was consistently high. Selectivity for H_2 for the four samples had a similar trend as they increased to stabilization without an obvious decrease in selectivity.

4. Conclusions

In this study, $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ perovskite-type oxides were prepared by a combustion method and used as oxygen carriers in CLR technology. The performance of the perovskite-type oxides that reacted with CH_4 was investigated by TGA and in a fixed-bed reactor. The desorption of the adsorbed oxygen on the catalyst surface was responsible for the complete oxidation of CH_4 to CO_2 and H_2O , while the bulk lattice oxygen was responsible for the deep reduction of Fe^{3+} to Fe^{2+} , and this was suitable for the partial oxidation of CH_4 to H_2 and CO. $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ gave good repeatability, and no significant deactivation was observed over five redox cycles. Sr substitution improved the amount of adsorbed oxygen in the perovskites,

and inhibited CH_4 decomposition in the methane reaction. The optimal range of Sr substitution was found to be $x = 0.3\text{--}0.5$ for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ from a CH_4 conversion rate point of view, the $n(\text{H}_2)/n(\text{CO})$ ratio, and selectivity toward CO and H_2 .

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Graphical Abstract

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$\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ perovskites as oxygen carriers for the partial oxidation of methane to syngas

Kun Zhao, Fang He*, Zhen Huang, Anqing Zheng, Haibin Li, Zengli Zhao
Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences;
University of Chinese Academy of Sciences

The lattice oxygen in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ is suitable for the production of syngas by the partial oxidation of methane. $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$ were found to be the best for CH_4 conversion, the $n(\text{H}_2)/n(\text{CO})$ ratio, and for selectivity toward H_2 and CO.

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La_{1-x}Sr_xFeO₃钙钛矿型氧化物中的晶格氧用于甲烷部分氧化制合成气

赵 坤^{a,b}, 何 方^{a,*}, 黄 振^a, 郑安庆^a, 李海滨^a, 赵增立^a

^a中国科学院广州能源研究所中国科学院可再生能源与天然气水合物重点实验室, 广东广州510640

^b中国科学院大学, 北京100049

摘要: 采用燃烧法制备了Sr掺杂钙钛矿型氧化物La_{1-x}Sr_xFeO₃ ($x = 0, 0.3, 0.5, 0.9$)载氧体, 对载氧体分别进行X射线衍射、扫描电镜和H₂程序升温还原反应表征, 在热重循环装置和固定床反应装置上考察甲烷与载氧体晶格氧的部分氧化反应. 结果表明, La_{1-x}Sr_xFeO₃氧化物中的晶格氧适用于甲烷部分氧化制合成气, 晶格氧的得失是一个可逆过程, Sr的掺杂提高了载氧体的供氧能力, 5次循环后载氧体得失晶格氧的能力没有明显的衰减. 从甲烷转化率、 $n(\text{H}_2)/n(\text{CO})$ 比以及H₂和CO的选择性等方面来考虑, $x = 0.3-0.5$ 比较理想, 甲烷转化率维持在70%左右, 气体产物中 $n(\text{H}_2)/n(\text{CO})$ 约为2, CH₄没有发生明显的裂解.

关键词: 钙钛矿; 晶格氧; 热重循环; 部分氧化; 合成气

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*通讯联系人. 电话: (020)87057721; 传真: (020)87057737; 电子信箱: hefang@ms.giec.ac.cn.

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1. 前言

随着经济的快速发展, 我国石油对外依赖程度越来越高, 预计2015年我国石油缺口将达1.9–2.0亿吨, 占总需求量的50%以上^[1], 因此开发洁净廉价的燃料替代石油已成为能源领域的研究热点. 天然气作为一种清洁、环境友好的能源, 将在全球能源和化工原料方面取代石油并占主导地位, 成为21世纪的主要能源. 天然气的主要成分是甲烷, 利用甲烷为原料制取液体燃料和化学品的工艺中, 通常需要先要将甲烷转化为以H₂和CO为主要组分的合成气, 然后再经费托合成等途径转化为液体燃料.

将甲烷转化为合成气一般有三种方法: 甲烷水蒸汽重整^[2]、甲烷二氧化碳重整^[3]、甲烷部分氧化^[4]. 与甲烷水蒸气/CO₂重整比较而言, 甲烷部分氧化制合成气反应放热温和, 反应器体积小、效率高、能耗低; 在750–800 °C下, 生成的合成气中H₂/CO比接近2, 可直接用于甲醇及费托合成的原料气^[5]. 但该反应采用贵金属Pt或Pd等作为催化剂, 价格较昂贵; 而Ni基催化剂价廉易得, 但因积

碳而容易失活; 另一方面, 反应必须有纯氧参与, 极易把甲烷完全氧化为CO₂和H₂O, 降低合成气的产率^[6], 并且CH₄直接与O₂接触有爆炸的危险. 因此根据甲烷部分氧化制合成气的优缺点, 研究人员基于化学链燃烧技术^[7]提出了一种新颖的工艺, 利用载氧体中的晶格氧将CH₄部分氧化制取合成气, 即化学链重整技术(CLR)^[8–12], 反应原理如图1所示.

在重整反应器, CH₄与载氧体部分氧化制得合成气(式1):

在空气反应器, 还原态的载氧体被空气重新氧化, 恢复晶格氧(式2):

由于CLR技术的新颖性、简洁性与高效性而备受关注. 在反应过程中, 载氧体在重整反应器和空气反应器之间循环传递晶格氧, 同时也可将空气反应器中的热量传递到重整反应器, 因此载氧体的选择至关重要. Ryden等^[10]采用Ni基氧载体, 在循环流化床反应器中研究

了天然气的CLR技术,验证了其可行性,天然气重整制合成气的转化率高达96%–100%。Luis等^[11]以Ni基氧载体,在900Wth的CLR实验平台中研究了CH₄的CLR技术,CH₄转化率达到98%以上。Zhu^[12]等采用浸渍法制备了CeO₂-Fe₂O₃氧载体,考察了两步法甲烷-水蒸气化学链重整过程,850 °C反应可产生 $n(\text{H}_2)/n(\text{CO}) = 2$ 的合成气,还原后的氧载体能分解水产生高纯度的H₂。李然家等^[13]以La_{0.8}Sr_{0.2}FeO₃钙钛矿作为氧载体用于甲烷选择性氧化制取合成气,结果表明CH₄能与La_{0.8}Sr_{0.2}FeO₃中的晶格氧反应生成CO和H₂,失去晶格氧的La_{0.8}Sr_{0.2}FeO₃能在空气气氛下氧化恢复其晶格氧,重复氧化还原循环反应。该课题组还考察了不同的钙钛矿AFeO₃ (A = La, Nd, Sm, Eu)作为氧载体用于天然气的CLR过程^[14,15],通过控制实验条件,钙钛矿型氧化物可以选择性地将CH₄部分氧化为合成气,钙钛矿具有良好的反复失氧得氧能力。

本文采用燃烧法制备钙钛矿型氧化物La_{1-x}Sr_xFeO₃ (x = 0, 0.3, 0.5, 0.9),利用X射线衍射仪(XRD),扫描电镜(SEM),和H₂程序升温还原(H₂-TPR)技术对其进行表征,然后在热重循环反应装置和固定床反应装置上考察La_{1-x}Sr_xFeO₃催化甲烷部分氧化反应性能。

2. 实验部分

2.1. 载氧体的制备

采用燃烧法制备钙钛矿型氧化物La_{1-x}Sr_xFeO₃。按照化学计量比称取一定量的La(NO₃)₃·6H₂O, Fe(NO₃)₃·9H₂O和Sr(NO₃)₂,用去离子水溶解,配制成一定浓度的硝酸盐溶液。按照甘氨酸:硝酸根(摩尔比) = 1.05的比例来称得一定量的甘氨酸,先溶解在去离子水中,再与硝酸盐溶液混合。所得混合溶液在70 °C不断搅拌直至水分蒸发形成棕红色的粘稠状,然后放入250–260 °C的马弗炉中,使其瞬间燃烧得到蜂窝状的催化剂前驱体,再研磨约10 min,最后在750 °C焙烧1 h, 900 °C焙烧6 h,再次研磨即获得所需的载氧体。

2.2. 载氧体表征

载氧体的物相分析采用荷兰帕纳科公司的X'Pert PRO MPD (PW3040/60) X射线衍射仪, Cu靶, 管电压40 kV, 管电流40 mA, 扫描范围 $2\theta = 5^\circ - 80^\circ$; 载氧体的形貌通过S-4800型场发射SEM表征, 工作温度为室温, 能量扩散度小于0.2 eV; H₂-TPR表征在全自动程序升温化学吸附分析仪上进行。

2.3. 热重循环实验

在热重反应器上进行载氧体与CH₄/air切换反应, 反应装置包括气体控制系统、加热测温系统、质量记录系

统以及石英管反应器, 反应温度设定为850 °C。实验过程中, 先在料盘中装入一定量的载氧体, 打开电炉电源, 在N₂气氛中将样品加热至设定温度后通入40% CH₄/N₂混合气, 同时由天平和电脑同步记录载氧体的质量变化。当载氧体被完全还原后切断CH₄, 通入N₂进行吹扫以防止CH₄和空气的混合。待石英管中的CH₄吹扫完毕后, 将气体切换至干空气, 载氧体被氧化恢复其晶格氧, 从而完成一个还原氧化过程。同时, 引入氧化程度X作为评价氧载体得失晶格氧的参数:

$$X = (m - m_{\text{red}}) / (m_{\text{ox}} - m_{\text{red}}) \quad (3)$$

其中, m 为天平实时测的氧载体的质量, m_{red} 为处于完全还原状态时氧载体的质量, m_{ox} 为处于完全氧化状态时氧载体的质量。

2.4. 固定床实验

固定床的反应器是一根石英管, 中间部分是一块石英砂烧制的能够通过气体的挡板。挡板上放置1 g的载氧体, 反应温度设定为850 °C。在升温过程中通入N₂进行吹扫, 待升至设定温度后, 通入40% CH₄/N₂混合气(20 ml/min)。石英管的两端采用不锈钢密封接头, 反应器出口收集的气体在气相色谱仪上测定气体成分。

3. 结果与讨论

3.1. 载氧体的表征

3.1.1. XRD结果

图2为新鲜La_{1-x}Sr_xFeO₃样品的XRD谱。可以看出, 各样品均出现了钙钛矿结构的主要特征峰, 表明所制备氧化物的钙钛矿结构已经形成; 随着 x 的增加, 最强衍射峰对应的 2θ 逐渐增大, 表明Sr的取代改变了钙钛矿结构的对称晶型, 晶系由正交型向菱方和立方型转变(表1); 同时, 最强衍射峰的半峰宽变大, 表明载氧体晶粒尺寸变小。这是由于LaFeO₃在A位掺杂Sr后, 离子半径较大的Sr²⁺ (0.144 nm)部分取代了A位离子半径较小的La³⁺ (0.136 nm), 导致B位的部分Fe³⁺氧化为Fe⁴⁺, 同时产生氧空位。而Fe⁴⁺的离子半径(0.0585 nm)则比Fe³⁺的(0.0645 nm)小^[16], 因此导致了晶粒尺寸的减小。

图3为四种载氧体还原之后的XRD图谱, 可以看出, 四种载氧体还原后仍然保持有钙钛矿的结构, 但同时也出现了La₂O₃, Fe₂O₃, Fe₃O₄和C的特征峰。Fe₂O₃和Fe₃O₄的出现是由于Fe⁴⁺/Fe³⁺ → Fe²⁺的还原, 而少量C的出现则是因为甲烷在还原过程中发生了部分裂解。经过5次还原-氧化循环反应后, 载氧体的XRD谱见图4。可以看出, 四种载氧体均恢复了钙钛矿的主要结构特征峰, 表明它们具有较好的循环反应再生能力。

3.1.2. H_2 -TPR结果

图5为各 $La_{1-x}Sr_xFeO_3$ 样品的 H_2 -TPR谱。当 $x=0$ 时, $LaFeO_3$ 载氧体还原过程中存在一个较宽的还原峰, 出峰温度为 $473\text{ }^\circ\text{C}$, 并在 $520\text{ }^\circ\text{C}$ 左右存在一个肩峰。第一个还原峰的出现是由于 $Fe^{4+} \rightarrow Fe^{3+}$ 的还原, 而肩峰则可能源于部分还原不彻底的 $Fe^{4+} \rightarrow Fe^{3+}$ 的还原以及部分 $Fe^{3+} \rightarrow Fe^{2+}$ 的还原峰的叠加^[17]。通过定量计算, 对于单位mol的载氧体, 这个还原峰和肩峰的 H_2 总消耗量为 0.1898 mol 。当 $x=0.3$ 时, 第一个还原峰降至 $445\text{ }^\circ\text{C}$, H_2 消耗量为 0.1681 mol ; 之后在 590 和 $770\text{ }^\circ\text{C}$ 分别出现第二个和第三个较弱的还原峰, 高温还原峰归属于载氧体表面和内部 $Fe^{3+} \rightarrow Fe^{2+}$ 的深层还原^[18], 表明Sr的加入增加了 H_2 的消耗量, 还原能力增强。这两个还原峰总的耗 H_2 量为 0.3425 mol 。随着 x 增至 0.5 , 样品的第一个低温还原峰出现在 $470\text{ }^\circ\text{C}$, H_2 消耗量为 0.1292 mol ; $805\text{ }^\circ\text{C}$ 附近出现第二个较小的高温还原峰, H_2 消耗量为 0.0393 mol 。对于 $La_{0.1}Sr_{0.9}FeO_3$ ($x=0.9$)样品, 只在 $475\text{ }^\circ\text{C}$ 出现一个还原峰, H_2 消耗量为 0.0782 mol , 未出现高温还原峰。对于这四种载氧体, 在整个温度范围内, 每mol载氧体总的耗 H_2 量分别为 0.1898 , 0.5106 , 0.1685 和 0.0782 mol 。研究表明^[19,20], 在钙钛矿型氧化物中存在两种不同性质的氧, 即低温下可脱附的表面吸附氧和高温段的晶格氧, 前者倾向于甲烷的完全氧化生成 CO_2 和 H_2O , 而后者则有利于甲烷的部分氧化生成合成气。综上可见, 在一定的范围内 Sr^{2+} 部分取代 La^{3+} 能够提高载氧体的还原性, $La_{0.7}Sr_{0.3}FeO_3$ 还原过程中消耗的 H_2 最多, 并且在 $750\text{ }^\circ\text{C}$ 的高温区出现两个还原峰, 对甲烷部分氧化制合成气较为有利。 $La_{0.5}Sr_{0.5}FeO_3$ 和 $LaFeO_3$ 消耗的 H_2 量接近, 但前者的出峰温度前移, 表明还原较易, 在 $750\text{ }^\circ\text{C}$ 之后的高温区存在一个还原峰; 而 $La_{0.1}Sr_{0.9}FeO_3$ 的还原效果最差。

3.1.3. SEM结果

图6为新鲜载氧体和5次循环反应后的载氧体SEM照片。可以看出, 新鲜载氧体以颗粒形态存在, 颗粒呈现空间堆积, 表面光滑。 $x=0$ 和 0.3 时, 载氧体的颗粒较分散, 粒径较均匀, 孔洞较多, 有利于晶格氧的传递。随着Sr掺杂量的增加, 载氧体表面孔洞变少, 微观形貌向层状发展; 至 $x=0.9$ 时, 载氧体颗粒变得大小不均。经过5次氧化还原反应后, 载氧体出现了轻微的烧结, 颗粒变大, 表面变得粗糙。但此时仍以颗粒形态存在, 颗粒之间存在孔洞结构, 还可以保持较好的反应性能。

3.2. 热重循环反应

氧化还原循环反应过程中四种载氧体的氧化程度

与反应时间的关系如图7所示。以 $LaFeO_3$ 为例, 在初始通入甲烷后, 与载氧体中的晶格氧发生反应, 载氧体的质量迅速降低, 最终的氧化程度为 0.65 , 表明 $LaFeO_3$ 中有 35% 的晶格氧参与到甲烷的还原反应过程。通入空气后, 载氧体的质量开始上升, 还原态的 $LaFeO_3$ 恢复晶格氧, 氧化程度基本可恢复到 0.95 以上, 失去的晶格氧几乎全部恢复。经过五次循环后载氧体的供氧能力没有明显的衰减, 仍保持较好的循环使用能力。 $La_{1-x}Sr_xFeO_3$ 在5次氧化还原过程中氧化程度随反应时间的变化列于表2。

可以看出, 当 $x=0.3$, 0.5 和 0.9 时, 对应载氧体最终的氧化程度分别为 0.5 , 0.54 和 0.58 , 表明随着Sr含量的增加, 载氧体中参与反应的晶格氧减少, 但供氧能力均高于 $LaFeO_3$ ($X_{red}=0.64$)。另外, 从反应时间来看, 随着Sr掺杂量的增加, 载氧体的反应速率变缓, 还原难度加大。陈永红等^[21]用甘氨酸-硝酸盐法合成了 $La_{1-x}Sr_xFeO_{3-\delta}$ ($x=0.0\text{--}0.6$)系列粉体, 采用碘滴定法测定了该系列产物中Fe元素的平均表现化合价和氧的非化学计量值, 结果表明, 随A位Sr掺杂量的增加, Fe的平均化合价逐渐升高, 在 $x=0.4$ 时达到最大值。钟子宜等^[22]对催化甲烷完全氧化反应前后的 $La_{1-x}Sr_xFeO_{3-\delta}$ 进行了Mössbauer谱学研究, 发现无序分布 Fe^{4+} 含量的增加, 提高了体系能量和晶格氧的反应活性, 在一定范围内催化氧化活性随 x 增加而增大。但随着 x 的继续增大, Fe^{4+} 的分布开始变为有序化, 伴随 $Fe^{4+} \rightarrow Fe^{3+}$ 留下的氧空位也开始变得有序化, 体系能量降低, 催化活性下降。因此, Sr的加入能提高载氧体的供氧能力, 但掺杂量要控制在一定的范围内。根据热重实验结果, $x=0.3$ 和 0.5 时载氧体的反应性能较好, 供氧能力较 $LaFeO_3$ 提高了 $17\%\text{--}39\%$, 这与 H_2 -TPR结果一致。

3.3. CH_4 在 $La_{1-x}Sr_xFeO_3$ 载氧体上的部分氧化活性评价

在固定床反应装置上考察 $La_{1-x}Sr_xFeO_3$ 载氧体与 CH_4 的反应活性, 图8(a)为 CH_4 转化率随反应时间的变化关系。可以看出, 在反应初始阶段 CH_4 转化率较高, 但是随反应进行迅速降低, 在 $4\text{--}6\text{ min}$ 左右达到最低值, 之后又随着反应的继续进行而逐渐升高。这是由于反应初期载氧体表面的吸附氧立即参与反应并迅速消耗, 而内部的晶格氧由于扩散能力所限, 此时没有足够的氧参与 CH_4 的还原反应中, 从而造成反应活性快速下降^[23,24]。随着反应的继续进行, 由于钙钛矿型氧化物形成固溶体而具有的良好氧传递能力, 内部晶格氧参与反应促使 CH_4 转化率又迅速升高。四种载氧体中, $LaFeO_3$ 上 CH_4 转化率最高, 但在 CH_4 转化率迅速升高的过程中伴随着(12

min之后) $n(\text{H}_2)/n(\text{CO})$ 迅速增大(图8(b)), 表明此时晶格氧供给不足, 甲烷发生大量裂解. $x = 0.3$ 和 0.5 时, 样品上 CH_4 转化率相近, 维持在70%左右; 而 $x = 0.9$ 时, CH_4 转化率最低, 最高仅为55%. 这三种载氧体上反应生成合成气的 $n(\text{H}_2)/n(\text{CO})$ 最终都在2附近, 效果较好, 没有发生明显的 CH_4 裂解.

图9为 CO 和 H_2 的选择性随反应时间的变化. 反应初期参与反应的吸附氧易造成 CH_4 的完全氧化, 因此 CO 和 H_2 选择性较低. 随着反应的进行, 具有选择性氧化能力的晶格氧逐渐占据主导地位, CO 和 H_2 选择性开始迅速升高. 晶格氧逐渐消耗, CO 的选择性开始降低, 其中 LaFeO_3 最先开始降低, 随着反应的进行迅速下降; 当 $x = 0.3$ 和 0.5 时, 相应载氧体上 CO 的选择性随反应的进行降低的较缓慢, 而 $x = 0.9$ 时 CO 选择性则一直维持在较高的

水平. 四种载氧体参与反应下的 H_2 选择性相差不大, 其升高后趋于稳定, 没有明显的下降趋势.

4. 结论

采用燃烧法制备了钙钛矿型氧化物 $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ 载氧体, 并将其用于甲烷化学链重整合成气反应中, 考察了 Sr 掺杂对载氧体反应性能的影响. 结果表明, $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ 氧化物中表面吸附氧倾向于甲烷完全氧化生成 CO_2 和 H_2O , 而内部晶格氧有利于 $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ 的深层还原, 适用于甲烷部分氧化制取合成气. 载氧体中晶格氧的得失是一个可逆的过程, 5次循环后载氧体的供氧能力没有明显的衰减. Sr 的加入能够提高载氧体的供氧能力, 同时较好地抑制了 CH_4 的裂解, 但 Sr 掺杂量要控制在合理的范围内, 当 $x = 0.3$ – 0.5 时, 载氧体催化性能最好.