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Article

$La_{1-x}Sr_xFeO_3$ perovskites as oxygen carriers for the partial oxidation of methane to syngas

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ABSTRACT

We prepared perovskite-type oxides $La_{1-x}Sr_xFeO_3$ (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 diffration, scanning electron microscopy and H_2 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 $La_{1-x}Sr_xFeO_3$ was suitable for the partial oxidation of methane to produce syngas. Their capacity to provide oxygen was enhanced by the partial substitution of La^{3+} by Sr^{2+} and the synthesized materials have good regenerability. The optimal degree of Sr substitution was found to be x = 0.3–0.5 for $La_{1-x}Sr_xFeO_3$ with regard to reactivity, selectivity, and oxygen-donating ability. CH_4 conversion was higher than 70%, and the $n(H_2)/n(CO)$ ratio remained about 2:1 and no obvious decomposition of CH_4 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 CH_4 and it is predominantly converted into syngas ($H_2 + CO$), 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 CH_4 to syngas: the steam reforming of CH_4 (SRM) [2], the CO_2 reforming reaction (CDR) [3], and the partial oxidation of CH_4 (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 H_2/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, CH_4 is easily completely oxidized to CO_2 and H_2O because

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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, CH_4 is partially oxidized to synthesis gas (H_2/CO = 2) by the lattice oxygen in the oxygen carrier. The reaction process is shown in Fig. 1.

In the reforming reactor, CH_4 is partially oxidized by the oxygen carrier as shown in Eq. (1):

$$Me_xO_y + CH_4 \rightarrow Me_xO_{y-1} + 2H_2 + CO \quad (1)$$

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

$$Me_xO_{y-1} + 1/2O_2 \rightarrow Me_xO_y \quad (2)$$

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 CH_4 conversion of 98%. CeO_2-Fe_2O_3 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 $La_{0.8}Sr_{0.2}FeO_3$ was used by Li et al. [13] in CLR technology, and their results show that CH_4 can be partially oxidized to CO and H_2 by the lattice oxygen in $La_{0.8}Sr_{0.2}FeO_3$. The reduced $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ can then be re-oxidized by air to recover the lattice oxygen. Various additional perovskite-type metal oxides $AFeO_3$ (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, $La_{1-x}Sr_xFeO_3$ 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 diffration (XRD), scanning electron microscopy (SEM), and H_2 temperature-programmed reduction (H_2-TPR) techniques. The reactivities of the $La_{1-x}Sr_xFeO_3$ were then investigated in a thermogravimetric analysis (TGA) reactor and in a fixed-bed reactor.

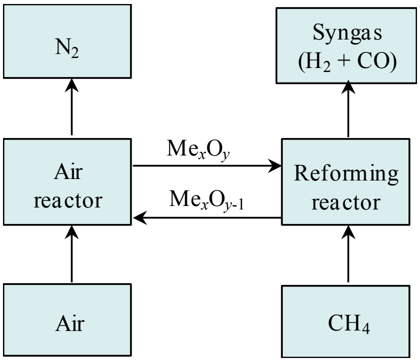

Fig. 1. Chemical looping reforming of CH_4.

2. Experimental

2.1. *Synthesis of $La_{1-x}Sr_xFeO_3$*

$La_{1-x}Sr_xFeO_3$ perovskite-type metal oxides (x = 0, 0.3, 0.5, 0.9) were prepared by a combustion method. First, the required amounts of $La(NO_3)_3\cdot6H_2O$, $Fe(NO_3)_3\cdot9H_2O$, and $Sr(NO_3)_2$ 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 ($H_2NCH_2CO_2H$) 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: $La_{1-x}Sr_xFeO_3$.

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 (2θ) scan range was from 5° to 80°. The morphology of the perovskite-type oxides was studied by SEM on a Hitachi S4800 instrument. H_2-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 N_2 to 850 °C. When the temperature reached a desired value, CH_4 (40 vol% CH_4 in N_2) and air were alternately introduced into the reaction tube. The degree of oxidation X was calculated as follows:

$$x = (m - m_{\rm red})/(m_{\rm ox} - m_{\rm red}) \quad (3)$$

where m is the instantaneous mass of the sample, $m_{\rm ox}$ is the mass of the sample when fully oxidized, and $m_{\rm red}$ 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 N_2 atmosphere at 850 °C. A mixture of 40.0 vol% CH_4 balanced with N_2 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.

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