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Preparation of double perovskite-type oxide $LaSrFeCoO_6$ for chemical looping steam methane reforming to produce syngas and hydrogen

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Abstract: Double-perovskite type oxide $LaSrFeCoO_6$ was used as oxygen carrier for chemical looping steam methane reforming (CL-SMR) due to its unique structure and reactivity. Solid-phase, amorphous alloy, sol-gel and micro-emulsion methods were used to prepare the $LaSrFeCoO_6$ samples, and the as-prepared samples were characterized by means of X-ray diffraction (XRD), hydrogen temperature-programmed reduction (H_2-TPR), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area. Results showed that the samples made by the four different methods exhibited pure crystalline perovskite structure. The ordered double perovskite $LaSrFeCoO_6$ was regarded as a regular arrangement of alternating FeO_6 and CoO_6 corner-shared octahedra, with La and Sr cations occupying the voids in between the octahedral. Because the La^{3+} and Sr^{2+} ions in A-site did not take part in reaction, the TPR patterns showed the reductive properties of the B-site metals. The reduction peaks at low temperature revealed the reduction of adsorbed oxygen on surface and combined with the reduction of Co^{3+} to Co^{2+} and to Co^0, while the reduction of Fe^{3+} to Fe^{2+} and the partial reduction of Fe^{2+} to Fe^0 occurred at higher temperatures. From the point of view of the oxygen-donation ability, resistance to carbon formation, as well as hydrogen generation capacity, the sample made by micro-emulsion method exhibited the best reactivity. Its redox reactivity was very stable in ten successive cycles without deactivation. Compared to the single perovskite-type oxides $LaFeO_3$ and $LaCoO_3$, the double perovskite $LaSrFeCoO_6$ exhibited better syngas and hydrogen generation capacity.

Keywords: double-perovskite; CL-SMR; micro-emulsion; oxygen species; redox; rare earths

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As a novel technology, chemical looping steam methane reforming (CL-SMR) technology has been drawing wide attention for the conversion and utilization of methane. In CL-SMR technology, methane is partially oxidized to syngas by the lattice oxygen of the oxygen carrier in the reformer reactor, and the reduced oxygen carrier is oxidized by steam to recover lattice oxygen and simultaneously to produce hydrogen in the steam reactor. Usually, an air reactor is needed since the oxygen species in oxygen carrier cannot be completely recovered by steam oxidation[1,2]. Syngas and hydrogen can be simultaneously obtained through two steps:

Methane reduction:

$$M_xO_y+CH_4 \rightarrow M_xO_{y-\delta1-\delta2}+(2H_2+CO) \quad (1)$$

Steam oxidation:

$$M_xO_{y-\delta1-\delta2}+H_2O \rightarrow M_xO_{y-\delta1}+H_2 \quad (2)$$

Air oxidation:

$$M_xO_{y-\delta1}+O_2 \rightarrow M_xO_y \quad (3)$$

where M_xO_y is an oxygen carrier, $M_xO_{y-\delta1}$ and $M_xO_{y-\delta1-\delta2}$ are the corresponding reduced oxygen carrier. Compared to the traditional partial oxidation of CH_4, the syngas with molar ratio of H_2/CO close to 2:1 can be obtained in CL-SMR and then can be used as a feed gas for direct methanol or Fischer-Tropsch synthesis. Then in the steam oxidation step, pure hydrogen can be obtained just by cooling the H_2/steam mixture exiting the steam reactor, without requirement of additional gas treatments such as reforming or shifting and separation processes.

In the CL-SMR technology, the most important factor is the properties of oxygen carrier. High methane conversion, high syngas selectivity, high sintering resistance and good activity for water splitting to produce hydrogen are four dominating requirements for oxygen carrier. Various metal oxides such as Fe-based oxides, Ni-based oxides, Cu-based oxides, Mn-based oxides, Ce-based oxides, and complex mixed metal oxides have been investigated as oxygen carriers for this process in previous researches[3–10]. As a special mixed-metal oxide, perovskite-type metal oxides have attracted more and more attentions due to the high reactivity and thermal stability[11–14]. Perovskite-type metal oxides are a series of mixed-metal oxides with general formula ABO_3,

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where A is usually a lanthanide ion and/or alkaline earth metal and B is a transition metal ion. The catalytic activity of ABO_3 is mainly determined by the B site metal, while A site is non-catalyzed but affects the oxygen vacancy and valence states of B site elements[15]. Samples of $LaFeO_3$[16,17], $La_{1-x}Sr_xFeO_3$[18], $LaFe_{1-x}Co_xO_3$[19], $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$[20] and $LaFe_{1-x}Ni_xO_3$[21] have been used for CH_4 oxidation. Moreover, perovskite-type oxides can serve not only as lattice oxygen carriers but also as catalysts for CH_4 activation[22]. Therefore, more varied perovskite-type oxides are exploited to satisfy the requests for oxygen carriers in CL-SMR.

Double perovskite-type oxide is a type of special perovskites with formula A'A''B'B''O_6, where B'–O_6 and B'' –O_6 octahedras are arranged alternately by the way of corner-sharing[23]. Differing from the single perovskite-type oxide, the catalytic activities of double perovskite-type oxides can be effectively improved through the synergy and coordination of the metals in special structure of B'–O–B''. Hu and the co-workers[24–27] investigated double perovskite-type oxides La_2CuNiO_6, La_2CuMnO_6, $LaSrFeCoO_6$, and La_2CoAlO_6 for methane combustion. They found that the synergistic effect of B and B' metals could effectively enhance the catalytic activity. Zheng et al.[28] prepared $LaSrFeMo_{1-x}Co_xO_6$ for methane catalytic combustion and also demonstrated the synergistic effect of Fe^{3+} with Mo^{2+} and Co^{2+}. Therefore, the different configuration and different exchange interaction between A'/A'' and B'/B'' metals in double perovskite-type oxide may provide an extensive modeling space for researches. Due to the special structure, double perovskite- type oxides are widely used as magnetic materials[29], superconducting materials[30], and catalytic materials[31,32]. All the researches confirmed the excellent performance of the double perovskite-type oxides in catalysis and oxidation. But as far as we know, there is no report regarding the catalytic performance of double perovskites-type oxides for CL-SMR technology, especially from the points of both chemical reforming of methane and water splitting. Also the cyclic reactivity of double perovskite- type oxide for oxygen delivery has no research.

In this work, double perovskite-type metal oxide $LaSrFeCoO_6$ was used as oxygen carrier for the CL-SMR process. The properties of the oxides were characterized by means of X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area, H_2 temperature-programmed reduction (H_2-TPR) techniques, and X-ray photoelectron spectroscopy (XPS). Then the reactivities of $LaSrFeCoO_6$ were investigated in a fixed-bed reactor. Moreover, the behaviors of single perovskite-type oxides $LaFeO_3$ and $LaCoO_3$ were used to make comparison with $LaSrFeCoO_6$.

1 Experimental

1.1 Synthesis of the double perovskite-type oxides

The chemical reactions and physical changes during the preparation process are different for different preparation methods. The preparation methods would largely affect the properties of oxides, consequently to affect the oxidation reactivities. In this paper, solid-phase method, amorphous alloy method, sol-gel method and micro-emulsion method were used for the preparation of double perovskite-type oxide $LaSrFeCoO_6$. The required amounts of $La(NO_3)_3·6H_2O$, N_2O_6Sr, $CoN_2O_6·6H_2O$ and $Fe(NO_3)_3·9H_2O$ were weighed at a desired stoichiometric ratio and dissolved in deionized water to get a mixed nitrates solution.

1.1.1 Solid-phase method

The mixed nitrates were put into the ball mill to be grinded for 4 h. After that, the resulting solution was suction filtrated and dried at 110 ºC for 24 h. The powdered precursor was then thermally decomposed at 500 ºC for 2 h and calcined at 1000 ºC for 6 h. The resulting product was ground to obtain the fresh double perovskite-type oxides of $LaSrFeCoO_6$, which was named sample SP.

1.1.2 Amorphous alloy method

Slightly excessive ammonium bicarbonate was added in the mixed nitrates solution. All the mixed solutions were added into DTPA for pyro-condensation 30 min. The obtained viscous solution was then dried at 110 ºC for 24 h. Finally, the precursor was thermally decomposed at 500 ºC for 2 h and calcined at 1000 ºC for 6 h. The resulting product was ground to obtain the fresh double perovskite-type oxides of $LaSrFeCoO_6$, which was named sample AA.

1.1.3 Sol-gel method

Glycine was added into the solution of the mixed nitrates to reach a glycine/nitrates molar ratio of 1.05. The resulting solution was allowed to evaporate by stirring in a 100 mL beaker at 70 ºC until a viscous gel was obtained. The gel was then thermally decomposed at 500 ºC for 2 h and calcined at 1000 ºC for 6 h. The resulting product was ground to obtain the fresh double perovskite-type oxides of $LaSrFeCoO_6$, which was named sample SG.

1.1.4 Micro-emulsion method

Surfactant Tritonx-100, cosurfactant n-butyl alcohol and oil phase cyclohexane were added to make a mixture of solution A. Meanwhile, the same ratio of surfactant Tritonx-100, cosurfactant n-butyl alcohol and oil phase cyclohexane were added into $(NH_4)_2CO_3$-NH_4OH to make a mixture of solution B. After that, the solution B was slowly dripped into solution A to form sediment under a water bath at 50 ºC. The sediment was allowed to settle for 2 h and filtered. Then the sediment was dried overnight in a convection oven at 110 °C. Finally, the as-prepared precursor was thermally decomposed at 500 ºC for 2 h and calcined at 1000 ºC for 6 h. The resulting