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CHEMICAL-LOOPING OXYGEN TRANSFER PROPERTIES OF PEROVSKITE-TYPE CATALYST $LA_{1-Y}CA_YCU_{0.1}NI_{0.9}O_3$

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ABSTRACT

This paper studies the experimental results of perovskite-based chemical looping combustion (CLC). Chemical looping combustion is a kind of combustion that can separate the fuel from air and avoid the mix of carbon oxide and air. This concept can realize the carbon oxide separation and storage without penalty. That key of CLC is focused on the oxygen carrier, e.g., metal oxide and perovskite. The study aims to assess the performance of a novel perovskite-type oxide as the oxygen carrier. We synthesized a series of La1-yCayCu0.1Ni0.9O3 (x=0, 0.1, 0.5, 0.9) by combustion method. These materials were characterized by using SEM, XRD, BET for unveiling the morphology, structure, and particle properties. Experiments were executed to investigate the reactivity of the redox materials in the thermogravimetric analyzer (TGA) in the respects of oxygen capacity, stability, and regenerability. Isothermal reaction and redox cycles are demanded to evaluate the performance. Hydrogen and methane as the fuel are both considered in this study. Besides, the effect of the temperature from 400 to 800 oC and the redox cycles were evaluated. The La1-yCayCu0.1Ni0.9O3 showed favorable reactivity in the CLC and achieved stable properties in the reaction cycles. The experimental results for CLC indicate that the La1-yCayCu0.1Ni0.9O3 has the potential to be used as the oxygen carriers for CLC system.

Keywords: chemical looping combustion; perovskite-type oxides; Hydrogen, oxygen transfer

NOMENCLATURE

Abbreviations	
CLC	Chemical looping combustion
OC	*oxygen carrier*
CCS	*carbon capture and storage*
CM	*calcium manganese*
LCCN	*La1-yCayCu0.1Ni0.9O3*
BET	*Brunauer Emmett-Teller*
XRD	*The X-ray diffraction*
FE-SEM	*field-emission scanning electron microscopy*
TGA	*Thermographic analysis*

1. INTRODUCTION

Chemical looping combustion (CLC) [1] is two-step combustion for realizing the exothermic reaction and separation of air and carbon oxides. As shown in Fig.1, the hydrocarbon fuels are partially oxidized in the reduce reactor and converted into syngas or CO2 and water[2]. Meanwhile, the oxygen carrier (OC) such as metal oxide is reduced into the metal with the oxygen supply. Then the reduced OC can be re-oxidized and scavenge oxygen from the air in the oxidizing reactor. The first reduction is endothermic, and the energy can be supplied from solar, industrial waste heat, and nuclear waste heat. In this regard, the CLC process can be considered as one of the compelling approaches for recycling of renewable energy and waste energy with no greenhouse gas emissions. The re-oxidation step is exothermic and can be combined with thermal cycles. This approach has shown promise in the power generation and the hydrogen/syngas generation. The advantages of CLC are that (i) the CO2 is separated and captured with no penalty; (ii) the combustion efficiency is not influenced

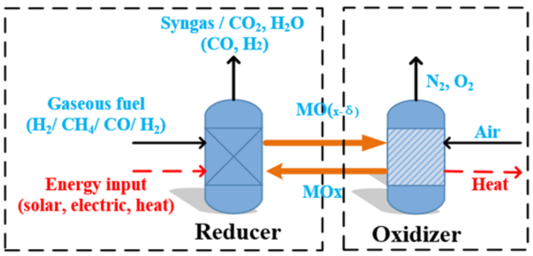

Fig 1 The schematic of Chemical-looping combustion combustion.

by the separation. (iii) renewable energy is used to drive the thermal cycles with high efficiency.

The oxygen carriers are considered as one of the most important factors in CLC, which based on metal oxides such as Fe, Co, Ni, Cu, Mn, etc. [3-6]. Previous researches have contributed to different metal oxides and their utilization mechanism. The NiO, Fe2O3, CuO, and CoO have been investigated by using TG or reactor. Jafarian et al. [7] discussed the influence of the type of oxygen carriers on the performance of a hybrid solar chemical looping combustion system. Therein, the NiO is considered as the most promising oxygen carrier for CLC from the standpoints of reactivity and systematic performance. Jin et al. [8] tested the NiO in the TG, and it showed the good reactivity and regenerability in the CLC. Hong et al. [9] analyzed the solar heat driven CLC system, and it indicated that the net solar efficiency is about 30%. That means the CLC shows comparable propertied both in the electricity generation and the carbon capture and storage (CCS) [10]. However, the carbon resistance still a barrier for the next development of the OC in CLC, especially for the nickel.

To deal with this problem, the perovskite, as a novel material alternative, was proposed to be used as the oxygen carrier in the CLC. In recent decades, perovskite-type oxides are investigated for the performance of oxygen transfer, oxygen capacity, and carbon resistance. Imanieh et al. [11] tested the calcium manganese (CM) perovskites for chemical looping combustion as well as the A-site doping CLMF, CLMZ, CSMF, and CSMZ. Lanthanum [12] and calcium-based perovskites [13] are mostly suitable for oxygen transportation, reactivity, regenerability, and the resistance to the carbon formation. Lima et al. [14] investigated the La1-xCaxNiO3 as the catalyst in dry reforming of methane, and the coking resistance is desirable and stable with x = 0.05 and 0.8.

Furthermore, the hydrogen, as renewable energy, renders the advantages as a gaseous fuel for chemical looping combustion for power generation. The hydrogen was used as a gaseous fuel since it is the major compound of syngas from biomass/coal gasification process. This study also aims to explore the oxygen transfer capacity of the materials under hydrogen as the fuel.

The object of this work was to investigate the oxygen transfer properties of the perovskite-type oxides, which can be used in CLC for power generation. La1-yCayCu0.1Ni0.9O3 were prepared and tested. The A-site substitution of La1-yCayCu0.1Ni0.9O3 (LCCN) that has been rarely reported was studied. The XRD, BET, SEM are used to characterize the structure of perovskite-type oxides. And the TPD, TPR, and isothermal reaction are used to test the performance of these perovskites.

2. EXPERIMENTAL

2.1 Perovskites preparation

The precursor perovskites LCCN were prepared by the combustion method. In the synthesis, La(NO3)3·6H2O, Ca(NO3)2·4H2O, Ni(NO3)2·6H2O, and Cu(NO3)2·3H2O(Aladdin, 99%) were used. The glycine (H2NCH2CO2H. 99%), as the complexing agent, was added into the mixture according to the volume ratio (1:1.05) of nitrate cations and glycine. The mixture was stirred until the viscous gel was formed. The viscous gel was dried until it changed to solid powder. Then it was ground and calcinated at 900 ^{o}C. Finally, the powders were finely ground to get the La1-yCayNi0.9Cu0.1O3 perovskites.

2.2 Characterizations

BET

The specific surface areas of the perovskites were quantified by using the Brunauer Emmett-Teller (BET) method. The perovskites were degassed at 350 ^{o}C for at least 12 h before tests. The mean pore sizes and total pore volume of the oxygen carriers were obtained from the experiments.

XRD

The X-ray diffraction (XRD) patterns of the perovskites were recorded on a Japan Rigaku Ultimal IV diffractometer instrument operating at 40 kV and 30 mA with Cu target Kα irradiation (λ = 1.54 Å). Diffraction curves of as-prepared samples were collected in the range of 2θ = 10~80° for measuring the mesoporous structure and analyzing the bulk phase composition, respectively.

SEM

The morphology of perovskites was analyzed by field-emission scanning electron microscopy (FE-SEM). The scanning electron microscope (SEM) experiments were carried out on a Zeiss MERLIN compact-62-11 equipped with an Oxford INCA X-ray Detector.

2.3 Reactivity test

The oxygen transfer properties were tested using a Thermographic analysis (TGA). The mass spectrometer was monitored during the reaction to analyze the oxygen transfer. The weight change of perovskites at different temperature for five cycles was detected. The weight change, the oxidation fractional, and oxygen release were considered as the evaluation indices for evaluating the redox performance of as-prepared perovskite-type oxides. Herein, the perovskite-type oxides were evaluated by hydrogen temperature-programmed reduction (H2-TPR), redox reaction (reduction and water splitting), and successive redox cycles.

3. RESULTS AND DISCUSSION

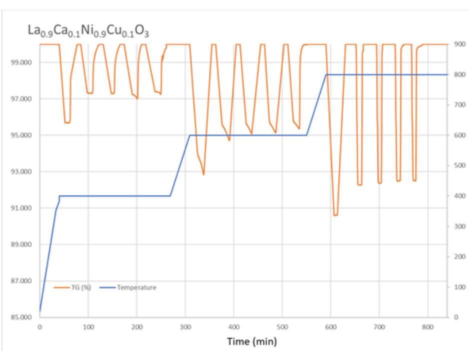

Fig 2 Five cycle reduction/oxidation cycles data for LCCN (y =0.1) at 400~800 oC with 10% H2/Ar.

Five-cycle redox cycles obtained for the LCCN (x = 0.1) oxygen carriers at 400~800 oC are shown in Fig. 2. When 10% of hydrogen was used as the fuel, the weight change of the sample was decreased with the temperature for the reduction step. In fig. 2, the mass changes are about 3% at 400oC, 5% at 600oC, and 8.5% at 800oC. It indicates that the mass change of perovskites is increased as the temperature is raised. The mass change is stable after five cycles, which means that the perovskites can make the oxygen transfer and uptake the oxygen again at the same extent for a long-term. It can promise the regenerability of the oxygen carrier which can be used in the chemical looping combustion system.

The oxygen transport capacities were calculated on the basis of TG data collected at 400, 600 and 800oC as a function of the cycle number shown in Fig. 3 (a, b, c), respectively. At the beginning of the CLC reactions, the oxygen transport capacities appeared to stabilize after 2 cycles. The oxygen transport capacities initially decrease slightly with increasing cycle number but stabilize after the second cycle. And it was increased with the temperature. It means the higher temperature can make the perovskite release more oxygen at the same gas conditions.

The calculated reaction rates for reduction are shown in Figs. 4(a, b, c). The reaction rates were calculated by differentiating the mass data versus time and they mean the rates at a maximum of DTG peak. The lowest reduction reaction rate of 0.15%/min was

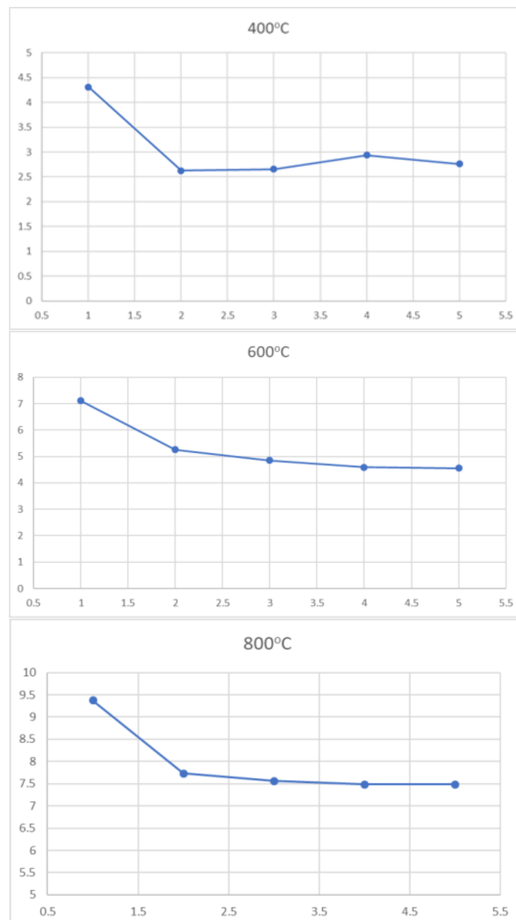

Fig 3 Oxygen transport capacity for LCCN (y =0.1) at versus cycle number at (a) 400°C, (b) 600 °C and (c) 800 °C.

observed at 400oC for LCCN (x =0.1), and the highest rate of 2%/min was observed. The reduction reaction rate was observed to raise with an increase in temperature.

4. CONCLUSIONS

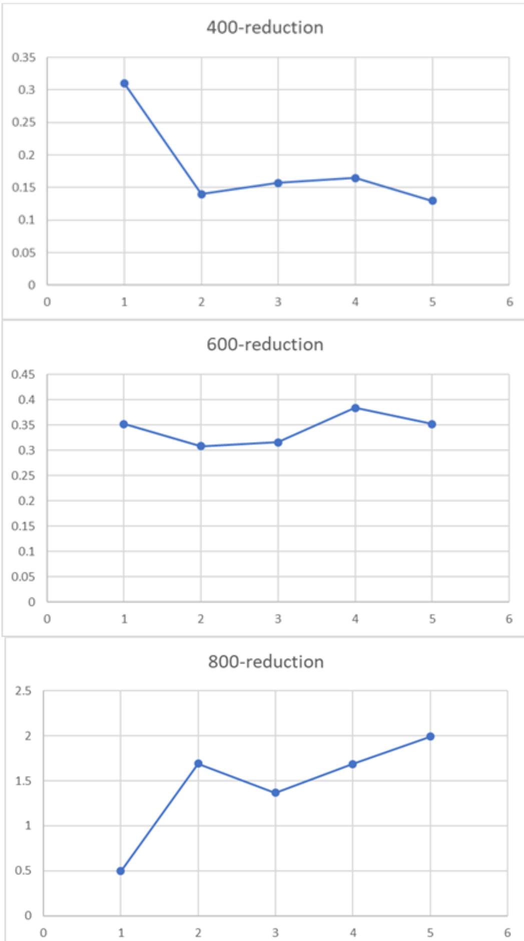

Fig 4 Reduction rate of LCCN (y =0.1) with the number cycle at (a) 400°C, (b) 600 °C and (c) 800 °C.

New perovskite-type lanthanum Ni-and Ca-based materials suitable for hydrogen chemical-looping combustion processes were proposed. All of the prepared perovskites as the oxygen carrier exhibited stable performance during five cycles of TGA tests at temperatures between 400 and 800 oC. The oxygen transport capacities were calculated from the TGA results. The effects of temperature and the Ca ratio were determined. These results indicate that the LCCN have the good performance and prone to be used in the CLC system.

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