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A thermogravimetric study of $CoTiO_3$ as oxygen carrier for chemical looping combustion

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ABSTRACT

CoTiO3 perovskite was investigated as an alternative oxygen carrier for chemical looping combustion. The cyclical reduction and oxidation reaction were performed in TGA equipment. When the CoTiO3 particles were reduced, oxygen transfer capacity was maintained at 10.2 wt% during 10th cycles with 15% H2/N2 and 10.5 wt % with 15% CH4/N2. It was similar to the theoretical oxygen transfer capacity, 10.3 wt%. The maximum oxygen transfer rate was 0.015 mmol O2/g/sec during the reduction process. For 15% CH4/N2, the transfer rate was 0.03 mmol O2/g/sec which was twice that resulting from using hydrogen. From XRD and TPR results, $CoTiO_3$ was transformed to Co/TiO_2 and CoC_x during reduction with hydrogen and methane, respectively. After all cycles, the particles were not agglomerated and appeared to be similar to its initial state. Conclusively, CoTiO3 could be a potential candidate as an oxygen carrier because $CoTiO_3$ shows an improved oxygen transfer capacity and rate.

1. Introduction

The demand for fossil fuels has increased since the industrial revolution to meet the increasing demand for energy resulting from human activities [1]. In the long term, fossil fuels are still the dominate energy source worldwide. However, the combustion of fossil fuels such as oil, gas and coal leads to CO_2 emissions into the atmosphere and is considered to be the largest source of greenhouse gases (GHGs) contributing to global warming. So, scientific and political communities are working on creating mitigating strategies to address the high concentrations of CO_2 in the atmosphere. Much attention has been paid to efforts that reduce CO_2 emissions by carbon capture, storage, and utilization. There are three major categories, such as pre-combustion, oxy-fuel combustion and post-combustion, where carbon capture is performed. Chemical looping combustion (CLC) offers promise as a technology within the oxy-fuel combustion category that allows for lower carbon capture costs [2–6].

Normally, CLC consists of two interconnected reactors: an air reactor, where the oxidation reaction occurs with reduced oxygen carriers and air or oxygen; and a fuel reactor, where fuel and oxygen from an oxidized carrier combust. The flue gas stream leaving the fuel reactor contains both CO_2 and H_2O. Pure CO_2 can be conveniently obtained using water condensation thereby saving the cost of CO_2 separation. Oxygen carriers circulate through these two reactors; therefore, it is very important for the oxygen carrier to provide the suitable activity and durability during CLC process. Some transition metal oxides such as NiO [7], Co_2O_3 [8], Mn_3O_4 [9] and Fe_2O_3 [10] have been studied as oxygen carriers. Although these metal oxides have the necessary activity for CLC, their activity would be lost by the agglomeration of particles as the cycle repeated. To improve durability, some supports such as Al_2O_3 [11], TiO_2 [12] and SiO_2 [13] have been adopted, but the loss of the activity per mass would be expected when using these supports as well. A metal oxide with a perovskite structure was introduced in order to overcome this obstacle due to its redox property and thermal stability.

Perovskite has an ABO_3 formula, where the oxidation state of A and B is 2^+ and 4^+, respectively. Studies have been conducted using $CaMnO_3{}^{-\delta}$ [14], $CaMn_{1-x}BxO_3{}^{-\delta}$ (B = Al, V, Fe, Co, and Ni) [15], $Ca_{1-x}A_xMnO_3$ (A = Sr and Ba) [16], and $CaMg_{0.1}Ti_{0.125}Mn_{0.775}O_{2.9}{}^{-\delta}$ [17] for CLC. Although the perovskite structure shows high thermal stability,

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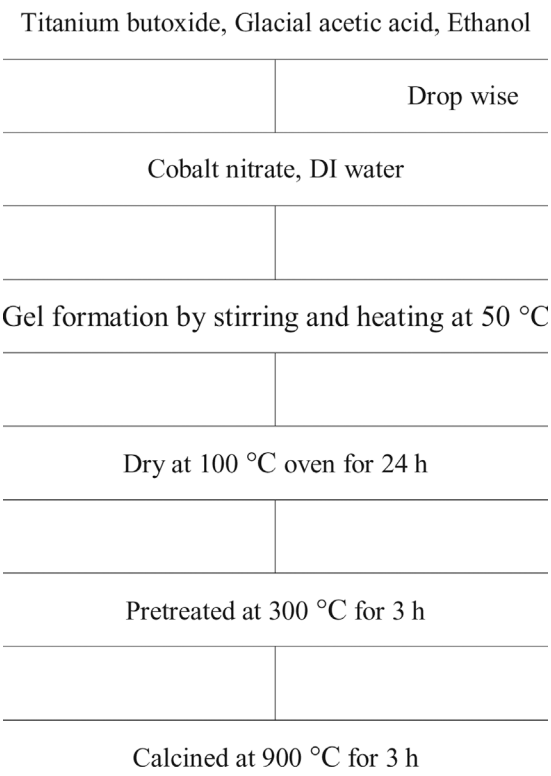

Fig. 1. Preparation procedure of $CoTiO_3$ oxygen carrier.

its oxygen transfer performance rates are lower than that of other transition metal oxides.

In this study, the activity and stability of $CoTiO_3$ with a perovskite structure was investigated as an oxygen carrier in CLC. Co was chosen because it has most active reactivity and oxygen transfer capacity when used as single metal oxide. In order to fabricate the perovskite structure with Co, Ti was selected as the second metal species.

2. Experimental

2.1. $CoTiO_3$ preparation

Fig. 1 shows the preparation procedure of the $CoTiO_3$ oxygen carrier. The $CoTiO_3$ oxygen carrier was produced by the sol-gel method. Precursors were obtained from Sigma-Aldrich. Solution A comprised titanium (IV) butoxide (97% purity, 0.01 mol) dissolved in 40 ml of glacial acetic acid (≥99.7% purity) and 10 ml anhydrous ethanol (≥99.99% purity). Solution B comprised cobalt nitrate (≥98% purity, 0.01 mol) dissolved in 30 ml of deionized (DI) water. Under continuous stirring, solution B was added a drop at a time into solution A. The resulting solution was then heated in a rotary evaporator at 50 °C for 1 h and concentrated to form a red gel. The gel was dried at 100 °C for 24 h and further calcined at 900 °C for 3 h after pre-treatment.

2.2. Thermogravimetric analysis

2.2.1. Experimental condition of thermogravimetric analysis

The cyclical reduction and oxidation reaction were performed in a thermogravimetric analyzer (TGA, SINCO N-1000). The oxygen carrier (30 mg) was placed into an aluminum pan and heated by furnace at 50 °C/min up to 900 °C with air. After reaching the set temperature, the experiment was started by exposing the oxygen carrier to alternating reducing and oxidizing conditions. To prevent the reducing and oxidizing gases from mixing, nitrogen was passed over the pan for 3 min after each process. The oxidizing and reducing processes continued until there was no mass change observed during each cycle. Air was used as the oxidizing gas and H2 (15%) and CH4 (15%) with N_2 base served as the reducing gas, respectively. The flow rate of each oxidizing and reducing gas was set to 150 ml/min.

2.2.2. Thermogravimetric analysis method

The reduction and oxidation activity of the oxygen carrier was analyzed in terms of its oxygen transfer capacity and oxygen transfer rate using TGA where mox was the mass after the complete oxidation of the oxygen carrier, and mred was the mass when fully reduced, and RO is the oxygen transfer capacity, or the maximum percentage of mass change by oxygen transfer under a given experimental condition:

$$R_O = \frac{m_{ox} - m_{red}}{m_{ox}} \quad (1)$$

Mass-based conversion(ω) is a measure of how much the mass has decreased and increased relative to the mass when fully oxidized,

$$\omega = \frac{m}{m_{ox}}, \text{ where } m_{red} \leqq m \leqq m_{ox} \quad (2)$$

Conversion for reduction and oxidation for the oxygen carrier are

$$\text{Conversion in reduction} = X_{red} = \frac{m_{ox} - m}{m_{ox} - m_{red}} \quad (3)$$

and

$$\text{Conversion in oxidation} = X_{ox} = \frac{m - m_{red}}{m_{ox} - m_{red}} \quad (4)$$

The oxygen transfer rate is expressed in terms of the amount of oxygen reacted per unit weight per unit time.

2.3. Characterization techniques

Temperature programmed reduction (TPR) and oxidation (TPO) experiments were performed with a BELCAT-M (BEL Japan, Inc.) equipped with a thermal conductivity detector (TCD) to investigate the reduction and oxidation properties of the oxygen carrier. Prior to analysis, each sample was pre-treated at 200 °C for 1 h in Ar flow to clean the surface then cooled to 100 °C. After the pre-treatment, gas mixture was passed through the sample cell at 30 ml/min and the temperature was raised from 100 to 900 °C at 5 °C/min. 5% H_2/Ar and 5% O_2/He were used as the reduction and oxidation gas, respectively.

To determine the oxygen carrier phase, X-ray diffraction (XRD) measurements were performed with an X'pert Powder (PANalytical) device using Cu Kα radiation and applied current and voltage 40 mA and 40 kV, respectively. The catalysts were scanned from 10° to 90° at 5°/min. Comparison of the observed results with the JCPDS database identified the oxide phases.

Morphology and particle size of the oxygen carrier was observed by field emission scanning electron microscope (FE–SEM, SUPRA40VP). Before analysis, the oxygen carrier was coated with gold by sputtering at 20 mA for 60 s using a coating machine. The analysis of chemical composition was performed using energy dispersive X-ray spectroscopy (EDS, HORIBA: EX-250).

The surface oxidation state analysis of the samples was carried out by X-ray photoelectron spectroscopy (XPS) (Kratos Analytical, AXIS Ultra DLD). The monochromatized X-ray Al Kα radiation (1486.6 eV) was used. The core levels were calibrated by reference to the first component of the C 1 s core level peak set at 284.5 eV.

3. Results and discussion

3.1. X-ray diffraction, SEM and XPS

The change of crystal structure during the oxidation and reduction process for the oxygen carrier was undertaken using XRD. Fig. 2(a) showed the crystal structure of $CoTiO_3$ particles after calcination and before reaction. It clearly showed the single crystal structure of $CoTiO_3$