Experimental Investigation of the Reactivity of the Copper-based Oxygen Carrier Used in Chemical Looping Air Separation

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Abstract. Chemical looping air separation is a novel oxygen production technology based on the reduction and oxidation cycle of the oxygen carrier. In this work, reactivity tests of the reduction and oxidation reactions with CuO supported on SiO2, TiO2, ZrO2, and Al2O3 were performed on STA409PC thermogravimetric analyzer under different temperatures and particle sizes. The results show that SiO2, TiO2, ZrO2 are the suitable binders for CuO. The reaction rates have the tendency of increasing as particle sizes decrease, but the influence is not apparent. The binders of SiO2, ZrO2 and TiO2 combined with CuO show high reactivity and conversion ratio. The reaction rates increase greatly as the temperature increases.

1. Introduction

CO2 is the main cause of global climate change and the CO2 concentration in the atmosphere has increased greatly during last decades. Several measures have been proposed to reduce the CO2 emission and oxy-fuel combustion is one of the effective measures [1, 2]. In oxy-fuel combustion, high purity of oxygen is needed [3-5]. However, the shortcomings and high price of the current air separation technologies restrict its application in industry widely [3-5]. Chemical looping air separation (CLAS) is a new air separation technology for oxygen production. The average specific power of the CLAS process is just 26 % of an advanced cryogenic air separation system [6]. The integration of CLAS and oxy-fuel combustion power plant has been investigated by Moghtaderi et al. The results indicated that for acceptable process kinetics CLAS can potentially run at much lower operating costs compared to an advanced cryogenic distillation system for oxy-fuel thermal power plant [5]. The CLAS system contains two interconnected reactors (oxidation and reduction reactors). Oxygen carrier is the bond of the two reactors. In the oxidation reactor, the oxygen carrier captures oxygen from air and in the reduction reactor, the oxygen carrier releases oxygen to carrier gas. The carrier gas used in the reduction reactor can be steam or flue gas to produce pure O2 or oxygen enriched gases. The key issue for large-scale application of CLAS is the capability of releasing oxygen of oxygen carriers under suitable temperature and oxygen concentration. In addition, some other properties are also needed, such as sufficient oxygen transport capacity, high reactivity and mechanical strength, chemical stability [7-9]. Ni-, Cu-, Co-, Fe- and Mn-oxides were the common oxygen carriers in chemical looping technologies [10, 11]. Besides the oxides, NiO and Fe2O3 cannot release oxygen even when the temperature are higher than 1600K. CuO, Mn2O3 and Co3O4 could evolve gaseous oxygen at suitable temperatures [12-14]. Among the three oxides, copper oxide has the highest oxygen transport capacity and has been studied widely. Gayán et al. [15] tested the oxidation-reduction reactivity and the stability of CuO supported on MgAl2O4 or ZrO2 in an abatch fluidized-bed reactor. The oxygen carriers were identified as suitable materials. Adánez-Rubio et al. [16, 17] evaluated the stability of
CuO/MgAl₂O₄ oxygen carrier under different temperatures. They found that both reduction and oxidation reaction rates were stable with cycles. Mattisson et al. [18] investigated the reactivity of CuO/ZrO₂ with petroleum coke in a small quartz laboratory fluidized bed reactor. In this work, SiO₂, TiO₂, ZrO₂, and Al₂O₃ as binders were prepared oxygen carriers [19]. Reactivity tests were performed on STA409PC under different temperatures and particle sizes.

2. Experimental

2.1. Materials

The materials used in the process were copper oxide combined with binders and these materials were prepared by mechanical mixing method. SiO₂, TiO₂, ZrO₂, and Al₂O₃ powders were used as binders. The preparation process could be seen from our previous studies [21]. Three particle sizes of oxygen carrier were obtained: 76–150μm, 150–200μm and 200–315μm.

The phases of oxygen carriers prepared were analyzed using XRD. The XRD patterns were shown in Figure 1. When ZrO₂, TiO₂, and SiO₂ were used, the phases in the oxygen carriers prepared were mainly CuO and the corresponding binders. When Al₂O₃ was used, CuAlO₂ were formed. The formation of CuAlO₂ followed the Eqs. (1) and (2).

\[ \text{CuO} + \text{Al}_2\text{O}_3 = \text{CuAlO}_2 \]  
\[ 4\text{CuAl}_2\text{O}_4 = 4\text{CuAlO}_2 + 2\text{Al}_2\text{O}_3 + \text{O}_2 \]  

Unlike Cu₂O, the phase of CuAlO₂ cannot be oxidized to CuAl₂O₄ in the oxidation process [22]. The phases of Al₂O₃ and CuAlO₂ all were binders in the Cu/Al oxygen carrier.

The BET surface area of the particles was evaluated by N₂-adsorption and the values were shown in Figure 2. The BET values of the oxygen carriers prepared by the four binders all increased with the binder adding ratio increasing. The effect of binder could increase the anti-sintering property of CuO. Among the four binders, the BET values of Cu/Al oxygen carriers were smallest. The probable reason was that the formation of CuAlO₂ increased the compactness of oxygen carrier.

![Figure 1 The XRD patterns of oxygen carriers](image1)

![Figure 2 The BET values of oxygen carriers](image2)

2.2. Experimental setup

Experimental tests were performed on the STA409PC. For reduction, the sample was heated to 700°C with heating rate of 30°C/min and kept at 700°C for 30min in air atmosphere to make the sample oxidized fully. Then the sample was heated to the required reduction temperatures. At these points, air was stopped and nitrogen was turned on. The reduction process was maintained for 30min to complete the full decomposition of oxygen carrier. For oxidation, the sample was cooled to the required oxidation temperatures in nitrogen atmosphere. Then nitrogen was stopped and air was turned on. The oxidation process was maintained for 30min to complete the full oxidation of oxygen carrier. The mass of sample at each experiment was 10mg.

The conversion ratio (α) can be calculated according to Eqs. (3) and (4).
For reduction: \[ \alpha_{\text{red}} = \frac{m_{\text{ox}} - m}{m_{\text{ax}} - m_{\text{red}}} \tag{3} \]

For oxidation: \[ \alpha_{\text{oxi}} = 1 - \frac{m_{\text{ox}} - m}{m_{\text{ax}} - m_{\text{red}}} \tag{4} \]

Where \( m, m_{\text{ox}}, m_{\text{red}} \) are the masses of the sample at each time, fully oxidized and fully reduced, mg.

3. Results and discussion

3.1. Effect of binder

Figure 3 shows the conversion ratio with time using different binders. The oxygen carriers with ZrO\(_2\), TiO\(_2\) and SiO\(_2\) supports had high reduction and oxidation conversion ratios. However, the oxygen carrier with Al\(_2\)O\(_3\) support had a conversion ratio only about 55%. The reason was that the spinel of CuAlO\(_2\) was formed during the preparation. Based on the maximum oxygen transfer capacity, ZrO\(_2\), TiO\(_2\) and SiO\(_2\) were the suitable binders for CuO. The reduction times of Cu/Zr and Cu/Ti oxygen carriers were small and the reduction rates were fast. The reduction rate of Cu/Si oxygen carrier was slow. The possible reason was that the BET values of Cu/Si oxygen carriers were small. Compared to the reduction rates, the oxidation rates of Cu/Zr, Cu/Si and Cu/Ti oxygen carriers were all high.

![Figure 3: The conversion ratio with time using different binders](image)

3.2. Effect of temperature

Figure 4 shows the conversion ratio with time under different reaction temperatures. The reduction processes were divided into two stages: incubation and rapid oxygen releasing stages. At the beginning of the reduction, the atmosphere in the reactor was air. With the nitrogen inletting, the oxygen concentration in the reactor decreased. When the concentration in the reactor was the equilibrium oxygen partial concentration, the reduction began. The equilibrium oxygen partial concentrations for 900, 950, 1000°C were 1.5%, 4.5% and 12.4% respectively. Thus, the times for incubation stage decreased with reduction temperature increasing. After the incubation stage, the oxygen releasing rates increased greatly. For oxidation, the equilibrium oxygen partial concentrations for 600, 650 and 700°C all were very low (lower than 0.01%). The oxygen concentration in the air (21.0%) was much higher than the equilibrium oxygen partial concentrations of the oxidation reactions. Thus the incubation times for oxidation were short. Moreover, the oxidation rates increased with the oxidation temperatures increasing. Under the oxidation temperatures investigated, high temperatures could promote the oxidation reactions [23].

![Figure 4: The conversion ratio with time under different reaction temperatures](image)
3.3. Effect of particle size

Figure 5 shows the conversion ratio with time under different particle sizes. For reduction, the time for overall conversion increased with the particle size increasing. During the reduction process, the oxygen released should diffuse from the inside of the oxygen carrier to outside. However, the effect of particle size on the reduction rate was not obvious and the reduction rates for the three sizes of oxygen carriers were all very high. The phenomenon was important for the fluidization operation in the CLAS technology. For oxidation, the curves of the three conditions were almost overlapping and the effort of particle size was little. The reason was that the oxygen concentration in the air (0.21) / equilibrium oxygen partial concentration ($5.8 \times 10^{-5}$) at 700°C was so high that the effect of particle size could be ignored. The oxidation rates were high and only about three minutes were needed to oxidize the Cu$_2$O to CuO.

4. Conclusions

TGA tests showed that the binders of SiO$_2$, ZrO$_2$ and TiO$_2$ combined with CuO show high reactivity and conversion ratio. The reaction rates had the tendency of increasing as particle size decreased in the reduction, but the influence was not apparent. The reaction rates increase greatly as the temperature increases.

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