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Study on the Kinetics of Chemical Looping Combustion of Copper-based Oxygen Carrier

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Abstract. Kinetics is the study of rates of chemical processes, which includes investigations of how different experimental conditions can influence the speed of a chemical reaction and the reaction's mechanism. In this paper, the influences of several parameters including particle size and mass of copper-based oxygen carrier, reaction gas flow rate and temperature on the conversion rate of oxygen carrier in chemical looping combustion was investigated. The results of experiment reveal that the conversion rate of oxygen carrier is influenced by the reaction temperature, mass of the oxygen carrier and the reaction gas flow rate. The conversion rate of oxygen carrier is improved with decreasing the mass of the oxygen carrier and increasing the reaction gas flow rate within a certain extent in the chemical looping combustion process. The particle size has very little effect on the conversion rate, and 800 °C is an advisable reaction temperature for chemical looping combustion process of copper-based oxygen carrier with methane and air.

Introduction

Chemical looping combustion (CLC) [1], a novel technology based on circulating oxygen carrier, which can be used to meet the demand on energy production without CO_2 emission, has attracted more and more attention. Reaction kinetics, in which the rate of CLC is studied as certain parameters are varied, has been studied and reported to increase the reaction rate of CLC. Ishida et al.[2] investigated the reaction dynamics performance of CLC with NiO mixed-YSZ (yttria-stabilized zirconia) as oxygen carrier. Cao et al.[3] simulated micro-reactor with simultaneous differential scanning calorimetry and thermo-gravimetric analysis（DSC-TGA or SDT) to investigate the reduction kinetics and the mechanism of the reduction product with copper-based oxygen carrier with coal, biomass and solid wastes. Monazam et al.[4] evaluated the rates of reduction of CuO impregnated in bentonite by 10 different rate models in a isothermal thermo-gravimetric analyzer, the results indicated that the transformation kinetics described by the Johnson-Mehl-Avrami (JMA) model was the best fit.

In this paper, experiment is conducted in a maglev thermo-gravimetric analyzer with copper-based oxygen carriers prepared by mechanical mixing, and the influence of reaction parameters such as the particle size and the mass of the oxygen carrier, reaction gas flow rate as well as the reaction temperature on the oxygen carrier conversion rate, is investigated.

Experimental section

The copper-based oxygen carrier containing 80% CuO and 20% SiO_2 was prepared by mechanical mixing [5] and extruded into a cylindrical shape particle, and then the cylindrical oxygen carrier was dried at 105 °C for 12h. The cylindrical copper-based oxygen carrier particle with 2~4mm length and 2mm in diameter was obtained after calcination for 6 h with a calcination temperature of 950 °C under air atmosphere.

A Rubotherm Dyntherm-HP high-pressure high-temperature maglev thermo-gravimetric analyzer (the Netherlands Ankersmid Corporation), can be applied in extreme conditions to conduct contactless analysis of the sample weight loss during a temperature programming run, was employed to oxygen carrier oxidation-reduction reactivity experiments. The instrument is equipped with four individually controlled different reaction gas, and can automatically switch to a different reaction atmosphere. High-purity methane is used as the reductant in the reduction stage of CLC while air as the oxidant in oxidation stage. The methane was introduced into the maglev thermo-gravimetric analyzer when the desired reaction temperature reached and then the reaction atmosphere was switched automatically to air after reduction stage finished, and the duration of both two stages is 1h.

The default experiment in this paper is conducted at the reaction temperature of 800 °C with a combination of gas flow rate of 50mL/min-100mL/min (50-100, the former is methane flow rate and the latter is air flow rate) in reaction sections and original size of fresh oxygen carrier with a mass of 0.1380g. Control variate method is used to examine the impact on the conversion rate of the oxygen carrier by changing one of these four parameters of mass and particle size of the copper-based oxygen carrier, reaction gas flow rate and reaction temperature.

Data in reduction–oxidation TGA tests is directly obtained as a sample weight evolution as a function of time. These weight data can be transformed into conversion data by using the following equations [6]:

For reduction: $X_{red} = (m_{ox} - m)/(m_{ox} - m_{red})$ (1)

For oxidation: $X_{ox} = 1 - X_{red} = 1 - (m_{ox} - m)/(m_{ox} - m_{red})$ (2)

Where m is the actual mass of sample, m_{ox} is the mass of the sample fully oxidized and m_{red} the mass of the sample in the reduced form.

Results and discussion

Influence of oxygen carrier mass. Chemical looping combustion of copper-based carrier involve gas adsorption, diffusion and lattice oxygen reaction with fuel gas molecular such as CH_4, and then desorption and diffusion of the product gas molecules such as CO_2 and H_2O. Therefore, the copper-based oxygen carrier weight gradually reduces as the duration of reaction increases. To analyze the influence of oxygen carrier mass on conversion rate, a set of experiment were carried out with different mass of copper-based oxygen carrier: 0.6885g, 0.3476g, 0.1380g and 0.0383g, but other parameters such as reaction gas flow rate, reaction temperature and oxygen carrier particle size were constant. The mass-change curves and conversion curves during the CLC process are shown in Fig. 1.

It can be seen that different weight loss and weight gain curve was obtained with different mass of the oxygen carrier sample used. As the increase in the mass of the oxygen carrier, the slope of reaction curve is decreasing, which can be concluded that the less the oxygen carrier used, the greater the rate of conversion. But when the mass reduces to a certain extent, the conversion rate will not change much. It also can be seen from the figures that the curve of 0.0383g is more fluctuant than the other three, which is due to the low difference between the fluctuation of the sample mass and the instrumental error of the TG. Therefore 0.1380g of oxygen carrier is chosen to conduct other influence experiments as a result of consideration both the two factors of weakening the effect of mass and reduction of measurement errors.

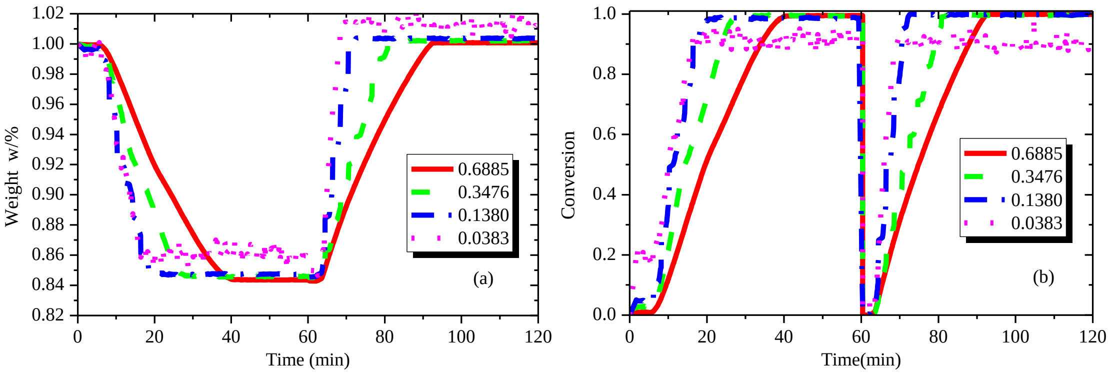

Fig. 1 Mass-change curves (a) and conversion curves (b) in CLC with different mass of oxygen carrier

Influence of particle size of oxygen carrier. In order to investigate the influence of particle size of oxygen carrier on the conversion rate, copper-based oxygen carrier was ground and screened into three particle sizes: less than 100 mesh, 40 ~ 80 mesh and the original particle. These three particle sizes of oxygen carrier with a mass of 0.1380g were used to conduct CLC respectively in the TGA. The mass-change curves and conversion curves during the CLC process are shown in Fig. 2.

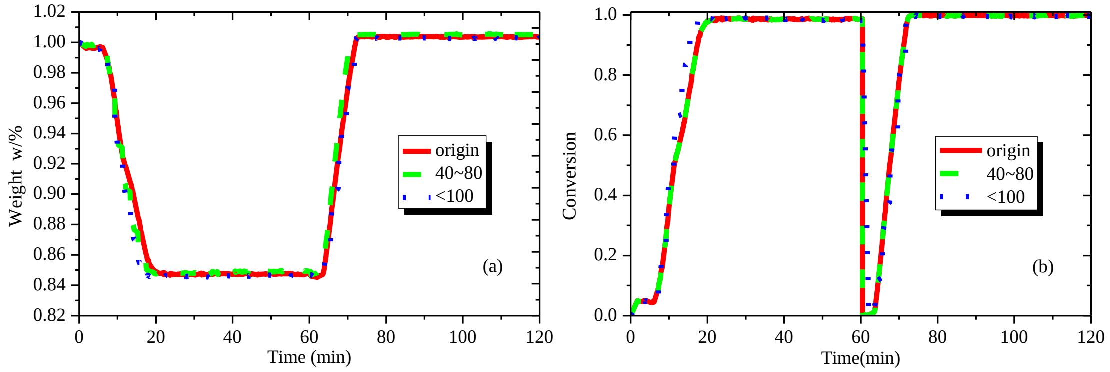

Fig. 2 Mass-change curves (a) and conversion curves (b) in CLC with different size of oxygen carrier

As can be seen from Fig. 2 (a) and 2 (b), similar curves were obtained in the CLC with oxygen carriers in three different particle sizes, which can be concluded that the particle size of oxygen carrier would barely affect the conversion rate of CLC fueled with gas fuels. This probably stem from the fact that the oxygen carrier based on SiO_2 is of large porosity and it’s easy for gas fuel to enter into the pore of oxygen carrier. The difference of the particle size has little affect on the gas-solid contact rate, and the particle size will not affect the reaction rate of chemical looping combustion of gas fuel as a result.

Influence of reaction gas flow rate. Considering that the gas flow rate is also an influence factor on the conversion rate, three different combinations of flow rate were designed: 25-50, 50-100 and 100-200. The mass-change curves and conversion curves during the CLC process using these three combinations of flow rate are shown in Fig. 3.

Similar steps can be found in the reduction stage of these three curves both in Fig. 3 (a) and 3 (b). And with the decrease of the flow rate combinations, step phenomenon becomes more and more obvious. Meanwhile, as the flow rate increases, the end time of both reduction and oxidation stage was brought forward. But when the flow rate increases to a certain extent, the conversion rate will not change much.

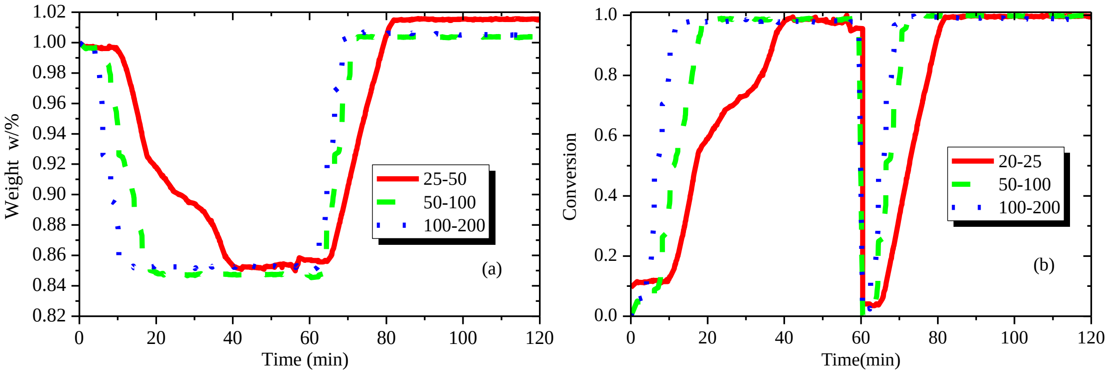

Fig. 3 Mass-change curves (a) and conversion curves (b) in CLC with different flow rate

Influence of reaction temperature. In a reducing atmosphere, the oxygen carrier will lost all lattice oxygen of the active constituent within a certain temperature range. Influence experiment of reaction temperature on conversion rate of oxygen carrier during CLC was carried out controlling reaction temperature at 750 °C, 800 °C, 850 °C and 900 °C, respectively. The mass-change curves and conversion curves during the CLC process are shown in Fig. 4.

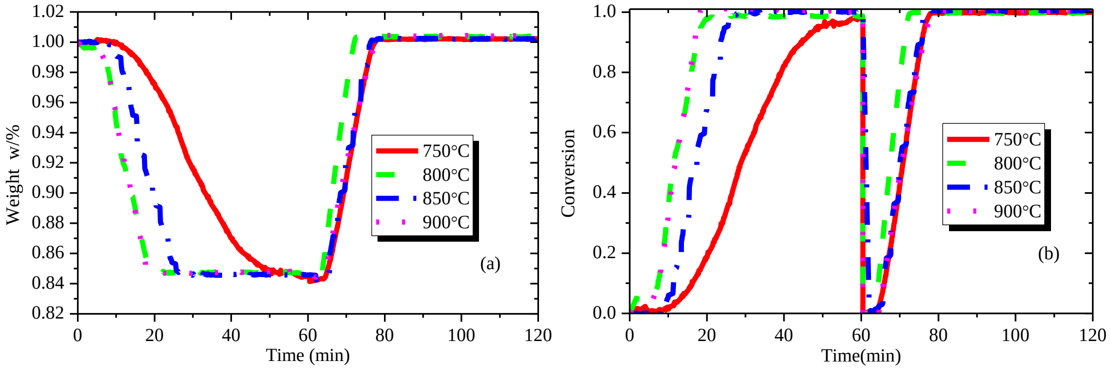

Fig. 4 Mass-change curves (a) and conversion curves (b) in CLC with different reaction temperature

As can be seen from Fig. 4 (a) and 4 (b), in the oxidation stage, four curves at different temperature are close or coincident and the reaction temperature showed little influence on the reaction curve, which can be concluded that the temperature needed to proceed oxidation stage of CLC normally ranges from 750 °C to 900 °C. In the reduction stage, the curves of 800 °C and 900 °C are adjacent and in the lead, followed by 850 °C, and the curve of 750 °C lags behind. Taking into account the low melting points [7, 8] and poor stability of copper-based oxygen carrier, 800 °C is advisable temperature for chemical looping combustion with copper-based oxygen carrier.

Conclusions

Influences of mass and particle size of copper-based oxygen carrier, reaction gas flow rate and temperature on conversion rate of oxygen carrier in CLC are investigated in a maglev thermo-gravimetric analyzer using control variate method and the experimental results are as follows: Within a certain extent, the lower the mass of the oxygen carrier and the greater the reaction gas flow rate, the faster the conversion rate of the oxygen carrier in CLC. The particle size has little effect on the conversion rate of CLC with gas fuel. The CLC can proceed normally when the temperature ranges from 750 °C to 900 °C, but the CLC reaction rate is slower and the duration of weight loss increases under reaction temperature of 750 °C. Considering thermal stability and melting point, 800 °C is advisable temperature for chemical looping combustion with copper-based oxygen carrier.

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References

[1] Richter, H., Knoche, K., “Reversibility of combustion processes,” ACS Symposium Series, 235, 71-86, 1983

[2] Ishida M., Jin H. G., Journal of Chemical Engineering of Japan, Vol. 27, No. 3, 296-301, 1994

[3] Cao Y., Casenas B., Pan W. P., Energy & Fuel, Vol. 20, No. 5, 1845-1854, 2006

[4] Monazam E. R., Siriwardane R., Breault R. W., Tian H. J., Shadle L. J., Richards G., Carpenter S., Energy & Fuel, Vol. 26, No. 5, 2779-2785, 2012

[5] L. F. de Diego, Garcia-Labiano F., Adanez J., Gayan P., Abad A., Corbella B. M., Palacios J. M., Fuel, Vol. 83, No. 13, 1749-1757, 2004

[6] Adanez-Rubio I., Gayan P., Abad A., de Diego L. F., Garcia-Labiano F., Adanez J., Energ Fuel, Vol. 26, No. 5, 3069-3081, 2012

[7] Adanez J., de Diego L. F., Garcia L. F., Gayan P., Abad A., Palacios J. M., Energy & Fuel, Vol. 18, No. 2, 371-377, 2004

[8] Mattisson T., Jardnas A., Lyngfelt A., Energy & Fuel, Vol. 17, No. 3, 643-651, 2003