

DEVELOPMENT OF A GRAIN MODEL ACCOUNTING FOR SOLID DIFFUSION TO DESCRIBE THE REDOX KINETICS OF $\text{CuO}/\text{Al}_2\text{O}_3$ PARTICLES FOR CHEMICAL LOOPING COMBUSTION

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Abstract

Chemical-looping combustion (CLC) has proven to be a promising technology for power production with integrated CO_2 capture. The selection of a suitable oxygen carrier is one of the most crucial steps in CLC because it determines to a large extent the overall process efficiency. Because of its fast reduction kinetics at relatively low temperatures, the use of $\text{CuO}/\text{Al}_2\text{O}_3$ has often been proposed. The redox kinetics as well as the morphological changes during the redox reactions has been investigated in detail. It was concluded that gas-phase diffusion limitations do not play a role in the sudden decrease in the reaction rate observed in all the redox cycles and that oxygen solid diffusion could be the responsible mechanism. A novel grain model based on the transport of oxygen vacancies has been developed with which the redox kinetics could be described with good agreement, not only in its initial slope but also in the sudden decrease in reaction rate and the final conversion, at different operating conditions.

Keywords

Solid diffusion, Oxygen vacancies, Redox kinetics in chemical looping combustion.

Introduction

Chemical-looping combustion (CLC) has proven to be a promising technology for power production with integrated CO_2 capture. Most of the CLC reactor concepts are based on interconnected fluidized-bed reactors, where an oxygen carrier (Me/MeO) is alternately reduced by a fuel (syngas or natural gas) in a fuel reactor and oxidized by air in an air reactor operating at atmospheric pressure. Because the separation of nitrogen from oxygen is already performed in the air reactor, a concentrated CO_2 stream is obtained from the fuel reactor which is ready for storage after steam condensation. To achieve higher overall efficiencies and be more competitive than other capture

technologies, CLC should be operated at very high temperatures and high pressures. The operation of interconnected fluidized-bed reactors at such conditions leads to a number of technical challenges especially related to the gas/solid separation and the loop seals. To circumvent these difficulties, a different CLC reactor concept has been developed, which is based on dynamically operated packed bed reactors (Norman et al., 2007), where the oxygen carrier is stationary and is alternately reduced and oxidized via periodic switching of the fuel and air streams. Therefore, the gas/particles

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separation is intrinsic and attrition of the reactor/particles due to moving particles is avoided.

The selection of a suitable oxygen carrier is one of the most crucial steps in CLC. $\text{CuO}/\text{Al}_2\text{O}_3$ has been studied because of its very high reduction rates at lower temperatures and its very good mechanical and chemical stability. The kinetics of $\text{CuO}/\text{Al}_2\text{O}_3$ have been measured with reduction (50% H_2 , 50% N_2)–oxidation (100% air) cycles at different temperatures using Thermogravimetric Analysis (TGA). In all the redox cycles, a slower reaction rate is observed after a certain percentage of conversion, typically around 80%, which must be better understood for a more accurate modeling of the process, in particular for packed bed chemical looping combustion, where a conversion from 0-100% is reached in every cycle.

Experimental section

To better understand the behavior of the $\text{CuO}/\text{Al}_2\text{O}_3$ oxygen carrier, different characterization techniques such as N_2 physisorption (BET) and SEM-EDX were used to study the morphological changes of the particles during the reduction and oxidation over many consecutive cycles. A significant increase in the pore size and particle porosity with the number of cycles and an exponential decrease in surface area were observed as a function of the number of oxidation and reduction cycles. However, after only two redox cycles a cyclic steady state in the redox kinetics was already obtained.

XRD analysis was carried out for the $\text{CuO}/\text{Al}_2\text{O}_3$ oxygen carrier after different numbers of redox cycles, observing that Cu_2O was present in both oxidized and reduced state, due to the possibility of oxygen uncoupling during the reduction cycle. An extensive study of different oxygen uncoupling reactions (CLOU) at 800 °C was performed, including TGA, XRD and SEM-EDX analysis.

This experimental study led to the following conclusions (San Pio et al., 2015): (1) the pore size distribution and particle porosity, and hence gas phase diffusion inside the pores of the particle, do not influence the redox kinetics, (2) copper increasingly agglomerates on the particle surface with increasing number of redox cycles but does not influence the redox kinetics, (3) the decrease in reaction rate is not related to inaccessible copper inside the particles.

After excluding gas-phase diffusion limitations, a study with a copper wire was performed, where it was observed that no full conversion in the oxidation-reduction cycles could be obtained even after 4 hours of reaction, indicating the possibility of CuO being shielded inside the wire making it difficult to be reached by gas components for reaction and confirming that solid diffusion limitations may be responsible for the observed characteristic redox kinetics.

Modeling development

In this work, a grain model for the redox kinetics of Cu-based oxygen carriers has been developed accounting for oxygen solid diffusion, following the work of Xu and Thomson (Thomson et al., 1999) who developed a model to describe the oxygen permeation through perovskite membranes by considering the transport of oxygen vacancies. This model accounts for the formation of oxygen vacancies at the outer surface of the grain and the consumption of oxygen vacancies at the Cu/CuO boundary during the reduction, and vice versa during the oxidation. The parameters in the developed model has been fitted to the available experimental data.

Conclusions

With the grain model including solid diffusion via the transport of oxygen vacancies to describe the redox kinetics of the Cu-based oxygen carriers, it is possible not only to predict the fast initial kinetics –important in fluidized bed reactors–, but also the sudden decrease in reaction rate and the final particle conversion –important in packed bed reactors– at different operating conditions (see *Figure 1* for a typical result).

Tables and Illustrations

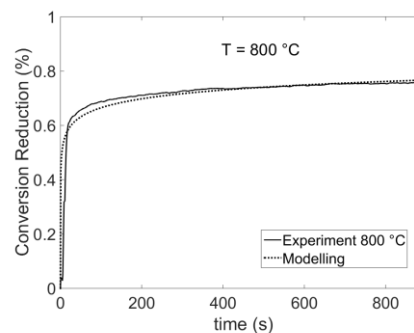


Figure 1. Reduction kinetics of a $\text{CuO}/\text{Al}_2\text{O}_3$ particle at 800 °C

Acknowledgments

The authors would like to acknowledge NWO for the financial support of this project under the ECHO-STIP grant 717.013.007.

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