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Effect of sintering on the reactivity of copper-based oxygen carriers synthesized by impregnation

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HIGHLIGHTS

- The sintering effect on reactivity of Cu-based OCs depends on the synthesis method.
- A model based on population balances is developed and experimentally validated.
- A mathematical expression for the aggregation frequency is proposed.
- Metallic copper sinters during oxidation in the chemical looping combustion process.

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ABSTRACT

A grain model based on population balances for redox reactions of copper-based oxygen carriers is developed. It considers the effects of grain size distribution and sintering, and a new expression for the aggregation frequency, which takes into account the sintering mechanisms and synthesis method, is deduced. In order to validate the model, six copper-based oxygen carriers were synthesized by excess wet impregnation and by incipient impregnation. They were characterized by BET surface area, BJH porosimetry, and SEM microscopy. Model results were compared with experimental data acquired by thermogravimetry during several redox cycles and the model was able to predict the conversion drop over the course of redox cycles due to sintering. It was found that copper-based oxygen carriers synthesized by incipient impregnation are more strongly affected by sintering than those prepared via excess wet impregnation, and finally it is shown that metallic copper sinters during oxidation, resolving a controversy in this regard that has existed in the literature.

1. Introduction

Fossil fuel combustion is one of the main forms of energy generation; however, this technology releases large amounts of CO_2 into the atmosphere as waste gas. Currently, advanced combustion technologies that capture and subsequently store CO_2 are the main method for mitigating the environmental impact produced by these CO_2 emissions. Existing advanced combustion technologies include post-combustion, pre-combustion, and oxy-fuel combustion; however, all of these technologies require additional energy and therefore reduce the overall efficiency of the process. Amongst CO_2 capture technologies, a new process known as Chemical Looping Combustion (CLC) is receiving increasing attention. CLC allows for the separation of CO_2 with low energy penalization, by using Oxygen Carriers (OCs) that are generally composed of a metallic oxide supported on an inert matrix. These OCs undergo redox reactions that allow for the inherent separation of CO_2 in a cyclical process that takes place in two interconnected fluidized bed reactors.

Some of the most studied OCs are the copper-based OCs, which have high oxygen transport capacity, high reactivity, exothermicity in both oxidation and reduction, and a low cost. Despite copper-based oxygen carriers had been discarded because of their tendency to sintering and agglomerating over the course of redox cycles, the have regained interest due to the recent improvement of the synthesis methods. de Diego et al. (2005) obtained agglomeration-resistant copper-based OCs by impregnating the active phase on Al_2O_3, and Gayán et al. (2011) found that copper-based OCs prepared by impregnation never agglomerate if these contain less than 20 wt% CuO. Maya and Chejne (2014) determined that OCs prepared by incipient impregnation require less precursor

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solution to obtain the same concentration of CuO in the Al_2O_3 support than those prepared by excess wet impregnation but they did not analyze the effect of sintering. As can be seen above, one of most important physical phenomena relating to copper-based OCs is the sintering, and therefore it must be thoroughly studied.

Regarding sintering in copper-based OCs, there is still no conclusion. de Diego et al. (2005) studied the agglomeration of copper-based OC particles in a fluidized bed using CH_4 as fuel. They suggested that carbon deposition followed by its combustion during oxidation produces the melting/sintering of metallic copper. However, this theory was discarded because agglomeration also occurred when using H_2 as fuel. It was also believed that metallic copper sintered during oxidation because of the temperature increase within the OC particle during the oxidation reaction. Nevertheless, García-Labiano et al. (2005) and Maya and Chejne (2014) modeled the redox reactions of OCs particles and they calculated temperature increases within the OC particle to be less than 10 K during oxidation. Hence, de Diego et al. (2005) ruled out the possibility of copper sintering due to OC particle temperature increase, although at the bulk temperature at which these authors performed their experiments (T = 800 °C), metallic copper has a significant sintering rate (Demirskyi et al., 2010).

Another factor that hinders the understanding of sintering in copper-based OCs is that existing mathematical models to study redox reactions are usually very simplified, neglecting the effects of sintering and OC microstructure. Amongst the most widely used models to simulate the redox reactions of CLC are the so-called empirical models (Kruggel-Emden et al., 2011), which have good agreement with experimental data at low computational cost, but they require the fitting of parameters that have no physical meaning. Another widely used model in CLC is the Shrinking Core Model (SCM) (Noorman et al., 2011), in which it is assumed that the particle is spherical and reacts at a reaction front, so the solid reactant core shrinks as the reaction proceeds and gases diffuse through the solid product layer. SCM can be correctly fitted to experimental data (Ishida et al., 1996; Son and Kim, 2006); however, it does not provide information regarding the development of OC microstructure during the redox reactions. To take into account microstructural changes of the solid, the so-called grain models are frequently used in CLC (García-Labiano et al., 2005; Abad et al., 2007; Song et al., 2008; Celaya, 2007). In these models it is assumed that a particle is made up of many non-porous grains with uniform initial size that react following a shrinking core mechanism. Pores are located at the interstices between grains, so that gases can access the inner surface of particle. However, grain models have several flaws, as they assume that all OC grains have initial uniform size, which rarely occurs. In addition, grain models neglect the sintering phenomenon that is particularly important at typical CLC temperatures, which can result in a decrease of surface area accompanied by grain growth.

In order to overcome the aforementioned shortcomings of grain models, improved models have been proposed in the literature. Ranade and Harrison (1981) and Manovic et al. (2006) used an enhanced grain model wherein sintering was modeled as a phenomenon of grain combination, although the grain size distribution effect was omitted. Concerning grain models that consider the grain size distribution, Maya and Chejne (2014) proposed a grain model with an initial grain radius distribution, and Bhattacharya and Purohit (2004) used a population balance for predicting the variation of grain size distribution over time, but neglected sintering. Recently, the "Changing Grain Size Distribution Model" (CGSDM) (Maya and Janna, 2016) has been proposed, which takes into consideration grain size distribution and sintering phenomenon simultaneously, by defining a parameter known as aggregation frequency. This parameter indicates the rate of sintering; however, the authors took this parameter as constant, which is a significant simplification since the sintering rate strongly depends on grain size (Rahaman, 2003).

As can be seen above, a better understanding of the sintering in copper-based OCs is necessary from both a theoretical and experimental point of view. In this way, the aim of this paper is to study the effect of sintering in copper-based oxygen carriers synthesized by impregnation over the course of redox cycles. For this purpose, a mathematical model based on CGSDM that takes into account sintering and grain size distribution was developed. In addition, an expression for the aggregation frequency that allows for the consideration of grain size and the methods of synthesis was derived. The model was experimentally validated with data taken by thermogravimetry for the redox reactions of six copper-based OCs prepared by incipient and excess wet impregnation.

2. The model

The mathematical model developed in this paper to simulate the redox reactions is based on the so called Changing Grain Size Distribution Model (CGSDM) (Maya and Janna, 2016), but also considers the aggregation frequency variation over time. Fig. 1 shows the scheme of the model for the oxidation reaction of a copper-based OC; however, this model applies equally for the reduction reaction. CGSDM supposes that an OC particle is formed by non-porous grains with non-uniform radius supported on an inert material also made of non-porous grains. Nonetheless, though the grains that make up the OC particle are considered non-porous, interstices between them constitute the OC particle pores, through which gas diffuses (see Fig. 1a). Each grain in the OC particle reacts following a Shrinking Core Model Mechanism as is shown in Fig. 1b. As reaction proceeds, grains of initial radii r'_o and r''_o reduce their unreacted core radii r'_r and r'_r, and increase their grain radii r'_g and r''_g because the molar volume of the CuO solid product is larger than that of the Cu reactant. At the same time as reaction occurs, grains can sinter with other adjacent grains by neck growth according to the widely known two-spheres model (Rahaman, 2003), as illustrated in Fig. 1c. Thus, a grain of characteristic radii r'_0, r'_r and r'_g combines with another grain of characteristic radii r''_0, r''_r and r''_g to form a new grain of characteristic radii r_0, r_r and r_g preserving the volume (see Fig. 1d). It should be noticed that sintering can occur simultaneously with the chemical reaction, so that $0 < t_1 \leqslant t_2 < t_3$.

The model assumptions are shown below:

- In SEM images, it has been observed that many OCs have a granular structure (Maya and Chejne, 2014; Ishida et al., 1996; de Diego et al., 2004). Hence, it is reasonable to suppose that the OC particle is spherical and made of nonporous spherical grains.
- Since the inert support is not significantly affected by sintering, which may produce densification (Rahaman, 2003), it is assumed that the OC particle retains its spherical shape and diameter during the reaction.
- Four resistances for the reaction are considered: external diffusion, internal diffusion between pores, diffusion through solid product layer, and surface chemical reaction.
- From observations of SEM micrographs and porosimetry measurements, it has been determined that grains of copper-based OCs have non-uniform sizes (Maya and Chejne, 2014; Maya and Janna, 2016). Therefore, it is assumed that, at the beginning of the reaction, grain sizes are distributed non-uniformly.
- It has been found that the transient temperature change inside the copper-based OCs particles during the redox reactions of CLC is very small (<10 K) García-Labiano et al., 2005. Thus, for