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Novel model for non catalytic solid–gas reactions with structural changes by chemical reaction and sintering

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HIGHLIGHTS

- A model for solid–gas reactions with sintering was developed.
- Variation in grain size distribution was modeled by using population balances.
- Porosity and surface area were calculated from moments of the distribution.
- Sintering increases the product layer mass transfer resistance.
- The model was able to predict the "die off" phenomenon present in some reactions.

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ABSTRACT

A new grain model for non-catalytic gas–solid reactions was proposed. It takes into account the grain size distribution and sintering simultaneously, which had not been achieved so far. The model considers the variation in grain size distribution due to the difference in density between solid product and solid reactant, and the effect of sintering. Two methods to deduce the initial grains size distribution were proposed. In the first method, grain size distribution was derived from porosimetry data; and in the second one, the grain size distribution was fitted to a simple distribution shape. In addition, a simplified solution for the model was deducted, which reduces strongly the computational cost and can be implemented in reactor models. Model predictions were validated with experimental data of the lime-sulfation reaction, the reaction between zinc oxide and hydrogen sulfide and the redox reactions of a copper-based oxygen carrier synthesized by wet impregnation.

1. Introduction

Non-catalytic gas–solid reactions have been widely studied for their industrial applications. Some of these reactions are the sulfation of lime and the reaction between zinc oxide and hydrogen sulfide, which have been widely used for waste gas desulfurization. Other reactions that have gained importance are the redox reactions of oxygen carriers in the chemical looping combustion process (CLC). Some of the most investigated oxygen carriers are the copper-based oxygen carriers, which have advantages over conventional materials such as high reactivity and exothermicity in both reduction and oxidation (Hossain and de Lasa, 2008). However, copper-based oxygen carriers are strongly affected by sintering at typical operating conditions of the CLC process, which reduces the reactivity of the material (Gayán et al., 2011).

In solid–gas reactions, kinetics and diffusivity depend strongly on the microstructure of solid, which may change because of the chemical reaction (difference in density between solid reactant and solid product) and the sintering phenomenon. Thus, to take into account of such microstructure variations have been proposed the so-called grain models. Classical grain models consider that particle is made up of non-porous grains with uniform initial grain size, among which are the pores. In 1979, Georgakis et al. proposed the so called Changing Grain Size Model (CGSM) (Georgakis et al., 1979), in which grains react according a shrinking core mechanism and change volume because of the difference in molar volume between solid reactive and solid product. CGSM has been the most widely used grain model to simulate solid–gas reactions (García-Labiano et al., 2002, 2005; Yu et al., 2012). Nonetheless, other models derived from the CGSM have been proposed. Dam-Johansen et al. (1991) developed a model of grains and micro-grains; which considers that particle is formed by grains, between

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which are the macropores, and these grains are formed of smaller micrograins, between which are the micropores. Niksiar and Rahimi (2009) evaluated thermal effects in the CGSM, and in recent years years Rahimi and Niksiar (2013) proposed a grain model with multiple reactions both in series and parallel, by introducing a parameter of fractional contribution of reaction.

Regarding to models that consider the grain size distribution, Szekely and Propster (1975) studied the effect of grain size distribution with a great computational effort. They concluded that grain size distribution strongly affects conversion, indicating that ignore such distribution leads to significant prediction errors. Bhattacharya and Purohit (2004) presented a model of distributed grains using a population balance, but neglecting the sintering phenomenon. Liu et al. (2012) proposed a model of random overlapped grains for discrete grain size distributions, which was applied to the reaction of carbonation of CaO (Zhou et al., 2013); and recently Maya and Chejne (2014) used an initial grain size distribution to modify CGSM considering heat transfer effects.

Due many solid–gas reactions occur at high temperatures, sintering phenomenon affects the structural properties at the same time the reaction. Amongst the approaches that consider sintering is the work of Ranade and Harrison (1979), in which sintering was represented as a phenomenon of aggregation between grains. This in order to simulate the increasing in mass transfer resistance in the solid product layer due to sintering. In more recent studies, empirical relationships to sintering modeling have been preferred. Manovic et al. (2006) employed an empirical equation to simulate the increase in grain size owing to sintering and Monazam et al. (2008) used a type Arrhenius equation, which required the adjustment of several parameters, to model the sintering in the reaction between zinc oxide and hydrogen sulfide. Must be mentioned that in latter models with sintering, a uniform initial grain size distribution was asumed.

Another weakness of classic grain models is that they are unable to predict the phenomenon known as “die off”. This phenomenon occurs when the solid reactant density is much higher than the one of solid product and grains located at the particle periphery grow more than grains near the center. Then, at the outside of the particle, intragrain mass transfer resistance increases and local porosity decreases until it becomes zero. At this point reaction ends, because of reactant gas can not diffuse into the particle. The “die off” phenomenon can also occur because of the mass transfer resistance in the solid product layer, which increases as reaction proceeds and makes the reaction to stop without necessarily zero porosity.

As can be seen above, studies that have been made so far take into account either grain size distribution or sintering, but not both effects simultaneously. This makes that classic grain models do not predict correctly the solid microstructure or phenomena like the so-called “die off”, which is most marked with sintering. Therefore, in this paper a generalized model for non catalytic gas–solid reactions that takes into account the variation of grain size distribution by chemical reaction and sintering was proposed. The model can predict conversion, porosity, and specific surface without the need of using additional empirical relations, and considering the phenomenon of sintering.

2. The model

Amongst grain models the most widely used is that of Georgakis et al. (1979). This model, called “the changing grain size model” (CGSM) considers that particle is formed of a great number of nonporous grains with initial radius r_o among which are the pores. As chemical reaction proceeds, grain radius r_p increases or decreases depending on the solid product molar volume, while the unreacted grain core radius r_c decreases (see Fig. 1). In this paper, a model based on the CGSM is proposed, but taking into account the grain size distribution and the sintering effect.

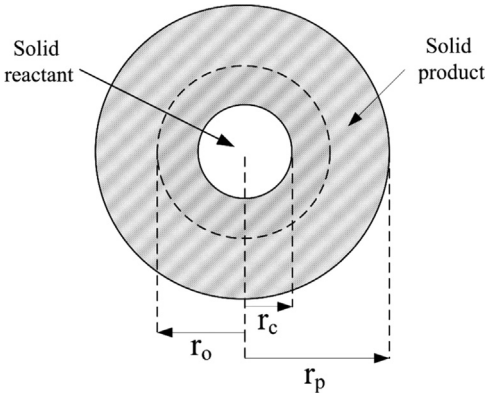

Fig. 1. Scheme of changing grain size model.

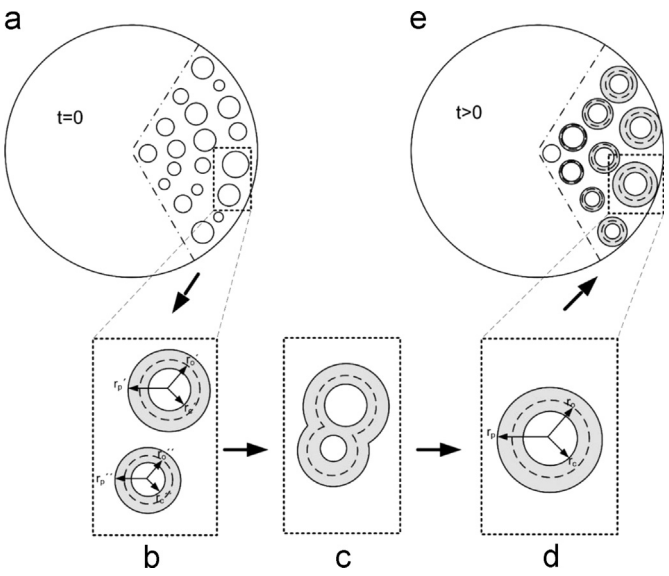

Fig. 2. Scheme of CGSDM.

The scheme of the model developed in this paper, called “the Changing grain size distribution model” (CGSDM) is illustrated in Fig. 2. Initially, particle is composed of a large number of grains of different radius r_o (see Fig. 2a). Then, when reaction begins the grains change their size due to chemical reaction (see Fig. 2b) and sintering (see Fig. 2c), simultaneously. When two grains of radii $r_{p'}$ and $r_{p''}$ coalesce (see Fig. 2c) a new grain of larger radius r_p is formed preserving volume (Fig. 2d). Similary, unreacted grain cores of radii $r_{c'}$ and $r_{c''}$ coalesce to form a new unreacted grain core of radius r_c preserving volume. The new grain will have a grain radius r_p, an unreacted grain core radius r_c and a hypotetical initial grain radius r_o, since the new grain did not exist at the beginning of reaction. At the end of reaction, number of grains will be lower than at the beginning of this, owing to sintering effect (see Fig. 2e). The modeling of sintering as a phenomenon of grains coalescence allows to represent the two main macroscopic effects of sintering: the decrease in specific surface area and grain growth (Ranade and Harrison, 1979). That is why this approach has also been adopted by other authors (Kruis et al., 1993; Monazam et al., 2008; Ranade and Harrison, 1979), since it allows to simplify the modeling and requires a minimal amount of parameters to fit. This approach is consistent with the widely used two spheres model for the initial stage of sintering (Kang, 2004). Therefore, it must be