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Kinetic Modeling Of Solid-Gas Reactions At Reactor Scale: A General Approach

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ABSTRACT

A rigorous simulation of industrial reactors in the case of solid-gas reacting systems is a complicated task due to several difficulties linked to the kinetic problem at the scale of the solid grains and to the problem of gas and heat transfers within the powder bed. Firstly it requires the knowledge of the kinetic model for the calculation of the speed of reaction in one part of the reactor and for given conditions of temperature and gas composition, and secondly it necessitates solving the material and heat balance equations for the thermohydraulic conditions settled in the reactor.

1. Introduction

Solid-gas reactions are of great interest in many industrial fields such as nuclear, chemistry, metallurgy, CO_2 capture, etc… Industrial reactors where these reactions take place are difficult to understand. Indeed the solid phase is a granular medium through which circulate gaseous reactants and products. The properties of such a medium are modified in space and time due to reactions occurring at a microscopic scale. The thermodynamic conditions are driven not only by the operating conditions but also by the heat and mass transfers in the reactor.

Several models have been developed to account for the complexity of these transformations such as the grain model [1] and the pore model [2] and all their improved derivatives. However most of these models are based on the law of additive reaction times of Sohn [3] which is only valid in some special cases: if the order changes from the gas is equal to one, and for a shrinking core model. In all other cases, it is necessary to consider another approach to understand the kinetics of these reactions.

2. Method

In this goal, we have developed a multi-physic approach combining the resolution of the thermohydraulic equations with kinetic laws describing the heterogeneous reactions, for aggregated or separate particles [4].

Indeed, rather than the restrictive equation

$$\frac{d\alpha}{dt} = A\exp(-\frac{E}{RT})\ f(\alpha) \qquad (1)$$

and with about a tenth of different laws only, depending on the expression of the function f(α), we propose a more general approach for kinetic modeling at microscopic scale, including instantaneous nucleation models, instantaneous growth model, surface-nucleation and growth models (anisotropic or isotropic growth), for the three usual symmetries (spheres, cylinders, planes), and other possible kinetic assumptions depending on where the rate-determining step occurs, and the sense of development of the new phase. This approach is based on the following equations

$$\frac{d\alpha}{dt} = \phi(T, P_i) S_m(t,...) \qquad (2)$$

where $\phi(T,P_i)$ is the areic reactivity of growth and $S_m(t,\ldots)$ is a molar space function. It allows to calculate about 45 various kinetic models (obviously including the classical ones as R3, D3, …) [5].

At macroscopic scale, heat and mass transfer terms entering in the balance equations depend on the kinetics evaluated at the microscopic scale. These equations give the temperature and partial pressure in the reactor, which in turn influence the microscopic kinetic behavior. The various equations corresponding to the thermal model, hydrodynamic and mass transport models can be found in [4].

At microscopic scale, the reaction fractional conversion is followed for a representative population of grains. By finite difference it is possible to evaluate the reaction rate dα/dt. This rate allows to calculate heat and mass sources produced by the reaction. So, using these sources terms, microscopic reactions have an impact on the spatial and temporal evolution of the thermodynamic processes at the reactor scale. Inversely since it modifies the kinetic parameters (areic frequency of nucleation γ and areic reactivity of growth ϕ), thermodynamics influences fractional conversion of the microscopic reaction.

3. Results and Discussion

In order to validate our approach we have chosen to study the dehydroxylation of kaolinite by means of thermogravimetry. Isothermal and isobaric curves were first obtained with about 25 mg of powder (corresponding to a 1 mm height powder bed). During the entire transformation, the sample weight was low enough to prevent any effect of pressure gradients in the powder layer. As expected, the reaction rate increases with temperature and decreases with water vapor pressure.

A second series of experiments was done with various heights of the powder bed. In the same crucible as previously, two distinct TGA experiments were performed at 450°C under a water vapor pressure of 7hPa: the first one with 50 mg of powder corresponding to a powder bed height of 3 mm; the second one with 300 mg corresponding to 10 mm. The kinetic curves and rates curves obtained with both bed heights are presented on Figure 2. One can see that the powder bed

height has an important effect on the kinetic curves since the maximum reaction rate obtained for 3 mm is about twice more that obtained with 10 mm (and is about twice less than that obtained with 1 mm).

In order to interpret the experimental curves obtained with thin powder beds (1 mm height), we used a model involving random nucleation followed by anisotropic growth of the nuclei first proposed by Nahdi et al. [6].

The optimization procedure of CIN4 provided the values of γ (in nb. nuclei m^{-2} s^{-1}) and ϕ (in mol m^{-2} s^{-1}) for each experiment so the laws of variation of these quantities with temperature and water vapor pressure could be expressed.

Concerning the results obtained with thick powder beds, the "macro" part of CIN4 was used in order take into account the heat and mass transfers between all the various places inside the reactor (sample bed, crucible, gas flow). The first step consisted in defining the domains of calculation. The system being axi-symmetric, we used weak forms written in cylindrical coordinates.

Inside the granular medium, heat and mass sources were calculated simulating the reaction phenomena at the microscopic level. Figure 1 shows the gas flow rate obtained as well as temperature and fractional conversion fields at a given time for bed height of 3 mm. Figure 2 presents a comparison of the whole rate of reaction versus fractional conversion between the experimental data and the simulation for both bed heights.

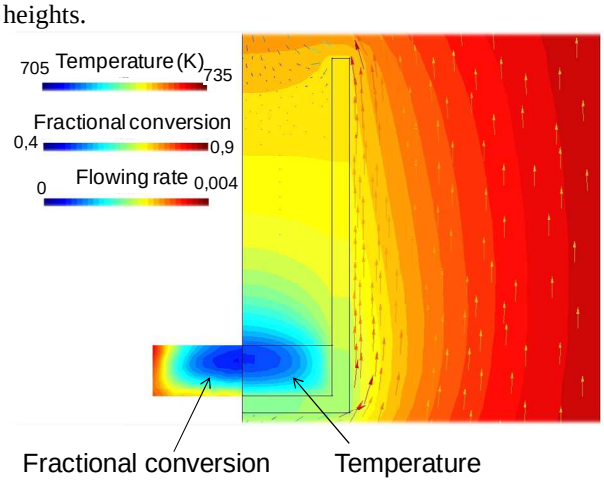

Fig. 1: Representation of the temperature field, the fractional conversion and the flowing rate (arrows) at a given time for 3 mm-height bed.

Figure 2 shows that the CIN4 simulation is able to discriminate the height of the powder bed from 3 to 10 mm. It is important to notice that these results at reactor scale are obtained by means of numerical simulation without any adjustment of parameters. Nevertheless the calculated curves are not perfectly superimposed with the experimental ones. Some improvements should be done in order to get better simulations. For example several points could be improved: at the grains scale ("micro" optimization), the particles size distribution could be taken into account to obtain more precise values of g and f, at the reactor scale, the change in the physical properties of the granular medium (including the porosity) due to the transformation of kaolinite into metakaolinite should be considered using appropriate relationships between the physical properties of the granular medium and fractional conversion.

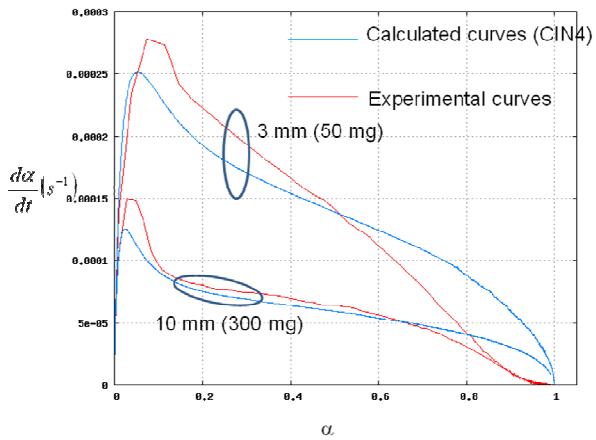

Fig. 2: Reaction rate vs. fractional conversion from the experiment and from the simulation for both powder bed heights.

4. Concluding remarks

CIN4 is a new software tool able to couple kinetics at grains population scale with both heat and mass transfers by means of the finite element method. Kinetic models are based on a general method agreeing with physical reality, offering the possibility to simulate more than 40 models depending on nucleation and growth processes, the shape of the grains, the growth type (isotropic or anisotropic), the development direction of the new phase and the localization of the rate determining step of growth (internal interface, external interface or diffusion volume). Heat and mass transfers are governed by differential equations and solved by a finite element method. Powder beds consisting in separate individual grains (micro and macro scales) or aggregates (micro-meso-macro scales) may be considered. CIN4 allows simulating not only reactions at laboratory scales such as thermobalances, but also industrial reactors.

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