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Original Research Paper

A multi-stage, multi-reaction shrinking core model for self-inhibiting gas–solid reactions

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ABSTRACT

Some thermal decomposition reactions display self-inhibiting behaviour, where the produced gas negatively influences the reaction progress. Further, a build-up of internal pressure caused by the product gas may alter the reaction pathway in a way that favours one pathway over others. Two well-known cases of this kind of reaction are the thermal decomposition of limestone and gibbsite, in which carbon dioxide and water vapour are the produced gases, respectively. A multi-stage, multi-reaction, shrinking core model is proposed for the simulation of this type of process. The model emphasises the role of the produced gas, not only in mass transfer, but also in the reaction kinetics. It includes parallel and series reactions, allowing for the formation of an intermediate species. The model has been applied to the conversion of gibbsite to alumina, including the formation of intermediate boehmite. Modelling results for gibbsite conversion, boehmite formation and its subsequent consumption, as well as alumina formation, agree well with literature data; the corresponding kinetic parameters are estimated for all reactions. Significantly, the experimentally-observed plateaux in the particle's temperature history are predicted by the model. The role of heating rate and particle size on boehmite formation is also evaluated using the model, and is in agreement with observation.

1. Introduction

Many modelling techniques have been reported on both catalytic and non-catalytic gas–solid particle reactions using a variety of approaches depending upon the physical and chemical properties of the solid and the type of reaction considered. Comprehensive reviews of the major modelling categories and their features are given by Ramachandran and Doraiswamy [1] and Molina and Mondragón [2]. The importance of developments in gas–solid reaction modelling is still high since a wide variety of reactions encountered in the process industries belong to this class. Combustion, gasification, roasting, calcination, reduction of metal ores, and catalyst regeneration are typical industrial gas–solid processes demanding new modelling tools for process intensification and product design. Modelling becomes crucial when prediction and control of transients during reaction at high conversion rates and at high temperature is the subject of investigation. In such cases deeper insight will be achieved by carefully establishing the relationships between dominant mechanisms, including reaction kinetics and transport processes, as well as structural changes taking place over the reaction period. Further, the combination of different sub-models at different time and length scales in a multi-scale modelling framework makes it possible to deal with product quality issues (small scale) via control of the process (large scale).

To date, particle reaction models have been mainly based on reactions with a positive order, particularly first order reactions. The variation of the reaction mechanism over the reaction period due to a change of internal conditions, like the build-up of gas pressure inside the particle, has not been extensively studied.

Mantri et al. [3] proposed a three-zone model comprised of a core, an outer product layer and a reacting zone in between them. The model is based on a single reaction and it is assumed that the reaction is first order with respect to gas concentration and zero order with respect to the solid. This model was applied by Chang and Kuo [4] to predict the transport of reactive gas in a packed bed of porous media. A variation of the shrinking core model with an intermediate layer was also proposed by Homma et al. [5]. In their work, fresh reactant is converted to an intermediate followed by conversion of the intermediate to a gas product without leaving any ash (solid) layer. This model was also based on a first order reaction with respect to the gaseous reactant. The intermediate component formed immediately and the final product was formed only via consumption of the intermediate. Suresh and Ghoroi [6] developed a model for solid–solid reactions in series for a single particle. In their work, multiple reactions were considered and

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Nomenclature

a, c, d, a', b', c', b'', c'', d''	stoichiometric coefficients (−)
C_{A0}	initial fresh solid concentration (mol/m^3)
C_{B0}	initial intermediate solid concentration (mol/m^3)
C_{C1}	gas concentration at r_1 (mol/m^3)
C_{C2}	gas concentration at r_2 (mol/m^3)
C_{Cb}	gas concentration in surrounding environment (mol/m^3)
C_{Cs}	gas concentration on particle surface (mol/m^3)
C_{G0}	initial gibbsite concentration (mol/m^3)
C_{Pe}	effective heat capacity (J/mol K)
C_{12}	gas concentration at reactant-product interface at t_{12} (mol/m^3)
D_e	effective diffusivity coefficient (m^2/s)
D_p	particle diameter (m)
E	activation energy (J/mol)
ΔH	heat of reaction (J/mol)
h	heat transfer coefficient (W/m^2 K)
k	surface reaction rate constant (mol^{-n} m^{3n+1}/s)
k_0	Arrhenius pre-exponential coefficient (mol^{-n} m^{3n+1}/s)
M	gas production/diffusion rate (mol/s)
Mw	molecular weight (g/mol)
Mw_e	average molecular weight (g/mol)
m	mass fraction (−)
$\dot{N}$	solid consumption rate (mol/s)
n	reaction order with respect to water vapour concentration (−)

P_{Cb}	environmental gas (C) pressure (kPa)
R	gas constant (J/mol K)
R_p	particle radius (m)
r_G	gibbsite surface reaction rate (mol/m^2 s)
r_s	solid surface reaction rate (mol/m^2 s)
r_1	unreacted fresh reactant core radius at any time (m)
r_{12}	reactant-product interface location at t_{12} (m)
r_2	intermediate-product interface location at any time (m)
r_{23}	intermediate-product interface location at t_{23} (m)
T	temperature (K)
T_b	environmental temperature (K)
T_0	initial particle temperature (K)
T_{12}	particle temperature at t_{12} (K)
T_{23}	particle temperature at t_{23} (K)
t	time (s)
t_{12}	time for transition from stages 1 to 2 (s)
t_{23}	time for transition from stages 2 to 3 (s)
t_∞	reaction completion time (s)
X	reactant conversion (−)

Greek letters

ϑ_1, ϑ_2, ϑ_3	ratio of stoichiometric coefficients: (c/a), (c'/a'), (c''/b'') (−)
ρ_e	average density (kg/m^3)

reaction rates were first order with respect to the solid concentrations.

The objective of this paper is to expand on a new version of the shrinking core model for a particular class of gas–solid reactions in which the released gas reduces the reaction rate and changes the reaction mechanism, and in which an intermediate solid species may form (Amiri et al. [7]). Calcination and thermal dehydration/decomposition of solid particles belong to this category of gas–solid reactions. The prediction of the formation and consumption of an intermediate species is a leading feature of this model. This kind of information is needed for maximisation or minimisation of the amount of the intermediate in the product via process control. The involvement of multiple reactions with different orders, and determination of a reaction–switching time are other notable features of this new version of the shrinking core model.

As a case study, the calcination of gibbsite to alumina, in which boehmite forms as an intermediate, is the focus of this article. Gibbsite calcination, which is an important stage in alumina production via the Bayer process, has been studied for many years. The majority of publications related to gibbsite calcination have focused on reaction kinetics and phase transitions (Stacey [8]; Whittington and Ilievski [9]; Wang et al. [10]; Ruff et al. [11]; Gan et al. [12]; Zhu et al. [13]). Little work has been reported on coupling hydrodynamics and reaction kinetics (Marsh [14]), and no work appears to be available specifically on multi-scale modelling of alumina calcination equipment, apart from our own preliminary efforts (Amiri et al. [15]). For gibbsite calcination, and similar thermal dehydration reactions, the gaseous species (water) is a reaction product, not a reactant, which is different from many other gas–solid reactions. There is a lack of particle-scale conversion and species distribution models for reactions of this type, although we have made some recent contributions in this area (Amiri et al. [7,16]). This paper is part of a study to develop a multi-scale model for the thermal dehydration of gibbsite in a fluidised bed reactor. A single gibbsite particle undergoing calcination is studied in this paper to establish a predictive three-stage model for particle conversion at high temperatures relevant to industrial operations. The paper explores the effect of water vapour pressure inside the particle on competing reactions and it includes the reaction orders with respect to vapour concentration for the various gibbsite calcination reactions.

Parameter estimation is performed by using two sets of experimental data from Wang et al. [10], then the model is validated against another data set at a different temperature. While gibbsite calcination is the focus of this paper, the model developed is general enough to be applied to other reactions in which a gaseous species is a reaction product only, for example pyrolysis of carbon-based materials, thermal decomposition of some organic and inorganic compounds, and the reduction of metal oxides.

2. Reaction kinetics and modelling assumptions

Unreacted core models for gas–solid reactions, in which the reaction rate is based on the reactant gas concentration, have been used in a wide range of applications in the literature. The majority of previous investigations have focused on gas–solid reactions that were generally represented by a reaction such as gas + solid → solid + gas.

The reaction was usually assumed to have first order kinetics with respect to the reacting gas concentration. However, in several applications, including thermal dehydration, gas-phase species are reaction products only. In this study there is no gaseous reactant and three reactions are involved. The following stoichiometric equations are used to represent parallel and series gas–solid reactions in a single particle: