A generalized mathematical model for non-catalytic gas-solid reactions

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Based on a general classification and characteristic comparison of the existing models, a new model for non-catalytic gas-solid reactions is proposed and a general formulation for the model in terms of the solid conversion, X, is presented in this paper. The model, referred to the generalized model, is demonstrated to be applicable to any solid reactant of general structure ranging from highly porous to nonporous materials. It is shown that the generalized model incorporates the grain and pore structure for a solid pellet and can be reduced to the grain and random pore models as extreme cases.

Keywords Non-catalytic conversion, gas-solid reactions, mathematical model, structure of solid reactants

Introduction

Non-catalytic gas-solid reactions occur in many important chemical and metallurgical industrial processes, such as extractive metallurgy, control of gaseous pollutants, coal gasification, combustion of solid fuels, catalyst manufacture, *etc*. The mathematical understanding of these systems is important in order to interpret laboratory data and design and scale-up reactors. All classes of gas-solid reactions have been extensively studied in the past decades. Some of the major developments in this area have been summarized in a book by Szekely[1] *et al*. and in monograph by Sohn and Wadsworth.[2] Comprehensive and critical journal reviews are available (Wen;[3] Sampath and Hughes;[4] Ramachandran and Doraiswamy[5]). It is seen that a number of models and modifications for gas-solid reactions have been proposed and mathematically formulated. However, there are limitations in applying them to systems of general interests. The validity of each model often has to be defined when applied to a system. There is still a need to evaluate the models in order to develop a general model with the least limits of its applicability.

In the present paper, a characteristic comparison of the existing models will be presented based on a general classification of the models. A generalized model for non-catalytic gas-solid reactions will be developed and demonstrated to be more general and applicable to wider range of systems.

Existing models and their formulations

General classification

Models that have been proposed to describe the non-catalytic gas-solid reactions may be classified into one of the following four categories according to the surface on which the reaction initiates and the diffusion characteristics of gaseous reactant:

(i) *Homogeneous models*[6,7] When the solid reactant is porous, the gas can penetrate into the solid without significant diffusion resistance. Reaction is assumed to take place throughout the volume of the pellet from the very beginning. Reactions described by this type of models are usually considered as being under chemical kinetics control.

(ii) *Unreacted shrinking core models*[1,5] These

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models may be further subdivided into two different headings, namely, "sharp-interface" and "finite thickness reaction zone" models. The main assumption for these models is the solid being relatively non-porous or significantly high temperature for porous solids, the reaction being diffusion-controlled and a sharp moving interface or finite thickness reaction zone being visualized. Apparently the reaction always occurs on the external surfaces of the pellet or the unreacted core.

(iii) *Grain models*[8-12] In these models, the solid pellet is assumed or visualized to be consisting of a number of small nonporous sub-units known as grains or particles. Surrounding these grains are macropores through which the gaseous reactant diffuses to reach the various grains. The reaction is assumed to occur at the surface of each grain according to the sharp-interface model. A product layer will form with time in the outer region of each grain and these will in turn offer some resistance to diffusion. The gas-solid reactions which fit the grain model may be either under kinetics control or under diffusion control.

(iv) *Pore structure models*[13-18] Pore structure models proposed emphasize that the reaction is initiated on pore surface within the solid pellet. The principal assumption is that the solid pellet is composed of a number of pores (of single size or distributed size) with a matrix of their associated wall solids, while the pellet may be visualized as a porous network, and the reaction occurs along the pore walls resulting in a buildup of product layer. Various models have been proposed to describe the pore structure of porous materials, such as isolated pore models,[27,19] Lattice models,[11] Random pore models[16] and pore tree model.[20-22] Among these models, random pore structure models are widely used in modeling of gas-solid reactions. As an extension of the random pore model the pore tree model has been lately developed by Simons, which has shown a good prospect in modeling of gasification of solid fuels.[23]

General mathematical formulation of the existing models

A general type of gas-solid non-catalytic reaction may be assumed to proceed according to the following stoichiometric equation:

$$A_{(g)} + \gamma_B B_{(s)} \Rightarrow \gamma_p P_{(g)} + \gamma_q Q_{(s)} \qquad (1)$$

in which the stoichiometric coefficient of reactant A is taken as unity and that a gas and a solid react to give gas and solid products. In some cases a gas and solid may yield only solid products (*i.e.* $\gamma_p = 0$), whilst in some cases a solid reactant decomposes to give gaseous and solid products. Cases where only gaseous products are formed are often encountered in industrial processes.

To formulate a mathematical model, it is accepted that some assumptions on the system are made, which are usually (i) isothermal conditions; (ii) the reaction rate is first order with respect to gas reactant A and nth order with respect to solid reactant, (iii) the pellet retain its size and shape during the course of reaction; (iv) the effects of bulk flow and external gas film mass transfer resistance are negligible; (v) the reaction is under pseudo-steady state.

The reaction rate expression per unit volume of the solid pellet at radial position r may be represented by the following equation

$$R_A = k_v[A][B]^n \qquad (2)$$

Thus, the mass continuity equations for the system can be directly cast in a dimensionless form as

$$\nabla_y^2 a = \frac{\Phi^2}{D}\frac{dX}{d\tau} \qquad (3)$$

$$\frac{db}{d\tau} = -\frac{dX}{d\tau} = -\frac{a}{f(X)} \qquad (4)$$

with the following boundary and initial conditions:

$$y = 0, \ \frac{da}{d\tau} = 0 \qquad (5)$$

$$y = 1, \ a = 1 \qquad (6)$$

$$t = 0, \ a = 0, \ b = 1 \qquad (7)$$

where $\nabla_y^2 a = y^{-\alpha}\frac{\partial}{dy}\left(D\frac{\partial y^\alpha}{\partial y}\right)$; α is the pellet shape factor ($\alpha = 0, 1, 2$ for flat, cylindrical and spherical pellet, respectively); $D = (D_e/D_{e0})$ and Φ^2 is the initial Thiele Modulus based on D_{e0}.

In this general formulation, $f(X)$ is defined as a function of the local rate of reaction in terms of solid

conversion X. Different forms of $f(X)$ characterizing the existing models for non-catalytic gas-solid reactions are given in Table 1.

Table 1 Local rate forms for various gas-solid reaction models

Model	f(X)	Equation
Volumetric model[5]	$(1-X)^{n}$	(8)
Shrinking core model[24]	$-(1-X)^{1/3}+(1-X)^{2/3}$	(9)
Grain model[10]	$-1-\frac{(1-X)^{1/3}}{Bi}+\frac{(1-X)^{2/3}}{Bi}$	(10)
Random pore model[17]	$\frac{1+(\beta Z_v/\Psi[(1-\Psi\ln((1-X))^{1/2}-1]}{(1-X)[1-\Psi\ln(1-X)]^{1/2}}$	(11)
Modified grain model[14]	$-1-\frac{(1-X)^{1/3}}{Bi}+\frac{(1-X)^{2/3}}{Bi[Z_v+(1-Z_v)(1-X)]^{1/3}}$	(12)

Dimensionless parameters and variables ϕ, a, b, Bi, β, Ψ and Z_v *etc*. are defined in Table 2.

A characteristic comparison of the existing models

There are four types of models prevailed in the literature of non-catalytic gas-solid reactions proposed. All these models can be represented by the same form of equations and distinguished by a local reaction rate function $f(X)$ essentially reflecting the structure of the solid reactant. Apparently the more consideration giving to the solid structure, the more complicated the rate equation is. It is also noted that a model with more complicated structural depiction always incorporates the simple one, *i.e.* the former can reduce to the latter under some conditions. From this point of view, the applicability of a model for non-catalytic gas-solid reactions is basically dependent on its assumption on the pore structure of solid reactant. The more reasonable the structure description of the solid is, the more general the model is. The following discussion will be devoted to the comparison of the characteristics of various models in the light of their applicability.

Table 2 Definitions of dimensionless parameters and variables

Parameter	Notation	Definition
Thiele Modulus	ϕ	$[R^2 k_v B_0/D_e]^{1/2}$
Biot number for the grain	Bi	$D_{eG}/k_s r_{G0}$
Pore structural parameter	Ψ	$4\pi L_0(1-\varepsilon_0)/S_0^2$
Ratio of product to reactant	Z_v	$\frac{\gamma_Q \rho_B M_Q}{\gamma_B \rho_Q (1-\varepsilon_0) M_B}$
Concentration of gas reactant	a	A/A_0
Concentration of solid reactant	b	B/B_0
Group β	β	$\frac{2k_s \rho_B (1-\varepsilon_0)}{\gamma_B M_B D_{eG} S_0}$

For instance, if $\Psi=0$, Eq. (11) reduces to the homogeneous model with $n=1$. As shown in Table 1, the rate functions for homogeneous reaction model and shrinking core model are of simple forms. Actually homogeneous model and shrinking core model are simple representations for the majority of gas-solid reactions. Often the shrinking core model is frequently used in design of gas-solid reactor. However, limitation of its applicability should be noted. Since the model is based on the assumption that the solid reactant is relatively non-

porous and diffusion is the rate controlling step, it is not applicable to a slow reaction with a very porous solid. Do[24] was the first to rigorously evaluate the validity of this type of model and point out that the condition to apply this model is that the reaction rate is much faster than the diffusion rate ($\phi >> 1$). There is only one exceptional case in which the shrinking core model is applied, *i.e.* high temperature reaction of a porous solid.

While the homogeneous reaction model is assumed to be applicable at relatively low temperature or in the case where the solid is highly porous. Homogeneous reaction may also occur in a nonporous solid when the temperature is so low that gas can penetrate into the solid without significant reaction. In this sense, the homogeneous model is a more general description of reaction in the solid. But in most gas-solid reaction systems, the reaction rate for a nonporous solid is much faster than that of diffusion into solid due to relatively high temperature for non-catalytic reactions. It is, therefore, concluded that neither the homogeneous model nor the shrinking core model can be ideally used in a non-catalytic reaction system of solid reactant with general structure.

Considering the grain models and pore structure models (mainly random pore models), it may be noted that those two types of models are the generalized forms of shrinking core model and homogenous model, respectively. Although there are a number of modified grain models taking account of structure change,[11,14,25,26] the basis of the model has never changed. The applicability of these models is limited in the same way as the shrinking core model and homogeneous model. Since the grain models are generally based on the assumption that the solid pellet is composed of a number initially nonporous small grains, it is particularly useful for the case where the pellet is formed by compaction of particles of very fine size. The grain size has a clear physical meaning for this case.[5] It is obvious that the grain models are not applicable for the case where a pellet is formed through physical chemical changes such as calcination, pyrolysis, *etc*. On the contrary, the pore structure models may find application in the case where a pellet is highly porous, while pore structure models can not be described as a pellet formed by compaction of relatively nonporous grains.

It is, therefore, desirable to develop a general model that is applicable to all types of materials, from nonporous metals to highly porous charcoal.

A generalized model

As indicated earlier, the structure of solid reactant is the most important factor in the reaction modeling. The starting point to develop such a general model should be a general description of the solid structure with nonporous and highly porous structures as extreme cases.

Assume that the solid pellet may be visualized to be a collection of N small grains of significant porosity, which can be referred to as the micropore porosity ε_{mi}, whilst the voidage between these grains constitutes the macropore porosity of the pellet ε_{ma}.

Then the overall porosity of the pellet might be described as

$$\varepsilon_p = \varepsilon_{mi} + \varepsilon_{ma} \tag{13}$$

A geometric consideration gives

$$\varepsilon_{ma} = 1 - \sum_{i=1}^{N} r_i^3/R_p^3 \tag{14}$$

where R_p is the radius of the pellet; r_i the radius of grain i, $i = 1,2,\ldots..N$

Evidently,

$$(1 - \varepsilon_p) = \frac{M_p}{\rho_s \frac{4}{3}\pi R_p^3} \tag{15}$$

where ρ_s is the true density of the solid matrix, and M_p the mass of the solid pellet.

Combining Eqs. (13), (14) and (15) yields

$$\varepsilon_{mi} = \sum_{i=1}^{N} [r_i^3 - 3M_p/4\pi\rho_s]/R_p^3 \tag{16}$$

Here two extreme cases existed:

i) $N = 1$, $r_i = R_p$; $\varepsilon_{ma} = 0$, $\varepsilon_{mi} = \varepsilon_p$

In this case, the pellet is just one composed of distributed sized pores, which is most likely formed physio-

chemically. The random pore models are applicable to this extreme case.

ii) $N \to \infty$, $\sum_{i=1}^{\infty} \frac{4}{3}\pi r_i^3 = M_p/\rho_s$ which means that infinite numbers of grains just make up the matrix of solid body of a pellet. Thus, it can be assumed

$$\varepsilon_{mi} = 0, \ i.e. \ \varepsilon_{ma} = \varepsilon_p$$

This case presents a pellet consisting of a great number of nonporous grains, possibly formed by physical or mechanical processes such as mechanical compaction, compression by high pressure and high temperatures. This pellet is actually the nonporous platelet while $\varepsilon_{mi} = 0$, $i.e.$ $\varepsilon_{ma} = \varepsilon_p$. The large number of these platelets could be overlayed each other to produce non-porous pellets. The existing grain models can be described as the extreme case fairly well.

It is expected that most solid reactants in the gas-solid reaction systems, regardless the way they are formed, would fall into the case between these two extremes. A mathematical formulation of the reacting pellet as generally depicted above is given below.

Formulation of the generalized model

Assume that

1. The pellet is a collection of N porous small grains of N porous small grains of unique size r_G;
2. Isothermal reaction conditions;
3. The reaction between a gas and solid occurs simultaneously at surfaces of the pore walls in each grain according to the random pore model;
4. The pore structure characteristics of each grain is identical, $i.e.$ the local reaction rates of each grain are equal;
5. As reaction proceeds, the grain remains its shape and size, while as the pore structure of the grain varies with time.

A general representation for irreversible reaction and diffusion in the pellet described above may be given by Eq. (3) and the local reaction expression is given as

$$\frac{db}{d\tau} = -\frac{a}{f(X)} \tag{17}$$

where $f(X)$ is actually resistance term to the local reaction.

Since the reaction at surfaces of each grain initiates at the same time, the total reaction resistance in the pellet may be described as the form of

$$f_p(X) = \frac{1}{N} f_G(X) \tag{18}$$

where $f_G(X)$ is the reaction resistance in one grain which can be represented by Eq. (11) as:

$$f_G(X) = \frac{1 + (\beta_G Z_\nu/\Psi_G)[\{1 - \Psi_G \ln(1 - X)\}^{1/2} - 1]}{(1 - X)\{1 - \Psi_G \ln(1 - X)\}^{1/2}} \tag{19}$$

We have

$$f_p(X) = \frac{\frac{1}{N} + \frac{\beta_G Z_\nu}{N\Psi_G}[\{1 - \Psi_G \ln(1 - X)\}^{1/2} - 1]}{(1 - X)\{1 - \Psi_G \ln(1 - X)\}^{1/2}} \tag{20}$$

where β_G is the Biot Modulus of each grain given by

$$\beta_G = \frac{2k_s\rho_s(1 - \varepsilon_{mi})}{\gamma_B M_p D_{eG} S_{G0}} \tag{21}$$

Ψ_G is grain pore structure parameter as

$$\Psi_G = \frac{4\pi L_0(1 - \varepsilon_{mi})}{S_{G0}^2} \tag{22}$$

Defining

$$\Psi_p = N\Psi_G = \frac{4\pi N L_0(1 - \varepsilon_{mi})}{S_{G0}^2} \tag{23}$$

as a generalized structure parameter of the pellet.

Considering the geometric relation, Ψ_p is written as

$$\Psi_p = 4\pi(1 - \varepsilon_{ma})(1 - \varepsilon_{mi})(\frac{R_p}{r_G})^3 L_o/S_{G0}^2 \quad (24)$$

Eq. (20) can be rewritten as

$$f_p(X) = \frac{\frac{1}{N} + \frac{\beta_G Z_\nu}{\Psi_p}[\{1 - \frac{\Psi_p}{N}\ln(1 - X)\}^{1/2} - 1]}{(1 - X)\{1 - \frac{\Psi_p}{N}\ln(1 - X)\}^{1/2}} \quad (25)$$

It can be then seen that a mathematical formulation of the generalized model for non-catalytic gas-solid reactions is represented by a group of Eqs. (3)—(7) and (25). Eq. (3) can be transformed to a second-order differential equation in terms of X through the concept of cumulative concentration

$$\Phi = \int_0^\tau a\,d\tau = \int_0^X f(X)dX \quad (26)$$

which was proposed and used by Ramachandran and Smith.[14]

Characteristics of the generalized model

To find out the characteristics of this generalized model, let us consider two extreme cases.

Case I. $N = 1$, $\varepsilon_{ma} = 0$, $\varepsilon_{mi} = \varepsilon_p$ and $r_G = R_p$

Eq. (24) can be reduced to

$$\Psi_p \mid_{N=1} = 4\pi L_o(1 - \varepsilon_p)/S_{G0}^2 = \Psi_G \quad (27)$$

And,

$$f_p(X) \mid_{N=1} = f_G(X) \quad (28)$$

which means that the random pore model is just one special case of the generalized model at $N = 1$.

Case II. $N = M$ where M is an infinite number and rather accesible to infinite number that enables the micropore porosity to be zero, *i.e.*, $\varepsilon_{ma} = \varepsilon_p$

Then, $S_{G0} = \left(\frac{4\pi r_G^2}{\frac{4}{3}\pi R_p^3}\right) = \frac{3r_G^2}{R_p^3}$; $L_o = \frac{L'_o}{\frac{4}{3}\pi R_p^3}$ and $\beta_G = \frac{2k_s\rho_s R_p^3}{3\gamma_B M_p D_{eG} r_G^2}$

Substituting the parameters above into Eq. (24) and Eq. (25), it can be obtained,

$$f_p(X) \mid_{N=M} = \left(\frac{\frac{1}{M} + \frac{2k_s\rho_s R_p^3}{3\gamma_B M_p D_{eG} r_G^2} \frac{Z_\nu 3r_G}{(1 - \varepsilon_p)\left(\frac{R_p}{r_G}\right)^6 L_o'}[G(X) - 1]}{(1 - X)G(X)}\right)$$

$$= \frac{\frac{1}{M} + \frac{P_G Z_\nu}{Bi}[G(X) - 1]}{(1 - X)G(X)}$$

$$= \frac{(1 - X)^{-1}K(X)}{M} + \frac{P_G Z_\nu (1 - X)^{-1}[1 - K(X)]}{Bi} \quad (29)$$

where P_G is defined as a new structure parameter by

$$P_G = \frac{2\rho_s}{\gamma_B M_p(1 - \varepsilon_p)}\left(\frac{r_G}{R_p}\right)^3\left(\frac{r_G}{L_o}\right) \quad (30)$$

and

$$K(X) = \frac{1}{G(X)} = \left\{1 - \frac{1}{3}\left(\frac{R_p}{r_G}\right)\frac{L_0}{r_G}\ln(1 - X)\right\}^{-1/2} \quad (31)$$

It is seen that Eq. (29) is very similar to Eq. (10), which indicates that the grain model behavior can be closely approximated by the generalized model at $N = M$. Thus, it can be concluded that the generalized model presented in this paper applies to any solid reactant from very nonporous to highly porous materials.

Conclusion

With the conceptual classification of the existing models for non-catalytic gas-solid reactions, a general formulation for the models is presented in this paper, which may be very useful in comparison of models. Based on a critical comparison of the prevailing models in terms of their characteristics, a generalized model incorporating microporous grains has been developed. It is shown that the generalized model can be reduced to the random pore model and grain model as two extreme cases, thus it is applicable to gas-solid reaction systems involving any solid reactant ranging from nonporous to highly porous materials.

References

1. Szekely, J.; Evans, J.W.; Sohn, H.Y., *Gas-Solid Reactions*, Academic press, New York, 1976.
2. Sohn, H.Y.; Wadsworth, M.E., *Process of Extractive Metallurgy*, Plenum, New York, 1979.
3. Wen, C.Y., *Ind. Eng. Chem.*, **60**, 34(1968).
4. Sampath, B.S.; Hughes, R., *Chem. Eng.*, Oct., 485 (1973).
5. Ramachandran P.A.; Doraiswamy, L.K., *AIChE J.*, **28**, 881(1982).
6. Ausman, J.M.; Watson, C.C., *Chem. Eng. Sci.*, **17**, 323(1962).
7. Ishida, M.; Wen, C.Y., *AIChE J.*, **14**, 311(1968).
8. Szekely, J.; Evans, J.W., *Met. Trans.*, **2**, 1691 (1971).
9. Szekely, J.; Evans, J.W., *Met. Trans.*, **2**, 1699 (1971).
10. Szekely, J.; Evans, J.W., *Chem. Eng. Sci.*, **25**, 1091(1970).
11. Hartman, M.; Coughlin, R.W., *AIChE J.*, **22**, 490 (1976).
12. Sohn, H.Y.; Szekely, J., *Chem. Eng. Sci.*, **27**, 763 (1972).
13. Petersen, E.E., *AIChE J.*, **3**, 443(1957).
14. Ramachandran, P.A.; Smith, J.M., *Chem. Eng. J.*, **14**, 137(1977).
15. Thiele, E.W., *Ind. Eng. Chem.*, **31**, 961(1939).
16. Bhatia, S.K.; Perlmutter, D.D., *AIChE J.*, **26**, 379 (1980).
17. Bhatia, S.K.; Perlmutter, D.D., *AIChE J.*, **27**, 247 (1981).
18. Gavalas, G.R., *AIChE J.*, **26**, 577(1980).
19. Hashimoto, K.; Silverston, P.L., *AIChE J.*, **19**, 259 (1973).
20. Simons, G.A.; Finson, M.L., *Combust. Sci. Tech.* **19**, 217(1979).
21. Simons, G.A., *Combust. Sci. Tech.*, **19**, 227(1979).
22. Simons, G.A., *Proceedings of the 19th International Symposium on Combustion*, 1982, p.1067.
23. Simons, G.A., *Prog. Energy Combust. Sci.*, **9**, 269 (1983).
24. Do, D.D., *Chem. Eng. Sci.*, **37**, 1477(1982).
25. Ranade, P.V.; Harrison, D.P., *Chem. Eng. Sci.*, **34**, 427(1979).
26. Georgakis, C.; Chang, C.W.; Szekely, J., *Chem. Eng. Sci.*, **34**, 1072(1979).
27. Wheeler, A., *Adv. Catal.*, **3**, 249(1951).

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