Solid-state Diffusion and Crystal Growth: Two Important Steps for Gas-solid Reactions
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Solid-state diffusion and crystal growth: two important steps for gas-solid reactions

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The importance of solid-state diffusion and crystal growth of the solid product in a gas-solid reaction with solid product formation (GSRSPF) are discussed with direct sulfation of limestone as a representative example. A GSRSPF usually involves nucleation and crystal growth of the solid product, which are necessary processes for the formation of the new phase of the solid product. Solid-state diffusion is a process which is responsible for the transport of atoms or ions of the solid reactant and product during the reaction and crystal growth of the solid product. For a GSRSPF, the conversion of the solids may involve steps such as gas film diffusion, pore diffusion in product layer, chemical reaction, solid–state diffusion and crystal growth. The overall kinetics is usually significantly influenced by the relatively slow and highly activated solid–state diffusion. Due to the involvement of nucleation and crystal growth of the solid product, crystallographic properties of the solid reactant and product have a large influence on the overall kinetics as well since those properties determine how nucleation and crystal growth proceed.

Keywords: gas-solid reaction, nucleation, solid–state, diffusion, crystal growth.

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Introduction

For a gas–solid reaction with solid product formation (GSRSPF), it is observed that nucleation and subsequent crystal growth of the solid product (it is shortened as "crystal growth" later on in the text) usually take place as necessary intermediate steps during the formation of the new product phase. There are numerous such reactions. Sulfation of limestone (Duo et al. 2000, Hu et al. 2007a,b,c), sulfation of iron oxide (Bolsaitis and Nagata 1980), oxidation of iron (Shao et al. 1997), reduction of iron oxides (Hayes and Grieveson 1981) and decomposition of pyrite (Fegley and Lodders 1995) are just a few examples. Solid–state diffusion is believed to be responsible for the transport of ions and atoms which are necessary for the reaction and crystal growth of the solid product. However, in kinetic modeling of gas–solid reactions, crystal growth and solid–state diffusion are either not considered or not considered properly. For example, in the well known shrinking unreacted core model (SUCM) (Szekely et al. 1976), only gas film/intraparticle diffusion, product layer diffusion and chemical reaction are considered. Because of the simplified description of the reaction process, SUCM or other similar models are relatively simple and easy to use. However, these models are often not sufficient for assessing kinetic parameters of the real physical and chemical phenomena taking place during a GSRSPF. In this article, the important roles of solid–state diffusion and crystal growth of the solid product in the kinetics of a GSRSPF are discussed mainly on basis of experimental observations of the direct sulfation of limestone.

Crystal growth

As mentioned above, crystal growth is the physical process by which the new phase of the solid product is formed. Nucleation of the solid product normally does not take place until sufficient amount of atoms or ions of the solid product is produced which creates conditions for the formation of stable product nuclei (West 1999). However, the mechanism of crystal growth of the solid product can be very different depending on the crystallographic properties of both the solid reactant and product, and the reaction conditions. Crystals are built up of atoms or ions in regular and three–dimensional arrangements. Crystal lattice structures of the solid reactant and product usually have large influence on how crystal growth proceeds, and are therefore particularly important for a GSRSPF (Figlarz et al.1990, West 1999, Hu et al.2007a,b,c).

Grains (in the following, a grain is defined as a whole piece crystal without pores and cracks, while a particle is a collection of the grains) of the solid reactant by its nature expose always different lattice planes at different sides. In case of epitaxial or topotaxial (two–dimensional or three–dimensional similarity in lattice structure, respectively) match in the lattice plane of a particular side of the solid reactant grain and a lattice plane in the solid product, oriented nucleation and crystal growth of the solid product may take place at this side because the energy barrier is relatively low for epitaxial and topotaxial nucleation and growth (Figlarz et al. 1990).

A good example to illustrate this is the nucleation and crystal growth of anhydrite during direct sulfation of limestone (Hu et al. 2007a,c). Figure 1a shows the SEM image of a sulfated Iceland Spar (a pure, naturally occurring calcite crystal) grain.
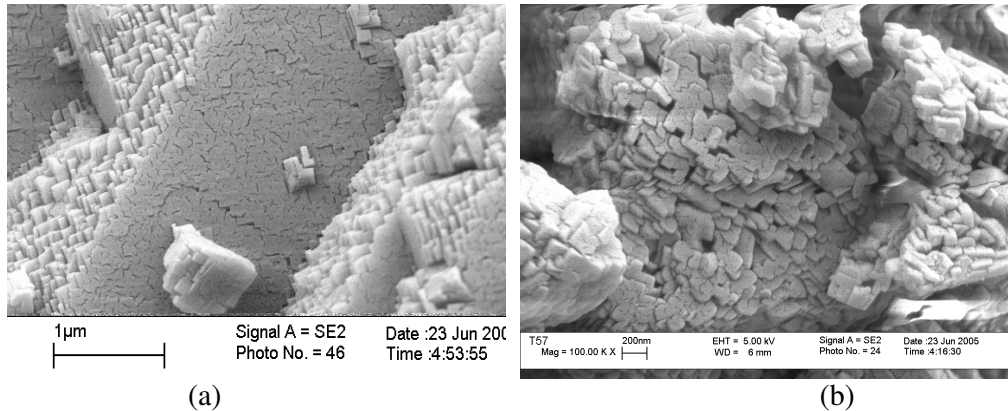

| 1µm | Signal A = SE2 | Date :23 Jun 200 |
| | Photo No. = 46 | Time :4:53:55 |

(a)

| T57 | 200nm | EHT = 5.00 kV | Signal A = SE2 | Date :23 Jun 2005 |
| Mag = 100.00 K X | | WD = 6 mm | Photo No. = 24 | Time :4:16:30 |

(b)

Figure 1 SEM images of Iceland Spar (a) and Faxe Bryozo (an porous bryozoan limestone from Denmark) (b) particles sulfated at 973 K to conversions of about 2.7% and 4.5%, respectively in a gas containing 1800 ppm SO_2 3% O_2 and 30 % CO_2 and 86.8 % N_2 (Hu et al. 2007a)

This SEM image demonstrates that crystal growth of the solid product (anhydrite) takes place only at the fractures of the grain. Nothing happens at the cleavages (the smooth sides). The nucleation and growth is oriented. This is because, as shown by Hu et al. (2007c), the side of the fractures have a close epitaxial match with a particular lattice plan in anhydrite crystals. Figure 1a demonstrates that all the fracture surfaces are active, as crystal growth of the solid product takes place overall the fracture surfaces. An important fact with oriented nucleation and crystal growth is the direct connection between the lattices of the substrate and the product as is well demonstrated in Figure 1a. As a consequence of the formation of product nuclei and their subsequent growth the free calcite grain surface area is reduced accordingly. This is most likely one of the main reasons for the initial (a few seconds) fast decrease in limestone conversion rate during the direct sulfation of limestone as observed by Hu et al. (2007a).

Figure 1b is a SEM image of sulfated Faxe Bryozo. Faxe Bryozo is a porous bryozoan limestone consisting of primary particles of 1-3 micrometer (Dam-Johansen et al. 1991a,b,c,d). The primary particles are a collection of small calcite grains. This SEM image shows that anhydrite crystal grains are formed overall the particle surface, very different from the situation with Iceland Spar mainly because of the relatively small size of the calcite grains. However, the growth is clearly oriented as well as with Iceland Spar.

Crystal growth can also be non–oriented most likely because of mismatch in lattice structure or high solid–state mobility of atoms or ions in the solid reactant and product caused by high temperature or dopants. The latter is well demonstrated by Hu et al. (2007b) with the direct sulfation of limestone doped with various additives. Figures 2 and 3 show a couple of examples.

Figure 2 shows a series of SEM images of NaCl–doped limestone particles sulfated to different conversions. These SEM images demonstrate non–oriented growth of totally deformed product crystals with relatively long distance between the initially formed nuclei. The product crystals coalesce when in contact. A poreless product layer is formed at higher conversions. Figure 3 shows a SEM image of sulfated limestone particles doped with KCl. This figure demonstrates non-oriented growth of well shaped product crystals. The non–oriented growth of product crystals can also be seen in the SEM images of sulfated iron oxide particles presented by Bolsaitis and Nagata (1980) and the SEM images of oxidized iron particles presented by Shao et al. (1996).

As it is demonstrated in Figures 1–3, the product layer structure and shielding of the surface of the solid reactant grain by the product crystals can be very different depending on the growth pattern, physical properties of the solid reactant and reaction conditions such as temperature, dopants and conversion level.
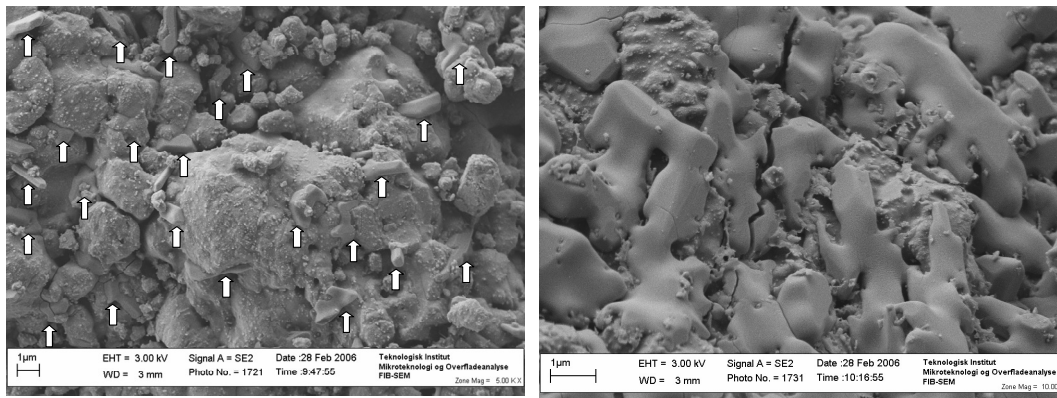
2a Sulfated at 873 K for 5 minutes (x = ca. 1.9 %) (the white arrows indicate the crystal grains)

2b Sulfated at 873 K for 10 minutes (x = ca. 4.4 %)
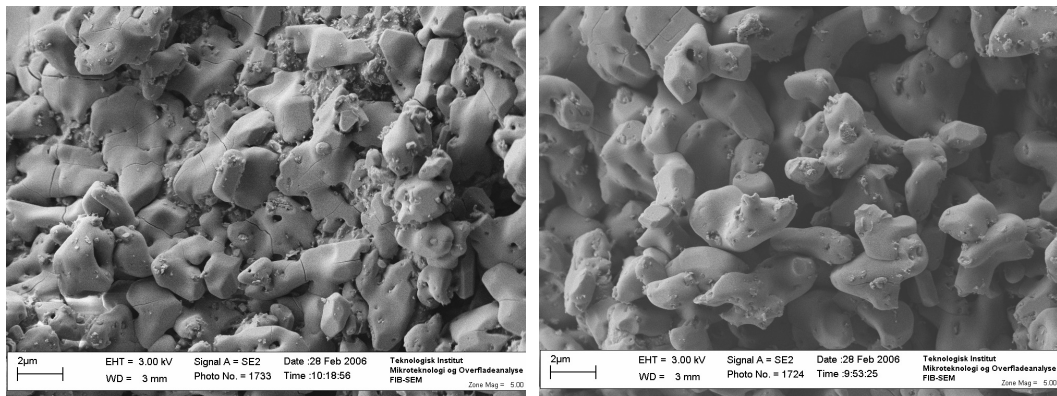
2c Sulfated 873 K for 20 minutes (x = ca. 9.0 %)

2d Sulfated at 873 K for 60 minutes (x = ca. 14.8%)

Figure 2 SEM images of Faxe Bryozo particles doped with 2 % NaCl and sulfated at 873 K to different conversions (other conditions: P: 0.11 MPa; inlet SO_2: 1800 ppm; O_2: 3 %; CO_2: 30 %; N_2: balance)(Hu et al. 2007b)
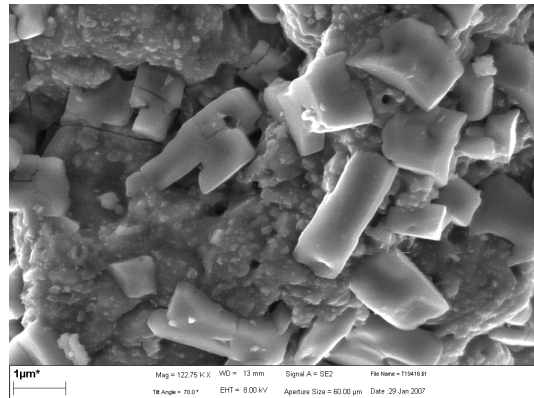
Figure 3 SEM image of Faxe Bryozo doped with 2 % KCl and sulfated at 823 K for 30 minutes (x = ca. 6 %) (other reaction conditions: P: 0.11 MPa; inlet SO_2: 1800 ppm; O_2: 3 %; CO_2: 30 %; N_2: balance) (Hu et al. 2007b).

Solid–state diffusion

The phenomenon of solid–state diffusion was discovered for more than 100 years ago by William Chandler Roberts–Austen (1896). About thirty years later it was further found that solid–state diffusion proceeds by point defects in crystals (Frenkel 1926, Wagner and Schottky 1930). Point defects are vacant lattice sites left by missing atoms or ions that normally should occupy the sites. Atoms and ions simply migrate by jumping from one vacancy to another. Solid–state diffusivity increases with increasing concentration of point defects in the solid materials. Point defects can be intrinsic when they are formed by thermal motion and can be extrinsic when they are formed by incorporation of aliovalent ions into the crystal lattice of the solid materials (West 1999). Solid–state diffusivity can thus be affected by addition of dopants and in some cases by varying gas compositions. The influence of CO_2 in the gas phase on the sintering of calcite particles (Beruto et al. 1986, Tetard et al. 1999) is an example of the influence of a gas on solid–state diffusivity in a solid.

For a crystal grain, it was found that diffusivity at the grain surface/interface is significantly (can be several orders of magnitude) higher than diffusivity in the inner part of the grain (Barnes 1950, LeClaire 1951, Fisher 1951, Hoffman and Turnbull 1951), most likely due to the unsaturated (ions or atoms at the surface are not surrounded by the same number of other ions or atoms as inside the grain) and more defective nature of the grain surface. For a GSRSPF, grain–boundary diffusion is particularly important because the movement of atoms or ions during such a reaction take place mostly at the grain surface.

In a GSRSPF, reaction and crystal growth of the solid product are facilitated by solid-state diffusion. As illustrated in figure 4, chemical reaction may take place at the surface of the solid reactant grain, the interface between the solid reactant grain and the product crystals or the surface of the product crystals. No matter on which surface the reaction takes place, the transport of the relevant component must proceed by solid-state diffusion. In Case (a), product atoms or ions formed at the surface of the

solid reactant grain need to diffuse in solid state to the nucleation and growth sites of the solid product. In Case (b), the gaseous reactant needs to diffuse in solid state through the product crystal to participate the reaction at the interface between the solid reactant and product. In Case (c), the atoms or ions of the solid reactant need to diffuse in solid state through the product crystal to participate the reaction at the surface of the product crystal.
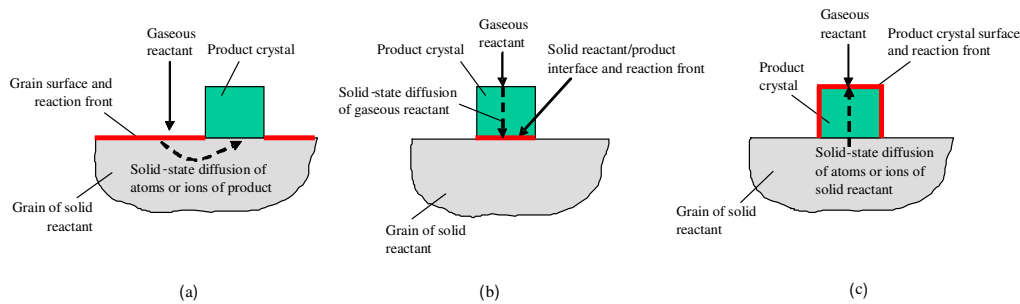

Figure 4 Illustration of possible solid–state diffusion routes in gas–solid reactions

The conversion of the limestone particles shown in Figure 2b is about two times the conversion of the limestone particles shown in Figure 2a. However, by visual judgement, the amount of product crystals on the limestone surface shown in Figure 2a is far less than half the amount of product crystals on limestone particles shown in Figure 2b. It can be estimated that at least more than 1% of the formed sulfate ions are distributed in the limestone phase. This is a confirmation of reaction taking place at the uncovered limestone grain surface. Diffusion of formed product ions (Cu^+ and Br^-) to nucleation and growth sites during the reaction between Cu and gaseous Br_2 observed by Nakakura et al. (1999) with scanning tunnelling microscopy is another example that demonstrates that reaction and crystal growth can take place at different locations, i.e. Case (a). Figure 2d can be an example of Case (b) or (c), as the sulfation reaction continues after the limestone particles are fully covered by a poreless product layer. Because diffusion of electrically neutral molecules through an ionic crystal material is expected to be much more difficult than diffusion of ions, Case (c) is therefore believed to have practical meaning with ionic product crystals.

The results with the direct sulfation of limestone indicate that solid–state diffusion may take place at different locations such as at the grain surface of the solid reactant or through the product layer depending very much on the physical properties of the formed product crystals and the conversion level.

Kinetic behavior

Hu et al. (2007a), on basis of their study on the direct sulfation of limestone, pointed out that a GSRSPF can involve the following 5 processes:

1). Gas film diffusion of the gaseous reactants and products
2). Pore diffusion of the gaseous reactants and products in case of porous particles and product layer
3). Chemical reaction between the gaseous reactants and solid reactant

4). Solid–state diffusion of atoms or ions of the solid reactant and product
5). Nucleation   and   crystal   growth   of   the   solid   product

Figure 5 illustrates the relative relations between these processes by considering only Cases (a) and (c) illustrated in Figure 4.
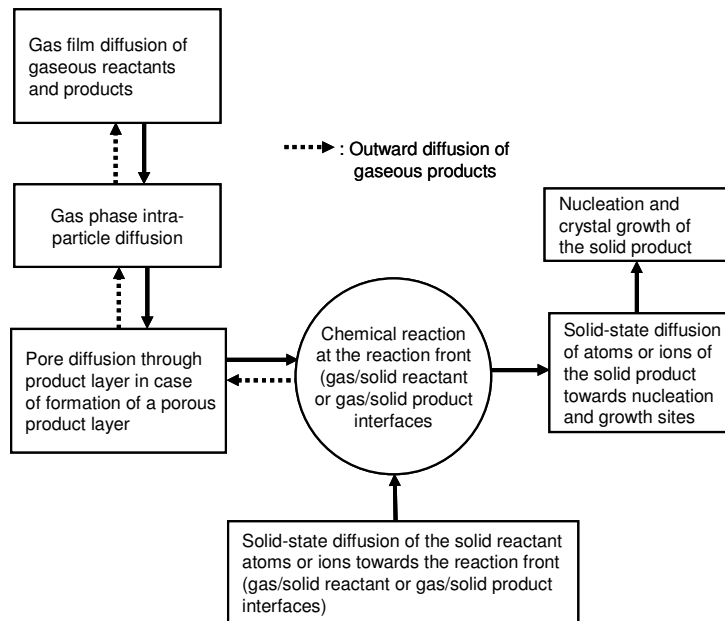

Figure 5 Illustration of the relative relations between the different processes in a gas–solid reaction with solid product formation

The reaction may be controlled by gas film diffusion, pore diffusion, chemical reaction or solid–state diffusion. Crystal growth of the solid product is a process for the formation of the new product phase. This process may have significant influence on the overall reaction rate because of its influence on the area of gas/solid reactant interface directly available for the reaction and the properties of the product layer which usually have significant influence on both gas phase and solid–state diffusion. However, crystal growth should not control the reaction because it is not a necessary intermediate step for the reaction to take place.

Kinetic behaviour of a GSRSPF is reflected in its conversion or conversion rate vs. time curves. The majority of the conversion rate vs. time curves that are found in the literature can be divided into the following two types:

1) Conversion rate decreases monotonically with reaction time.
2) Conversion rate increases at the start but decrease after it reaches a maximum.

These two types of conversion rate vs. time curve with corresponding conversion vs. time curve are illustrated in Figure 6.
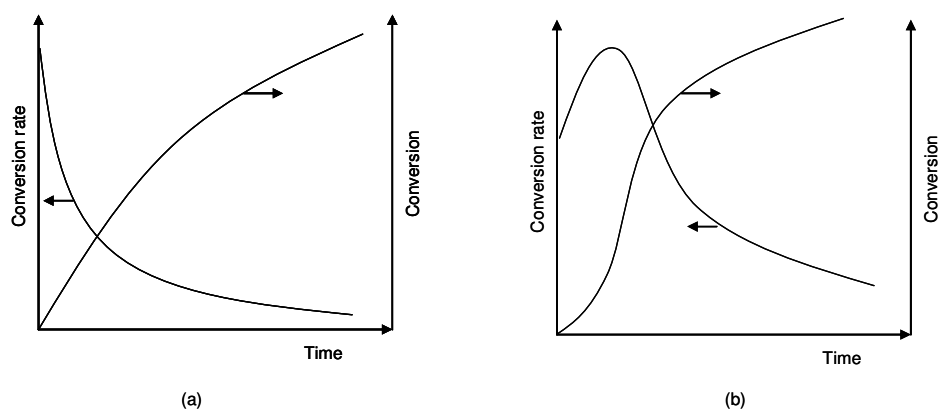
Figure 6 Illustration of different conversion (rate)
vs. time curves of gas–solid reactions

Direct sulfation of limestone (Hu et al. 2007a), sulfation of CaO (Dam–Johansen and Østergarrd 1991a,b,c,d, Duo et al. 2000) and reduction of iron oxide with CO (Piotrowski et al. 2005) are examples among the reactions which show type (a) curve in Figure 6, while reduction of iron oxide with hydrogen (Piotrowski et al. 2005), oxidation of copper sulfide (Ganguly and Mukherjee 1967) and thermal decomposition of pyrite (Schwab and Philinis 1947), limestone (Khraisha and Dugwell 1989, Haji–Sulaiman and Scaroni 1992, Khinast et al. 1996) and anhydrous nickel nitrate (Criado et al. 1987) are examples among the reactions which show type (b) curve in Figure 6. For some reactions the shape of their conversion rate vs. time curves can change with reaction conditions. For example, the direct sulfation of limestone can have type (b) curve when the limestone is modified with dopants (Hu et al. 2007b); sulfation of CaO under certain conditions can show type (b) curve as well as shown by Murthi et al. (1971), Laursen et al. (1999) and Duo et al. (2000). For some reactions, the shape of the conversion rate vs. time curve transforms gradually from type (b) to type (a) with increasing temperature (Piotrowski et al. 2005 and 2007, Criado et al. 1987, Hayashi et al. 1991)

The recent study of the direct sulfation of limestone by Hu et al. (2007a,b) indicates that the sigmoid conversion vs. time curves are most likely caused by a combined effect of the significant influences of solid–state diffusion and a gradual shielding of the grain surface of the solid reactant by the growing crystal grains of the solid product. All GSRSPFs may therefore have the potential of showing a sigmoid conversion vs. time curve.

Temperature, the type of nucleation and growth and properties of the solid reactant grain are among the factors that can have influence on the form of the conversion/conversion rate vs. time curve. Results presented by Criado et al. (1987), Hayashi et al. (1991), Piotrowski et al. (2005 and 2007) and Hu et al. (2007b) indicate that higher temperatures may create conditions for type (a) curve. The explanation could be a significantly reduced resistance of solid–state diffusion at higher temperatures. Results presented by Hu et al. (2007a,b) indicate that oriented nucleation and growth may create conditions for type (a) curve due to the fast coverage of the solid reactant grain surface by small grains of the solid product, which most likely make the period with increasing conversion rate very short and

difficult to be noticed. The influence of properties of the solid reactant grain on the curve type was demonstrated by the results obtained by Duo et al. (2000) in their study of CaO sulfation. The study showed that CaO directly from limestone calcination has type (b) curve, whereas CaO sintered at high temperatures showed type (a) curve.

Modeling

In the literature, two mathematical models are widely used to simulate the conversion or conversion rate vs. time curves. One is shrinking unreacted core model (SUCM) (Szekely et al. 1976). The other is Avrami–Erofeev equation (Avrami 1939, 1940 and 1941, Erofeev 1946).

In SUCM, the conversion of a non-porous solid reactant particle is assumed to take place with a shrinking unreacted core and a product layer surrounding the unreacted core. It is assumed that there is a clear boundary between the unreacted core and the product layer. 5 steps are considered. They are:

1). Inward diffusion of gaseous reactants through a gas film surrounding the particle.
2). Inward diffusion of gaseous reactants through the product layer.
3). Chemical reaction at the surface of the unreacted core of the solid reactant.
4). Outward diffusion of gaseous products through the product layer.
5). Outward diffusion of gaseous products through the gas film.

With a porous particle, intra–particle diffusion is also considered. This model has been treated in great details in the book by Szekely et al. (1976). There are a number of variants of SUCM such as the random pore model (Petersen 1957, Bhatia and Perlmutter 1980, 1981, Szekely 1976), the grain model (Szekely 1976) and the grain–micrograin model (Dam–Johansen et al. 1991a,b,c,d). These models basically assume the same steps as in SUCM. The only difference is additional pore/grain structure considerations in these models.

With a non–porous particle or grain (a porous particle can always be considered to consist of smaller and primary non–porous units/grains), the assumption of shrinking core in this model seems to hold based on the observations of various reactions such as decomposition and oxidation of pyrite (Jorgensen and Moyle 1982, Dunn et al. 1989a,b, Fegley and Lodders 1995) and sulfation of limestone (Hajaligol et al. 1988).

However, the assumptions about the involved steps or processes in a GSRSPF do not fully match the reality because nucleation and crystal growth of the solid product are not considered. The treatment of diffusion in the product layer is often not sufficient, either. As discussed earlier, the properties (such as porosity and pore size) of a product layer can be significantly influenced by reaction conditions such as temperature, dopants, reaction time and conversion level. In case of the formation of a non–porous product layer, the species that diffuse through the product layer may be atoms or ions of the solid reactant in stead of the gaseous reactants and products. These are most likely among the main reasons for the wide variation of kinetic parameters (such as activation energy, effective diffusion coefficient and reaction orders of gases) of the same reaction when measured or assessed through model simulations by using data obtained under different reaction conditions.

Decomposition of pyrite (Hu et al. 2006a) and direct sulfation of limestone (Hu et al. 2006b, Hu et al. 2007a,b) are two typical examples.

The Avrami–Erofeev equation is deduced based on the theory of germ nucleation and growth of crystal grains of a new phase in the whole volume of a mother phase or media without consideration of influences from such as chemical reaction and mass transport. The equation has the following form:

$$x = 1 - e^{-Bt^n} \qquad (1)$$

Here, x: conversion of the solid reactant; B: constant; t: reaction time; n: constant.

This equation produces a sigmoid curve which matches type (b) curve in Figure 5. Because of this reason, this equation has frequently been used to model GSRSPFs showing sigmoid conversion vs. time curves. The sigmoid conversion vs. time curves are also frequently used as an argument for nucleation and growth controlled process.

However, as discussed above, the sigmoid shape of a conversion vs. time curve is most likely related to the significant influence of solid–state diffusion and not because of control by crystal growth of the solid product. If the sigmoid shape of a conversion vs. time curve was an indication for control of nucleation and crystal growth, the influences of gaseous reactants should be negligible and the apparent activation energy should not vary significantly with gas concentrations. Results shown by Viricelle et al. (1995a,b), Ganguly and Mukherjee (1967) and Hu et al. (2007b) demonstrate that this is actually not the case.

For the purpose of process simulation, Equation (1) has its advantage because of its simplicity. However, it is not sufficient to conclude the reaction is controlled by nucleation and growth simply on the basis of a reasonable fit between experimental data (usually only part of the data) and the model.

In addition to process simulation, modeling is frequently used to judge reaction mechanism and assess kinetic parameters such as rate constant, activation energy, diffusion coefficient, etc. For this purpose, it is important that the model includes all the real and significant processes. For a GSRSPF, the kinetic parameters obtained by considering only gas phase diffusion and chemical reaction can be misleading if they are assumed to relate real physical processes. The following are two examples about effective diffusivity and apparent activation energy, respectively.

In SUCM, the effective diffusivity in a porous product layer is evaluated across the whole thickness of the product layer. When pore diffusion is the controlling mechanism, the evaluated effective diffusivity can thus be related to gas phase diffusivity and porosity in the product layer. However, when the resistance of solid–state diffusion is most likely the major diffusion resistance and this resistance of solid–state diffusion is most likely located at the surface of the unreacted core or in a relatively thin layer near the unreacted core, the effective diffusivity evaluated in such a way is no more than a model parameter and does not represent any physical properties of diffusion in the gas phase or in the solid phase. A typical example is the direct sulfation of limestone (Hu et al. 2006b). For the direct sulfation of limestone,

there has been a discussion about the controlling diffusion mechanism. The reason for the discussion is that the evaluated diffusivity is relative higher which, plus the fact of a porous product layer, give reasons for some authors to conclude gas phase diffusion control. However, another fact, a relatively high activation energy associated to the diffusion process disapproves this conclusion and gives reason for some other authors to conclude solid–state diffusion control. However, by considering solid–state diffusion in a thin layer (probably only a few nanometers) at the unreacted core surface, then the diffusivity will be several orders of magnitude lower than the value evaluated across the whole product layer. The magnitudes of the diffusivity and the activation energy then make a sense to represent a solid–state diffusion process.

The consistence between the apparent activation energies evaluated with the same GSRSPF under different reaction conditions and conversions are often very "poor". Decomposition of pyrite (Hu et al. 2006a) and direct sulfation of limestone (Hu et al. 2006b) are two examples. However, as it has been discussed earlier, GSRSPFs are usually significantly influenced by solid–state diffusion and crystal growth. If we take this into consideration and realize that the reaction is usually under mixed control by both chemical reaction and solid–state diffusion (Hu et al. 2007a,b), then the "poor" consistence is a result as it should be.

Today, with the development of analysis technologies, especially in advanced SEM and related technologies, it has become possible for us to "see" gas–solid reactions in great details. We begin to understand the mechanism much better than before. It is believed that with more sophisticated models that integrate all significant processes such as solid–state diffusion and crystal growth, model simulations will become more realistic and more powerful. The kinetic parameters assessed through model simulations will also be more "pure", more consistent from case to case and thus more universal for different applications.

Conclusion

Solid-state diffusion and crystal growth of the solid product are two important processes in gas-solid reactions with solid product formation. Crystal growth is the process through which the new phase of the solid product is formed. This process is complicated and can proceed in different ways depending on the crystallographic properties of the solid reactant and product and the reaction conditions such as gaseous reactants, temperature and dopants. Solid-state diffusion is responsible for the transport of atoms or ions of the solid reactant and product during the reaction and crystal growth of the solid product. Grain-boundary diffusion, a much faster diffusion process than lattice diffusion, is particular relevant and important for such reactions.

Solid-state diffusion and crystal growth of the solid product usually have large influence on the kinetic behavior of gas–solid reactions with solid product formation. Integration of these two factors into the mathematical models describing the reaction is necessary for better process simulation and assessment of kinetic parameters related to real processes.

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