TG measurement of gas–solid reactions.
The effect of the shape of the crucible on the measured rate

G. Hakvoort

Delft University of Technology, Chemistry Department, Julianalaan 136, 2628 BL Delft (The Netherlands)

Abstract

The effective rate of gas–solid reactions does not only depend on the chemical reaction rate, but also on the transport of the active compounds through the surrounding gas phase and through the pores of the solid sample. The gas phase transport strongly depends on the shape of the sample holder. Therefore TG measurements of gas–solid reactions show a great range in measured rate and apparent kinetic mechanism, depending on the specific sample holder used.

Investigations have been made of the absorption of sulfur oxide onto spherical CaO/ Al_2O_3 pellets. A shrinking-core model was applied for the description of the reaction. So the rate constants of the separate processes can be calculated. In this way the effect of any specific type of sample holder can be quantitatively determined.

INTRODUCTION

In our laboratory, regenerable sorbents are developed for in situ desulfurization of combustion gases during the fluidized bed combustion (FBC) of coal. This process, proceeding at relatively low temperatures of 800–1000°C, has several advantages over other processes such as powder coal combustion or fixed bed combustion, which proceed at much higher temperatures (about 1400°C), namely because of the low temperatures, nitrogen and oxygen from the air do not react to form NO_x; and the reaction of sulfur oxides with solid sorbent materials proceeds very easily because of the very good gas–solid contact in a fluidized bed [1, 2].

Several conditions must be fulfilled in order to develop a good sorbent pellet: an open, porous structure for good, fast reactions with gases, a good regeneration behavior, and sufficient mechanical strength for cyclic use.

Pellets of alumina with CaO are the best. Three kinds of pellets have been prepared and tested [2, 3, 4]: cylindrical α-Al_2O_3 pellets, impregnated with CaO: cylindrical γ-Al_2O_3 pellets, impregnated with CaO; and spherical Al_2O_3/CaO pellets, prepared by means of a sol-gel process.
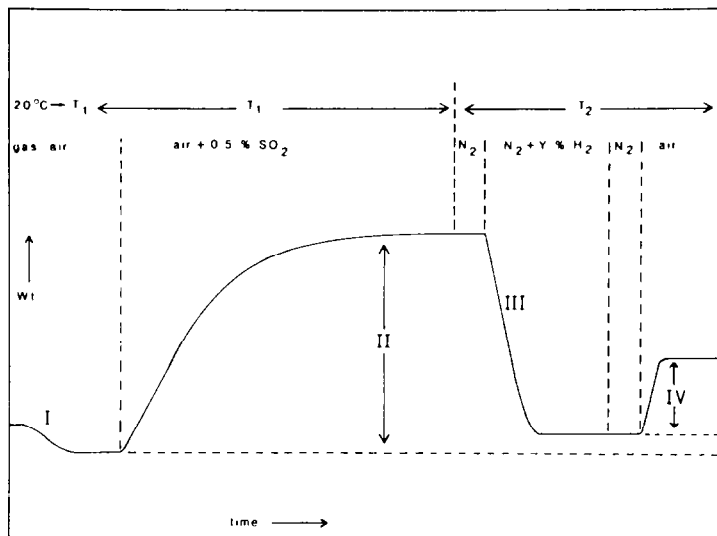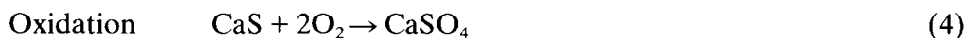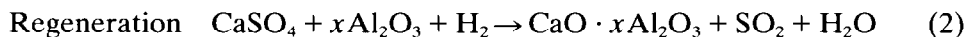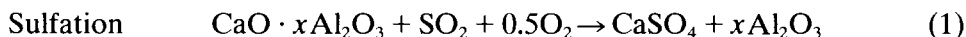
Fig. 1. TG curve of an absorption/regeneration cycle: I, calcination; II, sulfation; III, regeneration; IV, oxidation [4].

The reactions concerned are (see Fig. 1)

Sulfation $CaO \cdot xAl_2O_3 + SO_2 + 0.5O_2 \rightarrow CaSO_4 + xAl_2O_3$ (1)

Regeneration $CaSO_4 + xAl_2O_3 + H_2 \rightarrow CaO \cdot xAl_2O_3 + SO_2 + H_2O$ (2)

                $CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O$ (3)

Oxidation $CaS + 2O_2 \rightarrow CaSO_4$ (4)

Reaction (3) is undesirable; no active sulfation sorbent is formed. For thermodynamic reasons, reaction (3) normally proceeds at low temperatures (800–1000°C), unless Al_2O_3 molecules are in the direct vicinity of the $CaSO_4$ crystals, when the thermodynamically more stable compound $CaO \cdot xAl_2O_3$ is formed during regeneration.

For this reason, porous Al_2O_3 with a monolayer of CaO on the alumina surface forms the best sorbent. This can be made by a sol-gel process [2]. The other sorbents, α- or γ-Al_2O_3, impregnated with CaO, are less satisfactory, because the CaO layers made by impregnation have an irregular thickness, resulting in the formation of relatively more CaS during reduction. In addition, γ-Al_2O_3 pellets are not mechanically strong enough for cyclic use.

This article deals in particular with the kinetics of the sulfurization reaction (1) for sol-gel pellets. It was found that the measured rate depends strongly on the nature of the crucible used.
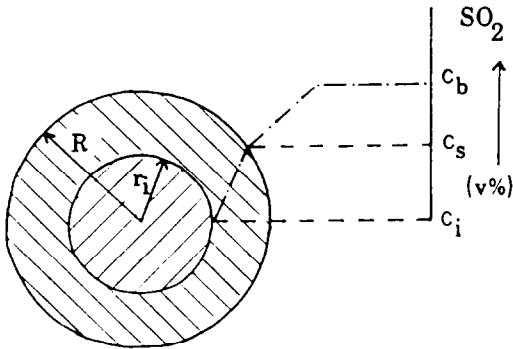
Fig. 2. SO_2 concentration profile in and around a sorbent sphere, according to the shrinking-core model: c_b, SO_2 concentration in the gas phase; c_s, SO_2 concentration on the outer surface of the sorbent particle with radius R; c_i, SO_2 concentration on the boundary of the shrinking core with radius r_1 [5].

DERIVATION OF EQUATIONS

At least three processes are involved in the absorption process (see Fig. 2)

(i) Transport of the active components (SO_2 and O_2) through the gas phase into the outer surface of the sorbent pellets.

(ii) Diffusion of these active components through the pores of the shell of reacted sorbent.

(iii) Chemical reaction with active sorbent.

Because processes in series are involved, the slowest process is the most rate-determining. For sol-gel pellets with narrow pores, the diffusion reaction (ii) is much slower than the chemical reaction (iii).

This can be proved by comparing the normal sol-gel pellets and pellets impregnated with about 0.1% of platinum [3,5]. It was found that the overall rate of the sulfation reaction does not increase, although platinum is a good catalyst for the chemical reaction. This means that even in the uncatalyzed process, the chemical reaction is sufficiently fast that it is not rate determining. So two possible rate-determining processes are left: diffusion through the gas phase (i), with a rate constant k_g; and diffusion through the pores of the reacted sorbent (ii), with a diffusion coefficient D. This last reaction can be described by a shrinking-core model.

It was found that the overall rate also depends on the type of crucible, which influences the gas transport, as well as on the progress of the reaction inside the pellets. So both processes (i) and (ii) influence the rate. Both are transport processes, by which SO_2 and O_2 are transported successively through the gas phase and through the pores of the sorbent. In fact, only the transport of SO_2 is rate-determining, because oxygen, with a high concentration and with a greater diffusion coefficient than SO_2, is

transported relatively rapidly compared to SO_2. The following formulae can be derived for a spherical sol-gel pellet.

Transport of SO_2 through the gas phase

$$\Phi_e = k_g(c_b - c_s)4\pi R^2 \text{ mol s}^{-1} \tag{5}$$

Transport of SO_2 through the pores of reacted sorbent

$$\Phi_i = D(dc/dr)4\pi r^2 \text{ mol s}^{-1} \tag{6}$$

With the assumption that SO_2 does not accumulate inside the pores of the reacted sorbent, eqn. (7) can be derived from eqn. (6)

$$\Phi_i = 4\pi D(c_s - c_i)/(1/r_i - 1/R) \text{ mol s}^{-1} \tag{7}$$

where Φ is the molar flow of SO_2 into one sorbent pellet (mol s^{-1}), Φ_i, the internal flow, Φ_e, the external molar flow, k_g, the transport coefficient of SO_2 through the gas phase (m s^{-1}), D, the effective diffusion coefficient of SO_2 through the layer of reacted sorbent (m^2 s^{-1}), c, the concentration of SO_2 (mol m^{-3}), c_{in}, the concentration in the inlet gas, c_b, the concentration in the bulk gas phase surrounding the pellet, c_s, the concentration on the outside of the pellets, c_i, the concentration at the inner unreacted core of the pellet with radius r_i (because the chemical reaction is fast, we assume $c_i = 0$), R, the radius of the sorbent pellet (m), r_i, the radius of the unreacted core (m), and r the radius between R and r_i.

In the absence of accumulation of SO_2, one obtains:

$$\Phi = \Phi_e = \Phi_i \tag{8}$$

or

$$k_g(c_b - c_s)4\pi R^2 = 4\pi D(c_s - c_i)/(1/r_i - 1/R) \tag{9}$$

For n pellets one obtains:

$$dW/dt = n\Phi M_{SO_3} \tag{10}$$

where dW/dt is the measured weight increase (kg s^{-1}) and M_{SO_3} is the molar mass of SO_3 (0.080 kg mol^{-1}).

The bulk gas concentration c_b depends on the sorption efficiency η, which is the relative amount of SO_2 that is actually absorbed

$$\eta = (dW/dt)/(dW/dt)_{max.poss.} \tag{11}$$

where $(dW/dt)_{max.poss.}$ is the rate of weigh increase when all the sulfur oxide in the gas phase is absorbed. Then the SO_2 concentration in the bulk gas becomes zero, so that

$$c_b = (1 - \eta)c_{in} \tag{12}$$

The relative degree of progress of the reaction can be given by the reaction

parameter α. At the beginning of the reaction $\alpha = 0$ and the weight $W = W_0$, while the radius of the core of unreacted sorbent $r_i = R$.

After completion of the absorption, $\alpha = 1$ and the measured weight $W = W_\infty$, while the radius of the core of unreacted sorbent $r_i = 0$.

So it can be derived that

$$\alpha = (W - W_0)/(W_\infty - W_0) = 1 - (r_i/R)^3 \tag{13}$$

Combining eqns. (9)–(13) gives

$$(1 - \eta)/(d\alpha/dt) = \kappa f(\alpha)/D + \kappa/(Rk_g) \tag{14}$$

with

$$\kappa = (W_\infty - W_0)/(4\pi RnM_{SO_3}c_{in}) \tag{15}$$

and

$$f(\alpha) = (1 - \alpha)^{-1/3} - 1 \tag{16}$$

Because

$$\eta(d\alpha/dt)^{-1} = (W_\infty - W_0)/(dW/dt)_{max.poss} \tag{17}$$

eqn. (14) can be written as

$$1/(d\alpha/dt) = (\kappa/D)f(\alpha) + [\kappa/(Rk_g) + (W^\infty - W_0)/(dW/dt)_{max.poss}] \tag{18}$$

or

$$Y = bX + a \tag{19}$$

Plotting Y against X gives a straight line, from which the slope b and the intercept a can be determined. From these figures, the values of k_g and D can be calculated. From the value of k_g, it is possible to determine the dimensionless Sherwood number

$$Sh = 2Rk_g/D_{bulk} \tag{20}$$

where D_{bulk} is the gas phase diffusion coefficient of SO_2. For SO_2 in air, $D_{bulk} = 1.018 \times 10^{-4} \, m^2/s^{-1}$.

The Sherwood number is a measure for the contact of the sorbent spheres with the surrounding gas atmosphere. For a free hanging sphere in a gas phase, the value of the Sherwood number would be $Sh = 2$. As we will see, the experimental value of the Sherwood number is much lower than 2, depending on the type of crucible applied and the number of pellets packed together.

From the measured value of the effective diffusion coefficient D, the tortuosity τ can be calculated, according to

$$\tau = D_{Kn}\varepsilon/D \tag{21}$$
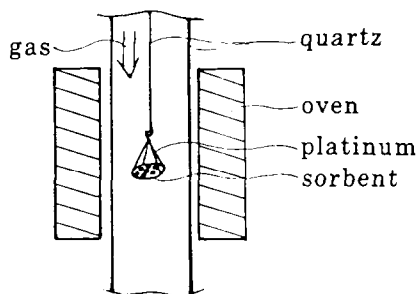
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Fig. 3. Geometry of sample holder III (a flat sheet of platinum gauze), suspended in a quartz tube in the thermobalance [5].

where D_{Kn} is the Knudsen diffusion coefficient in the sorbent pores with radius r_p (m)

$$D_{Kn} = (2/3)r_p(8RT/(\pi M))^{1/2} \tag{22}$$

In these formulae, ε is the porosity of the sorbent (m^3 pores per m^3 sorbent), R is the gas constant (8.3143 J mol^{-1} K^{-1}), T the temperature (K) and M the molar mass of the diffusing compound, SO_2: M being 0.064 kg mol^{-1}.

The value of the tortuosity τ gives information about the structure of the porous sorbent. The theoretical limits for τ are $\sqrt{2} \leq \tau \leq 6$ [6].

EXPERIMENTAL

Apparatus

A home-made thermobalance was used, made from a C.I. Electronics balance [4, 7]. The sample hang-down geometry is shown in Fig. 3. Three kinds of crucibles were tested (see Fig. 4): I, a cylindrical alumina crucible,
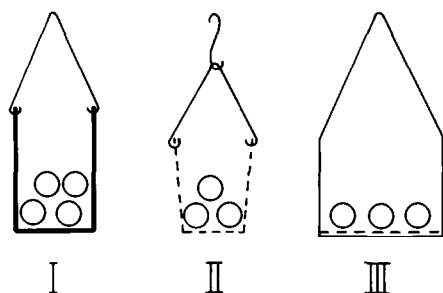

Fig. 4. Cross-sections of the three sample holders used: I, cylindrical alumina crucible: height 13 mm; diameter 8 mm; II, basket made of platinum gauze: height 10 mm, diameter 8 mm; III, flat sheet of platinum gauze: diameter 12 mm.

with an opening only at the top; II, a basket, made of platinum gauze; III, a flat sheet of platinum gauze, with the sample placed on that sheet. The contact of the sample with the gas phase increases from $I \to II \to III$.

Sample

The preparation of the sol–gel pellets is described elsewhere [2]. The radius R of the spherical pellets was measured before each experiment. In addition, the pore radius r_p and the porosity ε were determined by BET analysis.

Experimental conditions

The experiment was made with n sorbent pellets. The sample was heated in air (100 ncc min^{-1}) up to 850°C. When a constant weight was reached, the gas was changed into a gas mixture of air with SO_2 (0.25 or 0.50 vol.%) and the weight was recorded as a function of time. When the maximum absorption was reached, the weight became constant. From the weight–time plot, the values of α and $(d\alpha/dt)$ were determined.

RESULTS AND DISCUSSION

Figure 5 gives a plot of the relative reaction rate $(d\alpha/dt)$ as a function of the reaction degree α for the three different kinds of crucibles: (a), crucible
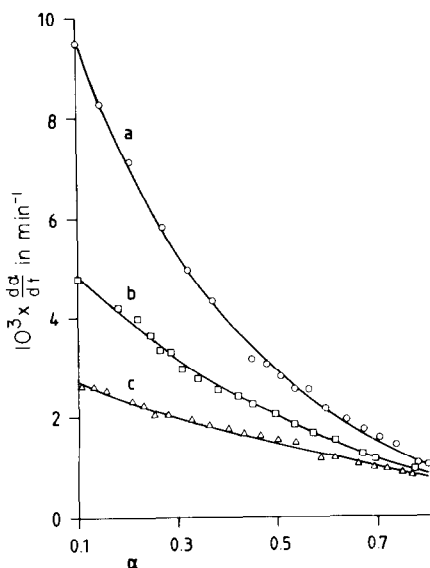

Fig. 5. The relative reaction rate $(d\alpha/dt)$ as a function of the reaction parameter α for the three different sample holders; (a), sample holder III; (b), sample holder II; (c), sample holder I.
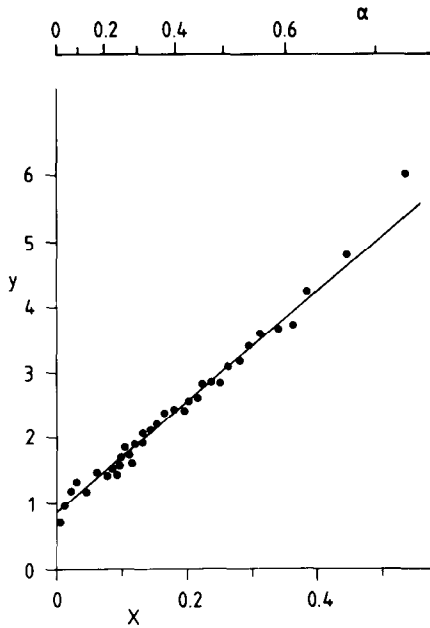
Fig. 6. Graph according to the shrinking-core model for experiment (b) with sample holder II: $Y = 10^{-4}/(d\alpha/dt)\,s$; $X = f(\alpha) = [(1 - \alpha)^{-1/3} - 1]$. The intercept is 8750 s and the slope is 83300 s.

III (sheet); (b) crucible II (basket); and (c), crucible I (alumina crucible). Experiment (b) is analysed in Fig. 6. In this figure, Y is plotted against X, according to eqns. (17) and (18); $Y = a + bX$. From this figure, the values of a and b can be determined: $a = 8750\,s$ and $b = 83300\,s$.

Further data for experiment (b), crucible II are: number of pellets $n = 14$; total weight 229.2 mg; mean diameter of pellets, $\bar{d} = 2.69\,mm$ yielding $R = 1.345 \times 10^{-3}\,m$; mean pore diameter, $r_p = 6.316 \times 10^{-9}\,m$; porosity $\varepsilon = 0.47$. The experimental conditions were $T = 850°C$ (1123 K); gas phase, $p = 1$ bar air + 0.25% SO_2, 100 ncc min^{-1}. Therefore, $C_{in} = 0.02717$ mol SO_2 m^{-3} and $(dW/dt)_{max.poss} = 0.89286$ mg SO_3 min^{-1} = 0.01488 mg s^{-1}. With $W_\infty - W_0 = 24.15$ mg

$$\eta/(d\alpha/dt) = 24.15/0.01488 = 1623\,s \tag{17}$$

$$Y = a + bX \tag{19}$$

$$a = \kappa/Rk_g + \eta/(d\alpha/dt) = 8750\,s \tag{18}$$

$$b = \kappa/D = 83300\,s \tag{18}$$

$$\kappa = (W_\infty - W_0)/(4\pi RnM_{SO_3}c_{in}) = 46.96\ 10^{-3}\,m^2 \tag{15}$$

TABLE 1

Experimental conditions ($T = 850°C$)

Experiment	Crucible	n [a]	R/mm [b]	r_p/nm [c]	ε [d]	$[SO_2]$/vol.%
(a)	III	8	1.660	6.54	0.47	0.50
(b)	II	14	1.345	6.32	0.47	0.25
(c)	I	12	1.785	6.54	0.47	0.50

[a] n, number of pellets. [b] R, diameter of pellets. [c] r_p, pore diameter. [d] ε, porosity.

Therefore, $Rk_g = 6.59 \times 10^{-6} \, m^2 \, s^{-1}$ and $D = 0.564 \times 10^{-6} \, m^2 \, s^{-1}$; and for SO_2/air, $D_{bulk} = 1.018 \times 10^{-4} \, m^2/s$. This gives

$$Sh = 2Rk_g/D_{bulk} = 0.13 \tag{20}$$

$$D_{Kn} = (2/3)r_p(8RT/\pi M_{SO_3})^{1/2} = 2.566 \times 10^{-6} \, m^2 \, s^{-1} \tag{22}$$

So the tortuosity $\tau = D_{Kn}\varepsilon/D = 2.14$ (from eqn. (21)).

The experiments are compared in Tables 1 and 2. Table 1 gives the experimental conditions, while Table 2 lists the results.

From the results in Table 2, it is shown that the tortuosity τ does not change very much, but that the Sherwood number is a strong function of the type of crucible. For a closed alumina crucible (I), the Sherwood number is more than 10 times lower than for the open, flat sheet (III). Also the relative error of the determined Sherwood number is the greatest in experiment (a) because the effective transport in the gas phase is so fast that the overall rate is nearly totally determined by pore diffusion. Nevertheless, the measured value of the Sherwood number in experiment (a) is also much lower than in the case of a free hanging sphere (Sh = 2) because the contact between gas phase and a particular sorbent pellet is hindered by the crucible and by the other sorbent pellets.

TABLE II

Comparison of results

Experiment	Crucible	$10^6 \times D$ in $(m^2 \, s^{-1})$ [a]	$10^6 \times Rk_g$ in $(m^2 \, s^{-1})$ [b]	Sh [c]	τ [d]
(a)	III	0.58 ± 0.02	28 ± 15	0.56 ± 0.30	2.11 ± 0.08
(b)	II	0.56 ± 0.01	6.6 ± 1.7	0.13 ± 0.03	2.14 ± 0.05
(c)	I	0.51 ± 0.02	2.5 ± 1.0	0.05 ± 0.02	2.45 ± 0.08

[a] D, effective diffusion coefficient. [b] k_g, transport coefficient of SO_2. [c] Sh, Sherwood number. [d] τ, tortuosity.

TABLE 3

Rate proportion P for the different experiments

Experiment	Crucible	Rate proportion P		$P_{\alpha=0.1}/P_{\alpha=0.8}$
		$\alpha = 0.1$	$\alpha = 0.8$	
(a)	III	3.28	0.34	9.65
(b)	II	2.39	0.42	5.69
(c)	I	1.82	0.59	3.09

The measured value of the tortuosity (2.11–2.45) is in very good agreement with the theoretical values [6]. This value, being a sample property, is virtually independent of the type of crucible. In Fig. 5, the rate of reaction $(d\alpha/dt)$ is plotted against the progress of reaction α for the experiments. From this figure, the rate proportion P can be determined: $P_i = (d\alpha/dt)_{\alpha=i}/(d\alpha/dt)_{\alpha=0.5}$. These values are summarized in Table 3 which shows that the apparent kinetics is strongly dependent on the applied type of crucible. The effect of using a different crucible is not simply a rate change with a constant value or proportion, but a change in the mechanism, because two reactions in series are involved. Depending on the type of crucible, the relative contribution of each reaction toward the overall reaction rate will change.

CONCLUSIONS

Thermogravimetry is a good technique for studying the kinetics of gas–sorbent reactions. TG experiments give information about the mechanism and the kinetic rate constants. The overall rate not only depends on the sorption reaction itself, but also on the transport of reactants through the gas phase. This gas transport is strongly influenced by the type of crucible used.

It is possible to derive suitable equations to separate the rate-determining processes. The reaction in the solid sorbent can be described with a shrinking-core model. The rate inside the sorbent for sol-gel pellets depends only on pore diffusion in the reacted shell. When the kinetics is deconvoluted in the correct way, the calculated kinetic constants can be used for rate calculations with totally different experimental conditions, for instance in fluidized bed combustion experiments.

This investigation proves that, in TG experiments, one may expect a strong influence of the type of crucible on the rate measurements of solid–gas reactions. This effect is so important that not only the absolute rate, but also the apparent kinetic mechanism may change with different types of sample holders.

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