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A THERMOGRAVIMETRIC STUDY OF THE SOLID-STATE REACTION BETWEEN ALUMINA AND STRONTIUM CARBONATE

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The kinetics of the solid-state reaction between alumina and strontium carbonate were studied by thermogravimetry. The effects of the structure (η or α) and/or doping (with Li^+ or Cd^{2+}) of the alumina on the kinetics of the reaction were examined. The results obtained were correlated with the phase composition and structural changes, followed by a number of physicochemical analyses (DTA, XRA and IRA) throughout the course of the reaction.

In earlier work [1], thermogravimetric techniques have shown unlimited reliability in efforts to tackle the everlasting problem inherent in studies on the kinetics of solid-state reactions, i.e. the problem of determining the fraction of reaction completed [2]. This could be fulfilled by measuring precisely the change in weight due to gas evolution (CO_2) occurring as a result of a simultaneous reaction ($Al_2O_3 + BaCO_3$).

The present study has been designed to extend the earlier theme and method of investigation [1] to an analogous reaction system, so as to explore the effect of change in the nature of the mobile alkaline earth oxide [3] on the kinetics of formation of the corresponding technically important aluminate [4]. To accomplish this objective, phase composition and structural changes were observed closely throughout the course of the reaction. Moreover, the kinetics of the reaction were studied with emphasis on: (a) the rate equation which best fits the experimental data, i.e. the fraction of reaction completed (x) vs. time (t) data; (b) whether the reaction is phase boundary or transport-controlled; (c) the distribution of the product phase with respect to the reactant phase; (d) the effect that changes in the structural characteristics of one of the reactants (alumina) may have on the overall reaction; (e) the reaction rates and some of the factors influencing them.

Experimental

The solid-state reactions:

$$\alpha\text{- or } \eta\text{-}Al_2O_3 + SrCO_3 \rightarrow \text{Sr-aluminate} + CO_2$$

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$$y\%\ \text{M-doped}\ \alpha\text{-}Al_2O_3 + SrCO_3 \rightarrow \text{Sr-aluminate} + CO_2$$

$$y\%\ \text{M-doped}\ \eta\text{-}Al_2O_3 + SrCO_3 \rightarrow \text{Sr-aluminate} + CO_2$$

(where $y\%$ ranges between 0.5 and 10.0 atom M% atom Al, and M is either Li^+ or Cd^{2+} ions) were studied isothermally between 800 and 920°, and weight changes were monitored as a function of time with a sensitivity of 0.1 mg by means of thermogravimetry, in a dynamic atmosphere of air (20 ml min^{-1}), using the apparatus and technique described earlier [1]. From the recorded weight loss curves, the fraction of reaction completed (x) was calculated as the ratio of the weight loss at time t to the theoretical total weight loss. The reaction time was corrected according to the method described by Yamashita et al. [5]. The data (x and t) were analysed kinetically using a computer-oriented scheme [6] based on rate law equations corresponding to four basically different mechanisms. These equations have been reviewed comprehensively by Geiss [7] and Sharp et al. [8].

To follow up phase composition and structural changes pertaining to the reaction progress, a parallel set of these reactions was run independently in a muffle furnace. Heating was interrupted after 2 h at different reaction temperatures (800–1200°). The reaction mixtures thus obtained were subjected to thorough differential thermal (DTA), X-ray (XRA) and ir-absorption (IRA) analyses, adopting the apparatus and techniques given elsewhere [9].

The $SrCO_3$ used was a high-purity (99.9%) Merck product. The preparation of the pure or doped aluminas involved was described earlier [1]. The homogeneity of the solid solutions of doped aluminas thus obtained was confirmed, except for the 10% Cd-doped α-Al_2O_3. For this sample the co-existence of small proportions of CdO and $CdAl_2O_4$ was demonstrated.

The procedures followed in preparing and calcining the homogeneous equimolar powder mixtures of reactants were described in detail previously [10].

Results and discussion

Earlier thermal analysis results [11] have shown that $SrCO_3$ begins to liberate CO_2 at 950° in air, whereas all the reactions concerned in the present study start to release CO_2 at a temperature well below 950°. At around 850°, the completed fraction of most of the reactions concerned was between 70 and 80% in 2 h, while under identical conditions no CO_2 evolution was detected from $SrCO_3$ [11]. This fact ensures that the change in weight due to gas evolution actually represents the rate of the reaction. It is worth mentioning that the XRA results for the reaction mixtures calcined at different temperatures (800–1200°) for 2 h showed no diffraction pattern for SrO, thus further indicating that the gas evolution was associated with the reaction between $SrCO_3$ and alumina (pure or doped) to form a product phase, and not with the decomposition of $SrCO_3$ to SrO.

Effect of alumina structure on the kinetics of the reaction

The computer-oriented kinetic analysis of the isothermal solid-state reaction between $SrCO_3$ and α- or η-Al_2O_3 was performed for each set of data (x and t) and the results are given in Tables 1 and 2, respectively.

The results in Table 1 ($SrCO_3 + \alpha$-Al_2O_3) reveal the effect of the reaction temperature on the type of the rate-controlling process. At 807–859°, the product growth may be controlled by nuclear growth, whereas at higher temperatures (880–920°) the controlling process tends to be diffusion of the reactants through a product layer. A similar temperature-dependence of the rate-controlling process in the reaction with η-Al_2O_3 is observed from the results in Table 2.

Table 1 Kinetic results obtained by computer-oriented analysis of the isothermal change in the fraction completed (x), at time t, of the solid-state reaction between $SrCO_3$ and α-Al_2O_3

	Reaction temperature, °C					
	807[a]	830[a]	859[a]	880[b]	907[b]	920[b]
Rate constant, min^{-1}	$31 \cdot 10^{-6}$	$54 \cdot 10^{-5}$	$15 \cdot 10^{-4}$	$32 \cdot 10^{-4}$	$51 \cdot 10^{-4}$	$73 \cdot 10^{-4}$
Activation energy, kJ mol^{-1}	743	743	743	321.7	321.7	321.7
m[c]	0.20	0.24	0.25	0.45	0.49	0.58

[a] Product growth controlled by nuclear growth. Most appropriate kinetic equation: nuclear growth equation (Eq. (1)). [b] Product growth controlled by diffusion of reactants through a continuous product layer. Most appropriate kinetic equation: Ginstling–Brounstein equation (Eq. (2)). m[c] = The exponent of the nuclear growth rate law equation (Eq. (1)).

The results in Tables 1 and 2 indicate that the nuclear growth rate law equation

$$\ln (1 - x) = (kt)^m \tag{1}$$

with m in the range 0.20–0.25, and the Ginstling–Brounstein equation

$$kt = 1 - \frac{2}{3}x - (1 - x)^{\frac{2}{3}} \tag{2}$$

are the most appropriate mathematical representations of the kinetics of the reaction at the temperatures indicated.

The kinetic parameters computed with the aid of Eqs (1) and (2) (given in Tables 1 and 2) show that the presence of η-Al_2O_3 promotes the faster formation of strontium aluminate. A similar conclusion was reached earlier for the formation of barium aluminate [1]. This was ascribed to the higher surface area and the spinel-like structure of η-Al_2O_3, which facilitate faster boundary reactions and easier build-up of the aluminate product phase, respectively. Overall, however, the promoting effect of η-Al_2O_3 is more obvious when it reacts with $SrCO_3$ than with $BaCO_3$ [1]. The positive contribution of $SrCO_3$ may be accomplished by means of its relatively high surface

Table 2 Kinetic results obtained by computer-oriented analysis of the isothermal change in the fraction completed (x), at time t, of the solid-state reaction between $SrCO_3$ and η-Al_2O_3

	Reaction temperature, °C					
	812[a]	833[a]	855[a]	880[a]	905[b]	920[b]
Rate constant, min^{-1}	$15 \cdot 10^{-6}$	$97 \cdot 10^{-5}$	$50 \cdot 10^{-4}$	$64 \cdot 10^{-4}$	$75 \cdot 10^{-4}$	$95 \cdot 10^{-4}$
Activation energy, kJ mol^{-1}	530	530	530	530	289.4	289.4
m[c]	0.22	0.23	0.25	0.31	0.36	0.50

[a] See footnote [a], Table 1, [b] see footnote [b], Table 1, [c] see footnote [c], Table 1.

area [12] (initiating faster boundary reactions) and/or of the smaller size (0.113 nm) of the diffusing Sr^{2+} ions as compared to that (0.143 nm) of the Ba^{2+} ions [13] (facilitating easier diffusion through a product layer). Moreover, the lower heat of dissociation of Sr—O (468.9 J/kg mol) than that (573.6 J/kg mol) of Ba—O [13] may decrease the energy barrier of the diffusion process [14]. The intensively hydrated nature (DTA, XRA) of the strontium aluminate product layer (from di- to tetrahydrated $SrO \cdot Al_2O_3$ (XRA, IRA)) might also help such an easy cationic diffusion [15].

According to the possible mechanisms of the solid-state formation of spinels in binary oxide systems, reviewed by Schmalzried [14], this cationic diffusion (structure-sensitive) and an "oxygen-vapour" transport are the two routes via which the unidirectional diffusion of SrO [3] throughout the product layer is believed to take place. The oxygen-vapour transport is controlled by the energy required to release the oxygen into the vapour phase [2], and subsequently by the conjugate mobility through the product layer maintaining local electrical neutrality [14]. If, according to results compiled elsewhere [13], SrO is an n-type semiconductor whereas BaO is of p-type, the higher electrical conductivity measured preliminarily for pelletized $SrAl_2O_4$ (the calcination product at 1200° for 72 h) than that reported earlier for $BaAl_2O_4$ [1] is conceivable. Thus, the oxygen-vapour transport is expected to be faster across the strontium aluminate product layer, thus accounting for the higher activity of $SrCO_3$.

Effect of doping

Computer-oriented kinetic analysis was also performed on the data (x and t) of the isothermal reaction between $SrCO_3$ and Li- or Cd-doped Al_2O_3 (α or η) The results obtained maintained the validity of both the nuclear growth and Ginstling—Brounstein rate law equations. The results showed that doping affected the kinetics of the diffusion-controlled part of the reactions only. Table 3 gives the effect of doping, with either Li^+ or Cd^{2+}, on the activation energy of the reaction, calculated using the Ginstling—Brounstein equation.

It is to be expected [16] that Li^+ ions are incorporated substitutionally, whereas the larger Cd^{2+} ions may incorporate interstitially [16]. It was found [17] that

Table 3 The effect of doping on the calculated activation energy value[a]

% Doping	Activation energy, kJ mol^{-1}
0.5% Li-doped α-Al_2O_3 + $SrCO_3$	234.4
10.0%	157.1
0.5% Li-doped η-Al_2O_3 + $SrCO_3$	275.9
5.0%	252.8
10.0%	217.1
0.5% Cd-doped α-Al_2O_3 + $SrCO_3$	321
10.0%	348
0.5% Cd-doped η-Al_2O_3 + $SrCO_3$	251.1
5.0%	234.4
10.0%	210.4

[a] Calculated for the diffusion-controlled part of the reactions.

interstitially incorporated ions (viz. Cd^{2+}) could create electron-donor centres. The effect of the substitutionally incorporated ions, however, depends mostly on the valency of the doping ion relative to that of the host. Our preliminary electrical conductivity measurements on pellets of strontium aluminate-based Li^+ or Cd^{2+} (5%) solid solutions (obtained after prolonged calcination (72 h) at 1200°) reflected a considerable decrease in the resistance of the aluminates. Accordingly, Li^+ ions are also anticipated to create electron-donor centres.

The observed increase of the diffusion-controlled reaction rate (Table 3) as a result of doping with Li^+ ions may be understood in terms of the expected pertinent enhancement of the rate of the oxygen-vapour transport across the product layer. It is worth mentioning that the contribution of the binding energy of Sr—O cannot be considered since the dopant is incorporated into the stationary oxide (Al_2O_3) only.

The trend of variation of the activation energy of the reaction between $SrCO_3$ and Cd-doped η-Al_2O_3 as a result of the increase of the % doping (Table 3) is compatible with the expected increase of the electronic conduction of the product layer. Surprisingly, however, this pattern is not followed in the case of Cd-doped α-Al_2O_3.

The results of physicochemical analyses showed that $CdAl_2O_4$ spinel was formed only in the 10% Cd-doped α-Al_2O_3 calcined at 600° for 5 h. In this spinel, Cd^{2+} ions should replace the octahedrally situated Al^{3+} ions. The formed layer of $CdAl_2O_4$ would occupy grain boundaries of the Al_2O_3 and consequently an additional isolating layer might be built up at the $SrCO_3$/α-Al_2O_3 phase boundary. The diffusion process throughout such a multi-phase product layer may therefore be expected to take place rather slowly.

The foregoing results may suggest analogously [1] that oxygen-vapour transport depends primarily on the mobility of O^{2-} valence electrons throughout the reaction product layer, rather than on the magnitude of the binding energy (metal-oxygen) of the diffusing oxide.

References

1 M. I. Zaki, G. A. M. Hussien and R. B. Fahim, Thermochim. Acta, 74 (1984) 167.
2 S. F. Hulbert and J. J. Klawitter, J. Am. Ceram. Soc., 50 (1967) 484.
3 T. Iseki, K. Yamaguchi and H. Tagai, J. Am. Ceram. Soc., 69 (1970) 425.
4 O. Henning, Wiss. Z. Hochsch. Archit. Bauwes., Weimar, 3 (1968) 315.
5 M. Yamashita, T. Maruyama and W. Komatsu, Z. Phys. Chem. N. F., 105 (1977) 187.
6 The program listing and subroutines are available on request.
7 E. A. Geiss, J. Am. Ceram. Soc., 46 (1963) 374.
8 J. H. Sharp, G. W. Brindley and B. N. Narahari Achar, J. Am. Ceram. Soc., 49 (1966) 379.
9 R. B. Fahim, M. I. Zaki and R. M. Gabr, Surf. Tech., 11 (1980) 215.
10 R. B. Fahim, M. I. Zaki, A. M. El-Roudi and A. M. A. Hassaan, J. Res. Inst. Catal., Hokkaido Univ., 29 (1981) 25.
11 R. B. Fahim, M. I. Zaki and G. A. M. Hussien, Powder Technol., 33 (1982) 161.
12 A. Amin and S. A. Selim, J. Chem. Tech. Biotechnol., 30 (1980) 183.
13 G. V. Samsonov, The Oxide Handbock, IFI/Plenum, New York, 1973.
14 H. Schmalzried, Solid State Reactions, Verlag Chemie, Weinheim, 2nd edn., 1981.
15 P. Kofstad, Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides, Wiley—Interscience, New York, 1972.
16 Z. M. Jarzebski, Oxide Semiconductors, Pergamon Press, New York, 1973.
17 R. B. Fahim, R. M. Gabr and M. I. Zaki, Indian J. Chem., 19A (1980) 829.

Zusammenfassung — Die Kinetik der Festkörperreaktion zwischen Aluminiumoxid und Strontiumcarbonat wurde thermogravimetrisch untersucht. Die Effekte der Struktur (η und α) und/oder des Dopens des Aluminiumoxids (mit Li^+ oder Cd^{2+}) auf die Kinetik der Reaktion wurde untersucht. Die erhaltenen Ergebnisse wurden mit der Phasenzusammensetzung und mit durch physikalisch-chemische Analysenverfahren (DTA, XRA und IRA) während des Reaktionsverlaufs verfolgten strukturellen Veränderungen in Beziehung gebracht.

Резюме — С помощью термогравиметрии изучена кинетика твердотельной реакции между окисью алюминия и карбонатом стронция. Изучено влияние структурных форм (η или α) окиси алюминия и легированной ионами Li^+ или Cd^{2+} окиси алюминия на кинетику реакции. Полученные результаты коррелировались с фазовым составом и структурными изменениями, установленными методом ДТА, рентгенофазовым анализом и ИК спектроскопией в процессе протекания реакции.

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