

A THERMOGRAVIMETRIC STUDY OF THE KINETICS OF THE SOLID STATE REACTION BETWEEN ALUMINA AND BARIUM CARBONATE

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ABSTRACT

The kinetics of the reaction between alumina and barium carbonate were studied using thermogravimetric analysis to monitor the fraction of reaction completed vs. time. The kinetics of the reaction are described by either the nuclei-growth equation or the Ginstling–Brounstein equation, depending on the reaction temperature range. Effects of structure (η or α) and/or doping (with Li^+ or Cd^{2+}) of alumina on the kinetics of the reaction are also examined.

INTRODUCTION

The solid state reaction formation of barium aluminate has drawn the attention of a number of research groups [1–3] for its exceeding technical importance [4]. Earlier results [5] of physicochemical analyses of the reaction mixture indicated the formation of $\text{BaO} \cdot \text{Al}_2\text{O}_3$ at the expense of $3 \text{BaO} \cdot \text{Al}_2\text{O}_3$ on calcination at $\geq 1000^\circ\text{C}$. In addition, the tendency of formation of rather stable hydrate-type intermediates, at room temperature, was observed.

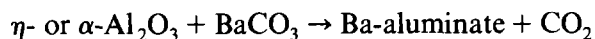
In order to characterize the optimal conditions for the preparation of barium aluminate, a better understanding of the mechanism of the solid state reaction formation is indispensable. To accomplish this objective, the kinetics of the reaction were studied with emphasis on: (a) the rate equation which 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) distribution of product phase with respect to the reactant phase; (d) the effect that changes in structural characteristics of one of the reactants (alumina) may have on the overall reaction; and (e) reaction rates and some of the factors influencing them.

The specific reaction concerned in the present investigation was chosen after careful consideration of the everlasting problem inherent in making a study of the kinetics of solid state reactions, i.e. the problem of determining the fraction of reaction completed [6]. This problem was overcome by

choosing a reaction in which a gaseous product is evolved. Thus, by measuring the change in weight due to gas evolution, a continuous record of the fraction of reaction completed, as a function of time, could be obtained adopting thermogravimetric techniques.

EXPERIMENTAL

The solid state reactions



(where $y\%$ ranges between 0.5 and 10 atom M% atom Al^{3+} , and M is either Li^+ or Cd^{2+} ion) were studied isothermally between 760 and 937°C, and weight changes—with a sensitivity of 0.1 mg—as a function of time were monitored thermogravimetrically, in a dynamic atmosphere of air (20 ml min^{-1}), using a Shimadzu TG-30H automatic recording thermobalance (Japan). 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.

In all experimental kinetic runs, some time was required to reach thermal equilibrium. The reaction time, therefore, was corrected according to the method described by Yamashita et al. [7].

A computer-oriented kinetic analysis [8] of the data, i.e. (x) and (t), was devised using rate law equations corresponding to four basically different mechanisms. These equations have been reviewed by Geiss [9] and Sharp et al. [10].

RESULTS AND DISCUSSION

When the rate of formation of product phase is indirectly measured, as by the change in weight due to gas evolution, the question arises as to whether the measurement actually represents the rate of the reaction. Earlier thermogravimetric and differential thermal analyses [11] showed that BaCO_3 begins to liberate CO_2 at 1050°C in air, whereas all reactions concerned in the present investigation start to liberate CO_2 at a temperature well below 1050°C. At around 900°C, the fraction completed of most of the reactions concerned was between 70 and 80% in 2 h. No CO_2 evolution was detected from BaCO_3 at $\leq 1000^\circ\text{C}$. It is worth noting that earlier X-ray diffraction results [5], for reaction mixtures calcined at different temperatures (800–1200°C), showed no diffraction pattern for BaO, thus further indicat-

ing that the gas evolution was associated with the reaction between BaCO_3 and alumina (pure or doped) to form a product phase, and not with the decomposition of BaCO_3 to BaO .

Effect of alumina structure on the kinetics of the reaction

The computer-oriented kinetic analysis of the isothermal solid state reaction between BaCO_3 and α - or η - Al_2O_3 was performed for each set of data

TABLE 1

Kinetic results obtained by a computer-oriented analysis of the isothermal change of the fraction completed (x), at time (t), of the solid state reaction between BaCO_3 and α - Al_2O_3

	Reaction temp. ($^{\circ}\text{C}$)						
	808 ^a	830 ^a	857 ^a	875 ^b	904 ^b	923 ^b	937 ^b
Rate constant (min^{-1})	30×10^{-7}	74×10^{-6}	10×10^{-5}	11×10^{-5}	28×10^{-5}	44×10^{-5}	73×10^{-5}
Activation energy (kcal mol^{-1})	201.4	201.4	201.4	214.6	214.6	214.6	214.6
m^c	0.25	0.33	0.49	0.49	0.60	0.65	0.65

^a Product growth controlled by nuclei growth. Most appropriate kinetic equation: nuclei-growth equation [eqn. (1)].

^b Product growth controlled by diffusion of reactants through a continuous product layer. Most appropriate kinetic equation: Ginstling-Brounstein equation [eqn. (2)].

^c m = The exponent of the nuclei-growth rate law equation [eqn. (1)].

TABLE 2

Kinetic results obtained by a computer-oriented analysis of the isothermal change of the fraction completed (x), at time (t), of the solid state reaction between BaCO_3 and η - Al_2O_3

	Reaction temp. ($^{\circ}\text{C}$)					
	760 ^a	780 ^a	801 ^a	830 ^b	845 ^b	860 ^b
Rate constant (min^{-1})	63×10^{-6}	34×10^{-5}	52×10^{-5}	69×10^{-5}	99×10^{-5}	13×10^{-4}
Activation energy (kcal mol^{-1})	62.8	62.8	62.8	234.6	234.6	234.6
m^c	0.38	0.43	0.44	0.52	0.52	0.60

^a See footnote ^a, Table 1.

^b See footnote ^b, Table 1.

^c See footnote ^c, Table 1.

(x and t) and the results are summarized in Tables 1 and 2, respectively.

The results summarized in Table 1 reveal the effect of reaction temperature on the type of rate-controlling process. At 808–857°C, product growth may be controlled by nuclei growth, whereas at higher temperatures (875–937°C) the controlling process tends to be diffusion of reactants through a product layer. A similar temperature-dependence of the rate-controlling process of the reaction between BaCO_3 and $\eta\text{-Al}_2\text{O}_3$ can be realized in terms of the results summarized in Table 2. It is worth mentioning that the reaction between BaCO_3 and $\eta\text{-Al}_2\text{O}_3$ had to be studied at a temperature range well below that over which the reaction between BaCO_3 and $\alpha\text{-Al}_2\text{O}_3$ was studied, so as to avoid being beyond the range of thermal stability of $\eta\text{-Al}_2\text{O}_3$ [12].

The results summarized in either Table 1 or Table 2 indicate that the nuclei-growth rate law equation

$$\ln(1 - x) = (kt)^m \quad (1)$$

(with m in the range 1/2–2/3), and the Ginstling–Brounstein equation

$$kt = 1 - 2/3x - (1 - x)^{2/3} \quad (2)$$

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

The kinetic parameters computed with the aid of eqns. (1) and (2) (cited in Tables 1 and 2) show that the presence of $\eta\text{-Al}_2\text{O}_3$ helps a comparatively faster nuclei growth and induces a slightly slower diffusion of reactants through a product layer.

Equation (1) is based on the transport-controlled growth of a product phase of any shape from a constant number of nuclei in a matrix of different composition [13]. Since $\eta\text{-Al}_2\text{O}_3$ was found to assume a much higher surface area than the sintered $\alpha\text{-Al}_2\text{O}_3$ ($S_{\text{BET}} = 148$ and $23 \text{ m}^2 \text{ g}^{-1}$, respectively), the nuclei growth-controlled reaction with $\eta\text{-Al}_2\text{O}_3$ may be enhanced by the wide phase boundaries then available.

It has been reported [13], in terms of results of platinum-marker experiments, that the diffusing elements in the diffusion-controlled reaction formation of barium aluminate are those of BaO. According to the possible mechanisms of solid state reaction formation of spinels in binary oxide systems, reviewed by Schmalzried [14], the unidirectional diffusion of BaO throughout a product layer is believed to take place via two routes: a cationic diffusion and an “oxygen-vapour” transport. In oxide spinels, the vapour-transport of oxygen is rather slow compared to the cationic diffusion [14]. Branson [15], studying the reaction between ZnO and Al_2O_3 , stated that the rate of the reaction changed as the partial pressure of oxygen changed in the furnace, suggesting that the “oxygen-vapour” transport is the determining step of the diffusion-controlled reaction.

Cationic diffusion is supposed to take place via interstitial voids [6] of the

lattice of a product layer, i.e. it is a structure-sensitive process. Oxygen-vapour transport, on the other hand, is controlled by the energy required to release the oxygen into the vapour phase [6], and subsequently by the conjugate-electronic mobility through the product layer maintaining local electrical neutrality.

It is plausible to suggest, beforehand, that the effect of alumina structure on the kinetics of the reaction (Tables 1 and 2) may show how far Ba^{2+} diffusion could be explained in terms of structural aspects only.

Physicochemical analyses [5] indicated that the high-temperature major phase comprising product layer of the reaction formation of barium aluminate, whatsoever the structure assumed by alumina was (either η - or α - Al_2O_3), is the monobarium aluminate ($\text{BaO} \cdot \text{Al}_2\text{O}_3$). Since η - Al_2O_3 crystallizes in a spinel-like structure (XRA [5]) and can form mixed crystals with other spinels [12], the build-up of monobarium aluminate spinel layer may take place in a most continuous form when bedded on η - Al_2O_3 rather than on the hexagonal α - Al_2O_3 . Accordingly, the observed η - Al_2O_3 -induced retarded diffusion is conceivable. The variation of the corresponding calculated activation energies given in Tables 1 and 2 is consistent with the conclusive remarks described above, though they do not agree with those reported for diffusion-controlled reaction formation of other alkaline earth aluminates [16]. This disagreement could be ascribed to the different nature of the diffusing ions.

Effect of doping

Computer-oriented kinetic analysis was also performed on the data (x and t) of the isothermal reactions between BaCO_3 and Li- or Cd-doped Al_2O_3 (η or α). The results obtained maintained the validity of both the nuclei-growth and Ginstling-Brounstein rate law equations. The results also 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:

Aluminium oxide is of extremely low electrical conductivity which confirms that the defect concentration is rare and effect of impurities, or doping with foreign ions, would critically affect its conduction [17]. Li^+ ions are expected to incorporate substitutionally, whereas the larger Cd^{2+} ions may incorporate interstitially [18]. It was found [19] that interstitially incorporated ions (viz. Cd^{2+}) would create electron-donor centres. The effect of substitutional incorporation of 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 barium aluminate-based Li^+ or Cd^{2+} solid solutions (5% M), obtained after a prolonged calcination (72 h) at 1200°C , reflected a considerable decrease in the resistance of the aluminate.

TABLE 3

The effect of % doping on the calculated activation energy value ^a

% Doping	Activation energy (kcal mol ⁻¹)
0.5% Li-doped α -Al ₂ O ₃ + BaCO ₃	83.2
10.0%	38.3
0.5% Li-doped η -Al ₂ O ₃ + BaCO ₃	76.6
5.0%	46.0
10.0%	27.6
0.5% Cd-doped α -Al ₂ O ₃ + BaCO ₃	79.3
10.0%	247.8
0.5% Cd-doped η -Al ₂ O ₃ + BaCO ₃	67.2
5.0%	54.6
10.0%	31.9

^a Calculated for the diffusion-controlled part of the reactions.

Accordingly, Li⁺ ions are also expected 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 a pertinent enhancement of the rate of the oxygen-vapour transport which is presumably due to the assumed increase of the electronic conduction of the product layer. It is worth mentioning that the contribution of the binding energy of Ba-O is not considered, since the dopant, being incorporated into the stationary oxide (Al₂O₃), is not likely to affect it.

Although it is known [17] that the substitutional incorporation of foreign ions does not depend on the structure of the host lattice, the effect of Li⁺ incorporation was clearer in case of η -Al₂O₃. This may be related to the tendency of η -Al₂O₃ (being of spinel-type structure) to accommodate Li⁺ ions in the tetrahedral holes [12]. The observed splitting of the characteristic IR absorption bands of 3 BaO · Al₂O₃ and BaO · Al₂O₃ [5], as a result of η -Al₂O₃ doping with Li⁺ ions, may provide experimental evidence for the consequent tetragonal deformation.

The trend of variations of the activation energy of the reaction between BaCO₃ and Cd-doped η -Al₂O₃ as a result of the increase of % doping (Table 3) is compatible with the expected increase of the electronic conduction of the product layer. Surprisingly, this pattern is not followed in the case of Cd-doped α -Al₂O₃.

Results of physicochemical analyses [5] showed that CdAl₂O₄ spinel was formed in the 10% Cd-doped α -Al₂O₃ which was calcined at 600°C for 5 h. In this spinel, Cd²⁺ ions should replace the octahedrally situated Al³⁺ ions. The formed layer of CdAl₂O₄ would occupy grain boundaries of the Al₂O₃ and consequently an additional isolating layer might be built up at the phase

boundary $\text{BaCO}_3/\alpha\text{-Al}_2\text{O}_3$. Therefore, the diffusion process throughout such a multi-phase product layer may be expected to take place rather slowly.

In conclusion, it is plausible to suggest that oxygen-vapour transport may depend primarily on the mobility of O^{2-} valence electrons throughout the reaction product layer, rather than the magnitude of the binding energy (metal-oxygen) of the diffusing oxide. The latter alternative failed to explain the effect of doping the diffusing oxide (ZnO) on the rate of the reaction formation of ZnAl_2O_4 in terms of the quasi-chemical theory of solids [6].

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