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STUDY OF REACTION OF FINELY-DIVIDED SILICA WITH BARIUM CARBONATE BY TG AND DTA

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The reaction between equimolar silica and barium carbonate powders in oxygen, air or carbon dioxide was studied by means of TG and DTA. The particle size of the silica showed appreciable effects on the reactivity of the silica, on the activation energy of the reaction, and on the formation of an intermediate silicate, Ba_2SiO_4. The formation of Ba_2SiO_4 is depressed by a decrease in the silica particle size or by an increase in the partial pressure of carbon dioxide in the ambient atmosphere.

It is well known that the reactivity of powder materials depends largely on the particle size as well as the history. Quantitative studies on the effects of particle size on the reactivity, however, have been carried out only rarely. In the present paper, the effects of the particle size of silica on its reaction with barium carbonate are investigated by using fine silica powders whose particle-size distributions are known quantitatively. Such a study may contribute to the preparation of finely-divided double oxides by solid-state reactions.

Experimental

Materials

The silica powders used were prepared by the oxygenolysis of $SiCl_4$ with oxygen at 1200°, and consisted of nearly-spherical silica particles [1]. The particle-size distribution of the silica powders as measured from electronmicrographs are shown in Fig. 1. These silica samples may be divided into two groups depending on the particle size: group S in which the particles smaller than 600 Å comprise more than 85 wt. %, and group L in which the particles smaller than 600 Å comprise less than 50 wt. %. These silica samples contain 7 wt. % water about 94% of which is released on heating up to 500°. The barium carbonate used was of reagent grade and had a BET surface area of 1.6 m^2/g. The carbonate showed no appreciable weight change up to 1000° on heating in oxygen. Equimolar mixtures of silica and barium carbonate was prepared by mixing these two powders by ultrasonic agitation in 99.5% ethanol for 10 min.

TG and DTA measurements

TG was performed with an RG electrobalance (Cahn Co.), up to 1000°, in a flow of oxygen or carbon dioxide, at a heating rate of 5.3°/min. The oxygen was pretreated by passing it through a solid KOH column. In the measurements involving an oxygen flow, the carbon dioxide evolved was determined by absorbing it in 0.1 N $Ba(OH)_2$ solution. The results agreed well with TG. A platinum crucible with the shape and size shown in Fig. 2 was used as the sample vessel and 200 to 250 mg of the reactant mixture was lightly packed in it.

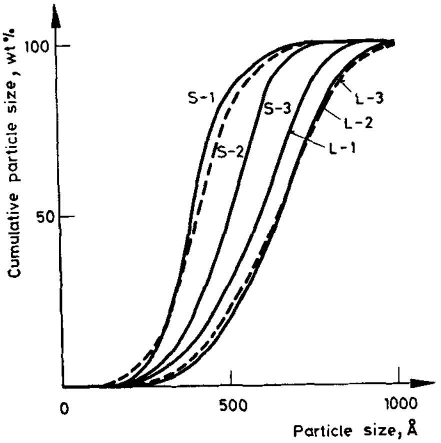

Fig. 1. Particle size distributions of silica powders.

DTA was carried out with a DTA apparatus (Rigaku Denki Co.), up to 1000° in oxygen, air or carbon dioxide, at a heating rate of 5°/min. A platinum vessel with the shape and size shown in Fig. 2 was used and 250 to 300 mg of the reactant mixture was taken in it.

The reaction products were analyzed by X-ray diffraction (CuK_α).

Results and discussion

Reaction in oxygen

TG curves in oxygen are shown in Fig. 2. There are large differences between groups *S*. In group *S*, the reaction starts at about 500° and proceeds in one step to completion at about 810°. On the other hand, the reaction proceeds in two steps in group *L*. In group *L*, although the reaction starts at about 500° as in group *S*, the conversion of barium carbonate is only 30 to 40% at 810° and 50 to 60% at 1000°. Curve *M* shows the reaction of silica gel (chromatographic grade, Merck Co.) finer than 200 mesh, with a BET surface area of 94 m^2/g. In *M*, the reaction begins at about 650° and the conversion of barium carbonate at 1000° is only 40%. Further, *M* does not show the high reactivities observed on groups *S* and below 810°. The surface areas of *S*-2 and *L*-1 were 353 and 254 m^2/g, respectively.

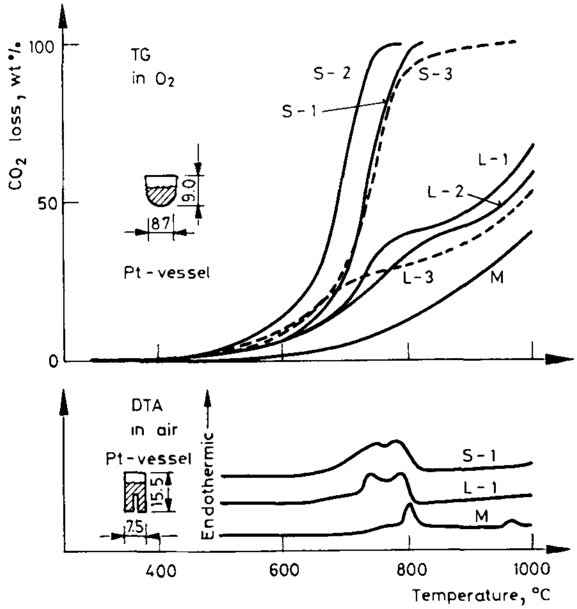

Fig. 2. TG and DTA curves of equimolar SiO_2 – $BaCO_3$ mixtures in O_2 and in air (values for Pt vessel size, mm). TG (in O_2); heating rate, 5.3°C/min. DTA (in air); heating rate, 5.0°C/min.

The particle size of the silica in *M* is therefore considered to be about three times larger than that in *L*-1. Thus, the results in Fig. 2 show that the particle size of the silica affects the reactivity markedly.

DTA

DTA curves of silica-barium carbonate mixtures in air are shown in Fig. 2. Groups *S* and *L* each show two endothermic peaks up to 810°. The second peak in group *L* is shifted to a slightly higher temperature than in group *S*, and overlaps the transition peak of barium carbonate (805°). In *M*, the endothermic peak due to the reaction is small and the two transition peaks of barium carbonate, 805° and 970°, appear clearly.

Up to 810°, two peaks are observed, in the DTA curves, whereas the weight decreases proceed in one step. This poor correspondence between TG and DTA may be due to the difference of the effective atmospheres, caused by the difference in the geometries of sample holder and apparatus in the two measurements, as discussed by many investigators [2–5]. In the present DTA measurements, the sample holder is deep and further triply shielded with ceramics to ensure homogeneous heating. In comparison with TG measurements, therefore, the dispersion of carbon dioxide produced by the reaction may be more difficult, resulting in a higher carbon-dioxide content of the ambient atmosphere in DTA measurements. This may perhaps be responsible for the discrepancy between the two measurements.

Reaction in carbon dioxide

TG and DTA curves in carbon dioxide are shown in Fig. 3. The weight decrease up to 810°, which occurred in one step in oxygen, is seen to be a two-step process in carbon dioxide. The separation of the two peaks in the DTA curves also becomes clearer and the correspondence between TG and DTA is better in carbon dioxide.

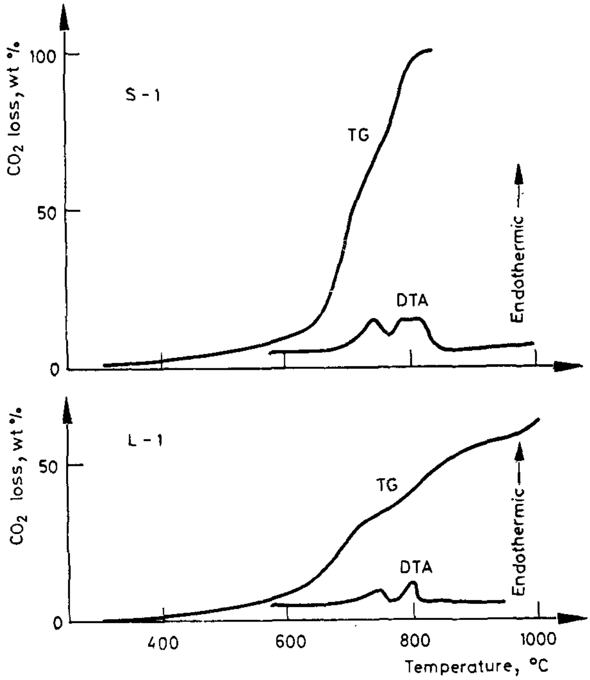

Fig. 3. TG and DTA curves of equimolar SiO_2-BaCO_3 mixtures in carbon dioxide. TG; heating rate, 5.3°C/min. DTA; heating rate, 5.0°C/min

Reaction processes between silica and barium carbonate

X-ray analysis of the reaction products in DTA measurements showed the formation of $BaSiO_3$ and Ba_2SiO_4. Their relative amounts were determined from the peak intensities of the strongest diffraction lines, $2\theta = 26.6$ ($BaSiO_3$) and $2\theta = 29.6$

(Ba_2SiO_4). Fig. 4 shows the conversion of barium carbonate into the two silicates. The X-ray diffraction intensities of the two silicates may change with the degree of their crystallinities. The following discussion, may be valid however, since the relative amounts of the two silicates varied markedly depending on the reaction conditions and starting materials. The effects of the silica particle size and the ambient atmosphere are also observed. The reaction products of *L*-1 at 810° were Ba_2SiO_4 alone in air, and $BaSiO_3$ alone in carbon dioxide. After heating up to 1000°, the product was a mixture of Ba_2SiO_4 and $BaSiO_3$ in both atmospheres. For *L*-2 and *L*-3, similar results were obtained. The reaction product of sample *M* in air was Ba_2SiO_4 alone, even at 1000°, and $BaSiO_3$ could not be detected.

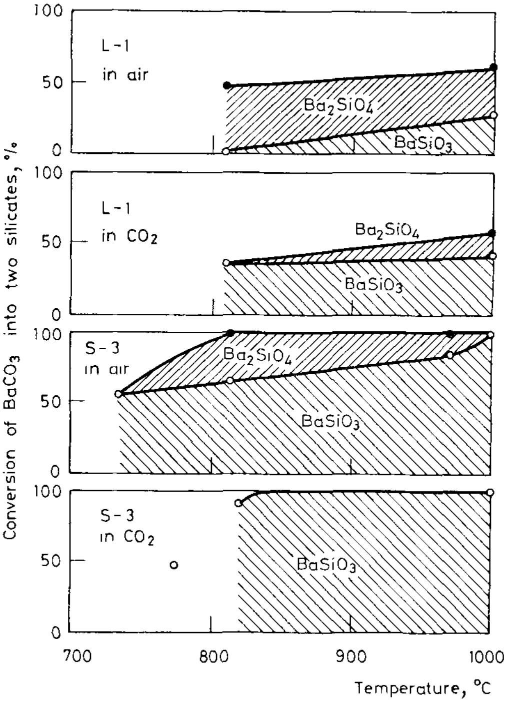

Fig. 4. Product distributions

The reaction products of *S*-3 in air were $BaSiO_3$ only at 735°, a mixture of $BaSiO_3$ and Ba_2SiO_4 at 810° where all the barium carbonate was consumed, and again $BaSiO_3$ alone at 1000°. In carbon dioxide, the reaction product was $BaSiO_3$ alone, and Ba_2SiO_4 could not be detected in the course of heating up to 1000°. *S*-1 and *S*-2 gave similar product distributions.

From these results, it may be concluded that in the reaction of equimolar mixtures of silica and barium carbonate the formation of the intermediate silicate,

Ba_2SiO_4, is facilitated by an increase in the particle size of the silica, and by a decrease in the partial pressure of carbon dioxide in the ambient atmosphere.

Grube et al. [6] carried out the reaction between silica and barium carbonate at temperatures from 700 to 1100° and proposed the following reaction steps on the basis of the chemical analysis of the products:

$$BaCO_3 + SiO_2 = BaSiO_3 + CO_2 \tag{A}$$

$$BaSiO_3 + BaCO_3 = Ba_2SiO_4 + CO_2 \tag{B}$$

$$Ba_2SiO_4 + SiO_2 = 2\ BaSiO_3. \tag{C}$$

On the other hand, Jander et al. [7] investigated the reaction of equimolar barium carbonate – silica mixtures at 750, 800 and 1010°, and concluded from the chemical analysis of the reaction products that the initial product was not $BaSiO_3$, but Ba_2SiO_4, and that differences in the starting materials and the method of chemical analysis might be responsible for the inconsistency with the results of Grube et al. In the present study, the product distributions in Fig. 4 suggest that the initial reaction product between silica and barium carbonate is $BaSiO_3$, and that Ba_2SiO_4 is formed by reaction (B), in accordance with the reaction processes proposed by Grube et al. The fact that $BaSiO_3$ could not be detected in the reaction products of *L*-1 in air at 810° and of *M* at 1000° may be due to the conversion of all the $BaSiO_3$ initially formed into Ba_2SiO_4. A similar consideration may be applied to the conclusion made by Jander et al.

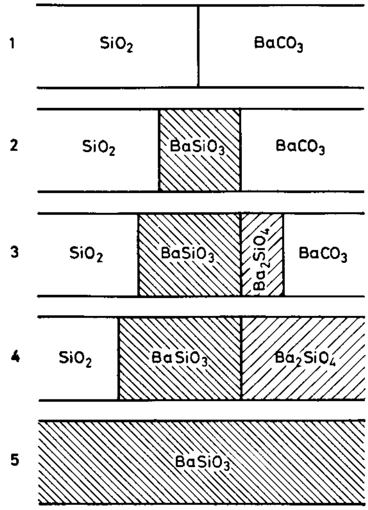

Fig. 5. Reaction model for SiO_2—$BaCO_3$ mixtures (numbers show the progress of reaction)

On the basis of the above considerations, the reaction processes in an equimolar $BaCO_3-SiO_2$ mixture may be represented schematically as in Fig. 5; this is similar to the reaction scheme for $CaO-SiO_2$ proposed by Jander et al. [8]. The first step is the formation of $BaSiO_3$ at the interface between SiO_2 and $BaCO_3$ by reaction (A) ($\Delta G^\circ = -23$ kcal/mole at 800°). The second step is the diffusion of BaO through the $BaSiO_3$ layer towards the $SiO_2-BaSiO_3$ interface to form $BaSiO_3$ by reaction with SiO_2, and the formation of Ba_2SiO_4 at the $BaSiO_3-BaCO_3$ interface by reaction (B) ($\Delta G^\circ = -13$ kcal/mole at 800°). Estimated by using data from the literature [9]. In the calculations, the heat capacities of barium silicates were assumed the same as those of the corresponding calcium silicates. When all the barium carbonate is consumed, the reaction product consists of $BaSiO_3$, Ba_2SiO_4, and SiO_2 equimolar to the Ba_2SiO_4. In the final step, the remaining SiO_2 is converted into $BaSiO_3$ by reaction (C), which may occur in that BaO in the Ba_2SiO_4 phase diffuses through the $BaSiO_3$ layer towards the $SiO_2-BaSiO_3$ interface. The relative amounts of $BaSiO_3$ and Ba_2SiO_4 in the course of the reaction vary, depending on the particle size of the silica and the partial pressure of carbon dioxide in the ambient atmosphere, as described above. Carbon dioxide depresses the formation of Ba_2SiO_4. As regards this effect, Grube et al. [6] considered that reaction (B) was thermodynamically impossible below 800° in an atmosphere of carbon dioxide. By the authors' estimation, however, the free energy change for reaction (B) is negative above 475° and the reaction is possible at the temperatures involved. In order to confirm this point, the reaction between equimolar $BaSiO_3$ and $BaCO_3$ was investigated by DTA in air and in carbon dioxide. The DTA curves showed endothermic peaks from 700 to 805° in both atmospheres, and the formation of Ba_2SiO_4 was confirmed by X-ray analysis. The conversions of barium carbonate at 805° were 71 and 79% in carbon dioxide and in air, respectively, showing little effect of the ambient atmosphere on reaction (B). Accordingly, the depression of the formation of Ba_2SiO_4 by carbon dioxide is not due to a thermodynamic reason. The authors tentatively consider that carbon dioxide may facilitate the diffusion of BaO the through the $BaSiO_3$ layer and as a result bring about the decrease of the Ba_2SiO_4 layer.

Analysis of reaction rates

Jander's equation (1), derived on the basis that a diffusion process is rate-determining, is a widely-used rate equation for solid-state reactions between powder materials:

$$(1 - \sqrt[3]{1 - \alpha})^2 = (k/r^2)t \tag{1}$$

where α, r and k are the fraction of the volume that has already reacted, the radius of the reacting particle, and the rate constant, respectively. Although several modifications [10–12] have been proposed to the equation, Jander [13] has shown that equation (1) holds for the reaction between equimolar SiO_2 and $BaCO_3$ and obtained 49 kcal/mole as the activation energy. The authors made an attempt to apply equation (1) for the analysis of TG curves obtained in oxygen, based on a method commonly used in thermoanalytical techniques [14, 15].

In TG, in which the temperature rises at a constant rate, the rate constant, k, is a function of time. For a uniform heating rate,

$$T = T_0 + at \quad (\mathrm{K}) \tag{2}$$

where T_0 is the temperature of commencement of the determination and a is the heating rate as defined by the equation $dT/dt = a$ (°/min). The temperature-dependency of the rate-constant may be expressed by an Arrhenius equation,

$$k = k_0 \exp(-E/RT) \tag{3}$$

where E is the activation energy of the reaction. Jander et al. [13] showed that expression (3) holds for the reaction between barium carbonate and silica. Substituting (2) and (3) into equation (1), one obtains

$$(1 - \sqrt[3]{1-\alpha})^2 = (k_0/r^2)(T - T_0/a)\exp(-E/RT) \tag{4}$$

Differentiation of both sides of (4) with respect to t gives

$$\frac{2}{3}(1 - \sqrt[3]{1-\alpha})(1-\alpha)^{2/3}\frac{d\alpha}{dt} = \frac{k_0}{r^2}\left(\frac{E}{RT} + 1\right)\exp(-E/RT) \tag{5}$$

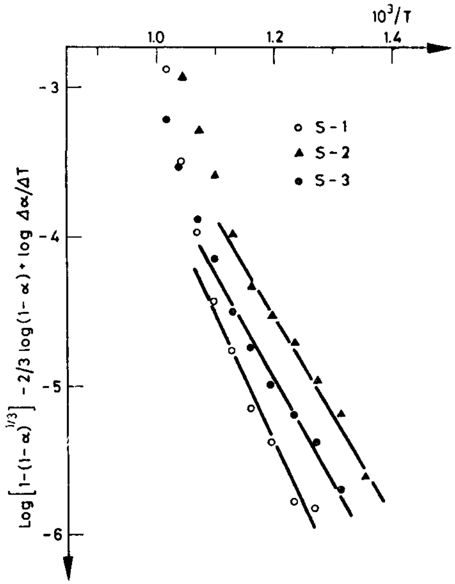

Fig. 6. Application of Jander's equation for TG curves in O_2

From (2), $d\alpha(dt) = a\, d\alpha/dT$. With the approximation $d\alpha/dT = \Delta\alpha/\Delta T$, equation (5) becomes

$$\log\left(1 - \sqrt[3]{1-\alpha}\right) - \frac{2}{3}\log(1-\alpha) + \log\frac{\Delta\alpha}{\Delta T} =$$

$$= \log C + \log\left(\frac{E}{RT} + 1\right) - \frac{E}{4.575\,T} \qquad (6)$$

where $C = 3\,k_0/2ar^2$. The value of the left side of (6), (y), can be calculated from the observed TG curves.

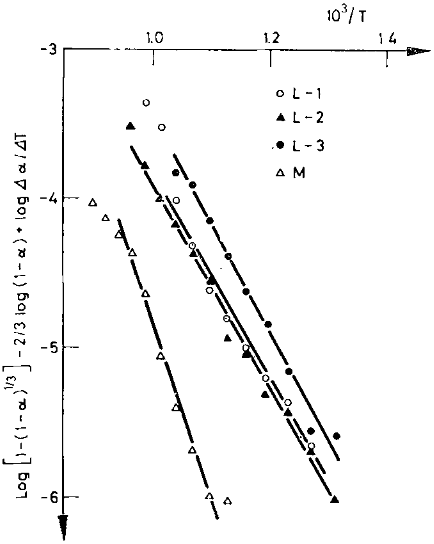

Fig. 7. Application of Jander's equation TG curves in O_2

The temperature range over which the analysis can be applied, as seen in Fig. 2, is from 500 to 800°. In this temperature range, the temperature-variation of the second term of the right side of (6) may be neglected in comparison with that of the third term. When this is the case, y should show a linear correlation with $1/T$. The results are shown in Figs. 6 and 7, in which the calculations were done by taking $T = 25°$. Linear relationships are observed between y and $1/T$ up to $\alpha = 0.16$ for groups S and L. From the slopes, the activation energies are calculated as 40 kcal/mole for S-1, and 32 kcal/mole for the others. For M, a linear relation also holds up to $\alpha = 0.11$, and gives 54 kcal/mole as the activation energy. It should be noted that the activation energy for M is close to that obtained by Jander et al., and is appreciably larger than those for groups S and L. The insignificant difference in the activation energy between groups S and L may be due to the fact that the silica particles which participated in the reaction up to 800° in group L samples were mainly the silica particles which had sizes comparable with those in group S.

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Résumé — On a étudié, par TG et ATD, la réaction de mélanges équimolaires pulvérulents de silice et de carbonate de baryum dans l'oxygène, l'air ou l'anhydride carbonique. La taille des particules de silice influence considérablement la réactivité de celle-ci, l'énergie d'activation de la réaction ainsi que la formation d'un silicate intermédiaire, Ba_2SiO_4. La diminution des dimensions des particules de silice ou l'augmentation de la pression partielle de l'anhydride carbonique réduisent la formation de Ba_2SiO_4.

Zusammenfassung — Die Reaktion zwischen äquimolaren Siliciumdioxid und Bariumcarbonatpulvern wurde in Sauerstoff, Luft oder Kohlendioxid mittels TG und DTA studiert. Die Teilchengröße von Siliciumdioxid zeigte eine bedeutende Wirkung auf die Reaktivität desselben und auf die Aktivierungsenergie der Reaktion, sowie die Bildung eines intermediären Silikats der Formel Ba_2SiO_4. Die Bildung des Ba_2SiO_4 wird durch die Abnahme der Teilchengröße des Siliciumdioxid sowie durch die Zunahme des Partialdrucks des Kohlendioxids in der Atmosphäre zurückgedrängt.

Резюме — Посредством ТГ и ДТА в атмосфере кислорода, воздуха и двуокиси углерода изучена реакция между крменеземом и карбонатом бария, взятыми в виде порошков в эквиполярных количествах. Показано, что размер зерен кремнезема значительно влияет на реакционную способность кремнезема и энергию активации реакции, а также на образование промежуточного силиката, Ba_2SiO_4. Образование Ba_2SiO_4 уменьшается с уменьшением размера зерен кремнезема или с увеличением парциального давления двуокиси углерода окружающей атмосферы.