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THE REACTIVITIES OF TiO_2 (RUTILE AND ANATASE) FOR THE SOLID-STATE REACTIONS WITH $BaSO_4$ AND $BaCO_3$

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DTA and isothermal kinetic studies were carried out on the reactions of $BaSO_4$ or $BaCO_3$ with TiO_2 (anatase and rutile) to $BaTiO_3$.

In the initial steps, the reactions of $BaSO_4$ with TiO_2 (anatase) proceeded to $BaTi_4O_9$, of $BaSO_4$ with TiO_2 (rutile) to $BaTi_3O_7$, and of $BaCO_3$ with TiO_2 (anatase and rutile) to Ba_2TiO_4, respectively. These reactions were connected with the formation of binary metal oxide through some intermediates, which are $BaSO_4$ or $BaCO_3$ incorporated with TiO_2. The reactivity of anatase was higher than that of rutile in all reaction systems.

Many investigations on the solid-state reaction between TiO_2 and $BaCO_3$ have been reported [1—5], but these results are not always consistent with each other from the viewpoint of the reaction processes and the reactivities of TiO_2. On the other hand, studies on the $BaSO_4-TiO_2$ system are rarely found. The present paper is concerned with DTA and isothermal kinetic studies on the reactivities of TiO_2 (anatase and rutile) in the $BaSO_4-TiO_2$ and $BaCO_3-TiO_2$ systems.

In a previous paper [6], the influence of the preparation history of the TiO_2 on its reactivity for the solid-state reaction in $CaSO_4-TiO_2$ systems was studied by means of TG, DTA and isothermal kinetic experiments, and it was concluded that the reactivity of TiO_2 was dependent on the structure difference due to the different preparation histories, whereas in the $CaCO_3-TiO_2$ systems there was no distinct influence of the structure difference of TiO_2 was recognized.

Experimental

Materials

TiO_2 (anatase) and $BaSO_4$ were prepared by calcining commercial TiO_2 (anatase) and $BaSO_4$ (GR reagents from Kanto Chemical Co.) at 500° for 1 hr in air. TiO_2 (rutile) was prepared by calcining TiO_2 (anatase) at 1200° for 1 hr in air. $BaCO_3$ was prepared by calcining commercial $BaCO_3$ (GR reagent from Kishida Chemical Co.) at 500° for 1 hr in air. All starting materials were ground to pass through a 250 mesh sieve. The samples used for DTA and isothermal experiments were prepared by mixing $BaSO_4$ and TiO_2 (1 : 1 mol), and $BaCO_3$ and TiO_2 (1 : 1 mol) in an agate mortar for 30 min.

DTA experiments

The gas flow type DTA apparatus [7] was used with a sample of 0.5 g, a flowing nitrogen atmosphere of 100 ml/min and a heating rate of 5.6 – 7.4°/min. α-Al_2O_3 (200 mesh) used as reference material was prepared by calcining activated alumina (Merk) at 1300° for 3 hr in air. X-ray analysis of the samples taken out at various temperatures (shown by arrows) in the course of DTA experiments was carried out at room temperature to study the reaction mechanism involved. The X-ray diffractometer used was a Geigerflex 2141 (Rigaku Denki Co.), operated under the following conditions: CuKα radiation, Ni filter, 25 kV and 10 mA.

Isothermal experiments

For $CaSO_4$ – TiO_2 systems, 100 mg sample was placed in an alumina boat and heated in the isothermally operated furnace in a current of N_2 (100 ml/min). The degree of decomposition of $BaSO_4$ and the compositions of the products were determined by gas analysis of SO_3 (SO_2) in the outlet gas and by X-ray analysis of the products as a function of reaction time, respectively. The quantity of SO_3 (SO_2) was determined on the basis of the titration of SO_3 absorbed in 0.1% hydrogen peroxide solution (40 ml) containing dilute $CuCl_2$ solution (10 ml) with 0.05 *N* NaOH solution.

Results and discussion

DTA of $BaSO_4$ – TiO_2 systems

Figure 1 shows the DTA curves for *(a)* $BaSO_4$ alone, *(b)* $BaSO_4$ – TiO_2 (anatase) and *(c)* $BaSO_4$ – TiO_2 (rutile) systems in flowing N_2. Curve *(a)* reveals no thermal deflection except for a sharp endothermic peak due to the transition of $BaSO_4$ at 1170°. In the course of the reaction up to 1400° trace amounts of SO_3 were detected, but the fractional decomposition of $BaSO_4$ at 1400° was less than 0.1%. No BaO (BaO_2) was identified in the sample at 1400° by X-ray analysis.

Curve *(b)* shows that an endothermic deflection begins at about 1000°, followed by three endothermic peaks, at 1120°, 1170° and 1260°. The sharp endothermic peak at 1170° corresponds to the transition of the $BaSO_4$ remaining. X-ray diffraction patterns showed that the reaction to $BaTiO_3$ is completed up to 1400°, but BaO is absent in all temperature ranges. On the basis of these results, it may be concluded that the decomposition of $BaSO_4$ (reaction (1)) is promoted by TiO_2 and proceeds through two steps, which results in the peaks at 1120 and 1260°, this reaction not involving the intermediate formation BaO (BaO_2) from the decomposition of $BaSO_4$:

$$BaSO_4 + TiO_2 \rightarrow BaTiO_3 + SO_3 \uparrow \tag{1}$$

Curve *(c)* shows, in a similar manner as curve *(b)*, a slight endothermic deflection at 1000 – 1250°, followed by two endothermic peaks, at 1170° and 1330°. The reaction to $BaTiO_3$ was completed up to 1370°, but BaO (BaO_2) was absent. It is

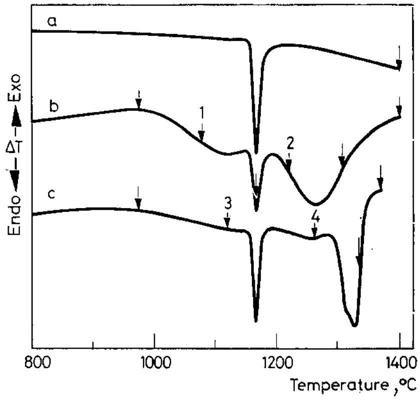

Fig. 1. DTA curves for $BaSO_4$ and $BaSO_4-TiO_2$ systems in flowing N_2. *a*, $BaSO_4$; *b*, $BaSO_4-TiO_2$ (anatase); *c*, $BaSO_4-TiO_2$ (rutile)

thought that the reaction proceeds through two steps, at 1000–1250° and 1330°. Compared with curve *(b)*, however, the endothermic deflection for the initial reaction step is small, the peak due to the transition of the $BaSO_4$ remaining is large, and the endothermic peak at higher temperatures is shifted from 1260° to 1330°. This means that the reactivity of anatase is higher than that of rutile in this reaction system.

In order to follow the reaction processes, especially in the initial reaction step, X-ray analysis was carried out on samples cooled from the temperatures indicated by the arrows on the DTA curves in Fig. 1. In the $BaSO_4-TiO_2$ (anatase) system, at 970° the same diffraction pattern as that of the starting sample was obtained, but at 1080° the formation of $BaTi_4O_9$ and the transition of a certain amount of anatase to rutile occurred. At 1160° the formation of $BaTiO_3$ began. The amount of $BaTiO_3$ increased with increasing temperature, and at 1400° only $BaTiO_3$ was identified. BaO (BaO_2) as a decomposition product of $BaSO_4$, was not identified in any temperature range.

On the basis of these results, it was assumed, similarly as for the $CaSO_4$-oxide system [7], that the promoting effect of TiO_2 (anatase) on the decomposition of $BaSO_4$ is connected with the formation of binary oxide through some intermediates, $BaSO_4$ incorporated with TiO_2, in the initial step of the reaction:

$$BaSO_4 + 4\,TiO_2 \rightleftarrows (BaSO_4 \cdot 4\,TiO_2) \tag{2}$$

$$(BaSO_4 \cdot 4\,TiO_2) \rightarrow BaTi_4O_9 + SO_3(SO_2 + 1/2O_2)\uparrow . \tag{3}$$

Reaction (3) is probably the rate-controlling step and corresponds to the endothermic peak at about 1120°. This initial reaction is followed by the second step:

$$BaTi_4O_9 + 3\,TiO_2 \rightarrow 4\,BaTiO_3 + 3\,SO_3\,(SO_2 + 1/2O_2). \tag{4}$$

In the $BaSO_4-TiO_2$ (rutile) system, at 970° the same diffraction pattern as that of the starting sample was given, but at 1120° the formation of $BaTi_3O_7$ was found, in contrast with $BaTi_4O_9$ in the $BaSO_4-TiO_2$ (anatase) system. At 1260° the formation of $BaTiO_3$ began. The amount of $BaTiO_3$ increased with increasing temperature, and at 1340° only $BaTiO_3$ was identified. BaO (BaO_2) was not found in the entire temperature range. In a similar manner as in the anatase system, the following processes were considered in the initial step:

$$BaSO_4 + 3\,TiO_2 \rightleftarrows (BaSO_4 \cdot 3\,TiO_2) \tag{5}$$

$$(BaSO_4 \cdot 3\,TiO_2) \rightarrow BaTi_3O_7 + SO_3(SO_2 + 1/2O_2)\uparrow . \tag{6}$$

This initial reaction is followed by the second step:

$$BaTi_3O_7 + 2\,BaSO_4 \rightarrow 3\,BaTiO_3 + 2\,SO_3(SO_2 + 1/2O_2). \tag{7}$$

The intermediate-like materials denoted by ($BaSO_4 \cdot 4\,TiO_2$) and ($BaSO_4 \cdot 3\,TiO_2$) were not identified in the X-ray diffraction patterns of the samples cooled to room temperature. This is probably due to the fact that reactions (2) and (5) proceed reversibly.

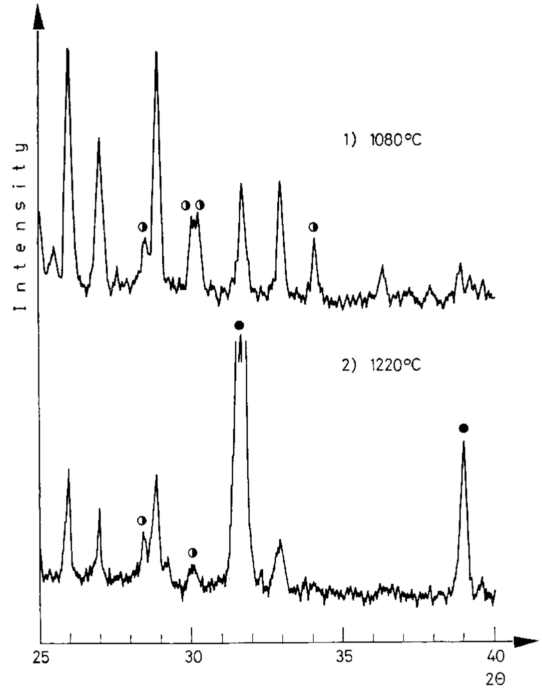

Fig. 2. X-ray diffraction patterns of samples 1 and 2 in the DTA curve for the $BaSO_4-TiO_2$ (anatase) system (curve b in Fig. 1). ◑, $BaTi_4O_9$; ●, $BaTiO_3$; no mark, $BaSO_4$ or TiO_2

Figure 2 shows the X-ray diffraction patterns of samples 1 and 2 corresponding to the temperatures 1080° and 1220° in DTA curve *(b)* in Fig. 1 for the $BaSO_4-TiO_2$ (anatase) system. The variations of the intensities of the characteristic diffraction peaks of $BaTi_4O_9$ ($2\Theta = 29.9$ and 30.1° ASTM) and $BaTiO_3$ (31.5, 31.6 and 38.9° ASTM) are given. Figure 3 shows the patterns of samples 3 and 4 at 1120° and 1260° in DTA curve *(c)* in Fig. 1 for the $BaSO_4-TiO_2$ (rutile) system. The characteristic peaks of $BaTi_3O_7$ (28.4, 31.3, 32.1 and 33.6° ASTM) and $BaTiO_3$ are given. In the rutile system no peaks are recognized at $2\Theta = 29.9$ and 30.1°.

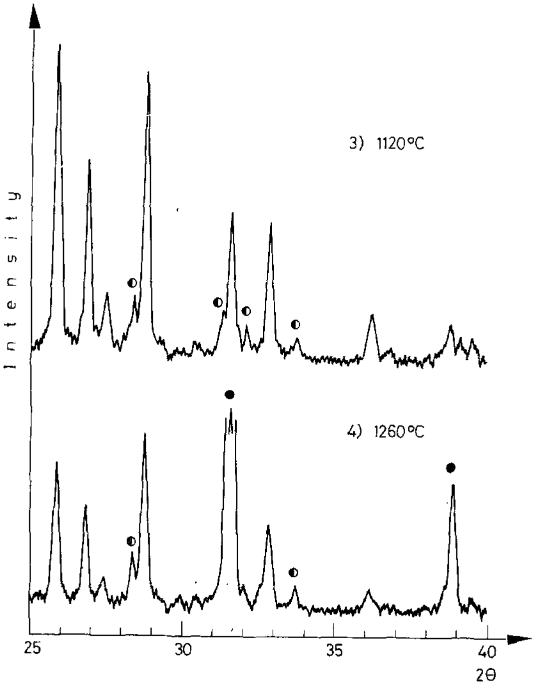

Fig. 3. X-ray diffraction patterns of samples 3 and 4 in the DTA curve for the $BaSO_4-TiO_2$ (rutile) system (curve c in Fig. 1). ◐, $BaTi_3O_7$; ●, $BaTiO_3$; no mark, $BaSO_4$ or TiO_2

Isothermal studies of $BaSO_4-TiO_2$ systems

Figure 4 shows plots of the isothermal kinetic data obtained in the temperature ranges where the initial reactions occur (1000–1100° for the anatase system, and 1100–1150° for the rutile system) as indicated by the DTA curves in Fig. 1. Jander's equation based on diffusion, $kt = [1 - (1 - \alpha)^{1/3}]^2$, provides a good fit to the data. The results reveal that the reactivity of anatase is higher than that of rutile. X-ray analysis of the samples at various temperatures and times substantiated the reaction processes suggested by the DTA experiments. Furthermore, the

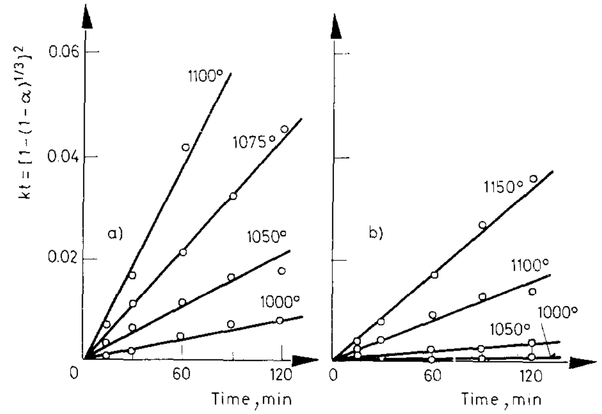

Fig. 4. Jander's plots of the isothermal kinetic data obtained in the temperature ranges where the initial reactions occur. *a*, $BaSO_4-TiO_2$ (anatase); *b*, $BaSO_4-TiO_2$ (rutile)

X-ray results showed that when the reaction time is long, the reaction in the second step proceeded simultaneously with that in the initial step. For example, in the $BaSO_4-TiO_2$ (anatase) system, reaction (3) proceeded under conditions of 1050° and 60 min, reactions (3) and (4) at 1100° and 30 min, and reaction (4) at 1100° and 60 min (reaction (3) disappeared), whereas in the $BaSO_4-TiO_2$ (rutile) system, no reaction products appeared at 1050° and 60 min, and reactions (6) and (7) proceeded at 1100° and 30–60 min.

DTA of $BaCO_3-TiO_2$ systems

In order to compare the reactivity of TiO_2 in $BaSO_4-TiO_2$ systems with that in $BaCO_3-TiO_2$ systems, DTA studies of $BaCO_3-TiO_2$ systems were carried out. Isothermal kinetic studies of $BaCO_3-TiO_2$ systems have already been made by many investigators.

Figure 5 illustrates the DTA curves for *(a)* $BaCO_3$ alone, *(b)* $BaCO_3-TiO_2$ (anatase) and *(c)* $BaCO_3-TiO_2$ (rutile) systems in flowing N_2. Curve *(a)* exhibits three endothermic peaks. X-ray analysis showed that there are no decomposition products at 990 and 1090°, and that BaO_2 is formed at 1180°. Therefore the endothermic peak at about 1140° corresponds to the decomposition of $BaCO_3$. The X-ray result at 1350° showed that the decomposition of $BaCO_3$ is completed. The endothermic peaks at about 810 and 990° correspond to the $BaCO_3$ transitions from rhombic to hexagonal and from hexagonal to cubic systems, respectively. A qualitative analysis of CO and CO_2 in the outlet gas was carried out with the use of $PdCl_2-HCl$ solution and $BaCl_2-NH_4OH$ solution, respectively. No CO was detected in the experimental temperature range; trace amounts of CO_2 were detected at about 700°. On the basis of these results, it is thought that the decomposition of $BaCO_3$ (reaction (8)) proceeds gradually from 700° and rapidly at about 1100°:

$$BaCO_3 \rightarrow BaO + CO_2 \uparrow . \qquad (8)$$

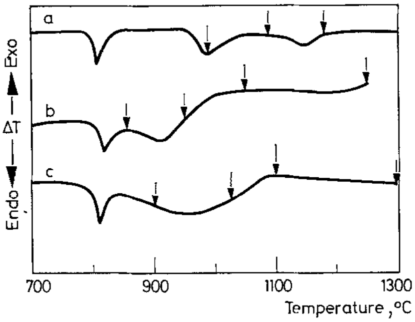

Fig. 5. DTA curves for $BaCO_3$ and $BaCO_3-TiO_2$ systems in flowing N_2. *a*, $BaCO_3$; *b*, $BaCO_3-TiO_2$ (anatase); *c*, $BaCO_3-TiO_2$ (rutile)

The BaO_2 formation at 1180°, mentioned above, is due to the oxidation of BaO by aerial O_2 in the course of the X-ray analysis.

Curve *(b)* shows that an endothermic peak due to the transition of $BaCO_3$ appears at 820°, followed by an endothermic peak at about 910°. X-ray analysis of the samples indicated by arrows demonstrated that the decomposition of $BaCO_3$ is promoted by TiO_2 (anatase), that the bulk of the $BaCO_3$ decomposes at 1050° into $BaTiO_3$ and CO_2 through the formation of Ba_2TiO_4, and that the decomposition is completed at 1250°.

Curve *(c)* shows that the transition peak of $BaCO_3$ appears at 815°, followed by a broad endothermic peak at 800 – 1100°. X-ray analysis revealed that, in a similar manner as for *(b)*, the decomposition is promoted, the bulk of the $BaCO_3$ decomposes at 1300° into $BaTiO_3$ and CO_2 through the formation of Ba_2TiO_4, and the decomposition is completed at 1370°. In contrast with $BaSO_4-TiO_2$ systems, in both $BaCO_3-TiO_2$ systems *(b* and *c)* the DTA peaks corresponding to the formation of $BaTiO_3$ are simple and Ba_2TiO_4 seemed to be the main product before $BaTiO_3$ formation (some unknown X-ray peaks appeared).

On the basis of the results given above, it was assumed that mainly the following reaction sequence proceeds in both anatase und rutile systems:

$$2\,BaCO_3 + TiO_2 \rightleftarrows (2\,BaCO_3 \cdot TiO_2) \tag{9}$$

$$(2\,BaCO_3 \cdot TiO_2) \rightarrow Ba_2TiO_4 + 2\,CO_2 \uparrow \tag{10}$$

$$Ba_2TiO_4 + TiO_2 \rightarrow 2\,BaTiO_3\,. \tag{11}$$

The influence of the crystal forms of TiO_2 on the composition of the intermediate in the initial reaction step was not evident in these systems, but the difference in reactivity due to the crystal form difference, anatase > rutile, did appear.

Kubo *et al.* [1] and Trzebiatowski *et al.* [8], in accordance with the interpretation by Templeton *et al.* [2], agree that first some $BaTiO_3$ and then Ba_2TiO_4 forms at the surface of contact, and finally the Ba_2TiO_4 combines with the remaining TiO_2 to form $BaTiO_3$, but they do not agree on the process of Ba_2TiO_4 formation.

Kubo *et al.* concluded that Ba_2TiO_4 is produced from $BaTiO_3$ and $BaCO_3$, whereas Trzebiatowski *et al.* suggested that Ba_2TiO_4 is formed directly from $BaCO_3$ and TiO_2. Templeton *et al.* concluded that a small amount of $BaTiO_3$ is formed first, and then the reaction becomes diffusion-controlled, and both $BaTiO_3$ and Ba_2TiO_4 are produced, with Ba_2TiO_4 being formed in much larger amounts.

In the present paper, there are not enough data to reexamine the above works, but the promotion of the reaction of $BaSO_4$ or $BaCO_3$ with TiO_2 was connected with the formation of binary metal oxide through intermediates, $BaSO_4$ or $BaCO_3$ incorporated with TiO_2, in the initial step of the reaction, and the reactivities of the TiO_2 were compared. It is interesting that the compositions of these intermediates and the reactivities are affected by the crystal forms of TiO_2.

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Résumé — La réaction de $BaSO_4$ ou $BaCO_3$ avec TiO_2 (anatase et rutile) en $BaTiO_3$ a fait l'objet d'une étude par ATD et en cinétique isotherme.

La réaction de $BaSO_4$ avec TiO_2 (anatase) en $BaTi_4O_9$, de $BaSO_4$ avec TiO_2 (rutile) en $BaTi_3O_7$ et de $BaCO_3$ avec TiO_2 (anatase et rutile) en Ba_2TiO_4 se produit dès le début. Ces réactions sont liées à la formation d'oxyde du métal binaire à l'aide de quelques intermédiaires, notamment $BaSO_4$ ou $BaCO_3$ incorporés au TiO_2. La réactivité de l'anatase est plus élevée que celle du rutile, dans tous les systèmes réactionnels étudiés.

Zusammenfassung — DTA und isotherme kinetische Untersuchungen der Reaktionen von $BaSO_4$ oder $BaCO_3$ mit TiO_2 (Anatas und Rutil) zu $BaTiO_3$ wurden durchgeführt.

In den Anfangsphasen verliefen sowohl die Reaktion von $BaSO_4$ mit TiO_2 (Anatas) zu $BaTi_4O_9$, von $BaSO_4$ mit TiO_2 (Rutil) zu $BaTi_3O_7$ als auch die von $BaCO_3$ mit TiO_2 (Anatas und Rutil) zu Ba_2TiO_4. Diese Reaktionen waren mit der Bildung binärer Metalloxide über einige Zwischenstufen, welche aus $BaSO_4$ odet $BaCO_3$, in Verbindung mit TiO_2 bestanden, verknüpft. Die Reaktivität von Anatas war in allen Reaktionssystemen höher, als die vom Rutil.

Резюме — Проведены ДТА и изотермические кинетические исследования реакций $BaSO_4$ и $BaCO_3$ с TiO_2 (анатаз и рутил) с образованием $BaTiO_3$. На начальных стадиях реакция $BaSO_4$ с TiO_2 (анатаз) протекает до $BaTi_4O_9$, $BaSO_4$ с TiO_2 (рутил) до $BaTi_3O$, реакция $BaCO_3$ с TiO_2 (анатаз и рутил) до Ba_2TiO_4. Эти реакции протекают с образованием двойных окислов металлов через промежуточные продукты, в которых $BaSO_4$ и $BaCO_3$ внедрялись в TiO_2. Во всех реакциях реакционная способность анатаза была выше, чем рутила.