Journal of Thermal Analysis, Vol. 18 (1980) 527—537

THE REACTIVITY OF TiO_2 WITH DIFFERENT PREPARATION HISTORIES IN SOLID-STATE REACTIONS IN $CaSO_4-TiO_2$ SYSTEMS

T. ISHII, R. FURUICHI and Y. OHSHIMA

Department of Applied Chemistry, Faculty of Engineering,
Hokkaido University, Sapporo, 060 Japan

(Received September 7, 1979)

Influences of the preparation histories of TiO_2 on its reactivity in solid-state reactions in $CaSO_4$—TiO_2 systems were studied by means of TG, DTA and isothermal kinetic experiments.

In order to estimate the reactivities of solids, it was necessary to note the behaviors in the initial reaction step in the selected reaction system. It was concluded that the reactivity of TiO_2 was dependent on the structure difference due to the different preparation histories, and the greater the stability of the anatase form, up to higher temperature, the higher the reactivity of TiO_2.

In a previous paper [1], the solid-state reactions in mixed systems of $CaSO_4$ with 12 metal oxides were investigated by means of gas-flow type DTA. In the $CaSO_4-[\text{oxide}]_{II}$ systems, where $[\text{oxide}]_{II}$ can be any one of Al_2O_3, SiO_2, TiO_2, Cr_2O_3, MnO_2 or $\alpha\text{-}Fe_2O_3$, decomposition of $CaSO_4$ was promoted by the oxide. It was supposed that this promotion is connected with the formation of binary metal oxide through intermediates, which are $CaSO_4$ incorporated with an oxide, in the initial steps of the reaction:

$$CaSO_4 = (CaO \cdot SO_3) \quad (1)$$

$$(CaO \cdot SO_3) + [MO_2]_{II} = (MO_2 \cdot CaO \cdot SO_3) \quad (2)$$

$$(MO_2 \cdot CaO \cdot SO_3) = CaMO_3 + SO_3(SO_2 + 1/2O_2) \quad (3)$$

where parentheses show the intermediates which suggest the distortion of the lattice, and $[MO_2]_{II}$ shows $[\text{oxide}]_{II}$. It seems reasonable to assume that step (3) determines the overall rates, because the rate of decomposition of the $CaSO_4-[\text{oxide}]_{II}$ system was markedly affected by the atmospheres used.

The present paper is concerned with TG, DTA and isothermal studies on the influence of the preparation history of TiO_2 on its reactivity as regards the initial reaction step in TiO_2-CaSO_4 systems.

Experimental

Materials

Six TiO_2 samples and their preparation methods and physical properties are shown in Table 1. Sample S–2 was prepared by calcining a precipitate, obtained by the hydrolysis of 20 g $TiCl_4$ in 100 ml H_2O, at 900° for 2 hr in air. S–3 was

Table 1

TiO_2 samples

Preparation methods			Physical properties		
samples	starting materials	calcining[c]	anatase contents, F_A, wt. %	SO_3 contents, C_{SO_3}, wt. %	BET surfaces, S, m^2/g
C-A	Commercial anatase[a]	700°, 2 hr	100	0.01	10.9
C-R_1	C-A	1200°, 1 hr	0	–	–
C-R_2	Commercial rutile[b]	700°, 1 hr	0	–	13.4
S-2	Hydrolyzed $TiCl_4$, (S-2′)	900°, 2 hr	0	0	1.4
S-3	Hydrolyzed $TiCl_4$ with $(NH_4)_2SO_4$, (S-3′)	700°, 2 hr	100	0.50	18.0
S-5	Hydrolyzed $Ti(SO_4)_2$, (S-5′)	700°, 2 hr	62.7	0.12	14.6

[a] Kanto Chemical Co.
[b] Commercial pigment.
[c] In air.

prepared by calcining a precipitate, obtained by the hydrolysis of 20 g $TiCl_4$ with 5 g $(NH_4)_2SO_4$ additive in 100 ml H_2O, at 700° for 2 hr in air. S–5 was prepared by calcining a precipitate, obtained by the hydrolysis of 19.5 g $Ti(SO_4)_2$ in 100 ml H_2O, at 700° for 2 hr in air. All the hydrolysis reactions were carried out at 100°. Each precipitate (hydrated TiO_2, S–2′, S–3′ or S–5′) was washed with warm water until the washings had no Cl^- or SO_4^{2-}, followed by filtration and drying at 100°. $TiCl_4$, $(NH_4)_2SO_4$ and $Ti(SO_4)_2$ were GR reagents from Kanto Chemical Co., and were used without further purification. C-A, C-R_1 and C-R_2 were prepared by calcining commercial TiO_2 under the conditions shown in Table 1. $CaSO_4$ was prepared by calcining commercial $CaSO_4 \cdot 2\,H_2O$ (GR reagent from Kanto) at 550° for 1 hr in air.

Prior to the preparation of the mixture used for the solid-state reaction in the TiO_2-CaSO_4 system, the TiO_2-CaSO_4 system, the TiO_2 and $CaSO_4$ were ground to pass a 325 mesh sieve. Particle sizes in the range 0.3–1.0 μm was measured under an electron-microscope, except for the C-R_1 sample, where it was about 2 μm. Equimolar mixtures of TiO_2 and $CaSO_4$ were blended in an agate mortar for 45 min. Completeness of mixing was checked by measuring the amount of Ca^{2+} in several parts of the sample after mixing.

TG and DTA

The TG apparatus used for the reactivity tests of five TiO_2 samples with different preparation histories consisted of a quartz spring (sensitivity 3.26 mg/mm) and a quartz reaction tube (d = 40 mm) connected to a vacuum system. The sample of 0.1 g of a mixtures of TiO_2 and $CaSO_4$ was placed in a cylindrical quartz dish

(10×10 mm) and the weight decrease of the sample under 150 torr N_2 was measured with a cathetometer as a function of temperature. A temperature increasing rate of 5°/min was used. The net weight decrease was estimated from the difference between the data measured in the TiO_2-CaSO_4 system and the baseline obtained for α-Al_2O_3. Temperature was measured with a CA thermocouple attached at the outer wall of the reaction tube.

The gas-flow type DTA apparatus [1] was used under the conditions of flowing N_2 (100 ml/min) and a heating rate of 5.8°/min for TiO_2 (C-A and C-R_1)$-CaSO_4$ systems.

In order to characterize the preparation histories of the samples S−2, 3 and 5, the calcination processes of hydrated TiO_2, S−2′, 3′ and 5′, were investigated by means of TG and DTA. TG experiments were carried out with a Cahn electrobalance Model RG. A heating rate of 4.5°/min and a static atmosphere of 150 torr N_2 were used. DTA experiments were carried out with a Thermoflex 8001 apparatus (Rigaku Denki). A heating rate of 10°/min and static air atmosphere were used.

Isothermal experiment

The TG apparatus was also used for the isothermal study in TiO_2-CaSO_4 systems in the temperature range 900 to 1000°. In order to start the reaction, the sample tube was inserted into the furnace heated up to the prescribed temperature, followed by the measurement of the weight decrease of the sample under 150 torr N_2 as a function of time. There was some uncertainty in the fractional conversion measured in an initial period of time, because about 15 minutes was required to attain the fixed reaction temperature after the sample was inserted into the heated furnace. Consequently, the data after 20 minutes were used for the kinetic considerations.

Fractional conversion (α)

The fractional decomposition of $CaSO_4$ was estimated from the weight decrease of the sample by assuming the reaction:

$$CaSO_4 + TiO_2 = CaTiO_3 + SO_3(SO_2 + 1/2O_2)\uparrow \qquad (4)$$

The fractional formation of $CaTiO_3$ was determined separately by chemical analysis. Chelatometry was used to determine the amount of Ca^{2+} unreacted. $CaTiO_3$ was the only product, and no CaO was detected. The values obtained by TG were 1−2% higher than those by chemical analysis. However, this is within the experimental error in the accuracy of chemical analysis.

Anatase content (F_A), SO_3 content (C_{SO_3}) and surface area (S)

The F_A (wt%) of the sample was estimated on the basis of the following equation [2].

$$F_A = \frac{1}{1 + 1.26 I_R/I_A} \qquad (5)$$

where I_A and I_R are the X-ray diffraction intensities at $2\theta = 25.3°$ for anatase and 27.5° for rutile, respectively. The C_{SO_3} (wt%) of the sample was determined by the chemical analysis of SO_3 and/or SO_2 liberated when the sample was calcined at 1200° in flowing O_2. The S (m^2/g) of the sample was estimated by the BET method from the amount of N_2 adsorbed at −195°.

Results and discussion

Changes of hydrated TiO_2 *during calcining*

Figure 1 shows the DTA and TG curves for three hydrated TiO_2 samples. An endothermic peak which corresponds to the dehydration appears at 150−200° for each sample. An endothermic peak which corresponds to the decomposition appears at about 600° for samples S−3′ and 5′. The weight decreases shown in the TG curves correspond to these endothermic peaks. The TG curve of S−2′ shows a weight decrease in only one step, which corresponds to the dehydration. Assuming that the weight decrease above 500° is due to the release of SO_3 [3, 4], the compositions of S−2′, 3′ and 5′ were evaluated to be $TiO_2 \cdot 0.49\,H_2O$, $TiO_2 \cdot 0.82\,H_2O \cdot 0.13\,SO_3$ and $TiO_2 \cdot 0.60\,H_2O \cdot 0.15\,SO_3$, respectively. It is thought that the exothermic peaks at 400° for S−2′ and at 870° for S−3′ correspond to the crystallization of rutile and the transition from anatase to rutile, respectively.

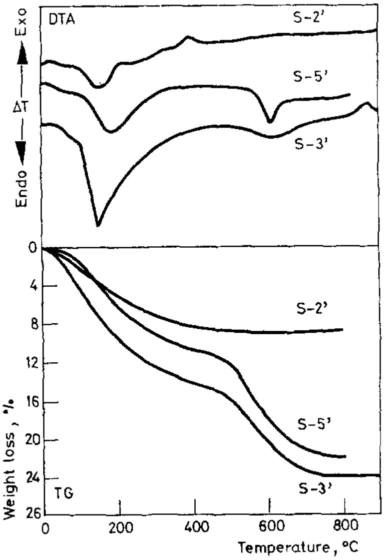

Fig. 1. DTA and TG curves for hydrated TiO_2. Heating rate: 10°/min; atmosphere: static air

Figure 2 shows the changes of F_A, C_{SO_3} and S as functions of the calcination temperature. The calcination time of samples for F_A values is 1 hr, and for C_{SO_3} or S values is 2 hr. In S–3′ and S–5′, C_{SO_3} decreases with increasing calcination temperature. It is thought that the C_{SO_3} decrease results from the transition from anatase to rutile, or the decrease of F_A and S. The inflection points of the F_A curves, which are taken as a measure of the temperature at which the transition to rutile proceeds with the greatest violence, were 1025° in C-A, 775° in S–3′ and 765° in S–5′. The transitions in S–3′ and 5′ seem to start as C_{SO_3} becomes less than about 1 %.

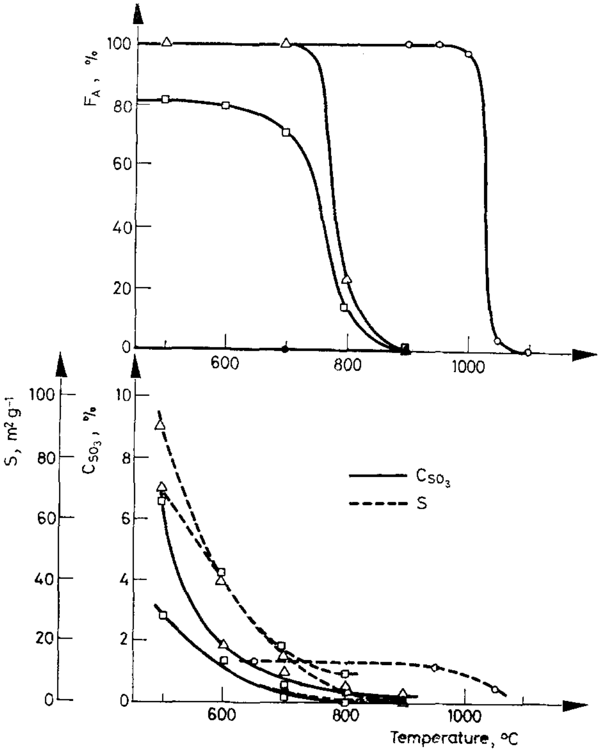

Fig. 2. F_A, C_{SO_3} and S of hydrated TiO_2 and commercial anatase as functions of the calcination temperature. Calcination time is 1 hr for F_A, and 2 hr for C_{SO_2} and S. Hydrated TiO_2: ●, S–2′; △, S–3′; □, S–5′; ○, commercial anatase (C-A)

DTA of $CaSO_4$–TiO_4 *and* $CaCO_3$–TiO_2 *systems*

Figure 3(A) shows the DTA curves for $CaSO_4$ alone (a) and for $CaSO_4$–TiO_2 systems (b and c) in flowing N_2. X-ray analysis and chemical analysis of samples at the various temperatures shown by arrows on the DTA curves were carried out to study the reaction mechanisms involved. The outlet gas was analyzed qualitatively to determine the onset temperature of decomposition of $CaSO_4$.

Curve (a) shows that an endothermic deflection of the DTA curve begins at about 1100°, followed by a sharp endothermic peak at 1220°. X-ray analysis of the sample taken at 1300° showed the presence of CaO and $CaSO_4$, which suggests that the endothermic deflection starting at 1100° is due to thermal decomposition of $CaSO_4$. The sharp peak at 1220° is due to the II $\rightleftarrows$ I transition of remaining $CaSO_4$. No endothermic or exothermic peak was observed below 1000°.

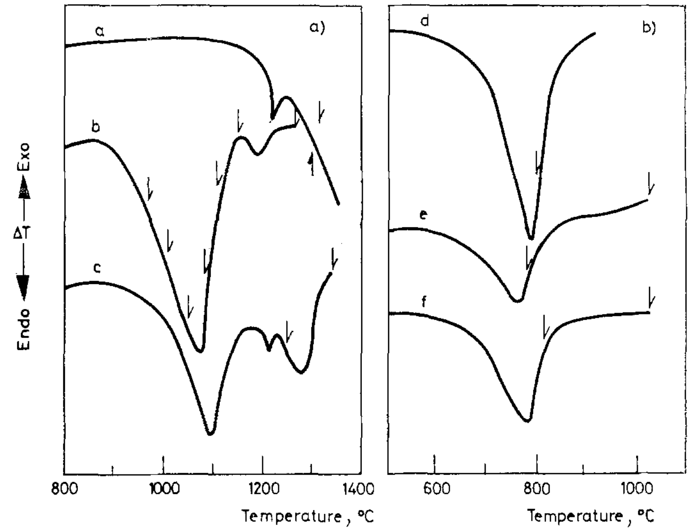

Fig. 3. DTA curves for $CaSO_4$–TiO_2 systems (A), and for $CaCO_3$–TiO_2 systems (B). Heating rate: 5.8°/min; atmosphere: N_2 flow (100 ml/min). Systems: (a) $CaSO_4$ alone; (b) $CaSO_4$ – (C-A); (c) $CaSO_4$–(C-R_1); (d) $CaCO_3$ alone; (e) $CaCO_3$–(C-A); (f) $CaCO_3$–(C-R_1)

(b) is the DTA curve for the $CaSO_4$–TiO_2 (anatase) system. An endothermic deflection begins at 880°, followed by two endothermic peaks, at 1070 and 1190°. Evolution of SO_2 and SO_3 was observed at about 500°. The large endothermic peak at 1070° corresponds to reaction (4). Some $CaSO_4$ remains at 1110° and the reaction was completed at 1265°, but CaO was absent over the entire temperature range. On the basis of these results, it is thought that reaction (4) proceeds in two steps, at 1070 and 1190°.

(c) is the curve for the $CaSO_4$–TiO_2 (rutile) system. As in the case of (b), it is thought that reaction (4) proceeds in two steps, at 1100 and 1280°. An endothermic peak at 1210° corresponds to the transition of residual $CaSO_4$. The reason why reaction (4) proceeds stepwise may be that the rapid reaction occurs at the point of contact between two particles in the initial step, followed by the second step, which is possibly a diffusion-controlled step through the product layer. The differences in peak temperature and size for C-A and C-R_1 are probably due to the differences in both the structure and particle size of TiO_2.

These results were compared with those in the $CaCO_3-TiO_2$ systems. Figure 3(B) shows the DTA curves for $CaCO_3$ alone (d) and $CaCO_3-TiO_2$ systems (e and f) in flowing N_2. (d) shows that an endothermic deflection begins at 550°, with a peak temperature of 780°. This peak corresponds to the decomposition of $CaCO_3$ to CaO, as CaO was identified in the X-ray diffraction pattern of the sample taken at 800°. (e) and (f) are the curves for $CaCO_3-TiO_2$ (anatase) and $CaCO_3-TiO_2$ (rutile), respectively. There is no distinct difference between $CaCO_3$ alone and the $CaCO_3-TiO_2$ systems, as opposed to the $CaSO_4-TiO_2$ systems. After completion of the DTA experiments, X-ray analysis of the samples showed the presence of $CaTiO_3$ and CaO. On the basis of these results, it is considered that the reactions in the $CaCO_3-TiO_2$ systems proceed in two steps:

$$CaCO_3 = CaO + CO_2 \tag{6}$$

$$CaO + TiO_2 = CaTiO_3 \tag{7}$$

In this reaction system, no distinct difference in reactivity between anatase and rutile was recognized.

TG of $CaSO_4-TiO_2$ *system*

On the basis of the discussions in the preceding section, it is understandable that the investigation in the TiO_2-CaSO_4 systems make it possible to examine the reactivity of TiO_2 with different preparation histories.

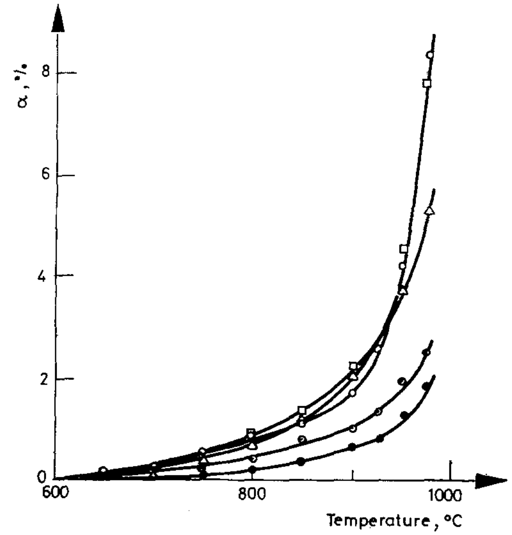

Fig. 4. TG curves for $CaSO_4-TiO_2$ systems. Heating rate: 5°/min; atmosphere: N_2 static (150 torr). TiO_2: ○, C-A; ⊙, C-R_2; ●, S–2; △, S–3; □, S–5

Figure 4 shows the TG curves of the reaction between $CaSO_4$ and five TiO_2 samples. All the curves were adapted so that the weight decrease starts at 600°, because the weight change was negligibly small below 600°. The curve for the $CaSO_4$–TiO_2 (C-A) system corresponds well to the DTA curve (b) in Fig. 3. The reactivity of the anatase group (C-A, S–3 and S–5), the fractional conversion of which increases rapidly at about 900°, is much higher than that of the rutile group (C-R_2 and S–2).

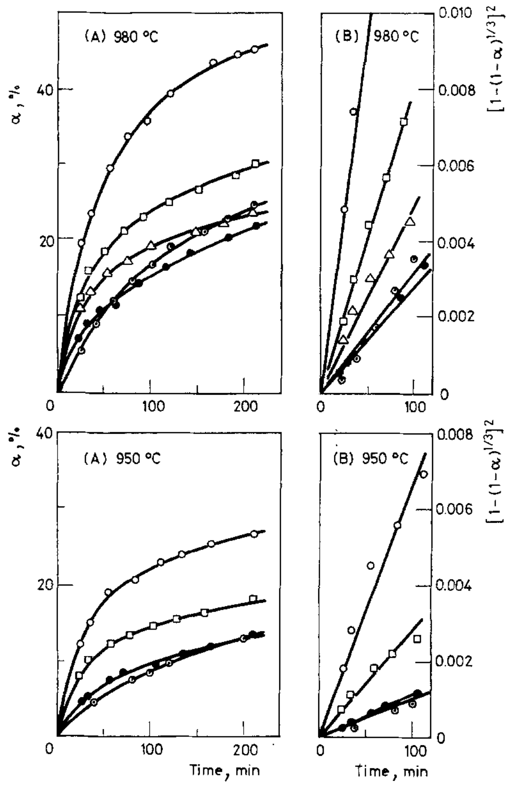

Fig. 5. (A): Isothermal TG curves at 980 (978–982°) and 950° for $CaSO_4$–TiO_2 systems in static N_2 (150 torr). (B): Jander's plots of (A) in the initial reaction step. TiO_2: ○, C-A; ⊙, C-R_2; ●, S–2; △, S–3; □, S–5

It is found that the reactivity of TiO_2 is more dependent on the crystal form rather than the particle size (*D*) or BET surface (*S*), because no distinct difference in the *D* or *S* values of the samples at the preparation temperature (700°) was recognized, except for sample S–2 (preparation temperature 900°). The question arises that *S* or *D* may decrease in a different manner with increasing temperature (Fig. 2), and this change influence the reactivity of TiO_2 at reaction temperatures above 700°. However, the *S* values of S–2 and S–3 are approximately the same at 900°, and no good correlation is obtained between the reactivity and S. On the basis of these considerations, it is thought that the formation of the intermediate thin layer, ($MO_2 \cdot CaO \cdot SO_3$), assumed in reaction (2), could be affected by the crystal form of TiO_2 at temperatures below around 900°, before the formation of $CaTiO_3$ becomes significant. If the TiO_2 samples are regarded as spherical in shape and 0.5 μm in diameter, an intermediate thin layer of about 300 Å is evaluated when the fractional conversion is 30%.

Isothermal study in $CaSO_4-TiO_2$ *system*

Figure 5(A) shows the isothermal TG curves at 980 (978–982°) and 950° for the reaction between $CaSO_4$ and five TiO_2 samples with different preparation histories. From the slopes of the α vs. t curves, a great difference in reaction rate can be found between the TiO_2 samples (C-A > S–5 > S–3 > S–2 ≈ C-R_2), as regards the initial reaction step up to about 60 min, while no distinct difference is recognized after 100 min.

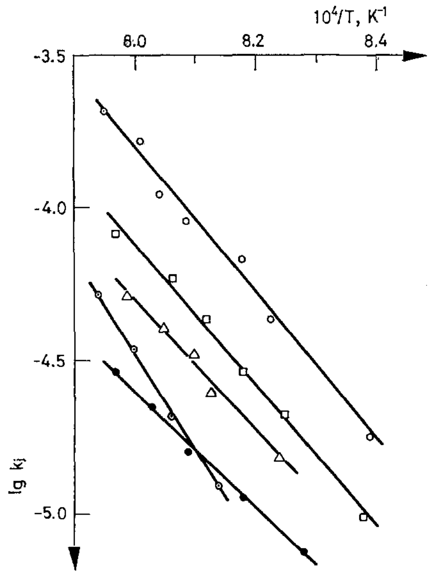

Fig. 6. log k_j as a function of $1/T$ for $CaSO_4$—TiO_2 systems. TiO_2: ○, C-A; ⊙, C-R_2; ●, S–2; △, S–3; □, S–5

Figure 5(B) shows the plots of the data for the initial reaction step as a function of time, according to Jander's equation, $k_j t = (1\text{-}/1\text{-}\alpha/^{1/3})^2$, which is based on diffusion. Kinetic data, log k_j as a function of $1/T$, are shown in Fig. 6 for five $CaSO_4-TiO_2$ systems. Activation energies estimated on the basis of Arrhenius' equation were 452, 527, 368, 389 and 435 kjoule/mole for C-A, C-R_2, S–2, S–3 and S – 5, respectively. No interesting information in connection with the reactivity of TiO_2 was obtained from the activation energy values estimated.

Figure 7 shows the relations between log k_j obtained in the initial reaction step as a measure of the reactivity of TiO_2 (in Fig. 6) and the transition temperatures of anatase to rutile (inflection points of the curves in Fig. 2) at the reaction temperatures of 950 and 980°. It is seen that the greater the stability of the anatase form up to higher temperature, the higher the reactivity of TiO_2.

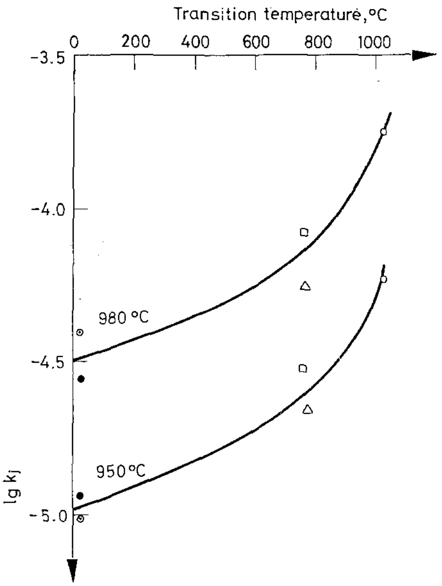

Fig. 7. log k_j at 980° and 950° for $CaSO_4-TiO_2$ systems vs. transition temperatures of TiO_2 samples. The symbols are the same as in Fig. 6

Conclusions

(1) In order to estimate the reactivities of solids, it is necessary to note the behaviors in the initial reaction step in the selected reaction system, because the reactivity is occasionally governed by the initial reaction step [5] occurring prior to the main reaction generally used for the reactivity measurements of solids.

(2) In the present study of the initial reaction steps of $CaSO_4-TiO_2$ systems, it was thought that the reactivity of the TiO_2 is dependent on the structure difference due to the different preparation histories.

References

1. T. ISHII, R. FURUICHI and H. MATSUSATO, J. Appl. Chem. Biotechnol., 28 (1978) 157.
2. R. A. SPUR and H. MYERS, Anal. Cnem., 29 (1957) 760.
3. W. F. SULLIVAN and S. S. COLE, J. Am. Ceram. Soc., 42 (1959) 127.
4. F. IMOTO and M. KANEKO, J. Chem. Sco. Japan (Ind. Chem. Sec.), 74 (1971) 591.
5. T. ISHII, Bul. of the Faculty of Engineering, Hokkaido Univ., No. 91 (1978) 103, 113.

RÉSUMÉ — On a étudié par TG, ATD et expériences cinétiques isothermes l'influence du mode de préparation de TiO_2 sur sa réactivité lors de la réaction en phase solide des systèmes $CaSO_4$ — TiO_2.

Afin d'estimer la réactivité des solides, il a été nécessaire d'observer leurs comportements lors de l'étape initiale de la réaction dans le système réactionnel choisi. On en a conclu que la réactivité de TiO_2 dépend des différences de structure dues aux différents modes de préparation et que ce composé est d'autant plus stable, à températures élevées, sous la forme d'anatase, que la réactivité de TiO_2 est forte.

ZUSAMMENFASSUNG — Der Einfluß der Herstellungsgeschichten von TiO_2 auf seine Reaktivität bei der Festphasenreaktion im System $CaSO_4$ — TiO_2 wurde durch TG, DTA und isotherme kinetische Versuche untersucht.

Zur Abschätzung der Reaktivität der Festkörper mußte ihr Verhalten während des Anfangsschrittes der Reaktion im gewählten System beobachtet werden. Es wurde gefolgert, daß die Reaktivität des TiO_2 von den durch verschiedene Herstellungsgeschichten verursachten Strukturdifferenzen abhängt und bis zu höheren Temperaturen umso stabiler in der Anatas-Form ist, je höher die Reaktivität des TiO_2 ist.

Резюме — С помощью ТГ, ДТА и изотермических кинетических методов было изучено влияние способов приготовления TiO_2 на его реакционную способность в твердотельной реакции в системе $CaSO_4$—TiO_2. Для установления реакционной способности твердых образцов, было исследовано их термическое поведение в начальной стадии реакции в избранной реакционной системе. Сделано заключение, что реакционная способность TiO_2 зависит от его структурных особенностей, обусловленных различными способами приготовления и наиболее устойчива в форме анатаза к высоким температурам и где более высокая реакционная способность TiO_2.