The Thermal Decomposition Process of Calcium Sulfite

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The thermal decomposition of calcium sulfite at temperatures below 880 °C in an argon stream was examined. Also, the reaction between calcium sulfate and calcium sulfide, which were formed during the decomposition process of calcium sulfite, was examined. The thermal decomposition process of calcium sulfite can be represented as follows: on heating calcium sulfite, the reaction, $CaSO_3 \rightarrow CaO + SO_2$, occurs above about 600 °C. Above about 680 °C, the reaction, $4CaSO_3 \rightarrow 3CaSO_4 + CaS$, occurs besides the above reaction. Furthermore, the reaction between calcium sulfate and calcium sulfide which are formed during the decomposition process of calcium sulfite, $3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2$, occurs above about 780 °C.

As regards the thermal decomposition process of calcium sulfite, Foerster and Kubel[1] have reported that the reaction, $4CaSO_3 \rightarrow 3CaSO_4 + CaS$, occurs above about 600 °C, and that the reaction, $CaSO_3 \rightarrow CaO + SO_2$, occurs besides the above reaction above about 650 °C in a nitrogen stream. Zawadzki[2] has briefly reported that the reaction, $4CaSO_3 \rightarrow 3CaSO_4 + CaS$, occurs above about 600 °C, and that the reaction, $3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2$, occurs above about 800 °C. On the other hand, Ketov and Nichkovskiĭ[3] have reported that the reactions, $CaSO_3 \rightarrow CaO + SO_2$, $4CaSO_3 + 2SO_2 \rightarrow 4CaSO_4 + S_2$, and $4CaO + 3S_2 \rightarrow 4CaS + 2SO_2$, take place successively over the temperature range of 600—800 °C in a nitrogen atmosphere.

In this report, the thermal decomposition process of calcium sulfite at temperatures below 880 °C will be described.

Experimental

A sample of $CaSO_3$ was prepared by dehydrating $CaSO_3 \cdot 1/2H_2O$ at 330 °C in an argon stream. The $CaSO_3 \cdot 1/2H_2O$ was prepared from a guaranteed reagent, $CaCO_3$, by the method based on the report of Kelly and Moore.[4]

The results of the chemical analysis of the $CaSO_3$ obtained were Ca 33.3_8, SO_3 66.4% (Calcd for $CaSO_3$: Ca 33.36, SO_3 66.64%). The Ca content in the $CaSO_3$ was determined by complexometric titration[5] after the $CaSO_3$ had been dissolved in dilute hydrochloric acid. The SO_3 content in the $CaSO_3$ was determined by decomposing the $CaSO_3$ with hydrochloric acid to convert the SO_3 to SO_2 gas in an argon atmosphere. The amount of SO_2 gas evolved was determined by volumetric iodometry.[6]

The X-ray analysis of the sample was performed with an X-ray powder diffractometer, equipped with a proportional counter, using Ni filtered Cu radiation. The X-ray diffraction data of the $CaSO_3$ are shown in Table 1. The data reported by Matthews and McIntosh,[7] which are cited in the ASTM X-ray diffraction data file, are also shown in Table 1.

The thermogravimetry(TG) and differential thermal analysis (DTA) were performed in an argon stream. A heating rate of 2.5 °C/min was employed. The sensitivity of the quartz helix used for TG was about 0.14 mg/0.01 mm. α-Al_2O_3 was used as a reference for DTA.

Table 1. X-RAY DIFFRACTION DATA OF $CaSO_3$

This work				ASTM card			
d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
5.61	5	2.468	10	5.50	2	1.63	2
4.93	5	2.417	20	3.80	5	1.57	5
3.66	10	2.362	10	3.49	5	1.47	15
3.51	15	2.338	10	3.12	100	1.40	2
3.24	55	2.259	10	2.90	60	1.28	15
3.07	100	2.151	25	2.79	5		
2.98	60	2.006	20	2.71	5		
2.92	25	1.824	20	2.61	5		
2.805	55	1.791	10	2.53	80		
2.747	55	1.647	5	2.34	20		
2.644	60	1.585	5	2.11	40		
2.592	25	1.388	5	1.93	15		
2.536	75			1.82	15		

Results and Discussion

The TG and DTA curves of $CaSO_3$ on heating are shown in Fig. 1. It was observed that the weight loss on heating $CaSO_3$ was accompanied by the evolution of SO_2 gas. The results of the X-ray analysis[8] of the samples heated up to Points A(800 °C) and B(1000 °C) are also shown in Fig. 1.

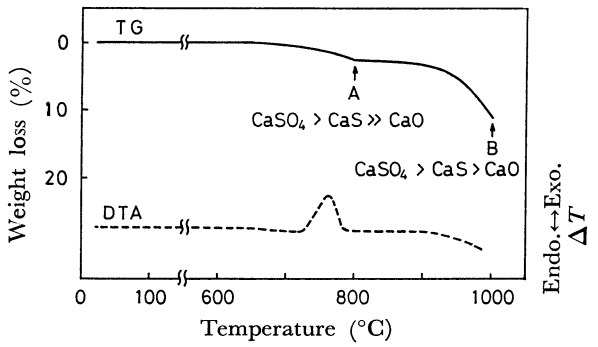

Fig. 1. TG and DTA curves of $CaSO_3$ on heating in an argon stream.

From the facts that CaO was observed in the sample heated up to Point A, and that SO_2 gas was evolved during the weight loss, it was considered that the reaction, $CaSO_3 \rightarrow CaO + SO_2$,[1,3] occurred. Also, an exothermic peak was observed at about 760 °C in the DTA curve, and the formations of $CaSO_4$ and CaS were observed in the sample heated up to Point A. From these facts, it was considered that the reaction, $4CaSO_3 \rightarrow 3CaSO_4 + CaS$,[1,2,9] occurred besides the above reaction.

Furthermore, from the facts that the X-ray diffraction intensity of CaO in the sample heated up to Point B was stronger than that in the sample heated up to Point A, and that the evolution of SO_2 gas was observed during the weight loss from Point A to Point B, it was considered that the reaction, $3CaSO_4+CaS \rightarrow 4CaO+4SO_2$,[2] occurred.

To clarify the thermal decomposition process of $CaSO_3$ in more detail, 1 g of $CaSO_3$ was placed in a quartz boat of 48 mm length, and decomposed in a straight quartz tube (26 mm i. d. and 300 mm heating length) at an argon flow-rate of 100 ml/min for 3 h under isothermal conditions at temperatures below 880 °C. The product obtained in the boat was examined by X-ray analysis. Also, the amount of SO_2 gas formed by the decomposition of $CaSO_3$ was examined. The results are shown in Table 2.

Table 2. Results of heating experiments on $CaSO_3$

Heating temp (°C)	Amount of SO_2 formed (mg)	Sample in the boat
580	—	$CaSO_3$
600	det.	$CaSO_3$
620	3	$CaSO_3$
640	4	$CaSO_3 \gg CaO$
660	10	$CaSO_3 \gg CaO$
680	19	$CaSO_3 > CaSO_4 > CaS \gg CaO$
700	33	$CaSO_4 > CaS \gg CaSO_3 > CaO$
720	31	$CaSO_4 > CaS \gg CaO \fallingdotseq CaSO_3$
740	28	$CaSO_4 > CaS \gg CaO$
760	19	$CaSO_4 > CaS \gg CaO$
780	14	$CaSO_4 > CaS \gg CaO$
800	18	$CaSO_4 > CaS \gg CaO$
840	37	$CaSO_4 > CaS > CaO$
880	83	$CaSO_4 > CaS > CaO$

From the results that the formations of SO_2 gas and CaO were observed at 600—660 °C, it was clarified that the reaction, $CaSO_3 \rightarrow CaO+SO_2$, occurred above about 600 °C. Above 680 °C, the formations of $CaSO_4$ and CaS in addition to CaO were observed; the $CaSO_3$ decreased with the increase in the temperature and was not observed above 740 °C. From these results, it was made clear that the reaction, $4CaSO_3 \rightarrow 3CaSO_4+CaS$, occurred above about 680 °C in addition to the reaction, $CaSO_3 \rightarrow CaO+SO_2$.

Above 800 °C, the amount of SO_2 gas formed was again increased; the X-ray diffraction intensity of the CaO in the product also increased with the increase in the temperature. These facts were considered to indicate a reaction between the $CaSO_4$ and CaS formed during the decomposition process of $CaSO_3$, $3CaSO_4+CaS \rightarrow 4CaO+4SO_2$. Therefore, the reaction between $CaSO_4$ and CaS was examined.

A sample of $CaSO_4$ was prepared by adding an aqueous $CaCl_2$ solution to an aqueous Na_2SO_4 solution.[10] Both the salts used were guaranteed reagents. The resulting precipitate was washed with water and dehydrated at 800 °C. A sample of CaS was prepared by heating the CaO formed by the thermal decomposition of a guaranteed reagent, $CaCO_3$, in a stream of H_2S gas at 1000 °C.[11]

One g of a mixture of $CaSO_4$ and CaS (in a molar ratio of $CaSO_4$: CaS=3 : 1) was heated at a specified temperature below 880 °C for 3 h in an argon stream. The product obtained in the boat and the amount of SO_2 gas formed were examined. The results are shown in Table 3.

Table 3. Results of heating experiments on $(3CaSO_4+CaS)$

Heating temp (°C)	Amount of SO_2 formed (mg)	Sample in the boat
760	—	$CaSO_4 > CaS$
780	3	$CaSO_4 > CaS \gg CaO$
800	9	$CaSO_4 > CaS \gg CaO$
840	21	$CaSO_4 > CaS \gg CaO$
880	71	$CaSO_4 > CaS > CaO$

The formations of SO_2 gas and CaO were observed above 780 °C, and the amount of SO_2 gas formed increased appreciably with the increase in the temperature. Also, the X-ray diffraction intensity of CaO in the product increased with the temperature. These results made it clear that the reaction, $3CaSO_4+CaS \rightarrow 4CaO+4SO_2$, occurred above about 780 °C.

From the above-mentioned experimental results, the thermal decomposition process of calcium sulfite can be represented as follows: on the heating of calcium sulfite, the reaction, $CaSO_3 \rightarrow CaO+SO_2$, occurs above about 600 °C. Above about 680 °C, the reaction, $4CaSO_3 \rightarrow 3CaSO_4+CaS$, also occurs. Furthermore, the reaction between calcium sulfate and calcium sulfide which are formed during the decomposition process of calcium sulfite, $3CaSO_4+CaS \rightarrow 4CaO+4SO_2$, occurs above about 780 °C. The thermal decomposition process of calcium sulfite revealed in this work differs from the previously reported processes mentioned above.[1-3]

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