Thermochimica Acta, 61 (1983) 375–378
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Note

THE INFLUENCE OF TITANIUM DIOXIDES, ALUMINA AND CALCIUM CARBONATE ON THE THERMAL STABILITY OF BARIUM CARBONATE

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(Received 3 August 1982)

Following our investigations on the thermal decomposition of barium carbonate in mixtures generating double oxides [1,2], in the present work we present the results concerning its thermal stability in the presence of titanium dioxides, alumina, and calcium carbonate, as reflected in the nonisothermal kinetic parameters of the reaction

$$BaCO_3(s) \rightarrow BaO(s) + CO_2(g) \qquad (I)$$

The results concerning the activation energy of the phase transition

$$BaCO_3(\text{orthorhombic}) \rightarrow BaCO_3(\text{hexagonal})$$

for different contents of alumina are also discussed.

EXPERIMENTAL

The following mixtures were used
(1) 70 wt.% $BaCO_3$, 30 wt.% TiO_2 rutile
(2) 69.6 wt.% $BaCO_3$, 29.8 wt.% TiO_2 rutile, 0.6 wt.% Al_2O_3
(3) 69.6 wt.% $BaCO_3$, 29.8 wt.% TiO_2 anatase, 0.6 wt.% Al_2O_3
(4) 70 wt.% (0.97 mole $BaCO_3$ + 0.03 mole $CaCO_3$), 30 wt.% rutile
(5) 1 mole $BaCO_3$, 0.006 mole Al_2O_3
(6) 1 mole $BaCO_3$, 0.06 mole Al_2O_3
(7) 1 mole $BaCO_3$, 1 mole Al_2O_3

A MOM derivatograph (Budapest), Paulik–Paulik–Erdey type, was used to record the decomposition curves.

Identification of the components of the mixtures and measurement of particle size were performed with the aid of a Phillips diffractometer using

0040-6031/83/0000-0000/$03.00

CrK_α radiation. Using Scherrer's formula [3] the following mean sizes were obtained: $BaCO_3$, 250 Å; TiO_2 (rutile), 350 Å; TiO_2 (anatase), 650 Å.

RESULTS AND DISCUSSION

For mixtures (1)–(4), the TG and DTG curves on the derivatograms exhibit the following two-step decomposition

$$3\ BaCO_3(s) \rightarrow (BaCO_3)_2 \cdot BaO(s) + CO_2(g) \qquad (II)$$

$$(BaCO_3)_2BaO(s) \rightarrow 3\ BaO(s) + 2\ CO_2(g) \qquad (III)$$

with the following temperatures corresponding to the maximum reaction rate

Mixture	t_{max} (°C)	
	Reaction(II)	Reaction (III)
1	910	1140
2	885	1090
3	840	1110
4	860	1140

The barium oxide reacts at higher temperatures with the titanium oxides until after heating at 1500°C, barium titanate ($BaTiO_3$) was evidenced by its diffraction lines. The intermediate of the decomposition $(BaCO_3)_2 \cdot BaO$ is a eutectic with quite a high thermal stability and was also evidenced during the decomposition of pure barium carbonate [2].

The kinetic parameters of reactions (II) and (III) were obtained using the Coats and Redfern method [4]. For both reactions the value of the apparent reaction order was found to be zero.

Values of the pre-exponential factor and activation energy for reactions (II) and (III) are given in Tables 1 and 2, respectively. In the last column of these Tables the values for the rate constants at 800°C for reaction (II) and 1000°C for reaction (III) are given.

In the case of reaction (II) a strong effect of calcium carbonate on the activation energy is observed. The important decrease of the activation energy is probably induced by calcium carbonate whose thermal stability is less than that of barium carbonate. In spite of a compensation effect (the values of the pre exponential factor vary in the same way as those of the activation energy) which determines little differences between the kinetic constants, the order of the last three $k_{800°C}$ values shows the same thermal stability range as the temperatures corresponding to the maximum reaction rate.

As far as reaction (III) is concerned, the data given in Table 3 show a decreasing effect of alumina on the thermal stability of the intermediate. This effect results from the order of the temperatures corresponding to the

TABLE 1

Pre-exponential factor, activation energy and rate constant at 800°C for reaction (II)

Mixture	Heating rate (β) (K min^{-1})	A (s^{-1})	E (kcal mole^{-1})	$k_{800^\circ} \times 10^4$ (s^{-1})
1	6.4	11	22	4.2
2	6.7	83	26	4.4
3	6.5	16	22	6.3
4	6.7	0.8	16	5.3

Table 2

Pre-exponential factor, activation energy and rate constant at 1000°C for reaction (III)

Mixture	Heating rate (β) (K min^{-1})	A (s^{-1})	E (kcal mole^{-1})	$k_{1000^\circ} \times 10^4$ (s^{-1})
1	6.4	3.7×10^5	56	2.1
2	6.7	5.6×10^4	44	4.6
3	6.5	1.0×10^4	43	3.5
4	6.4	1.1×10^2	32	3.1

TABLE 3

Activation energy values for the phase transition
$BaCO_3$(orthorhombic) → $BaCO_3$(hexagonal)

Mixture	Heating rate (β) (K min^{-1})	T (K)	E (kcal mole^{-1})
Pure $BaCO_3$		1103	517
5	2.5	1071	341
	1.0	1086	
6	2.5	1068	153
	6.7	1087	
7	2.5	1068	154
	5	1079	

maximum reaction rate as well as from the order of values of $k_{1000^\circ C}$. A compensation effect could also be observed in this case.

The resolution of reactions (II) and (III) is not so good in mixtures (5), (6) and (7) so it was not possible to determine the kinetic parameters in these cases.

In these last three systems the phase transition

$BaCO_3$(orthorhombic) → $BaCO_3$(hexagonal)

was clearly evidenced. The method given by Kissinger [5], which uses the shift of the DTA peaks with the heating rate, was used to determine the activation energy values of this phase transition. In Table 3 these values are compared with the corresponding value for pure barium carbonate [6].

A decreasing effect of alumina on the activation energy of the phase transition up to a critical value of its contents has to be noticed.

CONCLUSIONS

Alumina shows relative important effects in decreasing the thermal stability of barium carbonate in systems generating barium titanate, as well as in decreasing the activation energy for the phase transition

$BaCO_3$(orthorhombic) → $BaCO_3$(hexagonal)

Calcium carbonate induces a strong decrease of the activation energy for barium carbonate decomposition.

REFERENCES

1 S. Solacolu, M. Bulzan and E. Segal, Rev. Roum. Chim., 21 (1976) 545.
Marina Bulzan and E. Segal, Rev. Roum. Chim., 21 (1976) 651.
2 E. Segal, R. Weiss and D. Fătu, Rev. Chim. (Bucharest) 29 (1978) 533.
3 D. Bally, L. Benes and R. Mănăilă, The Diffraction of X-Rays and Neutrons, Editura Tehnică, Bucharest, p. 274 (in Romanian).
4 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 68.
5 H. Kissinger, Anal. Chem., 29 (1957) 1702.
6 R.M. Rao and P.N. Mehrotra, J. Therm. Anal., 17 (1979) 539.