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IRON COMPOUNDS IN HIGH OXIDATION STATES. IV *. KINETIC ANALYSIS OF THE REACTION BETWEEN Na_2O_2 AND $FeSO_4$

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ABSTRACT

The isothermal kinetic analysis of sodium ferrite formation by reaction between Na_2O_2 and $FeSO_4$ shows that the rate-controlling step is nuclei growth. This mechanism differs from that established in the case of the BaO_2–$FeSO_4$ system (diffusion-controlled). The appearance of Fe_2O_3 as intermediate here might be the primary cause of this different behaviour. Non-isothermal procedures appear unsuccessful in our analysis of the reaction between Na_2O_2 and $FeSO_4$.

INTRODUCTION

In a recent paper [1], we discussed the suitability of non-isothermal thermogravimetric procedures for studying formal kinetics of reactions between solids. It was then shown that, when a reaction occurs in one simple stage (as previously established for $2\ BaO_2 + FeSO_4 \rightarrow BaFeO_3 + BaSO_4 + 1/2\ O_2\uparrow$ [2]), only a single TG curve is required in order to determine the mechanism type and the kinetic parameters.

On the other hand, it was found that the oxidation of $FeSO_4$ by Na_2O_2 according to the total equation

$$3/2\ Na_2O_2 + FeSO_4 \xrightarrow[300^\circ C]{N_2} NaFeO_2 + Na_2SO_4 + 1/2\ O_2\uparrow$$

probably involves a complex mechanism. Thus, not only do the solid products obtained appear in various crystalline forms but the process (even though it is associated with one sharp and intense exothermic peak on the DTA curve [3]) implies two consecutive overlapping steps [3].

Elucidation of the formal kinetics of this reaction is the main purpose of the present paper. At the same time, the possibility (or not) mentioned above

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* For parts I–III, see Thermochim. Acta, 91 (1985) 249; 97 (1986) 243; 98 (1986) 167, respectively.

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of the exclusive use of non-isothermal procedures to analyse this kind of reaction will be argued.

EXPERIMENTAL

Samples were prepared as previously described [3] containing Na_2O_2/$FeSO_4$ at molar ratios of 5/2. Although the stoichiometric Na_2O_2/$FeSO_4$ ratio corresponding to the proposed equation is 3/2, it was shown that only in the presence of at least this excess of Na_2O_2 (5/2) does the reaction go to completion. The excess Na_2O_2 remains unreacted (in the experimental conditions used) in the reaction mixture [3].

Isothermal experiments were performed under a dynamic N_2 atmosphere (using a Setaram instrument [2]) on accurately weighted samples (ca. 200 mg) at 198, 205, 216 and 233°C.

The weight-loss data required in the non-isothermal analysis were provided by a TG curve obtained from a similar sample heated at 0.13°C min^{-1} (under the same N_2 atmosphere).

RESULTS AND DISCUSSION

In accordance with the conclusions reached in our previous work [1], we first approached the reaction by a non-isothermal kinetic study. To do this, we used the method and data treatment described in ref. 1, for checking the same models. However, the results achieved were highly unsatisfactory. Thus, in all cases, the correlation coefficient values obtained are lower than 0.9. Likewise, an inspection of the plot of α (fraction reacted) vs. T showed an inflection point in the curve (around $\alpha = 0.5$) so that the experimental points might be grouped into two sub-sets. Analysing each sub-set led to no concluding result. Only when the analysis was carried out using solely α values in the range 0.5–1.0 were the correlation coefficients obtained acceptable. Notwithstanding, even in this case, the calculated kinetic parameter values varied widely for each mechanism type and, in this way, their previous evaluation using a mathematical approach [1] could not differentiate between them.

Hence, these considerations support the previous supposition of the existence of a large difference (as shown by the oxidation states reached and also by the appearance, now in situ, of a stable intermediate) between the oxidative action of sodium and barium peroxides towards $FeSO_4$ [3]. Although problems occurring during sample handling as well as those associated with proper development of the process are higher than those observed for the BaO_2–$FeSO_4$ system [3], the experimental conditions have been thoroughly controlled. In this way, it seems unlikely that the inoperativity of the results could be attributed to a defective experimental method. The only possible alternative in the present situation seems to be the application of isothermal procedures.

Isothermal procedures

In Fig. 1 we have plotted α as a function of time (t) at several temperatures (T). Using the kinetic data (α, t pairs) obtained from the 205°C isotherm, we have assayed the same models (those proposed by Hulbert [4]) analysed for the BaO_2–$FeSO_4$ system [1]. The result of this test is shown in Fig. 2. It can be noted that, at this temperature, only model F_7 [nucleation; the m value to be used in the equation $F_7(\alpha) = K_7t^m = \ln(1-\alpha)^{-1}$ is calculated by means of the Handcock and Sharp method [5]; at 205°C, m is 0.26] yields a linear dependence over practically the whole time range. Also, this model is the only one for which the rate constant remains essentially unchanged with time. On the other hand, there is no case in which a sharp discontinuity in slope of the curve would allow it to be broken into two straight-line sections.

The validity of this model has been checked over the entire working temperature range. From the slopes of the straight lines obtained for $F_7(\alpha)$ vs. t, the following rate constant (K_7) values (s^{-1}) are extracted: K_7^{198} ($m = 0.27$) $= 9.8 \times 10^{-2}$; K_7^{205} ($m = 0.26$) $= 1.3 \times 10^{-1}$; K_7^{216} ($m = 0.24$) $= 1.6 \times 10^{-1}$; K_7^{233} ($m = 0.23$) $= 2.1 \times 10^{-1}$.

The kinetic parameters, E_a and Z, can be calculated from an Arrhenius plot ($\log K_7$ vs. T^{-1}) constructed using the above K_7 values. The data fit well to a straight line and the least-squares analysis gives $E_a = 9.8$ kcal mol^{-1} and $Z = 3.3 \times 10^3$ s^{-1}.

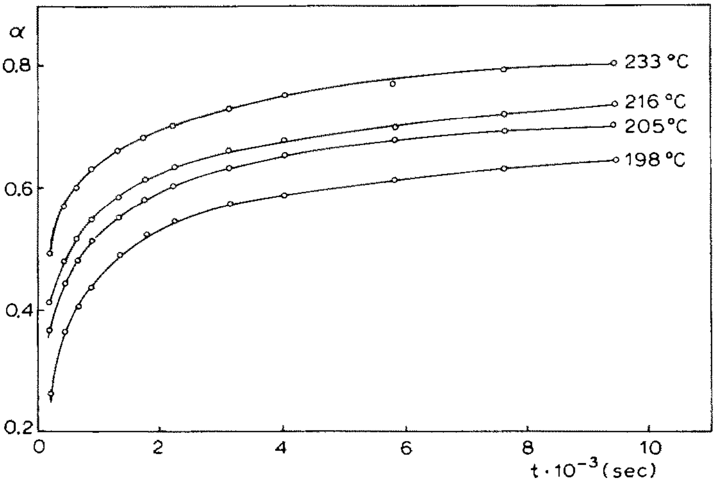

Fig. 1. Dependence of the fraction of reaction vs. temperature as a function of time.

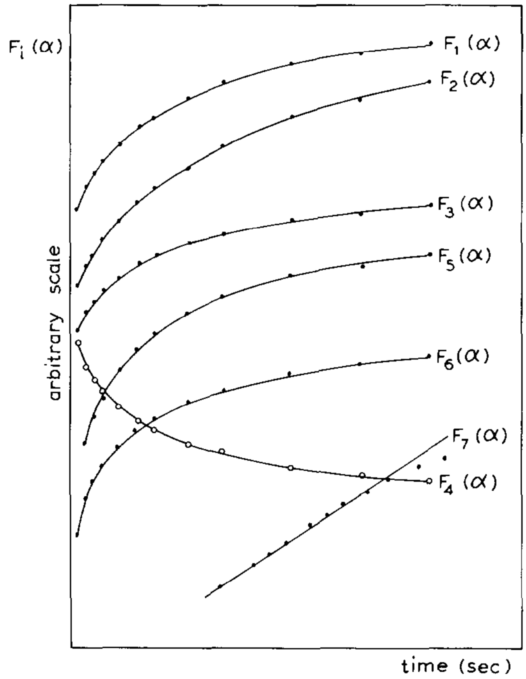

Fig. 2. Analysis of the models studied (F(α) vs. time functions).

It can be noted that these last values are significantly lower than those obtained for the BaO_2–$FeSO_4$ system ($E_a = 86.5$ kcal mol^{-1} and $Z = 2.1 \times 10^{25}$ s^{-1}).

This result is consistent with some empirical experimental observations. Thus, the DTA exothermic peaks associated with the reactions appear at 300 and 370°C for Na_2O_2 and BaO_2, respectively [2,3]. Likewise, to obtain an initially operative non-isothermal TG curve, the working heating rate must now be appreciably lower. To sum up, the reaction between Na_2O_2 and $FeSO_4$ proceeds very rapidly as compared with that occurring between BaO_2 and $FeSO_4$, thus contributing to the experimental difficulties found during its study.

After the foregoing discussion, an important question remains unanswered. Given that isothermal procedures lead to coherent results, what is the reason for the non-isothermal ones being unsuitable? It was already shown that reactions between solids occurring in one single step can be adequately analysed using only non-isothermal procedures [1]. However, in this case, not only is there disagreement between the isothermal and non-isothermal procedures but the results of the latter, when considered as a whole, are insignificant. The fact that the reaction involves two consecutive but overlapping steps, as well as the possibility of a variation in mechanism during the linear increase of temperature, might be two of the causes of this failure of non-isothermal procedures. This is an open, interesting problem which we will approach in the future.

CONCLUDING REMARKS

As has been previously shown [3], when $FeSO_4$ is oxidized by Na_2O_2 to give the sodium ferrite, $NaFeO_2$, Fe_2O_3 appears as an intermediate according to

$$FeSO_4 + 1/2\ Na_2O_2 \rightarrow 1/2\ Fe_2O_3 + 1/2\ Na_2SO_4 + 1/2\ SO_3$$

and

$$1/2\ Fe_2O_3 + 1/2\ SO_3 + Na_2O_2 \rightarrow NaFeO_2 + 1/2\ Na_2SO_4 + 1/2\ O_2 \uparrow$$

The results obtained here by isothermal kinetic analysis show that the rate-controlling process in the above two-step reaction is nucleation. Given the enhanced reactivity of the low-temperature generated oxides, it seems reasonable to assume that nuclei growth of the intermediate is the slower step of the mechanism.

Therefore, the fact that the rate of reaction between BaO_2 and $FeSO_4$ is determined by diffusion of the reactants, whereas now the oxidation follows a different mechanism type, could be attributed to the appearance of Fe_2O_3 as an intermediate. The different sizes of Na^+ and Ba^{2+} cations, allowing, in this last case, stabilization of the Fe(IV) oxidation state by means of highly favoured lattices, might be the origin of the distinctive experimental behaviour.

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