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INVESTIGATION OF BASIC ZINC SULFATE THERMAL DECOMPOSITION UNDER NITROGEN AND CARBON MONOXIDE ATMOSPHERE

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ABSTRACT

The thermal decomposition of basic zinc sulfate in nitrogen flux in the range 1070–1150 K and the reduction of this compound with carbon monoxide in the range 970–1030 K were investigated. In both cases the reaction product contained zinc oxide and, in the case of reduction, an admixture of zinc sulfide.

Hypotheses have been advanced that propose that the thermal decomposition is controlled by the reaction at the interface, whereas the thermal decomposition with reduction by carbon monoxide is limited by the nucleation processes.

The activation energies of thermal decomposition are 215.4 ± 10.9 kJ mol^{-1} for tablet samples and 253.7 ± 9.9 kJ mol^{-1} for powdered samples, whereas the activation energies for reduction by carbon monoxide are 128.6 ± 4.5 kJ mol^{-1} for tablet samples and 134.2 ± 4.9 kJ mol^{-1} for powdered samples.

INTRODUCTION

Basic zinc sulfate is a compound occurring in some metallurgical materials but not in nature. Under laboratory conditions it can be obtained by synthesizing from zinc oxide and zinc sulfate.

Basic zinc sulfate is formed at the first stage of zinc sulfate thermal decomposition [1]. It may occur as an intermediate product in reactions of zinc sulfide oxidation [2], zinc sulfate reduction with gaseous reducing agents [3] and in solid phase reaction between zinc sulfate and zinc sulfide [4].

The behavior of basic zinc sulfate at high temperatures as a function of the composition of the gaseous atmosphere is quite interesting from the viewpoint of practical metallurgy. Therefore many studies have dealt with the problem and the results obtained are reported in the literature. Most studies have been concerned with the thermal decomposition of basic zinc sulfate. Ingraham and Marier [5], Izaki and Torigama [6] and Togawa and

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Saija [7] showed that the rate of $ZnO \cdot 2ZnSO_4$ decomposition under a nitrogen atmosphere is limited by the reaction at the substrate/product interface.

However, no information is available on the kinetics of basic zinc sulfate reduction with gaseous reducing agents.

This study is an attempt to rectify this lack of information by presenting results of investigations carried out on basic zinc sulfate thermal decomposition and on the reduction of this compound with carbon monoxide.

TESTING

For determining the kinetics of basic zinc sulfate reduction with carbon monoxide several series of thermogravimetric measurements were carried out.

Reaction rates were measured for various gaseous atmosphere compositions, temperatures and sample types. Moreover the reacting agents were subjected to X-ray phase analysis and microscopic examination.

Test materials

The materials used in testing were analytically pure heptahydrous zinc sulfate (POCh, Gliwice), analytically pure zinc oxide (Reachim, Moscow) and formic acid (POCh, Gliwice). The first step consisted of sulfate dehydration by roasting at 373, 533 and 653 K. Then the mixture of anhydrous zinc sulfate and zinc oxide with a correct proportion of excess zinc sulfate was sintered twice, at 873 and 973 K. For stabilizing purposes the second sintering was carried out in an atmosphere containing sulfur dioxide. The product obtained ($ZnO \cdot 2ZnSO_4$) was subjected to X-ray phase analysis.

The preparations used for testing were in the form of a powder (0.3–0.5 mm) and cylindrical tablets (6 mm diameter, about 1 mm high). The tablets were pressed in a steel die under a pressure of 500 MPa.

Carbon monoxide was obtained from formic acid and hydrogen contained in a cylinder (Polgaz, Pszczyna).

Apparatus and testing method

The reaction rate was determined thermogravimetrically in a Mettler TA-1 thermobalance.

Samples of powdered zinc sulfate were placed into small alumina crucibles (6 mm in diameter, 10 mm high) and tablet samples were placed on a perforated platinum plate. After the sample had been introduced into the reacting zone on the balance pan, air was pumped out of the space, the reacting mixture was introduced into it and the flow rate was determined under atmospheric pressure. Then the samples were preheated to the preset temperature at a constant rate of 15 K min^{-1}; the flow rate was measured under the sample with a Pt–PtRh10 thermocouple. Consequently, under critical conditions (when a constant temperature was reached) the samples were already partly reacted.

A gas flow rate of 16 l h^{-1} was established experimentally so as to allow the influence of external mass transport on the rate of mass decrement to be disregarded. Nitrogen or a carbon monoxide–nitrogen mixture was apportioned by means of a system of rotameters, a gas mixer and an Infralyt 2T analyzer. The magnitudes of the weighed portions were also chosen experimentally. When varying the initial mass within the 25–400 mg range all samples with a mass below 100 mg were found to have similar kinetic curves. This may indicate that within this range the influence of intergranular diffusion on the reaction kinetics may be disregarded.

The weighed portions of the samples used for the measurements were 40 and 50 mg. The products were subjected to X-ray phase analysis (Kristalloflex 4) and microscopic examination in a JEOL microscope.

RESULTS

Measurements of the rate of basic zinc sulfate thermal decomposition in nitrogen flux

The test temperature was varied within the range 1070–1150 K. Figure 1 shows a typical example of the pattern of the kinetic curves, where full lines refer to the tablet sample and broken lines refer to the powdered preparation.

The relationships presented prove that for the tablet sample the rate of thermal decomposition decreases according to a convex curve, whereas for the powdered sample a constant decrease is observed. Such patterns explain why an R-type kinetic model (control at the interface) is adopted to interpret the experimental data [8].

The best representations of these curves were obtained using an R2 model for the tablets and an R1 model for the powder in the crucible. This is illustrated in Figs. 2 and 3. On this basis it may be assumed that the rate of thermal decomposition

$$ZnO \cdot 2ZnSO_4 = 3ZnO + 2SO_2 + O_2 \qquad (1)$$

is controlled by the reaction at the substrate/product interface.

Reaction (1) stoichiometry was determined from the composition of the product obtained using X-ray phase analysis.

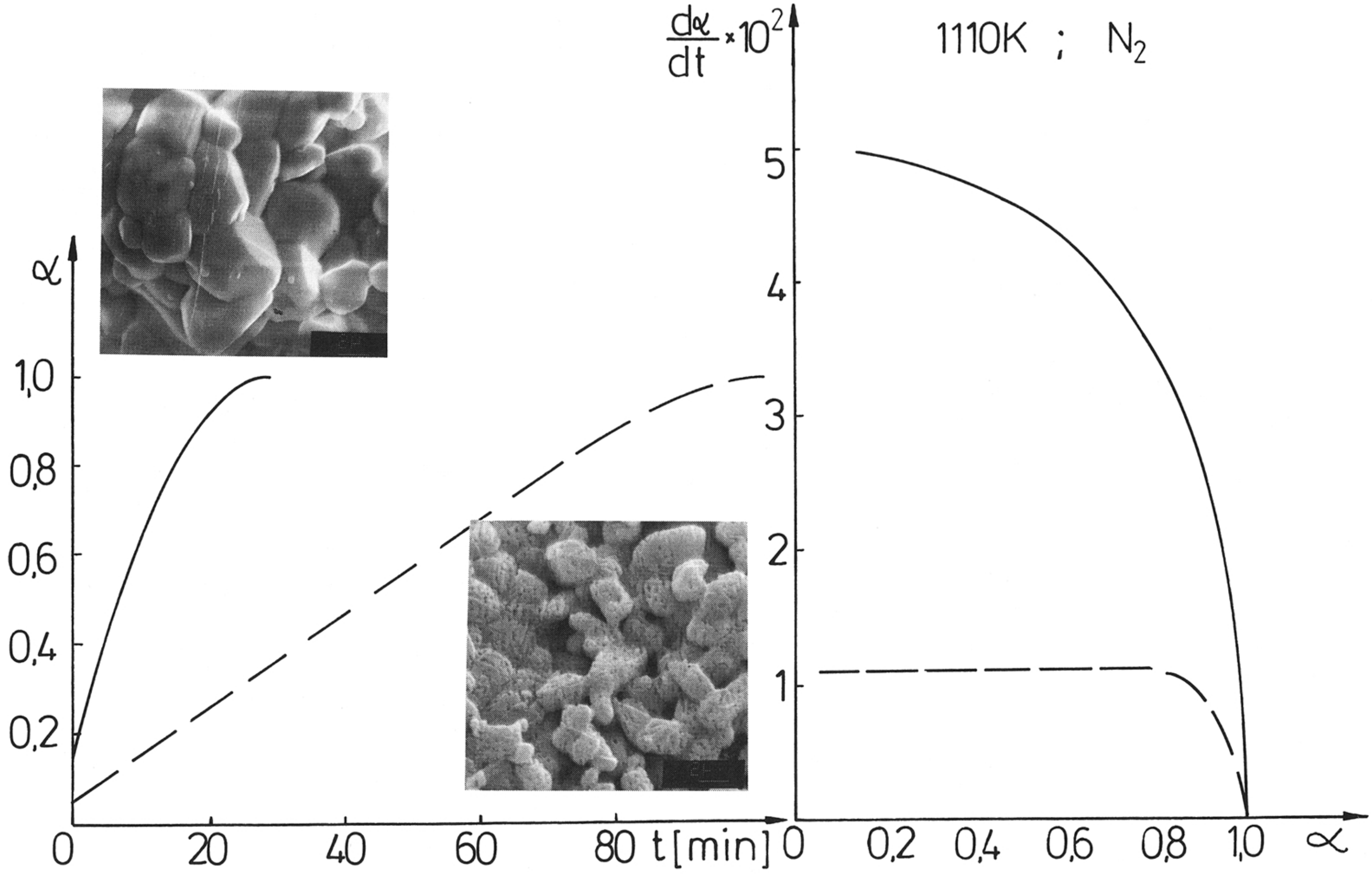

Fig. 1. Kinetic curves and scanning photomicrographs for basic zinc sulfate thermal decomposition in nitrogen flux: (a) decomposition degree vs. time; (b) decomposition rate vs. decomposition degree (upper photograph, substrate; bottom photograph, product).

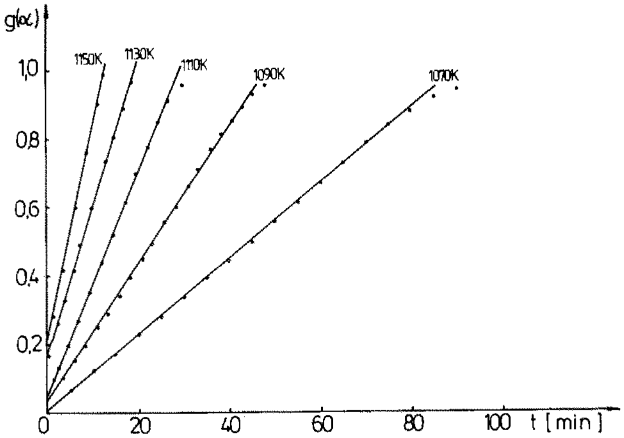

Fig. 2. Illustration of the R2 kinetic model; $g(\alpha)=1-(1-\alpha)^{1/2}$, matching with the experimental data obtained for the thermal decomposition of the $ZnO \cdot 2ZnSO_4$ tablet.

Measurements of the rate of basic zinc sulfate reduction with carbon monoxide

The rate of basic zinc sulfate reduction was measured at 1046 K with a carbon monoxide concentration of between 5 and 50% in the mixture with nitrogen and in the range 970–1130 K with a carbon monoxide concentration of 20%.

The kinetic curves obtained for various CO concentrations (Fig. 4) prove that a proportional relationship exists between the reaction rate and the reducing agent concentration.

Figure 5 is an illustration of the influence of the type of sample on the reduction reaction kinetics. The patterns of the curves are sigmoidal, show-

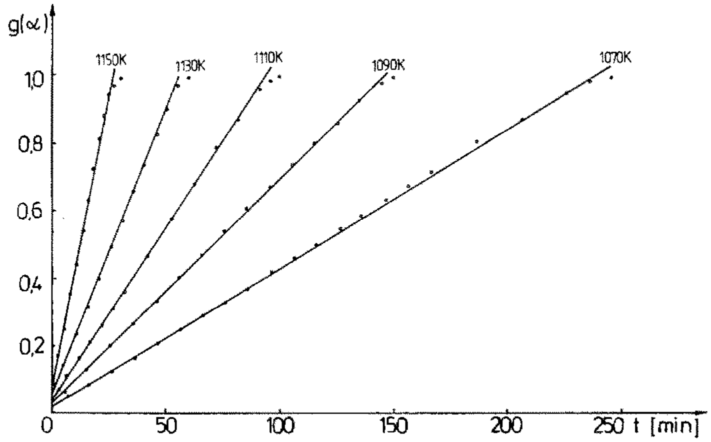

Fig. 3. Illustration of the R1 kinetic model; $g(\alpha)=\alpha$, matching the experimental data obtained for the thermal decomposition of $ZnO \cdot 2ZnSO_4$ powder in a crucible.

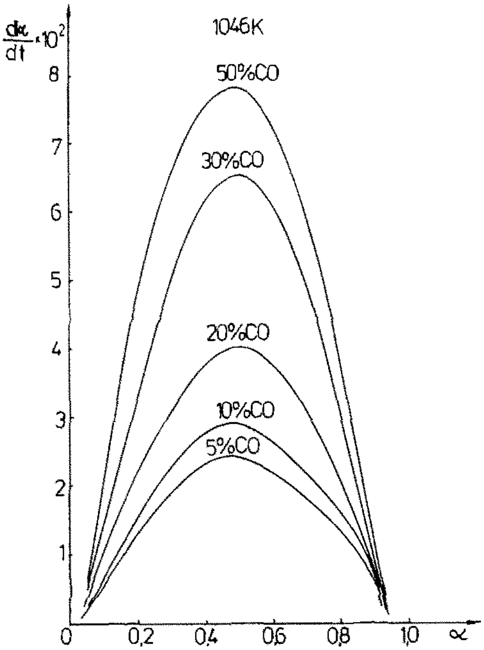

Fig. 4. Influence of carbon monoxide concentration in the mixture with nitrogen on the rate of basic zinc sulfate reduction at 1046 K [9].

ing a reaction rate maximum. This explains why nucleation models can be applied for interpreting these curves. It was found that the curves are best represented by a Prout–Tompkins (F4) model which is confirmed by the diagrams in Fig. 6.

The phase analysis revealed the occurrence of a two-phase product. The prime product was zinc oxide with zinc sulfide as an admixture. The fraction of the latter in the products decreased with increasing temperature.

Such a result may be attributed to the following chemical reactions

$$ZnO \cdot 2ZnSO_2 + 2CO = 3ZnO + 2CO_2 + 2SO_2 \qquad (2)$$

$$ZnO + 3CO + SO_2 = ZnS + 3CO_2 \qquad (3)$$

Reaction (3) should be considered as secondary.

DISCUSSION OF RESULTS AND SUMMING UP

The photographs presented (taken using a scanning microscope) show that both in the thermal decomposition and in the reduction reactions a system of gaps and pores develops inside the samples and the product grains are smaller than the substrate grains. Therefore mass transport resistances inside the samples may be disregarded.

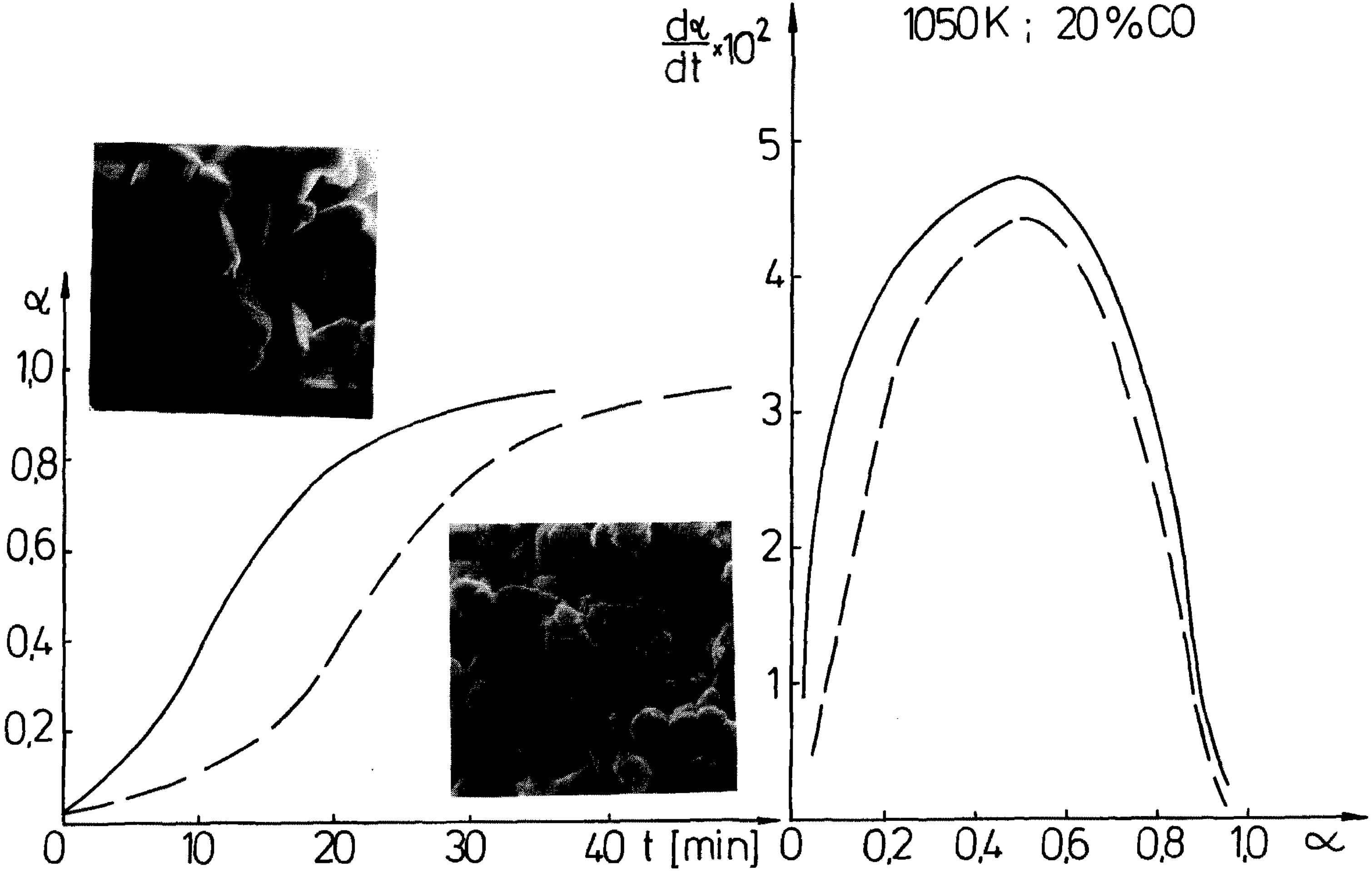

Fig. 5. Kinetic curves and scanning photomicrographs for basic zinc sulfate reduction with carbon monoxide: (left) reduction degree vs. time; (right) reduction rate vs. reduction degree (upper photograph, substrate; bottom photograph, product).

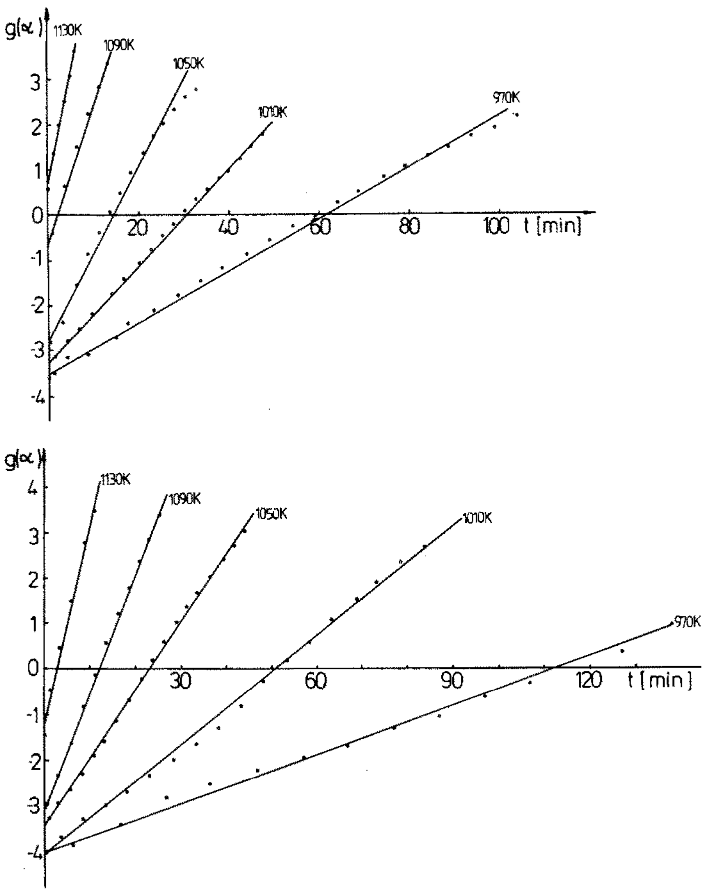

Fig. 6. Illustration of F4 model, $g(\alpha) = \ln(\alpha/(1-\alpha))$, matching the experimental data obtained for the reduction of basic zinc sulfate with carbon monoxide: (top) samples as tablets, (bottom) samples as powder in a crucible.

The analysis of the patterns of the kinetic curves and the adoption of the methods of kinetic model differentiation reported in ref. 8 have allowed us to advance a hypothesis concerning the control of the rates of the reactions investigated.

It is presumed that in the case of thermal decomposition the process is limited at the substrate/product interface, whereas for reduction with carbon monoxide the rate is controlled by the processes of nucleation and nuclei growth in branched chains.

The energies of the processes examined can be determined using the Arrhenius equation. Figures 7 and 8 are illustrations of the Arrhenius relationships for the thermal decomposition and reduction of basic zinc sulfate. The parameters of the Arrhenius equation were determined on the basis of reaction rate constants calculated both by integration and differentiation.

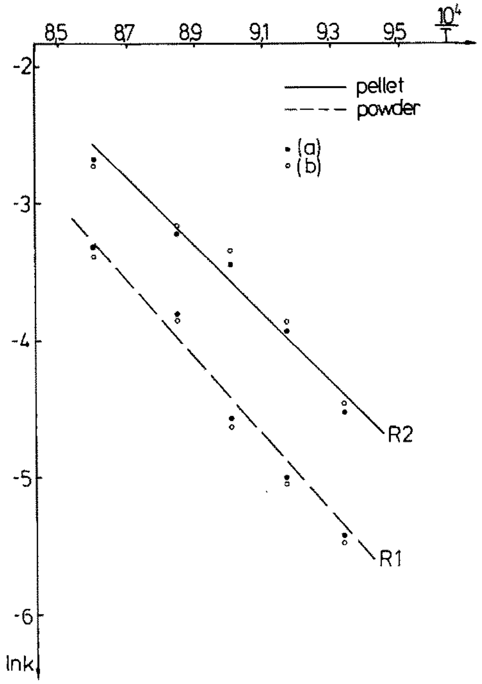

Fig. 7. Arrhenius relationship for basic zinc sulfate thermal decomposition in nitrogen.

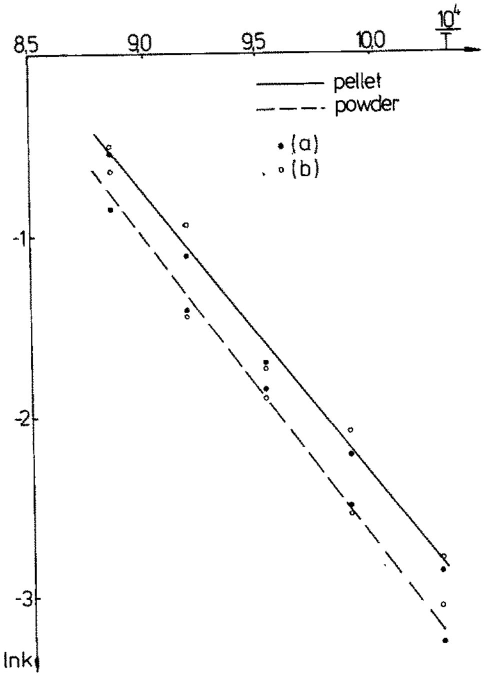

Fig. 8. Arrhenius relationship for basic zinc sulfate reduction with carbon monoxide.

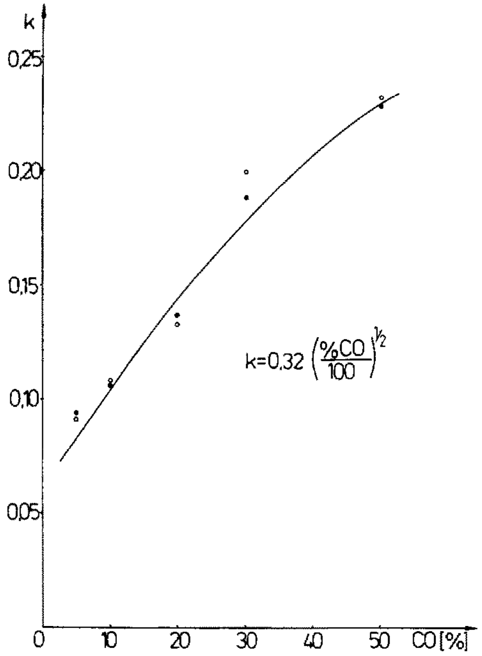

Fig. 9. Influence of carbon monoxide concentration in the mixture with nitrogen on the reduction reaction [9].

The activation energy values obtained for the thermal decomposition reaction are 215.4 ± 10.9 kJ mol^{-1} for tablets and 253.7 ± 9.9 kJ mol^{-1} for powder. These values are close to those reported in the literature and to those obtained for rate control at the interface: 243.9 kJ mol^{-1} [5], 245.2 kJ mol^{-1} [6] and 238.5 kJ mol^{-1} [7].

The activation energies obtained for the reduction of basic zinc sulfate with carbon monoxide are 128.6 ± 4.5 kJ mol^{-1} for tablets and 134.2 ± 4.9 kJ mol^{-1} for powder.

The activation energy of reduction is lower than the activation energy of thermal decomposition despite the similarity in the composition of the products.

It may be concluded that the reduction reaction proceeds at a lower potential barrier than the reaction of thermal decomposition. This is also illustrated by the comparison of reduction and decomposition initial temperatures. Under experimental conditions their values are 943 K and 1033 K, respectively.

The influence of the concentration of reducing agent on the constant rate of the reduction reaction is shown in Fig. 9. At a constant temperature the reduction of basic zinc sulfate is of the order $\frac{1}{2}$ with respect to the concentration of the reducing agent in the carbon monoxide–nitrogen mixture.

CONCLUSIONS

The following conclusions may be formulated on the basis of the reported results.

1. Basic zinc sulfate undergoes thermal decomposition in a nitrogen atmosphere at temperatures above 1033 K. In a carbon monoxide atmosphere basic zinc sulfate undergoes reduction at temperatures above 943 K. Zinc oxide is formed in both cases. A zinc sulfide admixture appears in the products in the presence of carbon monoxide as a result of a secondary reaction between zinc oxide and sulfur dioxide.

2. The rate of basic zinc sulfate thermal decomposition is controlled at the substrate/product interface.

3. The reduction of basic zinc sulfate by carbon monoxide is controlled by nucleation and nuclei growth in branched chains. The reaction is of the order $\frac{1}{2}$ with respect to the carbon monoxide concentration in the mixture with nitrogen.

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