Thermochimica Acta, 92 (1985) 177-180
Elsevier Science Publishers B.V., Amsterdam

THERMAL DECOMPOSITION OF $CuCrO_4$

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ABSTRACT

The kinetics, mechanism and activation energy of isothermal decomposition of $CuCrO_4$ was studied using isothermal TG measurements and X-ray high temperature technique in air and flowing atmosphere.

The rate of oxygen release in the decomposition measured by the isothermal TG method obeys Avrami-Erofeev equation with $n = 2$ and with activation energy values /248±8/ and /229±8/ kJ/mol in air and flowing atmosphere of nitrogen, respectively.

Decomposition of the crystalline portion of $CuCrO_4$ studied by X-ray diffraction follows the first order kinetics with activation energy E =/262±4/ kJ/mol.

INTRODUCTION

By thermal decomposition of $CuCrO_4$, a well known Adkins catalyst may be obtained /1-3/ according to the equation

$$2\ CuCrO_4 \longrightarrow CuO + CuCr_2O_4 + 1.5\ O_2 \qquad (1)$$

The system $CuO + CuCr_2O_4$ is active in several oxidation, hydrogenation, dehydrogenation, alkylation etc. reactions.

In this paper, we have studied the isothermal decomposition of $CuCrO_4$ according to the eq. (1) by TG method and X-ray analysis in order to determine the kinetics, mechanism and activation energy of the process.

EXPERIMENTAL

Copper chromate was obtained by the mixing of aqueous solutions of $Cu/NO_3/_2$ and $/NH_4/_2Cr_2O_7$ according to the scheme

$$2\ Cu^{2+} + /Cr_2O_7/^{2-} + 2\ /OH/^- = 2\ CuCrO_4 + H_2O \quad (2)$$

The solutions were evaporated to the dryness. The precursor thus obtained was heated at 500 K in air for 4 h in order to eliminate the volatile components and to decompose the nitrate. The phase purity of the powder sample of $CuCrO_4$ was checked by X-ray diffraction and by weight loss during heating according to the reaction (1).

The kinetics of the isothermal decomposition were studied thermogravimetrically in the static air and the flowing atmosphere of N_2 /1 cm^3s^{-1}/ using a DuPont 990 Thermoanalyzer /TGA 951 module/

Proceedings of ICTA 85, Bratislava

on 15-20 mg powder samples. Fraction decomposed α was calculated from the isothermal weight losses in time "t" divided by the theoretical total weight loss of the reaction (1) : 13.37 % 0 /found 13.30 %/. The plots of α vs. t for decomposition in the static air and in the flowing N_2 are shown in Fig. 1 and 2.

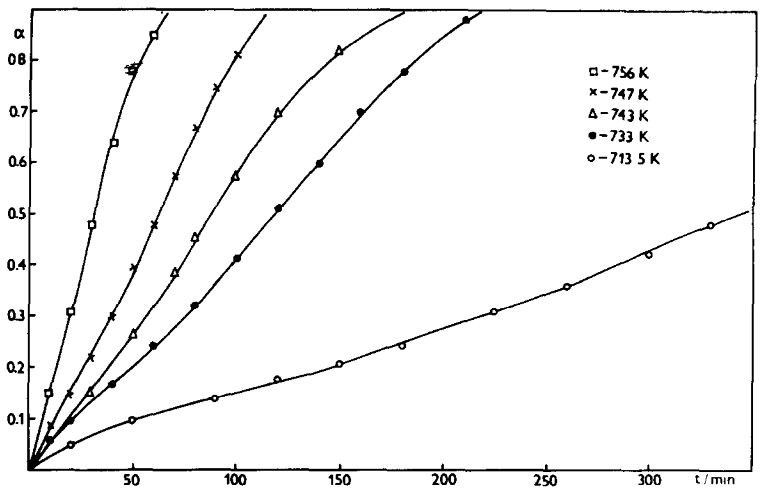

Fig. 1. TG isothermal patterns $\alpha = f/t/$ for decomposition of $CuCrO_4$ in static air.

The rate of $CuCrO_4$ decomposition was also checked by the high temperature X-ray powder diffraction method in static air using a Rigaku Denki high temperature powder diffraction device and CuK_α radiation. The change of the integral intensities of the selected h, k, l - reflections corresponding to the dissociating crystalline $CuCrO_4$ were evaluated as a function of time at different temperature levels. Fraction decomposed α was calculated from the relation $\alpha = (1 - I_t/I_o)$, where I_t is the integral intensity I_{hkl} at time "t" and I_o the same reflection at the beginning of the reaction. The results of these measurements are shown in Fig. 3.

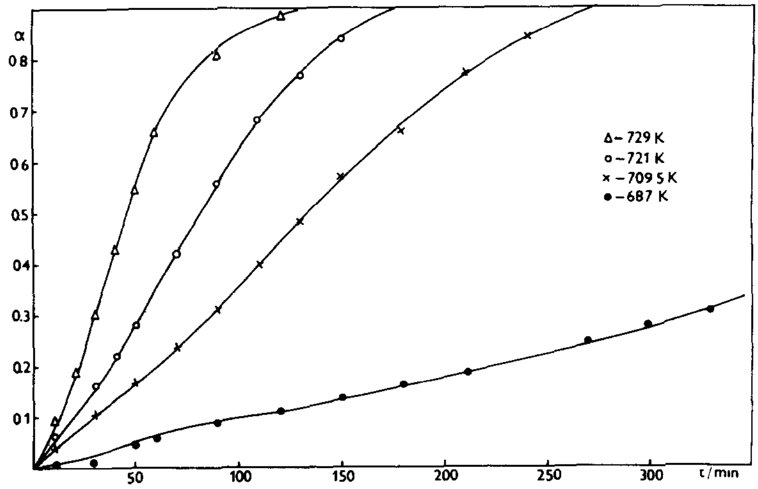

Fig. 2. TG isothermal patterns α = f/t/ for decomposition of $CuCrO_4$ in flowing N_2.

RESULTS AND DISCUSSION

The TG isothermal plots for decomposition of $CuCrO_4$ in both static /air/ and dynamic /N_2/ atmospheres exhibite less pronounced induction period followed by typical acceleratory and decay periods. Isothermal data were compared with the model functions based on diffusion, nucleation and growth and on the phase boundary control of the rate limiting step /4, 5/. Isothermal TG plots in both experimental conditions obey the model of Avrami-Erofeev equation

$$[- \ln (1 - \alpha)]^{0.5} = kt \qquad (3)$$

over the range α = 0.2-0.9. This indicates that the oxygen release according to the eq. (1) is controlled through the flat nuclei formation and its growth followed by the overlapping of the product nuclei and the decreasing of the reaction rate in decay period. From Arrhenius relation the values of activation energy E = /248±8/ kJ mol^{-1} /in static air/ and E =/229±8/ kJ mol^{-1} /in flowing nitrogen/ were found.

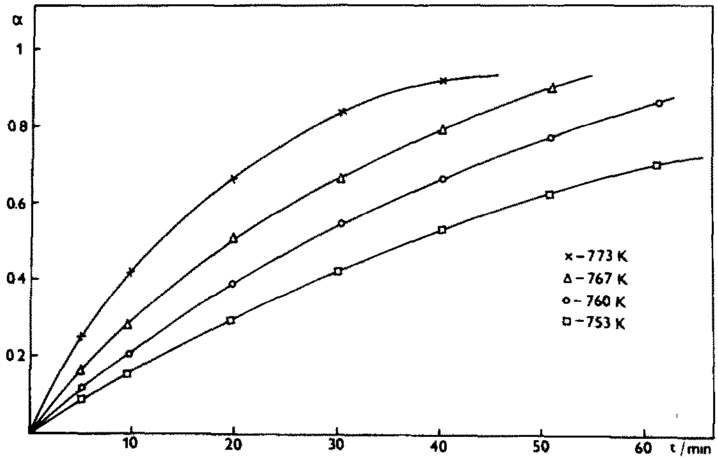

Fig. 3. Isothermal patterns $\alpha = f/t/$ for decomposition of $CuCrO_4$ in static air determined by X-ray high temperature diffraction method.

The decomposition of the crystalline portion of $CuCrO_4$ studied by high temperature X-ray diffraction method /Fig. 3/ obeyed the first-order kinetic equation

$$\ln /1 - \alpha/ = - kt \quad (4)$$

The corresponding activation energy for the transformation of the crystalline $CuCrO_4$ into amorphous form in air in /262±4/ kJ mol^{-1}.

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