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SIMULTANEOUS TG AND DTA FOR STUDY OF KINETIC OF ALKALIC SUPEROXIDES DECOMPOSITIONS

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INTRODUCTION

Special attention has been given to studies of reactions with alkalic superoxides. particularly from the standpoint of their application in practice. Some papers on reaction rate of decomposition reaction of sodium potassium superoxide are known[1.2]. Iz was shown that the presence of moisture and carbone dioxide[3] was very important for the reaction.

Macrokinetics investigations including observation of the reaction kinetics under real conditions to take into consideration mass and heat transfer.

As following of the kinetics is associated with dependance of the reaction rate on the parameters defining the given system (temperature. pressure. composition. particle distribution and size. concentracion etc.). the procedure used for determination of the kinetic parameters has the principal role in this work. Definition of the formal reaction order-n. activation energy-E and pre-exponentional factor (frequency factor)-Z may be carried out on the basis of the non-isothermal thermogravimetric method or differential thermal analysis.

Definition of the kinetic parameters on the basis of the non-isothermal thermogravimetric method is known as the dynamic thermogravimetric method. Differential or integral procedure of TGA is applied.

1. EXAMINATED SYSTEM

For the examination of experimental system was used the simultaneous TG DTA analyser - Stanton Redcroft Ltd. model TR-HT(TGA) and STA 661/667 (DTA) with general technical characteristics:

- max temperature	1400°C
- rate of heating	1 revolution on 3.6. 8. 12. 24 or 168 hours. t.i. 5°C/min
- atmosphere	air or protective gas
- weight of sample	2.10^{-2} - 20 g
- registration DTA. μV/mm	0.16 - 1.6

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- registration of temperature on TGA .... 0.2 - 0.5°C/cm
- registration of temperature on DTA .... 0.005 - 0.5°C/cm

The sodium superoxide was the comercial product of 70.5 % w. NaO_2 11% w. Na_2O. 3% w. NaOH, 0.5% w. Na_2CO_3 and 15% w. CaO.

The potassium superoxide was sintetised in own laboratory with 92 - 95% w. of KO_2.

2. EXPERIMENTAL WORK

Thermogravimetric examinations were not performed up to the decompositional sodium and potassium superoxides to their lowest oxides. i.e. to NaO_2 and KO_2. As only superoxide oxygen. in literature known as "active" oxygen. was interest for kinetic measurements. the samples were heated up to 300°C. Above this temperature it was characteristic that there occured solid solutions with above 380-400°C. losing oxygen. turn into peroxides. For our investigations. was used the kinetic expression according Coats - Redfern[5,6]:

$$\log \frac{1-(1-\alpha)^{1-n}}{T^2\,(1-\alpha)} = \log \frac{Z\cdot R}{Q\cdot E}\left(1-\frac{2RT}{E}\right)\frac{-E}{2.3\,R} \qquad \dots (1)$$

Our experimental data were presented in Fg. 1 (for NaO_2) and fg. 2 (for KO_2). The results indicated the existance of linear dependence for the reaction order n = 2,3 (Fg. 1) and n = 1.89 (Fg. 2). The activation energy in those cases are 142 kJ/mol for sodium superoxide and 175 kJ/mol for potassium superoxide.

The kinetic expression according Vachuska-Voboril:

$$\frac{(d^2\alpha/dt^2)T^2}{(d\alpha/dt)(dT/dt)} = -n\,\frac{d\alpha/dt}{1-\alpha}\cdot\frac{T^2}{dT/dt}+\frac{E}{R} \qquad \dots (2)$$

gived the results for sodium superoxide. n = 2,08 and E = 147 kJ/mol and for the potassium superoxide. n = 1.89 and E = 179 kJ/mol.

For the decomposition reaction macrocinetics was used. also, the defined dependence between the factor of DTA curve form and reaction order. We carried out the calculation of the kinetic parameters of the thermal decomposition reaction of sodium and potassium superoxide applying the equation according to Kissinger.[6]:

$$\frac{E\,dT/dt}{R\cdot T_m^2} = Z\cdot n\left(\frac{x}{V_m}\right)^{n-1} e^{-E/RT_m} \qquad \dots (3)$$

or

$$S = 0.63\ n^2 \qquad \dots (4)$$

where S-is the factor of curve forme. By analysing the experimental values for the factor of forme -S it was obtained the next results.

for sodium superoxide - NaO_2

S-factor	1.92 and 2.40
formal kinetic order reaction-n	2.0 ± 0.07 and 2.14 ± 0.17

for potassium superoxide - KO_2

S-factor	1.448 and 1.458
formal kinetic order reaction-n	1.91 ± 0.09 and 1.76 ± 0.06

In the basis of the data obtained in this vay the calculated activation energy of decomposition of sodium superoxide is 175 kJ/mol and of potassium superoxide is 239 kJ/mol.

CONCLUSION

For styding the decomposition reaction kinetics of sodium and potassium superoxides there were applied the method of the thermogravimetry and of the differential thermal analysis. On the basis of dynamic kinetic express according Coats - Redfern. Vachuska - Voboril and Kissinger it was found that the value of the activation energy for the thermal decomposition reaction of potassium superoxide was 198 kJ/mol (midle value) and for the decomposition reaction of sodium superoxide was 179 kJ/mol (midle value).

The mean value for the formal order of the decomposition reaction of sodium superoxide was 2.08 and for decomposition reaction of potassium superoxide was 1.86.

By comparing the values for the activation energy of decomposition reaction of sodium superoxide and potassium superoxide. one can state that the activation energy value for KO_2 was slightly greater than the value for NaO_2.

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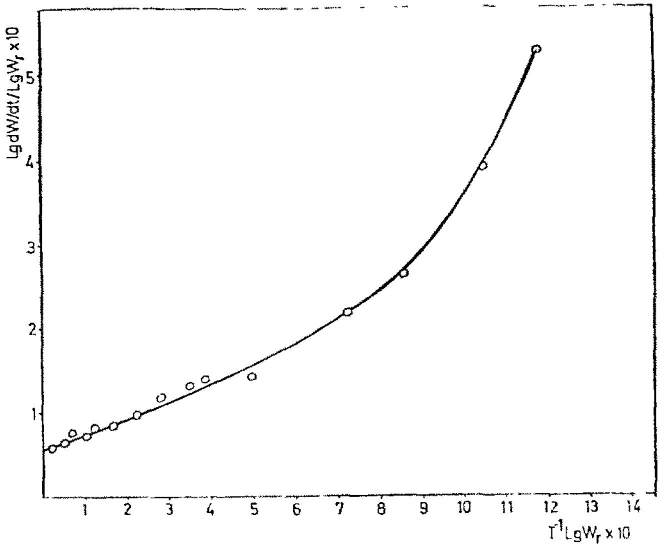

Fig. 2. Decomposition kinetics of sodium superoxide (the Freeman Carroll equation)