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CALCULATION OF KINETIC PARAMETERS FROM TG CURVE ON THE BASE OF DEHYDRATION PROCESS OF HYDROUS TITANIUM DIOXIDE

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A direct method of evaluating of kinetic equation parameters based on TG curve is proposed. The method was applied to calculate kinetic parameters of the process of dehydration of hydrous titanium dioxide.

Very often during investigations of reactions proceeding in nonisothermal conditions it is essential to define parameters of kinetic equation. In literature a number of methods is described to solve this problem. The well known methods are Freeman and Carrol [1], Coats and Redfern [2] etc. This kind of methods belongs to graphic group. The other technique is calculation of kinetic equation parameters by substituting a properly reduced approximating function for a kinetic equation [3]. These methods introduce an error, which in some cases may occur too significant.

In this paper a direct method of evaluating of kinetic equation parameters of the process of dehydration of hydrous titanium dioxide on the base of TG curve is presented.

Kinetics of dehydration process

Reaction of thermal decomposition in a solid state can be expressed by the common equation:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

where $d\alpha/dt$ is the reaction rate, α - degree of transformation defined as:

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$$\alpha = \frac{w}{w_\infty} \tag{2}$$

The rate constant k is related to temperature by Arrhenius type equation:

$$k = A \exp(-E/RT) \tag{3}$$

The function of $f(\alpha)$ is expressed by frequently used form:

$$f(\alpha) = (1-\alpha)^n \tag{4}$$

where n - the order of reaction, in this case has only empirical significance. Substituting (4) and (3) into Eq. (1) gives:

$$\frac{d\alpha}{dt} = A \exp(-E/RT)(1-\alpha)^n \tag{5}$$

Considering a constant rate of temperature changes:

$$\frac{dT}{dt} = q \tag{6}$$

Eq. (5) can be transformed as follows:

$$\frac{d\alpha}{dT} = \frac{A}{q} \exp(-E/RT)(1-\alpha)^n \tag{7}$$

Separating variables:

$$\frac{d\alpha}{(1-\alpha)^n} = \frac{A}{q} \exp(-E/RT)\, dT \tag{8}$$

Integrating:

$$\frac{1-(1-\alpha)^{n-1}}{(n-1)(1-\alpha)^{n-1}} = \frac{A}{q} \int_0^T \exp(-E/RT)\, dT \tag{9}$$

Transformation in relation to α leads to:

$$\alpha = 1 - \left[\left(A\,(n-1) \int_{0}^{T} \exp(-E/RT)\,dT + q \right) / q \right]^{-\frac{1}{n-1}} \tag{10}$$

Experimental

The above equation was applied to calculate kinetic parameters from TG curve obtaining during thermal decomposition of hydrous titanium dioxide. The sample of hydrous TiO_2 previously dried up to constant mass in the temperature of 105° was investigated using MOM 1500 derivatograph.

On the basis of the experimental data and Eq. (10) applying the Romberg's and Marquardt's methods the following values of the parameters were evaluated:

$$A = 142127.4\ \text{min}^{-1}, \quad E = 49366.5\ \text{J/mol}, \quad n = 4.64.$$

On Fig. 1 the experimental data and the values calculated from Eq. (10) are presented. Both experimental and calculated values are in good agreement.

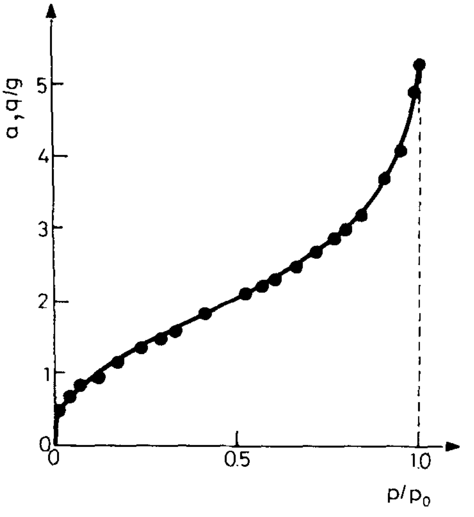

Fig. 1 Experimental and calculated values of degrees of transformation for the process of dehydration of hydrous titanum dioxide • - experimental data, — - calculated values

Conclusions

The method mentioned is relatively simple and enables to calculate values of the parameters with a required accuracy for various types of kinetic equations. The method omits the step of tabling, graphics and finding approximation functions.

References

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2 C. D. Doyle, J. Appl. Polym. Sci., 5 (1961) 285.
3 R. K. Agraval, J. Thermal Anal., 32 (1987) 149.

Zusammenfassung — Es wird ein direktes Verfahren zur Bestimmung der Parameter der kinetischen Gleichung auf der Basis von TG-Kurven gegeben. Das Verfahren wurde zur Berechnung der kinetischen Parameter des Dehydratationsprozesses von wasserhaltigem Titandioxid benutzt.