

Kinetics of thermal destruction of highly porous anion-exchange resin TOKEM-320Y

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Abstract. Temperature characteristics, stages and thermal effects of the processes occurring during the thermolysis of TOKEM-320Y anion-exchange resin in an atmosphere of air were determined by differential thermal analysis. The activation energies and the orders of reactions of thermal decomposition of the resin were calculated by the Kissinger and Metzger-Horowitz methods using the TG curves obtained at different heating rates of the resin. Models are proposed that most accurately describe the decomposition of TOKEM-320Y in air in the temperature range 25–800 °C.

1. Introduction

A great deal of attention is currently paid to hollow spheres of metal oxides which are intensively investigated for applications like controlled release capsules for drugs, fillers, filters [1], gas sensitive materials [1, 2] and catalysts [3–6].

Among other core-shell techniques of hollow spheres production, thermal decomposition of ion-exchange resins preliminarily loaded with the metal ions is truly a low-cost, easy scale-up and facile method [1, 3–5]. The crystalline framework in the obtained spherical agglomerates will have high structural stability at higher temperature and/or other rigorous conditions [4]. This method has been studied since the 1989s [7]. Later this procedure was used for preparing spherical particles of Fe₂O₃ [8], porous ZrO₂/Al₂O₃ macrobeads [4], catalytically active TiO₂-SiO₂/M_xO_y spheres (M = Co, Cr) [6], MoO₃ microspheres [1] and MoO₃-TiO₂-SiO₂ composites [5]. A number of studies have shown that the properties of oxide materials with spherical form of agglomerates depend not only on the chemical composition of the oxides but also on ion-exchange resins [1, 3–6]. Despite numerous studies, it is still an urgent problem to select an ion-exchange resin, which allows one to obtain strong spherical agglomerates. Researchers use different ion-exchange resins, which do not always allow obtaining strong spheres of oxide composites and there is no explanation for this. We believe that the formation of strong spherical agglomerates is primarily influenced by the mechanism of thermal destruction of the ion-exchange resin. Therefore, it is necessary to study the kinetics of the decomposition of resins.

The aim of this work was studying the thermal decomposition of TOKEM-320Y anion-exchange resin in an atmosphere of air and determination the kinetic parameters that make it possible to describe the individual stages.



2. Materials and research methods

TOKEM-320Y anion exchange resin was purchased from the TOKEM production Association.

Synchronous thermal analysis was conducted using an STA 449 F1 Jupiter thermoanalyzer interfaced with a QMS 403 Aëolos gas mass spectrometer (Netzsch-Gerätebau GmbH, Germany). The sample was heated in the atmosphere of air in the temperature range 25–1000°C at heating rates of 7, 10 and 12 °C/min. The kinetic parameters of the decomposition of anion exchanger were established using the methods: Kisenger, Metzger-Horowitz. According to the Kissinger method [9, 10], at a constant rate of heating of a solid substance, the maximum decomposition rate (β) of a substance is achieved at temperature (T_{\max}), which is related by the equation:

$$\frac{d\left(\ln\frac{\beta}{T_{\max}^2}\right)}{d\left(\frac{1}{T_{\max}}\right)} = -\frac{E}{R}$$

Therefore, the activation energy can be calculated from the slope of the line between $\ln(\beta/T_{\max}^2)$ and $1/T_{\max}$. In this equation, the activation energy is independent of the order of the reaction (n). The reaction order (n) can be calculated from shape index (S) of endothermic or exothermic peaks: $n = 1.26 \cdot S^{0.5}$ [10]. The activation energy was also determined using the Metzger-Horowitz method [11]. The Metzger-Horowitz equation is as follows:

$$\frac{(1-\alpha)^{1-n} - 1}{1-n} = -\frac{RT_{\max}^2}{Ea} \exp\left[-\frac{Ea}{RT}\left(1 - \frac{\Theta}{T_{\max}}\right)\right],$$

where Θ – the difference between the maximum temperature and the current temperature, α - degree of conversion.

If the order of the reaction is known, the activation energy is calculated from the angle of the line obtained as a graphical dependence $\frac{(1-\alpha)^{1-n}-1}{1-n}$ on Θ . The rate of decomposition reaction reaches a maximum when $\Theta = 0$ and then $(1-\alpha)_{\max} = n^{1/(1-n)}$. The Metzger-Horowitz method was used for approximate estimation of the reaction order since there is an error in determining $(1-\alpha)_{\max}$. The reaction order, determined by the method of Kissinger also was used to calculate the activation energy according to the method of Metzger Horowitz. The kinetic equation for each stage of decomposition of the studied sample was selected by the Shatava method [12]. This method is also called trial and error. The linearity of the $-\log(g(\alpha))$ function as a function of $1/T$ for different kinetic equations was tested by trial and error. From several tested kinetic equations, we selected one with the highest correlation coefficient.

3. Results and discussion

TOKEM-320Y is a weakly basic anion-exchange resin of porous structure with the styrene – divinylbenzene matrix and tertiaryamine functional groups. The composition of resin is as follows: $[-\text{CH}_2-\text{CHC}_6\text{H}_5-]_n-\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2\text{OH}-]_m$. The TG/DTG curves for TOKEM-320Y resin heated in air are shown in figure 1.

The shape of the TG curves obtained at different heating rates of resin, as well as the shape of the DTA curve presented on the thermogram indicate that TOKEM-320Y undergoes four-stage thermal decomposition. The peak T_{\max} temperatures of each stage at different heating speeds are shown in table 1.

Table 1. T_{\max} of peaks of each step at different heating rates of TOKEM-320Y.

β , °C/min	Stage I	Stage II	Stage III	Stage IV
7	95.3	248.1	360.4	561.1
10	100.2	255.0	365.1	565.1
12	112.1	259.3	368.2	567.5

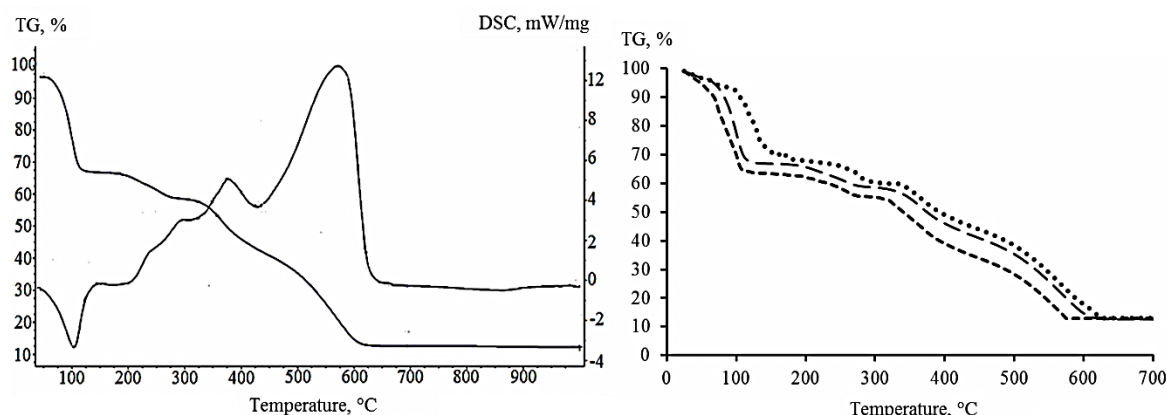


Figure 1. Thermogram ($\beta = 10$ °C/min) and TG-curves of degradation of TOKEM-320Y at β 7 (---), 10 (—), 12 (·····) °C/min.

Kinetic parameters were determined using modified Kissinger and Metzger-Horowitz methods. The Kissinger plots (figure 2) were done using the data for T_{\max} at various heating rates, listed in table 1.

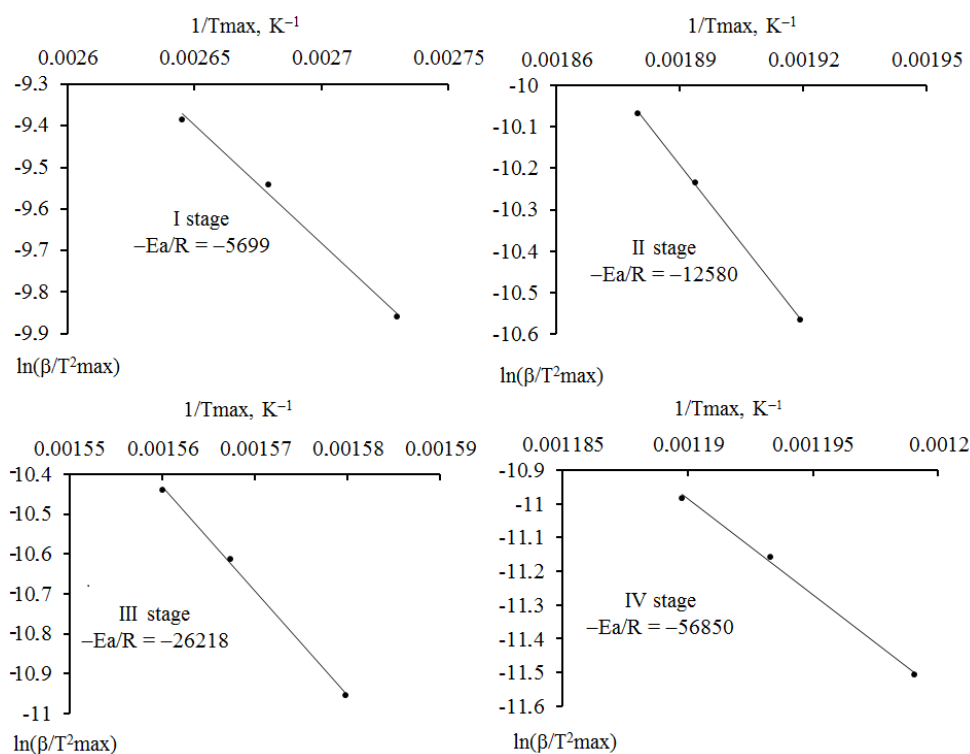


Figure 2. Kissinger plots for the decomposition of TOKEM-320Y.

The Metzger-Horowitz plots constructed using the data of thermogram of TOKEM-320Y decomposition at the rate of 10 C/min are shown in figure 3.

The reaction order obtained by the Kissinger method was used to determine the activation energy by the Metzger-Horowitz method, since there is an error in the Metzger-Horowitz method when determining $(1-\alpha)_{T_{\max}}$, which can lead to an incorrect value of the n . However, the n for all stages of thermal decomposition of the resin couldn't be determined by the Kissinger method, since lines on the DSC curve for II stage have no clearly defined basis. The limitation of the applicability of the Metzger-Horowitz method does not allow us to determine the reaction order of the third stage of the

decomposition of TOKEM-320Y [11]. The kinetic parameters of each stage of thermal decomposition of resin are presented in table 2.

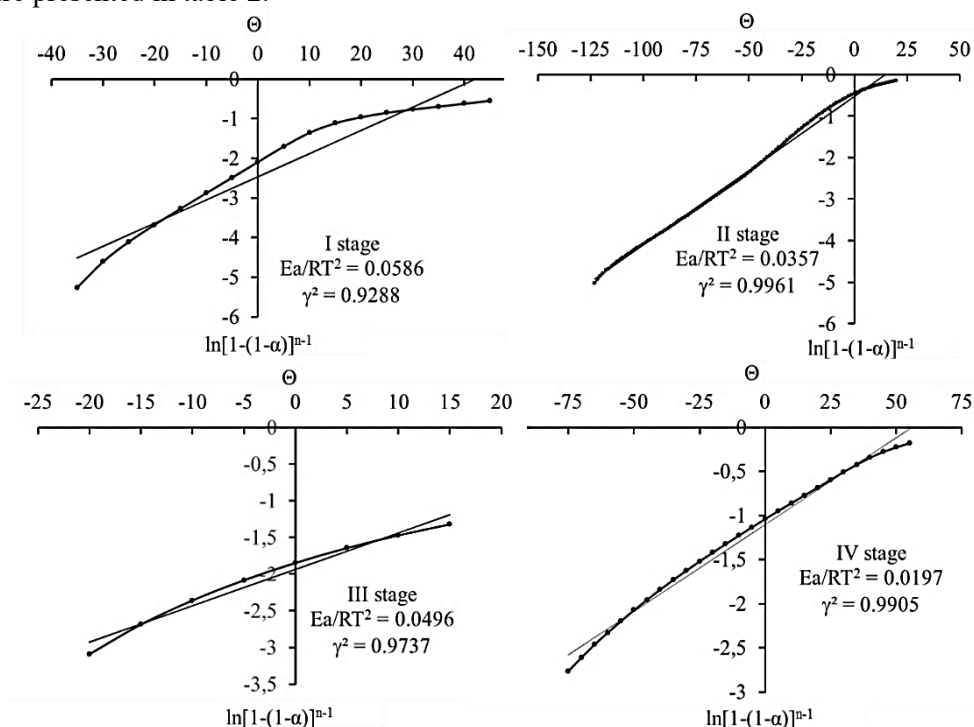


Figure 3. Metzger-Horowitz plots for the decomposition of TOKEM-320Y.

Table 2. Kinetic parameters of the decomposition of TOKEM-320Y resin.

Method	Stage I	Stage II	Stage III	Stage IV
	Ea, kJ/mol / n			
Kissinger	47.38	104.59	217.98	472.65
Metzger-Horowitz	72.98/0.98	81.12/0.93	–	137.79/0.86
Metzger-Horowitz (n Kissinger)	67.86/0.87	–	167.91/1.44	115.02/0.59

The activation energy (47.38–67.86 kJ/mol) for the first stage (25–150 °C) of the decomposition of the TOKEM-320Y resin with endothermic effect, as well as the mass spectra (figure 4) of its decomposition products, suggest that at this stage the most mobile water molecules adsorbed on the resin are removed. Also, water molecules, formed as a result of the destruction of weakly basic anion exchanger, are removed. The Shatava method (figure 5) showed that the dehydration of resin is described by the Avrami kinetic equation $-\ln(1-a) = k\tau$ ($n \approx 1$) and corresponds to the process of diffusion of water molecules through a layer of a solid phase with random nucleation and their growth.

The activation energies of the second stage of decomposition of the studied resin (table 2) indicate chemical destruction of the resin’s matrix which is accompanied by exothermic effects (160–325 °C). As can be seen from figure 4, at this stage in the gas phase, hydrocarbon fragments $C_3H_7^+$, $C_3H_4^+$ with mass numbers $m/z = 40$, $m/z = 43$ were found. In addition, the presence of CO ($m/z = 28$) and H_2O ($m/z = 18$) in the mass spectra of resin is also observed, which indicates the oxidation of hydrocarbon structures. The decomposition rate of the TOKEM-320Y resin polymer matrix can be described by the equation with the maximum coefficient in the correlation coordinates of the linearity of the function $-\log(g(\alpha))$ from $1/T - (1-\alpha)^{1/2} = k\tau$ ($n \approx 2$) (figure 5), which corresponds to the description of the reaction at the phase boundary of cylindrical symmetry.

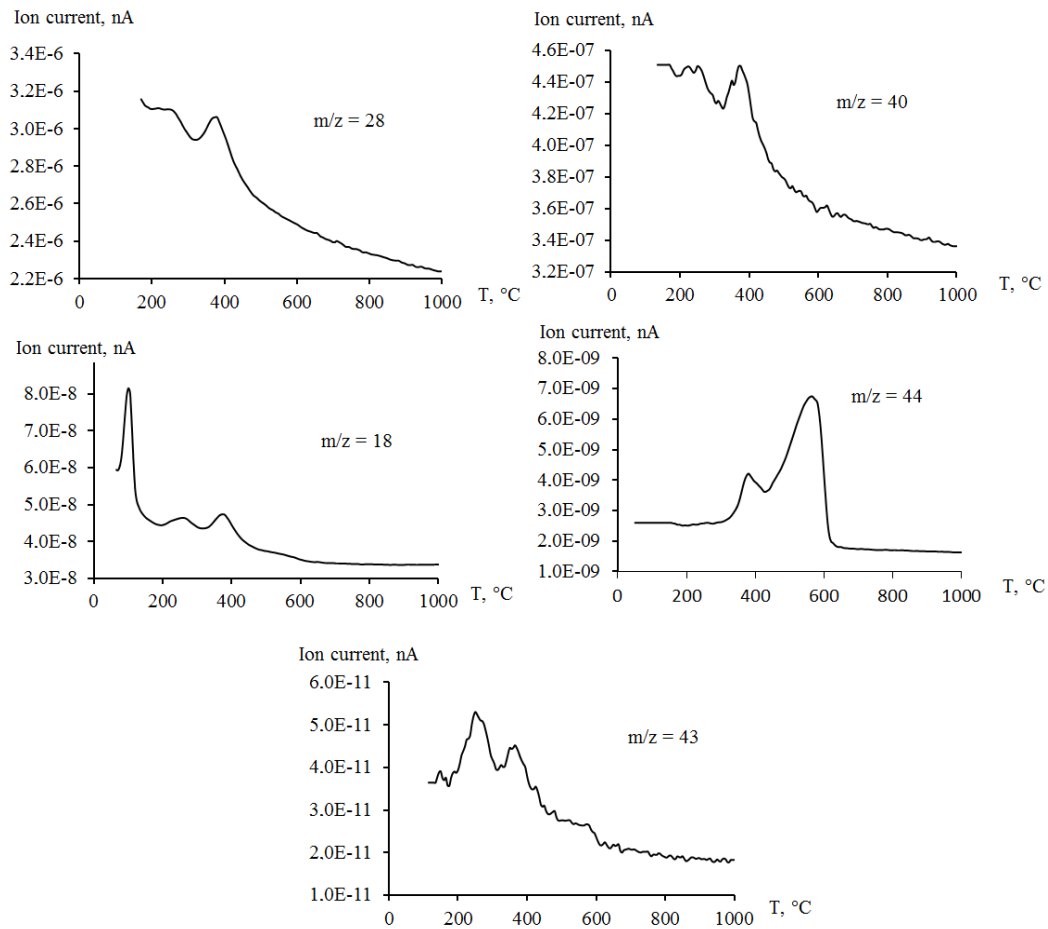


Figure 4. Mass-spectrometric data for degradation products of TOKEM-320Y.

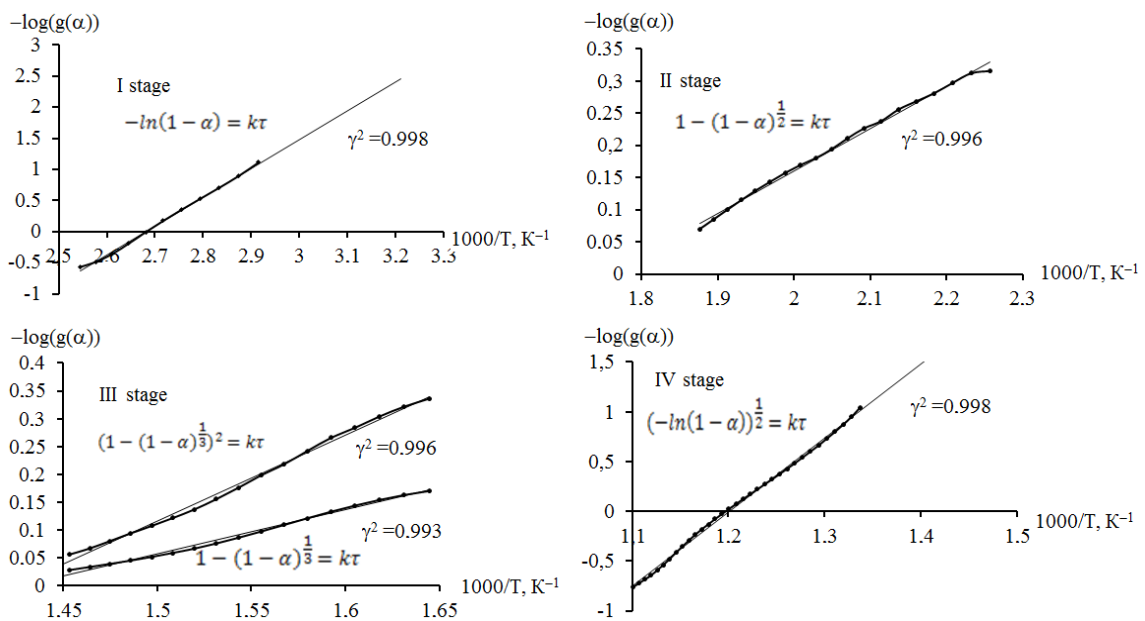


Figure 5. The linearity of the function $\log(g(\alpha))$ of $1/T$ decomposition of TOKEM-320Y.

The decomposition rate of the TOKEM-320Y polymer matrix at the third stage (330–445 °C) is described by the Yander equation $k\tau = [1 - (1-\alpha)^{1/3}]^2$ and the equation $k\tau = 1 - (1-\alpha)^{1/3}$ (figure 5) describing the reaction at the phase boundary of spherical symmetry. Therefore, the decomposition rate of anion exchange resin in the temperature range 330–445 °C with the formation of CO (m/z = 28) and CO₂ (m/z = 44), hydrocarbon residues (m/z = 40, 43), H₂O (m/z = 18) products (figure 4) is determined by the movement of the reagent or its individual components to the reaction interface and the removal of products from it. The rate of advancement of the reaction boundary at the interface of the TOKEM-320Y intermediate is the same in all directions (spherical symmetry). At the fourth stage of TOKEM-320Y, the anion exchange resin burns out with the formation of CO₂ and H₂O (figure 4) in the temperature range 450–660 °C. The limiting stage is described by the Avrami equation $-\ln(1-a)^{1/2} = k\tau$ (figure 5) with n=2. The residual mass of unburned carbon at a heating rate of anion exchange resin 7–12 °C/min is 13.5–13.6 mass. %.

4. Conclusions

Thus, in this work the kinetic analysis of the decomposition process of TOKEM-320Y anion exchange resin in nonisothermal conditions has been performed. The removal of the adsorption water from TOKEM-320Y is most accurately described by the Avrami equation. Instant nucleation changes the reacting particle homothetically (like itself). The shape of the anion exchange resin does not change. The chemical decomposition of the resin begins above 150 °C, which is confirmed by an increase in the activation energies of subsequent stages. Nucleation is limited by crystallographic surfaces in the temperature range 160–325 °C (II stage), and the reaction proceeds only at the edges of the TOKEM-320Y particles. The number of directions of advancement of the interface increases with increasing temperature (330–445 °C, III stage) and decomposition is enhanced by diffusion processes. The destruction of TOKEM-320Y at this stage is most accurately described by the Yander model and the reaction equation at the phase boundary (spherical symmetry). The combustion of intermediate products of TOKEM-320Y thermal decomposition to carbon dioxide at the final stage is most accurately described by the Avrami equation. The discrepancy between the reaction order values in model equations and the reaction orders obtained by the Kissinger and Metzger-Horowitz methods proves the low sensitivity of the latter methods in multistage processes, since they do not allow calculating the reaction order of the limiting stage.

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