RAPID THERMAL ANALYSIS OF PROCESSES OF THERMAL DECOMPOSITION OF MINERAL SALTS

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Kinetic curves of thermal decomposition and synthesis of mineral salts are obtained in the conditions of rapid heating approaching the heating conditions in a low-temperature plasma flow. The kinetic characteristics are used in calculations of transformations in the path of a chemical plasma reactor.

Keywords: kinetics, mineral salts, rapid TA

Introduction

Many kinds of polymineral raw materials and industrial wastes are decomposed by acids with formation of salts in dissolved or gaseous state. The obtained salts may serve as marketable products or semiproducts which shall be converted to other compounds, oxides or metals. For economic and ecological reasons, it is necessary regeneration of the maximum quantity of the acid consumed for decomposition of the initial raw materials to be assured.

The thermal treatment of salts in a low-temperature plasma flow possesses important advantages compared to the traditional technologies of precipitation and thermal treatment (drying) which require very much time (multistage processes of precipitation, filtration, drying, etc.). In a plasma reactor, a solid product of thermal treatment is obtained practically in one stage. Owing to a high temperature of heat-transfer agent and small sizes of raw material particles, the heat- and mass-transfer processes are intensified, which decreases the necessary contact times of the raw material with the heat-transfer agent and the overall dimensions of the reaction equipment by many orders of magnitude.

For the technological calculations of processes of thermal treatment of salts in a plasma flow, for determination of the reactor dimensions, the flow rate, and other parameters, it is necessary to have data about the kinetics of the thermal

decomposition and synthesis reactions which proceed with the heating rates of 10 to 10^3 K/s. The traditional thermal analysis instruments prove to be of little use in order to obtain such data because of their considerable thermal inertia. At the same time, rapid thermal analysers with heating devices of contact type allow sufficiently high heating rates to be obtained which are commensurable with those observed in plasma reactors. An advantage of such heating devices is also comparatively simple methods of experimental data processing [1, 2].

Experimental

The data about the kinetics of transformations (both thermal decomposition and thermal synthesis) of the studied mineral salts have been obtained by means of the method of contact heating of samples. The samples located in foil were weighed before and after an exposure at a constant temperature; based on the weighing results, the relative mass of the residue was determined. The samples in foil were located into a metallic heat-transfer agent. The detailed description of the method is given in earlier publications and in the report at the ESTAC–4 Conference [3]. An important peculiarity of the method of contact heating of samples is the possibility of obtaining kinetic curves beginning from 1 s after the heating beginning up to a preset temperature. The results of the tests of three different substances (aluminium nitrate nonahydrate, mixture of sodium nitrate and aluminium nitrate nonahydrate, and mixture of nitrates from nepheline concentrates) are given in Figs 1, 2, 3. On the indicated figures, time in seconds is plotted on the abscissa and the relative residue mass $\omega = M/M_o$ where M_o is the initial sample mass is plotted on the ordinate.

Processing of the test results

We shall give an example of processing the test results for aluminium nitrate nonahydrate. The thermal decomposition reaction rate is calculated according to the formula

$$k = \frac{1}{t_1 - t} \cdot \ln \frac{\omega - \omega_\infty}{\omega_1 - \omega_\infty} \tag{1}$$

where t_1 is the heating end temperature ($t_1 \cong 1$ s), ω_∞ is the equilibrium value of relative mass (concentration), for aluminium nitrate nonahydrate $\omega_\infty = 0.136$.

Based on the reaction rates found at different temperatures, the plot of $\ln k$ vs. $1/T$ was constructed. In the indicated coordinates, in conformity with the Arrhenius equation, right up to the temperatures by 50 to 100 degrees lower than
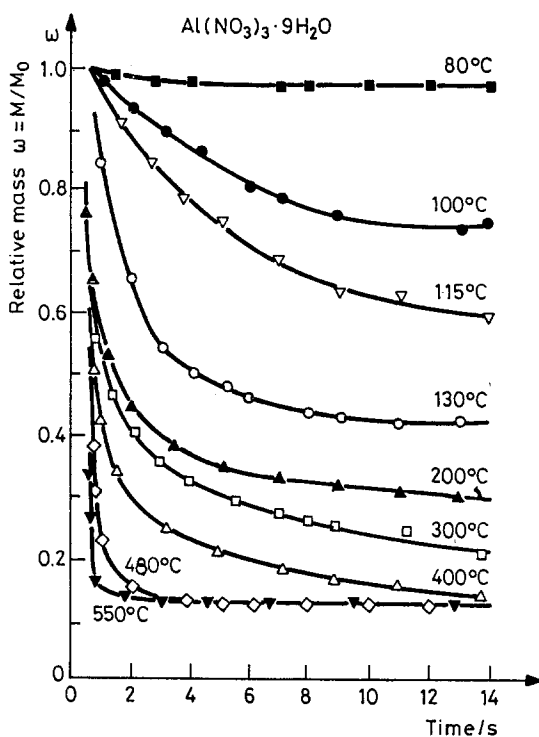
Fig. 1 Kinetic curves of mass loss for thermal decomposition of aluminium nitrate
nonahydrate. The numbers at the curves are temperatures, °C

the limiting ones, i.e. those which limit 'from above' the temperature range of
substance decomposition at the given stage, the plot is a straight line. Because
of existence of a spread of the experimental data, the least-squares technique
was used to obtain results which uniformly correspond to the kinetic curves. Ac-
cording to this technique, it is necessary, in the $\ln k - 1/T$ coordinates, to find
the straight line equation:

$$\ln k = C_0 + \frac{C_1}{T} \tag{2}$$

Using the procedure of the least-squares technique, we shall obtain the fol-
lowing expressions for the coefficients $C_0 = \ln k_0$ and $C_1 = -E/R$:
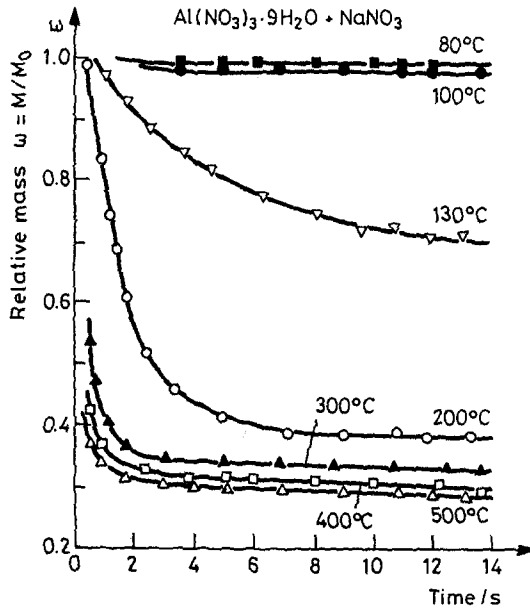
$$C_0 = \frac{bc - ad}{(n+1)b - a^2}$$

Fig. 2 Kinetic curves of mass loss for thermal decomposition and thermal synthesis of mixture of stoichiometric ratio $Al(NO_3)_3 \cdot 9H_2O$ + $NaNO_3$. The numbers at the curves are temperatures T, °C

$$C_1 = \frac{(n+1)d - ac}{(n+1)b - a^2}$$

where

$$a = \sum_{j=0}^{n} T_j^{-1} ; \qquad b = \sum_{j=0}^{n} T_j^{-2} ; \qquad c = \sum_{j=0}^{n} \ln k_j; \qquad d = \sum_{j=0}^{n} \frac{\ln k_j}{T_j};$$

Let's notice that j = 0, 1, 2..., n where $n+1$ is the number of isothermic tests. For example, if 5 isothermic tests are carried out, n = 4 etc.

On finding C_0 and C_1, we have

$$k_o = \exp(C_o); \qquad E = -C_1 R$$

The calculations carried out according to the above formulae have given for aluminium nitrate nonahydrate the following values of the kinetic characteristics:

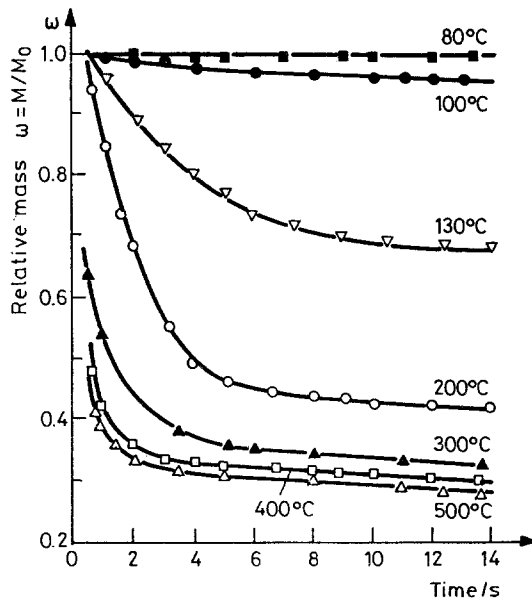$$E = 13.34 \text{ kJ/mol}, \qquad k_o = 12.03 \text{ 1/s}.$$

Fig. 3 Kinetic curves of mass loss for thermal decomposition of mixture of nitrates from nepheline concentrates. The numbers at the curves are temperatures T, °C

As it is seen from Fig. 1, at the temperature of 550°C the decomposition time has the value of about 1 s. Hence, the limiting temperature (the upper temperature of thermal decomposition range, the temperature of stability loss of anharmonic oscillators responsible for the given transformation or chemical reaction) may be adopted equal to $T = 560°C = 833$ K. In such a way, in the temperature range from the initial (20°C) to the final (560°C) temperatures, the temperature dependence of the rate constant is expressed by the following modified Arrhenius equation:

$$k = k_0 \exp\left(-\frac{E}{RT} - \frac{A}{1/T - 1/T_1 + \Delta} \right)$$

where A and Δ are correction factors.

In Fig. 4, with the solid line the straight line is shown constructed by means of the least-squares technique; separate experimental points are also shown for aluminium nitrate nonahydrate. While processing the experimental data, the data at the temperatures of 80° and 100°C have not been taken into account because at these temperatures, simultaneously with thermal decomposition, processes of phase transitions (melting, evaporation) of the initial substance and separated water take place. The kinetic curves of mass loss for mixtures submit to more

complicated relations in which it is necessary to take into consideration, parallel with thermolysis, also synthesis processes.
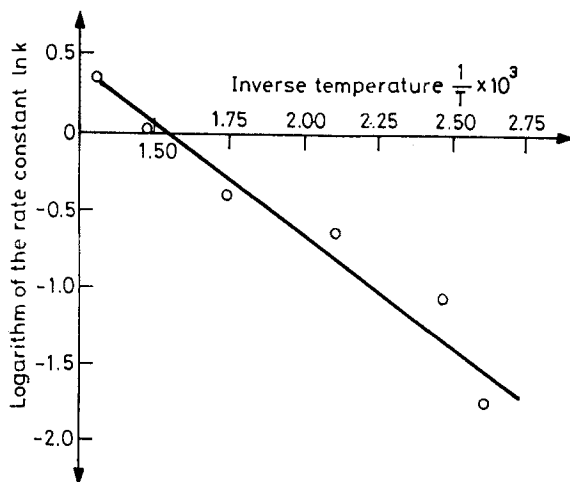

Fig. 4 Dependence of the thermal process rate of aluminium nitrate nonahydrate on inverse temperature. The points are experimental results, the solid line is the result of processing the experimental data by the least-squares technics

Results and discussion

The kinetic characteristics determined allow the mass loss function of the initial substance to be calculated at its heating in the path of a plasma reactor $\omega(T, t)$.

As an example, let's give the results of calculation of the dependence $\omega(T)$ in the process of thermal decomposition of aluminium nitrate nonahydrate at different heating rates similar to those which take place in plasma reactors. A linear law of temperature change $T = T_0 + bt$ has been adopted where T_0 is the initial temperature equal to 20°C. The calculation according to the equation of 1st order reaction kinetics has been carried out with help of the numerical Runge-Kutt method of integration of differential equations. The calculation results for three heating rates ($b = 500, 1.000, 2.000$ K/s) are given in Fig. 5. On the same figure, isochronic experimental curves are indicated at $t = 2$ s and $t = 10$ s.

As one may see from the plots, at the indicated heating rates, an appreciable mass loss which determines the degree of completion of the thermolysis reaction (10 to 20%) takes place already at the temperatures of 500 to 600 K, which corresponds to processes in the real heating conditions. The whole stage of decomposition of aluminium nitrate to alumina (Al_2O_3) comes to an end at the

temperature of $T_1 = 833$ K, which also corresponds to the experimental data obtained at a laboratory plasma generator. It is important to be noticed that the similar calculations carried out according to the kinetic characteristics obtained by means of a standardized thermal analysis (TA) equipment (at a standardized derivatograph, at the heating rate of up to 20 deg/min, the activation energy values of $E = 26$ cal/mole were obtained; $k_o = 1.4$ 1/s) have shown that there is practically no decomposition at high heating rates at the same temperatures. Such a difference is explained by the fact that the kinetic characteristics determined at standardized instruments concern not the initial, rapid stage of the thermal process, but its final stage which has small rates.
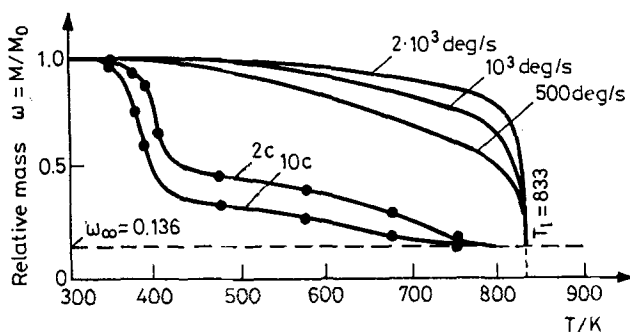

Fig. 5 Results of calculation of completion of the thermal decomposition of aluminium nitrate nonahydrate by means of integration of the differential equation of kinetics. The numbers at the curves are heating rates, deg/s.
Below, isochronic curves are given at $t = 2$ (top curve) and $t = 10$ s (bottom curve) obtained by reconstruction of the kinetic curves taken from Fig. 1 (analogues of derivatograms). The points are experimental data

So, contact heaters may be used to simulate processes which take place in plasma reactors. Such a simulation allows the procedure of election of composition of mixtures to be accelerated for obtaining final products (in chemical analysis of samples).

Conclusion

By means of the method and instrument for contact heating of samples, kinetic curves of thermal decomposition and synthesis of mineral salts are obtained, beginning from 1 s of heating of samples. A small delay time allowed the process of thermolysis to be recorded at its initial stage which is important for designing plasma reactors (heating rates up to 500 K/s).

References

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2 O. F. Shlensky and E. F. Vaynshteyn, J. Thermal Anal., 35 (1989) 1477.
3 Transactions of the European Conference in Jena, ESTAC-4, 1987. (in Russian)

Zusammenfassung — Für thermische Zersetzung und Synthese von Mineralsalzen wurden die kinetischen Kurven unter den Bedingungen schnellen Aufheizens in Annäherung der Aufheizbedingungen in einem Niedertemperatur-Plasmastrom ermittelt. Die kinetischen Eigenschaften wurden zur Berechnung der Umwandlungen bei einem chemischen Plasmareaktor verwendet.