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THERMAL DECOMPOSITION OF AMMONIUM NITRATE DISPERSED IN A MULTICOMPONENT NITRATE SYSTEM

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To obtain the kinetic curves of thermal decomposition of ammonium nitrate occurring together with decomposition of metal nitrates contained in a mixture, the ammonia contents evolved from samples heated under thermoanalytical conditions were determined by the Kjeldahl method.

The object of the investigation was the powdered precursor of the catalyst for the oxidation of propylene to acrolein: a mixture of Mo, Ni, Co, Fe, Bi, Al, K and NH_4 nitrates and SiO_2 [1]. These nitrates are subsequently thermally decomposed to obtain the catalytic material. NH_4NO_3 is well known to undergo explosive decomposition [2]. Accordingly, it indispensable to establish the existence or non-existence of the danger of the explosive decomposition of this substance during calcination of the catalyst precursor.

The thermoanalytical investigation was made to determine the principles of the thermal decomposition of the nitrates comprising the precursor, and especially to find the kinetic parameters of the thermal decomposition of ammonium nitrate dispersed among heavy metal nitrates. The experiments were made with a Mettler TA–2 thermal analyser.

When heated in air at a constant heating rate, the catalyst precursor reveals two steps of mass loss up to 600° (Fig. 1). The first step (Δm_1) is caused by the evaporation of moisture (the investigated material contained 9.1% of water; $m_1 = 0.09\ m_s$). The second step (Δm_2) is a consequence of the thermal decomposition of ammonium and metal nitrates. It was ascertained that the total mass loss in this step is equal to 28.85% of the mass of dry substance i.e. $\Delta m_2^{max} = 0.2885\ m_1$. From the ammonium content (determined by the Kjeldahl method), it was evaluated that the dry mass of the precursor contains 17.07% of ammonium nitrate, i.e. $m_{an}^0 = 0.1707\ m_1$. The above findings make it impossible to establish the kinetic curve for the thermal decomposition of ammonium nitrate from the TG data alone. Separation of the TG curve (Δm_2) was needed: Δm_{an} and

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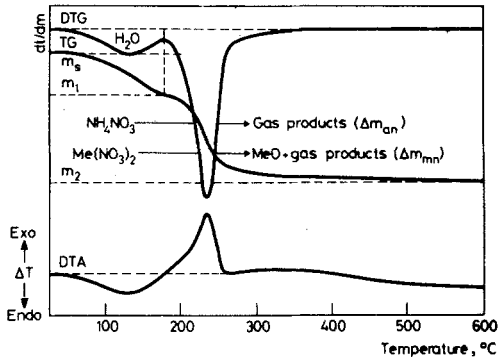

Fig. 1 TG, DTG, DTA curves of the catalyst precursor in air at the heating rate 6 deg/min

Δm_{mn}. Therefore, the ammonia content was determined for samples partially decomposed under thermoanalytical conditions. The ammonium nitrate content was evaluated from the ammonia content and the TG data (Δm_2). By subtracting this from the initial amount of ammonium nitrate contained in the dry mass of the sample (m^0_{an}), the amount of ammonium nitrate decomposed during the experiment (Δm_{an}) was determined. The degree of conversion of ammonium nitrate was then calculated as $\alpha = \Delta m_{an}/m^0_{an}$.

The kinetic curves $\alpha = f(t)$ at constant temperature $T = 190$, 200, 210 or 220° were then estimated via the equation $dc/dt = k_T \cdot (1-\alpha)$, where $k_T = k_0 \cdot \exp(-E/RT)$. Isothermal measurements gave $k_0 = 0.128 \times 10^{17}$ min^{-1} and $E = 162$ kJ·mol^{-1}, while non-isothermal ones gave $k_0 = 0.198 \times 10^{16}$ min^{-1} and $E = 154$ kJ·mol^{-1}.

Conclusions

The results obtained testify to the possibility of the safe calcination of the catalyst precursor; it was established that the thermal decomposition of the nitrates comprising the precursor may be stopped at any time through a temperature decrease, and that the thermal decomposition of ammonium nitrate occurs in a temperature range which is known to be safe [3].

References

1 Polish Pat. 122963 (1984).
2 A. Kolaczkowski et al., Pr. Nauk. Inst. Tech. Nieorg. Pol. Wrocł., 22 (1981) Konf. 9, p. 3–14.
3 Kirt-Othmer, Encyclopedia of Chemical Technology, New York, 1963, Ed. 2, Vol. 2, p. 323.

Zusammenfassung — Der aus unter thermoanalytischen Bedingungen erhitzten Proben freigesetzte Ammoniakgehalt wird durch das Kjeldahlverfahren bestimmt, um die kinetischen Kurven der thermischen Zersetzung von Ammoniumnitrat zusammen mit der Zersetzung von Metallnitraten in Gemischen zu erhalten.

Резюме — Для ролучения кинетических кривых термического разложения нитрата аммония в смеси с продуктами разложения нитратов металлов, содержание аммиака, выделяющегося при термоаналитическом нагреве образцов, определяли по методу Кьельдаля.