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KINETICS OF THERMAL DECOMPOSITION OF MANGANESE(II) OXALATE

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Abstract

The kinetics of manganese(II) oxalate thermal decomposition in the helium atmosphere was studied on the basis of isothermal measurements in the temperature range from 608 to 623 K. Manganese(II) oxide, MnO, was found to be the final product of reaction. The Avrami–Erofeev kinetic equation was used to describe all the experimental data in the range of decomposition degrees from 0.1 to 0.9. The determined activation energy equals 184.7 kJ mol^{-1} with standard deviation ±5.2 kJ mol^{-1}. The estimated value of parameter n is 1.9 with standard deviation ±0.01 what suggests that the rate limiting step of MnC_2O_4 decomposition is the nucleation of new MnO phase and that the rate of nuclei growth is rising during decomposition.

Keywords: kinetics of decomposition, manganese(II) oxalate, thermal decomposition

Introduction

The oxalates of transition metals are used as precursors to produce mixed metal oxides of the required stoichiometry at relatively low temperature [1]. They are also widely used to preparation of modern ceramic materials as well as for obtaining metallurgical powders or catalysts. The procedure of preparation of transition metals oxides and metallic alloys powders is very important because technological properties like specific surface area, shape of grains and chemical composition of material depend on a way of their preparation.

Thermal decomposition of *d*-metal oxalates has been an object of investigations for many years [2–5]. Many of these salts form hydrates, so their thermal decomposition occurs in two stages: dehydration followed by decomposition of anhydrous salt. The products of oxalates thermal decomposition can be corresponding metal and/or metal oxide and CO_2 and/or CO. Mechanism of *d*-metal oxalates decomposition can depend on the surrounding atmosphere. As manganese oxalate is concerned it exists in the form of dihydrate salt. There is common agreement that the final solid product of MnC_2O_4 decomposition is MnO when reaction proceeds in inert atmosphere or Mn_3O_4 when reaction proceeds in air [3–9]. However it is also reported that Mn_3O_4

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can be a final product of MnC_2O_4 decomposition in nitrogen atmosphere [10]. The gaseous products of decomposition in this case are CO and CO_2. This reaction was reported frequently as a one stage process however in one paper [7] the double endothermic DTA peak for decomposition in air has been observed.

Kinetics of thermal decomposition of MnC_2O_4 was studied in few works. For example in work [3] the thermal decomposition was performed in vacuum and degree of conversion was defined from quantitative analysis of CO and CO_2 by instrumental method. Measurements were done in four different temperatures in range from 659 to 685 K and determined activation energy was estimated as 170.8 kJ mol^{-1} using Avrami–Erofeev kinetic equation with exponent $n=1$. In work [7] isothermal decomposition of MnC_2O_4 was performed in nitrogen atmosphere in temperature range 658–698 K by TG method . In this case kinetics of decomposition was described by Avrami-Erofeev equation with exponent $n=1$ also but published value of activation energy was in range 155.3–180.3 kJ mol^{-1} in dependence on the method of its calculation. The chosen temperature range of measurements in cited above papers is questionable because our experiments show, that in these temperature ranges decomposition is very fast and is very difficult to record the kinetic data at these conditions. In view of available data the kinetics of MnC_2O_4 requires additional investigation which we have performed and presented in this paper.

Experimental

Manganese(II) oxalate dihydrate was prepared by precipitating from appropriate amounts of solution of manganese(II) chloride and oxalic acid. The solution was acidified by HCl to pH=3.3 and heated to 343 K for five h. The precipitate was filtered and washed out by dilute oxalic acid and next in absolute alcohol. The obtained oxalate was dried at 333 K and exposed to air. Diffractometric analysis showed that the obtained substance was $MnC_2O_4\cdot 2H_2O$ (Fig. 1a).

Thermal decomposition of $MnC_2O_4\cdot 2H_2O$ was performed on thermoanalyzer (SDT 2960 TA Instruments), which allowed simultaneous detection of mass changes and heat effect of reaction. The samples were heated in standard platinum crucible of 120 μL volume. All experiments were done in helium atmosphere with flow rate 6 $dm^3\ h^{-1}$. The mass of the sample was 6.0 mg. Gaseous products of reaction were analysed by quadrupole mass spectrometer (QMD 300 ThermoStar Balzers). The QMD was operated with an electron impact ionizer at an emission current of 2.00 mA with an electron energy of 70 eV. Gas probing quartz capillary of diameter 0.015 mm and 80 cm long, placed few millimeters above crucible with reacting sample, was connected with QMS analyser. The capillary was surrounded by heating jacket having temperature of 380 K to prevent condensation of gases. Faraday detector was used and the ion currents for M/q values equal to 18, 28 and 44 were monitored (where M is molecular mass of particle and q is the particle charge). Selected M/q values correspond to the following parent ions and fragmentation ions which can form during decomposition of oxalates: H_2O^+, CO^+, CO_2^+.

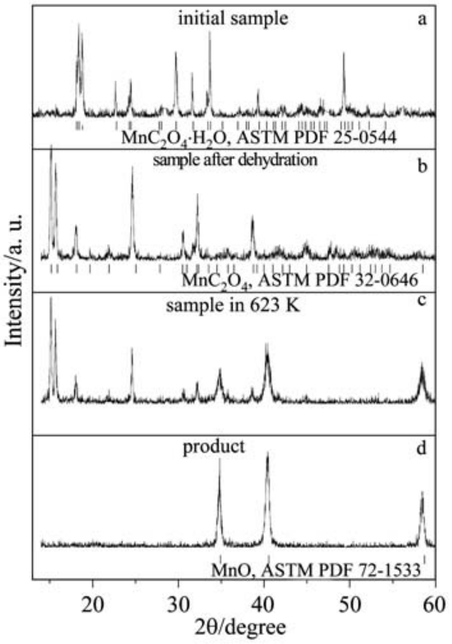

Fig. 1 X-ray diffraction patterns recorded during decomposition of samples in high temperature chamber in nitrogen atmosphere (heating rate 2 K min^{-1}): a – initial sample, b – sample after dehydration at 570 K, c – sample during decomposition at 623 K and d – final product of decomposition at 670 K

Non-isothermal measurements were performed at heating rate β=2 min^{-1}. The kinetics of anhydrous manganese(II) oxalate decomposition was studied on the basis of isothermal measurements carried out in the temperature range of 608–623 K. Temperature range chosen assured stable course of reaction. First samples were heated in 393K for 20 min to obtain complete dehydration, than furnace temperature was raised up with rate β=50 K min^{-1} to reach as fast as possible temperature of isothermal measurement.

Substrate and solid products of decomposition were analysed by X-ray diffraction using CuK_α radiation (Siemens D5005, Bruker-AXS, Germany with X-ray high-temperature chamber).

Results and discussion

Thermal decomposition of $MnC_2O_4{\cdot}2H_2O$ proceeds in two stages (Fig. 2). First stage is dehydration of oxalate which finishes at 393 K. Dehydration is confirmed by mass loss calculations and signal on H_2O^+ intensity line. X-ray analysis of the product after dehydration showed that it consists of anhydrous MnC_2O_4 (Fig. 1b). Second stage is decomposition of anhydrous oxalate which begins at about 523 K. In this stage the gaseous products of reaction are only CO and CO_2. The solid product of MnC_2O_4 decomposition in helium atmosphere is MnO (Fig. 1d). Intermediate solid products of decomposition were not found (Fig. 1c).

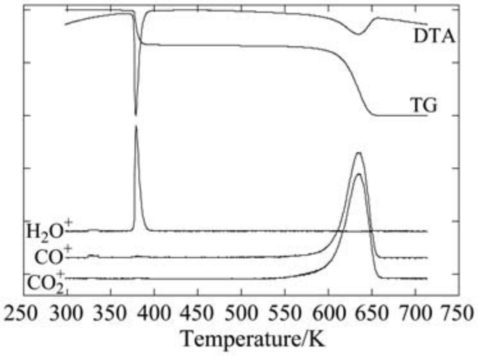

Fig. 2 Normalized TG and DTA curves and ionic current of gaseous products obtained during decomposition of $MnC_2O_4 \cdot 2H_2O$ at heating rate 2°C min^{-1}

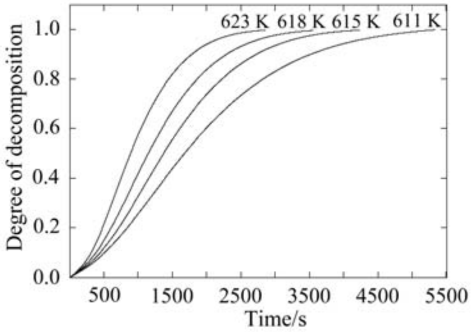

Fig. 3 Kinetic curves $\alpha(t)$ recorded during decomposition of MnC_2O_4 in helium atmosphere in different temperatures

Figure 3 shows as example $\alpha(t)$ curves obtained during isothermal decomposition of MnC_2O_4 in several different temperatures. Degree of decomposition α was calculated from the mass loss of samples. The kinetic curves $\alpha(t)$ have sigmoidal shape which suggests that nucleation of new phase is a rate limiting step in the initial period of reaction. The way of performing decomposition in isothermal conditions described in experimental part was the reason that temperature for the first 200 s actually was not constant.

It was found that Avarmi–Erofeev kinetic equation (1) describes $\alpha(t)$ curves with high accuracy:

$$\alpha = 1 - e^{-kt^{n}} \tag{1}$$

where n is constant related to the mechanism of reaction and k is connected with reaction rate constant K by the following relationship:

$$K = nk^{1/n} \tag{2}$$

The values of n and k parameters in Avrami–Erofeev equation were fitted by the least square method by minimization of the following expression:

$$\sum_i [\alpha_i - (1 - e^{-kt_i^n})]^2 \to 0 \tag{3}$$

where α_i and t_i are experimental values for degree of conversion and suitable time. Fitting was performed for the range of decomposition degree $0.1 < \alpha < 0.9$. Figure 4 shows as example result of fitting Eq. (1) to experimental data for the measurement performed at 618 K.

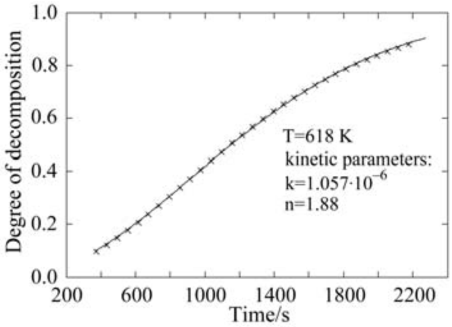

Fig. 4 Example of fitting equation $\alpha=1-e^{-kt^n}$ (line) to experimental data (points)

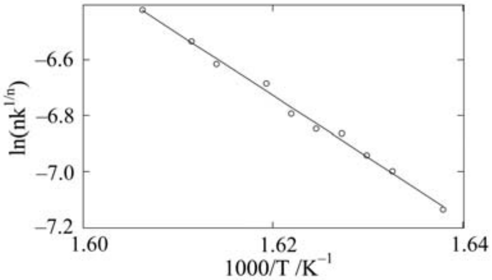

Fig. 5 $\ln(nk^{1/n})$ as a function of T^{-1}

The value of parameter n with its standard deviation was determined to be 1.9±0.01 taking all the measurements done. It was stated that n does not depend on temperature. When we assume that reaction rate constant K fulfils Arrhenius equation $K=K_0e^{-E_a/RT}$, where E_a is activation energy, R is gas constant and K_0 is a preexponential constant then the activation energy can be calculated from the slope of the straight line given by Eq. (4) (Fig. 5) and it is equal to 184.7 with standard deviation of 5.2 kJ mol^{-1}.

$$\ln nk^{1/n} = \ln K_0 - \frac{E_a}{RT} \tag{4}$$

The estimated value of exponent n in Avrami–Erofeev equation is 1.9 and it is close to 2 but statistically significantly different from 2 and also differs from values of n published earlier [3, 7]. This could suggest that the limiting step of MnC_2O_4 decomposition is nucleation of new MnO phase and that the rate of nuclei growth is rising during decomposition. The nuclei growth can be realised either by topochemical reaction or by diffusion.

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