THE INFLUENCE OF OXYGEN PRESSURE ON THE KINETICS OF THE THERMAL DECOMPOSITION OF Co_3O_4

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Abstract

The kinetics of the thermal decomposition of Co_3O_4 has been examined in the 1123–1200 K temperature and 2.66–20.73 kPa oxygen pressure range. The kinetics of this process has been described in terms of a mixed-control model of reaction. The values of activation energies of diffusion and chemical reaction as well as the observed activation energy have been given. The strong dependence of the decomposition rate on temperature and oxygen pressure has been explained.

Keywords: Co_3O_4, kinetics, thermal decomposition

Introduction

In our previous paper [1] the kinetics of the thermal decomposition of Co_3O_4 single crystals and polycrystalline powder at an oxygen pressure of 0.67 Pa has been presented. It has been stated that the decomposition kinetics can be described in terms of the mixed-control model of the reaction, in which the assumption is made that simultaneously diffusion and chemical reaction are the rate limiting steps of the process. The kinetic Eq. (1) has been derived based on the mixed-control reaction model:

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{1}{3}} + s[1 - (1 - \alpha)^{\frac{1}{3}}] = k_r t \qquad (1)$$

$$\text{where:} \quad k_r = \frac{2v_m \Delta p D}{R_o^2} \qquad (2)$$

$$s = \frac{2D}{R_o k} \qquad (3)$$

α – degree of decomposition, D – diffusion coefficient, k – reaction rate constant, v_m – molar volume, R_o – radius of grain, $\Delta p = p_r - p_o$, p_o – external pressure, p_r – equilibrium pressure.

The activation energy of diffusion, E_d, and activation energy of chemical reaction, E_r, have been determined:

for single crystals:

$$E_d = 11.8 \text{ kJ/mol}; \ E_r = 164.0 \text{ kJ/mol}$$

for polycrystalline powder:

$$E_d = 22.8 \text{ kJ/mol}; \ E_r = 153.0 \text{ kJ/mol}$$

It has also been concluded that the rate of the process is directly dependent on the value of the observed activation energy, E_{obs}, which is a function of temperature, external oxygen pressure and conversion degree. For the mixed-control kinetic model, the observed activation energy can be given by the following equation:

$$E_{obs} = \frac{RT^2 D \dfrac{d \ln k}{dT} + R_o \, kf_1 f_2 RT^2 \dfrac{d \ln D}{dT}}{kR_o f_1 f_2 + D} + RT^2 \dfrac{d \ln \Delta p}{dT} \qquad (4)$$

where: $f_1 = (1 - \alpha)^{1/3}$, $f_2 = 1 - f_1$

For the thermal decomposition of Co_3O_4 at an oxygen pressure close to zero, Eq. 4 takes the form:

$$E_{obs} = \frac{sE_r + 2f_1 f_2 E_d}{2f_1 f_2 + s} + \Delta H \qquad (5)$$

In the preliminary studies a very strong effect of external oxygen pressure on the rate of the thermal decomposition of Co_3O_4 has been noticed. In the present paper an attempt will be made to use the mixed-control kinetic model for the description of the effect of oxygen pressure on the kinetics of the thermal decomposition of Co_3O_4.

Experimental

Co₃O₄ polycrystalline powder (99.95%, Cerac Inc.) was used in the experiments. The apparatus used to measure the kinetics of the thermal decomposition of Co_3O_4 ensures a constant oxygen pressure and temperature during the measurement. A calibrated mercury buret allowed for expanding the system by definite increments of volume, while oxygen was evolved during the decomposition.

During preliminary measurements it has been noticed that at constant oxygen pressure, temperatures of the minimum and maximum reaction rate differ by about 7 degrees. Additionally a small change of the oxygen pressure caused the range of temperature to move, that forced us to make experiments in a nontypical way. A series of measurements was made in the oxygen pressure range 2.66–20.73 kPa, and for each oxygen pressure the temperature was chosen so as to provide the appropriate rate of the process (i.e. convenient for recording).

The procedure was as follows: an accurately weighed sample (30–200 mg, depending on the oxygen pressure value) in a platinum crucible, hanging on the iron pin, was placed in the open end of the vertical quartz tube. The open end of the tube was mechanically connected with the apparatus (beyond reach of the high temperature, to avoid decomposition of the sample) and the other end was placed in the furnace. Then the system was evacuated to the pressure of about 1 Pa and simultaneously the temperature of the furnace was raised to the required value. After the temperature was fixed, the oxygen was let into the apparatus up to the definite pressure. At this moment the platinum crucible with the sample was moved down into the high temperature area.

The temperature was controlled to within ±0.2°C by the programmable thermoregulator using a Pt–PtRh–10 thermocouple. The constancy of the oxygen pressure was within ±1 Pa.

The changes of the system volume were recorded as function of the time, taking the moment when the sample was placed in the furnace as $t=0$.

The degree of decomposition α, was defined as the ratio of the oxygen volume evolved till the moment t, to the total oxygen volume, evolved after complete decomposition of the sample under the given conditions.

Results and discussion

A series of measurements was made at oxygen pressures between 2.66 and 20.73 kPa and in the temperature range 1123–1200 K.

Figure 1 shows several representative $\alpha(t)$ curves obtained in the measurements. The kinetic curves of the thermal decomposition of Co_3O_4 belong to the
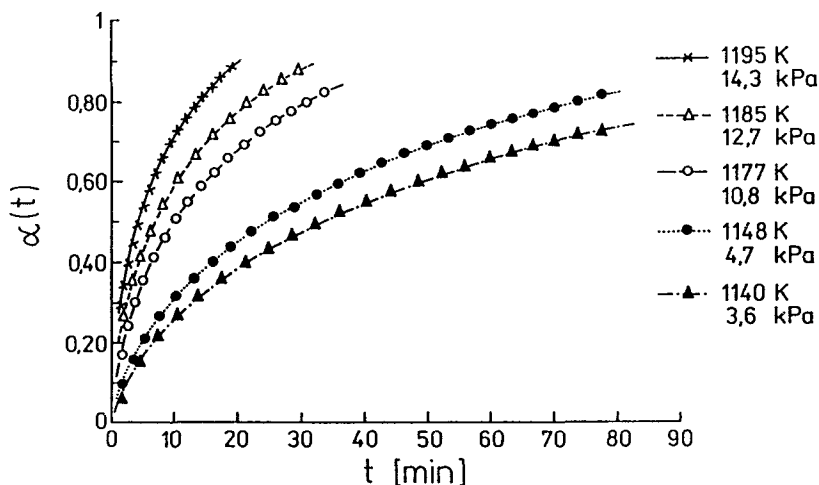
Fig. 1 $\alpha(t)$ curves of the thermal decomposition of Co_3O_4 (points – experimental data, lines – calculated curves)

group of maximum initial rate of the reaction and their shape does not depend on the experimental temperature, oxygen pressure and weight of sample.

On the basis of experimental data the parameters s and k_r of Eq. (1) for each measurement were determined, using a minimization procedure with the following condition:

$$\sum_{i=1}^{n} [F(\alpha_i,s) - k_r t_i]^2 \rightarrow \text{min} \tag{6}$$

where $F(\alpha_i,s)$ – the function on the left hand side of Eq. (1), α_i, t_i – conversion degree and time of i point, n – number of experimental points.

The quality of fitting Eq. (1) to experimental data is illustrated in Fig. 1 (lines correspond to calculated curves, obtained by use of the determined parameters s and k_r in Eq. (1)). Standard deviations of α calculated from the difference ($\alpha_{calc} - \alpha_{exp}$) were lower than 0.01 for each measurement (α_{calc} – value of α calculated from Eq. (1), α_{exp} – experimental value of α).

The above results allowed to state that Eq. (1) describes the kinetics of Co_3O_4 thermal decomposition with a very high accuracy in the experimental temperature and oxygen pressure range.

Kinetic analysis

It is possible to calculate the values of activation energies of the particular processes, e.g. diffusion and chemical reaction, since the determined parameters s and k_r of Eq. (1) depend on E_r and E_d.

It is known that:

$$D = D_o \exp\left(-\frac{E_d}{RT}\right) \qquad (7)$$

$$k = k_o \exp\left(\frac{E_r - E_d}{RT}\right) \qquad (8)$$

where: D_o, k_o – constants

If we take this into account, expressions (2) and (3) will take the form:

$$s = s^o \exp\left(\frac{E_r - E_d}{RT}\right) \qquad (9)$$

$$k_r = k_r^o \Delta p \exp\left(-\frac{E_d}{RT}\right) \qquad (10)$$

where s^o, k_r^o are constants.

Figures 2 and 3 show the plots of ln s and $\ln(k_r/\Delta p)$ vs. $1/T$ (p_r values were calculated from the thermodynamic data presented in [2]).
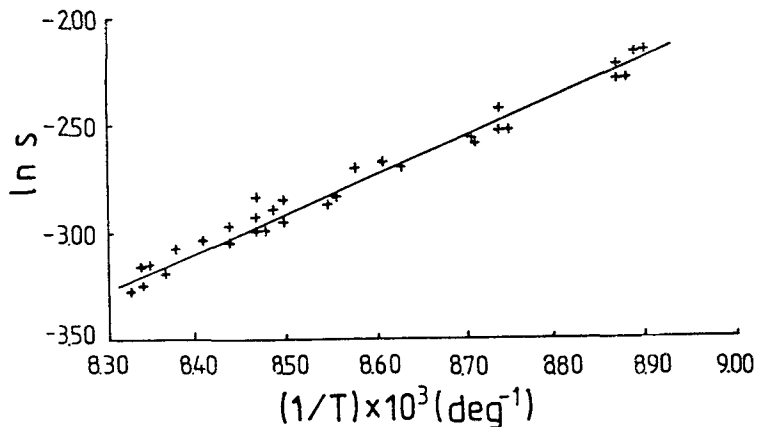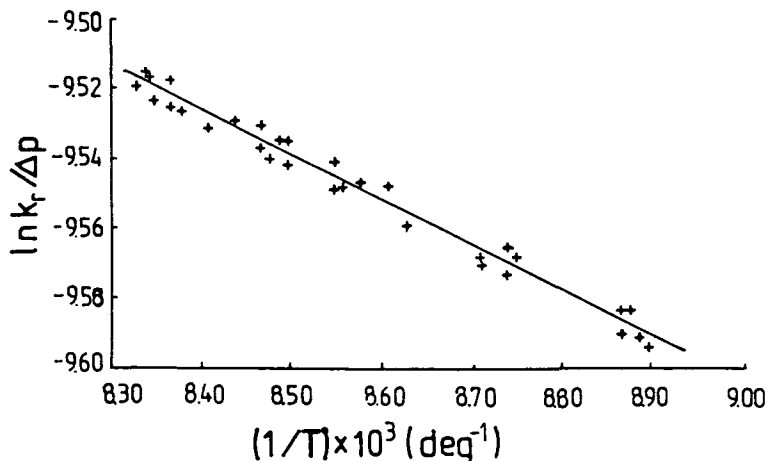

Fig. 2 Plot of ln s vs. $1/T$

Fig. 3 Plot of ln $(k_r/\Delta p)$ vs. $1/T$

Plots 2 and 3 are rectilinear; parameters of the straight lines are presented in
Table 1 Parameters of Eqs (9) and (10)

Figure 2	$\dfrac{E_r - E_d}{R}$	17.95 ± 0.42 K
	ln s°	-18.252 ± 0.359
	r	0.9915
Figure 3	$\dfrac{E_d}{R}$	1.28 ± 0.03 K
	ln k_r°	-8.443 ± 0.028
	r	0.9898

Table 1, together with the regression coefficients r.

The values of E_r and E_d were determined using data from Table 1:

$$E_r = 160 \pm3.8 \text{ kJ/mol} \quad E_d = 10.7 \pm0.27 \text{ kJ/mol}$$

The above values are comparable with those given in [1].

The values obtained for E_r and E_d do not explain the experimentally observed strong dependence of the rate of the process on temperature and oxygen pressure. In fact, when the process rate is controlled both by chemical reaction and diffusion, it depends on the parameter called observed activation energy, E_{obs}.

E_{obs} is given by expression (4). Taking Eqs (7), (8) and (9) into account and the following one:

$$p_r = p_r^o \exp\left(-\frac{\Delta H}{RT}\right) \tag{11}$$

where: p_r^o– constant, ΔH – enthalpy of the reaction, we obtained the following equation for E_{obs}:

$$E_{obs} = \frac{sE_r + 2f_1f_2E_d}{2f_1f_2 + s} + 2\Delta H\frac{p_r}{p_r - p_o} \tag{12}$$

As it results from Eq. (12), E_{obs} is a function of three independent variables: temperature T, external oxygen pressure p_o and degree of decomposition α. The dependence of E_{obs} on T and p_o is particularly strong as illustrated in Figs 4–6 (for the experimental range of T and p_o).

For experimental temperatures and oxygen pressures the E_{obs} value ranged from 635 to 1600 kJ/mol.

Kinetic analysis based on the concept of observed activation energy explains the sudden increase of the reaction rate with increasing temperature, at constant oxygen pressure. A small increase in temperature causes a great decrease in the E_{obs} value, which directly influences the rate of the process. For example, raising T by 5 degrees results in an increase in the rate of the Co_3O_4 decomposition by a factor of 7 (calculated for $p_o = 9.3$ kPa, $\alpha = 0.5$).

Almost analogous is the dependence of the rate on the oxygen pressure. For p_o close to the equilibrium oxygen pressure at a given temperature, E_{obs} reaches a very high value and the process is kinetically inhibited. This is the explanation for the hysteresis of the reaction conditions noticed before [2]. It was found
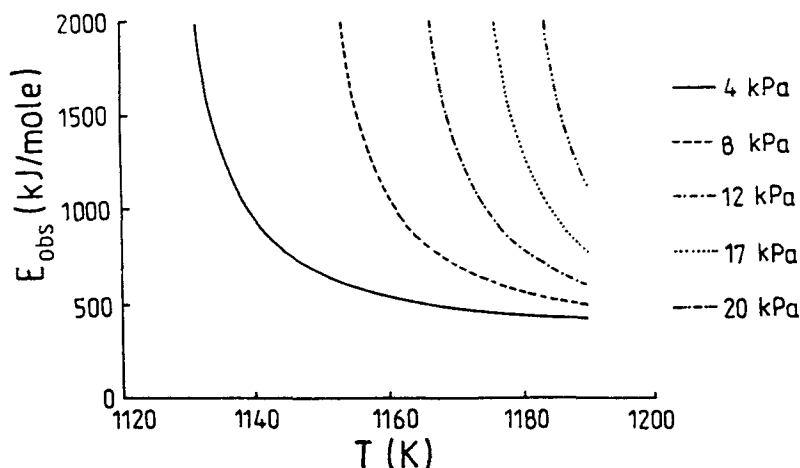

Fig. 4 E_{obs} as a function of temperature ($\alpha = 0.5$)

that the temperature of thermal decomposition of Co_3O_4 to CoO is about $30°$ higher than the temperature of oxidation of CoO to Co_3O_4 at atmospheric pressure.
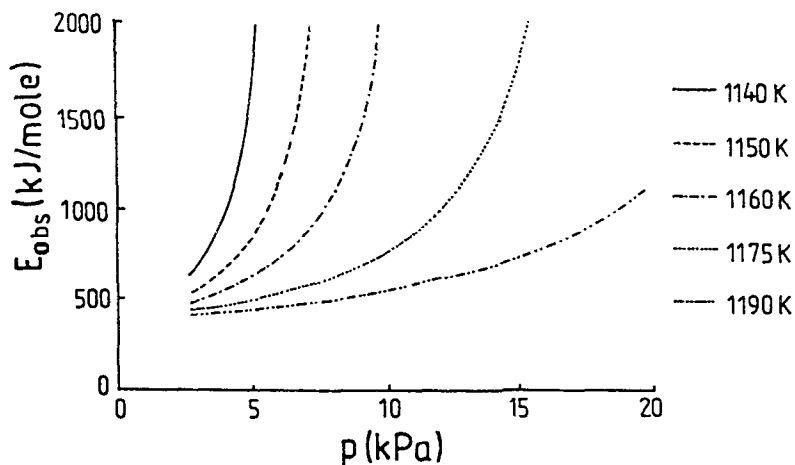

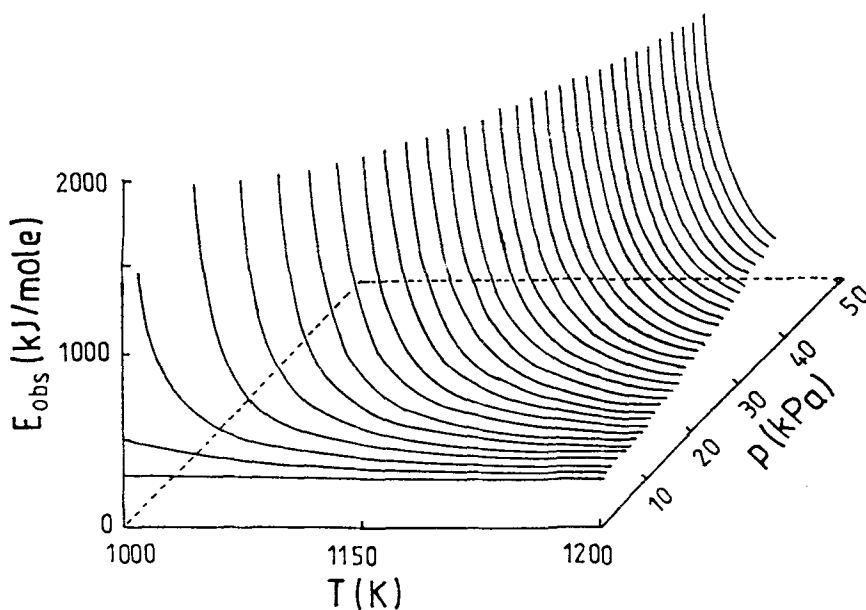Fig. 5 E_{obs} as a function of oxygen pressure ($\alpha = 0.5$)

Fig. 6 E_{obs} as a function of temperature and oxygen pressure ($\alpha = 0.5$)

The kinetic analysis presented also explains the great discrepancy between the values of activation energy of the thermal decomposition of Co_3O_4 given in other publications.

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Zusammenfassung — Im Temperaturbereich 1123–1200 K und im Sauerstoffdruckbereich von 2.66–20.73 kPa wurde die Kinetik der thermischen Zersetzung von Co_3O_4 untersucht. Die Kinetik wurde mit Hilfe eines Misch-Reaktionsmodelles beschrieben. Es wurden die Werte für die Aktivierungsenergie für Diffusion und chemische Reaktion als auch die gemessene Aktivierungsenergie angegeben. Die starke Abhängigkeit der Zersetzungsgeschwindigkeit von Temperatur und Sauerstoffdruck wurde erklärt.