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The mechanism and kinetics of thermal decomposition of $Co_{3-x}Ni_xO_4$

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Abstract

Thermal decomposition of $Co_{3-x}Ni_xO_4$, $x = 0.1$, 0.15 and 0.2, at oxygen pressures 2.7–20.0 kPa at linearly growing temperature was examined. Decomposition of $Co_{3-x}Ni_xO_4$ was found to be mixed-control diffusion–reaction process. Observed activation energy of studied process strongly depends on the oxygen pressure–dissociation pressure ratio. Comparison of the results obtained with earlier study on electrical conductivity of $Co_{3-x}Ni_xO_4$ showed linear correlation between activation energy of new phase nucleation and activation energy of electrical conductivity. Transport of electrons from oxygen ions to Co^{3+} ions leading to CoO nuclei formation was found to be one of two rate limiting steps of thermal decomposition of Co_3O_4. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneous kinetics; Reaction mechanism; Thermal decomposition; Cobalt oxide

1. Introduction

Thermal decomposition of Co_3O_4 is described by the following chemical equation $Co_3O_4 \rightleftharpoons 3CoO + 1/2O_2$. In the temperature range 1123–1200 K and in the oxygen pressure range 2.66–20.7 kPa thermal decomposition of Co_3O_4 proceeds according to Seth–Ross kinetic equation:

$$1 - \tfrac{2}{3}\alpha - (1-\alpha)^{2/3} + s\left[1 - (1-\alpha)^{1/3}\right] = k_r t, \qquad (1)$$

where α is a conversion degree, t is time, s and k_r are parameters dependent on the temperature and oxygen pressure [1]. Eq. (1) was derived for the mixed-control model of the heterogeneous gas–solid reaction, which assumes that the total reaction rate is simultaneously controlled by chemical reaction and by diffusion through the product layer [2]. For the thermal decomposition of Co_3O_4 the rate of chemical reaction was proportional to $(p_r - p)$, where p_r is dissociation pressure of Co_3O_4, p is oxygen pressure on the phase boundary $Co_{3-x}Ni_xO_4$/CoO, and the rate of diffusion was inversely proportional to the thickness of product layer.

As was found the rate of Co_3O_4 thermal decomposition strongly depends on temperature and oxygen pressure. This is connected with the high value of the observed activation energy E_a^{obs}, which is a function of temperature and oxygen pressure [1]:

$$E_a^{obs} = \frac{sE_r + 2f_1f_2E_d}{2f_1f_2 + s} + 2\Delta H \frac{1}{1 - p/p_r}, \qquad (2)$$

where f_1 and f_2 are functions of α, ΔH is the enthalpy of Co_3O_4 decomposition, E_r is the activation energy of chemical reaction and E_d is the activation energy of diffusion.

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While the kinetics of Co_3O_4 thermal decomposition is quite well described, the detailed mechanism of microscopic processes corresponding to diffusion and chemical reaction remains unknown. Doping of Co_3O_4 by Ni^{2+} ions should influence the electron transport process [3] that could help to explain the microscopic nature of Co_3O_4 thermal decomposition. The goal of the present work is to find the effect of nickel ions presence on the kinetics of the studied reaction.

2. Experimental

The powder samples of Co_3O_4 doped with Ni^{2+} ions used in experiments were prepared by thermal decomposition of cobalt(II) and nickel(II) nitrate(V) mixtures (analytically pure). The nitrate mixtures of appropriate composition were decomposed at 550 K in oxygen flow and next annealed for 1 h at 700 K [4].

The X-ray diffraction analysis of the samples prepared showed the presence of just one phase corresponding to Co_3O_4 spinel phase, with slightly shifted most intensive lines in the spectrum, that might be the effect of nickel ions built in the spinel structure. The grain size of the powder samples was lower than 30 μm and the specific area was 7.7–9.2 $m^2\ cm^{-3}$.

Gravimetric analysis and atomic absorption spectroscopy method were used to determine the chemical composition of the samples obtained. In experiments the samples of the following composition were used: $Co_{2.90}Ni_{0.10}O_4$, $Co_{2.85}Ni_{0.15}O_4$, $Co_{2.80}Ni_{0.20}O_4$.

The kinetics of decomposition of the prepared samples as well as Co_3O_4 was measured in the volumetric kinetic apparatus. The measurements were carried out at the constant oxygen pressure and at heating rate $\beta = 3\ K\ min^{-1}$. The experimental oxygen pressures were 2.7, 4.0, 6.7, 10.0, 13.3, 20.0 kPa.

The sample mass was 20–140 mg, depending on experimental oxygen pressure. In the preliminary measurements it was stated that mechanism of examined reaction is not influenced by the mass of sample in the mass range used in experiments.

The conversion degree α, was determined as a ratio of oxygen volume evolved from the sample till moment t, to oxygen volume evolved after the complete decomposition of sample.

3. Results and discussion

The preliminary measurements showed that decomposition of cobalt spinel doped by nickel ions carried out in constant temperature is diffusing inhibited, just like it was found for Co_3O_4 decomposition. In result only in the first, relatively short period the rate of reaction was high enough for recording. After this time diffusion processes took the control over the decomposition and the reaction rate has significantly decreased. Finally the reaction rate became so low that recording was almost impossible though the conversion degree has reached only 0.4–0.6, depending on the temperature. The way to omit this problem was to measure the kinetics of the process at constant oxygen pressure and in conditions of rising temperature.

At first the mixed-control model of reaction was tested for the kinetic analysis of the results obtained. The attempt to introduce temperature as a function of time into the mixed-control model of Co_3O_4 thermal decomposition has shown that analytical form of equation connecting conversion degree α, with the reaction time is impossible to derive. The main cause of this is that producing of the nuclei of new phase (CoO) and the rate of its growth are the complex functions of temperature. The consequence of this is that in discussed mixed-control model of reaction, the ratio of chemical reaction and diffusion in the rate of the whole process changes not only as a function of α, but also as a function of temperature and what is more, this function is unknown. In consequence it is impossible to obtain the simple equation that could be the analogue of Eq. (1) for non-isothermal conditions.

Fig. 1 shows how the rate of $Co_{2.85}Ni_{0.15}O_4$ decomposition changes during the course of reaction.

For the kinetic description of the obtained $\alpha(t)$ dependencies it was necessary to create the simplified model of reaction proceeding in non-isothermal conditions.

It was assumed that the rate of $Co_{3-x}NixO_4$ decomposition is proportional to $\Delta p = p_r - p$ and to nucleation rate J:

$$V = k(p_r - p) \cdot J \cdot g(\alpha), \qquad (3)$$

where $g(\alpha)$ is some function of decomposition degree which has to satisfy condition:

$$\lim_{\alpha \to 1}[g(\alpha)] = 0. \qquad (4)$$

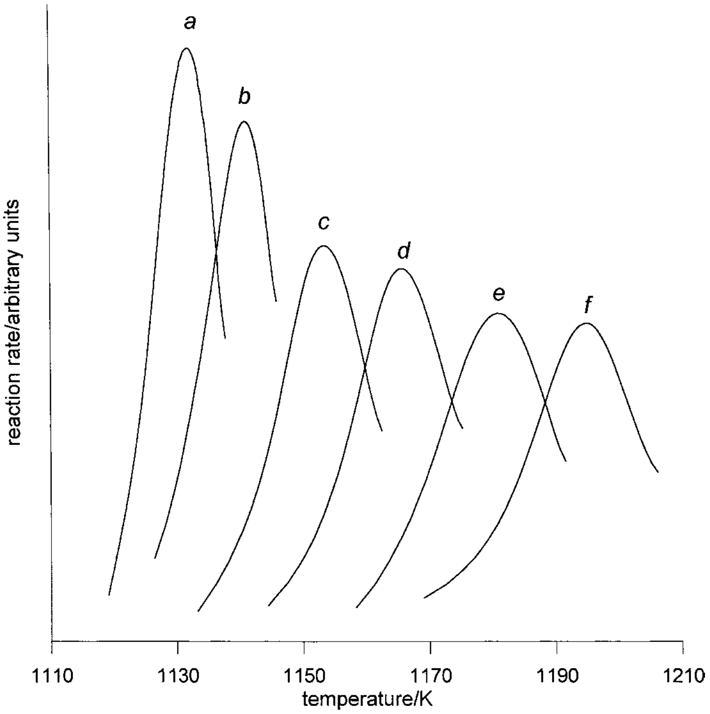

Fig. 1. The rate of $Co_{2.85}Ni_{0.15}O_4$ decomposition during the course of reaction conducted at different oxygen pressures: (a) 2.7 kPa, (b) 4.0 kPa, (c) 6.7 kPa, (d) 10.0 kPa, (e) 13.3 kPa, (f) 20.0 kPa.

It was additionally assumed that the rate of nucleation depends on deviation from equilibrium state and can be expressed by the following general dependence:

$$J = A'\left(\frac{p}{p_r}\right)^q, \tag{5}$$

where A' and q are constants. In experimental conditions it is justified to assume that oxygen pressure on the phase boundary $Co3_{-x}Ni_xO_4/CoO$ is equal to external oxygen pressure. Now Eq. (3) takes the following form:

$$V = K(p_r - p) \cdot (1/p_r)^q \cdot g(\alpha), \tag{6}$$

where $K = kA'p^q$. The logarithmic form of Eq. (6):

$$\ln\left(\frac{V}{p_r - p}\right) = \ln(K) + \ln[g(\alpha)] + q\ln\left(\frac{1}{p_r}\right) \tag{7}$$

allows to determine the value of constant q for each α, if K does not depend on temperature.

Fig. 2 illustrates, as example, the dependence $\ln(V/(p_r - p))$ vs. $\ln(1/p_r)$ for $Co_{2.80}Ni_{0.20}O_4$ and $\alpha = 0.2$, 0.5 and 0.8. Linear correlation coefficients of this dependence for all samples were better than 0.975. p_r as a function of temperature was determined by the authors in separate measurements for all studied compounds. V was calculated by numerical differentiation of experimental curve $\alpha(t)$. In Table 1 the determined values of q for all examined samples are collected.

The significant linear correlation between parameter q and the contents of nickel, x, was stated which is shown in Fig. 3.

Table 1
Values of parameter q

Sample	q
Co_3O_4	1.227±0.008
$Co_{2.90}Ni_{0.10}O_4$	1.195±0.011
$Co_{2.85}Ni_{0.15}O_4$	1.199±0.014
$Co_{2.80}Ni_{0.20}O_4$	1.179±0.017

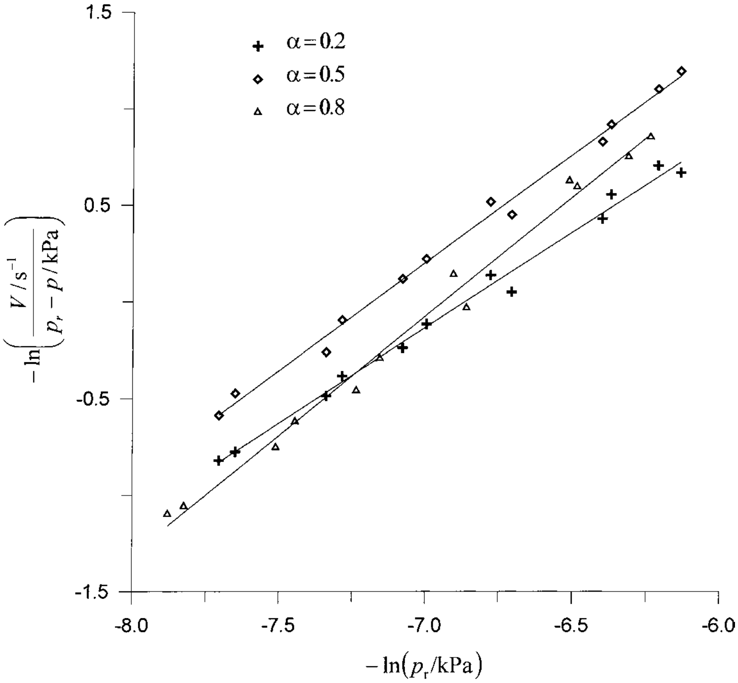

Fig. 2. Determination of parameter q as a slope of straight line in the system: $\ln(V/(p_r - p_o))$ vs. $\ln(1/p_r)$, for $Co_{2.80}Ni_{0.20}O_4$.

According to Eq. (5) parameter q is directly connected with the rate of nucleation J. Now it will be shown that parameter q is also connected with the observed activation energy, E_a^{obs}.

Using definition of E_a^{obs}, as a differential increment of reaction rate logarithm when temperature increases by dT [5]:

$$\frac{\partial \ln(V)}{\partial T} = \frac{E_a^{obs}(\alpha, T, p)}{RT^2} \tag{8}$$

and taking into account that $p_r = p_0\,e^{-2\Delta H/RT}$ (p_0 = const), the following expression for E_a^{obs} was obtained:

$$E_a^{obs}(\alpha, T, p) = RT^2 \frac{\partial G(\alpha)}{\partial T} - 2q\Delta H + 2\Delta H \frac{1}{1 - p/p_r}, \tag{9}$$

where $G(\alpha) = \ln(K) + \ln[g(\alpha)]$. The analytical form of $g(\alpha)$ is unknown; that is why E_a^{obs} can be calculated only for definite α value by numerical differentiation of experimental curve $\alpha(T)$.

Eq. (9) is in fact a sum of three components – one of them is dependent on oxygen pressure. This component can have any value, especially extremely high when p/p_r is close to 1. Moreover, during the experiments the strong dependence of reaction rate on oxygen pressure was noticed. That is why it is justified to assume that mainly the part of Eq. (9) dependent on oxygen pressure determines value of E_a^{obs}:

$$E_a^{obs}(T, p) \approx 2\Delta H \frac{1}{1 - p/p_r(T)}. \tag{10}$$

The strong dependence of E_a^{obs} on temperature is illustrated in Fig. 4 and explains experimental fact that changing temperature by 1 K causes change in reaction rate by several times, depending on oxygen pressure.

Eq. (9) is formally analogous to Eq. (2), which describes observed activation energy of pure Co_3O_4. First addend of Eq. (2) is related to chemical reaction and diffusion, being simultaneous rate limiting processes, while the second addend is related to deviation from equilibrium oxygen pressure. By comparison, it can be assumed that the following part of Eq. (9) is also related to chemical reaction and diffusion:

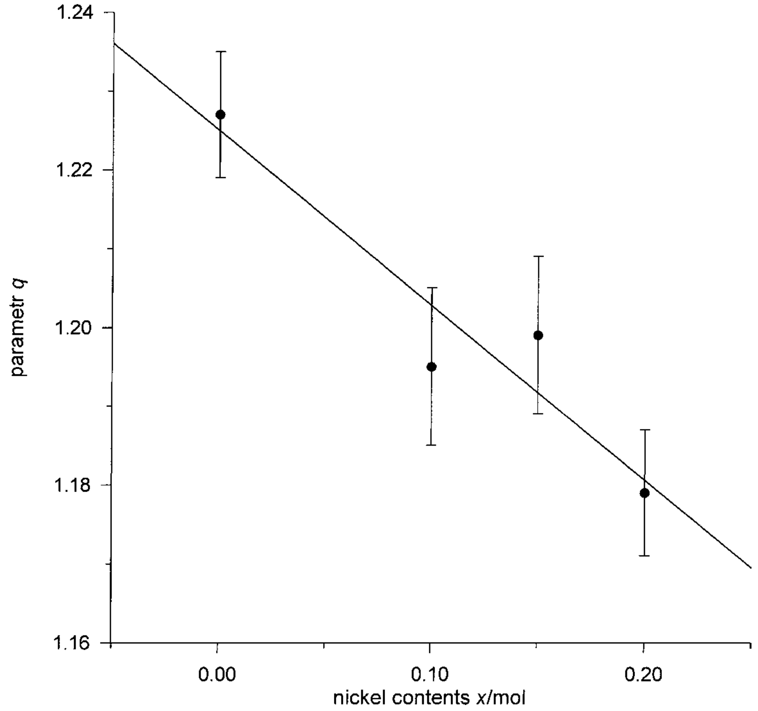

Fig. 3. Linear correlation between parameter q and nickel contents, x, in $Co_{3-x}Ni_xO_4$.

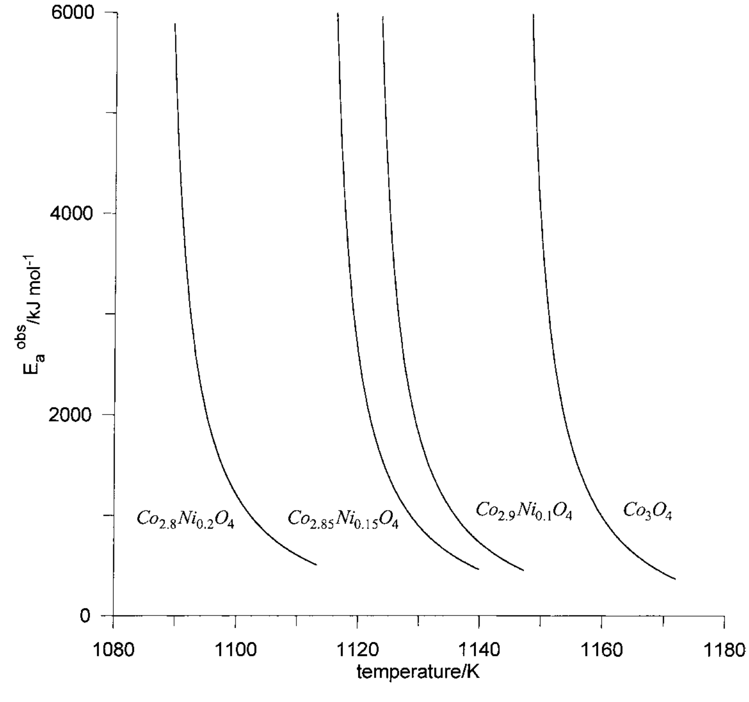

Fig. 4. Temperature dependence of observed activation energy E_{obs} of $Co_{3-x}NixO_4$ for oxygen pressure $p = 4.0$ kPa.

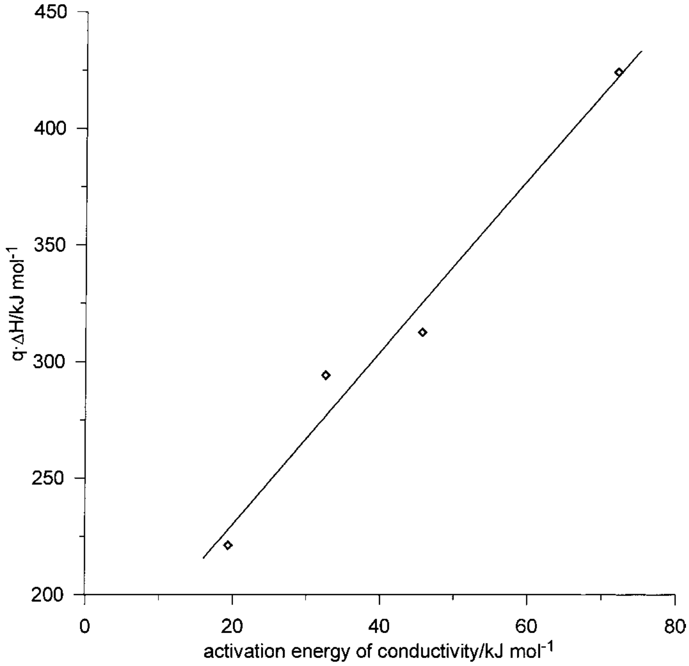

Fig. 5. Correlation between activation energy of nucleation and electrical conductivity for Co$_{3-x}$Ni$_x$O$_4$.

$$-2q\Delta H + RT^2\frac{\partial G(\alpha)}{\partial T}.$$

Notice that q is directly connected with the rate of nucleation which suggests that $-2q\Delta H$ can be interpreted as a part of observed activation energy related to activation energy of nucleation process.

It was found that activation energy of electrical conductivity of Co$_{3-x}$Ni$_x$O$_4$, E_s^σ, decreases when the contents of Ni^{2+}, x, increases [3]. The correlation between E_a^σ and x is nearly linear and the adequate regression line is calculated using values from [3] is given by:

$$E_a^\sigma = -263,2x + 72,0 \qquad (11)$$

This allowed for calculating values of E_a^σ for all studied samples. The statistical test F showed that hypothesis about correlation between E_a^σ and q obtained for examined samples cannot be rejected on the significance level >0.06. The lower q the higher activation energy of conductivity.

Above considerations allow for drawing conclusion that correlation exists between activation energy of nucleation and activation energy of electrical conductivity (Fig. 5). Thus transport of electrons from oxygen sub-lattice to Co^{3+} ions leading to CoO nucleus formation is the rate-limiting step of thermal decomposition of Co$_3$O$_4$, related to chemical reaction. The microscopic mechanism of diffusion process, which simultaneously controls observed rate of decomposition, remains still unexplained.

Acknowledgements

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