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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

A Study of the Kinetics of Synthesis of Potassium Superoxide from an Alkaline Solution of Hydrogen Peroxide

D. V. Zhdanov, M. A. Ul'yanova, and Yu. A. Ferapontov

Tambov Research Institute of Chemistry Federal Unitary Enterprise, Tambov, Russia

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Abstract—Kinetic aspects and the mechanism of shaping of particles of potassium superoxide in its synthesis from drops of an alkaline solution of hydrogen peroxide in a flow of a drying agent were studied.

The method for synthesis of potassium superoxide KO_2 is based on the fact that, being a weak acid, hydrogen peroxide enters, under certain conditions, into an exchange reaction with potassium hydroxide [Eq. (1a)] to give an intermediate adduct $K_2O_2 \cdot 2H_2O_2$ (potassium peroxide diperoxohydrate) [1]. This adduct disproportionates upon heating to above 40°C [Eq. (1b)] to give KO_2. The overall process of formation of potassium superoxide from the starting reagents is described by Eq. (1):

$$2KOH + 3H_2O_2 = K_2O_2 \cdot 2H_2O_2 + 2H_2O \quad (1a)$$

$$K_2O_2 \cdot 2H_2O_2 = 2KO_2 + 2H_2O \quad (1b)$$

$$2KOH + 3H_2O_2 = 2KO_2 \cdot 4H_2O. \quad (1)$$

Previously, this process has been carried out by spraying an alkaline solution of H_2O_2 onto the heated surface of a rotating drum blown over from the outside with an inert gas [2]. When the solution dries up, potassium superoxide is formed on the drum surface, cut-off with a blade, and discharged into the receiving bin.

However, this method has an important disadvantage: it is necessary to supply a saturated steam, which serves as a heat-transfer agent, into a rotating drum under elevated pressure and to remove the forming condensate from the drum. This impairs the reliability of the process and hinders its industrial application.

To eliminate these disadvantages, it is suggested to perform the process in a direct-flow spray reactor, with the synthesis of KO_2 and its drying in a dispersed state combined. The resulting powdered target product is separated from the drying agent in a cyclone and collected in a bin. Heated, dried, and purified (to remove CO_2) air or any inert gas can be used as a drying agent [3].

It is reasonable to assume that, under the experimental conditions, the disproportionation of $K_2O_2 \cdot 2H_2O_2$ may be accompanied by the following chemical side reactions:

$$2KO_2 + 3H_2O = 2(KOH \cdot H_2O) + 1.5O_2, \quad (2)$$

$$2KOH + CO_2 = K_2CO_3 + H_2O. \quad (3)$$

In the case of an intensive dehydration and low concentrations of H_2O and CO_2 vapor in the drying agent, the influence of these reactions can be neglected.

The rate of reaction (1) in a spray reactor depends on a number of factors (temperature, concentrations of the starting reagents, etc.). Therefore, determination and subsequent generalization of the fundamental kinetic aspects of this process and analysis of the shape of the forming grains is an obligatory stage in developing the scientific prerequisites for calculation of its performance and design parameters.

As shown by practical experience [4], the choice and substantiation of the optimal modes of synthesis of particular products should be primarily based on the information about the mechanism of internal processes and thermal characteristics of the substance being dried. It is the kinetics of heat-exchange processes in a separate particle that determines such important characteristics of the target product as dispersity, reactivity, bulk density of the powder, and its tendency toward caking.

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Physicochemically, the process being considered consists in dispersion of an alkaline solution of hydrogen peroxide and its subsequent crystallization to give potassium superoxide under drying, with a simultaneous occurrence of chemical reactions.

In studying under laboratory conditions the kinetics of the internal heat-and-mass-exchange processes and the mechanism of shaping in a separate particle, this particle was regarded as a unit element of the whole dispersed system present in the chamber of the reactor. Therefore, the primary goal in studying the kinetics of the process in question was to examine just those external conditions that are experienced by a unit element of the system in a real apparatus. This refers, in the first place, to the basic characteristics of the drying agent: temperature, pressure, relative velocity, and chemical composition.

The information that can be directly obtained in an experiment with a single drop of the solution with a drying agent is a set of data on how its temperature, mass, size, and shape vary in the course of synthesis. Processing of the resulting experimental data enables a conclusion about the nature of the internal heat-and-mass-transfer processes in a particle under varied external conditions.

EXPERIMENTAL

The kinetics of synthesis of potassium superoxide from an alkaline solution of hydrogen peroxide in a flow of a drying agent was studied on an experimental stand shown schematically in Fig. 1.

The drying agent is delivered by a gas blower *1* through a flow control valve *2* into a psychrometer *3* and rheometer *4*, which measure the humidity and flow rate, respectively. Then the drying agent is delivered for heating into an electric air heater *5* and, further, discharged via pipe *6* into the atmosphere through a nozzle 17 mm in diameter. A thermocouple *7* is fixed on a special bracket *8* connected to a high-precision electronic microbalance *9*. The temperature and mass of a drop suspended on the junction of the thermocouple is recorded by self-recorders *10* and *11*. The temperature of the drying agent is determined from the reading of the recorder *10* in the absence of drop suspended on the thermocouple after the stand attains a steady state. A video camera *12* with a microattachment enables a continuous video recording of the drop in the course of synthesis.

To make lower the radiation heating of the drop, the pipe *6* has a 90° elbow. To diminish the heating of the drop via thermal conduction, the diameter of the wires of the thermocouple is chosen to be the minimum possible. In the case in question, this diameter is 50 μm. All this is done with the only objective, to ensure a mainly convective heat supply and to make the experimental conditions as close as possible to the real process of dehydration of solution drops in an industrial apparatus.

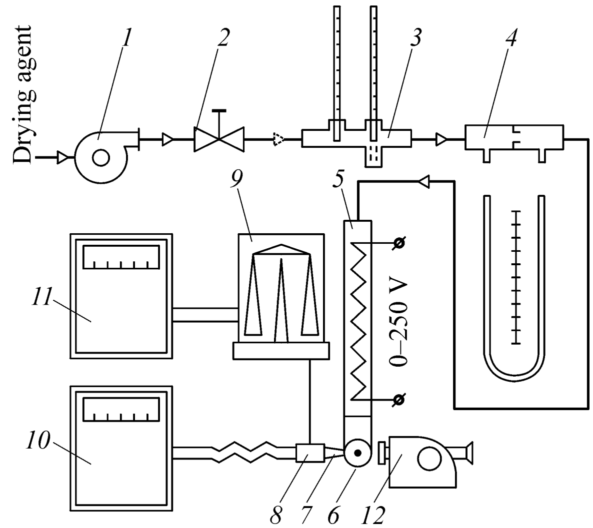

Fig. 1. Experimental stand for a study of the kinetics of synthesis of potassium superoxide from an alkaline solution of hydrogen peroxide in a flow of a drying agent.

The alkaline solution of hydrogen peroxide to be used in the study was prepared by mixing 50% solutions of KOH and H_2O [5].

A drop of the resulting solution was suspended on the junction of the thermocouple and blown over with the drying agent (for its parameters, see table). The following parameters were recorded in the course of the experiment: temperatures T_{dr} and T_{moist} of dry and moistened thermometer, respectively; flow rate G_A; and temperature T_{DA} of the drying agent. As a result, curves describing how the temperature [$T_d = f(\tau)$], mass [$m_d = f(\tau)$], and diameter [$d_d = f(\tau)$] of a drop under study vary with the time τ of the process were obtained.

Experimental conditions (drying agent, atmospheric air purified to remove CO_2)

Sample no.	T_{dr}, °C	T_{moist}, °C	G_{DA}, l min^{-1}	T_{DA}, °C
1	27.6	12.4	50	150
2	21.9	15.5	50	187
3	22.6	21.4	50	225

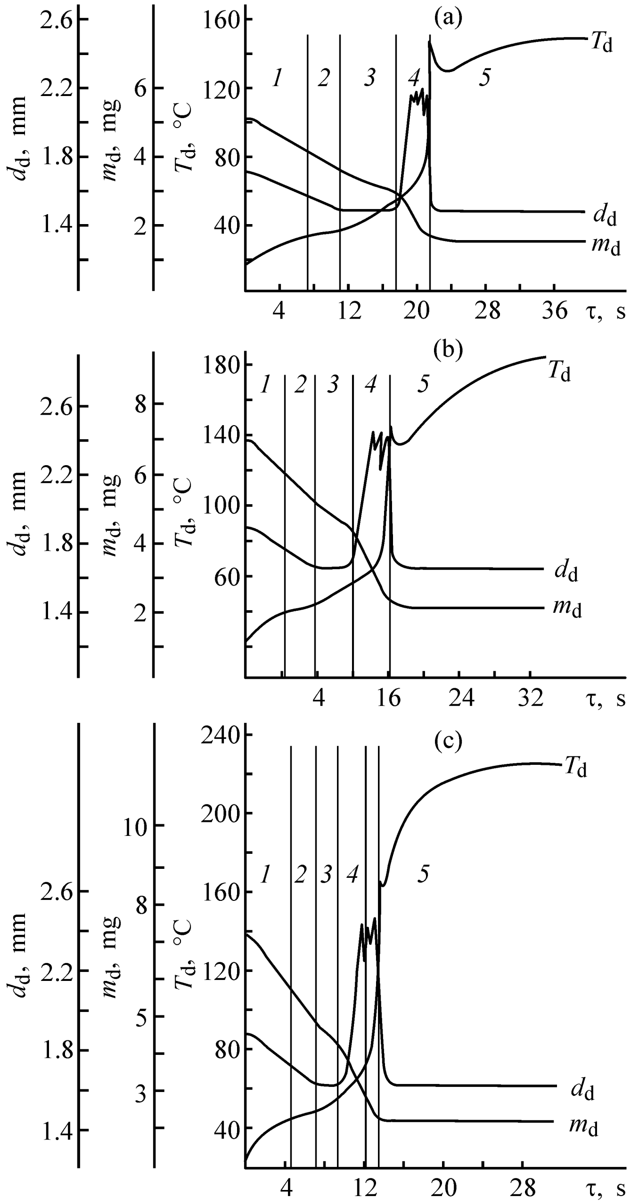

Fig. 2. Kinetic curves of synthesis of potassium superoxide for sample nos. (a) 1, (b) 2, and (c) 3. (d_d) Drop diameter, (m_d) drop mass, (T_d) drop temperature, and (τ) time. (*1*–*5*) Characteristic stages in synthesis of potassium superoxide.

The plots (Figs. 2a–2c) experimentally obtained at different temperatures and humidities of the drying agent make it possible to distinguish five characteristic stages in synthesis of potassium superoxide.

(1) The stage in which the drop is heated from the initial temperature T_0 to a temperature T_{eq}, which corresponds to the temperature of equilibrium evaporation of the solution at a given temperature and humidity of the heat-transfer agent.

(2) The stage of equilibrium evaporation, during which the moisture is intensively removed from the drop surface upon a slight increase in the temperature $T_{eq} = f(T_{DA}, \varphi_{DA}, c_s)$. The increase in the drop temperature at a fixed temperature T_{DA} and humidity φ_{DA} of the drying agent is due to a steady rise in the solution concentration c_s in the surface layer of the drop and to the resulting redistribution of heat flows in the heat exchange between the drop and the gaseous heat-transfer agent. During this period of time, the temperature of the drop at any given instant can be considered identical to the temperature of a moistened thermometer at the appropriate values of T_{DA} and φ_{DA}. The time of completion of this period is an important parameter of the kinetics of the internal processes, because it determines the instant of transition from the low-temperature stage of the process to the high-temperature stage.

(3) The stage of foam formation, which begins when the concentration of the dry substance reaches a value c_s = 40–43%, and continues at a constant drop diameter. The process of moisture removal is accompanied by an inconsiderable release of oxygen in thermal decomposition of the excess amount of hydrogen peroxide. The release of oxygen leads to agitation of the substance in the drop. This gives reason to believe that the temperature and concentration gradients in the material of the drop are negligible, i.e., the assumption that the temperature $T_d(r, \tau) = T_s(\tau) = T_d(\tau)$ and concentration $c_d(r, \tau) = c_s(\tau) = c_d(\tau)$ are constant over the cross-section of the drop is not too exacting. This assumption is confirmed by the experimental curves $m_d = f(\tau)$: the rate of loss of mass by the drop changes by an exceedingly insignificant amount during the entire period. The increase in the temperature of the drop is due to a rise in the concentration of the solution (temperature depression) and to the exothermic nature of its decomposition. A hollow particle starts to be formed during this period.

(4) The stage of synthesis of KO_2 via formation of an intermediate adduct $K_2O_2 \cdot 2H_2O$. According to the dependences presented above, this period of time begins at a drop temperature T_d = 53–57°C.

The crystallization of $K_2O_2 \cdot 2H_2O$ from solution is accompanied by decomposition of an excess amount of hydrogen peroxide by the reaction

$$2H_2O_2 = 2H_2O + O_2. \quad (4)$$

This results in an intensive release of oxygen and an abrupt increase in the particle diameter, with an inflation coefficient $k_{in} = d_4/d_3$ = 1.43–1.46. The absence of a boiling stage characteristic of most of solutions subjected to spray drying suggests that there are no internal limitations to moisture transfer in the crystallization of the solution.

Further, $K_2O_2 \cdot 2H_2O_2$ disproportionates to give KO_2 and free water in accordance with the reaction equation (1b). In this case, a side reaction (2) of decomposition of the target product inevitably occurs and the oxygen released inflates the drop, thereby intensively agitating the reaction mass.

The completion of this period is visually determined from an abrupt contraction of the drop with a contraction coefficient $k_c = d_4/d_5 = 1.43–1.46$, to give a solid hollow particle of yellow-canary color virtually instantaneously. The completion of this period is the most clearly seen from the presence of an exothermic peak in thermograms.

(5) The stage of a decreasing rate of drying, which begins at the instant of time when the rate of moisture removal from the particle starts to be limited only by the rate of transition of water bound to the material into the free state. During this period, the intensity of dehydration noticeably falls, which can be attributed to a decrease in the amount of remaining water and its stronger binding to the material. However, the drop mass remains virtually unchanged during this period, and, therefore, this time can be excluded from consideration in calculating the reactor.

In the course of synthesis, the drop was transformed into a grain with an elastic crust. In all the experiments performed, the dried particles were hollow, with thin, nearly spherical shells.

The data obtained can be used as a basis in calculations of performance and design parameters of the process of synthesis of potassium superoxide from potassium hydroxide and hydrogen peroxide in a spray reactor.

CONCLUSIONS

(1) A study of the basic kinetic aspects of the physicochemical process of synthesis of potassium superoxide from an alkaline solution of hydrogen peroxide in a flow of a drying agent yielded thermograms, gravimetric curves, and video records and made it possible to distinguish five characteristic stages of the process.

(2) It was established that drying is the rate-determining stage in the synthesis of potassium superoxide by the method suggested.

(3) It was established experimentally that particles of the target product, formed by the technique suggested, are hollow spheres.

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