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Hydrogen Peroxide Decomposition in Aqueous Alkali Suspensions of Fe(III) Oxide: The Nature of the Active Component

A. A. Lysova[1, 2], A. O. Kuz'min[2], and V. N. Parmon[1, 2]
[1] *Novosibirsk State University, Novosibirsk, 630090 Russia*
[2] *Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

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Abstract—The nature of the catalytically active components is studied in the steady-state decomposition of hydrogen peroxide in alkali media in the presence of an Fe_2O_3 suspension at 25°C in an intensively shaken reactor. It was found that a hydroxide colloid formed by the mechanical abrasion of the solid catalyst in an aqueous solution shows noticeable catalytic activity together with the initial solid-phase catalyst. As a result, the rate of the catalytic reaction becomes nonlinear with respect to the overall catalyst concentration.

INTRODUCTION

Many catalytic processes in the liquid phase are carried out in suspensions of solid catalysts under conditions of long intensive shaking or mixing. It is known that intensive mechanical treatment of the solid substance suspension may lead to its partial colloidization, and both initial solid particles of the suspension and the colloidal particles may be catalytically active. However, no special experiments are usually carried out to determine the contribution of each form of the catalyst to the overall catalytic activity of the systems under consideration. At the same time, knowledge of the true nature of the active component of the suspended catalyst is very important for creating stable catalysts and for the correct interpretation of the results of kinetic experiments.

Hydrogen peroxide decomposition is rather well studied in aqueous suspensions of heterogeneous catalysts based on oxides and hydroxides of many transition metals, including Fe(III) and Cu(II) (see [1, 2]). A detailed study of catalytically active sites has never been carried out for this reaction, although the heterogeneous catalyst is implicitly assumed to participate directly in hydrogen peroxide decomposition. This work shows that, when the suspended particles of iron oxide are used as a catalyst, both the initial suspended oxide and the Fe(III) colloid formed from the solid oxide upon the intensive mechanical treatment of the catalyst in the course of the reaction contribute to the catalytic activity.

EXPERIMENTAL

The following reagents were used: Fe(III) hydroxide (chemical purity grade, Reakhim), a 30% solution of H_2O_2 (extra purity grade), sulfuric acid (extra purity grade), hydrochloric acid (chemical purity grade), NaOH (analytical purity grade, Fluka), $TiCl_4$ (extra purity grade), $Ce(SO_4)_2 \cdot 4H_2O$ (chemical purity grade, Reakhim), *ortho*-phenanthroline, and hydroxylamine. Solutions were prepared in water prepared using a Milli-Q (Millipore, France) system for the fine purification of water. Argon was used without additional purification.

We used a catalyst obtained by calcining Fe(III) hydroxide at 450°C for 5 h in air and characterized by XRD as mostly crystalline α-Fe_2O_3 (S_{sp} = 20 m^2/g; microcrystallite size, ~400 Å). The calcined powder was ground in a mortar to a particle size of 10 μm. The uniformity of the phase composition of the samples was studied by the method of differential dissolution [3, 4] in a flow of a solvent mixture consisting of concentrated HCl, concentrated HNO_3, and water in a 0.5 : 0.5 : 1 volume ratio.

Before the reaction of hydrogen peroxide decomposition, a suspension of the catalyst in a 0.01 mol/l NaOH solution was intensively shaken for 15 min in the reactor purged with argon.

To obtain a supernatant, the catalyst suspension (1.15 g portion) in the 0.01 mol/l solution of NaOH (115 ml) was intensively shaken in a 152-ml reactor for 1 h. Then the liquid phase (supernatant) was separated by centrifuging for 10 min using an MPW 340 centrifuge (Poland) with an intensity of 2800 rpm.

Hydrogen peroxide solutions were prepared by dissolving the initial 30% solution of H_2O_2 in water. The exact concentration of H_2O was determined by spectrophotometry using a reaction with Ti(IV) [5] or by titration with Ce(IV) [6].

The steady-state concentration of hydrogen peroxide in the solution was controlled by the absorption of the H_2O_2–Ti(IV) complex [5]. To this end, 2 ml of the

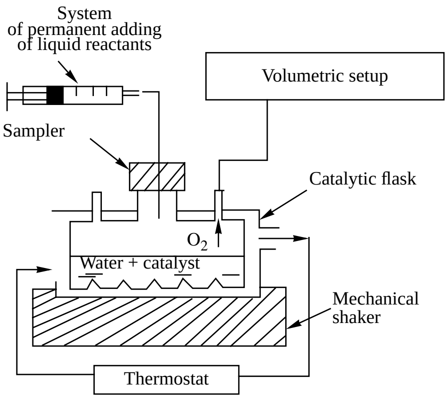

Fig. 1. Schematic of the catalytic setup with permanent adding of hydrogen peroxide.

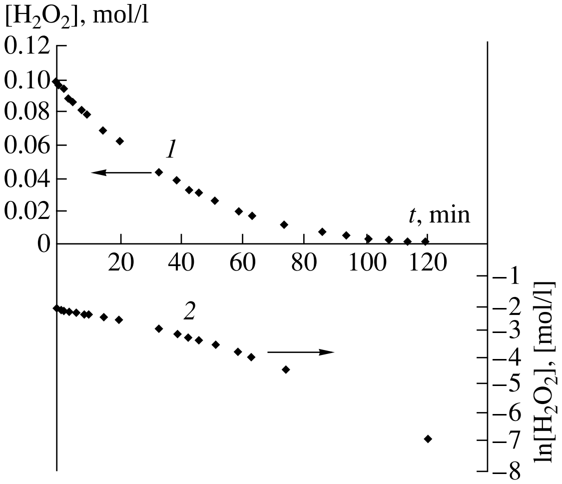

Fig. 2. (*1*) The kinetic curve and (*2*) its linearization in semilogarithmic coordinates for H_2O_2 decomposition in the presence of 0.1 g Fe_2O_3 under non-steady-state conditions. $[H_2O_2]_0 = 0.1$ mol/l; 25°C; 0.01 mol/l NaOH; the volume of the solution is 10 ml.

catalyst suspension in water was added to 2 ml of Ti(IV) in 4 mol/l H_2SO_4 (1 mg/ml) after interrupting hydrogen peroxide decomposition under conditions of permanent adding of H_2O_2 to the reaction mixture; the sediment was separated by centrifuging. The liquid phase obtained by the addition of the 2 ml of the suspension of the catalyst in water to 2 ml of 4 mol/l H_2SO_4 and sediment separation by centrifuging was used as a reference solution. The concentration of H_2O_2 was calculated using the extinction coefficient of the Ti(IV) peroxide complex with $\varepsilon = 700$ l mol^{-1} cm^{-1} at $\lambda = 405$ nm.

The concentration of Fe(III) in the solution after the reaction was determined by the absorption of the Fe(II) complex with *ortho*-phenanthroline (extinction coefficient $\varepsilon = 11000$ l mol^{-1} cm^{-1} at $\lambda = 505$ nm) after centrifugation, the decomposition of the colloid of concentrated HCl, and the reduction of Fe(III) to Fe(II) by a 10% solution of hydroxylamine [5, 7].

To register optical spectra in the UV and visible regions, a Shimadzu UV 300 spectrophotometer (Japan) was used. An EV-74 ion meter (USSR) was used to control the pH of the solutions.

The steady-state kinetic study of H_2O_2 decomposition was carried out in a system consisting of a thermostated several-necked catalytic flask (152 ml), a mechanical shaker (600 vibrations per minute), a thermostated volumetric device, and a system for the permanent adding of liquid reactants (Fig. 1). Permanent adding was necessary to maintain the steady-state of the system. This state is characterized by the stationary values of $[H_2O_2]$ and pH and therefore by the stationary composition of the catalyst surface, which is very probably because the state of the surface (the concentration of the surface hydroxy groups and peroxo complexes) is determined by the pH of the solution and by the H_2O_2 concentration. In our study, permanent adding maintained the supply of the H_2O_2 solution with a concentration of 0.3–1.2 mol/l at a constant rate (0.82 ml/h in most runs) during the whole period of a run. The amount of oxygen formed was measured during the reaction.

Under non-steady-state conditions, the system of permanent adding was not used: hydrogen peroxide was added to the shaken 72-ml reactor via a syringe and then the kinetics of O_2 formation was determined using a volumetric setup.

To increase the statistical reliability of the results, all experimental points were reproduced several times.

RESULTS AND DISCUSSION

The dependence of $[H_2O_2]$ on time in hydrogen peroxide decomposition under steady-state conditions in the presence of Fe_2O_3 is best linearized in semilogarithmic coordinates (Fig. 2). This fact suggests a first order of the reaction with respect to hydrogen peroxide concentration up to a hydrogen peroxide concentration of 9×10^{-3} mol/l, corresponding to 90% conversion.

When H_2O_2 is continuously supplied to the reaction medium, the rate of oxygen formation becomes constant for several minutes after the beginning of hydrogen peroxide dosing, indicating that some stationary state is established in the system (see Fig. 3). The constant value $[H_2O_2]$ under these conditions is confirmed by experiments on its determination in certain time intervals after the beginning of the reaction. The value of pH in the reaction medium during the experiment also remains constant (excluding the first minutes when the steady-state is established).

The steady-state kinetic experiments enabled the determination of the reaction order with respect to hydrogen peroxide at $[H_2O_2]$ ranging from 2.9×10^{-4} to 1.4×10^{-3} mol/l. Indeed, under steady-state conditions, the rate of hydrogen peroxide supply is equal to the rate

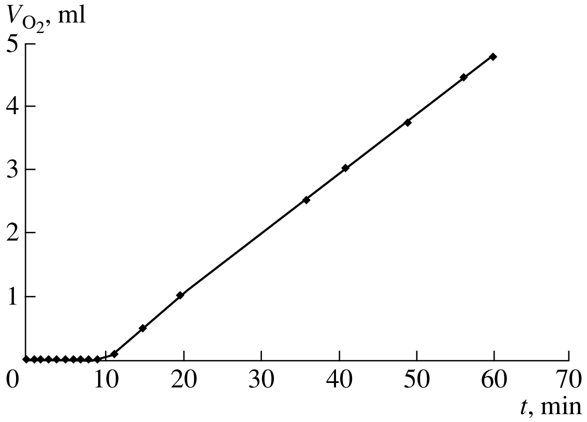

Fig. 3. The dependence of the volume of evolved oxygen on the time for H_2O_2 decomposition in the presence of 0.5 g Fe_2O_3 under conditions of permanent adding of H_2O_2 at 25°C.

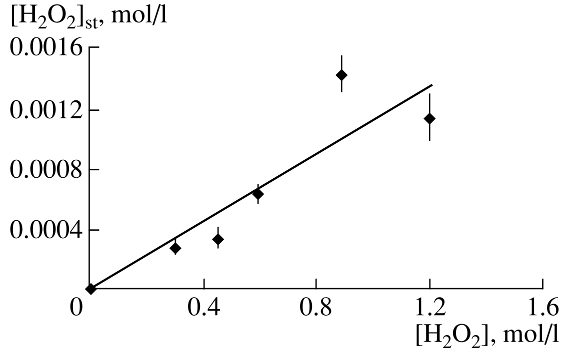

Fig. 4. Dependence of the steady-state concentration of hydrogen peroxide in the presence of 1.15 g Fe_2O_3 on the concentration of H_2O_2 solution supplied by the system of permanent adding. 25°C; 0.01 mol/l NaOH; the initial volume of the gas phase is 37 ml, and the initial volume of the liquid phase is 115 ml.

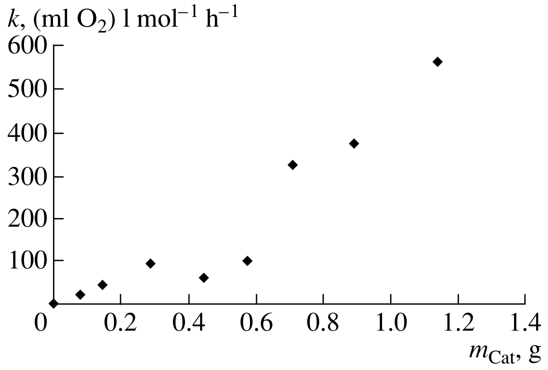

Fig. 5. Dependence of the apparent rate constant of H_2O_2 decomposition on the weight of the Fe_2O_3 catalyst loaded. The concentration of H_2O_2 in the supplied solution is 0.3 mol/l; 25°C; 0.01 mol/l NaOH; the initial volume of the gas phase is 37 ml; the initial volume of the liquid phase is 115 ml. The relative error in determining $k = w/[H_2O_2]_{st}$ is at most 10%.

of its consumption: $w_{suppl} = w_{cons} = k[H_2O_2]^n$, where k is the apparent rate constant and n is the reaction order with respect to hydrogen peroxide. The rate of hydrogen peroxide supply is set by the concentration of H_2O_2 in the solution dosed to the reactor.

Figure 4 shows the dependence of the steady-state concentration of H_2O_2 in the system on the H_2O_2 concentration in the solution supplied by the permanent adding system. This dependence is adequately described by a straight line, which is indicative of a reaction order close to the first with respect to hydrogen peroxide concentration under steady-state conditions. We assume that the first order with respect to H_2O_2 provides further evidence for the conclusion drawn in [1, 2] that hydrogen peroxide decomposition in alkali solutions in the presence of the Fe_2O_3 catalyst occurs via the molecular or hidden radical mechanism rather than via the free radical mechanism. Indeed, according to the free radical mechanism, the reaction order can be fractional.

Knowledge of the reaction order of hydrogen peroxide decomposition makes it possible to calculate the apparent rate constant of the reaction k and its dependence on the catalyst concentration. For that, we carried out experiments under steady-state conditions in the medium of 0.01 mol/l NaOH and various Fe_2O_3 loadings. The value of the coefficient k was determined as a ratio of the rate of oxygen formation to the steady-state concentration of hydrogen peroxide assuming that the reaction has the first order with respect to hydrogen peroxide.

Figure 5 shows the dependence of k obtained by averaging over several (up to five) independent experiments on hydrogen peroxide decomposition on the catalyst weight. This figure shows that, unlike the standard models of the dependence rates of heterogeneous catalytic reactions on the amount of the catalyst, this dependence is nonlinear and has several clearly seen regions. Although this plot has a rather complex shape, we can propose its qualitative interpretation. In our opinion, only the highly deficient or noncrystalline portion of the solid catalyst introduced into the systems has catalytic activity. This portion is on the surface of Fe_2O_3 microcrystallites and its presence is due to the sample history. This portion is capable of forming a colloid (unlike Fe_2O_3 microcrystallites) upon mechanical treatment when the system is shaken. The phase nonuniformity of the catalyst was confirmed by the method of differential dissolution, as is discussed in more detail below.

In this case, at low initial amounts of solid catalyst, its highly deficient or noncrystalline portion is in completely colloidal form, and H_2O_2 decomposition occurs on the colloidal Fe(III) hydroxide in the absence of catalytic activity of Fe(III) oxide in crystalline form. The amount of Fe(III) hydroxide is proportional to the overall concentration (m_{Cat}) of iron oxide introduced into the system. Then, if the properties of colloidal particles

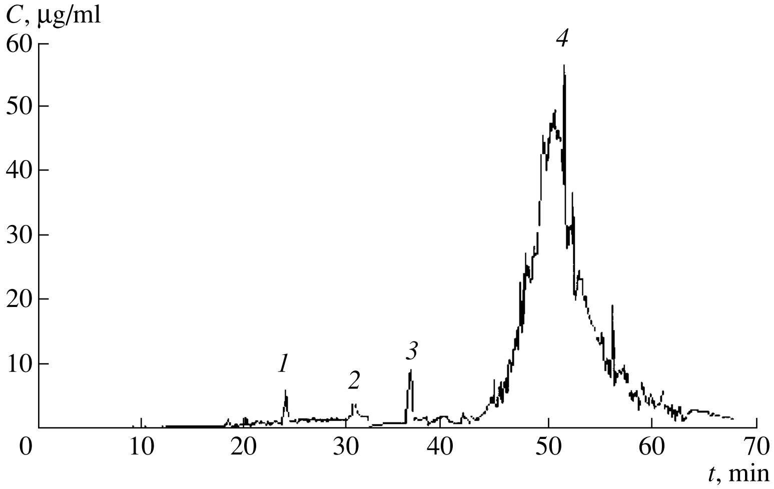

Fig. 6. Kinetics of the differential dissolution of the catalyst sample in a flow of the dissolving mixture: concentrated HCl, concentrated HNO_3, and H_2O with the volume ratio 0.5 : 0.5 : 1. $T = 20°C$; starting from the 43th minute, $T = 70°C$. C is the amount of the dissolved sample. The fraction of the first three peaks is 2.1% of the overall sample (2.75 mg).

remain constant, the reaction of H_2O_2 decomposition should have the first order with respect to the catalyst weight. Indeed, at low (<0.3 g) loadings of iron oxide, hydrogen peroxide decomposition has the first order with respect to the overall amount of the catalyst.

However, with an increase in m_{Cat} from 0.3 to 0.6 g, the reaction rate changes insignificantly. In our opinion, this is due to the fact that the colloid formed in the system is in equilibrium with a small amount of the remaining solid colloidized oxide phase in the given range of iron oxide concentration. This provides an approximate constancy of the colloid concentration and, as a consequence, an approximate constancy of the reaction rate when the overall catalytic activity of the solid particles is low, because the reaction mainly occurs on the colloidal Fe(III) hydroxide.

At $m_{Cat} > 0.7$ g, the dependence of the reaction rate is again almost linear with respect to the concentration of iron oxide introduced into the system. We suppose that a substantial amount of the catalytically active solid phase is in equilibrium with the colloid, and the rate of hydrogen peroxide decomposition on the solid catalyst, which is proportional to the amount remaining after colloidization, becomes comparable with the rate of decomposition on the colloid, which is in equilibrium with the solid phase and the concentration of which is independent of the Fe_2O_3 amount.

The phase nonuniformity of the Fe_2O_3 samples, which consists in the presence of a small amount of the phase that is more active in dissolution and colloid formation, is well known and depends on the sample history [8, 9]. Indeed, the direct study of the phase nonuniformity of the catalyst used in this work by the method of differential dissolution [3, 4, 8, 9] demonstrated the presence of a very small amount of the three phases in the sample that are more active in dissolution than the main body of the sample (see Fig. 6).

CONCLUSION

Experimental data obtained in this work suggest that both the solid phase of the catalyst and colloidal Fe(III) hydroxide are catalytically active in H_2O_2 decomposition in the presence of Fe_2O_3. Colloidal hydroxide is probably formed from the highly deficient or noncrystalline component of Fe_2O_3 on the surface of oxide microcrystallites in the initial biographically nonuniform sample of the catalyst. This explains the complex shape of the dependence of the hydrogen peroxide decomposition rate on the overall concentration of the catalyst.

To verify the assumption that the process of catalytic H_2O_2 decomposition in Fe_2O_3 suspension occurs not only on the surface of solid species but on the colloidized catalyst as well, we studied hydrogen peroxide decomposition in the presence of the supernatant separated from the mechanically destructed oxide catalyst (see the experimental section of this paper). Experiments on the decomposition of hydrogen peroxide under both non-steady-state and steady-state conditions (when the system of permanent adding was attached to the system), showed that the supernatant separated from the solid phase also has a noticeable catalytic activity.

The study of the supernatant by the method of small-angle X-ray scattering (SAXS) showed that this is a colloidal system that is almost uniform in particle size (diameters of ~30 Å). The concentration of Fe(III) in the colloidal solution formed after the reaction with 1.15 g Fe_2O_3 determined by the method described above was 6×10^{-5} mol/l. It is easy to check that a rather small concentration of iron in the colloidal solution approximately corresponds to the amount of Fe_2O_3 phases active in dissolution (2.1 wt % of iron, see Fig. 6). This confirms the assumption that only a portion of the solid catalyst transforms into the colloidal form rather than its main component, which is crystalline α-Fe_2O_3, which is apparently only slightly catalytically active.

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