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Study of Photocatalytic Activity of Layered Oxides: $NaNdTiO_4$, $LiNdTiP_4$, and $HNdTiO_4$ Titanates

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Abstract—The catalytic activity of the perovskite-like layered oxides $NaNdTiO_4$, $LiNdTiO_4$, and $HNdTiO_4$ in the reaction of the methyl orange dye decomposition under the action of UV irradiation was studied. Rate constants of the pseudo-first order were determined. It was found that in the series $NaNdTiO_4$, $HNdTiO_4$, and $LiNdTiO_4$ the photocatalytic activity of the layered oxides increases.

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Recently the possibility of using complex layered oxides (titanates, tantalates, and niobates) as catalysts of photoinduced processes is actively studied [1, 2]. Complex oxides of rare-earth and alkaline elements are considered as an alternative to binary oxides, in particular, to widely known and effective photocatalyst, titanium dioxide. The attractiveness of the complex oxides consists in a possibility of varying cationic composition, thus influencing their catalytic activity. Moreover, in complex oxides with a layered structure the intercalation of water molecules in the interplanar space [3, 4] is possible, which can be considered as an increase in the effective specific surface area of a photocatalyst. At present the effect of the nature of the interlayer space on the photocatalytic activity is insufficiently studied. Also experimental data are deficient on the photocatalytic activity of isostructural layered oxides in decomposition reactions of organic substances under identical conditions.

In this work we present the results of the study of photocatalytic activity of layered perovskite-like oxides with a similar structure, but different cationic composition. The comparative analysis of the photocatalytic activity of oxides has been fulfilled using the reaction of photoinduced decomposition of the methyl orange dye under UV irradiation.

The layered complex oxides $NaNdTiO_4$, $HNdTiO_4$, and $LiNdTiP_4$ belong to cation-ordered Ruddlesden–Popper phases and are built according to a block principle by jointing layers with the perovskite structure and fragments with the NaCl structure. In the structure of the oxides under consideration variously charged cations are completely ordered in different layers of the layered structure because of essential differences in sizes and charges of Nd^{+3} cations and cations of alkali metals (Na^{+1}, Li^{+1}) or a proton. It is the reason which is responsible for the possibility of the synthesis of $HNdTiO_4$ and $LiNdTiO_4$ by ion-exchange reactions from $NaNdTiO_4$, which can be obtained by a high-temperature solid-phase synthesis.

According to the X-ray analysis, samples of $NaNdTiO_4$, $HNdTiO_4$, and $LiNdTiO_4$ oxides, which were used for the study of catalytic activity, were monophase. According to the electron microscopy data, the particle size of layered titanates essentially exceeds that of titanium dioxide (50 nm) used for their synthesis. It is connected with the fact that $NaNdTiO_4$ was obtained by a ceramic method, which is characterized by the enlargement of particle sizes of synthesis products, as compared with reagents, due to caking at a high temperature. Particles of the complex oxides $NaNdTiO_4$, $HNdTiO_4$, and $LiNdTiP_4$ are close in morphology: particles have a lamellar shape with a width of ~200 nm. At the same time the specific surface area of $HNdTiO_4$ (3.5 $m^2\,g^{-1}$) is almost twice greater than that of $NaNdTiO_4$ (1.8 $m^2\,g^{-1}$) that can testify to a partial destruction of particles in the ion-exchange reaction, which proceeds in an acid solution, and to the appearance of surface defects and cracks.

As it was shown earlier [4], $NaNdTiO_4$ in aqueous solution is noticeably involved in an ion exchange, namely, sodium ions in a crystal phase are partially

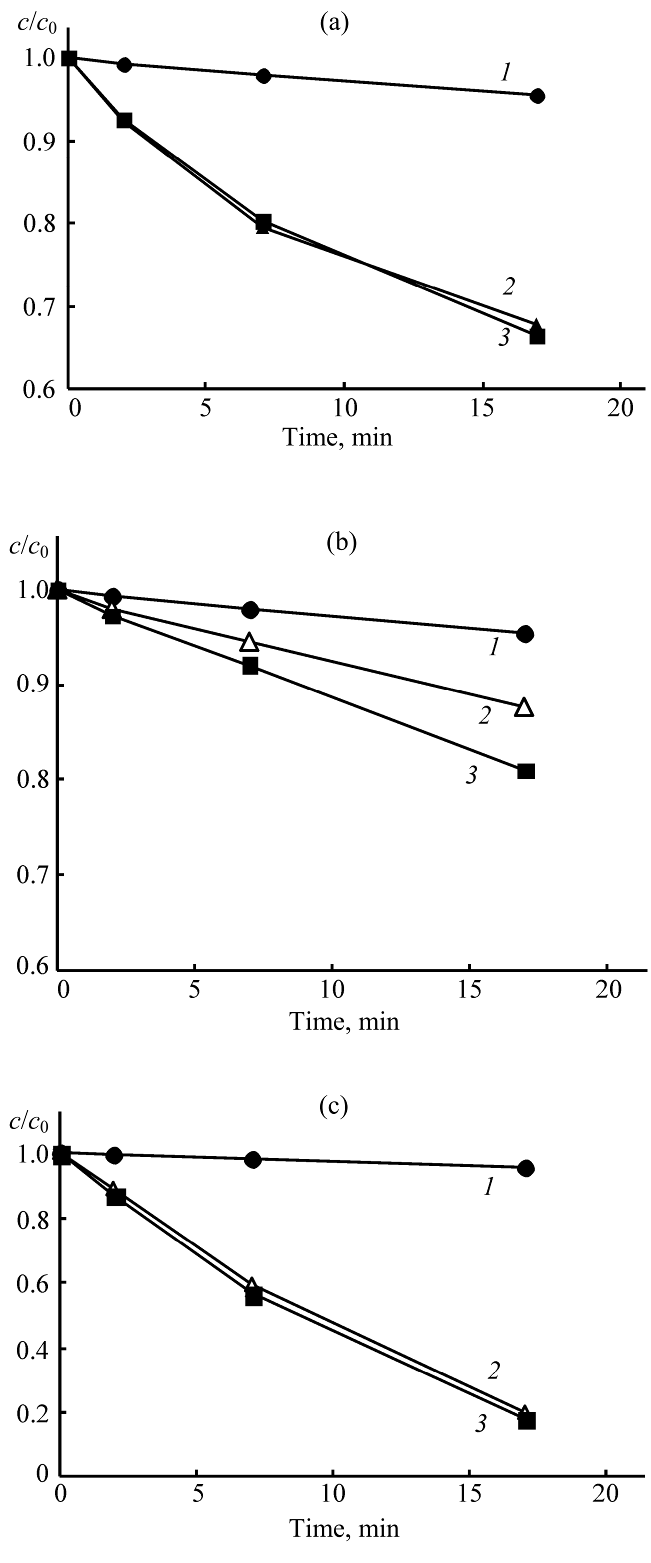

Fig. 1. Time dependence of the degree of methyl orange decomposition: (a) $NaNdTiO_4$, (b) $HNdTiO_4$, (c) $LiNdTiO_4$. (*1*) without catalyst, (*2*) 100 mg of a catalyst, and (*3*) 1 mmol of a catalyst.

replaced by protons, therefore the solution becomes alkaline. All the suspensions of the complex oxides to be studied had pH different from neutral. The results of the determination of pH of titanate suspensions are presented in the table. The acidity of HNdTiO suspensions$_4$ results from a partial dissociation of this solid acid. To find out the reason of the reaction acceleration, either the presence of a catalyst or a variation in pH, we have studied the dependence of the rate of the methyl orange decomposition on pH (from 5 up to 13) without a catalyst.

As a result in each spectrophotometric experiment we obtained a set of absorption spectra at various irradiation times. On the basis of these spectra we constructed kinetic curves describing a decrease in the methyl orange concentration in time. The degree of the dye decomposition (the ratio of the dye current concentration c to its initial concentration c_0 equal to 12 mg l^{-1}) is presented in Fig. 1. It is seen from Fig. 1a that the methyl orange decomposition rate in the presence of $NaNdTiO_4$ is 5–6 times greater than without a catalyst. It is seen from Fig. 1c that the rate of methyl orange decomposition in the presence of $LiNdTiO_4$ is 2.5–3 times higher than in the case of $NaNdTiO_4$. It is important to note that in the cases of $NaNdTiO_4$ and $LiNdTiO_4$ the photoreaction rate is independent of the catalyst amount in a suspension. It is seen from Fig. 1b that the presence of 1 g l^{-1} of $HNdTiO_4$ accelerates the photoreaction of methyl orange decomposition only by the factor of 2, and the increase in the concentration of the catalyst $HNdTiO_4$ results in a noticeable increase in the decomposition rate. It suggests that $HNdTiO_4$ possesses a low, but measurable, photocatalytic activity if the rate increase is not connected with the increase in the acidity of the medium. Kinetic curves obtained in the absence of the catalyst at various pH values (Fig. 2) show that the effect of pH of the solution on the rate of methyl orange decomposition is rather high. We have estimated pseudo-first order kinetic constants for all the experimental kinetic curves. The resulting values of the rate constant are presented in Fig. 3.

Dependences of the rate constant of methyl orange photolysis on pH in the presence of three studied layered oxides and in the absence of a catalyst are presented in Fig. 3. An examination of these data allows us the following conclusions. In the range of pH from 10.7 up to 13.0 a linear dependence of the rate constant of methyl orange decomposition on pH is observed. Points corresponding to $NaNdTiO_4$ lay under the plot of the rate constant vs. pH, i.e. this titanate does not render an accelerating action on the methyl orange photolysis in experimental conditions. Points corresponding to $HNdTiO_4$ are in the acid region and lay above the plot of the rate constant vs. pH. Thus, $HNdTiO_4$ renders an accelerating action on the reaction under study, however in the experimental conditions this effect is weak. Points corresponding to $LiNdTiO_4$ lay above the plot of the rate constant vs. pH, which points to a photocatalytic activity of the $LiNdTiO_4$ oxide.

Thus, the fulfilled research has demonstrated a catalytic activity of the perovskite-like layered oxides $MNdTiO_4$ (M = Na, Li, H) in the reaction of the photoinduced methyl orange decomposition under the action of UV irradiation. The comparative analysis has shown that the photocatalytic activity of the layered oxides increases in the sequence $NaNdTiO_4$, $HNdTiO_4$, $LiNdTiO_4$.

EXPERIMENTAL

The study was carried out using a UV-1650 PC spectrophotometer in the range of wavelengths 200–600 nm.

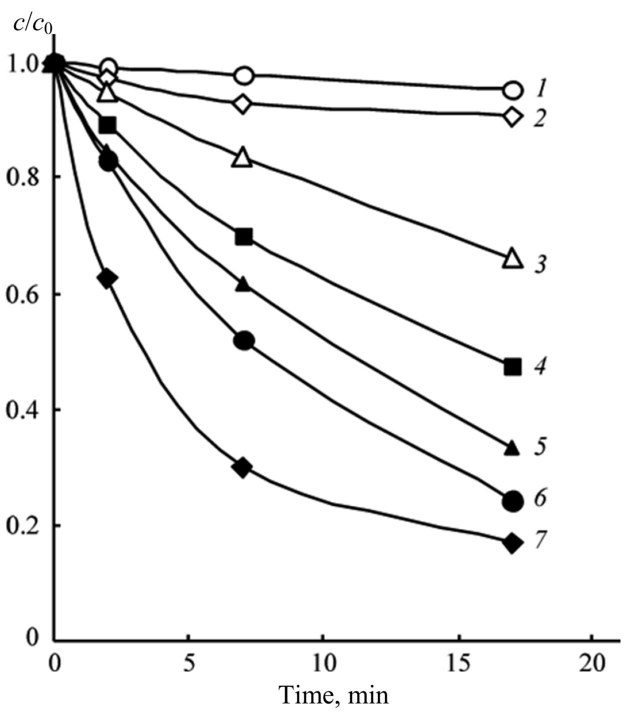

Fig. 2. Curves of methyl orange decomposition at various pH values. (*1*) 6, (*2*) 9.6, (*3*) 10.7, (*4*) 11.2, (*5*) 11.7, (*6*) 12.2, and (*7*) 13.

Values of pH of solutions and rate constants of methyl orange decomposition in the presence of catalysts

Catalyst	Weight of a catalyst, mg/100 ml	pH	k, min^{-1}
$NaNdTiO_4$	100	11.29	0.0253
$NaNdTiO_4$	279	11.59	0.0245
$HNdTiO_4$	100	5.42	0.0094
$HNdTiO_4$	257	5.21	0.0131
$LiNdTiO_4$	100	10.91	0.0910
$LiNdTiO_4$	263	11.19	0.0907

The layered titanate $NaNdTiO_4$ was synthesized by the solid-phase method in air under atmospheric pressure according to the procedure developed when studying the mechanism of its formation and its thermal stability [5, 6]. As initial reagents we used stoichiometric amounts of Na_2CO_3, TiO_2, and Nd_2O_3 corresponding to the equation of reaction (1).

$$Na_2CO_3 + 2TiO_2 + Nd_2O_3 \rightarrow 2NaNdTiO_4 + CO_2. \quad (1)$$

The purity of the reagents in use was 99.9%. Neodymium oxide was calcined at 1000°C within 10 h before weighing. Weighed samples of the reagents were ground in an agate mortar. The resulting blend was pressed in tablets, which then were calcined in a corundum crucible in Silit furnaces at 790°C within 3 h.

The protonated layered titanate $HNdTiO_4$ was obtained from $NaNdTiO_4$ by ion exchange [4]. For this

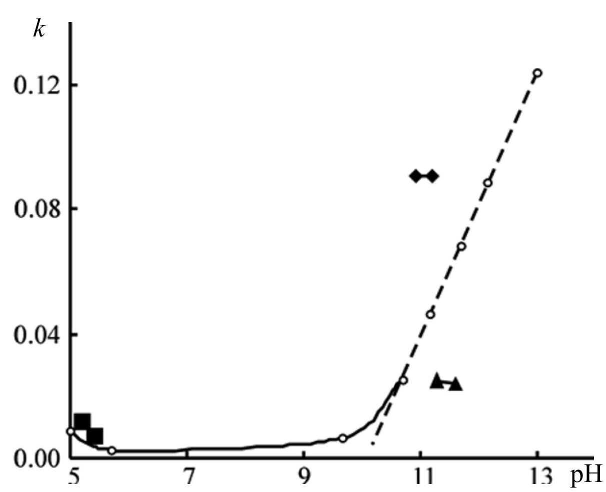

Fig. 3. Dependence of the rate constant of methyl orange decomposition on pH: (circles) without catalyst, (triangles) $NaNdTiO_4$, (squares) $HNdTiO_4$, and (rhombs) $LiNdTiO_4$.

purpose a 2.79 g (10 mmol) weighed sample of $NaNdTiO_4$ was placed in 100 ml of a 0.2 M solution of hydrochloric acid, which is twice as large as the stoichometry of reaction (2) required.

$$NaNdTiO_4 + H^+_{sol} \rightarrow HNdTiO_4 + Na^+_{sol}. \quad (2)$$

The resulting suspension was stirred within 2 h and a value of solution pH was determined using an IPL-103 ionometer and an ESL-43-07 H^+-selective electrode. Then a solid phase was filtered off on an acetate-cellulose filter in a vacuum. The resulting solid product was dried in a desiccator above $CaCl_2$ within 170 h.

The layered titanate $LiNdTiO_4$ was obtained from $NaNdTiO_4$ by ion exchange reaction (3) in a $LiNO_3$ melt.

$$NaNdTiO_4 + Li^+_{melt} \rightarrow LiNdTiO_4 + Na^+_{melt}. \quad (3)$$

A weighed sample of $NaNdTiO_4$ was mixed with a 50-fold excess of $LiNO_3$. The resulting mixture was heated up to 360°C and stirred for 10 h, then cooled to room temperature and separated from soluble nitrates using a 1 M LiOH solution to prevent the replacement of Li^+ by H^+ from water. Products of the synthesis were checked by X-ray analysis using an ARL X'TRA powder diffractometer (CuK_α radiation) in the range of 2θ angles from 5 up to 50.

The morphology of polycrystalline grains of the complex oxides was studied by means of a Carl Zeiss EVO 40 scanning electron microscope. Specific surface areas of $NaNdTiO_4$ and $HNdTiO_4$ were determined by the reversible nitrogen adsorption method (BET).

The rate of the photoinduced decomposition of a methyl orange dye was studied in an internal UV irradiation reactor at room temperature. The experiments were carried out in a vertical reactor constructed in such a way that a high efficiency was provided, first, of the light use due to the optimal ratio of an irradiated surface area to a reaction mixture volume and, second, of the reaction mixture intermixing by a magnetic stirrer and a stream of a gas moving from the bottom upwards. The reaction mixture (a dye solution and a suspended complex oxide) was arranged between exterior and interior quartz tubes, the distance between walls was 5 mm, and the exterior diameter 5 cm, which provided a 100 ml working volume of the reactor with a height of 20 cm. The irradiated area was 250 cm^2.

A catalyst was weighed to within 0.0001 g and placed into 100 ml of the dye solution (c_0 12 mg l^{-1}). The experiments were carried out at various amounts of a catalyst: 100 mg and 1 mmol (that, for example, corresponds to 279 mg in the case of $NaNdTiO_4$). A suspension obtained after adding a catalyst was stirred within 20 min, and then pH of the solution was determined. The study of the dependence of the methyl orange decomposition rate in the presence of titanium dioxide and without a catalyst was carried out at pH from 5 up to 13. The value of pH was maintained by a hydrophosphate buffer and Na_2CO_3 and NaOH solutions. A variation of methyl orange concentration during the decomposition reaction was determined by spectrophotometry from a set of absorption spectra at various times of suspension irradiation.

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