

Photochemical activity of some complex oxides – phase components of tropospheric aerosol

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Powdered samples of complex oxides (potassium niobates of the layered structure) were obtained by high temperature synthesis and subsequent grinding. Action spectra of photoinduced processes were determined over potassium niobates of the different phase composition for water and water-organic systems. It is shown that oxygen formation is caused by its photodesorption and is observed under illumination near the red boundary of intrinsic absorption band region. Hydrogen is formed as a result of photocatalytic dehydrogenation of residual adsorbed organic compounds, whereas photocatalytic decomposition of water does not occur. The quantum efficiency of photocatalytic dehydrogenation increases by an order of magnitude after adding the mixture of a hydrogen-containing organic compound to the reaction.

Introduction

Chemical phase composition of tropospheric solid aerosol has not been yet determined, however it is known that it is close to chemical phase composition of the Earth lithosphere.¹ Along with other processes of the earth crust formation, its formation also occurred in high temperature processes, which favor the synthesis of silicates, composite oxides – metal associations (Ni–Nb–Zr-association includes the perovskite group).² As its origin, a significant part of solid tropospheric aerosol (composite and simple oxides) has natural earth crust minerals, which underwent long-term changes. Therefore, the production of composite oxides, close to the parts of solid aerosol in texture and crystalline structure, is possible by means of high temperature synthesis of composite oxides after their further transformation to the powdered state.

In this work we present the results of investigation of photochemical activity of composite oxides belonging to the perovskite group. These oxides were produced by means of high temperature synthesis from niobium oxide and potassium carbonate (niobates of layered structure).

According to Refs. 3–7, niobates are active as photocatalysts of the hydrogen release. In order to increase the photocatalytic activity, niobates are modified by platinum,⁴ nickel,⁵ copper,⁶ caesium.⁷

In our experiment the photocatalyst was modified by intercalation^{4–8} of platinum in interlayer space of potassium niobate crystalline structure as more resistant to the influence of redox characteristics of a medium.

Experimental technique

To produce the potassium niobate, we used niobium pentoxide and carbonic potassium. The mixture of Nb₂O₅ and K₂CO was prepared either by

niobium pentoxide powder impregnation with K₂CO₃ water solution or by mixing their powders, or by grinding powder mixture in a mortar. Potassium niobate was produced by the fusion of the mixture in air in corundum crucible during 20 min at a temperature of 1573 K. The produced alloy was grinded in the corundum mortar to the powdered state.

According to the data of X-ray analysis, we obtained powdered samples with stoichiometric compositions, corresponding to the formulas presented in Table 1.

Table 1. Phase composition and the conditions of potassium niobate samples production

Sample	I	II	III
Stoichiometric formula	K ₄ Nb ₆ O ₁₇ (Nb ₂ O ₅ × × 2/3 K ₂ O)	K ₂ Nb ₄ O ₁₁ (Nb ₂ O ₅ × × 1/2 K ₂ O)	K ₂ Nb ₈ O ₂₁ (Nb ₂ O ₅ × × 1/4 K ₂ O)
Original ratio Nb ₂ O ₅ /K ₂ CO ₃	2.2	2.9	2.9
The conditions of mixing the components	Grinding in mortar	Mechanical mixing	K ₂ CO ₃ solution impregnation

To increase the activity of hydrogen release under the influence of light quanta, potassium niobates were modified with platinum according to the method described in Refs. 4 and 8. The powdered sample of potassium niobate was impregnated with [Pt(NH₃)₄]Cl₂ solution being constantly mixed with magnetic stirrer during 3 days. Then the sample was dried in water bath treated with hydrogen (*P* = 400 Torr) at a temperature of 473 K during 6 h in order to retrieve Pt(II) to metallic Pt(0).

After such an insertion (intercalation) of platinum in the interlayer space of the niobate layered structure, the metallic platinum was removed from the outer surface of the photocatalyst by boiling the niobate in aqua regis during 1 h. At the end stage of

photocatalyst preparation, it was filtered, rinsed with hot water and dried.

The $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ complex, which is necessary for the reaction of ion exchange in order to substitute potassium cations in interlayer space,⁹ was produced by the method described in Ref. 10. Water solution of platinum-hydrochloric acid was used as the original reagent.

Besides, before being loaded into reactor, the photocatalyst was heated, as in Ref. 8, in hydrogen at a temperature of 773 K and a pressure of 40 kPa and then in oxygen at a temperature of 473 K and a pressure of 16 kPa. The methodology of experiments on measuring the rates of oxygen and hydrogen formation in dark and under monochromatic illumination, as well as on determination of quantum efficiency of the photocatalytic reaction and the spectral dependence of the efficient quantum yield are described in Ref. 11.

Results and discussion

The oxygen and hydrogen release in the dark, found by us, was an unexpected result. Thus, in the initial state in the absence of illumination the hydrogen and oxygen are released with a rate of ~ 0.01 micromole/h. Note that in Pt/TiO₂ system this phenomenon is absent.¹¹ Such a difference is explained by the fact that niobates are catalysts of a layered structure,¹² microparticles of which have cavities of 2 nm (cavity of the I type) and of 0.5–0.6 nm (cavity of the II type).⁴ During preprocessing the photocatalyst, oxygen and hydrogen molecules are adsorbed on inner surfaces of the cavities. In the dark, a slow desorption of these gases, diffusion in the cavity of niobate crystalline structure, and the release into the gas phase proceed.

When the platinized potassium niobate is illuminated by DRSh-500 mercury lamp, the increase of hydrogen and oxygen release rate by orders of magnitude are observed. This fact agrees with the data presented in Refs. 3, 4, and 8. Hydrogen release rates for the systems with potassium niobate of different stoichiometric composition as photocatalyst are presented in Table 2.

Table 2. Hydrogen release rate under illumination of platinized potassium niobate by the OSL-1 illuminator with DRSh-500 mercury lamp

Photocatalyst	Hydrogen release rate, micromole /h
Pt (0.01 weight. %) / K ₄ Nb ₆ O ₁₇	0.8
Pt (0.01 weight. %) / K ₂ Nb ₄ O ₁₁	0.05
Pt (0.01 weight. %) / K ₂ Nb ₈ O ₂₁	0.017
No illumination	0.01

If several products are produced in photochemical and, particularly, in photocatalytic process, then the determination of spectral dependence of quantum yield of each product formation allows us in some cases to determine the nature of the reaction, which

leads to formation of these products, as well as to obtain the necessary information about the detailed mechanism of the reaction.^{11,13,14}

The determination of spectral dependence of quantum yield of oxygen and carbon dioxide from Pt/TiO₂ suspension allowed us to draw the conclusion that in this system oxygen release is caused by dehydrogenation of trace quantities of hydrogen-containing organic compounds, adsorbed on the surface of TiO₂ particles,¹¹ not by water decomposition as it was considered before.^{15–17}

The rate of oxygen release from the system that contain the platinized potassium niobate is maximal under the illumination by quanta with energy of 3.4 eV. The rate of oxygen release decreases with the increase of illumination time by quanta of the energy, corresponding to the limit of the potassium niobate intrinsic absorption; in about 3 hours of illumination the rate decreases virtually to zero. Then oxygen and hydrogen release rates in the dark also decrease to zero.

The observed oxygen release at the longwave boundary of potassium niobate intrinsic absorption range, as well as the termination of the oxygen release after the long-term illumination are typical for oxygen photodesorption from the surface of metal oxides.¹⁸

It can be assumed that in the system with potassium niobate the oxygen photodesorption from inner cavities of powdered photocatalyst particles proceeds under the influence of illumination quanta, followed by diffusion in the cavity and the release into the gas phase.

Measurements of the hydrogen release rate in the system with potassium niobate under the illumination by the monochromatic radiation allowed us to calculate the efficient quantum yield at different quantum energies.

The spectral dependence of the efficient quantum yield (per the incident radiation) of the hydrogen from the most photocatalytically active system is illustrated in Figure (curve 1). For comparison (curve 3), the optical density spectrum of potassium niobate diffuse reflection (K₄Nb₆O₁₇), registered by the KSVU-12 spectrophotometer, is also illustrated. Powdered magnesium oxide is given as the reflection standard.

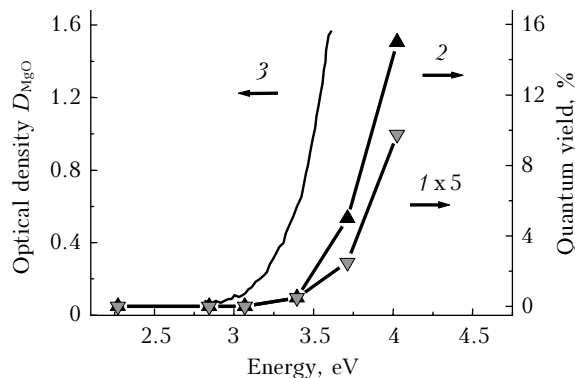


Fig. Spectral dependences of efficient hydrogen quantum yield from water (1, 5-fold magnification) and water-organic (2) suspensions Pt/K₄Nb₆O₁₇; optical density of Pt/K₄Nb₆O₁₇ diffusion reflection relative to reflection from the magnesium oxide standard (3).

The introduction of disodium salt of ethylenediaminetetraacetic acid (Na_2EDTA), which is a hydrogen-containing organic compound of 10^{-3} mole/l concentration to Pt/ $\text{K}_4\text{Nb}_6\text{O}_{17}$ system leads to an abrupt (by an order of magnitude) increase of efficient hydrogen quantum yield (curve 2), while spectrum remains virtually changeless (curves 1 and 3).

As is seen in the Figure, hydrogen release under illumination can be observed in the band of potassium niobate intrinsic absorption ($h\nu > 3.3$ eV) in the presence both of water in the reacting system and in water-organic mixture. This is typical for reactions of photocatalytic dehydrogenation of water-containing organic compounds at platinized semiconductor metal oxides.^{11,14,19}

Thus, investigation of the systems with photocatalysts of layered structure with the help of potassium niobates revealed that hydrogen and oxygen release occur in independent processes. Oxygen release is probably caused by its photodesorption, which kinetics is characterized by a rapid decrease of photodesorption rate to zero. Hydrogen formation in water systems is probably the consequence of photocatalytic dehydrogenation of trace quantities of water-containing organic compounds adsorbed on potassium niobate and not the consequence of water photodecomposition. In water-organic systems, the quantum efficiency of organic compound photocatalytic dehydrogenation, accompanied by the hydrogen release increases by an order of magnitude as compared to hydrogen release in the systems, containing only water.

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