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**Synthesis of Double Oxides TiO₂–SiO₂ with Low
Titanium Content by Hydrolysis
of Tetrabutoxytitanium–Tetraethoxysilane Mixture
in an Atmosphere of Water Vapor and Ammonia**

A. B. Shishmakov^a, O. V. Koryakova^a, A. S. Seleznev^a, L. A. Petrov^a, and S. A. Melkozerov^b

^aPostovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia
e-mail: sas@ios.uran.ru

^bUral State University of Forestry Engineering, Yekaterinburg, Russia

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Abstract—A series of TiO₂–SiO₂ binary xerogels with the titanium content lower than 7 mol % were prepared by joint hydrolysis of tetrabutoxytitanium and tetraethoxysilane in a desiccator in the atmosphere of vapor over 5% aqueous NH₃ solution under static conditions. The physicochemical properties of the material were examined by IR spectroscopy and by the kinetic method with hydrogen peroxide decomposition as model reaction.

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Double oxides TiO₂–SiO₂ are widely used as thin-film coatings, catalyst supports, selective sorbents, and photocatalysts [1, 2]. Of particular interest is the binary system TiO₂–SiO₂ with low titanium content (<7 mol %), which is characterized by homogeneous distribution of titanium dioxide with predominant formation of Ti–O–Si bonds [3].

The functional characteristics (catalytic activity, photoactivity, reactivity) of double oxides TiO₂–SiO₂, determined by the surface and bulk properties of this material, largely depend on the preparation procedure. The traditional sol–gel synthesis of TiO₂–SiO₂ xerogels involves hydrolysis of a mixture of titanium and silicon alkoxides in aqueous-alcoholic solutions in the presence of catalysts (acids or alkalis), followed by controllable drying. However, when organometallic compounds that strongly differ in hydrolysis rates, e.g., tetrabutoxytitanium (TBT) and tetraethoxysilane (TES), are used as precursors, it is difficult to perform simultaneous hydrolysis ensuring homogeneous distribution of titanium in the silica matrix. Therefore, it seemed appropriate to abandon the use of aqueous-alcoholic solutions and perform the hydrolysis of

the alkoxide mixture in an NH₃ + H₂O atmosphere. The use of such atmosphere favors simultaneous hydrolysis of the components. TBT undergoes hydrolysis already under the action of atmospheric moisture, and ammonia is the traditional catalyst of TES hydrolysis.

The goal of this study was to prepare a series of TiO₂–SiO₂ binary xerogels containing 1–6 mol % Ti by hydrolysis of a mixture of TBT and TES in an atmosphere of water vapor and ammonia and to examine the physicochemical properties of the material obtained.

EXPERIMENTAL

Hydrolysis was performed at 22°C in a 3000 cm³ desiccator containing a beaker with 100 ml of 5% aqueous ammonia solution. TES, TBT, and their mixtures were poured into 30-ml round-bottomed porcelain cups 60 mm in diameter and placed in the desiccator.

To prepare double oxides TiO₂–SiO₂ containing 6.1 (sample no. 1), 5.1 (no. 2), 3.9 (no. 3), 2.6 (no. 4), and 1.3 mol % TiO₂ (no. 5), 10 ml of TES was mixed with 1,

0.8, 0.6, 0.4, and 0.2 ml of TBT, respectively.

To prepare individual oxides SiO_2 and TiO_2 , we hydrolyzed 10 ml of TES or TBT.

The substances were kept in the desiccator for 93 h. IR data showed that the formed $\text{TiO}_2\text{-SiO}_2$ (nos. 1–5) and TiO_2 samples were free of the initial TES and TBT. The samples were dried in air at 24°C for 48 h and in an oven at 90°C for 24 h. Two-step drying ensures smaller amount of cracks in granules of the material. Then the samples were placed in a quartz reactor and calcined at 850°C (heating rate 10 deg min^{-1}) in an air flow (feed rate $0.075\text{ m}^3\text{ h}^{-1}$) for 1 h.

The total porosity of the xerogels for water was determined by keeping the cup contents in 40 ml of water for 2 h.

The IR spectra were recorded with a Spectrum One IR Fourier spectrometer (Perkin Elmer) in the frequency range $4000\text{--}370\text{ cm}^{-1}$ from solid powders, using a diffuse reflection attachment (DRA). The band assignments were based on data from [4]. The spectrum processing and calculation of band intensities were performed using special programs included in the spectrometer software.

The specific surface area of the samples was determined by thermal desorption of nitrogen with a SoftSorb-II ver. 1.0 device; the determination uncertainty did not exceed $\pm 5\%$.

Electron micrographs of $\text{TiO}_2\text{-SiO}_2$ were taken with a GSM-5900LV electron microscope.

Kinetic experiments were performed in a 40-ml reactor. The mixture was stirred at a rate of 1 s^{-1} . The $\text{TiO}_2\text{-SiO}_2$ granules ground to the particle size smaller than 0.1 mm were charged into the reactor ($\text{TiO}_2\text{-SiO}_2$ weighed portion 0.5–2.3 g, TiO_2 content in the reaction

space 0.04 g), and 30 ml of 1.05 M aqueous H_2O_2 solution was added. The reaction was performed at 24°C .

Kinetic measurements were performed by stopping the reaction and determining the content of the starting substance. The concentration functions were approximated by polynomials.

The hydrolysis product is a homogeneous solid mass. Sample nos. 1–3 are colorless and transparent, and sample nos. 4 and 5 are milky white. Individual SiO_2 and TiO_2 are loose white powders. We failed to perform complete hydrolysis of TES under the experimental conditions: SiO_2 particles are present in the form of suspension in a mixture of TES and liquid hydrolysis products.

Drying in air at 25°C causes cracking of sample nos. 1–3 in the cups. Calcination at 850°C did not noticeably increase the sample fracturing.

Figure 1 shows the electron micrographs of calcined sample no. 1. The globular, highly porous structure of the surface of the double oxide is clearly seen.

The total porosity of the binary material for water after calcination decreases with an increase in the titanium content (Fig. 2). It should be noted that the porosity determination revealed nonuniformity of the granules in the cup. Therefore, to obtain the mean porosity, we kept in water the whole cup contents.

The specific surface area of individual SiO_2 and TiO_2 was 27.8 and $0.7\text{ m}^2\text{ g}^{-1}$, respectively. An increase in the titanium content in the binary xerogel causes an increase in the specific surface area (Fig. 3). In the process, apparently, the structure with narrower pores, less accessible to water, is formed, which leads to the observed decrease in the total porosity for water in the series from sample no. 5 to sample no. 1.

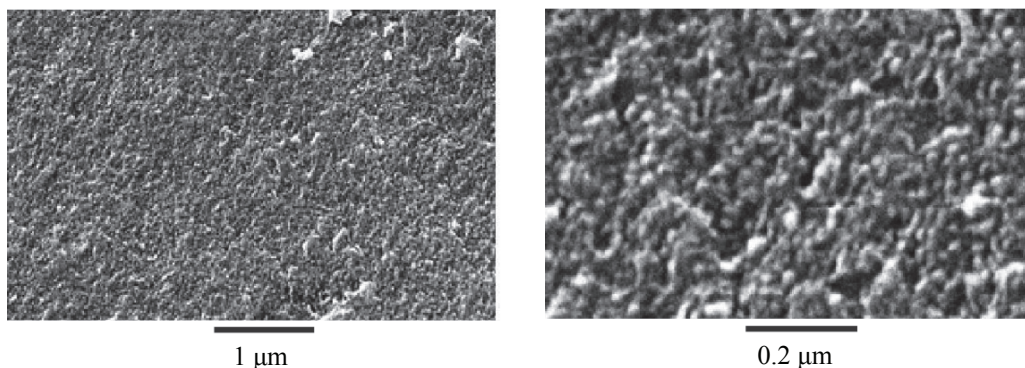


Fig. 1. Electron micrographs of sample no. 1.

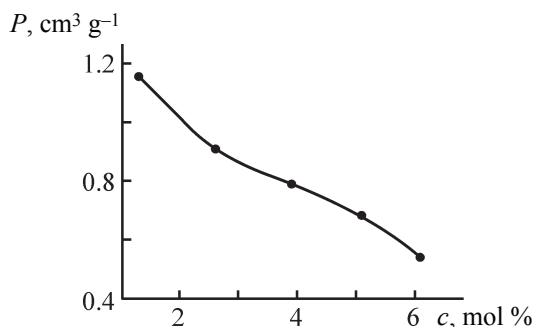


Fig. 2. Plot of the total porosity P of binary material granules for water vs. titanium content of the oxide c .

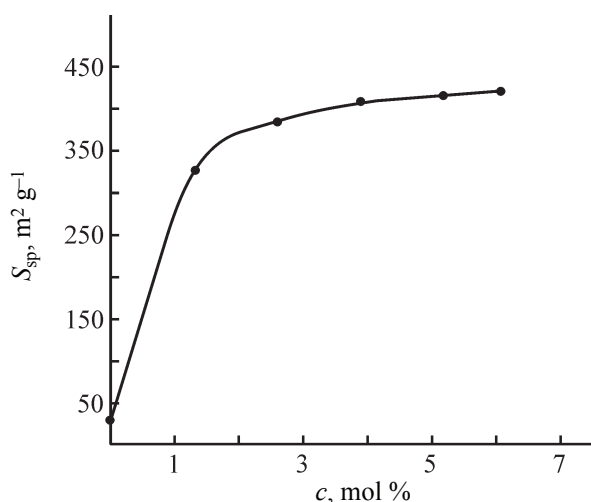


Fig. 3. Specific surface area S_{sp} of SiO₂ and sample nos. 1–5 as a function of the content c of titanium dioxide in the samples.

The IR spectrum of the SiO₂ xerogel (Fig. 4) has a strong absorption band of complex shape with a maximum at 1090 cm⁻¹ and an absorption band with a maximum at 803 cm⁻¹, corresponding to Si–O–Si stretching vibrations. The band of complex shape corresponds to asymmetric, and the medium-intensity band at 803 cm⁻¹, to symmetric stretching vibrations of SiO₄ tetrahedra [5]. The fact that the IR spectrum of silicon dioxide does not contain the band at 945 cm⁻¹, characterizing symmetric stretching vibrations of terminal Si–O⁻ bonds [6, 7], and the band at 3700–3000 cm⁻¹ (stretching vibrations of surface hydroxy groups and water) indicates that the xerogel surface after calcination is practically fully dehydroxylated.

The spectrum of the titanium dioxide xerogel contains a broad strong absorption band at 1000–400 cm⁻¹, corresponding to Ti–O stretching vibrations. As in the case of SiO₂, the TiO₂ surface after calcination is dehydroxylated, as indicated by the absence of the Ti–OH absorption bands (1126, 1095, and 1036 cm⁻¹).

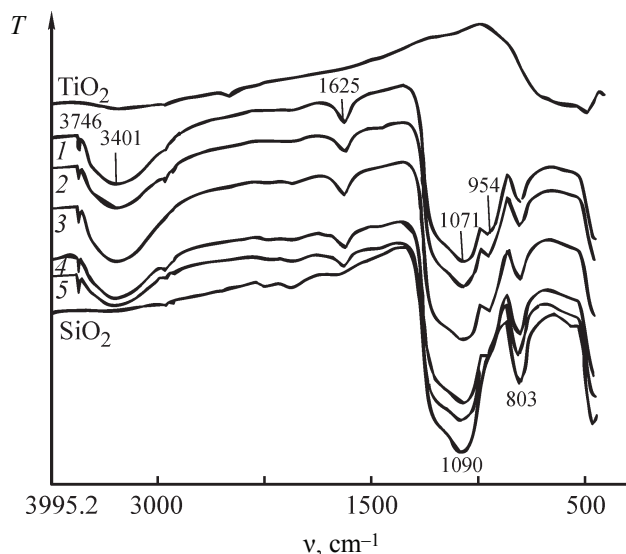


Fig. 4. IR spectra of SiO₂, sample nos. 1–5 (spectra 1–5, respectively), and TiO₂. (T) Transmittance and (ν) wavenumber.

In the spectra of double oxide nos. 1–5, there is a broad band with a maximum at 3401 cm⁻¹, corresponding to absorption of hydrogen-bonded hydroxy groups and water. The absorption band at 3746 cm⁻¹ corresponds to stretching vibrations of hydroxy groups not involved in hydrogen bonding, and the band with a maximum at 1625 cm⁻¹, to bending vibrations of water. The bands with maxima at 3401 and 1625 cm⁻¹ apparently originate from sorption of atmospheric moisture, as the binary xerogels are hygroscopic.

The band with the maximum at 954 cm⁻¹ in the spectra of the double oxides characterizes the Ti–O–Si vibrations.

The Si–O–Si absorption band with a maximum at 1090 cm⁻¹ in the spectrum of calcined SiO₂ is shifted toward lower frequencies in the spectra of sample nos. 5–1 and in the spectrum of sample no. 1 is observed at 1071 cm⁻¹.

A decrease in the frequency of the Si–O stretching vibration band near 1100 cm⁻¹ indicates that the SiO₄ tetrahedra are distorted owing to the presence of a heavier neighboring atom bonded to the Si–O system via O atom.

Thus, the IR data show that the TiO₂-SiO₂ binary xerogels contain Ti–O–Si groups.

Figure 5 shows how the intensity ratios of the Ti–O–Si absorption band and symmetric stretching vibration band of SiO₄ tetrahedra, $I(954 \text{ cm}^{-1})/I(803 \text{ cm}^{-1})$, and of the Ti–O–Si band and Si–O–Si asymmetric stretching vibration band, $I(954 \text{ cm}^{-1})/I(1090 \text{ cm}^{-1})$, in the IR spectra of double oxide nos. 1–5 depend on the double oxide

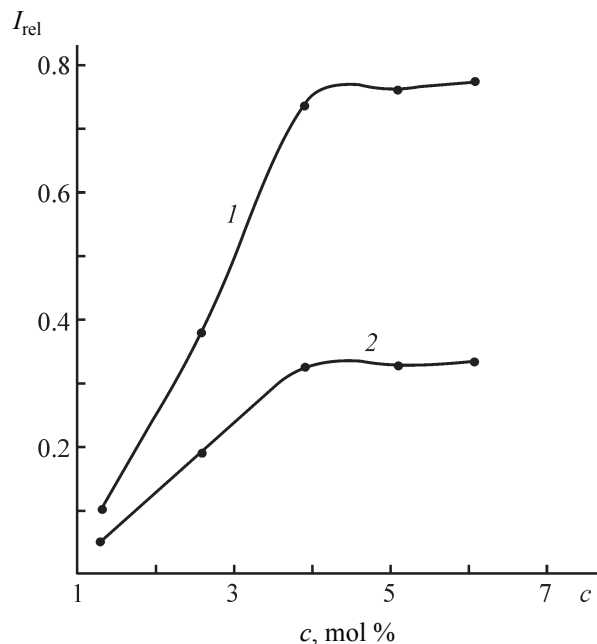


Fig. 5. Relative intensity I_{rel} of the band at 954 cm^{-1} as a function of the content c of titanium dioxide in the sample. (1) $I(954\text{ cm}^{-1})/I(803\text{ cm}^{-1})$ and (2) $I(954\text{ cm}^{-1})/I(1090\text{ cm}^{-1})$.

composition. As can be seen, as the titanium content of the double oxide is increased from 1 to 4%, the relative content of the Ti–O–Si groups in the xerogel structure increases practically proportionally. Apparently, at a low ($\leq 4\%$) concentration, titanium is incorporated in the silicon dioxide lattice with the formation of a Ti–O–Si bond. Further increase in the titanium dioxide fraction is accompanied by only insignificant increase in the relative content of the Ti–O–Si bonds. Probably, excess titanium over its 4% content in the double oxide mainly forms a separate TiO_2 phase.

According to [8–13], the presence of the heat-resistant Ti–O–Si bond stabilizes the crystalline phase of anatase (decelerates the growth of anatase crystallites in the course of heat treatment). Phase transition of anatase into rutile occurs when the size of primary anatase crystallites reaches a definite value (about 40–45 nm). As long as the anatase crystallite size is below this value, the anatase phase is stable and does not transform into the rutile phase [14]. Thus, it can be assumed (taking into account low content of titanium dioxide in the binary material) that the anatase modification prevails in the separate TiO_2 phase. In individual TiO_2 , heat treatment at 850°C leads to the prevalence of the rutile component [14, 15].

Figure 6 shows the kinetic curves of hydrogen peroxide decomposition in the presence of xerogel nos. 1–5 at

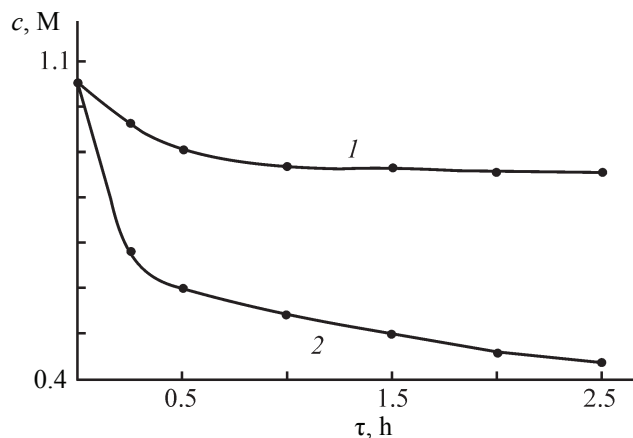


Fig. 6. Kinetic curves of hydrogen peroxide consumption. (c) H_2O_2 concentration and (τ) time. (1) Without catalyst and (2) in the presence of xerogel sample nos. 1–5.

equal amounts of titanium dioxide in the reaction zone (0.04 g). The kinetic data indicate that individual SiO_2 and TiO_2 do not affect the reaction of hydrogen peroxide decomposition, that titanium is the catalytically active component of the binary material, and that the titanium activity in the model process is independent of its content in $\text{TiO}_2\text{--SiO}_2$. The lack of the catalytic activity of individual TiO_2 may be due to its low specific surface area, $0.7\text{ m}^2\text{ g}^{-1}$.

CONCLUSIONS

(1) A series of $\text{TiO}_2\text{--SiO}_2$ binary xerogels containing 1–6% Ti were prepared by hydrolysis of a mixture of tetrabutoxytitanium and tetraethoxysilane in an atmosphere of water vapor and ammonia.

(2) An increase in the titanium content of the xerogel is accompanied by an increase in the specific surface area and by a decrease in the total porosity of the binary material for water.

(3) Ti–O–Si groups in the binary xerogels are detected.

(4) Titanium in the binary material catalyzes the model reaction of hydrogen peroxide decomposition. Its catalytic activity is constant throughout the examined range of material compositions.

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