ISSN 1070-4272, Russian Journal of Applied Chemistry, 2013, Vol. 86, No. 3, pp. 297−303. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.B. Shishmakov, M.S. Molochnikov, D.O. Antonov, O.V. Koryakova, A.S. Seleznev, L.A. Petrov, 2013, published in Zhurnal Prikladnoi Khimii, 2013, Vol. 86, No. 3, pp. 321−327.

INORGANIC SYNTHESIS
AND INDUSTRIAL INORGANIC CHEMISTRY

Synthesis of Cu(II)-Containing TiO_2–SiO_2 Binary Xerogels by Hydrolysis of a Mixture of Tetrabutoxytitanium, Tetraethoxysilane, and Copper(II) Chloride in a Water–Ammonia Atmosphere

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Received June 16, 2012

Abstract—A Cu(II)-containing binary xerogel TiO_2–SiO_2 was synthesized by joint hydrolysis of tetrabutoxytitanium, teraethoxysilane and copper(II) chloride dissolved in their mixture. The synthesis was performed in a vapor of 10% aqueous ammonia under static conditions. EPR spectroscopy was used to examine the state of Cu(II) in the xerogel matrix. Data on specific features of the behavior of saccharose within xerogel pores under heating were obtained. The catalytic activity of the xerogel was tested by the kinetic method on model reactions of hydrogen peroxide decomposition and oxidative dehydrogenation of trimethylhydroquinone.

DOI: 10.1134/S1070427213030014

Previous studies have shown [1–4] that the polyfunctional heterogeneous system having the form of a Cu(II)-containing titanium dioxide gel (xerogel) is constituted by self-organized copper structures of varied morphology, which are catalytically active in hydroxyarene oxidation reactions.

To proceed with research in this area, we suggest in the present study to use as a support the TuO_2–SiO_2 binary system with low content of titanium. This system is synthesized by the sol-gel method and has a homogeneous titanium dioxide distribution, with Ti–O–Si bonds formed [5]. The conventional synthesis of Cu(II)-containing xerogels of titanium and silicon consists in that a xerogel (gel) of TiO_2, SiO_2, or TiO_2–SiO_2 is formed by a particular method (sol-gel method, plasmochemical synthesis, vapor-phase deposition, etc.) and then impregnated with a copper(II) salt solution [6–11]. The most widely used method for synthesis of binary oxides TiO_2–SiO_2 is the sol-gel technique employing titanium and asilicon alkoxides as precursors. A mixture of these is hydrolyzed in an aqueous-alcoholicv medium in the presence of catalysts, acids and alkalis. This method does not require any intricate equipment and provides a homogeneous distribution of the components in the binary material. It has been suggested to perform the reaction of hydrolysis of organometallic precursors and copper(II) chloride simultaneously and without an aqueous-alcoholic medium, which can simplify the technology and yield a material with unusual sirface and structural characteristics.

The goal of our study was to synthesize a Cu(II)-containing binary TiO_2–SiO_2 xerogel by joint hydrolysis of tetrabutoxytitanium (TBT), tetraethoxysilane (TEOS), an copper(II) chloride dissolved in a mixture of these in a water–ammonia atmosphere and to examine the physicochemical properties of the material obtained.

EXPERIMENTAL

To synthesize the binary xerogel TiO_2–SiO_2

(7 mol % TiO_2), a mixture of 9 mL of TEOS and 1 mL of TBT was poured into a 30-mL round-bottom porcelain cup with a diameter of 60 mm.

To synthesize individual oxides SiO_2 and TiO_2, 10 mL of TEOS or TBT was poured into the cup.

To obtain a Cu(II)-containing containing sample TiO_2–SiO_2–Cu(II), a weighed portion (0.01 g) of $CuCl_2 \cdot 2H_2O$ was preliminarily dissolved in TEOS/TBT.

The cups with the precursors were placed in a desiccator (volume 3000 cm^3) containing a vessel with 100 mL of 10% aqueous ammonia. The temperature in the desiccator was 20°C.

The substances were kept in the desiccator for 93 h and the contents of a cup were dried in air at 20°C for 48 h and in a drying box at 90°C for 24 h. Further, samples from the cup were charged into a quartz reactor and calcined at 850°C)heating rate 10 deg min^{-1}) in a flow of air (feed rate 0.075 $m^3 h^{-1}$) for 1 h.

The total porosity of the TiO_2–SiO_2 xerogel for water was calculated from the difference between the mass of a sample kept in 20 mL of water for 20 h and its before the soaking (0.5 g) related to 1 g of the sample.

IR spectra of solid powders were recorded with a Perkin–Elmer Spectrum One IR Fourier spectrometer with a diffuse reflection attachment (DRA) at frequencies in the range 4000–370 cm^{-1}. The band assignment was made using the data of [12]. The band intensities were processed and calculated using special applied software of the spectrometer.

The specific surface area Ssp f the samples was determined by the method of thermal desorption of nitrogen on a SoftSorbi-II ver. 1.0 instrument with an error not exceeding ±5%.

Electron micrographs of TiO_2–SiO_2 were taken with a GSM-5900LV electron microscope.

To study the behavior of saccharose within pores of TiO_2–SiO_2–Cu(II) (TiO_2–SiO_2), a calcined xerogel heated to 90°C was impregnated to saturation with a hot (90°C) aqueous solution of saccharose (700-g L^{-1}) and then the grains were dried at 90°C for 2 days.

Kinetic experiments were carried out in a thermostated reactor equipped with a reflux. The reaction mixture was agitated by bubbling of air at a flow rate of 3.1 L h^{-1}. TiO_2–SiO_2–Cu(II) (TiO_2–SiO_2) grains to be used in experiments were crushed to a <0.1 mm fraction and wee kept in water for 15 min prior to addition of the substrate.

To study trhe decomposition of hydrogen peroxide, the reactor was charged with 30 mL of an aqueous solution of H_2O_2 (1.05 M of H_2O_2) and a weighed portion (0.5 g) of a calcined TiO_2–SiO_2–Cu(II) (TiO_2–SiO_2) sample. The reaction was performed at 24°C with a thermostating accuracy of ±0.2°C.

The reaction of trimethylhydroquinone (TMHQ) oxidation was performed at 50°C. The reactor was charged with 10 mL or an aqueous-ethanolic (water : ethanol = 1 : 1) solution of TMHQ with a concentration of 66 mM and a weighed portion (0.9 g) of a calcined TiO_2–SiO_2–Cu(II) (TiO_2–SiO_2) sample was introduced. The content of Cu(II) in the reaction space was 0.024 mmol.

The kinetic measurements were made by terminating the reaction and determining the content of the starting substance. The thus obtained concentration functions were approximated with polynomials. The initial reaction rates were found by numerical differentiation and interpolation. The determination error did not exceed ±10%.

TMHQ was quantitatively determined by GLC on a Chrom-4 chromatograph as described in [13].

The 0.01-g weighed portion of copper(II) chloride is completely dissolved in TBT/TEOS without hydrolysis of organometallic compounds.

After the mixture is kept in a desiccator in a water–ammonia atmosphere for 0.5 h, a light blue precipitate, copper(II) hydroxide, is formed in the cup. In the course of time, with increasing amount of ammonia dissolved in TBT/TEOS, the precipitate is partly dissolved, with the mixture colored dark blue as an ammonia complex of copper(II), $[Cu(NH_3)_4](OH)_2$, is formed. No hydrolysis of the organometallic precursors is observed in this stage of the process. After the reaction mixture is kept in the desiccator for 93 h, a solid transparent mass can be found in the cup. This mass is divided by cracks into 3–8-mm fragments and its color is light blue in the main bulk and bright blue at the up bottom. Apparently, the ammonia complex of copper(II) is blocked within pores of the xerogel formed at the liquid–gas phase boundary.

Drying at 90°C leads to an insignificant cracking of particles of the material, with their transparence and coloration remaining unchanged.

BY the end of the annealing (850°C), the particles of the material are green. On being kept in air, fine particles again became light blue, with coarse articles remaining green. It should be noted that the material with the morphological features described above is only obtained if the cup contents were not agitated in the course of hydrolysis in the desiccator. Otherwise, strongly cracked nontransparent dirty blue particles are obtained immediately after the annealing.

After the whole contents of the cup were ground, the content of copper(II) in the binary matrix of the calcined material was 0.027 mmol of Cu(II) per gram of TiO_2–SiO_2.

On being calcined at 850°C, the TiO_2–SiO_2 binary oxide matrix itself has the form of transparent colorless particles with grain sizes of 7–8 mm and S_{sp} = 254.3 m^2 g^{-1} (the grains are inhomogeneous, the porosities of separate grains are within the range 0.28–0.73 cm^3 g^{-1}).

The electron micrographs (Fig. 1) reveal the highly porous globular structure of the oxide matrix.

The values of Ssp for calcined SiO_2 and TiO_2 were 27.8 and 0.7 m^2 g^{-1}, respectively.

Figure 2a shows the IR spectra of the oxides upon their hydrolysis and drying at 90°C.

The IR spectrum of the SiO_2 xerogel contains a strong absorption band of complex shape and peaks at 1155 and 1062 cm^{-1} and an absorption band peaked at 798 cm^{-1}, associated with stretching vibrations of Si–O–Si bonds. The complex-shape band is associated with asymmetric stretching vibrations of SiO_4 tetrahedra, and the medium-intensity band at 798 cm^{-1}, with their symmetric stretching vibrations [14]. The absorption band peaked at 945 cm^{-1} characterizes symmetric stretching vibrations of nonbridging Si–O– bands [15, 16]. The high-intensity band at 435 cm^{-1} characterizes deformation vibrations of polyhedra. Absorption bands associated with stretching vibrations of hydroxyl groups and water molecules appear in the range 3700–3000 cm^{-1}. A broad medium-intensity band at 1626 cm^{-1} corresponds to deformation vibrations of water.

The spectrum of the titanium dioxide xerogel

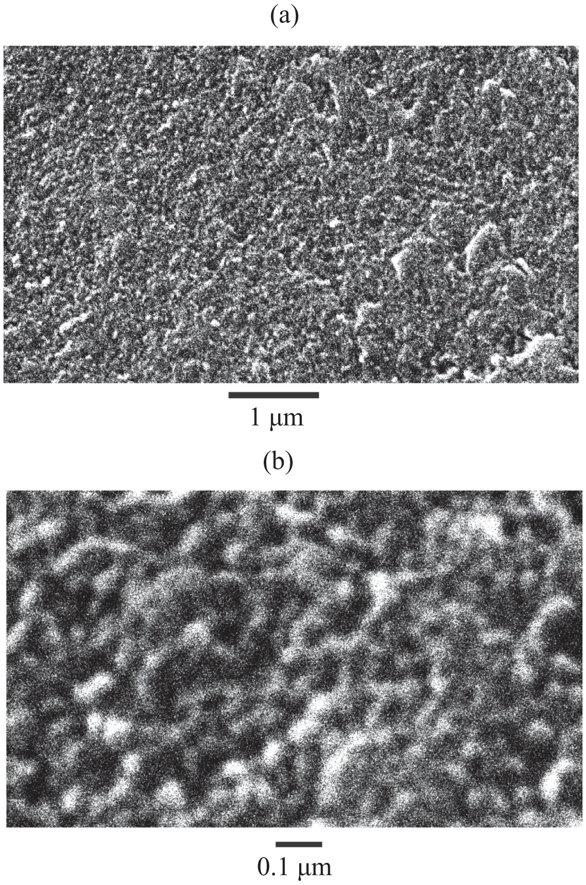

Fig. 1. Electron micrographs of the TiO_2–SiO_2 surface.

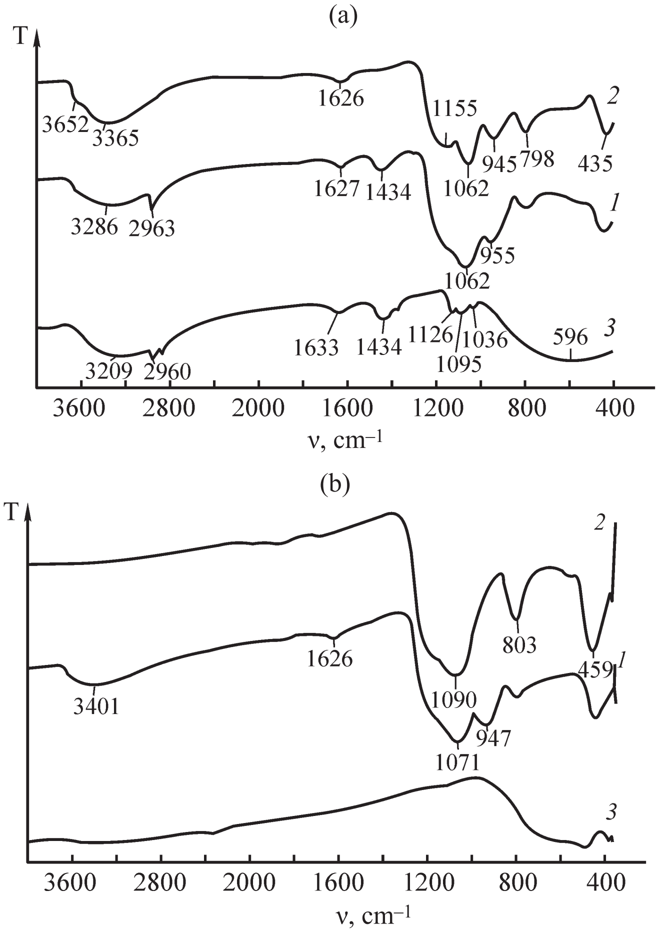

Fig. 2. IR spectra of (*1*) TiO_2–SiO_2, (*2*) SiO_2, and (*3*) TiO_2 after (a) drying at 90°C and (b) calcination. (*T*) Transmission and (ν) wave number; the same for Fig. 4.

(Fig. 2a) contains a single broad high-intensity absorption band in the range 1000–400 cm^{-1}, which is peaked at 596 cm^{-1} and corresponds to stretching vibrations of Ti–O bonds. The broad absorption band peaked at 3209 cm^{-1} is associated with the absorption by hydroxyl groups and xerogel-bound water. The absorption band peaked at 1633 cm^{-1} corresponds to deformation vibrations of water. Three absorption bands peaked at 1126, 1095, and 1036 cm^{-1} are associated with deformation vibrations of Ti–OH groups. Organic products formed in hydrolysis of TBT, present in the xerogel, appear as absorption bands at 3000–2800 cm^{-1} (stretching vibrations of C–H) and bands at 1500–1350 cm^{-1} (deformation vibrations of $–CH_3–$ and $–CH_3$.

The low content of titanium in the binary TiO_2–SiO_2 sample gives now way of unambiguously stating on the basis of the IR spectra that the Ti–O–Si bond is formed; however, the observed shift of the peak of the absorption band associated with symmetric stretching vibrations of Si–O nonbridging bonds from 945 (SiO_2) to 955 cm^{-1} (TiO_2–SiO_2) can be regarded as resulting from a superposition of the given band on the absorption band of the Ti–O–Si group (940–960 cm^{-1}) [5, 17].

An analysis of the IR spectrum of TiO_2–SiO_2–Cu(II) demonstrated that it is fully identical to that of TiO_2–SiO_2, which is apparently due to the low content of Cu(II) in the binary matrix.

Figure 2b shows IR spectra of a material calcined at 850°C. Calcination causes nearly full surface dehydroxylation of a SiO_2 sample, which is indicated by the fact that the spectrum contains no absorption bands at 3700–3000 cm^{-1} and those associated with Si–O– nonbridging bonds. As a result of calcination, the absorption bands of Ti–OH groups (1126, 1095, and 1036 cm^{-1}) disappear from the spectrum of titanium dioxide.

Parameters of the EPR spectra of Cu(II) in xerogels

Sample	Treatment conditions	$g_{II} \pm 0.005$	$A_{II} \pm 0.3$, mT
TiO_2–SiO_2	Drying at 20°C	2.241	17.7
	Drying at 90°C	2.276	16.2
	Calcination at 300–850°C	2.354	12.5
TiO_2 [18]	Drying at 20°C	2.352	13.2
SiO_2 [19]	The same	2.322	14.3
$Cu(NH_3)_4^{2+}$ [20]		2.239	18.5

The absorption bands of water (3700–3000, 1625 cm^{-1}) are present in the TiO_2–SiO_2 spectrum, which apparently results from sorption from the atmosphere.

The absorption band of Si–O–Si, peaked at 1090 cm^{-1} in calcined SiO_2, is shifted in the TiO_2–SiO_2 spectrum to lower frequencies to 1071 cm^{-1}.

The fact that the frequency of the absorption band associated with stretching vibrations of Si–O bonds becomes lower (to ~1100 cm^{-1}) indicates that SiO_4 tetrahedra are distorted by the presence of a heavier neighboring atom bound via an oxygen atom to the Si–O system under study.

Thus, the IR spectroscopic data indicate that Ti–O–Si groups are present in the structure of the calcined TiO_2–SiO_2 xerogel.

The IR spectrum of TiO_2–SiO_2–Cu(II) is fully identical to that of TiO_2–SiO_2.

The EPR study of TiO_2–SiO_2–Cu(II) yielded an anisotropic EPR spectrum with a well resolved hyperfine structure in the range of the parallel orientation of the magnetic moment of copper complexes with respect to the external magnetic field, which indicates that isolated copper complexes having the D_{4h} axial symmetry are formed. The complexes are situated rather far from each other, which results in that there is no dipole-dipole or exchange interaction between these complexes. It follows from published data that, for this to be observed, the distance between neighboring copper ions should be no less than 2.5 nm.

The parameters of the Cu(II) EPR spectra in the samples under study and some published data are listed in the table.

According to the parameters of the EPR spectrum of TiO_2–SiO_2–Cu(II) dried at 20°C after being synthesized, ammonia molecules are contained in copper complexes. Each complex contains four ammonia molecules in the equatorial plane of the elongated octahedron constituting the nearest environment of copper ions. This conclusion follows from the fact that the parameters measured for the EPR spectra are close to those observed for ammonia complexes of copper(II) in perfluorinated sulfocation-exchange membranes [20] (see table) and in ANKB-35 amphoteric ion exchanger ($g_{II} = 2.247$, $A_{II} =$ 16.8 mT [21]. The remaining two coordination places are occupied by oxygen atoms of dissociated hydroxy groups on the TiO_2–SiO_2 surface, which form covalent bonds with copper ions.

Upon a short-term (up to 3 h) drying of a sample at 90°C, the parameters of the EPR spectrum and, consequently, the composition of copper complexes in the sample remained unchanged, characteristic of copper tetraammoniates. The stability of complexes of this kind against heating to up to 100°C has also been noted for perfluorinated membranes [20, 22].Upon more prolonged drying, the parameters of the EPR spectra changed (see table). The changes in the parameters of the EPR spectra reflect the decrease in the number of nitrogen atoms in the first coordination sphere of copper ions to two [23]. Presumably, the places freed by ammonias molecules in the environment of copper ions are occupied by oxygens of the binary matrix, with bonds formed by the donor-acceptor mechanism.

After TiO_2–SiO_2–Cu(II) was calcined at various temperatures, the same parameters of the EPR spectra were observed, different from those for the uncalcined sample. Comparison values measured in the spectra with published data (see table) shows that complexes with titanium dioxide functional groups are formed in a calcined sample (Fig. 3), and this is just titanium dioxide, rather than silicon dioxide for which smaller values of g_{II} and larger values of A_{II} are characteristically observed [19]. It turns out that, under the experimental conditions, Ti–O fragments of the binary xerogel are more active ligands with respect to copper(II) ions than similar formations based on silicon dioxide.

Repeated EPR studies carried out a year after samples were prepared demonstrated that tetraammonia copper complexes in a sample dried at 20°C degraded, with a part of ammonia molecules substituted by water molecules from air or by oxygens from the binary matrix. The parameters of the EPR spectra had the following values: $g_{II}| = 2.295$ and $A_{II} = 15.3$ mT, which indicates that only a single molecule of ammonia is present in the first coordination sphere of copper ions [23]. At the same time, the EPR parameters of samples calcined at temperatures of 300–850°C remained unchanged.

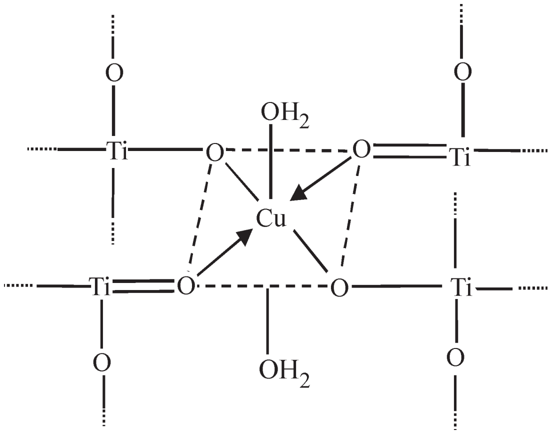

Fig. 3. Scheme of Cu(II) ion complexes in the TiO_2–SiO_2 matrix.

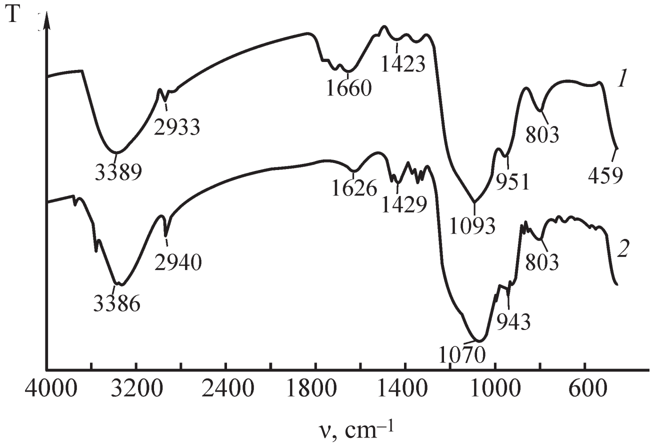

Fig. 4. IR spectra of (*1*) TiO_2–SiO_2/saccharose upon drying and (*2*) mechanical mixture of TiO_2–SiO_2 and saccharose.

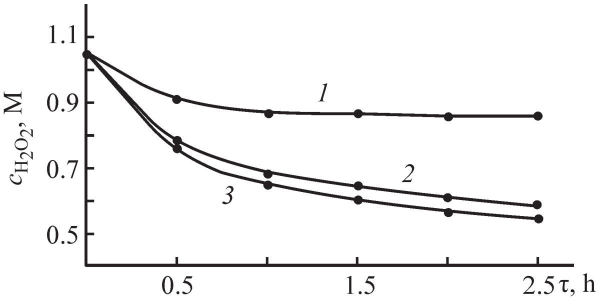

Fig. 5. Kinetic curves of hydrogen peroxide consumption. ($c_{H_2O_2}$) H_2O_2 concentration and (τ) time. (*1*) Without a catalyst and in the presence of (*2*) TiO_2–SiO_2 and (*3*) TiO_2–SiO_2–Cu(II); the same for Fig. 6.

Drying of a TiO_2–SiO_2 xerogel impregnated with a saccharose solution results in that grains of the material gradually change their color: become dark brown from colorless, which indicates that saccharose undergoes caramelization in pores of the binary oxide in the course of dehydration. As additional evidence in favor serve IR spectroscopic data, which demonstrate that the spectrum of the thermally treated (90°C, 48 h) binary xerogel with saccharose markedly differs from that of the TiO_2–SiO_2/saccharose mechanical mixture (Fig. 4). A similar behavior is observed for saccharose in pores of TiO_2–SiO_2–Cu(II). It should be noted that no caramelization is observed when saccharose is subjected to drying in an individual TiO_2 or SiO_2.

An analysis of the decomposition of hydrogen peroxide on the samples synthesized in the study demonstrated that TiO_2–SiO_2 exhibits a catalytic activity in the model process (Fig. 5). Comparison of the kinetic data suggests that, even though copper(II) exhibits activity in the binary matrix, its influence on the reaction is insignificant. It should be noted that the interaction of H_2O_2 with TiO_2–SiO_2 leads to washing-out of titanium from the binary oxide, as evidenced by the appearance of a yellow solution coloration characteristic of peroxy compounds of titanium. Keeping TiO_2–SiO_2 in an aqueous solution of hydrogen peroxide (H_2O_2 concentration 1.05 M), with periodic replacement of the yellowed solution, demonstrated that the coloration intensity of the solution decreases in the course of time, with the solution becoming nearly colorless in 60 h. The IR spectrum of TiO_2–SiO_2 at 850–1100 cm^{-1} and the intensity ratio of the Ti–O–Si absorption band and that associated with asymmetric stretching vibrations of Ti–O–Si (947 cm^{-1}) remained unchanged after the sample was reacted with $H2O_2$. This suggests that titanium is washed out mostly due to the rupture of Ti–O–TI bonds.

To find out whether the Cu(II)-containing binary material can be used as a catalyst in organic syntheses, we examined the effect of TiO_2–SiO_2–Cu(II) on the liquid-phase reaction of TMHQ oxidation by atmospheric oxygen into 23,6-trimethylbenzoquinone (TMBQ).

The kinetic data obtained are presented in Fig. 6. The reaction of TMHQ oxidation occurs with a 98% selectivity with respect to TMBQ, both without TiO_2–SiO_2–Cu(II) (TiO_2–SiO_2) and in its presence. Introduction of the binary oxide TiO_2–SiO_2 (0.9-g portion) into the reaction sphere has no effect on the course and parameters of the TMHQ oxidation process (Fig. 6, curve 1); the initial TMHQ oxidation rate was 40 mM h^{-1}.

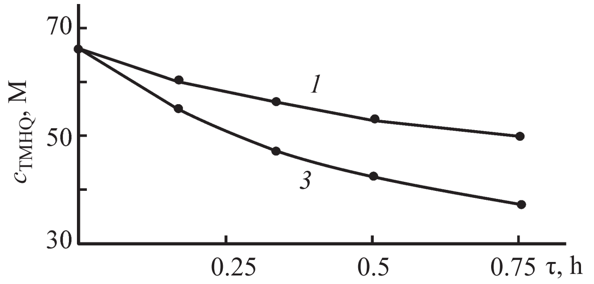

Fig. 6. Kinetic curves of TMHQ consumption. (c_{TMHQ}) TMHQ concentration and (τ) time.

Presence of TiO_2–SiO_2–Cu(II) (copper(II) content 0.024 mmol) accelerates the reaction, with its initial rate becoming 84 mM h^{-1}. Thus, the initial reaction rate in the presence of a Cu(II)-containing xerogel is 2.1 times the initial rate of an uncatalyzed process. Comparing the catalytic activity of copper(II) in TiO_2–SiO_2–Cu(II) with the previously obtained data on the activity of copper monocomplexes in TiO_2 and SiO_2 gels (with Ssp 320 m^2 g^{-1}) [1], we can conclude that copper monocomplexes localized in the binary material exhibit a substantially higher catalytic activity. The initial oxidation rate of the substrate in the presence of Cu(II)-containing gels of titanium and silicon dioxides [copper(II) content in the reactor, 0.059 mmol] is only 1.2–1.3 times the reaction rate in the absence of copper and gels [1]. It should be noted that TiO_2–SiO_2 has no effect on a noncatalytic process because the surface of the binary xerogel becomes dehydroxylated as a result of calcination. Presence of hydroxyl groups on the surface of TiO_2 and SiO_2 gels leads to TMHQ sorption by the surface of the gels, which inhibits the oxidation of the substrate in its noncatalytic oxidation by atmospheric oxygen. The easy separation of TiO_2–SiO_2–Cu(II) grains from the reaction product makes this catalyst more technologically convenient as compared with gel-type catalytic systems.

CONCLUSIONS

(1) A single-stage procedure for synthesis of a Cu(II)-containing TiO_2–SiO_2 binary oxide was developed.

(2) It was shown that, in TiO_2–SiO_2–Cu(II) calcined at 850°C, copper(II) is present in the form of complexes and is coordinated with titanium dioxide functional groups.

(3) It was demonstrated that impregnation of both TiO_2–SiO_2 and TiO_2–SiO_2–Cu(II) with a saccharose solution, followed by keeping at 90°C, results in the caramelization of saccharose.

(4) It was found that Cu(II) contained in the TiO_2–SiO_2 matrix exhibits catalytic activity in model processes of hydrogen peroxide decomposition and trimethylhydroquinone oxidation by atmospheric oxygen.

ACKNOWLEDGMENTS

The study was financially supported by the Ural Branch of the Russian Academy of Sciences (grant no. 12-I-3-2058.

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