SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

# SiO<sub>2</sub>-TiO<sub>2</sub> Binary Aerogels: Synthesis in New Supercritical Fluids and Study of Thermal Stability

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Abstract—A comparative analysis of properties of  $SiO_2$ —TiO<sub>2</sub> binary aerogels prepared by supercritical drying using different supercritical fluids (isopropanol, hexafluoroisopropanol, methyl *tert*-butyl ether, and CO<sub>2</sub>) has been performed. The use of different supercritical fluids allows preparation of both homogeneous amorphous  $SiO_2$ —TiO<sub>2</sub> binary aerogels (by supercritical drying in hexafluoroisopropanol and CO<sub>2</sub>) and composite aerogels containing nanocrystalline anatase (by supercritical drying in isopropanol and methyl *tert*-butyl ether). The thermal treatment of the aerogels at temperatures up to 600°C does not lead to considerable change in the porous structure and phase composition of the aerogels.

DOI: 10.1134/S0036023616110048

Aerogels (AGs) is a special kind of solid-state materials with open porous structure formed by the sequential binding of nanoparticles or polymer molecules [1, 2]. Aerogels derived from SiO<sub>2</sub> are the most widespread; they are unique mesoporous materials with low density, high porosity and specific surface area [3]. The possibility to prepare SiO<sub>2</sub>-based composite AGs that combine the above characteristics with high catalytic activity also attracts a considerable interest [1]. In particular, it was suggested to use  $SiO_2$ -TiO<sub>2</sub> composite aerogels as catalysts for isomerization and epoxidation of alkenes [4, 5], and as photocatalysts promoting photoinduced decomposition of organic contaminants in water and air [6-8]. Silicon dioxide imparts these AGs required texture characteristics (specific surface area, porosity), while titanium dioxide produces catalytic (photocatalytic) activity.

The physicochemical properties and functional characteristics of AGs based on  $SiO_2$ -TiO<sub>2</sub> are considerably affected by preparation method. Chemical homogeneity and high content of bridging Si-O-Ti groups is important factor for catalytic applications [4, 5, 9, 10] and employment as a catalyst support [11, 12]. Along with high matrix porosity, uniform distribution of crystalline TiO<sub>2</sub> is also required when AGs derived from SiO<sub>2</sub>-TiO<sub>2</sub> are used as photocatalysts [13-16].

SiO<sub>2</sub>-TiO<sub>2</sub> binary aerogels are obtained by different variations of sol-gel method followed by supercritical (SC) drying [17, 18]. The most universal method of their synthesis consists in the cohydrolysis and condensation of silicon and titanium alcoholates [19, 20]. Lower aliphatic alcohols (MeOH, EtOH, and *i*-PrOH) and CO<sub>2</sub> are usually employed as supercritical fluids (SCF) for the synthesis of aerogels, including binary ones [3]. The character of effect of SCF type on the physicochemical properties of SiO<sub>2</sub>- $TiO_2$  binary aerogels remains unexplored, however, it is known that drying with the use of alcohols results in formation of nanocrystalline titanium dioxide (usually as anatase) in SiO<sub>2</sub> matrix, whereas materials obtained using CO<sub>2</sub> or by drying under atmospheric pressure are homogeneous and X-ray amorphous [21–23].

It is of special interest to extent the variety of used SCF, first of all with the aim of supplementary chemical modification of AG surface. According to our data, the type of SCF used in the synthesis of oxide aerogels considerably affects AG microstructure [24–27]. Thus, the specific surface area of AG based on  $SiO_2$ ,  $Al_2O_3$ , and  $ZrO_2$  prepared by supercritical drying in diethyl and methyl *tert*-butyl ethers and in hexafluoroisopropanol is approximately twice as large as that of aerogels obtained by drying in traditionally used ethanol; their porosity is also considerably larger. The thermal treatment of AG based on  $SiO_2-TiO_2$ at 300–500°C leads to increase in their specific surface area ( $S_{sp}$ ), which is commonly associated with removal of residual organic compounds, while the annealing at higher temperatures (>500°C) results in decrease of  $S_{sp}$  and porosity on account of partial structure degradation [28–31]. As a rule, the phase composition of these AGs remains intact after thermal treatment. Thus, the annealing at 800°C of SiO<sub>2</sub>-TiO<sub>2</sub> aerogels prepared with the use of CO<sub>2</sub> as SCF does not lead to emergence of crystalline phases within them [6, 32].

In this work, we have studied the effect of type of supercritical solvent, including methyl *tert*-butyl ether and hexafluoroisopropanol, and thermal treatment conditions on the texture characteristics, phase composition, and morphology of  $SiO_2$ -TiO<sub>2</sub> composite aerogels with different TiO<sub>2</sub> content.

## **EXPERIMENTAL**

Initial chemicals used were as follows: tetramethoxysilane Si(OCH<sub>3</sub>)<sub>4</sub> (TMOS, Aldrich, 99%), titanium(IV) isopropoxide Ti(*i*-OPr)<sub>4</sub> (TIP, Acros, 98 + %), isopropanol (Acros, 99.5 + %), HF (Acros, 40% aqueous solution), acetylacetone (acacH, reagent grade), methyl *tert*-butyl ether (MTBE, Acros, 99%), hexafluoroisopropanol (HFIP, Aldrich, 99%), and distilled water.

#### Synthesis of Lyogels

To increase the homogeneity of SiO<sub>2</sub>–TiO<sub>2</sub> binary aerogels, lyogels were prepared using the following approach: a solution obtained by mixing TIP and acetylacetone was added to a preliminary hydrolyzed solution of TMOS. The initial reagents were taken in the following molar ratios: TMOS : Ti(*i*-OPr)<sub>4</sub> : acacH : *i*-PrOH : H<sub>2</sub>O : HF = 1 –  $\alpha$  :  $\alpha$  :  $2\alpha$  : 3.0 : 4.0 : 0.04 ( $\alpha$  = 0, 0.05, 0.10, 0.20, 0.50).

Let us describe the synthesis of sample with  $TiO_2$ nominal molar content of 20% ( $\alpha = 0.2$ ) as an example. The total volume of solvent (*i*-PrOH) of 13.8 mL was divided into two equal portions. TMOS (7.14 mL) was added to the first portion on constant magnetic stirring. A solution of HF was prepared by addition of 0.12 mL of HF into 4.32 mL of water. The hydrofluoric acid solution was added to the TMOS solution. The preliminary hydrolysis of TMOS was conducted in an ice bath for 5-7 min. The second solution was obtained by addition of 2.45 mL of acetylacetone to the second portion of the solvent at constant stirring. Next, 3.56 mL of TIP was added to the second solution and the resultant mixture was stirred for 3-5 min to form titanium complexes of composition  $Ti(i-PrO)_{4-x}(acac)_x$ (x = 1, 2) [33]. After stirring, the titanium-containing solution was added to the silicon-containing solution. After vigorous stirring of the reaction mixture for 40–

60 s, the resultant sols were transferred into cylindrical polypropylene containers (3–5 mL). Lyogel formed during 40–60 min. Next, the lyogels were kept at ambient temperature for 24 h and then washed with selected solvent (*i*-PrOH, MTBE, HFIP) once a day for five days (to replace the liquid in the pores by the pure solvent). The gels for supercritical drying in  $CO_2$  were washed with isopropanol.

# Supercritical Drying

Solvents selected for supercritical drying were isopropanol ( $T_{cr} = 235.1^{\circ}$ C,  $P_{cr} = 47.6$  atm), carbon dioxide ( $T_{cr} = 31^{\circ}$ C,  $P_{cr} = 72.8$  atm), hexafluoroisopropanol ( $T_{cr} = 182.0^{\circ}$ C,  $P_{cr} = 30.2$  atm) and methyl *tert*butyl ether ( $T_{cr} = 224.1^{\circ}$ C,  $P_{cr} = 34.3$  atm).

A glass test tube containing a lyogel under a solvent layer (14–16 mL) was placed into an autoclave with capacity of 38 mL. The autoclave was placed into a furnace, heated at a rate of ~100 K/h to prescribed temperature, and kept at this temperature for 10–15 min. The isothermal treatment temperatures for *i*-PrOH, MTBE, and HFIP were 250–260°C (100–120 atm), 235–245°C (100–120 atm), and 200–210°C (100– 120 atm), respectively. Then the pressure in the heated autoclave was gradually decreased to atmospheric, the autoclave was evacuated for 30 min (0.03–0.04 atm), cooled, and opened.

The supercritical drying in CO<sub>2</sub> was conducted in an installation composed of a SSI Supercritical 24 (USA) high-pressure pump for CO<sub>2</sub>, a 50-mL steel reactor, and a Waters Goregulator BPR back pressure regulator (USA). The sample was washed with liquid CO<sub>2</sub> for 2 h at 20°C and 150 atm, next temperature in the reactor was elevated to 50°C and the sample was washed with supercritical CO<sub>2</sub> (120 atm) for 2–2.5 h. Then the pressure in the hot autoclave was gradually decreased (for 30–40 min) to atmospheric, the autoclave was cooled and opened.

The annealing of aerogels was carried out in a muffle furnace in air at 400, 600, 800, and 1200°C for 1 h at heating rate 10 K/min.

Hereinafter, we designate the samples of binary aerogels as xSTy, where x corresponds to the nominal content of TiO<sub>2</sub> in aerogels (in mol %), while y indicates supercritical solvent (Pr, isopropanol; CO<sub>2</sub>, carbon dioxide; MTB, methyl *tert*-butyl ether; HFP, hexafluoroisopropanol). For example, 5STPr designates SiO<sub>2</sub>-TiO<sub>2</sub> aerogel with nominal molar content of TiO<sub>2</sub> of 5% prepared by drying in *i*-PrOH, while 20STMTB is an aerogel with nominal TiO<sub>2</sub> content of 20 mol % dried in MTBE.

#### Analysis of Aerogel Characteristics

The specific area of aerogel surface and full nitrogen adsorption/desorption isotherms were determined



Fig. 1. The results of thermogravimetric analysis coupled with mass spectroscopy of gaseous thermolysis products for AG samples with nominal TiO<sub>2</sub> content of 20 mol % dried in MTBE (a) and HFIP (b). The values of m/z are presented at the corresponding temperature dependences of ionic current.

by low-temperature nitrogen adsorption/desorption using a Katakon ATKh-06 analyzer (Russia). On the basis of obtained data, the specific surface area of the samples was calculated using the Brunauer–Emmett– Teller (BET) model from 5 points in partial pressure range 0.05–0.25. The samples were degassed prior to measurements in a nitrogen flow at 200°C for 35 min.

Thermogravimetric analysis and mass spectral determination of gaseous products evolved during thermal decomposition of samples was conducted with the use of a Netzsch TG 209 F1 thermobalances equipped with a Netzsch QMS 403 C Aëolos mass spectrometer. The analysis was performed in air atmosphere at heating rate 10 K/min up to 800°C.

X-ray powder diffraction analysis of solid samples was performed on a Bruker D8 Advance diffractometer (Cu $K_{\alpha}$  radiation) at goniometer rotation speed of 5°2 $\theta$ /min.

The microstructure of samples was studied with a Carl Zeiss NVision 40 scanning electron microscope equipped with an Oxford X-Max X-ray spectral detector at accelerating voltage of 1 and 20 kV. Magnification was from 3000 to 300000.

## **RESULTS AND DISCUSSION**

Previously [20], we characterized  $SiO_2$ -TiO<sub>2</sub> binary aerogels of various composition prepared using different SCF including *i*-PrOH, CO<sub>2</sub>, and MTBE.

We performed a thermal analysis of aerogel samples to determine the features of behavior on heating of AGs obtained using different solvents. Figure 1 exhibits the thermograms of 20STMTB and 20STHFP samples. The examination of data of thermal analysis allows us to draw a conclusion that the thermal degradation of all aerogel samples proceeds in two main stages: the first, within 50–150°C, the second, at 300–600°C. Weight loss at the first stage relates to the removal of physically sorbed solvent and water molecules (m/z =18, 69). Weight change at the second stage of thermolysis corresponds to the removal of chemically bound molecules of solvent, acetylacetone, and water (m/z =18, 44). The obtained data clearly demonstrate that SC drying in alcohols can result in alkylation of surface  $\equiv$ Si–OH groups (this is evidenced, in particular, by the

presence of signal of  $CF_3^+$  ion at 400–500°C, Fig. 1b, m/z = 69). This conclusion agrees well with the results presented in the work [25]. Furthermore, the corresponding data of mass spectral analysis of gaseous thermolysis products indicate the presence in the obtained materials of chemically bound acetylacetone removable at 300–400°C (m/z = 39, 43, data not given in Fig. 1). The values of total weight loss for AG samples are given in Table 1.

One can see that weight loss is maximal for samples dried in  $CO_2$  and HFIP. In the first case, this seems to be due to low solubility of isopropanol in supercritical  $CO_2$  (the gels were washed with isopropanol prior to drying) and low drying temperature, which can give rise to incomplete removal of isopropanol from initial lyogel. As for the samples dried in HFIP, such a large weight loss can be caused by the removal of sorbed molecules of hexafluoroisopropanol and chemically bound  $-O-CH(CF_3)_2$  groups having high molecular weight.



**Fig. 2.** Diffractograms of initial and annealed AG samples of 5ST (a, c, e) and 50ST series (b, d, f) obtained by SC drying in MTBE (a, b), HFIP (c, d), and  $CO_2$  (e, f).

To study the changes in the phase composition and texture characteristics of aerogels, they were annealed at 400, 600, 800, and 1200°C.

Figure 2 displays X-ray powder diffraction patterns for initial and annealed AGs of 5ST (a, c, e) and 50ST (b, d, f) series. The X-ray powder diffraction patterns of samples obtained in *i*-PrOH are similar to those of samples obtained in MTBE and not shown in the figure. The X-ray powder diffraction patterns of samples obtained by the annealing of AG at  $800^{\circ}$ C are also not shown in the figure because they are similar to those of samples obtained at  $600^{\circ}$ C.

Initial AGs obtained with the use of HFIP and CO<sub>2</sub> are X-ray amorphous irrespective of titanium content.

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Sample	SCF					
	CO <sub>2</sub>	HFIP	<i>i</i> -PrOH	MTBE		
0ST	21	34	22	11		
10ST	31	38	14	16		
20ST	36	37	—	15		
50ST	41	39	16	12		

On the contrary, the samples dried in *i*-PrOH and MTBE initially contain crystalline anatase. The marked broadening of diffraction maxima indicates a small size of  $TiO_2$  particles.

The formation of crystalline anatase in the samples dried with the use of *i*-PrOH and MTBE is obviously associated with the fact that the critical parameters of these solvents (and therefore the temperature of SC drying for these AGs) are considerably higher than the corresponding values for CO<sub>2</sub> and HFIP. The amorphous nature of AGs prepared by drying in HFIP may be also caused by the hydrophobic properties of lyogel surface, which, in turn, results from the substitution of surface –OH groups by –O–CH(CF<sub>3</sub>)<sub>2</sub>. The hydrophobic properties of the gels prevent the dissolution/crystallization processes of titanium compounds.

The formation of metastable anatase rather than rutile, thermodynamically stable polymorphous modification of titanium dioxide, under supercritical condition is often associated with the occurrence of topotactic crystallization of gel which was formed upon hydrolysis of titanium compounds and characterized by the short-range structural ordering typical for anatase [34].

Figure 2 shows that increase in annealing temperature for samples initially containing crystalline  $TiO_2$ (obtained in *i*-PrOH and MTBE) does not lead to considerable change in the corresponding X-ray diffraction patterns, which contain halo related to amorphous phase along with anatase reflections (Figs. 2a) and 2b). Rutile never formed in any case. The lack of anatase  $\rightarrow$  rutile phase transition in similar systems was observed in other works as well [9, 35]. The effect of anatase stabilization seems to result from dimensional factor or effect of admixtures, for example silicon. The crystallization of anatase in samples obtained in HFIP is observed after annealing at 600°C, whereas the samples obtained in CO<sub>2</sub> produce anatase only upon annealing at 1200°C. Lower crystallization temperature of anatase for samples prepared by drying in HFIP in comparison with samples obtained in  $CO_2$  is likely to result from their lower homogeneity (lower content of Si-O-Ti bonds) because of higher temperature of synthesis in HFIP.

Table 2 shows the results of treatment of diffractograms using Scherrer formula for AG samples containing nanocrystalline anatase.

For the samples initially containing anatase (prepared in *i*-PrOH and MTBE), the size of TiO<sub>2</sub> particles up to 600°C changes insignificantly and constitutes 10–20 nm in all cases. A considerable growth of TiO<sub>2</sub> particles in these AGs occurs only upon annealing at 1200°C.

When initially amorphous AGs (obtained in HFIP and  $CO_2$ ) were annealed at 1200°C, the coherent-scattering region (CSR) of anatase for samples of *x*STHFP series are considerably larger than similar values for

**Table 2.** The size of CSR of anatase (in nm) for initial AGs and samples annealed at different temperatures

SCF	<i>T</i> , °C	5ST	10ST	20ST	50ST
<i>i</i> -PrOH	Init.	15	14	17	14
MTBE		11	12	14	19
CO <sub>2</sub>		*	-	-	
HFIP		_	_	_	_
<i>i</i> -PrOH	400	22	16	17	15
MTBE		13	12	15	19
CO <sub>2</sub>		_	_	_	_
HFIP		_	_	_	_
<i>i</i> -PrOH	600	18	16	15	16
MTBE		13	12	14	18
CO <sub>2</sub>		—	—	_	_
HFIP		_	_	23	20
<i>i</i> -PrOH	1200	71	42	39	55
MTBE		22	22	31	60
CO <sub>2</sub>		_	_	18	28
HFIP		_	70	66	62

\* X-ray amorphous phase.

the samples of xSTCO2 series. This fact also confirms the above assumption on the different homogeneity of titanium distribution in these AGs. Let us note that the annealing of 50STCO2 sample (with high titanium content) at 1200°C retains extremely small size of anatase particles (~30 nm).

The data of scanning electron microscopy for initial and annealed AG samples in reflected electron detection mode (compositional contrast) presented in Fig. 3 show satisfactory fit to the results of X-ray powder diffraction analysis for samples presented in Fig. 2 and Table 2. The annealing up to 600°C does not lead to considerable change of TiO<sub>2</sub> particle size for samples initially containing anatase (Figs. 3a and 3b), while annealing at 1200°C causes their considerable growth (Fig. 3c). Moreover, the annealing at 600°C of initially amorphous AG 50STCO2 does not lead to a considerable change of image in reflected electrons (Figs. 3d



**Fig. 3.** Electron micrographs (in reflected electrons detection mode) for 20STMTB (a–c) and 50STCO2 (d–f) samples: initial (a, d) and annealed at 600 (b, e) and 1200°C (c, f).

and 3e), however, the annealing at 1200°C brings about the emergence of bright regions related to crystalline anatase in the micrographs of the corresponding sample.

<i>T</i> , ⁰C	SCF	0ST	5ST	10ST	20ST	50ST
Init.	<i>i</i> -PrOH	950	830	710	610	700
	MTBE	1250	1050	890	600	680
	CO <sub>2</sub>	1060	790	570	250	320
	HFIP	830	930	790	670	660
400	<i>i</i> -PrOH	1140	1060	800	500	430
	MTBE	1190	900	800	490	450
	CO <sub>2</sub>	1230	670	630	190	240
	HFIP	1040	1080	720	630	670
600	<i>i</i> -PrOH	1060	1050	710	400	500
	MTBE	970	870	740	450	480
	CO <sub>2</sub>	1010	620	530	110	150
	HFIP	310	690	430	390	670
800	<i>i</i> -PrOH	650	790	760	210	280
	MTBE	660	650	570	210	280
	CO <sub>2</sub>	640	510	380	60	40
	HFIP	500	490	400	100	310

**Table 3.** Specific surface area  $(S_{sp})$  for initial and annealed at different temperatures AG samples

Table 3 shows the values of specific surface area  $(S_{sp})$  of initial and annealed at different temperatures AGs.  $S_{sp}$  of initial AG samples decreases when titanium content in AG increases irrespective of the type of used SCF. In our opinion, this effect may be caused by lower availability of pores and segregation of TiO<sub>2</sub> in AG pores [20].

Figure 4c exemplifies the dependence of  $S_{sp}$  on annealing temperature for AG samples prepared in MTBE (Fig. 4a) and for aerogels of 20ST series dried in different solvents (Fig. 4b).

Figure 4a shows that the value of  $S_{sp}$  for AG with various titanium content obtained in MTBE regularly decreases when annealing temperature increases owing to the gradual degradation of their porous structure. The same trend is observed for samples dried in other solvents. Moreover, a slight growth of  $S_{sp}$  is observed for certain samples (Table 3) after annealing of initial AGs at 400°C, which seems to result from the removal of physically and chemically bound organic compounds and water.

As a whole, the analysis of the character of  $S_{sp}$  dependence on annealing temperature for the samples of aerogels dried in different solvents (Fig. 4b, Table 3) shows that the annealing at 600°C of samples prepared in *i*-PrOH, MTBE, and HFIP does not lead to marked degradation of aerogels structure and they retain high values of  $S_{sp}$  (>400 m<sup>2</sup>/g). The considerable decrease of  $S_{sp}$  for these AGs is observed upon annealing at 800°C, while the annealing at 1200°C causes the disappearance of porosity (specific surface area for all samples is not larger 2 m<sup>2</sup>/g). Let us note that



Fig. 4. Dependences of  $S_{sp}$  on annealing temperature for SiO<sub>2</sub>-TiO<sub>2</sub> aerogels: (a) prepared in MTBE; (b) AG of 20ST series prepared in different solvents.

the least values of  $S_{sp}$  for AG with high titanium content are observed for samples obtained in CO<sub>2</sub> (Fig. 4b).

Thus, in this work, we have prepared  $SiO_2-TiO_2$ binary aerogels by supercritical drying using common (isopropanol and carbon dioxide) and novel supercritical fluids (methyl *tert*-butyl ether and hexafluoroisopropanol), the aerogels have high specific surface area (up to ~1000 m<sup>2</sup>/g). We have shown that the selection of SCF for the synthesis of  $SiO_2-TiO_2$  binary aerogels has a considerable effect on their phase composition, texture characteristics, and thermal stability.

## ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation (project no. 14-13-01150).

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Translated by I. Kudryavtsev