

# Methyl *tert*-Butyl Ether As a New Solvent for the Preparation of SiO<sub>2</sub>–TiO<sub>2</sub> Binary Aerogels

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**Abstract**—SiO<sub>2</sub>–TiO<sub>2</sub> binary aerogels have been synthesized for the first time using methyl *tert*-butyl ether as supercritical fluid. It has been shown that the aerogels prepared in methyl *tert*-butyl ether and isopropanol contain nanocrystalline anatase and that amorphous SiO<sub>2</sub>–TiO<sub>2</sub> aerogels with a homogeneous distribution of their components can be obtained in CO<sub>2</sub>. A considerable contribution to the large specific surface area of the aerogels is made by micropores, especially when supercritical drying is carried out in CO<sub>2</sub> and isopropanol.

**Keywords:** SiO<sub>2</sub>–TiO<sub>2</sub> binary aerogels, supercritical drying, methyl *tert*-butyl ether

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## INTRODUCTION

SiO<sub>2</sub>-based aerogels are unique mesoporous materials with low density, high porosity, and large specific surface area [1]. The possibility of producing composite aerogels that combine these characteristics with high catalytic activity is of special interest [2]. In particular, SiO<sub>2</sub>–TiO<sub>2</sub> composite aerogels were proposed as catalysts for alkene isomerization and epoxidation [3, 4] and as photocatalysts promoting photoinduced decomposition of organic pollutants in water and air [5–7].

SiO<sub>2</sub>–TiO<sub>2</sub> binary aerogels can be prepared using a variety of sol–gel processes, followed by supercritical drying [8, 9]. For example, Kwon et al. [10] added titanium dioxide powder during the formation of SiO<sub>2</sub> lyogel. In a number of studies, SiO<sub>2</sub> lyogels were impregnated with titanium alkoxides [11] or TiO<sub>2</sub> suspensions [10]. The most universal synthesis method is the cohydrolysis and condensation of silicon and titanium alkoxides [12–14]. Since the rates of the hydrolysis and polycondensation of titanium alkoxides considerably exceed those of silicon alkoxides, two synthetic tricks are used. One is prehydrolysis of silicon alkoxides [12] and the other is prechelation of titanium alkoxides [13].

Lower aliphatic alcohols (MeOH, EtOH, and *i*-PrOH) and CO<sub>2</sub> are typically used as supercritical

fluids (SCFs) in the synthesis of aerogels, including binary ones [1]. The effect of the nature of the SCF on the physicochemical properties of SiO<sub>2</sub>–TiO<sub>2</sub> binary aerogels is essentially unexplored. Note that our data demonstrate that, in the synthesis of oxide aerogels, characteristics of the SCF are of prime importance [15–18]. In particular, the specific surface area of SiO<sub>2</sub>-, Al<sub>2</sub>O<sub>3</sub>-, and ZrO<sub>2</sub>-based aerogels prepared through supercritical drying in diethyl ether, methyl *tert*-butyl ether (MTBE), or hexafluoroisopropanol is about twice the surface area of aerogels produced by conventional drying in ethanol, and their porosity is also considerably higher. Aerogels prepared in different solvents may also differ in phase composition. In particular, ZrO<sub>2</sub> aerogel produced through drying in ethanol is crystalline and consists of a mixture of the tetragonal and monoclinic phases of zirconium dioxide, whereas drying in ethers yields amorphous ZrO<sub>2</sub> aerogels.

In this paper, we examine the effect of the nature of the solvent used in supercritical drying on the properties of binary aerogels based on SiO<sub>2</sub>–TiO<sub>2</sub> with various compositions and present an experimental study of the feasibility of preparing SiO<sub>2</sub>–TiO<sub>2</sub> aerogels containing titanium dioxide in an amorphous or nanocrystalline state.

## EXPERIMENTAL

The starting chemicals used were tetramethoxysilane (TMOS),  $\text{Si}(\text{OCH}_3)_4$  (Aldrich, 99%); titanium tetrakisopropylate (TTIP),  $\text{Ti}(\text{-O}i\text{Pr})_4$  (Acros, 98+%), isopropanol (Acros, 99.5+%), HF (Acros, 40% aqueous solution), acetylacetone (reagent grade), methyl *tert*-butyl ether (Acros, 99%), and distilled water.

**Synthesis of lyogels.** The following approach was used to improve the homogeneity of  $\text{SiO}_2$ – $\text{TiO}_2$  binary aerogels: to a prehydrolyzed TMOS solution was added TTIP chelated by acetylacetone. We used the following molar ratios of the starting chemicals:  $\text{TMOS} : \text{Ti}(\text{O}i\text{Pr})_4 : \text{acacH} : i\text{-PrOH} : \text{H}_2\text{O} : \text{HF} = 1 - \alpha : \alpha : 2\alpha : 3.0 : 4.0 : 0.04$  ( $\alpha = 0, 0.05, 0.10, 0.20, 0.35, 0.50$ ).

As an example, we describe the synthesis of a sample with a nominal  $\text{TiO}_2$  content of 20 mol % ( $\alpha = 0.2$ ). The total volume of the solvent (*i*-PrOH, 13.8 mL) was divided into two equal parts. To one part was added 7.14 mL of TMOS with constant stirring on a magnetic stirrer. A HF solution was prepared separately, by adding 0.12 mL of HF to 4.32 mL of water. The HF solution was added to the TMOS solution. TMOS was prehydrolyzed in an ice-water bath for 5–7 min.

Another solution was prepared as follows: Acetylacetone (2.45 mL) was added to the other part of the solvent, also with constant stirring on a magnetic stirrer. Next, 3.56 mL of TTIP was added to the resultant solution. Chelation by acetylacetone was performed for 3–5 min. 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 to cylindrical polypropylene containers (3–5 mL). Gelation took 40–60 min. Next, the gels were stored at room temperature for 24 h and then washed with the solvent chosen (*i*-PrOH or MTBE) every 24 h during five days (in order to replace the liquid in the pores by a pure solvent). The gels for supercritical drying in  $\text{CO}_2$  were washed with isopropanol.

**Supercritical drying.** As solvents for supercritical drying, we used isopropanol, carbon dioxide, and MTBE.

A glass tube containing gel under a solvent layer (14–16 mL) was placed in an autoclave ( $V = 38$  mL). The autoclave was mounted in a furnace, heated at a rate of  $\approx 100^\circ\text{C}/\text{h}$  to a temperature exceeding the critical temperature of the solvent, and held at that temperature for 10–15 min. The drying temperatures for *i*-PrOH and MTBE were 250–260 (6.0–7.0 MPa) and 235–245°C (6.0–7.0 MPa), respectively. Next, the pressure in the heated autoclave was gradually lowered to atmospheric pressure and the autoclave was evacuated for 30 min (0.03–0.04 atm), cooled, and opened.

Supercritical drying in  $\text{CO}_2$  was carried out in a system that comprised a Supercritical 24 high-pressure pump for  $\text{CO}_2$  (SSI, USA), a 50-mL steel reactor, and

a BPR back pressure regulator (Goregulator, Waters, USA). The sample was washed with liquid  $\text{CO}_2$  for 2 h at a temperature of  $20^\circ\text{C}$  and pressure of 15 MPa. The temperature in the reactor was then raised to  $50^\circ\text{C}$  and the sample was washed with supercritical  $\text{CO}_2$  (15 MPa) for 2–2.5 h. Next, the pressure in the heated autoclave was gradually (30–40 min) lowered to atmospheric pressure and the autoclave was cooled and opened.

Hereafter, the binary aerogel samples are denoted as  $x\text{TS}$ , where  $x$  is the nominal  $\text{TiO}_2$  content of the aerogel (in mole percent). For example, 0TS denotes aerogel based on individual  $\text{SiO}_2$ , and 20TS denotes aerogel based on  $\text{SiO}_2$ – $\text{TiO}_2$  with a nominal  $\text{TiO}_2$  content of 20 mol %.

**Characterization of the aerogels.** Using low-temperature nitrogen adsorption measurements with ATK-06 analyzer (KATAKON, Russia), we determined the specific surface area of the aerogels and plotted full nitrogen adsorption/desorption isotherms. From these data, we evaluated the specific surface area of the samples using the BET model, with five data points at partial pressures in the range 0.05–0.25. The pore size distribution was assessed by the Barrett–Joyner–Halenda (BJH) method using adsorption isotherms at partial pressures in the range 0.4–0.97. The micropore volume and specific surface area were determined by the  $t$ -plot method. As a reference, we used the adsorption isotherm proposed by Gregg and Sing (Sing's  $\alpha_s$  method) and refined at the laboratories headed by V.B. Fenelonov (Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Russia) and M. Jaroniec (Kent State University, USA). Before measurements, the samples were degassed in flowing nitrogen at  $200^\circ\text{C}$  for 35 min.

The phase composition of solid samples was determined by X-ray diffraction on a Bruker D8 Advance diffractometer ( $\text{CuK}_\alpha$  radiation) at a continuous scan rate of  $5^\circ/2\theta/\text{min}$ .

The micromorphology and elemental composition of the samples were assessed by scanning electron microscopy on a Carl Zeiss NVision 40 equipped with an Oxford Instruments X-Max energy dispersive X-ray detector, at accelerating voltages of 1 and 20 kV, respectively. Magnification was varied from  $3000\times$  to  $300000\times$ .

## RESULTS AND DISCUSSION

After the completion of supercritical drying with the use of different supercritical fluids, we successfully obtained monolithic aerogels in all cases (Fig. 1).

The actual titanium and silicon contents of the aerogel samples were determined by X-ray microanalysis. The actual titanium content was evaluated as

$$\frac{\chi(\text{Ti})}{\chi(\text{Ti}) + \chi(\text{Si})} \times 100$$
, where  $\chi$  is the atomic percent of the corresponding element as determined by X-ray

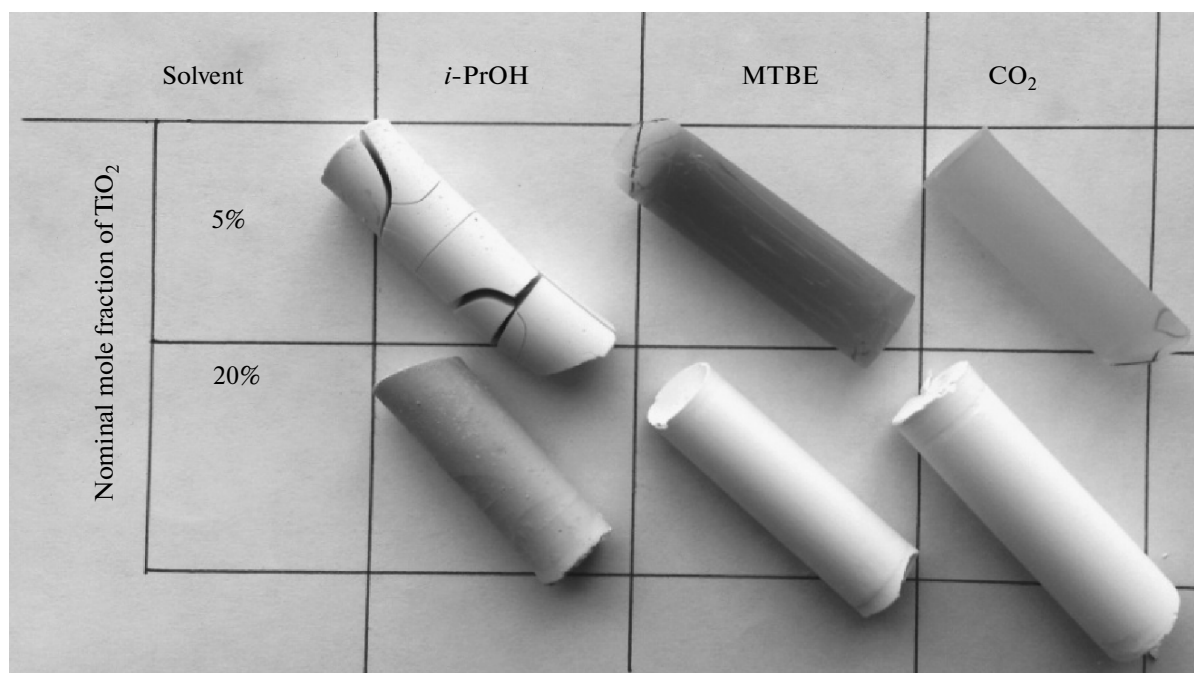


Fig. 1. Appearance of some  $\text{SiO}_2$ – $\text{TiO}_2$  binary aerogels.

microanalysis (the nominal content was evaluated in an analogous way). According to X-ray microanalysis data, the actual titanium content of the samples was lower than the nominal content (Fig. 2). It seems likely that the washing and supercritical drying of the lyogels led to removal of titanium in the form of complexes.

According to Fig. 2, the distinction between the actual and nominal titanium contents increases with increasing TTIP concentration in the reaction mixtures. At a given concentration, the highest titanium concentration is observed in the samples prepared using MTBE. One possible reason for this is that, because of its low polarity, MTBE is less prone to reactions with titanium complexes during washing and drying. It is worth pointing out that titanium leaching during supercritical drying of titanium-containing binary aerogels was also reported by Yoda et al. [5].

All of the synthesized  $\text{SiO}_2$ – $\text{TiO}_2$  mixed aerogels had a large specific surface area (200–1200  $\text{m}^2/\text{g}$ ) (Fig. 3). As seen in Fig. 3, the specific surface area of the  $\text{SiO}_2$ – $\text{TiO}_2$  binary aerogels decreases markedly with increasing nominal  $\text{TiO}_2$  content. A similar decrease in the specific surface area of  $\text{SiO}_2$ – $\text{TiO}_2$  aerogels was observed previously in a number of studies [12, 19, 20].

Data similar to ours have been interpreted in several ways. In particular, the decrease in specific surface area with increasing titanium content was assumed to be due to the larger atomic weight of titanium in comparison with that of silicon. Moreover, an increase in titanium content may impair pore accessibility

because of the  $\text{TiO}_2$  segregation in pores of aerogels. Clearly, the observed changes in specific surface area can be understood in terms of the key features of the hydrolysis and condensation processes during gelation. In particular, our data demonstrate that increasing the titanium content of reaction mixtures reduces the gelation time. A similar relation was reported by Miller et al. [12]. The increase in gelation rate is due to the higher rate of the formation of  $\text{Si-O-Ti}$  bridges owing to the higher reactivity of  $\text{Ti-O-R}$  in comparison with  $\text{Si-O-H}$ . In models dealing with diffusion-

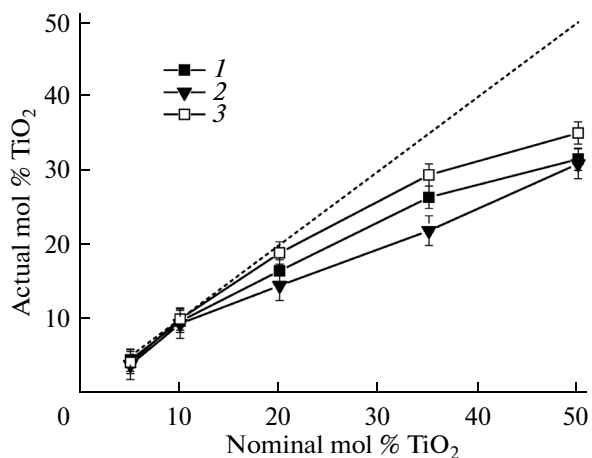
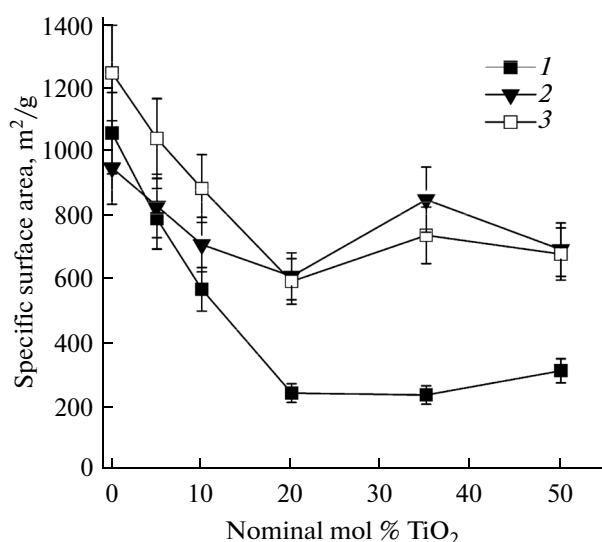


Fig. 2. Actual  $\text{TiO}_2$  content of the  $\text{SiO}_2$ – $\text{TiO}_2$  binary aerogel samples produced by supercritical drying in (1)  $\text{CO}_2$ , (2)  $i\text{-PrOH}$ , and (3)  $\text{MTBE}$ .



**Fig. 3.** Specific surface area as a function of nominal TiO<sub>2</sub> content for the SiO<sub>2</sub>-TiO<sub>2</sub> aerogels produced by supercritical drying in (1) CO<sub>2</sub>, (2) *i*-PrOH, and (3) MTBE.

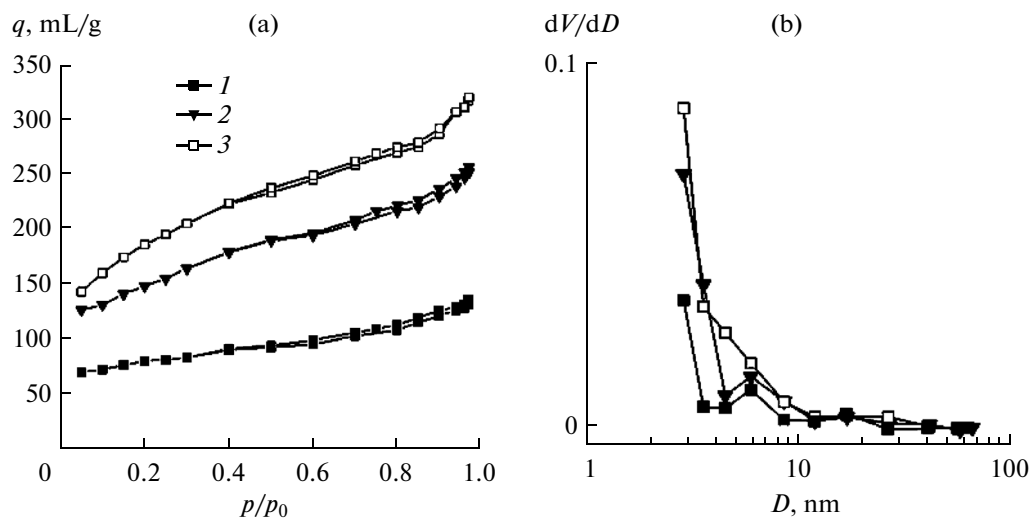
limited aggregation (DLA) and cluster-cluster aggregation (CCA) [9], gel structures with various pore sizes can be formed, depending on the rate of the hydrolysis of the starting compounds and that of the polycondensation of sol particles. If the hydrolysis rate exceeds the polycondensation rate, loose particle aggregates are formed. The opposite relationship between the rates of these processes leads to the formation of denser aggregates.

As follows from the data in Fig. 3, the samples prepared using supercritical CO<sub>2</sub> have a relatively small specific surface area in comparison with the materials obtained in the other solvents. Since the drying temperature in CO<sub>2</sub> is low ( $\approx 50^\circ\text{C}$ ) in comparison with the other solvents ( $\approx 200\text{--}250^\circ\text{C}$ ), drying in CO<sub>2</sub> removes not all organic impurities (especially acetylacetone).

Figure 4 shows full nitrogen adsorption/desorption isotherms for the 50TS aerogel samples and the corresponding pore size distributions. It can be seen from the data in Fig. 4 that the absolute adsorption values for the samples dried in MTBE and *i*-PrOH are higher than those for the samples dried in CO<sub>2</sub>. All of the isotherms are type IV in the IUPAC classification and have narrow, type H1 hysteresis loops, characteristic of materials containing cylindrical pores open on both sides. It follows from the pore size distributions in these samples that a major contribution to the pore structure of the samples comes from small mesopores (2–15 nm), whereas pores more than 20 nm in size are essentially missing.

Using a comparative  $\alpha_s$  method [21] for aerogels based on SiO<sub>2</sub>-TiO<sub>2</sub>, we determined the micropore and mesopore areas (Fig. 5).

It can be seen that micropores make a significant contribution to the specific surface area of the sample prepared using CO<sub>2</sub>. By contrast, their contribution is insignificant in the samples prepared in MTBE. With increasing titanium content, the contribution of micropores to the pore structure of the aerogels also increases. This trend is probably also due to a change in the gelation mechanism from CCA (loose structure) to DLA (dense structure).



**Fig. 4.** (a) Nitrogen adsorption/desorption isotherms for the 50TS samples prepared by supercritical drying in (1) CO<sub>2</sub>, (2) *i*-PrOH, and (3) MTBE, and (b) the corresponding pore size distributions.

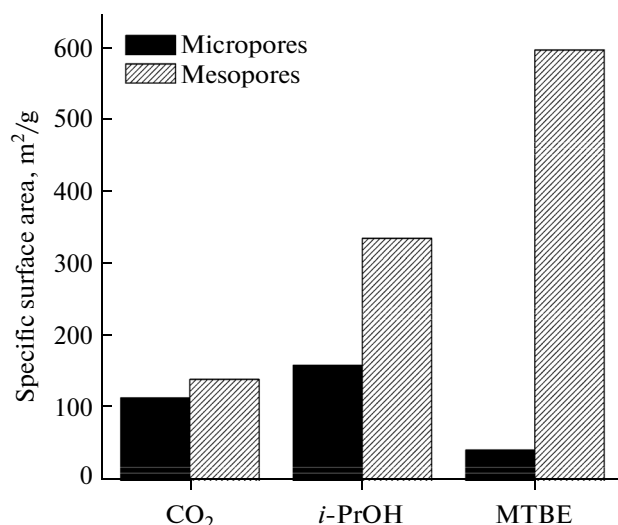


Fig. 5. Specific surface areas of meso- and micropores in the 50TS aerogel samples.

On the whole, MTBE as a solvent for the preparation of SiO<sub>2</sub>–TiO<sub>2</sub> aerogels allows one to produce materials with a considerable contribution of mesopores. This suggests that they will exhibit higher activity in heterogeneous catalytic processes owing to their large specific surface area and its better accessibility.

Figure 6 shows X-ray diffraction patterns of the synthesized aerogels. It can be seen that the aerogels

prepared using CO<sub>2</sub> are X-ray amorphous, independent of titanium content. The samples dried in *i*-PrOH and MTBE contain crystalline anatase. The marked broadening of the diffraction peaks attests to a small size of the TiO<sub>2</sub> particles.

The formation of crystalline anatase in the samples prepared using *i*-PrOH and MTBE is most likely due to the fact that the critical parameters of these solvents (and, accordingly, the supercritical drying temperature of these aerogels) considerably exceed those of CO<sub>2</sub>. It is worth pointing out that the preparation of amorphous aerogels via drying in CO<sub>2</sub> and the formation of anatase during drying in the alcohols were also reported previously [5, 13, 22].

The results obtained by analyzing X-ray diffraction data are presented in the table. It follows from these data that the anatase particles range in size from 10 to 20 nm and that the particle size is a weak function of the nominal titanium concentration in the aerogels.

Nevertheless, it can be seen that, with increasing titanium concentration in the aerogels prepared using MTBE, the particle size of anatase increases slightly (from ≈12 to ≈19 nm), whereas it remains essentially unchanged when *i*-PrOH is used as SCF.

Note that the formation of metastable anatase under supercritical conditions, instead of rutile, a thermodynamically stable titanium dioxide polymorph, is often attributed to topotactic crystallization of gel resulting from the hydrolysis of titanium compounds, whose structure has short-range ordering similar to one in anatase [23].

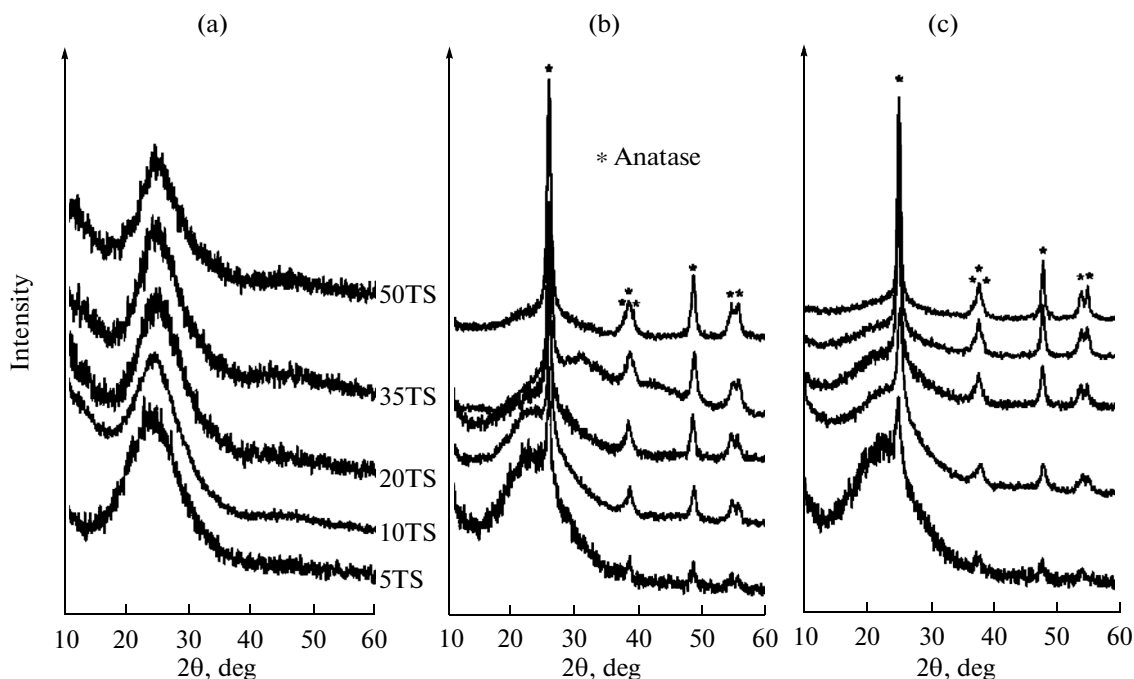


Fig. 6. X-ray diffraction patterns of aerogels prepared using (a) CO<sub>2</sub>, (b) *i*-PrOH, and (c) MTBE as solvents and containing different percentages of TiO<sub>2</sub>.

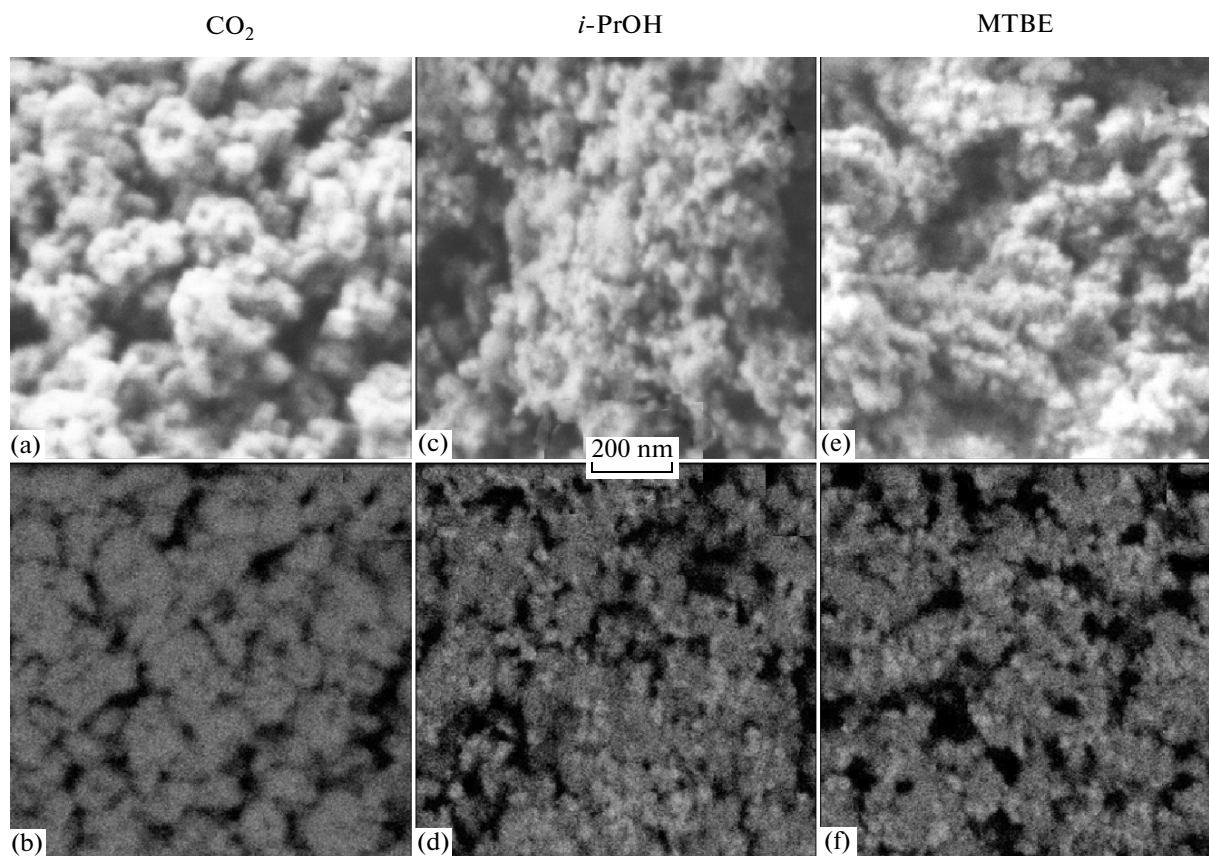
Particle size of anatase in the aerogels, as evaluated from X-ray diffraction data

Solvent	Particle size, nm					
	0TS	5TS	10TS	20TS	35TS	50TS
<i>i</i> -PrOH	XRAP*	15	14	17	14	14
MTBE	XRAP	12	12	14	16	19
CO <sub>2</sub>	XRAP	XRAP	XRAP	XRAP	XRAP	XRAP

\* X-ray amorphous phase.

The phase composition of the aerogels, as determined by X-ray diffraction, correlates well with scanning electron microscopy data. Figure 7 shows micrographs of the 20TS aerogel samples. It can be seen that, even though prepared using different solvents, the aerogels are similar in morphology.

Analysis of the micrographs taken using a backscattered electron detector (Figs. 7b, 7d, 7f) indicates that the aerogel samples dried in *i*-PrOH and MTBE contain separate anatase particles, which are uniformly distributed over the aerogel matrix, whereas the samples dried in CO<sub>2</sub> are homogeneous on a nanometer scale.



**Fig. 7.** Micrographs of the 20TS aerogel samples prepared through supercritical drying in (a, b) CO<sub>2</sub>, (c, d) *i*-PrOH, and (e, f) MTBE.

## CONCLUSIONS

SiO<sub>2</sub>–TiO<sub>2</sub> binary aerogels with a large specific surface area ( $\approx 1000 \text{ m}^2/\text{g}$ ) have been prepared via supercritical drying using a new SCF: methyl *tert*-butyl ether. It has been shown that, using different supercritical media, one can obtain both amorphous SiO<sub>2</sub>–TiO<sub>2</sub> aerogels, with a homogeneous distribution of their components (CO<sub>2</sub>), and composite aerogels containing nanocrystalline anatase (isopropanol and MTBE). The SiO<sub>2</sub>–TiO<sub>2</sub> aerogels contain no large mesopores (greater than 20 nm in diameter), independent of the nature of the supercritical fluid used. A considerable contribution to the large specific surface area of the aerogels is made by micropores, especially when supercritical drying is carried out in CO<sub>2</sub> and isopropanol.

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