

## **MESOPOROUS TITANIUM-CONTAINING SILICAS Synthesis and geometrical characteristics**

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### **Abstract**

Mesoporous titanium-containing silicas with TiO<sub>2</sub> contents from 1 up to 70 mol% were prepared. The obtained samples have been characterized by the powder X-ray diffraction data, the diffuse reflectance infrared Fourier transform method, and nitrogen adsorption at 77 K. Specific surface area, total pore volume, distribution pore volume on pore sizes were determined from nitrogen adsorption isotherm for synthesized titanosilicas.

**Keywords:** DRIFT, mesoporous titanosilicas, pore volume distribution, powder XRD, template synthesis

### **Introduction**

A remarkable achievement of the last decade in the field of synthesis of ordered mesostructural materials is the preparation of a new class MCM-41 periodic silicates and aluminosilicates [1–3] with pore diameter from 15 up to 100 Å and high specific surface area (more than 1000 m<sup>2</sup> g<sup>-1</sup>) with the use of surfactants as supramolecular templates. Such materials are used as catalyst carriers due to their unique geometrical structure, high thermal stability and adsorptivity [4–6]. Recently, considerable attention has been focused on synthesis of MCM-41 materials containing the ions of transition metals in their structure, in particular titanium [5–13], for the preparation of materials with high catalytic activity and which are stable at heating and under the conditions of hydrothermal treatment [7]. So, in the work [7], hydrothermal stability up to 800°C and the stability in acid medium (pH=2) were compared for the obtained Ti-MCM-41 materials in contradistinction to zeolites which are much less stable under the same conditions. The inclusion of titanium into the skeleton of mesoporous silica matrices permits one to create new materials with pore diameter in the range 15–100 Å, high specific surface area and with catalytic activity in oxidation reactions of large organic molecules, for which the adsorption space of known perspective

Ti-containing catalysts of TS-1, TS-2 and Ti- $\beta$  types is inaccessible [8]. Works [9, 10] dealing with synthesis of Ti-MCM-41 and Ti-HMS must be pointed out in this respect. It has been shown that Ti-MCM-41 materials, along with TS-1 and Ti-HMS, are effective catalysts for the hydroxylation reaction of benzene to phenol. The catalytic activity of Ti-HMS and Ti-MCM-41 in the reaction of 2,6-di-*tert*-butyl phenol oxidation was also demonstrated [9].

The aim of this work is to continue systematic research in the field of synthesis and characterization of titanium-containing mesoporous materials bearing various amounts of titanium.

## Experimental

For the preparation of titanium-containing mesoporous materials tetraethyl orthosilicate (TEOS) was used as a silica source and titanium(IV) tetraisopropoxide was chosen as a titanium source. Cation-active surfactant – octadecyl trimethylammonium chloride (ODTMAC) was applied as a micellar template.

Mesoporous titanosilicas with molar ratios Ti/(Ti+Si) equal 1, 15, 30, 50, and 70% were synthesized using the technique described in the work [9]. The necessary  $\text{Ti}(i\text{-OC}_3\text{H}_7)_4$  amount was added in small portions by stirring to TEOS solution in mixture of ethanol and isopropanol. The weighed portion of ODTMAC was dissolved during intensive stirring in water with addition of a small amount of concentrated HCl. The obtained homogeneous milk-white suspension was added to initial mixture during intensive stirring and heating up to 60°C for the gel preparation (for 1.5 h). The gel was subjected to ageing for 18 h on air. Samples were dried up at 120°C for 3 h, and were then calcinated at 540°C for 6 h on air.

The characterization of the synthesized samples was performed by the powder X-ray diffraction (XRD) data (automated diffractometer DRON-3M,  $\text{CuK}_\alpha$  radiation) and nitrogen adsorption isotherm measurements at 77 K using ASAP-2000 Micromeritics equipment. The average pore diameter was estimated by the Gurvich method ( $d=4V/S$ ). The specific surface area,  $S_{\text{BET}}$ , was determined from the linear part of the BET equation (at  $p/p_s=0.05\text{--}0.35$ ). Pore volume distribution was calculated from the desorption branch of an isotherm of nitrogen adsorption using the Barrett–Joyner–Halenda (BJH) formula [14, 15].

## Results and discussion

Diffractograms of the obtained titanium-containing materials are represented in Fig. 1.

The availability of low-angle peak on XRD pattern of the mesoporous silica, containing 1 mol% of titanium, testifies existence in this sample of ordered structure. For other samples the peak intensity in the region  $2\theta\approx 25^\circ$  is characteristic of anatase structure tending to increase with the increase of the metal contents in titanium-containing silicas.

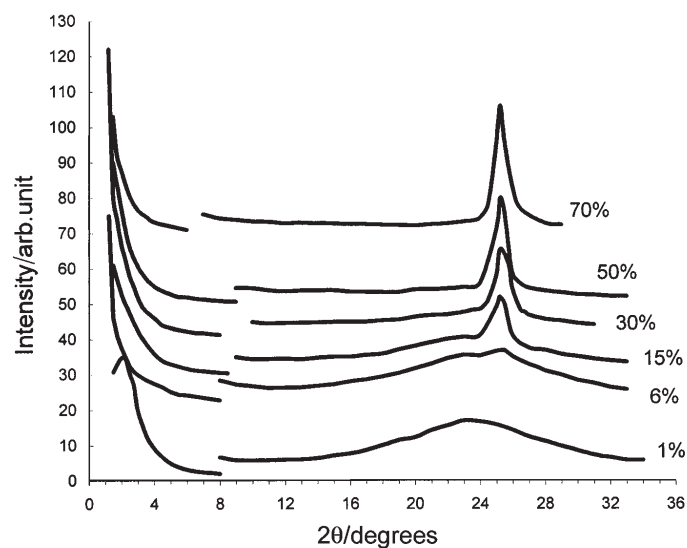


Fig. 1 Powder X-ray diffraction patterns of silicas with various titanium contents (in mol%)

In DRIFT spectra (Fig. 2) of the titanium-containing silicas the absorption band of silanol groups  $3750\text{ cm}^{-1}$  is observed, and there is the absorption band in the region  $920\text{--}960\text{ cm}^{-1}$  characteristic of stretching vibrations of Si–O bonds in titanosilicates. IR spectrum of the sample with maximum titanium contents is shown in Fig. 2. The intensity of this band grows in accordance with the increase of the titanium contents in the obtained samples. Some attention must be paid to the fact that the studied materials have a wide high-intensity band in the region of O–H stretching vibrations and bending vibrations of adsorbed water molecules ( $1640\text{ cm}^{-1}$ ) that testifies high hydroxylation and a hydration degree of the synthesized titanium-containing silica surfaces. The marked circumstance is obviously important for the chemical modification of the obtained sample surfaces with the purpose of the immobilized catalytically-active preparations produced.

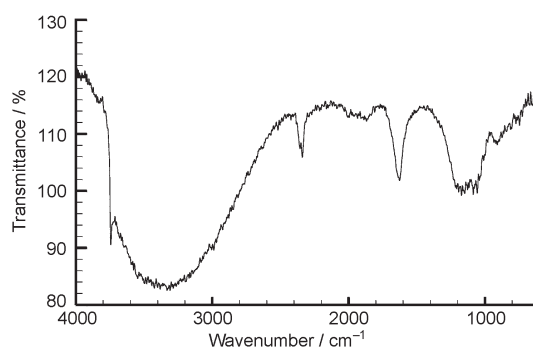


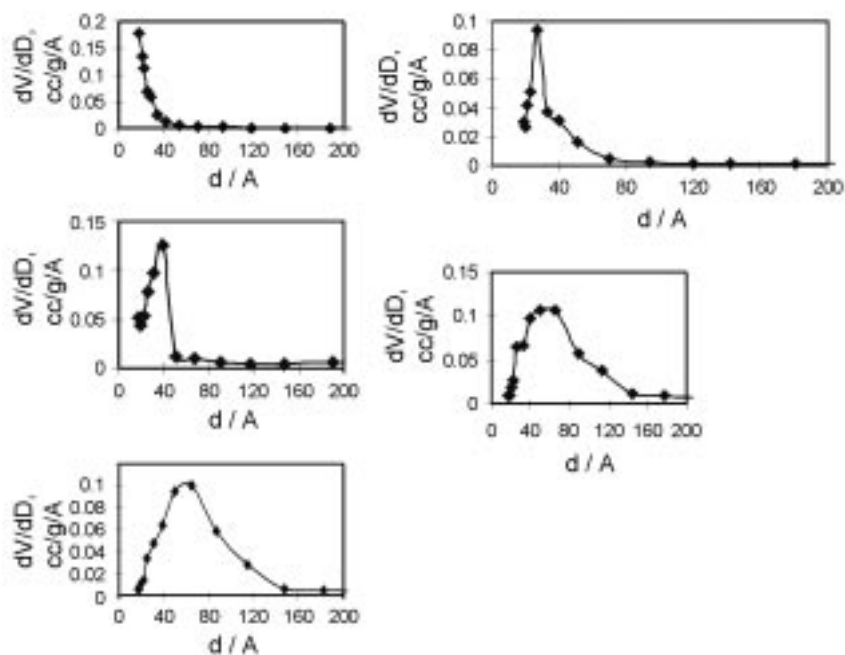
Fig. 2 DRIFT spectrum of mesoporous silica with 70 mol% titanium

The study of nitrogen ad(de)sorption isotherms permits one to receive the most complete and reliable information on the mesoporous structure of materials. Based on adsorption research it was shown that the values of the specific surface area in the titanium-containing silicas, determined by BET method, linearly decrease with the increase of the titanium contents from  $925 \text{ m}^2 \text{ g}^{-1}$  for the sample with titanium contents equal to 1 mol% up to  $350 \text{ m}^2 \text{ g}^{-1}$  for the sample, containing 70 mol% of titanium (Table 1).

**Table 1** Geometrical characteristics of mesoporous titanium-containing silicas

| TiO <sub>2</sub> contents/<br>mol% | Pore diameter/<br>Å | Total pore volume/<br>cm <sup>3</sup> g <sup>-1</sup> | BET surface area/<br>m <sup>2</sup> g <sup>-1</sup> |
|------------------------------------|---------------------|-------------------------------------------------------|-----------------------------------------------------|
| 1                                  | 20                  | 0.47                                                  | 924                                                 |
| 15                                 | 22                  | 0.45                                                  | 805                                                 |
| 30                                 | 30                  | 0.52                                                  | 702                                                 |
| 50                                 | 46                  | 0.59                                                  | 529                                                 |
| 70                                 | 51                  | 0.45                                                  | 353                                                 |

In this situation, the pore diameters calculated by Gurvich method are increased from 20 up to 51 Å at slightly varying total pore volume ( $0.45\text{--}0.60 \text{ cm}^3 \text{ g}^{-1}$ ). As the titanium content in the samples is increased, the shape of the nitrogen adsorption isotherms is changed from I up to IV type with occurrence of hysteresis loops characteristic of



**Fig. 3** Pore volume distribution for mesoporous silicas containing 1, 15, 30, 50, and 70 mol% titanium (1–5 respectively)

mesoporous structures and close under form to H1 type [14]. The curves of pore volume distributions on pore diameter for the synthesized titanium-containing mesoporous materials are given in Fig. 3. At small titanium contents in samples (down to 30 mol%) the narrow volume pore distribution on pore diameter is observed.

## Conclusions

The obtained experimental data testify the opportunity of template synthesis of mesoporous titanium-containing silicas with high titanium contents and advanced specific surface areas. More ordered structures characterized by similar distributions of pore volume can be prepared at small titanium contents. At increase of titanium contents a separate phase of titanium dioxide with anatase structure was formed. A high hydroxylation degree of the titanosilicas surface was marked, that it is important for their chemical modification in order to create catalytically active surface sites.

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R. Lebeda and J. Skubiszewska-Zieba express their thanks for support by KBN Grant number 3TO9A.

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