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SYNTHESIS AND CHARACTERIZATION OF SBA-15 AND Ti-SBA-15 NANOPOROUS MATERIALS FOR DME CATALYSTS

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ABSTRACT

Amorphous SiO_2 known as SBA-15 (Santa Barbara Amorphous) has been synthesized mixing consecutively water solutions of poly(ethylene glycol) $C_3H_6O.C_2H_4O$ (P123), 2M HCl and tetraethoxysilan 98 % $C_8H_{20}O_4Si$ (TEOS) at 60°C. The mixture has been dried at 100°C and calcinated at 500°C. The synthesized SBA-15 samples have been characterized by X-ray diffraction (XRD), FTIR spectroscopy, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), and N_2 physisorption analysis.

The Ti-SBA-15 has been prepared by impregnation using a solution of Ti-isoporopoxide in isopropanol with different concentrations (1, 5, 10, 15, 25 mass %). During the impregnation TiO_2 nanoparticles have been incorporated into the SBA-15 hexagonal channels. N_2-adsorption/desorption analysis has been carried out to investigate the specific surface area, pore size and pore diameter of Ti-SBA-15 to be used as a DME catalyst.

Keywords: SBA-15, Ti-SBA15, nanoporous DME catalysts, FT-IR spectroscopy, XRD, SEM, TEM, N_2 physisorption.

INTRODUCTION

Dimethylether (DME) is widely used as a raw material for obtaining chemicals and aerosol propellants. DME is an important chemical for the production of gasoline components, ethylene, aromatics and other chemicals [1-4]. Its applications as a fuel or a fuel additive for vehicles and family cooking have been studied [5-7]. In view of the environmental protection, the applying of DME as a substitute of freon, which is used in aerosol sprays [8] and as a refrigerant is being considered [9]. Nowadays, the commercial DME is produced by a dehydration of methanol using as a catalyst acidic porous materials such as zeolites, sillica–alumina, alumina etc. (Eq. 1) [10] and the methanol respectively can be produced from CO/H_2 (Eq. 2 and 3).

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad (1)$$

According to [11-13] DME can be synthesized directly from CO/H_2 according Eqs. (2) and (3) using metal supported catalysts with a high specific surface area. This pathway is much more thermodynamically and economically favorable.

$$2CO + 4H_2 \rightarrow CH_3OCH_3 + H_2O, \quad (2)$$

$$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2, \quad (3)$$

The mesoporous materials, including mesoporous amorphous SiO_2, known as SBA-15, can be applied as a support of the nanocatalysts for DME processes. Both the larger pore diameter and higher specific surface area of SBA-15 as a support, are useful for the accommodation of catalytically active metal nanoparticles [14-17].

The aim of this work is firstly , to synthesize and characterize mesoporous SBA-15 material. A second task is to obtain on its base a Ti-SBA-15 catalytic

nanomaterial by impregnation with a solution of Ti-isoporopoxide in isopropanol with different concentrations. It is expected TiO_2 nanoparticles to be incorporated into the suitable SBA-15 hexagonal channels. Thirdly, an aim is to investigate the optimal concentration of the impregnation solution for obtaining of nanoporous material suitable for DME catalysts.

EXPERIMENTAL

Synthesis of mesoporous SBA-15

Three samples of The SBA-15, denoted as S1 (sample 1), S2 (sample 2) and S3 (sample 3) have been prepared by the so-called Stucky's and coworkers method [18 - 20]. Synthesis of SBA-15 samples using water solutions of poly(ethylene glycol) $C_3H_6O.C_2H_4O$ (P123), 2M HCl and tetraethoxysilan 98 % $C_8H_{20}O_4Si$ (TEOS) has been performed stage by stage according to the scheme shown in a Fig. 1.

TEOS
Stirring – I stage
T=60 °C; τ = 5-6h
Stirring – II stage
T=40 °C; τ = 22-24h
Drying
T=100 °C; τ = 24h
Filtering and drying at 25 °C
T-313K;
Heating up to
T=500 °C; τ =8h
Calcination
T=500 °C; τ =6h
P123 H_2O 2M HCl
SBA-15

TEOS has been added to the mixture of P123, 2M HCl and H_2O at 40°C throughout 22 - 24 hours. The final synthesis has been carried out at 60°C for 5 - 6 hours. During the synthesis mechanical stirring using a magnetic stirrer has been used. It is followed by drying at 100°C for 24 hours and filtering at room temperatute and by calcination at 500°C for 14 hours. The last stage is cooling up to 70°C.

Preparation of the Ti-SBA-15 catalyst

An impregnation method was developed to incorporate the Ti-O_2 – basic structural units into the porous SBA-15 material. The Ti-incorporated SBA-15 (Ti-SBA-15) was prepared in a glove bag using pure Ar gas. The impregnation was accomplished with a mixture of titanium isopropoxide ($C_{12}H_{28}O_4Ti$) in isopropanol using a different amounts of a titanium

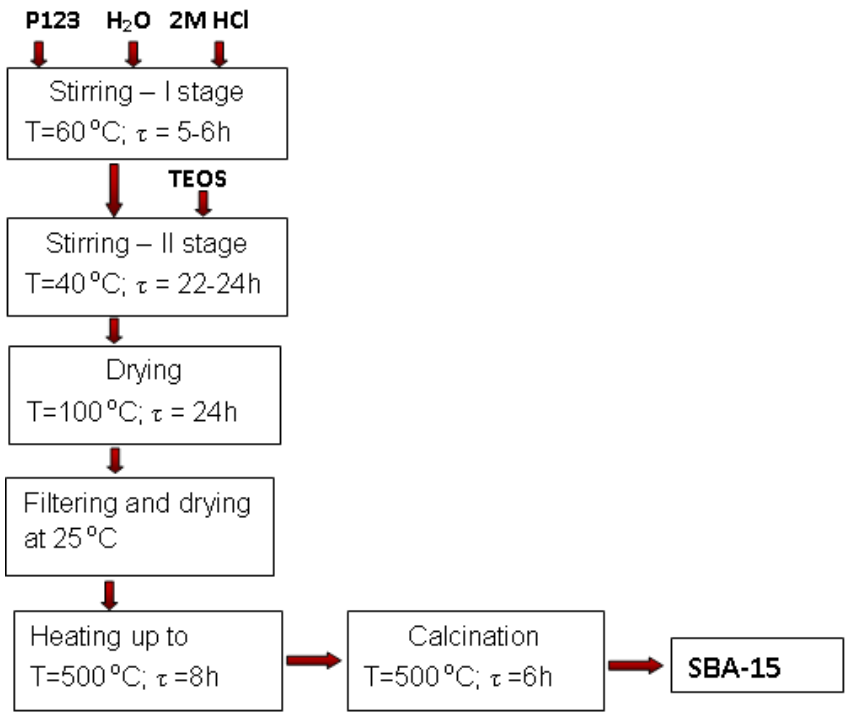


Fig. 1. Block scheme of the SBA-15 synthesis.

isopropoxide in isopropanol solution (different mass ratio of Ti-isoPr: isopropanol): 1 % $_{mass}$, 5 % $_{mass}$, 10 % $_{mass}$, 15 % $_{mass}$, 25 % $_{mass}$. The data about the impregnation solution with different concentration of Ti-isopropoxide are presented in Table 1.

The preparation process of Ti/SBA-15 follows the scheme: firstly, the required amount of titanium isopropoxide in isopropanol solution was prepared (1, 5, 10, 15, 25 % $_{mass}$) and then 0.5 g of SBA-15 was added to the thus prepared mixture. Immediately after that, the mixture obtained was heated at 25°C for 72 hours followed by calcination for 8 hours up to 500°C and keeping this temperature for 6 hours. It is expected that the titanium isopropoxide would be incorporated inside of the SBA-15 hexagonal channels.

The Ti - SBA-15 samples have been prepared from the sample 2 (S2) of the SBA-15.

Methods for characterization

XRD, FTIR, SEM and TEM investigations of the SBA-15 samples have been carried out. The X-ray diffraction patterns of SBA-15 were collected within the 2θ range from 10° to 95° with a constant step of 0.03° and time 1 s/step on a Philips PW 1050 diffractometer using CuKα radiation. The FT-IR spectroscopy study of the SBA-15 samples has been realised in mid-IR region (4000 - 400 cm-1) and the FT-IR spectra have been taken with a FTIR spectrophotometer Equinox 55 (Brucker). The morphology of the different samples was examined by means of a JEOL JSM 5300 (Japan) scanning electron microscope with an accelerating voltage of 20 kV. The TEM micrographs have been used to identify the hexagonal channels. The transmission electron microscopy (TEM) images of SBA-15 were obtained on a JEOL2100 (Japan) transmission electron microscope with an accelerating voltage of 200 kV. N_2 adsorption– desorption analysis has been carried out to determine the specific surface areas, pore volumes and pore sizes of the SBA-15 samples.

BET (Brunauer-Emmett-Teller) analysis provided precise specific surface area evaluation of the materials by nitrogen multilayer adsorption measured as a function of relative pressure with a fully automated analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in m^2/g yielding important information when studying the effects of surface porosity and particle size in many applications. Rapid single point and multipoint specific BET surface area determinations included:

- Full BET surface area characterization of disperse, nonporous or macroporous materials pore diameter >50 nm and mesoporous materials with pore diameter between 2 nm and 50 nm.

- BET surface area characterization of microporous materials < 2 nm.

BJH (Barrett-Joyner-Halenda) analysis can also be employed to determine pore area and specific pore volume using adsorption and desorption techniques. This technique characterizes pore size distribution independent of the external area due to particle size of the sample.

- Pore volume and pore area distributions in the mesopore and macropore ranges using BJH analysis with full complement of adsorbate thickness models.

- BJH adsorption and desorption average pore diameter (4V/A) determinations.

- Modified Kelvin equation: Kelvin equation predicts pressure at which adsorptive will spontaneously

Table 1. Conditions for the impregnation of SBA-15 with different concentration of Ti-isopropoxide.

Content of TiO_2, $\%_{mass}$	SBA-15, g	Ti-isoPr	IsoPr
1	0.5	0.019	2.491
5	0.5	0.094	2.406
10	0.5	0.200	2.300
15	0.5	0.300	2.200
25	0.5	0.600	1.900

condense (and evaporate) in a cylindrical pore of a given size. Condensation occurs in pores that already have some multilayers on the walls. Therefore, the pore size is calculated from the Kelvin equation and the selected statistical thickness (t-curve) equation. The analysis severely underestimates the size of small to medium mesopores, but is acceptable for broad size distributions of medium to large mesopores.

For the studied samples these results have been ob tained from the Kinetics and Catalysis laboratory of AMU Poznan, Poland.

RESULTS AND DISCUSSION

Characterization of the synthesized mesoporous SBA-15 material

Structure investigations of the synthesized samples have been carried out. Fig. 2 shows the X-ray diffraction patterns of the three SBA-15 samples prepared according to the block scheme (Fig.1). It is obvious that all patterns display one broad peak of 2 theta at around 12 degrees and indicate that the obtained of SBA-15 samples are apparently amorphous. The diffraction peak at 12 degrees is the typical diffraction of amorphous SiO_2 [18], showing namely the Si-O short-order structure.

Fig. 3 shows the FTIR spectra of the investigated SBA-15 samples. The FTIR spectroscopy analysis of the synthesized SBA-15 samples has proved that in all speciments the observed bands of absorption characterize the creation of Si-OH, Si-O, Si-H, Si-O-C, Si-C, C-O and O-H bonds [17-19].

The broad bands of absorption at around 3450 cm^{-1} correspond to molecular water hydrogens bonded to each other and to Si-OH groups, they can be assigned to stretching vibrations of O-H and Si-OH bonds. The bands at around 1620 cm^{-1} could be related to bending vibrations of O-H bonds in OH groups, overlapped with C-O-C stretching vibrations. The bands at around 1080 cm^{-1} could be due to antisymmetrical stretching vibrations of Si-O-Si, overlapped with Si-O-C, C-O-C and Si-C bond vibrations. The bands in 980-950 cm^{-1} could be refered to stretching vibrations of free silanol (Si-OH) groups on the surface of the amorphous solid samples and C-O stretching vibration bonds are also placed in this range. Symmertical stretching vibrations of Si-O-Si bonds belonging to ring structures are observed around 795-790 cm^{-1}. The bands in 480-460 cm^{-1} could be assigned to associate Si-O-Si bond bending vibrations.

The identical peak position and peak intensity of the XRD patterns (Fig. 2) and FTIR spectra bands of

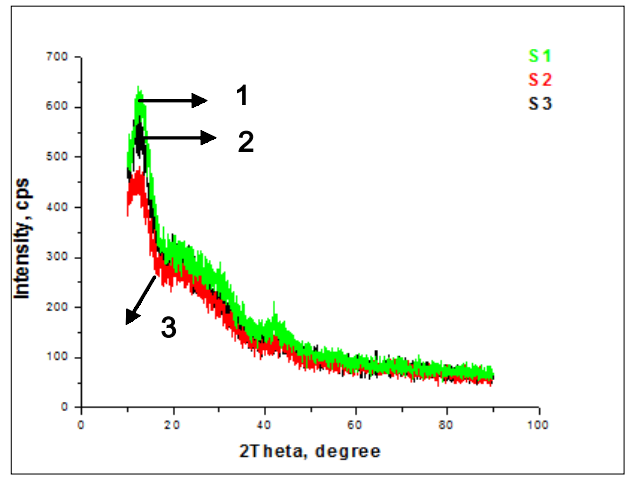


Fig. 2. XRD patterns of SBA-15 samples: S1 – sample 1, S2 – sample 2, S3 – sample 3.

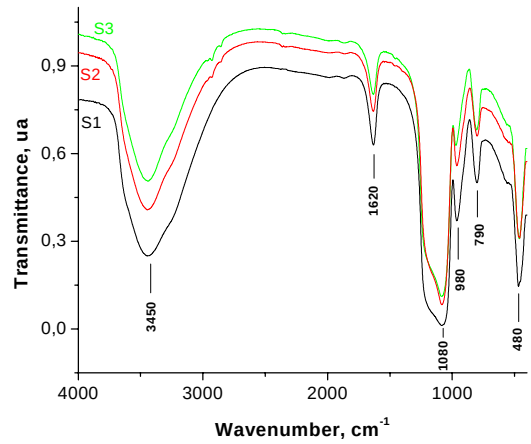


Fig. 3. FTIR spectra of SBA-15 samples.

absorption (Fig.3) prove the reproducibility of the conditions during the synthesis of the SBA-15 samples.

The results from SEM and TEM analysis of the SBA-15 structures are shown in Fig. 4 and Fig.5.

TEM micrographs, shown in Fig. 5, exhibit a hexagonal structure of the SBA-15 samples. The cross sections display the hexagonal channels regular by shape with dimensions from 6-7 nm to 9-10 nm and thickness of the channel walls ranging from 1.5 – 2.0 nm to 4.0 nm.

The results received from Brunauer-Emmett-Teller (BET) - Nitrogen adsorption-desorption analysis

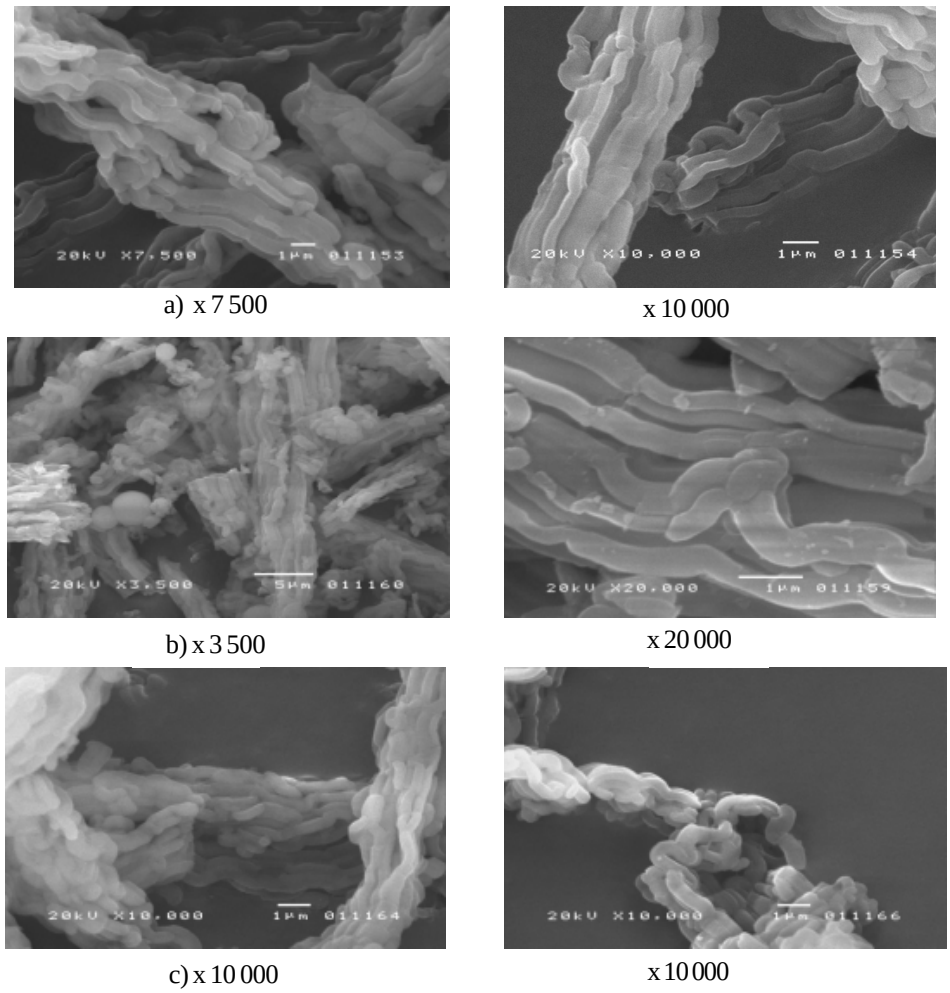


Fig. 4. SEM micrographs of SBA-15Ì at different magnifications: a – sample 1, b – sample 2, c – sample 3.

about the specific surface area (SSA, m^2/g), pore size and pore volume of the three SBA-15 samples are presented in Table 2 and also shown in Fig. 6.

It has been established that SSA is in the range from 606 to 522 m^2/g, the pore size varies from 6.3 to 6.8 nm and the pore volume – from 0.992 to 1.097 cc/g.

It could be seen from these results that the samples are characterized by a high specific surface area. Both the specific surface area and pore nanoscaled diameter will allow the metallic nanoparticles to be situated on the SBA-15 surface and incorporated in the hexagonal channels.

Characterization of the prepared Ti-SBA-15 nanocomposites

The Ti/SBA-15 samples prepared on the basis of the SBA-15 sample 2 (S2) by impregnation using a solution with different concentrations ($\%_{mass}$ TiO_2) have been investigated by BET metod. The obtained results about the specific surface area, pore size and pore volume of the sample are presented in a Table 3 and shown in Fig. 7.

It can be seen from Table 3 that the specific surface area, pore size and pore volume decrease with increasing the TiO_2 content from 1 $\%_{mass}$ to 25 $\%_{mass}$. From 1 % to 5 % the specific surface area decreases, while both the pore size and pore volume remain unchanged. It could be suggested that the TiO_2 nanoparticles have been accommodated only on the SBA-15 surface. Comparing the results from 5 to 10 $\%_{mass}$ it could be seen that not only the specific surface area decreases, but the pore size and pore volume decrease too. In this case the TiO_2 nanoparticles are probably situated not only on the surface, but also inside the pores. From 10 $\%_{mass}$ to 25 $\%_{mass}$ the investigated parameters also decrease, but not so sharply. In these cases some pores on the surface and inside of the SBA-15 hexagonal channels are occupied

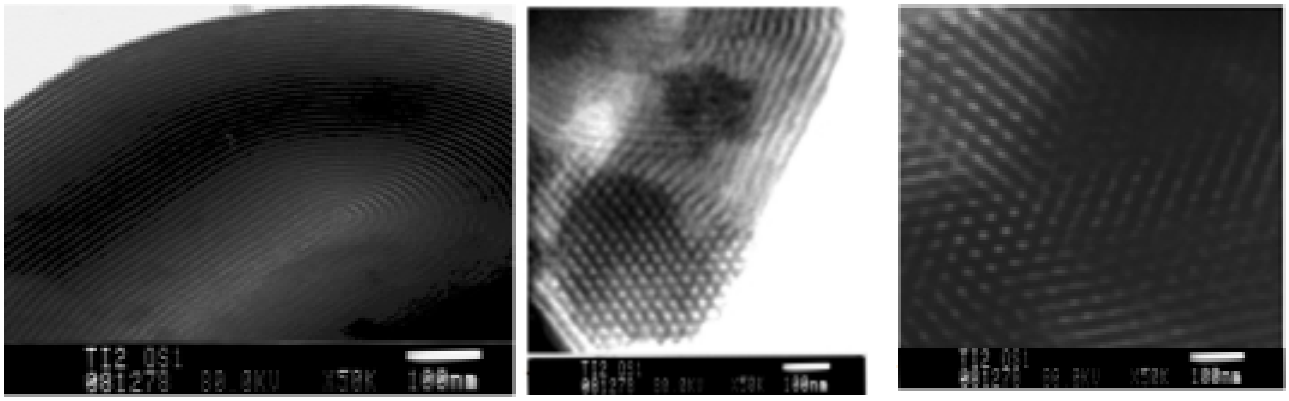


Fig. 5. TEM micrographs of a SBA-15 sample. Magnifications for all samples are x.

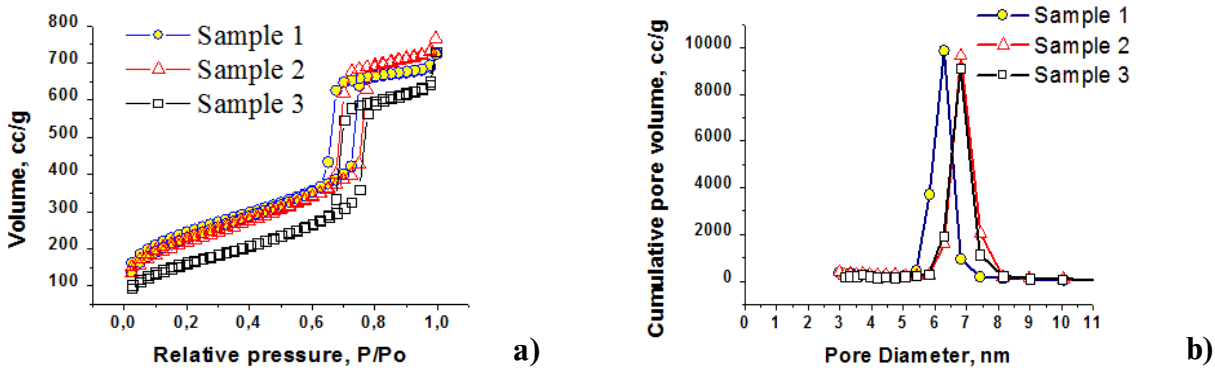


Fig. 6. Nitrogen adsorption-desorption isotherms (a) and pore size distributions (b) of SBA-15.

by the nanoparticles, which could not move any more. At TiO_2 concentration from 5 to10 $\%_{mass}$ the specific surface area and pore size are large enough so that the TiO_2 nanoparticles can move easily from one place to another. In these cases both the porous surface and the pores inside are an appropriate hosts for the TiO_2 nanoparticles, which could shift freely. Based on these results it follows that the TiO_2 content between 5 and 10 $\%_{mass}$ is suitable to be used for SBA-15 impregnation to obtain nanoporous catalytically active Ti-SBA-15 materials for DME catalysts.

Fig. 7 shows thechanges, respectively, of the pore diameter (a), pore volume (b) and specific surface area (c) of Ti/SBA-15 vs. different $\%_{mass}$ TiO_2.

Fig. 8 demonstrates the pore size distribution in the Ti-SBA-15 samples prepared with different content of TiO_2 after calcination at 500°C.

The nanostructure of the Ti -SBA-15 represents a set of stretched in one direction hexagonal channels with a cross section of about 8 nm and wall thickness of about 4 nm. The TiO_2 nanoparticles have an average size of about 4 to 8 nm.

CONCLUSIONS

Mesoporous silica SBA-15 has been synthesized using a mixture of polyethylene glycol P123, 2M HCl, tetraethyloxysilane TEOS and H_2O. The XRD analysis has proved that the synthesized SBA-15 samples are in an amorphous state. The SEM images have shown the surface morphology and nanoporous structure of the obtained samples. The FTIR study has establish the creation of Si-O and Si-OH bonds on the SBA-15 sample surface. Both the XRD and FT-IR spectroscopy inves-

Table 2. Results from the BET analysis of the SBA-15.

	Sample 1	Sample 2	Sample 3
Specific surface area, m^2/g	606	601	522
Pore size, nm	6.3	6.8	6.8
Pore volume, cc/g	0.992	1.079	1.097

Table 3. Results from BET analysis of Ti/ SBA-15 obtained at different TiO_2 content

Parameters	Content of TiO_2, wt.%					
	0	1	5	10	15	25
Specific surface area, m^2/g	601	591.2	550.12	539.4	528.4	520.8
Pore size, nm	6.8	6.8	6.8	5.8	5.8	4.7
Pore volume cc/g	1.079	1.064	0.977	0.900	0.850	0.750

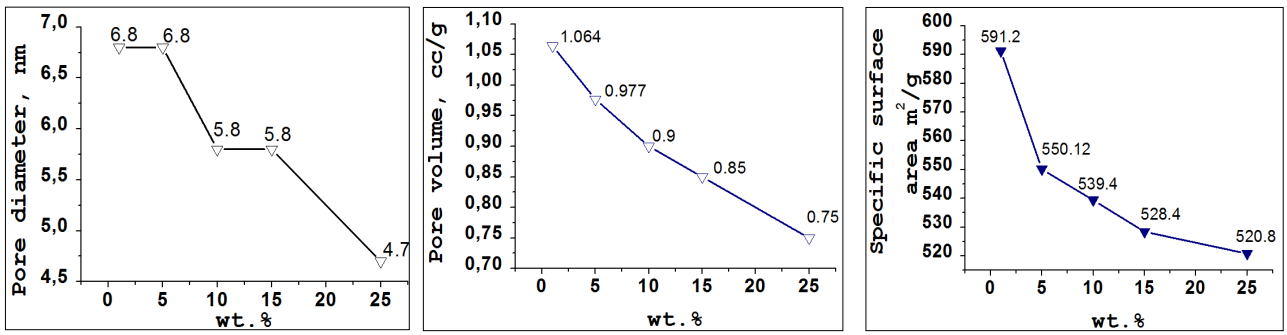
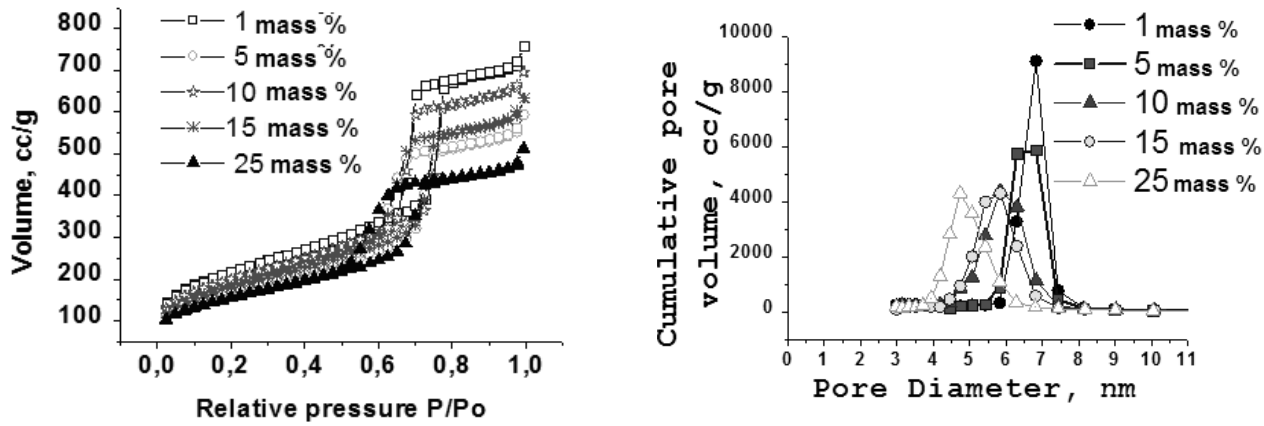


Fig. 7. Changes of the pore diameter (a), pore volume (b) and specific surface area (c) vs. mass % TiO_2.



a) b)

Fig. 8. Changes of the pore volume and BJH pore size distribution in the T-SBA-15 samples prepared with different content of TiO_2 after calcinations at 500°C.

tigations have proved the reproducibility of the method used for the synthesis.

Ti-SBA-15 has been prepared through impregnation of SBA-15 with a solution of titanium isopropoxide in isopropanol with different concentrations. The specific surface area, SSA m^2/g, measured by BET method has proved that the TiO_2 nanoparticles are located on the surface and inside of the nanostructured pores in the case of TiO_2 content from 5 to 10 $\%_{mass}$. The thus prepared Ti-SBA-15 nanoporous samples having a high specific surface area and large hexagonal channels can be an appropriate material for DME catalysts.

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