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# Efficient solid acid catalysts based on sulfated tin oxides for liquid phase esterification of levulinic acid with ethanol



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#### ABSTRACT

Tin oxide nanomaterials prepared by hydrothermal synthesis at 100 °C or 140 °C with or without template and further calcination step were modified with sulfate groups by post synthesis treatment. The catalysts were characterized by X-ray powder diffraction (XRD), N2 physisorption, UV Vis spectroscopy, TG analysis, XPS and solid state NMR spectroscopy. The acidity of the materials was characterized by temperature programmed desorption (TPD) of ammonia. The catalytic performance of nanosized SnO<sub>2</sub> catalysts and their sulfated analogues was studied in levulinic acid (LA) esterification with ethanol. Sulfated materials show significantly higher activity compared to non-sulfated ones. It was found that the synthesis parameters (temperature, template) for preparation of the parent SnO<sub>2</sub> nanoparticles influence significantly their textural properties and have a pronounced effect on the structural characteristics of the obtained sulfated tin oxide based materials and their catalytic performance in levulinic acid esterification. Skipping the calcination step during the preparation of parent SnO<sub>2</sub> samples synthesized without template resulted in the formation of new, highly crystalline phase based on hydrated tin(IV) sulfate [Sn(SO<sub>4</sub>)<sub>2</sub>.xH<sub>2</sub>O], tin(IV) bisulfate [Sn(HSO<sub>4</sub>)<sub>4</sub>.xH<sub>2</sub>O] and/or tin(IV) pyrosulfate [Sn(S<sub>2</sub>O<sub>7</sub>).xH<sub>2</sub>O] species in the sulfated nanomaterials with superior catalytic performance. The formation of this new and catalytically very active phase not reported so far in the literature for sulfated tin oxidebased materials is discussed. The catalytically active sites for esterification of levulinic acid with ethanol is suggested to result from the formation of strong Brønsted and Lewis acid sites with high density in the newly registered phase. The results indicate that the chemical structure and catalytic performance of the obtained sulfated tin oxide based materials strongly depend on the treatment of the SnO<sub>2</sub> nanoparticles before the sulfation procedure.

#### 1. Introduction

In the recent years, lignocellulosic biomass has been intensively studied for production of chemicals, fuels and energy. Levulinic acid and its esters are promising platform chemicals for the production of a broad range of sources for the biofuel, polymer and fine chemicals industry [1–5]. Levulinic acid (LA) is generally produced by the acid-catalyzed hydrolysis of cellulose, and can be converted into levulinate esters,  $\gamma$ -valerolactone, 1,4-pentanediol and 5-nonanone (via pentanoic acid) as well as diphenolic acid as an intermediate for the synthesis of epoxy resins and poly-carbonates [6–20]. Levulinate esters are also

valuble compounds that can be used as fuel additives, solvents and plasticizers. In particular, ethyl levulinate can directly be used up to 5 wt. % as a diesel-miscible biofuel in regular diesel car engines without modification because of its physicochemical properties similar to those of fatty acid methyl esters (FAME), i.e., biodiesel [6]. Therefore ethyl levulinate has the potential to decrease the consumption of petroleum-derived fossil fuels. Generally, levulinate esters are produced by ester-ification reactions using mineral acids such as HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>, resulting in the high yield of the corresponding products within a short reaction time. However, in such homogeneously catalyzed reactions, the acid catalysts are unrecyclable and often lead to technological

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problems, e.g., use of a large volume of base for neutralization and corrosion of equipment. The replacement of homogeneously catalyzed reactions with heterogeneously catalyzed analogues in which the catalysts are easily separable and reusable is thus highly desirable [20-30]. In comparison to zeolites, over sulfated metal oxide, e.g., SO4<sup>2-</sup>/Nb2O5, SO4<sup>2-</sup>/TiO2, SO4<sup>2-</sup>/SnO2, as catalysts higher conversions (up to 44% conversion on  $SO_4^{2-}/SnO_2$  at 70 °C) in the levulinic acid esterification is registered due to the presence of stronger acid sites. The acid site strength of  $SO_4^{2-}/SnO_2$  is reported to be higher than that of  $SO_4^{2-}/ZrO_2$  [2]. The increase in the surface acidity strength of the modified oxides leads to the raise in activity of the catalyst. The acidity generated by modification of SnO<sub>2</sub> with sulfate anions is even stronger than pure sulfuric acid. Thus it can be consider as super acid catalysts for many commercially important reactions, such as hydrocracking of paraffins, dehydration of alcohols, esterification, alkylation of olefins and protection of aldehydes, ketones and alcohols and olefins [31]. However, a detailed explanation on the nature of the active acid sites (Brønsted and Lewis) and the mechanism of their formation is still missing.

Different procedures are suggested in the literature for the preparation of sulfated tin oxide with strong acid sites. H. Miyazaki et al. [32] reported the preparation of a highly active sulfated tin oxide from tin oxide gel, precipitated by the hydrolysis of SnCl<sub>4</sub>. A. A. Dabbawala et al. [33] revealed the role of different sulfur content (1–8 wt%) during thermal decomposition of stannous sulfate during the preparation of sulfated tin oxides]. The sulfation procedure was carried out by impregnation of tin(IV) hydroxide with 0.5 M sulfuric acid resulting in the preservation of tin(IV) oxide tetragonal phase, decrease of the crystallite size and increase in the specific surface area. The effect of sulfate content and calcination temperature on the structure, acidity and catalytic activity of tin oxide was studied by A.S. Khder et al. [34] as well. They found that the sulfation enhances the concentration of Brønsted acid sitesand increases the strength of Lewis acidity when 20 wt.%  $SO_4^{2-}$  groups are applied and calcination is carried out at 550 °C.

In the already published papers the SnO<sub>2</sub> phase detected in sulphated materials showed similar crystalline properties to the parent SnO<sub>2</sub> materials thus suggesting that the sulfation procedures affected only surface of SnO<sub>2</sub> nanoparticles while their bulk structure remained unchanged. The increased catalytic activity of the sulfated tin oxides is considered to be a result of the formation of  $SO_4^{2-}/SnO_2$  chelate structures of different coordination modes between  ${\rm SO_4}^{2-}$  and  ${\rm SnO_2}$ which is associated with an increased concentration of Brønsted and Lewis acid sites. However the problem related to the low stability in liquid phase reactions and the considerable leaching of the active phase of surface  $SO_4^{2-}/SnO_2$  species during the catalytic experiments which is more pronounced in comparison to  $SO_4^{2-}/ZrO_2$  remains a major challenge [2,35,36]. Despite the strong acidity of the sulfated metal oxides their application is limited due to the leaching of sulfate groups during the reaction which is the most important drawback of this type of catalysts [33,34]. Moreover, to the best of our knowledge the exact chemical and structural nature of the active sites in sulfated tin oxide nanoparticles are still not fully clarified in the literature.

In the present study, a series of sulfated tin oxide based catalysts and their catalytic activity in the esterification of levulinic acid with ethanol were studied. We used different approaches to prepare active sulfated species in tin oxide based nanomaterials and to stabilize them on the support during the catalytic reaction. The parent  $SnO_2$  materials were synthesized by hydrothermal treatment with or without further calcination step and in the presence or absence of a template. The influence of the textural and morphological properties of the parent  $SnO_2$  prepared under different synthesis conditions on the properties of the sulfated  $SnO_2$  based catalysts was investigated.

#### 2. Experimental part

#### 2.1. Synthesis of nanosized SnO<sub>2</sub> materials

Nanosized SnO<sub>2</sub> samples were synthesized by precipitation of SnCl<sub>4</sub> solution with 20% NH<sub>4</sub>OH in the presence or absence of template followed by hydrothermal treatment. In a typical preparation, N-hexadecyl-N,N,N-trimethylammoniumbromide (12.0 g) was dissolved in 100 ml distilled water. To this solution was added slowly and under vigorous stirring a second solution of SnCl<sub>4</sub> (7.60 g) in 50 ml distilled water. Then the temperature was raised to 50 °C and stirred for 30 min before adding dropwise 40 ml NH<sub>3</sub> (12.5%). The resulting mixture was stirred overnight at 50 °C. Then it was transferred into an autoclave and treated at 100 °C or 140 °C for 24 h. The hydrothermal treatment was followed by filtration of the solution and washing with distilled water, then drying at room temperature was applied. Some of the samples were calcined up to 500 °C with a ramp of 1° per minute and a swelling time of 15 h at the final temperature. In the case of template-free samples the SnCl<sub>4</sub> (7.60 g) was added to 100 ml distilled water instead of 50 ml.

#### 2.2. Functionalization of nanosized $SnO_2$ by $SO_4^{2-}$ groups

Nanosized SnO<sub>2</sub> samples were mixed with 10% wt. H<sub>2</sub>SO<sub>4</sub> solution (40 ml/1 g SnO<sub>2</sub>). The suspension was dried at ambient temperature and calcined at 300 °C for 3 h. The samples after sulfation are denoted as  $SO_4^{2-}/SnO_2(x)(y)$  or  $SO_4^{2-}/SnO_2(x)T(y)$ , where x is temperature of hydrothermal synthesis; y is the calcination temperature and T indicates the use of template during the synthesis.

#### 2.3. Characterization

Powder X-ray diffraction (XRD) patterns were collected within the range of  $10-80^{\circ}$  20 with a constant step of  $0.02^{\circ}$  20 and counting time of 1 s/step on Bruker D8 Advance diffractometer equipped with Cu K $\alpha$  radiation and LynxEye detector. Mean crystallite sizes were determined by the Topas-4.2 software package using the Laue formula for the integral breadth (IB) of the diffraction peaks and fundamental parameters peak shape description for the instrumental broadening and diffractometer geometry.

Nitrogen physisorption measurements were carried out at -196 °C using Tristar 3000 Micromeritics volumetric adsorption analyzer. Before the analysis, the samples were outgassed under high vacuum for 2 h at 250 °C. The pore-size distributions were calculated from the desorption isotherms by the BJH method.

Ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD) was carried out using a Micromeritics 2920 Autochem II Chemisorption Analyser. The catalyst was pre-treated at 500 °C (at 300 °C for  $SO_4^{2-}$ /SnO<sub>2</sub>(100) and  $SO_4^{2-}$ /SnO<sub>2</sub>(140)) under the stream of helium for 60 min. Then the temperature was decreased to 80 °C. A mixture of 9.8% NH<sub>3</sub> in He was passed over the catalyst at a flow rate of 25 mL/min for 60 min. The excess NH<sub>3</sub> was removed by purging with helium for 25 min. The temperature was then raised gradually to 900 °C by ramping at 10 °C/min under the flow of helium and desorption data were recorded. The TCD signals were calibrated using various gas concentrations of NH<sub>3</sub> ranging from 0 to 10 wt. % NH<sub>3</sub> in He. The desorbed amount of NH<sub>3</sub> was determined continuously in a thermal conductivity cell and by absorption in a trap containing 0.05 M H<sub>2</sub>S0<sub>4</sub> followed by titration with 0.05 M NaOH solution.

The surface chemical composition of selected samples was analyzed by X-ray photoelectron spectroscopy (XPS). The measurements were carried out on AXIS Supra electron spectrometer (Kratos Analitycal Ltd.) using monochromatic Al Ka radiation with photon energy of 1486.6 eV. The energy calibration was performed by normalizing the C1s line of adsorbed adventitious hydrocarbons to 284.6 eV. The binding energies (BE) were determined with an accuracy of  $\pm$  0.1 eV.



Fig. 1. XRD patterns of the obtained initial (A) and sulfated (B) SnO<sub>2</sub> samples.

The chemical composition of the samples was determined monitoring the areas and binding energies of O1s, Sn3d and S2p photoelectron peaks. Using the commercial data-processing software of Kratos Analytical Ltd., the concentrations of the different chemical elements (in at.%) were calculated by normalizing the areas of the photoelectron peaks to their relative sensitivity factors.

The bulk chemical analysis was performed by classical chemical methods. Hydrogen and tin content were defined by the speed method for determination of compounds containing carbon, hydrogen and one metal component, while sulfur content was determined by oxygen pyrophoric incineration method. The oxygen content was calculated as the difference to 100%.

SEM images and elemental analyses were made by a JEOL-JSM-6390 scanning electron microscope equipped with package (standardless method) of Oxford Instruments. Spectra collecting conditions: accelerating voltage – EDS with (Li, Si) detector. The characteristic X-Ray spectra were analyzed with the INCA software 20 KV, integral mode of spectra collection, current-50 spot size and collecting time 300 s.

 $^{119}$ Sn solid state NMR spectra of precursor SnO<sub>2</sub> samples were recorded on a Bruker Avance II + 600 NMR spectrometer operating at 600.01 MHz  $^{1}$ H frequency (223.75 MHz for  $^{119}$ Sn), using 4 mm solid state CP/MAS  $^{1}$ H/X dual probehead. The samples were loaded in 4 mm zirconia rotors and spun at magic angle spinning (MAS) rates of 14 and 11 kHz to identify the isotropic chemical shift values. NMR spectra were measured with single-pulse sequence, 16 K time domain data points, spectrum width of 2000 ppm, 6000 scans and a recycle delay of 5 s. The spectra were referenced with respect to neat SnCl<sub>4</sub> (isotropic chemical shift -145 ppm). Exponential window function was applied (line broadening factor 100) prior to Fourier transformation.

 $^{119}$ Sn solid state NMR spectra of sulfated samples were recorded on a Varian VNMRS spectrometer operating at 599.53 MHz  $^{1}$ H frequency (223.40 MHz for  $^{119}$ Sn), using 3.2 mm solid state CP/MAS  $^{1}$ H/X probehead. The samples were loaded in 3.2 mm zirconia rotors and spun at MAS rates of 20 kHz. The spectra were measured with single-pulse and Hahn-echo sequences, with 90- and 180-degree pulses of 1.9  $\mu$ s and 3.8  $\mu$ s, respectively. In the echo experiments the delay between the two

pulses was equal to one sample-rotation period ( $50 \mu s$ ). During acquisition high-power XiX proton decoupling was applied. Recycle delay between consecutive scans was 80 s, and numbers of scans ranged between 800 and 4200 for different samples. The spectra were referenced with respect to neat SnCl<sub>4</sub> (isotropic chemical shift -145 ppm).

FT-IR experiments were performed with Nicolet Compact 640 spectrometer by the self-supported wafer technique with pyridine (Py) (7 mbar) as probe molecule. Self-supported pellets ( $10 \times 20$  mm) were pressed from the samples, placed into the IR cell, heated up to 350 °C in high vacuum (10-6 mbar) with a rate of 10 °C/min and dehydrated for 1 h. Following 30 min contact with Py at 100 °C the sample was evacuated subsequently at 100, 200 and 300 °C, for 30 min. After each evacuation step a spectrum was recorded at IR beam temperature with a resolution of  $2 \text{ cm}^{-1}$ . The spectra were normalized to  $15 \text{ mg/cm}^2$  weight of the wafers for comparison.

#### 2.4. Catalytic experiments

Prior to the catalytic experiments the samples were pre-treated exsitu in oven for 1 h at 140 °C at static conditions. In a typical experiment, the reactor was charged with 1 g LA (Sigma-Aldrich, 98%), 7 ml etannol (Sigma-Aldrich,  $\geq$  99.8%) and 0.050 g powder catalyst (2.5 wt. % catalyst/LA) while the LA/ethanol weight ratio was maintained 1:5. The reactor was placed in an oil bath, heated under stirring with 200 rpm at the reaction temperature of 70 °C for 7 h. The thermocouple was positioned in the reaction mixture for accurate measurement of the reaction temperature. Samples were taken every hour from the reaction mixture starting from 1 h reaction time and analyzed using HP-GC with a WCOT FUSED SILICA  $25\,m\times0.25\,mm$  COATING CP-SIL 43CB column. The catalytic activity of all the studied samples in 7 h reaction time was represented as levulinic acid conversion (%) and TOF (calculated using the amount of the acid sites obtained by the TPD of NH<sub>3</sub> versus reaction time). The applied mass balance was based on C-containing products and reactants.

#### 3. Results and discussion

#### 3.1. Powder X-ray diffraction (XRD)

XRD data of all parent nanosized tin oxide samples show reflections typical of tetragonal SnO<sub>2</sub> phase, i.e. cassiterite, identified by PDF#41-1445 (Fig. 1A). In the case of hydrothermally treated samples (100 °C and 140 °C) without further calcination step, the reflections are much broader due to the formed very small tin oxide crystallites (2–3 nm). XRD data also support that their crystalline morphology is not well defined, and the presence of an amorphous phase cannot be excluded. In contrast, the hydrothermally treated SnO<sub>2</sub> samples calcined at 500 °C (SnO<sub>2</sub>(100)T(500), SnO<sub>2</sub>(140)T(500), SnO<sub>2</sub>(100)(500) and SnO<sub>2</sub>(140) (500)) are characterized by well-defined crystallites of about 10 nm. It can be also observed that the application of template does not influence significantly the size of the crystallites (Fig. 1A).

After treatment with sulfuric acid all samples were calcined at 300 °C (Fig. 1B). No observable differences in the XRD patterns of the SO4<sup>2-</sup>/SnO2(100)T(500) and SO4<sup>2-</sup>/SnO2(140)T(500) samples in comparison to their non-sulfated analogues was detected. This indicates that the sulfuric acid does not substantially change the already well crystallized tin dioxide phase formed in the presence of the template. However, powder diffraction patterns of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100)(500) and SO4<sup>2-</sup>/SnO2(140)(500) samples synthesized without template show additional reflections indicating the appearance of a new crystalline phase, the latter being better defined for  $SO_4/SnO_2(140)(500)$  (Fig. 1B). However, very substantial changes with the initial tin dioxide phase occurred during the sulfuric acid treatment of the hydrothermally obtained and non-calcined samples SO422/SnO2(100) and SO422/ SnO<sub>2</sub>(140) (Fig. 1B). The peaks corresponding to the finely dispersed tin dioxide disappeared completely at the expense of the appearance of a well crystallized new phase with layered-type organization. These results demonstrate that during the treatment with sulfuric acid, the very small tin dioxide crystallites (around 2-3 nm) undergo complete transformation into this new, very well defined crystalline phase (Fig. 1B). Detailed examination of the powder diffraction data showed that this pattern could not be assigned to any known phase in the database ICDD-PDF-2(2014). The preliminary analysis showed that the pattern seems to be comprised of only one phase without presence of any other known tin-containing phases. Indexing procedure of powder diffraction pattern of the new phase resulted in monoclinic lattice containing most probably pyrosulfate type species. This crystal phase is characterized by unit cell parameters of a = 16.914 Å, b = 10.127 Å, c = 12.167 Å and  $\beta = 91.08^{\circ}$ , and a unit cell volume that exceeds 2000 Å3. To perform crystal structure determination from powder diffraction data, a complete knowledge about the exact composition and formula unit of the phase is crucial for building the initial structure model.

Table 1			
Element distribution	from	SEM-EDX	analysis.

Samples	Element distribution, at. %		
	0	S	Sn
SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> (100) SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> (100)(500) – agglomerates of small particles SO <sub>4</sub> <sup>2-</sup> /SnO <sub>2</sub> (100)(500) – new phase with large crystallites	84.88 67.13 80.77	9.49 3.12 12.28	5.62 29.75 6.95

In order to get more information about the chemical composition of this new phase, SEM-EDX and XPS analyses (Figs. 2, S1) were performed in combination with TG experiments of the selected sample.

## 3.2. Scanning electron microscopy/energy X-Ray spectroscopy (SEM/EDX) and X-Ray photoelectron spectroscopy (XPS) analysis

The SEM images of  $SO_4^{2-}/SnO_2(100)$  showed that the new phase mentioned above consists of randomly distributed well shaped big rodlike particles (Fig. 2A). The SEM-EDX analysis gives the following chemical composition of this material: O – 84.9 at.%, S – 9.5 at.%, Sn 5.6 at.% (Table 1). Thus the S:Sn molar ratio in the new crystalline phase of  $SO_4^{2-}/SnO_2(100)$  sample is 1.7:1 which implies that approximately one Sn atom shares two  $SO_4$  moieties.

SEM images of  $SO_4^{2-}/SnO_2(100)(500)$  sample show the presence of two phases – a main phase consisting of large irregular aggregates composed of smaller (~8 nm) particles, and a second phase representing regions with the new crystalline phase (Fig. 2B). The SEM-EDS analyses show that the aggregates and the new phase with the large crystallites have different element composition (Table 1). The sulfur content of the aggregates in the main phase is very low with S:Sn molar ratio of 1:10 (3.1 at. % S and 29.8 at. % Sn) while in the regions of the new phase the S:Sn molar ratio corresponds to 1.8:1. The letter value is practically identical with that of determined for the  $SO_4/SnO_2(100)$ sample where only the new phase is present. This result leads us to the conclusion that the new phase could be present in all acid treated samples. However, its formation and crystallization was strongly favoured in the sulfated materials obtained from non-calcined hydrated SnO<sub>2</sub> samples, where some residual water can be preserved.

The chemical analysis of  $SO_4^{2-}/SnO_2(100)$  shows the following bulk element distribution: H – 2.7 at. %; S – 13.1 at. %, Sn – 6.4 at.%, O – 77.8 at.%. The performed bulk chemical analysis of  $SO_4^{2-}/SnO_2(100)$  shows similar chemical composition of this material to that obtained by SEM-EDS analysis.

The surface chemical composition of  $SO_4^{2-}/SnO_2(100)$  sample was studied by XPS analysis (Figure S1). The registered binding energy



Fig. 2. SEM images of  $SO_4^{2-}/SnO_2(100)$  (A) and  $SO_4^{2-}/SnO_2(100)(500)$  (B).



Fig. 3. TG (A), DTG (B) analysis of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100) and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub> (100)(500) samples and TG-DTA (C) analysis of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100) sample.

peaks of Sn3d3/2 (496 eV) and 3d5/2 (487.6 eV) should be assigned to Sn(IV) bonded to oxygen atoms in tetrahedral or octahedral environments [37]. The Ols peak centred at around 532.0 eV can be attributed to oxygen atoms in coordinated water, OH and/or sulfate groups. The S2p peak centred at 169.2 eV is characteristic for S connected to Sn species *via* oxygen bridges. The surface composition determined by the XPS analysis was: S – 15.4 at.%, Sn – 8.2 at.% and O – 76.4 at.% and the calculated S:Sn molar ratio is 1.9:1. Thus, the XPS data support the results about the chemical composition and S:Sn molar ratio of the newly formed phase determined by SEM-EDX agrees with that of the bulk chemical analysis.

#### 3.3. Thermogravimetric analysis

TG data show significantly higher weight loss for  $SO_4^{2-}/SnO_2(100)$  compared to  $SO_4^{2-}/SnO_2(100)(500)$  during heating of the samples in air up to 600 °C (Fig. 3A). Three well defined weight loss effects were found for both samples (Fig. 3B). The first one up to 160 °C can be assigned to physisorbed water. With further temperature increase (160–300 °C) a second step appeared that can be attributed to the release of the bound water. The third weight loss observed between 300 °C and 600 °C corresponds to the decomposition of the loaded sulfate groups [38]. The obtained results confirm the much higher amount of sulfate groups loaded in the  $SO_4^{2-}/SnO_2(100)$  sample due to the complete transformation of the initial finely dispersed  $SnO_2$  into the new sulfate containing phase in comparison with the  $SO_4^{2-}/SnO_2(100)$  (500) sample where only small regions with sulfur enriched crystalline phase were found by SEM analysis (Fig. 3B).

In order to confirm the presence of water and to follow more precisely its release with increasing temperature, we performed TG-DTA experiment in air up to 600 °C for  $SO_4^{2-}/SnO_2(100)$  sample (Fig. 3C). The results confirmed that the observed two, low-temperature weight loss steps are due to water release. In addition, TG-DTA results evidence that water is released even over 430 °C. This indicates, that also OH groups can be found in the structure, connected to the oxide phase, beside the presence of a high amount (about 10 wt. %) of bound water molecules.

#### 3.4. The textural properties

The textural parameters from nitrogen adsorption/desorption isotherms of the parent and sulfated tin oxide samples are listed in Table 2. The isotherms are of IV type (not shown), characteristic of mesoporous materials, and similar to those usually found in inorganic oxides synthesized by the hard-templating route [24–26]. The data demonstrate

Table 2	
Specific surface area S	nore volum

Specific surface area  $S_{\text{BET}},$  pore volume and pore diameter and particle sizes of the studied samples.

Samples	S <sub>BET</sub> , (m <sup>2</sup> /g)	Pore volume, (cm <sup>3</sup> /g)	Pore diameter, (nm)	Particle size, (nm)
SnO <sub>2</sub> (100)	180	0.30	4.1	2.8
$SO_4^{2-}/SnO_2(100)$	160	0.20	4.0	76.7
SnO <sub>2</sub> (140)	160	0.22	4.2	3.4
SO4 <sup>2-</sup> /SnO2(140)	120	0.18	4.0	57.0
SnO <sub>2</sub> (100)(500)	150	0.20	5.3	10.6
SO4 <sup>2-</sup> /SnO2(100)(500)	90	0.13	4.6	8.9
SnO <sub>2</sub> (140)(500)	130	0.19	5.1	8.3
SO4 <sup>2-</sup> /SnO2(140)(500)	100	0.15	4.5	7.9
SnO <sub>2</sub> (100)T(500)	220	0.36	5.2	9.1
$SO_4^{2-}/$ SnO <sub>2</sub> (100)T(500)	100	0.19	4.6	7.9
SnO <sub>2</sub> (140)T(500)	190	0.30	5.4	8.8
$SO_4^{2-}/SnO_2(140)T(500)$	90	0.14	4.9	7.5

that among the non-sulfated materials the samples prepared with the use of template show the highest specific surface area (190–220 m<sup>2</sup>/g) and pore volume (0.30–0.36 cm<sup>3</sup>/g). It was observed also that in all cases the increase of the temperature of hydrothermal treatment from 100 °C to 140 °C resulted in decrease in the surface area and pore volume. The calcined samples synthesized without template show the lowest surface area (90–100 m<sup>2</sup>/g) and pore volume (0.13–0.15 cm<sup>3</sup>/g).

Sulfation procedure followed by thermal treatment at 300 °C resulted in a significant change of the textural properties of all samples. Their specific surface area as well as pore volume and the pore sizes decreased. This effect is more pronounced for the calcined samples and particularly for the samples prepared with the template  $(SO_4^{2^-}/SnO_2(100)T(500))$  and  $(SO_4^{2^-}/SnO_2(140)T(500)))$  where a decrease of around 50% was observed. Therefore the role of the template in sulfated materials obtained from calcined precursor  $SnO_2$  is negligible since after the sulfation their surfaces area and pore volume are practically identical. The highest surface area, pore volume and pore sizes were detected for the sulfated samples obtained from the non-calcined parent  $SnO_2$  samples  $(SO_4^{2^-}/SnO_2(100))$  and  $SO_4^{2^-}/SnO_2(140))$ . Thus we can conclude that the applied mild conditions for the synthesis of the parent  $SnO_2$  samples resulted in preparation of sulfated materials with advantageous textural parameters.

#### Table 3

Concentration and surface density of acid sites and calculated TOF of the studied samples.

Samples	Amount of NH <sub>3</sub> desorbed, (mmol/g)	Surface density of acid sites, mmol/ $m^2$	TOF, h <sup>-1</sup>
SnO <sub>2</sub> (100)	2.2	0.012	0.62
$SO_4^{2-}/SnO_2(100)$	19.5	0.122	3.73
SnO <sub>2</sub> (140)	2.3	0.014	0.60
$SO_4^{2-}/SnO_2(140)$	21.8	0.182	3.44
SnO <sub>2</sub> (100)(500)	2.4	0.023	0.58
SO4 <sup>2-</sup> /SnO2(100)(500)	4.9	0.054	6.11
SnO <sub>2</sub> (140)(500)	2.1	0.016	0.60
SO4 <sup>2-</sup> /SnO2(140)(500)	5.8	0.058	5.40
SnO <sub>2</sub> (100)T(500)	2.3	0.010	0.58
SO4 <sup>2-</sup> /SnO2(100)T(500)	10.5	0.105	3.00
SnO <sub>2</sub> (140)T(500)	1.8	0.004	0.65
SO4 <sup>2-</sup> /SnO2(140)T(500)	8.4	0.093	3.00

## 3.5. Acidity characterizations by ammonia TPD experiments and FT-IR of adsorbed pyridine

Ammonia TPD measurements were performed for the determination of the amount and the strength of the acid sites of the parent and the sulfated materials. The calculated amounts of desorbed ammonia which correspond to the acid sites in the samples are listed in Table 1. All nonsulfated samples show significantly lower concentration of acid sites in comparison to their sulfated analogs. We suggest that the parent SnO<sub>2</sub> materials contain mainly physisorbed and/or weakly coordinated surface water molecules. During the thermal pre-treatment of the samples in the TPD experiment the weakly coordinated water molecules acting as Brønsted acid sites were removed and thus only Lewis acid sites, i.e., unsaturated Sn ions, remain in the parent SnO<sub>2</sub> materials. In the calcined samples due to their very well-defined crystalline structure the amount of the Lewis acid sites is generally low. This explains the dramatically low concentration of acid sites measured by the ammonia TPD (Table 3).

Two peaks with different intensities were detected for all sulfated

samples, the first is in the interval 400–600 °C and the second one is in the 600–800 °C temperature interval (Fig. 4), the former being more intensive. They can be associated with the formation of moderate and strong acidic sites, respectively. Although the TPD method does not allow discrimination between Brønsted and Lewis acid sites we suggest that both types of acid centres are present in the sulfated materials. Our previous experience showed that the formation of strong Brønsted acid sites that are essential for the studied catalytic reaction is usually associated with a peak over 500 °C in the TPD of ammonia [39].

The TPD curves of  $SO_4^{2-}/SnO_2(100)$  and  $SO_4^{2-}/SnO_2(140)$  samples, presented in Fig. 4A, show that the amount of desorbed ammonia is ten times higher in comparison to all other samples. This implies that the amount of acid sites with moderate and strong acidity in the  $SO_4^{2-}/SnO_2(100)$  and  $SO_4^{2-}/SnO_2(140)$  samples is significantly higher. Formation of such high amount of acid sites can be explained by the inclusion of water molecules in the new crystalline phase. This suggestion is in agreement with the trend observed for the acidity of the calcined samples (Fig. 4B). Among these samples the highest acidity was detected for  $SO_4^{2-}/SnO_2(140)(500)$  material, where a small amount of the new crystalline phase was formed within the parent  $SnO_2$ .

The nature of the acidic species i.e. Lewis and Brønsted acid sites in the studied samples was determined by FT-IR spectroscopic investigation of adsorbed pyridine (Py) (Fig. 5). Lewis acid sites can be associated with the ring vibrations of coordinatively bound Py at 1617 and 1458 cm<sup>-1</sup> (Py-L) [40,41]. Only the presence of weak Lewis acid sites is registered on non-sulfated samples (not shown). The FT-IR spectra of sulfated samples contain bands characteristic of both Lewis and Brønsted acid sites (Fig. 5). The protonated Py molecules coordinated to the conjugated base of the solid Brønsted acid (Py-B) exhibit bands at 1540 cm<sup>-1</sup> and 1639 cm<sup>-1</sup>. The FT-IR spectra of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100) and  $SO_4^{2}/SnO_2(140)$  samples show intensive bands at  $1540/1639 \text{ cm}^{-1}$ and at  $1458/1617 \text{ cm}^{-1}$  which is due to the much higher concentration of Brønsted and Lewis acid sites than that of the other samples. These observations are in a good agreement with the results obtained by TPD of desorbed ammonia. FT-IR data of Py desorbed at higher temperature is characteristic for the strength of the acid sites of the samples [41]. It can be seen that the amount of Brønsted and Lewis acid sites decreases



Fig. 4. TPD of adsorbed ammonia on the studied samples.



**Fig. 5.** FT-IR spectra of adsorbed pyridine on sulfated  $SnO_2$  samples. Self-supported pellets were pretreated at 350 °C in vacuum and contacted with Py (7 mbar) for 30 min. Spectra were collected after Py desorption at 100, 200 and 300 °C for 30 min, shown from top to bottom for each sample.

at a higher temperature but this effect is less pronounced for the  $SO_4^{2-}/SnO_2(100)$  and  $SO_4^{2-}/SnO_2(140)$  samples, indicating the presence of stronger Brønsted and Lewis acid sites in them. Investigating the S==O stretching vibration region of the FT-IR spectra, characteristic bands at around 1415 and 1335 cm<sup>-1</sup> can be found for all samples (not shown). According to FT-IR studies of sulfated metal oxides bands appearing over 1400 cm<sup>-1</sup> can be associated with polynuclear, disulfate species, whereas S==O bands at lower frequencies are characteristic of isolated sulfate groups localized on the SnO<sub>2</sub> crystal plates or on the defects sites [42]. After pyridine adsorption only a part of the band at 1424 cm<sup>-1</sup> disappeared and a band at 1416 cm<sup>-1</sup> remained which supports the assumption that part of the SO<sub>4</sub><sup>2-</sup> species are not accessible through pyridine adsorption. In the case of the SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100)(500) and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100)T(500) samples sulfation is incomplete, leading to the formation of weak Brønsted acid sites.

#### 3.6. Solid state NMR spectroscopy

Solid state <sup>119</sup>Sn NMR spectroscopy was applied to gain an insight to the structural characteristics of the precursor SnO<sub>2</sub> and sulfated SnO<sub>2</sub> samples at atomic level. <sup>119</sup>Sn chemical shifts depend on various factors among which the most important are the Sn oxidation state (valence charge density of the tin atom), its coordination number and coordination mode, the chemical environment (the immediate oxygen environment of the Sn atom) and to a lesser extent the arrangement of more distant neighbours around it [43].

#### 3.6.1. Parent SnO<sub>2</sub> samples

Solid state <sup>119</sup>Sn NMR spectra of all non-sulfated SnO<sub>2</sub> samples show similar spectral pattern with a single resonance with isotropic chemical shift centered at around -601 ppm, which is typical for SnO<sub>2</sub> [44]. This chemical shift value clearly proves the formation of pure SnO<sub>2</sub> phase and the absence of any SnO which has a chemical shift at around -200 ppm. Fig. 6 present the <sup>119</sup>Sn NMR spectra of samples SnO<sub>2</sub>(100), SnO<sub>2</sub>(100)(500) and SnO<sub>2</sub>(100)T(500), respectively. Recently Chen et al. [39] demonstrated the presence of different SnO<sub>2</sub> species in SnO<sub>2</sub> nanosheets using <sup>119</sup>Sn solid state NMR (single pulse and <sup>1</sup>H-<sup>119</sup>Sn CP-MAS spectra) in combination with <sup>119</sup>Sn NMR chemical shift DFT calculations. The <sup>119</sup>Sn spectrum of SnO<sub>2</sub>(100) sample (Fig. 6) shows broad resonance at around -601 ppm with two shoulders on both sides of the main peak and is practically identical with the spectrum observed by Chen et al. [44] for the SnO<sub>2</sub> species from different layers of the hydroxylated SnO<sub>2</sub> particles. Thus the main resonance at around -601 ppm (Fig. 6) could be assigned to the 6-coordinated Sn ions (SnO<sub>6</sub>) that are far from the surface within the bulk part of SnO<sub>2</sub> particles. The low-field shoulder at around -584 ppm could be assigned to the hydroxylated tin ions and the Sn ions with adsorbed water molecules from the first surface layer of the SnO<sub>2</sub> particles, while the high field shoulders at around -608 ppm and -629 ppm (Fig. 6) could be assigned to the tin ions from the clean surface of the second layer of the SnO<sub>2</sub> nanoparticles. The observed broad central resonance at around - 601 ppm is also an indication for the small size (2.8 nm, see Table 1) of the SnO<sub>2</sub> nanoparticles in SnO<sub>2</sub>(100) sample, which is in agreement with previous studies showing that the signal width increases as the particles size decreases [45]. Thus we can conclude that samples  $SnO_2(100)$  and  $SnO_2(140)$  obtained by hydrothermal treatment without calcination step represent hydrated tin(IV) oxide (SnO<sub>2</sub>.xH<sub>2</sub>O) which is characterized by small crystallites (2.8–3.6 nm). According to literature data drying of the precursor SnO2.xH2O gel at 110 °C results in formation of hydrated tin(IV) oxide that is rich in water and corresponds to the more reactive  $\alpha$ -form [43].

The <sup>119</sup>Sn NMR spectra of the two calcined samples SnO<sub>2</sub>(100)(500) and SnO<sub>2</sub>(100)T(500) are practically identical showing a central resonance at -604 ppm (Fig. 6). Comparison with the <sup>119</sup>Sn spectrum of the non-calcined sample  $SnO_2(100)$  shows that the overall resonance linewidth in the spectra of the two calcined samples is smaller and the two shoulders on both sides of the main resonance have much lower intensity. We suggest that the calcination at 500°C resulted in partial removal of the adsorbed water molecules and the decrease of the amount of hydroxylated SnO2 species, which explains the lower intensity of the respective resonances in the spectra of the calcined samples. Similar effect upon sample heating was reported also by Chen et al. [44]. The narrowing of the main resonance at -604 ppm observed in the spectra of the SnO<sub>2</sub>(100)(500) and SnO<sub>2</sub>(100)T(500) samples (Fig. 6) is also in agreement with the larger particle size measured for these samples (8.3-10.6 nm, see Table 1) [45]. Thus we suggest that the calcination of the precursor SnO<sub>2</sub>.xH<sub>2</sub>O gel at 500 °C resulted in formation of the inactive β-form which has less bound water [43]. The progressive increase of crystallite size with increasing temperature is also documented in the literature [46].

#### 3.6.2. Sulfated SnO<sub>2</sub> samples

The <sup>119</sup>Sn NMR spectra of samples  $SO_4^{2-}/SnO_2(100)$  and  $SO_4^{2-}/SnO_2(140)$  synthesized by sulfating of  $SnO_2$  precursors obtained without calcination step ( $SnO_2(100)$  and  $SnO_2(140)$ ) show that the



Fig. 6. <sup>119</sup>Sn NMR spectra of the parent SnO<sub>2</sub> samples synthesized at different conditions: SnO<sub>2</sub>(100), SnO<sub>2</sub>(100)(500) and SnO<sub>2</sub>(100)T(500).



Fig. 7.  $^{119}$ Sn NMR spectra of sulfated materials prepared from SnO<sub>2</sub> precursors synthesized at different conditions.

sulfation procedure resulted in disappearance of the signal at -601 ppm and in the appearance of new peaks at -769 ppm and -786 ppm (Fig. 7). To the best of our knowledge these peaks have not been observed so far in the <sup>119</sup>Sn spectra of sulfated SnO<sub>2</sub> and more detailed study is needed to identify their origin and the exact morphology and chemical nature of this new phase. The significant upfield shift of the tin resonance in the <sup>119</sup>Sn spectra of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100) and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(140) samples as compared to the spectra of the non-sulfated precursors (at -601 ppm) and the complete disappearance of the signal at around -600 ppm that is characteristic for SnO<sub>2</sub> implies that upon sulfation the initial SnO<sub>2</sub> phase is fully converted into a new phase with different structural characteristics. The very narrow NMR signals indicate the formation of large crystallites which is also in agreement with the XRD results, showing particle size of 77 nm for SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100) and 57 nm in case of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(140) (see Table 1).

With the aim to give further evidence about the potential formation of layered tin(IV)sulfate (pyrosulfate) based species as suggested by the XRD analysis, we recorded the <sup>119</sup>Sn spectrum of stannic sulfate, which is presented in Fig. S2. It is known that stannic sulfate is unstable and quickly hydrolyses thus the actual sample was the commercially available Sn(SO<sub>4</sub>)<sub>2</sub> sulfuric acid suspension. The <sup>119</sup>Sn spectrum shows two signals at -845 and -879 ppm which similarly to the resonances observed in the spectra of the SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100) SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100) and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(140) samples are shifted –upfield as compared to the chemical shift of the precursor SnO<sub>2</sub> (-601 ppm). We assume that the trend towards high field chemical shift values observed in the <sup>119</sup>Sn spectra of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100) and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(140) samples and of the stannic sulfate supports the plausibility of the proposed structural transformations.

The  $^{119}$ Sn spectra of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100)(500) and SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(140) (500) samples obtained after sulfation of the calcined precursor  $SnO_2$ show spectral pattern with broad resonance at around -598 ppm similarly to their non-sulfated calcined SnO<sub>2</sub> precursors and to the already observed in the literature resonances for sulfated SnO<sub>2</sub> (Fig. 7) [44]. More detailed analyses of the  $^{119}$ Sn spectra of SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100) (500) and  $SO_4^{2-}/SnO_2(140)(500)$  samples obtained after sulfation of the preliminary calcined at 500 °C precursors show that along with the strong broad resonance at around - 598 ppm there are additional broad resonances of very low intensity at around -769 and -816 ppm. These observations indicate that while the predominant phase in these samples (signal at -598 ppm) is similar to the original non-sulfated SnO<sub>2</sub> there is also a small amount that is transformed into the new phase (signals at -769 and -816 ppm). These results are in agreement with the results obtained by XRD and SEM-EDS. The XRD data indicate that along with the reflexes typical for the known SnO<sub>2</sub> phase which are dominant in the spectrum there are also additional signals of lower intensity corresponding to the new unknown phase which are more pronounced in the XRD spectrum of the  $SO_4^{2-}/SnO_2(140)(500)$ sample. SEM images of the  $SO_4^{2-}/SnO_2(100)(500)$  sample also confirm the presence of two phases one main phase consisting of agglomerates of small (~8 nm) particles and a second minor phase representing regions with large crystallites of  $\sim$  70 nm.

The <sup>119</sup>Sn NMR spectra of sulfated tin oxides  $(SO_4^{2-}/SnO_2(100)T(500))$  and  $SO_4^{2-}/SnO_2(140)T(500))$  obtained after sulfation of calcined precursor samples synthesized with the use of template, show only one broad signal at around – 600 ppm. No additional signals indicating the presence of the new phase were observed in the NMR spectra which is in agreement with the XRD spectra showing only the reflections typical for SnO<sub>2</sub> phase. These results indicate that the bulk structural characteristics of the SnO<sub>2</sub> phase in the sulfated SnO<sub>2</sub> samples are preserved and the sulfation most probably leads to only surface modifications of the SnO<sub>2</sub> particles. The lack of significant changes in the <sup>119</sup>Sn NMR spectra of the sulfated materials obtained from calcined at 500°C SnO<sub>2</sub> precursors synthesized with or without the template implies that in these samples there are no strong interactions between the SO<sub>4</sub> groups and the Sn ions and the presence of SO<sub>4</sub> moieties does

not influence significantly the bulk structural characteristics of the original well crystalized  $SnO_2$  phase obtained after calcination.

The surface structure of sulfated  $SnO_2$  and  $ZrO_2$  has been studied by various methods such as XRD, FTIR, XPS however no consensus has been achieved so far and different structures of the active sites have been proposed in the literature [36,47].

The integrated analysis of all structural data implies that the sulfation of the non-calcined and calcined  $SnO_2$  samples leads to different structural transformations of the parent  $SnO_2$  materials and to the formation of different amount of active acid sites (Brønsted and Lewis). A new crystalline phase containing high amount of acid sites is formed on the sulfated non-calcined  $SnO_2$  samples. The determination of the exact chemical composition and structure of this new phase is a subject of an ongoing investigation.

The XRD and NMR results reported here suggest that this new phase is composed of hydrated tin(IV) sulfate [Sn(SO<sub>4</sub>)<sub>2</sub>,xH<sub>2</sub>O], tin(IV) bisulfate [Sn(HSO<sub>4</sub>)<sub>4</sub>.xH<sub>2</sub>O] and/or tin(IV) pyrosulfate [Sn(S<sub>2</sub>O<sub>7</sub>).xH<sub>2</sub>O] based species which represent the main structural motifs of the newly formed highly crystalline phase obtained after drying of the suspension and its further calcination at 300 °C. According to previous studies the formation of these species is highly plausible since the two tin oxide hydrates  $SnO_2(100)$  and  $SnO_2(140)$  represent the reactive  $\alpha$ -form and hence they can interact with sulfuric acid during their impregnation with H<sub>2</sub>SO<sub>4</sub> solution [43]. The very small particle size of these two samples (2.8-3.6 nm) and their not very well defined crystalline morphology also facilitate the interaction of the SnO<sub>2</sub> particles with sulfuric acid. The suggested structural units based on the formation of hydrated tin(IV) sulfate [Sn(SO<sub>4</sub>)<sub>2</sub>.xH<sub>2</sub>O], tin(IV) bisulfate [Sn(HSO<sub>4</sub>)<sub>4</sub>.xH<sub>2</sub>O] and/or tin(IV) pyrosulfate [Sn(S2O7).xH2O] species are presented by Structures I and II in Scheme 1. The increased amount of acid sites in the sulfated non-calcined SnO<sub>2</sub> samples could be explained by the inclusion of coordinated water molecules within the crystalline structure and by the presence of S-OH groups that generate additional Brønsted acid centers, while the presence of unsaturated Sn ions act as Lewis acid sites.

The lower acidity of the sulfated samples obtained from calcined parent tin oxides ( $SnO_2(100)T(500)$ ,  $SO_4^{2-}/SnO_2(140)T(500)$ ,  $SO_4^{2-}/SnO_2(140)T(500)$ ) and  $SO_4^{2-}/SnO_2(140)(500)$ ) is most probably associated with the well-defined crystalline structure of the parent materials which prevents further structural transformations during sulfation. In addition to that according to literature data the non-hydrated beta-form tin oxide is non-reactive and therefore the interaction with the sulfuric acid is not expected. In these samples the active sites formed as a result of sulfation procedure are located on the surface of the tin oxide particles and therefore the structural characteristics of the parent materials are preserved (Scheme 1, Structure III) after sulfation.

#### 3.7. Catalytic activity for levulinic acid with ethanol

The catalytic activity of the sulfated and non-sulfated SnO<sub>2</sub> nanoparticles was studied in the esterification of levulinic acid with ethanol. The only detected products were ethyl levulinate and water. Non-sulfated SnO<sub>2</sub> samples show very low catalytic activity (around 1.5–2% after 6 h of reaction time) (not shown). The sulfation treatment of the Sn-containing samples leads to a significant increase in the catalytic activity resulting in a conversion up to 77% (Fig. 8). The following order of the catalytic activity for the sulfated catalysts was obtained: SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100)  $\cong$  SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(140) > SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(140) (500) > SO<sub>4</sub><sup>2-</sup>/SnO<sub>2</sub>(100)(500) > SO<sub>4</sub><sup>2-</sup>/

 $SnO_2(100)T(500) > SO_4^{2-}/SnO_2(140)T(500)$ . The highest catalytic activity (77%) was observed for the sulfated non-calcined  $SnO_2$  samples, obtained by hydrothermal synthesis at 100 °C and 140 °C without template. This very high activity can be attributed to the formation of the above mentioned new phase, possessing high density of Brønsted acid sites with moderate and high strength generated by the coordinated water molecules and the S–OH groups. It is important to note





Scheme 1. Proposed main structural units in the sulfated SnO<sub>2</sub> obtained without (Structures 1 and 2) and with (Structure 3) calcination step in the preparation of the precursor SnO<sub>2</sub>.



**Fig. 8.** Levulinic acid conversion in the esterification of levulinic acid with ethanol over sulfated  $\text{SnO}_2$  at 70 °C as function of reaction time. Reaction conditions: 0.050 g catalyst (2.5 wt. % catalyst/LA); LA/ethanol weight ratio = 1:5; reaction temperature -70 °C.

that besides the surface density of acid sites, their nature (Brønsted or Lewis) and strength distribution (weak, intermediate, or strong) also play a very important role for the activity of the catalysts. The simultaneous presence of Brønsted and Lewis acid sites is of key importance for the high catalytic activity of the studied sulfated catalysts. Previous investigations show that the presence of Lewis sites such as Sn<sup>+</sup> ions could additionally increase the strength of the Brønsted acid sites due to their synergistic effect [34,48-50]. The proposed reaction mechanism involving participation of both Brønsted and Lewis acid sites for catalytic esterification of levulinic acid with ethanol is presented in Scheme 2. The adsorption of levulinic acid on the Brønsted and Lewis acid sites of the catalyst is the first step which leads to the formation of a protonated levulinic acid intermediate. The nucleophilic oxygen atom from ethanol molecules interacts with the electrophilic carbonyl carbon resulting in the formation of an oxonium ion. Then the loss of water from the oxonium ion, and subsequent deprotonation are the following step in the formation of ester and the regeneration of the Brønsted and Lewis acid sites.

The very low catalytic activity of non-sulfated  $\text{SnO}_2$  materials can be explained with the low concentration of active acid sites as demonstrated by ammonia TPD and FT-IR spectra of adsorbed pyridine. As already discussed due to their crystalline structure these materials contain relatively small amount of mainly Lewis acid sites such as unsaturated Sn ions. Lewis type sites alone are considered to be inactive, but they can have a synergistic effect with the Brønsted acid sites for the esterification of levulinic acid to esters. Recently the synergistic effect



Scheme 2. Proposed reaction mechanism for esterification of levulinic acid with ethanol including the participation of the Brønsted acid sites from the sulfated tin oxides containing the new phase.



**Fig. 9.** Correlations between catalytic activity and surface density of acid sites (A) and specific surface area (B) on the studied samples.

of Brønsted and Lewis acid sites was reported for the catalytic activity of SO<sub>4</sub>/TiO<sub>2</sub> [34,48–50]. A linear correlation between the catalytic activity and surface density of acid sites/specific surface area of the studied samples was found (Fig. 9). The increase of surface density of acid sites leads to an increase of the catalytic activity of the studied samples (Fig. 9A). The highest surface density of acid sites was registered for the  $SO_4^{2-}/SnO_2(100)$  (0.122 mmol/m<sup>2</sup>) and  $SO_4^{2-}/$  $SnO_2(140)$  materials (0.182 mmol/m<sup>2</sup>) which also show the highest catalytic activity. However, the surface density of acid sites is not the only important parameter for the samples' activity in esterification reaction. The increase of the surface area of the samples leads also to an increase of their catalytic activity as could be seen in Fig. 9B. The highest surface area was registered for  $SO_4^{2-}/SnO_2(100)$  (160 m<sup>2</sup>/g) and  $SO_4^{2-}/SnO_2(140)$  samples (180 m<sup>2</sup>/g) (Table 3). This effect can be explained by the increasing of surface exposed Brønsted and Lewis acid sites which can improve the accessibility of organic reactants (LA and

ethanol) to the active acid sites. In our previous paper [55] the  $SO_4^{2^-}/Zr/KIL-2$  materials with textural mesoporosity were developed as highly active catalysts for glycerol esterification with acetic acid due to the enhance of the reactants access to the active acid sites in large pores of KIL-2 support. The  $SO_4^{2^-}/SnO_2(100)$  and  $SO_4^{2^-}/SnO_2(140)$  samples were characterized by the high surface density of sites and specific surface area which could explain their high catalytic activity (Fig. 9B).

The catalytic activity of the samples was recalculated as TOF (Table 3). The obtained results reveal that the  $SO_4^{2-}/SnO_2(100)(500)$  and  $SO_4^{2-}/SnO_2(140)(500)$  samples show higher catalytic activity per acid site. However, higher activity per mass of catalyst was registered on the  $SO_4^{2-}/SnO_2(100)$  and  $SO_4^{2-}/SnO_2(140)$  materials showing the important role of the formation of strong Brønsted and Lewis acid sites with high surface density which is predetermined by the applied synthesis procedure.

Our catalysts show much higher catalytic activity than that of similar solid catalysts studied in levulinic acid esterification with ethanol at the same reaction conditions [6,19,51–55]. D.R. Fernandes et al. [6]

Table 4
Esterification of levulinic acid with ethanol (reaction con
ditions: $T = 70$ °C, ethanol/acid molar ratio of 5:1 an
2.5 wt % of catalyst)

m-1.1. A

Catalysts	LA conversion, %	
Amberlist	54 [6]	
$SO_4^{2-}/ZrO_2$	9 [6]	
$SO_4^{2-}/SnO_2$	44 [6]	
SO4 <sup>2-</sup> /TiO2	39 [6]	
HMCM-22	13.5 [6]	
HUSY	8 [6]	
HBEA	5 [6]	
HMor	3 [6]	
$SO_4^{2-}/Nb_2O_5$	14 [6]	
HZSM-5	5 [6]	
Zr-h-Mordenite	42 [53]	
$SO_4^{2-}/ZrO_2$	80 [54]	
SO4 <sup>2-</sup> /ZrKIL-2	52.5 [55]	
SO42-/SnO2	77 this work	

reported 44% conversion of LA to ester on  $SO_4^{2-}/SnO_2$  at similar reaction conditions. Among the presented catalysts at the same reaction conditions (Table 4) only  $SO_4^{2-}/ZrO_2$  [54] shows slightly higher catalytic activity than the  $SO_4^{2-}/SnO_2$  catalysts developed in the present study.

Besides the catalytic activity, the stability and reusability of the solid catalysts are of particular importance. Based on the published results [2,33,34,36] the reusability of a SO<sub>4</sub>/SnO<sub>2</sub> catalyst is limited because of the high leaching of the active phase, i.e.,  $SO_4^{2-}$ , after the first reaction cycle. Our results show that the new catalytic phase in  $SO_4^{2-}/SnO_2(100)$  and  $SO_4^{2-}/SnO_2(140)$  materials is very stable since we did not observe any leaching after 3 cycles as demonstrated by the XRD and TG data of the spent catalysts. The spent catalysts were characterized by XRD in order to obtain more detailed insight into the catalyst durability. XRD patterns confirmed that the used catalysts remained crystallographically unchanged.

This stability is a result of the inclusion of the active acid sites within the crystalline framework of the new phase, which hampers their leaching during the reaction. The calcined sulfated materials in which the new phase is missing showed lower stability towards leaching. For example about 12% leaching of the active sites was detected for  $SO_4^{2-}/SnO_2(100)T(500)$  sample which is the main reason for the decrease of its catalytic activity by 25%, i.e., 77.0% vs. 57.8% of LA conversion after 7 h, in three reaction cycles.

#### 4. Conclusions

SnO<sub>2</sub> nanomaterials were prepared by hydrothermal synthesis at different temperatures in the presence or absence of a template. After post-synthesis modification with sulfate groups, the materials are highly active catalysts for the esterification of levulinic acid with ethanol. The results demonstrate that the morphology, chemical structure and catalytic activity of the obtained sulfated tin oxide-based materials strongly depend on the synthesis conditions and the structural characteristics of the precursor tin oxides. The hydrated SnO<sub>2</sub> samples obtained by hydrothermal synthesis at low temperature (100 °C and 140 °C) were characterized by very fine crystallites and not well defined crystalline phases. The sulfation of these materials results in complete transformation of the SnO<sub>2</sub> phase into a new, highly crystalline phase based on hydrated tin(IV) sulfate [Sn(SO<sub>4</sub>)<sub>2</sub>.xH<sub>2</sub>O], tin(IV) bisulfate [Sn (HSO<sub>4</sub>)<sub>4</sub>.xH<sub>2</sub>O] and/or tin(IV) pyrosulfate [Sn(S<sub>2</sub>O<sub>7</sub>).xH<sub>2</sub>O] species as suggested from structural characterization by XRD and <sup>119</sup>Sn MAS NMR spectroscopy. Although the structure of this new phase is not completely determined, it shows the highest catalytic activity among all studied catalysts, due to the simultaneous presence of  $SO_4^{2-}$  anions and water molecules resulting in formation of a larger number of stronger Brønsted and Lewis acid sites with higher surface density. Detailed investigations are currently ongoing to clarify the exact nature of the new phase by additional XRD, NMR studies and theoretical calculations. The SnO<sub>2</sub> precursors obtained by hydrothermal synthesis with a further calcination step up to 500 °C were characterized by well-defined crystallites of  $\sim 10$  nm. These materials preserve the typical SnO<sub>2</sub> morphology after sulfation and only a very small part of the sample is transformed into a new phase. The well defined crystalline phase of the SnO<sub>2</sub> samples obtained by using the template and further calcination step at 500 °C resulted in complete preservation of the initial SnO<sub>2</sub> morphology after sulfation. The catalytic activity and the stability of these materials were also lower in comparison to that of sulfated SnO<sub>2</sub> from precursors synthesized without calcination. This study proves the potential of catalysts based on sulfated tin oxides for conversions that rely on a synergistic action of Lewis and Brønsted acid sites.

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