



J. Serb. Chem. Soc. 83 (1) 39–50 (2018)
JSCS–5057

Renewable glycerol esterification over sulfonic-modified mesoporous silicas

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(Received 6 March, revised 14 June, accepted 16 June 2017)

Abstract: SO₃H-functionalised mesoporous materials with different pore structures (SBA-15 and SBA-16) were prepared by the post-synthesis surface modification. The materials were thoroughly characterized by X-ray powder diffraction, nitrogen physisorption, temperature-gravimetric analysis, elemental analysis and solid state NMR spectroscopy. The acidic properties were investigated by the temperature-programmed desorption of ammonia. The catalytic performance of SO₃H-functionalised mesoporous materials was studied in glycerol esterification with acetic acid. The different amount of silanol groups in the initial SBA-15 and SBA-16 silicas predetermined the different amount of propylsulfonic groups which are formed in them and therefore significantly influenced the acidity and the catalytic performance in glycerol esterification. Much higher amount of Brønsted acid sites was generated in SO₃H modified SBA-15 catalyst, which exhibited higher activity to value-added triacetyl glycerol.

Keywords: glycerol esterification; SO₃H; mesoporous silica; SBA-15; SBA-16.

INTRODUCTION

The waste that is being generated through the food supply chain creates major environmental, economic and social issues¹. A novel approach is the utilization of waste through the development of green technologies for sustainable development. Food waste is a veritable source for a number of functional molecules (biopolymers, proteins, phytochemicals, *etc.*) and contains valuable extracts for different applications (*eg.* resins from cashew nutshell liquid). The food supply chain waste turned out to be a resource of great potential, which can be

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<https://doi.org/10.2298/JSC170306071P>

applied as raw material for the production of fuels and chemicals.¹⁻³ Used cooking oil (UCO) is currently one of the most attractive feedstocks for the production of biodiesel,¹⁻⁵ mostly due to the low market value of the feedstock. The byproduct of UCO conversion, glycerol can be converted into various valuable chemicals through numerous routes such as etherification,⁶ hydrogenolysis,⁷ oxidation,⁸ transesterification⁹ and dehydration.¹⁰ Besides, glycerol can be esterified with acetic acid to obtain valuable products of mono-, di- and triacetyl glycerols (named as MAG, DAG and TAG, respectively), which have found a wide range of industrial applications¹¹. MAG, DAG and TAG could be obtained in catalytic reaction of glycerol esterification in the presence of homogenous (mineral acids) or heterogenous catalysts (zeolites, sulfated zirconia *etc.*). MAG and DAG have applications in cosmetics, medicines and as a starting monomer for the production of biodegradable polyesters,^{1,11} whereas TAG has application as a biodiesel additive.¹² Mesoporous silica materials modified with acidic groups can be promising catalysts due to their high surface area, adjustable structure, chemical and thermal stability.¹³⁻²¹ Despite the numerous investigations, the problem how to develop highly acidic heterogeneous catalysts for the conversion of food waste derived chemicals and the development of green technologies to obtain valuable chemicals on their basis is not yet solved. MoO₃ functionalized fibrous hybrid SBA-15 catalysts exhibited high catalytic activity during glycerol esterification with acetic acid, as indicated by the complete glycerol conversion with 86 % selectivity to both DAG and TAG at 110 °C reaction temperature.²² Biswas *et al.*²³ reported the esterification of glycerol with acetic acid in the presence of the sulfonated γ -Al₂O₃ catalyst prepared by the impregnation of sulfuric acid on γ -Al₂O₃. The results demonstrated that sulfated alumina showed very high catalytic activity with glycerol conversion of over 90 %. Recently, we reported the glycerol esterification with acetic acid on sulfated ZrO₂-modified mesoporous KIL-2 silicas showing the high catalytic activity and the selectivity to di- and triacetyl glycerols.²⁴ However, it was not possible to avoid the leaching of sulfate groups especially when the amount of zirconia is increased. In order to improve the stability of the catalysts excluding the leaching we focus our attention on developing catalysts with high activity and selectivity and better stability. Other than the stability, the second reason for the continuing research in this field is to develop a cheap heterogeneous catalyst. The selection of an efficient support is of great importance in order to obtain catalysts with good performance, because the state and structure of the support strongly influence the type of the formed supported species and their dispersion. In the present paper we choose the mesoporous SBA family silicas as the catalyst's carriers. The mesoporous SBA-15 and SBA-16 materials are synthesized in the acidic media with different triblock copolymer surfactants. SBA-15 has the well-known hexagonal structure, whereas the pore structure of SBA-16 consists of two non-interpenetrating three-dimen-

sional channel systems with spherical cavities at the dividing of the channels.^{25,26} The development of an efficient procedure for the modification of SBA-15 and SBA-16 with acid groups is of great importance.

In the present study, SBA-15 and SBA-16 materials were modified with SO₃H groups. These catalysts seem to be the promising candidates for the glycerol esterification due to their strong acidity and stability at reaction conditions, demonstrated by minimized leaching of sulfonic groups.

EXPERIMENTAL

Synthesis of mesoporous SBA-15 and SBA-16 materials

The parent silica SBA-16 material was synthesized according to the procedure of Hu *et al.*²⁷ Pluronic F127 triblock copolymer and cetyl trimethyl ammonium bromide (CTAB) were used as templates and tetraethyl ortosilicate (TEOS) as silica source. In a typical synthesis, 1.0 g F127 and 0.12 g CTAB were completely dissolved into a solution of 130 ml water and 10 ml concentrated HCl, followed by the addition of 4.0 ml TEOS under stirring. After 1 h of stirring at 313 K, the mixture was heated at 353 K for 24 h under static conditions. The solid product was filtrated, washed with water and dried at 323 K.

SBA-15 silica was prepared following the method described by Zhao *et al.*²⁸ In brief, 2 g of P123 was dissolved in a solution of 60 ml deionized water and 6.18 ml HCl (2 M) at 308 K, followed by the addition of 4 g TEOS. The mixture was stirred at 308 K for 24 h before autoclaving in a Teflon[®] bottle at 368 K for 24 h. The solid product was filtered and washed with deionized water. The template was removed by calcination in air at 823 K for 5 h with a heating rate of 1 K/min for both types of silica.

The initial SBA-15 and SBA-16 materials were functionalized with 4.28 mmol/g 3-mercaptopropyl trimethoxysilane by dispersing in toluene at refluxed condition for 6 h and then filtered, washed and dried in oven at 328 K for 3 h. The obtained mercaptopropyl functionalized silica materials were dispersed in H₂O₂ and stirred for 24 h at room temperature. The oxidized products were filtered and dried in vacuum at 323 K for 8 h, and were denoted as SBA-15SO₃H and SBA-16SO₃H.

Characterization

The textural characterization of the prepared catalysts was performed using X-ray powder diffraction (XRD) and N₂ physisorption measurements. XRD patterns were recorded on a Pananalytical X'Pert PRO (HTK) diffractometer using CuK α radiation (1.5418 Å) in the 2 θ range between 0.5–5°. The nitrogen physisorption measurements were carried out at –196 °C using Thermo Scientific Surfer automatic volumetric adsorption analyzer. Before the analysis, the parent silica samples were outgassed under high vacuum for 2 h at 523 K. The pore-size distributions were calculated from the desorption branch of isotherms by the Barret–Joyner–Halenda (BJH) method for SBA-15 materials and from the adsorption isotherms by non-localized density functional theory (NLDFT) for SBA-16 ones.

The thermogravimetric measurements were performed with a Setaram TG92 instrument with a heating rate of 5 K/min up to 873 K in air in order to determine the amount of propyl-sulfonic groups.

The sulfur content of the samples was determined using a Vario EL III CHNOS elemental analyzer. The ammonia temperature programmed desorption (NH₃-TPD) was carried out using a Micromeritics 2920 Autochem II chemisorption analyser. In the NH₃-TPD experiments, the catalyst was pre-treated at 473 K under the stream of helium for 60 min. Then at 353 K a

gas mixture of 9.8 % NH_3 in He passed over the catalyst at a flow rate of 25 mL/min for 60 min. The excess NH_3 was removed by purging with helium for 25 min. The temperature was then raised gradually to 1173 K by ramping at 10 K/min under the flow of helium and ammonia desorption data was recorded. The thermal conductivity detector (TCD) signals were calibrated using various gas concentrations of NH_3 ranging from 0 to 15 mmol of NH_3 in He.

^1H spin echo MAS NMR spectra were recorded on a 600 MHz (14.1 T) Varian VNMRS spectrometer using a 1.6 mm NB triple resonance HXY FastMAS probe. Larmor frequency for the ^1H nucleus was 599.662 MHz. The chemical shift axis was referenced to tetramethylsilane. The spectra were recorded with a 5 s repetition delay and 16 scans were accumulated. The samples were spun at 36 kHz under the magic angle during measurements. Before the measurements the samples were dried for 16 h at 473 K.

FTIR spectra were recorded in KBr pellets (99 wt.% of KBr) on a Bruker Vector 22 spectrophotometer. The samples were calcined at 500 °C for 4 h before measurements to eliminate the physically adsorbed water. The amount of the silanols is evaluated by the integrated intensity of the bands at 3200–3750 cm^{-1} , which corresponded to the isolated Si–OH groups (narrow band in the range of 3745–3750 cm^{-1}) and silanol groups participating in hydrogen bonding (band at 3200–3700 cm^{-1}).^{27,28}

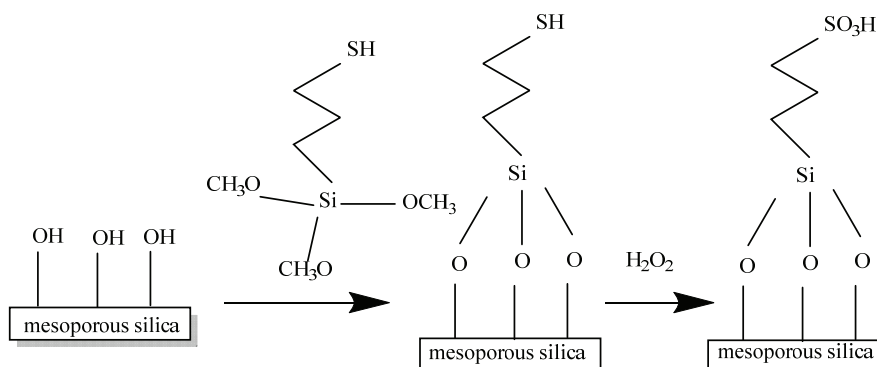
Catalytic activity measurements

Prior to the catalytic experiments the samples were pretreated *ex-situ* for 1 h at 423 K. A batch reactor equipped with magnetic stirrer was used to perform the acetylation reaction. In a typical experiment, the reactor was charged with 2 g glycerol and 0.05 g catalyst, glycerol/ acetic acid weight ratio of 1:5. The reactor was heated to the desired reaction temperatures (343–403 K) for 1 h. The analysis of the reaction products was performed using HP-GC with a WCOT fused silica 25 m×0.25 mm coating CP-SIL 43CB column.

RESULTS AND DISCUSSION

Preparation of SO_3H -modified mesoporous SBA-15 and SBA-16 materials

SO_3H functionalized silicas were prepared by a two-step procedure. At first propyl mercapto-modified mesoporous silicas were obtained in a reaction with mercaptopropyl-silane followed by an oxidative treatment with H_2O_2 in argon medium at room temperature resulting in the formation of sulfonic propyl modified mesoporous silicas (Scheme 1).



Scheme 1. Reaction pathway for the preparation of sulfonic propyl functionalized silica.

Physicochemical properties

XRD data of the initial SBA-15 and SBA-16 silica materials and their SO_3H -containing analogs at low 2θ region confirmed the preservation of the mesoporous structure after the modification procedure (Fig. 1). Compared to the parent materials some broadening, intensity decrease, and structure deterioration can be observed, especially for the modified SBA-16 sample.

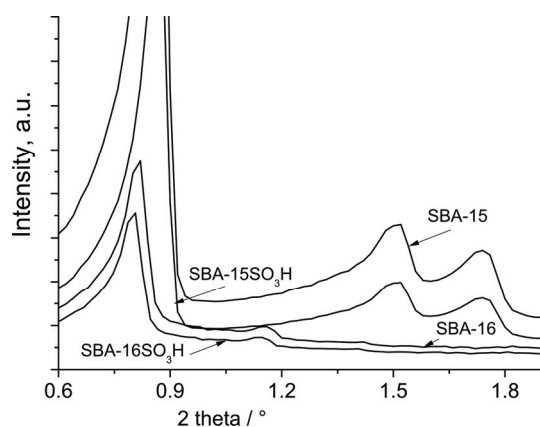


Fig. 1. XRD patterns of the studied samples.

The nitrogen physisorption isotherms of the parent and functionalized SBA-15 and SBA-16 materials display type IV isotherms with H1 and H2 type hysteresis loops, respectively (Fig. 2).

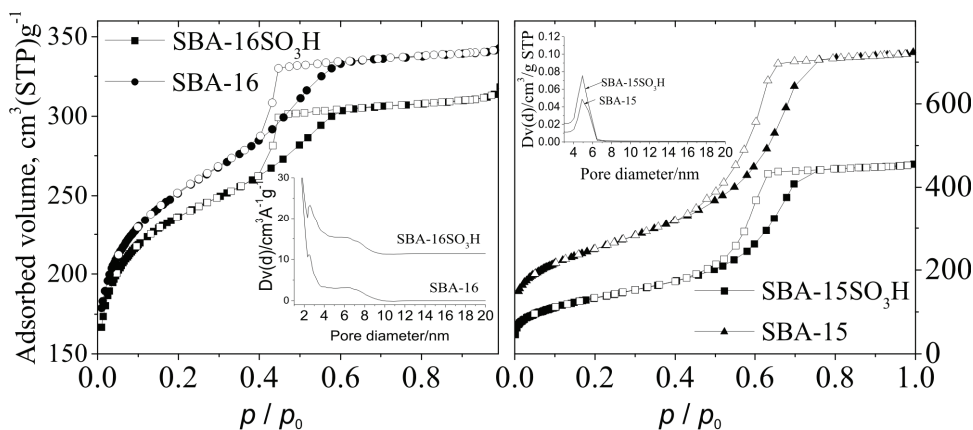


Fig. 2. N₂ physisorption isotherms of the studied samples.

Both SO_3H -modified silica samples show lower adsorbed volume than the parent one. The textural parameters are summarized in Table 1. Sulfonic func-

tionalization of SBA-15 and SBA-16 samples also led to the decreased specific surface area and pore volume which is more pronounced for SO₃H/SBA-15.

The pore diameter of SO₃H/SBA-15, Table I, is also reduced from 5.5 to 5.1 nm. More significant pore size reduction was observed for SO₃H/SBA-16 catalyst. The spherical pores are reduced from 7.9 nm to 6.5 nm, whereas the diameter of the interconnecting channels is not changed after the modification procedure (2.5 nm). These data support the fact that a significant part of propyl sulfonic groups are situated inside the channels and cavities of mesoporous supports. In the case of SBA-16 the decrease of adsorbed volume can be due to the decreased cavity volumes and pore blocking of narrower pore entrances.

TABLE I. Physicochemical properties of the studied samples; mean pore diameter, *PD*, calculated by the BJH method (desorption branch) for SBA-15 samples and by NLDFT method for SBA-16 samples (adsorption branch);

Sample	S_{BET} $\text{m}^2 \text{g}^{-1}$	Pore volume cm^3/g	<i>PD</i> nm	Content of (CH ₂) ₃ SO ₃ H, wt.%	Desorbed NH ₃ ^a mmol/g
SBA-15	878	1.14	5.5	–	–
SBA-16	1128	0.64	7.90 (2.5)	–	–
SO ₃ H/SBA-15	463	0.60	5.1	7.6 ^b (6.9) ^c (0.54) ^d	0.60
SO ₃ H/SBA-16	921	0.53	6.50 (2.5)	4.1 ^b (4.0) ^c (0.31) ^d	0.40

^acalculated by TPD of NH₃; ^bdetermined by TG analysis; ^ccalculated from elemental analysis; ^dcalculated in mmol/g

Thermogravimetric curves of the sulfonic-modified samples are shown in Fig. 3. The weight loss over 130 °C is due to the decomposition of propyl sulfonic groups. The TG profile of sulfonic SBA-15 sample shows much higher weight loss above 723 K (7.6 wt.%) in comparison to the corresponding SBA-16 one (4.1 wt.%, Table I). It indicates that the special pore structure of SBA-16 with narrower pore entrances hinder the penetration of mercaptopropyl trimethoxy silane into the pores and also its reaction with the silanol groups, by a pore blocking effect. Additionally the amount of propyl sulfonic groups was determined by elemental analysis of sulfur (Table I). A good correlation between the data obtained from TG analysis and data from elemental analysis was found. The difference in the amount of the formed propyl sulfonic groups is due to the different amount of silanols in the initial SBA-15 and SBA-16 silicas and their accessibility. The amount of silanols was determined by FTIR spectroscopy and it is 6.2 mmol/g in SBA-15 and 3.6 mmol/g in SBA-16 silicas. This result is in good accordance to the TG data.

The formation of Brönsted acid sites can be evidenced by ¹H-NMR investigations. The signal at 6.5 ppm in the spectrum of SO₃H/SBA-15 sample (Fig. 4) is characteristic for the acidic proton in the sulfonic group. With the increasing concentration of sulfonic groups this –SO₃H proton signal is shifted towards higher chemical shifts.²⁹

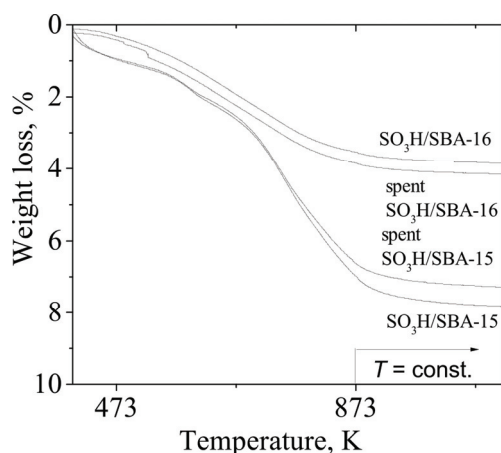
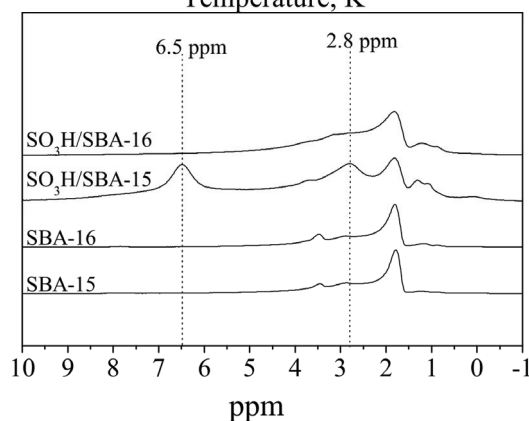


Fig. 3. TG analysis of the studied samples.

Fig. 4. ^1H -NMR spectrum of the initial and SO_3H -modified samples.

According to Kanthasamy *et al.*²⁹ the 6.5 ppm chemical shift can be witnessed only above 5 wt.% of the propyl sulfonic group loading in the sample. In accordance, this proton signal cannot be observed in $\text{SO}_3\text{H}/\text{SBA-16}$ sample due to its lower propyl sulfonic group content compared to $\text{SO}_3\text{H}/\text{SBA-15}$. Also the proton signal characteristic for propyl groups at 2.8 ppm is more intensive for the latter one. The proton NMR investigations supported also the presence of the Brønsted acid sites in higher concentration on the functionalized SBA-15 sample.

Additionally, the ammonia TPD was performed for the determination of the amount and strength of acid sites (Fig. 5). The quantity of the NH_3 desorbed was calculated from a detailed deconvolution of NH_3 -TPD profile. In the TPD profile of the prepared catalysts, the weak acidic sites between 373–673 K, the moderate acidic sites between 673–873 K and the strong acidic sites above 873 K can be observed. The calculated amount of adsorbed NH_3 corresponds to the amount of acid sites determined by TG (Table I). The peak over 823 K in the TPD curve can be probably associated with the strong Brønsted acidity of the samples and also with the partial decomposition of SO_3H groups, and it is more intensive for

SO₃H/SBA-15 sample compared to SO₃H/SBA-16. The results from ammonia TPD are in good agreement with our former TG and NMR data.

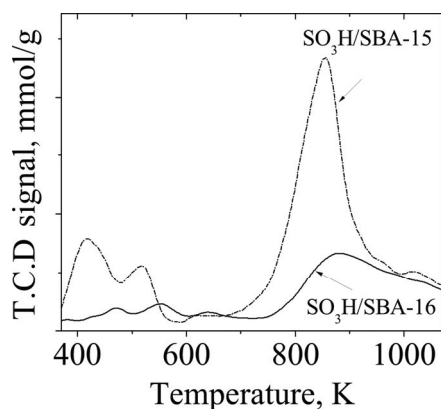


Fig. 5. TPD of ammonia of the studied samples.

It seems that the peculiarities of the pore system of silica structure significantly influence the acidic properties of the catalysts prepared by the post-synthesis modification with the propyl sulfonic groups. We also can conclude that the formed acid sites on two supports possess the same strength regardless the silica support structure. The silica texture influences mainly the amount of acid sites formed.

Catalytic activity for glycerol esterification with acetic acid

The catalytic activity of SO₃H/SBA-15 and SO₃H/SBA-16 samples in glycerol esterification with acetic acid is presented in Fig. 6. At a lower reaction temperature (343 K) both samples show low catalytic activity. A significant activity increase was observed for both catalysts with the increasing reaction temperature, reaching total conversion at 130 °C only for SO₃H/SBA-15.

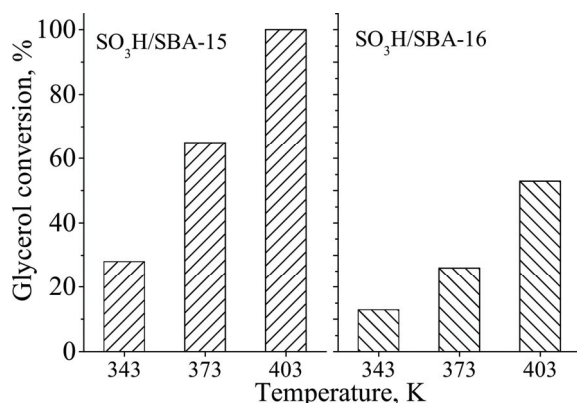


Fig. 6. Catalytic results in esterification of glycerol with acetic acid on the SO₃H-modified samples.

The selectivity data to mono-, di- and triacetyl glycerols is presented in Table II. Better selectivity to more valuable products (DAG and TAG) is registered for SO₃H/SBA-15, probably due to its higher catalytic activity in the consecutive reactions of monoacetyl glycerols esterification to di- and triacetyl glycerols.

TABLE II. Selectivity to monoacetyl glycerols (MAG), diacetyl glycerols (DAG) and triacetyl glycerol (TAG) of SO₃HSBA-15 and SO₃HSBA-16 catalysts

Catalyst	T / K								
	353			373			403		
	MAG	DAG	TAG	MAG	DAG	TAG	MAG	DAG	TAG
SO ₃ H SBA-15	50.0	39.0	11.0	37.0	44.0	19.0	21.3	57.2	21.5
SO ₃ H SBA-16	54.1	32.7	13.2	48.1	35.9	16.0	35.5	46.4	18.1

The stability test (Fig. 7) of the latter catalysts at 403 K in 3 reaction cycles showed a negligible decrease (from 100 to 93 %). TG curve of the spent catalysts after the third reaction cycle (Fig. 3) evidenced that there is no significant leaching of sulfonic groups during the reaction. The curves for the weight loss are not changed significantly – the weight loss from SBA-15SO₃H is decreased to 7.2 and 3.8 % for SBA-16SO₃H. Therefore, the formed sulfonic groups are active and stable during the catalytic reaction.

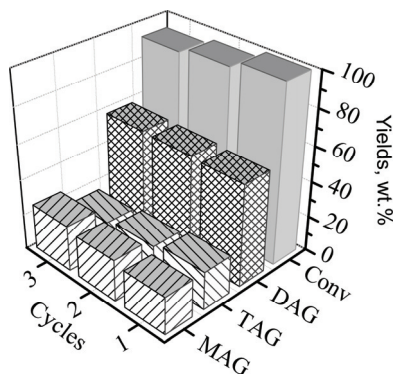


Fig. 7. Stability of the SO₃H/SBA-15 catalyst in glycerol esterification at 130 °C.

The better catalytic performance of SO₃H/SBA-15 sample can be explained by the formation of higher amount of strong Brønsted acid sites and their easier accessibility for the reactants in the wider and straight 2D channels of SBA-15 structure compared to that of 3D channels of SBA-16 as evidenced by textural, NMR and TPD data.

The formation of a higher amount of acid sites can be due to the presence of a higher amount of accessible silanol groups in SBA-15 during the functionalization process in comparison to SBA-16, where the grafted silane can easily block the narrower pore entrances. Kim *et al.*³⁰ published the results for the act-

ivity of SO₃H/SBA-15 prepared by the modification with chlorosulfonic acid in glycerol esterification. Their catalyst shows the total glycerol conversion at lower temperature (343 K) but the loaded catalysts in the catalytic experiment is two times higher (5 wt.%) than the one used in our experiment (2.5 wt.%). Moreover, the authors observed significant decrease in the catalytic activity after the first catalytic test. Recently, Dalla Costa *et al.*³¹ presented similar catalytic activity of SO₃H/SBA-15 prepared by the direct synthesis in glycerol esterification but they also used a higher amount of catalyst (4 wt.%). Ziarani *et al.*³² also found the SO₃H/SBA-15 is a highly active green recyclable catalyst in various chemical reactions, especially organic synthesis, but the detailed characterization of the catalyst, in particular of its acidity, is not available.

CONCLUSIONS

The esterification of glycerol with acetic acid results in the formation of glycerol acetates which turned out to be valuable products. It was proved that the sulfonic functionalized, solid acid type mesoporous silica can be an efficient solution for glycerol esterification with acetic acid. SBA-15 type mesoporous silica with its straight, easily accessible channels and the affordable amount of silanol groups for the post synthesis modification is a better choice as a catalyst, in the studied reaction, compared to SBA-16 structure with its bimodal pore system. Functionalized SBA-15 catalyst showed total conversion of glycerol and about 80 % selectivity to di- and triacetyl glycerols at 130 °C reaction temperature in 3 h reaction time. The good catalytic stability and resistance of the latter catalyst toward sulfonic groups leaching was also demonstrated.

Acknowledgements. Financial support by the COST action TD1203 (DKOST 01/05) and by the Bulgarian–Hungarian Inter-Academic exchange program is greatly appreciated.

ИЗВОД

ОБНОВЉИВА ЕСТЕРИФИКАЦИЈА ГЛИЦЕРОЛА НА МЕЗОПОРОЗНИМ СИЛИКАТИМА МОДИФИКОВАНИМ СУЛФОНСКИМ ГРУПАМА

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SO₃H-функционализовани мезопорозни материјали са различитом структуром пора (SBA-15 и SBA-16) добијени су поступком модификације површине, након синтезе почетних мезопорозних силиката. Добијени материјали окарактерисани су рендгенском дифракцијом X-зрака на праху, физисорпцијом азота, термогравиметријском анализом, елементалном анализом и NMR спектроскопијом чврстог стања. Температурно-програмираном десорпцијом амонијака одређена је киселост материјала. Каталитичка активност испитана је у естерификацији глицерола са сирћетном киселином. Различита количина силанолских група у полазним SBA-15 и SBA-16 утицала је како на количину про-

пилсулфонских група тако и на киселост и каталитичку активност материјала у естерификацији глицерола. Значајно већа количина Brönsted киселих центара настаје код SO₃H модификованог SBA-15, који је показао већу каталитичку активност уз образовање триацетил глицерола, што је додатна добит овог катализатора.

(Примљено 6. марта, ревидирано 14. јуна, прихваћено 16. јуна 2017)

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