Development of niobium containing acidic catalysts for glycerol esterification

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ABSTRACT

Mesoporous silicate and niobiosilicate materials of SBA-15 type were prepared and post-synthesis modified with MPTMS, i.e. (3-mercaptopropyl)trimethoxysilane, followed by oxidation of thiol species. The samples obtained were characterised by different techniques (N2 adsorption/desorption, XRD, elemental and thermal analyses) and applied as catalysts in glycerol esterification with acetic acid. The focus was on the comparison of the role of niobium in the formation of sulphonic species and its stability in the post-synthesis modified materials (prepared within this work) with those, already published, prepared by one-pot synthesis method. The most important finding is that the presence of niobium in the SBA-15 structure improves the efficiency of –SH oxidation by hydrogen peroxide towards sulphonic species like in case of one-pot synthesised samples. However, contrary to the latter samples the presence of niobium does not increase the stability of the modifier (oxidized MPTMS). This has an impact on faster deactivation of samples prepared. Samples prepared with post-synthesis modification exhibit much higher activity in glycerol esterification.

1. Introduction

Glycerol esterification process is one of the possible methods, which can be applied to utilize this waste alcohol obtained in transesterification of vegetable oils with short chain alcohols [1]. The latter process is carried out to obtain biodiesel, a fuel that is considered to have a positive impact on environment [2–4]. As an alternative to fossil fuel the usage of biodiesel causes the protection against emission of addition amounts of CO_2 (the cycle of production and usage of CO_2 by plants – sources of biodiesel – is completed) [5,6]. However, so-called eco-fuel obtained by transesterification of vegetable oils shows some drawbacks like poor oxidation stability and high boiling point. These properties can be improved by the usage of different additives. One of them is triacetylglycerol, i.e. the product of glycerol esterification with acetic acid (Fig. 1) [1,7,8]. The application of triacetylglycerol as an additive for biodiesel composition does not only improve viscosity or enhance cold resistance and anti-knocking properties [2], but also increases a total yield of biodiesel obtained in the transesterification process, which is realized by switching the waste product (glycerol) into biodiesel additive.

Typically, the glycerol esterification processes are carried out using mineral acids [3,6,9]. However, these technologies are not environmentally friendly and much attention is put to develop new techniques that apply heterogeneous catalysts having strong acidic

sites. Nevertheless, the bulky character of products demands also high porosity of catalyst with rather broad pore diameter. Taking into account these features the mesoporous silicas can be considered as such solids [10,11]. Unfortunately, even aluminosilicate mesoporous samples do not show enough strong acidity [12] and therefore are not attractive for glycerol esterification with acetic acid [13]. However, this feature can be improved by modification of mesoporous materials with sulphonic groups [1,14–30] originating from diverse sulphur containing organosilica compounds. Such modification can be performed by two different methods, i.e. one-pot synthesis [1,14,17,18,27,28] or post-synthesis procedure [20–26,29,30]. The use of such obtained catalysts in glycerol esterification with acetic acid allowed obtaining high conversion of glycerol (ca. 90%) and high selectivity towards di- and triacetylglycerol (ca. 85%) [1].

In our previous study we have developed a one-pot synthesis method of niobium containing SBA-15 type catalyst having sulphonic species on the surface generated from (3-mercaptopropyl)trimethoxysilane (MPTMS) [31]. We have showed that the addition of niobium enhances the oxidation of thiol species to sulphonic ones by hydrogen peroxide. Moreover, it was evidenced that niobium stabilizes such obtained sulphonic species that resulted in possible reuse of catalyst in glycerol esterification process. In this context the question appeared whether the post-synthesis introduction of MPTMS into niobium containing SBA-15 gives rise to the same effect as described above for the one-pot synthesis. The advantage of post-synthesis modification with MPTMS is in the better-controlled amount of modifier loaded and its location preferentially on the walls of mesopores. Therefore, the

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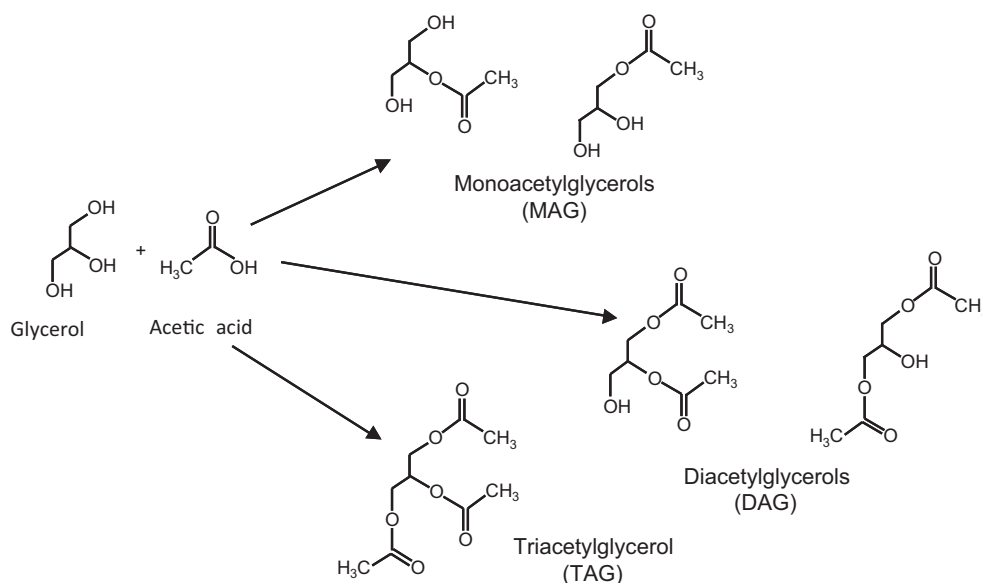*E-mail address:* tmaciej@amu.edu.pl (M. Trejda).

Fig. 1. Scheme of glycerol esterification with acetic acid.

aim of this study was to prepare the mesoporous silica and nio-biosilicate materials of SBA-15 type modified with MPTMS by the post-synthesis procedure and to examine the role of niobium on the formation of sulphonic species, their stability and activity in glycerol esterification with acetic acid.

2. Experimental

2.1. Preparation of SBA-15 type materials

Mesoporous molecular sieves of SBA-15 type were synthe-sised according to the standard synthesis procedure reported by Stucky [32] with some modification for niobiosilicate materi-als. The reaction mixture consisted of water, hydrochloric acid (CHEMPUR), Pluronic P123 (BASF) and TEOS (Fluka), at the molar ratio: 1 SiO_2:0.005 Pluronic P123:1.45 HCl:124 H_2O. After dissolv-ing Pluronic P123 in hydrochloric acid solution a source of silica was added. Ammonium niobate (V) oxalate (Aldrich) was also added to the gel (for niobiosilicate samples) keeping−TEOS/Nb molar ratio = 64 or 32. The mixture was stirred at 328 K for 8 h and then moved into a PP bottle and heated without stirring at 353 K for 16 h. The solid was filtered off, washed with water and finally dried at 333 K for 12 h. The template was removed by calcination at 823 K for 8 h in air in static conditions (temperature ramp 5 K/min).

2.2. Functionalisation of SBA-15 samples

Prior to the modification, mesoporous samples were heated at 623 K for 4 h in the oven. 1.5 g of anhydrous sample was placed in the round bottom flask equipped with the reflux. Next 60 ml of anhydrous toluene (Aldrich) and MPTMS, i.e. (3-mercaptopropyl)trimethoxysilane (Aldrich), were added. Three different ratios of Si/MPTMS were applied, i.e. 1:10, 1:5 and 1:1. Mixture obtained was heated at 373 K for 20 h keeping anhydrous conditions. Next product was separated by filtration and washed subsequently with toluene (150 ml), ethanol (150 ml) and water (700 ml). Finally the product was dried at 373 K for 12 h.

2.3. Oxidation of modifier

The oxidation of modifier was carried out using H_2O_2 and H_2SO_4 (CHEMPUR) solution. To perform the oxidation, the catalyst was immersed in hydrogen peroxide (Merck, 35%) and stirred for 2 h at room temperature. After decantation the material was washed with a mixture of ethanol and water (1:1). Then the catalyst was immersed in 1 M H_2SO_4 and stirred for 2 h at room temperature. Finally, the product was washed with a mixture of ethanol and water (1:1) and dried at room temperature.

2.4. Catalyst characterisation

XRD patterns were recorded at room temperature on a Bruker AXS D8 Advance apparatus using CuKα radiation (λ = 0.154 nm), with a step of 0.02° and 0.05° in the small-angle and in the wide-angle ranges, respectively.

N_2 adsorption/desorption isotherms were obtained on a Quan-tachrome Instruments autosorb iQ2. The samples (200 mg) were pre-treated in situ under vacuum at 423 K. The surface area was calculated using the BET method.

Elemental analyses (C, S, H) of the solids were carried out with Elementar Analyser Vario EL III.

Infrared spectra were recorded with a Bruker Vector 22 FTIR spectrometer using an in situ vacuum cell. Samples were pressed under low pressure into a thin wafer of ca. 8 mg cm^{-2} and placed inside the cell. Catalysts were evacuated at different temperatures. After each evacuation FTIR spectra were scanned. The spectrum of the IR cell without any sample ("background spectrum") was subtracted from all recorded spectra.

UV–vis spectra were recorded using a Varian-Cary 300 Scan UV-Visible Spectrophotometer. Catalyst powders were placed into the cell equipped with a quartz window. The spectra were recorded in the range from 800 to 190 nm. Spectralon was used as a reference material.

Thermogravimetry measurements were carried out in air atmo-sphere using SETARAM SETSYS-12 apparatus with temperature ramp 5 K/min. The measurements were performed from room tem-perature to 1000 K.

Titration of acidic sites was performed using 100 mg of catalyst. Solid was immersed in a 2 molar NaCl solution (60 cm^3) and stirred for 18 h. Then the solution was titrated with a 0.005 molar NaOH solution.

2.5. Glycerol esterification with acetic acid

The reaction of glycerol and acetic acid was performed in a liquid phase in batch reactor (30 cm^3) without the usage of any
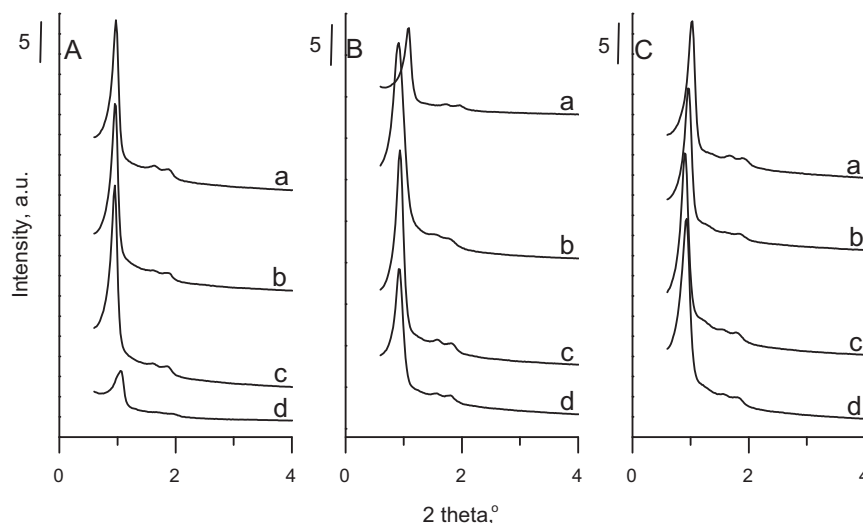
Fig. 2. XRD patterns of: (A) SBA-15; (B) NbSBA-64; (C) NbSBA-32; (a) pristine sample; (b) MP(10); (c) MP(5); (d) MP(1).

solvents. Reactor was equipped with reflux. The reaction was carried out under nitrogen atmosphere (1 atm) at 423 K for 4 h using 100 mg of catalyst. Molar ratio of glycerol to acetic acid was 1:9 (2.5 g of glycerol and 14.67 g of acetic acid). For selected catalysts the reuse test was performed. Prior to this process the catalyst after first reaction was separated from reactant mixture by centrifugation and than dried overnight at 373 K. The same mass of catalyst was applied for the second and third run. Products were analysed by a gas chromatograph (Varian CP 3800) equipped with 60 m VF-5 ms capillary column and FID detector. The column was heated as follows: at 333 K for 5 min, then 10 K/min up to 453 K.

3. Results and discussion

3.1. Texture/structure characterisation

The XRD patterns of materials modified with MPTMS species as well as those of the pristine supports are shown in Fig. 2 (the samples modified with MPTMS are indexed with MP(x), where x stands for Si/MPTMS molar ratio during the preparation procedure). Pristine materials show a characteristic feature of mesoporous ordered solids, which is demonstrated by Bragg peaks, from (1 0 0) face, at 2θ ca. 1° and two peaks in the range from 1.5° to 2°. The most intense peak is due to the regular interspace distance between silica (or niobiosilicate) walls of hexagonal tubes. These tubes are oriented in similar direction making some ordering inside the solid. Two less intense peaks in XRD patterns demonstrate this ordering. The incorporation of MPTMS does not significantly change both, hexagonal structure and material ordering, as it is shown in Fig. 2.

The mesoporous character of samples prepared is also supported by the N_2 adsorption/desorption isotherms (selected isotherms are shown in Fig. 3). According to IUPAC classification they can be assigned as type IV, which is characteristic of mesoporous materials [33]. For all samples the hysteresis loop is observed that is typical of SBA-15 type materials. The presence of this hysteresis loop is related to the condensation of nitrogen inside the mesopores. The profile of these hysteresis loops is similar for
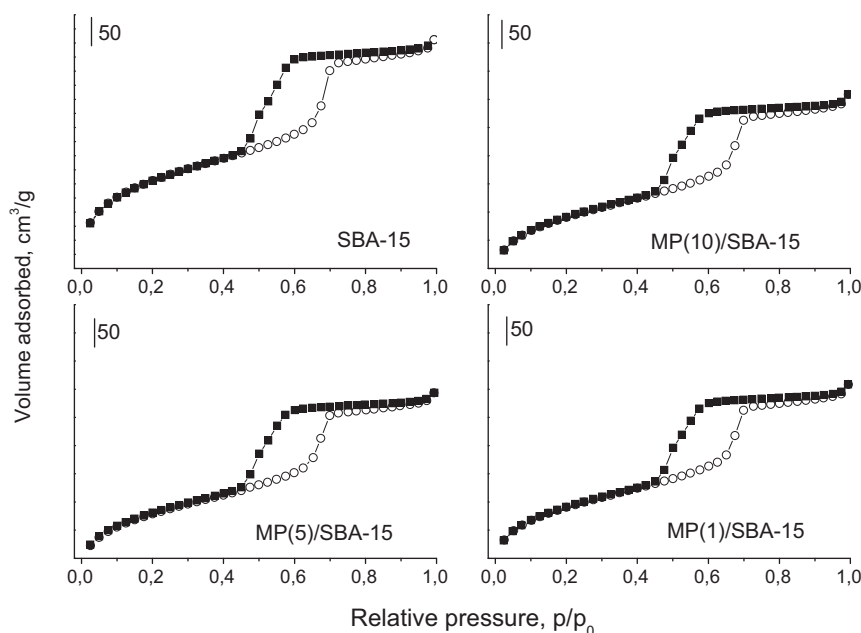

Fig. 3. N_2 adsorption/desorption isotherms.

Table 1
Textural/structural characterisation.

Catalyst[a]	Surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Mesopore diameter (PSD) (nm)
SBA-15	835	0.48	6.8
MP(1)/SBA-15	630	0.42	6.8
MP(5)/SBA-15	600	0.42	6.3
MP(10)/SBA-15	580	0.36	6.3
NbSBA-15-64	810	0.52	7.4
MP(1)/NbSBA-15-64	615	0.47	6.8
MP(5)/NbSBA-15-64	540	0.42	6.8
MP(10)/NbSBA-15-64	530	0.40	6.8
NbSBA-15-32	780	0.51	6.8
MP(1)/NbSBA-15-32	565	0.38	6.8
MP(5)/NbSBA-15-32	525	0.40	6.3
MP(10)/NbSBA-15-32	540	0.36	6.3

[a] MP – stands for MPTMS; the last number in the symbol of niobiosilicate materials means Si/Nb molar ratio in the synthesis gel.

Table 2
Results of elemental analysis and titration of acidic sites.

Catalyst	C (mmol/g)	S (mmol/g)	H⁺ (mequiv./g)
MP(1)/SBA-15 (SH)[a]	3.89	0.63	–
MP(1)/SBA-15	1.54	0.35	–
MP(5)/SBA-15	1.88	0.51	–
MP(10)/SBA-15	2.38	0.62	0.56
MP(1)/NbSBA-15-64 (SH)[a]	4.53	0.88	–
MP(1)/NbSBA-15-64	1.27	0.39	–
MP(5)/NbSBA-15-64	2.17	0.60	–
MP(10)/NbSBA-15-64	2.40	0.72	0.72
MP(1)/NbSBA-15-32	2.01	0.58	–
MP(5)/NbSBA-15-32	2.23	0.65	–
MP(10)/NbSBA-15-32	2.33	0.66	0.50

[a]Results concerning materials prior oxidation procedure.

all the samples indicating the comparable shape of pores inside the solids.

The textural/structural parameters of materials prepared are collected in Table 1. The surface areas of all samples are relatively high and reach values from 525 to 835 $m^2 g^{-1}$. The highest surface areas are reported for non-modified pristine materials. The immobilization of MPTMS species leads to a decrease in the surface area. The incorporation of MPTMS also causes the reduction of other two texture parameters, i.e. pore volume and pore diameter. The decrease of these two values indicates that MPTMS is grafted on the materials surface. Opposite trend was observed for MPTMS immobilized into the SBA-15 structure in the one-pot synthesis [31].

3.2. Efficiency of MPTMS incorporation

To establish the efficiency of modifier incorporation the elemental analysis was performed. The collected results are shown in Table 2. The molar ratio of carbon to sulphur in MPTMS molecule is equal to 3. Similar molar ratio of these elements should be found after introduction of MPTMS onto the silica or niobiosilicate surface. However, the results of elemental analysis give higher values of carbon. This is due to the presence of residual carbon on the material surface originating from surfactant (Pluronic P123) used in the synthesis. The existence of remaining carbon in the pristine materials was confirmed by FTIR spectroscopy (spectra not shown here). Therefore, the amount of sulphur should be used as an indicator of incorporation efficiency.

Data in Table 2 point out, that the higher Si/MPTMS ratio (during modification procedure), the higher amount of MPTMS
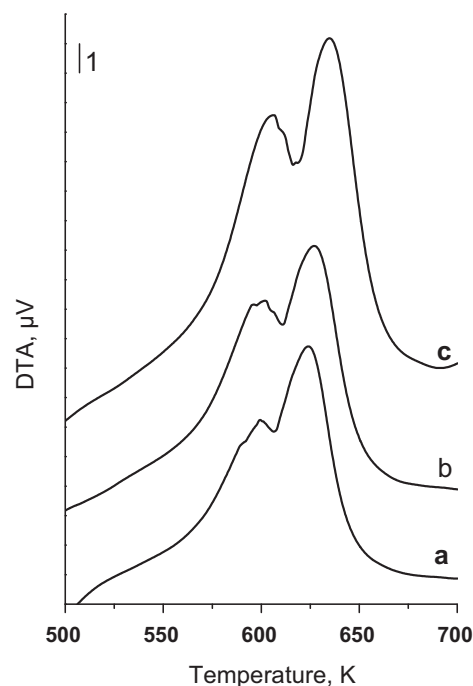

Fig. 4. DTA profiles of modified silica samples prior oxidation: (a) MP(1)/SBA-15 (SH); (b) MP(5)/SBA-15 (SH); (c) MP(10)/MCM-15 (SH).

incorporated on material surface. However, the increase of modifier loading is not proportional to its concentration in the solution used for modification. The difference between the highest and the lowest loadings is less than twice. It is worthy to notice that the one-pot synthesis procedure of the similar samples allowed incorporation of ca. 1 mmol of MPTMS per 1 g of the solid [31]. Thus, the effectiveness of MPTMS inclusion into SBA-15 is much higher in one-pot synthesis. Interestingly, a significant part of MPTMS is removed during oxidation with H_2O_2 of the samples post-synthesised modified (the comparison of the results for the samples before and after oxidation—Table 2). For silica as well as for niobiosilicate samples the oxidation route applied in this study leads to decrease in sulphur content. This suggests that a part of MPTMS incorporated on the material surface is not stable and it could be easy removed from the sample.

3.3. Efficiency of modifier oxidation

Determination of the state of MPTMS bounded on silica or niobiosilicate surface can be performed by thermal analysis [14,31]. Different temperatures of thiol and sulphonic species decomposition make this estimation possible. Thiol species decompose at temperature of 600–650 K, whereas sulphonic ones are more stable and the temperature of ca. 800 K is necessary to remove these species from the surface.

Fig. 4 shows DTA data of modified silica materials prior to the oxidation procedure. As expected, sulphonic species were not detected, thus Fig. 4 is focused on the thiol species decomposition region. Two maxima on each curve are observed. The higher MPTMS/Si ratio applied for pristine sample modification, the better resolution of maximum at lower temperature is observed. This data indicate the existence of two kinds of MPTMS species, which can vary in the bounding strength with silica surface. It should be mentioned that Diaz et al. observed similar feature for MCM-41 samples modified by methyl- or propyl-trimethoxysilane [27]. Basing on the thermal analysis combined with the mass spectrometry
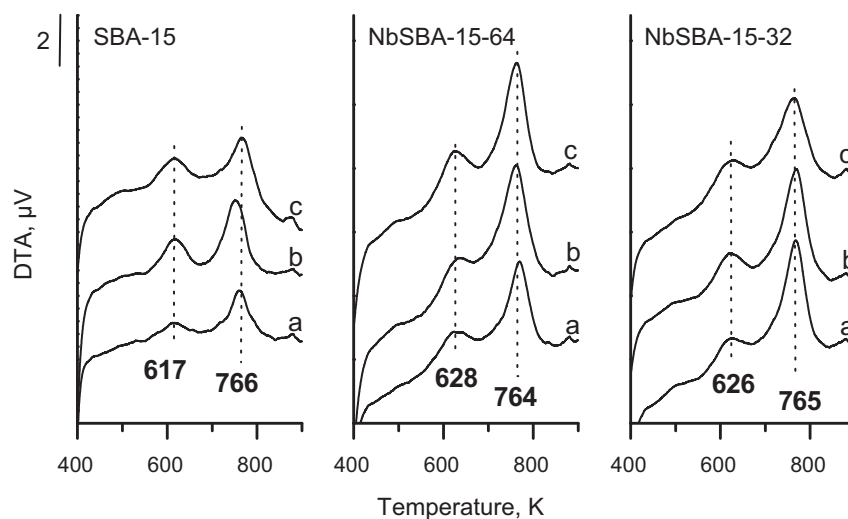
Fig. 5. DTA profiles of modified samples after oxidation: (a) MP(1); (b) MP(5); (c) MP(10).

they postulated the presence of disulphide species on the material surface. The presence of such species could also explain the phenomena observed in Fig. 4. However, as mentioned in [27], the origin of dimethylsulphide detected by MS can also be due to the recombination of methylthiol in the gas phase.

After oxidation procedure just one maximum is reported in the temperature region of 600–650 K (Fig. 5), thus the change of material surface composition is caused by the oxidation procedure. These results are in line with those of elemental analysis (Table 2), which indicated the partial lose of sulphur after thiol species oxidation. The UV–vis spectra, which show a remarkable decrease of intensity of a band assigned to charge transfer in thiol species, support the decrease of these species after oxidation procedure as well (spectra not shown here).

Fig. 5 presents the DTA data of silica and niobiosilicate samples after oxidation procedure. The maximum at ca. 765 K is present in all curves and can be assigned to the decomposition of sulphonic species [14,31]. However, all samples also contain a part of MPTMS, which is not oxidized. Basing on the intensity of peaks higher oxidation efficiency can be proposed for niobiosilicate samples. Comparable feature on thiol oxidation in one-pot synthesis procedure of similar materials was reported in [31]. This was explained by the interaction of niobium with hydrogen peroxide to form peroxy species able to oxidize different organic molecules [34,35]. Moreover, the higher stability of sulphonic species in the presence of niobium was also described for one-pot synthesis modification [31]. However, the post-synthesis modification (and oxidation) technique applied in this study does not allow obtaining a difference in stability of sulphonic species depending on chemical composition of mesoporous matrix. Therefore, a different mechanism of promoting effect of niobium species on oxidation of SH groups to sulphonic ones in both cases (one-pot synthesis and post-synthesis modification) can be proposed. Whereas in the course of one-pot synthesis modification a formation of peroxy species in the presence of niobium was postulated [31], the rather homogeneous cleavage of H_2O_2 on Nb incorporated into the SBA-15 walls can be anticipated for post-synthesis modification. The later leads to the formation of $HO^\bullet$ radicals able to oxidize –SH species. The preferential grafting of MPTMS on silanols explains the same stability of sulphonic species in silica and niobiosilicate materials.

Additional information concerning the oxidation efficiency of modifier can be obtained by the acidic sites titration [36]. Table 2 shows such results for the samples containing the highest sulphur loadings. The analyses performed indicate that most of

Table 3
Conversion and selectivity of glycerol esterification with acetic acid process.

Catalyst	Conversion (%)	Selectivity (%)		
		MAG	DAG	TAG
Blank test	63	24	58	18
MP(1)/SBA-15	85	12	54	34
MP(5)/SBA-15	64	12	53	35
MP(10)/SBA-15	78	9	51	40
MP(1)/NbSBA-15-64	92	11	51	38
MP(5)/NbSBA-15-64	92	11	50	39
MP(10)/NbSBA-15-64	92	11	50	39
MP(1)/NbSBA-15-32	94	11	52	37
MP(5)/NbSBA-15-32	94	11	51	38
MP(10)/NbSBA-15-32	93	11	51	38

Reaction temperature: 423 K; glycerol to acetic acid ratio = 1:9. MAG – monoacetylglycerols; DAG – diacetylglycerols; TAG – triacetylglycerol.

modifier was oxidized to sulphonic species. Moreover, it can be also concluded that acidic sites formed on the material surface are accessible and can be used as active sites in the catalytic processes.

3.4. Glycerol esterification with acetic acid

The esterification of glycerol with acetic acid was performed in liquid phase without usage of any solvents. To exclude the glycerol oxidation by molecular oxygen all reactions were carried out under nitrogen atmosphere. This allowed obtaining only products of glycerol esterification (monoacetyloglycerols, diacetologlycerols and triacetyloglycerol) and carbon balance close to 100%. The impact of temperature and molar composition of reactants was examined in [31] thus in this study the optimised conditions were applied, i.e. temperature of 423 K and glycerol to acetic acid ratio 1:9.

The results of glycerol esterification with acetic acid are collected in Table 3. This process can be driven just by the temperature, which is demonstrated by the results of the reaction carried out without catalyst addition (blank test). The conversion in this case reaches 63%, whereas the main products are di- and monoacetylglycerols. The usage of catalysts obtained in this study allows increasing the conversion value. Silicates materials, with exception to MP(5)/SBA-15, rise the conversion up to ca. 80%, meanwhile niobiosilicates samples are even more active (above 90% of conversion). It can be noticed that catalysts obtained in one-pot synthesis procedure showed lower activity (ca. 70%) [31], despite of higher
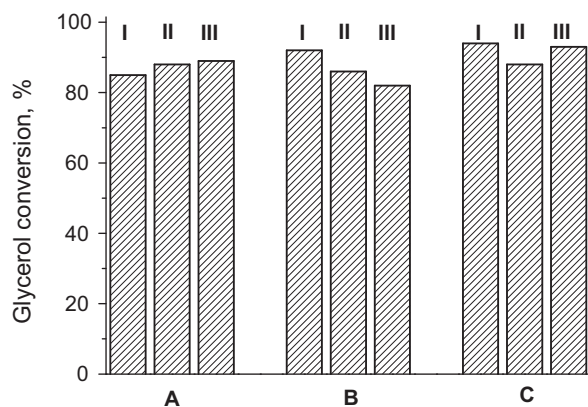
Fig. 6. Glycerol conversion in esterification of glycerol with acetic acid after I, II and III run on: (A) MP(1)/SBA-15; (B) MP(1)/NbSBA-15-64; (C) MP(1)/NbSBA-15-32.
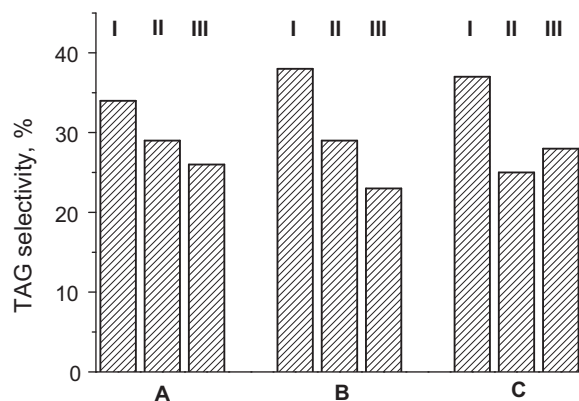

Fig. 7. TAG selectivity in esterification of glycerol with acetic acid after I, II and III run on: (A) MP(1)/SBA-15; (B) MP(1)/NbSBA-15-64; (C) MP(1)/NbSBA-15-32.

MPTMS loading. This can be explained by a better accessibility of active sites to the reactants for materials obtained by post-synthesis modification. The application of catalysts does not only change the conversion, but also strongly affects the selectivity. The dominant product is still diacetylglycerol, however, the selectivity to triacetylglycerol reaches almost 40%.

The application of catalysts in industrial scale demands not only sufficient activity and selectivity. The very important factor is reproducibility of catalyst behaviour after its regeneration. To check the possible application of materials obtained the reuse tests were performed. Catalysts after reaction were separated and dried at 373 K prior to the next usage. The results of such experiments for selected samples are shown in Figs. 6 and 7. Glycerol conversion does not significantly change after second and third run with exception to MP(1)/NbSBA-15-64. For the latter material a systematic slide decrease of conversion is observed (Fig. 6). However, the selectivity to triacetylglycerol remarkably goes down in the second run for all catalysts. This decrease is much higher compare to materials modified in one-pot synthesis [31] and testifies the lower stability of sulphonic species determined by thermal analysis.

4. Conclusions

The post-synthesis modification procedure applied in this study allowed incorporation of (3-mercaptopropyl)trimethoxysilane species into the SBA-15 structure (silica and niobiosilicate). A remarkable excess of MPTMS in the modification procedure did not allow introducing a significant higher amount of this species onto

material surface. The presence of niobium in the structure of matrix enhanced the transformation of thiols to sulphonic species via oxidation by hydrogen peroxide in comparison with silica material. It is the same effect as in case of one-pot synthesis in the presence of MPTMS and H_2O_2 [31]. However, the stability of sulphonic groups was not depended on the chemical composition of SBA-15 material testifying a low strength interaction of modifier with niobium. It is contrary to the previous results related to one-pot synthesis [31]. The samples prepared within this work were active in glycerol esterification process with acetic acid. They allow obtaining ca. 40% selectivity to triacetylglycerol, i.e. valuable product for biodiesel composition. Nevertheless, the catalysts were not stable during the reuse tests leading to the decrease of yield of triacetylglycerol.

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