



# The role of Nb in the formation of sulphonic species in SBA-15 and MCF functionalised with MPTMS

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## ABSTRACT

Mesoporous silica and niobosilicate materials of SBA-15 and MCF types were prepared in the presence of MPTMS, i.e. (3-mercaptopropyl)trimethoxysilane and hydrogen peroxide. The samples obtained were characterised by different techniques ( $N_2$  adsorption/desorption, XRD, elemental and thermal analyses) and applied as catalysts in glycerol esterification with acetic acid. The role of niobium species on the formation of sulphonic species and stability of organosilane modifier was explored. The most important finding is that the addition of niobium to the synthesis gel improves the efficiency of –SH oxidation by hydrogen peroxide towards sulphonic species. This behaviour is not dependent on the type of structure of mesoporous materials (SBA-15 or MCF). However, the kind of mesoporous solid influences the efficiency of Nb incorporation and on the esterification process. MCF matrix improves the catalytic performance of the MPTMS modified catalyst.

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## 1. Introduction

The role of acid catalysts in an industrial processes, especially in the field of hydrocarbon chemistry, is remarkable and very important [1]. Solid acid catalysts are often used for the most industrially important processes like cracking, isomerisation, alkylation or MTO [1]. However, there are still a lot of industrial operations that employ acidic catalysts in homogeneous phase, like for example the esterification processes involving mineral acids [2–4]. Because of their negative environmental impact, much effort is made to replace such processes by heterogeneous catalysis.

Development of solid acid catalysts dedicated to liquid phase processes needs to overcome some drawbacks, among others those related to the properties of host materials or acidic modifier. The size of catalyst pores determines the size of organic substrates which can be used for the catalytic reaction. Thus, the catalysts considered for esterification processes usually have relatively large pore diameters to enhance the formation of bulky products. So far for this purpose such materials like MCM-41 [5–10] or SBA-15 [11–15] have been applied. To generate the acidic properties, different organosilanes were deposited on the surface of the silica matrix, and sulphonic species were usually generated in the final product.

The formation of sulphonic species from mercapto-species immobilised on catalyst surface can be prompted by using

hydrogen peroxide as oxidant, either during the hydrothermal synthesis of solid materials or in post-synthesis oxidation. The latter procedure is more complicated because of the application of hydro-sulphuric acid and the need of some additional steps. Therefore, the efficiency of thiol group oxidation during the hydrothermal synthesis is very important and should be also taken under investigation.

Niobium compounds exhibit special properties, among them strong metal–support interaction and unique reversible interaction with several reagents are most important [16]. These features are essential for the catalyst preparation. Mesoporous materials containing this element have been synthesised and applied for the liquid phase oxidation of thioethers and cyclohexene with hydrogen peroxide [17–20]. The role of niobium in the catalysts mentioned above is to prompt the formation of peroxy species that are very active in oxidation processes. In this study the possible impact of niobium species on oxidation of thiols during the formation of two different mesoporous solids (SBA-15 and MCF) is examined and discussed.

## 2. Experimental

### 2.1. Preparation of SBA-15 type catalysts

Modified SBA-15 catalysts with MPTMS, (3-mercaptopropyl)trimethoxysilane, were prepared via modified hydrothermal synthesis [21] previously described by Margolese et al. [11]. The synthesis was performed in polypropylene bottle (PP). The synthesis procedure was as follow. To the PP bottle the Pluronic P123 (Poly(ethylene glycol)-block-Poly(ethylene

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glycol)-block-Poly(ethylene glycol)-block) (Aldrich – 4 g), HCl (Chempur 35% – 8.64 g) and water (116.36 g) were added. When the surfactant was dissolved a TEOS (Aldrich – 7.8 g) was dropwise inserted. After 45 min MPTMS (Aldrich – 0.7694 g) and hydrogen peroxide (Merck 30% – 1.258 g) were added. Ammonium niobate(V) oxalate ( $C_4H_4NNbO_9$  – Aldrich) was also added to the gel (10 min after TEOS addition) keeping Si/Nb ratio of 64 in case of the preparation of niobosilicate materials. The final mixture of: 1 TEOS: 0.018 Pluronic P123: 0.1 MPTMS: 0.3  $H_2O_2$ : 2.2 HCl: 181  $H_2O$  was stirred at 313 K for 20 h and then heated at 373 K under static conditions for 24 h. The product was washed by 600  $cm^3$  of water. The template was removed from the as-synthesized material by refluxing in ethanol for 24 h. Finally, the material was allowed to dry at room temperature.

The following notation was used for the catalysts prepared: MP-SBA-15 and MP-NbSBA-15 denote, respectively, the silica SBA-15 and niobosilicate NbSBA-15 materials modified with MPTMS.

## 2.2. Preparation of MCF type catalysts

Modified MCF catalysts with MPTMS were synthesised via modified procedure described by Kustrowski et al. [22]. The synthesis was performed in polypropylene bottle (PP). First, Pluronic P123 (Aldrich – 8 g) was dissolved in water (282.48 g) and HCl (Chempur 35% – 17.52 g) at 308–313 K. Second, 1,3,5-trimethylbenzene (Aldrich – 4 g) and  $NH_4F$  (Aldrich – 0.0934 g) were added under vigorous stirring. Following 1 h of stirring, TEOS (Fluka – 17.054 g) was added. MPTMS (Aldrich – 1.6788 g) and hydrogen peroxide (Merck 35% – 2.62 g) were slowly added to the solution 45 min after TEOS addition. Ammonium niobate (V) oxalate ( $C_4H_4NNbO_9$  – Aldrich) was also added to the gel (10 min after TEOS addition) keeping Si/Nb ratio of 64 in case of the preparation of niobosilicate materials. The final mixture of 1 TEOS: 0.017 Pluronic P123: 0.4 TMB: 0.03  $NH_4F$ : 0.1 MPTMS: 0.3  $H_2O_2$ : 2.07 HCl: 201  $H_2O$  was stirred at 308–313 K for 20 h and then heated at 373 K under static conditions for 24 h. The template was removed from the as-synthesized material by refluxing in ethanol for 24 h. Finally, the material was allowed to dry at room temperature.

One silica MP-MCF sample was prepared with the addition of higher amount of hydrogen peroxide (MPTMS/ $H_2O_2$  = 1:9).

The following notation was used for the catalysts prepared: MP-MCF and MP-NbMCF denote, respectively, the silica MCF and niobosilicate NbMCF materials modified with MPTMS. MP-MCF\* stands for modified silica MCF prepared with the higher amount of  $H_2O_2$ .

## 2.3. Catalyst characterisation

XRD patterns were recorded at room temperature on a Bruker AXS D8 Advance apparatus using  $CuK\alpha$  radiation ( $\lambda = 0.154$  nm), with a step of  $0.02^\circ$  and  $0.05^\circ$  in the small-angle range and in the high-angle range, respectively.

$N_2$  adsorption/desorption isotherms were obtained on a Quantachrome Instruments autosorb iQ2 (for MCFs) and Micrometrics ASAP (for SBA-15). The samples (200 mg) were pre-treated in situ under vacuum at 423 K. The surface area was calculated using the BET method, pore volume and diameter was estimated according to Broekhoff-de Boer method [23] for MCF materials and BJH method for SBA-15 samples.

Elemental analyses of the solids were carried out with Elementar Analyser Vario EL III.

Infrared spectra were recorded with a Bruker Vertex 70 FTIR spectrometer using an in situ 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 373 K for 6 h before spectra were recorded.

**Table 1**  
Textural/structural characterisation.

Catalyst <sup>e</sup>	Surface area, $m^2\ g^{-1}$	Pore volume, $cm^3\ g^{-1}$	Average pore diameter, nm
MP-SBA-15	670	1.0 <sup>a</sup>	5.8 <sup>a</sup>
MP-NbSBA-15	810	1.1 <sup>a</sup>	6.6 <sup>a</sup>
MP-MCF	420	1.5 <sup>b</sup>	22.6 <sup>c</sup> , 11.3 <sup>d</sup>
MP-MCF*	410	1.9 <sup>b</sup>	28.0 <sup>c</sup> , 10.2 <sup>d</sup>
MP-NbMCF	700	1.7 <sup>b</sup>	22.4 <sup>c</sup> , 6.1 <sup>d</sup>

<sup>a</sup> Determined from adsorption branches of  $N_2$  isotherms (BJH method).

<sup>b</sup> Determined from adsorption branches of  $N_2$  isotherms (BdB-FHH method).

<sup>c</sup> Cells diameter determined from adsorption branches of  $N_2$  isotherms (BdB-FHH method).

<sup>d</sup> Windows diameter determined from desorption branches of  $N_2$  isotherms (BdB-FHH method).

<sup>e</sup> MP stands for MPTMS.

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 atmosphere using SETARAM SETSYS-12 apparatus with temperature ramp 5 K/min.

## 2.4. Glycerol esterification with acetic acid

The reaction of glycerol and acetic acid was performed in a liquid phase in batch reactor without usage of any solvents. The reaction was carried out under nitrogen atmosphere 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 this process the catalyst after first reaction was separated from reactant mixture by centrifugation and then 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-5ms capillary column and FID detector.

## 3. Results and discussion

### 3.1. Impact of niobium on the material structure

In this study two different mesoporous silica materials SBA-15 and MCF, modified with (3-mercaptopropyl)trimethoxysilane (MPTMS) were synthesised. Moreover, both SBA-15 and MCF solids were also prepared with addition of niobium source into the synthesis gel so that two types of solids that vary in the chemical composition were obtained. The catalysts prepared are mesoporous as evidenced by  $N_2$  adsorption/desorption isotherms, texture parameters (Table 1, Fig. 1) and XRD analyses (not shown here). The  $N_2$  adsorption/desorption isotherms shown in Fig. 1 are typical of mesoporous solids and can be classified as type IV according to IUPAC classification [24]. Both materials show relatively high surface area in the range from 670 to 810  $m^2\ g^{-1}$  and from 420 to 700  $m^2\ g^{-1}$  for SBA-15 and MCF, respectively. Niobium addition to the synthesis gel has remarkably impacted on this texture parameter. The surface area of niobosilicate samples increased ca. 1.2 times for SBA-15 structure and 1.65 for MCF. This feature is important especially for the possible application of the materials obtained in the field of catalysis. Niobosilicate samples (prepared with the same amount of  $H_2O_2$  as silica samples) showed also higher pore volume than silicas. However, the pore diameter is remarkably higher only for NbSBA-15 samples. For MCF

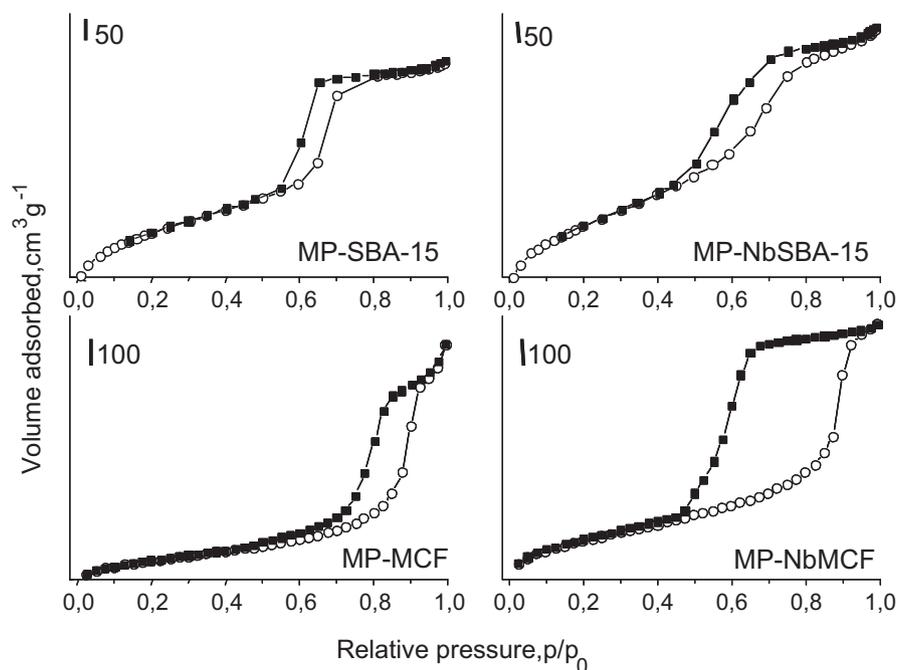


Fig. 1. N<sub>2</sub> adsorption/desorption isotherms.

materials the addition of niobium results in the smaller window size of cells. The cellular foams structure was identified for all MCFs prepared as it is exemplary shown in TEM image of MP-MCF\* sample (Fig. 2).

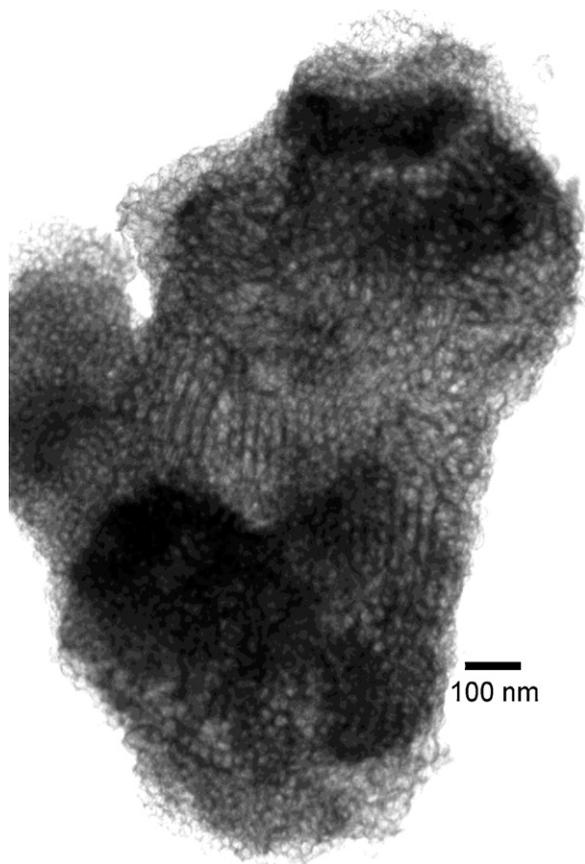


Fig. 2. TEM image of MP-MCF\* sample.

### 3.2. Impact of niobium on the efficiency of MPTMS functionalisation

The functionalisation of mesoporous solids by MPTMS was performed aiming to obtain acidic catalysts (after thiol groups oxidation to sulphonic species). Therefore, the efficiency of MPTMS incorporation and in particular the number of sulphonic species present in the final material is very important. Table 2 presents a comparison of MPTMS amounts introduced to all samples. The quantity of modifier expressed in mmol of sulphur per gram of the solid is given in Table 2. In both structures the silica matrix allows obtaining a higher MPTMS loading than the niobosilicate one. Moreover, this loading is also higher for SBA-15 structure than for MCF. It can be also noticed that the efficiency of niobium incorporation in the final material depends on the solid structure and it is higher for SBA-15. However, in spite of this difference, the decrease in MPTMS incorporation is similar for both kinds of niobosilicate solids. In our previous work concerning the functionalisation of SBA-15 structure we have shown that the MPTMS concentration on the silicate surface is almost independent of the niobium concentration in the synthesis gel in the range of Si/Nb molar ratio from 16 to 64 [21]. Thus, it could be concluded that the results obtained for NbMCF structure are in line with the results reported for NbSBA-15 materials and presented in [21]. To summarise, although the presence of niobium improves the textural parameters as described in previous section, it allows incorporating less amount of MPTMS on the surface of mesoporous solids.

Table 2  
Results of elemental analysis.

Catalyst	Si/Nb molar ratio		C, mmol/g	S, mmol/g
	Assumed	Real		
MP-SBA-15	–	–	10.2	1.1
MP-NbSBA-15	64	65	10.5	0.8
MP-MCF	–	–	19.7	0.9
MP-MCF*	–	–	11.1	0.7
MP-NbMCF	64	<300	13.0	0.6

### 3.3. Impact of niobium on modifier anchoring

The modification of silica or niobiosilicate surface by MPTMS is realised with the participation of methoxy species from organosilanes and OH groups from the surface of silica or niobiosilicate. Usually, one or two methoxy species take part in the functionalisation [25]. The synthesis procedure applied in this study involves the addition of hydrogen peroxide, which is necessary for oxidation of thiol species. In such conditions not only thiol species but also methoxy species can be oxidised. To examine in details the state of organic part of the modifier, the FTIR spectra of the materials prepared were recorded and they are shown in Fig. 3.

All spectra show a band assigned to the  $\delta_{as}(\text{CH}_3)$  vibrational mode in methoxy groups at  $1455\text{ cm}^{-1}$  [26–28]. It indicates that after functionalisation of silica or niobiosilicate surface, Si atom from MPTMS is still connected with at least one methoxy group. The bands corresponding to  $-\text{SH}$  vibrations are not detected for all the samples similar like in [21]. This could be explained by low concentration of  $-\text{SH}$  species. In the spectra of silica samples another band at  $1720\text{ cm}^{-1}$  is present. It is assigned to  $\text{C}=\text{O}$  vibrations [26–28]. The presence of this band suggests that a part of hydrogen peroxide is used for oxidative dehydrogenation of methoxy species. The spectra of the niobium containing samples exhibit a different character. Only for MP-NbMCF a low intense band at  $1720\text{ cm}^{-1}$  could be found. This feature points to the role of niobium, which favours the selective oxidation of thiol species. FTIR spectra can partially confirm this hypothesis. In all spectra a band at ca.  $1380\text{ cm}^{-1}$  is observed. Its appearance can be assigned to sulphonic [21] as well as to  $\delta_{sym}(\text{CH}_3)$  species [29]. The later species can come from non-hydrolyzed TEOS ( $\nu_{sym}(\text{CH}_3)$  from ethoxy species), which gives rise to the IR band at  $1377\text{ cm}^{-1}$ . Indeed, for niobiosilicate materials the band at ca.  $1380\text{ cm}^{-1}$  is more intense pointing to the presence of sulphonic species. These observations are in line with the results of thermal analyses described in the next section. Thus, it can be concluded that the addition of niobium to the synthesis gel enhances the selective oxidation of thiol species (methoxy species are not oxidised).

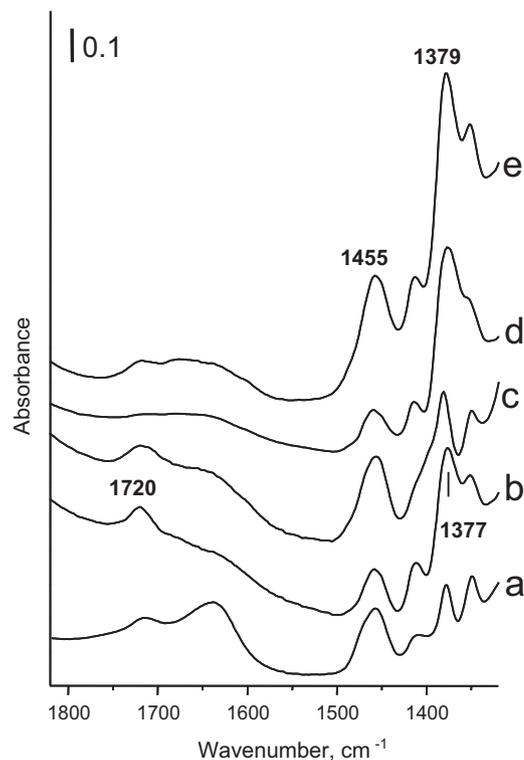


Fig. 3. FTIR spectra of: (a) MP-MCF\*; (b) MP-SBA-15; (c) MP-MCF; (d) MP-NbSBA-15; (e) MP-NbMCF.

### 3.4. Impact of niobium on the oxidation of thiol species

Successful incorporation of MPTMS species on the surface of mesoporous solids does not guarantee the acidic character of the catalyst obtained. To achieve the acidity required the thiol species must be selectively oxidised to sulphonic ones. For this purpose the hydrogen peroxide was added to the synthesis gel. To estimate the

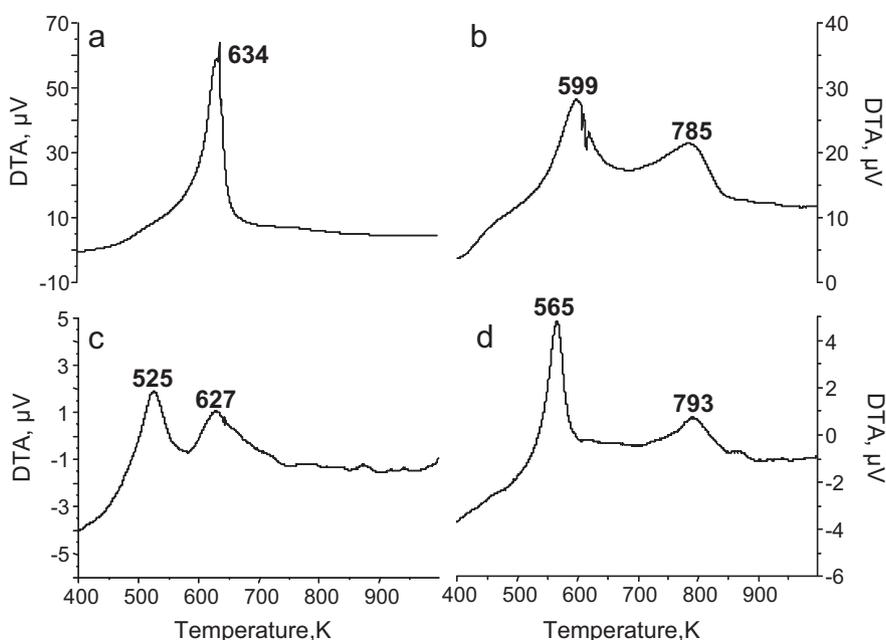


Fig. 4. DTA profiles of: (a) MP-SBA-15; (b) MP-NbSBA-15; (c) MP-MCF; (d) MP-NbMCF.

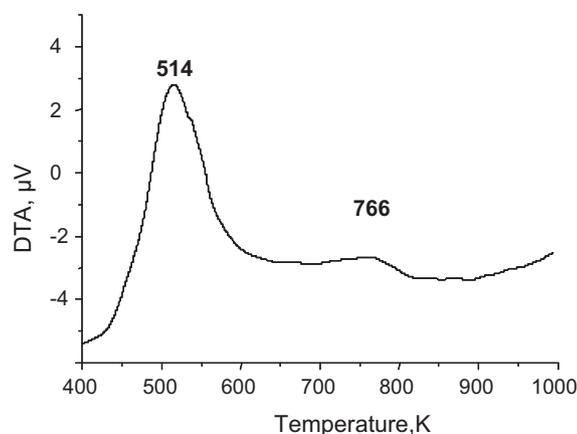


Fig. 5. DTA profile of MP-MCF\*.

oxidation efficiency, the final products were subjected to thermal analyses.

The types of organosilane modifier can be distinguished on the basis of different decomposition temperatures of thiol and sulphonic species. The former decompose at ca. 600–650 K, whereas the temperature of sulphonic species decomposition is around 800 K [11]. The DTA curves of silica and niobosilicate materials modified with MPTMS are presented in Fig. 4. The addition of hydrogen peroxide in the process of synthesis of silica samples of both structures does not allow obtaining sulphonic species. The DTA curves of these samples show exothermic peaks only below 650 K, which are assigned to the decomposition of thiol species. Moreover, in the curves of MCF two exothermal effects are observed. This feature suggests the existence of two types of MPTMS on the silica MCF surface characterised by different thermal stabilities. A similar observation was done for MCM-41 samples modified with methyl- or propyl-trimethoxysilane [9]. On the basis of the results of thermal analysis interpreted together with the mass spectrometry data, the presence of disulphide species on the material surface was postulated in [9]. The presence of disulphide species could explain the appearance of the two maxima shown in Fig. 4. However, as mentioned in [9], the origin of dimethylsulphide detected by MS can also be the recombination of methylthiol in the gas phase. The possible formation of disulphide species on the MCF surface could be enhanced by a more open structure of this material than SBA-15 one. Nevertheless, for niobosilicate MCF sample only one maximum below 650 K is observed on the DTA curve (Fig. 4). To check if this feature could be related to the thiol species oxidation efficiency, the MP-MCF\* sample was prepared with a higher H<sub>2</sub>O<sub>2</sub> to MPTMS ratio of 9. The DTA curve of this sample (Fig. 5) shows only one maximum below 650 K (at 514 K). Moreover, another exothermic effect at 766 K is visible pointing to the partial oxidation of thiol species. Thus it can be concluded that when the oxidation of modifier is possible and takes place (for higher H<sub>2</sub>O<sub>2</sub> amount or Nb presence) only one kind of thiol species is left on the MCF surface. This fact could be also related to a possible competition between the sulphonic and disulphide species formation.

The surface composition of niobosilicate samples functionalised by MPTMS is more complex. Besides the thiol species, the DTA curve shows another exothermic effect at temperature of ca. 790 K, testifying to the existence of sulphonic species. These results can be explained by the unique properties of niobium manifested when in the contact with hydrogen peroxide. It has been observed that niobium containing amorphous materials exhibit very promising activity in liquid phase oxidation with hydrogen peroxide [16,30]. The activity of niobium containing materials in the catalytic routes involving hydrogen peroxide as oxidant is related to

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-SBA-15	54	26	58	16
MP-NbSBA-15	66	11	53	36
MP-MCF	73	27	58	15
MP-MCF*	85	12	54	34
MP-NbMCF	76	12	54	34

Reaction temperature: 423 K; glycerol to acetic acid molar ratio = 1:9.

MAG: monoacetylglycerols, DAG: diacetylglycerols, TAG: triacetylglycerol.

the ability of formation of peroxy complexes [16,30]. Such activated hydrogen peroxide species are able to selectively oxidate different molecules, e.g. thiols [18,31]. The interaction of hydrogen peroxide with niobium species in the materials studied in this work, towards the peroxy complexes causes a further selective oxidation of SH groups towards sulphonic species. The role of niobium could be to promote stronger interaction between the methoxy groups from MPTMS and the OH groups from the surface. Such interaction would facilitate decomposition of SH groups, evidenced by the lower temperature of the exothermic peak in DTA curve (Fig. 4) and could be also the reason for easier (faster) oxidation of SH species to sulphonic one.

The results presented above clearly show the important role of niobium in the oxidation of thiol species. The formation of sulphonic species in the conditions of synthesis applied in this study would not be possible without the addition of niobium source into the synthesis gel.

### 3.5. Glycerol esterification with acetic acid

To verify the acidic character of niobosilicate SBA-15 and MCF, functionalised with MPTMS, the esterification of glycerol with acetic acid was performed. This process requires the presence of strong acidic sites to obtain a high yield of triacetylglycerol. To exclude the glycerol oxidation by molecular oxygen all reactions were carried out under nitrogen atmosphere. This allowed obtaining only products of glycerol esterification (monoacetylglycerols, diacetylglycerols and triacetylglycerol) and carbon balance close to 100%.

The results of glycerol esterification process carried out at 423 K (glycerol to acetic acid molar ratio = 1:9) are shown in Table 3. As can be observed, the esterification of glycerol takes place without catalyst addition (blank test) and the conversion value reaches 63%. However, the main products of blank test are DAG and MAG. The mesoporous silica SBA-15 and MCF materials functionalised with MPTMS show similar selectivity to DAG and MAG, which points out the lack of sulphonic acidic centres on the catalyst surface. Different behaviour shows MP-MCF\* sample prepared with much higher H<sub>2</sub>O<sub>2</sub> addition in the synthesis. A higher conversion and selectivity to triacetylglycerol testify the presence of sulphonic species generated in this sample.

The presence of strong acidic centres should switch the product formation to TAG, i.e. the consecutive reactions should take place. Indeed, for MP-NbSBA-15 and MP-NbMCF samples the product selectivity is different, i.e. the amount of MAG decreases, whereas the amount of TAG increases (in relation to non-niobium containing materials). In consequence, the combined selectivity to DAG and TAG reaches ca. 90%. Such a catalytic behaviour strongly points to the presence of acidic centres in these two samples. It leads to a conclusion that the presence of niobium in the synthesis gel makes the formation of acidic centres possible.

#### 4. Conclusions

The one-pot synthesis procedure applied in this study allowed incorporation of (3-mercaptopropyl)trimethoxysilane species into the silica and niobosilicate materials of both, MCF and SBA-15 structures. The mesoporous structure of the latter allowed obtaining a higher concentration of niobium as well as MPTMS species in the final material. The positive effect of niobium on the oxidation of thiol species was found to be independent of the type of mesoporous material. The same can be deduced concerning the impact of niobium on the drop of oxidation of methoxy species. The latter species are stable in the presence of niobium. The niobosilicate samples prepared within this work are active in glycerol esterification with acetic acid. They allow obtaining 66% and 76% of glycerol conversion for MP-NbSBA-15 and MP-NbMCF, respectively. The higher conversion of glycerol on MP-NbMCF material indicates that the more “open” structure (MCF) favours the increase in the reaction rate. The selectivity to triacetyl glycerol is similar for both samples and reached ca. 35%.

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#### References

- [1] G. Busca, *Chem. Rev.* 107 (2007) 5366–5410.
- [2] M. Lopez Granados, A.C. Alba-Rubio, F. Vila, D. Martin Alonso, R. Mariscal, *J. Catal.* 276 (2010) 229–236.
- [3] B.M.E. Russbueldt, W.F. Hoelderich, *J. Catal.* 271 (2010) 290–304.
- [4] C.-H. Zhou, J.N. Beltramini, Y.-X. Fan, G.Q. Lu, *Chem. Soc. Rev.* 37 (2008) 527–549.
- [5] I. Diaz, F. Mohino, T. Blasco, E. Sastre, J. Perez-Pariente, *Microporous Mesoporous Mater.* 80 (2005) 33–42.
- [6] M. Alvaro, A. Corma, D. Das, V. Fornes, H. Garcia, *J. Catal.* 231 (2005) 48–55.
- [7] M. Roman-Aquirre, Y.P. Gochi, A.R. Sanchez, L. de la Torre, A. Aguilar-Elguezabal, *Appl. Catal. A: Gen.* 224 (2008) 59–64.
- [8] A.C. Carmo Jr., L.K.C. de Souza, C.E.F. da Costa, E. Longo, J.R. Zamian, G.N. da Rocha Filho, *Fuel* 88 (2009) 461–468.
- [9] I. Diaz, C. Marquez-Alvarez, F. Mohino, J. Perez-Pariente, E. Sastre, *J. Catal.* 193 (2000) 283–294.
- [10] I. Diaz, C. Marquez-Alvarez, F. Mohino, J. Perez-Pariente, E. Sastre, *J. Catal.* 193 (2000) 295–302.
- [11] D. Margolese, J.A. Melero, S.C. Christiansen, B.F. Chmelka, G.D. Stucky, *Chem. Mater.* 12 (2000) 2448–2459.
- [12] G. Morales, G. Athens, B.F. Chmelka, R. van Grieken, J.A. Melero, *J. Catal.* 254 (2008) 205–217.
- [13] J.A. Melero, R. van Grieken, G. Morales, M. Paniagua, *Energy Fuel* 21 (2007) 1782–1791.
- [14] W. Shen, Y. Gu, H. Xu, D. Dube, S. Kaliaguine, *Appl. Catal. A: Gen.* 377 (2010) 1–8.
- [15] F. Martinez, G. Morales, A. Martin, R. van Grieken, *Appl. Catal. A: Gen.* 347 (2008) 169–178.
- [16] M. Ziolk, P. Decyk, I. Sobczak, M. Trejda, J. Florek, W. Klimas, H. Golinska, A. Wojtaszek, *Appl. Catal. A: Gen.* 391 (2011) 194–204.
- [17] M. Ziolk, *Catal. Today* 90 (2004) 145–150.
- [18] M. Ziolk, I. Sobczak, A. Lewandowska, I. Nowak, P. Decyk, M. Renn, B. Jankowska, *J. Catal.* 70 (2001) 169–181.
- [19] M. Ziolk, I. Sobczak, I. Nowak, P. Decyk, A. Lewandowska, J. Kujawa, *Microporous Mesoporous Mater.* 35/36 (2000) 195–207.
- [20] J. Xin, J. Suo, X. Zhang, Z. Zhang, *New J. Chem.* 24 (2000) 569–570.
- [21] M. Trejda, K. Stawicka, M. Ziolk, *Appl. Catal. B: Environ.* 103 (2011) 404–412.
- [22] P. Kustrowski, L. Chmielarz, J. Surman, E. Bidzinska, R. Dziembaj, P. Cool, E.F. Vansant, *J. Phys. Chem. A* 109 (2005) 9808–9815.
- [23] W.W. Lukens Jr., P. Schmidt-Winkel, D. Zhao, J. Feng, G.D. Stucky, *Langmuir* 15 (1999) 5403–5409.
- [24] K.S.W. Sing, D.H. Everet, R.A.W. Haul, L. Moskou, *Pure Appl. Chem.* 57 (1985) 603–619.
- [25] D. Blasco-Jimenez, I. Sobczak, M. Ziolk, A.J. Lopez-Peinado, R.M. Martin-Aranda, *Catal. Today* 152 (2010) 119–125.
- [26] G. Busca, A.S. Elmi, P. Forzatti, *J. Phys. Chem.* 91 (1987) 5263–5269.
- [27] G. Busca, J. Lamotte, J.-C. Lavalley, V. Lorenzelli, *J. Am. Chem. Soc.* 109 (1987) 2502–5197.
- [28] A.E. Lewandowska, M.A. Banares, M. Ziolk, D.F. Khabibulin, O.B. Lapina, *J. Catal.* 255 (2008) 94–103.
- [29] M.A. Peluso, E. Pronsato, J.E. Sambeth, H.J. Thomas, G. Busca, *Appl. Catal. B: Environ.* 78 (2008) 73–79.
- [30] M. Ziolk, *Catal. Today* 78 (2003) 47–64.
- [31] M. Ziolk, A.E. Lewandowska, M. Renn, I. Nowak, *Stud. Surf. Sci. Catal.* 154 (2004) 2610–2617.