J Mater Sci (2009) 44:6693–6700
DOI 10.1007/s10853-009-3599-0

Synthesis, characterization and catalytic behavior of SnTf/MCM-41 and SnTf/UVM-7 as new green catalysts for etherification reactions

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Received: 22 October 2008 / Accepted: 14 May 2009 / Published online: 2 June 2009

Abstract Strong Lewis acid SnTf-MCM-41 and SnTf-UVM-7 catalysts with unimodal and bimodal pore systems were prepared in a two-step synthesis in which the triflic acid (OTf) was incorporated into previously synthesized mesoporous tin-containing silicas. The Sn incorporation inside the pore walls was carried out through the Atrane method. The SnTf-UVM-7 catalysts were prepared by aggregating nanometric mesoporous particles defining a hierarchic textural-type additional pore system. Catalysts with different Si/Sn ratios in the range 21.8–50.8 for SnTf-MCM-41 and 18.4 for SnTf-UVM-7 were found to be efficient catalysts for the etherification of primary alcohols to symmetrical long chain ethers and the selective etherification of ethylene glycol with 1-octanol to nonionic surfactants structures. The processes are green, environmentally safe, and heterogeneous.

Introduction

The etherification of symmetrical primary alcohols is an acid catalyzed reaction frequently used in the fine chemical industry. Obtained ethers are used in important industrial applications as, for example, emulsifiers in cosmetic products [1] and additive for diesel fuels [2]. The most commonly used protocol for the preparation of ethers is Williamson synthesis [3] but needed strong basic conditions are hazardous to complex molecules carrying base sensitive functional groups. Therefore, a more attractive method is the use of solid Brønsted [4–11] or homogeneous Lewis acid catalysts [12]. Unfortunately, in both cases, reactions suffer from a series of disadvantages from environmental point of view, the most important being connected with the formation of considerable amounts of wastes [10, 13]. It is widely acknowledged that there is a growing need for more environmentally acceptable processes in the chemical industry, e.g., avoiding the use of toxic and/or hazardous substances, eliminating waste at source. In this context, solid Lewis acids would contribute to overcoming many of the environmental limitations of homogeneous Lewis acids [14].

Due to their versatile formulating characteristics, insensitivity to water hardness ions, outstanding detergency action on oily soils, and rapid biodegradation in the environment, non-ionic surfactants are widely used in household, industrial and institutional cleaning products, pharmaceuticals, and agrochemicals [15–19]. The main procedure in the synthesis of these surfactants involves the reaction of primary alcohols with ethylene oxide in the presence of a suitable catalyst [20]. Since ethylene oxide is dangerous both for the human health and environment it is interesting to consider an alternative procedure for their synthesis involving less toxic raw materials. The etherification of glycols with fatty alcohols appears in this context as a solution.

Usually in heterogeneous acid catalysis, isolated species are much more active than oligo- and polymeric species.

6th International Mesostructured Materials Symposium, September 8–11, 2008, Namur, Belgium.

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Atrane route [21] is, for example, an effective solution to achieve a good dispersion of monomeric species in, e.g., the silica network. Recently we obtained, with this preparation method, a high concentration of well-dispersed Sn triflate species into the framework of the mesoporous silica [22]. The obtained materials are active and highly selective into the acylation of aromatic sulfonamides with acetic acid as acylating agent and the synthesis of (*dl*)-[α]-tocopherol [22].

Here we disclose a new catalytic application of these materials as efficient, easily recyclable, and water-tolerant Lewis acid catalysts for the etherification of primary alcohols to symmetrical long chain ethers and the selective etherification of ethylene glycol with 1-octanol to non-ionic surfactants structures. These acid-catalyzed reactions have been chosen due to the high added value of the produced ethers in bulk and fine chemicals industry.

Experimental

Catalysts preparation and characterization

The unimodal (SnTf-MCM-41) and bimodal (SnTf-UVM-7) porous catalysts were prepared in a two-step synthesis procedure: (a) the Sn incorporation inside the pore walls using the Atrane method [21]; (b) the triflic acid incorporation into previously synthesized mesoporous tin-containing silicas. Detailed preparation procedure is described elsewhere [22]. Following this procedure, catalysts with different Si/Sn ratios were obtained. The resulted materials were designated SnTf(22)-MCM-41 (Si/Sn = 21.81), SnTf(47)-MCM-41 (Si/Sn = 47.32), SnTf(51)-MCM-41 (Si/Sn = 50.84), and SnTf(18)-UVM-7 (Si/Sn = 18.40). All catalysts were analyzed using techniques as nitrogen adsorption–desorption isotherms, X-ray powder diffraction (XRD), diffuse reflectance UV–vis and FTIR spectroscopy, transmission electron microscopy (TEM), electron probe microanalysis (EPMA), and NH_3-chemisorption measurements. All procedures are described in detail elsewhere [22].

Catalytic tests

Etherification of 1-octanol

1-Octanol (15 mmol, 1.95 g), and Sn triflate-based catalyst (60 mg) were stirred at 150 °C for 2–24 h. After the reaction was stopped, the catalyst was filtered off and the reaction product was analyzed through GC. The products were characterized by GC-MS.

Etherification of ethylene glycol

In a typical procedure, 5.0 mmol (0.31 g) of ethylene glycol were mixed with 15.0 mmol (1.95 g) of 1-octanol and 60 mg of catalyst in a 10-mL glass vessel (ethylene glycol/1-octanol molar ratio = 1/3). Tests were also conducted using an ethylene glycol/1-octanol molar ratio of 2/1–1/2. All reactions were carried out at 150 °C for 1–24 h under vigorous stirring. After the reaction was stopped, the catalyst was filtered off and the reaction product was analyzed through GC. The products were characterized by GC-MS.

Results and discussion

Physical characteristics of Sn- and SnTf-based catalysts

The selection of the pH conditions at the first step of the catalysts synthesis allowed us to prepare two different catalyst types with a unimodal or bimodal pore system. At high pH values, unimodal Sn-MCM-41, in the form of large micrometric particles, was obtained; working under moderately basic conditions, Sn-UVM-7 materials (a nanometric version of the typical M41 solids) were isolated. These latter catalysts were constructed by aggregating nanometric mesoporous particles defining a hierarchic textural-type additional pore system (UVM-7-like materials). The unimodal and bimodal porous character of MCM-41 and UVM-7-like catalysts was confirmed by N_2 adsorption–desorption isotherms (Fig. 1A, B).

As Fig. 1 shows the isotherm types, the number of N_2 adsorption steps and even the pore sizes after the second reaction step was practically unaltered both for MCM-41 and UVM-7-like materials. Only a certain decrease in the surface areas is observed after reaction with triflic acid. These features confirm that the respective pore systems remain practically unaltered after reaction under strong acid conditions.

The symmetry and order degree of the catalysts before and after reaction with triflic acid were also studied by XRD and TEM. Figure 2 shows the XRD patterns corresponding to Sn-MCM-41, SnTf-MCM-41, Sn-UVM-7, and SnTf-UVM-7 samples. All materials display XRD patterns in the low-angle region with one strong diffraction peak, usually associated with the (100) reflection when a hexagonal cell is assumed. Apart from the intense peak at low 2θ values, two other resolved small signals that can be indexed to the (110) and (200) reflections can be observed in the case of MCM-41 material. These features indicate that the ordered hexagonal mesopore symmetry typical of pure MCM-41 silica was maintained after the Sn incorporation (first step) and even after the reaction with triflic

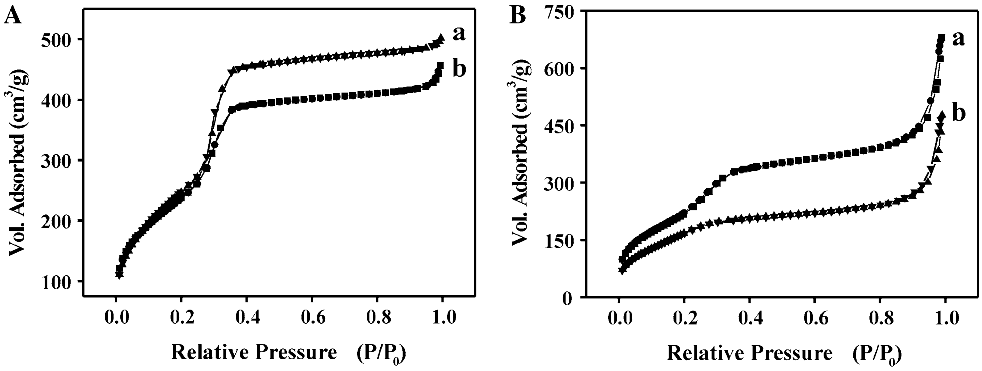


Fig. 1 N_2 adsorption–desorption isotherms of **A** (*a*) Sn-MCM-41 and (*b*) SnTf-MCM-41 catalysts and **B** (*a*) Sn-UVM-7 and (*b*) SnTf-UVM-7 catalysts

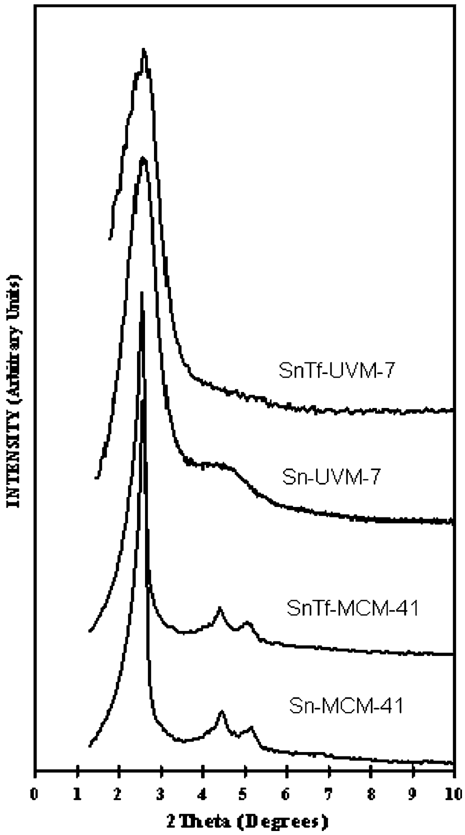


Fig. 2 Low-angle XRD patterns of Sn and SnTf-based catalysts

acid (second step). On the other hand, a broad signal of relatively low intensity can be indexed to the overlapped (110) and (200) reflections of the typical hexagonal cell in the case of the Sn-UVM-7 derivative (first step) that practically disappeared after reaction with triflic acid (second step).

In both series (MCM-41 and UVM-7 like), the peak positions remained practically unchanged. This finding confirms that the mesostructures were not practically altered after reaction with triflic acid. In fact, only a slight signal intensity decrease is observed after the second reaction step. However, this small loss of X-ray intensity observed in the XRD corresponding to SnTf-MCM-41 and SnTf-UVM-7 (compared with Sn-MCM-41 and Sn-UVM-7, respectively) must be attributed to a certain phase-cancellation phenomena associated to the introduction of scattering material (triflate anions) into the pores, although the possibility of a slight decrease in symmetry cannot be absolutely discarded. In all samples, the absence of XRD peaks at high angle values indicates that no phase segregation leading to SnO or SnO_2 bulk oxides occurred.

The TEM images (Fig. 3) were completely correlated with XRD and N_2 adsorption–desorption isotherm features. The observation in both cases of a dominant (single-type) particle morphology supports the monophasic nature of the catalysts. Typical morphologies—hexagonal ordered large particles and aggregates of disordered nanoparticles—were observed for the SnTf-MCM-41 and SnTf-UVM-7 catalysts. Moreover, TEM images (insets in Fig. 3) of both catalysts also showed small dark spots (average size ca. 2 nm) that could be due to Sn-rich domains.

A summary of the textural characteristics of the prepared catalysts is given in Table 1.

Chemical characteristics of Sn- and SnTf-based catalysts

Figure 4 shows evidence on the formation of the Sn triflate species. FTIR spectra indicate that both MCM-41 and UVM-7 supports did not retain even a trace of triflate. In contrast, on doped Sn-silica samples, triflic acid was incorporated in amounts that increased with increasing Sn content. No anchoring occurred on the silica wall, but anchoring was obvious on the Sn sites and on the Sn silica.

Regardless of the support type (MCM-41 or UVM-7), UV–vis characterization suggested the presence of highly dispersed tetrahedral isolated Sn^{4+} with an absorption band centered at 250 nm, ascribed to charge transition from O^{2-} to Sn^{4+} in a tetrahedral coordination environment [23]. In the SnTf(18)-UVM-7 sample, these Sn sites seemed to be the dominant Sn^{4+} species. However, in the SnTf-MCM-41 catalysts, the additional observed band (centered at ca. 289 nm, assigned to charge transitions

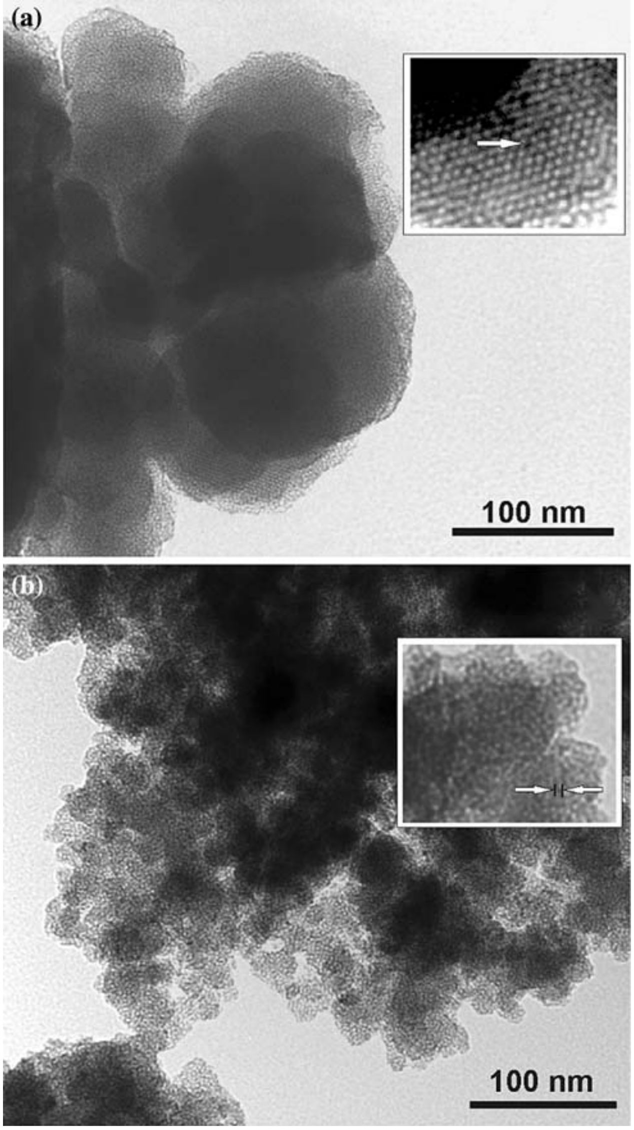


Fig. 3 TEM images of **a** SnTf-MCM-41 [the inset shows an enlarged (×5) image], **b** SnTf-UVM-7 catalysts [the inset shows an enlarged (×3) image]

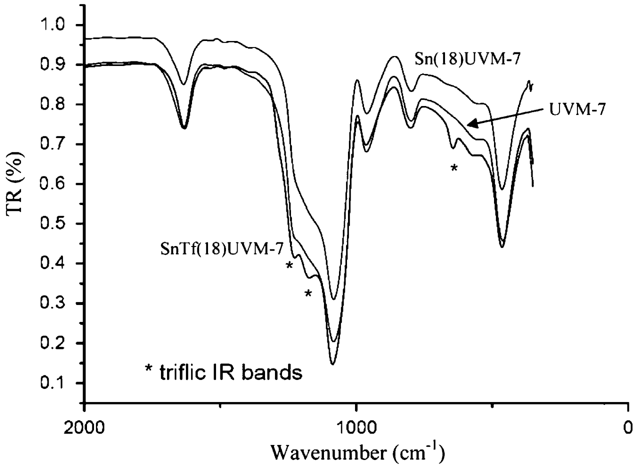


Fig. 4 Comparative FTIR spectra of UVM-7, Sn(18)-UVM-7, and SnTf(18)-UVM-7 samples

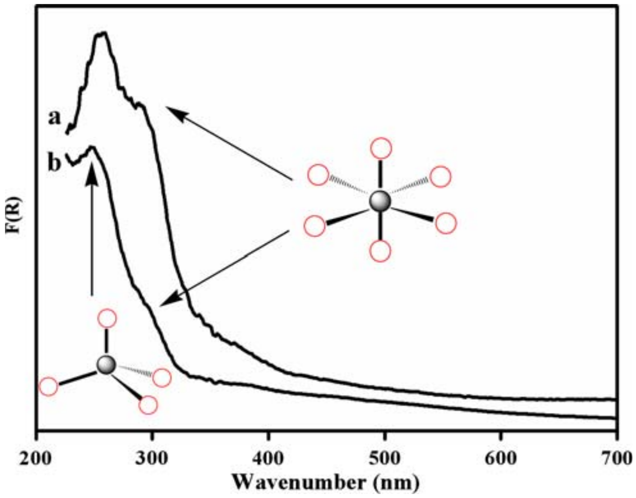


Fig. 5 Diffuse reflectance UV–vis spectra of (*a*) SnTf-MCM-41 and (*b*) SnTf-UVM-7 catalysts

from O^{2-} to Sn^{4+} in octahedral environments with a certain degree of polymerization [24]) could be associated with the existence of small casiterite-like nanodomains (Fig. 5) with a subsequent decrease in active sites from ca. 30 to 50% for low and high Sn-containing MCM-41 samples, respectively.

Table 1 Physical characteristics of the prepared catalysts

Samples	d_{100} (nm)	S_{BET} (m^2/g)	Small pore (nm)	Large pore (nm)
MCM-41	3.9	1050	2.6	–
Sn-MCM-41	4.0	937	2.5	–
SnTf(51)-MCM-41	3.7	812	3.1	–
SnTf(47)-MCM-41	3.7	878	2.6	–
SnTf(22)-MCM-41	4.1	725	2.5	–
UVM-7	4.2	1075	3.0	66.5
Sn-UVM-7	4.8	820	2.4	32.3
SnTf(18)-UVM-7	4.5	646	2.1	36.6

Table 2 Chemical characteristics of the prepared catalysts

Samples	Si/Sn	Sn/S	Number centers/m^2 [a]	$Sn_y(O,OH)_z$ (% moles)	$Sn(OTf)_x$ (% moles)
SnTf(22)-MCM-41	21.8	2.3	2.31×10^{20}	2.47	1.90
SnTf(47)-MCM-41	47.3	1.4	1.29×10^{20}	0.58	1.45
SnTf(51)-MCM-41	50.8	1.3	1.22×10^{20}	0.43	1.44
SnTf(18)-UMV-7	18.4	1.1	2.66×10^{20}	0.48	4.72

[a] Based on the NH_3-chemisorption measurements

This tendency to form Sn–O–Sn bonds is due to the higher pH values used for preparing MCM-41 materials compared with that used for preparing UVM-7.

NH_3-chemisorption data showed that mesoporous tin precursors practically do not chemisorb ammonia suggesting the absence of any acidity. Based on the NH_3 chemisorbed uptake (cm^3 (STM)/g), the highest number of acid centers was determined for the SnTf(22)-MCM-41 and SnTf(18)-UMV-7 catalysts, namely for those for which it was determined the higher tin amount (Table 2). Therefore, based on these results, one can conclude that indeed the active sites correspond to triflates anchored on highly dispersed tin species.

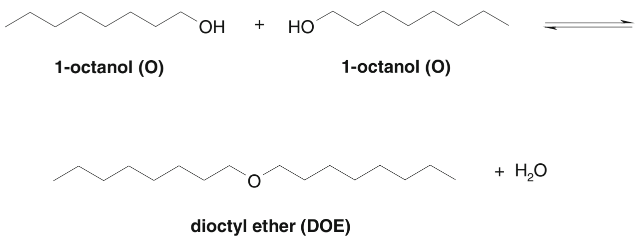
A summary of the chemical characteristics of the prepared catalysts is given in Table 2.

Catalytic tests

Etherification of 1-octanol

Mesostructured SnTf-based catalysts were primarily assessed in the etherification of 1-octanol, a reaction relevant for the synthesis of emulsifiers for cosmetic applications and of additives for diesel fuels (Scheme 1). The relatively large molecular size of the reactant (1-octanol) and product (dioctyl ether) makes them more readily manageable over catalytic materials within the mesoporous range of pore size, in comparison with a more traditional acid-based catalyst such as microporous zeolites (e.g., BEA zeolite, [11]).

Figure 6 shows the evolution of the conversion of 1-octanol on time over SnTf-based catalysts in the batch reactor. Under the selected reaction conditions (150 °C and 3 wt% of catalyst) all the catalysts displayed moderate conversions. After 24 h only on SnTf(18)-UMV-7 it reached 75%. This catalyst (2.66×10^{20} acid centers/m^2, 0.48% moles $Sn_y(O,OH)_z$, and 4.72% moles $Sn(OTf)_x$, Table 2) is more active than other samples, the poorest catalyst being SnTf(22)-MCM-41 (2.32×10^{20} acid centers/m^2, 2.47% moles $Sn_y(O,OH)_z$, and 1.90% moles $Sn(OTf)_x$, Table 2). This fact indicates that the acid strength is strongly correlated with the population of highly dispersed $Sn(OTf)_x$ species. On the contrary, a small population of these species is corresponding to a low activity for this reaction. Moreover, a high amount of small casiterite-like $Sn_y(O,OH)_z$ nano-domains, exhibiting a basic character, led to a strong decrease of the conversion of 1-octanol (e.g., SnTf(22)-MCM-41 sample).



Scheme 1 Etherification of 1-octanol to dioctyl ether (DOE)

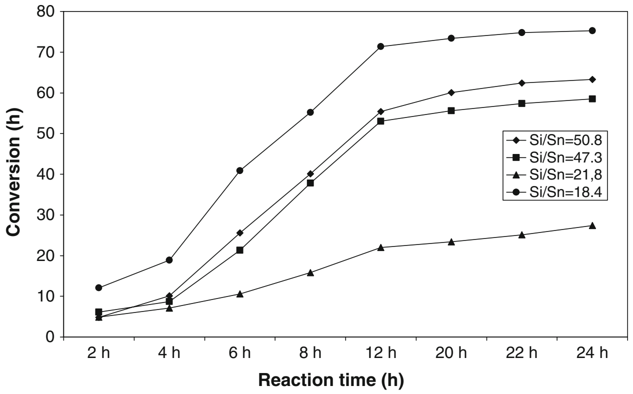


Fig. 6 The evolution of the conversion of 1-octanol on time

Obviously, acid solids are subjected to poisoning by water in reactions where this highly polar molecule is involved as solvent, reactant, or product [14]. This effect may explain the differences observed among the SnTf-MCM-41 catalysts. SnTf(22)-MCM-41 catalysts contains a higher population of $Sn(OTf)_x$ species (1.90% moles $Sn(OTf)_x$, Table 2) than SnTf(51)-MCM-41 (1.44% moles $Sn(OTf)_x$, Table 2) and in concordance it was expected to exhibit a higher activity. However, the stronger interaction between the acid groups of this catalyst and water molecules generated during the reaction is responsible for the partial blocking of active sites hindering the access of the alcohol molecules to the triflic sites and, in consequence, the progress of the etherification. It is well known that the hydrophilicity of the catalysts is of a paramount importance in determining their activity in water-mediated reactions.

In a reaction medium where the different chemical species show large differences in polarity, the hydrophilic–hydrophobic balance on catalyst's surface is an important parameter modulating the transformation rates [25]. Both 1-octanol (dielectric constant at 50 °C: 10.3) and the resultant dioctyl ether (DOE, dielectric constant at 50 °C: 5.3) display low polarities in contrast with water molecules (dielectric constant at 50 °C: 80.4). Thus, in media as the present one, resulted water is generating water microenvironments surrounding acidic moieties via hydrophilic interactions.

High reaction temperature (150 °C) disrupts the water microenvironments liberating part of the active sites while the high-surface area of silica acts as a dehydrating support. Evidence in this sense is the fact that working below 100 °C the conversion was less then 30% irrespective of the catalyst used.

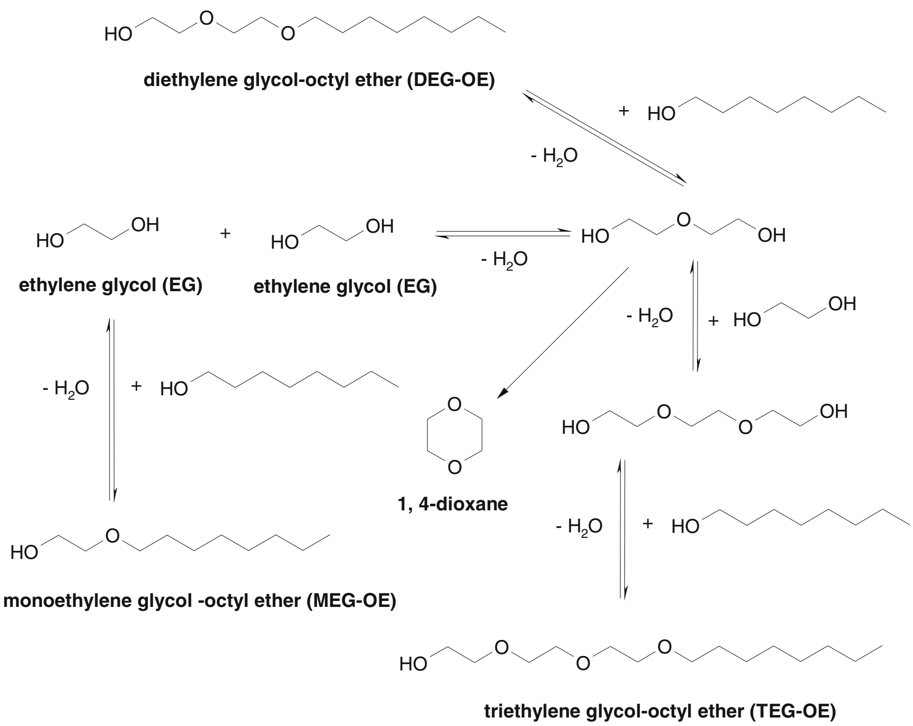
Regardless of the relative amount of heteroelements, a very similar density of silanol groups at the silica surface occurs for both MCM-41 and UVM-7-based catalysts [26]. Then, no significant differences dealing with the hydrophobic/hydrophilic character are expected, and a similar dehydrating ability for the pure silica domains at the catalyst surface must be assumed. However, the pore system architecture is playing a key role in the evolution of water molecules. Hence, the typical hierarchic pore system of UVM-7 materials (with intra-particle mesopores of nanometric length) confers them a remarkable open nature, this favoring the accessibility of the reagents to the active sites and also the evolution of the reactants (DOE and water). On the contrary, the presence of unimodal, non-interconnected, and long (micrometric) mesopores in MCM-41-like catalysts constitutes a clear handicap for water evolution when compared to UVM-7-like materials. The result is a lower proportion of water inside the pores under working conditions leading to an "apparent" relative hydrophobic character of the catalyst. Therefore, the high activity of SnTf(18)-UVM-7 sample can be related, not only to the strong acidity of highly dispersed $Sn(OTf)_x$ species but also to the "apparent" hydrophobic character of the silica surface which reduces the acid site blockage associated with the adsorption of water generated by the reaction.

Etherification of ethylene glycol with 1-octanol

Ethoxylated surfactants can be tailor-made with a high precision with regard to the average number of oxyethylene units added to a specific hydrophobe, e.g. a fatty alcohol. However, the ethoxylation invariably gives a broad distribution of chain lengths. If all hydroxyl groups, i.e., those of the starting alcohol and of the resulted glycol ethers have the same reactivity, a Poisson distribution of oligomers would be obtained [27].

The etherification of ethylene glycol (EG) with 1-octanol is a complex acid catalyzed consecutive reaction leading to mono-, di-, and tri-oxyethylene units. Moreover, 1-octanol can react itself leading to symmetric alkyl ethers, while ethylene glycol is generating low amounts of 1,4-dioxane (Schemes 1 and 2). This is an advantage upon the homogeneous acid catalyzed ethoxylation (e.g., $SnCl_4$ or

Scheme 2 Possible reaction pathways in the etherification of ethylene glycol with 1-octanol



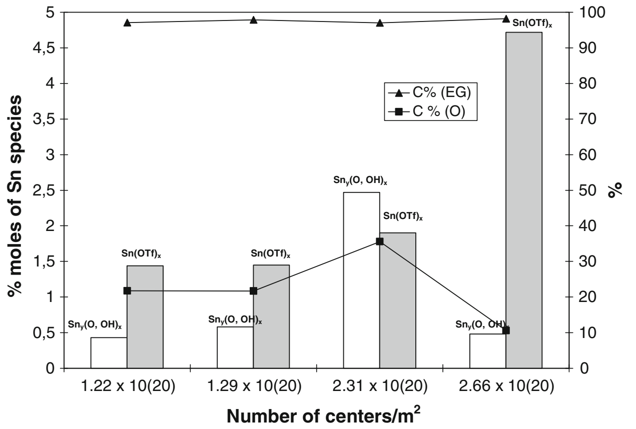


Fig. 7 The variation of the ethylene glycol (EG) and 1-octanol (O) conversions as a function of the sites density on m^2 and the % moles of Sn species (EG/O = 1/3, 150 °C, 1 h)

BF$_3$ Lewis acids) which suffers from the drawback of 1,4-dioxane being formed in considerable quantities as by-product [28].

As Fig. 7 shows, EG is converted in a high degree on all used catalysts (>97%), while 1-octanol is transformed only in a low degree (10–22%).

On the other hand, if the conversion of EG is almost constant irrespective of the density of acid sites or the nature of the Sn species, the conversion of 1-octanol depends not only on the density of acid sites but also on the nature of Sn species. Indeed, when Sn(OTf)$_x$ species predominates in the favor of Sn$_y$(O, OH)$_x$ species the conversion of 1-octanol decreases.

The high conversion of ethylene glycol can be assigned to its higher dielectric constant (37.0, 50 °C) in comparison with that one of 1-octanol (10.3, 50 °C). In fact, the distribution of the reaction products is the result of the competition between the two molecules for the active sites.

As for the etherification of 1-octanol, the distribution of the reaction products varies as a function of the population of the Sn(OTf)$_x$ species (Fig. 8). The etherification of ethylene glycol to diethylene glycol ether, followed by its condensation with 1-octanol to DEG-OE occurs on all catalysts, but the level of the selectivity depends on the population of the Sn(OTf)$_x$ species. A small population of Sn(OTf)$_x$ species is corresponding to a low selectivity. This explains the results obtained on SnTf(51)-MCM-41 where the coupling of ethylene glycol to 1,4-dioxane and the etherification of 1-octanol to dioctyl ether become favored leading to a decrease of the selectivity for the etherification of ethylene glycol with 1-octanol (Fig. 8).

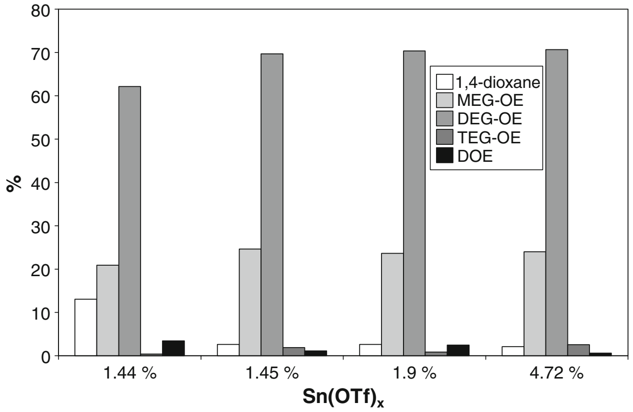


Fig. 8 The distribution of the reaction products as a function of the Sn(OTf)$_x$ species content and the support nature (EG/O = 1/3, 150 °C, 1 h)

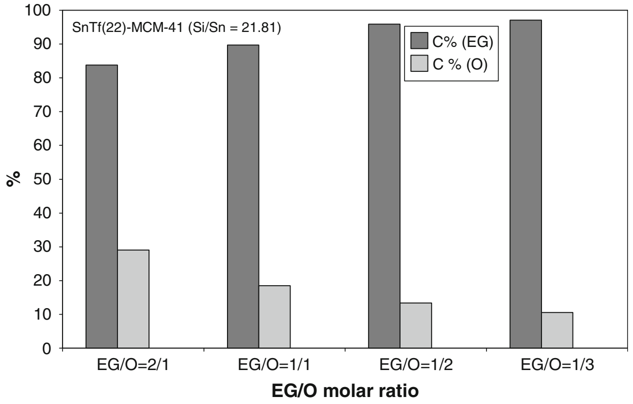


Fig. 9 The influence of the EG/O molar ratio upon the activity of SnTf(22)-MCM-41 (Si/Al = 21.81) catalyst (150 °C, 1 h)

The effect of the ethylene glycol to 1-octanol molar ratio was studied on SnTf(22)-MCM-41 (Si/Sn = 21.81) catalyst ranging this ratio from 2:1 to 1:3. The conversion of ethylene glycol increased from 83.8 to 97.1% as the mole ratio of ethylene glycol to 1-octanol increased from 2:1 to 1:3 (Fig. 9). On the other hand, when the 1-octanol initial concentration was five times higher (EG/O = 1/3 instead 2/1) the conversion of 1-octanol was approximately three times lower (10% instead of 29%). This indicates that when the catalyst surface is fully covered with alcohol the reaction rate is lower than in the case of a partially covered catalyst surface. Such a behavior suggests an additional inhibiting effect exerted by the reactant itself, i.e., the 1-octanol, than an inhibition of ethylene glycol.

A similar behavior was reported by Françoise and Thyron [29] for ethanol in the synthesis of ethyl *tert*-butyl ether catalyzed by Amberlyst-15. They ascribed this behavior to the occurrence of two different mechanisms depending on the concentration of ethanol. A high concentration of ethanol induces a salvation of the acid sites decreasing their acidity strength. In our case the conversion of EG paralleled the selectivity to DEG-OE (Fig. 10).

As Fig. 10 shows the selectivity to by-products like 1,4-dioxane and dioctyl-ether is quite high at an excess of

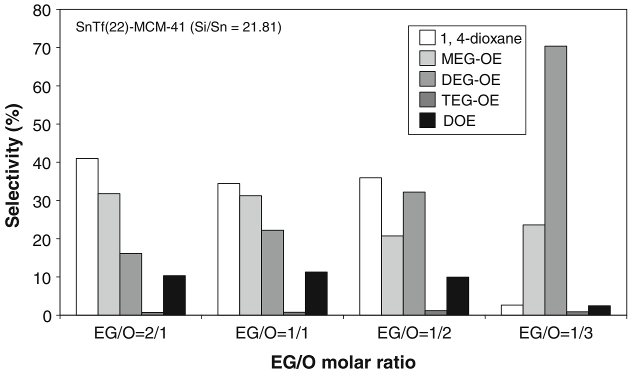


Fig. 10 The distribution of the reaction products as a function of the EG/O molar ratio in the presence of SnTf(22)-MCM-41 (Si/Al = 21.81) catalyst (150 °C, 1 h)

ethylene glycol in the reaction mixture (EG/O = 2/1). Once the concentration of 1-octanol start to increase (from EG/O = 2/1 to EG/O = 1/3), the formation of by-products starts to be suppressed in the favor of an increased selectivity to DEG-OE.

Longer reaction times (until 24 h) correspond to higher 1-octanol conversions. After 1 h the conversion of ethylene glycol was already higher than 97%. As expected, after that 1-octanol was further converted to dioctyl ether. After 24 h the selectivity in this product reached 62%.

Recycling these catalysts for five times in the above reactions was not accompanied by any visible loss in activity and selectivity. Moreover, the chemical analysis of the reaction products clearly indicated no leaching of the active species.

Conclusions

Our data demonstrate that on the investigated SnTf-MCM-41 and SnTf-UVM-7 catalysts, triflate is associated with well dispersed tin species. The synthesis of these catalysts was achieved in two steps, generating triflic acid incorporated into previously synthesized mesoporous tin-containing silicas.

Both SnTf-MCM-41 and SnTf-UVM-7 catalysts showed activity in the preparation of symmetrical long chain ethers and non-ionic surfactants structures. A high density of highly dispersed $Sn(OTf)_x$ species (e.g., SnTf(22)-MCM-41 catalyst) is detrimental for symmetrical long chain ethers synthesis. A low population of $Sn(OTf)_x$ species (e.g., SnTf(47)-MCM-41 and SnTf(51)-MCM-41) led to a low selectivity to non-ionic surfactants structures, the formation of 1,4-dioxane as a by-product being favored.

Under these conditions the hydrophobicity of the catalyst surface was found to be important. The combination of the concentration of the acidic sites with a relative high "apparent" hydrophobic character of the support (e.g., SnTf(18)-UVM-7 sample) is effective for the etherification of glycol with 1-octanol.

Acknowledgements The authors thank the MEC (CTQ2006-15456-C04-03/BQU) for financial support. Jamal El Haskouri thanks the Ministry of Science and Technology from Spain for a Ramon & Cajal contract. We also thank the CNCSIS (Grant 44GR/2008, COD CNCSIS 1071, and PNCDI II 40/2007) for the financial support.

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