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Etherification of benzyl alcohols with 1-hexanol over organosulfonic acid mesostructured materials

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Abstract

Etherification of benzyl alcohols with 1-hexanol was performed in liquid-phase over propyl- and arene-SO$_3$H-modified mesostructured SBA-15 silica. H$_2$O TPD measurements indicate a stronger interaction of arene-sulfonic acid sites with water molecules than that occurring in propyl-sulfonic groups. Hence, the higher catalytic activity of propyl-sulfonic-modified SBA-15 material is related to the more hydrophobic microenvironment of –SO$_3$H sites which reduces the acid site deactivation associated with adsorption of water generated during the reaction. Moreover, propyl- and arene-sulfonic functionalized SBA-15 materials show a clear improvement of the catalytic performances as compared to other commercial homogeneous and heterogeneous acid catalysts in this particular reaction.
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1. Introduction

Conventional homogeneous acid catalysts, such as H$_2$SO$_4$, HF or AlCl$_3$ are widely used in the industrial chemical processes to synthesize bulk and fine chemicals, but they have serious drawbacks concerning hazards in handling, corrosiveness, difficult separation, and production of toxic waste. Restrictions in environmental legislation are driving the chemical industries to consider alternative processes to avoid the use of these conventional homogenous mineral acids as catalysts [1,2]. The heterogenisation of homogeneous catalysts and their use in the production of fine chemical synthesis has become a major research area, since the potential advantages of these materials (simplified recovery and reusability) over homogeneous systems can introduce positive environmental consequences [3,4]. Most of the novel acid-solid catalysts are based on silica supports, primarily because silica displays some advantageous properties, such as excellent stability (chemical and thermal), good accessibility due to high surface areas, and the fact that organic moieties can be robustly anchored to the surface to provide heterogeneous catalytic acid sites. However, a suitable system must

not only give environmentally more benign processes, but also should exhibit activities and selectivities comparable or superior to the existing homogeneous route.

In the present work the etherification of benzyl alcohols, such as the vanillyl alcohol (4-hydroxy-3-methoxybenzyl alcohol) which is a derivative of vanilline, with a middle length-chain linear alcohol such as the 1-hexanol, has been studied. The selection of benzyl alcohols as etherification substrates has two major reasons: on the one hand due to their interest in some fine chemistry applications for the production of fragrances and flavourings and on the other hand because they are relatively bulky molecules which are not readily worked up over microporous catalysts such as conventional acid-zeolites. In the etherification of benzyl alcohols, the most used homogeneous catalyst is H$_2$SO$_4$, and when heterogeneous catalyst has been proposed as alternative, acid-zeolites and sulfonic acid functionalized resins have been the predominant materials. A German patent application DE-4434823 [5] discloses the preparation of ethers from benzyl alcohols reacting a hydroxybenzyl alcohol with an aliphatic one in the presence of a SO$_3$H-functionalized polystyrene resin (Amberlyst® A21). This kind of resin is hardly regenerable and the reaction yields are not too high. These drawbacks limit the feasibility of an industrial application. U.S. Patent No. 6362378 [6] shows a complete study including several etherifications with different benzyl alcohols employing a solid-acid catalyst

comprising certain amounts of acid-zeolites (Beta, Y, X, mordenite, ZSM family, etc.). Catalytic results obtained over these catalysts are acceptable for the majority of substrates.

New kind of acid-solids have emerged in the last years based on sulfonic acid groups contained in mesostructured MCM-41, HMS and SBA-15 materials [7–12]. Likewise, the increasing of acid strength by close attachment of different electron-withdrawing moieties to the sulfonic site (arene-sulfonic [12] and perfluorosulfonic groups [13,14]) as well as the hydrophobicity control of the microenvironment surrounding sulfonic acid sites [15] have opened up definitively the catalytic application of these materials. These sulfonated mesoporous silicas have been already tested in a broad variety of acid catalyzed reactions (esterifications [10,16,17], condensations and additions [8,18,19], etherifications [20], rearrangements [21–23], Friedel–Crafts acylations [24] and alkylations [23], ...) and in most of the cases showing better catalytic performance than conventional homogenous and heterogeneous catalysts.

Herein, a detailed study of the catalytic performance of these sulfonic acid-modified SBA-15 materials on the liquid-phase etherification of benzyl alcohols with 1-hexanol, never reported before, is carried out. Attention was brought on the comparison of their catalytic properties with other acid catalysts and on the effect of water production during the reaction, since these materials are expected to be hydrophilic and hence poisoning by water might occur [25].

2. Experimental

2.1. Catalysts preparation

Propyl-sulfonic acid functionalized mesostructured silicas (Samples 1 and 2) were synthesised as follows: 4 g of Pluronic 123 (Aldrich) were dissolved under gentle stirring in 125 g of 1.9 M HCl at room temperature. The solutions were heated to 40 °C and then tetraethylorthosilicate (TEOS, Aldrich) was added. A prehydrolysis time for TEOS species of 45 min was considered. Following this TEOS initial hydrolysis stage, mercaptopropyltrimethoxysilane (MPTMS, Aldrich) and an aqueous solution of H_2O_2 (30 wt%, Merck) were added at once. The resulting mixtures were stirred at 40 °C for 20 h and aged at 100 °C for an additional time of 24 h under static conditions. After synthesis, the solid products were recovered by filtration and air-dried overnight. Template molecules were removed from as-synthesised materials by washing with ethanol under reflux for 24 h (2 g of as-synthesised material per 200 mL of ethanol). The molar composition of the mixture, relative to 4 g of copolymer, was: $(0.0369 - X)$ TEOS:$(0.0041 + X)$ MPTMS:$(0.0369 + 9X)$ H_2O_2:0.24 HCl:≈6.67 H_2O. The amount of sulfur precursor (MPTMS) was fixed to provide 10% or 20% of total silicon atoms functionalized with sulfonic groups ($X = 0$ and 0.0041 for Samples 1 and 2, respectively).

Arene-sulfonic acid functionalized mesostructured silicas (Samples 3 and 4) were synthesised as described for the functionalized mesostructured solid above. Following TEOS prehydrolysis, chlorosulfonyl-propyl-trimethoxysilane (CSPTMS,

Gelest) was added and the resulting mixtures were stirred at 40 °C for 20 h, and aged at 100 °C for an additional period of 24 h under static conditions. The solid products were recovered and the template removed as previously described. The molar composition of the mixtures for 4 g of polymer was: $(0.0369 - X)$ TEOS:$(0.0041 + X)$ CSPTMS:0.24 HCl:≈6.67 H_2O. The amount of the precursor for arene-sulfonic acid groups (CSPTMS) was fixed at 10% or 20% of total silicon atoms ($X = 0$ and 0.0041 for Samples 3 and 4, respectively).

Other commercial acid catalysts. Methanesulfonic acid (CH_3SO_3H), *p*-toluenesulfonic acid ($C_7H_7SO_3H$), Nafion-SiO_2 composite (SAC-13) and Amberlyst-15 were supplied by Sigma–Aldrich. Arene-sulfonic acid and propyl-sulfonic acid functionalized non-ordered silica materials were acquired from Silicycle. Zeolite Al-beta (Si/Al molar ratio = 41) was synthesized in our research group following standard fluoride-mediated procedures [26].

2.2. Catalyst characterization

Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics TRISTAR 3000 system. The data were analysed using the BJH model and the pore volume (V_p) was taken at $P/P_o = 0.975$ single point. X-ray powder diffraction (XRD) patterns were acquired on a PHILIPS X'PERT diffractometer using Cu Kα radiation. The data were recorded from 0.6 to 5° (2θ) with a resolution of 0.02°. Cation-exchange capacities corresponding to the sulfonic acid mesostructured materials were determined using aqueous solutions of sodium chloride (NaCl, 2 M) as cationic-exchange agent. In a typical experiment, 0.05 g of solid was added to 15 g of aqueous solution containing the sodium salt. The resulting suspension was allowed to equilibrate and thereafter was titrated potentiometrically by dropwise addition of 0.01 M NaOH (aq). Sulfur and organic content were determined by means of Elemental Analysis (HCN) in a Vario EL III apparatus, and by means of thermogravimetry analysis (SDT 2960 Simultaneous DSC-TGA, from TA Instruments). Aluminum content in the zeolitic catalyst was determined by atomic emission spectroscopy with induced coupled plasma (ICP-AES) collected with a Varian Vista AX system. Table 1 summarizes the most relevant physicochemical properties for sulfonic acid-modified mesostructured material, and Table 2 incorporates characterization data (textural properties and acid capacities) corresponding to the commercial acid catalysts.

Temperature programmed desorption (TPD) experiments were carried out in a Micromeritics AutoChem 2910 equipment provided with thermal conductivity detector (TCD) using helium as carrier gas. Previously to the TPD experiment, the adsorbent sample was introduced in a quartz tube and outgassed in 30 cm^3 min^{-1} He flow by thermal treatment at 150 °C for 15 min, heating at 50 °C min^{-1} from room temperature. After cooling to 40 °C, the material was contacted with the gas-phase water until saturation by successive injections of adsorbate pulse, in amounts ranging from 0.1 to 2 μL under He flow. The reversibly adsorbed water was then removed in He flow for 2 h at 40 °C. The completion of this physidesorption process was confirmed

Table 1
Physicochemical, textural and acidic-related properties for sulfonic acid-modified mesostructured materials

Sample	Type	Textural properties				
		d_{100}[a] (Å)	Pore size[b] (Å)	BET area (m²/g)	Pore volume[c] (cm³/g)	Wall thickness[d] (Å)
1	Pr-SO₃H (10%)	97	82	666	1.23	30
2	Pr-SO₃H (20%)	98	62	630	0.68	51
3	Ar-SO₃H (10%)	102	80	720	0.93	37
4	Ar-SO₃H (20%)	103	76	733	0.81	43

Sample	Type	Acid capacities[e]			
		Titration[f]	Sulfur content[g]	Theoretical sulfur content[h]	S incorporation[i] (%)
1	Pr-SO₃H (10%)	1.58 (1.21)	1.52 (1.17)	1.67 (1.29)	91
2	Pr-SO₃H (20%)	2.74 (1.97)	2.85 (2.05)	3.33 (2.36)	86
3	Ar-SO₃H (10%)	1.71 (1.24)	1.66 (1.20)	1.67 (1.21)	99
4	Ar-SO₃H (20%)	2.87 (1.78)	2.87 (1.78)	3.33 (2.06)	86

[a] d (1 0 0) spacing, measured from small-angle X-ray diffraction.
[b] Pore size (D_p) from adsorption branch applying the BJH model.
[c] The pore volume (V_p) was taken at $P/P_o = 0.975$ single point.
[d] Pore wall thickness calculated by a_o-pore size ($a_o = 2d(1 0 0)/\sqrt{3}$).
[e] All the acid capacities defined as mmol of H⁺ per gram of SiO₂ (the amount of SiO₂ was obtained as the final residue in the TG analysis up to 700 °C) and as mmol of H⁺ per gram of sample (in brackets).
[f] Titration using NaCl 2N as ionic exchanger.
[g] Sulfur content calculated from elemental and TG analysis.
[h] Expected acid capacity at 100% of incorporation of sulfur precursors (MPTMS or CSPTMS).
[i] Sulfur incorporation estimated from sulfur content and theoretical content, assuming 100% incorporation of TEOS.

by the recovery of the baseline from TCD. TPD tests were carried out by heating the sample with a ramp of 15 °C min⁻¹ between 40 and 300 °C with constant He flow, finally keeping constant the latter temperature for an additional period of 15 min. The water concentration in the effluent is continuously monitorized by the TCD detector during all the experiment. Two parameters are derived from the TPD curves: the amount of water retained and desorbed by the solid (W_{H_2O}) and the temperature corresponding to the maximum of the desorption peak (T_{H_2O}).

2.3. Catalytic tests

Etherification runs were performed in liquid-phase at 50 °C in a stirred teflon-lined stainless-steel autoclave under autogenous pressure (with an initial nitrogen pressure of 4 bar in order to ensure liquid-phase for both reactants). Reaction temperature was controlled using a thermocouple immersed into the reac-

Table 2
Physicochemical and textural properties for commercial acid catalysts

Catalyst	S_{BET} (m²/g)	Pore size (Å)	Acid capacity[a]
Methanesulfonic acid	–	–	10.4
Toluenesulfonic acid	–	–	5.3
Propyl-SO₃H silica	301	20–200	1.0
Arene-SO₃H silica	279	20–200	0.8
Amberlyst-15	45	Macroporous	4.8
SAC-13 (Nafion™-SiO₂)	200	>100	0.12
Beta zeolite	400	5.6 × 6.5, 5.7 × 7.5	0.40 (Si/Al = 41)[b]

[a] mmol of acid centers per gram of catalyst.
[b] Al content by ICP-AES analysis.

tion mixture. In order to monitor the reaction, samples were withdrawn periodically at time intervals ranging from 0 to 2 h. Typically, the weight composition of the reaction mixture was: 30 g of 1-hexanol (which acted also as solvent), 3 g of benzyl alcohol (vanillyl, anisyl or 4-hydroxybenzyl alcohol) and a catalyst loading of 0.03 g (0.1 wt%). Reaction samples were analyzed by GC (Varian 3900 chromatograph) using a CP-SIL 8 CB column (30 m × 0.25 mm, d.f. = 0.25) and a FID detector. Benzyl ether was the unique detected reaction product. Control tests were carried out where no vanillyl alcohol was added (just 1-hexanol and catalyst), in order to evaluate the possible homo-condensation of 1-hexanol. No activity was detected as no ether ("di-hexyl ether" in this case) was observed. Thus, selectivity of vanillyl alcohol towards benzyl ether was considered to be 100%. Likewise, selected reaction conditions yielded no conversion of benzyl alcohols in absence of catalyst. Catalytic results are shown either in terms of absolute conversion of the corresponding benzyl alcohol or in terms of initial reaction rate values (mmol of reacted alcohol per gram of catalyst and minute), calculated for the first 5 min of reaction. In order to distinguish among the catalytic activity of different acid groups from different surface microenvironments, a specific initial reaction rate per acid site has also been utilized (mmol of reacted alcohol per minute and mmol of acid site after 5 min of reaction).
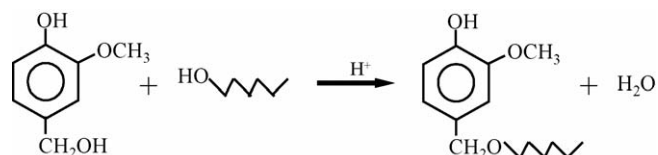
3. Results and discussion

Physicochemical properties of sulfonic acid-modified SBA-15 materials are summarized in Table 1. Data from XRD and nitrogen adsorption isotherms evidence high mesoscopic ordering of the different propyl- and arene-sulfonic acid-modified mesostructured SBA-15 materials (Samples 1–4). Likewise,

Scheme 1. Etherification of vanillyl alcohol with 1-hexanol.

high surface areas along with narrow pore size distributions around 7 nm are obtained (size enough to avoid the steric constraints imposed by the pore size when relatively bulky substrates such as benzyl alcohols are considered). It is important to note that every synthesised sample shows close agreement between ion-exchange capacity (measured by acid titration) and sulfur loading (determined by elemental analysis) independently of the synthesis conditions (acid capacities, Table 1). This is clear evidence indicating that most of the SO_3H groups are located on the pore walls, thus being accessible and useful for adsorption and catalytic reaction processes. In order to test the relevancy of the acid strength corresponding to each catalytic site in this particular reaction, two sulfonic acid moieties with different nature (propyl and arene) have been considered.

Mesostructured sulfonic acid catalysts were primarily assessed in the etherification of a benzyl alcohol, specifically the vanillyl alcohol (4-hydroxy-3-methoxybenzylalcohol), with 1-hexanol to yield 4-hydroxy-3-methoxybenzyl-1-hexyl ether, a reaction relevant to the production synthesis of flavourings and fragrances (Scheme 1).

This acid-catalyzed reaction has been chosen as an appropriate example due to the high added value of the produced ethers in fine chemicals industry. Furthermore, the relatively large molecular size of the reactants (benzyl alcohols) and products (benzyl ethers) makes them more readily manageable over catalytic materials within the mesoporous range of pore size, in comparison with more traditional acid-based catalyst such as microporous zeolites.

Fig. 1a shows the evolution of conversion of vanillyl alcohol with reaction time in the batch reaction over Samples 1 and 3 (10 mol% propyl- and arene-SO_3H functionalized SBA-15, respectively). Both catalyst displayed high conversion rates using the selected reaction conditions (50 °C and 0.1 wt% of catalyst), reaching values over 70% after 2 h. In contrast with other reported catalytic applications for the same samples [21,23,24], the 10 mol% propyl-SO_3H-modified material (Sample 1) provides higher reaction rates and conversion values than the 10 mol% arene-SO_3H one (Sample 3). This fact indicates that the acid strength of alkyl-sulfonic acid group is high enough to effectively catalyze this chemical transformation, and an increase in acid strength (arene-SO_3H groups as compared with propyl ones, [12]) supposes a decay in the activity for this reaction. Surprisingly, when materials with higher loading of sulfonic acid groups (20 mol%, Samples 2 and 4, Fig. 1a) are used, reaction rates and conversion values are decreased, which is also in contrast with previous catalytic tests concerning these materials where a high accessibility of acid sites for catalytic purposes was readily demonstrated [21,24]. In summary, there are evidences of
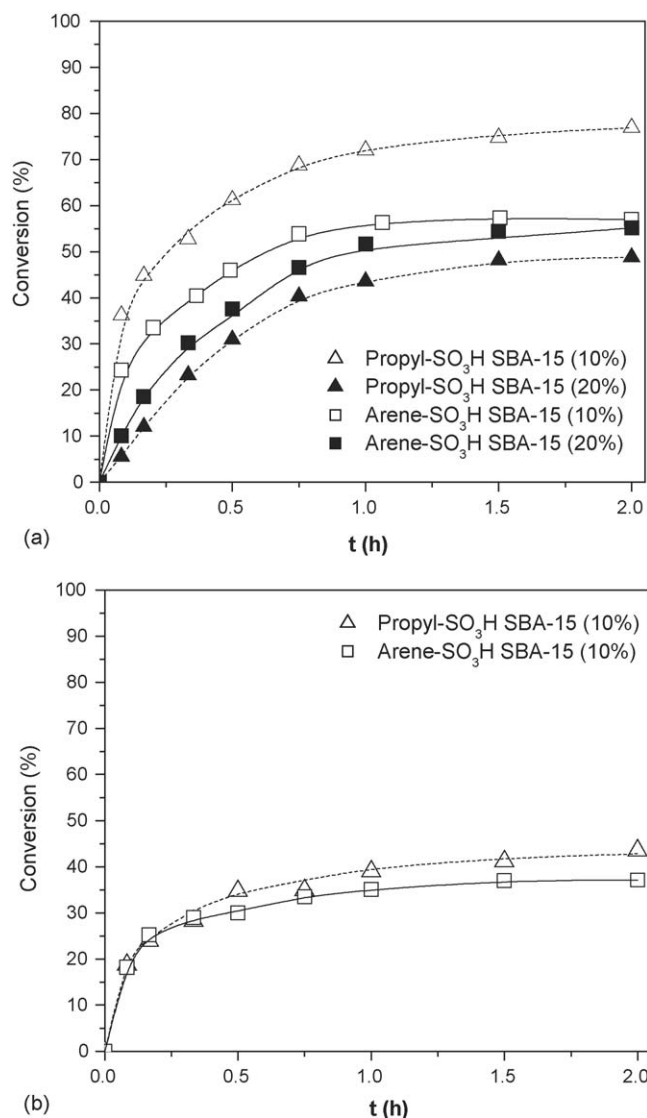

Fig. 1. (a) Conversion of vanillyl alcohol over SBA-15 materials functionalized with 10 and 20 mol% of propyl- and arene-SO_3H groups (Samples 1–4). (b) Conversion of vanillyl alcohol over SBA-15 materials functionalized with 10 mol% of propyl- and arene-SO_3H groups (Samples 1 and 3); when small amounts of water (1 wt% referred to total reaction mass) are added to reaction medium.

detrimental effects coming from increasing either acid strength or density of the SO_3H moieties.

Acid solids are subjected to poisoning with water in reactions where this highly polar molecule is involved as solvent, reactant or product. Hence, the lower catalytic performance displayed by the arene-SO_3H sample, despite of its higher acid strength, and by the highly SO_3H-loaded samples might be attributed to a stronger interaction between the sulfonic acid groups of these catalysts and water molecules generated during reaction. This interaction would lead to the partial deactivation of active sites hindering the access of alcohol molecules to the sulfonic sites. Such moieties constitute relatively highly hydrophilic groups, especially in the case of the more acidic arene-sulfonic acid groups or when they are in high concentrations [27]. Then, the hydrophilicity of the catalysts is of paramount

Table 3
Water TPD results over different catalysts

Sample	Type	T_{H_2O}[a] (°C)	W_{H_2O}[b]		
			(mg/g)	(mmol/g)	(mmol/mmol H$^+$)[c]
SBA-15	Silica	83	0.74	0.04	–
1	Propyl-SO$_3$H (10%)	119	13.81	0.77	0.64
3	Arene-SO$_3$H (10%)	139	14.55	0.81	0.81

[a] Temperature corresponding to the maximum of the water desorption peak.

[b] Water amount retained and desorbed by the solid in a temperature range of 50–200 °C.

[c] Water amount retained and desorbed by the solid referred to the number of acid sites.

importance in determining their activity in water-mediated reactions.

To compare the hydrophilicity of the samples, H$_2$O-TPD measurements were carried out. Table 3 summarises the amounts of water desorbed for Samples 1, 3 and pure-silica SBA-15 (control sample). It must be noted that the adsorbed-desorbed amounts of water, showed in Table 3, correspond to results obtained in dynamic experiments carried out in continuous helium flow and with a previous physidesorption step to remove all the reversibly retained adsorbate. Accordingly, the adsorption amounts shown account only for the adsorbate which is strongly linked to the adsorbent by direct interaction with the internal pore walls, being significantly smaller than the adsorption capacity corresponding to the total pore filling of the adsorbent (pore volumes shown in Table 1). The TPD curves for water over sulfonic acid-modified SBA-15 samples show two desorption peaks, the first one corresponding to the desorption of water (100–200 °C) and the second one over 200 °C arising from the decomposition of propyl and arene-SO$_3$H moieties and from dehydration of surface Si-OH groups. In this work, we have assumed that desorption below 200 °C essentially derives from water molecules interacting strongly with acid sites. This assumption is valid since decomposition of SO$_3$H moieties occurs at higher temperature ranges (observed in TGA data [11,12]). Shimizu et al. also employed this approximation for TPD results over sulfonic acid-modified silica samples [28]. Thus, amounts of desorbed water and temperature corresponding to the maximum of the desorption peak in TPD experiments, shown in Table 3, can be used to compare hydrophilicity of the samples.

As can be concluded from data shown in Table 3, both SO$_3$H-modified mesostructured samples are more hydrophilic than the non-functionalized one. They adsorb about 20 times more water (expressed as mg g^{-1}) than the pure-silica material. Additionally, the temperature corresponding to the maximum desorption peak is also higher, which indicates stronger interaction between the solid and H$_2$O molecules. Comparing both types of SO$_3$H groups, arene-SO$_3$H ones give higher W_{H_2O} and T_{H_2O} values to that observed for propyl-sulfonic groups. Furthermore, considering the results related to the number of acid centers of each sample, the higher water retention properties of the arene-SO$_3$H groups are clearly evidenced. In conclusion, arene-SO$_3$H moieties are shown to be more hydrophilic than propyl-SO$_3$H ones.
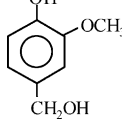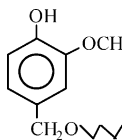
In a reaction medium where the different chemical species show large differences in polarity, hydrophilic–hydrophobic balance on catalyst's surface is an important parameter modulating the transformation rates. Table 4 summarises the dielectric constants of the species involved in the etherification of vanillyl alcohol with 1-hexanol. Both alcohols (linear and benzyl) and the resultant benzyl ether display low polarities in contrast with water molecules.

The presence of polar water molecules as reaction products in a non-polar reaction medium wherein catalytic sites are hydrophilic is likely hindering the progress of the etherification. In media as the present one, it is postulated the formation of water microenvironments surrounding sulfonic acid moieties due to hydrophilic interactions (see Scheme 2). This effect prevents the access for new reactant alcohol molecules to the acid sites.

In order to qualitatively evaluate the effect of water on these catalytic systems, water-doped experiments were also carried out (Fig. 1b). Small amounts of deionized water, equivalent to the water formed after completion of reaction (about 1 wt% referred to total initial reaction mass), were added to the reactor previously to the initiation of the reaction. As can be observed in the Fig. 1b, the catalytic performance of both catalysts (Samples 1 and 3) is drastically reduced, being the effect over the propyl-SO$_3$H sample more noticeable than over the arene one. The influence of water molecules on the performance of sulfonic acid sites has been previously reported for the 1-butanol etherification [29]. The authors proposed a strong competition effect between water and alcohol molecules for –SO$_3$H active sites, associating highest activities with most hydrophobic natures of SO$_3$H group environments for sulfonic-modified periodic mesoporous organosilica materials.

Table 4
Approximate dielectric constant (κ) values at 25 °C

Substance	Molecular formula	κ (25 °C)
Water	H$_2$O	78
1-Hexanol	HO⌄⌄⌄	14
Vanillyl alcohol		13
Benzyl ethers		4
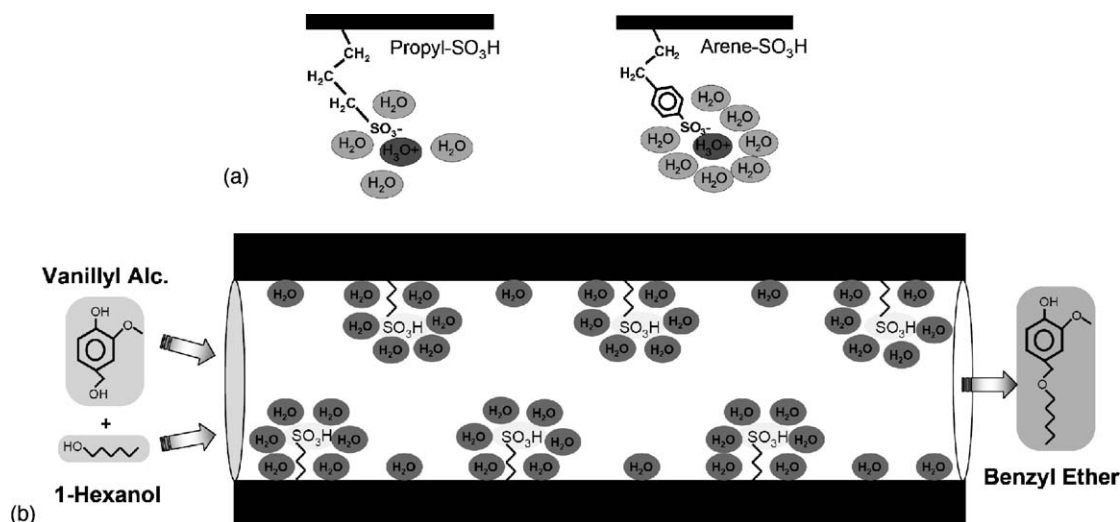
Scheme 2. (a) Simplified scheme of water/sulfonic acid interaction for propyl-sulfonic acid group (Sample 1) and arene-sulfonic acid group (Sample 3). (b) Schematic representation of a mesopore in sulfonic acid-modified SBA-15.

Summarizing, the detrimental effect of water formation on catalytic activity will occur in a greater extent over the more hydrophilic systems arising from the use of either high acid-strength (Sample 3) or high concentrations (Samples 2 and 4) of SO_3H groups, than over the 10 mol% propyl-SO_3H-modified material, as illustrated in Fig. 1a. Note that propyl-sulfonic-modified SBA-15 material with a moderate density of sulfonic acid sites is shown as an interesting water-tolerant acid catalyst.

In order to generalize the activity of Pr-SO_3H SBA-15 (Sample 1) for the etherification of different benzyl alcohols, 4-hydroxybenzyl and anisyl alcohols have also been selected as etherification substrates (Scheme 3).

Catalytic activities of Sample 1 with the different benzyl alcohols are depicted in Fig. 2. Reaction conditions were fixed at 50 °C, 1-hexanol/benzyl alcohol starting mass ratio of 10/1 and 0.03 g of catalyst (0.1 wt%). The use of anisyl alcohol as substrate gives acceptable conversion values, presenting similar reaction rates to those exhibited by Sample 1 with vanillyl alcohol (Fig. 2). However, in the case of 4-hydroxybenzyl alcohol higher catalyst loadings are needed to reach similar conversions. Increasing the amount of catalyst to 0.3 wt% (×3) provides final conversion values of 4-hydroxybenzyl alcohol over 70%. Acti-

vation degree of benzyl alcohols for etherification is the main factor behind the different behaviours. The reaction mechanism progresses via nucleophilic substitution and the presence of activating moieties as methoxy groups increases the etherification rates. Thus, methoxy-substituted benzyl alcohols as vanillyl or anisyl ones are more readily converted to the corresponding ether than 4-hydroxybenzyl alcohol. In conclusion, the promising etherification results obtained could be extended to other benzyl alcohols by simply adjusting the severity of reaction conditions (catalyst loading and/or temperature).

Finally, the catalytic activity of 10% propyl-sulfonic and arene-sulfonic SBA-15 for the etherification of vanillyl alcohol with 1-hexanol was benchmarked with the activities of several acid solid catalysts. Reaction conditions were fixed at 50 °C
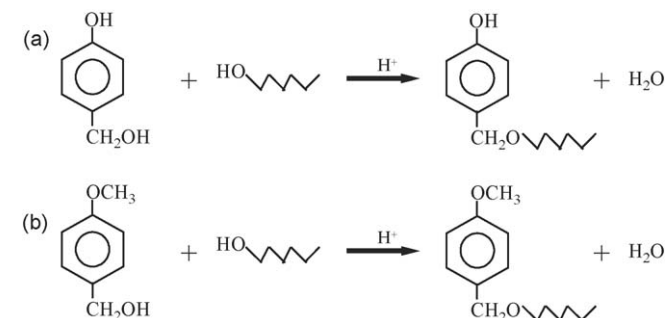
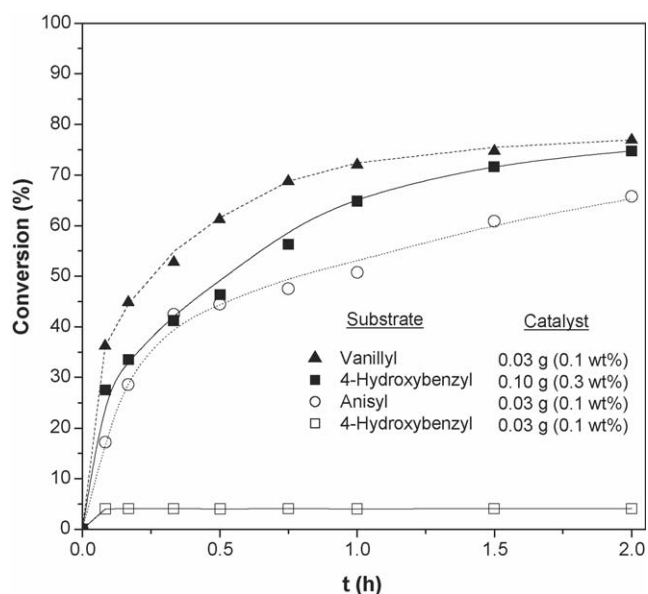Scheme 3. Etherification of (a) 4-hydroxybenzyl and (b) anisyl alcohols with 1-hexanol.

Fig. 2. Etherification of different benzyl alcohols with 1-hexanol over 10 mol% propyl-SO_3H SBA-15 (Sample 1).

Table 5
Catalytic activity of several acid solids in the etherification of vanillyl alcohol with 1-hexanol[a]

Catalyst	X_{vain}[b] (%, 5 min)	X_{vain}[b] (%, 120 min)	r_o[c]	r_o[d] (specific)
Propyl-SO_3H SBA-15 (Sample 1)	36	77	44.4	37.0
Propyl-SO_3H silica	15	25	18.5	18.5
Methanesulfonic acid	32	84	39.5	3.8
Arene-SO_3H SBA-15 (Sample 3)	24	57	29.6	23.9
Arene-SO_3H silica	10	22	12.3	15.4
p-Toluenesulfonic acid	58	92	71.6	13.5
Amberlyst-15	10	15	12.3	2.6
SAC-13 (Nafion^{TM}-SiO_2)	6	11	7.4	61.7
Zeolite Beta	4	9	4.9	12.3

[a] For all the catalysts, benzyl ether is the only detectable reaction product. No evidence of homo-condensation of 1-hexanol is observed. Therefore, selectivity of vanillyl alcohol towards benzyl ether is 100% for all the catalysts.

[b] Conversion of vanillyl alcohol at the indicated reaction time (5 and 120 min, end of reaction). Reaction conditions: 50 °C; 30 g 1-hexanol; 3 g vanillyl alcohol; 0.03 g catalyst.

[c] Initial reaction rate values [(mmol g_{cat}^{-1} min^{-1})] calculated from mmols of reacted vanillyl alcohol within the first 5 min of reaction and referred to catalyst's weight.

[d] Initial specific reaction rate values per acid site [(mmol mmol acid-center^{-1} min^{-1})] calculated from mmols of reacted vanillyl alcohol within the first 5 min of reaction and referred to mmol of acid sites in the catalyst.

under autogenous pressure, 1-hexanol/benzyl alcohol starting mass ratio of 10/1 and 0.03 g of catalyst (0.1 wt%). Catalyst loadings were kept constant for the different acid-solids tested. Catalytic performances of SO_3H-modified SBA-15 samples (S-1 and S-3 samples) were compared with those corresponding to conventional SO_3H catalysts, either homogeneous (methanesulfonic and p-toluenesulfonic acids) or heterogeneous (propyl- and arene-SO_3H-modified non-ordered silicas; and the resin-based materials Amberlyst-15 and SAC-13). Beta zeolite has also been tested as a representative of microporous acid-materials. Table 5 summarises the catalytic results obtained in this comparative study. Conversions of vanillyl alcohol at 5 and 120 min (end of reaction) are presented for all the catalysts. Initial reaction rate values are given to compare intrinsic activities avoiding equilibrium or deactivation perturbations. Additionally, in order to obtain a quantitative comparison of the performance of the different sulfonated catalysts, the specific initial reaction rates per acid center (mmol of converted vanillyl alcohol per mmol of acid site within the first 5 min of reaction) have been calculated and included in Table 5.

Highest conversion values are obtained over the homogeneous catalysts, either initially or at the final time. Almost complete absence of diffusional problems of reactants to acid sites makes them the most active catalysts in these conditions. Furthermore, in contrast with the results presented previously, the highest acid-strength of the phenyl-SO_3H group in the p-toluenesulfonic acid results in higher conversion values as compared to those obtained over alkyl-SO_3H moieties in the methanesulfonic acid. Despite their remarkable catalytic performances, homogeneous SO_3H catalysts still present the operational and environmental drawbacks generally attributed to homogeneous catalysis. Furthermore, due to their high acid capacities (Table 2), when considered in terms of specific activity per acid center their catalytic performances decrease significantly. Similar SO_3H moieties in Sample 1 (alkyl) and Sample 3 (phenyl) give higher specific activities. These catalytic results

demonstrate the high accessibility of the SO_3H centers for these modified mesostructured materials.

In order to evaluate the effect of the silica mesostructure, propyl- and arene-SO_3H non-ordered silicas were evaluated. Table 5 shows that the presence of a highly ordered mesostructured support with high surface area (as in SBA-15 materials) improves the catalytic activity of the SO_3H groups either in terms of absolute conversion of vanillyl alcohol or in terms of specific initial reaction rate. Commercially available sulfonated-resin-based catalyst (Amberlyst-15 and Nafion-silica composite) are used industrially in etherification processes. However, in the etherification of vanillyl alcohol they result in very low conversion values. Usually, low surface areas and lack of thermal stability are the main drawbacks of these catalysts, but in this case their poor activity is mainly attributed to their hygroscopic nature. Both types of sulfonic acid resins (sulfonated polystyrene in the case of Amberlyst and fluorinated alkyl-SO_3H chains in the case of Nafion) present higher acid-strengths and density of acid sites than sulfonated SBA-15 materials. Therefore, the above discussed detrimental effect for highly hydrophilic arene-SO_3H SBA-15 is observed over these polymer-based catalysts with an increased intensity. In the case of beta zeolite the conversion of vanillyl alcohol is quite low, confirming that the reaction is suppressed by the limited diffusion of the bulky reactants within the zeolite micropores. Moreover, the presence of aluminium atoms may favour the easy adsorption of water onto the surface and hence blocking the access of organic molecules towards the acid sites.

4. Conclusions

Propyl- and arene-SO_3H-modified mesostructured SBA-15 materials are shown as active catalysts in the preparation of benzyl ethers from benzyl alcohols. Despite their lower acid strength, propyl-SO_3H acid sites provide higher activity than arene-SO_3H groups as a consequence of the lower hydrophilicity

of the sulfonic acid site microenvironment of the former which reduces the poisoning effect by water molecules. Nevertheless, a high density of acid sites is detrimental for this reaction. Propyl-sulfonic-modified SBA-15 with a moderate concentration of acid sites combine a relative high hydrophobic character to avoid a significant blocking of water molecules and with an acid capacity enough to catalyze the etherification reaction. More-over, sulfonic acid-modified mesostructured materials display outstanding catalytic performances as compared with other com-mercial sulfonic acid-based homogeneous and heterogeneous acid catalysts. Further research is currently being addressed to the synthesis and catalytic application of surface-modified SO_3H-mesostructured materials, such as PMOs, in order to opti-mize the catalytic performance through the tuning of catalyst's hydrophobic–hydrophilic balance.

Acknowledgements

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