



Biodiesel production from crude palm oil using sulfonic acid-modified mesostructured catalysts

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ABSTRACT

Biodiesel production from crude palm oil containing high percentage of free fatty acids over sulfonic acid-functionalized SBA-15 materials (propyl-SO₃H, arene-SO₃H, perfluoro-SO₃H) has been studied. The catalytic results showed that sulfonic acid-modified mesostructured materials were more active than conventional ion-exchange sulfonic resins (Amberlyst-36 and SAC-13) in the simultaneous esterification of free fatty acids and transesterification of triglycerides with methanol. The reusability of the catalysts was also investigated showing high stability for propyl-SO₃H and arene-SO₃H-modified mesostructured materials. In contrast, ionic-exchange sulfonic acid resins displayed low-conversion rates, being stronger this decay of activity in the second consecutive catalytic run. Interestingly, perfluorosulfonic acid-functionalized SBA-15 sample yielded a dramatic loss of activity indicating that Si–O–C bonding is not stable under the reaction conditions as compared with Si–C bond present in propyl-SO₃H and arene-SO₃H catalysts. Further functionalization of arene-SO₃H SBA-15 catalyst with hydrophobic trimethylsilyl groups enhanced its catalytic performance. This material was able to produce a yield to FAME of ca. 95% as determined by ¹H NMR in 4 h of reaction with a moderate methanol to oil molar ratio (20:1), 140 °C and a catalyst concentration of 6 wt.% referred to starting oil.

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1. Introduction

Biodiesel production has become a very intense research area because of the growing interest on finding new resources and alternatives for conventional transport fuels [1]. The conventional production process consists on the use of alkaline catalyst—such as sodium hydroxide or sodium methoxide—[2,3], which lead good product yields in transesterification reactions. However, several drawbacks for these chemicals associated to the homogeneous nature [4,5] as well as limitations to the use of triglyceride feedstocks have also been reported [6–9]. Thus, for instance, homogeneous catalysts leads to impurification of products and alkaline catalysts cannot be used to treat raw materials containing more than 0.5 wt.% of free fatty acids [10]. One of the possibilities to overcome of these disadvantages is to use heterogeneous acid catalysts instead of homogeneous alkaline chemicals. Great advantages can be reached with this substitution [11], such as avoiding the use of a feedstock conditioning step—used for reducing FFA content—[12] or the possibility to use low-quality feedstock with high FFA content. Also, no catalyst neutralization wastewater is produced and thus, the glycerol by-product is achieved free of salts coming from the neutralization step [5].

In this way, since the two main factors affecting the cost of biodiesel production are related to the cost of raw materials and the cost of processing—number of steps—working with heterogeneous acid catalysts improves both economic issues, and thus, a better profitability of the biodiesel production process is expected [13].

Scarce examples of the application of heterogeneous acid catalyst to biodiesel production have been reported. It seems an ideal acid solid catalyst should join the following features: large pore size to minimize diffusional problems [14,15]; high concentration of acid sites; high catalytic stability against leaching and poisoning effects and the possibility to tune the hydrophobicity of the surface to promote the preferential adsorption of substrates and repulsion of highly polar compounds which could cause deactivation [16]. Most of these heterogeneous acid catalysts are based on modified inorganic oxides such as sulfated or tungstated zirconia [17–19] or supported heteropolyacids [20,21]. Usually, these materials lack of large textural properties to enhance mass transfer phenomena and several of them suffer deactivation under the reaction conditions. In this point, sulfonic functionalized materials, like cation-exchange resins, have revealed to be an interesting alternative as heterogeneous acid catalysts in many different applications, including biodiesel production [22–25]. However, their catalytic activity is conditioned by the swelling behavior of the polymer matrix in the reaction media since this affects the mass transfer phenomena inside the resin porous system. These inconveniences

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can be overcome using sulfonic acid-functionalized mesostructured silica [16,23,26] since the opened porous structure and large pore size of mesostructured materials ensures good mass transfer properties. Besides, tuning the hydrophobic/hydrophilic behavior of surface [16] can be easily done through surface silylation.

Within the scope of this work, we present the study on both the catalytic behavior and reutilization capability of mesostructured materials functionalized with different sulfonic acid groups, as well as the influence of several operation variables on the yield of crude palm oil towards fatty acid methyl esters. These studies have been completed through the comparison between an arene-sulfonic acid-functionalized mesostructured material—one of the mesostructured acid catalysts showing good catalytic performance—with an amberlyst-type commercial resin. Finally, the presence of inert hydrophobic groups ($-\text{CH}_3$) in the arene-sulfonic-modified catalyst has been also assessed in the simultaneous esterification and transesterification process.

2. Experimental

2.1. Materials

Crude palm oil (Cargill, see properties in Table 1) and methanol (ACS grade, Aldrich) were used as feedstocks for transesterification reactions. Tetraethyl orthosilicate (TEOS, 98%, Aldrich) was used as silica precursor in the synthesis of the silica-based mesostructured materials. 2-(4-chlorosulfonyl Phenyl)ethyltrimethoxy silane (ABCR), (3-mercaptopropyl) trimethoxy silane (Aldrich) and 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid beta-sultone (ABCR) were used as precursors for the different sulfonic acid groups. Pluronic (P123, Aldrich) was used as template in the synthesis of the mesostructured materials.

2.2. Synthesis of sulfonic acid-functionalized mesostructured materials

2.2.1. Propyl- SO_3H SBA-15 (Pr-SBA-15)

Propyl-sulfonic acid-functionalized SBA-15 material was synthesized following the procedure described by Margoese et al. [27]. 4 g of P123 were dissolved in 125 mL of 1.9N hydrochloric acid at room temperature. The clear solution was heated to 40 °C before adding the TEOS. The resultant white suspension was then stirred for 45 min before the addition of (3-mercaptopropyl)trimethoxy silane, together with the hydrogen peroxide used as oxidant. The mixture was then stirred for 20 h and hydrothermally aged at 110 °C for 24 additional hours. The material was then filtered and air dried. The surfactant was removed by ethanol washing under reflux for 24 h (1.5 g of as-made material per 400 mL of ethanol; see Scheme 1).

Table 1
Properties of crude palm oil used as feedstock for biodiesel production.

Property	Analysis method	Value
FFA content	ISO 660:96	5.6 wt.%
Humidity	UNE-EN-ISO 662:01 Met.B	0.22 wt.%
Rubber (P)	UNE 55.108-73	22.0 ppm
Iodine index	ISO 3961:00	57.7
Density (20 °C)	ISO 6883:00	928 kg m ⁻³
Stability against oxidation (AOM-97.8 °C)	ISO 6886:96	62 h
Fatty acid profile	ISO 5508:90/ISO 5509:00	Mass %
	Lauric acid (12:0)	0.16
	Myristic acid (14:0)	0.99
	Palmitic acid (16:0)	43.03
	Palmitoleic acid (16:1)	0.19
	Stearic acid (18:0)	4.31
	Oleic acid (18:1)	39.47
	Linoleic acid (18:2)	10.82
	Linolenic acid (18:3)	0.29

2.2.2. Arene- SO_3H SBA-15 (Ar-SBA-15)

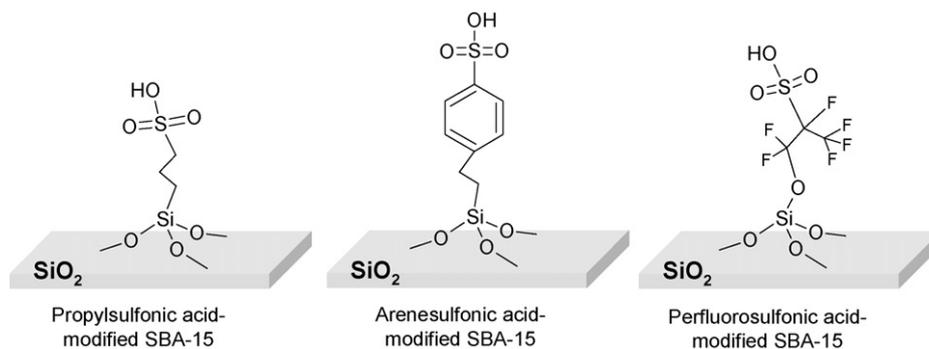
Arene-sulfonic acid-functionalized SBA-15 material was prepared using the method previously described in literature [28]. In essence the synthesis procedure involves the same steps already described for the preparation of propyl-sulfonic acid functionalized SBA-15 material. Nevertheless, since the sulfonic functionality is already present in the organosilicon precursor [2-(4-chlorosulfonylphenyl)ethyltrimethoxy silane] there is no need to add hydrogen peroxide to the synthesis medium. The rest of the preparation stages were the same previously described (see Scheme 1).

2.2.3. F- SO_3H SBA-15 (F-SBA-15)

This material was prepared, unlike propyl- and arene-sulfonic SBA-15 samples, through a post-synthetic pathway, following the same procedure already reported by Alvaro et al. [29]. In a typical preparation, 2 g of calcined pure silica SBA-15 material was treated with 1 g of the perfluorosulfonic acid precursor in 50 mL of dry toluene under reflux. The functionalization procedure was carried out for 6 h under nitrogen atmosphere before recovering the material by filtration. The resultant sulfonic-functionalized material was thoroughly washed with fresh toluene and oven-dried at 100 °C (see Scheme 1).

2.3. Commercial sulfonic acid-functionalized catalysts

Nafion[®]- SiO_2 composite (SAC-13) with resin content in the range of 10–20 wt.% was supplied by DuPont. Ionic-exchange sulfonic acid-based macroporous resin Amberlyst 36 wet was supplied by Rohm and Haas. Before use, it was treated by suspension in methanol under gentle stirring for 2 h, in order to displace water, and dried overnight at 85 °C. Both catalysts were ground



Scheme 1. Representation of the different sulfonic acid moieties incorporated on mesostructured SBA-15 silicas.

Table 2
Physicochemical properties corresponding to commercial sulfonic acid-based catalysts^a.

Catalyst	Acid capacity (meq H ⁺ /g)	BET area (m ² /g)	Average pore diameter (Å)	Maximum Op. temperature (°C)
Amberlyst-36 wet	≥5.40	33	240	150
SiliaBond [®] Tosic Acid	0.8	279 ^b	20–200 ^b	>200
Nafion [®] SAC-13	0.12	>200	>100	200

^a Properties provided by the suppliers.

^b Experimentally determined by N₂ adsorption isotherm.

to powder in order to minimize mass transfer limitations and thus avoid distortions in the catalytic results. Arene-sulfonic acid-functionalized non-ordered silica, under the commercial name SiliaBond[®] Tosic Acid, was acquired from Silicycle directly in powder form. Table 2 summarizes some relevant physicochemical properties corresponding to these commercial sulfonic acid-based catalysts.

2.4. Characterization techniques

The textural properties of the catalysts were assessed through N₂ adsorption–desorption experiments in a Micromeritics TriStar 3000 unit. Surface area values were calculated from isotherm data using the B.E.T. method. Pore sizes distributions were achieved through the B.J.H. method using the K.J.S. correction. Total pore volume was assumed to be that recorded at $p/p_0 = 0.985$. Structural ordering was further assessed by means of X-ray powder diffraction on a Philips X'Pert diffractometer using CuK α radiation in the 2 θ angle range of 0.6–5° with a resolution of 0.02°. Total organic content attached onto the catalyst was determined by TG analysis using a simultaneous DSC-TGA SDT 2960 thermogravimetric scale. The amount of incorporated sulfonic groups was calculated through the sulfur content determined by elemental analysis using an Elementar Vario EL III unit. Acid capacities were determined potentiometrically using 2 M NaCl (aq) as cationic-exchange agent, and a dropwise addition of 0.01 NaOH (aq) as titration agent. Single-pulse solid-state ²⁹Si MAS-NMR spectroscopy was used to characterize the environment of the silicon nuclei. NMR experiments were conducted at room temperature at a magnetic field strength of 9.4 T on a high-resolution Varian INFINITY PLUS 400 NMR spectrometer operating at a frequency of 79.41 MHz. Chemical shifts were referenced to tetramethylsilane, and the spectra were recorded using a 3.5 μ s $\pi/2$ pulse, a recycle delay of 60 s, and 1000 transients.

2.5. Catalytic experiments

All the experiments were carried out in a 25 mL teflon-lined stainless-steel batch reactor (Autoclave engineers) fitted with a

temperature controller, mechanical stirrer and a pressure transducer for monitoring the reaction conditions. In a typical assay, crude palm oil (5 g), methanol and the catalyst (6 wt.% referred to the amount of oil) were placed together inside the reactor and the temperature and stirring conditions (2000 rpm) were set up. The reactions were performed during 2 h (otherwise specified) and afterwards the reactor was cooled down using an ice-water bath. The products were recovered from the reactor and mixed with acetone (25 mL) used for cleaning the reactor vessel and stirrer. The final solution was then filtered to recover the catalyst before removing the residual methanol in a rotary evaporator. Further purification of FAME phase was not addressed.

The yield of fatty acid alkyl chains (comprising both free fatty acids and triglycerides) towards fatty acid methyl esters (FAME) was calculated on each experiment from ¹H NMR analyses performed in a Varian Mercury Plus 400 unit in a similar way to that described by Gelbond et al. [30].

2.6. Catalysts reusability and leaching tests

The catalyst separated from the reaction mixture by filtration was double-washed with methanol and n-hexane to remove both polar and non-polar compounds adsorbed on the surface [31]. Catalysts were used in recycling tests after drying overnight at 80 °C. Leaching of active species within the reaction mixture was investigated by sulfur elemental analysis.

3. Results and discussion

3.1. Catalyst structures, compositions and thermal stabilities

Table 3 summarizes the most relevant physicochemical properties for the synthesized sulfonic acid-modified mesostructured silicas. Data from XRD and N₂ adsorption isotherms evidence high mesoscopic ordering and high surface areas along with narrow pore size distributions around 8–9 nm (large enough to avoid the steric constraints imposed by pore size when relatively bulky substrates such as glycerides are considered).

Table 3
Physicochemical, textural and acidity-related properties corresponding to sulfonic acid-modified mesostructured silicas.

Sample	Textural properties					Acid properties		
	d_{100} ^a (Å)	Pore size ^b (Å)	BET area (m ² /g)	Pore volume ^c (cm ³ /g)	Wall thickness ^d (Å)	Acid capacity ^e (meq/g)		Organic incorporation ^f (%)
						Sulfur	H ⁺	
Pr-SBA-15	111	82	666	1.19	32	1.17	1.21	91
Ar-SBA-15	108	92	712	1.03	32	1.05	1.06	90
F-SBA-15	109	96	404	0.83	30	0.28	–	16

^a $d(100)$ spacing, measured from small-angle X-ray diffraction.

^b Mean pore size (D_p) from adsorption branch applying the BJH model.

^c The pore volume (V_p) was taken at $P/P_0 = 0.975$ single point.

^d Average pore wall thickness calculated by a_0 -pore size ($a_0 = 2 \times d(100)/\sqrt{3}$).

^e Acid capacities defined as milliequivalents of acid centers per gram of catalyst, obtained either directly by titration (meq H⁺/g) or indirectly from sulfur content by elemental analysis (meq S/g).

^f Organic incorporation estimated from actual sulfur content and maximum theoretical content.

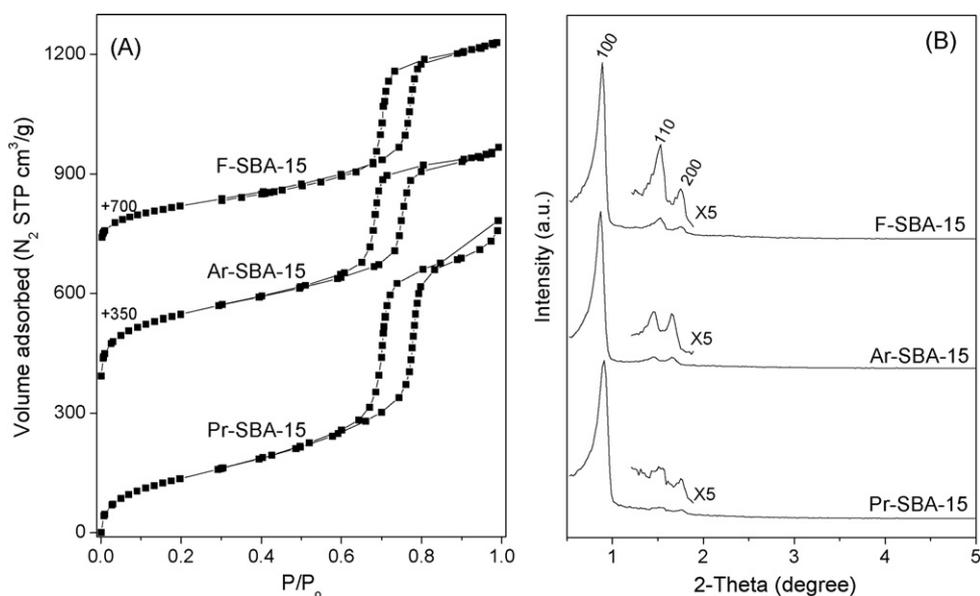


Fig. 1. (A) Nitrogen adsorption–desorption isotherms at 77 K, and (B) Small-angle X-ray scattering patterns for sulfonic acid-modified mesostructured SBA-15 silicas.

Fig. 1A depicts the nitrogen adsorption–desorption isotherms measured for the sulfonic acid-functionalized materials, which according to the IUPAC classification, can be ascribed as Type IV isotherms. The isotherms display a steep H1 hysteresis loop at relative pressures in the range 0.6–0.8, typical from narrow pore size distributions such as those usually reported for this kind of materials [27,28]. Powder X-ray diffraction analyses of propyl-, arene- and fluoro-sulfonic acid-functionalized samples give diffractograms that are typical signals for hexagonally ordered mesopores. Fig. 1B clearly evidences the presence of the typical small-angle X-ray scattering (SAXS) reflections associated with $p6mm$ symmetry: a single prominent SAXS reflection centered at 2θ below 1° , assigned to the crystallographic direction $[1\ 0\ 0]$, and low-intensity signals assigned to directions $[1\ 1\ 0]$ and $[2\ 0\ 0]$, indicative of long-range hexagonal ordering.

High incorporation yields for the sulfonic acid moieties (over 90%) are observed for propyl- and arene-sulfonic acid samples, both prepared by co-condensation of the different silanes (Table 3). In contrast, since the preparation method proceeds via a reactive-grafting procedure [29] for the F-SBA-15 material, the organic incorporation remains much lower (16%) than arene- and propyl-sulfonic acid samples. Elemental analyses and acid titration studies establish the incorporation of organic species within the silica framework and the accessibility of the sulfonic acid sites at the mesopore surfaces. Comparison of the sulfur concentration determined by elemental analysis and the proton concentration determined by cationic-exchange of the acid sites by sodium ions revealed that more than 95% of the acid catalyst sites are accessible.

Since acid-catalyzed transesterification of triglycerides requires a relatively high temperature, an important feature these materials must fulfil to be considered as appropriate catalysts for biodiesel production is an adequate thermal stability of the sulfonic acid active sites. The main advantage of using the co-condensation method for inclusion of functional species in mesoporous silicas, aside from a high degree of organic moieties dispersion, is the incorporation of the thermally-stable covalent Si–C anchoring bonds, in contrast to the Si–O–C anchoring bonds typically obtained by post-synthetic grafting methods as in the case of F-SBA-15 material. Thermogravimetric analyses carried out in air atmosphere (see Fig. 2) corresponding to propyl- and arene-sulfonic acid-functionalized mesoporous catalysts typically show weight loss

profiles that can be divided into three regions: (I) from room temperature to 150°C attributed to water desorption from the hydrophilic environment of the sulfonic acid sites [32], (II) between 150 and 350°C , attributed to remaining surfactant molecules and surface-adsorbed ethoxy groups from the ethanol-extraction to remove the surfactant species, and (III) above 350°C , from the thermal decomposition of sulfonic acid groups attached to the silica framework. In contrast, fluorosulfonic acid-modified SBA-15 displays a different weight loss pattern that can also be divided in three regions: (I) from room temperature to 150°C , attributed again to desorption of water, (II) from 150 to 250°C attributed to toluene retained within the pore structure after synthesis, and (III) above 250°C , where a progressive decomposition of perfluorosulfonic acid functions is observed. Thus, since its decomposition begins at lower temperatures, perfluorosulfonic acid moieties are expected to show lower thermal stability than propyl- or arene-sulfonic acid functions. The onset temperatures for thermal decomposition of the different sulfonic acid moieties considered in this study, although obtained in a thermally-controlled oven under a 5°C min^{-1} temperature ramp and not under the transesterification reaction conditions, suppose a valid indication of the high thermal stability of the sulfonic acid sites incorporated onto the SBA-15 mesostructured silicas.

3.2. Screening of sulfonic acid-containing catalysts for biodiesel production

The different acid solid catalysts were assayed for their catalytic activity in the transesterification of crude palm oil with methanol. Reaction conditions for the screening of catalysts were fixed as follows: temperature of 140°C , within the recommended range of working temperatures for all the compared catalysts—in this sense, the resin Amberlyst 36 is the catalysts closer to its limit, 150°C (see Table 2)—methanol to oil molar ratio 20/1; catalyst loading 6 wt.% referred to oil; and reaction time 2 h. Fig. 3 depicts the yields to fatty acid methyl esters (FAME), as defined in the experimental section, obtained over the different heterogeneous catalysts. A blank run carried out without catalyst has also been performed in the same conditions in order to determine the extension of thermally-driven reactions. This blank gave 7% yield to FAME, which can be mainly attributed to the thermal esterification of free fatty acids present in

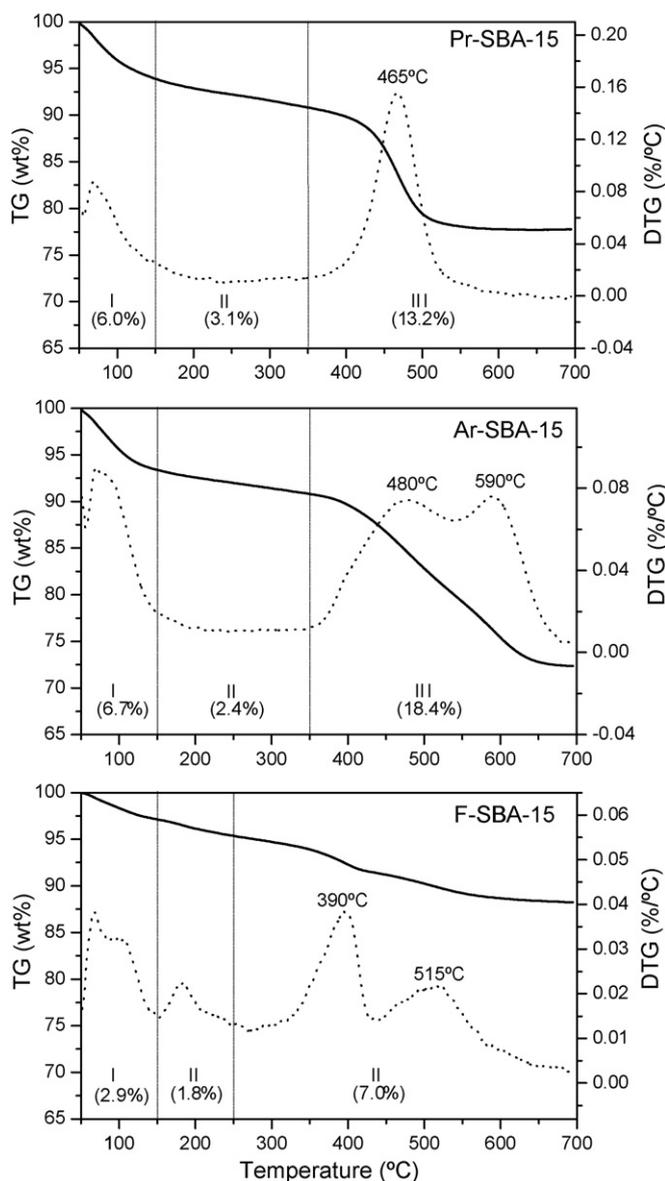


Fig. 2. Weight loss curves and derivative plots for sulfonic acid-modified mesostructured SBA-15 silicas.

the palm crude oil. Indeed, this value approximately corresponds to the 5.6 wt.% FFA content of the starting material (see Table 1). Likewise, it has been recently reported that the presence of high content of free fatty acids in cottonseed oil has been proved to be beneficial for the thermal transesterification reactions [33], so that the difference could be ascribed to auto-catalyzed transesterification. Nevertheless, such a reaction requires of higher temperature conditions, in the range of 170–220 °C.

The feasibility of tuning the acid strength of the sulfonic acid groups incorporated within mesostructured SBA-15-type silicas by close attachment of different moieties has previously led to improvements in the catalytic activity in several acid-catalyzed reactions [34]. Taking this into account, the catalytic performance of propyl-sulfonic acid-modified SBA-15 has been compared with that of arene-sulfonic acid-modified SBA-15 and fluoro-sulfonic acid-modified SBA-15 samples. The different nature of the molecular environment of the SO_3H sites in these three otherwise similar catalysts defines their acid strength. Thus, highly electronegative fluorine atoms provide higher acid strength than an aromatic ring, such as in arene-sulfonic acid sample, which in turn gives stronger

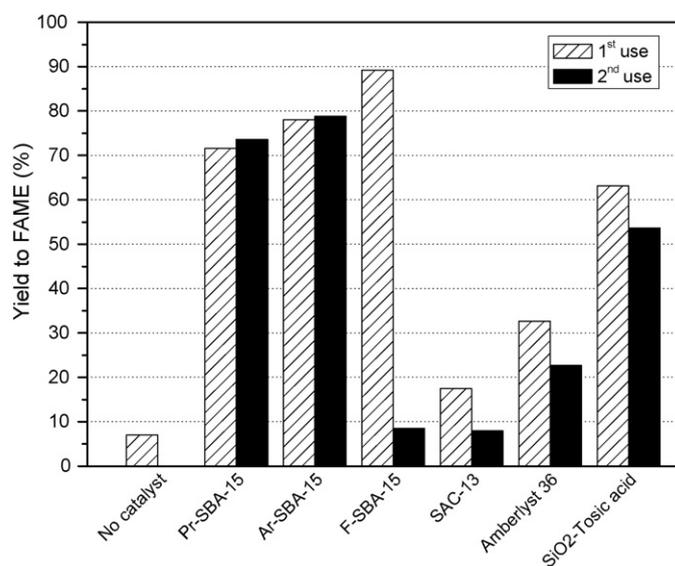


Fig. 3. Yields to FAME obtained over the different fresh catalysts and after catalyst recovery, washing and reuse. Reaction conditions: 140 °C; 2 h; methanol/palm oil molar ratio 20/1; catalyst 6 wt.% referred to oil.

acid sites than alkyl moieties like those in the propyl-sulfonic acid-modified material. Likewise, three commercially-available solid acid catalysts have also been evaluated: Amberlyst-36 as a representative of the family of sulfonic acid resins typically employed in many esterification and etherification industrial processes; SAC-13 as a resin-silica composite with high acid strength due to the perfluorosulfonic nature of the Nafion resin, and arene-sulfonic acid-modified non-structured silica (SiO_2 -Tosic acid) as a reference to analyze the influence of the presence of a mesostructured silica framework such as that shown in SBA-15 materials. Finally, the screening of catalysts has been completed with a reutilization assay in order to check the stability of the catalytic sites supported on the different materials upon reaction.

Data from Fig. 3 evidences the high activity of the sulfonic acid-functionalized mesostructured silicas for the transesterification reaction. In the first use they reach yields to FAME close to 70% (Pr-SBA-15), 80% (Ar-SBA-15) and 90% (F-SBA-15). As expected, this seems to indicate that a higher acid strength of the sulfonic acid active site can be translated into higher catalytic performance for palm oil methanolysis. Nevertheless, although propyl- and arene-sulfonic acid samples have been reused with no loss of activity, the recycling test for F-SBA-15 shows a dramatic loss of activity. A feasible explanation for this fact relies on the anchoring Si-O-C bonds of these perfluorosulfonic acid sites, whose stability has been shown to be critically compromised when used in polar solvents [35]. Thus, in the presence of high methanol concentration and temperature these moieties are likely being methanolized and released to reaction medium. Indeed, the activity recorded during the reuse of F-SBA-15 coincides with that of the blank reaction, which indicates a complete lack of activity for the solid catalyst. Therefore, SBA-15-supported arene-sulfonic acid functions can be selected as the best type of sulfonic acid sites both in terms of activity and stability.

On the other hand, commercial acid catalysts based on sulfonic acid resins Amberlyst 36 and Nafion- SiO_2 composite SAC-13 materials gave both very low yields to FAME. Furthermore, their recycling performances did not reach the initial yield values, indicating either a more intense deactivating effect or the necessity of profounder regeneration treatment after reaction for this sort of materials. Probably, the polymeric nature of the environment surrounding the active sites gives different and somehow detri-

mental molecular surface interactions in relation to those observed over the silica-supported catalysts, though deactivation has also been ascribed to pore blocking because of entanglement of the long fatty acid alkyl chains of the triglycerides. Finally, SiO₂-Tosic acid provided superior activity to that shown by the polymeric commercial acid catalysts but still approximately 15% in yield to FAME below the corresponding mesostructured material (Ar-SBA-15). Besides, surprisingly no complete regaining of activity after use and regeneration was achieved for this catalyst probably due to a partial leaching of low-stability active sites. Therefore, benefits from the presence of a mesostructured framework for the acid-catalyzed transesterification of crude palm oil with methanol have been demonstrated.

Though no great differences between propyl- and arene-sulfonic acid-functionalized SBA-15 materials have been observed, Ar-SBA-15 sample was chosen as catalyst for the rest of this investigation on the basis of its stronger acidity that leads to a higher catalytic activity.

3.3. Effect of reaction temperature and methanol to oil molar ratio

In order to determine the effect of several operation variables on the catalytic behavior of the arene-sulfonic acid-functionalized SBA-15 material, several reaction tests were carried out. Thus, the reaction temperature as well as the methanol to oil molar ratio were investigated in the ranges from 120 to 180 °C and from 3 (stoichiometric loading) to 40 respectively. Fig. 4 depicts the results obtained in these experiments.

Fig. 4 (black circles) shows the influence of the reaction temperature on the achieved yield towards FAME in the transesterification reactions. These experiments were carried out for 2 h using a methanol to oil molar ratio of 20 and 6 wt.% of catalyst referred to oil. The increase of the reaction temperature from 120 to 140 °C caused a great increase of the activity of the catalyst indicating

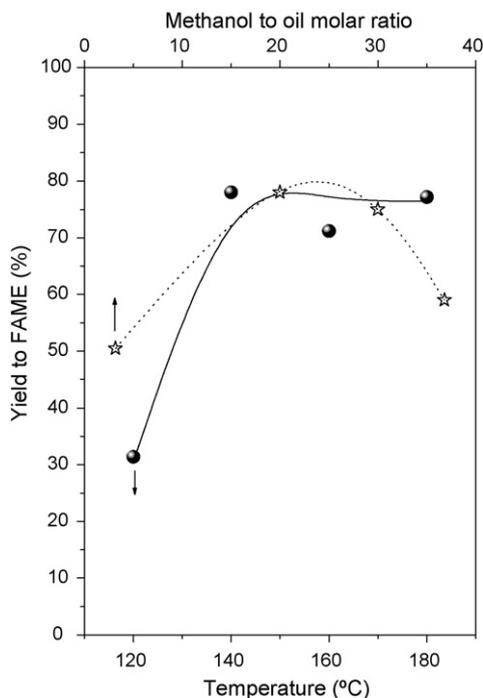


Fig. 4. Influence of (black circles) reaction temperature (methanol/palm oil molar ratio 20/1) and (hollow stars) methanol to oil molar ratio (reaction temperature of 140 °C) on the catalytic behavior of arene-sulfonic acid-functionalized SBA-15 material. Reaction conditions: 2 h; catalyst 6 wt.% referred to oil.

the enormous influence of this parameter on the transesterification reaction. Thus, more than twice the initial yield from palm oil towards FAME is achieved when operating at 140 °C. However, above this temperature, the results seem to be insensitive to this parameter, suggesting two opposite effects take place on the reaction at the same time. On one hand the increasing of the reaction temperature should lead to the usual increase of the reaction extent but also could cause acceleration of secondary by-reactions which reduce the yield towards the desired product. Since ¹H NMR experiments allowed discarding the presence of by-products, the attention was turned to the catalyst. Elemental analyses and acid–base titration were carried out in order to check the integrity of the catalyst acid sites before and after the reaction tests performed at different temperature. Table 4 lists the physicochemical properties thus obtained.

While the sulfur content remains in similar values to those obtained for the fresh catalyst, regardless the temperature conditions used for the catalytic tests, the acid loading suffers some decrease when increasing the reaction temperature. As result from both trends, the calculated hydrogen protons to sulfur molar ratio diminishes from the unit to 0.68 for the catalyst used at 180 °C, indicating that almost 30% of the initial acid loading has been removed. This fact could be explained attending to different possibilities: first, the amount of alkaline cations in crude palm oil is high enough to cause ion-exchange during the reaction step. On the other hand, the dependency of the acid loss with temperature suggests sulfonic acid sites are reacting, for instance with methanol to lead methyl sulfonates [36]. Whether the deactivation is caused by the first or the latter, the FAME yield is not increased when high reaction temperatures are used, in a similar way to that previously described for sulfated zirconia catalysts [37], though in this case no reasons were given for this fact.

Fig. 4 (hollow stars) also depicts the results achieved in the reaction tests carried out for determining the effect of the methanol to oil molar ratio. Reactions were performed at 140 °C in order to minimize the deactivation effect caused by temperature whereas noticeable FAME yield is achieved. Again, the catalytic tests were developed for 2 h using 6 wt.% catalyst referred to oil. In this case, a complete different behavior was found in the dependency of the catalytic behavior of the sulfonic acid-functionalized catalyst with the methanol initial loading. Thus, a maximum in the yield from crude palm oil towards FAME is achieved for methanol to oil molar ratios between 20 and 30. This behavior suggested a similar deactivation process to that previously described, though elemental analysis and acid–base titration experiments discarded this hypothesis. Several authors have also found optimal conditions for methanol to oil molar ratio in FAME production from triglycerides, attributing this trend to the different phase equilibria taking place at different methanol loadings [37,38]. Thus, high methanol loading makes possible that FAME and glycerol coexist in the same phase and react to lead triglycerides and methanol, the opposite transesterification reaction. Under these conditions, oil conversion and FAME yield are limited and thus a decrease in these param-

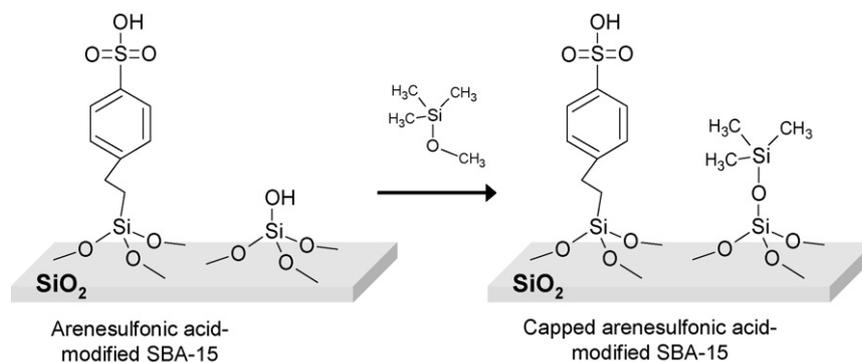
Table 4

Sulfur and acid loading for fresh and recovered catalysts (arene-sulfonic acid-SBA-15) after being used at different temperatures.

Temperature conditions	S content ^a (mmol S/g)	Acid loading ^b (meq H ⁺ /g)	H ⁺ /S molar ratio
Fresh catalyst	1.05	1.06	1.00
120 °C	1.06	1.05	0.99
140 °C	1.06	0.90	0.85
160 °C	1.08	0.94	0.87
180 °C	1.03	0.70	0.68

^a Calculated from elemental analyses.

^b Calculated by acid titration.



Scheme 2. Representation of the hydrophobization process of arene-sulfonic acid SBA-15 by capping of silanol groups.

ters are found for high methanol loadings, in a similar way to that described within this investigation.

3.4. Optimization of arene-sulfonic acid-modified SBA-15 catalyst for biodiesel production

Due to the highly hydrophobic nature of both the starting vegetable oil and the produced FAMES, their molecular transport within the pore framework is expected to be especially affected by surface interactions. Thus, an admissible optimization of mesostructured silica-based catalysts can be directed to modify its surface hydrophilicity–hydrophobicity balance. In fact, there are several examples in literature concerning the preparation of organic–inorganic hybrid materials to be used as catalysts in reactions combining the need for a certain level of acid strength with a demand for an adequate surface hydrophobicity. In this field, recent work has shown improved catalytic performance of sulfonic acid active sites supported on mesoporous organosilica–PMO—in hydrophobicity-sensitive reactions [39–42]. The higher catalytic activity obtained over these modified materials has been attributed to increased hydrophobicity near the sulfonic acid moieties and enhanced diffusion of reactant and products within the hydrophobic mesopores. More recently, highly acidic perfluorosulfonic moieties have been successfully incorporated into a PMO matrix by a procedure similar to that herein described for F-SBA-15 sample [43]. The resultant material led to an outstanding improvement in the alkylation of isobutene/1-butene as compared with SBA-15-supported perfluorosulfonic acid groups.

In this work, sample Ar-SBA-15 has been subjected to a surface hydrophobization procedure by capping the free surface Si-OH groups with an alkyl-based silane. In order to achieve this modification, 1 g of trimethylmethoxy silane was reacted with 1 g of overnight-dried arene-sulfonic acid material in dry toluene under reflux for 12 h (see Scheme 2).

Table 5 summarizes the structural characterization of the sample after the silylation procedure. X-ray diffraction pattern and N_2 adsorption isotherm (not shown) indicate that the modification of Ar-SBA-15 does not affect the mesostructure, since most of the textural properties are retained. The incorporation of new species on the silica mesopores produces an increase of the wall thickness accompanied by a slight decrease in pore volume and BET surface area.

The incorporation of the capping silane group has been assessed by means of solid-state MAS-NMR. A single-pulse method was used for the NMR analysis of ^{29}Si nuclei, enabling the direct quantification of the different silicon environments are shown: $Q^n = \text{Si}(\text{OSi})_n(\text{OX})_{4-n}$, wherein $n = 2-4$ (Q^2 at -90 ppm, Q^3 at -100 ppm y Q^4 at -110 ppm), $T^m = \text{RSi}(\text{OSi})_m(\text{OX})_{3-m}$, wherein $m = 2-3$ (T^3 at -65 ppm y T^2 at -57 ppm); $M = \text{R}_3\text{Si}(\text{OSi})$. M signal in the capped sample directly reveals the presence of trimethylsilane chemically attached to the silica structure, and hence can be utilized for the evaluation of the capping yield. Also, the disappearance of Q^3 and T^2 signals indicates the high efficacy of the capping process as it indicates a practically complete removal of free silanol groups. Thermogravimetric analysis of the resultant capped material is shown in Fig. 6 in comparison with the non-modified Ar-SBA-15 sample. Weight loss pattern is similar in both samples but notably, the mass loss assigned to water desorption—up to 150°C —is much lower in the hydroxyl-capped arene-sulfonic acid material compared to the non-modified material Ar-SBA-15: 1.7 wt.% vs. 6.7 wt.%. The difference in water retention supposes an indirect indication of the more hydrophobic nature of the trimethyl-modified material.

Catalytic performance of the hydroxyl-capped Ar-SBA-15 in the transesterification of crude palm oil with methanol was evaluated in the same conditions of the above screening of catalysts (Fig. 7). In this evaluation, a yield to FAME over 90% after only 2 h of reaction

Table 5
Physicochemical, textural and acidity-related properties corresponding to capped arene-sulfonic acid-modified mesostructured silica.

Sample	Textural properties					Acid properties	
	d_{100}^a (Å)	Pore size ^b (Å)	BET area (m ² /g)	Pore volume ^c (cm ³ /g)	Wall thickness ^d (Å)	Acid capacity ^e (meq/g)	
						Sulfur	H ⁺
Ar-SBA-15	108	92	712	1.03	32	1.05	1.06
Capped-Ar-SBA-15	114	83	533	0.75	48	1.01	1.04

^a $d(100)$ spacing, measured from small-angle X-ray diffraction.

^b Mean pore size (D_p) from adsorption branch applying the BJH model.

^c The pore volume (V_p) was taken at $P/P_0 = 0.975$ single point.

^d Average pore wall thickness calculated by a_0 -pore size ($a_0 = 2 \times d(100)/\sqrt{3}$).

^e Acid capacities defined as milliequivalents of acid centers per gram of catalyst, obtained either directly by titration (meq H⁺/g) or indirectly from sulfur content by elemental analysis (meq S/g).

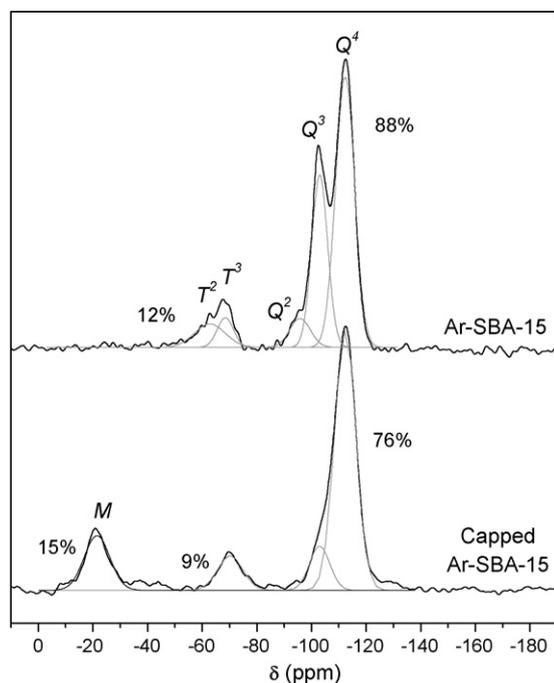


Fig. 5. ^{29}Si MAS-NMR spectra corresponding to arene-sulfonic acid-modified SBA-15 and hydroxyl-capped arene-sulfonic acid-modified SBA-15.

was achieved, which is approximately 10 points higher than that of unmodified Ar-SBA-15. Thus, the capping of free hydroxyl groups is demonstrated as a useful tool to achieve higher activities in this sort of reaction. Furthermore, reuse of this sample after double-washing gave almost the same yield, indicating a similar behavior to that of Ar-SBA-15 in terms of reusability.

In order to further increase the yield to FAME and get a biodiesel sample that fulfils standard specifications (minimum FAME content of 96.5 wt.% in the European Standard EN 14214), reaction time was increased up to 4 h. The results of these longer reactions are also shown in Fig. 7 for Amberlyst 36, Ar-SBA-15 and capped Ar-SBA-15. Sulfonic resin only gave a slight increase of the yield to FAME after 4 h, and its lack of activity does not appear to come from kinetics limitation. However, both arene-sulfonic acid-modified samples reached values over 95% as determined by ^1H NMR. Only after

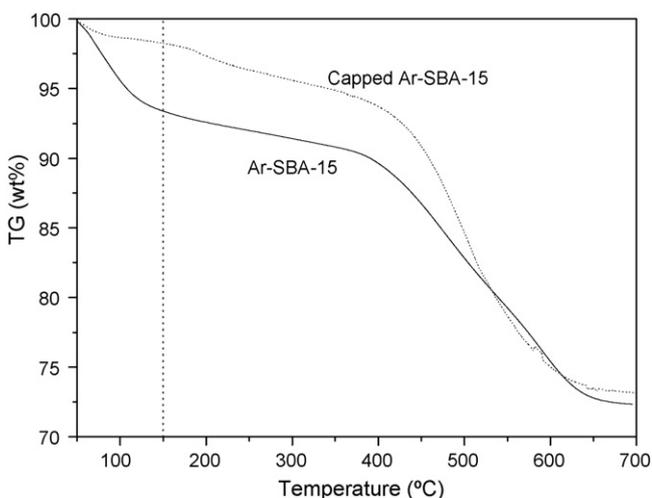


Fig. 6. Weight loss curves corresponding to arene-sulfonic acid-modified SBA-15 and hydroxyl-capped arene-sulfonic acid-modified SBA-15.

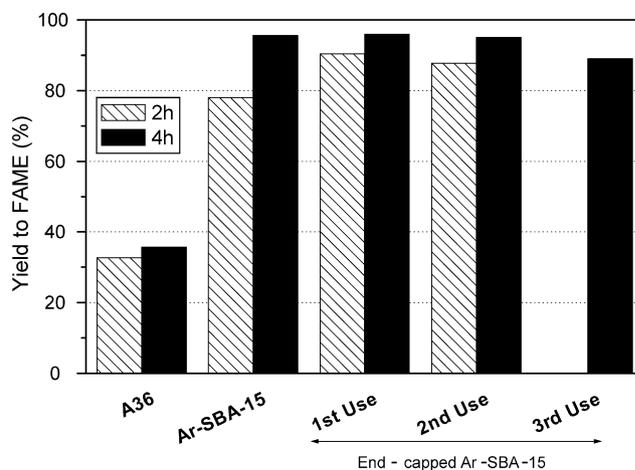


Fig. 7. Evolution with reaction time of yield to FAME over arene-sulfonic acid-modified SBA-15, Amberlyst-36, and capped arene-sulfonic acid-modified SBA-15. Reuse of capped Ar-SBA-15. Reaction conditions: 140 °C; methanol/palm oil molar ratio 20/1; catalyst 6 wt.% referred to oil.

three consecutive reaction cycles, a slight decrease on the catalytic activity of the end-capped Ar-SBA-15 material was observed. This suggests that surface silylation not only boost the catalytic activity of the sulfonic acid-functionalized material, but also provides the material with a noteworthy stability.

As this product has a high purity in FAMES, it was further analyzed by gas chromatography following the procedure described by the standard EN 14105 [44], for the analysis of un-reacted glycerides and free glycerol. The following contents were determined: monoglycerides 2.02 wt.%, diglycerides 0.65 wt.%, triglycerides 0.02 wt.%, and free glycerol 2.70 wt.%. In view of these results, free glycerol and monoglycerides and diglycerides contents clearly fall out of specification established by the EN 14214 standard. Especially, the high value of free glycerol could be a consequence of the formation of by-products such as ethers of glycerol and methanol [11], which would appear as free glycerol using the GC analysis established by EN 14105 standard. Formation of such ethers, far from being an undesired impurity, might even be taken as interesting additives [11]. Moreover, FAME phase after methanol removal was not further purified.

4. Conclusions

Arene-SO₃H SBA-15 catalyst has shown high activity and stability in the simultaneous esterification of FFA and transesterification of triglycerides to yield FAME using crude palm oil as feedstock. Further functionalization of arene-SO₃H SBA-15 catalyst by anchoring of hydrophobic trimethylsilyl groups effectively increased the reaction rate while keeping the stability at least for a second catalytic run. Methanol to oil molar ratio and temperature are crucial parameters to take into account in this catalytic system. A methanol to oil molar ratio of ca. 20 and a temperature of 140 °C seems to be the optimal values to achieve a high yield of FAME without damaging the catalyst. Upper values of these parameters are detrimental in terms of FAME production and catalyst reusability. However, ongoing work is being carried out over this catalyst using response surface methodology to understand the simultaneous influence of critical reaction parameters (temperature, catalyst loading and methanol to oil molar ratio) on the activity and stability of the catalyst. These sulfonic acid-based mesostructured catalysts have shown potential for biodiesel production from low-quality feedstocks containing high free fatty acids. Stability of acid sites and the control of surface properties to favour the diffusion of oily feedstock and to promote the expelling off of the polar compounds

(glycerol and water, etc.) are important challenges to be further studied in the future.

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