

Deactivation of sulfonated hydrothermal carbons in the presence of alcohols: evidences for sulfonic esters formation

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Abstract

Sulfonated hydrothermal carbons show high activity for esterification of palmitic acid with alcohols. However, the catalyst is significantly deactivated upon recovery. Leaching of sulfonated species does not account for this deactivation, which is observed even by pretreatment only with the alcohol under reflux. Solid state NMR shows the presence of chemically bound alkyl groups coming from the alcohol, clearly different from strongly physisorbed species obtained by pretreatment at room temperature. The formation of sulfonate esters accounts for the deactivation behavior in reactions taking place in alcohols as solvents, mainly with methanol due to its higher reactivity.

Keywords: sulfonated hydrothermal carbons; esterification; deactivation; acid catalysts

1. Introduction

The use of catalytic processes seems to be one of the most important Green Chemistry principles with regard to chemical production [1]. Mineral acids are among the most ubiquitous catalysts in industry but their corrosion and toxicity problems have prompted to the search for recoverable and reusable heterogeneous acid catalysts [2,3]. Fatty acid esters are present in a wide variety of daily used products, such as fuels, pharmaceuticals, cosmetics or foodstuffs. When the use of mixtures is allowed, they can be obtained by direct transesterification of fats and oils using either acid [4] or basic [5] catalysts. On the contrary, when the final application requires the use of a pure fatty acid ester, or free fatty acids are present in large amount in the triglycerides mixtures, the synthetic method of choice is the esterification of the fatty acid using an acid catalyst [6].

Among the huge amount of different solid acids, sulfonated carbons are emerging as an interesting alternative [7,8] due to the special features of those materials, including the sustainability issues in the case of carbons prepared from feedstock biomass instead of fossil fuels. In fact, sulfonated carbons obtained by partial carbonisation of glucose or cellulose have been used as catalysts for esterification reactions [9-13], as well as monoliths prepared by one-pot synthesis in the presence of *p*-toluenesulfonic acid [14]. Sulfonated mesoporous carbon was obtained by replication of SBA-15 pores through carbonisation of sucrose, leading to highly active solids [15]. Hydrothermal carbonisation (HTC) [16] is an attractive mild method of preparation of carbons with properties different from those prepared by more conventional methods. The accessible external surface densely functionalised with polar groups, such as carboxylic, hydroxyl or quinone [17], confers them high hydrophilicity and susceptibility to chemical modification. Sulfonated hydrothermal carbons, either prepared in two steps [18] or in one-pot synthetic method

[19], have been also used as acid catalysts for esterification reactions. Furthermore, hydrothermal carbon synthesis is a very versatile method to prepare materials with different porous structures [20-24] and shapes, such as hollow capsules [25-27], nanowires [28] or nanotubes [29]. Recently, it has been demonstrated by our group that HT carbon films can be also coated on a structured macroscopic support such as graphite felt [30].

Deactivation is a general problem in heterogeneous catalysis but it is a rather complicated phenomenon, related to coke formation, pore filling, structure modification, and a large variety of processes that depend on the type of catalyst and the catalytic reaction [31,32]. This is also the case of acid catalysts used in esterification reactions. In the case of sulfonated carbons, deactivation has been attributed to leaching of soluble polycyclic aromatics with sulfonic groups [14,33], simple physical loss of catalyst [15], or hydrolysis of sulfonic groups [34]. Other acid catalysts have also shown a similar behaviour with respect to stability in esterification reactions, that have been explained by leaching problems in sulfated zirconia [35], hydrocarbon accumulation in SAC-13 [36] and organosulfonic silica [37], and several reasons, including leaching of sulfonic species, water and glycerol adsorption, and even reaction with methanol in the case of sulfonic-acid modified SBA-15 [38,39].

In this manuscript the deactivation of sulfonated hydrothermal carbon in esterification reactions is studied, with evidences for different mechanisms, including the formation of sulfonic esters with the corresponding alcohol. The knowledge of these deactivation mechanisms may be the basis for designing catalytic processes which minimise this deactivation.

2. Experimental

2.1. Hydrothermal synthesis

An aqueous solution of glucose (25 ml, 1 M) was placed in a Teflon-lined autoclave and the hydrothermal synthesis was carried out under autogenous pressure at 195 °C for 19 h. After the synthesis, the autoclave was cooled down in a water bath at room temperature. The obtained material was washed thoroughly with distilled water and ethanol, and finally dried overnight in an oven at 105 °C.

The resulting material was then treated with concentrated (>96%) sulfuric acid (20 mL H₂SO₄/g solid) at 150°C under argon atmosphere for 16 h. The sulfonated sample was then washed thoroughly with hot distilled water and dried overnight at 105°C.

2.2. Characterization

Surface areas were determined by N₂ adsorption (BET) using a Micromeritics ASAP 2020 apparatus. Typically, a 0.2 g of solid was used for measurements. Prior to N₂ adsorption, the sample was outgassed for 4 h at 423 K. C,H,S analyses were carried out by combustion in a ThermoFlash 1112 elemental analyzer equipped with a TCD detector. For sample preparation, about 3 mg of sample are mixed with V₂O₅ in a crucible. Oxygen analysis was done by direct assay which involves pyrolysis of the sample.

SEM analysis was carried out with a microscope SEM EDX Hitachi S-3400 N with variable pressure up to 270 Pa and with an analyzer EDX Röntec XFlash de Si(Li). The samples were sputtered with gold previously to measurements. The images were obtained from the secondary electron signal.

For infrared analysis, samples were first ground in an agate mortar to produce fine powder that was mixed with pure KBr (Merck for spectroscopy) using a weight ratio of 1:20. About 30 mg of the mixture was used to prepare each pellet by compressing at 10

tonnes cm^{-2} using a hydraulic press. Infrared spectra were recorded with a Nicolet Avatar 360 spectrometer over the wavenumber range of $4000\text{-}400\text{ cm}^{-1}$ with 300 scans.

NMR spectra were recorded in a Bruker Avance III WB400 spectrometer with 4 mm zirconia rotors spun at magic angle in N_2 at 10 kHz. ^1H spectra (16 scans) were acquired using a single pulse excitation with $\pi/2$ pulse length of 3 μs . $^1\text{H}\text{-}^{13}\text{C}$ CP spectra (10000 scans) were measured using a ^1H $\pi/2$ pulse length of 2.45 μs , with a contact time of 2 ms, and spinal64 proton decoupling sequence of 4.6 μs pulse length. Direct polarization $^{13}\text{C}\{^1\text{H}\}$ spectra (60 scans) were measured using a ^{13}C $\pi/2$ pulse length of 4.5 μs , and continuous wave proton decoupling of 4.5 μs pulse length.

2.3. Catalytic tests

7.5 mmol of palmitic acid (1.92 g), 75.0 mmol of alcohol (3.04 ml of methanol, 4.38 ml of ethanol or 5.78 ml of isopropanol), 100 mg of catalyst and 2.1 mmol of 1-methylnaphthalene (0.30 g) as internal standard were stirred (≈ 1000 rpm) in a round flask immersed into a silicone bath at 85°C . Reaction was monitored by gas chromatography (HP-5890-II). The catalyst was filtered, washed with CH_2Cl_2 , dried under vacuum, and reused under the same conditions.

2.4. Deactivation tests

The catalyst (150 mg) was stirred under reflux in the corresponding solvent (40 ml) for 72 h (24 h in the case of methanol) or in 1-propanol at room temperature for 5 h under argon atmosphere. The solid was filtered at the same temperature and dried under vacuum at 105°C in the case of treatment under reflux or at room temperature in the case of treatment without heating. The solid was used in esterification of palmitic acid with methanol under the standard conditions. In some cases the activity of the extract was tested

by evaporating the extraction solvent (in case it was different from methanol), addition of methanol (if required), palmitic acid and internal standard and heating at 85°C.

3. Results and Discussion

3.1. Preparation and characterization of the sulfonated hydrothermal carbon

Hydrothermal carbons (HC) were prepared from aqueous solutions of glucose, using different concentrations (0.55 and 1 M), synthesis temperatures (180 and 195°C) and times (8, 19 and 43 h). At 180°C or after 8 h, the HC yield was very low. Thus the standard method included the use of glucose as starting material at 1 M concentration to maximize the productivity per volume and hydrothermal synthesis at 195°C for 19 h. The only effect of longer synthesis times was an increase in particle size, with little effect on composition or textural properties (surface area and porosity). Sulfonation was carried out by treatment with concentrated sulfuric acid at 150°C for 16 h under inert atmosphere, leading to sulfonated hydrothermal carbons (HC-SO₃H).

Hydrothermal carbon (HC) was obtained in the form of nanospheres (300-400 nm diameter, Figure 1), slightly smaller than those reported in analogous materials [40]. Longer synthesis times led to larger spheres, around 1.5 µm diameter after 43 h synthesis (not shown). Apparently the nanospheres were not modified by the sulfonation process. Surface area, determined by nitrogen adsorption isotherms, is always low, around 7 m²g⁻¹ for HC, slightly higher than values reported in the literature [18,40], in agreement with the smaller particle size. The microporous volume is also very low, around 0.2 µl g⁻¹.

Hydrothermal synthesis from carbohydrates leads to carbonaceous materials with relatively high oxygen content [40] (O/C ratio = 0.304, Table 1). Sulfonation produces a

significant increase in the oxygen content of the material [18] (O/C ratio = 0.528, Table 1), probably due to oxidation processes taking place besides sulfonation with sulfuric acid. The sulfur content corresponds to a functionalization of 0.55 mmol g⁻¹.

The chemical nature of the carbon was studied by IR and NMR spectroscopies. The most prominent IR bands (Figure 2) were the very broad one (3600-3000 cm⁻¹) corresponding the stretching of hydroxyl groups, that of aliphatic C-H at around 2900 cm⁻¹, the band of carbonyl groups at 1710 cm⁻¹, and bands attributable to skeletal C=C vibrations in the range of 1650-1400 cm⁻¹. Sulfonation modifies the spectrum, but sulfonic groups are not easily identifiable in the IR spectrum.

Due to the quite large hydrogen content (Table 1), hydrothermal carbons can be analyzed by NMR spectra in solid state using the cross-polarization technique (¹³C-CP-MAS-NMR). The spectra of the as-prepared samples (Figure 3) are in good agreement with the data reported in the literature [40,41]. Three distinct zones can be observed in the spectrum. The 0-60 ppm zone is typical for sp³ (aliphatic) carbons; the 100-160 ppm zone corresponds to sp² (aromatic and olefinic) carbons, and it can be divided in two wide bands, one in the normal interval of 100-140 ppm and another one at 140-160 ppm, typical for O=C=C; finally the peak at 200 ppm can be attributed to carbonyl groups. The high intensity of the aliphatic band demonstrates the presence of incompletely carbonized material, in agreement with the rather high oxygen and hydrogen contents. The aromatic groups in the hydrothermal carbon are mainly furans, as demonstrated by the band at 140-160 ppm, either with directly bound furan rings (bifuryl moieties) or with aliphatic or carbonyl spacers [40,41]. Simple sulfonation should not significantly modify this spectrum but it is not the case as shown in Figure 3. The increasing importance of the aromatic bands and the almost disappearance of the band for aliphatics demonstrate the existence of side reactions

in addition to the simple sulfonation. Some of those side reactions may be the oxidation of hydroxyl groups, the oxidation of benzylic methylene groups in α position to furans, the cross-linking and cyclization reactions of the polyfuran chains due to alkylation with hydroxyl or carbonyl groups, and the aromatization of partially saturated furan or benzene rings. In general all those types of reactions can be explained by either the strong acidic character of the sulfonation medium or the oxidant behavior of sulfuric acid, and they would account for the decrease in hydrogen content, the increase in oxygen content (Table 1), as well as the disappearance of the aliphatic bands in NMR. The lack of bands corresponding to carbonyl groups seems to indicate that they participate in the side reactions, for example alkylation of aromatics, and hence the high oxygen content must be due to phenol and ether groups, in addition to the furan rings.

3.2. Catalytic activity

Catalytic activity of the sulfonated carbons was tested in the esterification of palmitic acid with methanol (Figure 4). HC-SO₃H showed high catalytic performance in the first use, with yields of 46% after 1 h and 75% after 4 h. Initial TOF (mmol converted per mmol of catalyst per second) was calculated using conversion after 1 h and considering the total sulfur content (by elemental analysis) as SO₃H groups. The TOF value ($17.4 \times 10^{-3} \text{ s}^{-1}$, Table 2) is higher than values reported for sulfonated carbons in analogue reactions, (e.g. $1.6 \times 10^{-3} \text{ s}^{-1}$ with sulfonated mesoporous carbon [15] or $5.4 \times 10^{-3} \text{ s}^{-1}$ with sulfonated incompletely carbonized glucose [11] in esterification of oleic acid with methanol, Table 2) and similar to values obtained in esterification of lower acids ($16.7 \times 10^{-3} \text{ s}^{-1}$ with sulfonated partially carbonized cellulose in esterification of acetic acid with ethanol [13], Table 2). However, a significant drop in the catalytic activity upon reuse was observed

(Figure 4), with an initial TOF of 6.4×10^{-3} (Table 3). The deactivation behavior of sulfonated carbons has been described with different degree of detail in some cases [12,15,18,33], and also with other solid sulfonic acids [36]. On the contrary, some authors describe a complete stability of the sulfonated carbons in the same type of reactions [10,11]. Degradation of the catalyst might be due to a prolonged period of stirring under reaction conditions, and in a second test the reaction was stopped after only 6 h, reaching nearly 90% yield. In such case the drop in catalytic activity (Figure 4) was less pronounced (TOF = 13.8×10^{-3} , Table 3), showing the role of contact time between catalyst and reaction medium in the deactivation process.

Catalytic activity depends on the alcohol used in the esterification reaction, in the order methanol (TOF = $17.4 \times 10^{-3} \text{ s}^{-1}$) > ethanol (TOF = $10.6 \times 10^{-3} \text{ s}^{-1}$) >> isopropanol (TOF = $1.5 \times 10^{-3} \text{ s}^{-1}$), in agreement with the slower reaction with a sterically more hindered secondary alcohol. In all cases deactivation occurs, irrespective of the alcohol used.

3.3. Deactivation studies

The deactivation of sulfonated carbons had been ascribed, at least in part, to extraction of soluble sulfonated material into the liquid phase, both in the case of carbon prepared by pyrolysis of glucose [33] and in hydrothermal carbons prepared from *p*-toluenesulfonic acid/glucose/resorcinol mixtures [14]. The sulfur analysis of the recovered catalyst (Table 1) seems to confirm this hypothesis, although a loss of 18% in sulfur content cannot account for a loss of 65% in activity (Table 3). To assess the effect of leaching on deactivation, HC-SO₃H was pretreated with different solvents under reflux and the solid was tested after hot filtration to prevent deposition of the leached material. Figure

5 gathers the ester yield vs time graphs for pretreated catalysts in comparison with the untreated one (dashed lines) in successive cycles.

Properties of the treated solids, including sulfur content (Table 1) and catalytic activity (Table 3 and Figure 5), strongly depend on the solvent used in the pretreatment. Treatment with toluene under reflux for 72 h led to a solid with slightly lower sulfur content (0.49 mmol g^{-1}) but the same catalytic activity as the fresh catalyst. The low solubility of the highly oxygenated species of the hydrothermal carbon may account for this behavior. On the contrary, these species should be more soluble in acetone, and the analysis of the solid treated with acetone under reflux for 72 h (0.42 mmol g^{-1}) agrees with this point. In spite of the slightly higher degree of leaching compared with the analysis of the used catalyst (0.45 mmol g^{-1}), the decrease in activity is only minor, considering the weight of catalyst (Figure 5A) and even the sites on the solid show slightly higher activity (TOF, Table 3). Furthermore, the acetone extract was evaporated under vacuum and the residue was used as catalyst in another esterification reaction, with very low catalytic activity (Figure 5A), accounting for the difference in yield observed between the fresh catalyst and the treated one.

The situation is completely different when using an alcohol as solvent for treatment. Treatment with 1-propanol under reflux for 72 h produces an important degree of sulfur leaching, reducing its content (0.32 mmol g^{-1}) to less than 60% of the initial amount. Consequently, the activity of the solid is significantly reduced (Figure 5A) but the activity per site remains high (TOF $13.6 \times 10^{-3} \text{ s}^{-1}$ compared to $17.4 \times 10^{-3} \text{ s}^{-1}$ of the fresh catalyst). In the case of methanol, treatment under reflux was carried out only for 24 h (reaction conditions). The loss of sulfur is analogous to that observed under reaction conditions (Table 1) but deactivation is much higher (Figure 5A), leading to the lowest TOF among

the pretreated and recovered catalysts ($2.7 \times 10^{-3} \text{ s}^{-1}$),* similar to the activity of the untreated catalyst in the third cycle (Figure 5A and Table 3). On the other hand, the activity of the liquid extract obtained in the pretreatment was also tested to detect leaching of acidic species. The methanol extract showed the same low activity as that observed in the case of the extract in acetone (Figure 5A). Moreover this activity does not account for the drop in catalytic activity of the solid, demonstrating the existence of at least a second and more important deactivation mechanism based on the presence of methanol, or alcohols in general taking into account the deactivation in the esterification with ethanol or isopropanol. In fact, as deactivation is produced by simple pretreatment with alcohol, it cannot be ascribed to the presence of adsorbed products or by-products responsible for pore or acid sites blocking, as proposed for some sulfonic catalysts [36,37].

Recovery of pretreated catalysts (Figure 5B) shows that catalytic behavior is quite similar in all cases, with a very significant drop in catalytic activity, analogous to that observed in the fresh catalyst. Moreover, sulfur analysis of the recovered catalyst pretreated in toluene (Table 1) shows a drop in sulfur content, from 0.49 to 0.40 mmol g⁻¹, similar to that observed in the use of fresh catalyst, from 0.55 to 0.45 mmol g⁻¹. In view of all these results, the partially deactivated catalysts were analyzed by solid state NMR.

3.4. NMR study of deactivated catalysts

Pretreatment with toluene did not produce any significant modification of the ¹³C-CP-MAS-NMR spectrum of HC-SO₃H with respect to the freshly prepared catalyst (Figure 6), in agreement with the same catalytic activity observed. On the contrary, the solid pretreated with methanol, as well as the catalyst recovered after esterification (not shown),

* This seems to be the limit for deactivation with alcohol, as the pretreatment with methanol under reflux for 96 h leads to the same catalytic activity.

presents a prominent signal at 52 ppm. This signal is compatible with a methoxy (-OCH₃) group, with a chemical shift between those of methanol (49 ppm) and methyl p-toluenesulfonate (56 ppm). The line width (fwhm = 620 Hz) seems to indicate a lack of mobility, together with a possible distribution of different types of sites. Both effects may be due either to a strong physisorption of molecular methanol by formation of hydrogen bonds with the highly oxygenated structure of the hydrothermal carbon or to chemical reaction of methanol with some sulfonic groups leading to surface methyl sulfonates. Some authors have proposed this possibility in the deactivation of mesoporous silicas modified with sulfonic groups [38,39], but without experimental evidences.

Given that 1-propanol is also able to partially deactivate the catalyst, it was used to test the presence of weakly physisorbed alcohol, taking advantage of its lower volatility. In addition to the pretreatment under reflux, the catalyst was also treated with 1-propanol at room temperature for a shorter time (5 h) and the ¹³C-CP-MAS-NMR spectra of both samples were recorded (Figure 7). The spectrum of the sample pretreated under reflux shows the three signals typical for 1-propanol at 67.7, 21.3, and 8.7 ppm, but with highly restricted mobility as shown by the line widths, 460, 320 and 400 Hz, respectively. In the case of the sample pretreated at room temperature a double set of signals appears, with the minor ones at the same chemical shifts (only visible those corresponding to C1 and C2) with similar line width, and the major ones with line widths in the 120-170 Hz range appearing at 63.6, 25.5 and 9.8 ppm. The signals can be then tentatively assigned to chemically bound propyl groups, favorably formed at high temperature, and more mobile strongly adsorbed (hydrogen bonded) propanol molecules. In this case, as the solid was not washed or dried under vacuum, weakly physisorbed propanol should remain on the solid, but the high mobility of those molecules make them not detectable by CP technique due to

the fast relaxation. In order to confirm this point, the direct polarization $^{13}\text{C}\{^1\text{H}\}$ -MAS-NMR spectrum was also registered (Figure 7) showing the very narrow signals corresponding to liquid propanol at 66.2, 28.1 and 12.5 ppm.

A further confirmation of this point was obtained by ^1H -MAS-NMR spectroscopy (Figure 8). The spectrum of the sample pretreated under reflux shows only very broad signals in agreement with the strong H-H dipolar coupling due to the lack of mobility of the surface species. In the case of the sample pretreated at room temperature, the presence of highly mobile liquid propanol is clearly shown by the very narrow signals, including that of hydroxyl group at 5 ppm.

In order to confirm the presence of chemically bound propyl groups, solids pretreated with 1-propanol were thoroughly washed with acetone and the ^{13}C -CP-MAS-NMR spectra were registered after drying under vacuum (Figure 9). As can be seen the spectrum of the sample pretreated under reflux remains unchanged, showing that chemically bound propyl groups are mainly formed at high temperature. On the other hand, the spectrum of the sample pretreated at room temperature keeps only small signals at the same chemical shifts, whereas the second set of more intense signals has disappeared, confirming that it corresponded to strongly physisorbed alcohol, as well as those of the liquid propanol detectable by direct polarization (not shown). In agreement with the very low amount of chemically bound propyl groups, the solid pretreated at room temperature shows the same activity per site than the fresh catalyst (Table 2), and the drop in activity per weight is mainly due to leaching.

An additional proof for the effect of the reaction of sulfonated carbon with alcohol on deactivation is the correlation between the intensity of the alkyl signal in the CP-MAS-NMR spectrum and the TOF of catalysts pretreated under different conditions. Two

samples of HC-SO₃H were pretreated with methanol under reflux for 2 and 6 h, in addition to the sample pretreated for 96 h. The band corresponding to MeO groups was integrated and normalized with respect to the broad band of the HC structure at 200-80 ppm, and the initial TOF of the esterification reaction obtained with those three pretreated catalysts and the freshly prepared one was represented *vs* the normalized integral.[†] As can be seen in Figure 10 there exist a clear correlation between catalytic activity and the presence of the methoxy groups in the solid, showing that they are formed by covalent bonding at expenses of the acid sites.

The NMR study, together with the deactivation results, points to a general picture of the interaction between HC-SO₃H with alcohols (Scheme 1) in which at room temperature the formation of hydrogen bonds between the alcohol and the different protic groups of the material (sulfonic and carboxylic acids, hydroxyls of alcohols and phenols) is favored, whereas under heating those species evolve to alkyl esters (sulfonic and carboxylic) or alkyl ethers. Reactivity of the different groups in the solid will be different, also depending on the nature of the alcohol, with methanol being the most reactive and hence the most deactivating for the solid acid. Experiments are currently in progress to demonstrate the generality of this effect on different solid acids.

[†] The MeO band overlaps with that corresponding to residual aliphatic carbons in the catalyst. Hence the value of the integral was not zero in the case of the freshly prepared catalyst.

4. Conclusions

The sulfonated hydrothermal carbons are highly active for esterification of palmitic acid with different alcohols (methanol, ethanol, 1-propanol), but the catalysts suffer an important deactivation upon recovery. Leaching of sulfonated species has only a minor role in this deactivation, as shown by pretreatment in aprotic solvents. On the contrary, the main deactivation mechanism is produced by simple treatment with alcohol. This deactivation is highly dependent on the nature of the alcohol, with methanol as the most efficient for deactivation. Solid state NMR shows the presence of bound alcohol on the catalyst, strongly physisorbed in the case of solid pretreated at room temperature and chemically bound in the case of solid pretreated under reflux. The formation of sulfonate esters by reaction of the sulfonic groups in the solid with the alcohol at high temperature explains the strongly deactivating effect of alcohol.

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Table 1. Chemical composition ($\text{CH}_x\text{O}_y\text{S}_z$) and sulfur content of hydrothermal carbons.

Sample	Treatment	x	y	z	S (mmol g^{-1})
HC	–	0.796	0.304	0.000	0.00
HC-SO ₃ H	–	0.466	0.528	0.012	0.55
HC-SO ₃ H	Esterification ^a	0.563	0.492	0.010	0.45
HC-SO ₃ H	Esterifications (2) ^a	0.816	-	0.008	0.42
HC-SO ₃ H	Esterifications (3) ^a	0.497	-	0.009	0.41
HC-SO ₃ H	MeOH (24 h) ^b	0.597	0.533	0.010	0.46
HC-SO ₃ H	Toluene ^b	0.592	0.435	0.010	0.49
HC-SO ₃ H	Toluene ^b +esterification ^a	0.633	0.427	0.008	0.40
HC-SO ₃ H	Acetone ^b	0.575	0.439	0.008	0.42
HC-SO ₃ H	Acetone ^b +esterification ^a	0.518	-	0.007	0.36
HC-SO ₃ H	1-Propanol ^b	0.667	0.421	0.007	0.32
HC-SO ₃ H	1-Propanol ^b +esterification ^a	0.546	-	0.006	0.32
HC-SO ₃ H	1-Propanol ^c	0.606	0.508	0.008	0.36
HC-SO ₃ H	1-Propanol ^c +esterification ^a	0.484	-	0.007	0.35

^a Catalyst used in an esterification reaction of palmitic acid with methanol under reflux for 24 h. Successive recycles in parenthesis. ^b Treatment with the solvent under reflux for 72 h (unless otherwise stated). ^c Treatment at r. t. for 5 h.

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2 Table 2. Conditions and catalytic activity in esterification reactions of sugar-derived sulfonated carbons.

Ref.	Acid	Alcohol	Catalyst (functionalization)	Acid/catalyst ratio	T (°C)	t (h)	Yield (%)	initial TOF (s ⁻¹)
11	Oleic (10 mmol)	MeOH	140 mg (4.7% S)	48.5	reflux	0.5	20	5.4×10^{-3}
13	Acetic (100 mmol)	EtOH	200 mg (1.8 mmol S/g)	277.8	70	-	-	16.7×10^{-3}
15	Oleic (25 mmol)	MeOH	430 mg (= 1 mmol H ⁺)	25.0	reflux	1	23	1.6×10^{-3}
this work	Palmitic (7.5 mmol)	MeOH	100 mg (1.76% S)	136.4	reflux	1	46	17.4×10^{-3}

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Table 3. Catalytic activity of HC-SO₃H in esterification of palmitic acid with methanol.^a

Pretreatment	initial TOF (s ⁻¹) ^b
–	17.4 × 10 ⁻³
used ^c (24h)	6.4 × 10 ⁻³
used ^c (6h)	13.8 × 10 ⁻³
used twice ^c (24h)	3.0 × 10 ⁻³
MeOH (24 h) ^d	2.7 × 10 ⁻³
Toluene ^d	18.8 × 10 ⁻³
Toluene ^d + used ^c (24h)	4.2 × 10 ⁻³
Acetone ^d	20.4 × 10 ⁻³
Acetone ^d + used ^c (24h)	10.4 × 10 ⁻³
1-Propanol ^d	13.6 × 10 ⁻³
1-Propanol ^d + used ^c (24h)	5.9 × 10 ⁻³
1-Propanol ^e	17.5 × 10 ⁻³
1-Propanol ^e + used ^c (24h)	6.6 × 10 ⁻³

^a Under reflux for 24 h. ^b Calculated as: (initial mmol of palmitic acid × conversion after 1 h/100)/(mass of catalyst × S content × 3600). ^c Catalyst used in an esterification for the specified reaction time. ^d Treatment with the solvent under reflux for 72 h (unless otherwise stated). ^e Treatment at r. t. for 5 h.

Figure Captions

Figure 1. SEM image of HC.

Figure 2. IR spectra of HC (bottom) and HC-SO₃H (top).

Figure 3. ¹³C-CP-MAS-NMR spectra of HC (bottom) and HC-SO₃H (top).

Figure 4. Yield of methyl palmitate: (■) HC-SO₃H, reaction stopped after 24 h. (▲) HC-SO₃H, reaction stopped after 6 h, (◆) blank (HC). Solid line: first use. Dashed line: second use.

Figure 5. A) Yield of methyl palmitate after pretreatment of HC-SO₃H in refluxing solvents: (×) toluene, (▲) acetone, (◆) propanol, (■) methanol. Dotted line: activity of the acetone extract (see text). Dashed lines: results with fresh untreated catalyst in the successive cycles. B) Second use of treated catalysts.

Figure 6. ¹³C-CP-MAS-NMR spectra of as-prepared HC-SO₃H (bottom) and treated with toluene (middle) or methanol (top) under reflux.

Figure 7. ¹³C-CP-MAS-NMR spectra of HC-SO₃H treated with 1-propanol under reflux (top) and at rt (middle). Bottom: direct polarization spectrum of the sample treated at rt.

Figure 8. ¹H-MAS-NMR spectra of HC-SO₃H treated with 1-propanol under reflux (top) and at rt (bottom).

Figure 9. ¹³C-CP-MAS-NMR spectra of HC-SO₃H pretreated with 1-propanol and then washed with acetone: treatment under reflux (top) and at rt (bottom).

Figure 10. Initial TOF (h⁻¹) in esterification of palmitic acid with methanol vs normalized integral of the methoxy band in CP-MAS-NMR of the pretreated catalyst in methanol for different times.

