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Biobased catalyst in biorefinery processes: sulphonated hydrothermal carbon for glycerol esterification†

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Sulphonated hydrothermal carbon (SHTC), obtained from D-glucose by mild hydrothermal carbonisation and subsequent sulphonation with sulphuric acid, is able to catalyse the esterification of glycerol with different carboxylic acids, namely, acetic, butyric and caprylic acids. Product selectivity can be tuned by simply controlling the reaction conditions. On the one hand, SHTC provides one of the best selectivity towards monoacetins described up to now without the need for an excess of glycerol. On the other hand, excellent selectivity towards triacylglycerides (TAG) can be obtained, beyond those described with other solid catalysts, including well-known sulphonic resins. Recovery of the catalyst showed partial deactivation of the solid. The formation of sulphonate esters on the surface, confirmed by solid state NMR, was the cause of this behaviour. Acid treatment of the used catalyst, with subsequent hydrolysis of the surface sulphonate esters, allows SHTC to recover its activity. The higher selectivity towards mono- and triesters and its renewable origin makes SHTC an attractive catalyst in biorefinery processes.

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Introduction

Even though biodiesel production has decreased in the past years, the use of glycerol itself and glycerol derivatives has been the focus of the interest of many researchers, probably due to their availability, renewable origin and usefulness as building blocks¹ or as solvents² in industrial applications. Among glycerol derivatives, esters have been profusely used in industry, above all triacylglycerols. For instance, *ca.* twenty new applications for triacetin appear monthly. As some examples, triacetin has been used as a solvent for caffeine extraction from coffee or tea,³ as well as in ceramic preparation *via* enzymatic catalysis acting as a pH regulator when hydrolyzed in reaction media.^{4,5} On the other hand, monoacylglycerols with ester moieties with 1 to 7 carbon atoms have been used as solvents in antibacterial or anti-mould formulations,⁶ as well as cellulose plasticizers.⁷ Finally, acylglycerols have also been described as fuel additives.⁸

Acylglycerols have been used as reaction media but to a lesser extent. Diacetin, triacetin and tributyrin have been

used as solvents in three characteristic organic reactions, namely, nucleophilic substitution, Suzuki cross-coupling reaction and enzymatic asymmetric reduction.⁹ Triacetin plays simultaneously the roles of a solvent and an acyl donor in the synthesis of isoamyl acetate^{10,11} catalyzed by lipase CALB or Amberlyst 36 and in the one-pot synthesis of cinnamyl acetate from cinnamaldehyde,¹² and only that of a reaction medium in the production of paclitaxel,¹³ an anti-cancer drug.

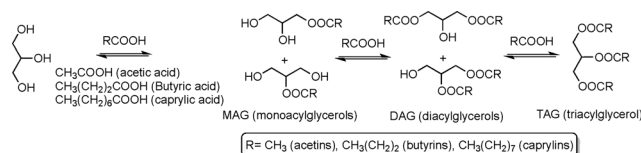
Due to the increasing interest in glycerol-derived esters, in the past few years great attention has been paid to glycerol acetylation with acetic acid (Scheme 1) and several studies have been published dealing with the use of solid acid catalysts, such as Amberlyst 15 or other sulphonic resins,^{14–17} mesoporous materials with anchored sulphonic groups,^{16,18,19} K10 montmorillonite,¹⁷ SnCl₂,²⁰ hydroxylated magnesium fluoride,²¹ and heteropolyacids.^{22,23} In general sulphonic solids, either resins or mesoporous materials, and K10 have shown much better performance than zeolites and other solid acids, such as niobic acid and sulphated zirconia.^{14,16,17}

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Scheme 1 Acylation of glycerol with carboxylic acids.

Some of these studies showed that glycerol conversion and reaction selectivity towards mono-, di- or triacetins strongly depend on the nature (hydrophobicity–hydrophilicity)¹⁴ of the catalyst surface and the density and strength of the acid catalytic sites.^{16,18,19}

In the past years, sulphonated carbons²⁴ have emerged as an interesting alternative to both organic and inorganic acidic materials, with the additional advantage of being prepared from renewables.²⁵ The use of sulphonated carbons in glycerol esterification has been recently described.^{26,27} Sulphonated pyrolysed (400 °C) sucrose provided excellent glycerol conversion and a maximum of 50% selectivity towards TAG at 180 °C.²⁶ Sulphonated activated carbon led to mixtures of 38% MAG, 28% DAG and 34% TAG at 120–135 °C with glycerol conversions over 90%.²⁷

Carbons prepared under mild conditions, such as hydrothermal carbon (HTC), are very attractive materials from a sustainability point of view. Sulphonated hydrothermal carbon (SHTC) has been used as a solid acid catalyst in esterification reactions of fatty acids,^{28–31} showing remarkable performance despite the apparently very low surface area. In this manuscript, we present a deep study of the acetylation of glycerol catalysed by sulphonated hydrothermal carbon (SHTC). Several reaction parameters have been studied, such as reaction temperature, excess of acid or catalyst loading, as well as the possibility of catalyst recovery. The activity of SHTC has been compared with that of some commercial sulphonic solids, and the optimised reaction conditions have been applied to the esterification of glycerol with butyric and caprylic (octanoic) acids, in order to broaden the scope of application of this catalyst.

Results and discussion

Preparation and characterization of the solids

Hydrothermal carbon (HTC) was prepared by introducing an aqueous solution (1 M) of glucose in a Teflon lined autoclave and keeping it at 195 °C for 19 h. HTC was obtained in the form of nanospheres (300–400 nm diameter), slightly smaller than those reported for analogous materials.³¹ Sulphonation of HTC was carried out by treatment with concentrated sulphuric acid at 150 °C for 15 h. Apparently, the nanosphere morphology was not modified by the sulphonation process.³² The main properties of both solids are collected in Table 1.

HTC is a carbonaceous material with relatively high oxygen and hydrogen contents (O/C ratio = 0.304; H/C ratio = 0.796). This composition corresponds to a structure based mainly on furan moieties directly bonded or linked through alkyl (methylene) or ketone bridges.³³ Sulphonation reduces the hydrogen content and increases the oxygen content, in agreement with an oxidation process, occurring in parallel with the sulphonation reaction. The surface area, determined by nitrogen adsorption isotherm measurement, was always low (6–7 m² g⁻¹), but slightly higher than the values reported in the literature,^{31,34} in agreement with the smaller particle size. The pore volume is also low (9–14 μl g⁻¹). However,

Table 1 Composition, textural properties and acidity of hydrothermal carbons

Sample		HTC	SHTC	Used SHTC
Composition ^a	H/C	0.796	0.514	0.616
	O/C	0.304	0.546	0.578
	S/C	0.000	0.009	0.007
N ₂ adsorption	S _A (m ² g ⁻¹)	7.0	5.9	n.d.
	V _p (cm ³ g ⁻¹)	0.014	0.009	n.d.
CO ₂ adsorption	S _A (m ² g ⁻¹)	142.5	224.3	256.0
	V _p (cm ³ g ⁻¹)	0.057	0.090	0.100
Acidity (mmol g ⁻¹)	Total ^b	3.42	5.43	4.61
	Sulphonic ^c	0.00	0.40	0.32
	Non-sulphonic ^d	3.42	5.03	4.29

^a Molar ratio determined by CHS combustion analysis and O analysis by pyrolysis. ^b Determined by back-titration. ^c Determined by sulphur analysis. ^d Calculated by difference.

higher values of surface areas were obtained (up to 224 m² g⁻¹) by CO₂ adsorption, demonstrating the presence of ultramicropores in the solid. Back titration with a solution of 0.01 M NaOH allowed the determination of the total acidity. In the case of SHTC, the total acidity was 5.43 mmol g⁻¹, whereas the number of sulphonic groups, calculated from the S content, is only 0.4 mmol g⁻¹. The rest of the acidic sites (5.03 mmol g⁻¹) corresponds to carboxylic and hydroxyl sites. This high functionalization forms a dense hydrogen-bond network responsible for the microporosity detected by CO₂ adsorption, which is not permanent as shown by the full access to the acid sites in the presence of a polar protic solvent.³⁵

Screening of reaction conditions

The activity of SHTC was first evaluated in the acetylation of glycerol with acetic acid. Screening of two reaction parameters was made, namely, the temperature (bath temperature 40, 80 and 115 °C) and the acetic acid/glycerol molar ratio (3:1, 6:1, and 9:1). Conversion of glycerol and selectivities towards mono-, di- and triacetins were chosen as response factors. A 10% w/w catalyst was used, that is 0.4% molar ratio of SO₃H sites with respect to glycerol. The reaction time was fixed at 10 h. The reaction was also carried out in the absence of the catalyst at 40 °C and 115 °C. The results are gathered in Table 2.

A big influence of the reaction temperature on glycerol conversion and reaction selectivity was observed. Thus at 40 °C, glycerol conversion reached 70% at 10 h of reaction time and monoacetins were the major products (up to 89% selectivity) regardless of the amount of acetic acid. To the best of our knowledge, this overall result is among the best ones described in the literature, comparable with the 84% MAG selectivity at 82% conversion with sulphonic SBA15 (ref. 19) or the 90% MAG selectivity at 55% conversion with K10 montmorillonite,¹⁷ without the need for an excess of glycerol.³⁶ At 40 °C, the reaction nearly did not take place in the absence of the catalyst, even with an excess of acetic acid.

Table 2 Glycerol conversion and product selectivities in the acetylation of glycerol with acetic acid catalysed by SHTC^a

Temp.	AcOH/gly	Conversion	%MAG	%DAG	%TAG
40 °C	3 : 1	32	85	15	0
	6 : 1	70	88	12	0
	9 : 1	70	89	11	0
Blank	9 : 1	7	100	0	0
80 °C	3 : 1	90	46	50	4
	6 : 1	93	33	57	10
	9 : 1	97	28	62	10
115 °C	3 : 1	99	9	51	40
	6 : 1	98	6	49	45
	9 : 1	98	5	38	57
Blank	9 : 1	95	32	57	11

^a Results determined by GC. Reaction time 10 h, 10% w/w catalyst.

An increase in temperature to 80 °C provided reaction mixtures in which diacetins are the major products, with more than 60% selectivity at a high acetic acid/glycerol molar ratio. Finally, good selectivity towards triacetin was obtained (57%) at higher temperature by using a larger excess of acetic acid. Interestingly, this high selectivity towards TAG is obtained with only small amounts of MAG in the reaction mixture. The triacetin selectivity can be improved up to 61% at 24 h of reaction time. This result is also remarkable, as in the literature^{14,16–19,23,23,26,27} the described triacetin yields are normally lower than the yields of diacetins, regardless of the temperature and the excess of acetic acid, whereas in our case triacetin is the major product. Just very recently, Khayoon *et al.*³⁷ described a similar triacetin selectivity, using Y-SBA as a catalyst, but in that case MAG selectivity was higher, up to 19%. When the reaction was carried out without the catalyst, good glycerol conversions are achieved but diacetin is in this case the major product, with very low triacetin selectivity.

As mentioned in the introduction, triacetin is an interesting product due to its industrial applications. Above this, triacetin is also the most challenging product and selectivity towards TAG can be used as an indicator of the catalytic activity. In view of this, the optimized conditions to obtain TAG, that is an acetic acid/glycerol molar ratio of 9:1 and 115 °C, were used to continue the study. First, a test to determine the influence of reducing the amount of catalyst from 10% w/w to 5% w/w and 1% w/w was carried out. Reactions were monitored with time and the results are presented in Fig. 1.

Although glycerol conversions were excellent in all cases at short reaction times (nearly quantitative in less than 1 h with 5% w/w), the product selectivity was strongly dependent on the amount of catalyst and reaction time. As can be seen, a reduction of the amount of catalyst from 10% to 5% w/w did not produce any significant change in glycerol conversion or in the yield of monoacetins, but had given rise to different TAG/DAG distributions. Thus, at 24 h of reaction time with the 10% w/w catalyst, triacetin was the major product, with a TAG/DAG ratio of 1.79, while with the 5% w/w catalyst the

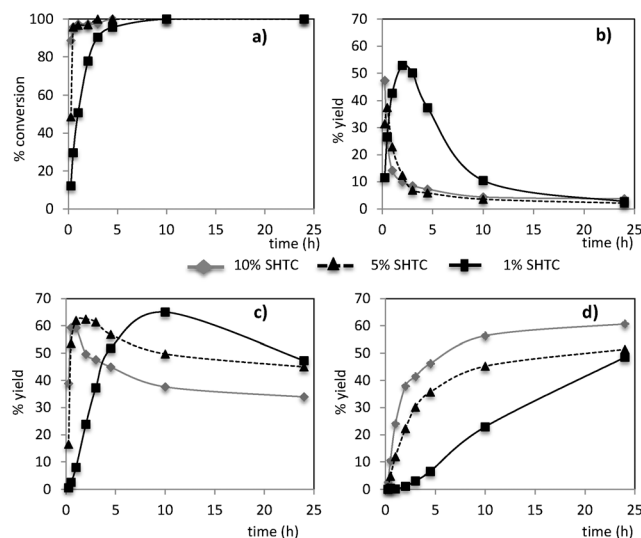


Fig. 1 Influence of the amount of catalyst in glycerol conversion (a) and yields of monoacetins (b), diacetins (c), and triacetin (d) in glycerol acetylation with acetic acid catalysed by SHTC (reaction temperature 115 °C, acetic/glycerol ratio 9 : 1; results determined by GC).

TAG/DAG ratio decreased to 1.15. When the 1% w/w catalyst was used, the results appeared to be identical to the ones in the blank reaction, that is 95.3% glycerol conversion in 4.5 h of reaction time with 41% yield of monoacetins, 51% yield of diacetins and only 7% yield of triacetin. These results can be considered as normal, given that the 1% w/w catalyst represents only 0.04 mol% of SO₃H with respect to glycerol.

Comparison of several solid acid catalysts

When we tried to compare the results of glycerol esterification catalysed by SHTC with those of other sulphonic solids, previously published, we found that the reaction conditions were different in many cases and conclusions about their relative activity were difficult to extract.

Two arylsulphonic resins (Amberlyst 15, Dowex 50W ×2) and one alkylsulphonic resin (Deloxan) were tested under the optimal reaction conditions (115 °C and 9 : 1 AcOH : glycerol molar ratio) to obtain triacetin. The weight of the catalyst was varied in order to maintain in all cases a constant ratio of the number of sulphonic sites per mol of glycerol, that is 0.4% molar ratio. The results are gathered in Table 3.

The TON value (productivity) with respect to the glycerol conversion is highly dependent on the initial glycerol/acid ratio, as the conversion is in general close to quantitative due to the easy first esterification reaction to produce monoacetins. Similar TON values are achieved with all the solids.

However, the synthesis of diacetins and triacetin represent two and three esterification reactions, respectively, and thus the TON calculated would be more significant with respect to esterification reactions, that is the number of acetate groups formed per acid site.

With this parameter, differences are observed when calculating TON with respect to the number of acetate groups

Table 3 Comparison of the productivity of SHTC and other sulphonic solids in the esterification of glycerol with acetic acid under the same reaction conditions

Catalyst	Reaction time 1 h		Reaction time 10 h	
	TON (conv) ^a	TON (acet) ^b	TON (conv) ^a	TON (acet) ^b
	SHTC	187	393(138)	189
Dowex 50W ×2	180	324(73)	189	453 (231)
Amberlyst 15	181	294(21)	188	436 (234)
Deloxan	181	307(36)	187	436 (236)

Reaction conditions: 0.4 mol% catalyst, acetic acid/glycerol ratio of 9:1, 115 °C. ^a Mol of glycerol converted per mol of sulphonic group.

^b Mol of acetic acid converted per mol of sulphonic group or acetate group formed per sulphonic acid site. In parentheses, the TON only of the third acetate in triacetin (mol of triacetin formed per mol of sulphonic group).

formed, especially triacetin. Thus at 1 hour of reaction time, SHTC and Dowex showed higher values than Ambelyst and Deloxan that exhibited similar activity. But SHTC provided twice the value of TON, with respect to triacetin, of Dowex. At 10 h of reaction time, acetate TON of the solids become similar but again SHTC exhibited higher values of TON in triacetin, demonstrating a higher activity of this catalyst under the same reaction conditions. This higher activity was also previously observed in the esterification of palmitic acid with methanol.³⁵ This behaviour was attributed to the cooperative effect of acid sites, due to their high density in the solid. The same cooperative catalysis by adjacent Brønsted acid sites has been also recently observed in fructose dehydration catalysed by HZSM5.³⁸ The authors reported that the multiple nearby sites can interact simultaneously with one reactant molecule to favour its activation. In our case, the favourable interaction of the catalyst surface with the polyfunctional diacetins could explain the higher reactivity to promote the esterification of the third hydroxyl group of glycerol with the nearby activated acetic acid and hence provoking an increased triacetin selectivity.

Reactions of glycerol with butyric and caprylic acids

Once the optimization of the reaction conditions and the screening of the catalysts were performed, SHTC was also tested in the esterification of glycerol with carboxylic acids having a longer hydrocarbon chain, such as butyric and caprylic acids. The idea of using butyric acid came from the interest in mono-, di- and tributyrins at an industrial level.^{39,40} The use of caprylic acid would demonstrate the general applicability of this solid even with fatty acids.

Reactions were carried out under the best conditions determined for acetylglycerol derivatives, that is 115 °C, 9:1 acid/glycerol molar ratio and 10% w/w catalyst. The results gathered in Table 4 show that, as in the case of using acetic acid, high glycerol conversions were achieved in only 1 hour and SHTC appeared to be also active in these reactions

Table 4 Glycerol conversion and product selectivities in SHTC^a catalyzed esterification of glycerol with butyric and caprylic acids^b

Acid	Time (h)	Conversion	%MAG	%DAG	%TAG
Butyric	1	95	43	52	5
	10	99	1	24	75
	24	99	1	18	81
Blank	24	99	11	62	27
	24	99	11	62	27
Caprylic	1	76	61	37	2
	10	98	2	42	56
	24	100	1	19	80
Blank	24	93	5	67	28

^a Another batch of SHTC was used, with a functionalization of 0.59 mmol of S per g. ^b Results determined by GC. Reaction conditions: 10% w/w catalyst, 115 °C, acid/glycerol molar ratio of 9:1.

providing high selectivities towards tributyrin and tricaprylin at longer reaction times.

Study of the recoverability of SHTC

The reuse of the catalyst was also studied and in all the cases SHTC was significantly deactivated upon recovery, as it happened in the esterification of palmitic acid.²⁸ At 10 h of reaction time, the fresh catalyst exhibited a TON of 188 for glycerol conversion while upon recovery, the TON slightly decreased to 152. However, the product distribution strongly varied, and with the reused catalyst MAG and DAG were the major products. For the sake of comparison, a carboxylic acrylic resin Dowex CCR-2 was tested in the acetylation of glycerol under the same conditions as SHTC and reused SHTC. The results gathered in Fig. 2 show that upon reuse, SHTC exhibited the same results as the carboxylic resin and as the blank reaction, behaving as if all the sulphonic groups were deactivated.

Analysis of the catalyst after the reaction (Table 1) revealed that 80% of the sulphur content remained in the solid and the surface area and pore volume did not decrease, thus deactivation could not be attributed to the leaching of

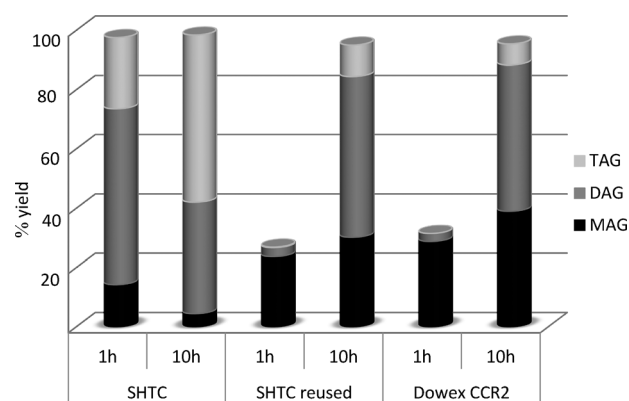


Fig. 2 Yields (determined by GC) of MAG, DAG and TAG in glycerol acetylation catalysed by SHTC, reused SHTC, and Dowex CCR2, at 115 °C and AcOH/glycerol ratio of 9:1.

sulphur, given that the reaction also takes place with half the amount of catalyst as shown in Fig. 1, nor to the blocking of the pores, as the textural properties (Table 1) are similar to those of the fresh catalyst.

In the case of the reaction of palmitic acid with MeOH, the esterification of the sulphonic sites was shown to be the main deactivation mechanism,^{28,35} and a similar effect may be also driven by glycerol. In order to confirm this hypothesis, the ¹³C-CP-MAS-NMR spectrum of the used catalyst was recorded and compared with that of the fresh SHTC (Fig. 3).

The ¹³C-CP-MAS-NMR spectrum of the catalyst used in the reaction at 115 °C (Fig. 3) shows the presence of new bands, a small one at 20 ppm, compatible with -OOC-CH₃ groups, and the most prominent one at 69 ppm, compatible with glycerol species that may have reacted with the acidic groups on the SHTC surface, as it happened in the case of esterification with methanol.^{28,35} To prove the nature of this band, SHTC was treated with glycerol under different conditions and the spectra are collected in Fig. 4.

First of all, glycerol was adsorbed on SHTC at room temperature, to prevent any reaction with the acidic groups. As can be seen (Fig. 4b), two signals at 73 and 64 ppm are obtained, typical for the carbons of the secondary and primary alcohols of glycerol, respectively. When SHTC is treated with glycerol at 115 °C and thoroughly washed with methanol, a broad signal at 69 ppm is obtained with a higher intensity for increasing treatment times (Fig. 4c and d). It is also significant that the signals of physisorbed glycerol are much thinner than those of the solids treated at 115 °C, in agreement with the higher mobility of the physisorbed molecules in comparison with that of those covalently bonded on the surface. In Fig. 4 the two possible types of surface species formed are also presented, bonded either with only one or with two covalent bonds. The question about the formation of surface sulphonates or only carboxylates was studied by

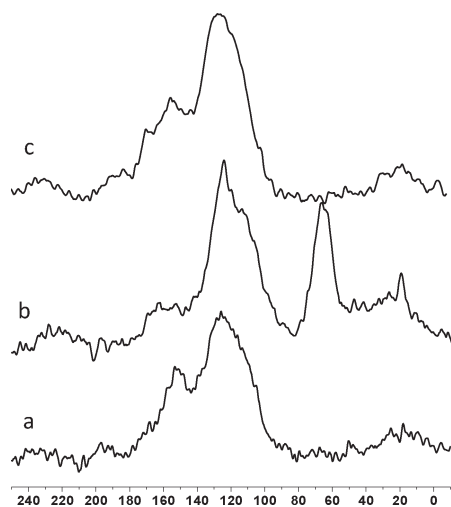


Fig. 3 ¹³C-CP-MAS-NMR spectra: a) SHTC, b) SHTC used in the reaction of glycerol with acetic acid at 115 °C, c) SHTC used and regenerated with H₂SO₄ (66%).

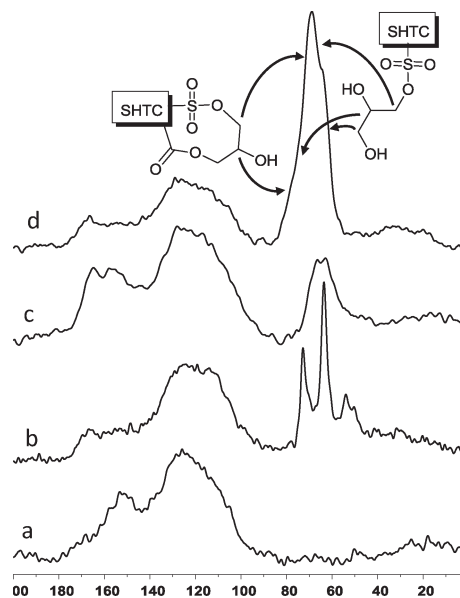


Fig. 4 ¹³C-CP-MAS-NMR spectra: a) SHTC, b) SHTC with glycerol physisorbed at room temperature, c) SHTC treated with glycerol at 115 °C for 4 h and washed with methanol, d) SHTC treated with glycerol at 115 °C for 24 h and washed with methanol.

adsorption of triethylphosphine oxide (TEPO) as a probe molecule. The bonding of triethylphosphine oxide (TEPO) to the acid site of a surface produces a systematic change in the ³¹P isotropic chemical shift that is proportional to the acid strength of the adsorption site.⁴¹ It has been also described that alkylsulphonic groups give the ³¹P chemical shift of TEPO in the range of 71–77 ppm, whereas the value for arylsulphonic groups in Amberlyst 15 is 86 ppm.^{35,42}

The intensity of the ³¹P-MAS-NMR band at 87 ppm, corresponding to TEPO adsorbed on sulphonic sites, is significantly reduced in the SHTC catalyst used in one reaction at 60 °C (Fig. 5), whereas it completely disappears in the solid treated with glycerol at 115 °C. Only the band at 62 ppm, corresponding to TEPO adsorbed on carboxylic sites, remains visible. This result demonstrates that sulphonic sites are involved in the formation of surface esters, the main mechanism for deactivation of SHTC. As the deactivation of the catalyst was due to the esterification of the sulphonic sites by glycerol, an attempt to recover the catalyst was done by acid treatment of the solid after the reaction. The catalyst was treated at 150 °C for 15 h with H₂SO₄ (98%) or H₂SO₄ (66%).

After thorough washing with water and drying overnight, the regenerated catalysts were reused in the acetylation of glycerol. Although a slight influence of the acid concentration is observed on the product distribution (Fig. 6), the solids treated with sulphuric acid behave as the fresh SHTC. Sulphur analysis of SHTC before and after acid treatment did not show any increase in sulphur content, precluding any additional sulphonation of HTC. On the contrary, the ¹³C-CP-MAS-NMR spectrum (Fig. 3c) showed that the bands assigned to bonded glycerol and acetate completely disappeared. Thus the recovery of the activity was due to

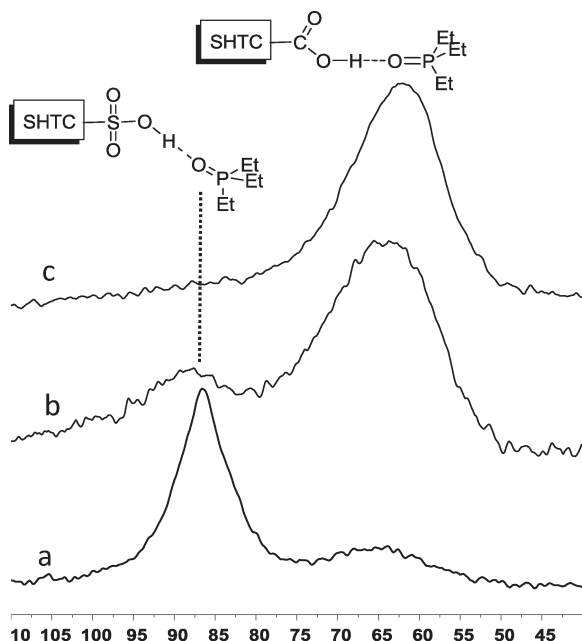


Fig. 5 ^{31}P -MAS-NMR spectra of TEPO adsorbed from methanol solutions on: a) SHTC, b) SHTC used in the reaction of glycerol with acetic acid at 60 °C for 4 h, and c) SHTC treated with glycerol at 115 °C for 24 h.

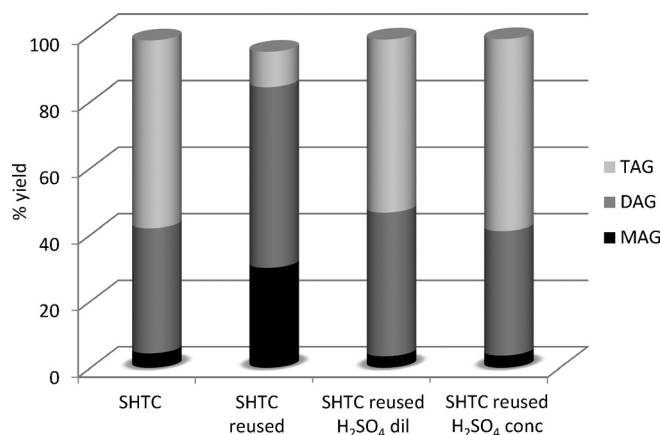


Fig. 6 Yields of products in acetylation of glycerol catalysed by fresh, used and regenerated SHTC (acetic acid/glycerol ratio of 9:1, 115 °C, time reaction 24 h, determined by GC).

hydrolysis of the sulphonated esters and hence confirmed that the esterification of the sulphonic groups was the reason for the catalyst deactivation.

Experimental

Esterification of glycerol

Glycerol (0.3 g, 3.25 mmol), acetic acid (0.6, 1.2 or 1.8 ml; 9.75, 19.5 or 29.25 mmol), SHTC (0.03 g, 0.012 mmol SO_3H), and 1-methylnaphthalene (0.03 g, 0.21 mmol) as an internal standard were stirred (≈ 1000 rpm) in a round flask immersed in a silicone bath at different temperatures (40 °C,

80 °C or 115 °C). The reaction was monitored by gas chromatography. At the end of the reaction, methanol was added to the reaction medium; the catalyst was filtered off, thoroughly washed with methanol and dried overnight at 115 °C prior to reuse. In the case of using sulphonic resins, the same loading of sulphonic groups (0.4 mol%) was used in each case. Reactions of glycerol with butyric and octanoic acid were carried out in the same way as acetylation reactions.

Regeneration of the catalyst by acid treatment

The catalyst recovered from the reaction medium as indicated in the prior section was treated with 96% or 65% sulphuric acid (15 ml g^{-1}) at 150 °C for 15 h and thoroughly washed with hot water (90 °C). Then the solid was dried overnight at 115 °C and reused under the same reaction conditions previously described.

Conclusions

SHTC showed a high activity in the esterification of glycerol with acetic, butyric and caprylic acids. Product selectivity could be tuned by adjusting the reaction temperature. Thus at 40 °C high selectivity toward monoacetylglycerol was obtained without the need for an excess of glycerol. When high reaction temperatures were used, triesters were mainly obtained. High reaction temperatures and long reaction times also favoured the deactivation of the catalyst by esterification of the sulphonic groups with glycerol. The superiority of the catalyst is attributed to cooperative effects. The acid treatment of deactivated SHTC made the recovery of the activity of the catalyst possible by hydrolysis of the surface sulphonic esters.

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