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Biobased Catalyst in Biorefinery Processes: Sulphonated Hydrothermal Carbon for Glycerol Esterification

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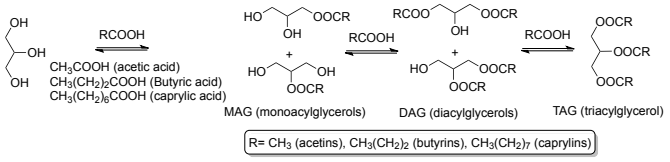
Sulphonated hydrothermal carbon (SHTC), obtained from D-glucose by mild hydrothermal carbonisation and subsequent sulphonation with sulphuric acid, is able to catalyse the esterification of glycerol with different carboxylic acids, namely acetic, butyric and caprylic acids. Product selectivity can be tuned by simply controlling the reaction conditions. On the one hand, SHTC provided one of the best selectivity towards monoacetins described up to now with no need of using 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 a partial deactivation of the solid. The formation of sulphonate esters on the surface, confirmed by solid state NMR, was the cause for this behaviour. Acid treatment of the used catalyst, with the 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.

Introduction

Even though biodiesel production has decreased in the last years, the use of glycerol itself and glycerol derivatives has focused the interest of many researchers, probably due to their availability, renewable origin and usefulness as building blocks[1] or as solvents[2] 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 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 the reaction media.[4,5] On the other hand, monoacylglycerols with ester moieties from 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, such as nucleophilic substitution, Suzuki cross-coupling reaction and enzymatic asymmetric reduction.[9] Triacetin plays simultaneously the roles of solvent and acyl donor in the synthesis of isoamyl acetate[10,11] catalyzed by lipase CALB or Amberlyst 36, in the one-pot synthesis of cinnamyl acetate from cinnamaldehyde[12] and only that of reaction medium in the production of paclitaxel,[13] an anticancer drug.
Due to the increasing interest in glycerol derived esters, in the last few years a great attention has been paid to glycerol acetylation with acetic acid (Scheme 1) and several works have been published dealing with the use of acid solid catalysts, such as Amberlyst 15 or other sulphonic resins,[14–17] mesoporous materials with anchored sulphonic groups,[16,18,19] K10 montmorillonite,[17] $SnCl_2$,[20] hydroxylated magnesium fluoride,[21] or heteropolyacids.[22,23] In general sulphonic solids, either resins or mesoporous materials, and K10 have shown much better performance than zeolites and other acid solids, such as niobic acid or sulphated zirconia.[14,16,17]



Scheme 1 Acylation of glycerol with carboxylic acids.

Some of these studies showed that glycerol conversion, and reaction selectivity towards mono, di or triacetin 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 last years, sulphonated carbons[24] are emerging 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 pyrolised (400ºC) sucrose provided excellent glycerol conversion and a maximum of 50% selectivity towards TAG at 180ºC.[26] Sulphonated activated carbon led to mixtures of 38% MAG, 28% DAG and 34% TAG at 120-135ºC with glycerol conversions over 90%.[27]

Carbons prepared under mild conditions, such as hydrothermal carbon (HTC), are materials very attractive from a sustainability point of view. Sulphonated hydrothermal carbon (SHTC) has been used as 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 carbons (SHTC). Several reaction parameters have been studied, such as reaction temperature, excess of acid or catalyst loading, as well as the possibility of the 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 (1M) of glucose in a Teflon lined autoclave and keeping it at 195ºC 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 a treatment with concentrated sulphuric acid at 150ºC for 15h. 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 bounded 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 to the sulphonation reaction. Surface area, determined by nitrogen adsorption isotherm, was always low (6-7 $m^2 g^{-1}$), but slightly higher than values reported in the literature,[31,34] in agreement with the smaller particle size. The porous volume is also low (9-14 $\mu l\ g^{-1}$)

However, higher values of surface areas were obtained (up to 224 $m^2\ g^{-1}$) by CO_2 adsorption, demonstrating the presence of ultramicropores in the solid. Back titration with a solution of NaOH 0.01M allowed the determination of 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 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 CO_2 adsorption, which is not permanent as shown by the full access to the acid sites in the presence of a polar protic solvent.[35]

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.

Screening of reaction conditions

The activity of the SHTC was first evaluated in the acetylation of glycerol with acetic acid. A screening of two reaction parameters was made, namely the temperature (bath temperature 40, 80 and 115ºC) and the acetic acid/glycerol molar ratio (3:1, 6:1, 9:1). Conversion of glycerol and selectivities towards mono, di and triacetin were chosen as response factors. 10% w/w catalyst was used, that is 0.4% molar ratio of SO_3H sites with respect to glycerol. Time reaction was fixed at 10h. The reaction was also carried out in the absence of catalyst at 40ºC and 115ºC. Results are gathered in Table 2.

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
40ºC	3:1	32	85	15	0
	6:1	70	88	12	0
	9:1	70	88	12	0
blank	9:1	7	100	0	0
80ºC	3:1	90	46	50	4
	6:1	93	33	57	10
	9:1	97	28	62	10
115ºC	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.

A big influence of the reaction temperature on glycerol conversion and reaction selectivity was observed. Thus at 40ºC, glycerol conversion reached 70% at 10h reaction time and monoacetins were the major products (up to 89% selectivity) regardless 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[19] or the 90% MAG selectivity at 55% conversion with K10 montmorillonite,[17] without the need of using an excess of glycerol.[36] At 40ºC the

reaction nearly did not take place in the absence of catalyst, even with an excess of acetic acid.

An increase of temperature to 80ºC provided reaction mixtures in which diacetins are the major products, with more than 60% selectivity at high acetic acid/glycerol molar ratio. Finally, a good selectivity towards triacetin was obtained (57%) at higher temperature and using 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 24h reaction time. This result is also remarkable, as in the literature[14,16–19,23,26,27,23] described triacetin yields are normally lower than yields of diacetins, regardless 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 similiar triacetin selectivity, using of Y-SBA as catalyst, but in that case MAG selectivity was higher, up to 19%. When carrying out the reaction without 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 that, the optimized conditions to obtain TAG, that is acetic acid/glycerol molar ratio of 9:1 and 115ºC, were used to continue the study. First, the test of the reduction of 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 represented in Figure 1.

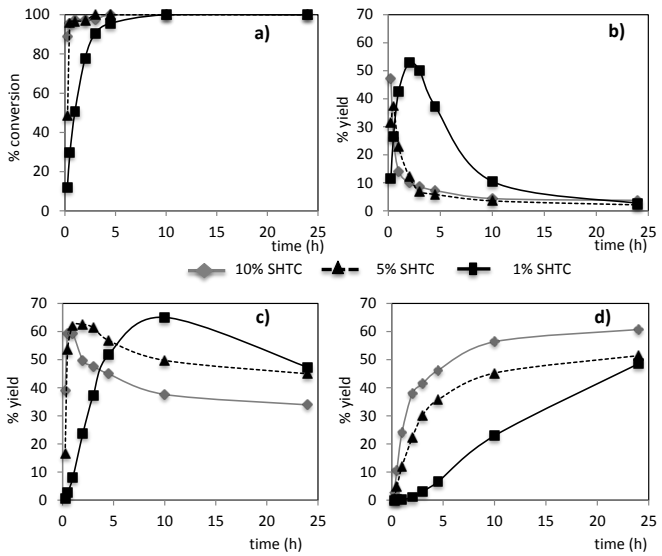


Figure 1 Influence of the amount of catalyst in glycerol conversion (a) and yields of monoacetins (b), diacetins (c), and triacetin (d) in the glycerol acetylation with acetic acid catalysed by SHTC **(reaction temperature 115°C, acetic/glycerol ratio 9:1, results determined by GC).**

Although glycerol conversions were excellent in all cases at short reaction times (nearly quantitative in less than 1h 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 produced any significant change in glycerol conversion or in yield of monoacetins, but provoked different TAG/DAG distribution. Thus, at 24h reaction time with 10%w/w catalyst, triacetin was the major product, with a TAG/DAG ratio of 1.79, while with 5%w/w catalyst the TAG/DAG ratio decreased to 1.15. When using 1%w/w catalyst, the results appeared to be identical to the ones in a blank reaction, that is 95.3% glycerol conversion in 4.5h reaction time with 41% yield of monoacetins, 51% yield of diacetins and only 7% yield of triacetin. This result can be considered as normal, given that 1%w/w catalyst represents only 0.04% mol of SO_3H with respect to glycerol.

Comparison of several solid acid catalysts

When trying to compare the results in glycerol esterification catalysed by SHTC with those of other sulphonic solids, previously published, we found that 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 (115ºC and 9:1 AcOH:glycerol molar ratio) to obtain triacetin. The weight of catalyst was varied in order to maintain in all cases a constant ratio of 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 are achieved with all the solids.

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

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 1h		Reaction time 10h	
	TON (conv)[a]	TON (acet)[b]	TON (conv)[a]	TON (acet)[b]
SHTC	187	393(138)	189	477 (324)
Dowex 50WX2	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 9:1, 115ºC. [a] Mol of glycerol converted per mol of sulphonic groups. [b] Mol of acetic acid converted per mol of sulphonic groups or acetate groups formed per sulphonic acid site. In parenthesis the TON only of the third acetate in triacetin (mol of triacetin formed per mol of sulphonic groups).

With this parameter, differences are observed when calculating TON with respect to acetate groups formed and specially triacetin. Thus at 1 hour 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 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 a cooperative effect of acid sites, due to the high density of them 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 invoked 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 diacetin 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 was made, 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 of mono, di and trybutirin 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 115ºC, 9:1 acid/glycerol molar ratio and 10% w/w catalyst. 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 providing high selectivities towards tributyrin and tricaprylin at longer reaction times.

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
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 S g^{-1}. [b] Results determined by GC . Reaction conditions: 10%w/w catalyst, 115ºC, acid/glycerol molar ratio 9:1.

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 10h reaction time, fresh catalyst exhibited a TON of 188 for glycerol conversion while upon recovery the TON slightly decreased to 152. However, 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. Results gathered in Figure 2 show that upon reuse, SHTC exhibited the same results as the carboxylic resin and as a blank reaction, behaving as if all the sulphonic groups were deactivated.

The analysis of the catalyst after the reaction (Table 1) revealed that 80% of the sulphur content remained in the solid and surface area and pore volume did not decrease, thus deactivation could not be only attributed neither to the leaching of sulphur, given that reaction also takes place with half amount of catalyst as shown in figure 1, nor to the blocking of the pores, as the textural properties (Table 1) are similar to the fresh catalyst.

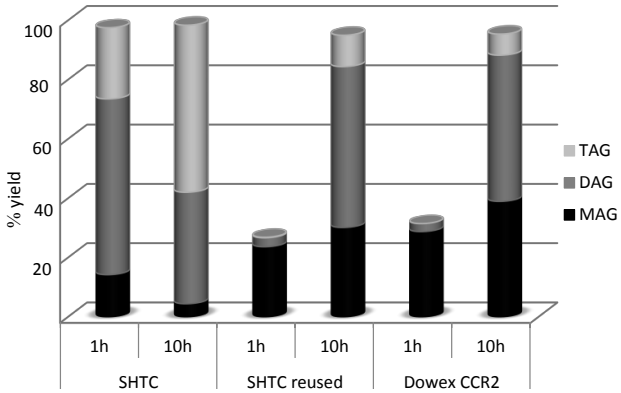


Figure 2 Yields (determined by GC) of MAG, DAG and TAG in glycerol acetylation catalysed by SHTC, reused SHTC, and Dowex CCR2, at 115°C and AcOH/glycerol ratio 9:1.

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 provoked by glycerol. In order to confirm this hypothesis, the ^{13}C-CP-MAS-NMR spectrum of the used catalyst was recorded and compared with that of the fresh SHTC (Figure 3).

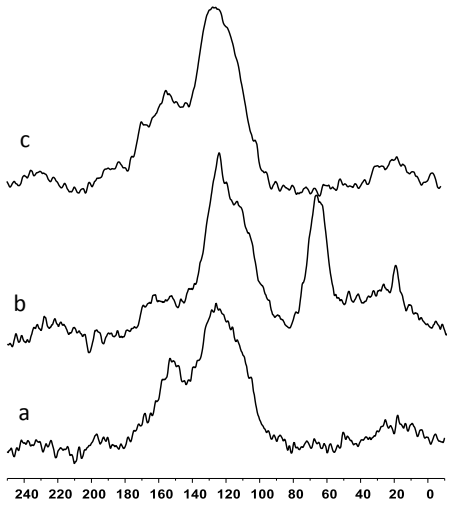


Figure 3 ^{13}C-CP-MAS-NMR spectra: a) SHTC, b) SHTC used in the reaction of glycerol with acetic acid at 115°C, c) SHTC used and regenerated with H_2SO_4 (66%).

The ^{13}C-CP-MAS-NMR spectrum of the catalyst used in a reaction at 115ºC (Figure 3) shows the presence of new bands, a small one at 20 ppm, compatible with –OOC-CH_3 groups, and the most prominent one at 69 ppm, compatible with glycerol species that may have been reacted with the acidic groups of the SHTC surface, as it happened in the case of esterification with methanol.[28,35] To proof the nature of this band, the SHTC was treated with glycerol under different conditions and the spectra are collected in Figure 4.

First of all, glycerol was adsorbed on SHTC at room temperature, to prevent any reaction with the acidic groups. As can be seen (Figure 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 115ºC and thoroughly washed with methanol, a broad signal at 69 ppm is obtained with higher intensity for increasing treatment times (Figure 4c and d). It is also significant that the signals of physisorbed glycerol are much thinner than those of the solids treated at 115ºC, in agreement with the higher mobility of the physisorbed molecules in comparison with those of those covalently bound to the surface. In Figure 4 the two possible types of surface species formed are also represented, bounded either with only one or with two covalent bonds. The question about the formation of surface sulphonates or only carboxylates was studied by adsorption of triethylphosphine oxide (TEPO) as a probe molecule. The bonding of triethylphosphine oxide (TEPO) to the acid site of a surface produced a systematic change in the ^{31}P isotropic chemical shift that is proportional to the acid strength of the adsorption site.[41] It has been also described that alkylsulphonic groups give TEPO ^{31}P chemical shift in the range of 71-77 ppm, whereas the value for arylsulphonic groups in Amberlyst 15 is 86 ppm.[35,42]

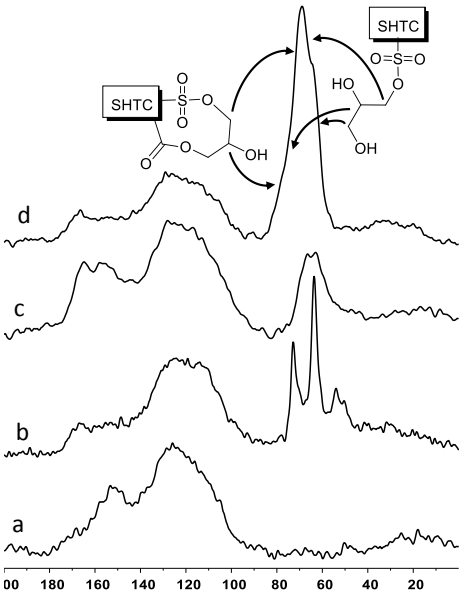


Figure 4 ^{13}C-CP-MAS-NMR spectra: a) SHTC, b) SHTC with glycerol physisorbed at room temperature, c) SHTC treated with glycerol at 115°C for 4 h and washed with methanol, d) SHTC treated with glycerol at 115°C for 24 h and washed with methanol.

The intensity of the ^{31}P-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 60ºC (Figure 5), whereas it completely disappears in the solid treated with glycerol at 115ºC. 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 of recovering the catalyst was done by acid treatment of the solid after the reaction. The catalyst was treated at 150ºC for 15h with H_2SO_4 (98%) or H_2SO_4 (66%).

After thoroughly 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 in the product distribution (Figure 6), the solids treated with sulphuric acid behave as the fresh SHTC. Sulphur analysis of the SHTC previous and after acid treatment, did not show any increase in sulphur content, precluding any additional sulphonation of HTC. On the contrary, the ^{13}C-CP-MAS-NMR spectrum (Figure 3c) showed that the bands assigned to bound glycerol and acetate completely disappeared. Thus the recovery of the activity was due to hydrolysis of the sulphonated esters and hence confirmed that the esterification of the sulphonic groups was the reason of the catalyst deactivation.

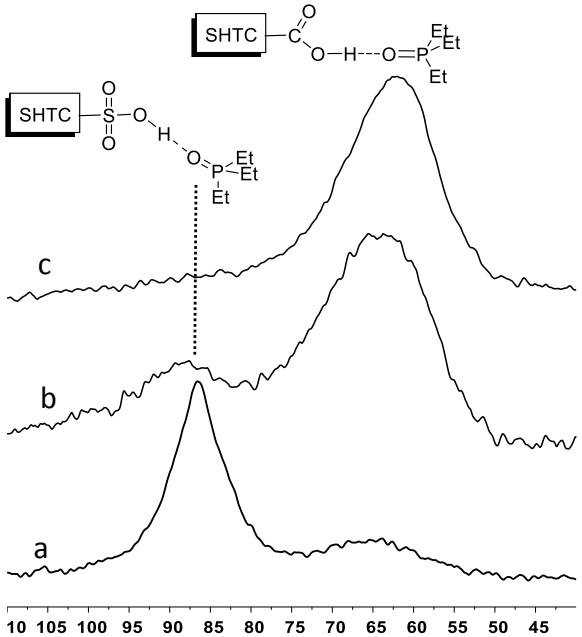


Figure 5 ^{31}P-MAS-NMR spectra of TEPO adsorbed from methanol solutions on: a) SHTC, b) SHTC used in the reaction of glycerol with acetic acid at 60°C for 4 h, c) SHTC treated with glycerol at 115°C for 24 h.

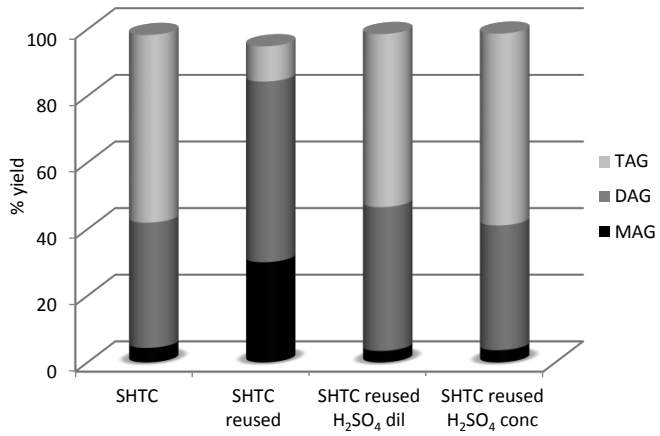


Figure 6 Yields of products in the acetylation of glycerol catalysed by fresh, used and regenerated SHTC. (acetic acid/ glycerol ratio 9:1, 115°C, time reaction 24h, determined by GC)

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 internal standard were stirred (≈ 1000 rpm) in a round flask immersed into a silicone bath at different temperatures (40ºC, 80ºC or 115ºC). Reaction was monitored by gas chromatography. At the end of reaction, methanol was added to the reaction medium, the catalyst was filtered off, thoroughly washed with methanol and dried overnight at 115ºC prior to reuse. In the case of using sulphonic resins, the same loading of sulphonic groups (0.5% 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) at 150ºC for 15h and thoroughly washed with hot water (90ºC). Then the solid was dried overnight at 115ºC and reused in 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 reaction temperature. Thus at 40ºC high selectivity toward monoacetylglycerol was obtained without the need of using an excess of glycerol. When using high reaction temperature, 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. Cooperative effects of acid sites are invoked for the superiority of the catalyst. The acid treatment of deactivated SHTC made possible the recovery of the activity of the catalyst by hydrolysis of the surface sulphonic esters.

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Notes

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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