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Alternative carbon based acid catalyst for selective esterification of glycerol to acetylglycerols

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ABSTRACT

Carbon-based acid catalysts with porous structure were prepared by sulfonation of carbonized sucrose. The catalysts have an amorphous porous structure with a good acid capacity and high thermal stability. The catalytic activity was evaluated by the esterification of glycerol with acetic acid. The sulfonated carbon catalysts showed that glycerol was completely transformed into a mixture of glycerol esters including a high selectivity of about 50% to triacetylglycerol (TAG).

1. Introduction

Glycerol is the main byproduct of the biodiesel production industry. The availability of glycerol can exceed current demand for the production of fine chemicals, cosmetics, pharmaceutical and food additives. The low cost of glycerol in addition that it is nontoxic, edible, and biodegradable has lead researchers to look for different alternatives for the conversion of glycerol into other valuable chemicals. It is known that a very large number of chemicals can be derived from glycerol by catalytic conversion processes, for example, oxidation, hydrogenolysis, dehydration, pyrolysis, gasification, transesterification, esterification, etherification, oligomerization, polymerization and carboxylation. Consequently, there is a great industrial and economical interest to investigate new ways for green and chemoselective catalytic materials for these processes [1–4].

The glycerol etherification reaction can be catalyzed by acidic homogeneous catalysts or preferentially by heterogeneous acid catalysts such as zeolites, strong acid ion exchange resins or sulfonic mesostructured silicas [5–8]. Large pore size materials are very active catalysts, in particular good results at 100% conversion of glycerol tert-butylation using isobutylene with selectivities to di- and tri-ethers up to 92% were obtained over strong acid macroreticular ion-exchange resins (Amberlyst type) [5]. Etherification of glycerol with isobutene over similar resins produced up to five different ethers [6].

In the case of glycerol esterification or transesterification, it is necessary to consider that the glycerol is a symmetrical molecule with the three hydroxyl groups which are not very different in reactivity. Therefore, the product of the direct esterification or transesterification of glycerol with acid and/or basic catalysts is a mixture of mono-, di-, and some triglyceride, plus glycerol that has not reacted. A theoretical study of glycerol acetylation using DFT theory determined the most stable structures of the reactants, intermediates and products between a large amount of conformers. Also it was found that the glycerol reaction with acetic acid is a thermodynamically favorable and that the outside hydroxyl bonds can be esterified before the center hydroxyl group [9]. Experimentally, in order to lower the reaction temperature for the direct esterification of glycerol with fatty acids usually an acid catalyst is required, for example, sulfuric acid, phosphoric acid, or organic sulfonic acids. It is therefore highly desirable to develop more environmentally friendly catalytic processes that can improve the yield of the desired products (*e.g.* monoester yield) using more economic reaction conditions. Solid basic materials such as metal oxides MgO, CeO_2, La_2O_3 and ZnO; Al–Mg hydrotalcites; Cs-exchanged sepiolite; and mesoporous MCM-41 have been used as potential basic catalysts for glycerol transesterification with triglycerides [4,10–14]. In these investigations it was found that when the basicity is significant, the catalyst becomes more active. Solid acids such as microporous zeolites or mesoporous silicas have also been tested for the catalytic esterification of glycerol with fatty acids. Mesoporous silicas are more easily accessible by large molecules like fatty acids and

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their esters than the zeolite microporosity. However, mesoporous silicas have lower strength of the acid sites [10–14].

Similar results were found in other researches [15,16]. It was found that glycerol esterification with acetic acid reaches conversions over 90% with a TAG selectivity of 13% using resins (such as Amberlyst-15 and Amberlyst-35) and zeolites (such as HZSM-5 and HUSY9) [15], the results showed that the acid exchange resin, Amberlyst-15, was the most active catalyst, achieving 97% conversion, followed by K-10 montmorillonite, niobic acid, HZSM-5 and HUSY. It was assumed that the poor performance of the zeolites might be related to diffusion problems of the acetylated esters inside the cavities. Also the same commercial resins and the HY and HZSM-5 were tested for the same reaction. Optimization of the reaction conditions indicated that an acetic acid to glycerol molar ratio of 9:1, at 378 K reaction temperature over Amberlyst-35 during 4 h yielded almost 100% of glycerol conversion and a selectivity to TAG near to 35% [16].

Silica-based mesoporous materials containing R–SO_3H groups have been evaluated for esterification of glycerol with fatty acids [13]. It was found that an optimum balance exists between the nature of the organic group which supports the sulfonic acid (aromatic or alkyl, length of the alkyl chain), the distance between the sulfonic group and the silica surface, and also the average pore size of the material. While mesoporous silica systems continue to be very important, over the past few years increasing attention has been paid to porous carbon materials with designed pore architecture. Some researchers consider nanoporous carbons as the next generation of mesoporous materials [17–19].

Porous carbon is an attractive catalytic material because it can be prepared from a wide variety of low-cost precursors, it is very stable under nonoxidizing conditions, it has low density, high thermal conductivity, good electrical conductivity, mechanical stability and the specific surface-area can be controlled. Compared to mesoporous silica, mesoporous carbon is more resistant to structural changes by hydrolytic effects in aqueous environments. Porous carbon materials functionalized with sulfonic acid groups have been investigated as potential, environment-friendly solid–acid catalysts; because functionalized carbons eliminate the need for liquid acids in certain catalytic reactions, and may be reused many times [19–21]. Mesoporous carbon can be produced by carbonization of starch and polysaccharides, and then sulfonated by suspension in fuming or liquid sulfuric acid at elevated temperature. The catalysts thus prepared were active and selective for several esterification reactions [18–24].

Carbon mesoporous materials can also be produced by pyrolysis of expanded starch and subsequently functionalized with sulfonated groups (Starbon type catalysts) [23]. These materials were tested for the esterification reaction of different diacids, under similar reaction conditions. The rates of esterification of diacids (succinic, fumaric and itaconic) were found to be between 5 and 10 times higher than any commercial alternative solid acid catalyst (zeolites, sulfated zirconias, acidic clays, etc.), a diester selectivity improvement (from 35 to 50% range for the majority of the solid acids to 90% for Starbon-400 at conversion levels of 90%) was also obtained. The recovered Starbon could be added to fresh substrate solutions giving almost identical behavior. Recently, a sulfonated carbon catalyst with mesoporous structure and high specific surface area was prepared by impregnating the cellulosic precursor (wood powder) with $ZnCl_2$ prior to activation and sulfonation [20]. The performance of the sulfonated porous carbon material as an acid catalyst was examined through the esterification of acetic acid in the presence of ethanol (343 K) and the benzylation of toluene in the presence of benzylchloride (373 K). It was found that the activity for the benzylation of toluene was depending on both the specific surface area and the acid density of the sulfonated porous carbon catalyst.

In summary, the sulfonated porous carbon materials according to the evidence catalytic capacity could be a viable alternative to improve the reactions of esterification of glycerol. Despite the increasing interest on glycerol conversion to valuable chemicals, few researches have been working on the esterification of glycerol with acetic acid. There is no information available concerning the performance of carbon acid catalysts prepared under mild conditions from polysaccharides to obtain selectivity to TAG derivate from glycerol, which is a biodiesel byproduct. In this research, sulfonated carbon catalysts were synthesized and used for the esterification of glycerol. Different methodologies were used for the carbonization and functionalization of the catalyst promoters. Catalytic esterification of the glycerol with acetic acid was carried out and the reaction conditions were optimized.

2. Experimental

2.1. Carbon preparation

Two different methods were used to obtain the porous carbons. The first one was a direct synthesis carbonization (here after called DC), in this case pure sucrose powder was carbonized in a tube reactor for 15 h under nitrogen atmosphere at 673 K. The second one was a template assisted carbonization process [25] (here after called TAC), in this method silica was used as template. The silica template was prepared in situ using Na_2SiO_3 and H_2O at 343 K, and then sucrose and HCl were added and then the mixture was left during two days for polymerization. The material was carbonized for 3 h under nitrogen atmosphere at three different temperatures: 673, 873 and 1123 K. The carbonized solids were stirred overnight at 393 K with NaOH 3 M solution and finally, filtered and washed with hot water in order to eliminate the template. The prepared materials were characterized by thermal analysis using a TA-Instruments Q-500 and IR spectroscopy using a Nicolet Magna 560 by a KBr disk method (0.5% of sample).

2.2. Carbon functionalization

In the sulfonation step the carbons samples were functionalized using two sulfonating agents to incorporate –SO_3H groups on the carbon surface. In one approach the carbon sample was left in contact overnight with fuming sulfuric acid (7% of SO_3). In the second approach the carbon sample was mixed with liquid H_2SO_4 (>98%), and heated during 10 h. The treated samples were washed repeatedly in boiling distilled water until impurities such as sulfate ions were no longer detected in the washing water, and then the sample was dried overnight in an oven at 373 K. The catalysts thus prepared are identified here after as TAC and DC; in reference to the template assisted and direct carbonization method respectively, following of the temperature of carbonization.

2.3. Catalyst characterization

Elemental analysis was used to determine the composition of the catalysts. The carbonaceous samples before and after sulfonation were characterized by infrared spectroscopy, by means of KBr disk (0.5% of sample) using a Nicolet Magna 560, to identify the functional groups bonded to the carbon surface. Surface acid capacity was determined by titration with different basic solutions, using Boehm's method [26], the concentration value were normalized and expressed as percentage. The surface and pore structure properties of sulfonic acid-carbons have been evaluated by means of nitrogen adsorption and desorption isotherm at 77 K, also carbon dioxide adsorption isotherm at 273 K using a Micromeritics ASAP 2010 system. Isotherm data were analyzed to obtain pore size distribution using the DFT model provided by Micromeritcs, the area

Table 1
Preparation conditions and sulfonic acid density of sulfonated based carbons.

Sample	Sulfonic agent	Carbonization temperature (K)	$-SO_3H$[a] density (mmol g^{-1})
DC-673	$H_2SO_{4\,(l)}$	673	0.14
DC-673	$H_2SO_{4\,(f)}$		0.36
TAC-673	$H_2SO_{4\,(l)}$	673	0.45
TAC-673	$H_2SO_{4\,(f)}$		1.35
TAC-873	$H_2SO_{4\,(l)}$	873	0.43
TAC-873	$H_2SO_{4\,(f)}$		0.77
TAC-1123	$H_2SO_{4\,(l)}$	1123	0.50
TAC-1123	$H_2SO_{4\,(f)}$		0.76

[a] Quantified from elemental sulfur.

Table 2
Characteristics of sulfonated carbon catalysts.

Sample	ITS[a] (K)	Surface and pore properties			
		N_2 adsorption[b]		CO_2 adsorption[c]	
		SA	VP	MSA	VP
DC-673	4	4	<0.01	nd	nd
TAC-673	2	556	0.51	333	0.13
TAC-873	8	616	0.57	432	0.17
TAC-1123	49	804	1.07	383	0.15

nd: no determined.

[a] Index of thermal stability, ITS = (% fixed carbon)/(% volatile material) from TGA experiment.

[b] Nitrogen adsorption at 77 K; SA: total surface area (BET) in $m^2\,g^{-1}$; VP: pore volume in $cm^3\,g^{-1}$ at $P/Po = 0.99$.

[c] Carbon dioxide adsorption at 273 K; MSA: micro surface area (DR) in $m^2\,g^{-1}$; VP: pore volume in $cm^3\,g^{-1}$ at $P/Po = 0.99$.

under the curve for every sample was integrated and normalized to obtain the percentage of every fraction of porosity, according to the IUPAC definition. Pore volume was taken at $P/Po = 0.99$ and 0.028 single point respectively to N_2 and CO_2 adsorption measure.

2.4. *Catalytic performance of the sulfonated carbons*

Esterification of oleic acid with high purity methanol was used as a reference reaction to probe the reaction system. The catalyst with the highest sulfur content was selected to optimize the time, catalyst load and temperature for the esterification of glycerol with acetic acid. The previous selected catalysts and a commercial ion-exchange resin (Amberlyst-15) were used to test the catalytic activity varying the temperature reaction from 378 to 473 K. These reactions were carried out in a reflux system using a high purity glycerol and acetic acid (HPLC grade), in a molar ratio acetic acid:glycerol of 1:9, the time reaction was 4 h and the catalyst load was 5% (w/w). After reaction the products were separated by filtration and analyzed by gas chromatography using Agilent GC and GC–MS 7890A instruments by means of a FID detector and a capillary column of polyetylene glycol (HP-Innowax 30 m × 0.32 mm × 0.25 μm), for the quantification of the main product, TAG, was used a column HP-5; other products were identified by GS–MS with a capillary column HP-5.

3. Results and discussion

3.1. *Structure*

All of the carbonized materials were functionalized using liquid or fuming sulfuric acid. The percentage of sulfur bonded to the surface was calculated from elemental sulfur analysis, the results, expressed as mass acid density, are shown in Table 1. There was a marked influence of the method used to introduce sulfur functionalities on the carbon surface, as well as of the carbonization procedure. The low surface area developed by the DC method induced poor surface sulfonation efficiency. On the other hand the TAC method developed larger surface areas and because of this, it was possible to increase the density of acid groups, of the SO_3H type, on the carbon surface. Therefore, the silica played an important role as a pore structure director. Comparison of both sulfonating agents leads to the assumption that the molecules in vapor phase have better diffusion properties and binding characteristics to the surface than the liquid. The highest amount of sulfur incorporated into the carbon surface was obtained with the material prepared using the TAC method with a previous carbonization at 673 K, in this way 1.35 mmol $SO_3H\,g^{-1}$ was obtained. This high sulfur uptake can be explained by the relatively mild carbonization temperature which produced an amorphous but more active surface towards sulfonation. It was proposed after structural characterization; using XRD, ^{13}C CP-MAS NMR and XPS, that sulfonated carbons prepared like TACs exhibit characteristics due to polycyclic aromatic carbon, and carboxyl groups which predominant at high temperature of preparation, to carbons obtained under similar temperature condition, like TAC-673, methylene groups and phenolic OH groups were confirmed. Also, it was found in other research that the density of SO_3H groups remains relatively constant with respect to carbonization temperature in the range of 523–723 K, but decreased with further increases in carbonization temperature [20]. The scientific literature reports also that for sulfonated (SO_3H-bearing) carbon the best acid density values ranging from 1.04 to 1.34 mmol of $SO_3H\,g^{-1}$ [20,21,24]. In particular a value of 1.34 was obtained to a material prepared from wood powder previously impregnated with $ZnCl_2$ and pyrolyzed at 873 K and then sulfonated with fuming sulfuric acid; this material with high densities of micro- and mesopores showed high catalytic performance for the esterification of acetic acid, the activity was attributed only on the acid density. For a sulfonated mesoporous silica there are reports of acid density value about 1.15 mmol g^{-1}; this material was also used to acetylation of glycerol and good selectivity to TAG was reported [7,14,20]. As was said above the material TAC-673 had a value of density acid (as SO_3H) of 1.35 mmol g^{-1}, which makes it comparable to the value before mentioned, for other catalysts such as carbons and silica functionalized with sulfonic groups.

Table 2 shows the correlation of the thermal characteristics, surface area and pore volume of the carbonized materials according to the method and the temperature of carbonization. It is presented in this table the index of thermal stability, ITS, which relates the carbon stable structures and hydrocarbon unstable structures. The last compounds volatilize after breakdown from the carbonaceous parental material in a TGA experiment at 1023 K in an inert atmosphere. Therefore the increase of the ITS value during the carbonization process can be attributed to the formation of random oriented amorphous carbon structure composed of aromatic sheets [17–21].

It was possible to observe from Table 2 that the direct carbonization of the sucrose at 673 K produces a non-porous material with a superficial area of 4 $m^2\,g^{-1}$, which was in the limit of detection of this analytical technique. It is shown in Table 1 that ITS was very low for a carbons obtained using DC method, also the mass yield using this method was very low. Due to these reasons, the DC method was not used to prepare other catalytic materials. In contrast the method using silica to mold the carbonaceous pore structural properties allowed obtaining materials with mixed micro- and mesoporosity material with a high specific surface area and high thermal stability, depending on the carbonization temperature. This is probably due to the control of the polysaccharide reactions of dehydration and condensation by the silica-template, avoiding in this way the massive decomposition of the parental material. High values of specific surface area (>500 $m^2\,g^{-1}$) and thermal stability were obtained from the carbonization process

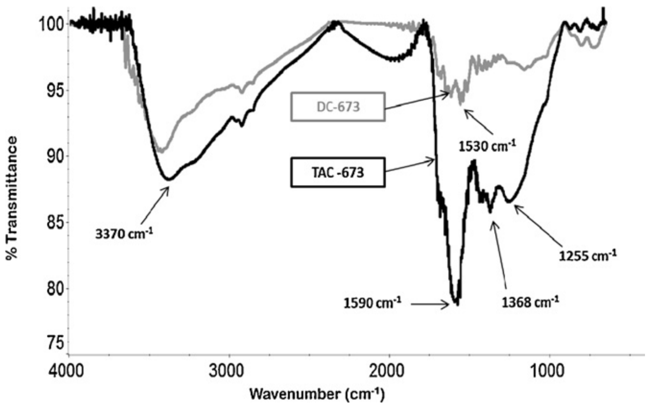


Fig. 1. Infrared spectra of the carbonized materials. Top: DC carbonized material at 673 K. Bottom: TAC carbonized material at 673 K.

at 850 K and 1123 K. It is happened in this kind of materials (i.e. active carbons) that the development of pore volume is caused by the widening of the size of pore in the range of mesoporosity more than the new porosity generation. In this case the volume of nitrogen adsorbed was major that the volume adsorbed of carbon dioxide in all materials produced for the TAC method. Therefore it is expected that TAC materials can have a pore size which can be accessed by molecules of the functionalizing agent but also by reactant molecules.

In this work the IR spectra was used to confirm the carbonization degree and the presence of the characteristics bands to identify sulfonic, carboxylic and polycyclic aromatic carbons, as was established early in this paper it is assumed that they were present in the carbon surface. Fig. 1 shows the infrared spectra of the carbonized materials at 673 K using the DC and TAC methods; the TAC carbonized material presents a well-resolved spectra. Both sucrose carbons showed a broad band centered at 3370 cm^{-1} was assigned to the –OH stretching vibration mode of the –COOH group. The main difference is exhibited in the region from 900 to 1900 cm^{-1} where the DC material shows an incipient resolution, in contrast TAC carbon present a strong band at around ~1590 cm^{-1} and other at 1368 cm^{-1} due to C=C stretching, also a broad band at 1255 cm^{-1} can be assigned to the aryl-hydroxyl stretching (Ar–OH).

Fig. 2 shows the effect of the temperature of carbonization on the surface functional groups for TACs carbons. The intensity bands at 1590, 1368 and 1260 cm^{-1} were decreased as the temperature becomes higher. The infrared spectra before and after sulfonation of the TAC-673 carbons are shown in Fig. 3. As shown in this figure, two bands appeared at 1035 and 1186 cm^{-1} in the sulfonated TAC-673 catalyst compared with the unsulfonated one that could be assigned to the SO_2 asymmetric and symmetric stretching vibration mode, which can be assigned to the $–SO_3H$ groups. For the sulfonated carbon the bands assigned to –COOH and C=C remained unaltered. The overall FTIR analysis suggests that the carbon-based catalysts consist of polycyclic aromatic carbon sheets containing $–SO_3H$, –COOH, and –OH functionalities, in agreement with the previous analysis. Elemental analysis of the TAC-673 sample is presented in Table 3. An increase of 4.3% sulfur content after functionalization is observed, a C/S ratio of 10.9 and O/S ratio of 10.6, is indicative of the chemical incorporation of sulfur. However the atomic ratio of oxygen increased in a proportion larger than the one of sulfonation. Therefore, it is assumed that was oxidation of the surface as carboxylic-type groups, because this information was correlated with FTIR data.

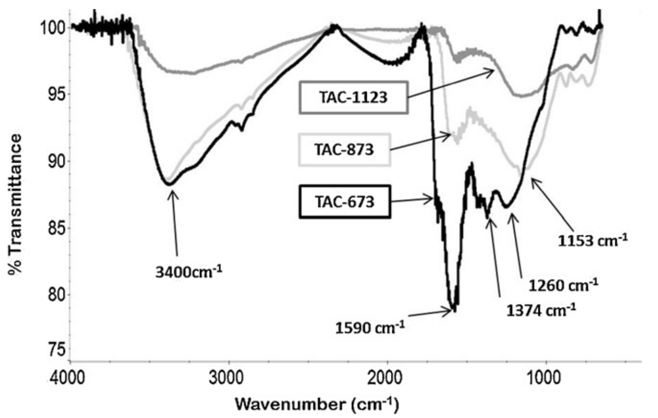


Fig. 2. Infrared spectra of the TAC carbonized materials at different temperatures.

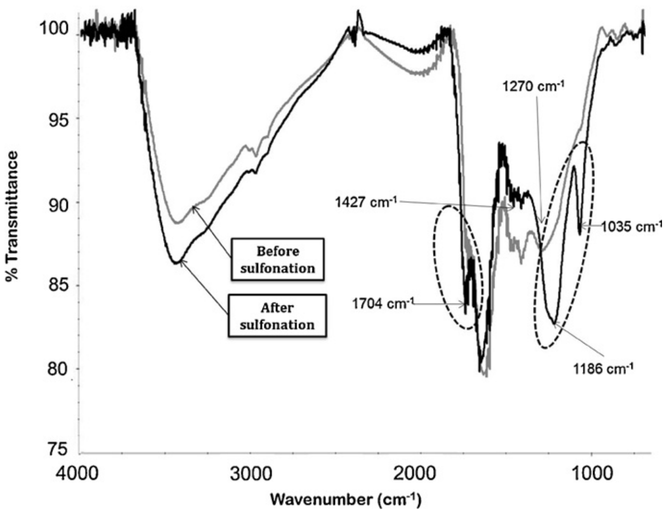


Fig. 3. FTIR spectra of the TAC-673 materials prepared from sucrose before and after sulfonation.

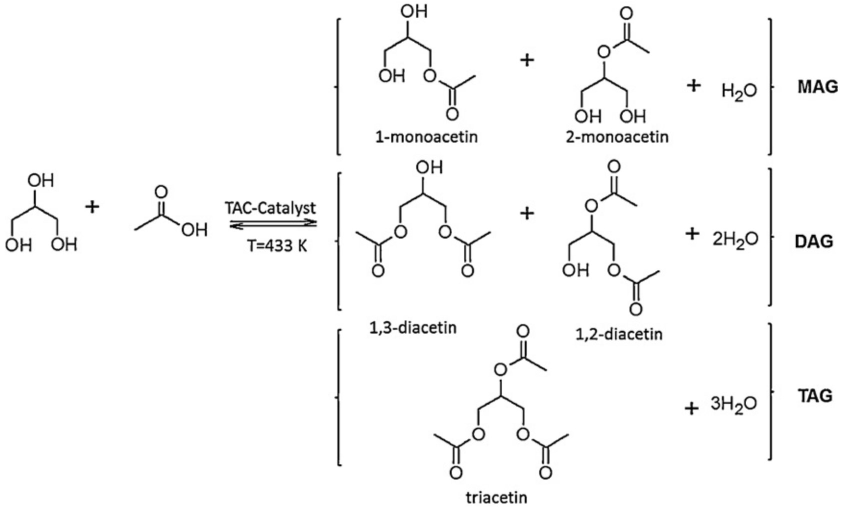
Table 3
Elemental analysis of the TAC-673 catalyst before and after sulfonation.

Element	Before sulfonation % (w/w)	After sulfonation % (w/w)
C	68.9	46.9
H	4.0	2.8
S	<0.1	4.3
O (by difference)	27.0	46.0

Table 4 shows the surface analysis for TAC-673 catalyst. This material has a bimodal pore size distribution, essentially between micro and mesoporosity in very similar proportions. Macroporosity was negligible. This pore size distribution is a desired composition for use in heterogeneous reactions due to diffusion requirements. The Boehm method provides evidence of how different bases can be linked with the functional groups of the surface catalyst, to determine this interaction NaOH, $NaCO_3$ and $NaHCO_3$ solutions were used to titrate the acid groups. It was found that there was a balanced distribution of the three kinds of acidic groups on the surface. As expected the strong acid groups on the surface had predomi-

Table 4
Acid capacity and pore size distribution of the TAC-673 catalyst.

Surface characteristics	
Acid capacity distribution by Boehm's method (%)	Mono-functional strong groups: 39 Bi-functional strong groups: 32 Weak groups: 29
Pore size distribution by N_2 and CO_2 adsorption (%)	Microporous 0–2 nm: 45 Mesoporous 2–50 nm: 51 Macroporous >50 nm: 4



Scheme 1. Reaction for production of actylglycerols.

nance. These characteristics make this material a potential catalyst for glycerol esterification reactions.

3.2. Catalytic performance

3.2.1. Oleic acid esterification with methanol

In the first step, the esterification reaction of oleic acid with methanol was used in order to determine the efficiency of the catalyst against a convencional catalyst. With the catalyst TAC-673 a conversion of 68.4% to the respective ester was obtained, while the commercial catalyst, Amberlyst-15, the conversion was 30.6%. That means, the catalyst obtained in this research yielded more than twice the selectivity of that obtained with Amberlyst-15 resin. This kind of resin is recognize for the macroporous structure and its catalytic activity for this reaction [17,27].

3.2.2. Esterification of glycerol with acetic acid

In this case the reaction of glycerol with acetic acid can yield products such as mono-, di- and triacetin. Our purpose was directed towards triacetin because this chemical is widely used in industry as a fixative of odors and flavors, biocides, cosmetics, plasticizing agent and recently as additive for biodiesel. Scheme 1 illustrates the different esterification products that can be obtained: monoacetylglycerol (MAG) or monoacetin, di-acetylglycerol (DAG) or diacetin, tri-acetylglycerol (TAG) or triacetin accompanied by water elimination. All the reactions gave conversions of glycerol higher that 99.6%.

The effect of the carbonization temperature on the catalytic activity of the sulfonated carbons is shown in Fig. 4. The catalyst activity is almost invariant for the materials carbonized at 873 and 1123 K (23.0%). However, it increases notably for the sample carbonized at 673 K (39.6%). Fig. 4 also shows the correlation between C–SO_3H acid density and the carbonization temperature. The comparison shows a similar pattern for the selectivity and acid density sites. The TAG formation takes place over sulfonated sites which are directly related to the porosity of the material. The samples carbonized at lower temperatures contain SO_3H groups and also high densities of hydrophilic functional groups such as OH and COOH, which were confirmed by FTIR data of TAC-673. It is therefore assumed that this sample can also adsorb large amounts of hydrophilic molecules such as alcohols and glycerol, among others.

For the esterification reactions the influence of the amount of catalyst and the reaction time were investigated keeping the acid–glycerol ratio of 9:1. Table 5 displays the TAG selectivity as function of the reaction time. When the time of reaction was 4 h the amount of catalyst did not affect the selectivity reached to TAG. The variation is from 37.6% to 41.0% for 1% to 7% respectively (weight of catalyst to weight of glycerol). To test the optimum reaction time the catalyst load was kept at 5%. A maximum, at 4 h, with a 39.6% of selectivity was found.

The effect of the reaction temperature was evaluated from 378 to 473 K. The results are plotted in Fig. 5. The conversion of glycerol was more than 99.6% for all of the experiments with a significant increase in the selectivity to triacetin (TAG) as the temperature reaction increased from 17% (at 378 K) to 50% (at 473 K). The maximum selectivity to TAG was 50% at 453 K. As seen in Scheme 1, in this particular type of reaction if the conversion of

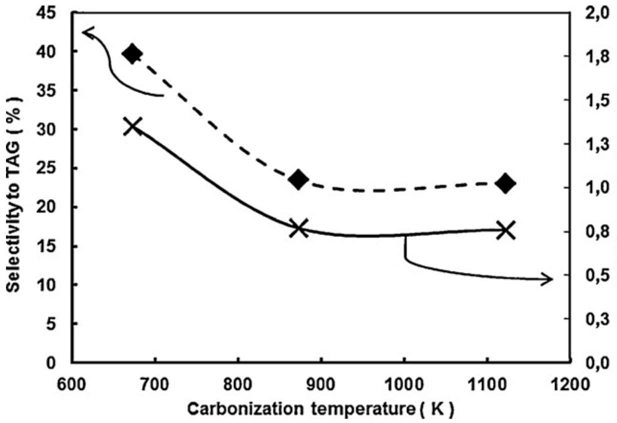


Fig. 4. Selectivity to TAG by esterification of glycerol with acetic acid (9:1 molar relation, at 433 K and 5% of catalyst load). (Black rhombus) effect of the temperature of carbonization of the catalysts. (Equis) effect of SO_3H density sites. The connecting lines in figure are just a guide for the eyes.

Table 5
Variation of the reaction time and load of the catalyst again selectivity for the esterification of glycerol with acetic acid at 378 K using TAC-673 catalyst.

		Selectivityto TAG (%)
Time (h)	2	34.6
	4	39.6
	6	31.4
Catalyst load (%)	1	37.6
	5	39.6
	7	41.0

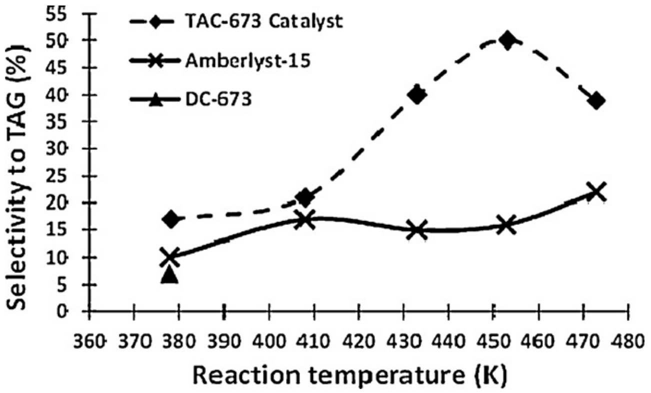


Fig. 5. Selectivity to TAG by esterification of glycerol with acetic acid (at 9:1 molar relation, 5% of catalyst load and 4 h of reaction time). Black rhombus for TAC-673. Equis for commercial catalyst (Amberlyts-15). Black triangle for DC-673 catalyst. The connecting lines in figure are just a guide for the eyes.

glycerol was 100%, the mono (MAG) and diacetin (DAG) compounds were transformed into triacetin with the increasing of the reaction temperature. In the same Figure, the selectivity to TAG obtained under the same conditions, at 378 K, using the catalyst prepared by the direct carbonization method, DC-673, was the lowest value (9%). This was a consequence of the poor structural characteristics developed; such as a non-porous material with the lowest increasing of sulfur incorporated into the surface, which is shown in Tables 1 and 2.

Finally, in order to make a comparative analysis of the selectivity between a carbon-based acid catalyst before analyzed (TAC-673) and a commercial catalyst (Amberlyst-15), the esterification reaction of both materials was run under the same conditions, (acid–glycerol molar ratio = 9:1, 5% of catalyst load and to the same reaction points of temperature). Fig. 5 shows that the selectivity to TAG using the commercial resin ranged from 10% to 22%. There was a decrease of 7% in the selectivity in comparison to the TAC-673 to 378 K, and a significant detriment of 28% in the point of maximum catalytic activity. From this graph, it is possible to affirm that the selectivity behavior of the commercial catalyst is less than TAC-673 at the temperature range studied (from 378 to 473 K), though there is a slight trend to increase the selectivity for the resin above of 453 K, there is an advantage for the material TAC-673 since its maximum selectivity was reached about this value of temperature, which is important thinking about its application. It has been reported that the acid capacity of Amberlyst is between 4.5 and 5.0 mmol g^{-1} [14]. That means more than 3 times the capacity of the TAC-673 catalyst. Nevertheless, the best catalytic performance evidenced by TAC-673 catalyst might be explained by the combination of several factors before approached in other sections; such as the diversity of active surface sites however the predominance of acid strong groups like $-SO_3H$ and the easy access of reactants caused by the pore system developed. Other structural studies should be realized to prove that statements. To the knowledge of the authors, the best catalytic result for the conversion of glycerol to TAG before this work, reported a selectivity value of 35% [16], using the Amberlyst-35 resin. In the present research a selectivity of about 50% to TAG were reached. This is a significant improvement in the selectivity yield for this application.

4. Conclusions

In this research the sulfonation of carbon-based materials prepared by controlled porous structure by sucrose carbonization produced a highly active, and stable solid acid catalyst for the glycerol acetylation reaction. The catalysts prepared exhibited an appropriated porous system of the interconnected micro- and mesoporosity that allowed the surface sulfonation using fuming sulfuric acid to form sufficient but variety catalytic active centers; type $C-SO_3H$. The combination of low temperature carbonization at 673 K using silica as template material and the sulfonation with fuming sulfuric acid produced the best active catalyst. The use of this catalyst in the esterification reaction of glycerol with acetic acid allowed conversions above 99% with selectivity towards triacetin around 50%, while the esterification at the same conditions using a conventional catalyst like Amberlyst-15 also gave over 99% conversion but with a selectivity to triacetin of about 10%. Therefore, these materials can be an alternative to other commercial heterogeneous acid catalyst such as commercial acid exchange resins.

To settle the potential industrial applicability of these solid acid catalysts, and as a continuation of the current research, the etherification of glycerol to fuel additives and use of crude glycerol from biodiesel production with true plant impurities are already under investigation.

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References

[1] B. Sels, E. D'Hondt, P. Jacobs, in: G. Centi, R.A. van Santen (Eds.), Catalytic Transformation of Glycerol, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2007, pp. 223–255.
[2] J. Janaun, N. Ellis, Renew. Sust. Energ. Rev. 14 (2010) 1312–1320.
[3] R.R. Soares, D.A. Simonetti, J.A. Dumesic, Angew. Chem. Int. Ed. 45 (2006) 3982–3985.
[4] C.H. Zhou, J.N. Beltramini, Y.X. Fan, G.Q. Lu, Chem. Soc. Rev. 37 (2008) 527–549.
[5] K. Klepácová, D. Mravec, M. Bajus, Appl. Catal. A 294 (2005) 141–147.
[6] R.S. Karinen, A.O.I. Krause, Appl. Catal. A 306 (2006) 128–133.
[7] J.A. Melero, G. Vicente, G. Morales, M. Paniagua, J.M. Moreno, R. Roldán, A. Ezquerro, C. Pérez, Appl. Catal. A 346 (2008) 44–51.
[8] Y. Gu, A. Azzouzi, Y. Pouilloux, F. Jerome, J. Barrault, Green Chem. 10 (2007) 164–167.
[9] X. Liao, Y. Zhu, S.-G. Wang, H. Chen, Y. Li, Appl. Catal. B 94 (2010) 64–70.
[10] K. Motokura, M. Tada, Y. Iwasawa, J. Am. Chem. Soc. 129 (2007) 9540–9541.
[11] H. Gurav, V.V. Bokade, J. Nat. Gas Chem. 19 (2010) 161–164.
[12] S.L. Barbosa, M.J. Dabdoub, G.R. Hurtado, S.I. Klein, A.C.M. Baroni, C. Cunha, Appl. Catal. A 313 (2006) 146–150.
[13] I. Diaz, F. Mohino, T. Blasco, E. Sastre, J. Pérez-Pariente, Micropor. Mesopor. Mater. 80 (2005) 33–42.
[14] J.A. Melero, R. van Grieken, G. Morales, M. Paniagua, Energy Fuel 21 (2007) 1782–1791.
[15] V.L.C. Gonçalves, B.P. Pinto, J.C. Silva, C.J.A. Mota, Catal. Today 133 (2008) 673–677.
[16] X. Liao, Y. Zhu, S.G. Wang, Y. Li, Fuel Process. Technol. 90 (2009) 988–993.
[17] A. Taguchi, F. Schüth, Micropor. Mesopor. Mater. 77 (2005) 1–45.
[18] M. Toda, A. Takagaki, M. Okamura, J.N. Kondo, S. Hayashi, K. Domen, M. Hara, Nature 438 (2005) 178.
[19] M. Hara, ChemSusChem 2 (2009) 129–135.
[20] M. Kitano, K. Arai, A. Kodama, T. Kousaka, K. Nakajima, S. Hayashi, M. Hara, Catal. Lett. 131 (2009) 242–249.
[21] X. Rong, L. Yueming, W. Yong, C. Li, W. Haihong, J. Yongwen, H. Mingyuan, P. Wu, Micropor. Mesopor. Mater. 105 (2007) 41–48.
[22] X. Mo, D.E. López, K. Suwannakarn, Y. Liu, E. Lotero, J.G. Goodwin Jr., C. Lu, J. Catal. 254 (2008) 332–338.
[23] J.H.C. Vitaly, L. Budarin, R. Luque, D.J. Macquarrie, Chem. Commun. 63 (2007) 4–637.
[24] A. Takagaki, M. Toda, M. Okamura, J.N. Kondo, S. Hayashi, K. Domen, M. Hara, Catal. Today 116 (2006) 157–161.
[25] S. Han, M. Kim, T. Hyeon, Carbon 41 (2003) 1525–1532.
[26] H.P. Boehm, Carbon 40 (2002) 145–149.
[27] R. Tesser, M. Di Serio, M. Guida, M. Nastasi, E. Santacesaria, Ind. Eng. Chem. Res. 44 (2005) 7978–7982.