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Synthesis of Oxygenated Fuel Additives from Glycerol

Jorge Sepúlveda, Mariana Busto, Carlos Vera,
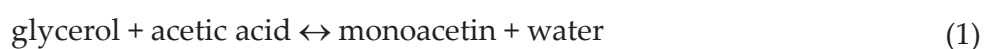Maraisa Gonçalves, Wagner Carvalho and
Dalmo Mandelli

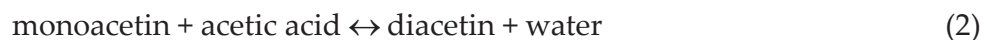Additional information is available at the end of the chapter

1. Introduction

The last years, a dramatic increase in the installed capacity for biodiesel fuel has taken place. This is a technically mature biofuel replacement of petrodiesel, with improved properties of cetane number, lubricity, biodegradability and flash point. This increasing biodiesel production has resulted in an excess production of the glycerol by-product (stoichiometrically 10 wt% of the product of a biodiesel plant). The transformation of bio-glycerol into glycerol-ethers and glycerol-esters via etherification and esterification reactions is considered to be a convenient alternative for glycerol utilization. These value-added chemicals have potential uses in many industrial applications. Particularly acetylation of bio-glycerol with acetic acid into glycerol-esters can produce di- and triacetin that have potential for vast quantity utilization as valuable biodiesel and petro fuel additives. In the case of the addition to biodiesel, the in-factory utilization of the product is quite advantageous. In addition, di- and triacetin are used as fuel additives for viscosity reduction. Triacetin meets the specifications of flash point (>374 K) and oxidation stability (6 h at 383 K) required by the standards EN 14214 and ASTM D6751 [1-3].

The esterification of glycerol with acetic acid produces mono-, di- and tri-acetates of glycerol. The mono- and di-acetates are known as monoacetin (2-monoacetyl-1, 3-propanediol or 3-monoacetyl-1, 2-propanediol, MAG) and diacetin (1, 2-diacetyl-3-propanol or 1, 3-diacetyl-propanol, DAG). The scheme of reaction is depicted below:

$$\text{glycerol + acetic acid} \leftrightarrow \text{monoacetin + water} \tag{1}$$

$$\text{monoacetin + acetic acid} \leftrightarrow \text{diacetin + water} \qquad (2)$$

$$\text{diacetin + acetic acid} \leftrightarrow \text{triacetin + water} \qquad (3)$$

Current glycerol esterification processes are carried out using mineral acids. However, these technologies are not environmentally friendly, and much attention has been put on the development of new techniques that use acidic heterogeneous catalysts. Recently, the synthesis of new supported materials containing immobilized sulfonic acid groups, which behave as active and selective catalysts for esterification, has been reported [4-6]. Other reports can also be found that deal with zeolites, poly vinyl sulfonic resins and niobic acid.

Sulfated zirconia obtained by the sol-gel method, was evaluated in the esterification of glycerol with acetic acid at 328 K; however, leaching of sulfur occurred during the reaction [7]. Propylsulfonic and fluorosulfonic acid functionalized mesostructured silica (SBA-15) was synthesized and have demonstrated excellent catalytic behavior in the acetylation of glycerol with acetic acid [8]. Sulfonation of carbon-based materials also produced a highly active, and stable solid acid catalyst for this reaction [9].

A great attention has been devoted to the conversion of glycerol into oxygenated additives for liquid fuels. In this context, an industrially relevant route for the conversion of glycerol into oxygenated chemicals is the etherification to tert-butyl ethers. Tert-butyl ethers of glycerol with a high content of di-ethers are considered promising as oxygenated additives for diesel fuels (smoke suppressors and pour point depressants for diesel, biodiesel and their mixtures).

It is found however that mono-tert-butyl ethers of glycerol (MBGEs) have a low solubility in diesel fuel and they are soluble in water. However, if the etherification of glycerol produces mainly di- and tri-ethers, the product is readily blended in the fuel, and other restrictions related to the fuel properties controlled by quality standards can also be met. Thus, when di- and tri-tertiary butyl ethers of glycerol are incorporated to standard 30–40% aromatic-containing diesel fuel, emissions of particulate matter, hydrocarbons, carbon monoxide and unregulated aldehydes decrease significantly [10, 11].

The alkylation of glycerol can be performed with many etherifying agents: isobutylene, tert-butyl alcohol and C_4 olefinic petrochemical fractions. Tert-butyl alcohol avoids the need to use solvents to dissolve glycerol; however, water is formed as a by-product that may deactivate the heterogeneous catalysts used. When isobutylene is used, two phases might be present depending on the reaction conditions. The existence of multiple phases may lead to some problems of mass transfer in the reactor.

Many heterogeneous catalysts have been used in the alkylation of glycerol and reported in the scientific literature: acidic ion-exchange resins (mainly Amberlyst15 and 35), acid form wide pore zeolites (e.g., H-Y and H-Beta), sulfonic mesostructured silicas, sulfonated niobia and pillared clays.

Reported homogeneous catalysts for etherification of glycerol are the p-toluenesulfonic acid and sulfuric acid. Glycerol etherification with tert-butyl alcohol (TBA) is an acid catalyzed

reaction, resulting in a mixture of mono-tert-butyl-glycerol (MTBG), di-tert-butyl-glycerol (DTBG) and tri-tert-butyl-glycerol (TTBG). Some unwanted by-products can also be formed that are mainly a result of polymerization reactions.

2. Experimental

2.1. Materials

An Amberlite 15W resin was supplied by Rohm & Haas and used as reference acid catalyst in most tests.

CNR 115 activated carbon (AC sample) was supplied by Norit. This activated carbon was sulfonated by three different procedures: (a) Immersion in hot (373 K) concentrated sulfuric acid (H_2SO_4 98%) for 10 h (ACa sample). (b) Immersion in aqua regia for 20 h at room temperature followed by rinsing with water until neutral pH and drying. Final sulfonation in hot concentrated sulfuric acid like in (a) (ACb sample). (c) Sulfonation with sulfuric acid and naphthalene. 0.3 g of naphthalene were dissolved in 20 ml of tetrahydrofuran at room temperature and 2 g of AC were immersed in this solution for 1 hour with gently stirring. Then the carbon was filtered and dried at 373 K. Finally the naphthalene doped AC sample was sulfonated with hot sulfuric acid like in (a) (ACc sample).

MWNT (multi-walled nanotubes) were supplied by Arkema (Lot number 6068). This MWNT were also sulfonated by three different procedures: (a) Immersion in hot (373 K) concentrated sulfuric acid (H_2SO_4 98%) for 10 h (MWNTa sample). (b) Immersion in aqua regia for 20 h at room temperature followed by rinsing with water until neutral pH and drying. Final sulfonation in hot concentrated sulfuric acid like in (a) (MWNTb sample). (c) Sulfonation in very hot concentrated sulfuric acid (503 K), H_2SO_4 98%) for 10 h (MWNTc sample).

Molybdophosphoric acid ($H_3PMo_{12}O_{40}.7H_2O$) (HPA) was supplied by Merck. HPA/AC was prepared by first treating AC with aqua regia (3 parts of HCl + 1 part HNO_3 + 1 part water H_2O), then rinsing with water and drying. 0.4 g of HPA were dissolved in 15 ml of water and 0.5 ml of HNO_3. AC was added to a solution of 10 ml of water and 0.3 ml of HNO_3. Then, the HPA solution was added to the AC solution while stirring gently. The solution was then kept at room temperature under constant stirring for 12 h. Then the carbon was washed repeatedly with hot water (373 K) and finally filtered and dried [12-14].

2.2. Characterization of the carbon-based catalysts

The functionalized carbon materials were characterized by Raman spectroscopy, thermogravimetry, FT-IR spectroscopy and chemical titration.

Raman spectroscopy analysis of the solid samples were performed at room temperature with a Jobin–Yvon Horiba Labram II micro-Raman system with an excitation laser wavelength of 632 and 514 nm. The incident power was kept well below 3 mW to avoid sample damage or laser-induced heating. For each sample, spectra were acquired at three different spots and averaged, except when large variations were observed.

Thermogravimetric analysis (TGA) was carried out in a N_2 atmosphere with a heating rate of 10 K min^{-1}, from 25 ºC to 800 ºC (TA Instruments, Q500 TGA).

The samples were analyzed by infrared spectroscopy using a Varian 3100 FT-IR Spectrometer. Spectra were acquired by accumulating 100 scans at 4 cm^{-1} resolution in the range of 400–1200 cm^{-1}.

The titration of the acidic sites was performed using 100 mg of catalyst and a back titration method. The sample was first immersed in 10 cm^3 of a 0.1 M NaOH aqueous solution and stirred gently for 1 h. Then the resulting solution was titrated with a 0.1 molar HCl solution.

2.3. Catalytic tests

Esterification of glycerol: the reagents were glycerol (99.5% purity, Sigma-Aldrich) and acetic acid (99.7% purity, Sigma-Aldrich). The reaction was carried out in liquid phase 20 at 80 ºC in a stainless steel PTFE lined autoclave. Typically, the mass composition of the reaction mixture was 2.5 g of glycerol, 10 g acetic acid, i.e. 6:1 acetic acid/glycerol molar ratio, and a constant catalyst mass of 0.1 g. Samples of the reacting mixture were analyzed by gas chromatography in a Varian 3900 chromatograph using a CP-SIL 8 CB column (30 m long, 0.25 mm ID, film thickness 0.25 μ) and a flame ionization detector.

Etherification of glycerol: the reagents were glycerol (99.5% purity, Sigma-Aldrich) and tert-butyl alcohol (99.7% purity, Sigma-Aldrich). The reaction was carried out in liquid phase in a stainless steel PTFE lined autoclave. The stirring rate was maintained at 1200 min^{-1} in order to limit the effects of external mass transfer phenomena. Experiments were performed under different reaction conditions, 70-90 ºC reaction temperature, 2-6 tert-butyl alcohol/glycerol ratio and 1-7 h reaction time. The catalyst concentration was constant, 5% with respect to the glycerol mass. The catalysts were dried before each catalytic test. In a typical run, 5 g of glycerol and 0.2 g of the dry catalyst were used. The reaction products were sampled periodically and analyzed off-line in a Shimadzu 2014 gas chromatograph equipped with a flame ionization detector and a capillary column (J&W INNOWax 19091N-213, 30 m length) using acetonitrile as internal standard.

3. Results and discussion

3.1. Catalyst characterization

Raman spectroscopy is a potentially useful technique to obtain information of carbon materials. Raman results of AC and MWNT exhibited some typical features of carbonaceous materials: The tangential G band around 1580 cm^{-1} and the defect D band around 1320-45 cm^{-1}.

Raman spectra of AC and MWNT are shown in Figure 1. The main difference between AC and MWNT is the intensity band D / band G; AC has a lower ratio than MWNT, indicating that there is a higher concentration of defects (sp^3) on MWNT.

The thermogravimetric analysis (TGA) shows an increased weight loss with respect to the raw materials. The evolution of the weight loss was between 400 and 700 K, and it can be concluded that AC and MWNT have been functionalized with sulfonic group. All the samples showed weight loss between 4 and 9 %.
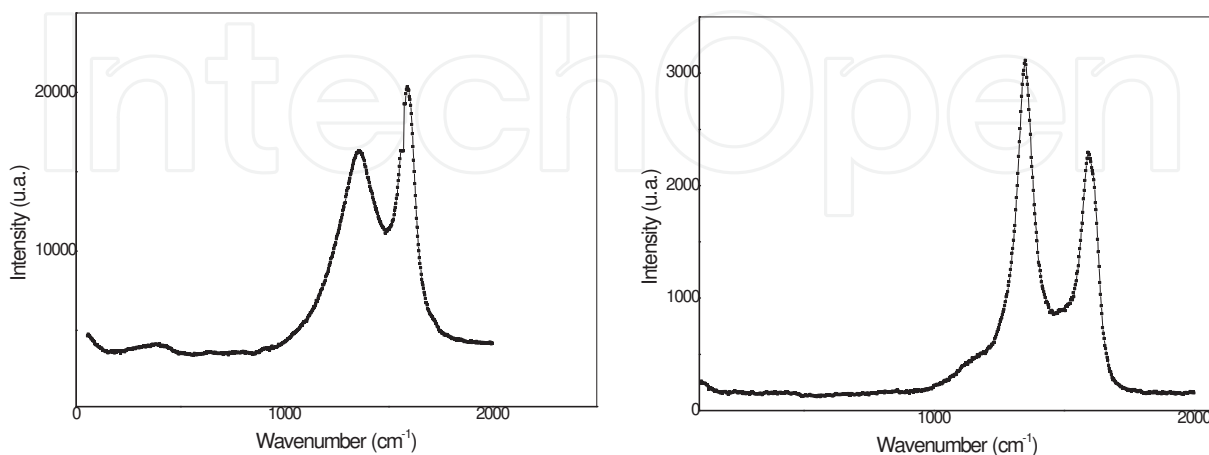
Figure 1. Raman spectra with excitation at 532 nm of AC (left) and MWNT (right).

Table 1 shows the specific surface area of the used catalysts. It can be seen that the acid treatment does not affect the physical properties of the activated carbon (AC). MWNT is also stable and not affected by the acid treatment. Only a shortening of the tubes or a slight variation of the length/diameter ratio might occur. The length of the nanotubes can range from several hundred nanometers to several micrometers, and the diameters from 2 to 100 nm [15, 16]. In the case of the catalyst of the last row of the table (HPA/AC), the HPA content (6.7%, mass basis) was determined by atomic absorption.

Catalyst	BET area ($m^2 g^{-1}$)	Mean pore radius (Å)	Acid content ($mEq\ g^{-1}$)
Amberlyst 15	45	280	4.8
AC	1970	19	
Aca	1850	20	0.9
Acb			1.2
Acc	1700	22	2.7
MWNT			
MWNTa			0.8
MWNTb			1.2
MWNTc			1.9
HPA	5		
HPA/AC	780	30	

Table 1. Textural and acid properties of the catalysts.

Some authors [17, 18] have posed that glycerol etherification reactions can show intraparticle diffusion problems, especially in the case of the formation of tri-tert-butyl-glycerol. In these reports, zeolites were used with a pore size of less than 10 Å. However, other authors have reported that using a beta zeolite as catalyst, glycerol can be etherified by 70-80% with tert-butyl alcohol with a 40% selectivity to di- and tri-ethers of glycerol [19]. The treatment of an HY zeolite with citric acid and/or nitric acid modifies the micropores and as a result selectivities to di- and tri-ethers of 85% and 58%, respectively, can be obtained when running the reaction at 343 K [11]. Therefore, the acidity strength significantly influences the formation of di- and tri-ethers of glycerol, although the accessibility of the glycerol to the acid sites must be guaranteed.

Table 1 also contains values of the total surface acidity of the catalysts. These concentration of acid sites can be considered as that of the strong sulfonic groups, because of the titrating method used. If other sites of weaker acid strength exist, they were not titrated by this method.

Regarding the sulfonation of carbonaceous materials, many reports have been published with values of surface sulfonic acid sites of 0.3-7 milimols H^+ g^{-1}. This big dispersion of values is due to the diverse nature of the starting carbons and the different ways of sulfonation used. Both sulfuric acid and óleum have been used and the temperature, time of sulfonation and method of titration have been varied.

In one approach, the carbon sample was left in contact overnight with fuming sulfuric acid (7% SO_3). In the second approach, the carbon sample was mixed with H_2SO_4 (>98%), and heated during 10 h [9]. SO_3H densities of about 1 mmol g^{-1} were got. In Ref. [20], the final sulfur content found was 3.29%, that corresponds to 1.03 mmol g^{-1}, after sulfonating at 453 K. 4-aminobenzene sulfonic acid at 278 K has also been used and functionalized carbons have been obtained with 1.16-1.86 mmol g^{-1} [21]. Some authors use more sophisticated sulfonation methods, like impregnation with 4-benzene-diazoniumsulfonate in ethanol/water solution in the presence of H_3PO_2. With this method, 1.70 mmol g^{-1} were obtained [22]. At 423 K with fuming sulfuric acid, the carbon with higher concentration had 1.1 mmol g^{-1} [23]. In a similar report at 423 K, a carbon with 7.07 %S was obtained that corresponds to 2.21 mmol g^{-1} [24]. Gomes et al. [25] found that impregnation at 353 K and 423 K with sulfuric acid yielded materials with 1 mmol g^{-1}. Other authors report that sulfonation at 423 K for 15 h yields a material with S content of 0.39 mmol g^{-1} [26] and 2.9-3.9 mmol g^{-1} calculated by titration with NaOH [27].

For the preparation of sulfonated carbon materials, only the sulfonation conditions have been varied. Other authors have focused their research efforts on the variation of the carbon precursor. For example, glucose and cellulose have been reported as carbon precursors, yielding materials with 7.2 and 7.3 mmol g^{-1} were obtained [28, 29].

All catalysts prepared from carbon supports (AC or MWNT) had an amount of acid sites lower than that of the resin. AC impregnated with naphthalene had a higher amount of sulfonic groups due to the incorporation of unsaturated surface carbons.

HPA/AC was also characterized by IR spectroscopy. Figure 2 shows that the four modes of vibration of HPA [12-14] can be found in the spectrum when the catalyst is the bulk one or when it is supported over activated carbon. These bands are attributed to the Keggin anion
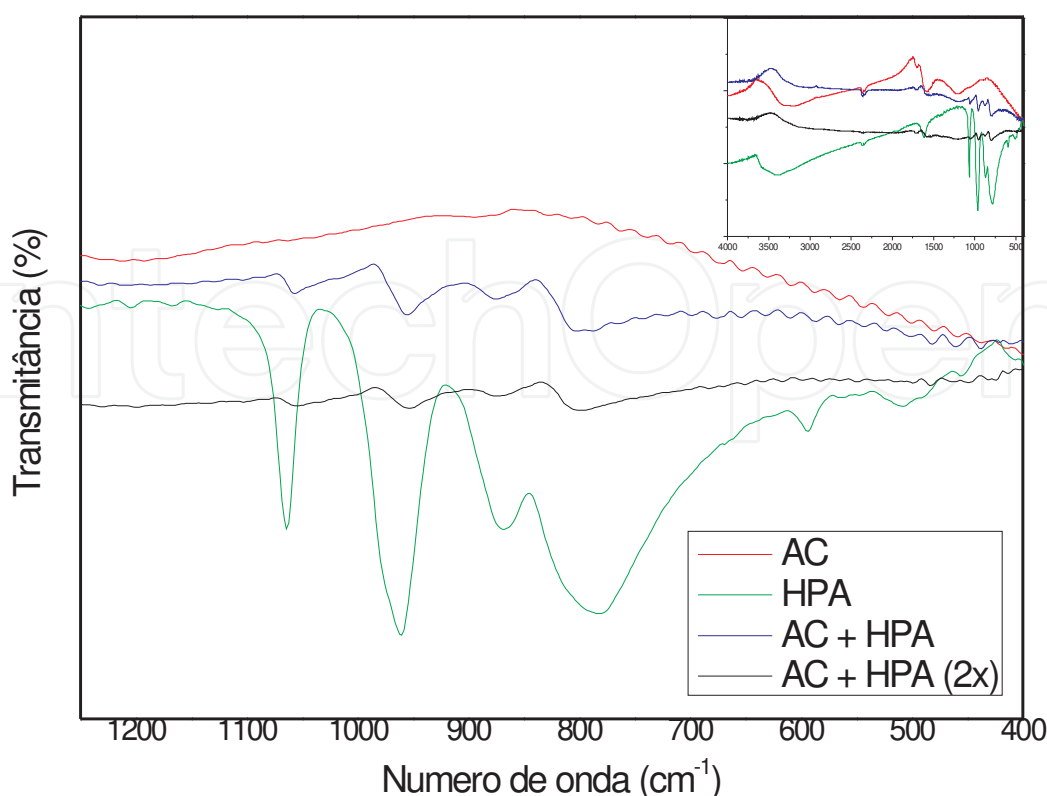
Figure 2. IR spectrum of HPA and HPA/AC.

$[PMo_{12}O_{40}]^{3-}$. The surface area of HPA/AC decreases due to the blocking of the micropores of AC by the heteropolyacid. In a previous work, we have demonstrated [12] that the acid treatments do not alter the total pore volume, though they decrease the fraction of micropores.

3.2. Esterification of glycerol

Some reported results on the esterification of glycerol with acetic acid are detailed in Table 2. One main variable is the molar ratio of acetic acid (AA) to glycerol (AA/Gly). This parameter varies widely from one report to the other. An inspection of the most active catalysts shows that these have an acid strength similar to that of pure sulfuric acid. Niobic acid that has an $H_o < 5.6$ (Hammett scale) is the least active.

It can also be seen that the temperatures used are those needed for reflux or 353-393 K. Variations of up to 100 K do not introduce meaningful changes in conversion, probably because of the low activation energy for this reaction.

The first assays of catalytic activity were performed at room temperature. The conversion of glycerol as a function of time can be seen in Figure 3.

The catalytic activity of the catalysts based on carbon catalysts, either AC or MWNT, was compared with that of the Amberlyst 15 resin. At 20 h of reaction time, the equilibrium was not achieved and the conversion was low. For the resin, conversion was 28% and for the other catalysts was about 20% or less.

Catalyst	AA / Gly	AA / Cat	T, K	X, %	MAG, %	DAG, %	TAG, %	Time, h	Ref.
Amberlyst 15	6/1	79	353	90	75	22	3	8	[30]
STARBON-400-SO$_3$H	1/1	6	373	98	78	20	2	0.16	[31]
Niobic acid	3/1	0.6	R	30	85	---	---	0.5	[32]
C-SO$_3$H	1/9	5 %	453	99.6	---	---	50	4	[33]
MP(10)/NbSBA-15-64	9/1	146	423	92	11	50	39	4	[34]
PMo1_NaUSY	16/1	105	R	60	33	62	4	3	[35]
Ag$_1$PW	10/1	100	393	96.8	48.4	46.4	5.2	0.25	[36]
MgF$_2$-87	3/1	72	373	94.2	---	60	30	22	[37]

Table 2. Reported values of catalytic activity and selectivity for the esterification of glycerol over several catalysts. MAG: selectivity to monoacetylglycerol; DAG: selectivity to diacetylglycerol; TAG: selectivity to triacetylglycerol; AA/Gly: molar ratio of acetic acid (AA) to glycerol (Gly); AA/Cat: mass ratio of acetic acid to catalyst; X: total conversion of acetic acid; R: reflux temperature. The resin was more active due to the higher concentration of acid sites. This was due to the fact that the resin has twice the concentration of acid sites of the carbon-based catalysts. The selectivity of the resin in these assays was 95% to monoacetin. For HPA/AC, ACc and MWNTc, the selectivity values to monoacetin were 92%, 93% and 94%, respectively. The selectivity to the other di- and tri- ethers was negligible.
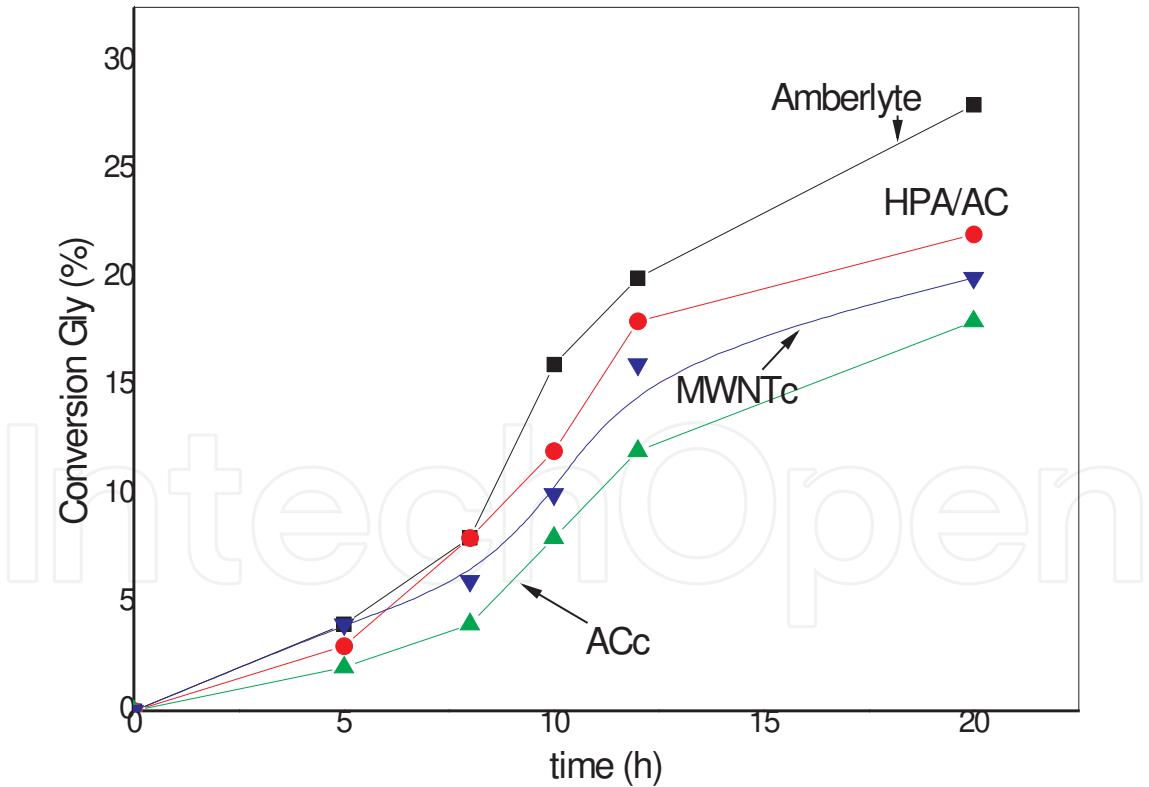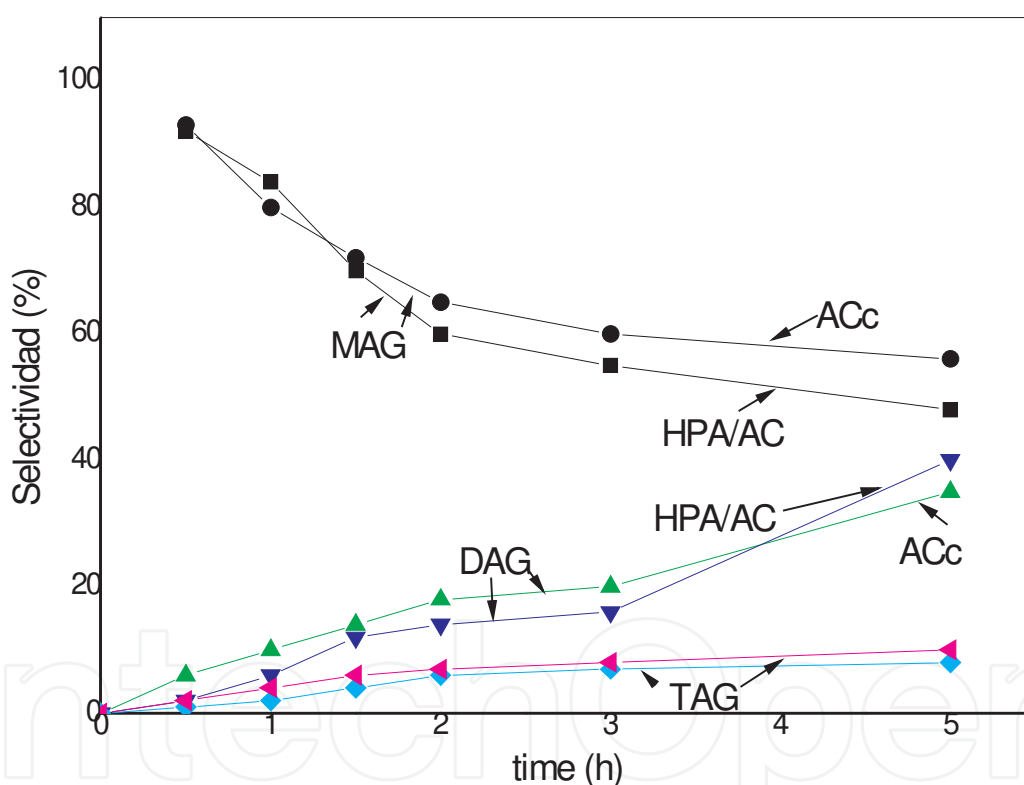

Figure 3. Conversion of glycerol during esterification with acetic acid at 293 K. Gly/AA=6, 0.1 g of catalyst.

Although the conversion achieved in these tests was relatively high, the reaction rate in these tests was fairly low and the thermodynamic equilibrium was not achieved. In these conditions,

monoacetin was the main product and could not be esterified with one or two additional glycerol molecules, as it could be expected from the consecutive reaction scheme depicted earlier.

A blank test was also performed to see the contribution of a non-catalytic path. Conversion was 4%, with a 90% selectivity to monoacetin. This conversion is not negligible in the reaction conditions used. The reactivity could be due to the protonic acid sites of acetic acid, that could autocatalyze the reaction.

Though the reaction can be performed at these conditions, the temperature was varied in order to maximize the glycerol conversion and the yield to di- and tri-acetylated products. The influence of the temperature was assessed by changing the reaction temperature to 373 K, keeping the other variables (AA/Gly molar ratio 6/1, 0.1 g catalyst mass) constant. Results for the catalysts with higher acidity (HPA/AC, MWNTc and ACc) are presented in Figure 4.

Figure 4. Selectivity in the reaction of esterification of glycerol with acetic acid at 373 K. Gly/AA=6, 0.1 g catalyst mass.

Conversion of glycerol reached 90-96% after 3-4 h of reaction time for all the catalysts tested. These results point to a higher reaction rate at higher temperatures and with favorable thermodynamics [38-41]. The equilibrium conditions are reached in a shorter time and the different selectivities can be inspected. Values of the selectivity to the diacetins (1, 3-DAG and 1, 2-DAG) and triacetin (TAG) can be seen in Figure 4. MAG concentration is decreased with reaction time while DAG and TAG are increased, showing the typical pattern of consecutive reactions.

Catalyst	AA/Gly	X, %	MAG, %	DAG, %	TAG, %
HPA/CB	1	90	56	37	7
	3	92	52	39	9
	6	92	49	41	10
CBc	1	88	62	32	6
	3	90	60	34	6
	6	94	56	36	8
MWNTc	1	86	64	30	6
	3	88	60	33	7
	6	90	58	32	10
Blank	1	27	66	32	2
	3	35	64	33	3
	6	44	62	36	2

Table 3. Conversion of glycerol and selectivity to acetates of glycerol. Esterification with acetic acid at 100 ºC, 0.1 g catalyst mass, 4 h reaction time. Notation as in Table 2.

HPA/AC showed the best yield to polyethers, with a 92% conversion at 3 h and a DAG+TAG selectivity next to 50%. Catalyst ACc that has the highest concentration of sulfonic sites also has a selectivity near to 45% for the products of interest.

Some additional tests were performed to check the reusability of the catalysts. These tests indicated that the catalysts were reusable and that surface sulfonic acid was not removed by leaching.

The influence of the molar ratio of acetic acid to glycerol (AA/Gly) was also assessed. The temperature was kept at 373 K and the values of AA/Gly used were 1, 3 and 6. The results are included in Table 3. It is especially noticeable that for the blank test at AA/Gly=6, the conversion was about 50%. This points to the autocatalytic role of the protons of acetic acid.

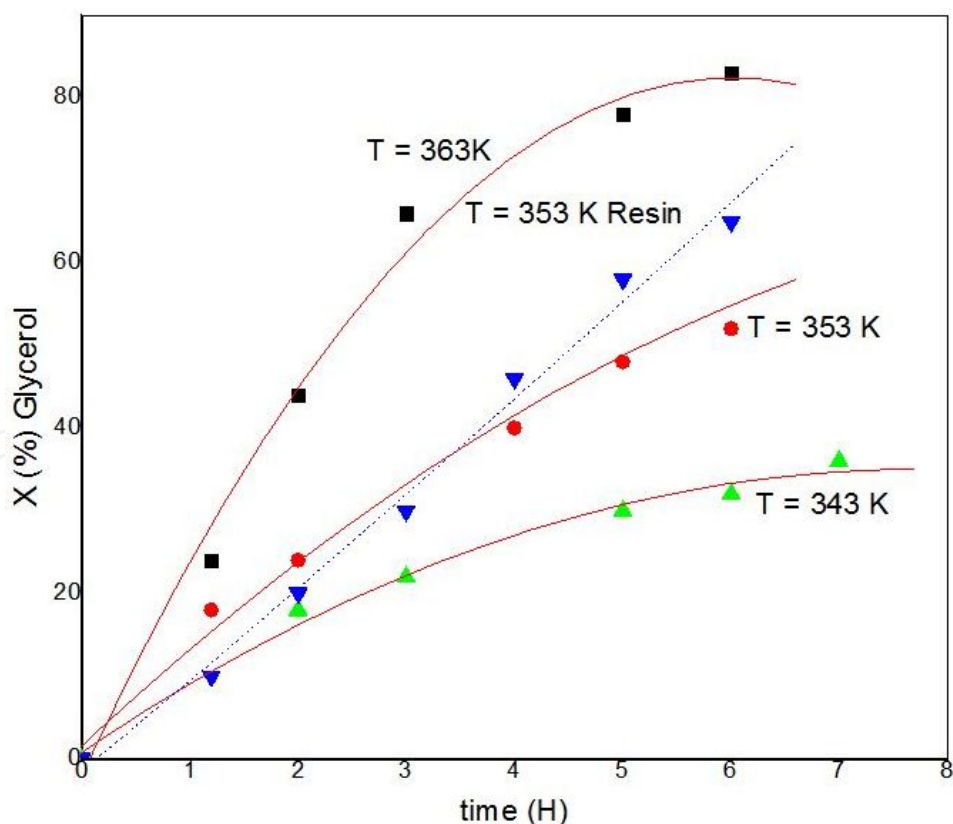### 3.3. Etherification of glycerol with tert-butyl alcohol

3.3.1. Effect of reaction temperature

Glycerol was etherified with tert-butyl alcohol with the same series of catalysts used in the previous section. The convenient temperature was first screened using the reaction with HPA and comparing with the results obtained with the resin. HPA catalysts with Keggin structure are widely used as acid catalysts because of their very strong Brönsted acidity. They however have low specific surface area. Variations have been prepared to increase their area by supporting HPA on carbon, silica, zeolites, etc.

Figure 5 shows that the conversion of glycerol is increased when increasing the temperature from 70 to 90 ºC. Although this could be foreseen, there is no agreement with the published

reports. Some authors have found that conversion of glycerol at 90 ºC is lower than conversion at 120 ºC [42]. It is also found that the maximum yield occurs at 90 ºC [43]. For the Amberlyst 15 resin, the maximum conversion is achieved between 70 and 90 ºC [44]. These differences can be due to the system not being in equilibrium in some cases and to the occurrence of other reactions. Degradative reaction would produce gases and increase the system pressure, thus modifying the reaction rate and the equilibrium [44].

In our experiments, 80 ºC was selected as optimal temperature for testing the activity and selectivity of the catalysts. First, HPA can be compared to the Amberlyst resin. According to the results of Figure 4, the initial reaction rate on HPA is higher than the reaction on the resin. After some time, the conversion however is lower with HPA, being 60% with the resin and 50% with HPA. At this temperature, a weight loss could also be detected. This could be due to the presence of degradation reactions catalyzed by the strong acid sites. *tert*-Butanol could be dehydrated to isobutylene and glycerol decomposed to acetaldehyde, acrolein, acetic acid, isobutylene, diisobutylene, etc. At 80 ºC, the reaction system with the resin had a weight loss of 3.8% and the system with HPA, 2.1%. In the first system, the amount of water formed was 3.2%; however, 2.3% water was formed when using the HPA catalyst. A blank test was performed in order to check the presence of autocatalytic reactions, but under similar conditions, the conversion of glycerol was negligible.

Figure 5. Conversion of glycerol during etherification of glycerol with *tert*-butanol at 80 ºC. *tert*-butanol/Gly=4, 0.2 g catalyst mass.

It can be seen that HPA is an optimal homogeneous catalyst with a great affinity for polar molecules. However, the resin, with its high concentration of active sites, is also very active. In both cases, no deactivation was detected due to the formation of water.

3.3.2. Influence of catalysts on the selectivity

Figure 6 shows values of conversion of glycerol and selectivities to the different glycerol ethers, when using catalysts ACc and MWNTc. Both catalysts have Brönsted acidity from sulfonic groups, the only difference being their concentration and their accessibility. In the case of the ACc catalyst, the average size of the pores is 22 Å. In the case of MWNTc, MWNTs have a greater amount of sp^3 carbons, and hence this catalyst should have a greater amount of defects of easier sulfonability. For a system of 5 nanotubes with 10 nm diameter (lower limit) and 10 tubes with 15 nm diameter (upper limit), 1 carbon atom out of 4.3-8.5 total atoms is on the surface. In this sense, 1 out of 6.4 carbon atoms is accessible for reaction with a liquid reagent [45].

The conversion of glycerol and the selectivity to different ethers was studied at 80 ºC and a *tert*-butyl alcohol/Gly molar ratio of 4. It is expected that high temperatures promote undesirable reactions. These could be the dehydration of *tert*-butyl alcohol to isobutene or the decomposition/reaction of glycerol. Usually, these side reactions produce an increase of the pressure in the system. There is in consequence an optimal temperature that some authors report as 75-85 ºC. Lower temperatures would not provide a sufficiently high reaction rate. Higher temperatures would lower the selectivity to the desired products [46]. Figure 5 shows values of the selectivity to the different glycerol ethers as a function of time, for a reaction temperature of 80 ºC.

The conversion of glycerol after 10 h reaction time was 50-60% on the ACc and MWNTc catalysts. Both catalysts were less active than the Amberlyst resin. This was attributed to their lower concentration of acid sites. With respect to the selectivity and according to the mechanism of consecutive reactions for this system, 5 glycerol ethers can be expected: 3-*tert*-butoxy-1, 2-propanediol, 2-*tert*-butoxy-1, 3-propanediol, 1, 3-di-*tert*-butoxy-2-propanol, 1, 2-di-*tert*-butoxy-3-propanol and tri-*tert*-butoxy-propane. Despite the high number of possible products, the selectivity was mostly to the monoether and to a lower extent to the di-ether. Only traces of the tri-ether could be detected. Several authors report that the acid strength of the catalyst should be increased [18] in order to improve the selectivity to di- and tri-ethers, or the temperature should be increased [41], or the water product eliminated from the reaction medium to help shift the thermodynamic equilibrium [43]. However, none of these modifications permits increasing the concentration of tri-ethers.

With respect to the MWNTc catalyst, we can safely say that the accessibility of the reactants to the acid sites is good, given the open structure of this catalyst. Another aspect to analyze is that of the surface density of acid sites. Once the glycerol monoether is formed, the availability of another active site nearby could permit the onset of a second etherification. Fluorinated beta zolite [18] permits the etherification of glycerol at 75 ºC with 75% conversion and 37% to di+tri ethers, but with a small amount of tri-ethers. Better results of higher catalytic activity and better selectivities to di- and tri-ethers have been published and concern the use of isobutylene as
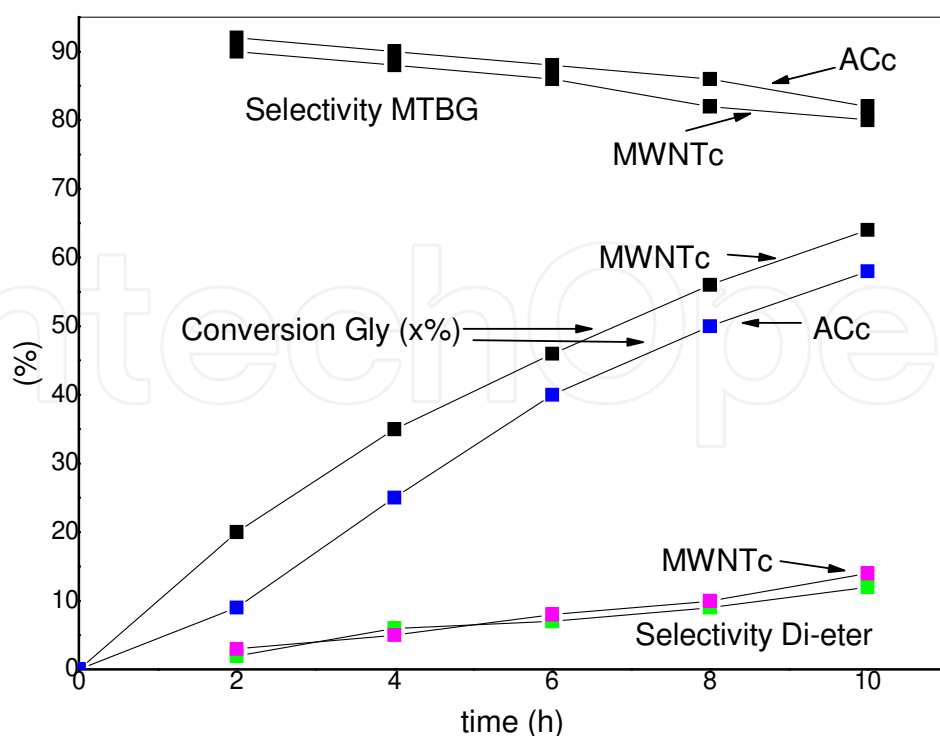
Figure 6. Conversion and selectivity as a function of time during etherification of glycerol with *tert*-butanol at 80 ℃ over different catalysts. *tert*-Butanol/Gly=4, 0.2 g catalyst mass.

etherifying agent. Under similar conditions of temperature and Gly/etherifying agent ratio, better results are obtained when using isobutylene than *tert*-butyl alcohol [18].

3.3.3. Effect of the molar ratio of tert-butyl alcohol to glycerol

The sulfonated carbons were also tested in the reaction of tert-butylation of glycerol at varying molar ratios of *tert*-butyl alcohol to glycerol. Only the most acidic catalysts were used. The temperature was kept at 80 ℃ and the catalyst mass used was 4% with respect to glycerol. The results are included in Table 4.

When a molar ratio in the range 2-6 and the resin Amberlyst 15 are used, the glycerol conversion increases as a function of the molar ratio from 68% to 82%. The reaction reaches equilibrium faster, although the selectivity is not significantly altered. Only a little increase of the selectivity to DTBG was observed in the case of the carbon-based catalysts. It can be seen that increasing the TBA/Gly molar ratio does not produce large modification in the activity or selectivity. This is probably a result of the similar acid strength of the catalysts due to the similar nature of the acid site (SO$_3$H). A change in activity or selectivity probably needs an increase of the acid strength, which might be obtained with another kind of acid sites. Some authors [19] observed that an increase in the Brönsted acid strength improved the yield of di- and tri-ethers of glycerol.

The effect of water on the activity and selectivity of these reactions must also be mentioned. In order to favor the consecutive reactions of glycerol over zeolite catalysts, Frusteri [44]

removed the water from the reaction system after 6 hours. He obtained an increase of the DTBG yield from 28.5% to 41.5% and demonstrated that the difficulty in obtaining tri-ethers is related to the presence of water.

Catalyst	TBA/Gly molar ratio	Gly conversion (%)	MTBG	DTBG	TTBG
	2	48	84	16	---
HPA/AC	4	56	82	18	2
	6	62	80	17	3
	2	52	85	15	---
ACc	4	60	84	16	2
	6	68	80	18	2
	2	50	84	16	---
MWNTc	4	58	82	15	3
	6	58	79	19	2
	2	68	80	20	---
Amberlyst 15	4	75	80	19	1
	6	82	78	18	4

Table 4. Conversion of glycerol and selectivity to tert-butyl ethers of glycerol at 80 ºC, 8 h reaction time and different TBA/Gly molar ratios. TBA: *tert*-butyl alcohol. MTBG: mono *tert*-butyl ether of glycerol. DTBG: di *tert*-butyl ether of glycerol. TTBG: tri *tert*-butyl ether of glycerol.

4. Conclusions

Carbon supports such as activated carbon and MWNTs can be irreversibly sulfonated to yield materials with sulfonic groups surface concentrations of about 3 milimols per gram.

Sulfonation of activated carbon does not yield materials with meaningful concentration values of surface acid sites unless a graphitic precursor such as naphthalene is coimpregnated during sulfonation.

MWNTs are more efficiently sulfonated at 230 ºC. In this case, only 1/6 of the surface carbon atoms are exposed.

Esterification of glycerol with acetic acid can be carried out at room temperature, but in these conditions, the selectivity is biased toward monoacetin because the esterification rate is low and monoacetin cannot be acetylated. The selectivity to TAG and DAG is increased at higher temperatures (e.g., 60% at 100 ºC).

Etherification of glycerol with tert-butyl alcohol is a complex reaction with many undesired by-products being produced. All catalysts tried were effective for converting glycerol, but obtaining selectivities higher than 70-80% to di- and tri-ethers is still a challenge.

Acknowledgements

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