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Biomass conversion: Preparation of glycerol carbonate esters by esterification with hybrid Nafion-silica catalyst.

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Abstract

Glycerol carbonate esters (GCEs) which are valuable biomass derivative compounds have been prepared by direct esterification starting from glycerol carbonate and long organic acids with different chain length, in absence of solvent and using acid organic resins, zeolites and hybrid organic-inorganic acid catalysts as heterogeneous catalysts. The best results in terms of activity and selectivity to glycerol carbonate esters have been obtained using a Nafion-silica composite. A full reaction scheme has been established and it has been found that an undesired competing reaction is the generation of glycerol and esters derived from a secondary hydrolysis of the endocyclic ester group due to water formed during the esterification reaction. The influence of temperature, substrates ratio, catalyst to substrate ratio and use of solvent has been studied and, under optimized reaction conditions and the adequate catalyst, it is possible to achieve 95% selectivity to the desired product at 98% conversion. It was found that reaction rate decreased as the number of carbons in the linear alkyl chain of the carboxylic acid increases for both p-toluenesulfonic acid and Nafion SAC-13. Fitting experimental data to a mechanistically based kinetic model, the reaction kinetic parameters for Nafion SAC-13 catalysis were determined and compared when reacting different carboxylic acids. A kinetic study showed that the lower reactivity of the carboxylic acid when increasing the chain length can be explained by inductive as well as steric effects.

Introduction

The production of fine chemicals, polymer precursors and commodities from biomass can contribute to decrease our current dependence on non-renewable energy sources. Chemical routes for catalytic biomass transformations have been recently reviewed^[1] and it has been presented that one of the foremost natural source of potentially relevant chemicals is glycerol. Moreover, the biodiesel industry, through the transesterification reaction of vegetable oils with methanol or ethanol, has contributed enormously to increase the production of glycerol^[2] and good results have been achieved in converting glycerol into a large number of industrial compounds, among them glycerol carbonate (GC)^[3]. Recently, we reported the synthesis of glycerol carbonate by transesterification of ethylene carbonate with glycerol catalyzed by basic oxides (MgO, and CaO) as well as by carbonylation of glycerol with urea with a Zn-Al mixed oxide catalyst^[4].

GC is a promising chemical intermediate which can be used as a solvent^[5] or it can react with alcohols, phenols and carboxylic acids^[6], and it is considered an excellent intermediate in the synthesis of glycidol and epichlorohydrin, products that have a large industrial application^[7]. On the other hand, glycerol carbonate esters (GCEs) are compounds with a polyoxygenate moiety due to the presence of both endocyclic and exocyclic ester groups. GCEs possess interesting physico-chemical properties such as a good thermal and oxidation stability, surfactant properties and biodegradability^[8,9]. The chain length of the carboxylic acid moiety determines the properties of the product for applications as surfactants, lubricants, plasticizers, or solvents. They have been prepared by reacting glycerol carbonate with an electrophile, as for instance an acyl halide^[10] in presence of triethylamine, acid anhydrides^[11] using *p*-toluenesulfonic acid (*p*TSA) as catalyst or isocyanates^[12]. Transesterification reaction may also be used for GCEs

synthesis in presence of MeONa and hydroquinone^[13] or by using zirconium acetylacetonate^[14] as catalyst. In the work of Ramaiah^[15], 4-[(Benzoyloxy)methyl]-1,3-dioxolan-2-one was synthesized with 68% yield from glycerol carbonate, potassium benzoate, triphenylphosphine and carbon tetrachloride at 55-60 °C for 5.5 h. Another synthetic route has been described that reacts natural oils with a carbonate source such as dimethylcarbonate and a strong base NaOCH₃ at 110-150 °C. In this case, GCEs were obtained with yields of 58%^[16]. GCEs have also been prepared by treating the corresponding glycidyl ester with carbon dioxide^[17]. Moreover, GCEs synthesis has been performed by direct esterification of the corresponding GC with carboxylic acids, in presence of homogeneous acid catalysts. In this sense, Jana et al.^[18] carried out the synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate with 67% yield using a coupling agent such as N,N'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine and in the patent literature^[19], acetic acid, glycerol carbonate, and *p*TSA were brought to reflux in toluene to remove the water, and a yield of up to 83% of the desired product was achieved. Interestingly, and as far as we know, there are not references in the literature for the preparation of GCEs with a heterogeneous catalytic process with solid acid catalysts. This is surprising since the development of green and sustainable chemistry focus on the use of solid catalysts that will avoid additional neutralization steps, and eliminate corrosion problems in the unit.

In this sense, the direct esterification of glycerol carbonate with carboxylic acids using solid acid catalysts can be of interest. In general, the most popular solid acids used to produce esters have been ion-exchange organic resins, such as Amberlyst-15^[20], zeolites^[21], and silica-supported heteropoly acids (HPA/silica)^[22,23]. However this type of catalysts exhibit limitations in applicability for catalyzing esterification due to: low

thermal stability (Amberlyst-15, < 140 °C), mass transfer limitations (zeolites)^[24], or leaching of active acid sites in the presence of a polar medium (HPA/silica)^[25].

Nafion[®] resins have been widely used in organic synthesis as acid catalysts^[26]. They exhibit an acidic character comparable to that of 100% sulfuric acid^[27] which, combined with a reasonable thermal stability, chemical resistance, and possible regeneration, makes Nafion[®] a safe and valued solid acid catalyst. However, because of the very low surface area (0.02 m²·g⁻¹) and the inaccessibility of most of the active sites, Nafion has low specific activity. Then the preparation of Nafion-silica nanocomposites (Nafion SAC-13), by immobilization of Nafion into a silica matrix reported by Harmer and co-workers^[28], has overcome some of the above limitations by providing nanocomposites with large surface area (150–500 m²·g⁻¹) and small Nafion particles (<100 nm) entrapped in a porous silica framework. Outstanding catalytic performance was found in various studies^[28-31] and it is now commercially available as Nafion SAC-13^[32].

In this work we have studied the synthesis of GCEs with organic acids with increasing chain length, and have shown the important role played by the adsorption terms in the kinetic equation on catalyst performance. From those results a proper coupling of the solid catalyst nature and the reaction conditions was found, that allow us to achieve conversions and selectivities above 95% using solid catalysts.

Experimental

Catalysts

Dowex 50-Wx2, Dowex Marathon C, Amberlyst-15, Nafion NR50, Nafion SAC-13 and *p*-toluenesulfonic acid (*p*TSA) were purchased from Sigma Aldrich. Beta (Si/Al = 13) and Mordenite zeolites were supplied by PQ Corp., in the acidic and the ammonium form respectively. The acid form of Mordenite was obtained by calcination, followed by

an acidic treatment to produce a sample with a final Si/Al ratio of 10. Beta zeolites with higher Si/Al ratio (47 and 100 respectively) were prepared following the synthesis procedure described in literature^[33]. MCM-22 zeolite with MWW structure^[34] with Si/Al = 15 was prepared and converted to its acid form following^[35]. ITQ-2 catalyst has been prepared by expansion and subsequent exfoliation of the corresponding laminar precursors of the MWW structure^[36]. Commercially available ZSM-5 with Si/Al = 10 was supplied by Tricat Zeolites GmbH. The commercial sample, supplied in their ammoniac form, was calcinated at 773K for 3 h in order to obtain the protonic zeolite

Reagents

Hexanoic, heptanoic, octanoic, nonanoic, lauric, and palmitic acids, as well as glycerol carbonate, nitrobenzene, pyridine, ferrous sulphate and hydrogen peroxyde 30% v/v were purchased from Sigma Aldrich, while toluene was supplied by Scharlab, and N,O-Bis(trimethylsilyl)trifluoroacetamide by Acros Organics.

Reaction procedure

The reactions were performed, in a two-neck round bottom flask of 10 mL. There 10 mmol (1.16 g) hexanoic acid (HA), 15 mmol (1.78 g) of glycerol carbonate (GC) and 3.5 wt% of just activated catalyst, respect to the total weight reactants, were introduced. Subsequently the reaction mixture was heated at 100 °C in a silicone bath fitted with a magnetic stirrer and a temperature controller. In order to remove the water formed in situ, the flask is coupled to a Dean Stark and this to a condenser, while a nitrogen flow of 20 mL·min⁻¹ was applied. In a series of preliminary experiments, the reaction mixture was stirred at 400, 800 and 1200 rpm. No influence of the stirring speed on initial reaction rate was observed being possible to conclude that, under our experimental

conditions, the reaction is not controlled by external diffusion. When the reaction was carried out under conditions of azeotropic distillation of water, 5 mL of toluene was used as a solvent and the reaction media was heated up to reflux temperature (111 °C).

In another series of experiments the same methodology was followed, but some of the reaction conditions were changed to study the effect of temperature, substrates ratio, substrates-to-catalyst ratio and solvent on reaction rate and selectivity.

The progress of the reaction was followed by taking samples at regular time periods that were analyzed by gas chromatography using a FID detector and a capillary column (HP5, 30 m × 0.25 mm × 0.25 μm). All samples were silylated with N,O-bis(trimethylsilyl)-trifluoroacetamide and dissolved in pyridine prior to analysis by gas chromatography. Nitrobenzene was used as external standard. At the end of the reaction the catalyst was filtered and washed with toluene. The catalyst, which contains organic material from the reaction, was regenerated by a Fenton's treatment (10 mL of H₂O, 0.1 g of FeCl₂, and 20 mL of H₂O₂ 35% v/v added drop wise over 3 hours by 1 g of catalyst)^[37].

Isolation of reaction products for NMR analysis was performed by vacuum distillation which allow to separate remaining carboxylic acid, remaining glycerol carbonate and monoglycerides from the reaction mixture. When necessary, and in order to eliminate remaining di and triglycerides, the distillation residue was dissolved in *n*-heptane and extracted with aqueous ethanol solutions according the procedure described in the patent US 2651646 (1953)^[38]. For instance, the case of glycerol carbonate lauric acid ester, it was purified under 10 mmHg at 250 °C and the isolated yield of the ester was 56%. The content of organic on the catalyst (wt% C, H, N and S) was measured by elemental analysis using EA-1108 CHNS Fisons analyzer and sulphanilamide as standard. The thermogravimetric analyses were carried out in a TGA 2050 by TA

Instruments, under an air flow and with a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$. Mass spectra were performed with a GC-MS HP Agilent 5973 with a 6980 mass selective detector. The FTIR spectra were collected on a Nexus Thermo FTIR spectrometer equipped with a DTGS detector (4 cm^{-1} resolution, 32 scans).

The calorimetric adsorption measurements were performed with a Calvet C80 Calorimeter from Setaram. Previously to the measurement, a pretreatment procedure of each sample was performed, which consists in heating the sample for 2 hours at a temperature of $250 \text{ }^\circ\text{C}$ under vacuum ($\sim 1\cdot 10^{-3} \text{ atm}$). After this time, the sample is sealed and it is ready to measure.

Results and discussion

Reaction network for GC esterification with carboxylic acids to GCEs

The esterification of glycerol carbonate (GC) with hexanoic acid (HA) was taken as reaction model and performed at $100 \text{ }^\circ\text{C}$, GC/HA molar ratio of 1.5 and catalyst (3.5 wt%). Perfluorinated sulfonic acid resin (Nafion NR-50) was used first to establish the reaction scheme. The main product of the reaction was the corresponding ester (2-oxo-1,3-dioxolan-4-yl)methyl hexanoate (GCE-6), but different by-products were also observed (Scheme 1). The by-products were identified by GC-MS as the glyceryl hexanoate (monoglyceride), glyceryl dihexanoate (diglyceride) and glyceryl trihexanoate (triglyceride). The formation of these by-products can be explained by following two different reaction routes: a) from the hydrolysis of the carbonate function of GCE-6 giving two monoglycerides which further esterifies with the carboxylic acid giving two di- and subsequently a triglyceride (see route I, Scheme 1), and b) by the hydrolysis of glycerol carbonate to glycerol followed by the fast acid catalyzed esterifications of glycerol with HA to give monoglycerides, diglycerides and

triglyceride (see route II, Scheme 1). The fact that free glycerol as well as β -monoglyceride, which only can be produced by glycerol esterification (route II), were detected at the beginning of the reaction suggests that the two routes described above can contribute to the formation of these by-products.

In Figure 1 the yields of the different by-products, i.e. mono, di and triglyceride versus time using Nafion NR-50 as catalyst are plotted. Monoglycerides appear as primary and unstable products, while diglycerides appear as secondary and unstable since they would be formed by esterification of monoglycerides, and further reaction will give the triglyceride by a consecutive esterification. The detection of those compounds, clearly indicate that the reaction proceeds via the two, a) and b), routes noted above.

Study of the catalyst

It appears that acid catalysts are adequate for performing the esterification reaction of glycerol carbonate with HA acid. Thus, when considering solid acids, the first catalyst choice was zeolites, and more specifically zeolites with higher silica to alumina ratios which are stable to the presence of acid reactants. Furthermore, the different pore dimensions and topologies of zeolites and their hydrophobic properties may be useful to achieve higher selectivities to the ester of the carbonate, i.e. 2-oxo-1,3-dioxolan-4-yl)methyl hexanoate (GCE-6). With this objective, we have selected aluminosilicate zeolites with relatively high Si/Al ratio (~15) and a system of unidimensional large pore (Mordenite), tridimensional large pore (Beta), a delaminated zeolite (ITQ-2) with high external surface area, and a bidimensional medium pore zeolite (ZSM-5).

The reactions were performed with a GC/HA of 1.5, with 3.5 wt% catalyst at 100 °C. Conversion and selectivity to GCE-6, together with the initial rates and turnover

frequencies (TOF), defined as mmol converted per mmol of nominal Brønsted acid sites (calculated from Al content) per minute, are given in Table 1. The results obtained with zeolites were disappointing since besides their low conversion, the selectivity was always lower than ~60%. Nevertheless, pore dimensions and site accessibility play an important role for the esterification reaction on these materials. Indeed, zeolites with medium pores were less active than those with large pore, and certainly less active than the delaminated ITQ-2 zeolite. This is even more visible when normalizing the activity (initial rate) per acid site. At this point we understood that the acidity of the zeolites was not adequate to operate at the relatively low temperature used here (100 °C), and/or it may also occur that the polarity of the zeolite is too high and it becomes rapidly deactivated by reactant and product adsorption, while catalyzing the hydrolysis of GC. In order to evaluate the last hypothesis, we have followed conversion and yield to GCE-6 with reaction time. The results given in Figure S1 clearly show that, regardless of the zeolite used, conversion rapidly stops with reaction time, indicating that the catalyst has been deactivated. Indeed, in the case of Beta zeolite, we have analysed by TGA and IR spectroscopy the total amount and type of products remaining on the catalyst after reaction, and the results indicate that 9 wt% of organic material remains on the catalyst surface after the catalyst was used and washed. The presence of IR bands at ~1730, 1780 and 1820 cm^{-1} associated to carbonyl groups and ~2800-3000 and 1450-1500 cm^{-1} associated to C-H bonds indicate the presence of adsorbed acid and also, probably, adsorbed esters of glycerol (see Figure S2). At this point, and with Beta zeolite, we have increased the hydrophobicity by increasing the Si/Al ratio by synthesis while decreasing the framework zeolite defects (internal Si-OH). This was achieved by synthesizing the Beta samples in fluoride media^[39]. The results given in Table S1, indicate that when increasing the Si/Al ratio of Beta zeolite, its activity increases (see initial reaction rates)

despite the fact that the number of acid sites decreases (see also total amount of nominal acid sites as well as Brønsted acid sites measured by pyridine adsorption and desorption at 250 °C). This would be an indication that the blocking of active sites by strong adsorption of reactant and products decreases when increasing the Si/Al ratio, as it was confirmed by TGA and IR spectroscopy (see Table S1 and Figure S3). Nevertheless, in the best case, conversion and selectivity are still in the order of 30 and 65 %, which are still too low. Then, we moved into catalysts with stronger Brønsted acid sites such as sulfonic and fluorosulfonic resins, including the hybrid Nafion-silica catalyst named Nafion SAC-13. As can be observed in Table 1 the most active catalysts (initial rate) are the perfluorinated sulfonic resins Nafion NR-50 and Nafion SAC-13 (entries 2 and 3). It follows the sulfonic acidic resins (entries 4-6), while the aluminosilicate catalysts are clearly less active (entries 7-11). However it should be noted that Nafion SAC-13 and Nafion NR-50, which give initial reaction rates close to sulfonic acids resins, have a lower concentration of Brønsted acid sites, and consequently the turnover frequency (TOF), i.e. activity per Brønsted acid site, is higher for the Nafion based catalysts (see Table 1). This fact could be attributed to the higher acidity of sulfonic groups in the perfluorinated resins with a Hammett acidity value (H_0) in the order of -12, while resins with sulfonic groups have $H_0 \sim -3$ ^[29]. On the other hand, when the activity per acid site is considered it can be observed that the composite Nafion SAC-13 is twelve times more active than Nafion NR-50, suggesting that the higher surface area of the former improves considerably the accessibility of reactants to the acid sites of the catalyst. In addition, the selectivity to the glyceryl carbonate ester (GCE-6) is higher with Nafion SAC-13 than with the other acid resins (Table 1), indicating a lower competitive hydrolysis of the cyclic carbonate moiety on the SAC-13. When, for comparative reasons, the reaction was performed with *p*-toluenesulfonic acid using the same

equivalents of acid sites that those existing in Nafion SAC-13 (entry 12), the activity of the homogeneous catalyst was higher but the selectivity to the ester was similar (see Figure 2 and Figure 3), indicating that even in Nafion SAC-13 not all the acid sites are accessible, or the acidity can be diminished by interaction of the Brønsted acid sites with silanol groups^[30].

Since it was possible to obtain a conversion close to 70% with selectivity to GCE-6 of 85%, we have attempted to improve those values by optimizing the process variables. Then, results in Figure S4 give the yield of GCE-6 versus conversion when the esterification was performed with different catalyst loadings (3.5, 8 and 15 wt%). As expected, an increase of conversion is observed when increasing catalyst loading, but selectivity to GCE-6 remains constant (85%) and it is practically independent of the level of conversion (see Table 2 and Figure S4). Then, the esterification was performed at 80, 100, 120 and 140 °C and, as expected, the initial rate of disappearance of HA increases with temperature, while selectivity to GCE-6 decreases significantly at conversions higher than 70% for reaction temperatures above 100 °C (Figure S5). This indicates that at higher temperatures, the opening of the cyclic carbonate is relatively more favorable than its esterification. Therefore, to maximize selectivity, one should work with strong solid acid catalysts that allow performing the reaction at lower temperatures.

Finally, the influence of the GC/HA molar ratio on conversion and selectivity was studied by performing the reactions with GC/HA molar ratio of 8, 4, 1.5, 0.25 and 0.125. The results in Figure S6 indicate that an increase in concentration of GC or HA, induces an increment of the initial rate of reaction while the selectivity to GCE-6 remains constant, being the conversion, yield and selectivity in the order of 95%, 81% and 85%, respectively, regardless the carbonate is or is not in excess.

Influence of the solvent

The results presented above have showed that working in absence of solvent and under optimized reaction conditions, selectivity to GCE-6 of 85% at 95% conversion can be achieved. The selectivity loss is due to the presence of water in the reaction media, because the impossibility to remove all the water formed during the esterification by applying a nitrogen flow and a Dean-Stark. Under these conditions, the presence of water causes the hydrolysis of the carbonate lowering the selectivity to GCE-6. To better eliminate the water from the reaction media, the reaction was performed under vacuum (10 torr), but no improvement was achieved in selectivity. Finally with the aim of avoiding the presence of water and maximising the yield and selectivity to GCE-6, the reaction was carried out under conditions of azeotropic distillation of water with toluene. From the results given in Figure 4 it can be observed that the selectivity to GCE-6 was increased up to 95% at 98% conversion of HA. Interestingly, when the reaction was performed using a conventional homogeneous acid catalyst such as *p*-toluenesulfonic acid, similar performance was achieved showing that Nafion SAC-13 constitutes a promising solid catalyst for this reaction.

Influence of the chain length of the carboxylic acid

To obtain products with different surfactant properties^[8], the esterification of GC has been performed with carboxylic acids of different chain length in conditions of azeotropic distillation. By doing that, it is possible to obtain molecules with different polar/apolar character and, therefore, with different surfactant properties. The yield of GCEs versus time is plotted in Figure 5 for hexanoic, heptanoic, octanoic, nonanoic, lauric and palmitic acids. It can be observed there that when increasing the chain length of the fatty acid from hexanoic to lauric and palmitic acid, the conversion decreases

drastically from 98% to 71% and 31% respectively. The observed reactivity trend for carboxylic acids can be conceptualized on the bases of well-established mechanistic model for the esterification reaction with homogeneous catalysis^[40]. It is believed that two factors may contribute to the decrease of carboxylic acid reactivity when increasing the number of carbon atoms in the carboxylic acid chain: an inductive and a steric effect^[41]. The inductive effect is a consequence of the increased electron-releasing capacity of the acid when increasing the alkyl chain. The inductive effect facilitates the protonation of the oxygen at the carbonyl group, however it also decreases the electrophilic character of the carbonyl carbon, resulting in a lower rate limiting nucleophilic attack by the alcohol. The second effect, i.e., the steric hindrance, increases when the alkyl chain in the carboxylic acid increases. This effect is originated by electronic repulsion between non-bonded atoms of reactants that decreases the electron density in the intermolecular region and disturbs bonding interactions^[42]. The steric component affecting carboxylic acid reactivity should certainly be examined for acid-catalyzed esterification^[41,43] specially when using solid acid catalysts.

In our case, we have observed that the decrease in conversion occurs regardless of using homogeneous (*p*TSA) or heterogeneous (Nafion SAC-13) catalysts (see Figure 6). Nevertheless the activity of the homogeneous catalyst was relatively higher than the heterogeneous ones for long chain carboxylic acids. These results are in good agreement with those reported by Liu et al.^[44] where it was observed the same trend when performing the esterification of methanol with carboxylic acids of different lengths in presence of homogeneous and solid acids. Thus, the higher activity observed for homogeneous catalyst with respect to heterogeneous ones, can be attributed to the fact that under homogeneous catalysis, large carboxylic acid molecules may assume equilibrium favored conformations that diminish contributions to steric hindrance^[45].

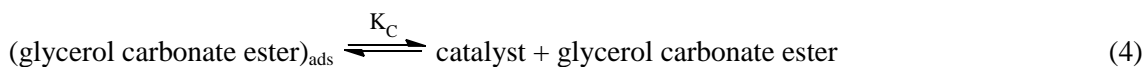
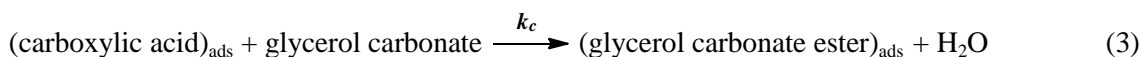
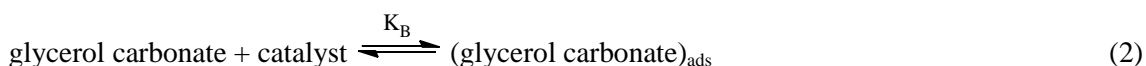
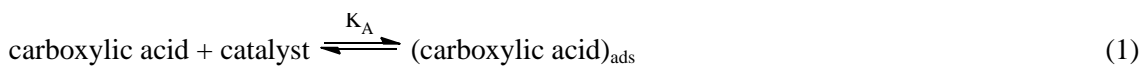
However, under heterogeneous catalysis the conformational effect has to be more important due to the limited conformational freedom of adsorbed alkyl chains on the SAC-13 catalyst. Moreover, as suggested by Liu et al.^[44] additional interactions of the adsorbed carboxylic acid on the acid site with polymeric Nafion nanodomains and/or adjacent silanol groups also may play a role on the reactivity of the carboxylic acid.

In order to further discuss these effects, we have carried out a full kinetic study on the glycerol carbonate esterification with different chain length carboxylic acids and the results have been compared on the bases of the kinetic rate constants, activation energies and heat of adsorptions.

Kinetic study of the reaction

The kinetic study was performed working at different carboxylic acids and glycerol carbonate concentrations, using toluene as a solvent (5 mL) and calculating initial reaction rates at a constant Nafion SAC-13 concentration (5.5 mg·mL⁻¹). The experiments were performed with three different carboxylic acids (hexanoic, nonanoic and lauric acid), at three different temperatures, 80, 100 and 111 °C (see Table S2).

Then, if one considers that the reaction follows an Eley–Rideal kinetic model with competitive carbonate adsorption, the mechanism for the esterification involves the following steps:



If we assume that the controlling step of the reaction corresponds to equation 3, and all the others are in equilibrium, then K_A , K_B , K_C and K_D are the equilibrium constants which are defined as:

$$K_A = \frac{[CA]_{ads}}{[CA] \cdot [C]} \quad (5)$$

$$K_B = \frac{[GC]_{ads}}{[GC] \cdot [C]} \quad (6)$$

$$K_D = \frac{[GCE] \cdot [C]}{[GCE]_{ads}} \quad (7)$$

and the rate of esterification is given by the following equation:

$$r_0 = \frac{d[CA]_0}{dt} = k_c \cdot [C] \cdot [CA]_{ads} \cdot [GC]_0 \quad (8)$$

where k_c is the kinetic constant and the script GC stands for glycerol carbonate; CA, for carboxylic acid; C, for catalyst; W, for water; and GCE, for glycerol carbonate ester.

Taking into account equations 5, 6, 7 and 8 and assuming that glycerol carbonate ester and water adsorbed on the catalyst is negligible under initial rate conditions, the kinetic rate equation becomes:

$$r_0 = \frac{k_c \cdot [C]_0 \cdot K_A \cdot [CA]_0 \cdot [GC]_0}{1 + K_A \cdot [CA]_0 + K_B \cdot [GC]_0} \quad (9)$$

which after linearization is converted into:

$$\frac{1}{r_0} = m \cdot \left(\frac{1}{[R]_0} \right) + n \quad (10)$$

where if $[R]_0$ is $[CA]_0$

$$m = \frac{1 + K_B \cdot [GC]_0}{k \cdot K_A \cdot [GC]_0} \quad (11)$$

$$n = \frac{1}{k \cdot [GC]_0} \quad (12)$$

whereas if $[R]_0$ is $[GC]_0$

$$m' = \frac{1 + K_A \cdot [CA]_0}{k \cdot K_A \cdot [CA]_0} \quad (13)$$

$$n' = \frac{K_B}{k \cdot K_A \cdot [CA]_0} \quad (14)$$

where k is the kinetic constant defined as

$$k = k_c \cdot [C]_0 \quad (15)$$

Thus, by plotting the inverse of the initial reaction rate versus the inverse of the initial concentration of carboxylic acid and glycerol carbonate, straight lines should be obtained, and from the slopes and intercepts at the origin of the fitted equations, the values of k_c , K_A and K_B can be deduced (Figure S7).

Moreover, activation energies E_{act} were calculated from the calculated kinetic rate constants at different temperatures according to the Arrhenius equation:

$$k_c = A \cdot e^{-E_{act}/RT} \quad (16)$$

$$\ln(k_c) = \ln(A) - \frac{E_{act}}{R} \cdot \left(\frac{1}{T}\right) \quad (17)$$

where A is the frequency factor, R is the molar gas constant and T is the reaction temperature.

Adsorption enthalpies ΔH and adsorption entropies ΔS of the corresponding carboxylic acids and glycerol carbonate on Nafion SAC-13 catalyst were calculated using the van't Hoff equation:

$$K_{ads} = A \cdot e^{-\Delta H/RT} \quad (18)$$

$$\ln(K_{ads}) = -\frac{\Delta H}{R} \cdot \left(\frac{1}{T}\right) + \frac{\Delta S}{R} \quad (19)$$

Figure S8 shows the variation of the logarithm of the kinetics k_c , and the adsorption constants K_{CA} and K_{GC} with the inverse of the temperature.

The kinetic parameters calculated are collected in Table 3. As expected, it can be observed that activation energies increase as carboxylic acid chain increases indicating that esterification reaction is less favored in kinetic terms due to the inductive effect of the alkyl chain which lowers the electrophilicity of the carbonyl group of the adsorbed carboxylic acid. On the other hand, and in good agreement with previously reported results^[44], adsorption constants of carboxylic acid decrease when lengthening the alkyl chain indicating that the catalyst surface coverage increases as the alkyl chain of the reacting carboxylic acid decreases. Additionally, in all cases constant adsorption values for carboxylic acids are between 2-3 times higher than for glycerol carbonate indicating the preferential adsorption of the carboxylic acid on the Bronsted acid sites. It can also be observed that adsorption constants of glycerol carbonate slightly increase when increasing the chain length of the acid indicating that adsorbed long chain carboxylic acids practically have not impact on the adsorption of the alcohol. These results are very different from those reported for the esterification of carboxylic acids with methanol^[44], where it was observed that adsorption constant of the alcohol decreases as the alkyl chain of the reacting carboxylic acid increases, which was attributed to the capacity of the long chain carboxylic acids to modify the catalyst surface, i.e. the adsorbed carboxylic acid increases surface hydrophobicity affecting therefore to methanol adsorption. This effect is not observed in our case, probably because the glyceryl carbonate is less polar than methanol. On the other hand, as the adsorption is an exothermic process, it can be observed that an increase of temperature causes a decrease of the adsorption constants for both reactants.

When the adsorption enthalpies of the carboxylic acids are examined we found a decrease for adsorption heat values when increase the carboxylic acid chain length. One can expect that adsorption of the carboxylic acid can take place by the interaction of the

carbonyl group with Bronsted acid sites as well as through Van der Waals interactions of the alkyl chain with the catalyst surface. Then, one should expect that the heat of adsorption of the acids will increase linearly with the number of carbons of the alkyl chain^[46], provided that all the methyl groups of the acids interact with the surface, i.e. they laydown linearly on the solid. However, the trend showed by the adsorption enthalpies suggests that long chain carboxylic acids do not adsorb in a linear way being they probably folded. This folding effect should be responsible of the steric hindrance attributed to long chain carboxylic acids that also contributes to decrease its reactivity in the esterification reaction.

The above results allow us to conclude that the lower intrinsic reactivity found when increasing carboxylic acid length is caused by both electronic (inductive) and steric effects, the later one being caused mainly by the folding of the alkyl chain of the adsorbed carboxylic acid.

Stability and reusability of Nafion SAC-13 catalyst

The reusability of solid catalysts is one of their main advantages over liquid homogeneous catalysts. To evaluate this characteristic for the Nafion SAC-13 catalyst, the esterification reaction of hexanoic acid with glycerol carbonate under azeotropic distillation of water was investigated by running consecutive reaction cycles using the same reaction conditions as described earlier. After each cycle, the catalyst was recovered by vacuum filtration, washed with ethanol through a Soxhlet extractor and dried. Then, a new reaction cycle was started with fresh reactants. The results of catalyst recycling are shown in Figure 7. As it can be seen, a continuous activity loss with each reaction cycle was observed.

The possibility that the water produced from esterification could be chemically and physically adsorbed on the surface, decreasing the catalytic activity from one reaction cycle to another, was disregarded since azeotropic distillation is performed during the reaction and, furthermore, the catalyst is dried before each reaction cycle.

Decomposition of sulfonic groups may also be a possible cause of the catalyst deactivation during multiple reaction cycles, as it is known to occur for $\text{SO}_4^{2-}/\text{ZrO}_2$ ^[47]. However, this cannot be the origin of catalyst deactivation in our case, since elemental analysis showed that the spent Nafion SAC-13 after four cycles maintained 92% of the original sulfur content.

It has been reported^[44] that the deactivation of the Nafion SAC-13 during the esterification of carboxylic acids with methanol occurred and was caused by entrapment of bulky reactants, intermediates, and products on the Nafion nanodomains. These compounds, which have to be resistant to the ethanol Soxhlet extraction performed in our case, seem to be the most probable cause of the activity loss. To check this hypothesis, the BET surface area of Nafion SAC-13 was measured before and after reaction and a decrease from 216 to 188 $\text{m}^2\cdot\text{g}^{-1}$ was observed indicating that some blocking of the pores may occur. FTIR spectroscopy was used to characterize the catalyst before and after reaction cycles and to find the type of compounds that remain adsorbed. Figure 8 shows IR spectra in the range 1300-3200 cm^{-1} for both fresh and spent catalyst samples. The peaks centered at 2900 and 1700 cm^{-1} adsorbed on the used catalysts can be assigned to the stretching frequencies of $-\text{CH}_2/-\text{CH}_3$ and $\text{C}=\text{O}$ groups, respectively. The presence of those bands together with the small band at 1460 cm^{-1} , which can be ascribed to the bending and/or stretching vibration of $\text{C}-\text{H}$, provide evidence of the strong adsorption of carboxylic acids on the catalyst surface. Moreover, the TG analysis of the used Nafion SAC-13 indicates that 9 wt% of organic material

remains on the catalyst after two reaction cycles. Therefore, we can conclude that catalyst deactivation is mainly due to the strong adsorption of organic compounds.

This strong adsorption of larger organic compounds may occur through a combination of two pathways, adsorption on acid Brønsted sites (see adsorption enthalpy constants in Table 3) or by interaction of long alkyl chains with the Nafion nanodomain polymeric chains. Both pathways will contribute to the acid site blockage by the large carboxylic acids, hindering access to active sites and inhibiting catalyst activity. If this is so, a stronger catalyst deactivation should occur when increasing the chain length of the organic acid. Indeed results from Figure 9 show that after three reaction cycles, catalyst deactivation is higher for lauric acid esterification, followed by nonanoic and hexanoic acids. The experimental calorimetric adsorption measurements on Nafion SAC-13 of the different carboxylic acids, as well as their correspondent glycerol carbonate esters, presented in Table 4 show that the deactivation of the catalyst should be mainly caused by the adsorption of the carboxylic acids since they have higher heats of adsorption than the ester compounds.

Catalyst regeneration could be achieved by burning off the adsorbed organic products. However, in this case classical regeneration by catalyst calcination cannot be carried out since the Nafion would also be destroyed or damaged. As an alternative to calcination we have attempted the oxidation of the adsorbed organic compounds by a low temperature Fenton oxidation^[37] (see experimental). This regeneration procedure works much better than extraction by Soxhlet (see Figure 10), and the activity of the regenerated catalyst clearly improves.

A possible regeneration method may involve the introduction of small amounts of Pt on the catalyst and to hydrocrack the adsorbed long chains of acid, and/or esters adsorbed, making easier desorption of the lower molecular weight products. This

possible catalyst regeneration route for the Nafion-silica hybrid catalyst is under study in our laboratory.

Conclusions

Nafion SAC-13 has proven to be an excellent catalyst for the esterification of glycerol carbonate with carboxylic acids, while other acidic ion exchange resins and micro and mesoporous aluminosilicates showed lower activity and selectivity. The highest activity is exhibited by the Nafion/silica composite Nafion SAC-13, despite its lower concentration of active sites, which can be attributed primarily to the greater strength of their acid sites and their better accessibility of the reactants to the active sites when compared with sulfonic resins, zeolites and perfluorinated resin. The optimization of the reaction conditions, including water removal, allows achieving 95% selectivity of GCE-6 at 98% conversion with Nafion SAC-13.

The esterification reaction of glycerol carbonate with acids of different carbon chain lengths showed that the reactivity decreases when increasing chain length. From a full kinetic study it was possible to conclude that this behavior can be attributed to both inductive as well as steric effects caused by the folding of the alkyl chain of the adsorbed carboxylic acid.

The activity loss after recycling is due to accumulation of carboxylic acid molecules/intermediates on the nanodomains of the Nafion resin. Such accumulation could be caused by the involvement of the carboxylic acids with the polymeric chains of the Nafion nanoparticles or by the adsorption of the reactants on the acid sites of the catalyst. Most of the activity of the fresh Nafion SAC-13 catalyst can be regenerated while maintaining high selectivity, by low temperature Fenton's treatment. Therefore, when comparing the heterogeneous esterification process described here with those

found in the literature using homogeneous coupling agents like dicyclohexylcarbodiimide and 4-dimethylaminopyridine^[18] or acid catalysts like *p*-toluenesulfonic acid^[19], it can be concluded that the Nafion SAC-13 heterogeneous catalyst can be an interesting green alternative for the synthesis of glycerol carbonate esters.

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Legends for Figures and Schemes

- Figure 1. Yields to monoglycerides (■), diglycerides (▲) and triglyceride (●) versus time in the esterification reaction of GC with HA. Reaction conditions: HA (10 mmol), GC (15 mmol), Nafion NR-50 (100 mg) at 100 °C.
- Figure 2. Conversion of HA using Nafion SAC-13 (■) and *p*-toluenesulfonic acid (▲) versus reaction time. Reaction conditions: HA (10 mmol), GC (15 mmol), 100 mg of Nafion SAC-13 (same H⁺ equivalents for *p*-toluenesulfonic acid) and 100 °C.
- Figure 3. Yield to GCE-6 using Nafion SAC-13 (■) and *p*-toluenesulfonic acid (▲). Reaction conditions: HA (10 mmol), GC (15 mmol), 100 mg of Nafion SAC-13 (same H⁺ equivalents for *p*-toluenesulfonic acid) and 100 °C.
- Figure 4. Conversion of HA versus time when the reaction was carried out by Nafion SAC-13 (◆) or *p*TSA (*). Reaction conditions: HA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions of azeotropic distillation of water.
- Figure 5. Yield to GCE versus time when the reaction was carried out by Nafion SAC-13 and different carboxylic acids: hexanoic (◆), heptanoic (■), octanoic (▲), nonanoic (●), lauric (×) and palmitic (*). Reaction conditions: CA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions of azeotropic distillation of water.
- Figure 6. Conversion of palmitic acid versus time when the reaction was carried out by Nafion SAC-13 (◆) and *p*TSA (*). Reaction conditions: Palmitic acid (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions of azeotropic distillation of water.
- Figure 7. Conversion of HA versus time when the reaction was carried out with fresh Nafion SAC-13 (■), Nafion SAC-13 reused (□), Nafion SAC-13 reused twice (Δ) and Nafion SAC-13 reused three times (○). Reaction conditions: HA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions of azeotropic distillation of water.
- Figure 8. IR spectra of Nafion SAC-13 samples: a) fresh catalyst sample and b) used catalyst recovered from HA esterification after two consecutive

reaction cycles. Spent catalyst sample was washed through ethanol Soxhlet extraction and then dried after each cycle.

Figure 9. Conversion of different carboxylic acids when the reaction was carried out with successive reuses using hexanoic acid (■), nonanoic acid (■) and lauric acid (□). Reaction conditions: CA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions of azeotropic distillation of water.

Figure 10. Conversion of HA when the reaction was carried out with successive reuses of Nafion SAC-13 cleaned by Soxhlet extraction (■) or Fenton's treatment (■). Reaction conditions: HA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions of azeotropic distillation of water.

Scheme 1. Proposed esterification pathway between glycerol carbonate and carboxylic acid.

TABLES

Table 1: Characteristics of different catalysts and catalytic results obtained for the esterification process between GC and HA.^[a]

Entry	Catalyst	S _{BET} (m ² ·g ⁻¹)	Si/Al Ratio	Topology	Acidity (meqH ⁺ ·g ⁻¹)	r ₀ (mmol·min ⁻¹)	TOF (min ⁻¹)	Conversion (%) ^[b]	Selectivity (%)	Yield (%) ^[b]
1	Blank	-	-	-	-	0.001	-	5	80 ^[b]	4
2	Nafion NR-50	0.02	-	-	1.08	0.102	0.944	65	73 ^[b]	47
3	Nafion SAC-13	218	-	-	0.13	0.067	5.608	67	85 ^[c]	57
4	DowexMarat.	-	-	-	3.10	0.073	0.235	79	64 ^[c]	42
5	Amberlist-15	0.35	-	-	5.43	0.088	0.162	76	66 ^[c]	47
6	Dowex-50	-	-	-	4.80	0.089	0.185	81	69 ^[c]	53
7	Mordenite	507	10	1D-12MR	1.51	0.027	0.179	23	58 ^[b]	13
8	MCM-22	465	15	2D-10MR	1.04	0.021	0.199	14	58 ^[b]	8
9	ZSM-5	368	10	2D-10MR	1.51	0.024	0.159	17	50 ^[b]	9
10	Beta	450	13	3D-12MR	1.19	0.026	0.218	25	57 ^[b]	14
11	ITQ-2	841	15	delaminated	1.04	0.031	0.295	31	61 ^[b]	19
12	<i>p</i> TSA ^[d]	-	-	-	5.81	0.137	10.438	72	81 ^[c]	58

[a] Reaction conditions: HA (10 mmol), GC (15 mmol) and catalyst (100 mg) at 100 °C. [b] After 8 h. [c] Selectivity to GCE-6 ester at 65% of conversion. [d] Same H⁺ equivalents that in 100 mg of Nafion SAC-13 were used.

Table 2. Influence of the amount of Nafion SAC-13 over the yield, selectivity and initial rate of esterification reaction.^[a]

Catalyst (wt%)	Time (h)	Conversion (%)	Selectivity (%)	Yield (%)
15	6	96	84	81
8	8	85	84	71
3.5	8	67	85	57

[a] Reaction conditions: HA (10 mmol), GC (15 mmol), 100 °C.

Table 3. Experimental values of the rate constant k_c , the adsorption constants K_{CA} and K_{GC} , the activation energy E_{act} , the adsorption enthalpies ΔH_{CA} and ΔH_{GC} , and the adsorption entropies ΔS_{CA} and ΔS_{GC} , at the three temperatures used in the kinetic study.

Carboxylic acid	T (°C)	$k_c^{[a]}$ (L·h ⁻¹ ·g ⁻¹)·10 ²	$K_{CA}^{[a]}$ (L·mol ⁻¹)	$K_{GC}^{[a]}$ (L·mol ⁻¹)	$E_{act}^{[a]}$ (KJ·mol ⁻¹)	$\Delta H_{CA}^{[a]}$ (KJ·mol ⁻¹)	$\Delta H_{GC}^{[a]}$ (KJ·mol ⁻¹)	$\Delta S_{CA}^{[a]}$ (J·mol ⁻¹ ·K ⁻¹)	$\Delta S_{GC}^{[a]}$ (J·mol ⁻¹ ·K ⁻¹)
Hexanoic acid	80	0.770	0.130	0.042					
	100	1.344	0.103	0.037	30.9	-13.8	-7.3	-55.9	-47.1
	111	1.805	0.089	0.034					
Nonanoic acid	80	0.091	0.122	0.047					
	100	0.198	0.098	0.042	41.1	-12.0	-8.4	-51.4	-49.1
	111	0.279	0.088	0.037					
Lauric acid	80	0.018	0.106	0.050					
	100	0.043	0.093	0.043	47.8	-9.8	-8.9	-46.3	-50.2
	111	0.068	0.080	0.039					

[a] Experimental error $\pm 5\%$.

Table 4. Experimental adsorption heat energies of different carboxylic acids and their correspondent glycerol carbonate esters.

Carboxylic acid	ΔH_{exp} ($\text{J}\cdot\text{g}^{-1}$)	Glycerol carbonate ester	ΔH_{exp} ($\text{J}\cdot\text{g}^{-1}$)
Hexanoic acid	-55.75	GCE-6	-30.12
Heptanoic acid	-48.96	GCE-7	-31.38
Octanoic acid	-44.89	GCE-8	-27.94
Nonanoic acid	-41.76	GCE-9	-26.89

FIGURES

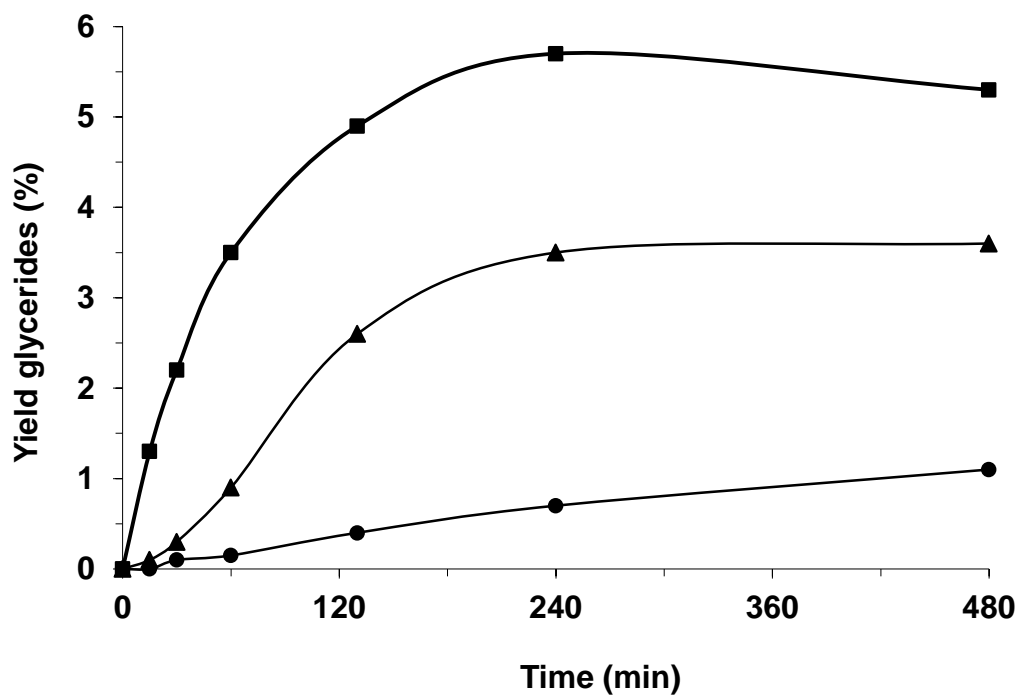


Figure 1. Yields to monoglycerides (■), diglycerides (▲) and triglyceride (●) versus time in the esterification reaction of GC with HA. Reaction conditions: HA (10 mmol), GC (15 mmol), Nafion NR-50 (100 mg) at 100 °C.

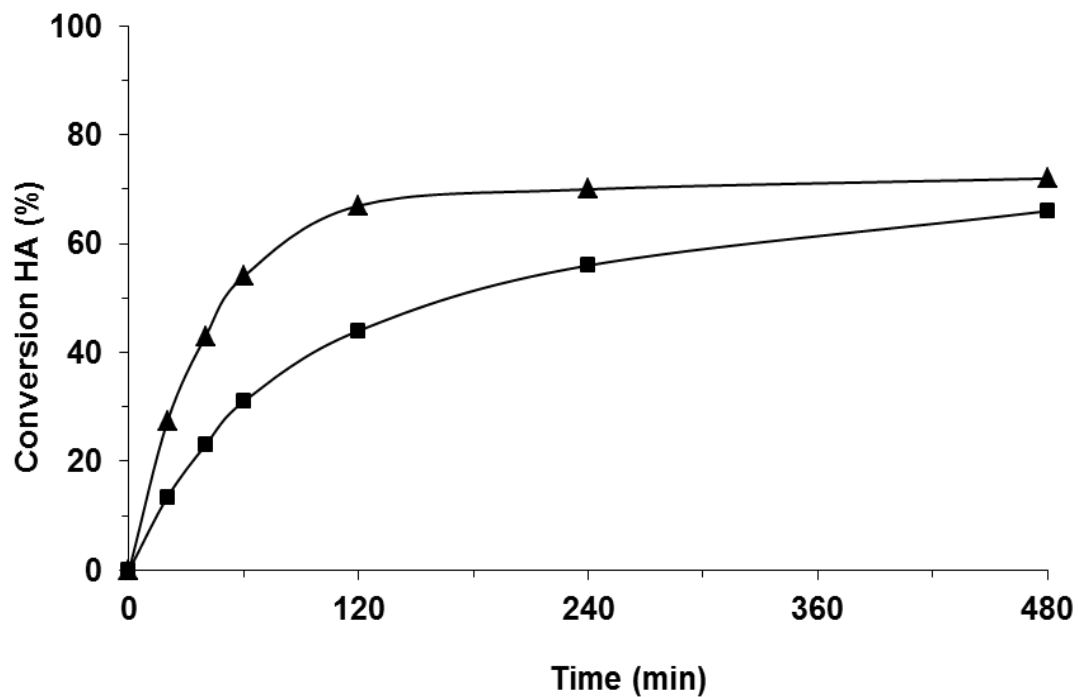


Figure 2. Conversion of HA using Nafion SAC-13 (■) and p-toluenesulfonic acid (▲) versus reaction time. Reaction conditions: HA (10 mmol), GC (15 mmol), 100 mg of Nafion SAC-13 (same H⁺ equivalents for p-toluenesulfonic acid) at 100 °C.

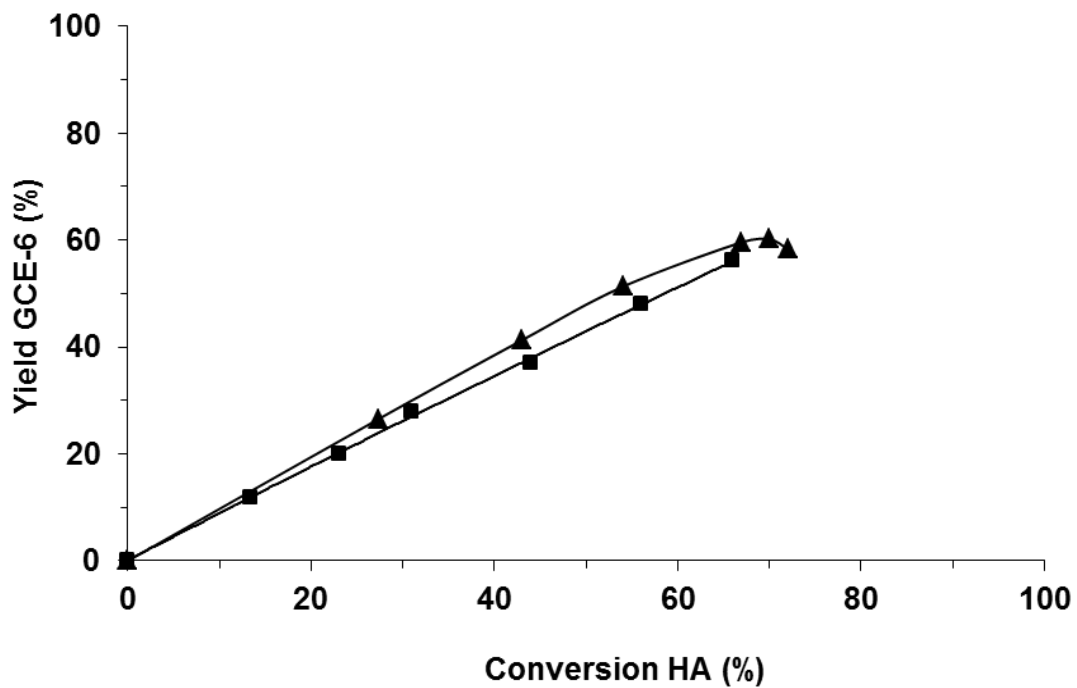


Figure 3. Yield to GCE-6 using Nafion SAC-13 (■) and *p*-toluenesulfonic acid (▲). Reaction conditions: HA (10 mmol), GC (15 mmol), 100 mg of Nafion SAC-13 (same H⁺ equivalents for *p*-toluenesulfonic acid) at 100 °C

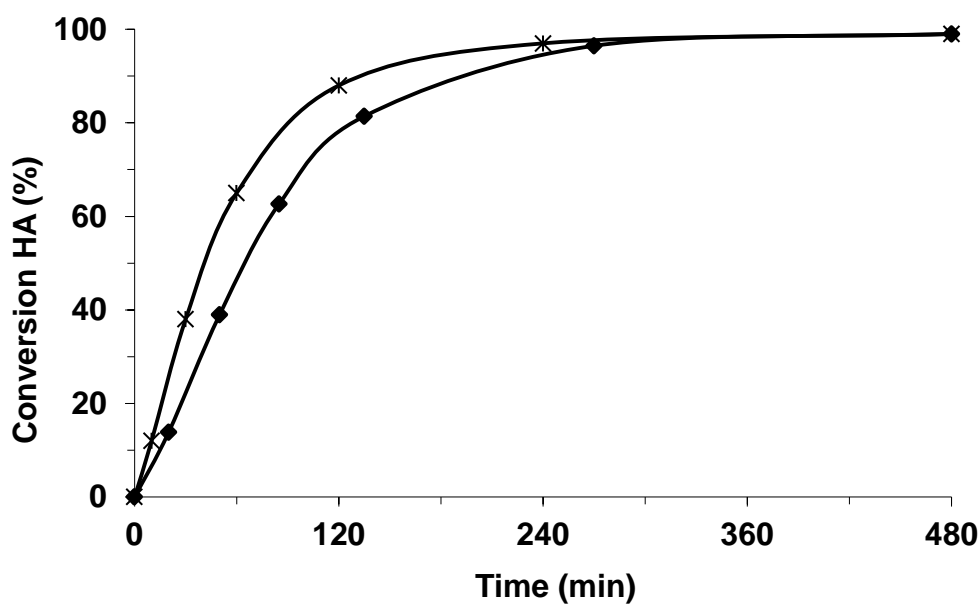


Figure 4. Conversion of HA versus time when the reaction was carried out by Nafion SAC-13 (♦) or *p*TSA (*). Reaction conditions: HA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions of azeotropic distillation of water.

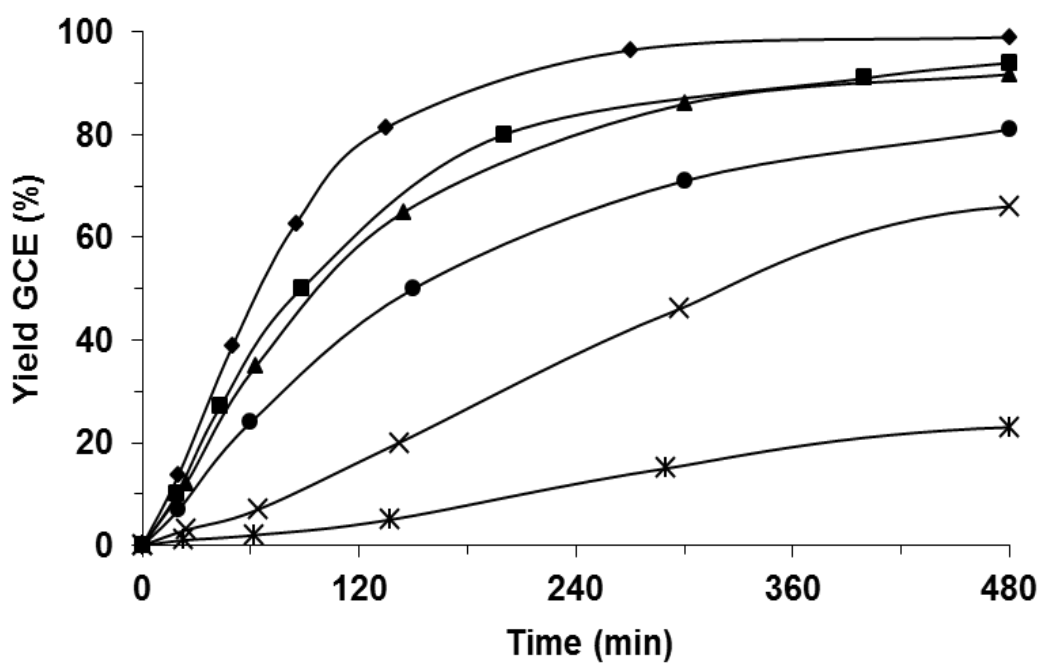


Figure 5. Yield to GCE versus time when the reaction was carried out by Nafion SAC-13 and different carboxylic acids: hexanoic (♦), heptanoic (■), octanoic (▲), nonanoic (●), lauric (×) and palmitic (*). Reaction conditions: CA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions of azeotropic distillation of water.

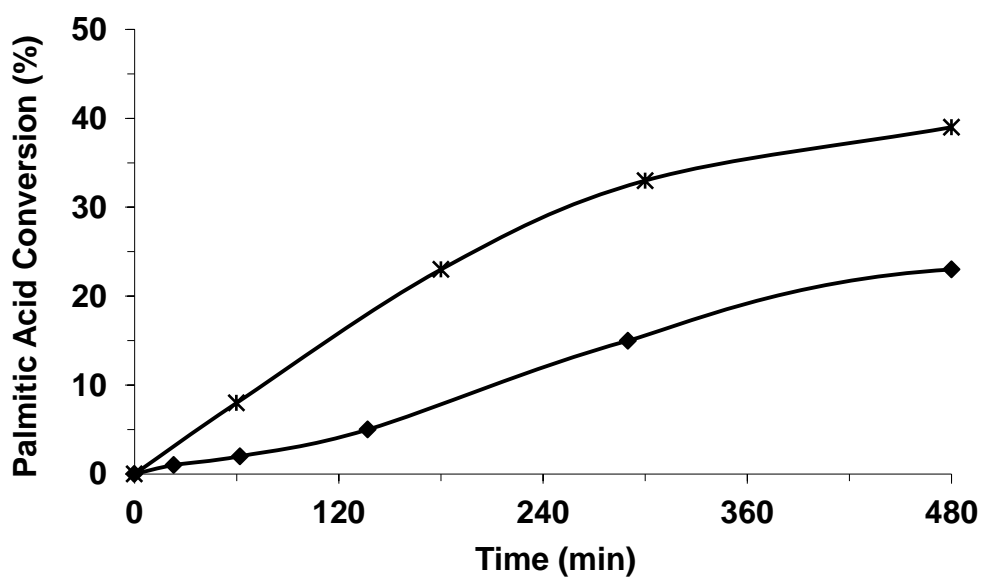


Figure 6. Conversion of palmitic acid versus time when the reaction was carried out by Nafion SAC-13 (◆) and p-toluenesulfonic acid (*). Reaction conditions: Palmitic acid (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions of azeotropic distillation of water.

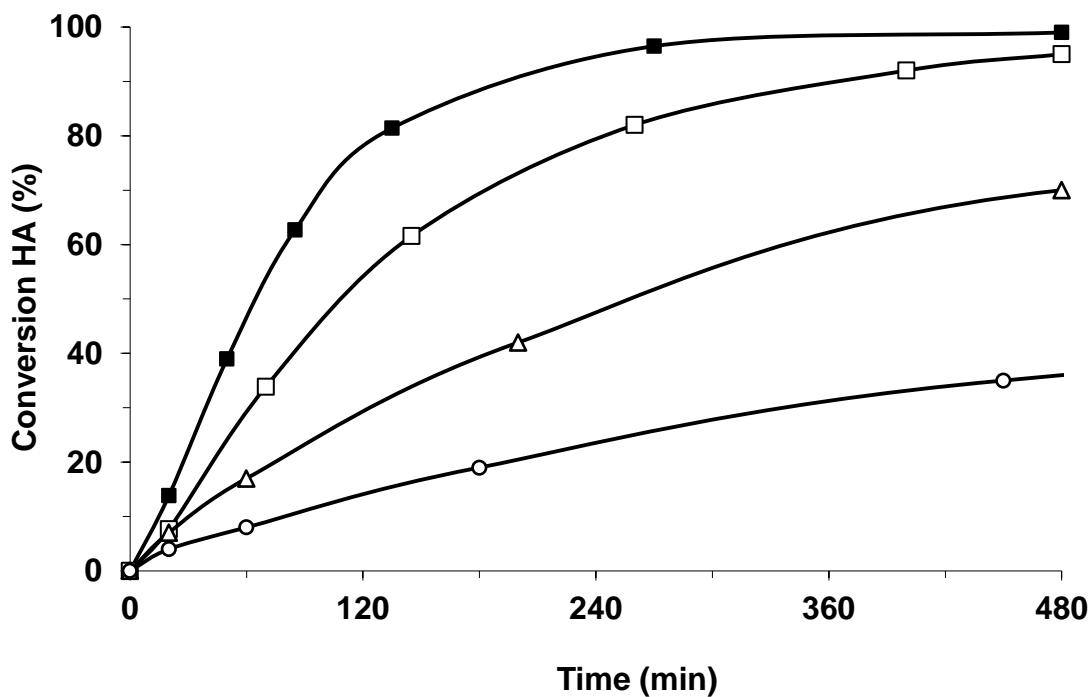


Figure 7. Conversion of hexanoic acid versus time when the reaction was carried out with fresh Nafion SAC-13 (■), Nafion SAC-13 reused (□), Nafion SAC-13 reused twice (△) and Nafion SAC-13 reused three times (○). Reaction conditions: HA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions of azeotropic distillation of water.

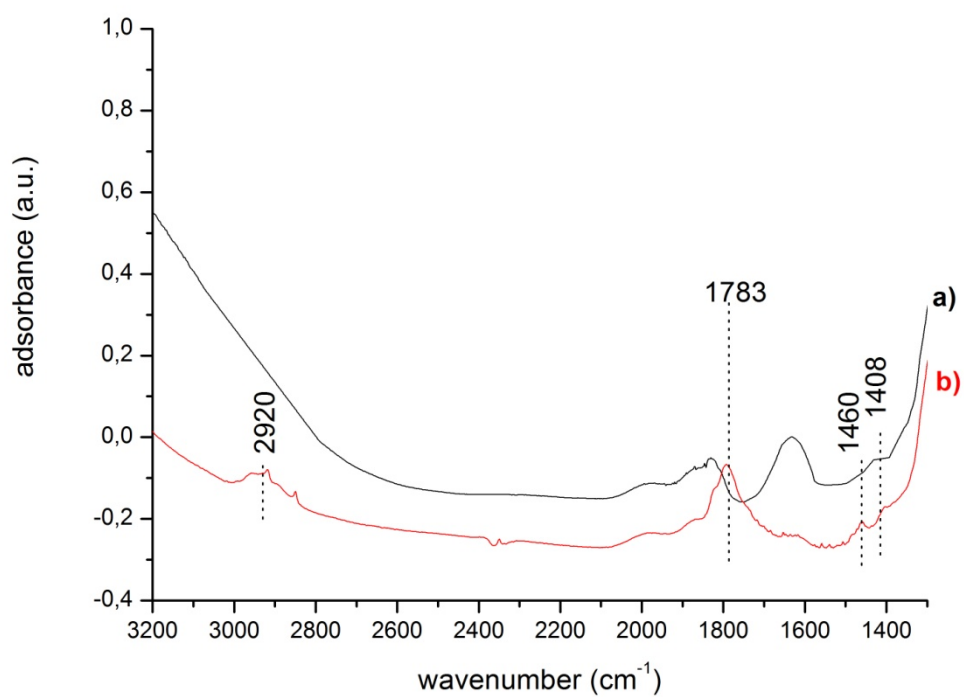


Figure 8. IR spectra of Nafion SAC-13 samples: a) fresh catalyst sample and b) used catalyst recovered from hexanoic acid esterification after two consecutive reaction cycles. Spent catalyst sample was washed through ethanol Soxhlet extraction and then dried after each cycle.

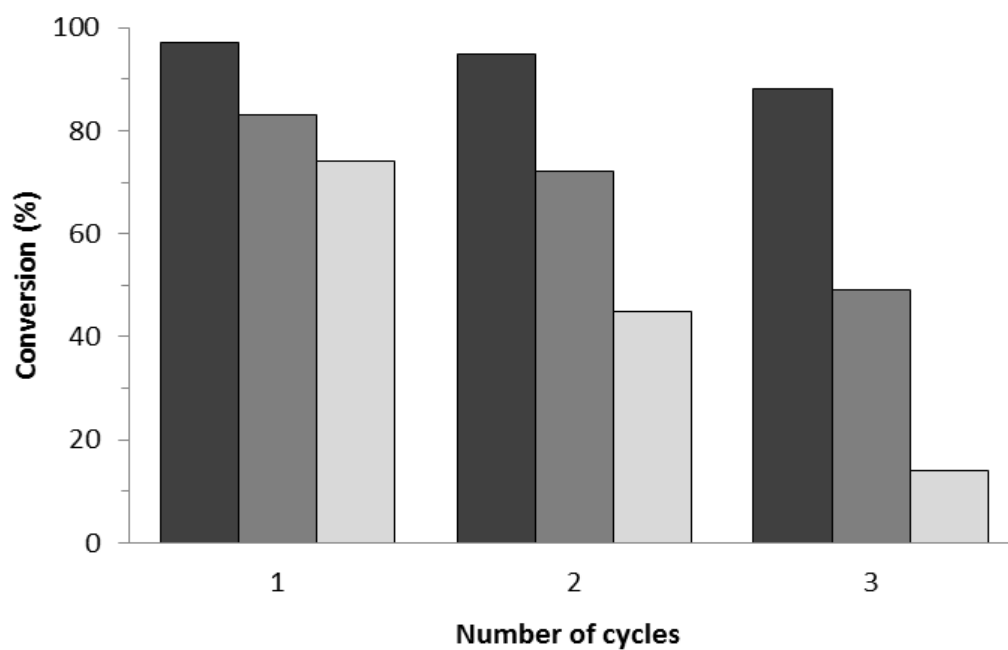


Figure 9. Conversion of different carboxylic acids when the reaction was carried out with successive reuses using hexanoic acid (■), nonanoic acid (▒) and lauric acid (□). Reaction conditions: CA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions of azeotropic distillation of water.

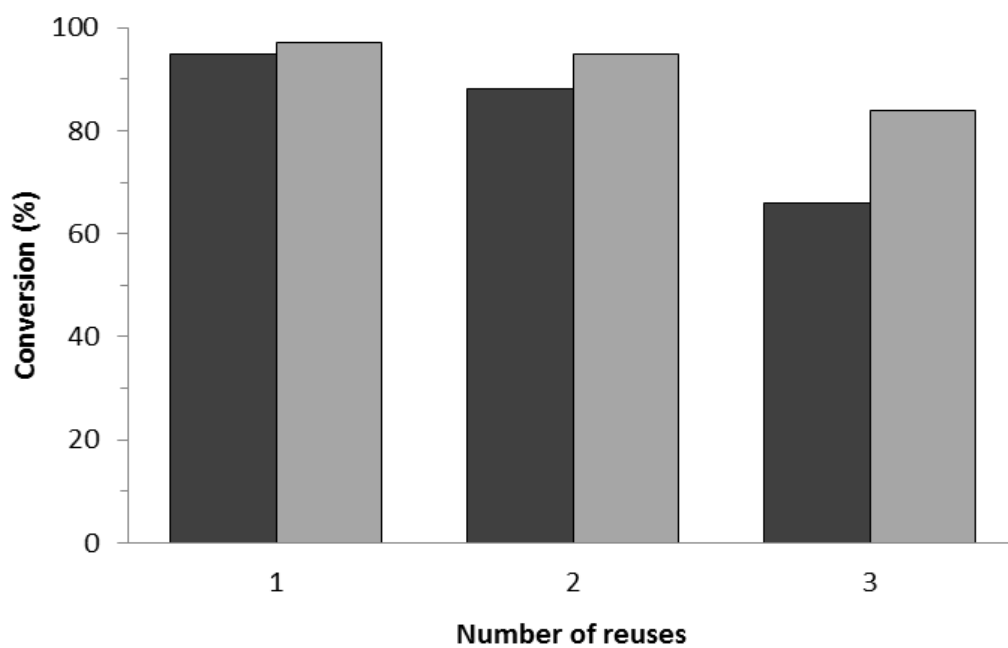
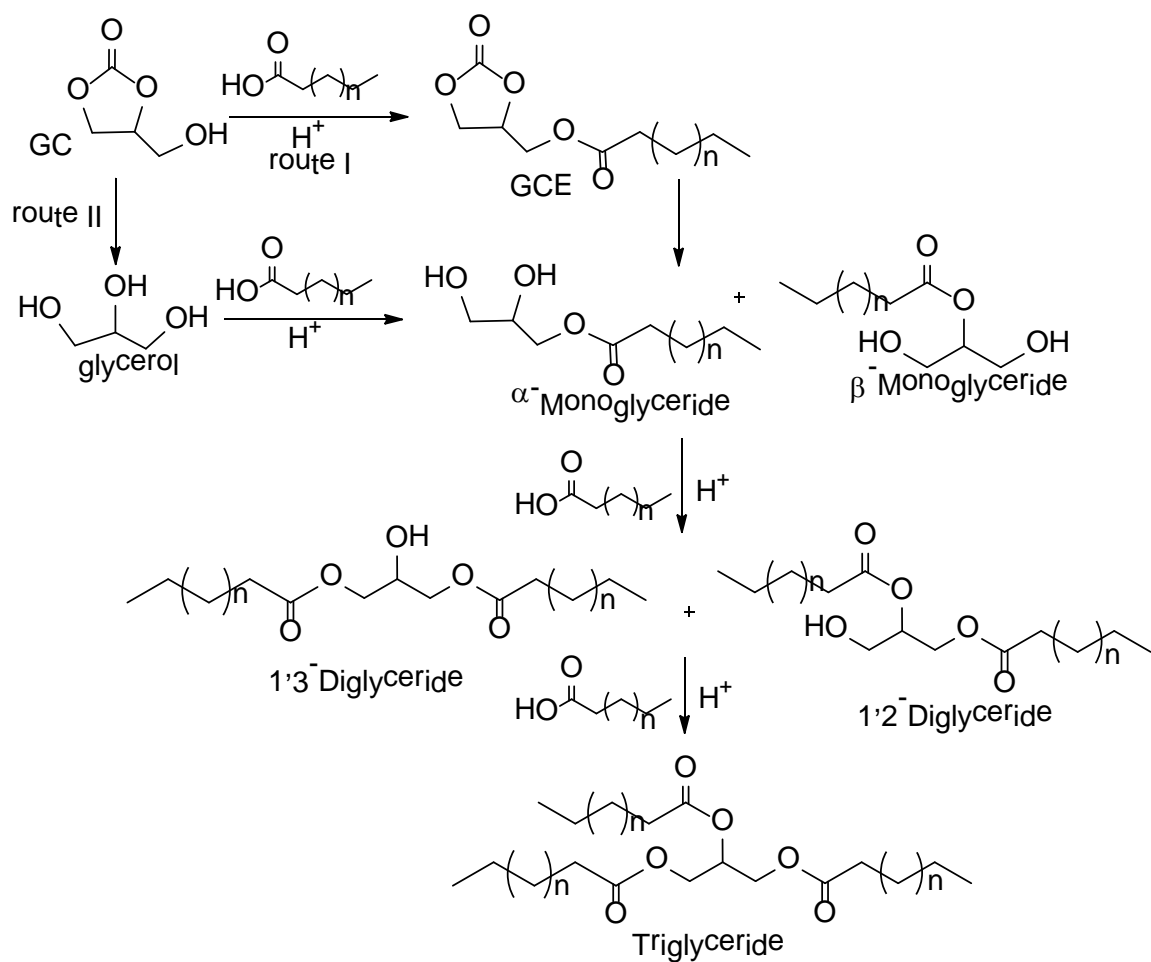


Figure 10. Conversion of hexanoic acid when the reaction was carried out with successive reuses of Nafion SAC-13 cleaned by Soxhlet extraction (■) or Fenton's treatment (■). Reaction conditions: HA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions of azeotropic distillation of water.

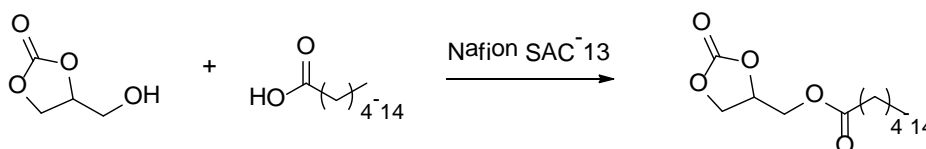
SCHEMES



Scheme 1. Proposed esterification pathway between glycerol carbonate and carboxylic acid.

Graphical Abstract

Nafion/silica composite Nafion SAC-13 is an excellent catalyst for the esterification of glycerol carbonate with carboxylic acids to produce glycerol carbonate esters which are valuable biomass derivative compounds.



Highlights

- Glycerol carbonate esters useful as surfactant molecules, have been prepared using heterogeneous acid catalyst.
- The optimization of the reaction conditions, including water removal, allows achieving 95% selectivity of (2-oxo-1,3-dioxolan-4-yl)methyl hexanoate at 98% conversion using Nafion SAC-13 as acid catalyst.
- The kinetic study of the esterification of glycerol carbonate with different carboxylic acids showed that the reactivity decreases when increasing the chain length of the acid. This behaviour can be attributed to both inductive as well as steric effects caused by the folding of the alkyl chain of the adsorbed carboxylic acid.
- Most of the activity of the fresh Nafion SAC-13 catalyst can be regenerated while maintaining high selectivity.

Keywords: glycerol carbonate ester, glycerol carbonate, Nafion SAC-13, heterogeneous catalysts, biomass.