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Preparation of Glycerol Carbonate Esters by using Hybrid Nafion–Silica Catalyst

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

Introduction

The production of fine chemicals, polymer precursors, and commodity chemicals from biomass can contribute to a decrease in our current dependence on nonrenewable energy sources. Chemical routes for catalytic biomass transformations have recently been reviewed and it has been presented that one of the foremost natural sources of the potentially relevant chemicals is glycerol.[1] Moreover, through the transesterification reaction of vegetable oils with methanol or ethanol, the biodiesel industry has contributed enormously to increase the production of glycerol.[2] 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 GC by transesterification of ethylene carbonate with glycerol catalyzed by basic oxides (MgO and CaO), as well as by carbonylation of glycerol with urea in the presence of a Zn–Al mixed-oxide catalyst.[4]

GC is a promising chemical intermediate that can be used as a solvent,[5] or it can react with alcohols, phenols, and carboxylic acids;[6] it is considered an excellent intermediate in the synthesis of glycidol and epichlorohydrin, which both have large industrial applications.[7] On the other hand, glycerol carbonate esters (GCEs) are compounds with a polyoxygenate moiety, owing to the presence of both endocyclic and exocyclic ester groups. GCEs possess interesting physicochemical properties such as 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. GCEs have been prepared by reacting GC with an electrophile, for instance an acyl halide in the presence of triethylamine,[10] acid anhydrides using *p*-toluenesulfonic acid (*p*TSA) as a catalyst,[11] or isocyanates.[12] The transesterification reaction may also be used for GCE synthesis in the presence of MeONa and hydroquinone,[13] or by using zirconium acetylacetonate as a catalyst.[14] In the work of Ramaiah, 4-[(benzoyloxy)methyl]-1,3-dioxolan-2-one was synthesized with a 68% yield from GC, potassium benzoate, triphenylphosphine, and carbon tetrachloride at 55–60 °C for 5.5 h.[15] Another synthetic route has been described that reacts natural oils with a carbonate source, such as dimethylcarbonate, and a strong base ($NaOCH_3$) 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, GCE synthesis has been performed by using direct esterification of the corresponding GC with carboxylic acids in the presence of homogeneous acid catalysts. In this sense, Jana et al.

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performed the synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl methacrylate with 67 % yield by using a coupling agent, such as *N*,*N*′-dicyclohexylcarbodiimide (DCC), and 4-dimethylaminopyridine.[18] In the patent literature, acetic acid, GC, 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.[19] Interestingly, and as far as we know, there are no previous reports for the preparation of GCEs through a heterogeneous catalytic process with solid acid catalysts. This is surprising because the development of green and sustainable chemistry focuses on the use of solid catalysts, which avoid additional neutralization steps and eliminate corrosion problems in the unit.

The direct esterification of GC with carboxylic acids by using solid acid catalysts is of interest. In general, the most popular solid acids used to produce esters are ion-exchange organic resins such as Amberlyst-15,[20] zeolites,[21] and silica-supported heteropoly acids (HPA/silica).[22,23] However, these catalysts exhibit limitations for catalyzing esterification because of low thermal stability (Amberlyst-15, < 140 °C), mass-transfer limitations (zeolites),[24] or leaching of the active acid sites in the presence of a polar medium (HPA/silica).[25]

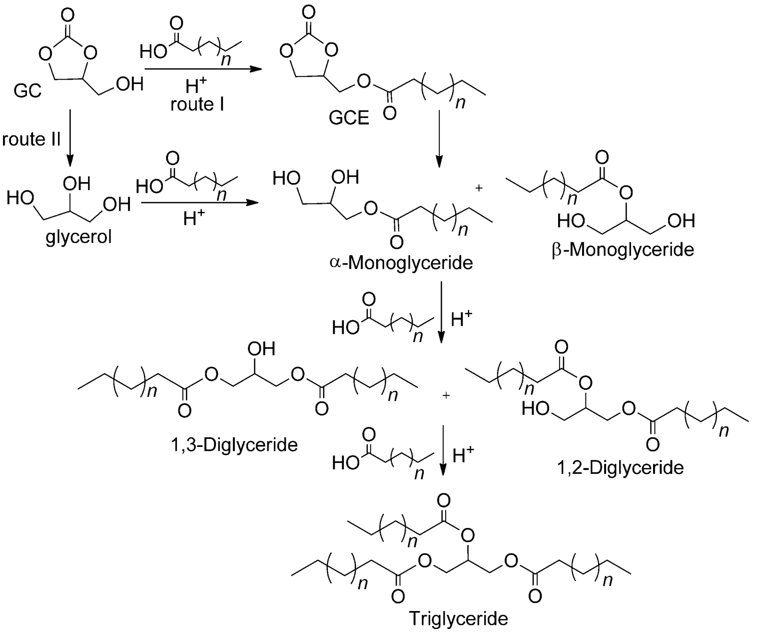
Perfluorinated sulfonic acid (Nafion) resins have been widely used in organic synthesis as acid catalysts.[26] They exhibit an acidic character comparable to that of 100 % sulfuric acid,[27] which, combined with a reasonable thermal stability, chemical resistance, and possible regeneration, renders Nafion a safe and valued solid acid catalyst. However, because of the very low surface area (0.02 $m^2 g^{-1}$) and the inaccessibility of most of the active sites, Nafion has a low specific activity. The preparation of Nafion–silica nanocomposites (Nafion SAC-13) through the 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 a large surface area (150–500 $m^2 g^{-1}$) and small Nafion particles (<100 nm) entrapped in a porous silica framework. Outstanding catalytic performance was observed by using this nanocomposite material 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 by using organic acids with increasing chain lengths, and have shown the important role played by the adsorption terms in the kinetic equation for catalyst performance. From those results, an optimal combination of the solid catalyst nature and the reaction conditions was identified, which allowed us to achieve conversions and selectivities above 95 % by using solid catalysts.

Results and Discussion

GC esterification with carboxylic acids to GCEs

The esterification of GC with hexanoic acid (HA) was taken as a reaction model and performed at 100 °C with a GC/HA molar ratio of 1.5 and using a catalyst (3.5 wt %); Nafion NR-50 was initially used as the catalyst to establish the reaction scheme. The main product of the reaction was the corresponding (2-oxo-1,3-dioxolan-4-yl)methyl hexanoate ester (GCE-6), but different byproducts were also observed (Scheme 1). The byproducts, identified by using GC–MS, were the glyceryl hexanoate (monoglyceride), glyceryl dihexanoate (diglyceride), and glyceryl trihexanoate (triglyceride). The formation of these byproducts could be explained by following two different reaction routes: a) from the hydrolysis of the carbonate group of GCE-6, resulting in two monoglycerides that could undergo further esterification with the carboxylic acid to yield two diglycerides and, subsequently, a triglyceride (see route I, Scheme 1); and b) by the hydrolysis of GC to form glycerol, followed by the fast acid-catalyzed esterification of glycerol with HA to yield monoglycerides, diglycerides, and triglyceride (see route II, Scheme 1). Because 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, it suggested that both routes described above could contribute to the formation of the byproducts.



Scheme 1. Proposed esterification pathways between GC and carboxylic acids.

Yields of the different byproducts, that is, mono-, di-, and triglycerides from the reaction that used Nafion NR-50 as the catalyst, are plotted in Figure 1 as a function of time. The monoglycerides appeared as the primary unstable products, whereas diglycerides appeared as secondary, and also unstable, prod-

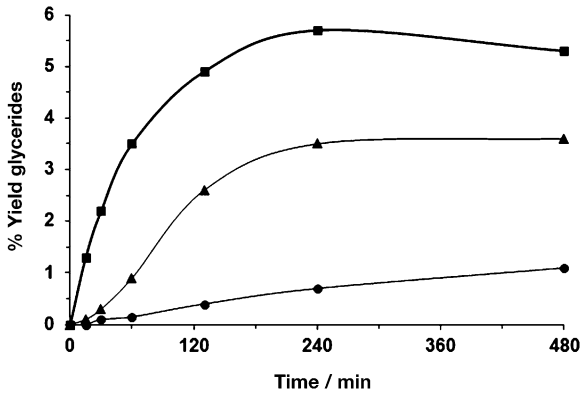


Figure 1. Yields of monoglycerides (■), diglycerides (▲), and triglyceride (●) versus time in the esterification reaction of GC with HA. Reaction conditions: HA (10 mmol), GC (15 mmol), Nafion NR-50 (100 mg) at 100 °C.

ucts because they were formed through the esterification of the first-formed monoglycerides; further reaction yielded the triglyceride by a consecutive esterification process. The detection of these compounds, clearly indicated that the reaction proceeded via both of the routes shown in Scheme 1.

Study of the catalyst

Acid catalysts appeared adequate for performing the esterification reaction of GC with HA. 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 could be useful to achieve higher selectivities towards the ester of the carbonate, that is, GCE-6. With this objective, we selected aluminosilicate zeolites with a relatively high Si/Al ratio (≈15) and systems with one-dimensional large pores (Mordenite) and three-dimensional large pores (Beta), as well as a delaminated zeolite with a high external surface area (ITQ-2), and a two-dimensional medium-pore-size zeolite (ZSM-5).

The reactions were performed at 100 °C with a GC/HA ratio of 1.5 in the presence of 3.5 wt % of the catalyst. Conversion and selectivity to GCE-6, together with the initial rates and turnover frequencies (*TOF*s, defined as mmol converted per mmol of nominal Brönsted acid sites, calculated from Al content, per minute), are detailed in Table 1. The results obtained with zeolites were disappointing because of their low conversion and because the selectivity was always lower than ≈60 %. Nevertheless, the pore dimensions and site accessibility played an important role in the esterification reaction of these materials. Indeed, zeolites with medium pores were less active than those with large pores, and certainly less active than the delaminated ITQ-2 zeolite. This was even more visible when normalizing the activity (initial rate) per acid site. Therefore, the acidity of the zeolites was not adequate to operate at the relatively low temperature used here (100 °C), and/or the polarity of the zeolite was too high; the zeolite became rapidly deactivated through reactant and product adsorption when catalyzing the hydrolysis of GC.

To evaluate the last hypothesis, we followed the conversion to GCE-6 and the yield as a function of reaction time. The results are detailed in Figure S1 (see the Supporting Information) and clearly show that, independent of the zeolite used, conversion rapidly decreased with reaction time, indicating that the catalyst had been deactivated. In the case of the Beta zeolite, we analyzed the total amount of products (and their type) remaining on the catalyst after the reaction by using thermogravimetric analysis (TGA) and IR spectroscopy; the results indicated that 9 wt % organic material remained on the catalyst surface after the catalyst had been 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 indicated the presence of adsorbed acid and, probably, adsorbed esters of glycerol (see Figure S2 in the Supporting Information).

Next, the hydrophobicity of the Beta zeolite was increased by increasing the Si/Al ratio, and the framework zeolite defects (internal Si–OH) were decreased. This was achieved by synthesizing the Beta samples in fluoride media.[33] The results de-

Table 1. Characteristics of different catalysts, and the 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 [$mEq.H^+ g^{-1}$]	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	*p*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 at 65 % conversion. [d] Same H^+ equiv. as in 100 mg of Nafion SAC-13.

tailed in Table S1 (see the Supporting Information) indicate that when the Si/Al ratio of the Beta zeolite was increased, its activity increased (see initial reaction rates) despite that the number of acid sites decreased (see also the total amount of nominal and Brönsted acid sites measured through pyridine adsorption and desorption at 250 °C). This was an indication that the blocking of the active sites, through strong adsorption of reactants and products, was decreasing as the Si/Al ratio was increasing, which was confirmed by using TGA and IR spectroscopy (see Table S1 and Figure S3 in the Supporting Information). Nevertheless, in the best case, the conversion and selectivity were still ≈30 % and 65 %, respectively, which was still too low.

Catalysts with stronger Brönsted acid sites, such as sulfonic and fluorosulfonic resins (including the Nafion SAC-13 hybrid), were investigated next. As can be observed in Table 1, the most active catalysts (initial rate) were the perfluorinated sulfonic resins Nafion NR-50 and Nafion SAC-13 (entries 2 and 3) and the sulfonic acidic resins (entries 4–6), whereas the aluminosilicate catalysts were clearly less active (entries 7–11). However, it should be noted that Nafion SAC-13 and Nafion NR-50, which resulted in initial reaction rates similar to the sulfonic acids resins, have a lower concentration of Brönsted acid sites, and consequently the *TOF*, that is, the activity per Brönsted acid site, was higher for the Nafion-based catalysts (see Table 1). This could be attributed to the higher acidity of the sulfonic acid groups in the perfluorinated resins with a Hammett acidity value (H_0) in the order of −12, whereas the resins with sulfonic acid groups have $H_0 \approx -3$.[29]

When the activity per acid site was considered, it could be observed that the Nafion SAC-13 nanocomposite was 12 times more active than Nafion NR-50, suggesting that the higher surface area of the former catalyst considerably improved the accessibility of the reactants to the acid sites of the catalyst. In addition, the selectivity towards GCE-6 was 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. For comparison, the reaction was performed by using *p*TSA with the same number of acid sites equivalents to those existing in Nafion SAC-13 (entry 12); the activity of the homogeneous catalyst was higher, but the selectivity towards the ester was similar (see Figure 2 and Figure 3), indicating that even in Nafion SAC-13, not all of the acid sites were accessible, or that the acidity could be diminished by the interaction between the Brönsted acid sites and the silanol groups.[30]

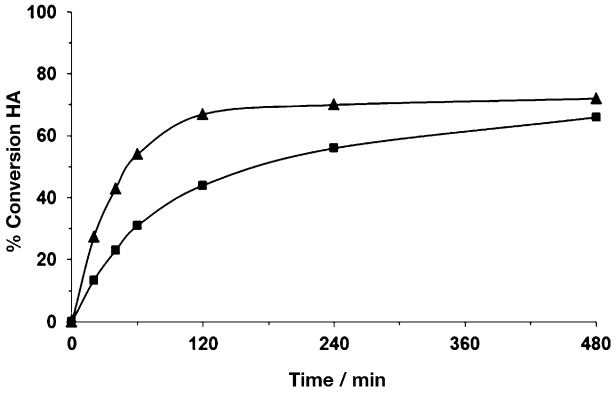


Figure 2. Conversion of HA in the presence of Nafion SAC-13 (■) and *p*TSA (▲) catalysts versus reaction time. Reaction conditions: HA (10 mmol), GC (15 mmol), 100 mg of Nafion SAC-13 (same H$^+$ equivalents for *p*TSA) and 100 °C.

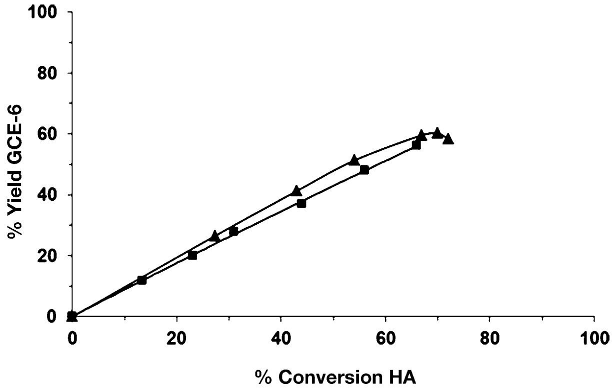


Figure 3. Yield of GCE-6 in the presence of Nafion SAC-13 (■) or *p*TSA (▲) catalysts. Reaction conditions: HA (10 mmol), GC (15 mmol), 100 mg of Nafion SAC-13 (same H$^+$ equivalents for *p*TSA) and 100 °C.

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

Concentration [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.

It was possible to obtain a conversion close to 70 % with selectivity towards GCE-6 of 85 % by using the Nafion SAC-13 catalyst; therefore, we attempted to improve these values by optimizing the process variables. The results in Figure S4 (see the Supporting Information) show the yield of GCE-6 versus HA conversion for the esterification performed with different catalyst loadings (3.5, 8, and 15 wt %). As expected, an increase in conversion was observed when the catalyst loading was increased, but selectivity towards GCE-6 remained constant (85 %) and was almost independent of the level of conversion (see Table 2 and Figure S4). The esterification was then performed at 80, 100, 120, and 140 °C and, as expected, the initial rate of the disappearance of HA increased with increasing temperature, whereas selectivity to GCE-6 decreased significantly at conversions higher than 70 % for reaction temperatures above 100 °C (Figure S5, see the Supporting Information). This indicated that at higher temperatures the opening of the cyclic carbonate was more favorable than its esterification. Therefore, to maximize selectivity, strong solid acid catalysts should be used that allow the reaction to be performed at lower temperatures.

Finally, the influence of the GC/HA molar ratio on the conversion and selectivity was studied by performing the reactions with GC/HA molar ratios of 8, 4, 1.5, 0.25, and 0.125. The results in Figure S6 (see the Supporting Information) indicate that an increase in the concentration of GC or HA induced an increase in the initial rate of reaction, whereas the selectivity to GCE-6 remained constant. The conversion, yield, and selectivity achieved 95 %, 81 %, and 85 %, respectively, regardless of whether or not the carbonate was in excess.

Influence of water

The results presented above have shown that working in the absence of a solvent and under optimized reaction conditions, a selectivity to GCE-6 of 85 % at 95 % conversion could be achieved. The selectivity loss was attributed to the presence of water in the reaction media, as it was impossible to remove all of the water formed during the esterification even by applying a nitrogen flow and a Dean–Stark. Under these conditions, the presence of water caused the hydrolysis of the carbonate, which lowered the selectivity towards GCE-6. To eliminate water from the reaction media, the reaction was performed under a vacuum (1.33×10^3 Pa), but no improvement in selectivity was achieved. Finally, with the aim of avoiding the presence of water and maximizing the yield and selectivity of GCE-6, the reaction was performed with the azeotropic distillation of water by using toluene. According to the results presented in Figure 4, the selectivity towards GCE-6 increased to 95 % at 98 % conversion of HA. Interestingly, when the reaction was performed by using a conventional homogeneous acid catalyst such as *p*TSA, a similar performance was achieved, which demonstrated that Nafion SAC-13 constituted a promising solid catalyst for this reaction.

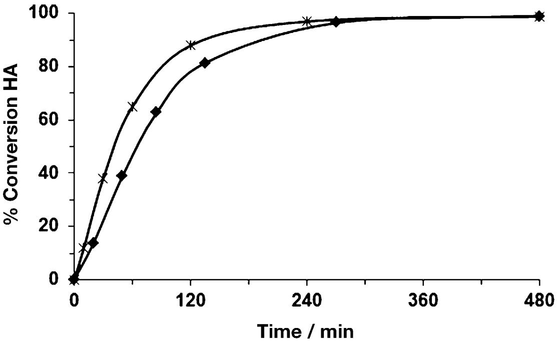


Figure 4. Conversion of HA versus time when the reaction was performed in the presence of Nafion SAC-13 (◆) or *p*TSA (*). Reaction conditions: HA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions for the azeotropic distillation of water.

Influence of the carboxylic acid chain length

To obtain products with different surfactant properties, the esterification of GC was performed under azeotropic distillation conditions with carboxylic acids of different chain lengths.[8] Therefore, it was possible to obtain molecules with different polar/apolar character and with different surfactant properties.

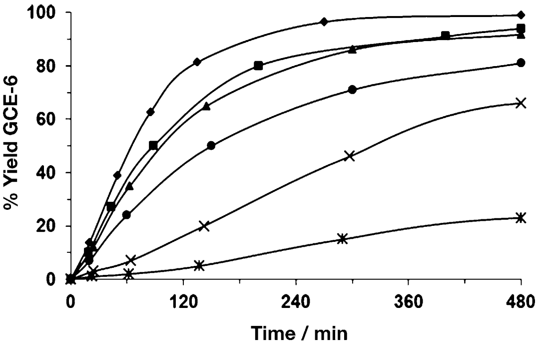


Figure 5. Yield of GCE versus time when the reaction was performed in the presence of Nafion SAC-13 and different carboxylic acids: hexanoic (◆), heptanoic (■), octanoic (▲), nonanoic (●), lauric (×), and palmitic (*) acid. Reaction conditions: Carboxylic acid (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions for the azeotropic distillation of water.

The yield of GCEs versus time is shown in Figure 5 for hexanoic, heptanoic, octanoic, nonanoic, lauric, and palmitic acids. Clearly, when increasing the chain length of the fatty acid from hexanoic to lauric and palmitic acid, the conversion decreased considerably from 98 % to 71 % and 31 %, respectively. The observed reactivity trend for carboxylic acids could be conceptualized on the basis of a well-established mechanistic model for the esterification reaction with homogeneous catalysts,[34] and two factors could contribute to the decrease in carboxylic acid reactivity when increasing the number of carbon atoms in the carboxylic acid chain, that is, an inductive and a steric effect.[35]

The inductive effect is a consequence of the increased electron-releasing capacity of the acid when the alkyl chain length is increased, and it facilitates the protonation of the oxygen of the carbonyl group; however it also decreases the electrophilic character of the carbonyl carbon, resulting in a rate-limiting nucleophilic attack by the alcohol. The steric hindrance effect increases as the alkyl chain length in the carboxylic acid increases, and originates from electronic repulsion between nonbonded atoms of reactants, which decreases the electron density in the intermolecular region and disturbs bonding interactions.[36] The steric component affecting carboxylic acid reactivity should be examined for acid-catalyzed esterification, especially when solid acid catalysts are being used.[35,37]

In our case, we observed that a 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 slightly higher than the heterogeneous catalysts for long-chain carboxylic acids. These results were in good agreement with a report by Liu et al.,[38] in which the same trend was observed when performing the esterification of methanol with carboxylic acids of different lengths in the presence of homogeneous and solid acid catalysts. Thus, the higher activity observed for the homogeneous catalyst with respect to the heterogeneous catalysts could be attributed to the ability of the large carboxylic acid molecules to assume equilibrium-favored conformations during homogeneous catalysis, which would diminish the contributions from steric hindrance.[39] However, under heteroge-

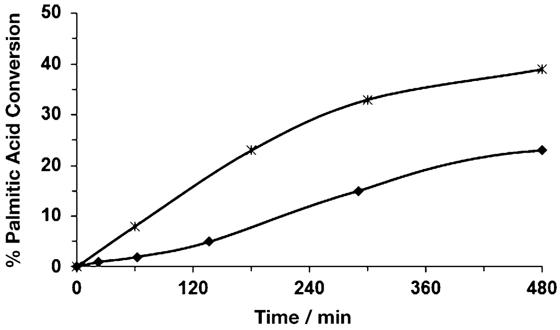


Figure 6. Conversion of palmitic acid versus time when the reaction was performed in the presence of Nafion SAC-13 (◆) or *p*TSA (*). Reaction conditions: Palmitic acid (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions for the azeotropic distillation of water.

neous catalysis the conformational effect must have been more important because of the limited conformational freedom of the adsorbed alkyl chains on the SAC-13 catalyst. Moreover, as suggested by Liu et al.,[38] additional interactions of the adsorbed carboxylic acid on the acidic site with polymeric Nafion nanodomains and/or adjacent silanol groups could also influence the reactivity of the carboxylic acid.

To further discuss these effects, we performed a full kinetic study on the GC esterification with different chain length carboxylic acids, and the results have been compared on the basis of the kinetic rate constants, activation energies, and heat of adsorptions.

Kinetic study of the reaction

The kinetic study was performed at different carboxylic acid and GC concentrations, with toluene as a solvent (5 mL), and by calculating the 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 in the Supporting Information).

It was considered that the reaction followed an Eley–Rideal kinetic model with competitive carbonate adsorption, and that the mechanism for esterification involved the following steps:

$$\text{carboxylic acid} + \text{catalyst} \overset{K_A}{\rightleftharpoons} (\text{carboxylic acid})_{ads} \quad (1)$$

$$\text{glycerol carbonate} + \text{catalyst} \overset{K_B}{\rightleftharpoons} (\text{glycerol carbonate})_{ads} \quad (2)$$

$$(\text{carboxylic acid})_{ads} + \text{glycerol carbonate} \overset{k_c}{\rightleftharpoons} (\text{glycerol carbonate ester})_{ads} + H_2O \quad (3)$$

$$(\text{glycerol carbonate ester})_{ads} \overset{K_D}{\rightleftharpoons} \text{catalyst} + \text{glycerol carbonate ester} \quad (4)$$

We assumed that the controlling step of the reaction corresponded to Equation 3, with a kinetic constant, k_c, and that all of the other processes were in equilibrium; therefore, K_A, K_B, and K_D would be the equilibrium constants, which could be 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 (r_0) could be described by using Equation 8:

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

in which CA stands for carboxylic acid, C stands for catalyst, and W stands for water.

Considering Equations 5, 6, 7, and 8 and assuming that the amount of GCE and water adsorbed on the catalyst was negligible under the initial rate conditions, the kinetic rate equation would be:

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

and after linearization could be converted into::

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

and if $[R]_0 = [CA]_0$ it could be rewritten as:

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

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

whereas, if $[R]_0 = [GC]_0$ it would be:

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

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

in which 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 GC, 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 could be deduced (Figure S7).

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

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

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

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

The adsorption enthalpy (ΔH) and adsorption entropy (ΔS) values for the corresponding carboxylic acids and GC on the Nafion SAC-13 catalyst were calculated by using the van't Hoff Equation:

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

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

in which K_{ads} is the adsorption constant. Figure S8 (see the Supporting Information) shows the variation of the logarithm of k_c, and the specific adsorption constants K_{CA} and K_{GC}, with the inverse of the temperature.

The calculated kinetic parameters were collected and are presented in Table 3. As expected, it can be observed that the E_{act} values increased as the carboxylic acid chain length increased, indicating that the esterification reaction was less favored in kinetic terms because of the inductive effect of the alkyl chain, which lowered the electrophilicity of the carbonyl group on the adsorbed carboxylic acid. On the other hand, and in good agreement with previously reported results,[38] K_{CA} and K_{GC} decreased when lengthening the alkyl chain, indicating that the catalyst surface coverage increased as the alkyl chain of the reacting carboxylic acid decreased. Additionally, in all cases, the K_{CA} values were two to three times higher than K_{GC}, indicating the preferential adsorption of the carboxylic acid on the Brönsted acid sites. Also, the K_{GC} values increased slightly when the chain length of the acid increased, indicating that the adsorbed long-chain carboxylic acids had very little impact on the adsorption of the alcohol. These results were very different from those reported for the esterification of carboxylic acids with methanol,[38] during which it was observed that the alcohol adsorption constant decreased as the alkyl chain length of the reacting carboxylic acid increased; this was attributed to the capacity of the long-chain carboxylic acids to modify the catalyst surface, that is, the adsorbed carboxylic acid increased the surface hydrophobicity; therefore, affecting methanol adsorption. This effect was not observed in our case, probably because the GC is less polar than methanol. However, as adsorption is an exothermic process, it could be observed that an increase in temperature caused a decrease in the K_{ads} for both reactants.

When the ΔH values of the carboxylic acids were examined, we observed a decrease for the adsorption heat values as the carboxylic acid chain length increased. It was expected that adsorption of the carboxylic acids would occur through the interaction of a carbonyl group with the Brönsted acid sites as well as through Van der Waals interactions of the alkyl chain with the catalyst surface. Therefore, it was expected that the heat of adsorption of the acids would increase linearly with the number of carbon atoms in the alkyl chain,[40] provided that all of the methyl groups of the acids interacted with the surface, that is, they laydown linearly on the solid. However, the trend shown by the ΔH values suggested that long-chain carboxylic acids did not adsorb in a linear way, it was more probable that they were folded. This folding effect was probably responsible for the steric hindrance attributed to long-chain carboxylic acids, which also contributed to a decrease in its reactivity in the esterification reaction.

The above results allowed us to conclude that the lower intrinsic reactivity observed when increasing the carboxylic acid chain length was caused by both electronic (inductive) and steric effects, the latter caused mainly by the folding of the alkyl chain of the adsorbed carboxylic acid.

Stability and reusability of the 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 HA with GC under the azeotropic distillation of water was investigated by running consecutive reaction cycles, under 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 onto the surface, decreasing the catalytic activity

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] [$\mathrm{L\,h^{-1}\,g^{-1}}$]$\times 10^2$	K_{CA}[a] [$\mathrm{L\,mol^{-1}}$]	K_{GC}[a] [$\mathrm{L\,mol^{-1}}$]	E_{act}[a] [$\mathrm{KJ\,mol^{-1}}$]	ΔH_{CA}[a] [$\mathrm{KJ\,mol^{-1}}$]	ΔH_{GC}[a] [$\mathrm{KJ\,mol^{-1}}$]	ΔS_{CA}[a] [$\mathrm{J\,mol^{-1}\,K^{-1}}$]	ΔS_{GC}[a] [$\mathrm{J\,mol^{-1}\,K^{-1}}$]
hexanoic	80	0.770	0.130	0.042	30.9	−13.8	−7.3	−55.9	−47.1
	100	1.344	0.103	0.037					
	111	1.805	0.089	0.034					
nonanoic	80	0.091	0.122	0.047	41.1	−12.0	−8.4	−51.4	−49.1
	100	0.198	0.098	0.042					
	111	0.279	0.088	0.037					
lauric	80	0.018	0.106	0.050	47.8	−9.8	−8.9	−46.3	−50.2
	100	0.043	0.093	0.043					
	111	0.068	0.080	0.039					

[a] Experimental error ±5%.

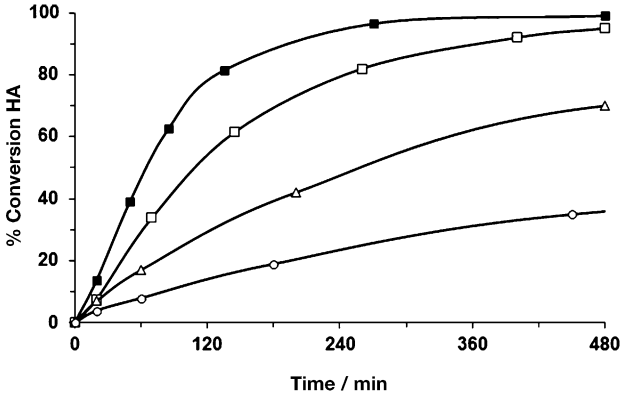


Figure 7. Conversion of HA versus time when the reaction was performed with Nafion SAC-13 that was fresh (■), reused once (□), reused twice (△) and reused three times (○). Reaction conditions: HA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions for the azeotropic distillation of water.

from one reaction cycle to another, was disregarded because azeotropic distillation was in place during the reaction and, furthermore, the catalyst was dried before each reaction cycle.

Decomposition of sulfonic groups could be a possible cause of catalyst deactivation during multiple reaction cycles, which is known to occur for SO_4^{2-}/ZrO_2.[41] However, this could not be the origin of catalyst deactivation in our case because elemental analysis showed that the spent Nafion SAC-13 catalyst maintained 92% of the original sulfur content after four cycles.

It has previously been reported that deactivation of Nafion SAC-13 occurred during the esterification of carboxylic acids with methanol, which was caused by the entrapment of bulky reactants, intermediates, and products on the Nafion nanodomains.[38] These compounds, which have to be resistant to the ethanol Soxhlet extraction process that was performed in our work, appeared to be the most probable cause of the activity loss. To check this hypothesis, the Brunauer–Emmett–Teller surface area (S_{BET}) of Nafion SAC-13 was measured before and after the reaction, and a decrease from 216 to 188 $m^2 g^{-1}$ was observed, indicating that some blocking of the pores had occurred. FTIR spectroscopy was used to characterize the catalyst before and after the reaction cycles, and to identify the type of compounds that remained adsorbed. Figure 8 shows IR spectra in the range 1300–3200 cm^{-1} for both the fresh and the spent catalyst samples. The peaks centered at 2900 and 1700 cm^{-1} adsorbed on the used catalysts could be assigned to the stretching frequencies of the $-CH_2-/-CH_3$ and C=O groups, respectively. There was also a small band at 1460 cm^{-1}, which could be ascribed to the bending and/or stretching vibration of C–H. The presence of these bands provided evidence for the strong adsorption of carboxylic acids on the catalyst surface. Moreover, TGA of the used Nafion SAC-13 indicated that 9 wt% of organic material remained on the catalyst after two reaction cycles. Therefore, we could conclude that catalyst deactivation was mainly cause by the strong adsorption of organic compounds.

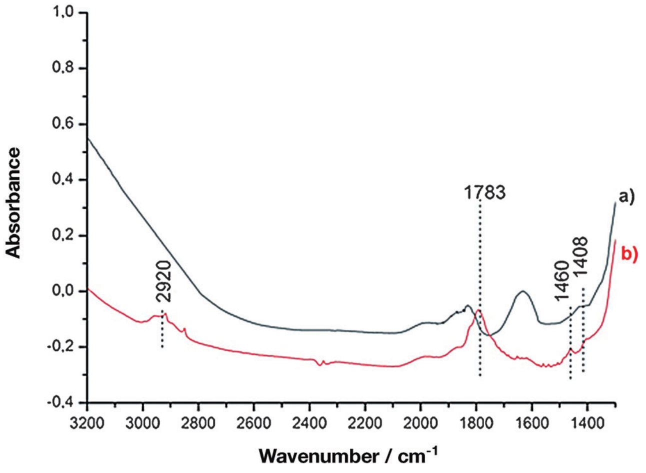


Figure 8. IR spectra of Nafion SAC-13: a) fresh catalyst sample and b) used catalyst recovered from HA esterification after two consecutive reaction cycles. The spent catalyst sample was washed through ethanol Soxhlet extraction and then dried after each cycle.

This strong adsorption of larger organic compounds could occur through a combination of two pathways, that is, through adsorption onto Brönsted acid sites (see ΔH values in Table 3) or through the interaction of the long alkyl chains with the Nafion nanodomains. Both pathways could contribute to the blockage of the acid sites by the large carboxylic acids, hindering access to the active sites, and subsequently inhibiting the catalyst activity. Therefore, stronger catalyst deactivation should have occurred when the chain length of the organic acid was increased. Indeed, results from Figure 9 show that after three reaction cycles, catalyst deactivation was 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 GCEs, presented in Table 4, showed that the deactivation of the catalyst was mainly caused by the adsorption of the carboxylic acids because they have higher heats of adsorption compared to the ester compounds.

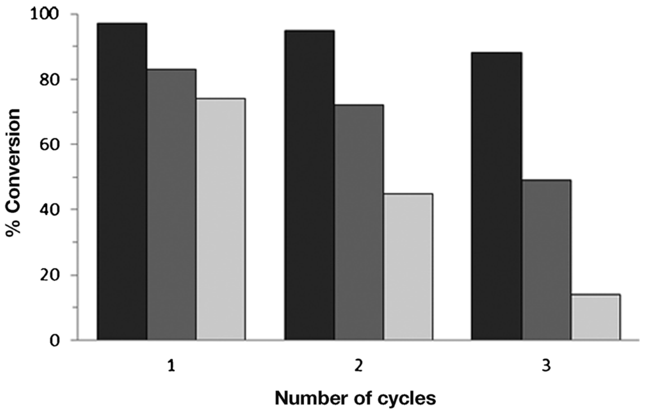


Figure 9. Conversion of different carboxylic acids when the reaction was performed with successive reuse of HA (■), nonanoic acid (▨), and lauric acid (□). Reaction conditions: Carboxylic acid (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions for the azeotropic distillation of water.

Table 4. Experimental adsorption heat energies of different carboxylic acids and their correspondent GCEs.

Carboxylic acid	ΔH_{exp} [J g^{-1}]	GCE	ΔH_{exp} [J g^{-1}]
hexanoic	−55.75	GCE-6	−30.12
heptanoic	−48.96	GCE-7	−31.38
octanoic	−44.89	GCE-8	−27.94
nonanoic	−41.76	GCE-9	−26.89

Catalyst regeneration could be achieved by burning off the adsorbed organic products. However, in this case, classical regeneration by catalyst calcination could not be performed because the Nafion would also be destroyed or damaged. As an alternative to calcination, we attempted the oxidation of the adsorbed organic compounds by using a low temperature Fenton oxidation[42] (see the Experimental Section). This regeneration procedure worked much better than Soxhlet extraction (see Figure 10), and the activity of the regenerated catalyst clearly improved.

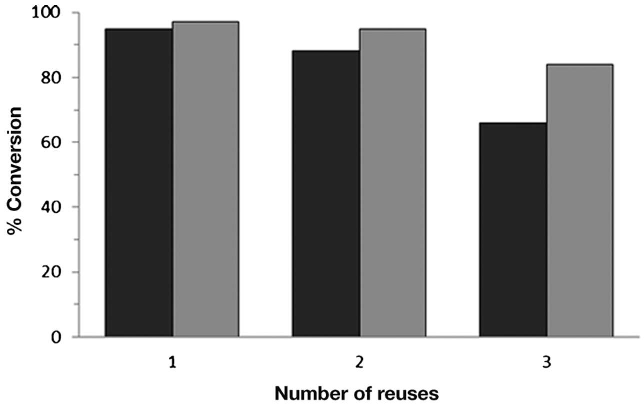


Figure 10. Conversion of HA when the reaction was performed with successive reuses of Nafion SAC-13 cleaned by using Soxhlet extraction (■) or the Fenton oxidation (▨). Reaction conditions: HA (10 mmol), GC (15 mmol), Nafion SAC-13 (450 mg), and conditions for the azeotropic distillation of water.

A possible regeneration method could involve the introduction of small amounts of Pt on the catalyst to hydrocrack the adsorbed long chains of the acids and/or esters; therefore, desorption of the lower molecular weight products would be easier. This possible catalyst regeneration route for the Nafion–silica hybrid catalyst is currently under study in our laboratory.

Conclusions

Nafion SAC-13 has proven to be an excellent catalyst for the esterification of GC with carboxylic acids, whereas other acidic ion-exchange resins and micro- and mesoporous aluminosilicates showed lower activity and selectivity. The highest activity was exhibited by the Nafion SAC-13 nanocomposite, despite its lower concentration of active sites, which could primarily be attributed to the greater strength of the acid sites and their better accessibility to the reactants compared to sulfonic resins, zeolites, and perfluorinated resin. The optimization of the reaction conditions, including water removal, enabled us to achieve 95 % selectivity towards GCE-6 at 98 % conversion.

The esterification reaction of GC with acids of different carbon chain lengths showed that the reactivity decreased when the chain length increased. From a full kinetic study, it was possible to conclude that this behavior could 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 was attributed to the 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 could be regenerated and high selectivity could be maintained by applying low-temperature Fenton oxidation. Therefore, when comparing the heterogeneous esterification process described herein to those detailed in the literature, with homogeneous coupling agents such as DCC and 4-dimethylaminopyridine,[18] or acid catalysts such as *p*TSA,[19] it was concluded that the heterogeneous Nafion SAC-13 catalyst could be an interesting green alternative for the synthesis of GCEs.

Experimental Section

Catalysts

Dowex 50-Wx2, Dowex Marathon C, Amberlyst-15, Nafion NR50, Nafion SAC-13, and *p*TSA were purchased from Sigma Aldrich. Beta (Si/Al = 13) and Mordenite zeolites were supplied by PQ Corporation in the acidic and the ammonium form, respectively. The acidic 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 ratios of 47 and 100 were prepared following the synthesis procedure described in a previously published report.[43] The MCM-22 zeolite with a MWW structure (Si/Al=15) was prepared and converted to its acid form following a previously published procedure.[44,45] The ITQ-2 catalyst was prepared by expansion and subsequent exfoliation of the corresponding laminar precursors of the MWW structure.[46] Commercially available ZSM-5 with Si/Al = 10 was supplied by Tricat Zeolites GmbH. The commercial sample, supplied in the ammonic form, was calcined at 773 K for 3 h to obtain the protonic zeolite

Reagents

Hexanoic, heptanoic, octanoic, nonanoic, lauric, and palmitic acids, as well as GC, nitrobenzene, pyridine, ferrous sulfate, and hydrogen peroxide 30 % *v/v* were purchased from Sigma Aldrich, whereas toluene was supplied by Scharlab, and N,O-bis(trimethylsilyl)trifluoroacetamide was obtained from Acros Organics.

Reaction procedure

The reactions were performed in a 10 mL two-necked round bottom flask. HA (10 mmol, 1.16 g), GC (15 mmol, 1.78 g), and the just-activated catalyst (3.5 wt% with respect to the total weight reactants) were added to the flask, and subsequently the reaction mixture was heated at 100 °C in a silicone bath fitted with a magnetic stirrer and a temperature controller. To remove the water formed in situ, the flask was coupled to a Dean–Stark and this was attached to a condenser, and 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 the initial reaction rate was observed and we concluded that under our experimental conditions, the reaction was not controlled by external diffusion. When the reaction was performed under the conditions for the azeotropic distillation of water, toluene (5 mL) 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, substrate ratio, substrate-to-catalyst ratio, and solvent on the reaction rate and selectivity.

The progress of the reaction was followed by taking samples at regular time periods that were then analyzed by using gas chromatography with a flame ionization 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 the external standard. At the end of the reaction, the catalyst was filtered and washed with toluene. The catalyst, which contained organic material from the reaction, was regenerated by using a Fenton oxidation (10 mL H_2O, 0.1 g $FeCl_2$, and 20 mL H_2O_2 35% *v/v* added drop wise over 3 h per 1 g of catalyst).[42]

Isolation of the reaction products for NMR analysis was performed by vacuum distillation, which allowed the remaining carboxylic acid, remaining GC, and monoglycerides to be separated from the reaction mixture. When necessary, and to eliminate any remaining di- and triglycerides, the distillation residue was dissolved in *n*-heptane and extracted with aqueous ethanol solutions according a previously reported procedure.[47] For instance, the case of (2-oxo-1,3-dioxolan-4-yl)methyl dodecanoate, it was purified under 1.33×10^3 Pa at 250 °C and the isolated yield of the ester was 56%. The content of organic material on the catalyst (wt% C, H, N, and S) was measured by using elemental analysis with an EA-1108 CHNS Fisons analyzer and a sulfanilamide standard. TGA was performed in a TGA 2050 (TA Instruments) under an air flow and with a heating rate of 10 K min^{-1}. MS was performed with a Agilent 5973 GC–MS HP 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 (Setaram). Prior to the measurement, a pretreatment procedure of each sample was performed, which consisted of heating the sample for 2 h at a temperature of 250 °C under vacuum ($\approx 1\times10^{-3}$ atm). After this time, the sample was sealed and it was ready to measure.

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Keywords: biomass · carboxylic acids · esterification · heterogeneous catalysts · solid-state structures

[1] a) G. Budroni, A. Corma, *J. Catal.* **2008**, *257*, 403–408; b) M. J. Climent, A. Corma, S. Iborra, *Green Chem.* **2011**, *13*, 520–540; c) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411–2502; d) P. Mäki-Arvela, B. Holmbom, T. Salmi, D. Y. Murzin, *Catal. Rev. Sci. Eng.* **2007**, *49*, 197–340; e) K. S. Arias, S. I. Al-Resayes, M. J. Climent, A. Corma, S. Iborra, *ChemSusChem* **2013**, *6*, 123–131.

[2] a) R. G. Bray in *Biodiesel Production*, PEP Report 251, Menlo Park, CA, **2004**. USA, SRI Consulting; b) G. Knothe, J. Krahl, J. van Gerpen, *The Biodiesel Handbook, 2nd ed.*, AOCS, Illinois, USA, **2010**, 302 pp.; c) G. Vicente, M. Martínez, J. Aracil, *Bioresour. Technol.* **2004**, *92*, 297–305.

[3] a) A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, *Green Chem.* **2008**, *10*, 13–30; b) Y. Zheng, X. Chen, Y. Shen, *Chem. Rev.* **2010**, *108*, 5253–5277; c) J. M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina, *Angew. Chem.* **2007**, *119*, 4516–4522; *Angew. Chem. Int. Ed.* **2007**, *46*, 4434–4440.

[4] M. J. Climent, A. Corma, P. De Frutos, S. Iborra, M. Noy, A. Velty, P. Concepción, *J. Catal.* **2010**, *269*, 140–149.

[5] B. Schäffner, F. Schäffner, S. P. Verevkin, A. Börner, *Chem. Rev.* **2010**, *110*, 4554–4581.

[6] a) M. O. Sonnati, S. Amigoni, E. P. Taffin de Givenchy, T. Darmanin, O. Choulet, F. Guittard, *Green Chem.* **2013**, *15*, 283–306; b) J. H. Clements, *Ind. Eng. Chem. Res.* **2003**, *42*, 663–674; c) R. B. Raether (BASF SE), WO 2012113616 A1, **2012**; d) S. Pelet, PhD Thesis, Institut National Polytechnique de Tolouse (France), n°1584, **1999**.

[7] a) J. W. Yoo, Z. Mouloungui, *Studies in Surface Science and Catalysis* **2001**, *135 (Zeolites and Mesoporous Materials at the Dawn of the 21st Century)*, 3806–3813; b) A. Dibenedetto, A. Angelini, M. Aresta, J. Ethiraj, C. Fragale, F. Nocito, *Tetrahedron* **2011**, *67*, 1308–1313; c) D. Balthasart, G. Patrick, K. Philippe (Solvay SA), FR 2966825, **2010**.

[8] Z. Mouloungui, S. Pelet, *Eur. J. Lipid Sci. Technol.* **2001**, *103*, 216–222.

[9] A. A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, *96*, 951–976.

[10] a) S. Hamaguchi, H. Yamamura, J. Hasegawa, K. Watanabe, *Agric. Biol. Chem.* **1985**, *49*, 1509–1511; b) J. Oehlenschläger, G. Gercken, *Lipids* **1978**, *13*, 557–562; c) D. V. Palaskar, P. S. Sane, P. P. Wadgaonkar, *React. Funct. Polym.* **2010**, *70*, 931–937; d) H. E. Katz, *Macromolecules* **1987**, *20*, 2026–2027; e) J. Britz, W. H. Meyer, G. Wegner, *Macromolecules* **2007**, *40*, 7558–7565.

[11] a) G. F. D'Alelio (Scott Paper Co.), US 3225063, **1965**; b) G. F. D'Alelio, T. Huemmer, *J. Polym. Sci. Part A* **1967**, *5*, 307–321; c) D. Grahe, D. Lachowicz (Dainippon Ink Chemical Industry Co.), EP 0328150, **1989**.

[12] a) J. J. Whelan, R. J. Cotter, US Pat., 3072613, **1963**; b) I. Frischinger, J. Cotting, J. Finter, J. François, EP 0881262, **2003**; c) B. Ochiai, Y. Ootani, T. Maruyama, T. Endo, *J. Polym. Sci. Part A* **2007**, *45*, 5781–5789.

[13] J. C. Fang (E. I. du Pont de Nemours & Co.), US 2967173, **1961**.

[14] B. Schmitt, M. Caspari, US Pat., 7414147, **2008**.

[15] M. Ramaiah, *J. Org. Chem.* **1985**, *50*, 4991–4993.

[16] J. M. Renga, F. D. Coms, E. R. Humphreys (Henkel Corp.), WO 9309111 A2, **1993**.

[17] G. Brindoepke, (Hoechst A.-G., Fed. Rep. Ger.), DE 3600602 A1, **1987**.

[18] S. Jana, H. Yu, A. Parthiban, C. L. L. Chai, *J. Polym. Sci. Part A* **2010**, *48*, 1622–1632.

[19] A. Lachowicz, G. F. Grahe (Dainippon Ink Chemical Industry Co.), DE 3937116, **1991**.

[20] G. D. Yadav, M. B. Thathagar, *React. Funct. Polym.* **2002**, *52*, 99–110.

[21] a) A. Corma, *Chem. Rev.* **1995**, *95*, 559–614; b) A. Corma, S. B. A. Hamid, S. Iborra, A. Velty, *ChemSusChem* **2008**, *1*, 85–90.

[22] W. Chu, X. Yang, X. Ye, Y. Wu, *Appl. Catal. A* **1996**, *145*, 125–140.

[23] J. H. Sepúlveda, J. C. Yori, C. R. Vera, *Appl. Catal. A* **2005**, *288*, 18–24.

[24] a) B. R. Jermy, A. Pandurangan, *Appl. Catal. A* **2005**, *288*, 25–33; b) S. R. Kirumakki, N. Nagaraju, K. V. R. Chary, S. Narayanan, *Appl. Catal. A* **2003**, *248*, 161–167.

[25] Y. Izumi, K. Urabe, *Chem. Lett.* **1981**, 663–666.

[26] a) "Nafion-H": Y. El-Kattan, J. McAtee in *e-EROS Encyclopedia of Reagents for Organic Synthesis*, Wiley, Chichester, **2001**; b) K. A. Mauritz, R. B. Moore, *Chem. Rev.* **2004**, *104*, 4535–4585; c) X. L. Feng, C. J. Guan, C. X. Zhao, *Chinese J. Org. Chem.* **2003**, *23*, 1348–1355.

[27] R. W. van Scoyoc, R. Warren, *Chemtech* **1987**, *17*, 438–441.
[28] a) M. A. Harmer, W. E. Farneth, Q. Sun, *J. Am. Chem. Soc.* **1996**, *118*, 7708–7715; b) M. A. Harmer, Q. Sun, A. J. Vega, W. E. Farneth, A. Heidekum, W. F. Hoelderich, *Green Chem.* **2000**, *2*, 7–14.
[29] M. A. Harmer, Q. Sun, *Appl. Catal. A* **2001**, *221*, 45–62.
[30] P. Botella, A. Corma, J. M. López-Nieto, *J. Catal.* **1999**, *185*, 371–377.
[31] a) A. Heidekum, M. A. Harmer, W. F. Hoelderich, *J. Catal.* **1999**, *181*, 217–222; b) A. Heidekum, M. A. Harmer, W. F. Hoelderich, *J. Catal.* **1999**, *188*, 230–232; c) B. Török, I. Kiricsi, Á. Molnár, G. A. Olah, *J. Catal.* **2000**, *193*, 132–138; d) M. C. Laufer, H. Hausmann, W. F. Hölderich, *J. Catal.* **2003**, *218*, 315–320.
[32] a) P. Beltrame, G. Zuretti, *Appl. Catal. A* **2003**, *248*, 75–83; b) I. Ledneczki, Á. Molnár, *Synth. Commun.* **2004**, *34*, 3683–3690; c) I. Ledneczki, M. Darányi, F. Fülöp, Á. Molnár, *Catal. Today* **2005**, *100*, 437–440; d) T. C. Wabnitz, J. Q. Yu, J. B. Spencer, *Synlett* **2003**, *7*, 1070–1072.
[33] a) R. F. Lobo, S. I. Zones, M. E. Davis, *J. Inclus. Phenom. Mol.* **1995**, *21*, 47–78; b) J. M. Chézeau, L. Delmotte, J. L. Guth, M. Soulard, *Zeolites* **1989**, *9*, 78–80.
[34] R. Rönnback, T. Salmi, A. Vuori, H. Haario, J. Lehtonen, A. Sundqvist, E. Tirronen, *Chem. Eng. Sci.* **1997**, *52*, 3369–3381.
[35] M. S. Newman, *Steric Effects in Organic Chemistry*, Wiley, New York, **1956**, 710 pp..
[36] H. Fujimoto, Y. Mizutani, J. Endo, Y. Jinbu, *J. Org. Chem.* **1989**, *54*, 2568–2573.
[37] M. Charton, *J. Am. Chem. Soc.* **1975**, *97*, 1552–1556.
[38] Y. Liu, E. Lotero, J. Goodwin, *J. Catal.* **2006**, *243*, 221–228.
[39] a) T. Fujita, C. Takayama, M. Nakajima, *J. Org. Chem.* **1973**, *38*, 1623–1630; b) D. Datta, D. Majumdar, *J. Phys. Org. Chem.* **1991**, *4*, 611–617.
[40] F. Eder, M. Stockenhuber, J. A. Lercher, *J. Phys. Chem. B* **1997**, *101*, 5414–5419.
[41] a) A. Corma, H. Garcia, *Catal. Today* **1997**, *38*, 257–308; b) F. Omota, A. C. Dimian, A. Bliek, *Chem. Eng. Sci.* **2003**, *58*, 3175–3185.
[42] a) I. Melian-Cabrera, *NPT Procestechnol.* **2006**, *13*, 12–14; b) I. Melián-Cabrea, F. Kapteijn, J. A. Moulijn, *Stud. Surf. Sci. Catal. A* **2006**, *162*, 37–46; c) I. Melián-Cabrera, A. H. Osman, E. R. H. van Eck, A. P. M. Kentgens, E. Polushkin, F. Kapteijn, J. A. Moulijn, *Stud. Surf. Sci. Catal. A* **2007**, *170*, 648–654.
[43] S. Valencia. PhD Thesis, Universitat Politècnica de València (UPV-CSIC), Valencia (Spain), **1997**.
[44] M. E. Leonowicz, J. A. Lawton, S. L. Lawton, M. K. Rubin, *Science* **1994**, *264*, 1910–1913.
[45] A. Corma, C. Corell, F. Llopis, A. Martínez, J. Pérez-Pariente, *Appl. Catal. A* **1994**, *115*, 121–134.
[46] A. Corma, V. Fornes, S. B. Pergher, T. Maesen, J. G. Buglass, *Nature* **1998**, *396*, 353–356.
[47] H. A. Goldsmith (Colgate-Palmolive-Peet Co.), US 2651646, **1953**.

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Preparation of Glycerol Carbonate Esters by using Hybrid Nafion–Silica Catalyst

Chain reaction: The esterification of glycerol carbonate with carboxylic acids to produce glycerol carbonate esters, which are valuable biomass-derivative compounds, has been investigated. A Nafion–silica nanocomposite is shown to be an excellent catalyst, and after fitting the experimental data to a kinetic model, the kinetic parameters were determined and compared for reactions involving different carboxylic acids.