From biomass to chemicals: Synthesis of precursors of biodegradable surfactant molecules by one pot two-steps selective acetalization and transacetalization of 5-hydroxymethylfurfural with zeolite catalysts

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Abstract

The selective acetalization of 5-hydroxymethylfurfural (HMF) with long chain alkyl alcohols has been performed to obtain precursor of molecules with surfactants properties. When direct acetalization of HMF with n-octanol is carried out in the presence of strong acids (homogeneous and heterogeneous catalysts), an increase in the etherification versus acetalization occurs. Beta zeolite catalyzes both reactions. However when the acidity of a zeolite (Beta) was controlled by partial exchange of H^+ with Na^+ the dioctyl acetal of HMF can be achieved with 95% yield by transacetalization. It is possible to achieve high yield in very short reaction time, through a one pot two-steps process which includes as first step the synthesis of dimethyl acetal of HMF followed by transacetalization with octanol. The one pot process could be extended to other alcohols containing between 6 to 12 carbon atoms affording 87-98% yield of the corresponding dialkyl acetal with selectivity higher than 96%. The optimized catalyst with adequate Na content (1.5NaBeta) could be recycled without loss of activity or selectivity.

Introduction

      5-Hydroxymethylfurfural (HMF) is considered as an important potential platform molecule for biorenewable fuels[1] and chemicals production[2] since it can be obtained by dehydration of fructose, glucose and cellulose.[2–4] HMF is a versatile molecule that can be converted into several derivatives with multiple applications, e.g. pharmaceuticals, antifungals, and polymer precursors. Recently, some transformations of HMF into monomers able to replace terephthalic, isophthalic, and adipic acids during manufacture of polyamides, polyesters and polyurethanes,[5] have been performed by our research group using heterogeneous catalysts.[6] With the aim to find other applications for HMF derivatives, we have investigated the conversion of this molecule into a new class of compounds with potential surfactant applications. Surfactants are commonly used in the composition of detergents, pharmaceuticals, cosmetics and food. They form micelles and vesicular microaggregates whose properties depend on the composition and structure of the polar head groups and on the length and shape of the hydrophobic hydrocarbon counterpart. With this in mind, we have studied the selective acetalization of the carboxaldehyde group of HMF with fatty alcohols using zeolites as acid catalysts. This type of molecules can be transformed in surfactant molecules by subsequent oxidation of the free hydroxyl group forming a carboxylic group or its salts (see Scheme 1). Although HMF derivatives have been mentioned as precursor of surfactant molecules we did not find reports in the literature.

Acetalization of carbonyl groups can be performed by reacting directly carbonyl compounds with alcohols or by transacetalization of dimethyl or diethyl acetals with other alcohols in the presence of acid catalysts. A wide variety of heterogeneous acid catalysts, such as Montmorillonite exchanged resin,[7] titania silicalite,[8] mesoporous materials[9] and zeolites[10] have been reported in the literature as solid catalysts to perform acetalization reactions with excellent results. Previously we have showed that zeolites, and mesoporous aluminosilicates[11] are suitable acid catalysts to obtain non-ionic surfactants, such as alkylglucosides, by selective acetalization of glucose with fatty alcohols. Then, for the selective acetalization of HMF, acid zeolites appear to be promising catalysts since, besides the general advantages associated with the use of solid catalysts, they can be synthesized with different crystalline structures, pore sizes, acid strength distribution and hydrophobicity. In the case of HMF, one should be taking

into account that HMF is a bifunctional molecule bearing alcohol and aldehyde functions, being both able to react with alcohols in the presence of acid catalysts to give ethers and acetals respectively. Therefore it would be of much interest to be able to tailor the solid catalyst selectively to direct the reaction either to ether or acetal, and will present here how this could be achieved by using zeolite catalysts.

Results and discussion

Taking into account the dimensions of the desired product (Scheme 2), we started our study by performing the acetalization of HMF with n-octanol in the presence of structured micro and mesoporous acid catalysts such as, a large pore tridirectional (Beta), and a monodirectional (Mordenite) zeolites, as well as with a mesoporous aluminosilicate (MCM-41) (Table 1). Thus, when the acetalization reaction of HMF was carried out with n-octanol in a n-octanol/HMF molar ratio of 40 in the presence of these catalysts at 65 ºC, it was observed that while Beta zeolite and the mesoporous MCM-41 gave high conversion of HMF, Mordenite gave sensibly lower conversion that could be attributed to the fast poisoning by pore blocking of the monodirectional pore zeolite catalyst. However, a complex mixture of products was always formed (Scheme 2), being the yield of the desired 5-(dioctoxymethyl)-2-hydroxymethylfurane (**3**) considerably low in all cases (see Table 2). The main byproducts observed were the ether 5-(octyloxymethyl)furfural (**4**) and its corresponding dioctyl acetal (**5**). However, compounds coming from the dimerization of HMF such as 5,5'-(oxy-bis(methylene))bis-2-furfural (OBMF, **6**) and the corresponding mono- and bis-dioctyl acetals (**7** and **8**) were also obtained (Table 2**).** As can be seen in Figure S1 the compounds **3, 4** and **6** have primary character while **5, 7** and **8** are secondary products. No octyl levulinate, coming from ring opening by hydrolysis of HMF followed by esterification in acidic media, was detected. In Scheme 2 the different possible routes for formation of the byproducts detected are presented. Additionally, when a solvent such as trifluorotoluene (TFT) was used, no improvement in selectivity to dioctyl acetal **3** was observed (see Table 2).

When the reaction was performed using p-toluenesulfonic acid (PTSA) as homogeneous Bronsted acid catalyst, the distribution of products obtained was similar to the one achieved with the Beta zeolite and the mesoporous material. The results indicate that under these reaction conditions the in the homogeneous catalyst of and the stronger ones strong acid sites existing in the aluminosilicate catalysts mainly favor the competitive

etherification reactions of the hydroxymethyl group (giving the compound **4**), as well as the dimerization of HMF (giving OBMF**, 6**) and its subsequent reactions with n-octanol (giving **7** and **8**). In Figure S2 is presented the selectivity to **3** versus conversion for the different catalysts tested**.**

Since etherification is a more demanding reaction from the point of view of the acid strength than acetalization, one way to increase the selectivity to the target compound (dioctyl acetal **3**) would be to decrease the number of strong Bronsted acid sites, and this could be achieved by a partial exchange of protons with Na cations in the zeolite framework. In order to check this, a series of Na exchanged Beta zeolites with sodium content from 0.26 to 3 wt% (calculated as of Na_2O), were prepared and tested in the reaction. In Figure 1 the IR spectra of pyridine adsorbed on the Beta samples with different percentage of Na content are displayed. There B and L correspond to pyridine protonated by Bronsted acids and pyridine coordinated with Lewis acids respectively. There, it can also be observed two absorption bands at 1592 and 1442 cm^{-1} which corresponds to interactions of sodium cations with pyridine and which intensity increase with increasing the sodium content.[12] In Table 3 (and Figures 2 and 3) the catalytic results obtained with these materials are displayed. As can be seen there, increasing the Na content leads to an increase in the selectivity to **3**. More specifically, with Beta zeolite samples with Na content higher than 1 wt% the formation of ethers, mainly OBMF, was drastically suppressed. Moreover, when all acid sites of the zeolite were exchanged by Na$^+$ cations**,** (3.1NaBeta) (see Table 1), the catalytic activity was totally suppressed.

The results presented in Table 3 and Figure S3 show that a Beta zeolite with a 1.5 wt% of sodium content is a very selective catalyst to perform the acetalization. Unfortunately the reaction stops after 8 h and the final yield obtained was 63 %. As can be observed in Figures 2 and 3a, Beta zeolite samples with Na content of 1 wt% and 1.5 wt% respectively, show similar kinetic behaviour (initial reaction rate) and both samples deactivate very fast. This deactivation could be associated to a strong adsorption of the products on the catalyst surface at lower reaction temperatures. In order to confirm this, the IR spectra of 1.5NaBeta after the acetalization reaction was obtained and a wide absorption band a 3500 cm^{-1} (associated to hydroxyl groups) and bands at 2900 cm^{-1} corresponding to C-H vibration and which can be associated to n-octanol alkyl chain were observed. In fact, when the used catalyst (1.5NaBeta) was Soxhlet extracted using acetonitrile as a solvent, n-octanol (11 wt%) was the only

compound detected by GC-MS in the organic extract. However, after the extraction process a 4 wt% of organic material remained on the solid catalyst according to the termogravimetric analysis of the sample. Then, the acetalization reaction of HMF with n-octanol was carried out in the presence of the catalyst submitted to Soxhlet extraction and the results show a decrease of the initial rate of reaction (0.20 mol min^{-1} g^{-1}) compared with the fresh catalyst (0.43 mol min^{-1} g^{-1}), though a similar yield (66 %) of dioctyl acetal of HMF could be obtained if the reaction time was prolonged (see Figure 3b). These results confirm that an important part of catalyst deactivation is reversible and is mainly due to the adsorption of the n-octanol on the surface of the catalyst. In fact the activity and selectivity to dioctyl acetal of HMF were totally recovered when the used catalyst was submitted to calcination at 580 ºC for 3h.

From an operational point of view, the amount of reactant and products adsorbed could be diminished by performing the reaction at higher temperature. Indeed, practically full conversion was achieved at temperature > 100 ºC (Table 4), though under these reaction conditions the selectivity to dioctyl acetal decreases and the competitive etherification reactions are promoted. It is worthy noticing that at 120 ºC, 52 % of dioctyl acetal ether **5** coming from **3** and **4** is the major product obtained (see Scheme 2).

The results presented up to now indicate that with zeolites, or at least with Beta zeolite, it is difficult to obtain high yields of the acetal of HMF with longer alkyl chain alcohols, even if zeolite acidity is optimized. It appears that n-octanol is strongly adsorbed at lower temperatures, competing with HMF for the zeolite adsorption sites, leading to a reversible deactivation of the catalyst.

At this point we thought that in principle, it could be possible to modify the relative adsorption of HMF and n-octanol by modifying the surface polarity of the zeolite. To do that, we have prepared two series of zeolite catalysts. In the first case zeolite Beta samples were synthesized in fluoride media and within different framework Si/Al ratios (Table 5). It is well known[13] that the synthesis in fluoride, instead OH$^-$ media, produces samples with a smaller amount of silanols, leading to less polar Beta samples. Moreover, for a given synthesis method, the higher the framework Si/Al ratio the less polar the zeolite will be. The second series of zeolite catalysts, correspond to Beta zeolite synthesis in OH$^-$ media and with different framework Si/Al ratios. IR results of two representative samples confirm that the Beta samples synthesized in fluoride media contain a smaller amount of silanols (see band at 3745 cm^{-1} in Figure 4).

The resultant samples were tested for the acetalization of HMF with n-octanol and the results are given in Table 6. It can be seen there that, regardless of the nature of the samples, selectivity to dioctyl acetal **3** is low for the sodium free HBeta sample. When the acetalization was carried out using Beta zeolite synthesized in hydroxy media, such as Beta15(B) and Beta25(B), which present a larger amount of silanol groups, a higher activity was obtained for the zeolite with the highest Si/Al ratio (Beta25(B)) indicating that some hydrophobicity is required in order to obtain good yield and selectivity of the dioctyl acetal **3** (see Figures 5a and b). However, when the more hydrophobic Beta zeolite samples i.e., those free of connectivity defects (Beta(F)), were studied the results in Table 6 show that the most active catalyst is the sample with a Si/Al ratio of 12 which represents a compromise between larger amount of acid sites and polarity (see Figures 5c and d). Additionally the reuse of Beta15(B) and Beta12(F) zeolites showed that some deactivation of the catalysts occurs during the reaction, however the selectivity to **3** is practically maintained. For instance, when Beta12(F) catalyst is used in a second cycle, the conversion decreases from 75 to 50 %. However, when the sample is calcined at 580 $^{\circ}$C the initial activity is restored (see Figure S4).

In conclusion, it appears that by controlling acidity, polarity and reaction temperature, it is possible to direct the reaction between HMF and n-octanol into dioctyl acetal or the ethers. The products formed can all of them act as surfactants though their properties will be different. Therefore, by using Beta zeolite synthesized with an adequate acidity and polarity it should be possible to maximize the yield of either product **3** or product **5.** However, and despite the larger ratios of n-octanol to HMF used and the optimization of acid sites and polarity, we could not obtain, by direct acetalization, yields to the desired product **3** larger than 70 %.

Transacetalization process

According with the results presented above, and taking into account that transacetalization reactions are thermodynamically and kinetically favored with respect to direct acetalizations, we have also explored an alternative route to obtain dioctyl acetal of HMF **3** which involves as a first step the preparation of dimethyl acetal of HMF (5-(dimethoxymethyl)-2-hydroxymethylfurane, **9**) followed by transacetalization with n-octanol.

Dimethyl acetal of HMF was prepared from HMF and MeOH using 1.5NaBeta zeolite as catalyst. The reaction was performed at 65 $^{\circ}$C, and after 2.5 h, 99 % of

selectivity to dimethyl acetal **9** at 99 % conversion of HMF could be obtained. Only traces of 5-(dimethoxymethyl)-2-methoxymethylfurane were detected in the reaction media. Then, starting from dimethyl acetal **9** we have performed the transacetalization reaction with n-octanol in the presence of Beta zeolite samples with different Na content (Table 7). Reactions were done with a previously optimized molar ratio of product **9** to n-octanol of 1:3.7, and 15 wt% of catalyst (respect to **9**) at 65 $^{\circ}$C, while MeOH was distilled off by using a Dean-Stark apparatus.

As can be observed in Table 7, HBeta zeolite gives low selectivity to dioctyl acetal **3**, and promotes mainly etherification reactions giving **4** and **5**, and hydrolysis of **9** giving HMF (**1**). However, the selectivity to dioctyl acetal (**3**) increases considerably when increasing sodium on the catalyst, reaching 95 % selectivity to the target compound when the Na content was 1.5 wt%. Dimerization of HMF to give OBMF was totally suppressed.

In Figures 6a and 6b the kinetics curves for HBeta and NaBeta are displayed. In the case of HBeta zeolite, (Figure 6a) the dioctyl acetal **3** reaches a maximum concentration and then decreases with time giving subsequent etherification to **5** and possibly hydrolysis to HMF (**1**). Indeed, HMF should be mainly formed by hydrolysis of dimethyl acetal **9** which undergo subsequent etherification to give ether **4.** Formation of HMF should be due to the water released during the etherification reactions as well as the water remaining on the zeolite. In fact the water content of the HBeta zeolite after the process of activation was still 12.5 wt%.

As can be seen in Figure 6b a different kinetic behavior is observed with 1.5NaBeta catalyst. 1.5NaBeta zeolite promotes the transacetalization of **9** with octanol giving initially an intermediate methyloctyl acetal of HMF (**11**), which further reacts with another molecule of n-octanol to give product **3** (Scheme 3). Meanwhile secondary reactions are minimized as a consequence of the lower acidity of the 1.5NaBeta catalyst (see Table 1). In this case formation of HMF should also be mainly attributed to the residual water present in 1.5Beta zeolite (10 wt%), although the rate of appearance of HMF was about twofold lower than in the case of HBeta, being the final HMF concentration in the reaction media considerably lower (see Table 7). These results indicate that the presence of strong acid sites on the catalyst is also detrimental for the transacetalization reaction since it catalyzes the hydrolysis of dimethyl acetal **9**. In order to avoid the hydrolysis of **9**, we did an additional experiment using octanol previously dried, in the presence of 1.5Beta zeolite. In this case, it was observed that the rate of

formation of HMF was an order of magnitude lower, though for long reaction time the concentration of HMF remained the same (see Table 7).

At this point, it appeared to us that one way to reduce the competitive hydrolysis of acetals could be by using catalysts with higher hydrophobic character that will adsorb lower amount of water (Table 5). In order to check this hypothesis, a more hydrophobic Beta zeolite prepared in fluoride media (Si/Al= 12) was exchanged with Na (1.5 wt%) and tested in the reaction. In this case although the rate of formation of HMF was also decreased by one order of magnitude a similar final result was obtained for long reaction times. Nevertheless, by properly controlling catalyst and reaction conditions, 95% yield of dioctyl acetal can be obtained through a transacetalization reaction between the dimethyl acetal and n-octanol.

The results presented above show that 1.5NaBeta zeolite is able to catalyze efficiently and selectively both, the acetalization of HMF with MeOH giving dimethyl acetal **9** and the subsequent transacetalization of **9** with n-octanol giving dioctyl acetal **3**. Taking into account these results it appeared to us that it would be of interest to design a one-pot process where both reactions occur in a single vessel. In order to do that, HMF was reacted first with MeOH in the presence of 1.5NaBeta zeolite at 65 ^{o}C during 2.5h to achieve the maximum yield of dimetyl acetal **9** (100 % HMF conversion with 99 % selectivity to **9**) . At this point, n-octanol was added to the reaction mixture in a molar ratio **9**:octanol of 1:3.7 while methanol was removed by bubbling a stream of nitrogen through the suspension. The results obtained are compared in Table 8 with those obtained with the most acidic HBeta zeolite. As can be seen there 1.5NaBeta zeolite is able to perform very efficiently the one pot process achieving 95 % yield of dioctyl acetal **3** in 30 min reaction time. It is interesting to notice that if the reaction time is prolonged up to 1h, a decrease in selectivity is observed due to the consecutive transformation of **3** into octyl ether **4** and octyl ether dioctyl acetal **5**. In Figure 7 the evolution of reactants and products with time is presented. It is observed there that at the beginning of the reaction there is an induction period in where **3** is not formed while the rate of disappearance of **9** is very low and HMF is the only product formed. This behaviour can be explained taking into account the experimental procedure. At the beginning of the reaction the excess of methanol used in the first step remains in the reaction media acting as solvent and reactant and shifting the equilibrium towards the formation of the dimethyl acetal of HMF (**9**). As methanol is distilled off,

transacetalization of dimethyl acetal **9** with octanol takes place at high reaction rate achieving maximum yield and selectivity to **3** after 30 min.

Comparatively, the most acidic HBeta zeolite was much less selective achieving only a maximum selectivity to dioctyl acetal of 47 % (Table 8).

Catalyst recycling in the one-pot process

In order to test the reusability of the 1.5NaBeta catalyst, it was reused in various cycles. After each reaction, the zeolite was filtered and washed thoroughly with acetone and activated under vacuum before each reuse, according to the experimental procedure. As can be observed in Figure 8, activity and selectivity was maintained at least during the four consecutive cycles studied here, without decrease in activity and selectivity.

Finally the one-pot process was extended to other aliphatic alcohols, since it is known that an important property of surfactant molecules is the biodegradability, which is related with the length and branching of the alkyl chain of the alcohol. For ours studies, we selected unbranched alkyl alcohols (between C6 and C12) to obtain in a one pot reaction the corresponding alkyl acetal. In Table 9 the results obtained show the general applicability of the catalyst and procedure to obtain precursors of molecules with surfactant properties.

Conclusions

It is possible to obtain surfactant precursor molecules by reacting HMF and fatty alcohols in the presence of solid acid catalysts. Beta zeolite appears to be a good catalyst for the above reaction, being the main products obtained: 5-(dioctoxymethyl)-2-hydroxymethylfurane (**3**), the ether 5-(octyloxymethyl)furfural (**4**) and its corresponding dioctyl acetal (**5**). By controlling zeolite acidity and polarity, as well as reaction temperature, it is possible to modify the product selectivity. Control of zeolite acidity is best performed by introducing different amounts of Na^+. Beta zeolite partially exchanged with Na^+ is also able to perform transacetalization with excellent conversions and selectivities within very reasonable reaction times.

Finally, a one pot two-step process involving acetalization of HMF with methanol to form the dimethyl acetal and transacetalization with n-octanol gives yields of dioctyl acetal of 95%. The one pot process catalyzed by Na partially exchanged Beta zeolite has been extended to alcohols from C6 to C12 with excellent activities and selectivities.

Experimental section

5-Hydroxymethylfurfural (≥99%), n-hexanol (≥98%), n-octanol (≥99%), n-decanol (98%), dodecanol (≥99%), hexadecane (99%), were purchased from Aldrich and methanol (99.99%) was purchased from Scharlau.

Materials

HBeta (CP811) and 0.58NaBeta (CP806) zeolites (Si/Al=12) were purchased from PQ Zeolites B. V. and before use were calcined at 580 ºC for 3 h. The MCM-41 (Si/Al=15) with a pore diameter of 3.5 nm, was prepared according to the literature.[14]

Na-exchanged Beta zeolites (0.26NaBeta, 0.49NaBeta, 1.0NaBeta, 1.5NaBeta, and 3.0NaBeta, where the number indicates the percentage, wt% of sodium content were prepared by impregnating the commercial HBeta zeolite with different aqueous solutions of sodium acetate followed by drying at 100 ºC overnight and then calcination at 580 ºC for three hours. The Na content of the samples was determined by chemical analysis (Varian 715-ES ICP-optical emission spectrometer) after dissolving the solids in a HNO_3/HF solution.

The acidity of the catalysts was measured by IR spectroscopy (Nicolet 710 FTIR spectrophotometer) combined with adsorption-desorption of pyridine[15] at 10^{-4} Torr at 150 ºC, 250 ºC and 350 ºC (Table 1) using self-supported wafers of 10 mg cm^{-2} that were degassed overnight under vacuum (10^{-4} to 10^{-5} Pa) at 400 ºC.

Specific surface area and pore diameters were measured by nitrogen adsorption at 77 K, using a Micrometrics ASAP 2000 apparatus. Thermogravimetric analysis (TG) were performed in a Netzsch STA 409 EP thermal analysis with about 20 mg of sample and heating rate of 10 ºC/min in air flow.

Reaction procedure

Direct acetalization of HMF with n-octanol

Micro- and mesoporous catalysts (51 mg) were activated *in situ* in a 10-ml batch glass reactor, by heating the solid at 200 ºC under vacuum (1 Torr) for 2 h. Then, the system was cooled to room temperature and a mixture of HMF and n-octanol (in a

molar ratio HMF:octanol of 1:40) previously heated at the desired reaction temperature was added onto the catalysts. The mixture was heated in a system equipped with a silicone bath, magnetical stirrer and a condenser. Samples were taken at regular times, diluted with acetone, and the catalyst was separated by centrifugation. The products in the solution were analyzed by GC-MS, and conversion of HMF and yields of the different compounds were determined by GC using hexadecane as external standard.

At the end of the reaction the catalyst was filtered and the reaction mixture was analized by GC-MS. The catalyst was submitted to continuous solid-liquid extraction with acetonitrile using a micro-Soxhlet equipment. After solvent removal, the residue was weighed and analyzed by GC-MS. In all cases the recovered material accounted for more than 90 % of the starting HMF.

*Synthesis of 5-(dimethoxymethyl)-2-hydroxymethyl furane (**9**)*

A solution of HMF (500 mg) in 28 ml of methanol heated at 65 °C was added over previously activated 1.5NaBeta zeolite catalyst (100 mg). The mixture was magnetically stirred during 2.5 h. After reaction the catalyst was filtered off and methanol was eliminated by heating under reduced pressure. The yellow concentrate obtained corresponds to dimethyl acetal of HMF (**9**) in ≥ 99% yield and it was used as prepared without any further purification in the transacetalization reactions.

GC-MS data of **9**: m/z (% relative intensity) M^+ 172 ($C_8H_{12}O_4$) (10), 141 (100), 125 (5), 109 (7), 97 (5), 81(14).

*Transacetalization of **9** with n-octanol*

The transacetalization reaction of dimethyl acetal of 5-hydroxymethylfurfural (**9**) with n-octanol was carried out in a batch glass reactor, equipped with a magnetic stirrer, immersed in a thermostated silicone bath with a reflux condenser, a Dean-Stark trap and nitrogen flow. Before reaction the catalyst (26 mg) was activated *in situ* as described above. A pre-heated (65 °C) mixture of dimethyl acetal of HMF (**9**) (1 mmol) and n-octanol (3.7 mmol), was added onto the catalyst and the mixture was stirred at 65 ºC during the required time. Samples were taken at regular times and were analyzed according to the procedure described above.

GC-MS data of **3**: m/z (% relative intensity) M^+ 368 ($C_{22}H_{40}O_4$) (2), 239 (100), 127 (96), 109 (18), 97 (5).

One-pot reaction

A solution of HMF (1 mmol) in methanol 5 ml (125 mmol) was added onto the previously activated catalyst (26 mg) and heated at 65 ºC for 2.5 h in a system equipped

with a silicone oil bath, magnetic stirrer, reflux condenser and Dean-Stark trap. During this first step dimethyl acetal of HMF (**9**) was obtained in yield ≥ 99% according to GC analysis. The second step of the reaction (transacetalization) was carried out by adding the fatty alcohol (3.7 mmol) while a stream of nitrogen was bubbled continuously through the suspension (50 ml min^{-1}) to facilitate the removal of methanol. Samples were taken at regular times and were analyzed according to the procedure described above.

Gas chromatography analyses were performed with a Varian 3900 chromatograph equipped with a flame ionization detector and HP-5 (5% crosslinked phenyl-methyl silicone, sizes 30m x 0.25mm x 0.25μm) capillary column. Mass spectra were performed by GC-MS (HP Agilent 5973 with a 6980 mass selective detector).

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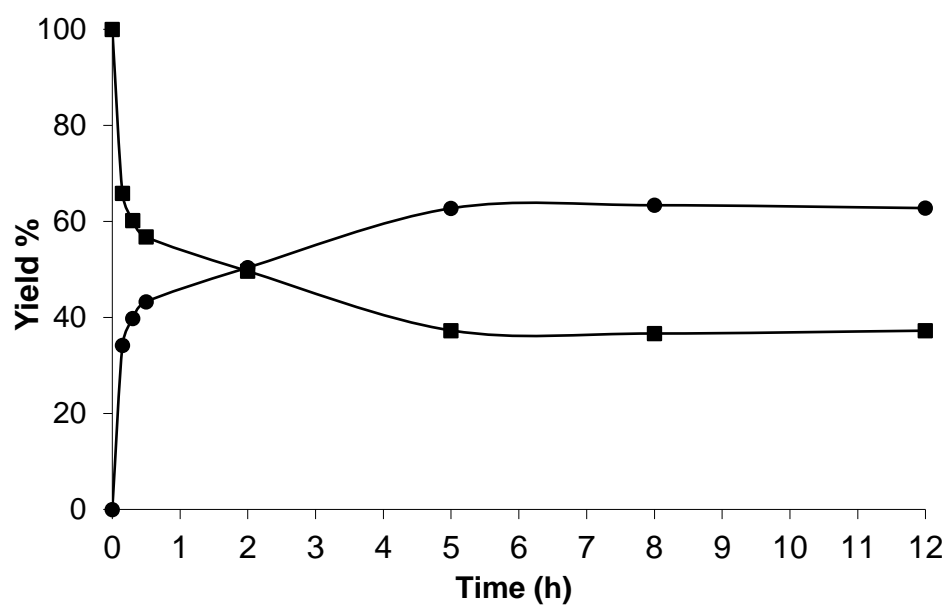
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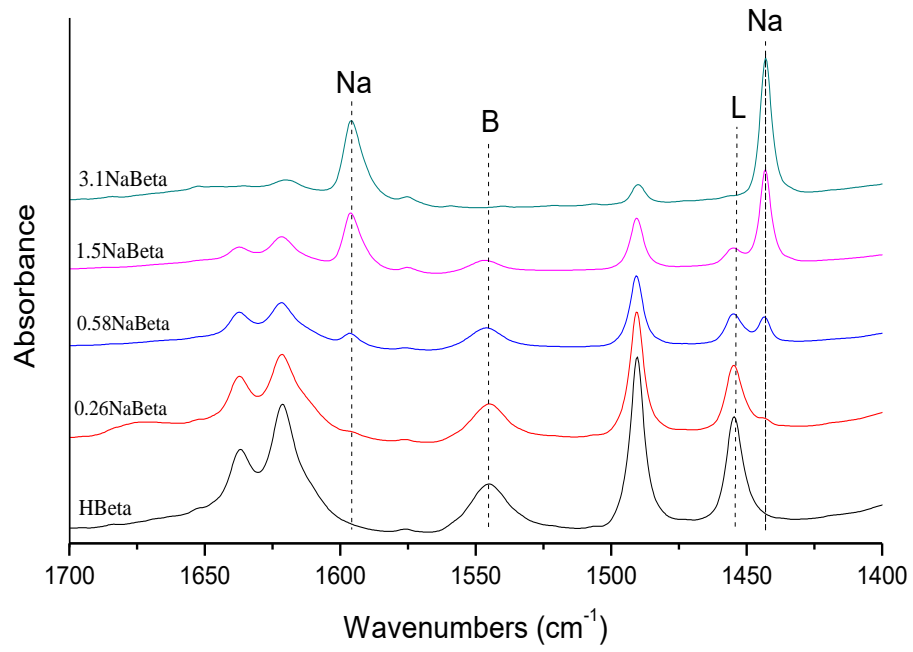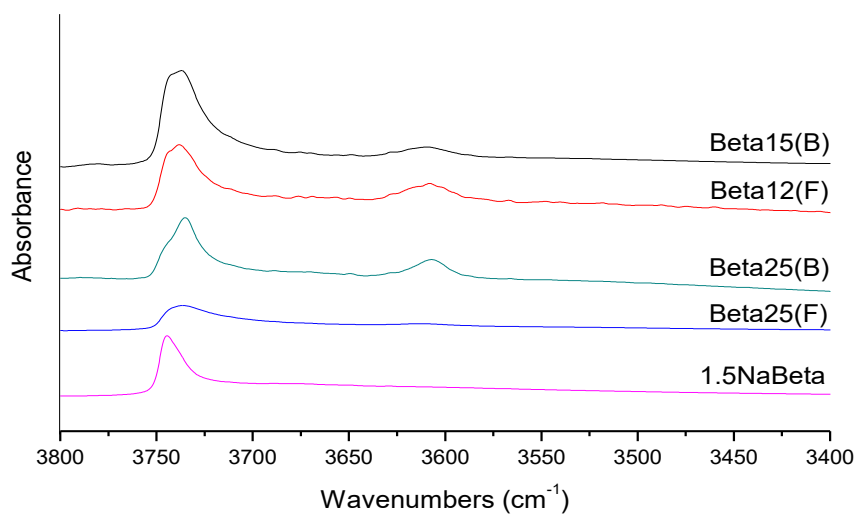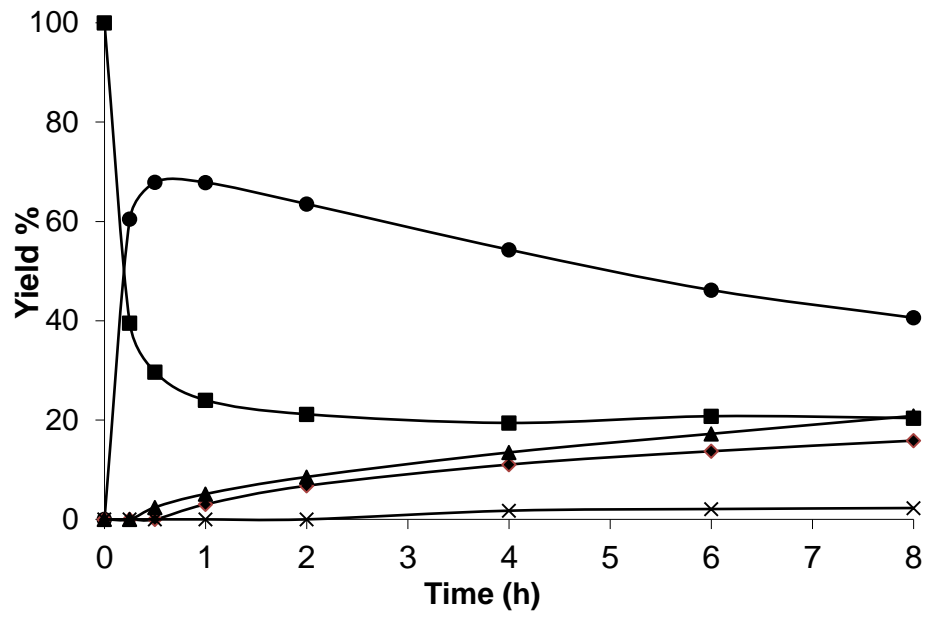
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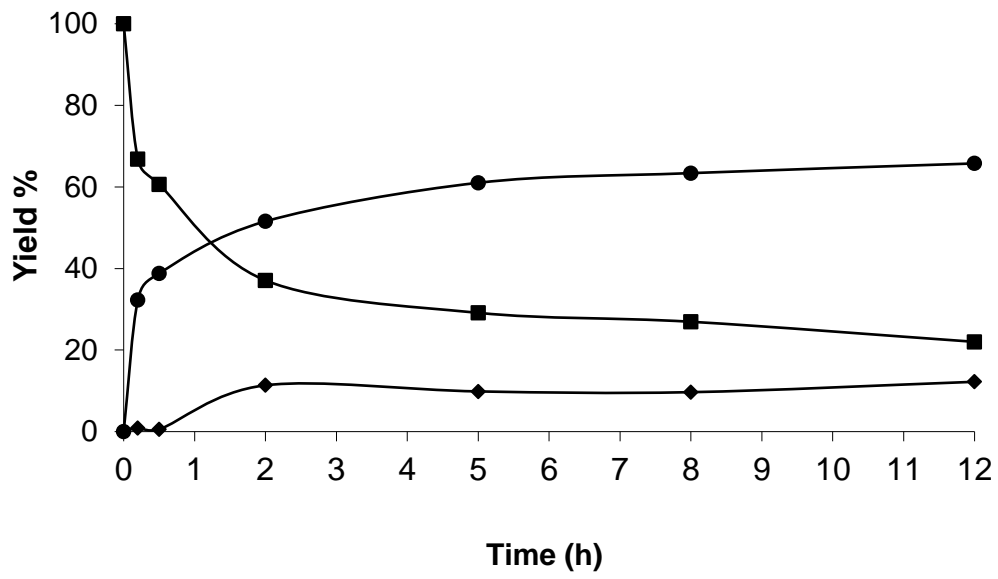
Figure 2

Figure 3a
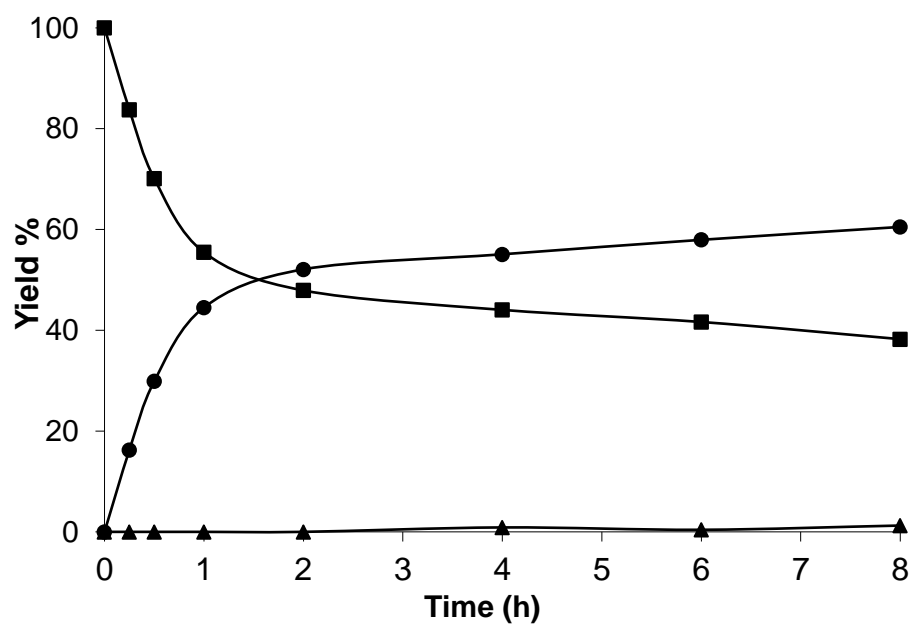
Figure 3b

Figure 4

Figure 5a
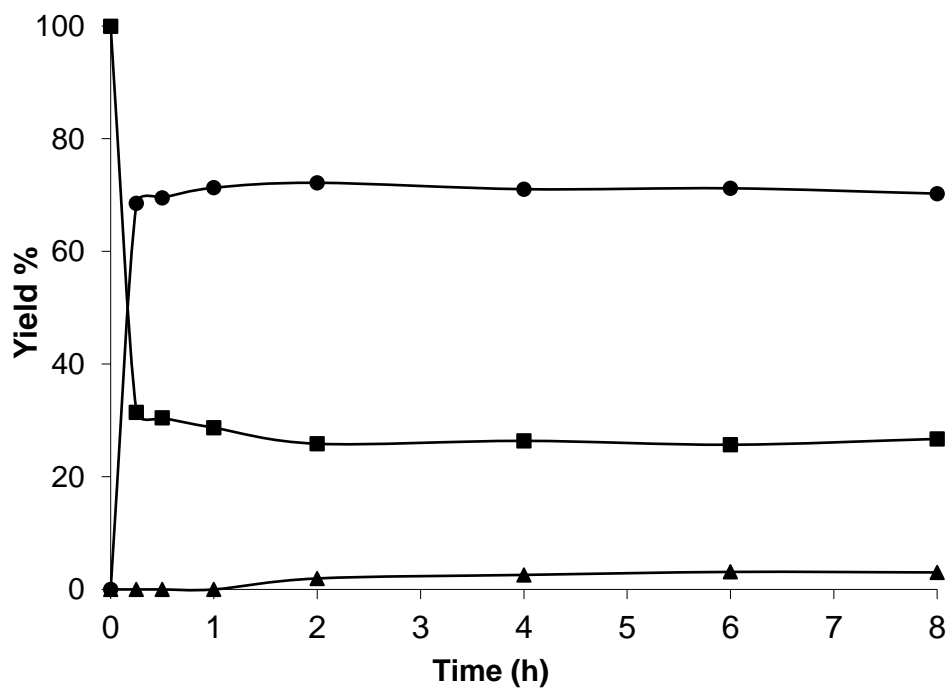
Figure 5b
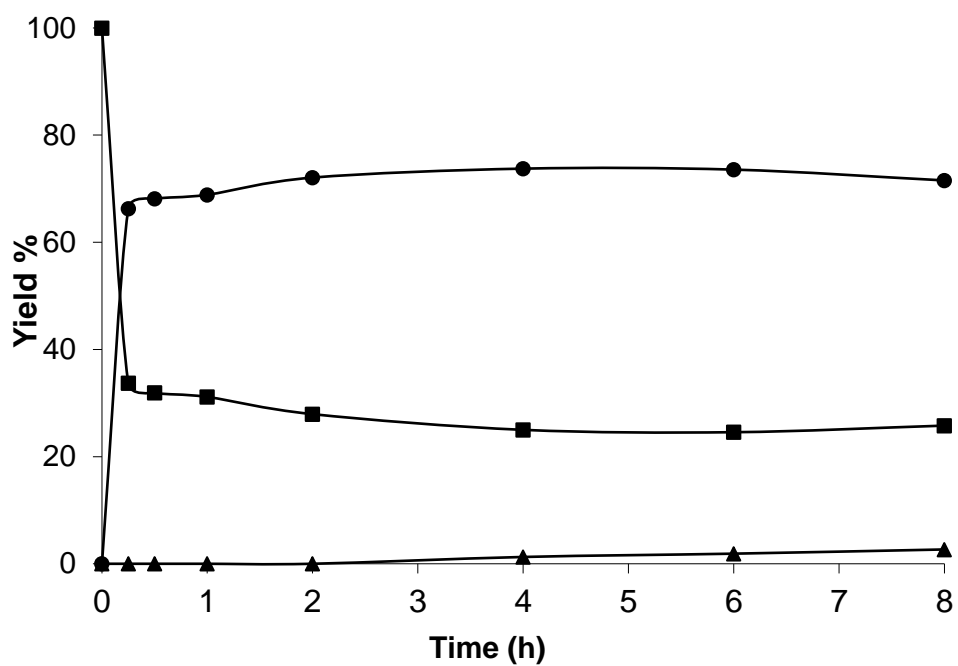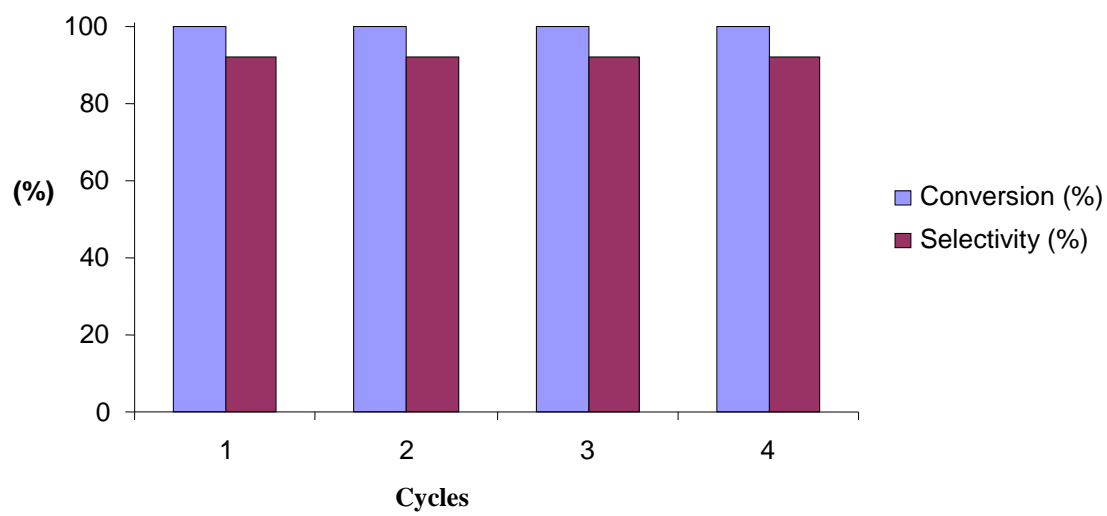
Figure 5c
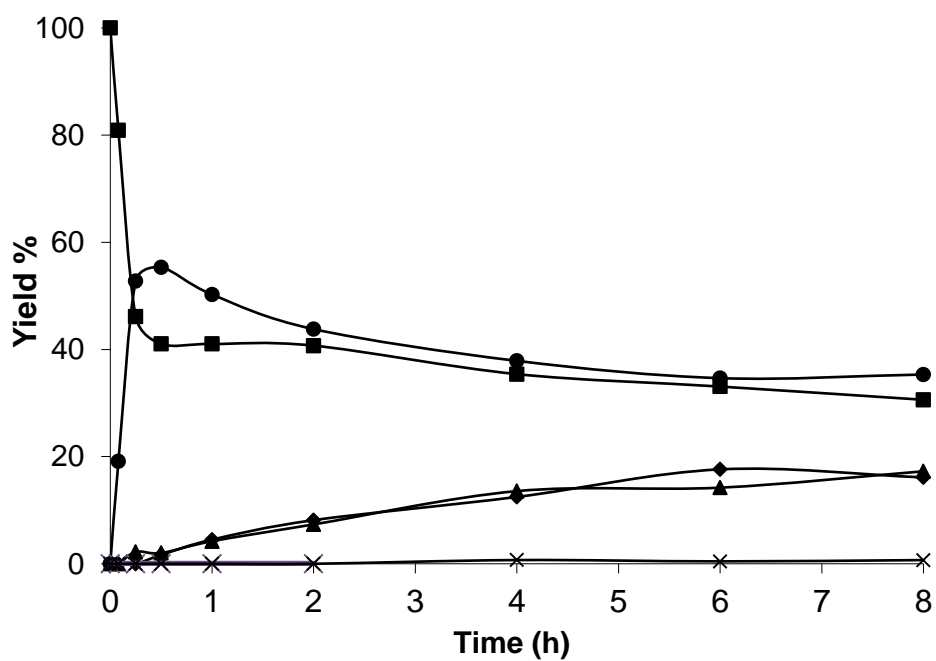
Figure 5d
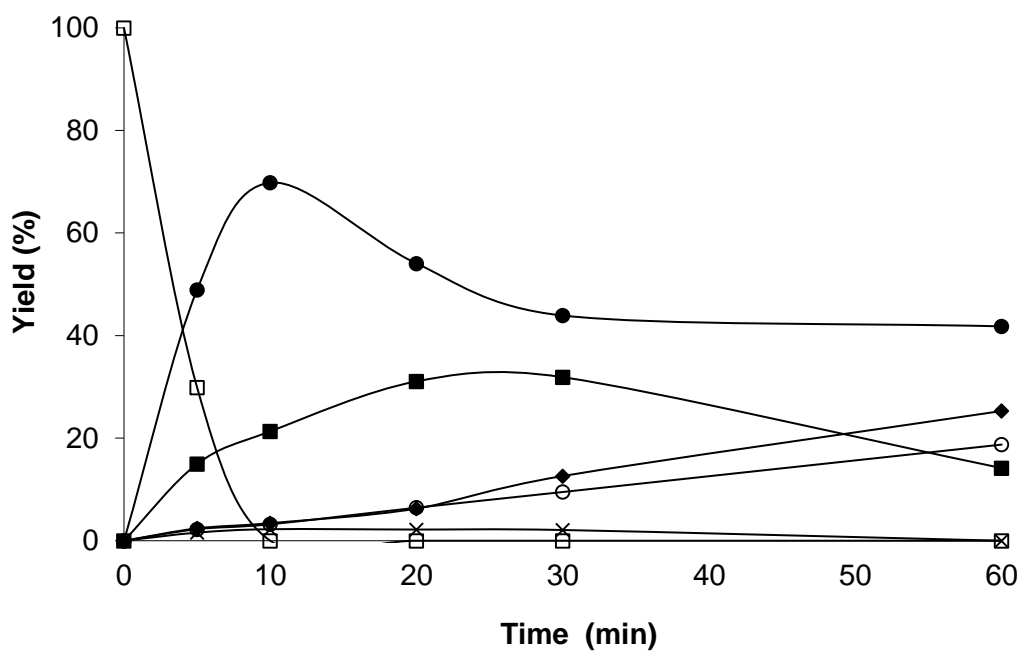
Figure 6a
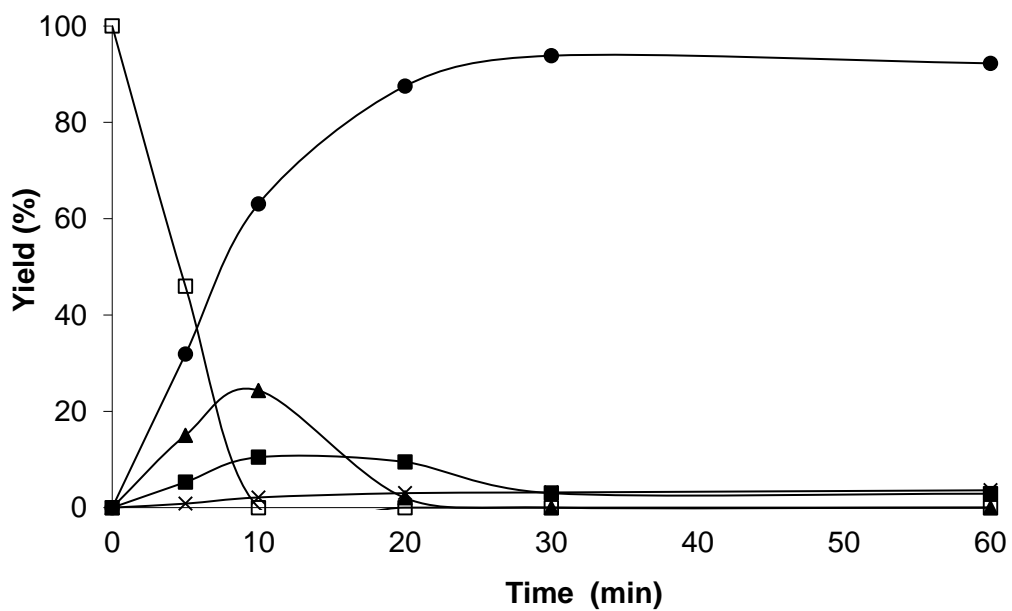
Figure 6b
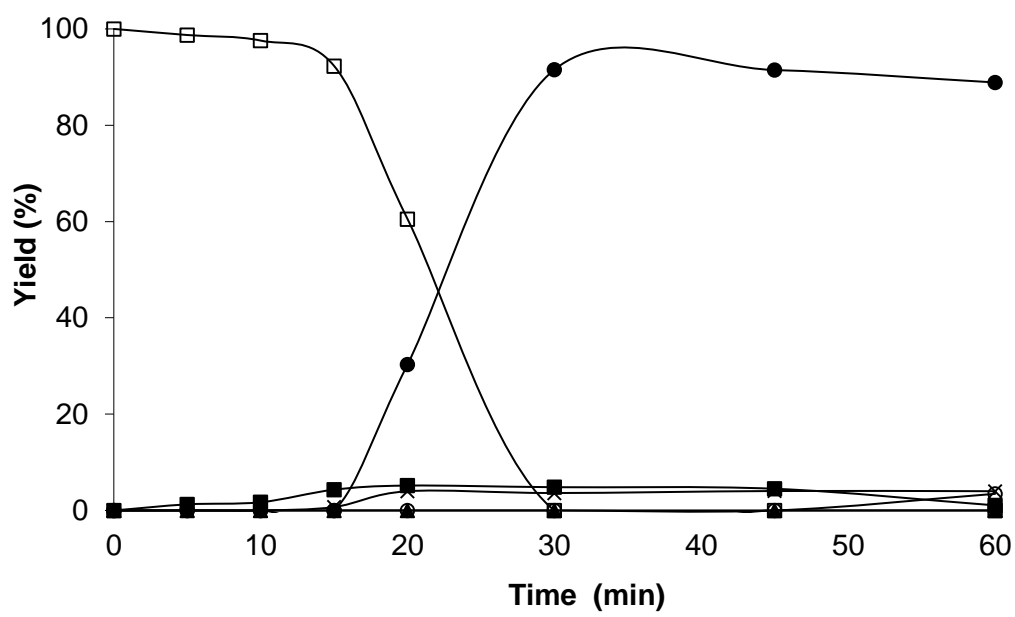
Figure 7

Figure 8
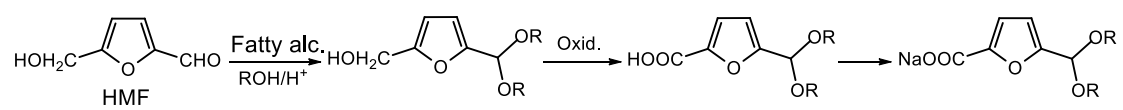
Scheme 1
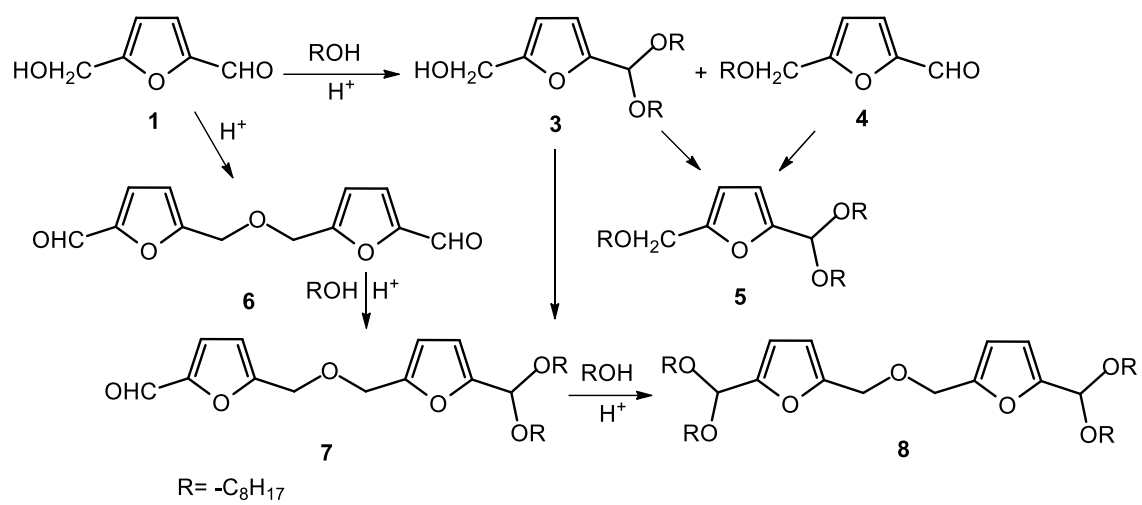
Scheme 2
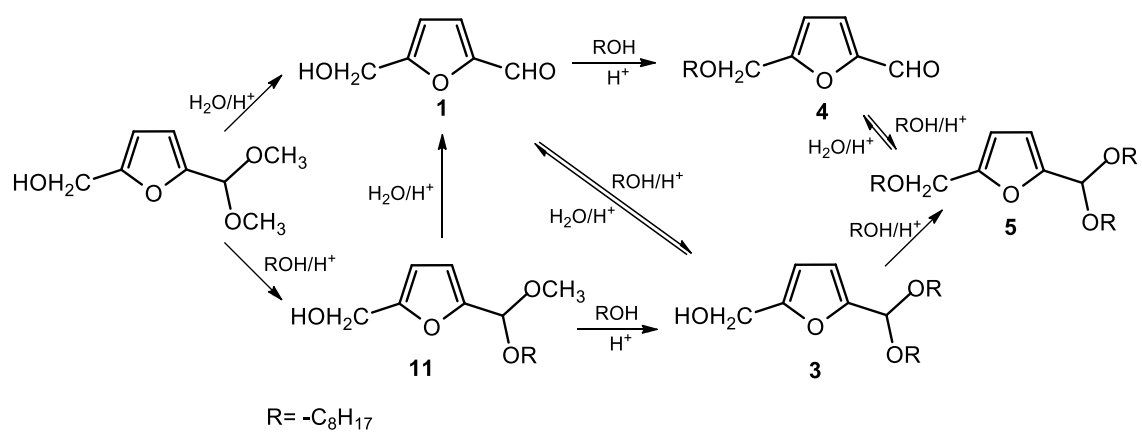
Scheme 3

Table 1. Main characteristic of the different catalysts.

Catalyst	Si/Al	BET (m²/g)	Pore vol. (cm³/g)	150 ºC[a]		250 ºC[a]		350 ºC[a]	
				Brönsted	Lewis	Brönsted	Lewis	Brönsted	Lewis
HBeta	12	602	0.36	65	69	58	56	25	29
0.26NaBeta	12	550	0.35	51	35	41	35	25	28
0.49NaBeta	12	556	0.34	41	28	35	27	23	23
0.58NaBeta	12	572	0.36	40	29	27	24	20	20
1NaBeta	12	556	0.34	33	27	23	21	12	16
1.5NaBeta	12	527	0.35	22	14	15	10	3	9
3.1NaBeta	12	536	0.36	0	0	0	0	0	0
MCM-41	15	1100	0.94	19	62	5	46	4	34
Mordenite	10	550	0.40	67	25	54	25	29	28

[a] Acidity (µmoles pyridine/g catalyst) at different temperatures, calculated using the extinction coefficients given in reference [15].

Table 2. Results of direct acetalization of HMF with n-octanol in the presence of acid catalysts.

Catalyst	Initial rate $(mol\ min^{-1}g^{-1})$	Conversion (%)	Yield (%) 3	4	5	6	7	8	Selectivity 3 (%)
HBeta	0.40	93	14	20	13	15	26	5	15
HBeta[a]	0.12	97	13	17	16	12	33	6	13
Mordenite	0.02	46	5	10	7	7	13	4	11
MCM-41	0.35	100	10	24	16	14	26	10	10
PTSA[b]	158	93	6	14	24	11	31	7	6

Reaction conditions: T=65 ºC, OctOH/HMF=40, 40 wt% (51 mg) of catalyst respect to HMF, 18h. [a] using TFT (5 ml) as a solvent. [b] 0.1 wt% PTSA respect HMF at 3h.

Table 3. Results of direct acetalización of HMF with n-octanol in the presence of Beta zeolite with different percentage of sodium content.

Catalyst	Conversion (%)	Yield (%)						Selectivity **3** (%)
		3	**4**	**5**	**6**	**7**	**8**	
0.26NaBeta	96	25	24	35	11	0	0	27
0.49NaBeta	92	27	25	28	12	0	0	29
1.0NaBeta	88	76	12	0	0	0	0	85
1.5NaBeta	63	63	0	0	0	0	0	100
3.1NaBeta	0	0	0	0	0	0	0	0

Reaction conditions: HMF (1 mmol, 126 mg), n-octanol (40 mmol), 51 mg Beta zeolite (40 wt% of catalyst respect HMF), 24h of reaction. At 65 °C.

Table 4. Influence of temperature in the direct acetalization of HMF with n-octanol using 1.5NaBeta as catalyst.

T (ºC)	Initial rate 3 (mol min^{-1}g^{-1})	Conversion (%)	Yield (%)						Selectivity 3[a] (%)
			3	**4**	**5**	**6**	**7**	**8**	
65	0.51	63	63	0	0	0	0	0	100
80	0.59	65	60	3	2	0	0	0	92
100	0.74	94	49	17	25	0	2	0	98
120	0.82	99	21	24	52	0	2	0	72

Reaction conditions: 126 mg HMF (1 mmol), octanol (40 mmol), 51 mg 1.5NaBeta zeolite (40 wt% of catalyst respect HMF), 5h of reaction. [a] Selectivity to **3** at 65 % of conversion of HMF.

Table 5. Main characteristic of Beta samples prepared in hydroxyl (B) and fluoride (F) media

Catalyst	Si/Al	BET Area(m^2g^{-1})	Water (%)	150 °C	Bronsted 250 °C	Acidity 350 °C
Beta15(B)	15	480	12	90	69	45
Beta25(B)	25	465	10.9	44	20	19
Beta12(F)	12	400	11.5	71	58	40
Beta25(F)	25	470	6.8	46	41	27
Beta50(F)	50	475	5.0	33	25	21

Table 6. Results of acetalization of HMF with n-octanol using Beta zeolite samples with different hydrophobic-hydrophilic character.

Catalyst	Time (h)	Conv. (%)	Yield (%)			Selec. **3** (%)
			3	**4**	**5**	
HBeta	0.5	66	11	18	5	17
	8	93	13	23	11	14
Beta15(B)	0.5	69	67	-	2	97
	8	80	40	18	20	50
Beta25(B)	0.5	70	70	-	-	100
	8	70	67	-	3	96
Beta12(F)	0.5	70	70	-	-	100
	8	75	70	1	4	93
Beta25(F)	0.5	68	66	1	1	97
	8	72	48	12	13	67
Beta50(F)	0.5	57	55	1	1	96
	8	68	35	16	17	52

Reaction conditions: HMF (1 mmol, 126 mg), octanol (40 mmol), 51 mg Beta zeolite (40 wt% of catalyst respect HMF), 8h, 65 °C.

Table 7. Results of the transacetalization of dimethyl acetal **9** with n-octanol in the presence of Beta zeolites with different Na content.

Catalyst	Conversion 9 (%)	Yield (%)					Selectivity 3 (%)
		4	**5**	**1**	**3**	**Others**[a]	
HBeta	100	13	10	32	44	2	44
0.26NaBeta	100	7	12	17	62	2	62
0.58NaBeta	100	5	9	17	66	3	66
1.5NaBeta	100	0	0	2	95	3	95
1.5NaBeta[b]	100	0	0	2	95	3	95
1.5NaBeta-F	100	0	0	2	95	3	95
3NaBeta[c]	9	1	0	6	1	1	7

Reaction conditions: molar ratio **9**:octanol of 1:3.7, catalysts 15 wt% (26 mg) at 65 ºC and 30 min reaction time, using a Dean-Stark apparatus and nitrogen flow. [a] octyl ether of **9** was observed. [b] Octanol was previously dried. Other is octyl ether of 9. [c] 24h of reaction.

Table 8. Comparative one-pot formation of dioctyl acetal (**3**) using HBeta and 1.5NaBeta catalysts[a].

Catalyst	Step 2					
	3	**4**	**5**	**HMF**	**Others**[b]	**S** (%)[c]
1.5NaBeta	95	0	0	2	3	95 (30min)
	90	3	4	1	3	90 (60min)
HBeta[d]	45	7	8	35	5	45 (30min)
	47	11	28	10	4	47 (60min)

[a] Reaction conditions: step 1, HMF(1 mmol), MeOH (5 ml, 123 mmol), 1.5NaBeta (26 mg), at 65 ºC, 2.5h; step 2, octanol (3.7 mmol) at 65 ºC and 30 min. [b] Others is octyl ether of **9**. [c] Selectivity to **3** is calculated as yield of **3** divided by the conversion of **9**. [d] 15 min reaction time during step 1.

Table 9. Results of the synthesis of alkyl acetals of HMF by of one pot process using 1.5NaBeta zeolite as catalyst.

Alcohol	Time (h)	HMF conversion (%)	Yield of dialkyl acetal (%)	Selectivity to dialkyl acetal (%)
Hexanol	0.5	100	98	99
Octanol	0.5	100	95	98
Decanol	2	93	90	97
Dodecanol	2	90	87	96

Reaction conditions: step 1, HMF (1 mmol), MeOH (123 mmol, 5 ml), 1.5NaBeta (26 mg), at 65 ^{o}C, 2.5h; step 2, alcohol (3.7 mmol) at 65 ^{o}C.

LEDGEND OF FIGURES

Figure 1. IR spectra of Beta zeolites with different percentage of Na content. B and L bands refer to Bronsted and Lewis acid sites determined by adsorption-desorption of pyridine at 150 °C. Additionally, adsorption bands at 1592 and 1442 cm-1 corresponds to interaction of sodium cations with pyridine.

Figure 2. Acetalization of HMF with n-octanol in the presence of 1.0NaBeta zeolite. HMF (■), **3** (●), 4 (♦).

Figure 3. Acetalization of HMF with n-octanol in the presence of a) fresh 1.5NaBeta zeolite and b) 1.5NaBeta submitted to Soxhlet extraction. HMF **(■), 3 (●), 5 (▲)**.

Figure 4. IR spectra of Beta samples at the OH stretching region, after heated at 400 °C under vacuum. The vibration band at 3745 cm^{-1} is assigned to the OH stretching of silanol group.

Figure 5. Results of acetalization reaction between HMF and n-octanol using Beta zeolite samples prepared in hydroxyl (B) and fluoride (F) media: a) Beta15(B), b) Beta25(B), c) Beta12(F), d) Beta50(F). HMF (■), **3** (●), 4 (♦), **5 (▲)**, others (×).

Figure 6. Yield versus time plot for transacetalization reaction of **9** with octanol in the presence of a) HBeta, b) 1.5NaBeta: HMF (■), **5 (○), 3 (●)**, 4 (♦), **9** (□),**11 (▲),** others (×).

Figure 7. One-pot formation of HMF dioctyl acetal using 1.5NaBeta as catalyst; HMF (■), **5 (○), 3 (●), 9** (□), others (×).

Figure 8. Reuses of 1.5NaBeta catalyst in the one-pot formation of HMF dioctyl acetal.

LEDGEND OF SCHEMES

**Scheme 1.** Synthesis of surfactant molecules from HMF

Scheme 2. Possible routes for formation of **3** and by-products through direct acetalization of **1** with n-octanol

Scheme 3. Routes for formation of of **3** and by-products through transacetalization of **9** with n-octanol

Graphical abstract

From biomass to chemicals: Synthesis of precursors of biodegradable surfactant molecules by one pot two-steps selective acetalization and transacetalization of 5-hydroxymethylfurfural with zeolite catalysts

K. S. Arias, Saud I. Al-Resayes, M. J. Climent,* A. Corma,* S. Iborra
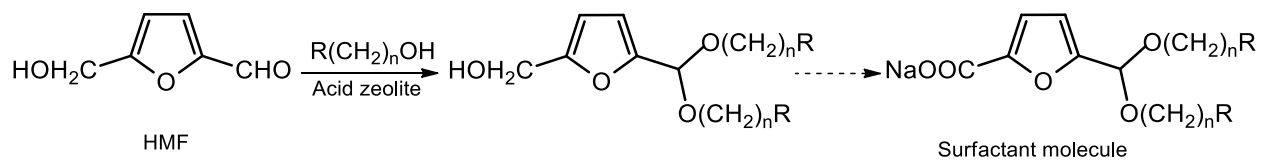
Precursors of surfactants molecules have been obtained by one pot two-steps selective acetalization and transacetalization of 5-hydroxymethylfurfural with long chain alkyl alcohols by controlling zeolite acidity and polarity