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From Biomass to Chemicals: Synthesis of Precursors of Biodegradable Surfactants from 5-Hydroxymethylfurfural

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

Introduction

5-Hydroxymethylfurfural (HMF) is considered as an important platform molecule for biorenewable fuel[1] and chemical production[2] as it can be obtained by the dehydration of fructose, glucose, and cellulose.[2–4] HMF is a versatile molecule that can be converted into several derivatives with multiple applications, for example, pharmaceuticals, antifungals, and polymer precursors. Recently, some transformations of HMF into monomers able to replace terephthalic, isophthalic, and adipic acids in the manufacture of polyamides, polyesters, and polyurethanes[5] have been performed by our group by 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 detergents, pharmaceuticals, cosmetics, and food. They form micelles and vesicular microaggregates, the properties of which depend on the composition and structure of the polar head groups and the length and shape of the hydrophobic hydrocarbon component. With this in mind, we have studied the selective acetalization of the carboxaldehyde group of HMF with fatty alcohols by using zeolites as acid catalysts. This type of molecule can be transformed into surfactants by subsequent oxidation of the free hydroxyl group to form a carboxylic group or its salts (Scheme 1). Although HMF derivatives have been mentioned as precursors of surfactants, we did not find any reports of such in the literature.

The acetalization of carbonyl groups can be performed by the direct reaction of carbonyl compounds with alcohols or by the 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 and ion-exchanger resins,[7] titania silicalite,[8] mesoporous materials,[9] and zeolites[10] have been reported as solid catalysts that perform acetalization reactions with excellent results. Previously we have shown that zeolites and mesoporous aluminosilicates[11] are suitable acid catalysts to obtain nonionic surfactants, such as alkylglucosides, by the selective acetalization of glucose with fatty alcohols. Therefore, for the selective acetalization of HMF, acid zeolites appear to be promising catalysts as, in addition to the general advantages associated with the use of solid catalysts, they can be synthesized with different crystalline structures, pore sizes, acid strength distributions, and hydrophobicity. Notably, HMF is a bifunctional molecule that bears alcohol and aldehyde functionalities, which are both able to react with alcohols in the presence of acid catalysts to give ethers and acetals, respectively. Therefore, it would be of interest to be able to tailor the solid catalyst selectively to direct the reaction to ethers or acetals, and we will present how this can be achieved by using zeolite catalysts.

Results and Discussion

Taking into account the dimensions of the desired product 5-(dioctoxymethyl)-2-hydroxymethylfurane (**3**) (Scheme 2), we started our study by performing the acetalization of HMF with *n*-octanol in the presence of structured micro- and mesopo-

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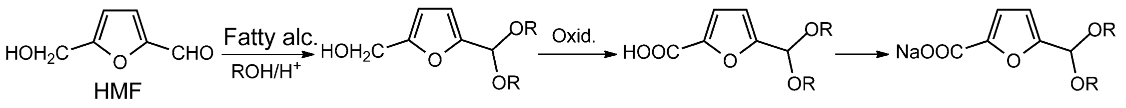
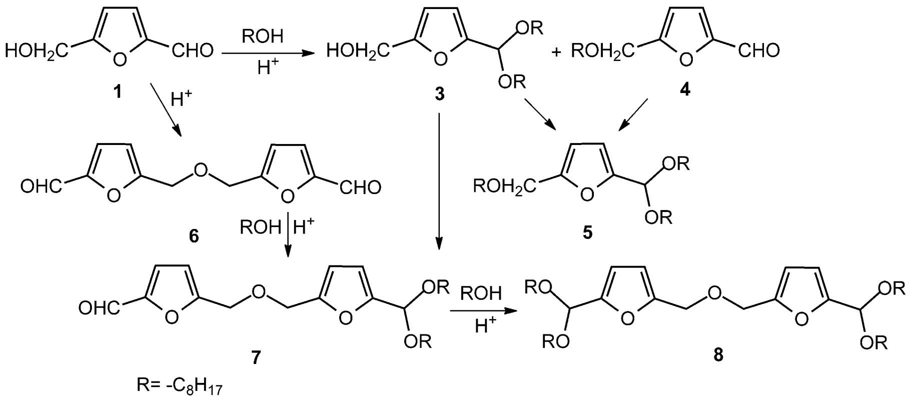


Scheme 1. Synthesis of surfactant molecules from HMF.

rous acid catalysts, such as a large pore tridirectional (Beta) and a monodirectional (Mordenite) zeolite, as well as a mesoporous aluminosilicate (MCM-41) (Table 1). Thus, when the acetalization reaction of HMF was performed with *n*-octanol in an *n*-octanol/HMF molar ratio of 40 in the presence of these catalysts at 65 °C, it was observed that although the Beta zeolite and the mesoporous MCM-41 gave rise to high conversions of HMF, mordenite gave rise to a lower conversion, which could be attributed to fast poisoning by pore blocking. However, a complex mixture of products was always formed (Scheme 2), and the yield of **3** was very low in all cases (Table 2). The main byproducts observed were the ether 5-(octyloxymethyl)furfural (**4**) and its corresponding dioctyl acetal **5**. However, compounds that came from the dimerization of HMF such as 5,5′-[oxy-bis(methylene)]bis-(2-furfural) (**6**) and the corresponding mono- and bis(dioctyl) acetals **7** and **8** were also obtained (Table 2). As shown in Figure S1, **3**, **4**, and **6** have a primary character, whereas **5**, **7**, and **8** are secondary products. Octyl levulinate, obtained from ring opening by the hydrolysis of HMF followed by esterification in acidic media, was not detected. Scheme 2 presents the different possible routes for the formation of the byproducts detected. Additionally, if a solvent such as trifluorotoluene (TFT) was used, no improvement in selectivity to **3** was observed (Table 2).

If the reaction was performed using *p*-toluenesulfonic acid (PTSA) as a homogeneous Brønsted acid catalyst, the distribution of products obtained was similar to that achieved with Beta zeolite and MCM-41. The results indicate that, under these reaction conditions, the strong acid sites in the homogeneous catalyst and the stronger ones that exist in the aluminosilicate catalysts mainly favor competitive etherification reactions of the hydroxymethyl group (to give **4**) as well as the dimerization of HMF (to give **6**) and its subsequent reactions with *n*-octanol (to give **7** and **8**).



Scheme 2. Possible routes for the formation of **3** and byproducts through the direct acetalization of HMF with *n*-octanol.

Table 1. Main catalyst characteristics.

Catalyst	Si/Al	BET [$m^2 g^{-1}$]	Pore volume [$cm^3 g^{-1}$]	Acidity[a] [$\mu mol_{pyridine} g_{cat.}^{-1}$]					
				150 °C		250 °C		350 °C	
				B[b]	L[c]	B[b]	L[c]	B[b]	L[c]
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 at different temperatures calculated from the extinction coefficients given in Ref. [15]. [b] Brønsted acidity. [c] Lewis acidity.

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

Catalyst	Initial rate [$mol\,min^{-1} g^{-1}$]	Conversion [%]	Yield [%]						Selectivity to **3** [%]
			3	**4**	**5**	**6**	**7**	**8**	
HBeta	0.40	93	14	20	13	15	26	5	15
HBeta[b]	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[c]	158	93	6	14	24	11	31	7	6

[a] Reaction conditions: 65 °C, OctOH/HMF = 40, catalyst (51 mg, 40 wt% with respect to HMF), 18 h. [b] TFT (5 mL) was used as a solvent. [c] PTSA (0.1 wt% with respect to HMF) after 3 h.

Figure S2 presents the selectivity to **3** versus conversion for the different catalysts tested.

As etherification is a more demanding reaction than acetalization from the point of view of the acid strength, one way to increase the selectivity to **3** would be to decrease the number of strong Brønsted acid sites, which could be achieved by a partial exchange of protons with Na^+ in the zeolite framework. To investigate this, a series of Na-exchanged Beta zeolites with Na contents from 0.26–3 wt% (calculated as Na_2O) were prepared and tested in the reaction. Figure 1 displays the IR spectra of pyridine adsorbed on the Beta samples with different Na contents. B and L correspond to pyridine protonated by Brønsted acids and pyridine coordinated with Lewis acids, respectively. Two absorption bands at 1592 and 1442 cm^{-1} were observed that correspond to the interactions of Na^+ with pyridine, which increase in intensity with increasing Na content.[12] Table 3 and Figures 2 and 3 show the catalytic results obtained with these materials. These results show that an increased Na content leads to an increased selectivity to **3**. More specifically, with Beta zeolite samples with a Na content higher than 1 wt%, the formation of ethers, mainly **6**, was drastically suppressed. Moreover, if all of the acid sites of the zeolite were exchanged by Na^+ (3.1NaBeta, see Table 1), the catalytic activity was totally suppressed.

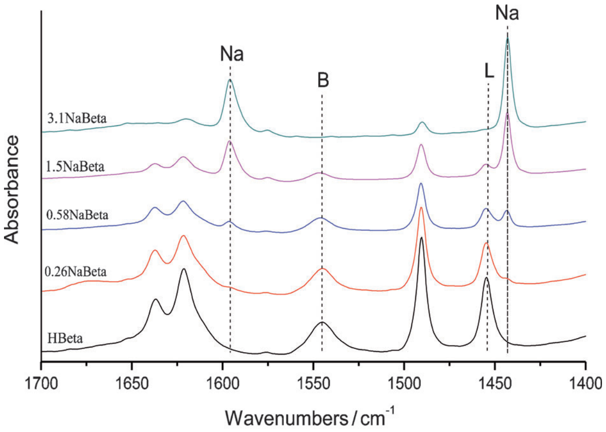


Figure 1. IR spectra of Beta zeolites with different Na contents. The B and L bands arise from Brønsted and Lewis acid sites determined by the adsorption–desorption of pyridine at 150 °C. Additionally, adsorption bands at 1592 and 1442 cm^{-1} correspond to the interaction of Na^+ with pyridine.

Table 3. Results of the direct acetalization of HMF with *n*-octanol in the presence of Beta zeolites with different Na contents.[a]

Catalyst	Conversion [%]	Yield [%]						Selectivity to **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	66	0	0	0	0	0	100
3.1NaBeta	0	0	0	0	0	0	0	0

[a] Reaction conditions: HMF (1 mmol, 126 mg), *n*-octanol (40 mmol), Beta zeolite (51 mg, 40 wt% catalyst with respect to HMF), 24 h, 65 °C.

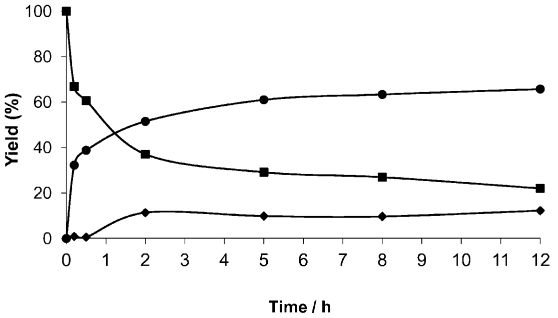


Figure 2. Acetalization of HMF with *n*-octanol in the presence of 1.0NaBeta zeolite. HMF ■, **3** ●, **4** ◆.

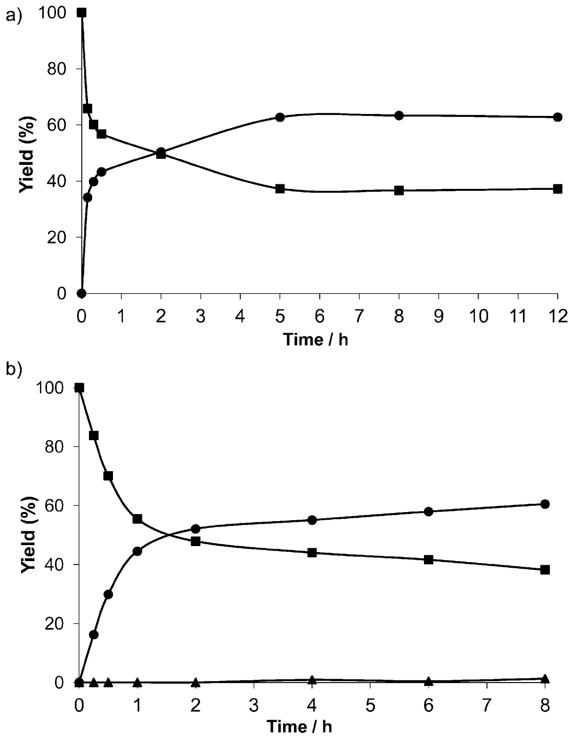


Figure 3. Acetalization of HMF with *n*-octanol in the presence of a) fresh 1.5NaBeta zeolite and b) 1.5NaBeta after Soxhlet extraction. HMF ■, **3** ●, **5**▲.

The results presented in Table 3 and Figure S3 show that a Beta zeolite with a Na content of 1.5 wt% is a very selective catalyst to perform the acetalization. However, the reaction stops after 8 h and the final yield obtained was 63%. The Beta zeolites with Na contents of 1 and 1.5 wt% show a similar kinetic behavior (initial reaction rate) and both catalysts deactivate quickly (Figures 2 and 3a). This deactivation could be associated with a strong adsorption of the products onto the catalyst surface at lower reaction temperatures. To confirm this, the IR spectrum of 1.5NaBeta after the acetalization reaction was obtained, and a wide absorption band at 3500 cm^{-1} (associated with hydroxyl groups) and bands at 2900 cm^{-1} (corresponding to C–H vibrations associated with the *n*-octanol alkyl chain) were observed. If the used 1.5NaBeta) was Soxhlet extracted by using acetonitrile as the solvent, *n*-octanol (11 wt%) was the only compound detected by GC–MS in the organic phase. However, after the extraction process, 4 wt% of organic material remained on the solid catalyst (thermogravimetric analysis). The acetalization reaction of HMF with *n*-octanol was performed in the presence of the catalyst after Soxhlet extraction, and the results show a decrease of the initial rate of reaction (0.20 mol min^{-1} g^{-1}) compared with that of the fresh catalyst (0.43 mol min^{-1} g^{-1}), although a similar yield (60%) of **3** was obtained if the reaction time was prolonged (Figure 3 b). These results confirm that an important part of the catalyst deactivation is reversible and is mainly a result of the adsorption of *n*-octanol onto the surface of the catalyst. The activity and selectivity to **3** were totally recovered when the used catalyst was calcined at 580 °C for 3 h.

From an operational point of view, the amounts of reactants and products adsorbed could be diminished by performing the reaction at a higher temperature. Indeed, practically full conversion was achieved at temperatures >100 °C (Table 4), although under these reaction conditions, the selectivity to **3** decreases and competitive etherification reactions are promoted. Notably, **5** (52%) is the major product obtained at 120 °C (Scheme 2).

These results 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 and competes with HMF for the zeolite adsorption sites, which leads to a reversible deactivation of the catalyst.

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

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

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

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

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

Catalyst	Si/Al	BET area [m^2 g^{-1}]	Water [%]	Brønsted acidity [µmol$_{\text{pyridine}}$ g$_{\text{cat.}}^{-1}$] 150 °C	250 °C	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

The resultant samples were tested for the acetalization of HMF with *n*-octanol, and the results are given in Table 6. By analysis of these results, it can be seen that, regardless of the nature of the sample, selectivity to **3** is low for the Na-free HBeta sample.

When the acetalization was performed by using Beta zeolite synthesized in OH$^-$ media, such as Beta15(B) and Beta25(B), which have large amounts of silanol groups, a higher activity was obtained for the zeolite with the highest Si/Al ratio (Beta25(B)), which indicates that some hydrophobicity is required to obtain a good yield and selectivity to **3** (Figure 5 a and b). However, if the more hydrophobic Beta zeolite samples (i.e., those free of connectivity defects, Beta(F)), were used, the results in Table 6 show that the most active catalyst has a Si/Al ratio of 12, which represents a compromise between a large amount of acid sites and polarity (Figure 5 c 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 maintained. For instance, if Beta12(F) is used in a second cycle, the conversion decreases

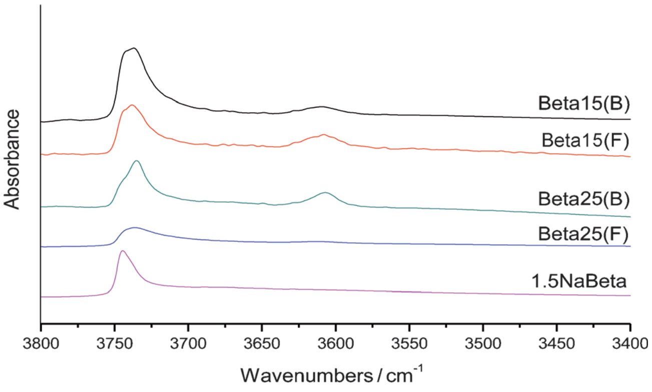


Figure 4. The OH stretching region of the IR spectra of Beta samples after heating at 400 °C under vacuum. The vibration band at 3745 cm^{-1} is assigned to the OH stretch of the silanol group.

Table 6. Results of the acetalization of HMF with *n*-octanol by using Beta zeolites with different hydrophobic/hydrophilic characters.[a]

Catalyst	*t* [h]	Conversion [%]	Yield [%] 3	4	5	Selectivity to **3** [%]
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

[a] Reaction conditions: HMF (1 mmol, 126 mg), *n*-octanol (40 mmol), Beta zeolite (51 mg, 40 wt% catalyst with respect to HMF), 8 h, 65 °C.

from 75 to 50%. However, when the sample is calcined at 580 °C the initial activity is restored (Figure S4).

In conclusion, it appears that by controlling the acidity, polarity, and reaction temperature, it is possible to direct the reaction between HMF and *n*-octanol to **3** or the ethers **4** and **5**. All of the products formed can 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 **3** or **5.** However, despite the large ratios of *n*-octanol to HMF used and the optimization of acid sites and polarity, we could not obtain, by direct acetalization, yields of **3** greater than 70%.

Transacetalization

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

Compound **9** was prepared from HMF and MeOH by using 1.5NaBeta zeolite as the catalyst. The reaction was performed at 65 °C, and after 2.5 h, 99% selectivity to **9** with 99% conversion of HMF was obtained. Only traces of **9** were detected in the reaction media. Then, starting with **9**, we performed the transacetalization reaction with *n*-octanol in the presence of Beta zeolites with different Na contents (Table 7). The reactions were performed with the previously optimized molar ratio of **9** to *n*-octanol of 1:3.7, and 15 wt% of catalyst (with respect to **9**) at 65 °C, and MeOH was removed by distillation by using a Dean–Stark apparatus.

Analysis of the results in Table 7 shows that HBeta zeolite gives a low selectivity to **3** and promotes mainly etherification

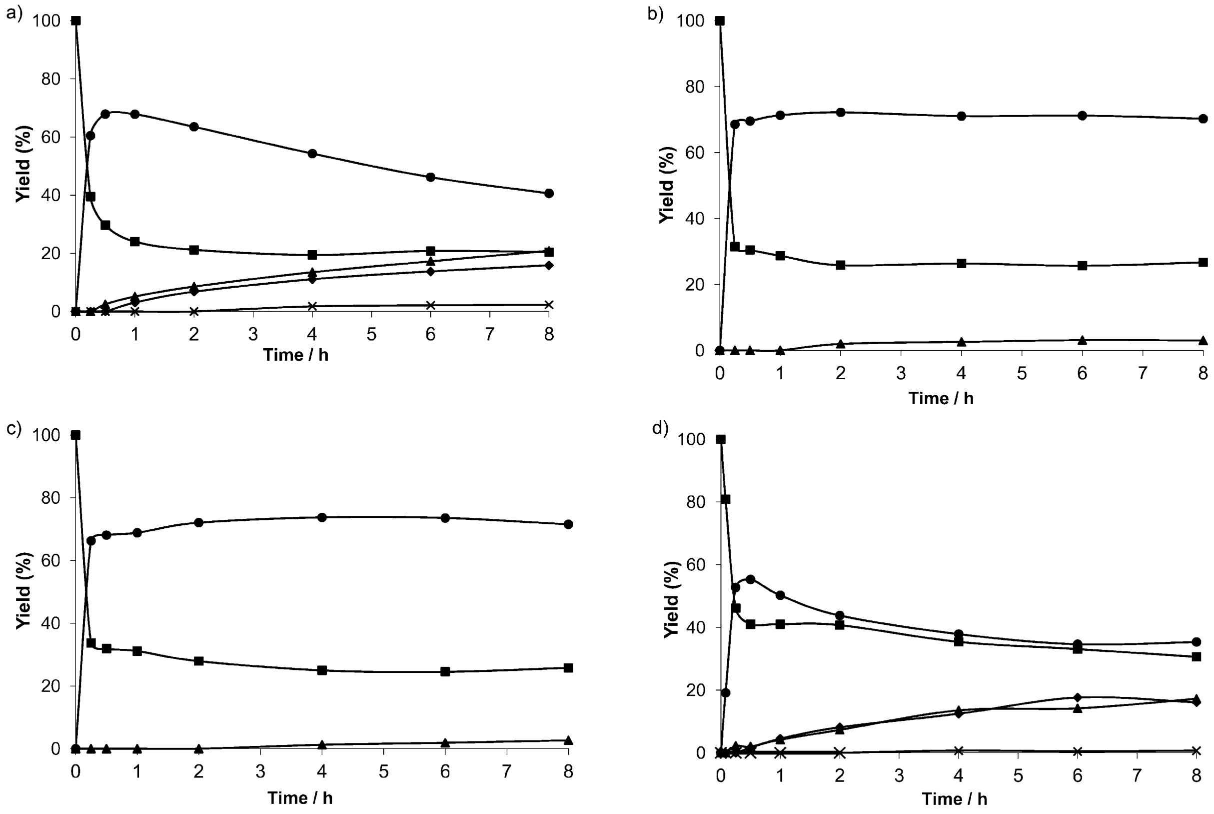


Figure 5. Results of acetalization reaction between HMF and *n*-octanol that used Beta zeolite samples prepared in hydroxyl (B) and fluoride (F) media: a) Beta15(B), b) Beta25(B), c) Beta12(F), d) Beta50(F). HMF ■, **3**●, **4**◆, **5**▲, others×.

Table 7. Results of the transacetalization of **9** with *n*-octanol in the presence of Beta zeolites with different Na contents.[a]

Catalyst	Conversion of **9** [%]	Yield [%] **4**	**5**	**1**	**3**	others[b]	Selectivity to **3** [%]
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[c]	100	0	0	2	95	3	95
1.5NaBeta-F	100	0	0	2	95	3	95
3NaBeta[d]	9	1	0	6	1	1	7

[a] Reaction conditions: Molar ratio of **9**/*n*-octanol 1:3.7, catalyst (26 mg, 15 wt%), 65 °C, 30 min, using a Dean–Stark apparatus and N_2 flow. [b] Octylether of **9** was observed. [c] n-Octanol was previously dried. [d] 24 h reaction time.

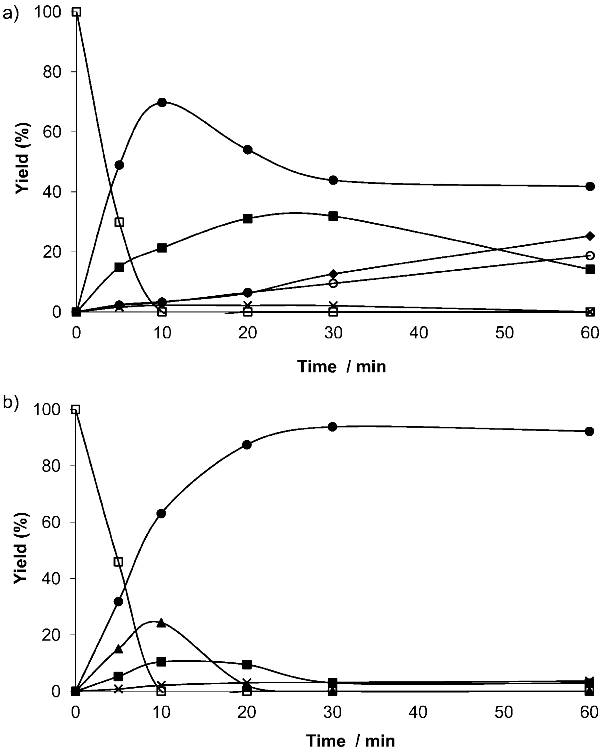


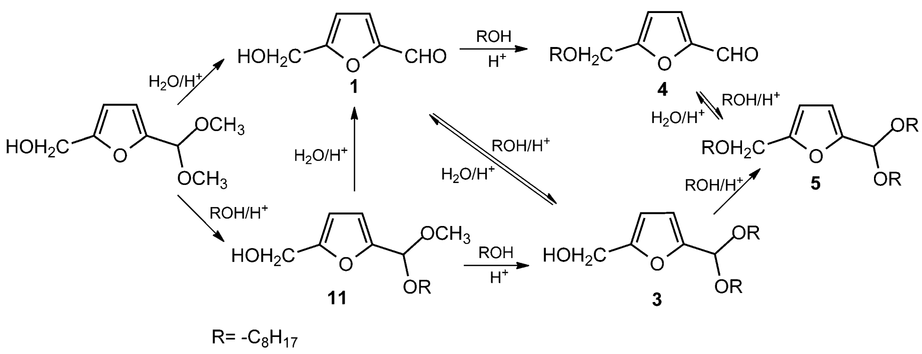
Figure 6. Yield vs. *t* plot for the transacetalization reaction of **9** with *n*-octanol in the presence of a) HBeta, b) 1.5NaBeta. HMF ■, **5**○, **3**●, **4**◆, **9**□, **11** ▲, others×.

reactions to give **4** and **5** and the hydrolysis of **9** to give HMF. However, the selectivity to **3** increases considerably with a catalyst with an increased Na content to reach 95% selectivity if the Na content was 1.5 wt%. Dimerization of HMF to give **6** was totally suppressed.

Figure 6a and b display the kinetics curves for HBeta and NaBeta. In the case of HBeta zeolite (Figure 6a), **3** reaches a maximum concentration and then decreases with time as etherification to **5** and possibly hydrolysis to HMF occur. Indeed, the hydrolysis of **9** mainly gives HMF, which undergoes subsequent etherification to give **4**. The formation of HMF is a result of the water released during the etherification reactions as well as the water that remains on the zeolite. The water content of the HBeta zeolite after activation was 12.5 wt%.

A different kinetic behavior is observed with the 1.5NaBeta catalyst (Figure 6b). 1.5NaBeta zeolite promotes the transacetalization of **9** with *n*-octanol to give an intermediate methyloctyl acetal of HMF **11**, which further reacts with another molecule of *n*-octanol to give **3** (Scheme 3). Meanwhile, secondary reactions are minimized as a consequence of the lower acidity of the 1.5NaBeta catalyst (Table 1). In this case, the formation of HMF is also mainly attributed to the residual water present in 1.5Beta zeolite (10 wt%), although the rate of the formation of HMF was approximately twofold lower than that with HBeta, and the final HMF concentration in the reaction medium was considerably lower (Table 7). These results indicate that the presence of strong acid sites on the catalyst is also detrimental for the transacetalization reaction as they catalyze the hydrolysis of **9**. To avoid the hydrolysis of **9**, we performed an additional experiment by using dry *n*-octanol in the presence of 1.5NaBeta zeolite. In this case, the rate of formation of HMF was an order of magnitude lower than that with undried *n*-octanol, although the concentration of HMF remained the same over a long reaction time (Table 7).

At this point, it appeared to us that one way to reduce the competitive hydrolysis of the acetals could be by using catalysts with a higher hydrophobic character, which would adsorb less water (Table 5). To test 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.



Scheme 3. Routes for the formation of **3** and byproducts through the transacetalization of **9** with *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 to give **9** and the subsequent transacetalization of **9** with *n*-octanol to give **3**. Taking into account these results, it appeared to us that it would be of interest to design a one-pot process in which both reactions occur in a single vessel. To achieve this, HMF was reacted first with MeOH in the presence of 1.5NaBeta zeolite at 65 °C for 2.5 h to achieve the maximum yield of **9** (100 % HMF conversion with 99 % selectivity to **9**). At this point, *n*-octanol was added to the reaction mixture in a molar ratio of **9**/octanol of 1:3.7, and MeOH was removed by bubbling a stream of N_2 through the suspension. The results are compared with those obtained with the most acidic HBeta zeolite in Table 8. 1.5NaBeta zeolite is able to perform very efficiently in the one-pot process to achieve a 95 % yield of **3** in 30 min. If the reaction time is prolonged to 1 h, a decrease in selectivity is observed owing to the consecutive transformation of **3** into **4** and **5**. Figure 7 presents the evolution of the reactants and products with time. At the beginning of the reaction, there is an induction period in which **3** is not formed, the rate of disappearance of **9** is very low, and HMF is the only product formed. This behavior can be explained by taking into account the experimental procedure. At the beginning of the reaction, the excess MeOH used in the first step remains in the reaction media as a solvent and reactant, which shifts the equilibrium towards the formation of **9**. As the MeOH is removed, the transacetalization of **9** with *n*-octanol occurs with a high reaction rate to achieve the maximum yield and selectivity to **3** after 30 min.

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

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

[a] Reaction conditions: step 1: HMF(1 mmol), MeOH (5 mL, 123 mmol), 1.5NaBeta (26 mg), 65 °C, 2.5 h; step 2: *n*-octanol (3.7 mmol), 65 °C, 30 min. [b] Others is octylether of **9** in this case. [c] Selectivity to **3** is calculated as the yield of **3** divided by the conversion of **9**. [d] 15 min reaction time in step 1.

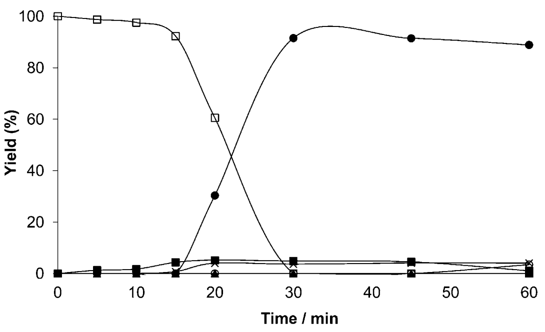


Figure 7. One-pot formation of **3** that used 1.5NaBeta zeolite as catalyst. HMF ■, **5** ○, **3**●, **9**□, others×.

Comparatively, the most acidic HBeta zeolite was much less selective achieved only a maximum selectivity of 47 % to **3** (Table 8).

Catalyst recycling in the one-pot process

To test the reusability of the 1.5NaBeta catalyst, it was reused in various cycles. After each reaction, the zeolite was collected by filtration, washed thoroughly with acetone, and activated under vacuum before each reuse. Figure 8 shows that the activity and selectivity were maintained at least for the four consecutive cycles studied without a decrease in activity or selectivity.

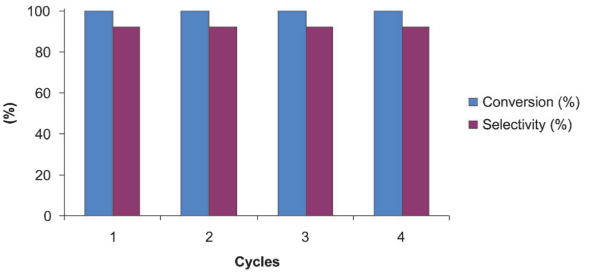


Figure 8. Reuse of 1.5NaBeta zeolite catalyst in the one-pot formation of **3**.

Finally the one-pot process was extended to other aliphatic alcohols as it is known that an important property of surfactant molecules is biodegradability, which is related to the length and branching of the alkyl chain of the alcohol. We selected unbranched alkyl alcohols (between C_6 and C_{12}) to obtain the corresponding alkyl acetal in a one-pot reaction. The results obtained show the general applicability of the catalyst and procedure to obtain precursors of molecules with surfactant properties (Table 9).

Table 9. Results of the synthesis of alkyl acetals of HMF by a one-pot process that used 1.5NaBeta zeolite as a catalyst.[a]

Alcohol	*t* [h]	HMF conversion [%]	Formation of dialkyl acetal	
			yield [%]	selectivity [%]
hexanol	0.5	100	98	99
octanol	0.5	100	95	98
decanol	2	93	90	97
dodecanol	2	90	87	96

[a] Reaction conditions: step 1: HMF (1 mmol), MeOH (123 mmol, 5 mL), 1.5NaBeta (26 mg), 65 °C, 2.5 h; step 2: alcohol (3.7 mmol), 65 °C.

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 this reaction, and the main products obtained are 5-(dioctoxymethyl)-2-hydroxymethylfurane (**3**), the ether 5-(octyloxymethyl)furfural (**4**), and its corresponding dioctyl acetal **5**. By controlling the zeolite acidity and polarity as well as the reaction temperature, it is possible to modify the product selectivity. Control of the 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 two-step one-pot process that involved the acetalization of HMF with MeOH to form the dimethyl acetal **9** and transacetalization with *n*-octanol gave rise to yields of **3** of 95 %. The one-pot process catalyzed by partially Na-exchanged Beta zeolite has been extended to alcohols from C_6 to C_{12} with excellent activities and selectivities.

Experimental Section

HMF ($\geq$99 %), *n*-hexanol ($\geq$98 %), *n*-octanol ($\geq$99 %), *n*-decanol (98 %), dodecanol ($\geq$99 %), and hexadecane (99 %) were purchased from Aldrich and methanol (99.99 %) was purchased from Scharlau.

Materials

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

Na-exchanged Beta zeolites (0.26NaBeta, 0.49NaBeta, 1.0NaBeta, 1.5NaBeta, and 3.0NaBeta, in which the number indicates the percentage [wt %] of Na) were prepared by impregnating commercial HBeta zeolite with different aqueous solutions of CH_3COONa followed by drying at 100 °C overnight and then calcination at 580 °C for 3 h. The Na contents of the samples were determined by chemical analysis (Varian 715-ES inductively coupled plasma optical emission spectrometer) after dissolution of the solids in a HNO_3/HF solution.

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

Specific surface areas and pore diameters were measured by N_2 adsorption at 77 K by using a Micrometrics ASAP 2000 apparatus. Thermogravimetric analysis (TGA) was performed by using a Netzsch STA 409 EP thermal analysis with approximately 20 mg of sample and a heating rate of 10 °C min^{-1} in an 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 °C under vacuum (1 Torr) for 2 h. The system was cooled to room temperature, and a mixture of HMF and *n*-octanol (1:40) previously heated to the desired reaction temperature was added to the catalysts. The mixture was heated by using a system equipped with a silicone bath, magnetic stirrer, and condenser. Samples were taken at regular intervals, diluted with acetone, and the catalyst was separated by centrifugation. The products in the solution were analyzed by using GC–MS, and the conversion of HMF and yields of the different compounds were determined by using GC with hexadecane as the external standard.

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

Synthesis of **9**: A solution of HMF (500 mg) in MeOH (28 mL) heated to 65 °C was added to activated 1.5NaBeta zeolite (100 mg), and the mixture was stirred for 2.5 h. The catalyst was removed by filtration and the MeOH was eliminated by heating under reduced pressure. The yellow concentrate obtained corresponded to **9** ($\geq$ 99 %) and was used without any further purification in the transacetalization reactions.

GC–MS for **9**: m/z (%) = 172 [M^+, $C_8H_{12}O_4$] (10), 141 (100), 125 (5), 109 (7), 97 (5), 81(14).

Transacetalization of **9** with *n*-octanol: The transacetalization reaction of **9** with *n*-octanol was carried out in a batch glass reactor equipped with a magnetic stirrer, a reflux condenser, and a Dean–Stark trap immersed in a thermostated silicone bath under a N_2 flow. Before reaction, the catalyst (26 mg) was activated in situ as described above. A preheated (65 °C) mixture of **9** (1 mmol) and *n*-octanol (3.7 mmol) was added to the catalyst, and the mixture was stirred at 65 °C for the required time. Samples were collected at regular intervals and analyzed according to the procedure described above.

GC–MS data for **3**: m/z (%) = 368 [M^+, $C_{22}H_{40}O_4$] (2), 239 (100), 127 (96), 109 (18), 97 (5).

One-pot reaction: A solution of HMF (1 mmol) in MeOH (5 mL, 125 mmol) was added onto the previously activated catalyst (26 mg) and heated at 65 °C for 2.5 h in a system equipped with a magnetic stirrer, reflux condenser, and Dean–Stark trap in a silicone oil bath. During this first step, **9** was obtained in a yield $\geq$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 N_2 was bubbled continuously through the suspension (50 mL min^{-1}) to facilitate the removal of MeOH. Samples were collected at regular intervals and analyzed according to the procedure described above.

GC analyses were performed by using a Varian 3900 chromatograph equipped with a flame ionization detector and HP-5 (5 % cross-linked phenyl methyl silicone 30 m × 0.25 mm × 0.25 μm) capillary column. Mass spectra were obtained by using a GC–MS (HP Agilent 5973 with a 6980 mass selective detector).

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Keywords: alcohols · surfactants · zeolites · biomass · synthesis design

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