Zr-containing UiO-66 Metal-Organic Frameworks as highly selective heterogeneous acid catalysts for the direct ketalization of levulinic acid

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Abstract

Zr-containing UiO-66 materials are active and reusable heterogeneous catalysts for the selective ketalization of levulinic acid (LA) with 1,2-propanediol, affording selectivities of up to 91-93% at full LA conversion, with very low levels of ester or ketal-ester byproducts. This allows preparing the target ketal directly from LA and avoiding intermediate esterification steps of LA to levulinate esters to minimize the formation of unwanted side-products. The catalytic activity of UiO-66 is found to depend critically on the hydration degree of the solid and the amount of missing linker defects. The most likely active sites for ketalization in (defective) UiO-66 are Brønsted-induced acid sites arising from the strongly coordination and polarization of H_2O molecules onto accessible Zr^{4+} associated to missing linker defects. A progressive deactivation is observed upon catalytic reuse, which is attributed to adsorbed reaction products poisoning the catalytic sites. These adsorbed products are easily removed by washing the spent catalyst with a dilute 2% HCl ethanolic solution, which completely restores the initial catalytic activity while maintaining the crystallinity of the solid intact.

Introduction

Levulinic acid (4-oxopentanoic acid, LA) is one of the top twelve platform molecules derived from biomass. It is produced from lignocellulosic biomass by acid catalyzed transformation of C_5 and C_6 carbohydrates.[1],[2] Formation of LA from C_6 carbohydrates requires a two-step process of dehydration followed by hydrolysis of 5-hydroxymethylfurfural in the presence of strong Brønsted acid catalysts in water.[3–6] Alternatively, alkyl levulinates are instead formed when alcohols are used as solvents, by alcoholysis of hexoses (see Scheme 1). LA or levulinic esters can also be synthetized by alcoholysis of furfuryl alcohol derived from furfural in the presence of strong Brønsted acid catalysts.[7–9]
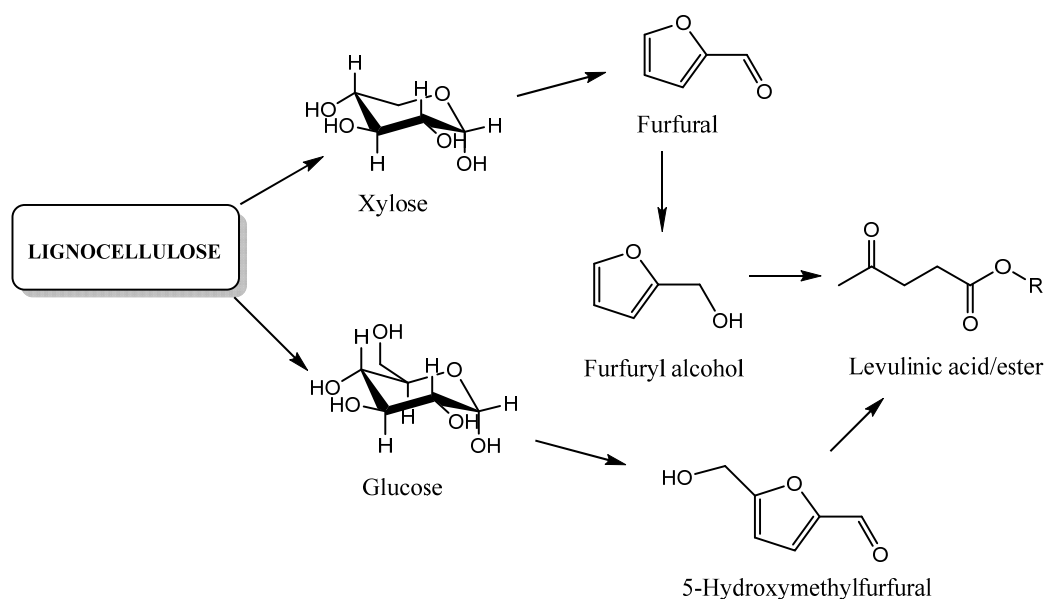
Scheme 1. General routs of synthesis of levulinic acid or levulinic esters from lignocellulosic biomass.

LA contains two highly reactive functional groups, a carbonyl and a carboxylic group, which provides the possibility of wide range of chemical transformations. Several value added chemicals can be synthetized from LA, such as succinic acid, diphenolic acid, ɣ-aminolevulinic acid, ɣ-valerolactone, as well as various esters and ketals, which are important building blocks for the synthesis of pharmaceuticals, fragrances, plasticizers, cosmetics or fuel additives[10–14] (Scheme 2).
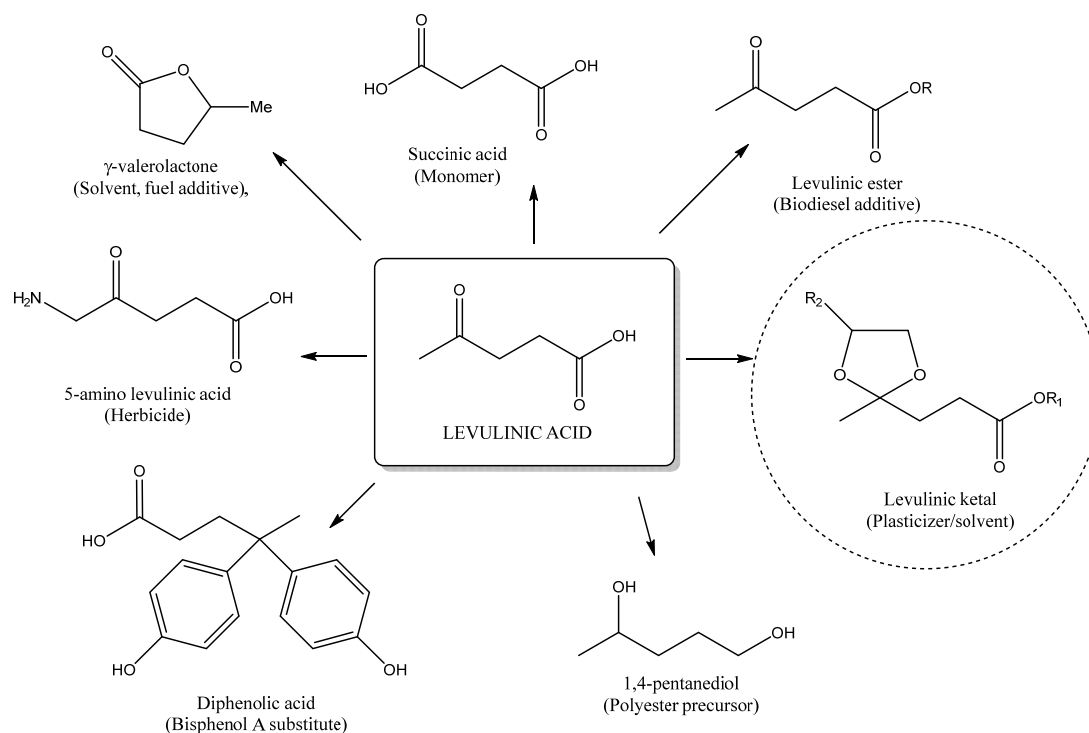
Scheme 2. Principal value added LA derivatives and their applications.

In this context, levulinic ketals are promising valuable biobased chemicals that have potential applications as additives for biofuels[12] as well as building blocks for producing plasticizers[13] and surfactants.[15] Reaction of LA with polyalcohols can lead to the formation of the corresponding ketals and/or esters. Ketalization and esterification reactions are both acid catalyzed reactions; therefore, the condensation of polyols with LA can result in competing ketalization and esterification reactions leading to nonselective mixtures of ketal, ester and ketal-ester products. For this reason, most of the methods described in the literature for the synthesis of levulinic ketals involve the reaction of ethyl levulinate (EL) with polyalcohols, thus avoiding the competing (trans)esterification reaction and improving the ketalization selectivity. Selifonov et al. described an efficient method for producing ketals from both LA and EL using mineral sulfuric acid as homogeneous catalyst.[16],[17] Although a high selectivity of ketals was achieved, the use of sulfuric acid as catalyst causes severe corrosive, toxic and waste treatment problems, which introduce important environmental concerns. Ketalization of EL have been studied using both homogeneous and heterogeneous acid catalysts, including *p*-toluenesulfonic acid (*p*-TSA), NbP, Amberlyst-70 or H-ZSM-5[15] (see Table S1 in the Supporting Information). Conversely, the direct ketalization of LA instead of levulinic esters to produce the corresponding ketals is a rather unexplored area. Recently, Amarasekara and Animashaun studied the condensation of LA with polyols in the presence of Amberlyst-15 and *p*-TSA as catalysts.[18] The authors explored the effect of homogeneous and heterogeneous catalysts on the competitive esterification and ketalization reactions. The highest ketal yield (88 %) was achieved with 1,2-propanediol using

Amberlyst-15 as a catalyst; whereas 88 % of ketal-ester was obtained when *p*-TSA was used as catalyst. According to the authors, their results indicate that the selectivity to one of the products can be improved by controlling the structure of the catalyst as well as the nature, the accessibility and the number of active sites.

In this context, Metal-Organic Frameworks (MOFs) can be an attractive alternative to the conventional homogeneous and heterogeneous acid catalysts generally used for ketalization reactions. The unique structural properties of MOFs such as well-defined pore structure, high specific surface area and flexible nature make them attractive for use as heterogeneous catalysts.[19–21] In particular, UiO-66 and other related Zr-MOFs have demonstrated excellent activity in a variety of acid catalyzed reactions, including esterifications and transesterifications,[22–27] isomerizations,[28] CO_2 cycloaddition to olefins,[29] Meerwein-Ponndorf-Verley reactions,[30–32] etc. In particular, we have reported the use of UiO-66 as an efficient catalyst for the esterification of free fatty acids[26] and LA[22,23,25] with different alcohols. We have shown that the catalytic activity of UiO-66 strongly depends on the number of missing linker defects generated during the synthesis of the MOF and the hydration state of the catalyst. These missing linkers create coordinatively unsaturated (*cus*) Zr^{4+} sites, which behave as Lewis acid sites. However, in the hydrated state, H_2O molecules are adsorbed and strongly polarized by these Zr^{4+} *cus*, resulting in relatively strong Brønsted acidity. Therefore, we have recently shown that it is possible to tune reversibly the acidity (and, thus the catalytic performance) of UiO-66 from Lewis to Brønsted acid centers by a simple hydration/dehydration treatment.[25,30]

Recently, Bakuru et al. have reported on the efficient acetalization of glycerol with acetone using UiO-66 containing Hf, Zr or Ce.[33] It was suggested that the acidity of the metal centers in UiO-66 depends on the oxophilicity of their metal ions. However, to the best of our knowledge, the activity of UiO-66 for the selective ketalization of LA has not been reported so far. In this work, we continue exploring the possibilities of UiO-66 as heterogeneous acid catalyst for synthesis of biomass-derived chemicals. In this context, the selective ketalization of LA with 1,2-propanediol in the presence of UiO-66 as heterogeneous catalyst is presented. Note that this study, along with the work by Amarasekara and Animashaun discussed above,[18] represent one of the few reports so far describing on the direct selective ketalization of LA with a heterogeneous acid catalyst. In particular, the effect of the amount of missing linker defects and hydration degree of the MOF in the catalytic activity and selectivity to the ketal product is analyzed, as well as the method used for the regeneration of the spent catalyst.

Results and discussion

Ketalization reaction of LA with 1,2-propanediol (1,2-PD)

Ketalization of LA with 1,2-PD was carried out in the presence of UiO-66 as heterogeneous acid catalyst. Note that the UiO-66 samples used in this study are referred to as

UiO-66-x%, where x% indicate the percentage of missing linker defects, as determined from the corresponding TGA curves (see Experimental Section for details). To ensure complete conversion of LA, the reaction was performed with an excess of 1,2-PD (2 equivalents) and toluene was used as solvent under reflux conditions. A Dean Stark apparatus was used to remove the water formed during the reaction. Owing to the bifunctional nature of LA, different reaction products can be observed. Thus, the ketal product (LA Ketal) is formed by acetalization of the carbonyl group with 1,2-PD, while the levulinic ester (LA Ester) comes from the esterification of the carboxyl group. Finally, LA Ketal and LA Ester can undergo successive esterification and acetalization resulting in the formation of LA Ketal-Ester. The main reaction routes and products formed during the reaction are shown in Scheme 3. Note that, although all these reactions should be in principle reversible and controlled by the equilibrium, using a Dean Stark trap to remove water generated during the forward reactions precludes the occurrence of the corresponding inverse reactions.
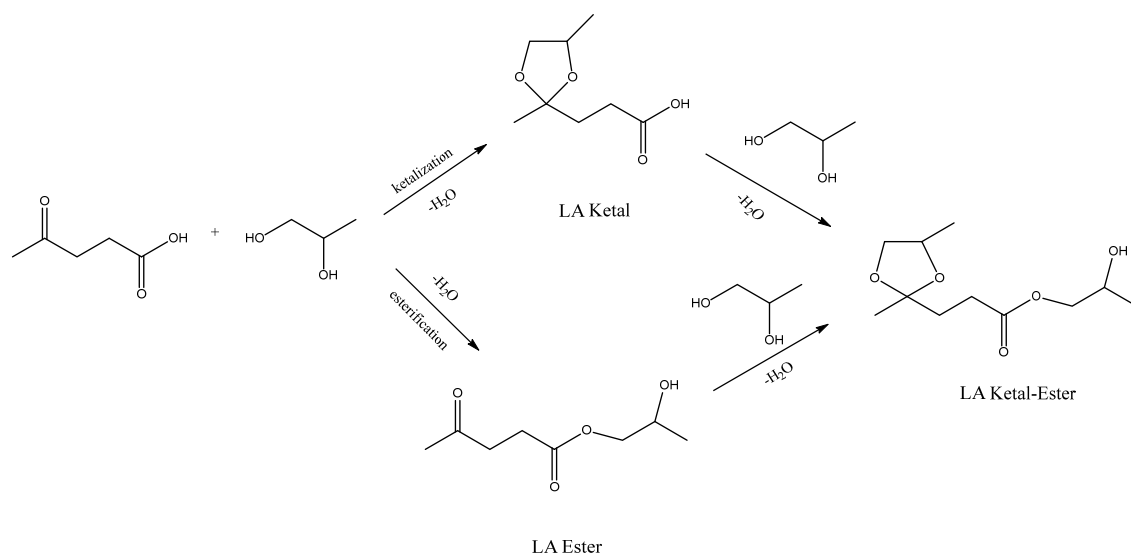
Scheme 3. General route of condensation reaction of levulinic acid with 1,2-propanediol.

In a preliminary experiment using UiO-66-6% as a catalyst (i.e., an UiO-66 sample containing 6% of missing linker defects) under non-optimized conditions, LA Ketal was obtained as a main product with 54 % yield and 96,4 % selectivity after 1 h of reaction (see Figure and Table 1). A slight decrease of the LA Ketal selectivity was observed at higher LA conversions (longer reaction times) due to the formation of small amounts of the ester and ketal-ester side products (< 5mol% of each). Nevertheless, a final LA conversion of 72% was attained after 7 h of reaction, with 63% LA Ketal yield and a still very good selectivity of 87.5% to the target ketal (see entry 2 in Table). In comparison, a blank experiment in the absence of any catalyst (autocatalytic process) produced only 16% conversion of LA after 22 h of reaction, being LA Ester the main reaction product, while only 2% LA Ketal yield was attained (entry 1).

In order to improve further these results and maximize the production of LA Ketal, different reaction parameters were analyzed, including thermal pre-activation of the catalyst, the alcohol excess used, and the amount of missing linker defects of the catalyst. The results obtained are summarized in Table 1.
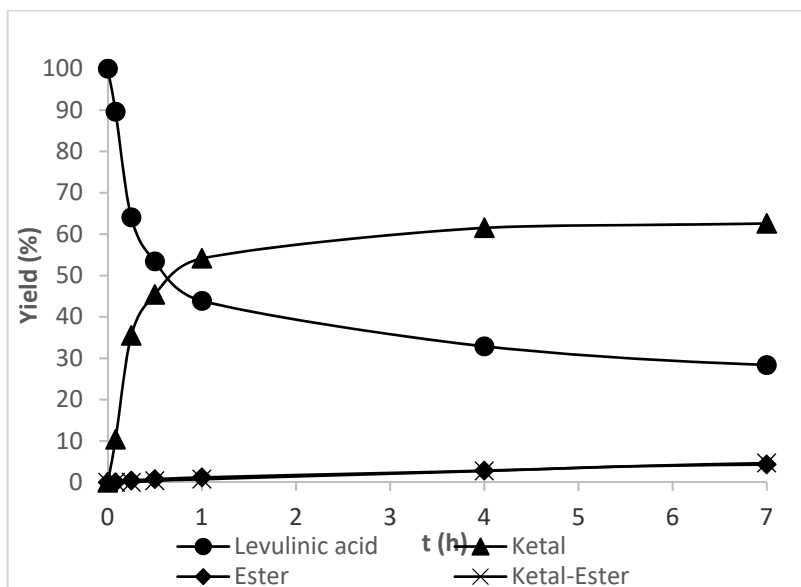

Figure 1. Time-conversion plots of condensation reaction between LA and 1,2-PD in the presence of UiO-66-6%.

Table 1. Results of ketalization of levulinic acid (LA) with 1,2-propanediol (1,2-PD) in the presence of UiO-66

Entry	Catalyst	time (h)	LA:1,2PD Molar ratio	Metal (mol%)	Conv.[a] (mol%)	Selectivity (mol%)[b]		
						Ketal	Ester	Ketal-Ester
1	Blank	22	1:2	-	16	12.5	84.4	3.1
2	UiO-66-6%	7	1:2	15.5	72	87.5	5.6	6.9
3	UiO-66-6%[c]	9	1:2	15.5	29	82.8	13.8	3.4
4	UiO-66-12%	7	1:2	15.5	86	93.0	2.4	4.6
5	UiO-66-16%	7	1:2	15.5	92	91.3	2.2	6.5
6	UiO-66-18%	7	1:2	15.5	93	91.4	3.2	5.4
7	UiO-66-16%	24	1:1	15.5	78	85.9	6.4	7.7
8	UiO-66-16%	7	1:4	15.5	89	69.7	9	21.3
9	UiO-66-16%	8	1:2	3.5	40	88.6	7.6	3.8

[a] Conversion of LA, determined by GC. [b] Selectivity to the indicated products, determined by GC. [c] The catalyst was pre-activated before ketalization reaction at 150 °C under vacuum. Reaction was performed at 110 °C using toluene as a solvent and Dean Stark apparatus.

Effect of catalyst dehydration

According to our previous studies, the hydration state of UiO-66 determines the presence of either Brønsted of Lewis acid sites in the solid catalyst.[23,25,30] To explore the effect of catalyst dehydration on ketalization and esterification reactions, UiO-66-6% was dehydrated at 150 °C under vacuum before use. Comparative results of ketalization reaction in the presence of hydrated or dehydrated UiO-66-6% are shown in Figure.
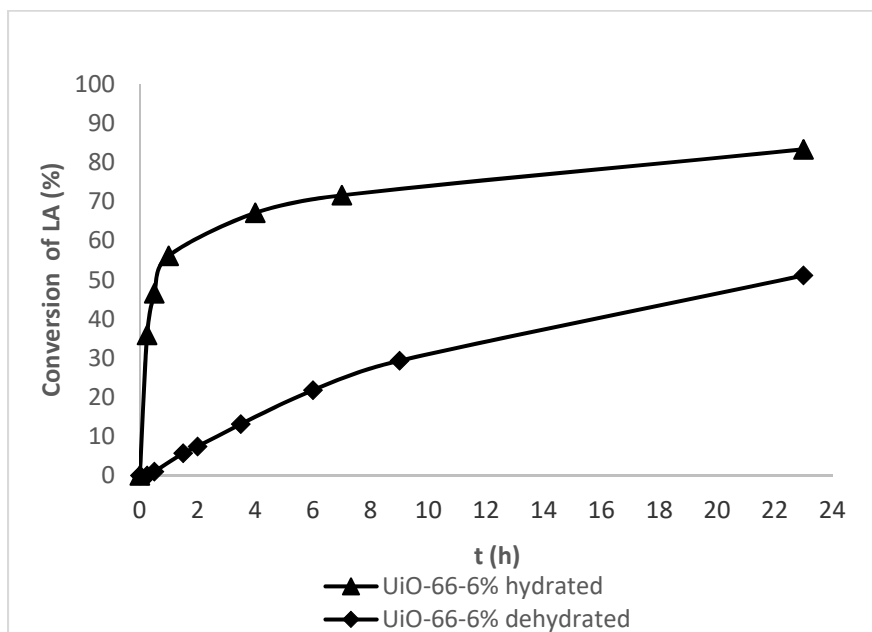

Figure 2. Conversion of LA obtained in the presence of hydrated and dehydrated UiO-66-6%.

As it can be observed in Figure, the catalytic performance of UiO-66 is significantly better for the hydrated MOF than for the dehydrated solid. The overall reaction is slower for the dehydrated material, while final selectivities to LA Ketal are similar in both cases, slightly higher by ca. 5% for the hydrated catalyst (compare entries 2 and 3 in Table 1). A similar effect of catalyst dehydration was observed previously for the esterification of LA over UiO-66,[25] for which the catalytic activity decreased upon dehydration. That result was attributed to a decrease of the Brønsted acidity of the solid upon dehydration. Therefore, the results obtained herein indicate that both esterification and ketalization reactions are preferentially catalyzed by (and compete for) the same Brønsted acid sites of the solid. However, a participation of Lewis acid sites to some extent, or even a synergy between Lewis and Brønsted acid sites, is not excluded.

Effect of amount of missing linker defects

Considering that Brønsted acid sites of hydrated UiO-66 arise from strongly polarized water molecules adsorbed onto accessible Zr^{4+} sites associated to missing linker defects, the number of such defects on the solid must have a direct impact on its catalytic activity. To evaluate this effect, four different samples of UiO-66 were prepared containing different amounts of linker

defects, ranging from 6% to 18%, as determined from the corresponding TGA curves.[34] These amounts of missing linker defects correspond to average coordination number of the Zr_6 oxoclusters moving from 12 (in the ideal, defect-free UiO-66), to 11.28 (in sample UiO-66-6%) and down to 9.84 (in sample UiO-66-18%). Then, these four UiO-66 samples were tested for the ketalization of LA with 1,2-PD under otherwise identical conditions. The results obtained are presented in Figure 3 and Table 1.

A direct correlation can be observed between the number of linker defects and the catalytic activity of UiO-66. Specifically, the conversion of LA after 7 h of reaction increases from 72 % to 93 % as the number of defects increase from 6% to 18 % (Figure 3a) while the selectivity to LA Ketal slightly increases from 87.5% up to 93 and 91% for the more defective samples. As it is seen in Figure 3b, a linear dependence can be observed for the corresponding turnover frequencies (TOFs), calculated for each material as moles of LA Ketal formed per hour and taking into account the total amount of zirconium used in the reaction (TOF_{tot}). Thus, the values calculated for TOF_{tot} range between 9.2 h^{-1} and 20.3 h^{-1} for samples UiO-66-6% and UiO-66-18%, respectively. However, TOFs can also be calculated by considering only the Zr^{4+} sites that are actually accessible to the reactants; i.e., those associated to missing linker defects (TOF_{def}). In the ideal structure of UiO-66, each terephthalate linker is coordinated to four Zr ions. When one linker molecule is missing, two Zr^{4+} are saturated by ^-OH groups to preserve the electrical neutrality of the system, while the other two Zr^{4+} become accessible. Therefore, the total amount of accessible Zr^{4+} sites is twice the amount of missing linker defects of the material. When TOFs are recalculated considering only the accessible Zr^{4+} sites, the values obtained are considerable higher than TOF_{tot}, and they are roughly constant for all the UiO-66 samples studied and close to ~ 68 ± 5 h^{-1} (see Figure 3c). Note that this value reflects the "intrinsic" catalytic activity per active site that participates effectively in the reaction. The fact that this value remains roughly constant irrespective of the amount of missing linkers of the solid indicate that all of them are basically isolated and act independently from the others. From this point of view, UiO-66 can thus be considered a true single-site catalyst.[21]
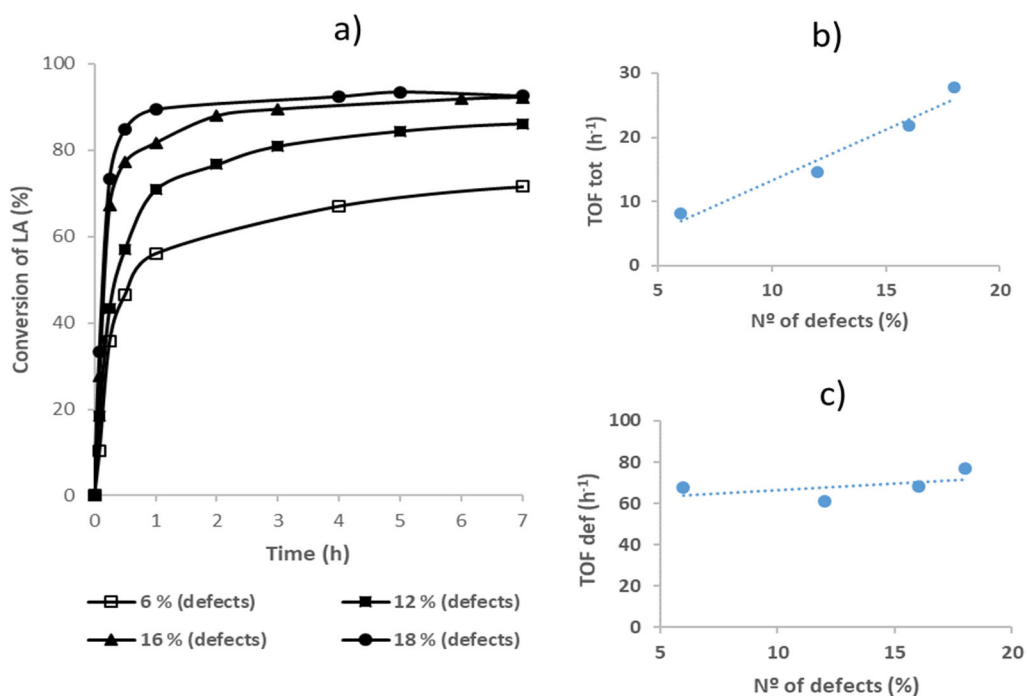
Figure 3. (a) Conversion of LA in the presence of UiO-66 with different amount of linker defects, ranging from 6% to 18%. Evolution of TOF_{tot} (b) and TOF_{def} (c) for the ketalization reaction of LA with the amount of linker defects.

Effect of LA/1,2-propanediol ratio and catalyst amount

Finally, we have also determined the effect of LA:1,2-PD molar ratio and the amount of catalyst used on the ketalization reaction of LA in the presence of UiO-66-16%. When an equimolar ratio of LA and 1,2-PD was used (Table 1, entry 7) full conversion of levulinic acid was not achieved even after 24 h of reaction time (78 % LA conversion). This was accompanied by a slight increase of the selectivity to LA Ketal-Ester, which is due to the longer reaction time analyzed (24 h versus 7 h), which favors the formation of the secondary product of the reaction. The same effect was observed when the excess of 1,2-PD used with respect to LA moved from 1:2 to 1:4, favoring also the formation of LA Ketal-Ester (which consumes two molecules of 1,2-PD per LA), up to a final selectivity of 21.3 % (Table 1, entry 8). Therefore, a LA:1,2-PD molar ratio of 2 was found to be the optimum ratio to achieve both, a high and fast conversion of LA and an excellent selectivity to the desired LA Ketal. A larger excess of 1,2-PD, as well as longer reaction times, both promote the subsequent esterification of LA Ketal giving rise to large amounts of undesired LA Ketal-Ester. Finally, when the amount of catalyst used was reduced from 15.5 mol% to 3.5 mol% of total Zr^{4+} with respect to LA, the reaction rate decreased considerably (compare entries 5 and 9 in Table 1), while the selectivity to LA Ketal was still close to 90%. Note that the lower level of LA conversion attained resulted in a concomitant decrease of the selectivity to the secondary reaction product, LA Ketal-Ester.

To put into context the catalytic activity of UiO-66 obtained in this work, we have also tested different homogeneous and heterogeneous catalysts under the same reaction conditions. These results are summarized in Table 2 and Figure S4 (see SI). As shown above, the catalytic performance of UiO-66-18% is excellent, attaining 85% conversion of LA after only 0,5 h of reaction with 99% selectivity to LA Ketal (see Table 2, entry 1). An UiO-66-NH$_2$ sample containing 12% of linker defects showed also very good activity and high selectivity toward LA ketal (entry 2). However, the TOF calculated per accessible Zr^{4+} site in UiO-66-NH$_2$ was considerably lower than in UiO-66 (40 vs 77 h^{-1}), which is most likely due to the higher steric hindrance introduced by the amino groups. In contrast, when the catalyst used was MOF-808 (another Zr-containing MOF with similar Zr$_6$ oxoclusters than UiO-66), only 35% LA conversion was attained after 23 h, with a poor selectivity to the ketal (48%) at a similar LA to total Zr^{4+} molar ratio (entry 3). The difference in activity of UiO-66 and MOF 808 can be attributed to the different structure and nature of their acid sites: While hydrated UiO-66 contain relatively strong Brønsted acid sites, these Brønsted sites are much weaker in MOF 808.[30] Note also that in MOF-808 all the Zr^{4+} sites should become accessible (as Lewis acid sites) upon removal of the six capping formate ligands (used as modulator in the synthesis). However, dehydration of MOF-808 at 150 °C before ketalization reaction (results not shown) did not improve its catalytic activity, which confirms that Lewis acid sites are not active for the ketalization reaction, and rather Brønsted acid sites are required to promote this type of transformation.

Table 2. Results of ketalization between LA) and 1,2-PD in the presence of different homogeneous and heterogeneous catalysts.[a]

Entry	Catalyst	Acid sites (mol.%)	time (h)	Conv. (mol%)	Selectivity (mol%)			TOF[b] (h^{-1})
					Ketal	Ester	Ketal-Ester	
1	UiO-66-18%	14.4 (Zr^{4+})	0,5	85	99	0	1	77
2	UiO-66-NH$_2$-12%	17.0 (Zr^{4+})	1	79	98	1	1	41
3	MOF-808	15.8 (Zr^{4+})	23	35	48	47	4	0.055
4	p-TSA*H$_2$O	3.5 (H$^+$)	0,5	96	38	5	57	56
5	Amberlyst-16	5.7 (H$^+$)	0,5	75	85	4	11	36
6	0,8% Zr-Beta	0.4 (Zr^{4+})	0,5	49	95	3	2	134
7	ZrO$_2$	17.2 (Zr^{4+})	0,5	2	100	0	0	0.063

[a] Reaction conditions: Levulinic acid (LA) 1 mmol, 1,2-propanediol (1,2-PD) 2 mmol, toluene 3 mL, 110 °C, Dean Stark apparatus, reaction time-0,5 h. [b] TOF is calculated as mol of ketal formed per hour and per mol of (accessible) acid sites.

In this sense, homogeneous *p*-TSA and heterogeneous resin Amberlyst-16 containing strong Brønsted acid sulfonic groups both showed high catalytic activity, achieving LA conversions of 96 and 75 %, respectively after 0.5 h of reaction time (entries 4 and 5). However, the selectivity of *p*-TSA to the ketal was very low (38 %), obtaining ketal-ester as a major product (57 %). In contrast, Amberlyst-16 gives good selectivity to the ketal (85 %) at 75 % of conversion, but it drops very fast at higher conversion of LA, leading to the formation of LA-Ester as a predominant product after 8 h of reaction (see Figure S4 in the SI for the corresponding time-conversion plots). Finally, we evaluated the catalytic activity of other heterogeneous catalysts containing Zr^{4+} sites. Thus, a Beta zeolite containing 0,8wt% Zr (entry 6) show good activity and selectivity toward LA-ketal at short reaction times, with a TOF of 134 h^{-1}. However, a fast deactivation of the catalyst was observed at longer reaction times, with a concomitant decrease of selectivity toward ketal. Thus, the LA conversion was only 83% after 24 h, while the selectivity to LA Ketal dropped to 74 %. Finally, amphoteric ZrO_2 exhibited poor activity for ketalization reaction, affording only 12 % LA conversion after 6 h (entry 7).

Reusability and regeneration of UiO-66

To complete the characterization of the catalytic activity of UiO-66, its recyclability was evaluated upon several consecutive reaction cycles. At the end of the reaction, the solid catalyst was recovered by filtration, washed with ethanol and dicloromethane, and dried at room temperature. However, while the crystallinity of the solid remained almost intact, a considerable decrease of the catalytic activity of MOF was observed (see Figure 4). The conversion of LA dropped from 93 % to 67 % after the first reuse, and down to 54% after the second reuse. This decrease of catalytic activity is most likely due to the adsorption of reactants or products on the surface of the catalyst that are not completely removed during the washing procedure, as clearly evidenced by FTIR spectroscopy and TGA (see Figures S5 and S6 in the SI). In order to improve the catalytic activity of the spent catalyst, the washing procedure was modified by treating the recovered solid with a 2% HCl solution in ethanol was employed[35]. Thus, after regeneration of UiO-66 with a 2% HCl ethanolic solution, a complete recovery of the catalytic activity was observed (Figure 4). This reactivation of the catalyst can be attributed to the regeneration of the Brønsted acid sites, as well as a better desorption and washing of adsorbed products from the catalyst surface.
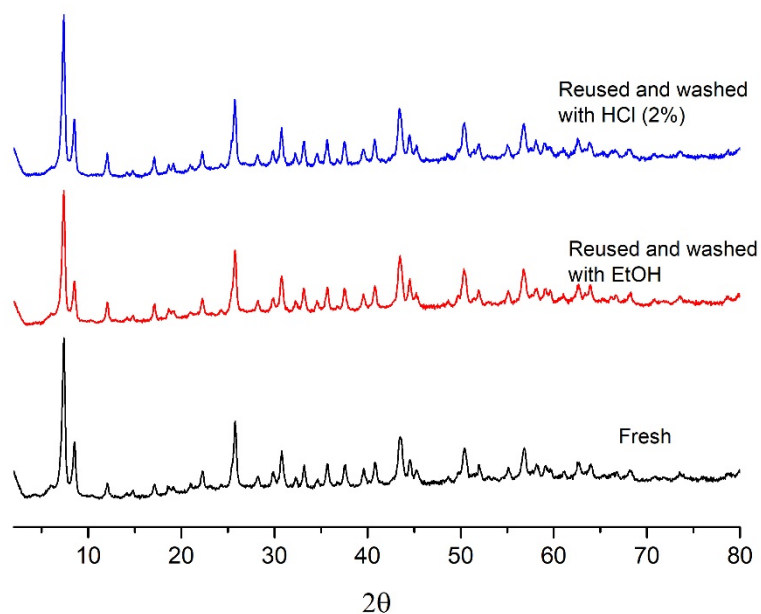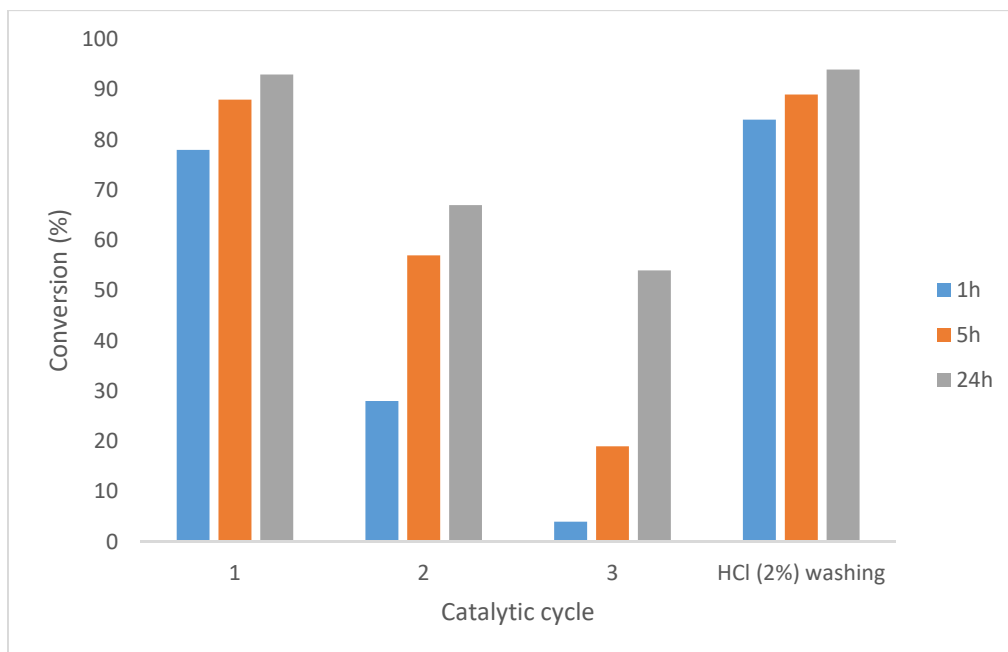
Figure 4. (*Top*) Conversion of LA obtained (after 1, 5 and 24 h of reaction) during several catalytic cycles of UiO-66-18%. (*Bottom*) XRD patterns of fresh UiO-66-18% and washed with either EtOH and CH_2Cl_2 or HCl (2%) in EtOH after reuse.

Conclusion

Herein, we have shown that Zr-containing UiO-66 materials are active catalysts for the selective ketalization of LA with 1,2-PD. Selectivities as high as 91-93% to LA Ketal were achieved at full LA conversion, while keeping the amount of the ester and ketal-ester byproducts very low. The high selectivity of UiO-66 for the ketalization reaction allows preparing the target ketal directly from LA and avoiding intermediate esterification steps of LA to levulinate esters to minimize the formation of unwanted side-products. The observed catalytic performance was found to depend

critically on the hydration degree of the solid and the amount of missing linker defects. According to our results, the most likely catalytic active sites for ketalization are thus Brønsted acid sites associated with strongly polarized H_2O molecules adsorbed onto accessible Zr^{4+} sites, associated to missing linkers, though a participation of Lewis acid sites or even a synergy between Lewis and Brønsted acid sites is not excluded. Although the crystallinity of UiO-66 is preserved during the catalytic process, a progressive decrease of the catalytic performance is observed in consecutive runs. This is clearly associated with the pore clogging of the catalyst and poisoning of the acid sites due to the presence of strongly adsorbed reaction products, which cannot be removed during the washing process with ethanol and CH_2Cl_2. However, the use of an ethanolic solution of HCl (2%) during the catalyst washing is found to be efficient to remove adsorbed products and to recover completely the catalytic performance of the fresh catalyst.

Experimental section

Materials and reagents

$ZrCl_4$, $ZrOCl_2 \cdot 8H_2O$, *N,N*-dimethylformamide, benzene-1,3,5-tricarboxylic acid (BTC), Benzene-1,4-dicarboxylic acid (BDC), levulinic acid, toluene, 1,2-propanediol, ZrO_2 (nanopowder, <100 nm pore size), *p*-toluenesulfonic acid monohydrate and Amberlyst 16 hydrogen form (4.8 meq/g) were supplied from Sigma Aldrich and used as received.

Synthesis of catalysts

UiO 66-Zr samples with different number of defects were prepared using non-modulated method described by Kandiah et al [36] with slight modifications. Briefly, $ZrCl_4$ (375 mg, 1.6 mmol) was dissolved in 25 mL of *N,N*-dimethylformamide (DMF) and 1,4-benzenedicarboxylic acid (BDC) was dissolved in 20 mL of DMF. Then, both solutions were sonicated during 15 min at ambient temperature and mixed inside a screw-capped glass bottle. The resulting mixture was placed in the oven at 80 °C during 24 h and then the temperature was raised to 100 °C and the mixture was kept for another 24 h. The resulting white precipitate was recovered by filtration under vacuum and washed with DMF and CH_2Cl_2. Finally, the obtained solid was dried under vacuum at ambient temperature. Four different samples were prepared containing a different amount of missing linker defects. These samples are referred to as UiO-66-x%, where x% indicates the amount of missing linkers, as determined from the TGA curves (see below).

UiO-66-NH$_2$ was synthetized according to the same procedure described above for UiO-66 but using 2-aminoterephthalic acid (400 mg) as organic ligand instead of BDC.

MOF 808-Zr was prepared following the method described by Furukawa et al.[37] First, 364 mg of $ZrOCl_2 \cdot 8H_2O$ was dissolved in solvent mixture of formic acid (16,8 mL) and DMF (5,6 mL). Then, 158 mg of benzene-1,3,5-tricarboxylic acid (BTC) was dissolved in 11,2 mL of DMF. Both solutions were mixed and placed in a Teflon lined autoclave. Then, the autoclave was

introduced into an oven at 130 °C for 48 h. After cooling down to room temperature the material was recovered by centrifugation. Finally, the obtained solid was washed 3 times with DMF (changing the solvent every 15 min) and 3 times with ethanol (changing the solvent every 30 min). After removing the solvent by centrifugation the solid was dried in air at ambient temperature.

0,8 wt.%Zr-Beta was prepared by the method reported in the literature[38] and calcined at 580 °C in air for 3 h before use.

Characterization of the catalysts

All synthetized catalyst samples were characterized by Powder X-ray diffraction (Phillips X'Pert, Cu Kα radiation) to confirm the expected structure and crystallinity of the materials. XRD diffraction patterns of all synthetized UiO-66 solids are shown in Figure S1 (see Supporting Information).

Thermogravimetric analysis (TGA) of the synthetized MOFs was performed under a flow of air and a heating ramp of 10ºC min^{-1} using a NETZSCH STA 449 F3 Jupiter analyzer. The TG and corresponding derivative curves (DTG) are presented in Figure S2 (see SI). From these TG curves, the number of defects in each UiO-66 sample was determined following the method reported by Valenzano et al.[34] as described in the Supporting Information. Textural properties of UiO-66 samples were determined from the corresponding N_2 adsorption isotherms (at 77 K) and the results are summarized in Table S2 (Supporting Information).

General procedure for ketalization reaction of levulinic acid with 1,2-propandeiol

Typically, levulinic acid (1 mmol), 1,2-propanediol (2 mmol), toluene (3 mL) and the catalyst were placed into round bottom two-necked flask connected to a Dean Stark apparatus to remove water formed during the reaction. Then, the mixture was stirred at 700 rpm (we checked that this speed is high enough to avoid external diffusion control of the reaction), using a magnetic stirrer and heated up to 110 ºC in a hot plate at atmospheric pressure. The amount of catalyst used in each reaction depends on the type of catalyst used in the reaction. In the case of UiO-66, MOF 808-Zr, ZrO_2 and Zr-Beta, 50 mg were added. In case of *p*-TSA and Amberlyst-16 an amount of 5 mg and 11 mg was used, respectively. The reaction was followed by taking sample aliquots at regular times and analyzing them by gas chromatography with a Varian 3000 instrument equipped with a capillary column (HP5, 30 m x 0.25 mm x 0.25 µm) and a flame ionization detector (FID) and using dodecane as internal standard. All products were identified by mass spectrometry analysis (GC-MS) and by comparison with reference compounds. Conversion and selectivities were determined from the areas of the corresponding GC peaks upon correction by the response factor of each species determined for the pure compounds with respect to the internal standard

Regeneration and reuse of UiO-66-Zr

When the reaction was finished, the spent catalyst was separated from reaction mixture by simple vacuum filtration. Then, it was washed with EtOH and CH_2Cl_2 and dried overnight at room temperature. Alternatively, in order to regenerate the catalyst, the solid was soaked in a 2% HCl solution of ethanol for 4 hours and then filtered under vacuum. Finally, the regenerated sample was dried at room temperature before next catalytic cycle.

Conflict of interest

The authors declare no conflict of interest.

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