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Production of biomass-derived furanic ethers and levulinate esters using heterogeneous acid catalysts

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Reactions of the biorenewable substrates 5-hydroxymethyl-2-furfural and furfuryl alcohol with aliphatic alcohols to give bio-based furanic ethers and levulinate esters using, as heterogeneous acid catalysts, mesoporous aluminosilicates of the type Al-TUD-1, prepared via non-surfactant templating routes.

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Production of biomass-derived furanic ethers and levulinate esters using heterogeneous acid catalysts

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Mesoporous aluminosilicates of the type Al-TUD-1, prepared via "green", low-cost, nonsurfactant templating routes, are effective and versatile heterogeneous acid catalysts for the production of useful bio-based furanic ethers and levulinate esters, via the reactions of the biorenewable substrates 5-hydroxymethyl-2-furfural (Hmf) or furfuryl alcohol (FA) with aliphatic alcohols. The identification of reaction intermediates and products by comprehensive two-dimensional gas chromatography combined with time-of-flight mass spectrometry was carried out, giving mechanistic insights. Ethyl levulinate (EL) was formed from FA or Hmf as substrates, with higher EL yields being reached in the former case. Different types of alkyl levulinates may be synthesized from FA using Al-TUD-1 catalysts. On the other hand, 5-(ethoxymethyl)furan-2-carbaldehyde may be formed as the main product from Hmf. Modifications of the properties of Al-TUD-1 involved varying the Si/Al ratio and applying a post-synthesis acid treatment. The influence of these factors and of the reaction conditions on the catalytic reactions was investigated. The efficient regeneration and recyclability of Al-TUD-1 was assessed.

Hemicelluloses

Furfuryl alcohol (FA)

Introduction

Carbohydrate matter can be obtained from sustainable such non-edible forest/agriculture resources as residues/surpluses, municipal solid waste, effluents of the pulp and paper industries, and short-rotation energy crops.¹ Carbohydrates may be converted to valuable products,² such as furanic ethers and levulinate esters (these groups of compounds are denoted bioEs) via the furanic platform chemicals 5hydroxymethyl-2-furfural (Hmf) and furfural (Fur) (Fig. 1). The hydrogenation of Fur gives furfuryl alcohol (FA); the two compounds have wide application profiles, and have been produced industrially for decades from lignocellulosic biomass.³ The bio-based conversion processes of Hmf and FA to bioEs involve the reaction of these substrates with biomassgrade aliphatic alcohols in the presence of acid catalysts. Interesting bioEs include 2-(alkoxymethyl)-furans, 5-(alkoxymethyl)furan-2-carbaldehydes and alkyl levulinates, for the production of fuels and fuel additives.⁴ The furanic ethers 5-(alkoxymethyl)furan-2-carbaldehyde and 2-(alkoxymethyl)furan may be formed via the acid-catalysed reactions of Hmf^{4j,5} or FA^{41,6}, respectively, with aliphatic alcohols. On the other hand, levulinate esters are common products in the reactions of the two substrates Hmf^{5a,5b,5d,5i,7} and FA.^{6,8}

The use of inorganic, porous heterogeneous acid catalysts for the chemical valorisation of plant biomass is one of the most promising approaches.⁹ Zeolites are among the most commonly used heterogeneous catalysts in the chemical industry, e.g. oil refining and petrochemistry.¹⁰ Recently, Bell and co-worker^{5b} reported that zeolite catalysts used for the reaction of Hmf with ethanol suffered fast deactivation due to blockage of the micropores by organic matter. On the other hand, the diffusion inside the micropores may govern the overall reaction process, whereas it is preferable to operate under kinetic regime^{5d,5i}. In order to avoid these drawbacks, Lanzafame et al.^{5d} used the mesoporous acid catalysts Al-MCM-41 and SBA-15-supported sulfated zirconia in the conversion of Hmf to 5-(ethoxymethyl)furan-2-carbaldehyde (5Emf) and ethyl levulinate (EL). We recently reported that Al-TUD-1 is an effective mesoporous solid acid catalyst for the conversion of FA to EL, leading to better results when compared with zeolites and modified versions of zeolites (modified to introduce mesoporosity and enhance active site accessibility).^{6c}.

BIOMASS

Acid Catalysis

BOH / AI-TUD-1



Fig. 1 Production of biomass-derived furanic ethers and levulinate esters.

Cellulose

5-Hydroxymethyl-2-furfural (Hmf)

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Materials of the type TUD-1 are particularly interesting and versatile for catalytic applications since they combine high specific surface area (up to 1000 m² g⁻¹), tuneable pore sizes (3-25 nm) and a 3-D channel system (foam-type structure), allowing enhanced active site accessibility, and avoiding internal diffusion limitations (e.g. in relation to 1-D pore systems such as that present in MCM-41).¹¹ In contrast to other types of mesoporous materials, TUD-1 materials may be prepared via "green", low-cost, non-surfactant templating routes.¹² TUD-1 can be furnished with acid properties by introducing aluminium into the framework, which may be accomplished via a one-pot procedure based on the sol-gel technique.¹³

Here, the catalytic versatility of Al-TUD-1 is explored for the production of bioEs from Hmf and FA. Synthetic modifications of Al-TUD-1 included varying the Si/Al ratio and post-synthesis acid treatment. A comparative study of FA and Hmf as substrates for EL production, and, on the other hand, the catalytic reaction of FA with different types of aliphatic alcohols to give alkyl levulinates, was investigated. In order to get mechanistic insights, the identification of the reaction intermediates and products by comprehensive two-dimensional gas chromatography (GC×GC) combined with time-of-flight mass spectrometry (ToFMS) was carried out. Commercial AmberlystTM-15 was chosen as a benchmark catalyst for comparative studies since these types of sulfonic acid resins are very active catalysts for the conversion of furanic compounds to bioEs.^{50,50,6,6,8a,14}

Results and discussion

Characterisation of the catalysts

The acid and texture properties of the tested Al-TUD-1 catalysts are summarized in Table 1. Al-TUD-1(21) has been characterized in a previous paper.¹⁵ In the case of Al-TUD-1(4) the low angle X-ray powder diffraction pattern exhibits a single very broad peak centered at ca. $2^{\circ} 2\theta$ (Fig. S1), indicating that this material possesses a mesoporous structure of somewhat reduced order. No higher-angle peaks due to crystalline phases of alumina and/or silica were found. SEM images of Al-TUD-1(4) show particles of irregular shape and size (Fig. S2). The Si/Al ratio of the sample (determined by EDS, Table 1) is in agreement with the nominal Si/Al of 4 that was used in the synthesis mixture.

The nitrogen adsorption-desorption isotherm of the Al-TUD-1(4) catalyst exhibits a narrow hysteresis cycle at high relative pressures (p/p₀ > 0.85), indicating that the solid has large mesopores (Fig. 2). Moreover, the material has a broad mesopore size distribution, with a maximum at 36.3 nm (Fig. 2 inset). Al-TUD-1(4) has lower S_{BET} and larger mesopores than Al-TUD-1(21) (Table 1).

Table 1 Acid and texture properties of the catalysts.

Sample ^a	S_{BET} (m ² g ⁻¹)	d _p ^b (nm)	B+L ^c (µmol g ⁻¹)	L/B ^c	L ₃₅₀ /L ₁₅₀ ^d	B ₃₅₀ /B ₁₅₀ ^d
Al-TUD-1(21) ^e	757	4	197	2.3	0.6	< 0.05
Al-TUD-1(4)	417	36	190	3.0	0.5	< 0.01

^{*a*} Si/Al atomic ratio indicated in parenthesis; ^{*b*} Maximum of the mesopore size distribution curve derived from the adsorption branch. ^{*c*} Lewis (L) and Brönsted (B) acid sites, based on FT-IR of adsorbed pyridine as base probe (desorption at 150 °C). ^{*d*} L₃₅₀/L₁₅₀ and B₃₅₀/B₁₅₀ are the molar ratios of the

The nature of the Al species in Al-TUD-1(4) was investigated by 27 Al MAS NMR spectroscopy (Fig. S3). The spectrum exhibits three distinct signals at ca. 0, 28 and 52 ppm, similar to the spectrum reported in ref. 16b. The signal at around 52 ppm corresponds to tetracoordinated aluminium that was incorporated into the silica matrix, and is responsible for the Brönsted acidity. The dominant signals at around 28 and 0 ppm are ascribed to penta- (Al_{penta}) and hexacoordinated (Al_{hexa}) aluminium species.^{13,16,17} The total amount of acid sites (Lewis plus Brönsted) is similar for the two Al-TUD-1 catalysts, with the main differences being the higher L/B ratio, slightly weaker acidity and higher acid site density in the case of Al-TUD-1(4) (Table 1). These results are consistent with that discussed above regarding 27 Al MAS NMR which indicated the presence of Lewis and Brönsted acidity.

Al-TUD-1(4) was treated with 1 M HCl (giving Al-TUD-1(4)-at) in an attempt to increase the relative amount of Al_{tetra} , as described in ref. 16b. Al-TUD-1(4)-at had a Si/Al ratio of ca. 4, determined by EDS. Based on the ²⁷Al MAS NMR spectra (Fig. S3) and performing peak deconvolution and integration, the ratio $Al_{tetra}/(Al_{penta}+Al_{hexa})$ is ca. 0.3 and 0.6 for Al-TUD-1(4) and Al-TUD-1(4)-at, respectively. These results indicate that the relative amount of Al_{tetra} increased with the acid treatment, although a significant amount of the other Al species is still present.

45 40 35 (mmol g⁻¹) 30 25 n_{ads} 40 80 120 160 20 $d_{p}(nm)$ 15 10 5 0 0.2 0.0 0.4 0.6 0.8 1.0 p/p°

Fig. 2 Nitrogen adsorption-desorption isotherm at $-196 \,^{\circ}$ C, of Al-TUD-1(4). The inset shows the pore size distribution curve.

Catalytic tests

Reaction of the platform chemical Hmf with ethanol to give bioEs. The reaction of Hmf with ethanol in the presence of Al-TUD-1(21), at 140 °C, was complete at ca. 24 h (Fig. 3). Fig. 4 shows the TIC GC×GC-ToFMS representation for the reaction mixture obtained at 24 h, and the corresponding reaction products are listed in Table S1. The main reaction products were 5-(ethoxymethyl)furan-2-carbaldehyde (5Emf), ethyl levulinate (EL) and 5-(ethoxymethyl)furfural diethylacetal (5Emfda). 5Emf is formed via the etherification of Hmf, whereas the formation of 5Emfda involves the etherification



Fig. 3 Dependence of Hmf conversion on reaction time, in the presence of Al-TUD-1(21) (\square -110 °C, \triangle -140 °C) or Al-TUD-1(4) (\circ -140 °C). Reaction conditions: [Hmf]₀ = 0.3 M in ethanol, catalyst loading of 10 g_{cat}.dm⁻³.

Other reaction products included angelica lactone isomers, 5,5-diethoxy-2-pentanone, furanic compounds possessing different substituent groups (carbonyl, acetal and ether functional groups), as well as difuranic compounds. Ethyl formate was formed as a co-product in the conversion of Hmf to EL.²¹ Some products resulted from the non-productive consumption of ethanol, such as diethyl ether (DEE), triethoxymethane and ethoxyacetaldehyde diethyl acetal. Some of these products were also formed in the FA/ethanol/Al-TUD-1(21) system, under similar conditions.^{6c} Nevertheless, these products were always formed in relatively small amounts. The molar ratio of DEE/Hmf₀ (where Hmf₀ is the initial number of moles of Hmf) was ca. 0.1 at 24 h reaction, 140 °C.

Decreasing the reaction temperature from 140 °C to 110 °C led to a slower reaction of Hmf in the presence of Al-TUD-1(21) (Fig. 3), although comparable yields of bioEs products were reached at high Hmf conversion of ca. 97% (Fig. 5d, Table 2). Similarly high Hmf conversion and BioEs yields can be obtained in a much shorter reaction time at 110 °C by increasing the catalyst loading from 10 (48 h reaction) to 30 g_{cat} dm⁻³ (24 h reaction), Table 2. For a catalyst loading of 30 g_{cat} dm⁻³, a 2-fold increase in the initial molar concentration of Hmf ([Hmf]₀) led to slightly lower Hmf conversion at 24 h and 110 °C, in comparison to that for [Hmf]₀=0.3 M (93% and 98% conversion, respectively). However, comparable bioEs yields were reached, with 5Emf formed as the main product in 72% yield. Hence, a compromise between the initial amount of substrate and catalyst loading at 110 °C may lead to similar catalytic results as those obtained for the higher reaction temperature of 140 °C.

Decreasing the Si/Al ratio of Al-TUD-1 from 21 to 4 led to similar reaction rates of Hmf at 140 °C (Fig. 3). The similar

catalytic activities correlate with the similar total amount of acid sites for the two catalysts. The yields of the BioEs products were comparable until ca. 24 h, and afterwards higher EL yields were reached in the case of Al-TUD-1(21), whereas Al-TUD-1(4) gave the highest 5Emf yield. These results may be at least partly due to the lower L/B ratio and slightly stronger acidity of Al-TUD-1(21) in comparison to Al-TUD-1(4). The acid-treated Al-TUD-1(4)-at catalyst led to a fairly high 5Emf yield of 81% at 88% conversion, reached at 24 h reaction (Table 3), possibly due to the relatively weak acidity of Al-TUD-1(4)-at. Higher 5Emf selectivity than EL selectivity has been reported for most of the previously studied inorganic catalysts (Table 3).^{5a,5b,5d,5e,5i} According to Lanzafame et al.,^{5d} strong acid sites tend to favor the formation of EL. Somewhat consistent with this hypothesis is the fact that one of the best results in terms of EL yield reported in the literature for inorganic solid acids tested in the reaction of Hmf with ethanol is that for the Brönsted acid catalyst SO₃H-SBA-15 (Table 2).⁵ⁱ Nevertheless, Brönsted acid catalysts seem to be effective for 5Emf production at relatively low reaction temperatures. For example, the heteropolyacidbased compound [MimB(SO₃H)]₃PW₁₂O₄₀ (MimB(SO₃H)=4-(3-methyl-1-imidazolium)-1-butanesulfonic acid), tested in the reaction of Hmf at 70 °C, led to 91% 5Emf yield at 98% conversion (Table 3).5e It was claimed that while the butanesulfonic groups provided the active sites, the heteropolyanions promoted the insolubility of the catalyst.

Based on a comparison of the catalytic results for Al-TUD-1 catalysts with those reported in the literature for Al-MCM-41, the former are effective catalysts when 5Emf is the target product, with 80% 5Emf yield being reached in the case of Al-TUD1(4)-at (Tables 2, 3).^{5d} A quantitative analysis of the acid properties of Al-MCM-41 and catalyst loadings were not given in ref. 5d, making it difficult to explain the observed differences. It is worth emphasizing that Al-TUD-1 is advantageously prepared via "green", low-cost, non-surfactant templating routes.¹²

The originally white powdered Al-TUD-1 catalyst turned light brown after the catalytic reaction and remained so after washing and drying, suggesting the presence of carbonaceous matter (by-products). The successful regeneration of Al-TUD-1(21) by burning out the carbonaceous matter has been demonstrated previously for its application in different catalytic reactions related to the sugar platform based biorefinery.^{6c,15} In parallel with these results, the regenerated Al-TUD-1(21) (details given in experimental section) led to similar catalytic results (conversion and product selectivities) in consecutive 24 h-batch runs of the reaction of Hmf with ethanol, at 140 °C (Table 2). The leaching test for Al-TUD-1(21) led to lower Hmf conversion (16%) than for the non-catalyzed reaction, indicating that this material acts as a purely heterogeneous catalyst. The texture properties of the used and calcined catalyst $(S_{BET}=738 \text{ m}^2 \text{ g}^{-1}, \text{ and } d_p \text{ of ca. 4 nm})$ are similar to those of Al-TUD-1(21) (Table 1). The ²⁷Al MAS NMR spectrum of the used and calcined Al-TUD-1(21) catalyst is similar to that of Al-TUD-1(21)¹⁵, showing two distinct signals at ca. 52 ppm and 0 ppm, assigned to Altetra and Alhexa, respectively (Fig. S4). These results further support the high catalyst stability of Al-TUD-1. High catalyst stability has also been reported for H₄SiW₁₂O₄₀ supported on MCM-41 nanospheres, tested as catalyst in the same reaction; the results were based on catalytic activity, and the product selectivities or yields in the subsequent runs were not given (Table 2).5a The published work for Al-MCM-41(25) did not include catalyst recycling tests.^{5d}



Fig. 4 TIC GC×GC-ToFMS representation (one- and three-dimensional) of the reaction mixture of Hmf with ethanol (left), and of FA with 1-butanol (right) in the presence of Al-TUD-1(21). Reaction conditions: [Hmf]₀=0.3 M in ethanol or [FA]₀ = 0.3 M in 1-butanol, catalyst loading of 10 g_{cat}.dm⁻³, 140 °C, 24 h. EL = ethyl levulinate, 5Emf = 5-(ethoxymethyl)furan-2-carbaldehyde, 5Emfda = 5-(ethoxymethyl)furfural diethylacetal, 5 BL= butyl levulinate.



Fig. 5. Dependence of yields of the BioEs products 5Emf (▲,△), 5Emfda (●,○) and EL (■,□) on the time of the reaction of Hmf with ethanol (a, c), or on the Hmf conversion (b, d), in the presence of Al-TUD-1(21) (solid symbols) or Al-TUD-1(4) (open symbols) at 140 °C (a, b), or in the presence of Al-TUD-1(21) at 110 °C (c, d). Reaction conditions: [Hmf]₀ = 0.3 M in ethanol, catalyst loading of 10 g_{cat}.dm⁻³. The dashed lines are 10 visual guides.

		Reaction cor	nditions ^b			Bi	ioEs yield (%)		Ref.
Catalyst ^a	T (°C)	$[\mathrm{Hmf}]_0\left(\mathrm{M} ight)$	Cat. load (g _{cat} .dm ⁻³)	t (h)	Conversion ^c (%)	5Emf	5Emfda	EL	-
Al-TUD-1(21)	140	0.3	10	24	97 (99/99) ^d	70 (67/67) ^d	$3(4/3)^{d}$	$11(12/14)^{d}$	-
Al-TUD-1(21)	110	0.3	10	48	96	68	6	7	-
Al-TUD-1(21)	110	0.3	30	24	98	67	11	10	-
Al-TUD-1(21)	110	0.6	30	24	93	72	7	8	-
Al-TUD-1(4)	140	0.3	10	24	97	65	14	7	-
Al-TUD-1(4)-at	140	0.3	10	24	88	81	-	6	-
Al-MCM-41(25)	140	0.7	n.m.	5	100	37	-	47	5d
Al-MCM-41(50)	140	0.7	n.m.	5	100	68	-	10	5d
Al-MCM-41(75)	140	0.7	n.m.	5	61	-	-	-	5d
Al-SBA-15	140	0.7	n.m.	5	75	-	-	-	5d
ZrO ₂ /SBA-15	140	0.7	n.m.	5	100	76	-	23	5d
SO ₄ ²⁻ /ZrO ₂ /SBA-15	140	0.7	n.m.	5	100	62	-	35	5d
SO ₃ H-SBA-15	140	0.12	16	24	~ 100	~ 10	-	~ 75	5i
H-ZSM-5 (11.5)	140	0.12	16	24	~ 100	~80	-	~ 5	5i
H-Mordenite(10)	140	0.12	16	24	~ 100	~ 80	-	~ 5	5i
Silica sulfuric acid	75	0.39	4.3	24	100	36	25	7	5b
H-Y	70	0.2	6	24	10	9	-	-	5e
H ₄ SiW ₁₂ O ₄₀ /MCM-41	90	1.7	42	4	92	77	-	6	5a
[MimB(SO ₃ H)] ₃ PW ₁₂ O ₄₀	70	0.2	37.5	24	98	91	-	-	5e

^a Value in parenthesis (when applied) is the Si/Al molar ratio. ^b Reaction conditions: T=reaction temperature (°C), [Hmf]₀=initial molar concentration of Hmf (M), Cat. load=catalyst loading (g_{cat}.dm⁻³), t=time of reaction (h), n.m.=not mentioned.^c Hmf conversion.^d Results in parenthesis are for batch 2 and 3, respectively (24 h reaction for each batch).

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Table 3 Al-TUD-1 catalysts for the production of EL and different furanic ethers via the reactions of Hmf and FA with ethanol.^a

Catalyst	0.1.4.4	Conversion at 30 min/24 h/48 h (%)	Yields of BioEs products at 30 min/24 h/48 h (%)			
	Substrate		Emf	5Emf	EL	
Al-TUD-1(21)	Hmf	31/97/100	-	16/70/61	1/11/21	
Al-TUD-1(4)	Hmf	31/97/100	-	17/65/75	1/7/11	
Al-TUD-1(4)-at	Hmf	27/88/100	-	18/81/68	0/6/11	
Al-TUD-1-(21)°	FA	100/100/100	44/0/0	-	13/80/80	
Al-TUD-1-(4)	FA	95/100/100	40/4/0	-	5/51/60	
Al-TUD-1(4)-at	FA	97/100/100	52/19/2	-	5/36/59	

^a Reaction conditions: [substrate]₀=0.3 M; catalyst loading=10 g_{cat}.dm⁻³, 140 °C. ^b Yield of Emf and 5Emf for FA and Hmf as substrate, respectively. ^c Results taken from 6c

- EL production from the biorenewable substrates FA and 10 Hmf. The conversion of FA to EL involved 2- 30 with 1-butanol in the presence of Al-TUD-1(21), at 140 °C, (ethoxymethyl)furan (Emf) as intermediate, which has similar chemical features to 5Emf formed in the conversion of Hmf to EL.^{41,6} The two furanic ethers may be converted to a common alkyl levulinate.^{6c} Some of the products identified in the 15 reaction of Hmf, such as angelica lactones (ALs) and 5,5-
- diethoxy-2-pentanone (Table S1), have also been identified for the reaction of FA with ethanol.^{6c} These results suggest that the overall reaction mechanisms for the two substrates have similar pathways and intermediates. For the three Al-TUD-1
- yields and in shorter reaction times in comparison to Hmf as substrate (Figs 5 and 6, Table 3). In contrast to that for FA, the conversion of Hmf to EL is accompanied by the formation of ethyl formate as co-product. Hence, the theoretical carbon
- 25 atom efficiency for the production of alkyl levulinates is 45 identified as 5,5-dibutoxy-2-pentanone (DBPent), based on the higher for the substrate FA than for Hmf. FA therefore seems to be a more attractive substrate than Hmf for the production of alkyl levulinates.

Conversion of FA to alkyl levulinates. The reaction of FA was complete within 30 min. The reaction products were identified GC×GC-ToFMS. Initially. hv 2-(butoxymethyl)furan (Bmf) was formed in 24% yield at 30 min reaction, and then it was consumed with the concomitant

- 35 formation of butyl levulinate (BL); a maximum BL yield of 60% was reached at 24 h reaction (Fig. 6). Without adding a catalyst these products were not formed in measurable amounts (conversion at 24 h was 43%). These results show the important role of the catalyst for selectively producing bioEs.
- 20 catalysts prepared, the reaction of FA led to much higher EL 40 The above kinetic features are consistent with Bmf being an intermediate of the conversion of FA to BL. On the other hand, the increasing BL yields at 100% conversion suggest that the primary elementary step of the conversion of FA is faster than that of BL formation. Another intermediate was
 - mass fragmentation pattern (m/z 57, 159, 103, 229, 173; Fig. S4). This compound has similar chemical features to 5,5-

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dietoxy-2-pentanone formed when ethanol is used instead of

1-butanol.6c



Fig. 6 Dependence of $\text{Emf}(\mathbf{A}, \Delta)$ and $\text{EL}(\mathbf{u}, \Box)$ yields, or $\text{Bmf}(\mathbf{\Phi}, \diamond)$ and $\text{BL}(\mathbf{u}, \Box)$ yields, on the time of the reaction of FA with ethanol (a) or 5 1-butanol (b), respectively, in the presence of Al-TUD-1(21) (solid symbols) or Al-TUD-1 (4) (open symbols) at 140 °C. Reaction conditions: $[FA]_0 = 0.3$ M in alcohol reagent, catalyst loading of 10 g_{cat}.dm⁻³. The FA conversion was always \geq 95%. Data for Al-TUD-1(21)/ethanol/140°C taken from ^{6c}. The dashed lines are visual guides.

A comparison of the type of aliphatic alcohol reagent used 10 for producing different types of alkyl levulinates from FA, in the presence of Al-TUD-1(21) at 140 °C, indicated very fast reaction of FA regardless of the aliphatic alcohol used (100% be higher than BL ones (Fig. 6). The two alkyl levulinates BL 15 and EL are relatively stable under the reaction conditions used,

- since when they were used as substrates instead of FA, conversion at 24 h reaction was 3%. Somewhat in parallel with for the FA/isopropanol system than for the FA/tert-butanol one
- 20 using the catalyst [MimB(SO₃H)]₃PW₁₂O₄₀ at reflux temperature (these two aliphatic alcohols possess similar boiling points).^{6b} A common result between our study and that for the system involving the bulkier aliphatic alcohol, 25 suggesting that steric hindrance effects may be important.
- For the two alcohol systems, the curves of alkyl levulinate vields as a function of time reached a plateau after a certain reaction time, possibly due to catalyst deactivation (Fig. 6). The originally white catalyst turned brown in color after the
- 30 catalytic reaction, suggesting the presence of organic matter, similar to that discussed above for Hmf, with the catalyst regeneration being effectively accomplished by applying a thermal treatment to the used Al-TUD-1 solid.
- Several by-products were detected by GC×GC-ToFMS 35 analysis of the reaction mixture of the FA/1-butanol system at 24 h (Table S2). When comparing the chromatograms for the FA/1-butanol and FA/ethanol^{6c} systems in the presence of Al-TUD-1(21), at 24 h reaction (the instant at which maximum alkyl levulinate yields were reached; conversion was 100%), a
- 40 wider product spectrum is observed in the case of the 1butanol system (Fig. 4). Hence, it seems that less hindered FA/alcohol systems lead to more selective production of the levulinate ester.

Some of the identified byproducts (indicated by # in Table

- 45 S2) are common to the two alcohol systems, suggesting that the respective overall reaction mechanisms share common pathways and intermediates. In the case of the 1-butanol 4aliphatic compounds (e.g. 2-cyclopenten-1-one,
- 50 cyclopentene-1,3-dione), C₆ aromatic, and furyl compounds

(e.g. 1-(2-furyl)-butan-3-one). By-products such as 2,2'methylenebis(furan), 2-(2-furylmethyl)-5-methylfuran, 2,2'methylenebis(5-methylfuran), 2,5-bis(2-furylmethyl)furan and 2,2'-(2-furylmethylene)bis(5-methylfuran) may lead to coke conversion at 30 min). On the other hand, EL yields tended to 55 formation and consequent catalyst deactivation. Butyl ester products, such as butyl-2-furoate, were formed. Some byproducts are common to the catalytic reaction of FA with 1butanol, and to the reaction of 1-butanol as the sole substrate (without FA), at 140 °C: e.g. ethers (dibutylether (DBE), our results, higher alkyl levulinate yields have been reported 60 dibutoxyalkanes) and esters (acetic acid butyl ester, butanoic acid butyl ester). Hence, the "non-productive" consumption of 1-butanol may be due to self-reactions of the alcohol and, on the other hand, side reactions with FA.

- Decreasing the reaction temperature from 140 to 110 °C of ref. 6b is that lower alkyl levulinate yields were obtained 65 for the FA/1-butanol system led to similar reaction rates (100% FA conversion at 30 min), and lower BL yields up to 32 h reaction (Fig. 7). As the reaction time approached 48 h. the BL yields tended to similar values (60-62% yield, at 110-140 °C). A plateau of BL vield versus time was observed for
 - 70 the two reaction temperatures, although it was reached in shorter time at the higher reaction temperature of 140 °C. These results may be due to slower catalyst deactivation at lower reaction temperature.
 - A comparison of the Al-TUD-1 catalysts with Si/Al ratios 75 of 4 and 21, at 140 °C, reveals that higher alkyl levulinate yields were observed for Al-TUD-1(21), with the differences being more pronounced for the ethanol system than for the 1butanol one (Fig. 6). Possibly, for the former system the Brönsted acidity and strength are relatively important (the L/B
 - ratio is highest for Al-TUD-1(21)). Somewhat consistent with 80 this hypothesis is the fact that the strong Brönsted acid catalyst AmberlystTM-15 led to much higher EL yields^{6c} than BL ones (discussed below). In terms of Emf yield, one of the best results is that for Al-TUD-1(4) which led to 60% yield at
- 85 100% conversion reached at 1 h reaction, 140 °C (Fig. 6a). These results are somewhat in parallel with those discussed above for Hmf in that higher furanic ether yields were reached for Al-TUD-1(4) than for Al-TUD-1(21). Hence, depending on the target product being levulinate esters or furanic ethers, system, the identified products include cyclic and linear 90 the acid property requirements may differ, with Brönsted and strong acid sites being more favourable in the former case. Besides the acid properties, the texture properties may play a

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role in product yields; one may expect larger pores to be favourable for reaction systems involving bulky aliphatic alcohol reagents. Accordingly, an interplay of acid and texture properties may at least partly explain the smaller differences in

5 EL and BL yields in the case of Al-TUD-1(4) (possessing much greater pore sizes) in comparison to that observed for Al-TUD-1(21).

Al-TUD-1 versus AmberlystTM-15. For comparison, the 10 reaction of FA with 1-butanol was carried out in the presence of the ion-exchange resin AmberlystTM-15 (Table 4, Fig. 7). To the best of our knowledge this is the first report of AmberlystTM-15 tested as catalyst for the FA/1-butanol reaction system. AmberlystTM-15 led to 100% conversion 15 within 30 min reaction, similar to that observed for Al-TUD-1. However, higher BL yields were observed for AmberlystTM-15 than for Al-TUD-1(21) at 110-140 °C (Fig. 7), or Al-TUD-1(4) at 140 °C; e.g. while the acid resin led to 55% BL yield at 30 min reaction, 140 °C, Al-TUD-1(21) led to 29%. These
20 results may be due to the fact that the acid resin catalyst possesses a considerably higher amount of Brönsted acid sites (4600 μmol_{H+}g⁻¹) in comparison to Al-TUD-1. Several

- (4600 μmol_{H+}.g⁻¹) in comparison to Al-TUD-1. Several products identified by GC×GC-ToFMS for the FA/1-butanol/Al-TUD-1(21) system (discussed above) were also 25 formed with AmberlystTM-15 as catalyst (Table S2),
- suggesting that the overall reaction mechanism is similar for the two catalysts. On the other hand, in comparison to Al-TUD-1(21), AmberlystTM-15 led to relatively high amounts of dibutyl ether, a possible product of the "non-productive"
- **30** consumption of 1-butanol; the molar ratio DBE/FA₀ (where FA₀ is the initial number of moles of FA) was 1.2 and 0.01 for AmberlystTM-15 and Al-TUD-1(21) at 24 h/140 °C, respectively. Similar trends were observed for the lower reaction temperature; no measurable amount of DBE was
- **35** formed for Al-TUD-1(21) at 24 h, whereas DBE/FA₀ was 0.1 for AmberlystTM-15. For AmberlystTM-15, and the reaction temperature range 110-140 °C, the curves of BL yield versus reaction time reached a plateau without giving quantitative BL yield, suggesting that catalyst deactivation occurred. It has
- 40 been previously reported for AmberlystTM-15 tested as catalyst for the FA/ethanol reaction system, under similar reaction conditions to those used in the present work, that leaching of the active species and coke formation occurred.^{6c} Thermal or chemical treatments to remove organic deposits from the acid 80
 45 resin catalyst may decompose it.^{6c,8a} In contrast, Al-TUD-1 is
- 45 resin catalyst may decompose it.^{6c,8a} In contrast, Al-TUD-1 is a heterogeneous catalyst which can be effectively regenerated and reused.

Table 4 Catalytic performances of Al-TUD-1(21) versusAmberlyst TM -15 in the reaction of FA with 1-butanol.^a

Catalyst	Reaction temperature (°C)	BL yield (%)
Al-TUD-1(21)	110	51
Amberlyst TM -15	110	72
Al-TUD-1(21)	140	60
Amberlyst TM -15	140	68

50 ^a Reaction conditions: [FA]₀=0.3 M; catalyst loading=10 g_{cat}.dm⁻³; 24 h reaction; conversion was always 100%; no measurable amount of Bmf was obtained at 24 h.



1(4) at 140 °C; e.g. while the acid resin led to 55% BL yield at 30 min reaction, 140 °C, Al-TUD-1(21) led to 29%. These results may be due to the fact that the acid resin catalyst possesses a considerably higher amount of Brönsted acid sites (4600 μ mol_{H+}.g⁻¹) in comparison to Al-TUD-1. Several (4600 μ mol_{H+}.g⁻¹) in comparison (4

Conclusions

The mesoporous material Al-TUD-1 is a versatile heterogeneous acid catalyst for the conversion of the biorenewable substrates 5-hydroxymethyl-2-furfural (Hmf) 65 and furfuryl alcohol (FA) to furanic ethers or levulinate esters (bioEs) with applications in the biofuels sector. Levulinate esters can be obtained from the catalytic reactions of Hmf and FA with aliphatic alcohols. The highest alkyl levulinate yields were reached using Al-TUD-1 with Si/Al=21 as catalyst in the

- 70 reaction of FA. On the other hand, the highest 5Emf yield was reached using acid-treated Al-TUD-1 with Si/Al=4 as catalyst in the reaction of Hmf. FA seems to be a more attractive substrate than Hmf for producing EL, since it led to higher EL yields and, on the other hand, the theoretical carbon atom 75 efficiency is higher for the FA-to-alkyl levulinate system than
 - 5 efficiency is higher for the FA-to-alkyl levulinate system than for the Hmf-to-alkyl levulinate one. Depending on the target product being levulinate esters or furanic ethers, the acid property requirements seem to be different; Brönsted and strong acid sites favour the production of alkyl levulinates,
 - ³⁰ whereas the production of furanic ethers seems to be less demanding in terms of catalyst acidity. Although the strong Brönsted acid catalyst AmberlystTM-15 (chosen as a benchmark catalyst) led to higher BL yields than Al-TUD-1 in the reaction of FA with 1-butanol, Al-TUD-1 stands on a
- 85 higher footing in terms of thermal and chemical stability. Al-TUD-1 can be effectively regenerated, giving similar catalytic results in recycling runs.

Experimental

Catalyst preparation

- 90 The preparation and characterisation of the Al-TUD-1 catalyst with Si/Al atomic ratio of 21 (denoted Al-TUD-1(21)) has been reported elsewhere.¹⁵ The synthesis of the aluminosilicate Al-TUD-1 with Si/Al=4 (denoted Al-TUD-1(4)) was performed following the procedure reported in ref.
- 95¹⁵. Aluminium isopropoxide (6.12 g, Aldrich, >98 %) was added to a mixture of absolute ethanol (27.65 g, Fisher) and anhydrous 2-propanol (27.04 g, Aldrich, >99.5%), and kept at

45 °C. Tetraethylorthosilicate (24.99 g, Aldrich, >99 %) followed by tetraethyleneglycol (29.17 g, Aldrich, 99%) were added. After stirring for 1 h, a mixture of demineralised water (5.41 g), absolute ethanol (27.65 g) and anhydrous 2-propanol 65

- 5 (27.04 g) was added dropwise and the suspension stirred for 0.5 h at room temperature, followed by aging for 6 h. The wet gel was then dried at 70 °C for 21 h, at 98 °C for 2 h, and subsequently it was hydrothermally treated in a Teflon-lined autoclave at 160 °C for 19 h. The final solid was obtained by 70 sampling, the reactors were cooled to ambient temperature
- 10 calcination at 550 °C for 4 h (heating rate of 1 °C min⁻¹) followed by 10 h at 600 °C (heating rate of 1 °C min⁻¹). Al-TUD-1(4) was treated with HCl as described in ref.

16b. A mixture of Al-TUD-1(4) (1 g) and 1 M HCl (10 mL) was stirred for 30 min at 30 °C. The solid was separated by

- 15 centrifugation and thoroughly washed with distilled water until neutral pH, and finally dried at 65 °C overnight to give Al-TUD-1(4)-at.
 - cation-exchange resin AmberlystTM-15 The (a macroreticular styrene-divinylbenzene copolymer bearing
- 20 benzenesulfonic acid groups) was acquired from FlukaChemika. The resin was manually ground using an agate pestle and mortar and subsequently sieved to give a powder with particle sizes of less than 106 µm width.

Catalyst characterisation

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- 25 X-Ray powder diffraction patterns were measured on a PANalytical X'Pert MPD diffractometer at 45 kV and 40 mA with a step size of 0.04° and time per step of 6 s, using Cu Ka 90 radiation (λ = 0.1541 nm). Nitrogen sorption isotherms were measured at -196 °C with a Micromeritics ASAP 2010. Before
- 30 the measurements the samples were degassed at 90 °C for 1 h and then at 350 °C for 6 h. The pore size distribution curve was calculated using the BJH algorithm applied to the 95 desorption branch. ²⁷Al MAS NMR spectra were recorded at 104.26 MHz with a Bruker Avance 400 (9.4 T) spectrometer,
- 35 using a contact time of 0.6 μ s, a recycle delay of 0.8 s, and a spinning rate of 15 kHz. Chemical shifts are quoted in ppm from $Al(H_2O)_6^{3+}$. Scanning electron microscopy (SEM)100 images were recorded on a Hitachi SU-70 HR microscope operating at 15 kV coupled with a Bruker Quantax 400 energy 40 dispersive X-ray spectroscopy system.

The acid properties of Al-TUD-1(4) were measured using a Nexus-Thermo Nicolet FTIR instrument (64 scans and 105 by centrifugation and filtration using a 0.2 µm PTFE resolution of 4 cm⁻¹) equipped with a specially designed cell, using self-supported discs (5-10 mg cm⁻²) and pyridine as the

45 basic probe molecule. After in situ outgassing at 450 °C for 3 h (10^{-6} mbar) , pyridine (99.99%) was contacted with the sample at 150 °C for 10 min and then evacuated at 150 and 350 °C (30 min) under vacuum (10⁻⁶ mbar). The IR bands at ca. 1540 and 110 Identification of the reaction products by GC×GC-ToFMS 1455 cm⁻¹ are related to pyridine adsorbed on Brönsted and 50 Lewis acid sites, respectively, allowing their quantification.²

Catalytic experiments

micro-reactors with pear-shaped bottoms and equipped with an appropriate PTFE-coated magnetic stirring bar and a valve. In

- 55 a typical procedure, 0.3 M 5-(hydroxymethyl)-2-furfural (Hmf, Aldrich, 99%) or furfuryl alcohol (FA, Aldrich, 99%), powdered catalyst (loading of 10 g_{cat} dm⁻³), and 1 mL of 120 and a secondary oven. The detector was a high-speed ToF alcohol (ethanol (Riedel-de Haën, 99.8%) or 1-butanol (Alfa Aesar, 99.4%)) were added to the reactor. Individual
- 60 experiments were performed for a given reaction time and the presented results are the mean values of at least two replicates.

The reaction mixtures were heated with a thermostatically controlled oil bath (at 110 or 140 °C) under continuous magnetic stirring at 1000 rpm. Zero time (the instant the reaction began) was taken to be the instant the micro-reactor was immersed in the oil bath.

The evolution of the catalytic reactions was monitored by GC (for FA conversion, and the yields of the reaction products of FA and Hmf) and HPLC (for Hmf conversion). Prior to

- before opening and work-up procedure, and no pressurerelease was verified. The GC analyses were carried out using a Varian 3800 equipped with a capillary column (Chrompack, CP-SIL 5CB, 50 m \times 0.32 mm \times 0.5 μ m) and a flame 75 ionisation detector, using H_2 as carrier gas. Authentic samples
- of the substrates EL and BL were used as standards, and calibration curves were measured for quantification. The amount of Hmf was measured using a Knauer K-1001 HPLC pump and a PL Hi-Plex H 300 mm × 7.7 mm (i.d.) ion
- 80 exchange column (Polymer Laboratories Ltd., UK), coupled to a Knauer 2600 UV detector (280 nm). The mobile phase was 0.005 M H₂SO₄. Analysis conditions: flow rate 0.6 mL min⁻¹, column temperature 65 °C.
- The substrate (Sub) conversion (%) at reaction time t was 85 calculated using the formula: [(initial concentration of Sub)-(concentration of Sub at time t)]/(initial concentration of Sub)×100. The yield of product (Pro) (%) at reaction time twas calculated using the formula: [(concentration of Pro at time *t*)/(initial concentration of Sub)] \times 100. The bioEs products considered were EL, 5Emf plus 5Emfda for Hmf as the substrate, and Emf plus EL, or Bmf plus BL for FA as the substrate, where 5Emfda = 5-(ethoxymethyl)furfural diethylacetal, Emf = 2-(ethoxymethyl)furan and Bmf = 2-(butoxymethyl)furan. After a 24 h batch run, the solid catalyst was separated from the reaction mixture by centrifugation, thoroughly washed with ethanol, dried at 85 °C overnight, and finally calcined at 450 °C (heating rate of 1 °C min⁻¹) for 4 h to give the regenerated catalyst which was reused in consecutive 24 h batch runs.

Leaching tests were performed in order to check for soluble active species, and were carried out as follows. The catalyst was treated for 24 h at 140 °C under similar conditions to those used for the typical catalytic run, but without substrate; subsequently the solids were separated from the liquid phase membrane; the substrate was then added to the liquid phase giving a reaction solution with an initial substrate concentration of 0.3 M; the obtained reaction solution was stirred for 24 h at 140 °C, and finally analysed by GC.

analyses

The liquid phase of the reaction mixture (after separating the solid phase by centrifugation and filtration with a 0.2 µm PTFE membrane) was analysed by GC×GC-ToFMS. The Batch catalytic experiments were performed in tubular glass115 injection port (250 °C) was lined with a 0.75 mm I.D. splitless glass liner; splitless injections were used (30 s). The LECO Pegasus 4D (LECO, St. Joseph, MI, USA) GC×GC-ToFMS system consisted of an Agilent GC 7890A gas chromatograph, with a dual stage jet cryogenic modulator (licensed from Zoex) mass spectrometer. A non-polar/polar set of columns was used: a HP-5 column (30 m \times 0.32 mm I.D., 0.25 μ m film thickness, J&W Scientific Inc., Folsom, CA, USA) was used as first-dimension column and a DB-FFAP (0.79 m \times 0.25 mm 65

I.D., 0.25 μ m film thickness, J&W Scientific Inc., Folsom, CA, USA) was used as a second-dimension column. The carrier gas was helium at a constant flow rate of 2.0 mL min⁻¹. The primary oven temperature was programmed from 35 °C to

- 5 50 °C (0.2 min) at a heating rate of 2 °C min⁻¹, then to 220 °C (14 min) at a heating rate of 5 °C min⁻¹; the secondary oven temperature was programmed from 50 °C to 65 °C (0.2 min) at a heating rate of 2 °C min⁻¹, then to 235 °C (14 min) at a heating rate of 5 °C min⁻¹. The MS transfer line temperature 70
- 10 and the MS source temperature were 250 °C. The modulation time was 5 s, and the modulator temperature was kept at 20 °C offset (above primary oven). The ToFMS was operated at a spectrum storage rate of 100 spectra s⁻¹. The mass spectrometer was operated in the EI mode at 70 eV using a
- 15 range of m/z 33-500 and the detector voltage was 1626 V. 75 Total ion chromatograms (TIC) were processed using the automated data processing software ChromaTOF (LECO) at a signal-to-noise threshold of 100. Contour plots were used to evaluate the separation general quality and for manual peak
- 20 identification; a signal-to-noise threshold of 50 was used. Two commercial databases (Wiley 275 and US National Institute of 80 Science and Technology (NIST) V. 2.0 Mainlib and Replib) were used. The majority (62% and 87% for Hmf and FA catalytic systems, respectively) of the identified compounds
- 25 showed mass spectral similarity matches > 800. Furthermore, a manual inspection of the mass spectra was done, combined with the use of additional data, such as the retention index (RI) value, which was determined according to the Van den Dool and Kovats RI equation.²¹ For the determination of the RI, a
- 30 C_{8} - C_{20} *n*-alkane was used, and as some volatile compounds were eluted before C_8 , the solvent *n*-hexane was used as C_6 standard. The experimentally calculated RI values were 90 compared, when available, with values reported in the literature for similar chromatographic columns employed as 35 the first dimension.

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