Supplementary Information

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

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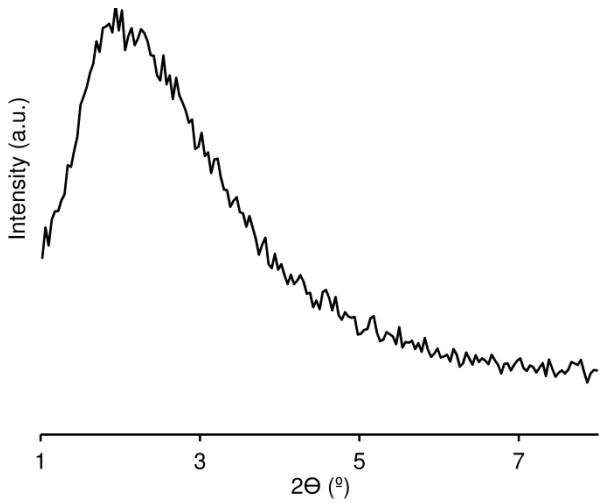


Fig.S1 Low angle X-Ray powder diffraction pattern of Al-TUD-1(4).

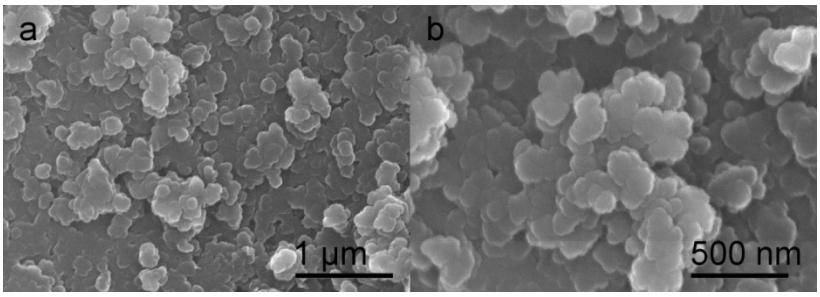


Fig. S2 SEM images of the Al-TUD-1(4) catalyst.

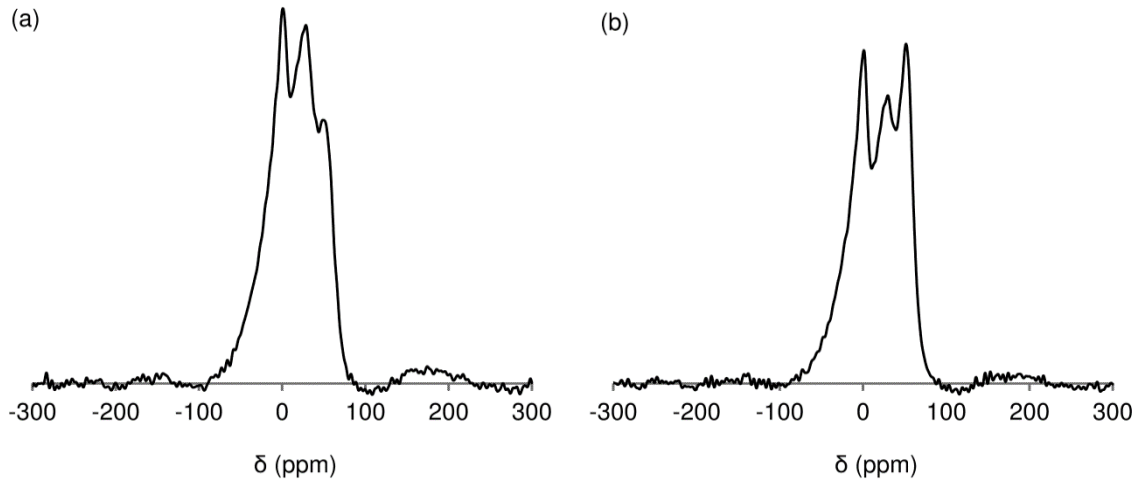


Fig. S3 ^{27}Al MAS NMR spectra of Al-TUD-1 (Si/Al=4) a) before and b) after HCl treatment to give Al-TUD-1(4)-at.

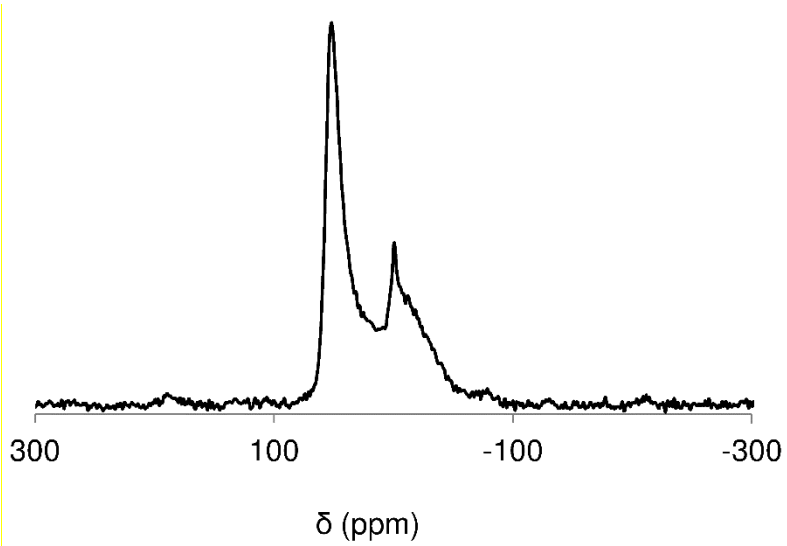
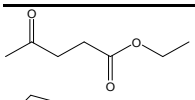
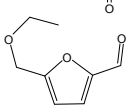
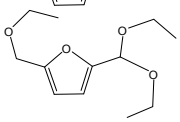
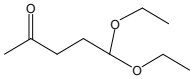
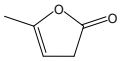
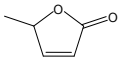
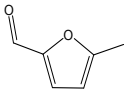
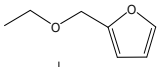
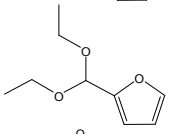
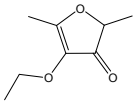
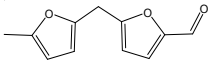
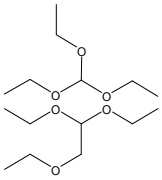


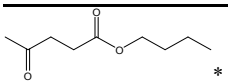
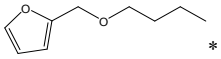
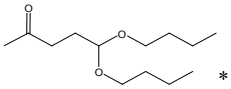
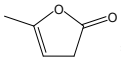
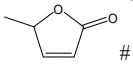
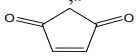
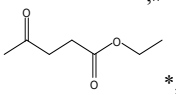
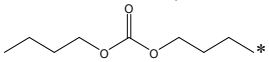
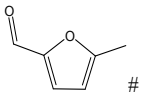
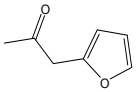
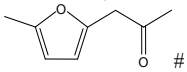
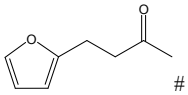
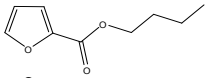
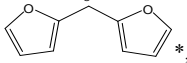
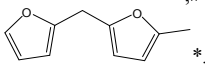
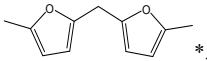
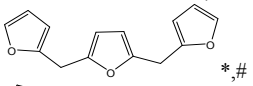
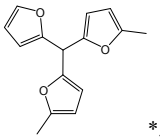
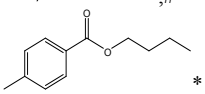
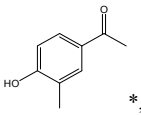
Fig. S4 ^{27}Al MAS NMR spectrum of the used-calcined Al-TUD-1(21) catalyst.

Table S1 Compounds detected by GC×GC-ToFMS for the reaction mixture of Hmf with ethanol in the presence of Al-TUD-1(21), at 140 ºC. [a]

Reaction product		Sim.[b]	RI[c]	RI [Ref][d]
Molecular structure	Name of compound			
	ethyl levulinate (EL)	959	1063	1070 [1]
	5-(ethoxymethyl)furan-2-carbaldehyde (5Emf)	876	1222	-
	5-(ethoxymethyl)furfural diethylacetal (5Emfda)	-[e]	1435	-
	5,5-diethoxy-2-pentanone	856	1158	1158 [2]
	α-angelica lactone	934	874	884 [3]
	β-angelica lactone	930	955	954 [3]
	5-methyl furfural	963	975	978 [4]
	2-(ethoxymethyl)furan	-[e]	917	913 [5]
	2-furaldehyde diethyl acetal	816	1079	1078 [2]
	4-ethoxy-2,5-dimethyl-3(2H)-furanone	824	1096	-
	5-[(5-methyl-2-furyl)methyl]-2-furancarboxaldehyde	815	1528	-
Products formed from ethanol				
	Triethoxymethane	940	913	-
	ethoxyacetaldehyde diethylacetal	917	1004	998 [5]

[a]Reaction conditions: $[Hmf]_0$=0.3 M, 10 g_{cat} dm^{-3}, 24 h reaction, at 140 ºC. [b] Mass spectral similarity. [c] Retention index (RI) obtained through the modulated chromatogram. [d] Retention index reported in the literature for one dimensional GC with 5%-phenyl-methylpolysiloxane GC column or equivalent. [e]The mass spectra was not available in the software's database.

Table S2 Compounds detected by GC×GC-ToFMS for the reaction mixture of FA with butanol in the presence of Al-TUD-1(21), at 140 ºC.[a]

Reaction Product[b]		Sim.[c]	RI[d]	RI [Ref.][e]
Molecular structure	Name of compound			
 *	butyl levulinate	921	1251	1257 [5]
 *	2-(butoxymethyl)furan (Bmf)	-[f]	1091	-
 *	5,5-dibutoxy-2-pentanone (DBPent)	-[f]	1776	-
 *,#	α-angelica lactone	952	895	884 [3]
 #	β-angelica lactone	954	960	954 [3]
 *,#	2-cyclopenten-1-one	922	871	835 [6]
 *,#	4-cyclopentene-1,3-dione	856	920	911 [7]
 *,#	ethyl levulinate (EL)	969	1068	1070 [1]
 *	carbonic acid, dibutyl ester	886	1176	-
 #	5-methyl furfural	941	980	978 [4]
	1-(2-furyl)-2-propanone	901	970	954 [8]
 #	1-(5-methyl-2-furyl)-2-propanone	863	1051	1056 [9]
 #	1-(2-furyl)-butan-3-one	863	1077	1089 [7]
	butyl-2-furoate	884	1248	-
 *,#	2,2'-methylenebis(furan)	817	1084	1086 [10]
 *,#	2-(2-furylmethyl)-5-methylfuran	939	1179	1195 [7]
 *,#	2,2'-methylenebis(5-methylfuran)	940	1277	1277 [5]
 *,#	2,5-bis(2-furylmethyl)furan	922	1650	1653 [5]
 *,#	2,2'-(2-furylmethylene)bis(5-methylfuran)	855	1627	1631 [5]
 *	o-toluic acid, 2-butyl ester	890	1449	-
 *,#	4-hydroxy-3-methylacetophenone	922	1311	1323 [11]

Products formed from 1-butanol

dibutyl ether	918	882	888 [12]
di-*sec*-butyl ether	941	860	-
1,1-diethoxybutane	879	925	929 [2]
1,1-dibutoxyethane	922	1098	-
2,2-dibutoxypropane	829	1127	-
1,1-dibutoxybutane	803	1259	1229 [12]
acetic acid, butyl ester	956	847	830 [13]
butanoic acid, butyl ester	958	1005	1002 [14]

[a] Reaction conditions: $[FA]_0$=0.3 M, 10 gcat dm^{-3}, 24 h reaction, at 140 ºC. [b] Symbols # and * indicate that the same product was also detected for the Al-TUD-1-21/FA/ethanol catalytic system at 140 ºC and 24 h[5], and for the Amberlyst™-15/FA/1-butanol system at 4 h and 140 ºC, respectively. [c] Mass spectral similarity. [d] Retention index (RI) obtained through the modulated chromatogram. [e] Retention index reported in the literature for one dimensional GC with 5%-phenyl-methylpolysiloxane GC column or equivalent. [f]The mass spectra is not available in the software's database.

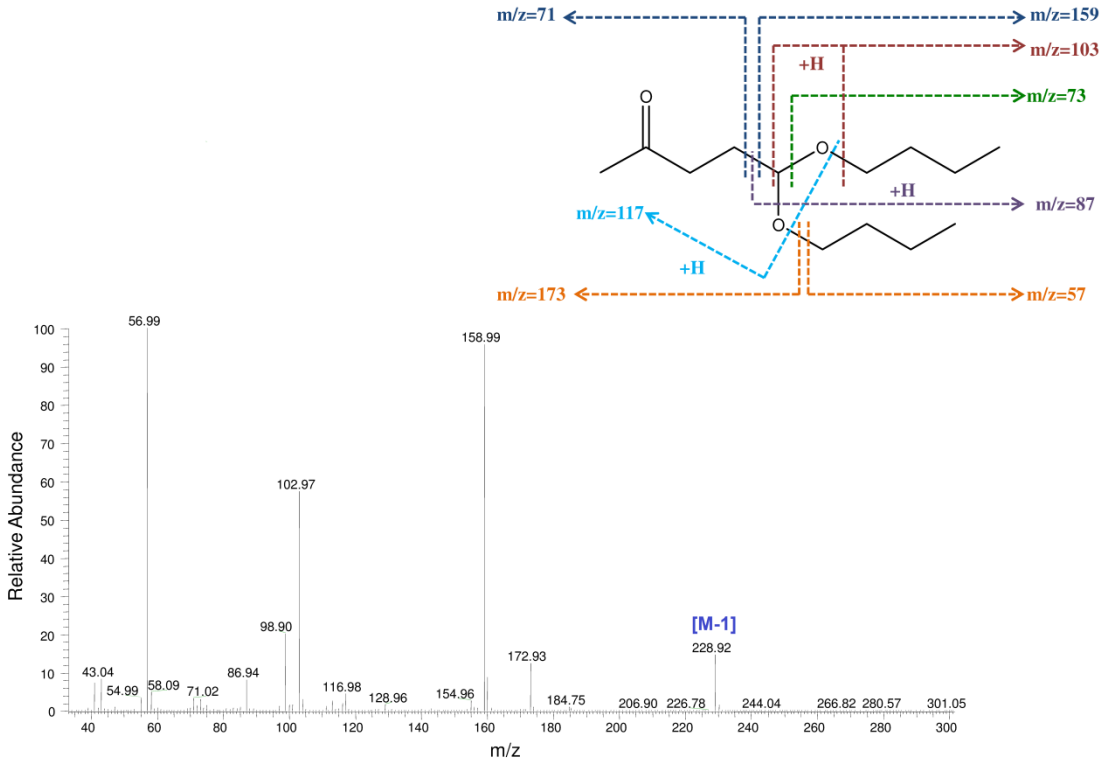


Fig. S5. Mass spectrum and proposed fragmentation mass spectrometry pattern of the intermediate DBPent (identified by GC×GC-ToFMS), for the reaction of FA and 1-butanol, in the presence of Al-TUD-1(21), at 140 ºC.

References

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