Electronic Supplementary Material (ESI) for Green Chemistry.

ELECTRONIC SUPPLEMENTARY INFORMATION.

Improving the production of maleic acid from biomass: TS-1 catalysed aqueous phase oxidation of furfural in the presence of γ-valerolactone

Y. Rodenas[a], R. Mariscal[a], J. L. G. Fierro[a], D. Martín Alonso[b,c], J. Dumesic*[b] and M. López Granados*[a]

---

[a] *Sustainable Energy and Chemistry Group, Institute of Catalysis and Petrochemistry (CSIC), Campus Cantoblanco, C/ Marie Curie 2, 28049 Madrid (Spain).*

[b] *Glucan Biorenewables LLC., Madison, WI 53719, USA.*

[c] *Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, WI 53706, USA.*

EXPERIMENTAL DETAILS OF THE CHARATERISATION TECHNIQUES

Qualitative and quantitative TXRF analysis of Ti and Si were performed with a benchtop S2 PicoFox TXRF spectrometer from Bruker Nano (Germany), equipped with a Mo X-ray source working at 50 kV and 600 µA, a multilayer monochromator with 80% of reflectivity at 17.5 keV (Mo K_{α}), a XFlash SDD detector with an effective area of 30 mm^2 and an energy resolution better than 150 eV for 5.9 keV (Mn K_{α}). The acquisition time was 300 s and 500 s for qualitative and quantitative analysis, respectively. For the analysis of solid samples, 10-15 mg of sample was ground in an agate mortar to a powder with a particle size less than 10 µm. Subsequently, 10 ml of high-purity water was added to the powder. The sample was homogenized for 15-20 min by ultrasonic disaggregation to disperse any possible agglomeration of particles. A 5 µl aliquot of the suspension was placed on a flat carrier of plastic after which the water was evaporated by vacuum. Further details can be found elsewhere [1].

Raman spectra were recorded on a single-monochromator Renishaw 1000 spectrophotometer equipped with a CCD cool detector (200 K), with an argon laser as the excitation source (λ = 532 nm), a single 1800/1200 lines/mm grating monochromator, and a supernotch filter. The collection optic was set at 50× objective. Raman spectra were recorded at room temperature with a laser power of 2-5 mW to prevent damaging the sample.

Thermogravimetric analysis (TGA) under a controlled atmosphere was carried out on a Mettler Toledo TGA/SDTA 851^e, using a heating rate of 10 K min^{-1} up to a maximum temperature of 1273 K under a flow of synthetic air.

X-ray photoelectron spectra (XPS) were acquired with a VG Escalab 200 R spectrometer equipped with a hemispherical electron analyser and a Mg Kα (1253.6 eV) X-ray source. The solids were outgassed at 393 K for 1 h at 10^{-5} mbar to remove water before transfer to the ion-pumped analysis chamber. Si 2p and Ti 2p spectra were scanned a sufficient number of times to obtain high signal-to-noise ratios (around 10 and 40-60 accumulations for Si 2p and Ti 2p core levels, respectively). The static charge of the samples was corrected by referencing binding energies (BEs) to the Si 2p peak (103.4 eV). The areas of the peaks were computed by fitting the experimental spectra to Gaussian/Lorentzian curves after removing the background (using the Shirley function). Surface atom ratios were calculated from peak area ratios normalised by using the corresponding atomic sensitivity factors [2].

1. R. Fernández-Ruiz and M. García-Heras, *Spectrochimica Acta - Part B Atomic Spectroscopy*, 2007, **62**, 1123-1129.
2. C. D. Wagner, *Journal of Electron Spectroscopy and Related Phenomena*, 1983, **32**, 99-102.

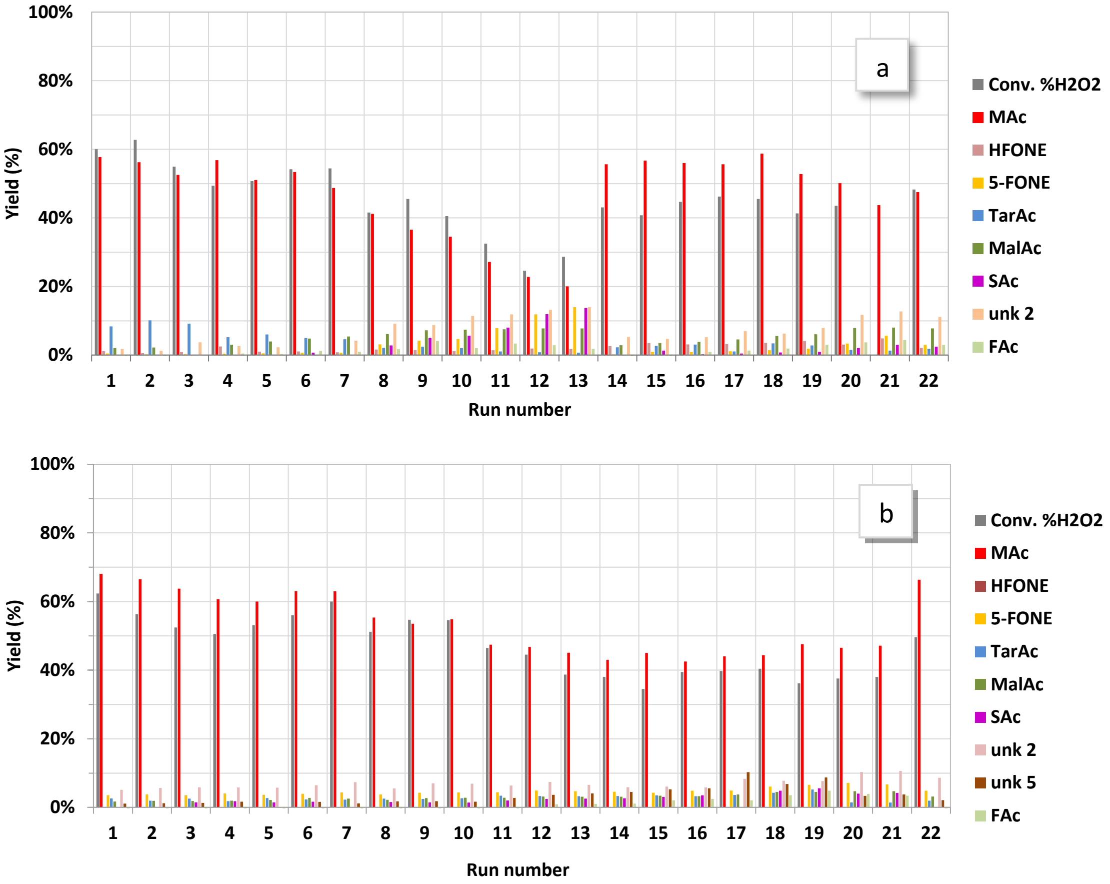

Figure ESI-1. Reutilization of TS-1 at 50 °C using high grade furfural: a) in H_2O, (77 wt. of H_2O) and (b) in GVL-H_2O solution, 42.5 wt.% of GVL and 34 wt.% of H_2O. Common reaction conditions: 5 wt.% of furfural (0.25 g), wt Ti/furfural = 0.016, mol H_2O_2/FUR = 7.5 and reaction time = 17 h. Unk2 and unk5 refers to the most important unknown products detected by HPLC.

Reutilization of TS-1 at 50 °C.

Figure ESI-1 shows the better reutilization properties in GVL-H_2O solutions, evident in the less intense deactivation after the 7th run and in the stabilization of the activity at around a MAc yield of 45 % after the 12th run. It is important to pay attention to the mino products because their yields become more important as the deactivation progresses. Deactivation is also evident in H_2O_2 conversion.

Kinetics of oxidation of high-grade furfural at 80 °C and 90 °C.

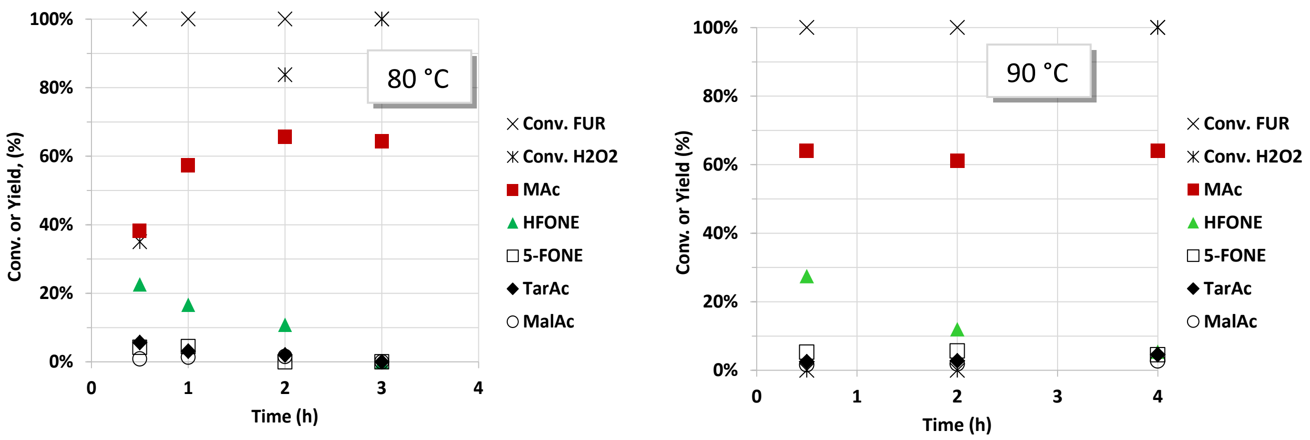

Figure ESI-2. Kinetics of the oxidation of high-grade furfural with TS-1 in GVL-H_2O medium at 80 and 90 °C. Common reaction conditions: 5 wt.% of furfural (0.1 g), wt. Ti/furfural = 0.016, 42.5 wt.% of GVL and 34 wt.% of H_2O, mol H_2O_2/FUR = 7.5.

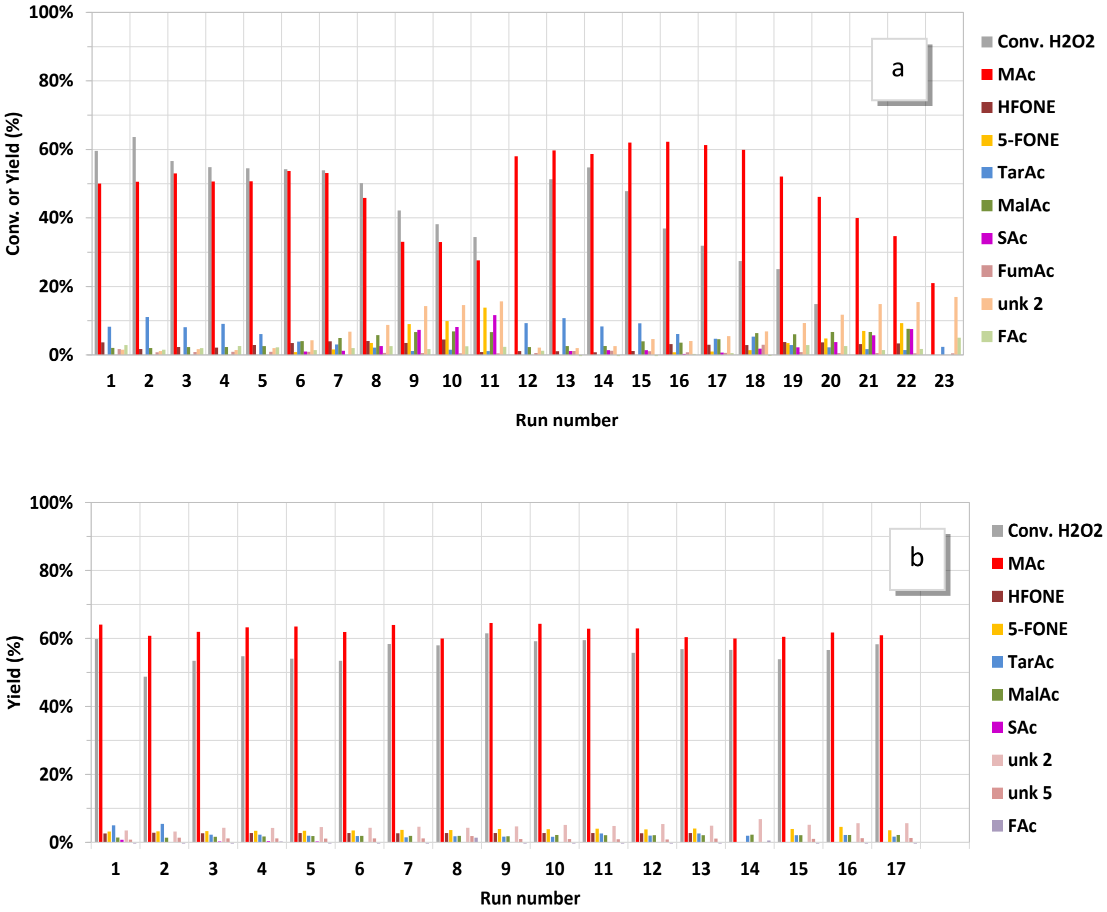

Figure ESI-3. Reutilisation properties of TS-1 at 70 °C using high-grade furfural: a) in H_2O (77 % wt. of H_2O) and (b) in GVL-H_2O solution, 42.5 wt.% of GVL, 34 wt.% of H_2O. Common reaction conditions: 5 wt.% of furfural, wt. Ti/furfural = 0.016, mol H_2O_2/FUR = 7.5 and reaction time = 4 h. Unk2 and unk5 refers to the most important unknown products detected by HPLC.

SEPARATION OF MAc FROM THE REACTION MIXTURE

Experimental details and details for toluene extraction and liquid CO_2 extraction

- Toluene extraction

The separation of GVL-H_2O solution into two phases (organic and aqueous) was explored by incorporation of toluene. The amounts of GVL, H_2O, toluene and MAc indicated in Table ESI-1 were incorporated to a closed vial and vigorously agitated for a few minutes. Two layers appears, the aqueous one was analysed by HPLC and found to have only 69.8 % of the initial MAc.

- Extraction with liquid CO_2.

A second attempt was the utilization of liquid CO_2 (see Table ESI-1 for experimental details). The amounts of MalAc, SAc, FumAc and FAc indicated in Table ESI-1 were dissolved in a mixture of GVL and H_2O (12 g and 8 g, respectively) and incorporated to a high pressure reactor. CO_2 at 6.5 MPa was admitted and let to equilibrate for 1 h. This step was conducted two more times. Once equilibrated, aliquots of the bottom (aqueous) and top (organic) were taken. The aqueous phase contained only 57.8 % of the initial MAc and moreover it could not be separated from the rest of the diacids (aqueous phase contained 84.6 %, 69.9 %, 47.3 % and 36.9 %, respectively, of the initial MalAc, SAc, FumAc and FAc).

Table ESI-1

Extraction with toluene[a]	Extraction with liquid CO_2[b]
MAc: 69.8%	MAc: 57.8% MalAc: 84.6% SAc: 69.8 % FumAc: 47.3 % FAc: 36.9 %

[a] GVL: 3 g, H_2O: 3 g, MAc: 0.125 g, Toluene: 3 g

[b] GVL: 8 g, H_2O: 12 g, MAc: 0.8112 g, MalAc: 0.0401g, SAc: 0.0428, FumAc: 0.0426 g, FAc: 0.03973 g

Experimental details and results for the precipitation of Na carboxylates by addition of NaOH

An aqueous NaOH solution (50 wt%) was incorporated to a GVL-H_2O solution (60-40 wt.%) containing different amounts of carboxylic diacids (see Table ESI-2 below). These amounts were selected to mimic the concentration found in the reaction mixture obtained after the oxidation of furfural with H_2O_2. When the NaOH incorporated represented more than 50 % of the acid protons, two layers appears and the bottom aqueous phase contained the precipitate of carboxylate salts. For lower amount of NaOH, there was no separation of phases. Consequently to make sure that all Na carboxylates are precipitated, water was removed in a rotary evaporator ($P < 50$ mbar, $T = 55$ °C). The precipitate was isolated by centrifugation and rinse with 5 cycles of acetone addition (ca. 5 mL)-centrifugation to remove any trace of GVL phase. The precipitate was dried overnight at 60 °C and dissolved in water for HPLC analysis (the HPLC analysis uses 5mM H_2SO_4 eluting solution, therefore the Na carboxylate salts are converted to acids when injected in the HPLC column).

Table ESI-2 summarises the main results obtained. In experiment 1, an excess of NaOH was added with respect to MAc, as to neutralise not only MAc but also the rest of the acids. This results in recovery rates of all the dicarboxylic acids close to 100 %. In the case of FumAc, the recovery is 125 %, well above the experimental error in HPLC analysis. It is very likely than part of MAc has been isomerized to FumAc during the experiment. The recovery of FAc is 85 % that indicates that part of the formate remained in the GVL phase or that FAc was not fully precipitated and evaporated during the rotary evaporation step.

Remarkably when NaOH is added to neutralize only the most acidic proton (first pK_a) of the MAc (experiment 2 in Table ESI-2 representing a mol NaOH/MAc = 1), MAc recovery rate was found to be close to 90 %. Minimum recovery rates were obtained for the rest of the acids, the maximum was 11 % for MalAc. The first pKa of MAc is 1.9, well below that of MalAc (3.4), SAc (4.2), FumAc (3.03) and FAc (3.73), consequently the first proton of MAc is first neutralised. When an excess of NaOH is added (with respect to this first neutralization) other acid protons are neutralized and precipitated.

Table ESI-2

Experiment 1			**Experiment 2**		
Amount incorporated to solution		% of acid recovered	Amount incorporated to solution		% of acid recovered
GVL (g)	3	-	GVL (g)	3	-
H_2O (g)	2	-	H_2O (g)	2	-
MAc (g)	0.1983	98 %	MAc (g)	0.2006	87%
MalAc (g)	0.0138	109%	MalAc (g)	0.0087	10%
SAc (g)	0.0166	100%	SAc (g)	0.0101	0%
FumAc (g)	0.0125	125%	FumAc (g)	0.0088	2%
FAc (g) (sol. 98 wt%)	0.0979	85%	FAc (g) (sol. 98 wt%)	0.1008	0%
NaOH (g) (sol. 50 wt.%)	0.6108		NaOH (g) (sol. 50 wt.%)	0.1406	-
mol NaOH/MAc	4.5	-	mol NaOH/MAc	1	-
% neutralized protons	123 %		% neutralized protons	29 %	-

Experimental details and results for the removal of TarAc by using $CaCl_2$

$CaCl_2$ (Sigma-Aldrich) was incorporated to a GVL-H_2O solution (60-40) containing different amounts of carboxylic diacids (see Table ESI-3 below). The amounts were again selected to mimic the concentration found in the reaction mixture obtained after the oxidation of furfural with H_2O_2. When a mol Ca/acids = 0.5 was used there was no separation of phases but for mol Ca/acid ≥ 1, two phases appear. The aqueous phase (bottom) and the organic phase were sampled and analysed by HPLC as explained in the experimental section.

Table ESI-3

Experiment 1			**Experiment 2**		
Amount incorporated to solution		% recovered in aqueous phase	Amount incorporated to solution		% recovered in aqueous phase
GVL (g)	6	-	GVL (g)	6	-
H_2O (g)	4	-	H_2O (g)	4	-
MAc (g)	0.4078	23%	MAc (g)	0.3855	25%
TarAc (g)	0.0236	95%	TarAc (g)	0.0223	100%
MalAc (g)	0.0212	55%	MalAc (g)	0.0277	83%
SAc (g)	0.0256	23%	SAc (g)	0.0183	31%
FumAc (g)	0.0175	25%	FumAc (g)	0.0233	14%
FAc (g) (sol. 98 wt%)	0.1918	16%	FAc (g) (sol. 98 wt%)	0.1996	18%
$CaCl_2$ (g)	0.9147		$CaCl_2$ (g)	1.1841	
mol. Ca/acids	0.93		mol. Ca/acids	1.95	

BLANK EXPERIMENTS OF THE OXIDATION OF GVL WITH H_2O_2 IN THE PRESENCE OF TS-1.

The Fig. ESI-4 presents GC-MS chromatograms of the reaction mixtures obtained at different reaction time when GVL is contacted with in H_2O_2 in the absence of furfural. The reaction conditions, indicated in the caption of the figure, were similar to those of Fig. 3a and 4a, except that furfural is now not incorporated. The liquids were analysed by GC-MS chromatograph equipped with a HP-5 Agilent column. Identification of the products was based on the library of the program used for the qualitative and quantitative analysis of the peaks. After 2h of reaction only a peak at around 2.9 min was observed, the fragmentation pattern of the compound matched that of GVL. After 4 h of reaction a weak peak at around 3.75 min was detected, which fragmentation pattern matched that of levulinic acid (LAc); LAc is formed by oxidation of GVL with H_2O_2. An estimation of the amount of LAc formed based on the areas of the peak indicate that much less than 1 wt. % of the initial GVL was oxidized to LAc. After 20 h of reaction the peak around 3.75 min (LAc) was clearly visible and represented a yield of LAc around 4 wt. %.

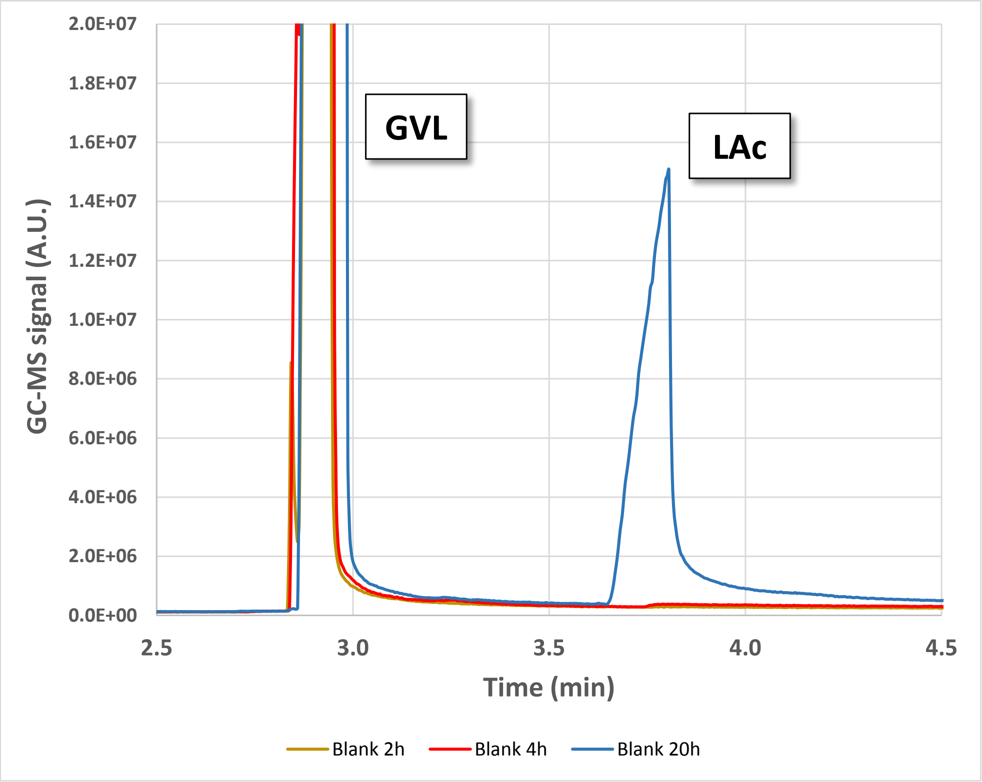

Figure ESI-4. GC-MS chromatogram of the oxidation of GVL with H_2O_2 in the presence of TS-1 catalyst. Reaction conditions: 43.7 wt.% of GVL, 35.7 wt.% of H_2O, 15.3 % of H2O2 and 70 °C.

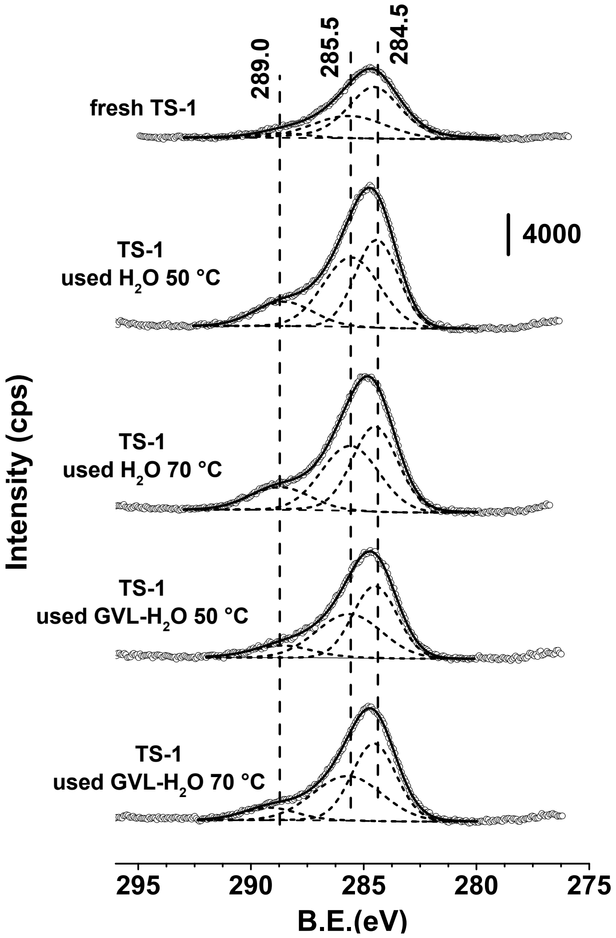

Fig. ESI-5. C1s XPS core levels for the fresh TS-1 catalyst and after being used with high-grade furfural. Open circles correspond to experimental data, dashed lines correspond to different C1s contributions obtained by deconvolution and the thicker solid line represents the addition of the deconvoluted peaks. The continuous thin line corresponds to the baseline.

C1s XPS core level.

The C1s signal in the fresh catalyst arises from the unavoidable and adventitious contamination of the surface by organic compounds ubiquitously present in ambient air. The C1s core level of the used catalysts is clearly more intense than that of fresh catalyst, demonstrating that by-products have been deposited over the catalysts during reutilisation. The intensity of all the contributions (at 284.5, at around 285.6 and at around 289.0 eV) is larger for used catalysts. However the used catalyst with the less intense peaks in comparison with the fresh catalyst is that being reutilised in GVL-H_2O mixtures.

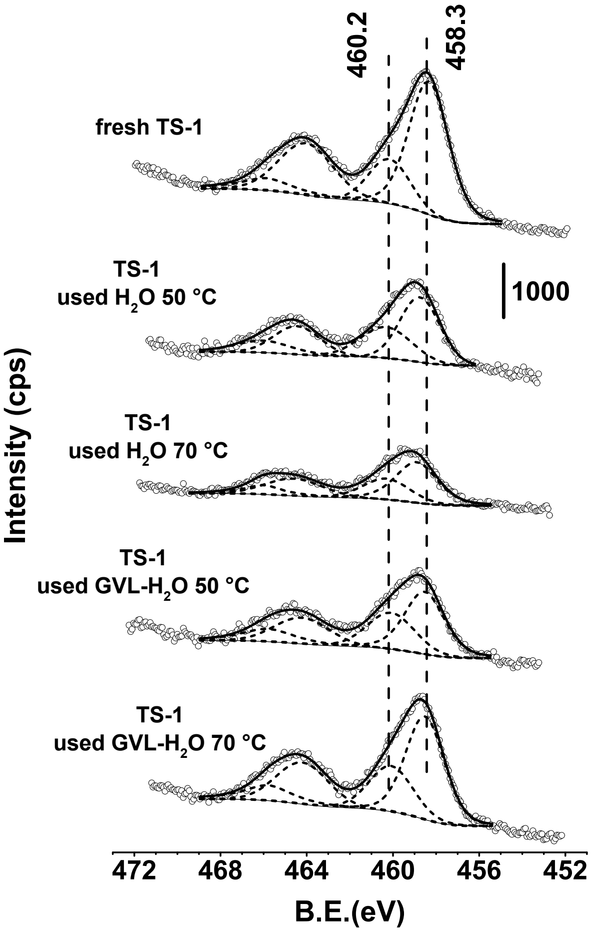

Fig. ESI-6. Ti2p XPS core level for the fresh TS-1 catalyst and after being used with high-grade furfural. Open circles correspond to experimental data, dashed lines correspond to different Ti2p contributions obtained by deconvolution and the thicker solid line represents the addition of the deconvoluted peaks. The continuous thin line corresponds to the baseline.

Ti2p XPS core level.

Ti2p core level displays a doublet due to the spin-orbit splitting, Ti2p$_{1/2}$ and Ti2p$_{3/2}$, the latter of higher intensity and at lower BE. In the samples studied in this article, a deconvolution statistically satisfactory was achieved by assuming that there are two Ti species, Ti$_{oct}$ and Ti$_{tet}$. For the deconvolution, the position and area of the Ti2p$_{1/2}$ contributions were restrained to have half the intensity and at 5.7 eV than the Ti2p$_{3/2}$ contribution. Ti$_{oct}$ arises from the presence of anatase and Ti$_{tet}$ is due to the Ti incorporated to the zeolite, substituting tetrahedral Si atoms of the framework.

A simple visual inspection of the figure clearly shows that the Ti peaks for the used samples, especially those used in water, are less intense than that of the fresh sample, indicating that the Ti concentration at the surface of the samples is smaller. This is due to the leaching of Ti that takes place during reusing. A simple visual inspection allows to conclude that the leaching affect mainly to the Ti$_{oct}$ contribution (at around 460.2 eV).

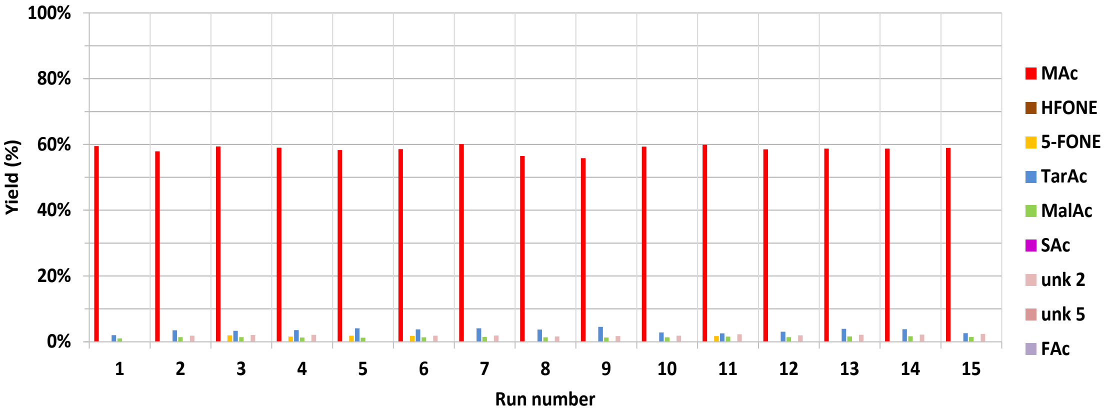

Fig. ESI-7. Reutilisation properties of TS-1 at 70 °C using low-grade furfural obtained by processing corn cobs. Reaction conditions: 3.5 wt.% of furfural (0.0725 g), wt. Ti/furfural = 0.021, 45 wt.% of GVL, 33 wt.% of H_2O, mol H_2O_2/FUR = 7.5 and time of reaction = 4 h. Unk2 and unk5 refers to the most important unknown products detected by HPLC.

Reutilization of TS-1at 70 °C using low-grade furfural.

Figure ESI-7 shows that at 70 °C the TS-1 there is no evidence of deactivation in any of the yields of the minor products.

Kinetics of oxidation of low-grade biomass-derived furfural at 70 °C.

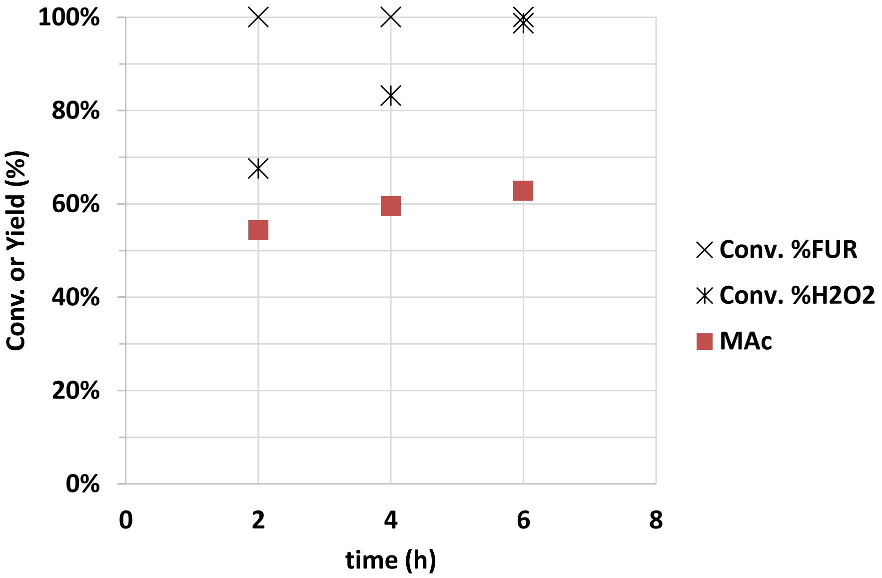

Figure ESI-8. Kinetic of the oxidation of low-grade furfural obtained from corn cobs using TS-1 in GVL-H_2O at 70 °C. Reaction conditions: 3.5 wt.% of furfural (0.0725 g), wt. Ti/furfural = 0.021, 45 wt.% of GVL, 33 wt.% of H_2O, mol H_2O_2/FUR = 7.5.

Fig. ESI-8 sumamrises the kinetic of the oxidation of low-grade furfural using TS-1 catalyst. For the sake of simplicity only MAc is included. The comparison of this figure with Fig. 3 in the article (high-grade furfural results) shows that when oxidising low-grade furfural the maximum yield of MAc that can be obtained (62 %) is smaller than that obtained with high-grade furfural (70%). The H_2O_2 conversion in Fig. ESI-8 is larger than those in Fig. 3 for all the reaction times studied and consequently less H_2O_2 is available for the selective oxidation to MAc. The oxidation of unaccounted contaminants may explain the larger H_2O_2 conversion.

Kinetics of oxidation of high-grade furfural at 70 °C using TS-1mod.

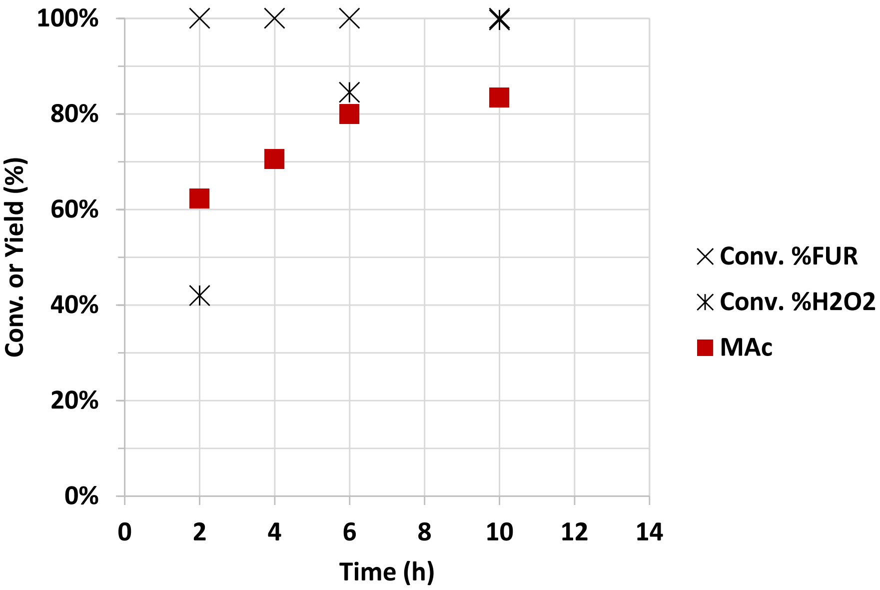

Figure ESI-9. Kinetics of oxidation at 70 °C in GVL-H_2O mixtures using TS-1mod and high-grade furfural. Reaction conditions: 5 wt.% of furfural (0.1 g), wt. Ti/furfural = 0.015, 43 wt.% of GVL and 34 wt.% of H_2O, mol H_2O_2/FUR = 7.5 and wt. GVL/H_2O = 1.3

Kinetics of oxidation of low-grade biomass-derived furfural at 70 °C using TS-1mod.

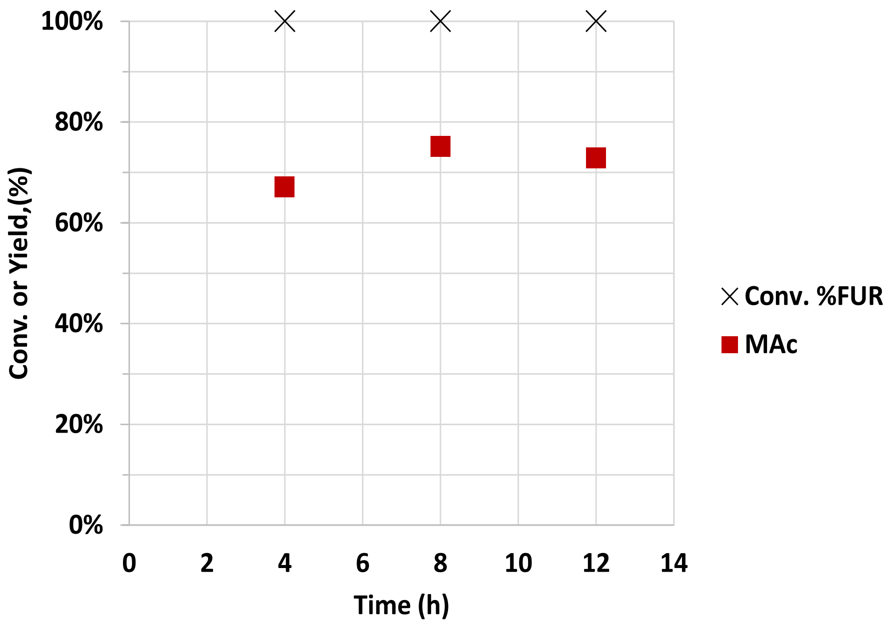

Figure ESI-10. Kinetics of oxidation at 70 °C in GVL-H_2O mixtures using TS-1mod and low-grade furfural. Reaction conditions: 4.1 wt.% of furfural (0.095 g), wt. Ti/furfural = 0.016, 56 wt.% of GVL, 24 wt.% of H_2O, mol H_2O_2/FUR = 7.5.

Reutilization of TS-1mod at 70 °C using low-grade furfural.

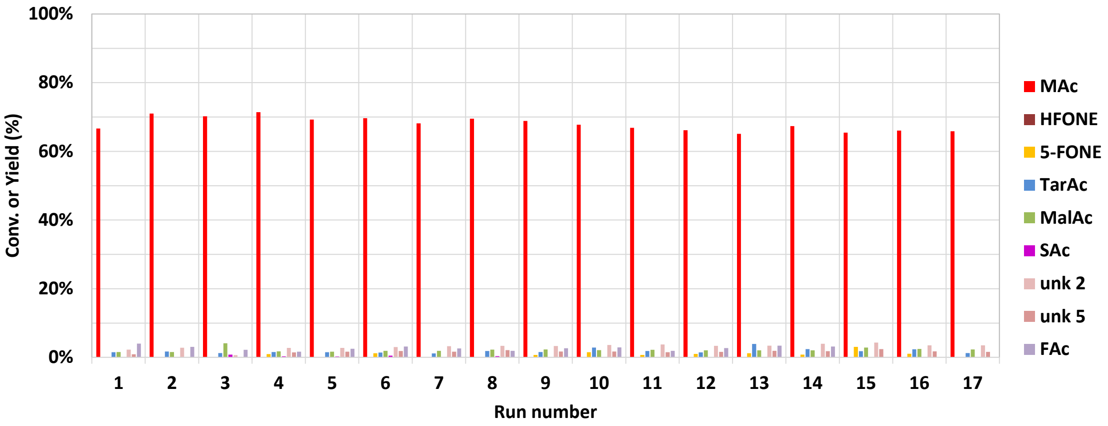

Fig. ESI-11. Reutilisation properties of TS-1mod at 70 °C using low-grade furfural obtained by processing corn cobs: Reaction conditions: 4.5 wt.% of catalyst (0.1 g), wt. Ti/furfural = 0.016, 56 wt.% of GVL, 24 wt.% of H_2O, mol H_2O_2/FUR = 7.5 and time of reaction = 4 h. Unk2 and unk5 refers to the most important unknown products detected by HPLC.

Figure ESI-11 shows that at 70 °C the TS-1 did not evidence any sign of deactivation in any of the yields of the minor products.

Characterisation of TS-1mod catalyst.

- N_2 isotherms

Fig. ESI-12 represents the isotherms of N_2 adsorption. The isotherm of TS-1 isotherm starts in the origin but, for the sake of clarity, that of TS-1mod is shifted upwards. Both isotherms are typical of microporous material (zeolite) with the presence of some mesoporosity, evident in the positive smooth steep at P/P_0 larger than 0.2 (filling of mesopores). After the DRP treatment with TPAOH, the hysteresis loop of TS-1mod is visibly larger, indicating that TS-1mod presents new and larger mesopores, not present in parent TS-1 sample.

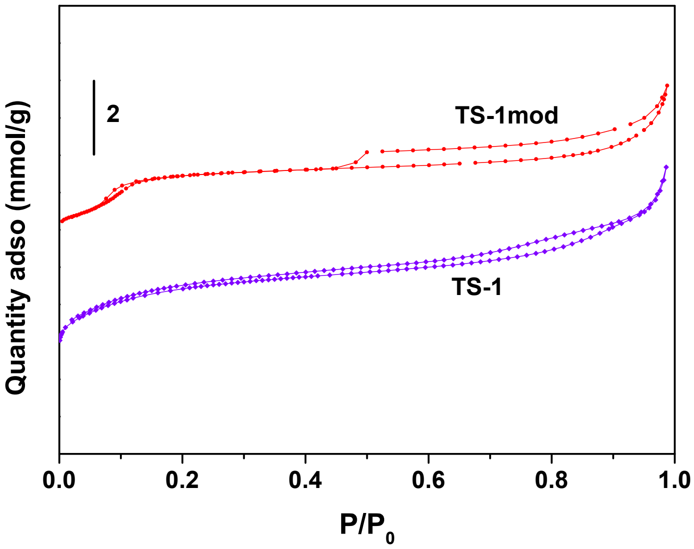

Fig. ESI-12. N_2 adsorption isotherms of TS-1 and TS-1mod.

- UV-VIS spectra

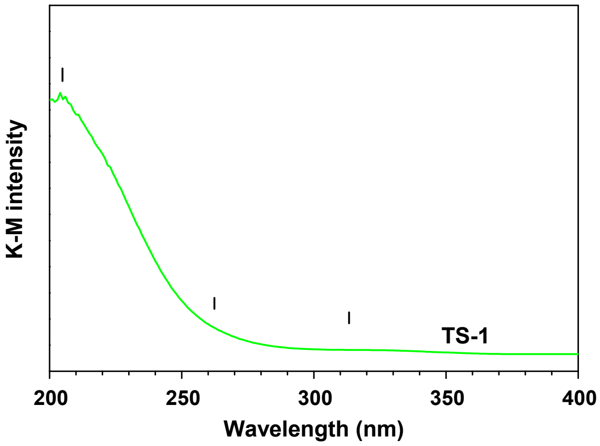

Fig. ESI-13. UV-VIS spectrum of TS-1 sample

The UV-VIS spectrum of the untreated TS-1 is represented in Figure ESI-13. The spectrum of TS-1 is dominated by the band at around 205 nm arising from tetrahedral Ti incopororated to the silica framework. Two much weaker bands could also be identified, between 250-300 nm and 300-350 nm, associated to octahedral extraframework Ti and to the residual presence of anatase, respectively. These bands are so weak that no change could be observed in the spectrum of the TS-1mod sample.

- Chemical analysis by XPS

Table ESI-4 compares the most relevant XPS parameters for both fresh and used TS-1mod catalysts (after reusing with low grade furfural, used catalyst of Fig. 8). Figs. ESI-11 a and b display, respectively, the corresponding C1s and Ti2p core levels and the contributions in which they were deconvoluted. The XPS results evidenced the deposition of by-products during the reutilization (C/Si at. ratio determined from XPS goes from 0.09 for fresh TS-1mod to 0.29 for used TS-1mod). As for high-grade furfural case, the deposits contained C-O and C=O functions as evidenced by the higher intensity of those contributions observed for the used catalyst. Regarding the Ti leaching, the XPS results indicate that leaching for TS-1mod is not as important as was for unmodified TS-1 catalyst. Thus the Ti/Si XPS ratio for the fresh TS-1mod (0.15) is quite similar to that found in used TS-1mod (0.13)

Table ESI-4. Binding Energy (BE) in eV and at. ratio (relative to Si) deduced from representative XPS core level for the fresh and used TS-1 catalysts.

	Ti $2p_{3/2}$		**C 1s**	
Catalyst	BE (eV)	at. Ti/Si	BE (eV)	at. C/Si
TS-1mod fresh	458.3	0.006	284.3	0.05
	460.2	0.008	285.3	0.03
		(0.015)[a]	288.7	0.01
				(0.09)[b]
TS-1mod used corn cobs GVL-H_2O 70 °C	458.5	0.007	284.5	0.13
	459.9	0.006	285.5	0.13
			288.9	0.03
		(0.013)[a]		(0.29)[b]

[a]Value between brackets corresponds to the total at. Ti/Si

[b]Value between brackets corresponds to the total at. C/Si

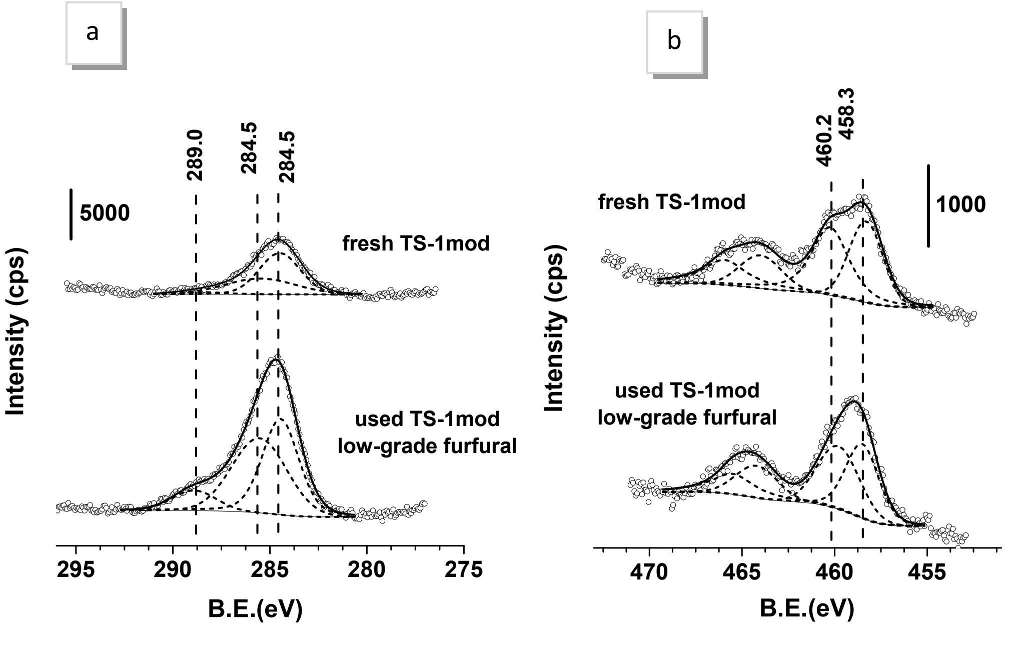

Fig. ESI-14. C1s (a) and Ti2p (b) XPS core levels for the fresh and used TS-1mod catalyst when conducting the reaction with low-grade biomass-derived furfural. Open circles correspond to experimental data, dashed lines correspond to different C1s and Ti2p contributions obtained by deconvolution and the thicker solid line represents the addition of the deconvoluted peaks. The continuous thin line corresponds to the baseline.