Supplementary Information

1. Experimental

1.1. Materials

5-hydroxy-furan-2(5H)-one was synthesised by a procedure adapted from P. Kumar et al.[1] consisting in the oxidation of furan with H_2O_2, using TS-1 as catalyst. Furan (2 g, 29 mmol) was added into a round-bottom flask with a magnetic stirrer containing 10 ml of acetonitrile, 0.4 g of TS-1 and 8 g of 30 wt.% H_2O_2 (70 mmol). The reaction was carried out for 8 h at 273 K and then at room temperature overnight. The catalyst was filtered off, and a sample of the filtrate was analysed by HPLC. The presence of 5-hydroxy-furan-2(5H)-one was confirmed, in addition to furan's total conversion. The filtrate was concentrated, and a white solid and an oily phase were formed. This mixture was filtered off and washed with diethyl ether. The solid was identified as MA, whereas HPLC analysis of the oily phase determined the presence of 5-hydroxy-furan-2(5H)-one and only traces of MA and FumA. The oily phase was dried and concentrated by vacuum and used for the determination of the chromatographic factor.

1.2. Catalytic activity measurements

Figure SI1 shows a typical chromatogram from the HPLC analysis of the reaction media. The retention times were 12.4 min for oxalic acid, 15.6 min for maleic acid, 17.6 min for malic acid, 21.3 min for succinic acid, 24.4 min for formic acid, 26.1 min for fumaric acid, 29.8 min for 5-hydroxy-furan-2(5H)-one, 48.7 min for furan-2(5H)-one, 53.6 min for furoic acid and 78.2 min for furfural (not shown in the figure because the chromatogram corresponds to a aliquot with full furfural conversion).
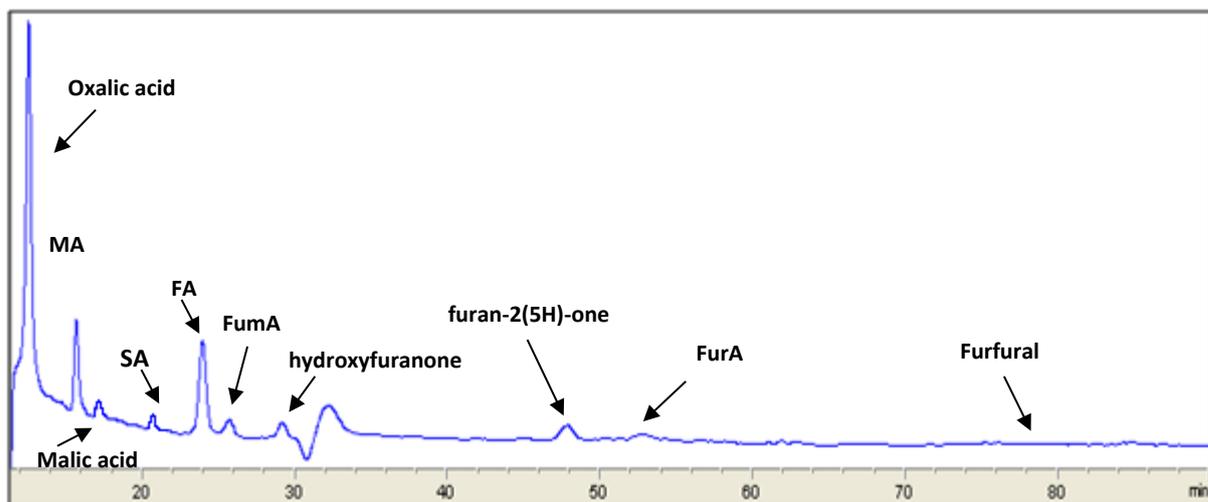
Figure SI1. Typical reaction chromatogram

2. Results and discussion

2.1 Parametric study

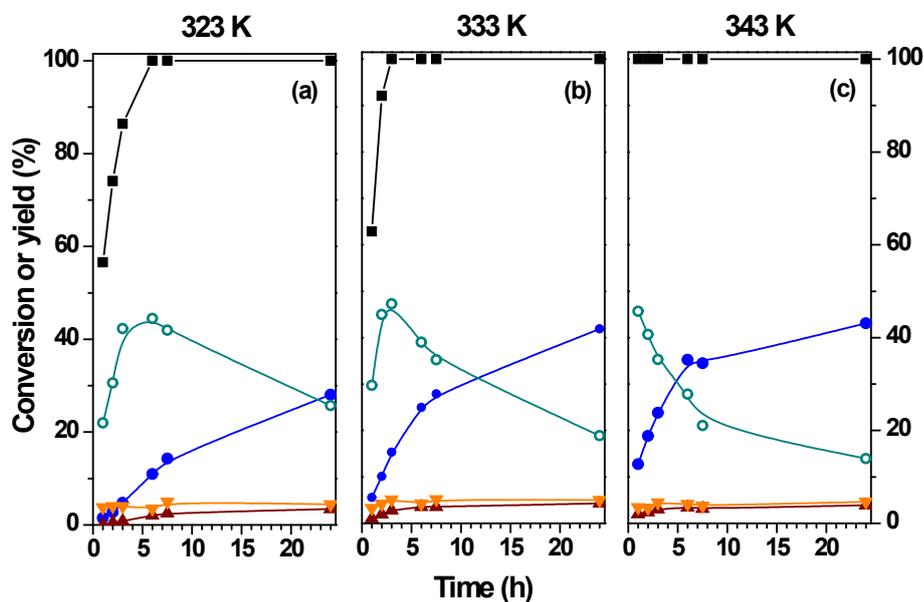*Temperature effect on catalytic activity*

Figure SI2. Effect of reaction temperature on the catalytic properties of TS-1 at three different temperatures: (a) 323 K, (b) 333 K and (c) 343 K. Reaction conditions: 4.6 wt. % of furfural, 2.3 wt. % of catalyst, 6.6 wt. % of H_2O_2, equivalent to a H_2O_2/F mol ratio = 4. Symbols: (O) furfural conversion; 5-hydroxy-furan-2(5H)-one yield (①); maleic acid yield (∞); formic acid yield (□); and malic acid yield (□).

The effect of reaction temperature on catalytic properties was also examined for a H_2O_2/furfural mol ratio of 4, equivalent to 6.6 wt. % of H_2O_2, and as shown in the results in Figure 1 of the main article, hydroxyfuranone, MA and FA were the main reaction products. Furfural conversion is also enhanced by temperature, and total furfural conversion was reached after 1 h when the reaction was carried out at 343 K. At short reaction times, hydroxyfuranone was the main product, and the MA yield increased for longer reaction times at the expense of the former. A notable positive effect was observed when the temperature increased from 323 to 333 K, and the MA yield after 24 h enhanced from 28 to 42 %. However, this positive effect is not evident for longer reaction times when the reaction is carried out at 343 K. Therefore, for low H_2O_2 concentrations, 333 K is the optimum temperature for the oxidation of furfural to MA.

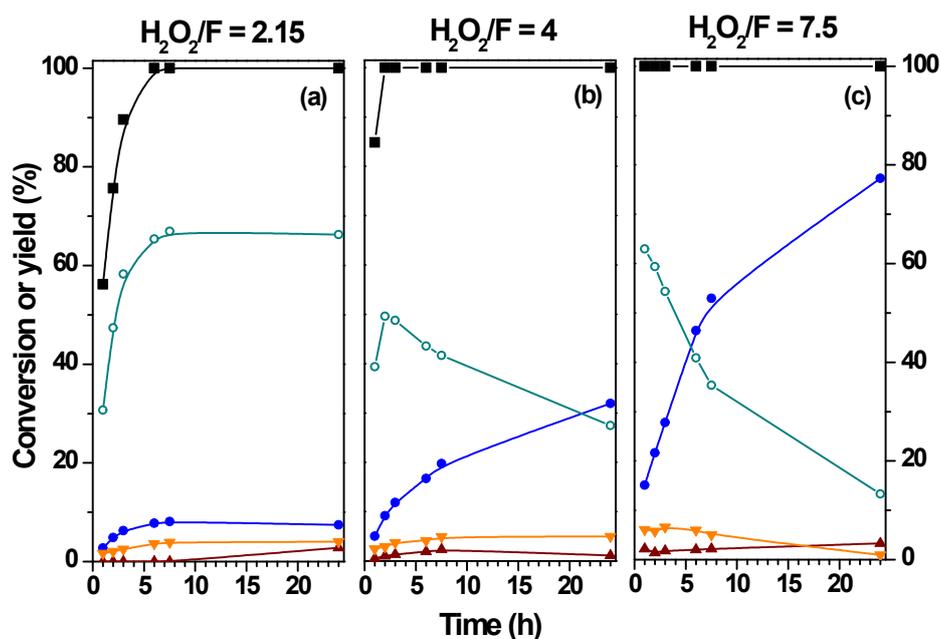### *Effect of H_2O_2 concentration on catalytic activity*

Figure SI3. Effect of H_2O_2 concentration on the catalytic properties of TS-1 for three different H_2O_2/furfural mol ratios (2.15, 4 and 7.5), corresponding to (a) 3.5, (b) 6.6 and (c) 12.3 wt. % of H_2O_2. Reaction conditions: 4.6 wt. % furfural, 323 K, 4.6 wt. % catalyst. Symbols: (**O**) furfural conversion; 5-hydroxy-furan-2(5H)-one yield (①); maleic acid yield (∞); formic acid yield (▢); and malic acid yield (▢).

H_2O_2 concentration had a remarkable positive effect on both the furfural conversion rate and MA yield. As shown in the above figure, three different H_2O_2/furfural mol ratios (2.15, 4 and 7.5) were studied for 4.6 wt. % of furfural and TS-1. When a low H_2O_2 concentration was used (H_2O_2/furfural mol ratio = 2.15), close to that needed for the

oxidation of furfural to hydroxyfuranone, the latter is the main product, with a yield close to 70 %. MA yield was negligible. The product yield remained constant after 6 h of reaction, most likely because after that reaction time, the H_2O_2 is fully consumed, and no more H_2O_2 is available for the oxidation of hydroxyfuranone to MA. In fact, with a larger H_2O_2/furfural mol. ratio, furfural conversion is faster and MA yield is higher.
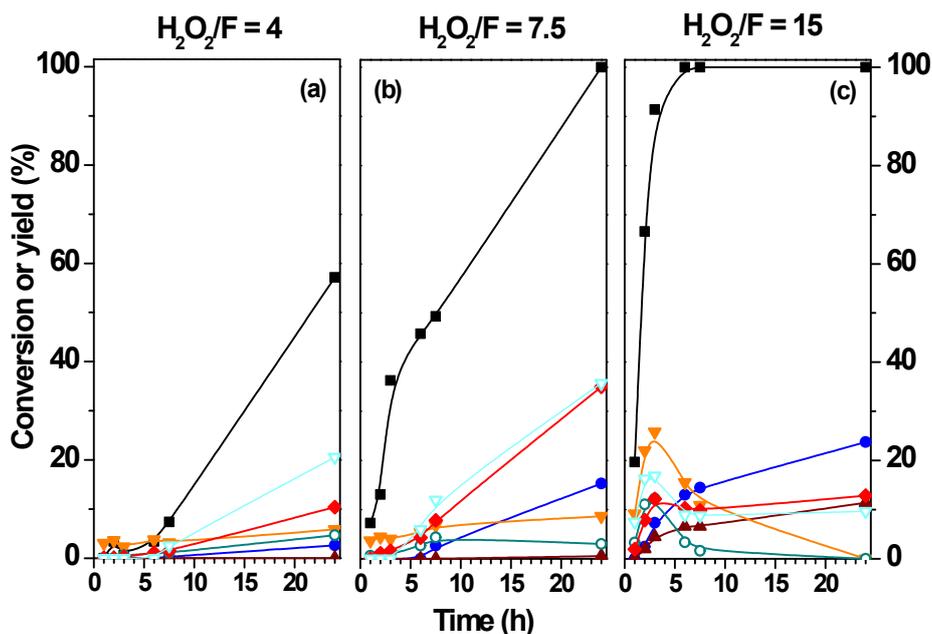
Autocatalytic reaction

Figure SI4. Auto-catalysed reactions with no catalyst for three different H_2O_2/furfural mol ratios (4, 7.5 and 15), which corresponds to (a) 6.6, (b) 12.3 and (c) 24.6 wt. % of H_2O_2. Reaction conditions: 4.6 wt. % furfural and 323 K. Symbols: (**O**) furfural conversion; 5-hydroxy-furan-2(5H)-one yield (⦶); maleic acid yield (⬗); formic acid yield (◻); malic acid yield (◼); furan-2(5H)-one yield (•); succinic acid yield (⊕).

Reactions without catalyst (autocatalytic reaction) and with different H_2O_2 concentrations were also carried out, and the results are plotted in Figure SI4. The furfural conversion rate is slower than in catalysed reactions, and for a H_2O_2/furfural mol ratio of 4, a reaction time of 24 h is needed to reach a conversion of ca. 60 %. The product distribution is also different to that when catalysed by TS-1, and now furan-2(5H)-one and succinic acid are the major products. The MA yield increases with H_2O_2 concentration, but only a maximum of 25 % is achieved after 24 h reaction when a H_2O_2/furfural mol ratio of 15 is used. For this highest H_2O_2 concentration, high yields of formic acid are obtained for short reaction times, but the yield starts to decrease after 3

h of reaction, most likely because overoxidation to CO_2 takes place due to the excess H_2O_2.

2.2. Selective vs. unselective conversion of H_2O_2 (thermal and catalytic decomposition of H_2O_2)

In principle, there are three routes to convert H_2O_2: conversion to organic products (including formic acid), catalytic decomposition and uncatalysed thermal decomposition. In an attempt to quantify these contributions, two blank experiments were conducted using 12.3 wt % H_2O_2 (the same as used for Figure 4b) in the absence of furfural: one in the absence of TS-1 (Figure 5a) and other in the presence of TS-1 (Figure 5b). Trace *a* accounts for uncatalysed thermal decomposition, and the difference between trace *b* and trace *a* (trace *c*) corresponds to catalysed decomposition in the absence of furfural. Apparently the catalysed decomposition in the absence of furfural is very intense and after 24 h is close to 65 %.
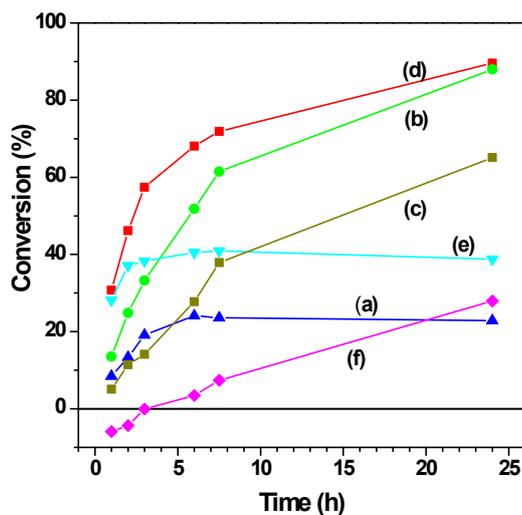

Figure SI5. Decomposition of H_2O_2. Symbols: (a) thermal decomposition of H_2O_2 in the absence of furfural and TS-1 (⊕); (b) decomposition of H_2O_2 by TS-1 (thermal plus catalytic) in the absence of furfural (∞); (c) difference between curve b and curve a, corresponding to catalytic decomposition of H_2O_2 in the absence of furfural (◯); (d) H_2O_2 converted when both furfural and TS-1 are present (◯); (e) H_2O_2 consumed to produce organic compounds, including FA, calculated from experimental results of Figure 4b (☐); (f) H_2O_2 catalytically decomposed by TS-1 in the presence of furfural (⊕) (curve f = curve d - curve e - curve a).

Figure SI5 also includes the experimental total conversion of H_2O_2 obtained when both TS-1 and furfural were present (trace *d*) and the H_2O_2 utilised to transform selectively furfural to all organic products, including formic acid (trace *e*); the latter was calculated from the yields of Figure 4b and the stoichiometry of the corresponding

reactions. The sum of trace *b* plus trace *e* (consumed in selective transformation in the presence of furfural) should result in trace *d* (overall H_2O_2 consumption), and a visual examination indicates that this hypothetical trace would be well above trace *d*. This imbalance strongly indicates that the catalytic decomposition of H_2O_2 is inhibited in the presence of furfural. The actual catalytic decomposition of H_2O_2 driven by TS-1 in the presence of furfural can in practice be estimated by subtracting both traces *a* and *e* from trace *d*. This is represented by trace *f*. It is evident that trace *f* is well below trace *c*. Even negative values are obtained for reaction times shorter than 3 h. After 24 h, the catalytic decomposition in the presence of furfural affects less than 30 % of the H_2O_2 (in comparison to 65 % when furfural is absent). Therefore, although TS-1 catalytically decomposes H_2O_2, the decomposition is remarkably inhibited by the presence of furfural.

2.3. Proposed reaction mechanisms

- *Reaction mechanism involving Baeyer-Villiger oxidation of furfural as first step.*

When using sulphonic-acid-based catalysts, it is accepted that the reaction starts with a Baeyer-Villiger oxidation of furfural to furanol formate ester, which is rapidly hydrolysed into the corresponding carboxylic acid and alcohol (formic acid and 2-hydroxyfuran, see scheme SI1). This first step explains the large concentration of formic acid that is always detected in the reaction mixture as the reaction progresses and fulfils the C atom loss required to go from a C_5 to a C_4 compound. 2-hydroxyfyuran is in equilibrium with the other two tautomeric isomers: furan-2(3H)-one and furan-2(5H)-one; the former yields SA and the latter MA after the corresponding oxidation steps. The presence of these tautomeric species explains why SA and MA are always simultaneously formed with acid catalysts and why the selectivity of SA (lower ratio) or MA (higher ratio) can be tuned by changing the H_2O_2/furfural ratio. MA requires more H_2O_2 to be formed (3 mol of H_2O_2 per mol of furfural).[2-5]
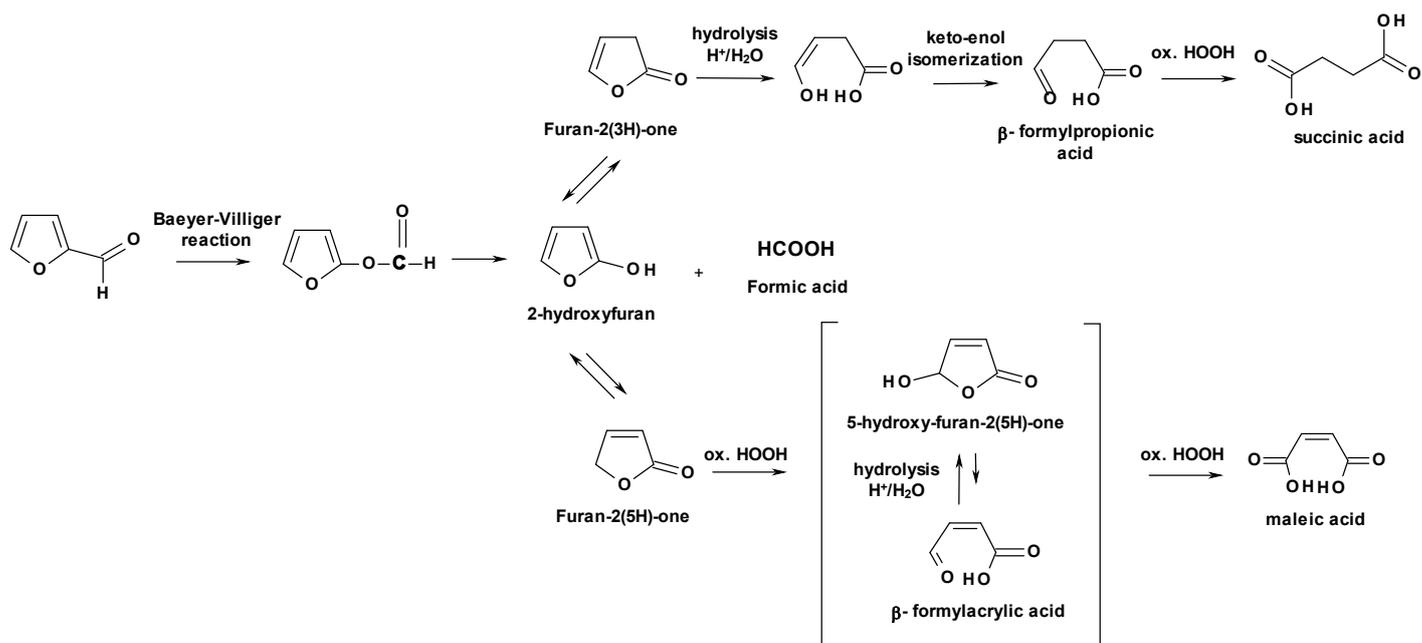
Scheme SI1. Reaction mechanism proposed for sulphonic-based catalysts starting with a Baeyer-Villiger oxidation of the aldehyde group of furfural [2-4, 6]

Furan-2(5H)-one is the compound initially produced by Baeyer-Villiger oxidation of furfural with H_2O_2. Furan-2(5H)-one is in tautomeric equilibrium with furan-2(3H)-one. Therefore, if the TS-1 oxidation of furfural utilised this mechanism, furan-2(5H)-one would be rapidly oxidised to either MA or SA. The oxidation of furan-2(5H)-one is plotted in Figure SI6 for a concentration of 4.6 wt. % of furanone and TS-1, a H_2O_2/furanone mol ratio of 7.5 and at 323 K. The oxidation of 5-furanone is very slow, the MA yield is very low and the yields of hydroxyfuranone and SA are negligible. Therefore, furan-2(5H)-one is not an intermediate when TS-1 is used as catalyst, so the first stage in the oxidation of furfural is not a Baeyer-Villiger reaction.
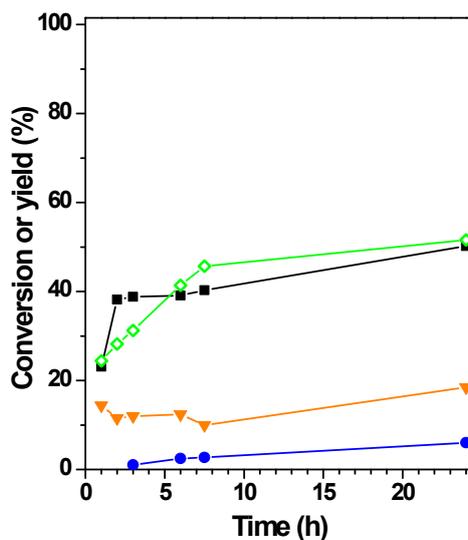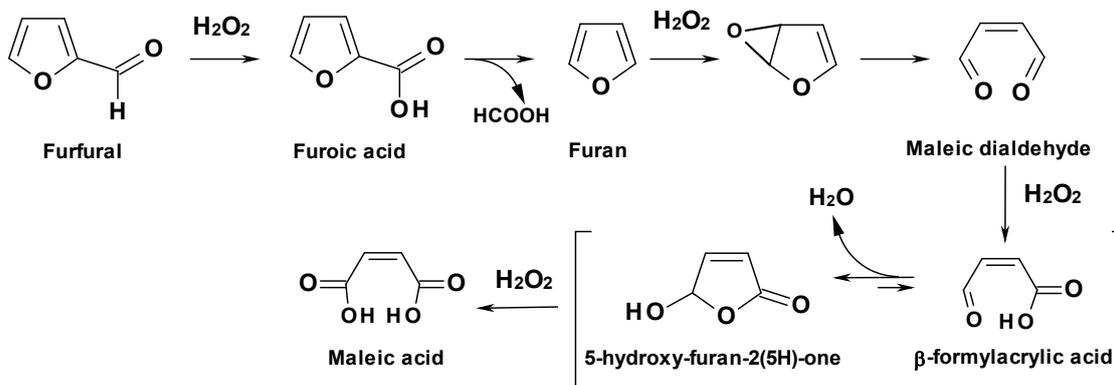
Figure SI6. Oxidation of furan-2(5H)-one with TS-1. Reaction conditions: 4.6 wt. % of furan-2(5H)-one, 4.6 wt. % of catalyst, 6.6 wt. % of H_2O_2, equivalent to a H_2O_2/furanone mol ratio = 7.5, and 323 K. Symbols: (**O**) furan-2(5H)-one conversion; maleic acid yield (⌀)formic acid yield (☐); H_2O_2 conversion (✳)

- *Mechanism of reaction involving the oxidation of furfural to furoic acid as the first step.*

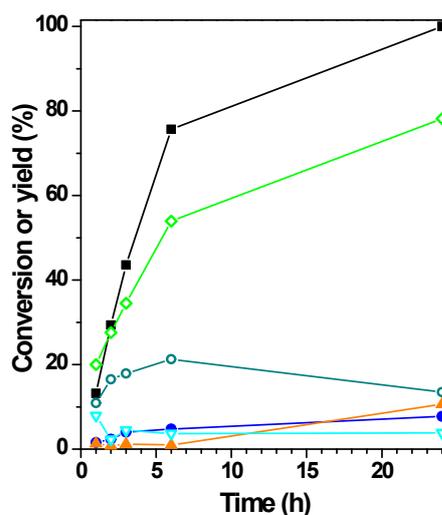**Scheme SI2.** Reaction mechanism through epoxidation of furoic acid and decarboxylation

Figure SI7. Oxidation of furoic acid. Reaction conditions: 2.3 wt. % furoic acid, 2.3 wt. TS-1, H_2O_2/FurA = 7.5, which corresponds to 5.4 wt. % H_2O_2, and 323 K. Symbols: (O) furoic acid conversion; 5-hydroxy-furan-2(5H)-one yield (①); maleic acid yield (∞); formic acid yield (■); furan-2(5H)-one yield (◆); H_2O_2 conversion (✳)

Taking into account Scheme SI2, it is proposed that furfural is initially oxidised to FurA and then the reaction proceeds to the subsequent epoxidation of furoic acid, the formation of maleic dialdehyde and hydroxyfuranone and finally MA. The results of Figure SI7 show that the oxidation of furoic acid with TS-1 is slow and not very selective. Thus, although hydroxyfuranone is the main reaction product, only a maximum of 20 % yield is achieved after 6 h reaction, and after that it starts to decrease (most likely because oxidation to formic acid takes place). Furan-2(5H)-one and MA are also detected, but in low concentration. Therefore, the conversion and yield patterns are not in agreement with those expected for the involvement of furoic acid in the reaction mechanism.

2.4. Stability of the catalysts
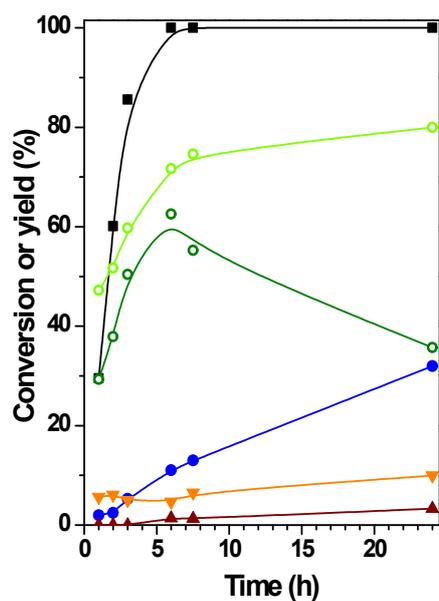
Oxidation of furfural obtained from biomass

Figure SI8. Oxidation of furfural obtained from biomass. Reaction conditions: 2 wt. % furfural from biomass, 2 wt. % catalyst, 323 K, H_2O_2/F = 7.5. Symbols: (O) furfural conversion; maleic acid yield (∞); malic acid yield (□); formic acid yield (□); 5-hydroxy-furan-2(5H)-one yield (①); H_2O_2 conversion (✳)

An aqueous solution of furfural obtained from lignocellulosic biomass was used as raw material. The concentration of furfural in this solution was 2.5 wt %, so the final concentration of furfural in the reaction media was 2 wt. %. Comparing the results in Figure SI7 with those in Figure 4a, where a reaction with 2 wt. % of commercial furfural was performed, it can be seen that the reaction rate is slower when furfural from biomass is used: a 6-h reaction time is needed to achieve the total conversion of furfural from biomass, while 2 h is enough when commercial furfural is used. As regards product yield, the values are lower when furfural from biomass is oxidised, though after 24 h reaction, the MA and FA yields are very similar. These results suggest that the impurities associated with furfural in the aqueous solution from biomass may interfere in the oxidation of furfural.
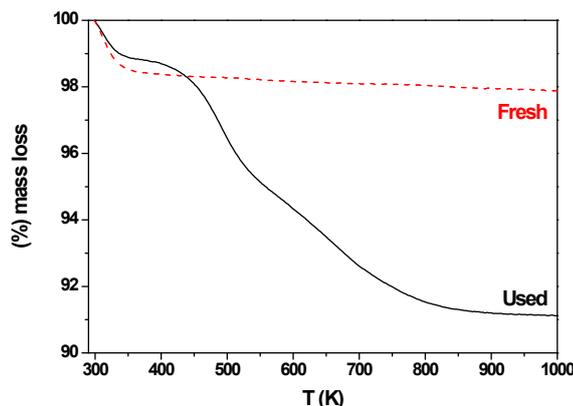
2.5. Catalyst characterisation

Figure SI9. Thermogravimetric analysis of fresh and used catalyst after 6 runs with commercial furfural

Thermogravimetric analyses of fresh and used catalyst are plotted in Figure SI8. For fresh TS-1, there is a main mass loss up to 373 K due to physisorbed water on the surface of the zeolite, but it is only 2 wt. % of the total. For higher temperatures, no great mass loss is observed. For used catalyst, in addition to the mass loss of physisorbed water, further mass losses are observed up to 800 K, most likely due to reaction product residues that are on the surface of the catalyst and that are burnt in the air atmosphere with increasing temperature. The total mass loss in the used catalyst is approximately 9 wt. %.
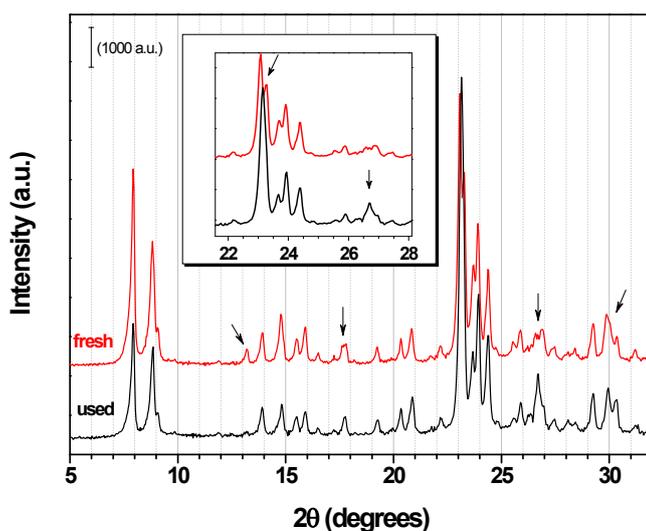

Figure SI10. XRD patterns of titanium silicalite 1, fresh and used 6 times

Analysis of X-ray diffraction patterns shows the presence of TS-1, with the main diffraction peaks of titanium silicalite. The use of the catalyst induces slight though significant changes to the crystal structure of titanium silicalite. Some of the differences are indicated in figure above with arrows. Peaks at 23.1º and 23.3º in fresh catalyst become only one diffraction peak at 23.2º, which has greater intensity. In addition, new peaks at approximately 27º and 13º appear after catalyst utilisation.

BET area and N_2 adsorption and desorption isotherms of fresh and use catalyst after six reaction cycles with commercial furfural were also measured. The results are summarized in Figure SI10 and in Table SI1. Fresh and used catalyst present a reversible type I isotherm, typical of microporous solids having relatively small external surfaces. Rouquerol methodology[7] was employed for the determination of BET surface area and t-plot method was used to estimate micropore area.[8] A loss of specific surface is observed which can be explained by the leaching, the modification of the framework, and the deposition of organics in the pore structure.
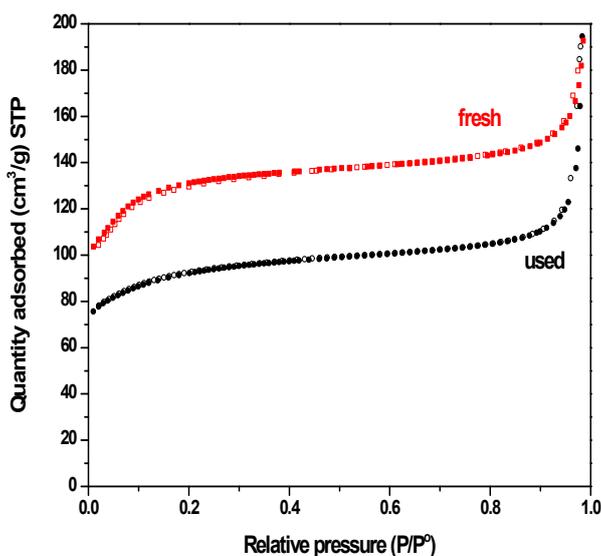

Figure SI11. N_2 adsorption-desorption isotherms of TS-1 catalyst, fresh and used (after six reaction cycles) (full symbols refer to N_2 adsorption and empty symbols to N_2 desorption isotherms)

Table SI1. Textural properties of fresh and used catalyst

Catalyst	BET area (m²/g)	Micropore area (m²/g)	Pore volume (cm³/g)	Micropore volume (cm³/g)	Micropores/total[a]
Fresh	494	419	0,27	0,17	0,85
Used	341	318	0,16	0,14	0,93

[a] Calculated as the ratio between micropores and total BET area

References

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