Electronic supplementary information ESI

Oxidation of fufural and furan derivatives to maleic acid in the presence of a simple catalyst system based on acetic acid and TS-1 and hydrogen peroxyde.

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Full experimental details:

1. Catalyst preparation TS-1

Catalyst samples were prepared with slight modifications of the procedure described by Tamarasso and others.[1][2] Optimum Ti insertion of \([\text{Ti}] / ([\text{Ti}]+[\text{Si}]) = 0.025\) or 2.5\% was targeted. Typically 1.26 g of tetraethyl orthotitanate (TEOT) were stirred in 45 g of tetraethyl ortho silicate (TEOS). Then 100 ml of 20\% aqueous solution of tetrabutylammonium hydroxide (TPAOH) was added slowly. This mixture was warmed under stirring at 333 K during three hours. Due to water and ethanol evaporation the volume of solution was maintained constant by addition of ultrapure water. The mixture was transferred in a Teflon-lined autoclaved and heated at 443K under autogenous pressure, without stirring, during three to six days. After cooling to room temperature, the organic phase was removed and the white solid was washed and rinsed several times with ultrapure water. Finally the solid was dried at 383K for two hours and finally calcined at 823K during six hours. Leading to the catalyst called TS1.

2. Catalysts characterizations.
Powder X-ray Diffraction (XRD) was conducted using a Siemens automatic Diffractometer (Siemens D5000) with monochromatized Cu-Kα radiation (λ=0.15406 nm) at a setting of 40 kV. Measures were commonly performed from 10 to 40.0° 2θ with a step of 0.025° 2θ, with a step time of irradiation of 2 sec, at room temperature.

Morphology of the catalyst was obtained with MEB Quanta Feg 250 at low vacum under 20kV in a range scale of 500 nm to 10 μm.

Fourier Transform Infrared Spectroscopy (FTIR, Jasco FT/IR 410) was employed in the range of 600–1000 cm\(^{-1}\) wave number with K-Br pellet method for observation of characteristic adsorption of TS-1.

3. Analytical methods

NMR analyzes of the products were conducted on a Brucker Ascend™ 400MHz device. The samples were prepared in deuterated water, DMSO or chloroform depending on their solubility. All products were analyzed and quantified by HPLC-MS (UFLC Shimadzu) with a diode array detector (Shimadzu SPD-M20A) an evaporative light scattering detector (Shimadzu ELSD-LTII) and coupled to mass spectrum detector (Shimadzu LCMS 2020). The HPLC instrument was equipped with a GRACE Prevail C18 5μ column (250 mm * 4.6 mm). The mobile phase was method 1: Eluent CH\(_3\)CN-H\(_2\)O with 0,01 mol.dm\(^{-3}\) Na\(_2\)HPO\(_4\) (1/9) pH=2,4 was adjust with H\(_3\)PO\(_4\) at a flowing rate of 1 ml.min\(^{-1}\) or method 2: MeOH-H\(_2\)O (10%-90%), the water phase contains Na\(_2\)HPO\(_4\) (0.01 mol.L\(^{-1}\)) and lead to a buffered solution with a pH adjust to 2.4 with H\(_3\)PO\(_4\). Flowing rate of the eluent was fixed at 1 mL.min\(^{-1}\) with both method 1 and 2. Temperature of the column was 303K. The injection volume was 5 μL. Before injection, all samples of reaction mixture were filtered through a 0.45 μm syringe filter. Retention times of product are given with the chromatogram below Fig.S5. Calibration curves were obtained from sample of commercial sources at the exception of 5-hydroxyfuranone which were prepared following the procedure described by Kumar et al.[3].

4. General procedure for the furfural oxidation
Typically, 2.6 mmol of furfural, hydrogen peroxide (aq. 35%) with a \( \text{H}_2\text{O}_2/\text{furfural} \) molar ratio between 4 to 10, and TS-1 as catalyst 0 to 0.2g) was stirred in 3.8 mL of solvent at a temperature between 333K to 373K during one to four hours. Then reaction mixture was cooled to room temperature, filtrated and evaporated or filtrated and diluted with water in volumetric flask before HPLC analysis.

Conversion and yields of all substrates and products were calculated by using the following formulas:

Conversion (mol%) = \((n^0 \text{ substrate} - n \text{ substrate})/(n^0 \text{ substrate})\)*100

Product yield (mol%) = \((n \text{ product} / n^0 \text{ substrate})\) * 100

Where \(n^0\) substrate corresponds to the mole quantity of furanic derivative initially loaded in 25 mL round bottom flask. In this study substrate is mainly furfural. \(n^0\) substrate or \(n\) product correspond to the mole quantity of substrate or product measure by HPLC analysis or weight after a given time.

Figure S1. Outline of potential chemical derivatives from maleic acid.
Figure S2. Acetic acid and formic acid, peracid equilibrium in presence of hydrogen peroxide.

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\begin{align*}
\text{H}_3\text{C} &\text{CO}_2\text{H} + \text{H}_2\text{O}_2 &\rightleftharpoons &\text{H}_3\text{C} &\text{O} - \text{O} - \text{H} \\
\text{H} &\text{O} \text{H} + \text{H}_2\text{O}_2 &\rightleftharpoons &\text{H} &\text{O} - \text{O} - \text{H}
\end{align*}
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Figure S3 (A) DRX fresh TS-1, (B) DRX used TS-1 after pyrolysis
Figure S4: SEM images of TS-1 (a) and (b) before synthesis, (c) and (d) after recycling followed by pyrolysis at 823K, 6h.
Figure S5 Additional SEM image. (A), (B), (C), (D) fresh TS-1; (E), (F), (G), (H), used TS-1 after pyrolysis.
Figure S6. FT-IR spectra of TS-1. Black curve: Fresh TS-1; Red curve: Used TS-1 after pyrolysis.
Figure S7. Typical H1-NMR (A) and C13-NMR (B) spectrum of maleic acid obtained without any further purification than filtration of TS-1 and evaporation of the reaction mixture. Only trace of impurities are visible on the baseline.
Figure S8. Typical HPLC Chromatogram, with method 1: Eluent CH$_3$CN-H$_2$O with 0,01 mol.dm$^{-3}$ Na$_2$HPO$_4$ (1/9) pH=2,4 was adjust with H$_3$PO$_4$ at 1 ml.min$^{-1}$: (A) Furfural 12,35 min, (B) Maleic Acid 3,86 min, (C) 5-hydroxy-
furan-2(5H)-one 4,30 min, (D) 2-(5H)-Furanone 5,39 min, (E) Fumaric Acid 4,78 min; with method 2: Eluent CH$_3$OH-H$_2$O with 0,01 mol.dm$^{-3}$ Na$_2$HPO$_4$ (1/9) pH=2,4 was adjust with H$_3$PO$_4$ at 1 ml.min$^{-1}$: (F) Furfural 18,24 min, (G) Maleic Acid 4,97 min, (H) 5-hydroxy-furan-2(5H)-one 4,71 min, (I) 2-(5H)-Furanone 7,17 min, (J) Fumaric Acid 7,45 min.

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