Electronic supplementary information ESI

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

Yuzhen Lou[a], Sinisa Marinkovic[b], Boris Estrine[b], Wei Qiang[a], Gérald Enderlin[a,*]

[a] Transformations Intégrées de la Matière Renouvelable, ESCOM, UTC, EA 4297 TIMR, 1 allée du réseau Jean-Marie Buckmaster, 60200 Compiègne, France
[b] Green Chemistry Department, Agro-industrie Recherches et Développements, Route de Bazancourt, Pomacle 51110, France

*Contact email: g.enderlin@escom.fr

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 [Ti]/([Ti]+[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 tetrapropylammonium 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 vaccum 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^{TM} 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_3CN-H_2O with 0,01 mol.dm^{-3} Na_2HPO_4 (1/9) pH=2,4 was adjust with H_3PO_4 at a flowing rate of 1 ml.min^{-1} or method 2: MeOH-H_2O (10%-90%), the water phase contains Na_2HPO_4 (0.01 mol.L-1) and lead to a buffered solution with a pH adjust to 2.4 with H_3PO_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 H_2O_2/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 substrate - n substrate)/(n^0 substrate))*100

Product yield (mol%) = (n product / n^0 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.

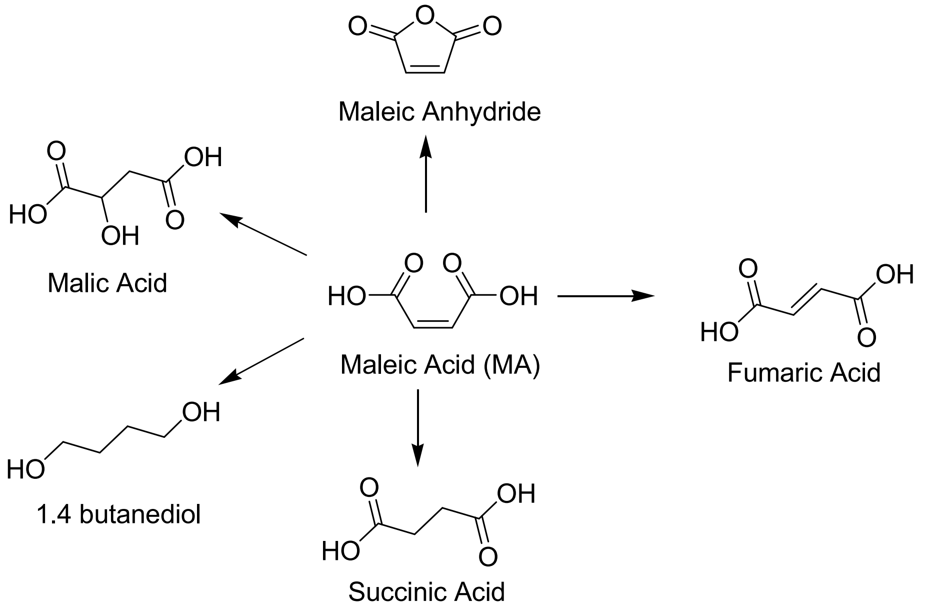
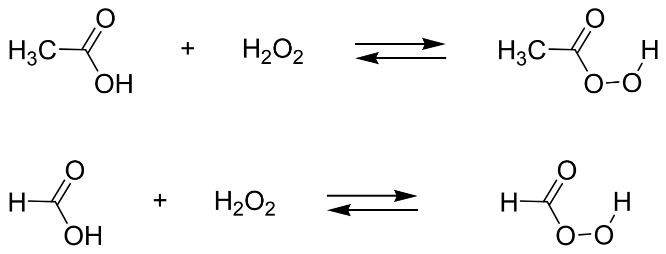
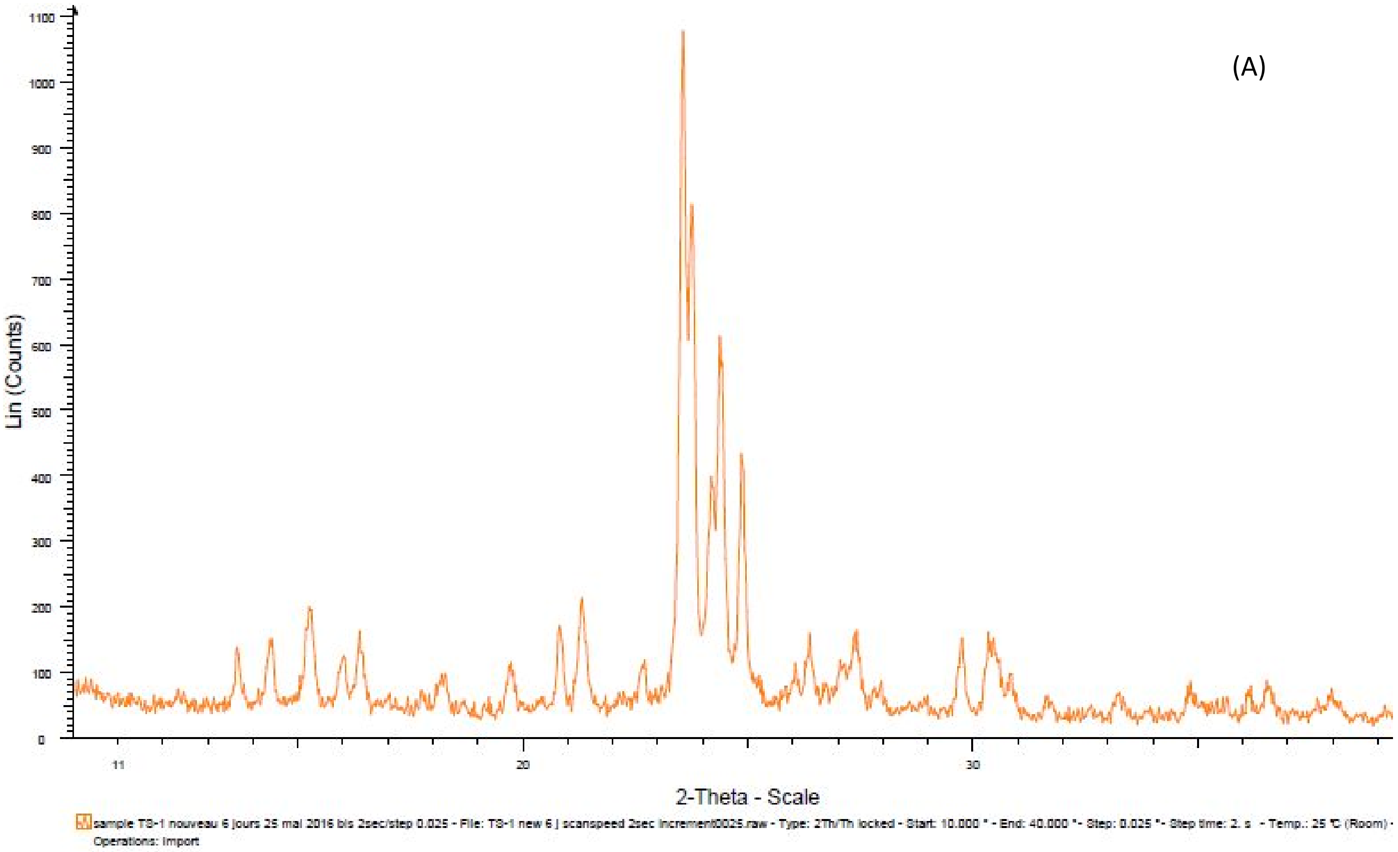


Figure S2. Acetic acid and formic acid, peracid equilibrium in presence of hydrogen peroxide.





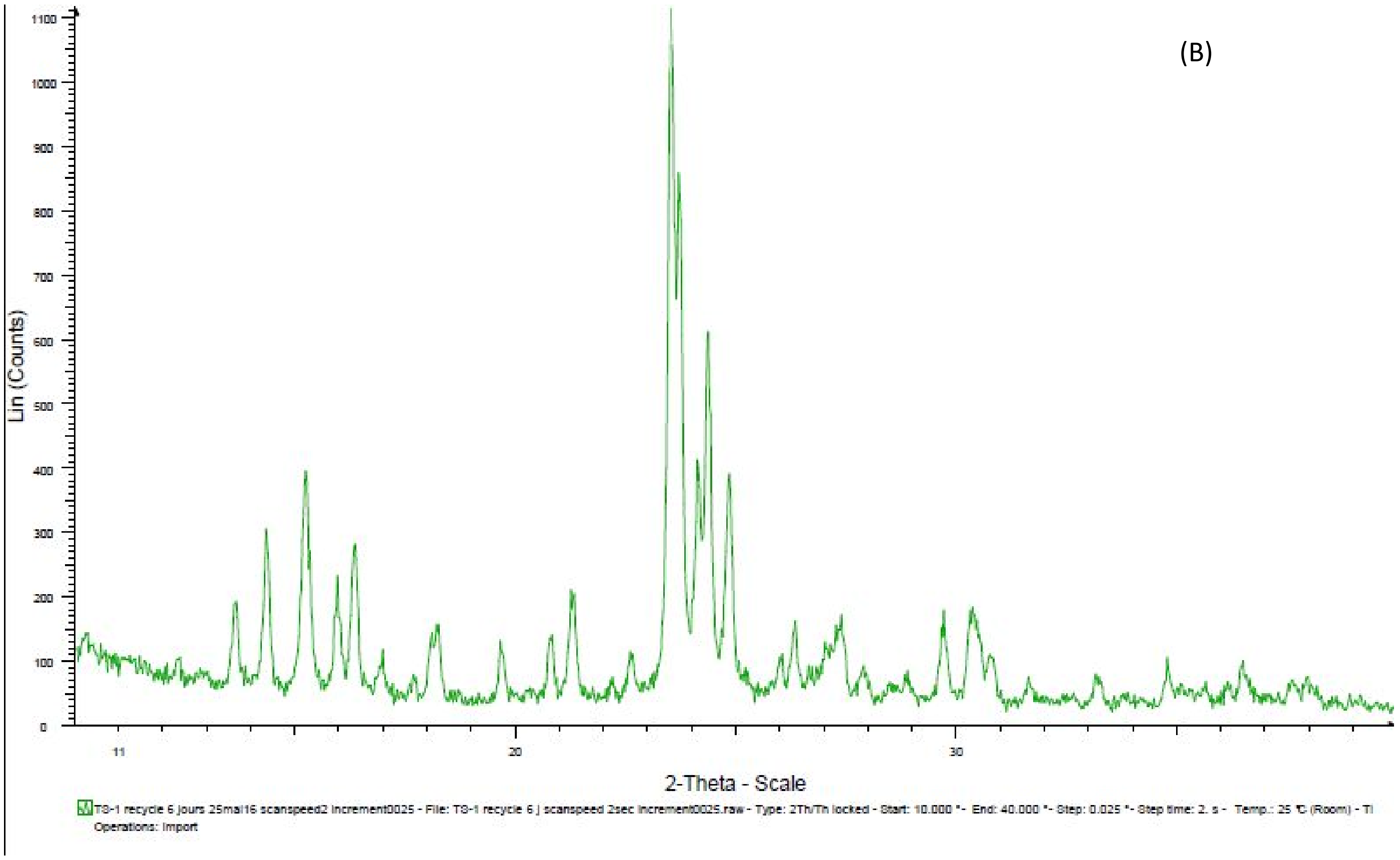


Figure S3 (A) DRX fresh TS-1, (B) DRX used TS-1 after pyrolysis

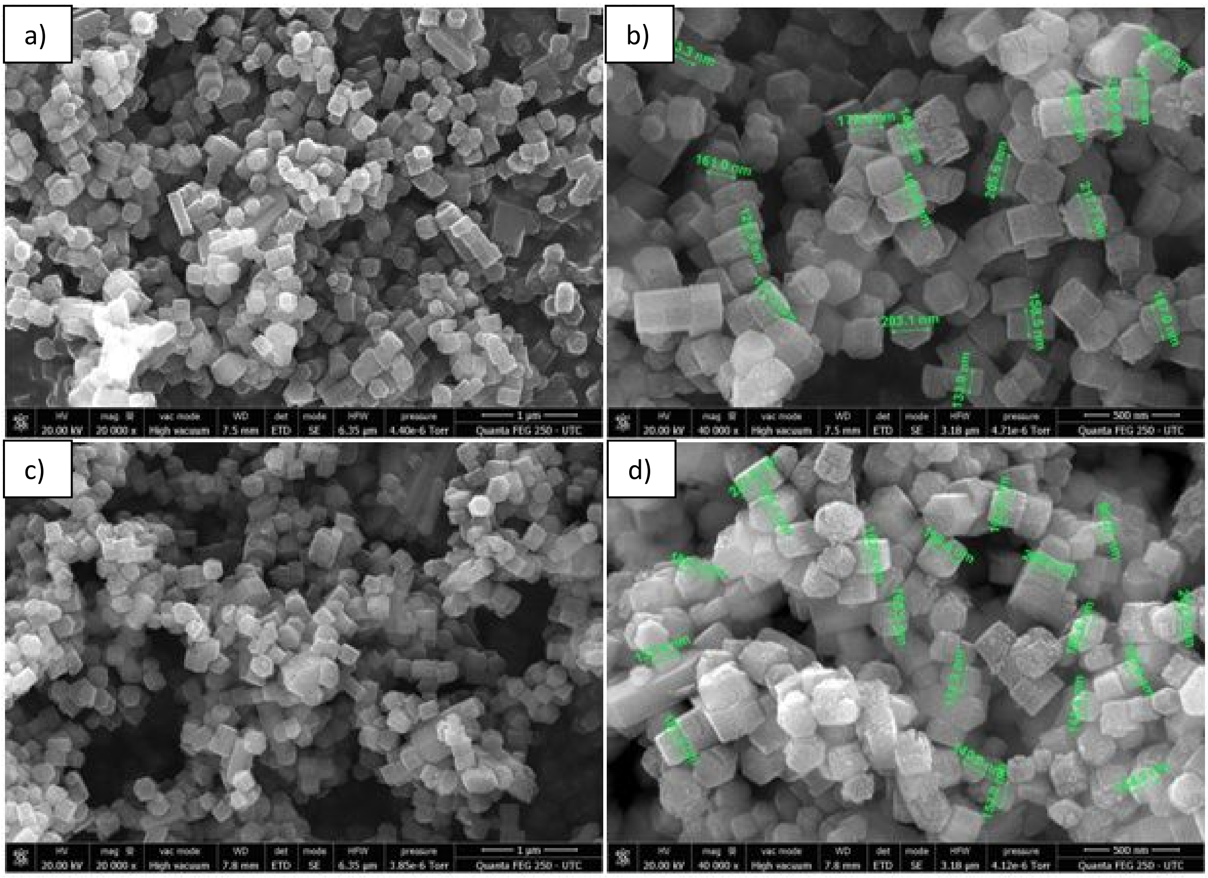
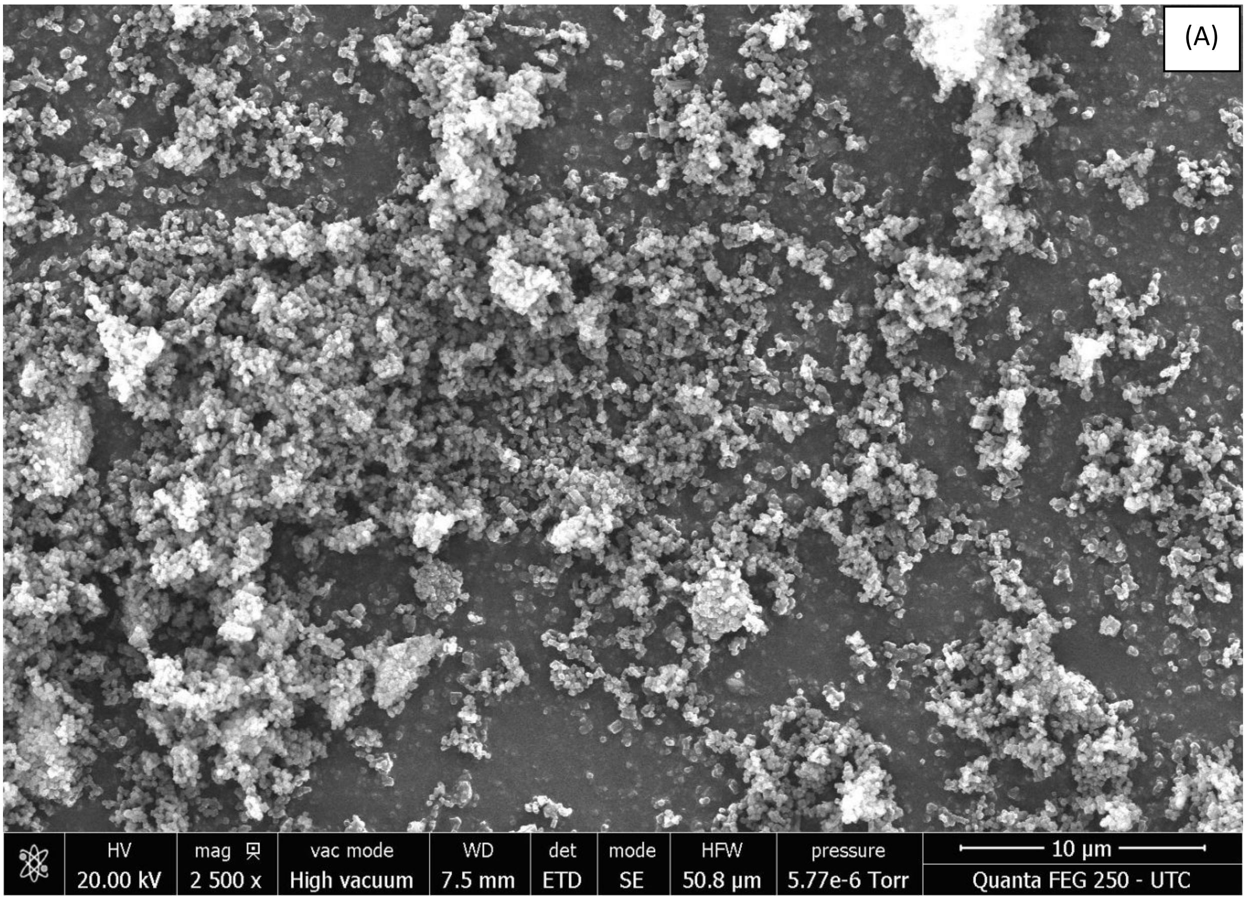
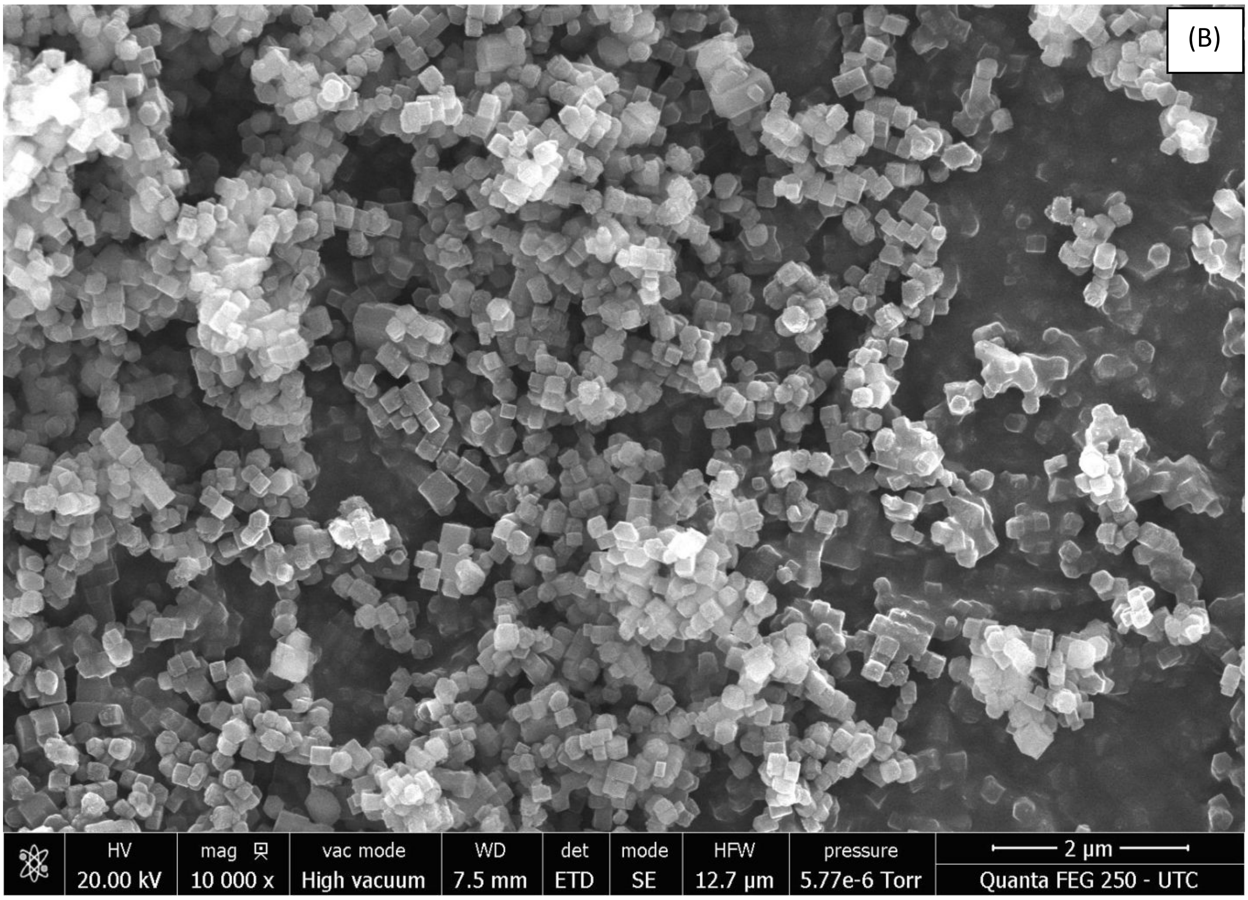
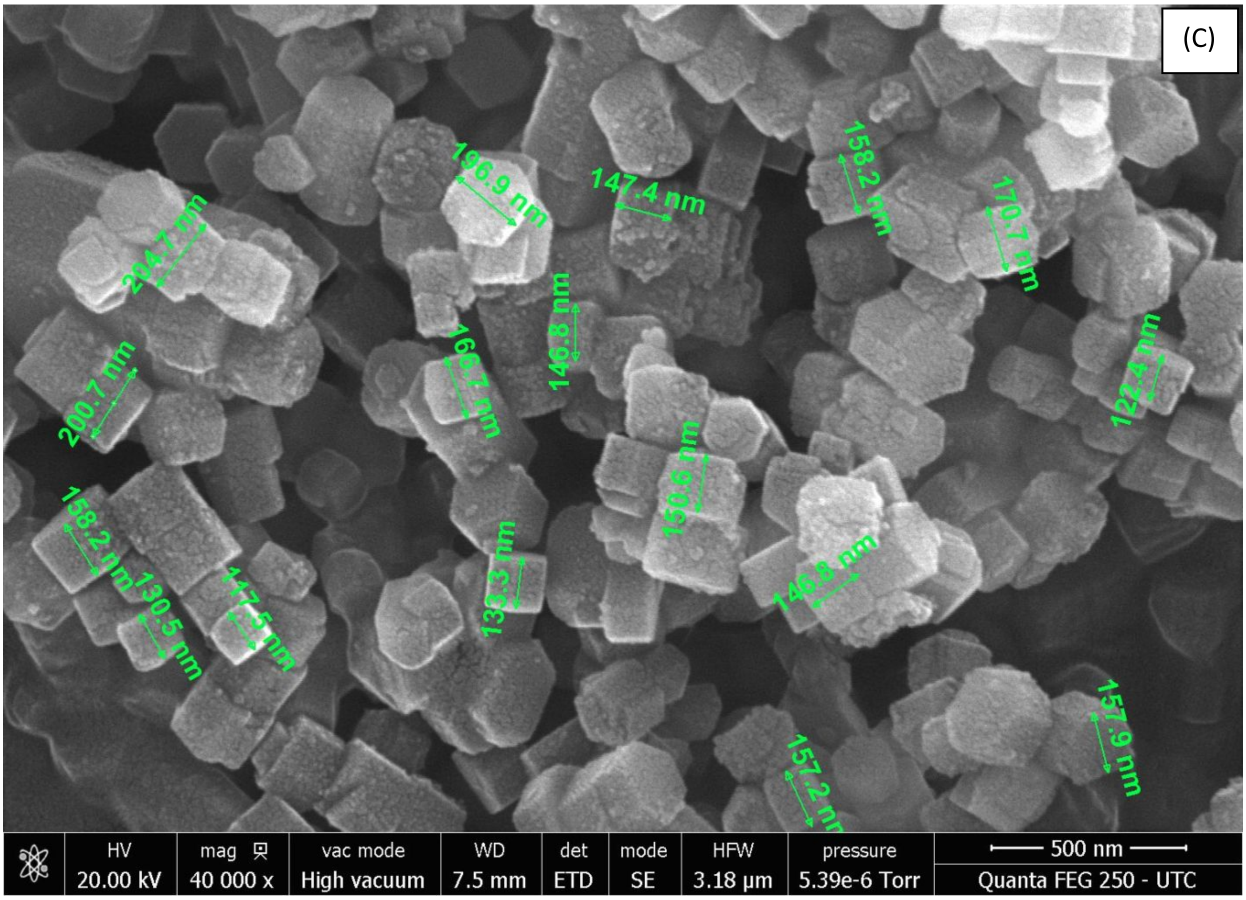
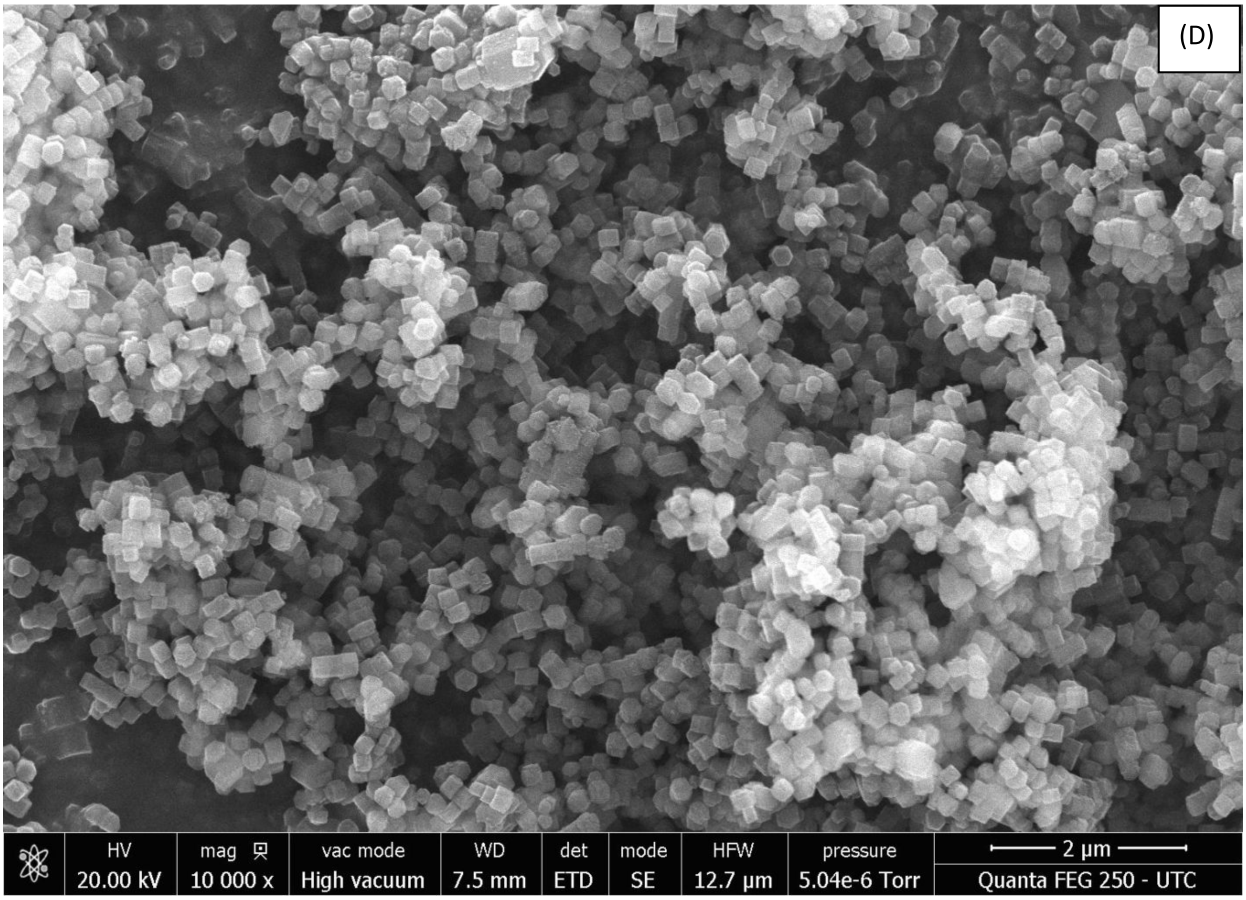


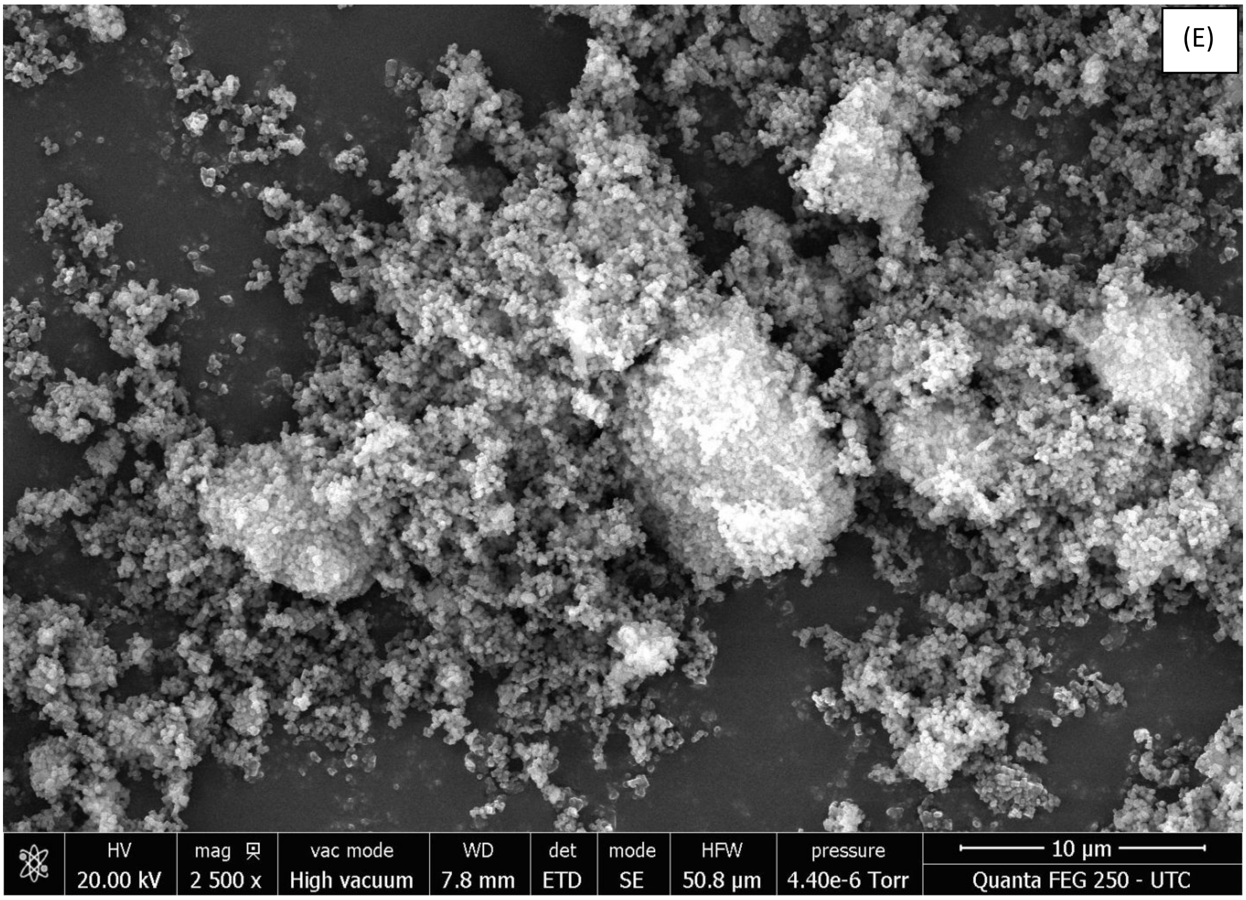
Figure S4: SEM images of TS-1 (a) and (b) before synthesis, (c) and (d) after recycling followed by pyrolysis at 823K, 6h.

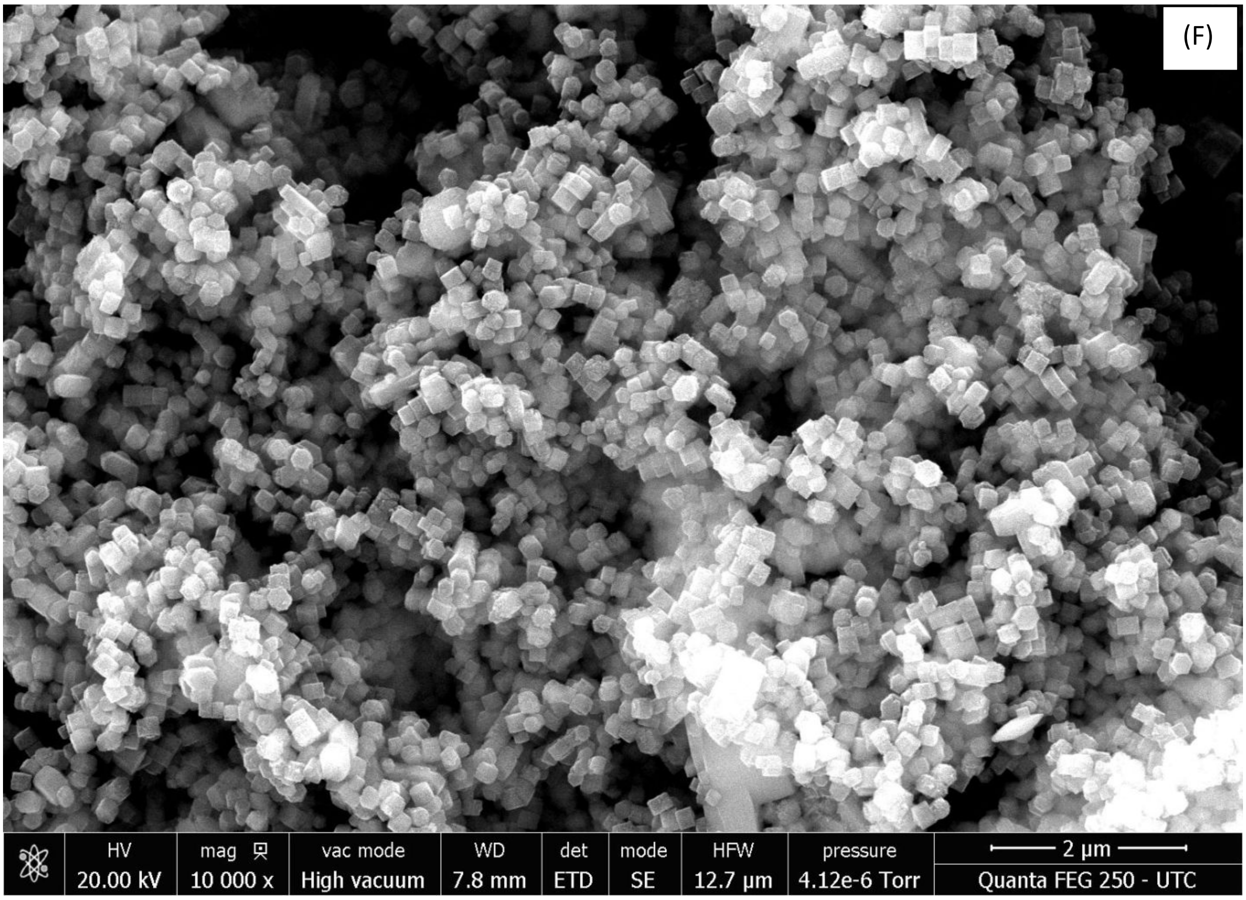


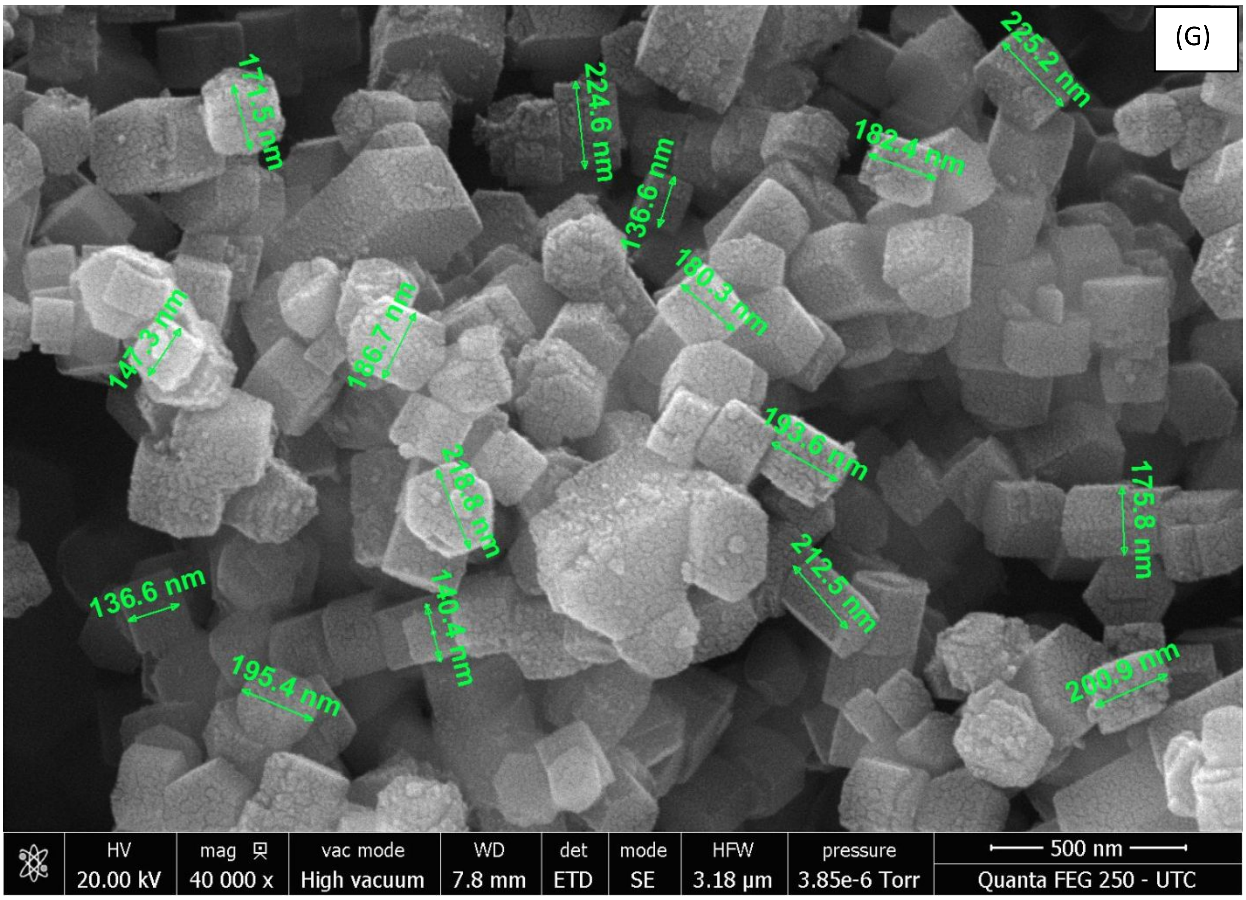

(B)
HV
20.00 kV
mag
10 000 x
vac mode
High vacuum
WD
7.5 mm
det
ETD
mode
SE
HFW
12.7 µm
pressure
5.77e-6 Torr
2 µm
Quanta FEG 250 - UTC


(C)
196.9 nm
147.4 nm
158.2 nm
170.7 nm
204.7 nm
146.8 nm
166.7 nm
200.7 nm
122.4 nm
150.6 nm
158.2 nm
130.5 nm
147.5 nm
133.3 nm
146.8 nm
157.9 nm
157.2 nm
HV
20.00 kV
mag
40 000 x
vac mode
High vacuum
WD
7.5 mm
det
ETD
mode
SE
HFW
3.18 µm
pressure
5.39e-6 Torr
500 nm
Quanta FEG 250 - UTC


(D)
HV
20.00 kV
mag
10 000 x
vac mode
High vacuum
WD
7.5 mm
det
ETD
mode
SE
HFW
12.7 µm
pressure
5.04e-6 Torr
2 µm
Quanta FEG 250 - UTC


(E)
HV
20.00 kV
mag
2 500 x
vac mode
High vacuum
WD
7.8 mm
det
ETD
mode
SE
HFW
50.8 µm
pressure
4.40e-6 Torr
10 µm
Quanta FEG 250 - UTC


(F)
HV 20.00 kV
mag 10 000 x
vac mode High vacuum
WD 7.8 mm
det ETD
mode SE
HFW 12.7 µm
pressure 4.12e-6 Torr
2 µm
Quanta FEG 250 - UTC


(G)
171.5 nm
224.6 nm
225.2 nm
182.4 nm
136.6 nm
180.3 nm
147.3 nm
186.7 nm
193.6 nm
218.8 nm
175.8 nm
212.5 nm
136.6 nm
140.4 nm
195.4 nm
200.9 nm
HV 20.00 kV
mag 40 000 x
vac mode High vacuum
WD 7.8 mm
det ETD
mode SE
HFW 3.18 µm
pressure 3.85e-6 Torr
500 nm
Quanta FEG 250 - UTC

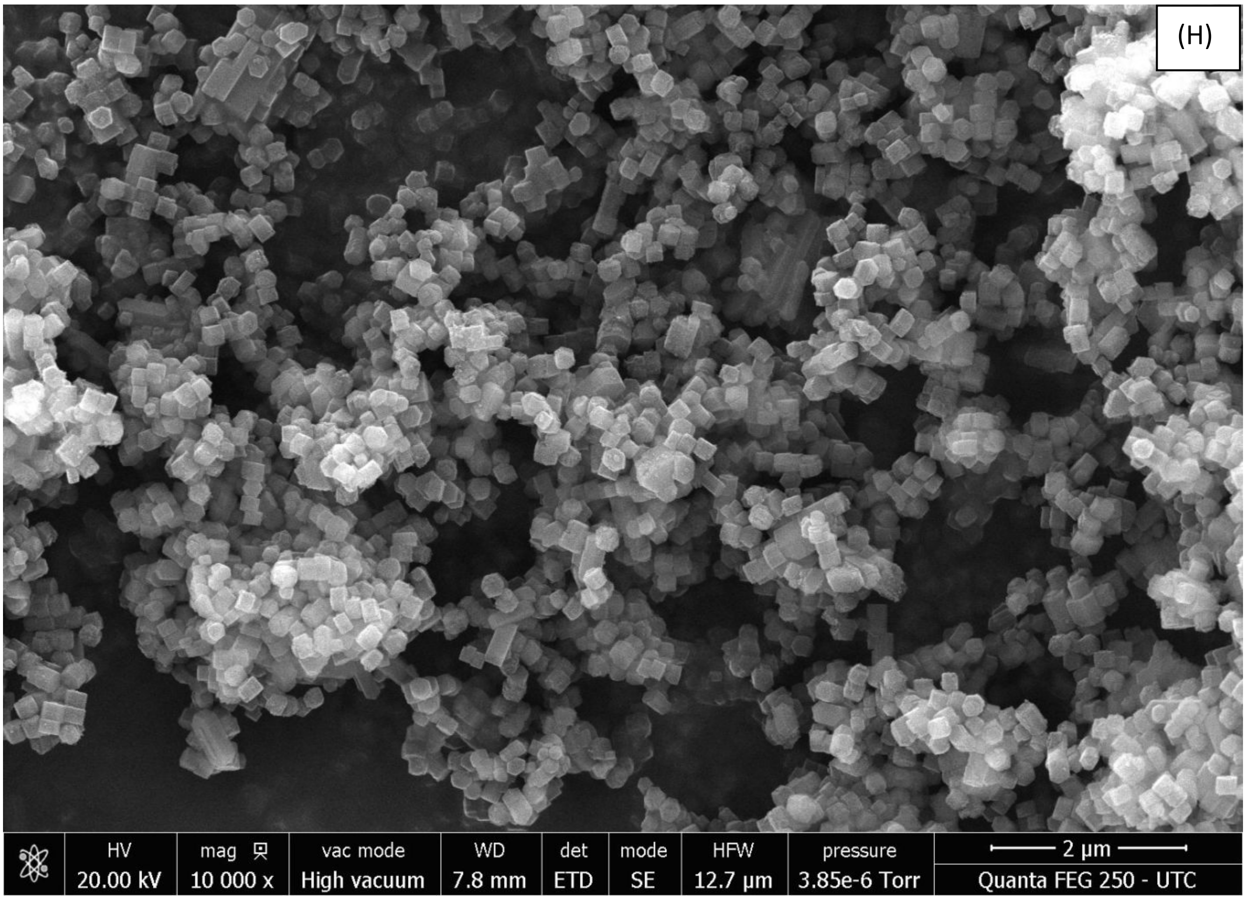


Figure S5 Additionnal SEM image. (A), (B), (C), (D) fresh TS-1; (E), (F), (G), (H), used TS-1 after pyrolysis.

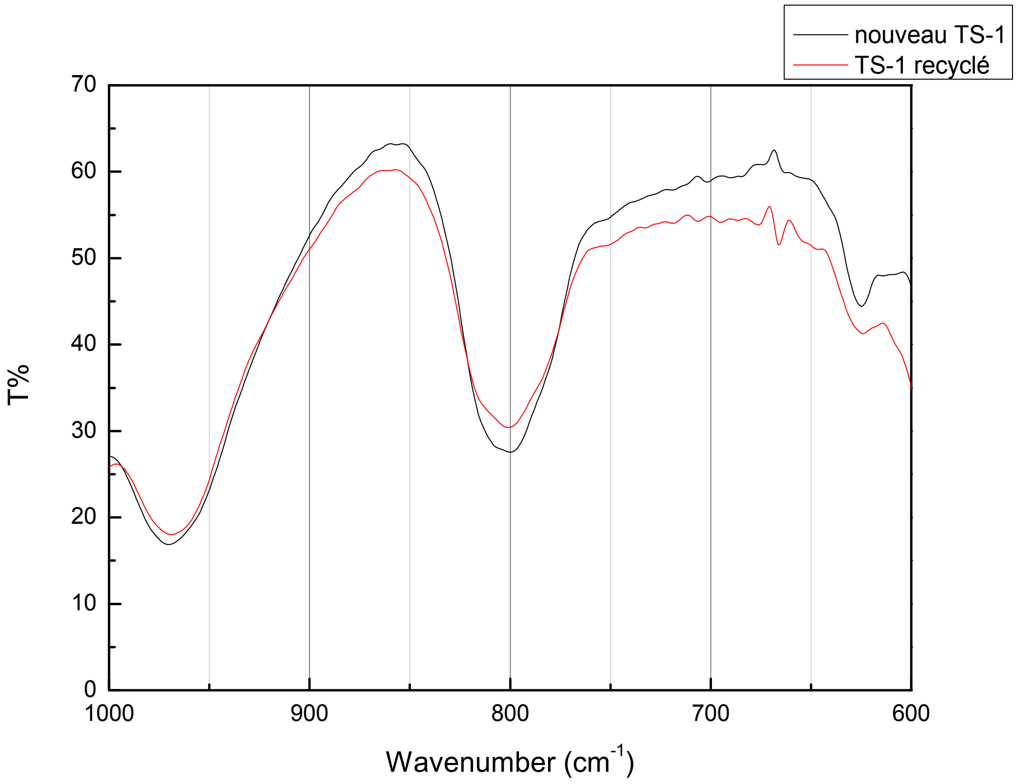
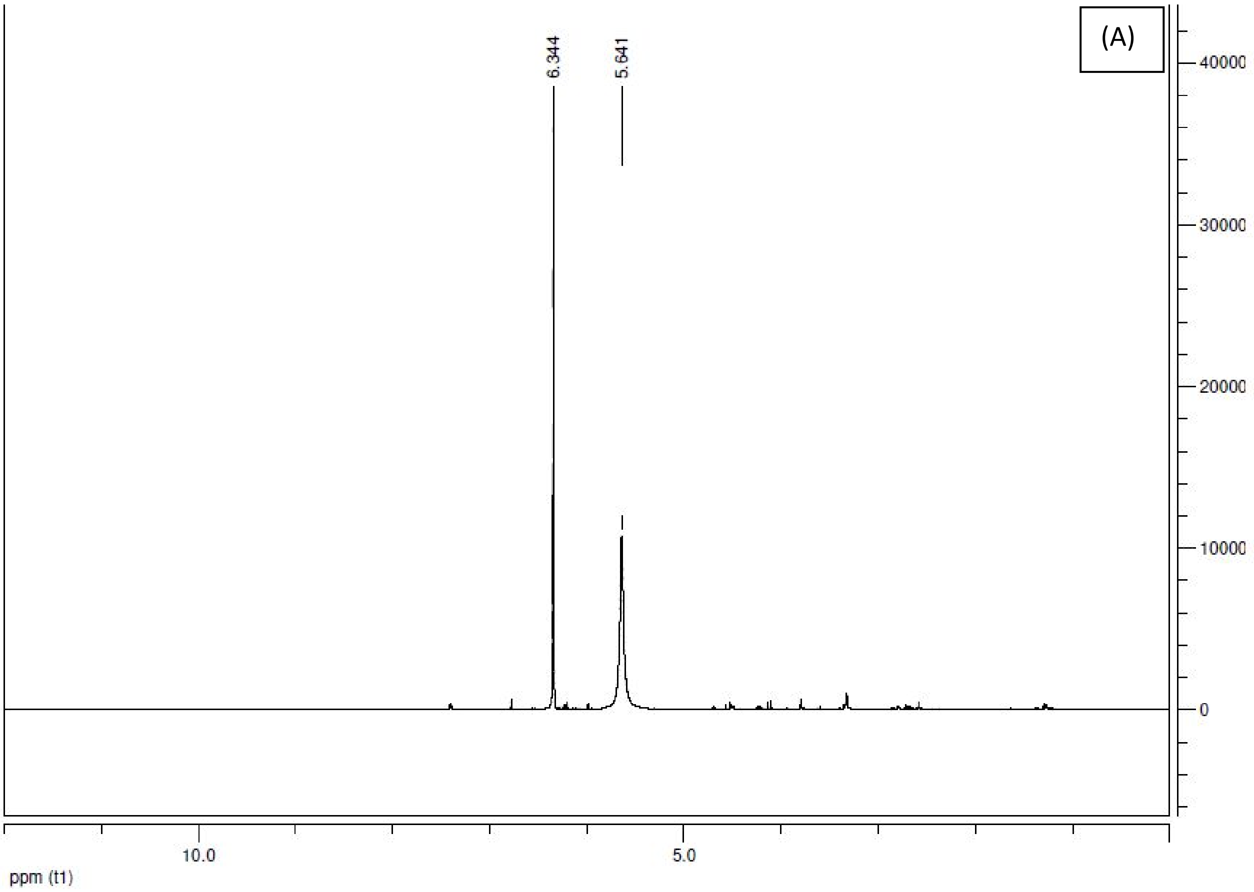


Figure S6. FT-IR spectra of TS-1. Black curve: Fresh TS-1; Red curve: Used TS-1 after pyrolysis.



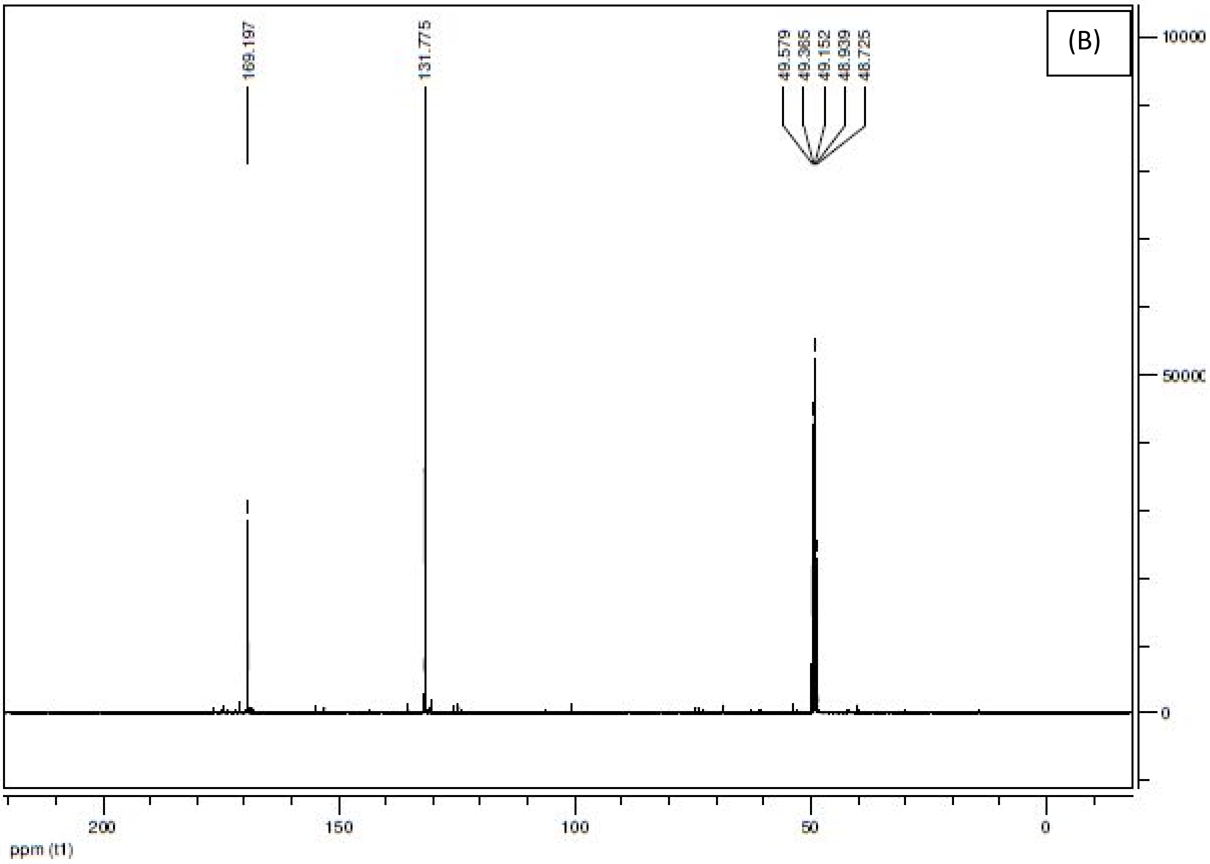
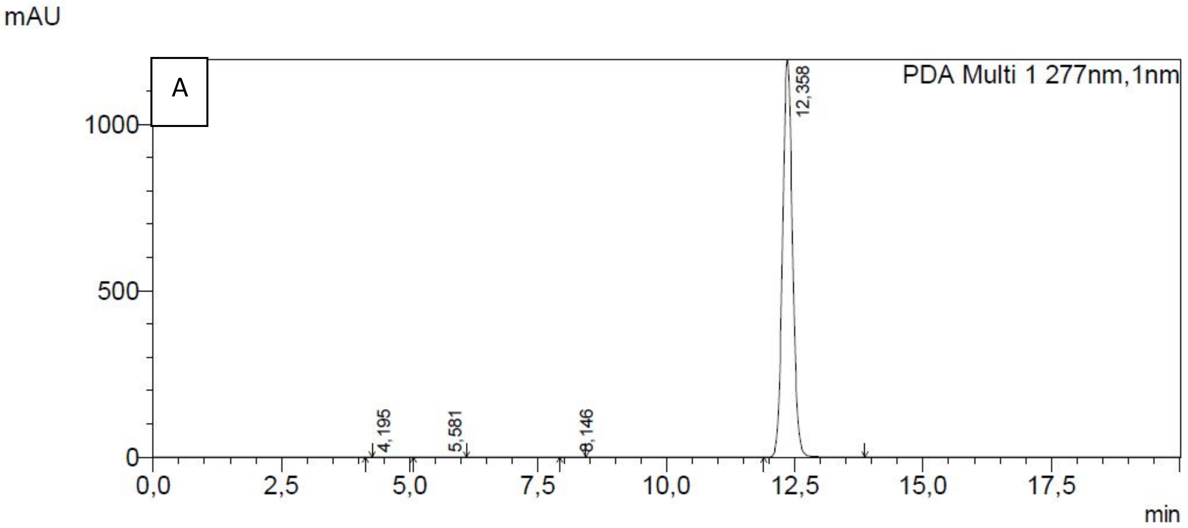
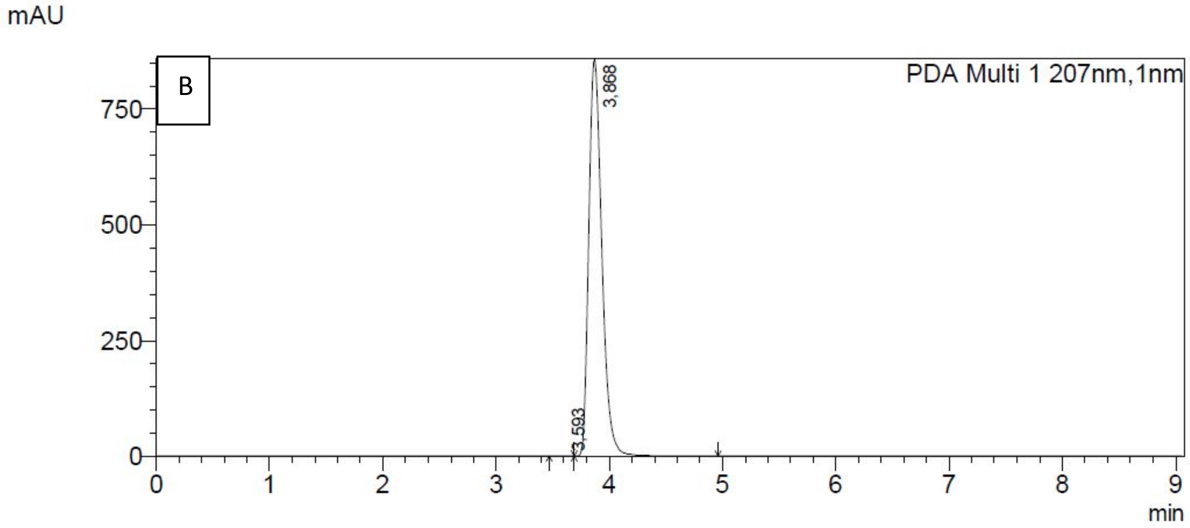
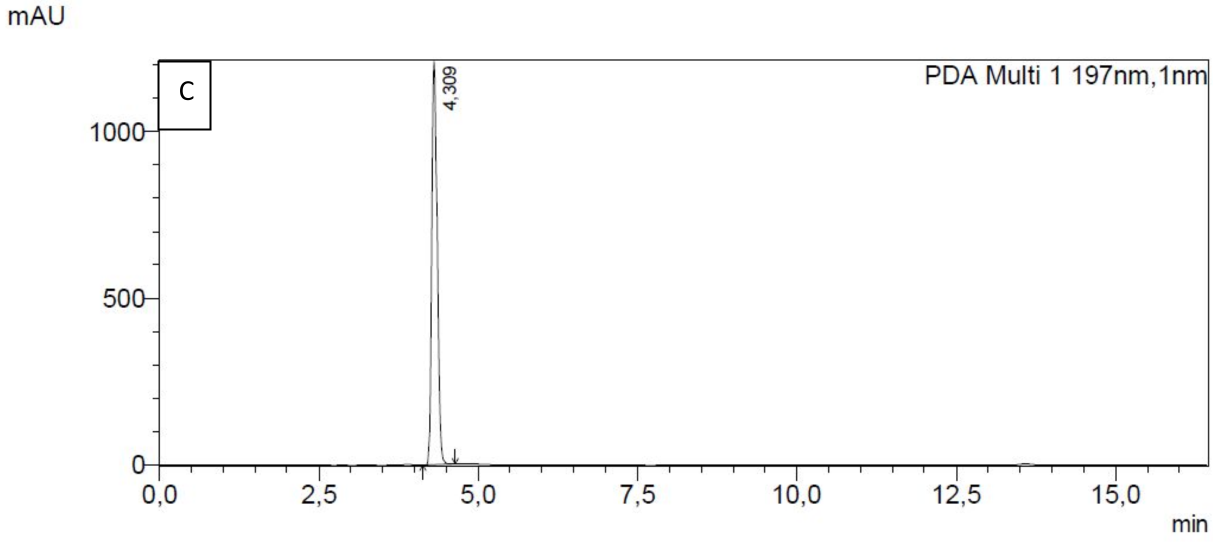
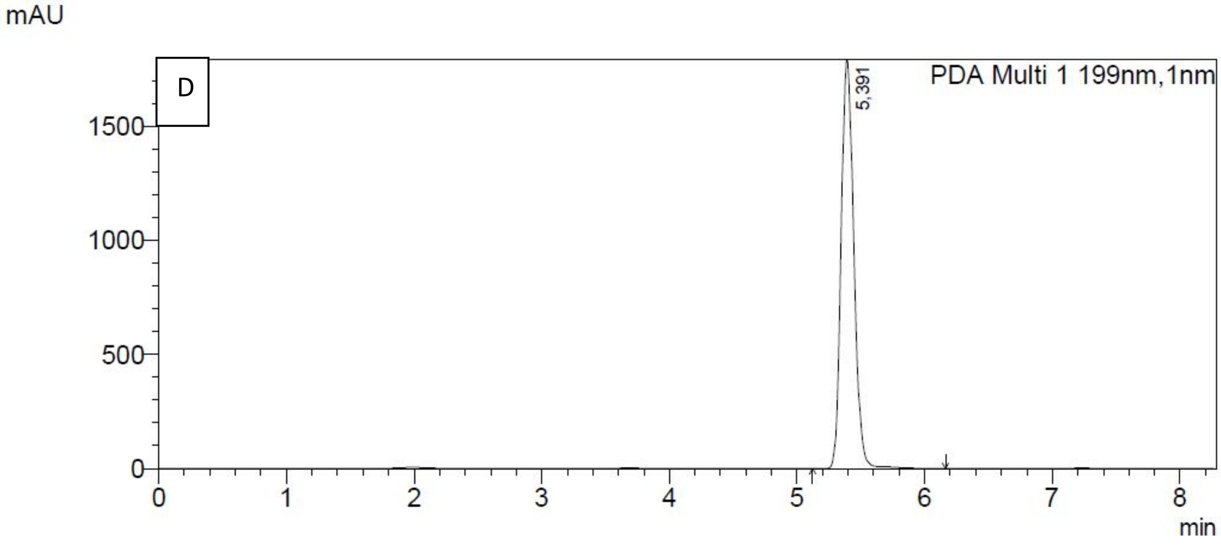


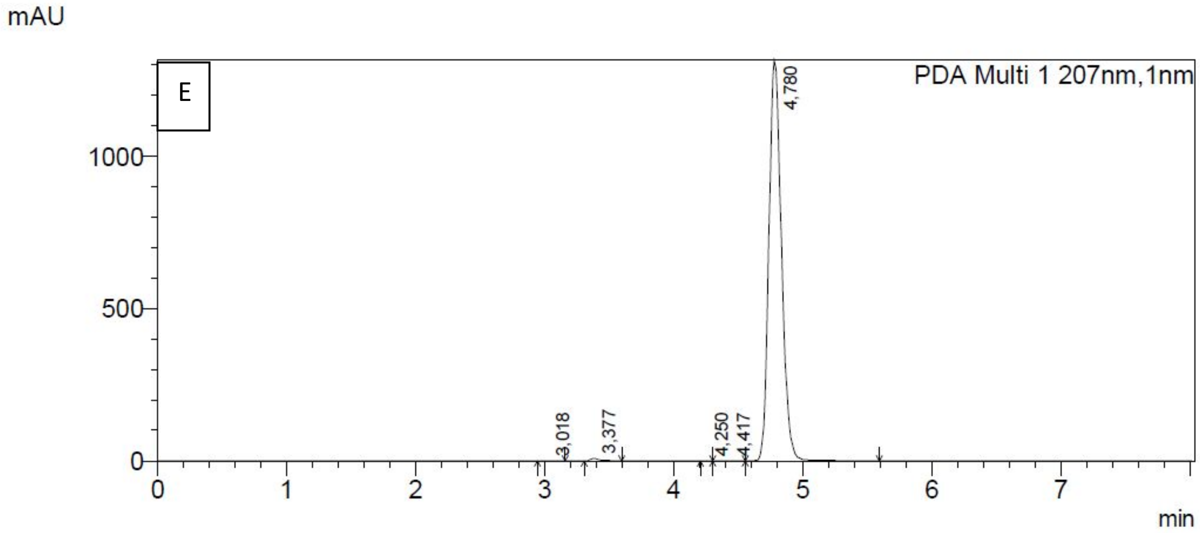
Figure S7. Typical H1-NMR (A) and C13-NMR (B) spectrum of maleic acid obtained without any further purification than filtration of TS-1 and evaporation of the reaction mixture. Only trace of impurities are visible on the baseline.

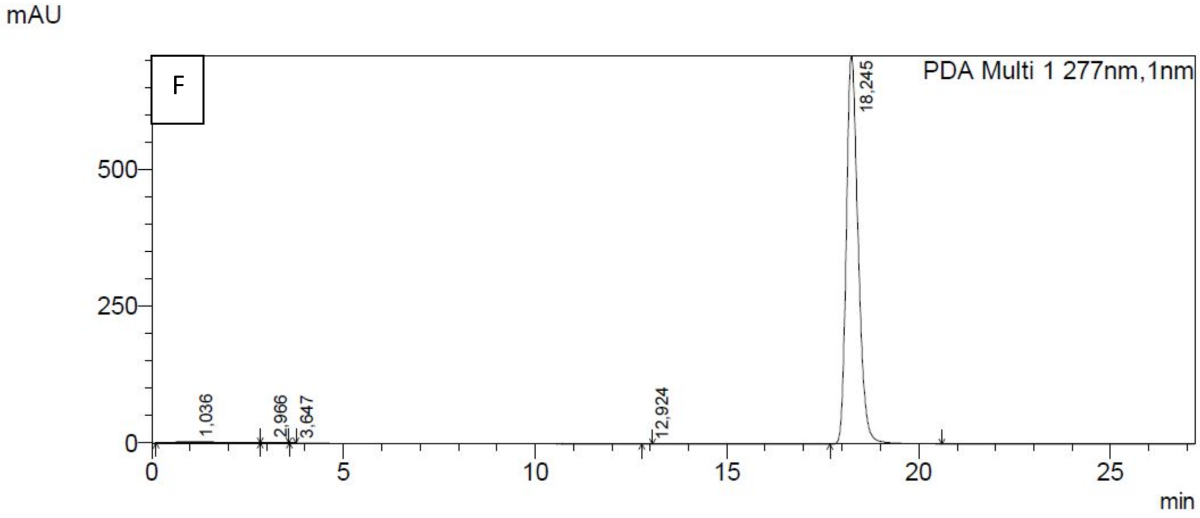


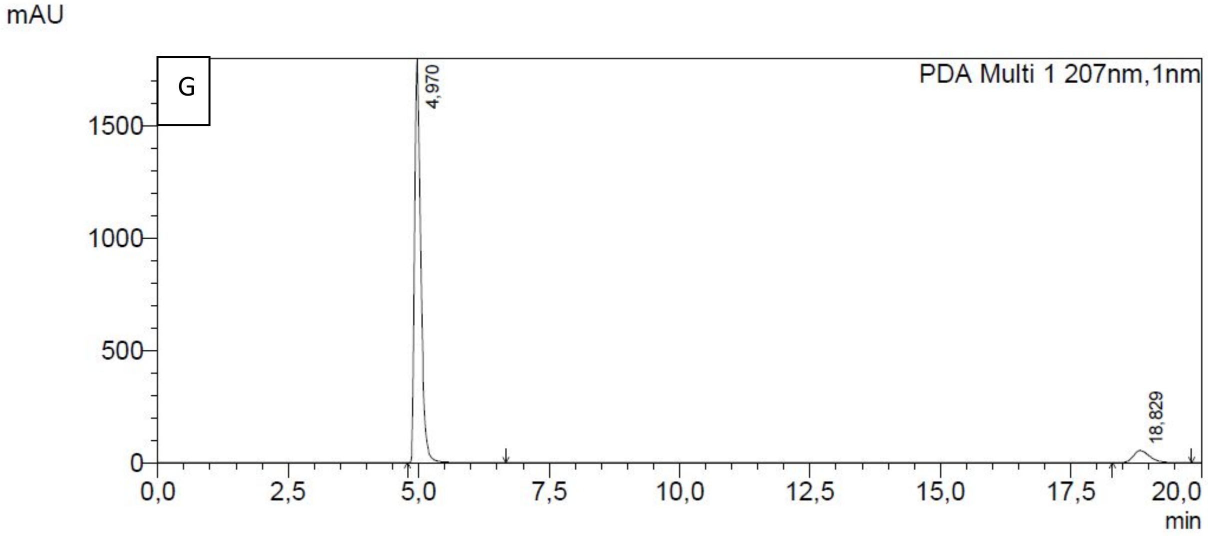

mAU
B
PDA Multi 1 207nm,1nm
3,868
3,593
750
500
250
0
0
1
2
3
4
5
6
7
8
9
min


mAU
C
PDA Multi 1 197nm,1nm
4,309
1000
500
0
0,0
2,5
5,0
7,5
10,0
12,5
15,0
min


mAU
D
PDA Multi 1 199nm,1nm
5,391
1500
1000
500
0
0
1
2
3
4
5
6
7
8
min


mAU
E
PDA Multi 1 207nm,1nm
1000
500
0
3,018
3,377
4,250
4,417
4,780
0
1
2
3
4
5
6
7
min


mAU
F
PDA Multi 1 277nm,1nm
500
250
0
1,036
2,966
3,647
12,924
18,245
0
5
10
15
20
25
min


mAU
G
PDA Multi 1 207nm,1nm
1500
1000
500
0
4,970
18,829
0,0
2,5
5,0
7,5
10,0
12,5
15,0
17,5
20,0
min

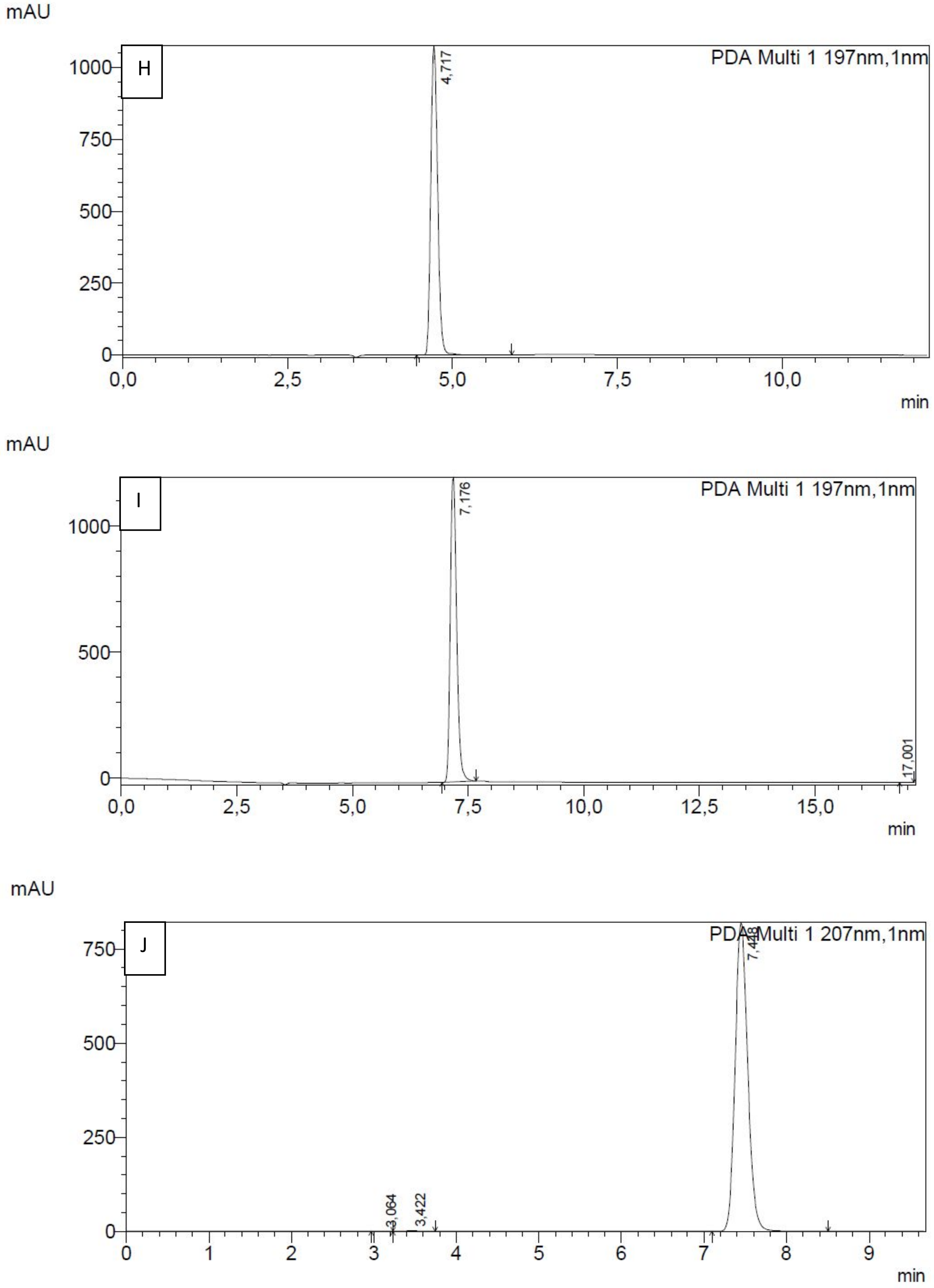


Figure S8. Typical HPLC Chromatogram, with method 1 : Eluent CH_3CN-H_2O with 0,01 mol.dm^{-3} Na_2HPO_4 (1/9) pH=2,4 was adjust with H_3PO_4 at 1 ml.min^{-1}: (A) Furfural 12,35 min, (B) Maleic Acid 3,86 min, (C) 5-hydroxy-furan-2(5H)-one 4,30 min, (D) 2-(5H)-Furanone 5,39 min, (E) Fumaric Acid 4,78 min; with method 2: Eluent CH_3OH-H_2O with 0,01 mol.dm^{-3} Na_2HPO_4 (1/9) pH=2,4 was adjust with H_3PO_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.

5. Acknowledgements:

For XRD and SEM characterizations, Frederic Nadau and François Oudet are gratefully acknowledged.
UTC Service d'Analyse Physico-Chimique, B.P 20529, 60205 Compiègne Cedex
frederic.nadaud@utc.fr; francois.oudet@utc.fr;

6. References:

[1] H. Xin, J. Zhao, S. Xu, J. Li, W. Zhang, X. Guo, E.J.M. Hensen, Q. Yang, C. Li, Enhanced catalytic oxidation by hierarchically structured TS-1 Zeolite, J. Phys. Chem. C. 114 (2010) 6553–6559. doi:10.1021/jp912112h.

[2] Z. Kong, B. Yue, W. Deng, K. Zhu, M. Yan, Y. Peng, H. He, Direct synthesis of hierarchically porous TS-1 through a solvent-evaporation route and its application as an oxidation catalyst, Appl. Organomet. Chem. 28 (2014) 239–243. doi:10.1002/aoc.3115.

[3] P. Kumar, R.K. Pandey, An efficient synthesis of 5-hydroxy-2(5H)-furanone: Using a titanium silicate molecular sieve catalyst, Green Chem. 2 (2000) 29–31. doi:10.1039/A907690E.