Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPORTING INFORMATION

Catalytic oxidative dehydrogenation of malic acid to oxaloacetic acid

Asmaa Drif,[a] Antonio Pineda,[a] Didier Morvan,[b] Virginie Belliere-Baca,[b] Karine De Oliveira Vigier[a] and François Jérôme[a]*.

---

[a] *Institut de Chimie des Milieux et Matériaux de Poitiers, CNRS-Université de Poitiers, 1 rue Marcel Doré, 86073 Poitiers (France). Email: francois.jerome@univ-poitiers.fr.*

[b] *ADISSEO, CINACHEM, 85 Rue des Frères Perret, 69192 Saint Fons (France)*

Catalysts preparation

The catalyst was prepared according to a protocol previously reported by Besson and co-workers.[1,2] Typically, 5 g of a commercially available Pt/C catalyst (Alfa Aesar – ref. 35849), with a nominal metal loading of 20 wt %, was pre-reduced at 40°C in 300 ml of an aqueous solution of glucose (30 wt%) under an inert atmosphere. The desired amount of $Bi(NO_3)_3.5H_2O$, dissolved in 15 mL of 1 M HCl, was then added dropwise to the suspension under continuous stirring. During all these operations, a nitrogen flow was maintained and the temperature was kept at 40 °C. After 2 h of reaction, the pH was increased to 9 with NaOH, and then the catalyst was filtered, washed, and dried at 100 °C overnight.

Experimental procedures

The catalytic oxidation of malic acid was performed in a three-neck-round bottom flask equipped with a reflux condenser. The reaction was followed by taking aliquots from the reaction media at different reaction times. Typically, malic acid (0.2 g, 1.49 mmol) was dissolved in 5 ml of ultrapure water. The pH was adjusted to 8 by the addition of NaOH. Then Pt-Bi /C catalyst (0.1 g) was added and the solution and stirred at 380 rpm. The oxidant (air) was bubbled through the solution during the catalytic reaction. The experiments were carried out at room temperature and at 50 °C.

Recyclability: To assess the reusability of the catalyst, the spent Bi_4-Pt_{20}/C was reused in malic acid dehydrogenation under the optimized conditions (4 wt% malic acid in MeOH, 2 wt% of catalyst, 50 mL/min of air, room temperature, pH 8). At the end of the reaction, the catalyst was recovered, washed with water, dried at 60 °C and then reused for the next cycle without any further purification. Elemental analysis using inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique, performed on a PerkinElmer Optima 2000 DV apparatus, was used to verify the leaching of platinum and bismuth into the reaction media.

Chromatographic conditions:

The reaction was analyzed by a Shimadzu HPLC equipped with a column ICSep COREGEL-107H (polystyrene/divinylbenzene, 5° particle size 8 μM), a pump (LC-20AD), a thermostated autosampler (SIL-20AC) and an oven heated at 40 ° C (CTO-20AC). The eluent consisted of an aqueous 7 mM H_2SO_4 solution with a flow rate of 0.8 mL/min. The eluted compounds were detected and quantified using two detectors (1) a UV detector (SPD-20A) at 210 nm wavelength and (2) a refractive index detector (RID-20A). A representative chromatogram with the different chemicals involved in the catalytic reaction is shown in Figure S1.

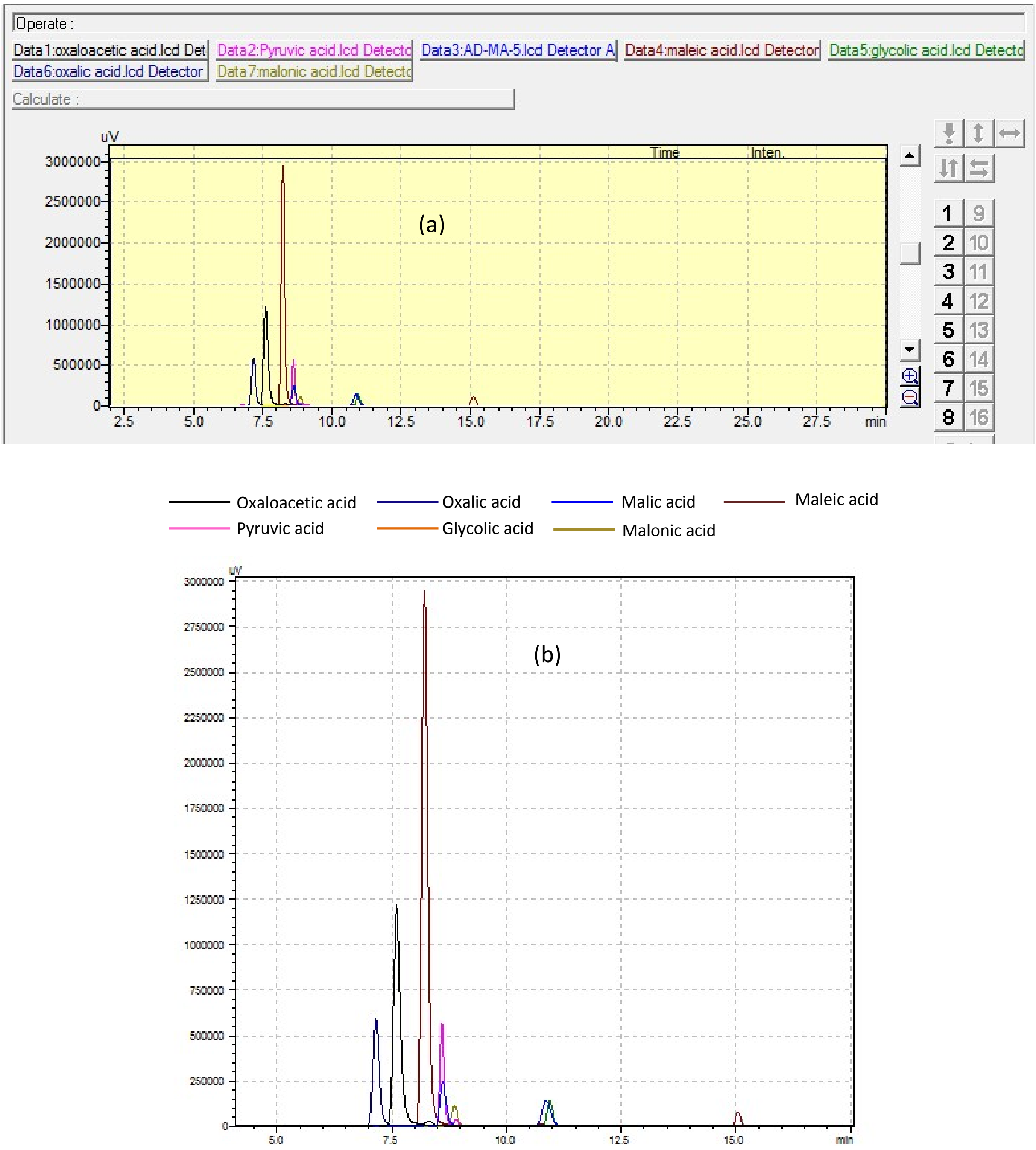


Figure S1. HPLC chromatogram for the different compounds that could be involved in the malic acid oxidation/dehydrogenation (UV detector λ=210 nm). (A) Original HPLC chromatogram from the Shimadzu HPLC and (B) for the sake of clarity, the original chromatogram was saved as an ascii file and re-plot with excel. Analysis conditions: 7 mM H_2SO_4, flow: 0.8 ml/min, ICSep COREGEL-107H Column (polystyrene/divinylbenzene) 5°, Particle size/ 8 µM, Column Temperature: 40 °C.

Table S1. Response coefficients of malic acid and reaction products on the ICSep COREGEL-107H Column

	Oxaloacetic acid	Pyruvic acid	Oxalic acid	Glycolic acid	Malic acid	Malonic acid	Maleic acid
Response coefficient	$7.\,10^{7}$	$6.\,10^{7}$	10^{8}	7.10^{6}	10^{7}	10^{7}	2.10^{8}

Thermodynamic calculations

The thermodynamic calculations were performed using the Spartan software [3]. The heat of formation ($\Delta H^{\circ}_{f,i}$) of the different compounds was computed using a T1 method, while the entropy of formation ($\Delta S^{\circ}_{f,i}$) was computed using the B3LYP hybrid functional method and a 6-311+G** basis set. All the calculations were conducted in the gas phase without taking into account of solvation effects.

X-ray photoelectron spectroscopy (XPS)

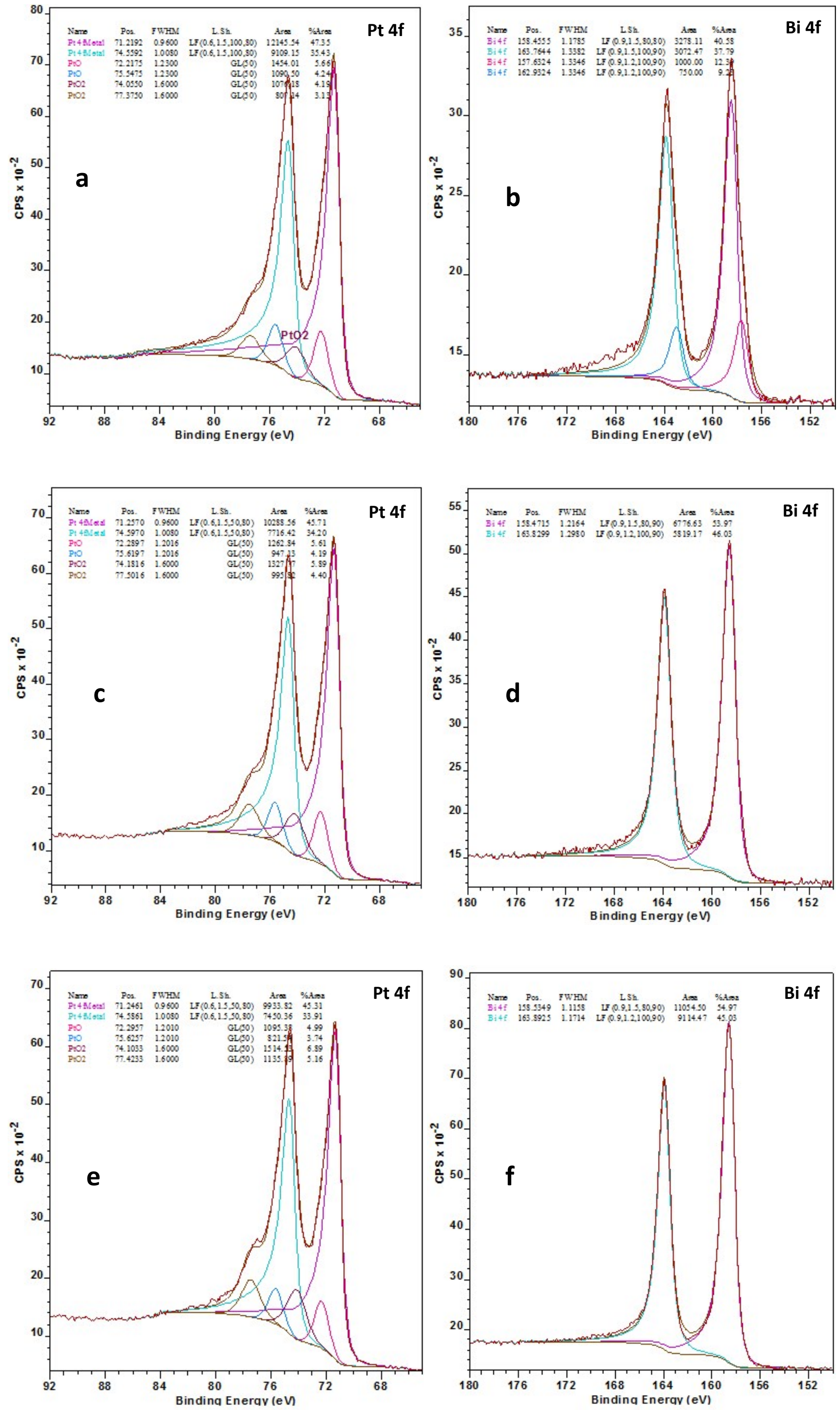
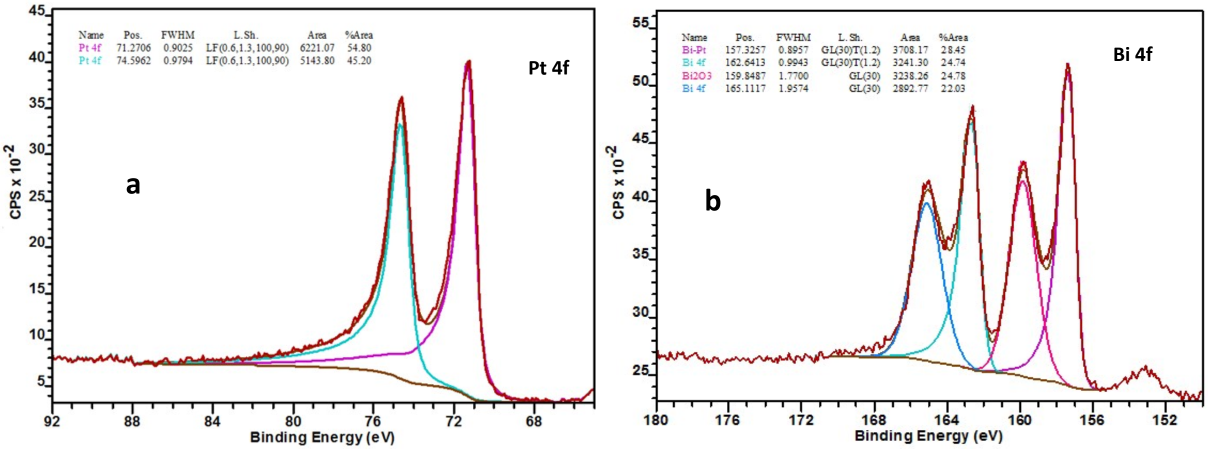


Figure S2. *Detailed XPS spectra for Pt 4f and Bi 4f orbitals on different Pt-Bi/C catalysts: (a-b) Bi_2-Pt_{20}/C, (c-d) Bi_4-Pt_{20}/C and (e-f) Bi_6-Pt_{20}/C.*

X-ray photoelectron spectroscopy (XPS) of the different Pt-Bi/C catalysts was performed on a Kratos Axis Ultra DLD apparatus equipped with a hemispherical analyzer and a delay line detector. The spectra were recorded using an Al monochromated X-ray source (10 kV, 15 mA) with a pass energy of 20 eV (0.1 eV per step) for high resolution spectra, and a pass energy of 160 eV (1 eV per step) for survey spectrum in hybrid mode and slot lens mode, respectively. XPS spectra were calibrated with respect to the C 1s orbital at 284.6 eV.

Remark: XPS measurements, performed on the spent Bi_4-Pt_{20}/C catalyst, indicates the presence of a large amount of sodium due to the basic reaction conditions, a result which was also observed by TEM analysis. According to XPS results (figure S3), after the catalytic reaction, platinum is in metallic form. The surface atomic ratio Bi/Pt of the catalyst determined by XPS showed that the bismuth concentration was higher than that of “bulk” composition estimated by TEM–EDX analysis, indicating that bismuth was mainly deposed on the platinum surface.



Name	Pos.	FWHM	L. Sh.	Area	%Area
Pt 4f	71.2706	0.9025	LF(0.6,1.3,100,90)	6221.07	54.80
Pt 4f	74.5962	0.9794	LF(0.6,1.3,100,90)	5143.80	45.20

Name	Pos.	FWHM	L. Sh.	Area	%Area
Bi-Pt	157.3257	0.8957	GL(30)T(1.2)	3708.17	28.45
Bi 4f	162.6413	0.9943	GL(30)T(1.2)	3241.30	24.74
Bi2O3	159.8487	1.7700	GL(30)	3238.26	24.78
Bi 4f	165.1117	1.9574	GL(30)	2892.77	22.03

Figure S3. *XPS spectra of Bi_4-Pt_{20}/C catalyst after 4 h of malic acid dehydrogenation reaction.*

Transmission Electron Microscopy (TEM)

Catalysts were characterized by transmission electron microscopy using a TEM/STEM JEOL 2100 UHR (200 kV, cathode LaB6, 0.19 nm resolution) equipped with an energy dispersive spectrometer EDX and High-Angle Annular Dark-Field HAADF. As shown in Table S2, the Pt/Bi ratio measured by EDX was close to the expected ratio.

Table S2. Determination of the Pt/Bi ratio by TEM-EDX analysis

	Mass ratio Pt/Bi	
Catalysts	Expected mass ratio	TEM–EDX analysis
Bi_2-Pt_{20}/C	10	9.3
Bi_4-Pt_{20}/C	5	4.78
Bi_6-Pt_{20}/C	3.33	3.05

The mean particle sizes and size distributions were determined by measuring the diameters of isolated particles using Image J free software [4]

Figure S4 presents a characteristic set of TEM images and the corresponding size distributions for the Bi-Pt/C catalysts with different bismuth loading. All samples display homogeneous distribution of Pt and Bi particles on the carbon support. TEM analyses indicated that the incorporation of bismuth leads to the increase of the Pt-Bi mean particle size from 2.3 nm for Bi_2-Pt_{20}/C to 2.9 nm for Bi_6-Pt_{20}/C.

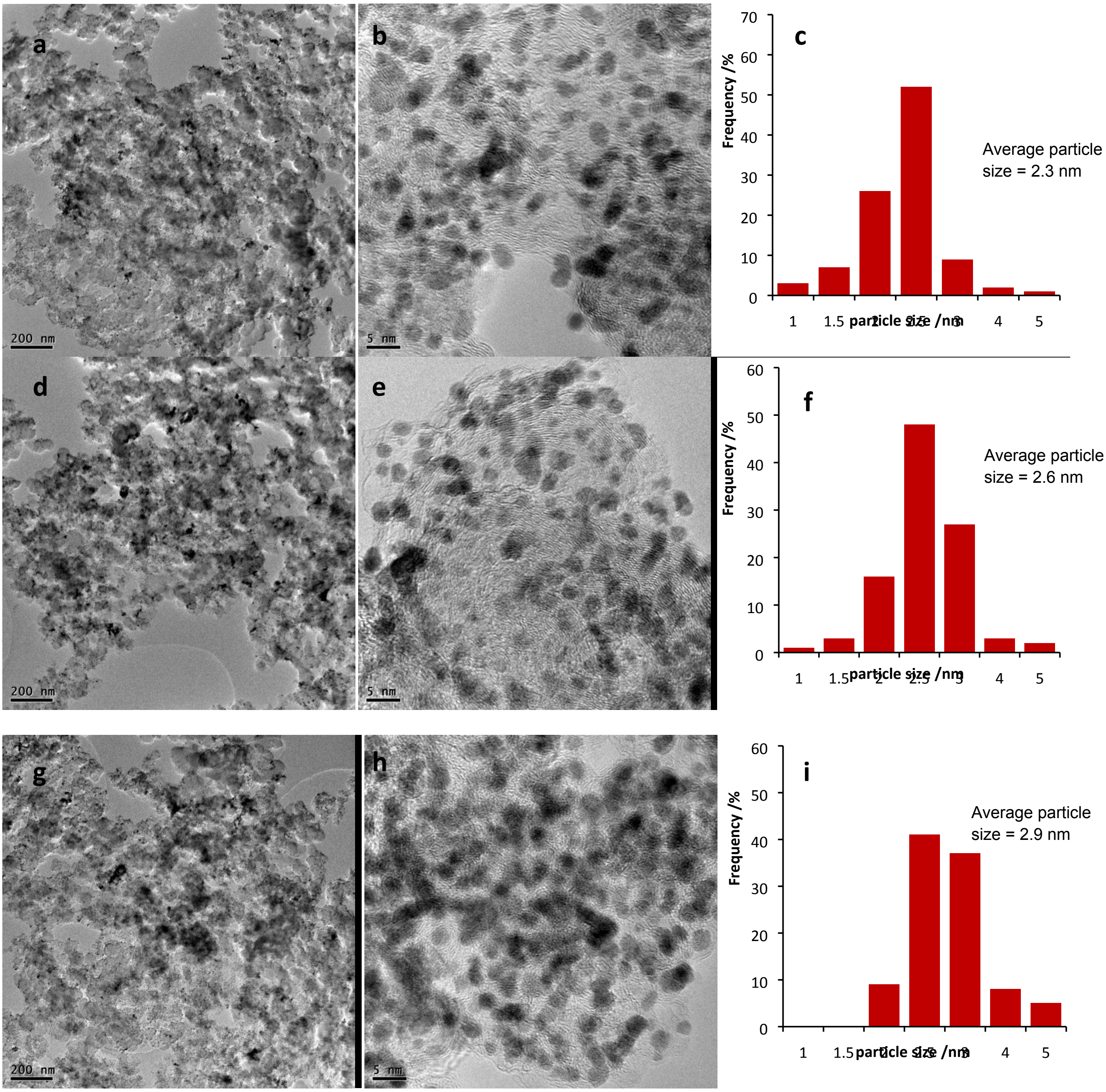


Figure S4. *TEM pictures and corresponding particles size distribution for the different Bi-P/C catalysts: (a-c)* Bi_2-Pt_{20}/C*, (d-f)* Bi_4-Pt_{20}/C *and (g-i)* Bi_6-Pt_{20}/C*.*

The TEM analysis of Bi_4-Pt_{20}/C catalyst after 4 h of malic acid dehydrogenation showed that the particle size of Pt-Bi remained almost constant compared with the fresh Bi_4-Pt_{20}/C catalyst (figure S5).

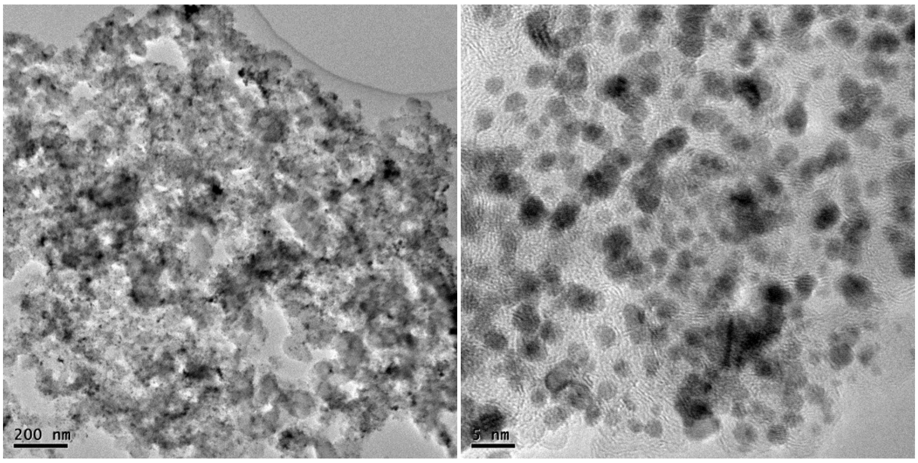


Figure S5. *TEM pictures of Bi_4-Pt_{20}/C catalyst after 4 h of reaction.*

H_2 chemisorption

Metal accessibility was determined by hydrogen chemisorption using a pulse chromatographic system. Typically, the catalyst sample (~100 mg) was reduced under H_2 (30 mL min^{-1}) at 500 °C for 1 h, then purged for 2 h with pure Ar (30 mL min^{-1}), and cooled down to room temperature. Pulses of H_2 were injected every minute up to saturation. The sample was degassed under pure Ar for 10 min to remove the hydrogen reversibly adsorbed (*i.e.* H_2 physisorbed). The amount of chemisorbed hydrogen was obtained by subtracting the amount of H_2 initially introduced with the amount of H_2 reversibly adsorbed on Pt, considering that one hydrogen atom chemisorbs on one accessible Pt atom.

The particle diameter was obtained as follows:

$$d\ (\mathrm{nm}) = 5.10^5 * \left(\frac{M}{\rho * \left(\frac{H}{Pt}\right) * S} \right)$$

with M the Pt molecular weight (g mol^{-1}), ρ the Pt volumetric weight (g.cm^{-3}), S the surface developed by one mole of Pt (m^2 mol^{-1}) and H (mol) the amount of H_2 chemisorbed.

Table S3 showed the obtained results of metallic accessibility and particle size measured by hydrogen chemisorption of the Bi-Pt/C catalysts.

Table S3 . *Metal accessibility and particle size determined by H_2 chemisorption at room temperature for Bi-Pt/C catalysts.*

Catalyst	H/Pt (%)	d (nm)
Bi_2-Pt_{20}/C	61	1.6
Bi_4-Pt_{20}/C	54	1.8
Bi_6-Pt_{20}/C	47	2.1

Characterization of the crude reaction medium

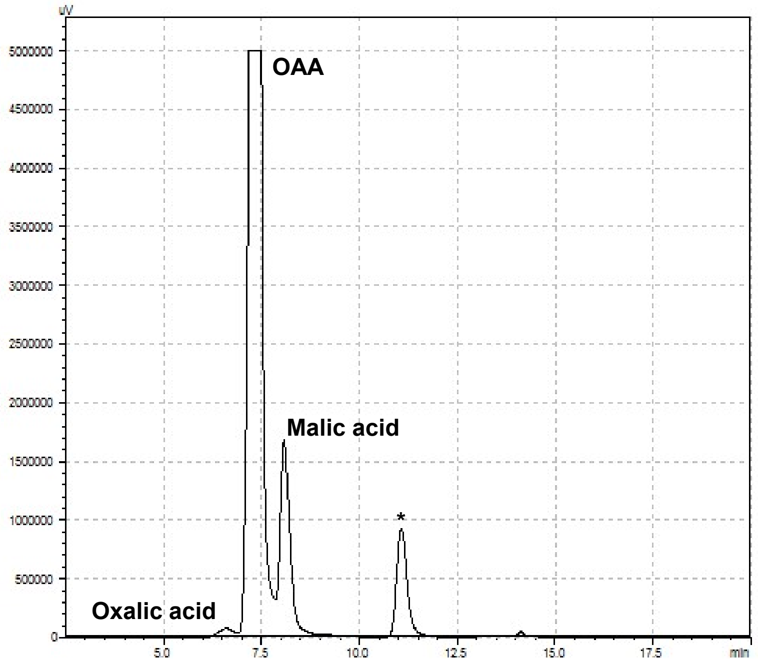


Figure S6. *HPLC chromatogram of the crude reaction mixture (plateau at 60 % OAA yield). Results collected under optimized conditions i.e. in a methanolic solution of malic acid (4 wt%) over a Pt_{20}-Bi_4/C catalyst (0.1 g), at pH=8, 25 °C, 4h and an air flow of 75 mL/min.*

* **Fumaric acid is an impurity contained in the starting malic acid lot** (ACROS Organics, CAS N°: 97-67-6). Fumaric acid stems from the isomerization of maleic acid, which is used as a precursor in the synthesis of malic acid. Even in a low amount, fumaric acid appears as an intense peak on the HPLC chromatogram. Indeed, at λ=210 nm, the response coefficient of fumaric acid (5.10^9) is 500 times higher than that of malic acid (1.10^7). Titration by HPLC has revealed that the amount of fumaric acid in malic acid is lower than 1%, in line with the specifications provided by ACROS Organics.

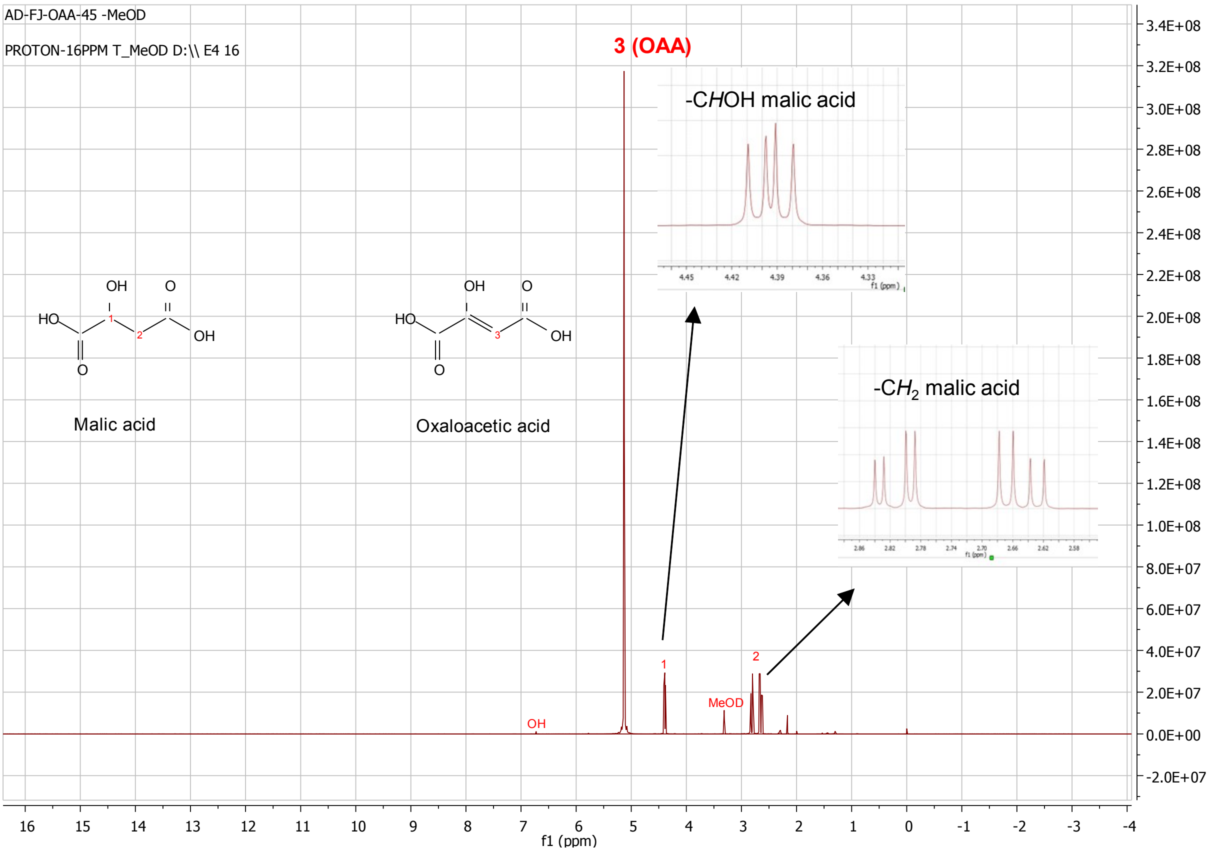


Figure S7. *^{1}H NMR of the crude reaction in CD_3OD, monitored at 60% conversion (oxidation of 4 wt % of malic acid in CD_3OD over the Pt_{20}-Bi_4/C catalysts. Only the enol form of OAA was detected*

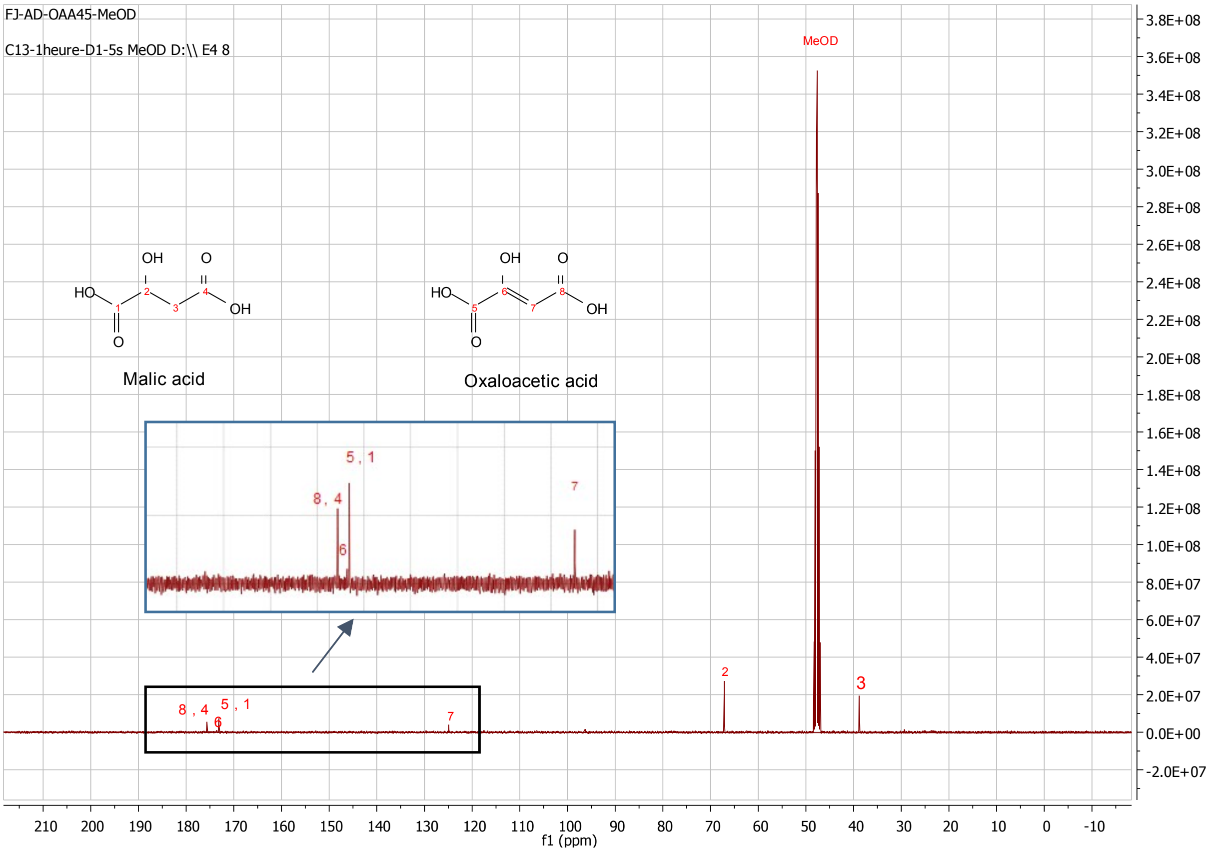
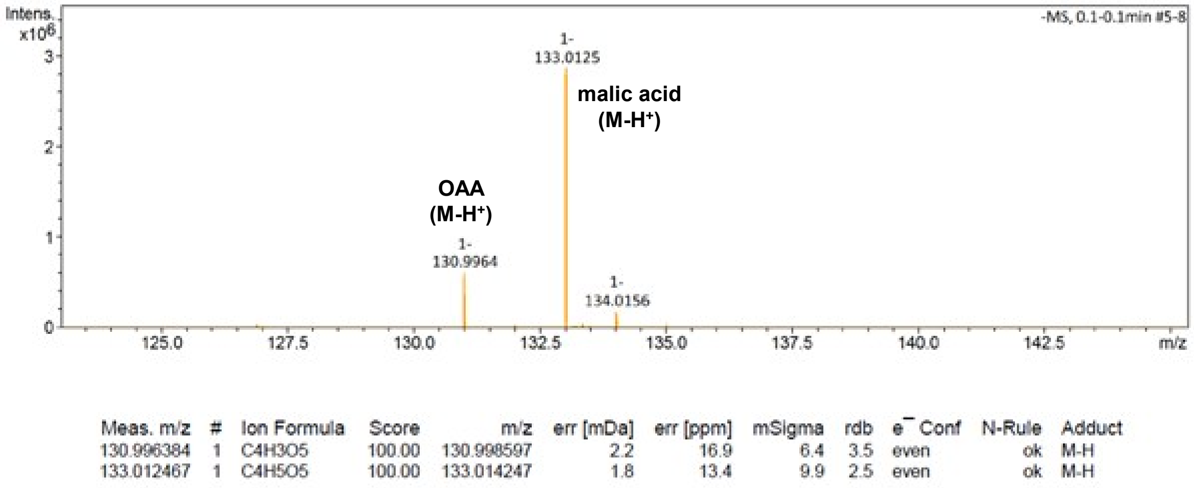


Figure S8. *^{13}C NMR of the crude reaction in CD_3OD, monitored at 60% conversion (oxidation of 4 wt % of malic acid in CD_3OD over the Pt_{20}-Bi_4/C catalysts. Note that the $–COO^-$,Na^+ of OAA and malic acid have similar chemical shift.*



Meas. m/z	#	Ion Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	Adduct
130.996384	1	C4H3O5	100.00	130.998597	2.2	16.9	6.4	3.5	even	ok	M-H
133.012467	1	C4H5O5	100.00	133.014247	1.8	13.4	9.9	2.5	even	ok	M-H

Figure S9. *Mas spectrometry of the crude reaction (oxidation of 4 wt % of malic acid in CD_3OD over the Pt_{20}-Bi_4/C catalysts. Note that the $–COO^-$,Na^+ of OAA and malic acid have similar chemical shift*

References

[1] M. Besson, F. Lahmer, P. Gallezot, P. Fuertes and G. Fleche, *J. Catal.*, 1995, **152**, 116–121.

[2] A. B. Crozon, M. Besson and P. Gallezot, *New J. Chem.*, 1998, **22**, 269–273.

[3] W.S. Rasband, Image J, US National Institutes of Health, Bethesda, MD, USA (2009), http://rsbweb.nih.gov/ij/.

[4] Spartan'16, Wavefunction, Inc., Irvine, CA. Except for molecular mechanics and semi-empirical models, the calculation methods used in Spartan have been documented in: Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko, S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. Simmonett, J.E. Subotnik, H.L. Woodcock III, W. Zhang, A.T. Bell, A.K. Chakraborty, D.M. Chipman, F.J. Keil, A.Warshel, W.J. Hehre, H.F. Schaefer, J. Kong, A.I.Krylov, P.M.W. Gill and M. Head-Gordon, Phys. Chem. Chem. Phys., 8, 3172 (2006).