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Supporting Information

Designed sol-gel precursors for atomically dispersed Nb and Pb within TiO_2 as catalysts for dihydroxyacetone transformation

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Experimental

General Procedures. We performed all the synthetic manipulations under an argon atmosphere using standard Schlenk and glovebox techniques. $Ti(OEt)_4$ and $Nb(OEt)_5$ (both Strem Chemicals) were distillated under vacuum prior to use, whereas *N*-methyl diethanolamine (Aldrich), stored under argon over 4 Å molecular sieves, was used as received. Anhydrous EtOH (Carlo Erba reagents) and lead oxide (Aldrich) were used as received. Anhydrous solvents (toluene, diethyl ether and *n*-hexane) were obtained using a solvent drier, MB SPS-800 (solvent purification system) from MBRAUN and stored under argon over 4 Å molecular sieves. Deuterated chloroform were stored into a Rotaflow flask over 4 Å molecular sieves. NMR spectra were recorded on Bruker AVANCE III 400MHz with a BBFO probe (Z gradient) using Topspin software. All chemical shifts were measured relatively to the residual protic solvent for ^1H NMR (in $CDCl_3$: $\delta = 7.24$ ppm singlet). FT-IR spectra were recorded from 4000 to 400 cm^{-1} at room temperature using Bruker Vector 22 and Opus software. Operation chamber is maintained under N_2 with constant gas flow. Samples were prepared under argon flow between KBr windows with Nujol (dried over 3 Å molecular sieves). TGA/DTA data of hydrolyzed products were collected in air on a Setaram 92 system with a thermal ramp of 5 °C/min. We used a Bruker D8 Advance A25 system with Cu Kα1 + 2 ($\lambda = 0.154184$ nm) radiation at 50 kV and 35 mA to measure the X-ray diffraction (XRD) patterns of the nanoparticles. The textural properties parameters were examined through nitrogen physisorption isotherms at −196 °C in a Micromeritics ASAP 2020 instrument. Previously, the samples were pre-treated for 3 h at 150 °C under 10^{-3} Torr. The BET multipoint method was used to measure the surface areas from the resulting isotherms. The STEM-ADF (annular dark field) experiments were performed with a FEI Titan ETEM G2 electron microscope, equipped with a Cs image aberration corrector and operated at 300 keV. The extraction voltage, camera length, acceptance angles, STEM resolution, and probe current were 4500 V, 245 mm, 29.2−146°, 0.14 nm, and <0.1 nA, respectively. For sample preparation, the powder was crushed and dispersed in ethanol through ultrasonication, dropped onto a holey carbon-coated 200 mesh Cu grid, and dried by a lamp. To avoid contamination during analysis and remove any residual carbon, the samples were Ar plasma-cleaned for 20 s (Plasma Prep 5, GaLa Instrumente).

Synthesis of molecular precursors

[Ti_2(mdea)$_2$(OEt)$_4$] (1)

N-methyldiethanolamine (6.6 mL, 58 mmol) was added drop-wise to a toluene solution (25 mL) of [Ti(OEt)$_4$] (13.18 g, 57.8 mmol) and the colourless solution obtained was stirred at room temperature for 3 h. Solvents were removed under vacuum to give a colourless viscous mass, which was crystallized from *n*-hexane + EtOH mixture at -20 °C as colourless solid. Yield, 11.9 g (78%). Anal. Calcd. for $C_{18}H_{42}N_2O_8Ti_2$: C 41.06, H 7.98, N 5.32. Found: C 42.40, H 8.10, N 5.40%. ν_{max} (Nujol)/cm^{-1}: 3300br, 2960s, 2961s, 2853s, 1452m, 1372w, 1351w, 1260w, 1255w, 1178w, 1145m, 1095s, 992m, 919m, 900m, 820m, 781m, 748m, 607m, 515s, 424s. δH (400 MHz; CDCl$_3$, ppm) 0.81 (t, 3H, C**H$_3$**CH$_2$OH), 1.23 (t, 12H, C**H$_3$**CH$_2$O), 2.29 (s, 6 H, N-**Me**), 2.61 (br, 8 H, N**CH$_2$**), 3.67 (br, 8H, O**CH$_2$**), 4.32 (br, 8H, CH$_3$C**H$_2$**O).

[Ti(O)(mdea)] (1a)

The partial hydrolysis of **1**, dissolved in 5 mL toluene, with a solution of water in ethanol (0.5 mL, 1 M, h = 0.2) led to crystallization of white, air-sensitive **1a** in 63% yield. The elemental analysis, FT-IR and ^{1}H NMR spectroscopic data as well as the unit sell parameters of this product matched well with the previously reported [Ti_6(O)$_6$(mdea)$_6$] obtained through the hydrolysis of the homoleptic derivative [Ti(mdea)$_2$].[25]

[Nb(mdea)(OEt)$_3$] (2)

Using a similar procedure as described for **1**, the derivative **2** was obtained as a viscous oil in quantitative yield from [Nb(OEt)$_5$] (3.06 g, 9.60 mmol) and *N*-methyldiethanolamine (1.10 mL, 10.0 mmol) in toluene at room temperature Anal. Calcd. for $C_{13}H_{31}NO_6Nb$: C 39.90, H 7.93, N 3.58. Found: C 40.81, H 8.22, N 3.67%. ν_{max} (Nujol)/cm^{-1}: 2964s, 2851s, 2704w, 1460s, 1417w, 1378s, 1350w, 1286w, 1253w, 1183w, 1091vs, 1063vs, 990m, 973w, 911s, 823s, 798m, 750m, 710m, 527s, 424m. δ H (400 MHz; $CDCl_3$, ppm) 1.13 (t, 9H, C**H**$_3$CH$_2$O), 2.23 (s, 3H, N-**Me**), 2.61 (br, 4 H, N**CH**$_2$), 3.58 (s, 4H, O**CH**$_2$), 4.26 (br, 6H, CH$_3$C**H**$_2$O).

[Nb(O)(mdea)(OEt)] (**2a**)

Partial hydrolysis of **2** in 5 mL toluene with a solution of water in ethanol (0.5 mL, 1 M) led to crystallization of **2a** as colourless blocks in 45% yield. The same product **2a** was obtained by reacting [Nb(OEt)$_5$] and mdeaH$_2$ directly in toluene + ethanol and hydrolysis (h = 0.3), albeit in lower yield (20%). Anal. Calcd. for $C_{24}H_{54}N_4O_{16}Nb_4$ (1026.3): C 28.06, H 5.26, N 5.45. Found: C 28.32, H 5.37, N 5.37%. ν_{max} (Nujol)/cm^{-1}: 3352br, 2930s, 2852s, 2722w, 2676w, 1459s, 1377s, 1291w, 1245w, 1088s, 992w, 914m, 847m, 753m, 694m, 654w, 563m, 517m. δ H (400 MHz; $CDCl_3$, ppm) 1.21 (t, 3H, C**H**$_3$CH$_2$O), 2.33 (s, 3 H, N-**Me**), 2.60 (br, 4 H, N**CH**$_2$), 2.97 (br, 4H, O**CH**$_2$), 3.70 (q, 2H, CH$_3$C**H**$_2$O).

[Pb(mdea)]. mdeaH$_2$ (3)

PbO (10 g, 45 mmol) and an excess of mdeaH$_2$ (11 mL, 92 mmol) were refluxed for 18 h in toluene (50 mL), running the condensate through a bed of molecular sieves before rejoining the reaction flask to remove water liberated from the reaction. After filtering the reaction medium, the solvent from the filtrate was removed and excess mdeaH$_2$ distilled off under reduced pressure. The resulting solid was recrystallized from boiling toluene affording colorless crystals of **3** on slow cooling. Yield, 17 g, 86%. The elemental analysis were not satisfactory, probably due to varying amount of solvated mdeaH$_2$ ligand in the lattice. ν_{max} (Nujol)/cm^{-1}: 3363br, 3169br, 1466vs, 1415m, 1380s, 1351s, 1294s, 1266s, 1242m, 1202m, 1180w, 1168w, 1138w, 1078s, 1043s, 992s, 987s, 890s, 878s, 802m, 768m, 753s, 724m, 593m, 575m, 541m, 462m, 425m. δ H (400 MHz, CD_3OD, ppm): 2.35 (s, CH_3 6H); 2.69 (NCH_2 8H, br); 4.31 (OCH_2 8H, br).

Complete hydrolysis of 1 to obtain undoped TiO_2 NPs

An aqueous solution of acetic acid (1.4 mmol in 2 mL of H_2O) was added to **1** (10.5 g, 20 mmol) dissolved in toluene (50 mL) and the reaction mixture was refluxed under stirring for 3 h. The solvent was recovered by distillation with a rotary evaporator and the obtained sol was dried under vacuum at 100 °C for 3 h. Calcination of the samples were carried out in static air by heating the samples to 500 °C at a rate of 1 °C/min and maintaining the final temperature for 4 h.

Using the above method, Nb or Pb-doped TiO_2 were also obtained by combining the precursor **1** either with **2** (to get Nb/TiO_2) or **3** (to get Pb/TiO_2) taken in toluene in appropriate molar ratio, followed by addition of aqueous solution of acetic acid, reflux the solution for 3 h, removal of the solvents and calcination of the resulting powders at 500 °C/4 h:

Nb/TiO_2: **1** (4 mmol), **2** (0.4 mmol) and aqueous solution of acetic acid (0.04 mmol in 1.1 mL of H_2O).

Pb/TiO_2: **1** (15 mmol), **3** (1.5 mmol) and aqueous solution of acetic acid (0.04 mL in 1.05 mL of H_2O).

X-ray crystallography: Crystals of **1, 2a** and **3** were obtained as described in the synthetic procedure. Crystal structures were determined using Mo radiation ($\lambda = 0.71073$ Å) on an Oxford Diffraction Gemini diffractometer equipped with an Atlas CCD detector. Intensities were collected at 150 K by means of CrysAlisPro software.[1] Reflection indexing, unit-cell parameter refinement, Lorentz-polarization correction, peak integration and background determination were carried out with CrysAlisPro software.[1] An analytical absorption correction was applied using the modeled faces of the crystal.[2] The resulting sets of *hkl* were used for structure solutions and refinements. The structures were solved with the ShelXT[3] structure solution program using intrinsic phasing and by using Olex2 as the graphical interface.[4] The model was refined with version 2018/3 of ShelXL using least squares minimization.[5] Some selected crystallographic and refinement data for **1, 2a** and **3** are given in the Table S1.

Table S1. Crystallographic and refinement data for **1, 2a** and **3**.

Compound	**1**	**2a**	**3**
Chemical formula	$C_{18}H_{42}N_2O_8Ti_2\cdot 0.5\ C_2H_6O$	$C_{12}H_{27}N_2Nb_2O_8$	$C_{10}H_{20}N_2O_4Pb_2$
Formula weight	1066.6	513.2	646.7
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$I2$	$I2/a$
a (Å)	9.7305 (3)	12.8106(13)	16.674(3)
b (Å)	10.3706 (4)	10.2674(13)	10.4513(13)
c (Å)	13.6626 (5)	18.4561(18)	22.478(3)
α (°)	78.159 (3)	90	90
β (°)	80.220 (3)	106.473(10)	108.767(15)
γ (°)	79.813 (3)	90	90
V (Å³)	1315.27 (8)	2327.9(5)	3709.0(9)
Z	1	4	8
μ (mm^{-1})	0.65	1.016	18.139
Temperature (K)	150	150	150
Measured reflections	27521	16317	16609
Independent reflections (R_{int})	6645 (0.034)	5581 (0.043)	4637 (0.063)
Restrains/Parameters	10/293	396/222	0/166
Goodness of fit	1.03	1.086	1.126
$R[F^2>2\sigma(F^2)]$	0.059	0.0979	0.0628
$wR(F^2)$	0.164	0.2488	0.1403
Residual electron density (e.Å^{-3})	−0.69 to 1.96	-1.752 to 3.208	-2.662 to 2.633
CCDC no.	1558717	2034796	2013426

Table S2. Lattice parameters of TiO_2, Nb/TiO_2 and Pb/TiO_2 calculated after Rietveld refinement of their powder XRD.

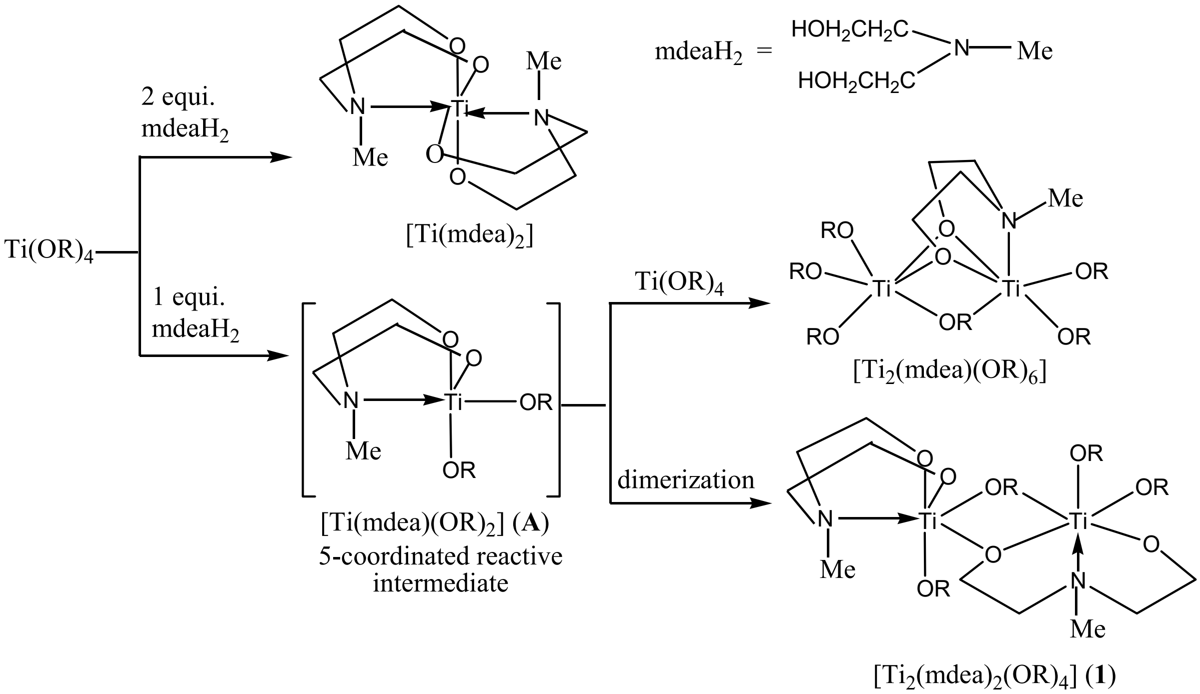
Compound	TiO_2	Nb/TiO_2	Pb/TiO_2
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space group	*I41/amd*	*I41/amd*	*I41/amd*
a (Å)	3.78779(9)	3.7952(7)	3.7856(4)
b (Å)	3.78779(9)	3.7952(7)	3.7856(4)
c (Å)	9.5163(2)	9.4300	9.4300
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V (Å³)	136.534(6)	135.83(3)	135.143(18)
Strain	0.30	1.75	0.64

Catalytic test

The conversion of dihydroxyacetone to lactic acid was carried out in aqueous medium, in a batch reactor coupled to a reflux condenser. The reaction was done using 20 mL of an aqueous solution of 0.1 mol/L of DHA, with a DHA/Catalyst weight ratio of 1, under air and temperature of 90 °C. When the system reached the temperature of 90 °C, the solid DHA was added to the solution under ambient pressure. Samples in the beginning and in some fractions of time were taken to be evaluated, after followed centrifugation, in a HPLC Shimadzu Prominence system, in order to quantify the amount of substrate and products in liquid phase.

References

1. CrysAlisPro Software System, Rigaku Oxford Diffraction, 2018.
2. R. C. Clark and J. S. Reid, The analytical calculation of absorption in multifaceted crystals. *Acta Crystallogr. Sect. A: Found. Crystallogr.* 1995, **51**, 887–897.
3. G. M. Sheldrick, ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.* 2015, **A71**, 3-8.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.* 2009, **42**, 339-341.
5. G. M. Sheldrick, Crystal structure refinement with ShelXL. *Acta Cryst.* 2015, **C27**, 3-8.



Scheme S1. Different course of reactions of Ti(OR)4 with the *N*-methyldiethanolamine ligand.

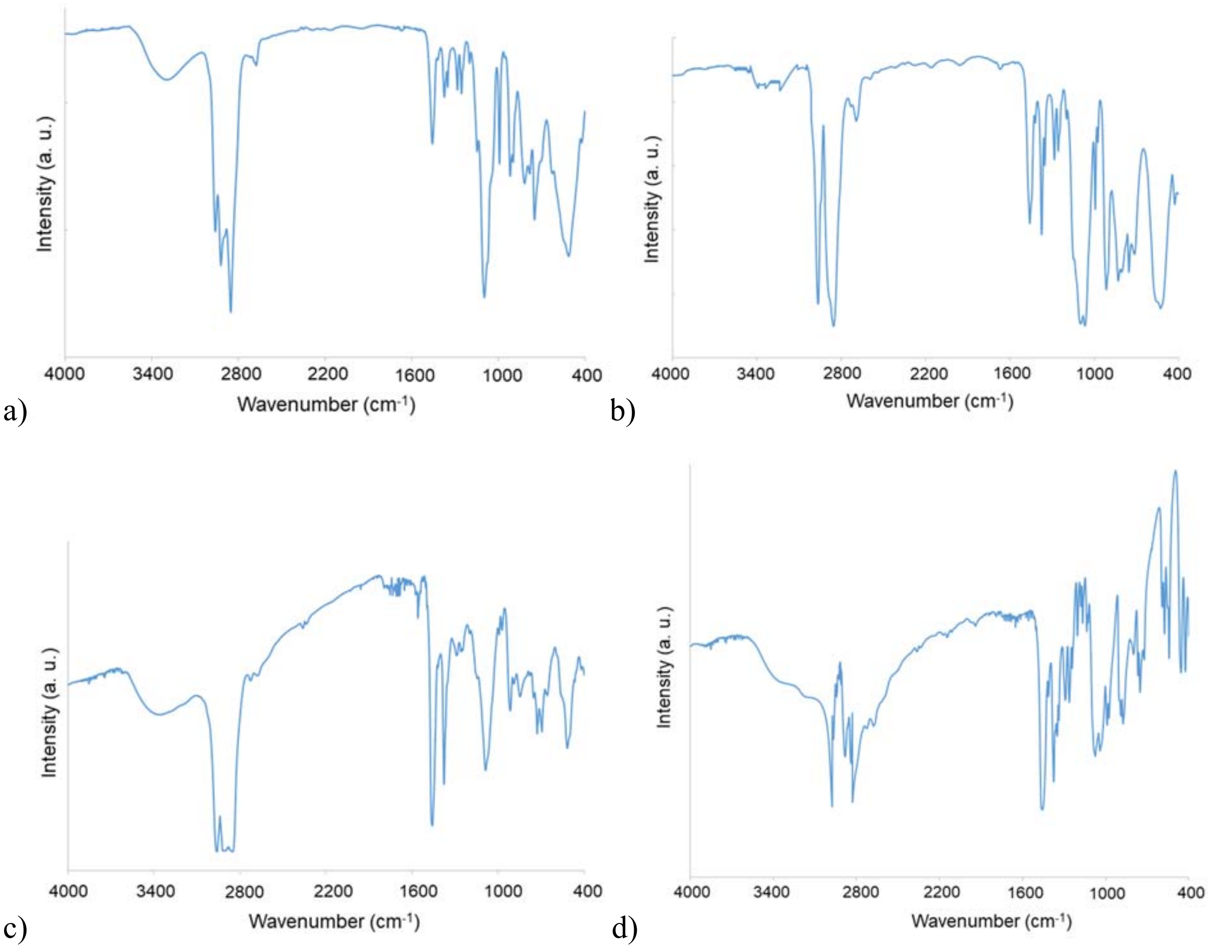


Figure S1. FT-IR spectra of **1** (a), **2** (b), **2a** (c) and **3** (d).

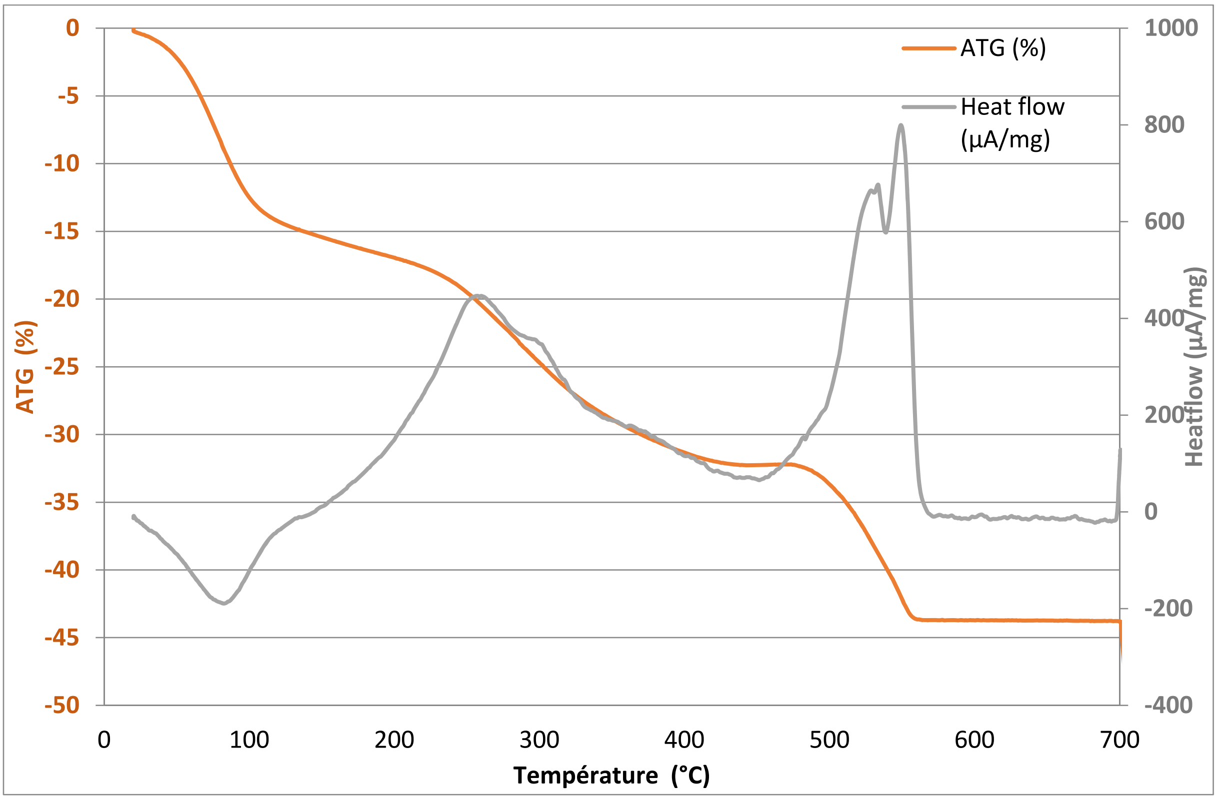


Figure S2. TG-DTA curves of the NPs obtained after the hydrolysis of **1**.

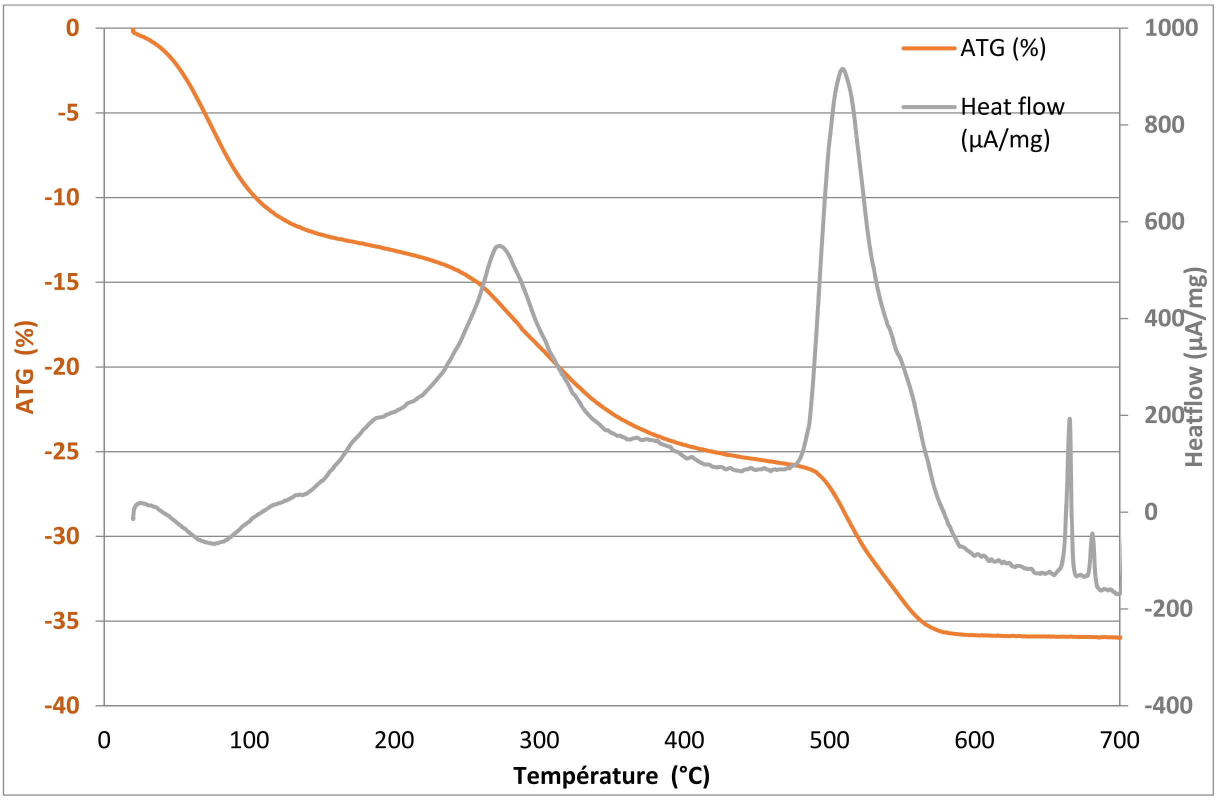


Figure S3. TG-DTA curves of the NPs obtained after the hydrolysis of a mixture of **1** + 10% **2**.

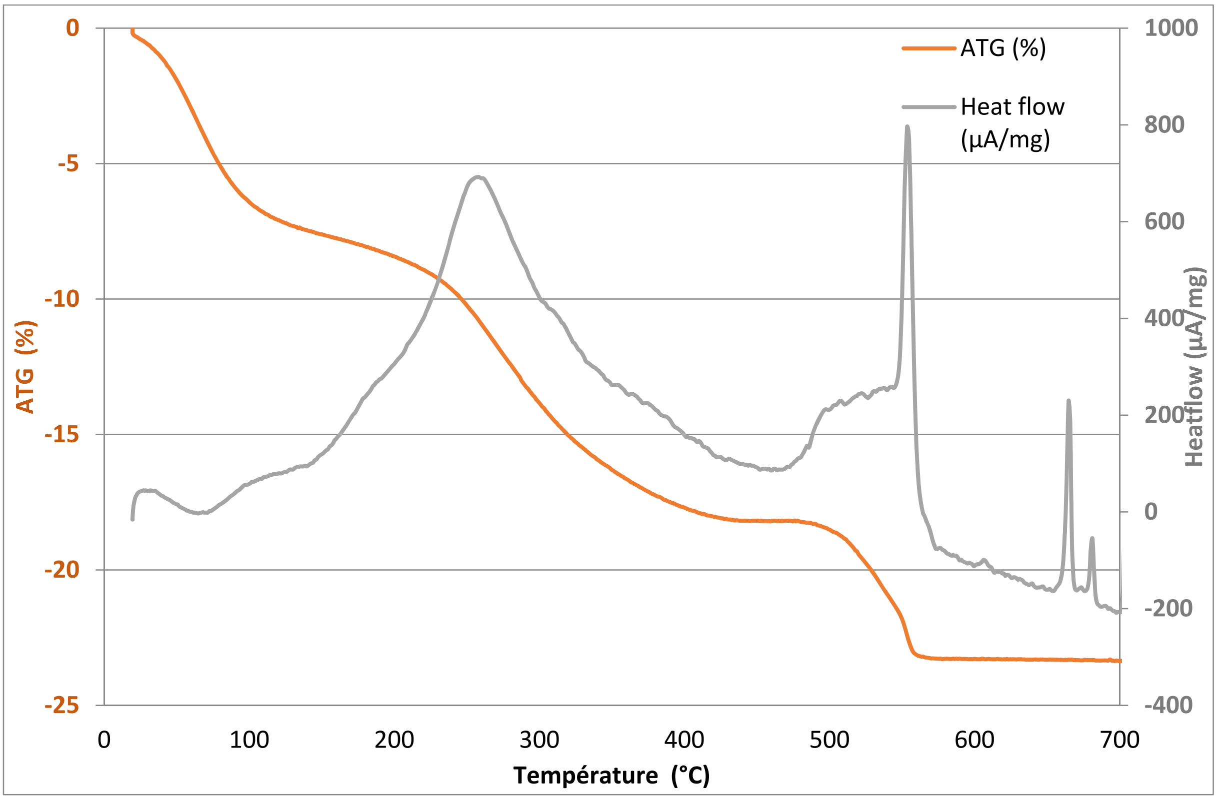


Figure S4. TG-DTA curves of the NPs obtained after the hydrolysis of a mixture of **1** + 10% **3**.

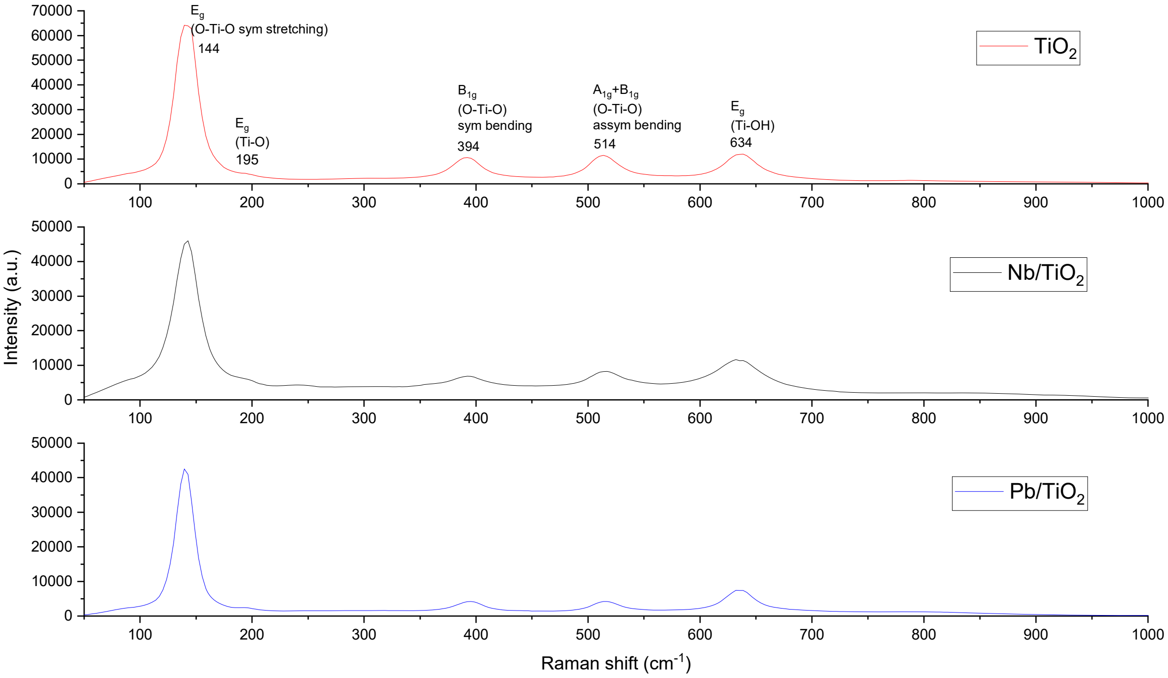


Figure S5. Raman spectra of TiO_2, Nb/TiO_2 and Pb/TiO_2.

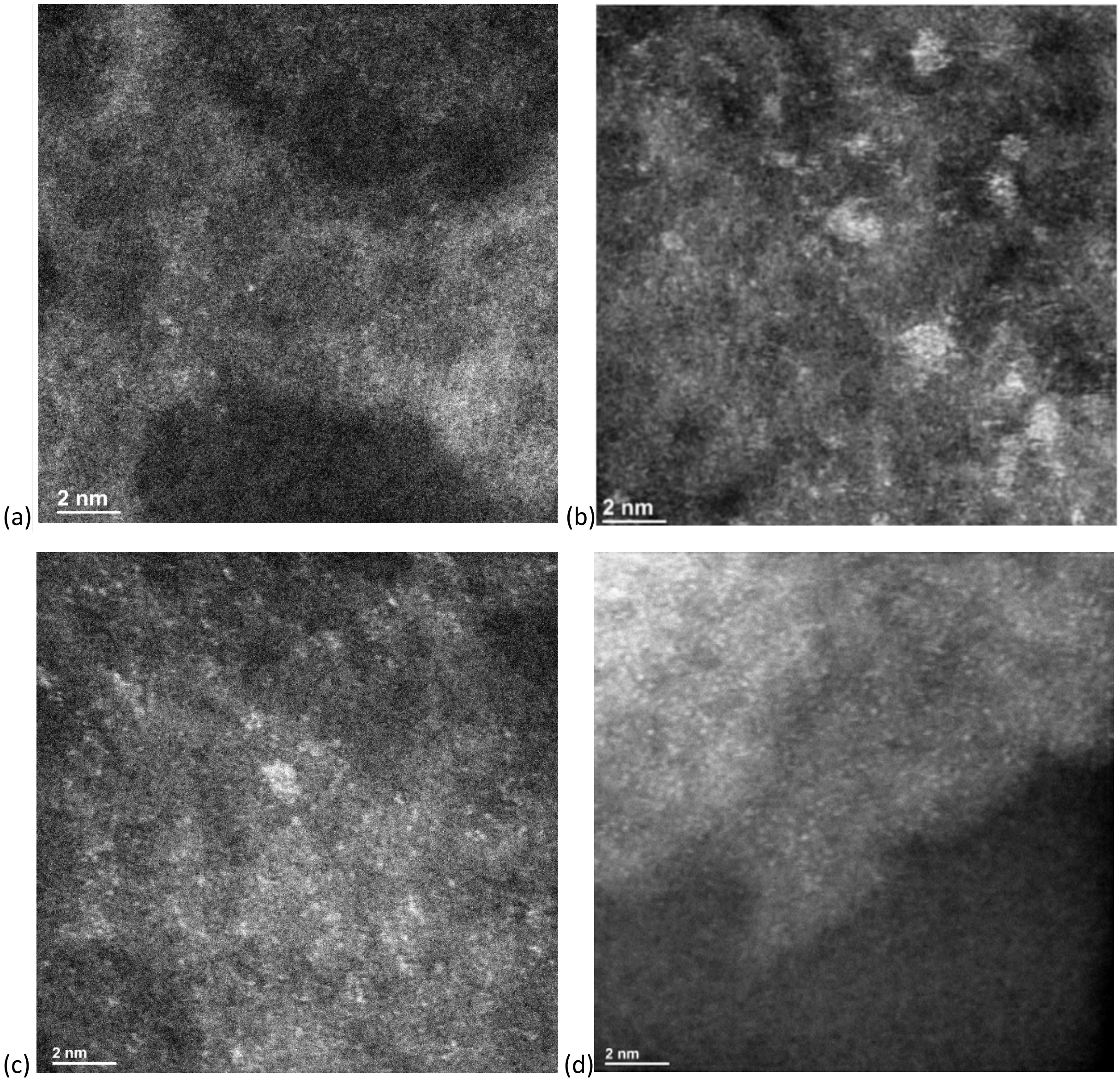


Figure S6. STEM-ADF images of Nb/TiO_2 (a,b) and Pb/TiO_2 (c,d).

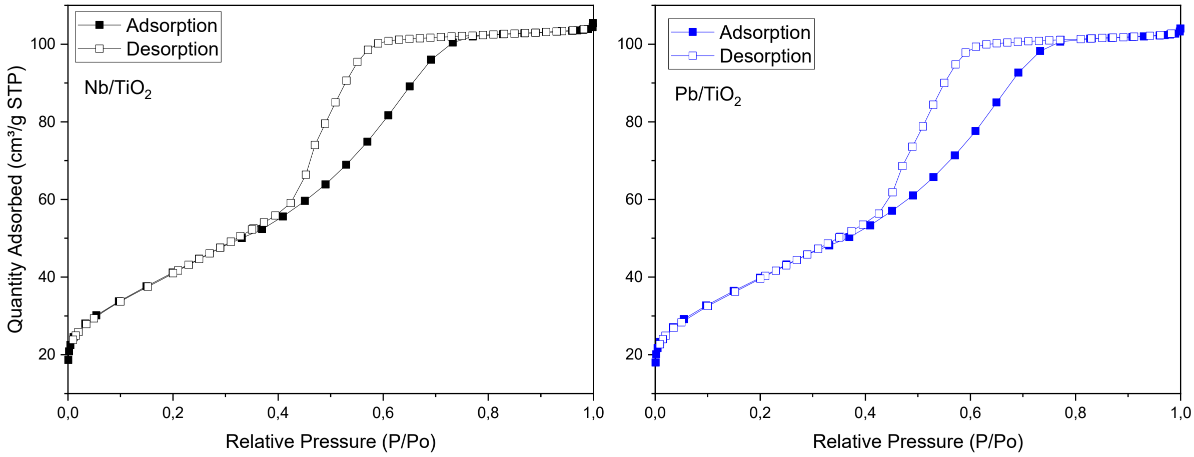


Figure S7. N_2 adsorption-desorption isotherms of Nb/TiO$_2$ and Pb/TiO$_2$.

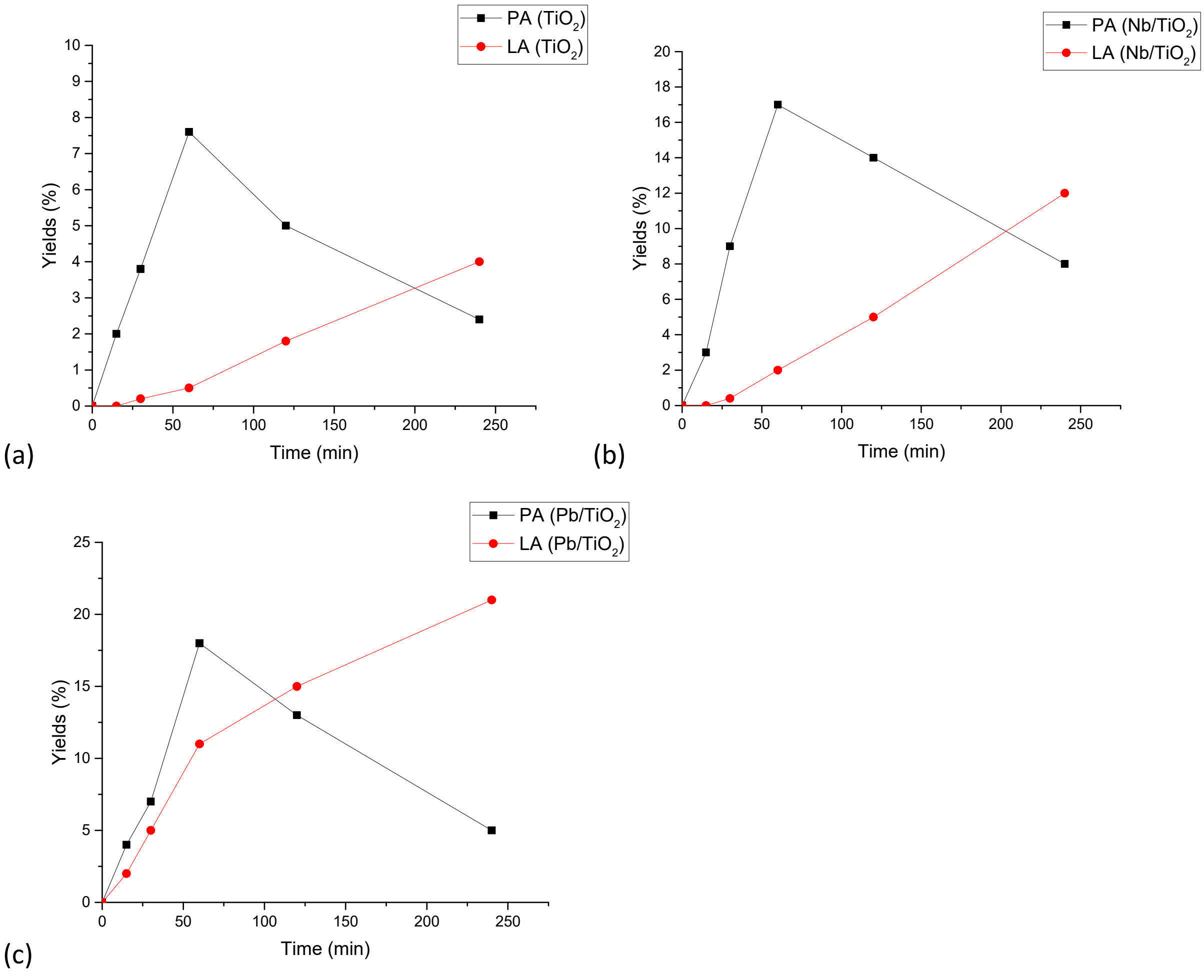


Figure S8. TiO$_2$ (a), Nb/TiO$_2$ (b) and Pb/TiO$_2$ (c) catalyzed DHA conversion as a function of time. Conditions: 20 mL of aqueous solution of DHA (0.1 mol/L), DHA/Catalyst wt ratio of 1, T = 90 °C.