

Molecular TiO₂ Modifications of Supported PPh₃-Capped Pd Nanocatalysts for CO₂ Hydrogenation into Formates

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1. Materials and Methods

Pd(dba)₂, PPh₃, TiO₂ (Titanium (IV) oxide nanopowder, 21 nm primary particle size (TEM), ≥ 99.5% trace metals basis, rutile-anatase mixture, specific surface area 35-65 m²/g) and the rest of compounds employed for modification were purchased from Sigma-Aldrich and used without any further purification. All solvents were dried

from a solvent purification system (SPS) and deoxygenated. Tetrahydrofuran was further dried by refluxing in the presence of sodium/acetophenone. Milli-Q water was employed in catalytic experiments. Any other solvent or reagent employed was reagent grade. Hydrogen (5.0) was purchased from Carbueros Metálicos and CO₂ (5.3) was purchased from Abelló Linde. All the synthesis were performed using Schlenk techniques under Argon and glovebox using nitrogen as inert gas. The synthesis of nanoparticles were carried in Fischer-Porter bottles and catalytic tests were performed in a stainless steel high-pressure reactor Hel CAT-7 (7 x 10 ml).

2. Characterization techniques

Transmission Electron Microscopy (TEM)

Measurements were performed at the “Unitat de Microscopia dels Serveis de Recursos Científics I Tècnics de la Universitat Rovira i Virgili” in Tarragona with JEOL 1011 electron microscope operated at 100 kV with resolution of 3 Å. The samples were prepared by deposition of several drops of the reaction crude onto a copper grid. The particles size distributions were determined by a manual analysis. At least 300 particles on a given grid were measured to obtain a statistical size distribution and mean diameter.

Environmental Scanning Electron Microscope (ESEM)

The equipment used was FEI ESEM Quanta 600 from “Unitat de Microscopia dels Serveis de Recursos Científics I Tècnics de la Universitat Rovira i Virgili” in Tarragona. This microscope has an integrated analysis system OXFORD INSTRUMENTS. Energy-dispersive X-ray spectroscopy (EDX) analysis was carried out using this technique (BSED detector and HV (20 kV)).

Field Emission Scanning Electron Microscope (FESEM)

The microscope used for FESEM analysis was Thermo Scientific Scios2. from “Unitat de Microscopia dels Serveis de Recursos Científics I Tècnics de la Universitat Rovira i Virgili” in Tarragona.

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

The inductively coupled plasma-optical emission spectrometer ICP-OES ARCOS FHS16 employed is in “Servei de Recursos Científics I Tècnics de la Universitat Rovira i Virgili” in Tarragona. The digestion of samples were made employing aqua regia in Milestone Ethos Easy Advanced microwave digestion system. Quantification of metals is performed by comparison with the respective calibration curve constructed in the range of 0-20 ppm.

Nuclear Magnetic Resonance (NMR)

The equipment used were Bruker Avance Neo 400 with probe Smart (PI HR-400-S1-BBF/H/D-5.0-Z SP N) and sample case of 24 positions VARIAN Varian NMRSYS 400 (reverse probe 5mm Auto-X 1H/31P-15N, probe 5mm autoswitchable PFG and 5mm probe One Probe). Measurements were performed in “Servei de Recursos Científics I Tècnics de la Universitat Rovira i Virgili” in Tarragona. Dry and deoxygenated 1,4-dioxane was used as internal standard for catalytic experiments.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis experiments were carried out with a Mettler Toledo TGA2 thermo-balance equipped with a gas flow system. For a typical TGA experiment, a small amount of sample (5-30 mg) was placed in an alumina crucible and heated at a rate of 10 °C/min in N₂ atmosphere (50 ml/min) within a temperature range of 30-900 °C.

Fourier Transform Infrared Spectroscopy (FT-IR)

The equipment used were FT/IR – 6700 Jasco. The FT-IR bands were examined in the range of 400–6000 cm⁻¹.

High Resolution Transmission Electron Microscopy (HR-TEM)

The morphology, crystallographic information and chemical analysis of the Pd nanoparticles were studied by Transmission electron microscopy in “Unitat de Microscopia dels Serveis de Recursos Científics I Tècnics de la Universitat Rovira i Virgili” in Tarragona.

TEM specimens were prepared by placing a drop of a Tetrahydrofuran (THF) solution containing the NPs onto a holey carbon coated copper micro-grid.

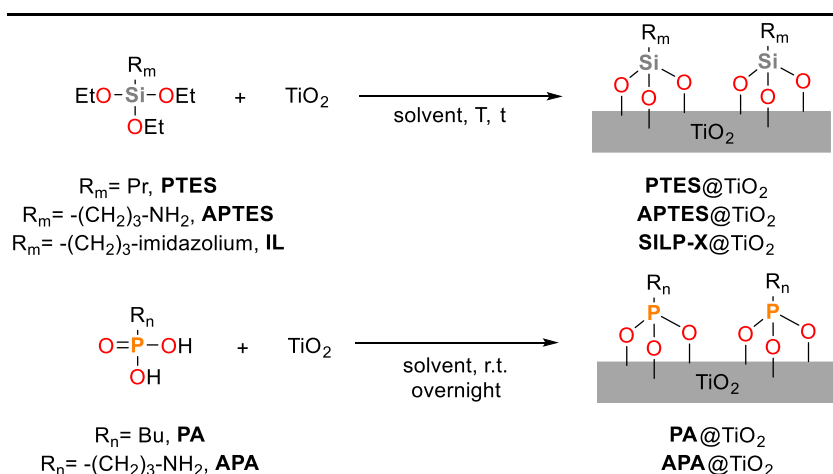
A JEOL F200 TEM ColdFEG operated at 200 kV was used for the Transmission Electron Microscopy characterization. TEM images were acquired with a Gatan OneView camera, a CMOS-based and optical fibre-coupled detector of 4096 by 4096 pixels. Gatan Digital Micrograph program was used to process the TEM images. STEM images (1024 x 1024 pixels) were recorded from the JEOL bright-field (BF) and High-Angle Annular Dark-Field (HAADF) detectors with a camera length of 400 mm. Samples were inserted in a JEOL beryllium double-tilt holder for energy dispersive X-Ray Spectroscopy (EDS). STEM-EDS mapping was recorded from an EDS Centurio detector (silicon drift) with an effective area of 100 mm² and 133 eV of energy resolution. STEM-EDS maps (512 x 512 pixels) were processed with the JEOL Analysis software.

X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were performed at room temperature with a SPECS PHOIBOS 150 hemispherical analyzer (SPECS GmbH, Berlin, Germany)) in a base pressure of 5×10^{-10} mbar using monochromatic Al K alpha radiation (1486.74 eV) as excitation source operated at 300 W. The energy resolution as measured by the FWHM of the Ag3d_{5/2} peak for a sputtered silver foil was 0.62 eV. The spectra were calibrated with respect to the C1s at 285.0 eV. Measurements were carried out in the Fundació Institut Català de Nanociència i Nanotecnologia (ICN2). The XPS data were curve-resolved using the CASAXPS software after Shirley background subtraction. The spectra were fitted with the minimum number of peaks needed to reproduce the spectral features. Analyses were carried out with CasaXPS software and calibrating with C1s at 285 eV in the overview spectra.

3. Synthesis and characterization of catalytic materials

Table S1. Optimization of synthesis conditions for TiO₂ modified with organosilanes, RSi(OEt)₃¹ and organosulphonic acids, RPO(OH)₂.²



Entry	[C], M	mmol/mg TiO ₂	T (°C)	Code
1	0.13	0.013	r.t.	TiO₂-1
2	0.01	0.003	r.t.	TiO₂-2
3	0.13	0.013	r.t.	TiO₂-3
4 ³	0.022	0.0009	80	TiO₂-4
5 ⁴	0.013	0.0013	80	TiO₂-5
6 ⁵	0.13	0.013	80	TiO₂-6
7	0.01	0.003	r.t.	TiO₂-7
8 ⁶	0.01	0.003	r.t.	TiO₂-8

¹Synthesis conditions: TiO₂ was added to a previously prepared solution of (A)PTES on mixture EtOH:milli-Q H₂O (95:5 v/v) and reacted at r.t. overnight. ²Synthesis conditions: TiO₂ was added to a solution of 10 mM of butylphosphonic acid (PA) in THF and the mixture was stirred at r.t. overnight. ³Suspension of 2 g of TiO₂ in 80 ml of milli-Q H₂O was added to a previously prepared solution of IL-Cl in 2 ml of milli-Q H₂O. The mixture was stirred at 80 °C during 12 h. ⁴TiO₂ was added to a solution of IL-OAc in EtOH:milli-Q H₂O mixture (95:5 v/v) and was heated at 80 °C overnight. ⁵Synthesis conditions: TiO₂ was added to a solution of 10 mM of butylphosphonic acid (PA) in THF and the mixture was stirred at r.t. overnight. ⁶Synthesis in milli-Q H₂O.

3.1. Modification of TiO₂ with *n*-propyltriethoxysilane (PTES) and (3-aminopropyl)triethoxysilane (APTES)

In a general synthesis of TiO₂-1-3, a solution (mixture EtOH:milli-Q H₂O 95:5 v/v), of the accorded concentration of PTES or APTES were prepared into a Schlenk (under Ar). Then, the corresponding amount of TiO₂ (mmol (A)PTES/mg TiO₂) was added to the solution under vigorous stirring (Table S1). Reaction was stirred at room temperature overnight. Then, the mixture was centrifuged. Supernatant was removed and the solid was washed several times with milli-Q H₂O and EtOH and was dried at 80 °C under vacuum for several hours.

Fourier Transform Infrared Spectroscopy (FT-IR)

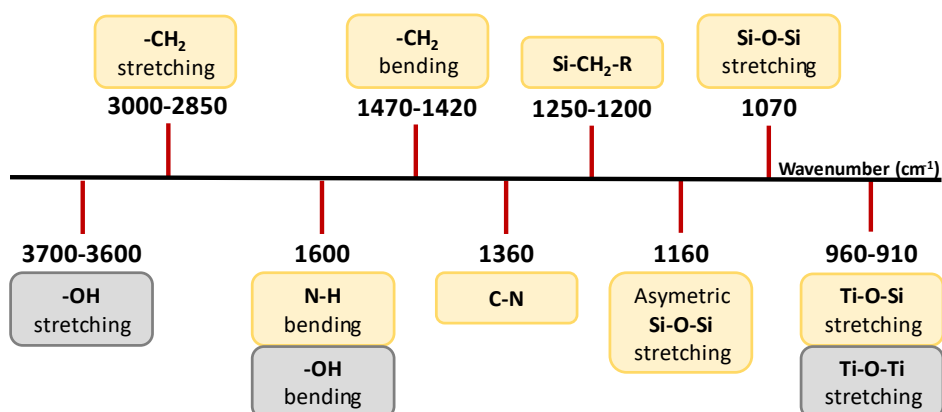
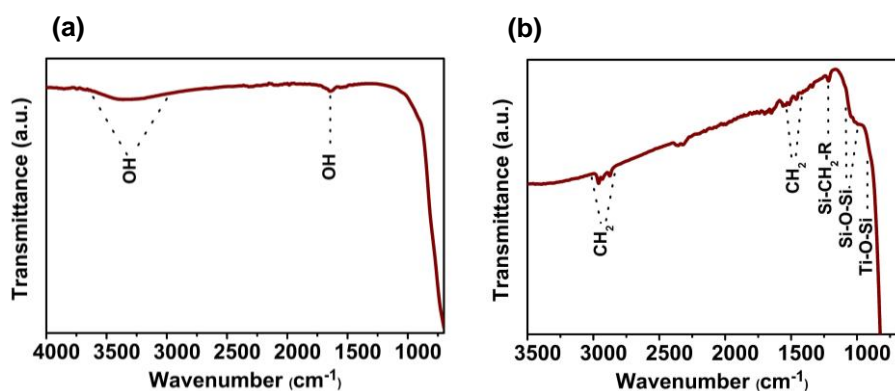


Figure S1. Organosilane modifiers used in this study.



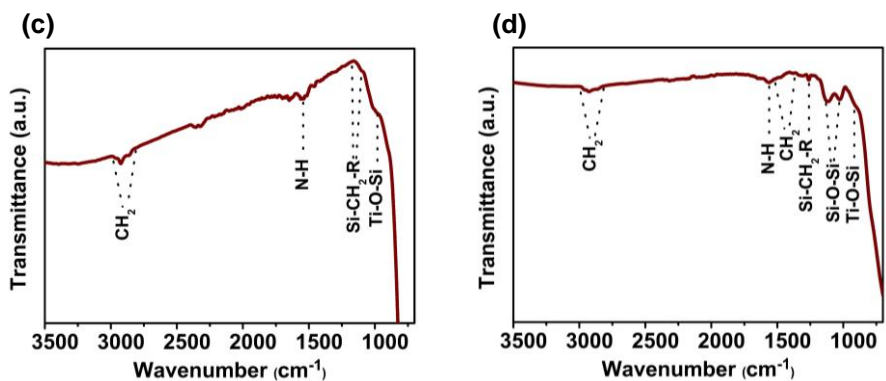


Figure S2. FT-IR of TiO₂ (a), TiO₂-1 (b), TiO₂-2 (c) and TiO₂-3 (d).

Thermogravimetric Analysis (TGA)

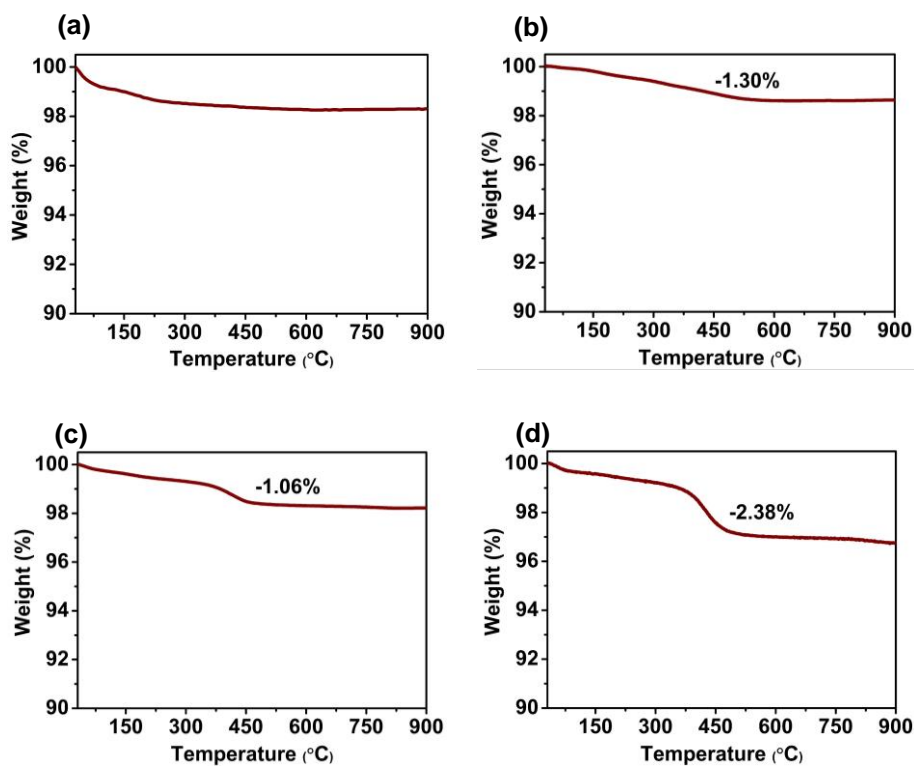
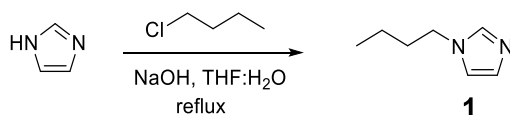


Figure S3. TGA of TiO₂ (a), TiO₂-1 (b), TiO₂-2 (c) and TiO₂-3 (d).

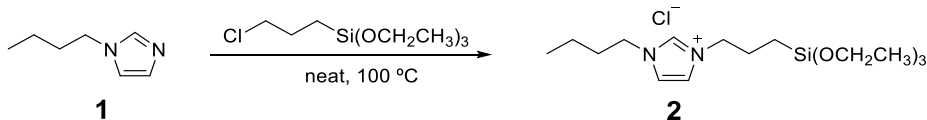
3.2. Synthesis of Ionic Liquids (ILs)

1. Synthesis of 1-*n*-butylimidazole



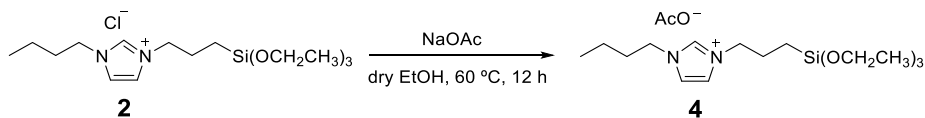
1: 1-*n*-butylimidazole was synthesized according to literature procedures [1] with some variations. In a round-bottom flask, imidazole (6.81 g, 0.1 mol) and NaOH (4 g, 0.1 mol) were added to a round-bottom flask with H₂O (4 ml) and stirred until the complete dissolution of imidazole. Then, 1-chlorobutane (11 ml, 0.105 mol) was diluted with THF (12.1 ml) and was added to the reaction flask. Reaction was left under reflux for 12 h. After this time, the crude was cooled to r.t. and was rotaevaporated to remove THF. Water was added (20 ml) and the product was extracted with DCM (3 x 40 ml). Organic phases were combined and washed with 10% NaOH solution (2 x 8 ml) and H₂O (3 x 8 ml) and dried over sodium sulfate. Filtration and evaporation of the volatiles provided the desired product as a yellow oil (9.04 g, 73%). NMR is in agreement with reported spectra [2]. ¹H-NMR (400 MHz, DMSO-*d*₆): δ 7.60 (s, 1 H), 7.15 (s, 1 H), 6.87 (s, 1 H), 3.94 (t, *J* = 7 Hz, 2 H), 1.71–1.62 (m, 2 H), 1.26–1.16 (m, 2 H), 0.87 (t, *J* = 7.4 Hz, 3 H).

2. Synthesis of 1-Butyl-3-[3-(triethoxysilyl)propyl]imidazolium Chloride



The product **2** was synthesized according to literature procedures [3] with some variations. In a 100 ml Schlenk, the product **1** (5.1 ml, 38.8 mmol) and (3-chloropropyl)triethoxysilane (9.35 ml, 38.8 mmol) were introduced. Then, the mixture was heated at 100 °C for 48 h and cooled to room temperature. The product was washed several times with Et₂O and dried under vacuum at 60 °C to obtain a yellow/orange oil (13.01 g, 92%). NMR is in agreement with reported spectra [4]. ¹H-NMR (400 MHz, DMSO-*d*₆): δ 9.44 (s, 1 H), 7.85 (s, 2 H), 4.23–4.13 (m, *J* = 7.0 Hz, 4 H), 3.73 (q, *J* = 7.0 Hz, 6 H), 1.87–1.73 (m, 4 H), 1.23 (m, 2 H), 1.13 (t, *J* = 6.9 Hz, 9 H), 0.88 (t, *J* = 7.44 Hz, 3 H), 0.51–0.46 (m, 2 H).

3. Synthesis of 1-Butyl-3-[3-(triethoxysilyl)propyl]imidazolium Acetate



The product **3** was synthesized according to literature procedures but including some variations [5,6]. In a 25 ml Schlenk, the product **2** (3 g, 8.2 mmol and NaOAc (783.8 mg, 9.55 mmol) were introduced. Dry EtOH was added (11 ml) and the mixture stirred at 60 °C for 12 h. At this point, the mixture was cooled to r.t. and the product was washed several times with EtOH and dried under vacuum at 60 °C to give an orange oil as product (2.95 g, 93% yield). $^1\text{H-NMR}$ (500 MHz, DMSO-d_6): δ 9.51 (s, 1 H), 7.82 (d, 2 H), 4.22-4.11 (m, 4 H), 3.74 (q, $J = 6.98$ Hz, 6 H), 1.87-1.73 (m, 4 H), 1.53 (s, 3 H), 1.28-1.20 (m, 2 H), 1.14 (t, $J = 7.08$ Hz, 9 H), 0.89 (t, $J = 7.32$ Hz, 3 H), 0.51-0.45 (m, 2 H).

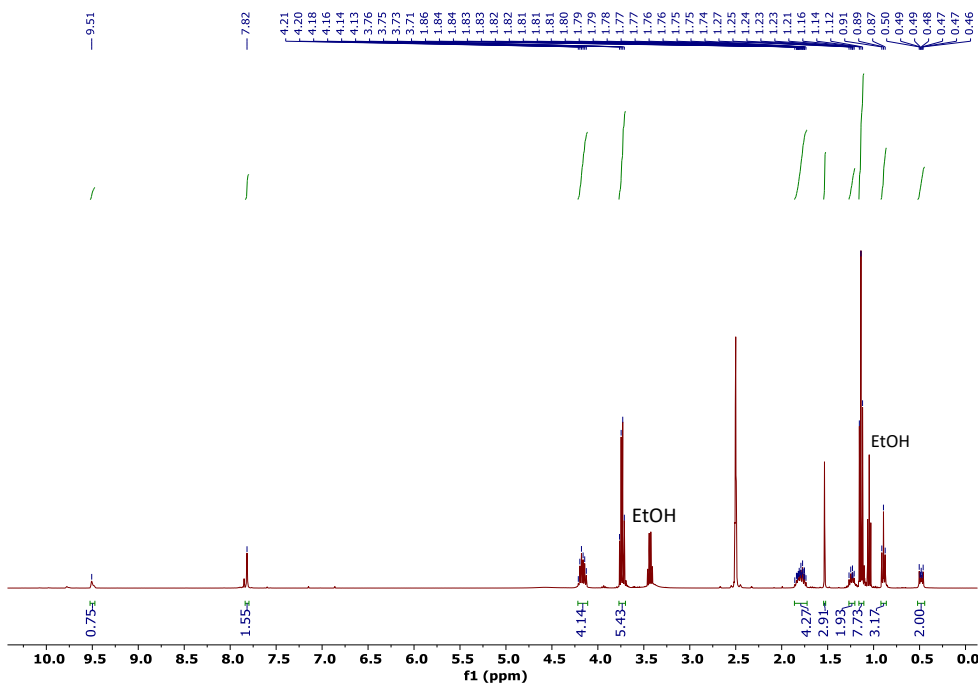


Figure S4. $^1\text{H-NMR}$ of compound **3** in DMSO-d_6 .

3.3. Modification of TiO₂ with Ionic Liquids (ILs)

The synthesis of **TiO₂-4** was performed according to reported procedures [3]. A suspension of 2 g of TiO₂ in 80 ml of milli-Q H₂O was added to a previously prepared solution of 659.08 mg (1.8 mmol) of IL-Cl in 2 ml of milli-Q H₂O. Mixture was stirred at 80 °C for 12 h (Table S1). After reaction, the mixture was centrifuged and washed twice with milli-Q and once with EtOH. After that, it was dried under vacuum at 60 °C.

For other ILs with AcO⁻ (**TiO₂-5** and **TiO₂-6**) as anion, TiO₂ was added to a solution of IL-OAc (mixture EtOH:milli-Q H₂O 95:5 v/v) and the mixture was heated at 80 °C overnight (Table S1). The product was washed with EtOH several times and dried under vacuum at 60 °C.

Fourier Transform Infrared Spectroscopy (FT-IR)

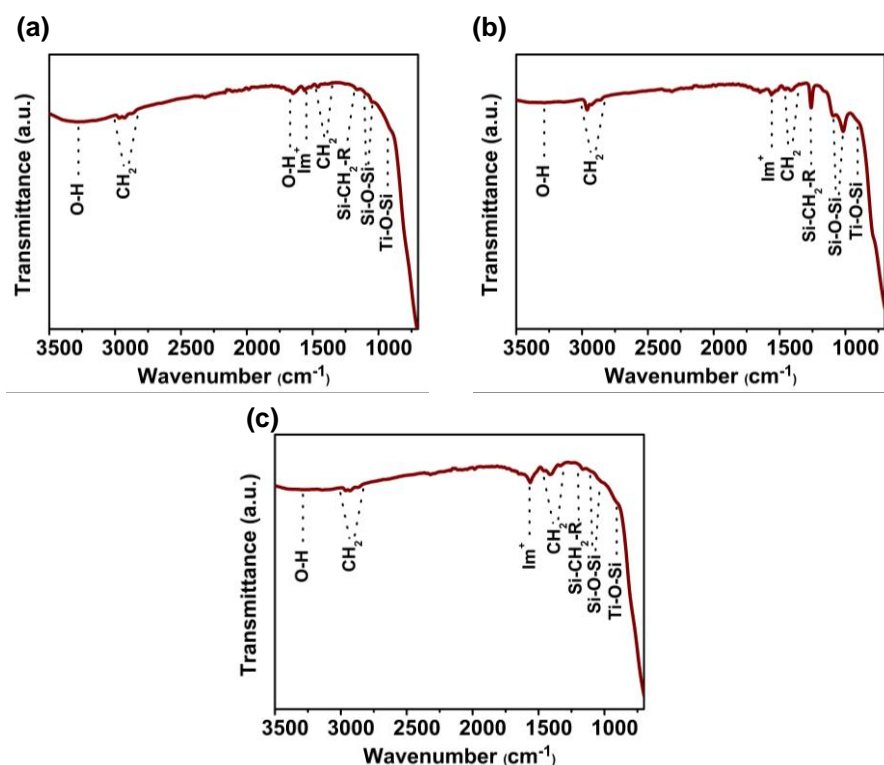


Figure S5. FT-IR of TiO₂-4 (a), TiO₂-5 (b) and TiO₂-6 (c).

Thermogravimetric Analysis (TGA)

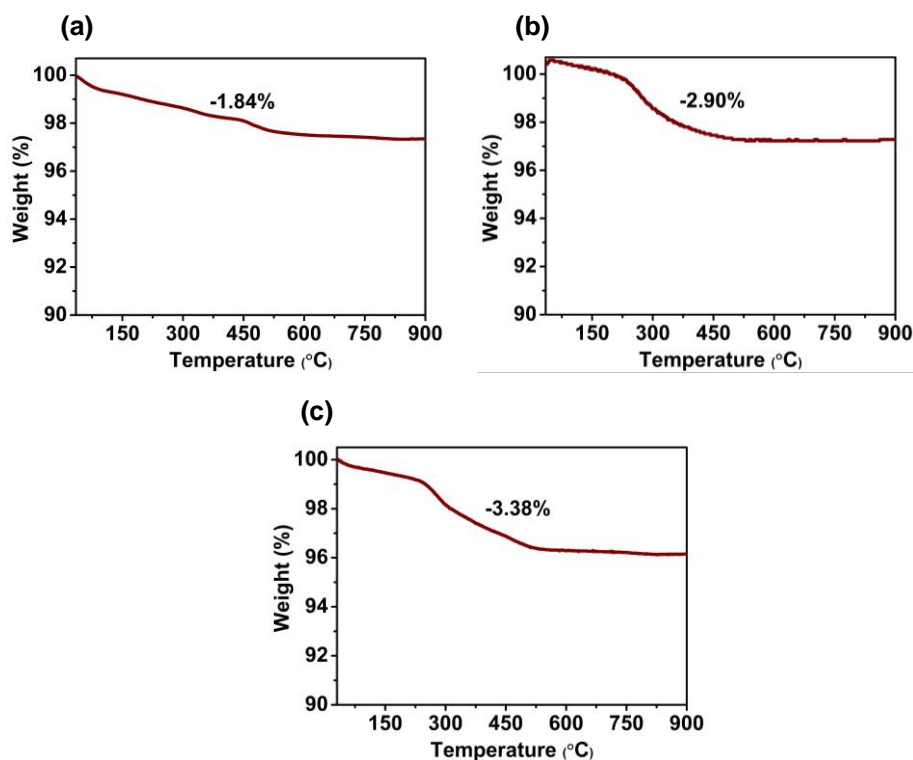


Figure S6. TGA of TiO₂-4 (a), TiO₂-5 (b) and TiO₂-6 (c).

3.4. Modification of TiO₂ with Phosphonic acids (PAs)

The modification of TiO₂ with PAs (TiO₂-7 and TiO₂-8) was performed according to literature procedures with some variations [7,8,9]. Solutions contained 83.35 μ mol of modifier per each square meter of TiO₂ nanopowder which corresponded approximately to a 10-fold excess in respect to build a monolayer in the surface of support (Table S1).

Solution 10 mM of 3-aminopropylphosphonic acid (APA) (TiO₂-8), (1.46 mmol, 202.84 mg) in 146 ml of milli-Q H₂O was prepared. Then, 0.5 g of TiO₂ was added and the mixture was stirred at r.t. overnight. After this time, the suspension was centrifuged, washed with abundant milli-Q water, EtOH and acetone. The solid was dried at 120 °C in an oven. It is necessary to produce condensation reactions to give

strong bonds between PAs and metal oxide [10]. So, in this case, after the reaction, the solid was separated by centrifugation, the solvent was removed and solid was placed into an oven at 100 °C overnight. After that, the solid was aged into a Quartz furnace at 120 °C under air flow during 6 h. Then, it was washed with abundant milli-Q water and centrifuged every time (5 times). The solid was dried overnight at 100 °C. When butylphosphonic acid was employed (PA) (**TiO₂-7**), the synthesis was performed under the same conditions (Table S1). The only difference was that THF was used as reaction media and for washing and centrifugation.

Fourier Transform Infrared Spectroscopy (FT-IR)

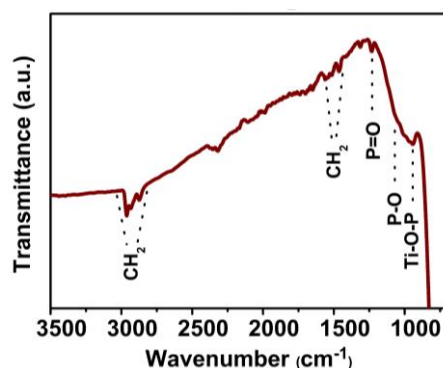


Figure S7. FT-IR spectrum of **TiO₂-7**.

Thermogravimetric Analysis (TGA)

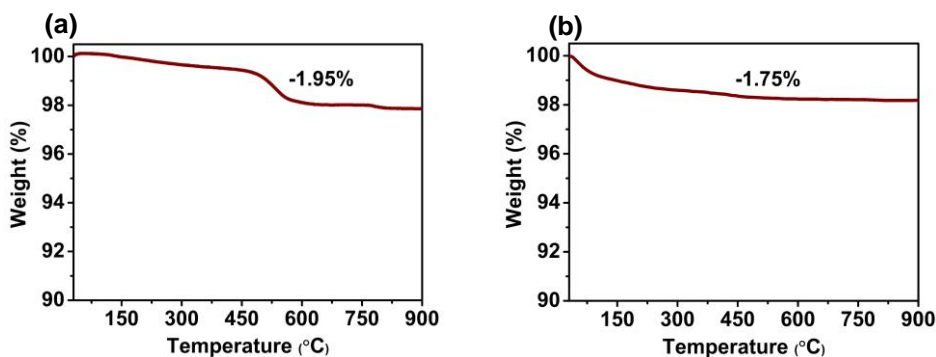


Figure S8. TGA of **TiO₂-7** (a) and **TiO₂-8** (b).

Summary of the Thermogravimetric Analysis (TGA) results obtained for the modification of TiO₂ with every type of modifier molecule

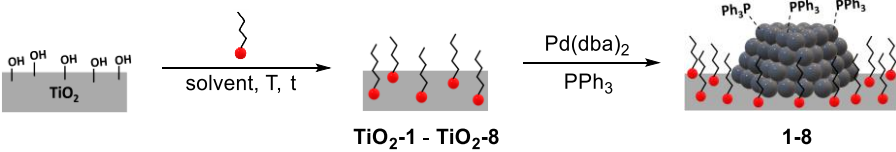
Table S2. Weight losses measured by TGA in TiO₂ modified with organosilanes, RSi(OEt)₃ and with organophosphonic acids, RPO(OH)₂.

Entry	System	Weight loss (%)
1	TiO ₂ -1	1.30
2	TiO ₂ -2	1.06
3	TiO ₂ -3	2.38
4	TiO ₂ -4	1.84
5	TiO ₂ -5	2.90
6	TiO ₂ -6	3.38
7	TiO ₂ -7	1.95
8	TiO ₂ -8	1.75

3.5. Synthesis of Pd NPs with PPh₃ as ligand over different modified TiO₂ supports through organometallic approach (1-8)

The catalysts were prepared following a previously reported methodology [11]. To obtain a 4 wt% theoretical content of Pd over TiO₂. In a common experiment, metal precursor (Pd(dba)₂), 0.2 eq. of stabilizer (PPh₃) and modified TiO₂ were weighted in the glove box and charged in a Fischer-Porter bottle. Then, solvent (THF) was added, the Fischer-Porter was closed, purged with hydrogen several times and then charged with 3 bar of H₂. The mixture was then heated at 60 °C and stirred at 700 rpm overnight. After the reaction, the mixture was cooled to room temperature and degassed. Samples for TEM analysis were prepared by deposition of several drops of the reaction crude onto a copper grid. The rest of the reaction crude was concentrated and washed several times with abundant hexane. The catalyst was dried under vacuum during several hours.

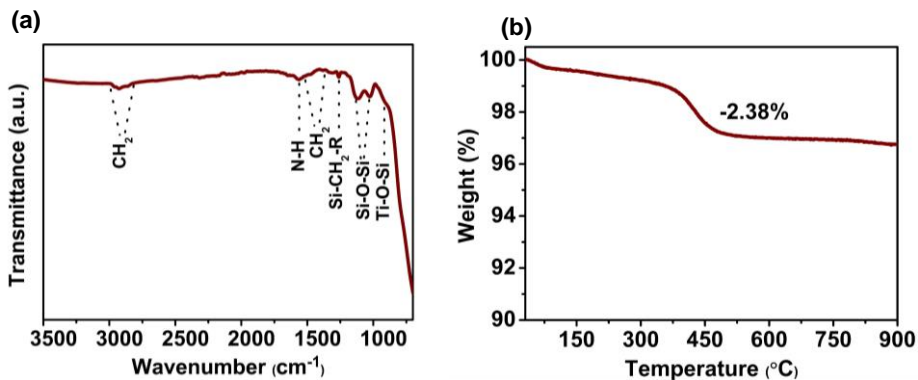
Table S3. Characterization data for 1-8 NPs using different conditions.¹



Entry	System	Size (nm) ²	Pd wt% ³	P wt% ³
1	1	5.75 ± 1.79	3.46	0.18
2	2	2.23 ± 0.78	2.75	0.19
3	3a	2.04 ± 1.05	3.07	-
4 ⁴	3b	2.52 ± 0.95	3.36	-
5	4	1.89 ± 0.82	3.25	-
6	5	2.43 ± 0.94	3.17	0.17
7	6a	1.99 ± 0.72	3.58	-
8 ⁴	6b	2.32 ± 0.99	3.60	-
9	7	Out of support	3.29	-
10	8	3.41 ± 1.72	3.29	-

¹ Synthesis conditions: Pd 4 wt% (metal precursor Pd(dba)₂), 0.2 eq. of PPh₃, previously synthesized TESs/TiO₂ or PAs/TiO₂, THF, 3 bar H₂, 60 °C, overnight. ² Determined by TEM. ³ Determined by ICP. ⁴ In absence of PPh₃.

Fourier Transform Infrared Spectroscopy (FT-IR) and Thermogravimetric Analysis (TGA)



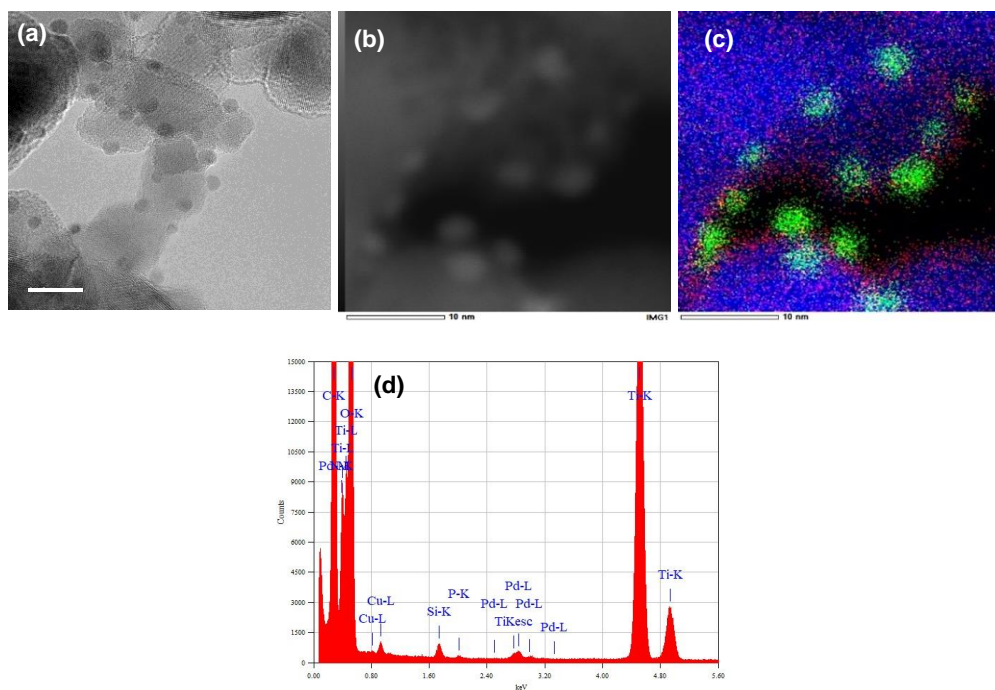


Figure S11. (a) HR-TEM image, (b) HR-HAADF STEM, (c) EDS mapping overlay (green, Pd; red, Si; blue, Ti), (d) spectrum of **3b**.

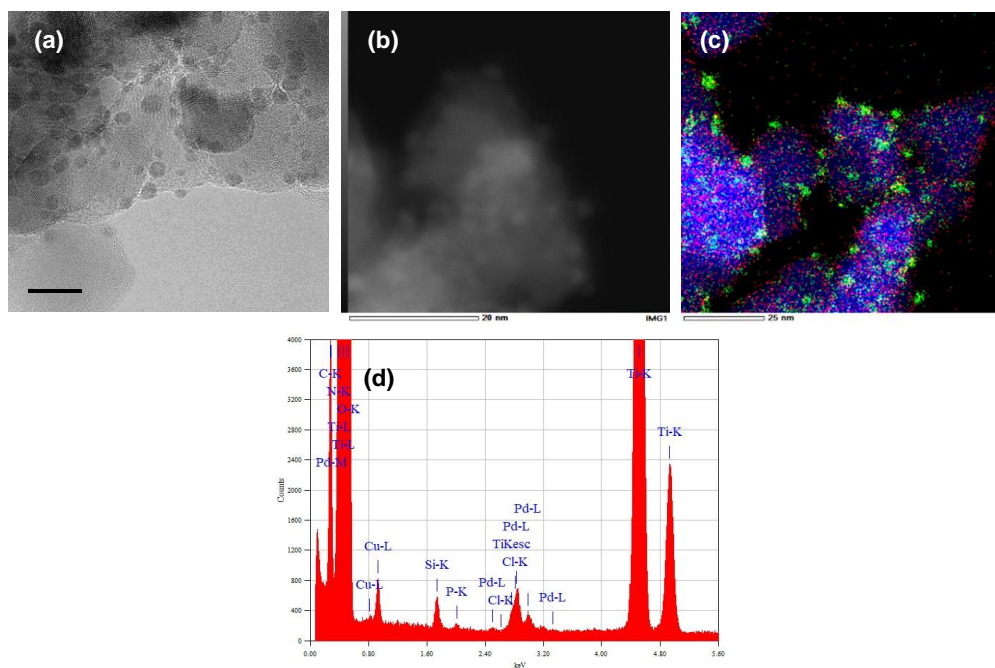


Figure S12. (a) HR-TEM image, (b) HR-HAADF STEM, (c) EDS mapping overlay (green, Pd; red, Si; blue, Ti), (d) spectrum of **4**.

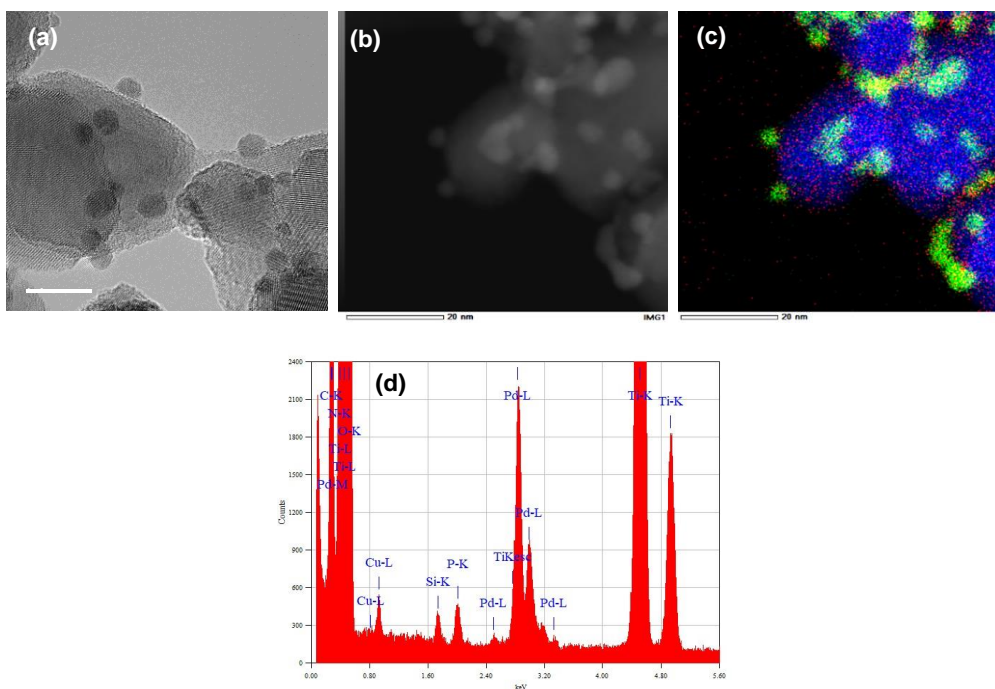


Figure S13. (a) HR-TEM image, (b) HR-HAADF STEM, (c) EDS mapping overlay (green, Pd; red, P; blue, Ti), (d) spectrum of **8**.

X-ray photoelectron spectroscopy (XPS)

Table S4. XPS results for Pd-PPh₃/TiO₂ and different Pd-PPh₃/mod@TiO₂-x catalysts.

Entry	System	Pd ^{δ+} (%)
1	Pd-PPh ₃ /TiO ₂	12.5
2	4	11.6
3	8	7.8

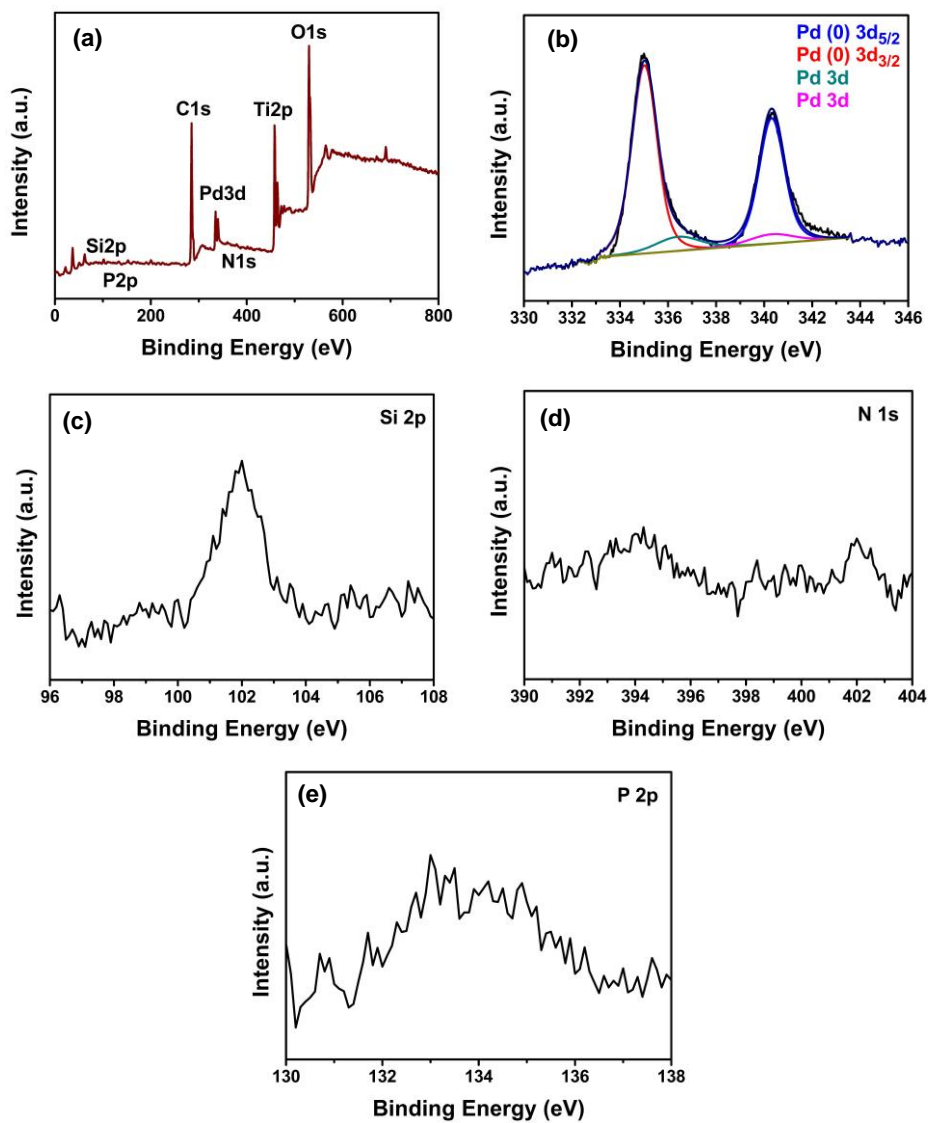


Figure S14. XPS images of **4**: overview (a), Pd3d (b), Si2p (c), N1s (d), P2p (e).

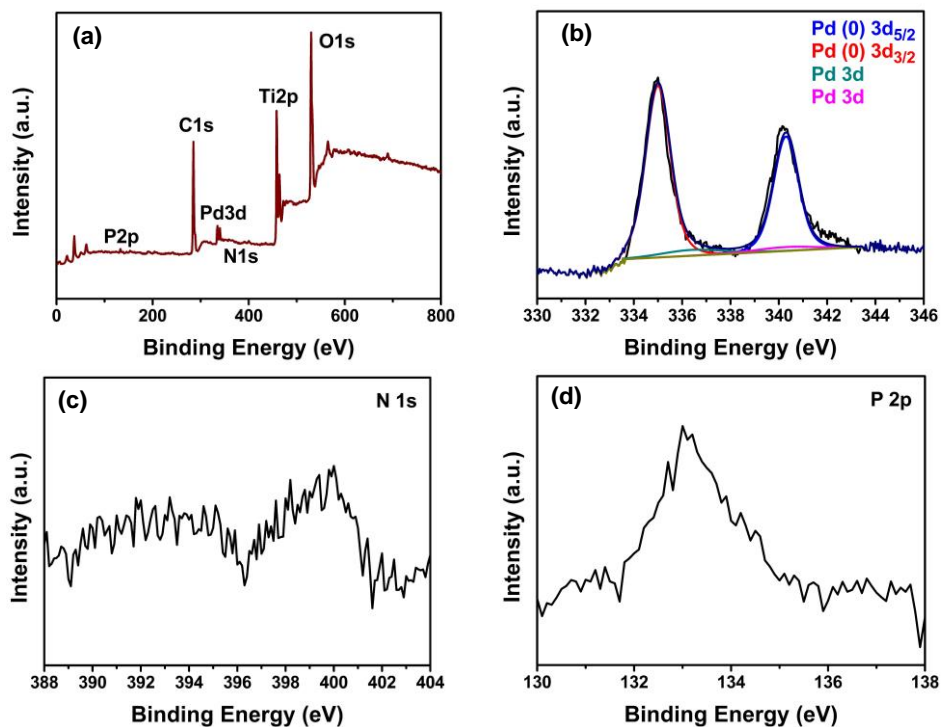


Figure S15. XPS images of 8: overview (a), Pd3d (b), N1s (c), P2p (d).

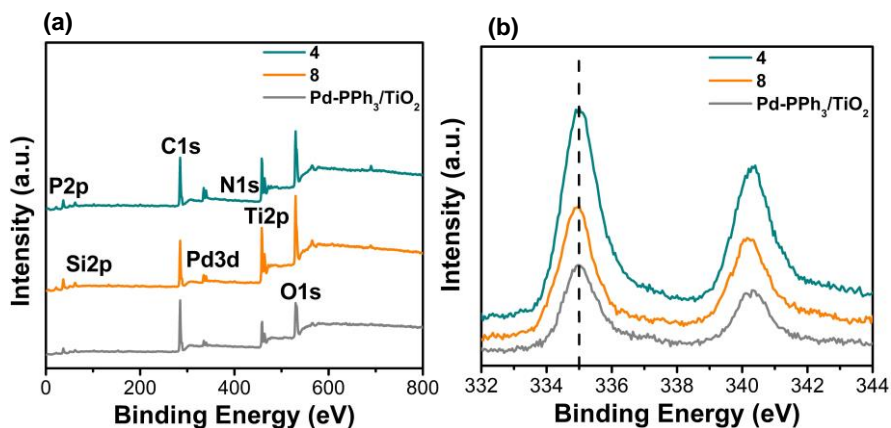


Figure S16. Stacked XPS image of overview (a) and Pd3d high resolution spectra (b) for the newly synthesized catalysts.

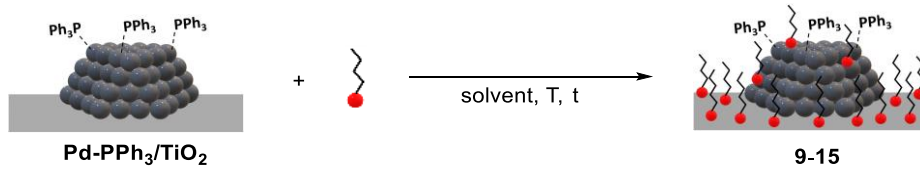
3.6. Deposition of modifier over previously synthesized Pd-PPh₃/TiO₂ systems (9-15)

PTES and APTES (9-11): Specified concentration of PTES or APTES (and determined mmol (A)PTES/mg: **Pd-PPh₃/TiO₂** ratio) (Table S5) and **Pd-PPh₃/TiO₂** previously synthesized were mixed. At r.t., the synthesis was carried out overnight in Schlenk using a mixture of 95% EtOH, 5% milli-Q H₂O, while reactions at 120 °C reaction were performed in an autoclave during 4 h using EtOH as solvent. In both cases, samples were dried overnight in an oven at 105 °C and stored inside the glove box.

ILs (12-13): Mixture of a specified concentration of IL-Anion and previously synthesized **Pd-PPh₃/TiO₂** system was prepared at r.t. using a mixture of 95% EtOH, 5% milli-Q H₂O, overnight (Table S5).

PAs (14-15): Mixture of a specified concentration of PAs and previously synthesized **Pd-PPh₃/TiO₂** system were mixed at r.t. using milli-Q H₂O as solvent (for synthesis with APA) or THF (for synthesis with PA), overnight (Table S5).

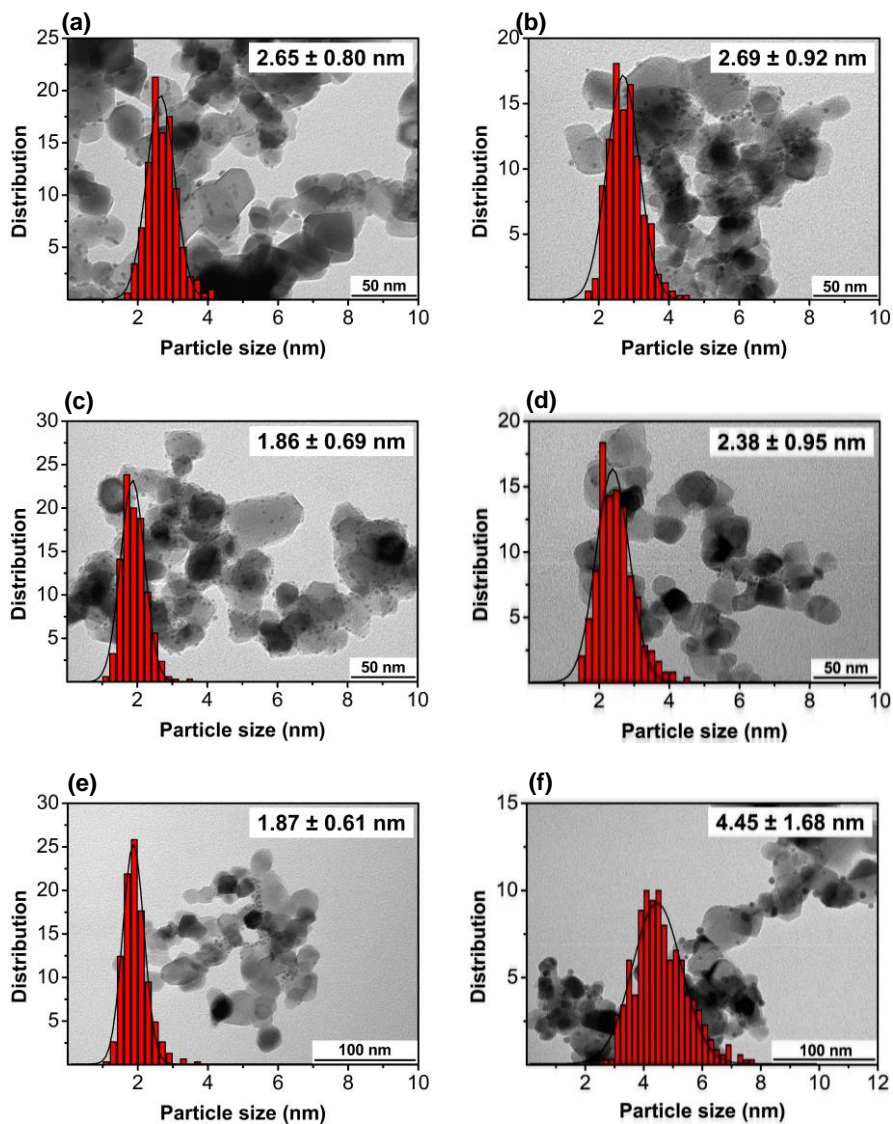
Table S5. Optimization of synthesis conditions for **Pd-PPh₃/TiO₂** modified with TESs and PAs.¹

			
Entry	[C], M	mmol/mg TiO ₂	Code
1	0.13	0.013	9
2	0.01	0.003	10
3	0.13	0.013	11
4	0.13	0.013	12
5	0.13	0.013	13
6 ²	0.01	0.003	14
7 ³	0.01	0.003	15

¹ Synthesis conditions: **Pd-PPh₃/TiO₂** previously synthesized was added to a solution of TESs (for determined mmol TESs/mg **Pd-PPh₃/TiO₂** ratio) on mixture EtOH:milli-Q H₂O (95:5, v/v) and it was let react at r.t. overnight. ² **Pd-PPh₃/TiO₂** system was added to a solution of PA on

THF and it was let react r.t. overnight. $^3\text{Pd-PPh}_3/\text{TiO}_2$ system was added to a solution of APA on milli-Q H_2O and it was let react r.t. overnight.

Transmission Electron Microscopy (TEM)



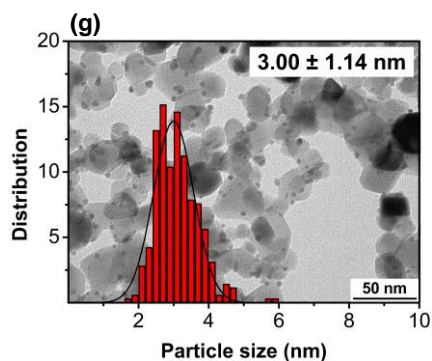


Figure S17. TEM images of 9 (a), 10 (b), 11 (c), 12 (d), 13 (e), 14 (f) and 15 (g).

Fourier Transform Infrared Spectroscopy (FT-IR) and Thermogravimetric Analysis (TGA)

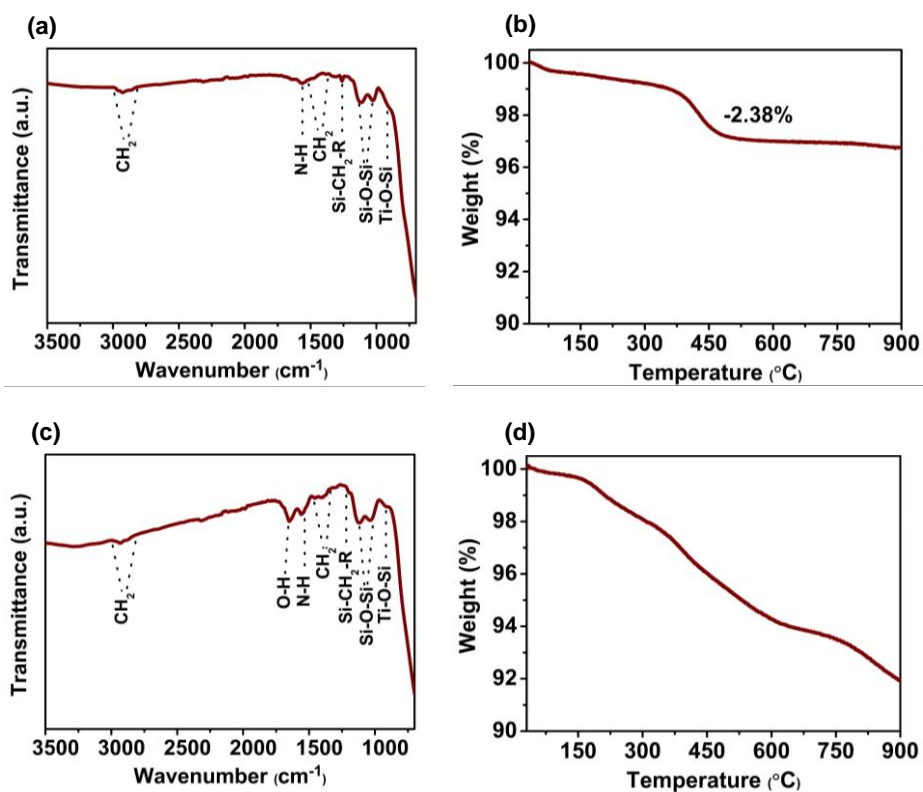


Figure S18. FT-IR spectra and TGA of TiO₂-3 (a), (b) and FT-IR spectra and TGA of 11 (c), (d).

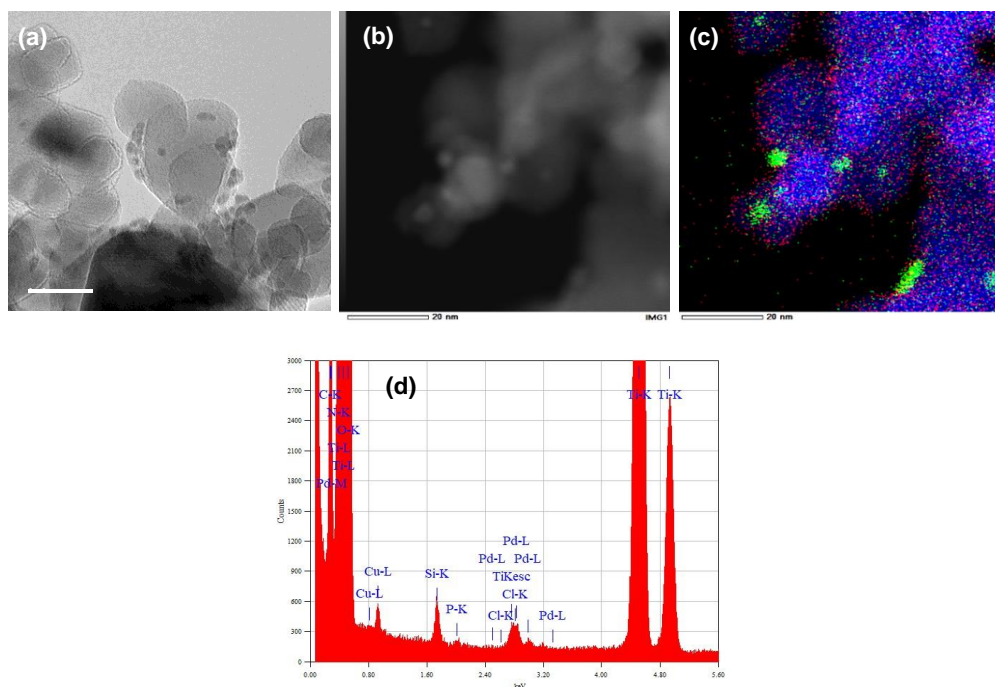


Figure S21. (a) HR-TEM image, (b) HR-HAADF STEM, (c) EDS mapping overlay (green, Pd; red, Si; blue, Ti), (d) spectrum of **12**.

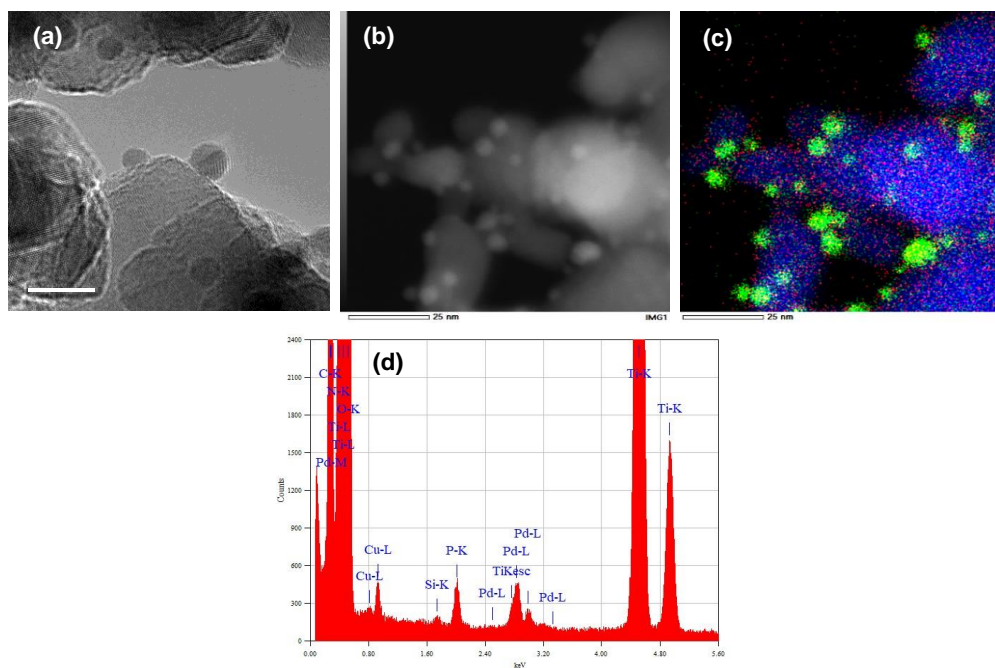


Figure S22. (a) HR-TEM image, (b) HR-HAADF STEM, (c) EDS mapping overlay (green, Pd; red, P; blue, Ti), (d) spectrum of **14**.

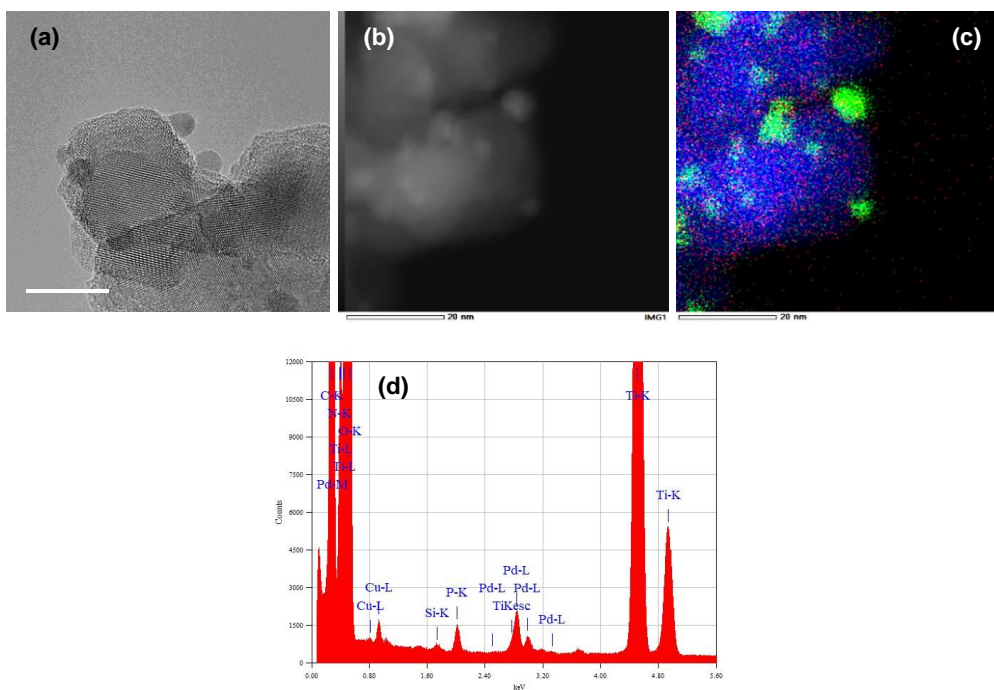


Figure S23. (a) HR-TEM image, (b) HR-HAADF STEM, (c) EDS mapping overlay (green, Pd; red, P; blue, Ti), (d) spectrum of **15**.

X-ray photoelectron spectroscopy (XPS)

Table S6. XPS results for Pd-PPh₃/TiO₂ and different mod@Pd-PPh₃/TiO₂-x catalysts.

Entry	System	Pd ^{δ+} (%)
1	Pd-PPh ₃ /TiO ₂	12.5
2	11	63.8
3	15	21.9

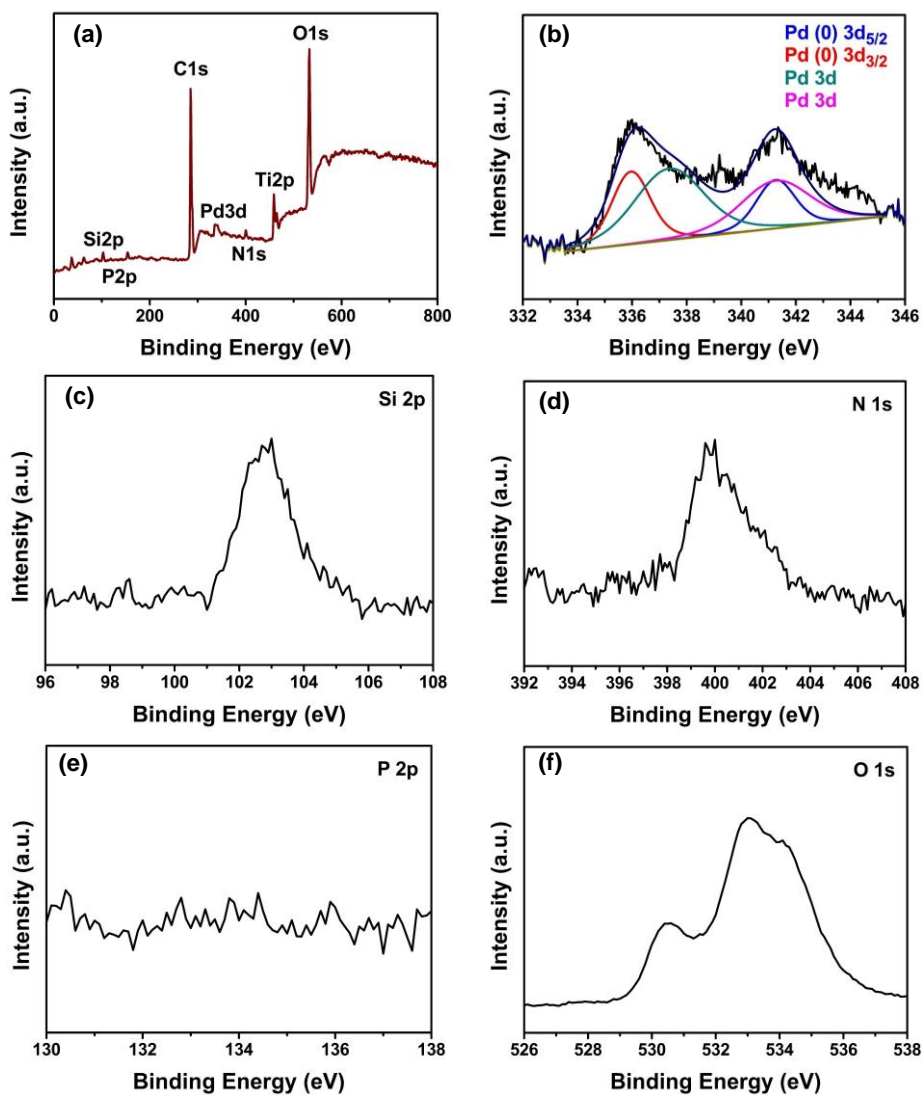


Figure S24. XPS images of 11: overview (a), Pd3d (b), Si2p (c), N1s (d), P2p (e) and O1s (f).

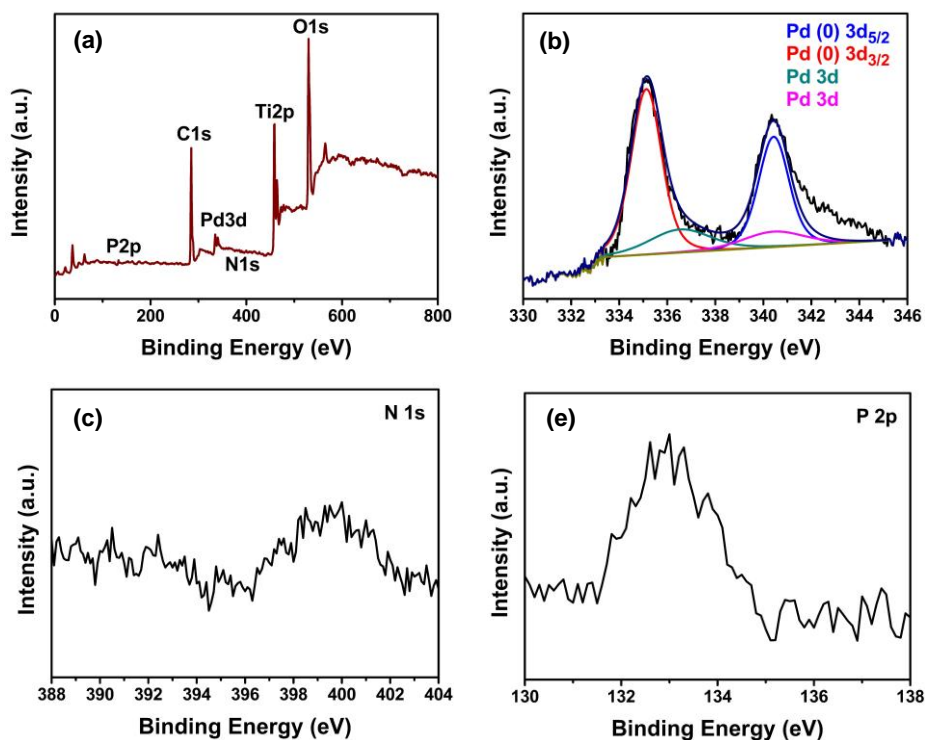


Figure S25. XPS images of 15: overview (a), Pd3d (b), N1s (c), P2p (d).

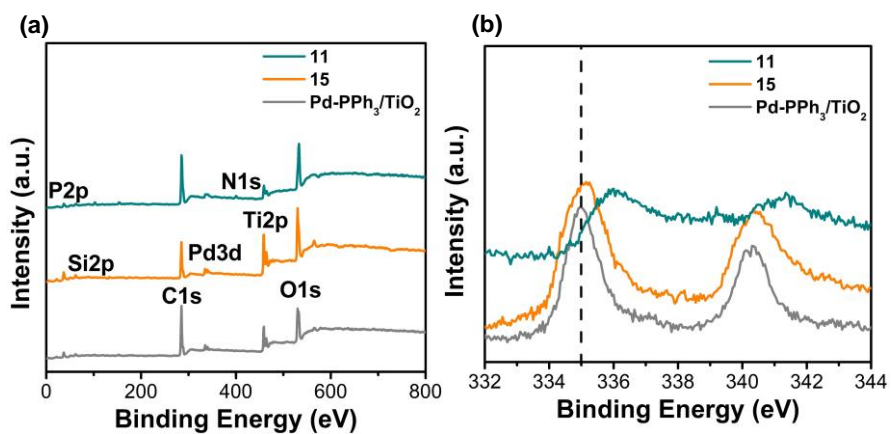


Figure S26. Stacked XPS image of overview (a) and Pd3d high resolution spectra (b) for the newly synthesized catalysts.

4. Catalytic experiments for CO₂ reduction to formate

Stainless steel high-pressure reactor HEL CAT-7 (7 x 10 ml) was charged with TiO₂ supported palladium nanoparticles (20 mg), 20 mg of 1,4-dioxane and 5 ml of a 4 M base solution employing milli-Q water. The reactor was first flushed with 3 cycles of hydrogen to remove the air. Then, the reactor was charged with 10 bar of H₂ and heated at 40 °C under stirring for twenty minutes. At this point, the reactor was depressurized, purged several times with CO₂ and charged with 18 bar of CO₂ and let under stirring for 20 minutes. Then, the reactor was charged with 18 bar of H₂ (1:1, CO₂:H₂) and heated to reach the temperature under 600 rpm of stirring. The experiment was left 15 h and after this time, the reactor was allowed to cool in an ice bath. When the reactor was cooled, it was depressurized and opened. A small amount of the sample was centrifuged and 100 µl of supernatant were analysed by NMR using D₂O as deuterated solvent.

- **Characterization data of spent catalysts after one catalysis**

Table S7. Loadings for Pd, P and Si of different systems before and after one catalytic experiment for CO₂ hydrogenation to formate.^{1,2}

Entry	System	Pd wt% ³	P wt% ³	Si wt% ³	Pd wt% ⁴	P wt% ⁴
1	1	3.46	0.18	0.85	3.30	0.06
2	2	2.75	0.19	0.57	2.55	0.03
3 ⁵	3b	3.36	-	0.81	3.40	0.01
4	4	3.25	-	-	3.37	0.05
5	5	3.17	0.24	0.89	3.35	0.03
6	14	3.10	0.82	-	3.23	0.04

¹ Reaction conditions: 20 mg of catalyst, 4 M KHCO₃, 5 ml milli-Q H₂O, 80 °C, p_{Total}= 36 bar, p(CO₂) = p(H₂), 15 h. ² Pd, P and Si contents were obtained by ICP. ³ Before catalysis. ⁴ After catalysis. ⁵ In absence of PPh₃

Table S8. Particle size of different systems before and after one catalytic experiment for CO₂ hydrogenation to formate.^{1,2}

Entry	System	Particle size (nm) ³	Particle size (nm) ⁴
1	1	5.75 ± 1.79	7.13 ± 0.06
2	2	2.23 ± 0.78	4.10 ± 1.35
3 ⁵	3b	2.52 ± 0.95	4.11 ± 0.77
4	4	1.89 ± 0.82	4.58 ± 1.86
5	5	2.43 ± 0.94	3.72 ± 0.21
6	14	4.45 ± 1.68	3.71 ± 2.14

¹ Reaction conditions: 20 mg of catalyst, 4 M KHCO₃, 5 ml milli-Q H₂O, 80 °C, pTotal= 36 bar, p(CO₂) = p(H₂), 15 h. ² Particle size was obtained by TEM. ³ Before catalysis. ⁴ After catalysis. ⁵ In absence of PPh₃.

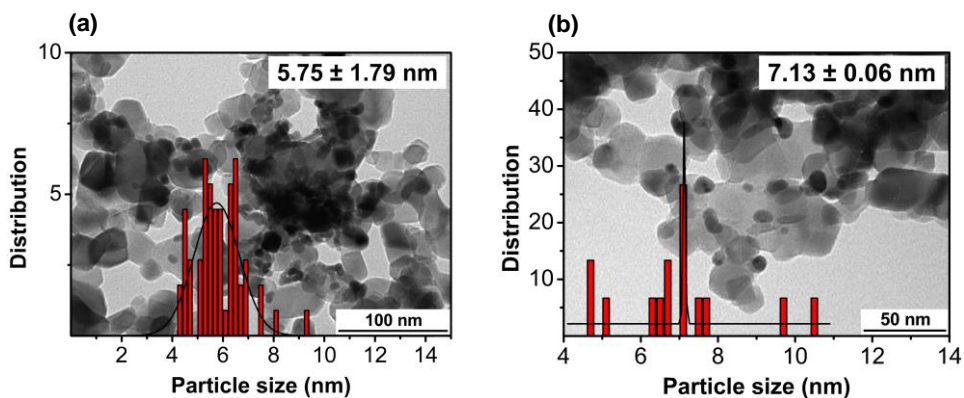


Figure S27. TEM images from **1** before (a) and after (b) catalysis at 80 °C.

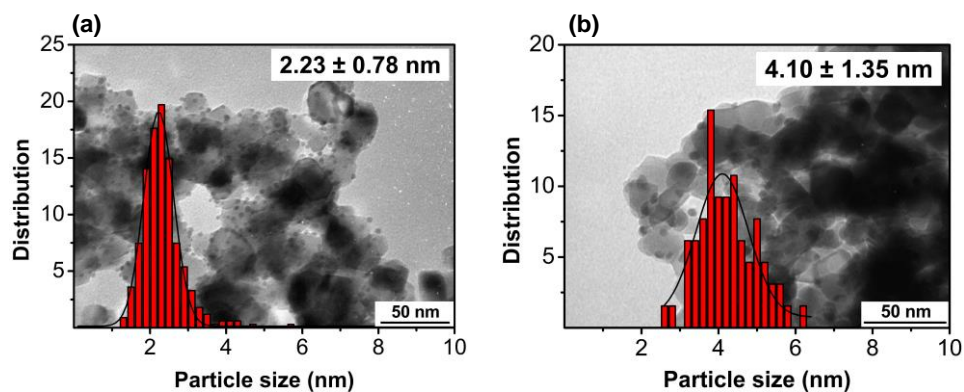


Figure S28. TEM images from 2 before (a) and after (b) one catalysis at 80 °C.

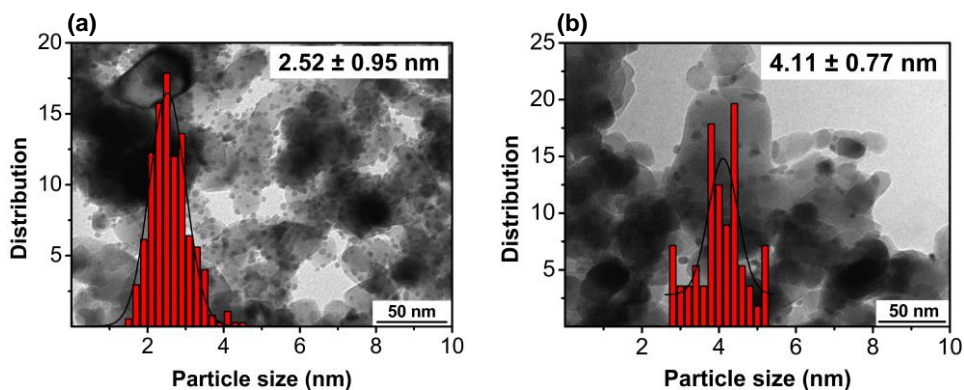


Figure S29. TEM images from 3b before (a) and after (b) catalysis at 80 °C.

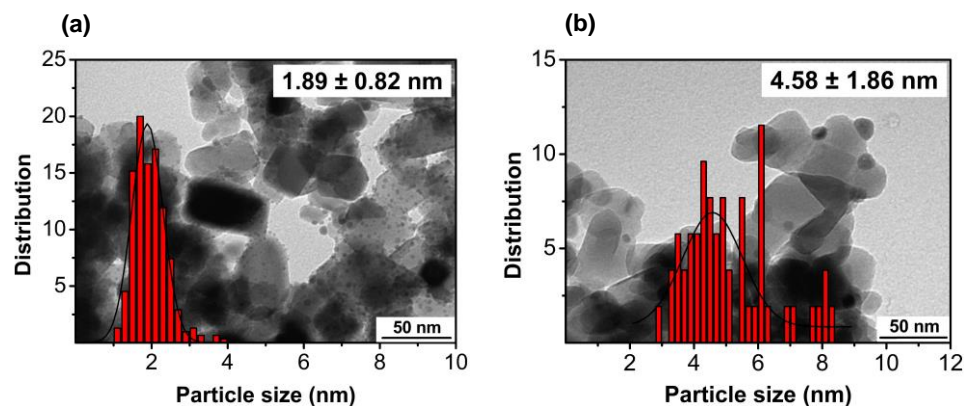


Figure S30. TEM images from 4 before (a) and after (b) catalysis at 80 °C.

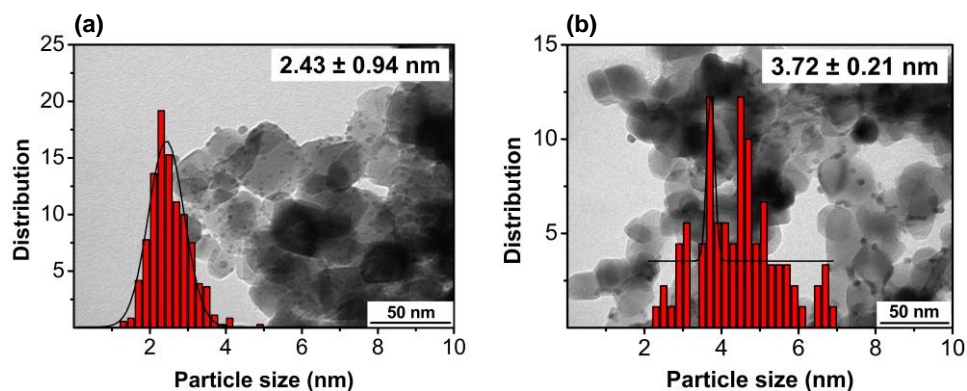


Figure S31. TEM images from 5 before (a) and after (b) one catalysis at 80°C .

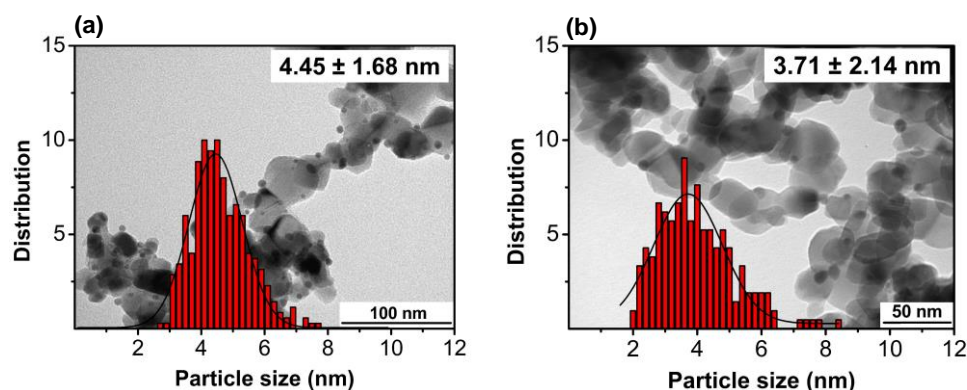


Figure S32. TEM images from 14 before (a) and after (b) catalysis at 80°C .

- Effect of time

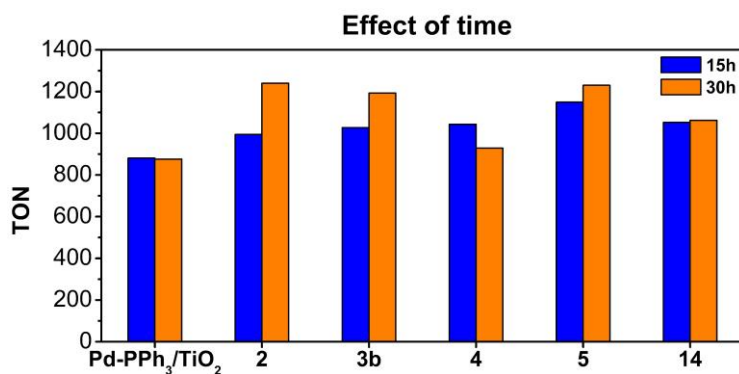


Figure S33. Effect of time in catalytic activity of different catalyst for CO₂ hydrogenation to formate. Conditions: 20 mg of Pd-PPh₃/modifier@TiO₂-x or modifier@Pd-PPh₃/TiO₂-x, 4 M

KHCO₃, 5 ml milli-Q H₂O, 80 °C, pTotal= 36 bar, p(CO₂) = p(H₂). TON= mmol formate/mmol total of Pd, calculated by NMR using 1,4-dioxane as internal standard.

Table S9. Effect of time in catalytic activity of different catalyst for CO₂ hydrogenation to formate.¹

Entry	System	Time (h)	TON ²
1	Pd-PPh₃/TiO₂	15	881
2	Pd-PPh₃/TiO₂	30	876
3	2	15	994
4	2	30	1240
5 ³	3b	15	917
6 ³	3b	30	1065
7	4	15	1043
8	4	30	929
9	5	15	1030
10	5	30	1103
11	14	15	912
12	14	30	920

¹ Reaction conditions: 20 mg of **Pd-PPh₃/modifier@TiO₂-x** or **modifier@Pd-PPh₃/TiO₂-x**, 4 M KHCO₃, 5 ml milli-Q H₂O, 80 °C, pTotal= 36 bar, p(CO₂) = p(H₂). ² TON= mmol formate/mmol total of Pd, calculated by NMR using 1,4-dioxane as internal standard. ³ In absence of PPh₃.

- Effect of temperature

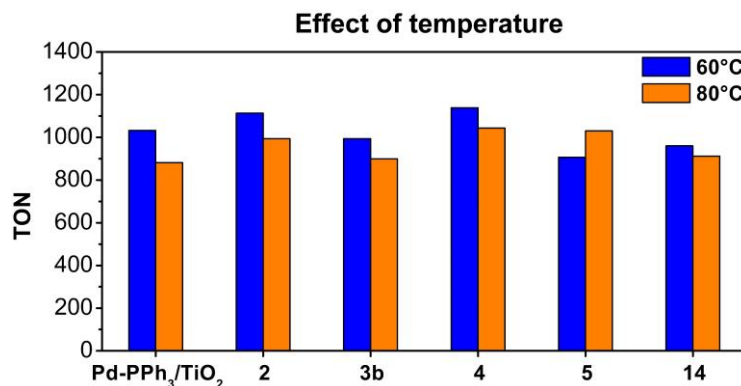


Figure S34. Effect of temperature in catalytic activity of different catalyst for CO₂ hydrogenation to formate. Conditions: 20 mg of **Pd-PPh₃/modifier@TiO₂-x** or **modifier@Pd-PPh₃/TiO₂-x**, 4 M KHCO₃, 5 ml milli-Q H₂O, pTotal= 36 bar, p(CO₂) = p(H₂), 15 h. TON= mmol formate/mmol total of Pd, calculated by NMR using 1,4-dioxane as internal standard.

Table S10. Effect of temperature in catalytic activity of different catalyst for CO₂ hydrogenation to formate.¹

Entry	System	Temperature (°C)	TON ²
1	Pd-PPh₃/TiO₂	60	1056
2	Pd-PPh₃/TiO₂	80	881
3	2	60	1113
4	2	80	994
5 ³	3b	60	994
6 ³	3b	80	899
7	4	60	1138
8	4	80	1043
9	5	60	907
10	5	80	1030
11	14	60	960

¹ Reaction conditions: 20 mg of **Pd-PPh₃/modifier@TiO₂-x** or **modifier@Pd-PPh₃/TiO₂-x**, 4 M KHCO₃, 5 ml milli-Q H₂O, pTotal= 36 bar, p(CO₂) = p(H₂), 15 h. ² TON= mmol formate/mmol total of Pd, calculated by NMR using 1,4-dioxane as internal standard. ³ In absence of PPh₃.

5. Recycling experiments

After every catalytic experiment, the content of a catalysis vial was filtered through a Nylon membrane. The solid was washed several times with abundant milli-Q H₂O and dried under vacuum for several hours. Then, a new catalysis was carried out.

• Reusability tests at different temperatures

Table S11. Recycling experiments with different systems at 60 °C for CO₂ hydrogenation to formate.¹

Entry	System	Fresh ²	1 st ²	2 nd ²
1	2	1118	943	380
2 ³	3b	963	802	408
3	14	915	531	206

¹ Reaction conditions: 20 mg of catalyst, 4 M KHCO₃, 5 ml milli-Q H₂O, 60 °C, pTotal= 36 bar, p(CO₂) = p(H₂), 15 h. ² TON= mmol formate/mmol total of Pd, calculated by NMR using 1,4-dioxane as internal standard. ³ In absence of PPh₃.

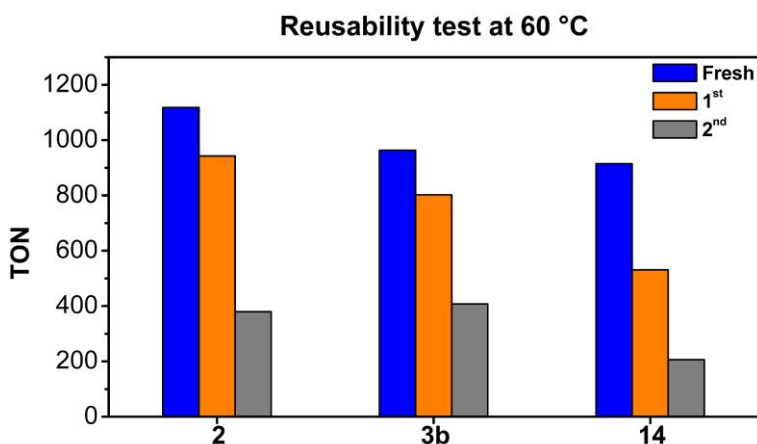


Figure S35. Recycling experiments with different systems at 60 °C for CO₂ hydrogenation to formate. Conditions: 20 mg of catalyst, 4 M KHCO₃, 5 ml milli-Q H₂O, pTotal= 36 bar, p(CO₂)

= p(H₂), 60 °C, 15 h. TON= mmol formate/mmol total of Pd, calculated by NMR using 1,4-dioxane as internal standard.

Table S12. Palladium content of different systems before and after recycling experiments for CO₂ hydrogenation to formate.^{1,2}

Entry	System	Pd wt% ³	P wt% ³	Si wt% ³	Pd wt% ⁴
1	2	2.75	0.19	0.57	2.43
2 ⁵	3b	3.36	-	0.81	3.57
3	14	3.10	0.82	-	3.25

¹ Reaction conditions: 20 mg of catalyst, 4 M KHCO₃, 5 ml milli-Q H₂O, 60 °C, pTotal= 36 bar, p(CO₂) = p(H₂), 15 h. ² Particle size was obtained by TEM. ³ Before catalysis. ⁴ After 2nd cycle. ⁵ In absence of PPh₃.

Table S13. Particle size of different systems before and after recycling experiments for CO₂ hydrogenation to formate.^{1,2}

Entry	System	Size (nm) ³	Size (nm) ⁴
1	2	2.23 ± 0.78	3.28 ± 0.65
2 ⁵	3b	2.52 ± 0.95	3.23 ± 1.03
3	14	4.45 ± 1.68	3.85 ± 0.91

¹ Reaction conditions: 20 mg of catalyst, 4 M KHCO₃, 5 ml milli-Q H₂O, 60 °C, pTotal= 36 bar, p(CO₂) = p(H₂), 15 h. ² Particle size was obtained by TEM. ³ Before catalysis. ⁴ After 2nd cycle. ⁵ In absence of PPh₃.

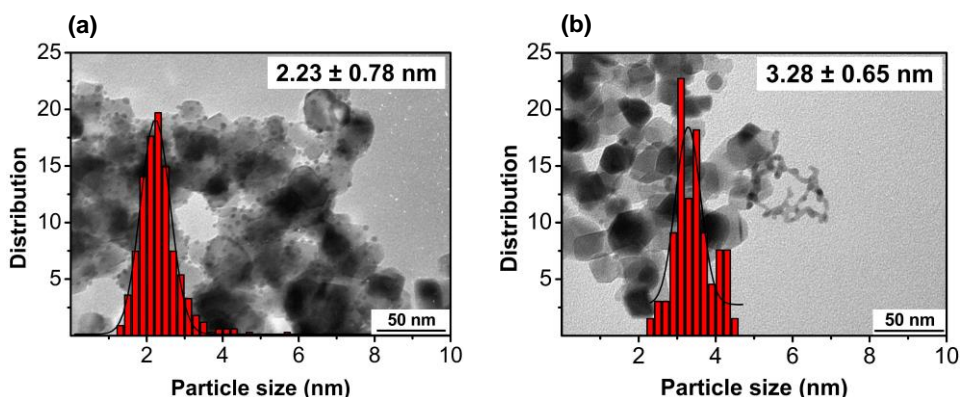


Figure S36. TEM images of **2** before (a) and after (b) two recovery experiments carried out at 60 °C.

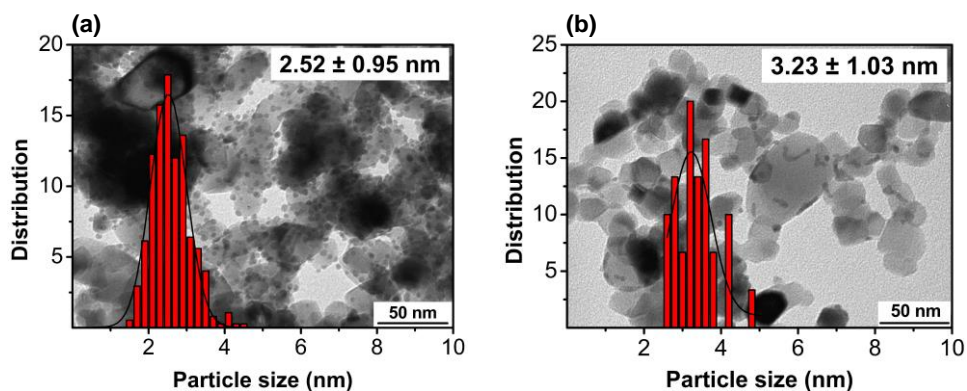


Figure S37. TEM images of **3b** before (a) and after (b) two recovery experiments carried out at 60 °C.

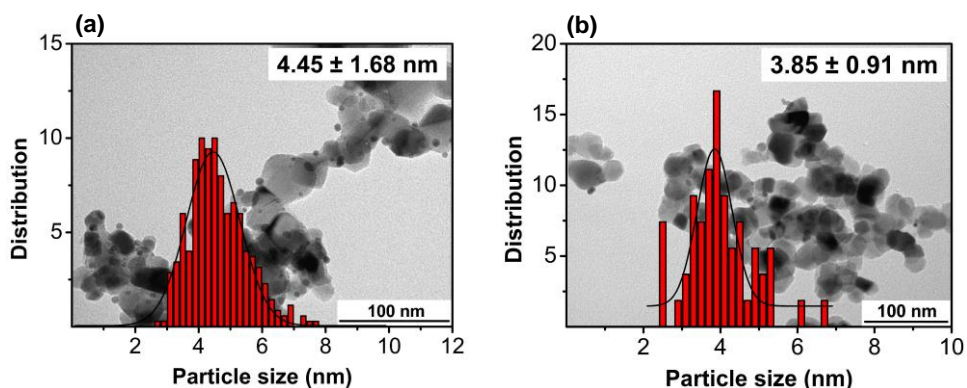


Figure S38. TEM images of **14** before (a) and after (b) two recovery experiments carried out at 60 °C.

Table S14. Recycling experiments with different systems at 80 °C for CO₂ hydrogenation to formate.¹

Entry	System	Fresh ²	1 st 2	2 nd 2
1	2	1117	987	510
2 ³	3b	954	838	516
3	14	827	723	369

¹ Reaction conditions: 20 mg of catalyst, 4 M KHCO₃, 5 ml milli-Q H₂O, 80 °C, p_{Total}= 36 bar, p(CO₂) = p(H₂), 15 h. ² TON= mmol formate/mmol total of Pd, calculated by NMR using 1,4-dioxane as internal standard. ³ In absence of PPh₃.

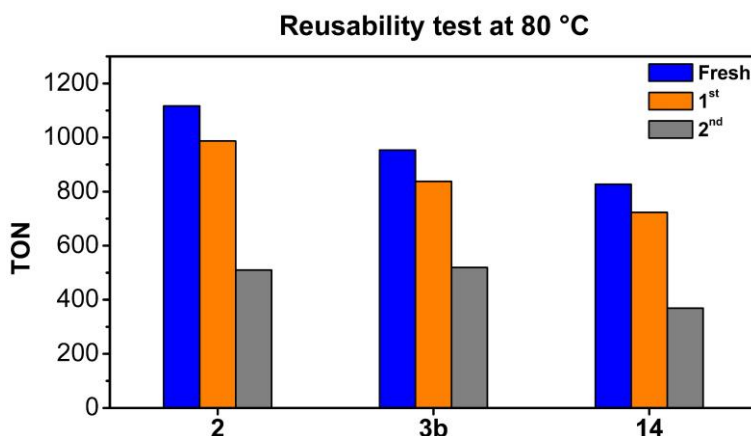


Figure S39. Recycling experiments with different systems at 80 °C for CO₂ hydrogenation to formate. Conditions: 20 mg of catalyst, 4 M KHCO₃, 5 ml milli-Q H₂O, pTotal= 36 bar, p(CO₂) = p(H₂), 80 °C, 15 h. TON= mmol formate/mmol total of Pd, calculated by NMR using 1,4-dioxane as internal standard.

Table S15. Palladium content of different systems before and after recycling experiments for CO₂ hydrogenation to formate.^{1,2}

Entry	System	Pd wt% ³	P wt% ³	Si wt% ³	Pd wt% ⁴
1	2	2.75	0.19	0.57	6.09
2 ⁵	3b	3.36	-	0.81	4.56
3	14	3.10	0.82	-	3.58

¹ Reaction conditions: 20 mg of catalyst, 4 M KHCO₃, 5 ml milli-Q H₂O, 80 °C, pTotal= 36 bar, p(CO₂) = p(H₂), 15 h. ² Particle size was obtained by TEM. ³ Before catalysis. ⁴ After 2nd cycle. ⁵ In absence of PPh₃.

Table S16. Particle size of different systems before and after recycling experiment for CO₂ hydrogenation to formate.^{1,2}

Entry	System	Size (nm) ³	Size (nm) ⁴
1	2	2.23 ± 0.78	3.50 ± 0.00
2 ⁵	3b	2.52 ± 0.95	3.44 ± 1.30
3	14	4.45 ± 1.68	3.59 ± 1.61

¹ Reaction conditions: 20 mg of catalyst, 4 M KHCO₃, 5 ml milli-Q H₂O, 80 °C, pTotal= 36 bar, p(CO₂) = p(H₂), 15 h. ² Particle size was obtained by TEM. ³ Before catalysis. ⁴ After 2nd cycle. ⁵ In absence of PPh₃.

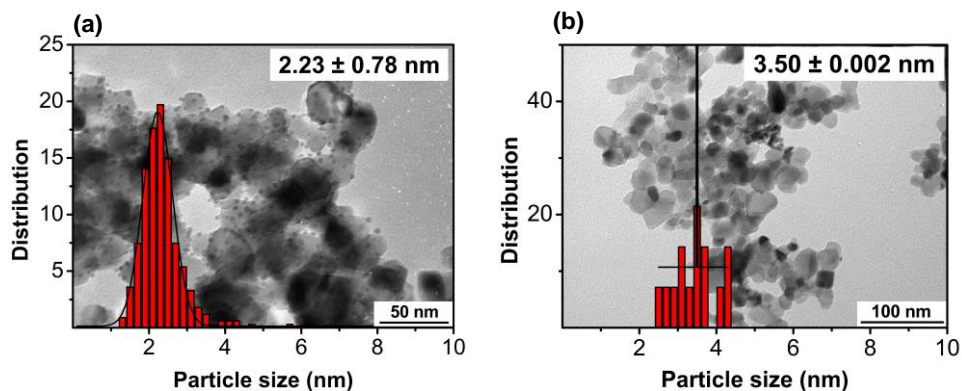


Figure S40. TEM images of **2** before (a) and after (b) two recovery experiments carried out at 80 °C.

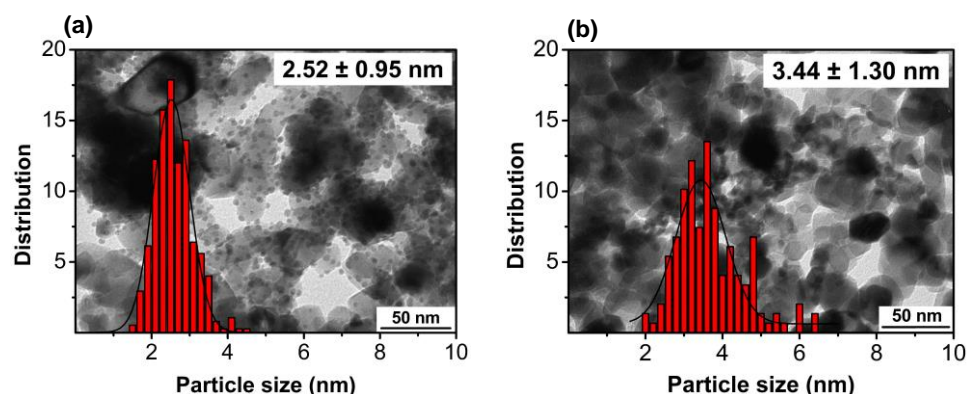


Figure S41. TEM images of **3b** before (a) and after (b) two recovery experiments carried out at 80 °C.

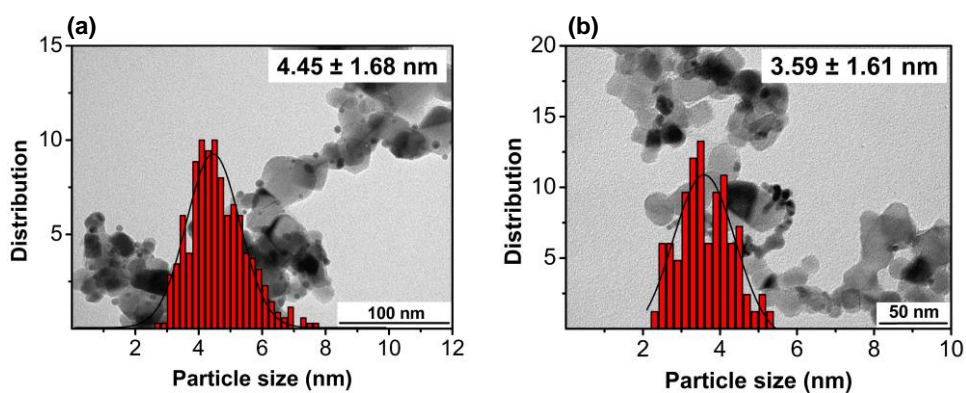


Figure S42. TEM images of **14** before (a) and after (b) two recovery experiments carried out at 80 °C.

- Recycling experiments with different types of modifiers include on the catalyst

Table S17. Recycling experiments with **Pd-PPh₃@modifier/TiO₂-x** for CO₂ hydrogenation to formate.¹

Entry	System	Fresh ²	1 st 2	2 nd 2	3 rd 2
1	2	1117	987	510	-
2 ³	3b	954	838	519	-
3	4	1005	434	404	221
4 ⁴	4	946	542	447	-
5	8	756	356	349	189

¹ Reaction conditions: 20 mg of **Pd-PPh₃/modifier@TiO₂-x**, 4 M KHCO₃, 5 ml milli-Q H₂O, 80 °C, pTotal= 36 bar, p(CO₂) = p(H₂), 15 h. ²TON= mmol formate/mmol total of Pd, calculated by NMR using 1,4-dioxane as internal standard. ³ In absence of PPh₃. ⁴ Same sample that entry 4 but recovery was different: in that case, the catalysis tube was let decanted, the solution was removed, solid was washed and solution and IS was added for the next cycle.

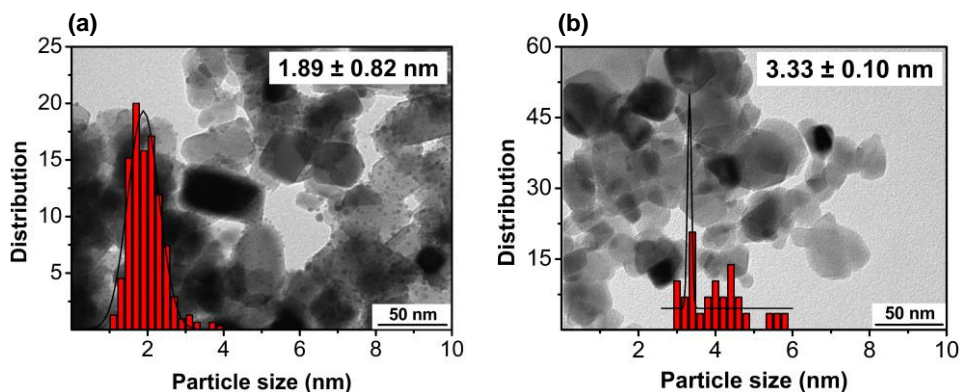


Figure S43. TEM images of 4 before (a) and after (b) two recovery experiments carried out at 80 °C.

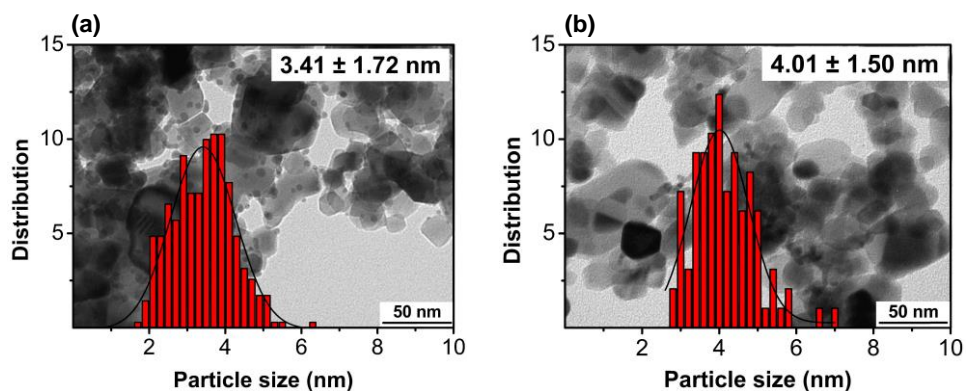


Figure S44. TEM images of **8** before (a) and after (b) two recovery experiments carried out at 80 °C.

Table S18. Recycling experiments with **modifier@Pd-PPh₃/TiO₂-x** for CO₂ hydrogenation to formate.¹

Entry	System	Fresh ²	1 st 2	2 nd 2	3 rd 2
1	11	904	724	662	524
2	12	405	249	367	209
3	14	827	723	369	-
4	15	873	332	326	201

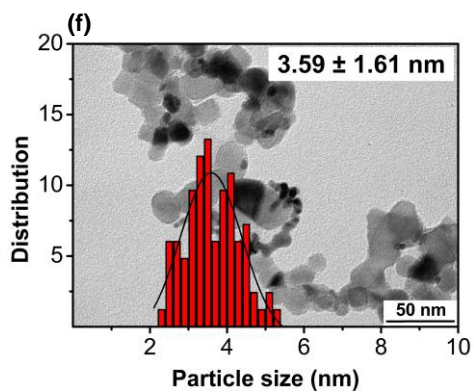
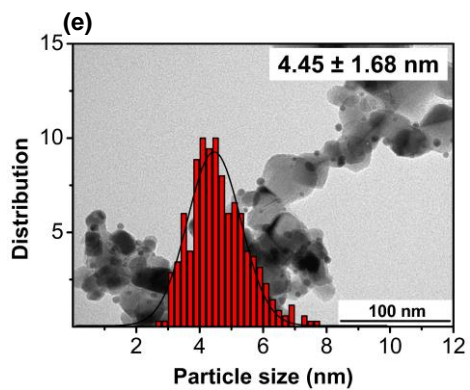
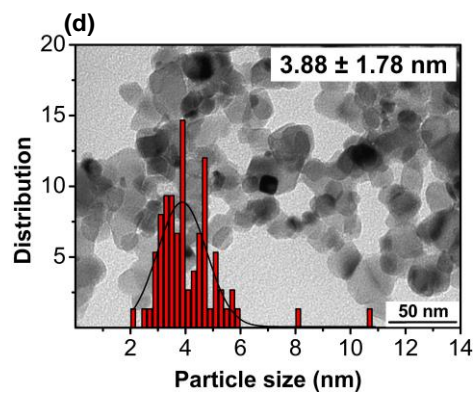
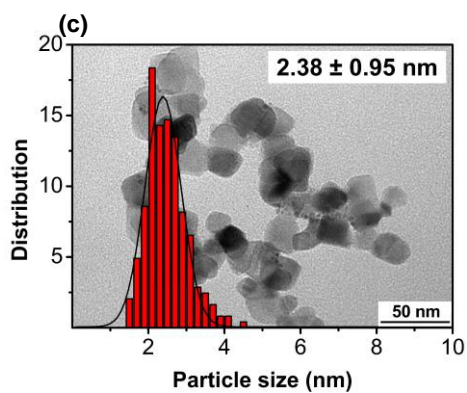
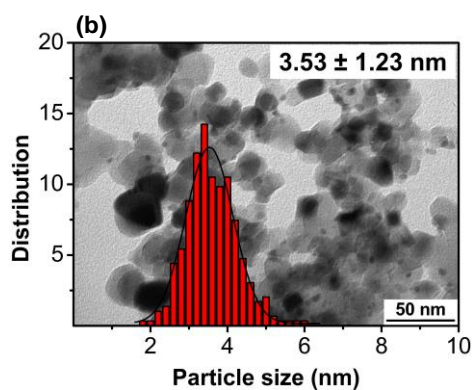
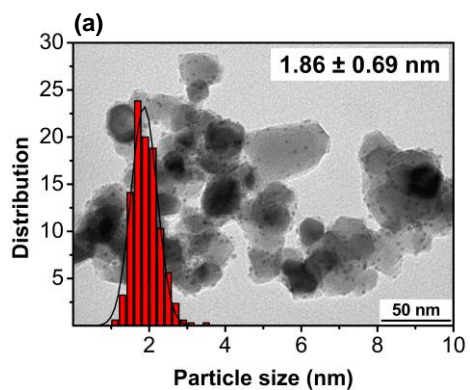
¹ Reaction conditions: 20 mg of **modifier@Pd-PPh₃/TiO₂-x**, 4 M KHCO₃, 5 ml milli-Q H₂O, 80 °C, pTotal= 36 bar, p(CO₂) = p(H₂), 15 h. ² TON= mmol formate/mmol total of Pd, calculated by NMR using 1,4-dioxane as internal standard.

Table S19. Particle size of different systems before and after two recovery experiments for CO₂ hydrogenation to formate.^{1,2}

Entry	System	Size (nm) ³	Size (nm) ⁴
1	11	1.86 ± 0.69	3.53 ± 1.23
2	12	2.38 ± 0.95	3.88 ± 1.78
3	14	4.45 ± 1.68	3.59 ± 1.61
4	15	3.00 ± 1.14	3.58 ± 1.10

¹ Reaction conditions: 20 mg of **modifier@Pd-PPh₃/TiO₂-x**, 4 M KHCO₃, 5 ml milli-Q H₂O, 80 °C, pTotal= 36 bar, p(CO₂) = p(H₂), 15 h. ² Particle size was obtained by TEM. ³ Before catalysis.

⁴ After 2nd cycle.



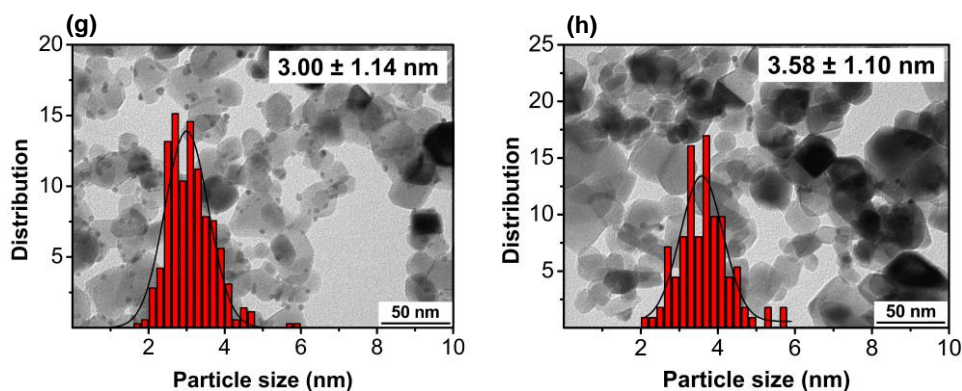


Figure S45. TEM images before and after two recovery experiments carried out at 80 °C of **11** (a), (b); **12** (c), (d); **14** (e), (f) and **15** (g), (h).

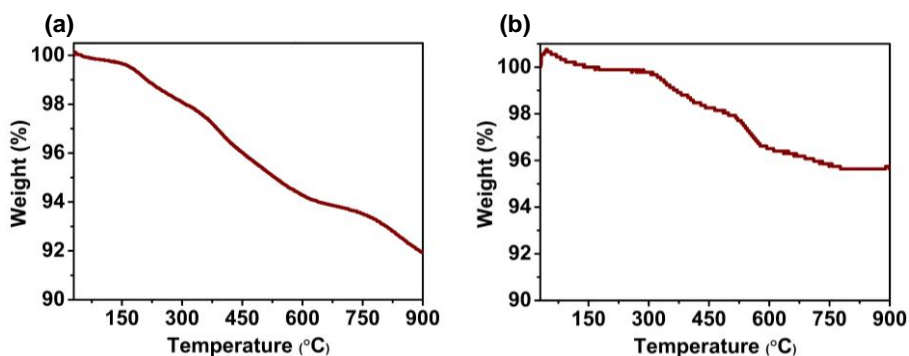


Figure S46. TGA before catalysis (a) and after three cycles (b) of **11**.

Table S20. Comparison of recycling experiments with **11**¹ and **Pd-PPh₃/TiO₂**² for CO₂ hydrogenation to formate.

Entry	System	Fresh ³	1 st ³	2 nd ³	3 rd ³
1	Pd-PPh₃/TiO₂	1056	733	377	188
2	11	904	724	662	524

¹ Reaction conditions: 20 mg of **11**, 4 M KHCO₃, 5 ml milli-Q H₂O, 80 °C, p_{Total}= 36 bar, p(CO₂) = p(H₂), 15 h. ² Reaction conditions: 20 mg of **Pd-PPh₃/TiO₂**, 4 M KHCO₃, 5 ml milli-Q H₂O, 60 °C, p_{Total}= 36 bar, p(CO₂) = p(H₂), 15 h. ³ TON= mmol formate/mmol total of Pd, calculated by NMR using 1,4-dioxane as internal standard.

6. References

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