Electronic Supplementary Material (ESI) for Chemical Science.

Implications of Ga Promotion and Metal-Oxide Interface from Tailored PtGa Propane Dehydrogenation Catalysts Supported on Carbon

Enzo Brack,[a] Milivoj Plodinec,[a,b] Marc-Georg Willinger[§,b] and Christophe Copéret*[,a]

a Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir Prelog Weg 2/10 CH-8093 Zurich, Switzerland.
b Scientific Center for Optical and Electron Microscopy (ScopeM) ETH Zurich, Otto-Stern-Weg 3, CH-8093 Zurich, Switzerland.
§ Present Address: Department of Chemistry, TU Munich, Arcisstraße 21, D-80333 Munich, Germany.

Table of Contents

EXPERIMENTAL DETAILS 3

Carbon Functionalisation 4

OH Titration 4

Synthesis of $Pt_x\_Si_z/C_{grafted}$ and $Pt_x/C_{grafted}$ 4

Synthesis of $Pt_x\_Si_z/C_{H2}$ and Pt_x/C_{H2} 4

Synthesis of $Ga_y\_Si_z/C_{grafted}$ and $Ga_y/C_{grafted}$ 5

Synthesis of $Pt_xGa_y\_Si_z/C_{grafted}$ and $Pt_xGa_y/C_{grafted}$ 5

Synthesis of $Pt_xGa_y\_Si_z/C_{H2}$ and Pt_xGa_y/C_{H2} 5

Synthesis of low loading $Pt_xGa_y\_Si_z/C_{H2}$ 5

XPS STUDIES 7

N_2 ADSORPTION ISOTHERM 8

CATALYTIC PROPANE DEHYDROGENATION STUDIES 9

XAS STUDIES 13

***EX SITU* (S)TEM & STEM-EDS STUDIES** 18

$Pt_{0.68}\_Si_{0.1}/C_{grafted}$ 18

$Pt_{0.68}\_Si_{0.1}/C_{H2}$ 19

$Pt_{0.60}/C_{H2}$ 22

$Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{H2}$ 25

$Pt_{0.26}Ga_{0.10}/C_{H2}$ 30

4D STEM MEASUREMENTS 33

Experimental Details

General Procedures & Considerations: All operations were performed in a M. Braun glove box under an Argon atmosphere or using high vacuum and standard Schlenk techniques. Pentane and benzene were purged with argon for 30 minutes and pre-dried using a MB SPS 800 solvent purification system, where columns were packed with activated alumina. Deuterated benzene was vacuum distilled from purple Na^0/benzophenone. All solvents were stored over 4 Å molecular sieves after being placed in the glove box. Molecular sieves as well as celite were activated at 350 °C under high vacuum overnight. Titration of the carbon supports was performed using $[Mg(Bn)_2(THF)_2]$ and Ferrocene which were purified via sublimation prior to use. $[Mg(Bn)_2(THF)_2]$[1], $[Pt(COD)(OSi(O^tBu_3)_3)_2]$[2], $[Ga(OSi(O^tBu_3)_3)_3(THF)]$[3], $[Ga(Mes)_3]$[4], platinum allyl-(N-N'-diisopropyl)acetamidinate ([Pt(AMD)])[5] and were prepared according to literature procedures.

Mesoporous carbon (>99.95% trace metal basis, Product Nr. 699624) was bought form Sigma-Aldrich. All other reagents were bought from commercial sources and used as received. Mikroanalytisches Labor Pascher located in Remagen, Germany, performed the elemental analysis.

Carbon Functionalisation

Mesoporous Carbon (6 g) was refluxed at 125 °C in 150 mL concentrated HNO_3 in a 250 mL round bottom flask equipped with a reflux condenser for 12 hours, as previously reported[6]. The solid was then filtered off using a glass filter and washed with large portions of water (3 x 100mL of milliQ water) and ethanol (2 x 100 mL), followed by drying under high vacuum (10^{-5} mbars) at 200 °C for 12 hours.

OH Titration

A solution of $[Mg(Bn)_2(THF)_2]$ (16.8 mg, 0.08 mmol) in C_6D_6 was added slowly to a suspension of mesoporous carbon (52.5 mg) while stirring. The resulting mixture was stirred for 24 hours, after which a ferrocene (6.4 mg, 0.03 mmol) solution was added and an NMR spectrum measured (recycle delay d1 = 60s).

Synthesis of $Pt_x\_Si_z/C_{grafted}$ and $Pt_x/C_{grafted}$

$Pt_{0.68}\_Si_{0.1}/C_{grafted}$ from $[Pt(OSi(O^tBu)_3)_2(COD)]$ precursor:

A solution of $[Pt(OSi(O^tBu)_3)_2(COD)]$ (103.4 mg, 0.125 mmol) in benzene was added slowly to a suspension of mesoporous carbon (750.3 mg) while stirring. The resulting mixture was stirred for 24 hours, then the carbon was filtered off, washed twice with benzene (5 mL) and followed by pentane (5 mL) and drying in high vacuum.

$Pt_{0.60}/C_{grafted}$ from [Pt(AMD)] precursor:

A solution of [Pt(AMD)] (52.9 mg, 0.140 mmol) in benzene was added slowly to a suspension of mesoporous carbon (844.0 mg) while stirring. The resulting mixture was stirred for 24 hours, then the carbon was filtered off, washed twice with benzene (5 mL) and followed by pentane (5 mL) and drying in high vacuum.

Synthesis of $Pt_x\_Si_z/C_{H2}$ and Pt_x/C_{H2}

$Pt_{0.68}\_Si_{0.1}/C_{H2}$ from $Pt_{0.68}\_Si_{0.1}/C_{grafted}$ precursor:

$Pt_{0.68}\_Si_{0.1}/C_{grafted}$ was subjected to a hydrogen flow treatment at 600 °C (300 °C/h ramp) and 1 bar of hydrogen for 12 hours, followed by evacuation under high vacuum and storage in a glovebox to give carbon supported platinum nanoparticles ($Pt_{0.68}\_Si_{0.1}/C_{H2}$).

$Pt_{0.60}/C_{H2}$ from $Pt_{0.60}/C_{grafted}$ precursor:

$Pt_{0.60}/C_{grafted}$ was subjected to a hydrogen flow treatment at 600 °C (300 °C/h ramp) and 1 bar of hydrogen for 12 hours, followed by evacuation under high vacuum and storage in a glovebox to give carbon supported platinum nanoparticles ($Pt_{0.60}/C_{H2}$).

Synthesis of $Ga_y\_Si_z/C_{grafted}$ and $Ga_y/C_{grafted}$

$Ga_{1.00}/C_{grafted}$ from $[Ga(OSi(O^tBu)_3)_3(THF)]$ precursor:

A solution of $[Ga(OSi(O^tBu)_3)_3(THF)]$ (118.7 mg, 0.13 mmol) in benzene was added slowly to a suspension of mesoporous carbon (748.9 mg) while stirring. The resulting mixture was stirred for 24 hours, then the carbon was filtered off, washed twice with benzene (5 mL) and followed by pentane (5 mL) and drying in high vacuum.

$Ga_{0.10}/C_{grafted}$ from $[Ga(Mes)_3]$ precursor:

A solution of $[Ga(Mes)_3]$ (91.9 mg, 0.22 mmol) in benzene was added slowly to a suspension of mesoporous carbon (1265.0 mg) while stirring. The resulting mixture was stirred for 24 hours, then the carbon was filtered off, washed twice with benzene (5 mL) and followed by pentane (5 mL) and drying in high vacuum.

Synthesis of $Pt_xGa_y\_Si_z/C_{grafted}$ and $Pt_xGa_y/C_{grafted}$

$Pt_xGa_y\_Si_z/C_{grafted}$ from $[Pt(OSi(O^tBu)_3)_2(COD)]$ precursor:

A solution of $[Pt(OSi(O^tBu)_3)_2(COD)]$ (47.4 mg, 0.06 mmol) in benzene was added slowly to a suspension of $Ga_{1.00}\_Si_z/C_{grafted}$ (340.2 mg) while stirring. The resulting mixture was stirred for 24 hours, then the carbon was filtered off, washed twice with benzene (5 mL) and followed by pentane (5 mL) and drying in high vacuum.

$Pt_xGa_y/C_{grafted}$ *from [Pt(AMD)] precursor:*

A solution of [Pt(AMD)] (42.7 mg, 0.11 mmol) in benzene was added slowly to a suspension of $Ga_{0.10}/C_{grafted}$ (674.2 mg) while stirring. The resulting mixture was stirred for 24 hours, then the carbon was filtered off, washed twice with benzene (5 mL) and followed by pentane (5 mL) and drying in high vacuum.

Synthesis of $Pt_xGa_y\_Si_z/C_{H2}$ and Pt_xGa_y/C_{H2}

The corresponding $Pt_xGa_y\_Si_z/C_{grafted}$ and $Pt_xGa_y/C_{grafted}$ materials were subjected to a hydrogen flow treatment at 600 °C (300 °C/h ramp) and 1 bar of hydrogen for 12 hours, followed by evacuation under high vacuum and storage in a glovebox.

Synthesis of low loading $Pt_xGa_y\_Si_z/C_{H2}$

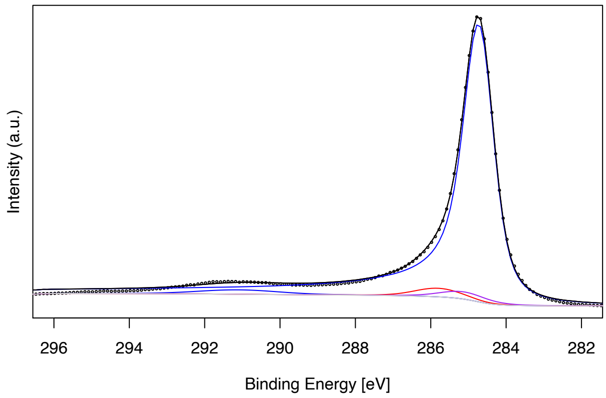
A solution of $[Ga(OSi(O^tBu)_3)_3(THF)]$ (11.6 mg, 0.12 mmol) in benzene was added slowly to a suspension of mesoporous carbon (750.0 mg) while stirring. The resulting mixture was stirred for 24 hours, then the carbon was filtered off, washed twice with benzene (5 mL) and followed by pentane (5 mL) and drying in high vacuum, giving $Ga_{0.10}\_Si_{0.31}/C_{grafted}$.

Then, a solution of [$Pt(OSi(O^tBu)_3)_2(COD)$] (6.1 mg, 0.007 mmol) in benzene was added slowly to the suspension of $Ga_{0.10}\_Si_{0.31}/C_{grafted}$ (340.2 mg) while stirring. The resulting mixture was stirred for 24 hours, then the carbon was filtered off, washed twice with benzene (5 mL) and followed by pentane (5 mL) and drying in high vacuum, giving $Pt_{0.15}Ga_{0.10}\_Si_{0.31}/C_{grafted}$.

$Pt_{0.15}Ga_{0.10}\_Si_{0.31}/C_{grafted}$ was then subjected to a hydrogen flow treatment at 600 °C (300 °C/h ramp) and 1 bar of hydrogen for 12 hours, followed by evacuation under high vacuum to give $Pt_{0.15}Ga_{0.10}\_Si_{0.31}/C_{H2}$, which was stored in a glovebox.

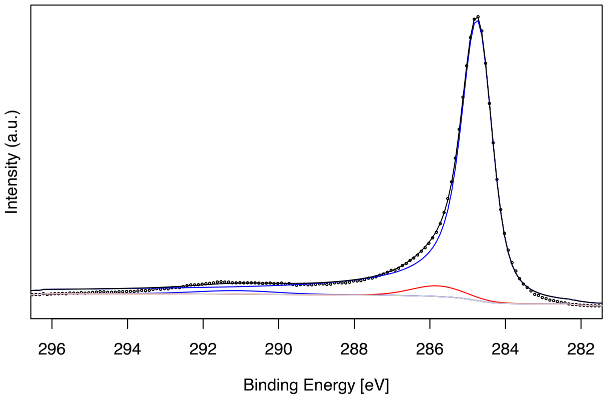
XPS Studies

XPS analysis was performed using the SIGMA II instrument equipped with an Al/Mg twin anode. The vacuum in the chamber was around 5x10^{-8} mbar during measurements. The analyses were carried out with a Mg-Kα source (energy = 1286.6 eV, 0.1 eV step size) in LAXPS mode with a pass energy of 16 eV. The curve-fitting was performed with Shirley background and line shape GL(30). C1s was used for referencing at 284.8 eV. RSFs were used to allow for semi-quantitative analysis of surface species.

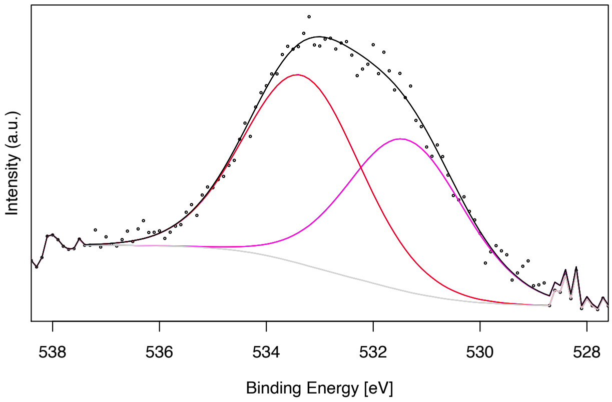


C 1s	Species
284.8	C-C
285.2	C sp^3
285.6	C-O

Figure S1. C 1s XPS spectrum of untreated mesoporous carbon as received from Sigma Aldrich.



C 1s	Species
284.8	C-C
285.8	C-O



O 1s	Species
531.4	OH
533.3	C=O

Figure S2. C 1s (*top*) and O 1s (*bottom*) XPS spectra of HNO_3-treated mesoporous carbon.

N_2 Adsorption Isotherm

Nitrogen adsorption isotherms were recorded on a Bel-Mini apparatus (BEL Japan, Inc.) at 77 K. Approximately 100 mg of the sample were loaded into the cells. Prior to the adsorption measurement, the samples coming from the glovebox, were evacuated under vacuum (ca. 10^{-3} mbar) at R.T. for 1 h. Data were fitted according to a BET theory to obtain the specific surface area.

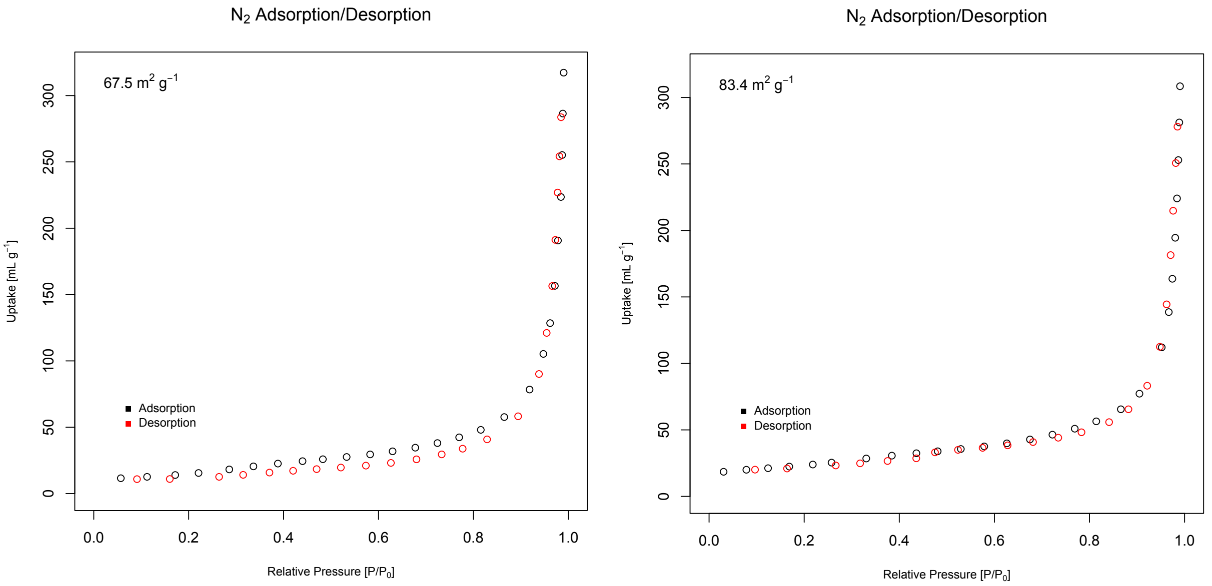


Figure S3. N_2 Adsorption isotherms of C before (*left*) and after (*right*) HNO_3 oxidative treatment.

Catalytic Propane Dehydrogenation Studies

Catalytic tests were performed utilizing a quartz flow reactor designed in our laboratories and a heating/flow setup designed and produced by Micromeritics Instrument Cooperation (PID Eng & Tech). Catalyst samples were loaded into quartz tubular reactor in an Ar filled glovebox. Prior to exposing the catalyst to flow conditions, a bypass was purged for 20 min with Ar (40 mL/min). The samples were then heated to 550 °C utilizing a tubular furnace under a flow of Ar (40 mL/min) and the temperature was maintained until fully stabilized. The propane containing gas mixture was subsequently mixed and purged through a bypass for 20 min at the desired flow rate for the reaction prior to contact with the catalyst. Reaction temperatures were maintained utilizing a quartz encased thermocouple maintained in contact with the catalyst dispersed in SiC to yield a total weight of ~2.5 g. The output gas composition was analysed automatically by a GC with a flame ionization detector (FID) which was programmed to sample the gas stream every 9 minutes throughout the time of reaction. Gases were purified by passing through a column with molecular sieves and Q5 catalyst prior to introduction to the flow reactor. Propane conversion, selectivity and the carbon balance were calculated according to following equations:

Conversion:

$$X_{C_3H_8} = 1 - \frac{n_{C_3H_8,out}}{n_{C_3H_8,out} + n_{C_3H_6,out} + n_{C_2H_6,out}/1.5 + n_{C_2H_4,out}/1.5 + n_{CH_4,out}/3}$$

Selectivity:

$$S = \frac{n_{i,out} * \#Carbonatoms/3}{n_{C_3H_8,out} + n_{C_3H_6,out} + n_{C_2H_6,out} * 2/3 + n_{C_2H_4,out} * 2/3 + n_{CH_4,out}/3}$$

Carbon Balance:

$$Carbon\ Balance = \frac{n_{C_3H_8,in}}{n_{C_3H_8,out} + n_{C_3H_6,out} + n_{C_2H_6,out} + n_{C_2H_4,out} + n_{CH_4,out}}$$

Deactivation constant:

$$k_D = \frac{\ln\left(\frac{1 - conv_{end}}{conv_{end}}\right) - \ln\left(\frac{1 - conv_{start}}{conv_{start}}\right)}{t}$$

Standard PDH conditions: 550 °C, 50 ml/min, 1 bar, 1:4 C_3H_8/Ar for varying times.

The catalytic activity of $Pt_{0.68}\_Si_{0.1}/C_{H2}$, $Pt_{0.60}/C_{H2}$, $Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{H2}$ and $Pt_{0.26}Ga_{0.10}/C_{H2}$ in the dehydrogenation of propane are summarized in Figure S32. For a typical catalytic test, varying amounts of catalyst (61.9 mg $Pt_{0.68}\_Si_{0.1}/C_{H2}$, 51.8 mg $Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{H2}$,124.1 mg $Pt_{0.60}/C_{H2}$ or 118.4 mg $Pt_{0.26}Ga_{0.10}/C_{H2}$) were used while maintaining identical gas composition and flow rate with a flow of 50 mL/min with 1:4 C_3H_8/Ar (any ratios of gases given is in volume ratio). In all cases conversions below equilibrium are achieved. The flow rates, temperatures and pressures used during the different catalytic tests are summarized in the following. Standard PDH conditions: 550 °C, 50 ml/min, 1 bar, 1:4 C_3H_8/Ar (v:v) for varying times.

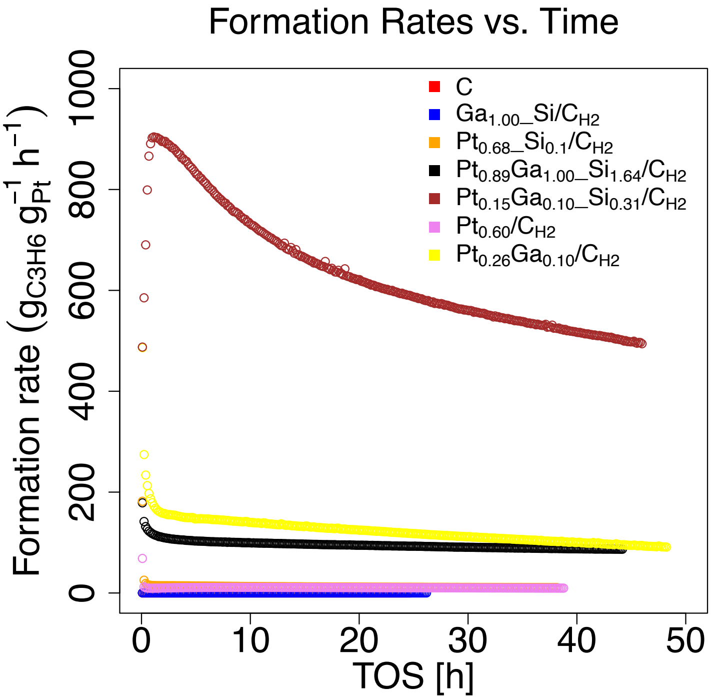


Figure S4. Formation rates as a function of time on stream (TOS) of

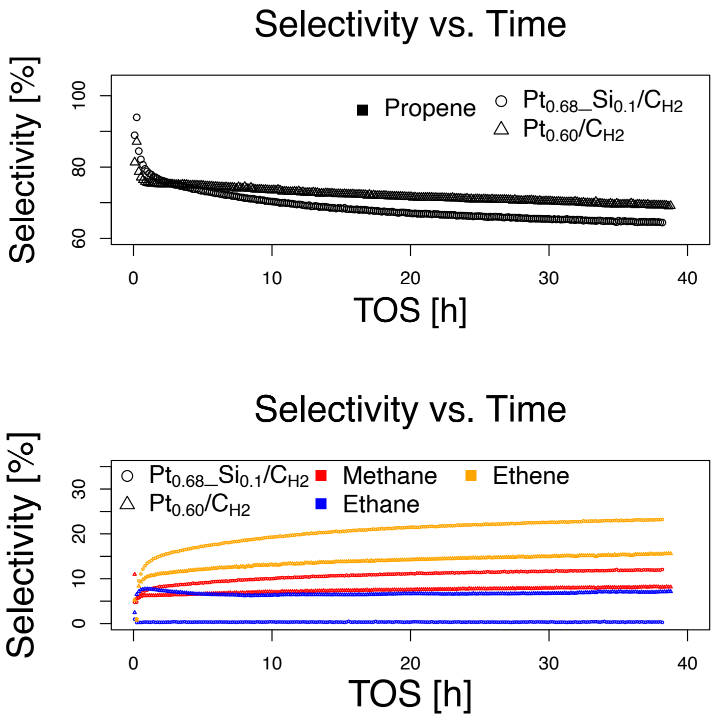


Figure S5. Product selectivities as a function of time on stream (TOS) of $Pt_{0.68}\_Si_{0.1}/C_{H2}$ and $Pt_{0.60}/C_{H2}$ catalysts.

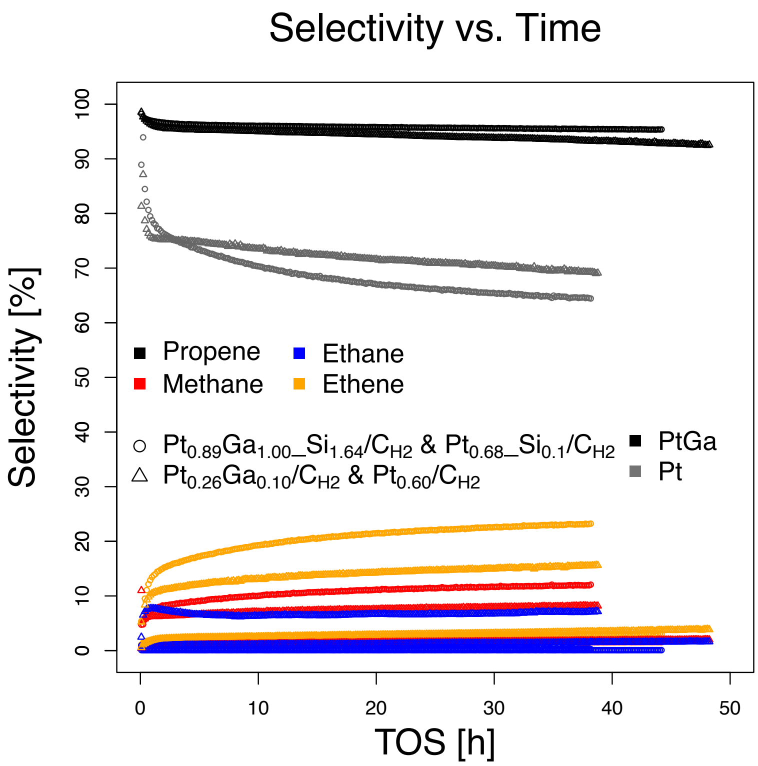


Figure S6. Product selectivities as a function of time on stream (TOS) of $Pt_{0.60}/C_{H2}$, $Pt_{0.68}\_Si_{0.1}/C_{H2}$, $Pt_{0.26}Ga_{0.10}/C_{H2}$ and $Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{H2}$ catalysts.

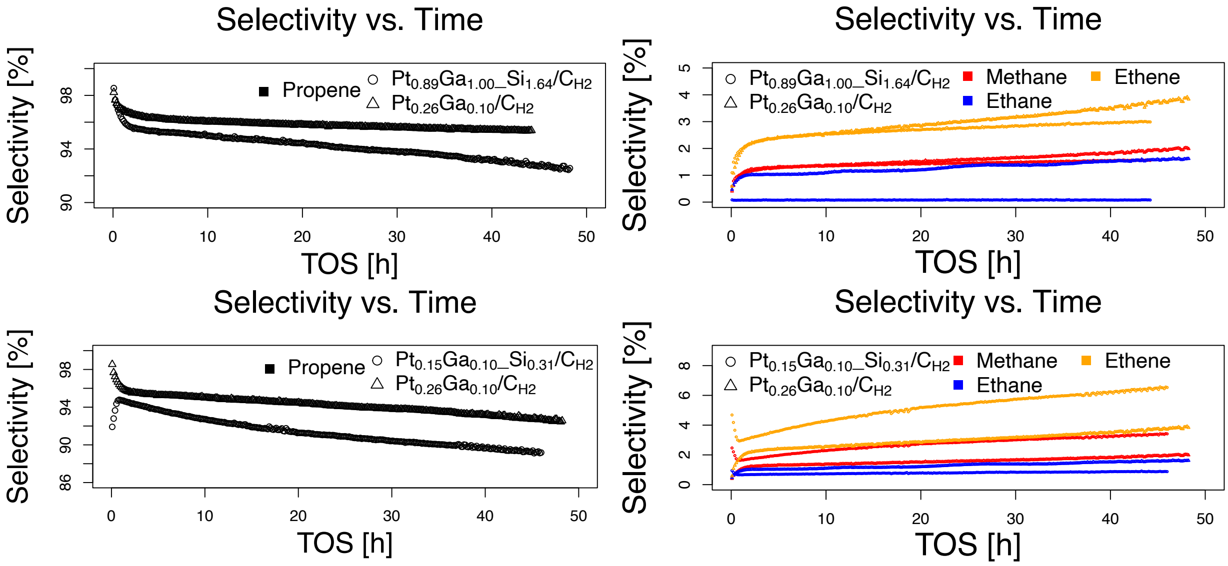


Figure S7. Product selectivities as a function of time on stream (TOS) of $Pt_{0.26}Ga_{0.10}/C_{H2}$, $Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{H2}$ and $Pt_{0.15}Ga_{0.10}\_Si_{0.31}/C_{H2}$ catalysts.

XAS Studies

XAS measurements were carried out at the Ga K-edge and Pt L_3-edge at the SuperXAS beamline at SLS (PSI, Villigen, Switzerland). The storage ring was operated at 2.4 GeV in top-up mode with a ring current of around 400 mA. The incident photon beam provided by a 2.9 T superbend magnet was selected by a Si(111) quick-EXAFS monochromator and the rejection of higher harmonics and focusing were achieved by a rhodium-coated collimating mirror at 2.5 mrad and a rhodium-coated torroidal mirror at 2.5 mrad. The beam size on the sample was 100 x 100 µm. During measurements, the monochromator was rotating with 1 Hz frequency in 2 deg angular range and X-ray absorption spectra were collected in transmission mode using ionization chambers specially developed for quick data collection with 1 MHz frequency.[7] The spectra were collected for 3 min and averaged. The beamline energy was calibrated with the Pt reference foil to the Pt L_3-edge position at 11564.0 eV. To avoid contact with air, all samples were sealed in a glovebox. For ex situ samples, pressed pellets (with optimized thickness for transmission detection) were placed in two aluminized plastic bags (Polyaniline (15 µm), polyethylene (15 µm), Al (12 µm), polyethylene (75 µm) from Gruber-Folien GmbH & Co. KG, Straubing, Germany) using an impulse sealer inside a glovebox; one sealing layer was removed immediately before the measurements. For in-situ measurements, catalyst beds of appropriate mass were supported with quartz wool in 3 mm quartz capillaries. Gas flow and composition were controlled using Bronkhorst mass flow controllers and a back-pressure regulator. Flow rates during H_2 reduction were maintained at 10 ml/min with a pressure of 1 atmosphere. Ar and H_2 were purified by passing through a column with molecular sieves and Q5 catalyst prior to introduction to the XAS quartz cell. Data processing was done by standard procedures using the ProXASGui software developed at the SuperXAS beamline, PSI, Villigen. The program package Demeter was used for data analysis.[8]

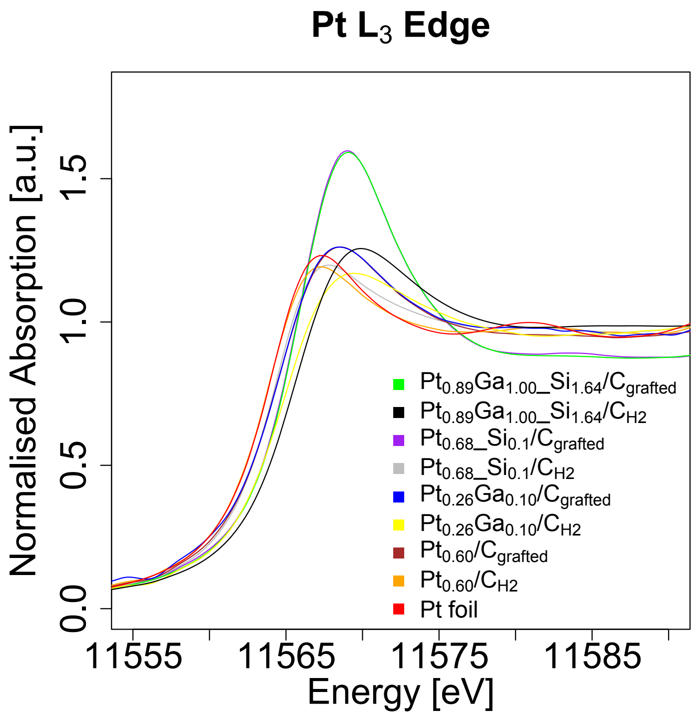


Figure S8. *Ex situ* Pt L_3-Edge XANES spectra of all prepared Pt catalysts and Pt foil reference.

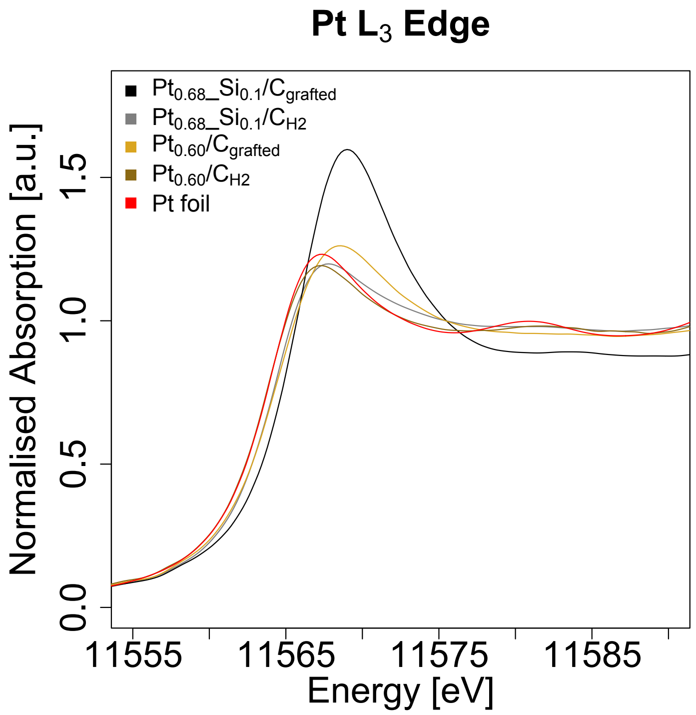


Figure S9. *Ex situ* Pt L_3-Edge XANES spectra of monometallic Pt catalysts and Pt foil reference.

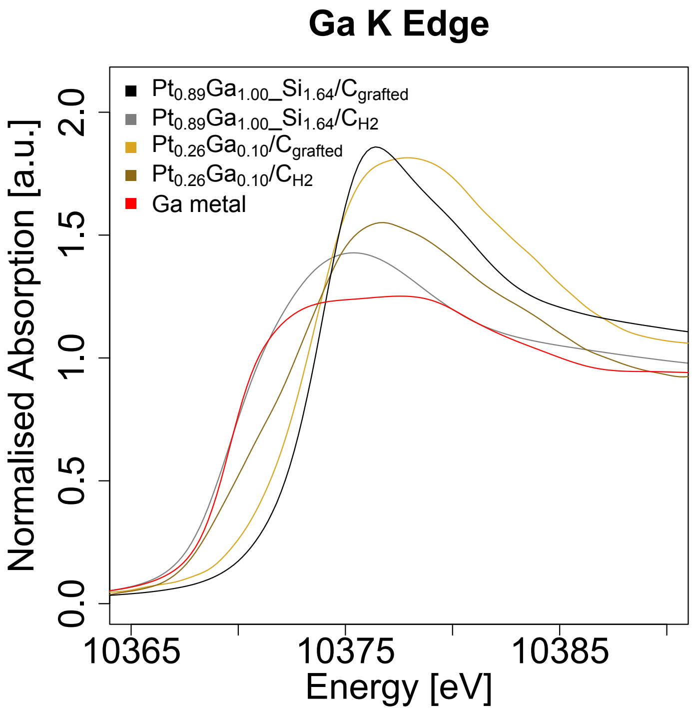


Figure S10. *Ex situ* Ga K-Edge XANES spectra of $Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{grafted}$, $Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{H2}$, $Pt_{0.26}Ga_{0.10}/C_{grafted}$, $Pt_{0.26}Ga_{0.10}/C_{H2}$ catalysts and Ga metal reference.

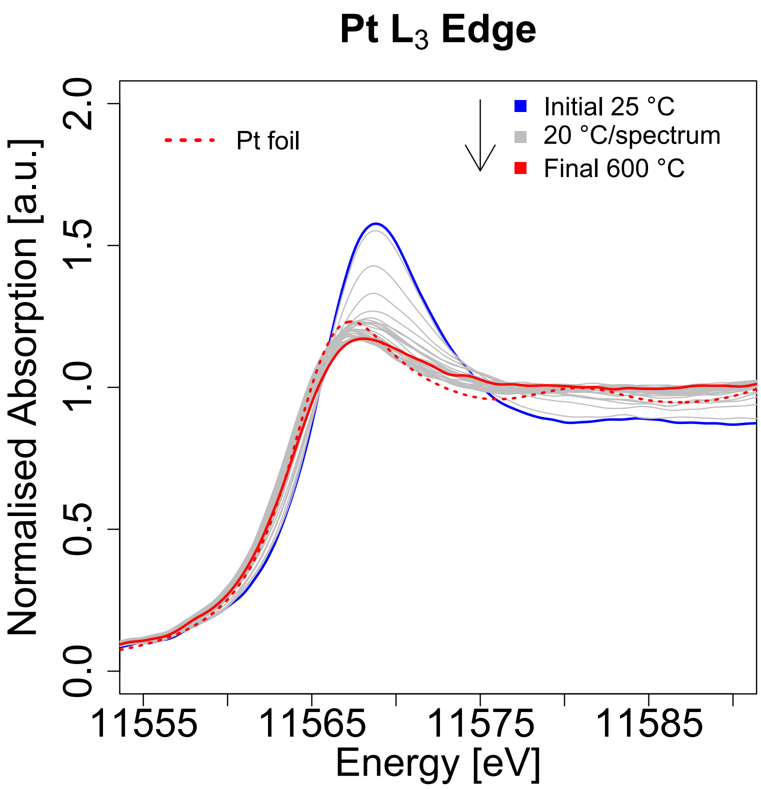


Figure S11. *In situ* Pt L_3-Edge XANES spectra of $Pt_{0.68}\_Si_{0.1}/C_{grafted}$ under a flow of 1 barg of H_2 (10 mL/min) and a temperature range of 25 °C to 600 °C.

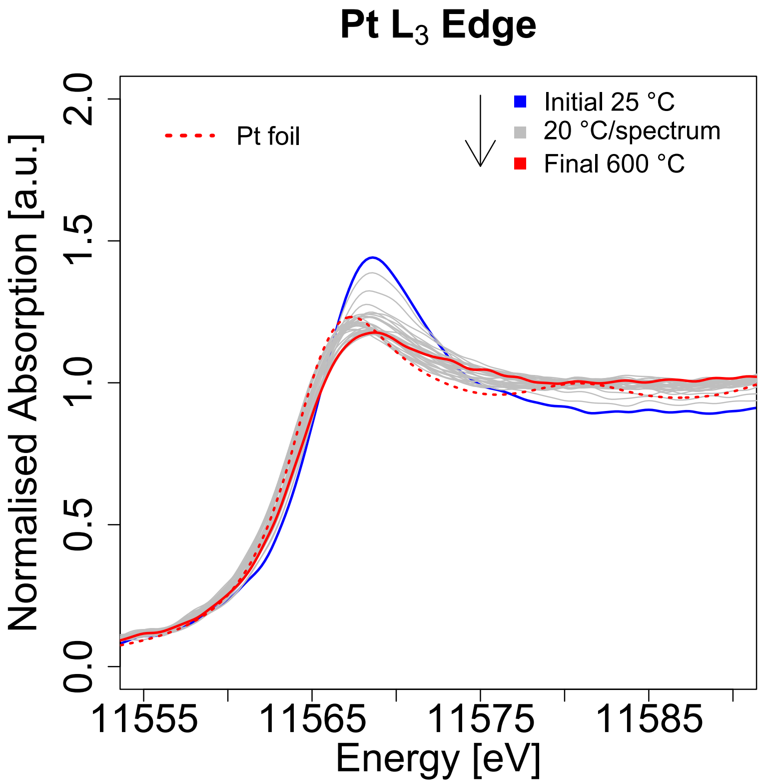


Figure S12. *In situ* Pt L_3-Edge XANES spectra of $Pt_{0.60}/C_{grafted}$ under a flow of 1 barg of H_2 flow (10 mL/min) and a temperature range of 25 °C to 600 °C.

Ex Situ (S)TEM & STEM-EDS Studies

TEM and STEM measurements were recorded on a double C_S corrected JEOL JEM-ARM300F Grand ARM "Vortex" (scanning) transmission electron microscope operated at accelerating voltages of 200 or 300 kV. Ga containing samples were dry casted as solid onto 200 mesh 5 nm thick C QUANTIFOIL copper grids in an Argon glovebox and mounted on a vacuum transfer holder (GATAN, MeI-Build).

$Pt_{0.68}$_$Si_{0.1}$/$C_{grafted}$

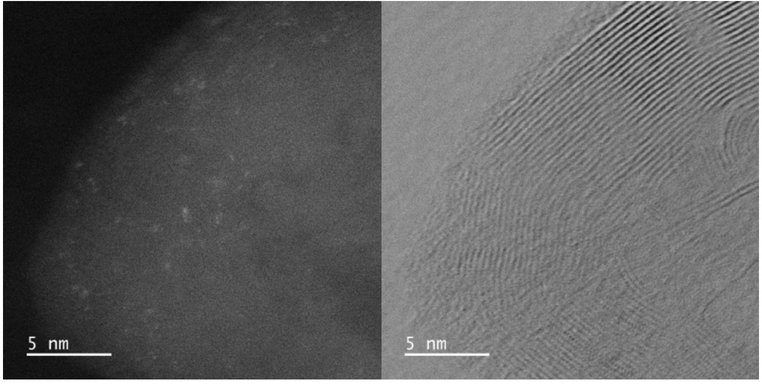


Figure S13. HAADF- (*left*) and ABF-STEM (*right*) images of $Pt_{0.68}$_$Si_{0.1}$/$C_{grafted}$.

$Pt_{0.68}\_Si_{0.1}/C_{H2}$

Fresh Catalyst

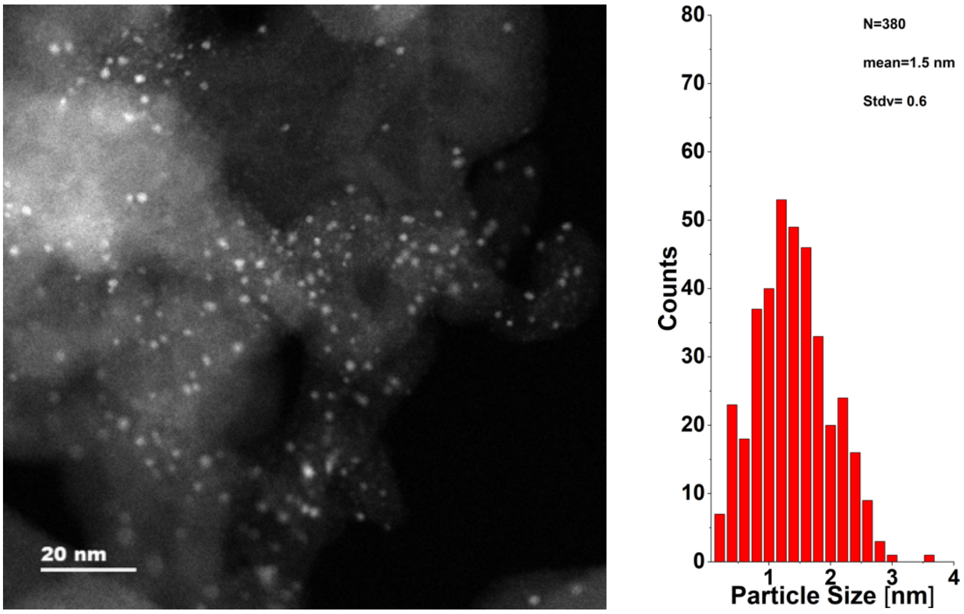


Figure S14. HAADF-STEM image of $Pt_{0.68}\_Si_{0.1}/C_{H2}$ (*left*) and particle size distribution (*right*).

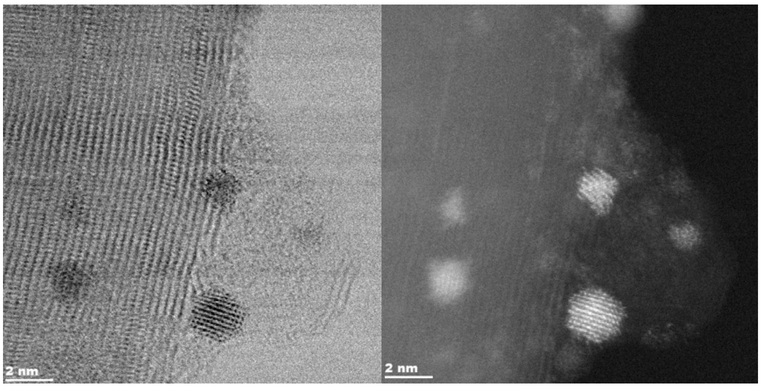


Figure S15. ABF (*left*) and HAADF-STEM (*right*) images of $Pt_{0.68}\_Si_{0.1}/C_{H2}$.

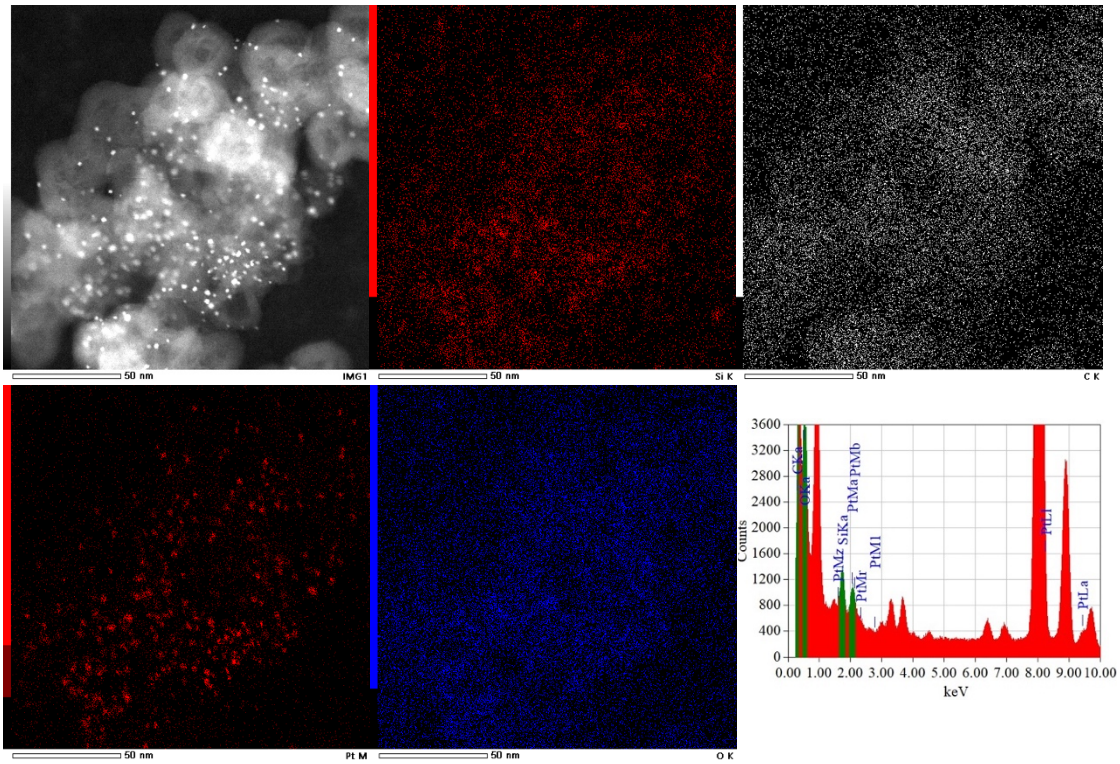


Figure S16. HAADF-STEM EDS maps and spectrum of $Pt_{0.68}\_Si_{0.1}/C_{H2}$.

Table S1. Quantification of STEM-EDS spectrum of $Pt_{0.68}\_Si_{0.1}/C_{H2}$.

Element	Energy (keV)	Mass%	Counts	Atom%
C K	-	n.q.	n.q.	n.q.
O K	0.525	45.72	19368	78.74
Si K	1.739	16.19	11567	15.88
Pt M	2.048	38.10	7142	5.38

Spent Catalyst

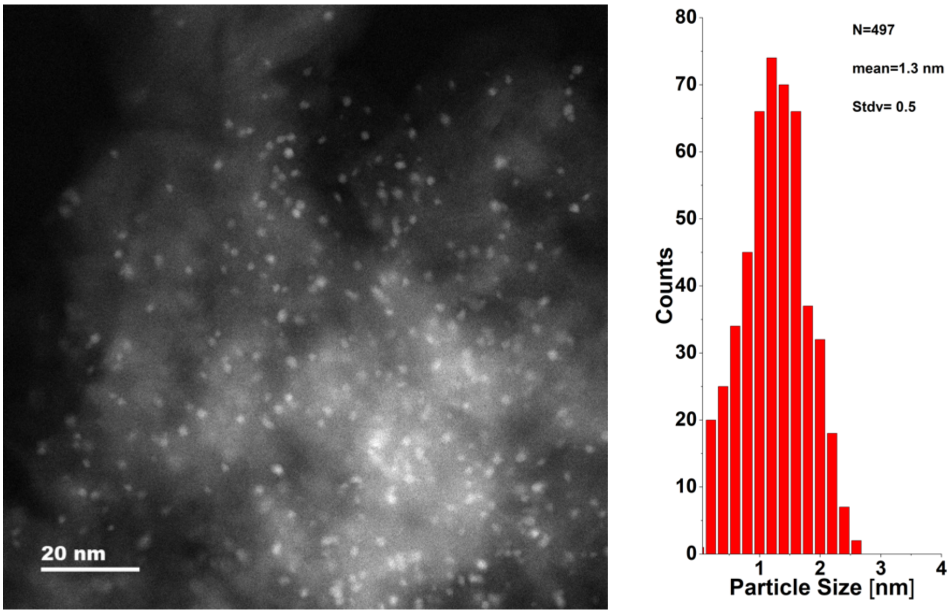


Figure S17. HAADF-STEM image of $Pt_{0.68}$_$Si_{0.1}/C_{H2}$ after catalysis (*left*) and particle size distribution (*right*).

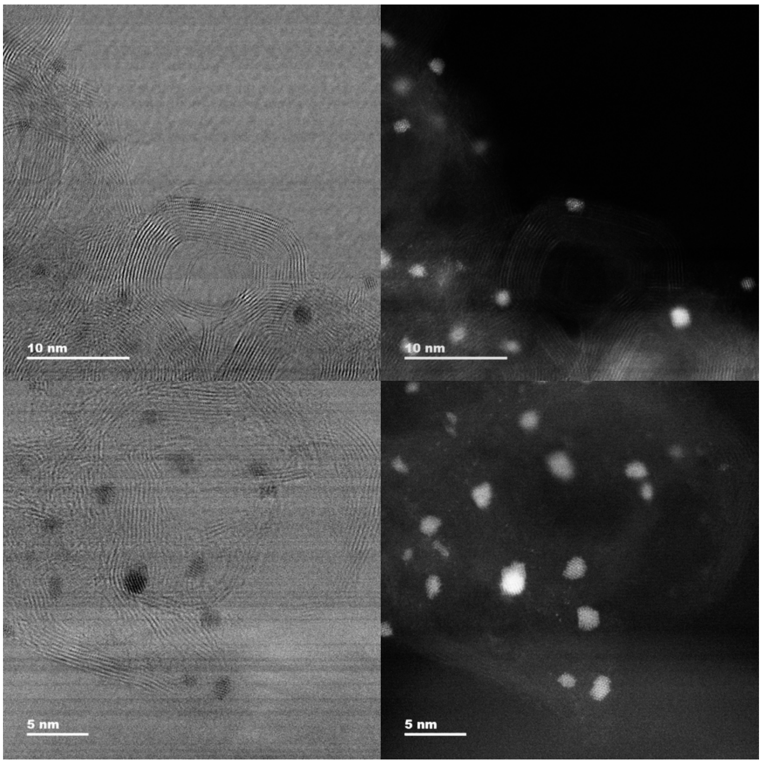


Figure S18. ABF (*left*) and HAADF-STEM (*right*) images of $Pt_{0.68}$_$Si_{0.1}/C_{H2}$ after catalysis.

$Pt_{0.60}/C_{H2}$

Fresh Catalyst

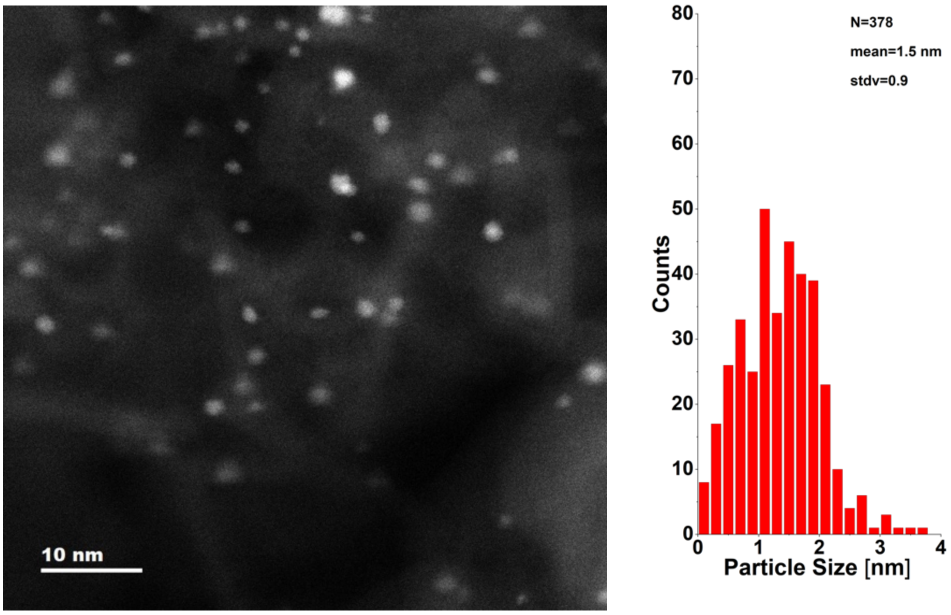


Figure S19. HAADF-STEM image of $Pt_{0.60}/C_{H2}$ (*left*) and particle size distribution (*right*).

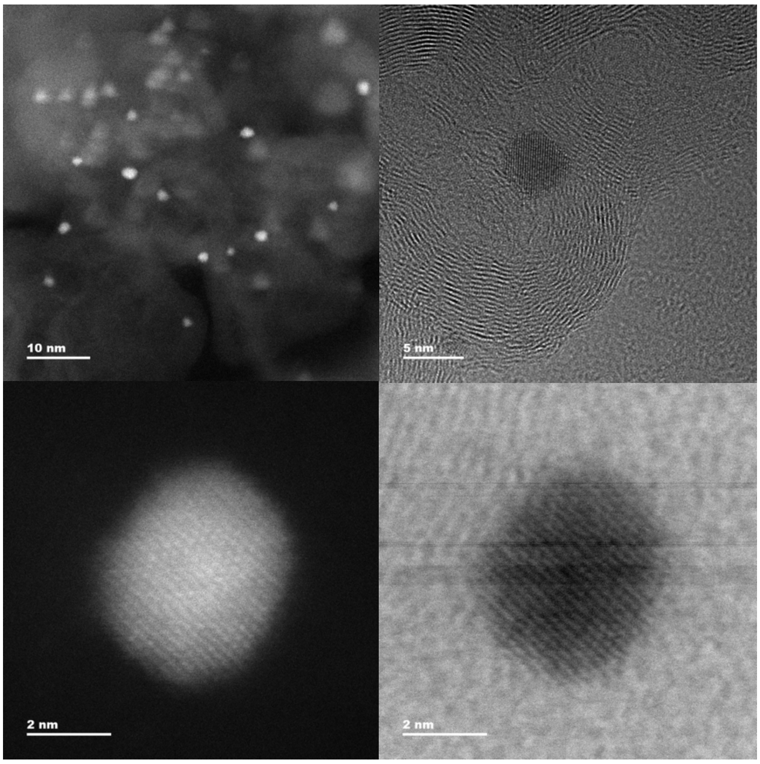


Figure S20. ABF (*bottom, right*) & HAADF-STEM (*left*) and TEM (*top, right*) images of $Pt_{0.60}/C_{H2}$.

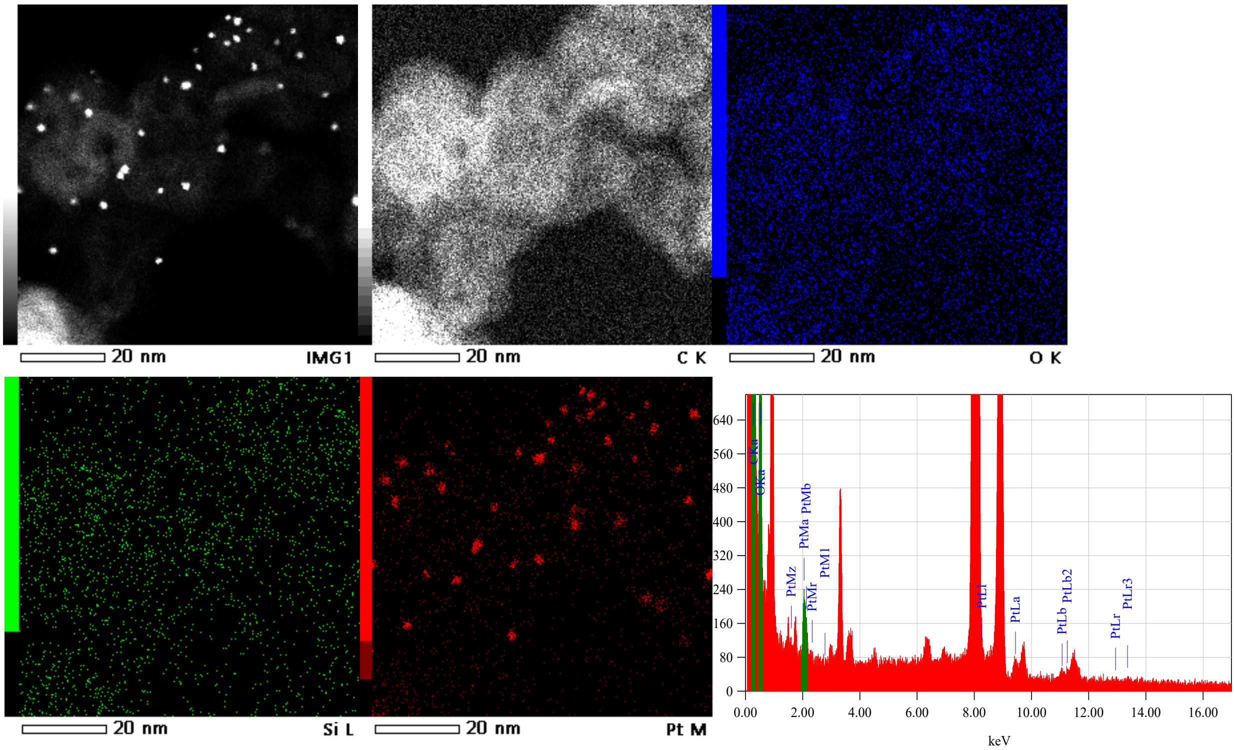


Figure S21. HAADF-STEM EDS maps and spectrum of $Pt_{0.60}/C_{H2}$.

Table S2. Quantification of STEM-EDS spectrum of $Pt_{0.60}/C_{H2}$.

Element	Energy (keV)	Mass%	Counts	Atom%
C K	0.277	98.32	300487	99.02
O K	0.525	1.26	7560	0.96
Si L	1.739	n.d.	n.d.	n.d.
Pt M	2.048	0.41	1425	0.03

Spent Catalyst

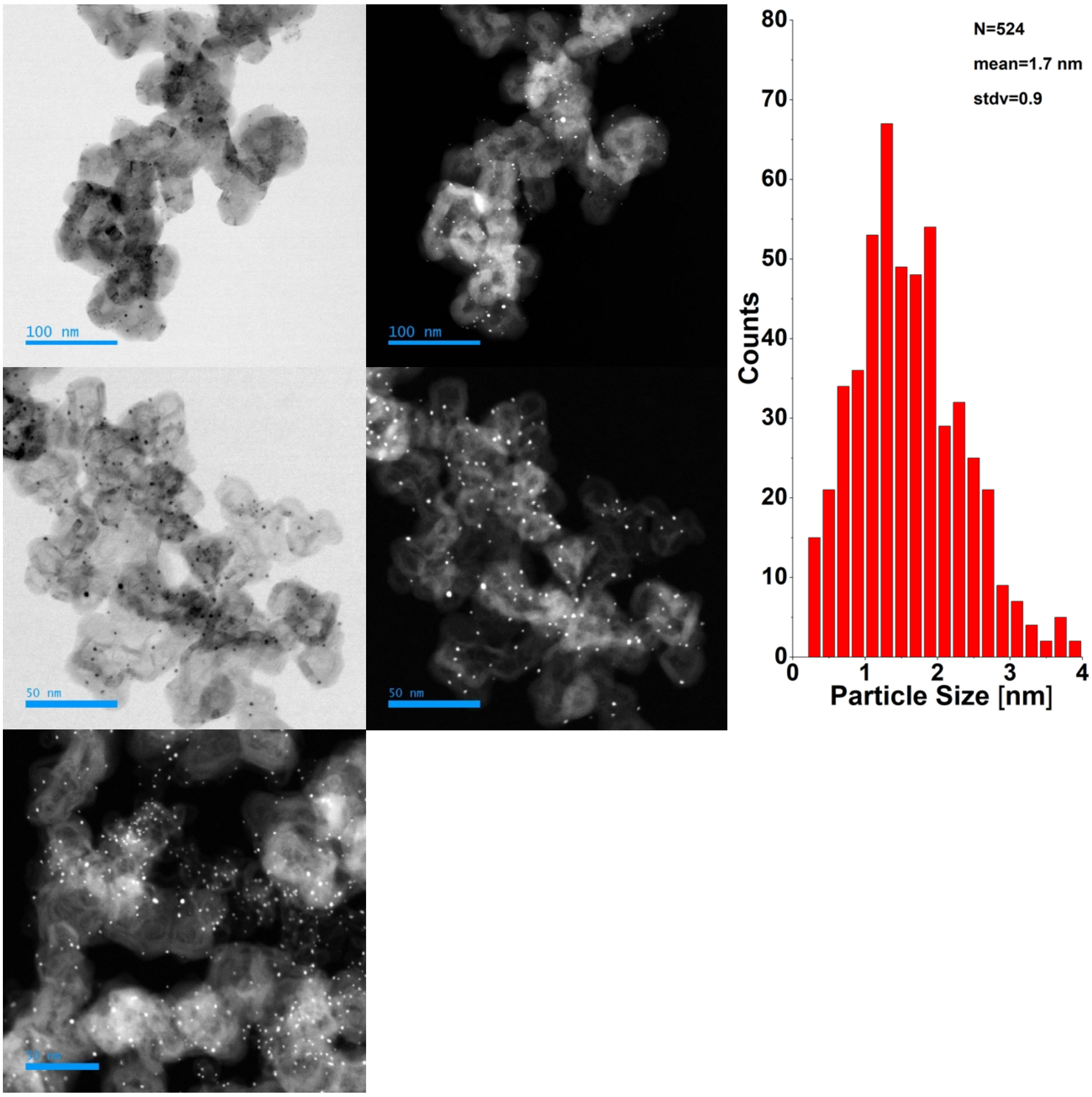


Figure S22. HAADF- and ABF STEM image of $Pt_{0.60}/C_{H2}$ after catalysis and particle size distribution.

$Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{H2}$

Fresh Catalyst

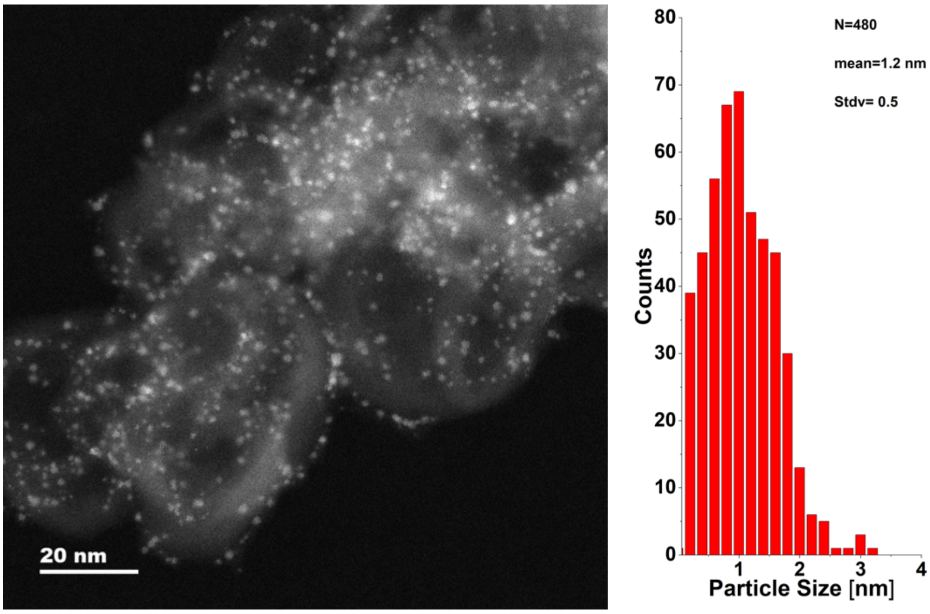


Figure S23. HAADF-STEM image of $Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{H2}$ (*left*) and particle size distribution (*right*).

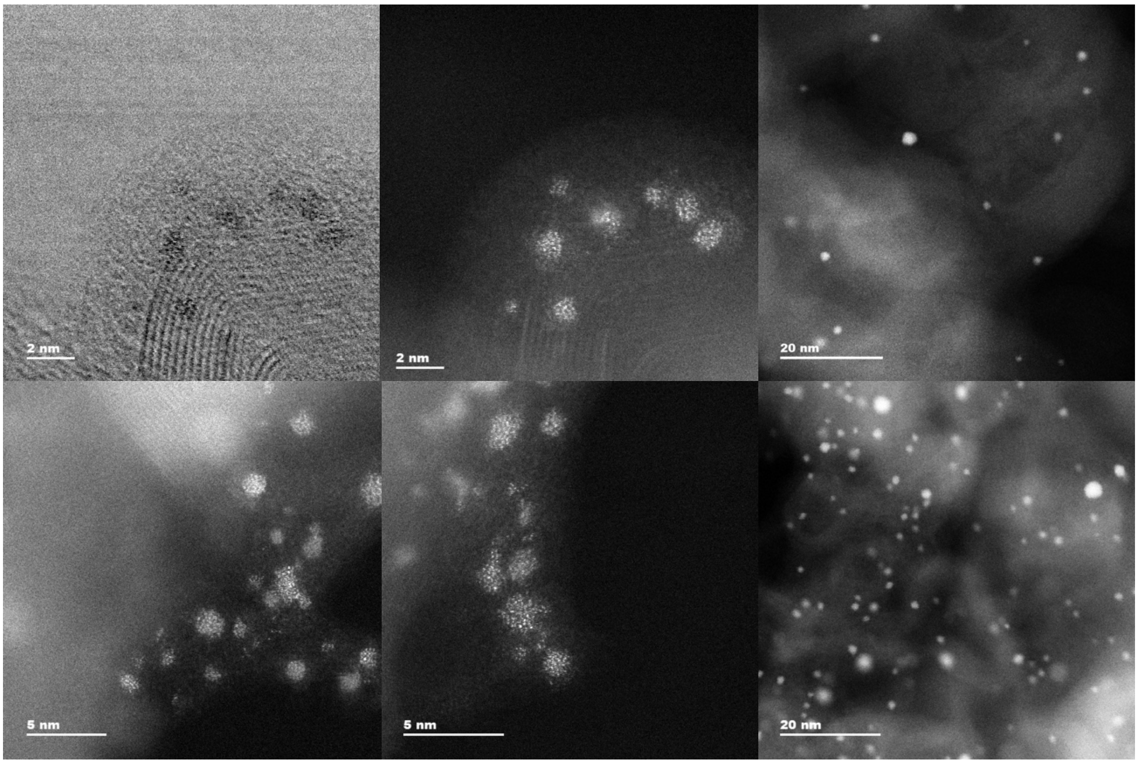


Figure S24. ABF (*top, left*) and HAADF-STEM (*rest*) images of $Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{H2}$.

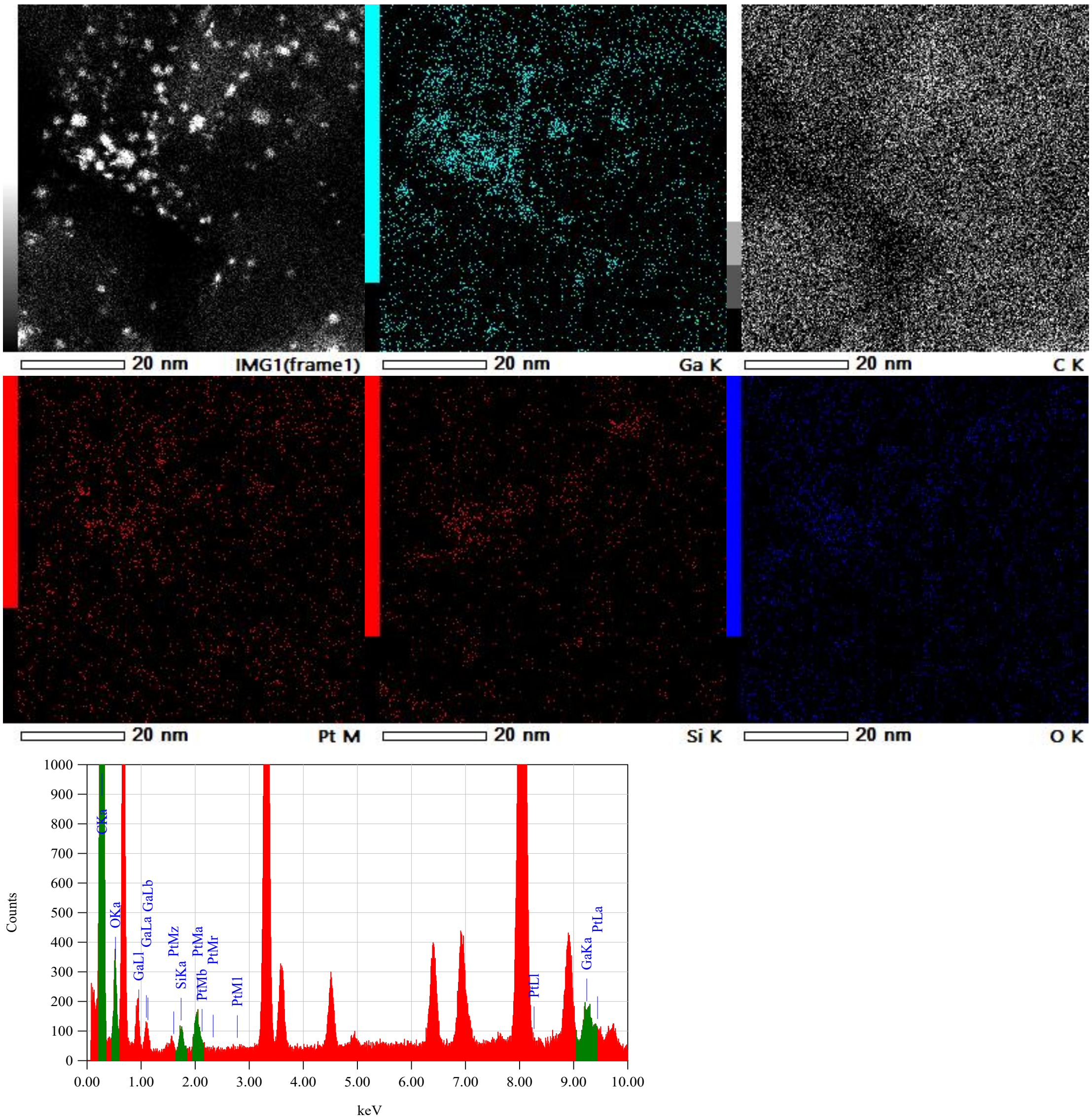


Figure S25. HAADF-STEM EDS maps and spectrum of Pt$_{0.89}$Ga$_{1.00}$_Si$_{1.64}$/C$_{H2}$.

Table S3. Quantification of STEM-EDS spectrum of Pt$_{0.89}$Ga$_{1.00}$_Si$_{1.64}$/C$_{H2}$.

Element	Energy (keV)	Mass%	Counts	Atom%
C K	0.277	94.28	48862	97.94
O K	0.525	1.75	2180	1.37
Si K	1.739	0.32	745	0.14
Pt M	2.048	0.87	2896	0.50
Ga L	1.098	2.78	530	0.06

Spent Catalyst

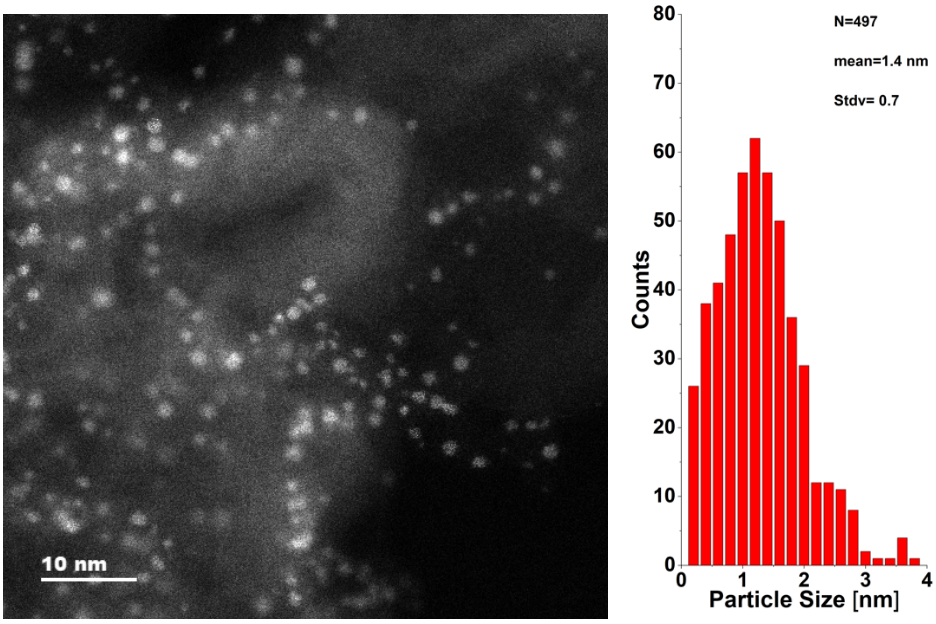


Figure S26. HAADF-STEM image of $Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{H2}$ after catalysis (*left*) and particle size distribution (*right*).

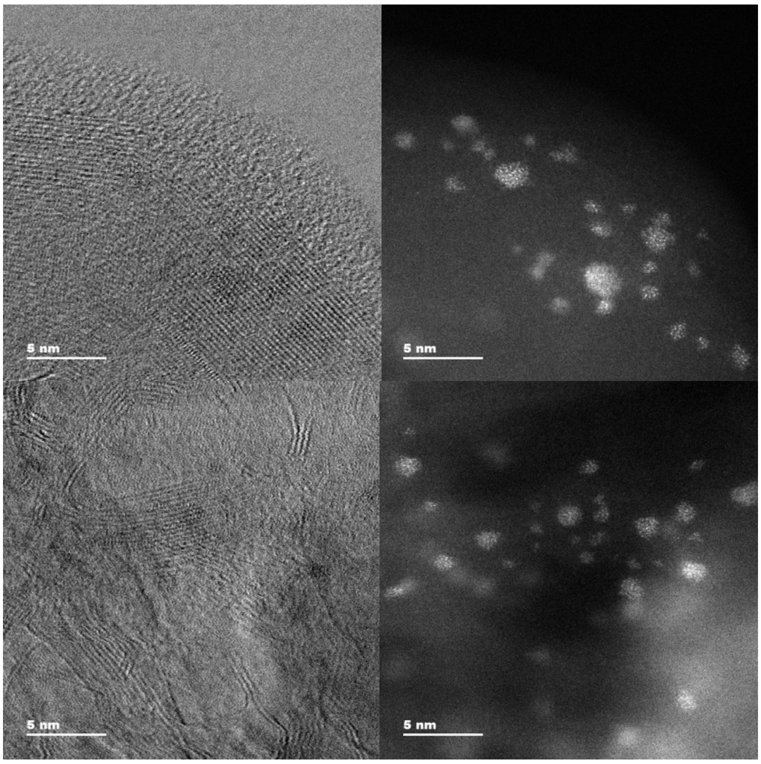
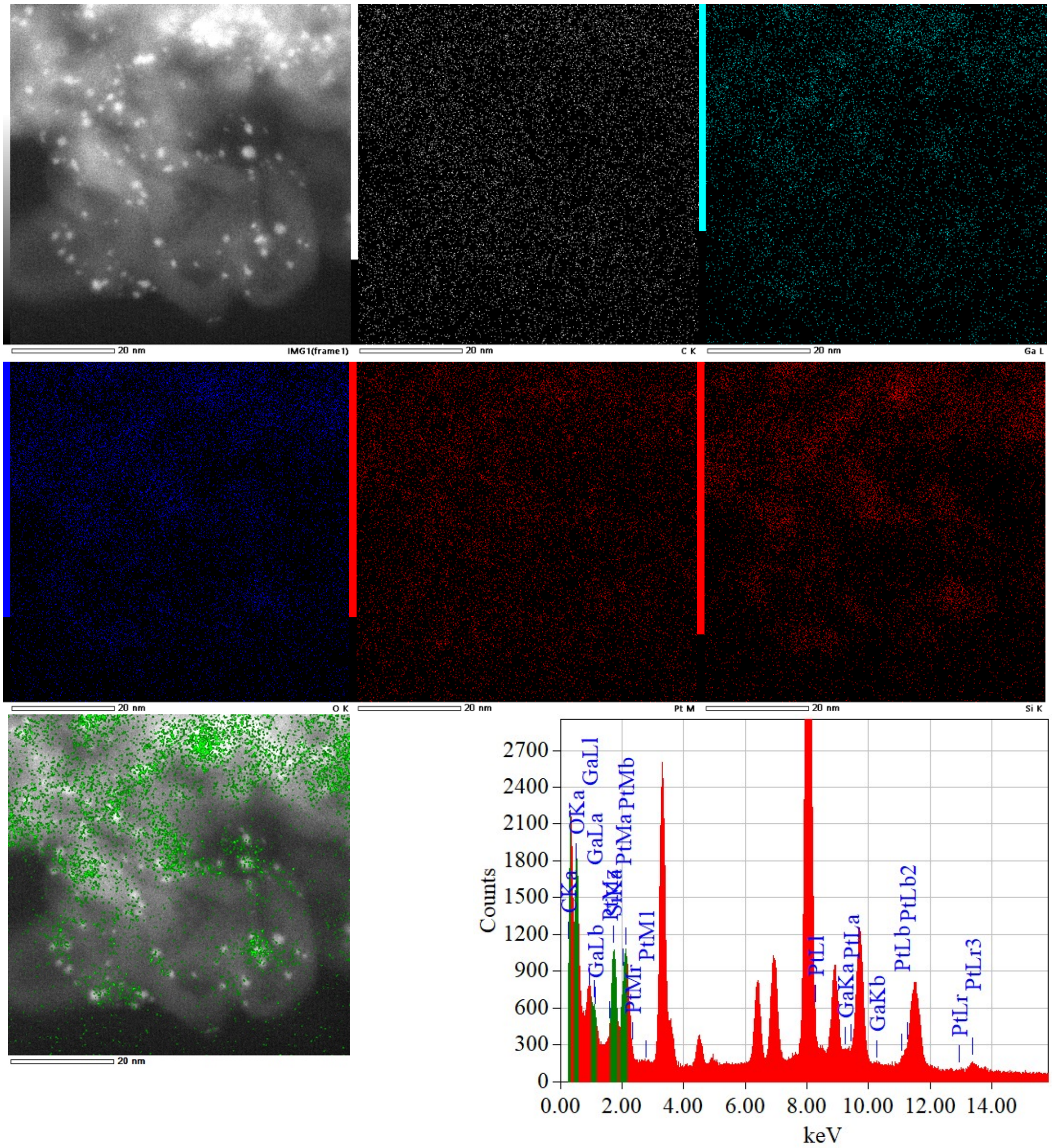


Figure S27. ABF (*left*) & HAADF-STEM (*right*) images of $Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{H2}$ after catalysis.



FigureS28. HAADF-STEM EDS maps and spectrum of $Pt_{0.89}Ga_{1.00}$_$Si_{1.64}$/C_{H2} after catalysis.

Table S4. Quantification of STEM-EDS spectrum of $Pt_{0.89}Ga_{1.00}\_Si_{1.64}/C_{H2}$ after catalysis.

Element	Energy (keV)	Mass%	Counts	Atom%
C K	0.277	2.73	412	6.96
O K	0.525	31.86	10956	60.90
Si K	1.739	20.60	11949	22.44
Pt M	2.048	35.32	5375	5.54
Ga L	1.098	9.50	1189	4.17

$Pt_{0.26}Ga_{0.10}/C_{H2}$

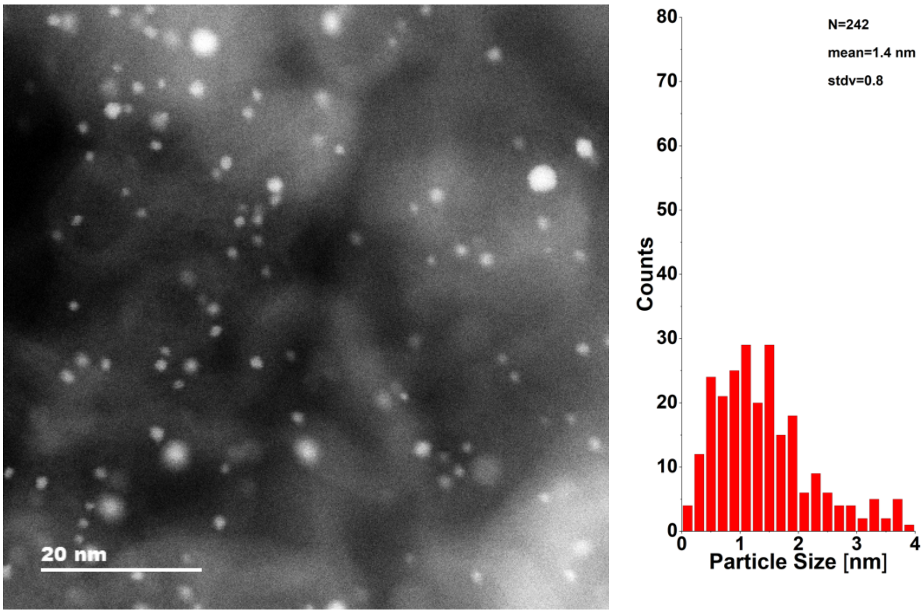


Figure S29. HAADF-STEM image (*left*) of $Pt_{0.26}Ga_{0.10}/C_{H2}$.and particle size distribution (*right*).

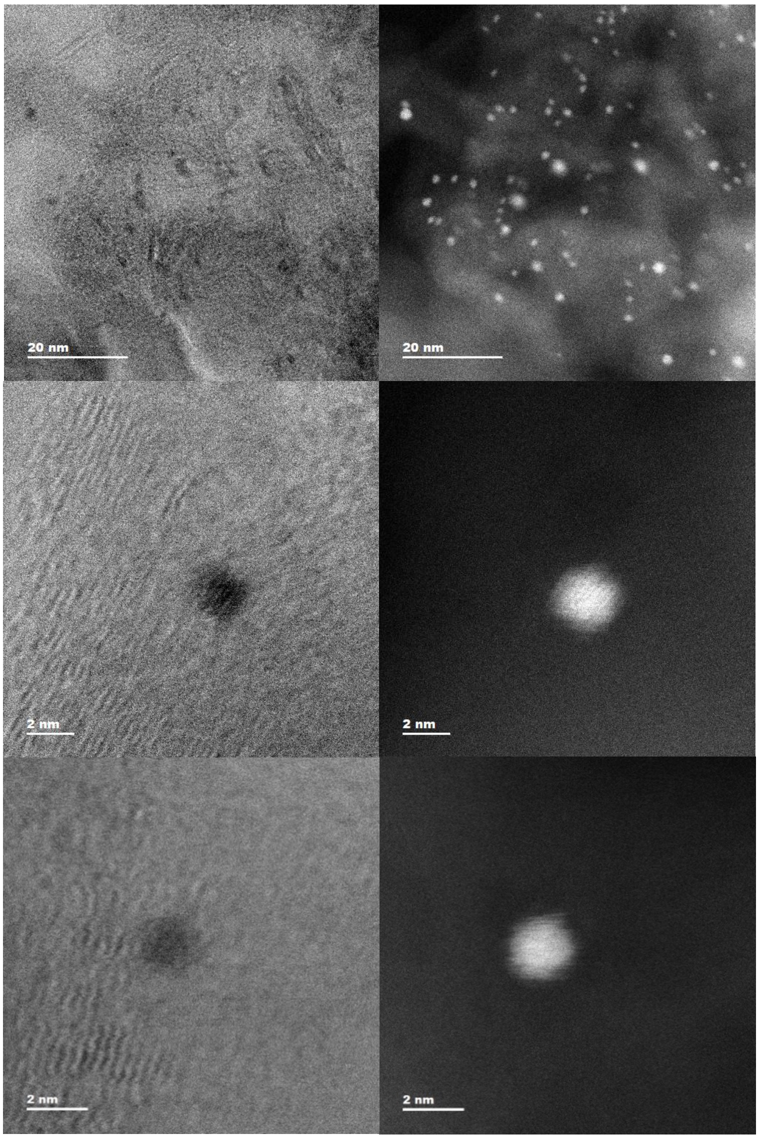


Figure S30. ABF (*left*) & HAADF-STEM (*right*) images of $Pt_{0.26}Ga_{0.10}/C_{H2}$.

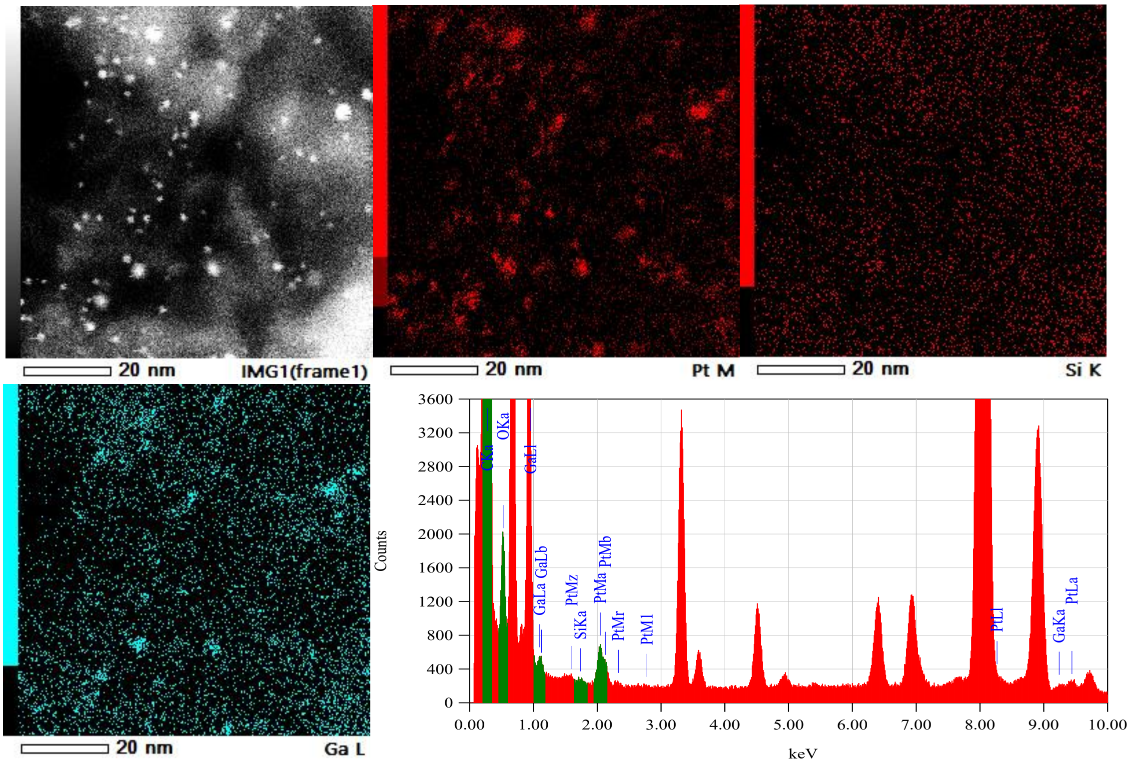


Figure S31. HAADF-STEM EDS maps and spectrum of $Pt_{0.26}Ga_{0.10}/C_{H2}$.

Table S5. Quantification of STEM-EDS spectrum of $Pt_{0.26}Ga_{0.10}/C_{H2}$.

Element	Energy (keV)	Mass%	Counts	Atom%
C K	0.277	98.83	845358	99.59
O K	0.525	0.43	8833	0.33
Si K	1.739	0.01	351	0.00
Pt M	2.048	0.38	2797	0.06
Ga L	1.098	0.35	3836	0.02

Spent Catalyst

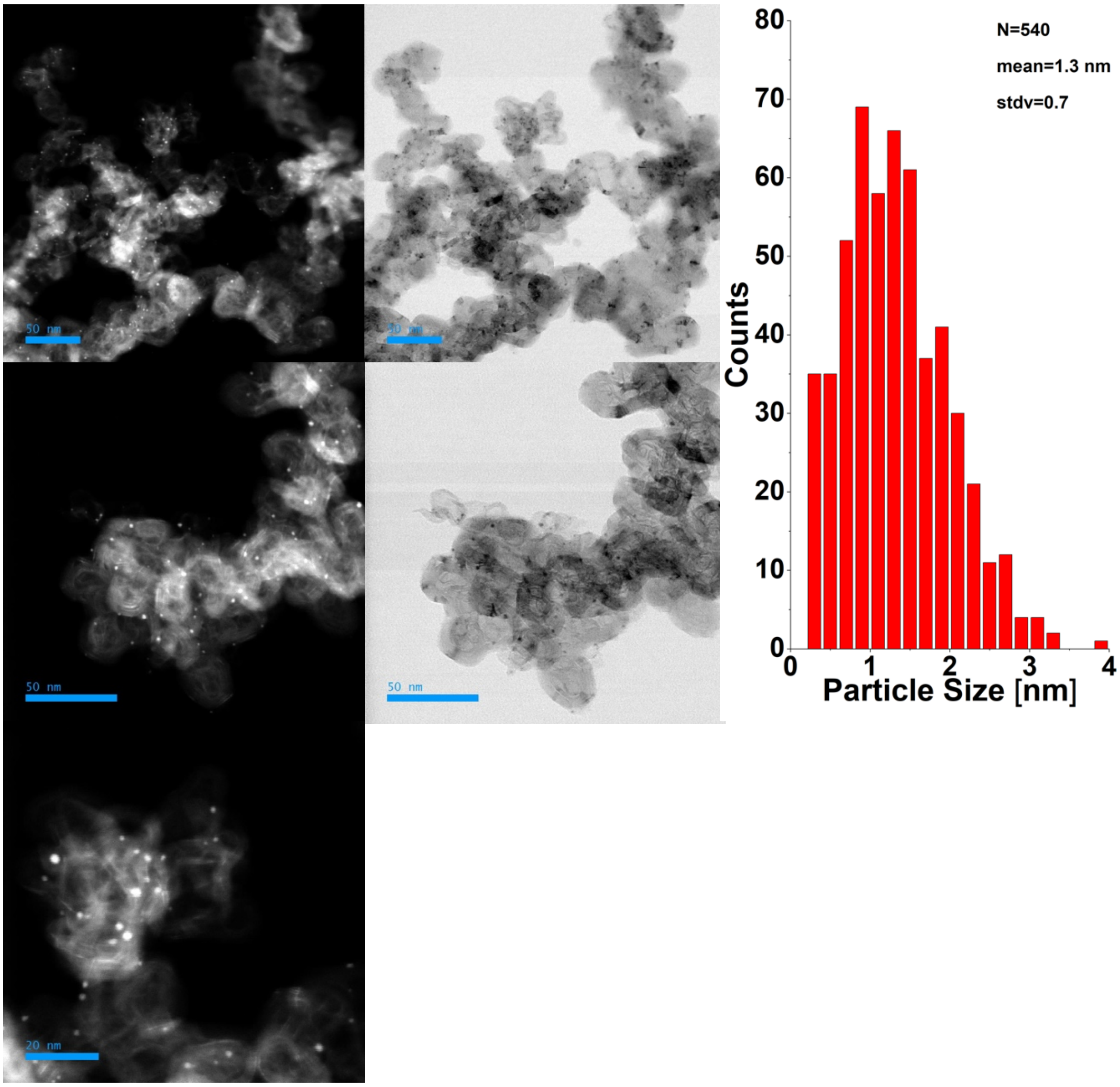


Figure S32. HAADF- and ABF STEM image of $Pt_{0.26}Ga_{0.10}/C_{H2}$ after catalysis and particle size distribution.

4D STEM Measurements

4D STEM measurements were performed on a JEOL JEM-F200 STEM microscope. The convergence-beam electron diffraction pattern at each probe position was recorded using a 4K Gatan RiO CMOS camera, operated at 160 frames per second. The camera acquisition and probe scanning were synchronized using a Gatan Digiscan3. Diffraction patterns were obtained over an area of 128×128pixels (pixel size: 0.024nmx0.024nm), with an acquisition time of 7ms and recorded in 1k resolution binned by 2. Ga containing samples were dry casted as solid onto 200 mesh 5 nm thick C QUANTIFOIL copper grids in an Argon glovebox and mounted on a vacuum transfer holder (GATAN, Mel-Build). For 4D STEM measurements, 200 mesh C QUANTIFOIL copper grids were used. All other samples were suspended in methanol by ultra-sonification and drop-casted onto 200 mesh 5 nm C QUANTIFOIL copper grids.

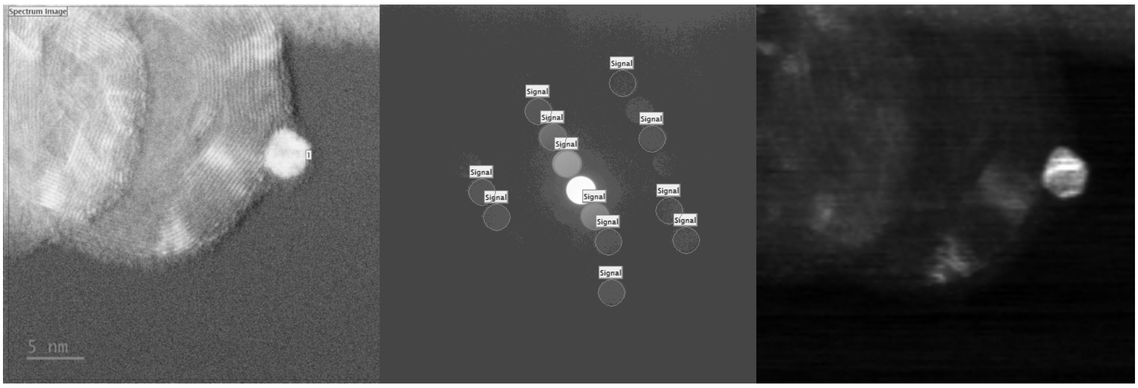


Figure S33. 4D STEM spectrum Image (*left*), diffraction pattern (*middle*) and signal (*right*) from selected diffraction disk of middle image of $Pt_{0.60}/C_{H2}$.

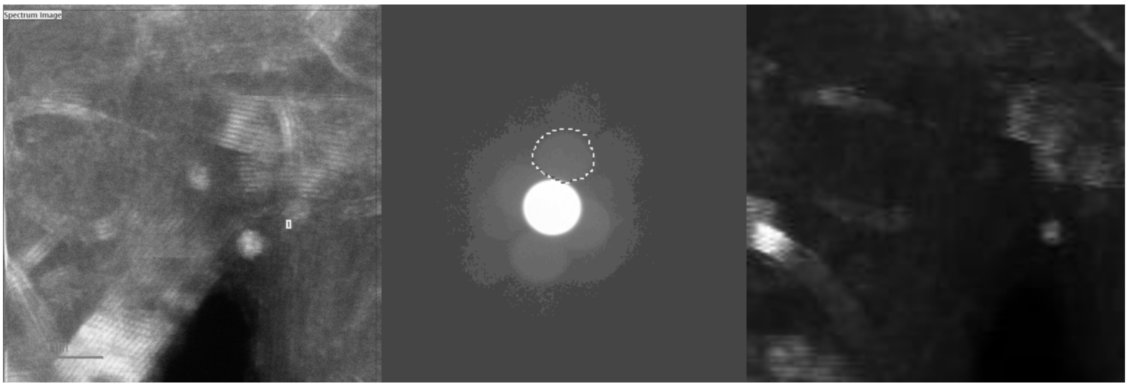


Figure S34. 4D STEM spectrum Image (*left*), diffraction pattern (*middle*) and signal (*right*) from selected diffraction disk of middle image of $Pt_{0.68}$_$Si_{0.1}/C_{H2}$.

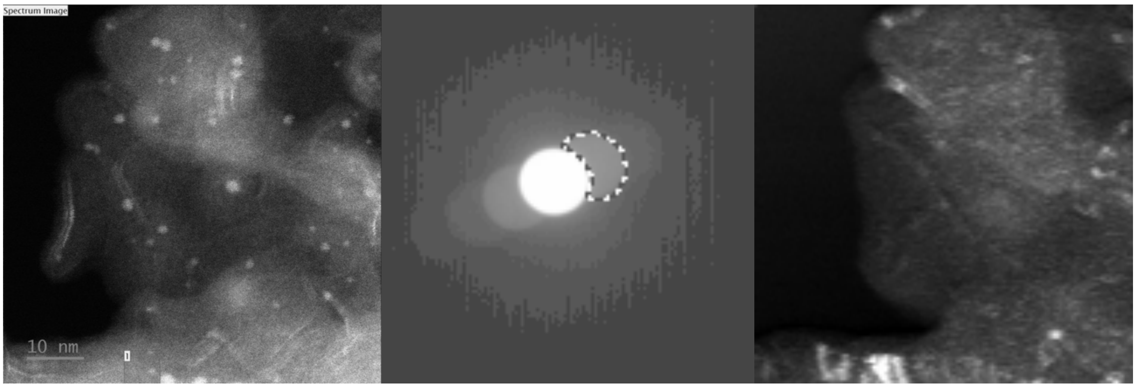


Figure S35. 4D STEM spectrum Image (*left*), diffraction pattern (*middle*) and signal (*right*) from selected diffraction disk of middle image of $Pt_{0.89}Ga_{1.00}$_$Si_{1.64}$/C_{H2}.

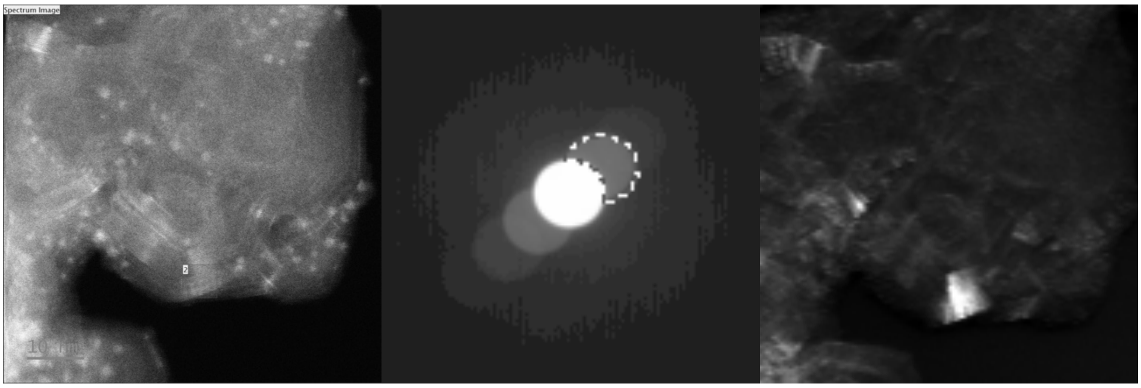


Figure S36. 4D STEM spectrum Image (*left*), diffraction pattern (*middle*) and signal (*right*) from selected diffraction disk of middle image of $Pt_{0.26}Ga_{0.10}$/C_{H2}.

References

1. J. J. Sandoval, P. Palma, E. Álvarez, J. Cámpora and A. Rodríguez-Delgado, *Organometallics* **2016**, 35, 3197-3204.
2. D. A. Ruddy, J. Jarupatrakorn, R. M. Rioux, J. T. Miller, M. J. McMurdo, J. L. McBee, K. A. Tupper and T. D. Tilley, *Chem. Mater.* **2008**, 20, 6517-6527.
3. K. Searles, G. Siddiqi, O. V. Safonova and C. Copéret, *Chem. Sci.* **2017**, 8, 2661-2666.
4. O. T. Beachley, Jr., M. R. Churchill, J. C. Pazik and J. W. Ziller, *Organometallics* **1986**, 5, 1814-1817.
5. C. Ehinger, X. Zhou, M. Candrian, S. R. Docherty, S. Pollitt and C. Copéret, *JACS Au* **2023**, *in press*, DOI: 10.1021/jacsau.3c00334.
6. C. K. Mavrokefalos, N. Kaeffer, H.-J. Liu, F. Krumeich and C. Copéret, *ChemCatChem* **2020**, 12, 305-313.
7. O. Müller, J. Stötzel, D. Lützenkirchen-Hecht and R. Frahm, *Journal of Physics: Conference Series* **2013**, 425, 092010.
8. B. Ravel and M. Newville, *Journal of Synchrotron Radiation* **2005**, 12, 537-541.