Supporting Information

PdGa Alloy Dynamics under CO_2 Hydrogenation from Surface Organometallic Chemistry on a Chip and *Operando* Transmission Electron Microscopy

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General Information

Reagents were purchased from Sigma-Aldrich ($\{Pd(\eta^3\text{-allyl})Cl\}_2$, $HOSi(O^tBu)_3$, MeLi (1.6M solution in diethyl ether), Apollo Scientific Ltd (N,N'-Bis(isopropyl)carbodiimide), Strem ($GaCl_3$) and Sasol (γ-Al_2O_3) and were used without further purification unless otherwise indicated. All operations regarding catalyst synthesis were performed in an M. Braun glovebox under an Argon atmosphere or using high-vacuum and standard Schlenk techniques. Benzene and pentane were pre-dried using a MB SPS800 solvent purification system, where columns were packed with activated alumina and degassed by three cycles of freeze-pump-thaw. Deuterated benzene was vacuum distilled from purple Na^0/benzophenone. All solvents were stored over 4 Å molecular sieves after being placed in the Argon glove box.

Operando (scanning) transmission electron microscopy (STEM) measurements were performed on a double aberration-corrected JEOL JEM-ARM 300F microscope operated at 300 kV within the facilities of ScopeM at ETH Zurich. A self-built gas mixing system was used in combination with an *in situ* Climate TEM holder from DENSsolutions and corresponding climate in situ gas Micro-Electro-Mechanical Systems (MEMS) chips. Mass spectra were collected using a HIDEN RGA-HAL 3F PIC mass spectrometer.

Ex situ (scanning) transmission electron microscopy (STEM) measurements were as well performed on an aberration-corrected JEOL JEM-ARM 300F microscope operated at 300 kV within the facilities of ScopeM at ETH Zurich. The samples were ground with a plastic spatula inside an Argon Glove Box and subsequently dry casted onto a 400 mesh Cu grid coated with ultra-thin carbon on lacey carbon from TedPella and transferred to the microscope under an inert atmosphere using a vacuum transfer holder from Gatan.

Sputtering was performed using a Safematic CCU-010 Metal Sputter Coater equipped with an Al target. The sputtering was performed at a pressure of 5.0×10^{-3} mbars and a current of 80.0 mA, with a selected thickness of 2.5 nm. Prior to sputtering the part of the chip where the contacts for heating are located, were covered with Aluminium foil.

The Climate *in situ* MEMS bottom chips were plasma cleaned using a Solarus II (model 955) plasma cleaner from Gatan prior to use, using an Ar plasma (30 sccm, 30 W) for 4 minutes.

Elemental analysis was performed by Mikroanalytisches Labor Pascher located in Remagen, Germany.

X-ray absorption spectroscopy (XAS) measurements were carried out at the Ga K-edge at the Balder beamline at MAX IV (MAX IV, Lund, Sweden). The storage ring was operated at 3 GeV with a ring current of around 400 mA. The incident photon beam was selected by a flat-bent VCM (Vertically Collimating Mirror), a fixed-exit DCM (Double Crystal Monochromator) with two pairs of flat Si111 and Si311 crystals and a VFM (Vertically deflecting Focusing Mirror) consisting of two cylinder-bent mirrors mounted in a single bender. The beam size on the sample was 100 x 100 µm. The beamline energy was calibrated with Ga_2O_3 and Ni foil to Ga K-edge position. For *ex situ* samples, quartz capillaries of 2 mm thickness were used and sealed with wax, grease and epoxy glue to avoid contact with air. For *in situ* measurements, catalyst beds of appropriate mass were supported with quartz wool in 2 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, CO_2 and H_2 were purified by passing through columns 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 and Fastosh software were used for data analysis.[1]

Preparation of the Ga and Pd Precursors

Preparation of $Ga(O(O^tBu_3)_3)_3(THF)$: $Ga(O(O^tBu_3)_3)_3(THF)$ was prepared following a previous literature report, yielding transparent crystals.[2]

Preparation of lithium diisopropylacetamidinate(THF) (LiDIA(THF)): LiDIA(THF) was prepared following a previous literature report to yield a white solid.[3]

Preparation of Pd(η_3 -allyl)-(N-N'-diisopropylacetamidinate) (Pd(η_3 -allyl)(DIA)): Pd(η_3 -allyl)(DIA) was prepared following a previous literature report to yield a yellow solid.[4]

Preparation of $PdGa/Al_2O_3$/Chip

The *in situ* MEMS bottom Chip were plasma cleaned for 4 minutes (30 sccm, 30 W) under an Ar atmosphere. Thereafter, the chip was dried under high vacuum (10^{-5} mbars) and 200 °C for 12 hours, followed by a transfer to an Argon filled glovebox. In the glovebox, the *in situ* MEMS bottom Chip was suspended to a continuously stirred solution of $Ga(O(O^tBu_3)_3)_3(THF)$ (10.0 mg) in 5 mL C_6H_6 in a vial and stirred for 5 hours, followed by washing with C_6H_6 (2 x 5mL) and subsequently

pentane (5mL). Thereafter, the *in situ* MEMS bottom Chip was dried for 12 hours under high vacuum (10^{-5} mbars) at 600 °C and transferred back to the glovebox. In the glovebox, the *in situ* MEMS bottom Chip was suspended into a continuously stirred solution of Pd(η_3-allyl)(DIA) (3.5 mg) in 5 mL of C_6H_6 for 5 hours, followed by washing with C_6H_6 (2x5mL) and subsequently pentane (5mL). Finally, the *in situ* MEMS bottom Chip was exposed to a flow of H_2 at 1 bar of pressure for 12 hours at 600 °C.

Preparation of PdGa/Si/$Al_2O_{3\text{-}600}$

γ-$Al_2O_{3\text{-}600}$ was prepared via calcination in air for 2 hours at 500 °C (ramp of 300 °C/h), followed by evacuation under high vacuum (10^{-5} mbar) at 500 °C for 5 hours, followed by heating to 600 °C (ramp of 60 °C/h), and holding at 600 °C for 12 hours. A suspension of $HOSi(O^tBu)_3$ (452 mg) in 10 mL benzene was added to γ-$Al_2O_{3\text{-}600}$ (1.065 g) in 10 mL benzene, and stirred at 150 rpm for overnight, followed by washing three times with 10 mL of pentane and drying under high vac (10^{-5} mbar) with a ramp of 5 °C/min for 1 hour at 300 °C, 400 °C, 500 °C each and then 13 hours at 600 °C, to give Si/$Al_2O_{3\text{-}600}$. Then, $Ga(O(O^tBu_3)_3)_3(THF)$ (160.0 mg) in C_6H_6 was added dropwise to a suspension of Si/$Al_2O_{3\text{-}600}$ (0.780 g) and left stirring at 150 rpm overnight, followed by washing with C_6H_6 and pentane, followed by a temperature treatment under high vacuum (10^{-5} mbar) at 600 °C (300 °C/h ramp) for 12 hours to give Ga@Si/$Al_2O_{3\text{-}600}$. A suspension of Pd(η_3-allyl)(DIA) (34.4 mg) in C_6H_6 was added dropwise to a suspension of Ga@Si/$Al_2O_{3\text{-}600}$ (0.745 g) and left stirring for 5 hours at 150 rpm, followed by washing with benzene and pentane and followed by a hydrogen flow treatment at 600 °C (300 °C/h ramp) for 12 hours.

Details of *operando* TEM Sample Preparation

The prepared *in situ* climate MEMS bottom Chip was removed from the glovebox and exposed to air, prior to mounting it on the *in situ* holder from DENS Solutions together with an untreated *in situ* climate MEMS top Chip. After checking the contacts, a leak check was performed using the plasma cleaning system from Gatan. Then, the holder was inserted into the microscope and flushed with Helium prior to any microscopy measurements.

Supplementary Movie Captions

Supplementary Movie S1: Continuous TEM imaging showing the reduction of a PdGa nanoparticle upon temperature programmed reduction in pure H_2.

Supplementary Movie S2: High-resolution ABF STEM movie showing the structural evolution of a single PdGa nanoparticle under CO_2 hydrogenation conditions at 230 °C and 1 bar of mixed H_2:CO_2 (3:1) atmosphere.

Supplementary Movie S3: High-resolution ABF STEM movie showing the dynamic movement of the core of the PdGa nanoparticle upon interaction with CO_2 hydrogenation conditions at 230 °C and 1 bar of mixed H_2:CO_2 (3:1).

Supplementary Movie S4: High-resolution ABF STEM movie showing the dynamic movement of the core of the PdGa nanoparticle upon interaction with CO_2 hydrogenation conditions at 230 °C and 1 bar of mixed H_2:CO_2 (3:1).

Supplementary Movie S5: High-resolution HAADF STEM movie showing the dynamic appearance and disappearance of an amorphous surface layer under CO_2 hydrogenation conditions at 230 °C and 1 bar of mixed H_2:CO_2 (3:1).

Supplementary Movie S6: Colorized HRTEM movie showing the restructuring of the bulk of a PdGa nanoparticle under CO_2 hydrogenation conditions at 230 °C and 1 bar of mixed H_2:CO_2 (3:1).

Supplementary Movie S7: HRTEM movie showing the restructuring of the bulk of a PdGa nanoparticle under CO_2 hydrogenation conditions at 230 °C and 1 bar of mixed H_2:CO_2 (3:1).

Analysis of the Washing Solution during synthesis of PdGa/Al_2O_3/Chip

The solution, in which the *in situ* climate MEMS bottom Chip was immersed, was analysed via solution ^{1}H NMR spectroscopy using ferrocene as an internal standard (7.5 mg and 5.5 mg for the Ga- and Pd-grafting step respectively).

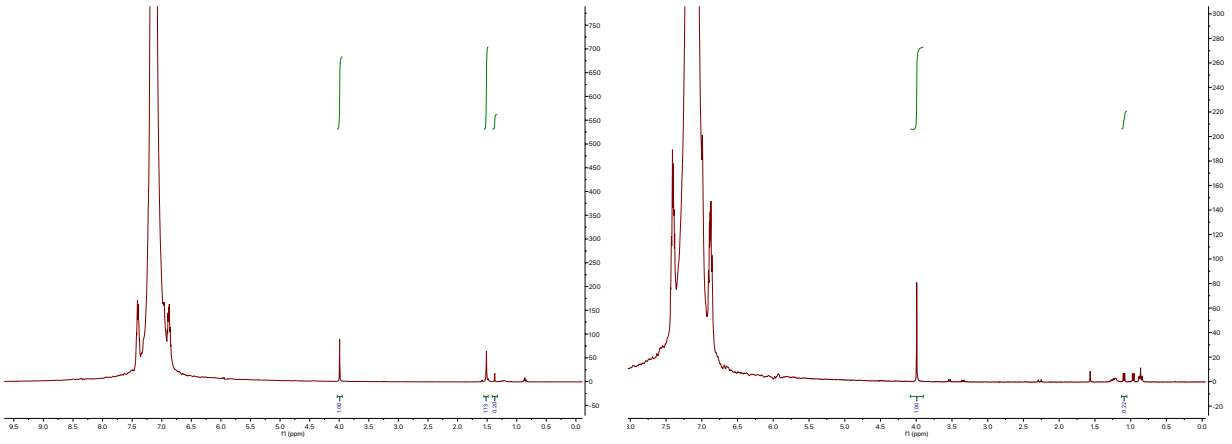

Figure S1. Washing analysis of the PdGa/Al_2O_3/Chip via solution ^{1}H NMR spectroscopy using ferrocene as an internal standard. (*left*) ^{1}H NMR spectrum of the solution after grafting of Ga(O(O^{t}Bu$_3$)$_3$)$_3$(THF), (*right*) ^{1}H NMR spectrum after grafting of Pd(η_3-allyl)(DIA).

Additional (Scanning) Transmission Electron Microscopy (STEM) Data under He

TEM and STEM Images

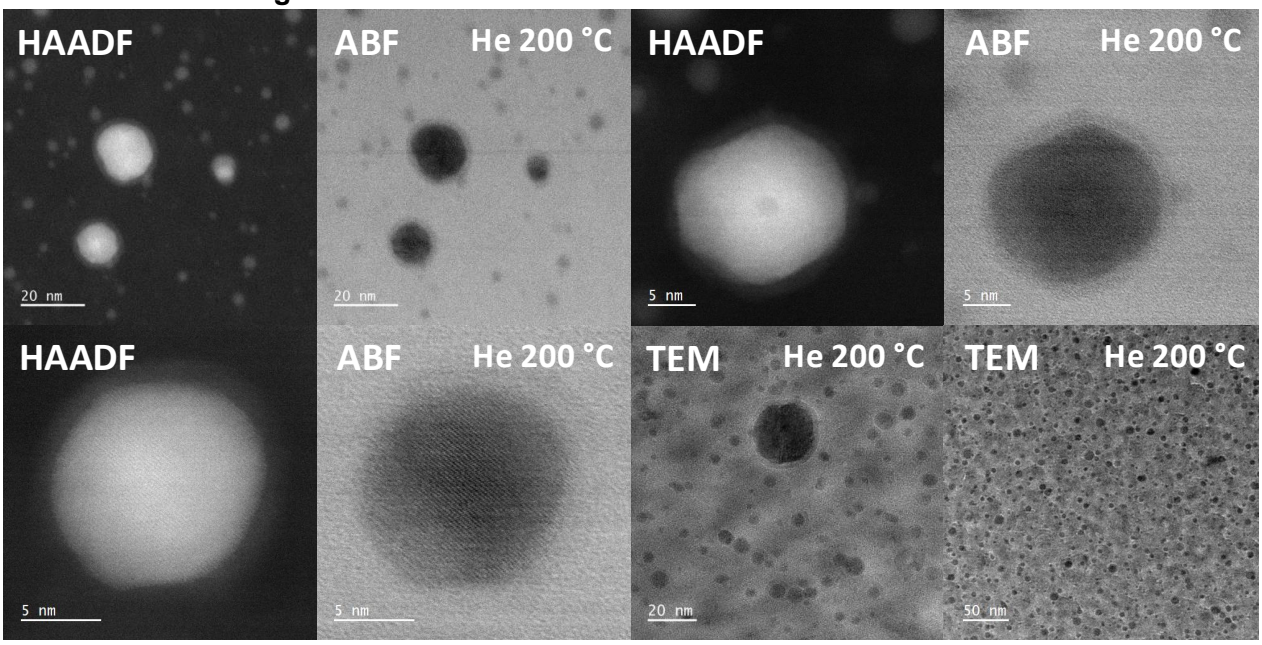

Figure S2. High-resolution HAADF/ABF STEM and TEM images of PdGa/Al_2O_3/Chip upon air-exposure under 1 bar of He at 200 °C.

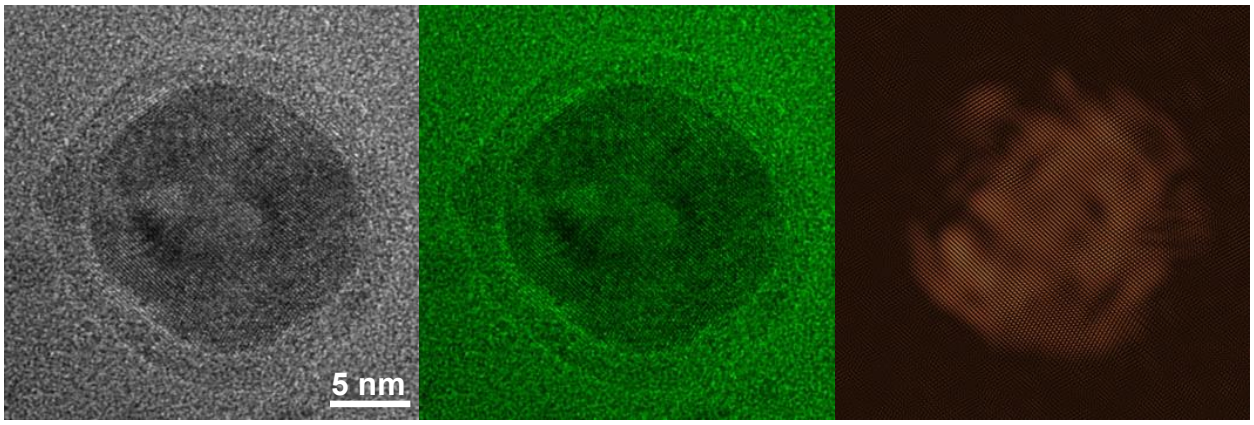

Figure S3. (*left*) Grayscale, (*middle*) colorized HRTEM image and (*right*) colorized inverse FFT image of the detected planes of a single nanoparticle of PdGa/Al_2O_3/Chip upon air-exposure under 1 bar of He at 200 °C.

STEM EDXS Maps and Spectra

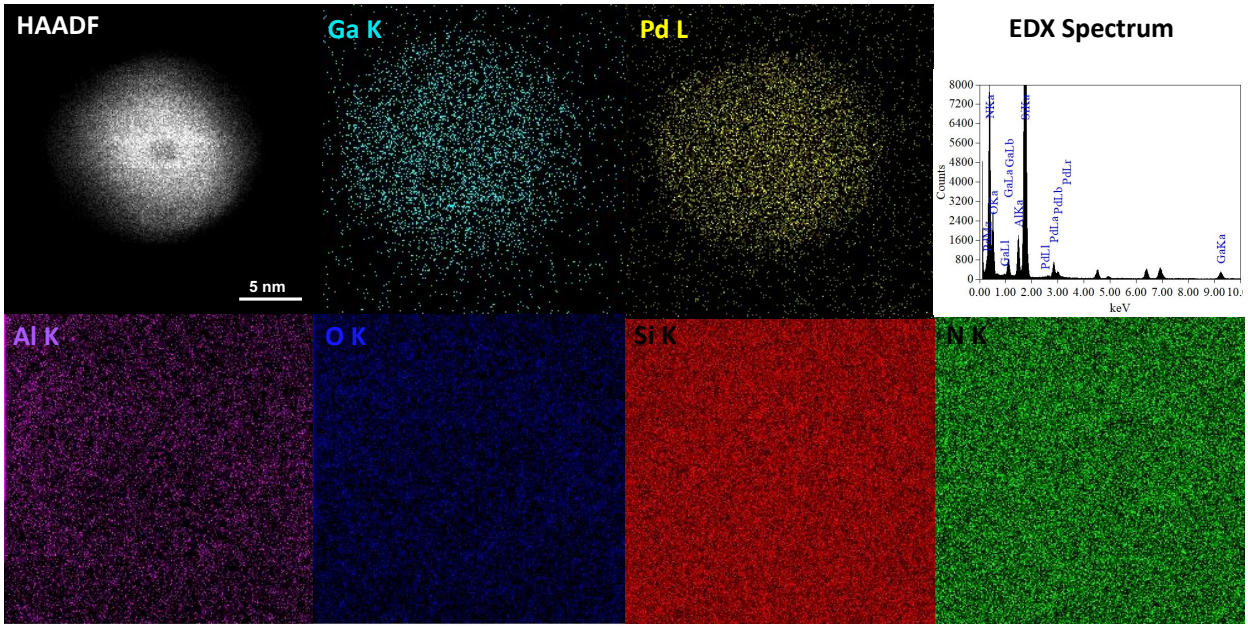

Figure S4. HAADF STEM image and EDXS maps of the Ga K, Pd L, Al K, O K, Si K and N K peak signal and spectrum of PdGa/Al_2O_3/Chip upon air-exposure under 1 bar of He at 200 °C.

Table S1. Quantification of the EDXS peak signals of Figure S4 of PdGa/Al_2O_3/Chip upon air-exposure under 1 bar of He at 200 °C.

Element	Atom %	Mass %	Element	Atom %	Mass %
Ga K	0.76	2.45	O K	10.97	8.14
Pd L	1.26	6.21	N K	45.89	29.80
Si K	38.07	49.58	Al K	3.06	3.83

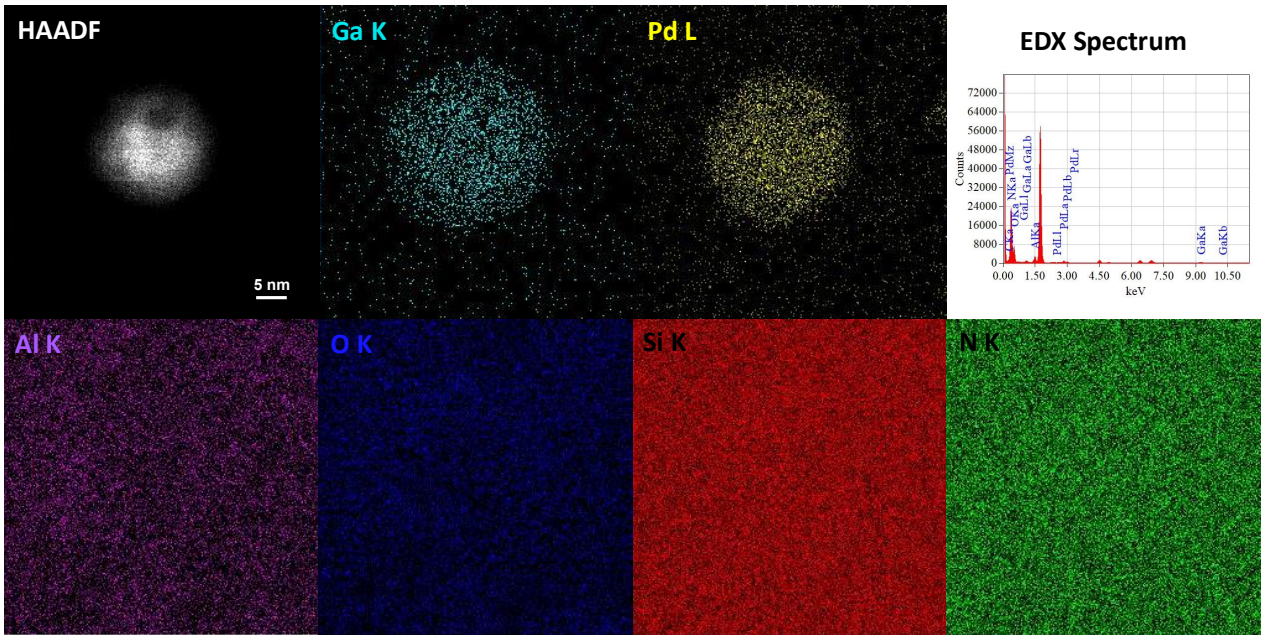

Figure S5. HAADF STEM image and EDXS maps of the Ga K, Pd L, Al K, O K, Si K and N K peak signal and spectrum of PdGa/Al_2O_3/Chip upon air-exposure under 1 bar of He at 200 °C.

Table S2. Quantification of the EDXS peak signals of Figure S5 of PdGa/Al_2O_3/Chip upon air-exposure under 1 bar of He at 200 °C.

Element	Atom %	Mass %	Element	Atom %	Mass %
Ga K	0.50	1.65	O K	11.17	8.46
Pd L	0.86	4.35	N K	45.92	30.46
Si K	38.06	50.62	Al K	3.49	4.46

Additional (Scanning) Transmission Electron Microscopy (STEM) Data under H_2

STEM EDXS Maps and Spectra

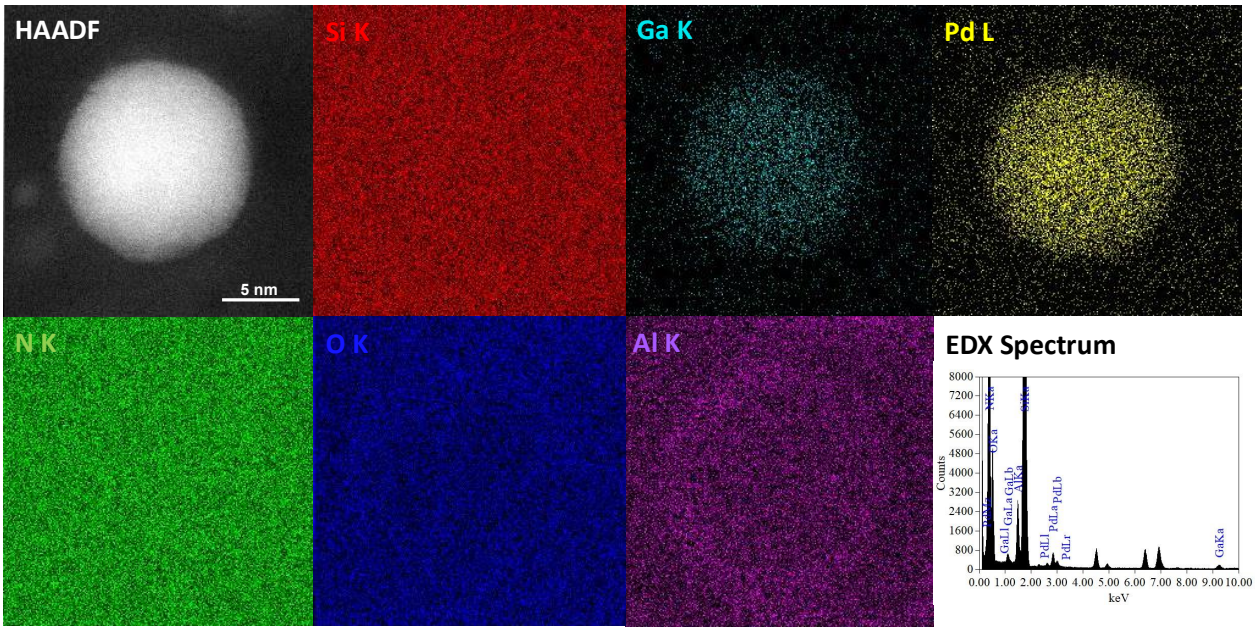

Figure S6. HAADF STEM image and EDXS maps of the Si K, Ga K, Pd L, N K, O K and Al K peak signal and spectrum of PdGa/Al_2O_3/Chip after H_2 at 600 °C.

Table S3. Quantification of the EDXS peak signals of Figure S6 of PdGa/Al_2O_3/Chip after H_2 at 600 °C.

Element	Atom %	Mass %	Element	Atom %	Mass %
Ga K	0.28	0.94	O K	12.15	9.19
Pd L	0.76	3.81	N K	43.74	28.98
Si K	40.50	53.80	Al K	2.57	3.28

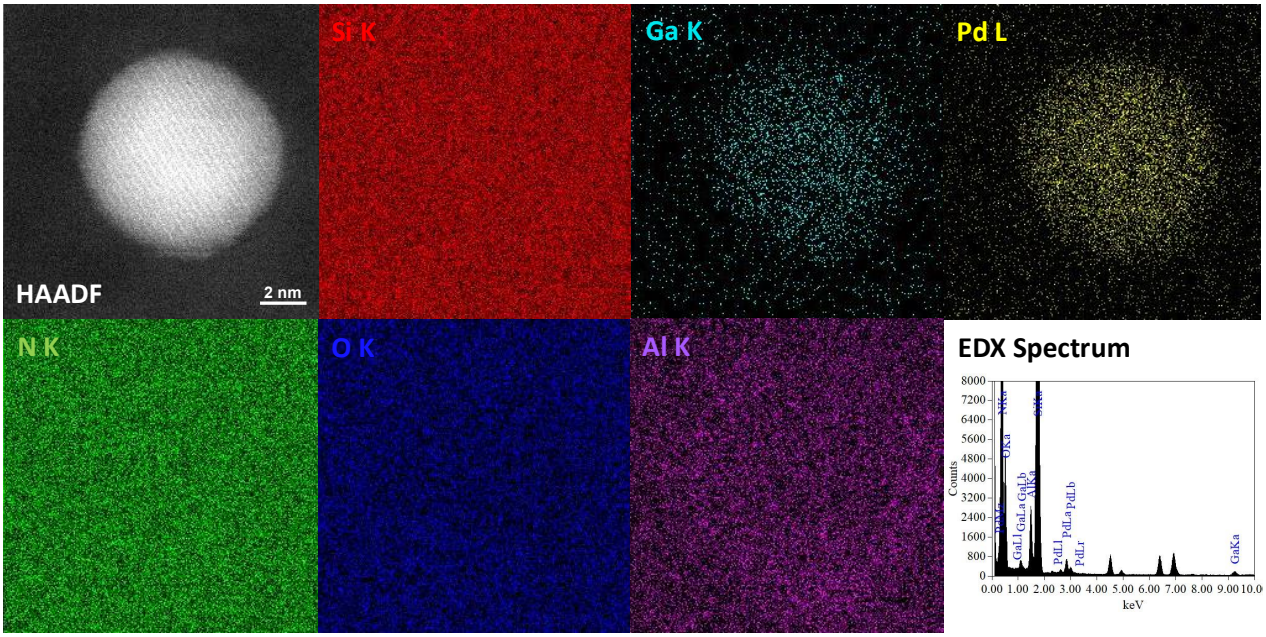

Figure S7. HAADF STEM image and EDXS maps of the Si K, Ga K, Pd L, N K, O K and Al K peak signal and spectrum of PdGa/Al_2O_3/Chip after H_2 at 600 °C.

Table S4. Quantification of the EDXS peak signals of Figure S7 of PdGa/Al_2O_3/Chip after H_2 at 600 °C.

Element	Atom %	Mass %	Element	Atom %	Mass %
Ga K	0.22	0.72	O K	10.24	7.67
Pd L	0.65	3.23	N K	43.13	28.30
Si K	43.44	57.14	Al K	2.33	2.94

TEM and STEM Images

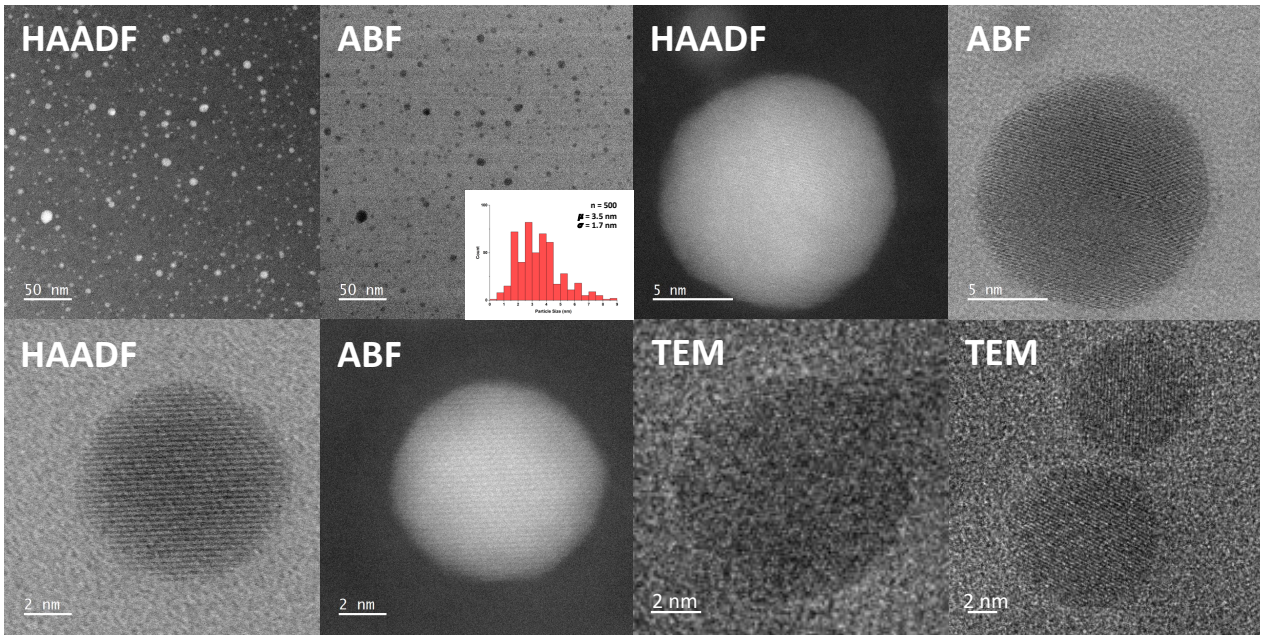

Figure S8. High-resolution HAADF and ABF STEM and TEM images of PdGa/Al_2O_3/Chip after 1 bar of H_2 at 600 °C for 1 hour.

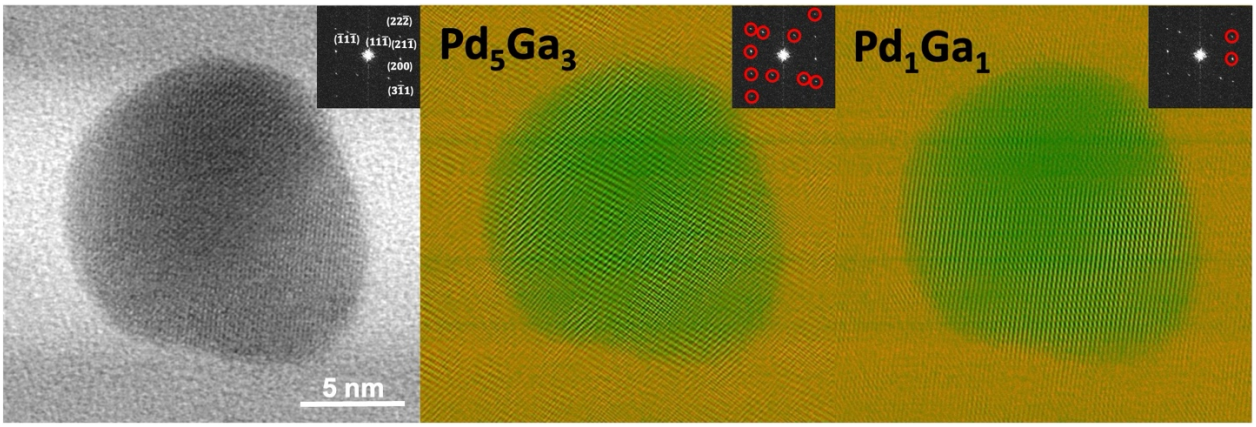

Figure S9. Denoised high-resolution ABF STEM image, FFT of the original image (*inset*) and colorized composite images of the denoised image with inverse FFT of the circled spots in the inset, matching Pd_1Ga_1 and Pd_5Ga_3 structures.

Additional (Scanning) Transmission Electron Microscopy (STEM) and Mass Spectrometry Data under CO_2 Hydrogenation Conditions

TEM and STEM Images

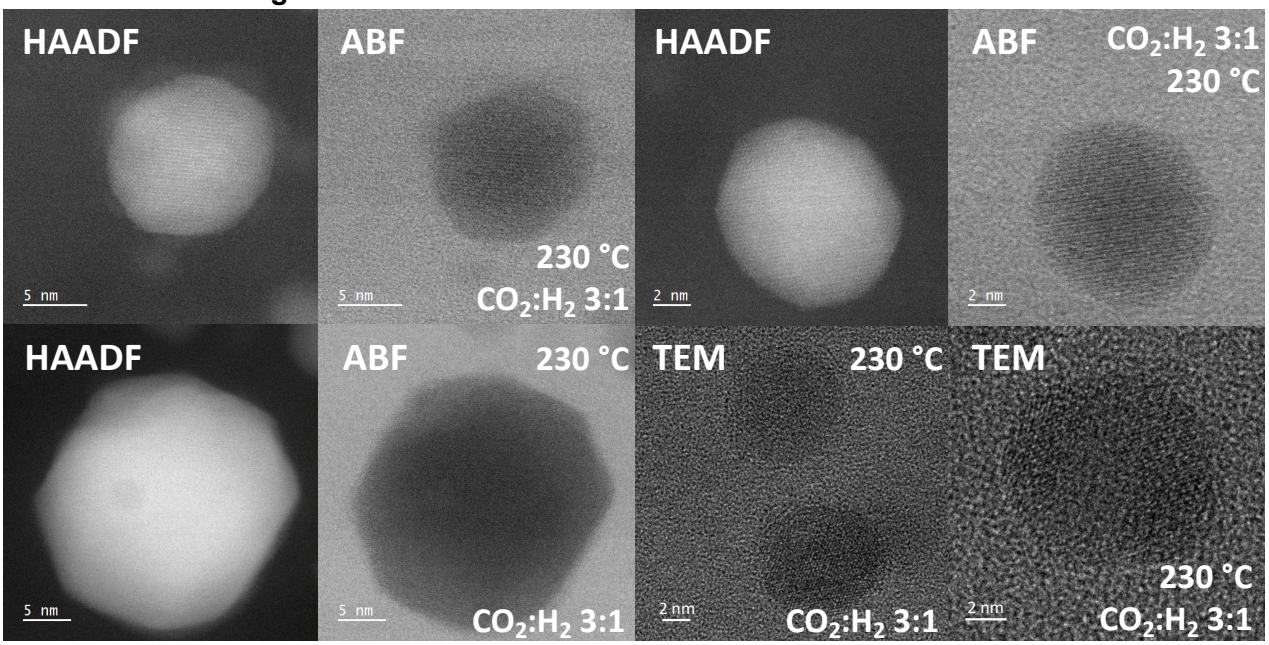

Figure S10. High-resolution HAADF/ABF STEM and TEM images of PdGa/Al_2O_3/Chip under 1 bar of H_2:CO_2 (3:1) at 230 °C.

Mass Spectrometry Data

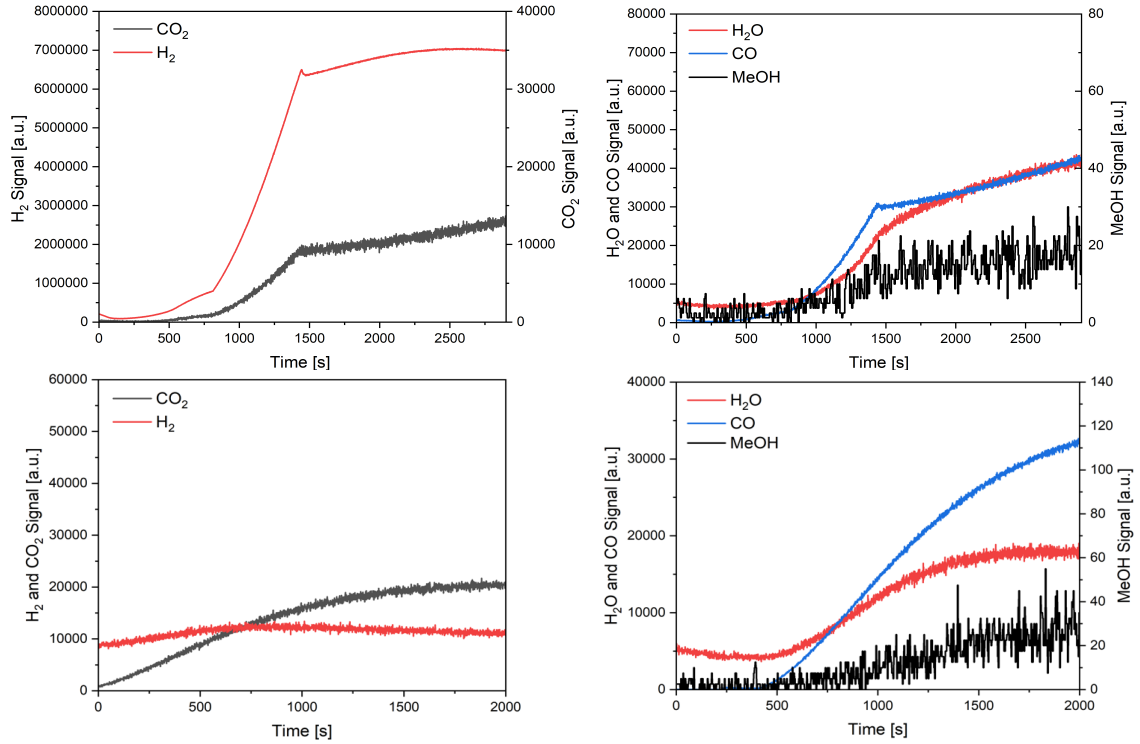

Figure S11. Additional mass spectrometry data of PdGa/Al_2O_3/Chip under 1bar of H_2:CO_2 (3:1) at 230 °C.

STEM EDXS Maps and Spectra

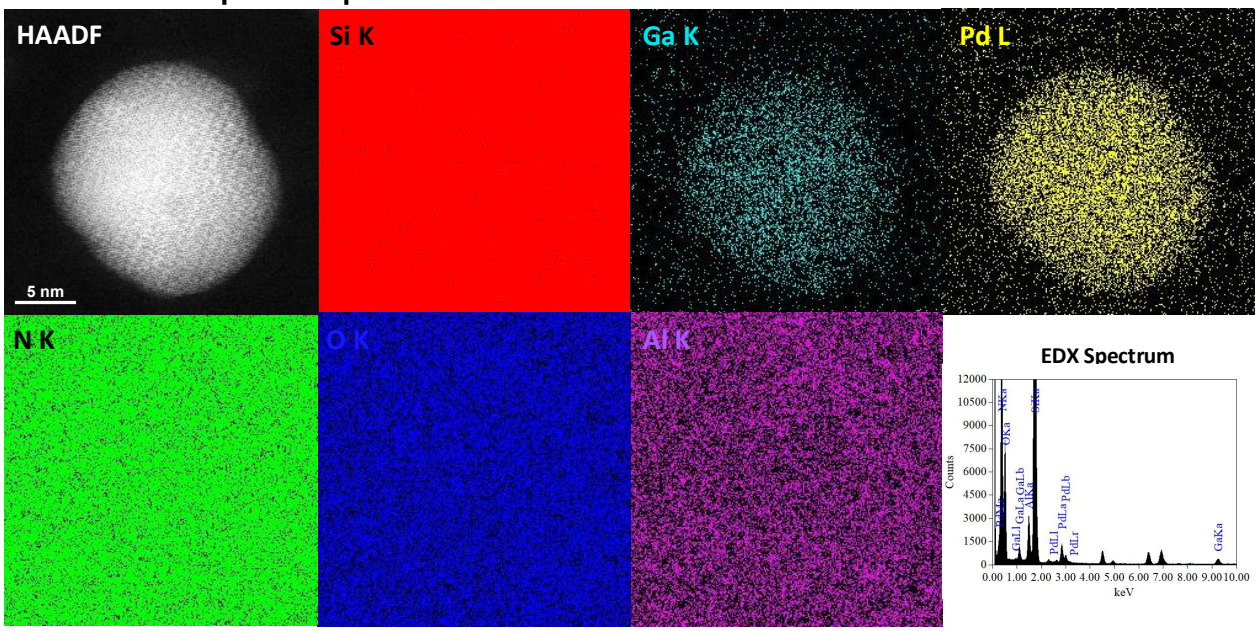

Figure S12. HAADF STEM image and EDXS maps of the Si K, Ga K, Pd L, N K, O K and Al K peak signal and spectrum of PdGa/Al_2O_3/Chip under 1 bar of H_2:CO_2 (3:1) at 230 °C.

Table S5. Quantification of the EDXS peak signals of Figure S12 of PdGa/Al_2O_3/Chip under 1 bar of H_2:CO_2 (3:1) at 230 °C.

Element	Atom %	Mass %	Element	Atom %	Mass %
Ga K	0.50	1.60	O K	16.81	12.33
Pd L	1.22	5.93	N K	38.22	24.55
Si K	40.68	52.40	Al K	2.57	3.19

Time Series

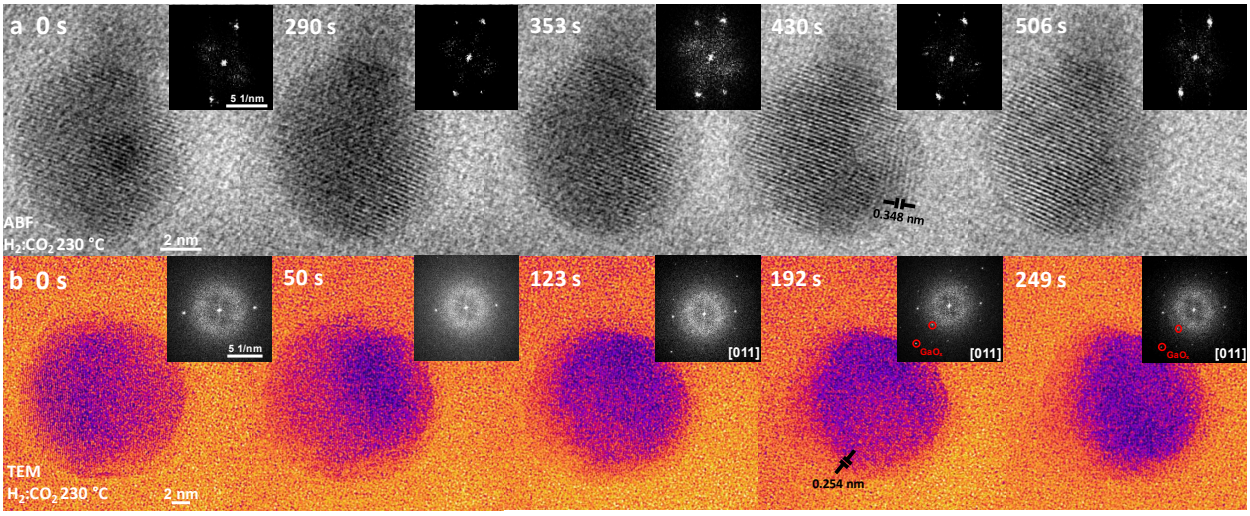

Figure S13. *Operando* high-resolution ABF STEM (**a.**) and TEM (**b.**) image series and corresponding FFT of a single PdGa nanoparticle of PdGa/Al_2O_3/Chip over time under 1 bar of H_2:CO_2 (3:1) at 230 °C.

Additional (Scanning) Transmission Electron Microscopy (STEM) Data under CO_2

TEM and STEM Images

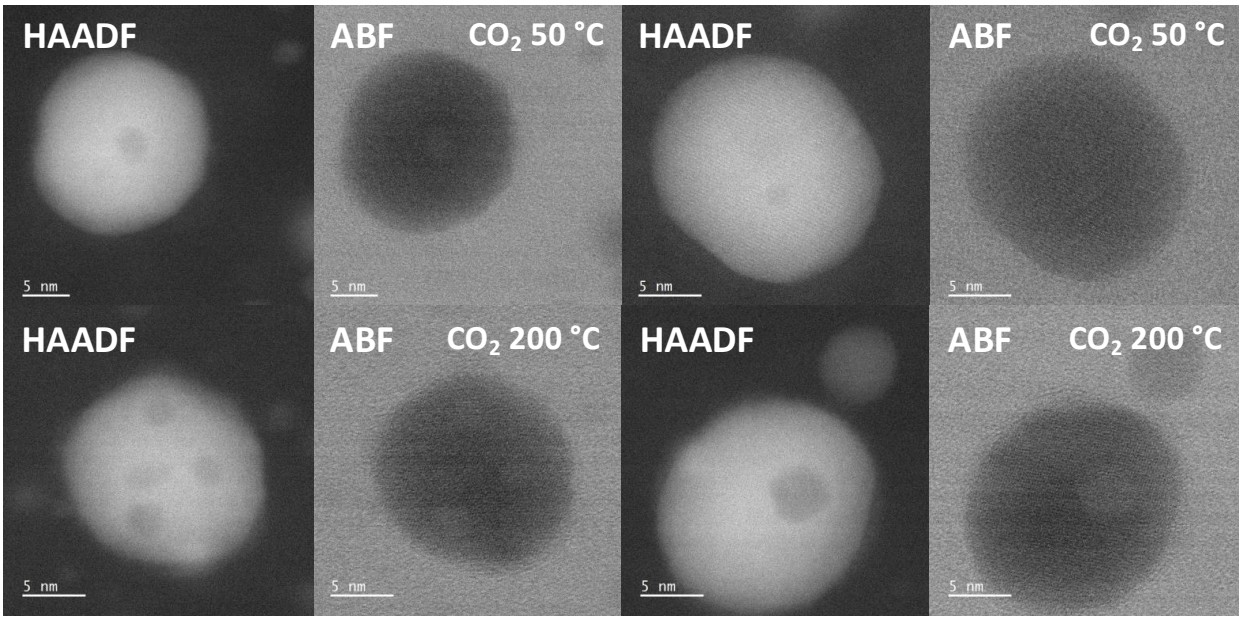

Figure S14. HAADF/ABF STEM images of PdGa/Al_2O_3/Chip under 1 bar of CO_2 at 50 °C and 200 °C.

STEM EDXS Maps and Spectra

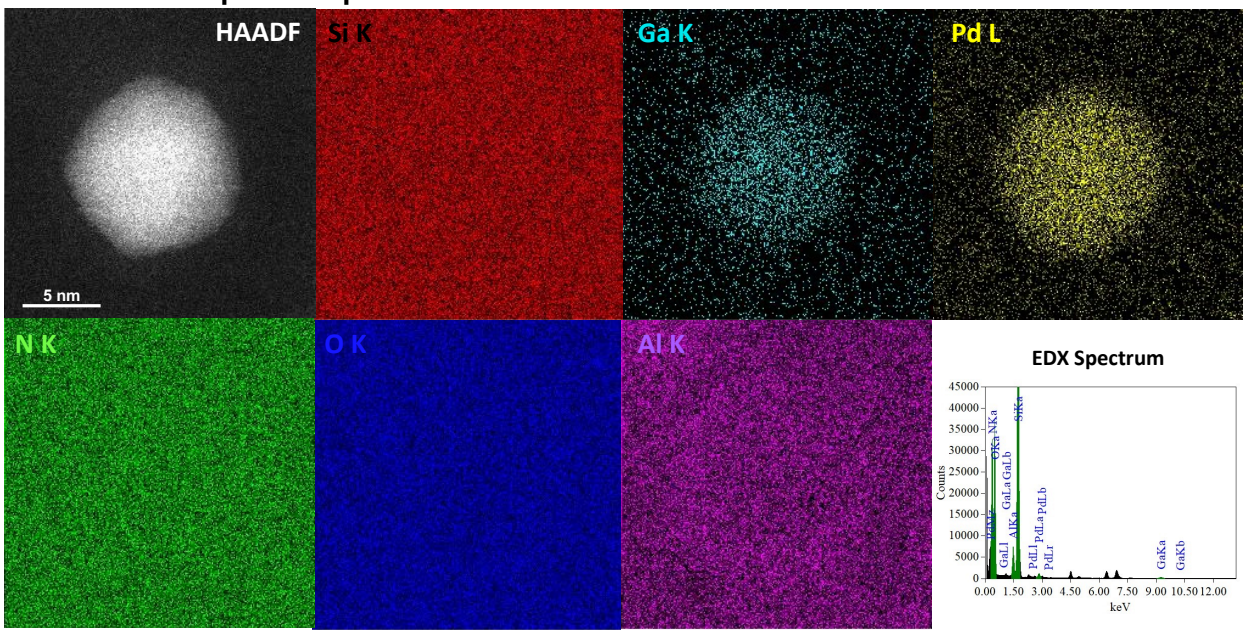

Figure S15. HAADF STEM image and EDXS maps of the Si K, Ga K, Pd L, N K, O K and Al K peak signal and spectrum of PdGa/Al_2O_3/Chip under 1 bar of CO_2 at 230 °C.

Table S6. Quantification of the EDXS peak signals of Figure S15 of PdGa/Al_2O_3/Chip under 1 bar of CO_2 at 230 °C.

Element	Atom %	Mass %	Element	Atom %	Mass %
Ga K	0.12	0.43	O K	31.48	24.84
Pd L	0.40	2.11	N K	30.88	21.33
Si K	34.67	48.03	Al K	2.45	3.26

Preparation of PdGa/Al_2O_3

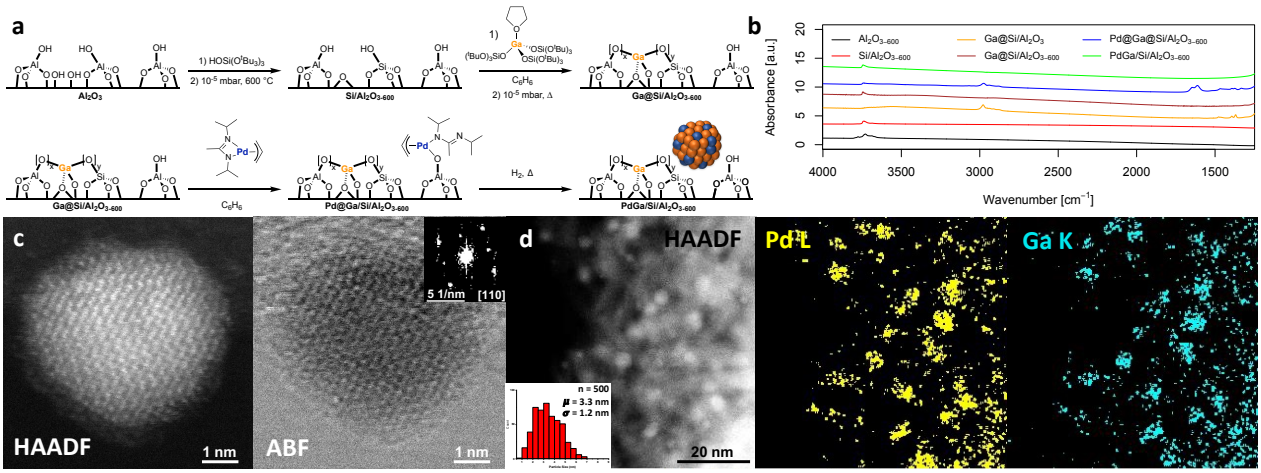

Figure S16. a. Synthesis of PdGa nanoparticles supported on Si doped $Al_2O_{3\text{-}600}$ via a SOMC approach. **b.** Corresponding FTIR spectra monitoring the preparation of PdGa/Si/Al_2O_3 throughout the synthesis. **c.** High-resolution *ex situ* HAADF and ABF STEM images and FFT thereof (*inset*) **d.** Pd L and Ga K EDXS maps and particle size distribution (*inset*) of PdGa/Si/Al_2O_3. The EDXS maps were processed using an averaging filter.

X-ray Absorption Spectroscopy

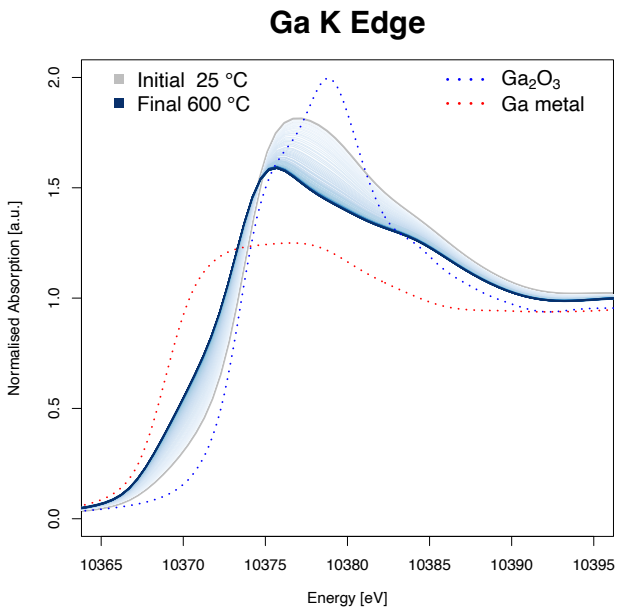

Figure S17. *In situ* X-ray absorption spectroscopy at the Ga K-Edge of air exposed PdGa/Si/$Al_2O_{3\text{-}600}$ under a flow of H_2 at 1 bar from 25 °C to 600 °C.

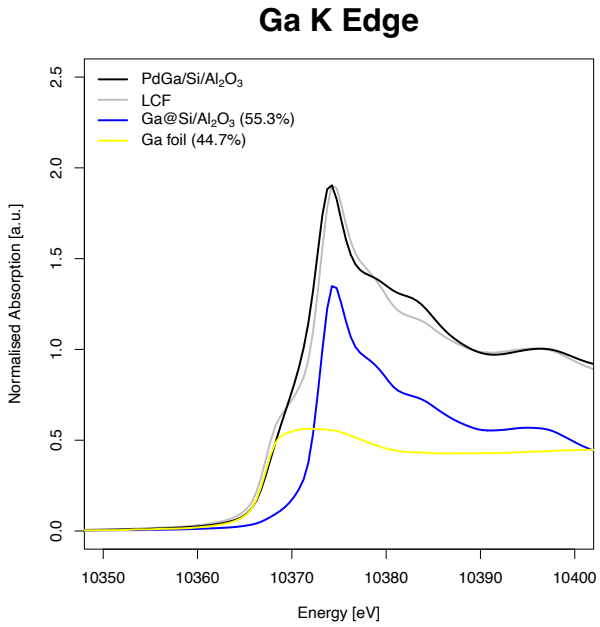

Figure S18. Linear combination fit at the Ga K-Edge of reduced PdGa/Si/$Al_2O_{3\text{-}600}$ using Ga@Si/$Al_2O_{3\text{-}600}$ and Ga foil references.

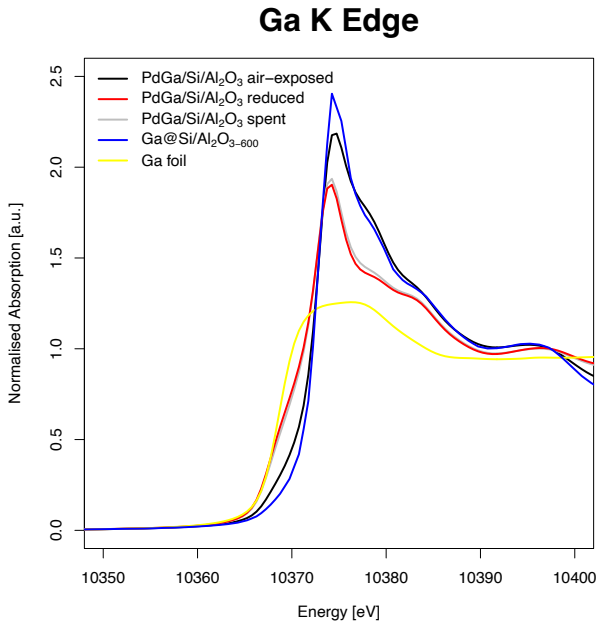

Figure S19. *Ex situ* X-ray absorption spectroscopy at the Ga K-Edge of air-exposed, reduced and spent PdGa/Si/$Al_2O_{3\text{-}600}$, Ga@Si/$Al_2O_{3\text{-}600}$ and Ga foil reference.

CO_2 Hydrogenation

CO_2 hydrogenation reactions were carried out on a fixed-bed flow reactor (PID Eng&Tech). Typically, 250 mg of catalyst were mixed with 4.0 g of SiC and packed in the reactor in air. Prior to CO_2 hydrogenation, the catalyst was reduced at 1 bar under 30 mL min^{-1} of H_2 for 1 h at 300 °C (5 °C/min ramp). After reduction, the furnace was cooled down to the reaction temperature (230 °C), and the reactor pressurized to the reaction pressure (25 bar) under CO_2 hydrogenation conditions (50 mL min^{-1} of 1:3:1 CO_2:H_2:Ar). The effect of conversion on product formation rates was probed by systematically varying the total gas flow rate from 6 mL min^{-1} to 100 mL min^{-1}. Finally, the initial flow rate was restored to check for potential catalyst deactivation. The effluent gases were analysed via online gas chromatography (Agilent 7890B equipped with Restek Rt-U-BOND (30 m x 0.53 mm x 20 µm) and Rt-Msieve 5A (30 m x 0.53 mm x 50 µm) columns) and quantified by using a flame ionization detector (FID) for CH_3OH, and C_{2+} hydrocarbons and a thermal conductivity detector (TCD) for Ar, CO_2, CO and CH_4. GC data was collected in increments of half an hour.

The CO_2 conversion and product selectivity were calculated using the following set of equations:

$$S_x = \frac{F_{X,out}}{\sum_{i=1}^{n} F_{i,out}}$$

$$X_{CO2} = \frac{\sum_{i=1}^{n} F_{i,out}}{F_{CO2,in}}$$

The product selectivity (S_x) is defined as the outflow of the component X, $F_{X,out}$, divided by the sum of the outlet flows of all carbon containing products $\sum_{i=1}^{n} F_{i,out}$. The CO_2 conversion X_{CO2} is defined as the sum of the outlet flows of all the carbon containing products $\sum_{i=1}^{n} F_{i,out}$, divided by the inlet flow of CO_2, $F_{CO2,in}$. Note, that all concentrations are normalized with respect to its number of carbon atoms to enable accurate comparison.

CO_2 Hydrogenation performance of $PdGa/Si/Al_2O_3$ at 1 bar

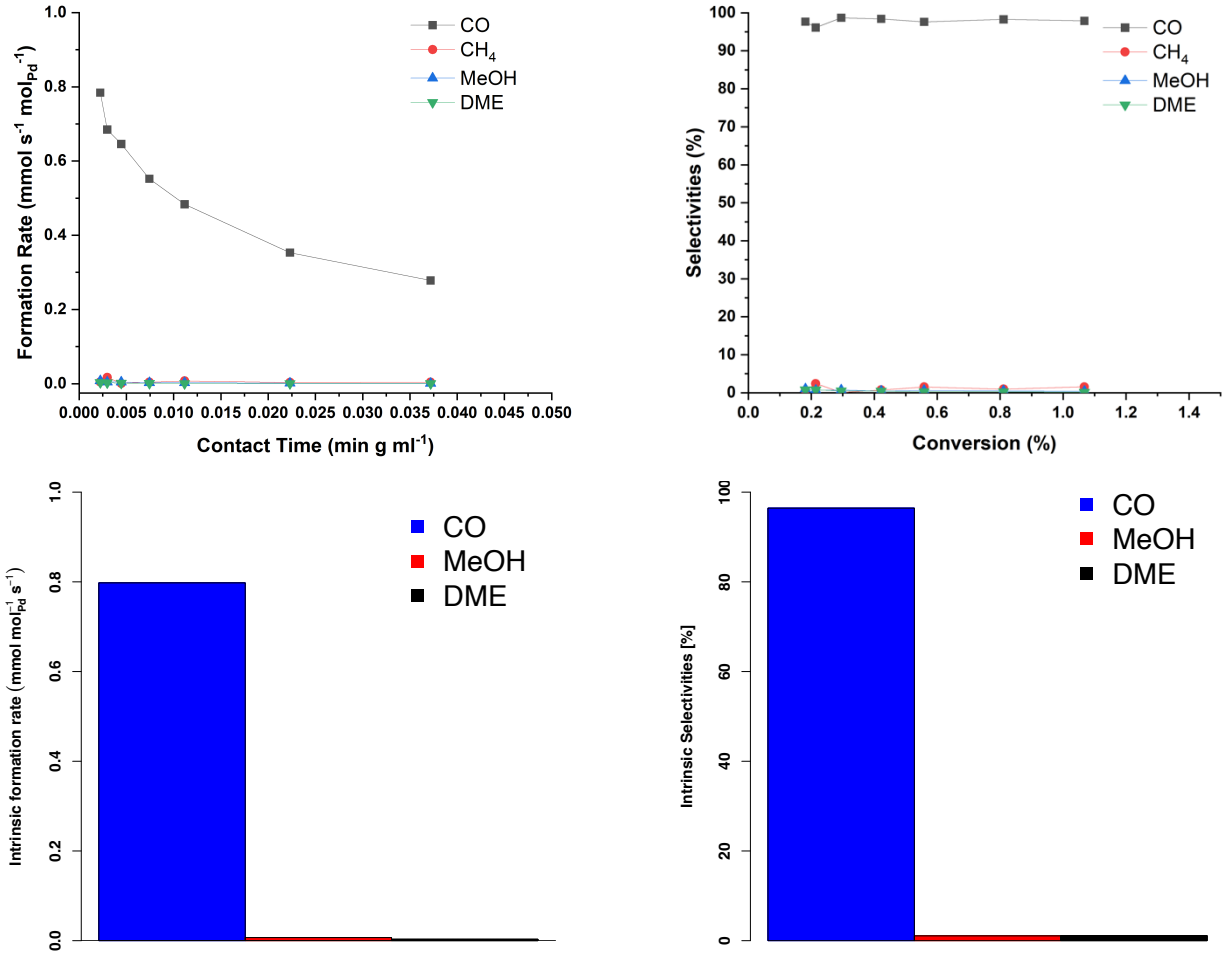

Figure S20. Catalytic performance of $PdGa/Si/Al_2O_{3\text{-}600}$ at 1 bar of H_2:CO_2:Ar (3:1:1) gas mixture at 230 °C across a span of CO_2 conversions, achieved by varying the flow rate of the reactant gas mixture.

CO_2 Hydrogenation performance of $PdGa/Si/Al_2O_{3\text{-}600}$ at 25 bars

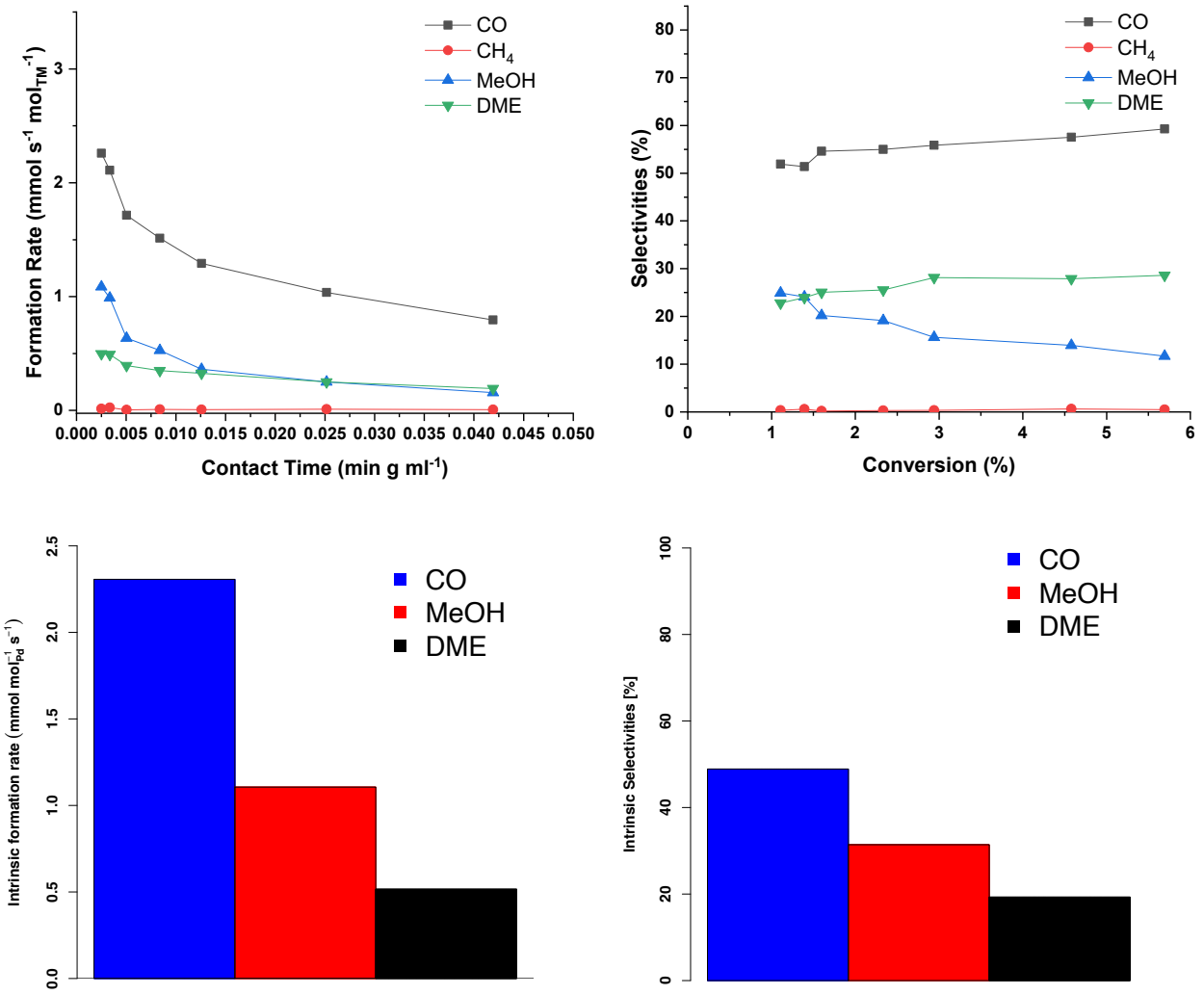

Figure S21. Catalytic performance of $PdGa/Si/Al_2O_{3\text{-}600}$ at 25 bars of H_2:CO_2:Ar (3:1:1) gas mixture at 230 °C across a span of CO_2 conversions, achieved by varying the flow rate of the reactant gas mixture.

Supplementary References

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