Supporting Information

Dynamics and Site Isolation: Keys to High Propane Dehydrogenation Performance of Silica-Supported PtGa Nanoparticles

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1. Synthesis Procedures

All operations were performed in a M. Braun glove box under an argon atmosphere. All solvents were dried using standard procedures prior to use. SiO$_2$-700 was prepared by heating Evonik AEROSIL® (200 m$^2$/g) to 500 °C (ramp of 5 °C/min) in air and calcine at this temperature for 12 hours, followed by evacuation to high vacuum (10$^{-3}$ mbar) while keeping at 500 °C for further 8 hours, heating to 700 °C (ramp of 1 °C/min), and maintaining 700 °C for 24 hours. Titration of the resulting SiO$_2$-700 using [Mg(CH$_2$Ph)$_2$(THF)$_2$] purified via sublimation prior to use, yielded an Si-OH density of 0.3 mmol/g, corresponding to 0.9 accessible Si-OH groups per nm$^2$.

The molecular complexes [Ga(OSi(OtBu)$_3$)$_3$(THF)] and [Pt(OSi(OtBu)$_3$)$_2$(COD)] were prepared according to a literature procedure$^1$ The material Pt(OSi(OtBu)$_3$)(COD)$_{Ga/SiO_2}$ was likewise prepared according to a reported procedure.$^2$

Pt(OSi(OtBu)$_3$)(COD)$_{Ga/SiO_2}$ was then added to a tubular quartz flow-reactor supported with a porous quartz frit. The reactor was heated to 100 °C (ramp of 5 °C/min) and kept at that temperature for 1 h under a steady flow of H$_2$ at 1 bar. The reactor was subsequently evacuated under high vacuum (10$^{-5}$ mbar) while cooling to rt. The material was transferred to an Argon filled glove box, half of the material was removed from the tube for further analysis, the other half of the material was reheated to 100 °C (ramp of 5 °C/min) and kept at that temperature for 10 h. Evacuation was done under the same conditions as mentioned before to obtain PtGa/SiO$_2$-100 as a black material. PtGa/SiO$_2$ was obtained similarly by heating to 600 °C (ramp of 5 °C/min) and keeping the temperature there for 10 h while applying a steady flow of H$_2$ at 1 bar. Evacuation under high vacuum (10$^{-5}$ mbar) while cooling to rt yielded PtGa/SiO$_2$ as a black material.

It has to be noted that in this work when the material is treated at 600 °C – instead of the 500 °C in the aforementioned publication$^2$ – the Ga-O coordination number ratio of initial/final material is approximately 4:1 which corresponds to only ca. 25 % remaining Ga$^{III}$ sites at the surface of the support, versus 50% of Ga$^{III}$ remaining at the support surface when the treatment has been done at 500 °C. This seems to indicate that a treatment at higher temperature allows for more Ga incorporation into the particle.

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1. (a) Searles, K; Siddiqi, G.; Safonova, O. V.; Copéret C. Chem. Sci., 2017, 8, 2661-2666; (b) Ruddy, D. A.; Jarupatrakorn, J.; Rioux, R. M.; Miller, J. T.; McMurdo, M. J.; McBee, J. L.; Tupper K. A.; Tilley, T. D. Chem. Mater., 2008, 20, 6517–6527.

2. Searles, K.; Chan, K. W.; Mendes Burak, J. A.; Zemlyanov, D.; Safonova, O. V.; Copéret, C. J. Am. Chem. Soc., 2018, 140, 11674–11679.
2. Optimization of PtGa bulk and surfaces

The most stable bulk structures are displayed in Figure S1. The general trend is that the more the Ga\(^{0}\) atoms are dispersed within the structure the more stable the bulk becomes. In other words, stable alloys minimize Ga\(^{0}\)-Ga\(^{0}\) interactions, in agreement with the very low energy of the Ga\(^{0}\)-Ga\(^{0}\) bond (112 kJ mol\(^{-1}\)) by comparison with the Pt-Pt one: 357 kJ mol\(^{-1}\)). This finding is fully consistent with the EXAFS data, where no Ga-Ga neighbors are found and with the experimentally known structure for crystalline Pt\(_{2}\)Ga.\(^4\)

Table S1 – Different bulk structures of Pt\(_{2}\)Ga and the average nearest neighbour. The energy is given in kJ mol\(^{-1}\) per atom in the unit cell, relative to the 225-7 structure.

| Label  | Rel energy | Pt-Pt | Pt-Ga | Ga-Pt | Ga-Ga |
|--------|------------|-------|-------|-------|-------|
| 225-3  | 28.6       | 10    | 4     | 2     | 8     |
| 225-10 | 14.3       | 8.5   | 3.5   | 7     | 5     |
| 225-8  | 14.3       | 9     | 3     | 6     | 6     |
| 225-13 | 11.3       | 8     | 4     | 8     | 4     |
| 225-14 | 9.1        | 8     | 4     | 8     | 4     |
| 225-9  | 9.1        | 8     | 4     | 8     | 4     |
| 225-11 | 7.8        | 8     | 4     | 8     | 4     |
| 225-2  | 4.8        | 7     | 5     | 10    | 2     |
| 225-6  | 4.4        | 7.5   | 4.5   | 9     | 3     |
| 225-1  | 3.7        | 7     | 5     | 10    | 2     |
| 225-12 | 3.6        | 7.5   | 4.5   | 9     | 3     |

\(^3\) Kerr, J. A., CRC Handbook of Chemistry and Physics 1999-2000 : A Ready-Reference Book of Chemical and Physical Data. CRC Press, Boca Raton, Florida, USA: 2000.

\(^4\) a) Chattopadhyay, T.; Khalaff, K.; Schubert, K. Zur Konstitution der Mischungen Platin-Gallium und Platin-Gallium-Germanium Metall 1974, 28, 1160-1168; b) Schubert, K.; Bhan, S.; Biswas, T. K.; Frank; Panday, P. K. Einige Strukturdaten metallischer Phasen. 13. Mitteilung Naturwissenschaften 1968, 55, 542-543; c) Ueber die Struktur von Phasen mit Kupfer Unterstruktur in einigen T-B Legierungen (T= Ni, Pd, Pt; B = Ga, In, Tl, Pb, Sb, Bi) J. Less-Comm. Metals 1969, 17, 73-90.
Table S2 – Lowest Surface energies for the four chosen Pt₃Ga bulk systems for many different Miller indices.

| System | Miller Indices (hkl) | $\gamma$ (J m⁻²) |
|--------|----------------------|------------------|
| 225-4  | (001)                | 1.23             |
|        | (111)                | 0.80             |
|        | (012)                | 1.21             |
|        | (310)                | 1.88             |
|        | (311)                | 1.04             |
|        | (113)                | 1.04             |
| 225-7  | (100)                | 1.49             |
|        | (111)                | 0.92             |
|        | (211)                | 0.64             |
|        | (922)                | 0.97             |
| 225-7  | (101)                | 1.24             |
|        | (111)                | 0.93             |
|        | (012)                | 2.28             |
|        | (311)                | 0.99             |

Figure S2 – Optimized surfaces corresponding to the 225-7 bulk, ordered according to their energy. Top left is the most unstable structure, bottom right is the most stable structure.
3. Interaction of Pt nanoparticles with amorphous oxides

Computational details of the optimization procedure:

**Step 1:** pre-run stabilization at 875 K

**QM:** rev-PBE\(^5\) with D3-BJ dispersion corrections\(^6\) (SCF convergence criteria: 5 \(10^{-7}\) a.u.), basis set: the mixed Gaussian and plane waves basis (GPW) were used DZVP-MOLOPT-SR-GTH for Pt and SZVP-MOLOPT-SR-GTH for Si, O and D with associated pseudo potentials (GTH-PBE).\(^7\)

**MD:** Born-Oppenheimer AIMD, ensemble canonical (NVT), time step: 1 fs, \(T = 875\) K (Temperature tolerance 50 K), thermostat: velocity rescaling (10.1063/1.2408420), time delay between rescalings (100 fs). Total simulation time 3000 fs. Hydrogen were replaced by deuterium atoms.

Here follows the evolution of the total energy (total energy with initial state as a reference, \(\Delta E\), kcal mol\(^{-1}\)) of the system as a function of time for a 38 atoms Pt-nanoparticle supported on 1) SiO\(_2\), 2) SiO\(_2\)-700 and 3) Ga-doped SiO\(_2\)-700:

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\(^5\) Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* 1996, 77 (18), 3865-3868; \(b\) Zhang Y.; Weitao Y., W. Comment on “Generalized Gradient Approximation Made Simple”. *Phys. Rev. Lett.* 1998, 80 (4), 890.

\(^6\) (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, S. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements. H-Pu. J. Chem. Phys. 2010, 132, 154104; (b) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory *J. Comp. Chem.* 2011, 32, 1456-1465.

\(^7\) (a) Blöchl, P. E., Projector augmented-wave method. *Phys. Rev. B* 1994, 50 (24), 17953-17979; (b) Kresse, G.; Joubert, D., From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* 1999, 59 (3), 1758-1775.
**Step 2:** annealing steps

Starting from selected energy minima obtained step 1.

**QM:** rev-PBE with D3-BJ dispersion correction (SCF convergence criteria: $5 \times 10^{-7}$ a.u.), basis set: the mixed Gaussian and plane waves basis (GPW) were used DZVP-MOLOPT-SR-GTH for Pt and Ga and SZVP-MOLOPT-SR-GTH for Si, O and D with associated pseudo potentials (GTH-PBE).

**MD:** Born-Oppenheimer AIMD, ensemble canonical (NVT), time step: 1 fs, no thermostat, velocity rescaling factor: 0.999. Total simulation time 2000 fs. Hydrogen were replaced by deuterium atoms.

Here follows the evolution of the total energy of the system with respect to the initial state ($\Delta E$, kcal mol$^{-1}$) and evolution of the temperature ($T$, K) of the system as a function of time for a 38 atoms Pt-nanoparticle supported on 1) SiO$_2$, 2) SiO$_2$-700 and 3) Ga-doped SiO$_2$-700:
**Step 3:** gradient descent optimization

**QM:** rev-PBE with D3-BJ dispersion correction (SCF convergence criteria: $5 \times 10^{-7}$ a.u.), basis set: the mixed Gaussian and plane waves basis (GPW) were used DZVP-MOLOPT-SR-GTH for all atoms (Pt, Si, O, Ga and H) with associated pseudo potentials (GTH-PBE). Convergence criteria: MAX_DR: 0.001, RMS_DR: 0.0003, MAX_FORCE: 0.0001, RMS_FORCE: 0.00003.
**Figure S3** – Model silica surfaces, **Left** – fully hydroxylated SiO$_2$ (7.2 OH per nm$^2$), **Right** – dehydroxylated SiO$_2$ (1.1 OH per nm$^2$), **Bottom** – dehydroxylated Ga-doped SiO$_2$ (1 Ga per nm$^2$; 1 OH per nm$^2$) Conventions: Ga (green), Si (blue), O (red), H (white).
Figure S4 – A – Initial guess structures of Pt nanoparticles (38 atoms) on SiO$_2$-700 surfaces; B - Optimized structures (Guess 1) obtained by *ab initio* molecular dynamic and subsequent gradient optimization; C - Optimized structures (Guess 2) obtained by *ab initio* molecular dynamic and subsequent gradient optimization. Electronic energy at DZ level (kcal mol$^{-1}$), interaction energy of the nanoparticle with the surface ($E_{tot}$), deformation energy between nanoparticle in vacuum and nanoparticle on surface ($E_{def}$), interaction energy between the distorted nanoparticle and surface ($E_{int}$) see the computational Section for definitions. Conventions: Si (blue), O (red), H (white), Pt (grey).
Figure S5 – Optimized structures of Pt nanoparticles (38 atoms) on SiO$_2$ surfaces optimized by ab initio molecular dynamic and subsequent gradient optimized, electronic energy at DZ level (kcal mol$^{-1}$), interaction energy of the nanoparticle with the surface ($E_{int}$); deformation energy between nanoparticle in vacuum and nanoparticle on surface ($E_{def}$); interaction energy between the distorted nanoparticle and surface ($E_{def}$) see the computational Section for definitions. Conventions: Si (blue), O (red), H (white), Pt (grey).
Figure S6 – Optimized structures of Pt nanoparticles (38 atoms) on Ga-doped SiO$_2$ surfaces optimized by \textit{ab initio} molecular dynamic and subsequent gradient optimized, electronic energy at DZ level (kcal mol$^{-1}$), interaction energy of the nanoparticle with the surface ($E_{\text{int}}$); deformation energy between nanoparticle in vacuum and nanoparticle on surface ($E_{\text{def}}$); interaction energy between the distorted nanoparticle and surface ($E_{\text{int}}$) see the computational Section for definitions. Conventions: Si (blue), O (red), H (white), Pt (grey) and Ga (green).
Figure S7 – Evolution of the total number of Pt-O, Pt-Si, Si-O and Pt-Pt bonds during isothermic and subsequent AIMD annealing on a 38 Pt atoms SiO$_2$-700 supported nanoparticle. Each color corresponds to a different starting time for the annealing process.
4. Interaction of Pt single atoms with oxides

The Silica and Ga-doped silica molecular clusters described below (Figure S8) are optimized using Gaussian 09 (Rev. D.01). The structures of all minima were fully optimized using the B3LYP functional with Grimme’s correction for dispersion combined with Beckett-Johnson damping function (D3BJ), without any symmetry constraint. Basis sets used for structural optimization was LANL2TZ/LANL2 on metal center and 6-31+G(d) on O and 6-31G(d) on Si. All stationary points were characterized as minima by analytical frequency calculations.

Fukui functions for acid sites were obtained by single point energy calculation of cation and anion using the optimized geometry of the neutral cluster. Electrophilic Fukui function ($f^+$) is defined as:

$$f^+(r) = \rho(r)_{\text{anion}} - \rho(r)_{\text{neutral}}$$

with $\rho_{\text{anion}}$ and $\rho_{\text{neutral}}$ the electronic density of the neutral and anionic cluster respectively. Nucleophilic Fukui function ($f^-$) is defined as:

$$f^-(r) = \rho(r)_{\text{neutral}} - \rho(r)_{\text{cation}}$$

with $\rho_{\text{cation}}$ the electronic density of the cationic cluster.

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9 a) A. D. Becke, A new mixing of Hartree–Fock and local density functional theories. J. Chem. Phys. 1993, 98, 1372-1377; b) C. Lee, W. Yang, R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density Physical Review B 1988, 37, 785-789; c) S. H. Vosko, L. Wilk, M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis Can. J. Phys. 1980, 58, 1200-1211; d) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields J. Phys. Chem. 1994, 98, 11623-11627.

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11 Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory J. Comp. Chem. 2011, 32, 1456-1465.
Figure S8. Electrophilic ($f^+$) and nucleophilic ($f^-$) Fukui functions of model Ga$^{III}$Si$_{3}$O$_{9}$H$_{3}$ cluster calculated at the D3-BJ-B3LYP level.
The amorphous silica surfaces and Ga-doped silica surfaces (Figure S3) used below (Figure S9-11) were optimized using CP2K Quickstep module\textsuperscript{12} with the revised Perdew–Burke–Ernzerhof (rev-PBE) exchange correlation functional and Grimme D3 correction for dispersion, the double-zeta Gaussian plane waves (GPW) basis set, and the Goedecker–Teter–Hutter (GTH) pseudopotentials. The construction of these models for amorphous silica surfaces we used were described in previous papers:\textsuperscript{13}

As expected, the affinity of Pt(0) modelled using a single Pt atom is much higher on silica doped with Ga(III) site (\(-65.7\) kcal mol\(^{-1}\)) than for pure SiO\(_2\) (\(-29.3\) kcal mol\(^{-1}\)). While with silica Pt can only bind through donation from the O-doublet - as evidenced by the positive coefficient on O in the nucleophilic Fukui function \((f^-)\) of the cluster (Figure S8) – with Ga\(^{\text{III}}\), Pt can bind both through both donation from the O atom \((f^-)\) and from back-donation into vacant sp type orbitals of Ga\(^{\text{III}}\) \((f^+)\).

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\textsuperscript{12} a) J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, QUICKSTEP: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach \textit{Comput. Phys. Commun.} \textbf{2005}, \textit{167}, 103-128; b) J. Hutter, M. Iannuzzi, F. Schiffmann, J. VandeVondele, cp2k: atomistic simulations of condensed matter systems \textit{WIREs Comput. Mol. Sci.} \textbf{2014}, \textit{4}, 15-25.

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S17
To have an idea of all possible behaviors of Pt atoms bound to SiO$_2$-$700$, several representative sites were selected (Figure S9), some of regular Td shape (site I) some distorted and featuring elongated Si-O bond (Sites II and III) some distorted but without elongated SiO (Sites IV and VI) and an hydroxo group (site V).

It is instructive to consider first extremal behaviors: while site I interacts weakly with Pt (-19.9 kcal mol$^{-1}$) through the O atom (Figure S9, site I-Pt) and site II has a strong affinity for Pt (-93.4 kcal mol$^{-1}$) and is inserting into the already elongated SiO bond (Figure S9, site II-Pt). All other SiO$_2$-$700$ sites (Sites III, IV, VI) have intermediate behavior. The hydroxo group (site V) behave like site I, interacting only weakly through the O-atom. Overall the interaction energy of Pt atom with SiO$_2$ sites is directly related to the most elongated length of the SiO bond (Figure S9, bottom).

An analogous linear trend, with an opposite slope was found for the cost of dehydration of this SiO$_2$ model as a function of the average distance of the new SiO bond length formed.$^{[7]}$ A significant interaction energy between Pt and silica can be obtained only on highly distorted sites (Si-O bond longer than 1.7 Å). However, if such sites are present in reasonable amount in dehydroxylated silica (SiO$_2$-$700$, see Figure S10, Top) they are very rare on hydrated silica (SiO$_2$, Figure S10, Top). This already seems to point toward a higher affinity of Pt clusters and nanoparticles for dehydroxylated silica compared to the hydrated one.

Then, the interaction of Pt with a representative variety of Ga$^{III}$ sites on SiO$_2$-$700$ was studied (Figure S11). Most Ga$^{III}$ sites are tri-coordinated (Figure S11, site I) in this case formation energy of a Pt-adduct range between -60.0 kcal mol$^{-1}$ and -68.3 kcal mol$^{-1}$, while for tetracoordinated sites (Figure S11, site IV-Pt) this energy decreases to -49.5 kcal mol$^{-1}$. In any case, the average affinity of these sites for Pt is much higher
than on pure SiO$_2$-700 (-60.6 kcal mol$^{-1}$ vs -20.7 for Ga$^{III}$ sites on SiO$_2$-700 and -17.1 for SiO$_2$) thus confirming the trends obtained with the cluster model.
5. Structure of PtGa nanoparticles on Ga-doped SiO$_2$-700

Figure S12 – Optimized structures of Pt$_2$Ga nanoparticles (12 Ga and 26 Pt) on Ga-doped (1 Ga per nm$^2$) SiO$_2$ surfaces optimized by ab initio molecular dynamic and subsequent gradient optimized, electronic energy at DZ level (kcal mol$^{-1}$), interaction energy of the nanoparticle with the surface ($E_{\text{tot}}$), deformation energy between nanoparticle in vacuum and nanoparticle on surface ($E_{\text{def}}$); interaction energy between the distorted nanoparticle and surface ($E_{\text{int}}$) see the computational Section for definitions. Conventions: Si (blue), O (red), H (white), Pt (grey) and Ga (green).
Figure S13 – Evolution of the total number of Ga-O, Pt-Si, OSi, Pt-Pt and Pt-Ga bonds during isothermic and subsequent AIMD anealing on a 38 Pt atoms SiO$_{2.700}$ supported nanoparticle. Each color corresponds to a different starting time for the anealing process.
Figure S14 – Top – *In-situ* Ga K-edge XANES spectra (Left) and first derivative (Right) of Pt(OSi(OtBu)3)(COD)Ga/SiO2 under reduction conditions (flow of H2, 1 bar, see Figure S15 for temperature ramp) recorded after 0, 6, 9, 18, 24, 31, 37, 45 and 61 min; – Down – *In-situ* Pt L3-edge XANES spectra (Left) and first derivative (Right) of Pt(OSi(OtBu)3)(COD)Ga/SiO2 under reduction conditions (flow of H2, 1 bar, see Figure S15 for temperature ramp) recorded after 0, 6, 9, 18, 24, 31, 37, 45 and 61 min.
Figure S15 – Top-Left – Fraction of the final material (x, %) obtained by LCF of the Ga K (green line) and Pt L3 (grey line) edges XANES spectra obtained during in situ during reduction of Pt(OSi(OtBu)_3)(COD)_Ga/SiO_2 under a flux (1 bar) of H_2, initial and final spectra were used as fitting components. – Top-Right – Temperature ramp during the reduction treatment. Bottom – LCF of the Ga K (green line) and Pt L3 (grey line) edges XANES spectra obtained during in situ during reduction of Pt(OSi(OtBu)_3)(COD)_Ga/SiO_2 under a flux (1 bar) of H_2, Pt^0 and Ga^III foils spectra and initial spectra were used as fitting components. Left – fraction of Pt^II (grey line) and Ga^III (green line), Right – fractions of Pt^0 (grey line) and Ga^0 (green line).

Here follows the fitted data, LCF of the Ga K and Pt L3 edges XANES spectra obtained during in situ during reduction of Pt(OSi(OtBu)_3)(COD)_Ga/SiO_2 under a flux (1 bar) of H_2, initial and final spectra were used as fitting components, used for the construction of Figure 4a and Figure S15 (Top-Right).
Here follow the fitted data, LCF of the Ga K and Pt L3 edges XANES spectra obtained during *in situ* during reduction of \( \text{Pt(OSi(OtBu)_3)(COD)} \_\text{Ga/SiO}_2 \) under a flux (1 bar) of \( \text{H}_2 \), \( \text{Pt}^0 \) and \( \text{Ga}^0 \) foils spectra and initial spectra were used as fitting components, used for the construction of Figure S15 (Bottom).
Figure S16 – Left – LCF of the Ga K-edge XANES spectrum of PtGa/SiO$_2$ 100: 18.3 % PtGa/SiO$_2$, 81.7 % Pt(OSi(OtBu)$_3$)(COD)$_2$/Ga/SiO$_2$. Right – 11.7 % Ga foil, 88.3% Pt(OSi(OtBu)$_3$)(COD)$_2$/Ga/SiO$_2$.

Table S3 – EXAFS fit parameters for PtGa/SiO$_2$ 100 at the Pt L$_3$ edge. $\chi^2=0.82$; $k$ range 3-14 Å; R range 1-3.2 Å; $k$ weight 2. Hanning window $dr=0.5$; R factor 0.026.

| Path  | $N$   | R (Å)          | $\sigma^2$ (Å$^2$) | $\Delta E_0$ (eV) |
|-------|-------|----------------|--------------------|-------------------|
| Pt-O  | 1.8 +/- 2.7 | 2.001 +/- 0.060 | 0.0302 +/- 0.0300  | 6.7 +/- 1.3       |
| Pt-Pt | 5.5 +/- 0.7  | 2.728 +/- 0.007 | 0.0075 +/- 0.0007  |                   |

As alluded in the main text, attempts to fit a Ga-Pt pathway at the Ga K-edge for PtGa/SiO$_2$ 100 leads to small coordination numbers with large error (Ga-Pt CN = 0.5 +/- 1.1), suggesting a low amount of Ga-Pt interaction with either alloyed Ga$^0$ or Ga$^{III}$ surface sites. Removal of this pathway leads to a statistically worse fit indicating that Ga-Pt interaction exists but is difficult to analyze purely via EXAFS analysis. For the same material fitting of a Pt-O pathway at the Pt L$_3$ edge led to a high error in coordination numbers (1.8 +/- 2.7) in accordance with low Pt-O interaction. Removal of this pathway resulted in a visual and statistically worse fit. The inclusion of a Pt-Ga pathway gave an unphysical fit which can be explained by a much higher Pt-Pt contribution compared to Pt-Ga contribution which both occur at a similar position in R space.
Figure S17 – Top – EXAFS data (black) and fits (red) in R-space PtGa/SiO$_2$ after 10 h at 100 °C under H$_2$ (1 bar, flux) at the Pt L$_3$-edge. Bottom-Right – LCF of the Pt L$_3$-edge XANES spectrum of PtGa/SiO$_2$: 77.5 % Pt foil, 22.5 % Pt(OSi(OtBu)$_3$)(COD)$_2$/SiO$_2$. Bottom-Left – LCF of the Pt L$_3$-edge XANES spectrum of PtGa/SiO$_2$: 90.2 % PtGa/SiO$_2$, 9.8 % Pt(OSi(OtBu)$_3$)(COD)$_2$/SiO$_2$. 
**Table S4** – EXAFS fit parameters for Pt foil reference at the Pt L3 edge. $S_0^2=0.82 +/- 0.03$; $k$ range 3-14 Å; $R$ range 1-3.2 Å; $k$ weight 2. Hanning window $dr=0.5$; $R$ factor 0.002. Values without errors are fixed.

| Path | $N$ | $R$ (Å)      | $\sigma^2$ ($Å^2$) | $\Delta E_0$ (eV) |
|------|-----|--------------|-------------------|-------------------|
| Pt-Pt| 12  | 2.763 +/- 0.001 | 0.0047 +/- 0.0002 | 8.2 +/- 0.3      |

**Table S5** – EXAFS fit parameters for Ga(acac)$_3$ reference at the Ga K edge. determined $S_0^2=1.21 +/- 0.09$; $k$ range 3-14 Å; $R$ range 1-2.2 Å; $k$ weight 2. Hanning window $dr=0.5$; $R$ factor 0.005. Values without errors are fixed.

| Path | $N$ | $R$ (Å)     | $\sigma^2$ ($Å^2$) | $\Delta E_0$ (eV) |
|------|-----|-------------|-------------------|-------------------|
| Ga-O | 6   | 1.956 +/- 0.007 | 0.0057 +/- 0.0009 | 2.7 +/- 1.0      |

**Table S6** – EXAFS fit parameters for PtGa/SiO$_2$ at the Ga K edge. $S_0^2=1.21$; $k$ range 3-11 Å; $R$ range 1-3.2 Å; $k$ weight 3. Hanning window $dr=0.5$; $R$ factor 0.022.

| Path | $N$   | $R$ (Å)        | $\sigma^2$ ($Å^2$) | $\Delta E_0$ (eV) |
|------|-------|----------------|-------------------|-------------------|
| Ga-O | 0.8 +/- 0.4 | 1.781 +/- 0.0121 | 0.0076 +/- 0.0048 | 2.2 +/- 2.5      |
| Ga-Pt| 2.4 +/- 0.6 | 2.610 +/- 0.012 | 0.0084 +/- 0.0018 |                   |
Table S7 – EXAFS fit parameters for PtGa/SiO$_2$-100 at the Ga K edge. \( S^2=1.21; \ \kappa \) range 3-13 Å; R range 1-3.2 Å; \( \kappa \) weight 2. Hanning window \( dr = 0.5; \ R \) factor 0.021.

| Path   | \( N \) | \( R \) (Å) | \( \sigma^2 \) (Å$^2$) | \( \Delta E_0 \) (eV) |
|--------|--------|-------------|----------------|-----------------|
| Ga-O   | 3.6 $\pm$ 0.5 | 1.807 $\pm$ 0.015 | 0.0086 $\pm$ 0.0018 | -2.0 $\pm$ 2.8  |
| Ga-Pt  | 0.5 $\pm$ 1.1  | 2.537 $\pm$ 0.059 | 0.0107 $\pm$ 0.0157 |                |

Table S8 – EXAFS fit parameters for Pt(OSi(OtBu)$_3$)(COD)$_2$-Ga/SiO$_2$ at the Ga K edge. \( S^2=1.21; \ \kappa \) range 3-12 Å; R range 1-3.2 Å; \( \kappa \) weight 2. Hanning window \( dr = 0.5; \ R \) factor 0.013.

| Path   | \( N \) | \( R \) (Å) | \( \sigma^2 \) (Å$^2$) | \( \Delta E_0 \) (eV) |
|--------|--------|-------------|----------------|-----------------|
| Ga-O   | 4.2 $\pm$ 0.4 | 1.813 $\pm$ 0.008 | 0.0067 $\pm$ 0.0011 | -0.4 $\pm$ 1.4  |

Figure S18 – STEM and STEM-EDX picture of PtGa/SiO$_2$-100.

Figure S19 – Histograms of the Pt-Pt distances during a 1 ps MD simulation at 875 K (the silica surface was frozen) for 1 nm (38 atoms) Pt and Pt$_2$Ga nanoparticle.
6. Adsorption Energies of Educts and Products on Surfaces

Table S9 – Optimized structures of propane adsorbed on (111) Pt and (311) Pt₂Ga surfaces, adsorption electronic energy \( E_{\text{ads}} \) (kcal mol\(^{-1}\)), defined as \( E_{\text{ads}} = E_{\text{propane/surface}} - [E_{\text{propane}} + E_{\text{surface}}] \), adsorption enthalpy \( H_{\text{ads}} \) (kcal mol\(^{-1}\)) adsorption free energy at 298 K and 875 K \( G_{\text{ads}} \) (kcal mol\(^{-1}\)), lowest CH frequency (cm\(^{-1}\)) and Pt-H distance (Å).

| Pt₂Ga (311) |  |  | Pt₂Ga (311) |  | Pt (311) |
|-------------|---|---|-------------|---|----------|
|              | 1 | 2 |              | 3 | 4        |
| a face       |   |   |              |   |          |
| c face       |   |   |              |   |          |
| \( E_{\text{ads}} \) | -9.4 | -11.1 | -10.2 | -9.7 |
| \( H_{\text{ads}} \) | -9.5 | -11.5 | -10.5 | -9.7 |
| \( G_{\text{ads}} \) (298 K) | -2.8 | -4.4 | -3.6 | -3.0 |
| \( G_{\text{ads}} \) (875 K) | +11.5 | +9.8 | +10.7 | +11.5 |
| CH freq      | 2900 | 2679 | 2892 | 2892 |
| Pt-H         | 2.866 | 2.269 | 2.412 | 3.050 |

| Pt₂Ga (311) | 5 | Pt₂Ga (311) |  | Pt (311) |
|-------------|---|-------------|---|----------|
|              |   |              |   |          |
| a face       |   |   |              |   |          |
| c face       |   |   |              |   |          |
| \( E_{\text{ads}} \) | -9.5 | -14.9 | -11.5 |
| \( H_{\text{ads}} \) | -9.6 | -15.4 | -11.7 |
| \( G_{\text{ads}} \) (298 K) | -13.3 | -7.8 | -5.4 |
| \( G_{\text{ads}} \) (875 K) | +10.5 | +9.9 | +8.2 |
| CH freq      | 2892 | 2691 | 2834 |
| Pt-H         | 3.050 |        | 2.735 |
Table S10 – Optimized structures of propene adsorbed on (111) Pt and (311) and (111) Pt$_2$Ga surfaces in π-conformation (π²-propene), adsorption electronic energy ($E_{ads}$, kcal mol$^{-1}$, defined as $E_{ads} = E_{propane/surface} - [E_{propane} + E_{surface}]$), adsorption enthalpy ($H_{ads}$, kcal mol$^{-1}$) and adsorption free energy at 298 K and 875 K ($G_{ads}$, kcal mol$^{-1}$).

| Pt$_2$Ga (311) | Pt1 | Pt2 | Pt3 | Pt4 |
|----------------|-----|-----|-----|-----|
| **b face**     | ![Image](image1) | ![Image](image2) | ![Image](image3) | ![Image](image4) |
| **c face**     | ![Image](image5) | ![Image](image6) | ![Image](image7) | ![Image](image8) |
| $E_{ads}$      | -22.0 | -23.6 | -22.7 | -14.8 |
| $H_{ads}$      | -20.6 | -22.6 | -21.5 | -13.7 |
| $G_{ads}$ (298 K) | -13.4 | -14.6 | -13.5 | -5.9 |
| $G_{ads}$ (875 K) | -0.4 | 0.0 | +0.9 | +7.9 |

| Pt$_2$Ga (111) | Pt-1 | Pt-2 | Pt (111) |
|----------------|------|------|----------|
| **b face**     | ![Image](image9) | ![Image](image10) | ![Image](image11) |
| **c face**     | ![Image](image12) | ![Image](image13) | ![Image](image14) |
| $E_{ads}$      | -24.8 | -27.9 | -25.7 |
| $H_{ads}$      | -23.9 | -26.8 | -24.5 |
| $G_{ads}$ (298 K) | -17.2 | -18.8 | -16.8 |
| $G_{ads}$ (875 K) | -5.7 | -4.4 | -11.5 |
Part of the lower affinity of propene for Pt₃Ga is due to geometric effects coming to the adjunction of Ga atoms to the Pt, which increases the distance between Pt atoms thus disfavoring the di-σ adsorption mode on Pt. By plotting the adsorption energy of propene on the Pt₃Ga (311) surface as a function of the distance between the two platinum atoms (Pt-x and Pt-y) in the case of σ-coordination (Figure S20), it is clear that the adsorption energy decreases with increasing distance between the two coordinating Pt atoms. However, for similar Pt-Pt distances, adsorption of propene is more favored on Pt (111) than on Pt₃Ga (Figure S20). Thus, part of the lower affinity of propene for Pt₃Ga must be related to electronic effects as well.

To understand these effects, the Density of State (DOS) for both Pt and Pt₃Ga surfaces were compared: addition of Ga induces a significant decrease of the Fermi level from 2.63 eV in pure Pt to 1.86 eV in Pt₃Ga (Figure S21-left). Consequently, one would expect a strong decrease of the electron donating ability of Pt surrounded by Ga, that is consistent with the decrease adsorption energies discussed above. In fact, analyzing the projected DOS on Pt and Ga atoms (Figure S21-right) shows that the d-orbitals of Pt interacts with the empty Ga p-orbitals, resulting in the observed stabilization of the Fermi level. Coordination of propene on the surface is typically due to i) donation from the π-orbital of the double bond to the low-lying empty d-orbitals of Pt, and the ii) back-donation from the d-orbitals of the metal to the low-lying π*- antibonding orbital of propene (Figure S22). The stabilization of the d-orbital of Pt by Ga induces a decrease of the π-back donation, as evidenced by the magnitude of the variation of the C-C bond length (Figure S22-d). This contrasts with a simpler view that the addition of Ga, a more electropositive element, would increase the electron density on Pt and thereby increase its π-bonding ability.

This model holds well for flat surfaces, however the distorted and unsaturated Pt₃Ga (111) surface – lower in energy than the (311) – is likely to have a different behavior. The particular activity of step sites was underlined in the case of a PtSn alloy. Structures and energies of propene adsorbed on Pt₃Ga (111) are provided in Tables S8-9. Both σ (-23.9 to -26.8 kcal mol⁻¹) and π-coordination of propene (-20.4 to -31.4 kcal mol⁻¹) are significantly more favored compared to adsorption of the flat (311) surface and close to the one on Pt (111) (Tables S8-S9). At 875 K the entropic contribution dominates and the π-coordination is favored, as found for pure platinum.

Figure S20 – Corelation between the Pt-Pt distance (pm) at the (311) Pt₃Ga and (111) Pt surfaces and the relative adsorption enthapy of propene ($\Delta E_{\text{ads}} = E_{\text{ads}} - E_{\text{ads,Pt3Pt2}}$).
Table S11 – Optimized structures of propene adsorbed (111) Pt and (311) and (111) Pt$_2$Ga surfaces in $\sigma$-conformation (adsorbed on two adjacent Pt sites), adsorption electronic energy ($E_{ads}$ kcal mol$^{-1}$, defined as $E_{ads} = E_{propene/surface} - [E_{propene} + E_{surface}]$), adsorption enthalpy ($H_{ads}$ kcal mol$^{-1}$) adsorption free energy at 298 K and 875 K ($G_{ads}$ kcal mol$^{-1}$).

| Pt$_2$Ga (311) | Pt1-Pt2 | _ | Pt2-Pt1 | _ | Pt1-Pt3 | _ | Pt3-Pt1 |
|----------------|---------|---|---------|---|---------|---|---------|
| a face         | ![Structure](image1.png) | ![Structure](image2.png) | ![Structure](image3.png) | ![Structure](image4.png) | ![Structure](image5.png) | ![Structure](image6.png) | ![Structure](image7.png) |
| c face         | ![Structure](image8.png) | ![Structure](image9.png) | ![Structure](image10.png) | ![Structure](image11.png) | ![Structure](image12.png) | ![Structure](image13.png) | ![Structure](image14.png) |
| $E_{ads}$      | -22.2   | -22.3 | -22.5   | -22.7 |
| $H_{ads}$      | -21.2   | -21.3 | -21.5   | -21.7 |
| $G_{ads}$ (298 K) | -12.5  | -12.8 | -13.1   | -13.2 |
| $G_{ads}$ (875 K) | +3.8   | +3.2  | +2.7    | +2.9  |

| Pt$_2$Ga (311) | Pt2-Pt3 | Pt3-Pt2 | Pt4-Pt3 | Pt2-Pt4 |
|----------------|---------|---------|---------|---------|
| a face         | ![Structure](image15.png) | ![Structure](image16.png) | ![Structure](image17.png) | ![Structure](image18.png) |
| c face         | ![Structure](image19.png) | ![Structure](image20.png) | ![Structure](image21.png) | ![Structure](image22.png) |
| $E_{ads}$      | -25.2   | -25.6   | -16.6   | -15.9   |
| $H_{ads}$      | -24.3   | -24.6   | -15.6   | -14.9   |
| $G_{ads}$ (298 K) | -15.8  | -16.1   | -7.2    | -6.5    |
| $G_{ads}$ (875 K) | +0.2   | -0.2    | +8.4    | +9.1    |

| Pt$_2$Ga (111) | Pt4-Pt1 | _ | Pt4-Pt2 | _ | Pt4-Pt3 | _ | Pt (111)  |
|----------------|---------|---|---------|---|---------|---|---------|
| a face         | ![Structure](image23.png) | ![Structure](image24.png) | ![Structure](image25.png) | ![Structure](image26.png) | ![Structure](image27.png) | ![Structure](image28.png) |
| c face         | ![Structure](image29.png) | ![Structure](image30.png) | ![Structure](image31.png) | ![Structure](image32.png) | ![Structure](image33.png) | ![Structure](image34.png) |
| $E_{ads}$      | -31.4   | -25.1   | -20.4   | -33.8   |
| $H_{ads}$      | -30.7   | -24.5   | -19.6   | -32.7   |
| $G_{ads}$ (298 K) | -21.6  | -16.4   | -10.5   | -24.1   |
| $G_{ads}$ (875 K) | -3.0   | -1.5    | +8.1    | -6.7    |
Figure S21 – Left - Total Density of State (DOS) for Pt (111) and Pt$_2$Ga (311). Right – Projected DOS (p-DOS) on a surface Pt and surface Ga atom of the (311) Pt$_2$Ga surface. Calculated with the same level of theory of this work.

Figure S22 – a – p-DOS and crystal orbital Hamilton population (COHP) bonding analysis of the C=C bond in ethene. b – p-DOS and COHP of C=C bond of adsorbed ethene on Pt (111) surface. c – p-DOS and COHP of C=C bond of adsorbed ethene on Pt$_2$Ga (311) surfaces. d – Effect of incorporated Ga on the length of the C=C bond.
7. Reactivity of PtGa₂ alloy compared to Pt

Table S12 – Optimized structures of propylgallium and propylplatinium intermediates adsorbed on Pt (111) and PtGa (311), adsorption electronic energy ($E_{ads}$ kcal mol⁻¹, defined $E_{ads} = E_{propyl/surface} + E_{H/surface} - (E_{propane} + 2 \times E_{surface})$), adsorption enthalpy ($H_{ads}$ kcal mol⁻¹) and adsorption free energy at 298 K and 875 K ($G_{ads}$ kcal mol⁻¹).

| Pt₂Ga (311) | Pt1 | Pt2 | Pt2-bis | Pt3 |
|-------------|-----|-----|---------|-----|
| a face      | ![Diagram](image1) | ![Diagram](image2) | ![Diagram](image3) | ![Diagram](image4) |
| c face      | ![Diagram](image5) | ![Diagram](image6) | ![Diagram](image7) | ![Diagram](image8) |
| $E_{ads}$   | -6.5 | -3.9 | -6.8    | -2.2 |
| $H_{ads}$   | -10.4 | -7.8 | -11.0   | -6.8 |
| $G_{ads}$ (298 K) | -2.4 | +0.5 | -2.3    | +1.4 |
| $G_{ads}$ (875 K) | +7.0 | +10.5 | +8.7    | +11.0 |

| Pt₂Ga (311) | Pt4 | Ga1 | Ga2 | Pt (111) |
|-------------|-----|-----|-----|----------|
| a face      | ![Diagram](image9) | ![Diagram](image10) | ![Diagram](image11) | ![Diagram](image12) |
| c face      | ![Diagram](image13) | ![Diagram](image14) | ![Diagram](image15) | ![Diagram](image16) |
| $E_{ads}$   | -1.1 | +12.3 | +12.6 | -12.9 |
| $H_{ads}$   | -5.1 | +8.3  | +6.1  | -15.3 |
| $G_{ads}$ (298 K) | +3.1 | +16.8 | +15.7 | -5.2 |
| $G_{ads}$ (875 K) | +13.0 | +27.5 | +31.8 | +2.9 |

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|            | Pt$_2$Ga (I1) | Pt4 | Pt4 bis |
|------------|---------------|-----|---------|
| **a face** |               |     |         |
| **c face** |               |     |         |

|        |     |     |         |
|-------|-----|-----|---------|
| $E_{\text{ads}}$ | -7.7 | -6.3 |         |
| $H_{\text{ads}}$ | -10.9 | -9.6 |         |
| $G_{\text{ads}}$ (298 K) | -4.4 | -2.9 |         |
| $G_{\text{ads}}$ (875 K) | +6.6 | +8.4 |         |
Table S13-a – Optimized structures of monoligated hydride intermediates adsorbed on Pt$_2$Ga (311), adsorption electronic energy ($E_{ads}$ kcal mol$^{-1}$, $E_{ads} = E_{H/face} - (1/2)E_{H_2} + E_{surface}$) adsorption enthalpy ($H_{ads}$ kcal mol$^{-1}$) and adsorption free energy at 298 K and 875 K ($G_{ads}$ kcal mol$^{-1}$).

|       | Pt1 | Pt2 | Pt3 | Pt4 |   |
|-------|-----|-----|-----|-----|---|
| c face |     |     |     |     |   |
| $E_{ads}$  | -8.6 | -8.0 | -6.5 | -4.8 |   |
| $H_{ads}$    | -8.2 | -6.8 | -5.6 | -3.7 |   |
| $G_{ads}$ (298 K) | -3.8 | -3.7 | -2.0 | -0.1 |   |
| $G_{ads}$ (875 K) | +3.9 | +5.2 | +6.0 | +8.3 |   |

Table S13-b – Optimized structures of bis-ligated hydride intermediates adsorbed on Pt$_2$Ga (311), adsorption electronic energy ($E_{ads}$ kJ mol$^{-1}$, $E_{ads} = E_{H/face} - (1/2)E_{H_2} + E_{surface}$) adsorption enthalpy ($H_{ads}$ kcal mol$^{-1}$) and adsorption free energy at 298 K and 875 K ($G_{ads}$ kJ mol$^{-1}$).

|       | Pt1-Pt4 | Pt2-Pt3 | Pt3-Pt4 |   |
|-------|---------|---------|---------|---|
| c face |         |         |         |   |
| $E_{ads}$  | -4.6    | -9.4    | -2.4    |   |
| $H_{ads}$    | -3.9    | -8.8    | -1.7    |   |
| $G_{ads}$ (298 K) | -0.2    | -5.3    | +2.0    |   |
| $G_{ads}$ (875 K) | +6.7    | +3.2    | -10.9   |   |

Table S13-c – Optimized structures of tris-ligated hydride intermediates adsorbed on Pt$_2$Ga (311), adsorption electronic energy ($E_{ads}$ kcal mol$^{-1}$, $E_{ads} = E_{H/face} - (1/2)E_{H_2} + E_{surface}$), adsorption enthalpy ($H_{ads}$ kcal mol$^{-1}$) and adsorption free energy at 298 K and 875 K ($G_{ads}$ kcal mol$^{-1}$).

|       | Pt2-Pt3-Pt4 |   |
|-------|-------------|---|
| c face |         |   |
| $E_{ads}$  | -3.0   |   |
| $H_{ads}$    | +0.7   |   |
| $G_{ads}$ (298 K) | +9.6   |   |
| $G_{ads}$ (875 K) | +9.6   |   |
Table S14 – Optimized structures of transition states corresponding to the first C-H activation of propane on Pt (111) and Pt$_2$Ga (311) and (111), adsorption electronic energy ($E_{ads}$, kcal mol$^{-1}$), $E_{ads} = E_{TS/surface} - (E_{propane} + E_{surface})$, adsorption enthalpy ($H_{ads}$, kcal mol$^{-1}$) adsorption free energy at 298 K and 875 K ($G_{ads}$, kcal mol$^{-1}$).

|                  | Pt (311) | Pt1-Pt2 |  | Pt2-Pt3 |  | Pt1-Pt4 |  |
|------------------|----------|---------|---|---------|---|---------|---|
|                  | a face   |         |   | c face   |   |         |   |
| $E_{ads}$        | +9.1     | +7.4    | +11.9 |
| $H_{ads}$        | +6.0     | +4.0    | +9.1  |
| $G_{ads}$ (298 K)| +12.7    | +10.6   | +16.2 |
| $G_{ads}$ (875 K)| +25.1    | +22.5   | +29.4 |

Table S15 – Optimized structures of transition states corresponding to the second C-H activation of propane on Pt (111) and Pt$_2$Ga (311) and (111), adsorption electronic energy ($E_{ads}$, kcal mol$^{-1}$), $E_{ads} = E_{TS/surface} - (E_{propane} + E_{surface})$, adsorption enthalpy ($H_{ads}$, kcal mol$^{-1}$) adsorption free energy at 298 K ($G_{ads}$, kcal mol$^{-1}$).

|                  | Pt1-Pt2Pt3 (311) | Pt2Pt3Pt4 (311) | Pt$_2$Ga (111) | Pt (111) |
|------------------|------------------|-----------------|----------------|----------|
|                  | a face           |                 |                |          |
| $E_{ads}$        | +11.6            | +28.0           | +4.4           | +4.2     |
| $H_{ads}$        | +4.8             | +20.7           | -1.7           | -1.8     |
| $G_{ads}$ (298 K)| +12.7            | +28.6           | +6.1           | +6.0     |
Table S16 – Optimized structures of transition states corresponding to the first C-H activation of propene on Pt (111) and Pt₂Ga (311), adsorption electronic energy (\(E_{ads}\) kcal mol\(^{-1}\)), adsorption enthalpy (\(H_{ads}\) kcal mol\(^{-1}\)) adsorption free energy at 298 K (\(G_{ads}\) kcal mol\(^{-1}\)).

|            | Pt₂Ga (311) | Pt (111) |
|------------|-------------|-----------|
| a face     |             |           |
| c face     |             |           |
| \(E_{ads}\)| -0.4        | -13.1     |
| \(H_{ads}\)| -2.0        | -15.5     |
| \(G_{ads}\) (298 K)| +7.0        | -6.4      |
| \(G_{ads}\) (875 K)| +23.6       | +11.2     |
Table S17 – Optimized structures of vinyl intermediates (CH\textsubscript{2}CHCH\textsubscript{2}) adsorbed on Pt (111) and Pt\textsub{2}Ga (311) and (111), adsorption electronic energy ($E_{ads}$, kcal mol\textsuperscript{-1}), $E_{ads} = E_{TS/surface} + E_{H/surface} - (E_{propene} + 2 \cdot E_{surface}$), adsorption enthalpy ($H_{ads}$, kcal mol\textsuperscript{-1}) adsorption free energy at 298 K ($G_{ads}$, kcal mol\textsuperscript{-1}).

|                | Pt\textsub{2}Ga (311) | Pt (111) |
|----------------|------------------------|----------|
| a face         |                        |          |
| c face         |                        |          |
| $E_{ads}$      | -17.0                  | -30.1    |
| $H_{ads}$      | -20.1                  | -32.2    |
| $G_{ads}$ (298 K) | -11.3                 | -23.3    |
| $G_{ads}$ (875 K) | +4.3                  | -8.5     |

Table S18 – Optimized structures of transition states corresponding to the second C-H activation of propene on Pt (111) and Pt\textsub{2}Ga (311) and (111), adsorption electronic energy ($E_{ads}$, kcal mol\textsuperscript{-1}), $E_{ads} = E_{TS/surface} + E_{H/surface} - (E_{propene} + 2 \cdot E_{surface}$), adsorption enthalpy ($H_{ads}$, kcal mol\textsuperscript{-1}) adsorption free energy at 298 K ($G_{ads}$, kcal mol\textsuperscript{-1}).

|                | Pt\textsub{2}Ga (311) | Pt (111) |
|----------------|------------------------|----------|
| a face         |                        |          |
| c face         |                        |          |
| $E_{ads}$      | +11.2                  | -8.8     |
| $H_{ads}$      | +5.0                   | -14.0    |
| $G_{ads}$ (298 K) | +14.0                 | -5.1     |
| $G_{ads}$ (875 K) | +30.1                 | +10.8    |
Table S19 – Optimized structures of propyne (CH\textsubscript{3}CCH) adsorbed on Pt (111) and Pt\textsubscript{2}Ga (311) and (111), adsorption electronic energy (\(E_{\text{ads}}\) kcal mol\textsuperscript{-1}, \(E_{\text{ads}} = E_{\text{TS/surface}} + 2 \cdot E_{\text{H/surface}} - (E_{\text{propene}} + 3 \cdot E_{\text{surface}})\), adsorption enthalpy (\(H_{\text{ads}}\) kcal mol\textsuperscript{-1}) adsorption free energy at 298 K (\(G_{\text{ads}}\) kcal mol\textsuperscript{-1}).

|           | Pt\textsubscript{2}Ga (311) | Pt (111) |
|-----------|-----------------------------|----------|
| a face    | ![Image](image1.png)        | ![Image](image2.png) |
| c face    | ![Image](image3.png)        | ![Image](image4.png) |
| \(E_{\text{ads}}\) | -7.4                        | -31.4    |
| \(H_{\text{ads}}\) | -13.7                       | -36.0    |
| \(G_{\text{ads}} (298 K)\) | -5.0                        | -27.4    |
| \(G_{\text{ads}} (875 K)\) | +9.8                        | -13.5    |

Table S20 – Optimized structures of transition states corresponding to the cleavage of the CC triple bond of propyne adsorbed on Pt (111) and Pt\textsubscript{2}Ga (311) and (111), adsorption electronic energy (\(E_{\text{ads}}\) kcal mol\textsuperscript{-1}, \(E_{\text{ads}} = E_{\text{TS/surface}} + 2 \cdot E_{\text{H/surface}} - (E_{\text{propene}} + 3 \cdot E_{\text{surface}})\), adsorption enthalpy (\(H_{\text{ads}}\) kcal mol\textsuperscript{-1}) adsorption free energy at 298 K (\(G_{\text{ads}}\) kcal mol\textsuperscript{-1}).

|           | Pt\textsubscript{2}Ga (311) | Pt (111) |
|-----------|-----------------------------|----------|
| a face    | ![Image](image5.png)        | ![Image](image6.png) |
| c face    | ![Image](image7.png)        | ![Image](image8.png) |
| \(E_{\text{ads}}\) | +37.1                       | -4.9     |
| \(H_{\text{ads}}\) | +28.                        | -11.1    |
| \(G_{\text{ads}} (298 K)\) | +37.9                       | -2.4     |
| \(G_{\text{ads}} (875 K)\) | +53.7                       | +12.6    |
Figure S24 – Enthalpy (kcal mol\(^{-1}\)) pathway for propene deep dehydrogenation and coking on (311) Pt\(_2\)Ga surface (red) and on pure (111) Pt (blue).

Table S21 – Comparison of electronic energy pathways (\(E\), kcal mol\(^{-1}\)) on the (311) and (111) Pt\(_2\)Ga \textit{ab initio} optimized surfaces, on the (012) Pt\(_2\)Ga surface obtained from the experimental bulk structure of Pt\(_2\)Ga\(^{14}\) and on (111) Pt.

|                  | \(E\) (012) XRD bulk | \(E_{\text{max}}\) (311) Optimized bulk | \(E_{\text{min}}\) (311) Optimized bulk | \(E\) (111) Optimized bulk | \(E\) (111) Pt |
|------------------|-----------------------|----------------------------------------|----------------------------------------|-----------------------------|----------------|
| Propane (g)      | 0                     | 0                                      | 0                                      | 0                           | 0              |
| Propane (ads)    | -10.6                 | -11.1                                  | -9.4                                   | -14.5                       | -11.5          |
| TS1              | 11.1                  | 7.4                                    | 12.8                                   | 1.6                         | 6.4            |
| Propyl (ads) + H (ads) | -7.8                 | -6.8                                  | -2.2                                   | -7.7                        | -12.9          |
| TS2              | 14.6                  | 11.6                                  | 28                                     | 4.4                         | 4.2            |
| Propene (ads) + 2H (ads) | -13.9                | -12.3                                  | -5.8                                   | -18.1                       | -20.5          |

\(^{14}\) a) Chattopadhyay, T.; Khalaff, K.; Schubert, K. Zur Konstitution der Mischungen Platin-Gallium und Platin-Gallium-Germanium \textit{Metall} \textbf{1974}, \textit{28}, 1160-1168; b) Schubert, K.; Bhan, S.; Biswas, T. K.; Frank.; Panday, P. K. Einige Strukturdaten metallischer Phasen. 13. Mitteilung \textit{Naturwissenschaften} \textbf{1968}, \textit{55}, 542-543; c) Ueber die Struktur von Phasen mit Kupfer Unterstruktur in einigen T-B Legierungen (T= Ni, Pd, Pt; B = Ga, In, Tl, Pb, Sb, Bi) \textit{J. Less-Comm. Metals} \textbf{1969}, \textit{17}, 73-90.
8. Metadynamic

Selected snapshots of the Metadynamic simulations are available below (Figure S25, S29-32), movies of these simulations are available as separated SI files:

i) PDH-Pt.mp4: Metadynamic simulation of PDH on silica supported Pt nanoparticle;

ii) PDH-PtGa.mp4: Metadynamic simulation of PDH on silica supported Pt$_2$Ga nanoparticle;

iii) coking-Pt.mp4: Metadynamic simulation of coking on silica supported Pt nanoparticle;

iv) coking-PtGa.mp4: Metadynamic simulation of coking on silica supported Pt$_2$Ga nanoparticle.
Figure S25 – Snapshots from the metadynamic simulation of PDH on silica supported Pt nanoparticle.

Figure S26 – Comparison between free energy pathway for PDH obtained from periodic DFT (doted-line) versus metadynamic (plain line), Left on Pt, right on Pt3Ga (311 surface, most favorable pathway). 1) free propane; 2) adsorbed propane; 3) first CH activation; 4) Pt-propyl intermediate; 5) second activation; 6) adsorbed propene; 7) free propene.

Figure S27 – FES of PDH on SiO2-700 supported Pt nanoparticles 1) as a function of CV2-CV4 2) as a function of CV1-CV3 as reconstructed from the metadynamics run.
Figure S28 – FES of PDH on Ga-doped SiO$_2$-700 supported Pt$_2$Ga nanoparticles as a function of CV1 and CV2 as reconstructed from the metadynamics run. (1) adsorbed propane; TS-1 first C-H activation (2) Pt-alkyl intermediate TS-2 second C-H activation (3) adsorbed propene.
Figure S29 – Snapshots from the metadynamic simulation of PDH on silica supported PtGa nanoparticle.
Figure S30 – Snapshots from the metadynamic simulation of coking on silica supported Pt nanoparticle.
Figure S31 – Snapshots from the metadynamic simulation of coking on silica supported Pt nanoparticle.
Figure S32 – Snapshots from the metadynamic simulation of coking on Ga doped silica supported Pt nanoparticle.