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Peer reviewed

*Supporting Information for*

**Templated Encapsulation of Pt-based Catalysts Promotes High-Temperature Stability to 1,100 °C**

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### *Sintering simulations in absence of diffusion limitations*

The theory behind the mean-field model for the simulation of PtO<sub>2</sub>(g) in absence of diffusion limitations is the same as described in the literature.<sup>1</sup> Neglecting diffusion limitations, immediate transport of PtO<sub>2</sub>(g) through the gas phase leads to a constant PtO<sub>2</sub>(g) pressure  $p_b$  in the entire system. The influx of PtO<sub>2</sub>(g) onto a given particle follows the ideal gas law based on pressure  $p_b$ , mass  $m$ , temperature  $T$ , and surface area of the particle  $A(r)$ :

$$J_{in} = \frac{S}{\sqrt{2\pi mkT}} \cdot A(r) \cdot p_b \quad (\text{S1})$$

The total flux according to the mean-field model is given by:

$$J_{tot} = \frac{S}{\sqrt{2\pi mkT}} \cdot A(r) \cdot [p_b - p_{eq}(r)] \quad (\text{S2})$$

Importantly,  $p_{eq}(r)$  depends only on the thermodynamic stability of PtO<sub>2</sub>(g) relative to the chemical potential of the particle and it is not an observable pressure. In the mean field model,  $p_b$  is then determined from the requirement of mass-conservation, which means that the sum of the fluxes  $J_{tot}$  of all particles is zero.

### *Sintering simulations and diffusion limitations*

Above, we considered the limiting case that fast diffusion will immediately equilibrate the gas phase containing all particles. We now study the opposite case, where diffusion through the encapsulating material is slow. In the limiting case of extremely slow diffusion, an equilibrium between the particles and PtO<sub>2</sub>(g) within the encapsulating material will be established with the local pressure  $p_{eq}(r)$ , which is different for each particle. Outside of the particle, fast diffusion is assumed to again establish a constant background pressure  $p_b$ . Diffusion through the encapsulating material with constant diffusion coefficient  $D$  and surface area  $A$  is described by Fick's first law:

$$J_{tot} = -AD\nabla c \quad (\text{S3})$$

Here,  $\nabla c$  is the concentration gradient of the diffusing species, PtO<sub>2</sub>(g). For an encapsulating wall of constant thickness  $d$ , we obtain a constant concentration gradient:

$$J_{tot} = -AD \left( \frac{c_{eq} - c_b}{d} \right) \quad (\text{S4})$$

Expressing the concentrations in terms of pressures using the ideal gas law, we obtain:

$$J_{tot} = \frac{D}{dkT} A(p_b - p_{eq}). \quad (\text{S5})$$

Equation S5 has the same functional form as equation S2. If we assume that the area of the encapsulating material, through which PtO<sub>2</sub>(g) diffuses, is proportional to that of the particle, then identical results are obtained with both types of simulations, if the pre-factors are equal:

$$\frac{S}{\sqrt{2\pi mkT}} \cdot A = \frac{D}{dkT} A \quad (\text{S6})$$

Consequently, the results of a sintering simulation with strong diffusion limitations and the parameters (D, d, T, A) give exactly the same results as simulations without diffusion limitations, if an appropriate value of  $S=S_{eff}$  is chosen. Here, we use  $S_{eff}$  rather than  $S$  to emphasize that it effectively captures diffusion limitations and is not the sticking coefficient of a clean surface.

#### *Effect of diffusion limitations on catalysis*

Assuming that the diffusion coefficient of  $PtO_2(g)$  and  $O_2(g)$  is the same, the effect of the diffusion limitations, as expressed through a given  $S_{eff}$  can be estimated. Under steady-state conditions, the rate of  $O_2$ -consumption per particle (TOF) equals the flux of  $O_2(g)$  through the encapsulating material.

$$TOF = J_{tot} \quad (S7)$$

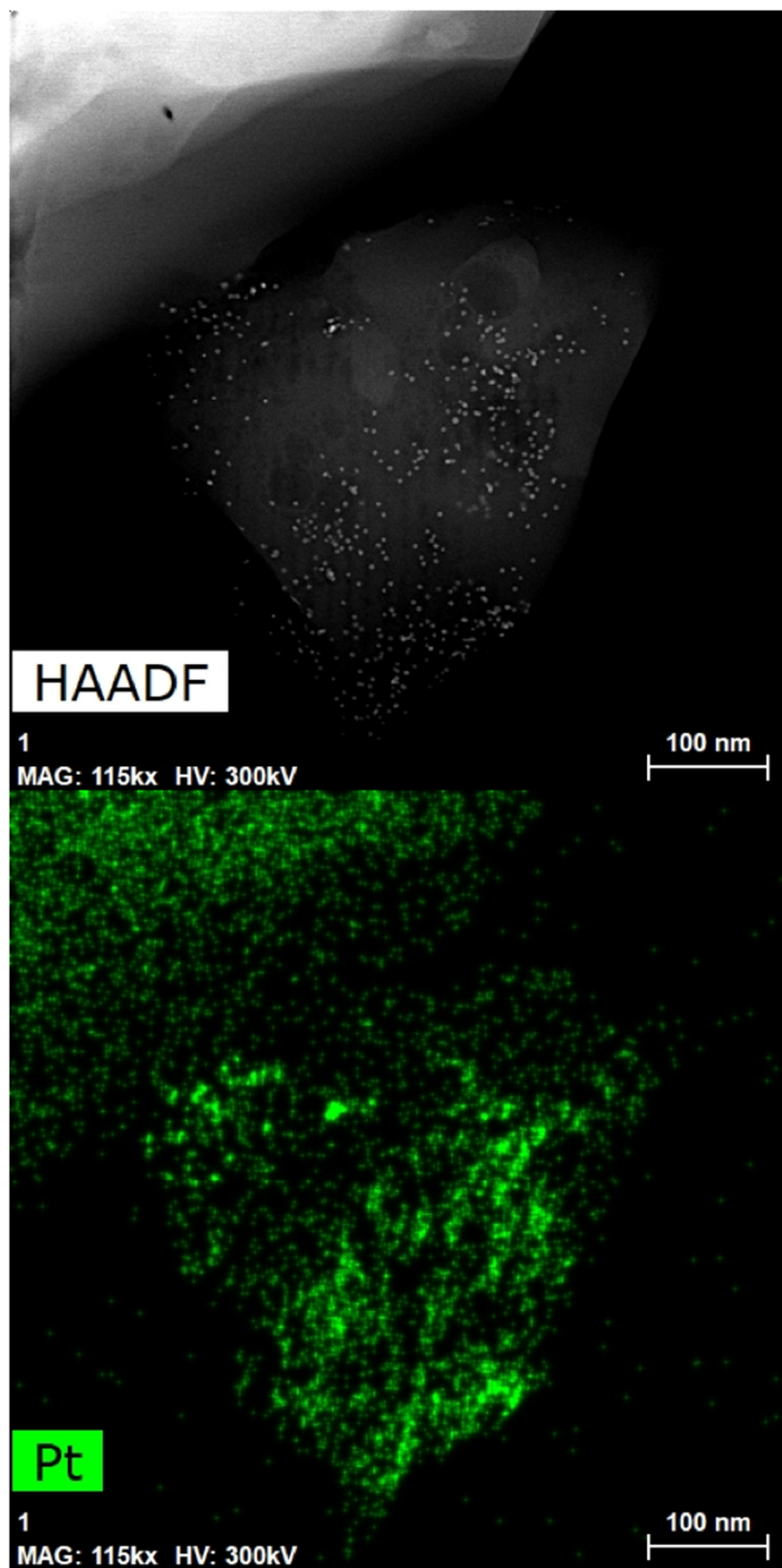
Using Eq. S5, we can determine the pressure drop  $\Delta p$  between the  $O_2$ -pressure outside and inside the encapsulation that is caused by the diffusion limitations:

$$\Delta p = TOF / \left( \frac{D}{dkT} A \right) \quad (S8)$$

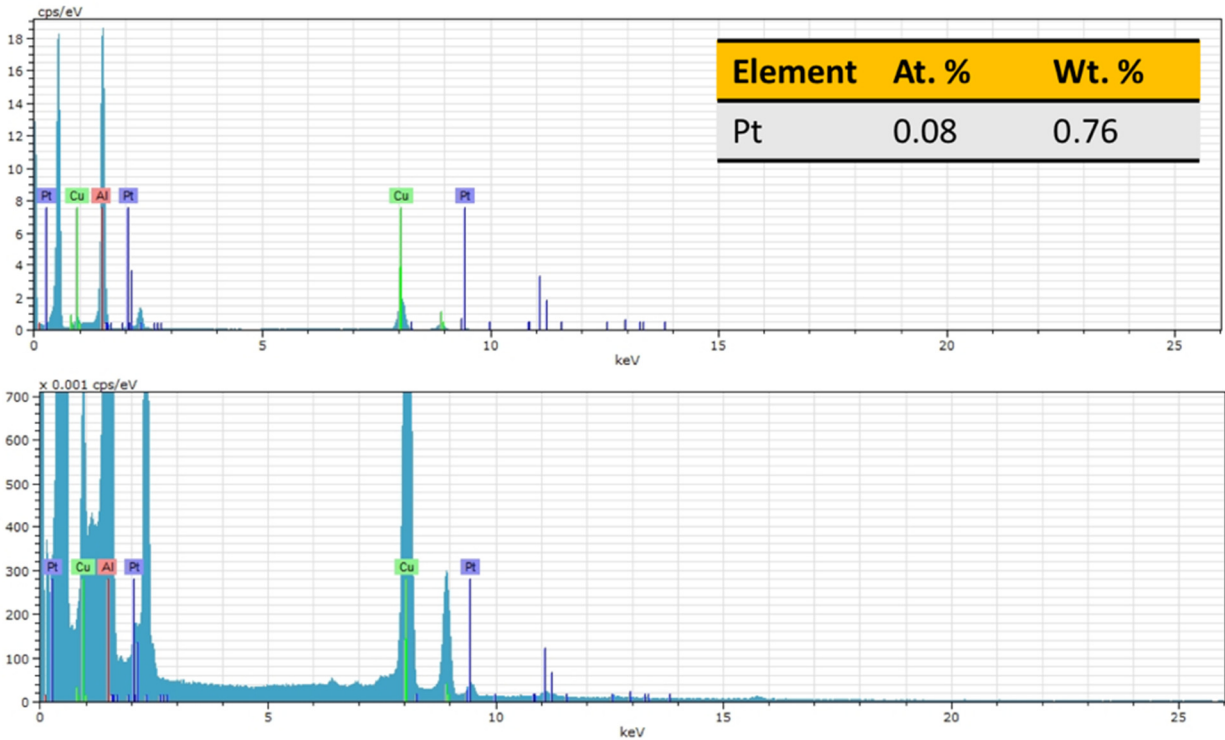
We will now study a worst-case scenario, where  $\Delta p$  becomes largest. The highest measured consumption rate of  $O_2(g)$  was determined as 695 molecules per second and nanoparticle at 202 °C. The smallest estimate of the diffusion limitations follows from Fig. 4b, for  $S_{eff} = 0.001$  at 800°C. In order to account for the fact that diffusion is expected to be slower at lower temperatures, we assume a temperature dependence of  $D \sim T^{3/2}$ . Using Eq. S8 and the surface area of a spherical particle with  $d=3.8$  nm, we obtain a pressure drop of  $\Delta p = 4.3 * 10^{-5} bar$ . For an oxygen pressure of 0.03 bar of  $O_2(g)$ , this means that the  $O_2$ -pressure is reduced by about 0.1%. The analogous calculation can be performed for propene. Since combustion per formula unit  $C_3H_6$  requires 9/2  $O_2$  molecules, the pressure drop is reduced by a factor of 2/9 to  $0.96 * 10^{-5} bar$ . Relative to the partial pressure of propene,  $1.5 * 10^{-3} bar$ , this is again a negligible pressure drop of 0.6 %.

The example above shows that the diffusion limitations assumed to be present for sintering via  $PtO_2(g)$  have no significant effect on catalysis. The reason for this is that the induced pressure gradient for  $O_2$  is very small compared to the pressure of  $O_2$ . For sintering, however, the situation is different, since the pressure of  $PtO_2(g)$  is typically on the order of  $10^{-9}$  bar. Therefore, much smaller pressure drops will already be significant for sintering.

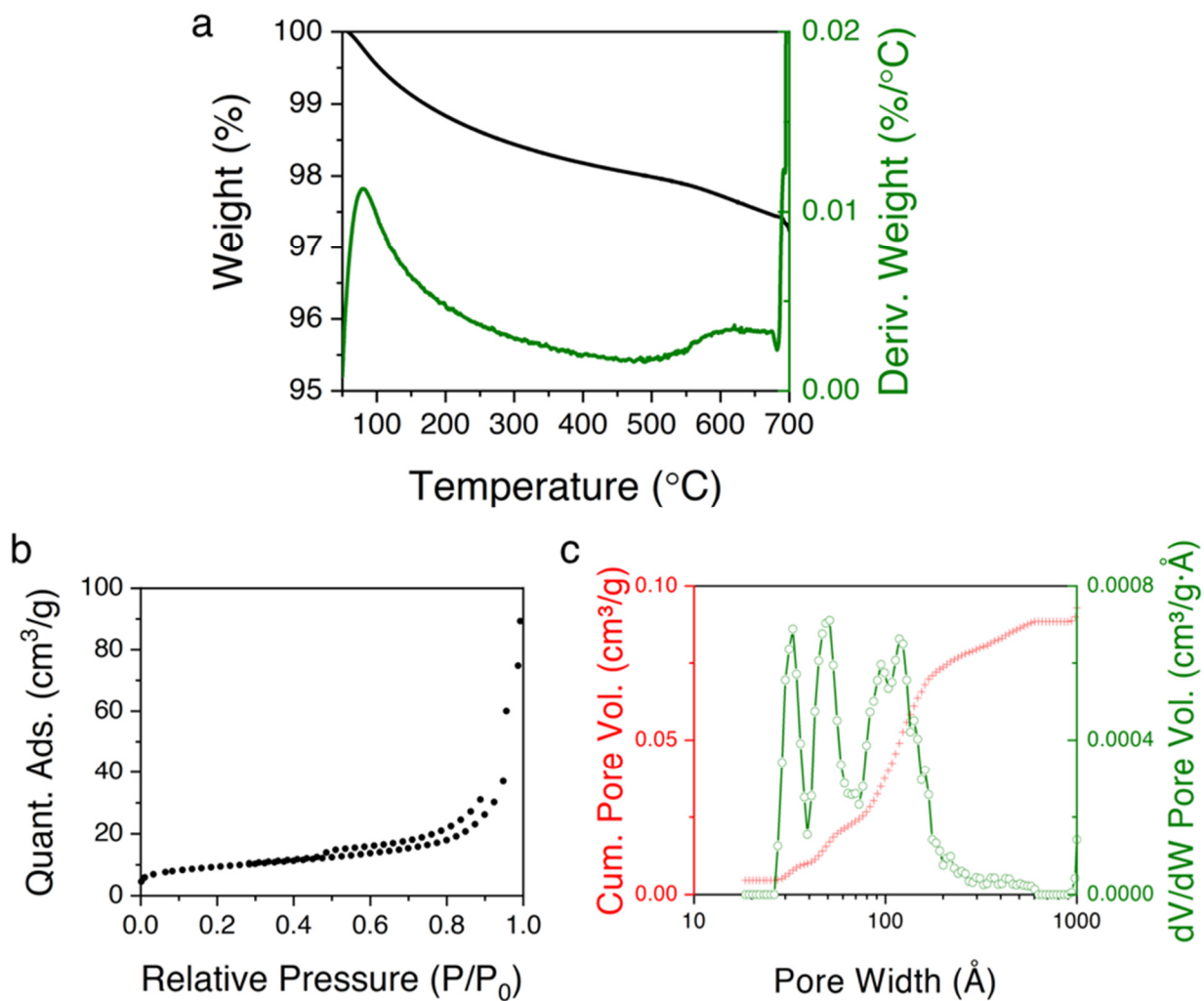
To study the effect of longer sintering time, a sintering protocol under alternating reducing/oxidizing conditions over 50 h was also considered (Table S5). Here, only a third of the 50 h is under oxidizing conditions, while the remaining time is spent under reducing conditions. Since the partial pressure of  $PtO_2(g)$  will be negligible under reducing conditions, we modeled this situation by only considering a sintering time of is  $50/3$  h  $\approx 16.67$  h under oxidizing conditions (900 °C and 1.5%  $O_2$ ). All other parameters were kept the same.



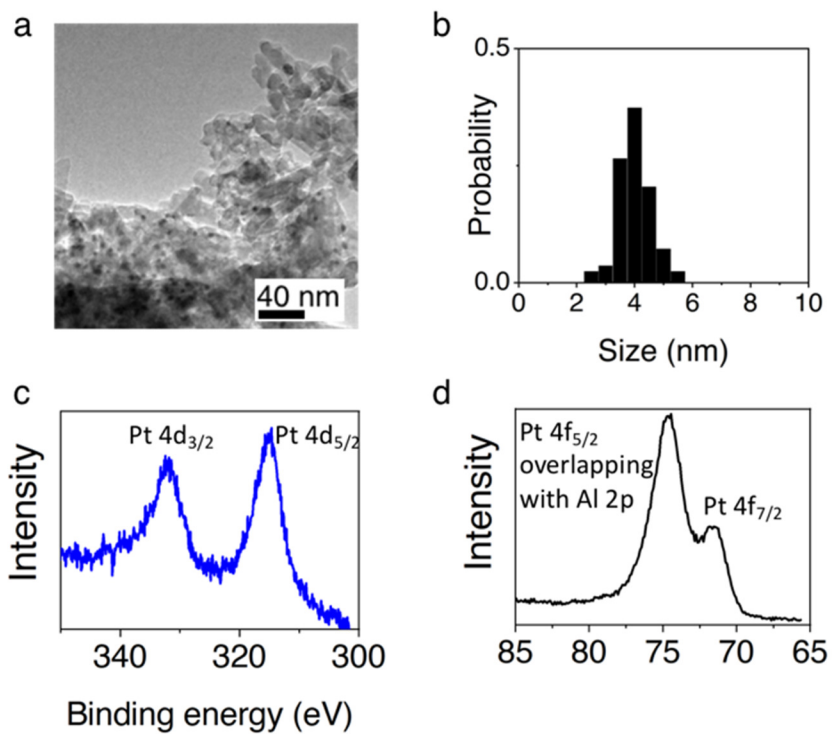
**Figure S1.** HAADF-STEM image and corresponding Pt-L edge EDS map of as-synthesized Pt@Al<sub>2</sub>O<sub>3</sub>.



**Figure S2.** EDS spectrum corresponding to the EDS map in Figure S1 showing Pt-L edge. Fe, Co, Cu, Zr, and Sn normal signal from the TEM column/holder. Pt atomic and weight percent concentrations measured from EDS: 0.08 at. % or 0.76 wt. %.

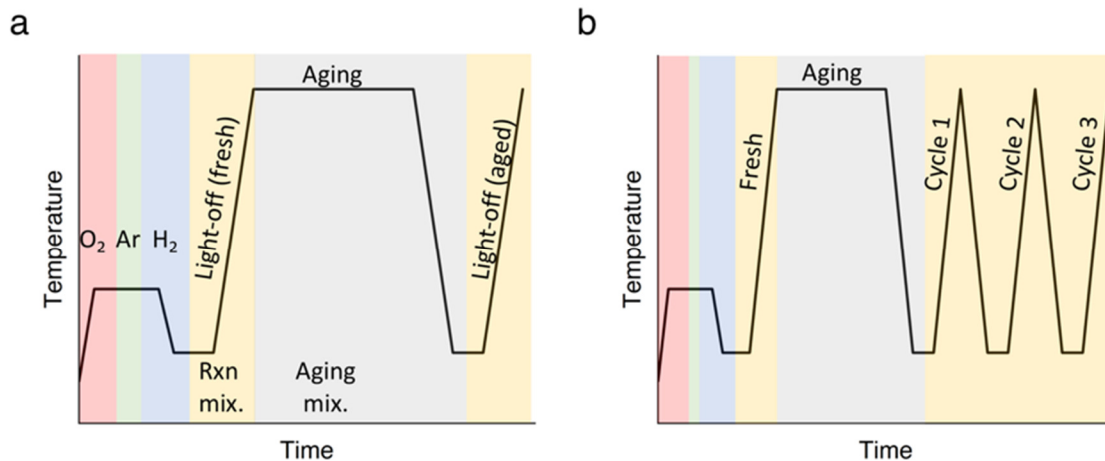


**Figure S3.** a-c) Characterization of Pt@Al<sub>2</sub>O<sub>3</sub>: a) TGA upon heating the sample in air to 700°C; b) N<sub>2</sub> physisorption isotherm; c) pore size distribution.

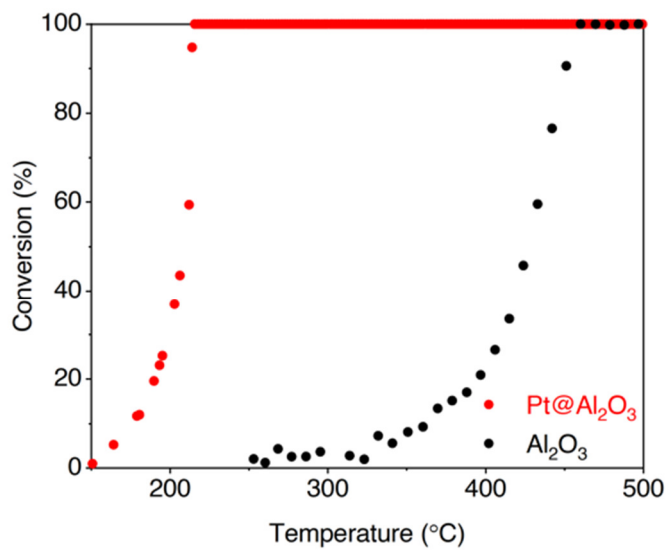


**Figure S4.** Characterization of Pt/Al<sub>2</sub>O<sub>3</sub>: a) Transmission electron microscopy image; b) NP size distribution; c-d) XPS of c) Pt 4d<sub>3/2</sub> (332.2 eV) and Pt 4d<sub>5/2</sub> (315.2 eV); d) Al 2p (74.7 eV) and Pt 4f<sub>5/2</sub> (71.5 eV) overlapping signals.

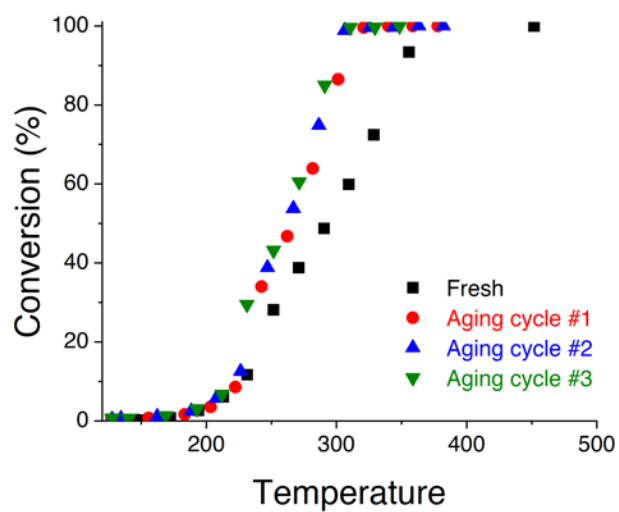




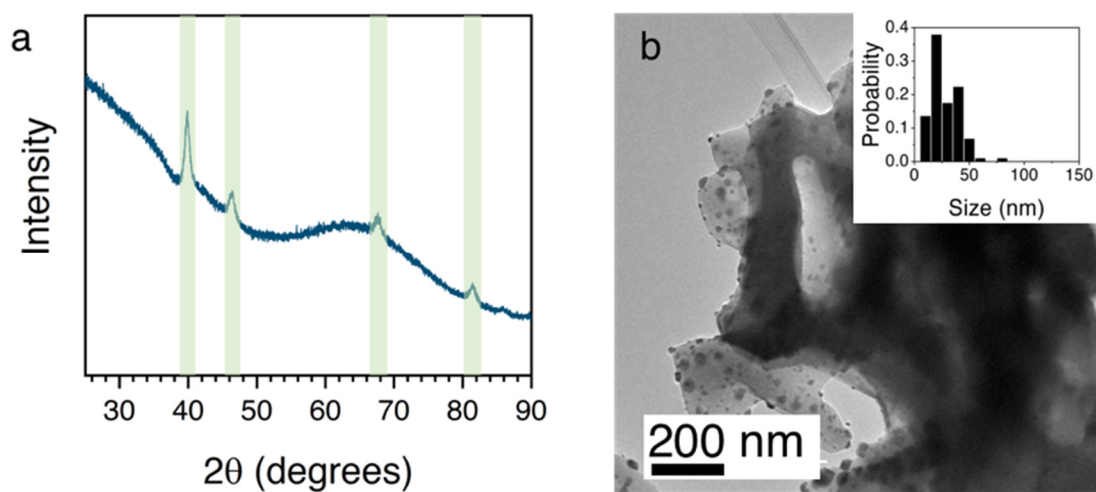
**Figure S5.** a) Temperature profile and catalyst environment for one aging cycle; b) Temperature profile and catalyst environment for three consecutive cycles.



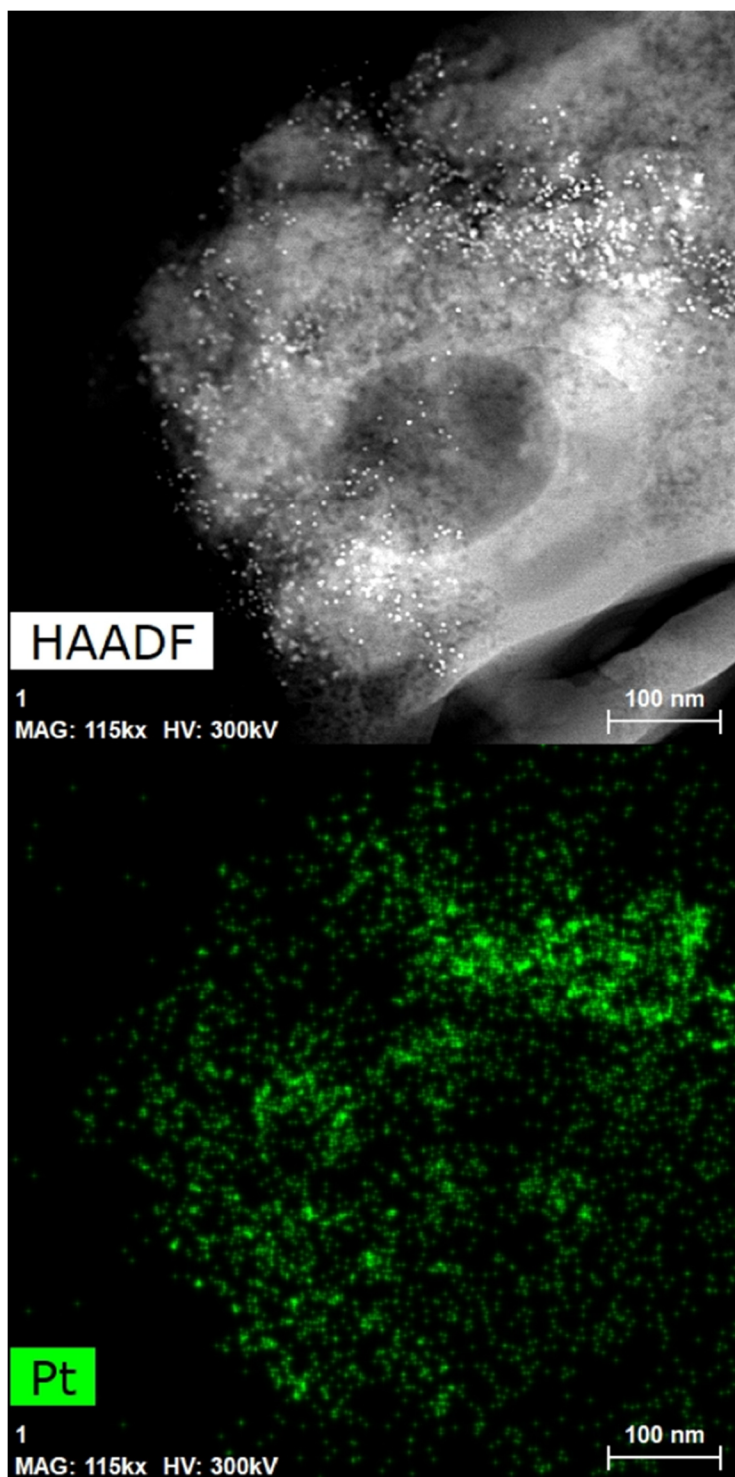
**Figure S6.** Light-off curves of fresh Pt@Al<sub>2</sub>O<sub>3</sub> and metal-free Al<sub>2</sub>O<sub>3</sub> support. Reaction mixture: 0.15 vol.% C<sub>3</sub>H<sub>6</sub>, 3 vol.% O<sub>2</sub>, and 5 vol.% steam (balance Ar).



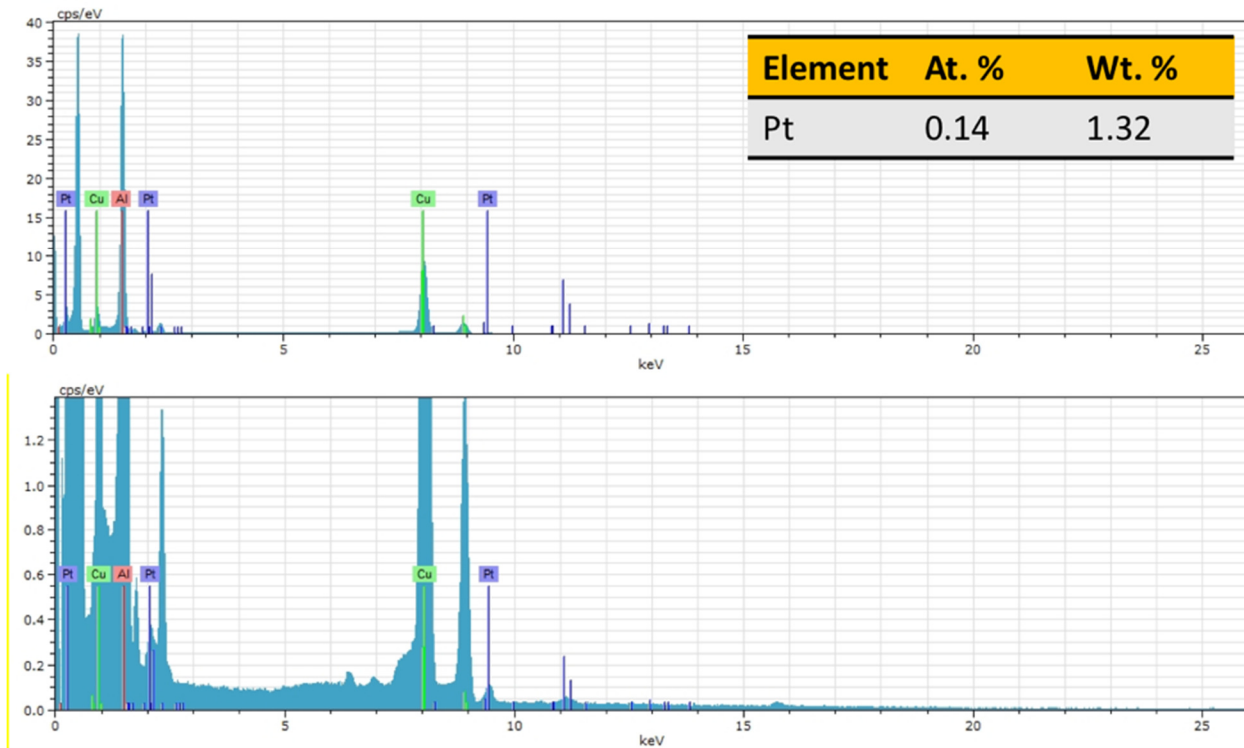
**Figure S7.** Propene combustion activity for as-prepared Pt@Al<sub>2</sub>O<sub>3</sub> and the aged catalyst after consecutive three cycles (aging performed at 800 °C for 2 h in the reaction mixture). 30 mg of the catalyst was mixed with 160 mg of SiC diluent. Catalyst pretreatment: 300 °C, 30 min 5 vol.% O<sub>2</sub> (40 mL/min), 10 min Ar (40 mL/min), 30 min 5 vol.% H<sub>2</sub> (40 mL/min). Reaction mixture: 0.15 vol.% C<sub>3</sub>H<sub>6</sub>, 3 vol.% O<sub>2</sub>, 5 vol.% H<sub>2</sub>O, balance Ar (50 mL/min total flow rate).



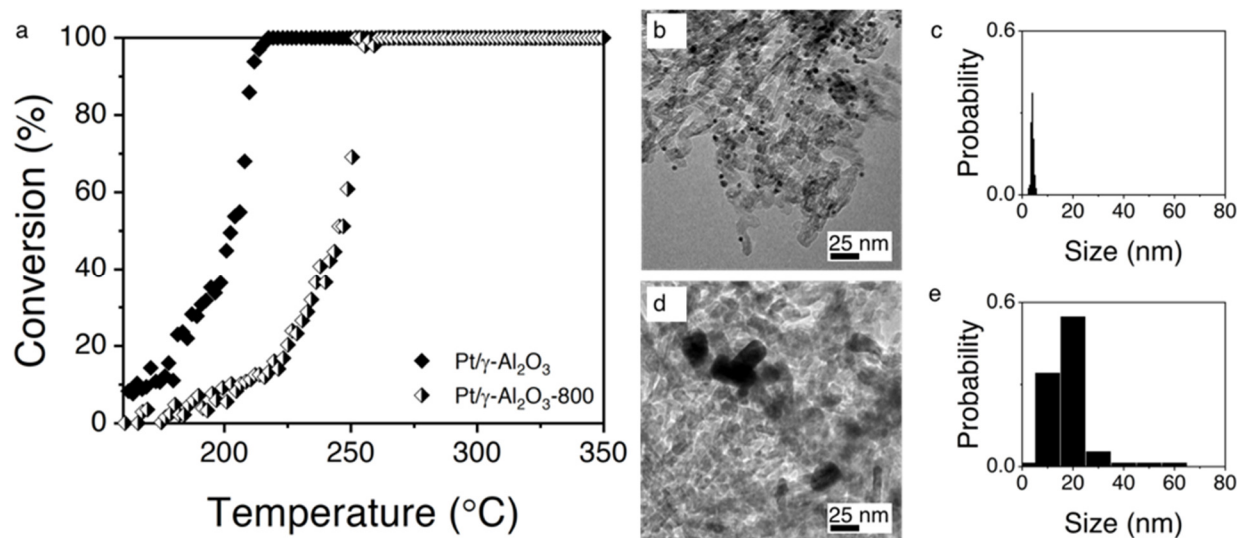
**Figure S8.** Characterization of Pt/ $\text{Al}_2\text{O}_3$  calcined at 600 °C. a) XRD: highlighted peaks are due to metallic Pt; b) TEM: upon calcination the average Pt NP size increases from 3.8 nm to 23.3 nm.



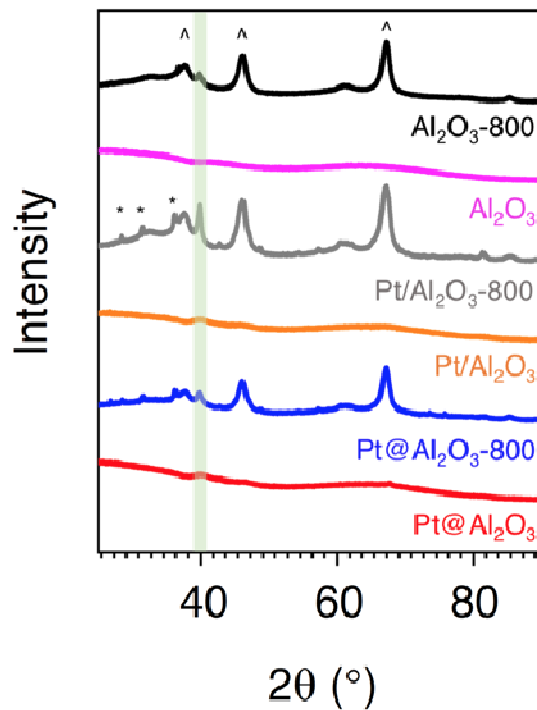
**Figure S9.** HAADF-STEM image and corresponding Pt-L edge EDS map of aged Pt@Al<sub>2</sub>O<sub>3</sub>-800.



**Figure S10.** EDS spectrum corresponding to the EDS map in Figure S9 showing Pt-L edge. Fe, Co, Cu, Zr, and Sn normal signal from the TEM column/holder. Pt atomic and weight percent concentrations measured from EDS: 0.14 at. % or 1.32 wt. %.

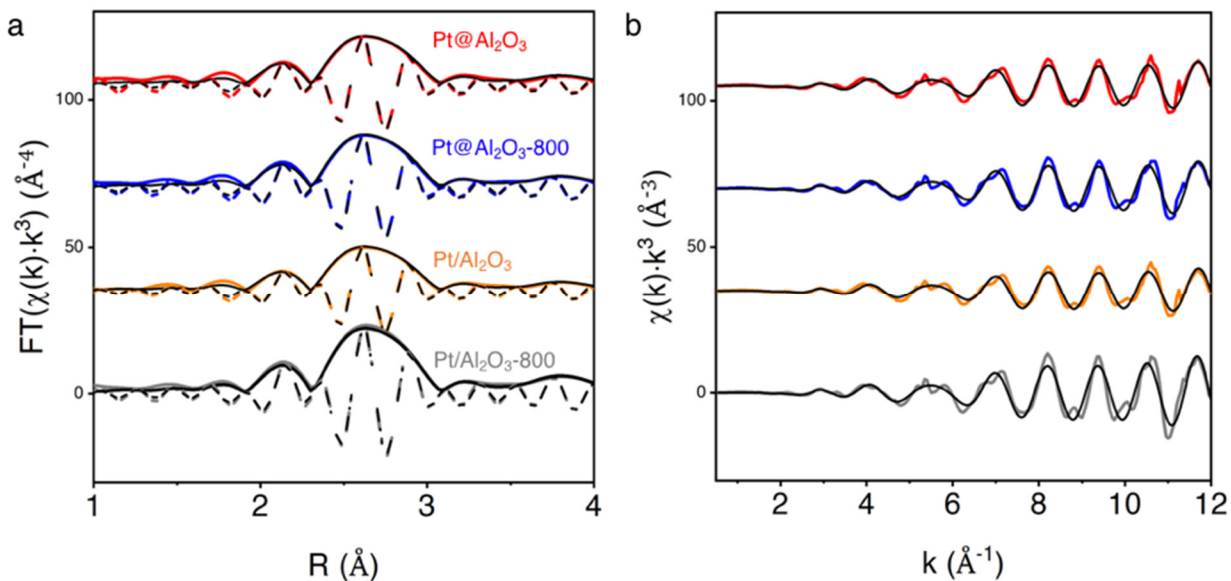


**Figure S11.** a) Light-off curve measurements of fresh and aged Pt/γ-Al<sub>2</sub>O<sub>3</sub>. Reaction conditions: 0.15 vol. % C<sub>3</sub>H<sub>6</sub>, 3 vol. % O<sub>2</sub>, and 5 vol. % steam, balance Ar (40 ml/min total flow). Aging performed in the reaction mixture at 800 °C for 2 h; b-e) Representative TEM images and particle size distributions of the fresh (b-c) and aged catalysts (d-e).

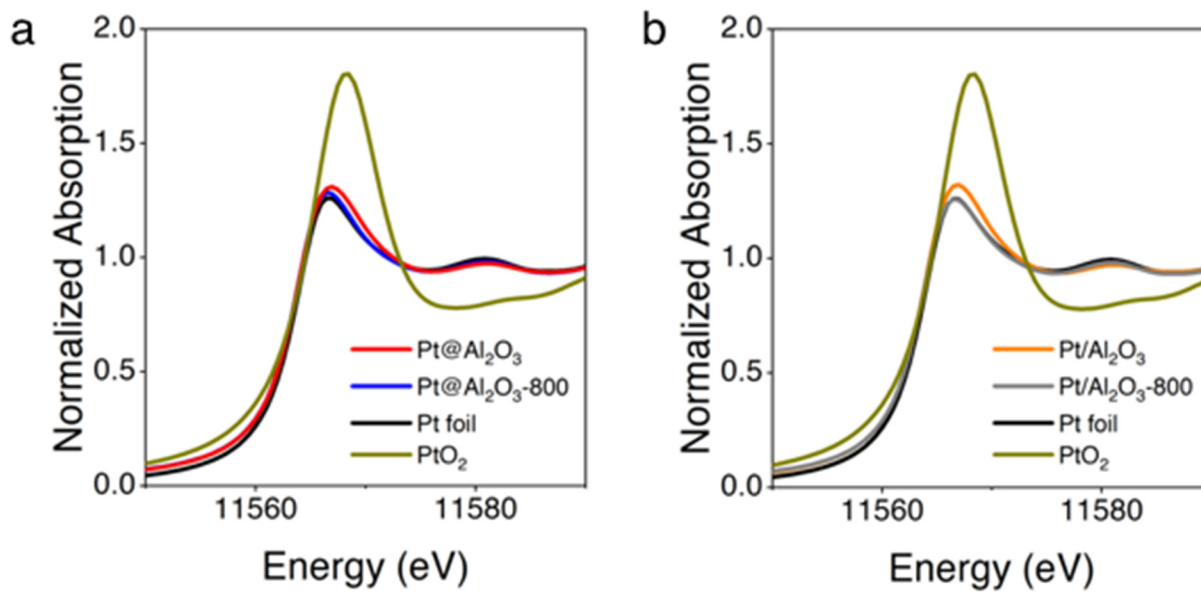


**Figure S12.** XRD patterns for the samples and the bare support. ^ and \* represent diffractions peaks due to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and quartz diluent, respectively. Highlighted region at 40° indicates overlapping  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pt(111) diffraction peaks.

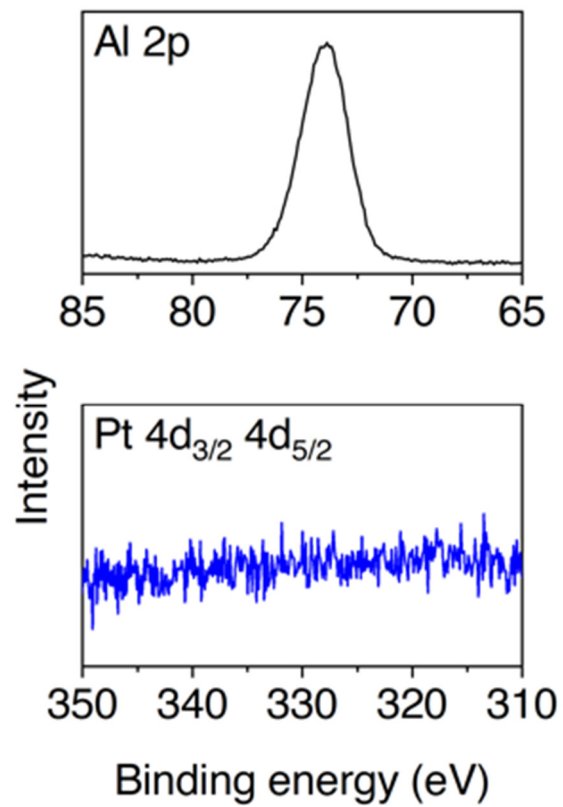




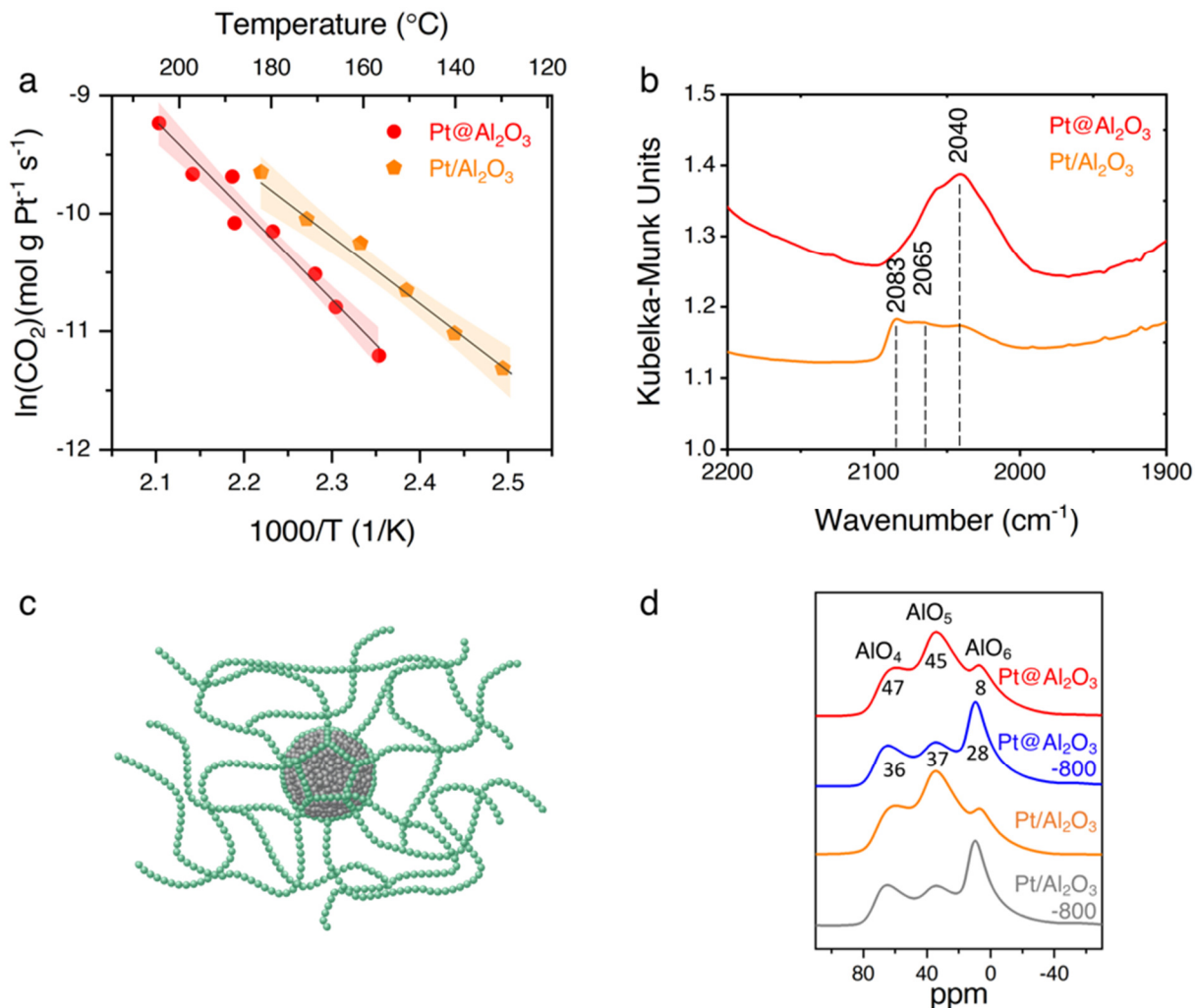
**Figure S13.** a) Magnitude and imaginary part of the Fourier Transform and b) EXAFS of the Pt L<sub>3</sub>-edge data and best-fits characterizing the encapsulated and supported Pt catalysts before and after aging at 800°C. Black lines indicate the fits.



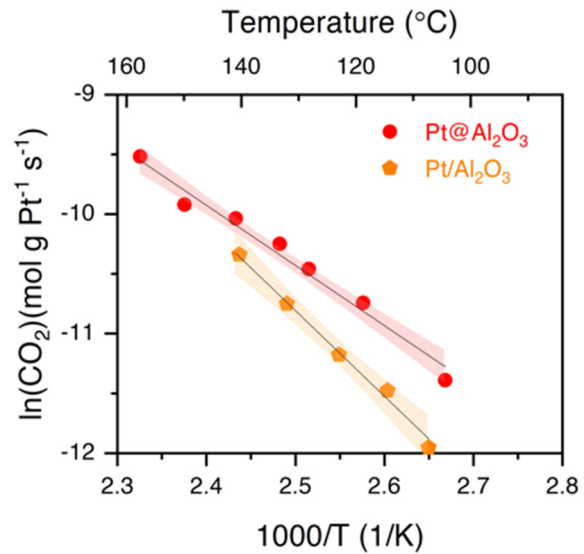
**Figure S14.** Pt L<sub>3</sub>-edge XANES: a) Pt@Al<sub>2</sub>O<sub>3</sub>; b) Pt/Al<sub>2</sub>O<sub>3</sub>.



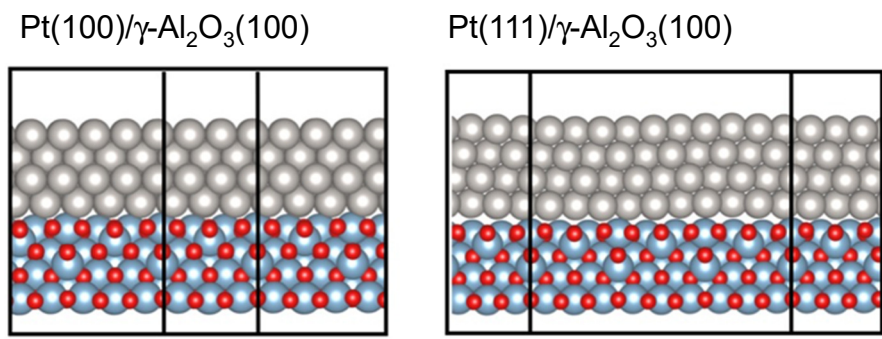
**Figure S15.** XPS characterization of Pt@Al<sub>2</sub>O<sub>3</sub>-800.



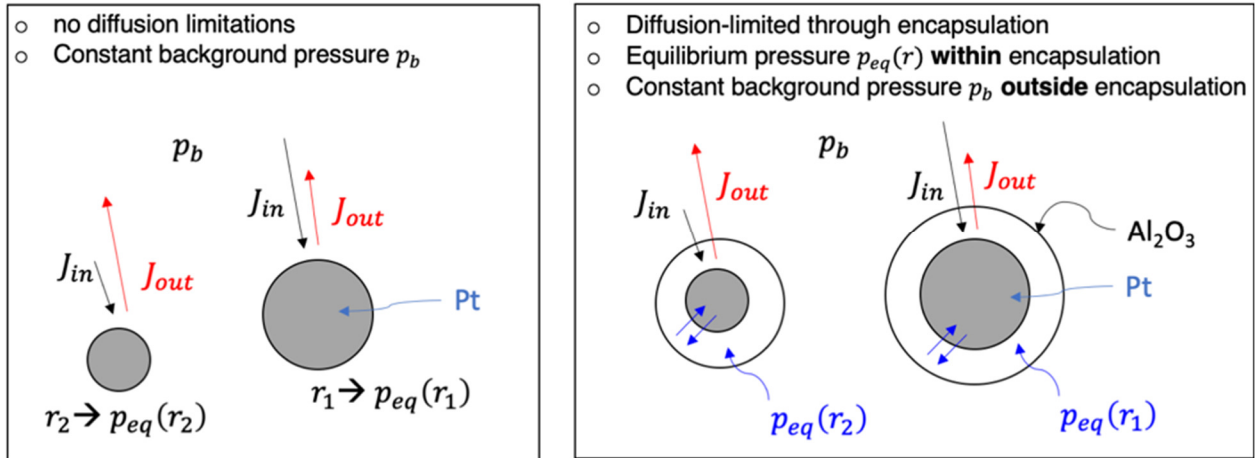
**Figure S16.** a) Arrhenius plots with 95% confidence intervals of Pt@Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> for propene combustion collected at conversions less than 5%. The data points are averages for three measurements; b) CO diffuse reflectance infrared spectroscopy; c) proposed model schematic of Pt@Al<sub>2</sub>O<sub>3</sub>; d) <sup>27</sup>Al MAS NMR spectra of fresh and aged Pt@Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub>. Peaks for four-, five-, and six-coordinated Al (AlO<sub>4</sub>, AlO<sub>5</sub>, AlO<sub>6</sub>) are labeled, with approximate percentages of each shown below the spectra.



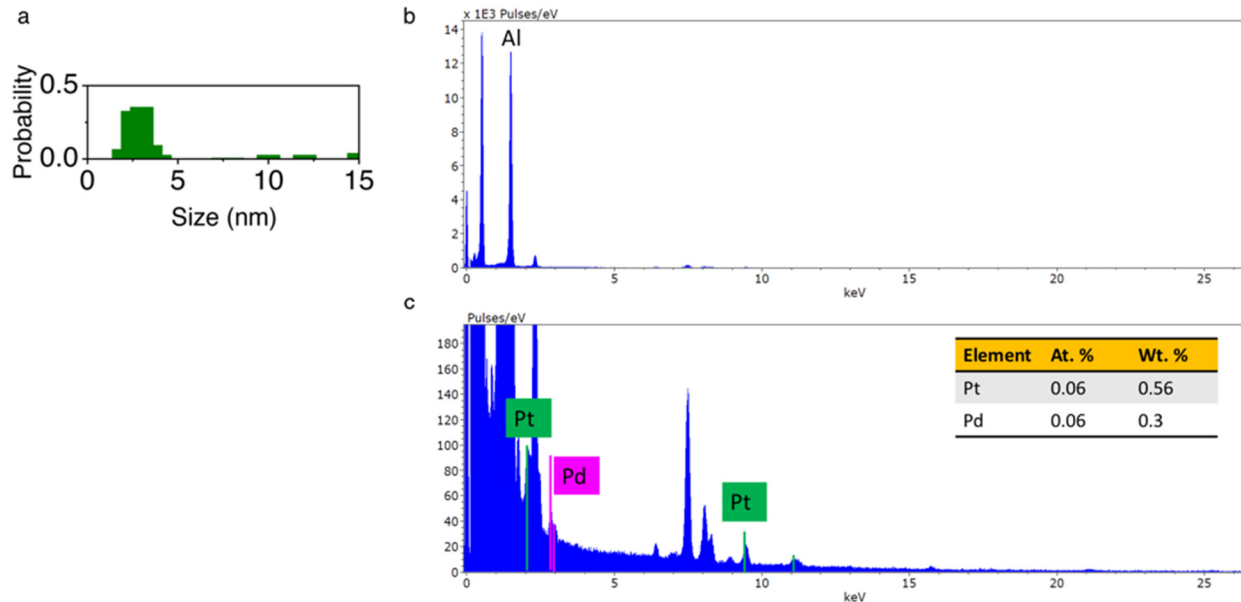
**Figure S17.** Arrhenius plots with 95% confidence intervals of Pt@Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> for CO oxidation collected at conversions less than 5%. The data points are averages for three measurements.



**Figure S18.** Side-on views of the atomic models optimized for the interfaces of Pt(100) and Pt(111) with the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(100) surface.

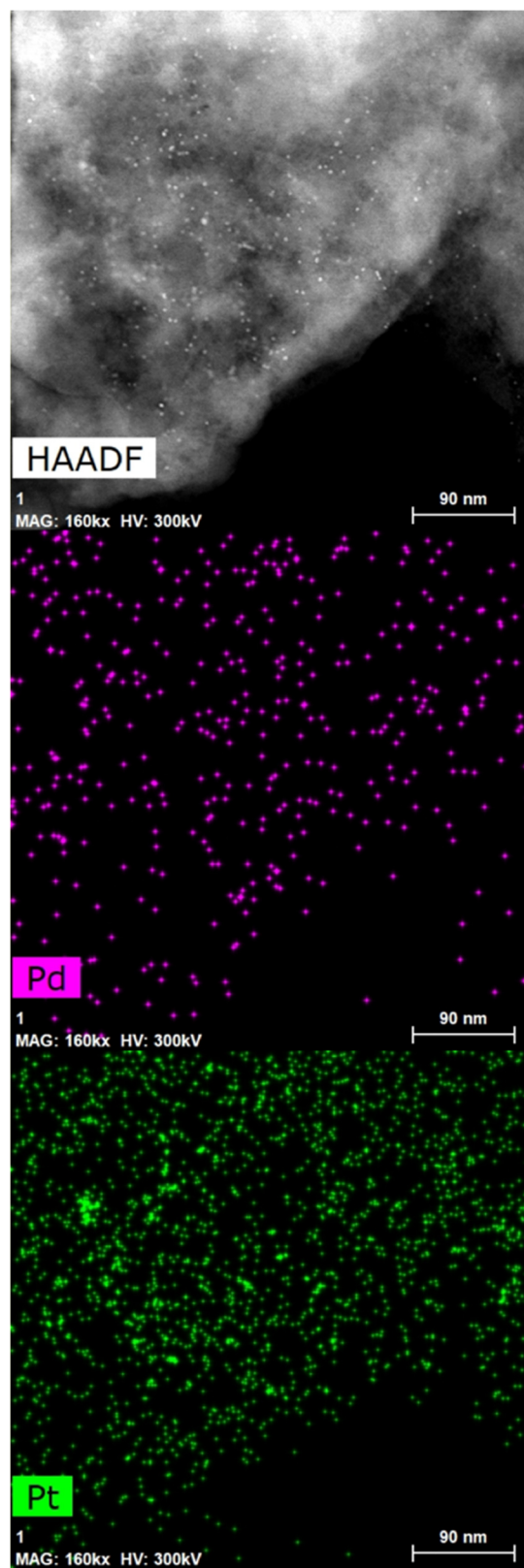


**Figure S19.** Illustration of sintering models and underlying assumptions: Left: No diffusion limitations lead to immediate equilibration within the gas phase and thus a constant background pressure  $p_b$ . Right: Significant diffusion limitations through the encapsulating material lead to local equilibration between particle and gas phase for each particle, so that locally the equilibrium pressure  $p_{eq}(r)$  is established.

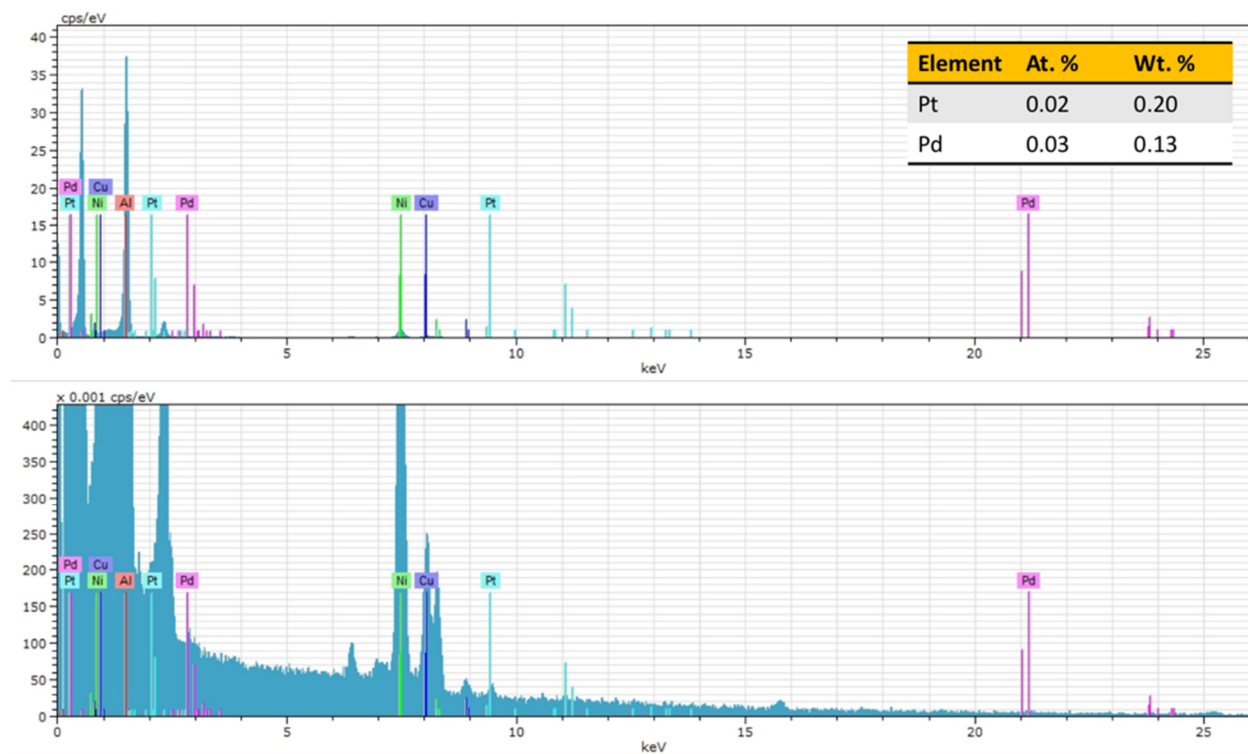


**Figure S20.** Characterization of as-synthesized PdPt@Al<sub>2</sub>O<sub>3</sub>: a) Particle size distribution; b) EDS full spectrum; c) EDS spectrum corresponding to the EDS maps in Figures 4b-c showing Pd-K edge and Pt-L edge on Ni grid. Fe, Co, Cu, Zr, and Sn normal signal from the TEM column/holder. Pt and Pd atomic and weight percent concentrations measured from EDS: Pt 0.06 at.%, 0.56 wt.%; Pd 0.06 at.%, 0.3 wt.%.

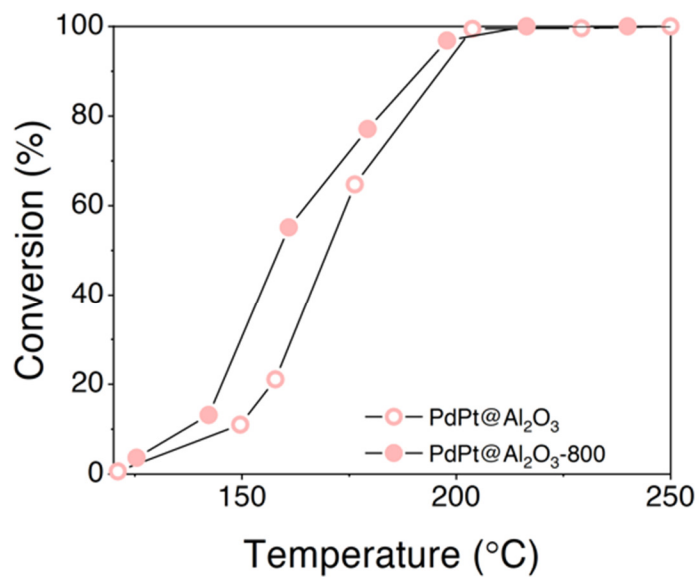




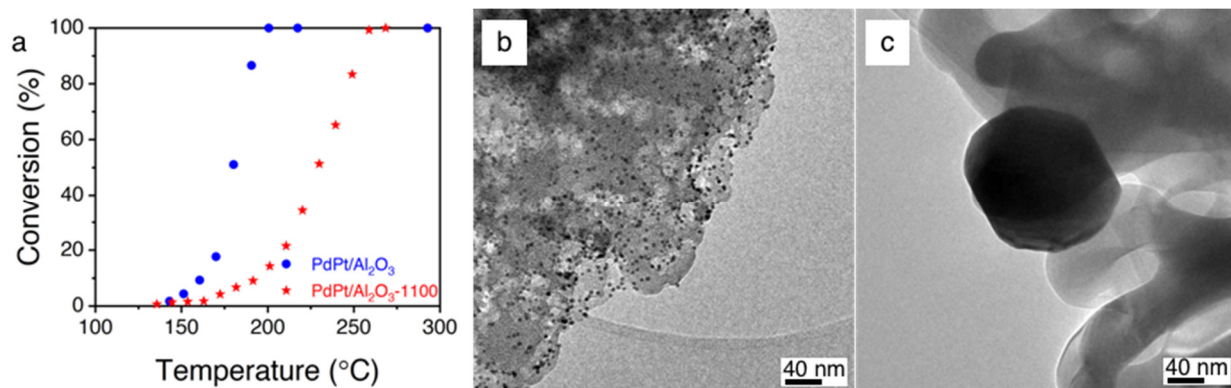
**Figure S21.** HAADF-STEM image and corresponding EDS maps (Pd-K edge and Pt-L edge) of as-synthesized PdPt@Al<sub>2</sub>O<sub>3</sub>.



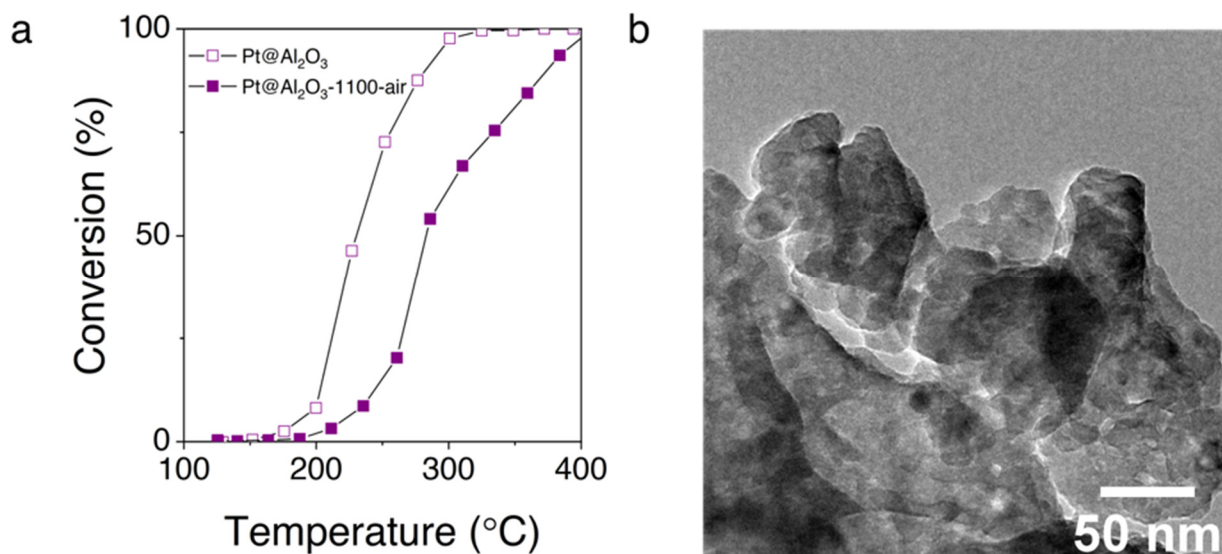
**Figure S22.** EDS spectrum of as-synthesized PdPt@Al<sub>2</sub>O<sub>3</sub> corresponding to the EDS maps in Figure S21 showing Pd-K edge and Pt-L edge on Ni grid. Fe, Co, Cu, Zr, and Sn normal signal from the TEM column/holder. Pt and Pd atomic and weight percent concentrations measured from EDS: Pt 0.02 at. %, 0.20 wt.%; Pd 0.03 at.%, 0.13 wt.%.



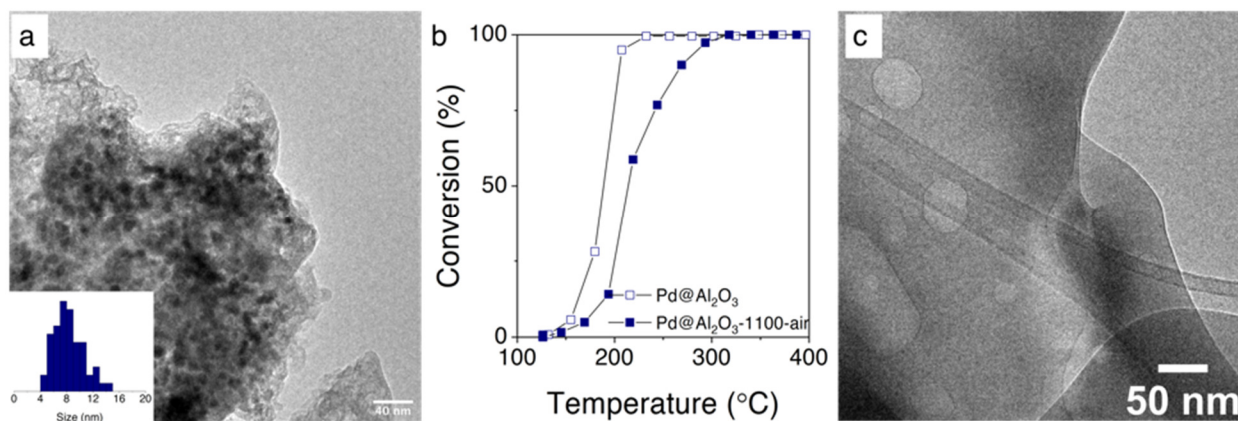
**Figure S23.** a) Propene combustion activity for as-prepared and 800 °C aged PdPt@Al<sub>2</sub>O<sub>3</sub>. Aging conditions: 800 °C for 2 h in the reaction mixture consisting of 0.15 vol. % C<sub>3</sub>H<sub>6</sub>, 3 vol. % O<sub>2</sub>, and 5 vol. % steam, balance Ar (40 ml/min total flow).



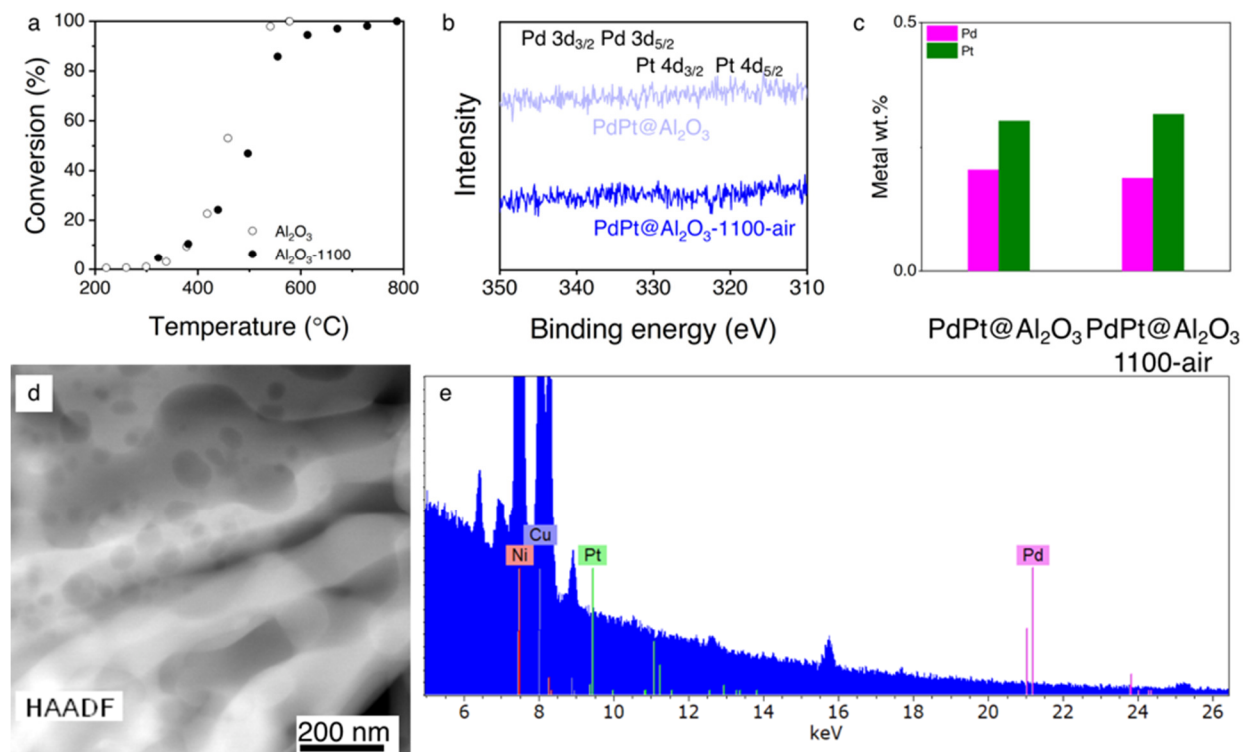
**Figure S24.** a) Propene combustion activity for fresh PdPt/Al<sub>2</sub>O<sub>3</sub> and aged PdPt/Al<sub>2</sub>O<sub>3</sub>-1100. PdPt@Al<sub>2</sub>O<sub>3</sub>-1100 is the fresh catalyst aged at at 1,100 °C for for 5 h in air with 10 vol.% steam (40 ml/min total flow). Reaction mixture: 0.15 vol.% C<sub>3</sub>H<sub>6</sub>, 3 vol.% O<sub>2</sub>, and 5 vol.% steam, balance Ar; b-c) Representative TEM images of fresh (b) and 1100°C aged (c) PdPt/Al<sub>2</sub>O<sub>3</sub>.



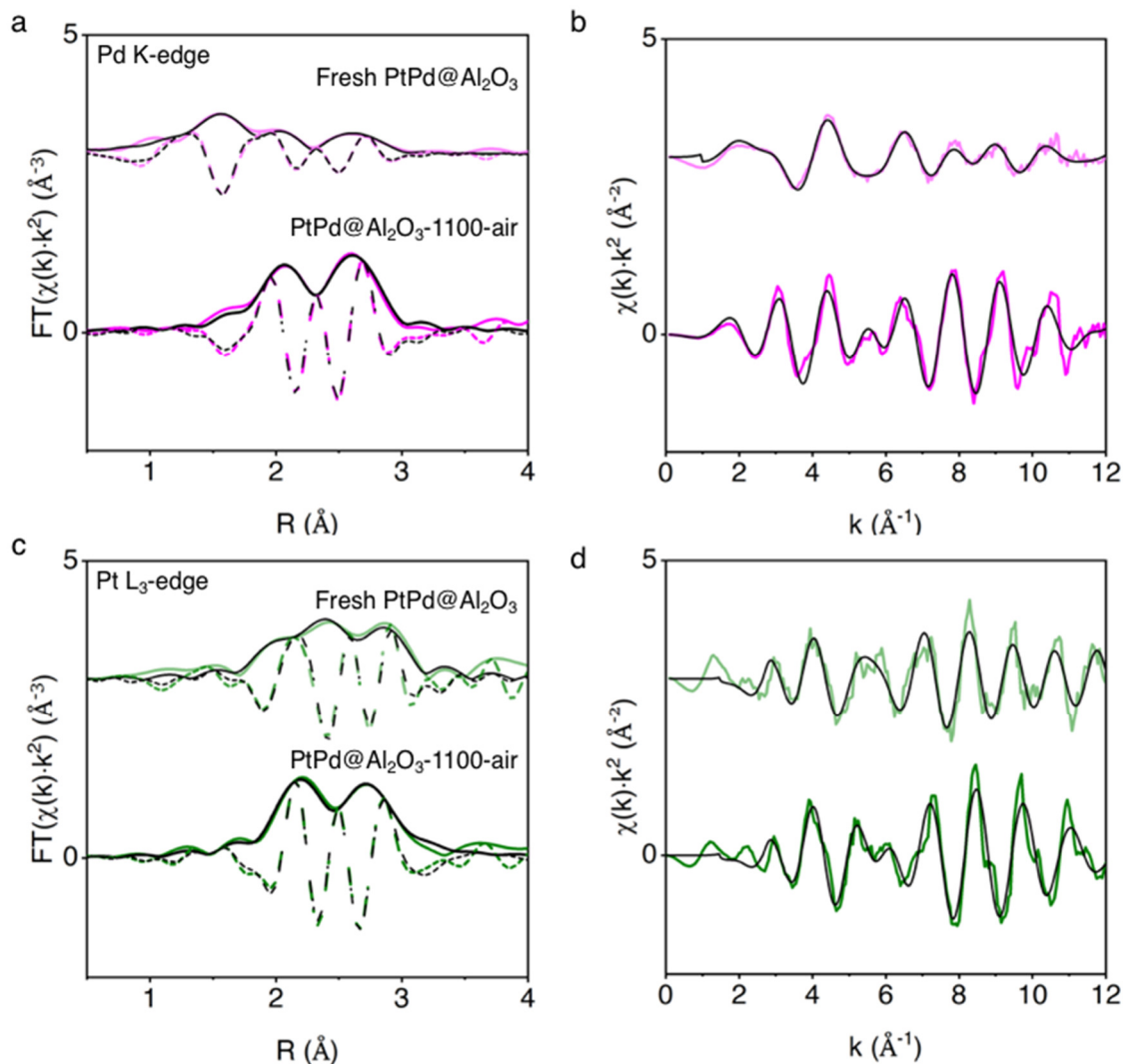
**Figure S25.** A) Propene combustion activity for fresh Pt@Al<sub>2</sub>O<sub>3</sub> and 1,100 °C aged Pt@Al<sub>2</sub>O<sub>3</sub>. Reaction mixture: 0.15 vol.% C<sub>3</sub>H<sub>6</sub>, 3 vol.% O<sub>2</sub>, and 5 vol.% steam. Aging performed at 1,100 °C for 5 h in air with 10 vol. % steam (40 ml/min total flow); b) TEM image of the 1,100 °C aged Pt@Al<sub>2</sub>O<sub>3</sub> catalyst.



**Figure S26.** a) TEM image and particle size distribution of as-synthesized Pd@Al<sub>2</sub>O<sub>3</sub>; b) Propene combustion activity for fresh Pd@Al<sub>2</sub>O<sub>3</sub> and 1,100 °C aged Pd@Al<sub>2</sub>O<sub>3</sub>. Reaction mixture: 0.15 vol.% C<sub>3</sub>H<sub>6</sub>, 3 vol.% O<sub>2</sub>, and 5 vol.% steam. Aging performed at 1,100 °C for 5 h in air with 10 vol. % steam (40 ml/min total flow); c) TEM image of the 1,100 °C aged Pd@Al<sub>2</sub>O<sub>3</sub> catalyst.

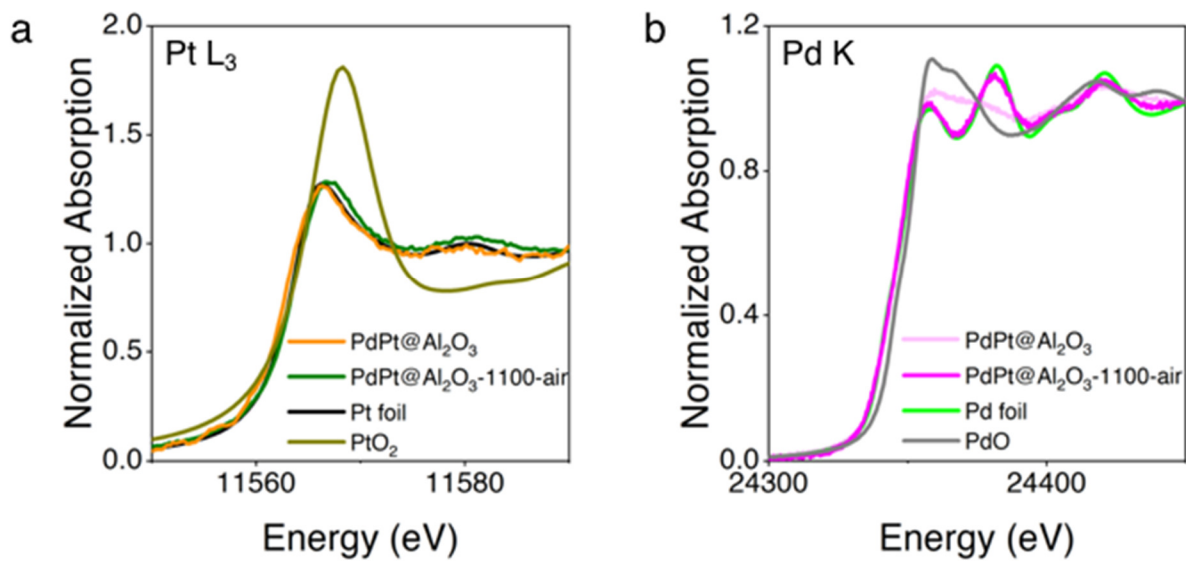


**Figure S27.** a) Propene combustion activity of the fresh and 1,100 °C aged metal-free alumina support. Reaction mixture: 0.15 vol.% C<sub>3</sub>H<sub>6</sub>, 3 vol.% O<sub>2</sub>, and 5 vol.% steam. Aging performed at 1,100 °C for 5 h in air with 10 vol. % steam (40 ml/min total flow); b-c) Characterization of the as-synthesized and 1,100 °C aged PdPt@Al<sub>2</sub>O<sub>3</sub>: b) XPS; c) XRF; d-e) Representative HAADF-STEM image of 1,100 °C aged PdPt@Al<sub>2</sub>O<sub>3</sub> and EDS spectrum showing no Pd or Pt detectable signal. Fe, Co, Cu, Zr and Sn normal signal from the TEM column/holder.

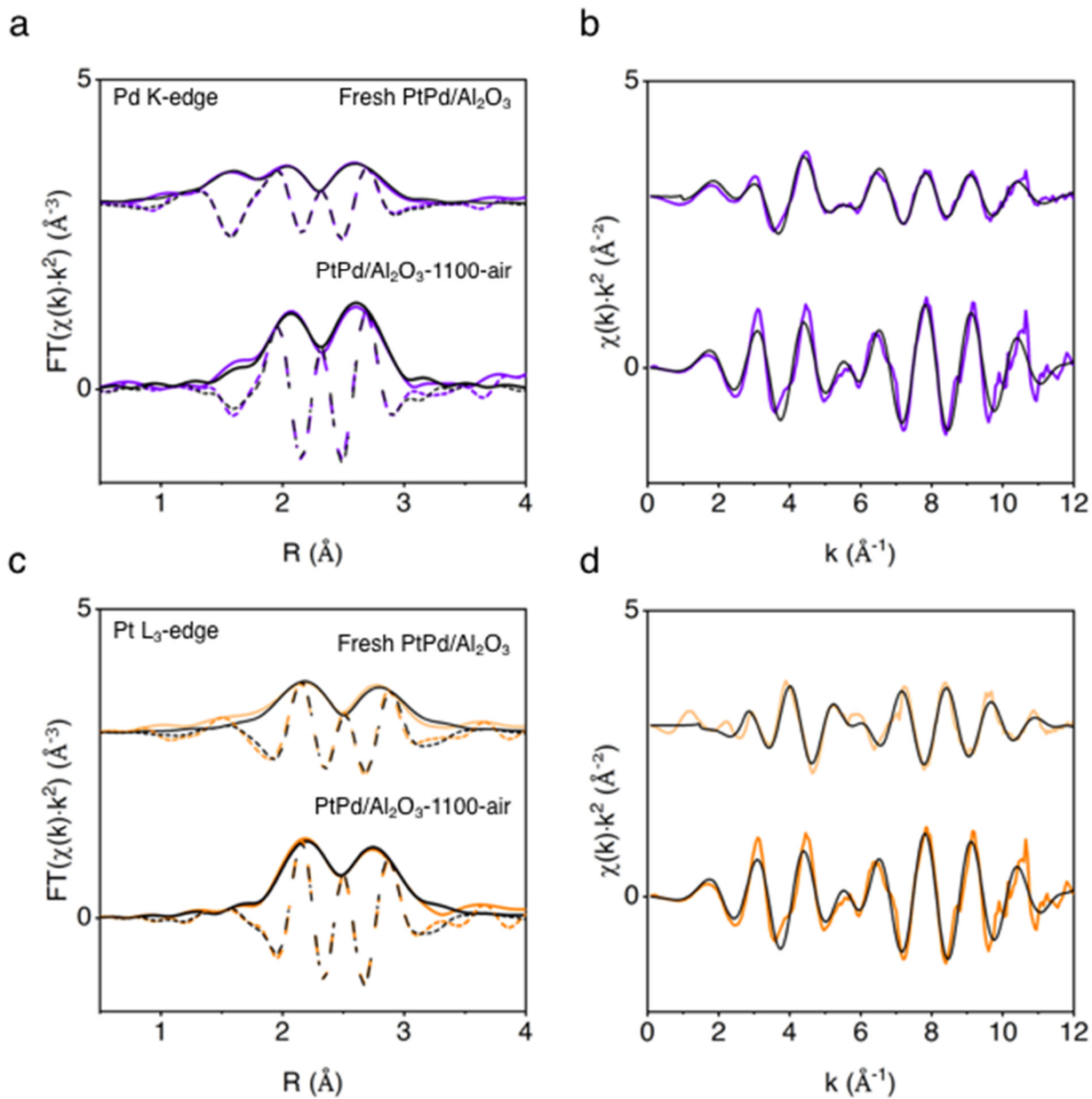


**Figure S28.** Magnitude and imaginary component of the Fourier Transform and EXAFS at the Pd K-edge (a-b) and Pt L<sub>3</sub>-edge (c-d) characterizing the fresh PdPt@Al<sub>2</sub>O<sub>3</sub> and PdPt@Al<sub>2</sub>O<sub>3</sub>-1100-air samples. Black lines indicate the fits. The range in R was 1.2-3.0 Å (Pd) and 1.7-3.2 Å (Pt); the range in k was 2.7-12.5 Å<sup>-1</sup> (Pd) and 3.1-12.0 Å<sup>-1</sup> (Pt).

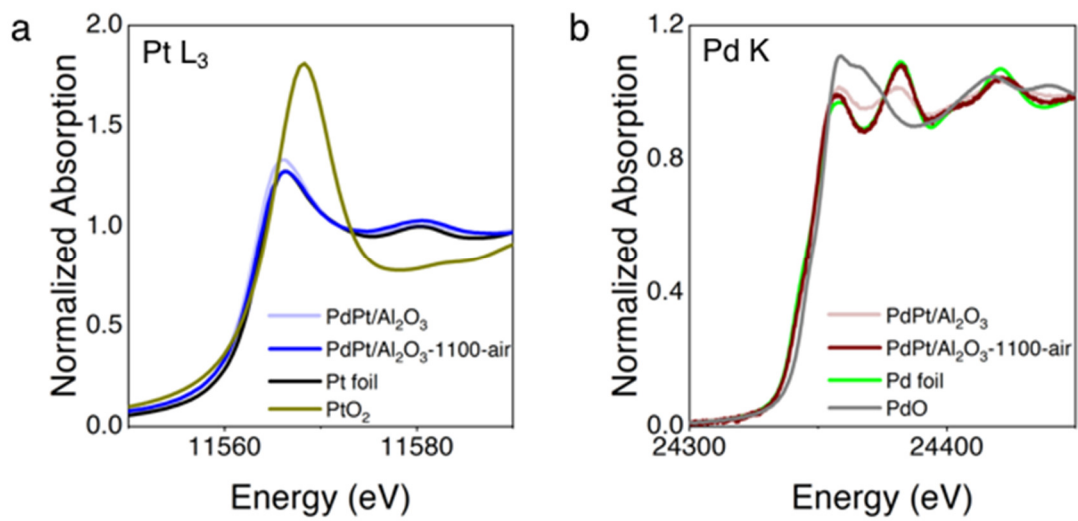




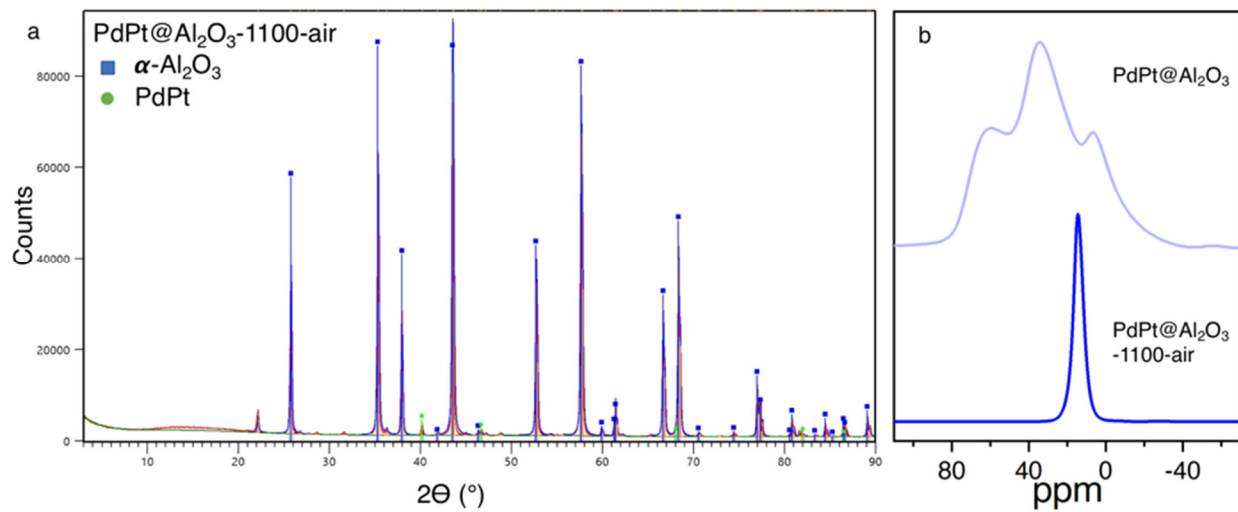
**Figure S29.** PdPt@Al<sub>2</sub>O<sub>3</sub> XANES: a) Pt L<sub>3</sub>-edge; b) Pd K-edge.



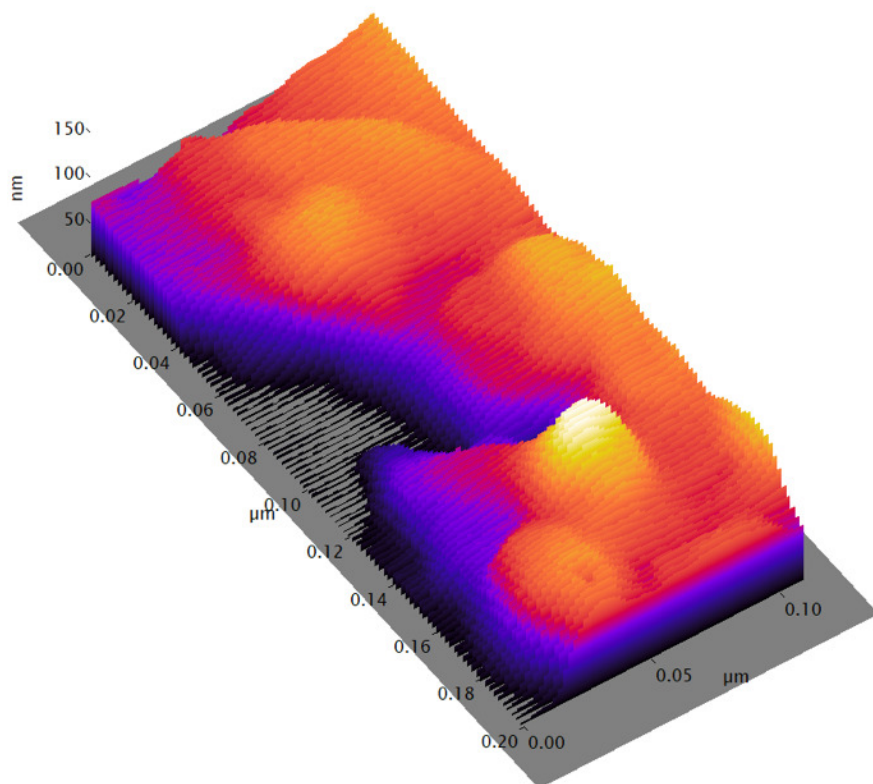
**Figure S30.** Magnitude and imaginary component of the Fourier Transform and EXAFS at the Pd K-edge (a-b) and Pt L<sub>3</sub>-edge (c-d) characterizing the fresh PdPt/Al<sub>2</sub>O<sub>3</sub> and PdPt/Al<sub>2</sub>O<sub>3</sub>-1100-air samples. Black lines indicate the fits. The range in R was 1.2-3.0  $\text{\AA}$  (Pd) and 1.7-3.2  $\text{\AA}$  (Pt); the range in k was 2.7-12.5  $\text{\AA}^{-1}$  (Pd) and 3.1-12.0  $\text{\AA}^{-1}$  (Pt).



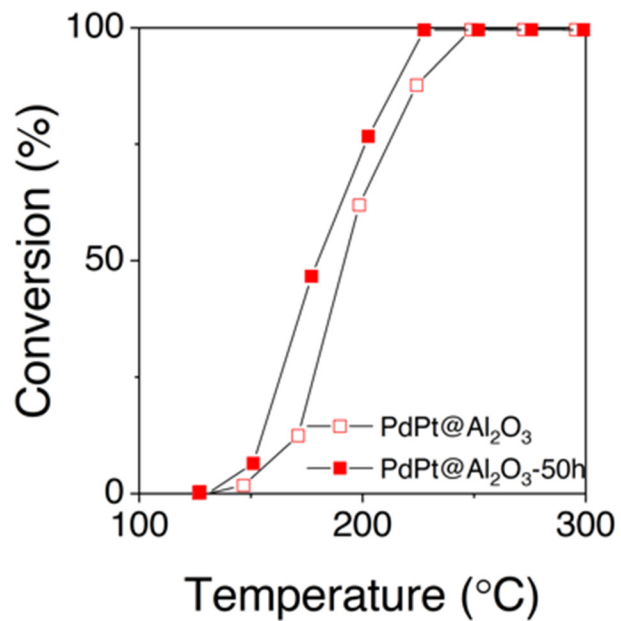
**Figure S31.** PdPt/Al<sub>2</sub>O<sub>3</sub> XANES: a) Pt L<sub>3</sub>-edge; b) Pd K-edge.



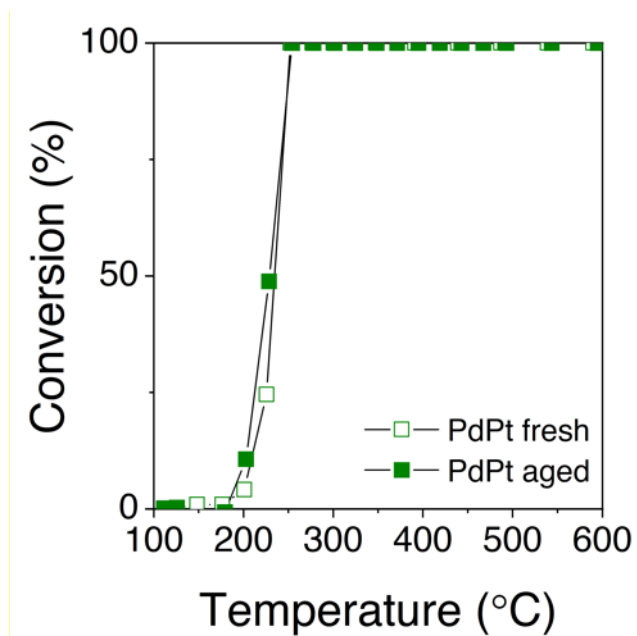
**Figure S32.** XRD (a) and  $^{27}\text{Al}$  NMR (b) characterization of as-synthesized and 1,100 °C aged  $\text{PdPt@Al}_2\text{O}_3$ .



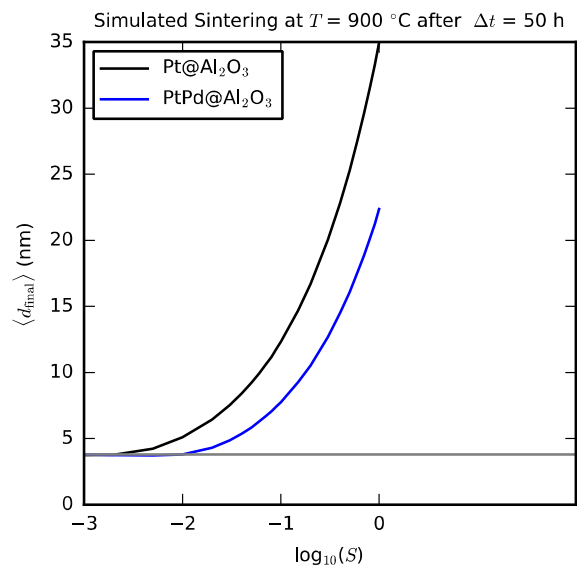
**Figure S33.** Thickness map of the supporting alumina layer in the as-prepared PdPt@Al<sub>2</sub>O<sub>3</sub> sample crystallized into the  $\alpha$  phase as determined from the log-ratio method of the low-loss portion of the EEL spectrum. Dimensions of the 3D surface plot are 200 nm x 110 nm x 167 nm (L x W x H).



**Figure S34.** Propene combustion activity for fresh and aged PdPt@Al<sub>2</sub>O<sub>3</sub>. Aging performed for 50 h at 900 °C under alternating reducing-oxidizing conditions described in Table S5.



**Figure S35.** Propene combustion activity for fresh and aged PdPt@Al<sub>2</sub>O<sub>3</sub>. Aging performed for 48 h at 800 °C in the reaction mixture consisting of 2 vol. % CO<sub>2</sub>, 0.2 vol. % CO, 0.1 vol. % C<sub>3</sub>H<sub>6</sub>, 0.1 vol. % C<sub>3</sub>H<sub>8</sub>, 5 vol. % H<sub>2</sub>O, 8 vol. % O<sub>2</sub> balance Ar and N<sub>2</sub> (113 ml/min total flow). Catalyst mass: 31 mg. GHSV = 113,000 h<sup>-1</sup>.



**Figure S36.** Sintering simulations at  $T = 900 \text{ }^\circ\text{C}$  for Pt@Al<sub>2</sub>O<sub>3</sub> and PdPt@Al<sub>2</sub>O<sub>3</sub> catalysts under 50 h of aging according to protocol reported in Table S5. The initial particle size distribution identical to that in Figure 3b. Since only sintering via PtO<sub>2</sub>(g) is considered, the effective sintering time is 50/3 h  $\approx$  16.67 h (see further details for this protocol in Table S5). The effect of alloying with Pd is accounted for as a reduction of the surface energy by 21%.



**Table S1.** Platinum-alumina catalysts used in the study.

<b>Catalyst</b>	<b>Description</b>	<b>Metal</b>	<b>Alumina support</b>	<b>Pt wt. % (XRF)</b>
Pt@Al <sub>2</sub> O <sub>3</sub>	Pt NPs inside Al <sub>2</sub> O <sub>3</sub>	Colloidal Pt NPs from the same batch	From polymer	0.44
Pt/Al <sub>2</sub> O <sub>3</sub>	Pt NPs on Al <sub>2</sub> O <sub>3</sub>		From polymer	0.54
Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Pt NPs on $\gamma$ -Al <sub>2</sub> O <sub>3</sub>		Commercial $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	0.50
Pt-free Al <sub>2</sub> O <sub>3</sub>	Metal-free Al <sub>2</sub> O <sub>3</sub>	-	From polymer	-

**Table S2.** EXAFS fitting of Pt foil.

<b>Sample</b>	<b><math>S_0^2</math></b>	<b><math>\Delta E_0</math>, eV</b>	<b><math>R</math>, Å</b>	<b><math>\sigma^2</math>, Å<sup>2</sup></b>	<b><math>CN_{Pt-Pt}</math></b>
Pt foil	$0.79 \pm 0.06$	$9.8 \pm 0.5$	$2.77 \pm 0.01$	$0.005 \pm 0.003$	12

**Table S3.** Pt dispersion from CO chemisorption.

<b>Sample</b>	<b>Pt@Al<sub>2</sub>O<sub>3</sub></b>	<b>Pt@Al<sub>2</sub>O<sub>3</sub>-800</b>	<b>Pt/Al<sub>2</sub>O<sub>3</sub></b>	<b>Pt/Al<sub>2</sub>O<sub>3</sub>-800</b>
Pt dispersion, %	8.0	7.5	9.0	0.3

**Table S4.** PdPt- and Pd-alumina catalysts used in the study.

<b>Catalyst</b>	<b>Description</b>	<b>Metal</b>	<b>Alumina support</b>	<b>Metal wt. % by XRF</b>
PdPt@Al <sub>2</sub> O <sub>3</sub>	PdPt NPs inside Al <sub>2</sub> O <sub>3</sub>	Colloidal PdPt NPs	From polymer	0.51
Pd@Al <sub>2</sub> O <sub>3</sub>	Pd NPs inside Al <sub>2</sub> O <sub>3</sub>			0.4
PdPt/Al <sub>2</sub> O <sub>3</sub>	PdPt NPs on Al <sub>2</sub> O <sub>3</sub>			0.53

**Table S5.** Aging conditions of PdPt-, Pt-, and Pd-alumina catalysts.

Temperature, °C	O <sub>2</sub> , vol. %	steam, vol. %	C <sub>3</sub> H <sub>6</sub> , vol. %	CO <sub>2</sub> , vol. %	CO, vol. %	H <sub>2</sub> , vol. %	C <sub>3</sub> H <sub>8</sub> , vol. %	Time, h	Catalyst
800	3	5	0.15	-	-	-	-	2	Pt@Al <sub>2</sub> O <sub>3</sub> Pt/Al <sub>2</sub> O <sub>3</sub> PdPt@Al <sub>2</sub> O <sub>3</sub>
800	3	10	-	-	-	-	-	2	Pt@Al <sub>2</sub> O <sub>3</sub>
800	3	5	0.15	-	-	-	-	2	Pt@Al <sub>2</sub> O <sub>3</sub>
1,100	21	10	-	-	-	-	-	5	Pt@Al <sub>2</sub> O <sub>3</sub> Pd@Al <sub>2</sub> O <sub>3</sub> PdPt@Al <sub>2</sub> O <sub>3</sub>
900	-/-1.5	10/10/10	-	3/3/3	0/0.9/0	0/0.3/0	-	50	PdPt@Al <sub>2</sub> O <sub>3</sub>
800	8	5	0.1	2	0.2	-	0.1	48	PdPt@Al <sub>2</sub> O <sub>3</sub>

**Table S6.** EXAFS results for the fresh (as-synthesized) PdPt@Al<sub>2</sub>O<sub>3</sub>.

Edge	Scattering path	Fresh			
		CN	$\sigma^2, \text{\AA}^2$	R, $\text{\AA}$	$\Delta E_0, \text{eV}$
Pd	Pd-O	2.1 ± 0.3	0.004 ± 0.001	2.03 ± 0.01	3.7 ± 1.1
	Pd-Pt	2.5 ± 0.6	0.006 ± 0.001	2.74 ± 0.03	-1.9 ± 0.6
	Pd-Pd	1.5 ± 0.3	0.005 ± 0.001	2.74 ± 0.03	-1.9 ± 0.6
Pt	Pt-Pt	10.5 ± 1.7	0.006 ± 0.001	2.74 ± 0.03	8.0 ± 0.6
	Pt-Pd	1.0 ± 0.8	0.006 ± 0.001	2.74 ± 0.03	8.0 ± 0.6

$\sigma^2$ , mean-square deviation in path length; CN, coordination number;  $\Delta E_0$ , inner potential correction.  $S_0^2 = 0.78$  and  $0.81$  was used for Pd K-edge and Pt L<sub>3</sub>-edge, respectively.

**Table S7.** EXAFS results for the 1,100 °C aged PdPt@Al<sub>2</sub>O<sub>3</sub>.

Edge	Scattering path	1,100 °C aged			
		CN	$\sigma^2, \text{\AA}^2$	R, $\text{\AA}$	$\Delta E_0, \text{eV}$
Pd	Pd-O	-	-	-	-
	Pd-Pt	$6.1 \pm 0.5$	$0.003 \pm 0.001$	$2.74 \pm 0.04$	$-2.0 \pm 0.3$
	Pd-Pd	$4.6 \pm 0.4$	$0.003 \pm 0.001$	$2.74 \pm 0.04$	$-2.0 \pm 0.3$
Pt	Pt-Pt	$5.4 \pm 0.7$	$0.003 \pm 0.001$	$2.74 \pm 0.04$	$8.3 \pm 0.5$
	Pt-Pd	$4.9 \pm 0.4$	$0.003 \pm 0.001$	$2.74 \pm 0.04$	$8.3 \pm 0.5$

**Table S8.** EXAFS results for the fresh (as-synthesized) PdPt/Al<sub>2</sub>O<sub>3</sub>.

Edge	Scattering path	Fresh			
		CN	$\sigma^2, \text{\AA}^2$	R, $\text{\AA}$	$\Delta E_0, \text{eV}$
Pd	Pd-O	1.4 ± 0.2	0.004 ± 0.001	2.03 ± 0.01	3.7 ± 1.1
	Pd-Pt	4.0 ± 0.5	0.006 ± 0.001	2.74 ± 0.03	-1.9 ± 0.6
	Pd-Pd	3.0 ± 0.4	0.005 ± 0.001	2.74 ± 0.03	-1.9 ± 0.6
Pt	Pt-Pt	6.3 ± 0.8	0.006 ± 0.001	2.74 ± 0.03	8.0 ± 0.6
	Pt-Pd	1.3 ± 0.5	0.006 ± 0.001	2.74 ± 0.03	8.0 ± 0.6



**Table S9.** EXAFS results for the 1,100 °C aged PdPt/Al<sub>2</sub>O<sub>3</sub>.

Edge	Scattering path	Fresh			
		CN	$\sigma^2, \text{\AA}^2$	R, $\text{\AA}$	$\Delta E_0, \text{eV}$
Pd	Pd-O	-	-	-	-
	Pd-Pt	6.5 ± 0.6	0.003 ± 0.001	2.74 ± 0.04	-2.0 ± 0.3
	Pd-Pd	5.0 ± 0.5	0.003 ± 0.001	2.74 ± 0.04	-2.0 ± 0.3
Pt	Pt-Pt	5.8 ± 0.7	0.003 ± 0.001	2.74 ± 0.04	8.3 ± 0.5
	Pt-Pd	4.4 ± 0.4	0.003 ± 0.001	2.74 ± 0.04	8.3 ± 0.5

## References

- 1 Wynblatt, P. & Gjostein, N. A. Particle growth in model supported metal catalysts—I. Theory. *Acta Metall.* **24**, 1165-1174 (1976).