Supporting Information

Dynamics of Pd Dopant Atoms Inside Au Nanoclusters During Catalytic CO Oxidation

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Experimental Details

Synthesis of [Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$]$. The synthesis was carried out following a protocol by Shivare et al.$^1$ 50 ml of THF and 500 mg of HAuCl$_4$ • 3H$_2$O were mixed with 1.2 eq. of TOAB and stirred for 10 min. Then, 0.85 ml of phenylethyl mercaptan was added to the solution and stirred until transparent. 480 mg of NaNBH$_4$ in 10 ml of ice-cold water was added at once, leading to a dark brown reaction mixture. The solution was stirred for 4 days under ambient conditions, before the solvent was evaporated and the precipitate was washed several times with methanol. The clusters were then separated by Size Exclusion Chromatography (SEC) and their purity evaluated by Ultraviolet-Visible (UV-Vis) spectroscopy and matrix-assisted laser desorption ionization (MALDI) mass spectrometry (Figure S1).

Synthesis of PdAu$_{24}$(SC$_2$H$_4$Ph)$_{18}$. PdAu$_{24}$(SC$_2$H$_4$Ph)$_{18}$ was synthesized following a modified protocol from Negishi et al.$^2$ Briefly, 112.1 mg Na$_2$PdCl$_4$ and 373.3 mg HAuCl$_4$ • 3H$_2$O were dissolved in 50 mL THF. The solution showed an orange color. 0.539 g phenylethyl mercaptan were added as a solution, the mixture was then stirred for 30 min at room temperature. Afterwards, 0.5669 g NaBH$_4$ were quickly mixed with cooled nanopure water and added to the mixture. Under cooling with ice (around 0 °C), the mixture (now a brown color) was stirred for 4 hours. Subsequently, the THF solvent was removed by rotary evaporation.

Separation and cleaning were performed according to Niihori et al.$^3$ The crude product was washed with methanol several times to remove excess thiols and then dissolved in toluene:hexane 3:5 and loaded onto a silica column. A mixture of PdAu$_{24}$(SC$_2$H$_4$Ph)$_{18}$ and Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$ was obtained after the elution of Pd complexes and other byproducts. Since PdAu$_{24}$(SC$_2$H$_4$Ph)$_{18}$ is more stable under such conditions, Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$ was decomposed by mixing a solution of 50 mg
clusters in 5 ml CH$_2$Cl$_2$ with 5 ml of a concentrated aqueous H$_2$O$_2$ solution and stirring for 4 h at room temperature. Afterwards, the aqueous phase was discarded, the organic phase washed with H$_2$O and centrifugated. CH$_2$Cl$_2$ was removed by rotary evaporation, the product re-dissolved in toluene:hexane 3:5 and loaded onto another silica column. After elution of the decomposed clusters and byproducts, PdAu$_{24}$(SC$_2$H$_4$Ph)$_{18}$ could be obtained. In case residual Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$ was still detected by MALDI-MS, the H$_2$O$_2$ oxidation step was repeated another time.

The final product was characterized by UV-Vis spectroscopy and MALDI-MS (Figure S2).

**Synthesis of Pd$_x$Au$_y$(SC$_2$H$_4$Ph)$_z$.** Pd$_x$Au$_y$(SC$_2$H$_4$Ph)$_z$ was synthesized following the same protocol from Negishi *et al.*$^2$ as for the PdAu$_{24}$(SC$_2$H$_4$Ph)$_{18}$ clusters, but with further modifications. Briefly, 112.1 mg Na$_2$PdCl$_4$ and 373.3 mg HAuCl$_4$ • 3H$_2$O were dissolved in 50 mL THF. The solution showed an orange color. 0.539 g phenylethyl mercaptan were added as a solution, the mixture was then stirred at room temperature until it turned colorless. Afterwards, 0.5669 g NaBH$_4$ were quickly mixed with cooled nanopure water and added. The mixture (now a brown color) was not cooled to 0 °C for this synthesis, but stirred at RT. In addition, the stirring was reduced from 4 hours to 2-2.5 hours. Subsequently, the THF solvent was removed by rotary evaporation. The same purification procedure as for PdAu$_{24}$(SC$_2$H$_4$Ph)$_{18}$ was applied. The UV/Vis spectrum can be found in Figure S3.

**Synthesis of Au nanoparticles.** Au nanoparticles (Au NPs) with an approximate particle size of 3.2 nm (estimated from UV-Vis$^4$) were synthesized following a protocol from Wang *et al.*$^5$ 2 ml of HAuCl$_4$ solution in H$_2$O (1% w/v) were added to 200 mL H$_2$O. The solution was cooled to 0 °C and 2 ml of an aqueous trisodium citrate solution (1% w/v) was added slowly under vigorous
stirring. The reduction was then initiated by addition of 2 ml of a NaBH₄ solution (0.075% w/v) in ice-cold H₂O. The mixture was allowed to slowly warm to room temperature over 5 hours, accompanied by a color change to ruby red, indicating the formation of nanoparticles. The UV-Vis spectrum of the nanoparticle solution and the DRS spectrum of the TiO₂ supported catalyst can be found in Figure S4.

**Synthesis of Pd nanoparticles.** Pd nanoparticles (Pd NPs) with an approximate particle size of 3.9 nm according to the literature were synthesized by the citrate method.⁶ A solution of PdCl₂ in 170 ml H₂O (0.118 mmol) was prepared, to which trisodium citrate (0.4 mmol) was slowly added. Subsequently, the reduction was initiated by addition of 11.8 ml of a NaBH₄ solution in ice-cold H₂O (0.075 wt%). The light grey solution was stirred at RT for 2 hours. The UV-Vis spectrum of the nanoparticle solution and the DRS spectrum of the TiO₂ supported catalyst can be found in Figure S5.

**Characterization Techniques**

UV-Vis spectra of nanoclusters dissolved in CH₂Cl₂ were recorded on a Perkin Elmer Lambda 750 UV-Vis spectrometer. Diffuse Reflectance Spectroscopy (DRS) of the nanoparticle catalysts was performed using the same instrument coupled to a 60 mm integration sphere.

All matrix-assisted laser desorption ionization (MALDI) mass spectrometric measurements were performed using a reflectron (RTOF) mass spectrometer (Shimadzu). For analytical experiments, 2,4,6-trihydroxyacetophenone (Sigma-Aldrich) was selected as MALDI-MS matrix. MALDI-RTOF mass spectra were acquired near threshold laser irradiance to obtain mass spectra of sufficient mass spectrometric resolution [3000–5000 at full width half-maximum (fwhm)]. All
displayed mass spectra were based on averaging 300–600 single and unselected laser pulses \((\lambda = 337 \text{ nm at } 50 \text{ Hz})\).

Transmission electron microscopy (TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed using a 200 kV FEI Tecnai F20 S-TWIN analytical (scanning) transmission electron microscopy \([(S)TEM]\) instrument equipped with a Gatan GIF Tridiem filter. The energy resolution was \(\leq 1 \text{ eV}\), the semiconvergence angle \(\sim 8 \text{ mrad}\), the semicollection angle \(\sim 15 \text{ mrad}\), and the spatial resolution on the order of 0.5 nm. Supported clusters were directly deposited on carbon-coated copper grids and plasma cleaning was applied to remove possible hydrocarbons and adsorbed water. Unsupported clusters were dissolved in dichloromethane and the solution dropcasted on carbon-coated copper grids, followed by plasma cleaning after evaporation of the solvent.

Chemical analysis with Total Reflection X-ray Fluorescence (TXRF) spectroscopy was performed with the supported cluster samples to determine the actual metal loading (%wt), using an ATOMIKA 8030C X-ray fluorescence analyzer. This spectrometer employs a total reflection geometry with an energy-dispersive Si(Li)-detector (energy resolution 160 eV). The measurements were done with monochromatized Mo-K\(\alpha\) excitation mode (17.48 keV) at \(\sim 70\%\) of the critical angle for total reflection of X-rays (1.2 mrad, angle of incidence), for 100 s live time, at 50 kV and 47 mA. Samples were attached to total reflecting quartz reflectors for the TiO\(_2\) matrix by using 1 mg of sample mixed with 5 \(\mu\)l of 1% poly-vinyl alcohol solution (for fixation). Blank measurements of the unloaded reflectors were performed prior to each specimen measurement in order to avoid cross contamination. Results for Au and Pd were scaled to 100% mass of Ti. Detection limits of the quantified elements (Au, Pd and Ti) are in the range of 10-100 \(\mu\)g/g.
UV-Vis spectra and MALDI mass spectra of the nanocluster samples in solution

Both the UV-Vis spectrum of $[\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}]^-$ (Figure S1, left) and the dominant peak at m/z ≈ 7394 in the MALDI mass spectrum (Figure S1, right) are in good agreement with the reported data.1

![UV-Vis spectrum and MALDI mass spectrum](image)

**Figure S1.** UV-Vis (left) and MALDI mass spectrum (right) of $[\text{Au}_{25}(\text{SC}_2\text{H}_4\text{Ph})_{18}]^-$.  

The UV-Vis fingerprint of $\text{PdAu}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{18}$ (Figure S2, left) agrees with reported spectra.7-8 In addition, the mass spectrum (Figure S2, right) shows only a single significant peak at m/z = 7309, corresponding to $\text{PdAu}_{24}(\text{SC}_2\text{H}_4\text{Ph})_{18}$. 
The UV-Vis spectrum of Pd$_x$Au$_y$(SC$_2$H$_4$Ph)$_z$ shows bands in similar regions as Au$_{25}$(SC$_2$H$_4$Ph)$_{18}$ and PdAu$_{24}$(SC$_2$H$_4$Ph)$_{18}$, although broadened. Unfortunately, due to upgrade of instrumentation no MALDI-MS spectrum of the Pd$_x$Au$_y$(SC$_2$H$_4$Ph)$_z$ samples could be obtained (strong fragmentation with the new equipment). However, STEM-HAADF indicated a mean particle size of 1.3±0.2 nm, very close to the particle size of Au$_{25}$ and PdAu$_{24}$ clusters, in line with a cluster size of around 20-30 metal atoms.

**Figure S3.** UV-Vis spectrum of Pd$_x$Au$_y$(SC$_2$H$_4$Ph)$_z$. Absorption maxima indicated are only approximate.
UV-Vis and DRS spectra of the Au and Pd nanoparticles

**Figure S4.** (a) UV-Vis spectrum of the Au NPs in H₂O and (b) DRS spectrum of Au NPs/TiO₂.

**Figure S5.** (a) UV-Vis spectrum of the Pd NPs in H₂O and (b) DRS spectrum of Pd NPs/TiO₂.
**Total metal loading & Pd/Au ratio of the nanocluster and nanoparticle catalysts**

The total metal loadings of the catalysts (Au$_{25}$/TiO$_2$, PdAu$_{24}$/TiO$_2$, Pd$_x$Au$_y$/TiO$_2$, Au NPs/TiO$_2$, Pd NPs/TiO$_2$) were determined by TXRF. As seen from Table S1, the Pd content in PdAu$_{24}$/TiO$_2$ was too low for detection by TXRF.

For Pd$_x$Au$_y$/TiO$_2$, a Pd:Au 1 : 4.2±0.4 atomic ratio was determined by TXRF. XPS measurements of Pd$_x$Au$_y$(SC$_2$H$_5$Ph)$_z$ dropcast on HOPG yielded a Pd:Au ratio of 1 : 3.1±0.3.

**Table S1.** Metal loading (wt%) of the nanocluster catalysts determined by TXRF.

|               | wt% Pd | wt% Au | wt% total | Pd:Au atomic ratio |
|---------------|--------|--------|-----------|-------------------|
| Au$_{25}$/TiO$_2$ | -      | 4.50   | 4.50      | -                 |
| PdAu$_{24}$/TiO$_2$ | n.d.*  | 2.70   | 2.70      | n.a.              |
| Pd$_x$Au$_y$/TiO$_2$ | 0.24   | 1.88   | 2.12      | 1 : 4.2±0.4       |
| Au NPs/TiO$_2$    | -      | 0.11   | 0.11      | -                 |
| Pd NPs/TiO$_2$    | 0.35   | -      | 0.35      | -                 |

* n.d.: not detected; TXRF-measurements can have a maximum relative error of 10%.

**(S)TEM of the TiO$_2$-supported PdAu$_{24}$, Pd$_x$Au$_y$ and Au$_{25}$ nanoclusters**

TEM and HAADF-STEM images were acquired for the nanocluster catalysts to determine the average particle size (Figure S6). For TiO$_2$-supported Au$_{25}$ and PdAu$_{24}$ the average diameter was 1.2 ± 0.2 nm, for Pd$_x$Au$_y$ nanoclusters it was 1.3 ± 0.2 nm.
Figure S6. (a) HAADF-STEM image of Au25 supported on carbon-film; (b) TEM image of PdAu24 supported on carbon-film, and (c) HAADF-STEM image of PdxAuy supported on TiO2.

Table S2. Mean particle sizes of the supported PdxAuy nanoclusters, as-prepared and after various treatments and reaction, estimated from HAADF-STEM.

|          | fresh catalyst | after pretO2 | after pretH2 | after pretO2-H2 | after COox |
|----------|----------------|--------------|--------------|-----------------|------------|
| PdxAuy/TiO2 | 1.3 ± 0.2      | 2.7 ± 0.7    | 2.6 ± 0.6    | 2.7 ± 0.5       | 2.8 ± 0.8  |

For PdxAuy/TiO2 catalyst, images were also taken after oxidative, reductive, and sequential treatments (pretO2-H2) and after CO oxidation (post-reaction), as shown in Figure S7. Upon pretreatment and reaction (Table S2), the particle size approximately doubled (2.8 ± 0.8 nm).
Figure S7. HAADF-STEM images of Pd_{x}Au_{y} supported on TiO_{2}: (a) pretO_{2}, (b) pretH_{2}, (c) pretO_{2}-H_{2} and (d) post-reaction.

Reusability of PdAu_{24}/TiO_{2} in CO oxidation

Reusability test with PdAu_{24}/TiO_{2} were conducted by subsequent CO oxidation reactions in the flow reactor set-up without removing the catalyst in between. After the first reaction, the sample was cooled to room temperature (under Ar). Once reached, a second CO oxidation reaction was initiated (same for the third catalytic test). As can be seen in Figure S8, activity increases in the 2\textsuperscript{nd} and 3\textsuperscript{rd} run, which indicates activation of PdAu_{24}/TiO_{2} at CO oxidation conditions.

Figure S8. Reusability tests with PdAu_{24}/TiO_{2} in CO oxidation.
Catalytic activity of TiO$_2$ supported Au and Pd NPs

TiO$_2$ supported Au and Pd nanoparticles (NPs) were employed in CO oxidation to contrast their activities to that of the nanocluster catalysts. The catalysts were pretreated by pretO$_2$-H$_2$ as described in the main paper. As can be seen in Figure S9, Au NPs/TiO$_2$ exhibited significantly higher conversion, which gradually increased with rising temperature. The CO conversion of the Pd NPs/TiO$_2$ catalyst was much lower and only increased above 200 °C, due to the much stronger CO poisoning on Pd. The low activity of Pd$_x$Au$_y$/TiO$_2$ indicates the presence of residual protecting ligands (or fragments thereof) even after the pretreatment steps, which are blocking the active sites.

Figure S9. Comparison of the catalytic activity of Au NPs/TiO$_2$, Pd NPs/TiO$_2$ and Pd$_x$Au$_y$/TiO$_2$. Activity was normalized to 1 wt% total metal loading and 1 mg of catalyst (as opposed to 15 mg for the measurements described in the main manuscript).
**DRIFT spectra: CO dosing and TiO₂ blank**

CO dosing experiments were performed with the pretreated catalysts before starting the CO oxidation reaction, which DRIFT spectra are depicted in Figure S11. The CO gas phase band is clearly visible in the 1% CO atmosphere spectra with maxima at around 2170 and 2115 cm⁻¹.

For Au₂₅/TiO₂, no significant formation of CO-adsorbate species could be detected. This correlates with its low CO oxidation activity. For the PdAu₂₄/TiO₂ catalyst, the spectra strongly depended on the pretreatment conditions. After only pretO₂, minimal formation of CO adsorbed on Au could be found, whereas after pretO₂-H₂, a pronounced CO-Pd band could be detected. This correlates with the better catalytic performance of the pretO₂-H₂ catalysts.

Blank experiments with the pure TiO₂ support without any impregnated Au clusters were performed as well (Figure S10). CO dosing experiments showed no formation of adsorbed CO species, yet still some CO₂ formation could be detected in the *in situ* DRIFTS measurements during CO oxidation, getting stronger at higher temperature. The same trend could be observed in the kinetic tests (Figure 1b in main manuscript).

**Figure S10. In situ** DRIFTS spectra of a TiO₂ blank experiment during CO oxidation (red). CO dosing after pretreatment (blue and green)
Figure S11. DRIFT spectra after CO dosing and subsequent He purging: (a) Au$_{25}$/TiO$_2$ pretO$_2$-H$_2$, (b) PdAu$_{24}$/TiO$_2$ pretO$_2$-H$_2$ and (c) PdAu$_{24}$/TiO$_2$ pretO$_2$. The pretreated samples were exposed to a 1% CO in He gas atmosphere and afterwards purged with He at RT, until no further changes in the spectra were observed.

Figure S12. MS analysis of CO conversion during DRIFTS experiments. Each run used 10 mg of catalyst.
**EXAFS Fitting**

XAS data have been processed according to standard procedures. Au L$_3$ and Pd K-edge spectra have been normalized by calculating and subtracting pre-edge and post-edge backgrounds as low order polynomial smooth curves. The corresponding EXAFS signal has been then extracted, k-squared weighted, and Fourier transformed (FT) in the range 2.8 Å$^{-1}$ and 10 Å$^{-1}$ and 2.6 Å$^{-1}$ and 12.6 Å$^{-1}$ at Au L$_3$ edge and Pd K-edge, respectively. The results are displayed in Figure S13.

**Pd K-edge EXAFS fit.** A two shell model (with Pd-S, Pd-Au contributions) has been considered to model the EXAFS data at Pd K-edge. For each spectrum of the dataset, we considered two coordination numbers $CN$ ($N_{Pd-S}$, $N_{Pd-Au}$) as fitting parameters and two correction factors for interatomic distances ($\Delta R_{Pd-S}$ and $\Delta R_{Pd-Au}$). We decided to use only two disorder parameters ($\sigma^2_{Pd-S}$ and $\sigma^2_{Pd-Au} = \sigma^2_{Au-Pd}$) for the whole dataset, plus the energy correction to photoelectron reference $\Delta E_0$ and the passive electron reduction factors $S_0^2$.

**Au L$_3$-edge EXAFS fit.** A three shell model (with Au-S, Au-Au, and Au-Pd contributions) has been considered to model the data. For each spectrum of the dataset, we considered three coordination numbers $CN$ ($N_{Au-S}$, $N_{Au-Au}$, and $N_{Au-Pd}$) as fitting parameters and two correction factors for interatomic distances ($\Delta R_{Au-S}$ and $\Delta R_{Au-Au} = \Delta R_{Au-Pd}$), which means that we constrained the Au-Pd and Au-Au distances. Due to the limited k range available and the strong intercorrelation between the fitting parameters, we decided to use only two disorder parameters ($\sigma^2_{Au-S}$ and $\sigma^2_{Au-Au} = \sigma^2_{Au-Pd}$) kept common for all the spectra in the dataset. Such assumption can be justified considering the limited temperature range of these *in situ* measurements (25-250 °C) and the fact that in general, the static structural disorder is higher than the temperature one for small clusters. This approach assures that the coordination numbers obtained from the analysis are consistent with all the experimental information available. Finally, we fit the energy correction to
photoelectron reference $\Delta E_0$ and the passive electron reduction factors $S_0^2$, again common to all the spectra.

**Figure S13.** EXAFS fitting.
In order to evaluate if there was a significant contribution of Pd-Pd in the EXAFS, a feff\textsuperscript{9} simulation\textsuperscript{10} was done. The results of the simulation are shown in Figure S14. From these simulations, it could be shown that in a bimetallic particle containing less than 30\% of Pd, a small contribution of Pd-Pd cannot be distinguished from Pd-Pd and Pd-Au. This would only be possible if there was a stronger contribution of Pd-Pd bonds.

**Figure S14.** EXAFS and XANES simulation to study Pd-Pd contributions in spectra of PdAu nanoparticles containing less than 30\% of Pd.
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