

Atomistic Engineering of Catalyst Precursors - Dynamic Reordering of PdAu Nanoparticles during Vinyl Acetate Synthesis enhanced by Potassium Acetate

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Transmission Electron Microscopy

TEM images were collected on a *JEM-2010-JEOL* microscope applying an acceleration voltage of 120 kV to electrons generated by a LaB₆ source. The resolution of the microscope is 0.2 nm. Before measurement the samples were dispersed in ethanol and dropped on a copper-grid supported film.

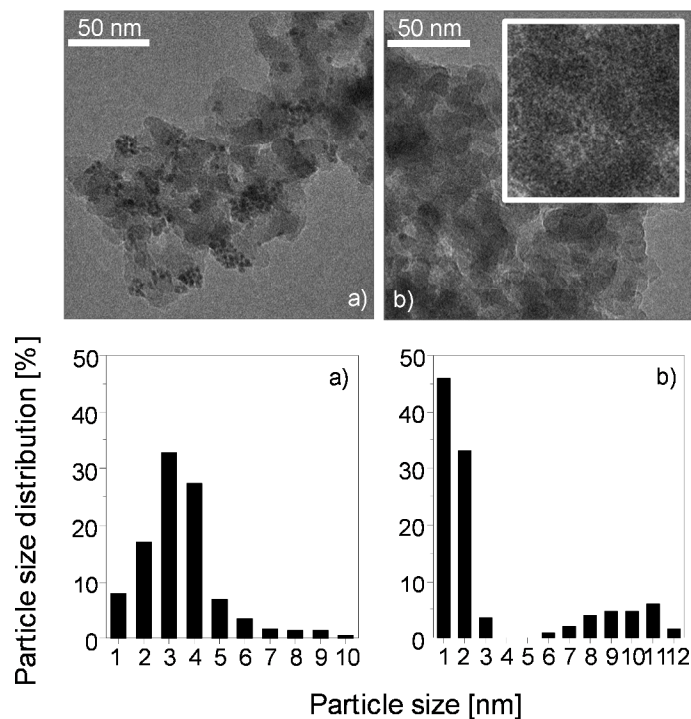


Figure S1 TEM images and particle size distribution of (a) fresh and (b) used (Pd+Au)/KOAc/SiO₂.

The particle size distribution of fresh (Pd+Au)/KOAc/SiO₂ (Figure S1a) revealed an average particle size of ~3.5 nm. After reaction (Figure S1b), small particles in the range of 1-2 nm were found together with bigger agglomerates in the range of ~5 to 12 nm. The small particles are associated with leached and reduced Pd⁰ clusters whereas the bigger particles are Au rich as indicated by XRD. A number of the large metal particles was encased within a low contrast shell, most likely consisting of acetate deposits.¹

Catalytic Result of (Pd+Au)/KOAc/SiO₂

The catalytic activity normalized to the total concentration of Pd and the selectivity of PdAu/KOAc/SiO₂ and (Pd+Au)/KOAc/SiO₂ (Figure S2) are almost identical. The overall activity contains contributions of the activity of Pd in PdAu and from Pd²⁺, which is about 20% less active than Pd in PdAu. (Pd+Au)/KOAc/SiO₂ contains 91% dispersed Pd whereas PdAu/KOAc/SiO₂ contains only 53%. Therefore, for (Pd+Au)/KOAc/SiO₂ dispersed Pd

contributes more to the overall activity than on PdAu/KOAc/SiO₂. On the other hand, the Au enriched PdAu particle surface (molar Pd/Au ratio on the surface of 1.1) on (Pd+Au)/KOAc/SiO₂ contributes less to the overall activity compared to PdAu/KOAc/SiO₂ (molar Pd/Au ratio on the surface of 2.0) both effects compensate and lead to the similar activity observed.

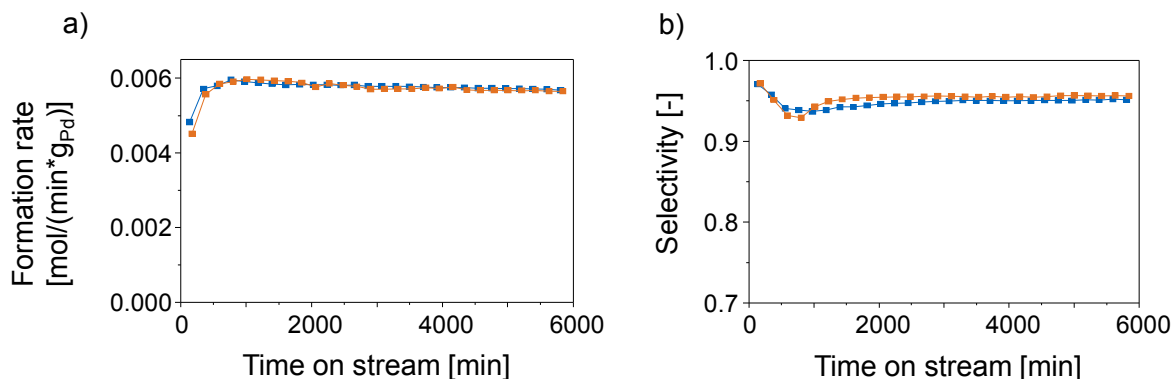


Figure S2. (a) Formation rates normalized to the total concentration of Pd and (b) selectivities for PdAu/KOAc/SiO₂ (blue) and (Pd+Au)/KOAc/SiO₂ (orange) with time on stream. Reaction conditions: 60 vol % C₂H₄, 13 vol % AcOH, 4.5 vol % O₂, balance N₂; total pressure, 8.8 bar; temperature, 150 °C.

IR Spectroscopy of Adsorbed CO on Silica

At -150 °C, 1.0 mbar CO adsorbed on the silica support (Figure S3) by interacting with cations (2184 cm⁻¹) and with the OH groups on silica (2157 cm⁻¹).²⁻³ Physically adsorbed CO appeared at 2135 cm⁻¹.⁴ The normalized absorbance (10⁻⁵) is about one order of magnitude lower than the absorbance on fresh and reacted samples (10⁻⁴).

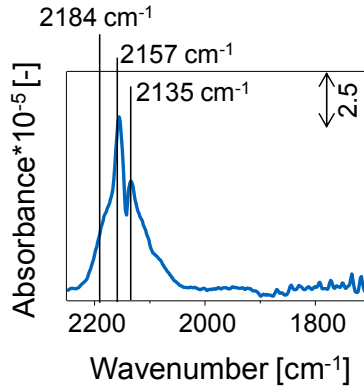


Figure S3. IR spectrum of 1.0 mbar CO adsorbed on SiO₂ at -150 °C.

Calculation of the Absorption Coefficients ϵ of CO on Au and Pd

Lambert-Beer law: $A = \epsilon \cdot c \cdot d$ $A = \epsilon \cdot c \cdot d$

A = Absorbance (height) or integrated area [cm^{-1}]

ϵ = Absorption coefficient [$\text{cm}^2 \text{mol}^{-1}$] (if IR band intensity is used) or [cm mol^{-1}] (if IR band area [cm^{-1}] is used)

c = Concentration of the absorbing substance [mol l^{-1}]

d = Thickness [cm]

with $c \cdot d = \frac{n_s}{S} = \text{const.}$

n_s = Number of total Au or Pd surface atoms [mol]

S = Surface of the wafer; $S = r^2 \cdot \pi$, r = radius of the wafer [0.6 cm]

$$A = \epsilon \cdot \frac{n_s}{S}$$

$$\epsilon = A \cdot \frac{S}{n_s}$$

$$\varepsilon = A \cdot \frac{r^2 \cdot \pi}{n_s}$$

$$\varepsilon = A \cdot \frac{r^2 \cdot \pi}{\frac{n_s}{\frac{g_{SiO_2}}{M_{Au}}} \cdot m_W}$$

m_W = mass of the wafer [g]

$$n_s = \text{Number of total Au or Pd surface atoms; } n_{Au} = \frac{\frac{m_{Au}}{g_{SiO_2}}}{M_{Au}} \cdot D \quad n_{Pd} = \frac{\frac{m_{Pd}}{g_{SiO_2}}}{M_{Pd}} \cdot D$$

$$\frac{m_{Au}}{m_{SiO_2}} \text{ Concentration of Au on SiO}_2 \text{ [g/g]; } \frac{m_{Pd}}{m_{SiO_2}} \text{ Concentration of Pd on SiO}_2 \text{ [g/g]}$$

$$M_{Au} = 197 \text{ g/mol; } M_{Pd} = 106.4 \text{ g/mol}$$

$$D = \text{dispersion} \quad (D = \frac{n_s}{n_{total}}) \quad (\text{Dispersion derived from average particle size in TEM})$$

$$\varepsilon_{Au} = \frac{A \cdot r^2 \cdot \pi}{\frac{\frac{m_{Au}}{g_{SiO_2}}}{M_{Au}} \cdot D \cdot m_W} \quad \varepsilon_{Pd} = \frac{A \cdot r^2 \cdot \pi}{\frac{\frac{m_{Pd}}{g_{SiO_2}}}{M_{Pd}} \cdot D \cdot m_W}$$

Calculation of the extinction coefficients of CO on Au ($\varepsilon_{l,Au}$)

$$\varepsilon_{l,Au} = \frac{6.28 \text{ cm}^{-1} \cdot (0.6 \text{ cm})^2 \cdot \pi}{\frac{0.024 \frac{g_{Au}}{g_{SiO_2}}}{197 \frac{g}{mol}} \cdot 0.26 \cdot 0.01606 \text{ g}}$$

$$\varepsilon_{l,Au} = 1.40 \cdot 10^7 \text{ cm mol}^{-1}$$

Calculation of the extinction coefficients of CO on Pd ($\varepsilon_{l,Pd}$, $\varepsilon_{b,Pd}$)

$$\varepsilon_{Pd} = \frac{A \cdot r^2 \cdot \pi}{\frac{\frac{m_{Pd}}{g_{SiO_2}}}{M_{Pd}} \cdot D \cdot m_W}$$

Attention: CO adsorbs in linear and bridged form on Pd atoms. (Equilibrium between linear and bridged CO depends on the partial pressure of CO.)

M.A. Vannice, S.Y. Wang, The Journal of Physical Chemistry 85 (1981) 2543-2546.⁵

$$\varepsilon_l = 3.3 \cdot 10^7 \text{ cm mol}^{-1} \quad \varepsilon_b = 85 \cdot 10^7 \text{ cm mol}^{-1}$$

Calculation of ε_l and ε_b (assuming $\frac{\varepsilon_b}{\varepsilon_l} = \frac{85}{3.3}$)

$$\frac{\varepsilon_b}{\varepsilon_l} = \frac{85}{3.3} \quad \varepsilon_b = \frac{85}{3.3} \cdot \varepsilon_l$$

$$n_s = n_l + 2 \cdot n_b \quad n_b = \frac{n_s - n_l}{2}$$

n_l = Number of linearly adsorbed CO on Pd [mol]

n_b = Number of bridged adsorbed CO on Pd [mol]

$$n_l = \frac{A_l \cdot S}{\varepsilon_l} \quad n_b = \frac{A_b \cdot S}{\varepsilon_b}$$

$$n_s = \frac{A_l \cdot S}{\varepsilon_l} + 2 \cdot \frac{A_b \cdot S}{\varepsilon_b} = \frac{A_l \cdot S}{\varepsilon_l} + 2 \cdot \frac{A_b \cdot S}{\varepsilon_l \cdot \frac{85}{3.3}}$$

$$n_s = \frac{(\frac{85}{3.3} \cdot A_l + 2 \cdot A_b) S}{\varepsilon_l \cdot \frac{85}{3.3}}$$

$$n_s = \frac{\frac{m_{Pd}}{g_{SiO_2}} \cdot D \cdot m_W}{M_{Pd}} = \frac{\frac{0.025 \text{ g}_{Pd}}{106.4 \frac{g}{mol}} \cdot 0.14 \cdot 0.01072 \text{ g}}{3.526 \cdot 10^{-7} \text{ mol}} = 3.526 \cdot 10^{-7} \text{ mol}$$

$$\varepsilon_{l,Pd} = \frac{(\frac{85}{3.3} \cdot A_l + 2 \cdot A_b) r^2 \pi}{n_s \cdot \frac{85}{3.3}}$$

$$\varepsilon_{l,Pd} = \frac{(\frac{85}{3.3} \cdot 2.562 \text{ cm}^{-1} + 2 \cdot 8.27 \text{ cm}^{-1}) (0.6 \text{ cm})^2 \pi}{\frac{85}{3.3} \cdot 3.526 \cdot 10^{-7} \text{ mol}}$$

$$\epsilon_{l,Pd} = 1.03 \cdot 10^7 \text{ cm mol}^{-1}$$

$$\epsilon_{b,Pd} = \frac{85}{3.3} \cdot \epsilon_{l,Pd}$$

$$\epsilon_{b,Pd} = 2.65 \cdot 10^8 \text{ cm mol}^{-1}$$

$$\frac{\epsilon_{l,Au}}{\epsilon_{l,Pd}} = \frac{1.40}{1.03} = 1.36$$

IR Spectroscopy of Adsorbed CO on Unwashed PdAu/SiO₂ after Reaction

As seen in Figure S4, the bright green band for CO linearly adsorbed on “Au next to Pd” dominated the spectrum compared to CO on “Au next to Au” (dark green), “Pd next to Pd” (bright blue) and “Pd next to Au” (blue). The lower Pd/Au ratio of 0.62 on unwashed compared to washed PdAu/SiO₂ after reaction of 0.83 indicated that the washing procedure leads to a slight overestimation of the Pd surface concentration, which is more pronounced on Au enriched PdAu particles.

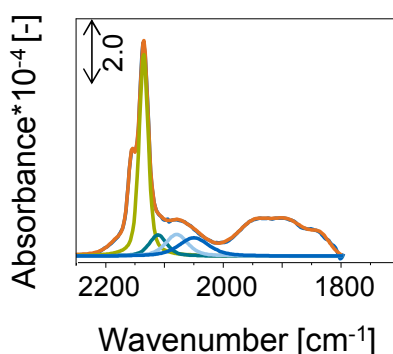


Figure S4. IR spectrum of 1.0 mbar CO adsorbed on spent, unwashed PdAu/SiO₂. Green lines represent CO on Au and blue lines CO on Pd at –150 °C.

X-Ray Diffraction on KOAc Free and KOAcP Pd(OAc)₂/SiO₂ after reaction

In order to estimate the reduction behavior of the reactive Pd₃(OAc)₆ and K₂Pd₂(OAc)₆ intermediates, two model catalysts, Pd(OAc)₂/SO₂ (Figure S5, blue) and Pd(OAc)₂/KOAc/SiO₂

(Figure S5, orange) were studied by XRD after reaction. The general lower values for the full width at half maximum and the narrower Pd reflections revealed the formation of bigger Pd particles on Pd(OAc)₂/KOAc/SiO₂. We associate the bigger Pd particles to a lower reduction stability of K₂Pd₂(OAc)₆ compared to Pd₃(OAc)₆.

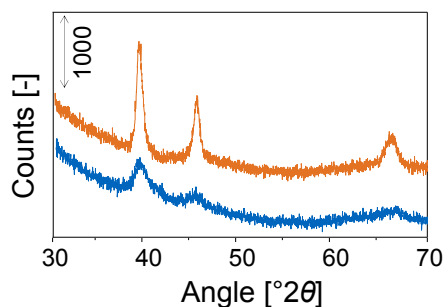


Figure S5. X-ray profile between 30 - 70 °2θ of Pd(OAc)₂/SO₂ (blue) and Pd(OAc)₂/KOAc/SiO₂ (orange) after reaction.

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