Supporting Information

Quantifying Oxygen Induced Surface Enrichment of a Dilute PdAu Alloy Catalyst

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1. Transient Pulse Response Experiments

The transient pulse-response experiments were carried out in a modified commercial TAP-2 type reactor.¹ The Pd_{0.08}Au_{0.92}-RCT-SiO₂ catalyst (7.1 mg, sieved to 100-300 μ m) was sandwiched in a thin zone configuration between two layers of inert SiC particles (~350 μ m) in a quartz microreactor 48.4 mm in length with an inner diameter of 3.75 mm. The length of the catalyst zone between the inert zones was 3 mm. An internal thermocouple was located at the center of the microreactor where the catalyst resided. One side of the microreactor was connected to a high-speed pulse valve (Parker, Model 009-1421-900) for the pulse experiments and the other side was connected to a vacuum chamber which is equipped with a quadrupole mass spectrometer (QMS, Stanford Research Systems, RGA200). The microreactor was evacuated to 10⁻⁸ torr before the pulse experiments.

$$N(Ar) = \frac{\Delta P V N_A}{RT} \tag{1}$$

The pulse size was calibrated with pulses of argon through the catalyst bed before the oxygen titration. A known volume (*V*) behind the pulse valve was filled with Ar at a given pressure (*P*), and the pressure drop (ΔP) after a certain number of pulses was used to quantify the total number of Ar atoms (*N*) in each pulse by using the ideal gas law (eqn (1)). With *N*_A being the Avogadro's number, *R* being universal gas constant, and *T* being temperature. The

scaling coefficient relating the raw mass spec signal and the number of molecules (*C*) was calculated by dividing the total number of molecules pulsed during the calibration by the total integrated area under the baseline-corrected pulse responses of m/z 40, defined as:

$$C = \frac{N(Ar)}{\sum_{i=1}^{\infty} \left[\int_0^t \{ I_i(Ar). \Delta t \} \right]}$$
(2)

with *I* being signal intensity, and *i* being pulse number.

The total number of CO₂ molecules produced in a pulse train can be calculated using eqn (3), with δ being the number of pulses in a pulse set and *TCF* being QMS sensitivity factor for m/z 44 (CO₂) relative to m/z 40 (Ar). The *TCF* for m/z 44 CO₂ was calculated to be 0.8169 by pulsing a known mixture of CO₂ and Argon.

$$N(CO_2) = \sum_{i=1}^{\infty} \left[\int_0^t \{ I_i(CO_2) \cdot \Delta t \} \ TCF \right] C \ \delta$$
(3)

For quantification of the CO signals during sequential pulses, the m/z 28 fragment from CO₂ production was subtracted from the measured CO transient.

The transient pulse responses shown in Figure 1 and Figure 3-inset are shown as a function of dimensionless time. For a TAP pulse response where the limiting transport factor is diffusion (e.g., in the case of an inert gas, or an instantaneously reacting species) it is possible to generate a *standard diffusion curve* which will be independent of the gas, bed length, bed packing, or reactor temperature, allowing for more accurate comparison.¹ For example, a TAP reactor in a "one zone" configuration, dimensionless time is defined as:

$$t_{dim} = t \frac{D}{\varepsilon L^2} \tag{4}$$

where t_{dim} is dimensionless time, t is time, D is the diffusivity, ε is the void fraction, and L is the reactor length. The benefit of using dimensionless time is that all physical characteristics of the reactor bed, along with the temperature and mass of the gas are removed, allowing for direct comparison of transient curves to the *standard diffusion curve*. Therefore, any deviation of an exit response from the *standard diffusion curve* solely arises due to interactions/reactions occurring on the catalytic surface for a TAP pulse. For reacting gases, the dimensionless time can be calculating by scaling the diffusivity measured for the inert gas response using the following relationship:

$$D = \frac{\varepsilon d_i}{3\tau} \left(\frac{8RT}{\pi M}\right)^{1/2} \tag{5}$$

where d_i is the diameter of the interstitial voids, τ is the tortuosity of the bed, T is the temperature, R is the universal gas constant, and M is the molecular weight of the gas. When Knudsen diffusion is the transport limiting process through the bed, the peak of the pulse response occurs at a dimensionless time of 0.17.¹

2. Synthesis of Pd0.08Au0.92-RCT catalyst

Details on the synthesis of the $Pd_{0.08}Au_{0.92}$ -RCT-SiO₂ catalyst were recently reported.² The $Pd_{0.08}Au_{0.92}$ RCT-SiO₂ catalysts were prepared using a multi-step colloid synthesis procedure. First, monodispersed citrate-stabilized gold nanoparticles were prepared using the procedure reported in the literature.³ After ligand exchange from citrate to polyvinylpyrrolidon (PVP), the gold nanoparticles (NPs) were attached to polystyrene colloids ($d_{PS} = 393$ nm) to create the "raspberry" colloids, and Pd was deposited on the AuNPs, using at low pH to ensure sufficiently slow reaction rates for selective Pd growth onto the NPs. After washing, the raspberry colloids were assembled into a colloidal crystal by solvent evaporation at 65 °C in air, and the resulting colloidal assembly was infiltrated with a pre-hydrolyzed silica solution to fill the interstitial spaces between the raspberry colloids. Finally, the polystyrene was removed via calcination in air at 500 °C , resulting in an ordered macro-porous silica matrix with well-distributed NPs.⁴ Based on TEM analysis, the NPs were 5.6±0.7 nm in diameter and were mostly embedded (85% of their surface on average) in the silica matrix.⁵

The palladium concentration in the nanoparticles was 7.8 atm%, and the total metal loading of the $Pd_{0.08}Au_{0.92}$ -RCT-SiO₂ catalyst was 4.0 wt%, as determined by inductively coupled plasma mass spectrometry (ICP-MS).

3. Calculations for number of surface atoms on particles

To calculate the number of surface atoms on the nanoparticles, the shape of the nanoparticles is assumed to be icosahedral with a diameter of 5.6 nm, as has been used previously.² The volume and surface area of an icosahedron particle were calculated using the following formulas:

$$V_{particle} = \frac{5}{12} (3 + \sqrt{5}) a^3$$
 (6)

$$S_{particle} = 5\sqrt{3} a^2 \tag{7}$$

$$r_{particle} \approx 0.95 \times a$$
 (8)

with *a* being the edge length of an icosahedron and r being the radius of a circumscribed sphere. Based on the ICP-MS results and using eqn(6)-(8), the total number of particles loaded into the bed and their surface area (S_{total}) were calculated as 2.83 x 10¹⁴ and 212.92 cm², respectively. Then, the total number of surface atoms was computed as 2.97 x 10¹⁷ by using the following equation:

$$\# of surface atoms = \frac{S_{total} \times \rho}{\pi \times r^2}$$
(6)

With ρ being the surface packing density (0.907) of a FCC (111) crystal facet, and r being the radius of an Au atom (0.144 pm). Since ~85% of the nanoparticle surface is embedded in the silica support⁵, the exposed surface contains 4.45 x 10¹⁶ atoms available for a reaction.

References

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