# Palladium-Gold Single Atom Alloy Catalysts for Liquid Phase Selective Hydrogenation of 1-hexyne

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## Supplementary Text

We prepared a sample with a higher Pd loading, having a Pd/Au atomic ratio of 1/5 with the same sequential reduction method. CO-IR data are shown in Figures S1 and S2. Bridging CO peak at around 1940 $cm^{-1}$ can be seen clearly. This is different from the CO-IR of PdAu SAA which shows no bridging CO.

We have performed STEM imaging and EDX mapping on PdAu SAAs to confirm the formation of single atom alloy. As shown in Figure S3, EDX elemental mapping over a large area of the sample does not show any monometallic Pd nanoparticles. And HAADF-STEM images show the isolated Pd atoms as darker atoms (Figure S4).

Selective hydrogenation of phenylacetylene with PdAu-SAA catalysts was conducted, as shown in Figure S5. It shows PdAu-SAA is active and selective for phenyacetylene hydrogenation to styrene.

Reaction rates of 1-hexyne hydrogenation over different Pd catalysts are compared in Table S1.

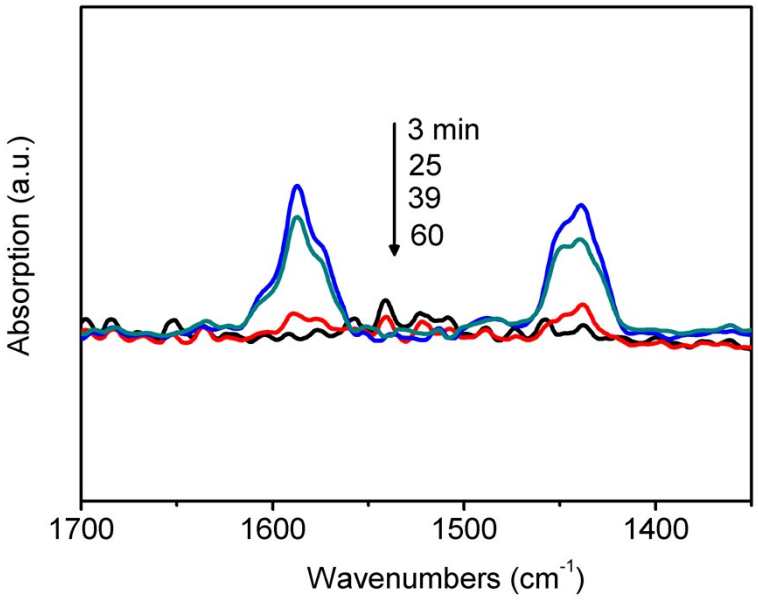


Figure S1. DRIFTS for adsorbed pyridine on Pd/C. Pd/C was pre-treated in $H_2$ at 150 °C. Pyridine vapor was carried in with He and flowed through the sample at room temperature followed by degassing in He at room temperature. The IR spectra were collected at different time point during degassing.

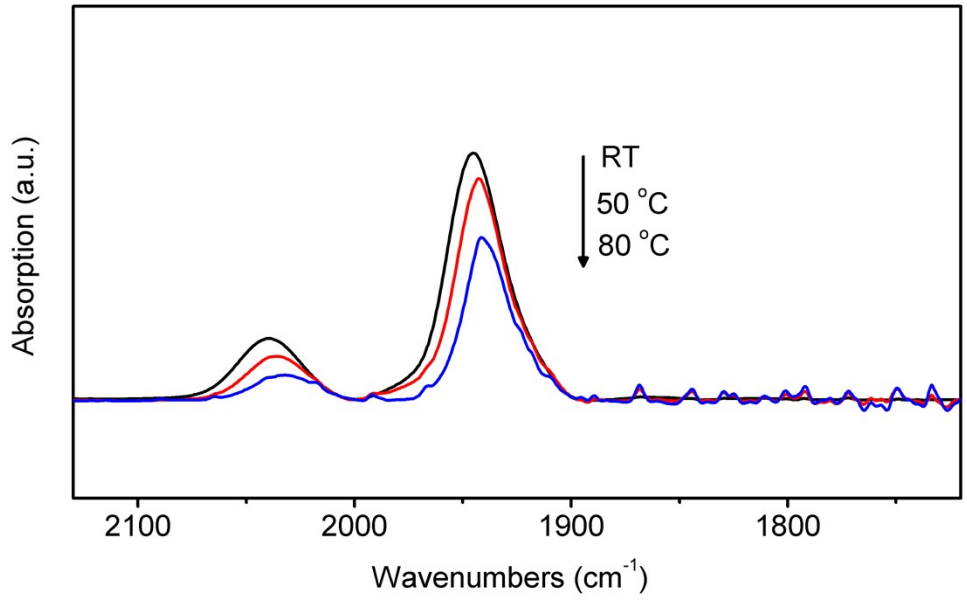


Figure S2. ATR-IR spectra of the CO stretch on $Pd_1Au_5$ sample. After pure CO flow through the ATR cell for 10 min, spectra were collected at different temperatures under He flow.

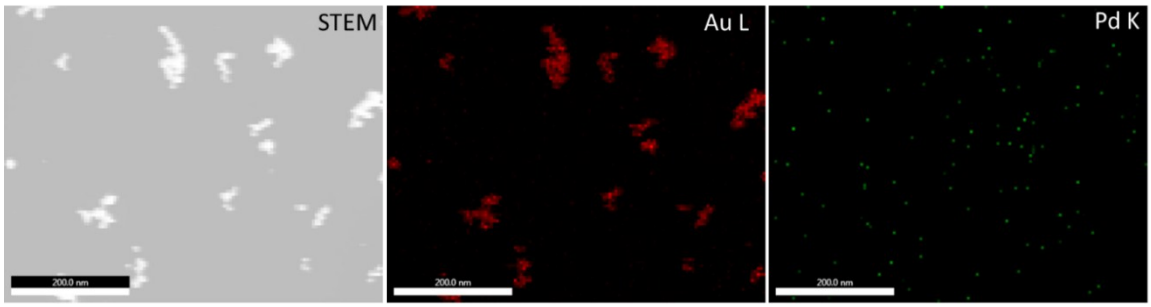


Figure S3. Dark field STEM image and Au and Pd EDX maps of PdAu-SAA.

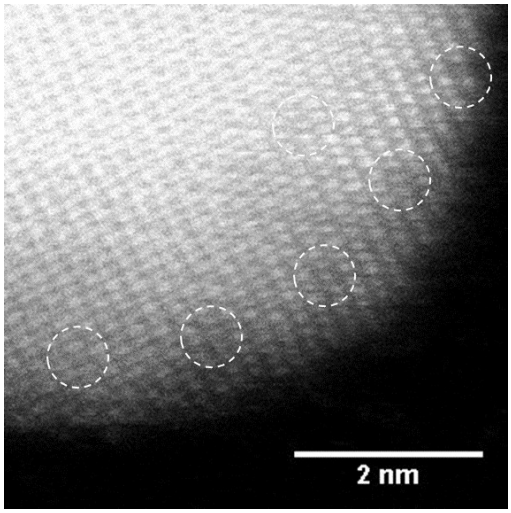


Figure S4. HAADF-STEM image of PdAu-SAA. The darker Pd atoms are highlighted by circles.

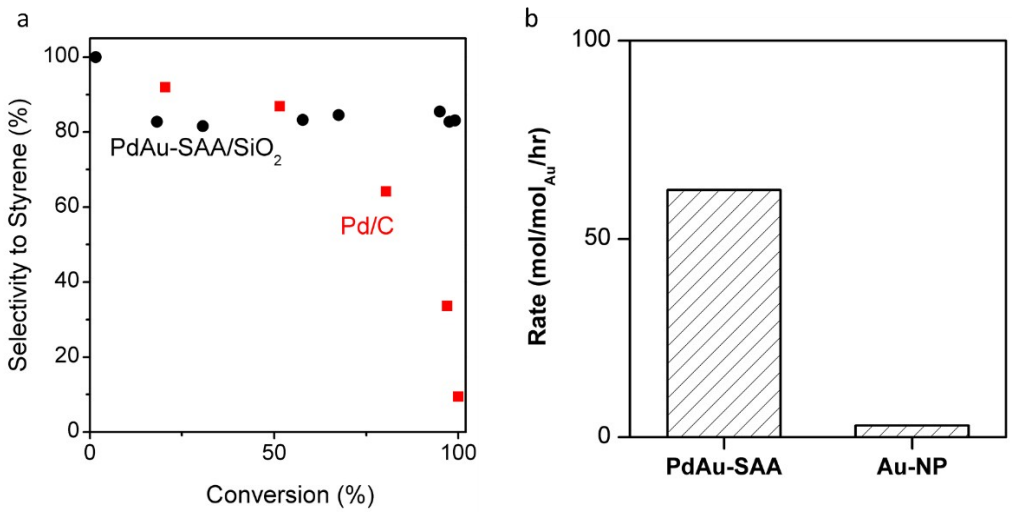


Figure S5. Partial hydrogenation of phenylacetylene. (a) selectivity to styrene as a function of conversion of phenylacetylene over PdAu-SAA/$SiO_2$ and Pd/C. (b) initial rate normalized by total Au of PdAu-SAA and Au-NP. (Batch reactor, 25 °C, 5 bar $H_2$, 600rpm, 1% phenylacetylene)

Table S1. Reaction rate of 1-hexyne hydrogenation over different Pd catalysts

| Catalyst | Rate (mol/$mol_{surf\ Pd}$/s) | Temperature (°C) | Reference |
|---|---|---|---|
| This work | 2.2 | 25 | -- |
| Bipyridine modified Pd | 29.5 | 30 | [1] |
| Unsupported Pd | | 30 | [2] |
| 6 - 11 nm | 0.5 | | |
| 13 nm | 6.6 | | |
| 1% $Pd/Al_2O_3$ | 6.3 | 25 | [3] |
| 5% $Pd/Al_2O_3$ | 3.2 | 25 | [3] |

## References


1 M. Crespo-Quesada, R. R. Dykeman, G. Laurenczy, P. J. Dyson and L. Kiwi-Minsker, *J. Catal.*, 2011, **279**, 66–74.

2 N. Semagina, A. Renken and L. Kiwi-Minsker, *J. Phys. Chem. C*, 2007, **111**, 13933–13937.

3 J. Anderson, J. Mellor and R. Wells, *J. Catal.*, 2009, **261**, 208–216.