Electronic Supplementary Material (ESI) for Green Chemistry.

Supplemental Information

Amination of 1-Hexanol on Bimetallic AuPd/TiO_2 Catalysts

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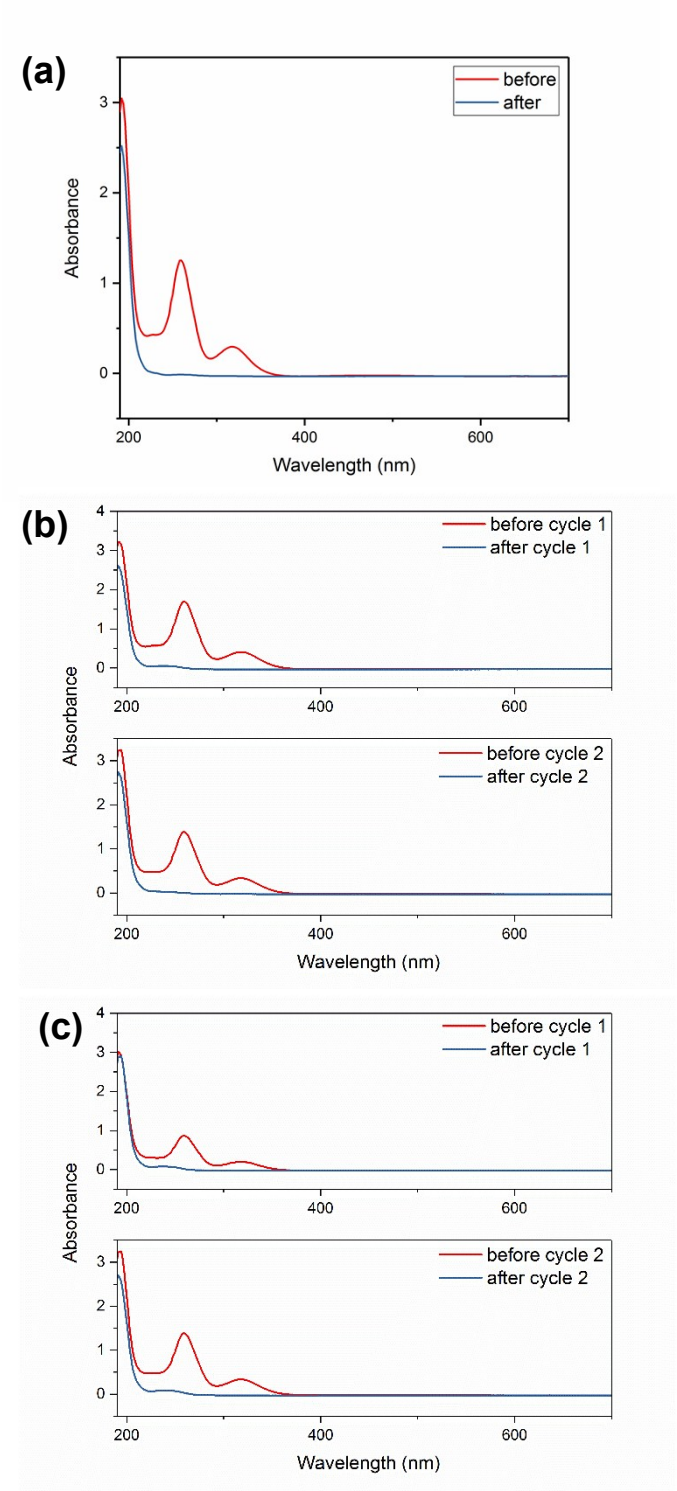

Figure S1. UV Vis Spectra of Cp(Pd)allyl solution before and after contact with Au/TiO_2 catalyst during synthesis of (a) $AuPd_{0.06}/TiO_2$, (b) $AuPd_{0.55}/TiO_2$, and (c) $AuPd_{0.67}/TiO_2$

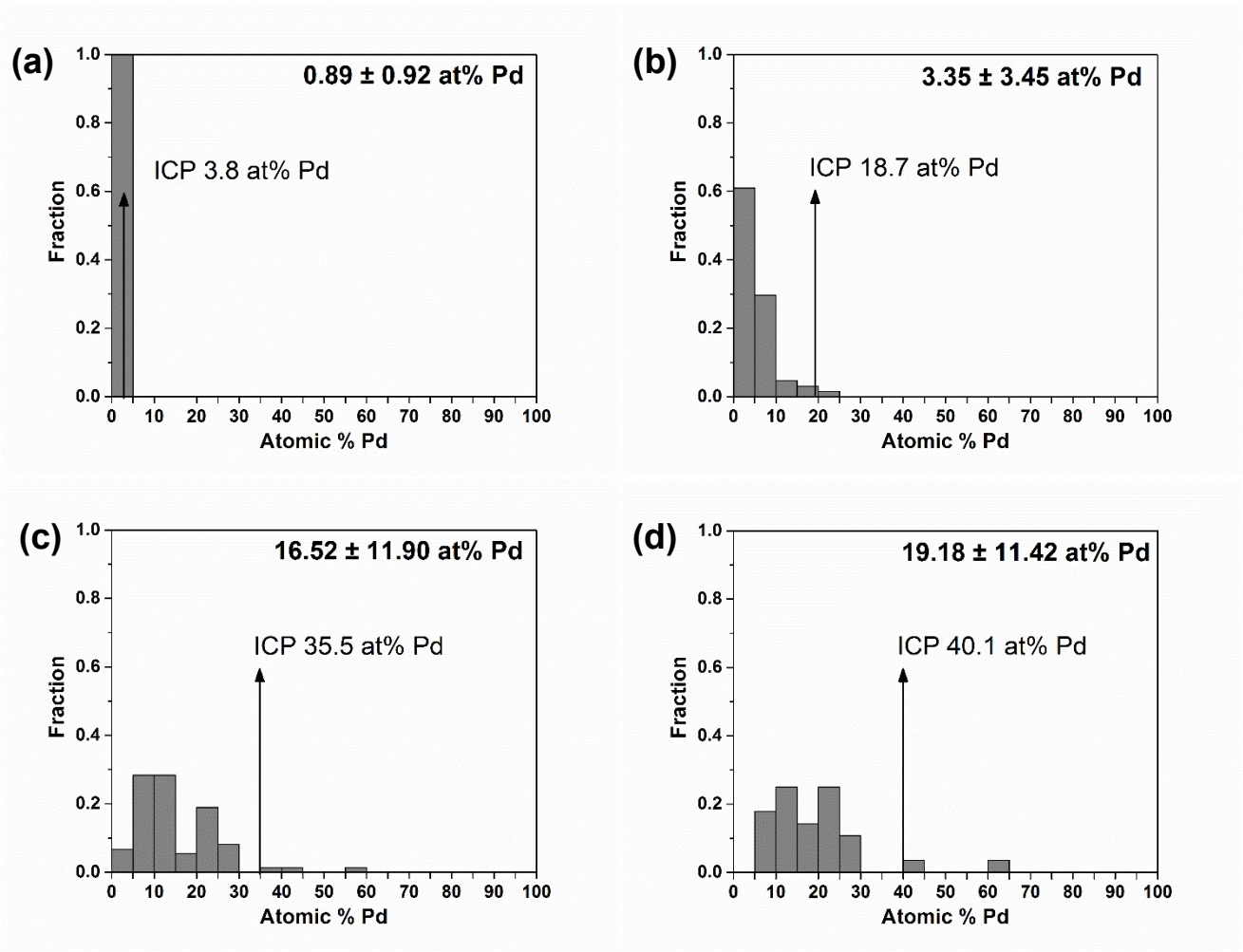

Figure S2. Composition distribution for (a) $AuPd_{0.06}/TiO_2$, (b) $AuPd_{0.23}/TiO_2$, (c) $AuPd_{0.55}/TiO_2$, and (d) $AuPd_{0.67}/TiO_2$ as measured by EDS analysis of individual nanoparticles. The average composition and standard deviation is shown and the composition as determined by ICP is shown by the arrow.

Table S1. Site density and dispersion from CO chemisorption experiments using different pretreatment conditions to determine the extent of strong metal support interaction effects

Catalyst	Pretreatment	Site density (µmol/g)	Dispersion (%)
$AuPd_{0.55}/TiO_2$	Red. 533 K	2.0	7.0
	Calc. 673K, Red. 533 K	1.1	3.8
Pd/TiO_2	Red. 533 K	7.3	15
	Red. 673 K	5.7	13

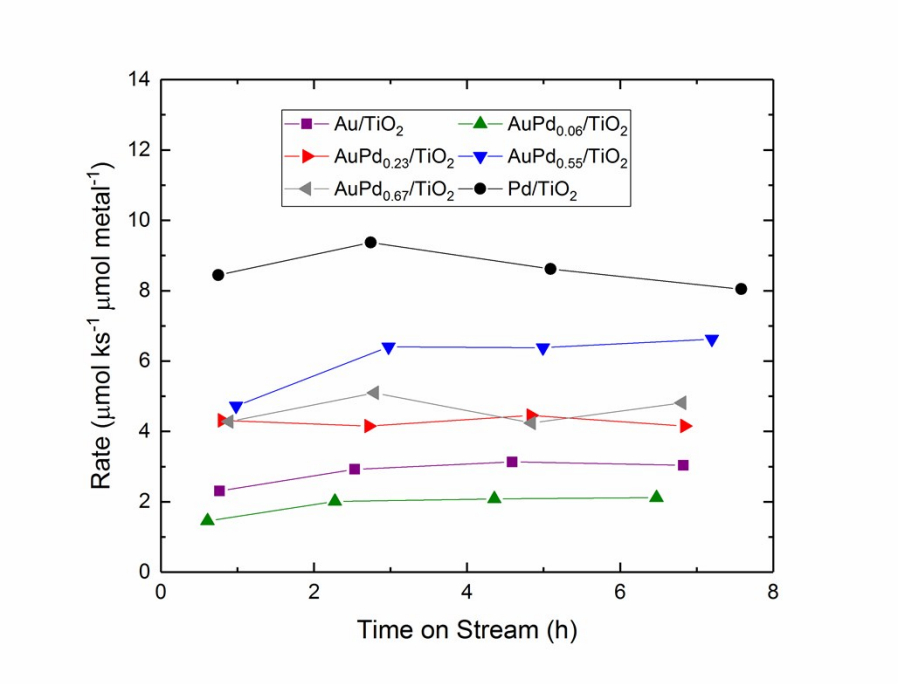

Figure S3. Hexanol conversion rates, based on product formation (weighted by the number of moles of hexanol required to form one mole of product), for the various catalysts versus time-on-stream. Conditions: 503 K, 1 atm (0.07 kPa hexanol, 2.5 kPa NH_3, 51 kPa H_2, and balance He), 16-24% hexanol conversion.

Table S2. Equilibrium constants for various steps in the amination of hexanol with ammonia, calculated from gas phase Gaussian calculations. The coupled cluster ccsd(t)/cc-pvtz method was used. Species were approximated by their two-carbon analogs (i.e. ethanol, ethanenitrile, diethylamine, etc.).

			K_{eq}
Hexanol +H_2	⇌	Hexane + H_2O	$6.4x10^{9}$
Hexanol	⇌	Hexanal + H_2O	$1.1x10^{-1}$
Hexanal + NH_3	⇌	Hexylimine + H_2O	$4.7x10^{-3}$
Hexylimine	⇌	Hexanenitrile + H_2	$1.7x10^{3}$
Hexylimine + H_2	⇌	Hexylamine	$1.0x10^{3}$
Hexylamine + Hexanal	⇌	N-hexylidene hexylamine + H_2O	$1.4x10^{-3}$
N-hexylidene hexylamine + H_2O	⇌	Dihexylamine	$2.1x10^{4}$
N-hexylidene hexylamine + hexanal +2H_2	⇌	Trihexylamine + H_2O	$6.2x10^{6}$

Using PBE+D3 and m062x/def2tzvp methods, it was confirmed that Gibbs free energy changes for the reaction steps approximated using C2 species were equivalent to the Gibbs free energy changes calculated for C6 species. The Gibbs free energy changes are shown for hexanenitrile + H_2 <-> hexylamine.

Method	**2C**	**6C**
PBE ΔG	0.06	0.05
MO6 ΔG	0.27	0.27