Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

Additional Details on Kinetic Simulation + Fitting

There are three principal regions in the experiment: benzaldehyde rich, benzyl alcohol rich, and toluene rich. The empty site concentrations can be assumed to stay within the same order of magnitude within each of these 3 regions. With this assumption, the empty catalytic sites can be lumped into observed rate constants, allowing pseudo-first order models for each reaction step. This provides a lower limit to the catalytic activity, since it corresponds to having an available site concentration of 100%. The rate expressions are then as follows:

$d[\text{Benzaldehyde}]/dt = -k_{1,obs}[\text{Benzaldehyde}]$

$d[\text{benzyl alcohol}]/dt = +k_{1,obs}[\text{Benzaldehyde}] - k_{2,obs}[\text{benzyl alcohol}]$

$d[\text{toluene}]/dt = +k_{2,obs}[\text{benzyl alcohol}]$

Fitting with these equations in Athena Visual Studio using Non-Linear Least Squares returned the reported rate constants and their respective 95% confidence intervals.

The direct results of the fits are presented in the table below, with the turnover frequencies as molecules per site per second. To convert to turnover frequencies we need to convert the rate constants from k1 into molecules per second and then divide by the number of sites. The liquid volume of the reactor was 10 mL, allowing us to convert to mol/s. Using the method of estimation from our previous study,[2016Savara et al.] we estimate 5.07E18 surface metal atoms in the reactor, which allowed us to convert to estimated lower limits for turnover frequencies. For turnover frequencies of this magnitude, if we assume that the product of the pre-exponential of reaction and surface coverage are on the order of 1E10 to 1E16, that suggests that the activation energies for both the first and second hydrogenation (over both catalysts) fall in the range of 70 kJ/mol - 120 kJ/mol.

Rate constant or rate	Pd	AuPd
k1 ($mol^1 L^{-1} s^{-1}$)	1.209546E-04 +/- 4.136E-05	4.128892E-04 +/- 1.913E-04
k2 ($mol^1 L^{-1} s^{-1}$)	2.120641E-04 +/- 1.357E-04	1.122587E-04 +/- 4.782E-05
r1 (TOF, s^{-1})	1.44E-01 +/- 4.91E-02	4.90E-01 +/- 2.27E-01
r2 (TOF, s^{-1})	2.52E-01 +/- 1.61E-01	1.33E-01 +/- 5.68E-02