Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Investigating deposition sequence during synthesis of SAM-modified Pd/Al_2O_3 catalysts

Supporting Information

Zachary Blanchette[a], Jing Zhang[a], Sadegh Yazdi[b,c], Michael B. Griffin[d], Daniel K. Schwartz[a], J. Will Medlin[a,*]

[a]*Department of Chemical and Biological Engineering, University of Colorado, Boulder, CO 80303, USA.*

[b]*Renewable & Sustainable Energy Institute, University of Colorado, Boulder, Colorado 80309, USA.*

[c]*Materials Science & Engineering Program, University of Colorado, Boulder, Colorado 80309, USA.*

[d]*Catalytic Carbon Transformation and Scale-up Center, National Renewable Energy Lab, Golden, Colorado 80401, USA.*

Catalyst Characterization

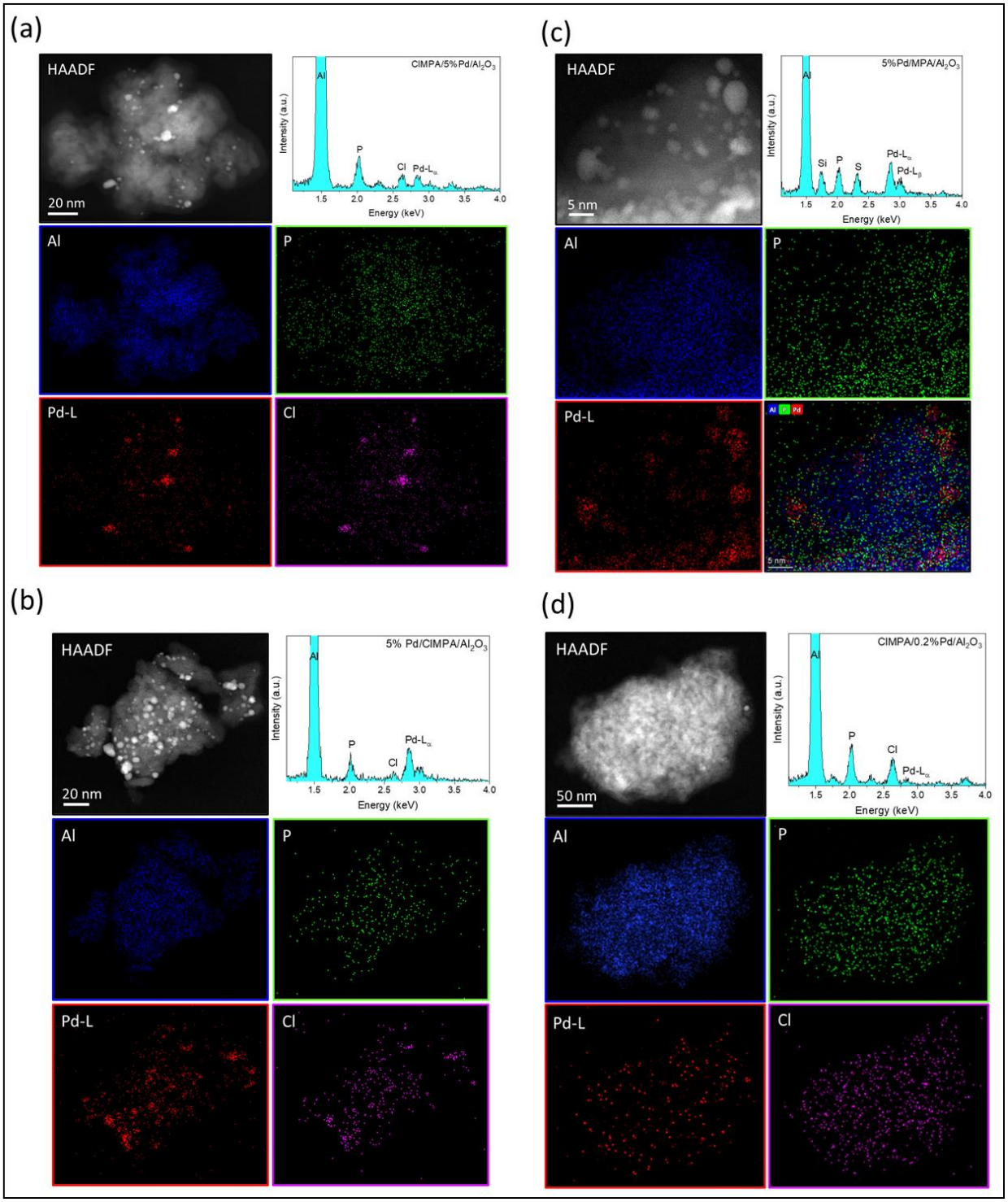

Fig. S1 STEM-EDS elemental mapping of catalysts synthesized with different deposition orders, PA modifier, and Pd weight loading. (a) ClMPA/5%Pd/Al_2O_3, (b) 5%Pd/ClMPA/Al_2O_3, (c) 5%Pd/MPA/Al_2O_3, (d) ClMPA/0.2%Pd/Al_2O_3. No attempt was made to deconvolute EDS intensity peaks to quantify the concentration of elements. Therefore, care should be taken when attempting to draw conclusions regarding the precise location of each element since, (for example) Pd K peaks and Cl L peaks are located at similar energies.

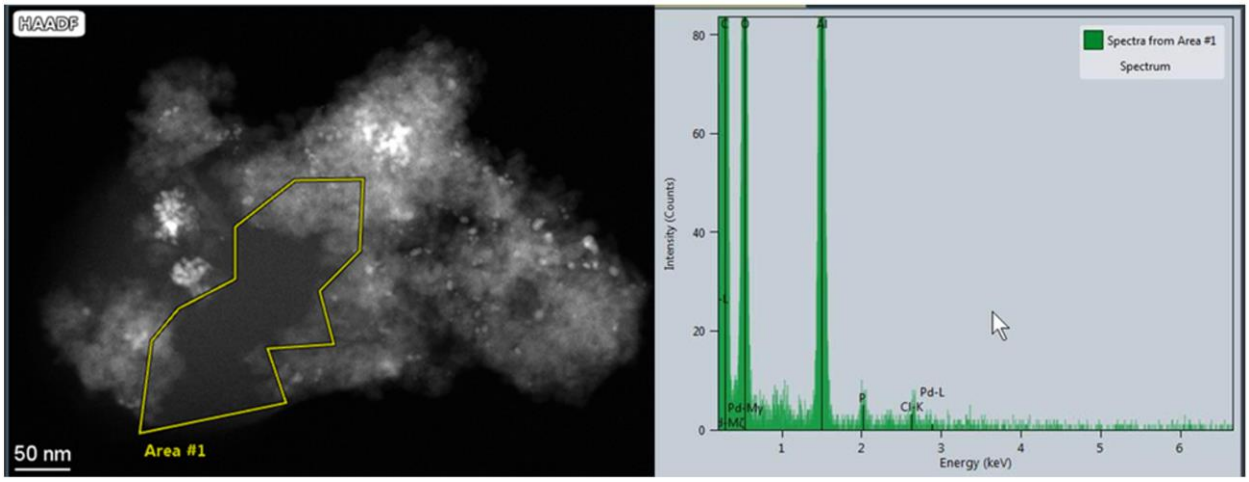

Fig. S2 STEM-EDS elemental mapping of an area on ClMPA/5%Pd/Al_2O_3 containing Cl but no Pd.

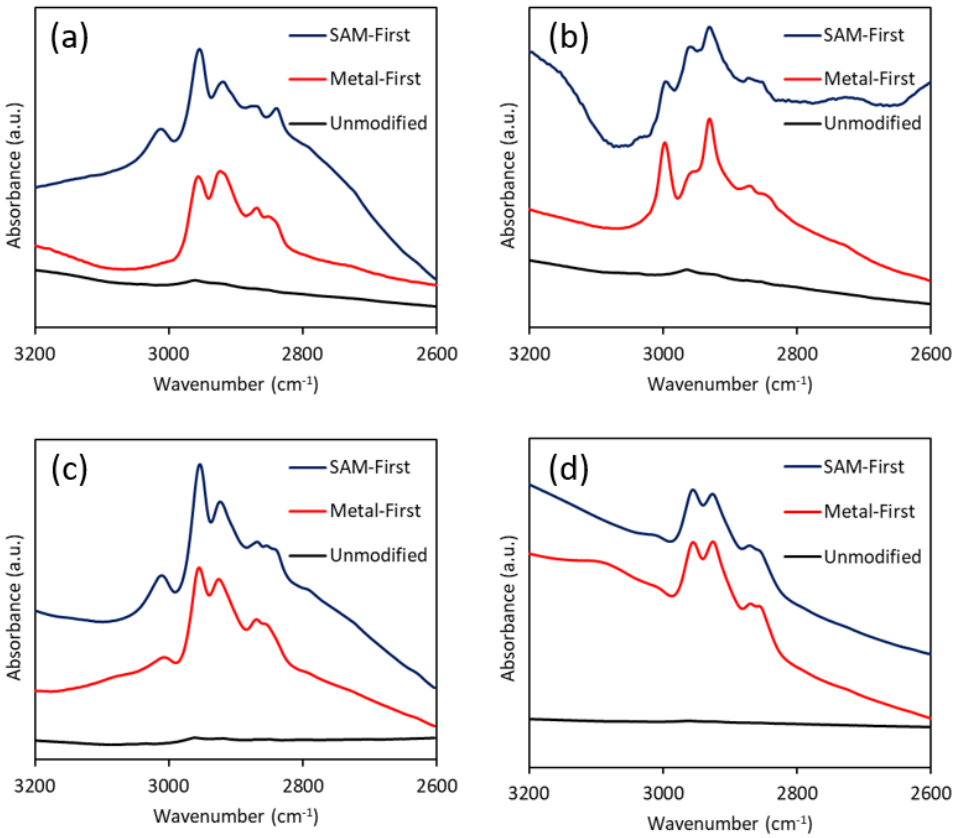

Fig. S3 DRIFTS spectra for Pd/Al_2O_3 catalysts, (a) 5%Pd/ Al_2O_3 modified with ClMPA, (b) 5%Pd/ Al_2O_3 modified with MPA, (c) 1%Pd/ Al_2O_3 modified with ClMPA, (d) 0.2%Pd/ Al_2O_3 modified with ClMPA

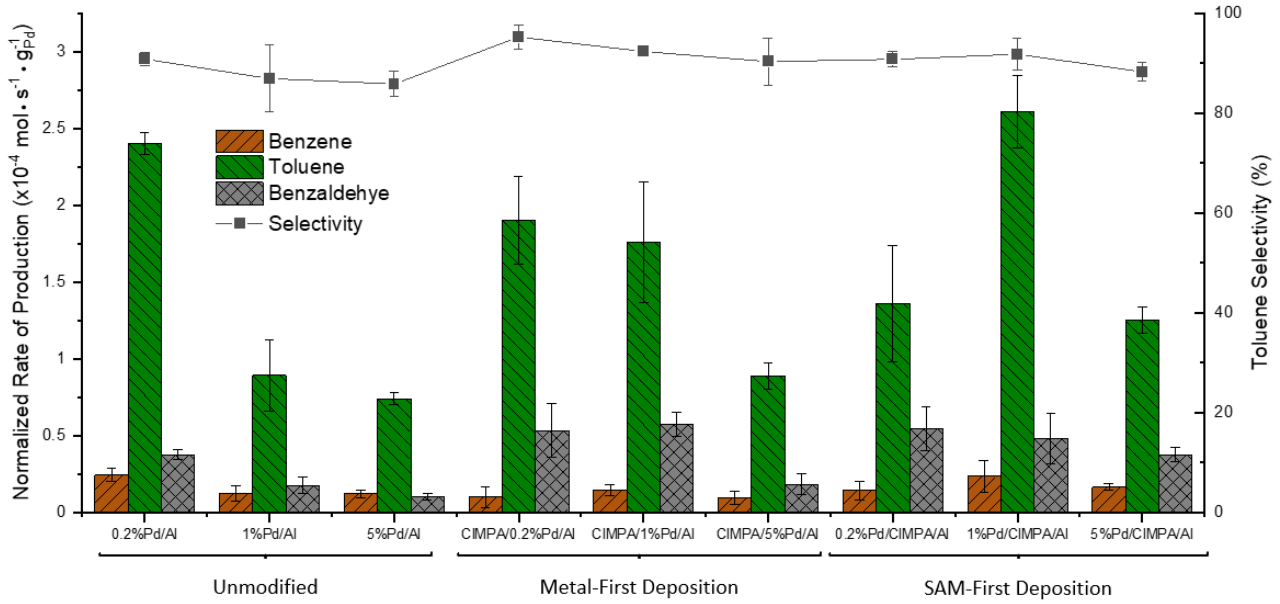

Fig. S4 Benzyl alcohol HDO performance over Pd/Al_2O_3 catalysts modified with ClMPA through both Metal-First (ClMPA/Pd/Al) and SAM-First (Pd/ClMPA/Al) deposition of varying Pd loading (5%, 1%, 0.2%).

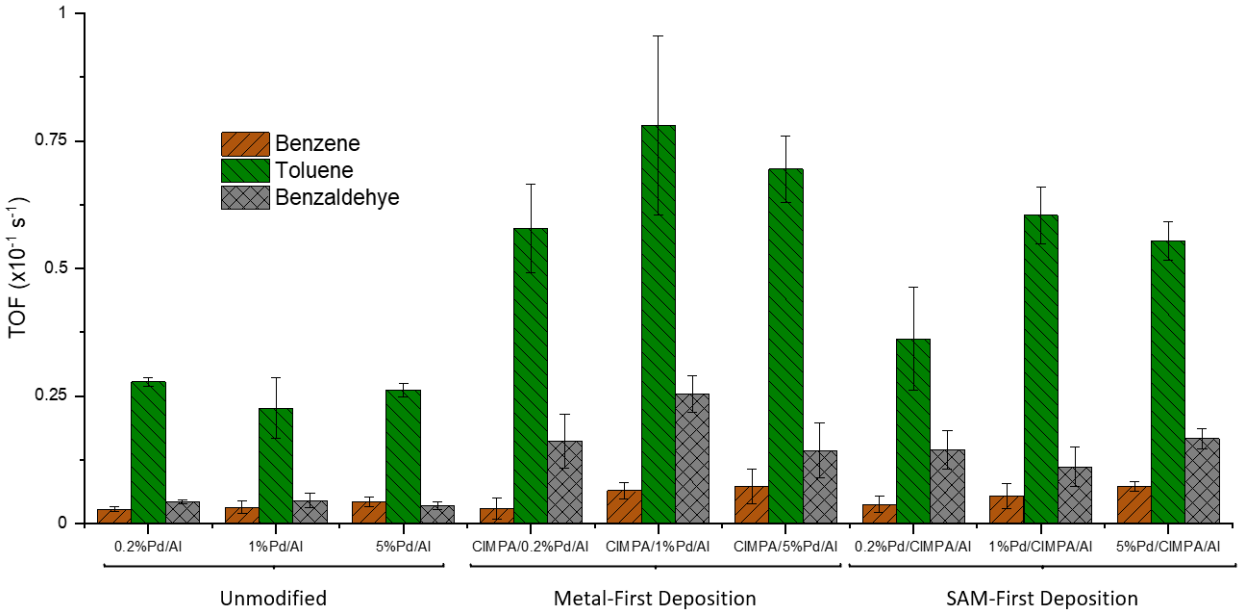

Fig. S5 Turnover Frequencies for Pd/Al_2O_3 catalysts modified with ClMPA through both Metal-First (ClMPA/Pd/Al) and SAM-First (Pd/ClMPA/Al) deposition of varying Pd loading (5%, 1%, 0.2%).

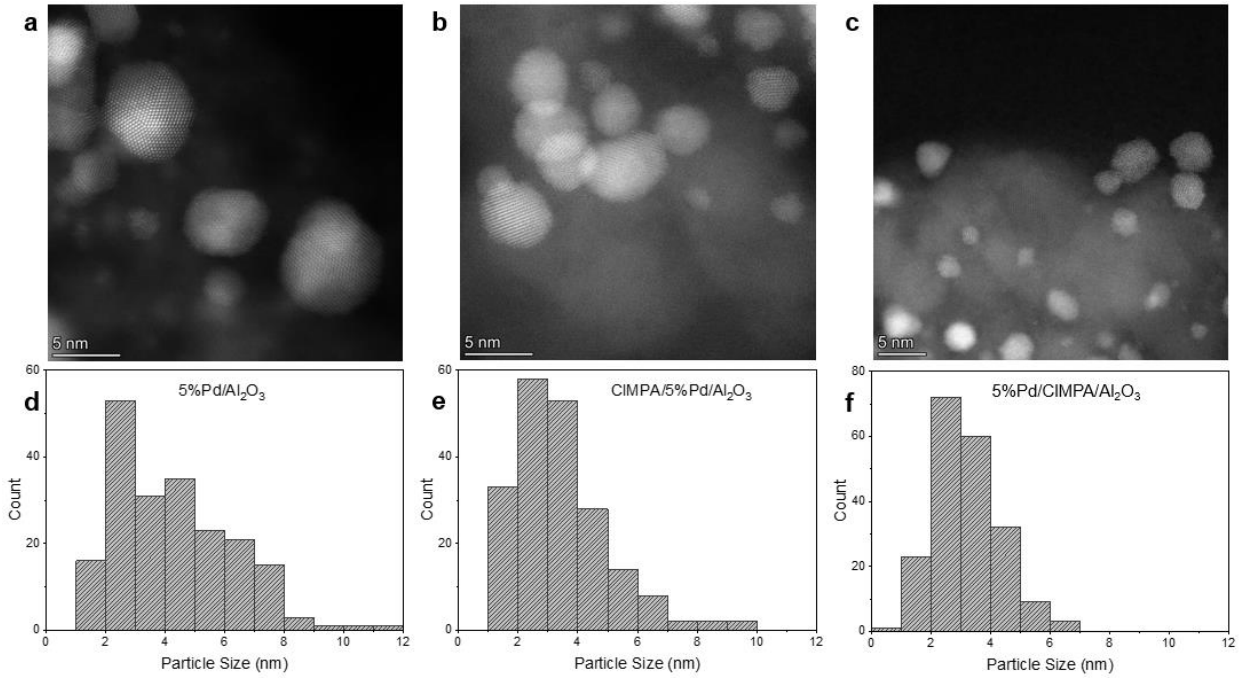

Fig. S.6 Representative HAADF-STEM images and particle size distribution for (a)&(d) 5%Pd/Al_2O_3, (b)&(e) ClMPA/5%Pd/Al_2O_3, (c)&(f) 5%Pd/ClMPA/Al_2O_3

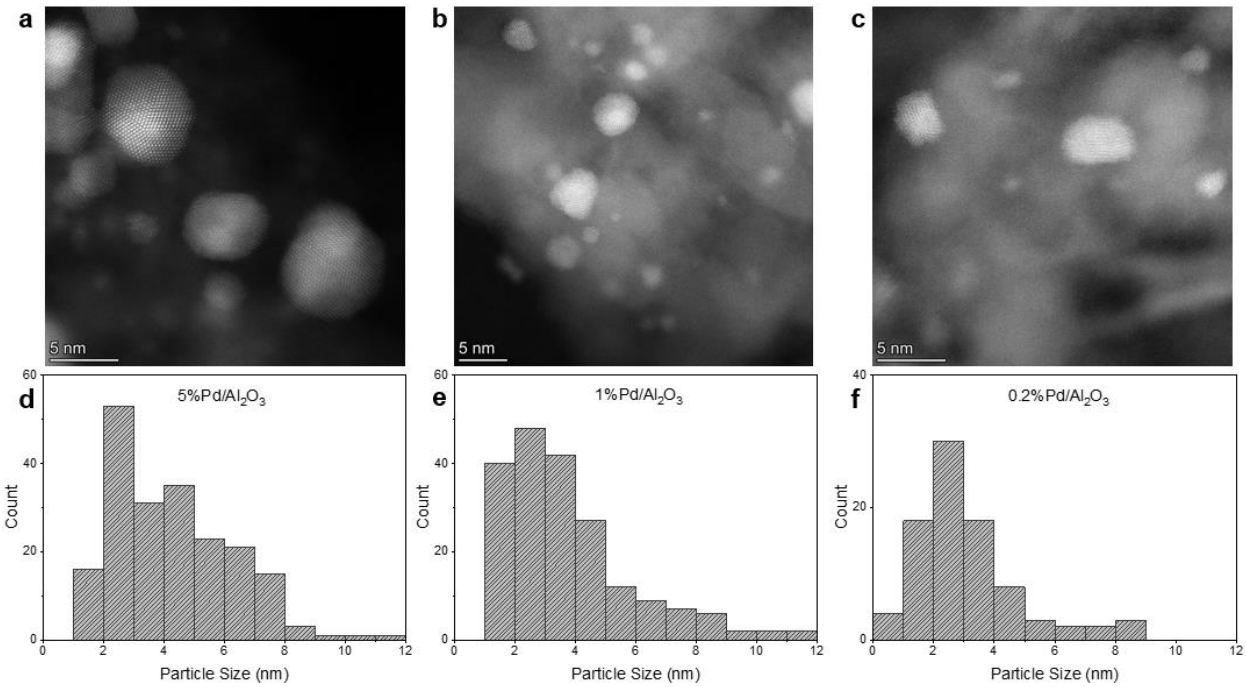

Fig. S7 Representative HAADF-STEM images and particle size distribution for (a)&(d) 5%Pd/Al_2O_3, (b)&(e) 1%Pd/Al_2O_3, (c)&(f) 0.2%Pd /Al_2O_3

Supplementary Discussion

Effect of Pd loading

Catalysts were synthesized and tested with Pd weight loadings of 1 wt% and 0.2 wt%. These lower weight loadings were expected to produce smaller particles with higher dispersions, meaning that lowering the weight loading should generally increase metal-normalized activities. Pd/Al_2O_3 catalysts for each weight loading were synthesized and tested using both metal-first and SAM-first deposition of ClMPA as a model PA.

First looking at the unmodified catalysts, the mass activity for toluene (Fig. S3) increased as the Pd loading was decreased. This is reflected in the properties determined using TEM and CO chemisorption (Table 1) in which the average particle size decreased from 4.3 nm to 3.1 nm and dispersion increased from 30% to 92% as the loading changes from 5%Pd to 0.2%Pd. Interestingly, for these unmodified catalysts, TOF (Fig. S4) was nearly identical for all three weight loadings and not a clear function of dispersion in this particle size range. In other words, TOF analysis is indicative of a largely structure-insensitive reaction for this series of Pd catalysts.

The metal-first deposition catalysts showed a similar trend to the unmodified case where lower weight loading provided a higher rate of production per mass of Pd, particularly when decreasing from 5 wt% to 1 wt%, with little improvement between 1 wt% and 0.2 wt%. This correlated well with trends seen in particle size and dispersion where these modified catalysts did not seem to change as much with weight loading as the unmodified case. TOF analysis for metal-first deposition catalysts again appeared to be similar across all weight loadings, consistent with low structure sensitivity.

For the SAM-first deposition catalysts, both the normalized rate of toluene production and TOF benefited from decreasing the Pd loading from 5 wt% to 1 wt%, in line with smaller particles and increased dispersion. Interestingly, both the rate and TOF decreased when decreasing the Pd loading to 0.2 wt%. It is interesting that 0.2 wt% also did not follow the trend in apparent dispersions as all other catalysts tested. The $0.2\%Pd/ClMPA/Al_2O_3$ has a dispersion of 40%, much closer to the metal-first deposition catalyst (36%) than the uncoated catalyst (92%).

For all weight loadings tested the trend in TOF (Fig. S4) was that metal-first deposition was the most active on a per site basis, followed by SAM-first deposition, and finally the unmodified catalyst. Again, this is likely because PAs provide Brønsted acid sites to promote HDO and metal-first deposition catalysts have a higher amount of these ligands compared to SAM-first deposition.

Supplementary Methods: STEM

TEM images were imported into ImageJ. The perimeter of individual particles was traced using the freehand tool and the area of each was determined. The area was then used to calculate the corresponding diameter (i.e., particle size) assuming that the particle was circular. Average particle size was determined using the average size of 200 particles. Error analysis was done using the

standard deviation of average particle size in each individual image (generally 10 – 20 images in total).