Supporting information

Relationship between Atomic Scale Structure and Reactivity of Pt catalysts: Hydrodeoxygenation of m-cresol over Isolated Pt Cations and Clusters

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Table S1: Comparison of reactivity of 0.1% Pt/SiO_2 and 0.1% Pt/TiO_2 for HDO of m-cresol.

Catalyst	0.1% Pt/SiO_2	0.1% Pt/TiO_2	0.1% Pt/SiO_2	0.1% Pt/TiO_2
W/F (h)	0.156	0.156	0.727	0.695
Conversion (%)	2.85	15.73	18.53	72.31
Product yields (%)				
Toluene	1.42	14.09	16.07	67.45
Dimethylbiphenyl		0.30		3.27
Methylcyclohexanone and methylcyclohexanol	0.30	0.22	0.61	0.00
Methycyclohexane	0.14	0.20	0.44	0.50
Phenol	0.11	0.14	0.18	0.00
p/o-Cresol	0.85	0.69	0.52	0.21
Xylenol	0.03	0.03	0.71	0.27

Reaction conditions: T=350°C; P=1atm H_2; TOS=20min.

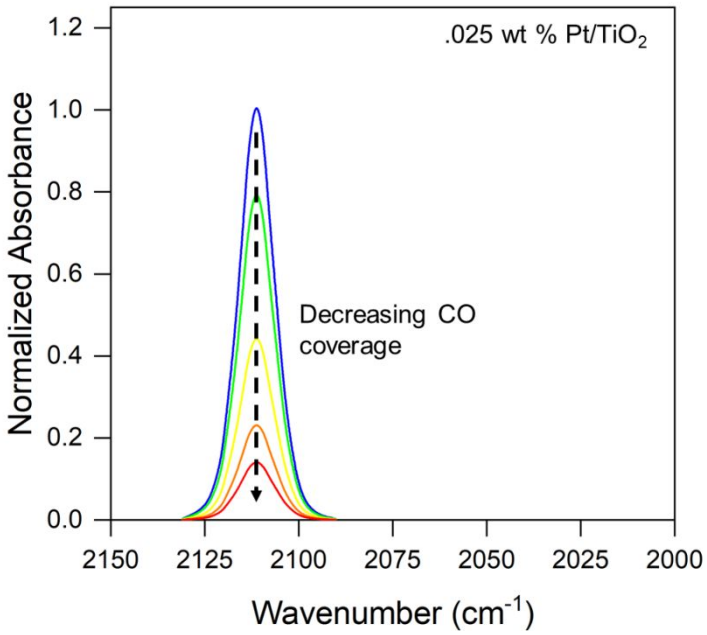

Figure S1: CO IR spectroscopy of All Pt_{iso} (0.025% Pt/TiO_2) during CO desorption. Lack of change in vibrational frequency or peak symmetry implied Pt sites sit at uniform, non-interaction sites on the oxide support.

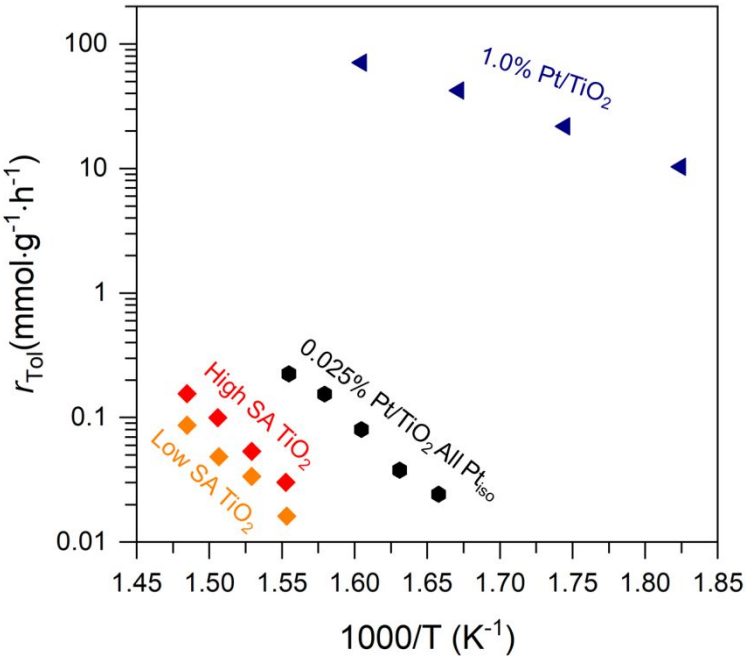

Figure S2: Comparison of activity for Pt/TiO_2 catalysts and pure TiO_2 supports. No significant differences in activity are observed for TiO_2 supports. Small differences in activity observed are likely due to differences in surface area of the two supports. Comparison of pure supports with 0.025% Pt/TiO_2 demonstrates Pt_{iso} does have catalytic activity for m-cresol HDO, although the reactivity is much lower than Pt clusters. Reaction conditions: T=275-350 °C for 1.0% Pt/TiO_2; T=330-370 °C for the catalyst containing only Pt_{iso}; T=375-400 °C for pure TiO_2. P=1atm H_2; TOS=20 min. Conversion was maintained below 15% by adjusting W/F.

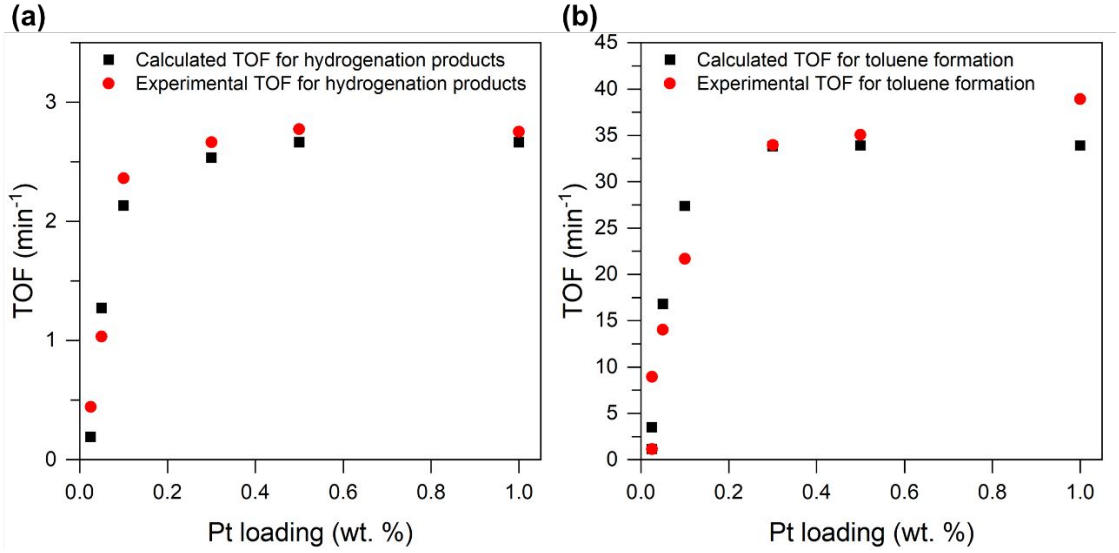

Figure S3: Correlating site fractions to reactivity data. Experimental and calculated TOF at (a) 220 °C and (b) 350 °C. Calculated values obtained from a linear combination of TOF values for Pt_{iso} and Pt clusters, weighted by the relative site fractions of each. Site fractions were obtained from fitting one consistent set of extinction coefficients for Pt_{iso} and Pt clusters to measured CO infrared data.

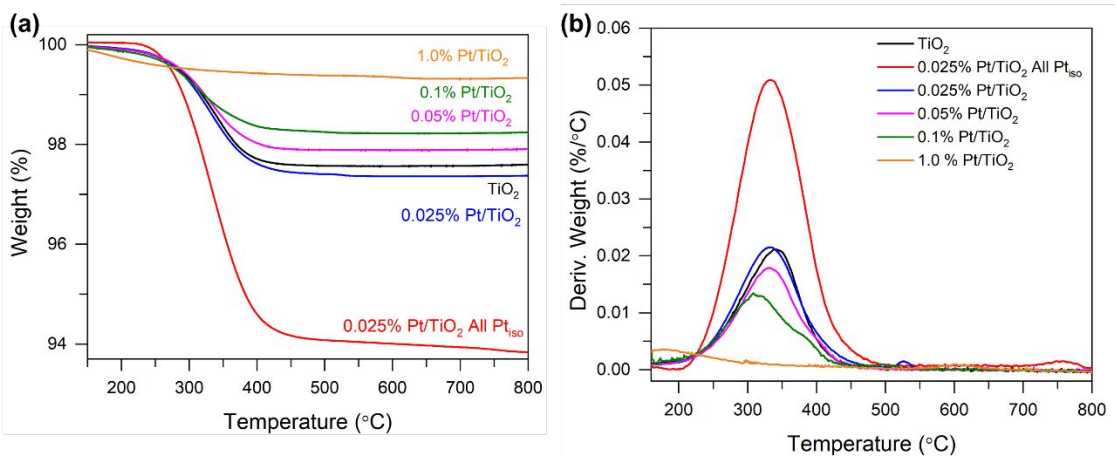

Figure S4: Thermogravimetric analysis of Pt/TiO_2 catalysts. (a) Mass loss and (b) Derivative of mass loss against temperature for Pt/TiO_2 catalysts at different Pt weight loadings. All samples were deposited on lower surface area TiO_2 support besides the sample labeled 0.025% Pt/TiO_2 All Pt_{iso}. The higher coke formation on this sample was the result of the higher surface area support. Reaction conditions for the spent catalysts: W=100mg; F=0.1ml/h; H_2=58ml/min; TOS=3.5h.

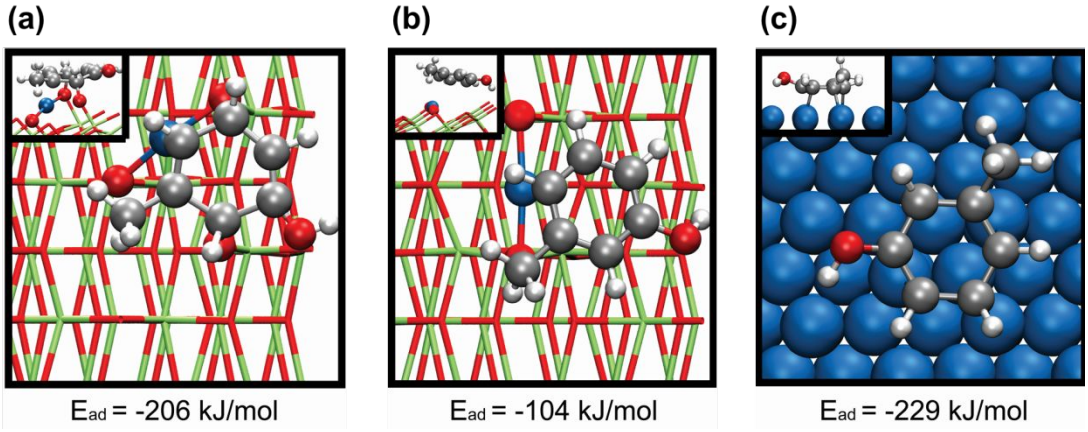

Figure S5: Adsorption of m-cresol on Pt structures. DFT optimized adsorbed structures with calculated heats of adsorption for (a,b) cresol adsorption over Pt_{iso} and (c) Pt (111). The balls refer to the atoms of H (white), O (red), C (grey), Pt (blue) and Ti (green), respectively.