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

Higher Loadings of Pt Single-Atom and Clusters over Reducible Metal Oxides: Application to C-O Bond Activation

Yunzhu Wang,[1] Seungyeon Lee,[1,2] Jiahua Zhou,[1,2] Jiayi Fu,[1,2] Alexandre Foucher,[3] Eric Stach,[3] Lu Ma,[4] Nebojsa Marinkovic,[4] Steven Ehrlich,[4] Weiqing Zheng,[1]* Dionisios G. Vlachos[1,2]*

1. Catalysis Center for Energy Innovation, University of Delaware, Newark, DE 19716, USA
2. Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA
3. Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, PA 19104, USA
4. National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973, USA

*Corresponding authors: Weiqing Zheng weiqing@udel.edu; Dionisios G. Vlachos vlachos@udel.edu

Table S1. XRF results of Pt/TiO_2 catalysts.

Sample	Pt (wt %)	TiO_2 (wt %)	I (wt %)
$1Pt_{NP}$	1.24	98.76	-
$1Pt_1$	1.18	97.86	0.95
$1Pt_1$-H_2	1.13	98.50	0.36
$1Pt_1$-Ar	1.18	98.18	0.64

Table S2. ICP-OES results of Pt/TiO_2 catalysts.

Sample	Theoretical Pt Loading (%)	Actual Pt Loading (%)
$1Pt_{NP}$	1	0.95
$1Pt_1$	1	0.89
$2Pt_{NP}$	2	1.53
$2Pt_1$	2	1.55

Table S3. The Pt/Ti atomic ratio, Ti^{3+} and Ti^{4+} percentage in 1 wt% and 2 wt% samples, obtained from XPS data.

Samples	Pt/Ti (atomic ratio)	Ti (III)	Ti (IV)
$1Pt_{NP}$	0.010588	3.72%	96.27%
$1Pt_1$	0.020079	2.53%	97.47%
$2Pt_{NP}$	0.016158	4.15%	95.85%
$2Pt_1$	0.056355	2.07%	97.93%

Table S4. Calculated CO binding energy on Pt_1-$(I)_m$-CO (m=1-4). A positive convention is used for favorable binding. ($E_{bind,CO} = E_{system} + E_{CO(gas)} - E_{system+CO}$)

Number of I● introduced on Pt_1-CO	$E_{bind,CO}$ (per CO) (eV)
1	2.19
2	3.06
3	2.88
4	1.80

Table S5. Calculated CO vibrational frequencies and Bader charge value of Pt for the configurations shown in Figure 3.

n	Pt_n		Pt_n-$(I)_2$	
	ν (cm^{-1})	bader Pt	ν (cm^{-1})	bader Pt
1	2084	0.12	2110	0.34
2	2055	-0.13	2079	0.11
3	2039	0.06	2085	0.14
4	2025	0.03	2099	0.40

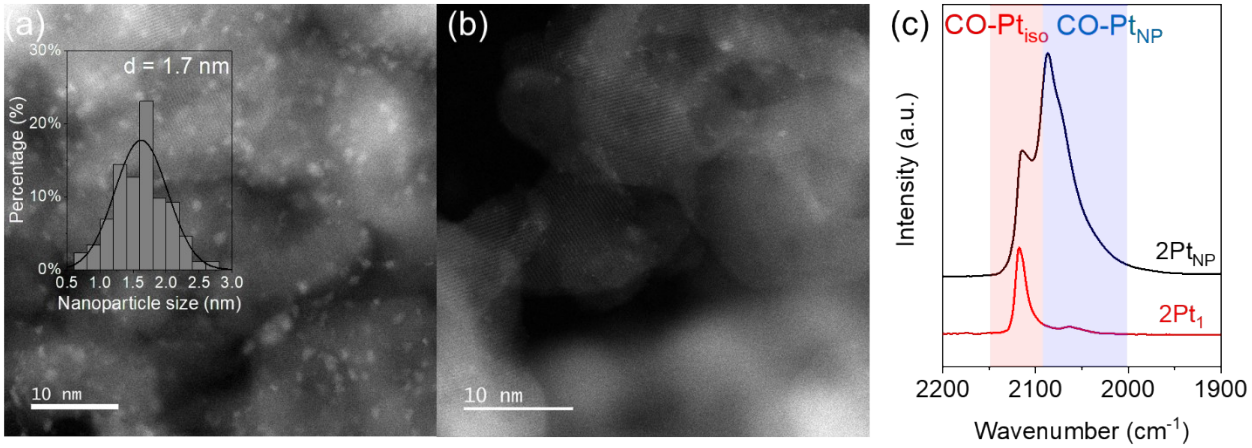

Figure S1. AC-HAADF-STEM images of (a) $2Pt_{NP}$, (b) $2Pt_1$, and (c) FTIR spectra of CO adsorption of $2Pt_{NP}$ and $2Pt_1$.

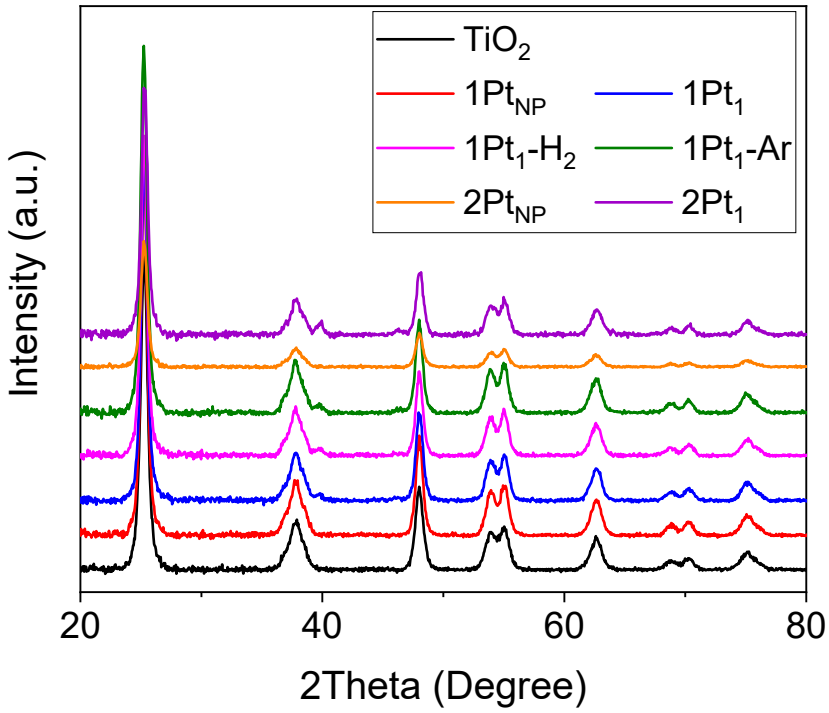

Figure S2. XRD patterns of Pt/TiO_2 catalysts before and after redispersion.

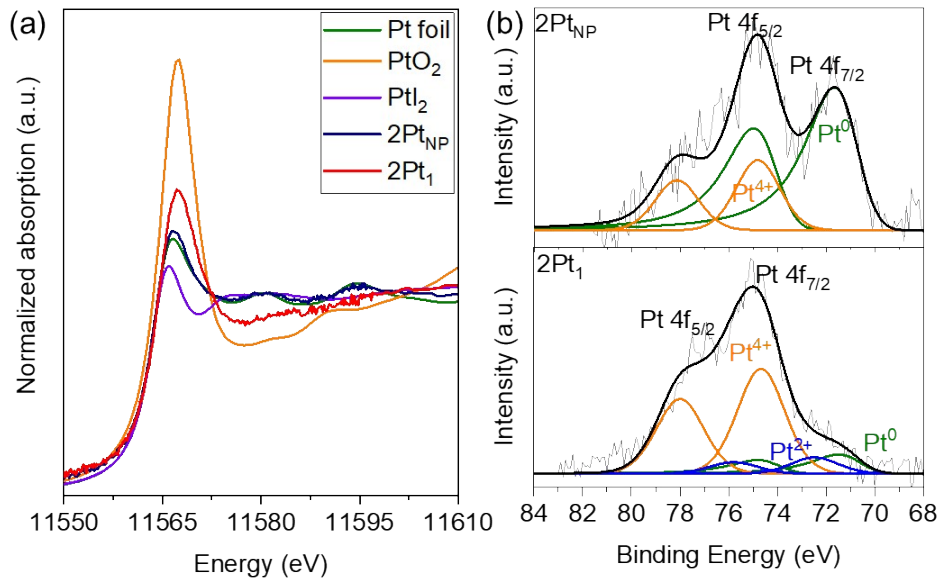

Figure S3. The Pt L_{III}-edge XAS and Pt 4*f* XPS data of the 2 wt% Pt/TiO_2 catalysts. (a) Normalized XANES spectra and (b) the Pt 4*f* XPS spectra.

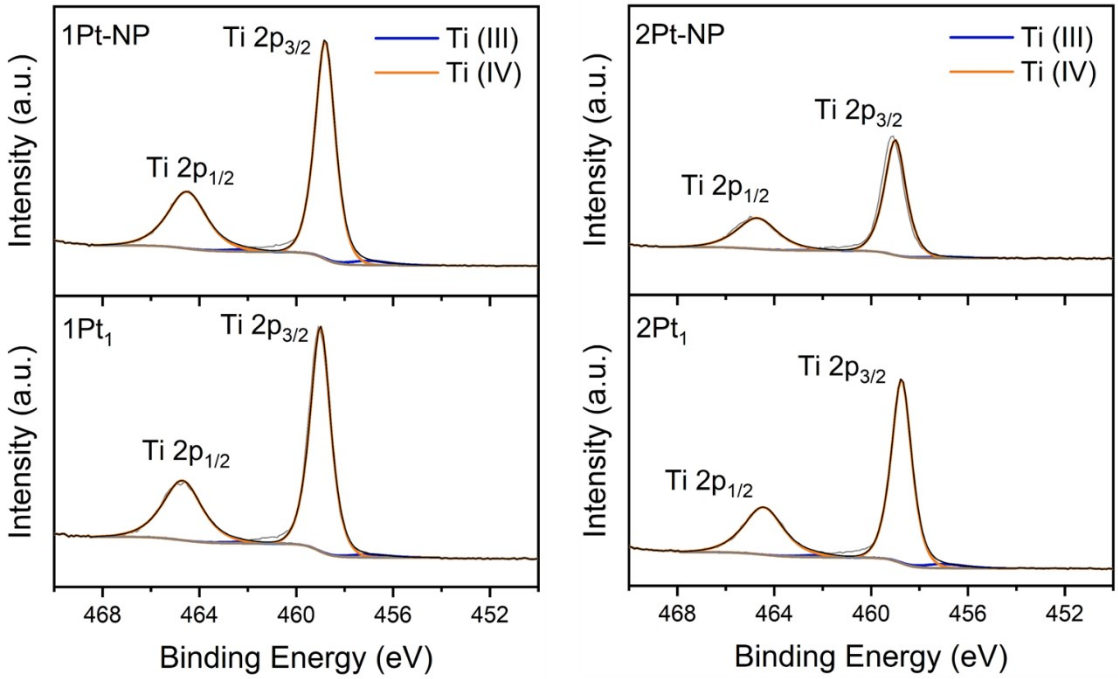

Figure S4. The Ti *2p* XPS spectra of 1 wt% and 2 wt% Pt/TiO_2 catalysts.

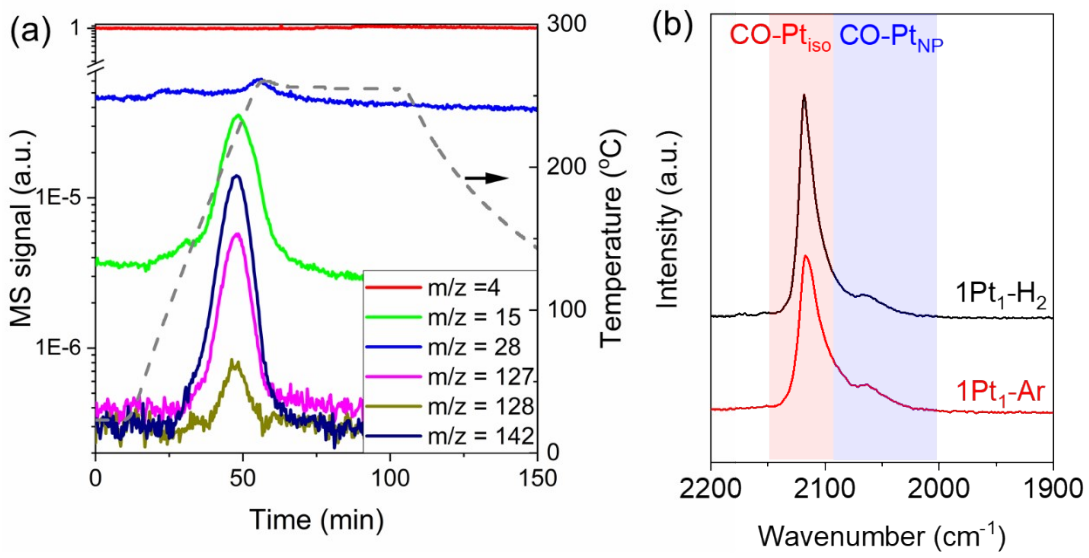

Figure S5. Catalyst thermal stability. (a) MS spectra of $1Pt_1$ sample upon thermal treatment under inert gas at 250 °C. Reaction conditions: 100 mg catalyst, 50 ml/min He. (b) FTIR spectra of CO adsorption of $1Pt_1$-H_2 and $1Pt_1$-Ar.

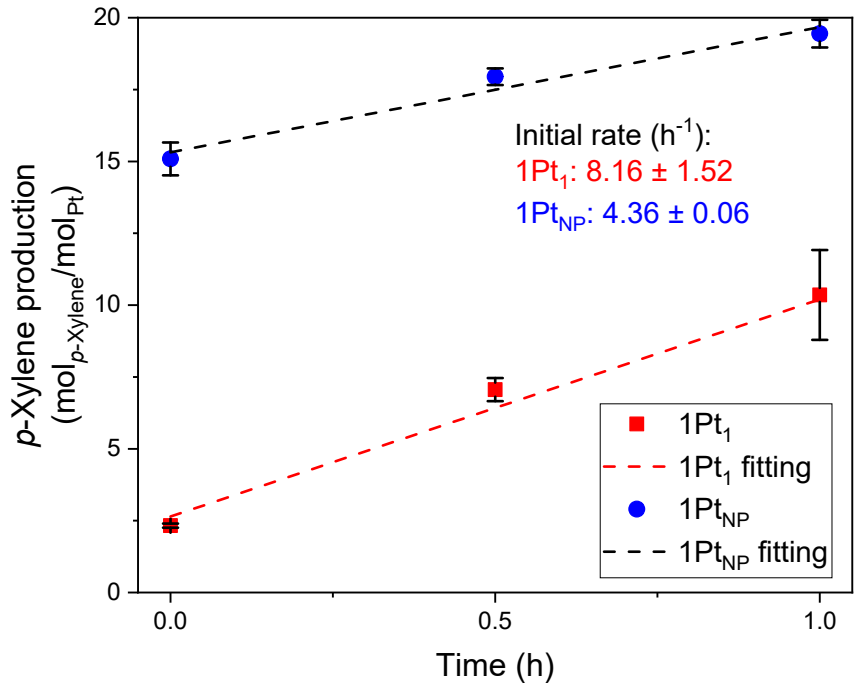

Figure S6. Measurement of the initial activities of $1Pt_1$ and $1Pt_{NP}$. The *p*-Xylene production was calculated by mole of *p*-Xylene produced over mol of surface Pt. Reaction conditions: 0.088 M 4MBA, 20 mL iso-propanol (IPA), 100 mg catalyst, 100 psi H_2 and 160 psi N_2 at room temperature, 180 °C.

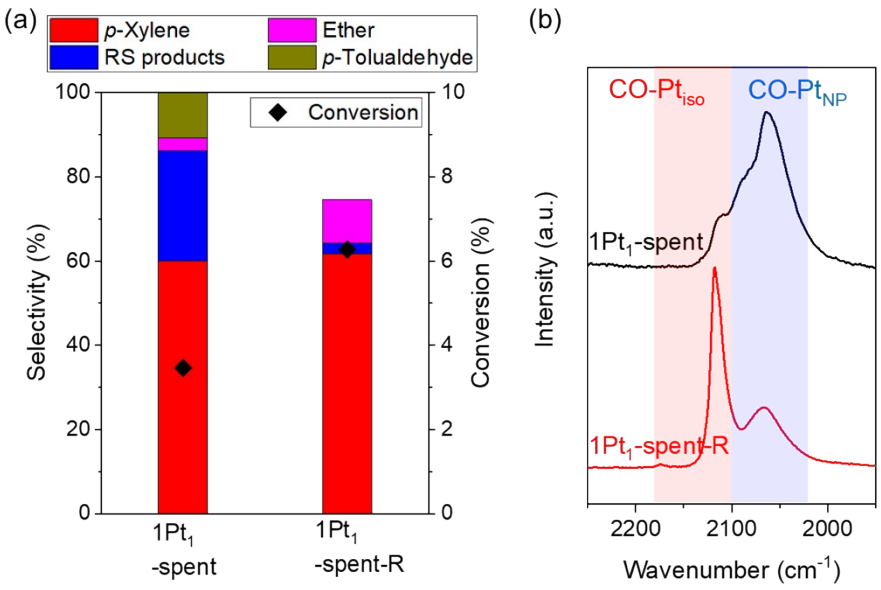

Figure S7. (a) Catalytic performance of spent and regenerated $1Pt_1$ catalysts for HDO of 4MBA. Reaction conditions: 0.088 M 4MBA, 20 ml iso-propanol (IPA), 100 mg catalyst, 100 psi H_2 and 160 psi N_2 at room temperature, 180 °C, 2 h. (b) FTIR spectra of CO adsorption of $1Pt_1$-spent and $1Pt_1$-spent-R.