

Supporting information for:

Insights into the Mechanism of Tandem Alkene Hydroformylation over a Nanostructured Catalyst with Multiple Interfaces

Ji Su,^{1, #} Chenlu Xie,^{2, #} Chen Chen,^{2, §, #} Yi Yu,² Griffin Kennedy,^{1, 2} Gabor A. Somorjai,^{*, 1, 2} Peidong Yang^{*, 1, 2, 3}

¹Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

²Department of Chemistry, University of California, Berkeley, California 94720, United States

³Kavli Energy NanoScience Institute, Berkeley, California 94720, United States

[§]Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China

[#]Contributed equally to this work.

Correspondence to:

* somorjai@berkeley.edu

* p_yang@berkeley.edu

S1 Experiment details for the synthesis of single interface catalysts.

S1.1 Synthesis of Pt@mSiO₂ single interface catalyst. The Pt@mSiO₂ core shell nanoparticles were prepared using the similar method as CeO₂-Pt@mSiO₂. The solution of pre-synthesized Pt nanoparticles (3.5 mg in 25 mL deionized water) was mixed with a solution of CTAB, which was prepared by dissolving 125 mg CTAB in 25 ml ethanol. An ammonia solution (0.1 mL) was added to the above solution with stirring. Then a controlled amount of 1 vol % TEOS diluted with ethanol was added under continuous magnetic stirring at room temperature. After 6 hours, the as-synthesized Pt@SiO₂ nanoparticles were obtained by centrifugation (6000 rpm, 5 minutes). The product was calcined at 350 °C for 1 hour in static air to remove ligands and generate Pt@mSiO₂ particles with clean interfaces.

S1.2 Synthesis of Pt nanoparticles. For the synthesis of Pt nanoparticles¹, 44.4 mg (NH₄)₂PtCl₆ and 36.8 mg TTAB and 21.8 mg PVP (M_w = 29000) were mixed with 20 mL of ethylene glycol in a 50 mL round bottom flask at room temperature. The mixture was heated at 80 °C for 20 min under argon protection and then quickly heated to 180 °C. The solution was kept at 180 °C for 1 h before it was cooled to room temperature, and the product was centrifuged at 12000 rpm for 10 min. The supernatant solution was separated and centrifuged again at 12000 rpm for 10 min, twice. The Pt nanoparticle colloids were collected and re-dispersed in 5 mL of deionized water by sonication for further use.

S2 Catalytic testing

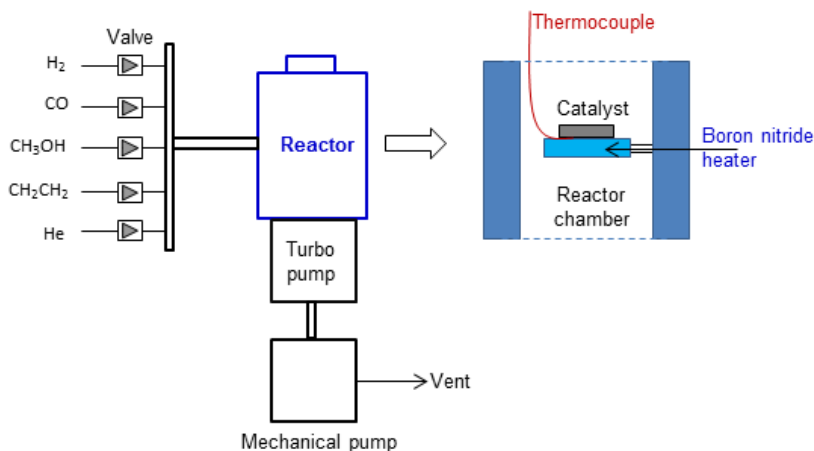


Figure S1. The schematic of the reactor.

The catalytic testing was performed using a batch-mode reactor (as illustrated in Figure S1). The batch reactor consists of a stainless steel chamber equipped with a boron nitride heater, a turbo pump, a mechanical pump and a circulator pump. In the gas feeding system, H₂, CO, ethylene and He lines as well as a methanol container were connected to the reactor, and were delivered via a series of independent needle valves. The molar ratio of each reactant gas was precisely controlled via their partial pressure. Pressure was monitored by a digital pressure gauge, and temperature was monitored by the thermocouple underneath the catalyst. The gases exiting the reactor were analyzed using a Hewlett Packard HP 5890 Series II chromatograph equipped with both FID and TCD detectors.

The turnover frequency (TOF) values are derived by the number of Pt active sites and the number of propanal molecules produced as monitored by GC. The TOF was calculated based on the experiment data with a total conversion of reactants below 20%. Number of active sites was calculated through two different methods. The first method was based on the geometric dispersion of Pt nanoparticles, by taking particle size from TEM and weight % Pt loading from ICP-AES, assuming the same atomic density on the Pt nanoparticle surface as Pt (111) and all the surface Pt atoms are accessible. The second method was based on actual measurement. Ethylene hydrogenation reaction, which was known to be structure-insensitive^{2,3,4} was performed to estimate the accessible number of Pt sites of the catalysts. The number of active sites derived was found to be 70% of the active sites from geometric determination, likely due to silica over coating. Therefore, the number of active sites estimated in this study was based on the second method.

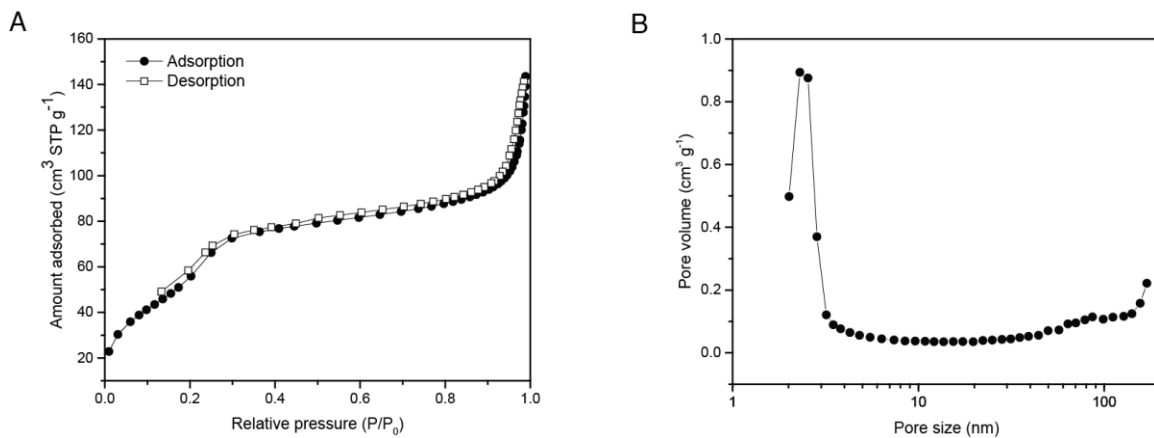


Figure S2. Porosity characterization of CeO₂-Pt@mSiO₂ nanoparticles calcined at 350 °C. (A) Nitrogen adsorption-desorption isotherms. (B) Pore size distribution calculated from the adsorption branch of the isotherms.

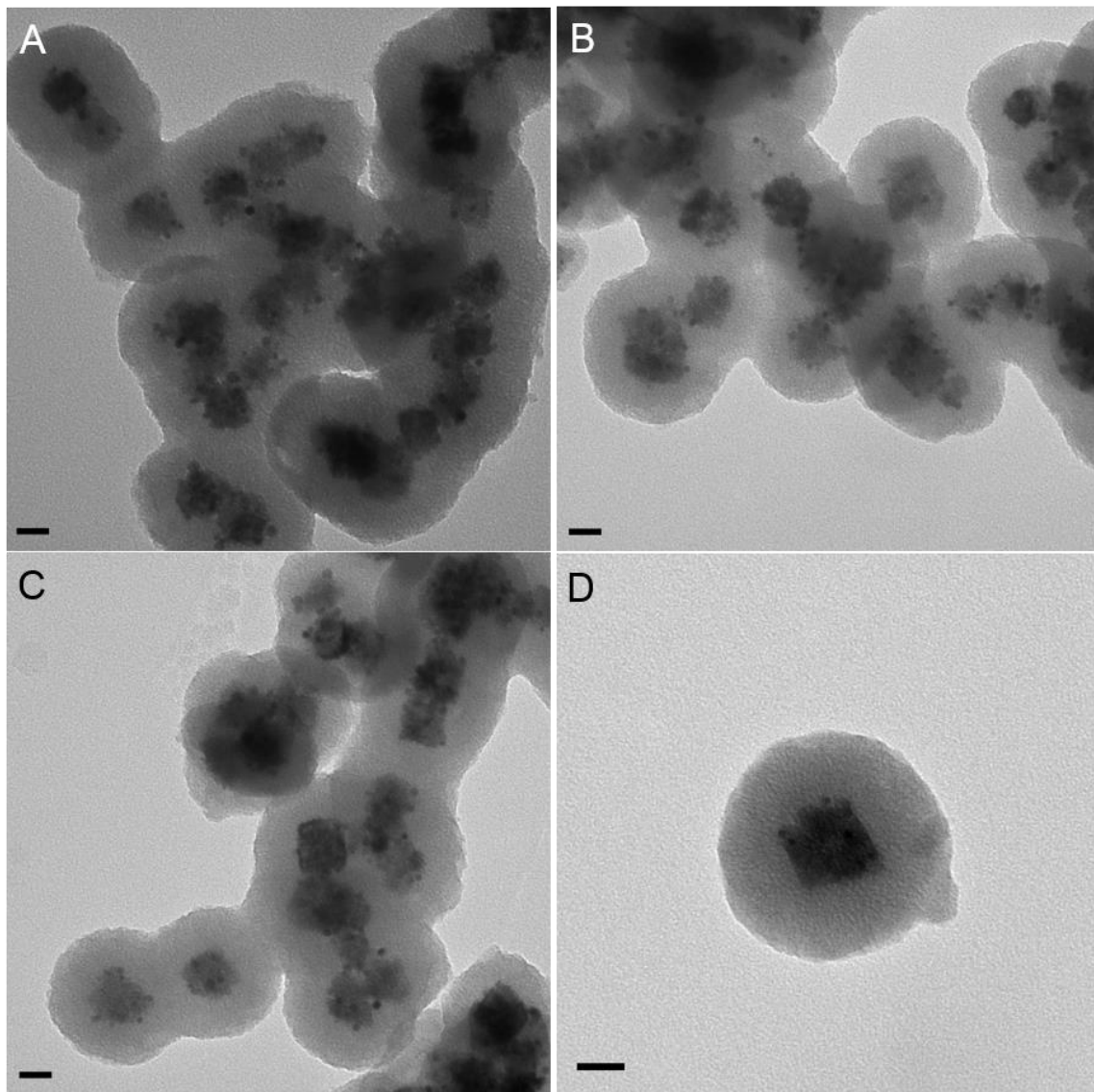


Figure S3. Stability of tandem catalyst $\text{CeO}_2\text{-Pt@mSiO}_2$. (A–D) TEM images of $\text{CeO}_2\text{-Pt@mSiO}_2$ particles after calcination at $350\text{ }^\circ\text{C}$ and hydroformylation reactions. Scale bar: 20 nm.

Table S1. Pt loading amount for the tandem catalyst $\text{CeO}_2\text{-Pt@mSiO}_2$ and single interface catalysts according to ICP-AES.

Catalyst	Pt loading amount
$\text{CeO}_2\text{-Pt@mSiO}_2$	5.14%
$\text{CeO}_2\text{-Pt}$	5.38%
Pt@mSiO_2	5.78%

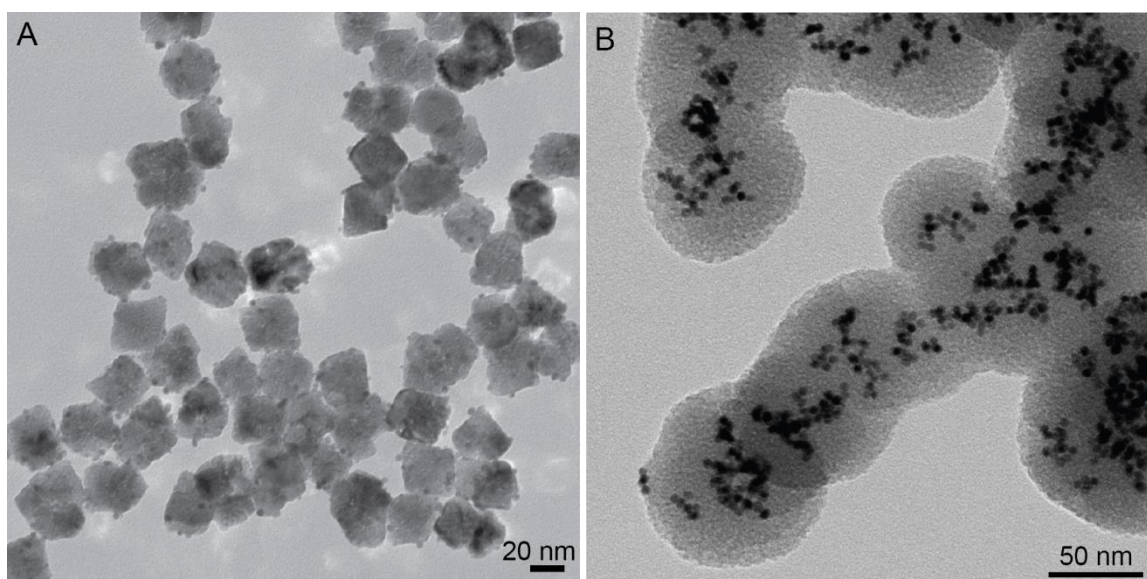


Figure S4. TEM images of single interface catalysts. (A) $\text{CeO}_2\text{-Pt}$ catalyst. (B) Pt@mSiO_2 catalyst. All the catalysts were calcined at $350\text{ }^\circ\text{C}$ for 1 hour in static air to remove ligands.

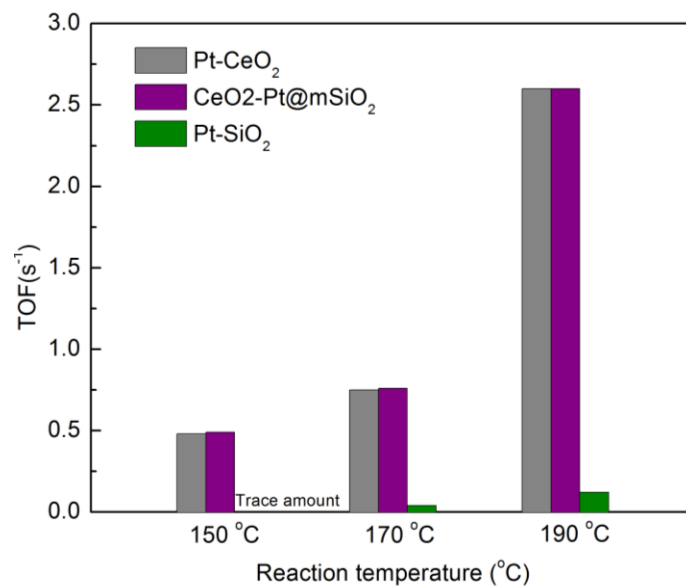


Figure S5. Methanol decomposition over 3D catalyst CeO₂-Pt@mSiO₂ and single interface catalysts: CeO₂-Pt and Pt@mSiO₂. (Methanol is 35 Torr, He is 735 Torr, reaction temperatures are 150 °C, 170 °C, 190 °C)

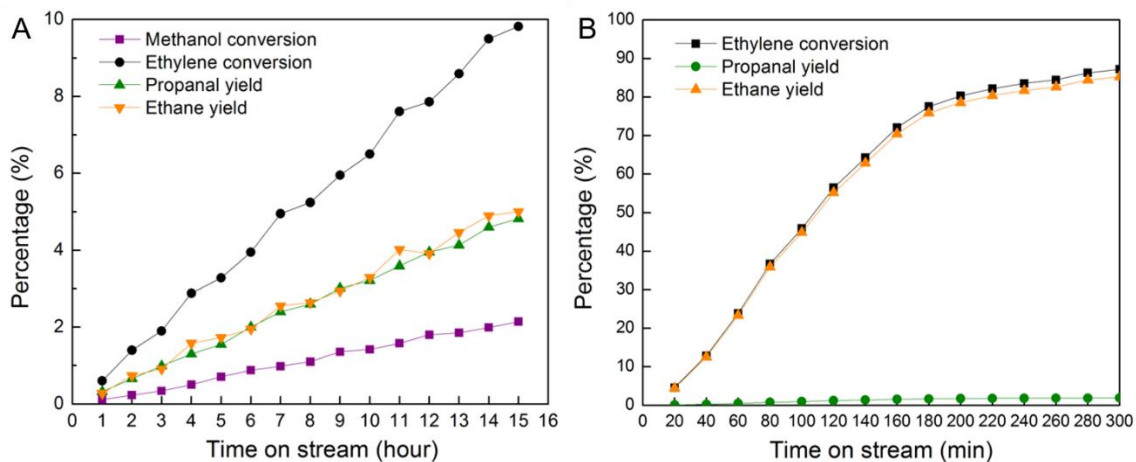


Figure S6. Time evolution of methanol and ethylene conversions and propanal and ethane concentrations in an effluent. Propanal yield = produced propanal/reactants fed in, ethane yield = produced ethane/reactants fed in. (A) Tandem ethylene hydroformylation with methanol. Reaction condition: methanol 35 Torr, ethylene 7.5 Torr, reaction temperature 150 °C. (B) Single-step hydroformylation with CO and H₂. Reaction condition: ethylene 7.5 Torr, CO 35 Torr, H₂ 70 Torr, reaction temperature 150 °C.

Table S2. Conversion of methanol and ethylene of tandem hydroformylation, single-step hydroformylation and tandem hydroformylation cofed with CO or H₂.

Reaction conditions ^a					Conversion		Date refer to
Methanol (Torr)	Ethylene (Torr)	H ₂ (Torr)	CO (Torr)	Time (h)	Methanol (%)	Ethylene (%)	
-	7.5	70	35	5	-	87.2	Figure 4A
35	7.5	-	-	15	2.1	9.8	Figure 4B
-	7.5	0.7	0.35	5	-	Trace amount	Figure 4C
-	7.5	3.5	1.75	5	-	4.3	Figure 4C
35	7.5	0.1	-	15	4.5	22.5	Figure 6A
35	7.5	0.2	-	15	10.7	41.6	Figure 6A
35	7.5	1	-	5	63.3	84.2	Figure 6A
35	7.5	1	-	15	100	100	Figure 6A
35	7.5	-	1	15	2.1	9.9	Figure 6B
35	7.5	-	10	15	3.0	13.9	Figure 6B
35	7.5	-	70	15	3.9	18.0	Figure 6B

a, Reaction conditions: 150 °C, total pressure is 1 atm.

Table S3. Selectivity of single-step ethylene hydroformylation with CO and H₂.

Entry ^b	Catalyst	Reaction conditions ^a			Products selectivity (%)	
		H ₂	CO	Ethylene	Ethane	Propanal
1	CeO ₂ -Pt@mSiO ₂	0.7	0.35	7.5	99.9	trace amount
2	CeO ₂ -Pt@mSiO ₂	3.5	1.75	7.5	98.6	1.4
3	CeO ₂ -Pt@mSiO ₂	70	35	7.5	97.8	2.2
4	Pt@mSiO ₂	0.7	0.35	7.5	99.9	trace amount
5	Pt@mSiO ₂	3.5	1.75	7.5	99.2	0.8
6	Pt@mSiO ₂	70	35	7.5	98.0	2.0

a, Reaction conditions: 150 °C, total pressure is 1 atm. b, Entry 1 to 3 are the same results with **Figure 4C**

Table S4. The inhibiting effect of different alkenes on methanol decomposition over CeO₂-Pt@mSiO₂ catalyst

Alkenes	Methanol decomposition TOF (s ⁻¹) ^a		
	150 °C	190 °C	230 °C
No alkene	0.49	0.86	2.6
Ethylene	0.0042	0.02	0.15
Propylene	Trace amount	0.0035	0.018
1-Butene	Trace amount	Trace amount	0.0023

a. Reaction condition: 35 Torr of methanol, 7.5 Torr of alkene, and 727.5 Torr of helium.

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