

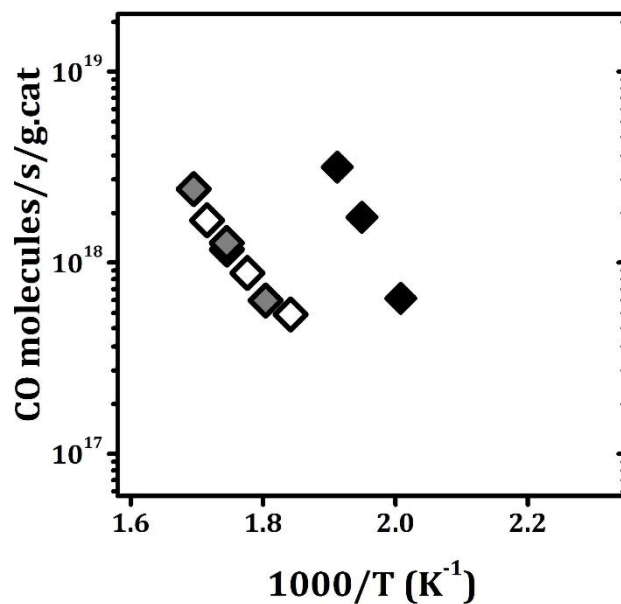
# “Intelligent” Pt Catalysts Studied on High-Surface-Area $\text{CaTiO}_3$ Films

*Chao Lin*<sup>a</sup>, *Alexandre C. Foucher*<sup>b</sup>, *Yichen Ji*<sup>a</sup>, *Christopher D. Curran*<sup>c</sup>, *Eric A. Stach*<sup>b</sup>, *Steven McIntosh*<sup>c</sup> & *Raymond J. Gorte*<sup>a,\*</sup>.

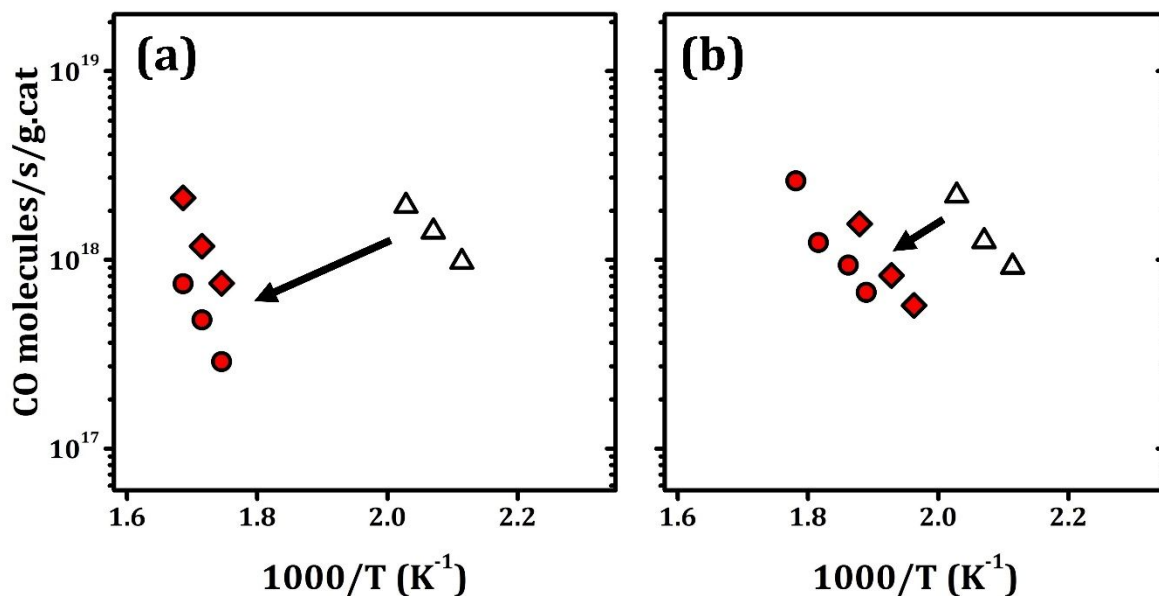
<sup>a</sup> Department of Chemical and Biomolecular Engineering, University of Pennsylvania, 34th Street, Philadelphia, PA 19104, United States

<sup>b</sup> Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States

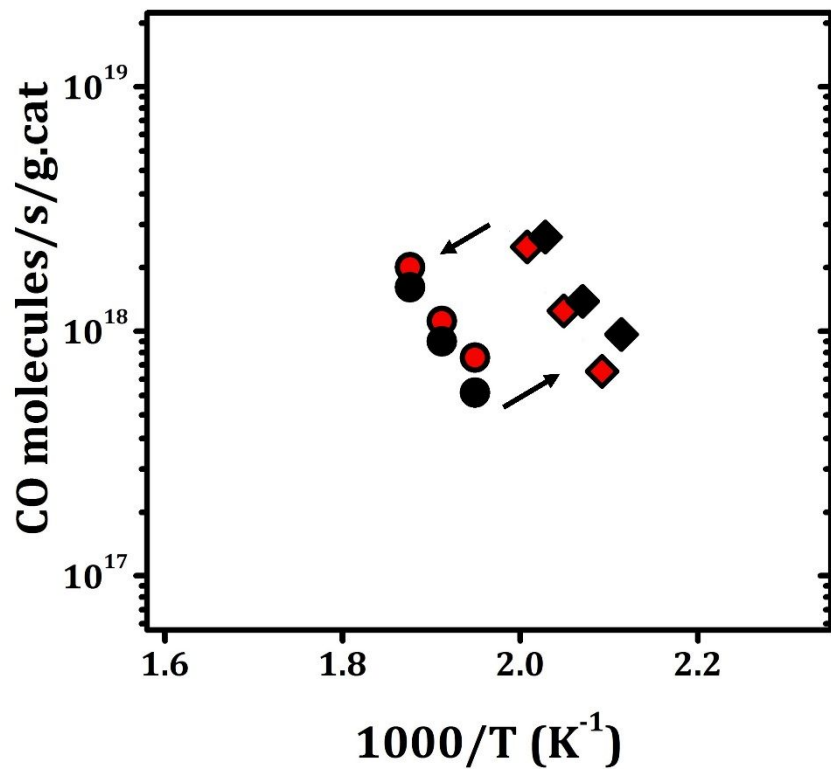
<sup>c</sup> Department of Chemical and Biomolecular Engineering, Lehigh University, 111 Research Drive, Bethlehem, PA 18015, United States.



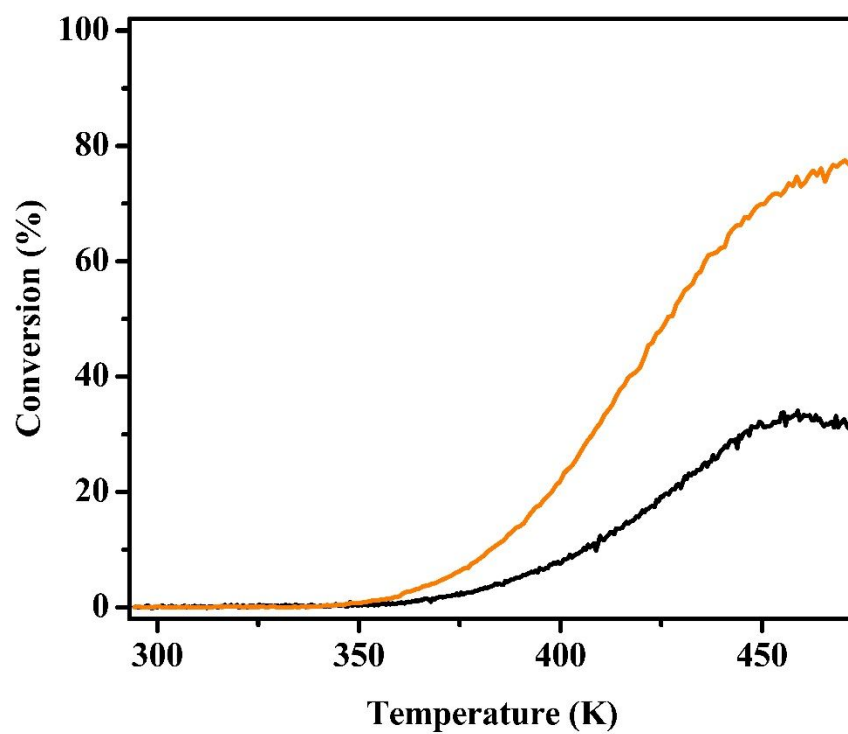
**Figure S1.** Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O<sub>2</sub> for Pt/CaTiO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub>. The rates were compared after the following pretreatment conditions: (white) two-hour oxidation in 10% O<sub>2</sub> in He at a flow rate of 100 mL min<sup>-1</sup> at 1073 K, followed by one-hour reduction at 773 K using 10% H<sub>2</sub> in He; (grey) two-hour oxidation in 10% O<sub>2</sub> in He at a flow rate of 100 mL min<sup>-1</sup> at 1073 K, followed by one-hour reduction at 973 K using 10% H<sub>2</sub> in He; (black) two-hour oxidation in 10% O<sub>2</sub> in He at a flow rate of 100 mL min<sup>-1</sup> at 1073 K, followed by one-hour reduction at 1073 K using 10% H<sub>2</sub> in He.



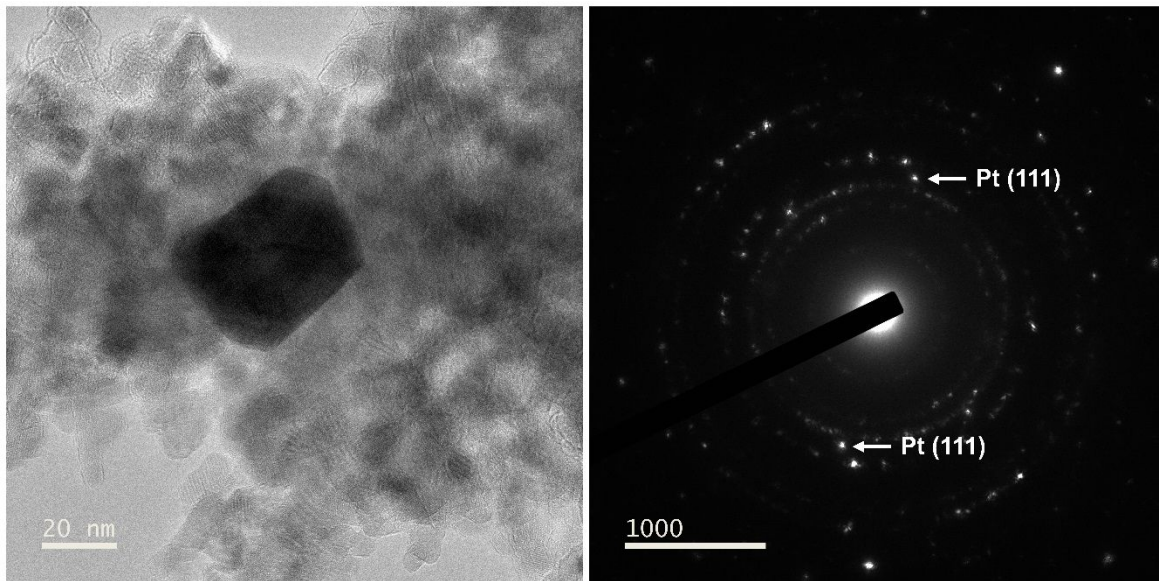
**Figure S2.** Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O<sub>2</sub> for (a) Pt/CaO/MgAl<sub>2</sub>O<sub>4</sub> and (b) Pt/TiO<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub>. The rates were compared for after following pretreatment conditions: (Δ) sample in its pristine state (573K calcination after Pt deposition); (●) Five high-temperature redox cycles, followed by an oxidation half cycle (two-hour oxidation in 10% O<sub>2</sub> in He at a flow rate of 100 mL min<sup>-1</sup>, followed by one-hour reduction at 773 K using 10% H<sub>2</sub> in He); (◆) Five high-temperature redox cycles, followed by a reduction half cycle (one-hour reduction at 1073 K using 10% H<sub>2</sub> in He).



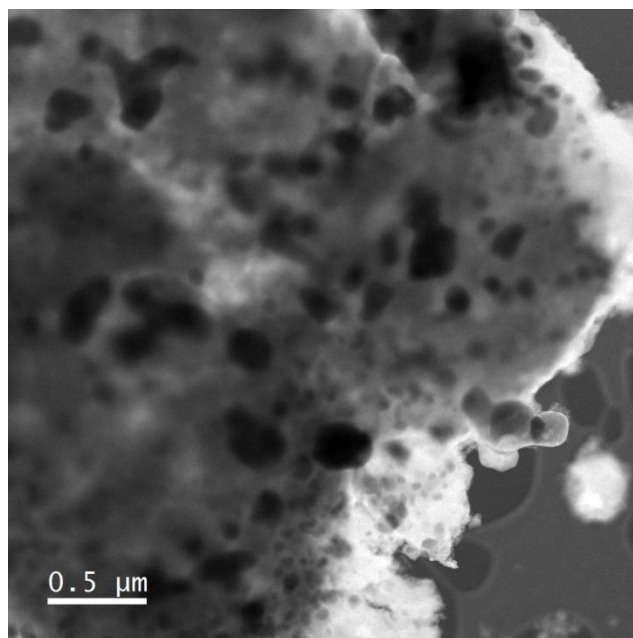
**Figure S3.** Steady-state, differential reaction rates for CO oxidation with 25 Torr of CO and 12.5 Torr O<sub>2</sub> for Pt/0.5 nm CaTiO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> after redox cycling. The rates were compared for after following pretreatment conditions: (●) two-hour oxidation in 10% O<sub>2</sub> in He at a flow rate of 100 mL min<sup>-1</sup>, followed by one-hour reduction at 773 K using 10% H<sub>2</sub> in He; (◆) one-hour reduction at 1073 K using 10% H<sub>2</sub> in He. Black symbols denote the first oxidation–reduction cycle, while red symbols represent the fifth cycle.



**Figure S4.** Light-off profiles for toluene hydrogenation over Pt/CaTiO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> after five redox cycles with the final treatment being (gold) oxidation and (black) reduction.



**Figure S5.** STEM result with SAED pattern for Pt/CaTiO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub>, after five 1073-K redox cycles, with the final step being reduction.



**Figure S6.** STEM result for Pd/CaTiO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub>, after five 1073-K redox cycles, with the final step being reduction.

Table S1. BET surface area for various samples after 1073 K calcination

Sample	$\text{MgAl}_2\text{O}_4$	CaO- $\text{MgAl}_2\text{O}_4$	$\text{TiO}_2$ - $\text{MgAl}_2\text{O}_4$	CaTiO <sub>3</sub> - $\text{MgAl}_2\text{O}_4$
BET surface area (m <sup>2</sup> /g)	125	63	95	50