

Highly selective single metal atom [Pt-O_x-(OH)]- species for the preferential oxidation of CO in H₂-rich streams

Sufeng Cao, Jilei Liu, Mengwei Li, and Maria Flytzani-Stephanopoulos*
 Department of Chemical and Biological Engineering, Tufts University, Medford, MA 02155, USA

Introduction:

H₂ is an important chemical for the chemical industry used in ammonia synthesis, methanol synthesis, hydrogenation reactions, and in clean power generation by fuel cells. When the source of H₂ is a fossil fuel, it is crucial to provide high purity H₂ with no or negligible amount of CO to protect the process catalysts from poisoning and deactivation. The preferential oxidation of CO (PROX) in hydrogen-rich streams is an attractive option to purify H₂, which significantly reduces the loss of energy and H₂. Good PROX catalysts must be active and selective at low temperatures and show good stability in realistic fuel gas streams which include water and CO₂ in large amounts.

Pt nanoparticles supported on alumina or other oxides are good PROX catalysts, but because they operate at moderately high temperatures (150-200 °C), they do not exceed 50-60% selectivity. Single Pt atoms doped in iron oxide surfaces have been reported as promising candidates for CO PROX at temperatures as low as 80 °C(1). However, a limited loading of dopant Pt (<0.2 wt.%) is possible in this approach. Here, we introduce an effective method to synthesize high loading single atom Pt catalysts (characterized by CO DRIFTS, STEM, and EXAFS), on any support oxide, including inert supports, with high selectivity at high PROX conversions. Alkaline ions are used to stabilize [Pt-O_x]-species previously reported as the active sites for the water-gas shift reaction (2, 3).

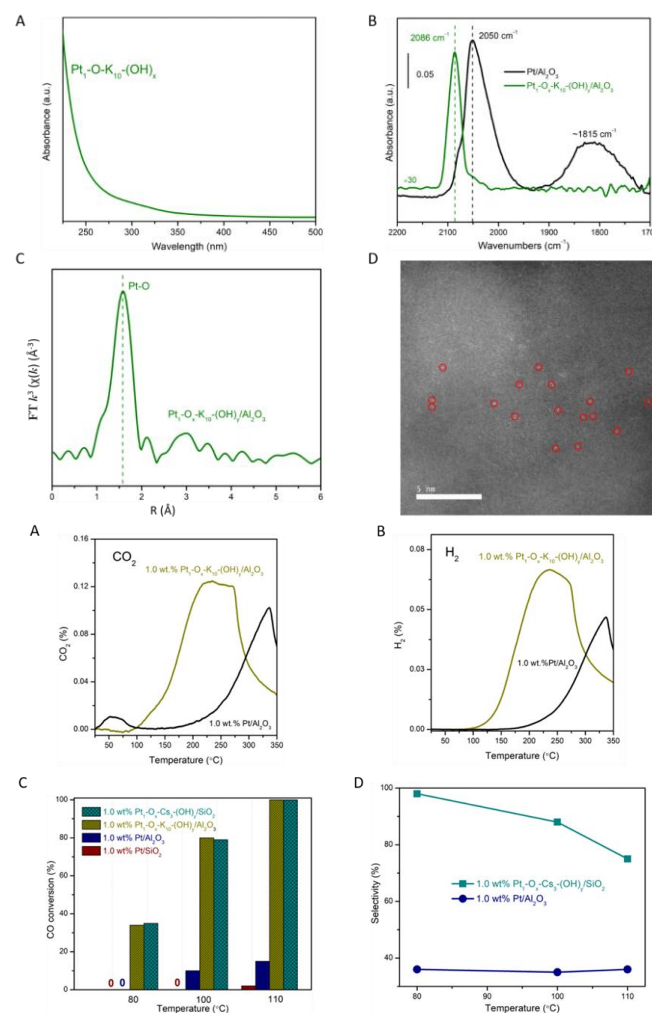
Materials and methods:

Single Pt atom oxo-clusters were synthesized in highly alkaline solutions of H₂Pt(OH)₆ and KOH (CsOH). The solution was applied on supports by incipient wetness impregnation (IWI).

Results and discussion:

The water-insoluble H₂Pt(OH)₆ reacts with KOH to produce a transparent yellow Pt uniform solution as found by UV-vis (Fig. 1A). CO was used as the probe molecule to characterize the Pt structure by DRIFTS. A narrow and symmetrical CO adsorption peak at 2086 cm⁻¹ that may be assigned to CO linearly adsorbed on single Pt atom sites(1) (Fig. 1B). EXAFS (no Pt-Pt bond) and STEM results corroborate the CO DRIFTS findings (Fig. 1C&D).

CO temperature programmed reduction (TPR) indicates that Pt₁-O_x-K₁₀-(OH)_y/Al₂O₃ has a higher number of surface OH groups compared to Pt/Al₂O₃ (Fig. 2A&B). OH has been proposed to promote the CO oxidation reaction(4). The single Pt atom catalysts, Pt₁-O_x-K₁₀-(OH)_y/Al₂O₃ and Pt₁-O_x-Cs₃-(OH)_y/SiO₂ show much higher activity and O₂ selectivity in CO PROX compared to the conventional Pt/Al₂O₃ and Pt/SiO₂ (Fig. 2C&D). Pt



nanoparticles are very active for H₂ oxidation and adsorb CO strongly, which makes them poor catalysts for the low temperature CO PROX reaction.

Fig. 1. Characterization of single Pt atom catalyst: A. UV-vis of Pt₁-O_x-K₁₀-(OH)_y solution; B. CO DRIFTS of Pt/Al₂O₃ and Pt₁-O_x-K₁₀-(OH)_y/Al₂O₃; C. EXAFS of Pt₁-O_x-K₁₀-(OH)_y/Al₂O₃; D. ac-HAADF-STEM image of Pt₁-O_x-K₁₀-(OH)_y/Al₂O₃.

Fig. 2. Catalytic tests over Pt/Al₂O₃ and Pt₁-O_x-K₁₀-(OH)_y/Al₂O₃: A. production of CO₂ from CO TPR; B. production of H₂ from CO TPR; C. conversion of CO at 80, 100, and 110 °C respectively over Pt/Al₂O₃ and Pt₁-O_x-K₁₀-(OH)_y; D. the selectivity of O₂ of Pt/Al₂O₃ and Pt₁-O_x-K₁₀-(OH)_y/Al₂O₃. All catalysts were calcined at 200 °C for 2h and then reduced in H₂ at 150 °C for 0.5h. CO TPR conditions: 10%CO, 30mL/min, 100mg catalyst, 5 °C/min; PROX test conditions: 1%CO, 1%O₂, 40% H₂, 20mL/min, 100mg catalyst, 5 °C/min.

Acknowledgment The financial support of the work by the U.S. Department of Energy, grant #DE-FG02-05ER15730, is gratefully acknowledged.

References

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