Palladium nanoparticles has been intensively pursued in heterogenous and homogenous catalysis. Palladium can catalyze myriad chemical reactions, such as CO oxidation, formic acid oxidation, and glycerol hydrogenolysis. Ceria (CeO$_2$) has been widely applied in catalysis. It has been known for a common catalyst used for oxidizing CO and NOx in automotive industry. It exhibits strong oxidation capacity based on the oxidation states +3 and +4 coupled with the oxygen vacancies. Relative to other oxide supports, ceria also enhances the performance of transition metal catalysts in a variety of other reactions including water-gas shift, steam reforming of oxygenates, and PROX. Vacancies also bind adsorbates more strongly than normal oxide sites and assist in their dissociation. Oxygen vacancies stabilize transition metal nanoparticles supported on oxide surfaces.

**Objectives**

Develop nanoscale cerium oxide decorated with sub-nanometer Pd clusters for the conversion of CO to CO$_2$ through oxidative catalysis.

- Synthesize and characterize Palladium decorated cerium oxide nanorods.
- Evaluate the oxidative potential of the oxide catalysts with respect to its capability for CO oxidation as a function of reaction time and temperature.
- Propose the mechanism of catalytic reaction.
- Examine the self-recharging ability of this catalyst.

**Material Synthesis**

$\text{K}_2\text{PdCl}_4 \xrightarrow{100\text{ sccm Air flow}} \text{Pd}$

$\text{Air} \xrightarrow{50^\circ \text{C}} \text{Ce}_2\text{(SO}_4\text{)}_3 + \text{NaOH} \rightarrow \text{Ce(OH)}_3 \xrightarrow{500^\circ \text{C}} \text{Ce}_2\text{O}_3/\text{CeO}_2 \xrightarrow{\text{Pd}}$  

**Catalyst Activation System**

- Air flow: 100 sccm Air flow
- Ramping rate: 14°C/min
- 400°C for 0.5h
- Pressure: 2.5~3.0 Torr

**Results and Discussion**

**TEM Characterization**

- Figure 1. (a) The TEM image and (b) HRTEM image of the as-synthesized 2 at% Pd on ceria nanorods

The high-resolution image shown is indeed typical of highly crystalline CeO$_2$. The nanocrystals are polyhedra displaying (111) facets as indicated. It has an inter planar spacing of 3.1Å. Ceria crystallizes in a cubic fluorite structure and exposes the thermodynamically most stable (111) surface. This surface is the oxygen termination of stoichiometric O-Ce-O trilayers stacked along the 111 direction and also represents the major fraction of the active surface in catalytic nanocrystals.

**XRD Characterization**

- Figure 2. The XRD patterns of the as-synthesized pure ceria nanorod and 2 at% Pd on ceria nanorod.

**XPS Characterization**

- Figure 3. Pd 3d spectra for the 2% Pd decorated CeO$_2$ samples

The peak at 336.7-336.9eV is assigned to Pd$^{2+}$ 3d$_{5/2}$. The binding energy for the Pd$^{2+}$ 3d$_{5/2}$ for the three samples shift to a high value of 337.5eV-337.8eV, which may be ascribed to co-existence of PdO(336.8eV) and PdO$_2$ (338.3eV).

**Catalytic Activity Test**

- Figure 4. The temperature dependent catalytic behavior of Pd-CeO$_2$ with different percentages Pd loading on catalytic CO oxidation.

**Long Term Catalytic Activity Test**

- Figure 5. Plot of carbon monoxide conversion or yield percentage versus reaction time at 20 °C for the Pd decorated on cerium oxide nanorod catalysts.

**Self-Recharging Ability Test**

- Figure 6. 24h Catalytic activity test of 1at. % Pd on ceria self-recharging for 24h

1. The catalytic behavior for low temperature CO oxidation of ceria-supported Pd has been investigated as a function of temperature. The $T_{50}$ for 2 at. % Pd on ceria is 18°C.

2. This catalyst is suitable for long use since its catalytic activity drops significantly during the first 8 hours, but stays almost unchanged for following long period of time.

3. The specific property of this catalyst, self-recharging was found under ambient conditions.

4. In this catalysis system, the active surface is a PdO$_2$ surface which may have adsorbed CO but not Pd metal.

**Conclusion**

We thank Nebraska Center for Energy Sciences Research for financial support.