Self-Recharging Palladia Nanoparticles on Cerium oxide Nanorod Support for Catalytic Oxidation

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Introduction

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 hydrogenoloysis.

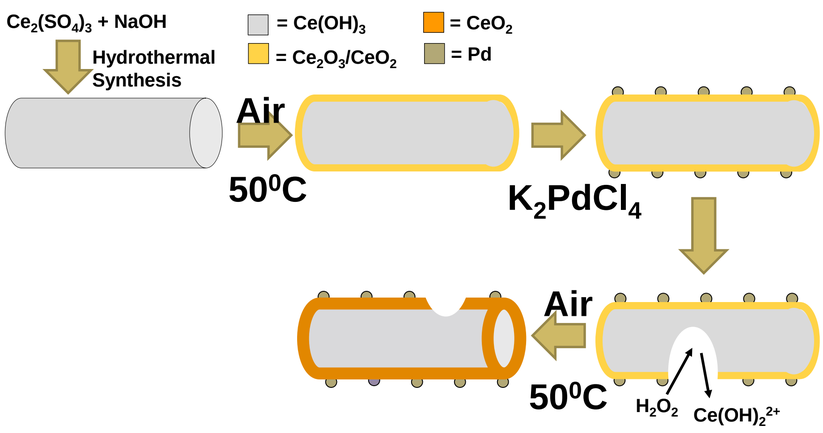
Ceria (CeO_{2-x}) has been widely applied in catalysis. It has been known for a common catalyst used for oxidizing CO and NO_x in automotive industry. It exhibits strong oxidation capacity based on the oxidation states +3 and +4 coupled with the oxygen vacancies. Relative to other oxide supports, ceria 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

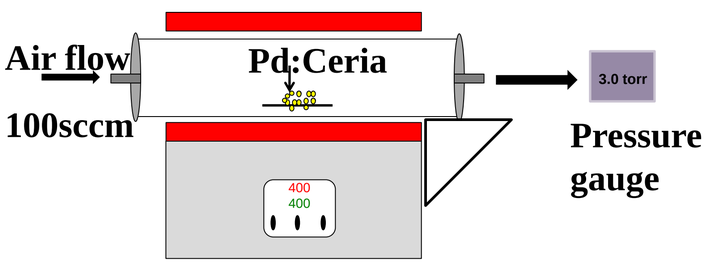
Develop nanoscale cerium oxide decorated with sub-nanometer Pd clusters for the conversion of CO to CO_2 through oxidative catalysis.

- 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

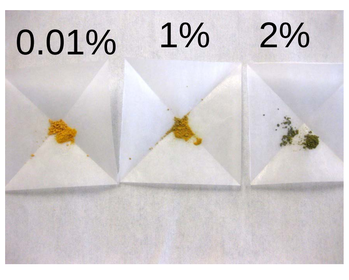
Material Synthesis



Catalyst Activation System



Activation conditions:
100 sccm Air flow
Ramping rate: 14⁰C/min
400⁰C for 0.5h
Pressure:2.5~3.0 Torr



Results and Discussion

TEM Characterization

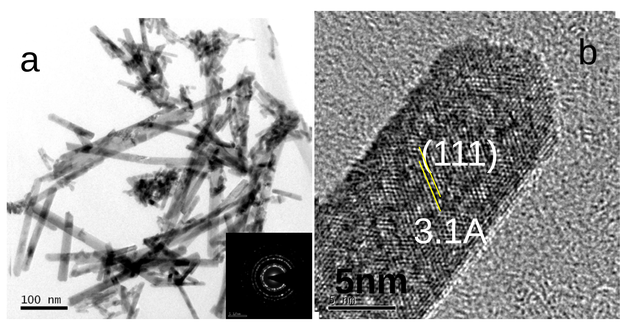


Figure 1. (a) The TEM image and (b) HRTEM image of of the as-synthesized 2 at% Pd on ceria nanorods

The high-resolution image shown is indeed typical of highly crystalline CeO2. The nanocrystals are polyhedra displaying (111) facets as indicated. It has a 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

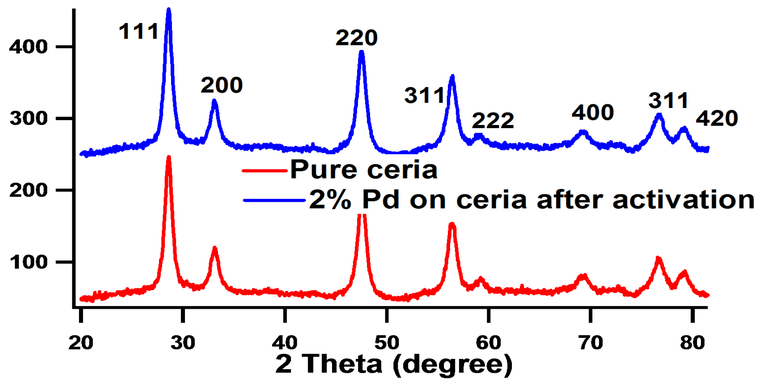


Figure 2. The XRD patterns of the as-synthesized pure ceria nanorod and 2 at% Pd on ceria nanorod.

XPS Characterization

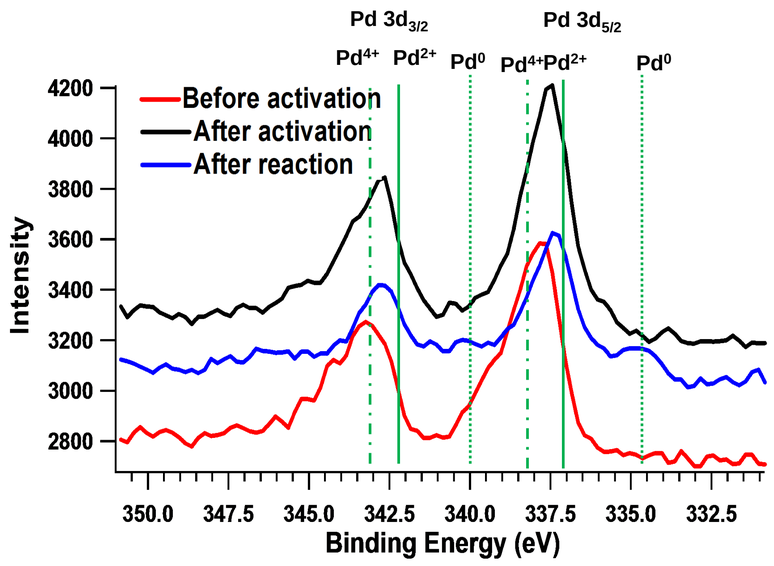


Figure 3. Pd 3d spectra for the 2% Pd decorated CeO2 samples

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

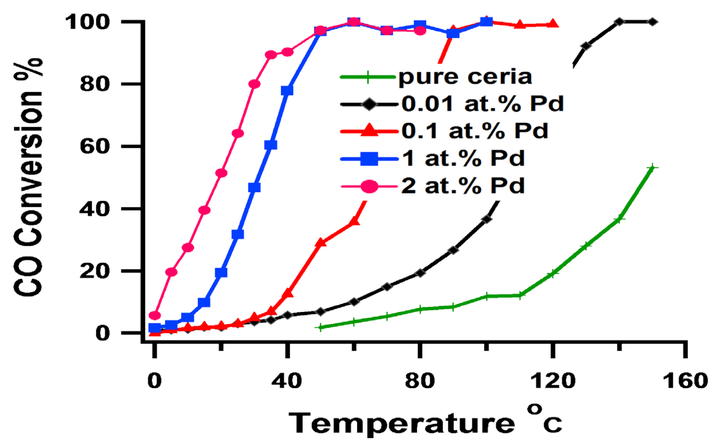


Figure 4. The temperature dependent catalytic behavior of $Pd:CeO_2$ with different percentages Pd loading on catalytic CO oxidation.

Long Term Catalytic Activity Test

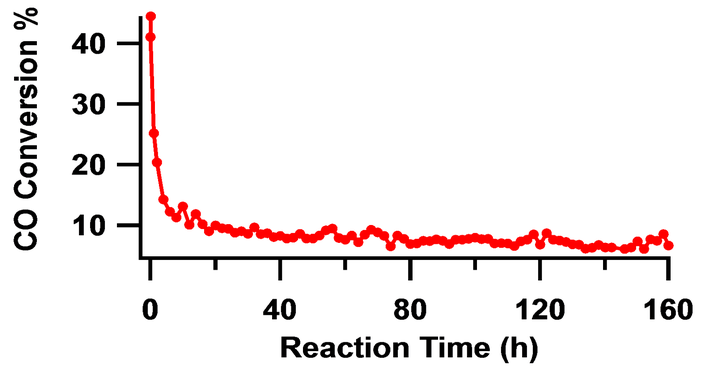


Figure 5. Plot of carbon monoxide conversion or yield percentage versus reaction time at 20 °C for the Pd decorated on cerium oxide nanorod catalysts.

Self- Recharging Ability Test

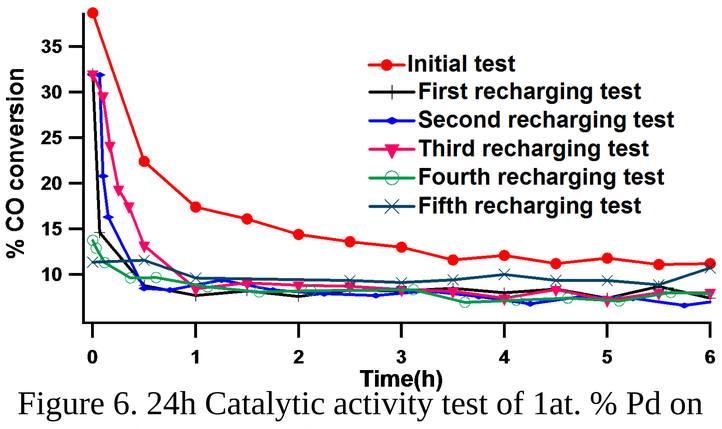


Figure 6. 24h Catalytic activity test of 1at. % Pd on ceria self-recharging for 24h

Conclusion

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 18⁰C.
2. This catalyst is suitable for last 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 surface which may have adsorbed CO but not Pd metal.

Acknowledgements

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