Impact of ZrO_2 Supports on the Durability and Low-Temperature Performance of Pd-based Diesel Oxidation Catalysts

Mi-Young Kim[1], Eleni A. Kyriakidou[1], Jae-Soon Choi*[,1], Todd J. Toops[1], Cyril Thomas[2], Andrew Binder[1], James E. Parks II[1], Viviane Schwartz[1], Jihua Chen[1]

1-Oak Ridge National Laboratory (ORNL): Fuel, Engines and Emissions Research Center; 2-UPMC Univ. Paris 06, UMP 7197, Laboratoire de Réactivité de Surface, Paris, France

Email: choijs@ornl.gov (Jae-Soon Choi), toopstj@ornl.gov (Todd J. Toops)

Motivation

- Future diesel oxidation catalysts (DOC) will need to perform effectively at increasingly low exhaust temperatures, arising from continued improvements in diesel engine efficiency.
- Recently, progress has been made in designing catalytic materials with enhanced low-temperature oxidation performance (e.g., Au and Ag nanoparticles combined with Cu, Mn, or Fe). However, significant technical barriers exist for implementing these novel materials into practice.
- We have recently reported that Pt dispersed on ZrO_2-coated SiO_2 supports are excellent CO oxidation catalysts with good hydrothermal stability and sulfur tolerance.
- In this work, we extended this ZrO_2-coated support concept to Pd, a popular metal due to its cost-competitiveness compared to Pt.

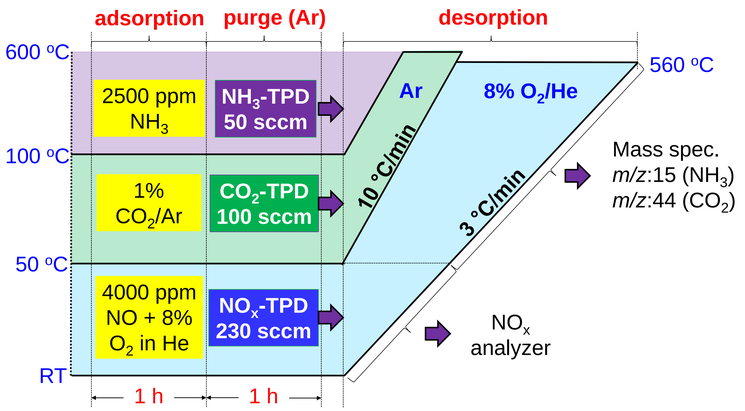
Objectives

- The goal of this work is to assess the impact of ZrO_2 supports on CO and C_3H_6 oxidation, sulfur tolerance, and hydrothermal stability.
- The physicochemical properties were examined using ICP, XRD, TEM, and NH_3-, CO_2-, and NO_x-TPD.
- The performance of Pd catalysts was evaluated in fresh, sulfated, and hydrothermally aged states, and compared with that of a commercial DOC.

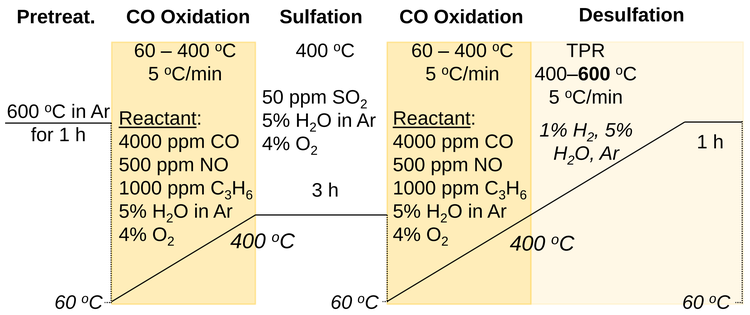
Experimental

TPD

Pretreatment:
NH_3 and CO_2-TPD → 600 °C in Ar for 0.5 h
NO_x-TPD → 500 °C in 20% O_2/He for 2 h



Evaluation

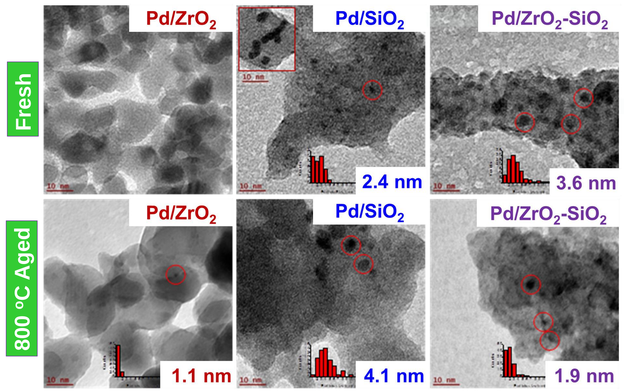


Loading: 100 mg Pd Catalyst/ Total Flow: 200 sccm/ SV: 60,000 h^{-1}

Mass. Spec.: *m/z*:26 (C_3H_6), 28 (CO), 44 (CO_2)

Catalysts Surface Characterization

TEM



Sample	Surface Area (m^2/g)
Fresh Pd/ZrO_2	92.6
Aged Pd/ZrO_2	*24.3*
Fresh Pd/SiO_2	447.4
Aged Pd/SiO_2	*300.9*
Fresh Pd/ZrO_2-SiO_2	404.4
Aged Pd/ZrO_2-SiO_2	*325.3*

Aging results into lowering of the Surface Area

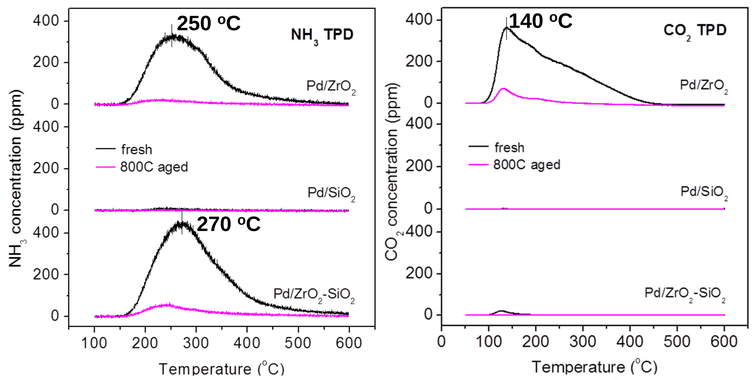
Incorporation of ZrO_2 on SiO_2 appears to enhance hydrothermal stability of Pd catalysts.

Well dispersed Pd on ZrO_2 (fresh). Sintering of Pd particles with aging.

Pd/PdO particle growth with aging

Presence of PdO particles with aging (XRD)

Surface Acidity and Basicity – NH_3-, CO_2-TPD



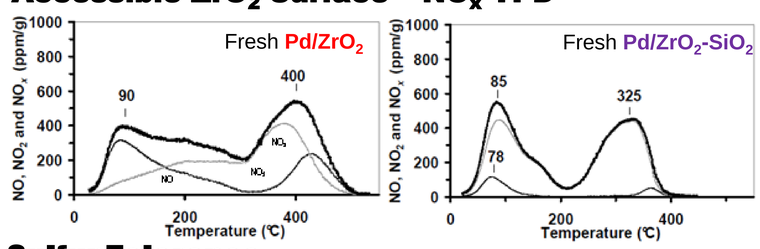
Acidity:
Pd/ZrO_2-SiO_2 > Pd/ZrO_2 > Pd/SiO_2

Basicity:
Pd/ZrO_2 > Pd/ZrO_2–SiO_2 > Pd/SiO_2

Pd/ZrO_2-SiO_2: relative high acidity and no basicity for high sulfur tolerance.

Hydrothermal aging: loss of surface acido - basicity for Pd catal.

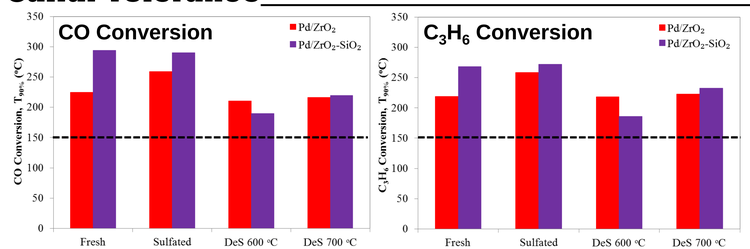
Accessible ZrO_2 Surface – NO_x-TPD



- Pd/ZrO_2: LowT peak < HighT peak
- Pd/ZrO_2-SiO_2: LowT peak > HighT peak

Pd/ZrO_2 more stable (due to higher basicity) adsorbed NO_x species than Pd/ZrO_2-SiO_2.

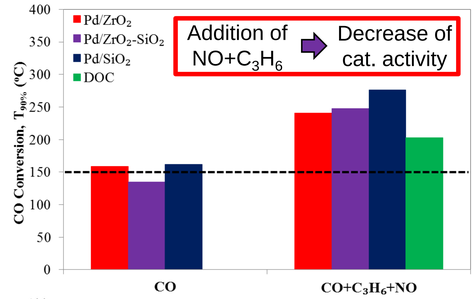
Sulfur Tolerance



Better S tolerance of ZrO_2-SiO_2

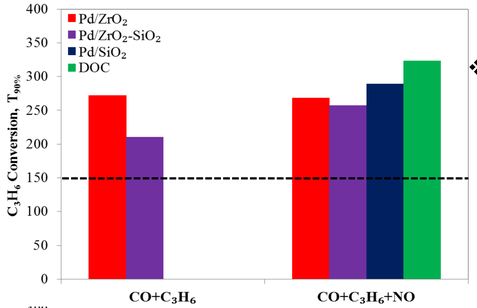
Lowest $T_{90\%}$ after DeS at 600 °C for Pd/ZrO_2-SiO_2

Catalytic Evaluation

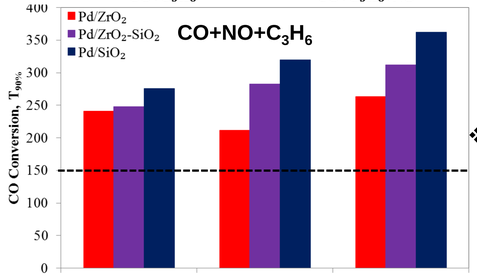


Reaction Conditions: 4000 ppm CO / 500 ppm NO / 1000 ppm C_3H_6 +4% O_2 + 5% H_2O in Ar, Total Flow: 200 sccm

Catalytic Activity is sensitive to the type of support as well as the catalytic state.



❖ **Pd/ZrO_2-SiO_2 shows better performance for HC oxidation**
- $T_{90\%}$ in CO+NO+HC
- Commercial DOC 323 °C
- Pd/ZrO_2-SiO_2: 257 °C



Aging Conditions: 800, 900 °C for 16 h in 10% O_2, 5% H_2O/Ar

Pd/SiO_2: significant performance loss due to Pd particle agglomeration.

❖ **After aging at 800 °C, Pd/ZrO_2 shows excellent stability**
- Increase in $T_{90\%}$ observed on Pd/ZrO_2-SiO_2
- improved zirconia adherence necessary

Conclusions

- Controlling morphology and accessible area of coated ZrO_2 layer appears to be critical for maximizing the performance of Pd oxidation catalysts.
- ZrO_2 layer on SiO_2 surface generated acidity and negligible basicity on the catalyst surface.
- **ZrO_2-containing catalysts** showed higher activity in both CO, C_3H_6 oxidation than Pd/SiO_2 (fresh state).
- Pd/ZrO_2-SiO_2 is more active than Pd/ZrO_2 after DeS at 600 °C.
- Hydrothermally aged (800, 900 °C) Pd/ZrO_2 showed higher activity than Pd/ZrO_2-SiO_2. which was in turn more active than Pd/SiO_2.
- Further research is necessary to enhance the thermal stability of ZrO_2-SiO_2 to maximize potential.

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