Mechanistic Insights into the emission and trapping of mobile species during sintering of Pt based DOCs

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Chang H. Kim, Gongshin Qi, Michelle Wiebenga, Se Oh, Wei Li & Mike Balogh
Improvement in CO Lightoff temperature for Pd/La-alumina

2.5 wt% Pd

Sub-nm clusters

Atomically dispersed Pd

Jason Gaudet, Andrew DeLaRiva, et al., ACS Catal, 2013

Motivation

• Catalyst durability is important for achieving low temperature reactivity

• Understanding sintering mechanisms may help us devise methods to improve long term stability of catalysts & improve low temperature performance
“Pd helps to improve the durability of Pt DOCs”

Underlying mechanism not well understood

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Pt</th>
<th>Pt-Pd</th>
<th>Physical Mixture</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>12</td>
<td>6</td>
<td>11</td>
<td>--</td>
</tr>
<tr>
<td>600</td>
<td>13</td>
<td>7</td>
<td>11</td>
<td>--</td>
</tr>
<tr>
<td>750</td>
<td>18</td>
<td>15</td>
<td>18</td>
<td>14</td>
</tr>
<tr>
<td>900</td>
<td>43</td>
<td>28</td>
<td>27</td>
<td>30</td>
</tr>
</tbody>
</table>

- Aged in 5% O₂ and 10% H₂O in N₂ for 3 hr
- Reduced in 1% H₂ at 500°C for 1 hr
- Alloying takes place between 600°C and 750°C

Graham et al., *Effect of alloy composition on dispersion stability and catalytic activity for NO oxidation over alumina-supported Pt-Pd catalysts*, Catalysis Letters, 2007
Mechanisms of Catalyst Sintering

- **Ostwald Ripening** - particles grow in size due to differences in surface energy. Larger particles grow at the expense of smaller ones.
- **Particle Migration and Coalescence** – dependent on the mobility of nanoparticles.

What is the contribution from each of these processes?
Model Catalysts Provide Mechanistic Insight

SiO$_2$/Si$_3$N$_4$/ SiO$_2$ membrane

TEM grids developed by Hans Niemantsverdriet (Eindhoven) allow heating of sample in air and observation of the same region of the sample.
At Atmospheric Pressure in Air, Pt/SiO$_2$ Sinters Through Ostwald Ripening

Initial $\rightarrow$ 15 s in 21% O$_2$/Ar at 650ºC $\rightarrow$ Aged

Avg Diameter: 3.3nm

Avg Diameter: 4.2nm

Pd transforms into PdO & does not sinter.
Pt-Pd/SiO$_2$ Also Sinters via Ostwald Ripening (No PdO left behind!)

Initial \[ \rightarrow \] 15 s in 21\% O$_2$/Ar at 650ºC \[ \rightarrow \] Aged

Avg Diameter: 3.5nm

Avg Diameter: 3.9nm

Rate of sintering similar to that of Pt alone
What are the mobile species? Pt, Pd, or both?

- **Answer:** Identical composition of aged nanoparticles in Pt-Pd catalysts, despite significant growth in particle size, **suggests similar mobility of Pt and Pd** – when emitted from **metallic** Pt-Pd particles.

DFT for Pt emission

DFT for emission from Pt-Pd

Mechanism 1: Atomic transport

Mechanism 2: Particle Migration
How does Pd improve the performance of Pt catalysts

- **Part I**: Addition of Pd lowers the vapor pressure of Pt (in oxidative atmospheres)
- **Part II**: Pt keeps Pd metallic, and metallic Pd is active for low temperature hydrocarbon oxidation
- **Part III**: PdO can trap mobile Pt species
Part I

Influence of Pd on the vapor pressure of Pt in Pt-Pd alloys
Emission of Atoms from Automotive Exhaust Catalysts

- The vapor pressure of the metal and oxide phases is significant to cause emission at temperatures used for accelerated aging.
  - Diesel oxidation catalysts are aged at 800 °C
    - Vapor pressure of PtO$_2$ $\sim$ 1x10$^{-5}$ Torr
  - Three way catalysts are aged at temperatures ranging from 900 °C to 1050 °C
    - While PdO is not volatile, it decomposes into Pd at temperatures $>$800 °C and then has significant vapor pressure.
Vaporization-Assisted Degradation of High Temperature Combustion Catalysts

J. G. McCarty, K.-H. Lau, and D. L. Hildenbrand
SRI International, 333 Ravenswood Avenue, Menlo Park, CA, 94025, USA

10^{-6} \text{ Torr} (1.3 \times 10^{-9} \text{ atm})
1 \text{ Langmuir} (1 \text{ monolayer/sec})
Rate of evaporation from a metal surface

At equilibrium, the rate of condensation from vapor is equal to the rate of emission from solid.

\[ \text{flux} = \frac{1}{2} \rho \cdot \overline{V}_1 \]

\[ m = \sqrt{\frac{M}{2\pi R_g T}} P \]

**Langmuir,** *Phys. Rev.* **2** 329 (1913)
Pd Only Catalyst Shows No Emission To The Vapor Phase at 800 °C

<table>
<thead>
<tr>
<th>Time</th>
<th>Image Description</th>
<th>Particle Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>Initial image</td>
<td>$d_{avg} = 3.7$ nm</td>
</tr>
<tr>
<td>Aged 650°C, 2 min</td>
<td>Image after aging 650°C, 2 min</td>
<td>$d_{avg} = 4.2$ nm, 3.6 nm after correction</td>
</tr>
<tr>
<td>Aged 800°C, 1.5 hr</td>
<td>Image after aging 800°C, 1.5 hr</td>
<td>$d_{avg} = 4.8$ nm, 4.1 nm after correction</td>
</tr>
</tbody>
</table>
At 800 °C We See Significant Emission Of Pt To The Vapor Phase

\[ d_{\text{max}} = 97 \text{nm} \]

\[ d_{\text{avg}} = 19.4 \text{nm} \]

\[ d_{\text{avg}} = 5.5 \text{nm} \]

\[ d_{\text{max}} = 31 \text{nm} \]

Aged 750°C, 1.5 hr

Aged 800°C, 1.5 hr

Pt 500 pm
Initial

Pt 315 pm
Aged 750°C, 1.5 hr

Pt 177 pm
Aged 800°C, 1.5 hr

At 800 ºC We See Significant Emission Of Pt To The Vapor Phase
Adding Pd Slows Emission of Pt

Aged 750°C, 1.5 hr
- d_max = 8.2 nm
- 28% Pt, 72% Pd
- d_avg = 4.5 nm

Aged 800°C, 1.5 hr
- d_max = 29 nm
- 32% Pt, 68% Pd
- d_avg = 12.4 nm

Aged 800°C, 1.5 hr
- Pt-Pd 500 pm
- Pt-Pd 429 pm
- Pt-Pd 449 pm

Adding Pd Slows Emission of Pt
Summary of Part I

- Vapor phase transport is a significant contributor to catalyst degradation at conditions used for accelerated aging.
- Pd lowers the vapor pressure of Pt in oxidizing conditions.
- Lowering the vapor pressure of Pt helps avoid the formation of abnormally large particles seen in Pt-only catalysts.
Part II

Pt keeps Pd in metallic form, improving catalytic activity for low temperature hydrocarbon oxidation
Calcination in air at 800 °C leads to Pt sintering

**CO Oxidation on 1wt% Pt/La-Al2O3**

- Fresh
- Aged 800°C 10 hr

**XRD of 1wt% Pt/La-Al2O3 aged 800°C 10hr**

- Intensity

**Micron-sized Pt particles after aging**
XANES shows that Pt remains metallic in air-aged catalysts. Pt is almost fully reduced even after aging for 10 hours at 750°C in air.
Pt transforms PdO into metallic Pt-Pd which sinters forming larger particles.

750°C air-aged 10 h
Air-Aged Samples Show Only Metallic Pt, No Pt Oxide

XRD patterns of La-Al$_2$O$_3$ support and 750°C air-aged Pt-Pd/La-Al$_2$O$_3$, Pt/La-Al$_2$O$_3$, and Pd/La-Al$_2$O$_3$.
XANES confirms Pd forms Pt-Pd alloy + excess PdO

Pd-only catalysts are fully oxidized while the bimetallics show Pd to be partly oxidized, even after aging at 750°C in air for 10 hours.
Excess PdO is seen as a dispersed phase on the Pt-Pd/La-alumina. Similar to particle sizes found via SEM and XRD.
No Core Shell Particles Seen

- Composition from overall EDS: 40% Pt, 60% Pd
- Composition from XRD: 68% Pt, 32% Pd
- Composition from spot EDS: 60% Pt, 40% Pd

(a) Pt: 61% Pd: 39%
(b) Pt: 62% Pd: 38%

Pt: 56% Pd: 44%
Pt: 53% Pd: 47%
Pt: 55% Pd: 45%

10 nm
20 nm
EDS Mapping Confirms Uniform Composition Within Nanoparticles & Existence Of Dispersed PdO

Pd – red
Pt - green

Mike Balogh, GM Research
Aged Bimetallic Catalysts Do Not Show Any Surface PdO on Pt-Pd Particles

Eric Stach
Titan 80-300 kV Aberration Image Corrector

HR-TEM image of Pt-Pd/La-Al$_2$O$_3$ aged at 750°C for 10 hours in air clearly showing no PdO on the surface of the nanoparticle.
Aging Physical Mixtures Of Pt/Al₂O₃ And Pd/Al₂O₃ Improves Catalytic Performance

- Improved performance after aging physically mixed Pt and Pd indicates formation of Pt-Pd alloys
- Samples were hydrothermally aged for 72 hours at 750 °C with 10% H₂O in flowing air

Reactant Gas Mixtures

<table>
<thead>
<tr>
<th>(ppm, molecular basis)</th>
<th>NO</th>
<th>C₃H₆:C₃H₈</th>
<th>C₈H₁₀:C₁₂H₂₆</th>
<th>CO</th>
<th>(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard (Std.)</td>
<td>200</td>
<td>260 : 90</td>
<td>-</td>
<td>-</td>
<td>8 8</td>
</tr>
<tr>
<td>Std. with CO</td>
<td>200</td>
<td>260 : 90</td>
<td>-</td>
<td>500</td>
<td>8 8</td>
</tr>
<tr>
<td>Std. with Heavy HC</td>
<td>200</td>
<td>-</td>
<td>295:146</td>
<td>-</td>
<td>8 8</td>
</tr>
<tr>
<td>Std. with High HC</td>
<td>200</td>
<td>1190 : 410</td>
<td>-</td>
<td>-</td>
<td>8 8</td>
</tr>
</tbody>
</table>

Summary of Part II
Origins of the improved performance of Pt-Pd catalysts

• Air aged PtPd particles are metallic, with a small amount of dispersed PdO on the support

• Only a very slight segregation of Pd to the surface of the nanoparticle

• The improved catalytic activity must be related to the presence of metallic Pd that is present under oxidizing conditions
Part III
Trapping of Mobile Pt by PdO

$\text{PdO traps mobile Pt species}$


Trapping of Mobile Pt Species by PdO Nanoparticles under Oxidizing Conditions

Cristiñan Carrillo, Tyne R. Johns, Haifeng Xiong, Andrew DeLaRiva, Sivakumar R. Challa, Ronald S. Goeke, Kateryna Artyushkova, Wei Li, Chang H. Kim, and Abhaya K. Datye

pubs.acs.org/JPCL
Aging for 2 minutes \textbf{in air} causes mobile Pt species to be trapped by PdO forming metallic Pt-Pd.
XPS Shows Formation Of Metallic Pt-Pd After Aging In Air

- Pd 3d

- PdO: 337.7 eV
- Pd: 335.8 eV

- Palladium

- Pt/Pd Atomic Ratio

- Percentage (%) vs. Aging Time (min)

- Binding energy, eV vs. cps
TGA of Chloroplatinic Acid and PdO decomposition in air

- CPA decomposed to Pt around 600 °C in agreement with the literature
- Theoretical weight loss for PdO$\rightarrow$Pd is $\sim$13%
TGA with a Physical Mixture of CPA+PdO Showed Formation of Metallic Pt-Pd

- CPA decomposed to Pt around 600 °C in agreement with the literature

- Theoretical weight loss for PdO→Pd is ~13%

- Theoretical weight loss for Pt+PdO→PtPd is ~5%

Bulk Thermodynamics Consistent With Lowering The Reduction Temperature Of PdO

We used the linearized equations versions of the Van’t Hoff equation from the work of Peuckert. Linearized versions lead to some error. PdO decomposition temperature is 792°C while TGA shows this decomposition at around 834°C.

Peuckert, M. Journal of Physical Chemistry 1985, 89, 2481
Trapping Pt by PdO in powder catalysts

- Physical mixture of Pt/MgAl₂O₄ with PdO aged in air 800 °C

What is the role of PdO particle size on trapping?

Xiong, Datye et al., Cat Today (2016)
Different Initial PdO particle sizes on Pd/La-Al₂O₃ catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>PdO particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Pd/La-Al₂O₃-300-a</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>2Pd/La-Al₂O₃-800-a</td>
<td>5.0</td>
</tr>
<tr>
<td>10Pd/La-Al₂O₃-300</td>
<td>4.2</td>
</tr>
<tr>
<td>10Pd/La-Al₂O₃-500</td>
<td>8.5</td>
</tr>
<tr>
<td>10Pd/La-Al₂O₃-800-a</td>
<td>9.9</td>
</tr>
<tr>
<td>10Pd/La-Al₂O₃-800</td>
<td>12.0</td>
</tr>
</tbody>
</table>

1 a means that the Pd salt is Palladium amine
2 The particle size was obtained from XRD
Small PdO particles trap Pt better than large particles

(physical mixture of Pt/MgAl$_2$O$_4$ and PdO/La-Al$_2$O$_3$)
Reactivity of Pt + PdO physically mixed catalysts

Methane oxidation \((0.5\%O_2; 0.2\%CH_4; \text{He as balance})\)

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}
\]

Pt, Pd, PdO are active, Pd is more active than PdO

Xiong, Datye et al., Catal Today (2016)
How Pd helps to improve durability of Pt DOCs

At 800 C in oxidizing conditions the vapor pressure of PtO₂ is very high leading to vapor phase transport.

Pd slows rate of Pt emission by lowering the vapor pressure.
Regenerative trapping of mobile Pt helps generate Pt-Pd and slow Ostwald ripening.

- PdO traps mobile Pt species
- Excess PdO on the support helps to regenerate Pt-Pd particles
Trapping of mobile species allows catalysts to be regenerated

• Stable atomically dispersed species can be formed via bonding through support oxygen atoms
• During reaction the atomically dispersed species transform into nanoparticles
• The atomically dispersed metal species can be regenerated by high temperature calcination in air
Role of Sn in the Regeneration of Pt/γ-Al₂O₃ Light Alkane Dehydrogenation Catalysts

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Low-temperature carbon monoxide oxidation catalysed by regenerable atomically dispersed palladium on alumina

After CO oxidation

Oxidative treatment in air at 700 °C causes redispersion of the Pd

Calcined at 700 °C
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