Degradation Mechanism of Pd/Zeolite Passive NOx Adsorbers: The Interchange Between Particles & Cations

Yuntao (Kevin) Gu, CLEERS Workshop, Sep 18th, 2020
What do we know about PNAs?

Pd/Zeolites exhibit great low temperature NOx storage capacity and reasonable NOx release temperature
  • Ion-exchanged Pd is responsible for the low temperature NOx storage
What do we know about PNAs?

NOx storage capacity can be maximized by atomically dispersing Pd

- 100% Pd ion-exchange leads to NO:Pd=1:1
What do we know about PNAs?

Pd/BEA irreversibly losses part of the NOx storage capacity when exposed to low temperature CO
- CO exposure leads to the detrimental formation of PdO particles

What do we know about PNAs?

Pd/SSZ-13 degrades similarly as Pd/BEA when exposed to CO during NO-TPD cycles

- CO induced degradation appears to be a universal behavior of Pd/zeolites
Today’s objective

What is the PNA degradation mechanism? How can we stop it?
Experimental Methods & Materials

- **Synthesis**
- **Pretreatment**
- **Simulate exhaust from bypass**
- **Switch from bypass to reactor**
- **Start temperature program**

**Dehydrated**

**Hydrated**

**Reduced**

**Support:** H/SSZ-13 (Si:Al = 9&16) — ACS Material
**Precursor:** Pd(NO$_3$)$_2$·2H$_2$O — Sigma Aldrich
**Solvent:** 28% NH$_4$(OH) — Sigma Aldrich

**Temperature**
- 80 °C: 2hr
- 105 °C: 10hr
- 600 °C: 4hr

**O$_2$** pretreatment (45 min.): 10% O$_2$ balanced by N$_2$, 600 °C
**PNA experiment:** 200 ppm NO, 200 ppm CO, 10% O$_2$, 5% H$_2$O balanced by N$_2$. (GHSV: 60,000 hr$^{-1}$)

**Adsorption Temperature:** 80 °C

**Time (hour)** 0 2 4 6 8 10 12 14 16

**Temperature (°C)** 0 200 400 600

**Concentration (ppm)** 0 50 100 150 200 250 300 350 400 450 500 550 600

**Time (s)** 0 800 1600 2400 3200

**Ramp rate:** 90 °C/min
Difference Between IE100 & IE50
Distinct results of repetitive NOx-TPD profiles

**IE100**: Pd/SSZ-13 – Si:Al=9

**IE50**: Pd/SSZ-13 – Si:Al=16

<table>
<thead>
<tr>
<th>Sample</th>
<th>Support</th>
<th>1&lt;sup&gt;st&lt;/sup&gt; NOx:Pd</th>
<th>4&lt;sup&gt;th&lt;/sup&gt; NOx:Pd</th>
<th>Si/Al</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Nominal</td>
<td>ICP</td>
<td>Target</td>
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<tr>
<td>IE100*</td>
<td>H-SSZ-13</td>
<td>1.05 ± 0.1</td>
<td>0.91 ± 0.1</td>
<td>10</td>
<td>9</td>
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<tr>
<td></td>
<td></td>
<td>1 wt.%</td>
<td>0.84 wt.%</td>
<td></td>
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<tr>
<td>IE50*</td>
<td>H-SSZ-13</td>
<td>0.55 ± 0.1</td>
<td>0.38 ± 0.1</td>
<td>15</td>
<td>16</td>
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<td></td>
<td></td>
<td>1 wt.%</td>
<td>0.79 wt.%</td>
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*EXAFS, H2-TPR and STEM Imaging were employed to characterize the samples studied
Difference Between IE100 & IE50
Distinct results of repetitive NOx-TPD profiles

IE100: Pd/SSZ-13 – Si:Al=9
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Difference Between IE100 & IE50
Distinct results of consecutive CO light-off behavior

IE100: Pd/SSZ-13 – Si:Al=9

IE50: Pd/SSZ-13 – Si:Al=16
CO Oxidation Kinetics
Effect of hydration, NO adsorption and Pd distribution

IE100: Pd/SSZ-13 – Si:Al=9

IE50: Pd/SSZ-13 – Si:Al=16

CO oxidation activity: **Hydrated** Pd cations > **Dry** Pd Cations > **Pd Particles** > **NO adsorbed** hydrated Pd cations
What Happened During NOx-TPD?

Key reactions:

1. \( \text{ZPd}^{\text{III}}(\text{NO})(\text{H}_2\text{O})_3 \rightarrow \text{Z}_2\text{Pd}^{\text{III}}(\text{H}_2\text{O})_4 + \text{NO} \)
   - NO desorption

2. \( \text{Z}_2\text{Pd}^{\text{III}}(\text{H}_2\text{O})_4 \rightarrow \text{Z}_2\text{Pd}^{\text{III}} + 4\text{H}_2\text{O} \)
   - H\text{O} desorption
Reduction of Pd$^{II}$ by CO
How do NOx trapping and CO oxidation affect each other?

IE100 - Si:Al=9
IE50 - Si:Al=16

CO – Temperature programmed reduction

Temperature (°C)

CO$_2$ Concentration (ppm)

Temperature (°C)

Temperature (°C)

Temperature (°C)
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3. $\text{Z}_2\text{Pd}^{\text{II}}(\text{H}_2\text{O})_4 + \text{CO} \rightarrow \text{Pd}^0 + \text{CO}_2 + 2\text{ZH} + 3\text{H}_2\text{O}$
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4. $\text{Pd}^0 + \frac{1}{2} \text{O}_2 \rightarrow \text{PdO}$
   - Pd Re-oxidation

5. $\text{PdO} + 2\text{ZH} \rightarrow \text{Z}_2\text{Pd}^{\text{II}} + \text{H}_2\text{O}$
   - Pd$^{\text{II}}$ regeneration (Protonolysis)
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Reduction and Reoxidation Dynamics
In-situ EXAFS Characterization of Pd/SSZ-13

Preoxidized

1st Shell Pd-O
CN=9.5
d_{Pd}=1.8 nm

Reduced

1st Shell Pd-O
CN=10.8
\textit{d}_{Pd}=4.7 nm

Reoxidized

O\textsubscript{2} @600 °C
O\textsubscript{2} + H\textsubscript{2}O @300 or 500 °C
CO + H\textsubscript{2}O @300 or 500 °C
O\textsubscript{2} @300 or 500 °C

Pd-Pd

500C Preoxidized
500C Reduced
500C Re-oxidized

Pd-O-Pd

300C Preoxidized
300C Reduced
300C Re-oxidized

Radial distance (Å)

k^2 * |\mathcal{F}(R)| (Å^{-3})
Deactivation Mechanism: Particle Agglomeration vs. Protonolysis

Increasing Particle size

Large PdO

Large PdO

Large Pd\(^0\)

Small PdO

Small PdO

Small PdO

Small Pd\(^0\)

Small Pd\(^0\)

Small Pd\(^0\)

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Summary & Conclusions

IE100 - Si:Al=9

IE50 - Si:Al=16

• CO + H₂O lead to the reduction of Pd^{II} and formation of Pd particles

• O₂ can re-oxidize Pd into PdO and regenerate Pd^{II} via protonalysis

• Particle agglomeration and protonalysis are competing reactions during reoxidation

• Only high temperature CO exposure leads to the formation of big PdO particles and irreversible PNA degradation
Proposed Solution
Integration of PNA with DOC

IE100 - Si:Al=9
IE50 - Si:Al=16

DOC – Pt/Al$_2$O$_3$
Proposed Solution
Integration of PNA with DOC

IE100 - Si:Al=9

IE50 - Si:Al=16

\[ \text{DOC} \rightarrow \text{Pt/Al}_2\text{O}_3 \]

<table>
<thead>
<tr>
<th>No. of Cycle</th>
<th>DOC+PNA</th>
<th>PNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>0.7</td>
</tr>
<tr>
<td>2</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>4</td>
<td>0.7</td>
<td>1.0</td>
</tr>
</tbody>
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\[ \text{NOx:Pd Ratio} \]

\[ \text{CO}_2 \text{ Concentration (ppm)} \]

\[ \text{Temperature (°C)} \]

\[ \text{CO conversion (%)} \]

\[ \text{Temperature (°C)} \]

\[ \text{Temperature (°C)} \]
Acknowledgement

Advisor: Bill Epling

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Yu-Ren Chen, Silvia Marino, Ryan Zelinsky, Yuntao(Kevin) Gu, Lai Wei, Natalia Diaz
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4. Pd agglomeration

5. $\text{Pd}^{0} + \frac{1}{2} \text{O}_2 \rightarrow \text{PdO}$
   - Pd Re-oxidation

6. PdO agglomeration

7. $\text{PdO} + 2\text{ZH} \rightarrow \text{Z}_2\text{Pd}^{\text{II}} + \text{H}_2\text{O}$
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