Rational Synthesis and Molecular Level Understanding of Pd/Zeolite Passive NOx Adsorbers (PNA)

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Why is it important to decrease NOx emissions?

- NOx is a very toxic free radical gas
- Causes serious respiratory problems
- Main ingredient in the formation of ground-level ozone
- Contributes to formation of acid rain
- Contributes to global warming

Source: EPA, 2005 (National Emission Trends)
Selective Catalytic Reduction (SCR) Cu/SSZ-13 materials are not active at low temperature.

- SCR catalysts are less active below 200 °C (during cold start and vehicle idle).
- 90% challenge: to remove 90% emissions at 150 °C.
- Solution: Passive NOx adsorber, previous Pd/Zeolite formulations.
Passive NOx adsorber (PNA): NOx storage at low temperature and release at higher temperature

- Our goals for PNA
  - Find the optimal Pd/SSZ-13 preparation route
  - Prepare and characterize well-defined materials
  - Effect of Si/Al ratio
  - Effect of Pd loading
  - Sulfur and aging
  - Understand PNA performance on a molecular level


Materials testing

- **PNA**

  - NOx adsorption tests were conducted in a plug-flow reactor system
  - Powder samples of Pd/Zeolite (120 mg, 60–80 mesh) were loaded in a quartz reactor
  - Flowing gas mixture contained ~200 ppm of NOx and CO, 14% O2, and 3.0% H2O balanced with N2 at a flow rate of 210 and 310 sccm (corresponding to 335 K/h respectively)
  - Concentrations of reactants and products were measured by an online MKS MultiGas 2030 FTIR gas analyzer with a gas cell maintained at 191 °C
  - The gas was flown through the reactor after 10 minutes, and allowed to equilibrate for 10 min at 100 °C, then temperature ramped at 10 °C/min to 650 °C
Performance of IWI 1 wt% Pd/H-Zeolite materials with the same Si/Al ratio 12

- Pd/Zeolite materials are active for PNA
- Pd/BEA and Pd/SSZ-13 are more active than Pd/MFI
- Pd-SSZ-13 has an attractive release temperature
- Effectiveness expressed as NO/Pd ratio < 1: Pd in underutilized and thus not used with maximum efficiency
Lowest NOx storage was observed for the aqueous ion exchanged sample (~0.9 wt% Pd) (NO/Pd=0.43)

NH4/SSZ-13 autoclaved in the presence of Pd showed better NOx storage than the IE sample.

Best NOx storage performance was measured over the incipient wetness impregnated NH4/SSZ-13: NO/Pd ratio increased to 0.87

In that sample, most of the Pd is effectively utilized to store NOx even under wet conditions at elevated temperature
Effect of Si/Al ratio on PNA performance for 1 wt% Pd/SSZ-13 prepared by IWI with NH4-SSZ

<table>
<thead>
<tr>
<th>Si/Al</th>
<th>6</th>
<th>12</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO/Pd</td>
<td>1</td>
<td>0.87</td>
<td>0.31</td>
</tr>
<tr>
<td>Storage (µmol/g)</td>
<td>94</td>
<td>80</td>
<td>29</td>
</tr>
</tbody>
</table>

- Progressive agglomerations of Pd as PdO as Si/Al ratio increases
- PdO is not active for PNA
- Atomically dispersed Pd is the true PNA active species
- In 1 wt% Pd/SSZ-13 with Si/Al=6 potentially all Pd is atomically dispersed and this sample utilizes each Pd atom for PNA storage
EXAFS characterization of 0.1 and 1 wt% Pd/SSZ-13 with Si/Al ratio 6

### Features

- Both 0.1 and 1 wt% Pd show no Pd-Pd contributions
- Pd is atomically dispersed
- Pd$_{1}$O$_{(3\text{-}4)}$ site
- NO$^+$ and Pd(I/II)-nitrosyl dominate upon NO adsorption: electron transfer takes place from NO to Pd(II):
  \[ \text{Pd(II)} + \text{NO} \rightarrow \text{Pd(I)} + \text{NO}^+ \]

- \( \text{Pd}^{2+}(\text{CO})_2 \) dominates upon CO adsorption.

- Pd atomically dispersed monomers next to cationic exchange positions.
DFT calculations for Pd/SSZ-13 and Pd-NO complexes

FTIR of adsorbed NO:
Pd(II) + NO → Pd(I) + NO

<table>
<thead>
<tr>
<th>Str.</th>
<th>$\nu$(L) $^a$</th>
<th>$d$(Pd-L) $^a$</th>
<th>$d$(Pd-O) $^{2+}$</th>
<th>$N_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$^{2+}$</td>
<td>221;222;225</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Pd$^{3+}$</td>
<td>215;218;224;228</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Pd(II)(NO)</td>
<td>1806</td>
<td>180</td>
<td>219;230</td>
<td>0</td>
</tr>
<tr>
<td>Pd$^{2+}$(NO)</td>
<td>1823;1748</td>
<td>196;201</td>
<td>223;236</td>
<td>1</td>
</tr>
<tr>
<td>Pd$^{3+}$(NO)$_2$</td>
<td>1818;1739;1717</td>
<td>201;202;207</td>
<td>238;240</td>
<td>0</td>
</tr>
<tr>
<td>Pd$^{4+}$</td>
<td>206;206;214;214</td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Pd$^{3+}$(NO)</td>
<td>1845</td>
<td>194</td>
<td>218;219;232;233</td>
<td>1</td>
</tr>
<tr>
<td>Pd$^{2+}$(NO)$_2$</td>
<td>1880;1824</td>
<td>197;199</td>
<td>226;226</td>
<td>0</td>
</tr>
<tr>
<td>Pd$^{3+}$(NO)$_3$</td>
<td>1872;1820;1797</td>
<td>202;206;218</td>
<td>228;231</td>
<td>1</td>
</tr>
</tbody>
</table>
Under dry conditions oxygen promotes NO storage via formation of NO$^+$ in cationic positions of SSZ-13
In the presence of water steam (and absence of CO) PNA storage decreases

Cryo HAADF-STEM images for 1 wt% Pd/SSZ-13 Si/Al ratio 6 of (a) unsteamed (b) steamed

- Mild steaming does not cause Pd aggregation
- Decrease in PNA performance is related to $\text{H}_2\text{O}$ competition for the first coordination sphere of Pd(II) with the formation of $[\text{Pd}(\text{II})(\text{H}_2\text{O})_4]^{2+}$ or $[\text{Pd}(\text{II})(\text{OH})_4]^{2-}/[\text{Pd}(\text{II})\text{H}_2\text{O})(\text{OH})_3]^{-}$ aqua complexes
- It prevents facile NO coordination to Pd(II) centers

PNA 1 wt% Pd/SSZ-13 with and without 200 ppm CO in the presence of steam (~3 v%)

- 200 ppm CO in the PNA feed even in the presence of steam improves PNA performance and shifts maximum NOx release peak to the higher temperature

FTIR and DFT provides evidence for selective formation of Pd(II)(NO)(CO) complex: $\text{Pd(II)-NO + CO} \rightarrow \text{OC-Pd(II)-NO}$

- NO binds much stronger than CO to Pd(I/II) due to a different coordination mode: CO binds linearly, NO binds in a bent fashion
- Pd(I)-NO does not bind CO

### Table: Complexes and Bond Distances

<table>
<thead>
<tr>
<th>Structure</th>
<th>$v(L)\text{ cm}^{-1}$</th>
<th>$d(\text{Pd-L})\text{ Å}$</th>
<th>$d(\text{Pd-O})\text{ Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$^{2+}$(CO)(NO)</td>
<td>2145/1822</td>
<td>193/199</td>
<td>213;218</td>
</tr>
<tr>
<td>Pd$^{2+}$(CO)$_2$(NO)</td>
<td>2129;2109/1825</td>
<td>198;198/231</td>
<td>219;220</td>
</tr>
<tr>
<td>Pd$^{2+}$(CO)(NO)$_2$</td>
<td>2145/1865;1811</td>
<td>199/214;214</td>
<td>240;240</td>
</tr>
</tbody>
</table>
How can the performance of PNA materials be maximized without sacrificing Pd efficiency?

Effect of SO₂ on PNA Performance: Essentially no effect

The samples were treated according to the standard SO₂ poisoning protocol: 5 ppm SO₂ in SO₂/10%O₂/N₂ mix for 5 hours at 300 °C
Comparison with materials described in the (patent) literature

- These are the best known PNA materials
- Up to 2 wt% Pd atomically dispersed
- Atomic dispersion is mandatory to utilize each Pd atom
- Previous generations of PNA materials contain agglomerated Pd and thus are not atom efficient
- Sulfur does not significantly affect PNA performance

<table>
<thead>
<tr>
<th>Material</th>
<th>NOx storage</th>
<th>NO/Pd ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 wt% Pd/SSZ-13 Si/Al=11&lt;sup&gt;1,2&lt;/sup&gt;</td>
<td>48 μmoles/g</td>
<td>0.5</td>
</tr>
<tr>
<td>1 wt% Pd/ZSM-5 Si/Al=12&lt;sup&gt;1,2&lt;/sup&gt;</td>
<td>55 μmoles/g</td>
<td>0.6</td>
</tr>
<tr>
<td>1 wt% Pd/BEA Si/Al=14&lt;sup&gt;1,2&lt;/sup&gt;</td>
<td>65 μmoles/g</td>
<td>0.68</td>
</tr>
<tr>
<td>2 wt% Pd/SSZ-13 Si/Al=22&lt;sup&gt;3&lt;/sup&gt;</td>
<td>26 μmoles/g</td>
<td>N/A</td>
</tr>
<tr>
<td>2 wt% Pd/ZSM-5 Si/Al=22&lt;sup&gt;3&lt;/sup&gt;</td>
<td>24 μmoles/g</td>
<td>N/A</td>
</tr>
<tr>
<td>1 wt% Pd/BEA Si/Al=25&lt;sup&gt;4&lt;/sup&gt;</td>
<td>20 μmoles/g</td>
<td>0.2</td>
</tr>
<tr>
<td>Pd/Pt on various Alumina, Ceria and Ceria-Zirconia supports&lt;sup&gt;5&lt;/sup&gt;</td>
<td>10-30 μmoles/g</td>
<td>N/A</td>
</tr>
<tr>
<td>1 wt% Pd/SSZ-13 Si/Al=6&lt;sup&gt;this work&lt;/sup&gt;</td>
<td>94 μmoles/g</td>
<td>1</td>
</tr>
<tr>
<td>1.9 wt% Pd/SSZ-13 Si/Al=6&lt;sup&gt;this work&lt;/sup&gt;</td>
<td>180 μmoles/g</td>
<td>1</td>
</tr>
<tr>
<td>3 wt% Pd/SSZ-13 Si/Al=6&lt;sup&gt;this work&lt;/sup&gt;</td>
<td>250 μmoles/g</td>
<td>0.9</td>
</tr>
</tbody>
</table>


Konstantin Khivantsev, Janos Szanyi, Nicholas Jaegers, Libor Kovarik, Feng Gao, Yong Wang (Provisional Patent)
PNA: Hydrothermal aging effects

- **Hydrothermal aging conditions:** 750 °C in flowing air containing 10% water vapor for 16 hours.

- **Two effects:** (1) always reduces NO\textsubscript{x} storage efficiency of Pd/Zeolite materials. (2) release temperature change. Reduction or removal of the high-temperature NO\textsubscript{2} desorption stage.

- **For 1-3 wt% Pd/SSZ-13 with Si/Al=6 HTA leads to loss of 10 to 20% performance**

- **Why does the performance decrease?**
1 wt% Pd/SSZ-13 Si/Al=6 HAADF-STEM imaging after HTA

- PdO nanoparticles form
- They are relatively large (>20 nm)
- Pd migrates out of the pore and agglomerates
High magnification HAADF-STEM imaging of HTA 1 wt% Pd SSZ-13 Si/Al = 6 sample

Crystal structure is largely preserved

Mesopore formation evident

PNA performance decreases

Decrease in PNA performance is related to the decrease in number of available isolated Pd(II) sites due to their agglomeration into PdO
Upon hydrothermal aging, a large number of $\text{Al}^{3+}_{\text{penta}}$ ions form on both materials (Si/Al=6 and 12).

HTA also results in the broadening of the $\text{Al}^{3+}_{\text{tetra}}$ $^{27}$Al NMR signal, possible due to the significant changes in the environment around these ions.

HTA leads to deterioration of Bronsted acidity and framework Al which are key in stabilizing isolated Pd ions.
Synchrotron high-energy cryo XRD and Pair Distribution Function (PDF) studies on HTA samples

- Synchrotron XRD and PDF have much higher sensitivity than regular XRD and can reveal the formation of minor phases.
- PDF indicates the formation of bulk-like PdO with typical Pd-O, Pd-Pd and Pd-Pd bond distances 203, 307 and 347 picometers, respectively.
- All data on HTA samples thus indicate that changes in PNA are related to dealumination with the following PdO agglomeration on the external area of SSZ-13.
We identified the factors governing performance of Pd/Zeolite materials through extensive characterization and PNA testing.

Ionically dispersed Pd(II) species are active PNA storage species: synthetic pathways to highly loaded 100% dispersed materials are identified with record-high loading of atomically dispersed Pd(II) in small-pore zeolite.

Various PNA storage pathways are identified under different PNA feeds.

CO promotes PNA in the presence of water steam in the PNA feed via formation of Pd(II)(NO)(CO) complex.

HTA effects clarified: water steam causes significant changes in Al (and hence proton) distribution; decrease in Bronsted acidity in the micropore leads to lower stabilization of ionically dispersed Pd(II) species and their sintering into PdO on the external crystal surface.
Acknowledgements

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- Franklin (Feng) Tao group (University of Kansas) EXAFS data
- EMSL, a DOE user facility, located at PNNL.
- CRADA partners (Cummins, Inc. and Johnson Matthey, Inc.)
Thank you!