Bifunctional Catalysts for the Selective Catalytic Reduction of NO by Hydrocarbons

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### Existing Methods of NO\textsubscript{x} Reduction

<table>
<thead>
<tr>
<th>Method</th>
<th>Typical Usage</th>
<th>Disadvantages</th>
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</thead>
<tbody>
<tr>
<td>NO\textsubscript{x} Sorption</td>
<td>Metal oxides in lean adsorption/rich reduction cycles</td>
<td>Limited capacity, Strict engineering controls</td>
</tr>
<tr>
<td>(NOx Traps)</td>
<td></td>
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<tr>
<td>NO\textsubscript{x} Reduction with NH\textsubscript{3}/Urea (NH\textsubscript{3} - SCR)</td>
<td>Metal oxides under lean conditions</td>
<td>NH\textsubscript{3} slippage, NH\textsubscript{3} (urea) storage</td>
</tr>
<tr>
<td>Plasma-Assisted Catalysis</td>
<td>Metal zeolites under lean conditions</td>
<td>Energy requirements of the plasma device</td>
</tr>
</tbody>
</table>

- **Advantages**
  - Hydrocarbon typically already in use on site
  - Can be used in lean-burn conditions
  - Minimal concerns with HC slippage

\[\text{NOx} + \text{HC} \rightarrow \text{N}_2 + \text{CO}_2\]
Catalyst Synthesis

- Prepared from step-wise addition of metal oxide to zeolite form via exchange or impregnation techniques
- CeO$_2$/Cu-ZSM-5 has been explored the most
  - other metals, oxides, and zeolites have similar improvements
  - Metals
    - Co, Ag, Fe, Cr, Y
  - Metal oxides
    - ZrO$_2$, MoO$_3$
  - Zeolites
    - Mordenite, Ferrierite,
    - Y, Beta
Minimal Formation of Side Products

Side Production Formation under Wet Conditions at 300°C

<table>
<thead>
<tr>
<th></th>
<th>Cu-ZSM-5</th>
<th>Forward CeO₂/Cu-ZSM-5</th>
<th>Reverse CeO₂/Cu-ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO Conversion</td>
<td>17.6%</td>
<td>34.8%</td>
<td>64.2%</td>
</tr>
<tr>
<td>NO₂ &amp; N₂O Selectivity</td>
<td>3.8%</td>
<td>0.1%</td>
<td>0.1%</td>
</tr>
<tr>
<td>CO Selectivity</td>
<td>11.0%</td>
<td>0.0%</td>
<td>0.2%</td>
</tr>
<tr>
<td>C₃H₆ Slippage</td>
<td>51.7%</td>
<td>0.6%</td>
<td>0.1%</td>
</tr>
</tbody>
</table>

- New catalysts are extremely selective
- Side product formation and slippages under typical EPA regulations
Technical Accomplishment Summary

• Lowered the temperature for maximum activity by 150 °C.
  - Using propylene.

• Improved the water stability from unstable in water to needing water for maximum activity.

• Drop-in replacement for existing NH3 SCR systems

• Optimized the individual reaction steps for maximum overlap
  - \( \text{NO} + \frac{1}{2} \text{O}_2 \rightarrow \text{NO}_2 \)
  - \( \text{HC} \rightarrow \text{HC (surface)} \)
  - \( \text{HC (surface)} + \text{NO}_2 \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O} \)

• Poster
Diesel Applications
Challenges in Moving to Diesel Reductant

- Lower reaction temperature
  - Optimized at 350°C
- Extended temperature range
  - Peaks at 350°C
- Use of diesel (or diesel derived hydrocarbons) as source of reductant
- Improved conversion at higher space velocity
- Higher O₂ content
  - Perhaps most problematic.
Diesel Composition Very Different from Pure Olefin

- High concentration of paraffins >75%
- Moderate concentration of aromatics
- No OLEFINS!!!
Effect of $O_2$ on HC-SCR with Hexane ($n$-$C_6$)

- While overall activities improve with lower $O_2$ concentration, still negatively affected by water
Addition of C₆ Olefin Greatly Improves Activity with No Side Products

![Graph showing conversion percentage vs. temperature with different reductant ratios.](image-url)
JP-8 vs. Low Sulfur Diesel

Ultra Low S Diesel – BP15

- API Gravity: 37.5
- Total Sulfur: 15 ppm
- Aromatics: 29.0%
- Olefins: 0.9%
- Saturates: 70.1%

JP-8 Fuel – Chevron Phillips

- API Gravity: 46.9
- Total Sulfur: 6 ppm
- Aromatics: 14.4%
- Olefins: 1.1%
- Saturates: 84.5%
DeNO$_x$ Reactor System

- Reactor conditions:
  - 40,000 Hr$^{-1}$ SV
  - 1000 ppm NO
  - 1000 ppm HC
    - 17% Aromatics
    - 13% C$_9$ and smaller
  - 2% O$_2$ (A/F = 16.9)
  - 10% H$_2$O
- Detectors allow quantification of NO$_2$, N$_2$O, and CO
JP-8 as a Reductant w/ and w/o H₂O
HC-SCR Mechanism

NO + O₂ → NO₂ 
(NO activation) 
(requires reducible sites)

CₓHᵧ + NO₂ → CO₂ + N₂ + H₂O 
(HC-SCR)

CₓHᵧ + O₂ → CO₂ + H₂O 
(HC oxidation) 
(very fast)

• Bifunctional catalyst needed to oxidize HC with NO₂ before O₂ oxidation
Additive Increases Low Temperature Activity But Does Very Little at the High End
Effect of JP-8 Reductant with Catalyst Additive

![Graph showing the effect of JP-8 reductant with and without oxidation additive on conversion percentage vs. temperature. The graph indicates a significant increase in conversion with the oxidation additive at certain temperatures, labeled as NO₂ Breakthrough.]
In Situ XAS shows no Cu(0) under reaction conditions
Additive promotes two electron Cu(II) → Cu(0)
Conclusions

• Paraffinic hydrocarbons are ineffective as reducing agents
  - Addition of small amounts of olefins helps
• **JP-8 (diesel) is effective**
  - Due to high aromatic content
  - Extends high temperature range up to 450 °C
• **Oxidation promoter lowers the overall activity**
  - Promotes NO $\rightarrow$ NO$_2$ reaction
  - Adversely effects the Cu
    - $Cu(II) \rightarrow Cu(0)$
• **No evidence yet of sulfur poisoning**
**Plans for further catalyst development**

- Further investigation of alternate reductants
- Change ion exchange metal
  - *Mixed metal systems*
- Improved additive phase
- Wider pore zeolites
- Alternate conditions
  - *Diesel & natural gas engines*
- Systems approach
  - Argonne on-board reformer
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