Selective reduction of NOx in oxygen rich environments with plasma-assisted catalysis: Catalyst development and mechanistic studies

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Talk Outline

• Introduction
  • Plasma-facilitated catalysis for NOx reduction
  • Active catalysts
  • What is the plasma doing?

• Catalyst synthesis and reactivity
  • What is the optimum catalyst composition?
  • Some optimization of catalyst synthesis

• Studies of the reaction mechanism
  • Differences in rates of the back reaction (NO₂ to NO) on different catalysts
  • Concept of the Cascade Reactor
This Technology is Hydrocarbon SCR with a Plasma “Reformer”

Schematic of Two Step Discharge/Catalyst Reactor

Exhaust Gas: NO, HC’s, etc.  →  Discharge Volume → Catalyst Volume → N₂, N₂O, CO₂, etc. → To exhaust

Reformed Exhaust

Electrical Power

DEER Workshop, August 24-28, 2003
Modeling of the Gas-Phase Plasma Reaction Mechanisms

- Under lean-burn engine exhaust conditions, a non-thermal plasma is oxidative.
  - A primary reaction is conversion of NO -> NO₂
  - The oxidation of NO in a NTP is promoted by added hydrocarbon.
  - Added hydrocarbon is partially oxidized, and aldehydes are a crucial product as they are most reactive as reductant for NOx.
  - *Thermal* catalytic reaction of aldehydes + NO₂ yield activities of >90% for reasonable flow rates.
  - Understanding the products of exhaust ‘reforming’ by the plasma has guided catalyst development efforts.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NO(_x) removal, %</th>
<th>Temperature, °C</th>
<th>Space velocity, hr(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO(_3)</td>
<td>No activity</td>
<td>180</td>
<td>12,000</td>
</tr>
<tr>
<td>Al(_2)O(_3) (active at higher temp.)</td>
<td>20</td>
<td>200</td>
<td>12,000</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>No activity</td>
<td>180</td>
<td>12,000</td>
</tr>
<tr>
<td>HZSM-5, HBeta</td>
<td>No activity</td>
<td>180</td>
<td>12,000</td>
</tr>
<tr>
<td>CuZSM-5</td>
<td>15-20</td>
<td>180</td>
<td>12,000</td>
</tr>
<tr>
<td>CaY</td>
<td>54</td>
<td>200</td>
<td>12,000</td>
</tr>
<tr>
<td>NaY</td>
<td>60-65</td>
<td>180</td>
<td>12,000</td>
</tr>
</tbody>
</table>

Subsequently, we have developed alkali- and alkaline earth-exchanged zeolite-Y catalysts for plasma-assisted NOx reduction.

Panov, et al., SAE 2001-01-3513
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What is the optimum cation substitution into Zeolite-Y?

Y-Zeolites are Crystalline Silica-Alumina Materials with 3-D Pore-Structures

- Cations compensate charged sites in zeolite present due to Al substitution.

\[
\text{Zeolite} \quad \overset{\text{Solution}}{\begin{array}{c}
\text{Na}^+ \\
\text{Ba}^{2+} + 2\text{NO}_3^- \\
\text{2Na}^+ + 2\text{NO}_3^- \\
\end{array}}
\]
Catalyst Synthesis by Ion Exchange

Ion exchange solution

Ex) 0.5 M solution of LiNO₃, KNO₃, CsNO₃ etc

2 ~ 4 times

Base zeolite

Ex) NaY(CBV100)

RT, >24 h

Stirring

DI water,
5 ~ 7 times

Filtering/Washing

100°C, air

Drying

Air, 500°C, 4 h

Calcination

(Me-Y, FAU)

(M = Li⁺, K⁺, Cs⁺ etc)
**Experimental Procedure and Apparatus**

**Catalyst**  
**Volume**  
**Analysis**

**Simulated Exhaust**

**Discharge Volume**

**Catalyst Volume**

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**Gas composition**  
(flow ~ 12,500 hr⁻¹)

- C₃H₆ – 525 ppm (C:N ~ 6)
- NO – 250 ppm
- Oxygen – 9%
- H₂O – 2%
- N₂ - balance

Reaction rates were measured at ‘steady-state’ to assure that NOx ‘reduction’ is not due to adsorption.

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**Plasma Power**

- ~ 10 Joules/liter

**Analysis**

- Chemiluminescent NOx Analyzer
Comparison of Alkali- and Alkaline Earth-Exchanged Na-Y

- Alkaline earth-exchanged catalysts are generally more active than alkali metal-Y materials.
- Ba-Y is most active and has high activity over a wide-temperature range.
Alkali- and Alkaline Earth-Substituted Zeolite Y: Activity variation vs ionic radius

* TOF = # of NOx converted/supercage•sec • 100000
** Alkali and alkaline earth 2-2 base
Activity is a monotonic function of Ba substitution for Na

Activity of Ba$^{2+}$ and Na$^+$ sites is simply additive
Some optimization of catalyst synthesis:

The role of calcination and its effect on catalytic activity

Catalyst Synthesis by Ion Exchange

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**Base zeolite**

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- 100°C, air

**Calcination**

- Air, 500°C, 4 h

**Me-Y, FAU**

(M = Li$^+$, K$^+$, Cs$^+$ etc)

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Ba$_{2+}$ ion-exchange – no intermediate calcination

Aqueous ion exchange solutions contained an excess of Ba$^{+2}$.

A single solution ion exchange was sufficient to ‘saturate’ the zeolite with Ba.
• Again, the aqueous ion exchange solutions contained an excess of Ba$^{+2}$.

• Each solution ion exchange was followed by a calcination step.

• Solid state cation exchange?

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For mechanistic insight, compare NO$_2$ conversion rather than NO conversion.

NO $\rightarrow$ NO$_2$ (in the plasma)
NO$_2$ $\rightarrow$ N$_2$, N$_2$O, HCN, etc. (over the catalyst)
NO$_2$ $\rightarrow$ NO (over the catalyst – different site?)

Tonkyn, Kwak, Szanyi, and Peden – in preparation
While virtually all NO$_2$ is reacted over alkaline earth zeolite-Y, a considerable fraction does not react over alkali-Y catalysts.

These differences suggest a significant difference in the reaction mechanism over these two classes of catalysts.
FTIR and TPD indicate much weaker adsorption of NO$_2$ on NaY relative to BaY

NO$_2$ TPD of NaY and BaY2-2
* Normalized based on the chemisorption amount

FTIR of NO$_2$ adsorbed on NaY and BaY2-2 during evacuation
NOx Conversion Chemistry

• **Fate of Nitrogen:**
  • NO $\rightarrow$ NO$_2$ $\rightarrow$ N$_2$ + N$_2$O + HCN + NO

• **Fate of Carbon:**
  • C$_3$H$_6$ $\rightarrow$ CH$_2$O + CH$_3$CHO + CO + CO$_2$
    + CH$_3$OH + C$_3$H$_6$

• **After Treatment by Plasma and Catalyst:**
  • > 50% propene remains
  • NOx is mainly NO again
New Multi-Step, “Cascade” System Design Achieves 90% NOx Conversion Target with NaY Catalyst!!

- Patent filed, 9/01.
- Modeling has provided insight into optimum system design for obtaining maximum NOx reduction concurrent with minimum fuel economy penalty.

R.G. Tonkyn and S.E. Barlow, SAE 2001-01-3510
S.E. Barlow, et al., SAE 2001-01-3509

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Summary and Conclusions

• Y-zeolites and alumina are very active for plasma-facilitated NOx reduction in different temperature ranges. NOx conversion levels of greater than 90% are achievable.

• The plasma reactor performs NO oxidation to NO$_2$ with chemistry that is coupled to partial hydrocarbon oxidation.

• Aldehydes, produced in the plasma, are excellent reductants for the *thermal catalytic* reduction of NOx over zeolite Y-based catalysts.

• Ba-Y catalysts are the most active with the widest temperature “window”. Improved catalyst synthesis procedures have been developed.

• Mechanistic studies point to some clear differences for the alkali- and alkaline earth-zeolite Y catalysts, especially with respect to the strength of NO$_2$ adsorption.
NOx emission control is a challenge in “lean-burn” engines

- Current “3-way” catalytic converters that use precious metal (Rh) for NOx reduction are ineffective for fuel-efficient ‘lean-burn’ engines.

New technologies for NOx reduction use oxides

- Ammonia (urea) selective catalytic reduction has been used for some time for “stationary” sources (e.g., power plants).
- NOx adsorbers based on barium oxides with “lean-rich” cycles.
- Reports of new zeolite oxide-based lean-NOx catalysts first appeared in 1990.
- Hybrid plasma-catalytic processes for NOx removal using alumina- and zeolite-based catalysts have been studied since the mid-1990’s.

• Reports in the literature claim many compounds for NOx reduction in conjunction with a plasma. Meaningful data is shown for only one of these compounds (Al₂O₃).
  – Co₂O₃, Fe₂O₃, CuO, Al₂O₃, TiO₂, ZrO₂, ZnO, Y₂O₃, MgO, Pt/SiO₂, SO₄/TiO₂, SO₄/ZrO₂, AlPO₄, NiSO₄/SiO₂, ZnCl₂/SiO₂, H-ZSM-5, H-Y, H-Mordenite, Na-ZSM-5, Cu-ZSM-5, BaTiO₃, SrTiO₃; perovskite, spinel, ilminite; Co, Cr, Cu, Ni, V, Pt/Al₂O₃, Pd/Al₂O₃Rh, Rh/ZnO₂, Fe₂O₃, Fe₃O₄; a ceramic, zeolite or perovskite with a coating of CuO or BaO, ZSM-5; oxides of V, Ti, W; and Pb or Ba niobate, titanate or zirconate.

• In general claims fall in several categories of materials: high dielectric constant materials, base metals, noble metals with known 3-way activity, zeolites with lean NOx reduction activity, and ammonia SCR catalysts.
Experimental Reactor

Tube Array Reactor (TAR)
Ion Exchange of Cations in Zeolites

Zeolite

\[
\text{Na}^+ \quad \text{Si} \quad \text{O} \quad \text{Al}^- \quad \text{Si} \quad \text{O} \quad \text{Si} \quad \text{O} \quad \text{Al}^- \quad \text{Si} \quad \text{O} \\
\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O}
\]

Solution

\[
\text{Ba}^{2+} + 2\text{NO}_3^- 
\]

\[
2\text{Na}^+ + 2\text{NO}_3^- 
\]
Faujasite Zeolite Structure and Ion Exchange Sites

JPC B 103, 8283 (1999)
NaY batch effect – A Caution!

16% lower activity in second batch of Na-Y!

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Is there ‘synergy’ between Na and Ba?

Ba exchange levels controlled by limiting Ba$^{+2}$ concentration in the ion exchange solution

Effect of varying $\text{Ba}^{2+}/\text{Na}^+$ ratio

* Sample label: based on solution concentration

![Graph showing NOx conversion (%)](image)

- NaY
- 25%Ba-NaY
- 44%Ba-NaY
- 59%Ba-NaY
- 62%Ba-NaY
- BaY2-2
- Ba-Y(1-1)
What is the plasma doing?

Panov, Tonkyn, Balmer, Peden, Malkin, and Hoard – SAE 2001-01-3513
• In the presence of unsaturated hydrocarbons, the primary reaction is oxidation of NO by the peroxo radicals leading to aldehyde production.

Plasma treatment of simulated exhaust

Other input gases included 2% H₂O and 8% O₂ with a N₂ balance.

<table>
<thead>
<tr>
<th>Plasma power</th>
<th>NO/NO₂, ppm</th>
<th>C₃H₆, ppm</th>
<th>CH₂O, ppm</th>
<th>CH₃CHO, ppm</th>
<th>CO/CO₂, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>off</td>
<td>210/5</td>
<td>660</td>
<td>0</td>
<td>0</td>
<td>0/0</td>
</tr>
<tr>
<td>40 J/l</td>
<td>0/175</td>
<td>425</td>
<td>120</td>
<td>160</td>
<td>90/55</td>
</tr>
</tbody>
</table>
Role for Partially Oxidized Hydrocarbons

- Penetrante, et al., SAE 982508 – “For some catalysts, the partially oxygenated hydrocarbons [formed in a plasma reactor] are much more effective compared to the original hydrocarbons in reducing NOx to N₂.”

- Tonkyn, et al., SAE 2000-01-2896 – “NOx reduction over NaY is more efficient with one or more partially oxidized propylene products than with propylene itself.”

  - $\text{NO} + \text{Propylene} + \ldots \rightarrow \text{plasma-catalyst} \rightarrow \sim55\% \text{ NOx Conversion}$
  - $\text{NO}_2 + \text{Propylene} + \ldots \rightarrow \text{catalyst only} \rightarrow \sim25\% \text{ NOx Conversion}$
**Fate of aldehydes over a zeolite catalyst**

- Input Gas ($S/V \sim 12,000 \text{ hr}^{-1}$)
  - 200 ppm NO
  - 500 ppm $C_3H_6$
  - 7.5:1 C:N ratio
  - 2% $H_2O$
  - 8% $O_2$
  - 400 ppm CO
  - 7% $CO_2$
  - $N_2$ Balance
  - 15 J/L

<table>
<thead>
<tr>
<th></th>
<th>NOx conversion to $N_2$, %</th>
<th>$CH_2O$ ppm</th>
<th>$CH_3CHO$ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma</td>
<td>0</td>
<td>55</td>
<td>75</td>
</tr>
<tr>
<td>Plasma and NaY</td>
<td>50</td>
<td>55</td>
<td>15</td>
</tr>
</tbody>
</table>

**Discharge Volume** → **Catalyst Volume** → **Analysis**
Experimental Procedure and Apparatus

Gas composition (flow ~ 12,000 hr⁻¹)
- HC – varying type and amount
- NO – 200 ppm
- Oxygen – 8%
- H₂O – 2%
- N₂ - balance

Reaction rates were measured at ‘steady-state’ to assure that NOx ‘reduction’ is not due to adsorption.

Analysis
- CLA
- FTIR

Catalysts
- Ba-zeolite Y
NOx Reduction with Acetaldehyde versus Temperature (no plasma!)

**Gas composition**
- CH$_3$CHO – 500 ppm
- NO$_x$ – 200 ppm
- Oxygen – 8%
- H$_2$O – 2%
- N$_2$ – balance

**Gas flow**
- 12,000 hr$^{-1}$

**Catalyst**
- Ba-zeolite Y

C:N ratio ~ 5
Higher aldehydes equally active on a C1 basis

Gas composition
- NO₂ – 200 ppm
- Oxygen – 8%
- H₂O – 2%
- N₂ – balance

Gas flow
- 12,000 hr⁻¹

Temperature
- 240 °C

Catalyst
- Ba-zeolite Y

C:N ratio ~ 5
Plasma-catalysis activity and NO$_2$ TPD of alkaline-earth exchanged zeolites

Activity correlates with higher-T NO$_2$ TPD feature.
NOx emission control is a challenge in “lean-burn” engines

- Current “3-way” catalytic converters that use precious metal (Rh) for NOx reduction are ineffective for fuel-efficient ‘lean-burn’ engines.

New technologies for NOx reduction use oxides

- Oxides are being used as NOx adsorbers in another ‘lean-burn’ engine NOx control technology.
- Reports of new zeolite oxide-based lean-NOx catalysts first appeared in 1990.
  - Early on, it became quite evident that the mechanism for NOx reduction on oxides was considerably different that what had been established to occur on metal surfaces.


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NOx reduction mechanism on oxide-based catalysts does not involve N-atom recombination.

For oxide-based NOx emission control, the nature of the active adsorbed NOx species is important but difficult to determine.
NO$_2^+$ CH$_3$CHO on Na-Y, FAU at 473K

a: t=0 (300K)  e: t=15min. (473K)  f: 5min. evacuation (300K)
Proposed Reaction Mechanism

\[
\text{ZeO}^{\cdots}\text{NO}^+\ \text{NO}_3^-\text{Na}^+ + \text{CH}_3\text{CHO} \rightarrow \text{ZeO}^{\cdots}\text{NO}^+\cdot\text{O=CHCH}_3\ \text{NO}_3^-\text{Na}^+
\]

\[
\{\text{O=N\cdotsO=CHCH}_3\}\text{Na}^+ \rightarrow \text{CH}_3\text{NO}_2 + \text{CO}_2 + \text{HONO} + \text{CH}_3\text{NO}
\]

\[
\text{HCNO} \rightarrow \text{HCN} \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O}
\]

\[
\text{HNCO} \rightarrow \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O}
\]