Development of a Durable Low-Temperature Urea-SCR Catalyst for CIDI Engines

by

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Ceramic Processing & Inorganic Materials

Diesel Engine Emission Reduction Conference

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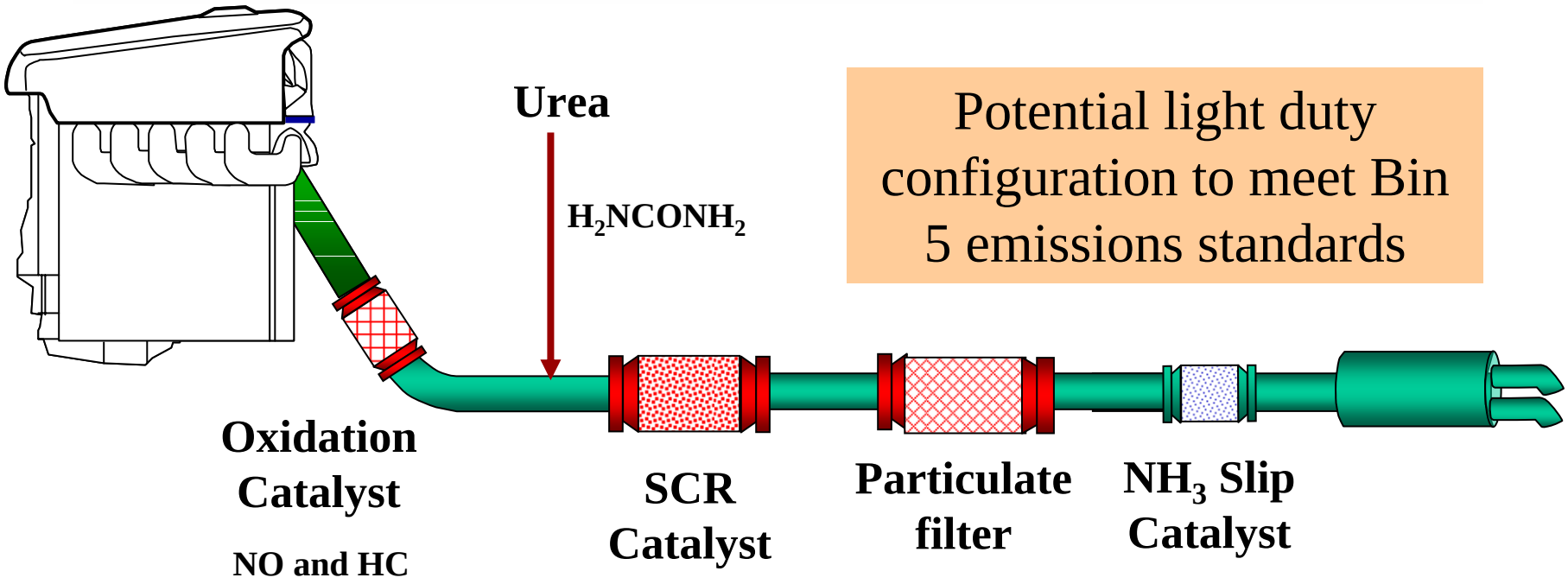
Diesel Emissions Control



Potential light duty configuration to meet Bin 5 emissions standards

$$4\ NH_3 + 4\ NO + O_2 \longrightarrow 4\ N_2 + 6\ H_2O \quad \text{(medium)}$$

$$4\ NH_3 + 2\ NO + 2\ NO_2 \longrightarrow 4\ N_2 + 6\ H_2O \quad \text{(fast)}$$

Take advantage of faster kinetics to increase conversion and expand temperature window

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Catalyst Development Issues

- High Selectivity
  - $NH_3 + NO_x + O_2 \longrightarrow N_2 + H_2O$
    - X $\dashrightarrow$ $N_2O + H_2O$
- Urea Decomposition to NH_3
  - $NH_2\text{-}CO\text{-}NH_{2(l)} \longrightarrow NH_3 + HNCO$
  - $HNCO + H_2O \longrightarrow NH_{3(g)} + CO_2$
- Minimize Competing Reactions
  - *Low T:* $2NH_3 + 2NO_2 \longrightarrow NH_4NO_3 + N_2 + H_2O$
  - *High T:* $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$
  - $4NH_3 + 4NO + 3O_2 \longrightarrow 4N_2O + 6H_2O$

Typical Experimental Conditions

Temperature (°C)	450-125
NO (ppm)	280-175
NO_2 (ppm)	70-175
NH_3 (ppm)	350
O_2 (%)	14
CO_2 (%)	5
H_2O (%)	4.6
GHSV (h^{-1})	30,000-140,000

20% NO_2 simulates cold-start conditions

- NH_3:NO_x in the feed is 1:1
- Powder catalysts diluted 1:1 with cordierite
- 450 – 125 °C decreasing, 30 minute isothermal holds
- NO_x conversion (%) defined as:

$$100 * \left(1 - \left[\frac{NO_{(out)} + NO_{2(out)}}{NO_{(in)} + NO_{2(in)}}\right]\right)$$

- N_2O selectivity (%) defined as: $\mathbf{N_2O / (N_2O + N_2)}$

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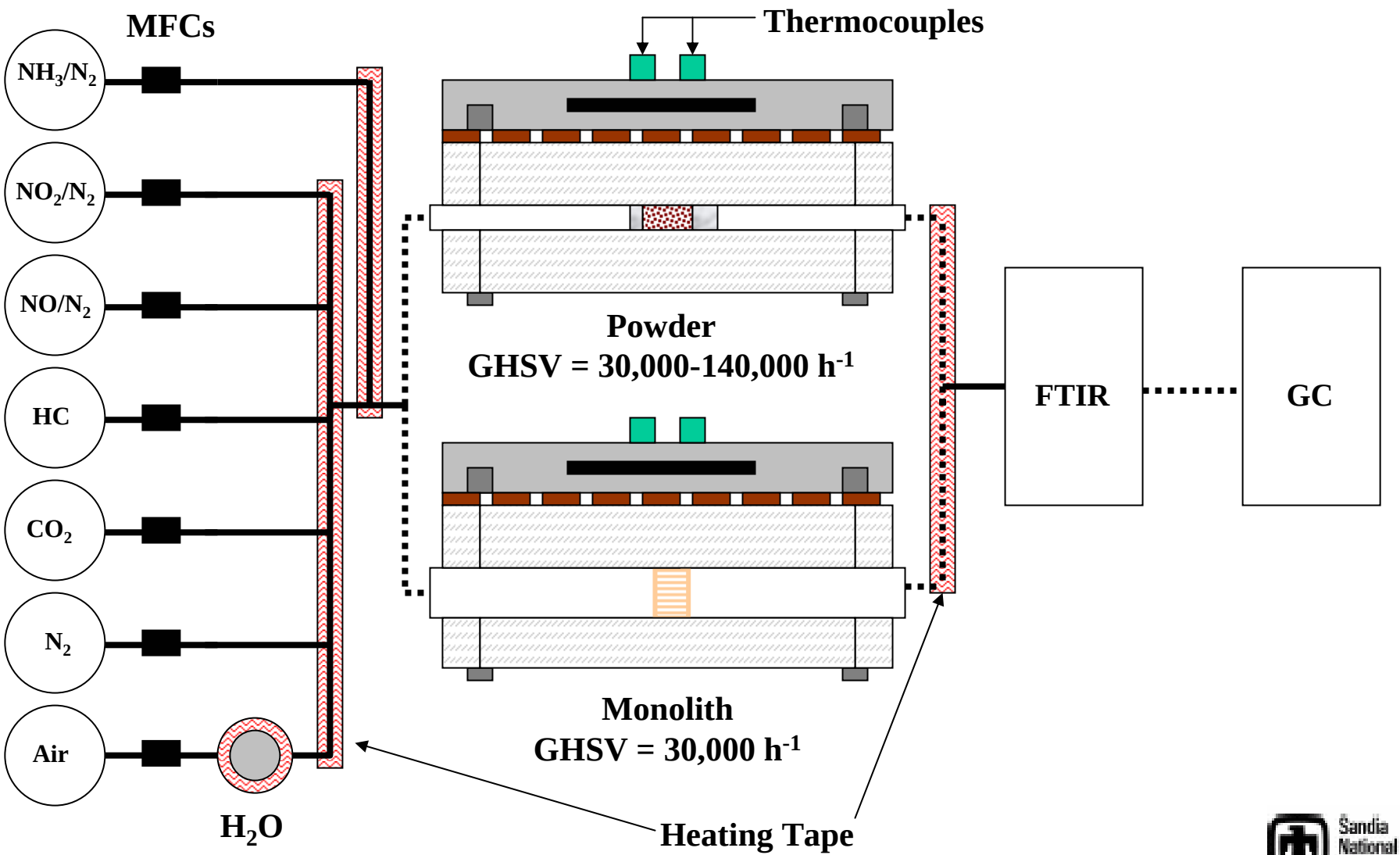
LEP Staged Testing Protocol

Catalyst performance evaluated:

1. Fresh, using stated typical experimental conditions
2. Fresh, as a function of NO:NO_2 ratio
   - 100% NO to 100% NO_2
3. After hydrothermal aging
   - 16 hours at typical experimental conditions at **600°C***, 700°C, and 800°C
4. After sulfur aging
   - 20 ppm SO_2 at **350°C*** or 670°C at typical experimental conditions (minus NH_3) for **24*** and 48 hours

* Items in **bold** represent minimum performance requirement

Experimental Apparatus



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Hydrous Metal Oxide Synthesis

- Hydroxide Addition

  Ti-alkoxide + Si-alkoxide + NaOH $\xrightarrow[\text{Methanol}]{}$ soluble intermediate

- Hydrolysis

  soluble intermediate $\xrightarrow[\text{Water}]{\text{Acetone}}$ $NaTi_2O_5H\downarrow$

- Acidification and Ion Exchange

  $M^{n+} + n\ NaTi_2O_5H \longrightarrow M(Ti_2O_5H)_n + n\ Na^+$

- Impregnation $\longrightarrow$ incipient wetness (powder)

- Activation/Pretreatment (600°C in air for 4 h) $\longrightarrow$ **Catalyst**

- Monolith

  Catalyst + Al_2O_3 + H_2O + grinding $\longrightarrow$ slurry

  slurry + monolith $\xrightarrow[\text{425°C in air for 4 h}]{}$ final monolith

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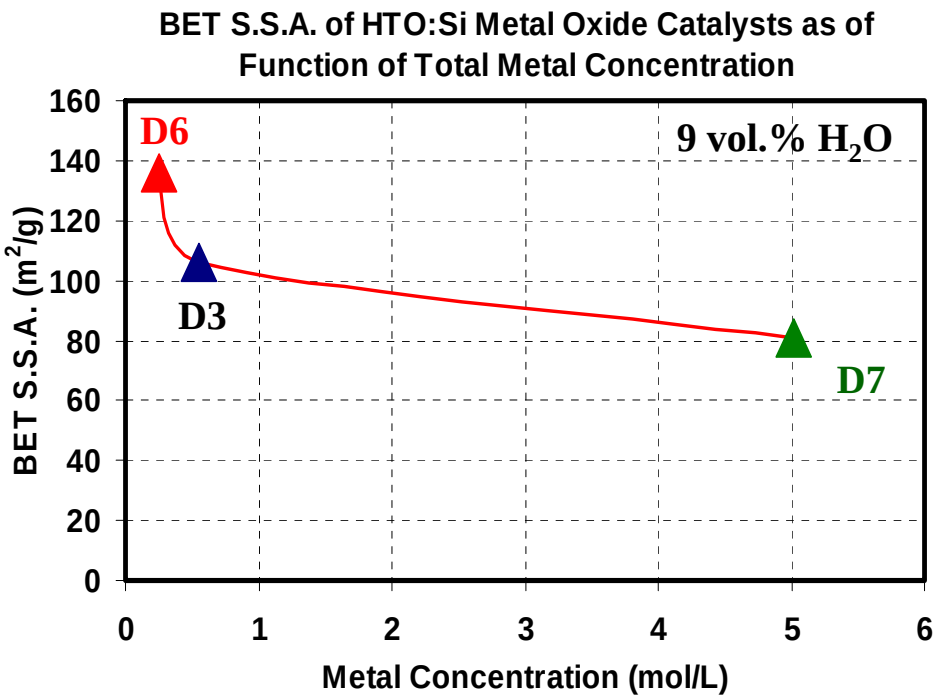
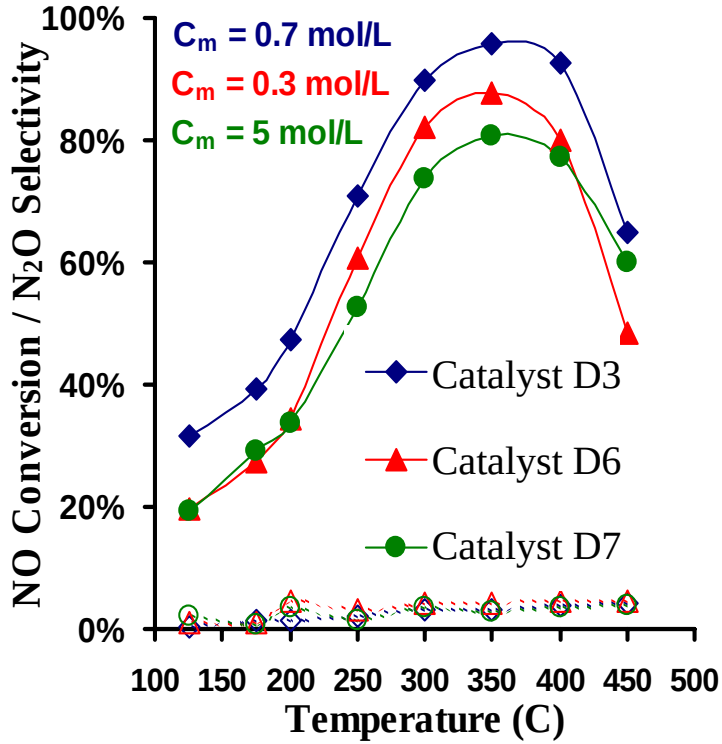
Effect of Synthesis Conditions on S.S.A.





- Less concentrated hydrolysis solution increases resulting surface area by 30%
- May be attributed to slower rate of hydrolysis from decreased metal concentration
- Similar results seen with supports only
- No linear relationship between catalytic activity and surface area
- All samples were calcined at 600°C in air and degassed at 400°C for 14 h

Powders

1:1

20% NO_2

140,000 h^{-1}

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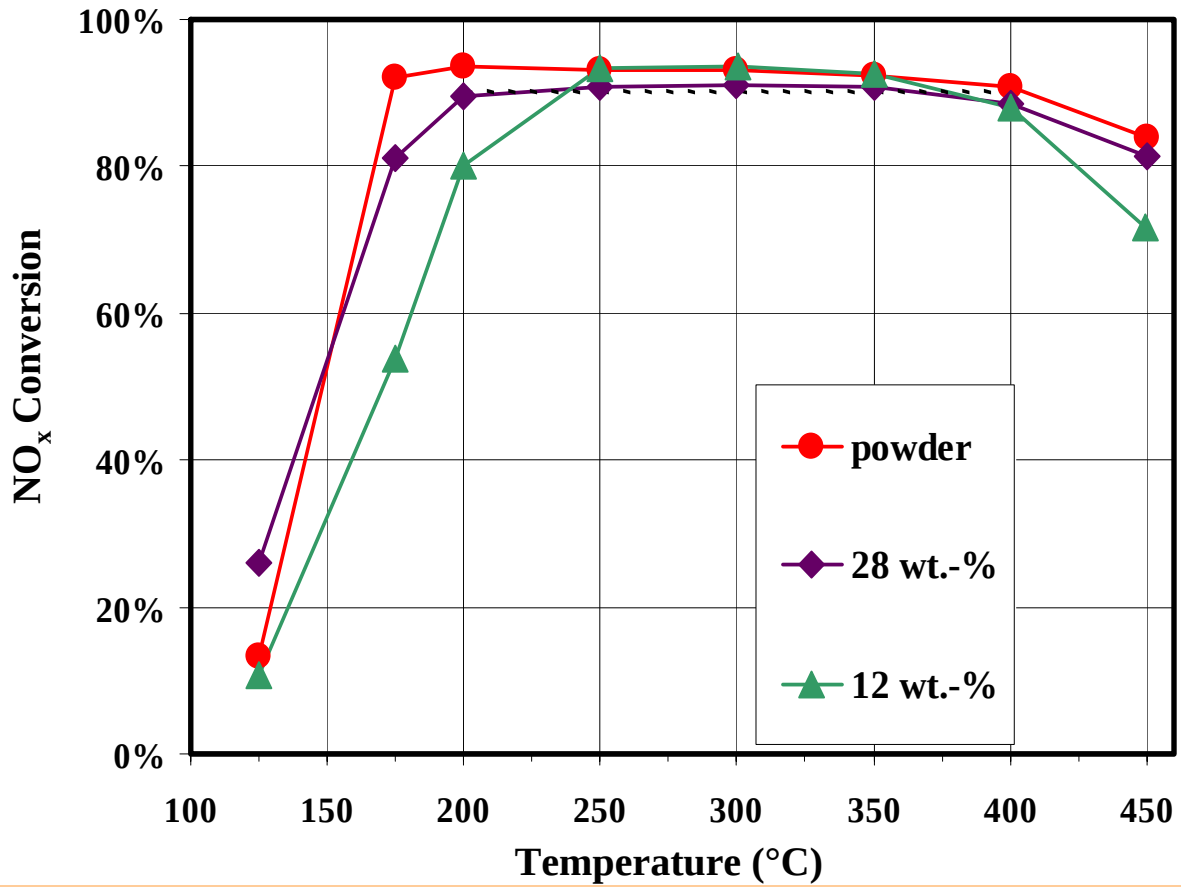
Comparison of Monolith and Powder Data



Powder
1:1
50% NO_2
140,000 h^{-1}

Monoliths
50% NO_2
30,000 h^{-1}

- Powders tested at high SV to simulate the contact time of 25 wt.-% catalyst on monolith
- High-loaded monoliths (>16 wt.-%) approach powder performance

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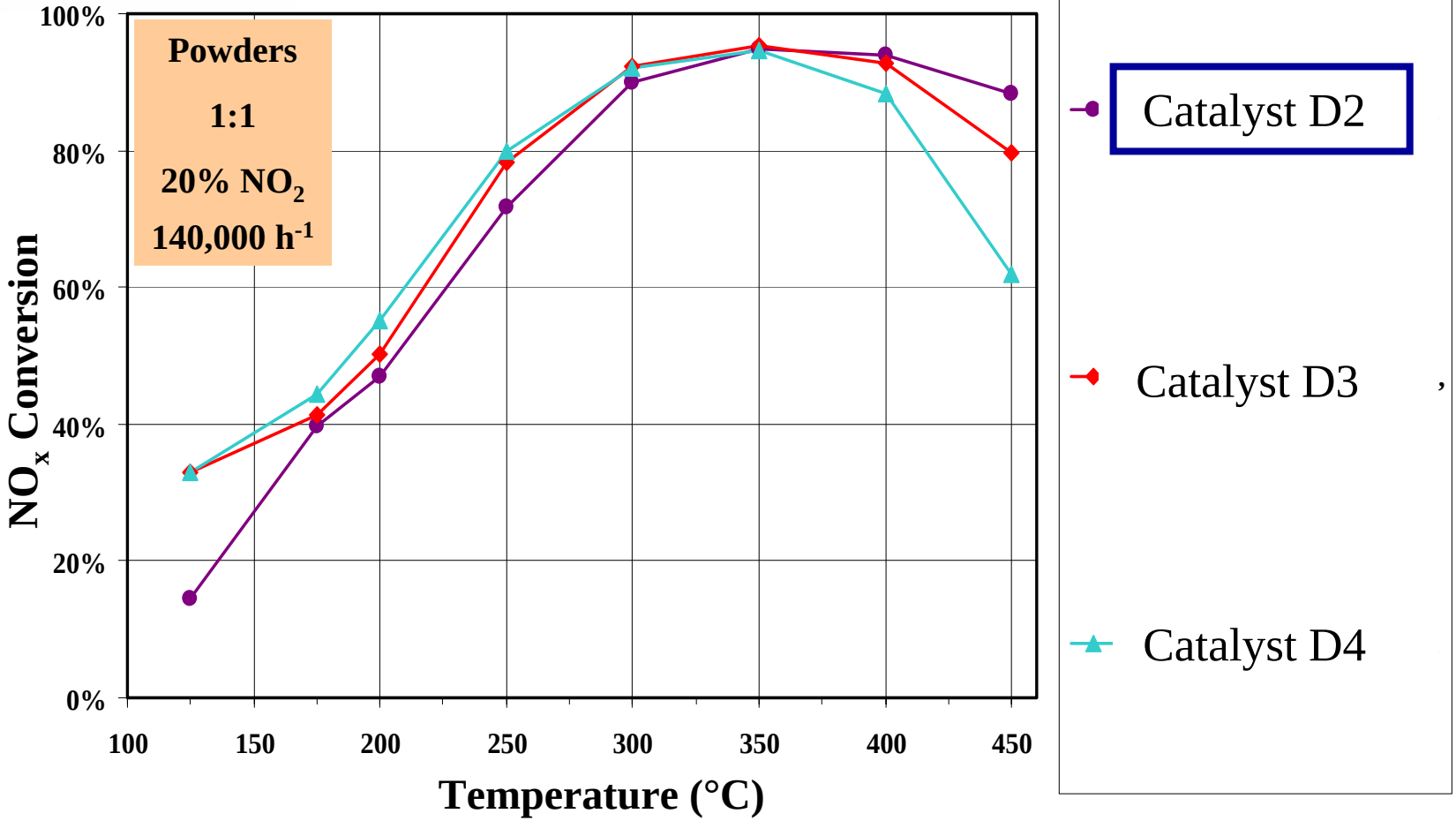
Optimization of Catalyst Composition



- Change concentration of same two components
- Have the ability to tune catalytic performance
  - tradeoffs in low and high temperature activity

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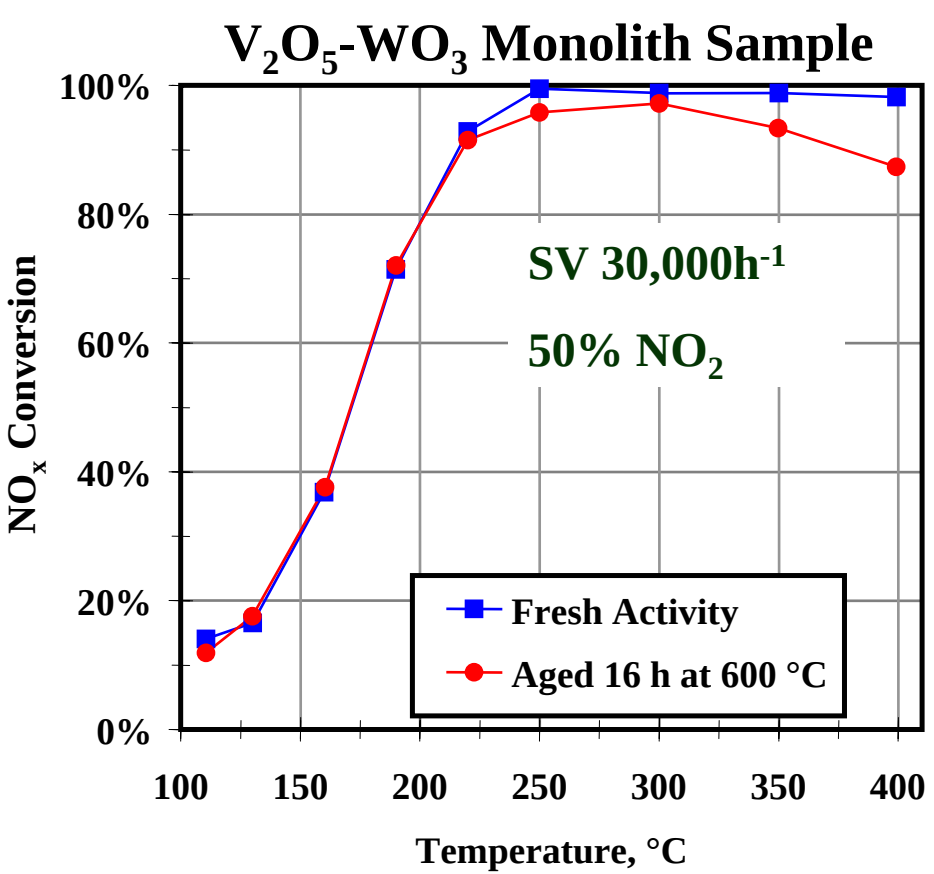
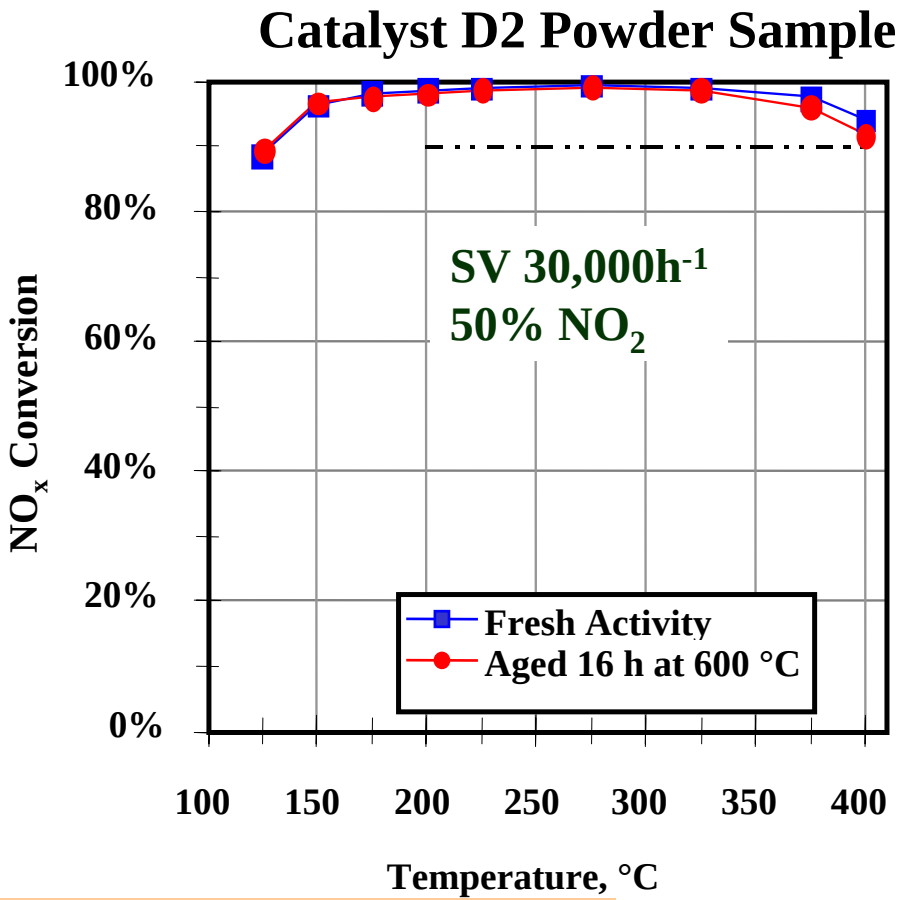
Hydrothermal Treatment





- Minor loss in activity after short term hydrothermal treatment
- More relative activity retained with D2
- Hydrothermal treatment at feed concentration (4.6% H_2O)

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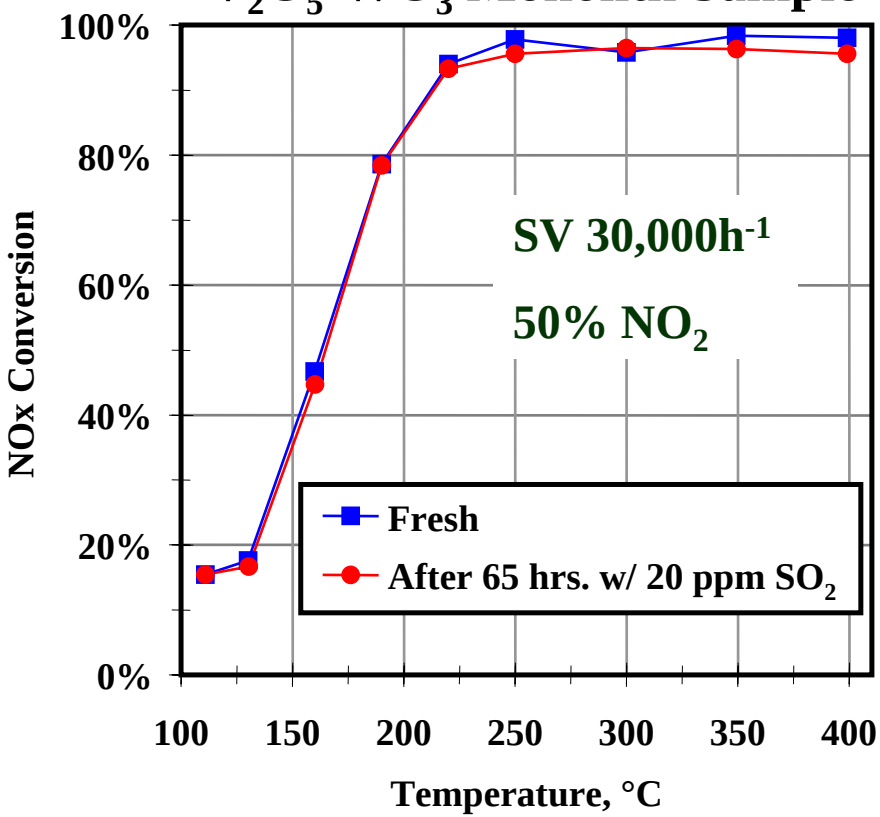
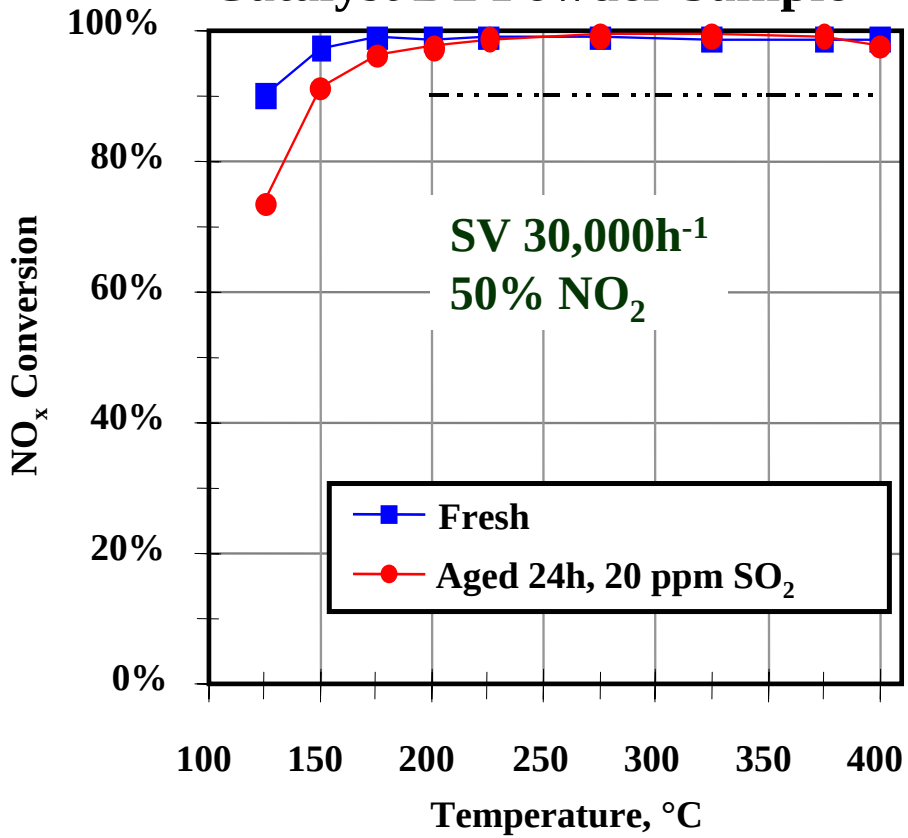
SO_2 Tolerance





- SO_2 Aging At 350 °C without NH_3
- Some loss in low temperature activity

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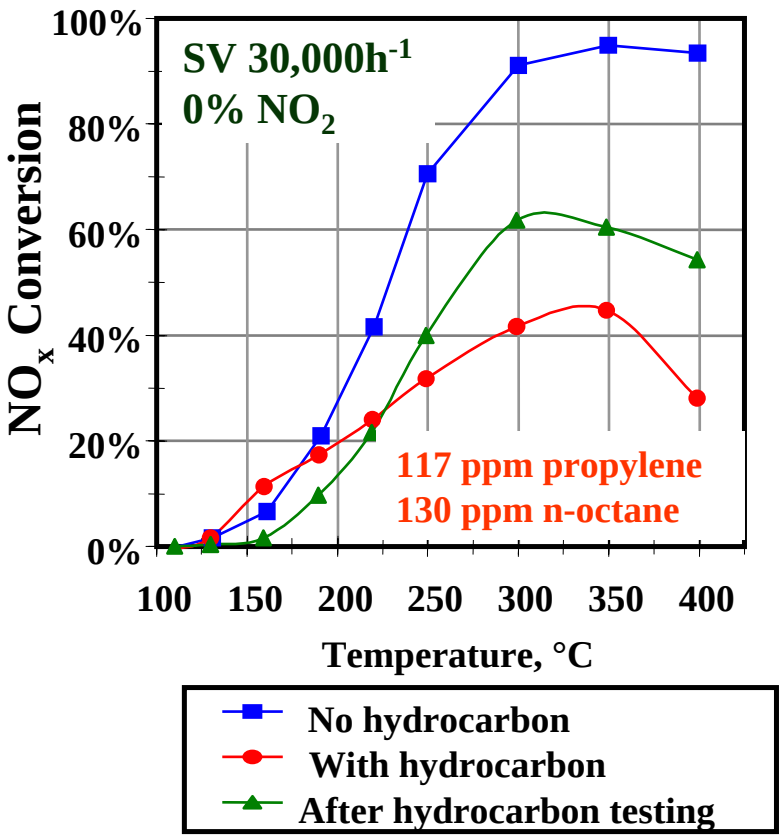
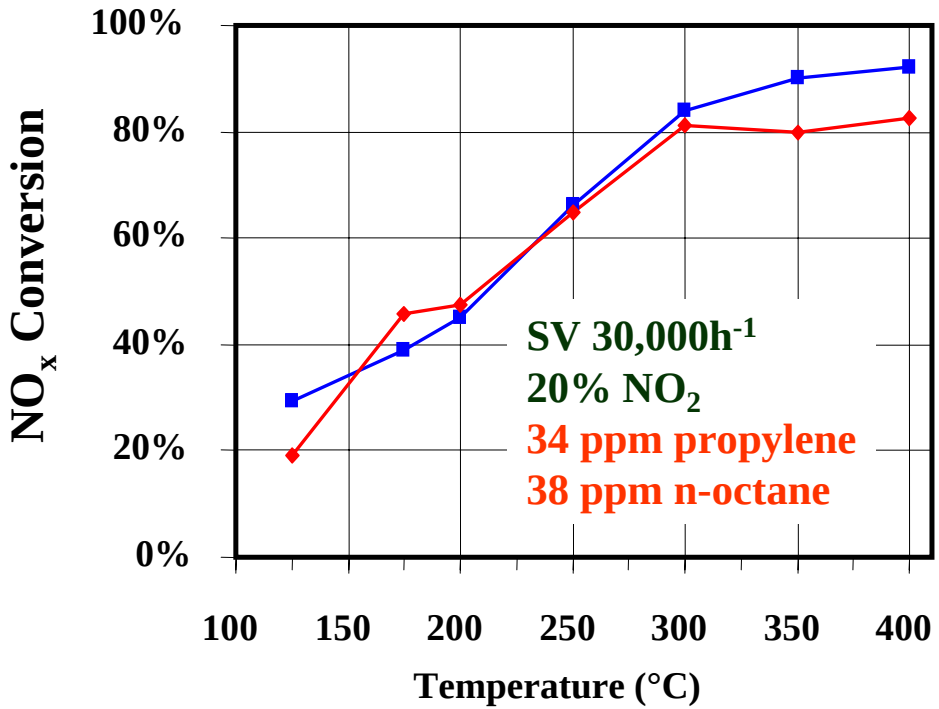
Hydrocarbon Testing

V_2O_5-WO_3 Monolith Sample



- Not a direct comparison
- Trends are important

Catalyst D2 Monolith Sample



- C_3 & n-C_8 suppress conversion *ca.* 10% above 300°C, (HC oxidation)
- No change on addition of 60 ppm toluene (>12 h TOS)
- Activity recovered when HCs removed

Summary

- Optimizing synthesis parameters leads to enhanced catalyst surface areas
  - Nonlinear relationship between activity and surface area
- Catalyst development performed under a staged protocol
- Catalytic materials with desired properties have been identified
  - Meet stage requirements
  - Performance can be tuned by altering component concentrations
  - Optimization still necessary at low temperatures
    - Better activity and tolerance to SO_2
  - V_2O_5-based materials ruled out because of durability issues
- Future work will focus on improving overall low temperature activity

Acknowledgements

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