Limitations of Supported Pt Catalysts for Active Lean-NOx (Hydrocarbon SCR) Applications

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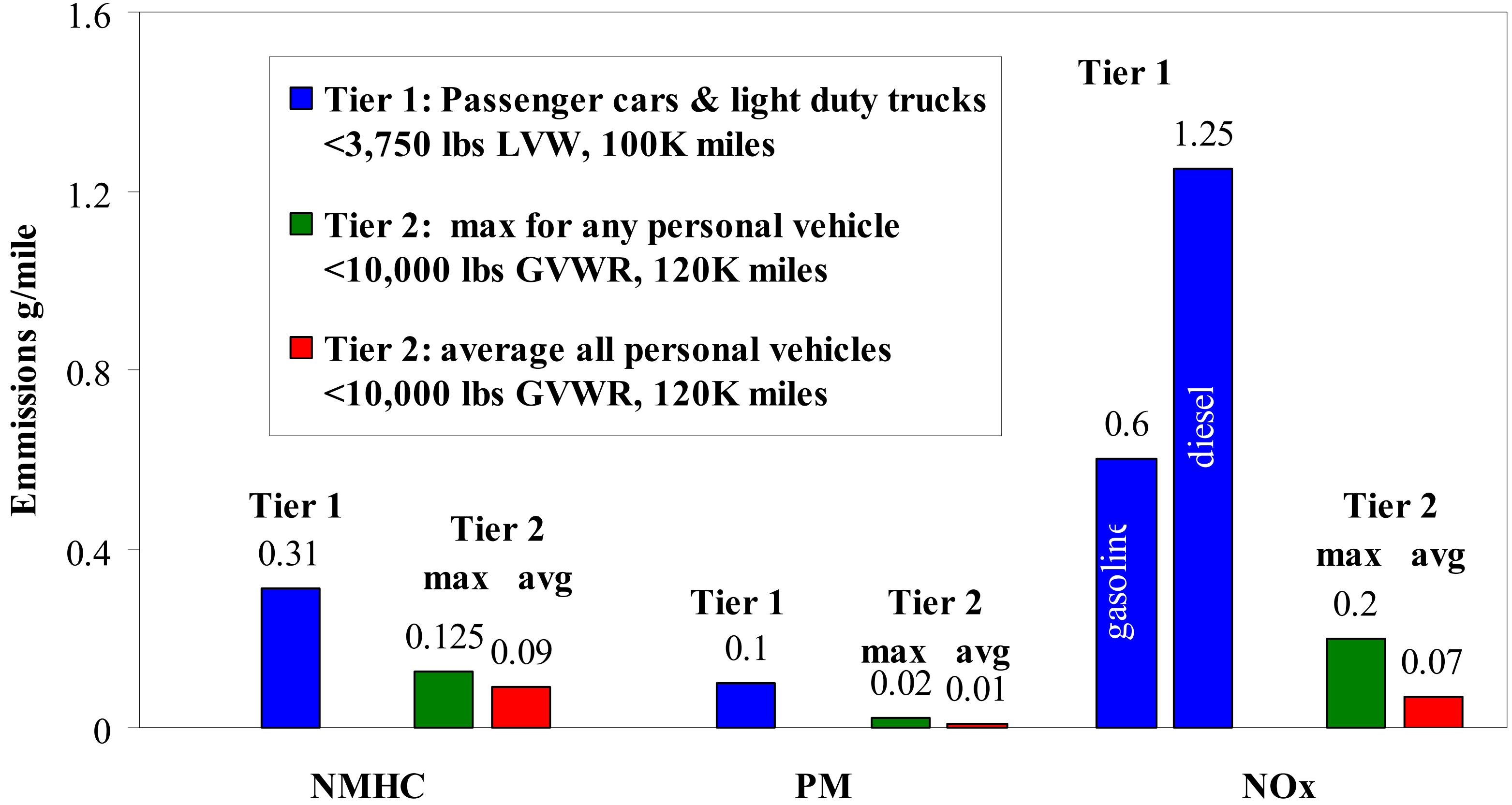
Advantages of Lean-Burn Combustion Systems (Diesel [CIDI] and SIDI)

- Improved Fuel Economy
  - Reduced Unburned Fuel
    - 5% to 15% Fuel Economy Advantage for Lean-Burn (SIDI) Gasoline Engines
    - CIDI Engines Typically 30-50% More Fuel Efficient Than Gasoline Engines
- Simpler Emissions Control Systems
- Lower Flame Temperature (Lower Engine-Out NOx)

Tier 1 vs. Tier 2 Emission Standards



Tier 2 Phased In for Passenger Vehicles and Light Duty Trucks 2004-2007
All Personal Vehicles Must Be In Compliance By 2009

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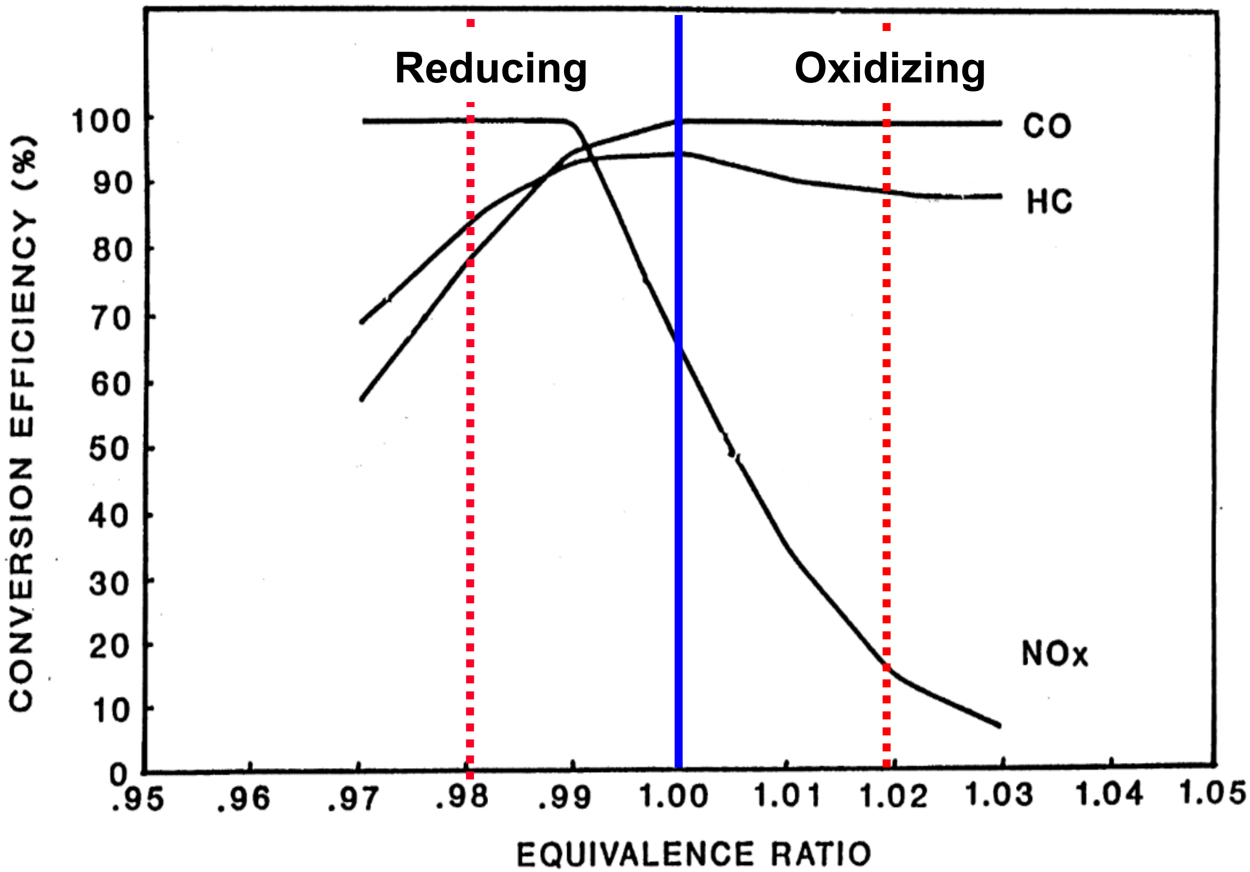
Current NOx Abatement Technology

Current 3-Way Catalysts Are Very Efficient Over a Narrow Air/Fuel Ratio Range



Lean-Burn Exhaust Environments:
A/F > 18:1
Eq. Ratio > 1.2

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CIDI and SIDI Exhaust Aftertreatment Provides Unique Challenges

- Highly Oxidizing Exhaust Environments
- New Catalyst Compositions are Required
- Exhausts Have Low Hydrocarbon Content
  - Typical Diesel HC/NOx Ratio ~1 (C1 HC Basis)
  - Additional Reductant Required for Effective NOx Reduction
- Potential Emissions Control Systems Options for NOx Abatement
  - Selective Catalytic Reduction of NOx
    - Hydrocarbon Reductant
    - Urea Reductant
  - NOx Adsorber Catalysts
  - Non-Thermal Plasma

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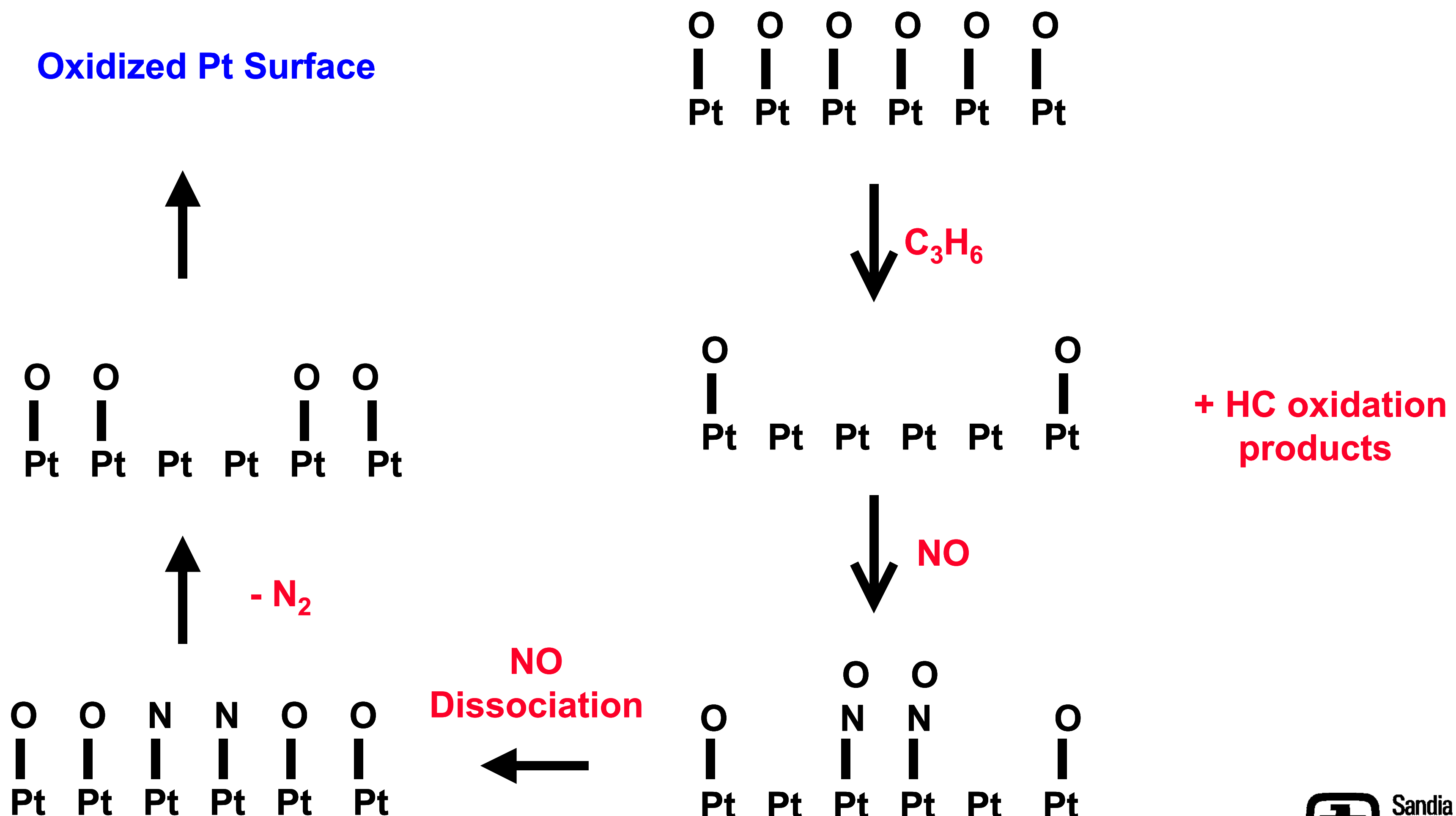
Catalytic Reactions Governing Pollutant Removal are Coupled

- **CO Oxidation**
  - $CO + 1/2\ O_2 \rightarrow CO_2$
- **Hydrocarbon Oxidation**
  - $C_3H_8 + 5\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O$
  - $C_3H_6 + 9/2\ O_2 \rightarrow 3\ CO_2 + 3\ H_2O$
- **NOx Reduction**
  - $NO + CO \rightarrow CO_2 + 1/2\ N_2$
  - $2\ NO + C_3H_8 + 4\ O_2 \rightarrow 3\ CO_2 + 4\ H_2O + N_2$
  - $2\ NO + C_3H_6 + 7/2\ O_2 \rightarrow 3\ CO_2 + 3\ H_2O + N_2$
- **Other Reactions**
  - $NO + 1/2\ O_2 \rightarrow NO_2$

Possible Reaction Mechanisms for NOx Reduction Under Oxidizing Conditions

- Oxidation of NO to NO_2, which then reacts with hydrocarbons
- Formation of a highly reactive partially oxidized hydrocarbon intermediate
- Formation of an isocyanate (-NCO) intermediate
- Reduction of the metal surface followed by NO dissociation on the metal
  - NO dissociation possibly assisted by other adsorbed species

Lean NOx Reduction Mechanism by Propylene in Oxidizing Environments over Supported Pt Catalysts (after Burch)



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HC-SCR Reaction Mechanisms

- **Possible Reaction Mechanisms on Supported Pt Catalysts for NOx Reduction Under Oxidizing Conditions with Relevant Hydrocarbons (After Burch)**
  - Propylene - Reduction of the oxidized Pt surface by the hydrocarbon, followed by NO dissociation on the metal
  - Propane - Bifunctional Mechanism: Oxidation of NO to NO_2 on Pt, with hydrocarbon reacting with an acid site on the support surface. NO_2 then spills over to support interface where reaction occurs with C_xH_y species
  - Octane - combination of above mechanisms:
    - Propylene-like for high octane:NOx ratios
    - Propane-like for lower octane:NOx ratios

HC-SCR Testing

- **Pt/HTO:Si Monolith Core Catalyst Synthesis**
  1. Hydroxide Addition

     $Ti(OC_3H_7)_4 + 0.2\ Si(OC_2H_5)_4 + NaOH \xrightarrow[\text{Methanol}]{}$ Soluble Intermediate
  2. Hydrolysis

     Soluble Intermediate $\xrightarrow[\text{Support}]{}$ HTO:Si-Coated Support
  3. Ion Exchange with Pt
  4. Activation/Pretreatment

- **NOx Measured With Chemiluminescence Analyzer**
  - Reported conversions include NO $\rightarrow$ N_2 and N_2O

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Simulated Exhaust Gas Formulations

- **Two Different Simulated Exhaust Gas Formulations Developed Through USCAR/LEP CRADA**
- **Native Lean-Burn Gasoline and Diesel Exhaust Have Insufficient Hydrocarbon Content for Effective HC-SCR**
  - **Additional Hydrocarbon (Fuel) Must Be Added**

Simulated Exhaust Gas Formulations

Species	Small Displacement CIDI	Lean-Burn Gasoline
NOx	75	250
Total HC (ppm as C1)	600	2100
n-C_8H_{18} (ppm as C1)	450	525 (C_3H_8)
C_3H_6 (ppm as C1)	150	1575
Total HC (as C1):NOx	8:1	8.4:1
C_3H_6 (as C1):NOx	2:1	6.3:1
CO (ppm)	600	400
H_2 (ppm)	200	133
CO_2 (%)	5.0	7.0
O_2 (%)	12	8
H_2O (%)	5.0	8.0
SO_2 (ppm) - Aging	1.5	15
SV (h^{-1})	25,000	50,000

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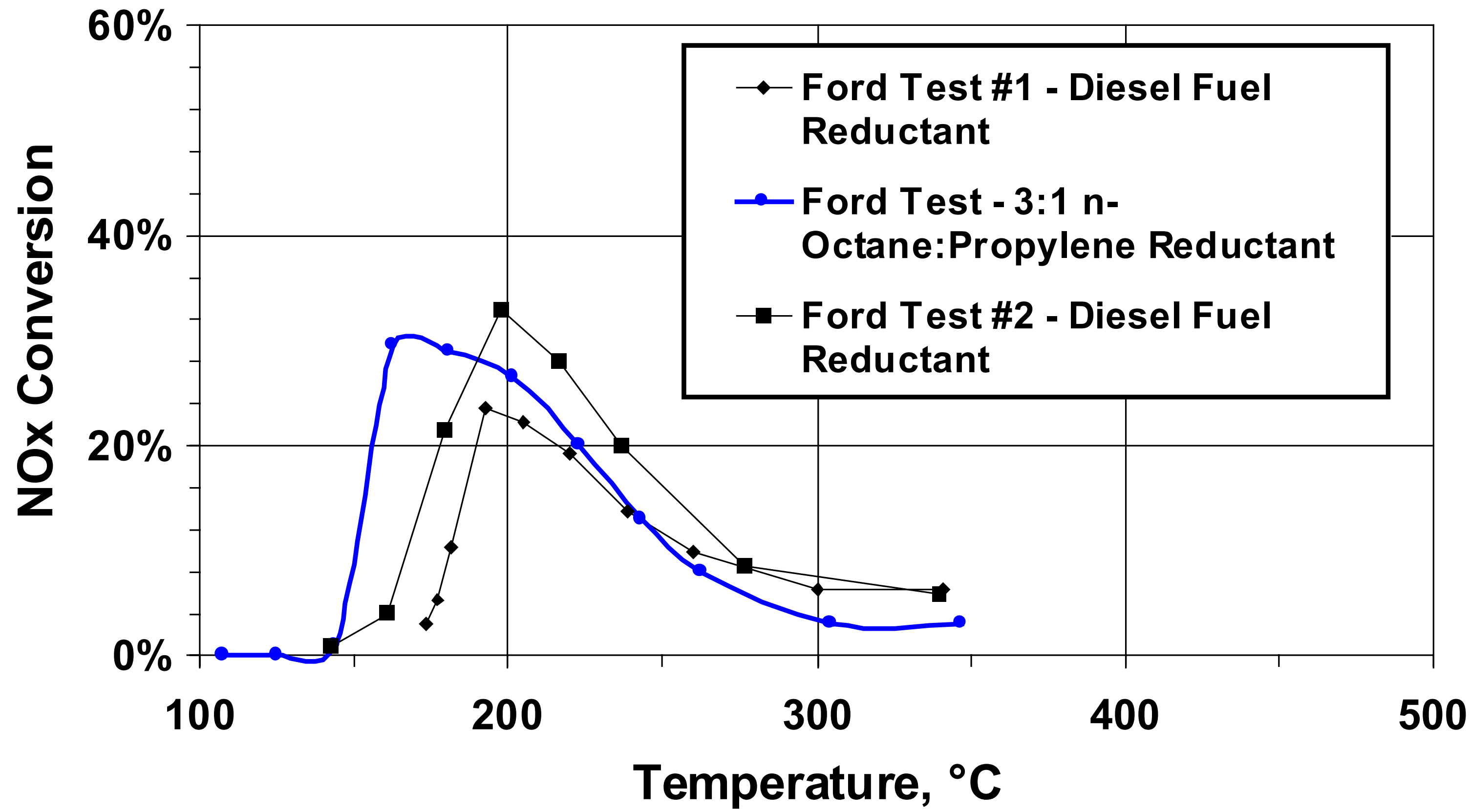
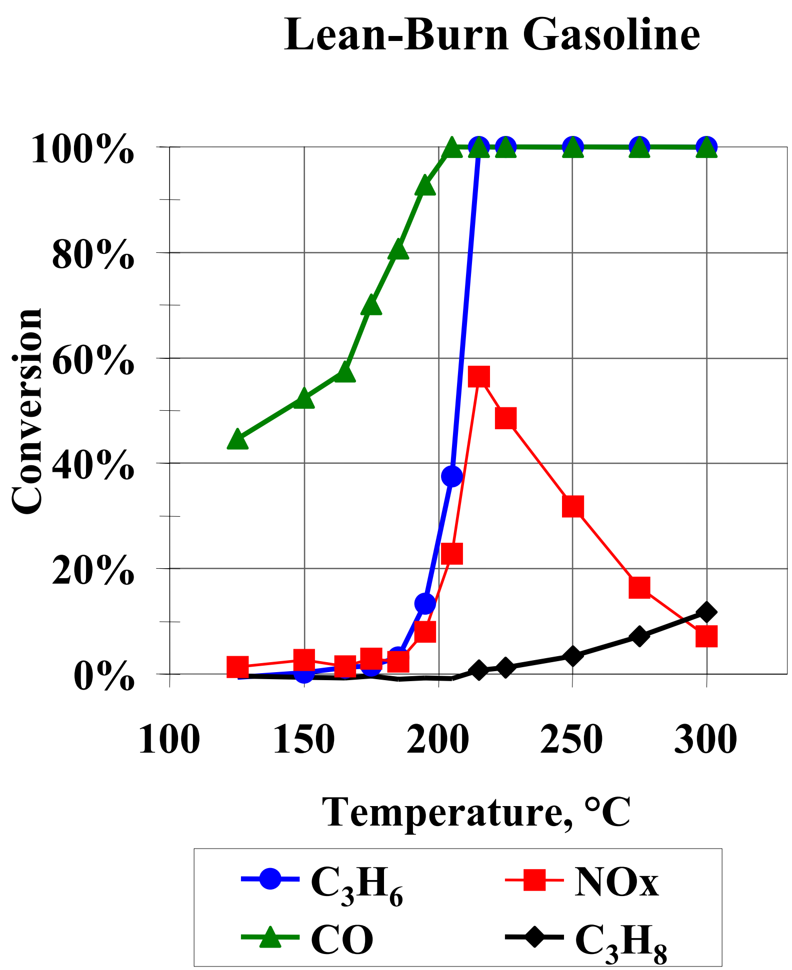
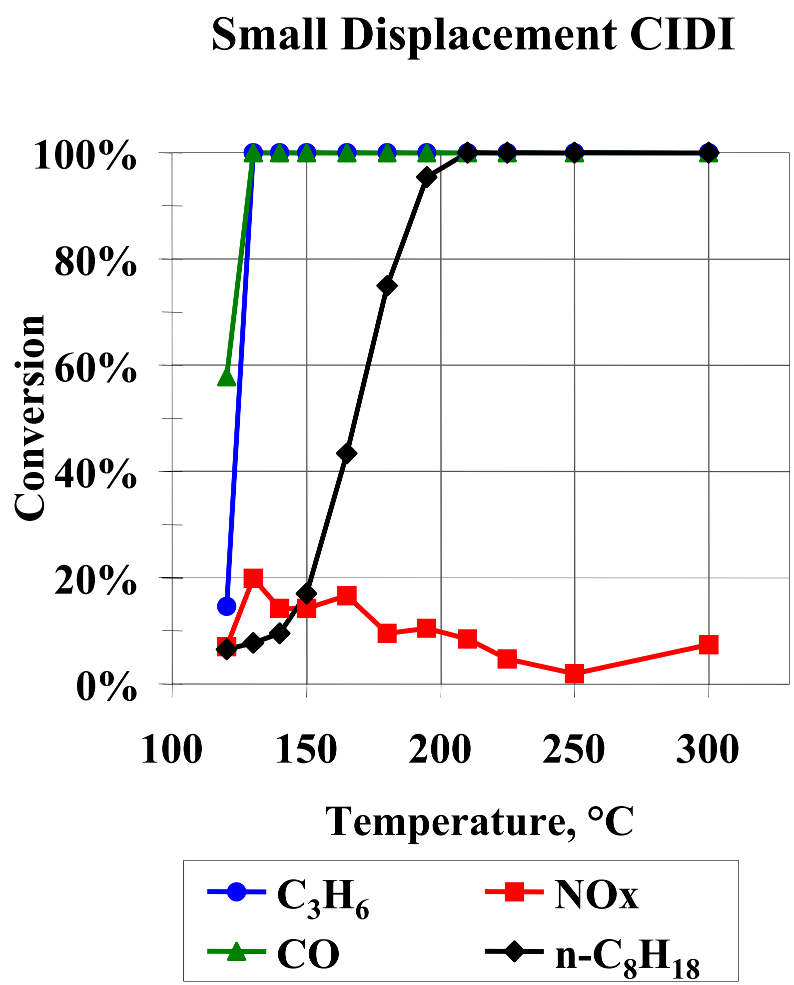
Ford Tests Determined Appropriate HC Mixture to Simulate Diesel Fuel Reductant



Data courtesy of John Cavataio and Bob Hammerle (Ford Motor Company)

Conversion Profiles





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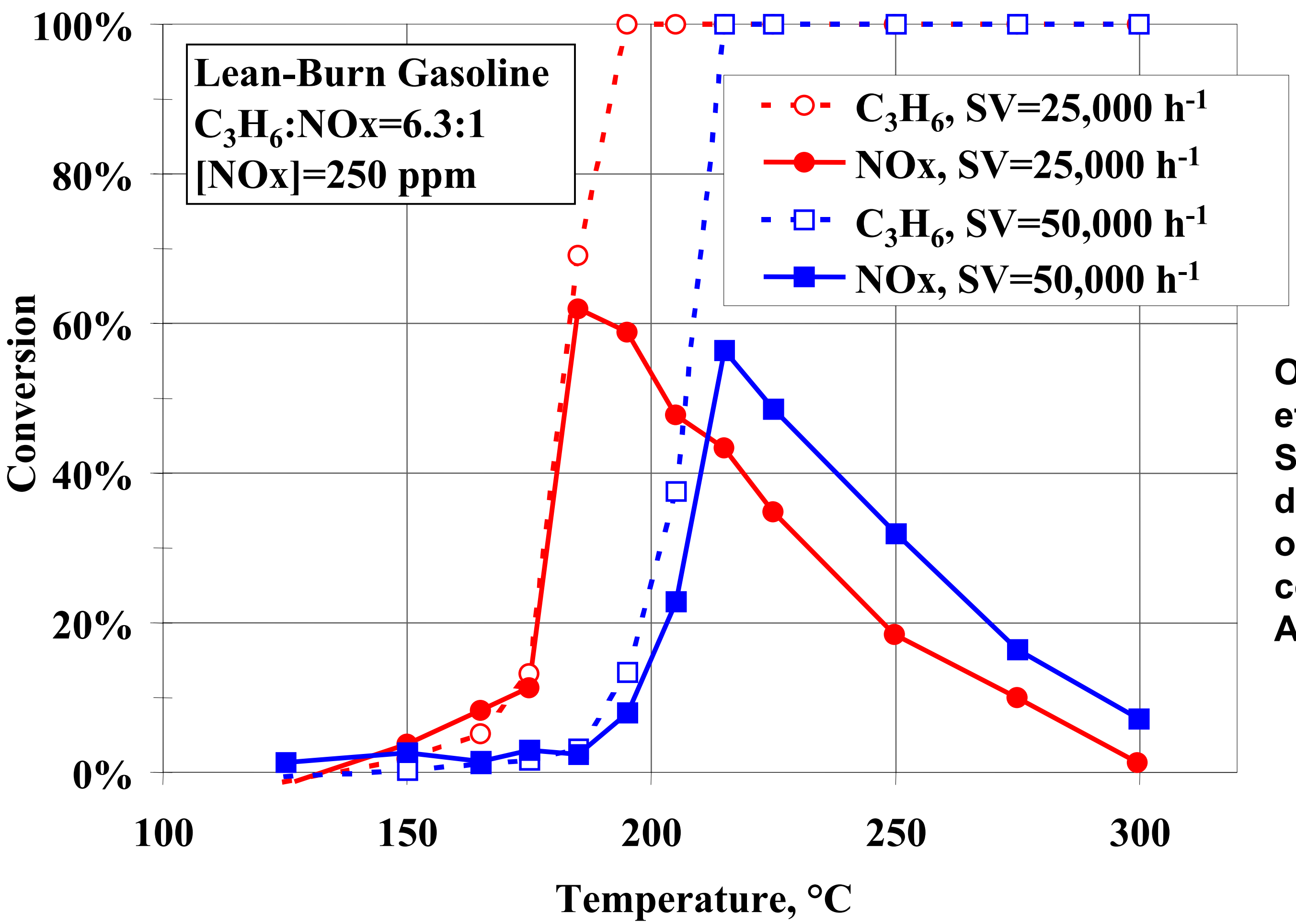
Effect of Space Velocity



On Pt based catalysts, Adams et al. also found that lowering SV from 50,000 to 25,000 hr^{-1} decreases light off temperature of C_3H_6 and increases the conversion of NO
Appl.Catal. B 10 (1996) 157-181

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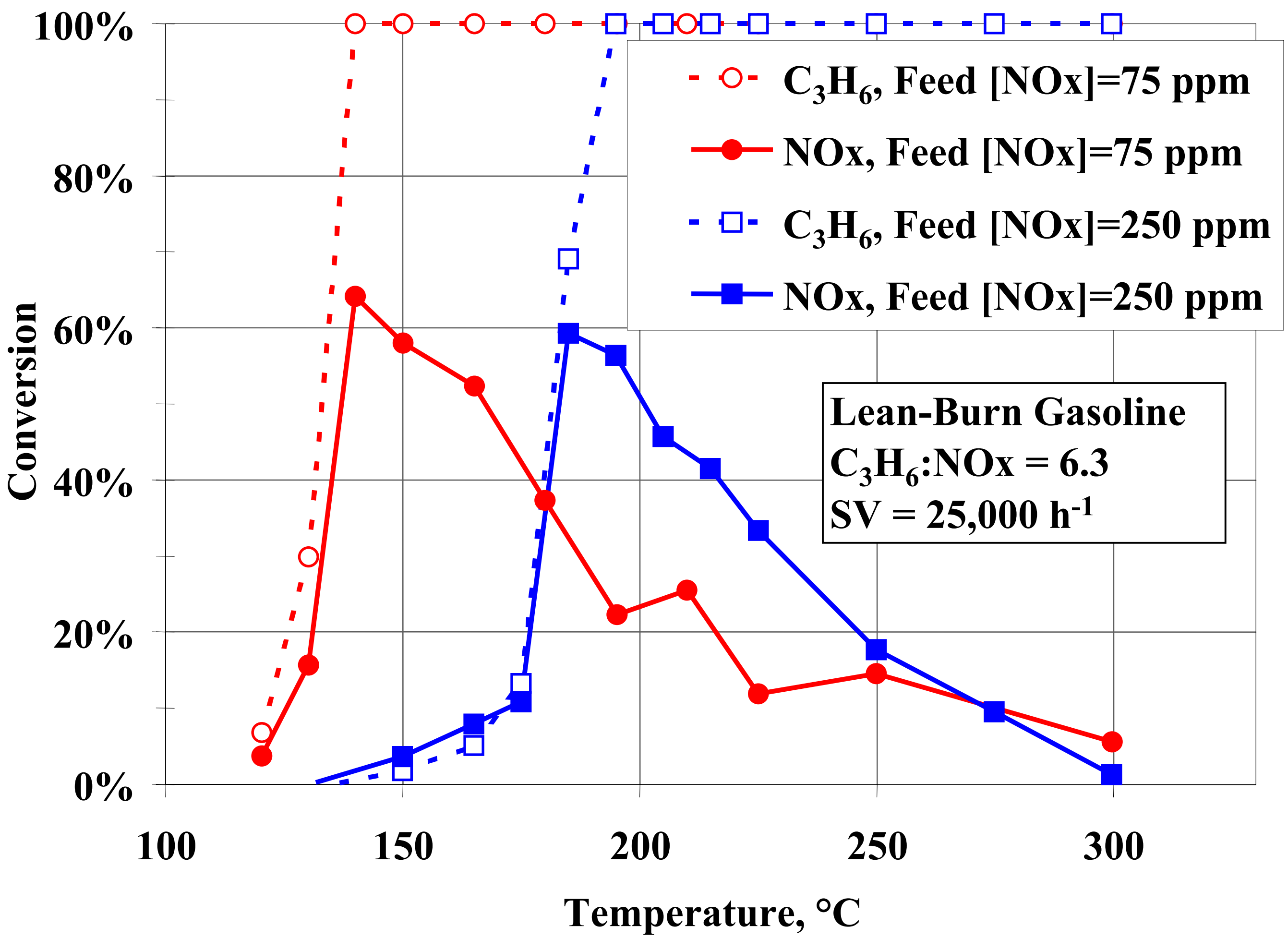
Effect of NOx Concentration



Several authors have also reported that NO increases the light-off temperature for C_3H_6:

Burch and Millington, Catal. Today, 29 (1996) 37-42

Lionta et al., Ind. Eng. Chem. Res., 35 (1996) 2508-2515

Roberts and Amiridis, Ind. Eng. Chem. Res., 36 (1997) 3528-3532

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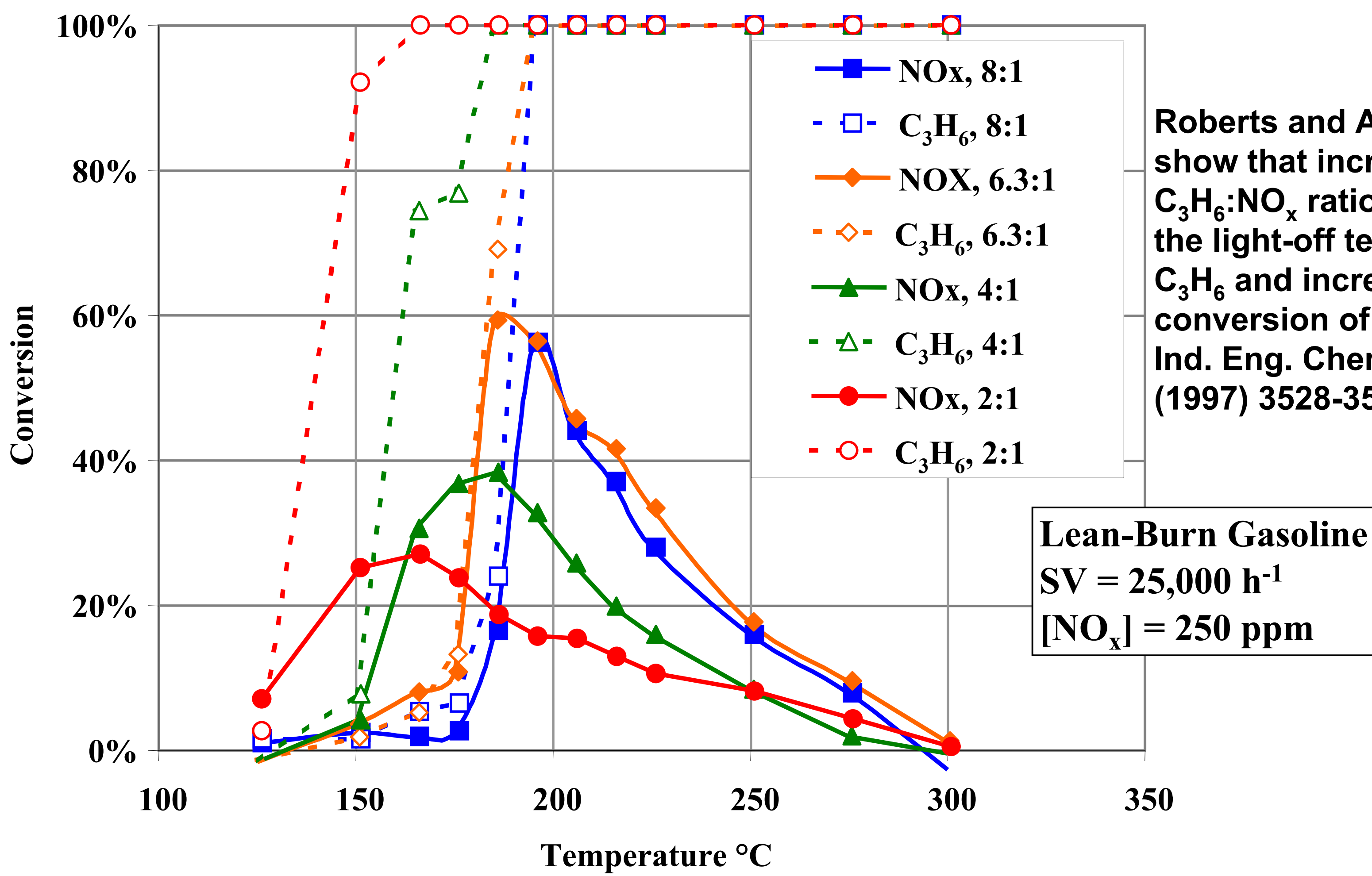
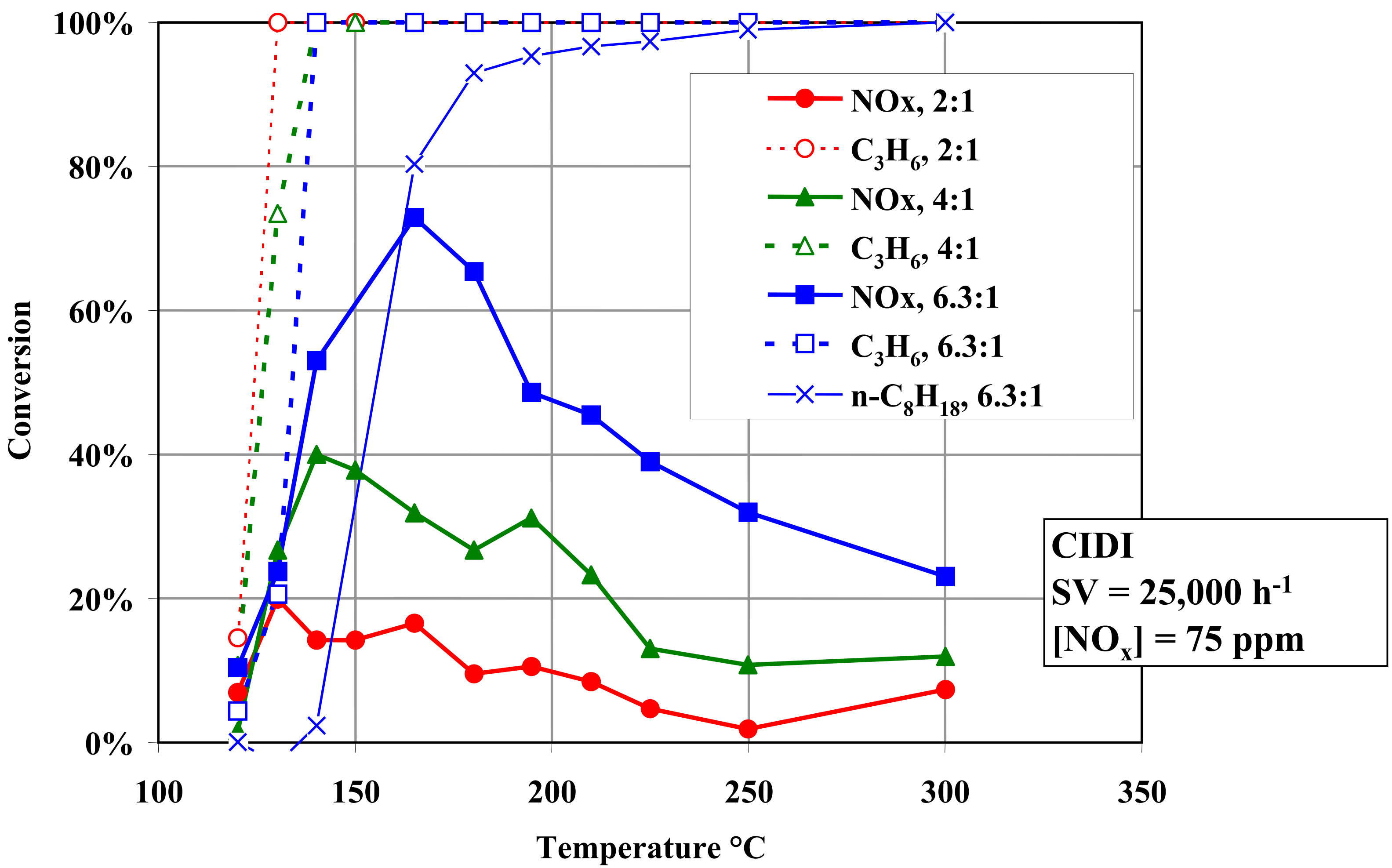
Effect of $C_3H_6:NO_x$ - Lean Burn Gasoline



Roberts and Amiridis, also show that increasing the $C_3H_6:NO_x$ ratio increases the light-off temperature of C_3H_6 and increases conversion of NO_x
Ind. Eng. Chem. Res., 36 (1997) 3528-3532

Effect of C_3H_6:NO_x - CIDI



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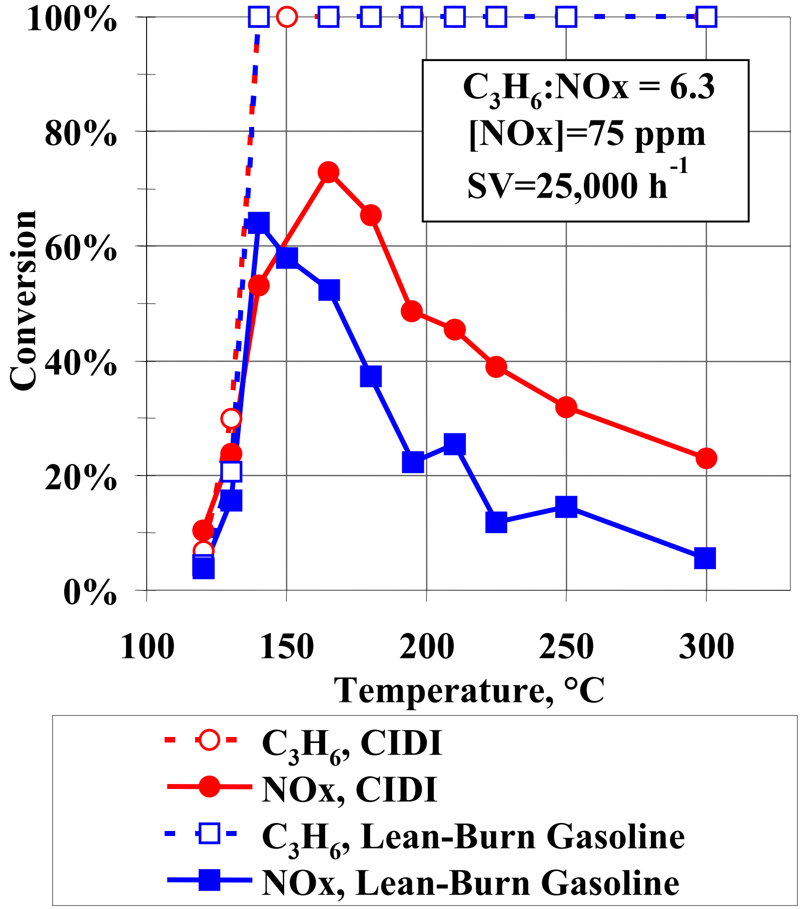
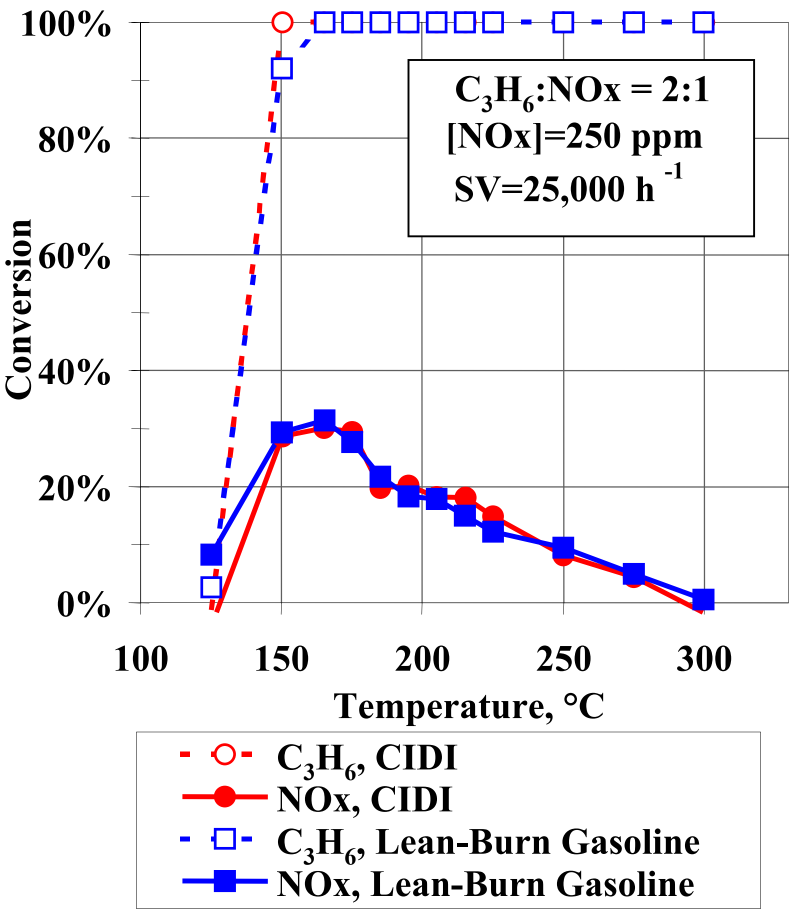
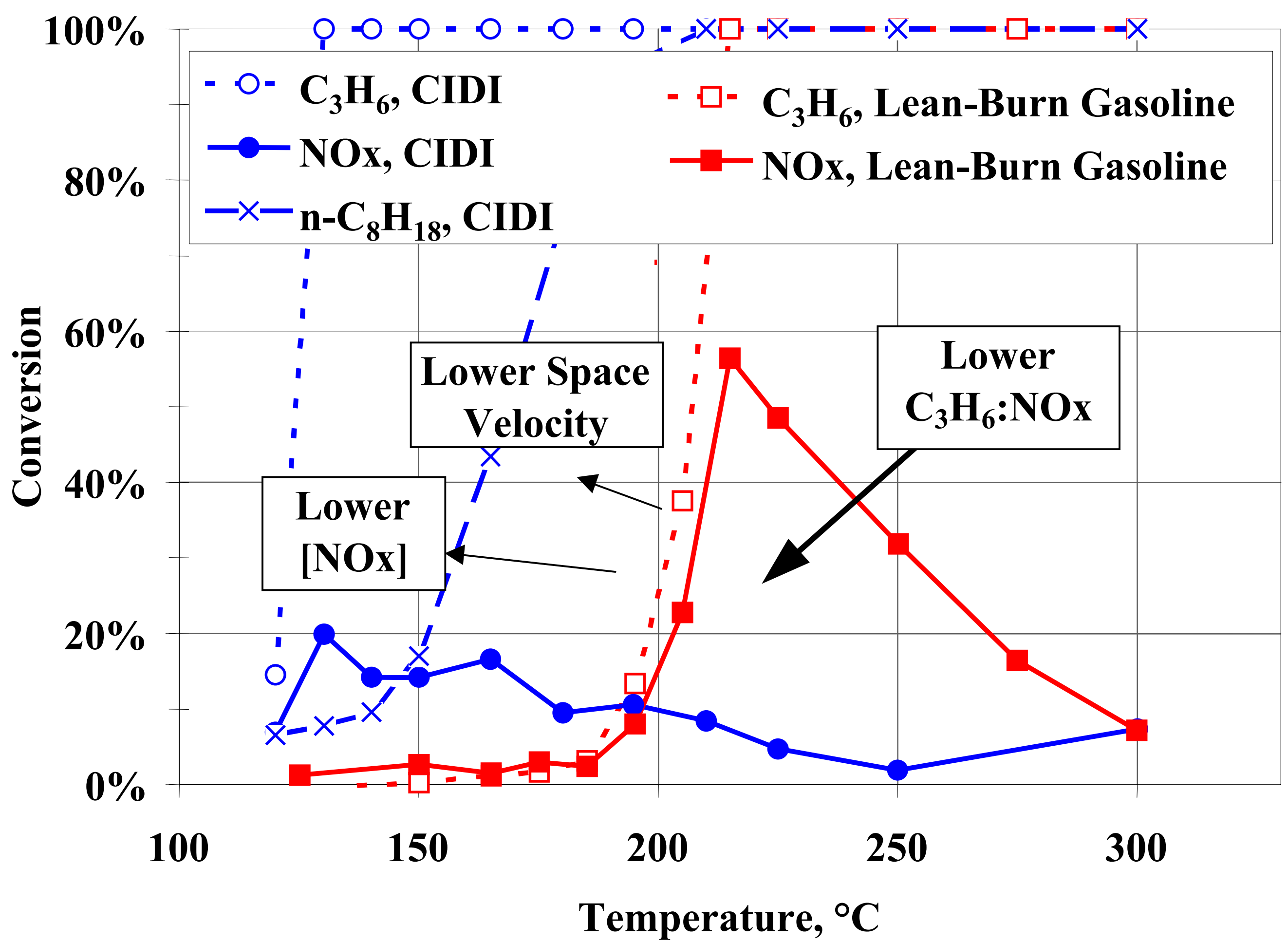
Exhaust Simulations Adjusted to Equal SV, C_3H_6:NOx, and [NOx]





Overall Effect Of Feed Parameters



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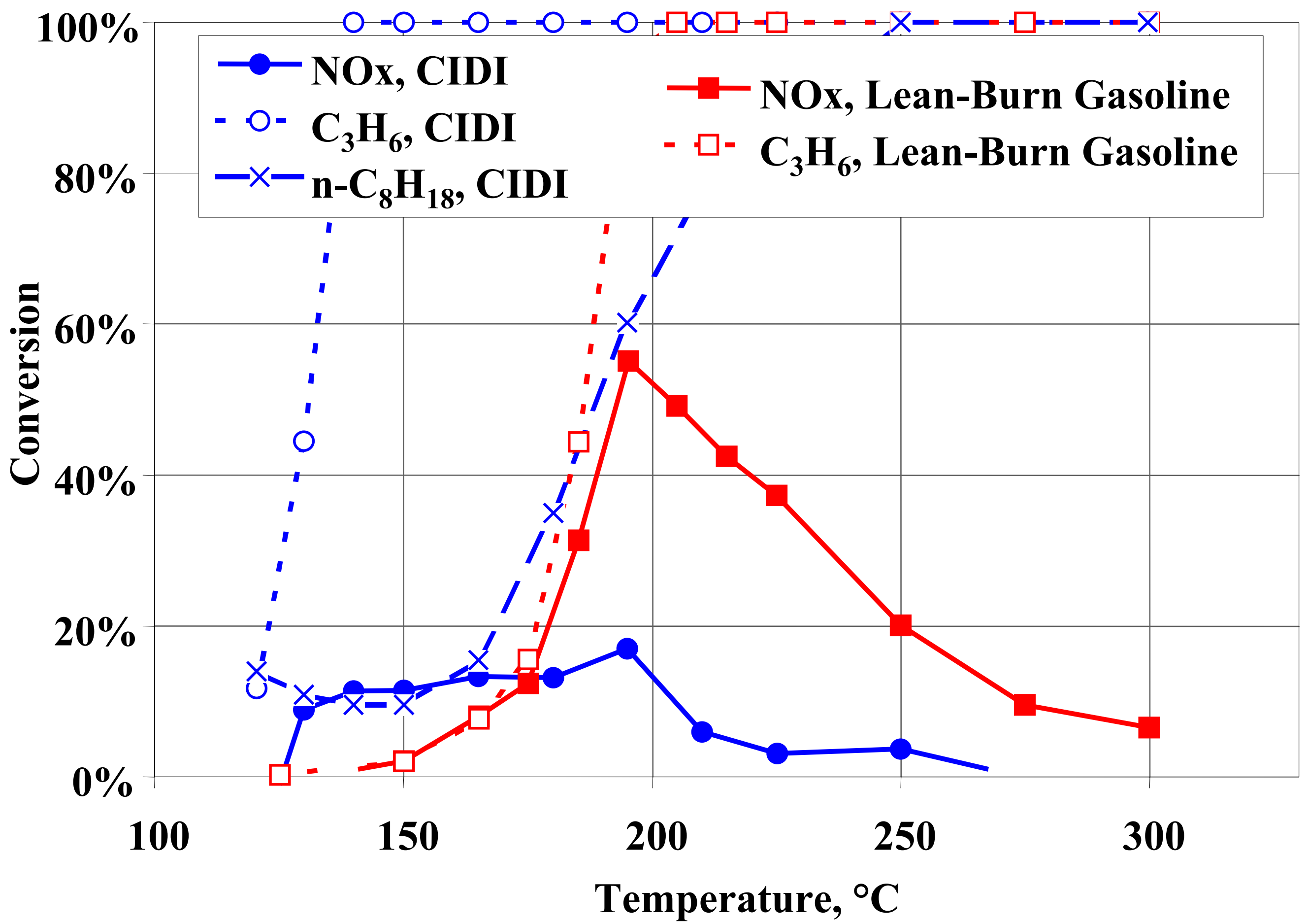
Commercially-Available Supported Pt Catalyst (76 g Pt/ft^3) Shows Very Similar Results



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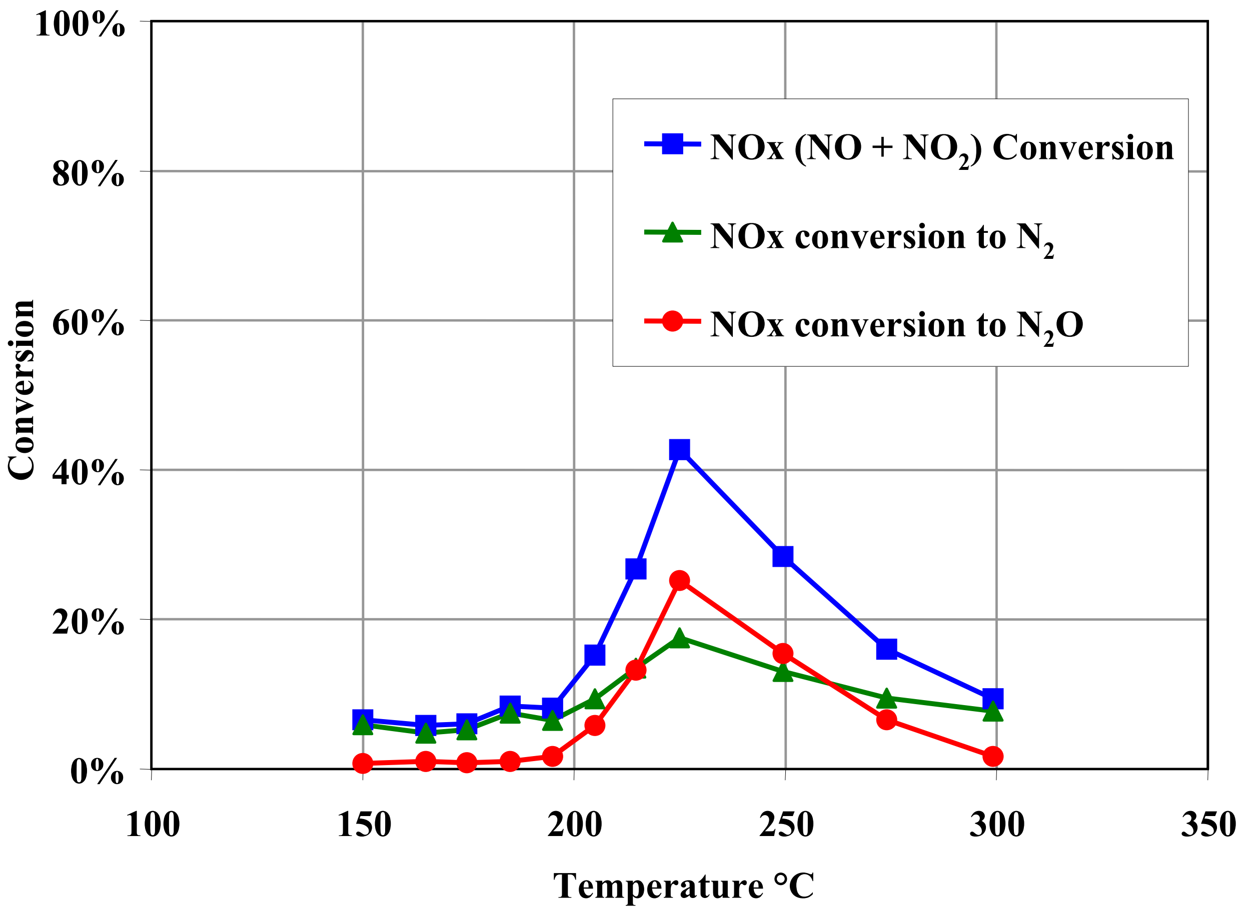
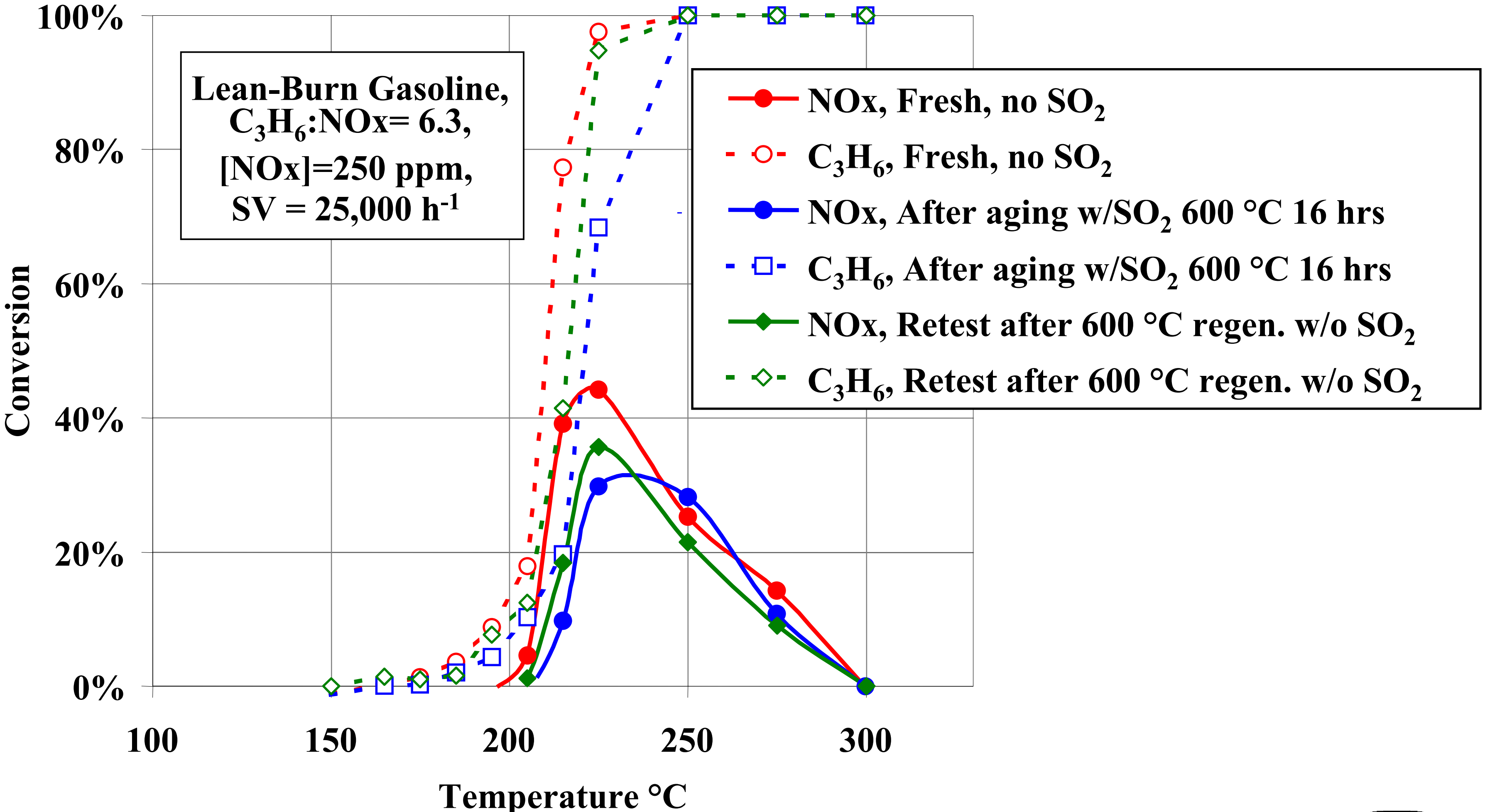
Poor Selectivity to N_2 is Also a Problem for Supported Pt Catalysts



0.6 wt% Pt/HTO:Si Monolith
Lean-Burn Gasoline
Space Velocity = 30,000 h^{-1}

SO_2 Aging Further Lowers Supported Pt Catalyst Activity



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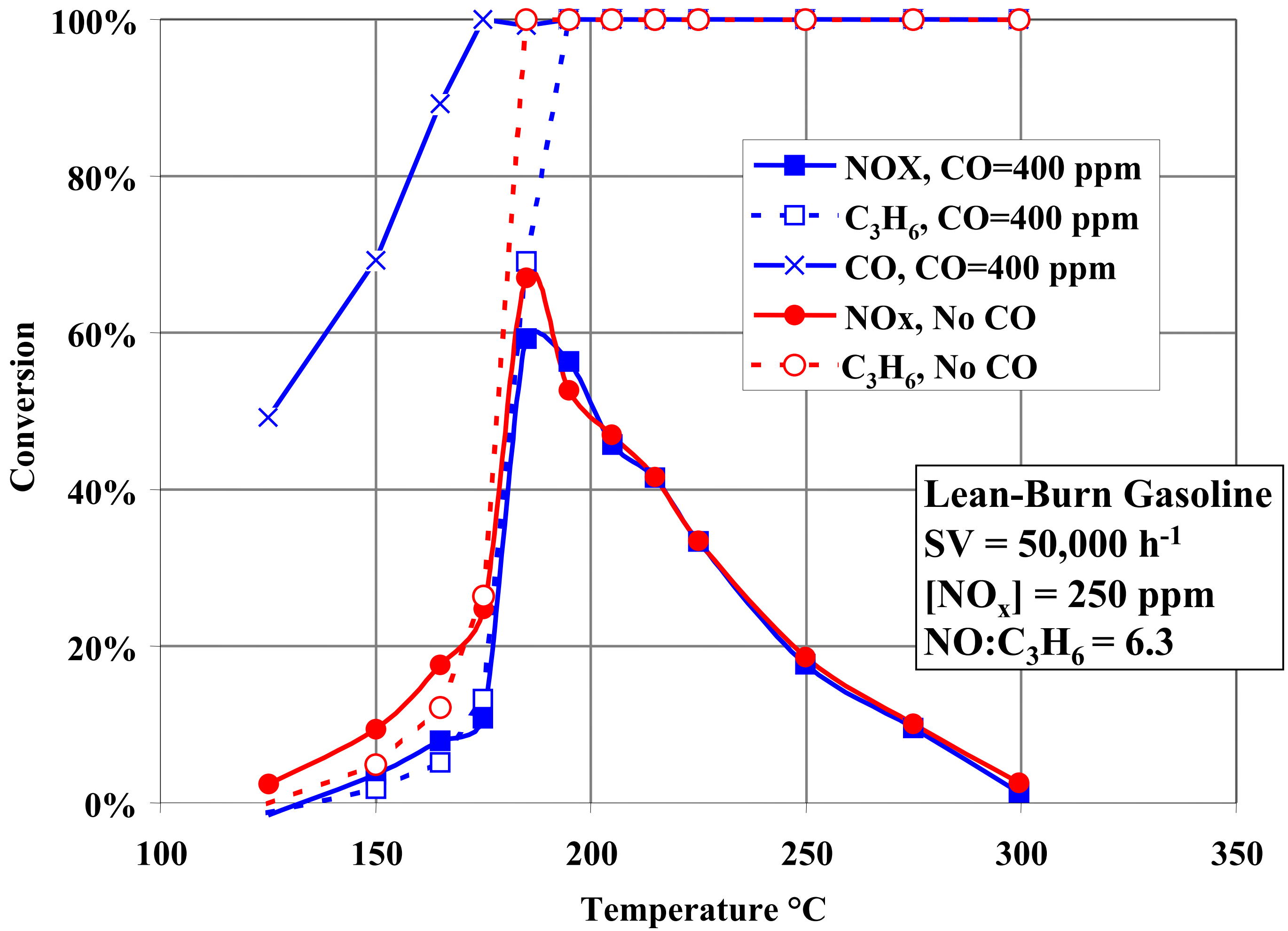
Pt-Based Catalysts for Selective Catalytic Reduction of NOx via Hydrocarbons: Summary

- **Problems with Current Pt-Based Catalysts for HC-SCR**
  - Low Maximum NOx Conversion
  - Narrow Temperature Window of Activity
  - High Hydrocarbon (e.g., C_3H_6):NOx Ratios are Required to Approach Necessary NOx Conversion Levels
  - Low N_2 Selectivity (N_2O Production)
  - SO_2 Further Decreases Fresh Catalyst Activity
- **Small Displacement CIDI Engines are Especially Difficult**
  - Lower SV, [NOx], and C_3H_6:NOx Lowers Light-Off Temperature
  - Low C_3H_6:NOx Results in Low Maximum NOx Conversion
- **Without a Significant Catalyst Breakthrough, Selective Catalytic Reduction of NOx via Hydrocarbons Over Supported Pt Catalysts is Not Likely to Meet EPA Tier 2 Requirements**
  - Systems Approach Likely Necessary

Effect of CO



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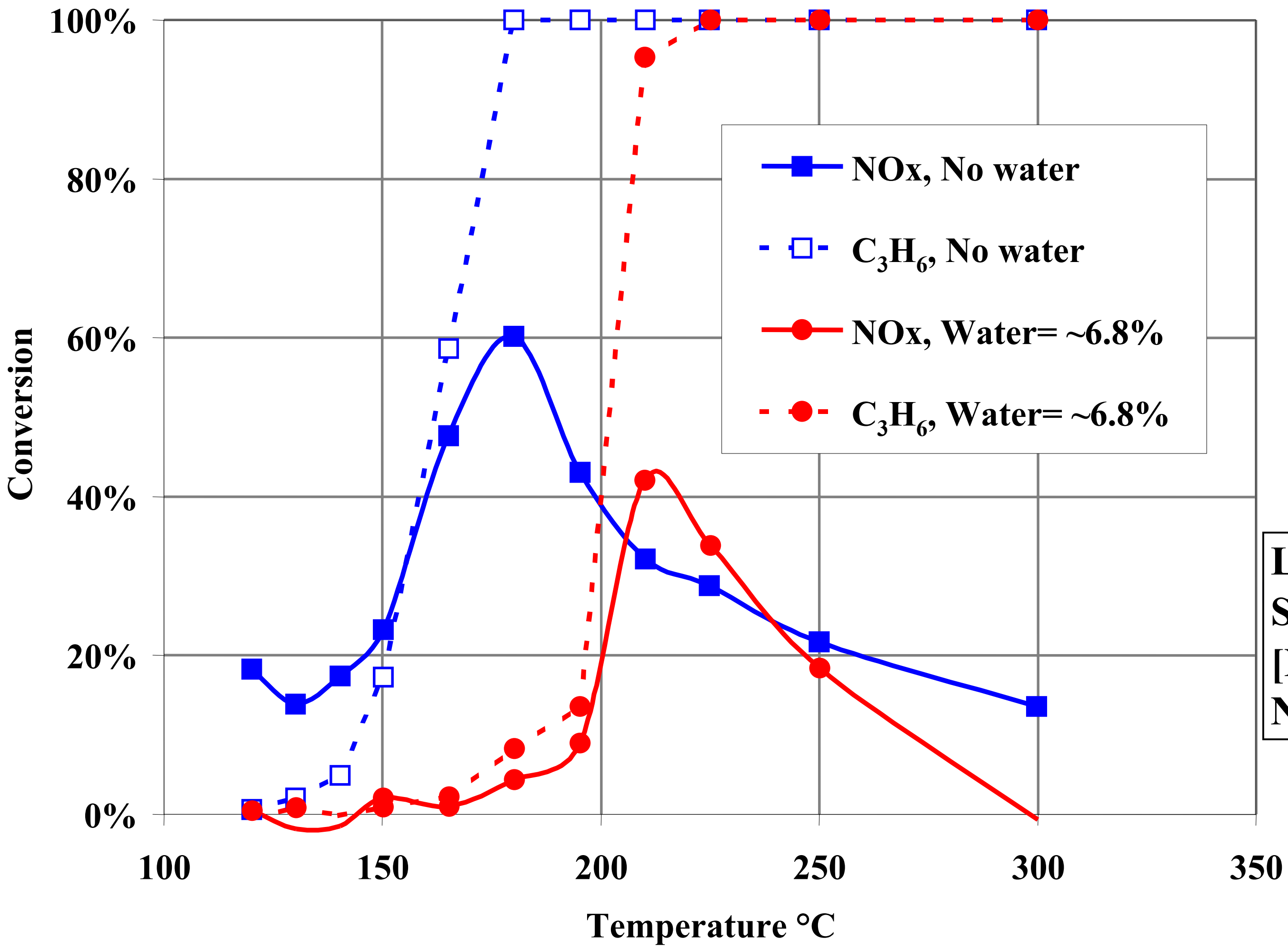
Effect of Water



Lean-Burn Gasoline
SV = 50,000 h^{-1}
$[NO_x]$ = 250 ppm
$NO:C_3H_6$=6.3

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