Bifunctional Catalysts for the Selective Catalytic Reduction of NO by Hydrocarbons

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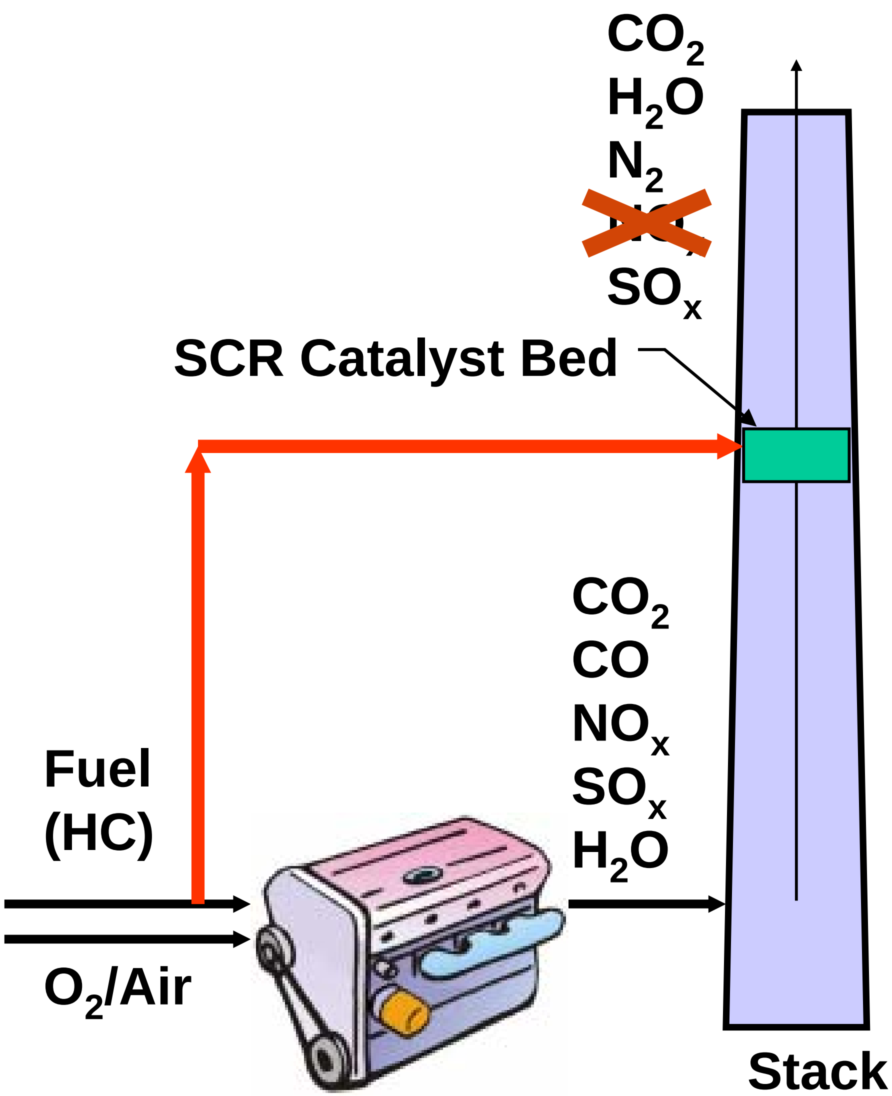
Existing Methods of NO_x Reduction

Method	Typical Usage	Disadvantages
NO_x Sorption **(NO_x Traps)**	**Metal oxides in lean adsorption rich reduction cycles**	**Limited capacity, strict engineering controls**
NO_x Selective Catalytic Reduction with NH_3/Urea **(SCR)**	**Metal oxides under lean conditions**	NH_3 slippage **and** NH_3/Urea storage

SCR With Hydrocarbons

- **SCR with light hydrocarbons**
  - Potential replacement for NH_3/urea-based systems
  - Slipstream of combustion fuel
  - Minimal slippage of hydrocarbons
  - Two classes of catalysts
    - *Metal-exchanges zeolites (Cu-ZSM-5, Co-FER)*
      - Very active
      - Deactivation/poison under wet conditions
    - *Supported metals (Pt/SiO_2)*
      - Water stable
      - Lower activity
      - Significant by-products (N_2O, NO_2)

Hydrocarbon Selective Catalytic Reduction (HC-SCR)



- **SCR with light hydrocarbons proposed as alternative deNO$_x$ method**

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

HC-SCR Mechanism

$NO + O_2 \rightarrow NO_2$ ***NO activation***

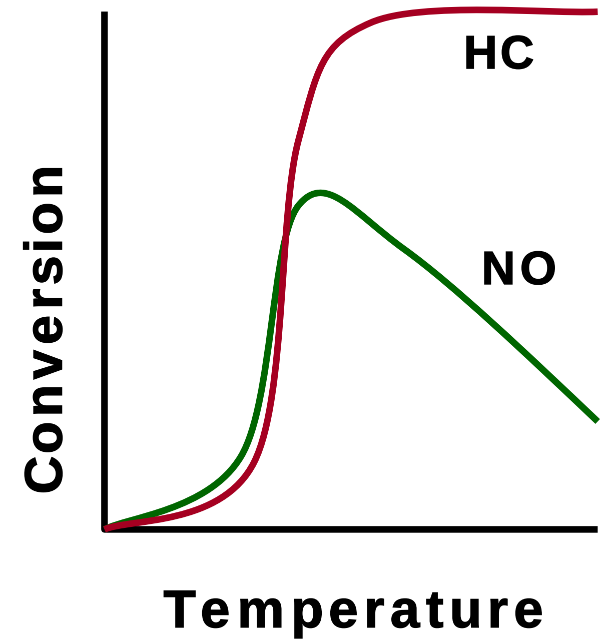
(requires reducible sites)

$C_xH_y + NO_2 \rightarrow CO_2 + N_2 + H_2O$ ***HC-SCR***

↕ ***Competition for Hydrocarbon***
(on oxidizable sites)

$C_xH_y + O_2 \rightarrow CO_2 + H_2O$ ***HC oxidation***

(very fast)



- Bifunctional catalyst needed to oxidize HC with NO_2 before O_2 oxidation

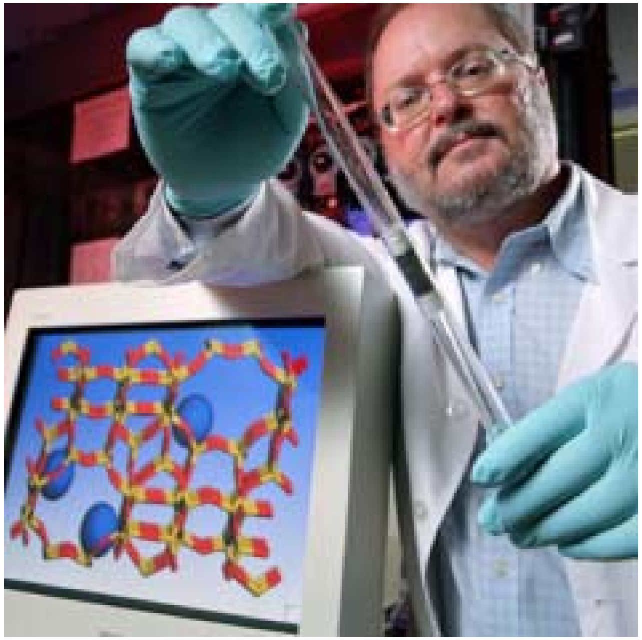
Novel DeNO$_x$ Catalyst Project Goals

Develop **bifunctional** catalysts for the selective catalytic reduction of NO_x using hydrocarbons to improve catalyst **activity and stability** under **wet conditions**

- **Use of two-phase catalysts to improve NO_x activity**
  - Metal-zeolite
    - *High SCR activity*
  - Metal oxide additives
    - *Improved water stability*
    - *Mechanistic improvements*

Catalyst Synthesis

- **Current catalysts samples**
  - Step-wise addition of metal and metal oxide to zeolite
    - *exchange or impregnation techniques*
- **CeO_2/Cu-ZSM-5 explored the most**
- **Other metals, oxides, and zeolites have been tested with similar improvements**
  - Metals
    - ***Co***, ***Ag***, ***Fe***, *Cr, Y*
  - Metal oxides
    - ***ZrO_2***, ***MoO_3***
  - Zeolites
    - ***Mordenite***, ***Ferrierite,***
    - *Y, Beta*

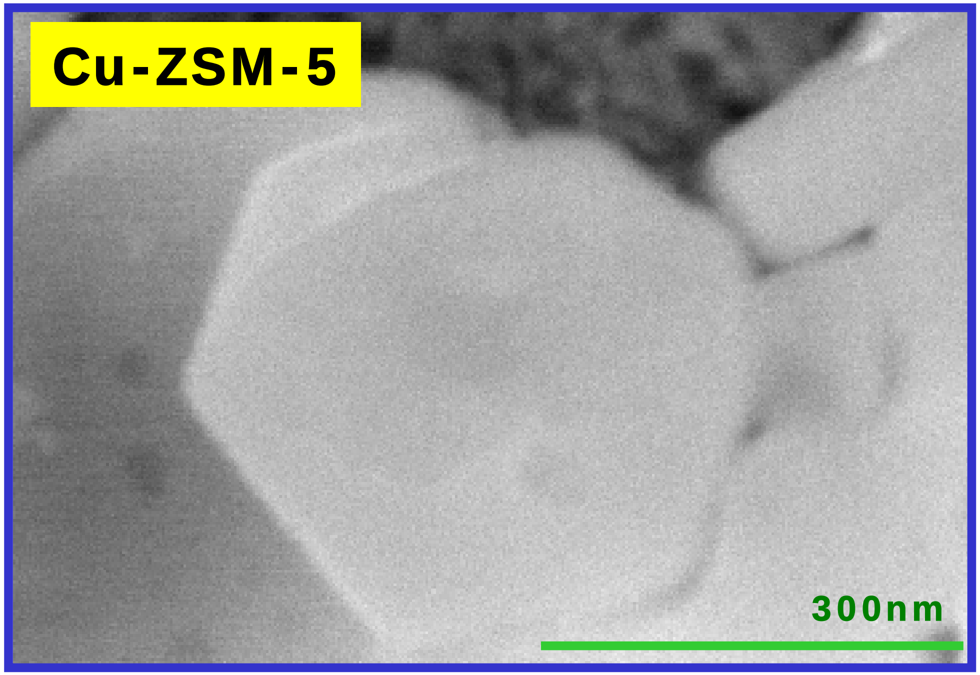


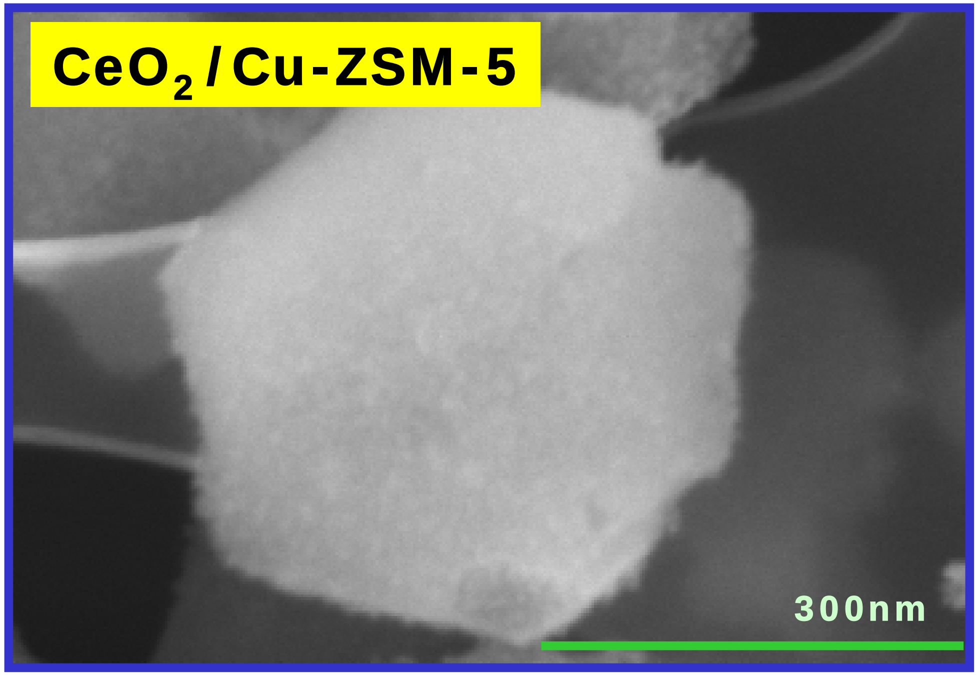
Catalyst Preparation Method

Step #	Method	
	Forward	**Reverse**
1	Ion Exchange zeolite with desired metal	Coating with nano sized metal sol (10 – 20 nm)
2	Coating with nano sized metal sol (10 – 20 nm)	Ion Exchange zeolite with desired metal
3	Calcination	Calcination

Synthesis of Bifunctional Materials

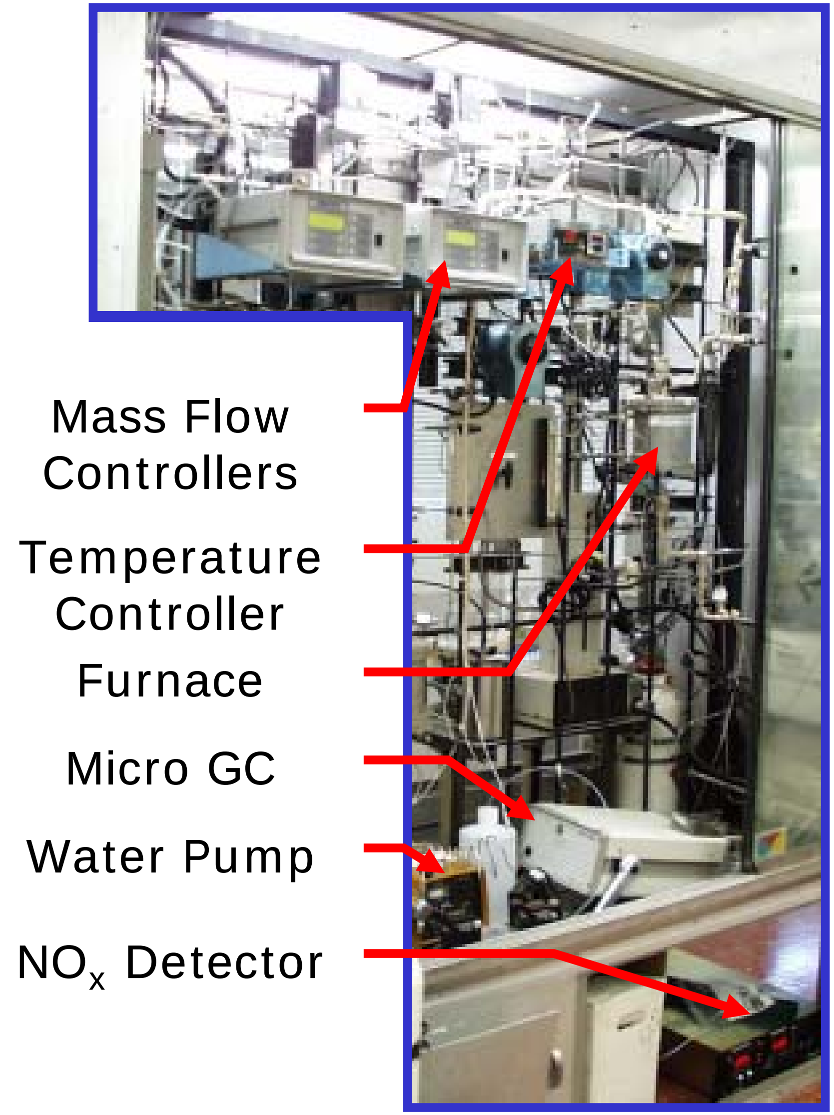
- **Zeolite + sol = coated zeolite**



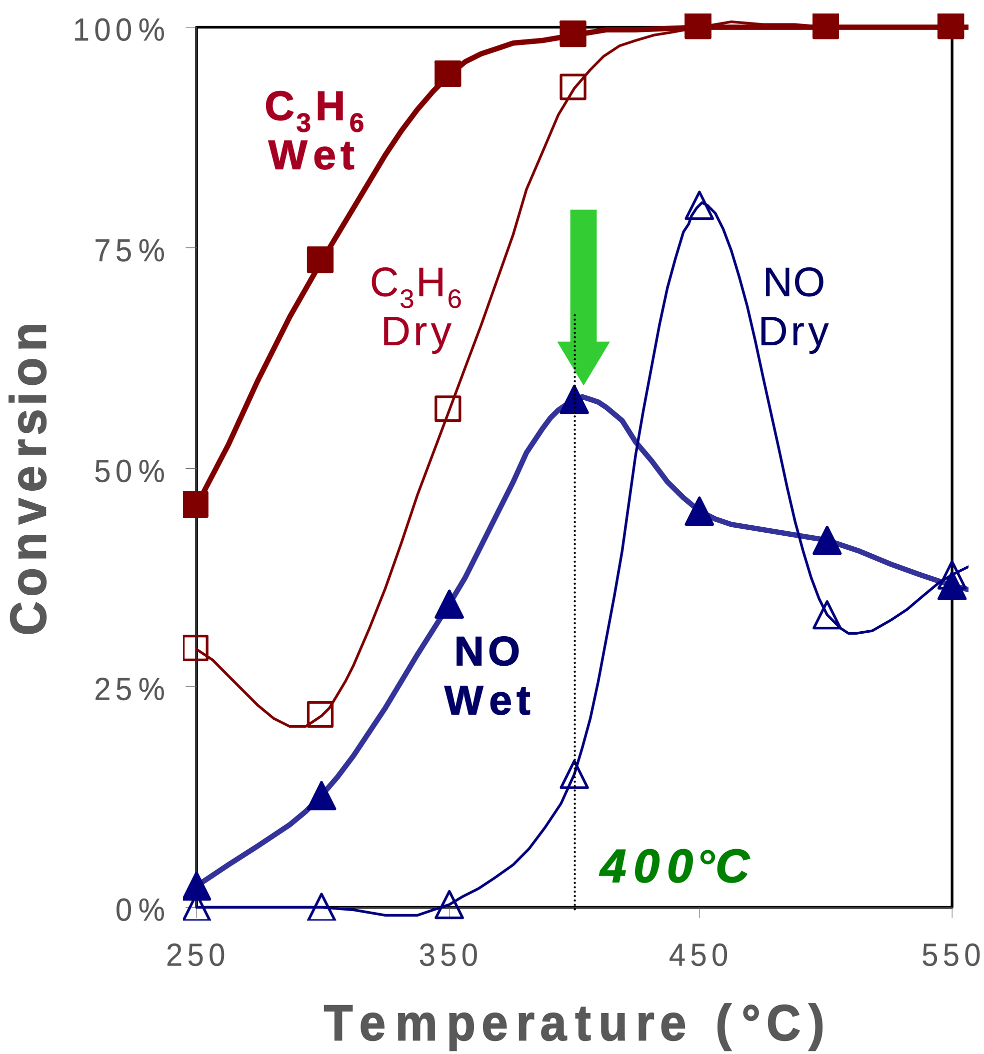


DeNO$_x$ Reactor System

- **Nominal conditions for stationary applications:**
  - 30,000 hr^{-1} SV
  - 1000ppm NO
  - 1000ppm C_3H_6
  - 2% O_2
  - 10% H_2O when used
- **Flexible design to test other NO$_x$ systems**
- **Detectors allow quantification of NO_2, N_2O, and CO**

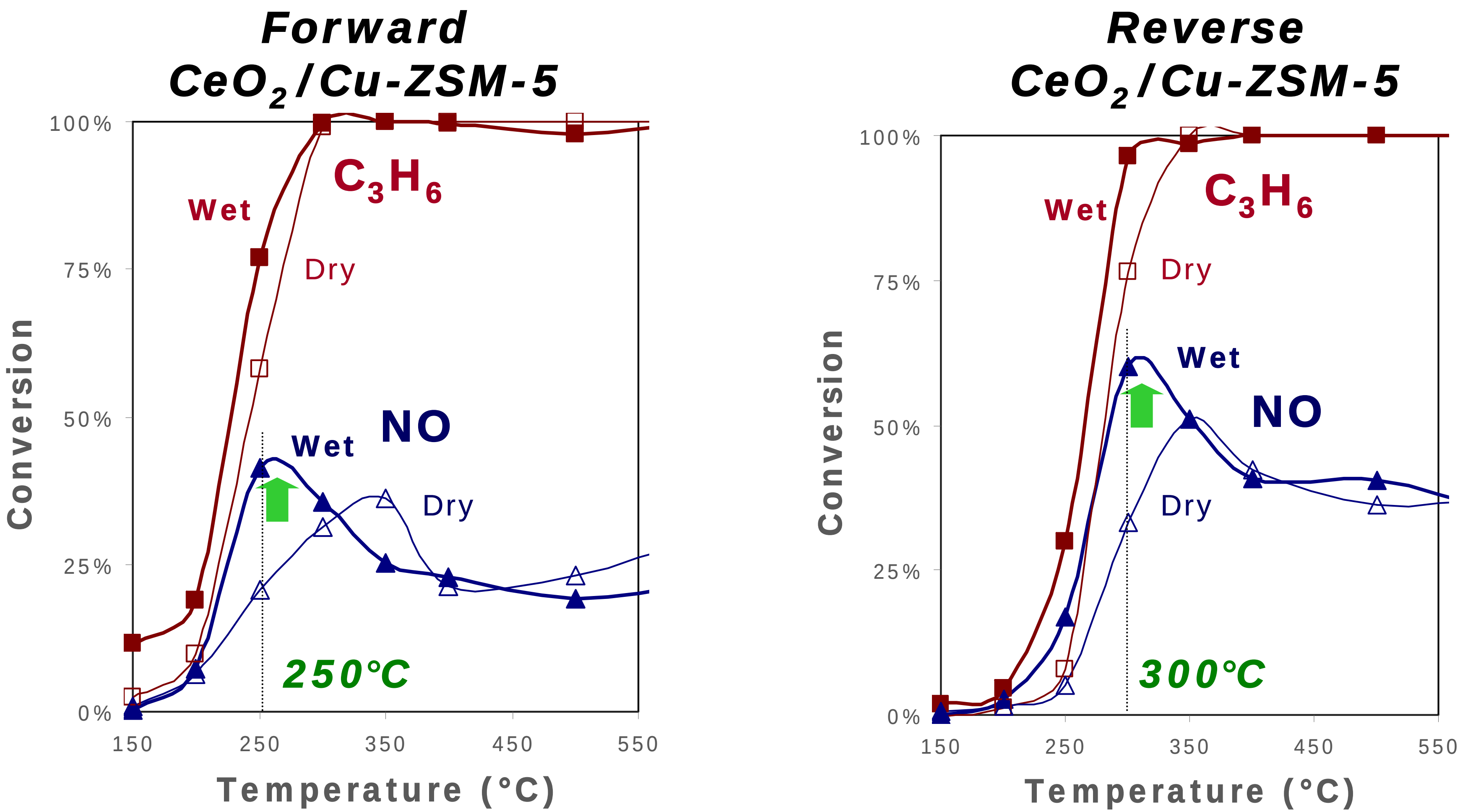


Typical DeNO$_x$ Over Cu-ZSM-5



- **Typical behavior as with literature**
  - Very active when dry
  - Suffers when water is present
    - *Hydrothermal deactivation of zeolite*
    - *Competition between H_2O and NO/C_3H_6 for active sites*
  - Typically ~400°C for maximum activity

$DeNO_x$ Over Bifunctional Catalysts



- **Bifunctional catalysts show improvement in SCR activity in the presence of water**

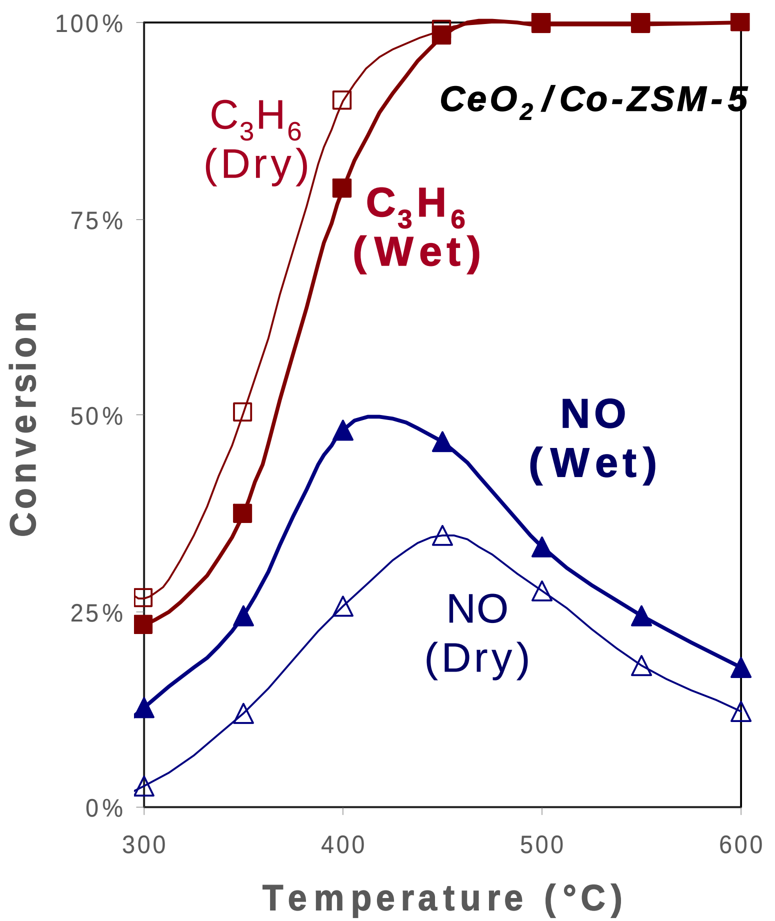
Minimal Formation of Side Products

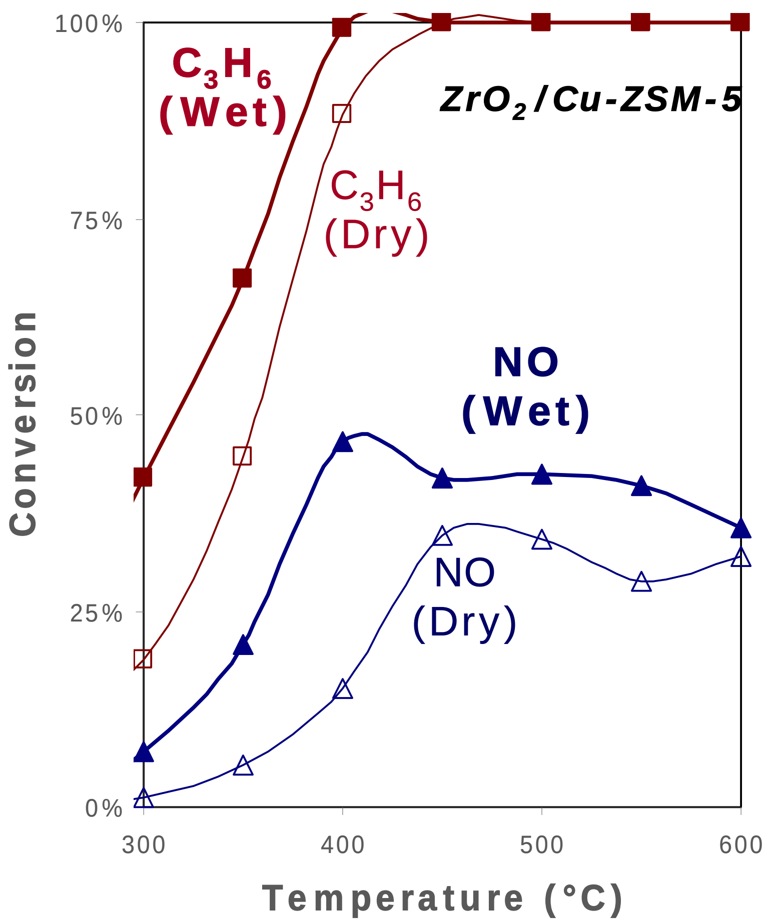
Side Production Formation under Wet Conditions at 300°C

	Cu-ZSM-5	Forward CeO_2/Cu-ZSM-5	Reverse CeO_2/Cu-ZSM-5
NO Conversion	**17.6%**	**34.8%**	**64.2%**
NO_2 & N_2O Selectivity	**3.8%**	**0.1%**	**0.1%**
CO Selectivity	**11.0%**	**0.0%**	**0.2%**
C_3H_6 Slippage	**51.7%**	**0.6%**	**0.1%**

- **New catalysts are very selective**
- **Side product formation and slippages under typical EPA regulations**

Alternate Bifunctional Modifications

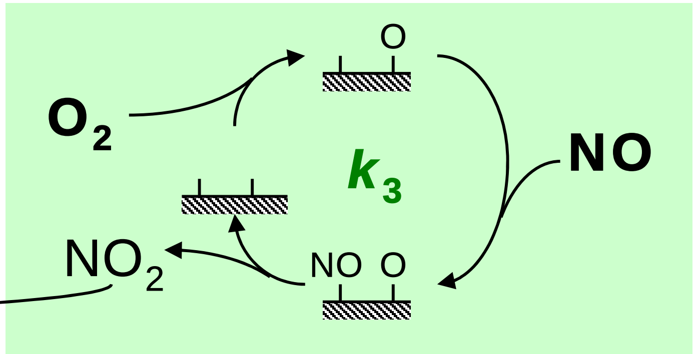




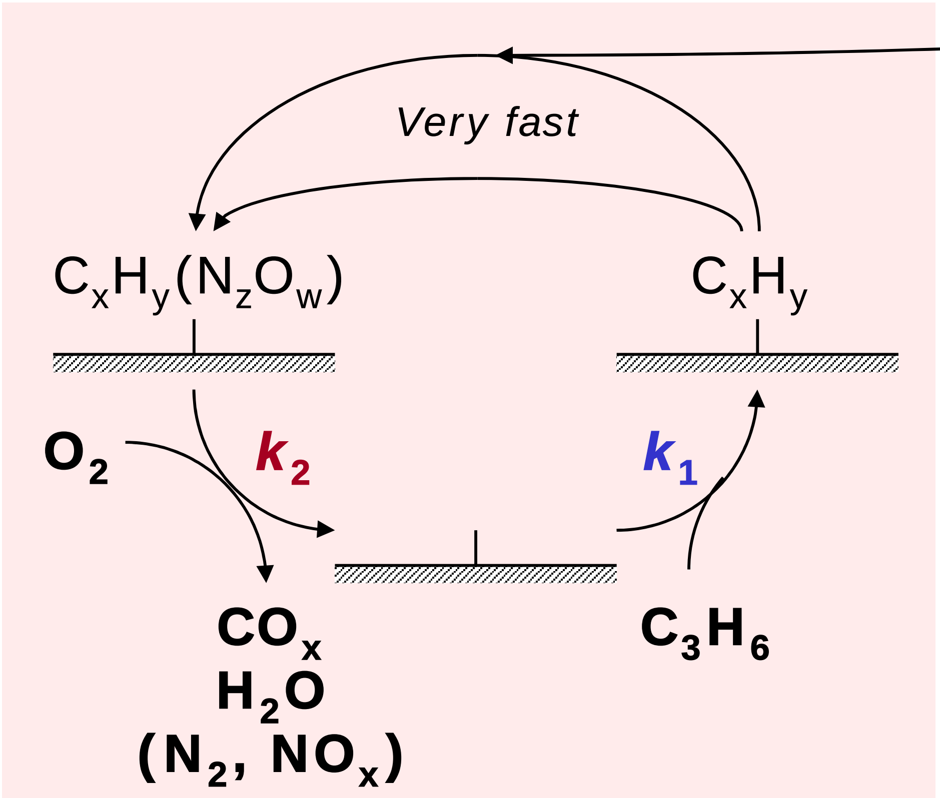
- **Can modify additive, base metal, zeolite, and combinations thereof to achieve similar benefits**

Tunable Bifunctional Mechanism

On Additive Phase



On Metal-Zeolite



Use combinations of phases to adjust kinetics

$k_1 \approx k_2$

(to maintain carbon layer)

$k_3 > k_2$

(but not $k_3 >> k_2$)

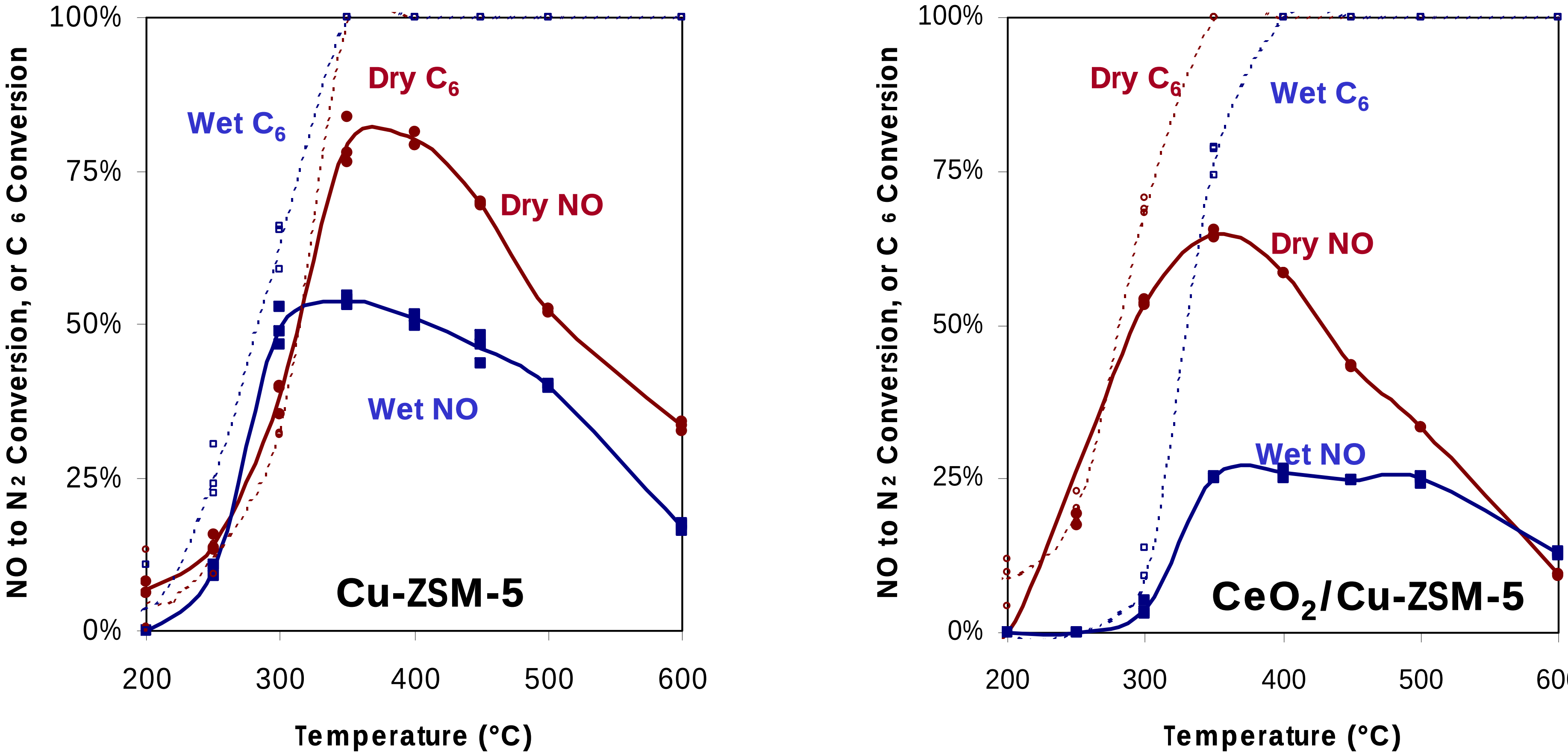
(to get NO_2 to oxidize with HC but not saturate surface)

Diesel Applications

HC-SCR with Hexane

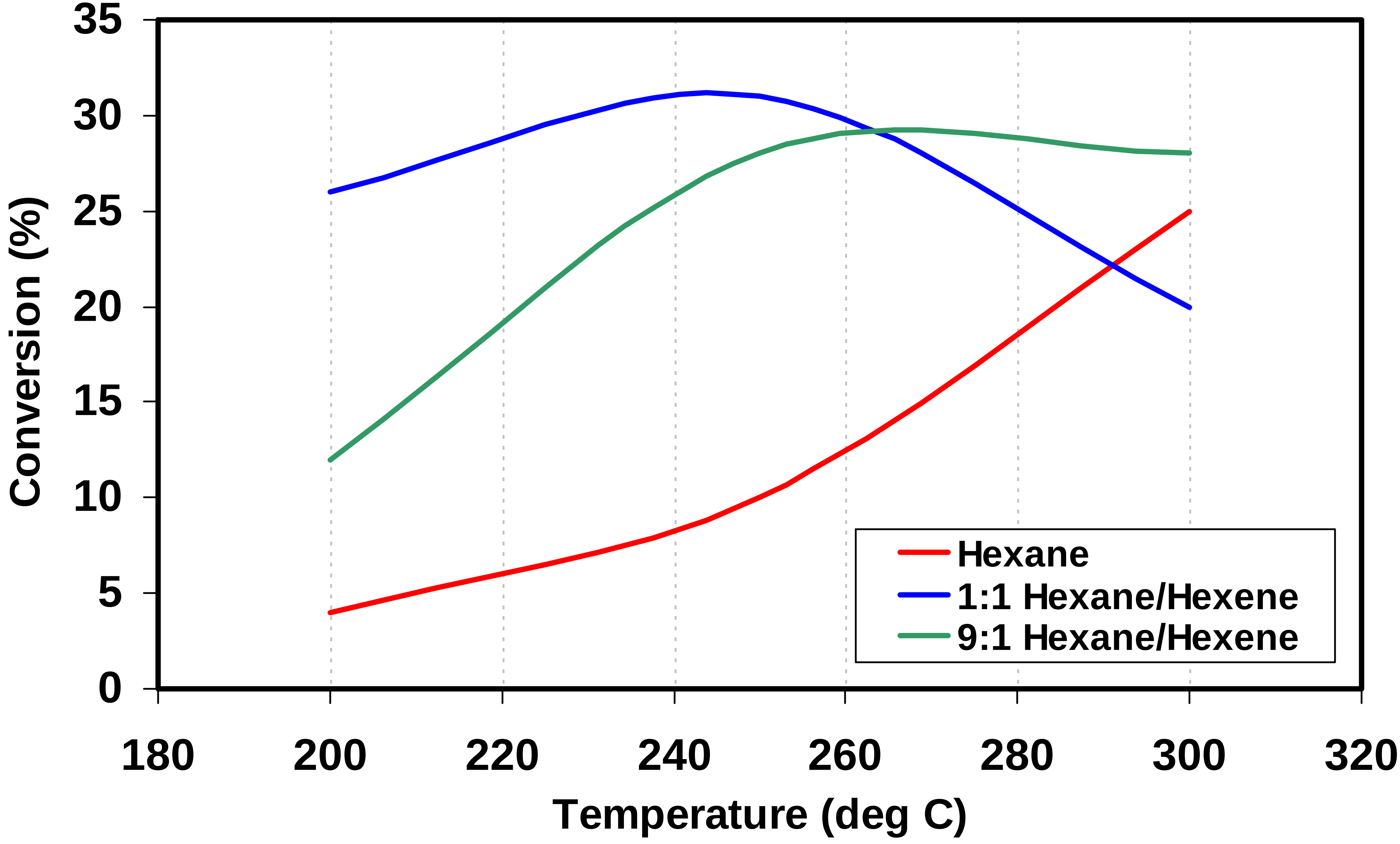
- **Current DeNO$_x$ reactor modified to achieve near-diesel conditions (from Caterpillar)**
  - 0.5% n-hexane/He gas cylinder used in place of propylene
  - O_2 delivered in higher concentration (up to 10%)
  - 1:6 N:C ratio of reagents, with 500ppm NO
  - SV ~ 30,000hr^{-1}

HC-SCR with C_6 And High O_2 Results



- **Bifunctional catalyst does not have the same benefit under these conditions as previously seen**

Addition of C_6 Olefin Greatly Improves Activity with No Side Products



Energy Advantages

- **Over Urea SCR**
  - No synthesis of urea necessary
  - No need to develop a entirely new infrastructure
  - No additional on-board storage
  - Stoichiometric use of hydrocarbon
  - Slip very minimal but (*only*) hydrocarbon

- **Over NO_x absorbers**
  - Non-precious metals
  - Very sulfur tolerant
  - Low pressure drop
  - Constant action

Conclusions

- **Developed novel bifunctional catalysts for HC-SCR**
  - Activated by water
  - Lower temperature activity compared to Cu-ZSM-5
  - Drop-in replacement for existing NH_3 SCR systems

- **Explored catalyst behavior and mechanism**
  - Catalytic behavior can be tuned through numerous phases
  - Good understanding of critical steps

- **Planned for further development of catalysts**
  - Alternate hydrocarbons (CH_4, C_3H_8, C_6H_{14})
  - Alternate conditions (diesel, coal-fired plants)

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Patents Pending

- **US Patent Application 2003/0073566**
- **World Patent Application WO 03/031781 A1**
  - Novel Catalyst for Selective NOx Reduction Using Hydrocarbons
  - C. L. Marshall & M. K. Neylon

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Marshall et al. (43) **Pub. Date: Apr. 17, 2003**

(54) **NOVEL CATALYST FOR SELECTIVE NOX REDUCTION USING HYDROCARBONS**

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(57) **ABSTRACT**

This invention discloses a catalyst and process for removing nitrogen oxides from exhaust streams under lean burn conditions using hydrocarbons as the reductant. Catalysts consists of two phases, a metal exchanged molecular sieve and a stabilizing metal oxide associated with the molecular sieve.