

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 NH₃/Urea (SCR)	Metal oxides under lean conditions	NH₃ slippage and NH₃/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

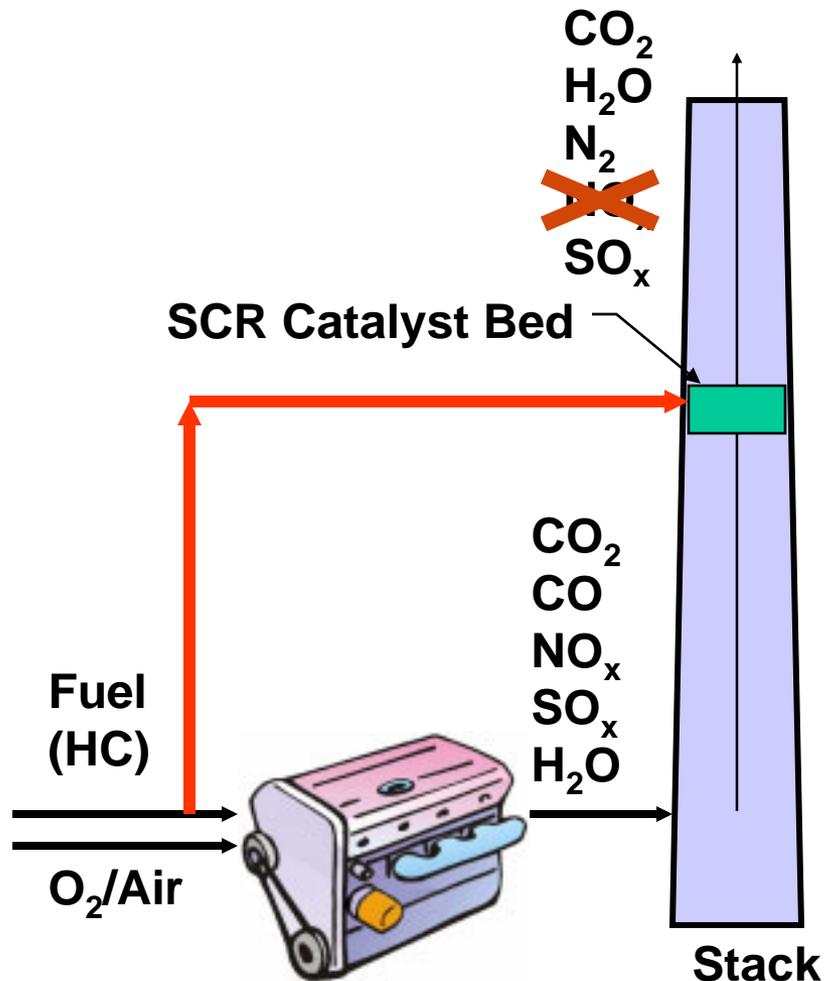
- *Supported metals (Pt/SiO₂)*

- Water stable

- Lower activity

- Significant by-products (N_2O , NO_2)

Hydrocarbon Selective Catalytic Reduction (HC-SCR)



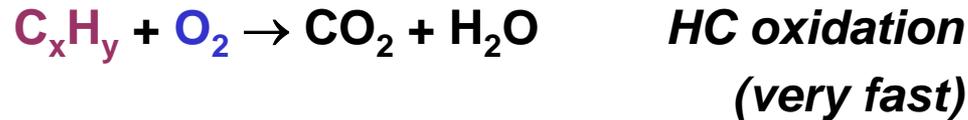
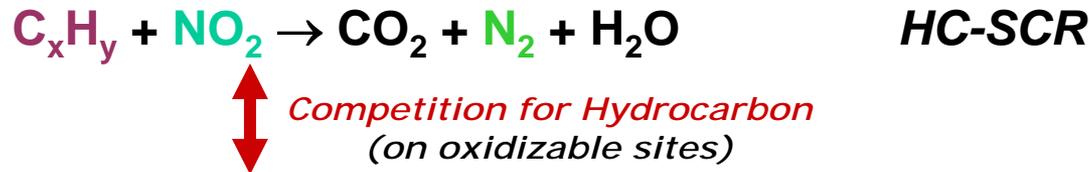
- **SCR with light hydrocarbons proposed as alternative deNO_x method**

- **Advantages**

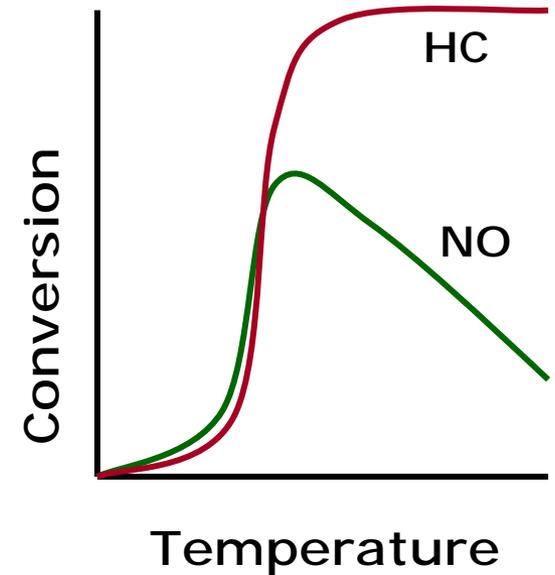
- Hydrocarbon typically already in use on site
- Can be used in lean-burn conditions
- Minimal concerns with HC slippage



HC-SCR Mechanism



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



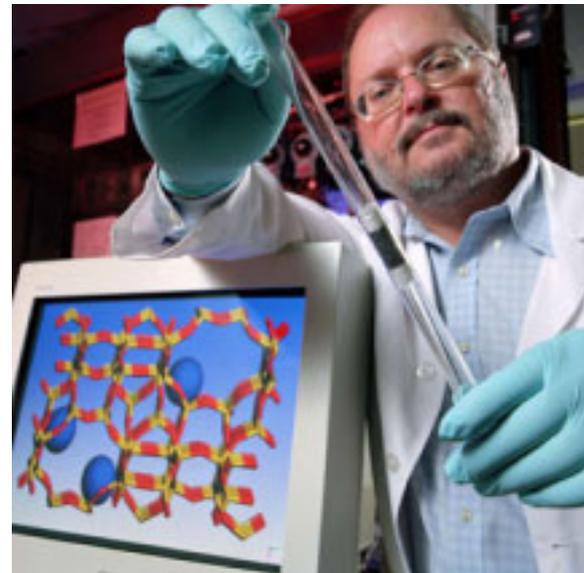
Novel DeNO_x Catalyst Project Goals

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*
- **CeO₂/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
 - **ZrO₂, MoO₃**
 - Zeolites
 - **Mordenite, Ferrierite,**
 - **Y, Beta**



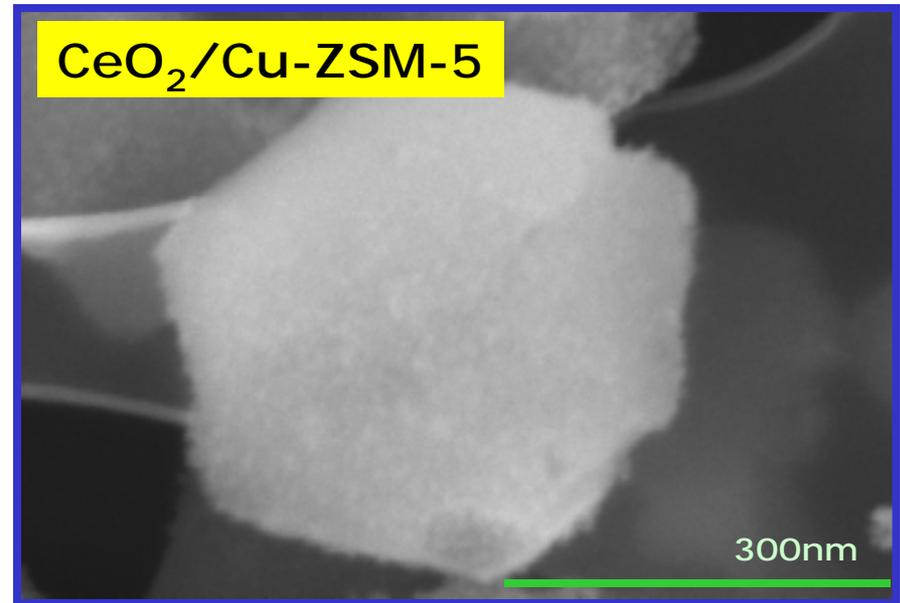
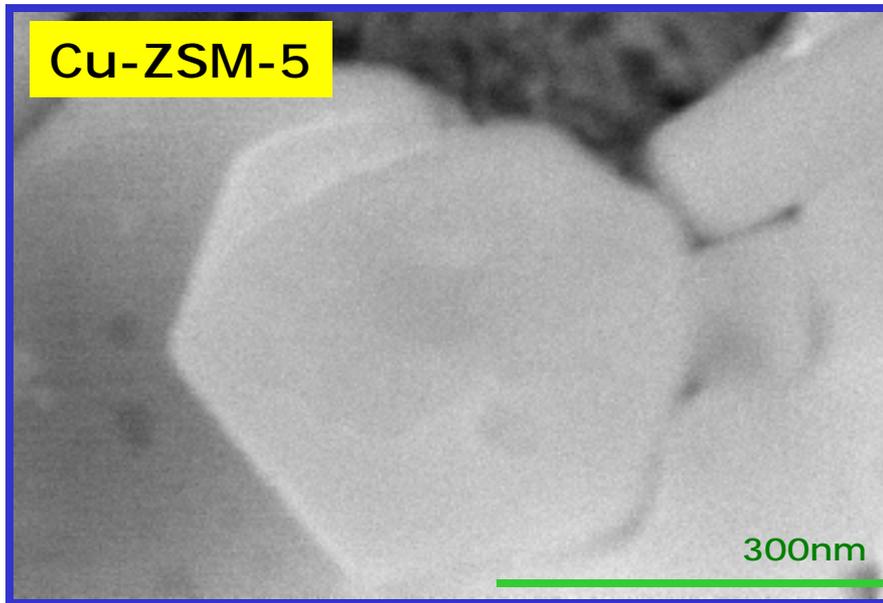
Catalyst Preparation Method

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



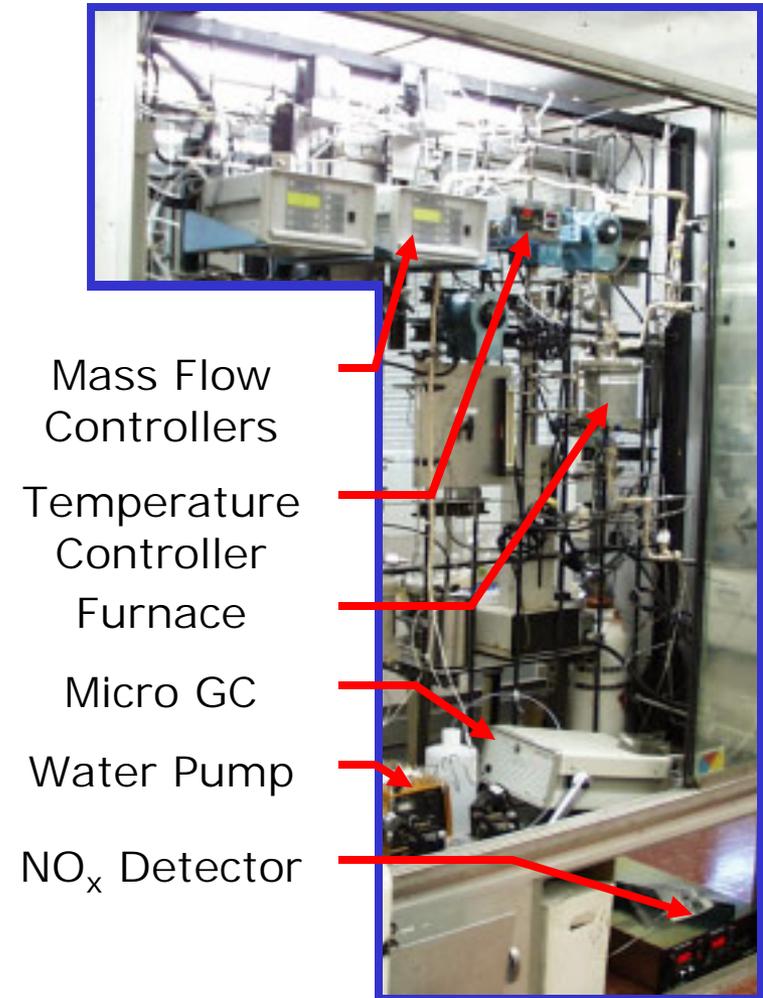
Synthesis of Bifunctional Materials

- **Zeolite + sol = coated zeolite**

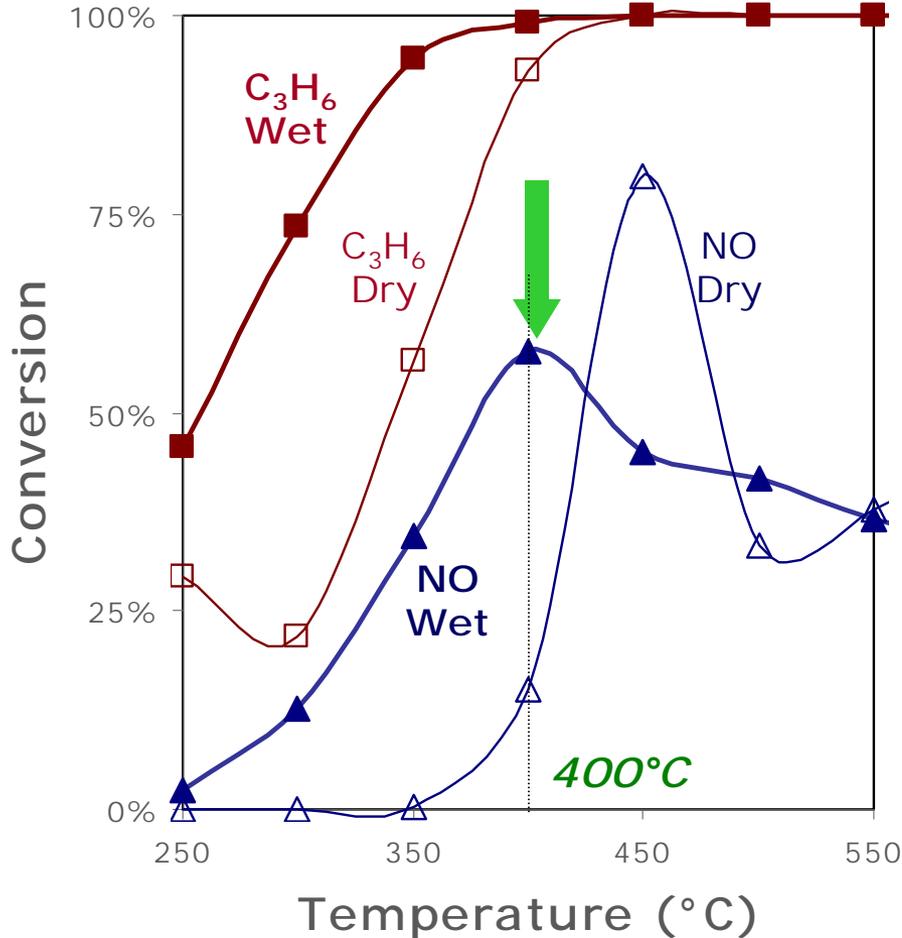


DeNO_x Reactor System

- **Nominal conditions for stationary applications:**
 - 30,000 hr⁻¹ SV
 - 1000ppm NO
 - 1000ppm C₃H₆ ←
 - 2% O₂
 - 10% H₂O when used
- **Flexible design to test other NO_x systems**
- **Detectors allow quantification of NO₂, N₂O, and CO**

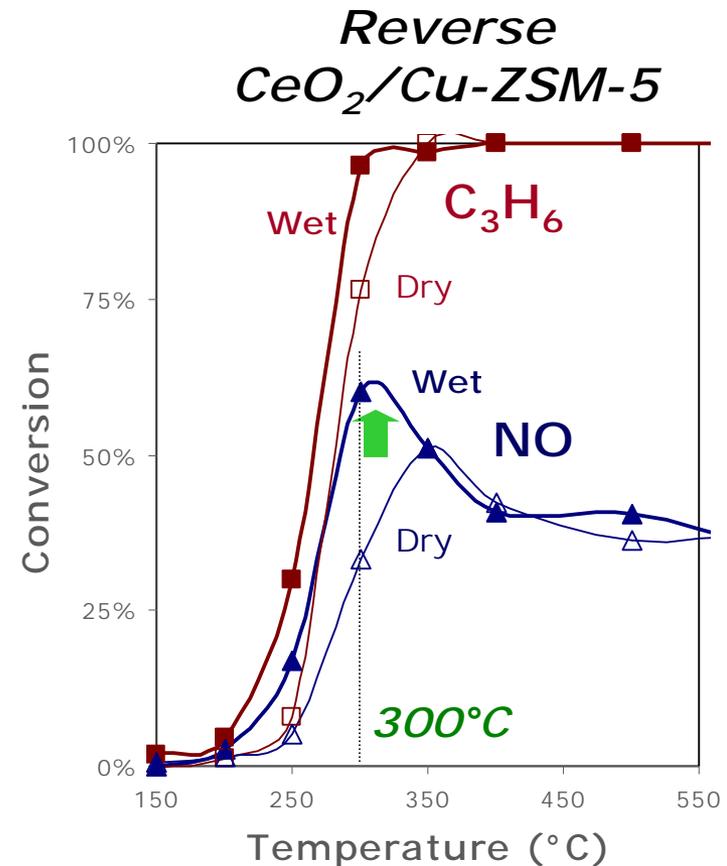
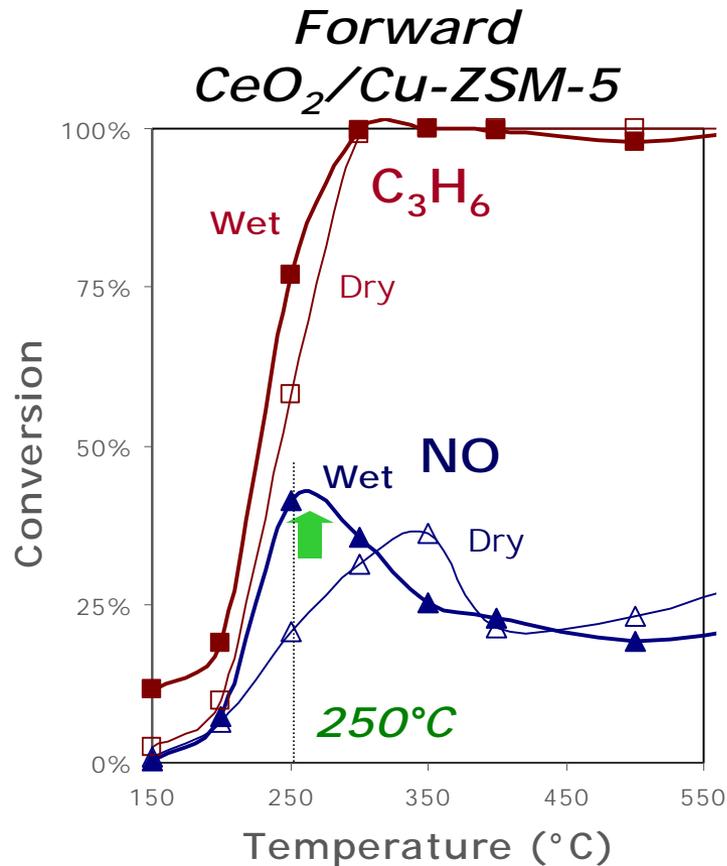


Typical DeNO_x Over Cu-ZSM-5



- **Typical behavior as with literature**
 - Very active when dry
 - Suffers when water is present
 - *Hydrothermal deactivation of zeolite*
 - *Competition between H₂O and NO/C₃H₆ 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**

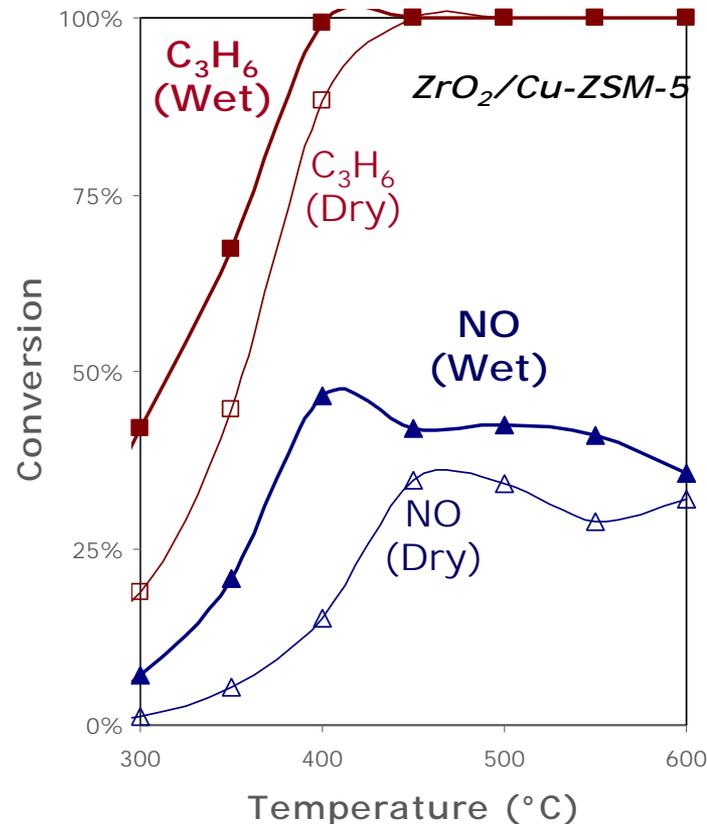
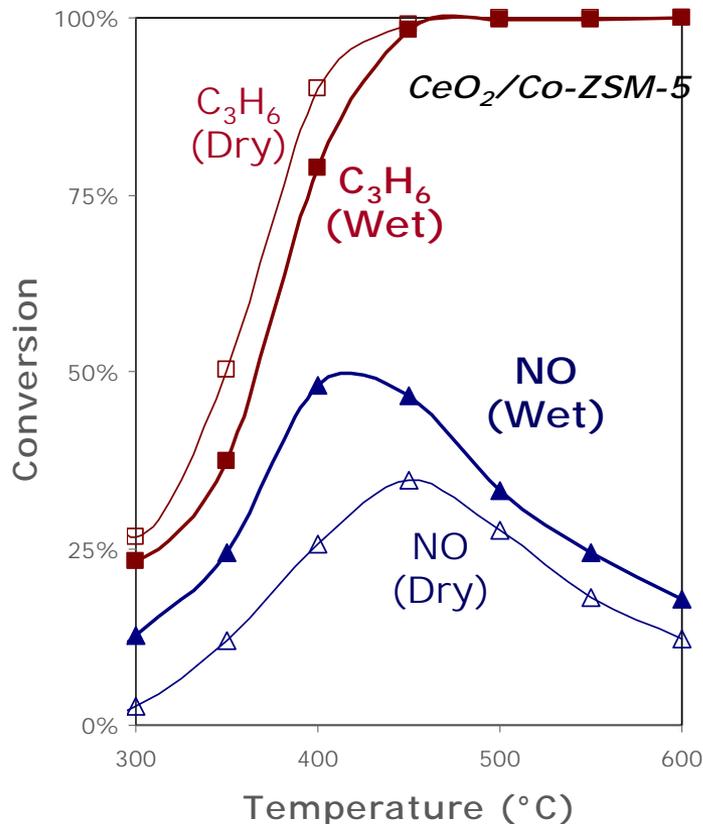
Minimal Formation of Side Products

Side Production Formation under
Wet Conditions at 300°C

	Cu-ZSM-5	Forward CeO₂/Cu-ZSM-5	Reverse CeO₂/Cu-ZSM-5
NO Conversion	17.6%	34.8%	64.2%
NO ₂ & N ₂ O Selectivity	3.8%	0.1%	0.1%
CO Selectivity	11.0%	0.0%	0.2%
C ₃ H ₆ Slippage	51.7%	0.6%	0.1%

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

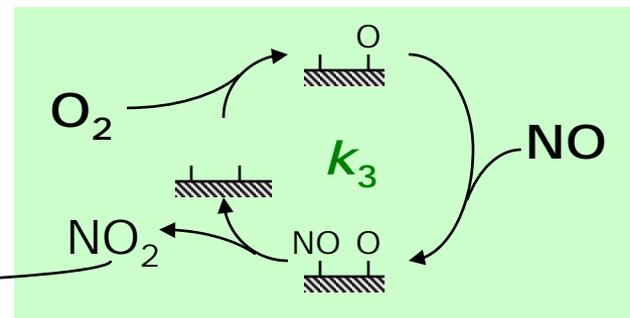
Alternate Bifunctional Modifications



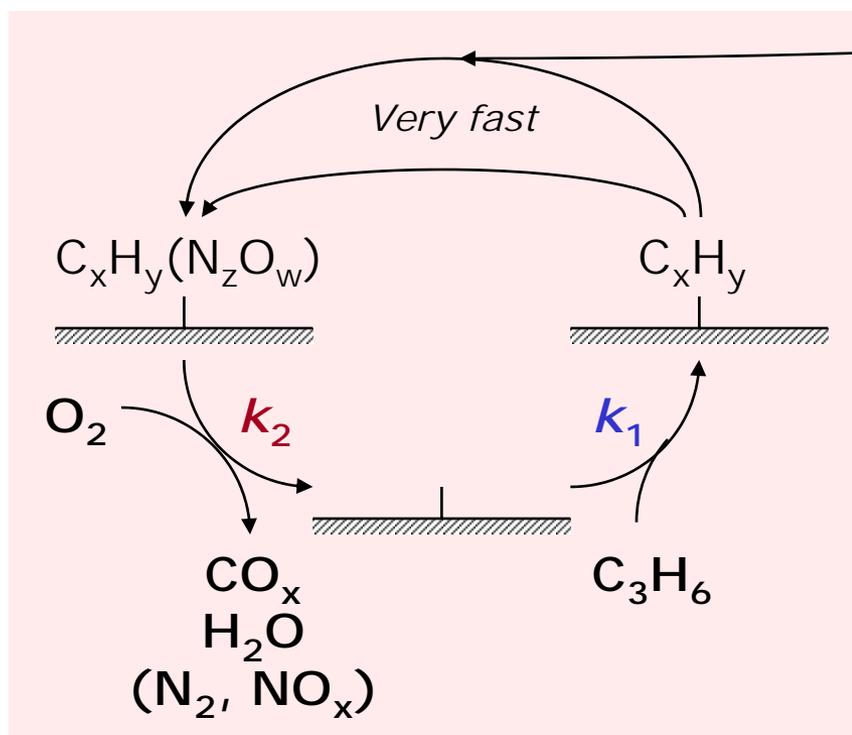
- **Can modify additive, base metal, zeolite, and combinations thereof to achieve similar benefits**

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)

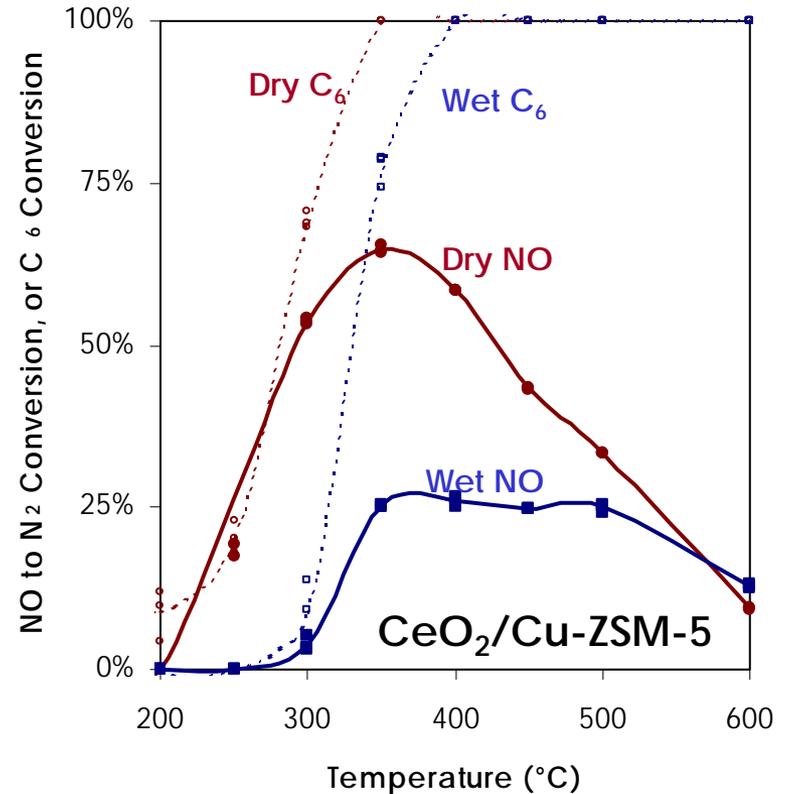
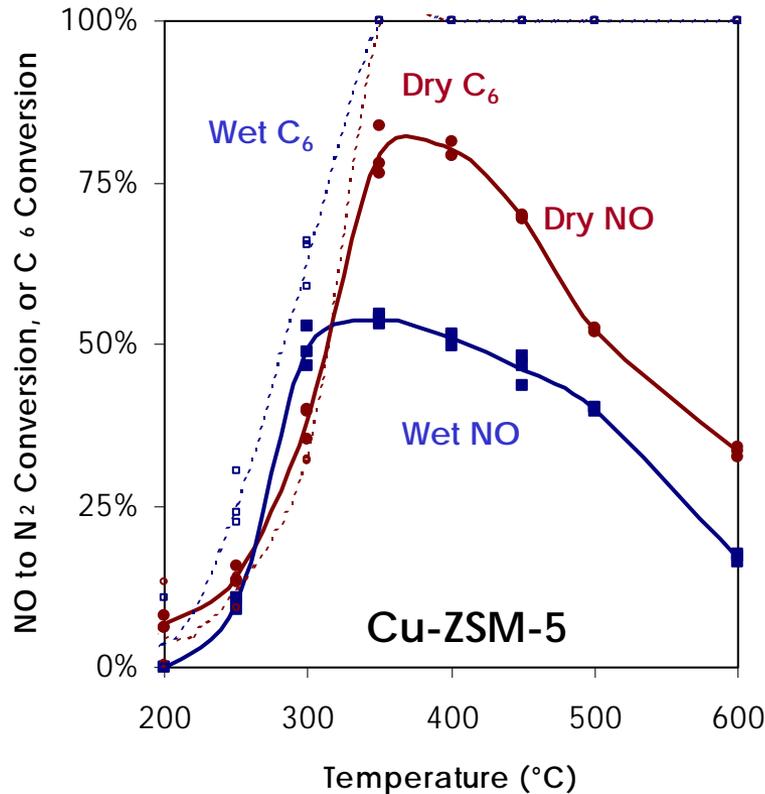
$k_3 > k_2$
(but not $k_3 \gg k_2$)
(to get NO_2 to oxidize with HC but not saturate surface)

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
 - O₂ delivered in higher concentration (up to 10%)
 - 1:6 N:C ratio of reagents, with 500ppm NO
 - SV ~ 30,000hr⁻¹

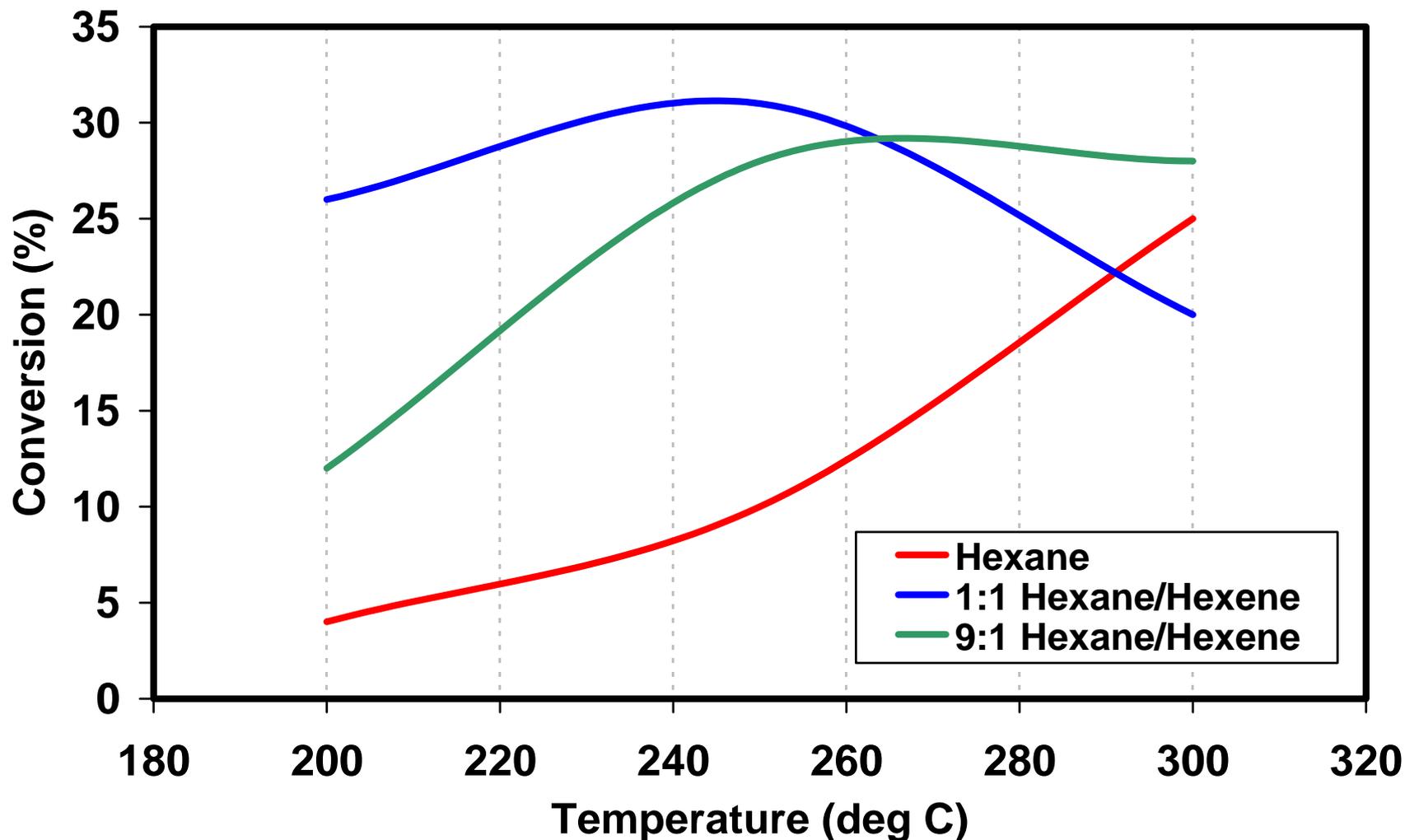
HC-SCR with C₆ And High O₂ Results



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



Addition of C₆ 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

(19) **United States**
(12) **Patent Application Publication** (10) **Pub. No.: US 2003/0073566 A1**
Marshall et al. (43) **Pub. Date: Apr. 17, 2003**

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

(76) **Inventors: Christopher L. Marshall, Naperville, IL (US); Michael K. Neylon, Naperville, IL (US)**

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(52) **U.S. CL 502/64; 502/66; 502/74; 502/78; 502/79**

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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.

(21) **Appl. No.: 09/975,708**

(22) **Filed: Oct. 11, 2001**