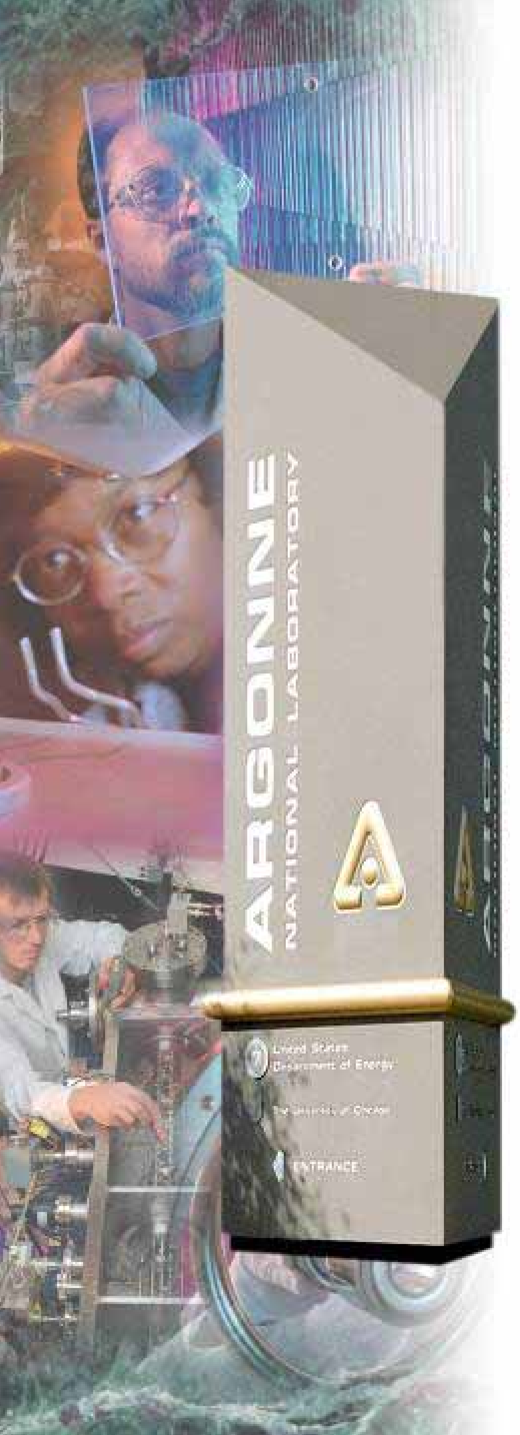

Bifunctional Catalysts for the Selective Catalytic Reduction of NO by Hydrocarbons

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Existing Methods of NO_x Reduction

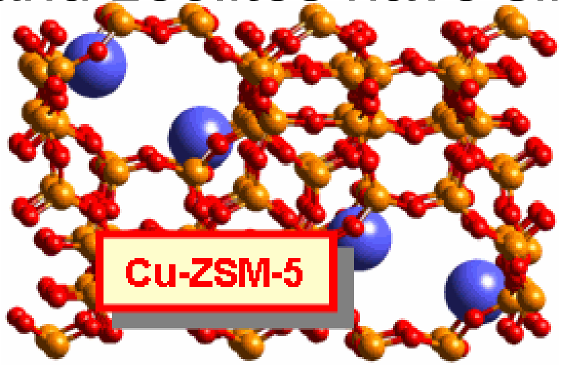
Method	Typical Usage	Disadvantages
NO_x Sorption (NOx Traps)	**Metal oxides in lean adsorption/rich reduction cycles**	**Limited capacity Strict engineering controls**
NO_x Reduction with NH_3/Urea (NH₃ - SCR)	**Metal oxides under lean conditions**	NH_3 slippage NH_3 (urea) storage
Plasma-Assisted Catalysis	**Metal zeolites under lean conditions**	Energy requirements of the plasma device

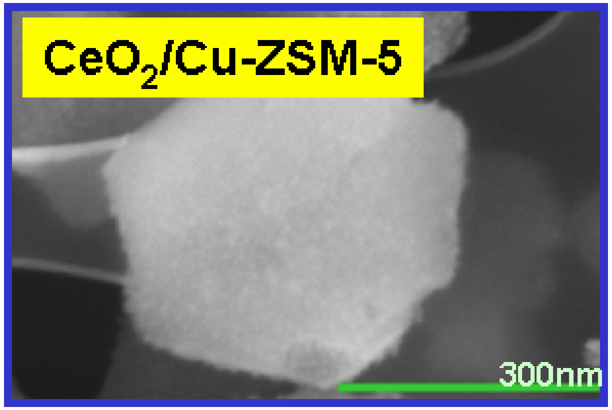
- **HC SCR completely passive**
- ***Advantages***
  - Hydrocarbon typically already in use on site
  - Can be used in lean-burn conditions
  - Minimal concerns with HC slippage

$$NOx + HC \rightarrow N_2 + CO_2$$

Catalyst Synthesis

- **Prepared from step-wise addition of metal oxide to zeolite form via exchange or impregnation techniques**
- **CeO_2/Cu-ZSM-5 has been explored the most**
  - other metals, oxides, and zeolites have similar improvements
  - Metals
    - ***Co***, ***Ag***, ***Fe***, *Cr*, *Y*
  - Metal oxides
    - ***ZrO_2***, ***MoO_3***
  - Zeolites
    - ***Mordenite***, ***Ferrierite,***
    - *Y*, *Beta*





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 extremely selective**
- **Side product formation and slippages under typical EPA regulations**

Technical Accomplishment Summary

- **Lowered the temperature for maximum activity by 150 °C.**
  - Using propylene.
- **Improved the water stability from unstable in water to needing water for maximum activity.**
- **Drop-in replacement for existing NH3 SCR systems**
- **Optimized the individual reaction steps for maximum overlap**
  - $NO + \frac{1}{2} O_2 \rightarrow NO_2$
  - HC → HC (surface)
  - HC (surface) + $NO_2 \rightarrow N_2 + CO_2 + H_2O$
- **Poster**

Diesel Applications

Challenges in Moving to Diesel Reductant

- **Lower reaction temperature**
  - Optimized at 350°C
- **Extended temperature range**
  - Peaks at 350°C
- **Use of diesel (or diesel derived hydrocarbons) as source of reductant**
- **Improved conversion at higher space velocity**
- **Higher O_2 content**
  - Perhaps most problematic.

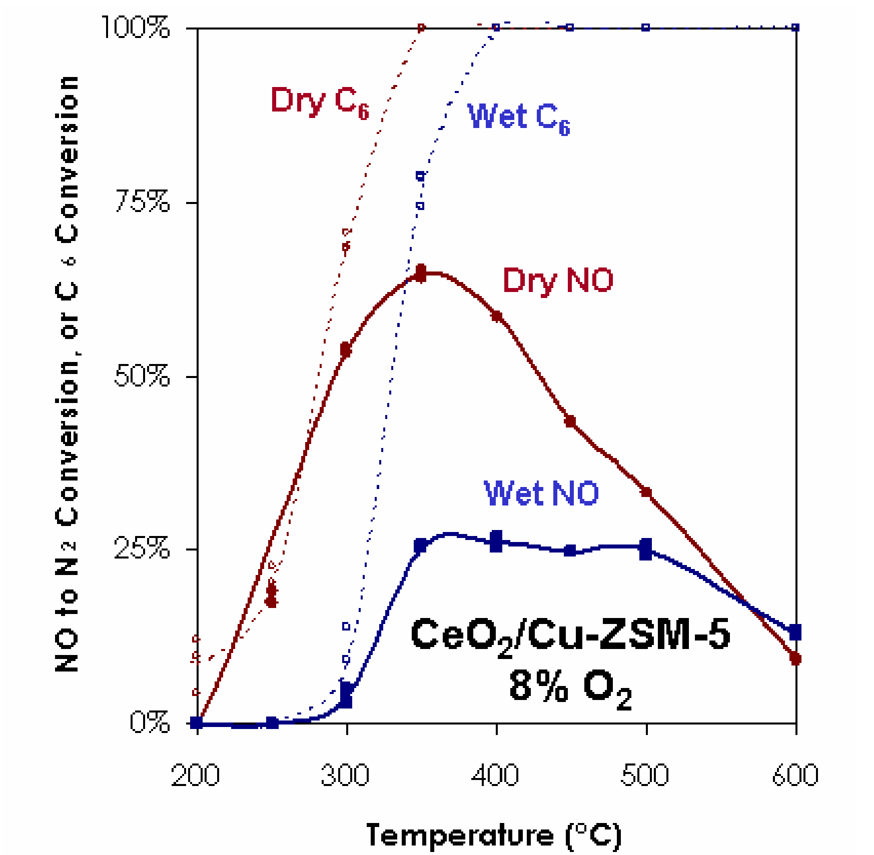
Diesel Composition Very Different from Pure Olefin

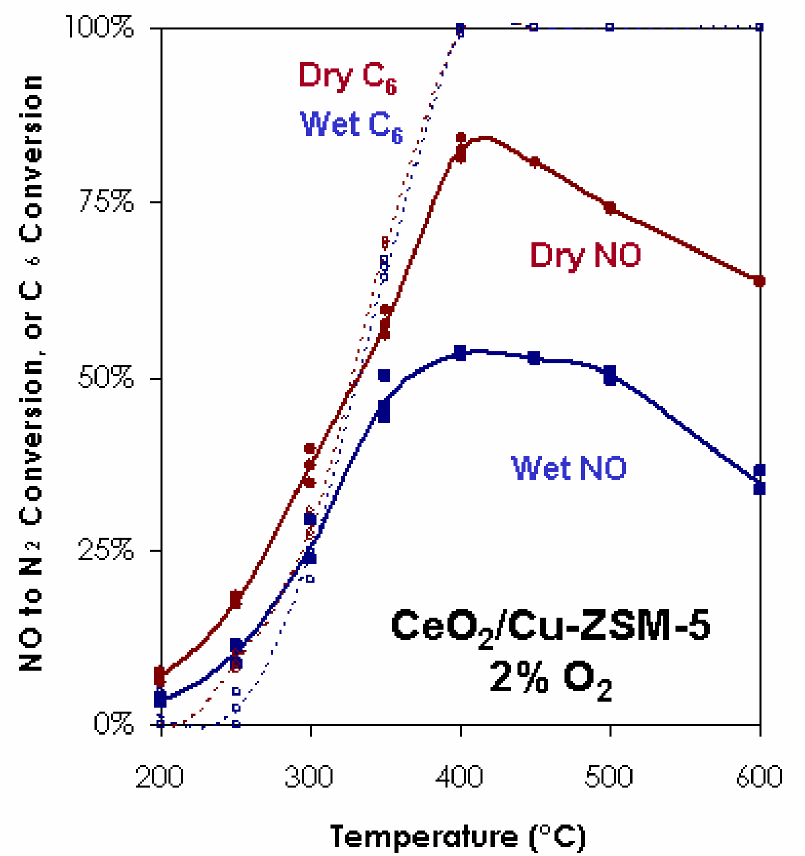
- **High concentration of paraffins**

  >75%

- **Moderate concentration of aromatics**
- **No OLEFINS!!!**

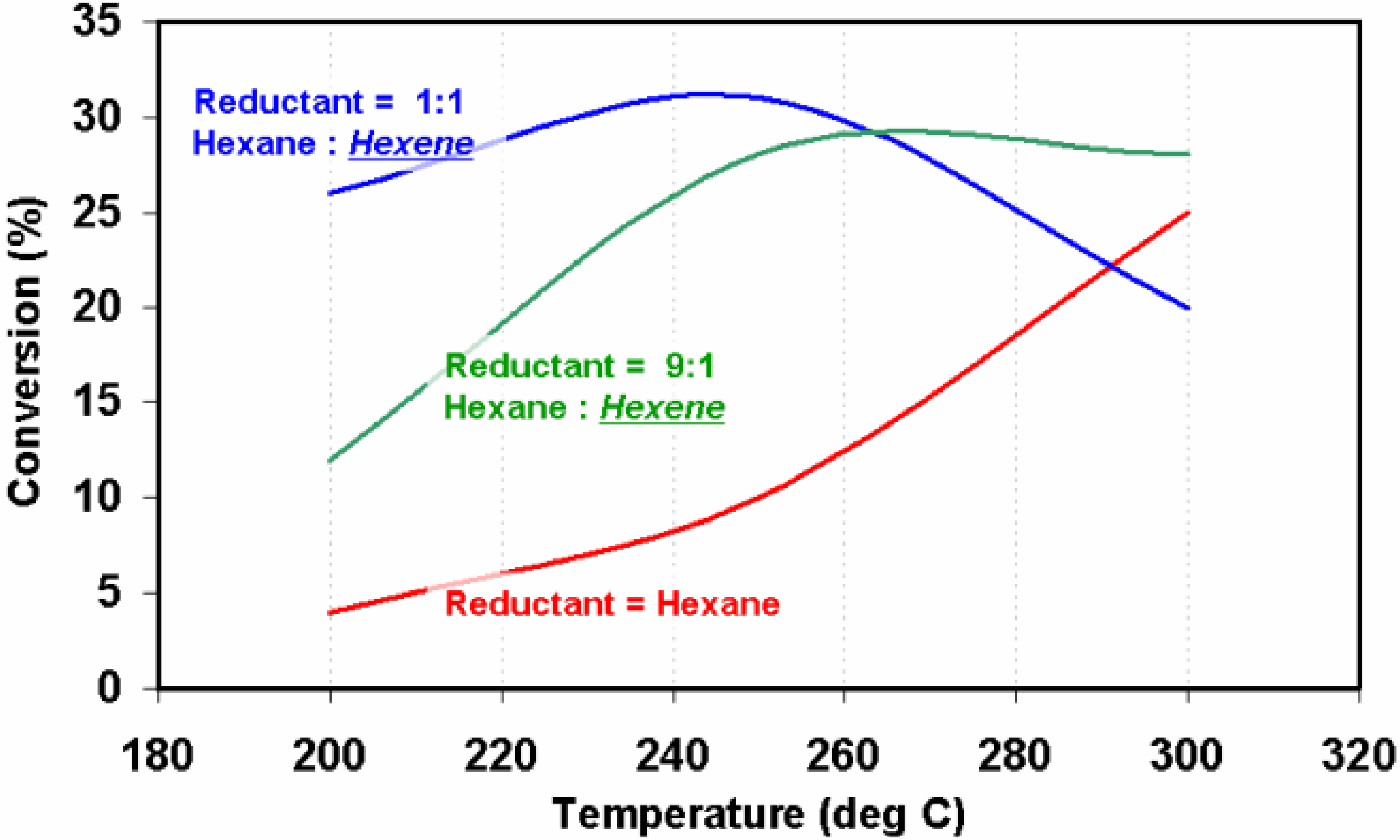
Effect of O_2 on HC-SCR with Hexane (n-C_6)



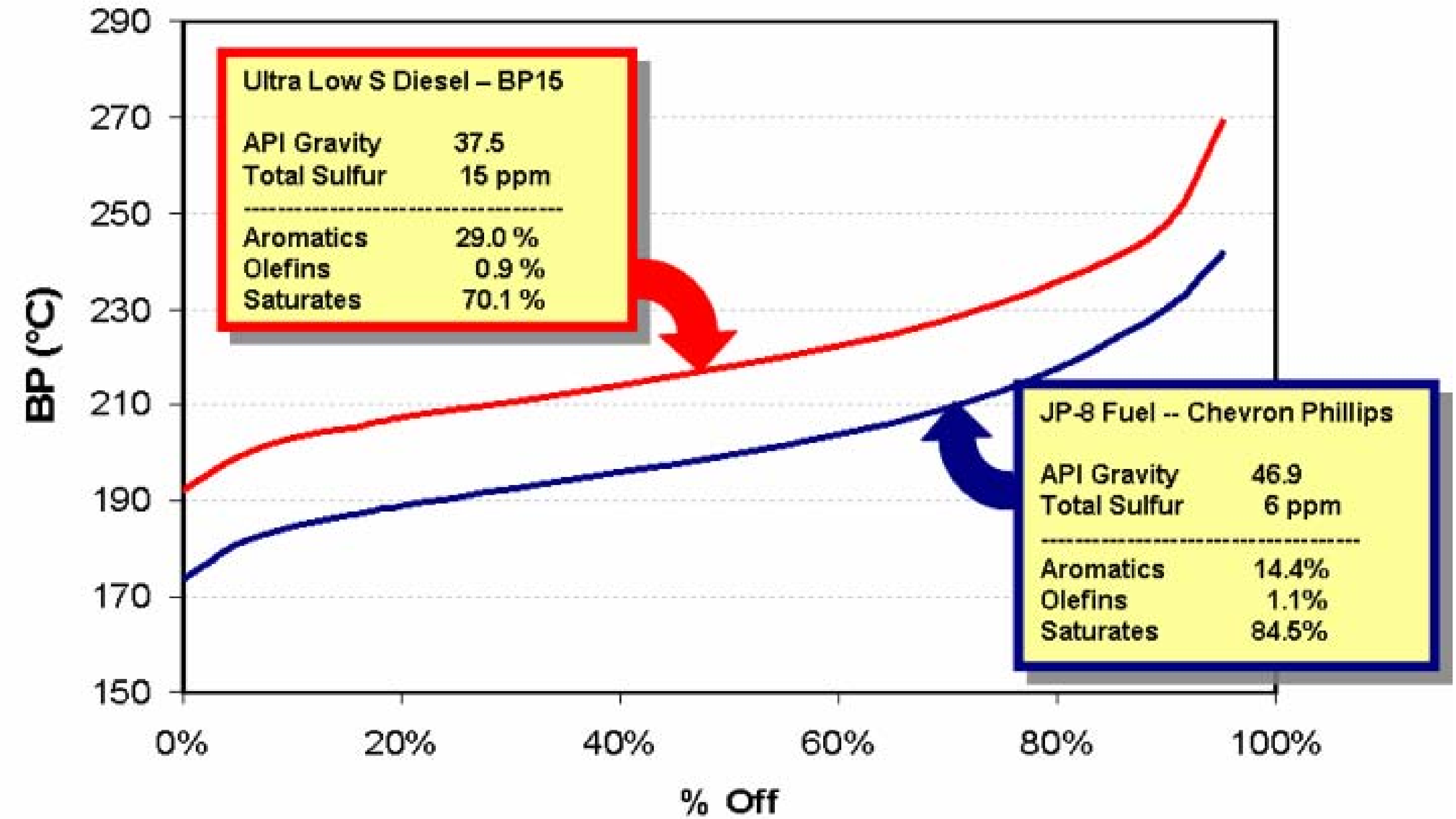


- **While overall activities improve with lower O_2 concentration, still negatively affected by water**

Addition of C_6 Olefin Greatly Improves Activity with No Side Products

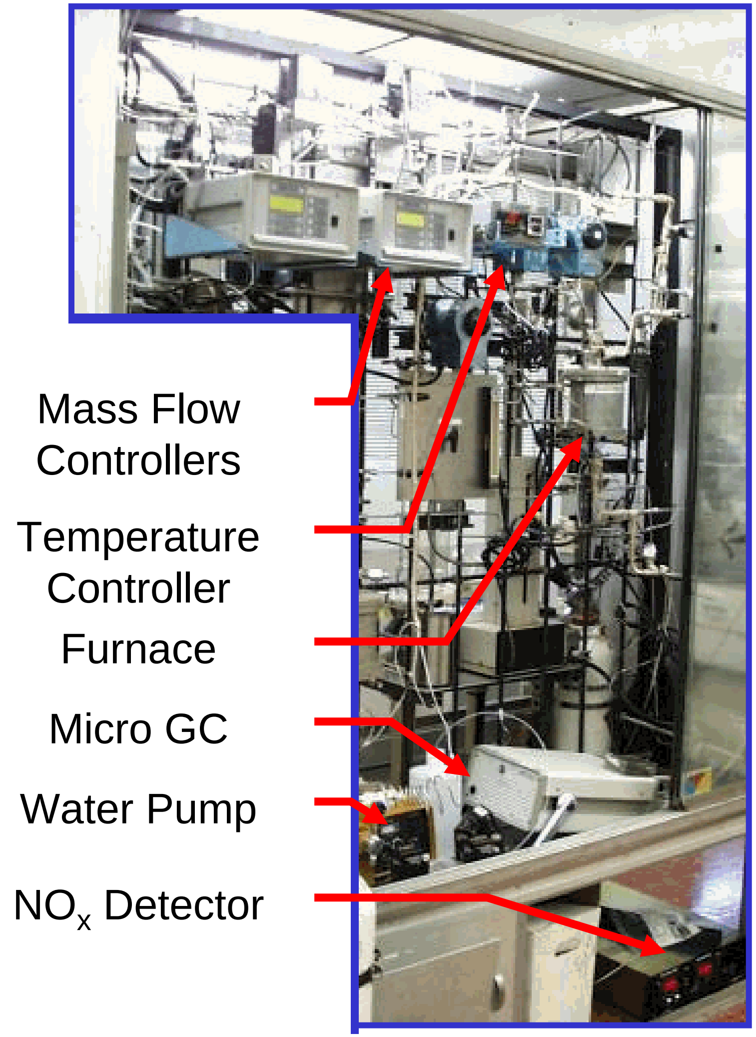


JP-8 vs. Low Sulfur Diesel

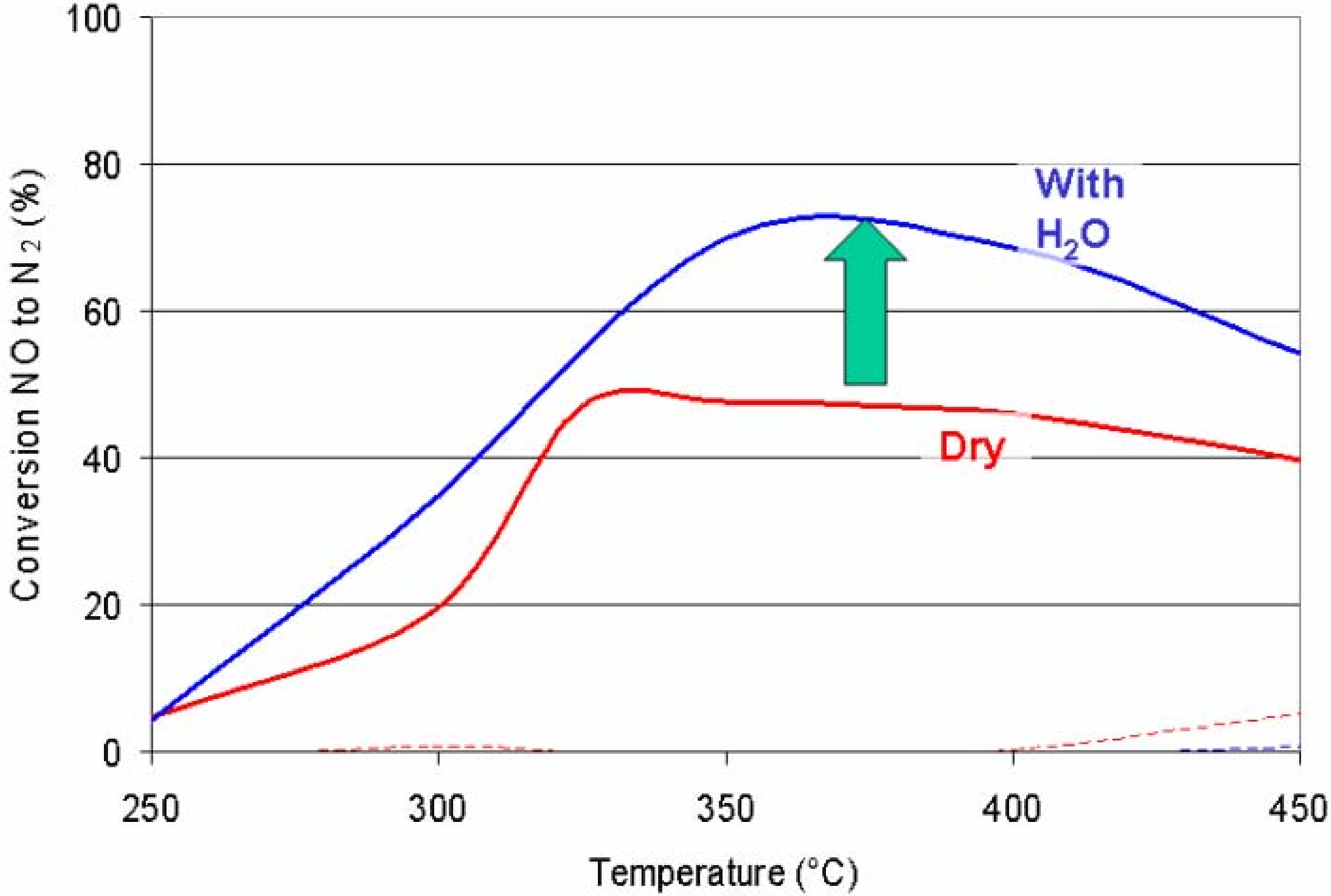


DeNO$_x$ Reactor System

- **Reactor conditions :**
  - 40,000 Hr^{-1} SV
  - 1000 ppm NO
  - 1000 ppm HC
    - *17% Aromatics*
      - 13% C_9 and smaller
  - 2% O_2 (A/F = 16.9)
  - 10% H_2O
- **Detectors allow quantification of NO_2, N_2O, and CO**



JP-8 as a Reductant w/ and w/o H_2O



HC-SCR Mechanism

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

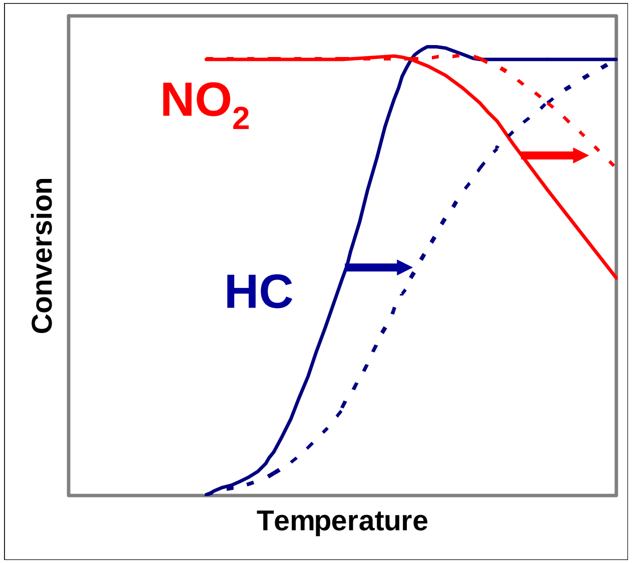
(requires reducible sites)

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

Competition for Hydrocarbon
(on oxidizable sites)

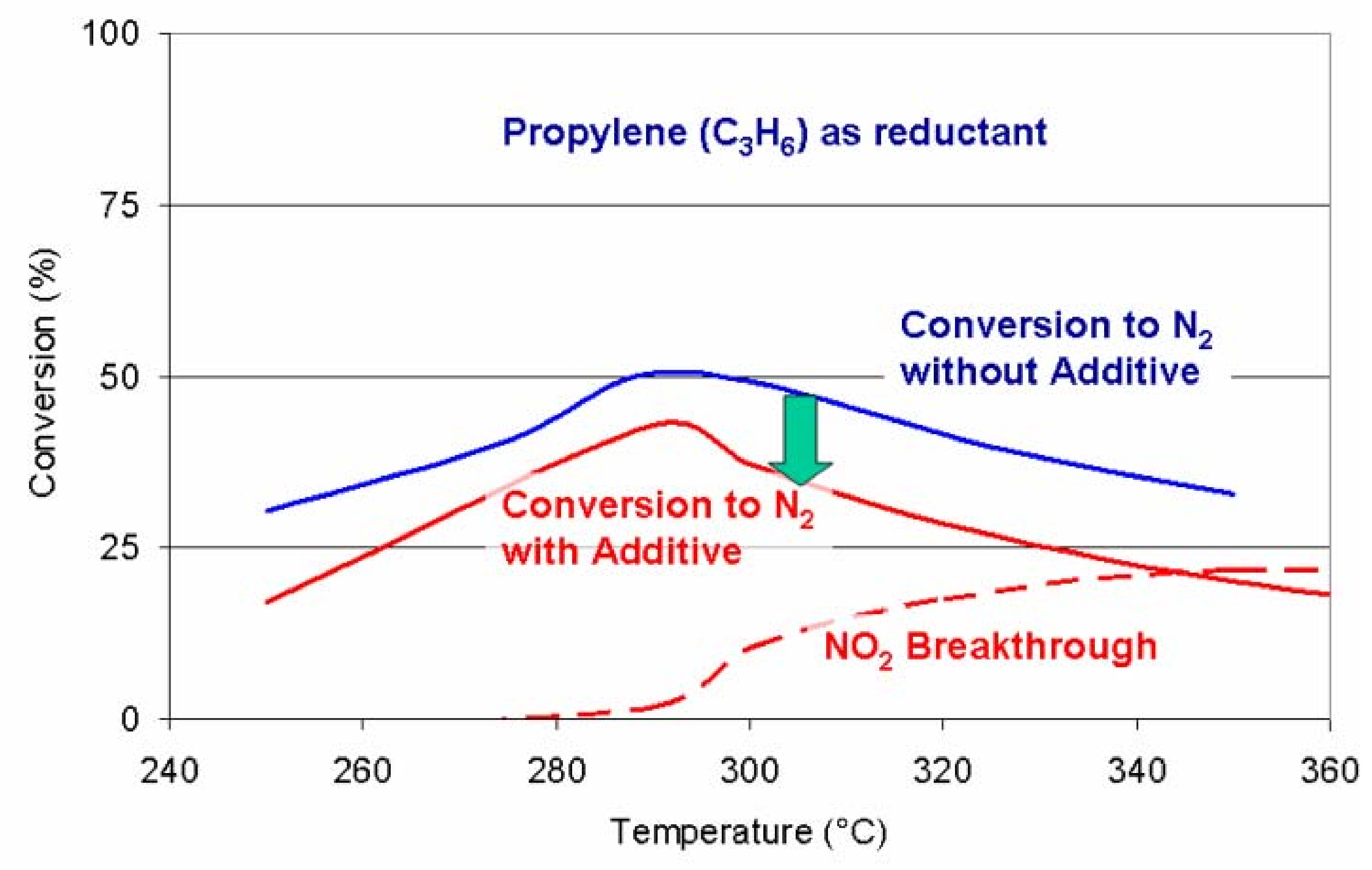
$C_xH_y + O_2 \rightarrow CO_2 + H_2O$ *HC oxidation*

(very fast)

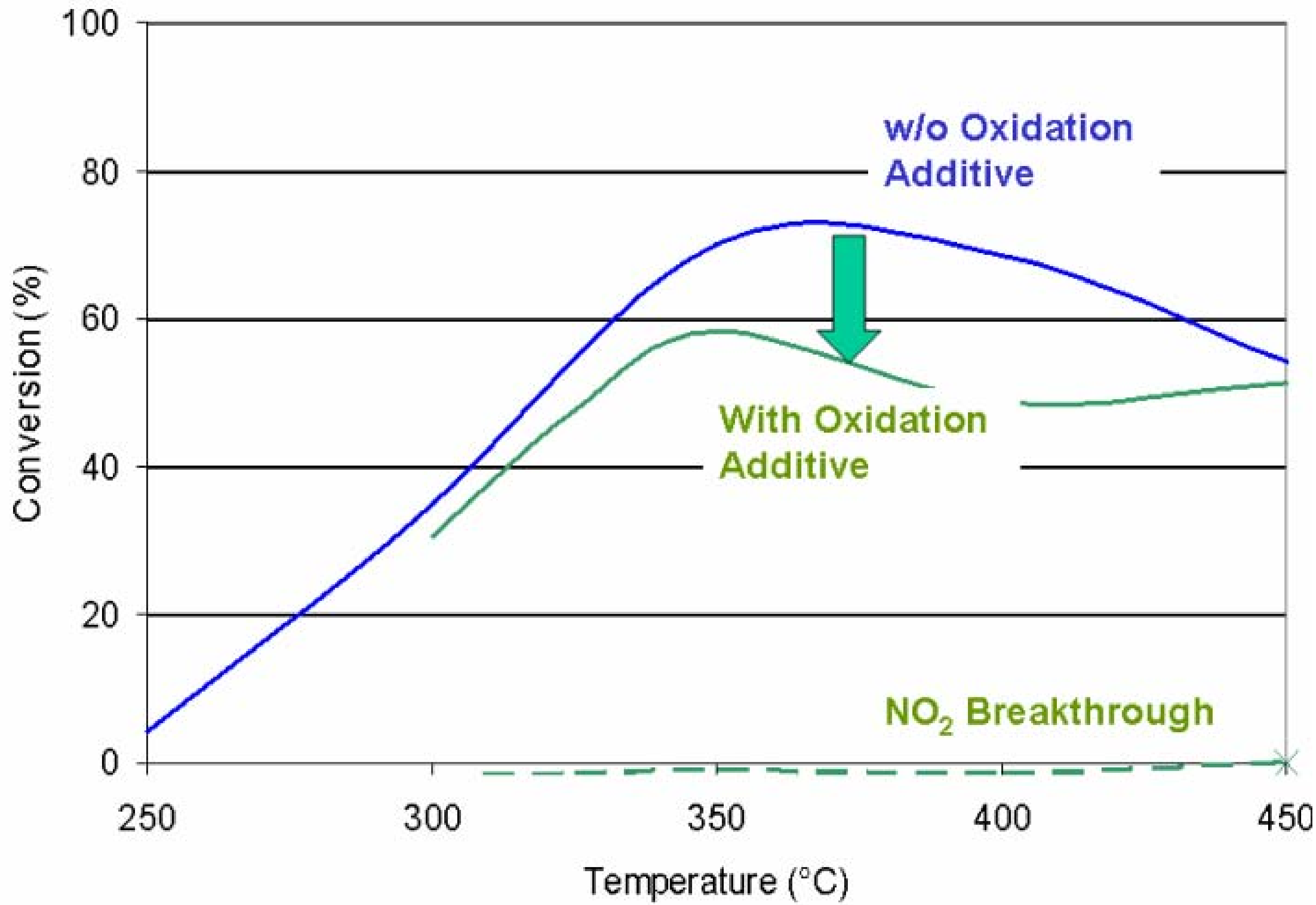


- Bifunctional catalyst needed to oxidize HC with NO_2 before O_2 oxidation

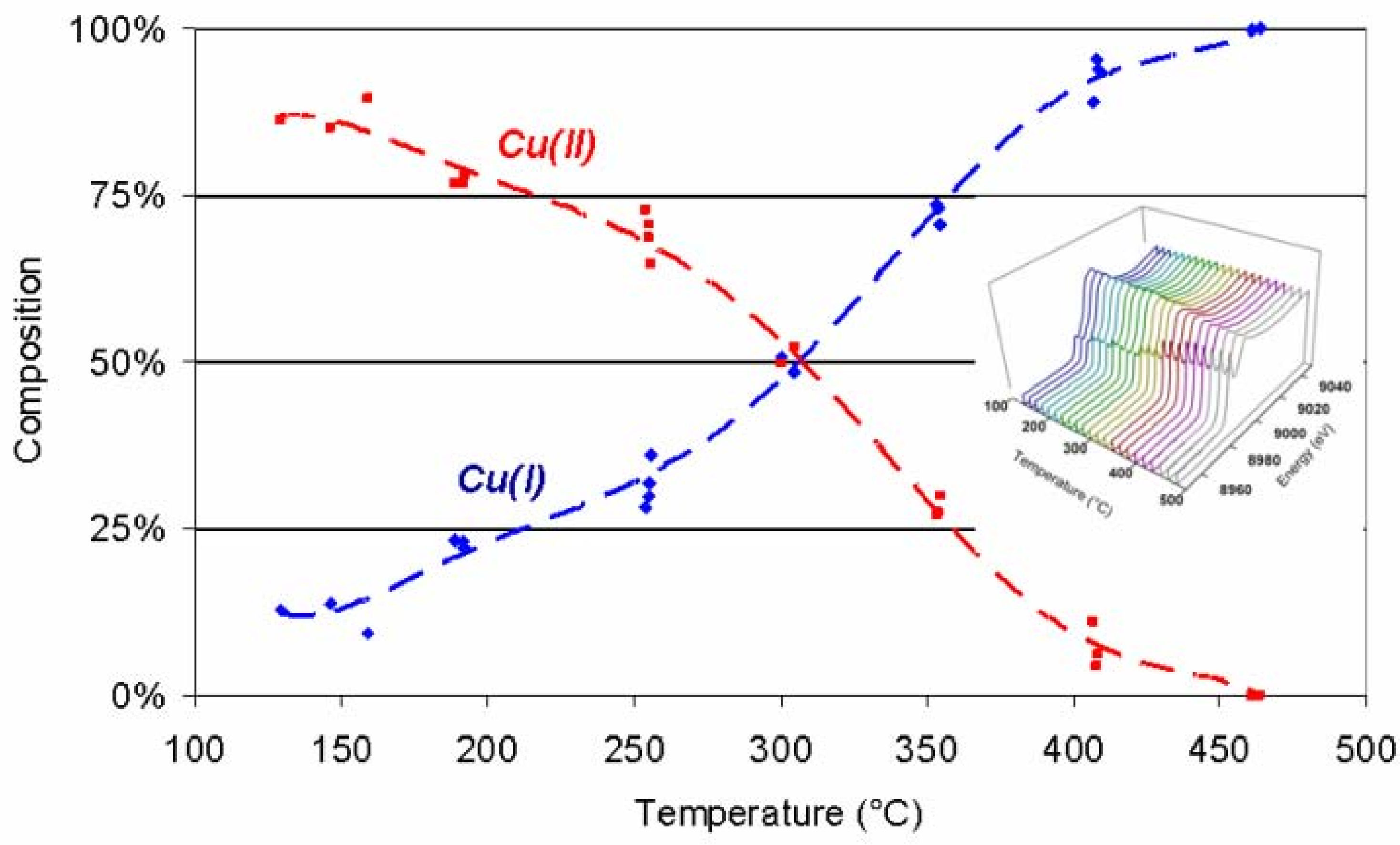
Additive Increases Low Temperature Activity But Does Very Little at the High End



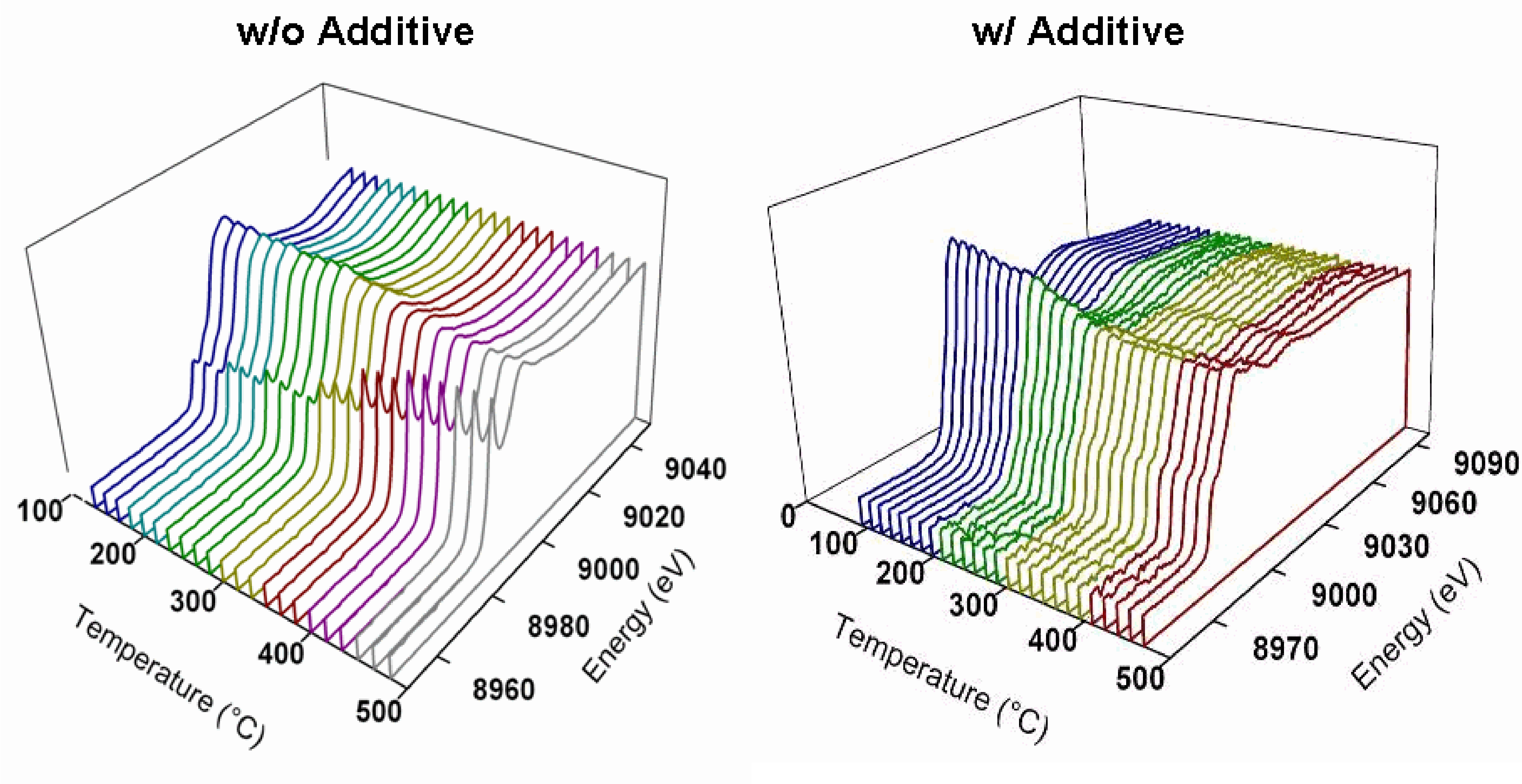
Effect of JP-8 Reductant with Catalyst Additive



In Situ XAS shows no Cu(0) under reaction conditions



Additive promotes two electron Cu(II) → Cu(0)



Conclusions

- **Paraffinic hydrocarbons are ineffective as reducing agents**
  - Addition of small amounts of olefins helps
- **JP-8 (diesel) is effective**
  - Due to high aromatic content
  - Extends high temperature range up to 450 °C
- **Oxidation promoter lowers the overall activity**
  - Promotes NO → NO_2 reaction
  - Adversely effects the Cu
    - *Cu(II) → Cu(0)*
- **No evidence yet of sulfur poisoning**

Plans for further catalyst development

- **Further investigation of alternate reductants**
- **Change ion exchange metal**
  - *Mixed metal systems*
- **Improved additive phase**
- **Wider pore zeolites**
- **Alternate conditions**
  - *Diesel & natural gas engines*
- **Systems approach**
  - Argonne on-board reformer

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