Bifunctional Catalysts for the Selective Catalytic Reduction of NOx With Hydrocarbons

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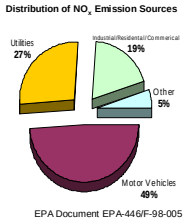
Overview

The Necessity of NOx Reduction

NO_x emissions are a significant pollutant

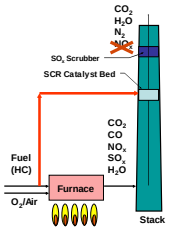
- Acid rain formation
- Smog generation
- Greenhouse gas

Increasing regulations on emissions to be in place by 2006 in several countries



EPA Document EPA-446/F-98-005

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

Goal of Research

Develop bifunctional catalysts that can effectively perform hydrocarbon SCR at lower temperatures under wet conditions

Addition of metal oxides to metal-exchanged zeolites to create two phases in close proximity

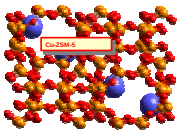
- Metal-zeolite phase provides catalytic sites and aids in reduction process
- Metal oxide phase can improve oxidation reactions

Possible formation of new, more active phases

Catalysis

Catalyst Synthesis

- Current catalyst samples are prepared from step-wise addition of metal and metal oxide to zeolite form via exchange or impregnation techniques
- CeO_2/Cu-ZSM-5 has been explored the most, but several other metals, oxides, and zeolites have been tested with similar improvements



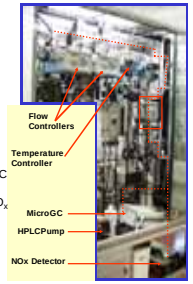
Step #	Method	
	Forward	Reverse
1	Ion Exchange	Coating with nano-sized metal sol
2	Coating with nano-sized metal sol	Ion exchange
3	Calcination	Calcination

NYACOL® COLLOIDAL CERIA

CeO_2 (wt.%)	*20*
Particle Size (nm)	*2 – 5 (TEM)*
Particle Charge	*Positive*
pH	*3.0*
Specific Gravity	*1.22*

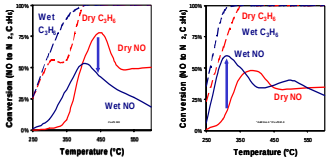
Reactor System

- Near both stationary and transportation conditions
  - 1000 ppm NO
  - 1000 ppm C_3H_6
  - 2% O_2
  - 10% H_2O when used
  - SV ~30,000 hr^{-1}
- Tested between 250° and 600°C
- Analysis with both GC and NO_x detector to quantify CO_x and NO_x products



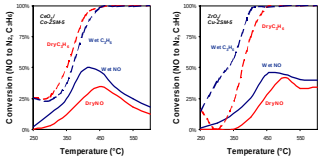
Activity

SCR Over Bifunctional Catalysts

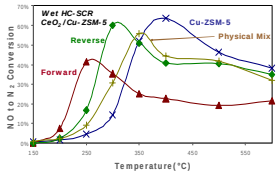


Unlike Cu-ZSM-5, ceria coated materials show improvements in SCR activity at lower temperatures under wet conditions

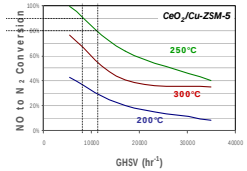
Other Bifunctional Catalysts



Co-ZSM-5 also very active in SCR using CH_4 – would be ideal reductant in several situations



- Intimate contact of two phases needed to improve catalysts
  - Short-lived intermediates
  - Phase synergy
  - New (as yet undetected) phase formed



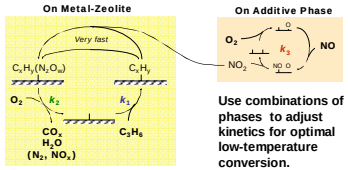
- Can achieve necessary 80-90% NO_x reduction at 250°C with SV ~ 10,000 hr^{-1}
- Economics would be similar to typical NH_3 SCR system – **potential drop-in replacement**

Selectivity

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% (11 ppm)	0.1% (4 ppm)	0.1% (14 ppm)
CO Selectivity	11.0% (120 ppm)	0.0% (0 ppm)	0.2% (67 ppm)
C_3H_6 Slippage	51.7% (517 ppm)	0.6% (5.6 ppm)	0.1% (1.4 ppm)

Mechanism



Use combinations of phases to adjust kinetics for optimal low-temperature conversion.

In Summary

A series of bifunctional catalysts have been synthesized and tested for hydrocarbon SCR of NOx. These materials:

- Activate in the presence of water
- Exhibit very high selectivity (>95%) to N_2
- React at relatively low temperatures (~350°C)
- Work effectively using hydrocarbons as the reductant

The additive appears to function by

- Adding water stability
- Lowering the reduction temperature of the copper in the zeolite

Patents filed for material and processes

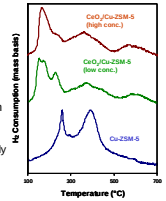
Argonne National Laboratory
Operated by The University of Chicago
for the U.S. Department of Energy, Office of Science

TPR / XAS

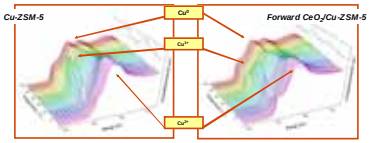
Temperature-programmed reduction in H_2 used to determine reducibility of phases

Addition of CeO_2 to Cu-ZSM-5 shows lower temperature reduction profile

- New phase at ~150°C
- Lower reduction temperature typically implies higher activity at lower temperatures

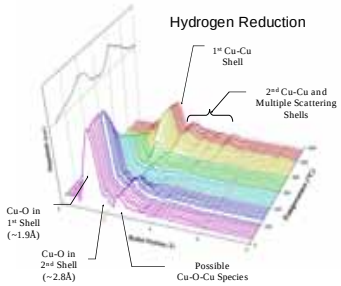


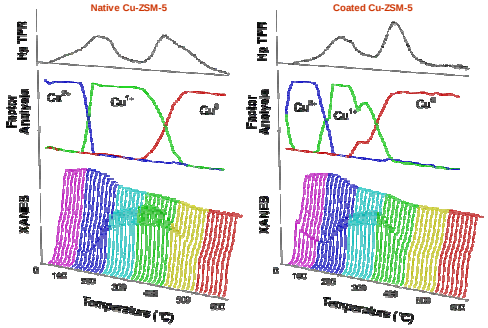
***In Situ* XANES Studies – H_2 Reduction**



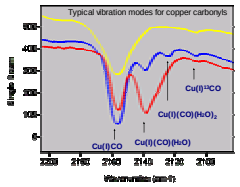
Pre-edge feature indicated presence of Cu^{1+}

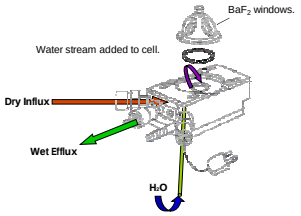
Shift in reduction temperatures apparent in bifunctional material

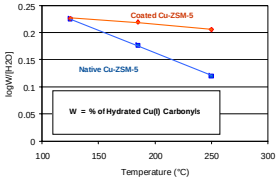




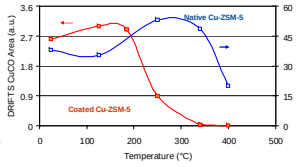
DRIFTS





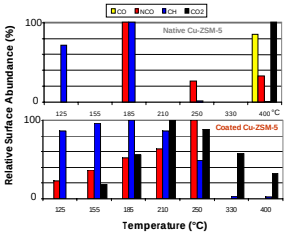


Fraction of hydrated Cu^+ carbonyls in the catalysts as a function of temperature

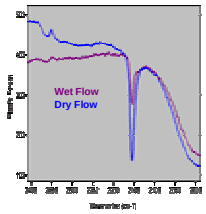


Cu^+ resistance to oxidation in the catalysts as monitored by its carbonyl intensity

Coating of catalyst retains water and hydrocarbons at higher temperatures, promotes NOx reactivity at lower temperatures and eases the combustion process.



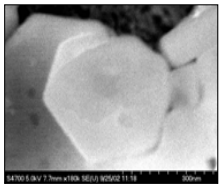
In situ DRIFTS: Observed intermediates during SCR of NO_x with C_3H_6 as reductant.



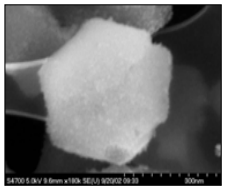
CO absorption on coated catalyst: Water promotes the $Cu^+ \rightarrow Cu^{2+}$ transition at lower temperatures.

Electron Microscopy

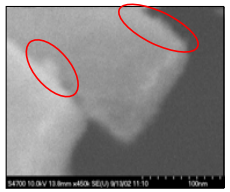
A uniform coating over the surface of the Cu-ZSM-5 crystals imparts high activity and selectivity to the catalyst even at high moisture contents.



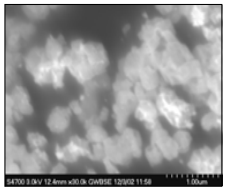
Field emission SEM image of the native Cu-ZSM-5



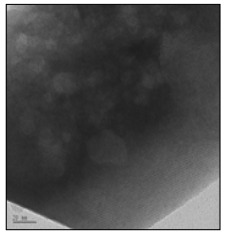
Field emission SEM image of the coated catalyst



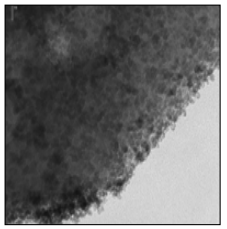
Coating is made of particles < 20 nm



Backscattered electron image of the coated Cu-ZSM-5 shows even distribution of the additive



TEM Image of Cu-ZSM-5



TEM Image of Forward Coating CeO_2/Cu-ZSM-5

Conclusions

- The uniform coating added to Cu-ZSM-5 crystals controls the water flux into the active sites, protecting the catalyst.
- Interface offers higher reactivity due to water promotion and lower redox potential.
- Complete combustion translates into lower by-products.

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Operated by The University of Chicago
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