Selective Catalytic Reduction of NO_x with Diesel-Based Fuels as Reductants

Mario J. Castagnola, A. Jeremy Kropf and Christopher L. Marshall*

Chemical Engineering Division, Argonne National Laboratory, Argonne, Illinois 60439

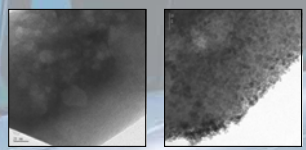
Overview

We have reported the development of bifunctional catalysts based on metal-exchange zeolites coated with metal oxide phases at the nanoscale level [1, 2]. In the case of C_3H_6-SCR, the application of the oxide coating lowers the NO reduction temperature by approximately 100-150°C and (unlike previous catalysts) shows higher activity under wet feeds. Results of deNOx studies over this catalyst using middle-distillate fuels as reductants are presented here.

Catalyst Preparation

To produce a nanoscale coating on the zeolite crystals, a nanoparticle ceria sol is added to partially exchanged Cu-ZSM-5 crystals by incipient wetness impregnation. The solvent is absorbed by the zeolite inner pores, while the cerium oxide nanoparticles agglomerate on the external surface of the crystals. Most of the absorbed water is removed by drying the crystals at 100°C, and the sol stabilizer (acetate) is removed by calcination at 500°C.

Ceria loadings varied from 1% to 25% (w/w).



TEM image of the native Cu-ZSM-5 | TEM image of the coated catalyst

TEM images obtained by Dr. Narma Castagnola at the electron microscopy facilities of The University of Chicago.

Catalyst Selectivity

Minimal Formation of Side Products

Side Product Formation under Wet Conditions (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)

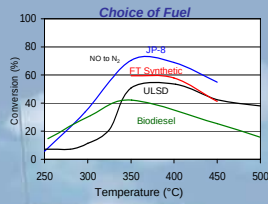
- New catalysts are very selective
- Side product formation and slippages under typical EPA regulations

References

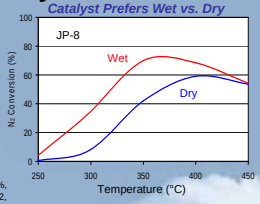
1. Neylon, M. K., Castagnola, M. J., Castagnola, N. B., and Marshall, C. L. *Catal. Today*, **96**, 53 (2004).
2. Castagnola, M. J., Neylon, M. K., and Marshall, C.L. *Catal. Today*, **96**, 61 (2004).

Diesel Activity

Choice of Fuel

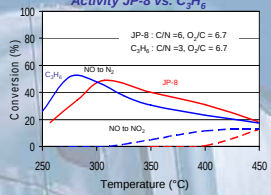


Catalyst Prefers Wet vs. Dry

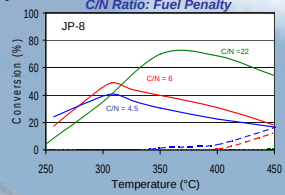


10% CeO_2/Cu-ZSM-5
NO = 1000 ppm, O_2 = 2%, (H_2O = 10.5%), C/N = 22, GHSV = 40,000 mL/gh

Activity JP-8 vs. C_3H_6

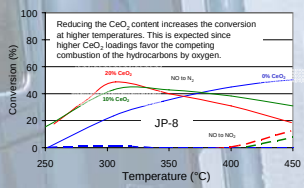


C/N Ratio: Fuel Penalty



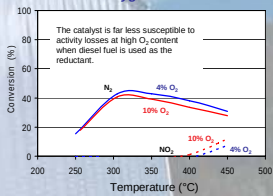
Coating of catalyst promotes NO_x reactivity at lower temperatures. Mixture of higher paraffins, naphthalenes and aromatics expands activity window and provides oxygen tolerance.

Effect of Ceria Content



CeO_2/Cu-ZSM-5, NO = 1142 ppm, H_2O = 10.5%, C/N = 6, GHSV = 40 000 mL/gh

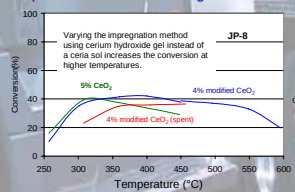
Effect of Oxygen on HC-SCR



10% CeO_2/Cu-ZSM-5, NO = 1142 ppm, H_2O = 10.5%, C/N = 6, GHSV = 40,000 mL/gh

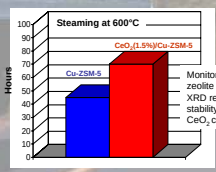
Optimization

Preparation Method of Coating Affects Activity



CeO_2/Cu-ZSM-5, NO = 1142 ppm, O_2 = 10%, H_2O = 10.5%, C/N =6 GHSV = 40 000 mL/gh

Hydrothermal Stabilization



Monitoring the integrity of the zeolite crystal structure by XRD reveals >50% longer stability for catalysts with 1.5% CeO_2 coating.

Accelerated Aging Test Performed at BP

Conclusions

The CeO_2/Cu-ZSM-5 system shows significant activity for NO to N_2 conversion when kerosene fuels are used as reductants. The system offers:

- *A wide temperature window of activity.*
- *Water-enhanced activity.*
- *O_2 tolerance.*
- *Tunable CeO_2 content for specific applications.*

It is proposed that in the CeO_2/Cu-ZSM-5 system, the aliphatic components of the fuel are responsible for the greater part of the NO conversion.

Acknowledgements: Work supported by the U.S. Department of Energy, Offices of Energy Efficiency and Renewable Energy, and Office of Energy Science, under Contract W-31-109-Eng-38. The Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, under Contract No. W-31-109-Eng-38. Work performed at MR-CAT is supported, in part, by funding from the Department of Energy under grant number DE-FG02-04ER46106.

Argonne National Laboratory is managed by The University of Chicago for the U.S. Department of Energy