Chemical and Physical Properties of Small Pore Cu- Zeolites Catalysts for NOx Selective Catalytic Reduction with NH_3

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Acknowledgments

U. S. DOE, Office of Energy Efficiency and Renewable Energy/Vehicle Technologies Program

Ja Hun Kwak, Feng Gao, Eric Karp, John Lee,* Diana Tran, Janos Szanyi, Eric Walter, and Haiyang Zhu, Institute for Integrated Catalysis, PNNL

Experiments performed in DOE/BER's Environmental Molecular Sciences Laboratory located at PNNL

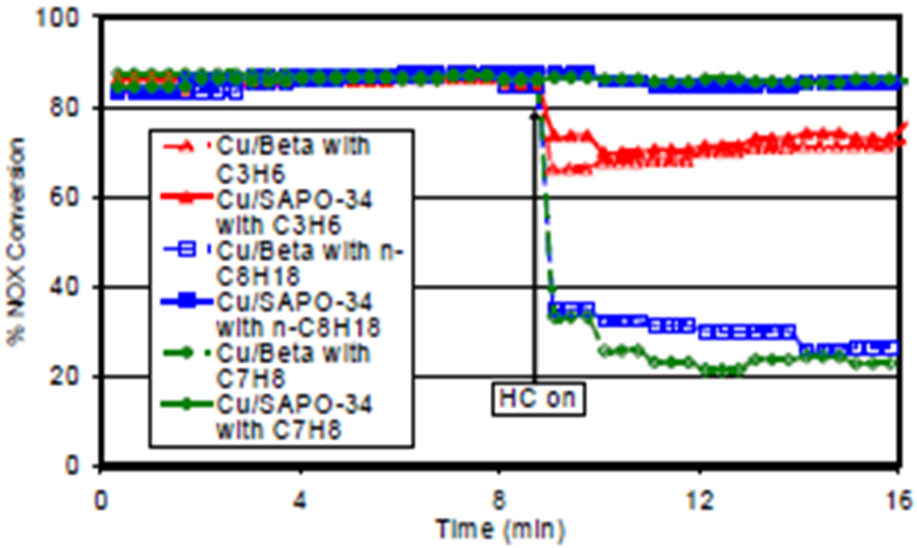
*Currently at Daimler Trucks N. Am.

Small-Pore Molecular Sieves Have Very Recently Become Primary Candidates for Commercial Cu-Zeolite Urea SCR Catalysts

- Recent patent literature has described the use of chabazite (CHA) zeolites for this application:
  - P.J. Andersen, J.E. Bailie, J.L. Casci, H.-Y. Chen, J.M. Fedeyko, R.K.S. Foo and R.R. Rajam, WO 132452 A2 (2008).
  - I. Bull, W.-M. Xue, P. Burk, R.S. Boorse, W.M. Jaglowski, G.S. Koermer, A. Moini, J.A. Patchett, J.C. Dettling, M.T. Caudle, US Patent, 7,601,662 (2009).
- SSZ-13 was invented by Stacy Zones at Chevron in the mid-1980s:
  - S.I. Zones, US patent 4,544,538 (1985).
- In a presentation at the recent (June, 2012) North American Catalysis Society meeting, Hai-Ying Chen (Johnson Matthey Inc.) described enhanced stability and hydrocarbon tolerance of a number of small-pore zeolites, including:
  - Cu/SAPO-34 chabazite (CHA) zeolite
  - Cu/ZSM-34 erionite (ERI) zeolite
  - Cu/SSZ-13 CHA zeolite

Small-Pore Molecular Sieves Display a Number of Beneficial Properties, Including Insentivity to Hydrocarbon Poisoning During Urea SCR

Effects of HC on "Standard" SCR Activity



H-Y Chen and coworkers
NACS Meeting Abstract #OB04

Small pore molecular sieve supported transition metal catalysts for the selective catalytic reduction of NOx with NH_3

Paul J. Andersen, John Casci, Hai-Ying Chen*, Jillian Collier, Joseph M. Fedeyko, Rodney Foo, and Raj Rajaram,
Johnson Matthey Inc., Emission Control Technologies, Wayne, PA 19087 (USA)
*chenh@jmusa.com

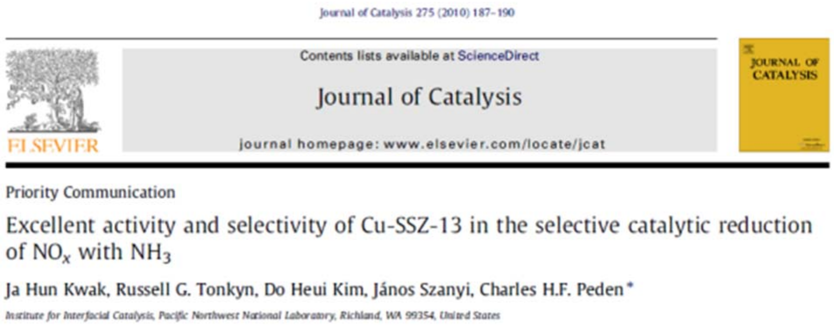
"Standard" SCR NOx Conversion and N_2O Formation

Catalysts	NOx conv.(%)	N2O (ppm)
Cu/beta (Fresh)	98	17
Cu/ZSM-5 (Fresh)	98	7
Cu/SAPO-34 (Fresh)	95	1
Cu/Nu-3 (Fresh)	97	1
Cu/beta (750°C/24h)	69	16
Cu/SAPO-34 (750°C/24h)	99	3
Cu/SSZ-13 (750°C/24h)	99	7
Cu/ZSM-34 (750°C/24)	98	3
Cu/beta (900°C/1h)	58	22
Cu/ZSM-5 (900°C/1h)	28	0
Cu/SAPO-34 (900°C/1h)	97	2
Cu/Nu-3 (900°C/1h)	98	4
Cu/SSZ-13 (900°C/1h)	99	7
Cu/Sigma-1 (900°C/1h)	85	4

Cu/beta (BEA) zeolite
Cu/SAPO-34 chabazite (CHA) zeolite
Cu/SSZ-13 CHA zeolite

Very little publicly known about the physical and catalytic properties of small-pore zeolites

- First open literature studies of the newest generation of Cu SCR catalysts (Kwak, et al., *J. Catal.* **275** (2010) 187-190).


Journal of Catalysis 275 (2010) 187–190

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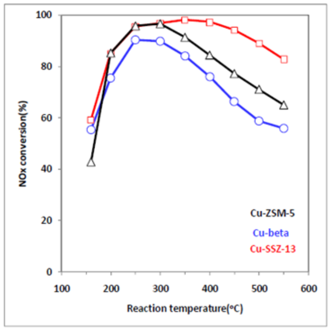
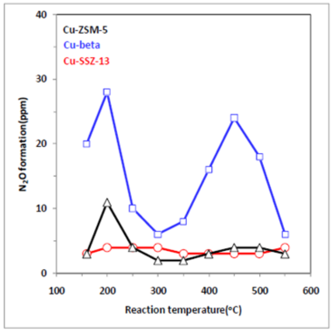
Priority Communication

Excellent activity and selectivity of Cu-SSZ-13 in the selective catalytic reduction of NO_x with NH_3

Ja Hun Kwak, Russell G. Tonkyn, Do Heui Kim, János Szanyi, Charles H.F. Peden *

Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, Richland, WA 99354, United States





- Today will provide a progress report on our recent studies of Cu/SSZ-13 CHA zeolite-based SCR catalysts.
  - Comparative reactivity and stability of Cu-zeolite catalysts – *Journal of Catalysis* **287** (2012) 203-209.
  - Effects of Cu loading – *Catalysis Letters* **142** (2012) 295-301.
  - Nature of the Cu species in Cu-CHA catalysts – *Chemical Communications* **48** (2012) 4758-4760.

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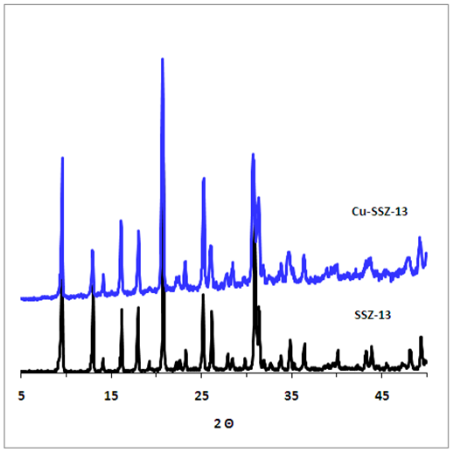
Catalyst Samples and Treatments

- Commercial zeolites: ZSM-5 (Si/Al_2=30), Beta (Si/Al_2=38) and Y (Si/Al_2=5.2), all from Zeolyst
- SSZ-13 (Si/Al_2=12) in house as per initial patent*
- Cu loading by solution ion exchange with an aqueous process $Cu(NO_3)_2$ solutions; varying levels of Cu^{2+} exchange.
  - Filtered and dried catalysts were pre-calcined at 500 ºC in laboratory air before reaction tests.
- HTA treatments: 800 ºC in air with 10% H_2O for 16 hours



XRD of SSZ-13 with and without Cu

	Cu-Y, FAU	Cu-beta	Cu-ZSM-5	Cu-SSZ-13
Si/Al_2	5.3	39.0	32.9	12.4
Cu/Al	0.35	0.34	0.53	0.40
Cu loading (wt.%)	7.2	1.73	2.83	4.3
Cu I.E. level (%)	70	69	106	79

*As described by DW Fickel and RF Lobo, Journal of Physical Chemistry C **114** (2011) 1633.

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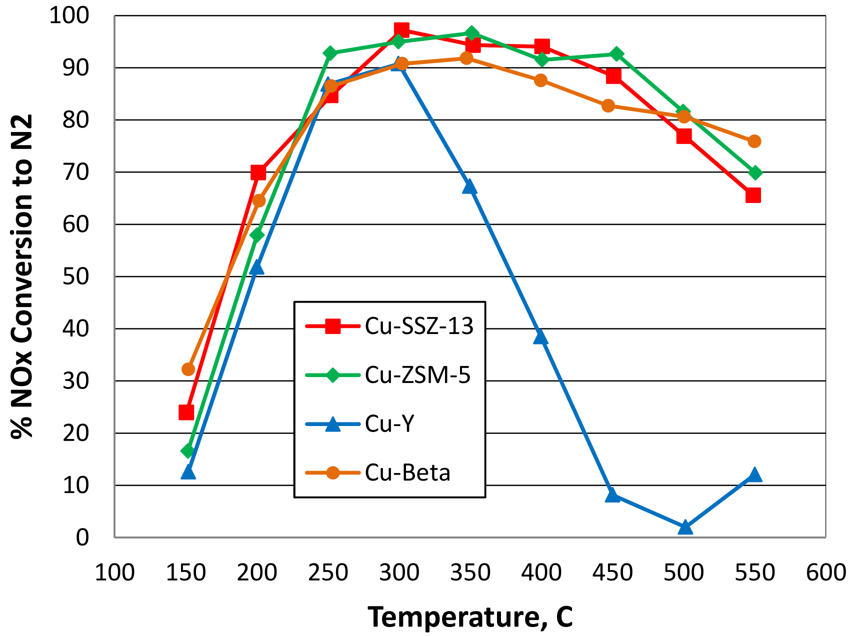
Reaction Conditions

Reaction tests:

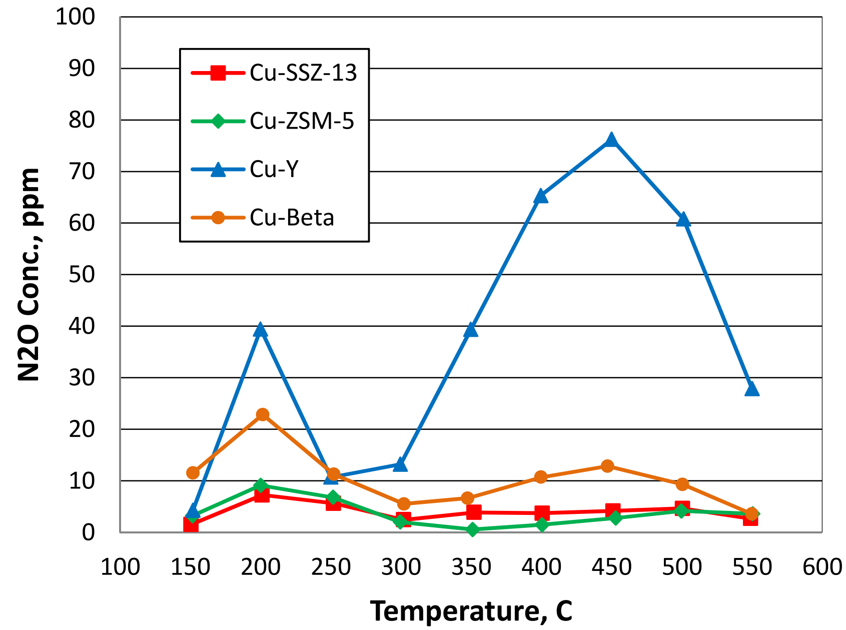
- NH_3-SCR, and NO and NH_3 Oxidation
  - Catalyst: 0.11g
  - 350 ppm NOx, 350 ppm NH_3, 14% O_2, 10%H_2O in N_2. GHSV ~30,000 hr^{-1}.
  - Both "standard" (NOx = NO only) and "fast" (NOx = ½ NO + ½ NO_2) SCR reactions were performed
- Product analysis with FTIR
- % NO_x conversion = $\{(NO + NO_2)_{inlet} - (NO + NO_2 + 2*N_2O)_{outlet}\}/(NO + NO_2)_{inlet}*100$

"Standard" SCR Reaction – Fresh Catalysts

NO Reduction to N_2 (estimated)



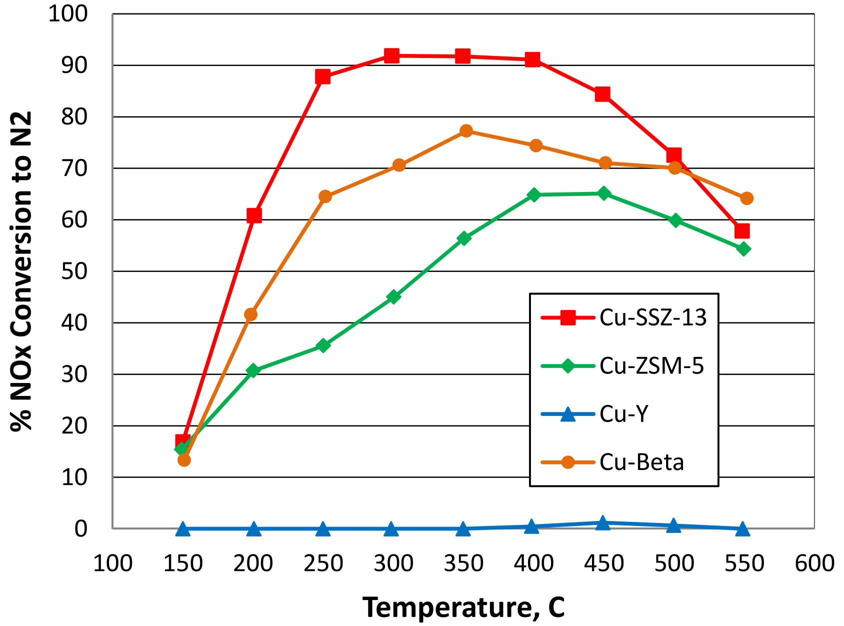
N_2O Formation



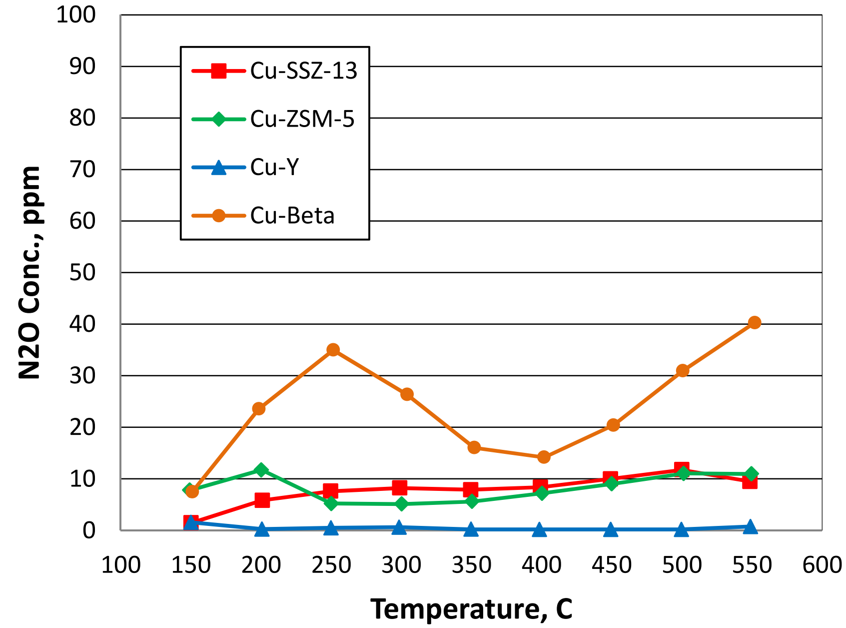
- **Cu/ZSM-5, Cu/beta and Cu/SSZ-13 are roughly equivalent in performance.**
- **Very low N_2O formation over Cu/SSZ-13 and Cu/ZSM-5.**
- **Cu/Y has low activity at higher temperatures due primarily to N_2O production.**
- **Effects of hydrothermal aging?**

"Standard" SCR Reaction – Hydrothermally Aged (HTA)

NO Reduction to N_2 (estimated)



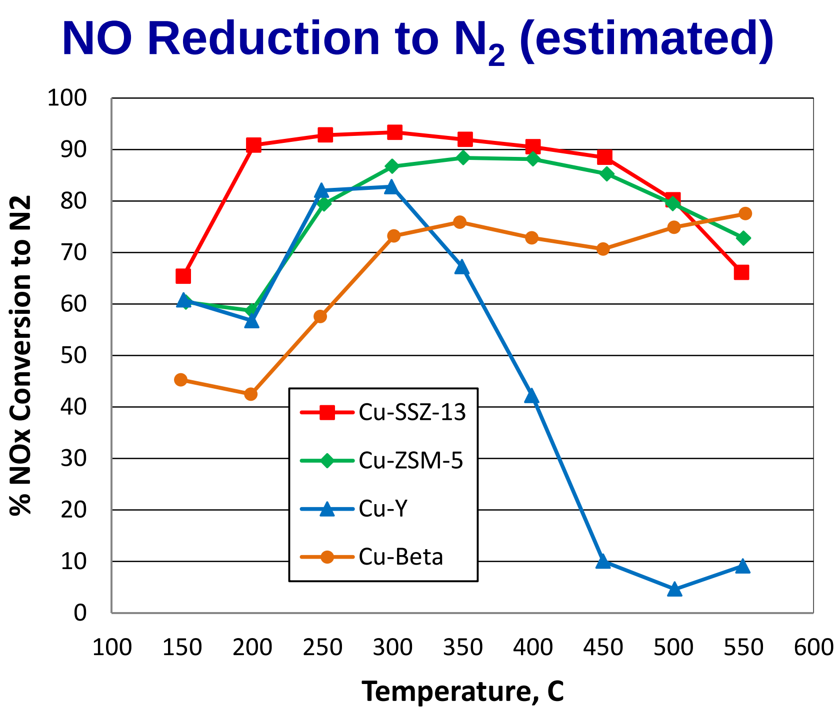
N_2O Formation

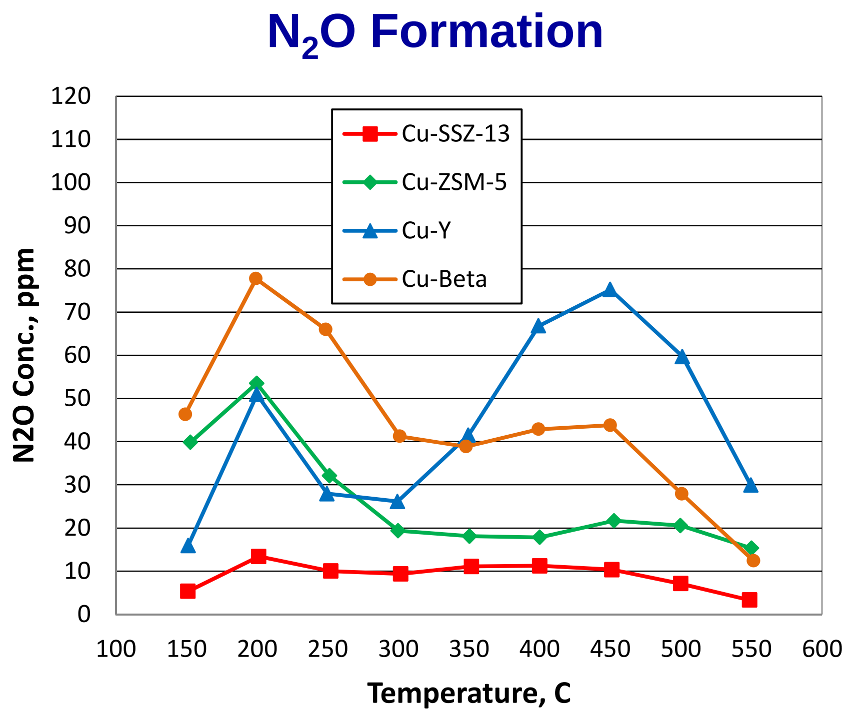


- Cu/SSZ-13 catalyst is quite stable to HTA
- Further reduction of performance for the other Cu catalysts due, in part, to increased N_2O formation after HTA
- Essentially complete loss of Cu/Y activity after HTA

JH Kwak, D Tran, SD Burton, J Szanyi, JH Lee, CHF Peden, Journal of Catalysis **287** (2012) 203.

“Fast” SCR Reaction – Fresh Catalysts





- **Again, very little N_2O formation over Cu-SSZ-13**
- **Lower NOx conversion to N_2 over other the Cu catalysts is a result of higher N_2O formation**
- **Further reduction over the other Cu catalysts due to increased N_2O formation after HTA**

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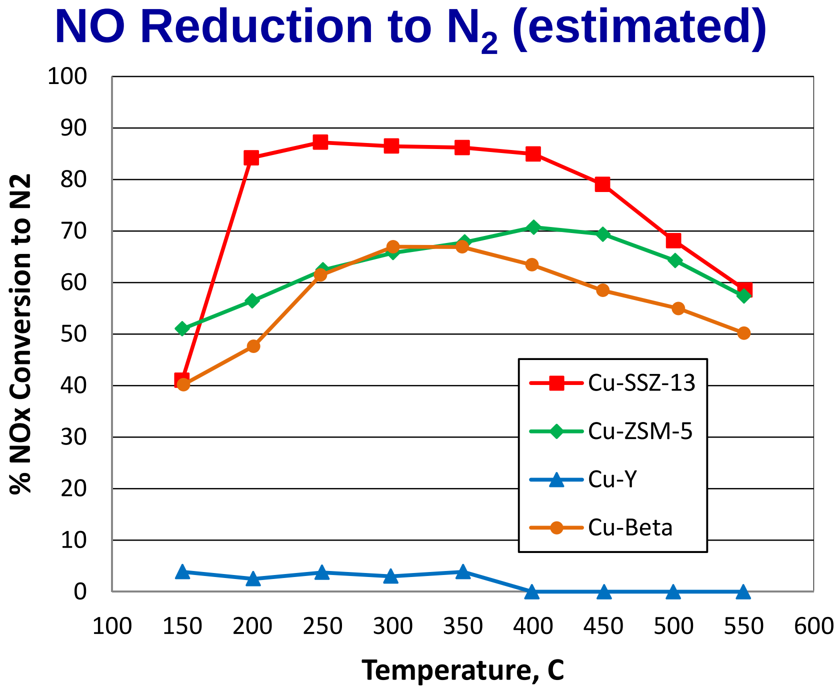
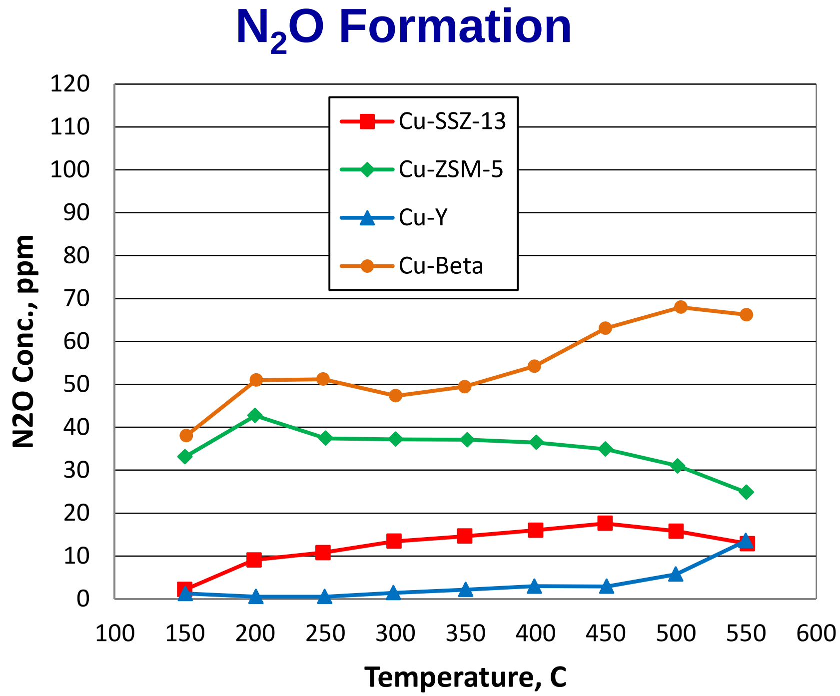
“Fast” SCR Reaction – Hydrothermally Aged (HTA)





- **While Cu/SSZ-13 catalyst is still stable, relative loss of performance for reduction to N_2 is more severe for “fast” SCR**
- **As before, complete loss of activity for Cu/Y**
- **Still very little N_2O formation over Cu/SSZ-13 and even higher N_2O formation over Cu/ZSM-5 and Cu/beta**

JH Kwak, D Tran, SD Burton, J Szanyi, JH Lee, CHF Peden, Journal of Catalysis, submitted (2011).

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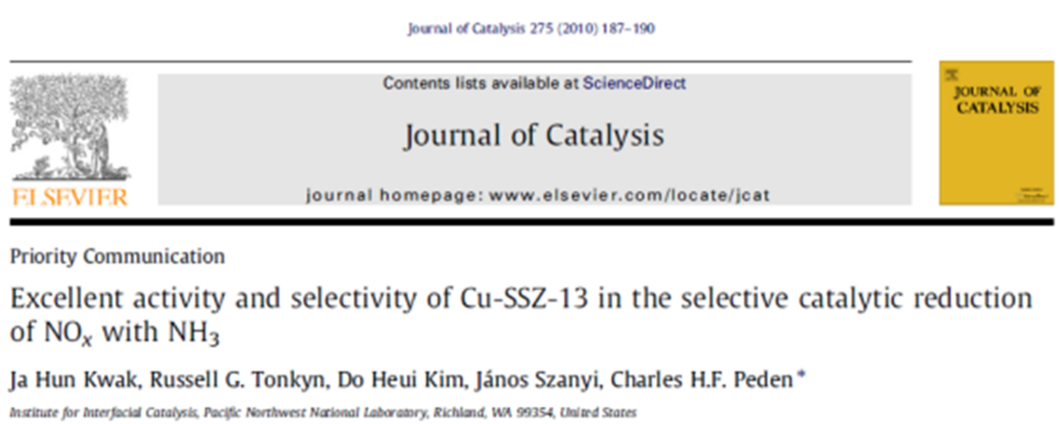
A Number of Unknowns about the Superior Performance of CHA-Zeolite SCR Catalysts


Journal of Catalysis 275 (2010) 187–190
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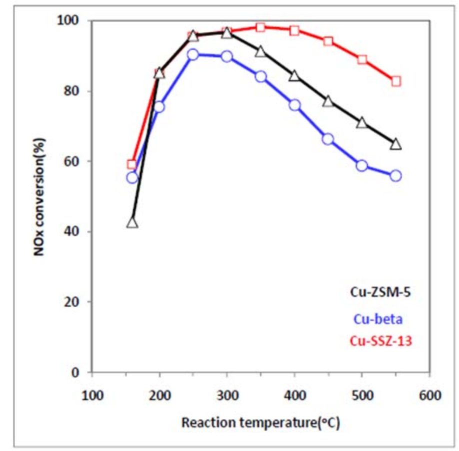
Priority Communication

Excellent activity and selectivity of Cu-SSZ-13 in the selective catalytic reduction of NO_x with NH_3

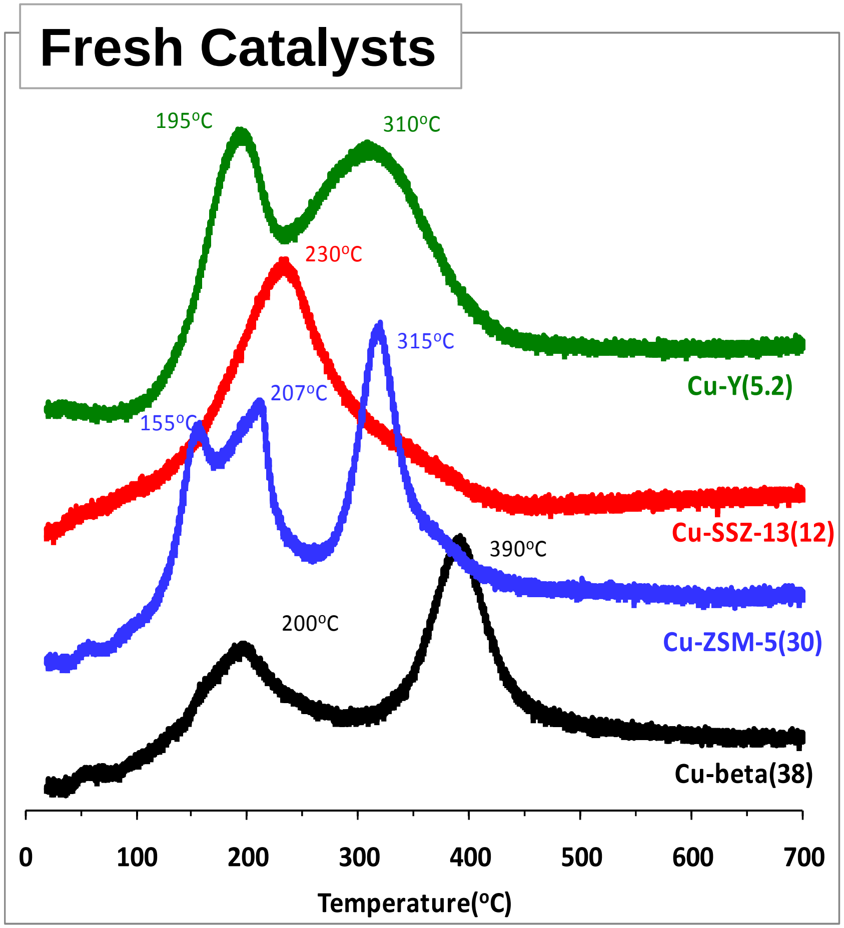
Ja Hun Kwak, Russell G. Tonkyn, Do Heui Kim, János Szanyi, Charles H.F. Peden *
Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, Richland, WA 99354, United States



- **Some questions:**
  - **Effects on zeolite structure of this specific hydrothermal treatment used here (800 ºC, 16 hours)?**
  - **What is the nature of the active Cu species in these various catalysts?**
  - **What gives rise to good selectivity (i.e., low N_2O formation)?**

JH Kwak, D Tran, SD Burton, J Szanyi, JH Lee, CHF Peden, Journal of Catalysis **287** (2012) 203.

Reduction of Cu Species Varies Considerably with Zeolite Type



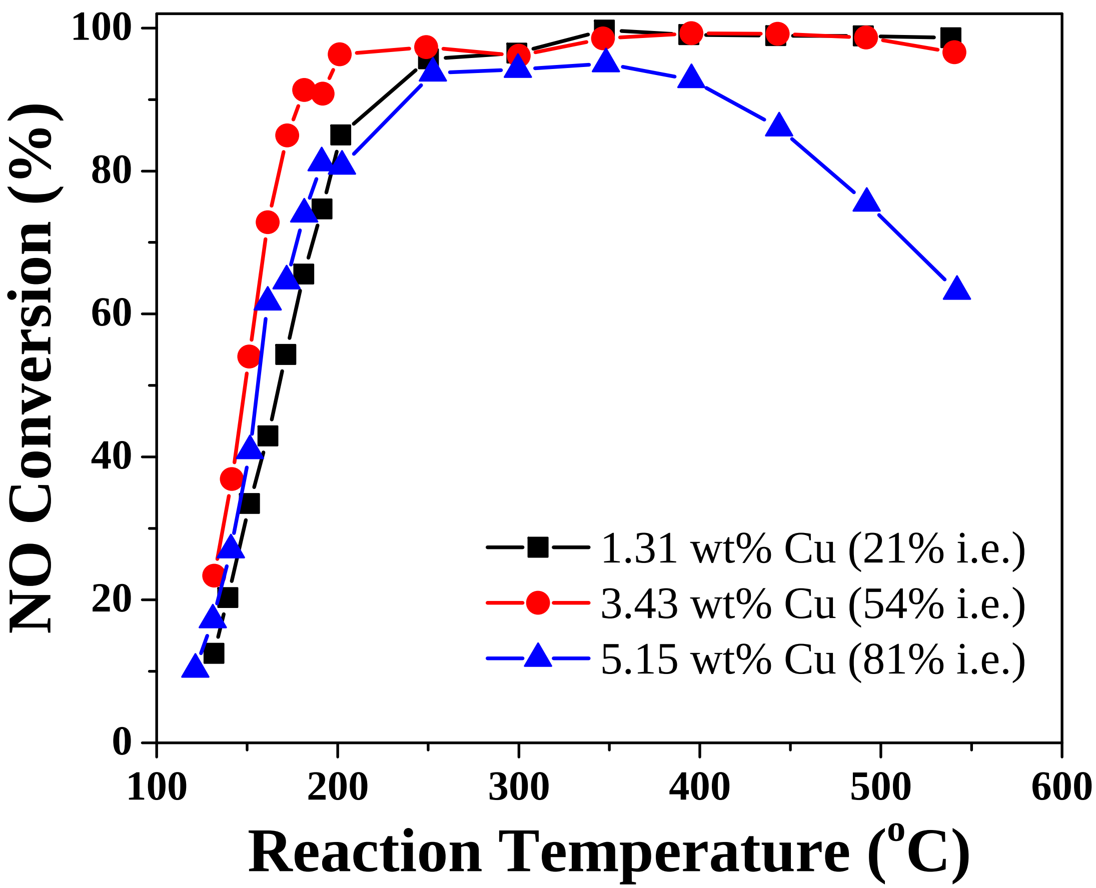
- Cu/beta and Cu/ZSM-5 fully reduced to Cu^0 by 500 ºC; according to Iglesia and coworkers, the two main features are due $Cu^{+2} \rightarrow Cu^{+1}$ and $Cu^{+1} \rightarrow Cu^0$. Catalyst powders were colored after reduction.
- Cu in Cu/Y and Cu/SSZ-13 remained as Cu^{+1} even after TPR to 700 ºC.
- Two peaks for Cu/Y due to two Cu species (in super- and sodalite-cages)
- Cu/SSZ-13 also has two peaks which may be two sites; *however, recent studies by Weckhuysen, Lobo and coworkers suggest a single Cu site*.

JH Kwak, D Tran, SD Burton, J Szanyi, JH Lee, CHF Peden, Journal of Catalysis **287** (2012) 203.

Questions about the state of Cu…

- Cu/ZSM-5 catalysts are likely to contain both monomeric and dimeric Cu species at the ion-exchange sites. The presence of dimeric Cu species may explain the ability of Cu/ZSM-5 to carry out NO decomposition ($NO \rightarrow ½N_2 + ½O_2$) – S.T. Korhonen, D.W. Fickel, R.F. Lobo, B.M. Weckhuysen, and A.M. Beale, *Chem. Comm.* **47** (2011) 800-802.
  - Lack of activity for NO decomposition by Cu/SSZ-13 then due to only monomeric Cu species?
- Why does Cu-SSZ-13 show two $Cu^{+2} \rightarrow Cu^{+1}$ TPR peaks if only a single Cu monomeric Cu species is present?
  - Study effects of Cu loading…

Effects of Cu Loading on “Standard” SCR



- Common reactivity measurements reveal small differences in performance as a function of Cu loading:
  - Enhanced low temperature performance from low to medium ion exchange levels.
  - Drop off in performance at both low and high temperatures at high Cu exchange levels.
- Characterization with TPR and FTIR.

JH Kwak, D Tran, J Szanyi, CHF Peden, JH Lee, Catalysis Letters **142** (2012) 295-301.

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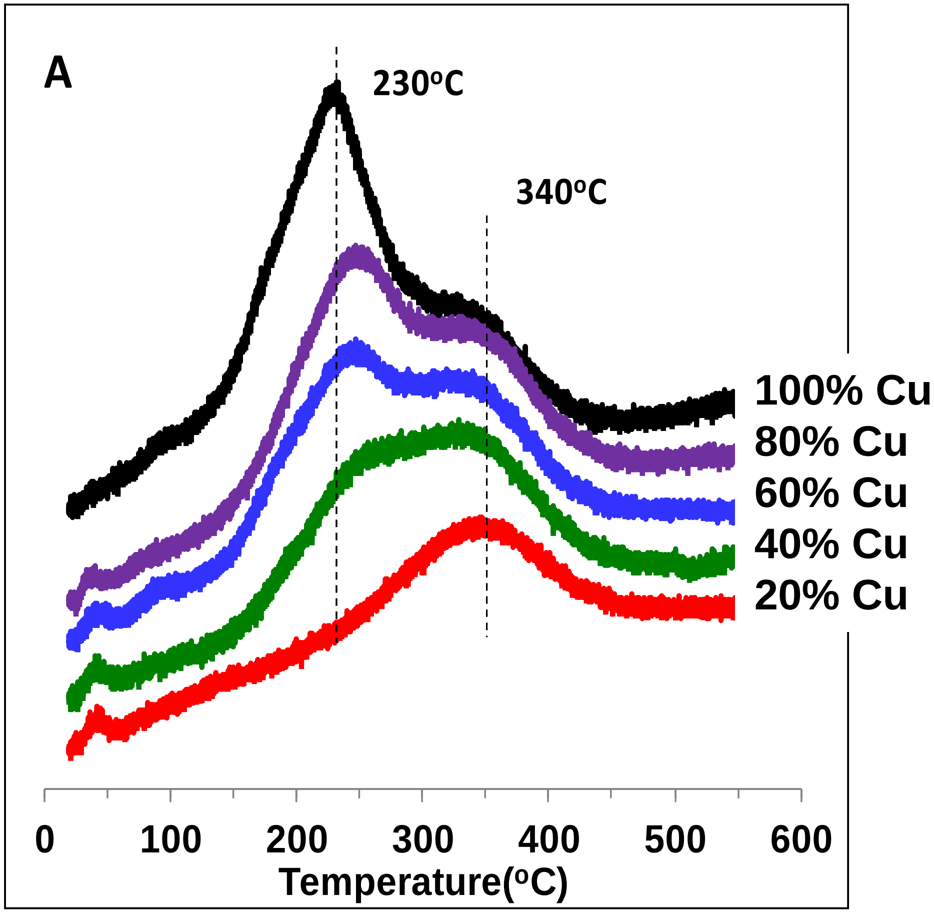
Effect of Cu Loading on the Reduction of Cu Species in Cu-SSZ-13 Zeolites Catalysts



- SSZ-13 (Si/Al_2=12) was synthesized by us.
- Controlled Cu loading via aqueous ion exchange.
- At low loading, only a single H_2 TPR reduction peak at ~340 ºC.
- At higher loadings, a second TPR peak appears at ~230 ºC, which monotonically increases in size with increasing Cu loading.

JH Kwak, H Zhu, JH Lee, CHF Peden, J Szanyi, Chemical Communications **48** (2012) 4758-4760.

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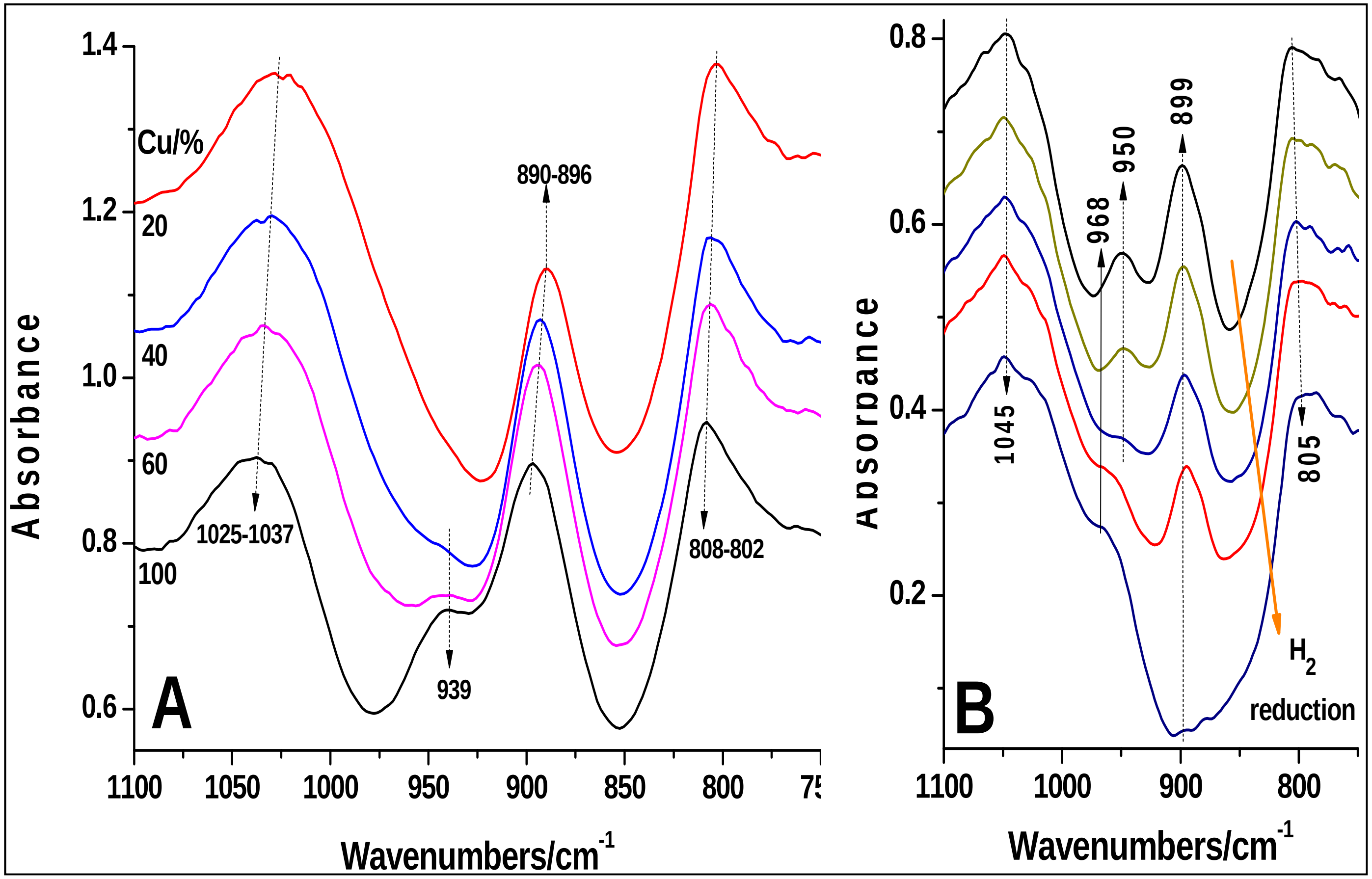
Perturbation of Zeolite Framework Vibrations also Suggest Multiple Cu Sites



- IR peak at ~940 cm^{-1} in T-O-T (Si-O-Si, Si-O-Al) region grows in with Cu loading.
- This ~940 cm^{-1} peak is removed first during H_2 reduction, followed by loss of ~899 cm^{-1} peak.
- Preliminary EPR results also strongly suggest two Cu species as a function of loading.

JH Kwak, H Zhu, JH Lee, CHF Peden, J Szanyi, Chemical Communications **48** (2012) 4758-4760.

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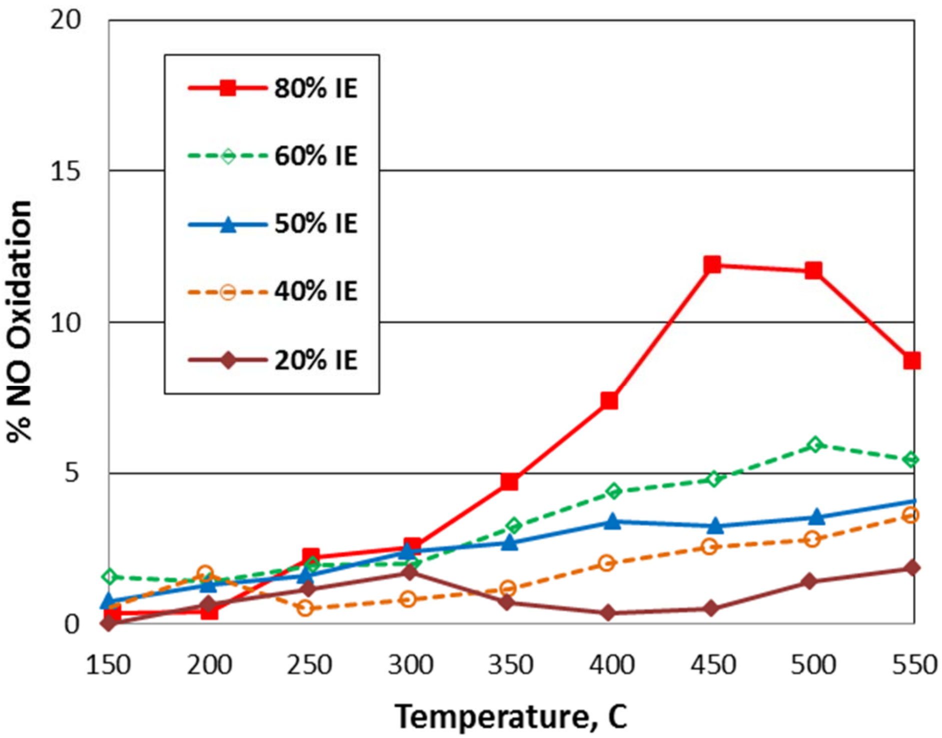
NO Oxidation over Cu-SSZ-13



Proposed Elementary Steps

(Nova, Tronconi and coworkers, J. Catal. 256 (2008) 312)

$$2\cdot NO + O_2 \longrightarrow 2\cdot NO_2 \longrightarrow NO^{+}\cdot NO_3^{-}$$

$$NO^{+}\cdot NO_3^{-} \xrightarrow{H_2O} HONO + HNO_3$$

$$HONO \xrightarrow{NH_3} NH_4NO_2 \longrightarrow N_2 + 2\cdot H_2O$$

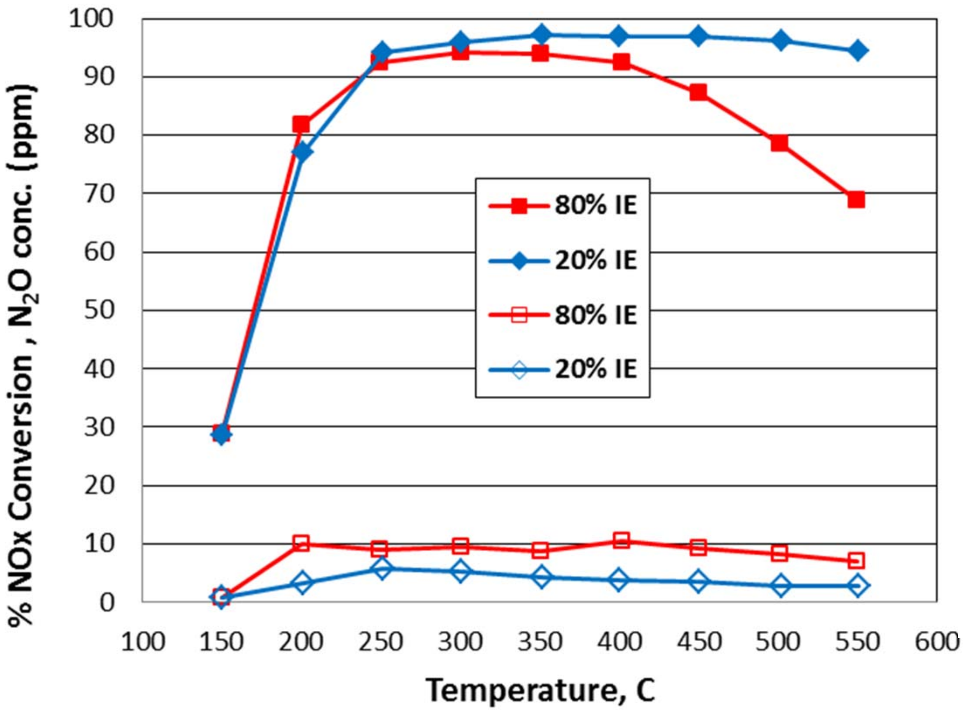
$$HNO_3 \xrightarrow{NH_3} NH_4NO_3 \xrightarrow[\text{slow}]{} N_2O + 2\cdot H_2O$$

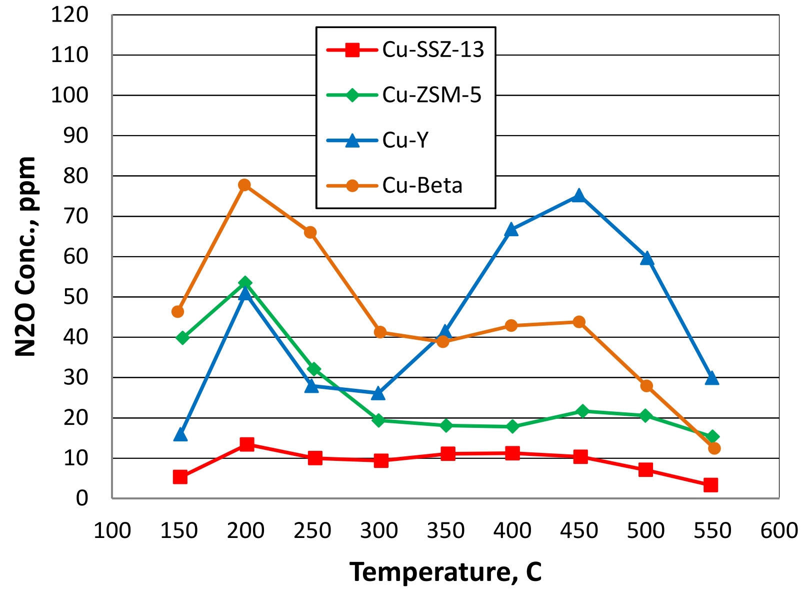
$$HNO_3 \xrightarrow{NO} HONO + NO_2$$

- ❑ Very low NO oxidation over Cu/SSZ-13.
- ❑ Very high NO reduction despite low NO oxidation suggests NO oxidation may not be critical over Cu/SSZ-13.

JH Kwak, D Tran, J Szanyi, CHF Peden, JH Lee, Catalysis Letters **142** (2012) 295-301.

Effect of Cu Loading on "Fast" SCR

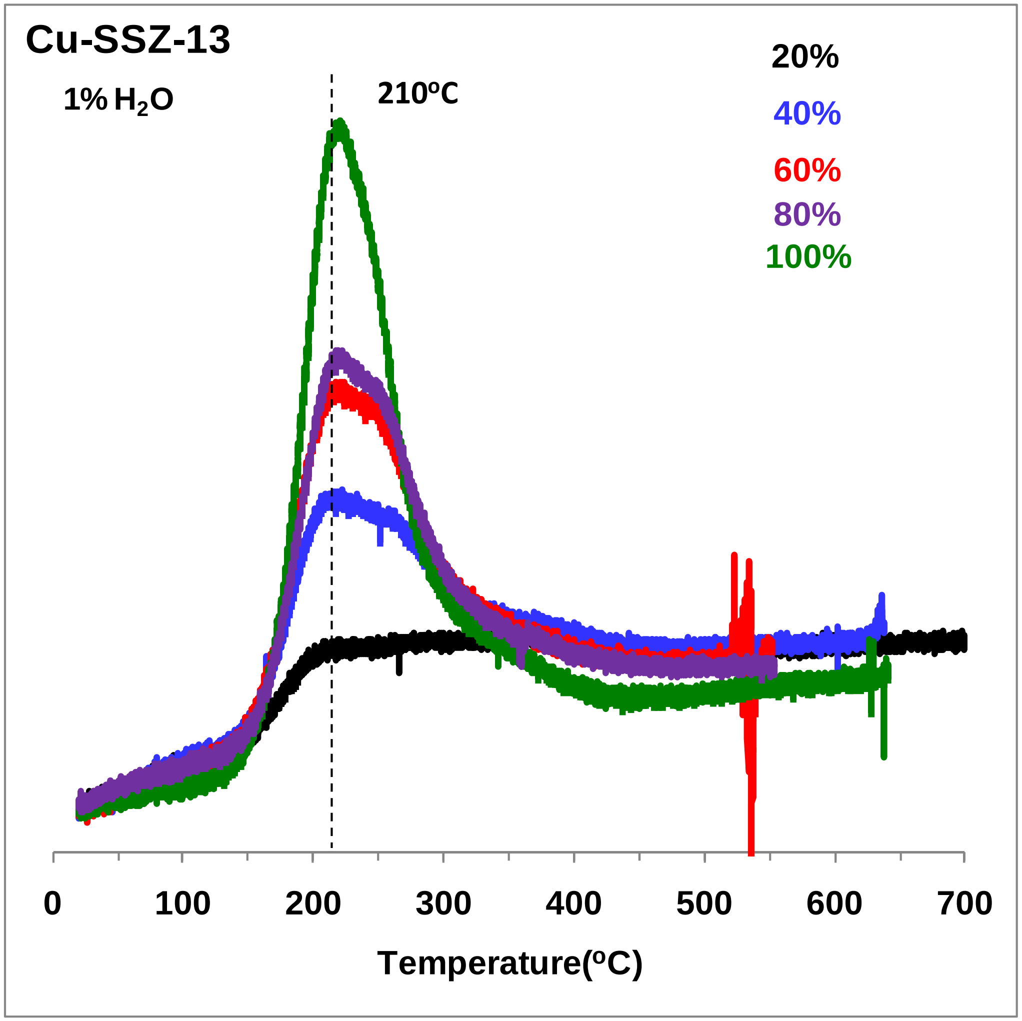




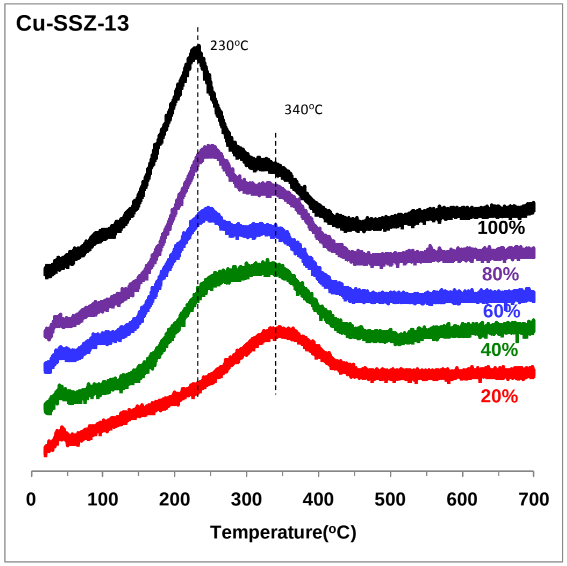
- ❑ **Limited N_2O formation, compared to other Cu/zeolite catalysts, suggests that NO reduction pathway involving NH_4NO_2 and NH_4NO_3 may not be important over Cu/SSZ-13.**
- ❑ **Cu/SSZ-13 only zeolite-based catalyst that shows low selectivity to N_2O during "fast" SCR.**

JH Kwak, D Tran, J Szanyi, CHF Peden, JH Lee, Catalysis Letters **142** (2012) 295-301.

Another significant open question…



- In presence of 1% H_2O, H_2-TPR shows only low-temp peak for all Cu loadings.
- It appears Cu species may move under reaction conditions.



JH Kwak, H Zhu, JH Lee, CHF Peden, J Szanyi, Chemical Communications **48** (2012) 4758-4760.

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Summary and Conclusions

- Cu/SSZ-13 catalysts display outstanding performance for both "standard" and "fast" NH_3 SCR relative to other Cu/zeolite-based catalysts.
  - Limited N_2O formation and NO oxidation over Cu/SSZ-13 suggests the SCR reaction pathway may not involve the formation and decomposition of NH_4NO_2 and NH_4NO_3.
- Significantly, the SSZ-13 small-pore zeolite provides considerably lower sensitivity to high-temperature hydrothermal aging. Reduction of performance for the other zeolite-based catalysts results from:
  - Cu/ZSM-5 and Cu/beta – increased selectivity to the undesirable N_2O product, and partial loss of zeolite structure;
  - Cu/Y – complete loss of zeolite structure.
- The nature of the active Cu site in CHA zeolites is an active area of research.
  - Two different Cu species within Cu/SSZ-13 were identified by H_2 TPR and FTIR
  - The relative distribution of Cu species is dependent on Cu loading levels and reaction conditions