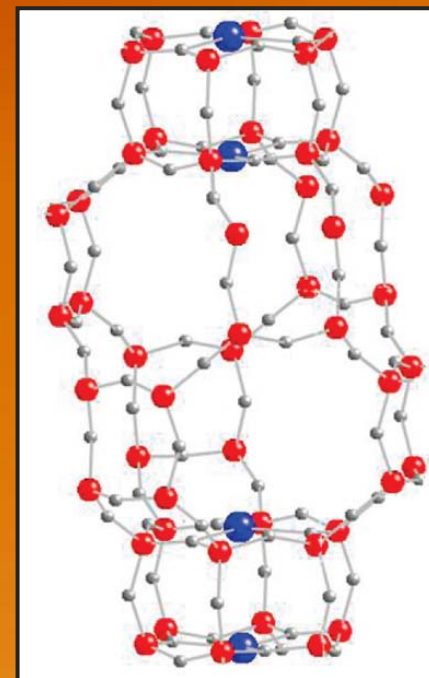


# Structure-activity relationships in $\text{NH}_3$ selective catalytic reduction of $\text{NO}_x$ over Cu/CHA catalysts as probed by reaction kinetics and EPR



Feng Gao; Eric Walter, Eric Karp, Ja Hun Kwak; Janos Szanyi; Chuck Peden  
Institute for Integrated Catalysis  
Pacific Northwest National Laboratory

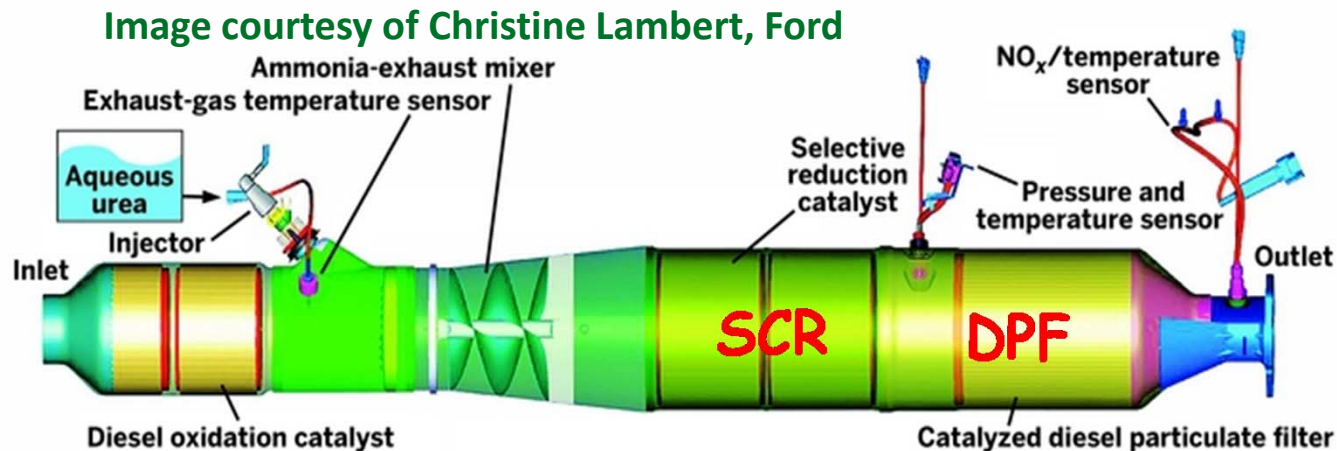
# Outline

## □ Short Intro

## □ Cu-SSZ-13

- Nature of active Cu
- **SCR reaction mechanism over SSZ-13 (and other CHA-based catalysts?)**

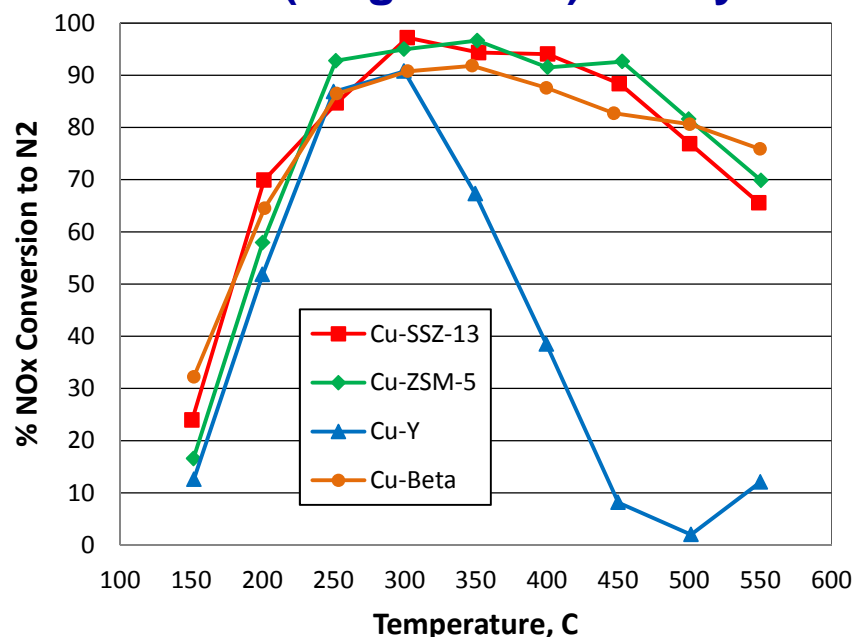
# Issues with zeolite catalysts



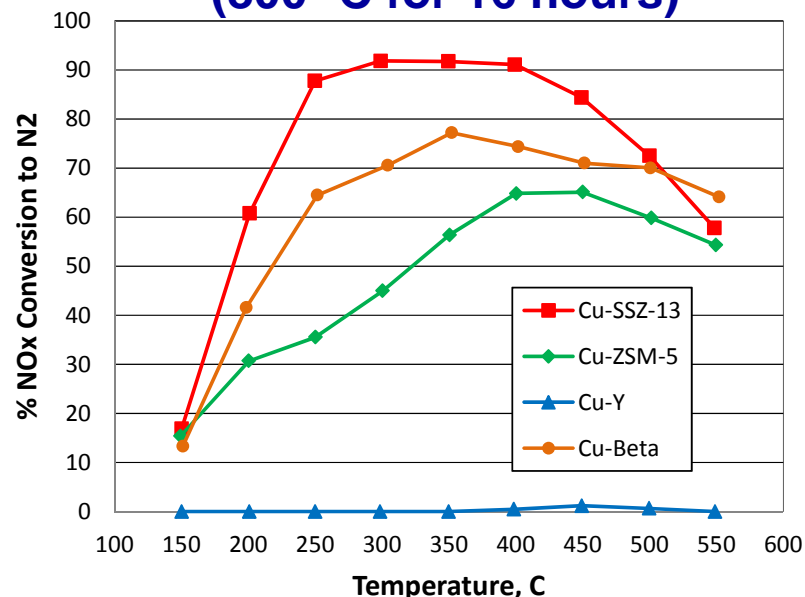
- Good SCR catalysts must survive during soot filter regeneration (hydrothermal, 600-700 °C.)
- Best catalysts a few years ago: Cu/Fe-ZSM-5, Cu/Fe-Beta zeolites. They deactivate dramatically during hydrothermal aging.
  - Dealumination (structural damage, active center migration and agglomeration).
  - Thermal damage (HC storage and burning).
  - Coking.

# “Standard” SCR Reaction – Fresh vrs. Aged Catalysts

## Fresh (‘degreened’) Catalysts



## After Hydrothermal Aging (800 °C for 16 hours)



- ▶ Fresh Cu/ZSM-5, Cu/beta and Cu/CHA (SSZ-13) are roughly equivalent in performance. Cu/Y has low activity at higher temperatures due primarily to N<sub>2</sub>O production.
- ▶ Cu/CHA catalysts are MUCH more hydrothermally stable.

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

# Small-Pore Molecular Sieves are very Insentive to Hydrocarbon Poisoning During Urea SCR

## “Standard” SCR NO<sub>x</sub> Conversion and N<sub>2</sub>O Formation

**Table 1:** NO<sub>x</sub> conversion (%) and N<sub>2</sub>O formation (ppm) at 250°C on various Cu SCR catalysts

Catalysts	NO <sub>x</sub> conv.(%)	N <sub>2</sub> O (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

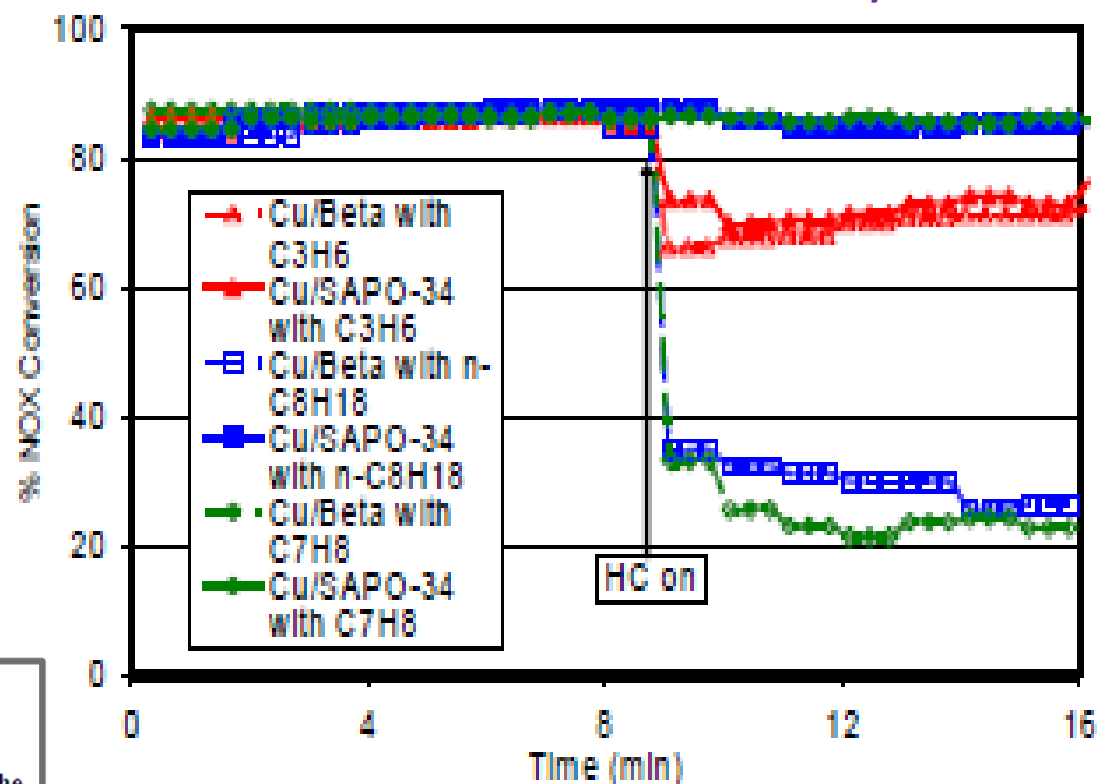
Cu/SSZ-13 CHA zeolite

### H-Y Chen and coworkers NACS Meeting Abstract #OB04

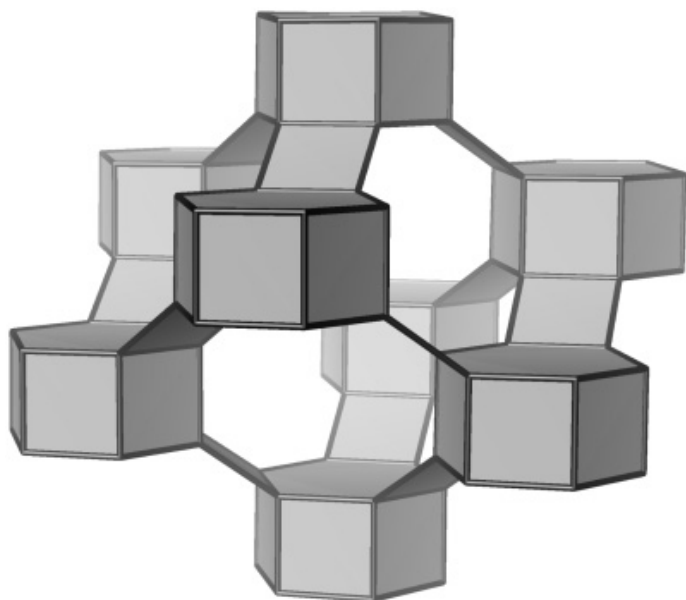
Small pore molecular sieve supported transition metal catalysts for the selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>

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@jmus.com

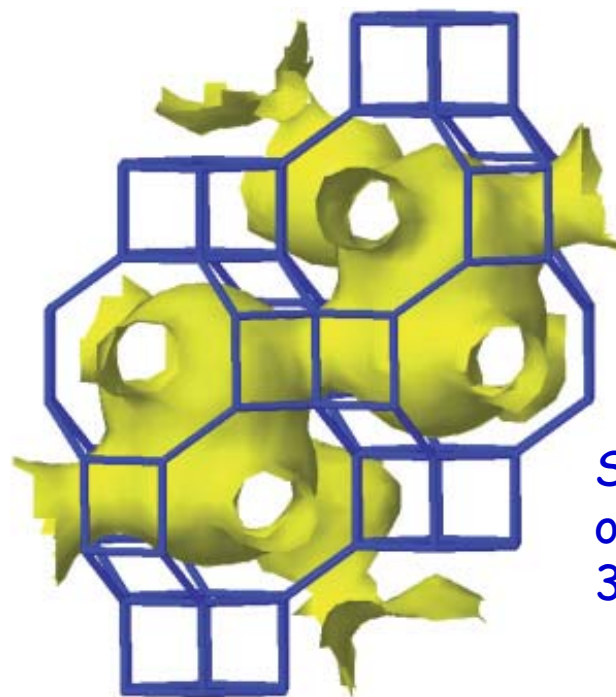
## Effects of HC on “Standard” SCR Activity



# Why is Cu/CHA so durable?



6-membered rings in an  
AABBCCAA sequence



Small pore  
opening ( $\sim 3.8 \text{ \AA}$ );  
3D channels.

- Much less dealumination ( $\text{Al}(\text{OH})_3$  kinetic diameter  $\sim 5.0 \text{ \AA}$ )\*
- No storage of large,  $\text{C}_6+$  HCs)\*\*
  - Much less thermal damage
  - Much less coking.

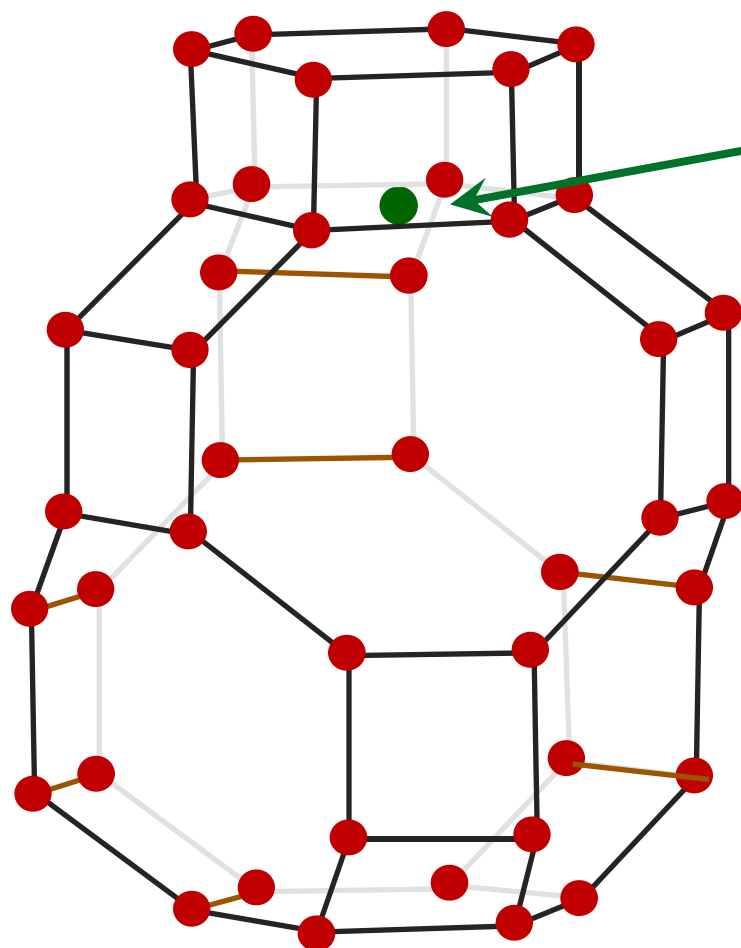
\*RF Lobo and coworkers, Applied Catalysis B 102 (2011) 441.

\*\*HY Chen and coworkers, Abstracts, North American Catalysis Society (June 2011).





# Location for Cu in SSZ-13 catalysts at low Cu loadings



$a = b = 13.719 \text{ \AA}$   
 $c = 14.953 \text{ \AA}$   
 $d = 3.8 \text{ \AA}$

“Cu/SSZ-13 contains mononuclear  $\text{Cu}^{2+}$  species, located in the *face of the double-6-ring subunit of the zeolite* after calcination where it remains under reaction conditions”

U Deka, A Juhin, EA Eilertsen, H Emerich, MA Green, ST Korhonen, BM Weckhuysen, AM Beale, *J Phys Chem C* **116** (2012) 4809.

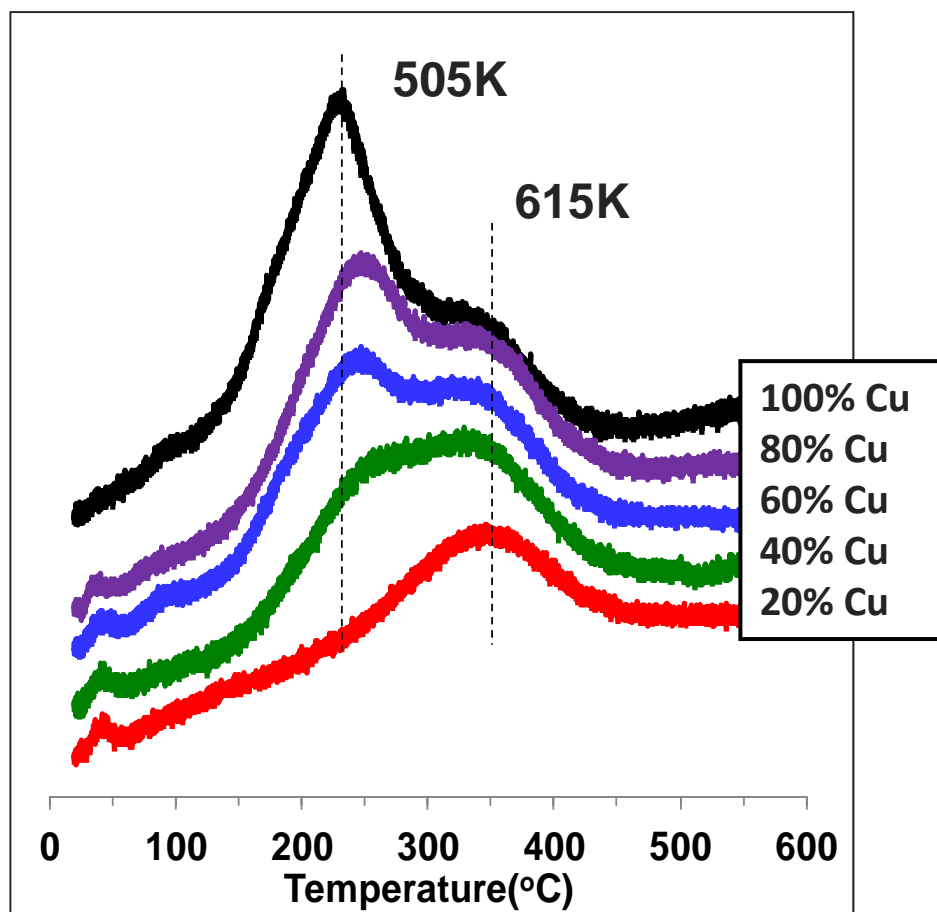
This location also identified in:

- DW Fickel, RF Lobo, *J Phys Chem C* **114** (2010) 1633.
- J-S McEwen, T Anggara, WF Schneider, VF Kispersky, JT Miller, WN Delgass, FH Ribeiro, *Catal Today* **184** (2012) 129.

Higher Cu loadings result in multiple Cu locations in the zeolite cages.



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

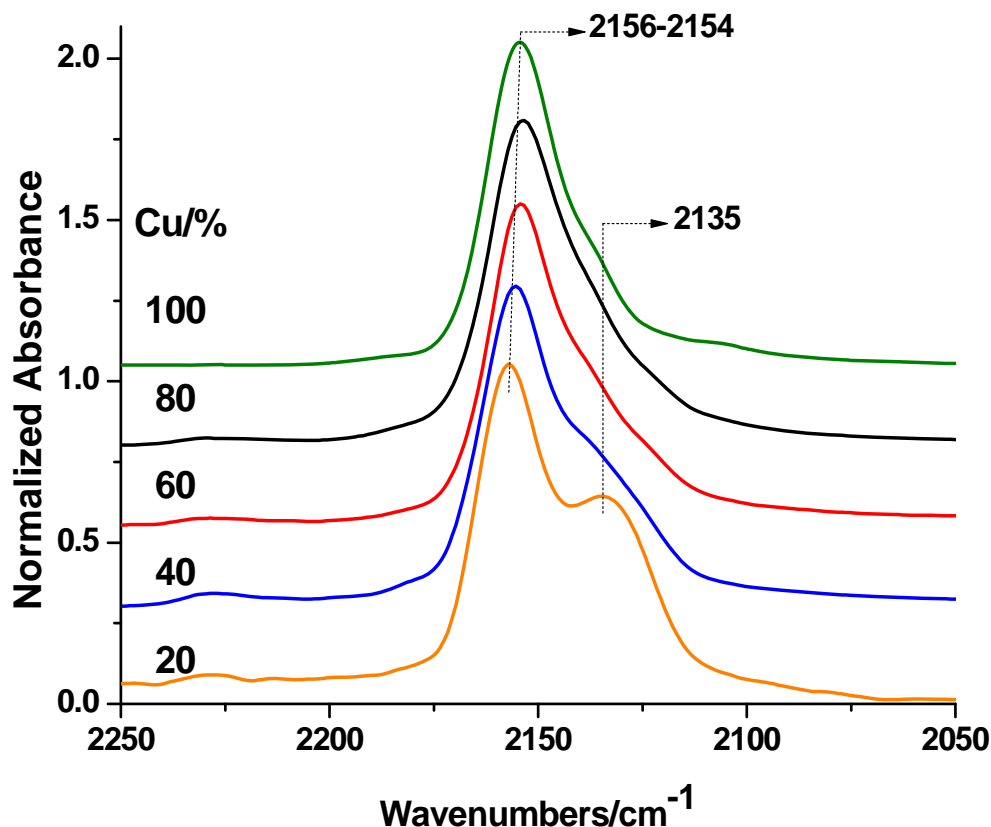


- ▶ At low loading, only a single H<sub>2</sub> TPR reduction peak at ~340 °C.
- ▶ At higher loadings, a second TPR peak at ~230 °C.
- ▶ Reduction of Cu<sup>+</sup> to Cu<sup>0</sup> does not occur until T>800 °C (data not shown).

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

F Gao, ED Walter, EM Karp, J Luo, RG Tonkyn, JH Kwak, J Szanyi, CHF Peden, *Journal of Catalysis* **300** (2013) 20.

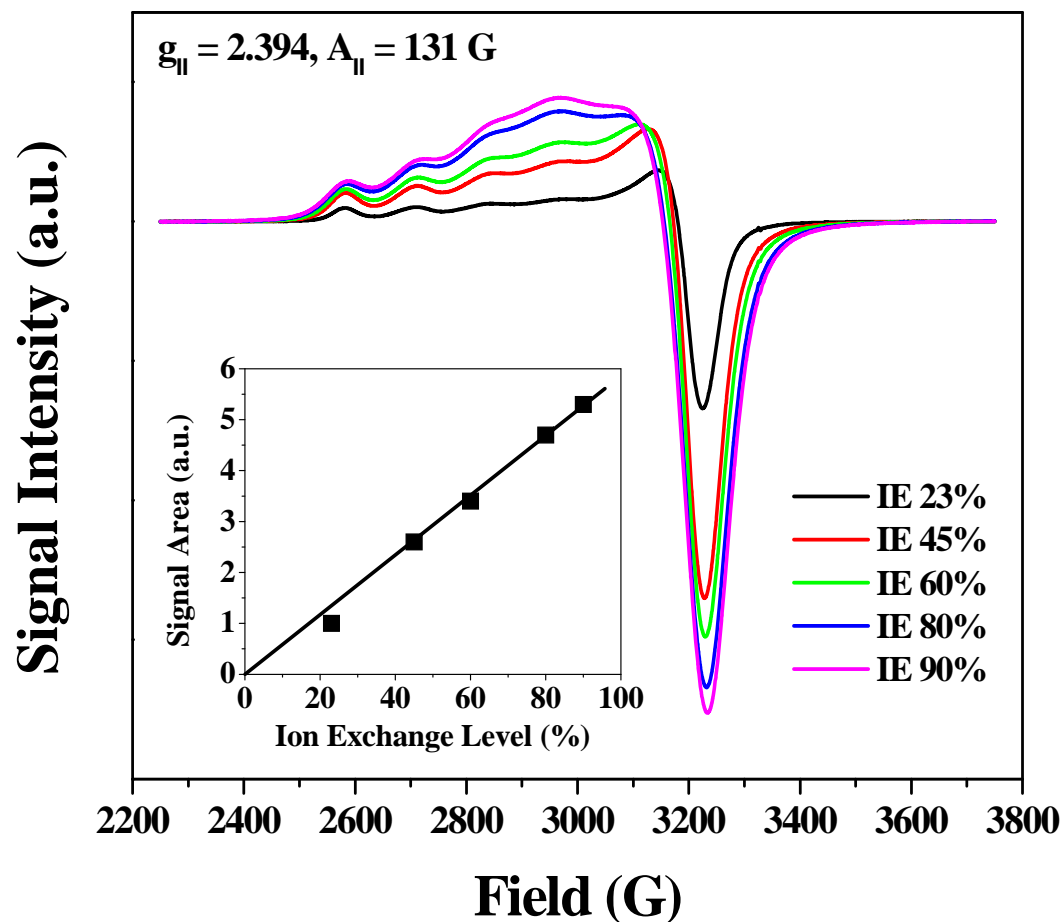
# CO Adsorption on Cu/SSZ-13



- ❑ Similar results obtained for NO chemisorption on catalysts with varying Cu loading.
- ❑ FT-IR of CO adsorption on Cu/SSZ-13 shows two CO-Cu<sup>+</sup> vibrational peaks at ~2155 and ~2135 cm<sup>-1</sup>.
- ❑ Change in relative intensities of the peaks with respect to Cu ion exchange levels suggest:
  1. two different Cu species in Cu-SSZ-13; and
  2. relative distribution of these species is dependent of Cu loading levels.

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

# Low Temperature EPR of Cu(various)/SSZ-13 Catalysts

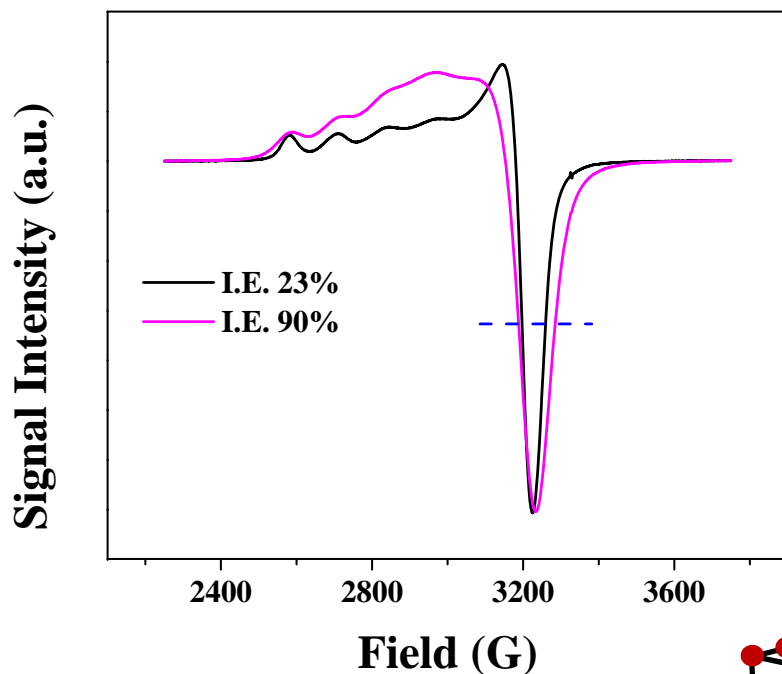


- Done at 155 K to freeze  $\text{Cu}^{2+}$  in place.
- Up to IE of 90%, linear relationship between signal intensity and Cu content. Suggests all  $\text{Cu}^{2+}$  are EPR active, i.e., all  $\text{Cu}^{2+}$  are isolated monomers.
- EPR parameters consistent with Cu in octahedral coordination.

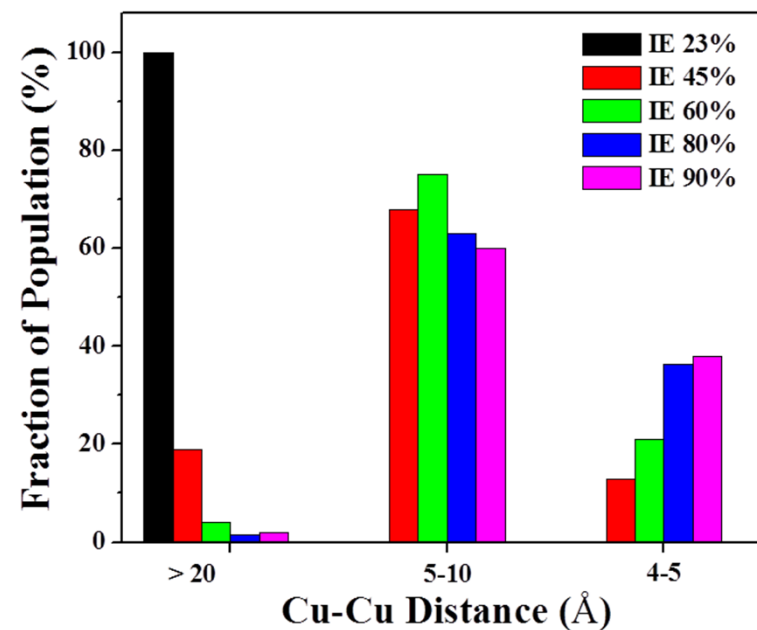
Line broadening is due to dipole-dipole interactions which are dependent on Cu-Cu distances. We use this to estimate these Cu-Cu distance.

# Active Sites & Locations: EPR

## "Normalized" EPR

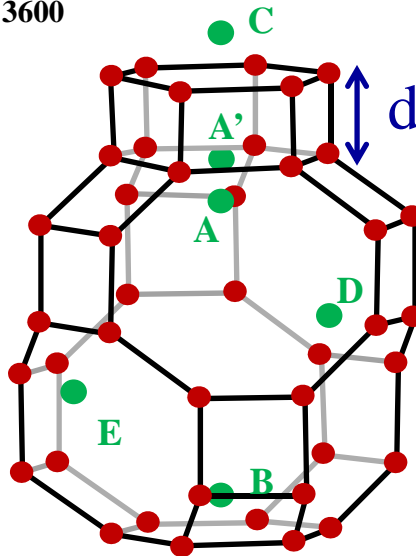


## Cu-Cu distance Estimation



$$\Delta E = g\mu_B H_0$$

$$\Delta E_{dd} = \frac{\mu_0}{4\pi} g^2 \mu_B^2 \frac{1}{r^3}$$

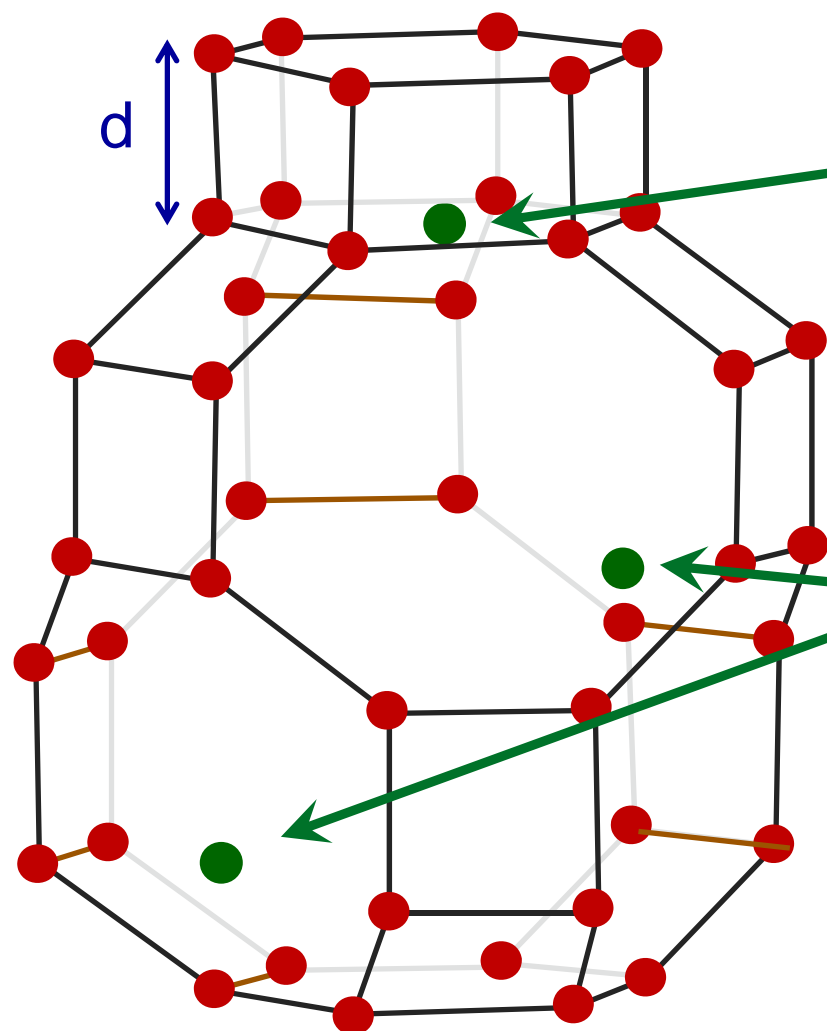


$$a = b = 13.719 \text{ \AA}$$

$$c = 14.953 \text{ \AA}$$

$$d = 3.8 \text{ \AA}$$

# Possible Locations for Cu in SSZ-13 Catalysts

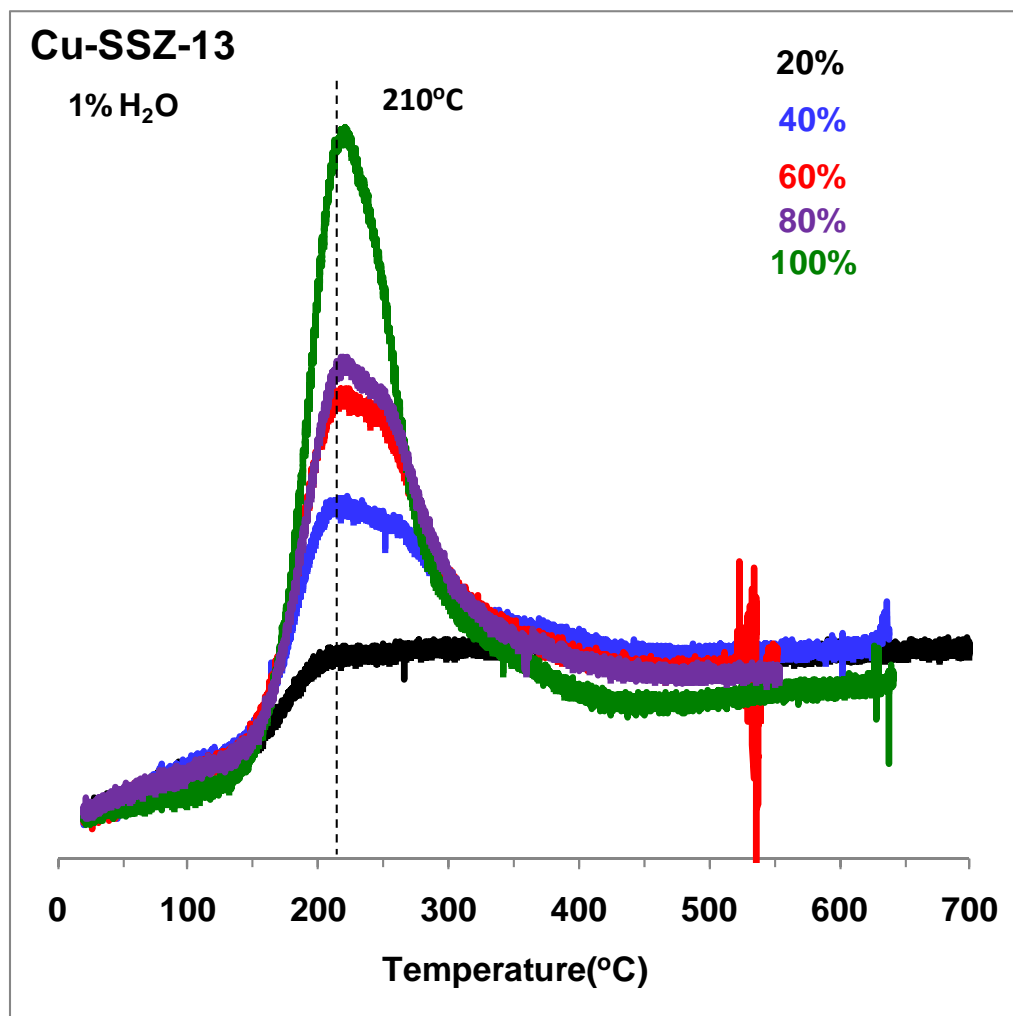


- ❑ Location at bottom of six-membered rings known from XRD and EXAFS studies of low-Cu loaded catalysts (Lobo, Weckhuysen and coworkers).
- ❑ Locations in large zeolite cage consistent with EPR and with more facile reducibility of Cu at higher loading.

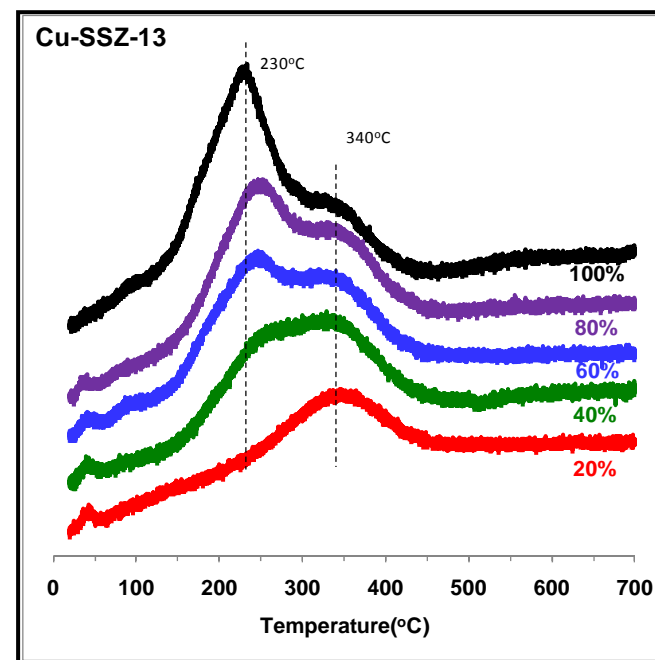
$$\begin{aligned}a &= b = 13.719 \text{ \AA} \\c &= 14.953 \text{ \AA} \\d &= 3.8 \text{ \AA}\end{aligned}$$

F Gao, ED Walter, EM Karp, J Luo, RG Tonkyn, JH Kwak, J Szanyi, CHF Peden, *Journal of Catalysis* **300** (2013) 20.

# A couple more significant open questions...



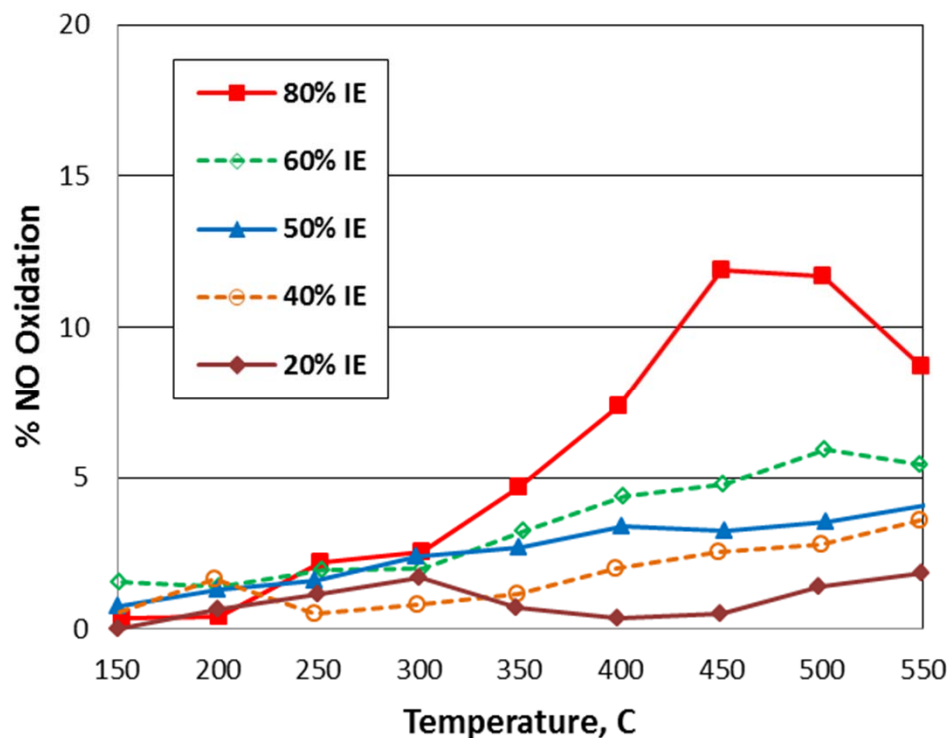
- ❑ Cu at low loadings is more difficult to reduce.
- ❑ In presence of 1% H<sub>2</sub>O, H<sub>2</sub>-TPR shows only low-temp peak for all Cu loadings.
- ❑ It appears Cu species may move under reaction conditions.



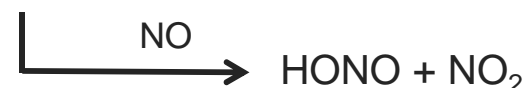
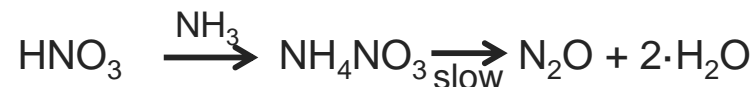
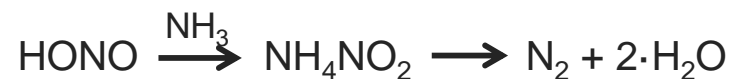
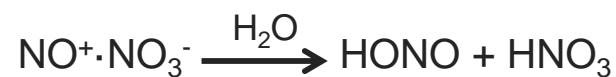
JH Kwak, H Zhu, JH Lee, CHF Peden, J Szanyi,  
Chemical Communications 48 (2012) 4758-4760.



# NO Oxidation over Cu-SSZ-13



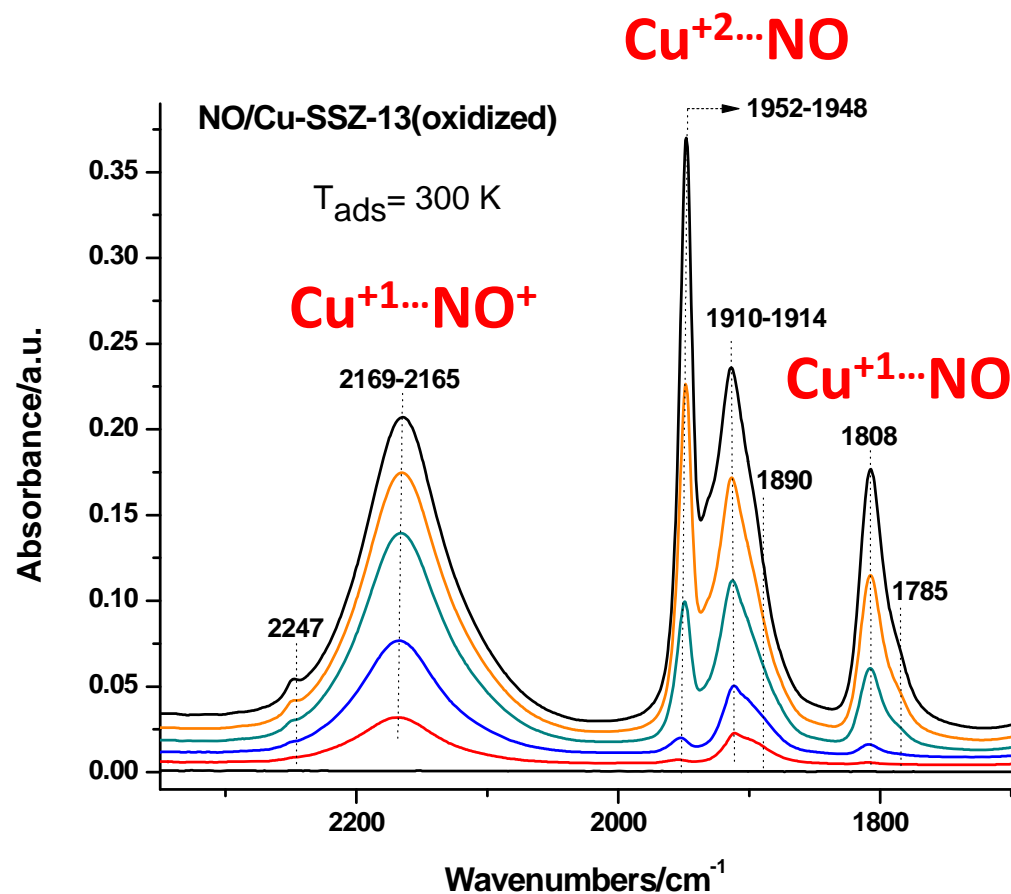
## Proposed Elementary Steps (From Weitz and coworkers, *Catalysis Today* 136 (2008) 55)



- Very low NO oxidation over Cu/CHA catalysts.
- Very high NO reduction despite low NO oxidation suggests NO oxidation may not be critical over Cu/CHA.
- N<sub>2</sub>O is an insignificant product of SCR reaction over Cu/SSZ-13.

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

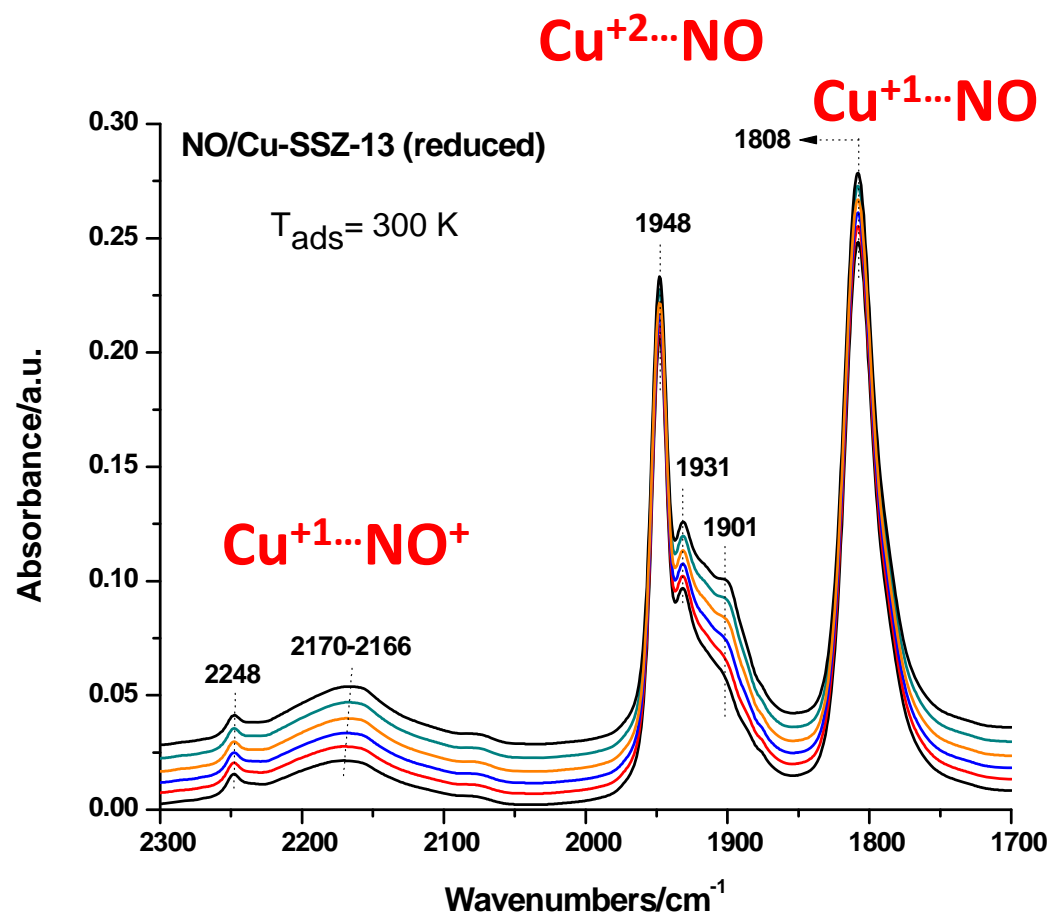
# NO Adsorption on oxidized Cu/SSZ-13



- Peaks between ~1850 and ~2000 cm<sup>-1</sup> can be assigned to NO adsorbed on Cu<sup>+2</sup>.
- Unusually high wavenumber (~2165 cm<sup>-1</sup>) peak is assigned to an NO<sup>+</sup> Species.
- Cu<sup>+1</sup> adsorbed NO species forms after NO<sup>+</sup>.
  - Some Cu<sup>+2</sup> reduced by NO?
  - NO then chemisorbs on Cu<sup>+1</sup>?

J Szanyi, JH Kwak, H Zhu, CHF Peden,  
PCCP 15 (2013) 2368-2380.

# NO Adsorption on reduced Cu/SSZ-13



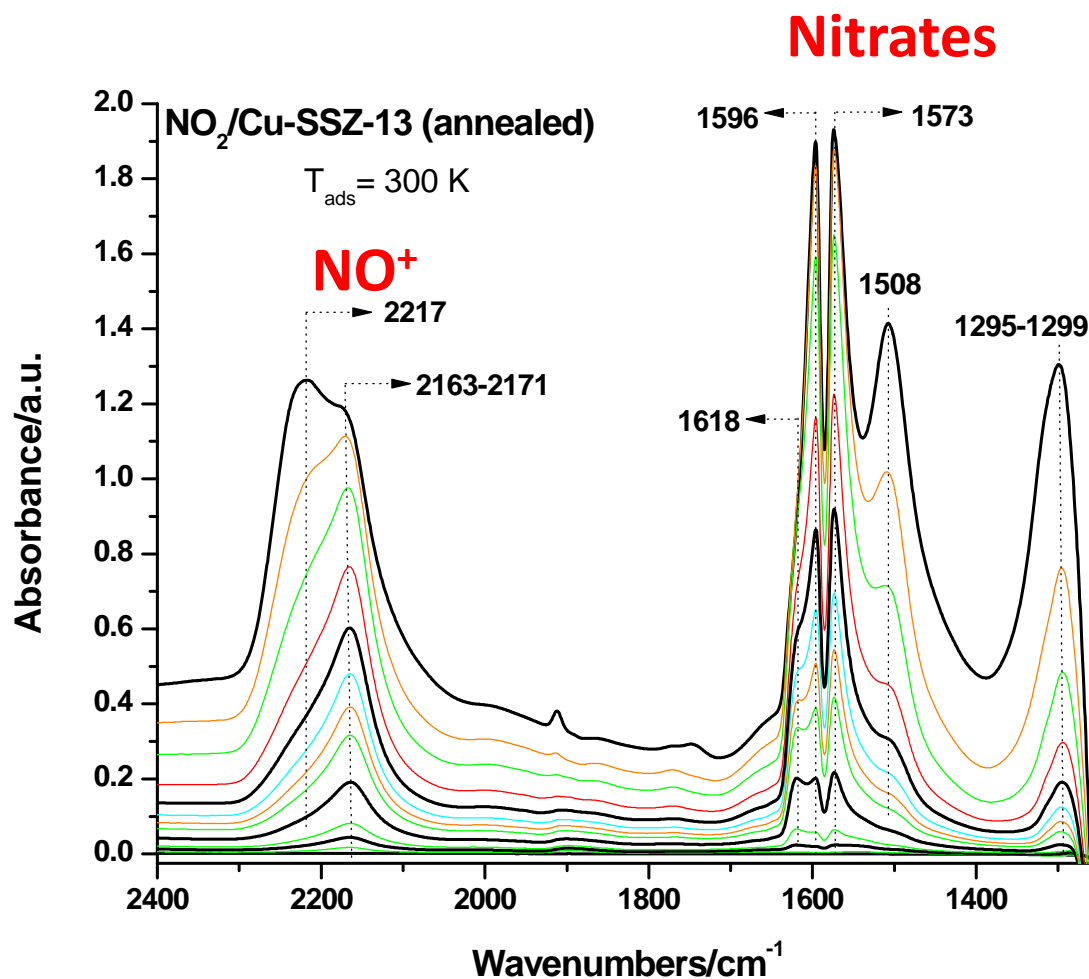
□ When Cu/SSZ-13 is reduced prior to NO adsorption:

- Significantly lower amounts of  $\text{Cu}^{2+}\dots\text{NO}$ ;
- Only very small amounts of  $\text{NO}^{+}$  species; yet
- $\text{Cu}^{+1}\dots\text{NO}$  is the dominant species present.

□ NOTE:  $\text{NO}^{+}$  species can be observed on zeolites after  $\text{NO}_2$  adsorption.

J Szanyi, JH Kwak, H Zhu, CHF Peden,  
PCCP 15 (2013) 2368-2380.

# NO<sub>2</sub> Adsorption on oxidized Cu-SSZ-13

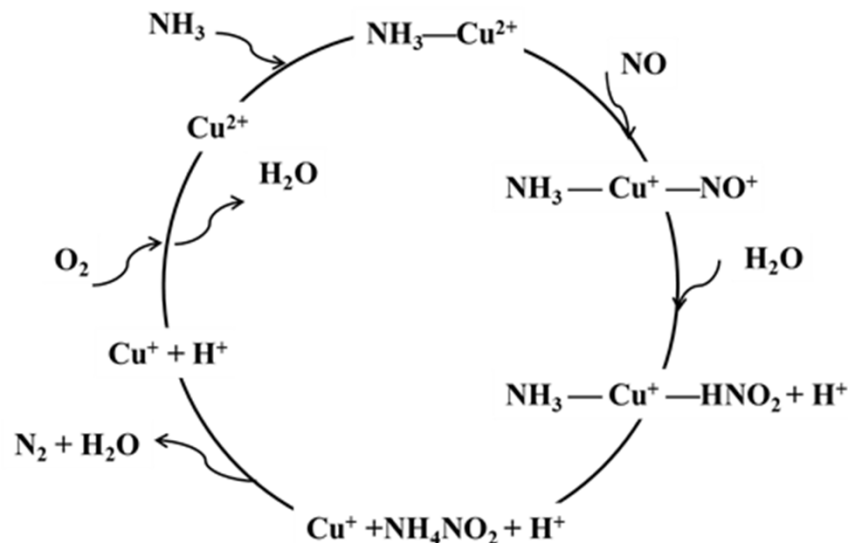
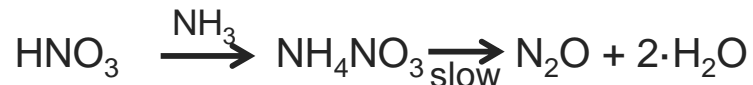
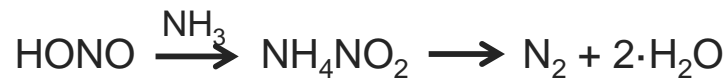
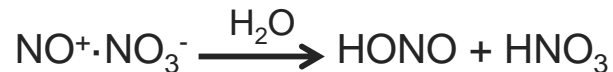


- Nitrates and NO<sup>+</sup> are the predominant species formed when NO<sub>2</sub> is adsorbed on Cu/SSZ-13 as expected from proposed mechanism.
- Have used <sup>15</sup>N NMR to learn more about the nature of the Cu<sup>1+</sup>-bound NO<sup>+</sup> species.

J Szanyi, JH Kwak, H Zhu, CHF Peden,  
PCCP 15 (2013) 2368-2380.

# Mechanistic Implications

## Proposed Elementary Steps

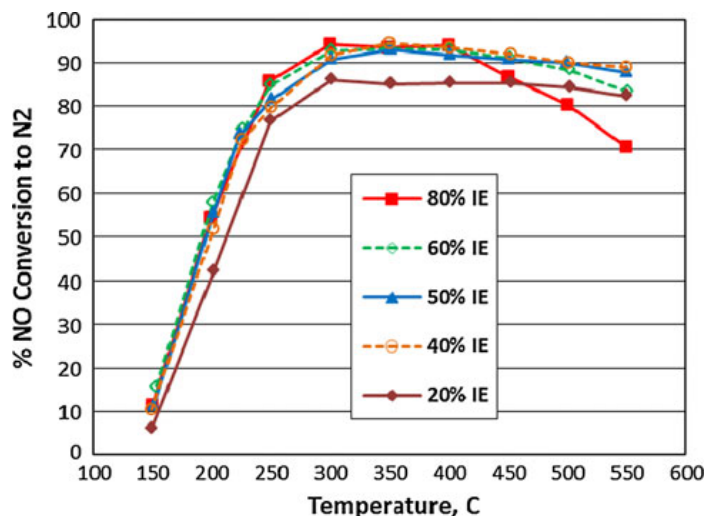


- N in +3 ( $\text{NH}_3$ ) and -3 ( $\text{NO}^+$ ) oxidation state are required.
- Nitrates and  $\text{NO}^+$  are proposed products of  $\text{NO}_2$  disproportionation.
- Nitrates +  $\text{NH}_3$  results in  $\text{N}_2\text{O}$  formation (*not observed for Cu/SSZ-13*).
- Formation of  $\text{NO}^+$  without nitrates for Cu/SSZ-13 can rationalize selectivity.
- $\text{Cu}^{+1}$  observed during SCR reaction with XANES – Ribeiro and coworkers, *Cat. Today* 184 (2012) 129-144.

# SCR Kinetics and Mechanisms Studies are Complicated by Mass Transfer Effects

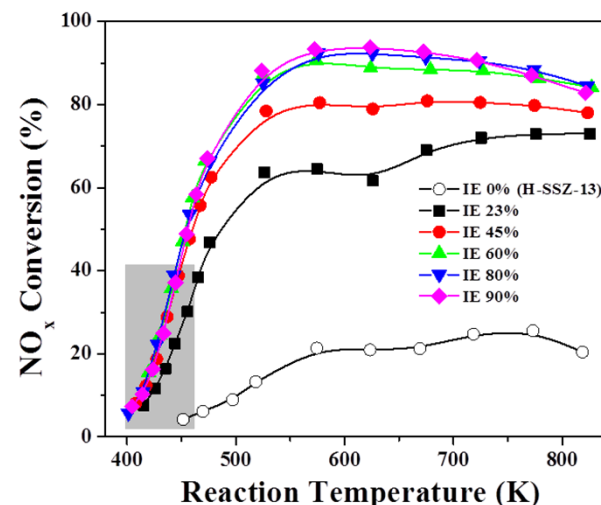


GHSV ~ 200,000 h<sup>-1</sup>



JH Kwak, D Tran, J Szanyi, CHF Peden, J Lee, *Catal. Lett.*, **142** (2012) 295.

GHSV ~ 800,000 h<sup>-1</sup>



F Gao, ED Walter, E Karp, J Luo, RG. Tonkyn, JH Kwak, J Szanyi, CHF Peden, *J. Catal.* **300** (2013) 20.

**SCR not reaction limited; rather mass-transfer limited.**

**We are also studying another CHA zeolite-based SCR catalyst, Cu-SAPO-34.**



# Summary and Conclusions

- Cu/SSZ-13 catalysts display outstanding performance for  $\text{NH}_3$  SCR relative to other Cu/zeolite-based catalysts.
- Significantly, the SSZ-13 small-pore zeolite provides considerably lower sensitivity to high-temperature hydrothermal aging.
- 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  $\text{H}_2$  TPR, EPR and FTIR.
  - The relative distribution of Cu species is dependent on Cu loading levels and reaction conditions.
- FTIR and NMR studies are addressing the mechanism of  $\text{NH}_3$  SCR:
  - Surprising is the presence of  $\text{Cu}^{+1}\text{-NO}$ , even for oxidized Cu/SSZ-13, evidently from the reduction of Cu by NO to form a  $\text{Cu}^{+1}\text{...NO}^+$  species.
  - This  $\text{NO}^+$  species without the formation of nitrates may explain high  $\text{N}_2$  selectivities (little, if any,  $\text{N}_2\text{O}$ ) of Cu/SSZ-13.
  - $^{15}\text{N}$  NMR results suggest that the structure of the  $\text{Cu}^{+1}\text{...NO}^+$  species involves side-on bonding of NO, similar to that in nitrite-reductase enzymes.
- We believe that solid-state ion exchange is a better method to incorporate Cu into SAPO-34 CHA catalysts for fundamental studies.

# Acknowledgments



Institute for  
INTEGRATED  
CATALYSIS

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



Haiyang Zhu and Russ Tonkyn,  
Institute for Integrated  
Catalysis, PNNL



Institute for  
INTEGRATED  
CATALYSIS

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

