



New Insights into the Role of the SCR Catalyst in Coupled LNT-SCR Systems

J. Wang¹, Z. He¹, Y. Ji¹, M. Crocker¹, M.-Y. Kim², J.-S. Choi²

¹ Center for Applied Energy Research, University of Kentucky

² Fuels, Engines & Emissions Research Center, Oak Ridge National Laboratory

April 30, 2012

LNT-SCR Concept: Utilization of *In Situ* NH₃

- “Classical” explanation:¹⁻³
 - LNT produces NH₃ during rich purges (similar to TWC under rich engine conditions)
 - NH₃ stores on downstream SCR catalyst
 - Stored NH₃ reacts with “breakthrough” NO_x during lean operation
 - Similar to urea-SCR except that NH₃ is generated “in-situ” or “passively” by the LNT
- NH₃ *in situ* mechanism does not appear to fully explain LNT+SCR vehicle data⁴

1. D. Chatterjee, P. Koči, V. Schmeisser, M. Marek, M. Weibel, B. Krutzsch, Catal. Today 151 (2010) 395

2. P. Forzatti, L. Lietti, Catal. Today 155 (2010) 131

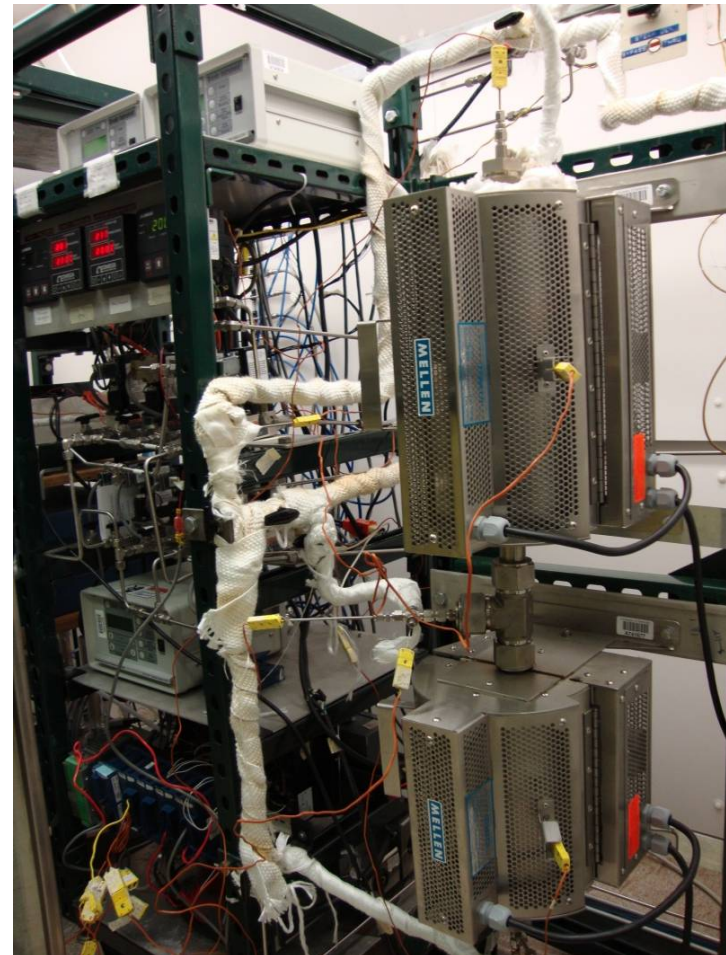
3. A. Lindholm, H. Sjövall, L. Olsson, Appl. Catal. B 98 (2010) 112

4. L. Xu, R. McCabe, M. Dearth, W. Ruona, SAE Technical Paper 2010-01-0305 (2010)

Reactor Studies

LNT-SCR studies:

- BASF catalysts:
Low PGM-loaded LNT +
Cu-chabazite SCR catalyst
- 3" x 0.9" cores, de-greened at 500 °C
for 5 h under L/R cycling
- Separate catalysts/reactors with gas
sampling at three positions
- 60 s lean/5 s rich cycles
- Gas analysis using FTIR gas analyzer

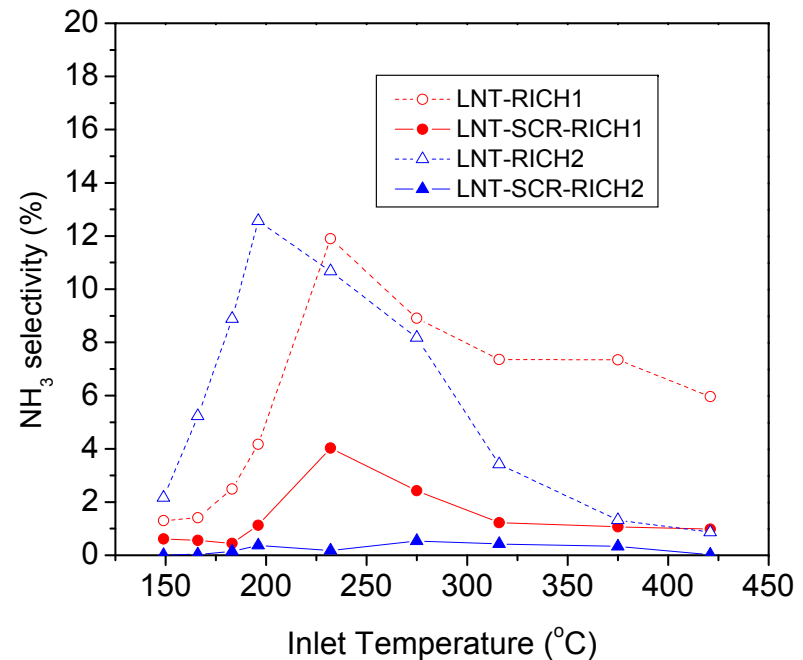
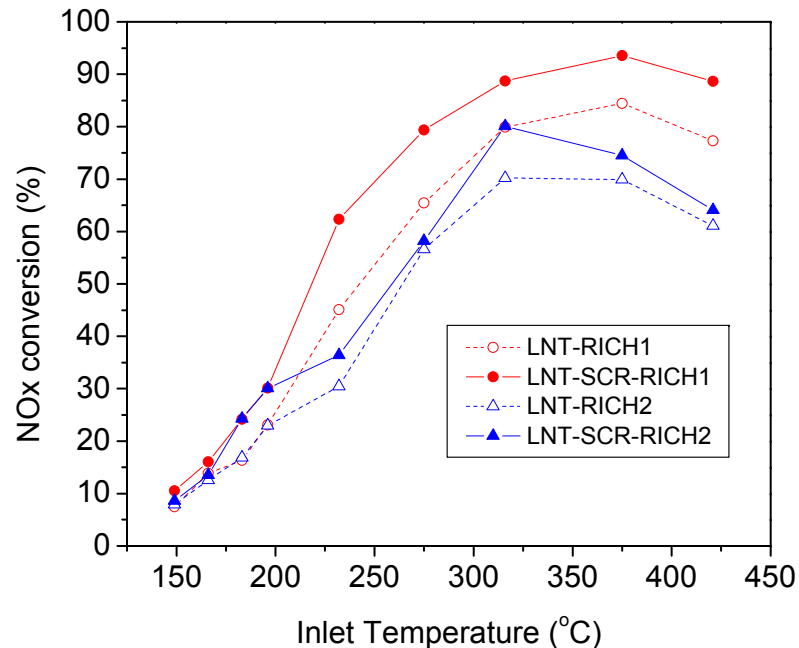


NO_x and NH₃ Conversion in LNT-SCR System: Effect of Added Propene (Rich Phase)

60 s lean – 5 s rich cycles:

Rich condition #1: 1% CO, 0.3% H₂, 3333 ppm C₃H₆

Rich condition #2: 1% CO, 0.3% H₂

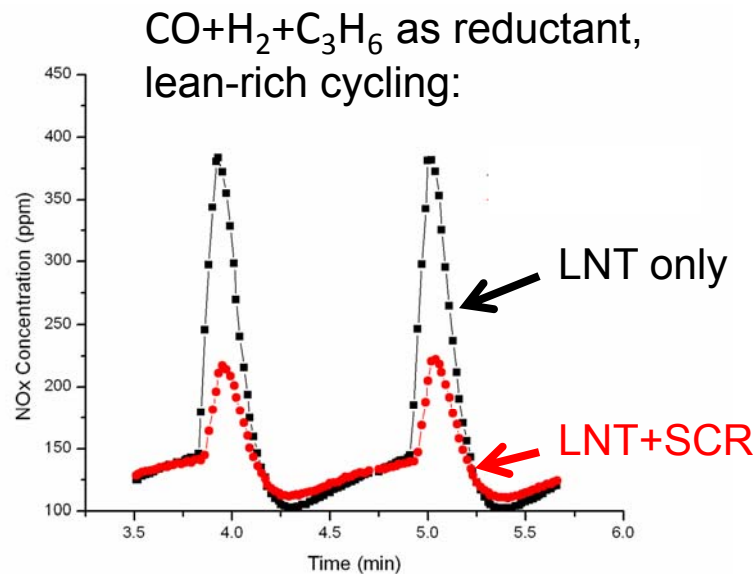


Benefit of SCR catalyst most apparent when hydrocarbon (propene) is present
→ SCR catalyst is able to utilize propene - or a derivative thereof - as a reductant

NOx Conversion in the LNT-SCR System: Results for Different Reductants (233 °C)

Reductant ^a	Total NOx conversion over SCR catalyst (%)	NOx conversion over SCR catalyst during lean phase (%)	NOx conversion over SCR catalyst during rich phase (%)
CO + H ₂ + C ₃ H ₆	15.3	5.9	9.6
CO + H ₂	3.6	3.45	0.15
C ₃ H ₆	8.0	0.8	7.2

^a CO = 1%; H₂ = 0.3%; C₃H₆ = 3333 ppm;



When propene is added as rich phase reductant, NOx conversion over SCR catalyst mainly occurs in rich phase (as opposed to lean phase for conventional NH₃ route)

Nitrogen Balance Across SCR Catalyst

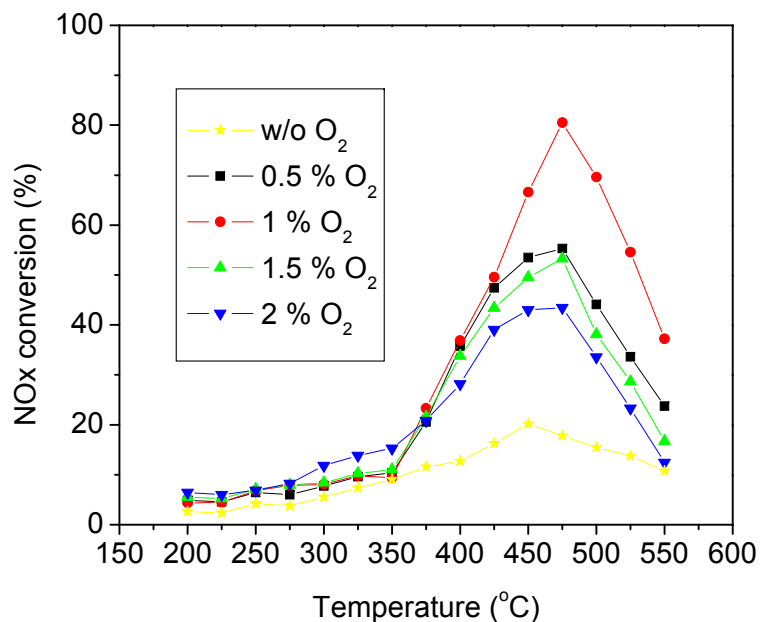
Reductant = 1% CO + 0.3% H₂ + 3333 ppm C₃H₆

LNT Inlet Temperature (°C)	NH ₃ converted over SCR catalyst (ppm)	NOx converted over SCR catalyst (ppm)	NH ₃ converted – NOx converted (ppm)
149	0.1	9.3	-9.1
166	0.3	6.7	-6.3
183	0.9	23.9	-23.0
196	1.9	21.5	-19.6
232	8.7	52.6	-43.9
275	11.9	42.4	-30.5
316	14.6	26.8	-12.2
375	15.9	27.7	-11.8
421	11.4	34.7	-23.3

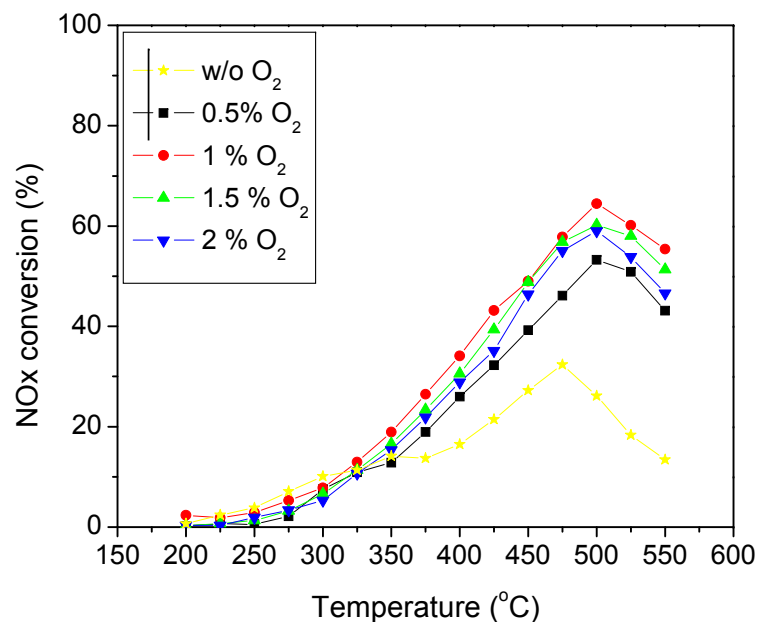
Steady State NOx Conversion over Cu-zeolite SCR Catalyst

Conditions: 300 ppm NO, 5% CO₂, 5% H₂O, N₂ balance, GHSV = 30,000 h⁻¹

3333 ppm C₃H₆ as reductant



5000 ppm C₂H₄ as reductant



- Propylene and ethylene show moderate activity for NOx reduction over SCR catalyst under steady-state and cycling conditions
- NOx conversion is sensitive to O₂ content of feed

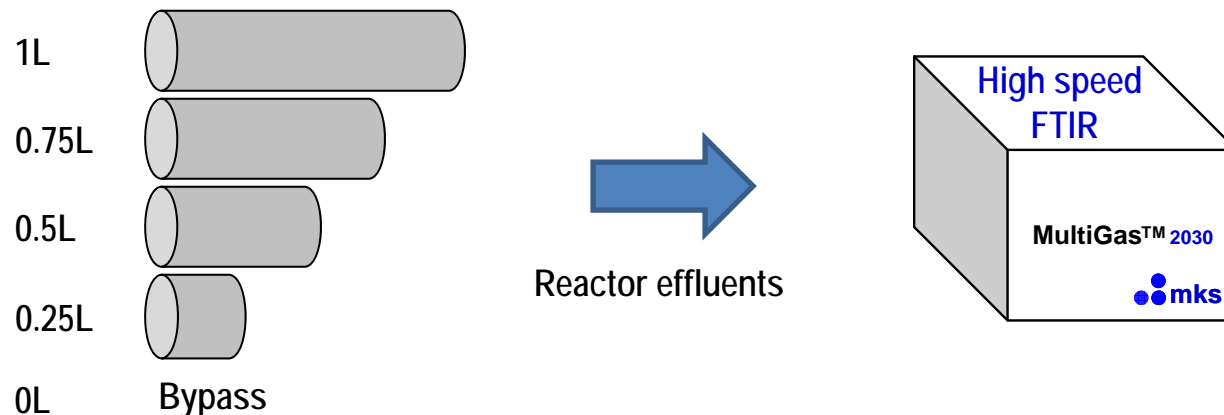
Spatiotemporal Analysis of NO_x Reduction by NH₃ & C₃H₆ over Cu-chabazite During Lean/Rich Cycling

- Bench-reactor experimental conditions

	NH ₃		C ₃ H ₆		NH ₃ + C ₃ H ₆	
	Lean (60 s)	Rich (5 s)	Lean (60 s)	Rich (5 s)	Lean (60 s)	Rich (5 s)
NO (ppm)	300	300	300	300	300	300
O ₂ (%)	8	1	8	1	8	1
C ₃ H ₆ (ppm)	0	0	0	3333	0	3333
NH ₃ (ppm)	0	300	0	0	0	300
CO ₂ (%)	5	5	5	5	5	5
H ₂ O (%)	5	5	5	5	5	5
N ₂ (%)	Balance	Balance	Balance	Balance	Balance	Balance

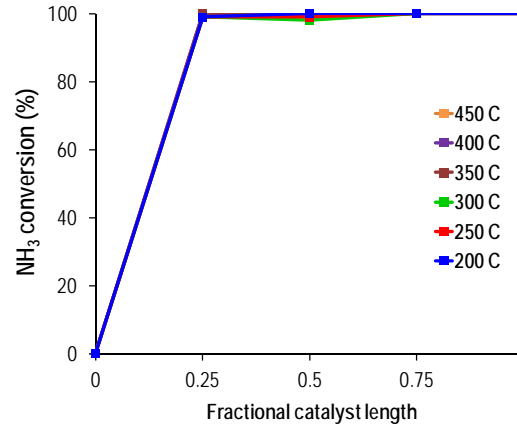
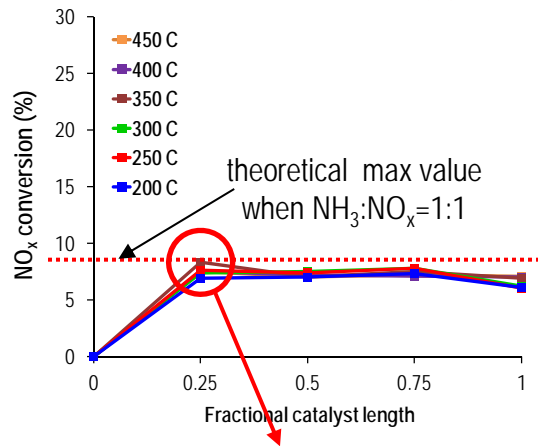
- Total flow: 13.7 L/min (equivalent to 30K SV for 3-in core: 1L)
- Temperature: 200, 250, 300, 350, 400, 450 °C

- Spatiotemporal resolution of reactions

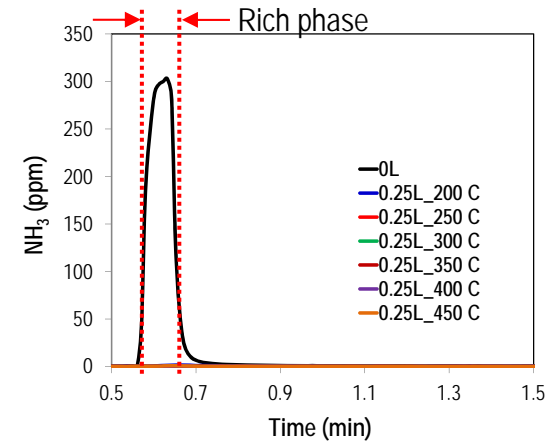
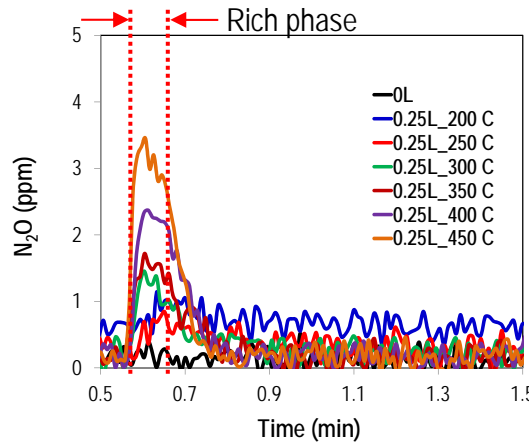
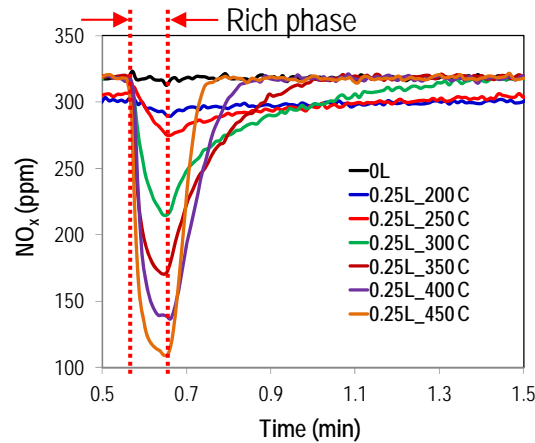


NO_x Reduction by NH₃

Reductant: 300 ppm NH₃



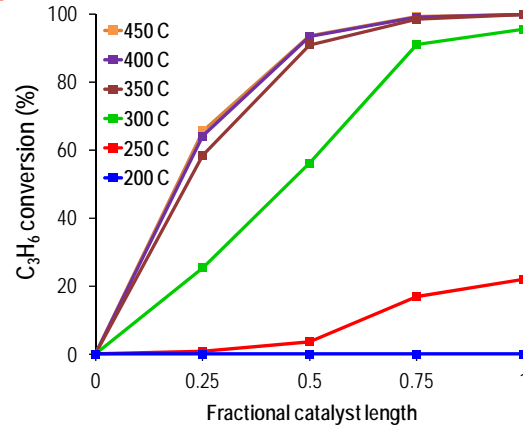
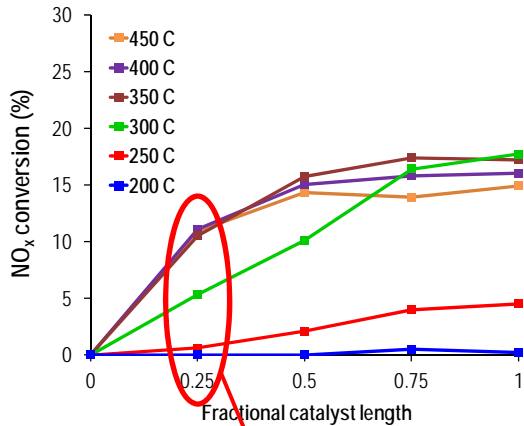
- Total consumption of NH₃ with near stoichiometric NO_x reduction within 1st ¼ catalyst at all temps.



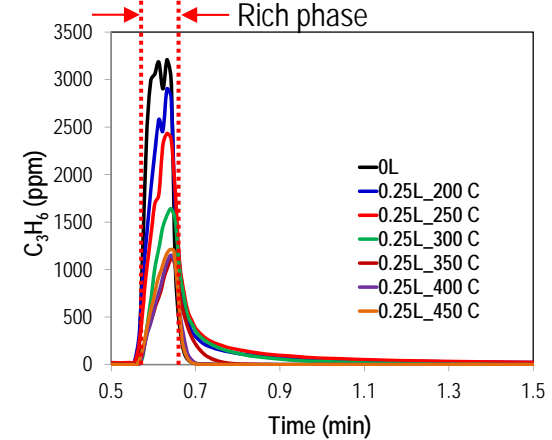
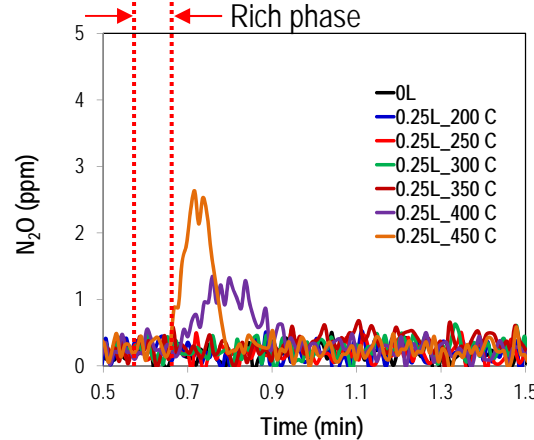
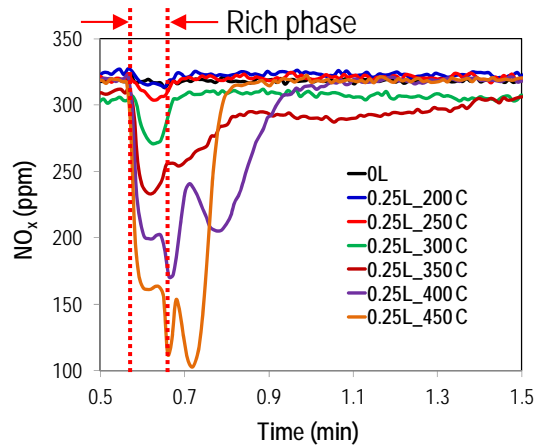
- NO_x reduction occurs both in rich & lean phases
- Greater portion of NO_x reduction in lean phase at lower temperatures
 - Due to lower reduction rate & higher NH₃ storage

Significant NOx Reduction by C₃H₆ Above 250 °C

Reductant: 3333 ppm C₃H₆



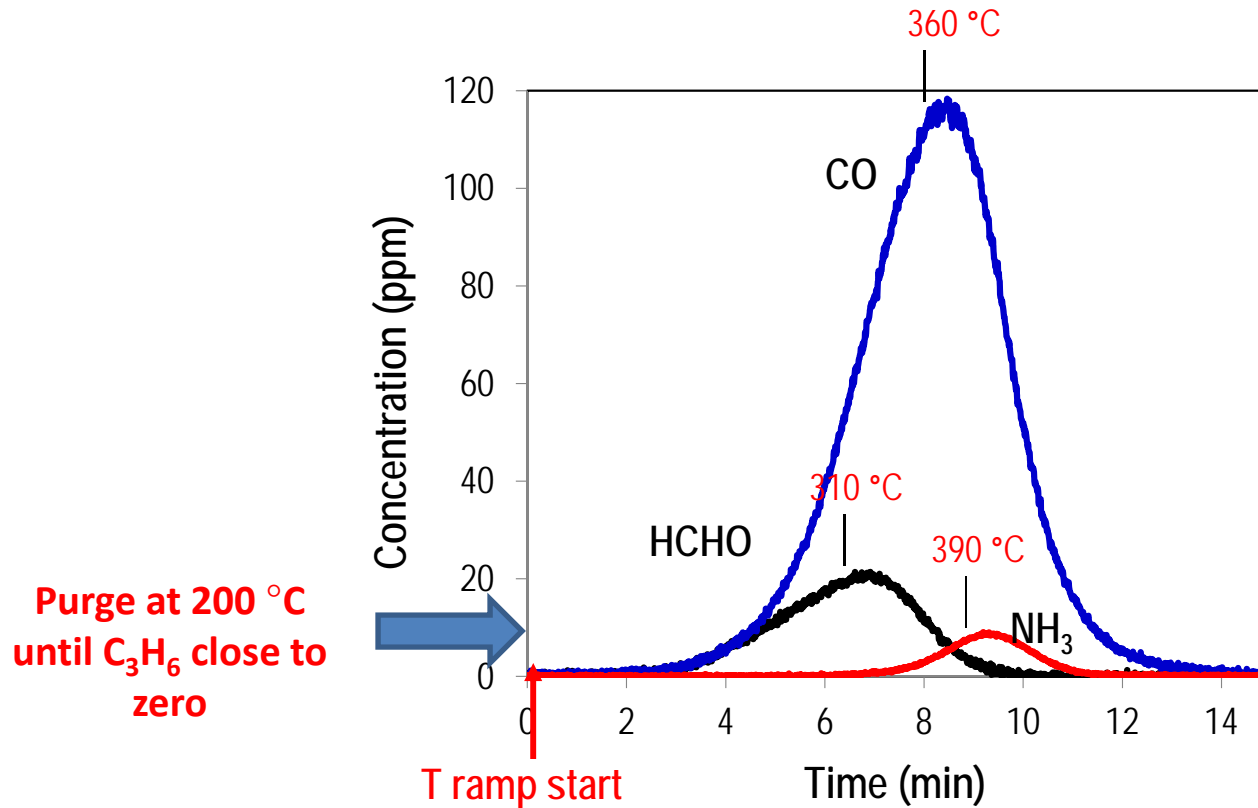
- Up to ~20% NOx conversion
- Best performance at 300-350 °C
- Entire length used except at 400-450 °C



- NOx reduction occurs both in rich & lean phases (3 “regimes” at 350, 400, 450 °C)
- Greater portion of NOx reduction in lean phase at lower temperatures
 - Due to lower reduction rate & higher C₃H₆ storage (see peak tails)

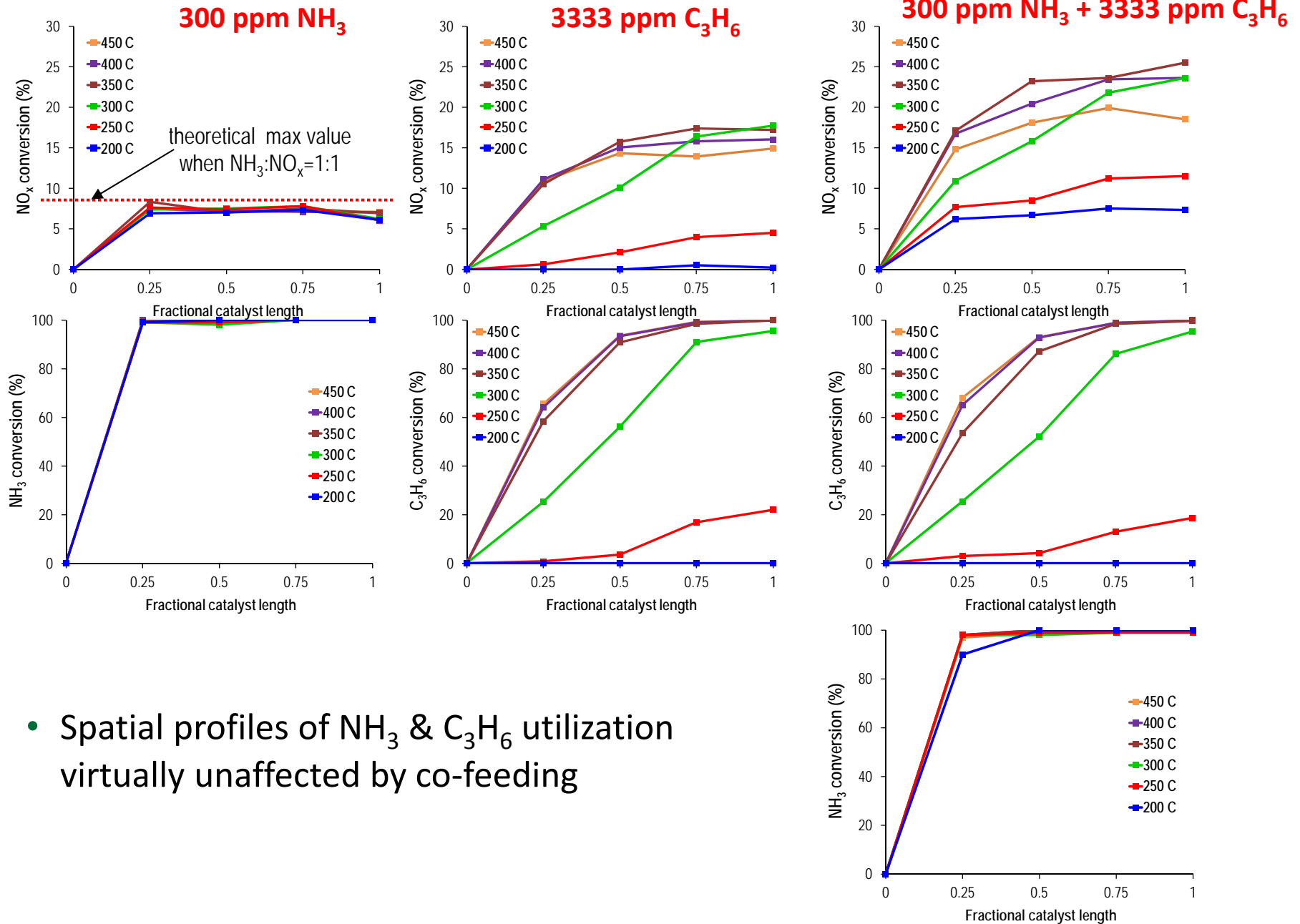
NH₃ Could be Surface Intermediate

Temperature ramp (200 → 500 °C) after C₃H₆ cycling at 450 °C → 200 °C;
catalyst was purged with O₂, H₂O and CO₂ at 200 °C before the TPD

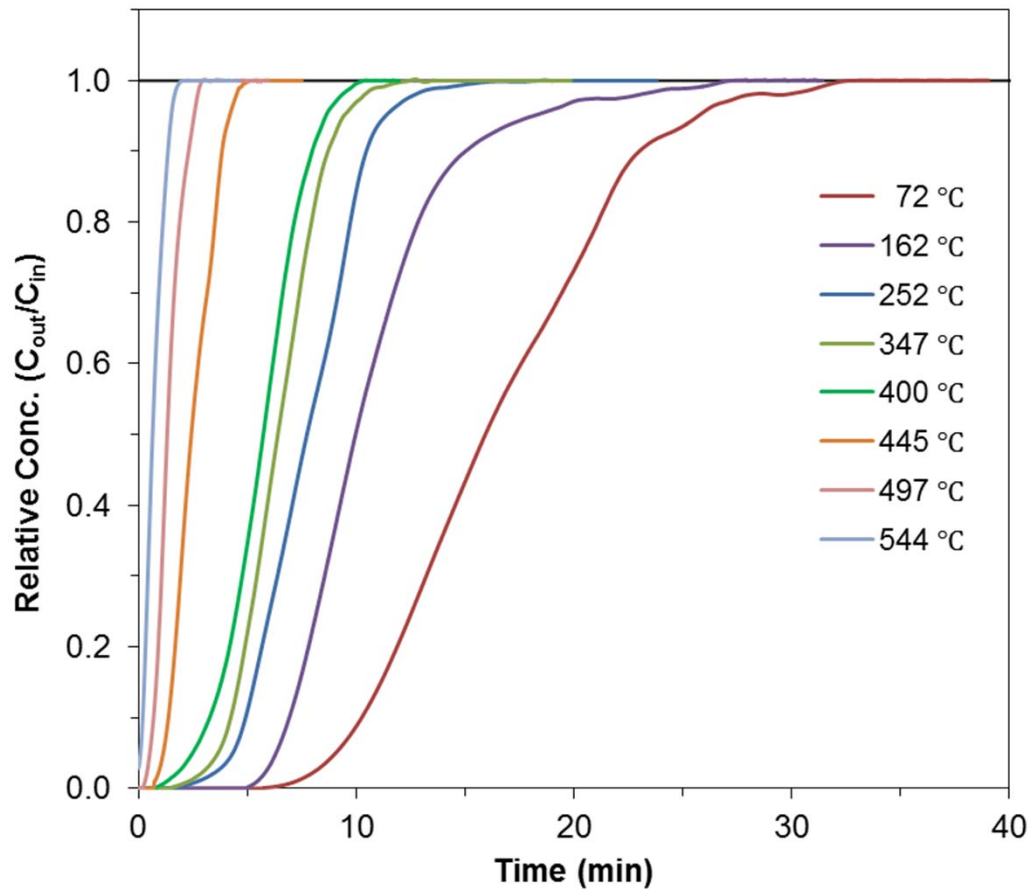


- High-T release of NH₃ suggests its formation, storage & usage on surface only
 - Could explain “3rd” NO_x reduction regime (peak in lean phase) observed during C₃H₆ cycling at 350, 400, 450 °C

Effects of NH_3 & C_3H_6 on NO_x Reduction are Additive



Adsorption of C_3H_6 on Cu-chabazite SCR Catalyst



Pre-treatment:

10% O_2/He at 550 °C for 1 h

Adsorbate:

1000 ppm C_3H_6 in He

GHSV: 30,000/h

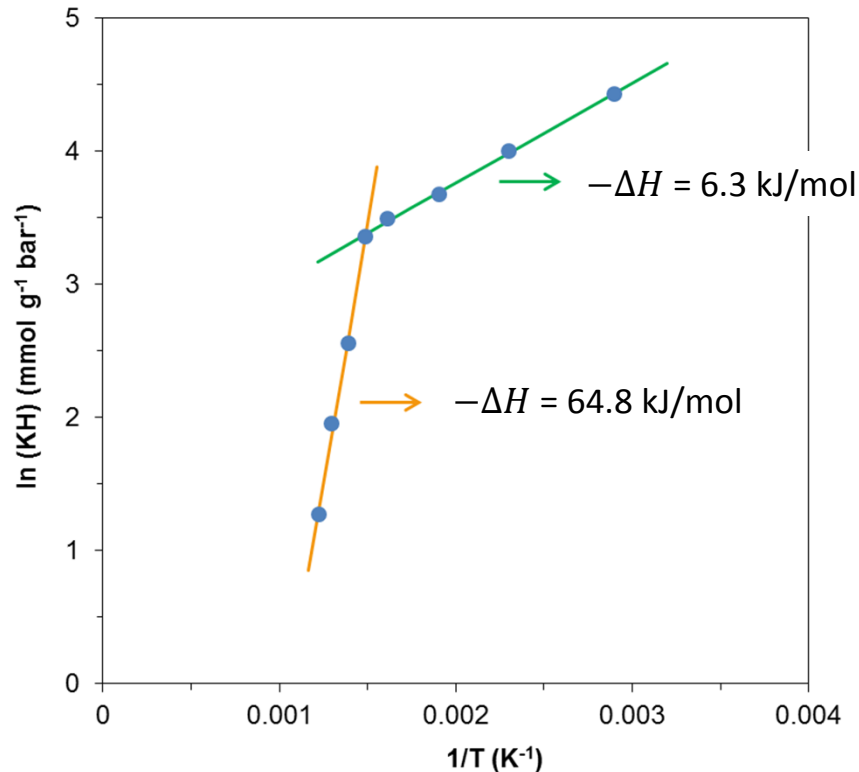
Maximum C_3H_6 loading

(72 °C) = 0.84 mmol/g

(36 mg/g)

➤ Breakthrough time decreases with increasing adsorption temperature

Heat of Adsorption of C₃H₆ on Cu-chabazite SCR Catalyst



N.A. Al-Baghli, K.F. Loughlin, *J. Chem. Eng. Data* **2005**, 50, 843-848:

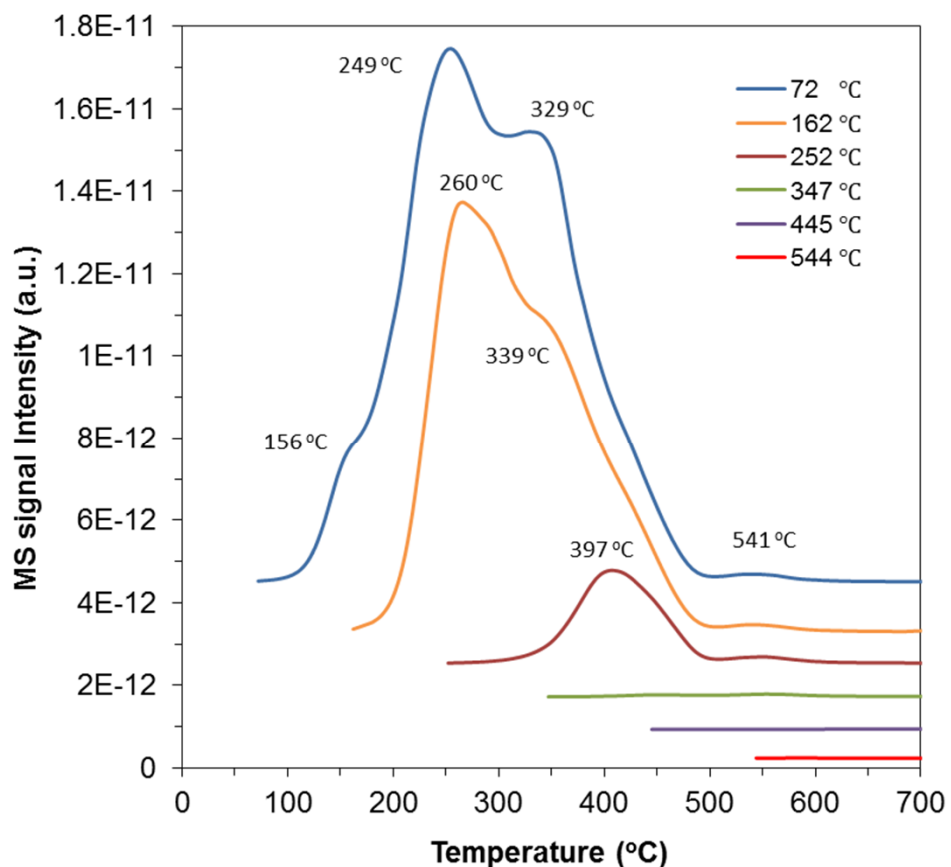
$$q = \frac{q_m K_a P}{1 + K_a P} \quad \text{where} \quad q_m = \frac{V_p}{V^*}$$

$$K_a = k_0 \left(\frac{-\Delta H}{RT} \right)$$

$$\ln(K_a) = \frac{-\Delta H}{R} \frac{1}{T} + \ln(k_0)$$

- Heat of adsorption of C₃H₆ obtained using Langmuir isotherm and Arrhenius eqns.
- Magnitude of heat of adsorption consistent with chemi- and physisorption; chemisorption is indicated to be strong (e.g., comparable with Li-exchanged zeolite 13X)

TPD of C₃H₆ Adsorbed on Cu-chabazite SCR Catalyst



Ramp rate 10 °C/min

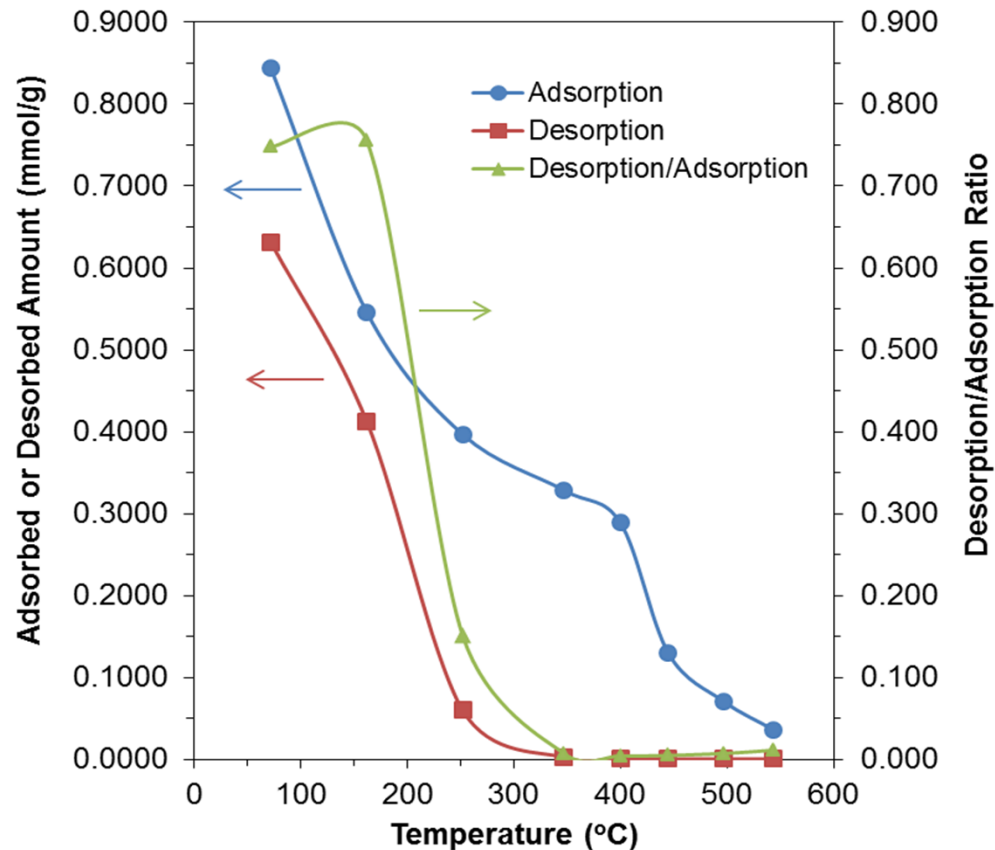
Flow rate: 40 mL/min (He)

In addition to propene,
many other desorbed
species are observed:

C₂H₂, C₂H₄, C₂H₆, C₄H₈, CO,
CO₂, H₂O, etc.

- After propene adsorption 72 °C, the TPD curve shows four peaks with a maximum intensity at 156, 249, 329, and 541 °C
- Possible adsorption sites: Cu species (e.g., Cu²⁺, Cu⁺, CuO) and Brønsted acid sites

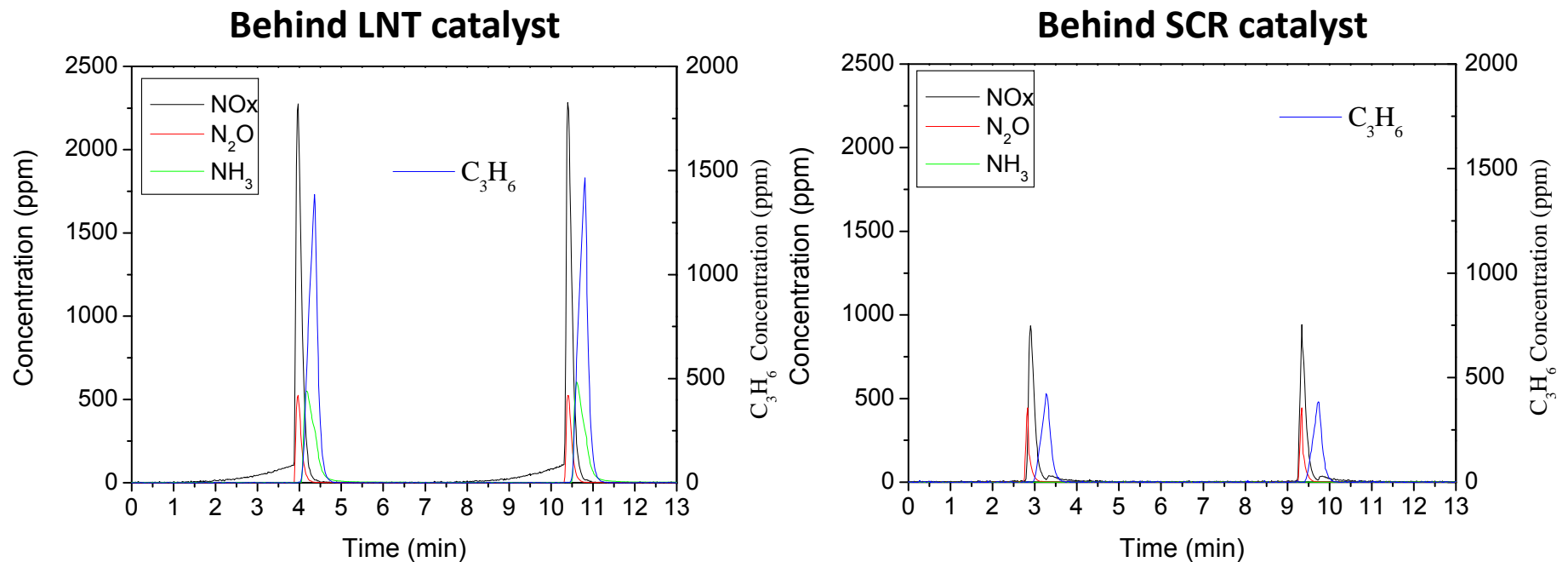
Adsorption and Desorption of C_3H_6 on Cu-chabazite SCR Catalyst



- Mismatch between amount of propene adsorbed and desorbed (particularly at > 300 °C) indicates high reactivity of propene in zeolite
- Implication is that many different species are available to react with NO_x

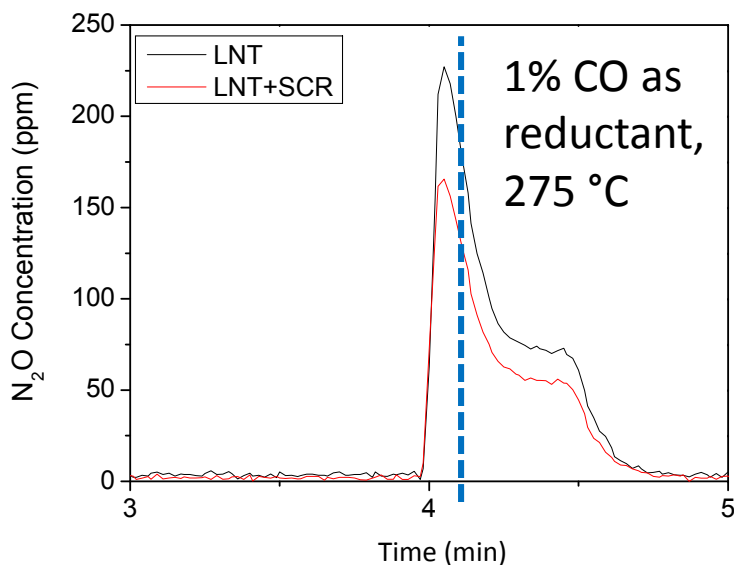
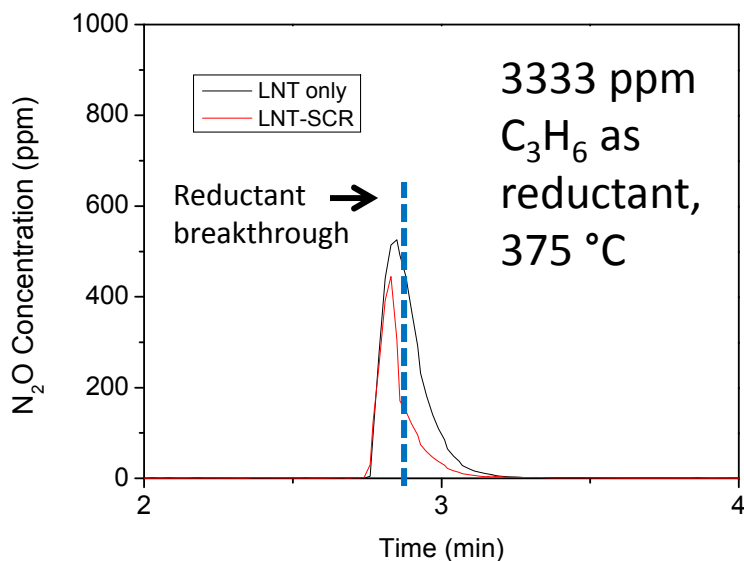
N₂O Reduction Over Cu-chabazite SCR Catalyst

Comparison of gas composition behind LNT and SCR catalysts during lean-rich cycling (1% C₃H₆ as reductant, 360 s lean, 30 s rich; 375 °C)



- Significant conversion of NO_x, NH₃, C₃H₆ and N₂O over SCR catalyst
- As expected NO_x and N₂O breakthrough LNT catalyst before NH₃ and C₃H₆

N₂O Reduction Over Cu-chabazite SCR Catalyst



Comparison of N₂O concentrations behind LNT & SCR catalysts (360 s lean, 30 s rich):

- Increased N₂O formation over LNT when using CO as reductant, compared to H₂ (consistent with Abdulhamid *et al.* and LePhuc *et al.*)
- For CO, N₂O formation observed at L-R and R-L transition (consistent with Elizundia *et al.*)
- Some N₂O conversion occurs before reductant has broken through, implying N₂O decomposition

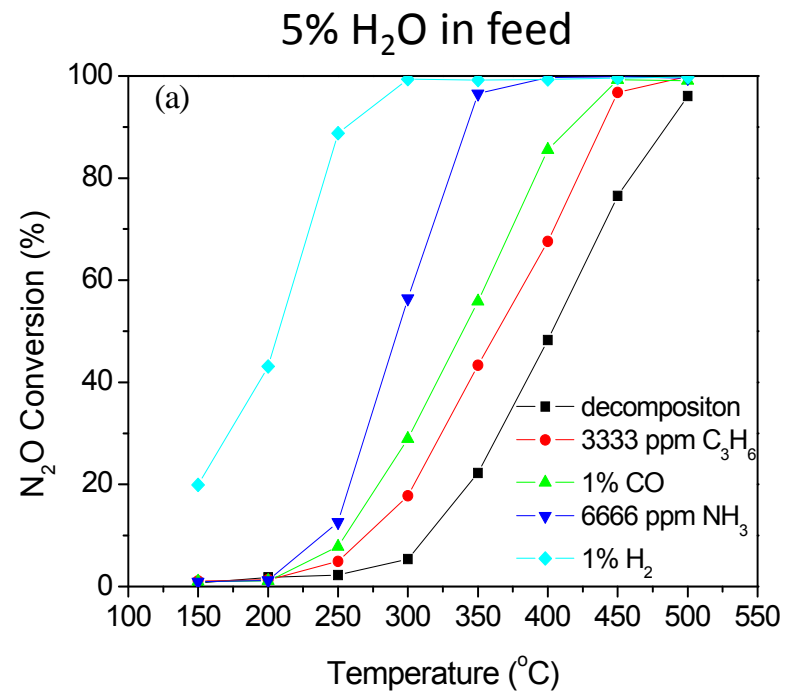
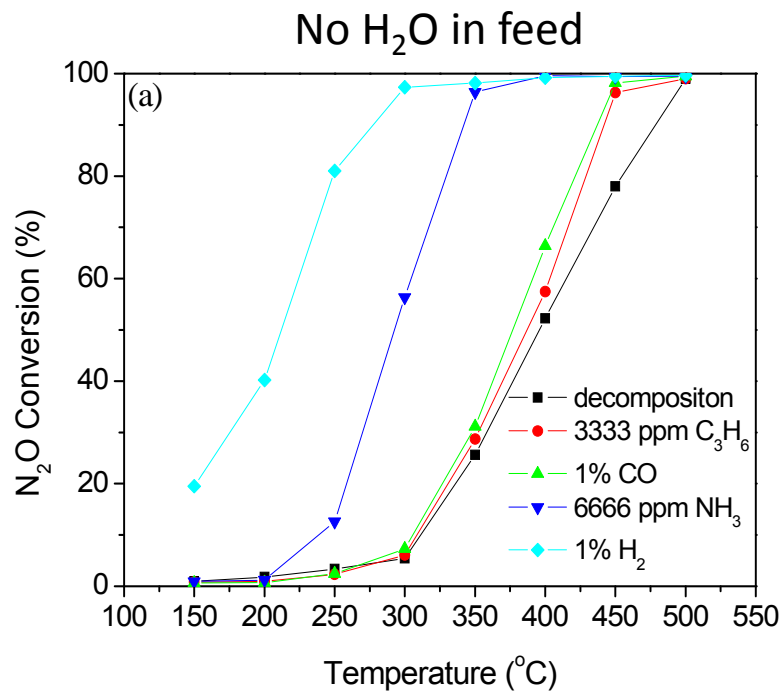
H. Abdulhamid, E. Fridell, M. Skoglundh, *Top. Catal.* 30/31 (2004) 161.

N. Le Phuc, X. Cortois, F. Can, S. Berland, S. Royer, P. Marecot, D. Duprez, *Catal. Today* 176 (2011) 424.

U. Elizundia, D. Duraiswami, B. Pereda-Ayo, R. Lopez-Fonscea, J.R. Gonzalez-Velasco, *Catal. Today*, 176 (2011) 324.

N₂O Reduction Over Cu-chabazite SCR Catalyst: Steady-state Continuous Flow

Feed: 100 ppm N₂O, 5% CO₂, reductant as shown, bal. N₂; GHSV = 30,000 h⁻¹



- H₂ best reductant, followed by NH₃
- N₂O reduction not inhibited by water; v. slight inhibition of decomposition reaction
- Slight promoting effect with water for reduction using CO or C₃H₆: implies *in situ* formation of H₂ via WGS or steam reforming

Summary

- Reactor studies have shown that a hydrocarbon-based NO_x reduction pathway (ethylene and propylene studied) can operate in a Cu-chabazite SCR catalyst in parallel with the NH₃-SCR pathway
- The contribution of hydrocarbons to NO_x reduction is most evident under conditions of low NH₃ availability
- Propene adsorbs strongly in the Cu-chabazite catalyst; significant storage of HC in the SCR catalyst can occur, even at high temperatures
- Preliminary results indicate that adsorbed propene undergoes oxidation, cracking and oligomerization reactions
- Significant N₂O reduction is observed over the SCR catalyst

Acknowledgements

- Funding:
Department of Energy, Office of Vehicle Technologies
- Project partners:
Ford Motor Co.: M. Dearth, B. McCabe
University of Houston: M. Harold, V. Balakotaiah, D. Luss
ORNL: T. Toops
BASF: C.Z. Wan