

# ***Selective reduction of NO<sub>x</sub> in oxygen rich environments with plasma-assisted catalysis: Catalyst development and mechanistic studies***

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EE/FreedomCar and Vehicle Technologies  
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# Talk Outline

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- Introduction
  - Plasma-facilitated catalysis for NO<sub>x</sub> reduction
  - Active catalysts
  - What is the plasma doing?
- Catalyst synthesis and reactivity
  - What is the optimum catalyst composition?
  - Some optimization of catalyst synthesis
- Studies of the reaction mechanism
  - Differences in rates of the back reaction (NO<sub>2</sub> to NO) on different catalysts
  - Concept of the Cascade Reactor



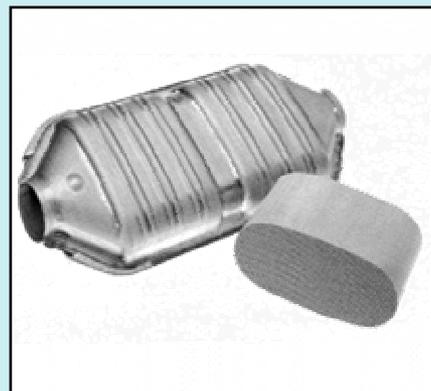
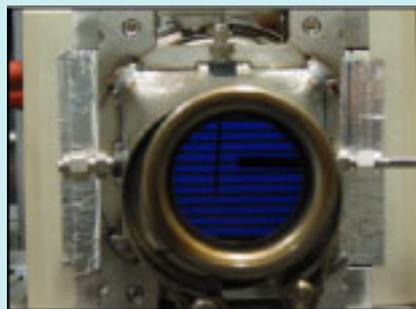
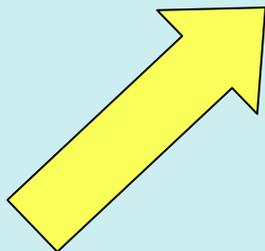
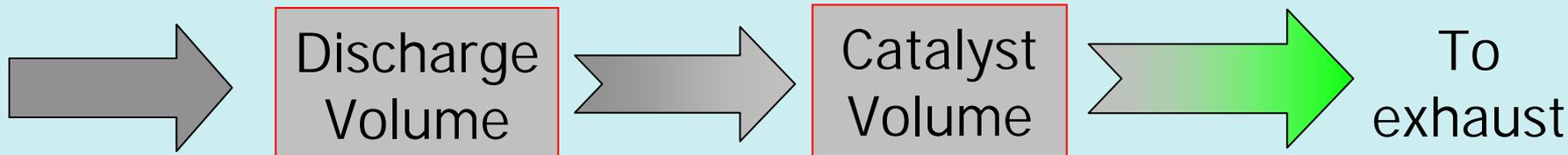
# This Technology is Hydrocarbon SCR with a Plasma “Reformer”

## Schematic of Two Step Discharge/Catalyst Reactor

Exhaust Gas:  
NO, HC's, etc.

**Reformed  
Exhaust**

N<sub>2</sub>, N<sub>2</sub>O,  
CO<sub>2</sub>, etc.



Electrical Power

# Modeling of the Gas-Phase Plasma Reaction Mechanisms

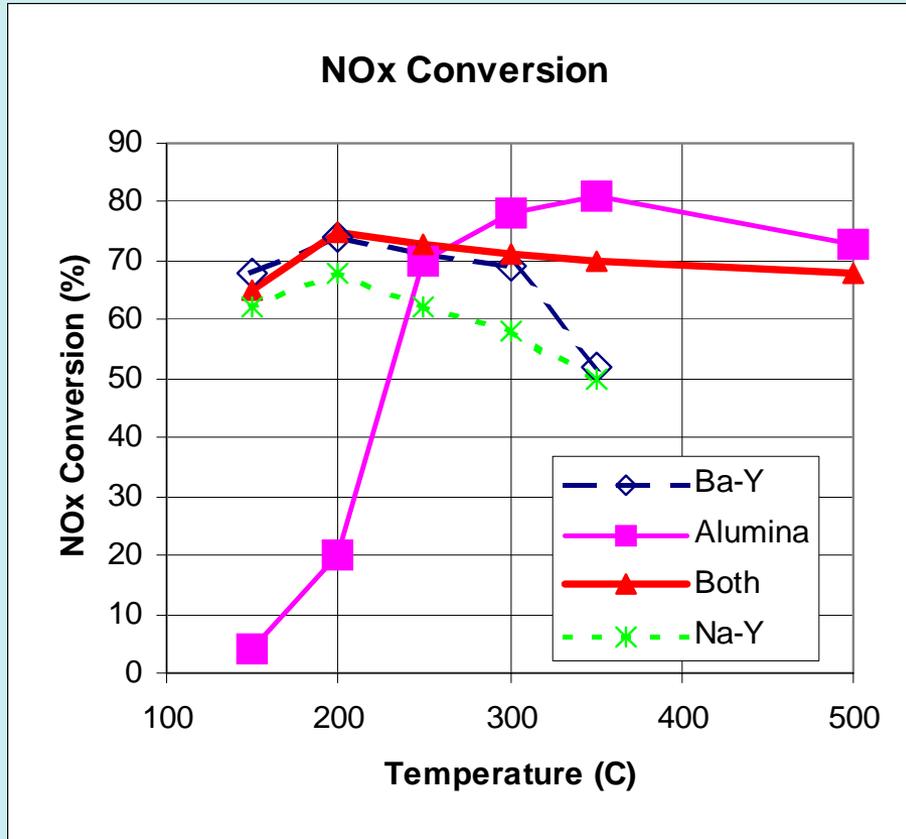
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- Under lean-burn engine exhaust conditions, a non-thermal plasma is oxidative.
  - A primary reaction is conversion of  $\text{NO} \rightarrow \text{NO}_2$
  - The oxidation of NO in a NTP is promoted by added hydrocarbon.
  - Added hydrocarbon is partially oxidized, and aldehydes are a crucial product as they are most reactive as reductant for NOx.
  - *Thermal* catalytic reaction of aldehydes +  $\text{NO}_2$  yield activities of >90% for reasonable flow rates.
  - Understanding the products of exhaust 'reforming' by the plasma has guided catalyst development efforts.

# From Balmer, et al., SAE 1999-01-3640 and Tonkyn, et al., SAE 2000-01-2896

Catalyst	NO <sub>x</sub> removal, %	Temperature, °C	Space velocity, hr <sup>-1</sup>
BaTiO <sub>3</sub>	No activity	180	12,000
Al <sub>2</sub> O <sub>3</sub> (active at higher temp.)	20	200	12,000
ZrO <sub>2</sub>	No activity	180	12,000
HZSM-5, HBeta	No activity	180	12,000
CuZSM-5	15-20	180	12,000
CaY	54	200	12,000
NaY	60-65	180	12,000

# Na-Y, Ba-Y, Alumina



- Alumina effective at high temperature
- Zeolite effective at lower temperature
- Combination effective over wide range

Panov, et al., SAE 2001-01-3513

Subsequently, we have developed alkali- and alkaline earth-exchanged zeolite-Y catalysts for plasma-assisted NOx reduction.

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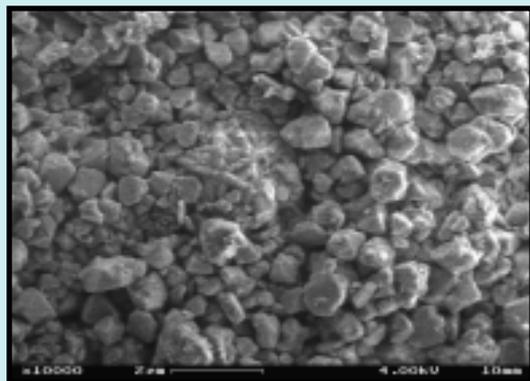
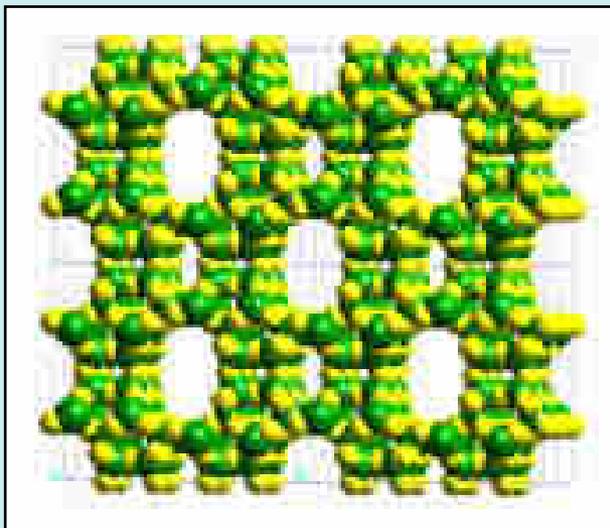
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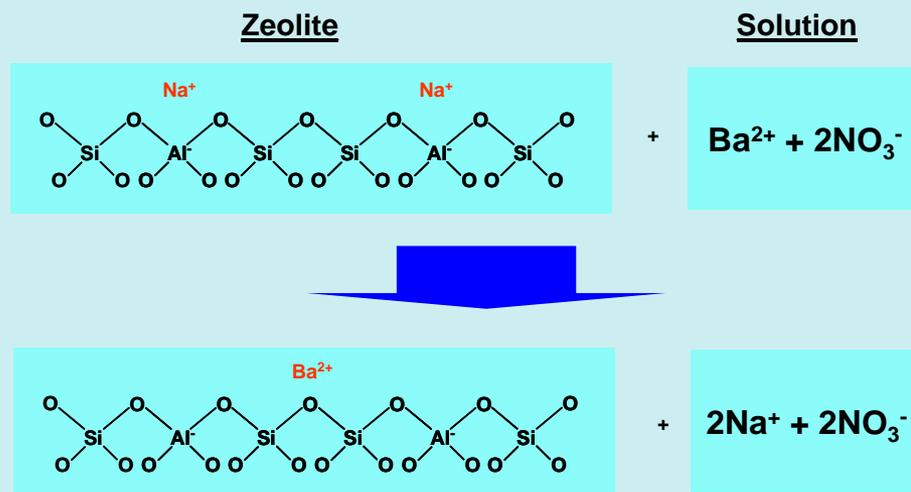
# What is the optimum cation substitution into Zeolite-Y?

Kwak, Szanyi, and Peden – Catalysis Today  
(2003) in press.

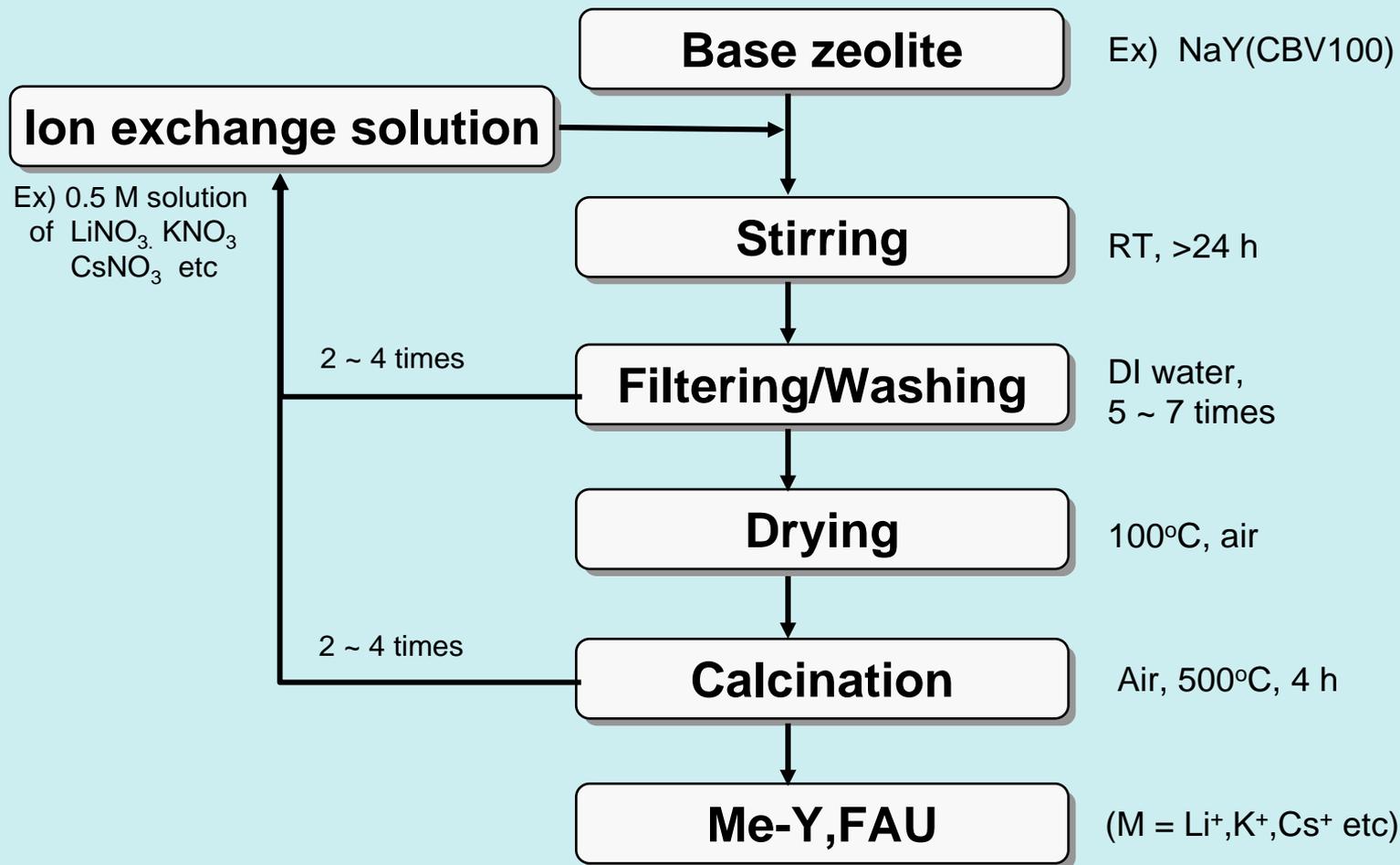
# Y-Zeolites are Crystalline Silica-Alumina Materials with 3-D Pore-Structures



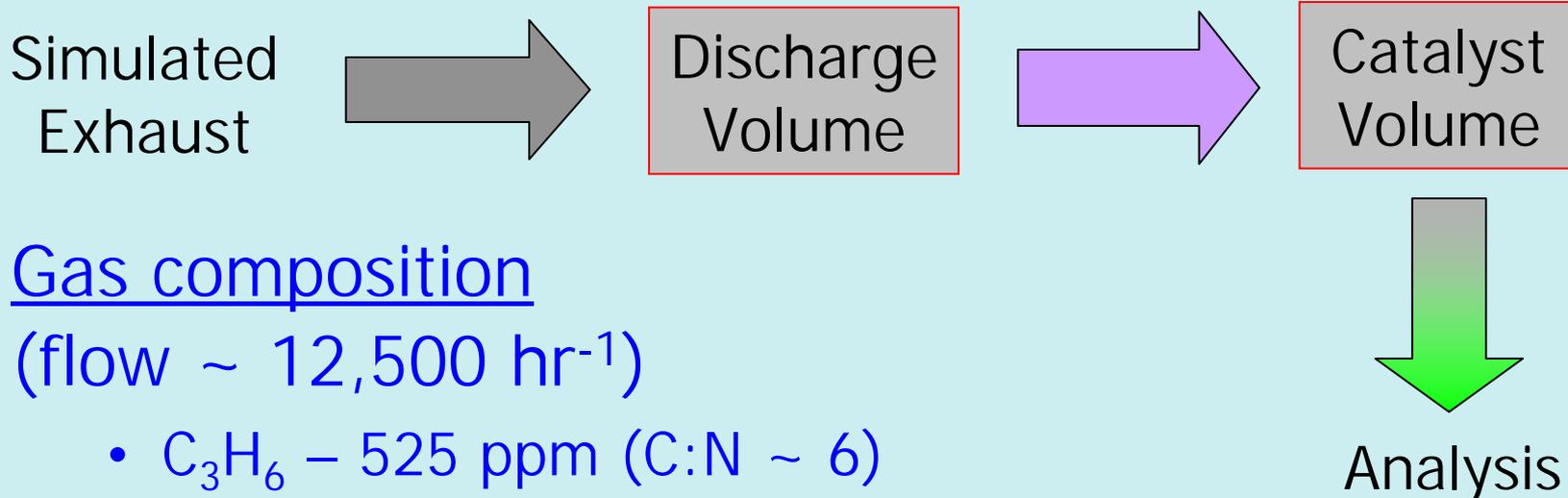
- Cations compensate charged sites in zeolite present due to Al substitution.



# Catalyst Synthesis by Ion Exchange



# Experimental Procedure and Apparatus



## Gas composition

(flow ~ 12,500 hr<sup>-1</sup>)

- C<sub>3</sub>H<sub>6</sub> – 525 ppm (C:N ~ 6)
- NO – 250 ppm
- Oxygen – 9%
- H<sub>2</sub>O – 2%
- N<sub>2</sub> - balance

Reaction rates were measured at 'steady-state' to assure that NOx 'reduction' is not due to adsorption.

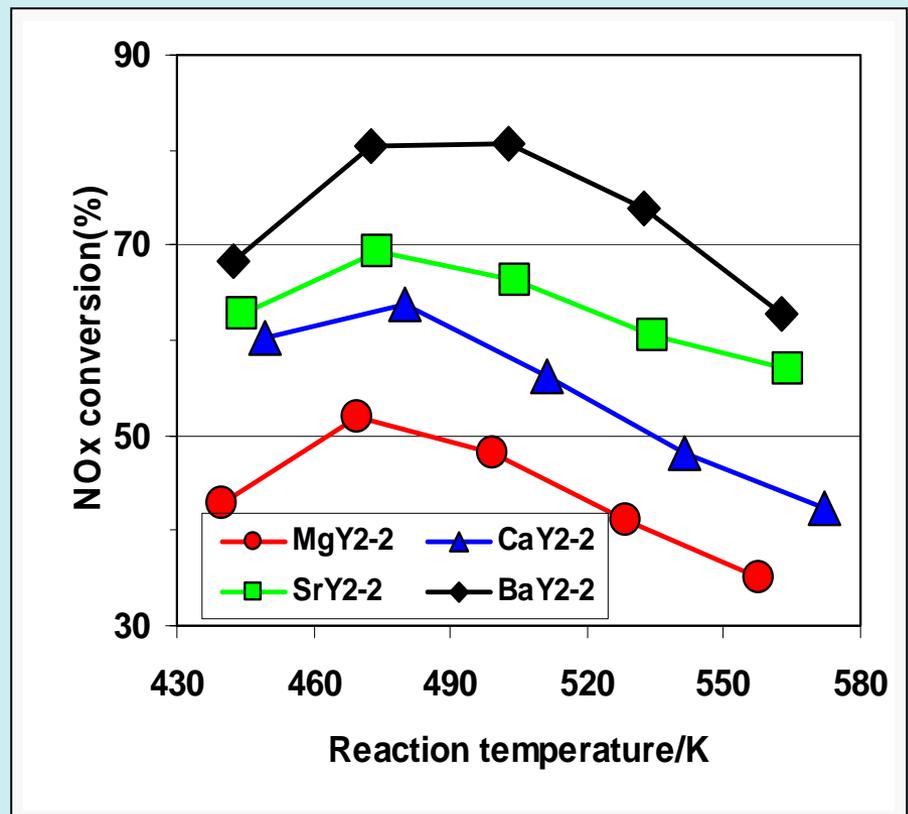
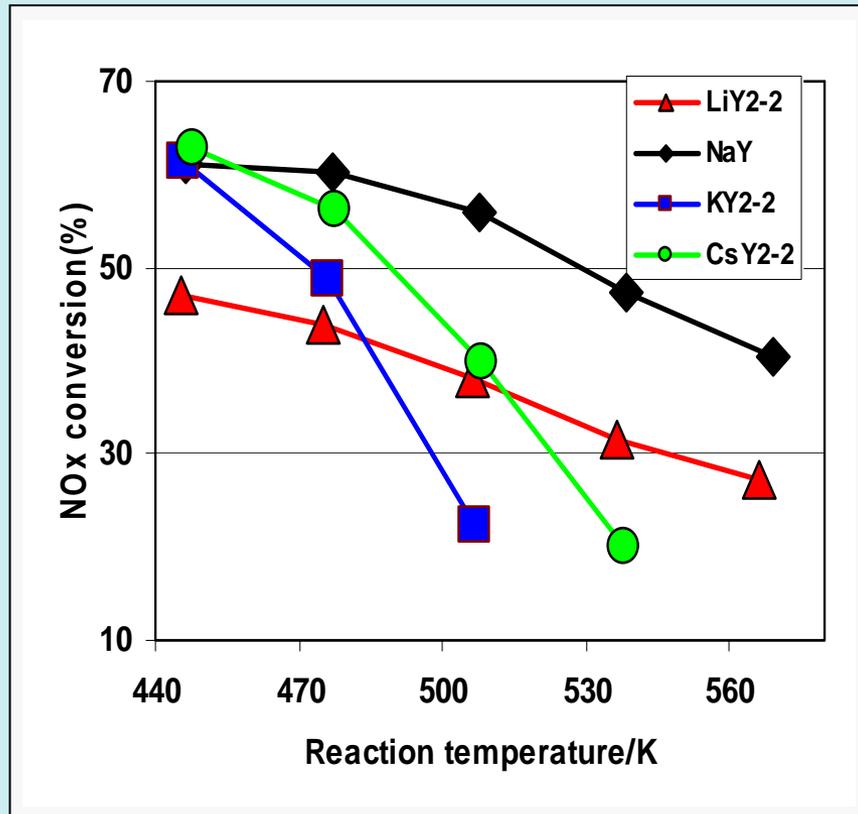
## Plasma Power

- ~ 10 Joules/liter

## Analysis

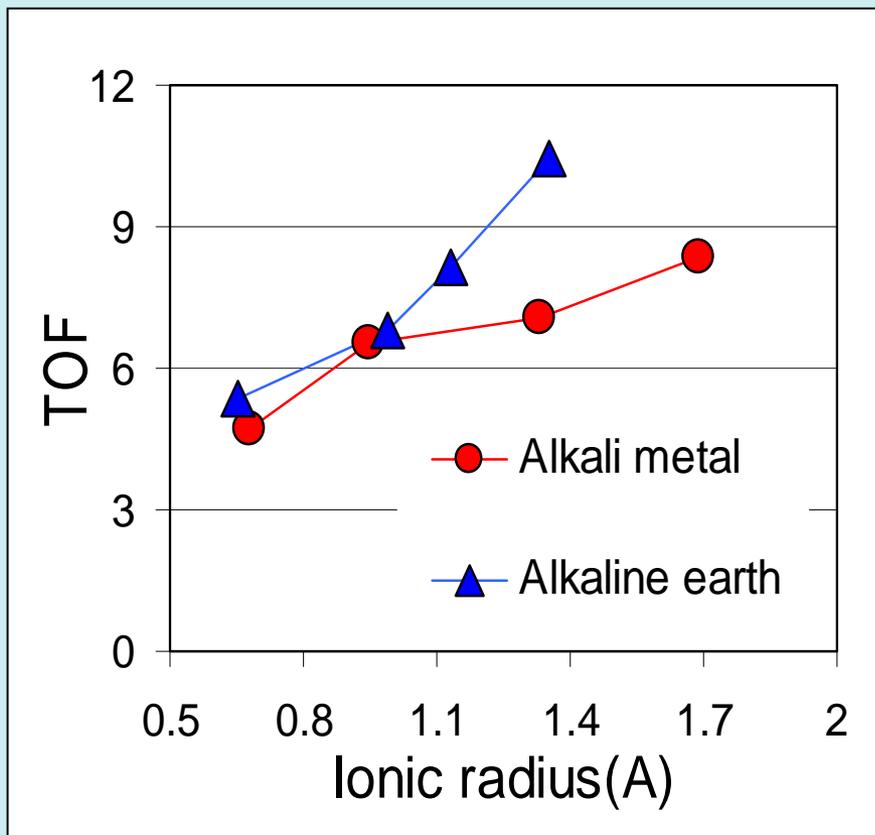
- Chemiluminescent NOx Analyzer

# Comparison of Alkali- and Alkaline Earth-Exchanged Na-Y



- Alkaline earth-exchanged catalysts are generally more active than alkali metal-Y materials.
- Ba-Y is most active and has high activity over a wide-temperature range.

# Alkali- and Alkaline Earth-Substituted Zeolite Y: Activity variation vs ionic radius



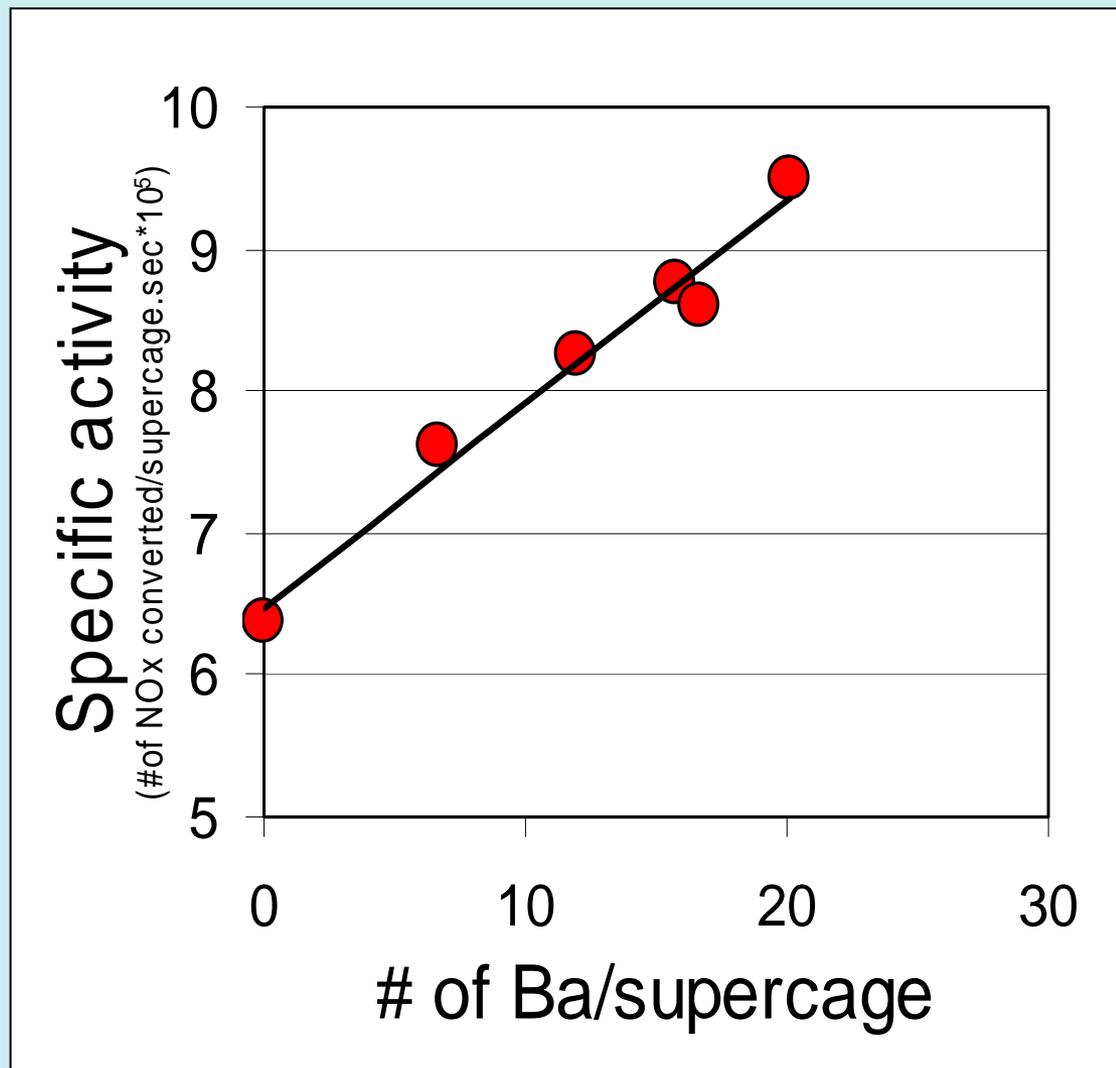
Ionic radius(Å)	
Li <sup>+</sup>	0.68
Na <sup>+</sup>	0.95
K <sup>+</sup>	1.33
Cs <sup>+</sup>	1.69
Mg <sup>2+</sup>	0.65
Ca <sup>2+</sup>	0.99
Sr <sup>2+</sup>	1.13
Ba <sup>2+</sup>	1.35

\* TOF = # of NO<sub>x</sub> converted/supercage•sec • 100000

\*\* Alkali and alkaline earth 2-2 base

# Activity is a monotonic function of Ba substitution for Na

Activity of  $Ba^{2+}$   
and  $Na^{+}$  sites is  
simply additive

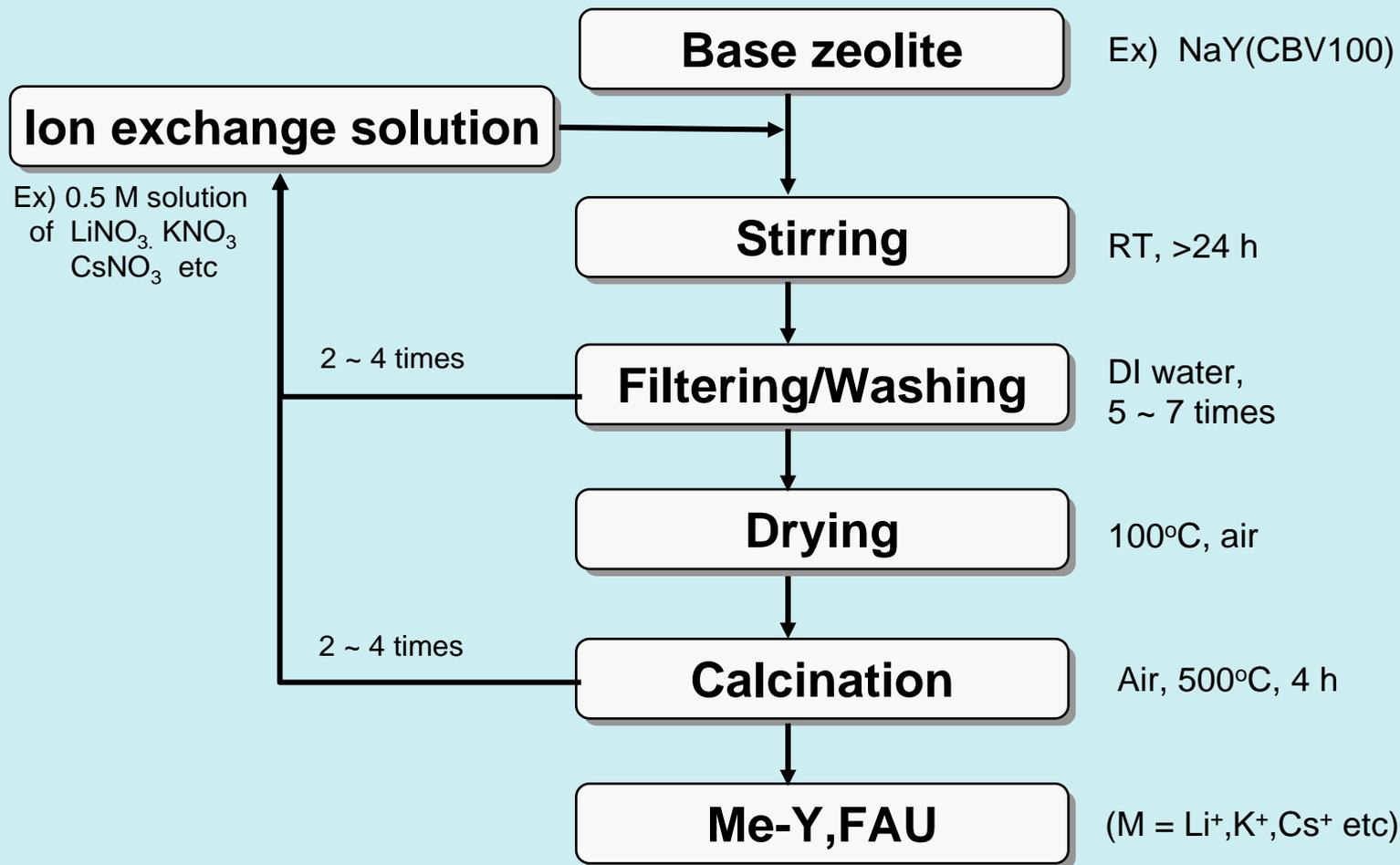


# Some optimization of catalyst synthesis:

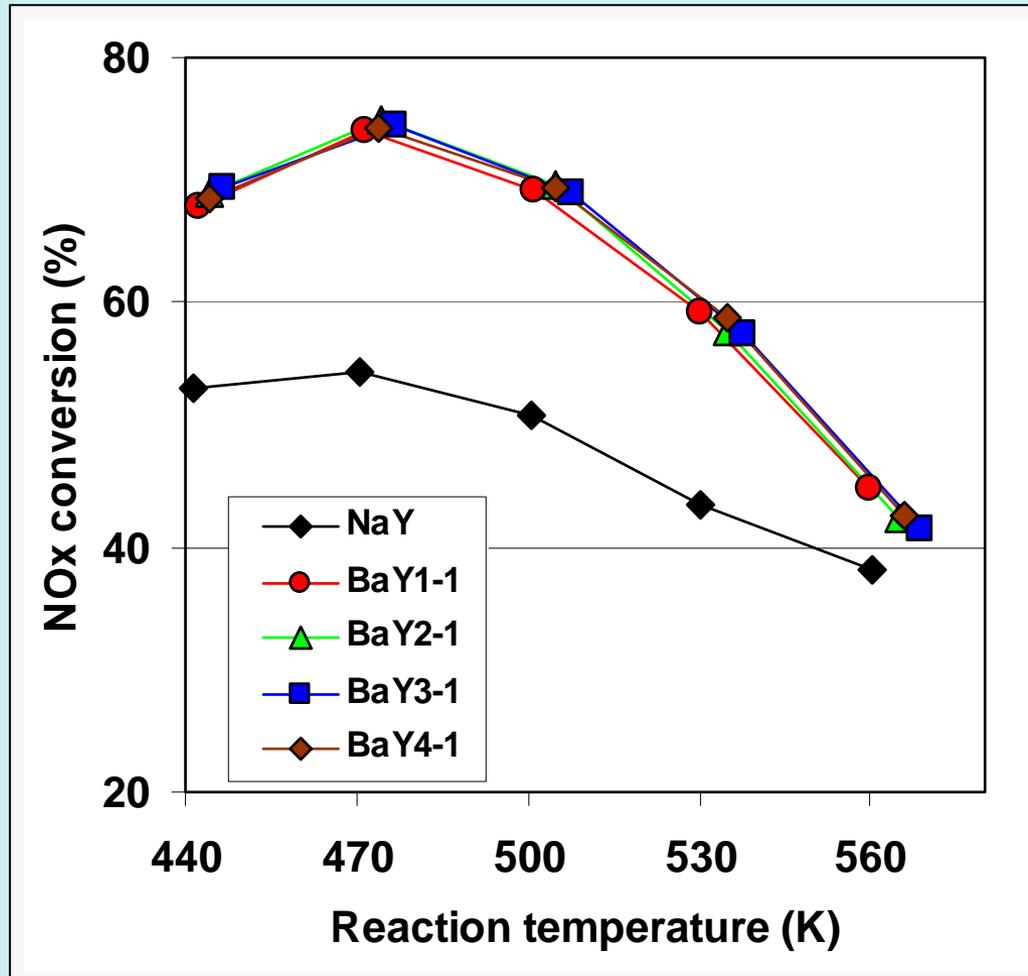
**The role of calcination and its effect on catalytic activity**

Kwak, Szanyi, and Peden – Journal of Catalysis (2003) in press.

# Catalyst Synthesis by Ion Exchange

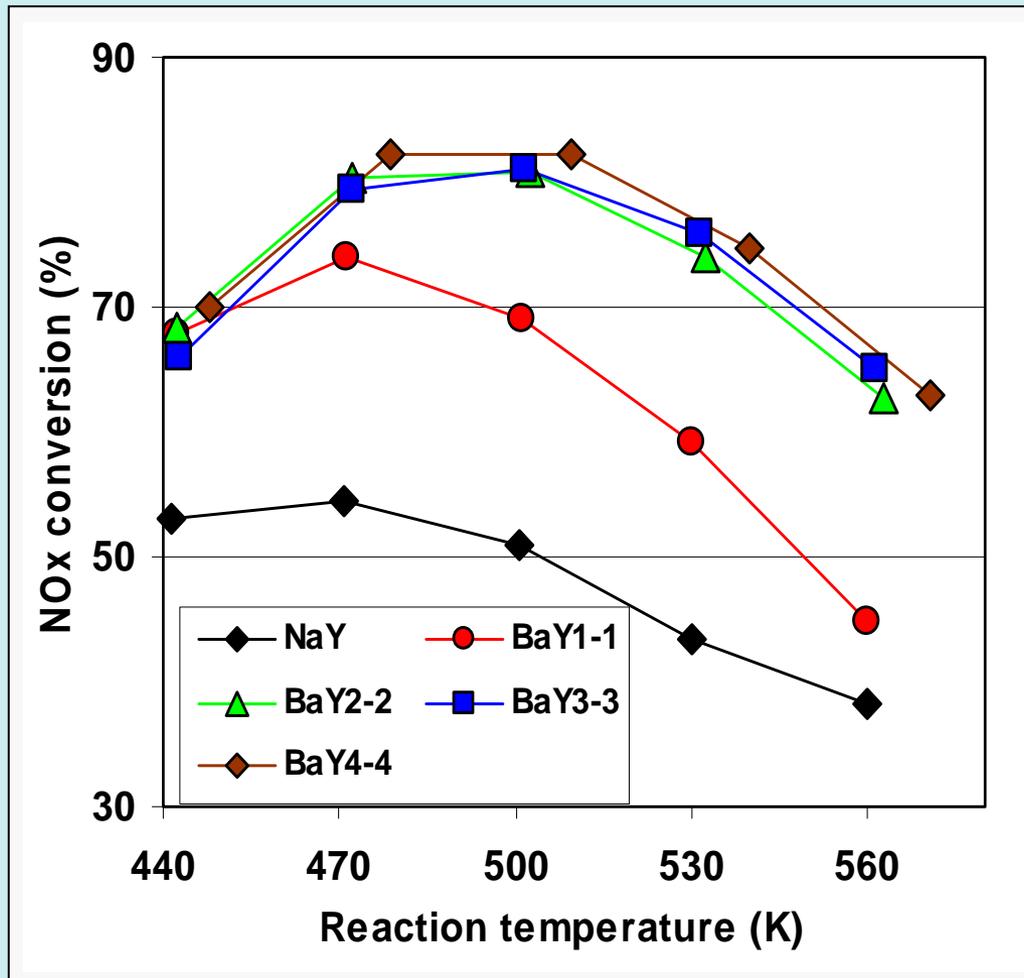


# Ba<sup>2+</sup> ion-exchange – no intermediate calcination



- Aqueous ion exchange solutions contained an excess of Ba<sup>+2</sup>.
- A single solution ion exchange was sufficient to 'saturate' the zeolite with Ba.

# Ba<sup>2+</sup> ion-exchange – calcined in air prior to additional exchange



- Again, the aqueous ion exchange solutions contained an excess of Ba<sup>2+</sup>.
- Each solution ion exchange was followed by a calcination step.
- Solid state cation exchange?

“Cation Migration in Zeolites: An *in Situ* Powder Diffraction and MAS NMR Study of the Structure of Zeolite Cs(Na)-Y during Dehydration”, Grey and coworkers, J. Phys. Chem. B **102** (1998) 839-856.

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For mechanistic insight,  
compare  $\text{NO}_2$   
conversion rather than  
 $\text{NO}$  conversion.

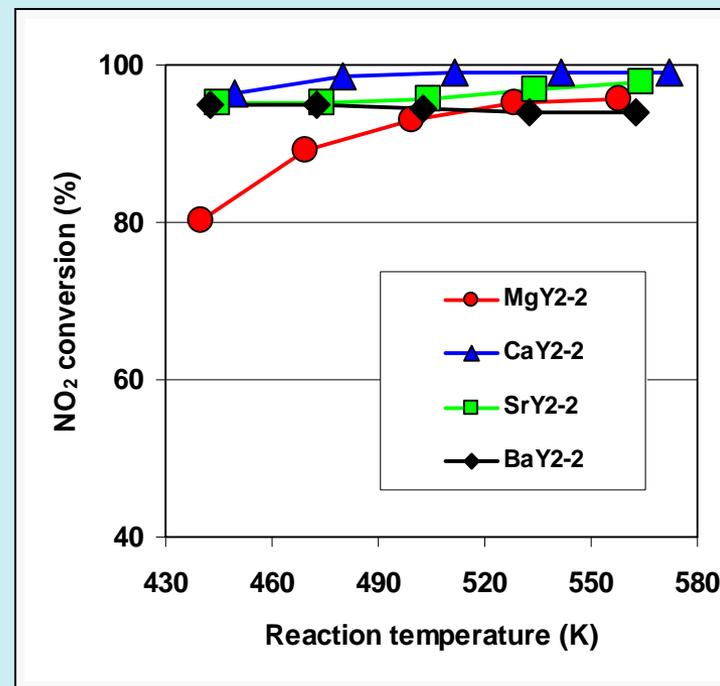
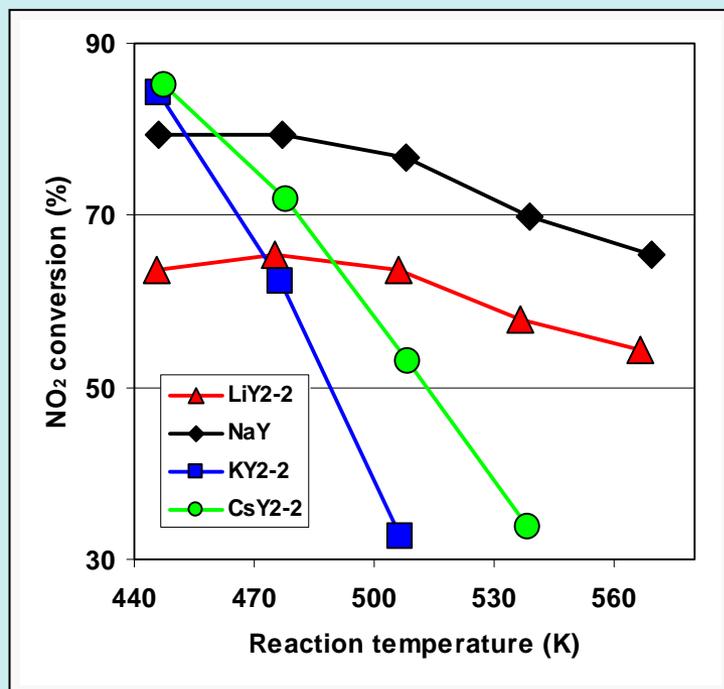
$\text{NO} \rightarrow \text{NO}_2$  (in the plasma)

$\text{NO}_2 \rightarrow \text{N}_2, \text{N}_2\text{O}, \text{HCN}, \text{etc.}$  (over the catalyst)

$\text{NO}_2 \rightarrow \text{NO}$  (over the catalyst – different site?)

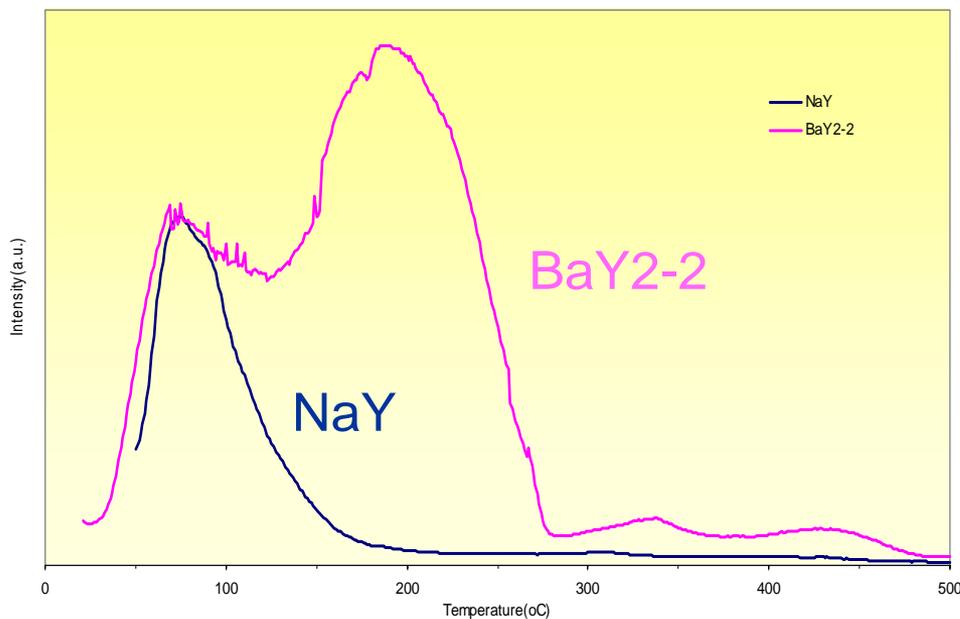
Tonkyn, Kwak, Szanyi, and Peden –  
in preparation

# Alkali- and Alkaline Earth-Exchanged Na-Y – NO<sub>2</sub> Conversion



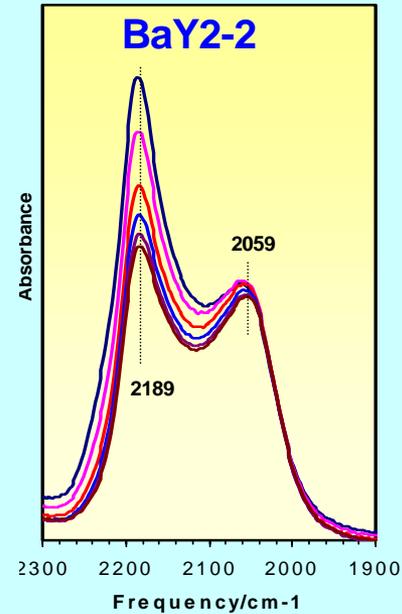
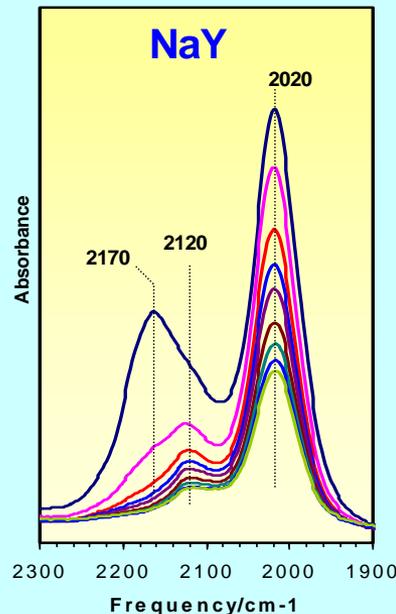
- While virtually all NO<sub>2</sub> is reacted over alkaline earth zeolite-Y, a considerable fraction does not react over alkali-Y catalysts.
- These differences suggest a significant difference in the reaction mechanism over these two classes of catalysts.

# FTIR and TPD indicate much weaker adsorption of NO<sub>2</sub> on NaY relative to BaY



NO<sub>2</sub> TPD of NaY and BaY2-2

\* Normalized based on the chemisorption amount

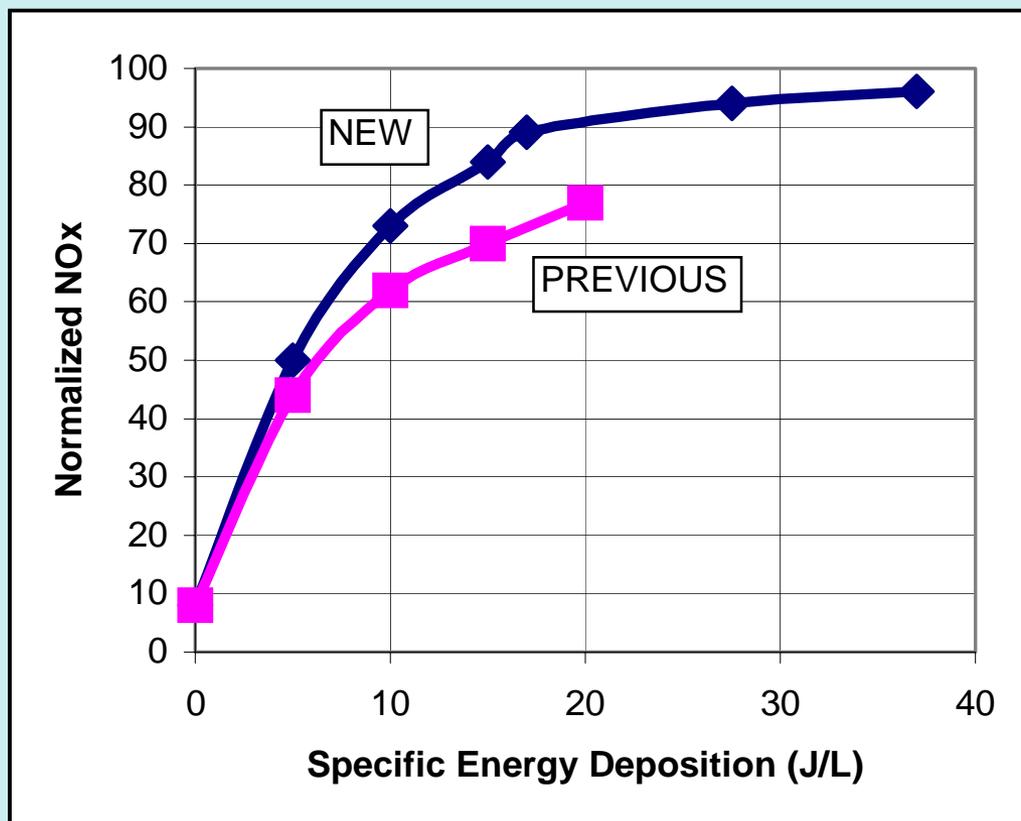


FTIR of NO<sub>2</sub> adsorbed on NaY and BaY2-2 during evacuation

# NOx Conversion Chemistry

- **Fate of Nitrogen:**
  - $\text{NO} \rightarrow \text{NO}_2 \rightarrow \text{N}_2 + \text{N}_2\text{O} + \text{HCN} + \text{NO}$
- **Fate of Carbon:**
  - $\text{C}_3\text{H}_6 \rightarrow \text{CH}_2\text{O} + \text{CH}_3\text{CHO} + \text{CO} + \text{CO}_2 + \text{CH}_3\text{OH} + \text{C}_3\text{H}_6$
- **After Treatment by Plasma and Catalyst:**
  - > 50% propene remains
  - NOx is mainly NO again

# New Multi-Step, "Cascade" System Design Achieves 90% NO<sub>x</sub> Conversion Target with NaY Catalyst!!



- Patent filed, 9/01.
- Modeling has provided insight into optimum system design for obtaining maximum NO<sub>x</sub> reduction concurrent with minimum fuel economy penalty.

R.G. Tonkyn and S.E. Barlow, SAE 2001-01-3510

S.E. Barlow, et al., SAE 2001-01-3509

# Summary and Conclusions

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- Y-zeolites and alumina are very active for plasma-facilitated NO<sub>x</sub> reduction in different temperature ranges. NO<sub>x</sub> conversion levels of greater than 90% are achievable.
- The plasma reactor performs NO oxidation to NO<sub>2</sub> with chemistry that is coupled to partial hydrocarbon oxidation.
- Aldehydes, produced in the plasma, are excellent reductants for the *thermal catalytic* reduction of NO<sub>x</sub> over zeolite Y-based catalysts.
- Ba-Y catalysts are the most active with the widest temperature “window”. Improved catalyst synthesis procedures have been developed.
- Mechanistic studies point to some clear differences for the alkali- and alkaline earth-zeolite Y catalysts, especially with respect to the strength of NO<sub>2</sub> adsorption.