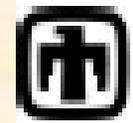




The University of New Mexico



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# Impact of SO<sub>2</sub> on Lean NO<sub>x</sub> Trap Catalysts

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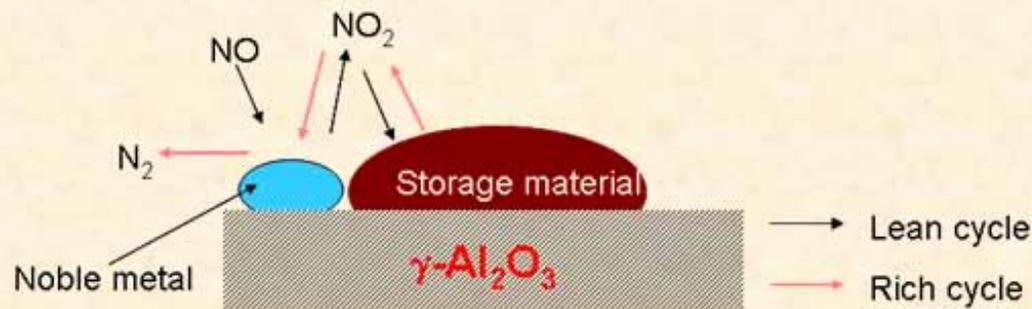
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# Introduction

- $\text{NO}_x$  Storage Reduction (NSR) reaction:
  - Simplified reaction mechanism
  - Lean cycle (oxidation):  $\text{NO} \longrightarrow \text{NO}_2$  (stored as nitrates)
  - Rich cycle (reduction): stored  $\text{NO}_x \longrightarrow \text{N}_2$  and  $\text{N}_2\text{O}$  (very low concentration)
- Lean  $\text{NO}_x$  trap catalyst:
  - Noble metal for oxidation and reduction
  - Alkaline oxide for  $\text{NO}_x$  storage.
- Limitations
  - Incomplete regeneration of the catalysts (during rich cycle).
  - Deactivation due to sulfur by sulfate formation.



# Objectives

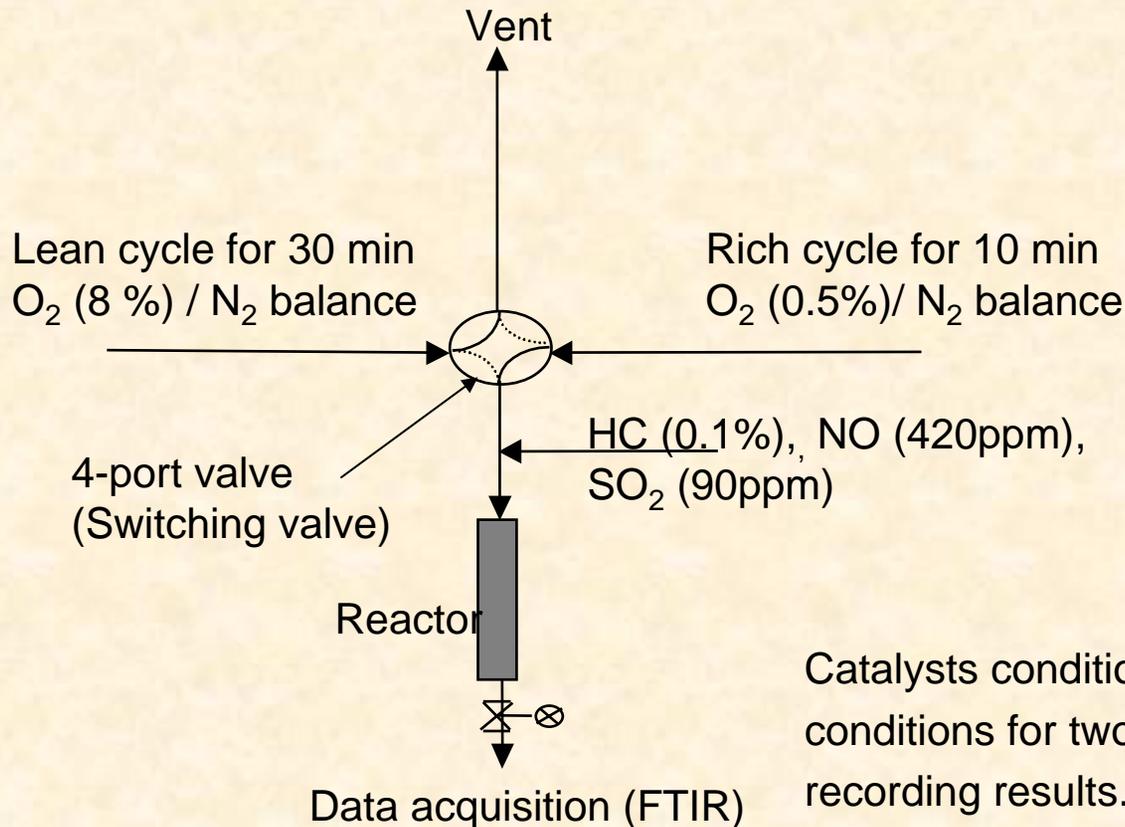
- Improve the sulfur tolerance of Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, the benchmark catalyst.
  - Investigate the impact copper addition has on the performance of Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.
    - Earlier studies showed that the addition of copper to Pt/hydrotalcite catalyst increased its tolerance for SO<sub>2</sub> (Ref. 1).
  - Understand the deactivation mechanism by SO<sub>2</sub> on the benchmark and the copper-modified catalysts.
- 
- [1] G. Centi et al. *Catalysis Today* 73 (2002) 287-296

# NSR Reaction Conditions

❖ Catalysts: 1% Pt-20% BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 1% Pt-2% Cu-20% BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

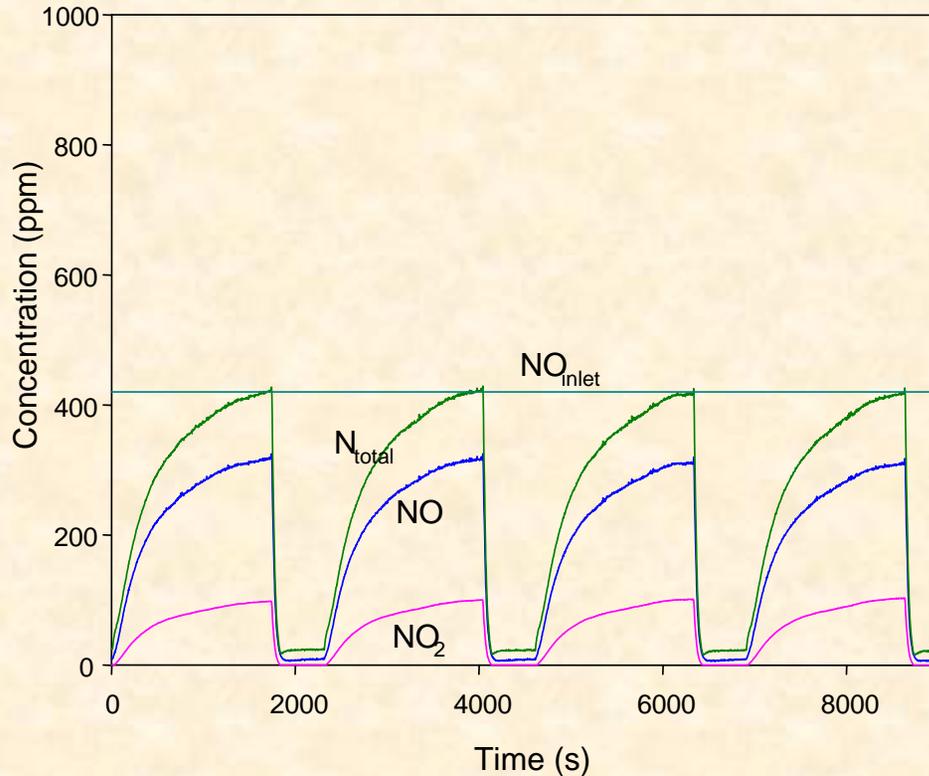
(incipient wetness impregnation). Calcination: 500°C for 4 hrs under static air.

❖ Reaction conditions: Temperature: 380°C, space velocity: 40000 hr<sup>-1</sup>

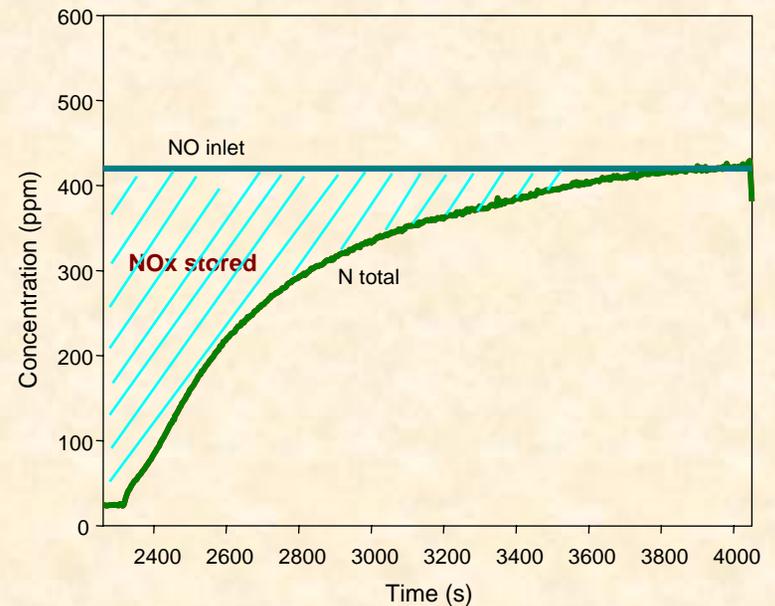


Catalysts conditioned under reaction conditions for two hours prior to recording results. Error on results:  $\pm 5\%$

# NSR Profile of Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>



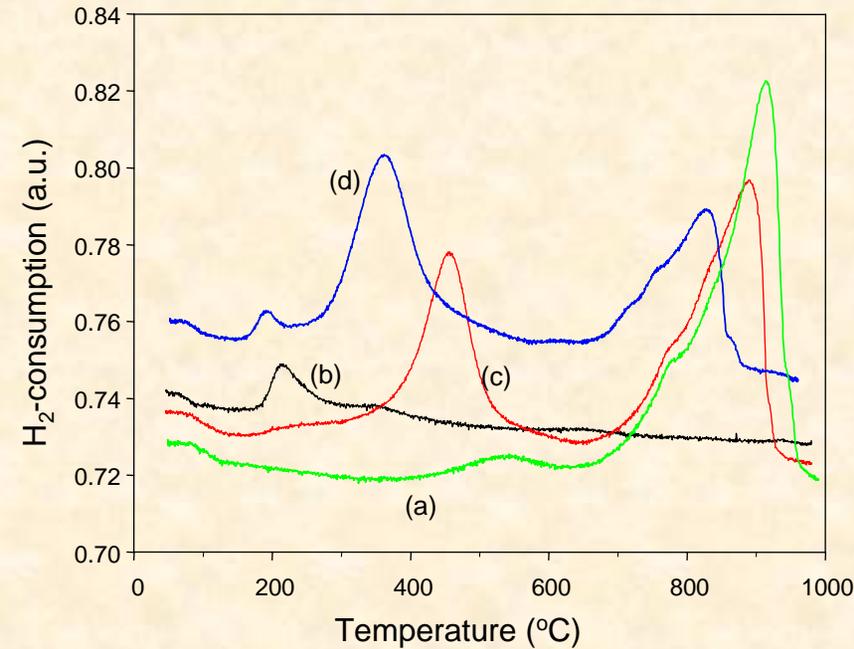
During lean cycle  
Amount of  $NO_x$  stored



During rich cycle

$$NO_x \text{ Conversion to } N_2 (\%) = 100 * (N_{inlet} - N_{total}) / N_{inlet}$$

# Evidence of Pt-BaO Interaction



Temperature Programmed Reduction (TPR) profiles of (a) BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (b) Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (c) Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and (d) (Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> + BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>)

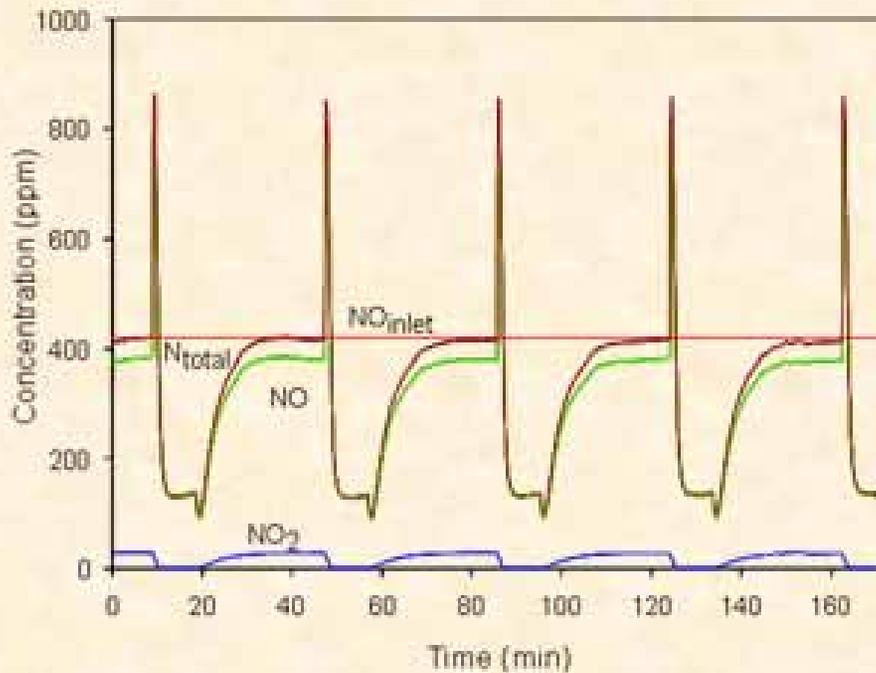
*Shift in Platinum reduction temperature with BaO addition is indicative of a strong interaction between Pt and BaO.*

Is this interaction important for Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to run as an NSR catalyst?

Catalyst	Amount of NO <sub>x</sub> adsorbed ( $\mu$ mol/gcat)
Pt-BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	107.7
Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> + BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	25.3

- (Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> + BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) is not a NO<sub>x</sub> storage catalyst- the amount of NO<sub>x</sub> stored is very low.
- Pt and BaO have to be in proximity to perform optimally in NSR reaction.

# NSR Profile of Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>



Amount of NO <sub>x</sub> adsorbed ( $\mu$ mol/gcat)	
Pt-BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Pt-Cu-BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>
107.7	69

NO <sub>x</sub> conversion (%)	
Pt-BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Pt-Cu-BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>
95	71

- A breakthrough in NO is present for Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, absent for Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.
- The performance of Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was higher than Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

# Impact of SO<sub>2</sub> on Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> & Pt-Cu-BaO/ $\gamma$ - Al<sub>2</sub>O<sub>3</sub>

Catalyst	Amount of NO <sub>x</sub> adsorbed ( $\mu$ mol/gcat) <sup>a</sup>		
	Standard reaction	40ppm SO <sub>2</sub> -12 hrs <sup>b</sup>	90ppm SO <sub>2</sub> -4 hrs <sup>b</sup>
Pt-BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	107.7	54	45
Pt-Cu-BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	69	56	53

a Experimental error =  $\pm 5$

b SO<sub>2</sub> added during lean and rich cycle

- Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has a higher resistance to SO<sub>2</sub> deactivation than Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.
- Sulfur concentration is an important factor.
- Lower concentration of SO<sub>2</sub> for longer time (more total sulfur exposure) deactivates the catalysts to a lesser degree.

# Is Sulfur Tolerance due Solely to Cu?

Catalysts	Amount of NO <sub>x</sub> adsorbed (μmol/gcat)		Loss in the storage capacity (%) <sup>b</sup>	Conversion (%)	
	Standard reaction	SO <sub>2</sub> <sup>a</sup> 90ppm-4hrs		Standard reaction	SO <sub>2</sub> <sup>a</sup> 90ppm-4hrs
Pt-BaO/γ-Al <sub>2</sub> O <sub>3</sub>	107.7	45	58	91	40
Pt-Cu-BaO/ γ-Al <sub>2</sub> O <sub>3</sub>	69	53	23	71	30
Cu-BaO/γ-Al <sub>2</sub> O <sub>3</sub>	68	38	44	20	11

Hypothesis: On Pt-Cu-BaO/γ-Al<sub>2</sub>O<sub>3</sub>

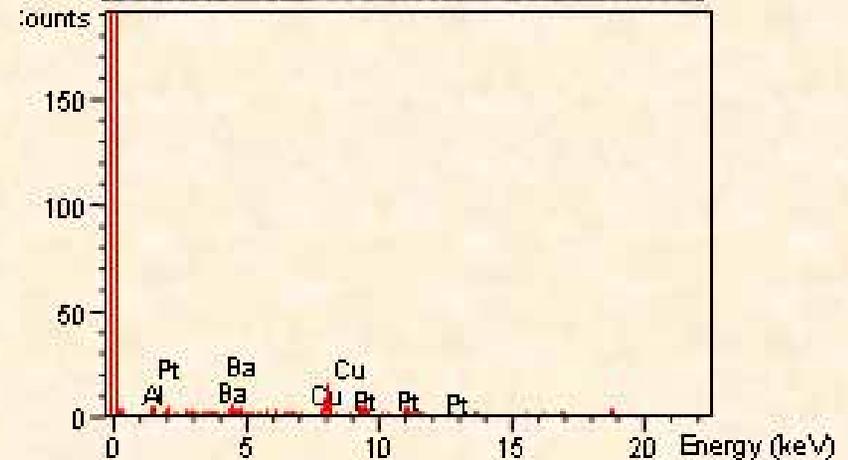
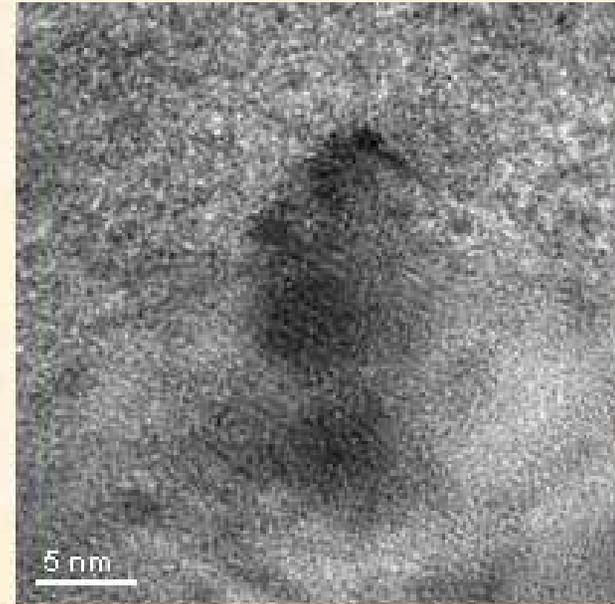
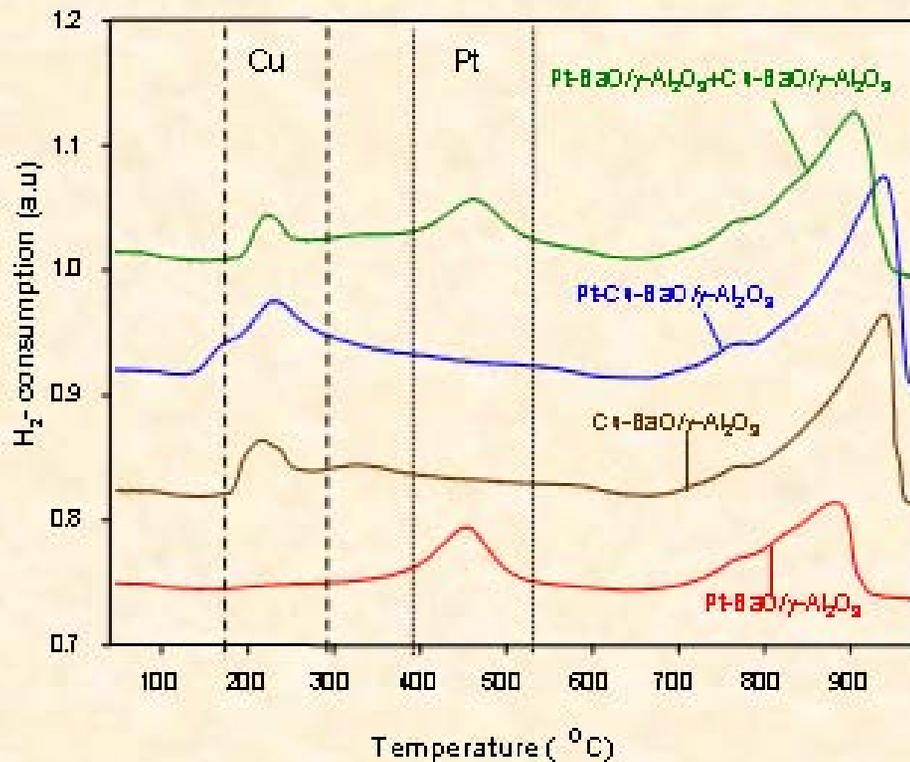
NO → NO<sub>2</sub> → BaNO<sub>3</sub> low oxidation rate

SO<sub>2</sub> → SO<sub>3</sub> → BaSO<sub>4</sub> low oxidation rate

*Not the case with Cu-BaO/γ-Al<sub>2</sub>O<sub>3</sub>*

The low deactivation rate of Pt-Cu-BaO/γ-Al<sub>2</sub>O<sub>3</sub> is the result of both Pt and Cu.

# Evidence of Pt-Cu Interaction



TPR and TEM results on Pt-Cu-BaO/γ-Al<sub>2</sub>O<sub>3</sub> suggest the presence of a Pt-Cu bimetallic phase.

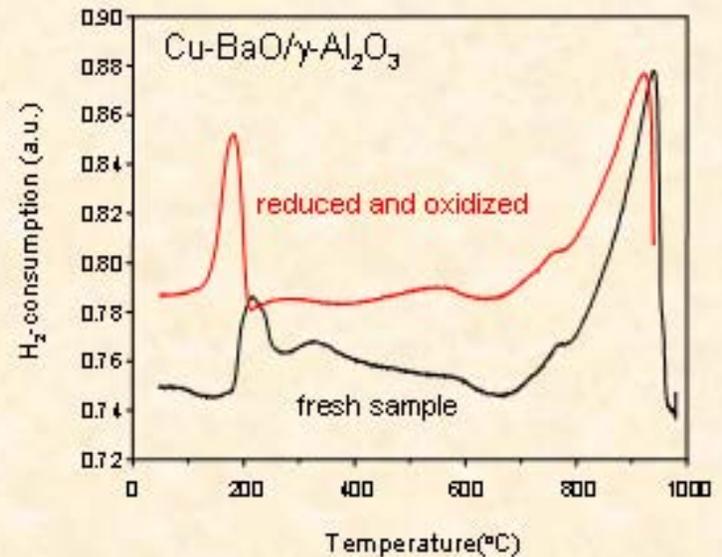
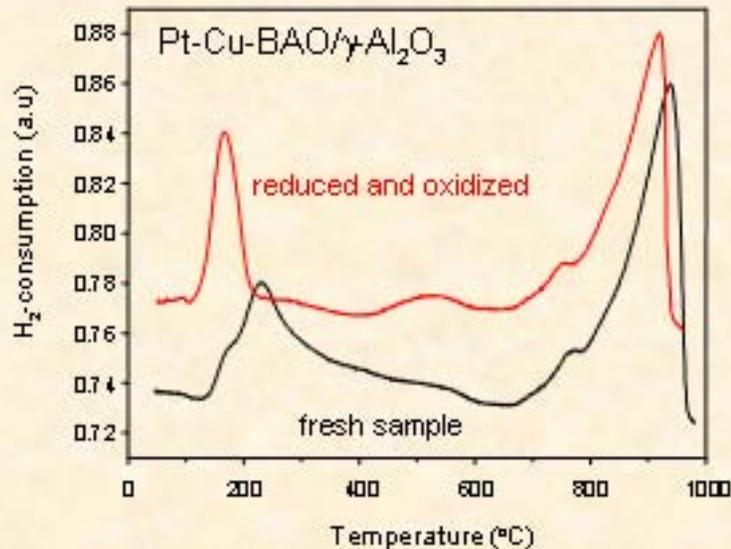
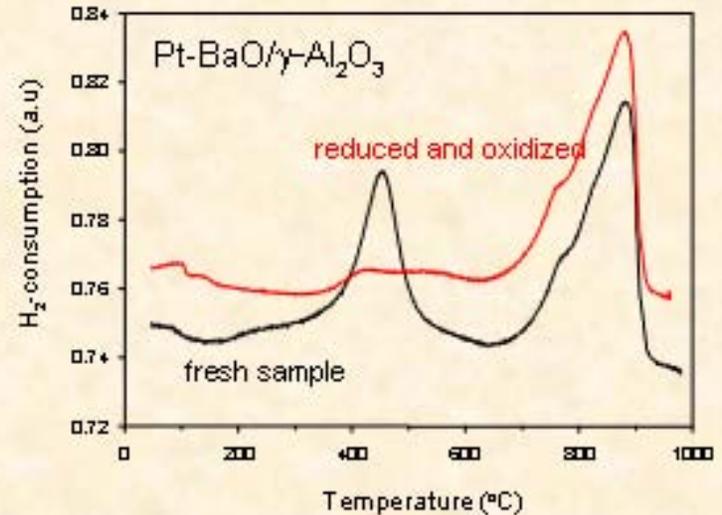
More Active Sites on Reduced Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.  
Effect of Reduction on Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>?

Reaction conditions	Amount of NO <sub>x</sub> adsorbed (μmol/gcat)		NO <sub>x</sub> conversion (%)	
	Pt-BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Pt-Cu-BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Pt-BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Pt-Cu-BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>
Standard reaction	107.7	69	91	71
SO <sub>2</sub> (90ppm-4hrs)	45	53	40	30
H <sub>2</sub> -pretreatment	116	62	92	45
H <sub>2</sub> -pretreatment SO <sub>2</sub> (90ppm-4hrs)	61	38.7	38	29
	Standard reaction	SO <sub>2</sub> 90ppm- 4hrs	Standard reaction	SO <sub>2</sub> 90ppm- 4hrs
Cu-BaO/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	68	38	20	11

- H<sub>2</sub>-pretreatment affects positively Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and negatively Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.
- The storage capacities of reduced Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and of Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were similar in both the presence and the absence of SO<sub>2</sub>.

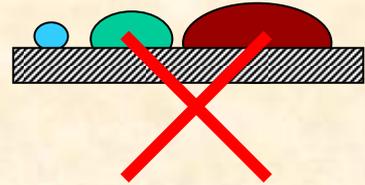
## Effect of H<sub>2</sub>-Pretreatment: TPR of Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

- Pt remained in a reduced state after re-oxidation of reduced Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.
- H<sub>2</sub>-pretreatment of Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> seems to remove the bimetallic phase.

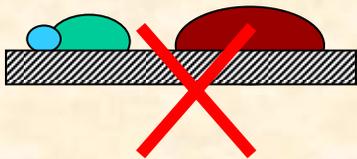


# How was Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> affected by H<sub>2</sub>?

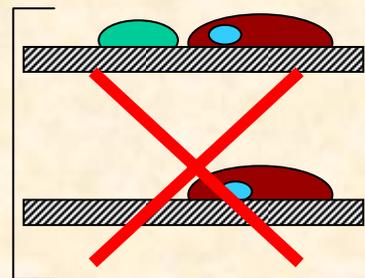
## Possible Cases:



NSR and Chemisorption results would be similar to Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>



NSR results would be similar to Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

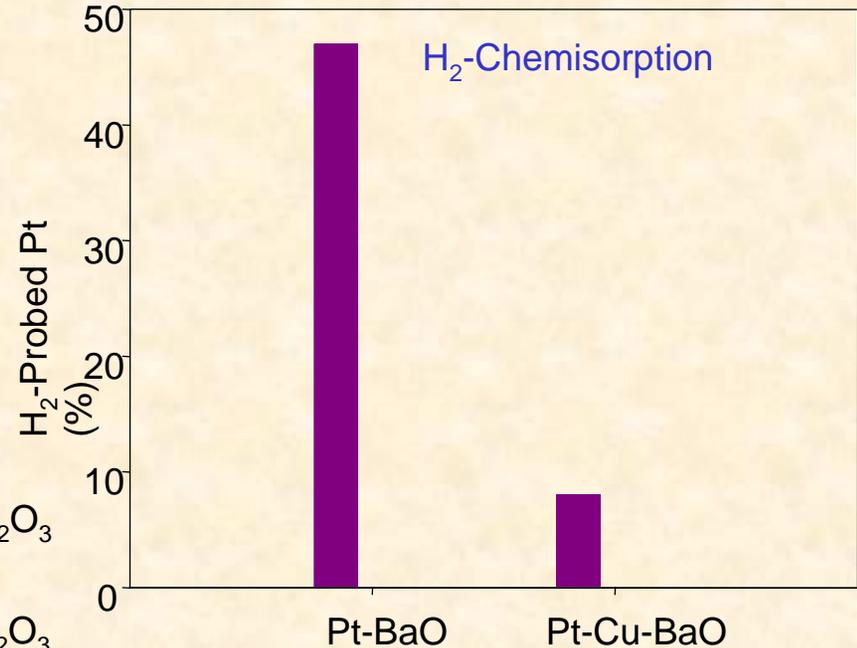
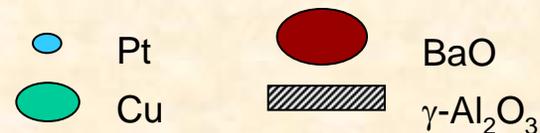


NSR results similar to Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

NSR results of reduced Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> better than the non-reduced.  
Pt can be probed during chemisorption



NSR results similar to Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>



# Summary

- Addition of Cu to the benchmark catalyst:
  - Decreases the NO<sub>x</sub>-storage capacity (no SO<sub>2</sub> exposure).
  - Increases the sulfur tolerance.
- There is evidence of a bimetallic Pt-Cu phase which may influence oxidation of SO<sub>2</sub> to SO<sub>3</sub>.
- H<sub>2</sub>-pretreatment:
  - Reduced Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is more active
  - Reduced Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> behaves like Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>
  - Surface enrichment of Cu relative to Pt
- In situ FTIR and TEOM experiments underway to elucidate the adsorption mode of NO/SO<sub>2</sub> on Pt-Cu-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and on Pt-BaO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.