

# DRIFTS Investigation of LNT Regeneration

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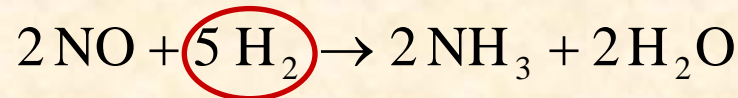
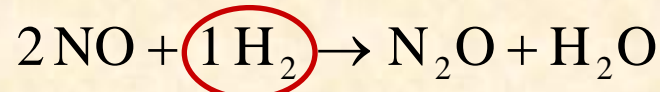
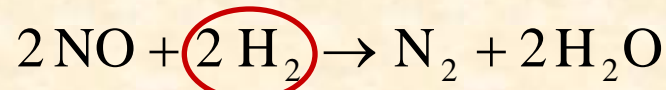
**10<sup>th</sup> CLEERS Workshop**

**Dearborn, Michigan**

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# Motivation

- Formation of  $\text{NH}_3$  and  $\text{N}_2\text{O}$  creates problems during conventional lean  $\text{NO}_x$  trap (LNT) operation:
  - Trading one pollutant ( $\text{NO}_x$ ) for another
    - $\text{N}_2\text{O}$ : potent greenhouse gas
    - $\text{NH}_3$ : toxic, corrosive, can be oxidized back to  $\text{NO}_x$
  - Reduction stoichiometry depends on product:



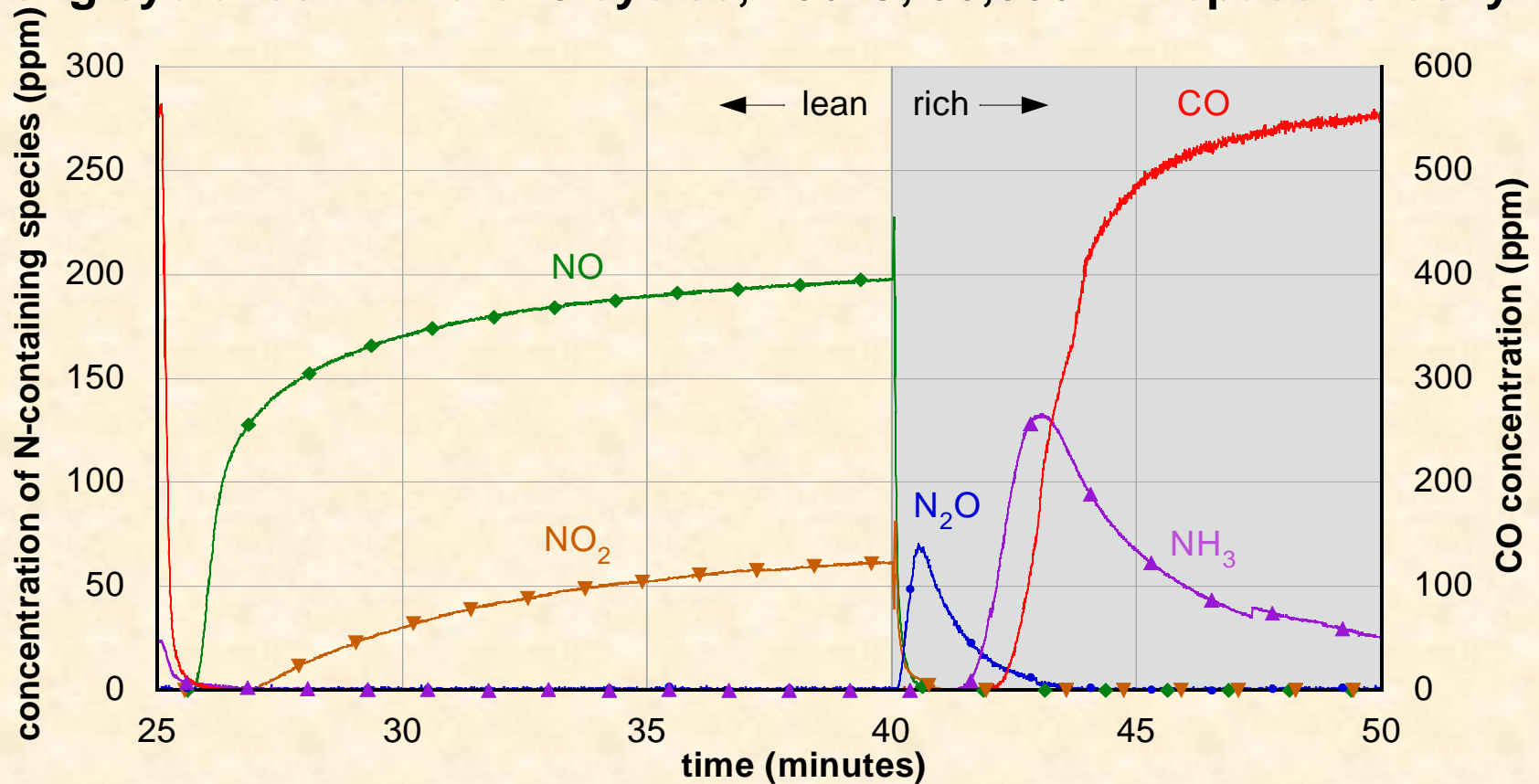
- $\text{N}_2\text{O}$  : reductant slip (CO and HC emissions)
  - $\text{NH}_3$  : incomplete regeneration or increased fuel penalty
- Optimization of  $\text{NH}_3$  formation essential for multi-component systems such as LNT-SCR

## Prior Work

- Performed bench scale flow reactor experiments on Umicore GDI LNT monolith core sample (9<sup>th</sup> CLEERS Workshop, SAE 2006-01-3441)
  - Short and long storage/reduction cycles (based on early version of CLEERS LNT focus group test protocol)
  - Steady flow temperature sweeps
    - Simultaneous flow of reactants (**not** switching)
    - Ramped from  $<100^{\circ}\text{C}$  to  $500^{\circ}\text{C}$  at  $5^{\circ}\text{C}/\text{min}$  under reactant flow
    - NO<sub>x</sub>/reductants: NO/H<sub>2</sub>, NO/CO, NO<sub>2</sub>/H<sub>2</sub>, NO<sub>2</sub>/CO
    - Secondary reactants: NH<sub>3</sub>/O<sub>2</sub>, NH<sub>3</sub>/NO, NH<sub>3</sub>, N<sub>2</sub>O/CO, N<sub>2</sub>O/H<sub>2</sub>
- Larson & Chakravarthy developed a detailed microkinetic LNT regeneration mechanism based on the steady flow experiments (stay tuned for the next talk)

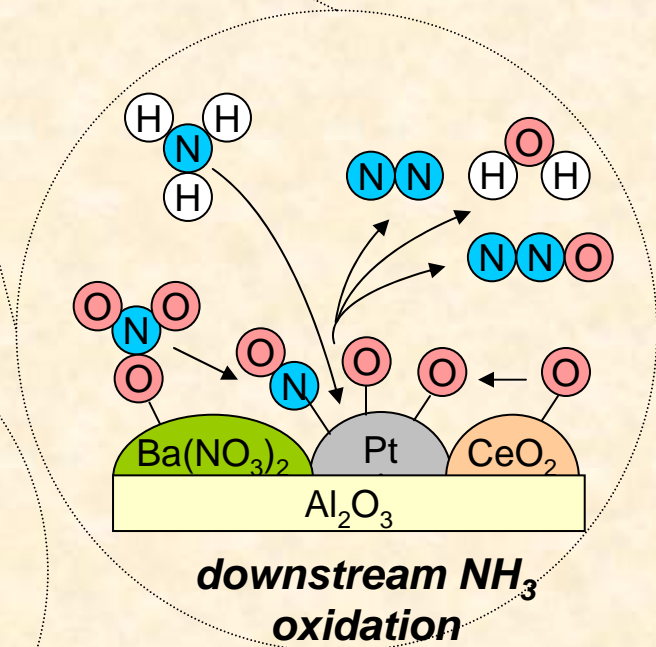
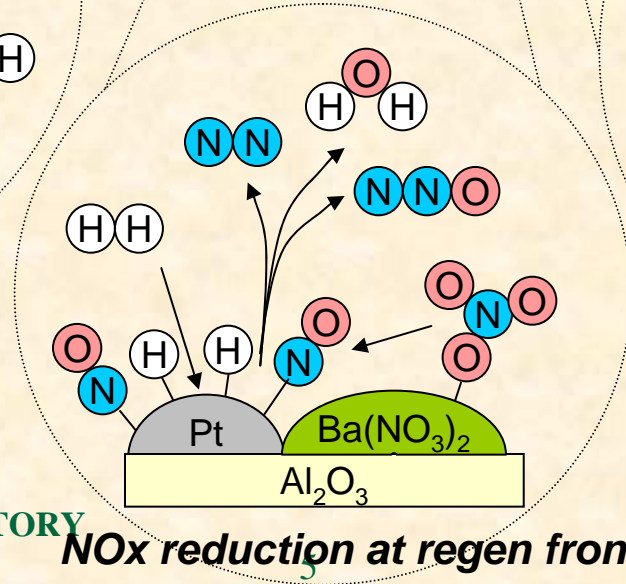
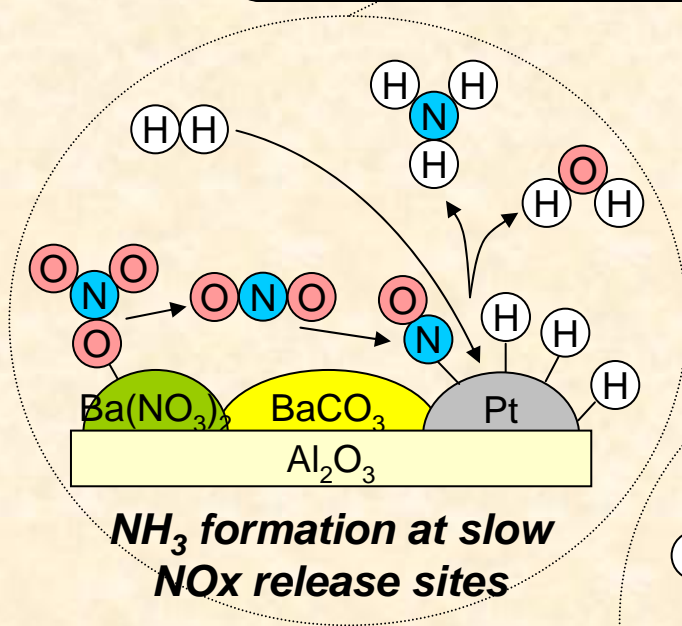
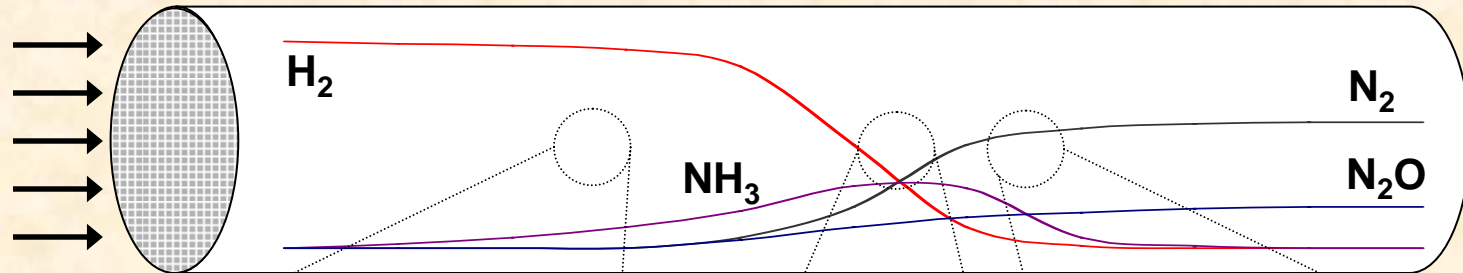
# Long storage/reduction cycles illustrate complicated product concentration profiles

Long cycle test – 2nd of 3 cycles, 200°C, 30,000 hr<sup>-1</sup> space velocity



# Proposed regeneration processes

“snapshot” of expected gas concentration profile inside monolith

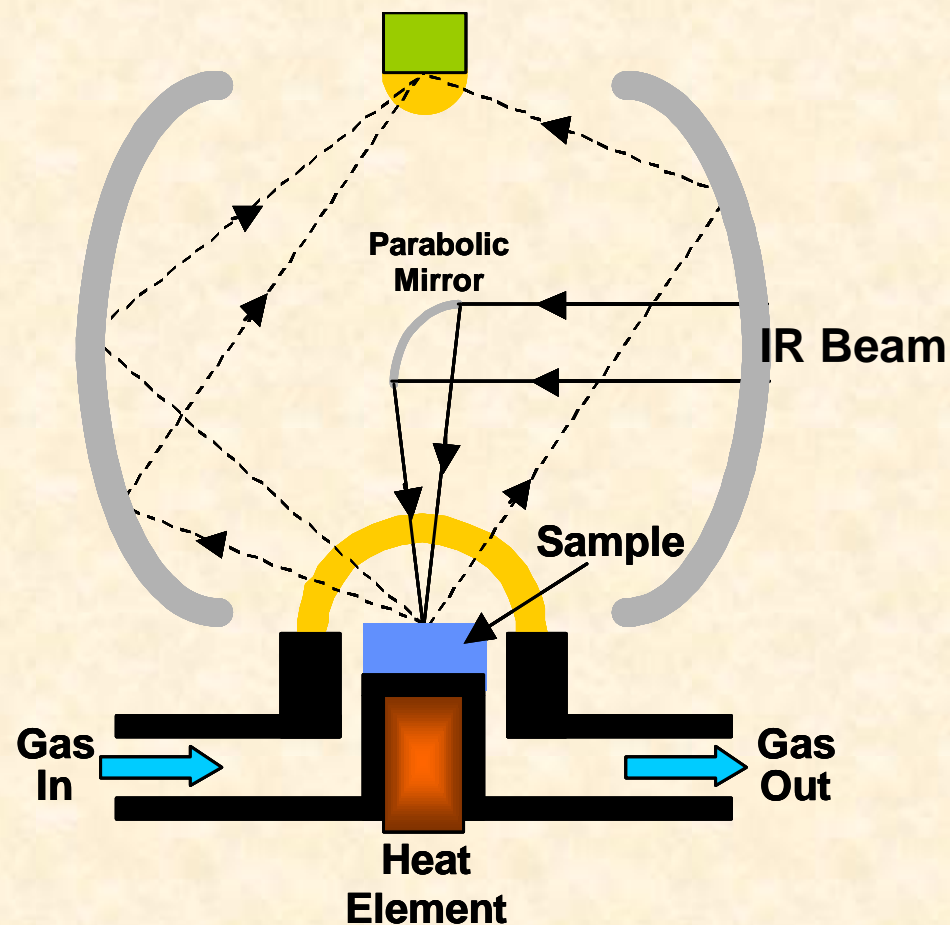


# Current Objectives

- Identify reaction intermediates involved in regeneration process
- Validate regeneration mechanism where possible
- Topics for investigation:
  1. Reduction of NO by CO
  2. NO<sub>x</sub> storage/reduction cycles
  3. Impact of sulfation on regeneration
  4. NH<sub>3</sub> oxidation

# Approach

- *In situ* DRIFTS measurements
  - Catalyst T up to  $\sim 550^{\circ}\text{C}$
  - Heated lines for  $>5\%$   $\text{H}_2\text{O}$
  - capable of (slow) lean/rich cycling
- MIDAC FTIR spectrometer
  - 2 Hz scan rate;  $2\text{ cm}^{-1}$  resolution
- Harrick Barrel Ellipse DRIFT
- Umicore GDI LNT catalyst (CLEERS reference material)
  - NO<sub>x</sub> storage: Ba
  - Oxygen storage:  $\text{CeO}_2$
  - Precious metals: Pt, Rh, Pd
- Cut single wall from degreened monolith



# Reduction of NO by CO



# Overview for reduction of NO by CO

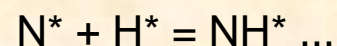
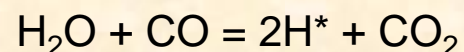
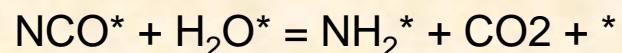
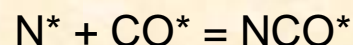
- **Observations from bench experiments:**

- Reduction product selectivity driven by NO<sub>x</sub>/reductant ratio
  - stoichiometric for N<sub>2</sub>: primarily N<sub>2</sub>
  - excess reductant: mostly NH<sub>3</sub>

- **Key questions:**

- Can we determine pathway for NH<sub>3</sub> formation from NO + CO?
- Is mechanism consistent with observable intermediates?

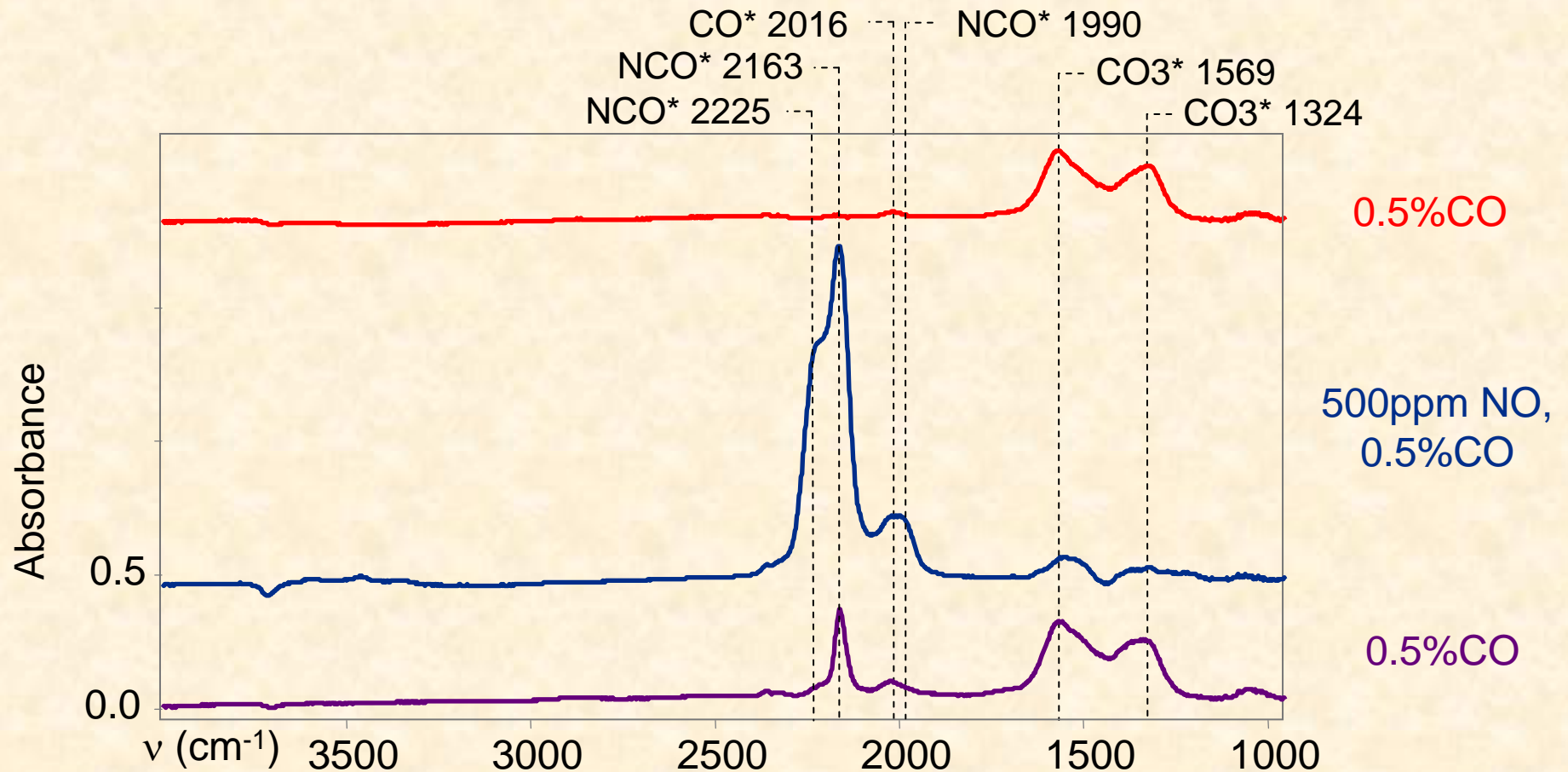
- **Relevant reactions from mechanism:**



- **DRIFTS experiments:**

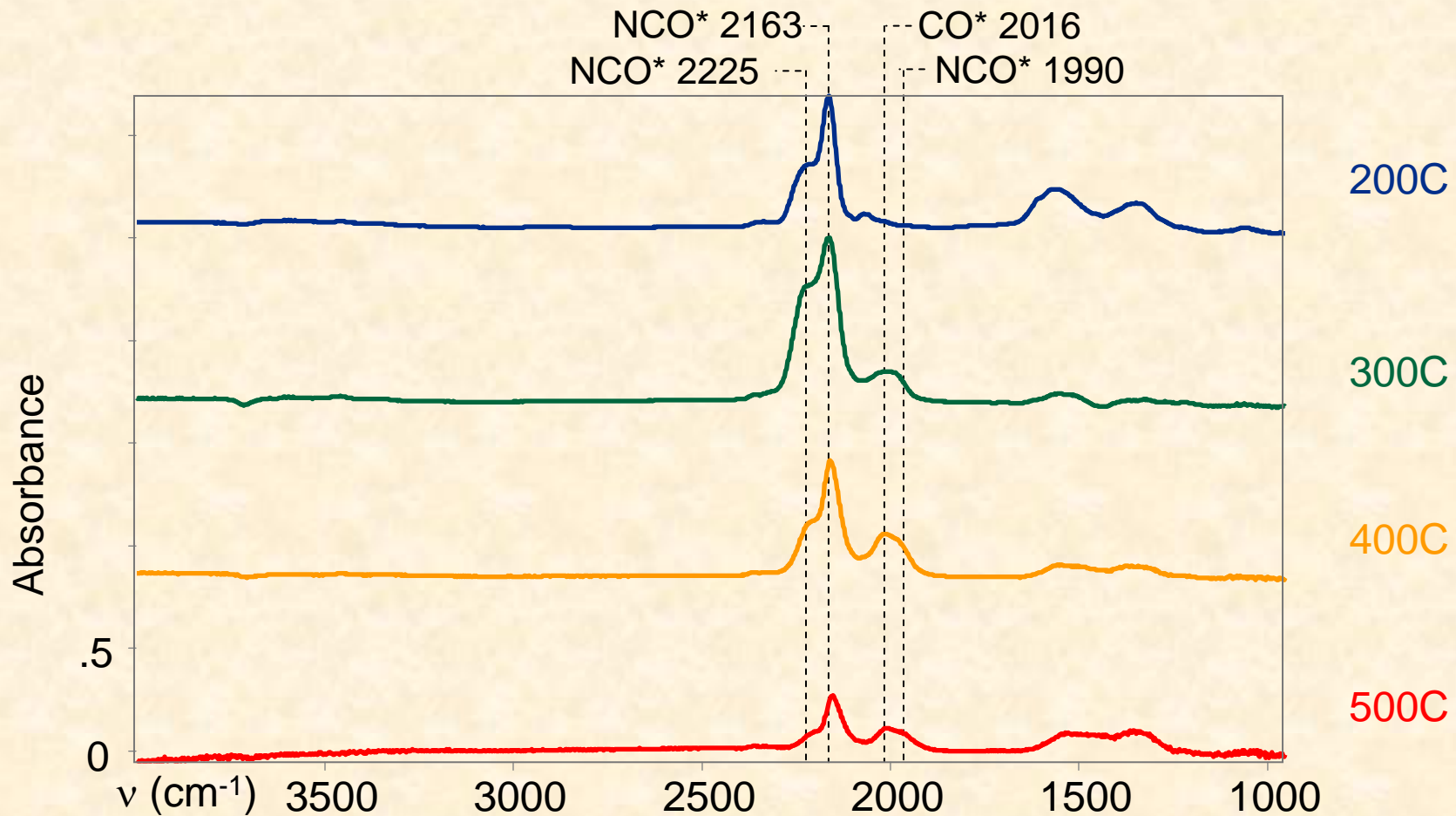
1. Reduced 500°C, cooled to experiment temperature under 0.5%H<sub>2</sub>
2. Sequentially exposed to reactant flows:
  - 0.5%CO, then 0.5%CO/500ppmNO, back to 0.5%CO
  - repeated with 5%H<sub>2</sub>O (subtracted clean H<sub>2</sub>O spectra)
3. Repeated at 200, 300, 400, 500°C

# NO+CO form considerable isocyanate at 300°C



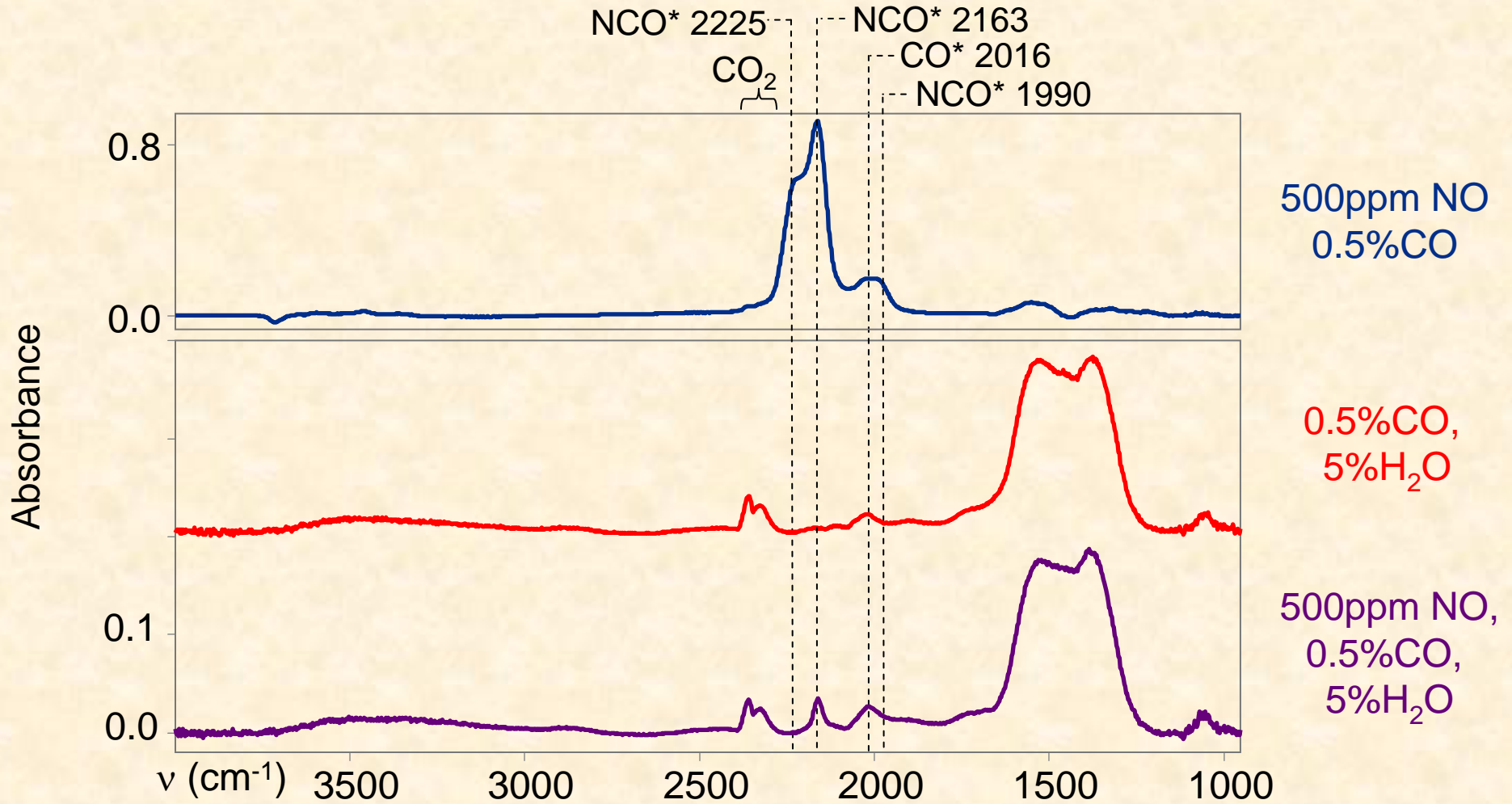
- Peaks at 2225 and 1990 cm<sup>-1</sup> correlate with loss and recovery of carbonate peaks at 1324 and 1569 cm<sup>-1</sup>; likely associated with NCO on oxides (CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) or storage material (Ba)

# NCO observed in all dry experiments



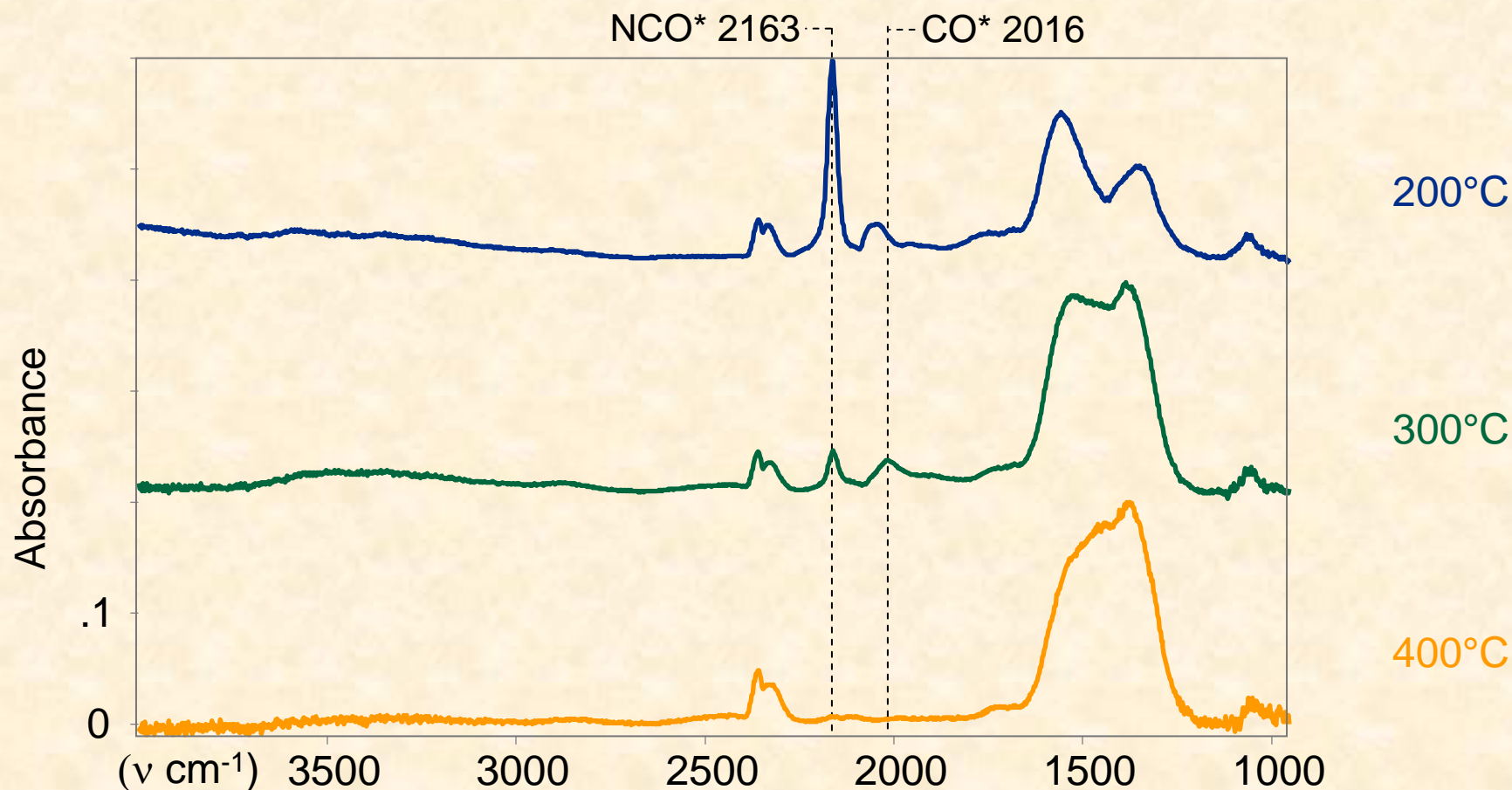
- NCO peaks increase from 200 to 300°C, then drop off with increasing temperature

# Water hydrolyzes NCO at 300°C



- Peak at 2163 much smaller; peaks at 2225 and 1990  $\text{cm}^{-1}$  (on oxides/storage material?) not visible

With H<sub>2</sub>O present, NCO decreases rapidly with increasing temperature



- Large drop in NCO from 200-300°C correlates with NH<sub>3</sub> formation increase from steady flow bench experiments

# NO<sub>x</sub> storage/reduction cycles

# Overview for NO<sub>x</sub> storage/reduction cycles

- **Key question:**

- Are the intermediates observed during steady state experiments relevant to cyclic operation?

- **DRIFTS experiments:**

1. Reduced 500°C, cooled to experiment temperature under 0.5% H<sub>2</sub>
2. Performed three cycle experiments (FTIR scan every 6 sec)

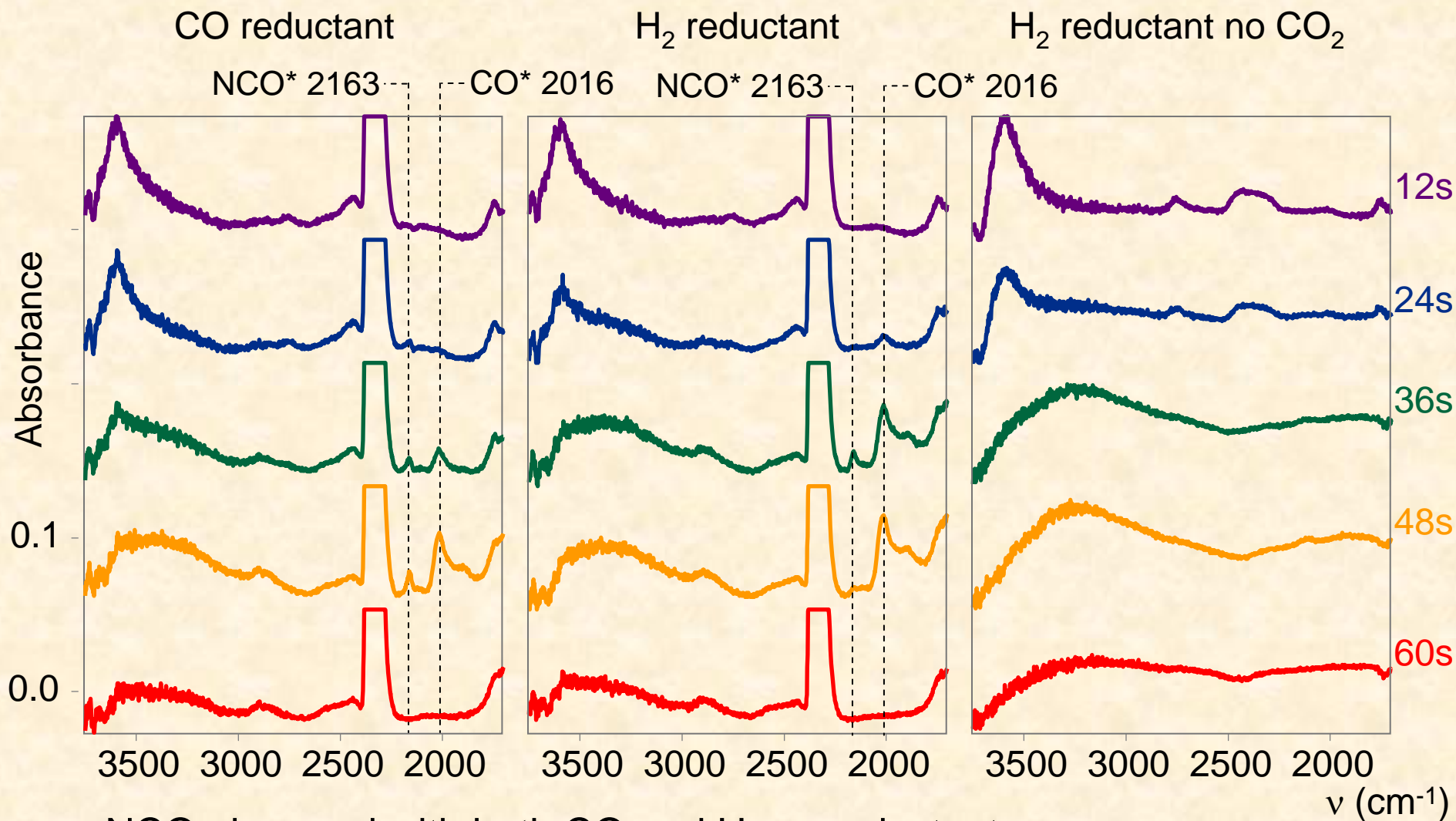
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H <sub>2</sub> (no CO <sub>2</sub> )	Lean	390 s	300ppmNO/10%O <sub>2</sub> /5%H <sub>2</sub> O
	Rich	60 s	0.9%H <sub>2</sub> /5%H <sub>2</sub> O
H <sub>2</sub>	Lean	390 s	300ppmNO/10%O <sub>2</sub> /5%CO <sub>2</sub> /5%H <sub>2</sub> O
	Rich	60 s	0.9%H <sub>2</sub> /5%CO <sub>2</sub> /5%H <sub>2</sub> O
CO	Lean	360 s	300ppmNO/10%O <sub>2</sub> /5%CO <sub>2</sub> /5%H <sub>2</sub> O
	Rich	60 s	0.9%CO/5%CO <sub>2</sub> /5%H <sub>2</sub> O

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3. Repeated at 200, 300, 400°C

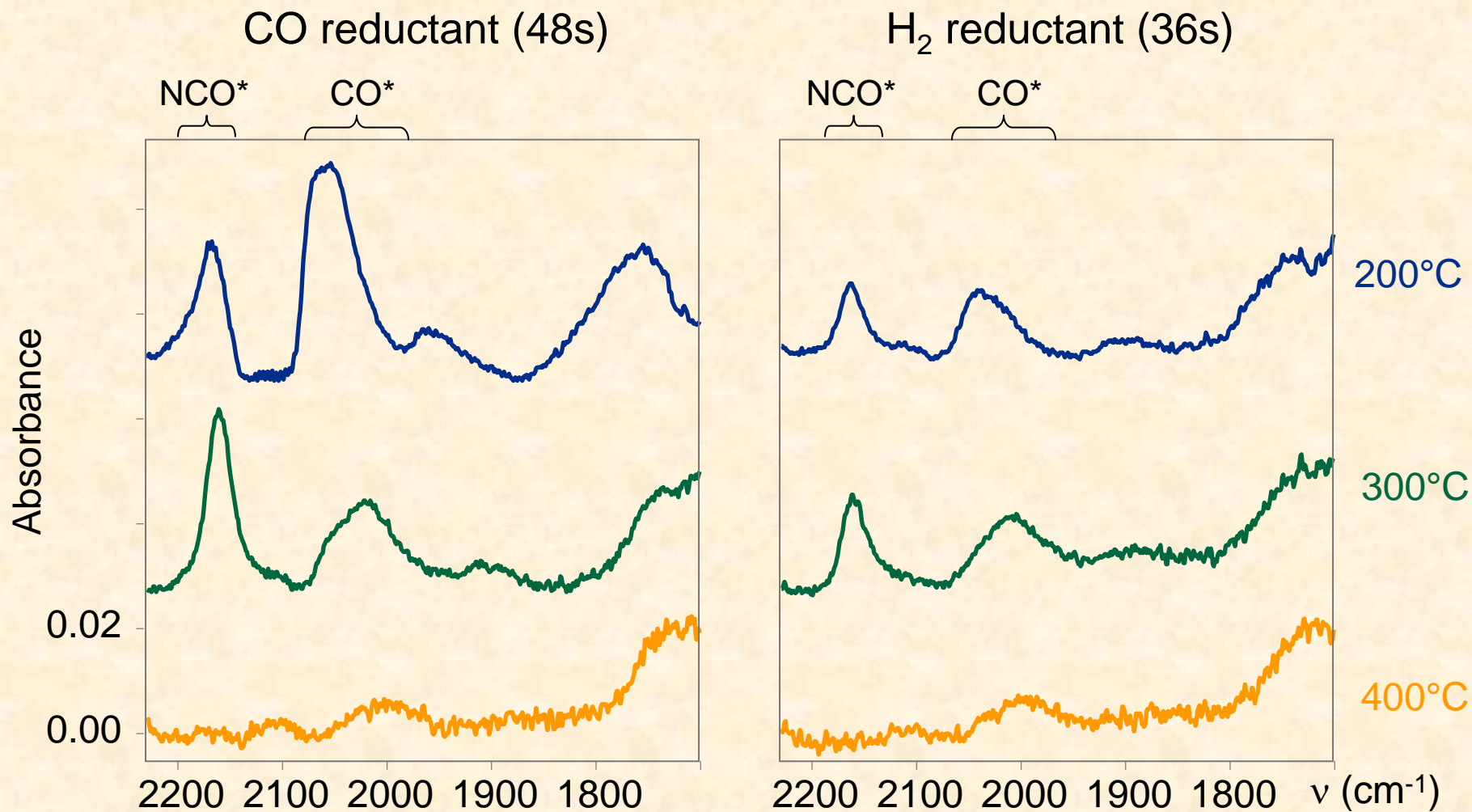
# NCO observed during 300°C cycle experiments



- NCO observed with both CO and H<sub>2</sub> as reductant



# NCO observed during cycles at 200 & 300°C

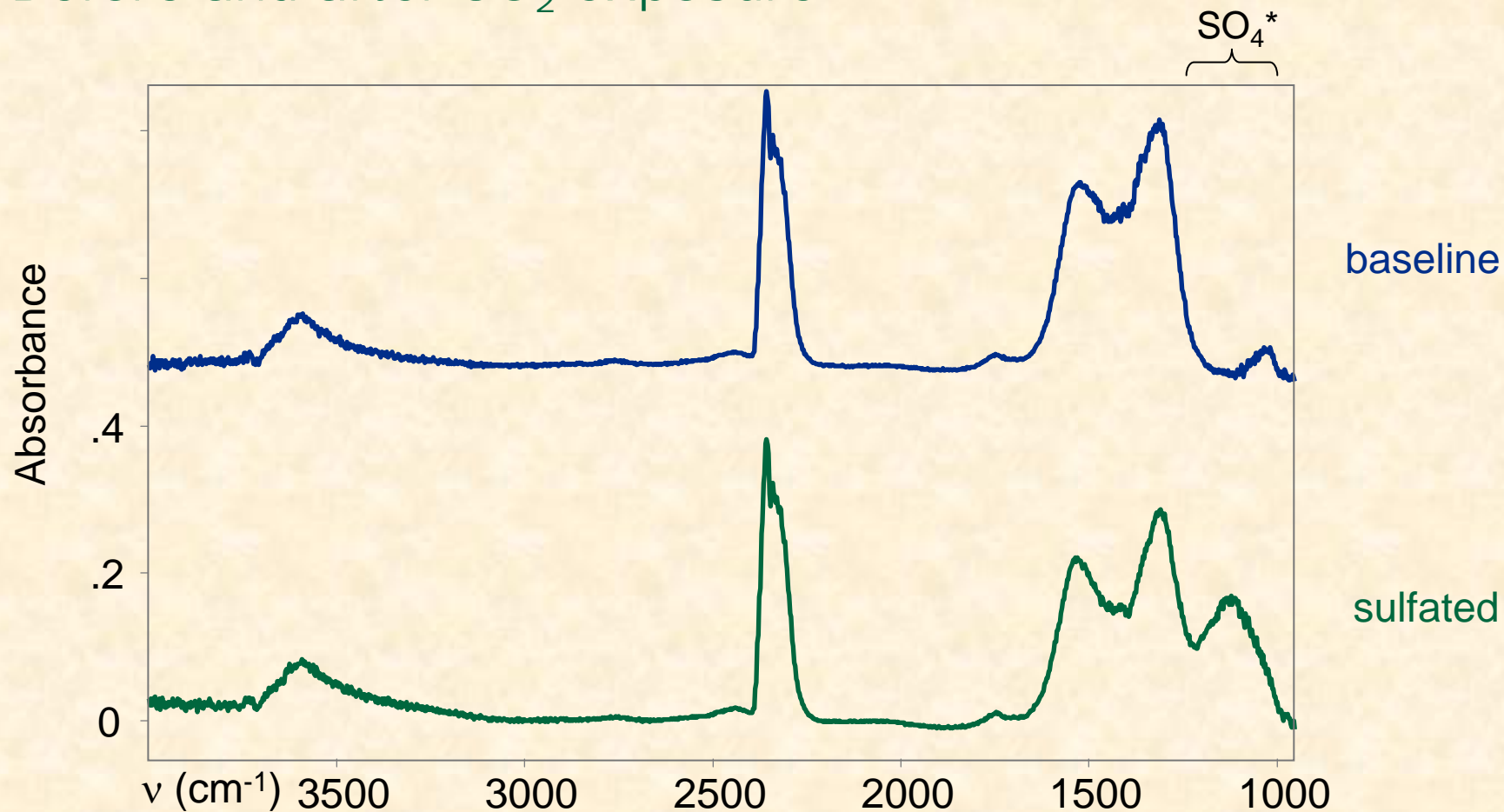


# Impact of sulfation on regeneration

# Overview for impact of sulfation

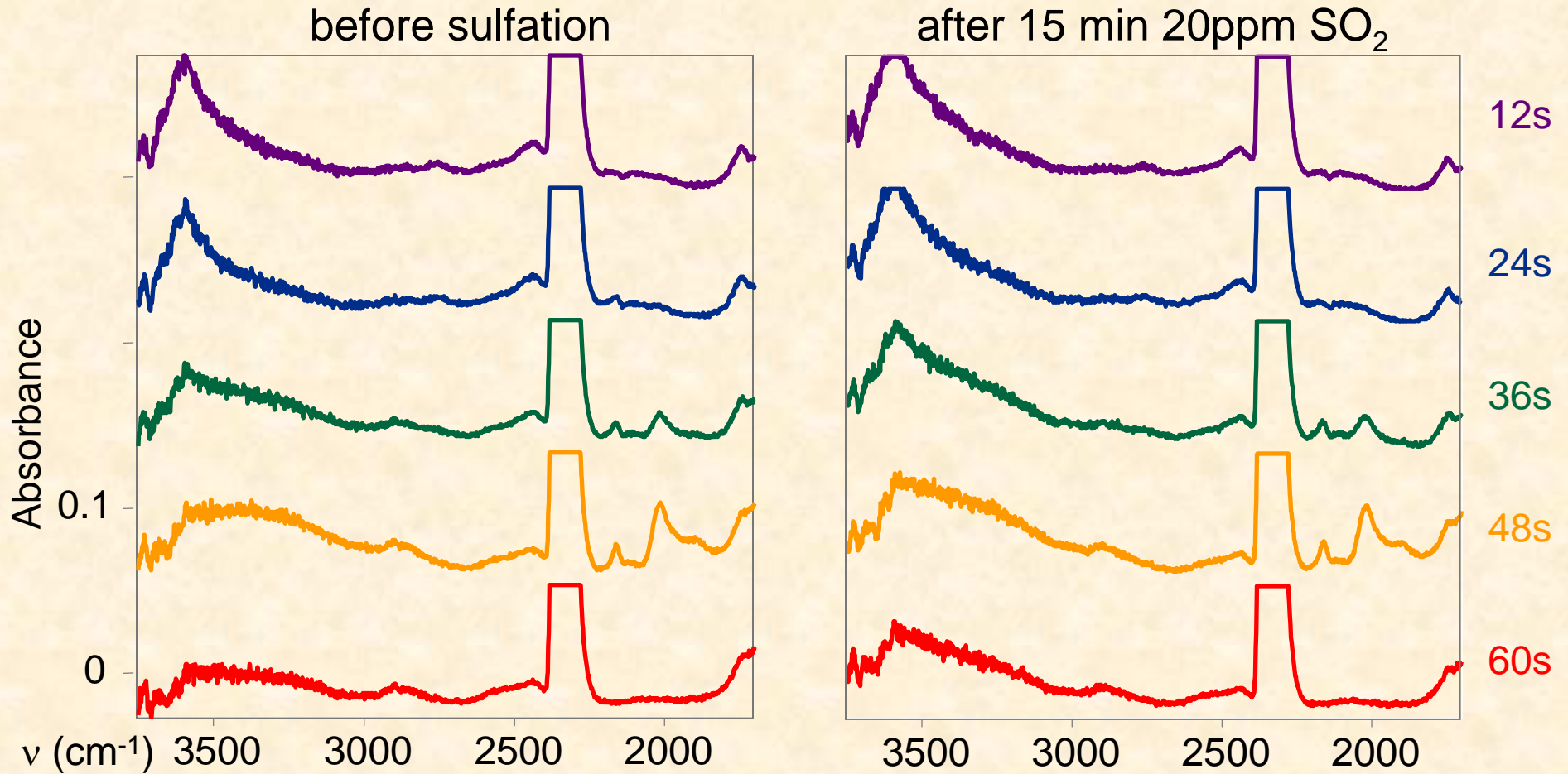
- **Observations from bench experiments:**
  - Large increase in  $\text{NH}_3$  slip with sulfur loading (Partridge, Choi, and Daw later today)
- **Key question:**
  - Does sulfation impact the regeneration reduction reactions?
- **DRIFTS experiments:**
  1. Reduced  $500^\circ\text{C}$ , cooled to  $300^\circ\text{C}$  under  $0.5\%\text{H}_2$
  2. Cycled with  $\text{H}_2$  reductant
    - lean:  $300\text{ppmNO}/10\%\text{O}_2/5\%\text{CO}_2/5\%\text{H}_2\text{O}$
    - rich:  $0.9\%\text{H}_2/5\%\text{CO}_2/5\%\text{H}_2\text{O}$
  3. Cycled with  $\text{CO}$  reductant
  4. Exposed to  $20\text{ ppm SO}_2$  15 min while cycling with  $\text{CO}$ 
    - ~15% reduction in storage capacity
  5. Cycled with  $\text{CO}$  reductant
  6. Cycled with  $\text{H}_2$  reductant

## Before and after SO<sub>2</sub> exposure

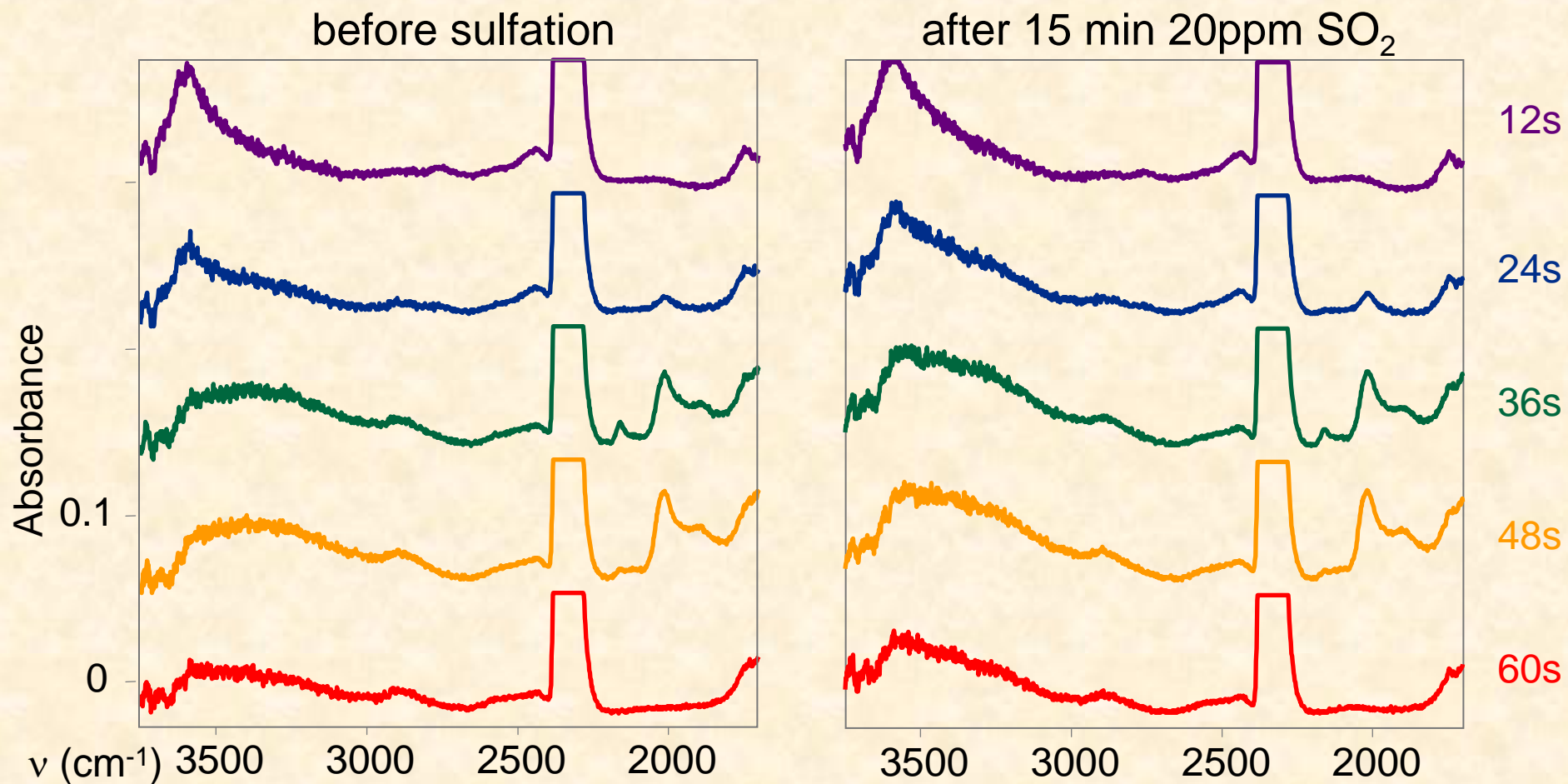


- Decrease in NO<sub>3</sub>\* & CO<sub>3</sub>\* peaks corresponds to loss of ~15% active storage material

No change observed in reduction behavior after light sulfation at 300°C for cycles with CO...



...or cycles with H<sub>2</sub> reductant



# NH<sub>3</sub> oxidation

# Overview for NH<sub>3</sub> oxidation

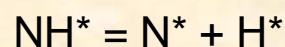
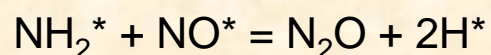
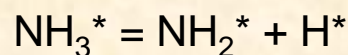
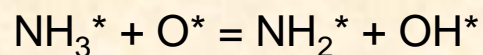
- **Observations from bench experiments:**

- NH<sub>3</sub> oxidized by both O<sub>2</sub> and NO over the LNT catalyst
- N<sub>2</sub>O formed from NH<sub>3</sub> oxidation by O<sub>2</sub> and NO

- **Key question:**

- Does NH<sub>3</sub> react with NO<sub>x</sub> and O<sub>2</sub> stored on catalyst surface?

- **Relevant reactions from mechanism:**

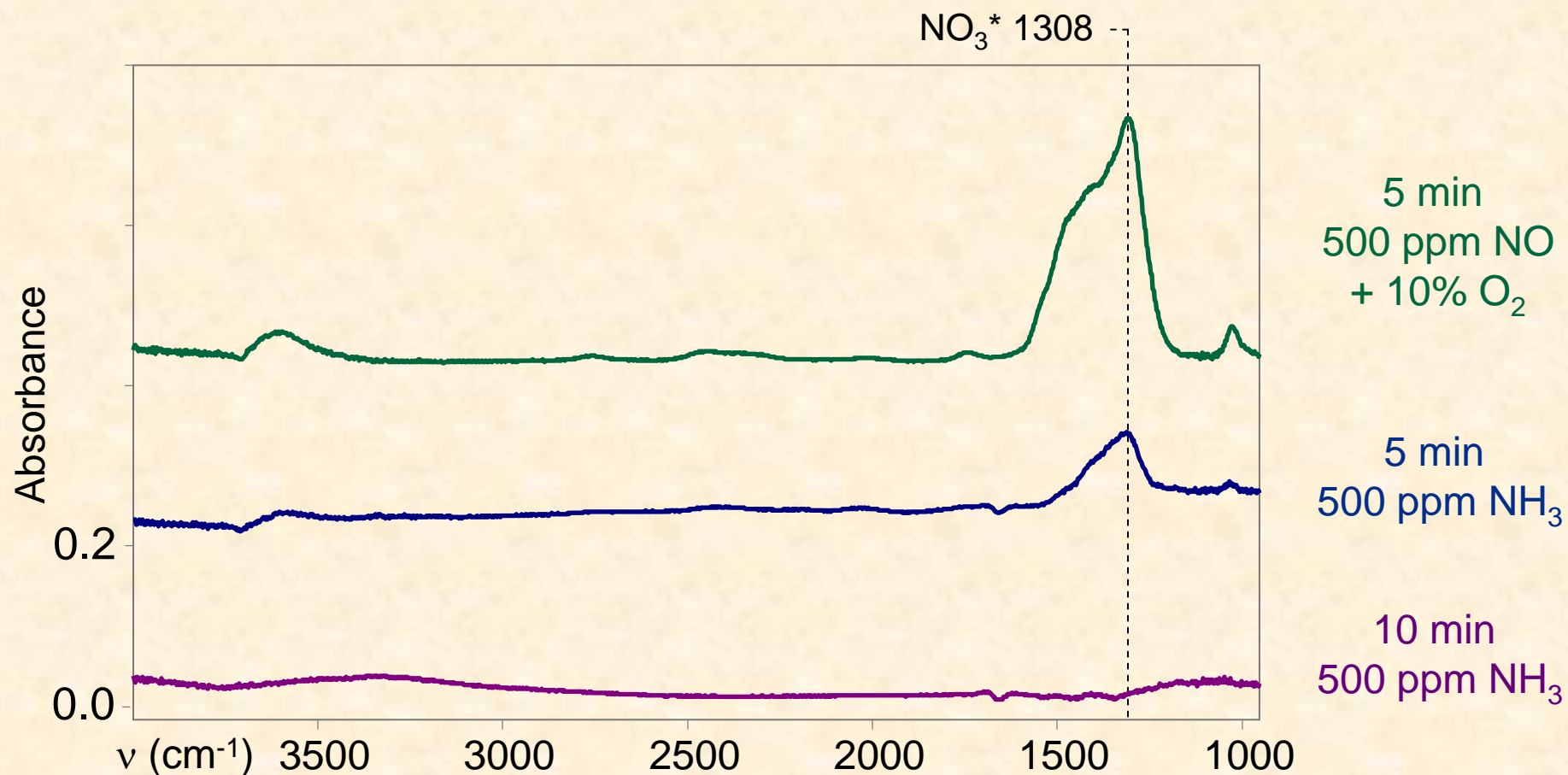


- **DRIFTS experiments:**

1. Reduced 500°C, cooled to experiment temperature under 0.5% H<sub>2</sub>
2. Exposed to oxidants for 5 minutes (10% O<sub>2</sub> or 300ppm NO/10% O<sub>2</sub>)
3. Purged in inert gas for 5 minutes
4. Exposed to 500ppm NH<sub>3</sub>; FTIR scan every 15 seconds
5. Repeated at 200, 300, 400, 500°C

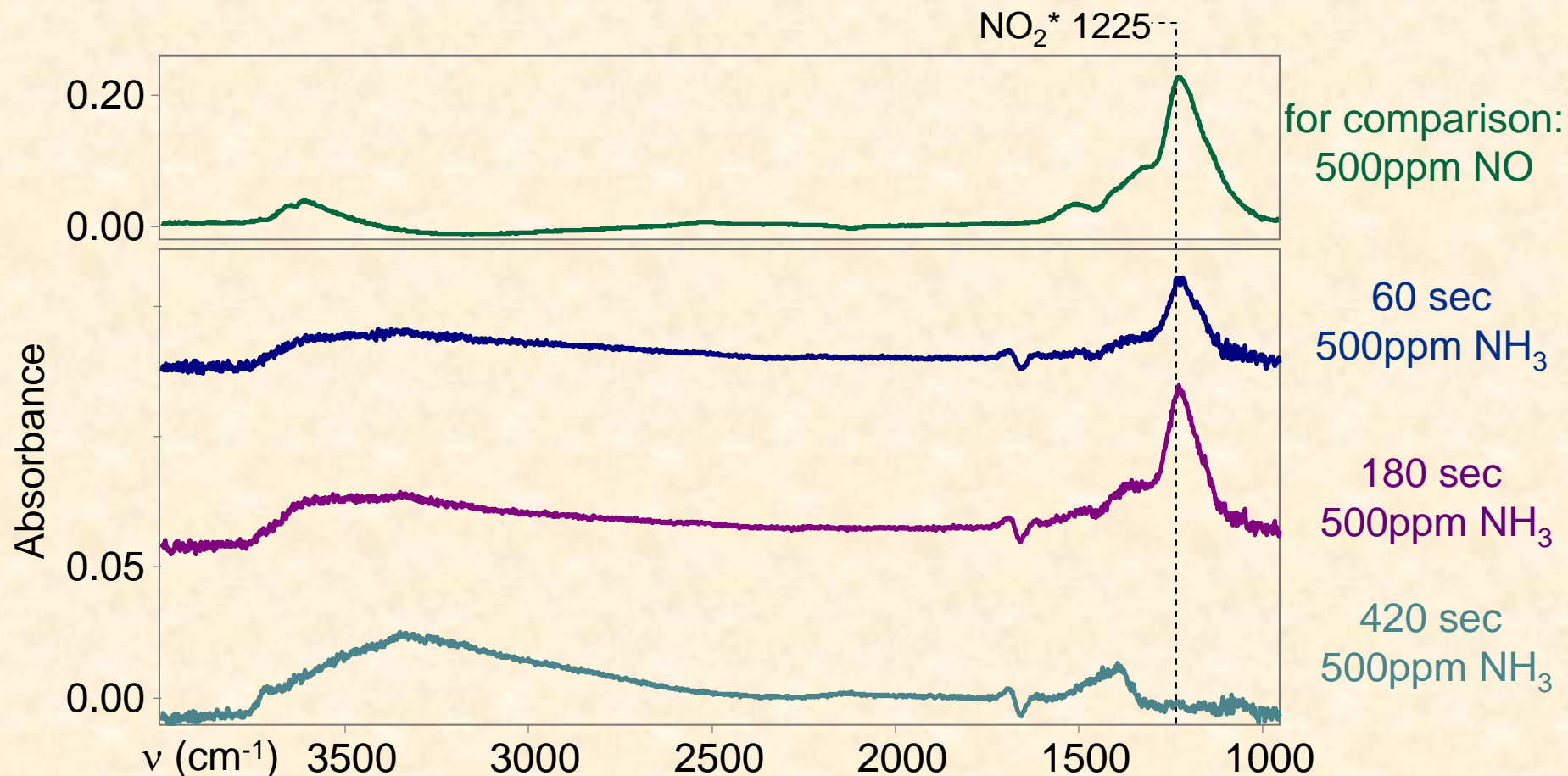


# NH<sub>3</sub> reduces NO<sub>x</sub> stored on the catalyst surface



- At 300°C, NH<sub>3</sub> reduces the adsorbed nitrates, regenerating the storage material; also observed at 200 and 400°C

# NH<sub>3</sub> initially forms nitrites over oxidized surface



- At 200°C, NH<sub>3</sub> initially oxidized and stored as nitrite; eventually incoming NH<sub>3</sub> eliminates oxidative capacity and reduces stored nitrites
- Also observed at 300 and 400°C; higher temperatures speed things up

# Conclusions

- Isocyanate:
  - formed in large quantities in the absence of water
    - some appears to be located on metal oxide components
  - rapidly hydrolyzed by water, reducing surface concentration
    - water appears to suppress NCO formation on metal oxides
    - temperature where NCO diminished correlates with increased  $\text{NH}_3$  selectivity in bench experiments
  - observed during cycling with both CO and  $\text{H}_2$  (on precious metals)
  - sufficient evidence to leave NCO  $\text{NH}_3$  pathway in mechanism
- Light sulfation of the catalyst had no observable impact on reduction chemistry
- $\text{NH}_3$  reacts with stored  $\text{NO}_x$  to regenerate the LNT
- When  $\text{NH}_3$  encounters an oxidized surface, it
  - is initially oxidized and stored as nitrite
  - eventually depletes oxidative capacity and reduces the stored nitrite

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