NO_x Adsorption of $Pt/K/Al_2O_3$ in the Presence of CO_2 and H_2O: an *In-situ* DRIFTS Study

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Project Overview

- **Investigate and quantify *in-situ* surface species on NO_x adsorber catalysts**
  - ***In-situ*, quantitative, and transient analysis**
  - **Pre-competitive, model catalyst used ($Pt/K/Al_2O_3$)**
  - **Ba is widely studied; limited effectiveness above ~350C**
  - **K improves overall storage capacity; few studies exist**

Objectives

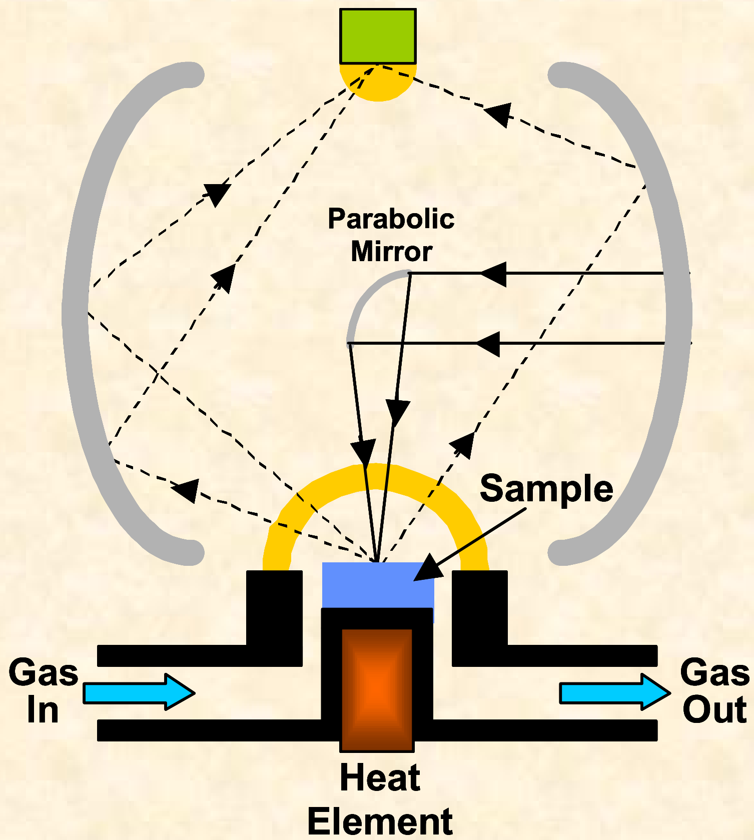
- **Establish a technique for quantifying surface species on $Pt/K/Al_2O_3$**
  - Provide dynamic *in-situ* measurements
  - Effective in the presence of H_2O and CO_2
- **Determine the role of the constituent parts of a multi-component NO_x adsorber catalyst**
  - Pt readily oxidizes NO to NO_2, but what is role of γ-Al_2O_3
- **Determine surface chemistry**
  - Intermediate and dominant NO_x storage species
  - Competing surface species that lessen capacity
  - Individual and synergistic role of exhaust constituents
  - Variation with temperature

Approach

- Powder catalysts studied
  - γ-Al_2O_3, Pt/Al_2O_3, K/Al_2O_3, $Pt/K/Al_2O_3$
  - Component effects studied by breaking down full catalyst
- DRIFTS reactor with simulated exhaust
  - Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)
  - Surface analysis based on characteristic spectroscopy
  - H_2O and CO_2 capable
  - Studied between 150 and 400C
- Adsorbates quantified with chemisorption
  - Chemisorption: chemically bound gas with surface

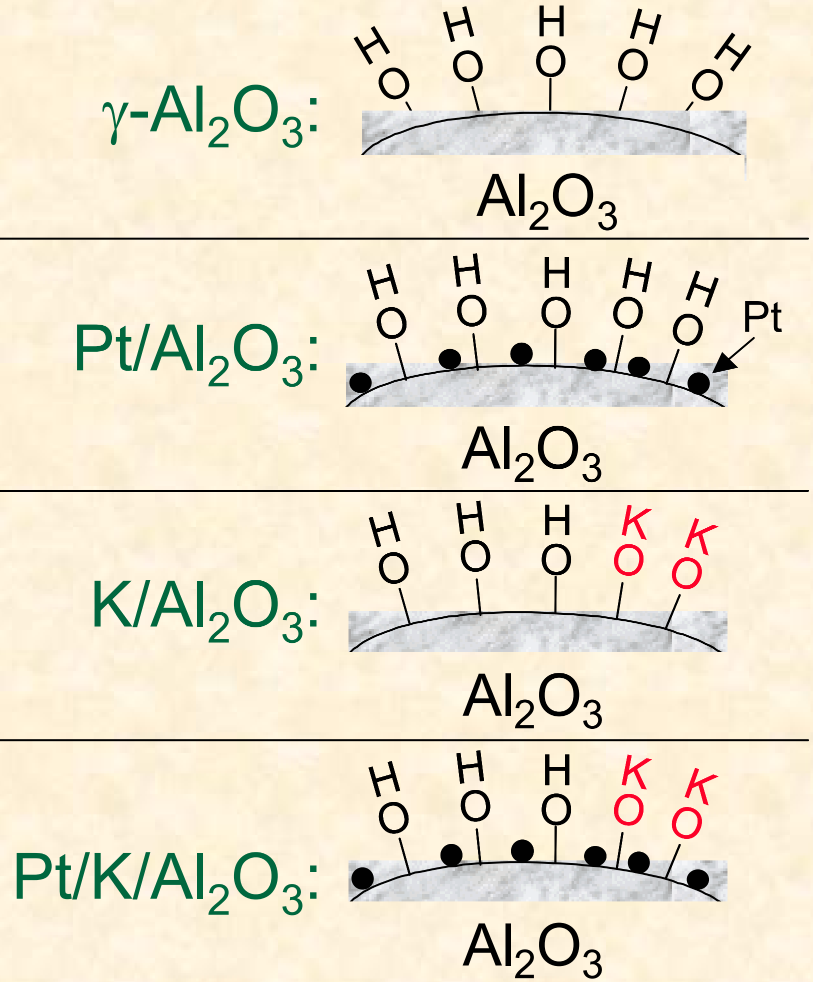
DRIFTS with High Sensitivity

- *In situ* DRIFTS measurements
  - Catalyst temperature up to ~500°C
  - Heated lines for up to 10% H2O
- MIDAC FTIR spectrometer
  - 2 Hz scan rate; 1 cm-1 resolution
- Harrick Barrel Ellipse DRIFT accessory
  - Design increases signal and sensitivity
  - LN_2 cooled MCT detector
- Chemisorption calibrates DRIFTS
  - Standards obtained to determine DRIFT response factors



State of Catalytic Components

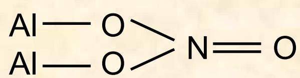
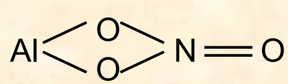
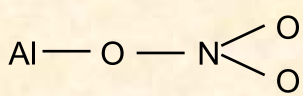
- **EmeraChem provided model catalysts**
- **1% Pt; 1-10 wt% K added by K_2CO_3**
  - **Above 200C –OH groups react with K_2CO_3 leaving –OK groups on the surface†**
  - **Highly dispersed potassium phase**

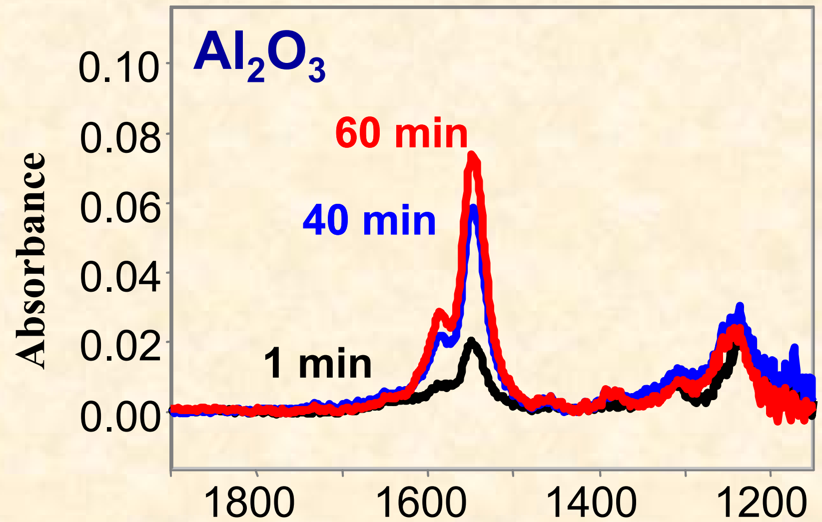


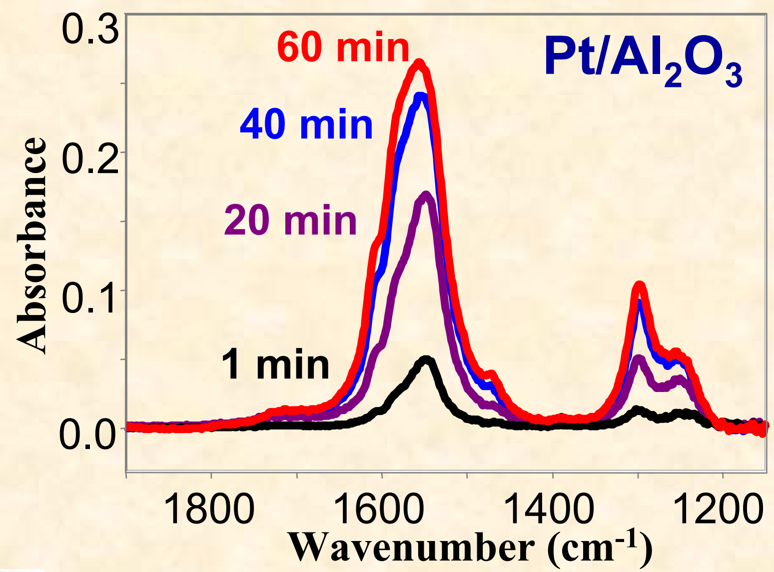
† - W. Stork and G. Pott, *J. Phys. Chem.*, 78 (1974) 2496; B. Krupay and Y. Amenomiya, *J. Catal.*, 67 (1981) 362; M. Kantschewa et al., *Appl. Catal.*, 8 (1983) 71.

Nitrates Adsorb on Alumina Support

- Alumina adsorbs NO_x
- Covalently bound nitrates
- Pt expedites adsorption; enables bridged form
- Spectra at 250C for 500 ppm NO + 5% O_2 at 10 sccm

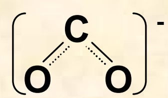
Peak Position	Infrared Stretch	Structure
1610 1210	N=O vibration NO_2 asymmetric	
1590 1237	N=O vibration NO_2 asymmetric	
1550 1257	NO_2 asymmetric NO_2 symmetric	

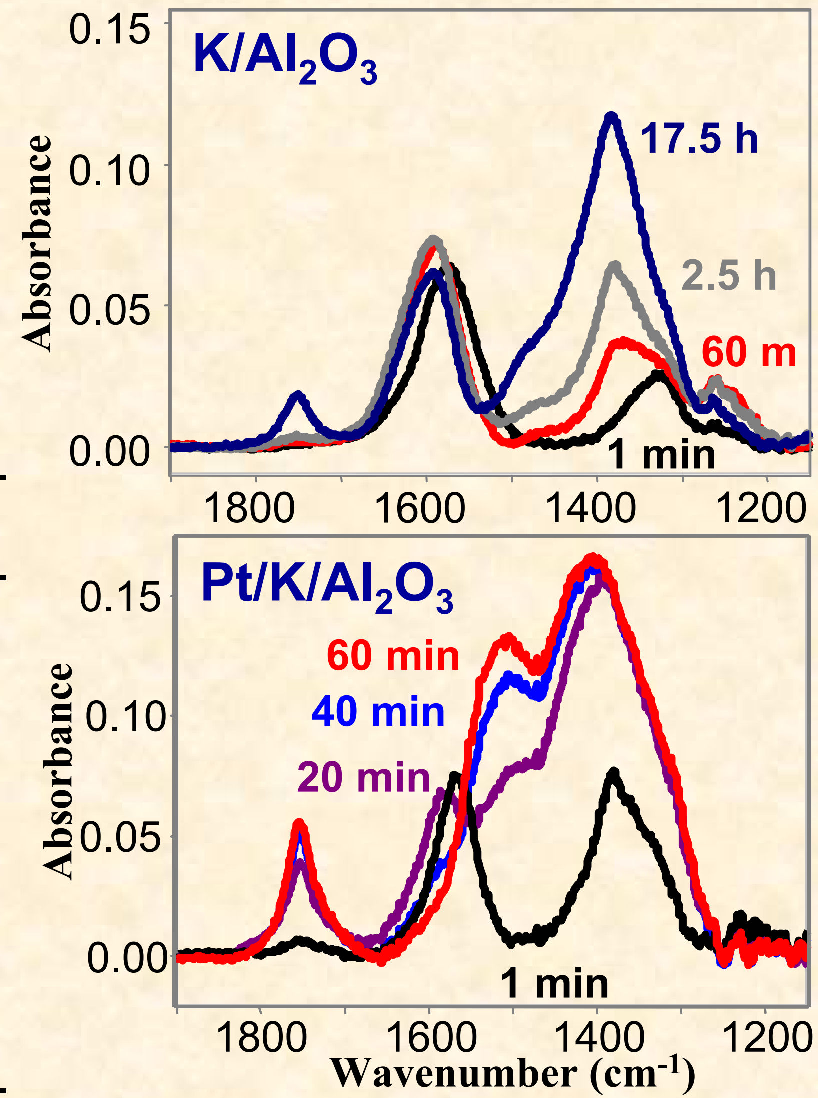




NO_3^- is Primary Nitrate Formed on K

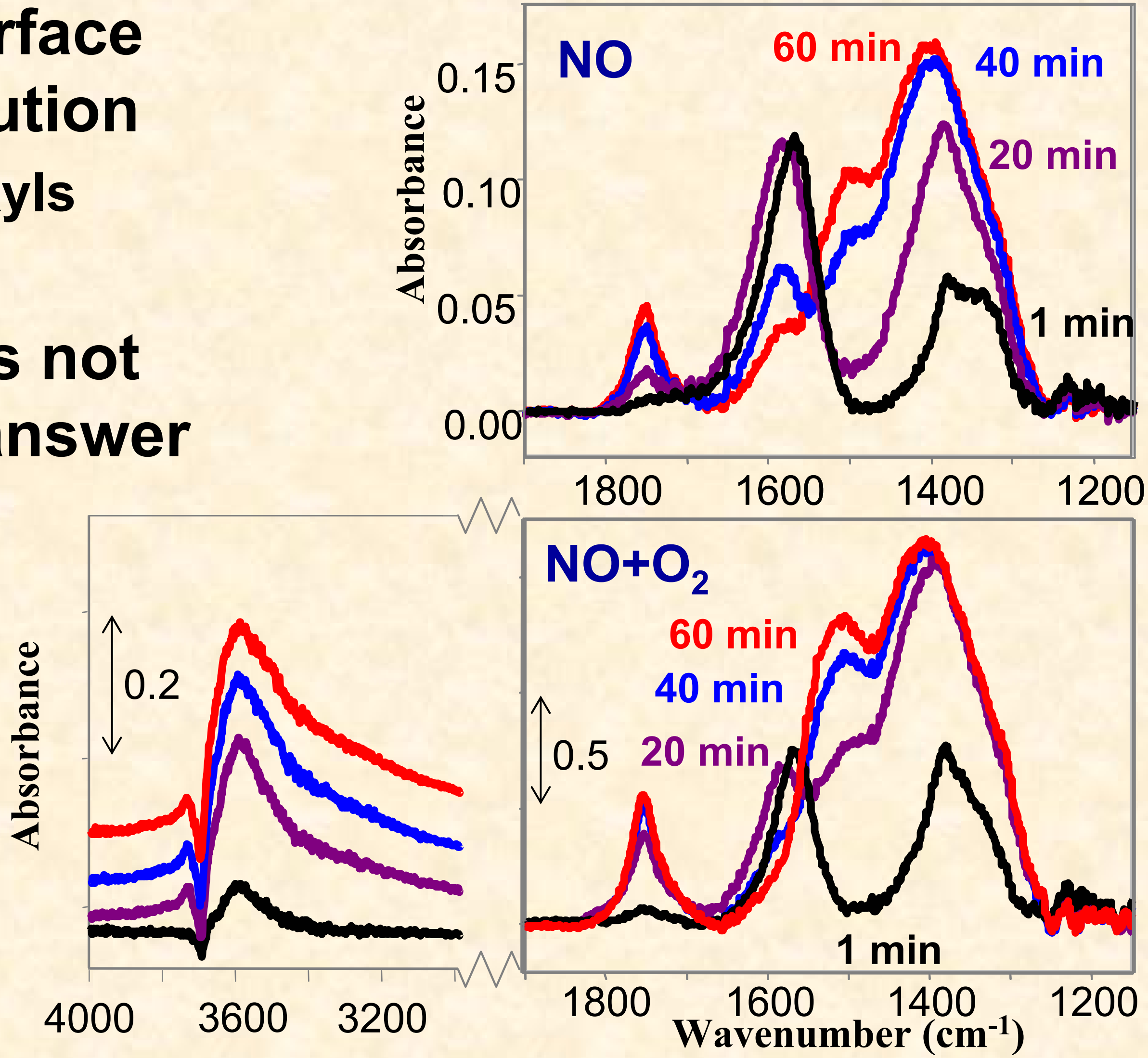
- **Ionic nitrate formed on K**
- **NO_2 formation essential for adsorption on K**
- **NO_x adsorbs on Al_2O_3**
- **Spectra at 250C for 500 ppm NO + 5% O_2 at 10 sccm**

Peak Position	Infrared Stretch	Structure
1600	COO^- asymmetric	
1310	COO^- symmetric	
1510	N=O & NO_2 asymmetric	Al_2O_3 nitrates
1260	NO_2(a) symmetric	
1380	free nitrate ion	NO_3^-
1250	free nitrite ion	NO_2^-



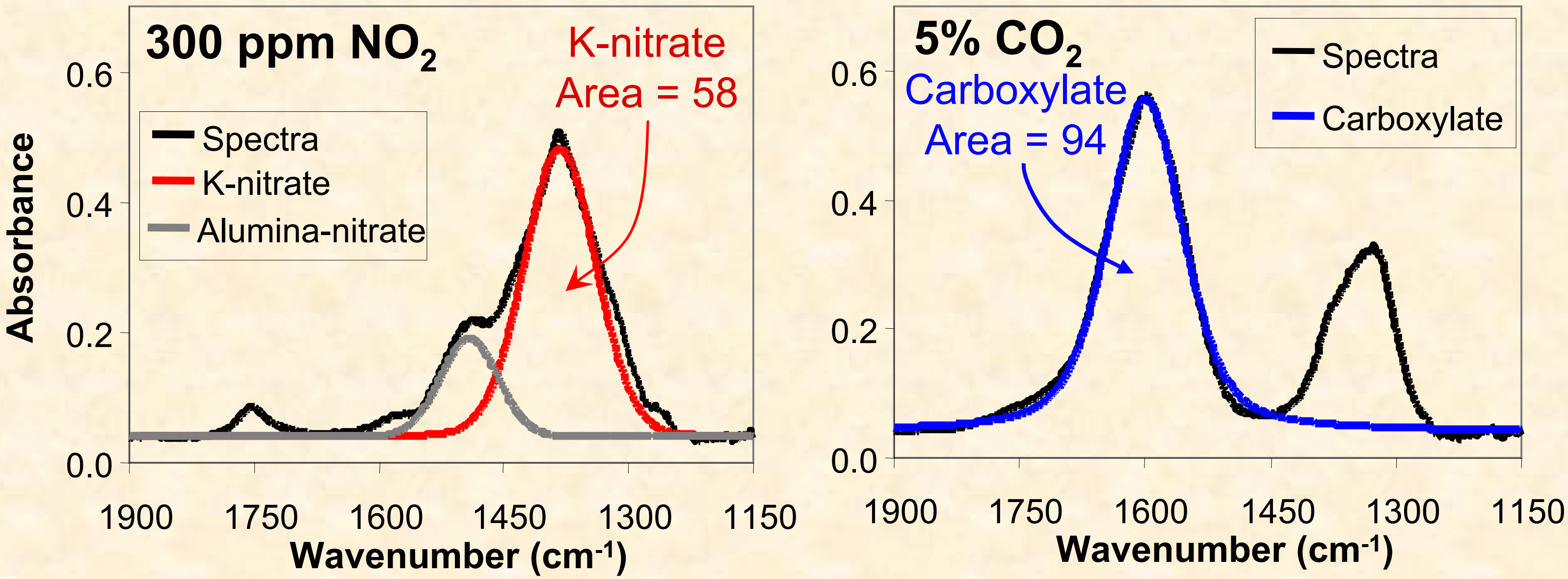
NO Readily Stored in Absence of O_2

- **Indicative of surface oxygen contribution**
  - Surface Hydroxyls
  - Lattice oxygen
- **-OH region does not give definitive answer**
  - Decreasing and increasing features observed
- **Also observed on γ-Al_2O_3**



DRIFTS Quantified with Chemisorption

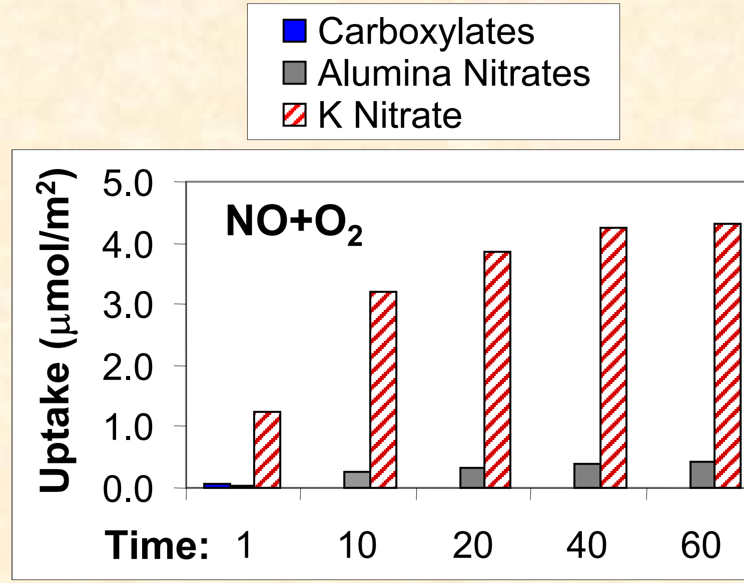
- NO_2 and CO_2 chemisorption on Pt/Al_2O_3 and $Pt/K/Al_2O_3$ enables calibration of DRIFTS features
  - Each adsorbate/surface must be calibrated separately

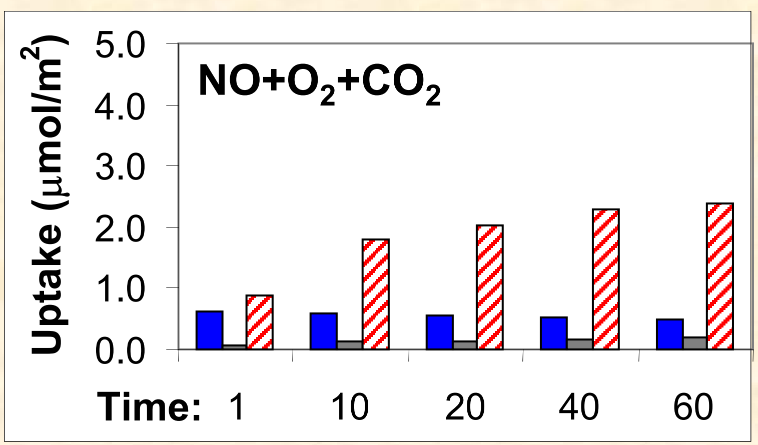


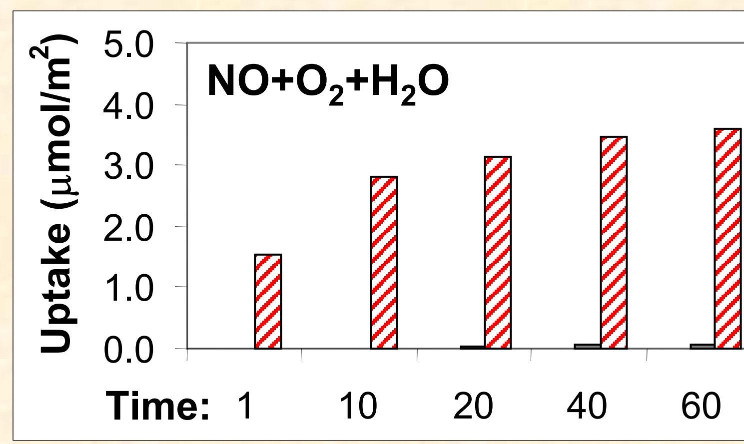
- Linear response allows uptake calculation
  - RF = uptake [μmols/m^2]/Peak Area [absorbance·cm^{-1}]
  - Uptake = RF*Peak Area

CO_2 and H_2O Inhibit NO_x Adsorption

- **CO_2 reduces NO_3^- formation by 45%**
  - **Competition for sites**
- **H_2O mildly reduces NO_3^- formation by 16%**
  - **Decreases alumina nitrate formation by 86%**

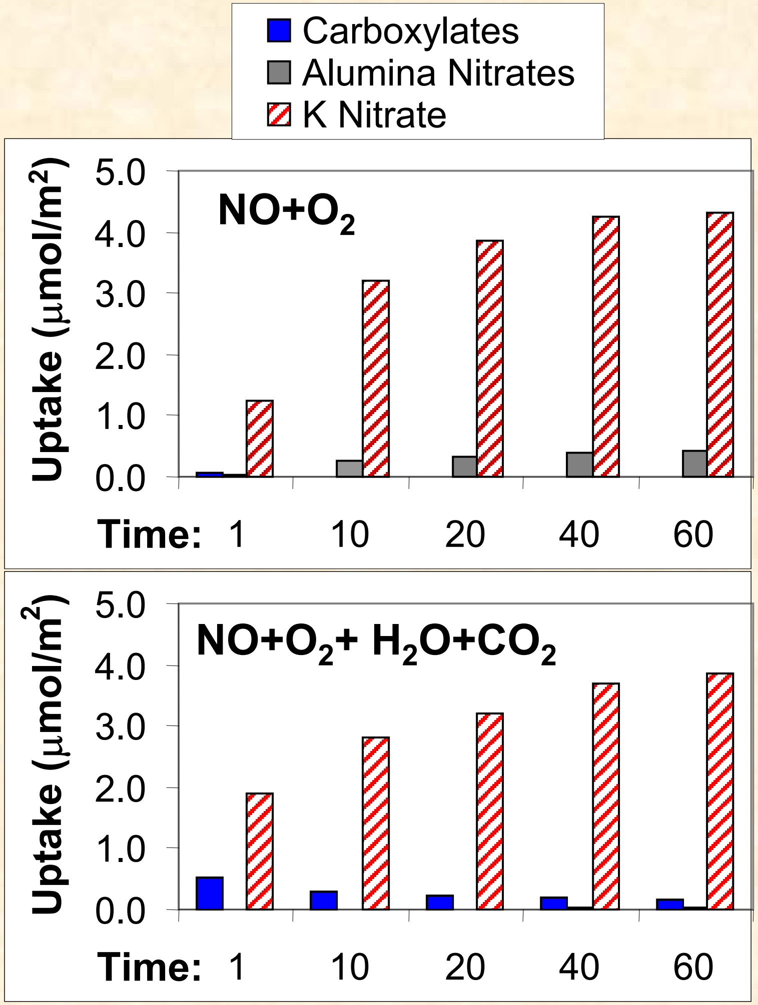






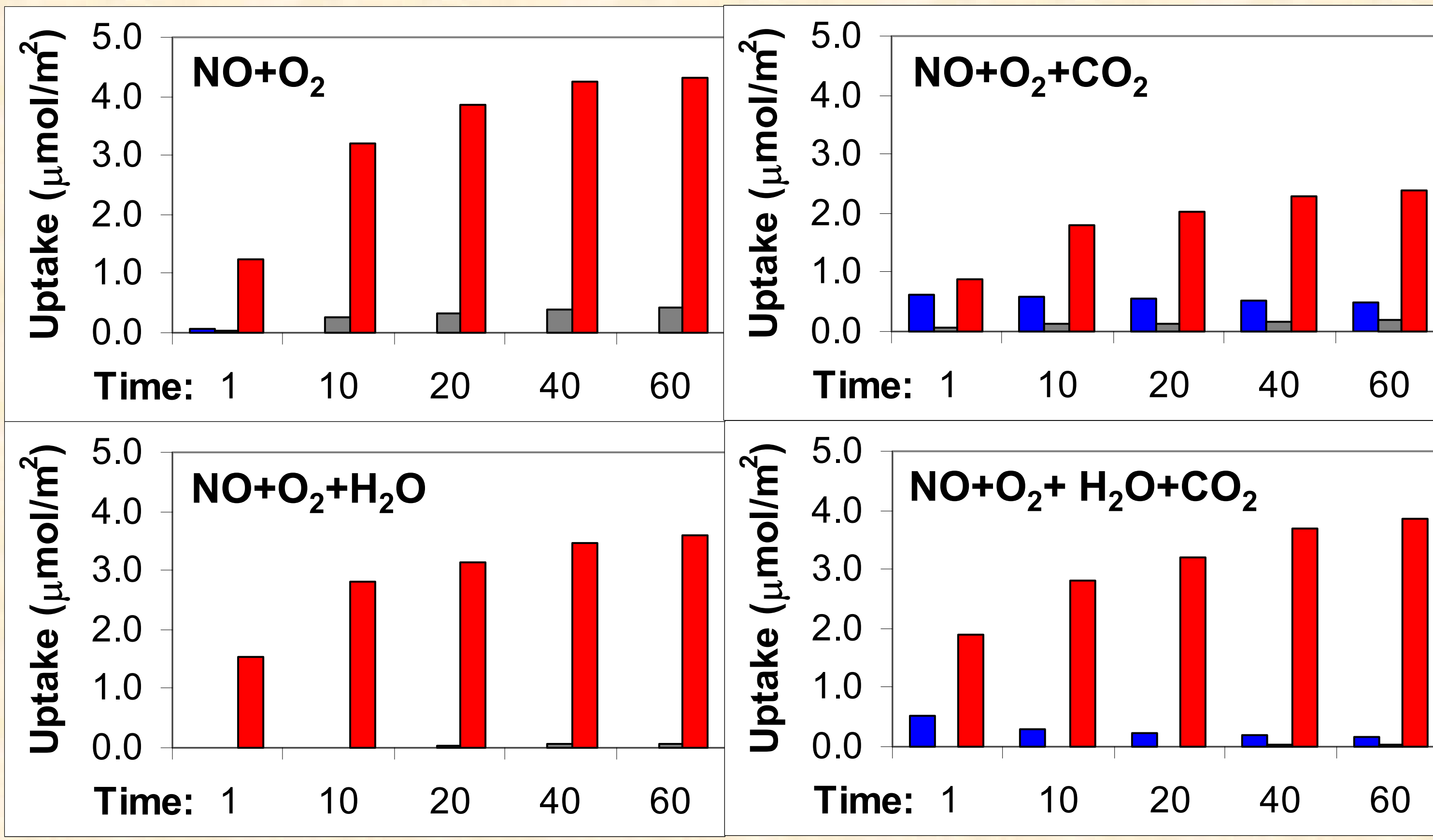
H_2O Reduces CO_2 Inhibition

- NO_3^- reduced by 11% with $CO_2 + H_2O$
- Al_2O_3 nitrates negligible in the presence of H_2O
- H_2O suppresses carboxylate formation
- Importance of hydroxyl groups (on Alumina) for adsorption behavior



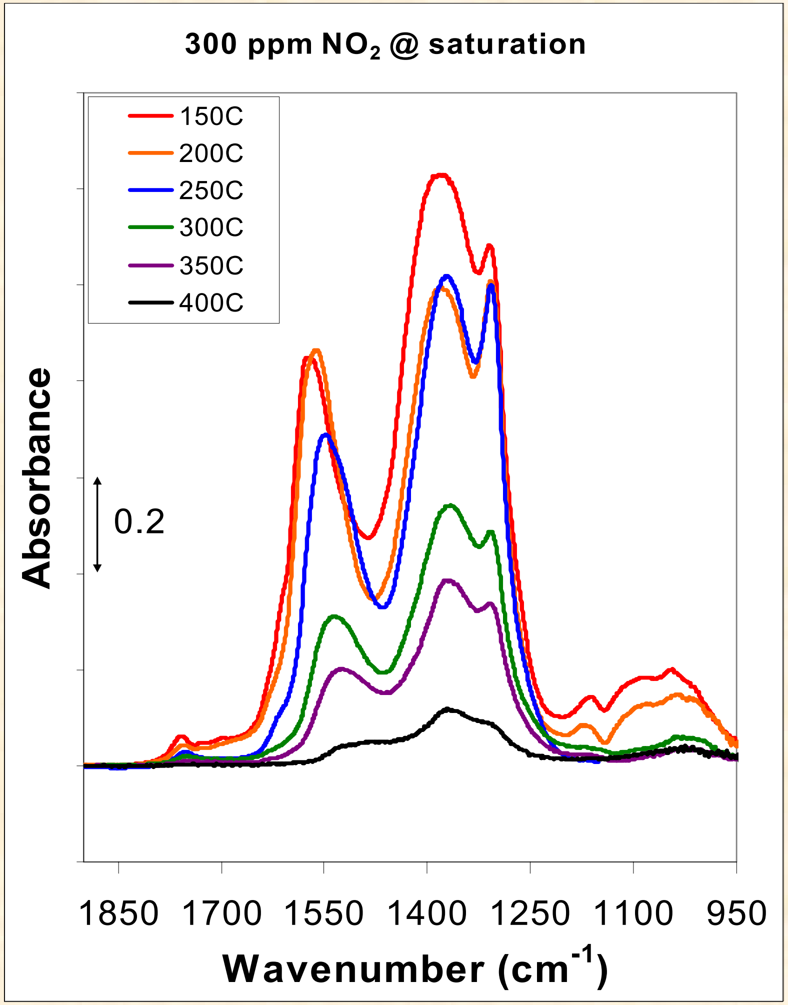
Adsorbate Summary

- Compared to $NO+O_2$ both CO_2 and water reduce nitrate formation
- H_2O effectively increases nitrate formation in the presence of CO_2
  - Leads to hydroxyls that react with carboxylates



Saturated Surface Similar at all Temp.

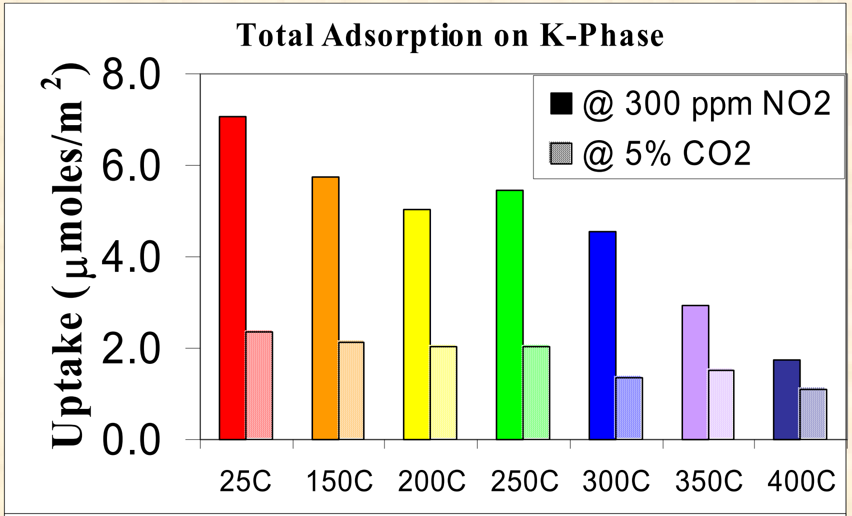
- Spectra very similar at all temps
- Decreasing intensity indicative of decreased storage and an artifact of IR spectroscopy
  - Must record calibration factors for each temperature

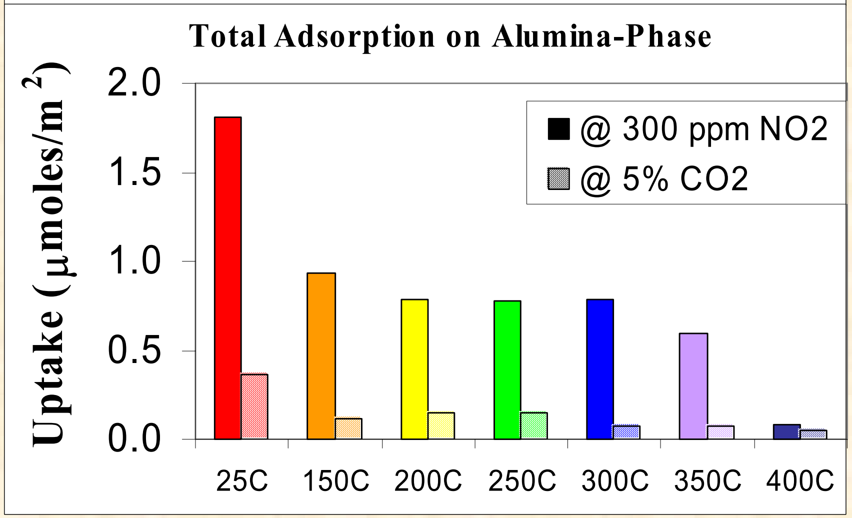


Maximum Capacity Decreases w/ T

- NO_x adsorption sites decrease with increasing temp
- CO_2 adsorption unchanged
  - Suggests greater impact of CO_2 at higher temp
- Alumina adsorption observed at all temperatures
  - Important for calibrated data
- Best conditions: 25-150C?
  - look at temporal effects

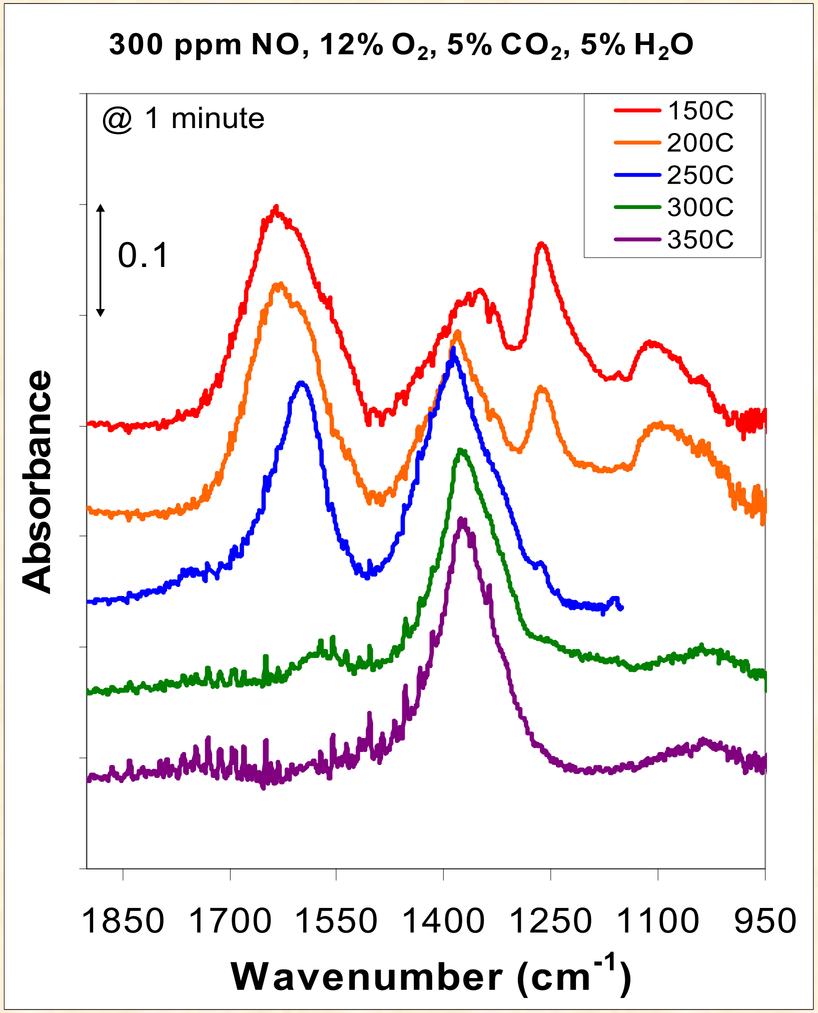
Total NO_2 and CO_2 Uptake





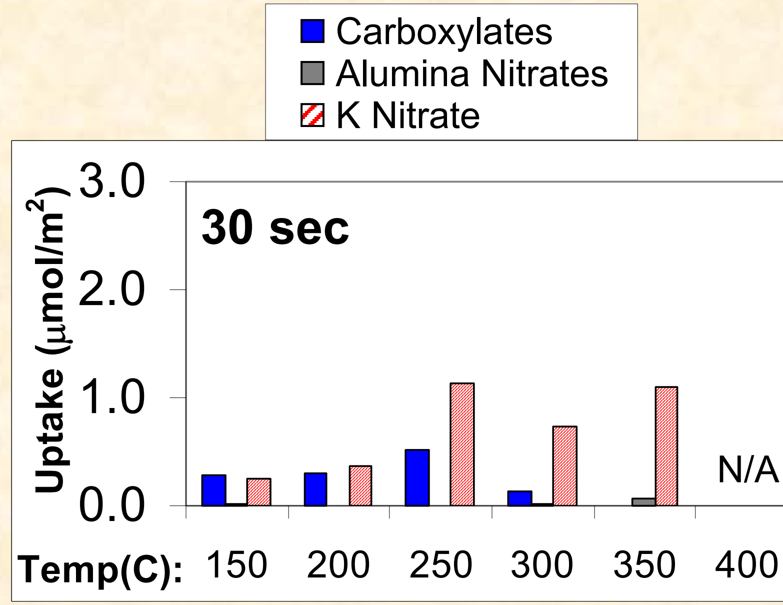
Initial Adsorption Vary with Temp.

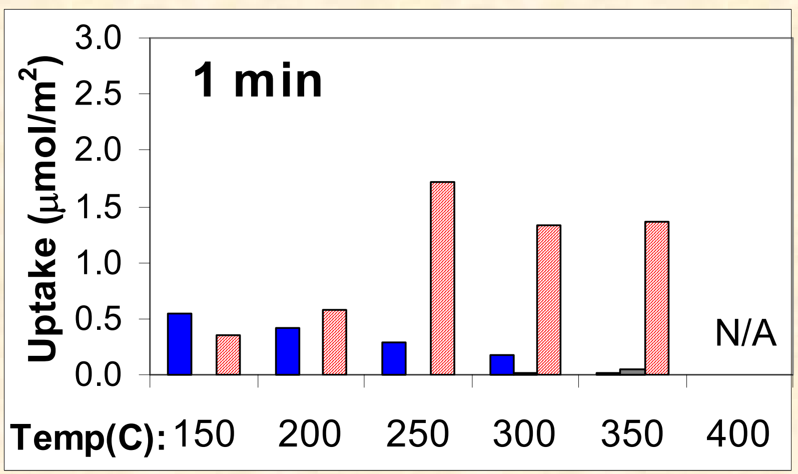
- Spectra recorded in the presence of CO_2 and H_2O
  - H_2O subtracted
- Carboxylate more prevalent at lower temperatures
- Linear nitrite clearly present below 250C
  - intermediate path to nitrate formation
  - Indicative of kinetic limitations
- Only ionic nitrate formation above 300C

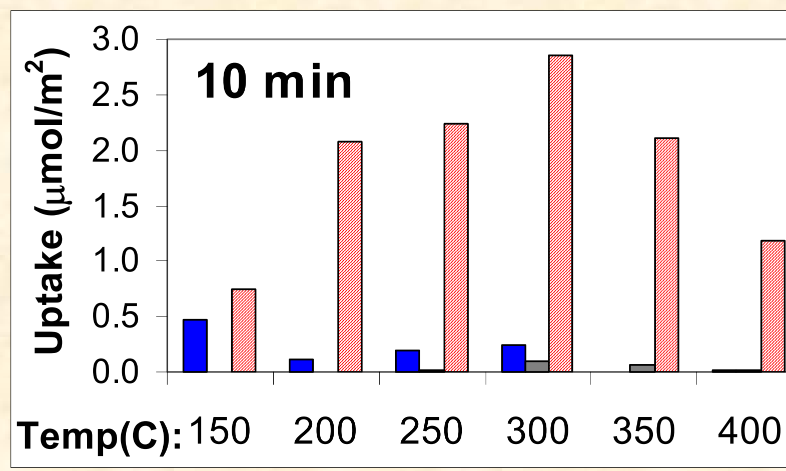


Kinetics Control Adsorption

- **Results for 300ppm NO, 12%O_2, 5% CO_2, and 5% H_2O**
- **Potential is not realized at lower temps due to kinetic limitations**
- **At higher temps adsorption is within 70% of saturation after 10 minutes**







Conclusions

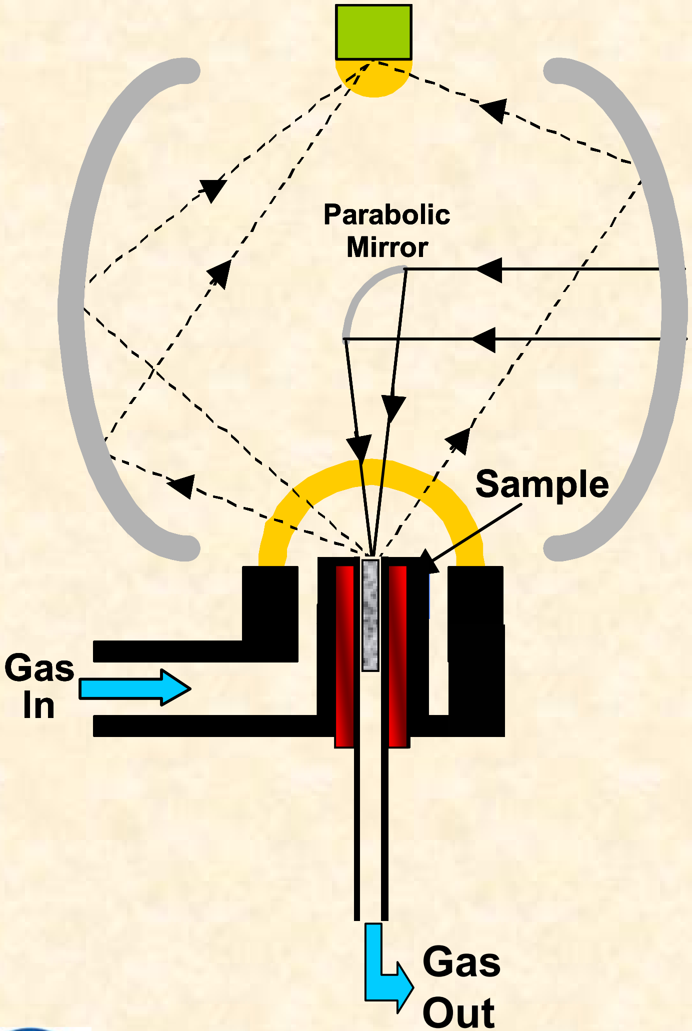
- Free nitrate ion, NO_3^-, is dominant NO_x storage
  - Most likely adsorption route through ionic nitrite
- Surface born oxygen participates in NO_x adsortpion
  - Hydroxyl or lattice oxygen is source
- H_2O mitigates inhibitory effects of CO_2
  - Also effectively eliminates Al_2O_3 adsorption effects
- NO_x storage on $Pt/K/Al_2O_3$
  - kinetics limited below 200C
  - storage site limited above 350C
  - Both important between 200 and 350C

Future Work

- Post-reactor gas analysis of products
  - Particularly of interest in regeneration reactions
  - Rates of reaction during regeneration
- Sulfur poisoning effects
- DRIFTS flow through reactor
- Barium based catalysts

Flow-Through DRIFTS Reactor

- Plug flow reactor with DRIFT spectra at front of bed
- Mass flow controller for effluent
- Simultaneous kinetic and surface chemistry data
- Possible to combine with SPACI-MS for gas analysis throughout catalyst bed



Pt/K/Al_2O_3 compares favorably with other NO_x adsorber catalysts under similar conditions

Temp. (C)	Adsorption time	Gas Components	Adsorbed NOx ($\mu mol/g_{cat}$)	Adsorbed NOx ($\mu mol/m^2$)
Pt(1.0%)/K(4.5%)/γ-Al_2O_3				
250	sat (~17h)	300 ppm NO-12% O_2-bal N_2	936	6.2
250	1h	300 ppm NO-12% O_2-bal N_2	797	5.3
250	1h	Standard + 5% CO_2 + 5% H_2O	658	4.4
250	1 min	300 ppm NO-12% O_2-bal N_2	215	1.4
250	1 min	Standard + 5% CO_2 + 5% H_2O	283	1.9
Pt(0.72%)/Rh(0.14%)/Ba/La/Washcoat				
250	sat (~2h)	500 ppm NO-7% O_2-bal N_2	333	-
Pt(0.76%)/Ba(15%)/γ-Al_2O_3				
250	sat (~20min)	1000 ppm NO + 3% O_2 + bal He	379	-
250	sat (~20min)	Standard + 0.3% CO_2 + 1% H_2O	166	-
250	~3 min	1000 ppm NO + 3% O_2 + bal He	181	-
250	~3 min	Standard + 0.3% CO_2 + 1% H_2O	97	-
Rh(1.0%)/CaO(5%)/γ-Al_2O_3				
300	3 min	1000 ppm NO + 7% O_2 + bal He	5000	14.4
300	1 min	1000 ppm NO + 7% O_2 + bal He	1700	4.9
Pt(1.0%)/CaO(5%)/γ-Al_2O_3				
300	3 min	1000 ppm NO + 7% O_2 + bal He	3400	9.8
300	1 min	1000 ppm NO + 7% O_2 + bal He	1380	4.0
Pd(1.0%)/CaO(5%)/γ-Al_2O_3				
300	3 min	1000 ppm NO + 7% O_2 + bal He	1660	4.8
300	1 min	1000 ppm NO + 7% O_2 + bal He	660	1.9
CaO(5%)/γ-Al_2O_3				
300	3 min	1000 ppm NO + 7% O_2 + bal He	820	2.4
300	1 min	1000 ppm NO + 7% O_2 + bal He	220	0.6

Maximum Capacity Decreases with T

- Adsorption sites decrease with increasing temperature
- Alumina adsorption observed at all temperatures
  - Important for calibrated data
- Best conditions at 25-150C?
  - Must look at temporal effects

Total NO_2 Uptake at 300 ppm