

# **Development of Materials Analysis Tools for Studying NO<sub>x</sub> Adsorber Catalysts**

A cooperative research and development  
agreement with Cummins Engine Company

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## 2. Introduction

- 2007 and 2010 emission regulations require significant reductions in NO<sub>x</sub> and Particulate Matter.
- Catalyst fundamentals and characterization techniques must be developed to support future diesel engine emissions reductions.
- Cummins and ORNL are developing the critical parameters and characterization techniques for catalysts.

# 3. Objective

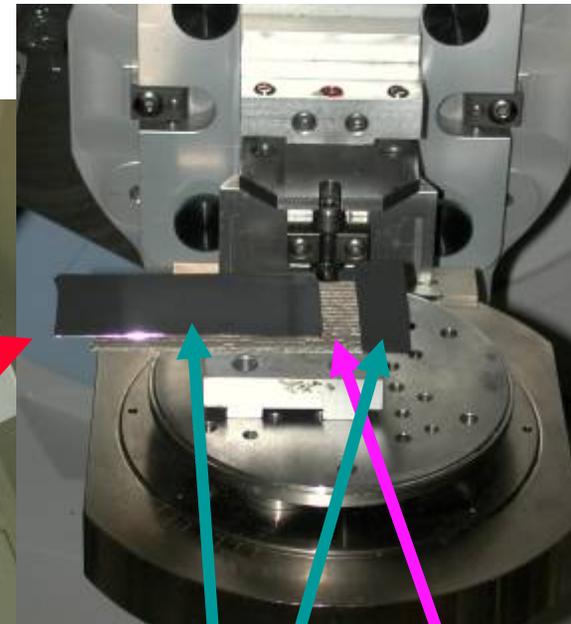
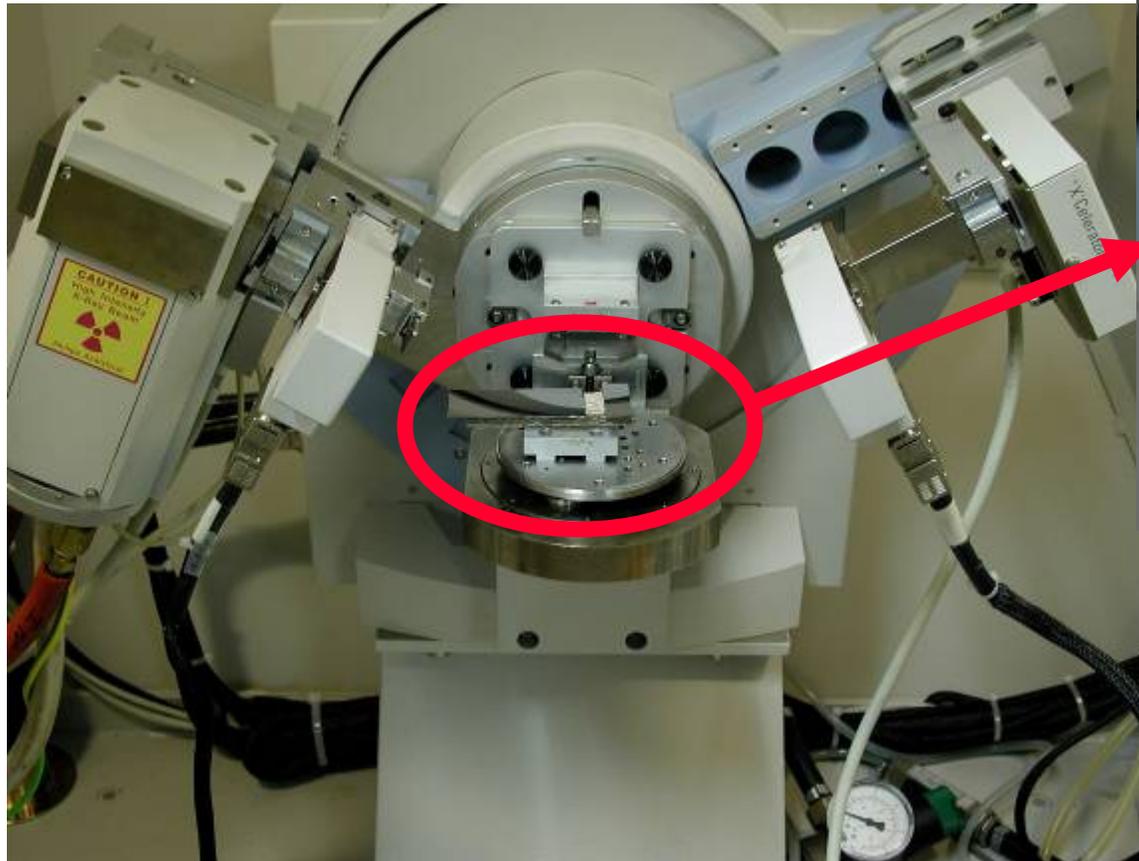
- The overall objective of this effort is to produce a quantitative understanding of the processing and in-service effects on NO<sub>x</sub> adsorber catalyst technology leading to an exhaust aftertreatment system with improved catalyst performance capable of meeting future emission requirements.
- Model systems selected:
  - Al<sub>2</sub>O<sub>3</sub>/Pt on cordierite
  - Al<sub>2</sub>O<sub>3</sub>/BaO/Pt on cordierite

# 4. Results: X-ray Diffraction

- X-ray diffraction (XRD) data were taken along the length of samples
- Peak width related to the crystallite size; monitored as a function of desulfation time
  - A crystallite is a region of coherent diffraction
  - Crystallites can be thought of as sub-grains, which are very small perfect single crystals
  - Typically, the crystallite size < the grain size of a material as observed on the SEM.
  - Significant contributions to peak broadening if crystallite size < 0.1  $\mu\text{m}$

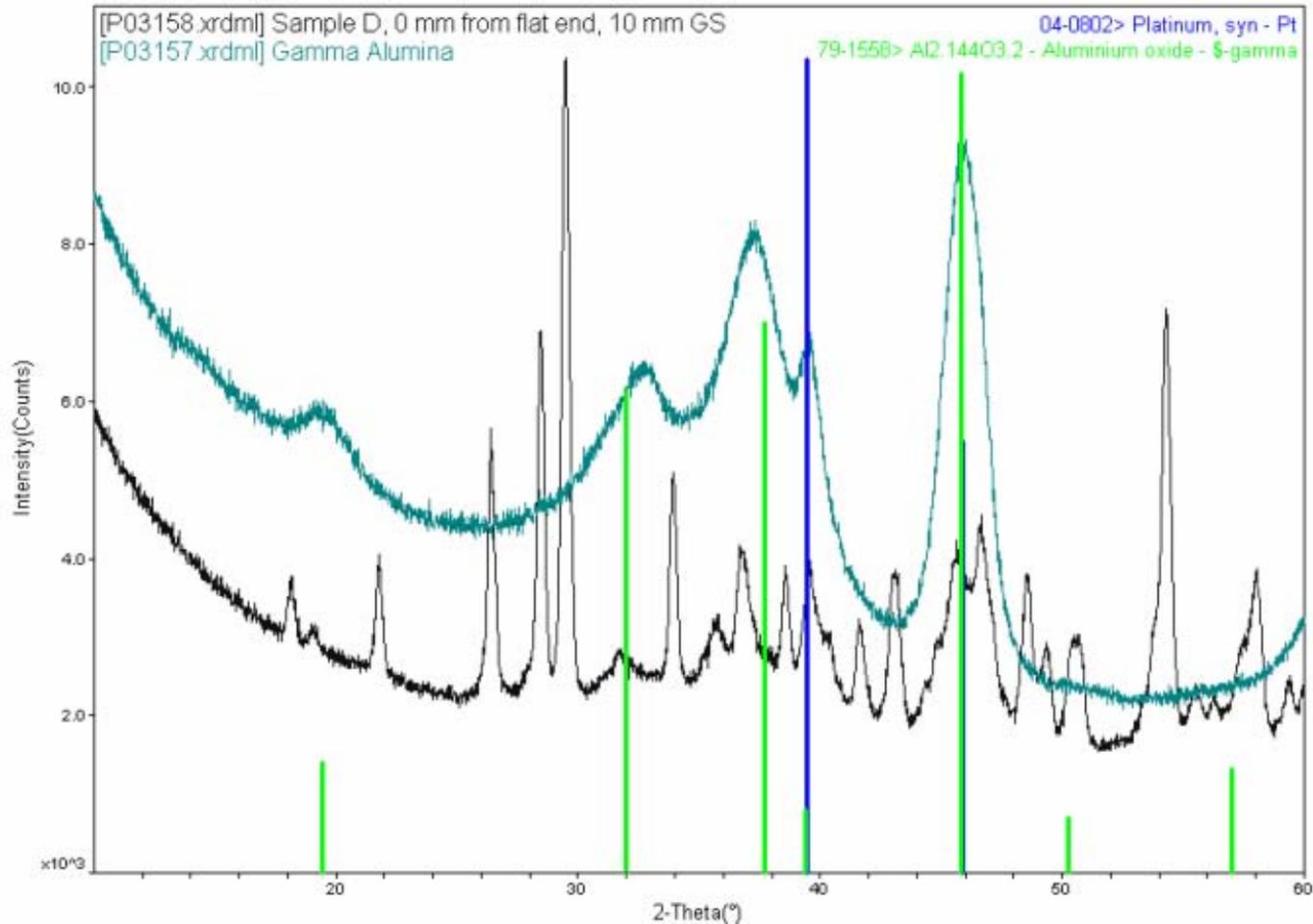
# 5. XRD: Data collected every 10 mm from 10 mm sections

PANalytical X'Pert Pro MPD employed



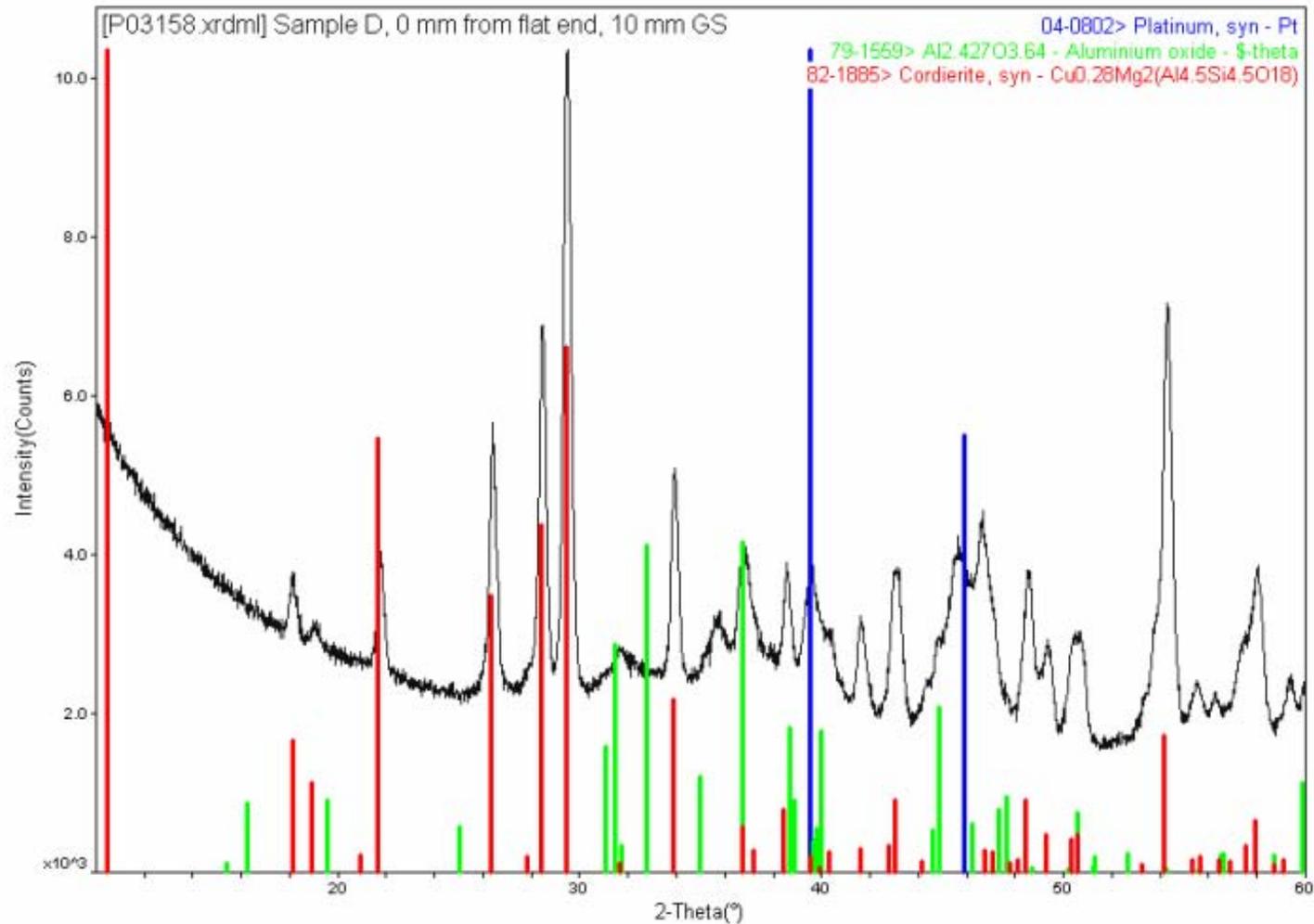
Sample  
Silicon wafer masks

# 6. Gamma alumina transformed to theta



Gamma-alumina crystallite size = 3nm

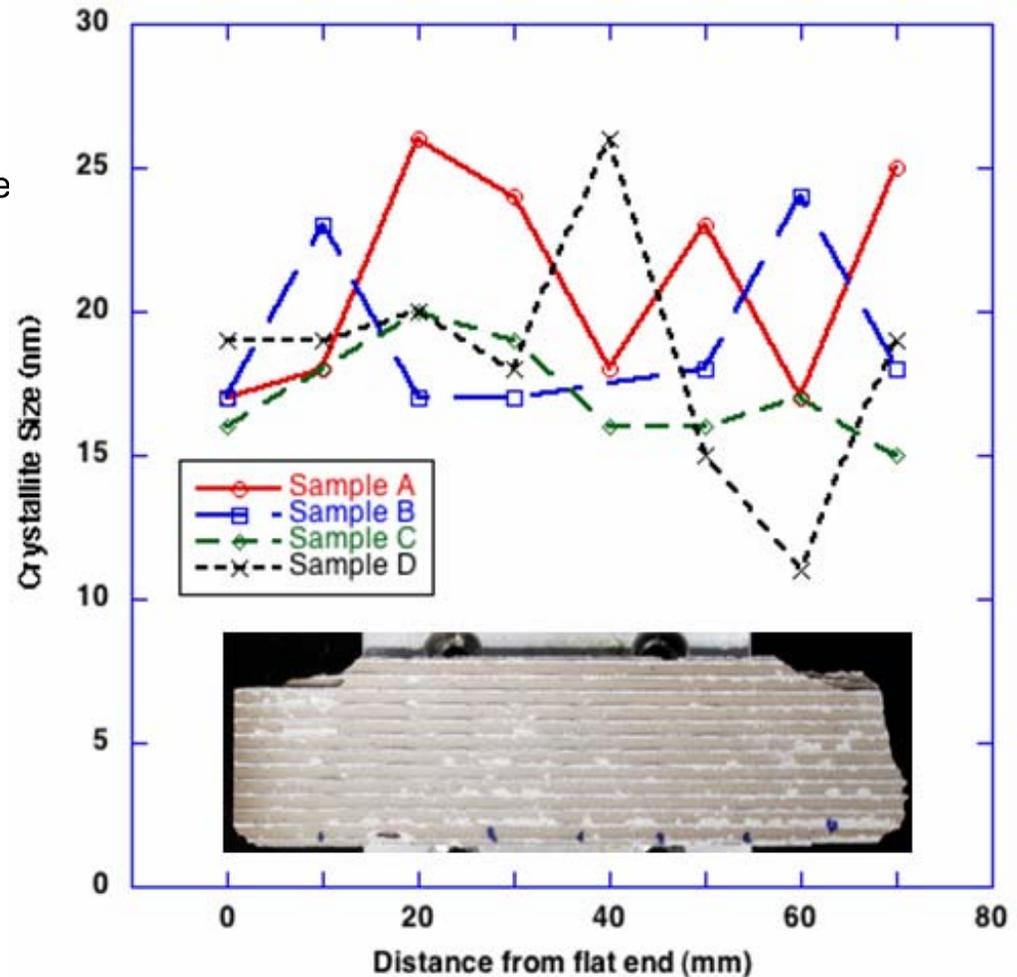
# 6. Pt peaks overlap with alumina peaks



# 7. No trends observed along length. Measured crystallites are large and likely from alumina

- Sample A-Baseline
- Sample B-6 hrs @350°C, Pulse
- Sample C-6 hrs @350°C, Pulse, Low Volume
- Sample D-6 hrs @450°C, Pulse

Surface area lost

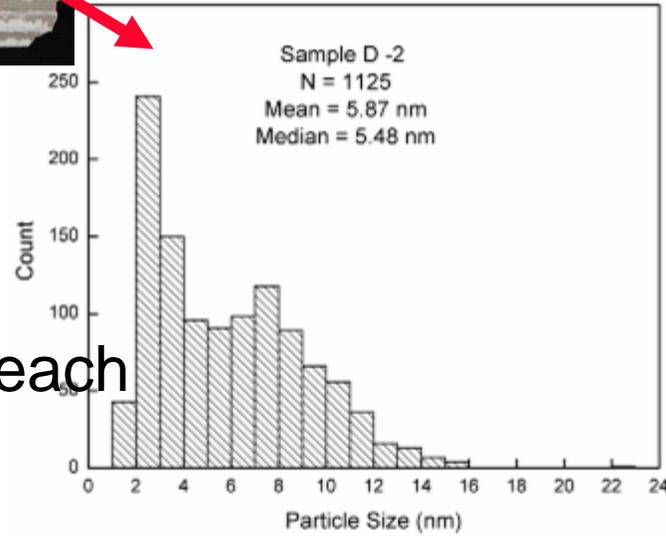
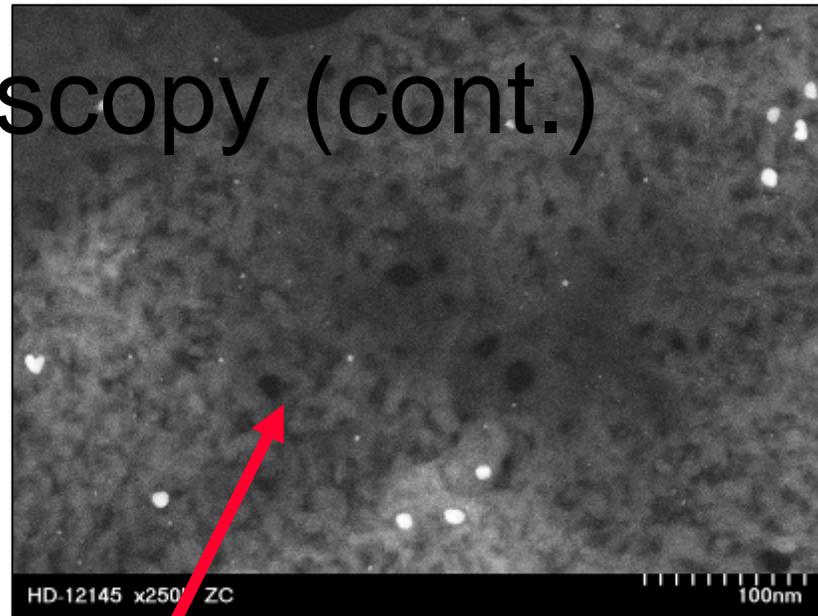
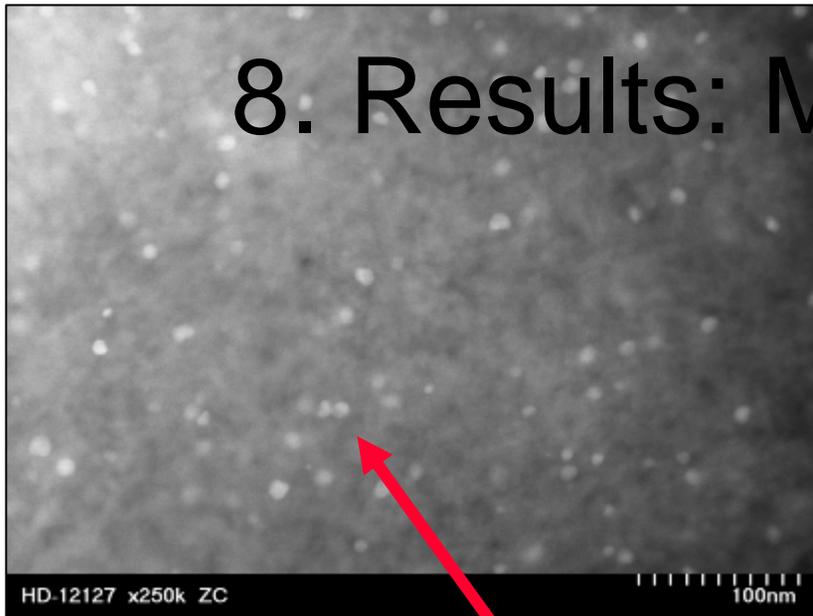


## 8. Results: Microscopy

- Hitachi HD-2000 dedicated Scanning Transmission Electron Microscope (STEM) employed
  - Multivariate Statistical Analysis - analysis procedure for spectral image datasets

9. Fairly uniform distribution spatial and in size of Pt

# 8. Results: Microscopy (cont.)

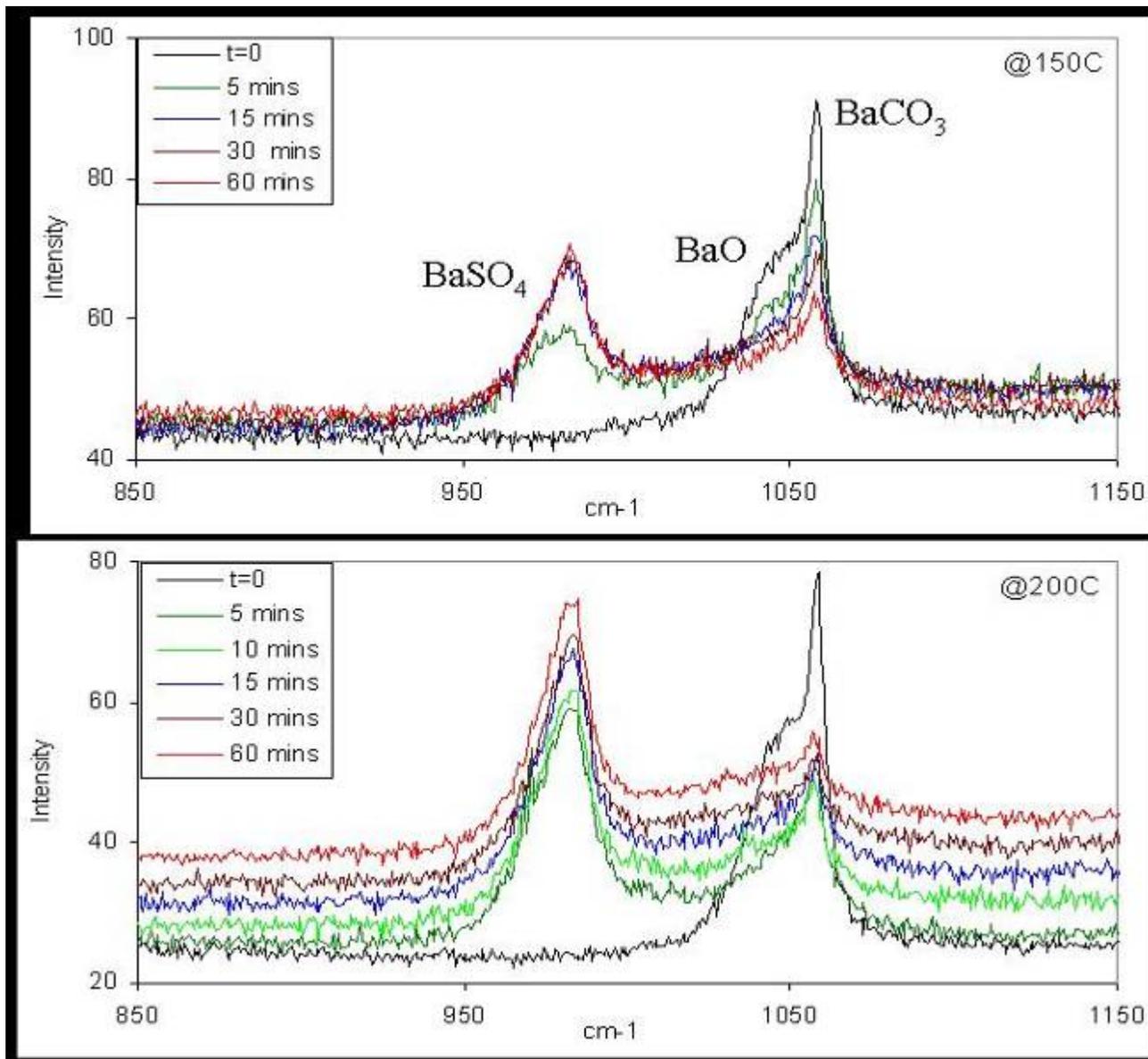


Based on 10 images each

# 10. Results: Spectroscopy

- Techniques employed to characterize the adsorbed species
  - Raman spectroscopy
  - X-ray Photoelectron Spectroscopy (XPS)
- Focus: Raman spectroscopy
  - Raman spectroscopy measures the characteristic vibrational energy levels of molecules and crystals; very sensitive to any changes in bonding, stoichiometry and phase/symmetry

# 11. Sulfation on BaO/1%Pt/Al<sub>2</sub>O<sub>3</sub> with 10 ml/min 1000 ppm SO<sub>2</sub>/air increases with temperature



# Activation Energies (kcal/mol) for Sulfation

<i>O<sub>2</sub> Present?</i>	<i>Pt Present?</i>	<i>BaO</i>	<i>BaCO<sub>3</sub></i>
No	No	17.8	25.4
No	Yes	11.0	17.9
Yes	No	11.6	15.9
Yes	Yes	7.4	13.1

- Pt reduces the activation energy.
- Oxygen reduces the activation energy.
- Sulfation of BaO is easier than BaCO<sub>3</sub>.

# 13. Summary

- Pt particles were not observed to increase along the length of catalyst
- XRD and TEM crystallite size results did NOT agree likely due to the overlapping alumina peaks in the XRD pattern
- Raman spectroscopy was used to monitor sulfation in-situ and calculate activation energies of sulfation

# 14. Acknowledgement

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