Dual Catalyst System for the Reduction of NO with CH_4 Under Lean Conditions

Department of Chemical and Biomolecular Engineering

Heterogeneous Catalysis Research Group

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2005 Review of DOE-ARES University Program

Argonne National Lab – July 12, 2005

Relevance

DOE Advanced Reciprocating Engine Systems Project

Natural gas-fired engines operating under very lean conditions to improve efficiency. Generally used as distributed energy and in pipeline service.

Improve Engine Efficiency
50%

Reduce Operating Costs
10%

Reduce NOx Emissions
90%

Current NOx reduction technologies are unsuitable for these engines.

- NH_3 SCR – Cost effective only on large scale, major infrastructure.
- Automotive TWC – Inactive in excess O_2 conditions.

Approach to Lean Reduction

Two-Stage Catalytic Reduction of NOx

NO Oxidation to NO_2

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

- Thermodynamically limited reaction.

NO_2 Reduction by Hydrocarbon

$$2\,NO_2 + CH_4 \rightarrow N_2 + CO_2 + 2\,H_2O$$

- Reaction must compete with hydrocarbon combustion with O_2.

NO_2 is a stronger oxidizing agent than NO, making it better able to compete with excess oxygen.

Excess oxygen will help to overcome the thermodynamic limitations on the oxidation reaction.

Project Objectives

Develop a two-stage catalytic NO_x reduction scheme active with hydrocarbons in high excess oxygen conditions.

- Design and synthesize NO oxidation and NO_2 reduction catalysts.
- Examine catalyst activity and stability through steady-state reaction experiments.
- Understand catalyst behavior through detailed characterization.

A 3-year university program supported by DOE.

HCRG NO_x Team

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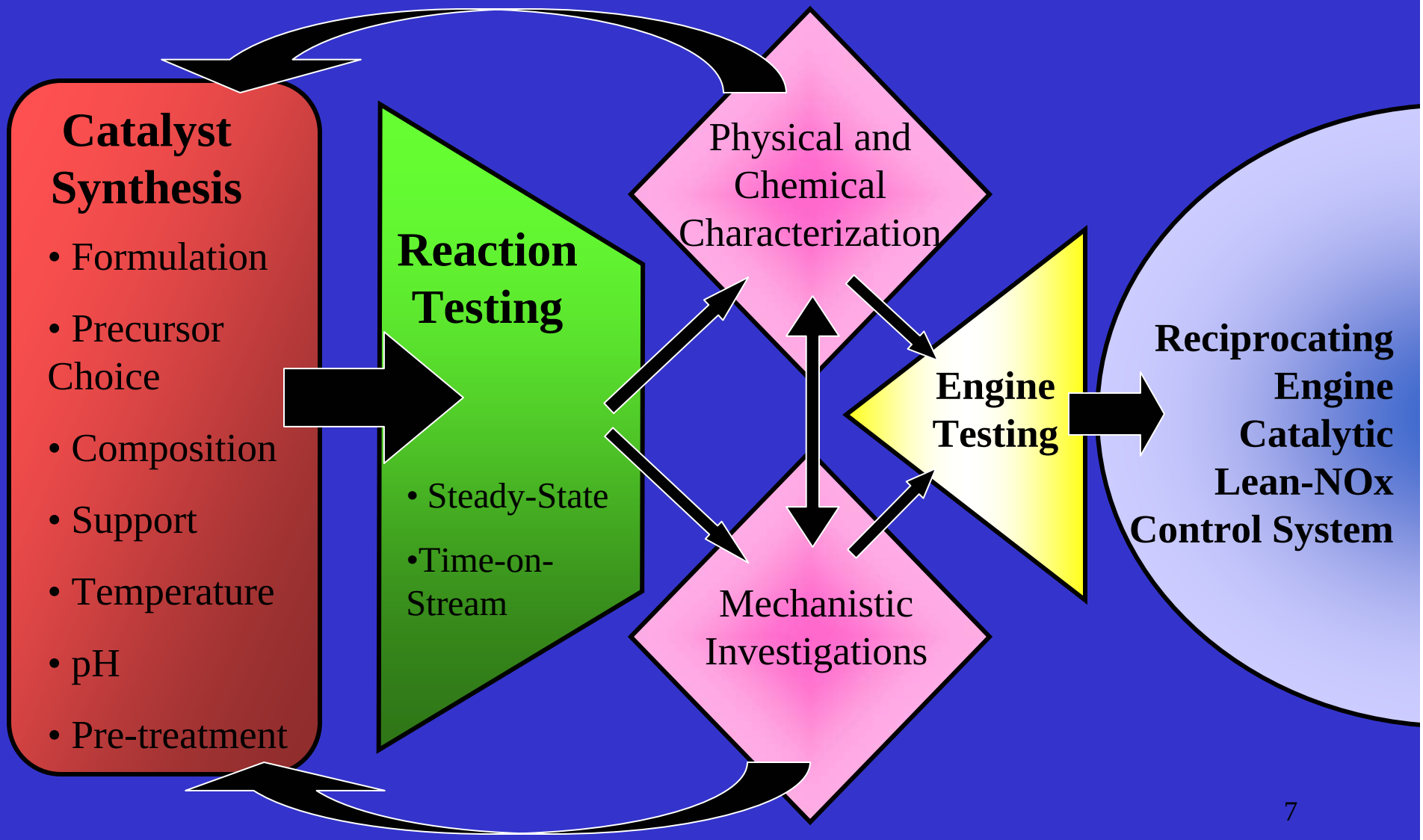
Catalysis Toolbox

- **Reaction experiments (micro or lab-scale reactors)**
  - Activity/selectivity
  - Kinetic parameters
  - Deactivation characteristics
  - Mechanistic studies
  - Online Mass Spectrometry
- **Physical characterization**
  - Surface area
  - Pore volume / pore size distribution
  - Dispersion
  - Particle size
- **Microscopy (SEM, TEM)**
  - Particle size / shape
  - Dispersion
  - Composition
  - Surface morphology
- **Surface characterization**
  - X-ray Photoelectron Spectroscopy (XPS)
  - Secondary Ion Mass Spectroscopy (SIMS)
  - Auger-Electron Spectroscopy (AES)
- **Bulk and structural characterization**
  - X-ray Diffraction (XRD)
  - X-ray Fluorescence (XRF)
  - Energy Dispersive X-ray Analysis (EDXA)
- **Molecular and in-situ characterization**
  - Laser Raman Spectroscopy (LRS)
  - Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)
  - Nuclear Magnetic Resonance (NMR)
  - Electron-spin Resonance (ESR)
- **Adsorption/desorption characterization**
  - Temperature Programmed Reduction (TPR)
  - Temperature Programmed Oxidation (TPO)
  - Temperature Programmed Desorption (TPD)
- **Thermal analysis**
  - Thermo-gravimetric Analysis (TGA)
  - Differential Thermal Analysis (DTA)
  - Differential Scanning Calorimetry (DSC)

An Iterative Approach



Catalyst Synthesis

Incipient Wetness Impregnation

- Pore volume addition of aqueous metal salt solution.

Sol-gel Synthesis

- Hydrolysis of metal alkoxide precursors.
- Atomic scale mixing of catalyst components.

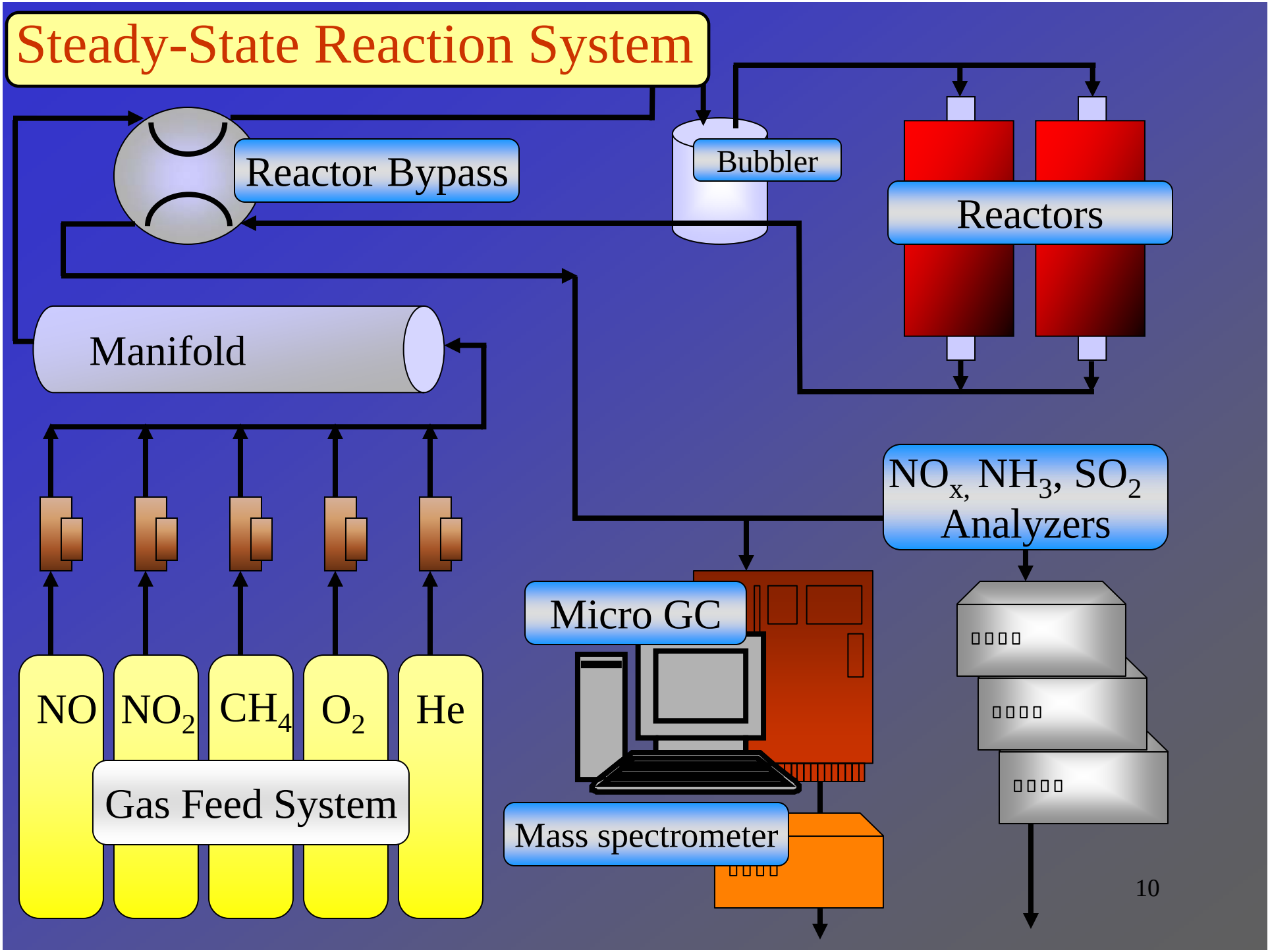
Precursors

- Cobalt nitrate, silver nitrate, palladium acetate, titanium isopropoxide.

Analytical System

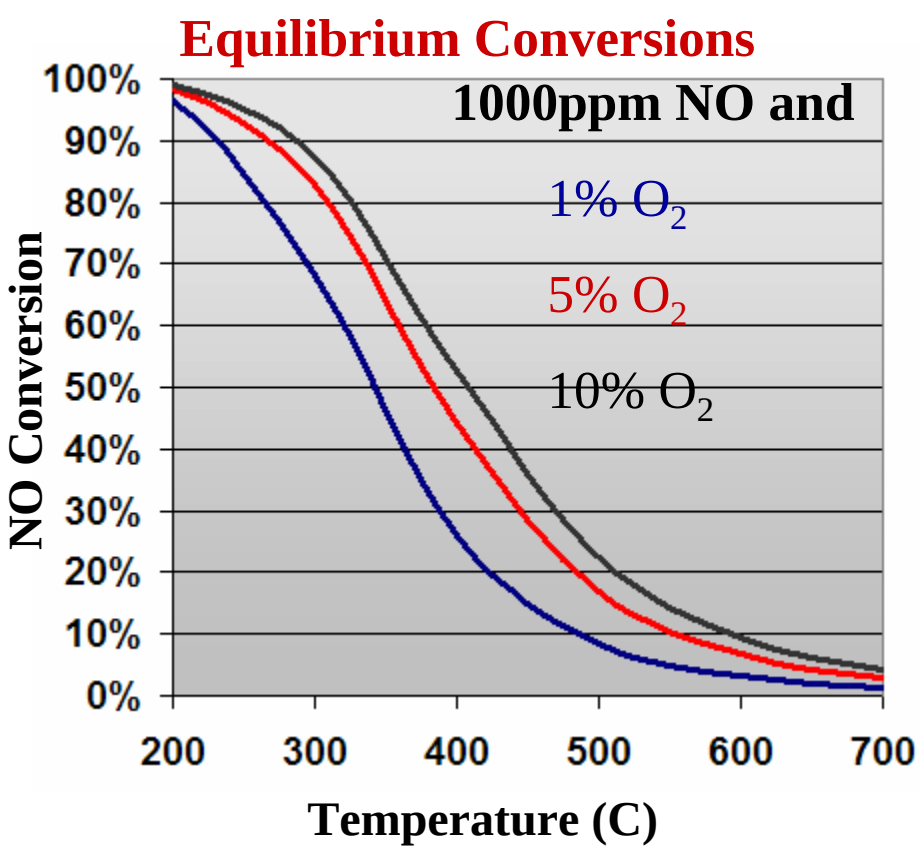
- Thermo Environmental Chemiluminescence NO_x Analyzer
- Thermo Environmental Pulsed Fluorescence SO_2 Analyzer
- Siemens Infrared NH_3 Analyzer
- Varian CP-4900 Micro Gas Chromatograph
- Thermoelectron Quadrupole Mass spectrometer

Steady-State Reaction System



Major Accomplishments and Progress

NO Oxidation to NO_2



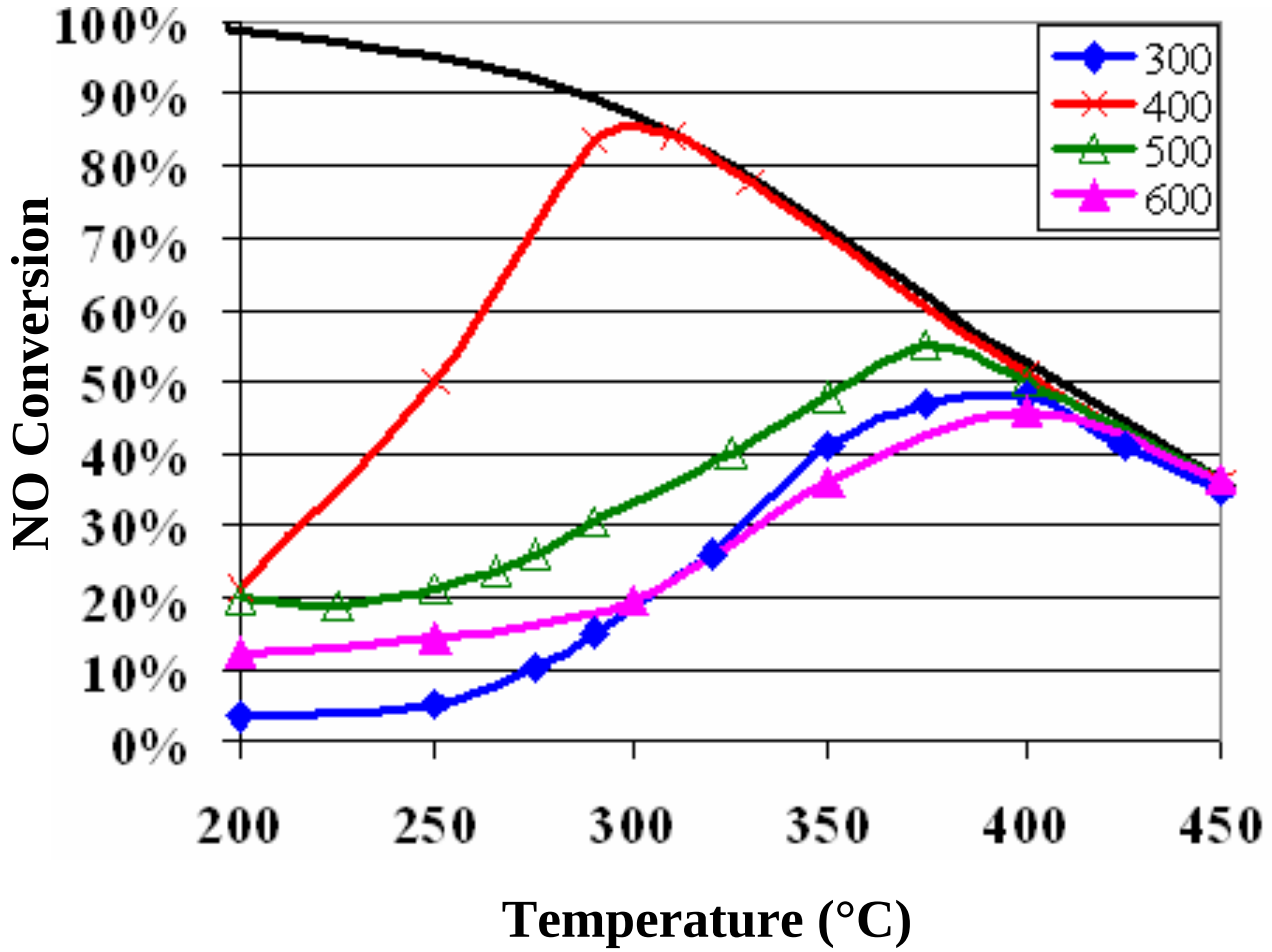
NO oxidation is an exothermic reaction and thus thermodynamically limited at high temperatures. High conversion will then require good activity at low temperatures.

Effect of Calcination Temperature

10%Co/TiO_2

Calcination Temperature

Sol-Gel Synthesis



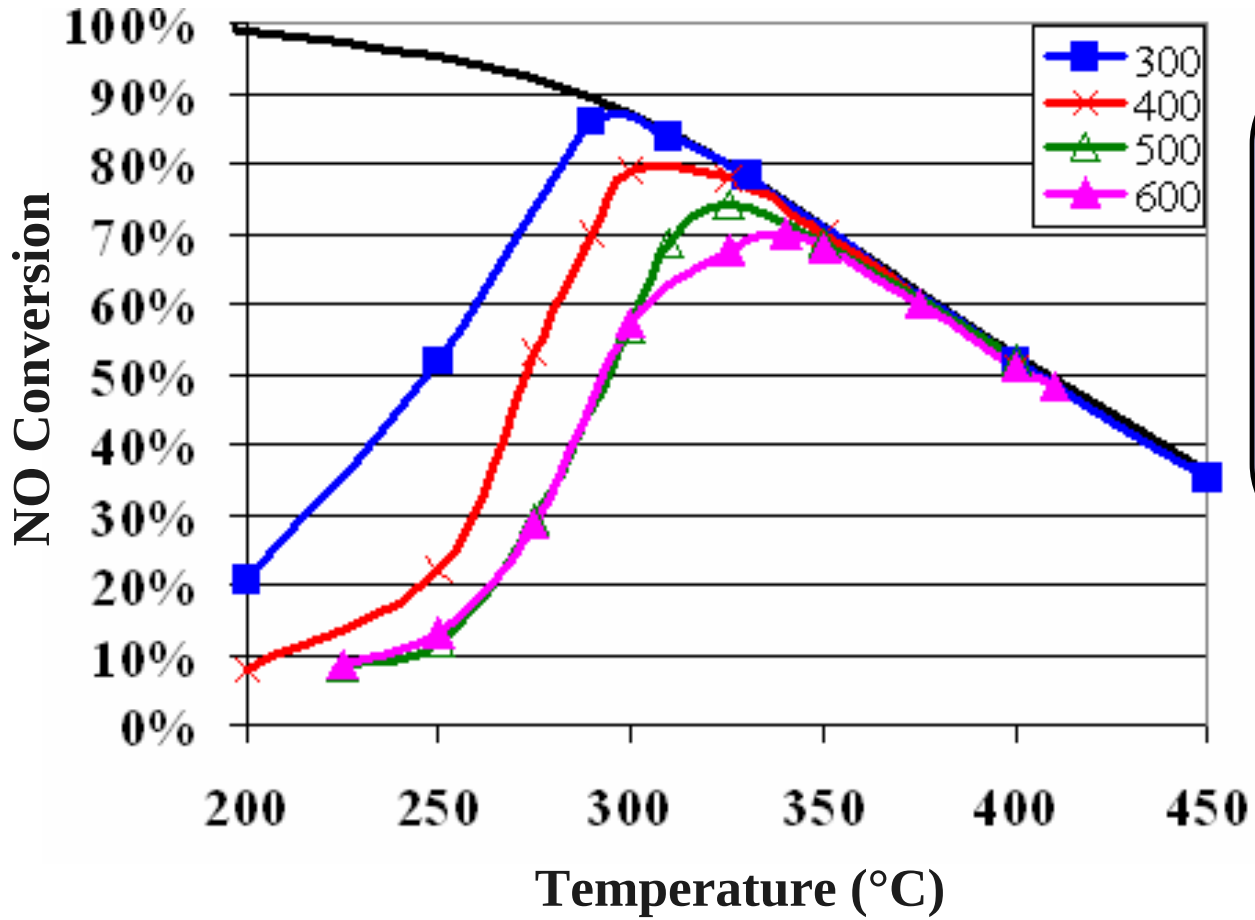
Except for the catalyst calcined at 300°C, the trend shows decreased reaction performance with increased calcination temperature.

1000ppm NO
10% O_2

Effect of Calcination Temperature

10%Co/TiO_2

Calcination Temperature



Incipient Wetness Synthesis

Reaction performance shows a decline when the synthesis calcination temperature is increased.

1000ppm NO
10% O_2

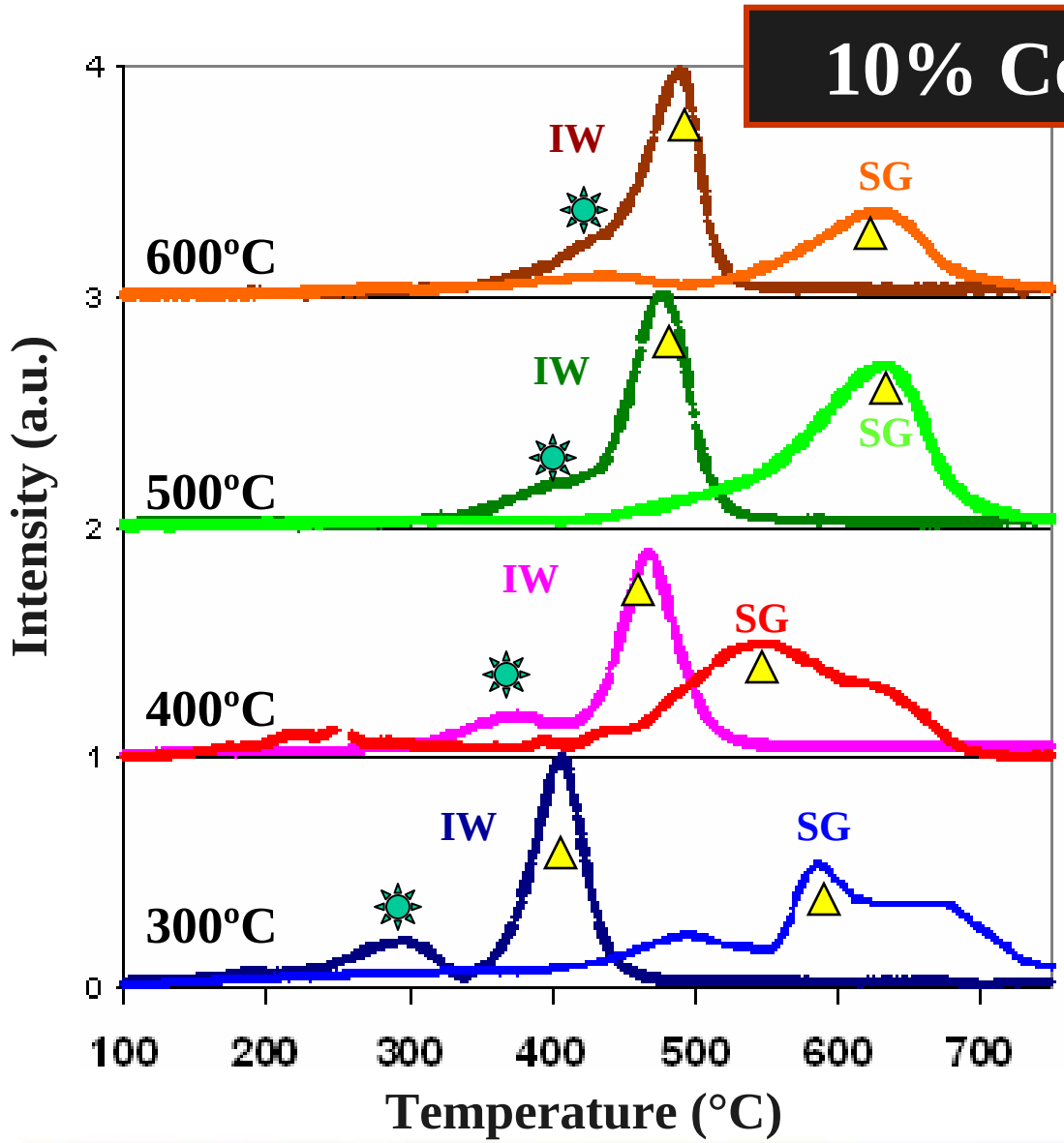
Temperature Programmed Reduction

- 5% H_2/He
- 10ºC/min
- Reducibility / accessibility to oxygen of supported metal.
- Measure H_2 consumption as a function of temperature.

Experimental

Oxidize at 300ºC in O_2; cool under N_2; ramp at 10ºC/min; reduce in 5% H_2; monitor signal by TCD.

Temperature Programmed Reduction



$Co^{3+} \rightarrow Co^{2+}$

$Co^{2+} \rightarrow Co^{0}$

- Increased calcination creates stronger metal-support interaction.
- Co^{3+} peak is most prominent on catalyst calcined at 300ºC and decreases with increasing calcination temperature.

X-ray Photoelectron Spectroscopy

XPS is a highly surface sensitive technique (10-50 Å) that yields chemical environment and oxidation state information on surface atoms.

- AXIS Ultra XPS Unit.
- Al (Mono) X-ray Source.
- Controlled atmosphere transfer capability.
- Charge balancing on C 1s peak.

XPS – Co $2p_{3/2}$

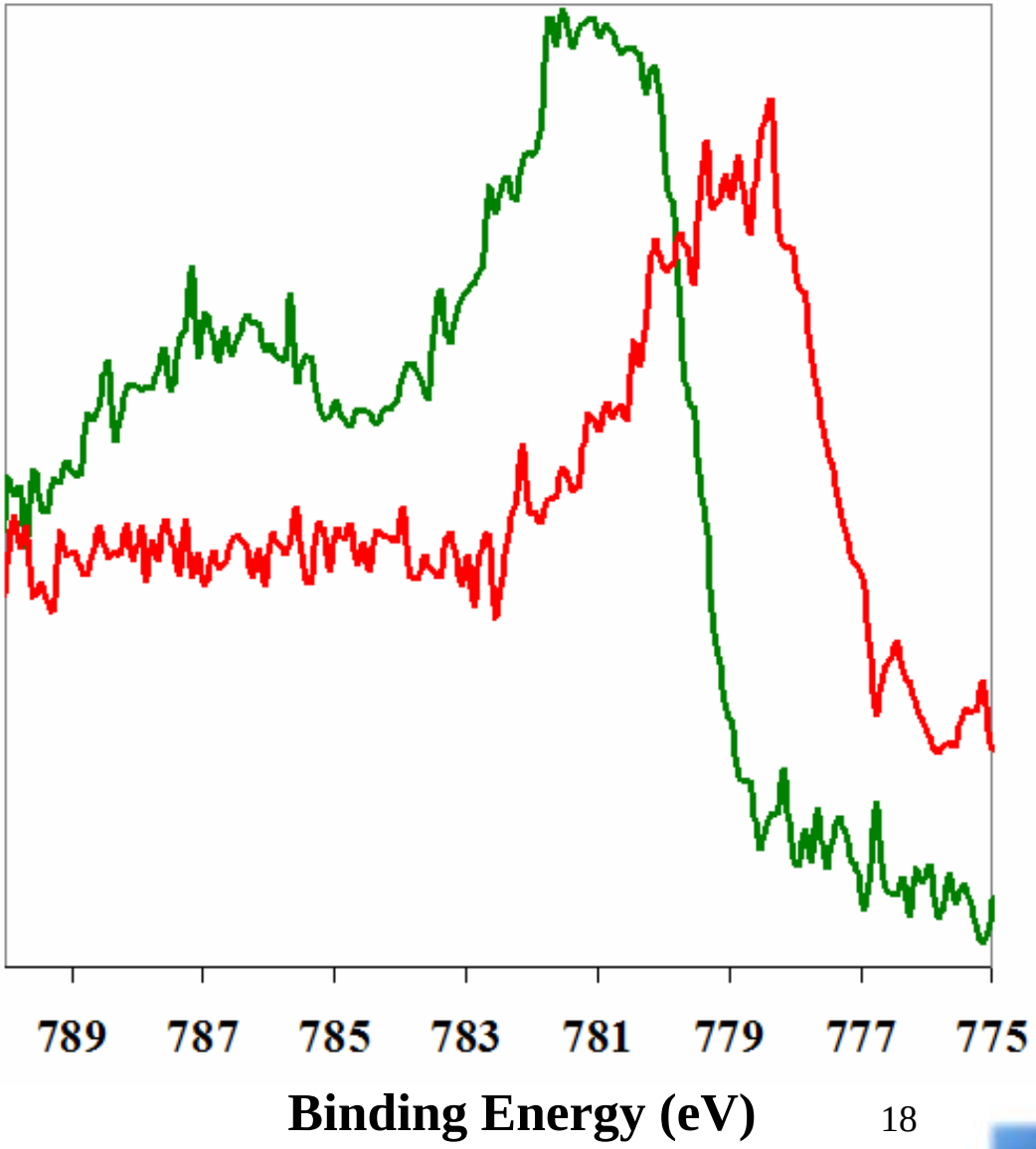
- **10%Co/TiO_2 SG300**

  781.0 eV – CoO (2+)

  786.7 eV – Shake-up effect

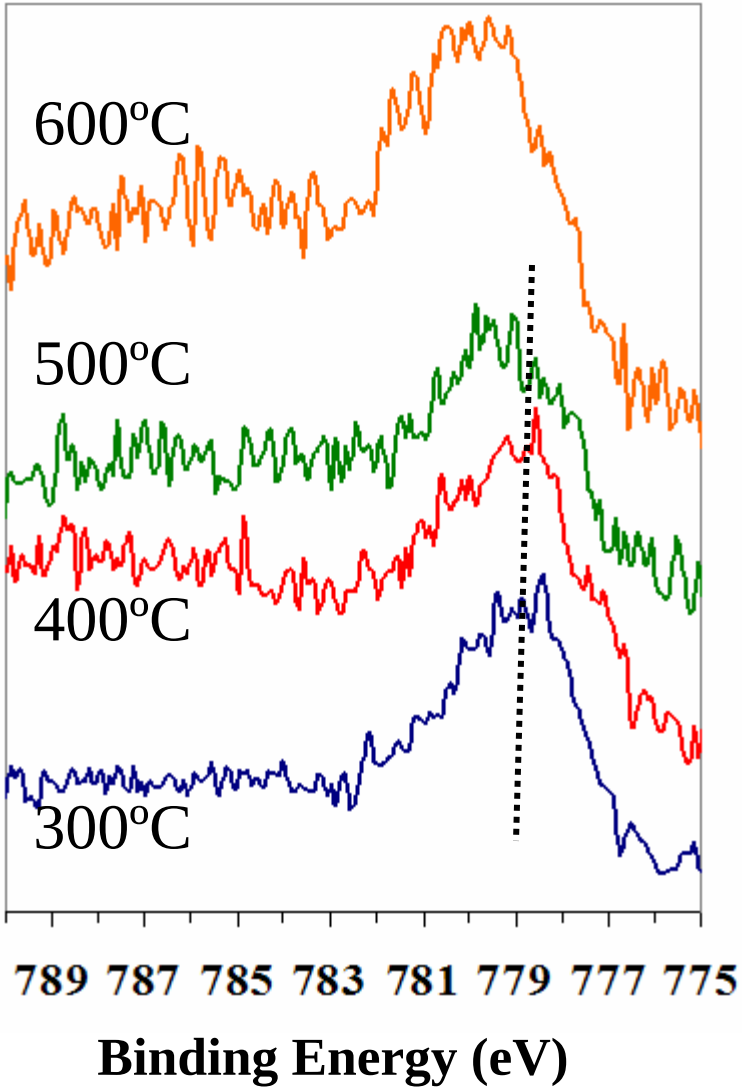
- **10%Co/TiO_2 IW300**

  778.5 eV – Co_3O_4 (3+)

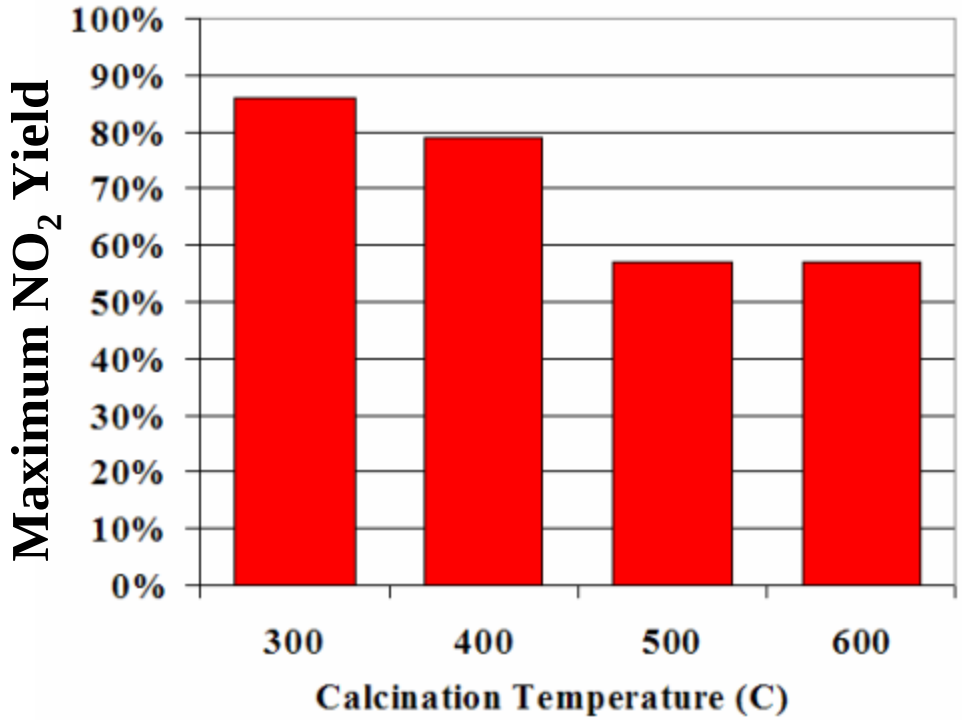


XPS – Co $2p_{3/2}$

Calcination T



10%Co/TiO_2 IW



1000 ppm NO

10% O_2

Thermogravimetric Analysis

Thermogravimetric analysis allow for the quantitative determination of mass changes associated with both surface and bulk effects. Mass changes due to adsorption, desorption, precursor decomposition, and crystallographic phase changes can all be observed.

Perkin-Elmer TGA 7

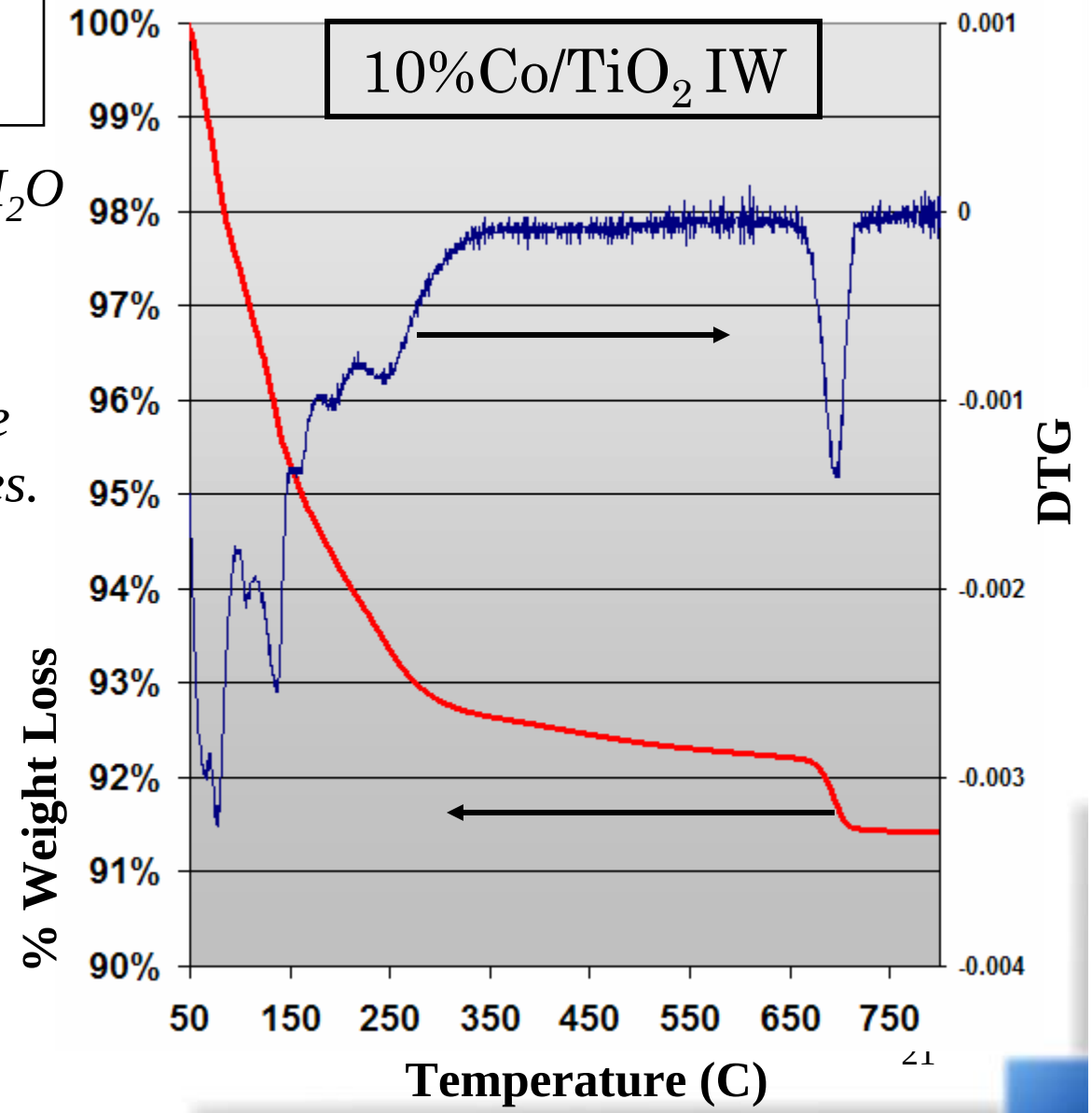
Maximum Temperature 1100C

TGA Calcination – 10%Co/TiO_2 IW

Calcined in Air
10°C/min

Initial weight loss due to H_2O loss and precursor decomposition.

Additional feature above 650°C due to bulk changes.



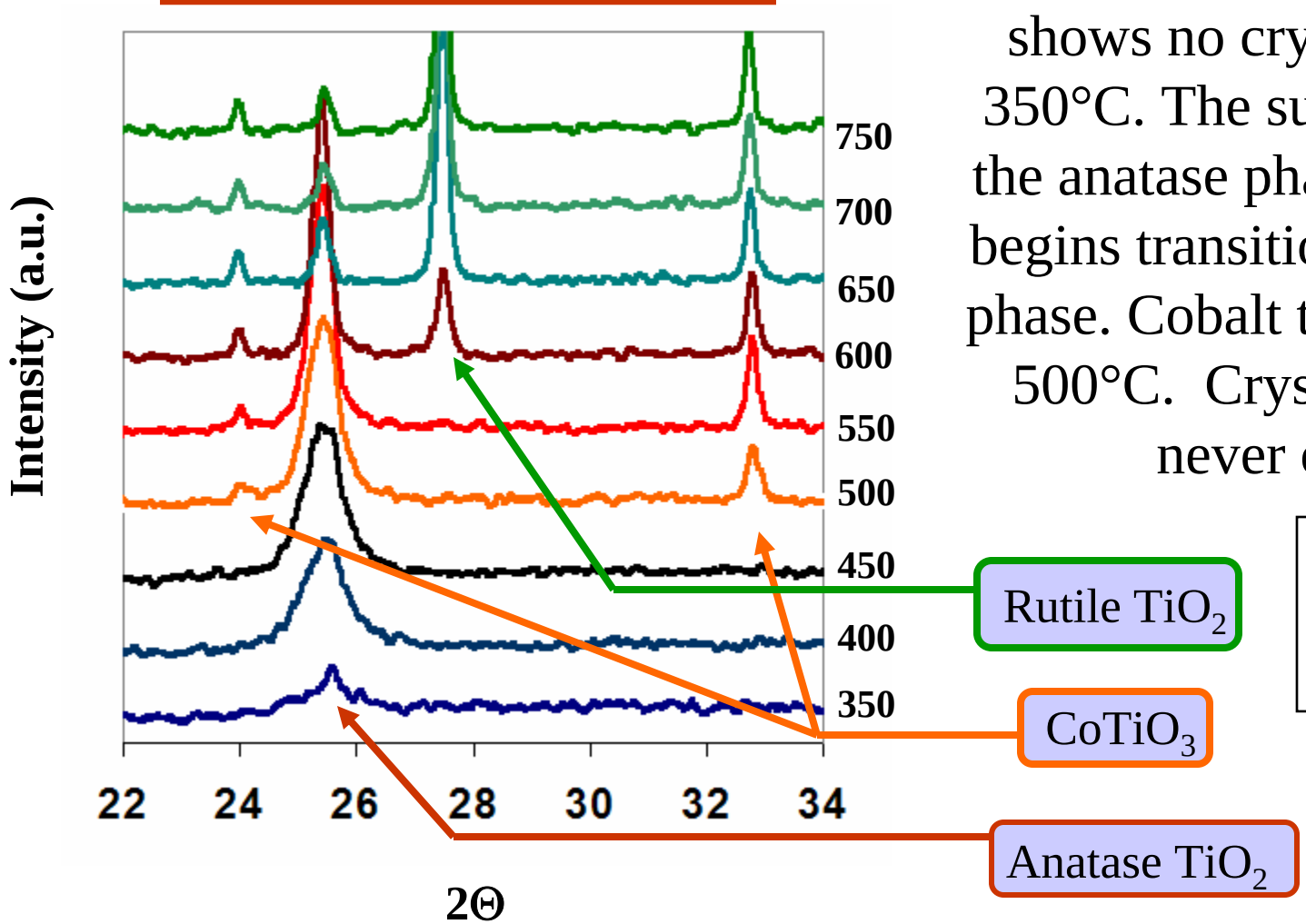
X-ray Powder Diffraction

X-ray powder diffraction is used for the detection and identification of bulk crystalline phases within the catalyst. With controlled atmosphere and temperature capability analysis of structural changes during synthesis can be examined.

- Bruker D8 Advance diffractometer.
- Cu Kα X-ray source.
- Position sensitive detector.
- Controlled atmosphere capability.
- Cryogenic to 1200 °C temperature programmed analysis

In-Situ XRD During Calcination

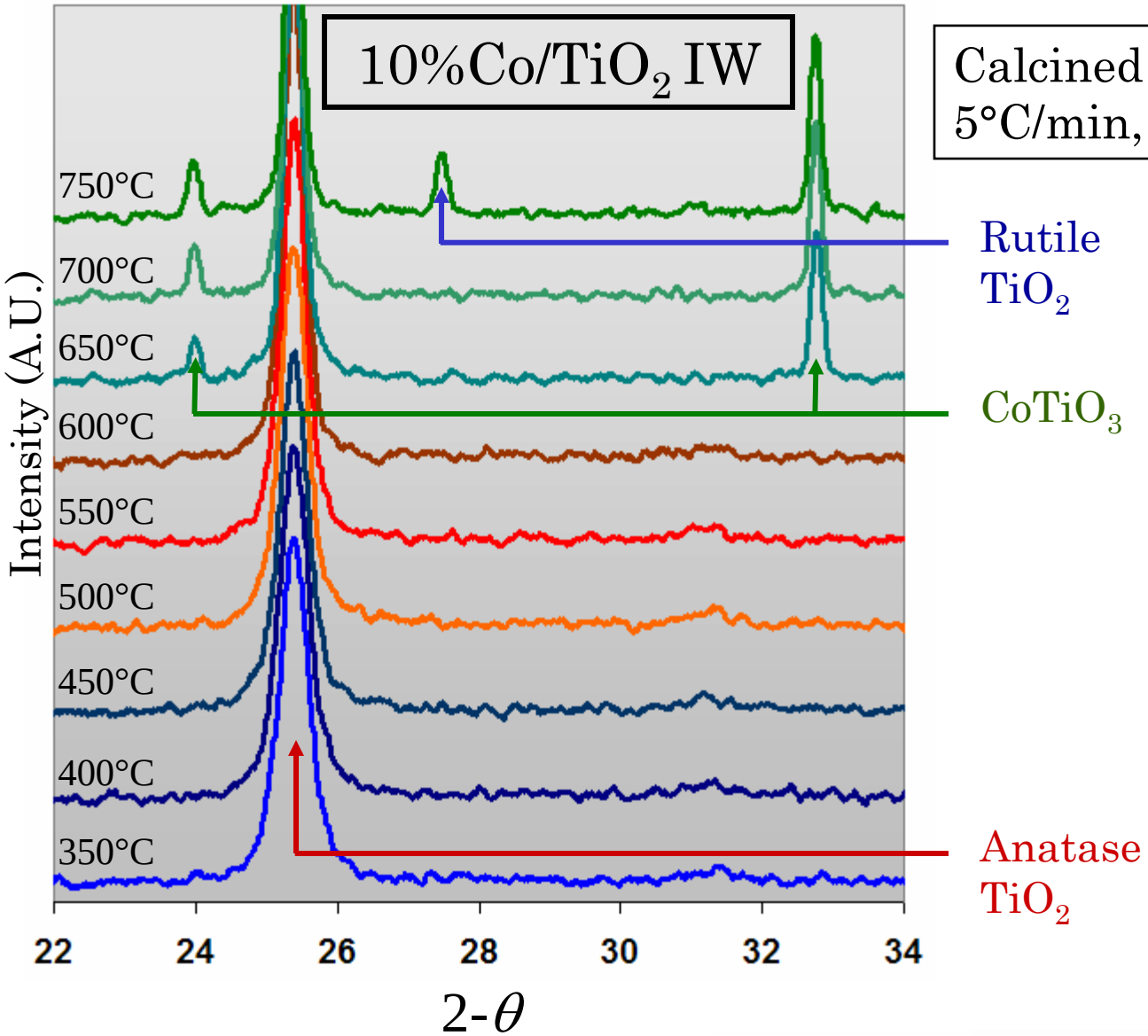
10% Co/TiO_2 SG



Sol-gel prepared Co/TiO_2 shows no crystallinity below 350°C. The support first forms the anatase phase, and at 600°C begins transitioning to the rutile phase. Cobalt titanate appears at 500°C. Crystalline cobalt is never observed.

Calcined in Air
5°C/min
Scans at 50°C

In-Situ XRD During Calcination



Calcined in Air
5°C/min, Scans at 50°C.

Co/TiO_2 prepared by incipient wetness shows the anatase form of the commercial support at all temperatures, with a small amount of rutile TiO_2 observed at 750°C. The formation of cobalt titanate is seen at 650°C.

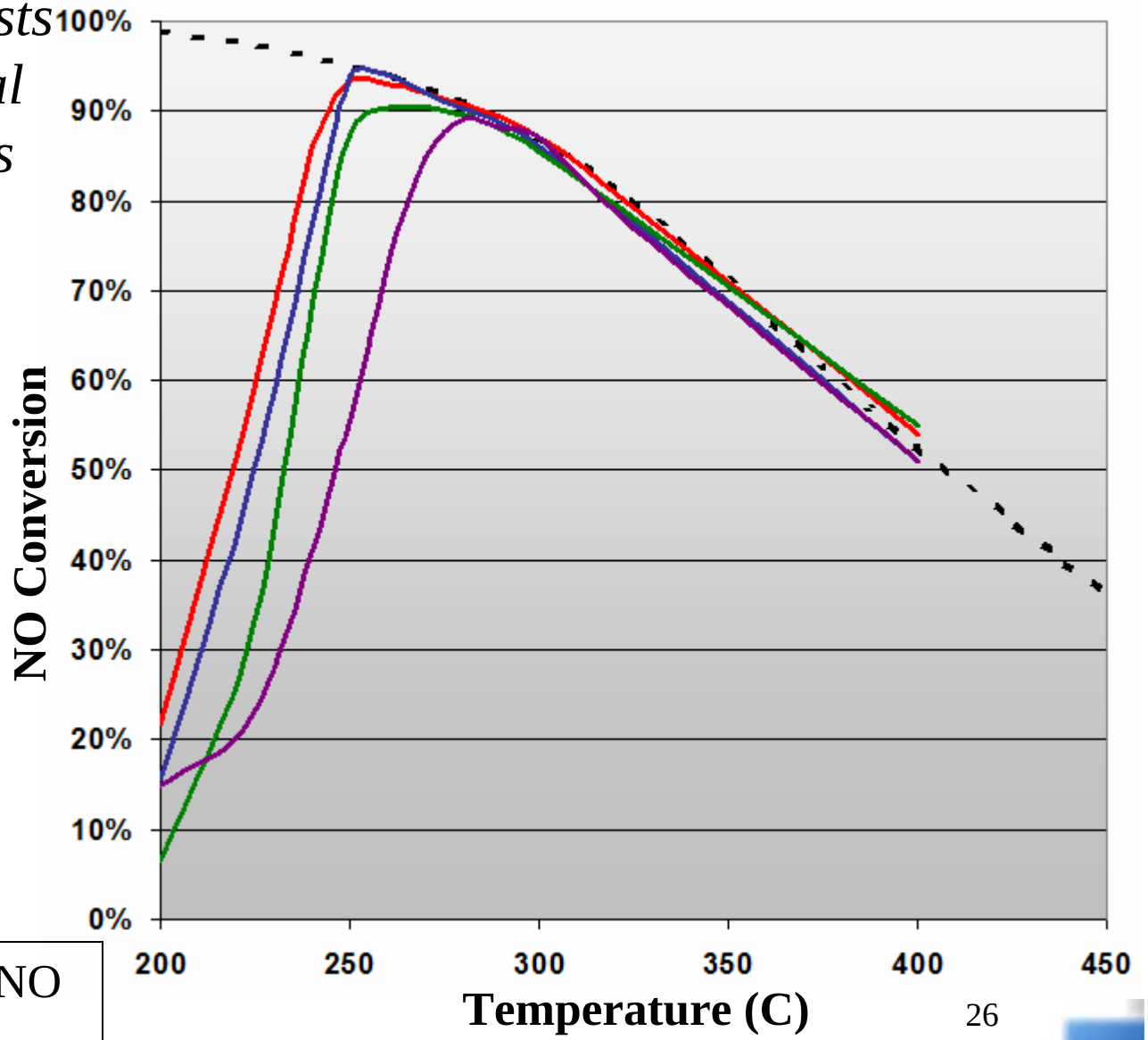
New formulations for NO oxidation catalyst

NO Oxidation – 10%Co/ZrO_2

10%Co/ZrO_2 catalysts show better thermal stability, as well as higher oxidation activity.

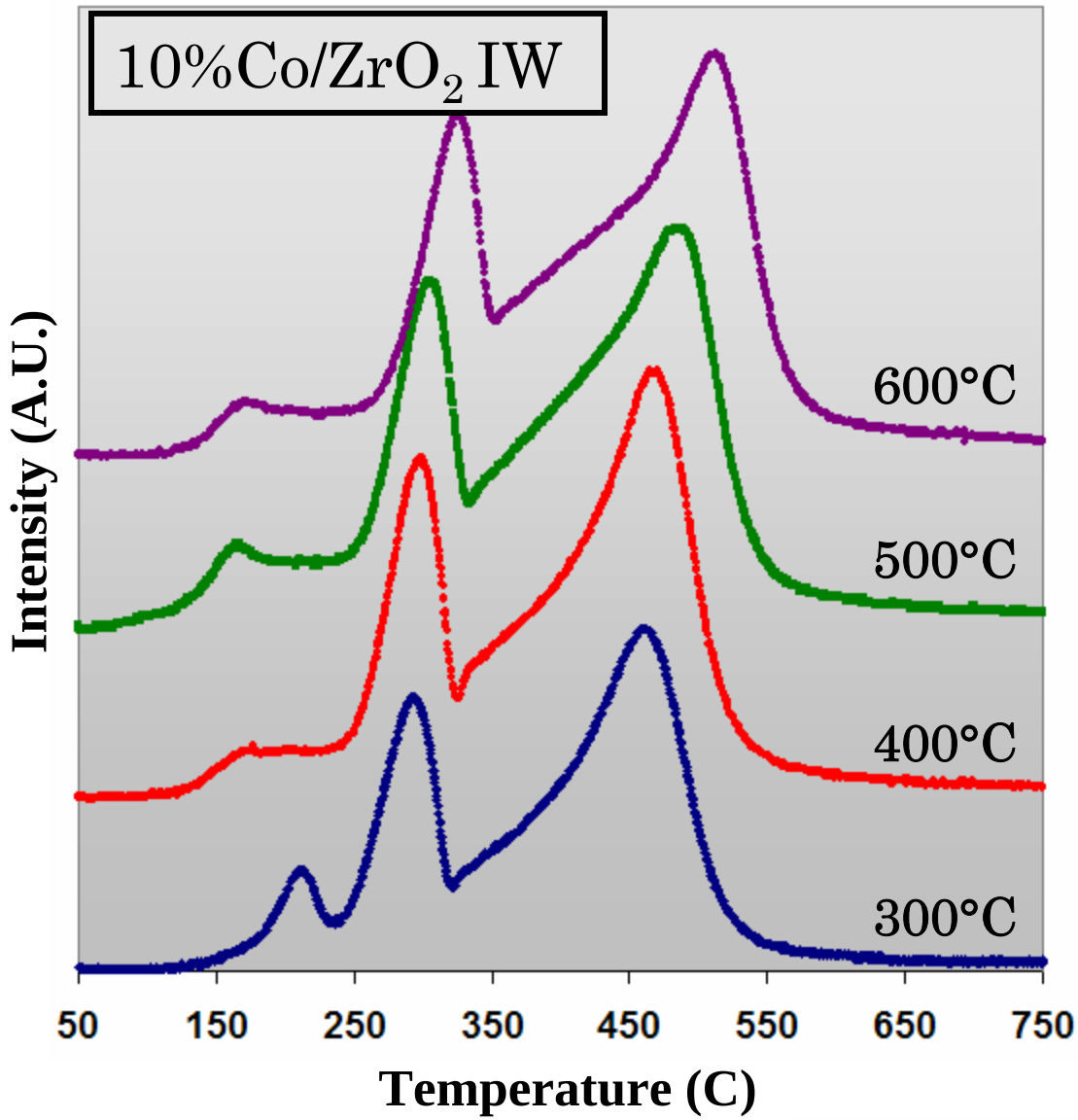
Temp (C)	S.A. (m^2/g)
300	43
400	42
500	41
600	37

- 10%Co/ZrO_2 300
- 10%Co/ZrO_2 400
- 10%Co/ZrO_2 500
- 10%Co/ZrO_2 600



1000ppm NO
10% O_2

TPR – 10%Co/ZrO_2



Over 10%Co/ZrO_2 the low temperature Co^{3+} reduction feature is much more prominent and is stable with increasing calcination temperature.

Reduced in 5% O_2
10°C/min

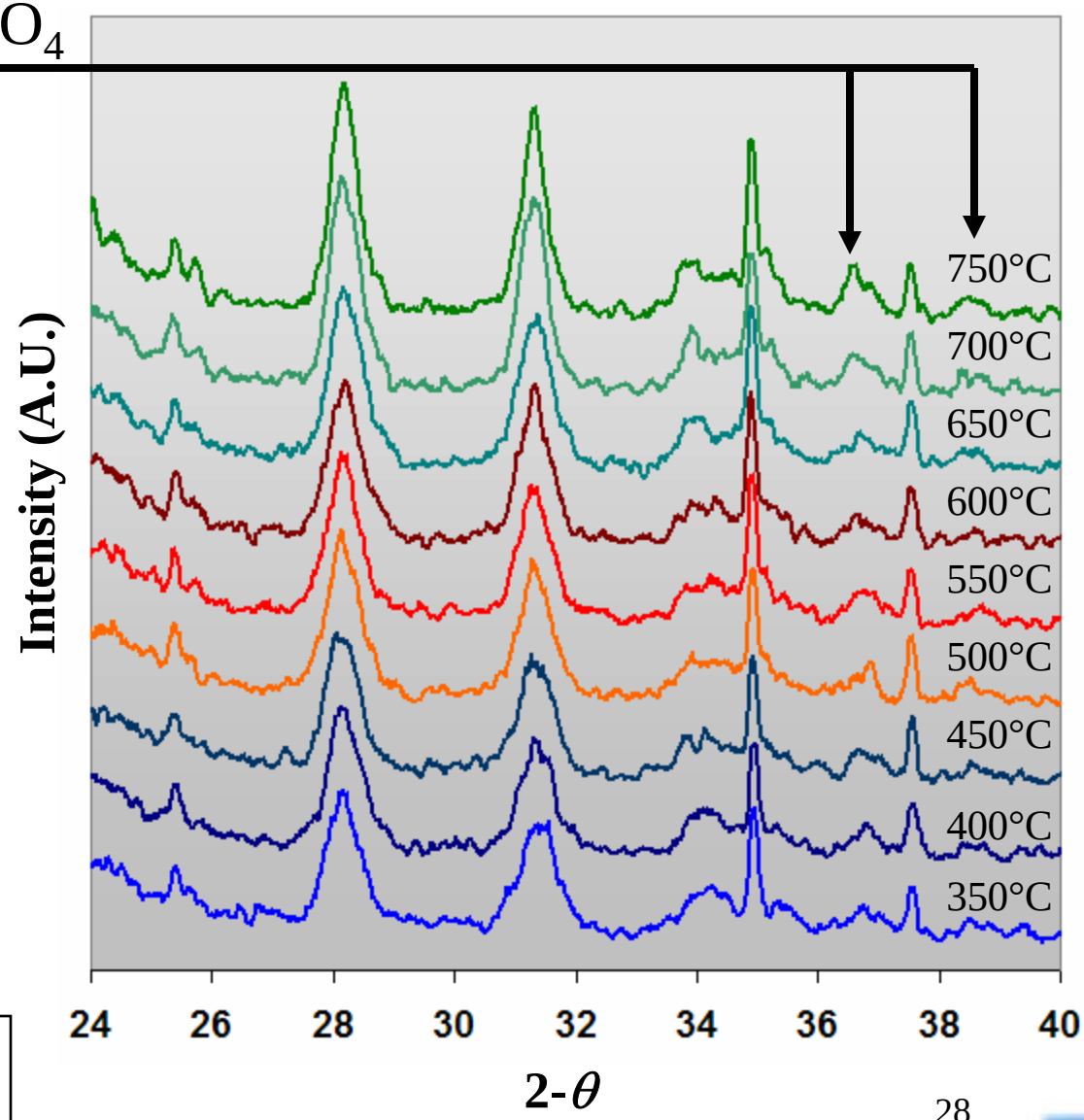
In-Situ XRD During Calcination

10%Co/ZrO_2 IW

Co_3O_4

In-situ X-ray diffraction during calcination demonstrates stable monoclinic zirconia, but also visible are peaks from Co_3O_4.

This indicates the formation of larger Co clusters on the ZrO_2 support as compared with TiO_2.



Calcined in Air
5°C/min, Scans at 50°C.

NO Oxidation Catalyst Development

Summary

- ***We have developed very active and stable NO oxidation catalysts based on Co-oxides.***

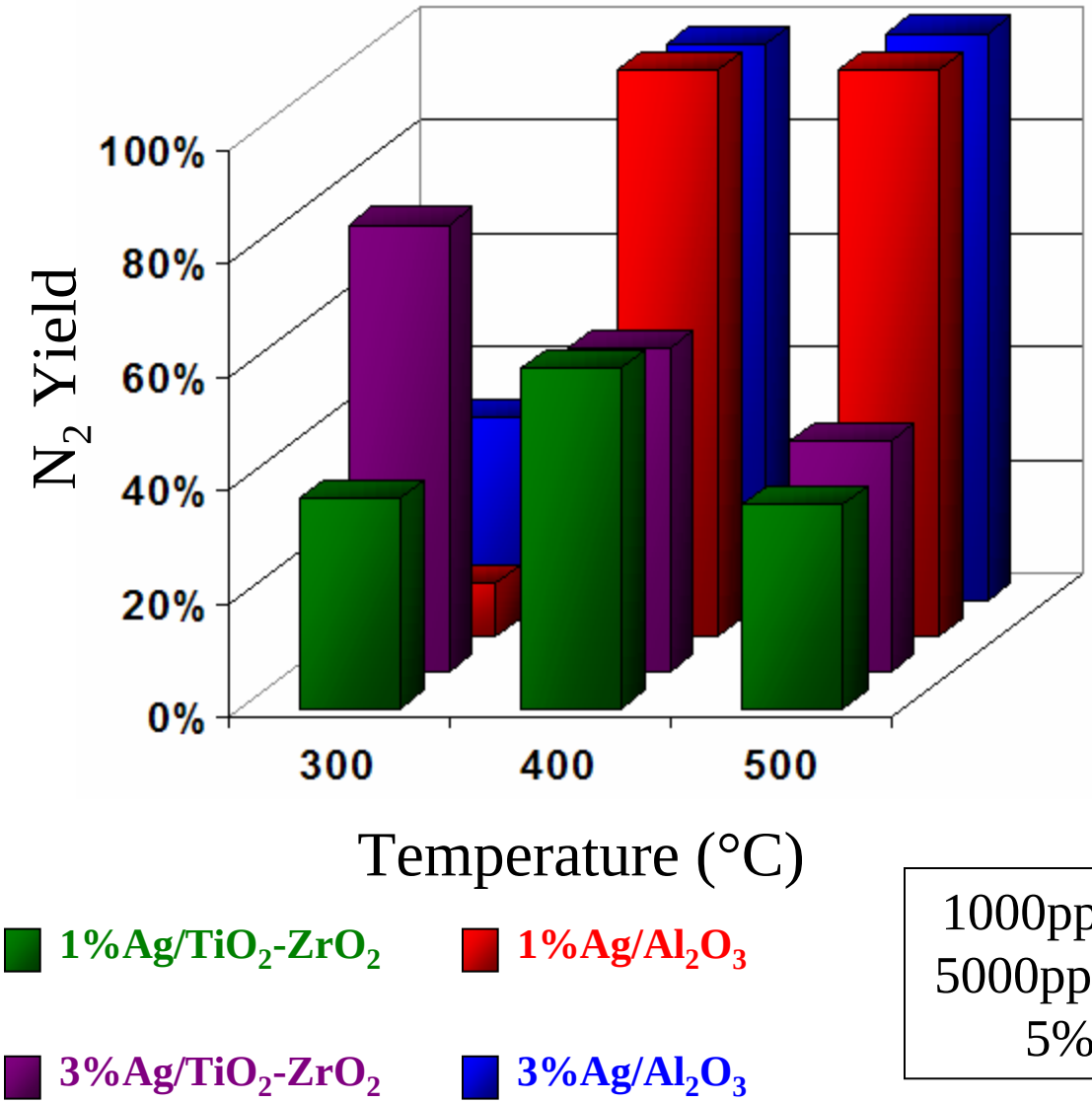
- ***The catalysts have high intrinsic activity even at temperatures as low as 250°C and high thermal stability.***

Catalyst development for NO_2 Reduction

Development of NO_2 Reduction Catalysts

- Low loadings of transition metals, particularly Ag, and Co, have been shown to have NO_x reduction activity with hydrocarbons. (2-6% O_2)
- Catalysts designed with metal oxide supports because of good mechanical and hydrothermal stability.
- Several lower hydrocarbons examined.

NO_2 Reduction with C_3H_6

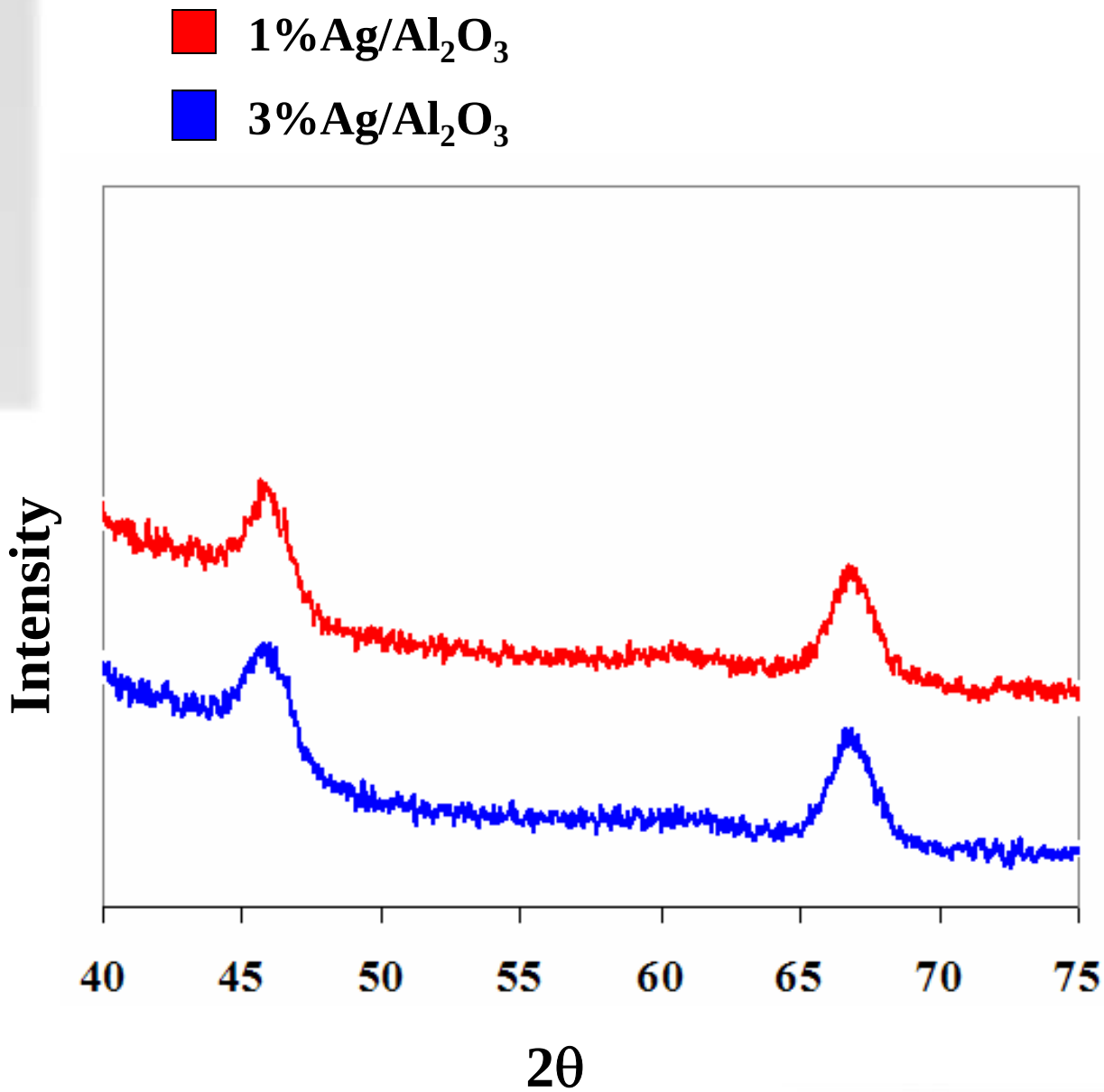


Ag-based catalysts supported on both Al_2O_3 and at TiO_2-ZrO_2 mixed oxide were shown to be active for the reduction of NO_2 with propene.

1% and 3%Ag/Al_2O_3 were most active, achieving over 95% N_2 yields at 400°C.

1000ppm NO_2
5000ppm C_3H_6
5% O_2

XRD – Ag/TiO_2



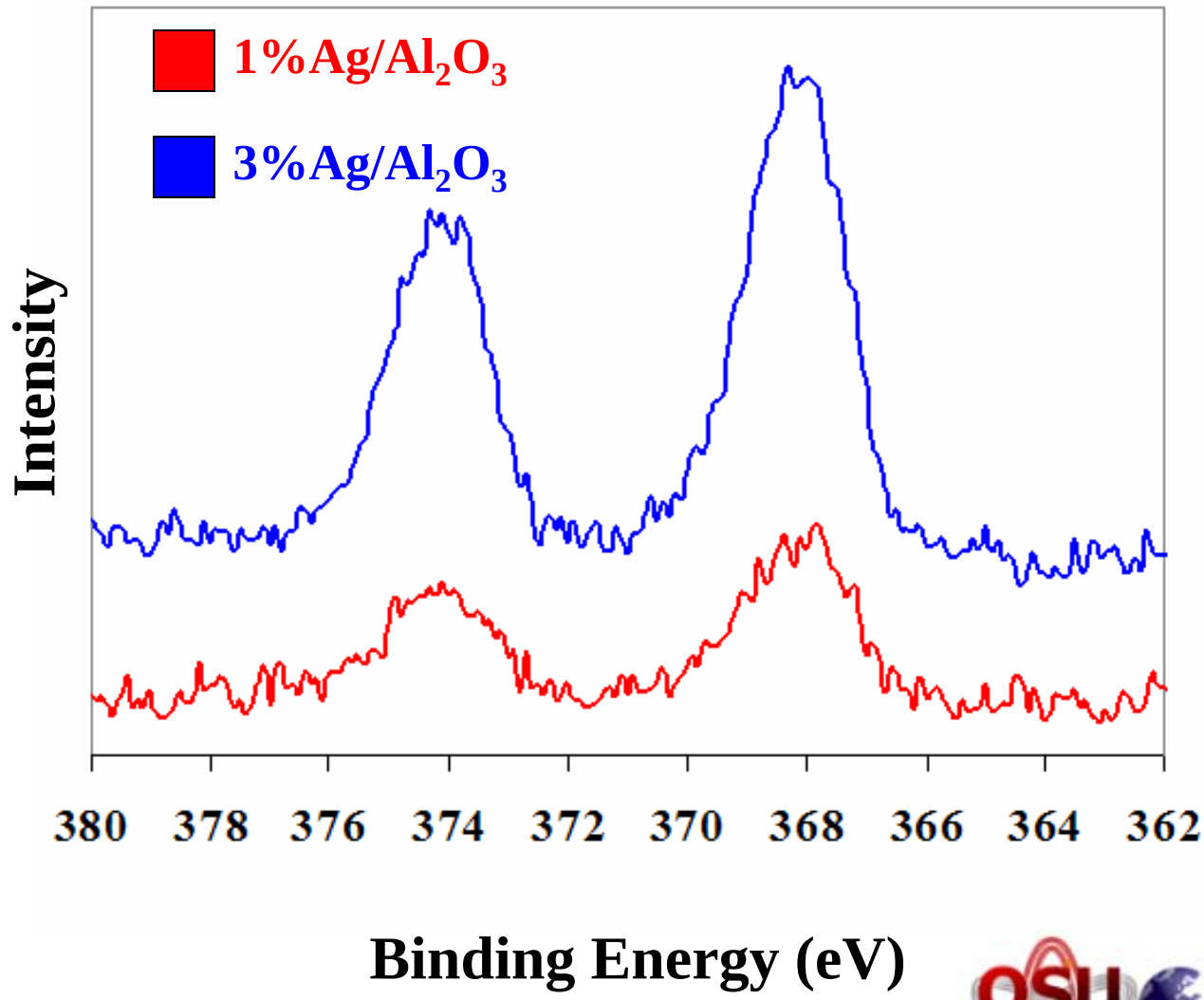
XRD structural characterization of the the active Ag/Al_2O_3 catalysts showed no crystalline Ag species, indicating that Ag is well dispersed over the surface of the catalyst.

Only gamma alumina is observed.

XPS – Ag 3d Region

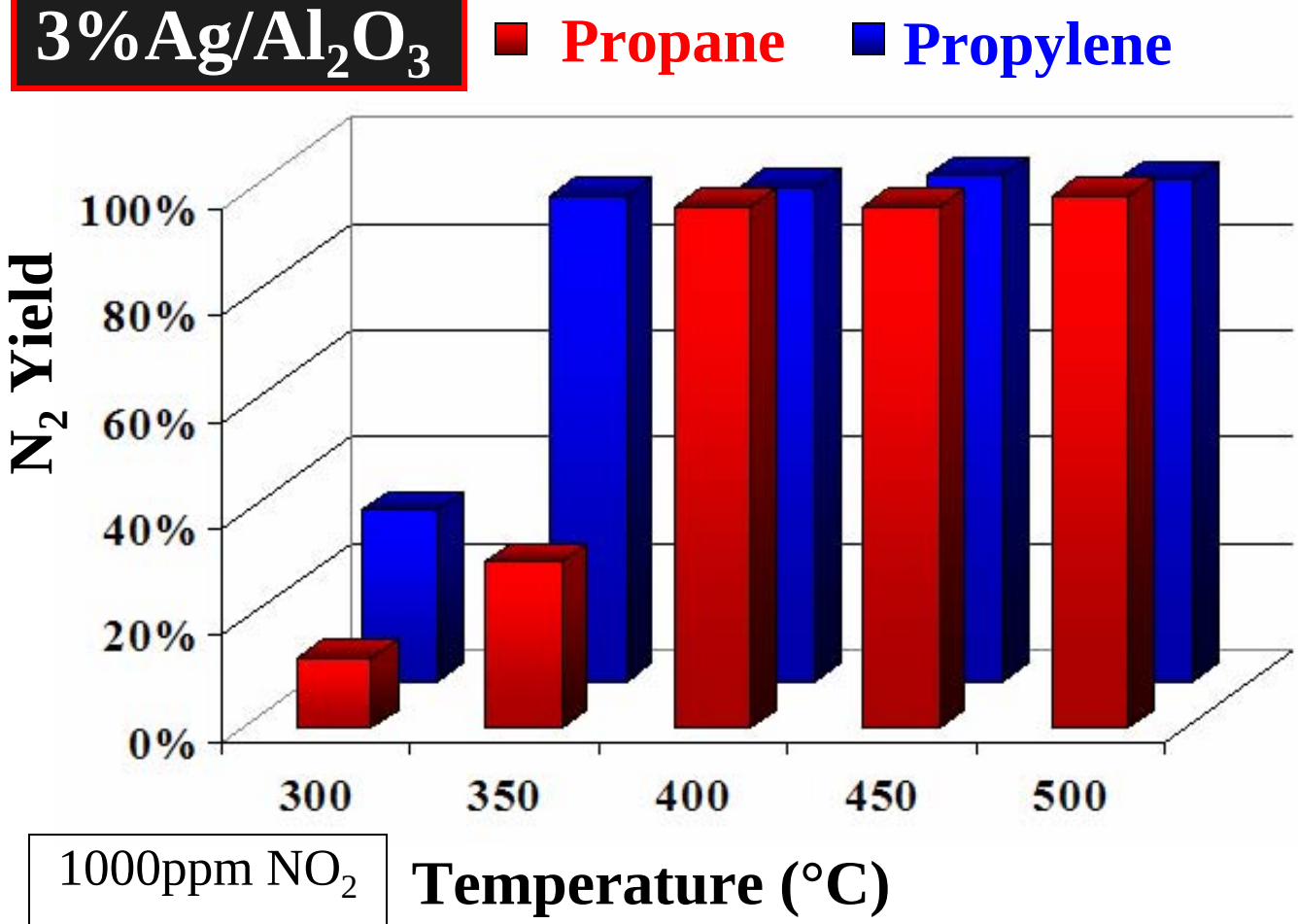
Surface analysis by XPS indicates that only one Ag phase is present on the Ag/Al_2O_3 catalysts. The binding energy of this species indicates that it is an oxide.

As expected the 3%Ag sample shows a larger intensity.



NO_2 Reduction over Ag/Al_2O_3

3%Ag/Al_2O_3



1000ppm NO_2
5000ppm HC
5% O_2

A more detailed comparison of NO_2 reduction activity with propane and propene was performed over 3%Ag/Al_2O_3.

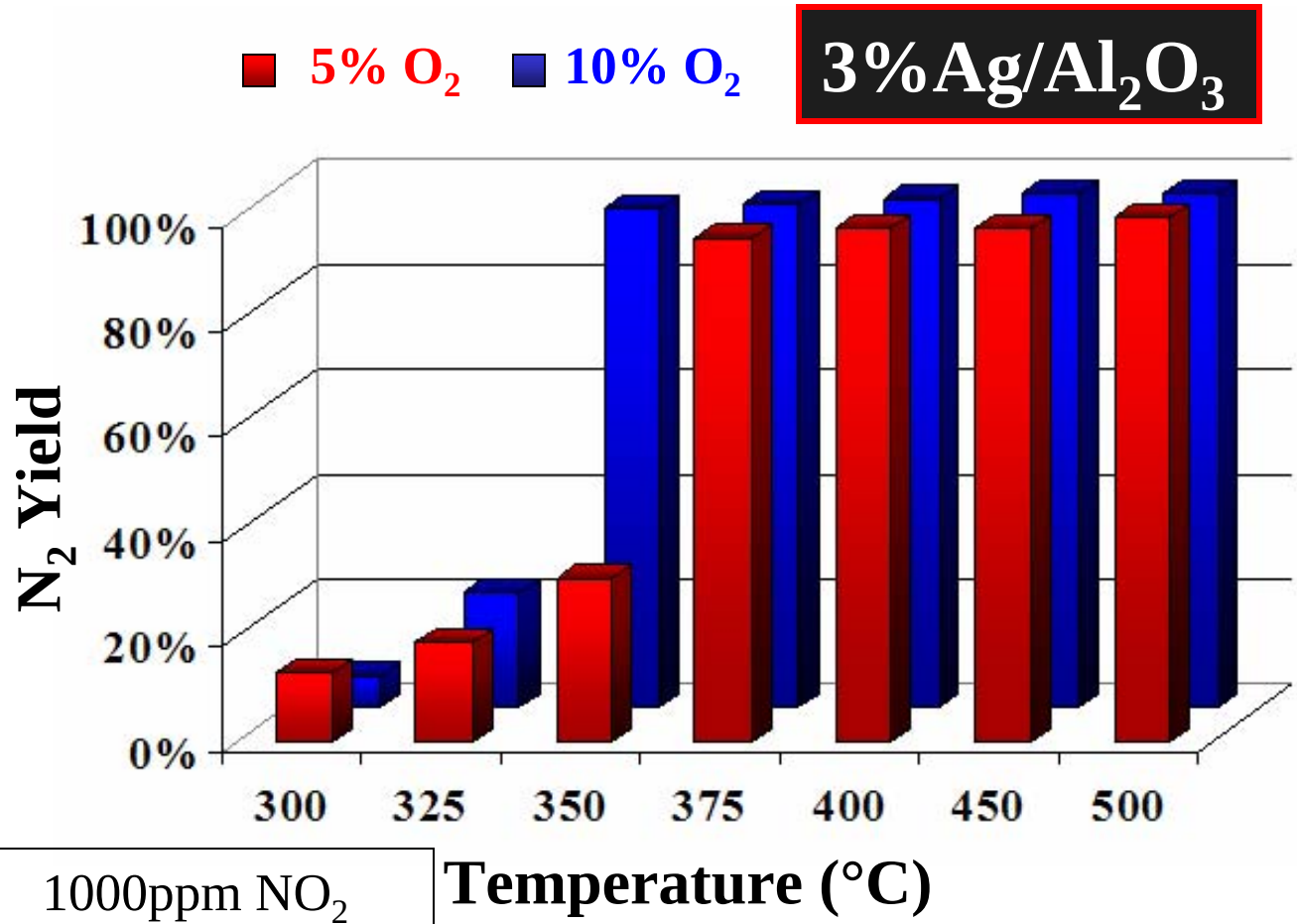
Propene lights off at lower temperature, but by 400°C activities are similar.

Slightly higher low temperature yields are observed with increased Ag loading.

NO_2 Reduction over Ag/Al_2O_3

A comparison of different reactant O_2 concentrations demonstrated that Ag/Al_2O_3 is capable of achieving above 90% N_2 yield in 10% O_2.

In fact performance at 350°C increased dramatically with increased O_2 concentration.



1000ppm NO_2

5000ppm C_3H_8

5% or 10% O_2

Summary

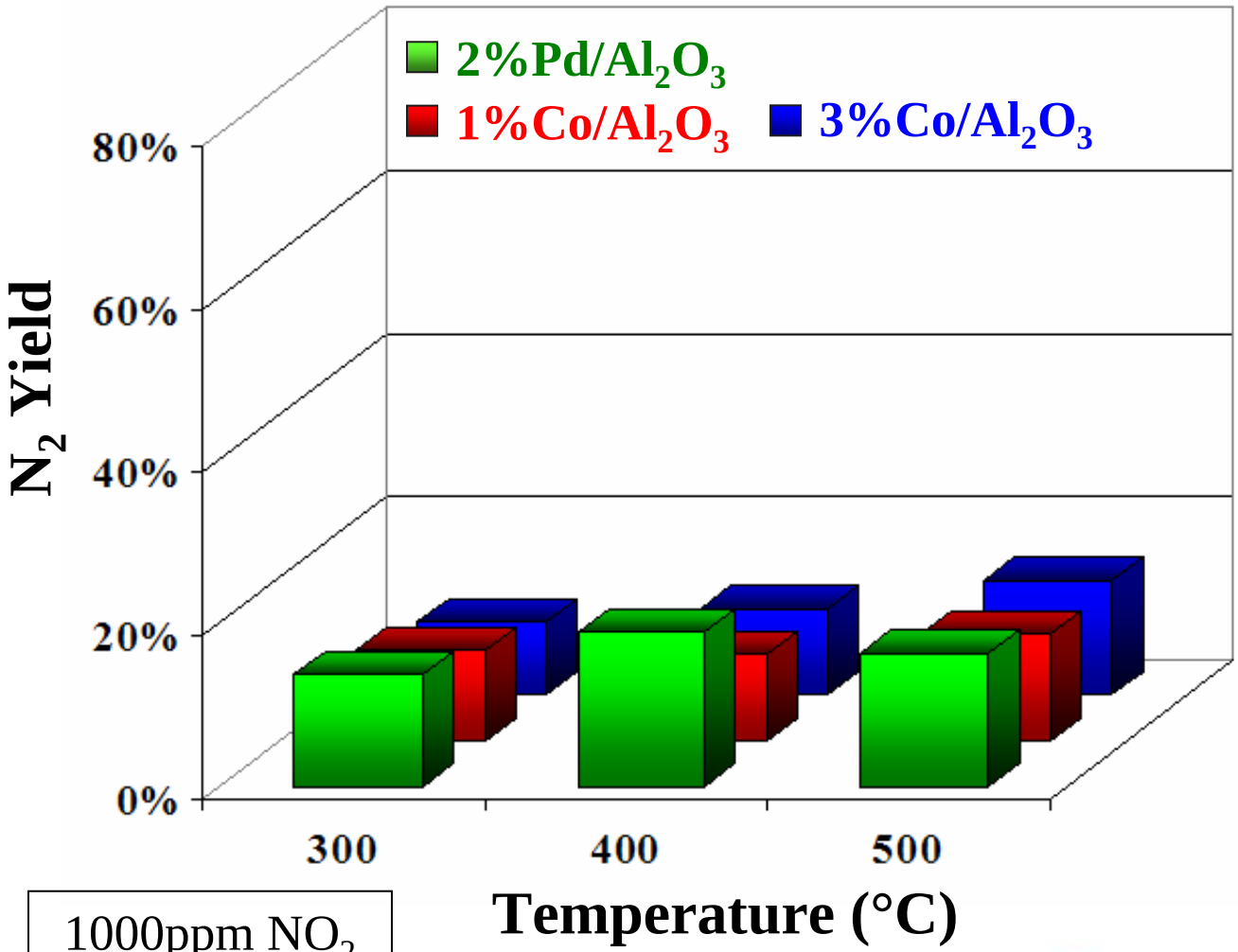
- Highly active NO_2 reduction catalysts that can work equally well with C_3 alkane or olefins.
- It may find application for recip engines used for wellhead gas compression where propane/propylene is readily available.

But how about reduction with *methane*?

NO_2 Reduction with CH_4

Although results with propane were very promising, demonstrating NO_2 reduction in high excess O_2, CH_4 would be the preferred reducing agent.

Catalysts from initial screening experiments were shown to be inactive with CH_4.



1000ppm NO_2
5000ppm CH_4
5% O_2

NO_2 Reduction with CH_4

New catalyst formulation

-Pd/sulfated zirconia

-Reported to be active with CH_4. (Resasco 1995, 2000) (Ohtsuka 2001)

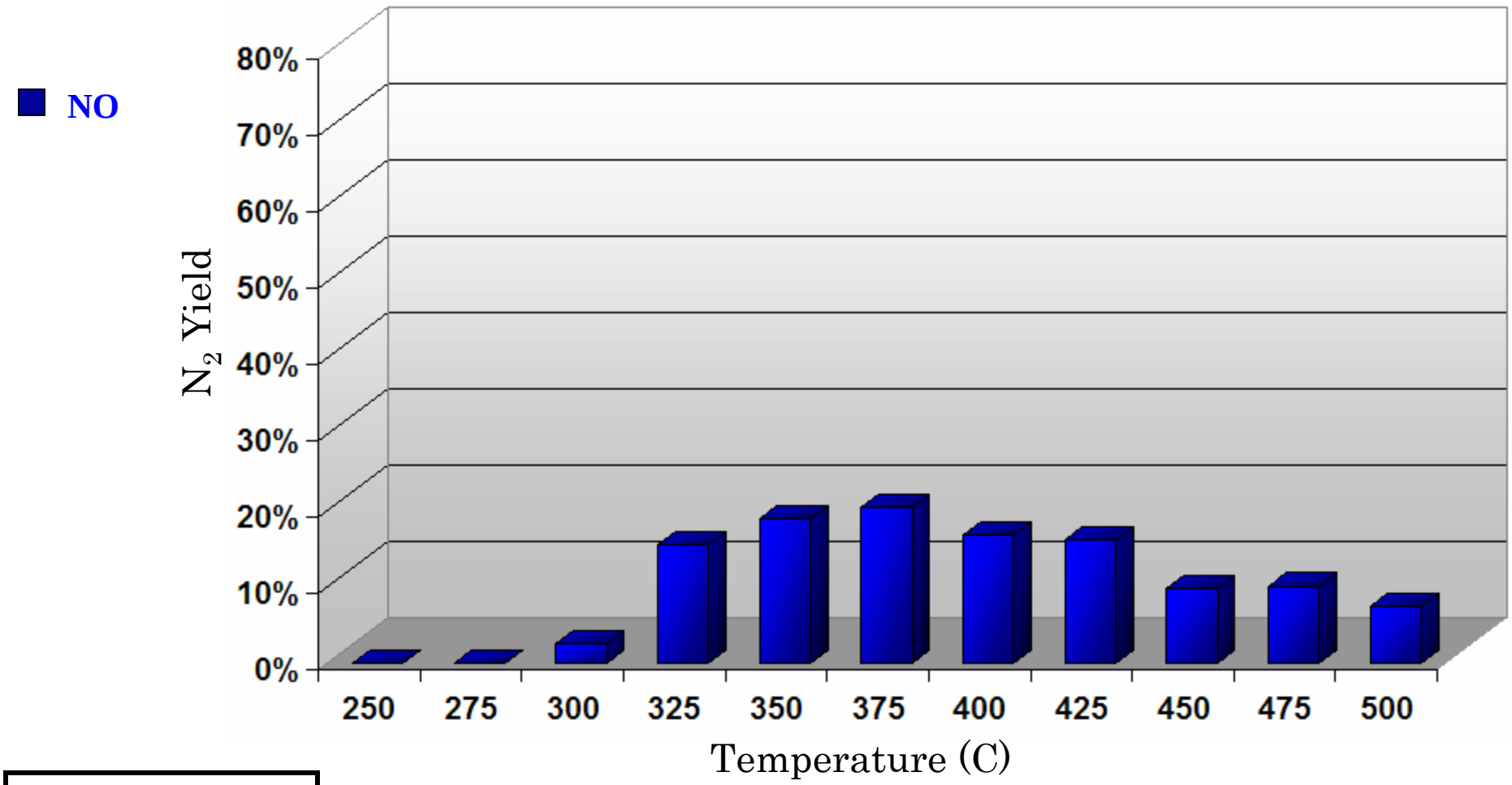
-High surface acidity.

Catalyst Preparation

Commercial monoclinic zirconia is sulfated using $(NH_4)_2SO_4$, dried and calcined at 500°C.

Pd is then added by incipient wetness, and the catalyst is again dried and calcined at 500°C.

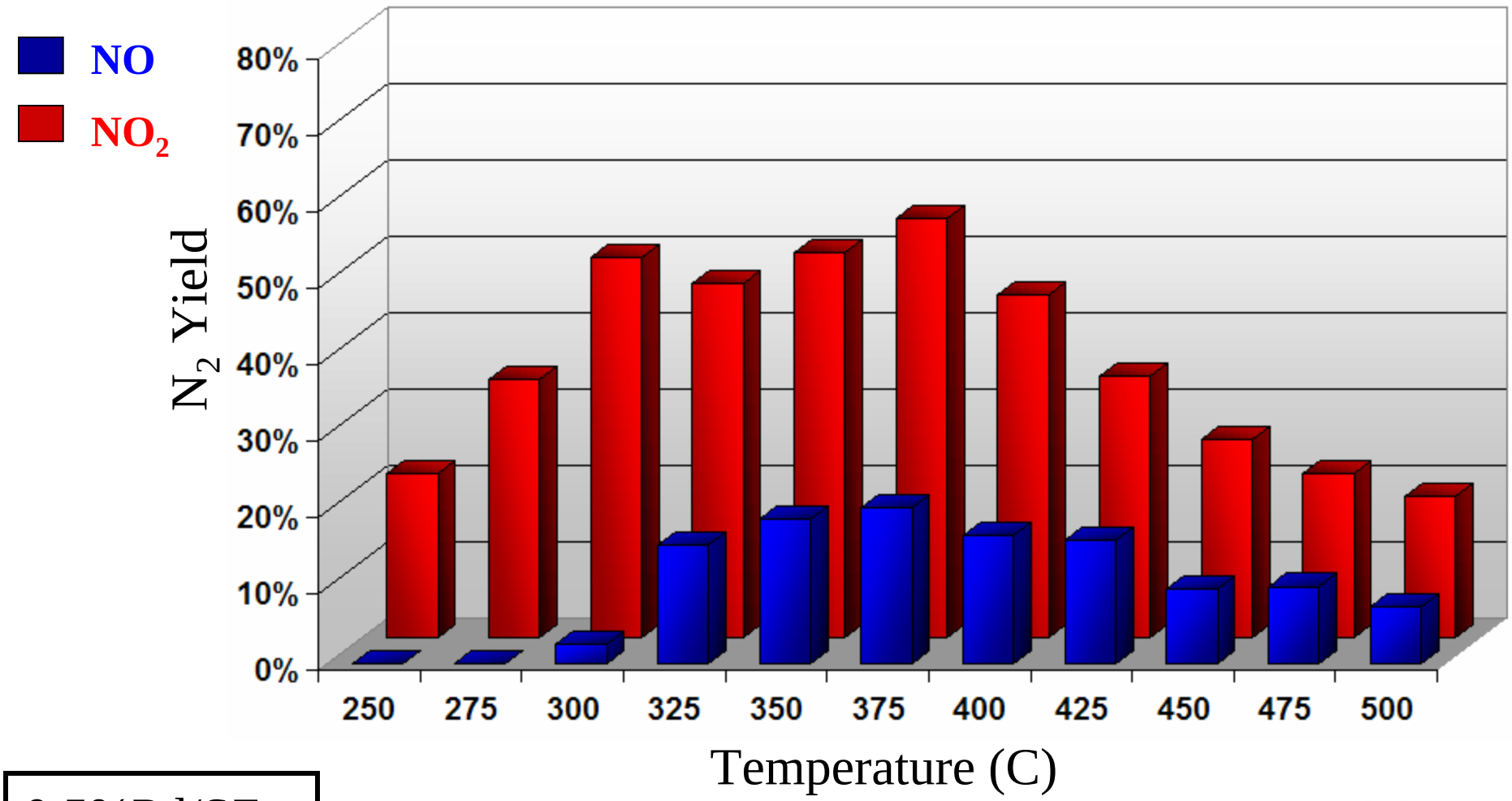
NO vs. NO_2 Reduction with CH_4



0.5%Pd/SZ

1000ppm NO_x	3000ppm CH_4
10% O_2	Balance He

NO vs. NO_2 Reduction



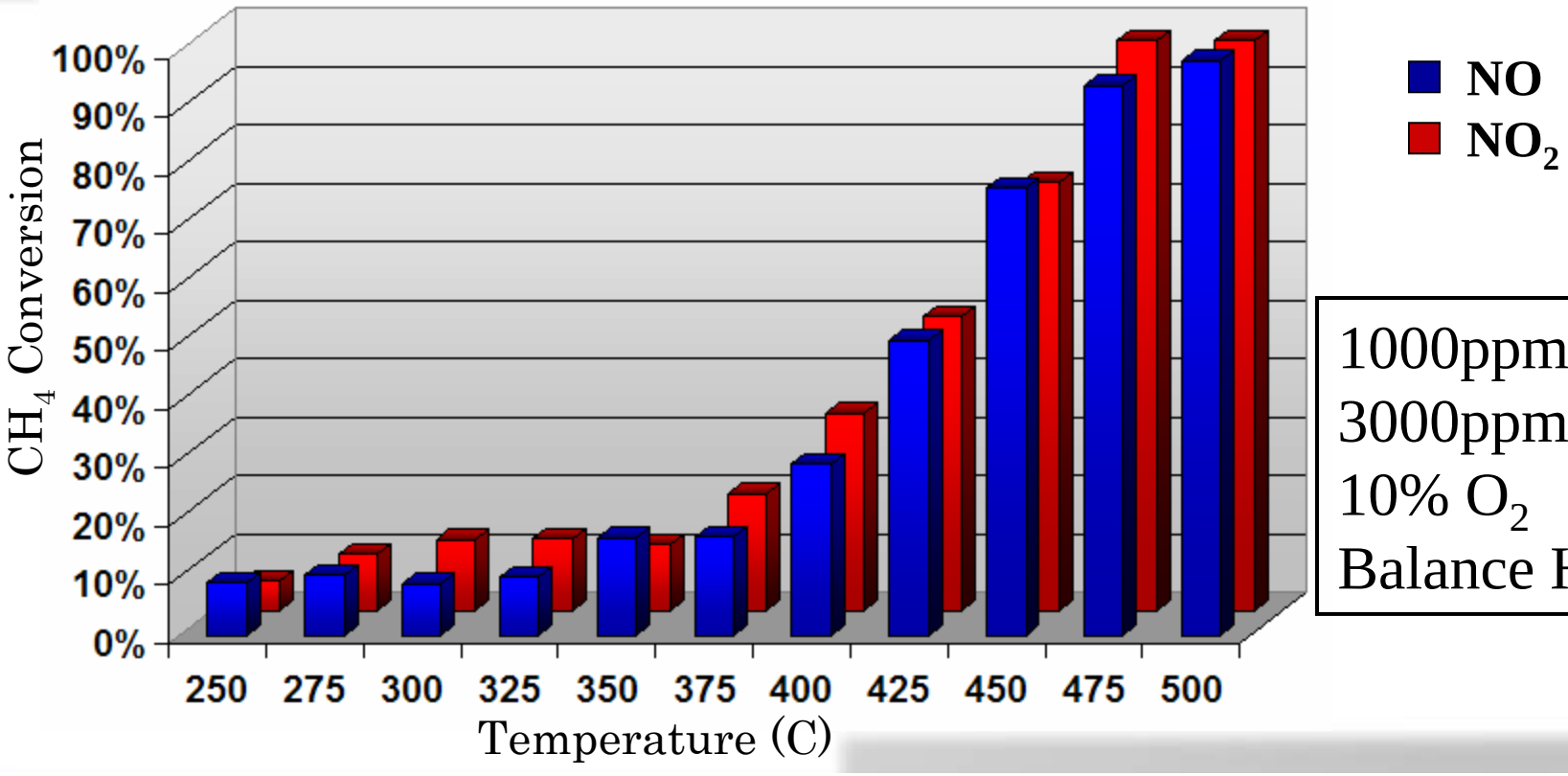
0.5%Pd/SZ

1000ppm NO_x	3000ppm CH_4
10% O_2	Balance He

NO vs. NO_2 Reduction

Despite high excess oxygen concentrations the catalyst is active for NO_x reduction at low temperatures. The reduction maximum is a function of increasing CH_4 combustion.

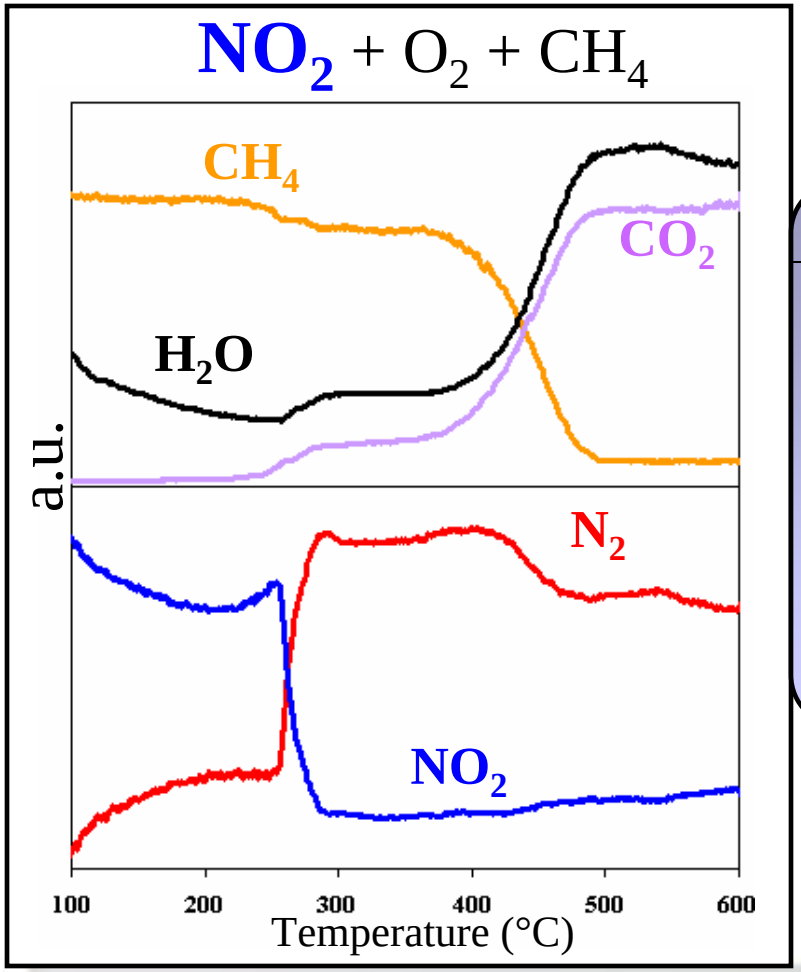
0.5%Pd/SZ



1000ppm NO_x
3000ppm CH_4
10% O_2
Balance He

Temperature Programmed Reaction

- Under temperature ramp, monitor reactants/products via mass spectrometry.
- Use of NO_2 rather than NO as the NO_x species gives higher N_2 yield, validating the two-stage concept.



Conditions

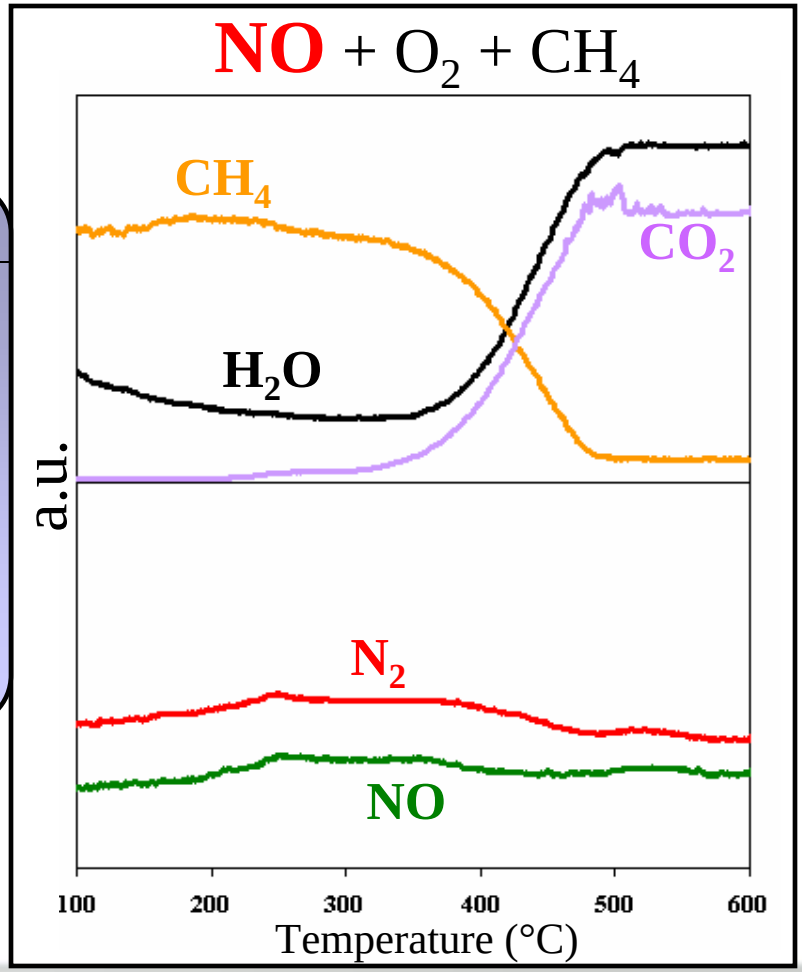
3000ppm CH_4

1000ppm NO_x

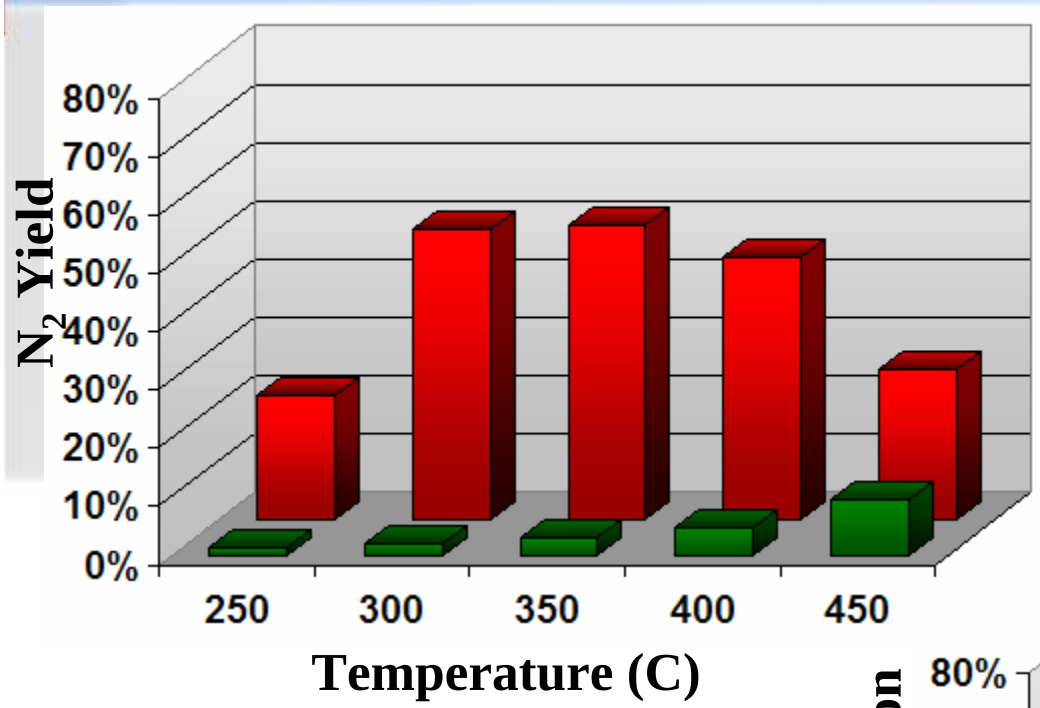
5% O_2

GHSV 20,000h^{-1}

10°C/min



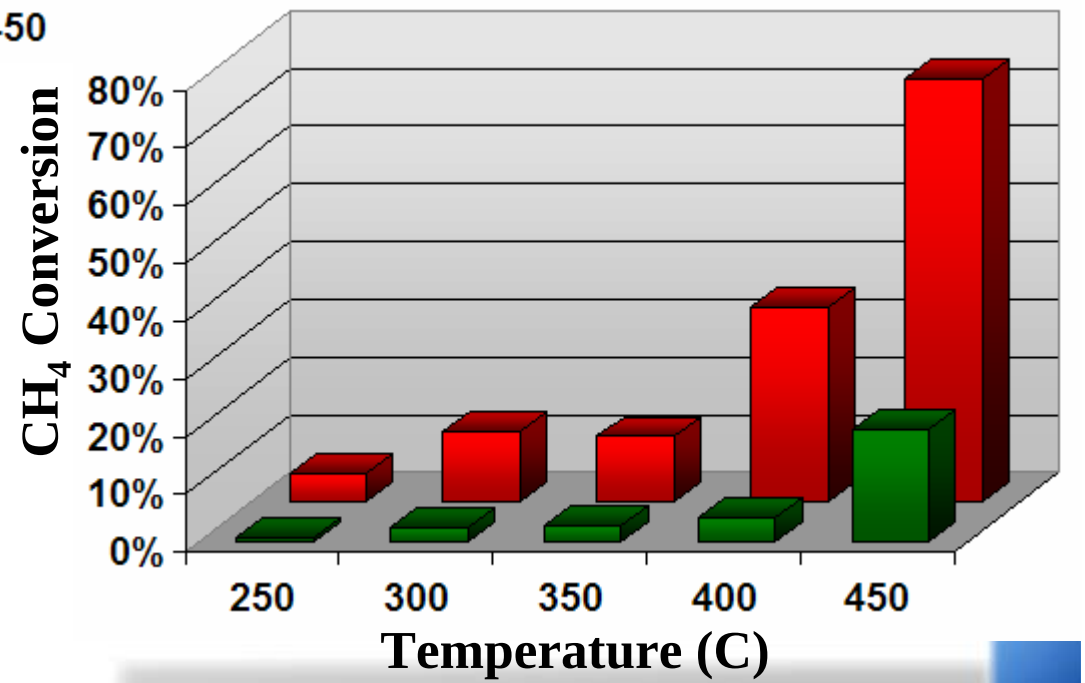
Effect of Sulfate Addition (Reduction Catalyst)



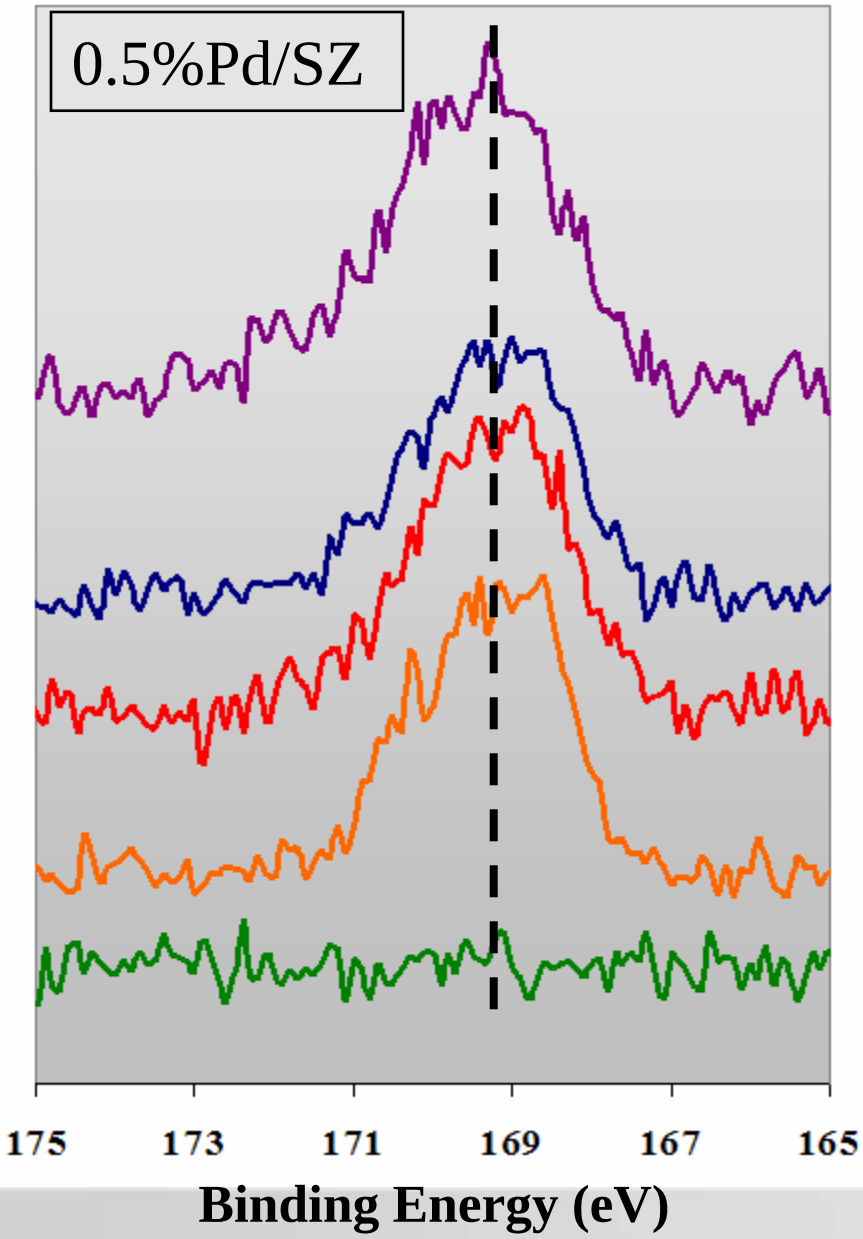
1000ppm NO_x
3000ppm CH_4
10% O_2
Balance He

0.5%Pd/SZ
0.5%Pd/ZrO_2

Sulfate loading is clearly key to activity, as observed in both N_2 yields and in CH_4 activation.



Catalyst Preparation XPS – S 2p



Examination of the catalyst surface after each step in the preparation shows the presence of sulfate groups (169.1 eV) that are stable throughout the procedure.

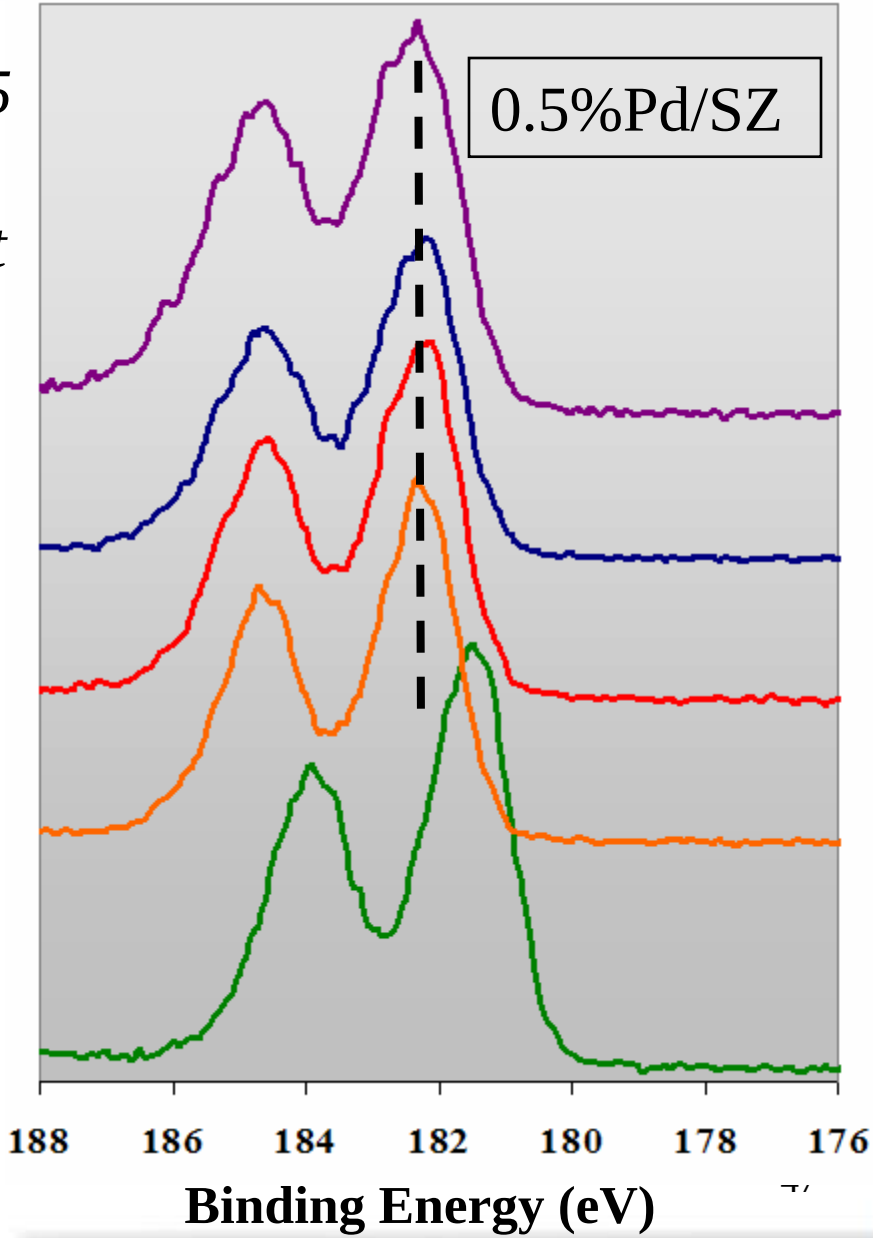
- Pd/SZ Calcined
- Pd/SZ Uncalcined
- SZ Calcined
- SZ Uncalcined
- Zirconia

Catalyst Preparation XPS – Zr 3d

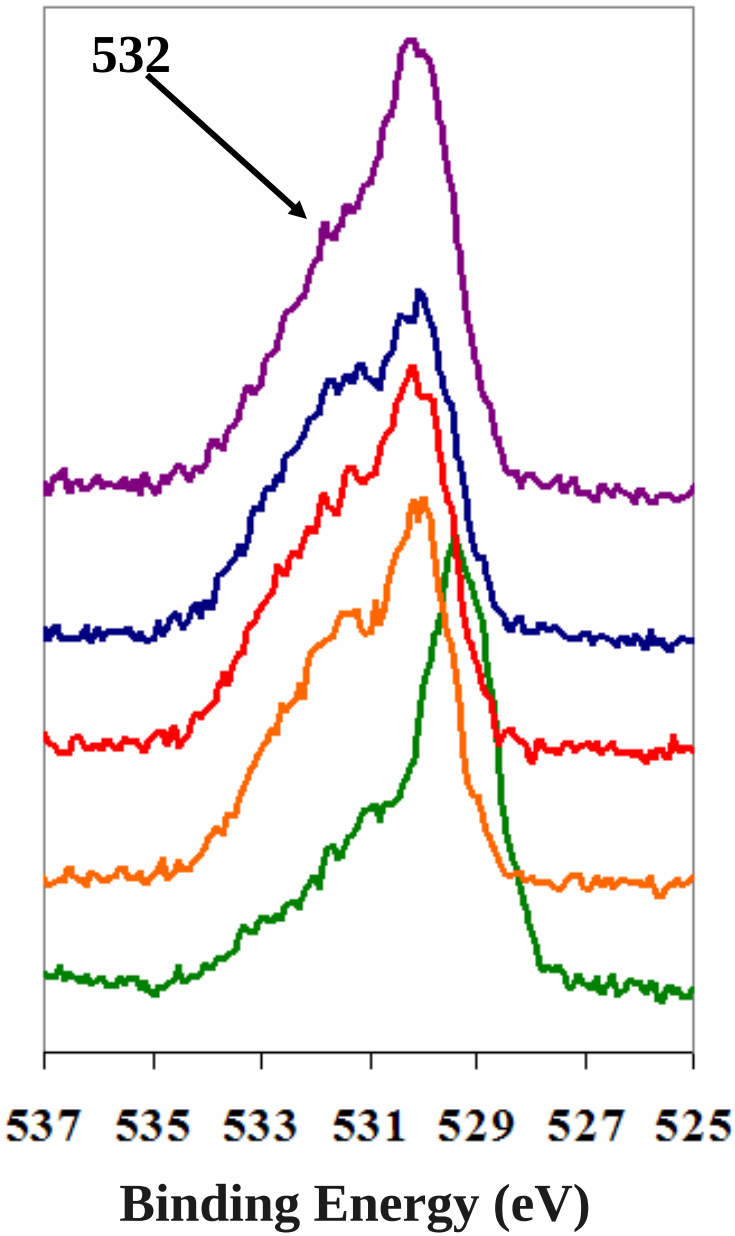
The Zr $3d_{5/2}$ from ZrO_2 at 181.5 eV is shifted to 182.2 eV after sulfidation treatment. This shift is due to decreased electron density around Zr atoms corresponding to increased surface acidity.

This shift is constant throughout subsequent preparation steps.

- Pd/SZ Calcined
- Pd/SZ Uncalcined
- SZ Calcined
- SZ Uncalcined
- Zirconia



Catalyst Preparation XPS – O 1s



Observation of the O_{1s} peak shows the development of a shoulder in the 532 eV range. This binding energy is typical of oxygen present in sulfate groups.

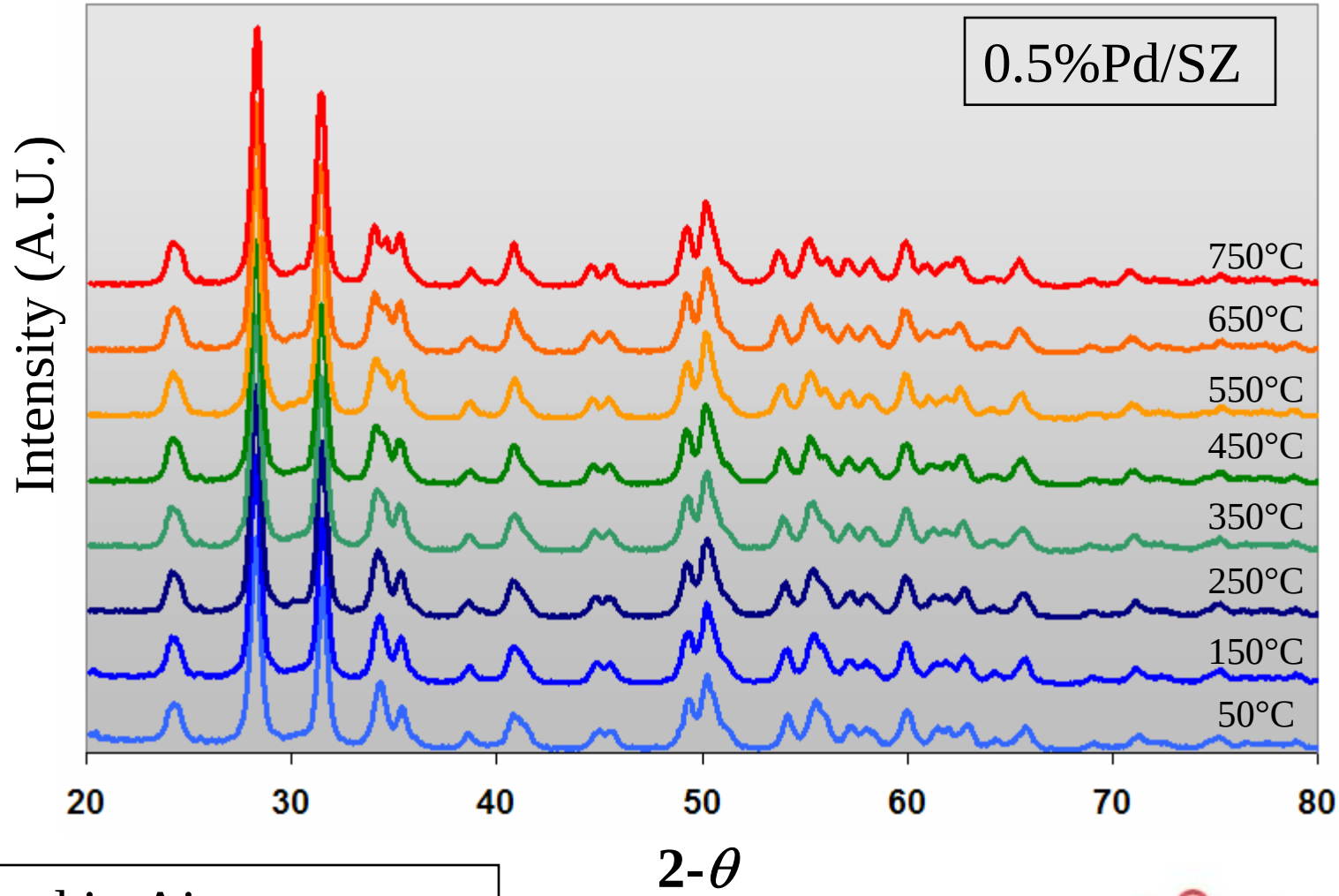
This shoulder is stable with further preparation steps, demonstrating stable sulfate species.

- **Pd/SZ**
- **Pd/SZ Uncalcined**
- **Sulfated Zirconia**
- **SZ Uncalcined**
- **Zirconia**

0.5%Pd/SZ

In-Situ XRD During Calcination

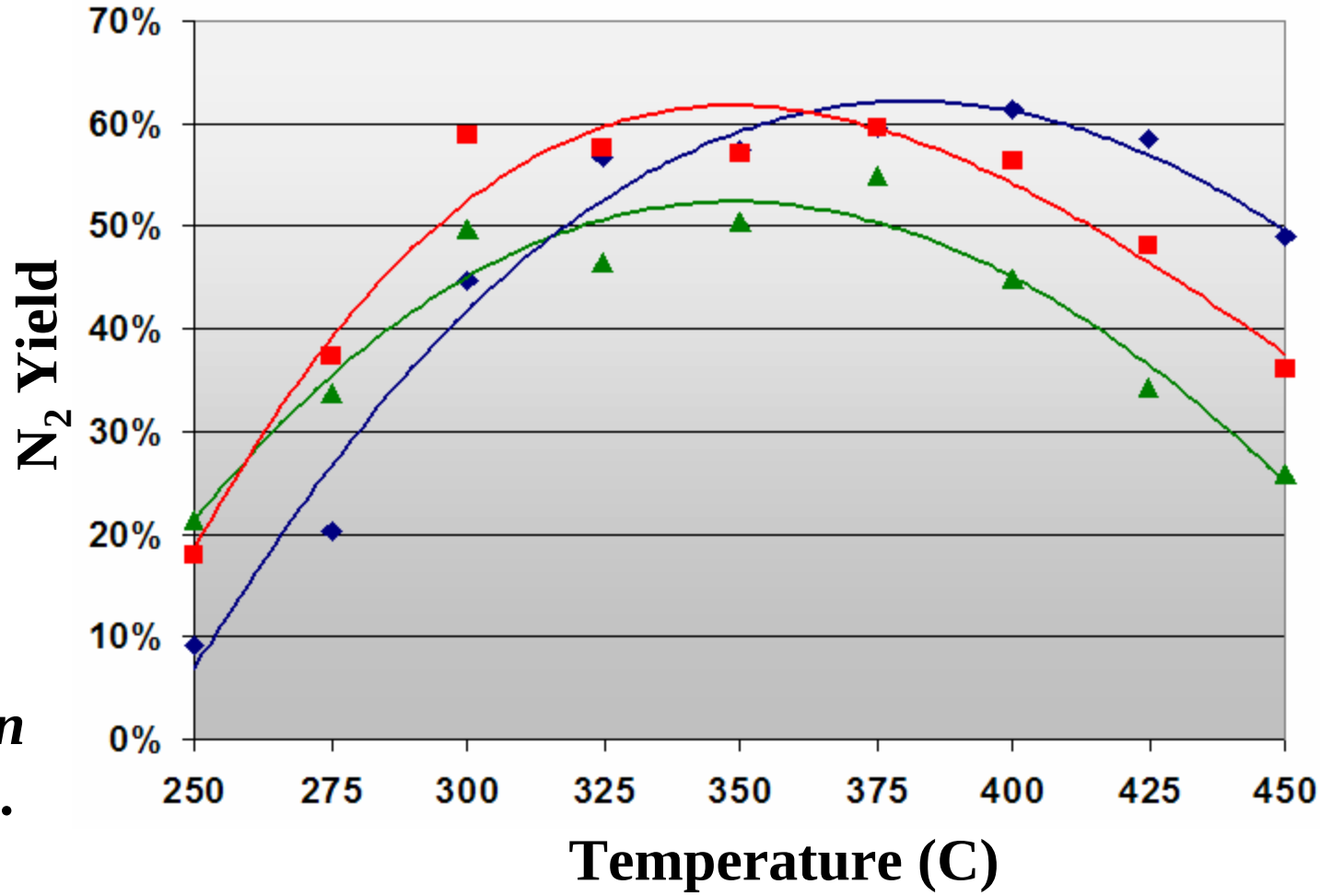
Only monoclinic zirconia is observed across the entire temperature range.



Calcined in Air
5°C/min, Scans at 50°C.

Effect of Pd Loading (NO_2 Reduction)

1000ppm NO_2
3000ppm CH_4
10% O_2
Balance He

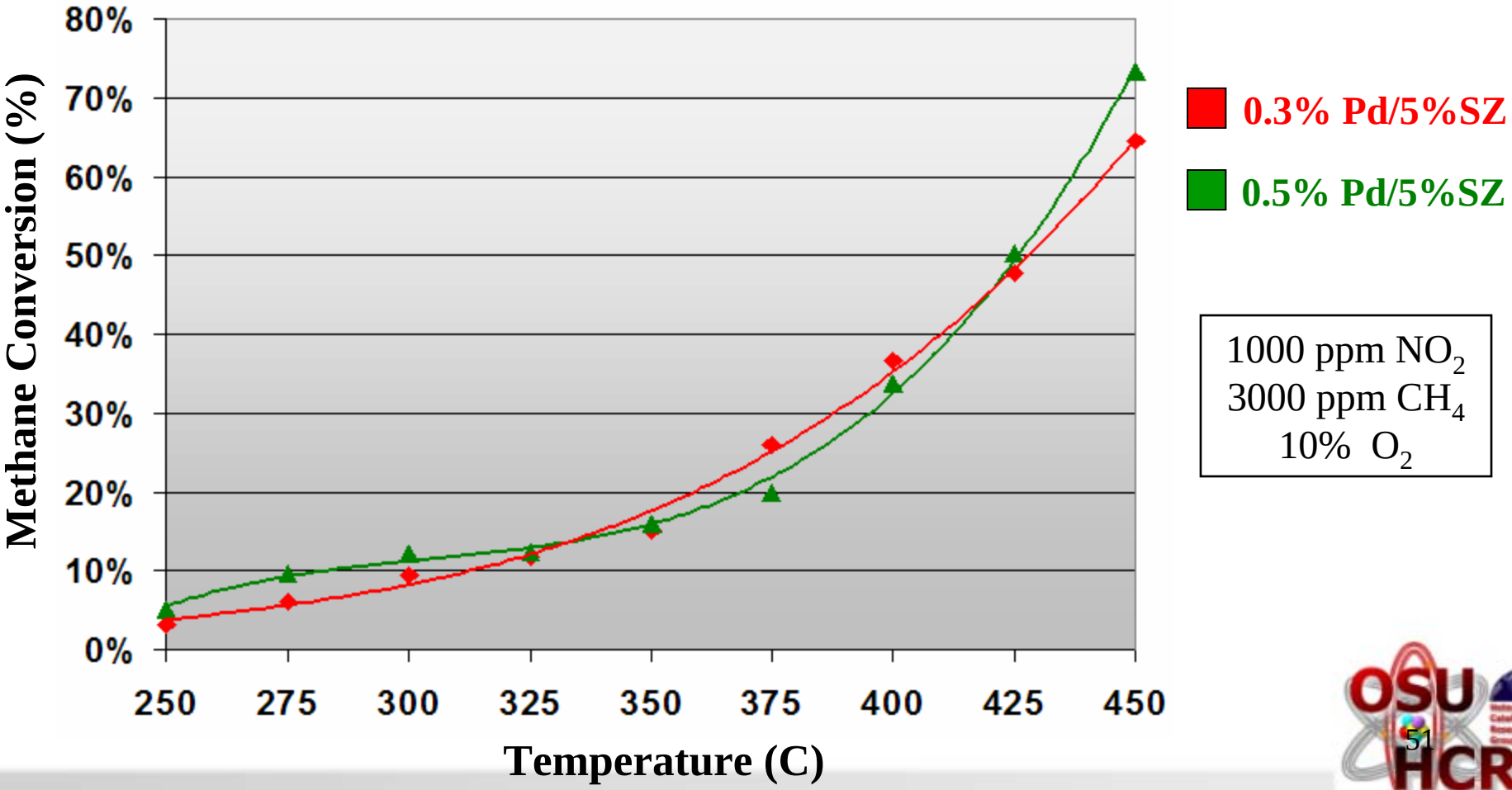


Decreased Pd loading results in higher N_2 yields.

0.5%Pd/SZ 0.3%Pd/SZ
0.1%Pd/SZ

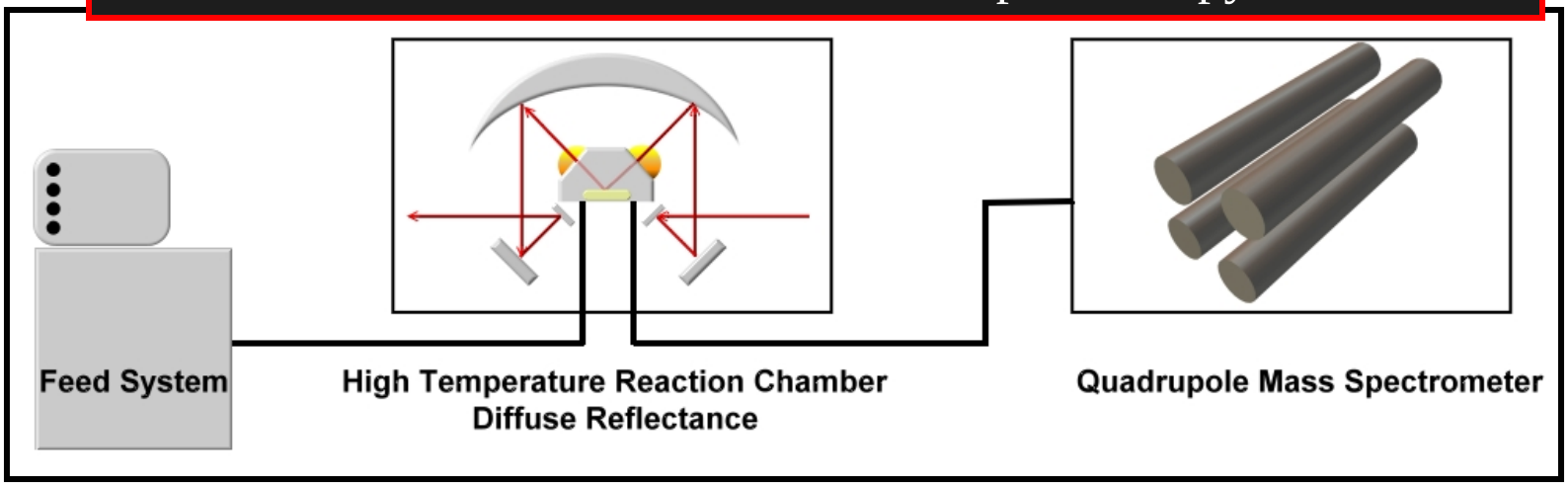
Effect of Pd Loading (NO_2 Reduction)

Higher temperatures result in higher CH_4 conversions, but still far from complete combustion, showing the selectivity of the reaction of the reaction for NO_2 reduction.



DRIFT Spectroscopy

Temperature Programmed Desorption – Diffuse Reflectance Infrared Fourier Transform Spectroscopy

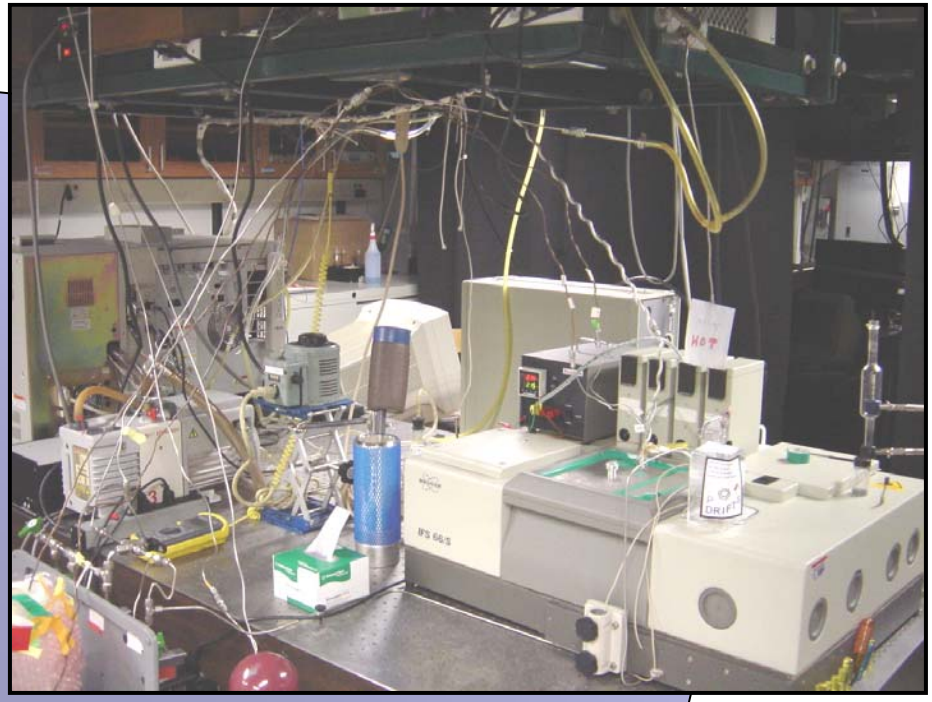


Bruker IFS66 MCT Detector, KBr Beamsplitter

Shimadzu Mass Spectrometer

DRIFT spectroscopy is ideal for powdered samples, allowing the identification of surface species associated with reactants, products, and intermediates. Combined with on-line mass spectrometry, the disappearance of surface species can be directly correlated to desorbed reaction products.

DRIFTS on 0.5%Pd/SZ Reduction Catalyst



0.5%Pd/5%SZ in KBr

- Observe IR bands from sulfate species and their interaction with NO_x

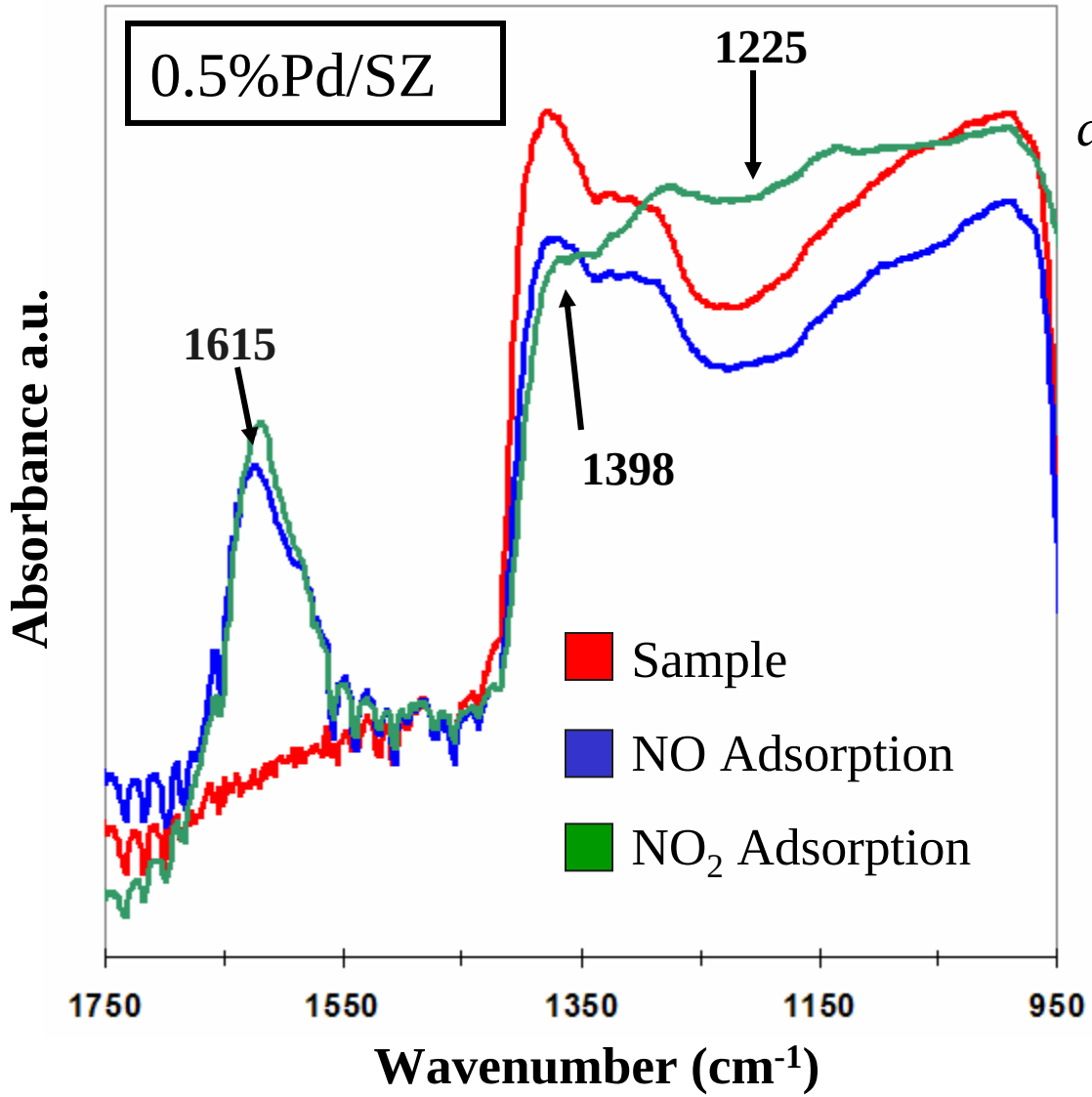
NO and NO_2 TPD

- Observe the thermal transformation of adsorbed NO_x species

TP-Reaction of adsorbed NO_x with CH_4/O_2

- Observe the transformation of adsorbed NO_x with CH_4 and O_2 present and observe the corresponding reaction intermediates

DRIFTS on 0.5%Pd/SZ



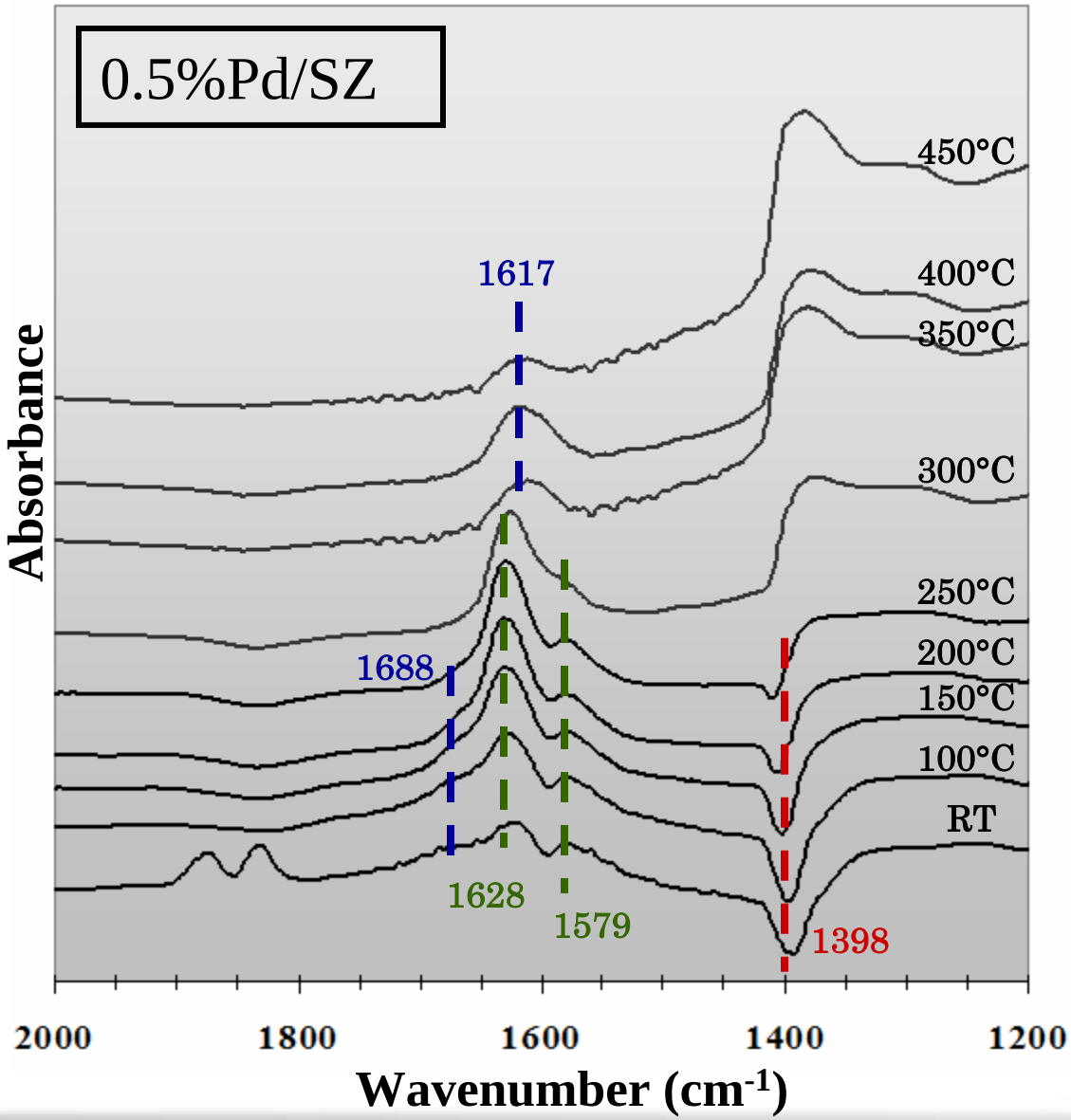
Spectra of catalyst mixed with KBr allows for the detection of species associated with the catalyst material. Spectra taken at 200°C. Sample 15 wt%.

The band at **1398 cm^{-1}** is characteristic of S=O, demonstrating the presence of surface sulfates.

With adsorption of NO or NO_2 a broad band appears ~**1615 cm^{-1}**, typical of bridging nitrates.

The adsorption of NO_2 yields additional nitrates in the 1225 cm^{-1} region.

NO TPD with DRIFTS

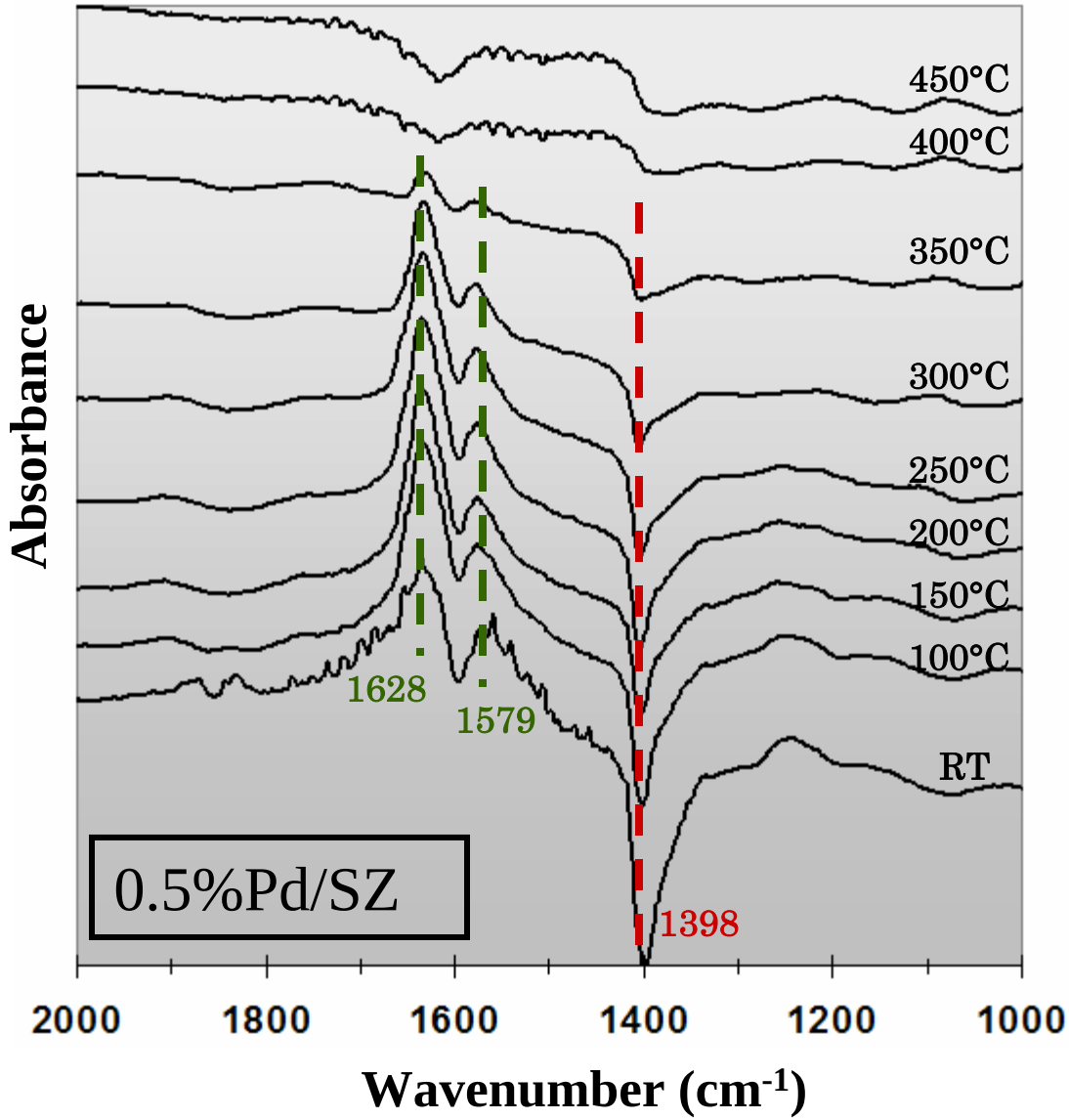


Adsorbed NO interacts with S=O groups **1398cm^{-1}**

1579, 1628cm^{-1}
Typical bands of adsorbed NO <u>or</u> NO_2 (Bidentate/Unidentate)

1617cm^{-1}
Bridging Nitrate Species

NO_2 TPD with DRIFTS

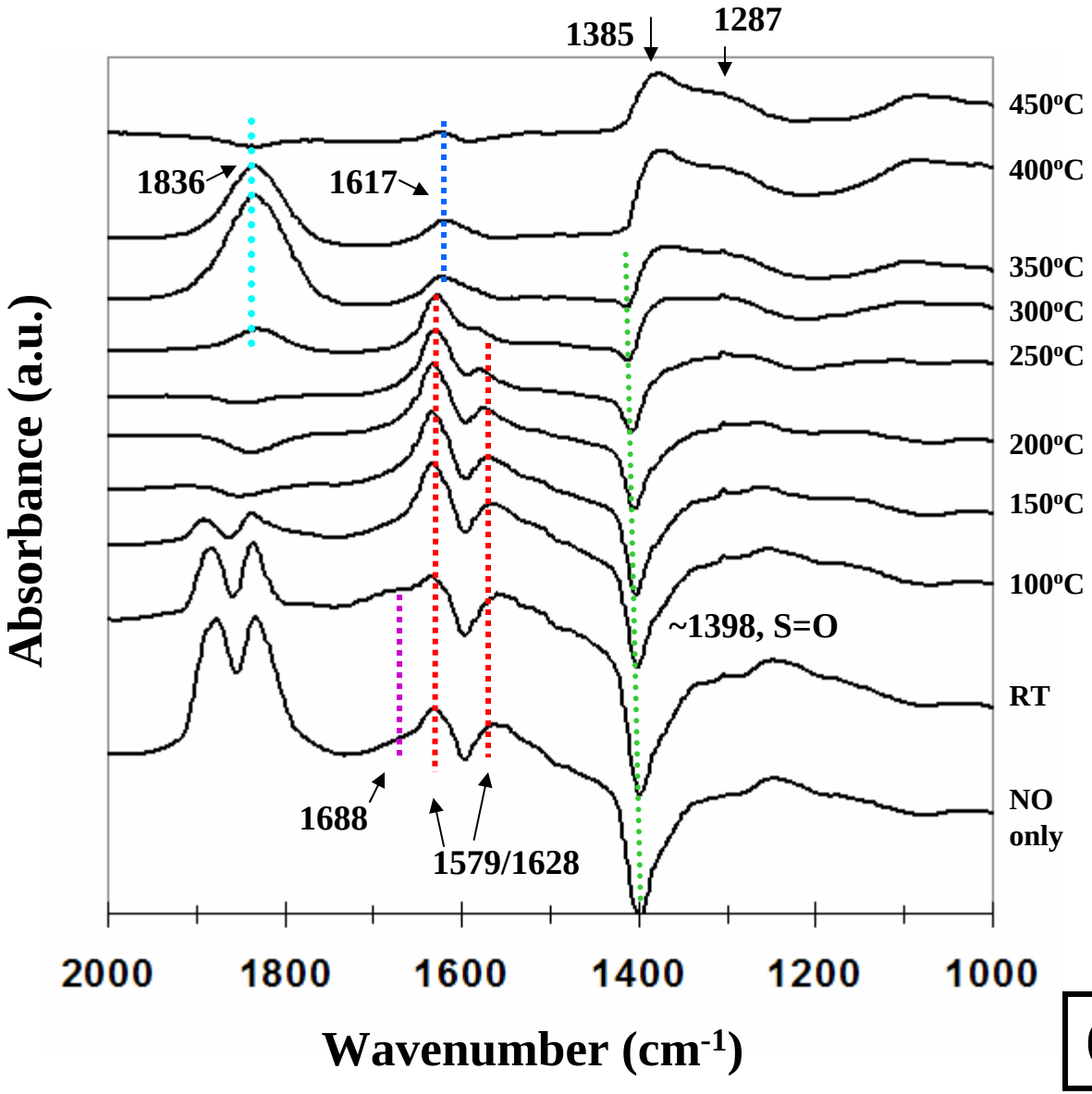


1398 cm^{-1}
Adsorbed NO_2 interacts more strongly with S=O groups than NO

1579, 1628cm^{-1} Typical bands of adsorbed NO <u>or</u> NO_2 (Bidentate/Unidentate)

No linearly adsorbed NO, bridged NO, or low wavenumber nitrates formed from NO_2

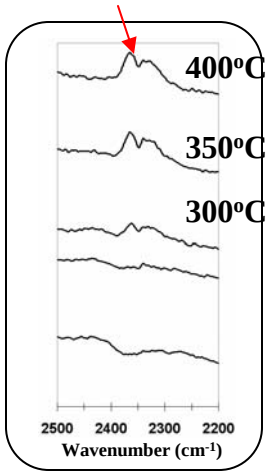
NO Adsorption followed by TPRxn with CH_4



Species form similar to NO adsorption alone.

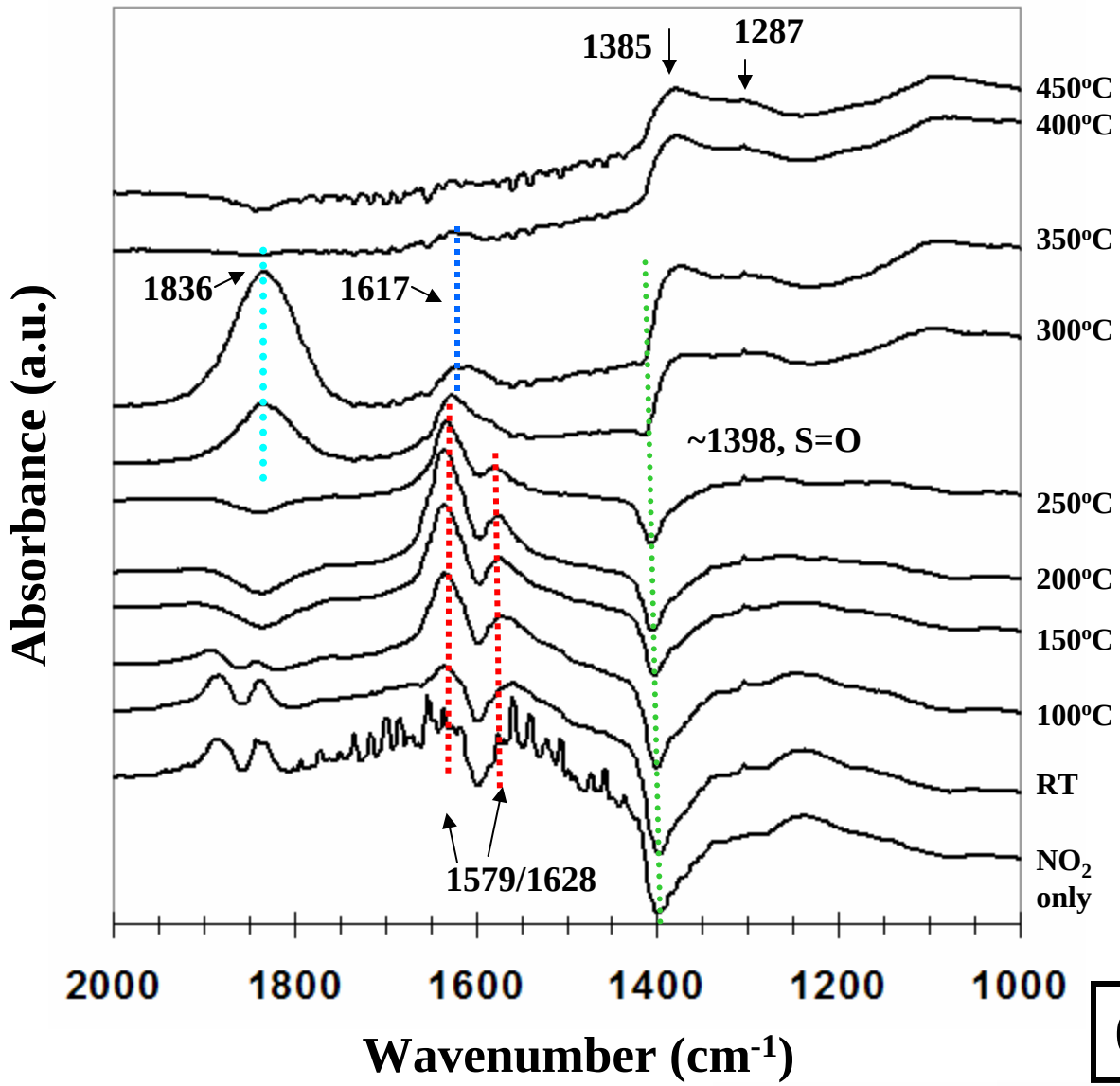
With methane in the gas phase: new band at 1836cm^{-1} appears at 300°C. It could be due to linearly adsorbed NO on Pd sites.

CO_2 formation appears at 300°C.



0.5%Pd/SZ

NO_2 Adsorption followed by TPRxn with CH_4



Ad-species are now converted above 300°C with the presence of methane, unlike NO_2 alone.

With methane in the gas phase the band at 1836cm^{-1} also appears at 300°C but disappears easier than with NO.

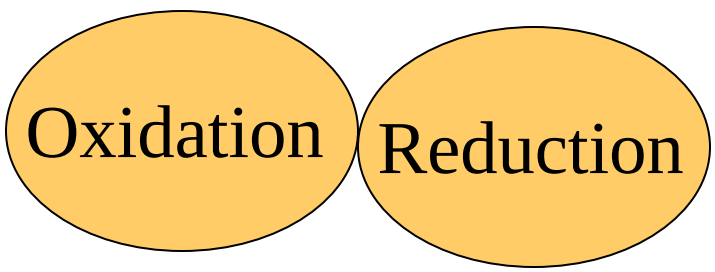
0.5%Pd/SZ

Can we combine the oxidation and reduction stages?

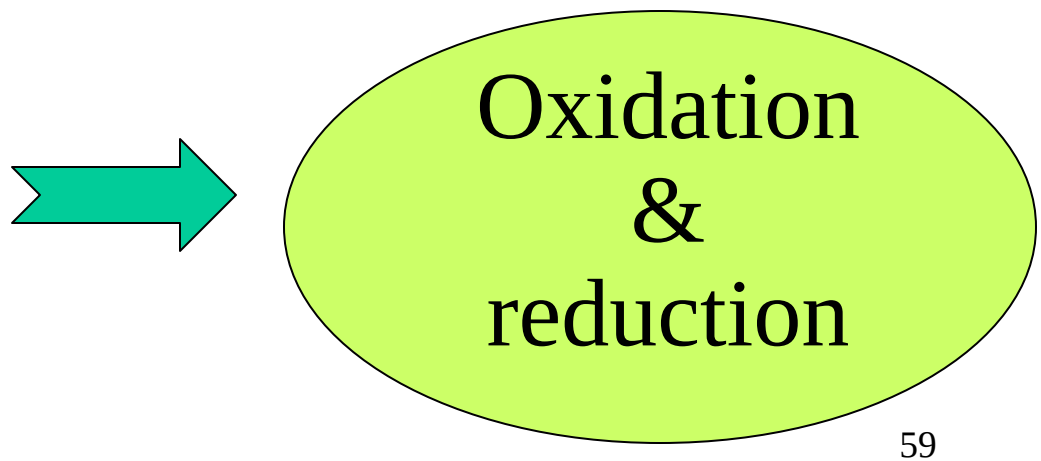
- ***Achieve NO to NO_2 conversion in close proximity to the reduction catalyst.***

- ***Help overcome thermodynamic limitations of the oxidation reaction.***

Two-stages



Single stage mixed catalyst bed

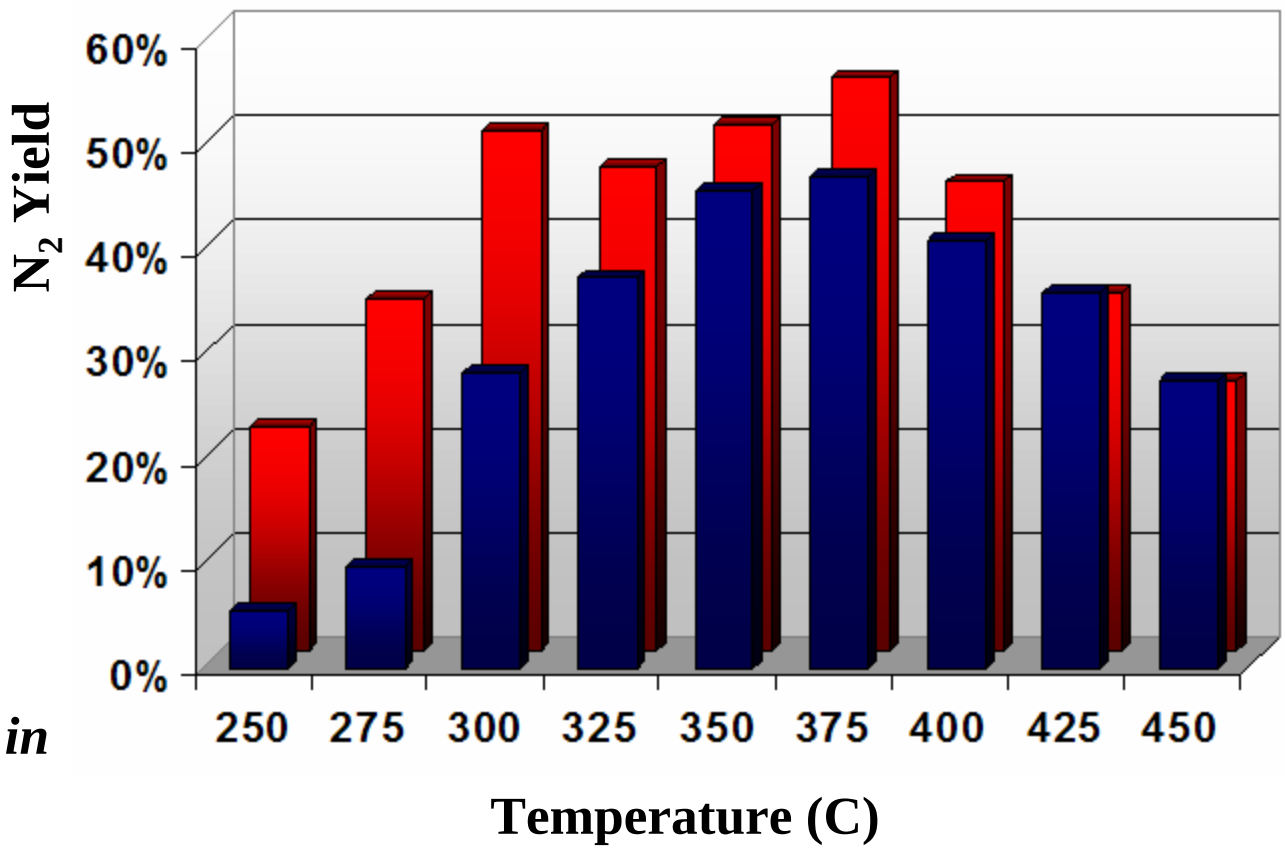


Mixed Catalyst Bed - *Initial Tests*

1000 ppm NO_x
3000 ppm CH_4
10% O_2

0.5% Pd/5%SZ – NO_2

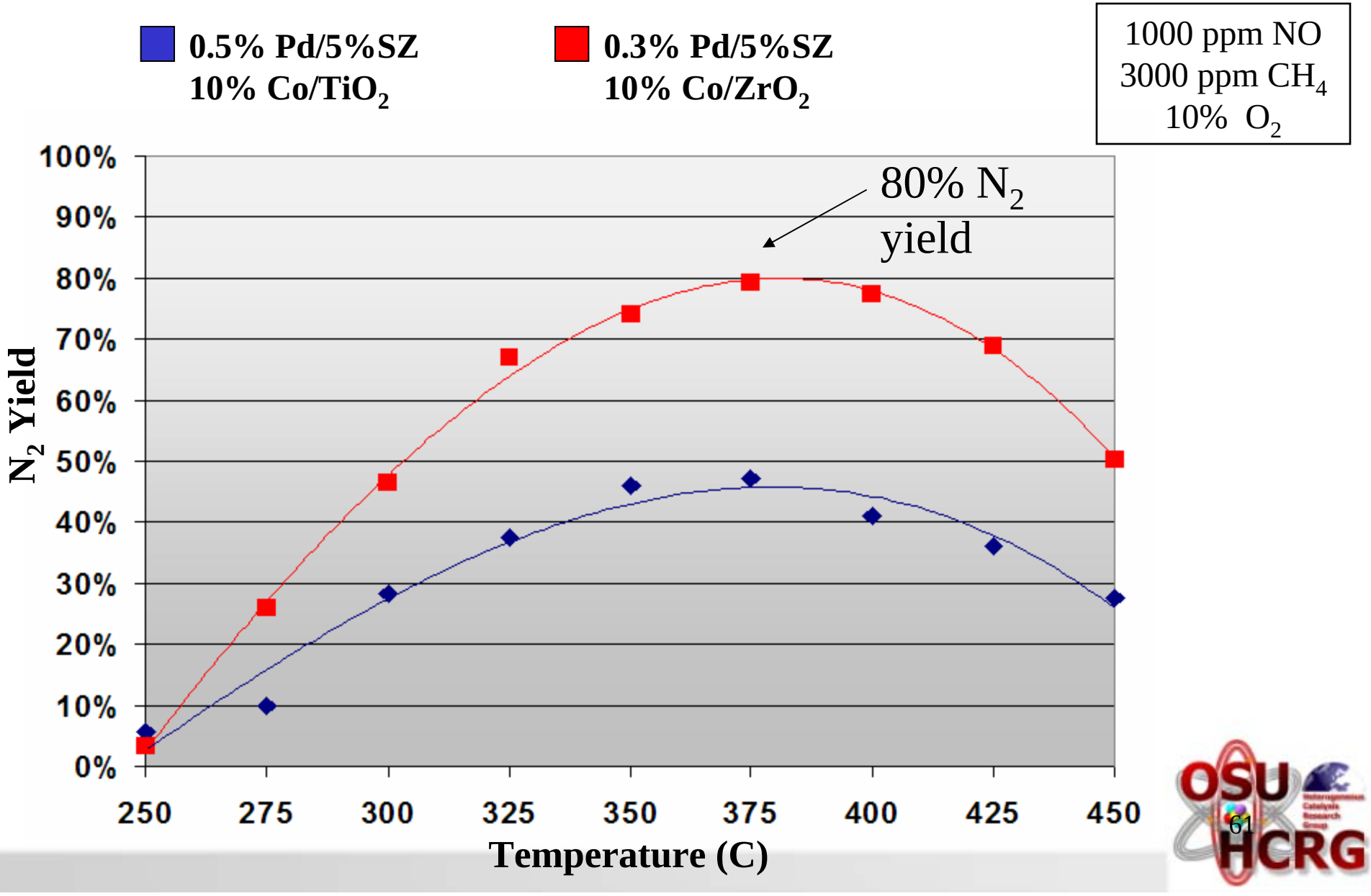
0.5% Pd/5%SZ – NO
10%Co/TiO_2 (1:1)



Catalysts are combined in a mixed bed.

Initial tests showed mixed-bed nearly matches direct NO_2 reduction over the reduction-only catalyst.

Mixed Catalyst Bed - New Formulations

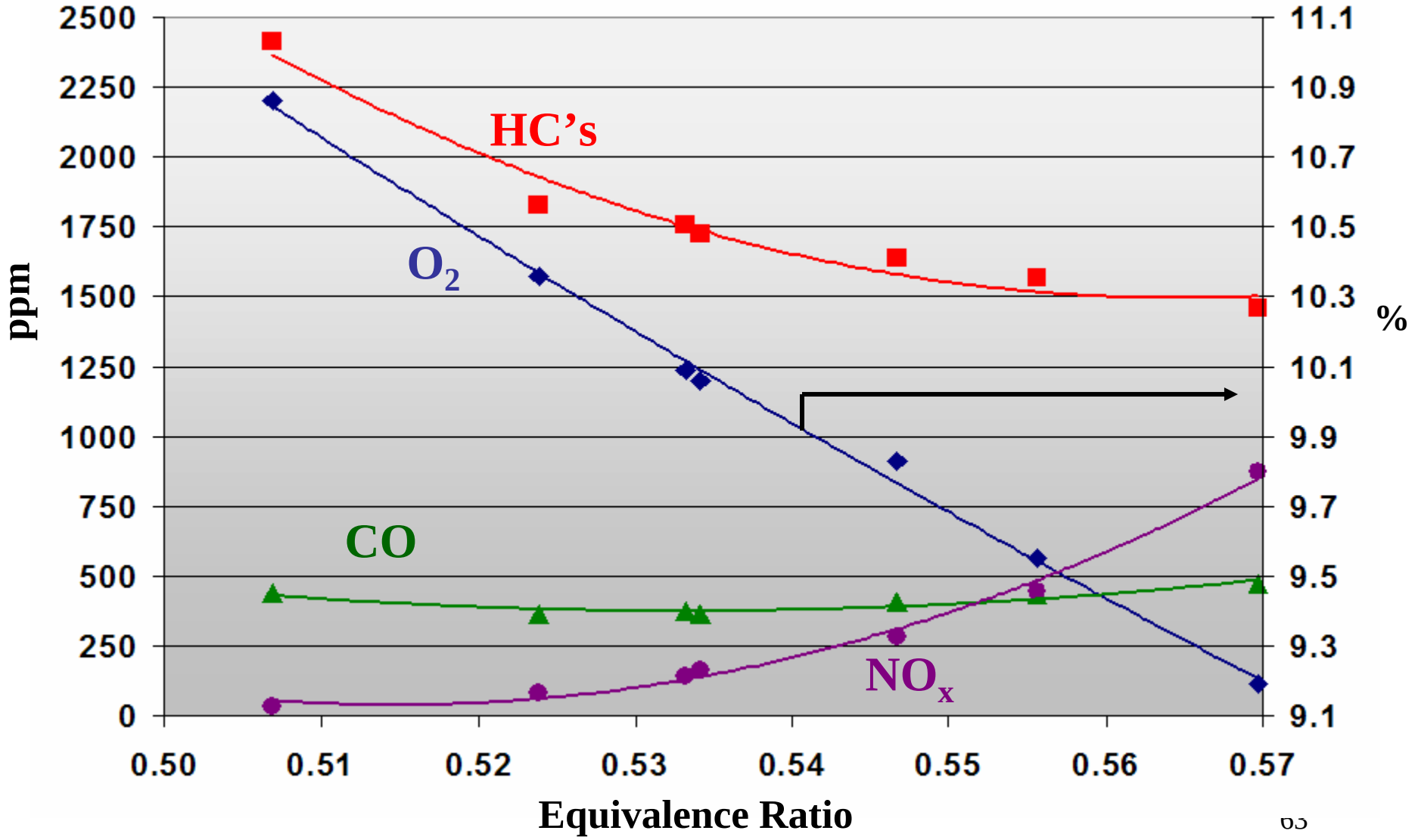


With no real optimization, the first trials show the dual catalyst bed to give 80% N_2 yield using "model" conditions of 1000 ppm NO, 3000 ppm CH_4 and 10% O_2 and in 350-450 °C range.

But, how do we relate these results to real engine exhaust concentrations?

ARES Class Engine 1-2 MW Operating at Constant Load

Hydrocarbons
NO_x
Carbon Monoxide
Oxygen



Moving closer to more typical exhaust concentrations…

- Lower HC concentrations, using simulated natural gas.
- Lower NOx concentrations

0.3%Pd/5%SZ

10% Co/ZrO2 IWI300

Methane : 1700 ppm
Ethane : 200 ppm
Propane : 100 ppm

NO : 400 ppm

O_2 : 10%

Reduction Catalyst : Oxidation Catalyst

Vary the ratios.

Mixed-Bed Results – N_2 Yield

Constant reduction catalyst loading, while varying oxidation catalyst amount.

Low loadings of oxidation catalyst results in higher N_2 yields.

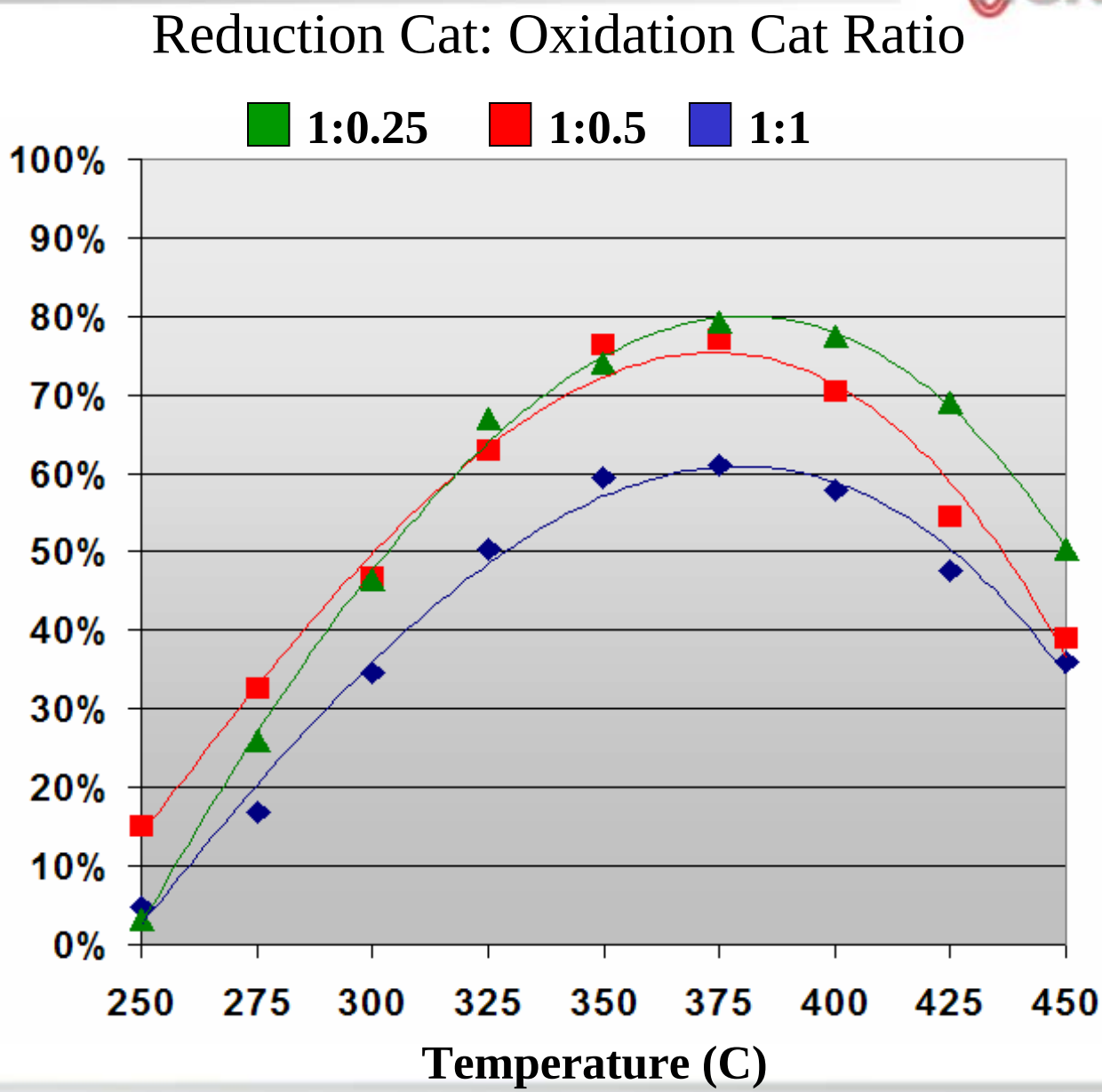
Methane : 1700 ppm

Ethane : 200 ppm

Propane : 100 ppm

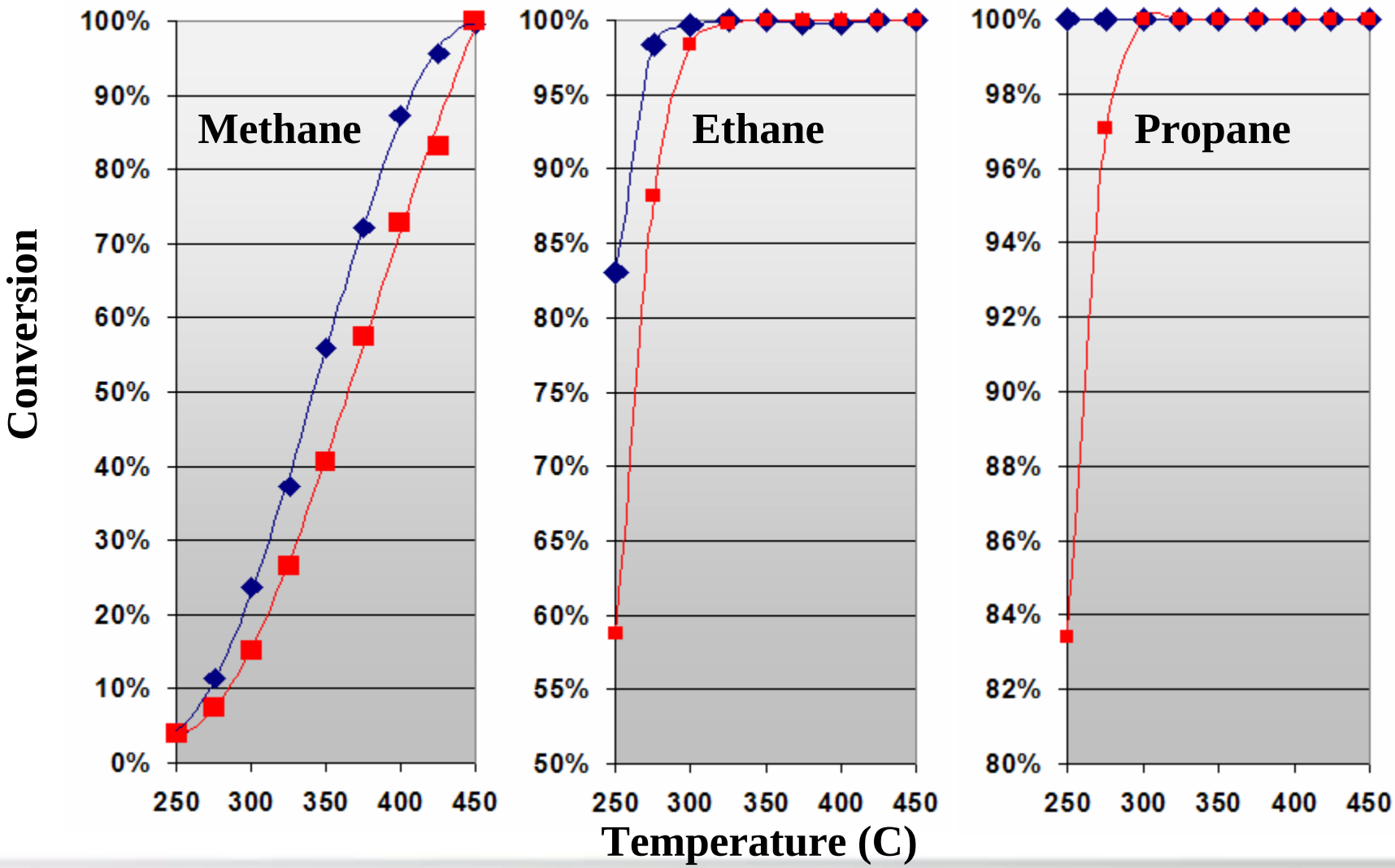
NO: 400 ppm

O_2: 10%



Mixed-Bed Results – Hydrocarbons

1:0.5 1:1 *Significant HC conversion activity.*



It appears that our NO to NO_2 conversion catalyst could work as an oxidation catalyst for unburnt hydrocarbons as well!

How about CO?

Catalyst : 10% Co/ZrO_2

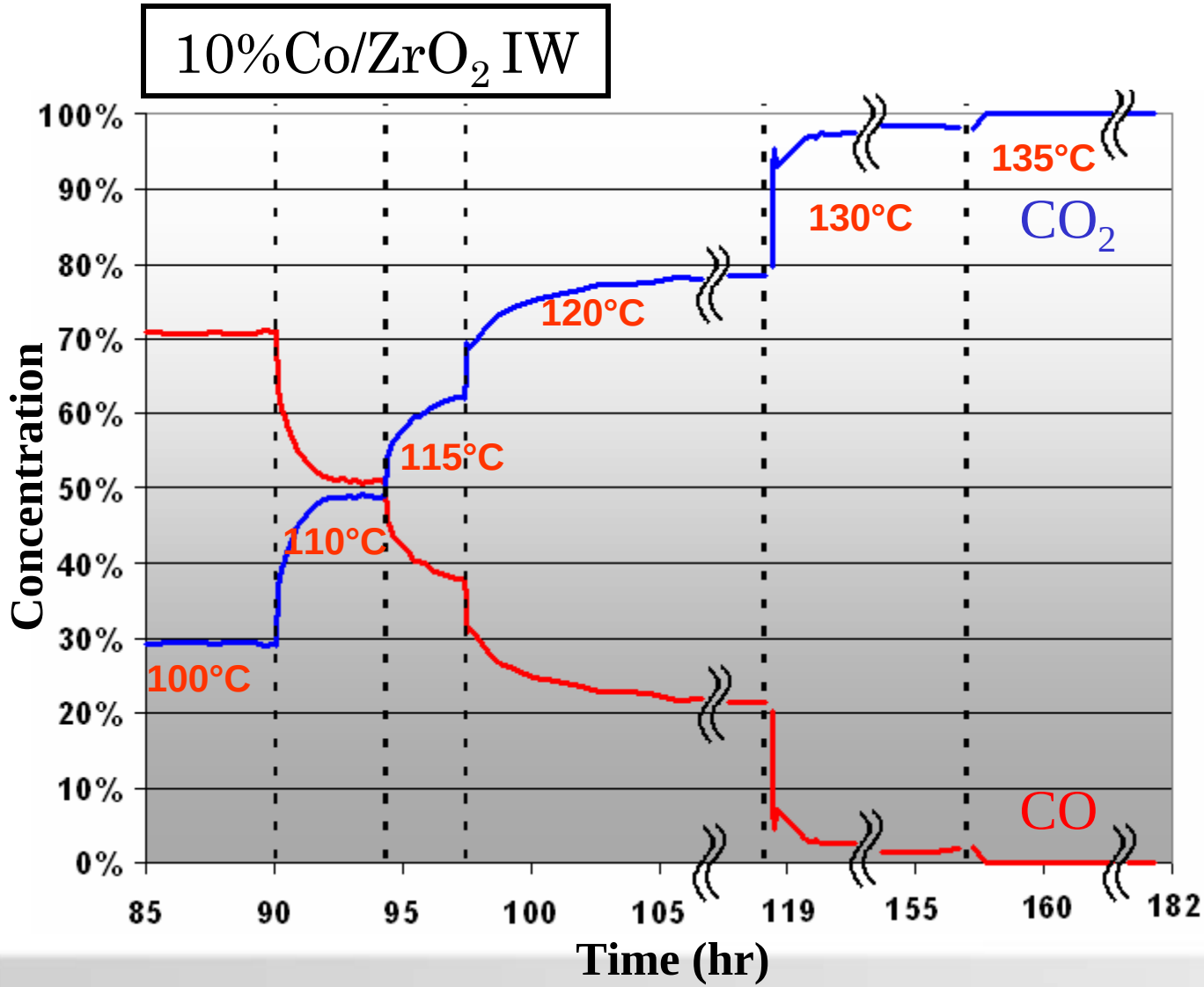
Feed composition: 600 ppm CO, 10% O_2

Temperature: 20 °C

Complete CO to CO_2 conversion at room temperature.

Carbon Monoxide Oxidation

How will it work at much higher CO concentrations?



Increasing CO concentration to **1.5%** causes some decrease in conversion. Complete conversion returns with slightly elevated temperature.

1.5% CO
10% O_2

CO
CO_2

Could this catalyst be used to eliminate CO in H_2 streams?

CO Oxidation in H_2 Streams

Oxidation performed in both wet and dry conditions:

2500 ppm CO

5000 ppm O_2

40% H_2

2500 ppm CO

5000 ppm O_2

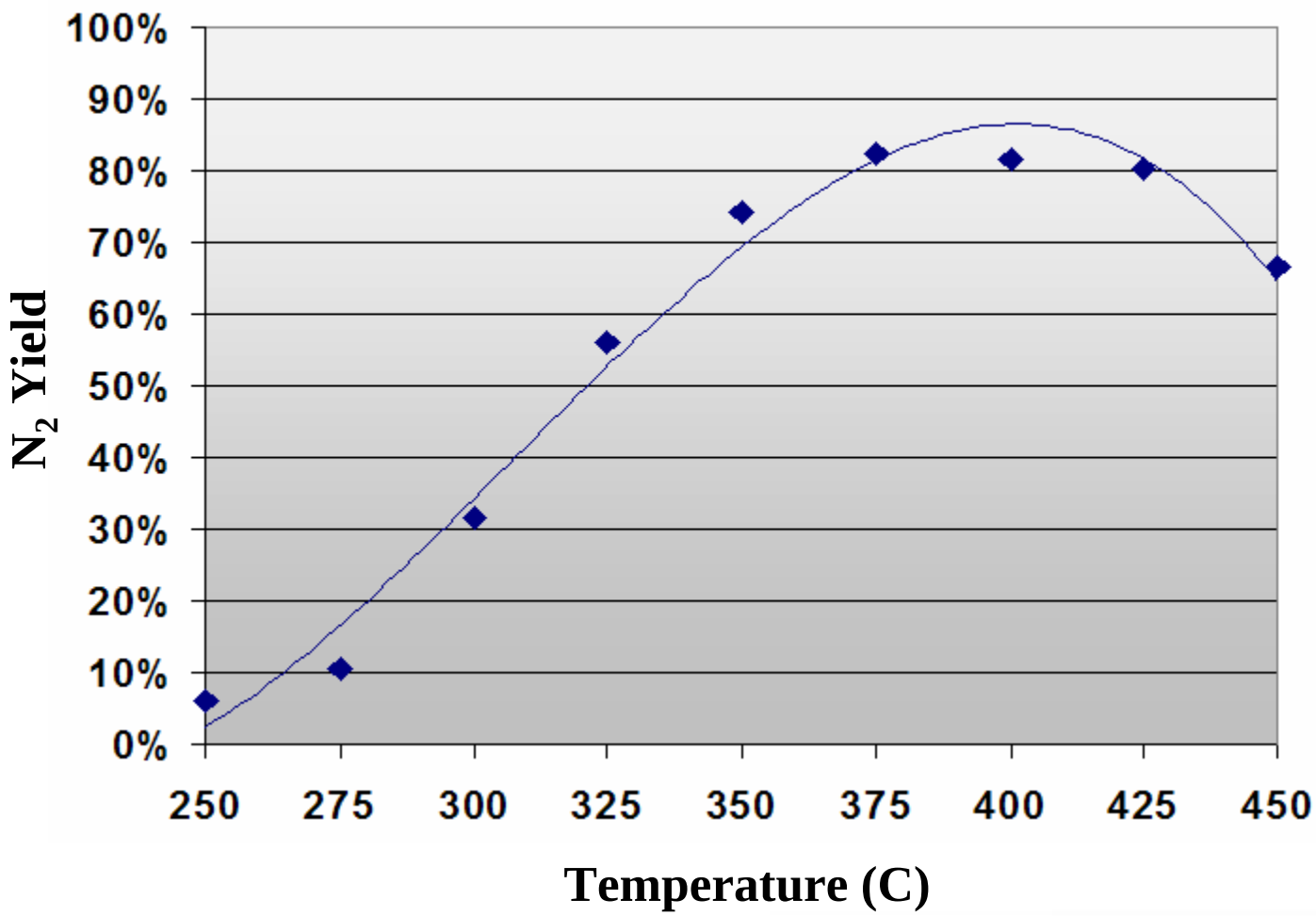
40% H_2

4% H_2O

Complete CO oxidation by 175°C under both conditions.

Mixed-bed reaction in the presence of CO&CO_2

With the addition of CO/CO_2, we still achieve N_2 yields around 80% between 375-425°C.



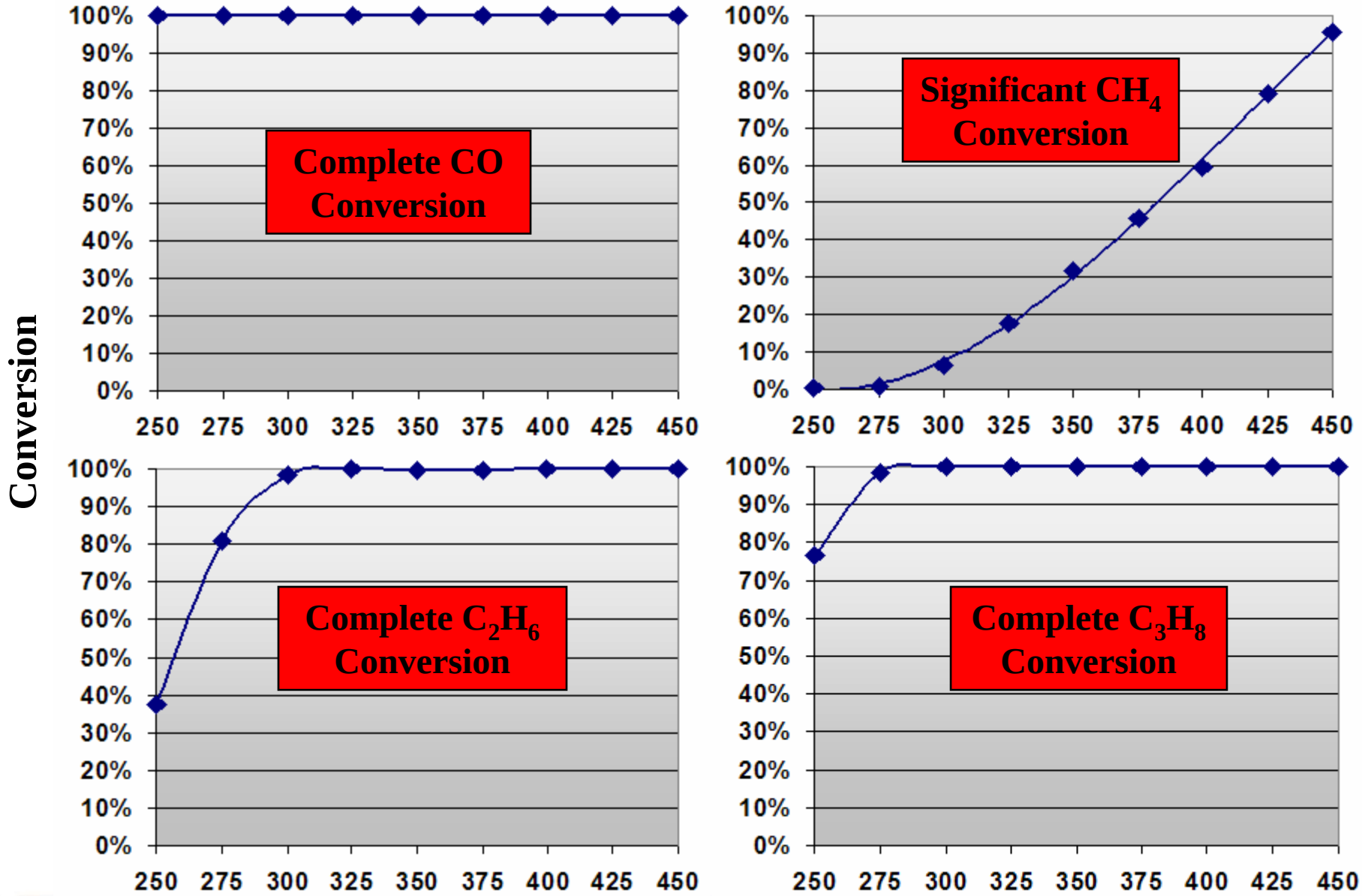
400ppm NO
10% O_2
2000ppm HC
600ppm CO
6% CO_2

0.3%Pd/5%SZ

10% Co/ZrO2
IW300

(1:0.25)

Mixed-Bed Reaction (cont'd)



Dual Catalyst Aftertreatment

Cleanup of NO, CO, and Hydrocarbons

Simulated Lean Exhaust in 375-425°C.

400 ppm NO	→	**80% N_2 Yield**
1700 ppm CH_4	→	**60-80% Conversion**
200 ppm C_2H_6	→	**100% Conversion**
100 ppm C_3H_8	→	**100% Conversion**
600 ppm CO	→	**100% Conversion**

Hydrothermal Stability: Preliminary Testing

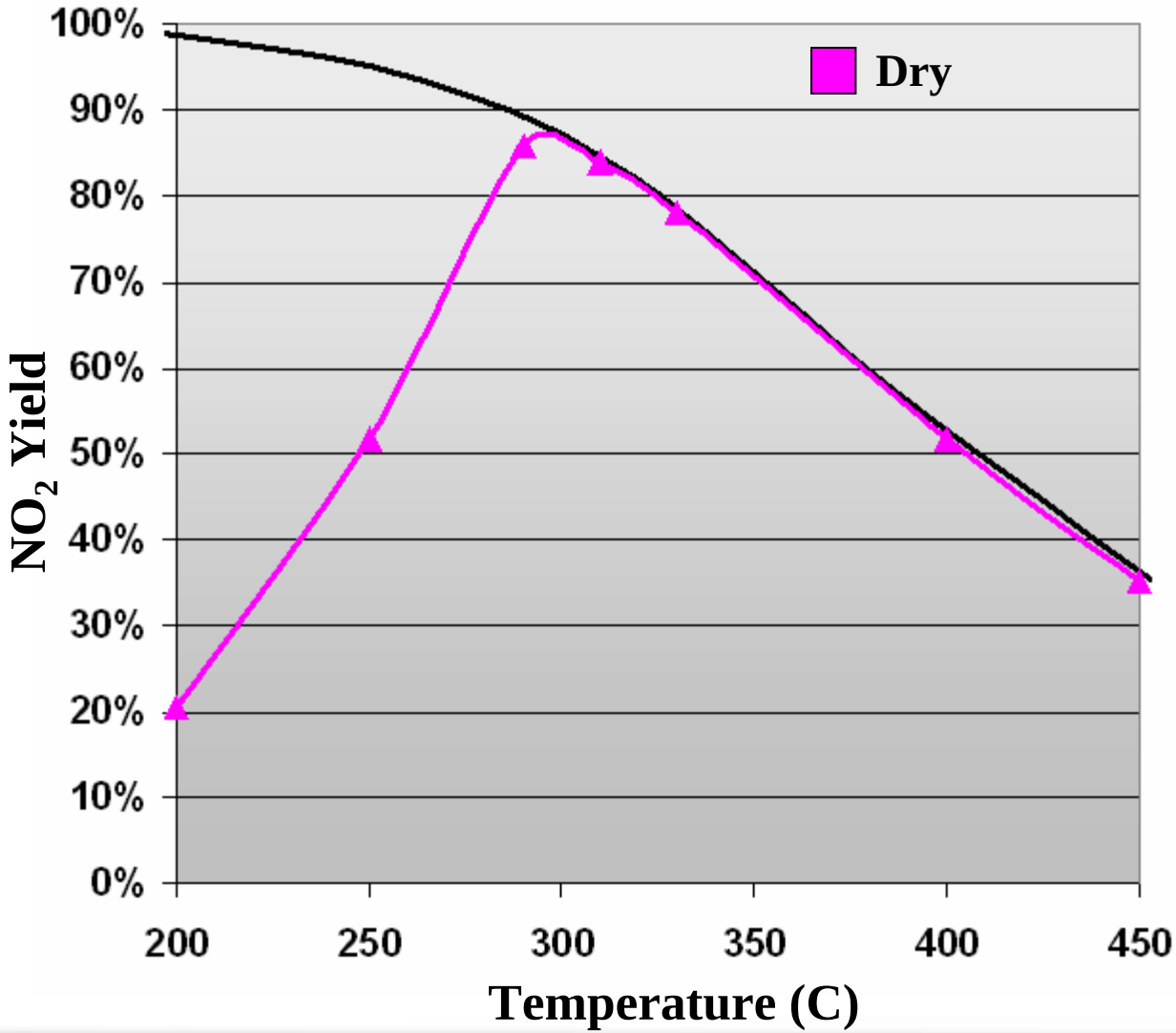
Effect of H_2O on NO Oxidation Catalyst

Oxidation catalyst

Catalyst

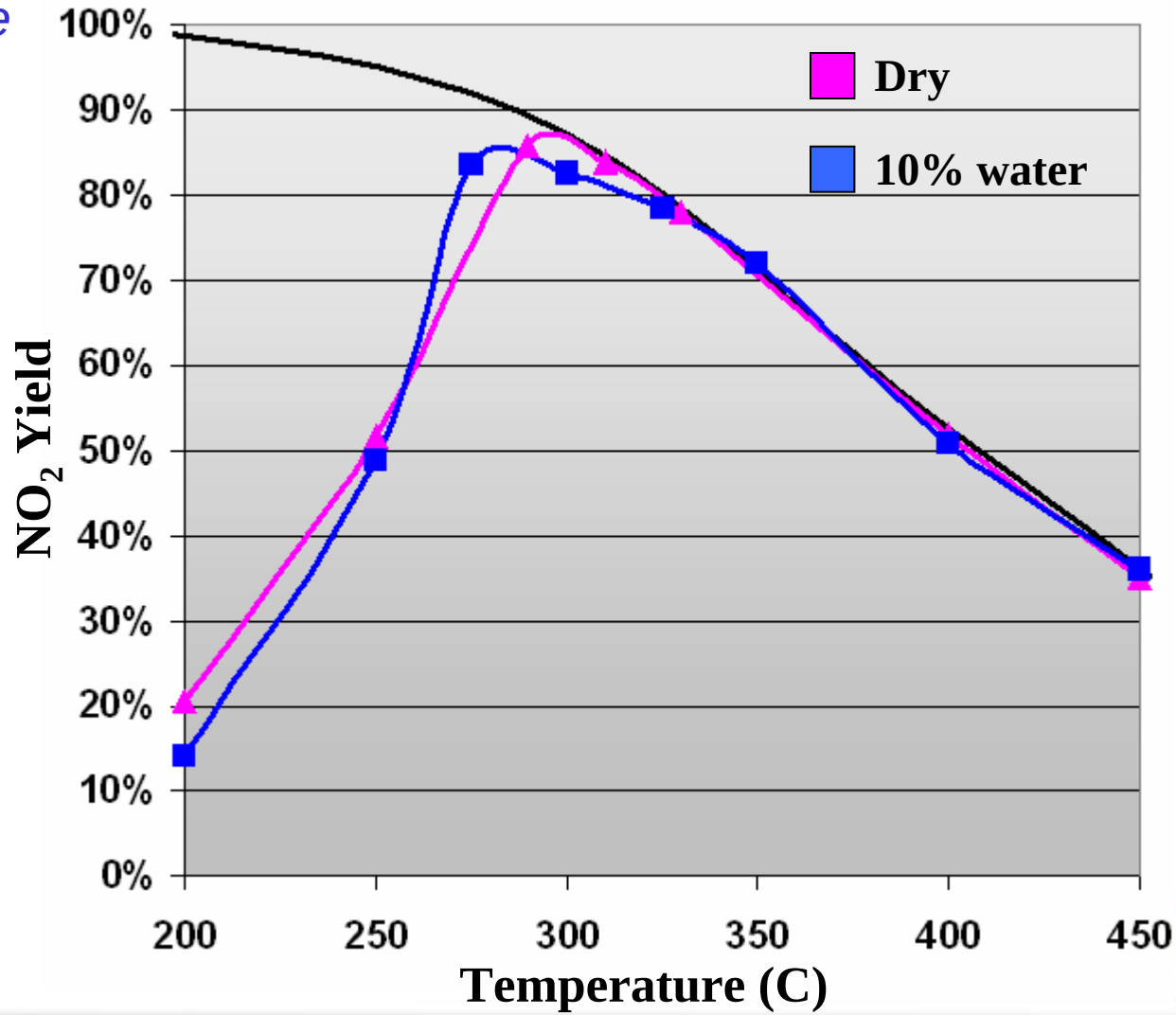
10% Co/TiO_2
IW300

1000 ppm NO
10% O_2



Effect of water on oxidation catalyst

Water has little effect on the catalyst's NO oxidation behavior.

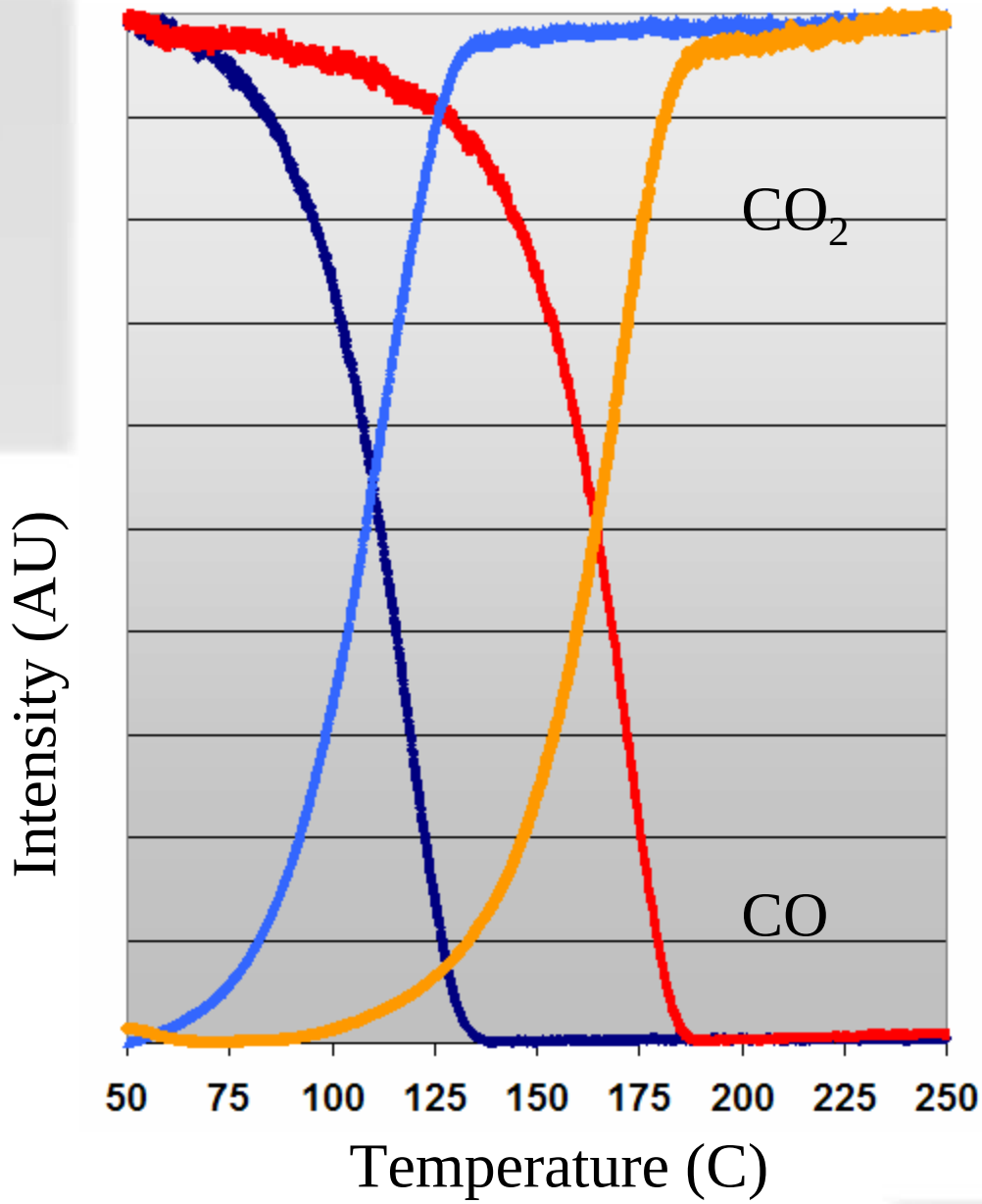


Catalyst

10% Co/TiO_2 IW300

1000 ppm NO
10% O_2
with
0% H_2O
or
10% H_2O

TPRxn CO Oxidation - Effect of Water



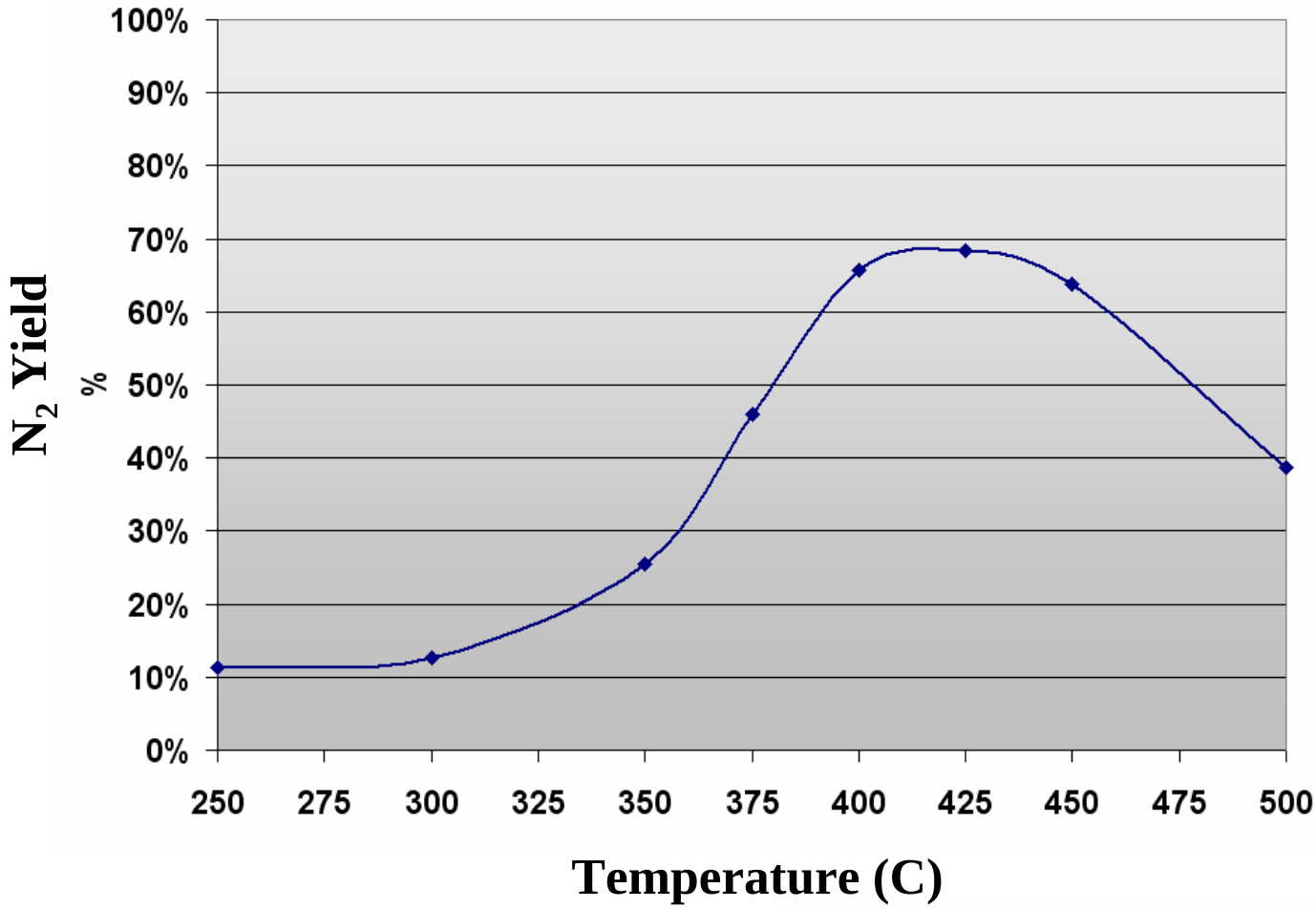
10% Co/ZrO_2 IW300

H_2O increases the light off temperature of CO oxidation by about 50°C, but complete conversion is still reached.

5000 ppm CO
1% O_2
2% H_2O

Steady-state reaction experiments performed between 300-500°C in 10% H_2O show complete CO conversion.

Mixed-bed reaction in the presence of H_2O



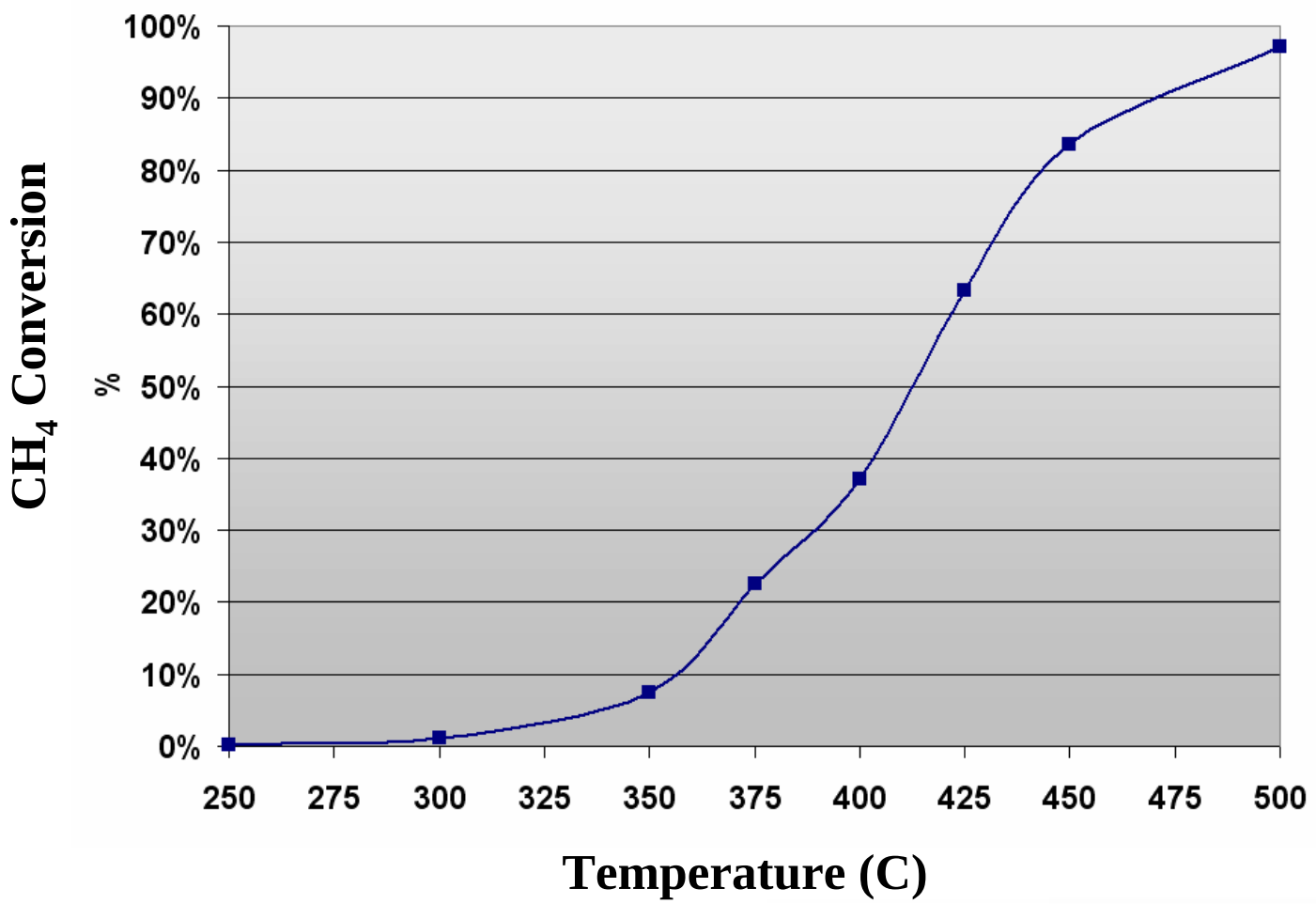
1000ppm NO
10% O_2
3000ppm CH_4
1% H_2O

0.5%Pd/5%SZ

10% Co/ZrO2
IW300

(1:0.25)

Mixed-bed reaction in the presence of H_2O



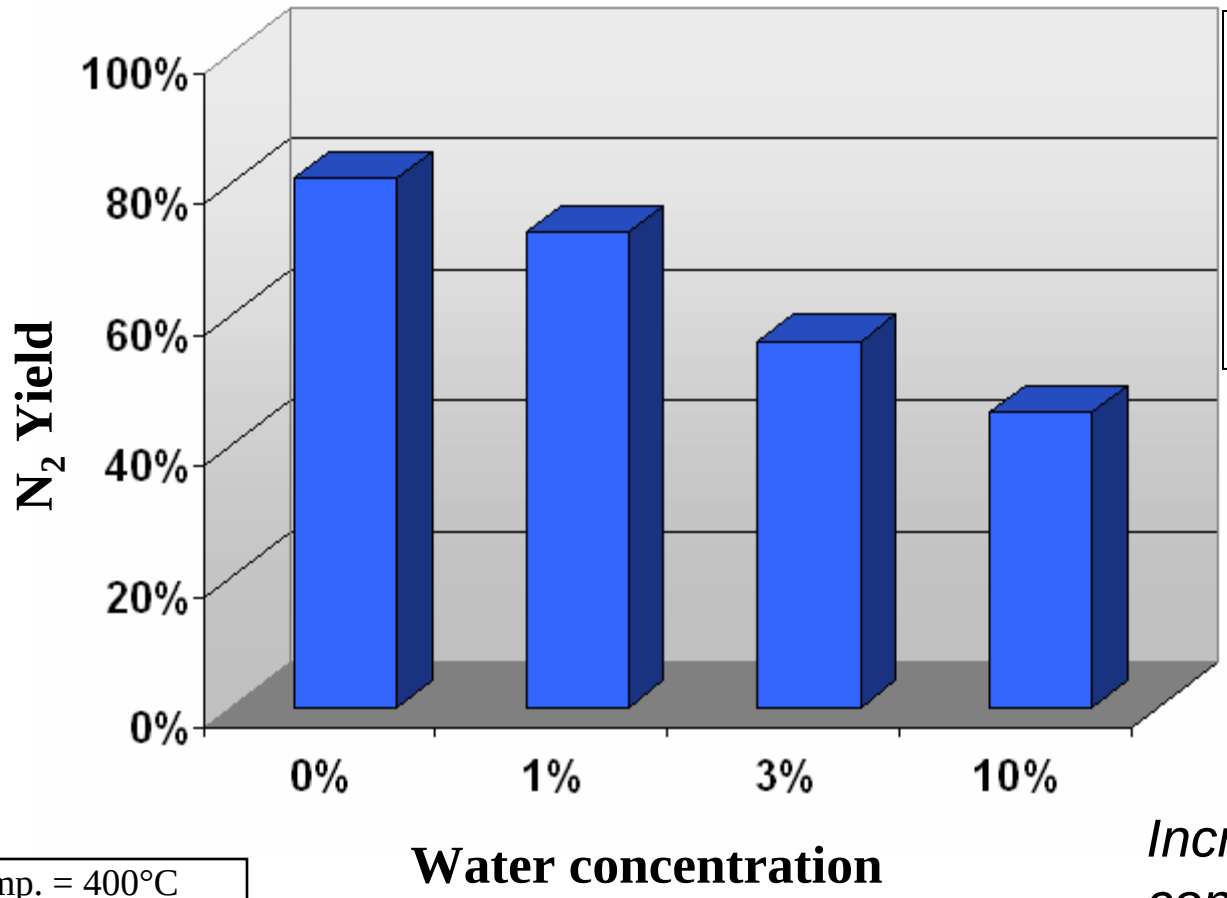
1000ppm NO
10% O_2
3000ppm CH_4
1% H_2O

0.5%Pd/5%SZ

10% Co/ZrO2
IW300

(1:0.25)

Mixed bed: Effect of water concentration



Catalyst mixture

0.3%Pd/5%SZ

10% Co/ZrO_2 IW300

(1:0.25)

Temp. = 400°C
1000 ppm NO
3000 ppm CH_4
10% O_2
0, 1, 3, or 10% H_2O

Increasing water concentration leads to lower N_2 yields.

Why is the N_2 yield lower?

Is the catalyst surface changing?

Do we lose sulfur from the surface?

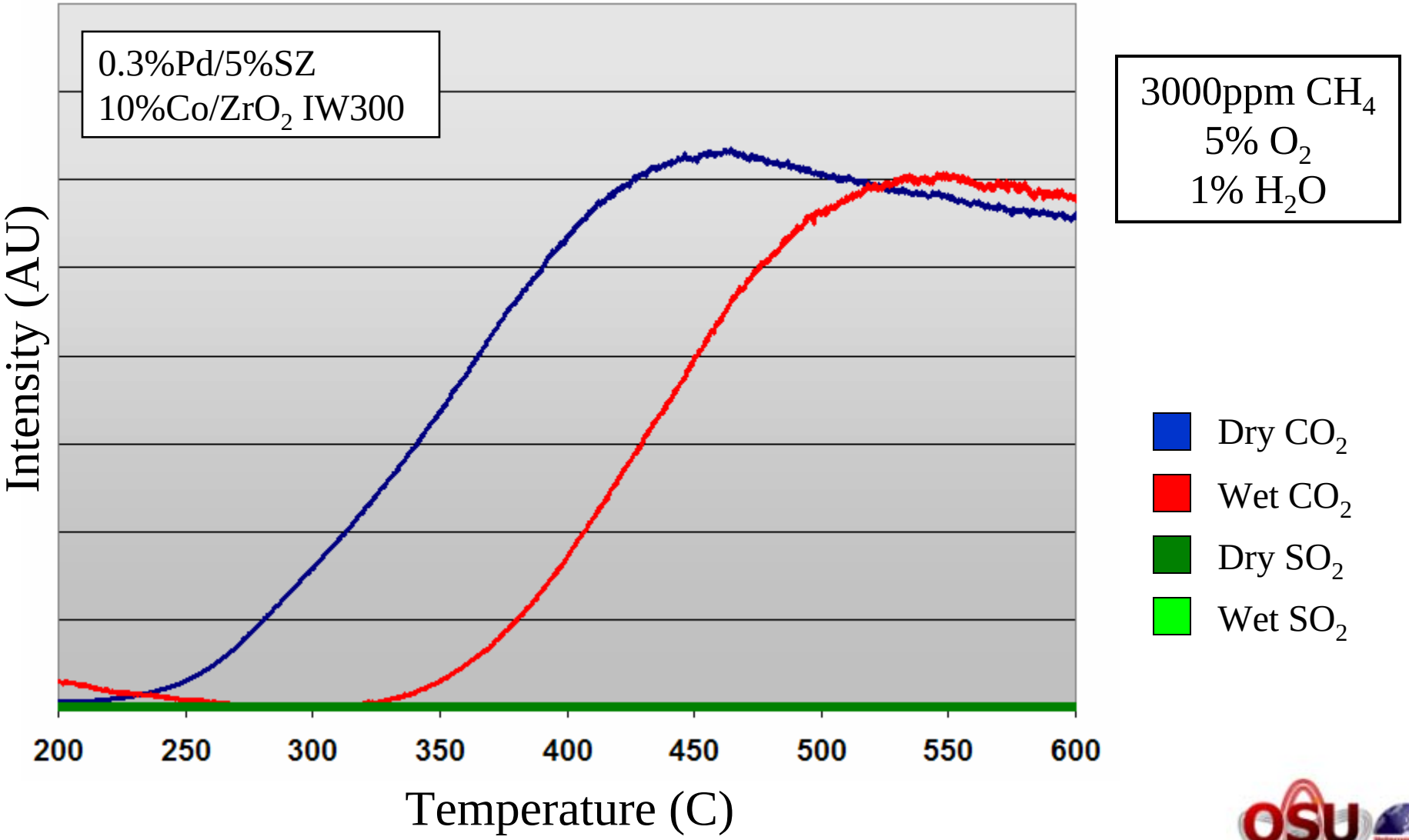
Temperature Programmed Desorption

Species leaving surface are monitored with a Mass Spectrometer while temperature is raised linearly

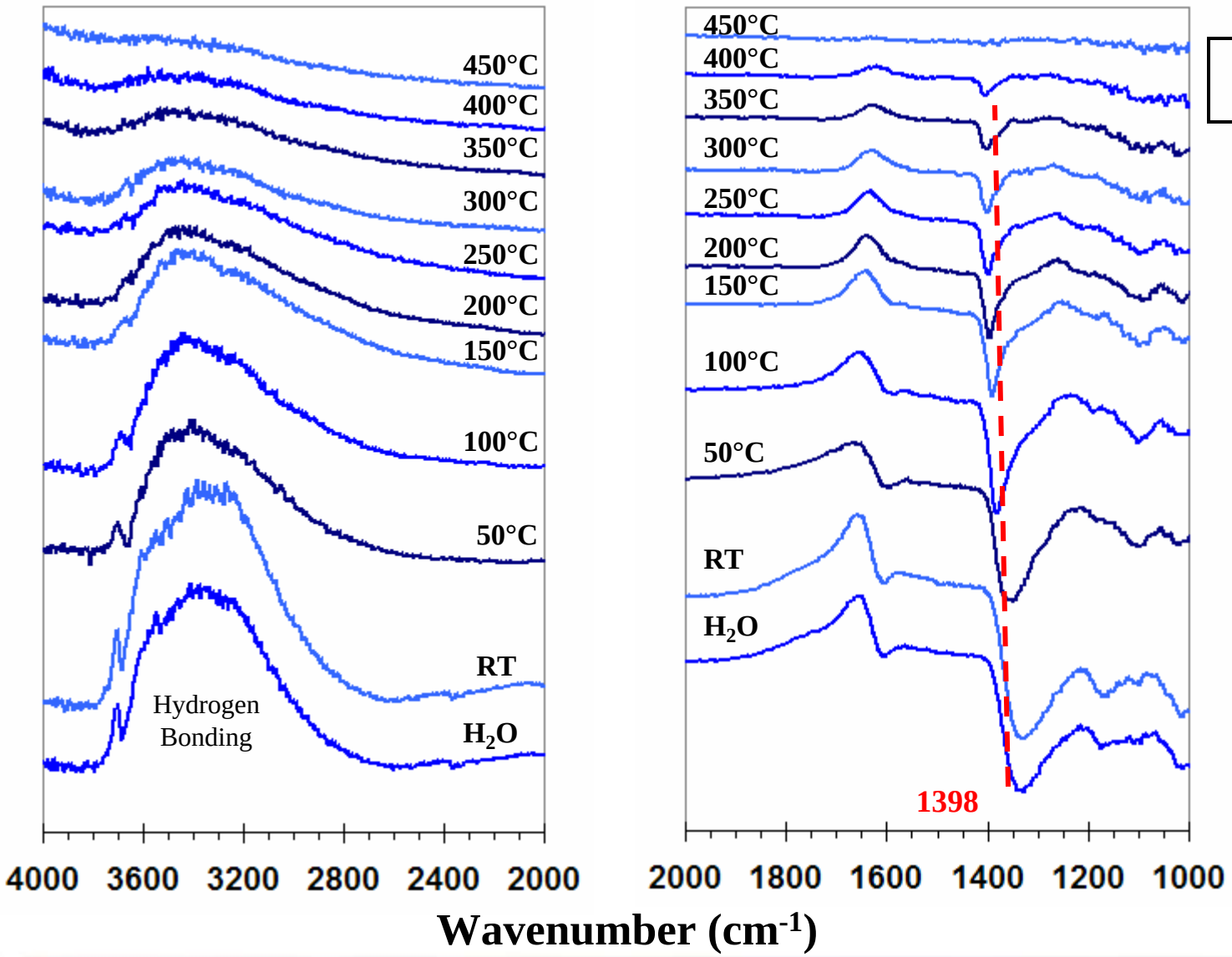
- Blank TPD in dry He
- Blank TPD in the presence of 2%H_2O in He

No loss of sulfate groups between 200-600ºC.

TPRxn of CH_4 Over Mixed-Bed



DRIFTS – H_2O TPD



0.5%Pd/5%SZ

H_2O peaks decrease and sulfate bands recover with increasing temperature.

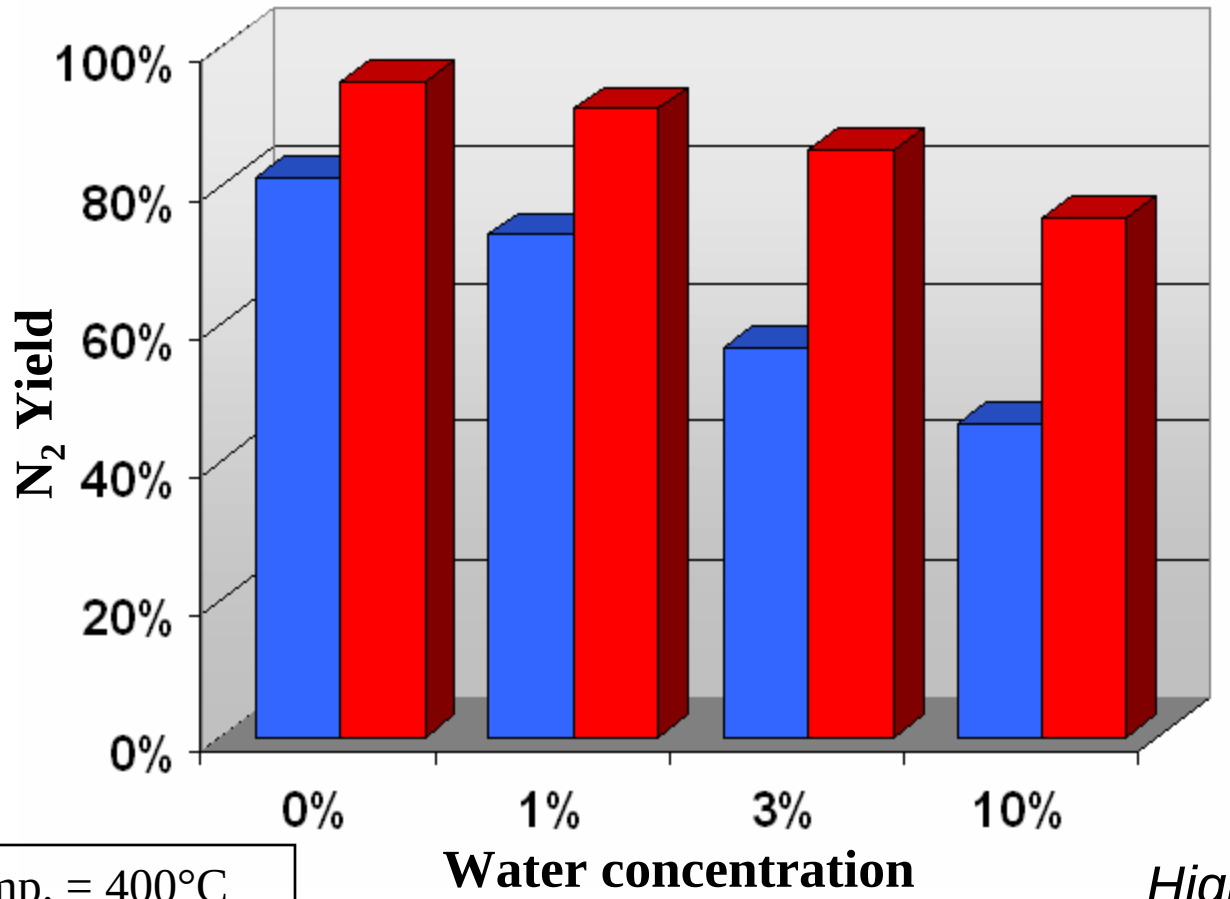
Complete desorption above 400°C, with full sulfate recovery.

It appears that the catalyst structure remains intact in the presence of water and the loss of activity is due to competitive adsorption of H_2O on S=O sites

Modify catalyst formulation

Increase the surface acidity

Mixed bed: Sulfate level comparison in water



Catalyst mixture

0.3%Pd/5%SZ

or

0.3%Pd/15%SZ

and

10% Co/ZrO2 IW300

(1:0.25)

Temp. = 400°C
1000 ppm NO
3000 ppm CH_4
10% O_2
0, 1, 3, or 10% H_2O

Higher sulfate levels show substantial improvement in N_2 yields.

Although still preliminary, the initial results are very promising in showing that we may be able to "tailor" the catalyst surface to optimize the active sites.

Dual Catalyst System Advantages

"Three-way catalyst" for lean systems

Zero fuel penalty → **Operates solely on engine exhaust. No fuel addition required.**

Replaces oxidation catalyst → **Oxidation of CO and hydrocarbons occurs over these catalysts, so they can replace current oxidation catalysts**

Ease of installation, retrofitting → **Works with existing engines without modification or additional control systems**

Results are very promising, but more work is needed.

Future Work (1/3)

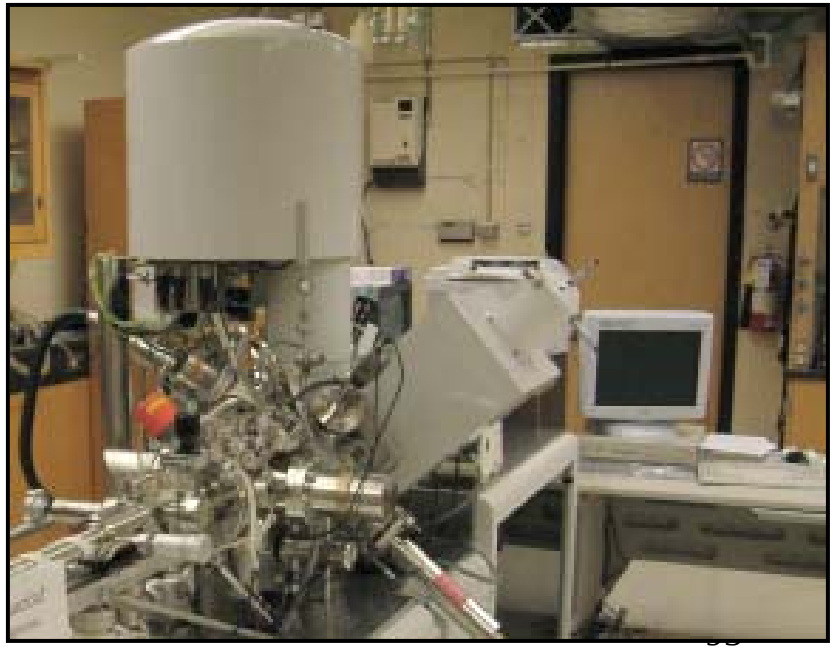
- **Catalyst formulation**
  - Surface acidity
  - Surface hydrophobicity
  - Addition of promoter/stabilizer materials
  - Replacement of Pd with transition metals
  - Combining oxidation and reduction sites on the same catalyst
  - Lowering metal content for cost savings

Future Work (2/3)

- **Catalyst characterization**
  - *In-situ* catalyst characterization to guide the catalyst formulation studies
- **Kinetic experiments**
  - Hydrothermal stability testing
  - Reaction parameters
  - Catalyst ratios and residence time
  - Detailed mechanistic studies
  - Time-on-stream studies
  - Deactivation / regeneration studies

Future Work (3/3)

- **Towards scale-up**
  - Optimization of mixed catalyst bed
  - Tests under realistic conditions
  - Catalyst manufacturability
    - Wash-coating
    - Pelletizing



- **Engine testing**

Technology Transfer

and

Collaboration with industry

Patents

Three Provisional Patent applications filed

- Two-stage catalytic system for nitrogen oxide reduction with methane under lean conditions
- Dual Catalyst System for Lean Exhaust Aftertreatment
- Low temperature oxidation of CO on Co/ZrO_2 catalysts

Industry Collaboration:

Site visit to Caterpillar's Lafayette Engine Plant on June 20th, 2005.

Discussions in progress for collaboration and future engine testing.

Discussions with Sud Chemie for catalyst development

Publications and Presentations

Publications in progress

- Holmgreen, E., Yung, M. and Ozkan, U.S., "Two-Stage Catalytic NOx Reduction with Hydrocarbons for Lean Burn Gas Fired Reciprocating Engines" Proceedings of ICEF04 ASME Internal Combustion Engine Division 2004 Fall Technical Conference **893**, 1-7 (2004).
- Yung, M., Holmgreen, E., and Ozkan, U.S., "Oxidation of NO to NO_2 over cobalt-based metal-oxide supported catalysts" to be submitted to *Journal of Catalysis*.
- Holmgreen, E., Yung, M. and Ozkan, U.S., "NO and NO_2 reduction of Pd-based sulfated-zirconia catalysts" to be submitted to *Journal of Molecular Catalysis*.
- Yung, M., Holmgreen, E., and Ozkan, U.S.,"Low-temperature CO oxidation of Co/ZrO_2 catalysts" to be submitted to Journal of Catalysis.
- Holmgreen, E., Yung, M. and Ozkan, U.S., "Two-stage catalytic reduction of NO with methane"to be submitted to *Applied Catalysis*

Presentations (1/2)

•“Oxidation of NO and CO over cobalt based metal oxide supported catalysts.” American Institute of Chemical Engineers Annual Meeting, Cincinnati OH, October 2005; to be presented

•“Dual-catalyst system for lean exhaust aftertreatment.” American Institute of Chemical Engineers Annual Meeting, Cincinnati OH, October 2005; to be presented.

•"Two-Stage Catalytic Reduction of NOx Methane Under Lean Conditions." North American Catalysis Society Annual Meeting, Philadelphia PA, May 2005.

•“Two-Stage Catalytic Reduction of NOx with Hydrocarbons in Lean Conditions.” Ohio State Hayes Graduate Research Forum, Columbus OH, April 2005. **1st Place Award**

•"Two-Stage Catalytic Reduction of NOx Under Lean Conditions." 2nd Annual Advanced Stationary Reciprocating Engines Conference, Moving Forward in Low-Emissions and High-Efficiency Technologies, U.S. DOE, California Energy Commission, Diamond Bar, CA, March 2005.

Presentations (2/2)

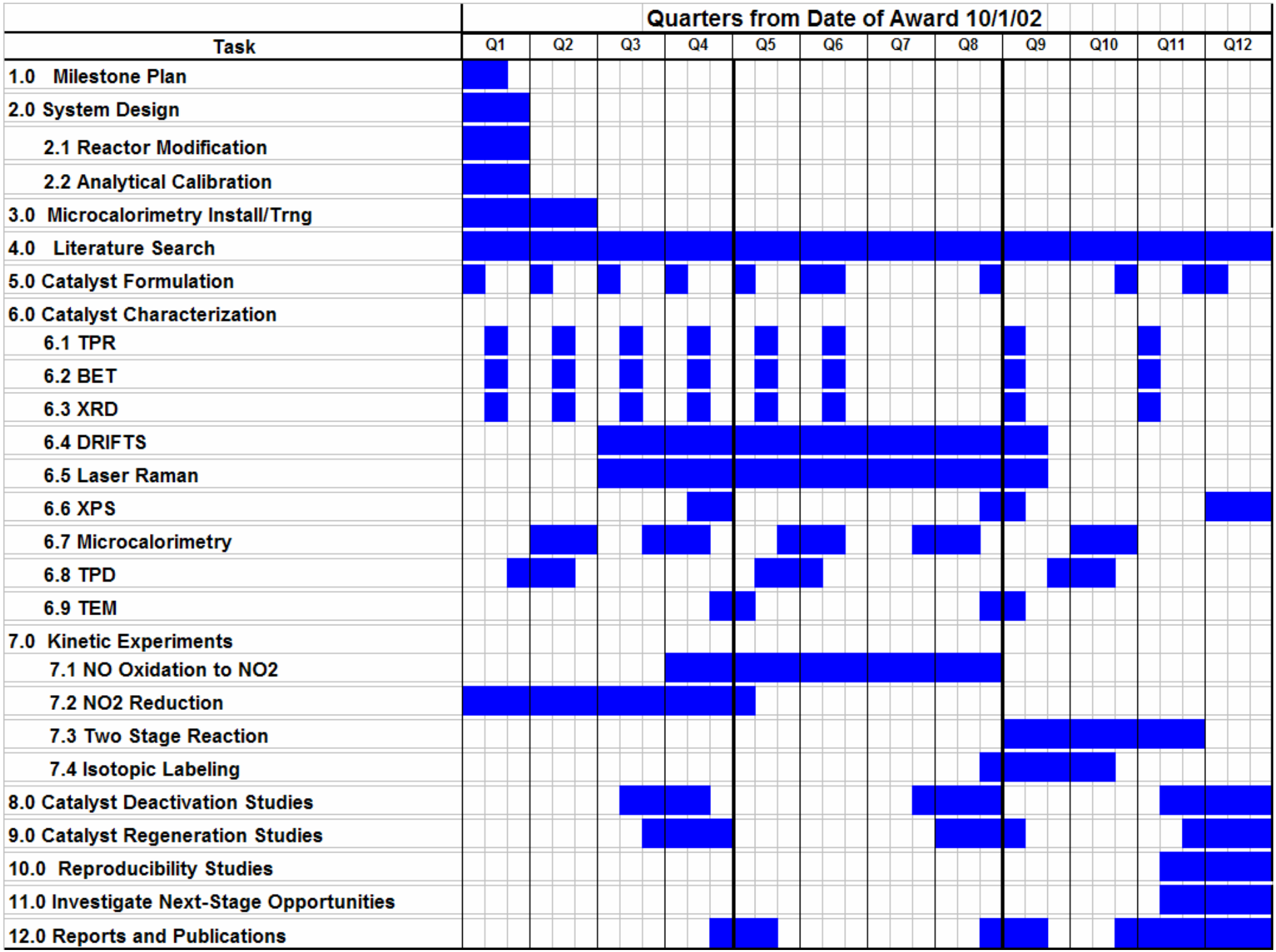
•"Two-Stage Catalytic Reduction of NOx Under Lean Exhaust Conditions." Ohio Air Quality Research Symposium, Athens OH, December 2004; Poster Presentation. **3rd Place Award**

•"Two-Stage Catalytic Reduction of NOx with Hydrocarbons." American Society of Mechanical Engineers, Internal Combustion Engine Division Meeting, Long Beach CA, October 2004.

•"Nitrogen Oxide Emission Control for Lean-Burn Engines by Two-Stage Catalytic Reduction with Hydrocarbons." Great Lakes Pollution Prevention Roundtable, Columbus OH, September 2004; Poster Presentation.

•"Two-Stage Catalytic Reduction of NOx with Hydrocarbons." ARES University Peer Review, Chicago IL, May 2004.

•"Two-Stage Catalytic Reduction of NO with Hydrocarbons in Lean Conditions." Distributed Energy Resources Peer Review Meeting, Washington DC, December 2003; Poster Presentation.


Quarters from Date of Award 10/1/02
Task
Q1
Q2
Q3
Q4
Q5
Q6
Q7
Q8
Q9
Q10
Q11
Q12
1.0 Milestone Plan
2.0 System Design
2.1 Reactor Modification
2.2 Analytical Calibration
3.0 Microcalorimetry Install/Trng
4.0 Literature Search
5.0 Catalyst Formulation
6.0 Catalyst Characterization
6.1 TPR
6.2 BET
6.3 XRD
6.4 DRIFTS
6.5 Laser Raman
6.6 XPS
6.7 Microcalorimetry
6.8 TPD
6.9 TEM
7.0 Kinetic Experiments
7.1 NO Oxidation to NO2
7.2 NO2 Reduction
7.3 Two Stage Reaction
7.4 Isotopic Labeling
8.0 Catalyst Deactivation Studies
9.0 Catalyst Regeneration Studies
10.0 Reproducibility Studies
11.0 Investigate Next-Stage Opportunities
12.0 Reports and Publications

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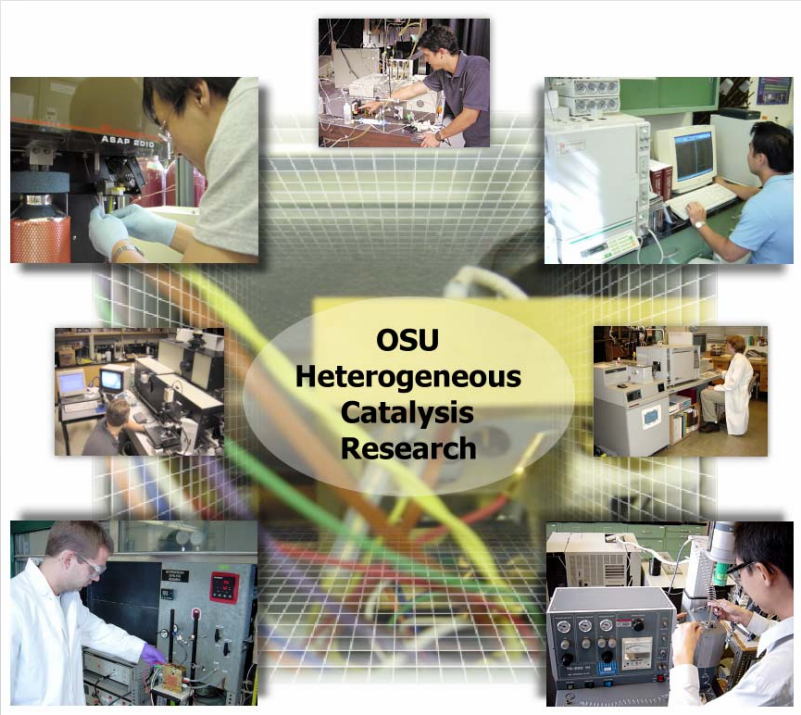

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