Investigation of Mixed Oxide Catalysts for NO Oxidation

ACE078

George Muntean
Ja Hun Kwak, Donghai Mei, Darrell Herling

Pacific Northwest National Lab

May 17, 2012

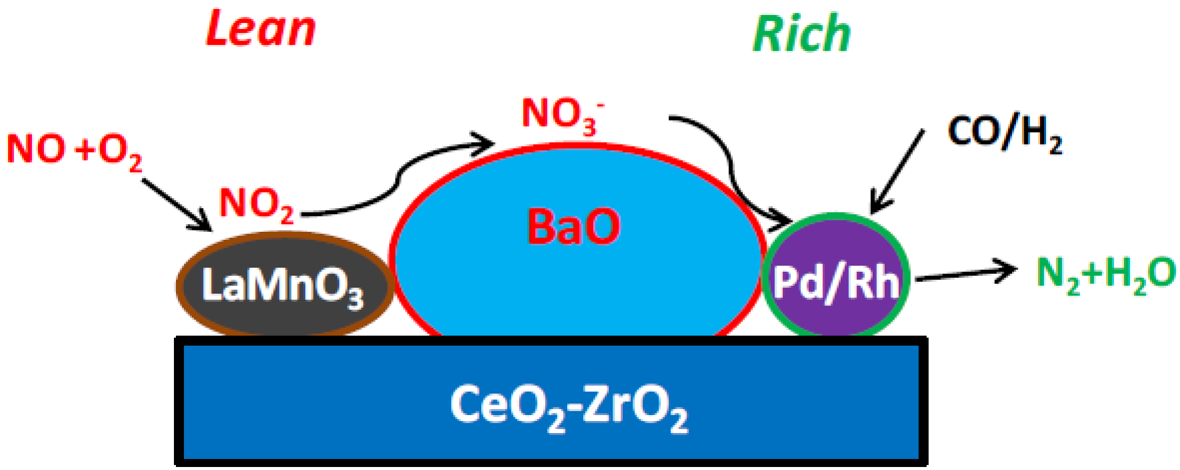
Overview

- **Timeline**
  - Start – Oct 2011
  - Finish – Sept 2014
  - 36-month CRADA
- **Budget**
  - Total project funding
    - DOE: $450k ($150k/year)
    - Matched 50/50 by GM per CRADA agreement
  - Funding authorized to-date: $186k
- **Barriers**
  - Reduce or optimize PGM usage as “critical materials” in emission control devices
  - Development of low-temperature oxidation catalysts
  - Better understanding of active sites and structure requirements in catalysts
  - Design and modeling of catalyst functions and structures
- **Partner**
  - General Motors
  - GM’s university partner in China (Tianjin University)

Objectives

This CRADA project aims to *develop and demonstrate a substitutive option for Pt oxidation function using mixed-metal oxide structures.*

- Improve the understanding of the nature and structure of active sites for mixed metal oxide catalysts intended for NO oxidation
- Study of synthesis and metal dopant on resulting structure and effectiveness of NO oxidation

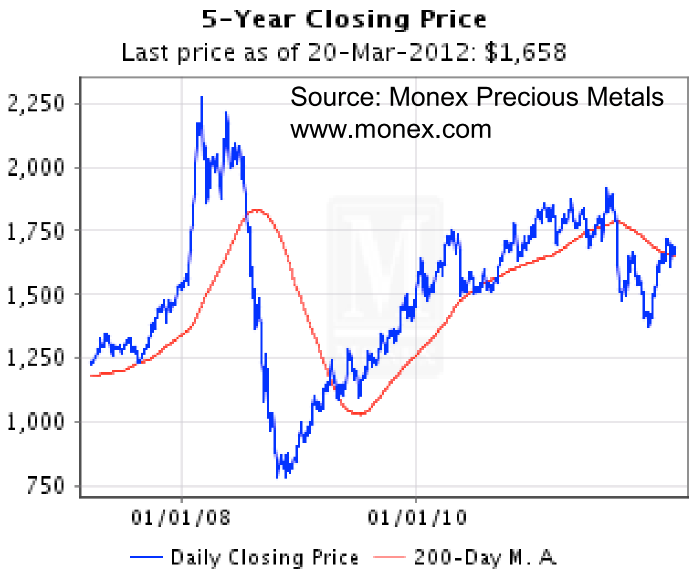


- Typical LNT catalyst structure (left)

Motivation and Relevance

- Higher efficiency engines often implies lower exhaust temperature, requiring better low-temp catalysis to meet emission regulations by inexpensive and reliable NOx emission control

- Pt commodity pricing is still high and volatile, although the rate of increase is leveling off



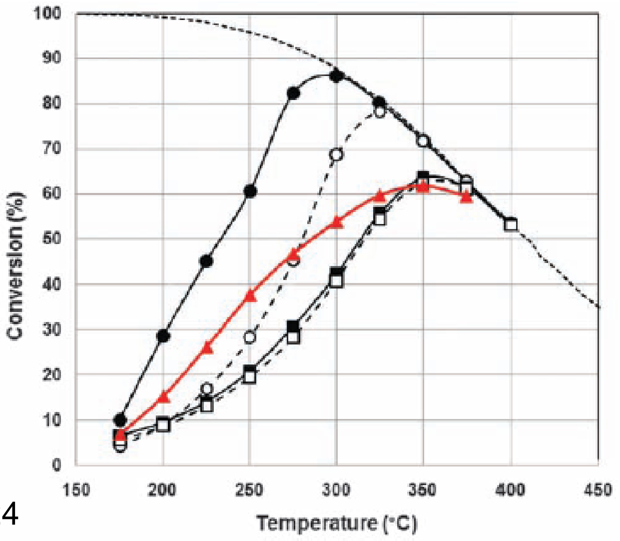
Source: Monex Precious Metals www.monex.com

- Thrifting or replacement of Pt in DOC and LNT catalysts desired for:
  - supply-chain stability
  - cost reduction as an enabler to advanced aftertreatment and combustion technologies
  - alternative technologies for oxidation reactions

Partnership with GM - CRADA

- Based on research reported by GM (Science 327 (2010) 1624)
  - CRADA initiated for PNNL assistance leveraging surface science and catalysis capabilities
  - Analytical assessment and computational model
- Scope split, but coordinated between GM and PNNL
  - GM - Catalyst formulation, aging and testing
  - PNNL - Characterize structure and active sites, along with alternative synthesis processes and assessment of the effect on performance

Fig. 1. NO oxidation activities for $LaCoO_3$ (○), $La_{0.9}Sr_{0.1}CoO_3$ (●), $LaMnO_3$ (□), $La_{0.9}Sr_{0.1}MnO_3$ (■), and commercial DOC (▲) at a gas hourly space velocity of 30,000 $hour^{-1}$; 400 parts per million (ppm) of NO and 8% of O_2 in a balance of N_2.



Science 327 (2010) 1624

Approach

- Prepare and evaluate both fresh and lab-aged catalyst materials to optimize the formulations for DOC and LNT applications

- Utilize catalysis expertise, state-of-the-art analytical techniques and computational analysis to investigate:
  - Surface and bulk properties of the catalyst materials with respect to the substitution of La by Mn and other dopants
  - Interaction between reactants and the potential active sites
  - And help inform more advanced catalyst formulations

Milestones and Planned 1st Year Tasks

- Characterization of fresh and lab-aged catalysts
  - Catalyst formulation and aging by GM
  - Characterize structure and number of active sites - XRD, TPD, TPO
- Determination of reaction mechanism
  - Source of oxygen, reaction between NO and oxygen, etc.
  - Effects of La substitution and aging on NO oxidation
- Computational analysis of active sites and reaction mechanism
  - Density function theory (DFT) calculations to help investigate the interaction between reactants and potential active sites

Milestone: Complete evaluation and characterization of the first round of fresh and aged DOC and LNT catalysts made of perovskite materials – September 2012 (on-schedule)

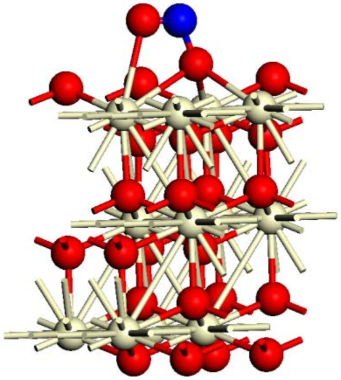
Insight into Reaction Mechanism
NO Oxidation on $CeO_2(111)$

$NO(g) + 1/2\ O_2(g)$ → $NO_2(g)$

ΔE = -1.16 eV

NO adsorption

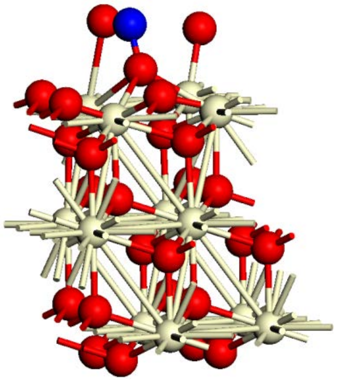
ΔE = -0.82 eV



$NO^* + 1/2\ O_2(g)$

O_2 adsorption

ΔE = +1.33 eV

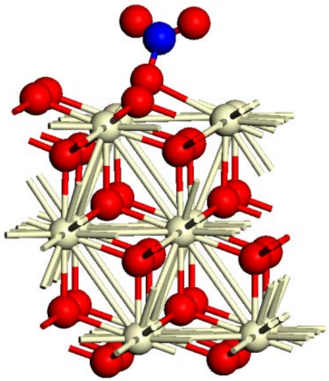


$NO^* + O^*$

NO oxidation

ΔE = -2.32 eV

NO_2^*

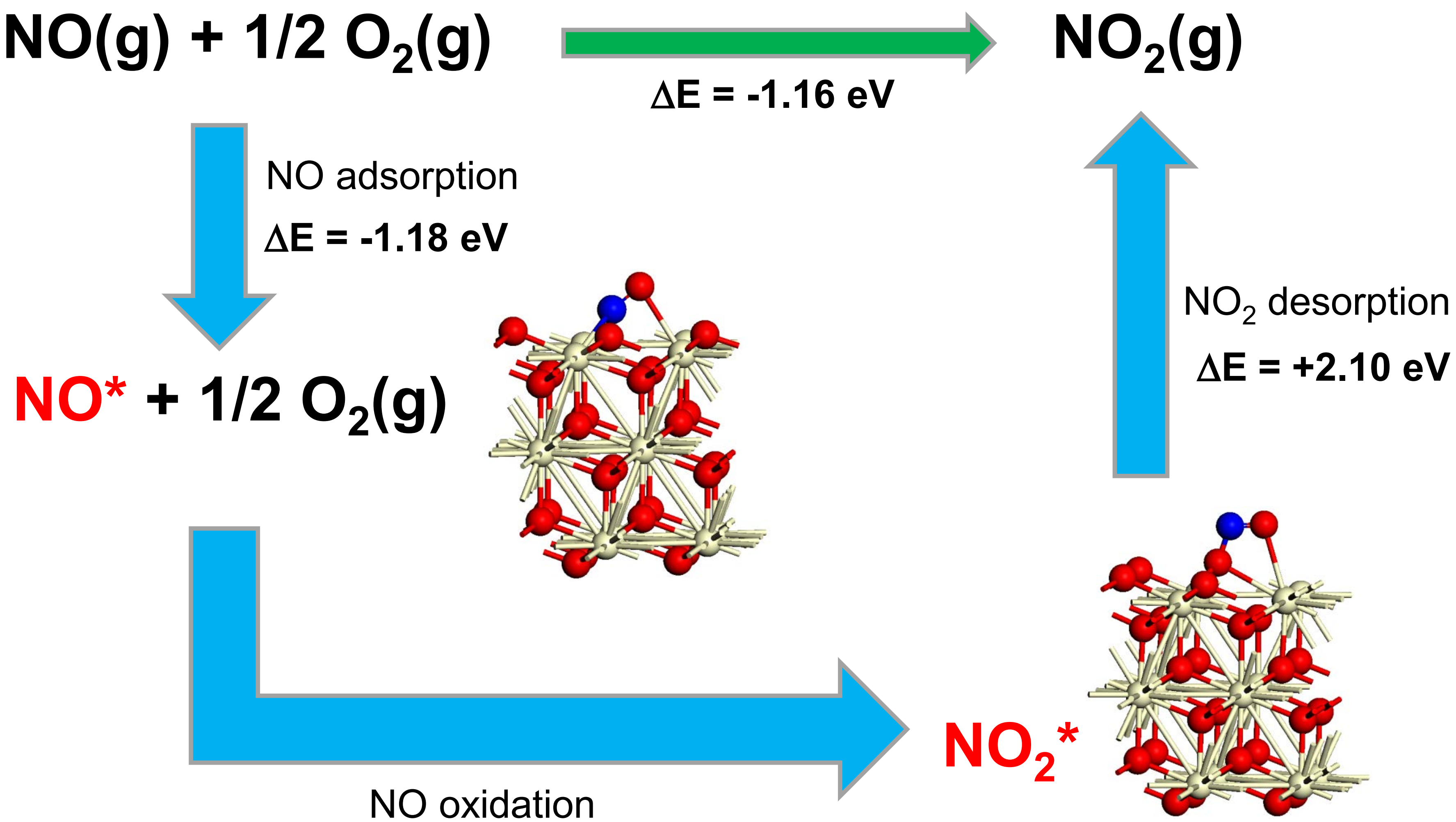


NO_2 desorption

ΔE = +0.65 eV

Insight into Reaction Mechanism

NO Oxidation on $CeO_{2-x}(111)$



$NO(g) + 1/2\ O_2(g)$ → $NO_2(g)$

$\Delta E = -1.16$ eV

NO adsorption

$\Delta E = -1.18$ eV

$NO^* + 1/2\ O_2(g)$

NO oxidation

$\Delta E = -2.00$ eV

NO_2^*

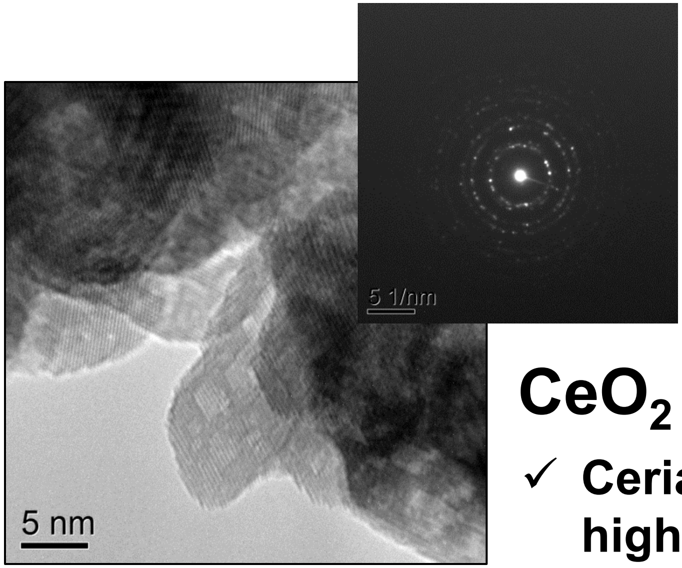
NO_2 desorption

$\Delta E = +2.10$ eV

Sample Preparation

- GM: synthesized by co-precipitation method
  - CeO_2
  - MnO_x
  - $Mn\text{-}CeO_x$ (Mn/(Mn+Ce) = 0.1)
  - $Mn\text{-}CeO_x$ (Mn/(Mn+Ce) = 0.3)
  - $Mn\text{-}CeO_x$ (Mn/(Mn+Ce) = 0.5)

Mn-CeO appears well mixed –
Co-precipitated structure is as desired

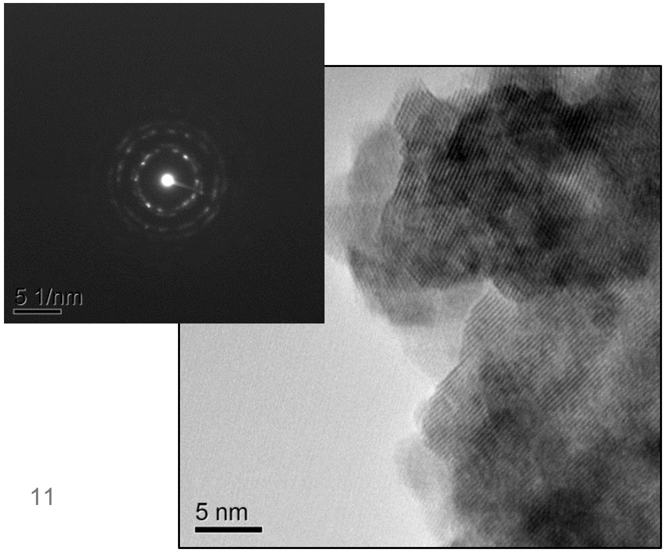


CeO_2

- ✓ Ceria shows highly crystalline status

Sample	Surface area(m^2/g)
CeO_2	37
MnO_x	14
$Mn\text{-}CeO_x$ (Mn/(Mn+Ce) = 0.1)	75
$Mn\text{-}CeO_x$ (Mn/(Mn+Ce) = 0.3)	88
$Mn\text{-}CeO_x$ (Mn/(Mn+Ce) = 0.5)	64

- ✓ Significantly higher BET surface area on MnO_x-CeO_2 samples compared to MnO_x or CeO_2



$Mn\text{-}CeO_x$ (Mn/(Mn+Ce) = 0.5)

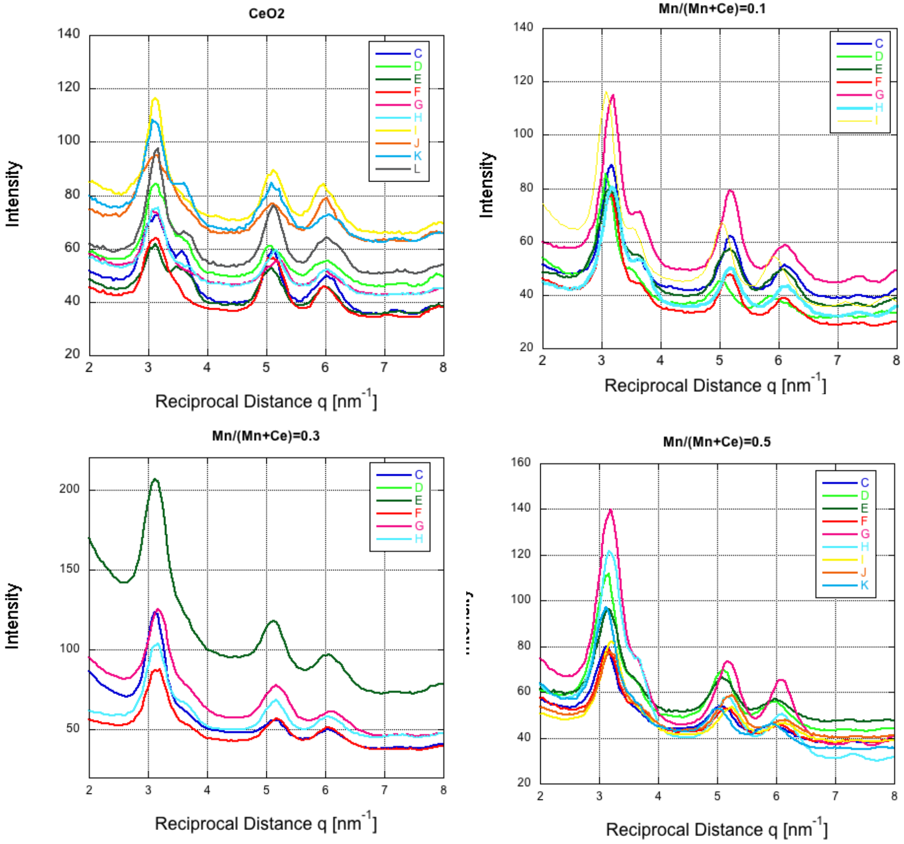
- ✓ MnO_x-CeO_2-0.5 sample shows relatively small domain size compared with CeO_2 but still well crystalline structure
- ✓ No evidence of separated MnO_x

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Institute for
INTEGRATED
CATALYSIS

So where is the Mn?

Electron diffraction



- ✓ **Diffraction pattern data confirms a crystalline structure in Mn-CeO_2-0.5 co-precipitated samples**
- ✓ **Electron diffraction effective to identify the crystallinity of small domain**

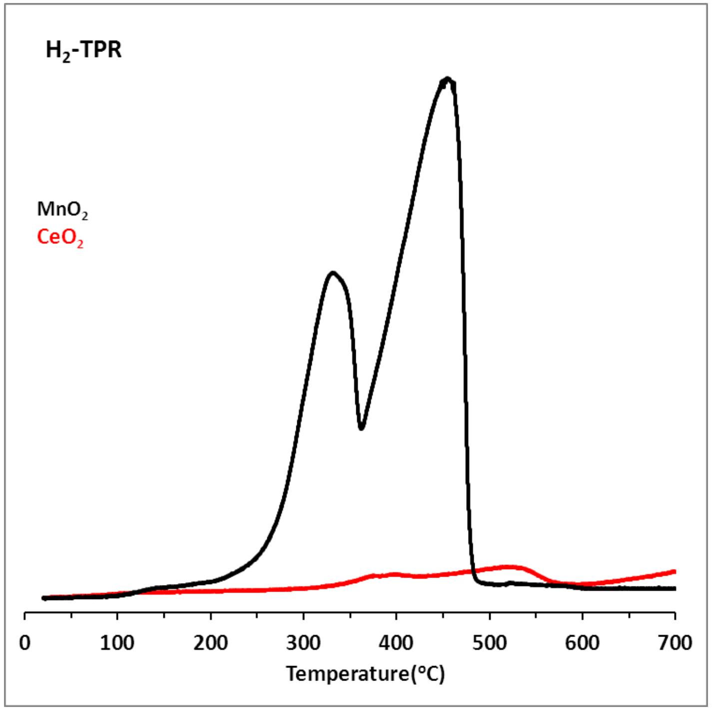
Lattice parameter from electron diffraction

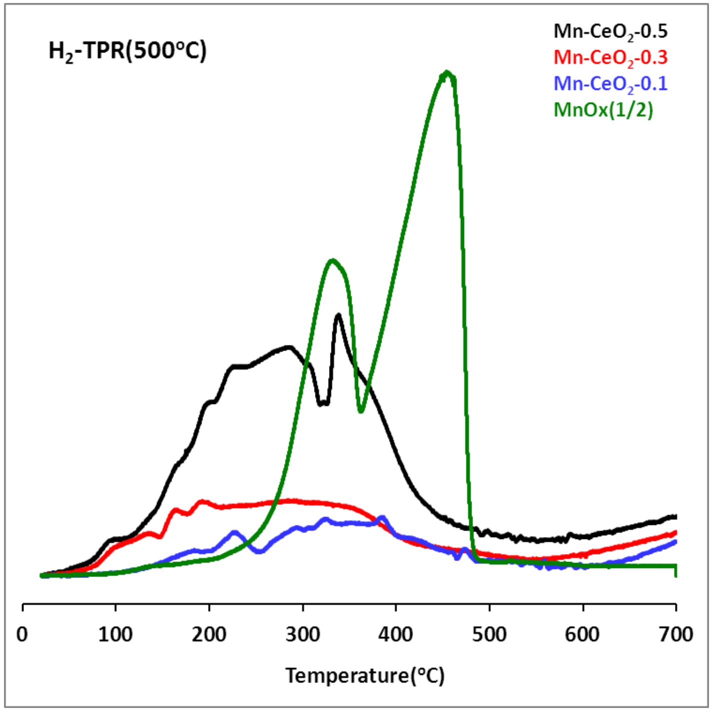
Sample	d(111) (Å)
CeO_2	3.233
Mn-CeO_x (Mn/(Mn+Ce) = 0.1)	3.193
Mn-CeO_x (Mn/(Mn+Ce) = 0.3)	3.200
Mn-CeO_x (Mn/(Mn+Ce) = 0.5)	3.167

- ✓ **Lattice parameter points to a lattice contraction with higher Mn loading, which suggests Mn within the ceria lattice as intended**
- ✓ **Unknown is if any Mn is on Ceria surface and the impact on NO oxidation performance**

Reduction behavior of the mixed oxides suggests broad Mn distribution

- ✓ Negligible H_2 consumption on ceria (baseline)
- ✓ MnOx shows stoichiometric reduction on Mn^{4+} to Mn^{3+} at ~ 320°C and Mn^{3+} to Mn^{2+} at ~ 450°C.
- ✓ Hydrogen consumption peaks are 0.27 and 0.49 (H/Mn) which suggests that even after calcined at 500°C MnO_x is mixture of MnO_2 and Mn_2O_3.

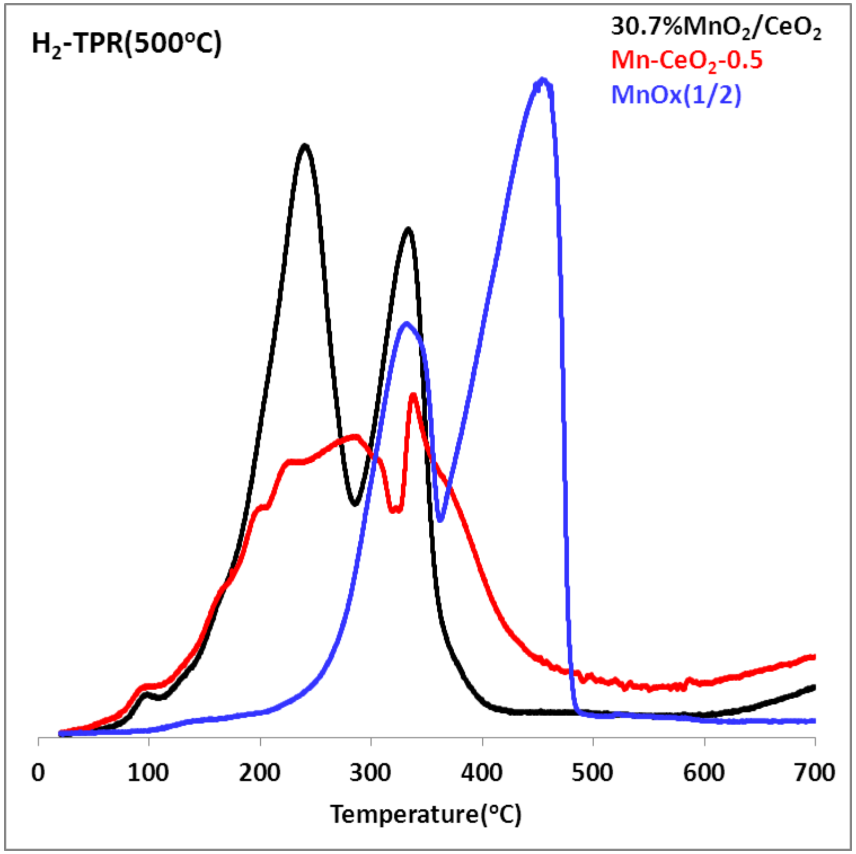




- ✓ Complex hydrogen reduction peaks suggests wide distribution of Mn species in the ceria lattice and on surface.
- ✓ Lower temperature reduction suggests more active oxygen state which should correlate with NO oxidation activity.

Is surface MnO_x active?

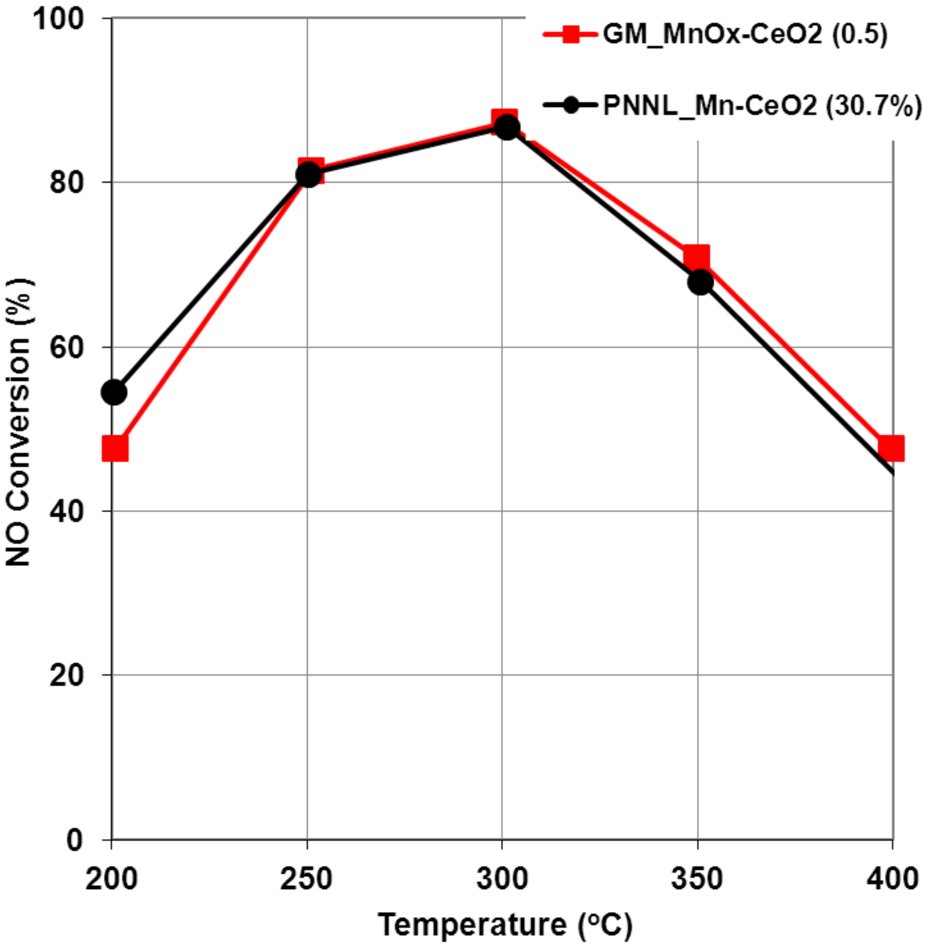
- Synthesized by incipient wetness method
- Support: high surface area CeO_2 (from GM S.A. = ~ 120m2/g)
- MnO_x loading: 3.4, 6.9, 14.3, 30.7 wt%



- ✓ **Impregnated sample shows relatively simple hydrogen consumption profile compared with co-precipitated sample.**
- ✓ **Significantly lower reduction temperature compare with MnO_x and higher Mn^{4+} to Mn^{3+} reduction peak intensity.**
- ✓ **Results suggest that ceria helps higher oxidation state of Mn species (mostly Mn^{4+})**
- ✓ **Confirmed that surface MnO_x is active.**

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965
Institute for INTEGRATED CATALYSIS

MnO_x on Ceria surface only supports NO oxidation reaction



- ✓ **Impregnated PNNL catalyst shows comparable NO oxidation activity with co-precipitated catalysts.**
- ✓ **MnO_x on ceria surface appears adequate for NO oxidation.**
- ✓ **Easier to synthesize with similar NO oxidation performance.**

Conclusion

- Impregnated catalysts show similar catalytic behavior on NO oxidation reaction with co-precipitated samples which suggests the Mn doping in the ceria lattice is not important - need to confirm.

- CeO_2 significantly lowers the reduction temperature of MnO_x promoting a higher Mn oxidation state compared to non-supported MnO_x

Summary & Future Work

- Project Q1 progress
  - Catalysts prepared and characterized
  - Initial NO oxidation reactions completed
  - Catalyst structure and parameters now available for modeling

- Continue catalytic reaction tests initiated Q1
- Comparison of the catalyst preparation methods
- Detailed characterization such as in-situ XPS and high resolution TEM