

Investigation of Mixed Oxide Catalysts for NO Oxidation

ACE078

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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)

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 increase is leveling off

▶ Thrifting or replacement of Pt in DOC and LNT catalysts desired for:

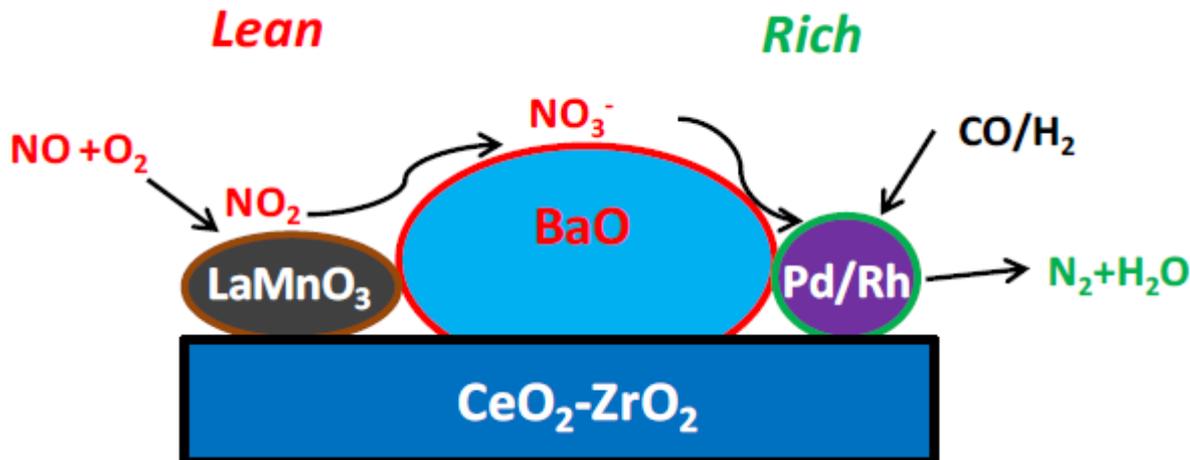
- supply-chain stability
- cost reduction as an enabler to advanced aftertreatment and combustion technologies
- alternative technologies for oxidation reactions



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 synthetic method and composition on resulting structure and on effectiveness of NO oxidation

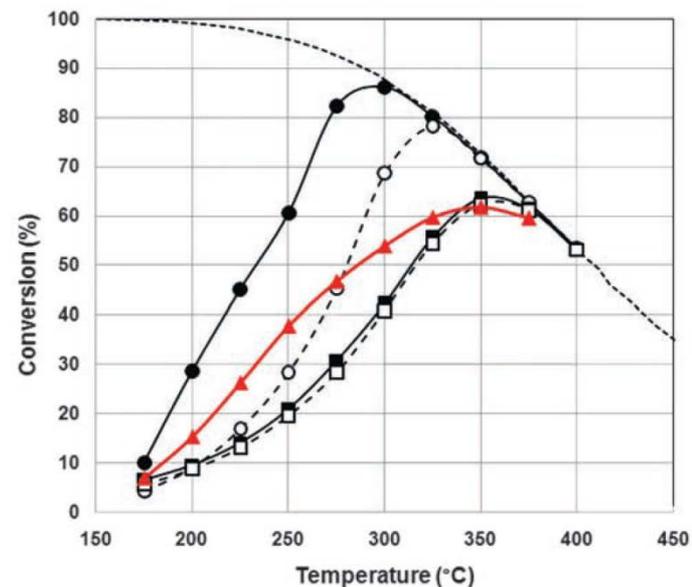


- Typical LNT catalyst structure (left)

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 (\circ), $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$ (\bullet), LaMnO_3 (\square), $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ (\blacksquare), and commercial DOC (\blacktriangle) at a gas hourly space velocity of $30,000 \text{ hour}^{-1}$; 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 changes in composition;
 - Interaction between reactants and the potential active sites
 - And help inform more advanced catalyst formulations

Milestones and Planned 2nd 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
 - Identified mixed metal oxide catalyst compositions and forms that show high activity for NO oxidation.
- ▶ **Determination of reaction mechanism**
 - Demonstrated that the $\text{MnO}_x\text{-CeO}_2$ catalyst both decreased the required temperature for formation and increased the quantity of labile oxygen needed for NO oxidation.
 - Showed that mixed metal oxide catalysts produced using a simple incipient wetness method compared favorably to those prepared by co-precipitation.
- ▶ **Computational analysis of active sites and reaction mechanism**
 - Density function theory (DFT) calculations established to help investigate the interaction between reactants and potential active sites

Catalyst Synthesis

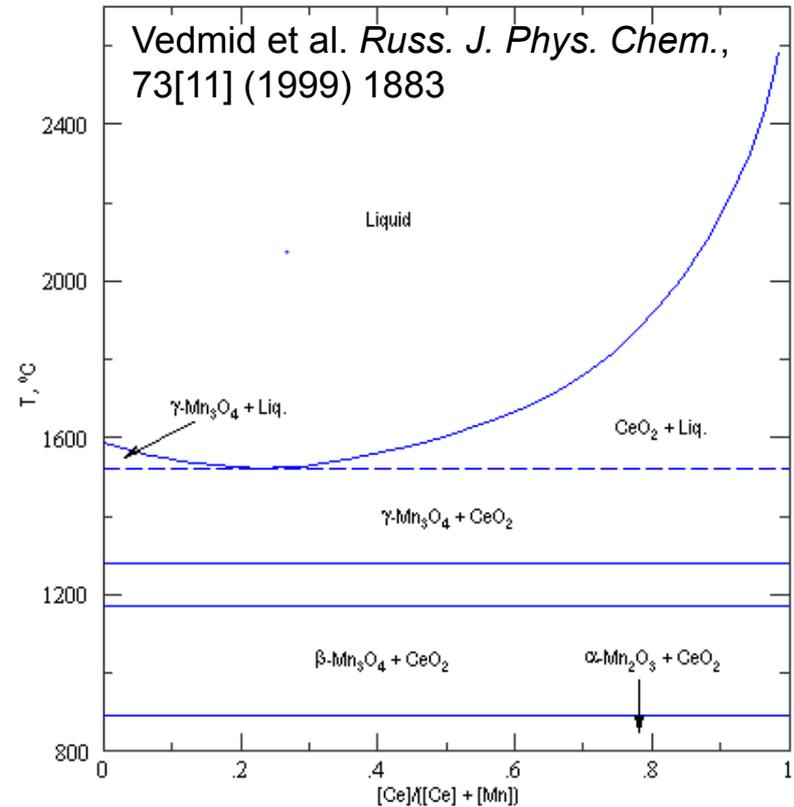
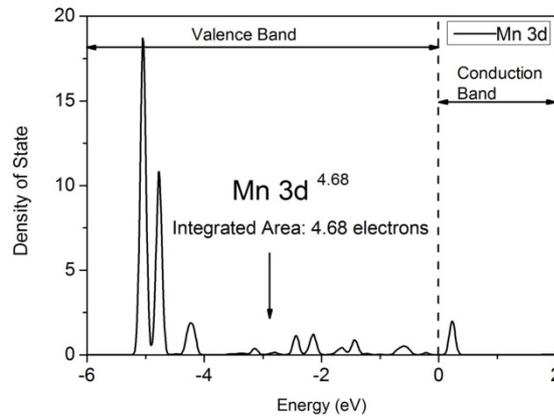
▶ GM: synthesized by co-precipitation method

- CeO_2
- MnO_x
- Mn-CeO_x (Mn/(Mn+Ce) = 0.04)
- Mn-CeO_x (Mn/(Mn+Ce) = 0.12)
- Mn-CeO_x (Mn/(Mn+Ce) = 0.30)

▶ PNNL

- 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%

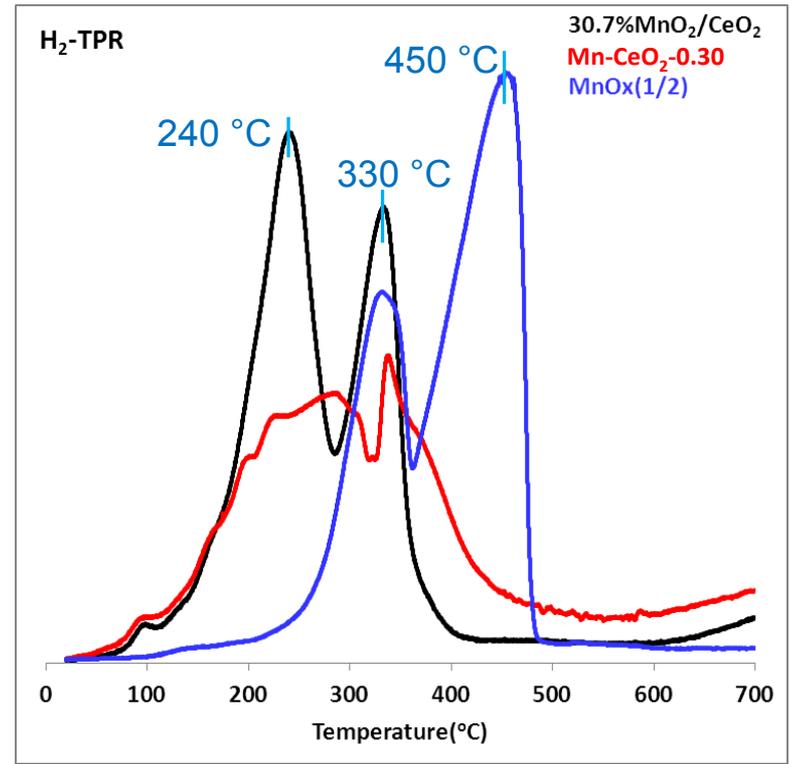
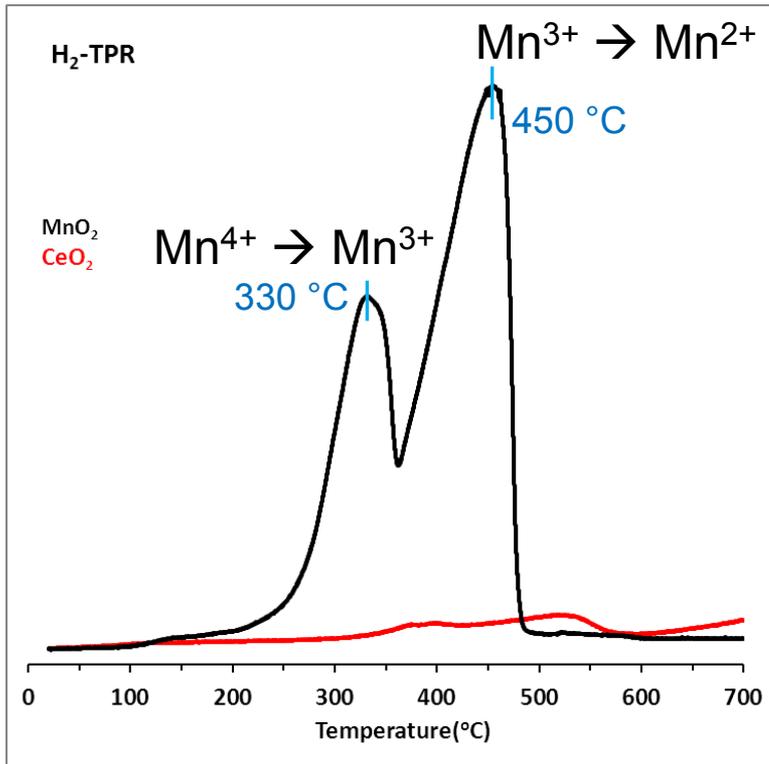
Electron configuration:
Mn⁰: 3d⁵ 4s²
Mn²⁺: 3d⁵



Mn %	The occupied Mn 3d states (Integrated area)		
	None-ov	1 oxygen vacancy	2 oxygen vacancies
3%	4.68	4.93	
6%	4.86	5.00	5.00

- ▶ As the concentration of **Mn** increases, the valence of Mn decreases from **+2.32 to +2**.
 - Mn incorporated in the CeO₂ lattice is expected to be in Mn²⁺ valence state.
- ▶ The ionic radius of Mn²⁺ (0.97 Å) is the same as that of Ce⁴⁺ (0.97 Å).

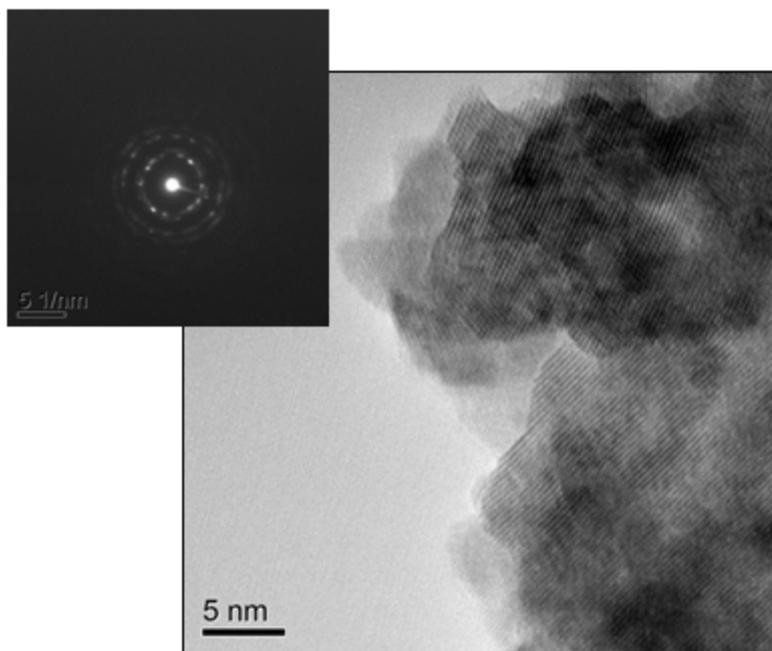
H₂ TPR Shows Strong Interaction Between Ce and Mn



- ▶ Impregnated sample shows relatively simple hydrogen consumption profile compared with co-precipitated sample.
- ▶ Significantly lower reduction temperature compare with MnOx and higher Mn⁴⁺ to Mn³⁺ reduction peak intensity.
- ▶ Results suggest that ceria helps stabilize higher oxidation state of Mn species (mostly Mn⁴⁺)
- ▶ Confirmed the accessibility of MnOx.

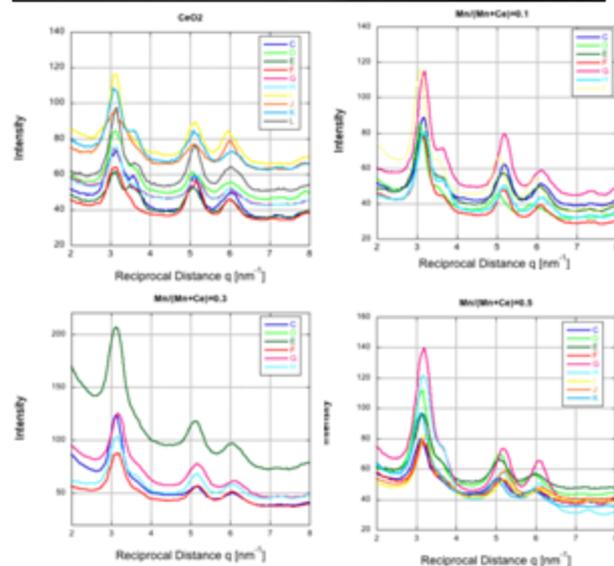
Mn-CeO Show Similar Lattice Spacing by TEM and XRD

Previously presented



Lattice parameter from TEM

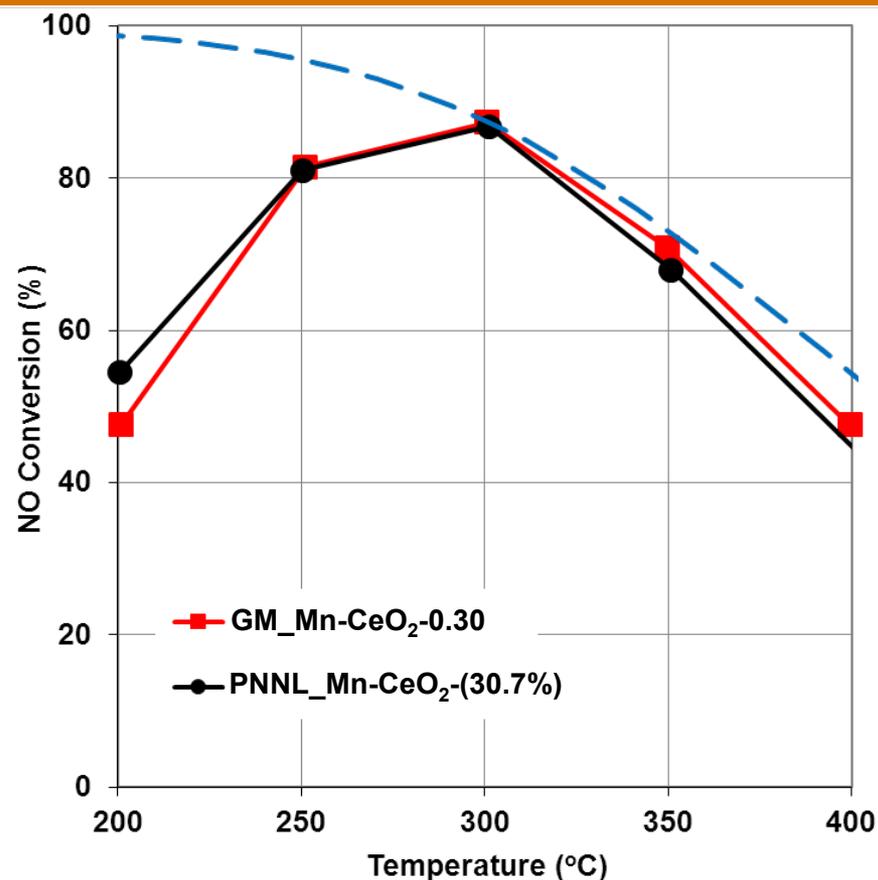
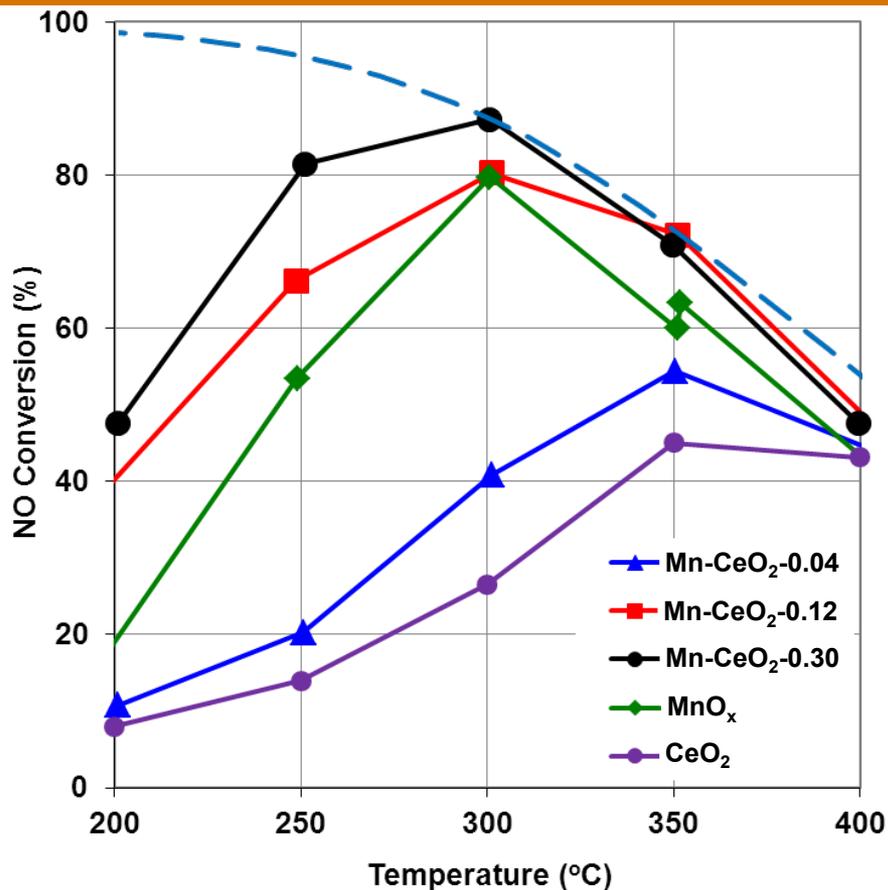
Sample	d(111) (Å)
CeO ₂	3.233
MnO _x -CeO ₂ (Mn/(Mn+Ce) = 0.04)	3.193
MnO _x -CeO ₂ (Mn/(Mn+Ce) = 0.12)	3.200
MnO _x -CeO ₂ (Mn/(Mn+Ce) = 0.3)	3.167



- ▶ DFT, TPR, TEM and XRD results suggest that MnO_x is mostly on the surface.

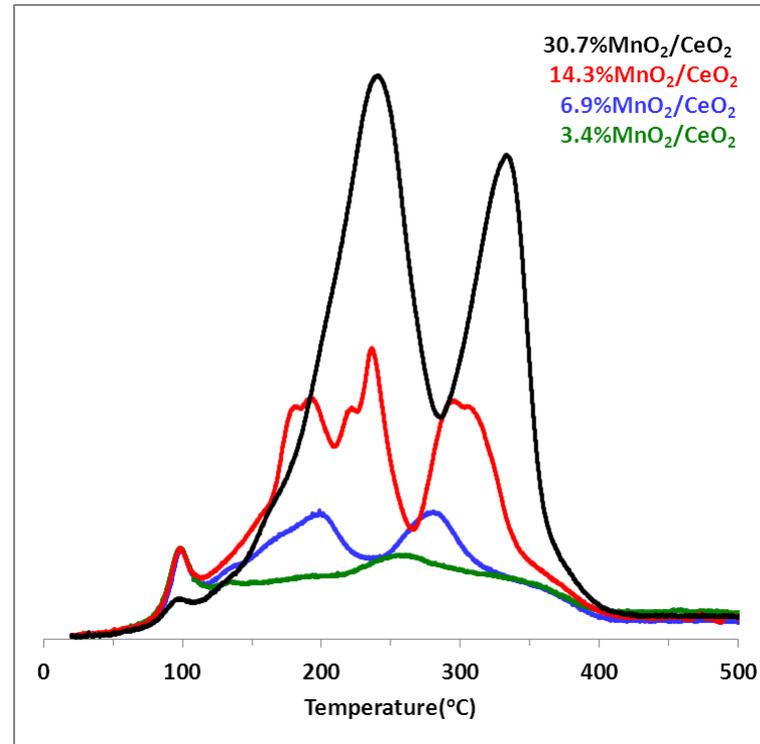
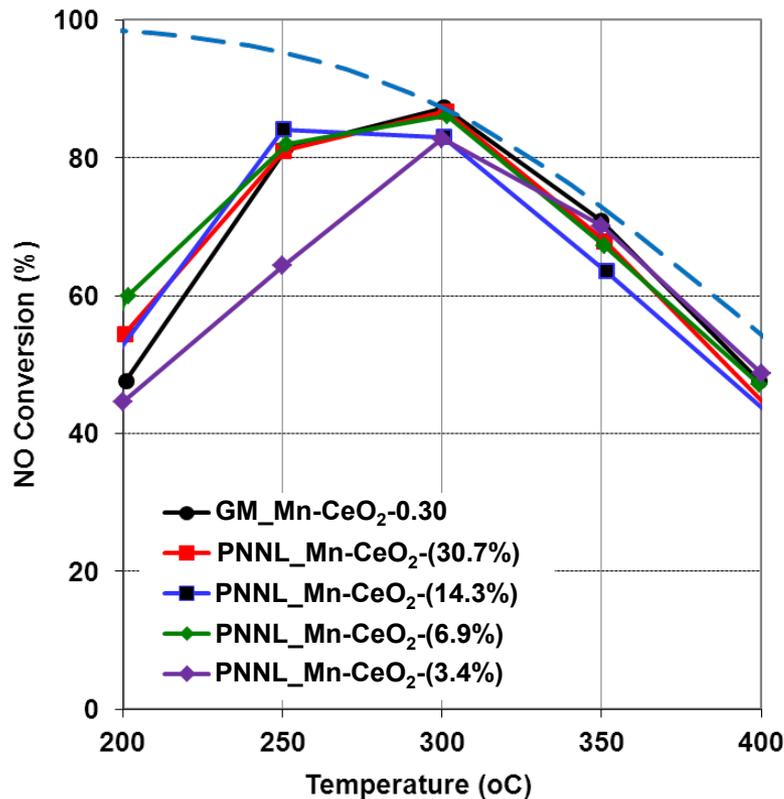
Electron diffraction

Ce-Mn Interaction Leads to Higher NO Oxidation Activity



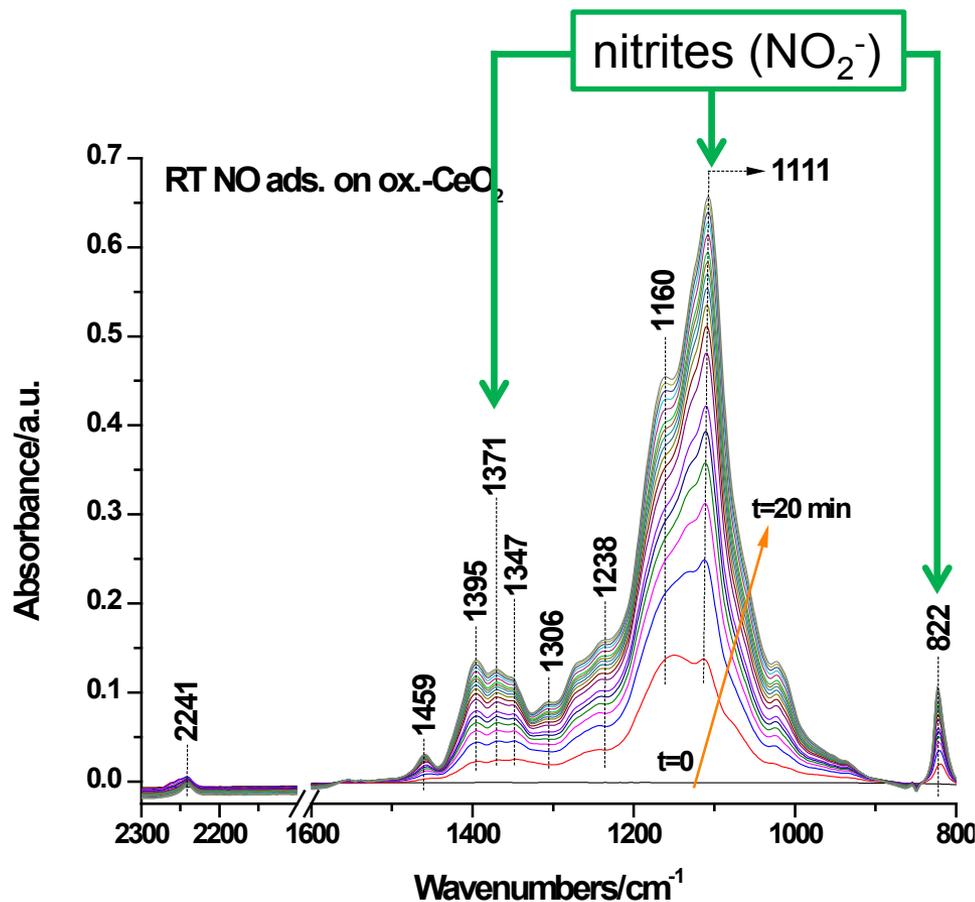
- ▶ MnO₂ is more active than CeO₂.
- ▶ MnO_x/CeO₂ is more active than pure CeO₂ or MnO₂ which is consistent with the TPR (more reducible MnO_x → more active oxygen).
- ▶ Impregnated PNNL catalyst show comparable catalytic activity with co-precipitated GM catalysts.

Activity is Weakly Dependent on Mn loading

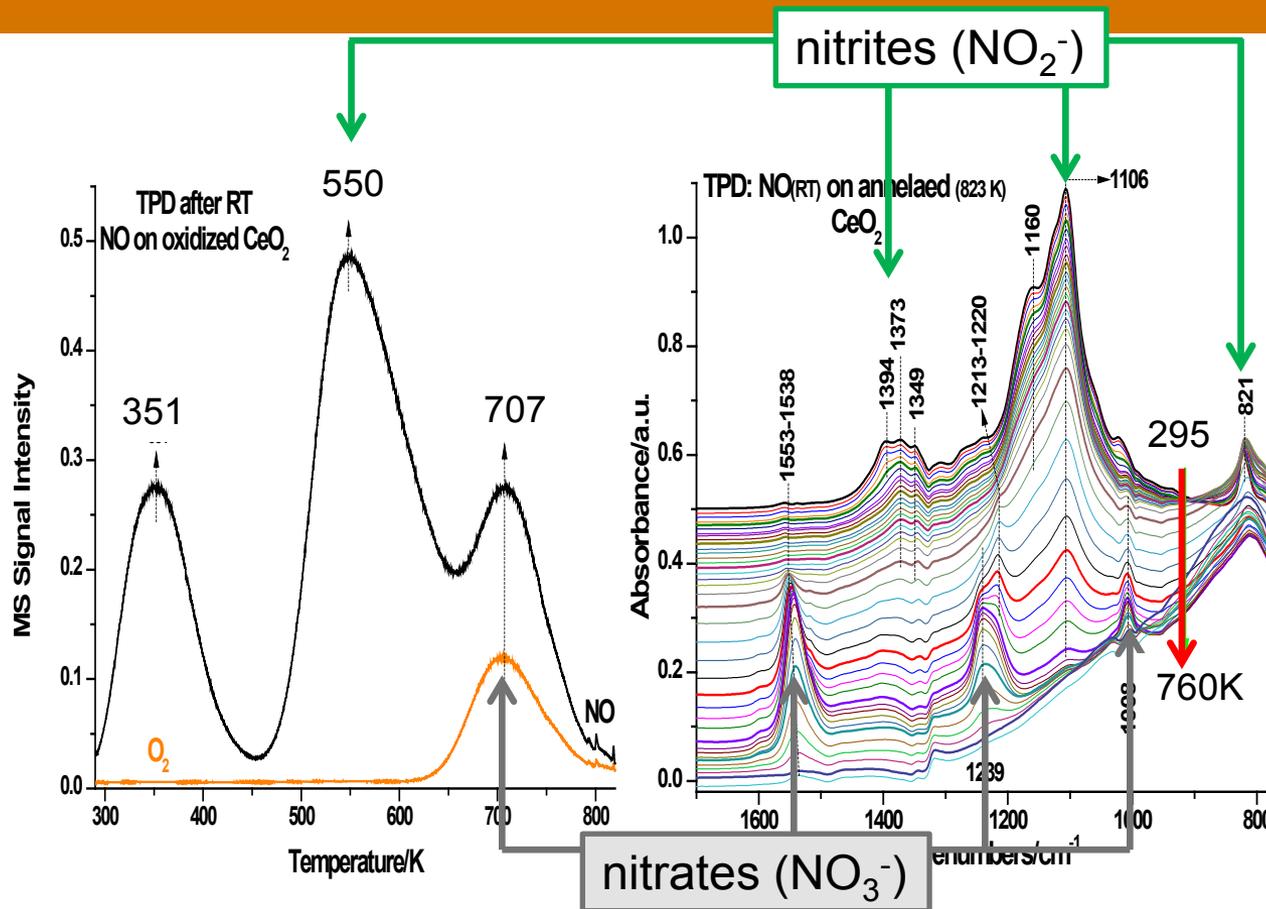


- ▶ Over 6.9wt%Mn show basically same catalytic behavior which is consistent with GM results (0.3 and 0.5 show similar activity).
 - The effect of loading on Mn oxidation state is being investigated (*in situ* XPS and XAFS).
- ▶ NO conversion to NO₂ is lower than total NO conversion, suggesting NO_x storage which is currently being investigated.

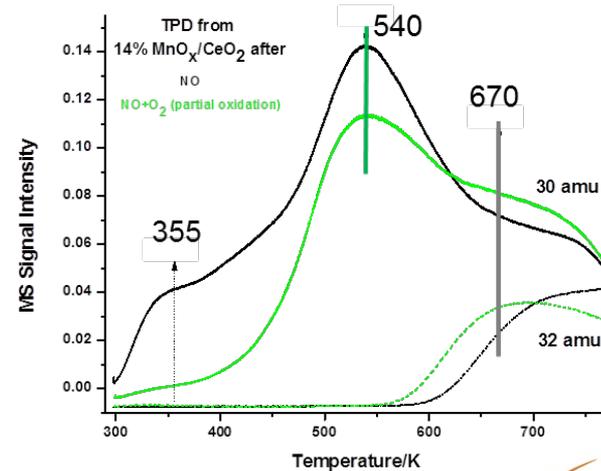
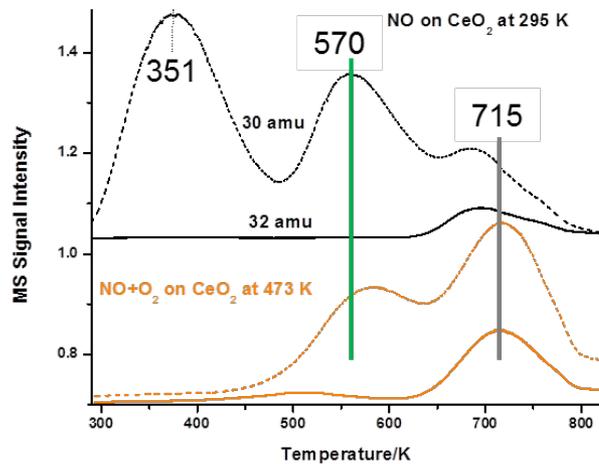
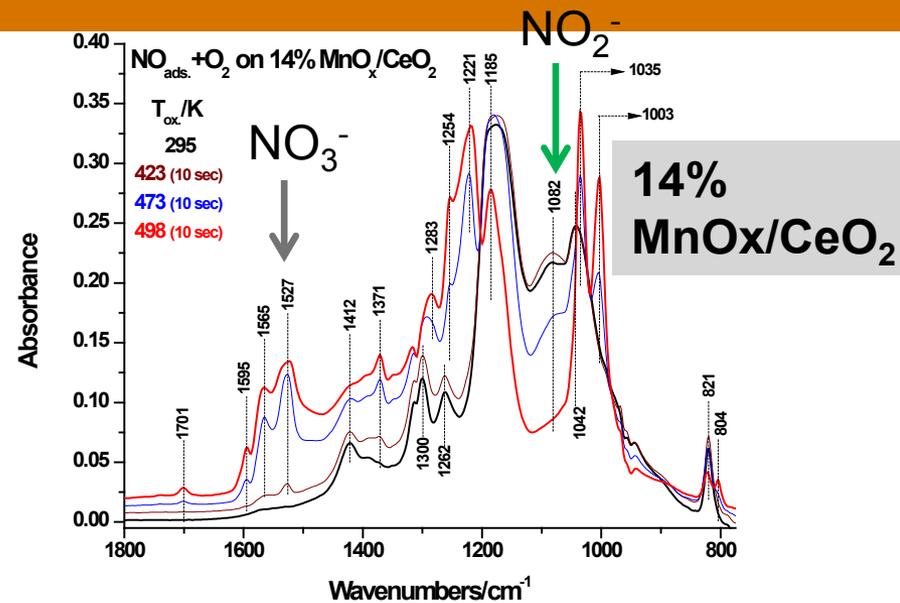
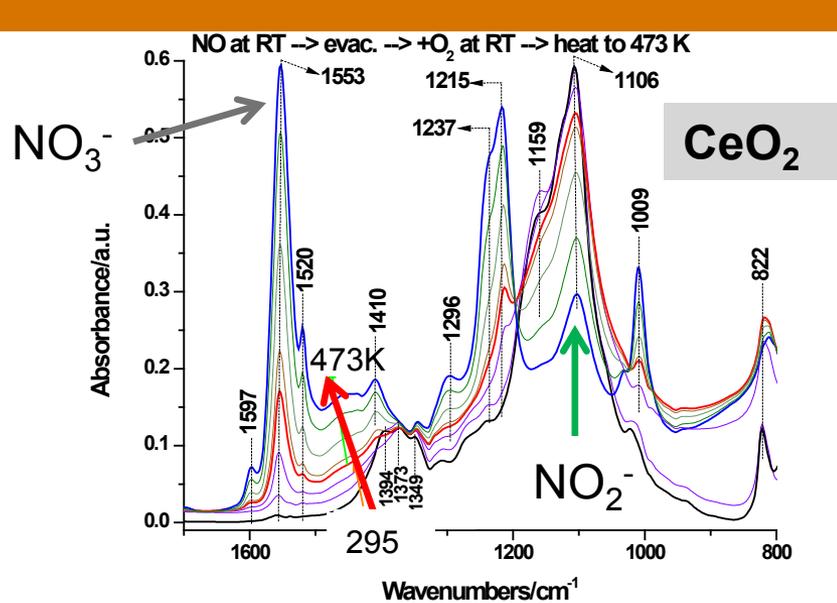
NO adsorption CeO₂ at 295 K Show Nitrite Formation



- ▶ 1. Fast nitrite formation
- ▶ 2. NO “heals” oxygen vacancies, that leads to the formation of N₂O



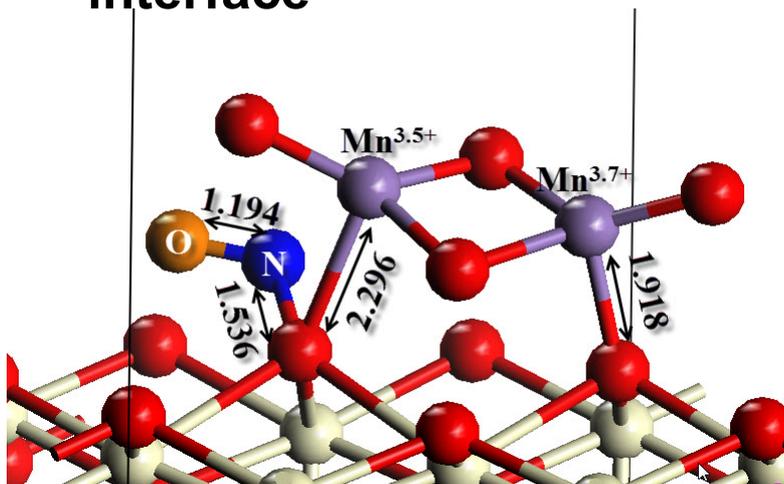
- ▶ Weakly adsorbed NO desorbs at T < 400 K.
- ▶ Part of the nitrites desorbs at ~560 K, the other part converts to nitrates during TPD.
- ▶ Nitrates decompose at ~700 K as NO + O₂.
- ▶ The amounts of NO₂⁻ and NO₃⁻ are higher on the oxidized CeO₂ than on the reduced one.



- ▶ Less weakly adsorbed NO on MnO_x/CeO₂ compared to CeO₂
- ▶ Nitrate formation and decomposition took place at lower temperature in the presence of MnO_x.

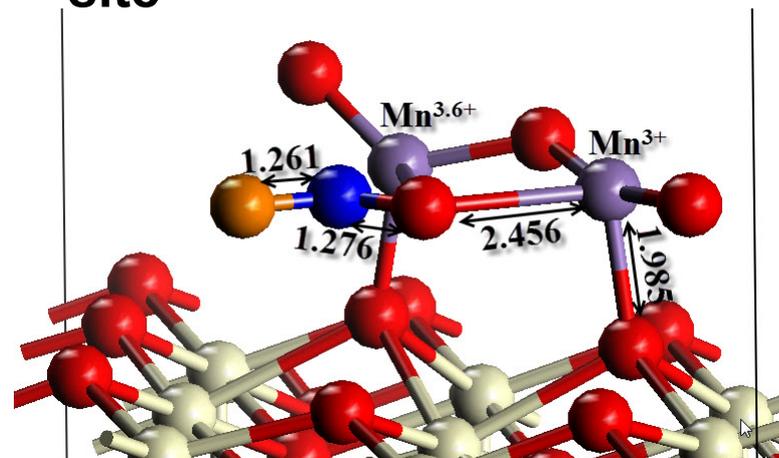


NO adsorption at interface



- No cation was reduced by NO adsorption.

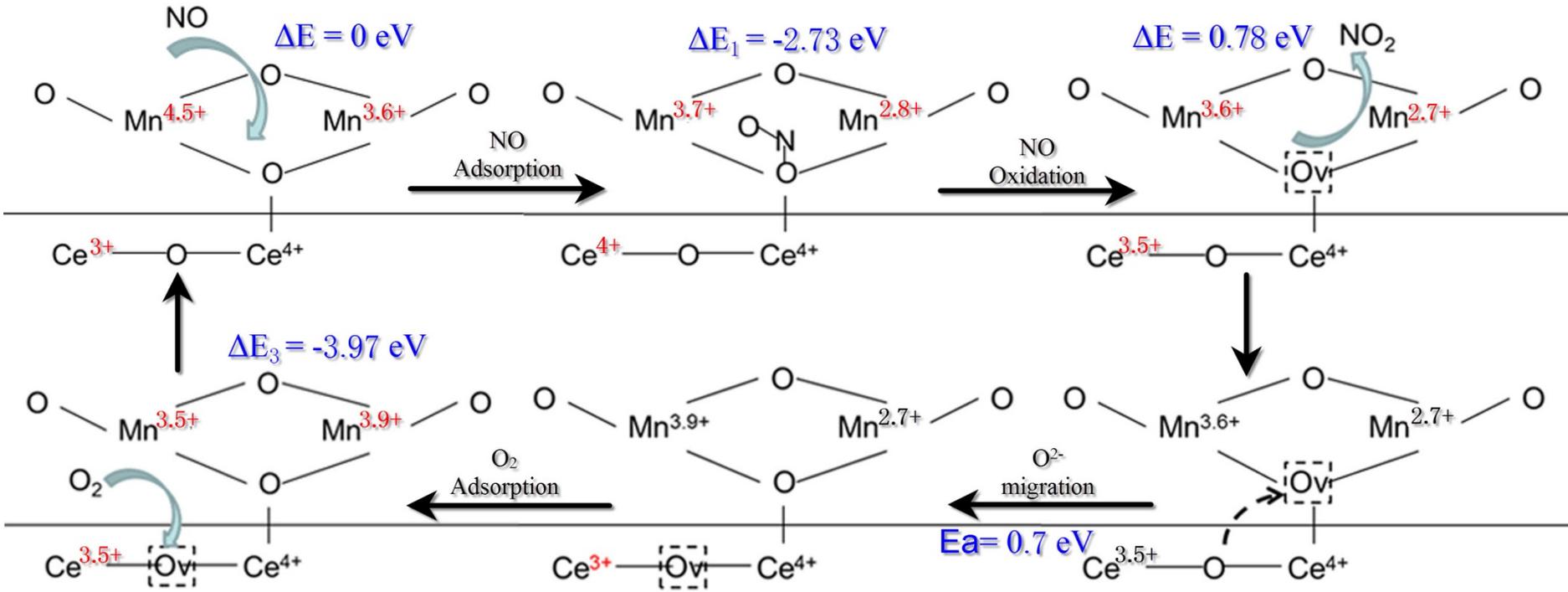
NO adsorption at cluster site



- Mn^{3.9+} → Mn^{3.6+} and Mn^{3.6+} → Mn^{3.0+}
- Mn – O bond (2.456 Å) was enlarged significantly.

NO Oxidation on $(\text{MnO}_2)_2/\text{CeO}_2(111)$ Model Catalyst

$\Delta E = 2.38 \text{ eV}$ for $\text{CeO}_2(111)$



$E_a = 1.50 \text{ eV}$ for $\text{CeO}_2(111)$

- ▶ Compared to the pure $\text{CeO}_2(111)$ and $\beta\text{-MnO}_2(110)$ surfaces, the proposed model catalyst shows higher activity for NO oxidation in terms of enhanced NO_2 desorption and easier oxygen replenish mechanism.
- ▶ The higher activity and lower desorption barrier are in agreement with the FTIR and catalytic activity results.

Summary and Conclusions

- ▶ Project progress
 - Catalysts prepared and characterized
 - NO oxidation reactions completed
 - The reaction mechanism was investigated by DFT and FTIR.
- ▶ CeO₂ helps stabilize Mn in a higher oxidation state (Mn⁴⁺)
 - in addition, the Mn is also easier to reduce.
- ▶ NO oxidation results on impregnated catalysts and DFT calculations suggest that Mn doping in the ceria lattice is not necessary.
- ▶ MnOx significantly lowers the temperature for the conversion of adsorbed nitrites to nitrates.
- ▶ The NO oxidation mechanism on the proposed (MnO₂)₂/CeO₂ model catalyst structure is in agreement with the FTIR and NO oxidation results.

Future Work

- ▶ Goal: Optimize mixed metal oxide catalyst compositions and active sites for NO oxidation, to enable the noble metal content of DOC and LNT catalysts to be reduced or eliminated.
 - Prepare MnO_x-CeO₂ catalysts using citrate and combustion synthesis methods.
 - Continue catalytic reaction tests to understand the role of NO_x storage capacity and type of NO_x (NO or NO₂) on the NO oxidation activity.
 - Detailed characterization by FTIR, *in situ* XPS, high resolution TEM and *in situ* XAFS
 - Study the effect of MnO₂ cluster size on the reaction mechanism by DFT.

Technical Back-Up Slides

BET

Sample	Surface area(m ² /g)	
	Fresh	After reaction
CeO ₂	37	
MnO _x	14	14.7
Mn/(Mn+Ce) = 0.04	75	71.0
Mn/(Mn+Ce) = 0.12	88	84.3
Mn/(Mn+Ce) = 0.3	64	64.4

- ✓ **PNNL catalysts shows high surface area due to the initial high surface area CeO₂.**
- ✓ **Negligible surface area reduction after reaction tests for both GM and PNNL catalysts.**

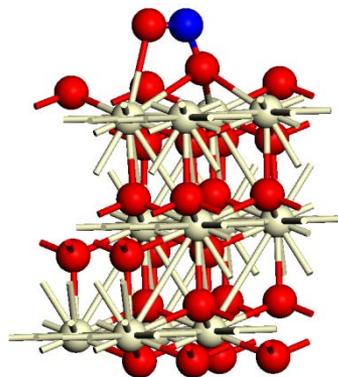
Sample	Surface area(m ² /g)	
	Fresh	After reaction
HAS-CeO ₂ (GM)	139.4	
3.4%MnO _x /CeO ₂	132.3	
6.9%MnO _x /CeO ₂	125.5	124.5
14.3%MnO _x /CeO ₂	114.8	111.5
30.7%MnO _x /CeO ₂	86.8	84.7

Insight into Reaction Mechanism

NO Oxidation on CeO₂(111)



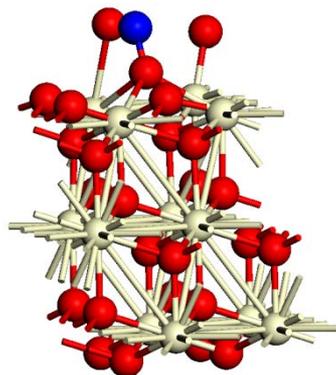
NO adsorption
 $\Delta E = -0.82 \text{ eV}$



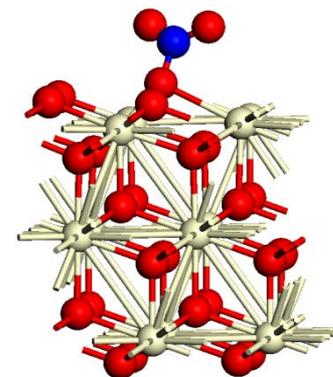
NO₂ desorption
 $\Delta E = +0.65 \text{ eV}$



O₂ adsorption
 $\Delta E = +1.33 \text{ eV}$

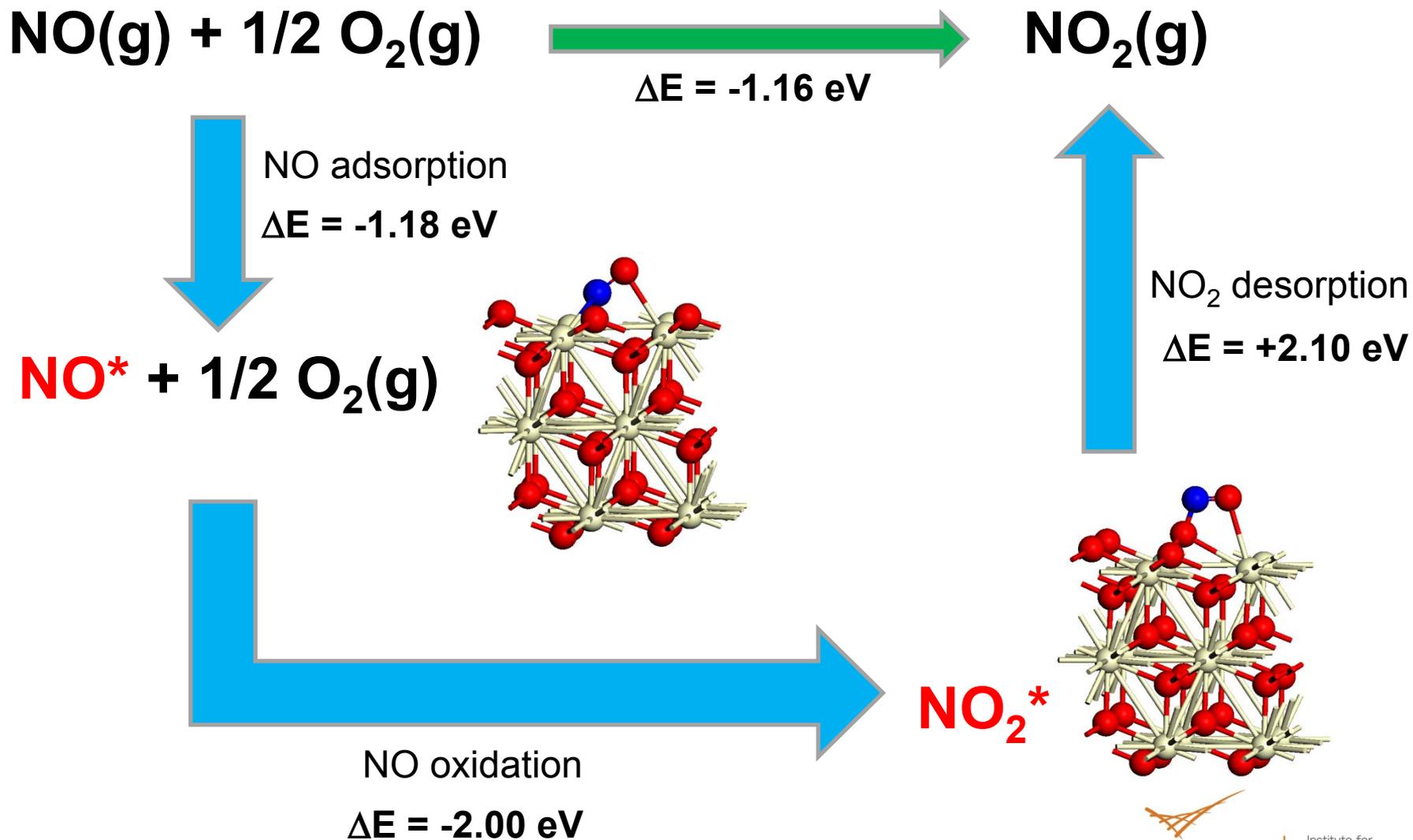


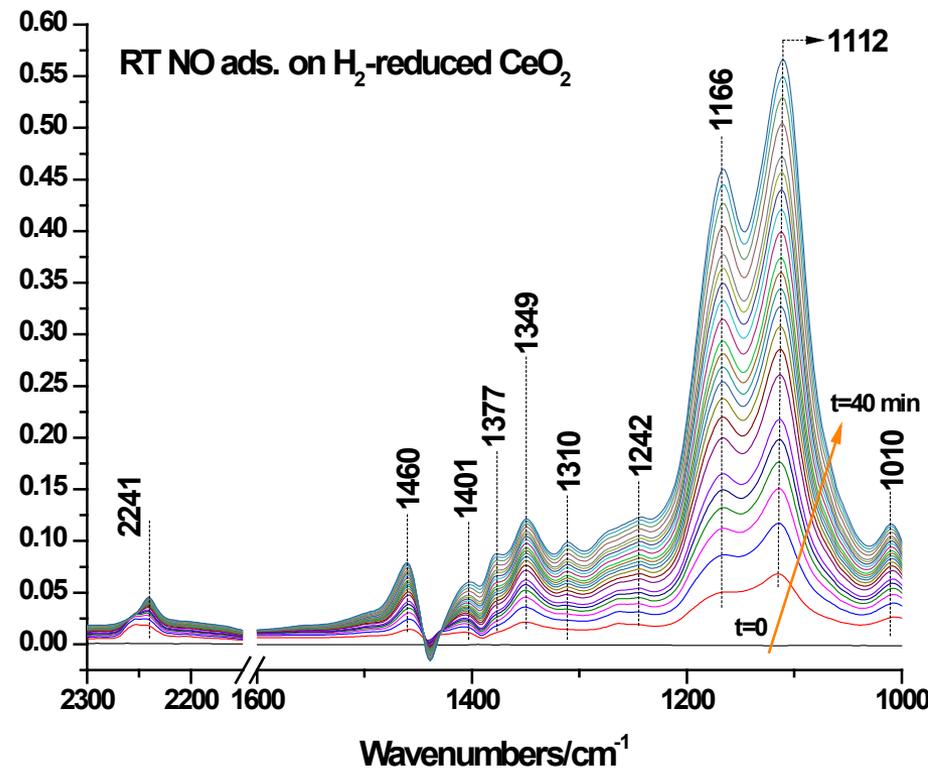
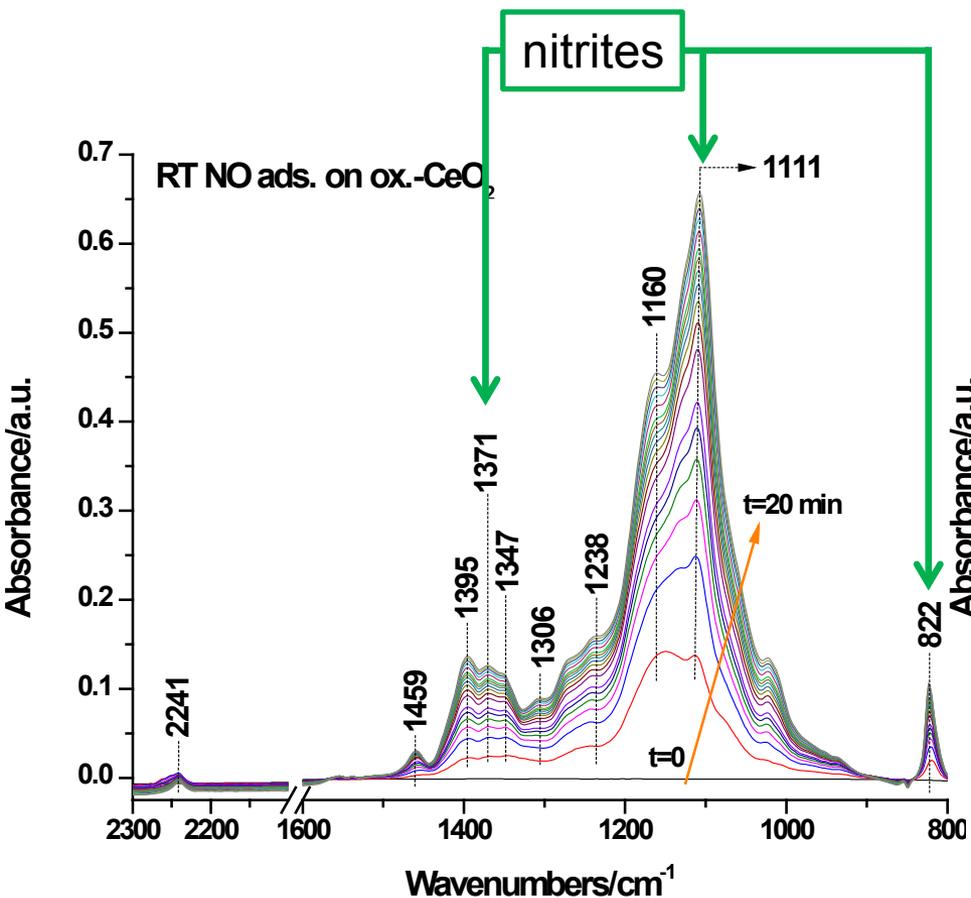
NO oxidation
 $\Delta E = -2.32 \text{ eV}$



Insight into Reaction Mechanism

NO Oxidation on $\text{CeO}_{2-x}(111)$

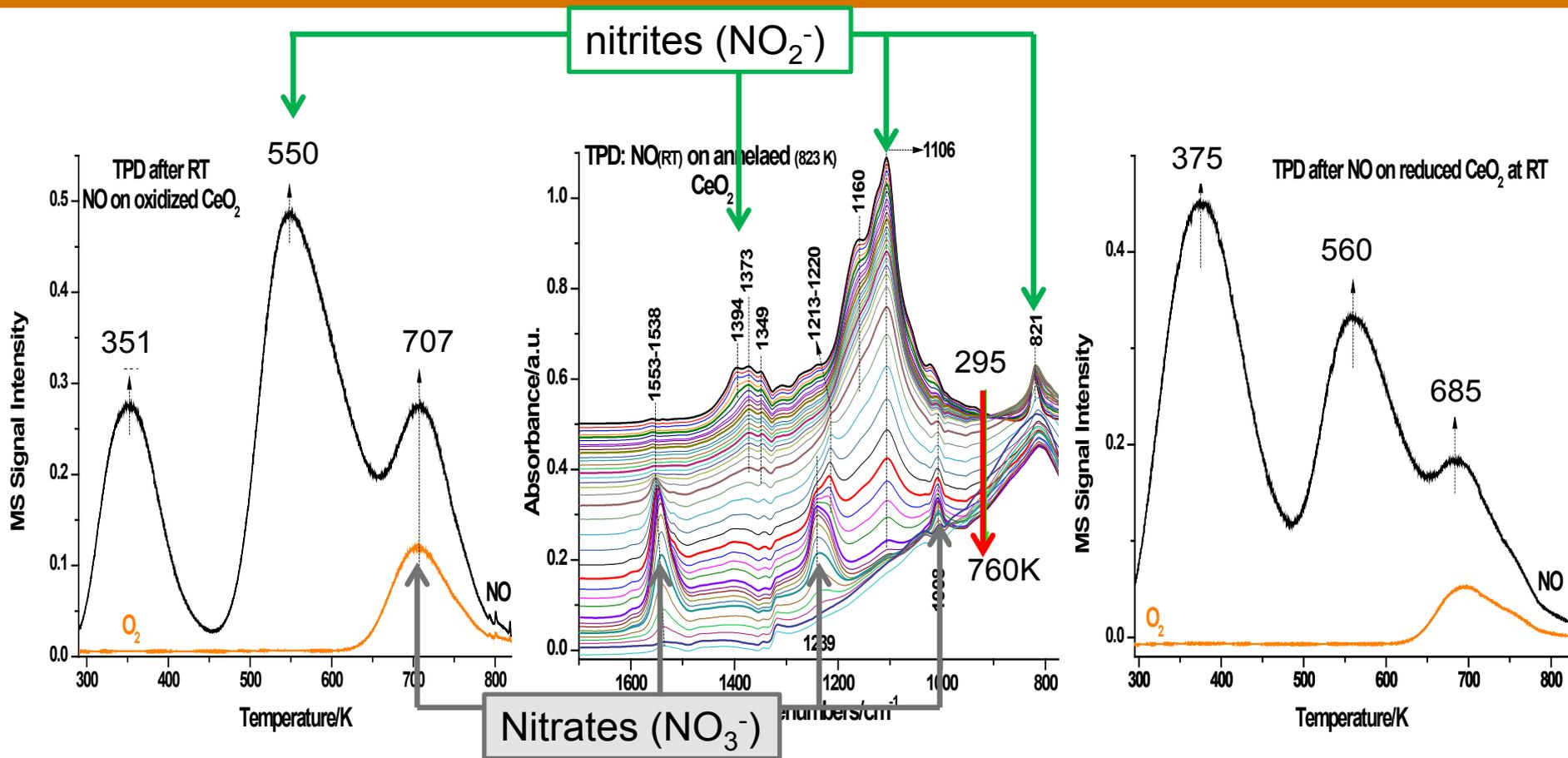




- ▶ 1. Fast nitrite formation on both samples
- ▶ 2. NO “heals” oxygen vacancies, that leads to the formation of N_2O



NO Temperature Programmed Desorption on CeO₂



- ▶ Weakly adsorbed NO desorbs at $T < 400$ K.
- ▶ Part of the nitrites desorbs at ~ 560 K, the other part converts to nitrates during TPD.
- ▶ Nitrates decompose at ~ 700 K as $\text{NO} + \text{O}_2$.
- ▶ The amounts of NO_2^- and NO_3^- are higher on the oxidized CeO₂ than on the reduced one.