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 imply 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.

Source: Monex Precious Metals
www.monex.com
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$_3$ (○), La$_{0.4}$Sr$_{0.4}$CoO$_3$ (●), LaMnO$_3$ (□), La$_{0.4}$Sr$_{0.4}$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 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 MnO$_x$-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. = ~ 120m$^2$/g)
- MnO$_x$ loading: 3.4, 6.9, 14.3, 30.7 wt%
As the concentration of Mn increases, the valence of Mn decreases from +2.32 to +2.

- Mn incorporated in the CeO$_2$ lattice is expected to be in Mn$^{2+}$ valence state.

- The ionic radius of Mn$^{2+}$ (0.97 Å) is the same as that of Ce$^{4+}$ (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 compared 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

Lattice parameter from TEM

<table>
<thead>
<tr>
<th>Sample</th>
<th>d(111) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>3.233</td>
</tr>
<tr>
<td>MnOₓ-CeO₂ (Mn/(Mn+Ce) = 0.04)</td>
<td>3.193</td>
</tr>
<tr>
<td>MnOₓ-CeO₂ (Mn/(Mn+Ce) = 0.12)</td>
<td>3.200</td>
</tr>
<tr>
<td>MnOₓ-CeO₂ (Mn/(Mn+Ce) = 0.3)</td>
<td>3.167</td>
</tr>
</tbody>
</table>

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

Electron diffraction
MnO₂ is more active than CeO₂.

MnOₓ/CeO₂ is more active than pure CeO₂ or MnO₂ which is consistent with the TPR (more reducible MnOₓ → 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 NOₓ storage which is currently being investigated.
NO adsorption CeO$_2$ at 295 K
Show Nitrite Formation

- 1. Fast nitrite formation
- 2. NO “heals” oxygen vacancies, that leads to the formation of N$_2$O
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 NO+O₂.
- The amounts of NO₂⁻ and NO₃⁻ are higher on the oxidized CeO₂ than on the reduced one.
NO+O₂ reaction over CeO₂ and 14% MnOₓ/CeO₂

Less weakly adsorbed NO on MnOx/CeO₂ compared to CeO₂.

Nitrate formation and decomposition took place at lower temperature in the presence of MnOx.
NO Adsorption on CeO$_2$ Supported MnO$_2$ Cluster

- No cation was reduced by NO adsorption.
- $\text{Mn}^{3.9+} \rightarrow \text{Mn}^{3.6+}$ and $\text{Mn}^{3.6+} \rightarrow \text{Mn}^{3.0+}$
- Mn – O bond (2.456 Å) was enlarged significantly.
NO Oxidation on \((\text{MnO}_2)_2/\text{CeO}_2(111)\) Model Catalyst

- Compared to the pure CeO\(_2\)(111) and \(\beta\)-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.

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

\[ \text{Ea} = 1.50 \text{ eV for CeO}_2(111) \]
Summary and Conclusions

- Project progress
  - Catalysts prepared and characterized
  - NO oxidation reactions completed
  - The reaction mechanism was investigated by DFT and FTIR.

- CeO$_2$ helps stabilize Mn in a higher oxidation state (Mn$^{4+}$)
  - 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.

- MnO$_x$ significantly lowers the temperature for the conversion of adsorbed nitrites to nitrates.

- The NO oxidation mechanism on the proposed (MnO$_2$)$_2$/CeO$_2$ 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 MnOx-CeO$_2$ catalysts using citrate and combustion synthesis methods.
- Continue catalytic reaction tests to understand the role of NOx storage capacity and type of NOx (NO or NO$_2$) on the NO oxidation activity.
- Detailed characterization by FTIR, \textit{in situ} XPS, high resolution TEM and \textit{in situ} XAFS
- Study the effect of MnO$_2$ cluster size on the reaction mechanism by DFT.
Technical Back-Up Slides
### BET

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Fresh</th>
<th>After reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CeO₂</strong></td>
<td></td>
<td>37</td>
<td></td>
</tr>
<tr>
<td><strong>MnOₓ</strong></td>
<td></td>
<td>14</td>
<td>14.7</td>
</tr>
<tr>
<td>Mn/(Mn+Ce) = 0.04</td>
<td></td>
<td>75</td>
<td>71.0</td>
</tr>
<tr>
<td>Mn/(Mn+Ce) = 0.12</td>
<td></td>
<td>88</td>
<td>84.3</td>
</tr>
<tr>
<td>Mn/(Mn+Ce) = 0.3</td>
<td></td>
<td>64</td>
<td>64.4</td>
</tr>
</tbody>
</table>

- 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.
Insight into Reaction Mechanism
NO Oxidation on CeO$_2$(111)

\[
\text{NO(g)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{NO}_2(g)
\]

\[\Delta E = -1.16 \text{ eV}\]

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

- NO$^*$ + \frac{1}{2} O$_2$(g)

- O$_2$ adsorption
  \[\Delta E = +1.33 \text{ eV}\]

- NO$^*$ + O$^*$

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

- NO$^*$ + 1/2 O$_2$(g)

- NO$_2$ desorption
  \[\Delta E = +0.65 \text{ eV}\]

- NO$_2^*$
Insight into Reaction Mechanism
NO Oxidation on CeO$_2$–x(111)

\[ \text{NO(g)} + \frac{1}{2} \text{O}_2(g) \rightarrow \text{NO}_2(g) \]
\[ \Delta E = -1.16 \text{ eV} \]

NO adsorption
\[ \Delta E = -1.18 \text{ eV} \]

\[ \text{NO}^* + \frac{1}{2} \text{O}_2(g) \rightarrow \text{NO}_2^* \]
\[ \Delta E = -2.00 \text{ eV} \]

NO oxidation
\[ \Delta E = +2.10 \text{ eV} \]

NO$_2$ desorption

Technical Progress
1. Fast nitrite formation on both samples
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+O<sub>2</sub>.

The amounts of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> are higher on the oxidized CeO<sub>2</sub> than on the reduced one.