Monolithic Metal Oxide based Composite Nanowire Lean NO$_x$ Emission Control Catalysts

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Outline

- Monolithic nanowire catalyst concept
- Goal and approaches
- Monolithic nanowire catalysts
  - Specific surface area
  - Thermal and chemical stability
  - CO and NO oxidation behaviors
Monolithic Nanowire Catalyst Concept

What is New?

• First conceptual composite nanocatalysts made from MeO_x/ABO_3 semiconductor/perovskite nanowires.

Advantages: 1) Ultrahigh surface area; 2) High thermal stability; 3) Strong adherence; 4) Low cost; 5) High tailoring ability; 6) Reduce or Eliminate PGM usage by incorporating ABO_3 perovskite.

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Potential Multifunctional Nanocatalysts

1) Selective adsorption/storage of excess oxygen (surface and lattice oxygen) and catalytic extraction of oxygen from NO_x, potentially allow direct reaction of CO, HC with NO_x in the lean-burn engine operation.

2) Mesoporous perovskite shell allows desulfurization via substitution reaction of metal oxide core into sulfide or sulfate, eliminating or reducing the surface poisoning tendency.

3) The strong adhesive forest-like composite nanocatalysts allow itself to survive in high flow-velocity exhaust conditions, and potentially function as an effective particular matter filter for the lean-burn diesel engines.

4) With dopants either Pt or Pd, or Sr, Ba, K, Ce, the 3D composite nanocatalysts could be tailored as an excellent candidate as either lean NO_x catalysts or LNT’s absorbents.
Monolithic Nanowire Catalyst Concept

Compare to other Technologies?

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Tech 1</th>
<th>Tech 2</th>
<th>Tech 3*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area</td>
<td>High</td>
<td>Average</td>
<td>Ultra-high</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>High</td>
<td>Average</td>
<td>High</td>
</tr>
<tr>
<td>Poison resistance</td>
<td>High</td>
<td>Poor</td>
<td>High</td>
</tr>
<tr>
<td>Tailoring capacity</td>
<td>Poor</td>
<td>Average</td>
<td>Excellent</td>
</tr>
<tr>
<td>Adhesion</td>
<td>Good</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Availability</td>
<td>Limited</td>
<td>Average</td>
<td>High</td>
</tr>
</tbody>
</table>

Technologies:
1. Noble metals (Pt, Pd, etc.)
2. Hybrid particle catalysts ABO₃ + noble metal
3*. 3D composite nanowire catalysts

Potential Applications

- Lean NOₓ emission control in vehicle and aircrafts
- Industrial combustion emission control (reactors, power plants)
Goal and Approaches

1) **Goal:** To reduce CO, NO$_x$, HC and PM emission by introducing a new concept composite nano-catalysts, eventually to replace or reduce the usage of the Pt-group metal (PGM) catalysts.

2) **Approaches**
   - **Synthesis:**
     \[(\text{ZnO, TiO}_2)/\text{(La, Sr)}(\text{Co or Mn})\text{O}_3\ \text{(LSCO or LSMO)}\] composite nanowire arrays rooted on monolithic cordierite or stainless steel.
   - **Characterization:**
     Structure, morphology, and chemical properties of composite nanowire arrays using a range of microscopy and spectroscopy techniques.
   - **Durability:**
     Thermal stability by using a variety of microscopy, spectroscopy and thermal analysis tools.
   - **Activity:**
     Catalytic behavior: CO oxidation and NO oxidation, storage and reduction, etc..
Composite nanowire arrays

ZnO/LSMO

ZnO/LSCO

TiO$_2$/LSMO

E
Large scale ZnO and TiO$_2$ nanowire arrays grown in monolithic substrates

Metal oxide nanowire arrays on monolithic substrates.
Structure and surface areas of TiO$_2$ nanoarrays on substrate

<table>
<thead>
<tr>
<th>Samples</th>
<th>TiO$_2$-Cordierite</th>
<th>TiO$_2$</th>
<th>800°C 24 hrs TiO$_2$-Cordierite</th>
<th>800°C 24 hrs TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Surface Area (m$^2$/g)</td>
<td>37.96</td>
<td>704.47</td>
<td>24.51</td>
<td>454.86</td>
</tr>
</tbody>
</table>
Thermal stability of TiO$_2$ nanorods array at 800°C for 24h
Thermal stability of TiO$_2$ nanoarrays under oxidative atmosphere

TGA and DSC of TiO$_2$ nanorods array on substrates
Thermal stability of TiO$_2$ nanowire based catalysts under reductive atmosphere

TPR-H$_2$ of Pt coated TiO$_2$ or TiO$_2$/LSMO nanowire arrays on substrates.
Thermal stability of ZnO/LSCO nanoarrays

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>424 m²/g</td>
</tr>
<tr>
<td>600°C</td>
<td>490 m²/g</td>
</tr>
<tr>
<td>800°C</td>
<td>268 m²/g</td>
</tr>
<tr>
<td>1000°C</td>
<td>262 m²/g</td>
</tr>
</tbody>
</table>
Thermal stability of ZnO nanowire catalysts under reductive atmosphere

TPR-H$_2$ of Pt coated ZnO/LSCO nanowire arrays on substrates.
CO oxidation behaviors of monolithic composite nanowire catalysts

Better performance in sol-gel processed nanowire catalysts;
- LSCO reduces the light-off temp in CO oxidation;
- TiO2/LSMO/Pt is better than ZnO/LSCO/Pt for CO oxidation.

CO 1%, O2 10%, N2 balance
Pt: <1%; SV: 45,454 h⁻¹
NO oxidation behaviors of monolithic composite nanowire catalysts

- **Conversion (%):**
  - Pt: <1%; SV: 166,667 h⁻¹

- **Temperature (°C):**

- **NO 500ppm, O₂ 10%, N₂ balance**

- **LSMO loading in ZnO/Pt catalyst seems to reduce the NO oxidation performance**
- **LSMO loading improved the NO oxidation**
- **High space velocity induced low conversion efficiency**
Conclusions

1) Monolithic metal oxide composite nanowire emission control catalysts demonstrated with achievable high specific surface area.

2) ZnO/LSCO have very good thermal stability under ambient condition, while tend to decompose at ~600°C due to reduction of ZnO, still with good structure integrity.

3) TiO$_2$/LSMO have good thermal stability under both ambient and reductive atmospheres with good structure integrity.

4) Monolithic composite nanowire catalysts are catalytically active to both CO and NO oxidation under high space velocity and low Pt loading;

5) LSCO and LSMO improve the CO oxidation conversion efficiency of ZnO/Pt nanowire catalysts; sol-gel processed nanowire catalysts have better catalytic performance than sputtering process.

6) LSMO improves the NO oxidation behavior in TiO$_2$/Pt nanowire catalyst, while LSCO seemed to degrade the catalytic performance in ZnO/Pt systems.