Microwave-Assisted Thermal Conversion of CO₂ and Methane Over Conductive Metal Oxides

Douglas R. Kauffman (NETL)
Catalytic CO$_2$ conversion at NETL

Excess Renewables

Waste heat

Polymers & Plastics | Ethylene | Hydrogen | Carbon Monoxide | Methanol | Fuels
Electrochemical catalyst design

Structure-controlled product selectivity

H$_2$O

CO$_2$

Products

Surface-science enabled electrocatalysis

10 nm

“Atomically Precise” nanocatalysts

Journal of Physical Chemistry
Cover (Dec. 2018)
Appealing thermal route: Dry Reforming of Methane (DRM)

Traditional thermal DRM is extremely challenging due to high temperatures (700+ °C)

\[ \text{CO}_2 + \text{CH}_4 \rightarrow 2(\text{CO} + \text{H}_2) \]

Synthesis Gas

- Methanol
- Fertilizers
- Fuel gas
- Polycarbonates
- Synthetic diesel and waxes
Our approach: microwave-active catalysts!

Leverages excess renewable (curtailed) electricity

Tunable catalyst composition “LSC-M”

\[
\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.9}\text{M}_{0.1}\text{O}_3
\]

Efficient Catalyst Heating

- Conductive mixed-metal oxide catalysts stable at high temps
- MWs selectively heat catalyst bed … not entire reactor volume!
- Dopants tune reactivity

Manuscript and patent application in preparation.
Doped LSC-M Catalysts

Tunable catalyst composition “LSC-M”

La$_{0.8}$Sr$_{0.2}$Co$_{0.9}$M$_{0.1}$O$_3$

*No evidence of significant dopant segregation

$\lambda = 0.24136$ Å (51.4 keV); APS 17-BM-B
Microwave-assisted heating

All catalysts show microwave heating & rapid on-off cycling (200-300°C / min)
Dopant control MW-DRM activity

**CH₄ Conversion**

**CO₂ Conversion**
Dopant control MW-DRM activity

**CH$_4$ Conversion**

- LSC
- LSC-Ni
- LSC-Cu

**CO$_2$ Conversion**

- LSC
- LSC-Ni
- LSC-Cu
Dopant control MW-DRM activity

Mn and Fe dopants drastically improve DRM conversion rates

** LSC-Mn: H$_2$/CO ratio: 0.92 ± 0.03 over 10 hours of operation @ 90W **
Monitoring ex-situ phase changes during MW-DRM

- Undoped LSC initially forms Ruddelson-Popper perovskitic phase
  (Δ RP: strong microwave absorber)

- After continued reaction
  - Significant loss of perovskitic phases
  - Formation of SrO_x, La_2O_3 and Co
  - Loss of MW absorptivity
Relative Stability of doped LSC-M Catalysts

* From post-reaction XRD; LSC-M, RP, La$_4$Co$_3$(M)O$_{10}$
Relative Stability of doped LSC-M Catalysts

Formation of Small Co NPs on LSC-Mn

*From post-reaction XRD
Electropositive dopants increase Oxygen Bader charge (ionicity) and prevent catalyst reduction.

Understanding Catalyst Stability

Less Reducible  More Reducible

LSC-Mn  LSC-Fe  LSC  LSC-Ni  LSC-Cu

O Bader Charge (e)

H₂ TPR Temperature (°C)

LSC-Mn  LSC-Fe  LSC  LSC-Ni  LSC-Cu

More Reducible

LSC-Mn  LSC-Fe  LSC  LSC-Ni  LSC-Cu

Less Reducible

Oxygen Bader Charge (e)
Understanding Catalyst Stability

Experimentally observed with electronic structure through O K-edge XAS

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>O Bader Charge (e)</th>
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</thead>
<tbody>
<tr>
<td>LSC-Mn</td>
<td>-1.140</td>
</tr>
<tr>
<td>LSC-Fe</td>
<td>-1.135</td>
</tr>
<tr>
<td>LSC-Ni</td>
<td>-1.130</td>
</tr>
<tr>
<td>LSC-Cu</td>
<td>-1.125</td>
</tr>
<tr>
<td>LSC</td>
<td>-1.120</td>
</tr>
</tbody>
</table>

Less Reducible → More Reducible

O ligand hole states

-1.110
-1.115
-1.120
-1.125
-1.130
-1.135
-1.140

LSC-Mn
LSC-Fe
LSC-Ni
LSC-Cu
What are the catalytically active sites?

We want to characterize the catalyst surface *during* DRM to better understand structure-property relationships.

- *Ex situ* studies reveal stability and phase changes *after* the reaction.
- Difficult to probe *in situ* changes within the microwave reactor.
- We have an optical measurement of catalyst temperature during MW DRM.
- Can we utilize thermal DRM to precisely monitor structure vs temperature under reaction conditions?
Thermal DRM confirms reactivity of LSC-Mn

- Thermal DRM starts around 775°C in traditional packed-bed, thermal reactor.
- Higher temperature than optically measured in MW reactor
  - Optical measurement averaged over a 5mm spot on catalyst bed
  - We likely underestimated MW temperature due to formation of micro-scale hot-spots
- Consistent structural changes based on post reaction thermal DRM up to 1000 °C
In situ synchrotron XRD: active site identification

In situ XRD with real-time product analysis excludes other potential active sites
In situ synchrotron XRD: active site identification

In situ XRD with real-time product analysis excludes other potential active sites

*DRM Coincides w/ Co NP Formation*

Perovskitic

Co\textsubscript{fcc}

Mass Spec Signal

H\textsubscript{2}  CO

Co NPs

Normalized Intensity (a.u.)

2 Theta

900 10 min
900 5 min
900 start
880
860
840
820
800
780
740
700
600
500
400
220
20

100 nm
Moving forward: pure gas DRM with LSC-Mn

- High single-pass conversion still possible with pure gases
  - 100% CO₂ + 100% CH₄

- Higher wattage required compared with dilute gases
Extrapolated System Performance

Conventional methane steam reforming: ~30 kWhr/Kg H₂
- Extremely carbon intensive: ~10 tonnes CO₂ / tonne H₂

2020 DOE (EERE FCTO) electrolyzer target: ~45 kWhr/Kg H₂ ($2/kg H₂)
- Scaling studies with larger MW reactor
Conclusions

1. **Doped LSC is promising catalyst for microwave-assisted DRM**
   - Reduced heat management may allow non-traditional reactor designs
   - Fast on/off cycling allows interrupted operation
   - Load following and/or reactant availability

2. **Mn-Doped LSC-Mn shows superior performance**
   - More electropositive dopants transfer charge density to oxygen atoms
   - Prevents catalyst reduction
   - Sustains MW absorbing perovskitic phases
   - Prevents formation of large Co particles

3. **In situ XRD identified Co nanoparticles as likely active sites**

4. **Next steps: Scaling, TEA/LCA, catalyst optimization (co-doping), contaminants**
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Questions or Comments?

Thank you for your attention!

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