Microwave Absorbing Perovskite Catalysts for Efficient Electrification of Syngas Production from CO_2 and Methane

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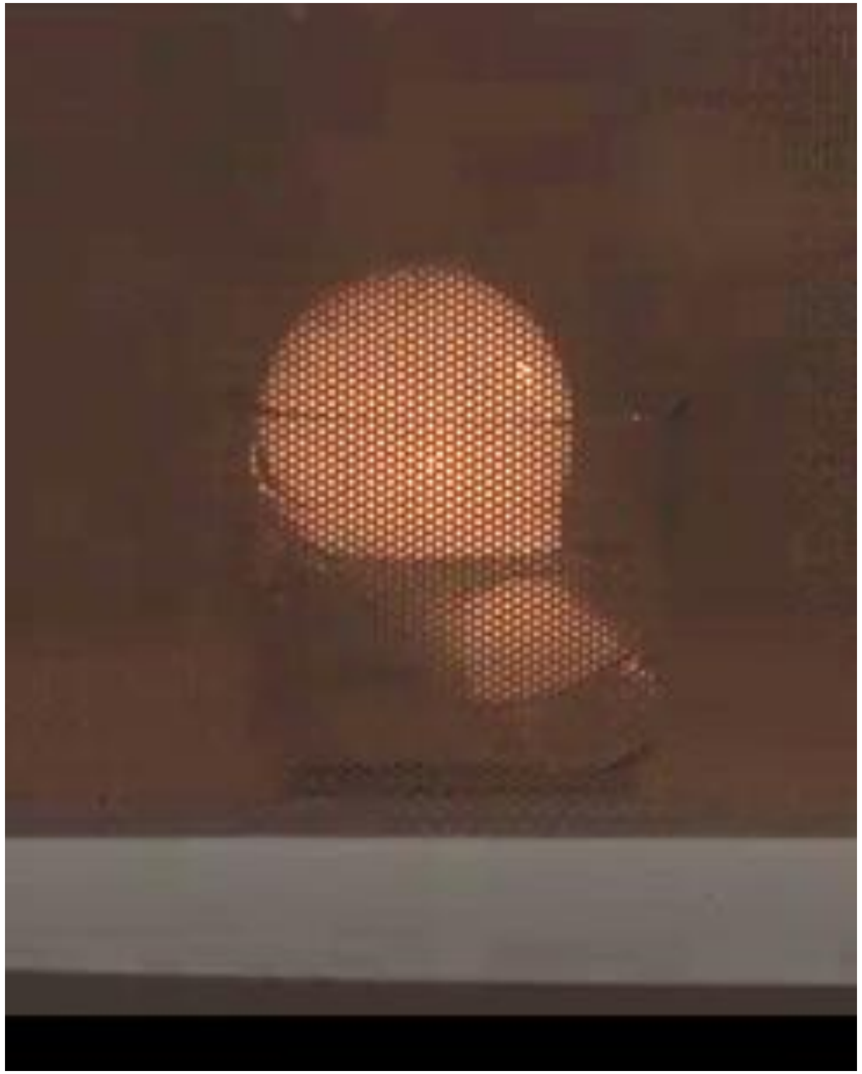
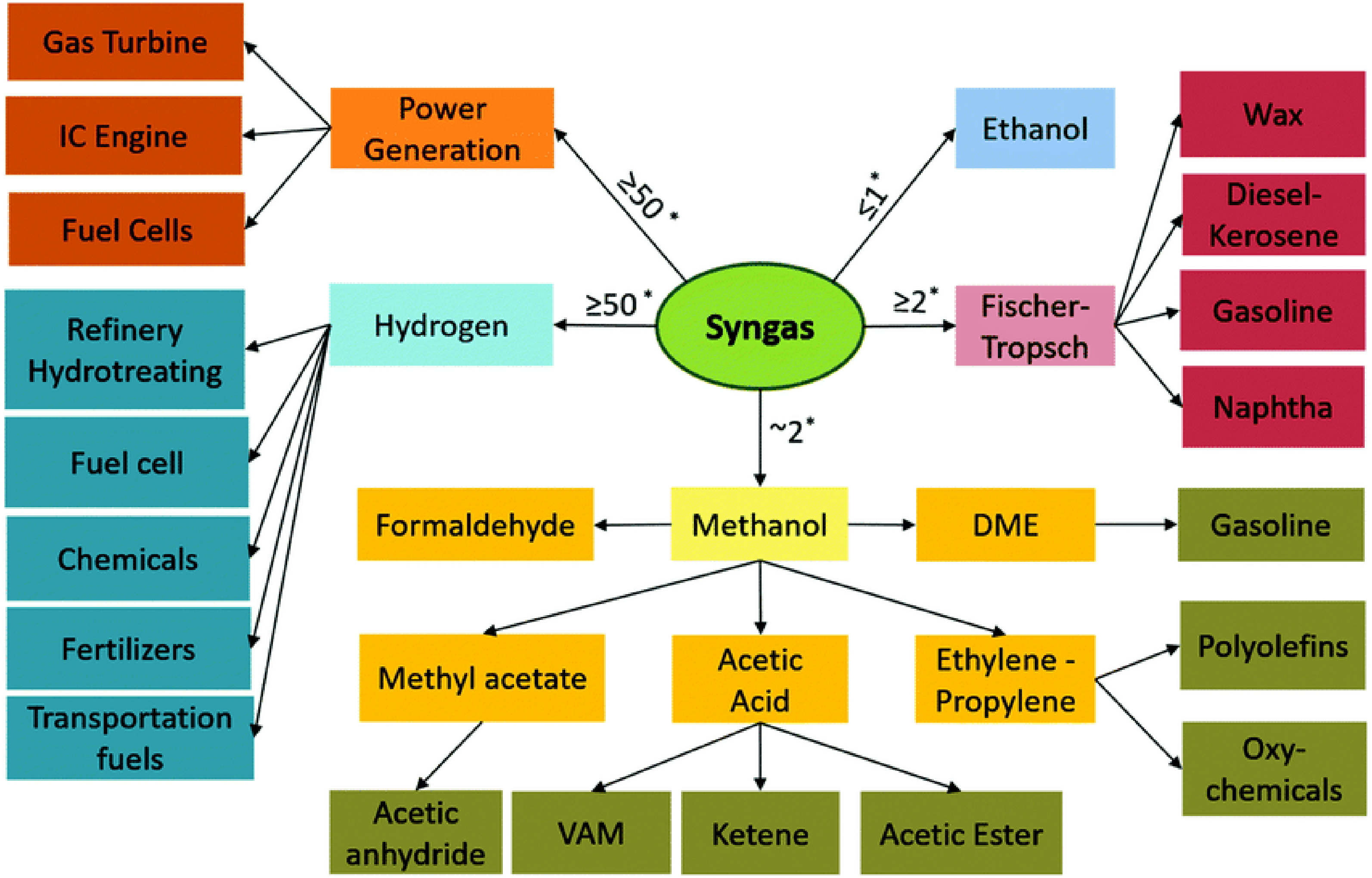
Talk Outline

- Methane reforming
- Microwave heating
- Catalysts/susceptors
- Conductive perovskites
- Fast failure performance screening
- Test results
- Efficiency gains
- Conclusions



Synthesis Gas

H_2:CO Ratio Determines Its Uses

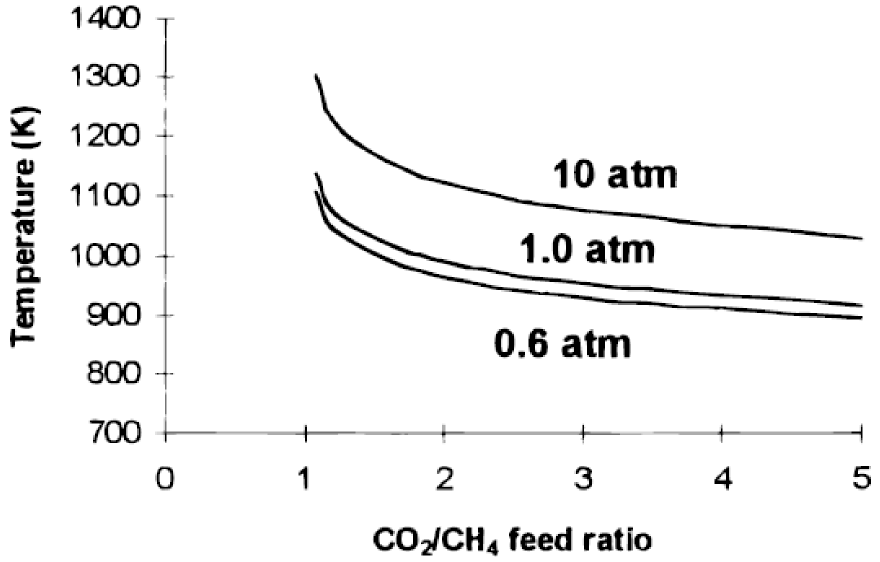


From Chae, Jung-il et al. Catalysts 10(1):99 2020 DOI: 10.3390/catal10010099

Methane Reforming

Methane to Syngas

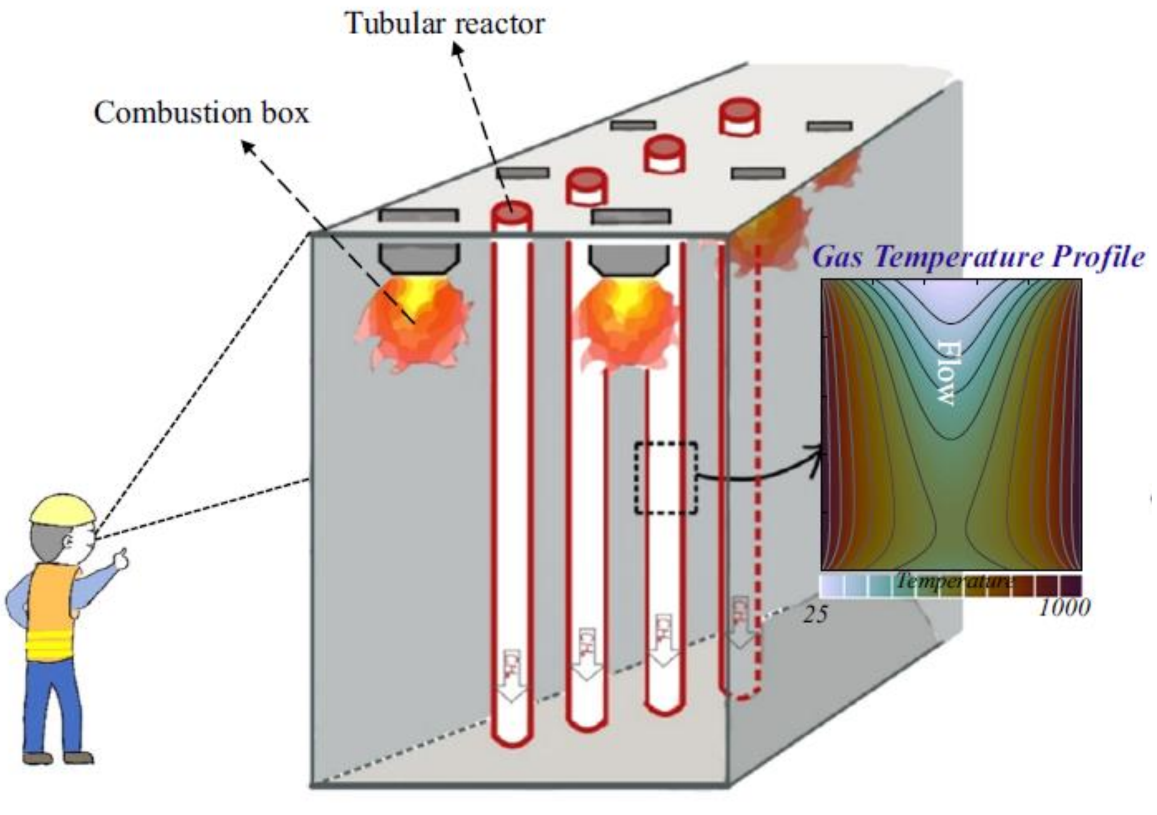
- Dry reforming of methane (DRM): $CO_2 + CH_4 \rightarrow 2CO + 2H_2$ **(1:1 syngas)**
- Steam methane reforming (SMR): $CH_4 + H_2O \rightarrow CO + 3H_2$ **(3:1 syngas)**
- Mixed reforming of methane (MRM): $CO_2 + 2H_2O + 3CH_4 \rightarrow 4CO + 8H_2$ **(2:1 syngas)**
- Commercially, only steam reforming is used due to ability to run at lower temperature and higher pressure
  - CO_2 much softer oxidizing power than steam
  - All 3 processes are spontaneous by 687 °C
  - For DRM, coking occurs below 860 °C



Wang et al. Energy & Fuels 1996

Conventional (Indirect) Heating

Heat Transfer Between a Fire and a Hot Place



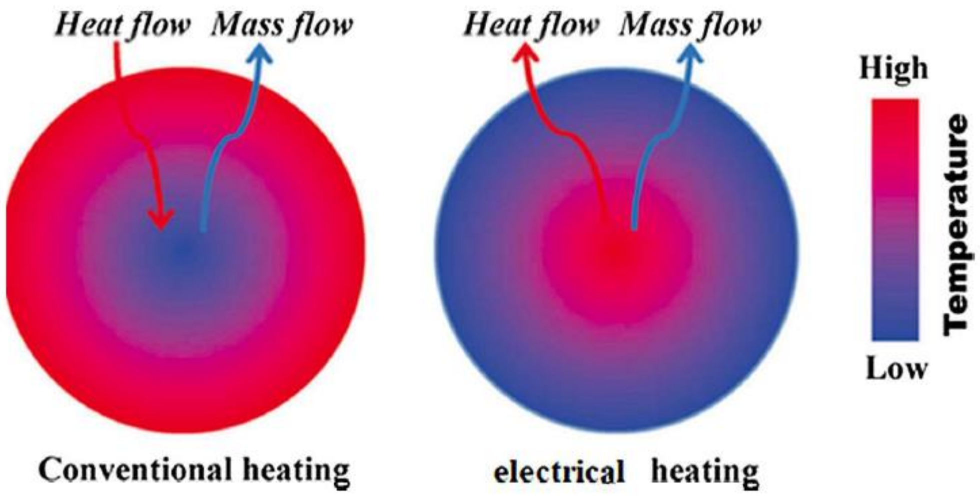
A. Conventional Heating

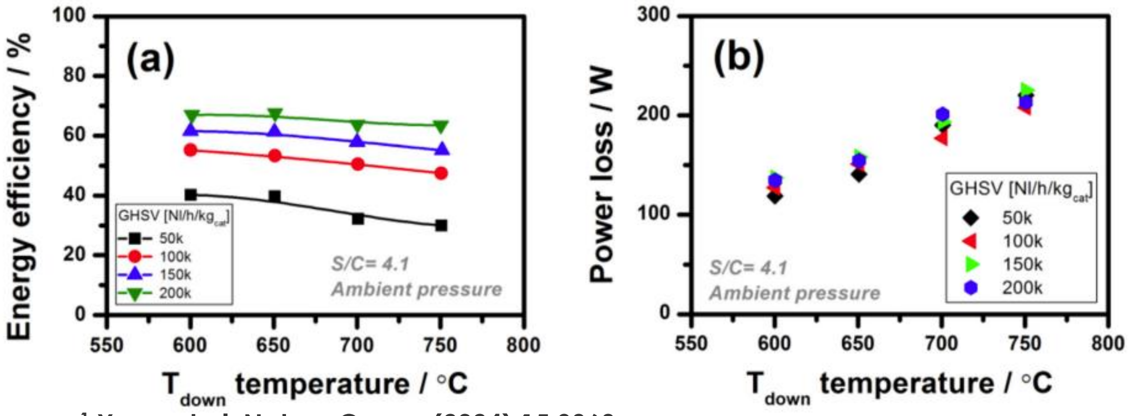
- Conventional SMR reactors use methane as both fuel and reactant
  - 8-10 kg CO_2 per kg H_2 with ~20% from heating[2]
- Long startup and cool down times due to reactor insulation
- Difficult to scale down efficiently due to heat transfer
  - Long tubes needed to ensure middle of channel gets warm
  - Many tubes due to low flow rates to ensure enough residence time

[1] Yang et al. Nature Comm (2024)15:3868
[2] Rapier, Robert. Forbes "Estimating the Carbon Footprint of H_2 Production June 6, 2020

Distributed Electrified (Direct) Heating

Warmth from Within



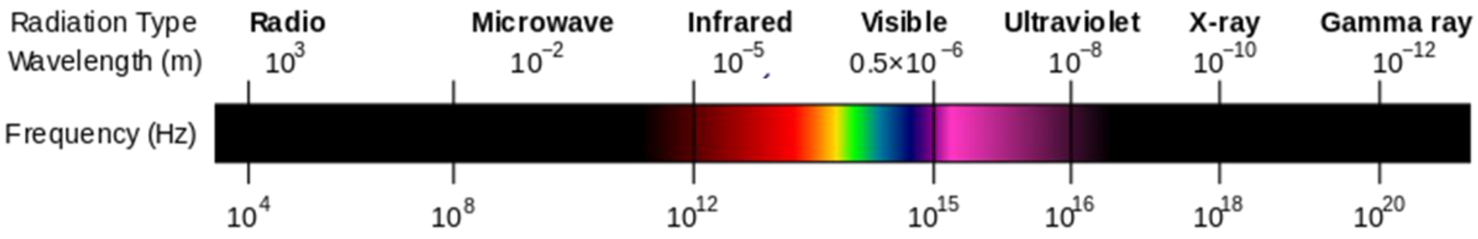


[1] Yang et al. Nature Comm (2024) 15:3868

[2] Zheng et al. International Journal of Hydrogen Energy (2023) 48:14681-14696

- Recent papers have highlighted the efficiency gains in endothermic reactions by internally (directly) heating the catalyst[1]
- Heat losses found to grow ~linearly with reactor temperature but ~independent from the space velocity so overall efficiency increases with flow rate[2]
- Approaches range between direct resistive (joule) heating the catalyst bed, inductive heating, and microwave heating

Microwave Heating



- Microwaves are electromagnetic waves from ~10 cm to ~1 mm
- Lower frequency than infrared
- Interact weakly with most matter allowing for wireless selective heating
- Microwave heating efficiency (susceptibility) determined by the loss tangent:

$$\tan\delta = \frac{\omega\varepsilon'' + \sigma}{\omega\varepsilon'}$$

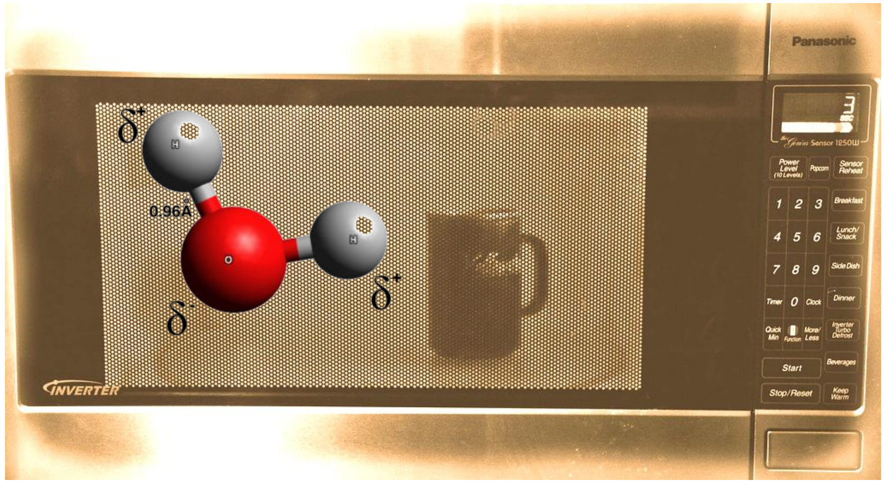
- ε'' and ε' are the imaginary and real permittivities, respectively, while σ is conductivity
- Materials with large tan δ either have large ε''/ε' ratios (like strongly polar materials) or large σ/ε' ratios (like salt solutions or graphite)

Microwave Heating

Saving Time in the Lunchroom

Water: tanδ ~ 0.003

Dipolar materials have large ε''/ε' ratio



Much higher tanδ in water than air allows selective heating of dipolar water in the cup

Saltwater: tanδ ~ 3 ($5.8M_{NaCl}$)

Conductivity improvements both raise σ and lower ε'

Salty liquids like soup absorb microwaves much more efficiently

Graphite: tanδ ~ 0.25-1.5

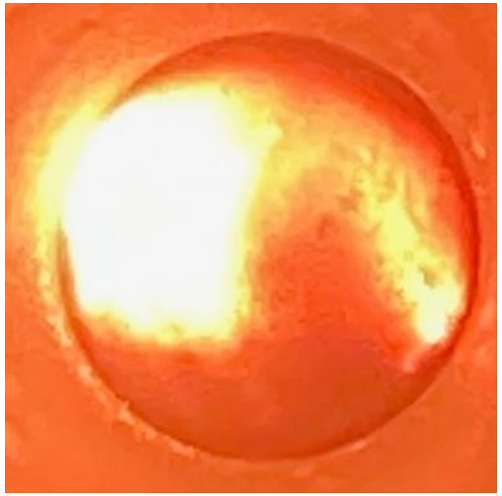
Conductivity rises with temperature causing loss tangent to vary

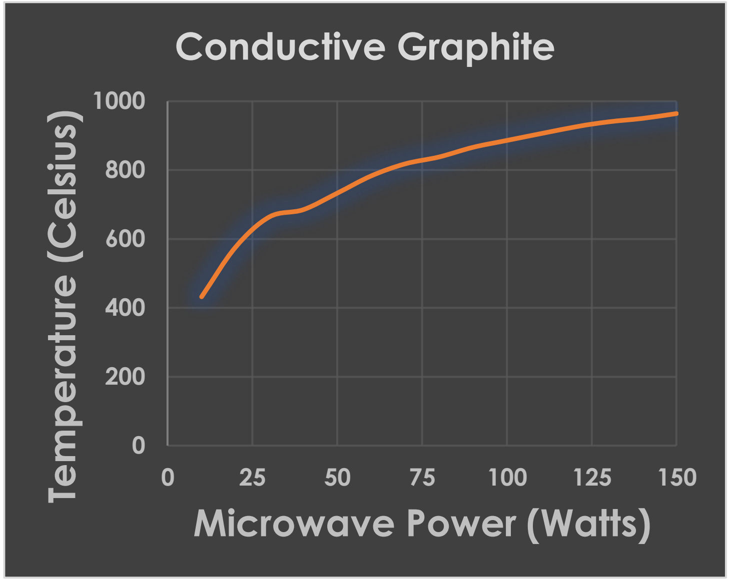
Graphite or other metallic susceptors absorb efficiently and have higher phase transition temperatures than water

Catalysts/Susceptors

Putting Microwave Hot Spots to Work

- Catalysis takes place on heterogenous surfaces so those are the only spots that need to be hot
- Metals make excellent microwave absorbers when they are fine enough to absorb instead of reflecting electromagnetic wave
- Once metals sinter or melt, end up with a large metal object in the microwave (which is microwave reflective)
- Want materials that heat like metals but do not sinter or melt like metals
- Graphite heavily used as a microwave susceptor, but conditions that remove coke also remove graphite
- For efficiency, the same material absorbing microwaves should be where catalysis occurs

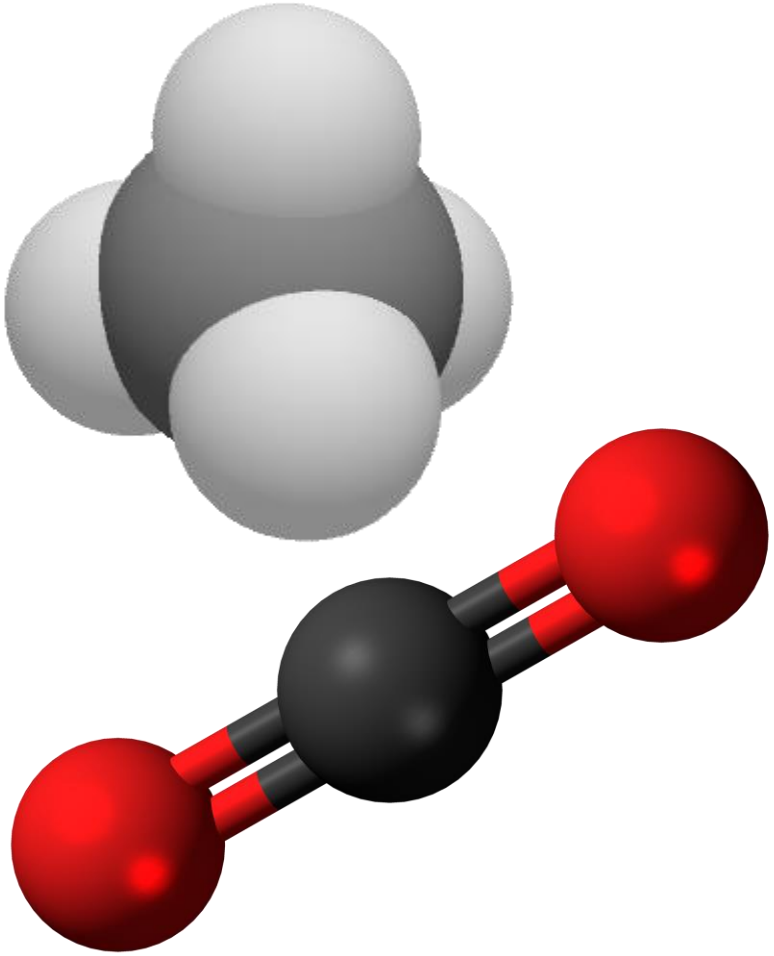




Methane Reforming Catalysts

Bringing Molecules Together

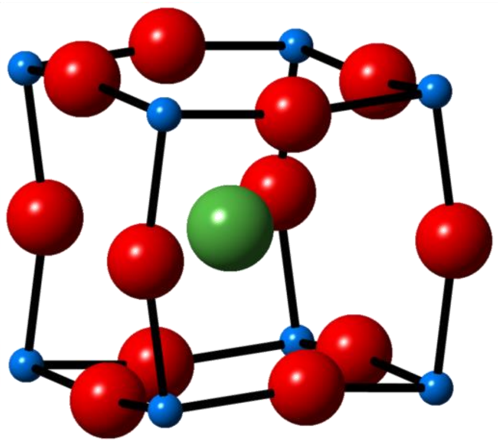
- CH_4 is symmetric and tough to crack
  - Generally, metals are used as active sites for CH_4 to bind to
- CO_2 is also symmetric, but does present Lewis acid sites
  - Basic oxides are often used as active sites for CO_2
- Typical methane reforming catalysts are metals (Pt, Ru, Ni, Co, etc.) on oxide supports with base sites (Na, Ca, Sr, etc.) to promote CO_2 interaction

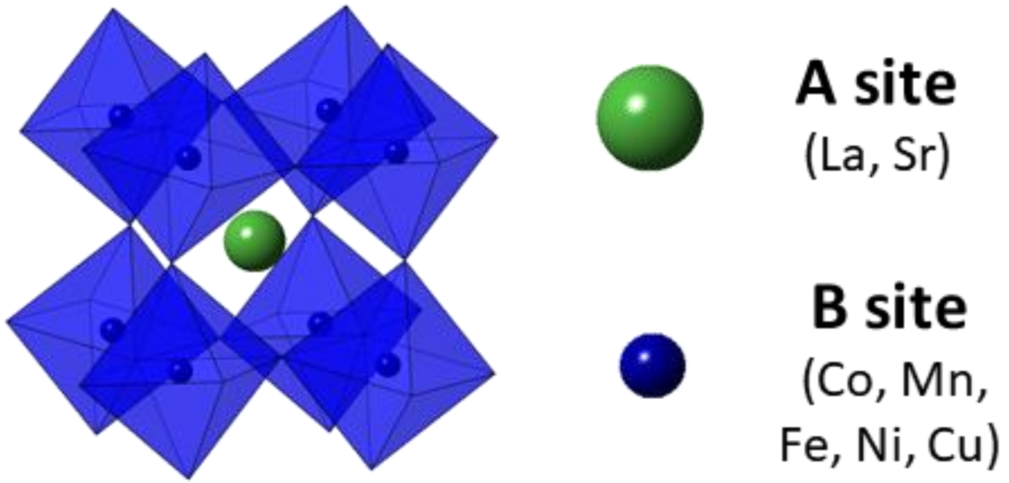


Conductive Perovskites

Making Oxygen Share

- The highest high temperature oxide conductivities belong to the perovskite family
- Perovskites have general form ABO_3 with A sites generally alkaline or rare earths and B sites generally transition metals
- B sites make up the structure backbone with each metal octahedrally coordinated with vertex sharing oxygen
- In the case of Sr doped $LaCoO_3$, highest known oxide conductivity ~4,400 S/cm and a melting point of 1700 °C

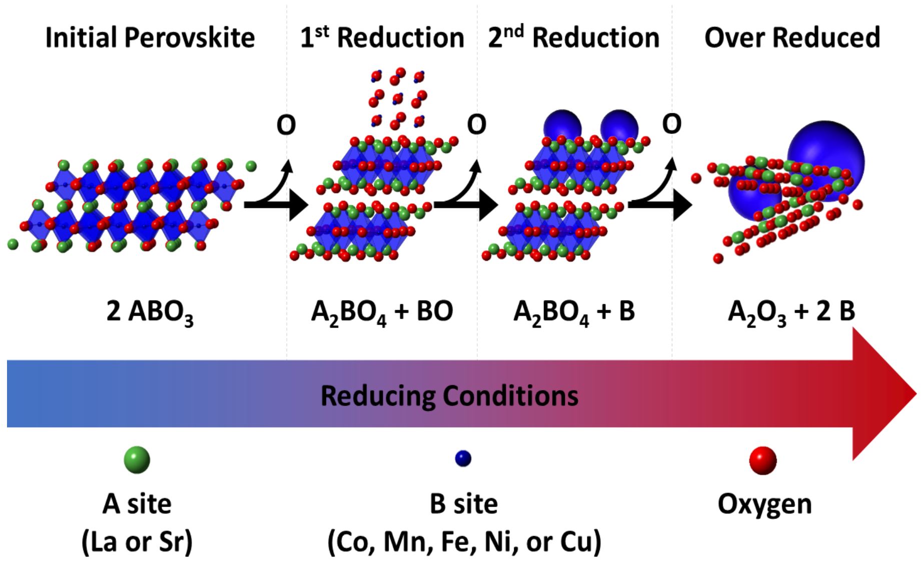


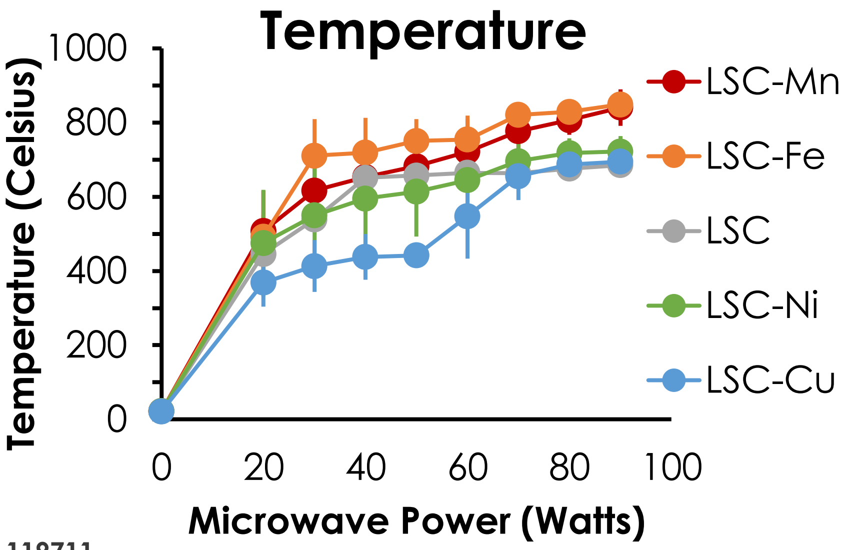


DRM with LSC

That's $CO_2 + CH_4 \rightarrow 2CO + 2H_2$ with $La_{0.8}Sr_{0.2}CoO_3$

- Under reducing conditions, $La_{0.8}Sr_{0.2}CoO_3$ kicks out Co metal sites and adopts a layered perovskite structure
- Under oxidizing conditions, catalyst can be converted back to parent perovskite
- When over-reduced, phase separation to microwave inactive La_2O_3 and SrO leads to sintering and to a catalyst that no longer heats efficiently
- Control of B site dopants effective for moderating phase transition temperatures



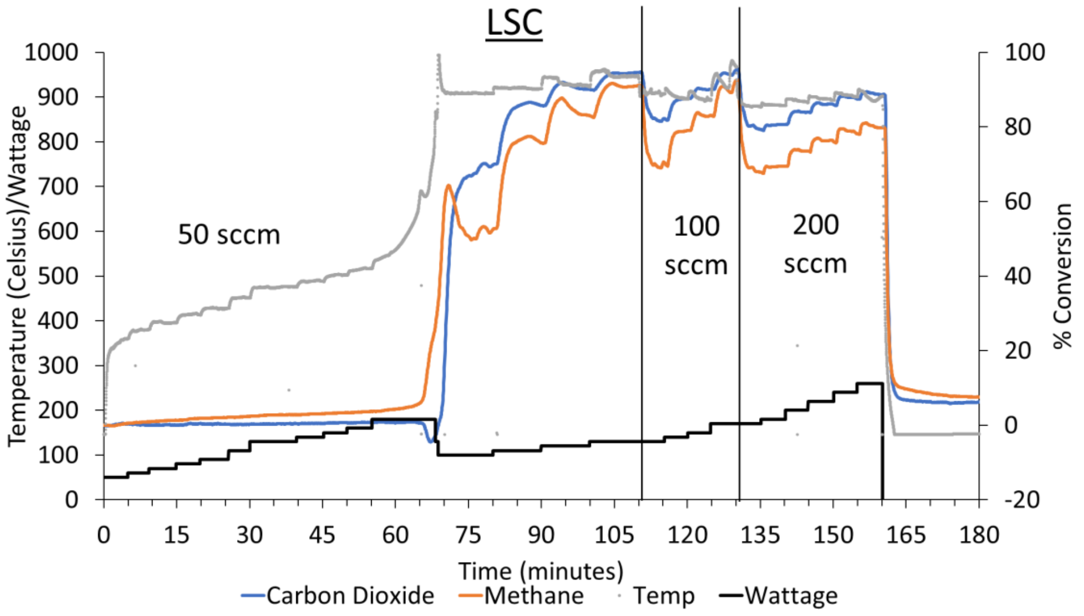


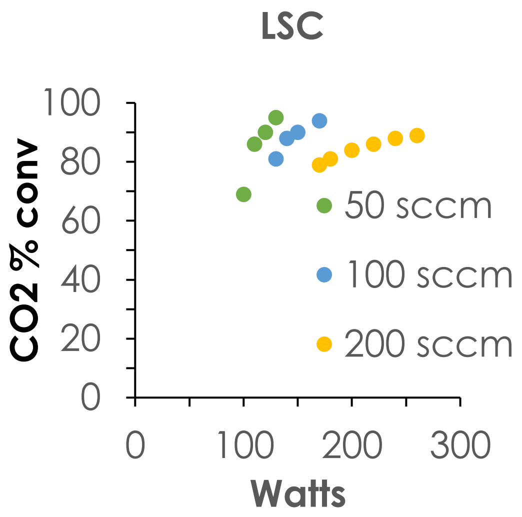
Marin et al. Applied Catalysis B 284 (2021) 119711

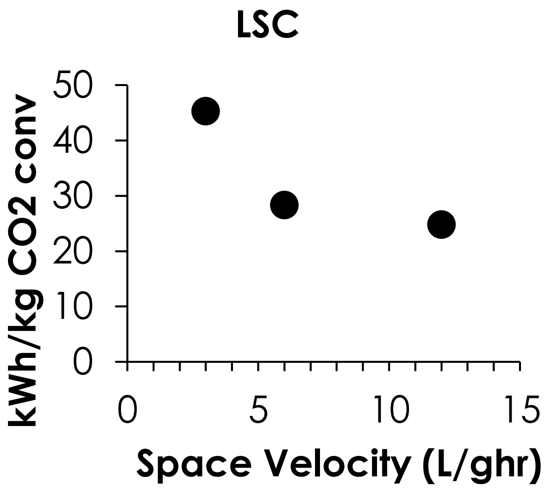
Fast Failure Performance Screening

If at First You Succeed, Try-Try Again

- Starting with 1g $La_{0.8}Sr_{0.2}CoO_3$ (LSC) and testing with 50:50 CO_2:CH_4
- Trying to find the least energy to convert a kg of CO_2 at 80-90% conversions
- If conversions below 90% of both CO_2 and CH_4, applied power raised
- If conversions of CO_2 and CH_4 ≥ 90%, increase the flow rates and repeat

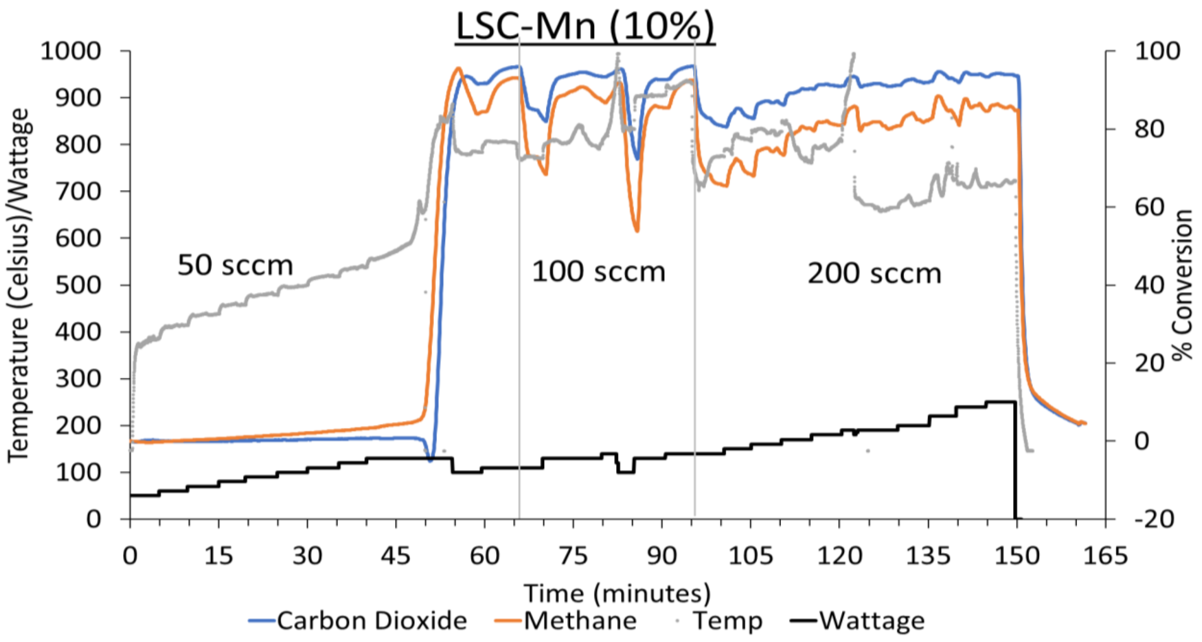


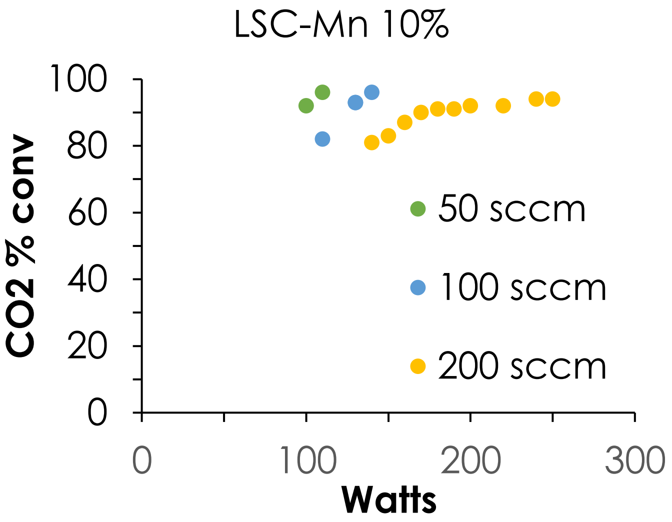


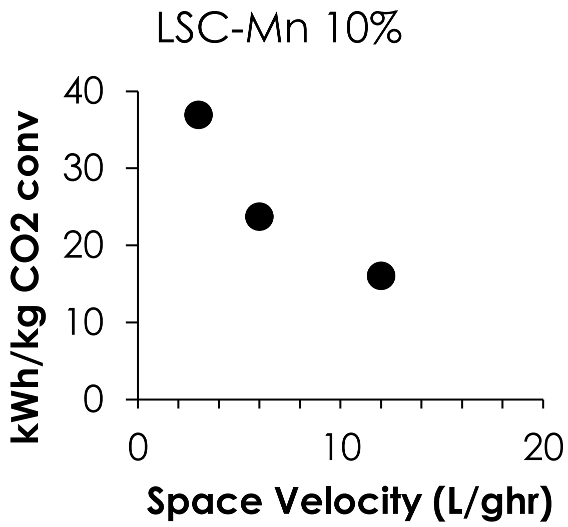


- 24.8 kWh/kg CO_2 conversion at 12 $Lg^{-1}hr^{-1}$

Fast Failure Performance Screening

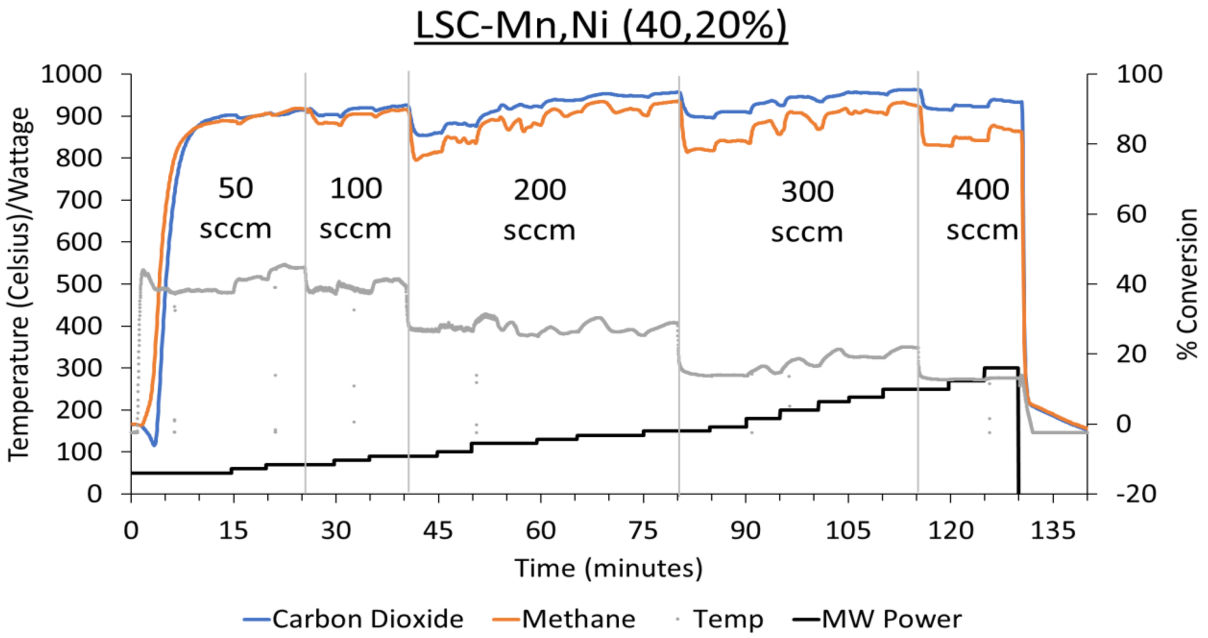


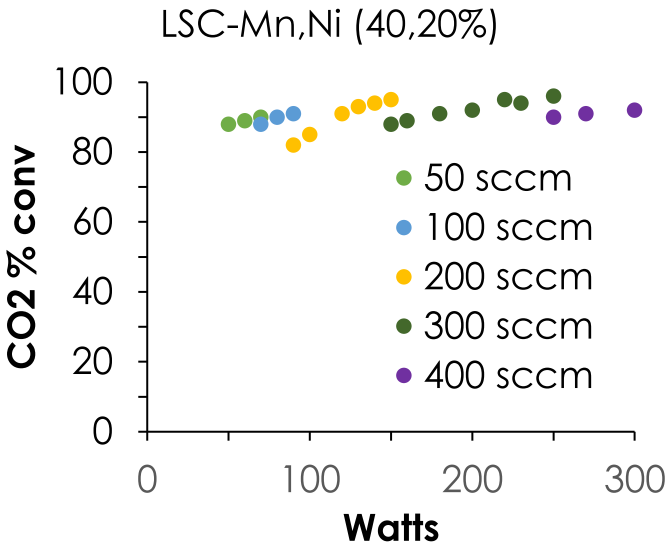


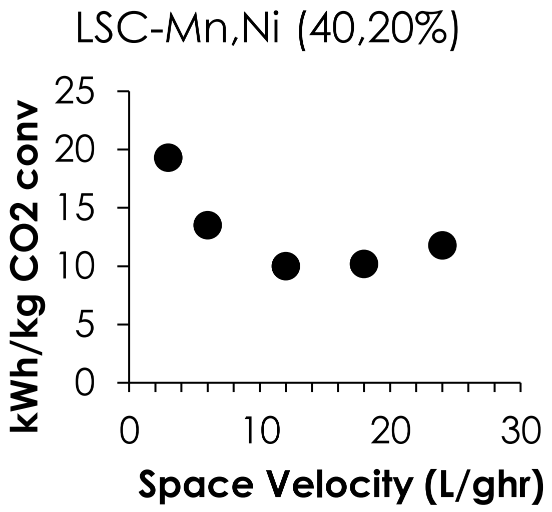


- **16.0 kWh/kg CO_2** conversion at 12 $Lg^{-1}hr^{-1}$

Fast Failure Performance Screening







- **<u>10.0 kWh/kg CO_2</u>** conversion at 12 $Lg^{-1}hr^{-1}$

Test Results $La_{0.8}Sr_{0.2}Co_{0.4}Mn_{0.4}Ni_{0.2}O_3$

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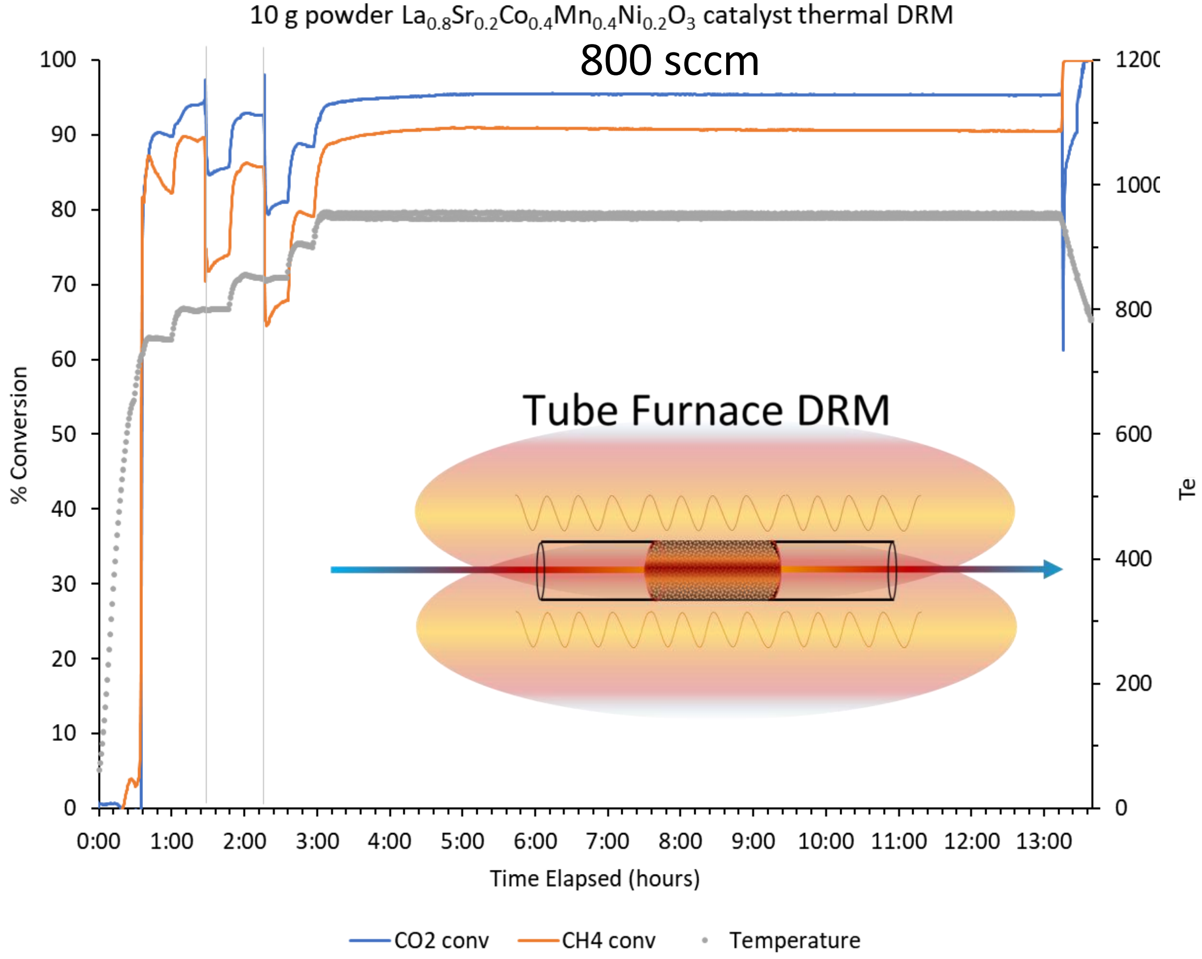
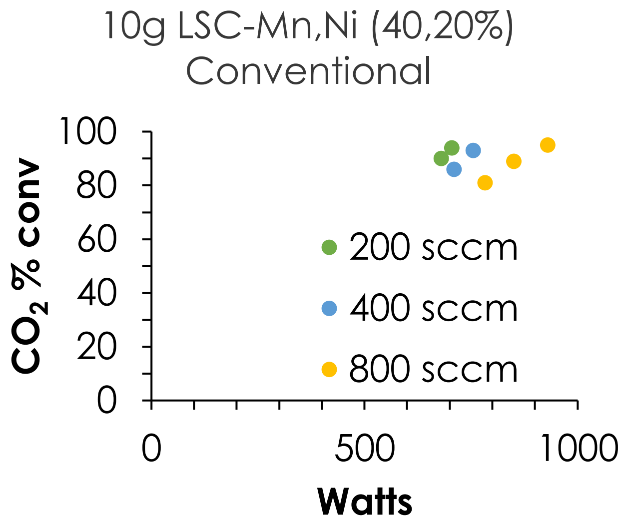
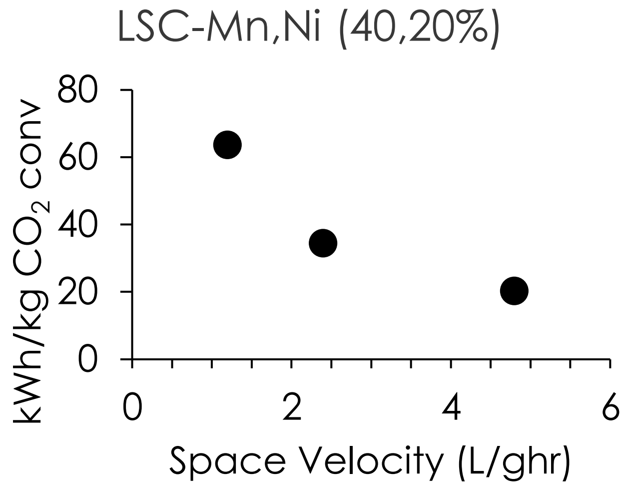
Conventional (Indirect) Heating



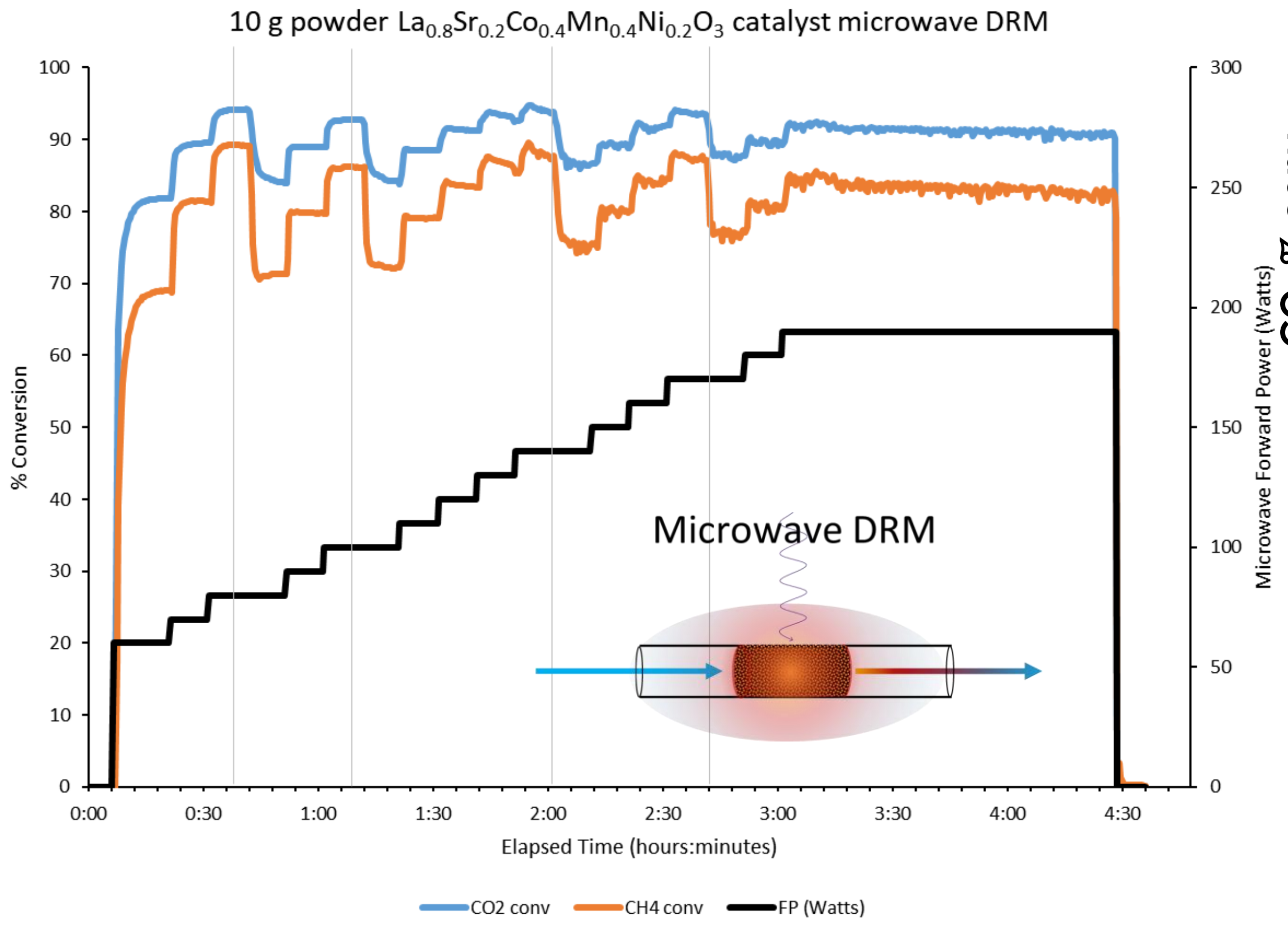


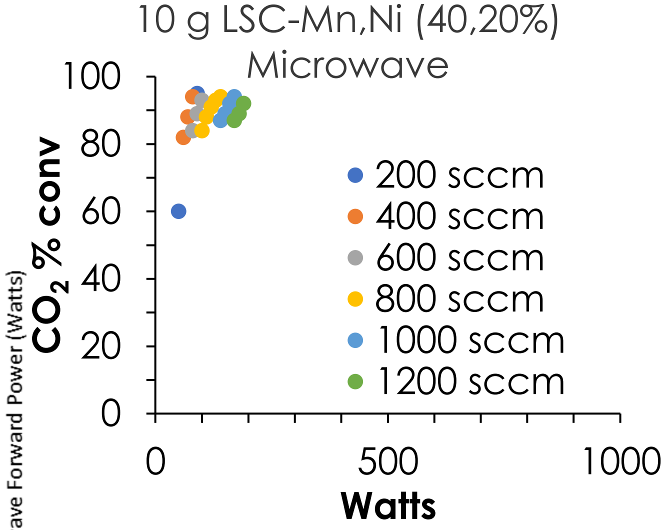


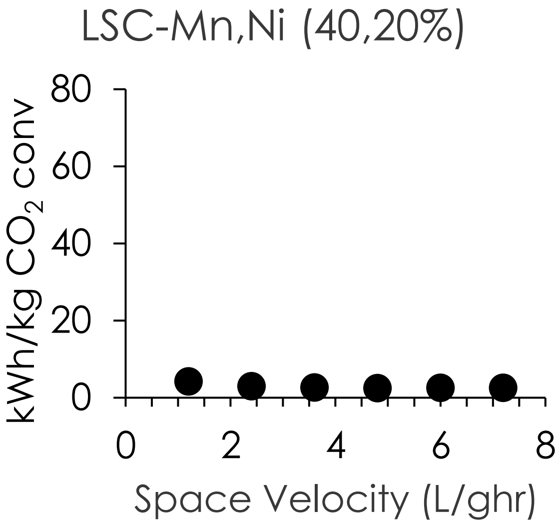
- In a conventional tube furnace reactor, only 20.3 kWh/kg CO_2 conversion at 4.8 $Lg^{-1}hr^{-1}$
- Efficiency improves with flow rate, but faster flow rates require much hotter side walls to keep catalyst bed at temperature
- Back pressure gradually rose forcing a test end after 10 hours with catalyst heavily sintered and coked up

Test Results $La_{0.8}Sr_{0.2}Co_{0.4}Mn_{0.4}Ni_{0.2}O_3$

Microwave (Direct) Heating



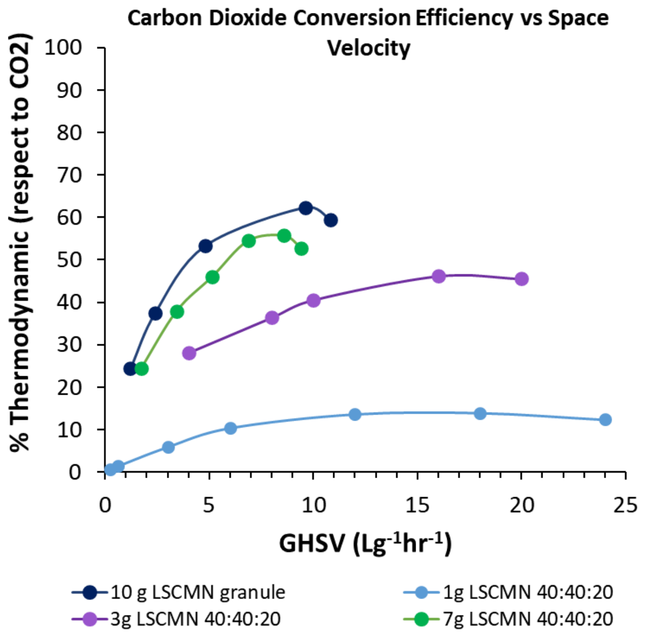


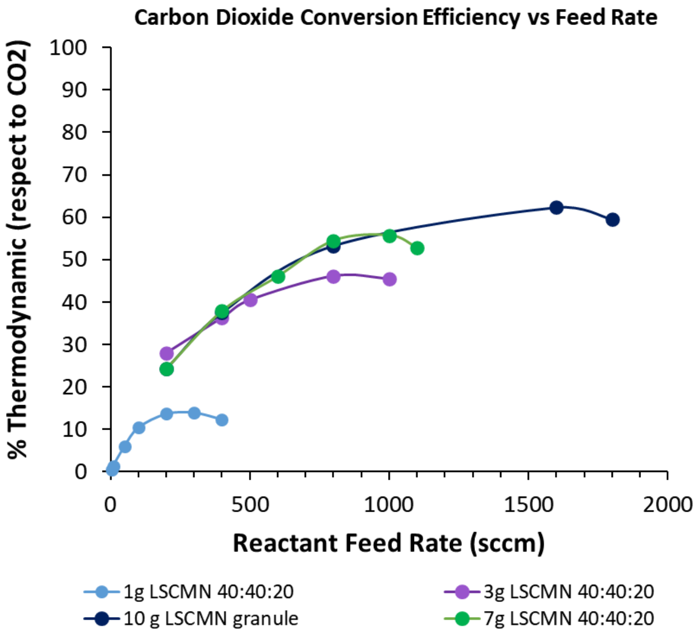


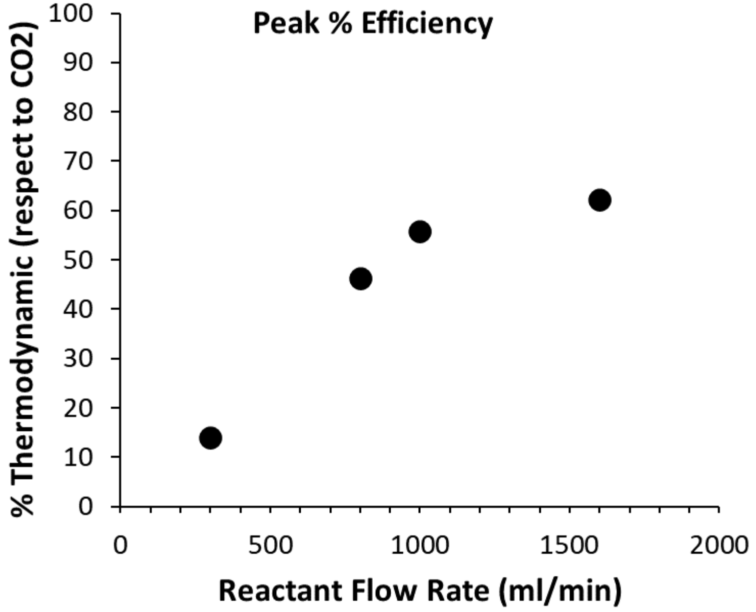
- In a microwave reactor, only 2.4 kWh/kg CO_2 conversion at 4.8 $Lg^{-1}hr^{-1}$ **~10x better efficiency**
- Efficiency improves with flow rate and higher flow rates were achievable with internally heated catalyst
- Ran catalyst for over 40 hours on stream before back pressure ran high

Efficiency

Working Smarter, Not Harder



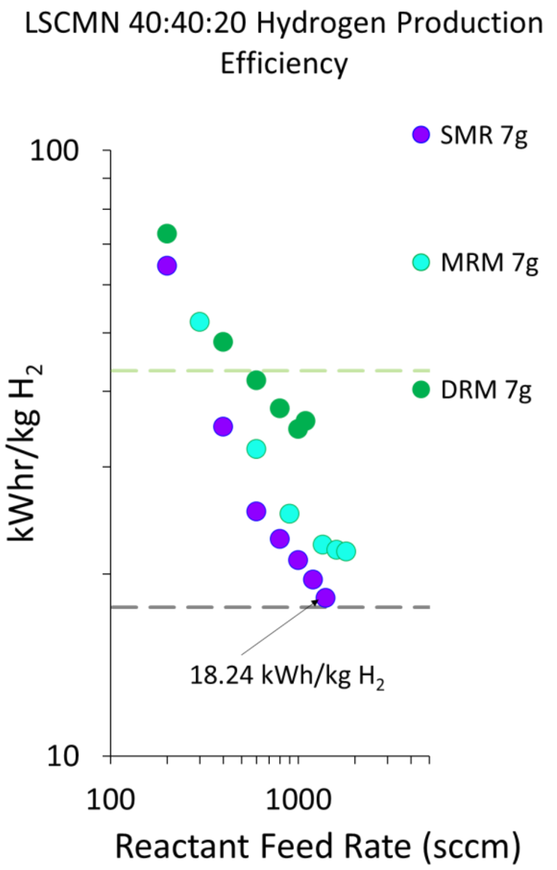


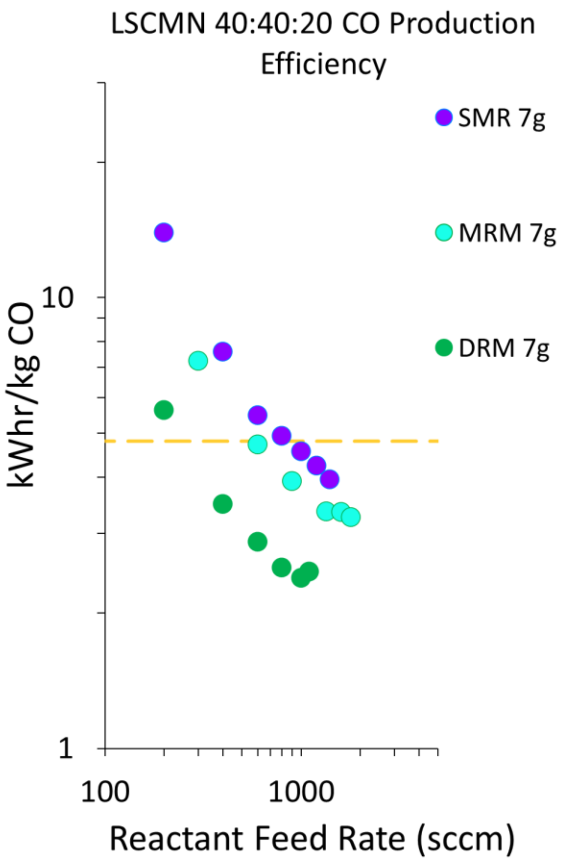


- Thermodynamic efficiency calculated assuming that at 100% only energy used is for dry reforming reaction enthalpy (+247 kJ/mol CO_2)
- Like other internally heated endothermic reactions, efficiency improving with flow rate
- Efficiency improving with flow rate even while keeping within the same space velocity range

Variable Methane Reforming

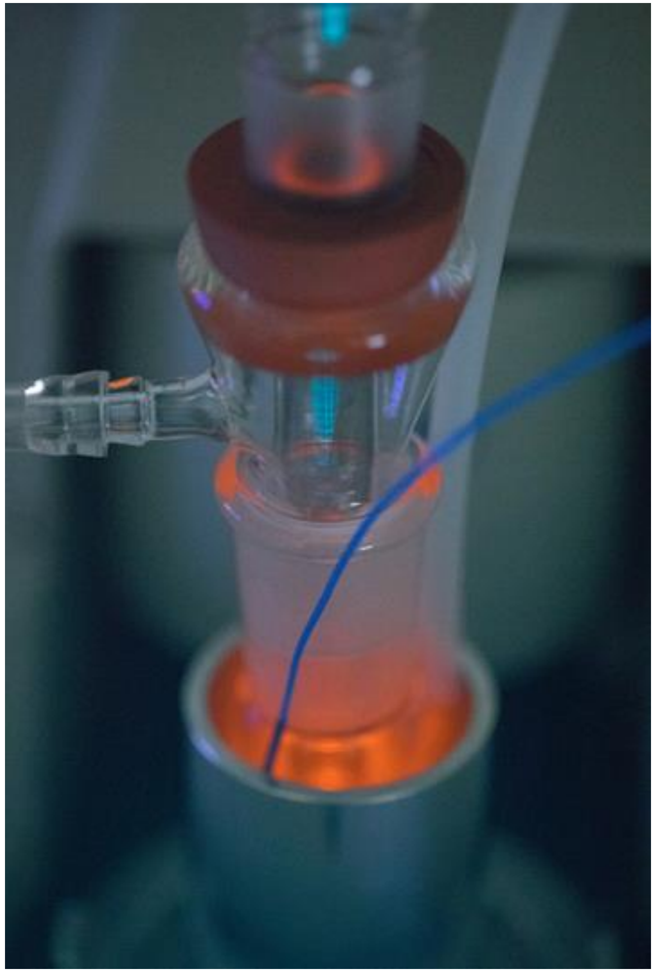
1:1 to 3:1 Syngas Ratios





- As LSC-Mn,Ni (40,20%) was developed for performance with dry reforming methane, catalyst also suitable for mixed and steam reforming
- Dry Reforming Methane ($CO_2 + CH_4 \rightarrow 2CO + 2H_2$) **1:1 syngas**
- Mixed Reforming Methane (in our case, $CO_2 + 2H_2O + 3CH_4 \rightarrow 8H_2 + 4CO$) **2:1 syngas**
- Steam Methane Reforming ($CH_4 + H_2O \rightarrow 3H_2 + CO$) **3:1 syngas**
- For all 3, efficiency has been improving with reactant feed rate

Conclusions



- High temperature endothermic reactions such as dry reforming methane run more efficiently with higher flow rates
- Directly heating of catalyst bed from within allows for better temperature uniformity and stability at high gas flow rates
- LSC optimized for microwave absorption and dry reforming stability with incorporation of Mn and Ni for overall formula $La_{0.8}Sr_{0.2}Co_{0.4}Mn_{0.4}Ni_{0.2}O_3$
- Catalyst found to be suitable for microwave dry, mixed, and steam reforming conditions

Acknowledgments

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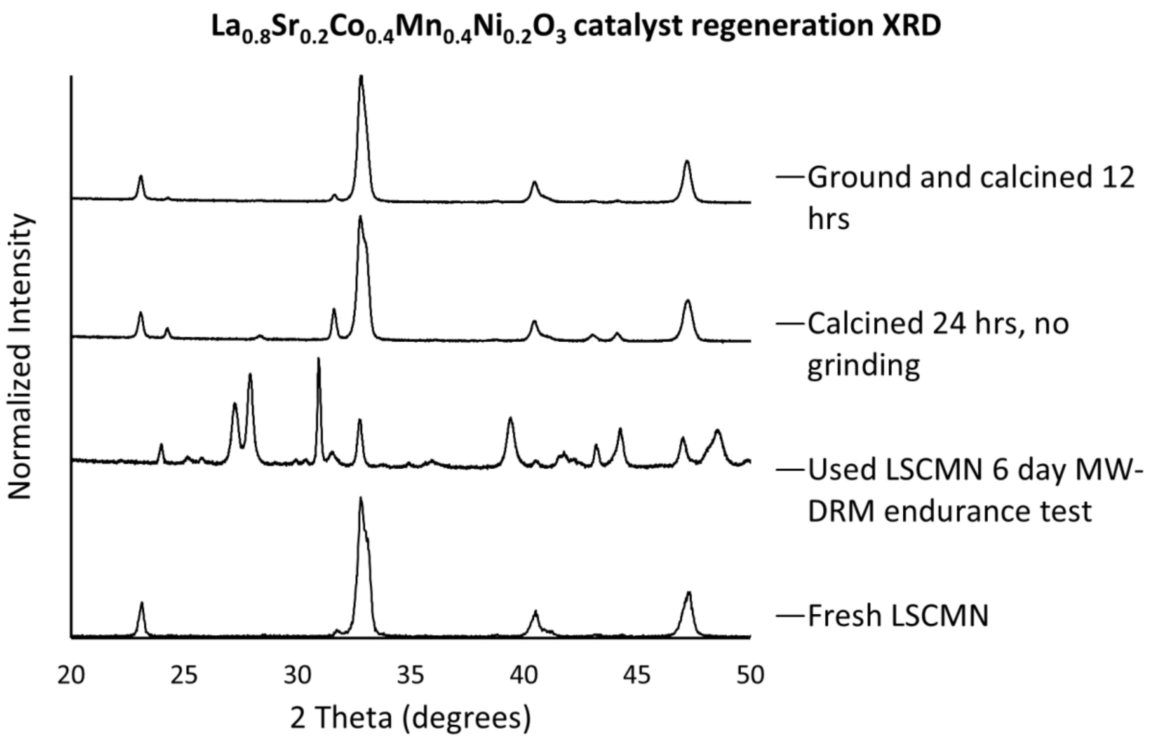
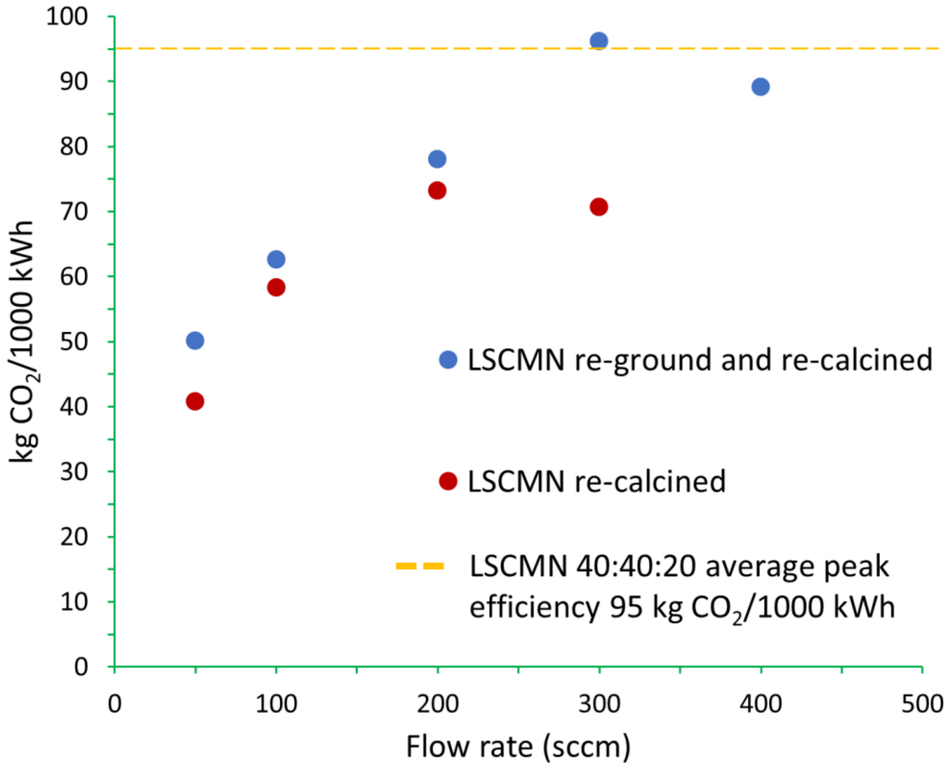
Supporting Information slides

LSC-Mn,Ni Regeneration





Supporting Information Slides

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some elementary reactions of SMR on Ni(111)

Reaction	
$CH_4 + 2^* \rightleftharpoons CH_3^* + H^*$	$CHO^* + {}^* \rightleftharpoons CO^* + H^*$
$CH_3^* + {}^* \rightleftharpoons CH_2^* + H^*$	$CHO^* + O^* \rightleftharpoons HCOO^{**}$
$CH_2^* + {}^* \rightleftharpoons CH^* + H^*$	$CO^* + O^* \rightleftharpoons CO_2^* + {}^*$
$CH^* + {}^* \rightleftharpoons C^* + H^*$	$H_2O^* + {}^* \rightleftharpoons OH^* + H^*$
$CH_3^* + OH^* \rightleftharpoons CH_3OH^* + {}^*$	$OH^* + {}^* \rightleftharpoons O^* + H^*$
$CH_2^* + OH^* \rightleftharpoons CH_2OH^* + {}^*$	$H_2O^* + O^* \rightleftharpoons OH^* + OH^*$
$CH^* + OH^* \rightleftharpoons CHOH^* + {}^*$	$CO^* + OH^* \rightleftharpoons COOH^* + {}^*$
$C^* + OH^* \rightleftharpoons COH^* + {}^*$	$COOH^* + {}^* \rightleftharpoons CO_2^* + H^*$
$CH_3^* + O^* \rightleftharpoons CH_3O^* + {}^*$	$HCOO^* \rightleftharpoons CO_2^* + H^*$
$CH_2^* + O^* \rightleftharpoons CHO^* + {}^*$	$H_2 + 2^* \rightleftharpoons H^* + H^*$
$CH^* + O^* \rightleftharpoons CHO^* + {}^*$	$H_2O + {}^* \rightleftharpoons H_2O^*$
$C^* + O^* \rightleftharpoons CO^* + {}^*$	$CO + {}^* \rightleftharpoons CO^*$
$CH_3OH^* + {}^* \rightleftharpoons CH_2OH^* + H^*$	$CO_2 + {}^* \rightleftharpoons CO_2^*$
$CH_2OH^* + {}^* \rightleftharpoons CHOH^* + H^*$	$CH_3OH + {}^* \rightleftharpoons CH_3OH^*$
$CHOH^* + {}^* \rightleftharpoons COH^* + H^*$	$C^* + H_2O^* \rightleftharpoons CH^* + OH^*$
$CH_3OH^* + {}^* \rightleftharpoons CH_3O^* + H^*$	$C^* + H_2O + {}^* \rightleftharpoons COH^* + H^*$
$CH_2OH^* + {}^* \rightleftharpoons CH_2O^* + H^*$	$COH^* + OH^* \rightleftharpoons CO^* + H_2O^*$
$CHOH^* + {}^* \rightleftharpoons CHO^* + H^*$	$HCOH^* + OH^* \rightleftharpoons HCO^* + H_2O^*$
$COH^* + {}^* \rightleftharpoons CO^* + H^*$	$H_2COH^* + OH^* \rightleftharpoons H_2CO^* + H_2O^*$
$CH_3O^* + {}^* \rightleftharpoons CH_2O^* + H^*$	
$CH_2O^* + {}^* \rightleftharpoons CHO^* + H^*$	

- Methane reforming composed of many elementary steps to strip H_2 from CH_4 and oxidize carbon back into a leaving group (CO and CO_2)
- CO_2 and H_2O closely interrelated by the water-gas shift reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$
  - Note: WGSR also not an elementary reaction
- Ratio of CO_2 and H_2O oxidizers use control the ratio of H_2:CO in product mix but elementary steps are the same either way
- Very complex microkinetics: thermodynamics treatment relied on for reforming reactions

Changming Ke, Reaction Chemistry & Engineering 2020(5) 10.1039/C9RE00460B