Microwave-Assisted Thermal Conversion of CO_2 and Methane Over Conductive Metal Oxides

NATIONAL ENERGY TECHNOLOGY LABORATORY

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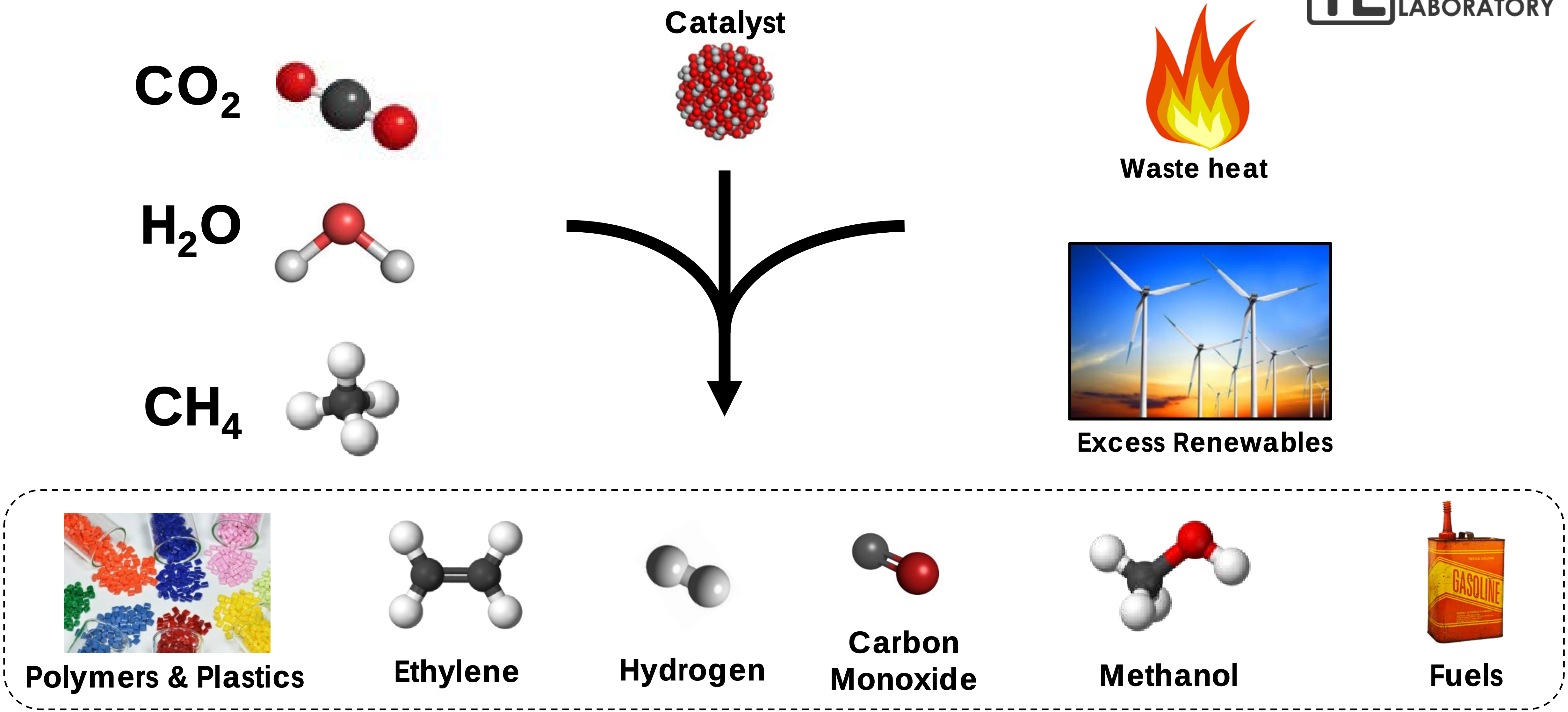
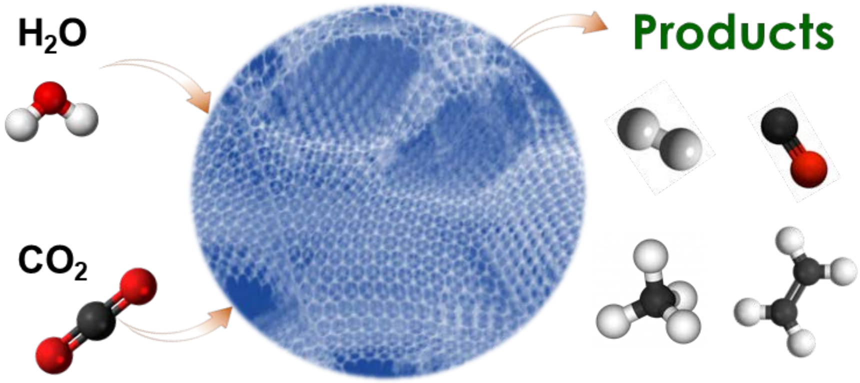
August 29, 2019

Catalytic CO_2 conversion at NETL

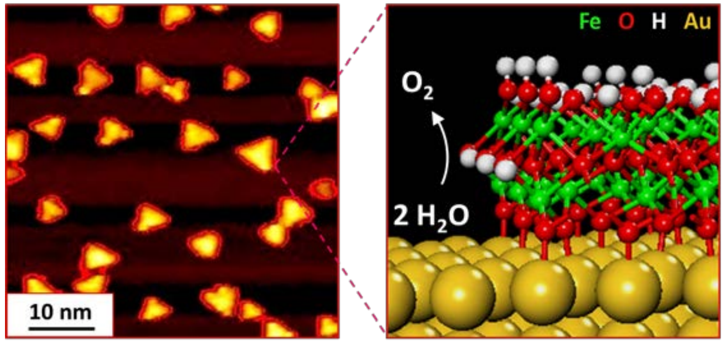


Electrochemical catalyst design

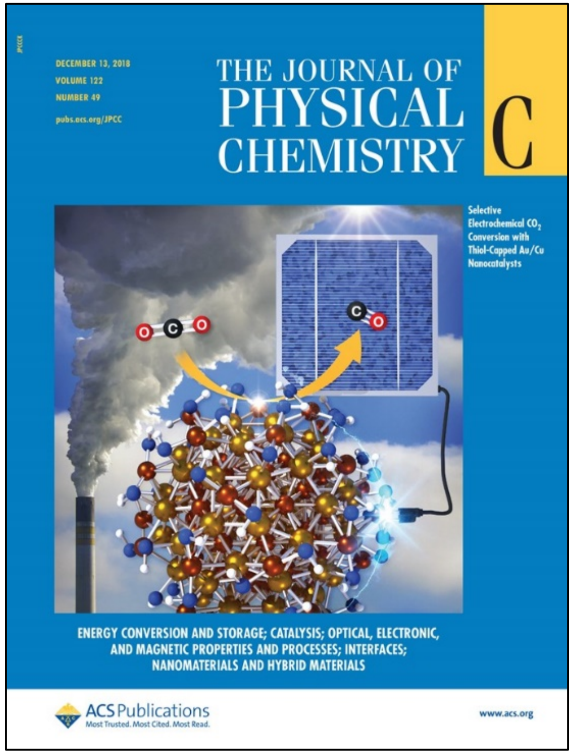
Structure-controlled product selectivity



Surface-science enabled electrocatalysis

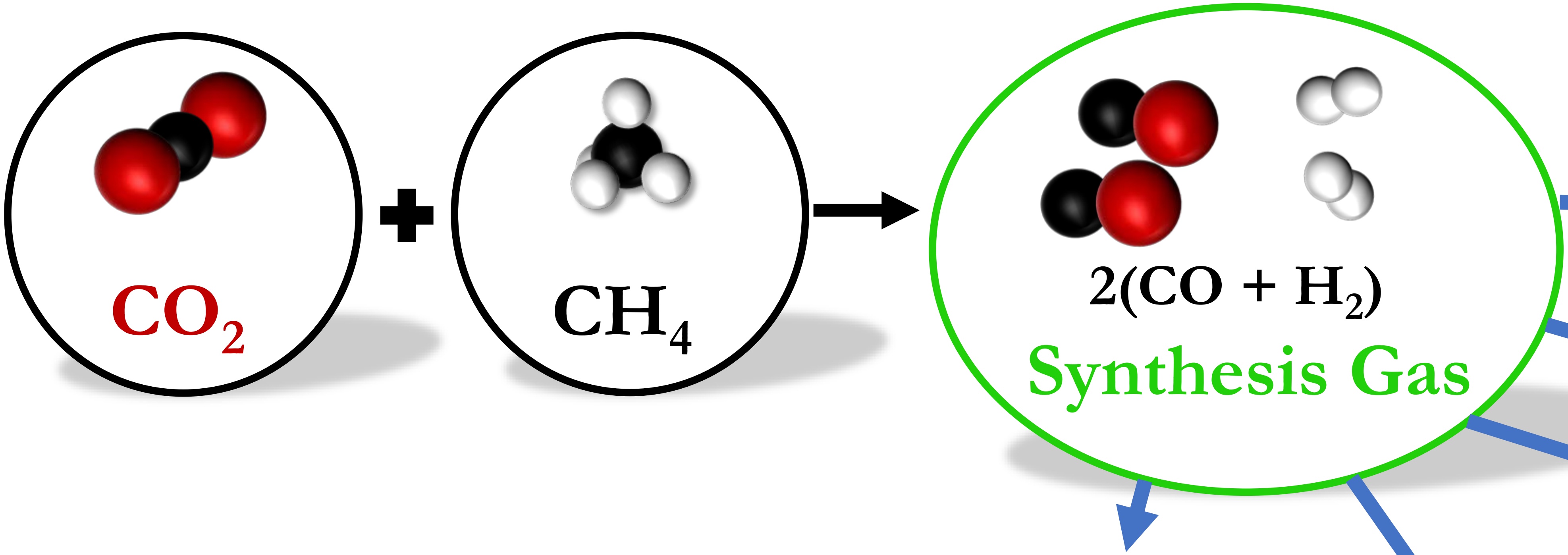


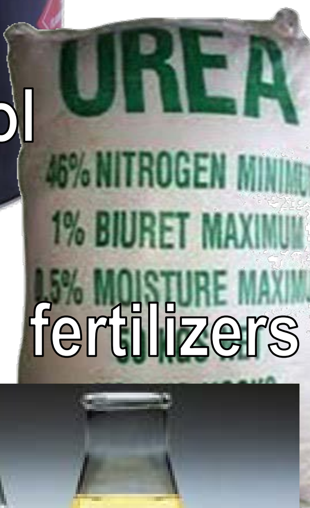
"Atomically Precise" nanocatalysts

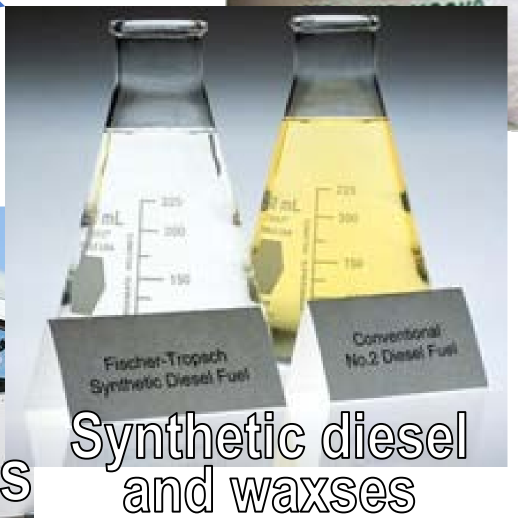


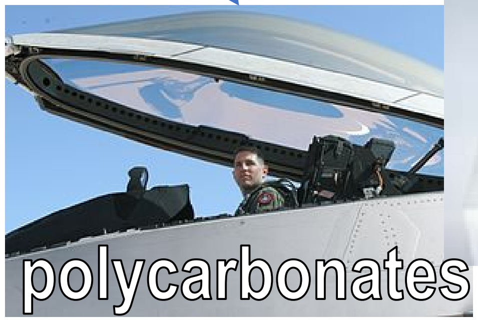
Journal of Physical Chemistry Cover (Dec. 2018)

Appealing thermal route: Dry Reforming of Methane (DRM)





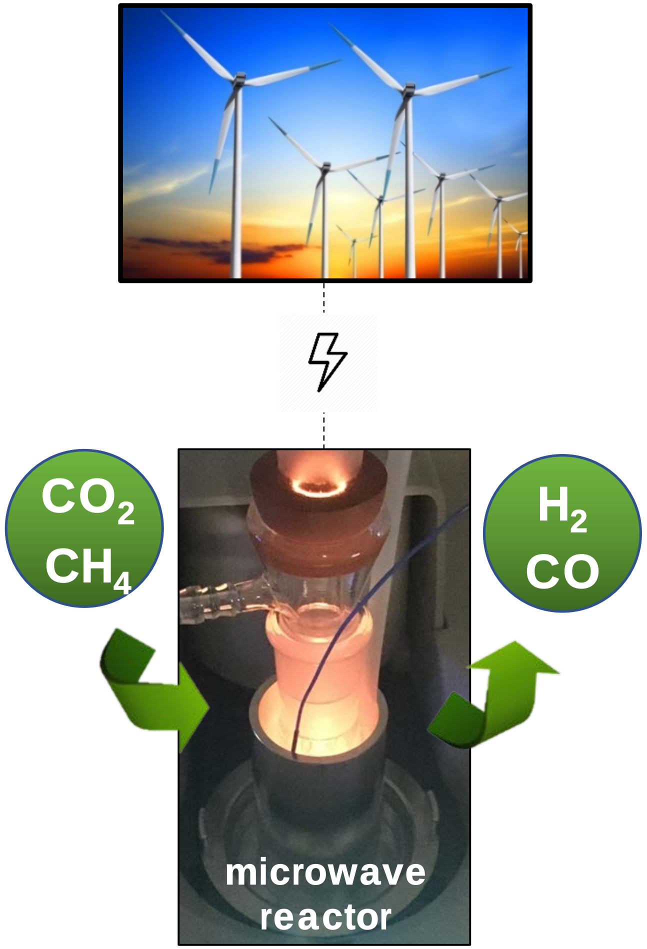




Traditional thermal DRM is extremely challenging due to high temperatures (700+ °C)

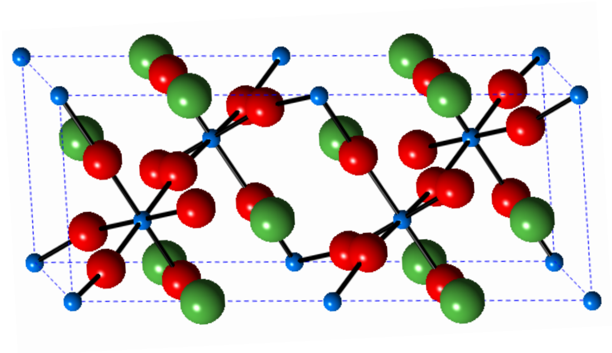
Our approach: microwave-active catalysts!

Leverages excess renewable (curtailed) electricity



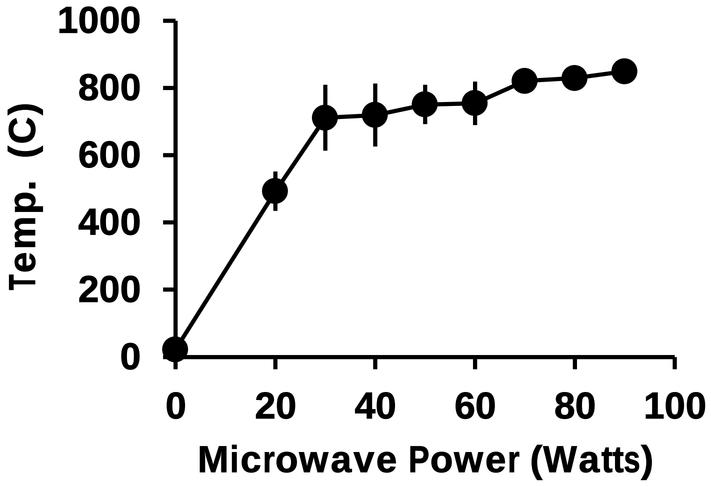
Tunable catalyst composition "LSC-M"

$La_{0.8}Sr_{0.2}Co_{0.9}M_{0.1}O_3$



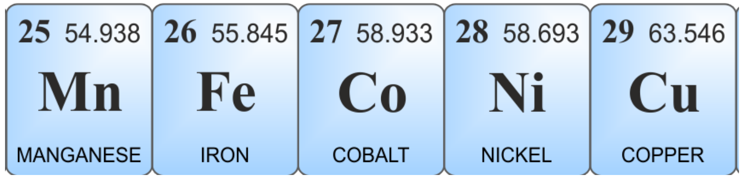
- La + Sr
- Cobalt and 10% dopant (Mn, Fe, Ni, Cu)
- Oxygen

Efficient Catalyst Heating



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

Doped LSC-M Catalysts



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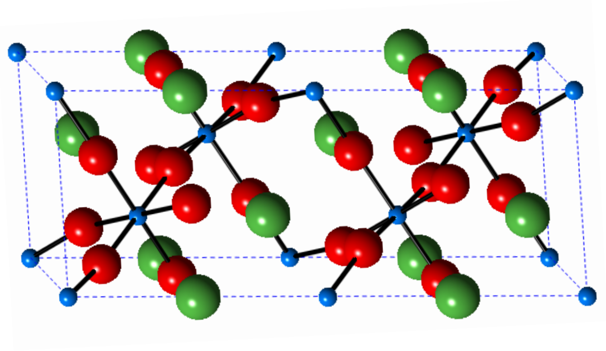
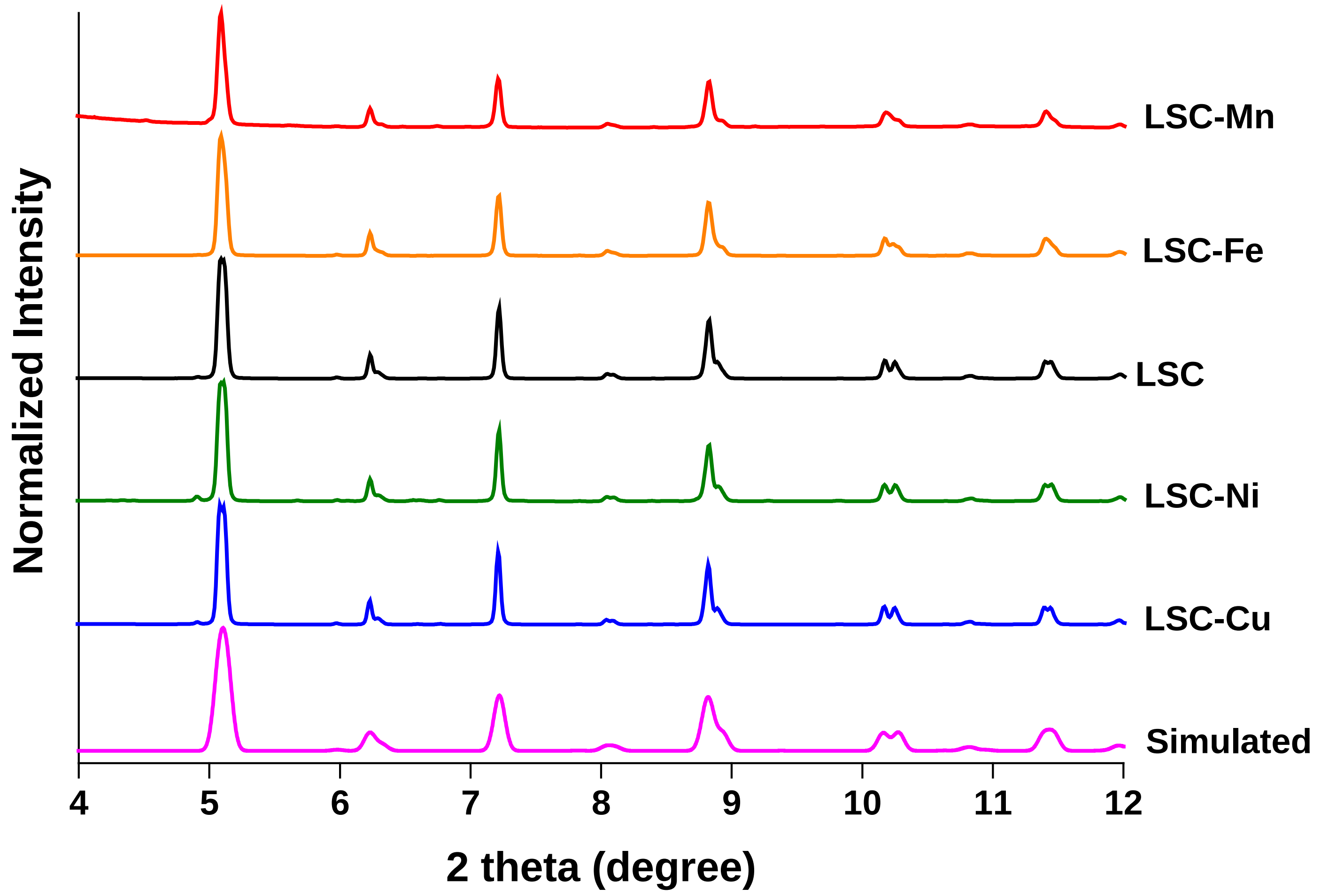


La + Sr

Cobalt and dopant (Mn, Fe, Ni, Cu; 10%)

Oxygen

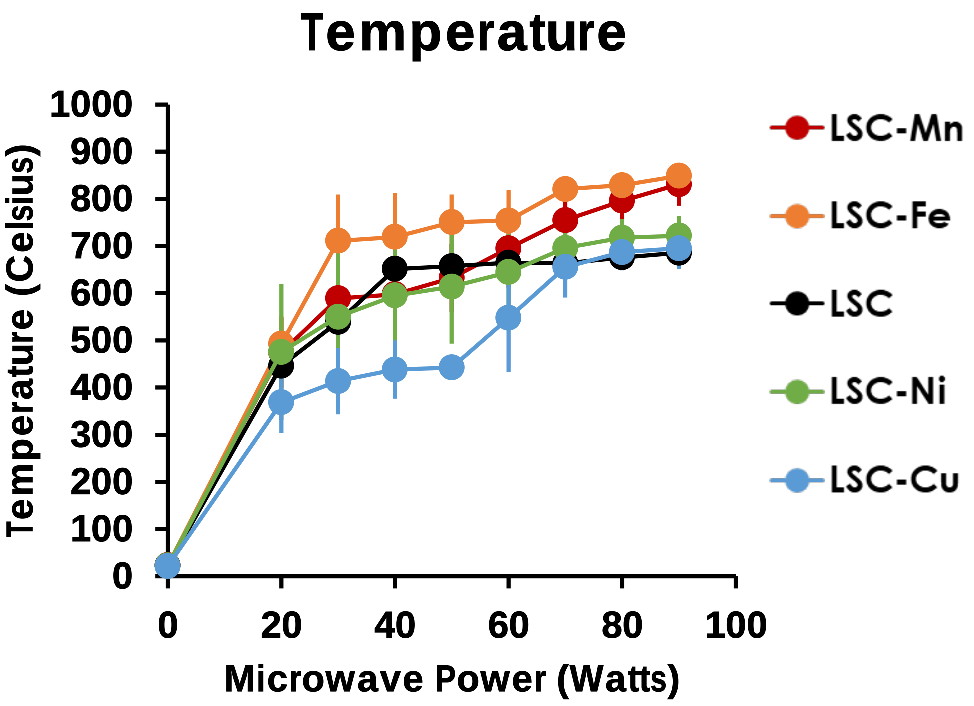


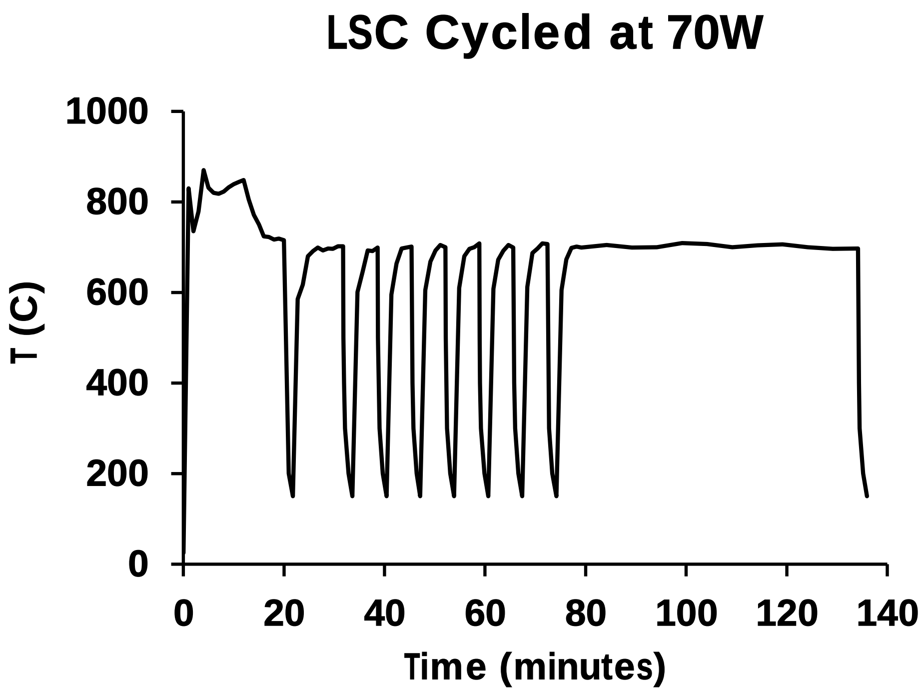
*No evidence of significant dopant segregation

λ = 0.24136 Å (51.4 keV); APS 17-BM-B

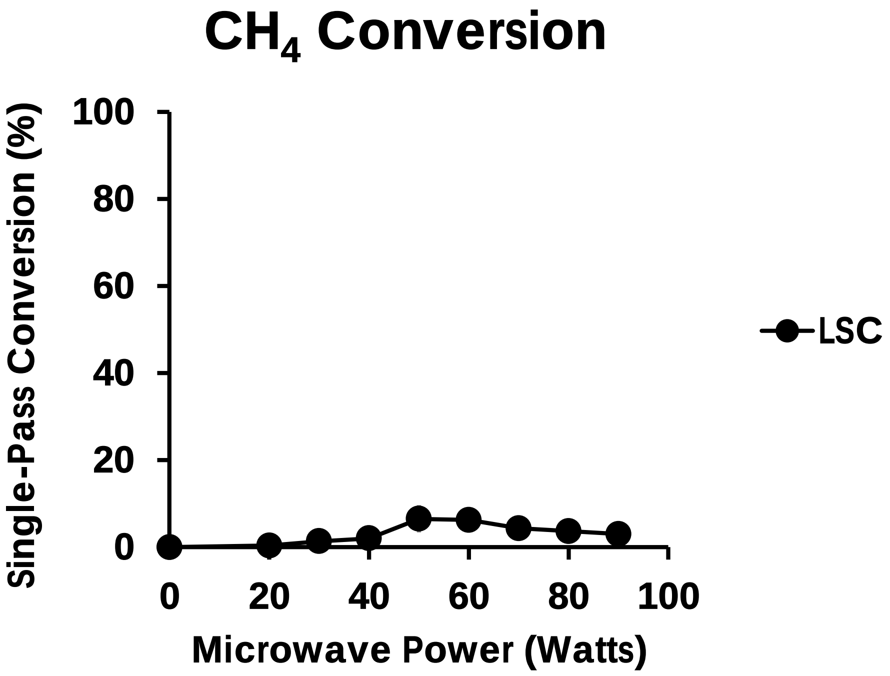
Microwave-assisted heating

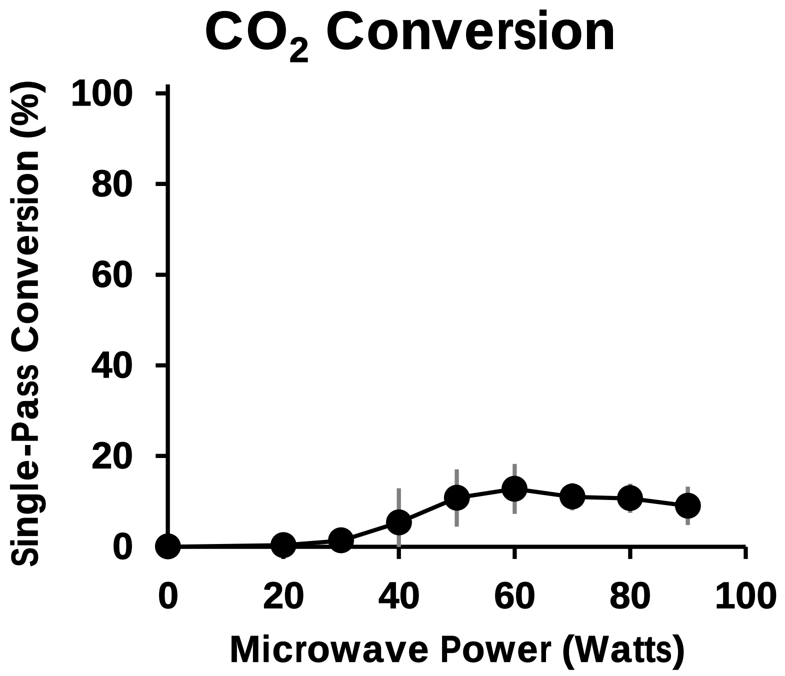
All catalyst show microwave heating & rapid on-off cycling (200-300°C / min)





Dopant control MW-DRM activity





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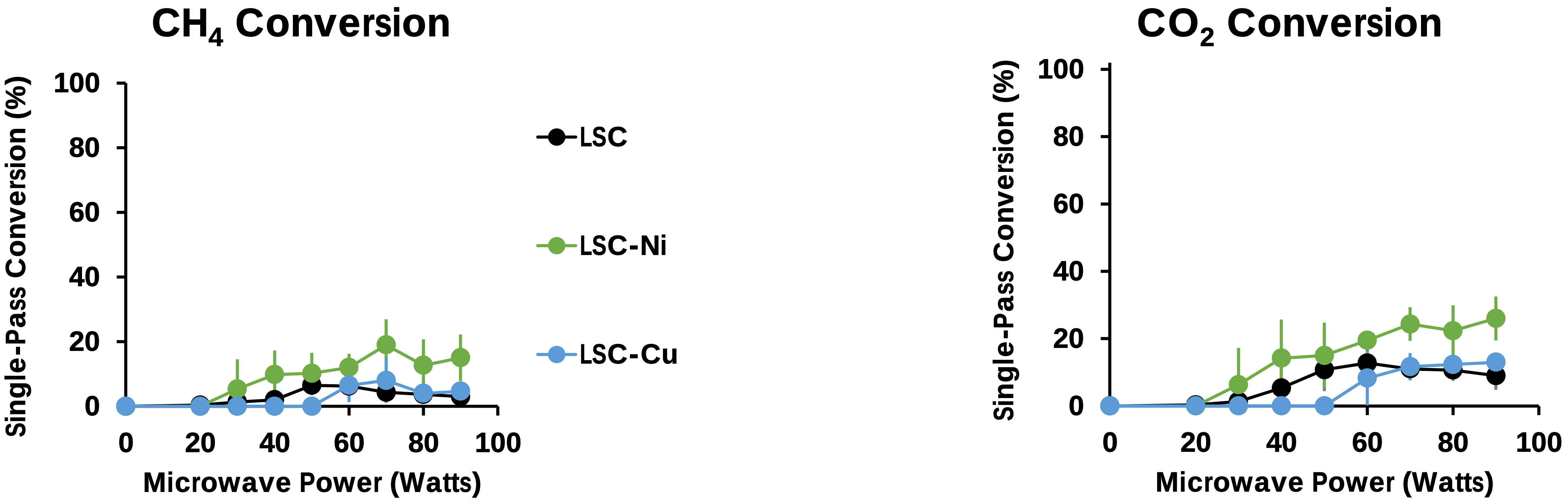
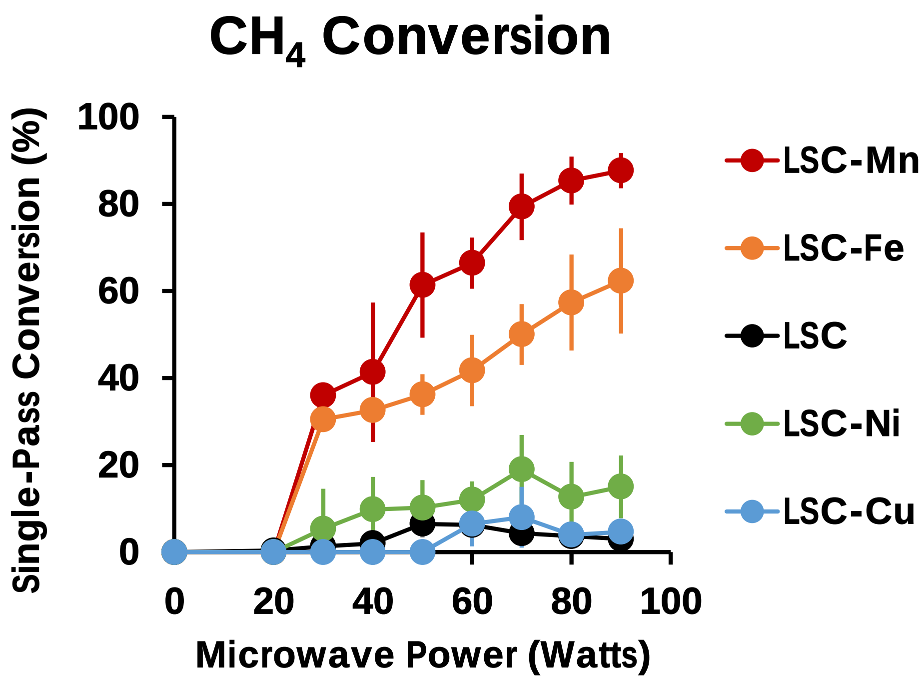
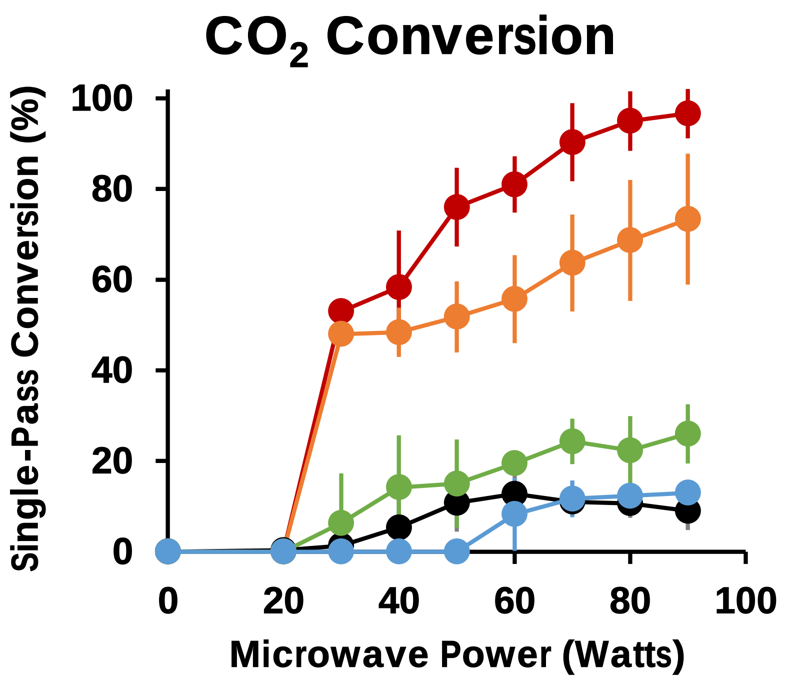


Dopant control MW-DRM activity

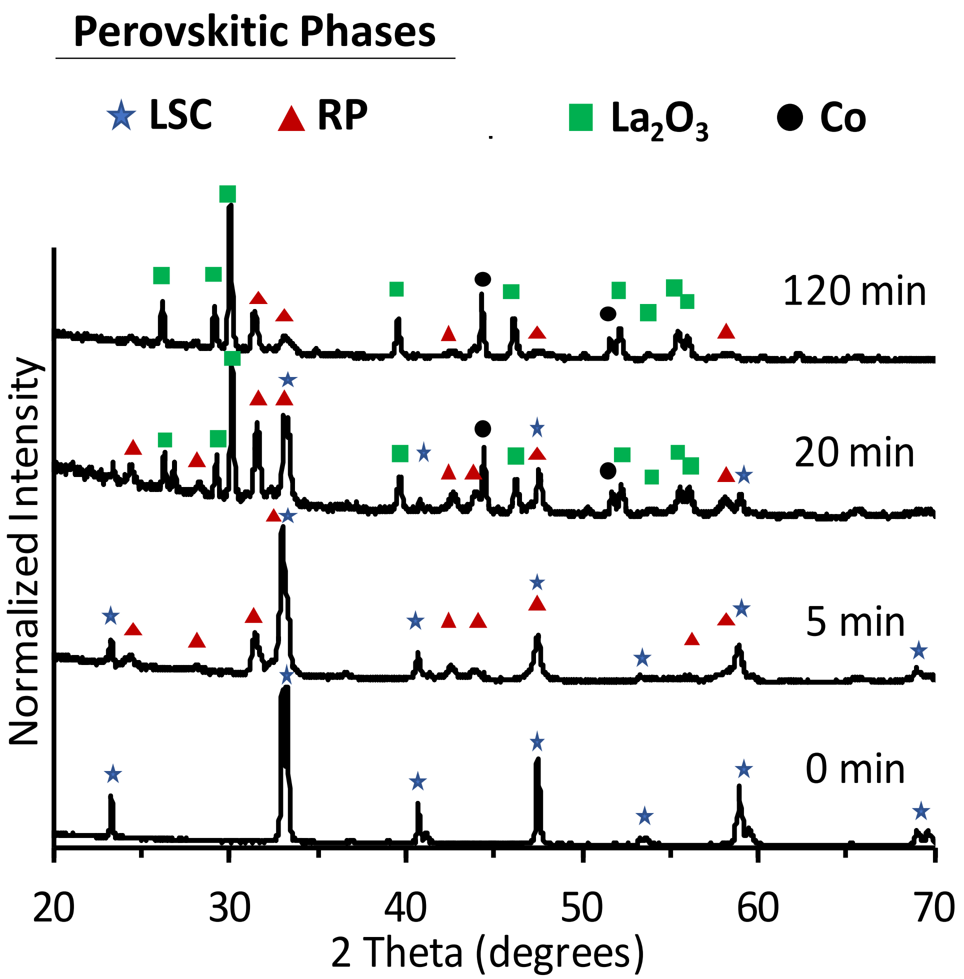
Mn and Fe dopants drastically improve DRM conversion rates





** LSC-Mn: H_2/CO ratio: 0.92 ± 0.03 over 10 hours of operation @ 90W **

Monitoring *ex-situ* phase changes during MW-DRM

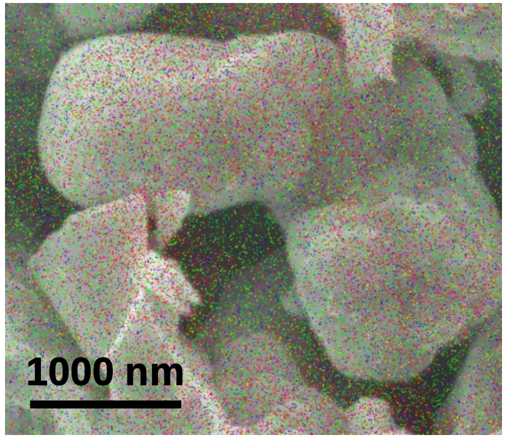


- **Undoped LSC initially forms Ruddelson-Popper perovskitic phase**
  (▲ RP: strong microwave absorber)

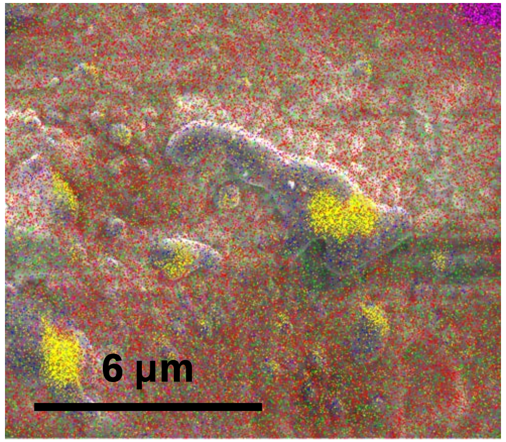
- **After continued reaction**
  - Significant loss of perovskitic phases
  - Formation of SrO_x, La_2O_3 and Co
  - Loss of MW absorptivity

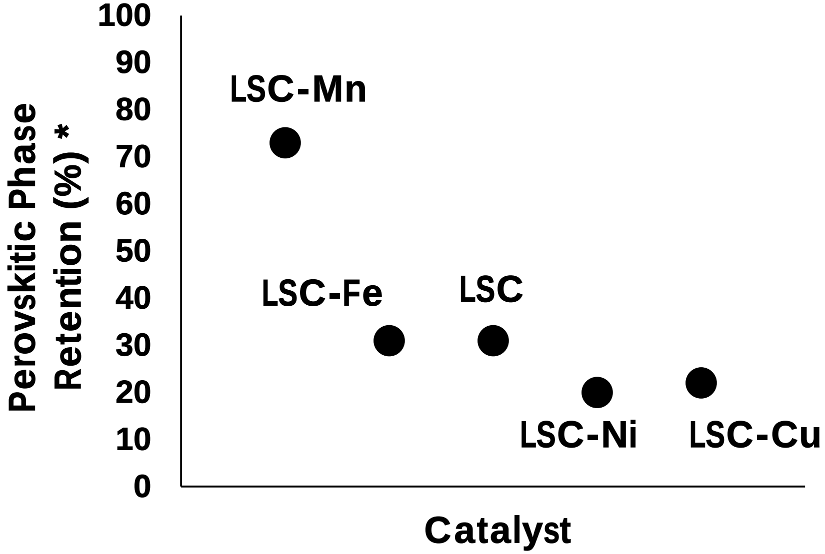
Relative Stability of doped LSC-M Catalysts

LSC-Mn



LSC-Cu

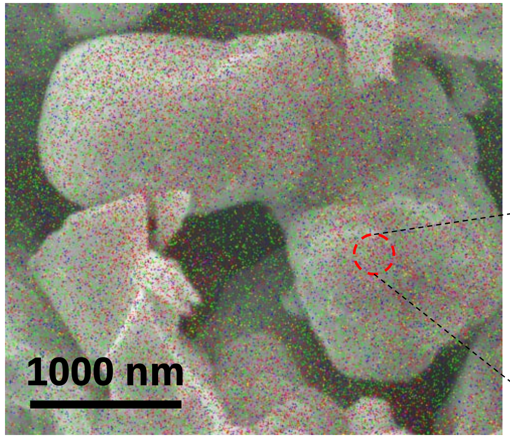




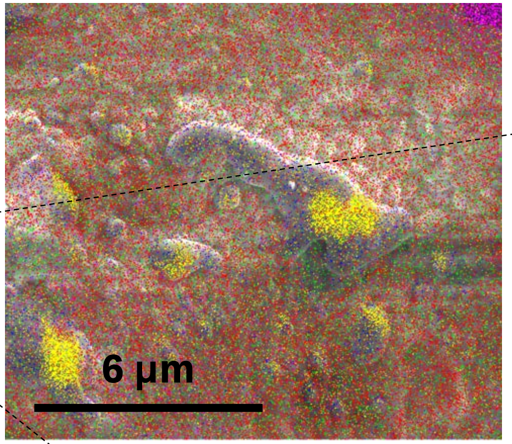
* From post-reaction XRD; LSC-M, RP, $La_4Co_3(M)O_{10}$

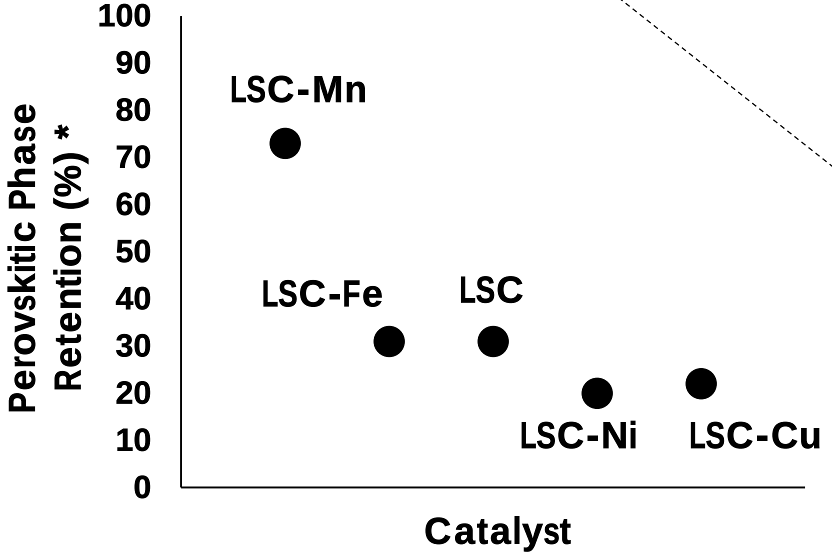
Relative Stability of doped LSC-M Catalysts

LSC-Mn

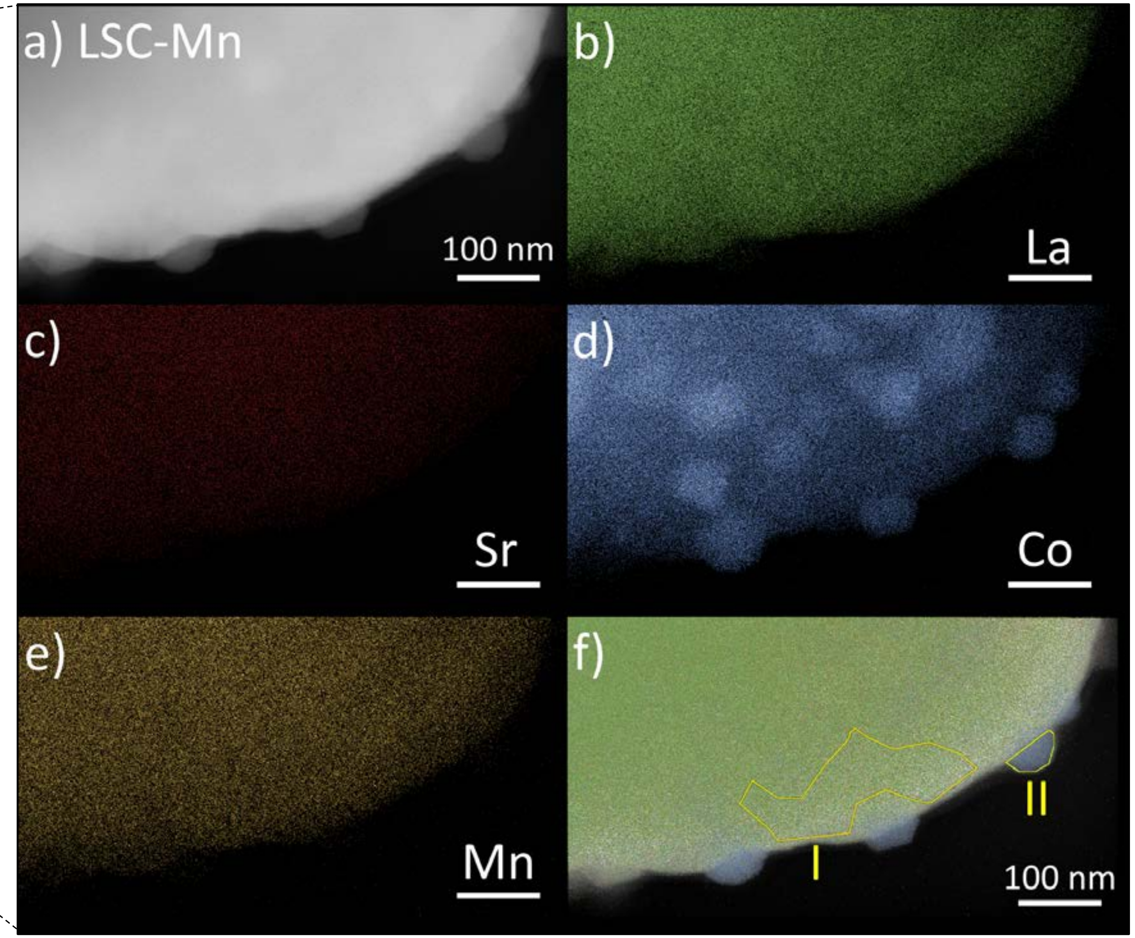


LSC-Cu





Formation of Small Co NPs on LSC-Mn

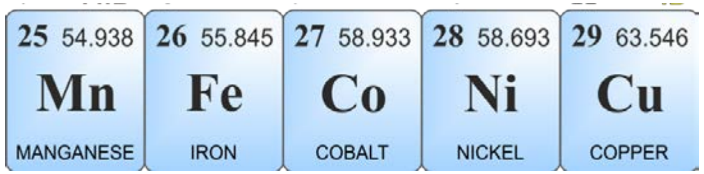


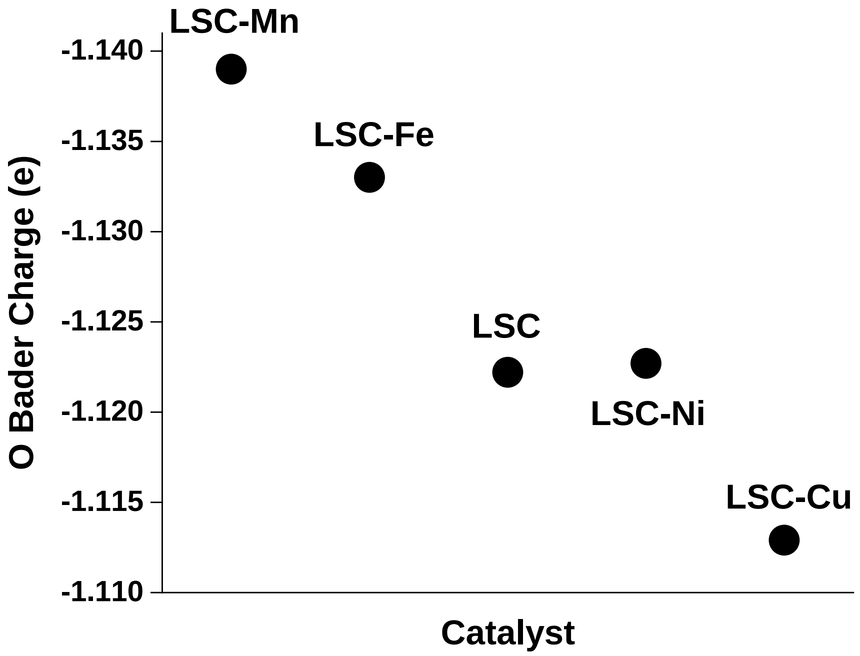
*From post-reaction XRD

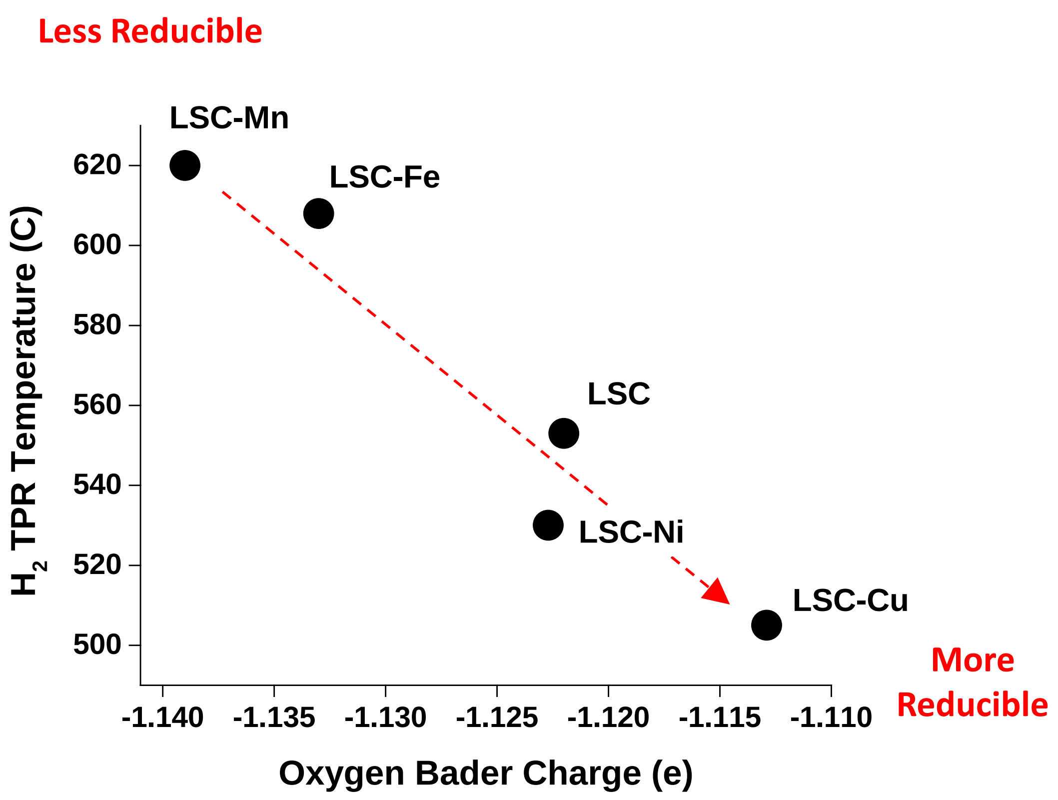
Understanding Catalyst Stability

Electropositive dopants increase Oxygen Bader charge (ionicity) and prevent catalyst reduction

Less Reducible → More Reducible

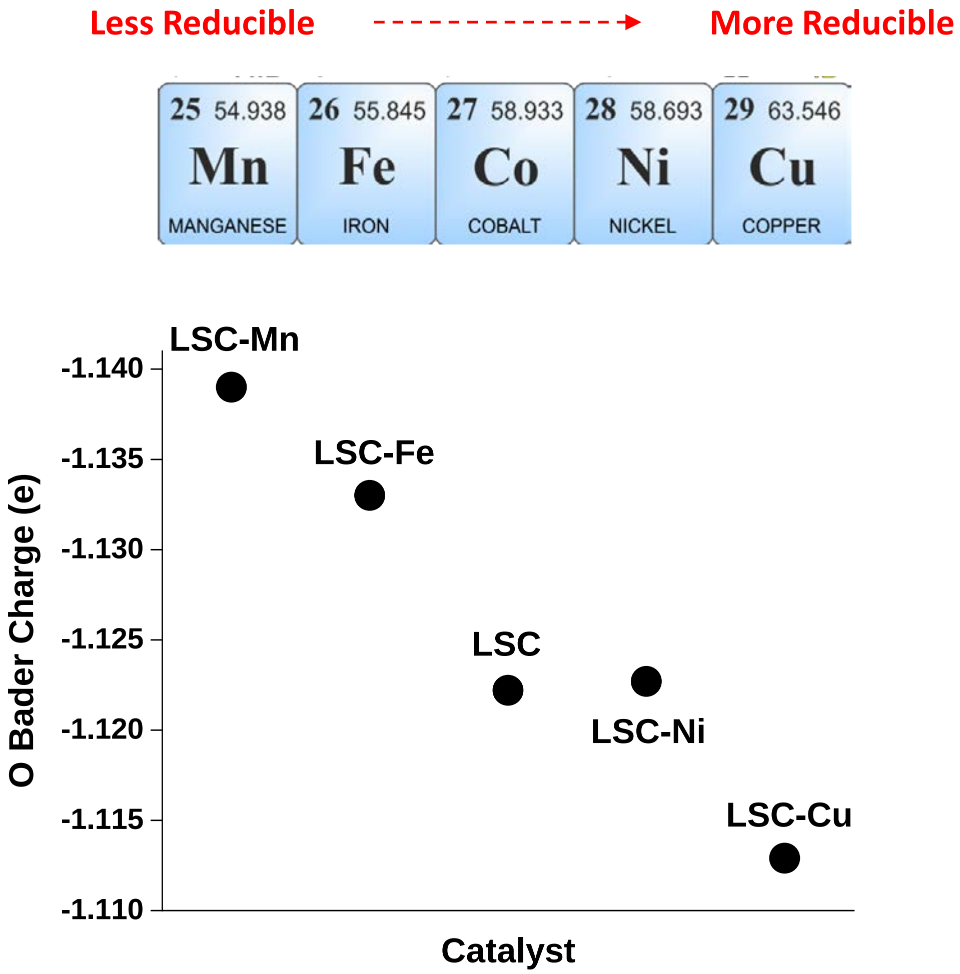


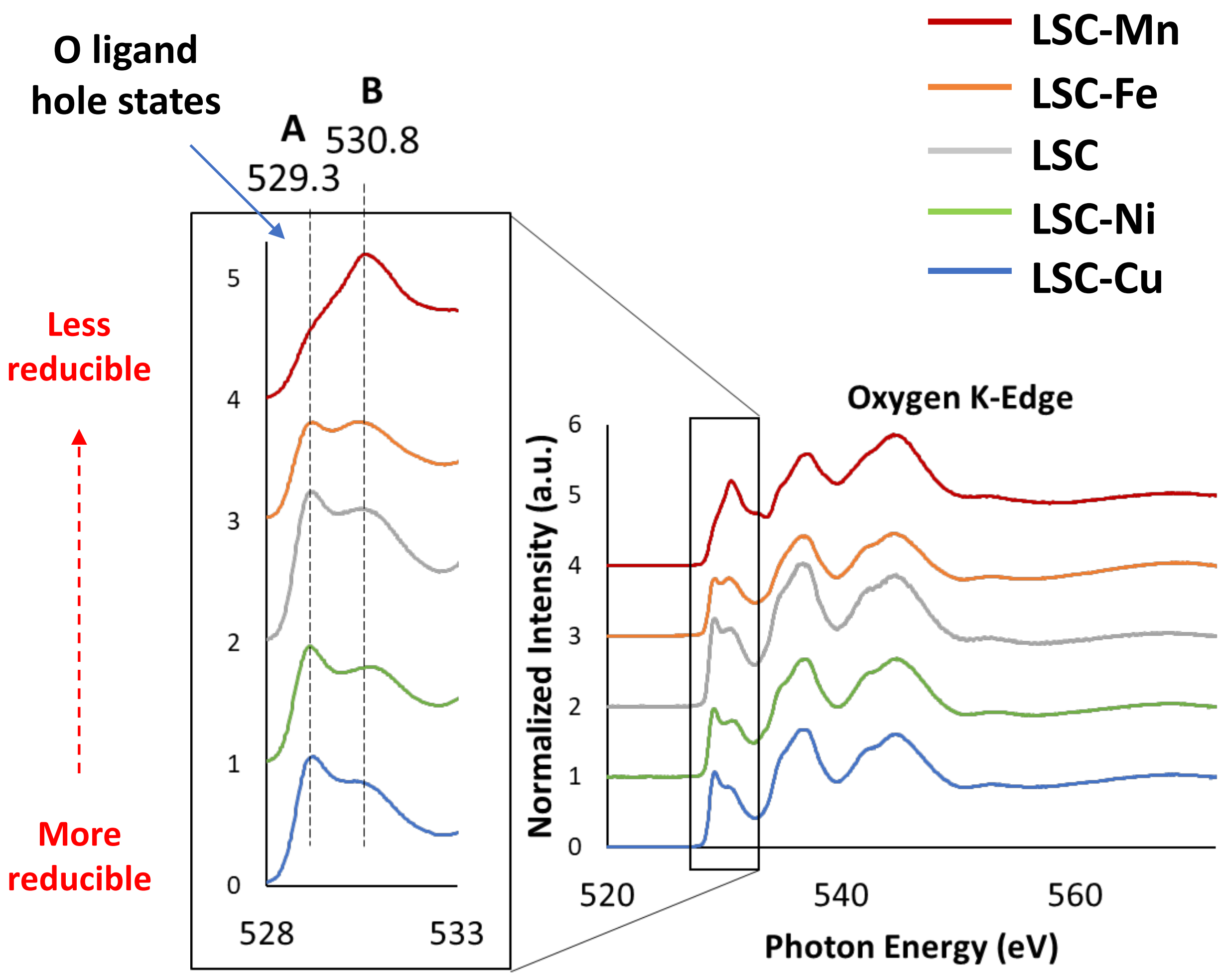




Understanding Catalyst Stability

Experimentally observed with electronic structure through O K-edge XAS



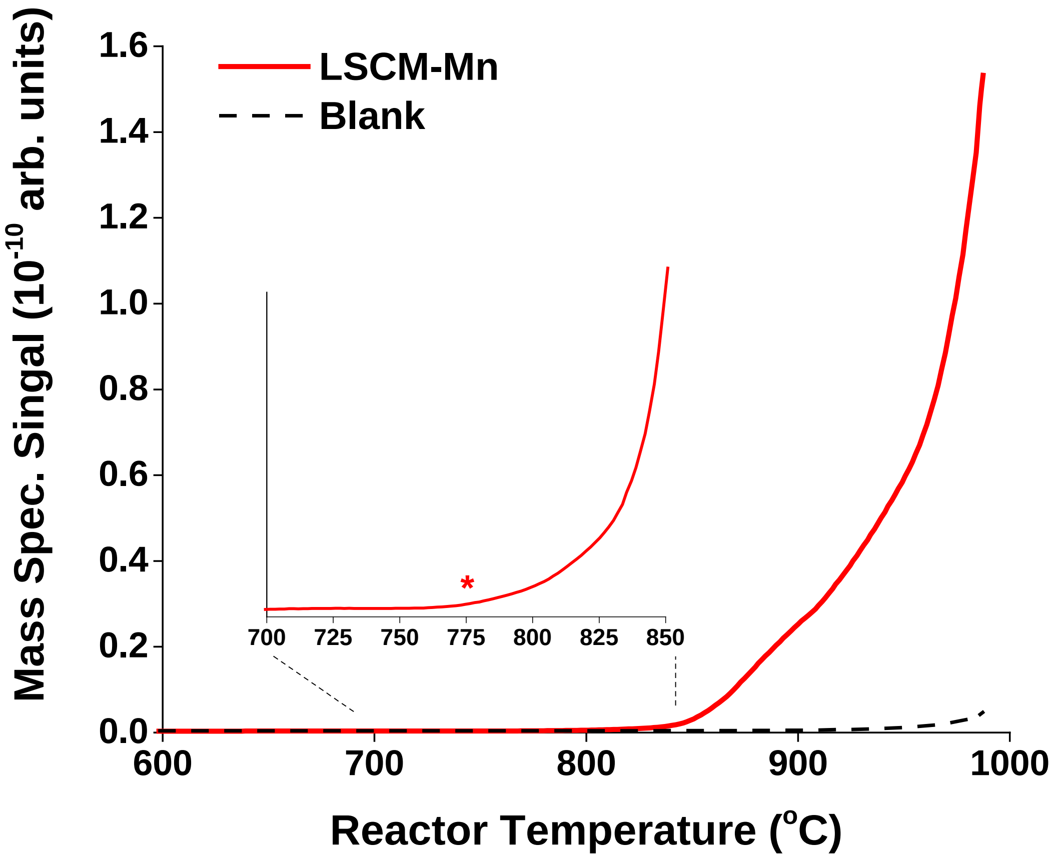


What are the catalytically active sites?

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

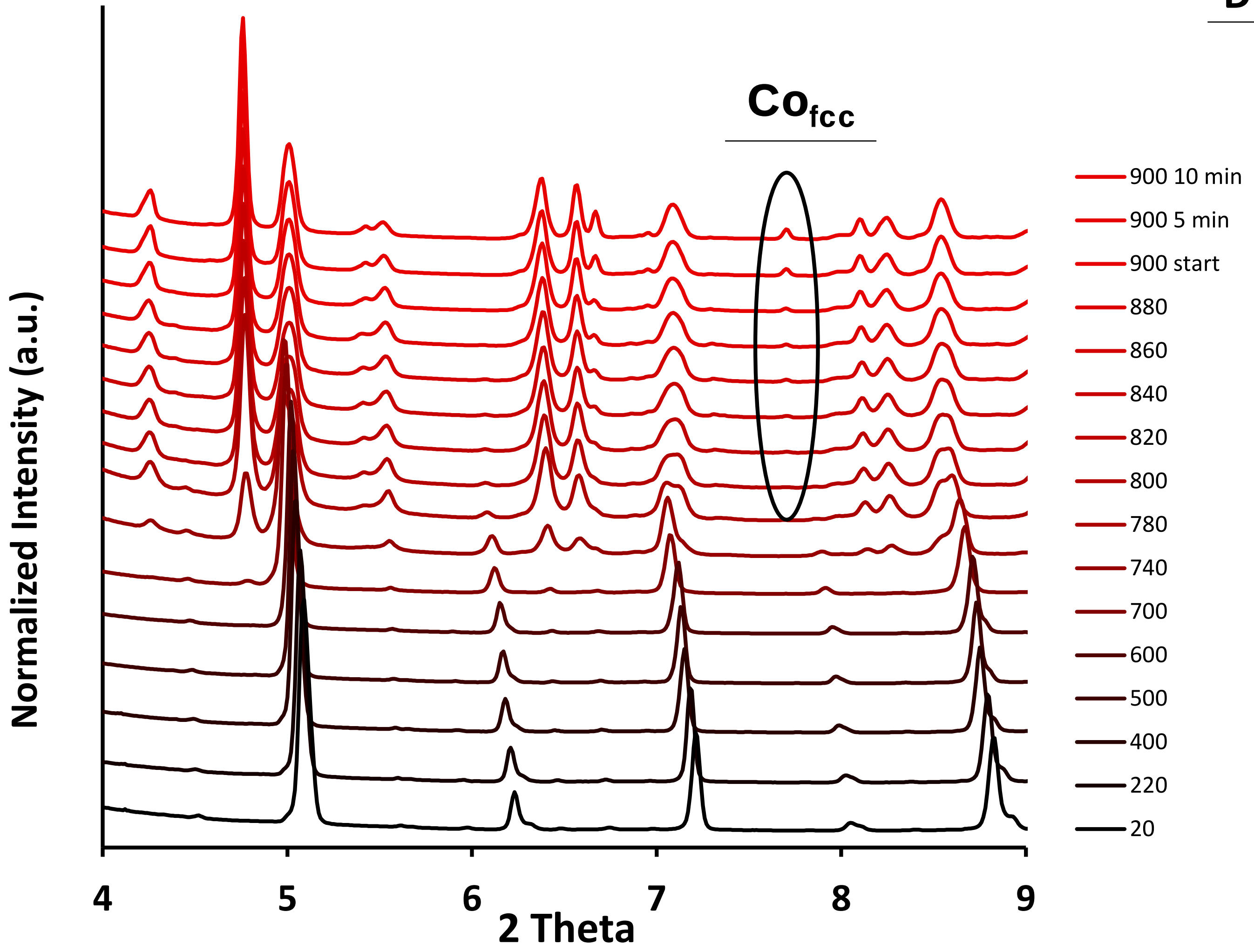
- ***Ex situ* studies reveal stability and phase changes *after* the reaction.**
- **Difficult to probe *in situ* changes within the microwave reactor.**
- **We have an optical measurement of catalyst temperature during MW DRM.**
- **Can we utilize thermal DRM to precisely monitor structure *vs* temperature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

Thermal DRM confirms reactivity of LSC-Mn

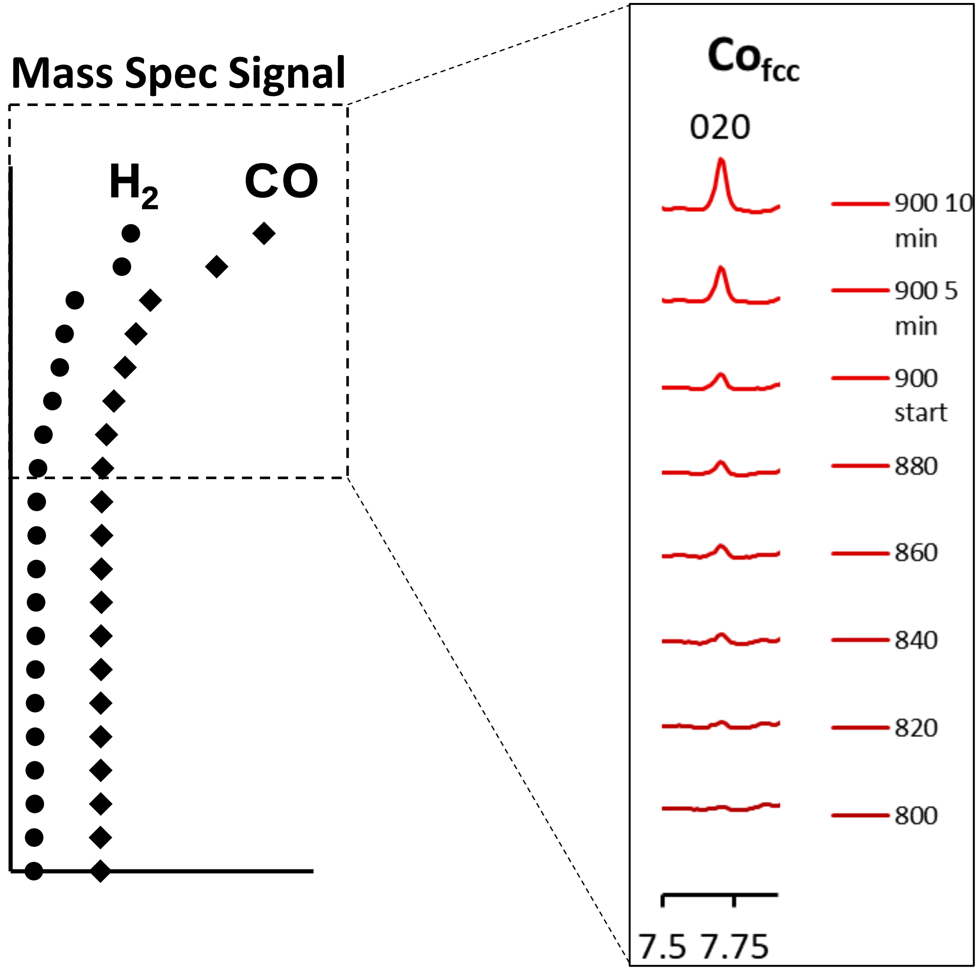


- **Thermal DRM starts around 775°C in traditional packed-bed, thermal reactor.**
- **Higher temperature than optically measured in MW reactor**
  - Optical measurement averaged over a 5mm spot on catalyst bed
  - We likely underestimated MW temperature due to formation of micro-scale hot-spots
- **Consistent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

In situ synchrotron XRD: active site identification



DRM Coincides w/ Co NP Formation



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

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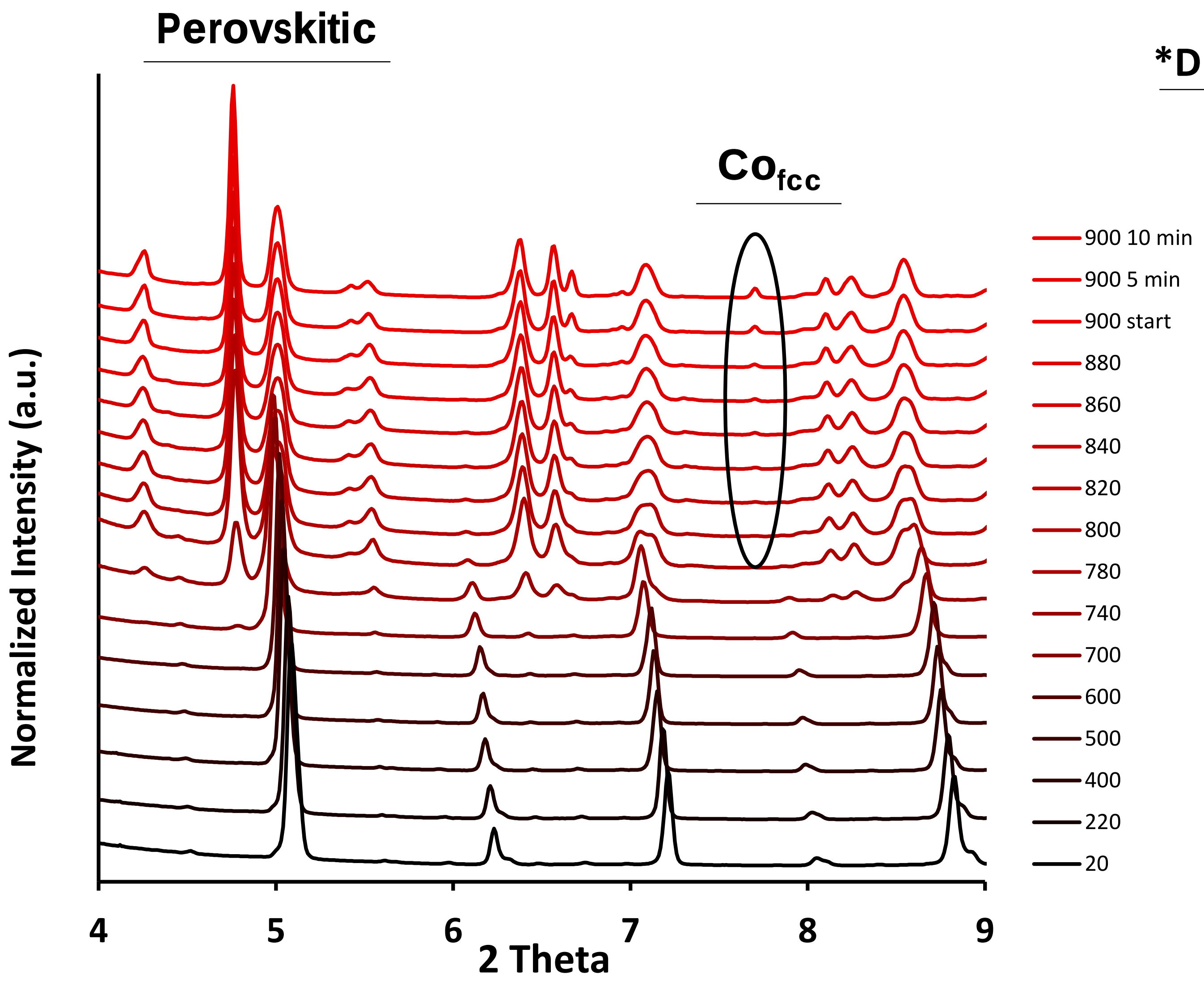

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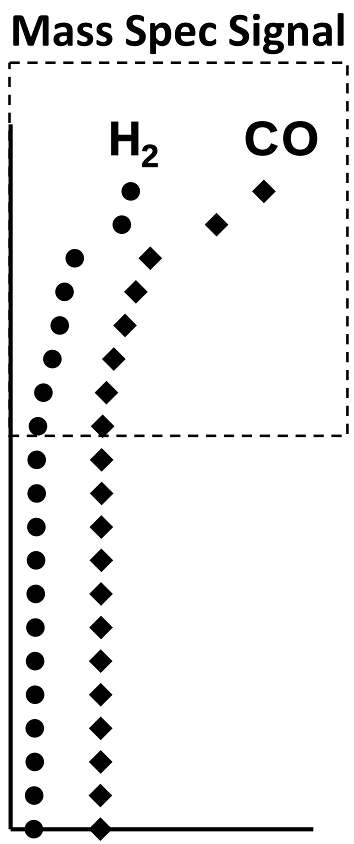
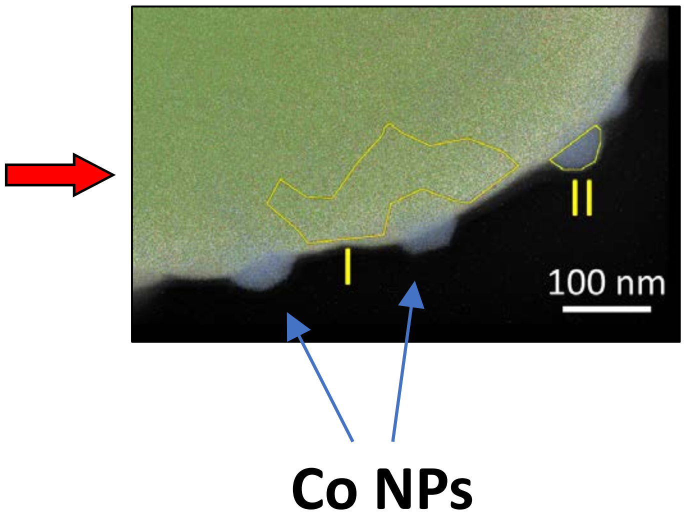
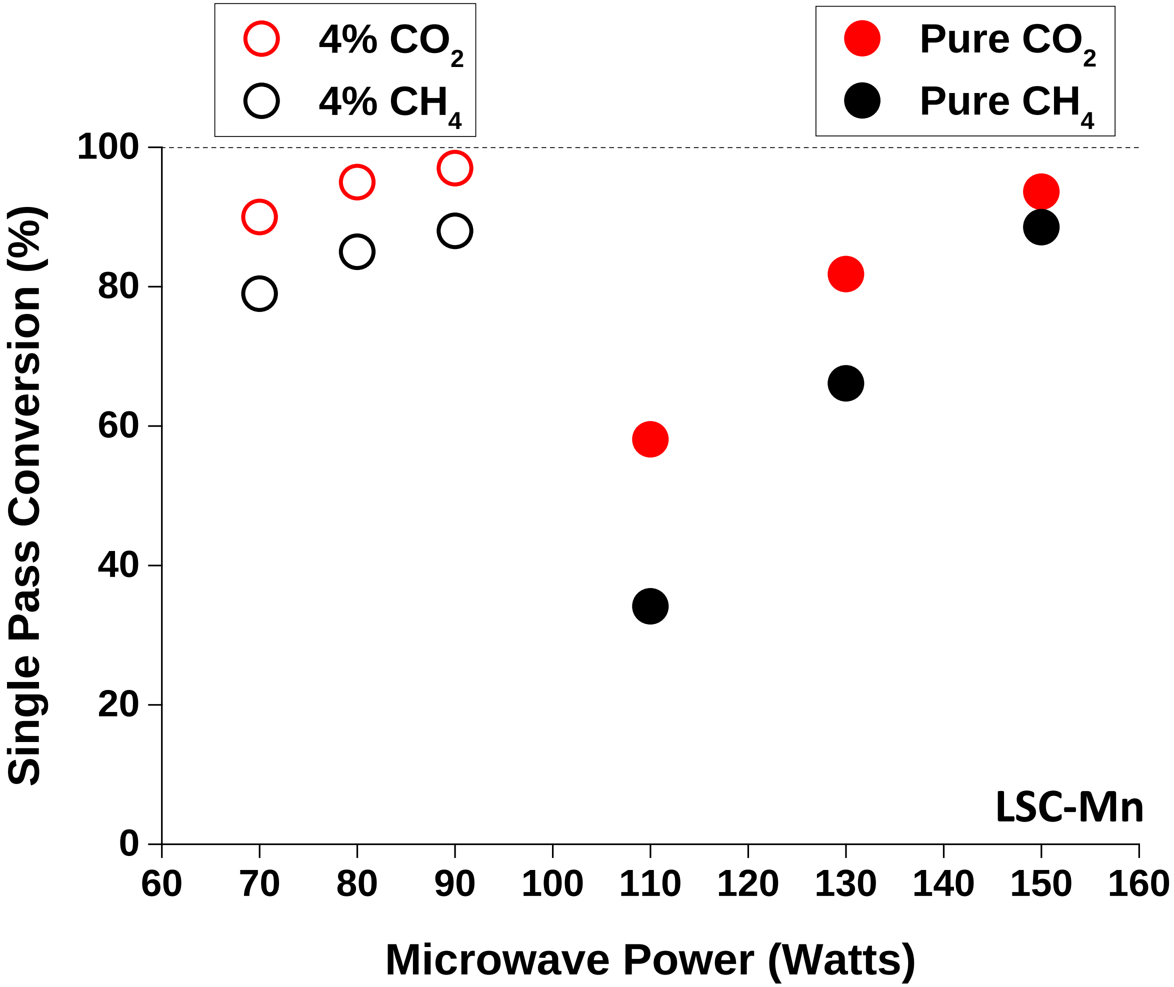




In situ **XRD with real-time product analysis excludes other potential active sites**

Moving forward: pure gas DRM with LSC-Mn



- **High single-pass conversion still possible with pure gases**
  - 100% CO_2 + 100% CH_4
- **Higher wattage required compared with dilute gases**

Extrapolated System Performance

Conventional methane steam reforming: ~30 kWhr/Kg H_2

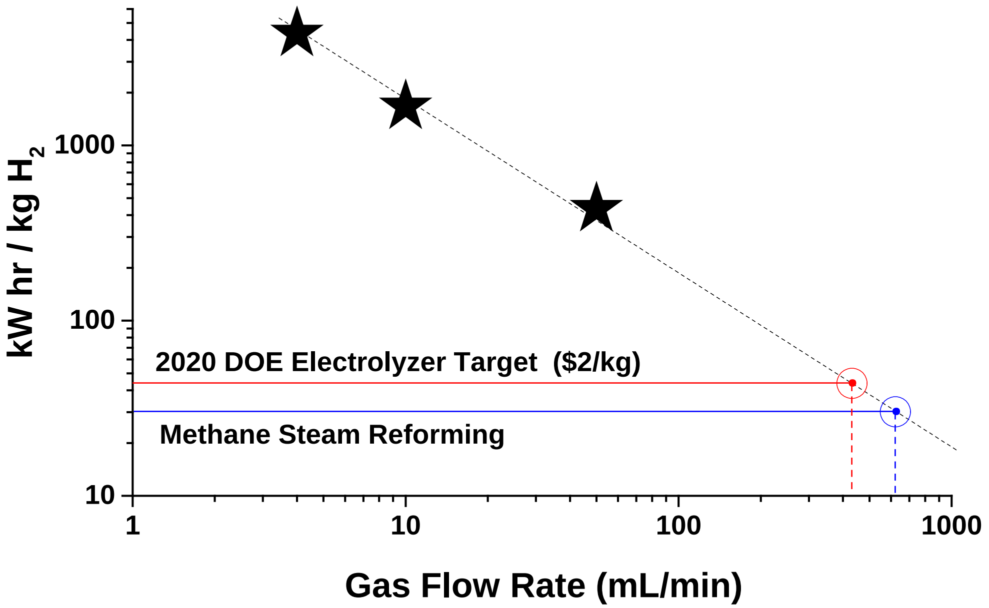
- Extremely carbon intensive: ~10 tonnes CO_2 / tonne H_2

2020 DOE (EERE FCTO) electrolyzer target: ~45 kWhr/Kg H_2 (\$2/kg H_2)

- Scaling studies with larger MW reactor

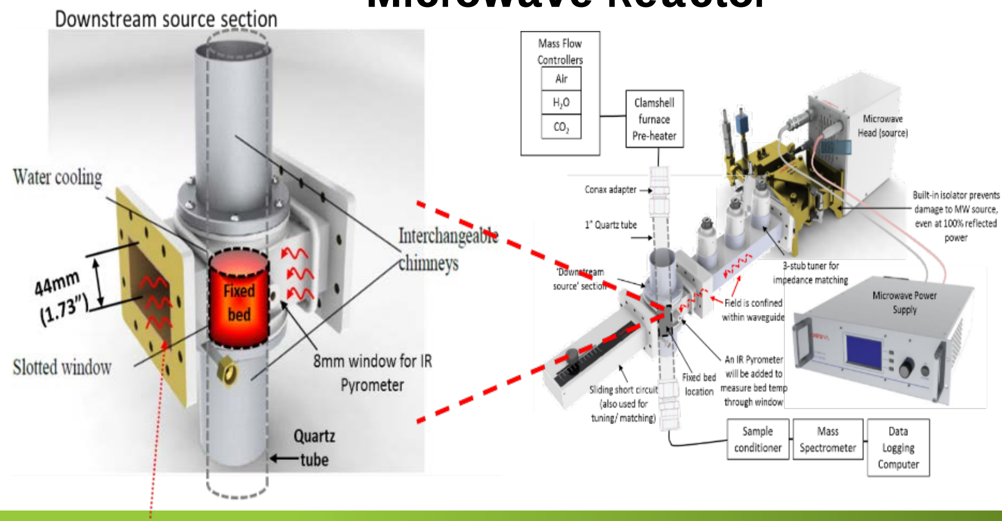
ReACT Facility

Reaction Activation and Chemical Transformation



Scaling Studies

Morgantown NETL Larger Scale Microwave 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**

Aknowledgements

NATIONAL ENERGY TECHNOLOGY LABORATORY

Microwave Studies (NETL): Christopher Marin

Computational Modeling (NETL): Dominic Alfonso & DeNyago Tafen

In situ XRD: Argonne APS line 17-BM-B; APS Staff Scientist: Wenqian Xu.

O K-edge XAS: Brookhaven NSLS-II line 23-ID-2; NSLS-II Staff Scientist: Ira Waluyo

Acknowledgement: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

Questions or Comments?

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Thank you for your attention!

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