C2C-1- POSTER #39

C2C Project 1
Poster #: 39

Novel perovskite oxide characterization and stability investigated via pulsed laser deposition of thin films

Luke H. Denoyer[1], Kannan P. Ramaiyan[1], Diego Lopez[2] , Angelica Benavidez[1], Andre S. Ferlauto[2], Fabio Coral Fonseca[3], Fernando H. Garzon[1]
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[2]Universidaded do Federal do ABC
[3]Universidade de São Paolo - IPEN

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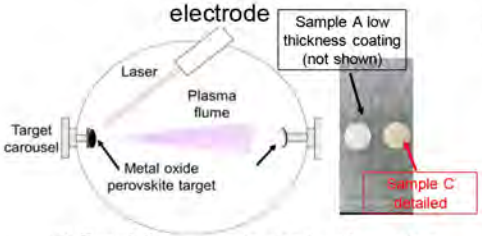
NSF Engineering Research Center
Center for Innovative and Strategic Transformation of Alkane Resources

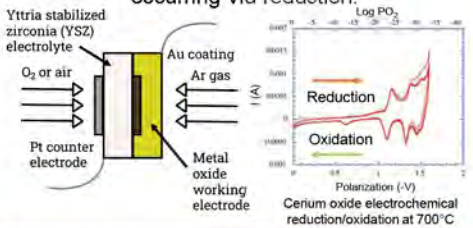
GOALS

Develop and characterize thin films for use in electrochemical stability setup:

1) Pulsed laser deposition of novel $BaCa_{0.33}Nb_{0.42}Fe_{0.25}O_{3-\delta}$ (BCNF25) electrode



2) Providing more in-depth information on electrode degradation pathways occurring via reduction.



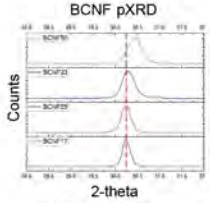
Cerium oxide electrochemical reduction/oxidation at 700°C

Electrochemical stability measurements featuring novel perovskite anode materials allow for precise gas environment control and redox stability probing.

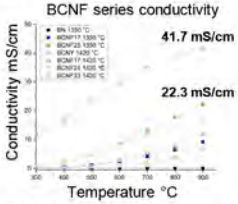
Bulk BCNF properties

$BaCa_{0.33}Nb_{0.67-x}Fe_xO_{3-\delta}$ (BCNF)

BCNF pXRD



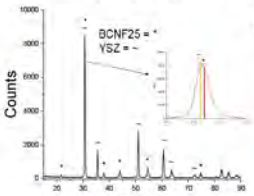
BCNF series conductivity



Pulsed laser deposition Parameters

ID	Substrate	Target	T(°C)	PO2 (mbar)	Tension (kV)	Freq (Hz)	Energy (mJ)	Fluence (J/Cm^2)	Distance to substrate (mm)	Time (min)
C	YSZ	BCNF25	700	1.00E-02	21.5	10	50	2.012	60	180
D	SiO_2	BCNF25	750	1.00E-03	27.0	10	50	2.000	47	120

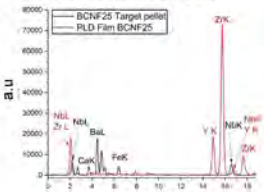
Grazing incidence XRD



Improved resolution for BCNF peaks via 4° theta angle fixed source

XRF/AFM thickness monitoring

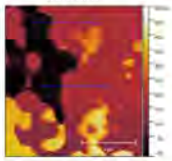
X-ray fluorescence for composition and film thickness **sample C** and BCNF25 standard pellet

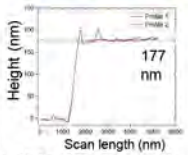


Orbis™ coating builder XRF estimate for film thickness

LD08 vs.Standard	9%	RIR
Estimate	0.431	film/standard
Thickness estimate	215.6	nm

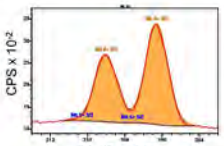
Atomic force microscopy ~~sample D~~ done to elucidate roughness and thickness of thin film



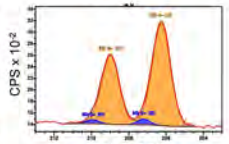


Niobium and iron XPS on thin film sample

BCNF25 Standard



Sample C thin film



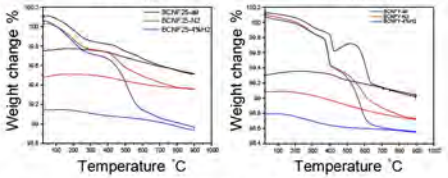
Sample	Nb 4+ % composition	Nb 5+ % composition
BCNF25 Standard	99.37	0.63
Sample C Thin Film	96.26	3.74

OUTCOMES

C2C

- Pulsed laser deposition for thin films
- New testing methodology for metal oxide perovskite stability and oxygen coordination
- Successfully formed thin films on yttria stabilized zirconia substrate

$BCNF_{25}$ $BCNF_{20}Y_{13}$



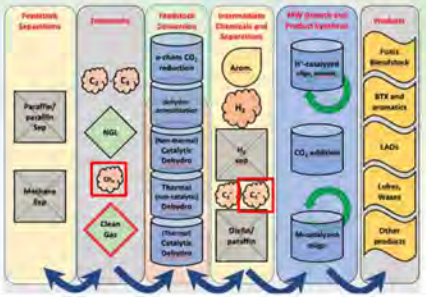
TGA of BCNF25 versus yttria doped sample

Can use high temperature electrochemical voltammetry testing to supplement and extend findings from thermogravimetric analysis (TGA).

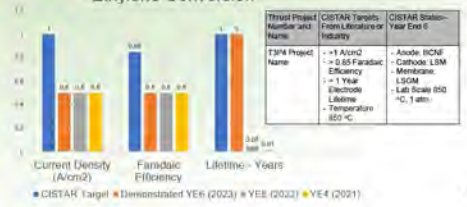
IP & INNOVATION

- IP includes perovskites with co-doped Mg/Ca and Fe.
- Chemical formula $BaMNb_{0.67-x}Fe_xO_{3-\delta}$
- M = Mg or Ca
- These materials have stable lattice configurations both before and after methane treatment.

SYSTEM DESIGN & BENCHMARKS



T3P4 Electrochemical Methane to Ethylene Conversion



Thrust Project Number and Name	CISTAR Targets From Literature or Industry	CISTAR Status- Year End 6
T3P4 Project Name	- >1 A/cm2 - > 0.65 Faradaic Efficiency - > 1 Year Electrode Lifetime - Temperature 850 °C	- Anode: BCNF - Cathode: LSM - Membrane: LSGM - Lab Scale 850 °C, 1 atm

IMPACT & FUTURE

- Examine novel perovskite reduction pathways under various partial pressures.
- Screening for next generation of E-OCM catalysts

1) Denoyer, L. H., Benavidez, A., Garzon, F. H., Ramaiyan, K. P. Highly Stable Doped Barium Niobate Based Electrocatalysts for Effective Electrochemical Coupling of Methane to Ethylene. *Advanced Materials Interfaces* **2022**, *9* (27), 2200796. https://doi.org/10.1002/admi.202200796.
2) Denoyer, L. H.; Benavidez, A.; Garzon, F. H.; Ramaiyan, K. P. Chemical Stability of $BaMg_{0.67}Nb_{0.67}Fe_xO_{3-\delta}$ in High Temperature Methane Environments [Under revision, *Energy and Fuels*, September 2023]

This paper/poster is based upon work supported primarily OR in part by the National Science Foundation under Cooperative Agreement No. EEC-1647722. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

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C2C-3 - POSTER #40

C2C
Poster #40

Investigation of Pt_3Mn Surface Structures for Propane Dehydrogenation Using A Cluster Expansion Approach

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[2]São Carlos Institute of Chemistry, University of São Paulo

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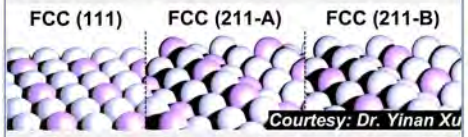
GOALS

Pt_3Mn was found to be a promising **catalyst candidate** for non-oxidative **propane dehydrogenation** reaction

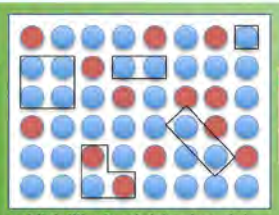
Wu et al., *JACS, 2018*

Bulk-terminated Pt_3Mn surfaces have **uniform distribution of Mn atoms**



- However, **Mn** can have preferential or non-preferential **distribution** to **the edge** and/or **the corner sites**
- There can be **segregation, islanding,** and/or **site isolation** by Mn atoms on the catalyst surface
- Previous studies showed that **PDH reactivity** can be sensitive to the **local ordering** of Pt and Mn atoms

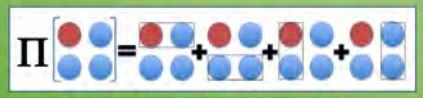
- **DFT-based screening** of surface structures become **non-tractable** due to too many arrangements
- A **faster and accurate method** is needed for **structure screening**
- Previous DFT calculations suggest activity and selectivity **descriptors** for PDH on bulk-terminated **smooth and step** Pt_3Mn surfaces
- Descriptors can be used to rapidly estimate **catalytic activity and selectivity** on the catalyst surface



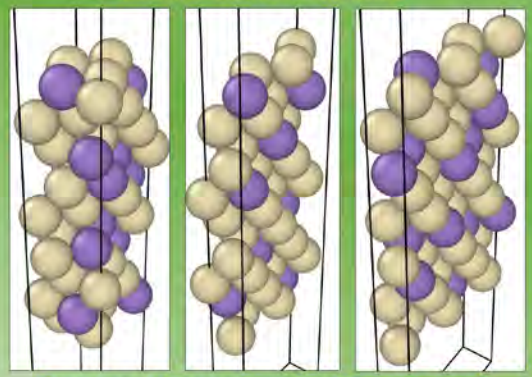
publish.illinois.edu/atomicscale/

Cluster Expansion Hamiltonian:

$$H(\sigma) = J_0 + \sum_{all\ clusters\ f} J_f \prod(\sigma)_f$$

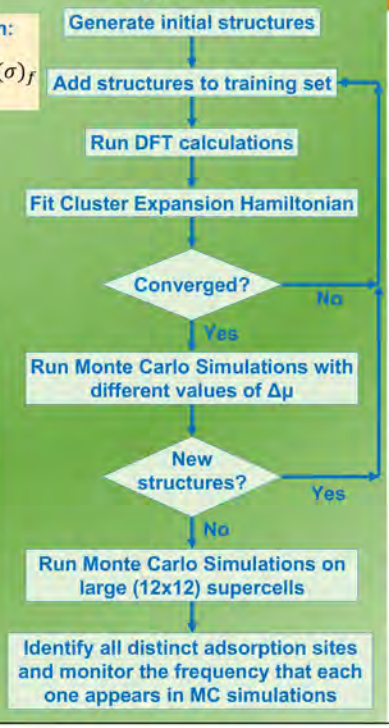


Example of cluster expansion

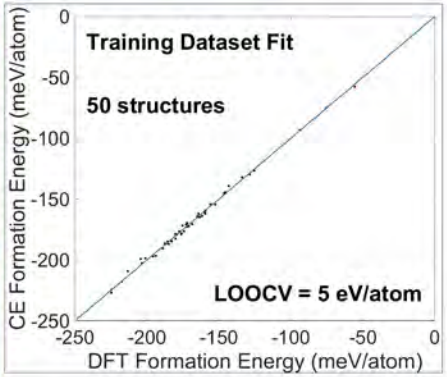


Sample Pt_3Mn Slabs from the Training Dataset

Algorithm



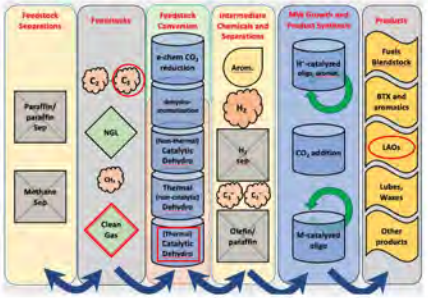
OUTCOMES



In the training dataset, **Mn atoms** with **anti-ferromagnetic** spin distributions show **higher thermodynamic stability** than their ferromagnetic spin configurations

1st round of *simulated annealing* generates Pt_3Mn surface slab structures with **clustered Mn atoms**

SYSTEM DESIGN



IMPACT & FUTURE

- Low energy surface configurations identified from the Monte Carlo simulations will lead to an understanding of **an average surface site ensemble**
- This study will elucidate how the nature of the **surface site distribution influences the overall reaction** as a function of the reaction conditions

Acknowledgments

Dr. Tim Mueller, Dr. Yinan Xu

Internship Candidate

This paper/poster is based upon work supported **primarily** by the National Science Foundation under Cooperative Agreement No. EEC-1647722.
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C2C-5 - POSTER #41

C2C-5
Poster #: 41

High Pressure Gas Separation Technology for the Removal of CO_2 from Natural Gas

Mariam Y. Balogun[1], Leonardo Hadlich de Oliveira[2], Cláudio Oller do Nascimento[2], Rita Maria de Brito Alves[2], Benny D. Freeman[1], Joan F. Brennecke[1]
[1]Department of Chemical Engineering, University of Texas at Austin
[2]Department of Chemical Engineering, University of São Paulo

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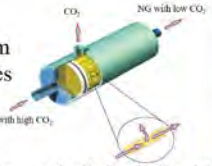
GOALS

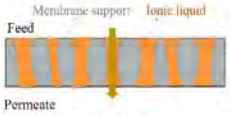
Background

- Natural Gas is a less carbon intensive fuel compared to coal and oil
- CO_2 concentration (10 – 80 mol %) largely depends on the source of extraction
- Pressures 130 – 500 bar

Research Goal

- Remove CO_2 directly from source under high pressures





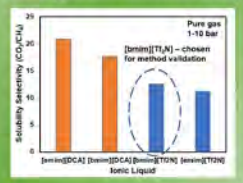
- Non- volatile ionic liquids
- Non-selective polymeric membrane support
- Solution-Diffusion Mechanism

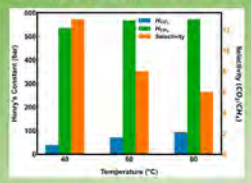
Research Aims

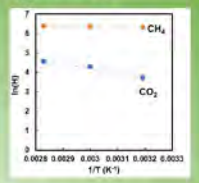
- **Aim 1**: Ionic Liquid (IL) development and testing
- **Aim 2:** Supported Ionic Liquid Membrane (SILM) development and testing

MAIN FINDINGS

- Pure gas solubilities in [bmim][Tf_2N] (Gravimetric Apparatus)

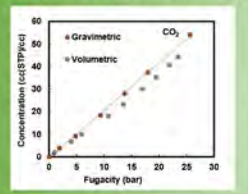


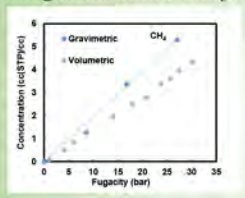




Gases	ΔH_{ab} (kJ/mol)
CO_2	-17.9 ± 0.3
CH_4	-1.5 ± 0.03

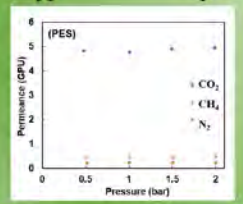
- Mixed Gas Solubilities: Pure gas solubilities in [bmim][Tf_2N] (Volumetric Apparatus)

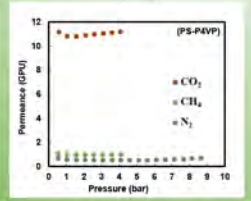




- Solubility – selectivity (CO_2/CH_4) ~ 12

- Supported Ionic Liquid Membranes (Asymmetric VS Isoporous Membranes Support)





- Perm – selectivity (CO_2/CH_4) ~ 11
  (CO_2/N_2) ~ 21
  [bmim][Tf_2N]

OUTCOMES

Conclusions

- Methane has weak interactions with ionic liquids from low enthalpy of absorption and temperature independent
- In – house built mixed gas sorption analyzer has pure gas measurement capability
- High pressure stability is observed with Isoporous SILMs while maintaining desired selectivity

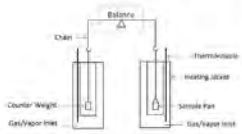
Future Work

- Measure mixed gas solubilities at these composition ratios 25:75, 50:50, 10:90 for CO_2/CH_4 separations
- Mixed gas solubilities will be performed at pressures up to 30 bar and temperatures from 40 – 80 °C
- Explore poly (ionic - liquids) for higher pressure stability

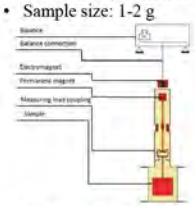
C2C COLLABORATION

Brennecke Research Group

Gravimetric Microbalance
- Xemis (Hiden Ischema)
- Sample size: 50 – 80 mg



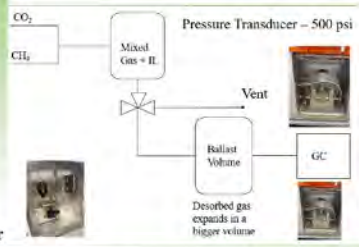
Magnetic Suspension Balance
- Rubotherm (TA Instruments)
- Sample size: 1-2 g



Temperature and pressure ranges from 0 - 150 °C and 0 - 150 bar

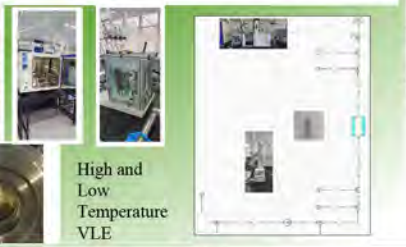
SYSTEM DESIGN & BENCHMARKS

Brennecke Research Group
Mixed Gas Solubility Apparatus



Oller Research Group
High Pressure Variable Volume Cell

Oller Research Group
High Pressure Absorption Column



High and Low Temperature VLE

IMPACT & FUTURE

- Students exchange will be facilitated between the research groups
- Leonardo from USP will visit UT Austin (March 2024 – September 2024)
- Mariam from UT Austin will visit USP (September 2024 – December 2024)

Leonardo Oliveira

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C2C-6 - POSTER #42

C2C-6
Poster #: 42

Sustainable Aviation Fuels (SAF) from Ethanol: An Integrated Systems Modeling Approach

Madelynn J. Watson[1], Aline Veronese de Silva[3], Pedro Gerber Machado[2], Celma de Oliveira Ribeiro[2], Cláudio Augusto Oller do Nascimento[2], and Alexander W. Dowling[1]

[1]Department of Chemical and Biomolecular Engineering, University of Notre Dame, [2]Department of Industrial Engineering, University of São Paulo, [3]Institute of Economics, Universidade Estadual de Campinas

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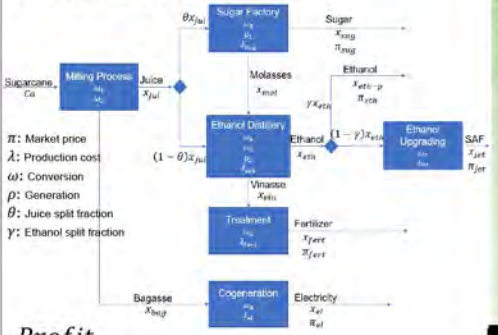
GOALS

Develop a rigorous modeling framework to enable SAF production with the lowest costs and environmental impact considering market uncertainty

Process Model



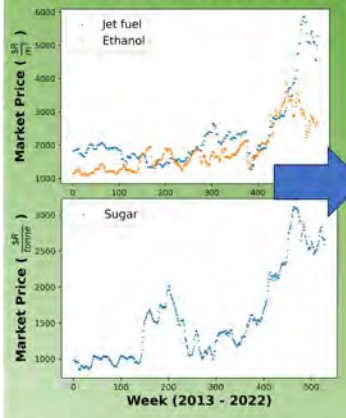
$$
\begin{aligned}
&Profit \\
&= (\pi_{sug} - \lambda_{sug})x_{sug} + \pi_{eth}x_{eth-p} \\
&- \lambda_{eth}x_{eth} \\
&+ (\pi_{jet} + \pi_{premium} - \lambda_{jet})x_{jet} \\
&+ (\pi_{el} - \lambda_{el})x_{el} + (\pi_{fert} - \lambda_{fert})x_{fert}
\end{aligned}
$$

$$
\begin{aligned}
&\max \ Profit \\
&\text{s.t.} \quad \text{mass balances} \\
&\qquad \text{capacity restrictions} \\
&\qquad \text{demand fulfillment}
\end{aligned}
$$

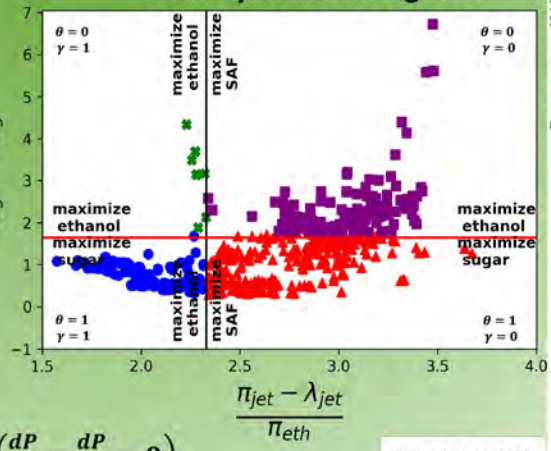
MAIN FINDINGS

Optimal operation depends on the relationship between sugar, ethanol, and SAF prices

Historical Market Prices



Four Operation Regions

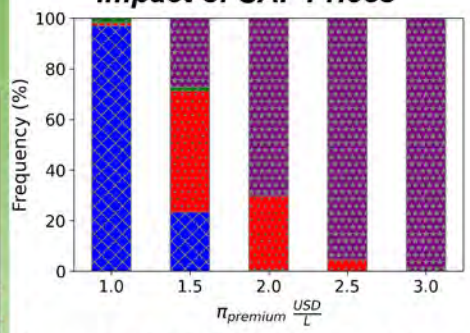


Operation Region Bounds $\left(\frac{dP}{d\theta} = \frac{dP}{d\gamma} = 0\right)$

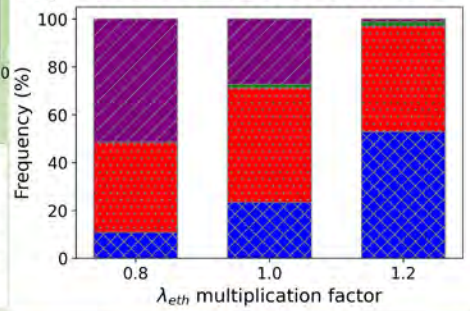
$$\frac{\pi_{eth-mod}}{\pi_{sug} - \lambda_{sug}} = \frac{\omega_3 - \omega_2\omega_4\rho_1}{\omega_2} \qquad \frac{\pi_{jet} - \lambda_{jet}}{\pi_{eth}} = \frac{1}{\omega_7}$$

OUTCOMES

Impact of SAF Prices



Impact of SAF Production Cost



C2C International Collaboration

Universidade de São Paulo
UNIVERSITY OF NOTRE DAME

Research Domain

IMPACT & FUTURE

Integrating Technology Scale-up, Process Design, Supply Chain Optimization and Life Cycle Analysis

PYOMO GREET LIFE-CYCLE MODEL

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C2C-7 - POSTER #43

C2C-7
Poster #: 43

Single Atom Ni Catalyst for Low Temperature Activation of CO_2 & CH_4 to Fuels and Chemicals

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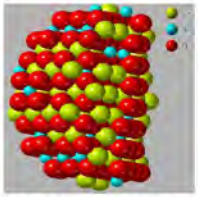
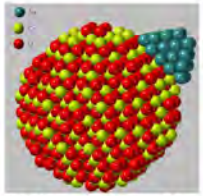
GOALS

- Brazil's natural gas has high levels of CO_2 hence there is interest in dry reforming of methane
- Metallic Ni particles are prone to coke deposition and catalyst fouling.
- Ni single nickel atoms are being studied to allow activation of CH_4 and CO_2
- Co-dopants and exsolution of Ni particles from the oxide support provide avenues to tailor performance.



Nickel single atoms doped into the ceria crystal lattice



Nickel nanoparticle bound to the ceria crystal

MAIN FINDINGS - CISTAR

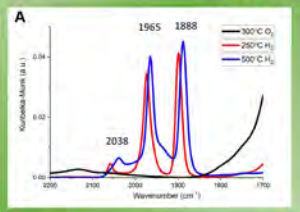


Figure 1: (A) CO-DRIFTS spectra of $Ce_{0.9}Ni_{0.1}O_{2-x}$ (B) CO-DRIFTS spectra of $Ce_{0.9}Ni_{0.05}Al_{0.05}O_{2-x}$.(C) CO-Drifts spectra of metallic Ni/SiO_2

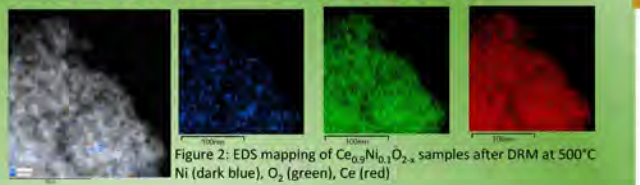


Figure 2: EDS mapping of $Ce_{0.9}Ni_{0.1}O_{2-x}$ samples after DRM at 500°C Ni (dark blue), O_2 (green), Ce (red)

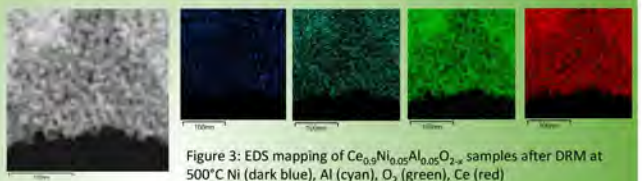


Figure 3: EDS mapping of $Ce_{0.9}Ni_{0.05}Al_{0.05}O_{2-x}$ samples after DRM at 500°C Ni (dark blue), Al (cyan), O_2 (green), Ce (red)

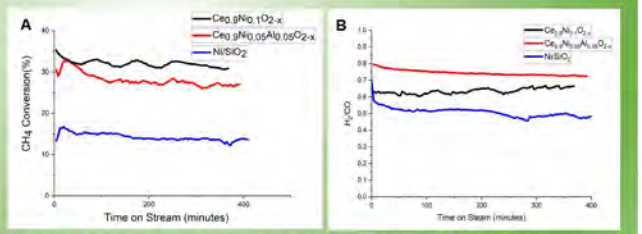
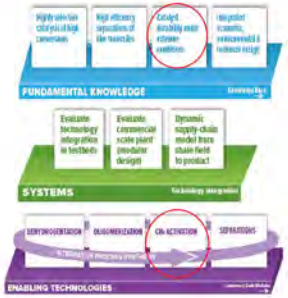


Figure 4: (A) CH_4 activity of $Ce_{0.9}Ni_{0.1}O_{2-x}$, $Ce_{0.9}Ni_{0.05}Al_{0.05}O_{2-x}$, Ni/SiO_2 at 500°C (B) Product ratio of $Ce_{0.9}Ni_{0.1}O_{2-x}$, $Ce_{0.9}Ni_{0.05}Al_{0.05}O_{2-x}$, Ni/SiO_2 at 500°C

OUTCOMES

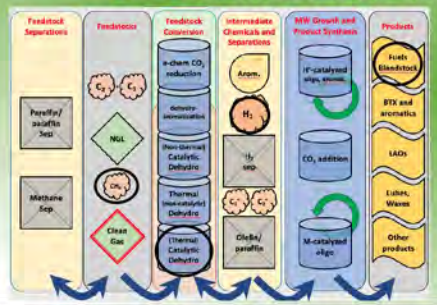
- Ni single atom catalyst is active without reduction for hydrogenation
- Metallic Ni exsolved from doped Ni-ceria shows no coke after DRM
- Observed product ratios are higher in Ni single nickel atoms than studies of metallic nickel at higher temperatures

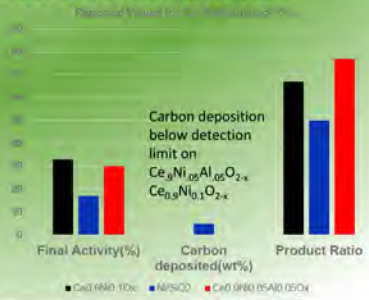


IP & INNOVATION

- Stable nickel catalyst that is highly coke resistant
- *Single Atom Metal Doped Ceria for CO Oxidation and Hydrocarbon Hydrogenation/Oxidation* (DeLaRiva et al., US 11,745,169 B1 issued Sep. 5, 2023)

SYSTEM DESIGN & BENCHMARKS





IMPACT & FUTURE

- Co-doping of Ni-ceria can control the Ni reactivity and stability
- The co-dopant helps retain a larger fraction of the Ni single atom species
- Single Ni atoms can activate CH_4 and CO_2 at low temperatures

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