INL/CON-23-71693-Revision-0

Chemical looping conversion of CH4/CO2 to syngas on 5wt.%Ni@Ce0.6Zr0.4O2 catalyst: Impact of dynamic accumulation of surface carbon and oxygen vacancies

March 2023

Changing the World's Energy Future

Rebecca R Fushimi, Zoe Cascade Benedict, Sherafghan Ifkithar, Debtanu Maiti, Fanxing Li, Yingchao Yang

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Idaho National Laboratory
Idaho Falls, Idaho 83415

http://www.inl.gov

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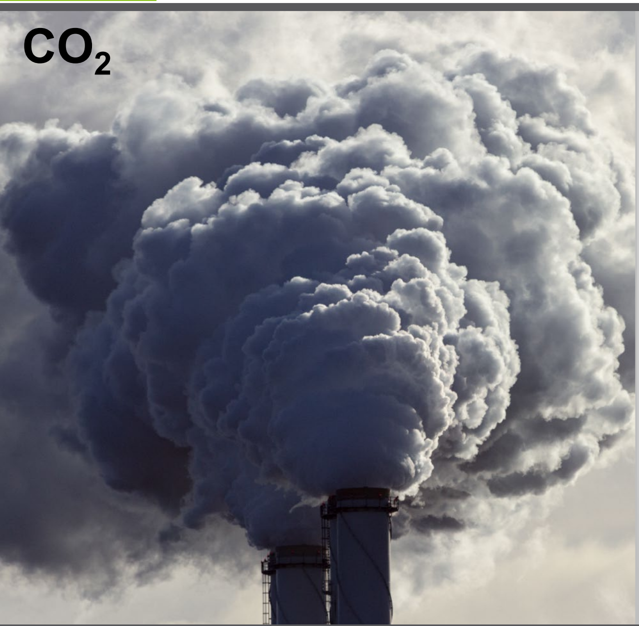
Zoe Benedict

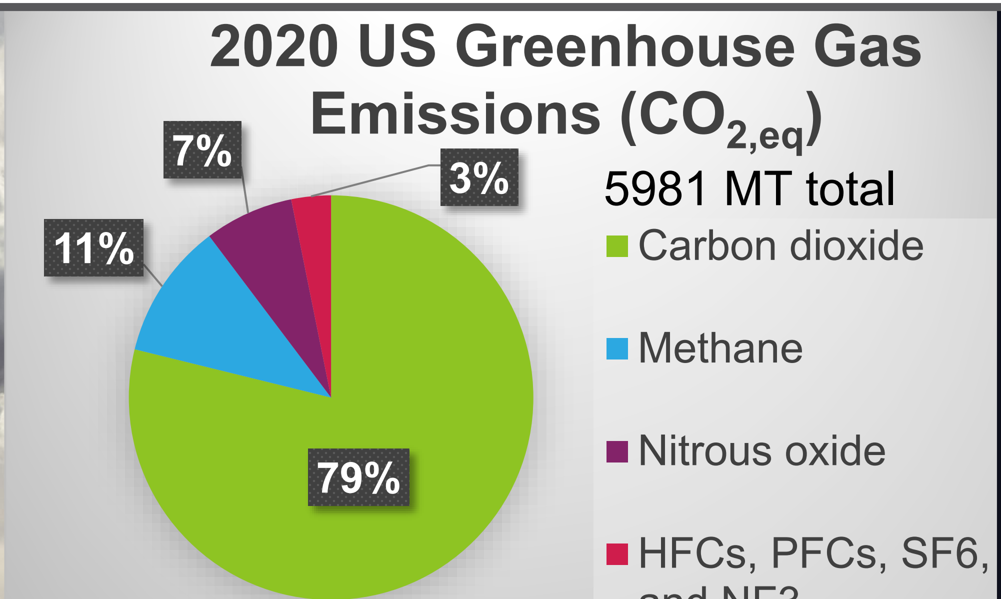
Chemical looping conversion of CH_4/CO_2 to syngas on 5wt.%Ni@$Ce_{0.6}Zr_{0.4}O_2$ catalyst

Advisors:
Dr. Yingchao Yang
Nanomaterials and Nanomechanics Laboratory
Dr. Rebecca Fushimi, Dr. Debtanu Maiti
Idaho National Laboratory

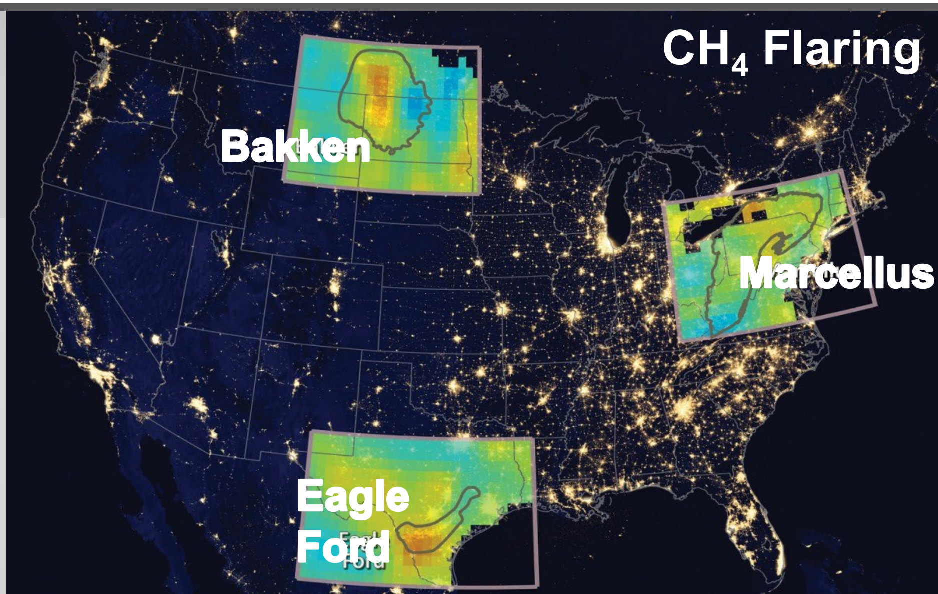
INL Idaho National Laboratory

Motivation

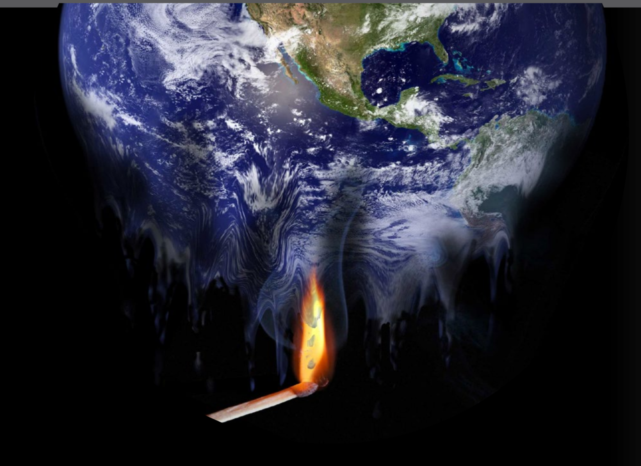




Data source: U.S. EPA, 2022



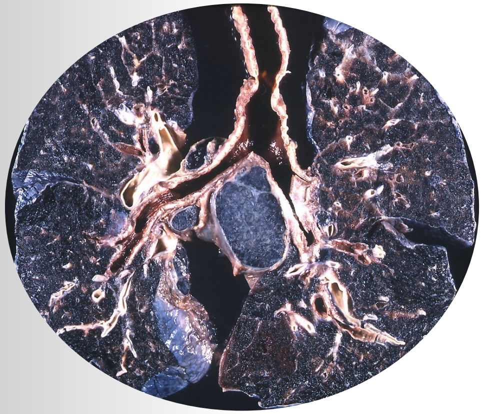
Rosen J., "Methane Leaks," *Eos*, ***2014***.



CLIMATE CHANGE

WILDFIRES

POLLUTION, LUNG DISEASE



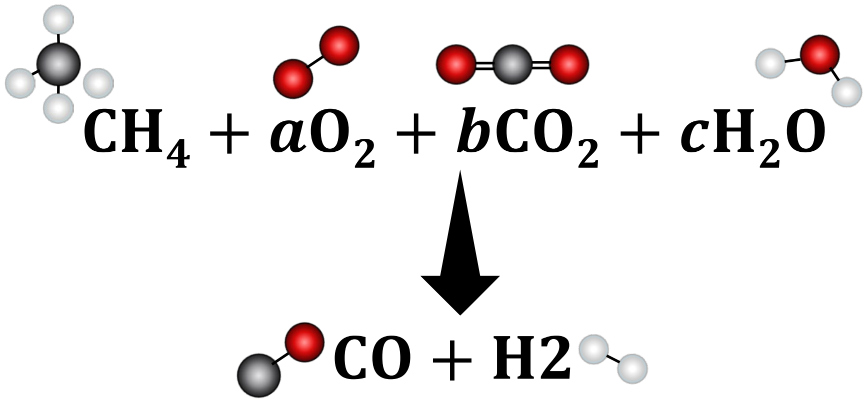
EXTREME WEATHER

Syngas

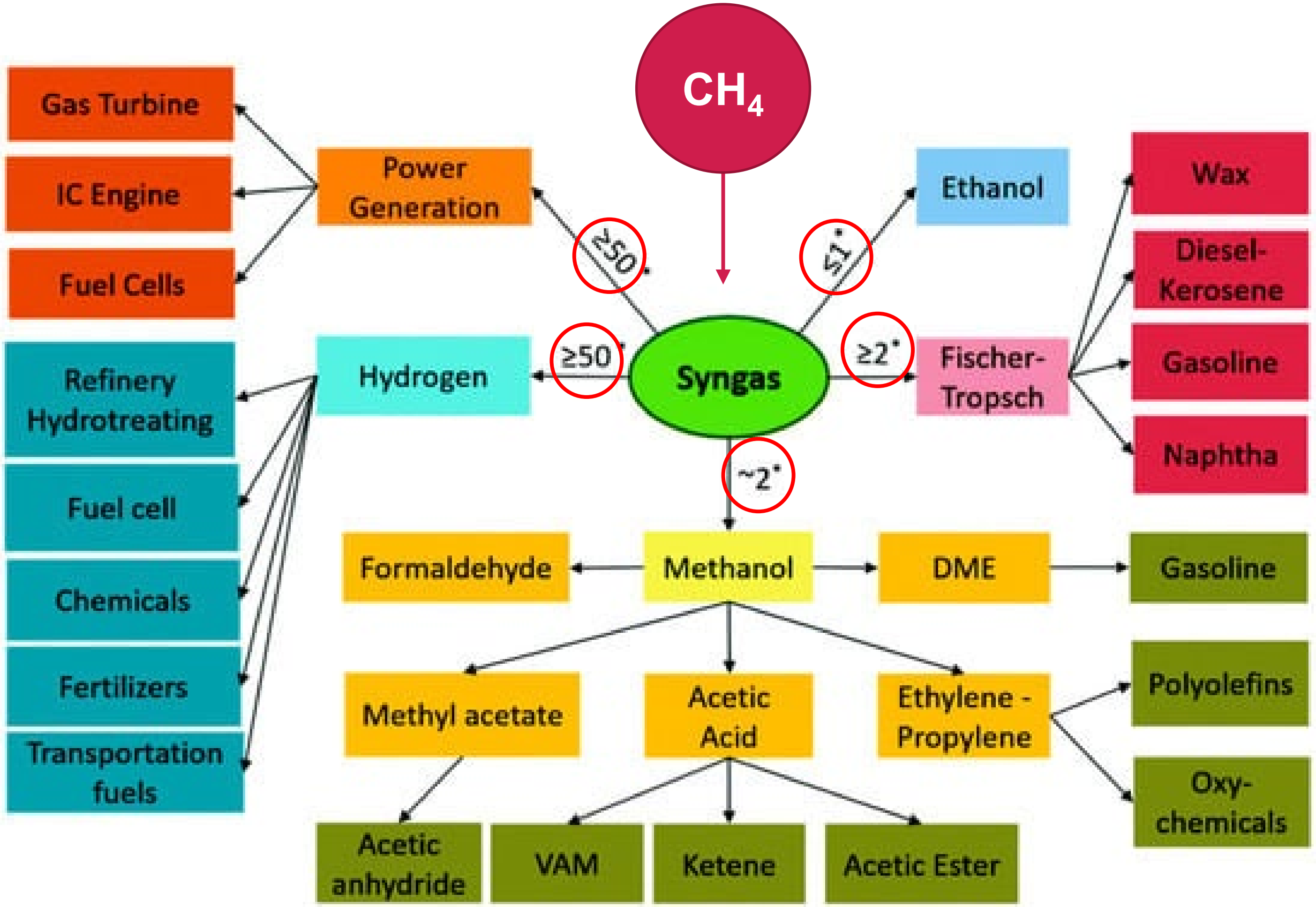
Syngas

H_2 + CO

Fuels and chemicals



$$CH_4 + aO_2 + bCO_2 + cH_2O \rightarrow CO + H2$$



* H_2/CO syngas ratio

De Smit, E. *Chem. Soc. Rev.* **2008**, 37, 2758-2781.

Syngas production

CATALYTIC PROCESSES

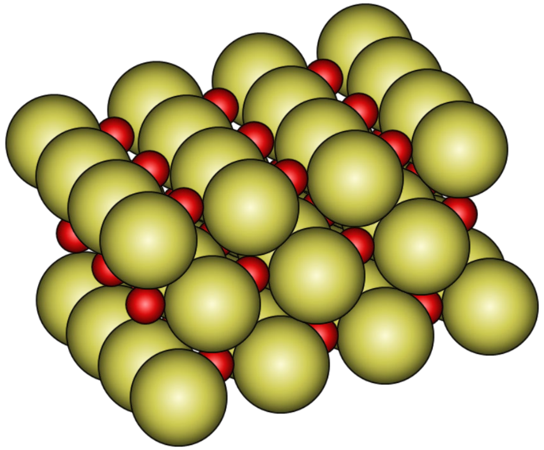
Dry Reforming of Methane (DRM)

Steam Reforming of Methane (SRM)

Partial Oxidation (PO_x)

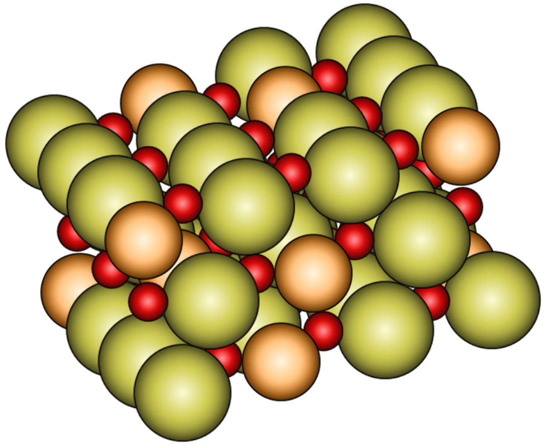
METAL OXIDE-BASED CATALYSTS

Binary M_xO_y



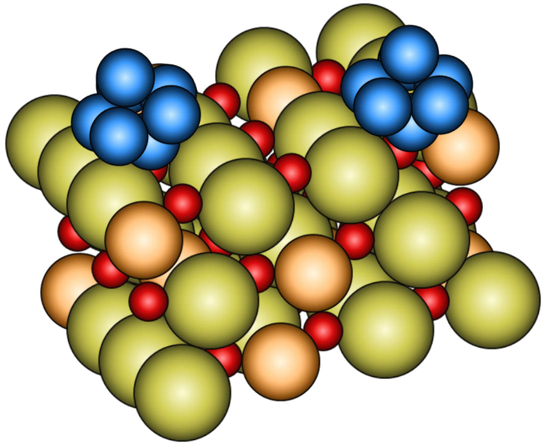
e.g. CeO_2

Mixed $M_{1,1-x}M_{2,x}O_y$



e.g. $Ce_{1-x}Zr_xO_2$

Active metal M_xO_y



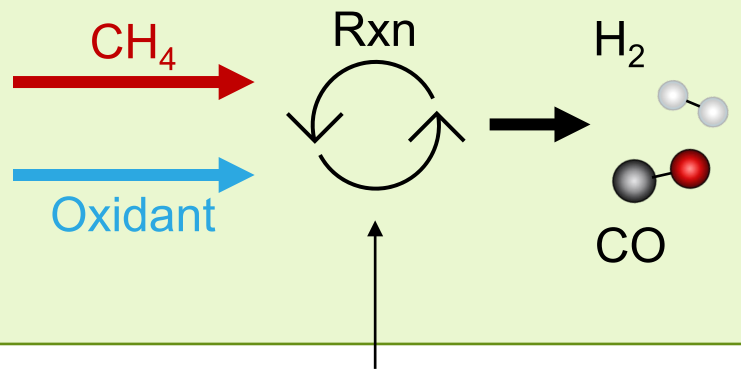
e.g. Ni@ $Ce_{1-x}Zr_xO_2$

Syngas production

CATALYTIC PROCESSES

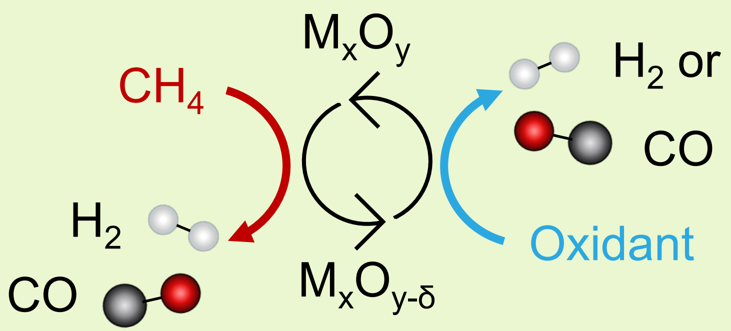
Dry Reforming of Methane (DRM)	Steam Reforming of Methane (SRM)	Partial Oxidation (PO_x)
$CH_4 + CO_2 \downarrow 2H_2 + 2CO$	$CH_4 + H_2O \downarrow 3H_2 + CO$	$CH_4 + 1/2\ O_2 \downarrow 2H_2 + CO$

CO-FEED

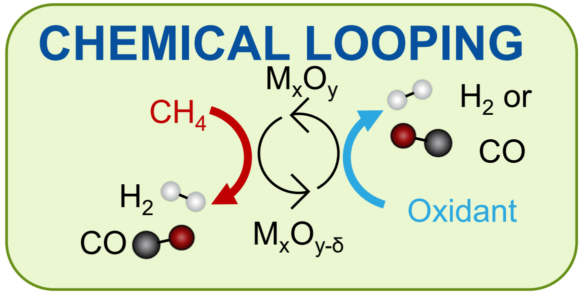


Prone to side reactions

CHEMICAL LOOPING



Syngas production



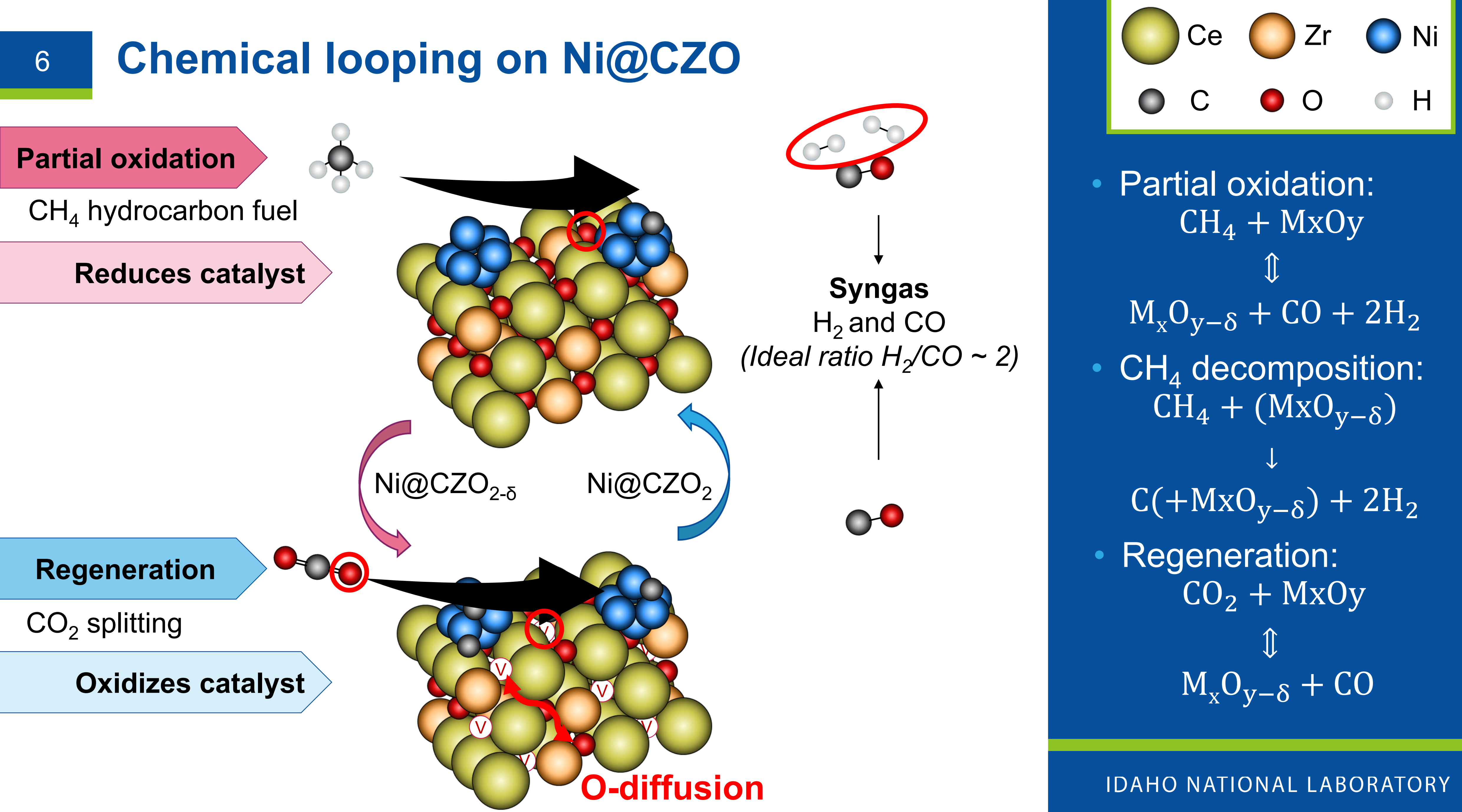
CATALYTIC PROCESSES

Dry Reforming of Methane (DRM)	Steam Reforming of Methane (SRM)	Partial Oxidation (PO_x)
$CH_4 + CO_2$ ↓ $2H_2 + 2CO$	$CH_4 + H_2O$ ↓ $3H_2 + CO$	$CH_4 + 1/2\ O_2$ ↓ $2H_2 + CO$

CATALYST REGENERATION

Carbon Dioxide (CO_2)	Steam (H_2O)	Oxygen (O_2)
$M_xO_{y-\delta} + \delta CO_2$ ↓ $M_xO_y + \delta CO$	$M_xO_{y-\delta} + \delta H_2O$ ↓ $M_xO_y + \delta H_2$	$M_xO_{y-\delta} + \delta 1/2\ O_2$ ↓ M_xO_y

Chemical looping on Ni@CZO



- Partial oxidation:

$$CH_4 + MxOy \Updownarrow M_xO_{y-\delta} + CO + 2H_2$$

- CH_4 decomposition:

$$CH_4 + (MxO_{y-\delta}) \downarrow C(+MxO_{y-\delta}) + 2H_2$$

- Regeneration:

$$CO_2 + MxOy \Updownarrow M_xO_{y-\delta} + CO$$

CL performance of Ni/CZO catalysts in literature

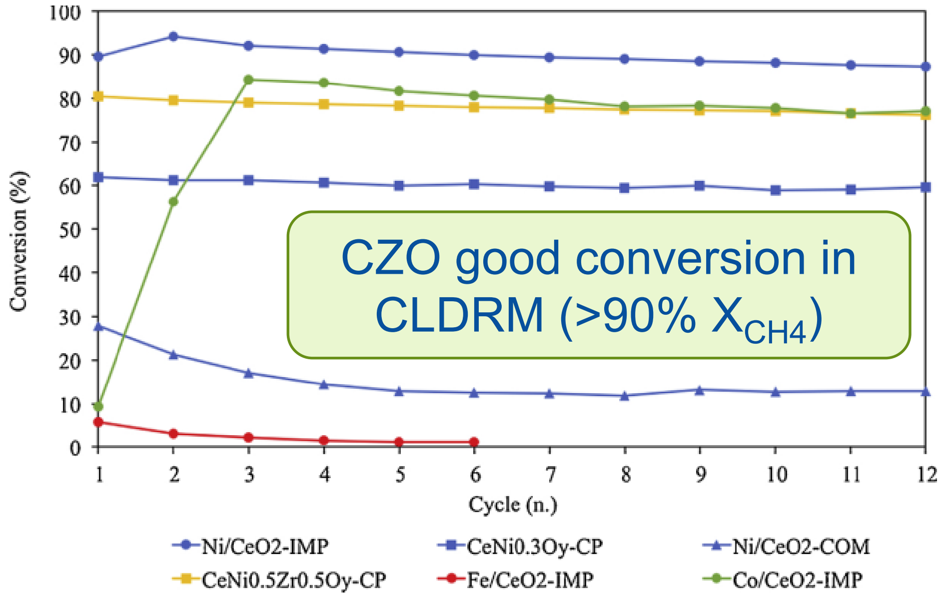


Fig. 2. CH_4 conversion on all studied carriers upon first exposure to CLDRM at 800 °C.

Guerrero-Caballero J., et al. *Catal. Today* (2019) 333, 251-258.

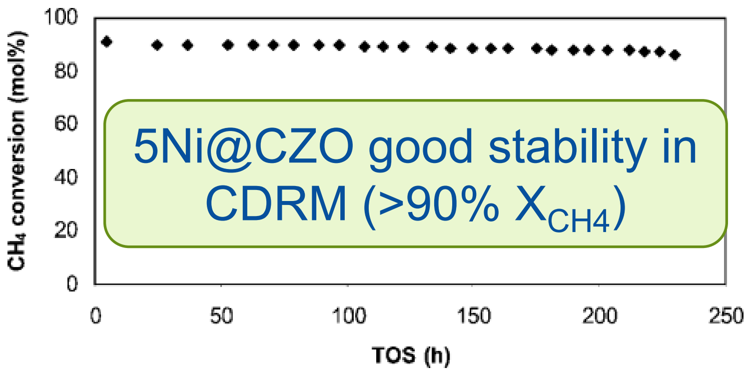


Figure 14. Long-term stability test of 5% Ni/$Ce_{0.6}Zr_{0.4}O_2$ (CTAB) catalyst at 800 °C, feed (CH_4:CO_2:N_2 = 2:2:1) rate of 5.04 × 10^4 mL/(h g-cat.), and reduction temperature of 710 °C.

Kumar P., et al. *Energy & Fuels.* (2007) 21, 3113-3123.

Table S2. Comparison of syngas yield, methane conversion and metal loadings for chemical looping methane-to-syngas.

Redox Materials	Syngas Yield (mmol/g_{cat})	Feed CH_4 (%)	CH_4 Conversion (%)	CO Selectivity (%)	Metal loadings (wt%)
Ni/CeO_2	3.30	5	95	96	8.8
Ni/CeO_2-TiO_2	4.54	1	100	76	5
$Ni_{0.5}WO_x/Al_2O_3$	2.85	16.7	58	95	5
Ni/$CeZrO_2$	1.92	5	87	87	3
Rh/$LaCeO_{3.5}$	0.50	10	98	90	0.5
5Ni/CeO_2	3.35	5	100	77.2	5[a]
1Ni/CeO_2	3.42	5	100	97.1	0.74[a]
0.1Ni/CeO_2	3.41	5	99.1	97.6	0.07[a]

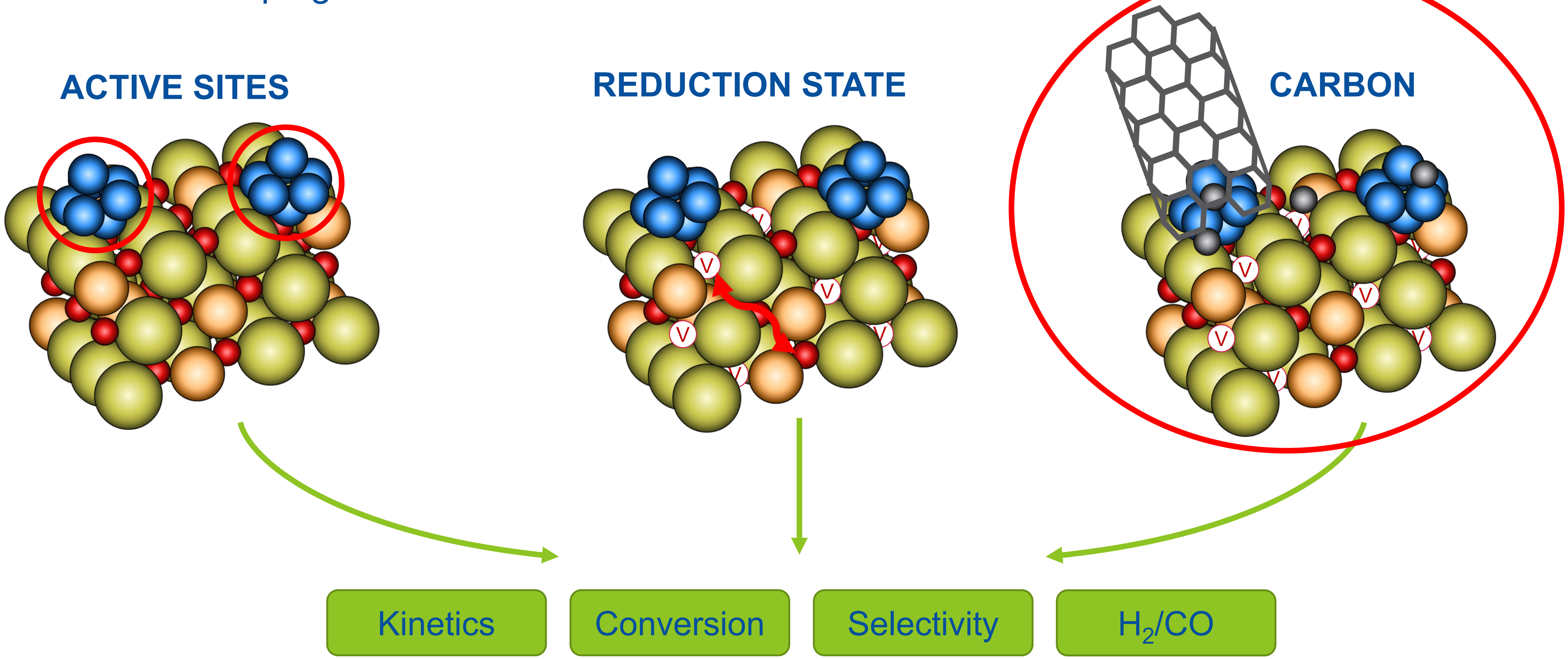
[a]Ni loadings are the mass percentage measured by ICP.

Han Y., et al. *ACS Sustain. Chem. Eng.* (2021)

Goal: near 100% conversion

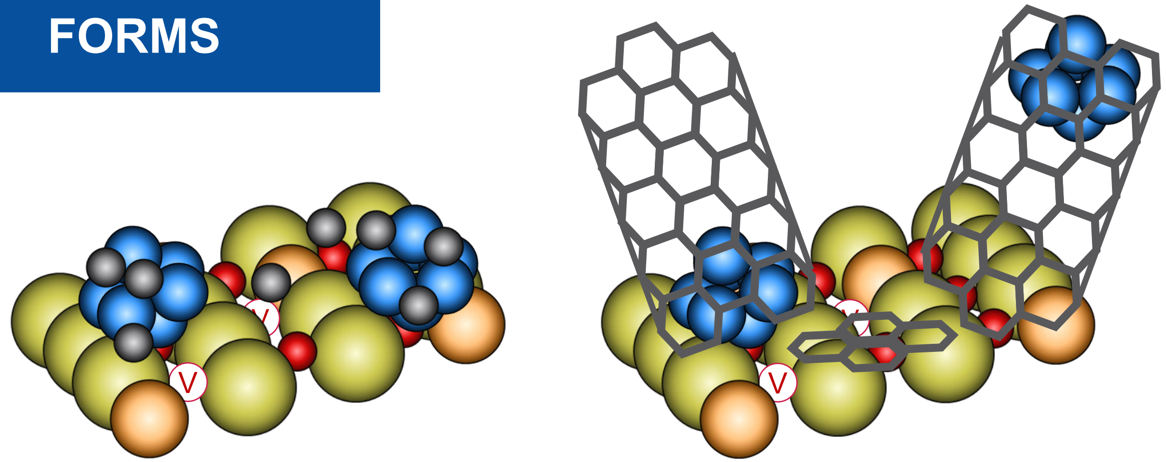
Investigation

- How do active sites, reduction state, and carbon formation affect syngas production in chemical looping?



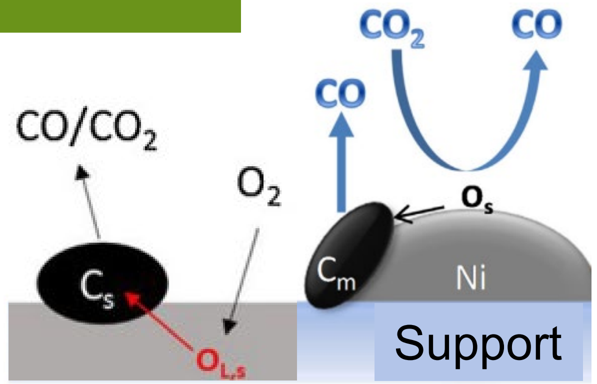
Carbon depositions

FORMS



AMORPHOUS GRAPHITIC

OXIDATION



Potential effects:

- Coverup active sites
- Maintain slightly reduced state
- "Pluck" off catalyst material

From support:

- Redox support O_L oxidation of C_s

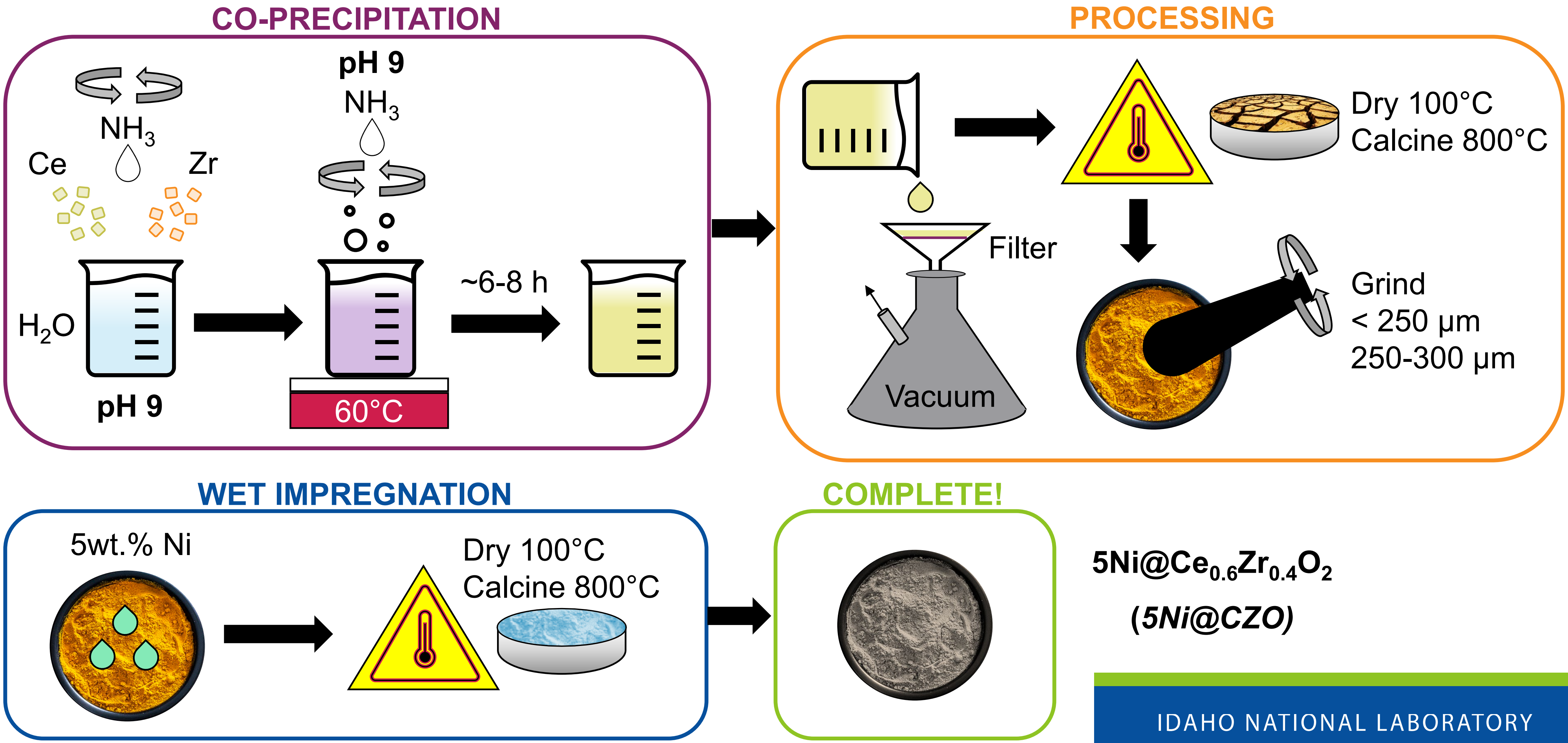
At active metal sites:

- Dissociation by Ni: O_s oxidation of C_m

S.A. Theofanidis, et al. *App;. Catal. B.* (2016) S.A. Theofanidis, et al. *Appl. Catal. B.* (2019)

C_s – surface carbon; C_m – metal carbon; O_s – surface oxygen; O_L – lattice oxygen

Material synthesis



$5Ni@Ce_{0.6}Zr_{0.4}O_2$

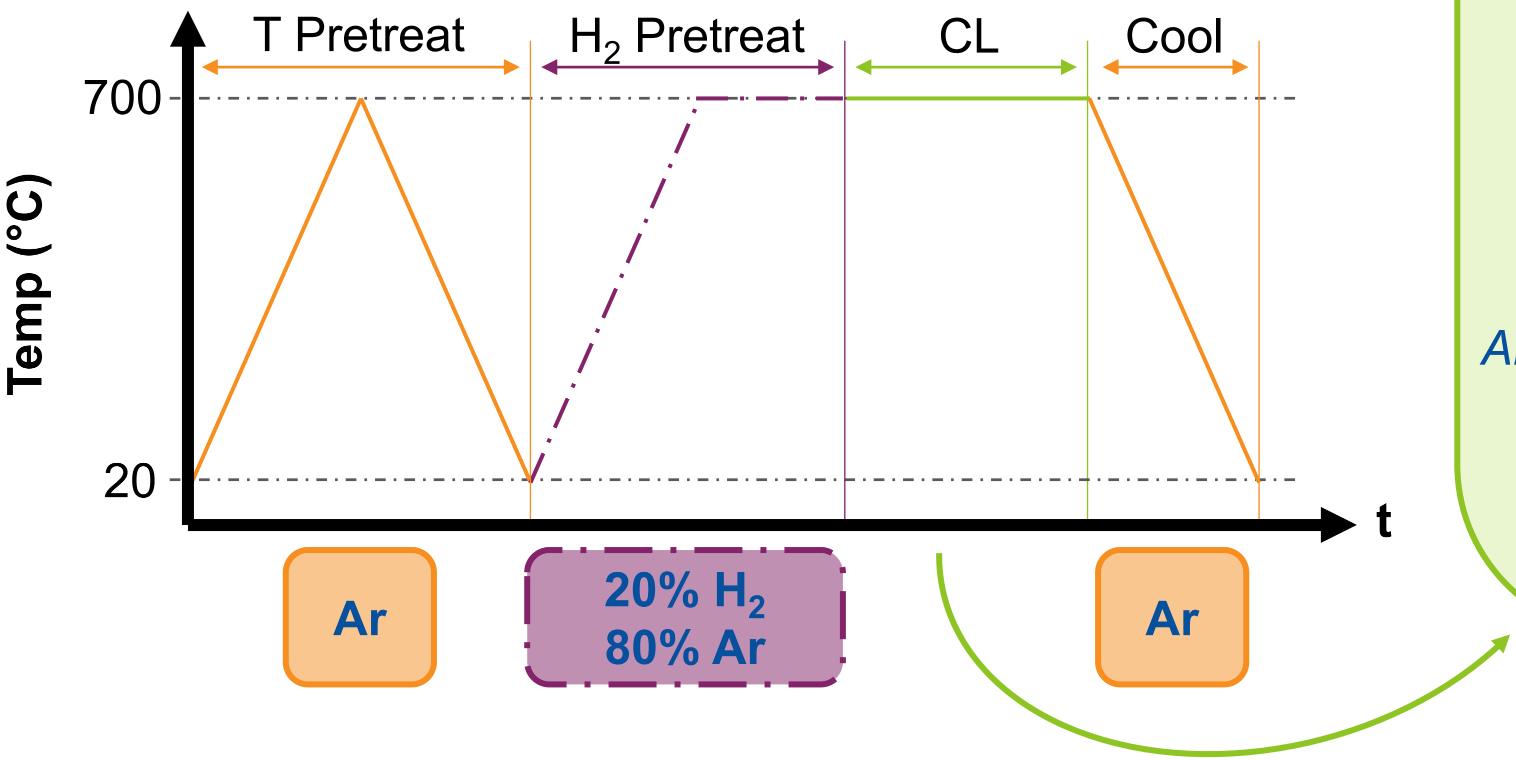
(5Ni@CZO)

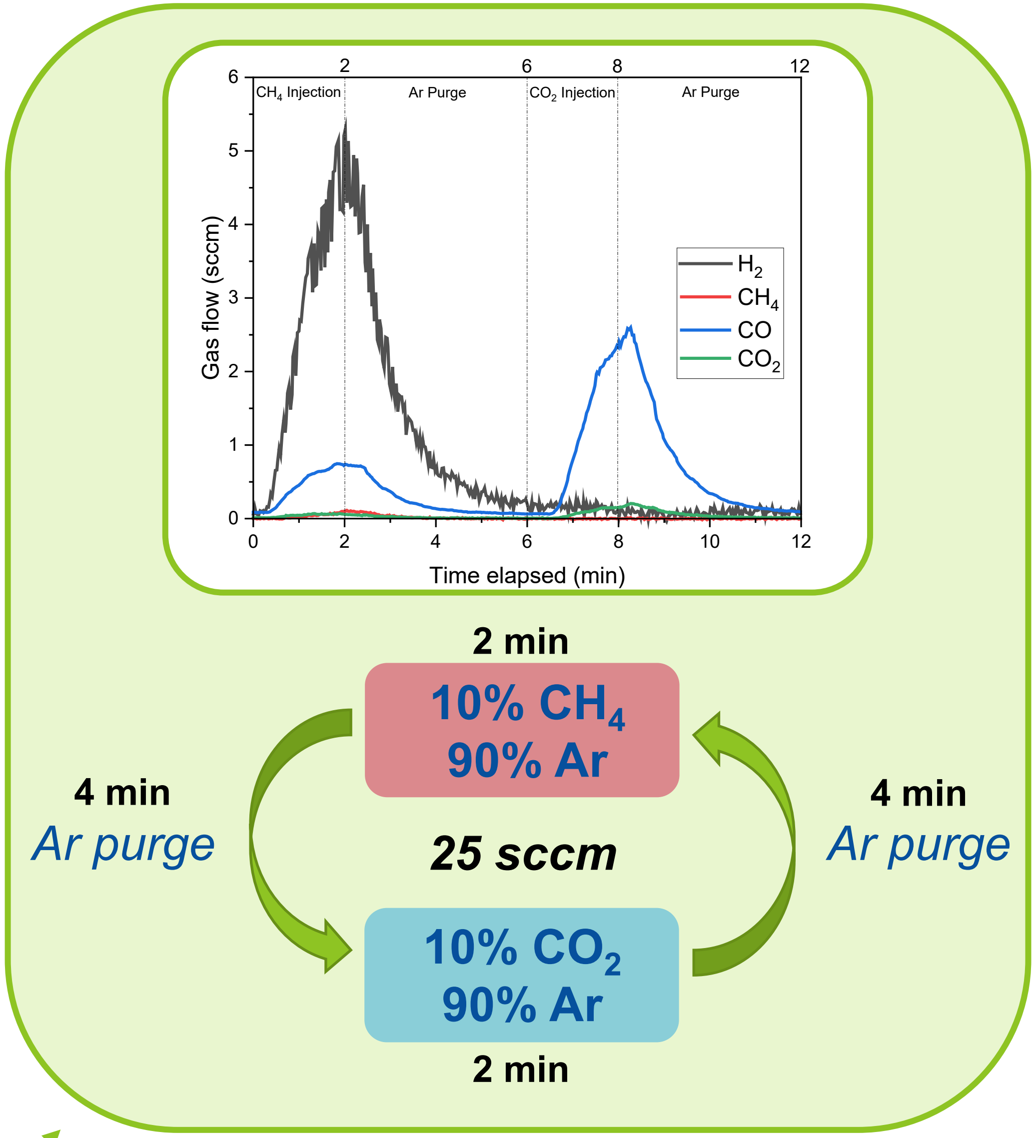
Reaction

- Gas Hourly Space Velocity: 108.12 h^{-1}

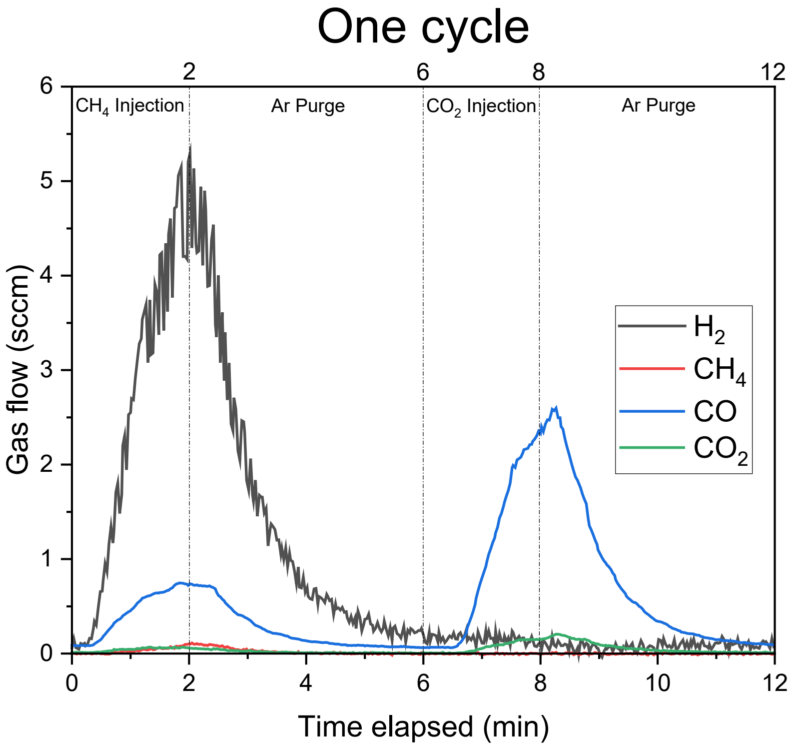
$$\frac{Vol.\,flow\,rate\,of\,gas/hr}{External\,vol.\,catalyst}$$

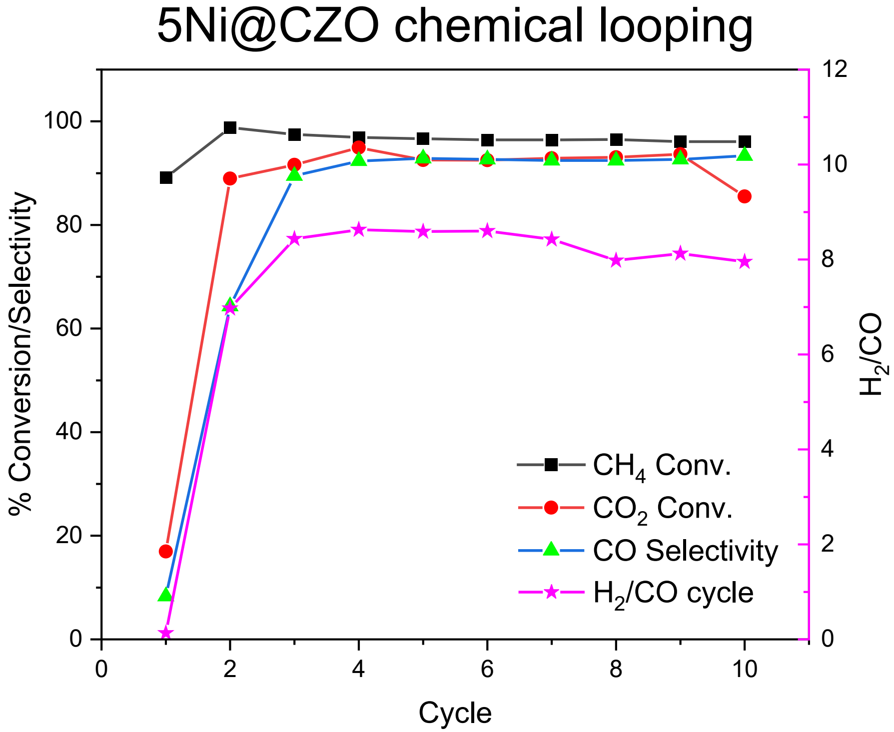
- Temperature ramp rates: ±10°C/min

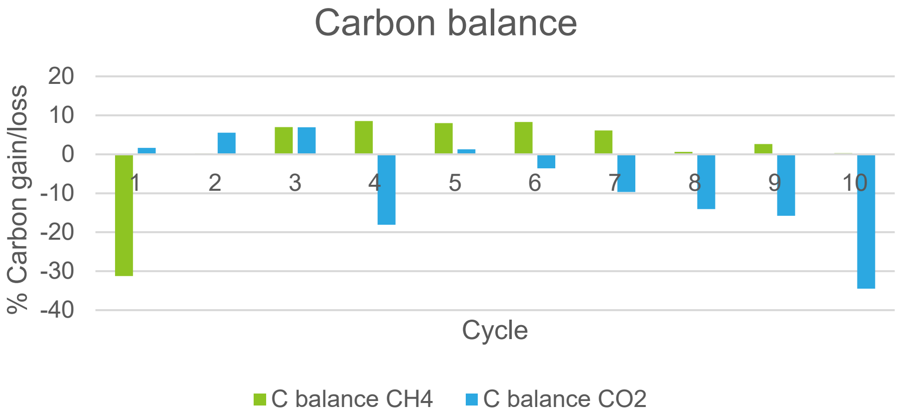




Reaction data







Performance	
X_{CH_4}	>96%
X_{CO_2}	>92.5%
S_{CO}	>92.5%
H_2/CO	~8

Conversion:

$$\%X_n = \frac{F_{n,in} - F_{n,out}}{F_{n,in}} * 100\%$$

Selectivity for CO during CO_2 flow:

$$\%S_{CO} = \frac{F_{CO}}{F_{CO} + F_{H2}} * 100\%$$

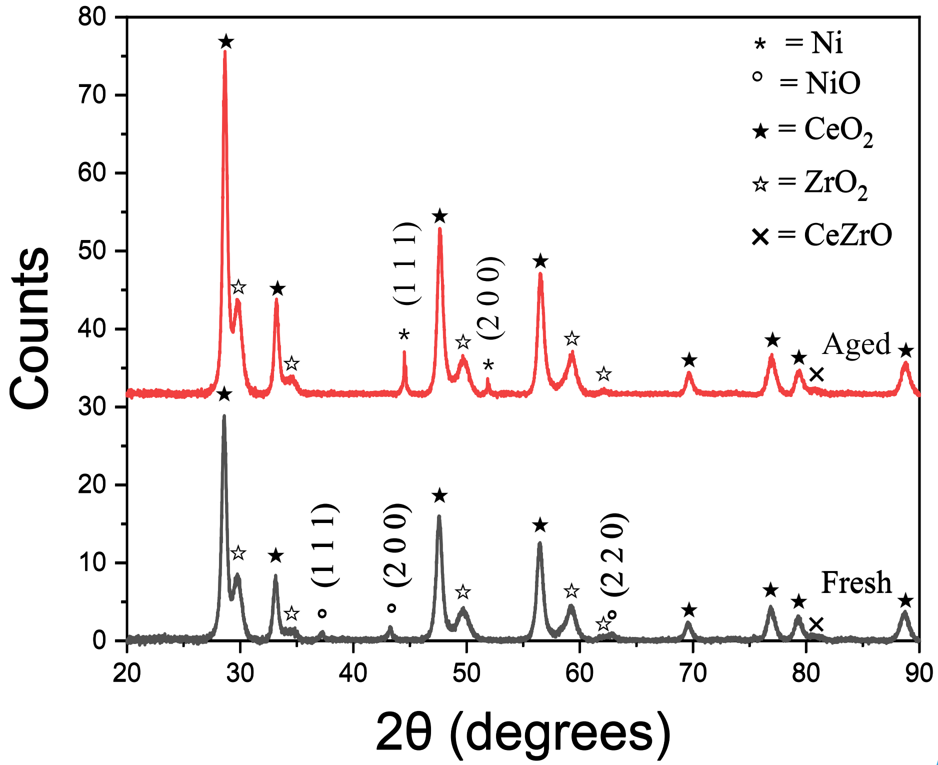
Carbon balance:

$$\%\Delta C = \frac{C_{in} - C_{out}}{C_{in}} * 100\%$$

Track deposition/oxidation of carbon during reaction

Material evolution – Fresh 5Ni@CZO

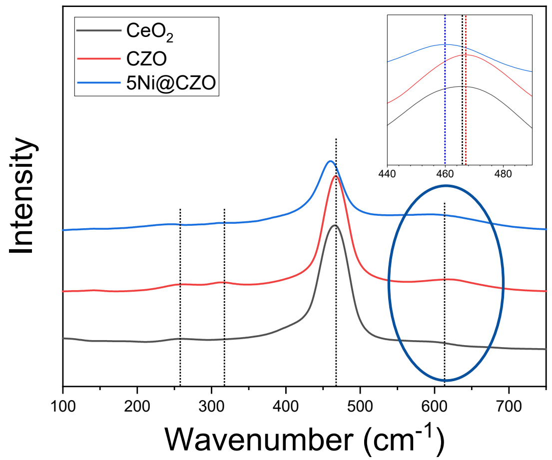
Bulk composition



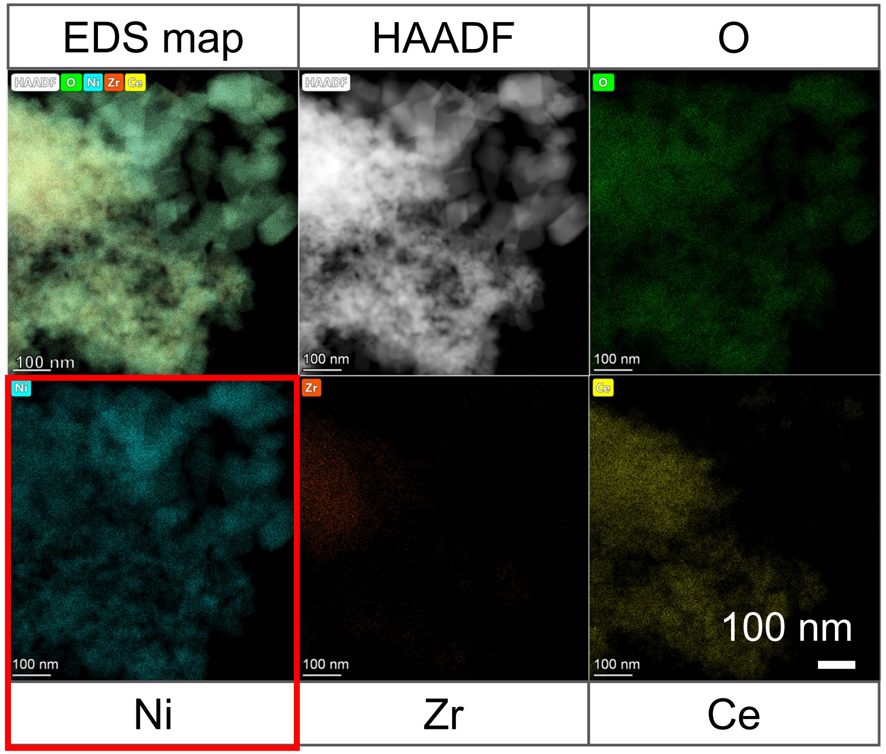
Separate Ce and Zr phases

Increased O_{vac}

Fresh Raman Shift



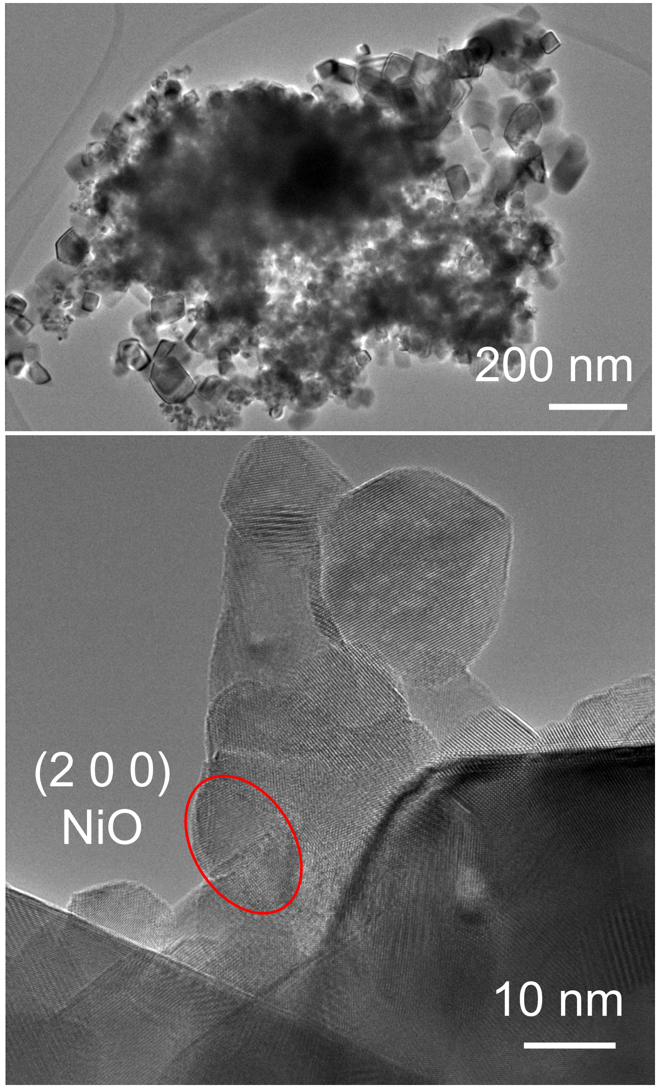
Well-distributed Ni



Material evolution - CL

BET (m^2/g)	Fresh	Aged	CLx5 no H2	CLx5 w H2
CZO	47	34		
5%Ni@CeO2	26	13		
5%Ni@CZO	28	27	25	24

FRESH



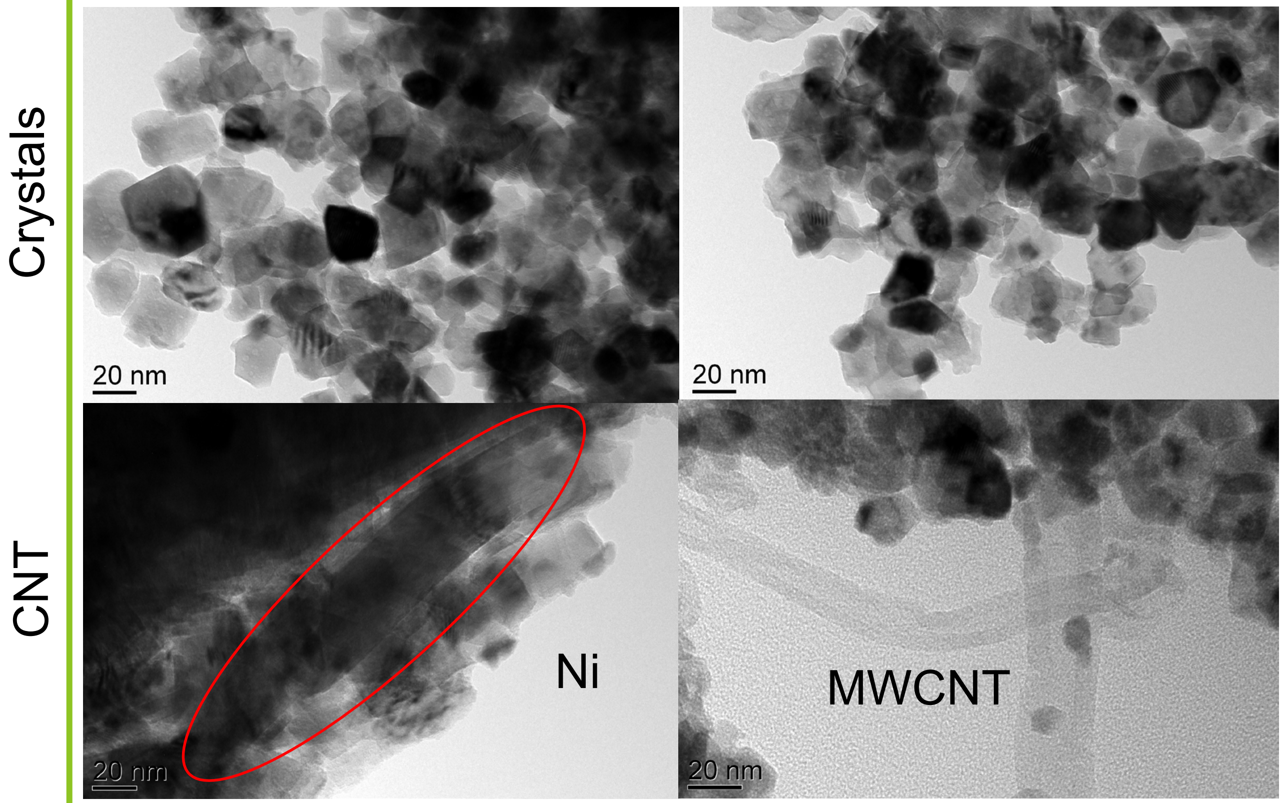
~20-40 nm

Thermal stability

NiO present

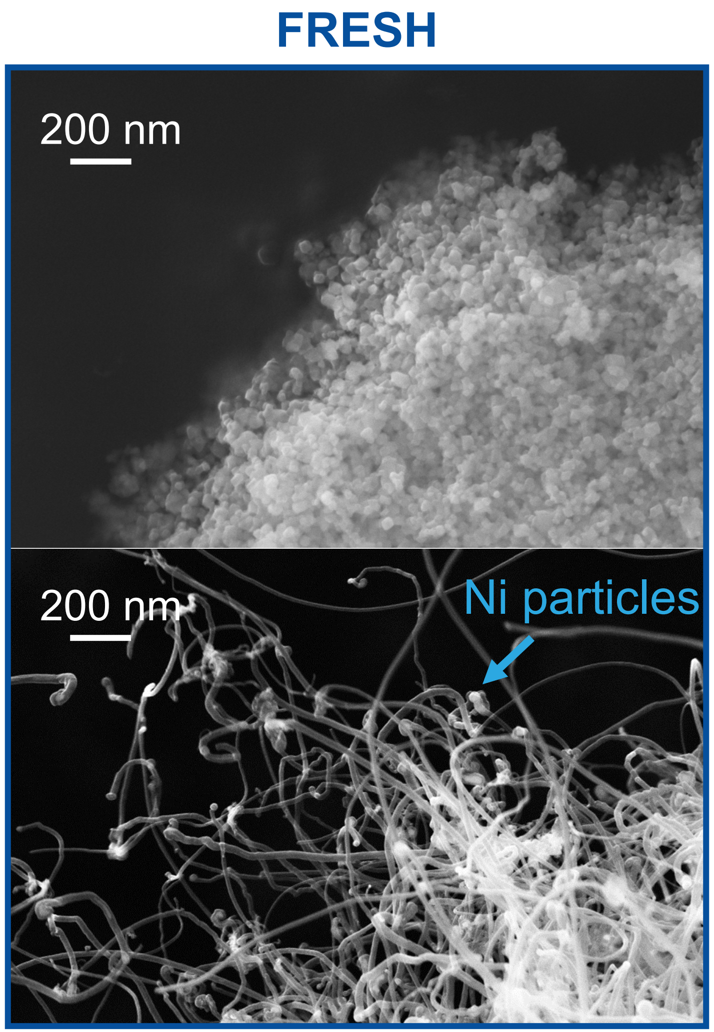
(2 0 0)
XRD

CLx5 no H_2 | CLx5 w/ H_2

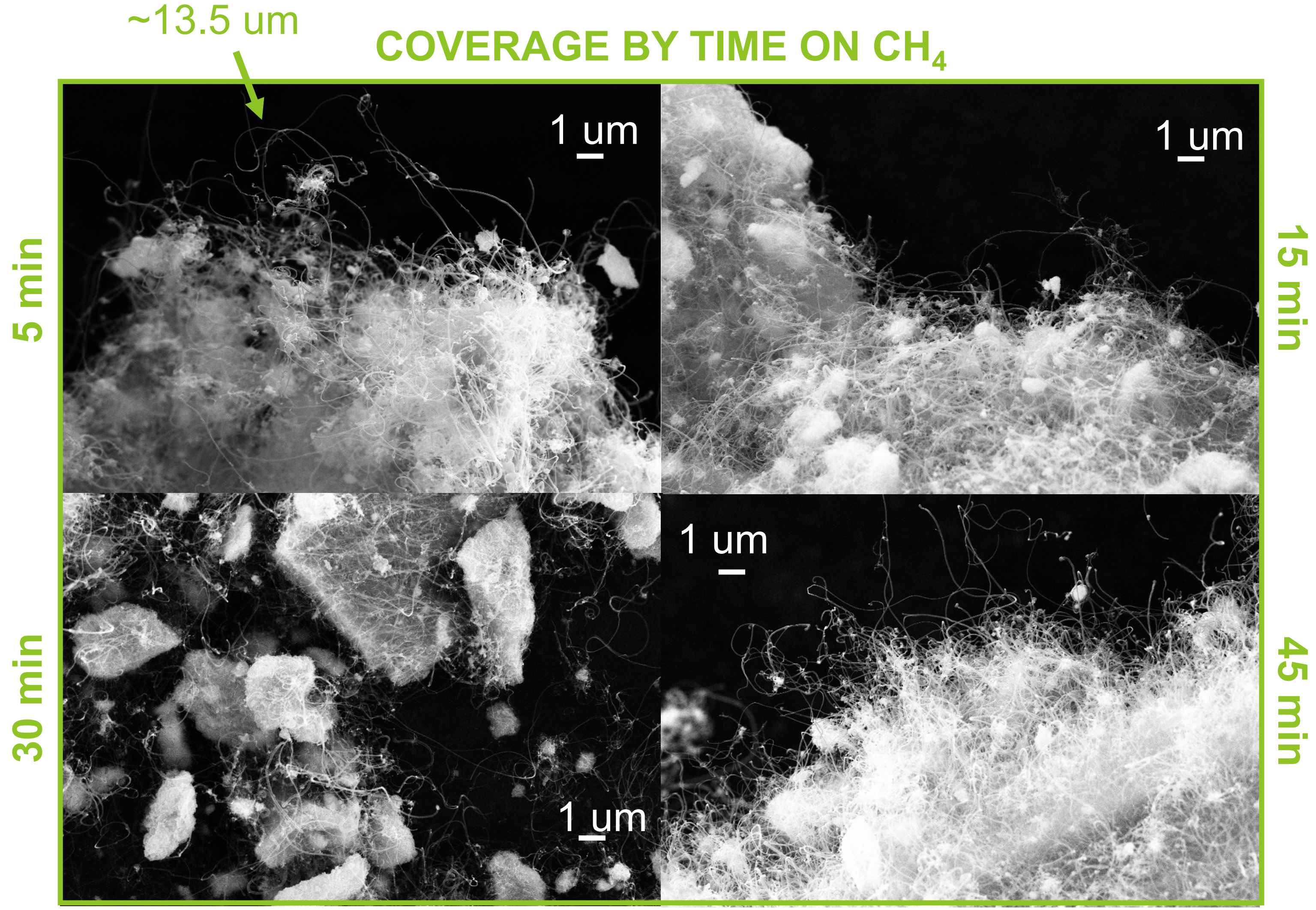


Evidence of CNTs

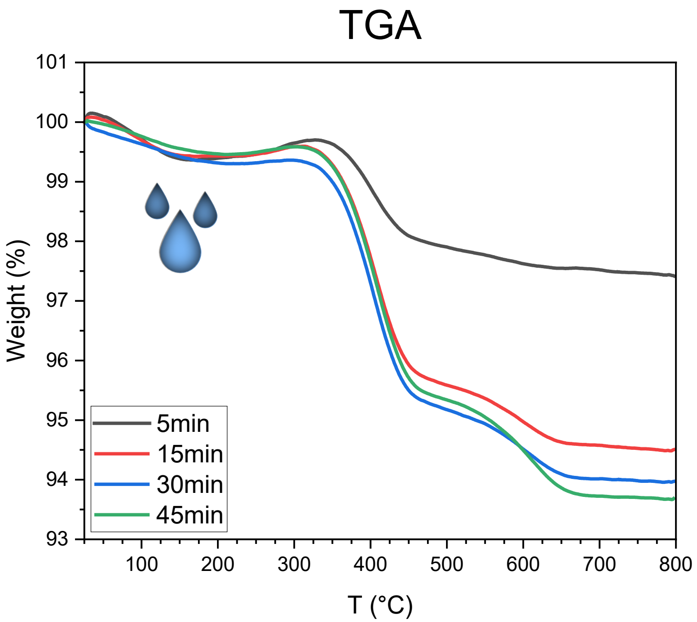
Material evolution – CNT growth with time

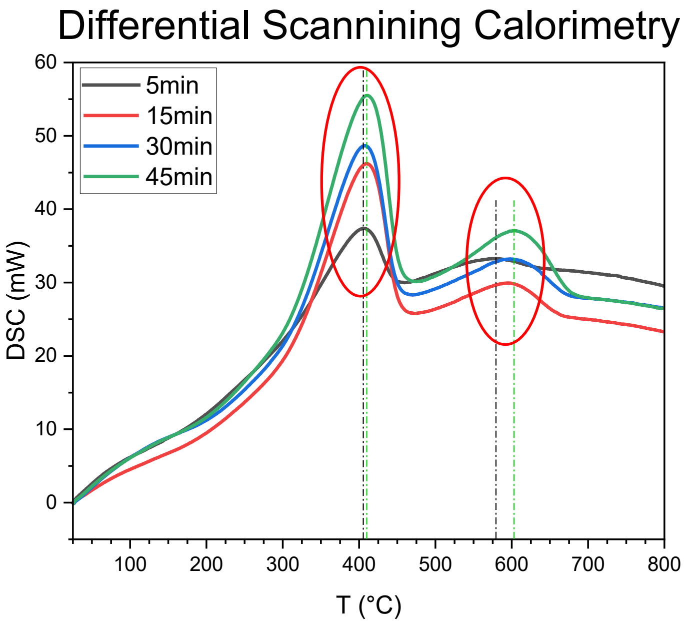


CH_4 45 MIN



Carbon quantification





CH_4 (min)	Transformation (C)	Qty. (%wt.loss)	Transformation (C)	Qty. (%wt.loss)	Total mass loss (%)
5	405.40	-1.87	579.37	-0.41	-2.28
15	409.17	-4.00	596.00	-1.09	-5.09
30	408.11	-4.19	598.10	-1.21	-5.40
45	410.08	-4.23	603.05	-1.69	-5.92

+

~405-410°C

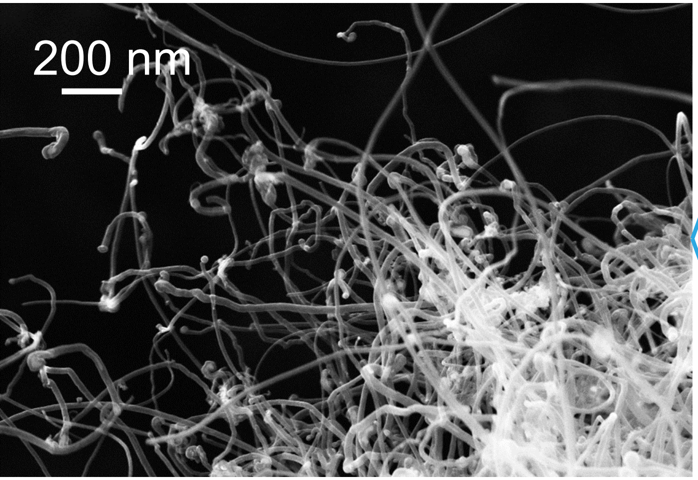
Amorphous C

~580-603°C

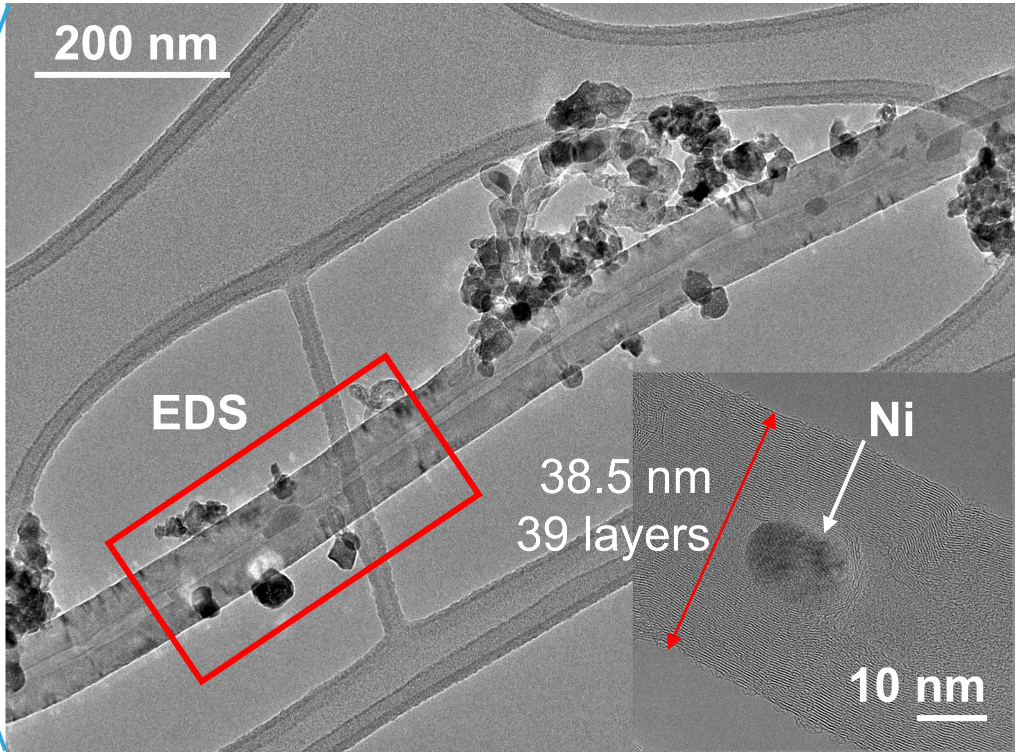
Structured C

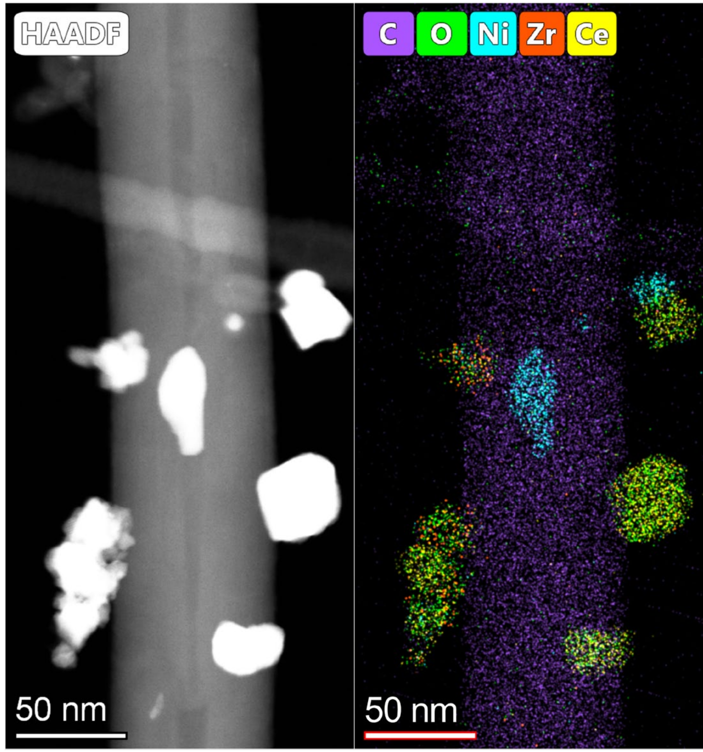
- Initial loss of H_2O and equilibration
- Two types of C deposits
  1. Amorphous
  2. Structured
- Increased C deposition with increasing time on CH_4

Carbon characterization



CH_4 45 MIN





- Particles ruptured from catalyst → CZO particles
- Average particle size: **20 nm**
- MWCNT
- Ni catalyzed

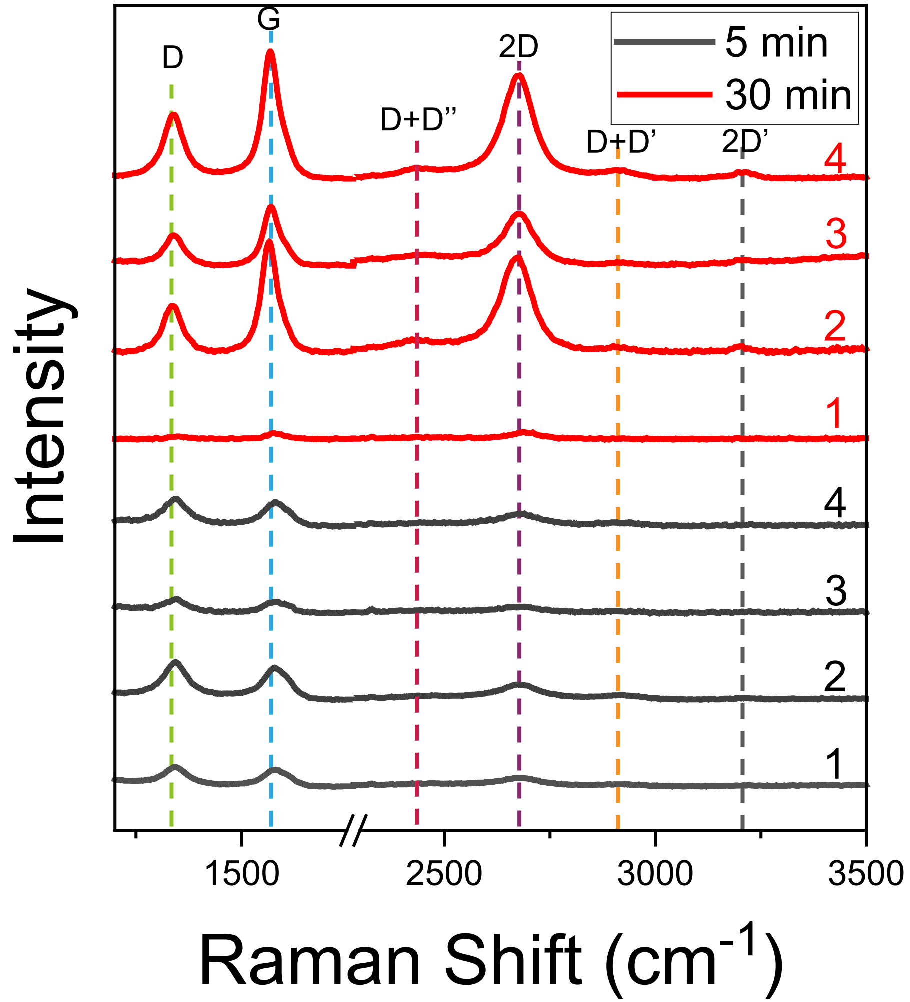
Carbon quality

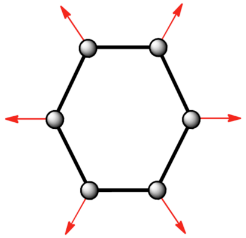
$I_{D/G}$

D
Defects, edge effects, dangling bonds

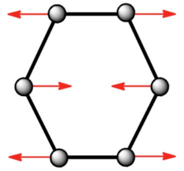
G
In plane sp^2 stretch

Ex situ Raman





D Mode
(A_{1g} - symmerty)



G Mode
(E_{2g} - symmerty)

Rosenburg, et al. *Materials* (**2018**), 11, 93.

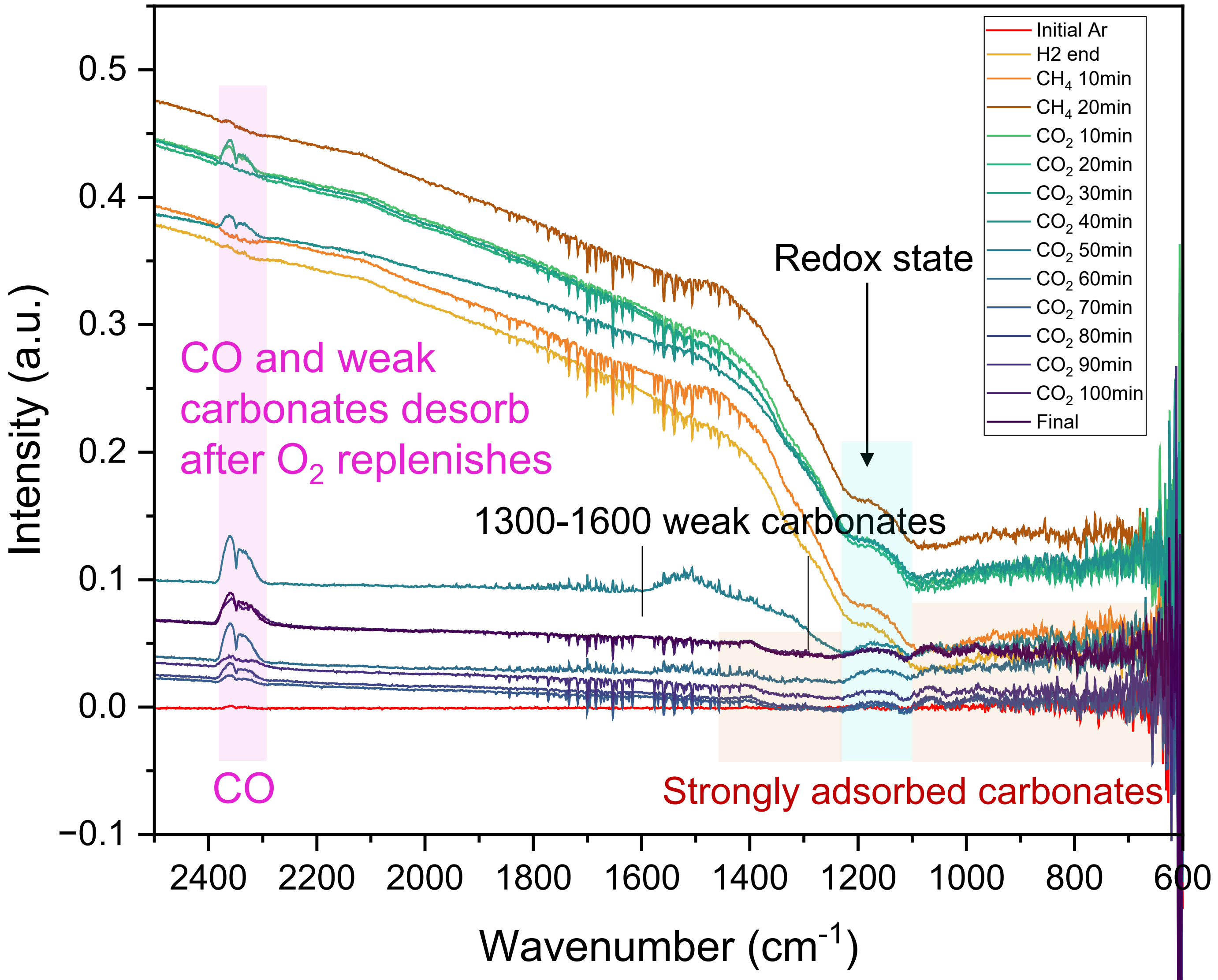
- ↓ defect concentration w/ time on CH_4
- Resonant peaks = MWCNTs

Cluster		$I_{D/G}$	D cm^{-1}	G cm^{-1}	2D cm^{-1}	2D /G	D+D'' cm^{-1}	D+D'' /G	D+D' cm^{-1}	D+D' /G	2D' cm^{-1}	2D' /G
30 min CH_4	4	0.49	1339	1568	2676	0.81	2433	0.08	2907	0.07	3214	0.05
	3	0.48	1340	1570	2677	0.86	2454	0.15	2908	0.04	3195	0.06
	2	0.42	1351	1575	2672	0.85	2424	0.11	2900	0.05	3201	0.05
	1	0.44	1351	1575	2686	1.15	2458	0.33	-	-	-	-
5 min CH_4	4	1.02	1346	1580	2678	0.55	2441	0.17	2905	0.17	-	-
	3	1.01	1346	1580	2680	0.55	2466	0.22	2902	0.18	3223	0.19
	2	1.09	1344	1579	2671	0.47	2479	0.11	2921	0.14	3207	0.05
	1	1.01	1341	1582	2675	0.53	2468	0.18	2911	0.14	-	-

Surface reactions

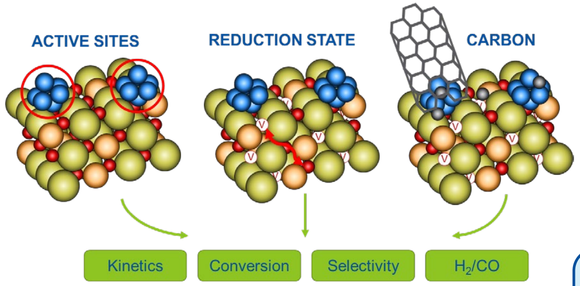
- Intensity increase of baseline related to increased oxygen vacancies
- Oxidation after reduction confirms (permanent peak ~1160 cm^{-1})
- 20 min_{eq} CH_4 → 100 min_{eq} CO_2
- Weak carbonates desorbed after 40-50 min_{eq} CO_2 (amorphous)
- CO desorbes after oxygen replenishes
- Strongly adsorbed carbonates remain after 100 min_{eq} CO_2 oxidation (graphitic)

H_2, CH_4 short/CO_2 soak



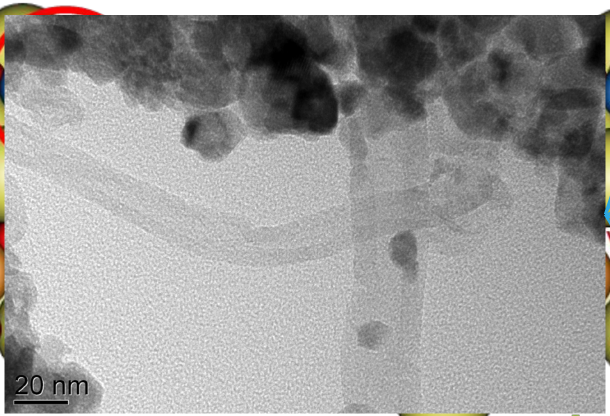
CO_2 successfully oxidizes catalyst, but CH_4 leaves residual strongly adsorbed carbonates

Current conclusions



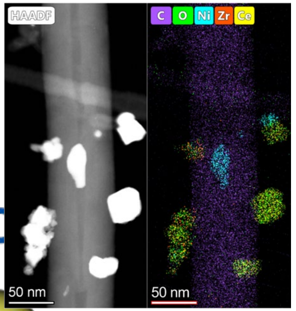
Good performance of 5wt.%Ni@$Ce_{0.6}Zr_{0.4}O_2$ catalyst in chemical looping of CH_4 and CO_2

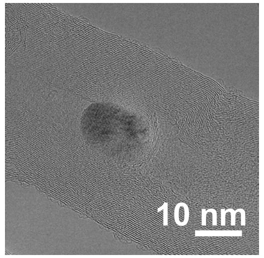
Evidence of amorphous and CNT on catalyst during CL

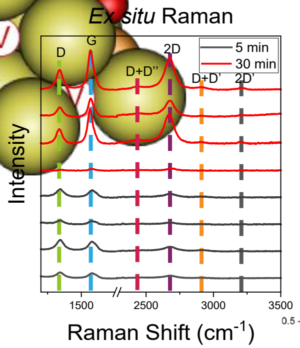


Performance	
X_{CH_4}	>96%
X_{CO_2}	>92.5%
S_{CO}	>92.5%
H_2/CO	~8

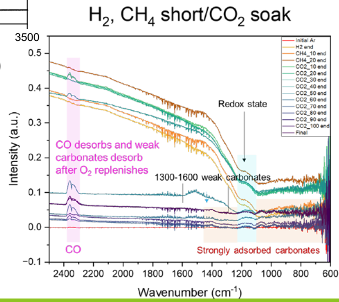
- Ni Catalyzed
- Ruptures CZO
- MWCNT
- Increasingly graphitic w/ TOS
- Harder to oxidize







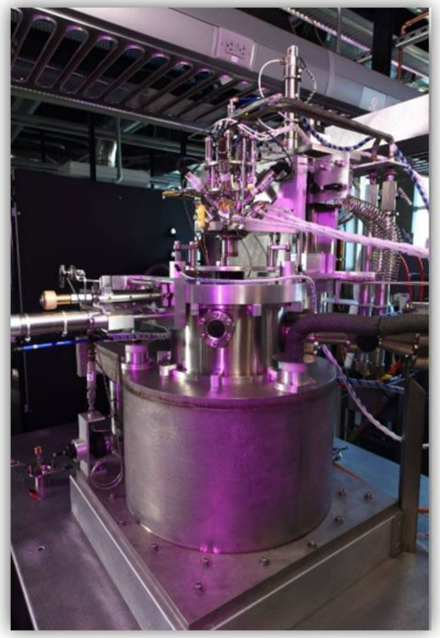
H_2/CO

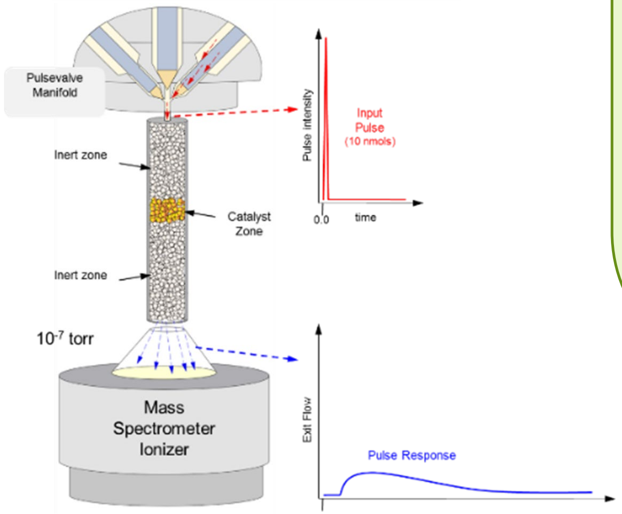


Help better predict reaction strategies to control C formation for the best chemical reaction kinetics with a stable catalyst

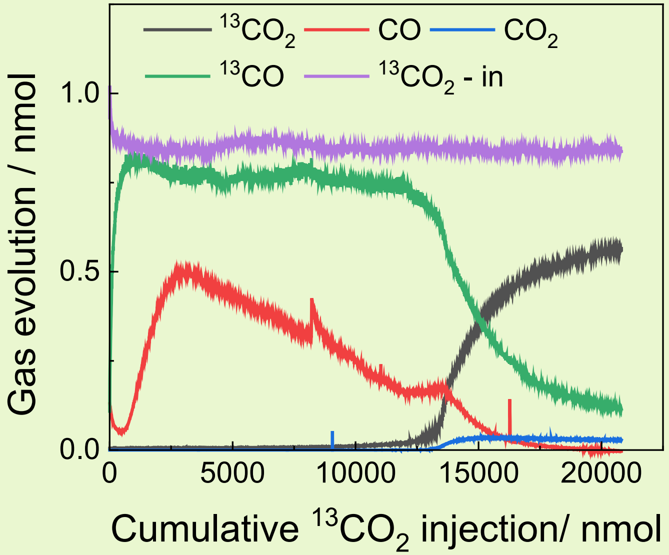
- E.g. Control CH_4 deposition of C to maintain easy to oxidize C

Future work





Temporal Analysis of Products



- Intrinsic surface reactions/kinetics
- Evolution as fn(reaction sites):
  - O_{vac}, C, Ni
- Reaction rate constants

XRD

- Bulk reduction state comparison at various redox states

In situ Raman

- Growth of surface C
- Role of different active sites during redox

Dynamic Oxygen Storage Capacity

- Total oxygen capacity
- Oxygen mobility rates

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- TEM/EDS

Questions?