Nano-engineered catalyst for the utilization of CO_2 in dry reforming to produce syngas

DOE Contract No. DE-FE0029760

Shiguang Li, ***Gas Technology Institute (GTI)***

Xinhua Liang, ***Missouri University of Science and Technology (Missouri S&T)***

CO_2 Capture Technology Project Review Meeting

August 21 - 25, 2017, Pittsburgh, PA

Project overview

- **Performance period**: July 1, 2017 – June 30, 2020
- **Funding**: $799,807 DOE ($200,000 co-funding), three year effort
- **Objectives**: Develop nano-engineered catalyst supported on high-surface-area ceramic hollow fibers for the utilization of CO_2 in dry reforming of methane ($CO_2 + CH_4 \rightarrow 2\ H_2 + 2\ CO$) to produce syngas
- **Team:**

Member	Roles
gti	• Project management and planning • Quality control, reactor design and testing • Techno-Economic Analysis (TEA) and life cycle analysis (LCA)
Missouri S&T	▪ Catalyst development and testing

Introduction to GTI and MS&T

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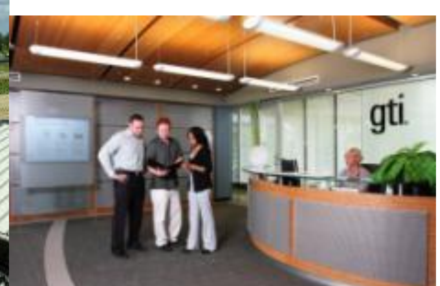
- **Not-for-profit** research company, providing energy and natural gas solutions to the industry since 1941
- **Facilities**: 18 acre campus near Chicago, 28 specialized labs



MISSOURI S&T
University of Science & Technology

- **Co-educational research university** located in Rolla, Missouri
- **Prof. Liang Group**: expertise in atomic layer deposition thin film coatings, catalyst synthesis and testing

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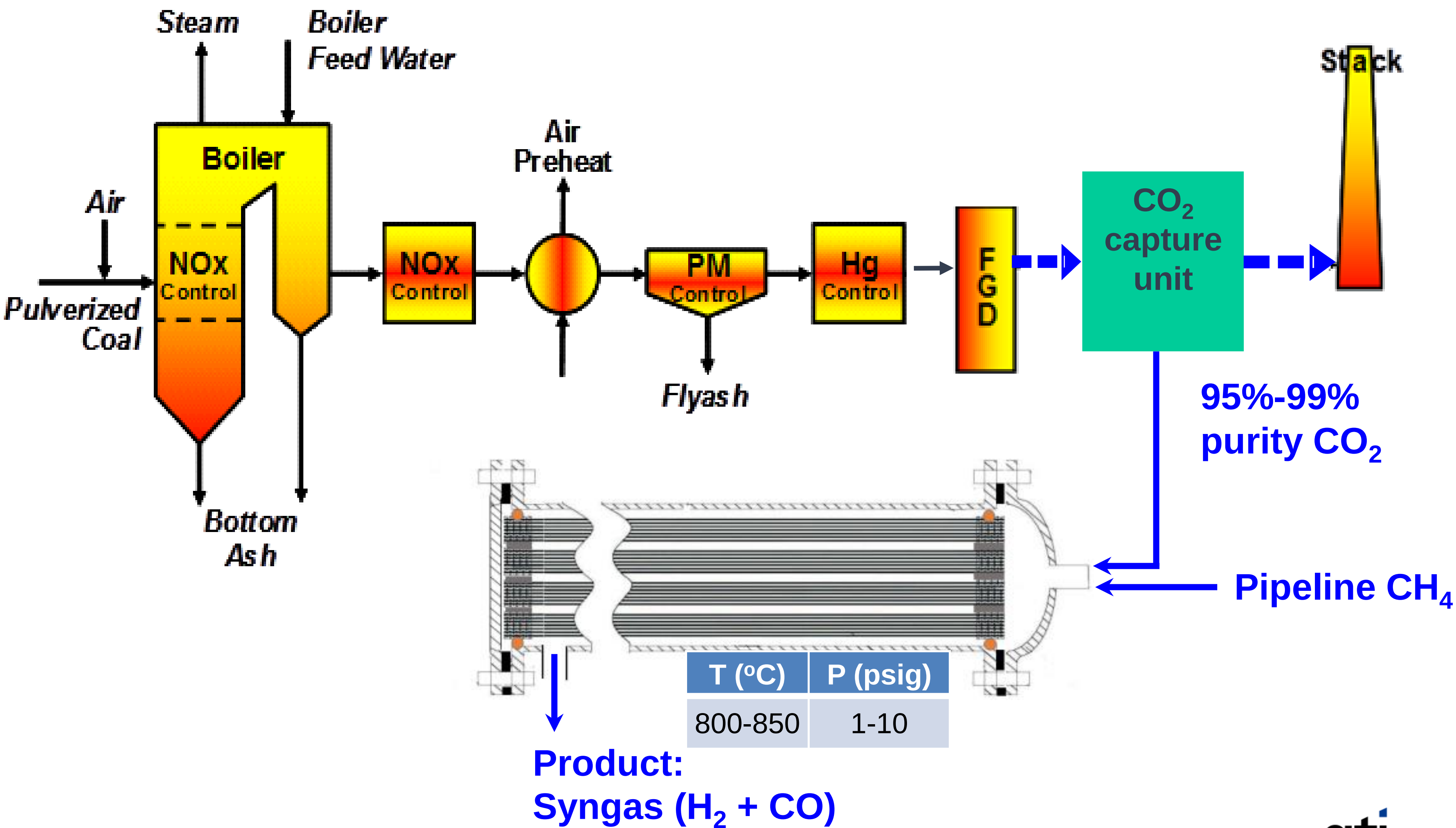
Process description



T (ºC)	P (psig)
800-850	1-10

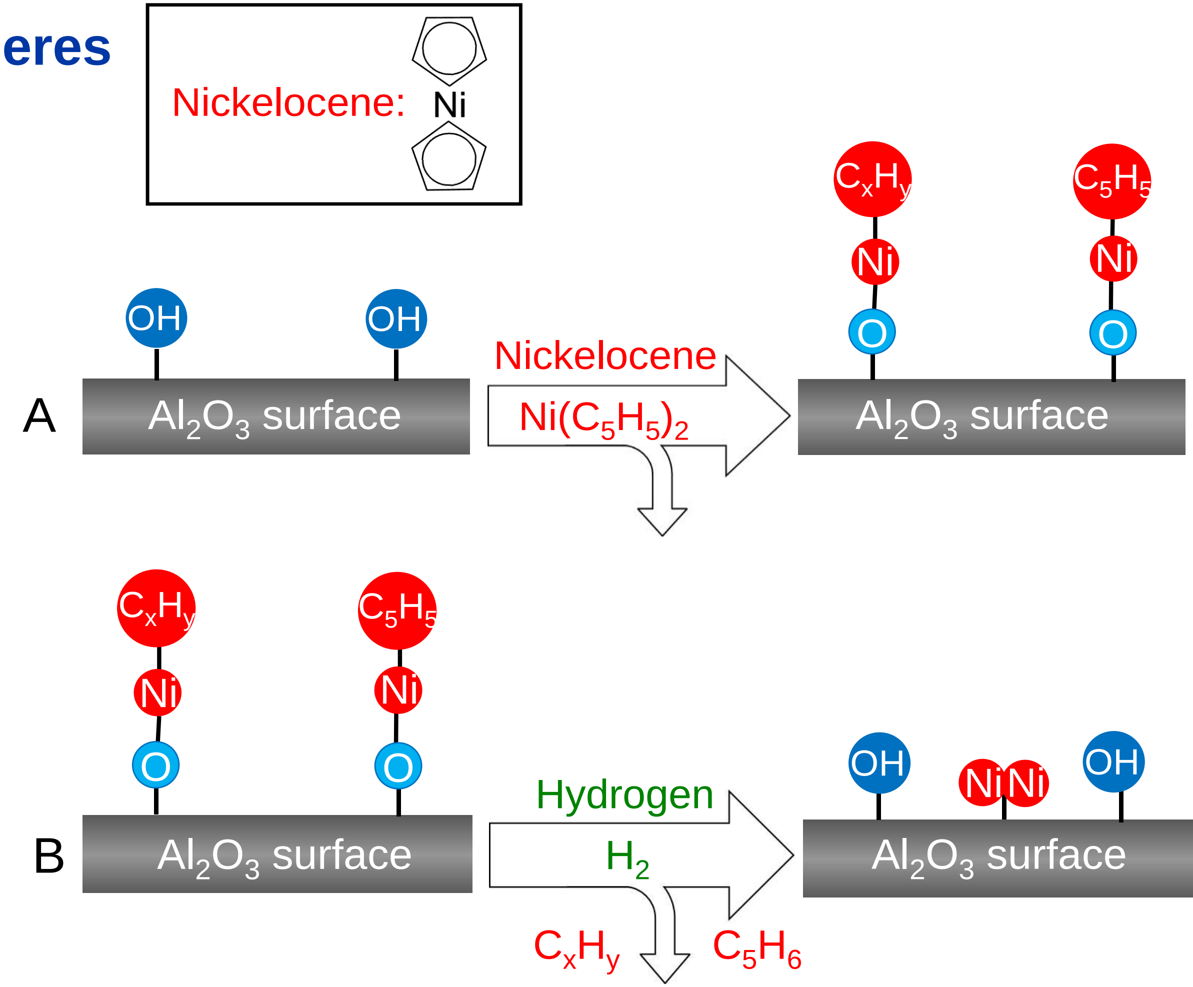
Dry reforming of methane using CO_2

- $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$ with H_2/CO ratio <1 due to the reverse water-gas shift reaction ($CO_2 + H_2 \rightleftharpoons CO + H_2O$)
  - Different from methane steam reforming ($CH_4 + H_2O \rightarrow CO + 3\,H_2$) where H_2/CO ratio >3 due to water-gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$)
- H_2/CO ratio can be adjusted by blending with products from steam reforming
- Typical catalysts:
  - **Precious metals** (Pt, Rh, Ru): expensive
  - **Low-cost Ni**: issue of sintering of the Ni particles

Nano-engineered Ni catalyst prepared by atomic layer deposition (ALD) may resolve sintering issue

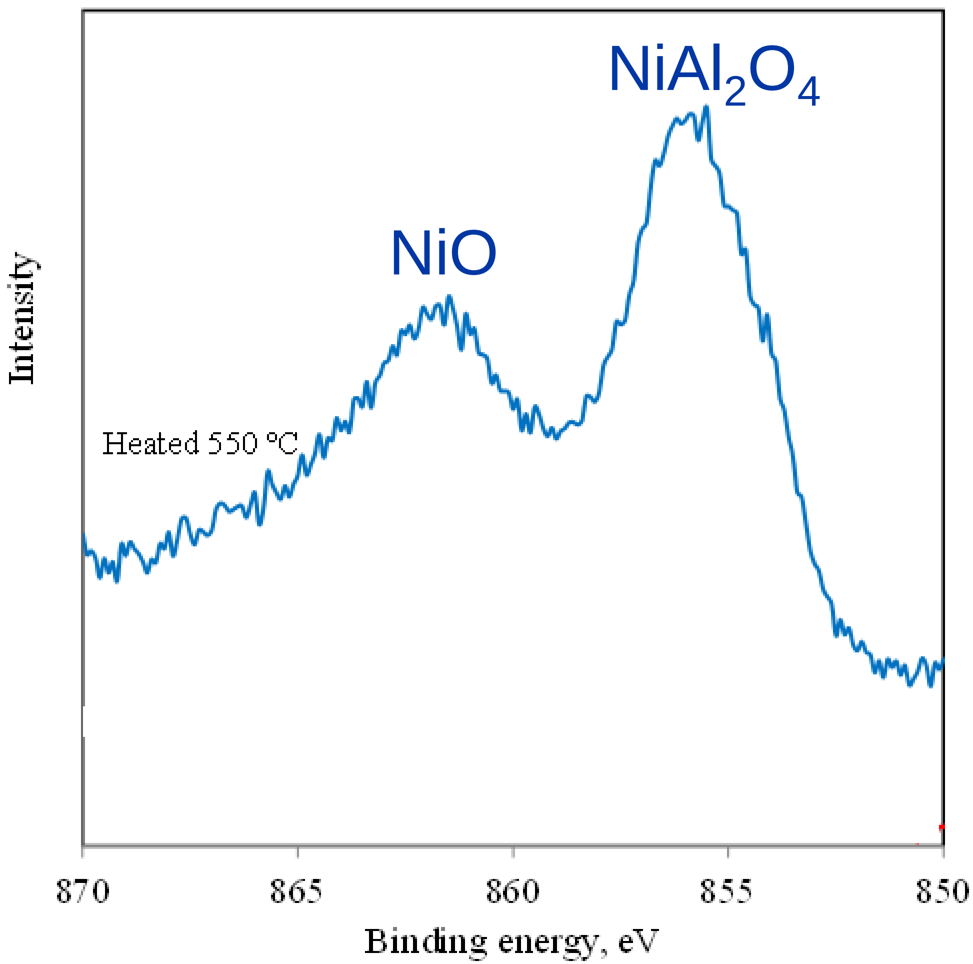
ALD of Ni on γ-alumina spheres

- Bis(cyclopentadienyl)nickel, $NiCp_2$, used as Ni precursor
- Self-limiting sequential surface chemical reaction



C Catalysts are calcined in air at 550 ^oC

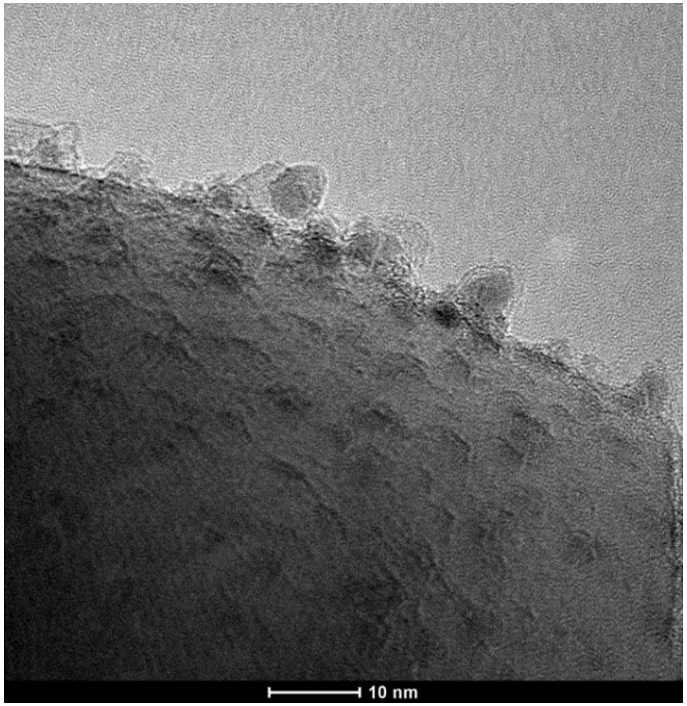
X-ray photoelectron spectroscopy (XPS) analysis

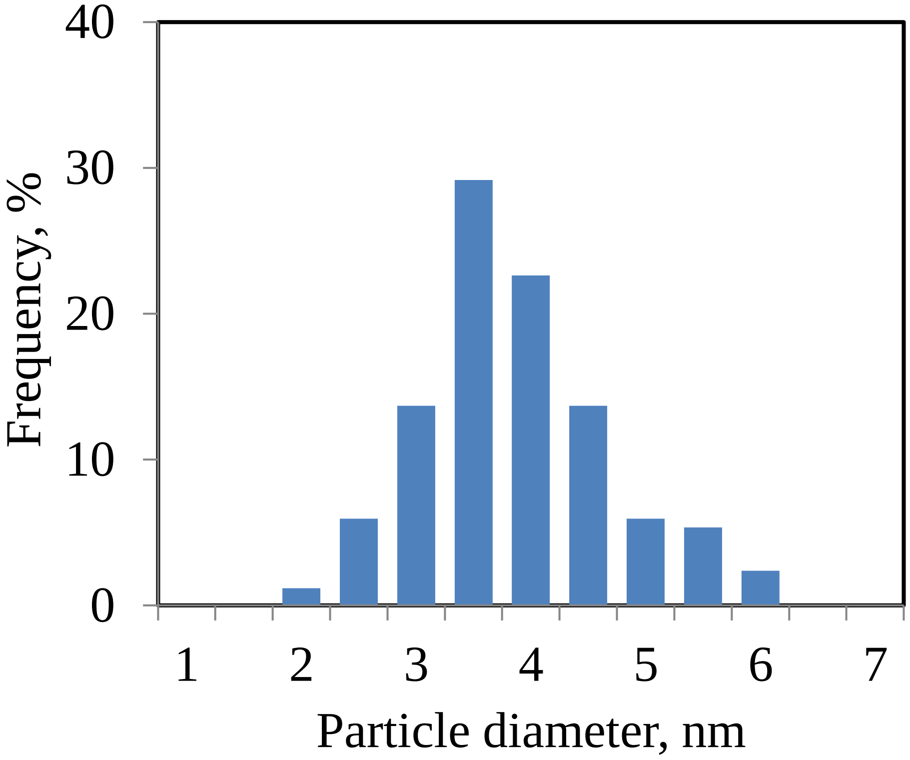


Z. Shang, et al., *Applied Catalysis B: Environmental*, 2017, 201, 302-309

TEM image of γ-Al_2O_3 supported Ni catalysts

- Particle size: 2-6 nm, average 3.6 nm
  - Particles prepared by traditional methods are ~10-20 nm





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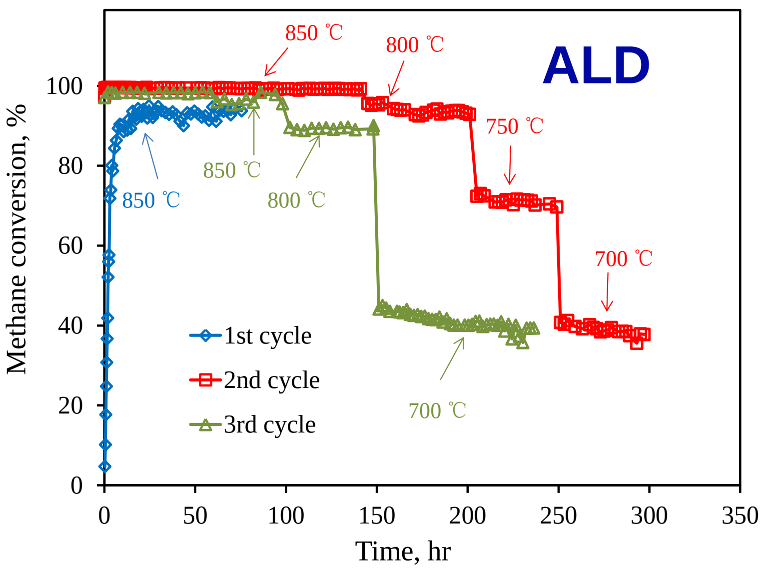
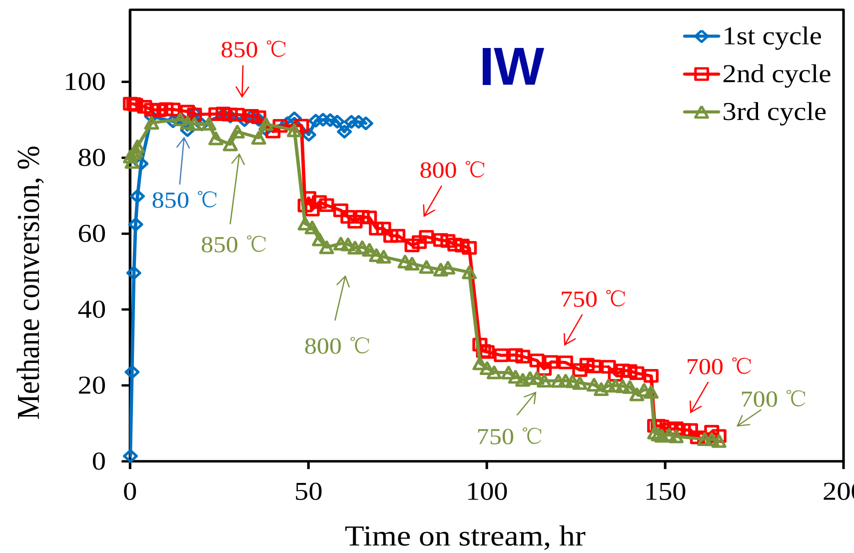
Advantages over traditional catalysts prepared by incipient wetness (IW)

- **Higher activity** due to highly dispersed nanoparticles: ~3.6 nm Ni particles compared to ~10-20 nm particles prepared by traditional method

Catalyst	CH_4 reforming rate ($L \cdot h^{-1} gNi^{-1}$)			H_2/CO ratio in the product		
	850°C	800°C	750°C	850°C	800°C	750°C
ALD	1840	1740	1320	0.82	0.78	0.68
IW	1700	1150	480	0.70	0.61	0.51

- **Better stability** due to strong bonding between nanoparticles and substrates since the particles are chemically bonded to the substrate during ALD





Novel α-Al_2O_3 hollow fiber with high packing density is being used as catalyst substrate in current project

Commercial substrates

Catalyst Geometry	SA/V (m^2/m^3)
1-hole	1,151
1-hole-6-grooves	1,733
4-hole	1,703
10-hole	2,013
Monolith	1,300
4-channel ceramic hollow fibers	**3,000**

Novel α-Al_2O_3 hollow fibers

- Four channels, 35 cm long
- OD of 3.2 mm and a channel inner diameter of 1.1 mm
- Geometric surface area to volume as high as 3,000 m^2/m^3
- Currently being tested in a packed bed reactor with catalyst supported on ~2-cm long fibers

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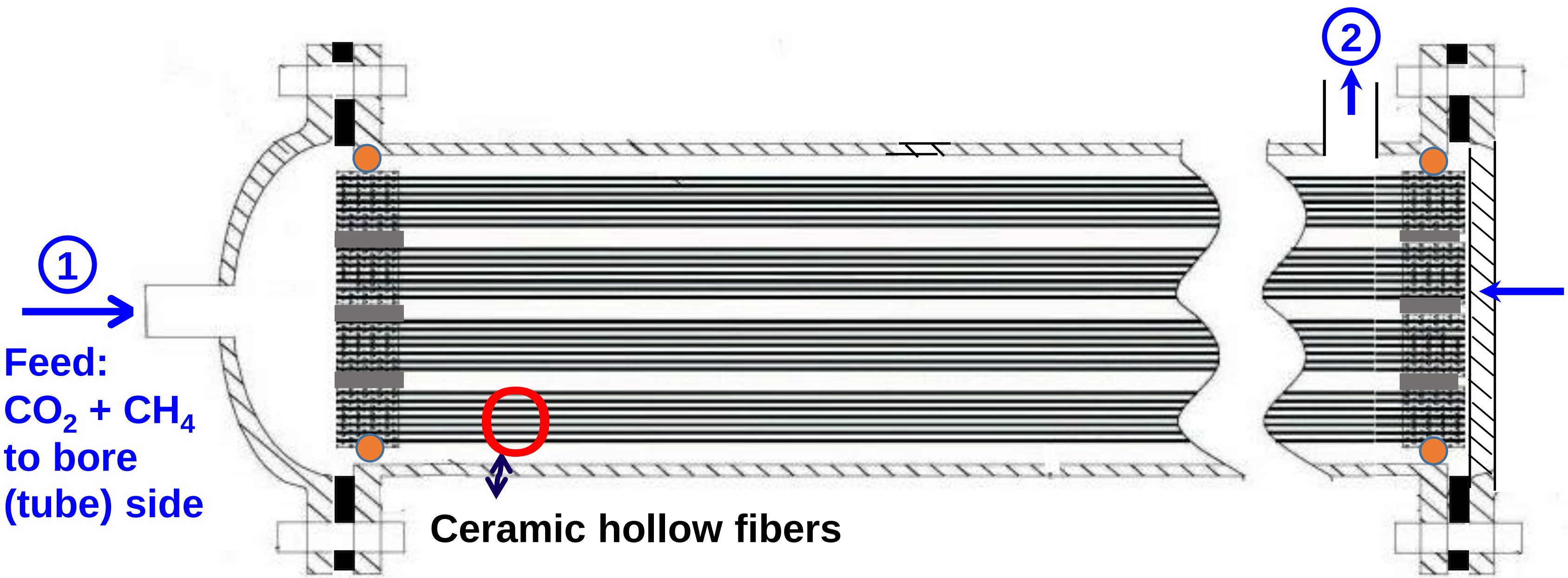
In addition to packed bed reactor, a pressure-driven transport reactor will be designed and tested

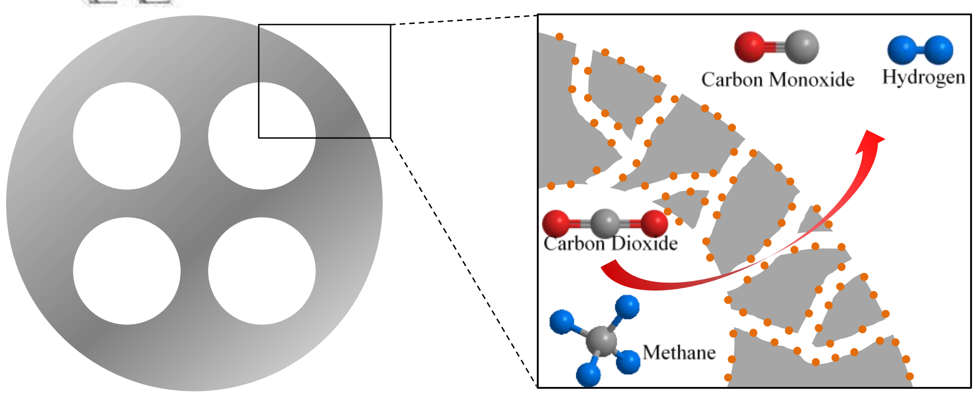
Product: syngas (H_2 + CO)
Collected from the shell side



Feed: CO_2 + CH_4 to bore (tube) side

Dead end

Ceramic hollow fibers



<u>Fiber internal surface, pores, and external surface</u> coated with catalysts for reactions:

$$CO_2 + CH_4 \rightarrow 2\ H_2 + 2\ CO$$

Overview/roadmap

Task 1: Project management and planning (*throughout the project*)

	Catalyst Development	System Design/Modification
BP1 (18 months)	Task 2.0 – Dry reforming catalyst (supported on ~2-cm long fibers) synthesis optimization, characterization and testing	Task 3.0 – Modification of ALD reactor for coating catalysts onto 20-cm long hollow fibers
	Task 4.0 – Deposition of catalyst onto 20-cm long hollow fibers using viscous flow ALD	
	Task 5.0 – Evaluation of 20-cm hollow fiber supported catalyst performance	
BP2 (18 months)	Task 6.0 – Further improvement of the hollow fiber supported catalyst	Task 7.0 – Design and construction of reactor containing multiple hollow fibers
	Task 9.0 – Catalyst support for deactivation and long-term stability tests	Task 8.0 – Catalytic reactor performance testing of the two configurations
		Task 10.0 – Catalyst deactivation and long-term stability tests
		Task 11.0 – Life cycle analysis and technical and economic feasibility study

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Key milestones and success criteria

Budget Period	Key Milestones	Planned Completion Date
1	**CH_4 conversion** >90%, **H_2/CO ratio** of 0.7-0.85, and **CH_4 reforming rate** >2,200 L/h/g_{Ni} at 800ºC and pressure of 15-25 psia	03/31/18
1	Hollow fiber supported catalyst shows CH_4 conversion >95%, H_2/CO ratio of 0.7-0.85, and CH_4 reforming rate >2,300 L/h/g_{Ni} at 800 ºC and 15-25 psia	12/31/18
1	200 hours testing shows CH_4 conversion decrease less than 20% at 800ºC and pressure of 15-25 psia	12/31/18
2	Reactor shows CH_4 conversion >95%, H_2/CO ratio of 0.7-0.85, and CH_4 reforming rate >2,200-2,500 L/h/g_{Ni} at 800ºC	09/30/19
2	**200 hours testing** shows CH_4 conversion decrease less than 10% at 800ºC	06/30/20
2	Issue topical report on TEA and LCA	06/30/20

Decision Point	Date	Success Criteria
Go/no-go decision points	12/31/18	1) Fiber supported catalyst shows CH_4 conversion >95%, H_2/CO ratio of 0.7-0.85, and CH_4 reforming rate >2,300 L/h/g_{Ni} at 800 ºC and 15-25 psia 2) 200 hours testing shows CH_4 conversion decrease less than 20% at 800ºC and 15-25 psia
Completion of the project	6/30/20	1) Catalytic reactor shows CH_4 conversion >95%, H_2/CO ratio of 0.7-0.85, and CH_4 reforming rate >2,200-2,500 L/h/g_{Ni} at 800ºC 2) 200 hours testing shows conversion decrease less than 10% at 800ºC

Preliminary risk assessment: technical challenges and mitigation strategies

Challenges/Risks

1) Longer-term stability of catalyst

Mitigation:
- 1a: Address any issues observed during a 200-hour testing
- 1b: Develop a catalyst regeneration process

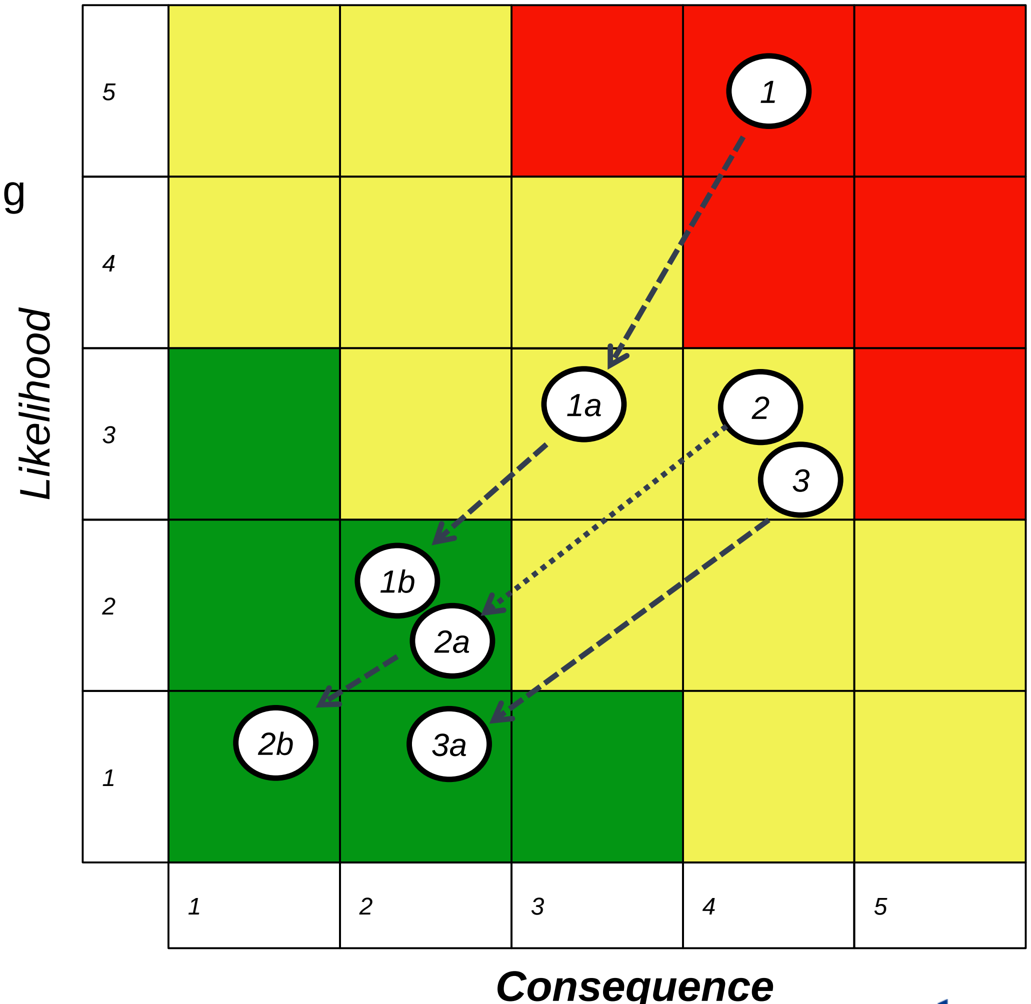
2) Catalytic reactor sealing/potting

Mitigation:
- 2a: Use advanced potting materials
- 2b: Leave the potting ends in a lower temperature zone

3) Pressure-driven transport configuration not as good as expected

Mitigation:
- 3a: Alternate designs

Risk summary



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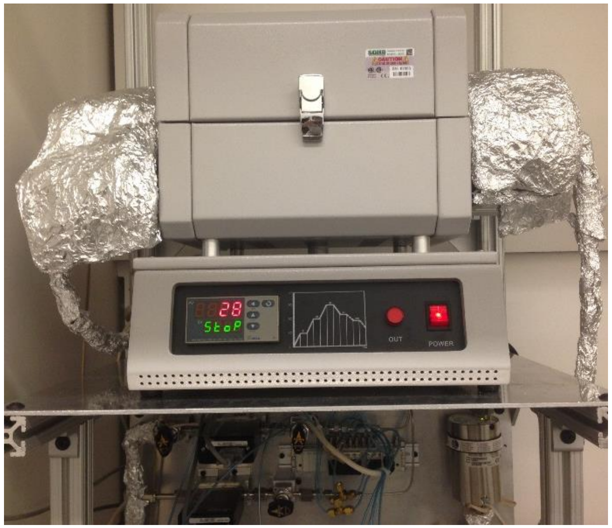
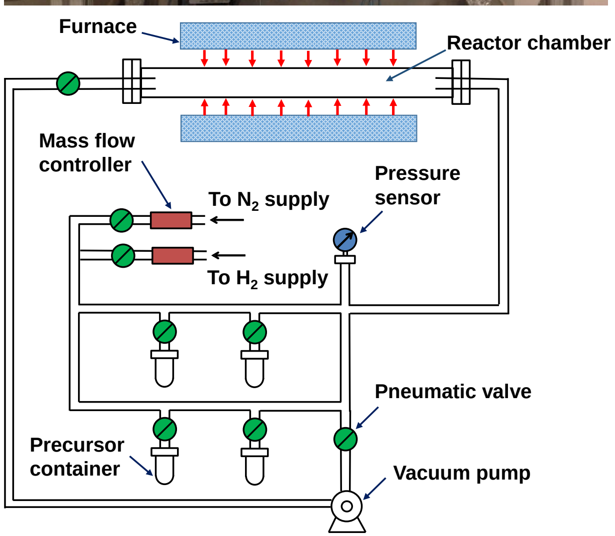
Equipment for catalyst development and testing





Horizontal ALD reactor at Missouri S&T

Packed bed catalytic reactor at Missouri S&T

Catalytic reactor at GTI

Preliminary results: ALD Ni/α-Al_2O_3 hollow fiber shows higher CH_4 reforming rate than ALD Ni/γ-Al_2O_3

- Nickel nanoparticles successfully deposited on α-Al_2O_3 hollow fibers by ALD
- Dry reforming performance:

Catalyst	CH_4 reforming rate ($L \cdot h^{-1} gNi^{-1}$)			
	850°C	800°C	750°C	700°C
ALD Ni/γ-Al_2O_3 porous particles	1840	1740	1320	720
ALD Ni/α-Al_2O_3 hollow fiber	1970	2040	1770	980

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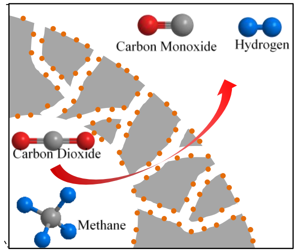
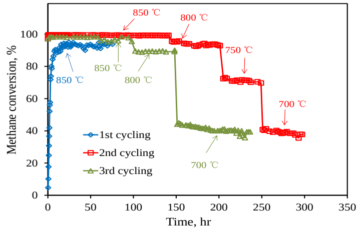
Summary

- We are developing ALD nano-engineered catalysts for utilization of CO_2 in dry reforming of methane to produce syngas
- ALD nano-engineered catalyst improves catalytic activity and stability
- Novel α-Al_2O_3 hollow fiber increases surface area, and enables pressure-driven transport reactor configuration
- Preliminary study indicated that Ni catalyst supported on α-Al_2O_3 hollow fiber had higher reforming rate than that on the γ-Al_2O_3 porous particles





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Acknowledgements

- **Financial and technical support**

U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

DE-FE0029760

- **NETL Project Manager Bruce Lani**

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