the Energy to Lead

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

DOE Contract No. DE-FE0029760

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Kickoff Meeting

September 12, 2017

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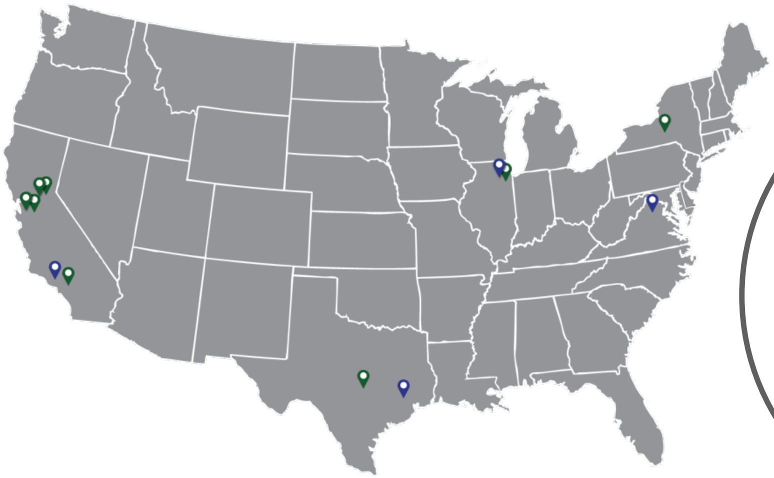
Outline

- Introduction to team members
- Project overview
- Technology fundamentals/background
- Research plan
- Preliminary results

Introduction to GTI

- Research organization, providing energy and environmental solutions to the government and industry since 1941
- Facilities: 18 acre campus near Chicago



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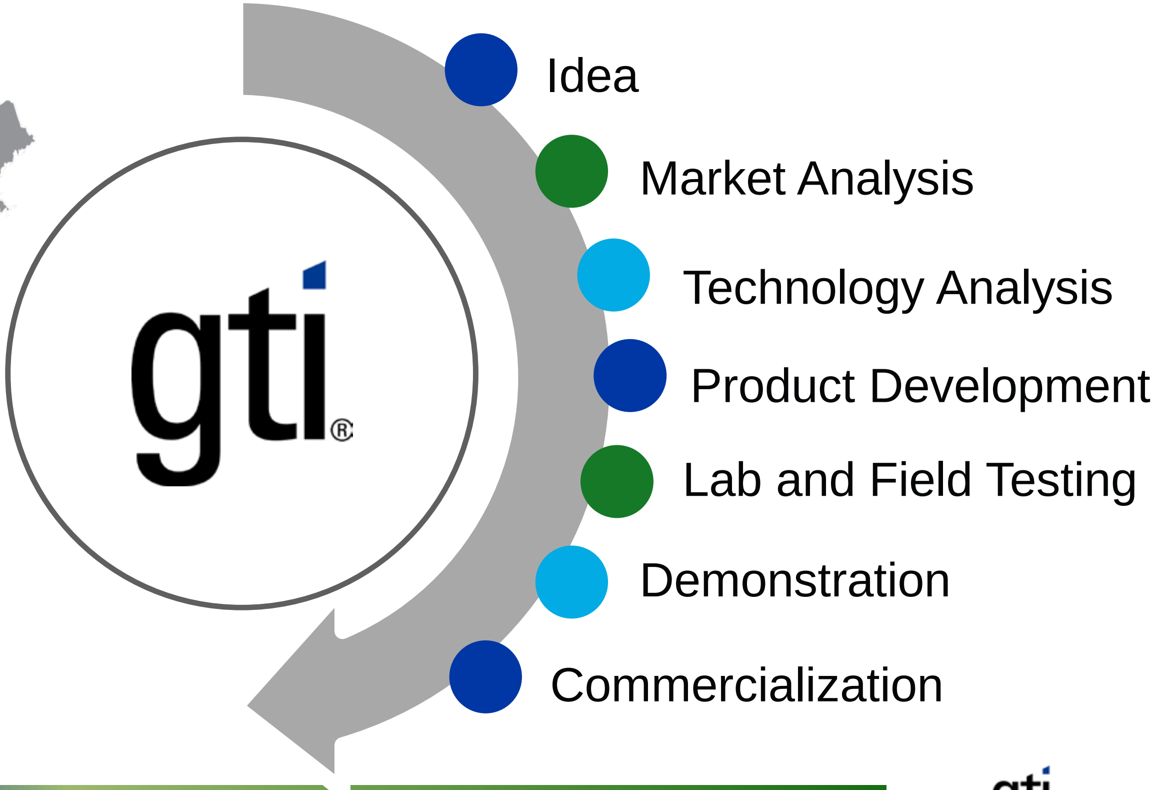

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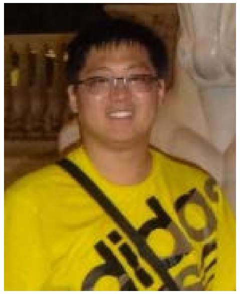
Introduction Missouri S&T

MISSOURI S&T
University of Science & Technology

- **<u>Co-educational research university</u>** located in Rolla, Missouri
- **<u>Prof. Liang Group</u>**: expertise in atomic layer deposition thin coatings, catalyst preparation, characterization, and testing

Dr. Xinhua Liang



Zeyu Shang

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Han Yu

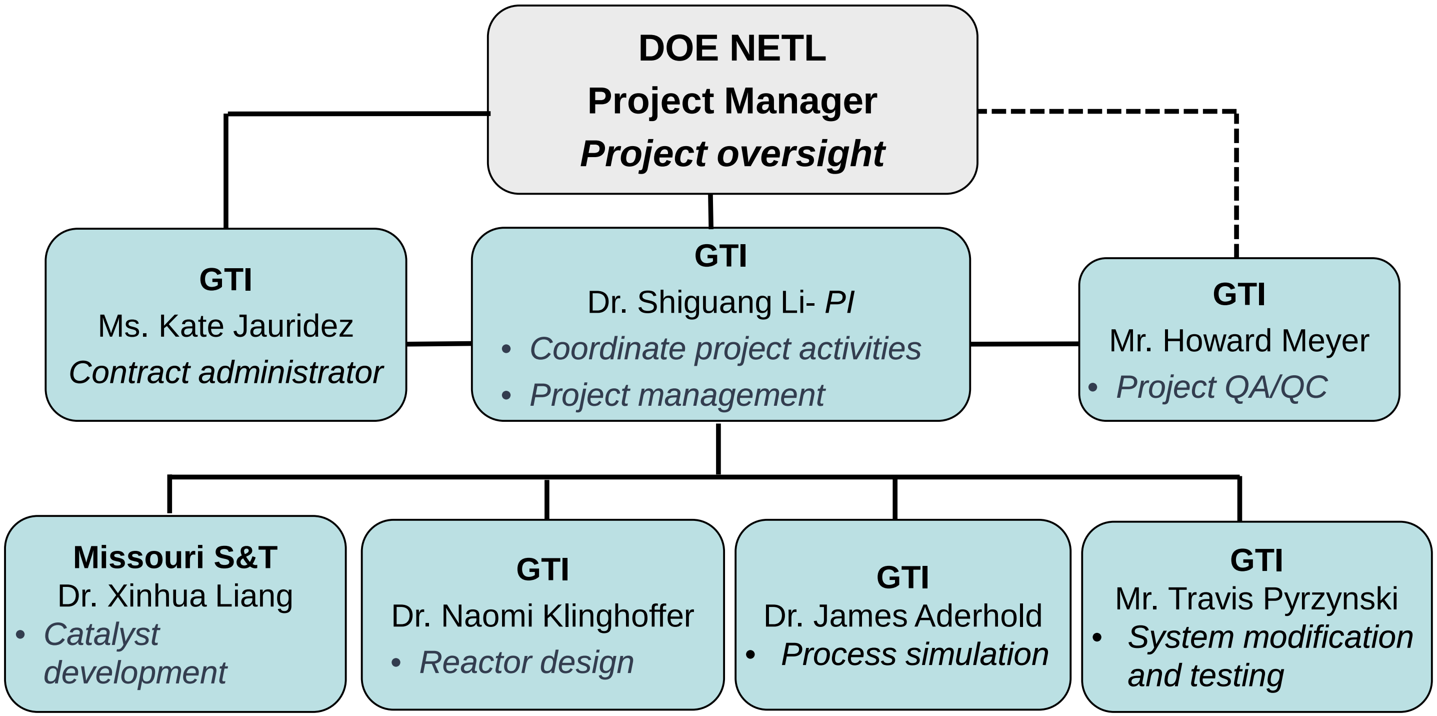
Ye Jin

Project overview

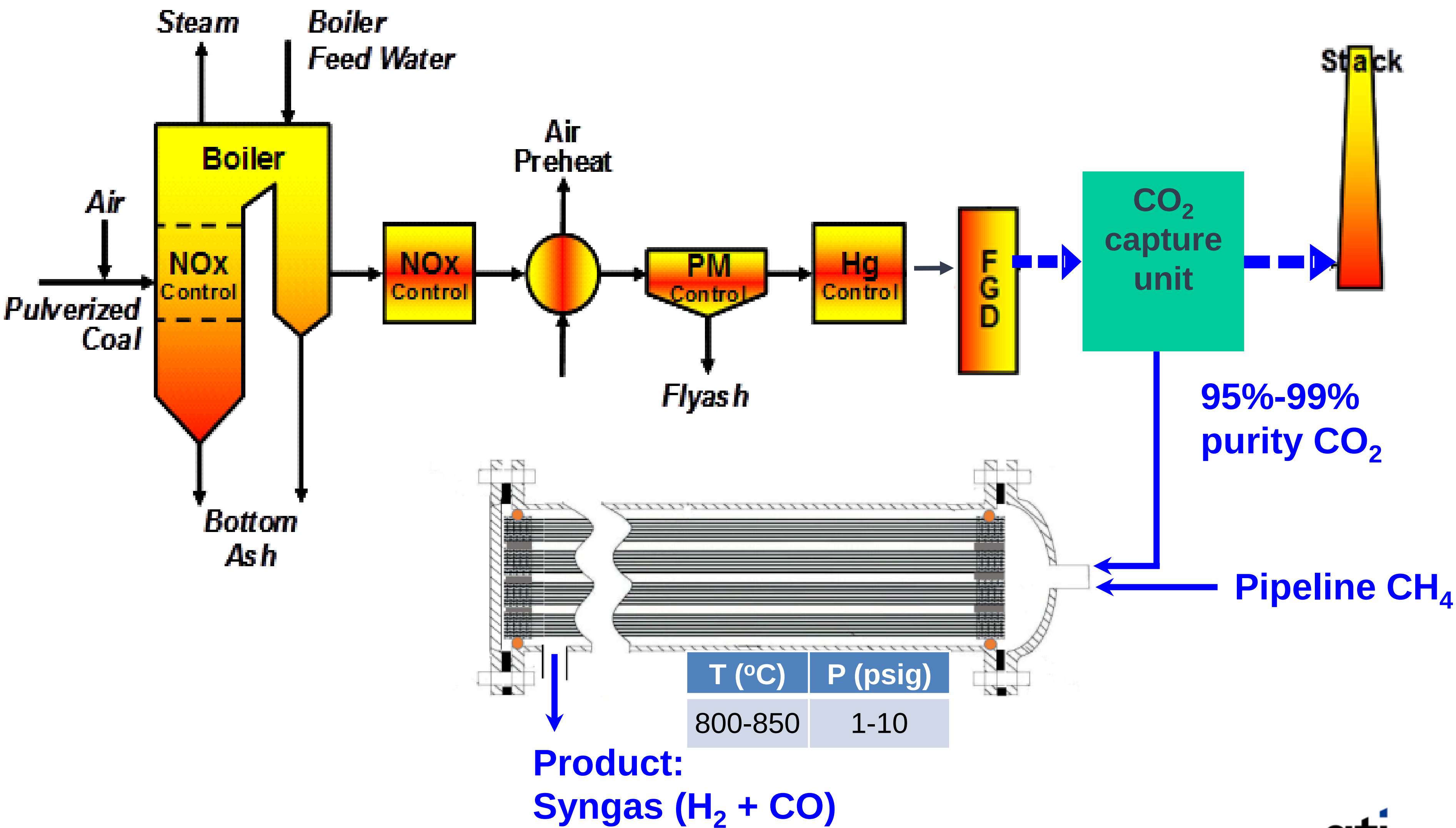
- **Performance period**: July 1, 2017 – June 30, 2020
- **Funding**: $799,807 DOE ($199,990 co-funding), three year effort
- **Objectives**: Develop nano-engineered catalyst supported on high-surface-area ceramic hollow fibers for the utilization of CO_2 in dry reforming of methane ($CO_2 + CH_4 \rightarrow 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

Project organization and structure



Process description



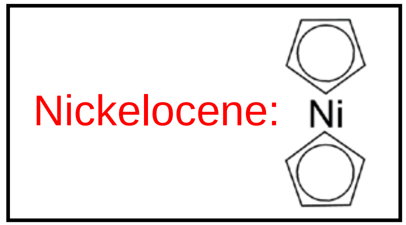
T (ºC)	P (psig)
800-850	1-10

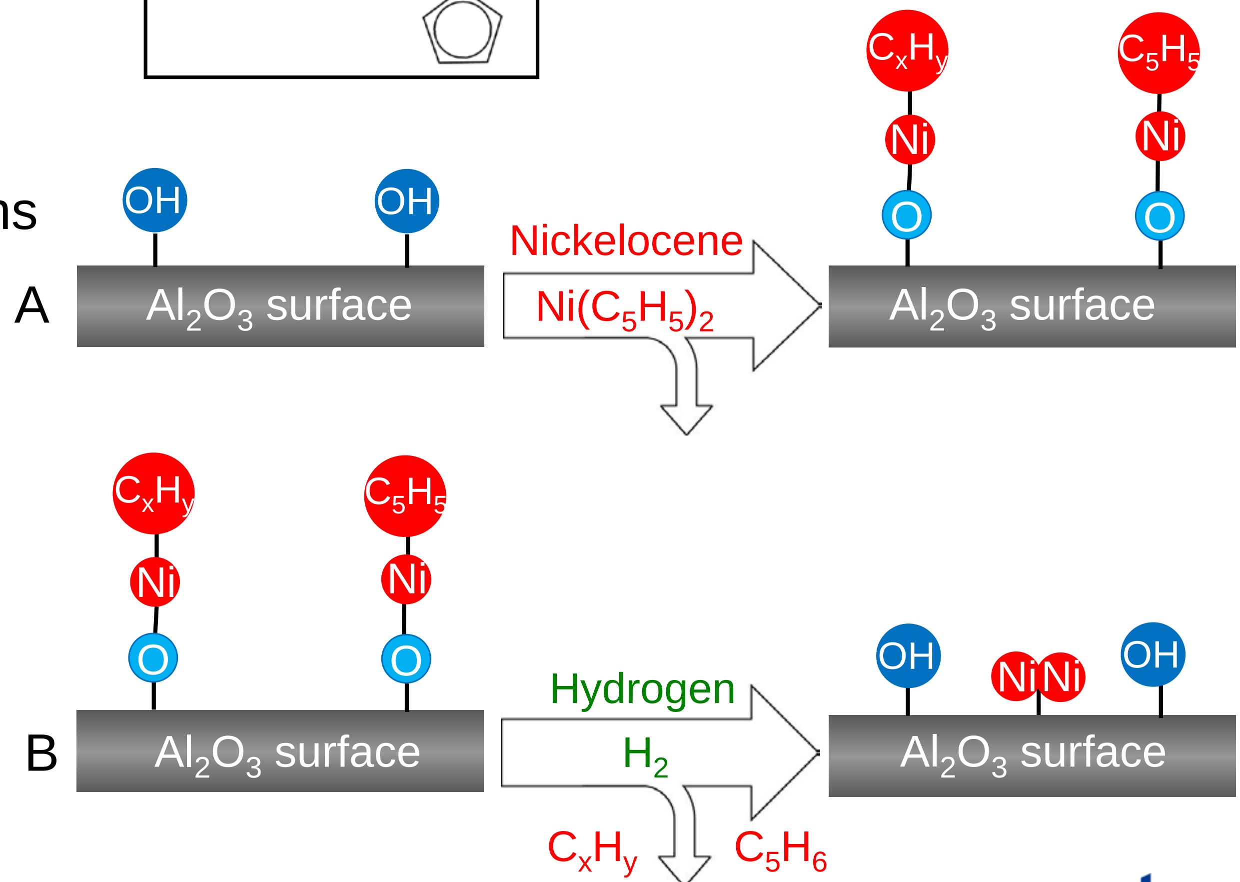
Dry reforming of methane using CO_2

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

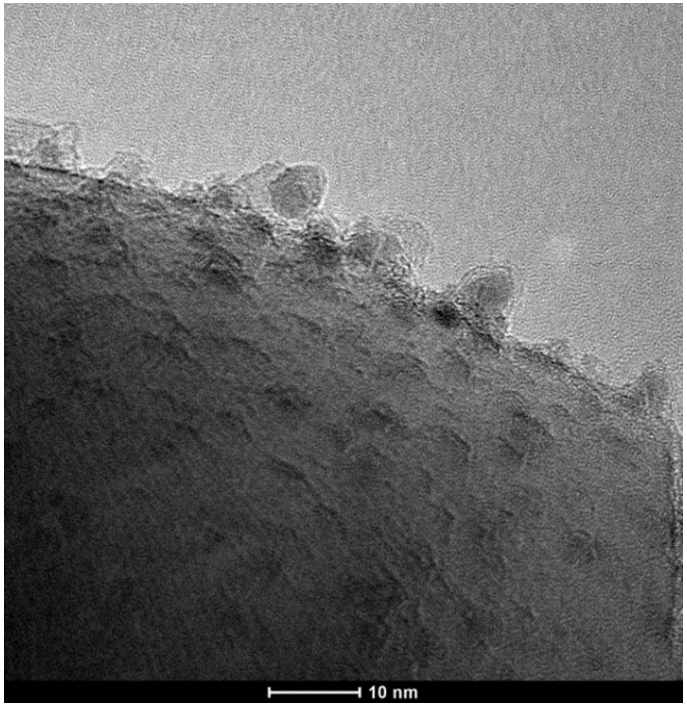
- Bis(cyclopentadienyl)nickel, $Ni(Cp_2)$, used as a precursor
- Self-limiting sequential surface chemical reactions

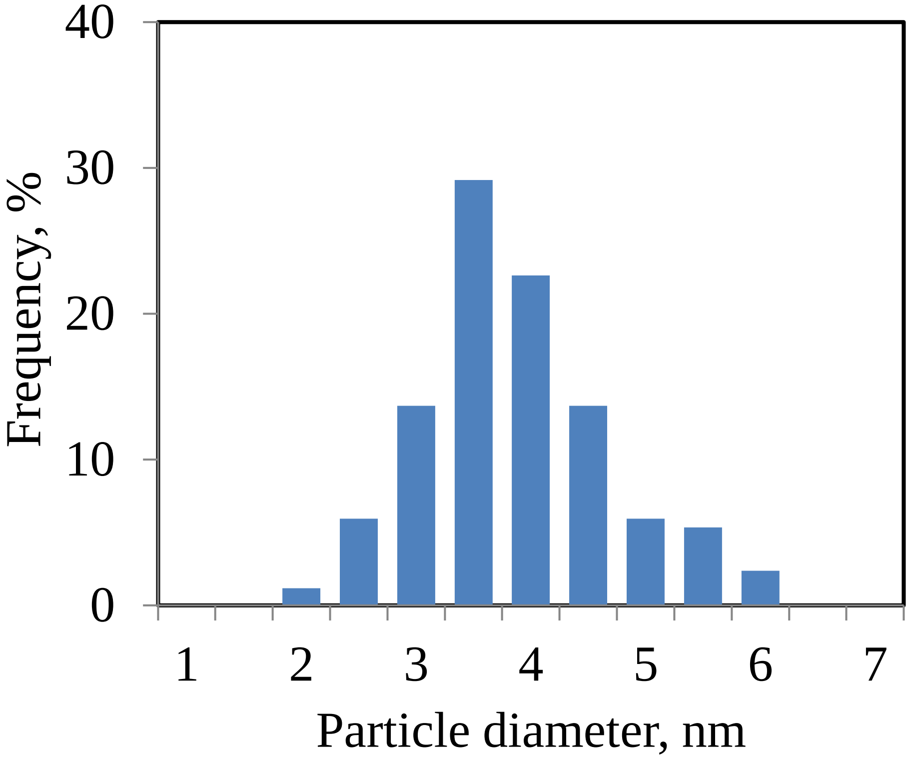




TEM image of γ-Al_2O_3 spheres supported Ni catalysts

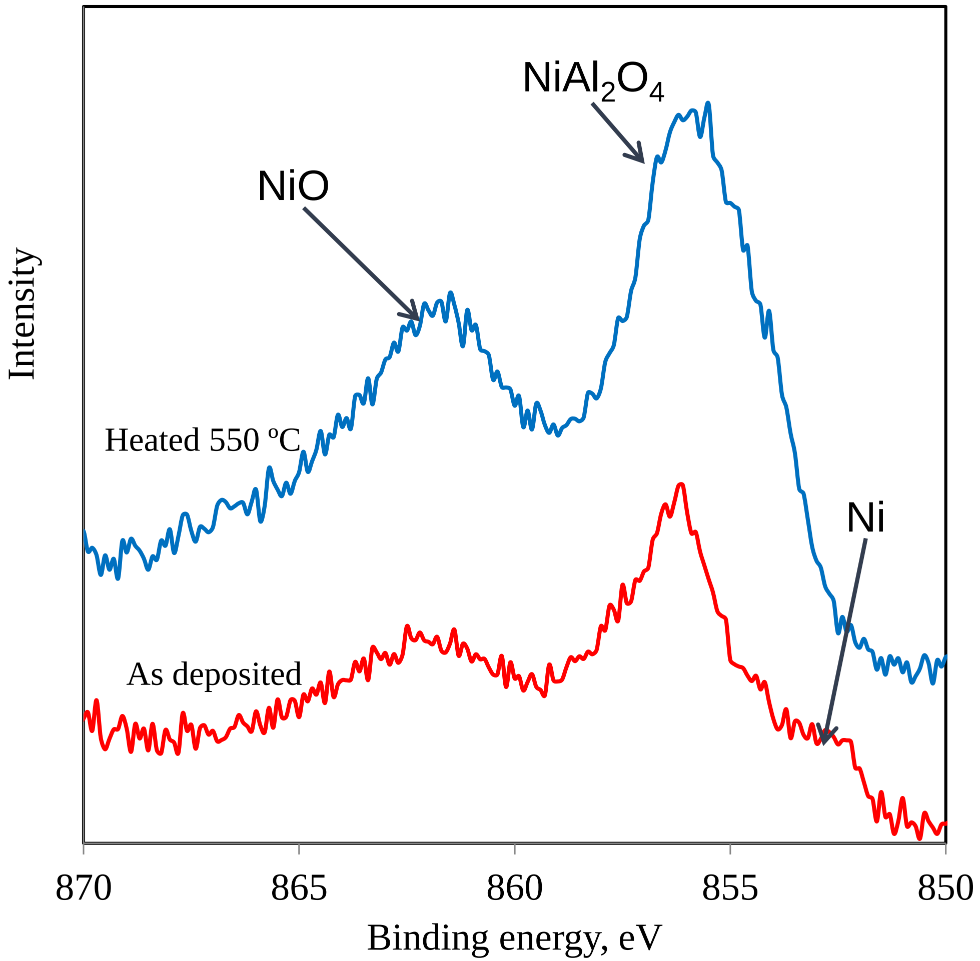
- Ni particle size: 2-6 nm, average 3.6 nm
  - Particles prepared by traditional methods are ~10-20 nm
- Smaller nanoparticles can increase active sites





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

X-ray photoelectron spectroscopy (XPS) analysis indicates the presence of $NiAl_2O_4$



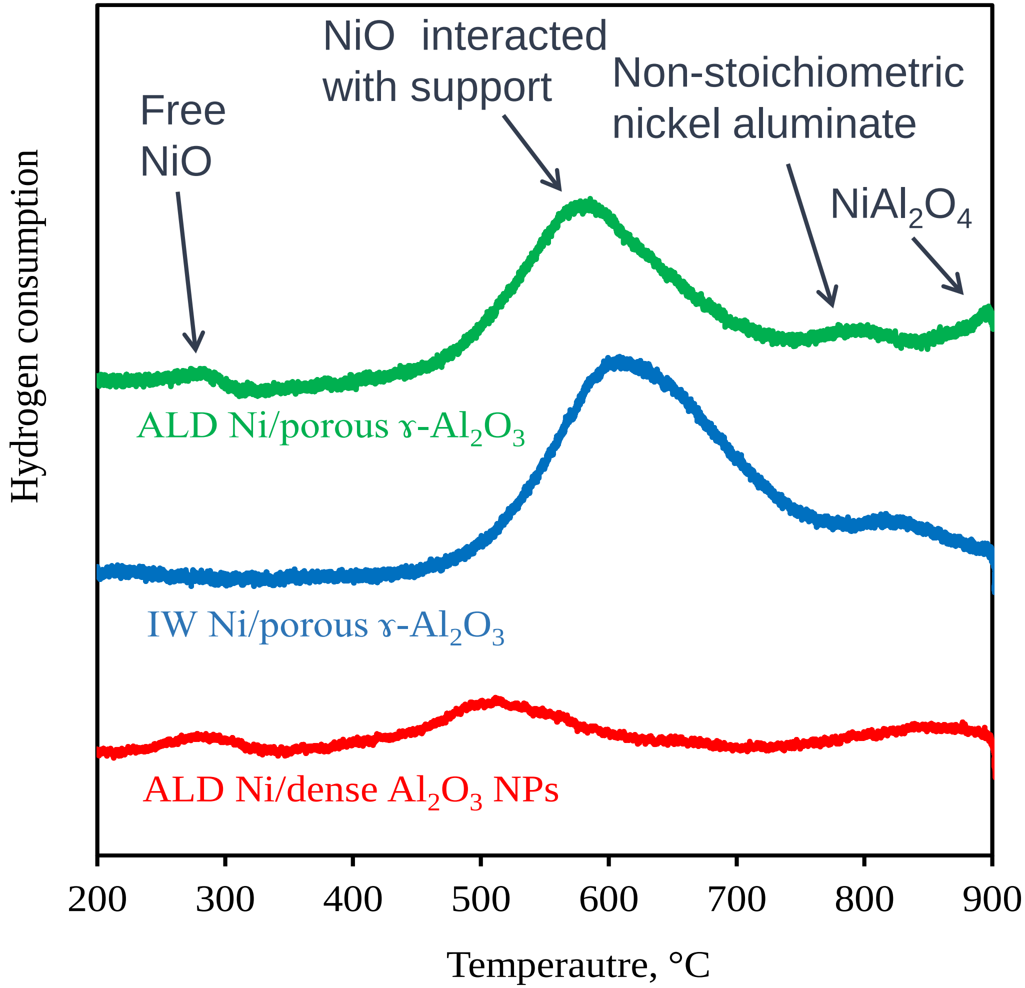
- Metallic Ni can be observed on as-deposited Ni/Al_2O_3 catalyst
- Metallic Ni was oxidized to NiO and $NiAl_2O_4$ when catalysts were calcined in air at 550ºC

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

H_2-Temperatrue programmed reduction (TPR) analysis

- $NiAl_2O_4$ spinel would form in the Ni ALD process.

- No $NiAl_2O_4$ spinel would form for Ni catalysts prepared by conventional method.



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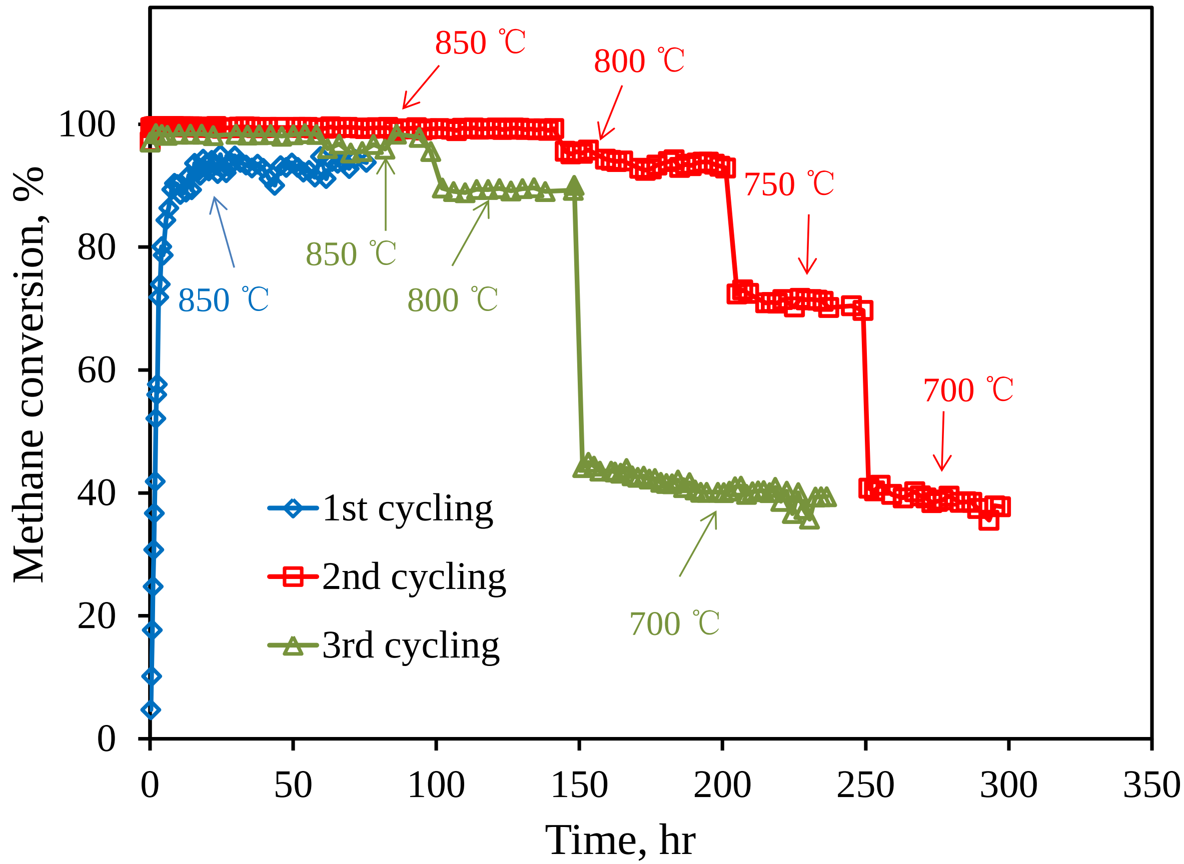
Performance of ALD Ni/γ-Al_2O_3 catalyst



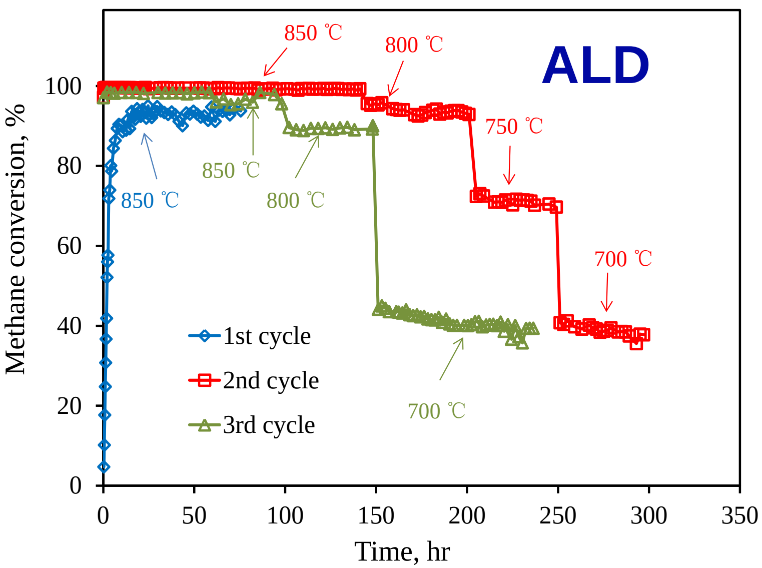
- Catalyst was regenerated by oxidation and reduction between cycles
- Conversion stable at 850 ºC after 140 hours in 2nd cycle
- Only slight deactivation at lower temperatures (<3% in 50 hours)

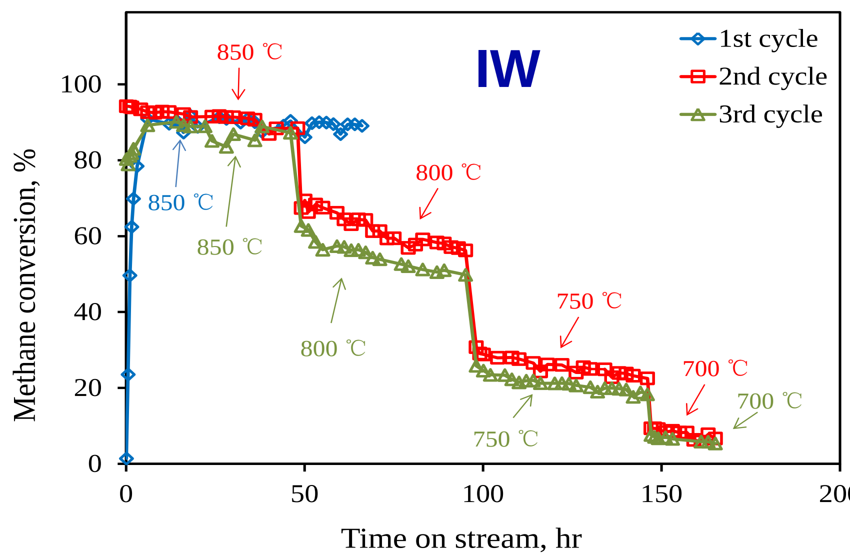
Advantages over traditional catalysts prepared by incipient wetness (IW)

- **<u>Higher activity</u>** due to highly dispersed nanoparticles: ~3.6 nm Ni particles compared to ~10-20 nm particles prepared by traditional methods

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

- **<u>Better stability</u>** 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

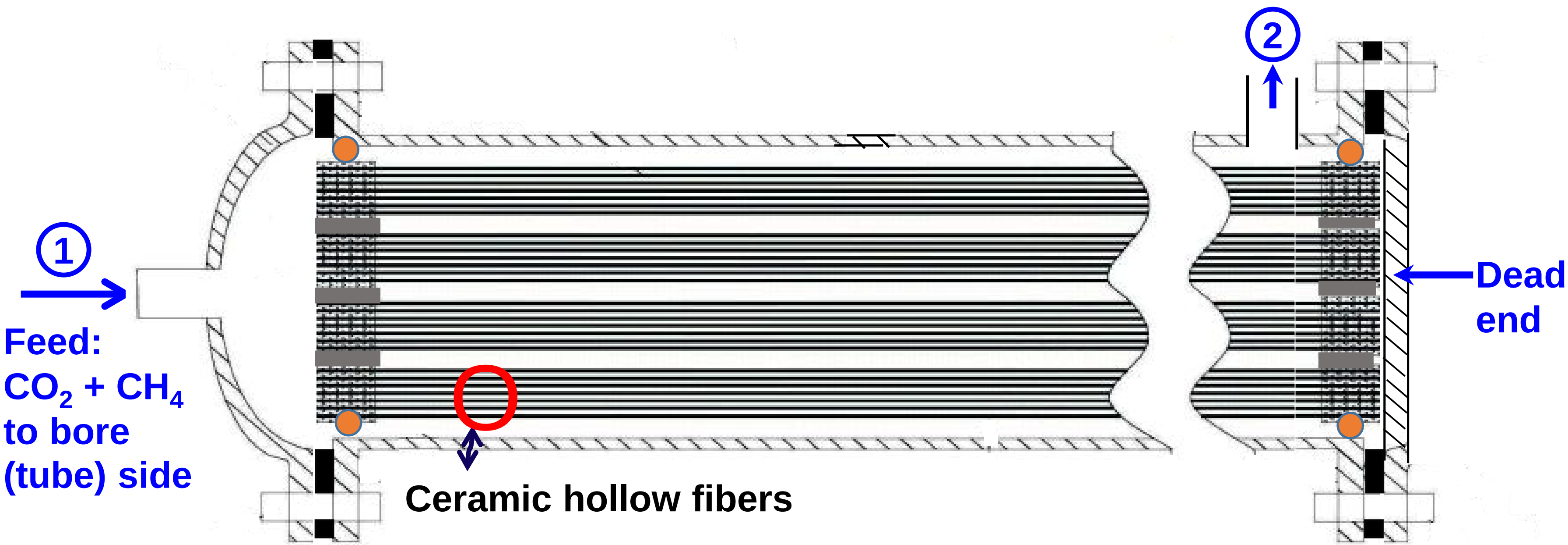
Commercial substrates

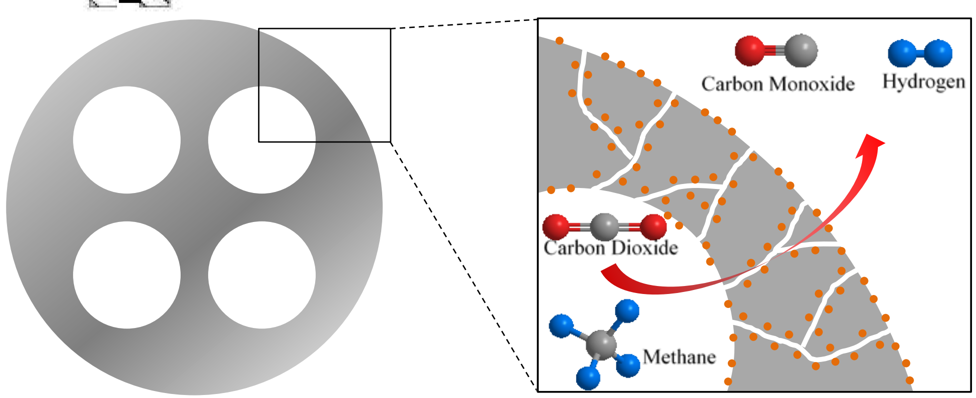
Catalyst Geometry	SA/V (m^2/m^3)
1-hole	1,151
1-hole-6-grooves	1,733
4-hole	1,703
10-hole	2,013
Monolith	1,300
4-channel ceramic hollow fibers	**3,000**

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

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





<u>Fiber internal surface, pores, and external surface</u> deposited 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 ~1-2-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

Project funding profile

	Budget Period 1		Budget Period 2		Total Project	
	07/01/2017-12/31/2018		01/01/2018-06/30/2020			
	Government Share	Cost Share	Government Share	Cost Share	Government Share	Cost Share
GTI	$70,026	$15,136	$329,775	$49,854	$399,802	$64,990
Missouri S&T	$230,830	$66,813	$169,176	$68,187	$400,005	$135,000
Total	$300,856	$81,949	$498,951	$118,041	$799,807	$199,990
Cost Share	79%	21%	81%	19%	80%	20%

Milestones

Budget Period	Task/ Subtask Number	Milestone Title/Description	Completion Date	
			Planned	Actual
1	1	Updated Project Management Plan.	08/31/17	07/03/17
1	1	Kickoff Meeting.	09/30/17	09/12/17
1	2	Catalyst showed 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 15-25 psia.	03/31/18	
1	3, 4	Hollow fiber supported catalyst showed CH_4 conversion >95%, H_2/CO ratio in the range of 0.7-0.85, and CH_4 reforming rate >2,300 $L/h/g_{Ni}$ at 800 ºC and pressure of 15-25 psia.	12/31/18	
1	5	200 hours testing showed CH_4 conversion decrease less than 20% at 800ºC and pressure of 15-25 psia.	12/31/18	
1	1	Submit Continuation Application.	10/01/18	
2	6	20 pieces of 20-cm long hollow fibers coated with catalysts shipped to GTI for testing in catalytic reactor.	09/30/19	
2	7	Reactors containing multiple hollow fibers passed commissioning testing.	03/31/19	
2	8	Catalytic reactor showed 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	9,10	200 hours testing in catalytic reactor showed conversion decrease less than 10% at 800ºC.	06/30/20	
2	11	Issue topical report on technical and economic feasibility and life cycle analysis	06/30/20	
2	1	Submit Final Technical Report.	07/30/20	

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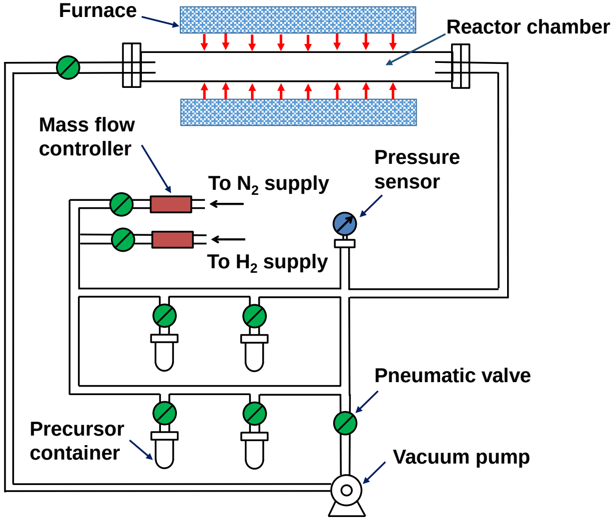
Success criteria

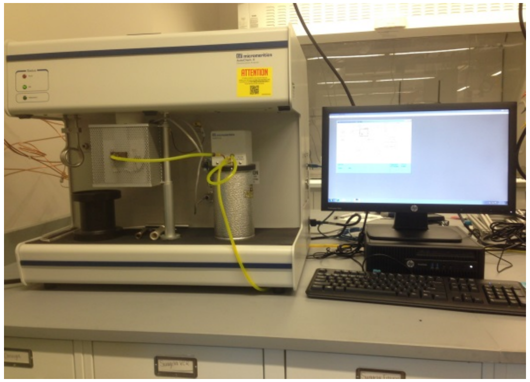
Decision Point	Date	Success Criteria
Go/no-go decision points	12/31/18	1) Fiber supported catalyst shows CH_4 conversion >95%, H_2/CO ratio of 0.7-0.85, and CH_4 reforming rate >2,300 $L/h/g_{Ni}$ at 800 ºC and 15-25 psia 2) 200 hours testing shows CH_4 conversion decrease less than 20% at 800ºC and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

Equipment for catalyst development at Missouri S&T



Horizontal ALD reactor

Autosorb-1 physisorption



AutoChem II 2920 chemisorption

Packed bed catalytic reactor

Catalyst development strategies

Current status

ALD Ni/α-Al_2O_3 hollow fiber (1-cm long)

⇩

Improvement

ALD Ni/α-Al_2O_3 hollow fiber (1-cm long)

⇩

Scale-up

ALD Ni/α-Al_2O_3 hollow fiber (20-cm long)

Equipment for catalyst testing at GTI

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:

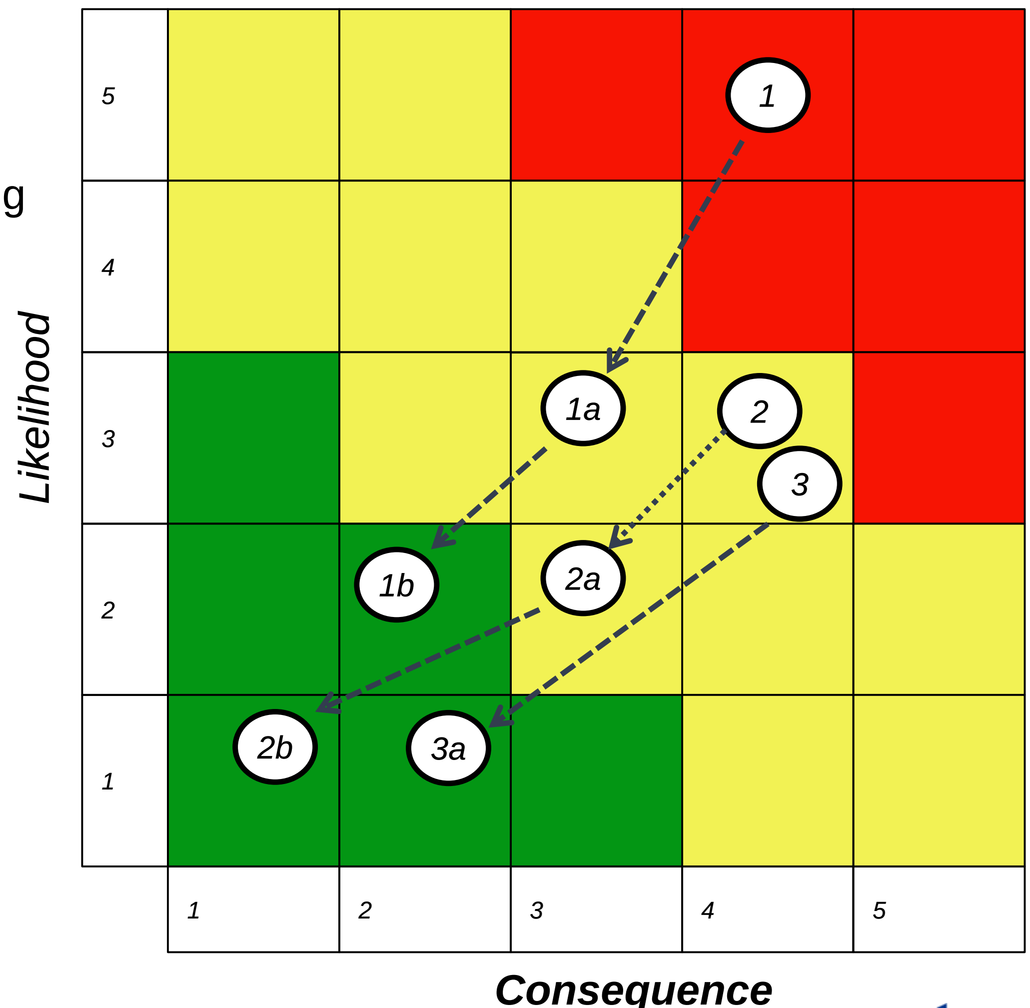
- 2a: Use advanced potting materials
- 2b: Leave the potting ends in a lower temperature zone

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

Mitigation:

- 3a: Alternate designs

Risk summary



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

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 sphere	1840	1740	1320	720
ALD Ni/α-Al_2O_3 hollow fiber	1970	2040	1770	980

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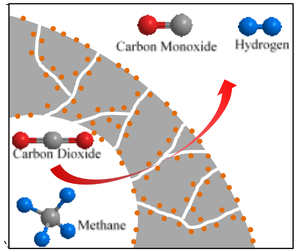
Plans for future development

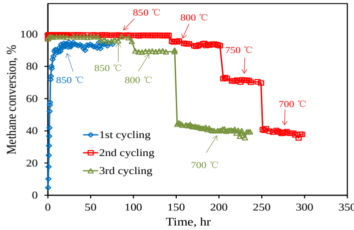
- **In this project**
  - Project just started, will focus on project work and meeting milestones

- **After this project**
  - Test with real captured CO_2 from our CO_2 capture system

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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- Financial and technical support

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