the Energy to Lead

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

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NATIONAL ENERGY TECHNOLOGY LABORATORY

CO_2 Capture Technology Project Review Meeting

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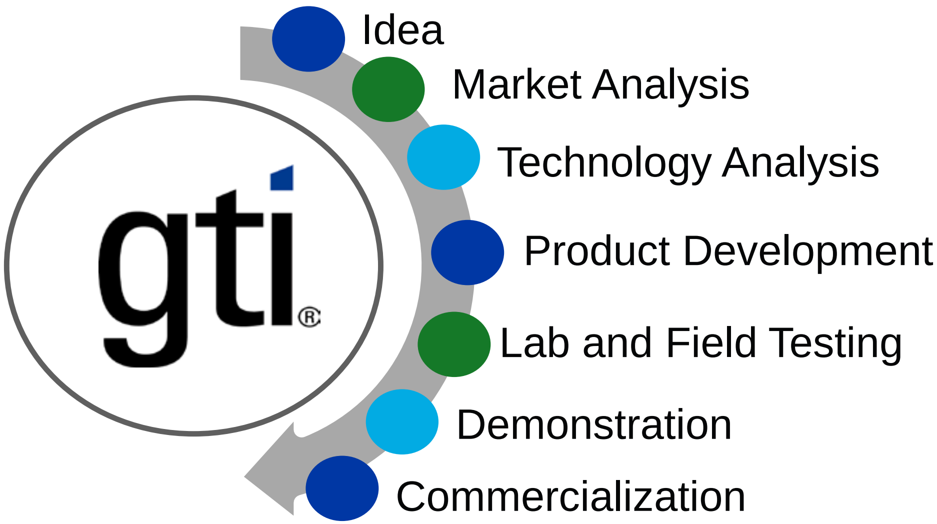
Project overview

- **Performance period**: July 1, 2017 – June 30, 2020
- **Funding**: $799,807 DOE ($200,000 co-funding)
- **Objectives**: Develop nano-engineered catalyst supported on high-surface-area ceramic hollow fibers for the utilization of CO_2 in dry reforming of methane ($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 Missouri S&T



- **<u>Not-for-profit</u>** research company, providing energy and natural gas solutions to government and industry since 1941

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

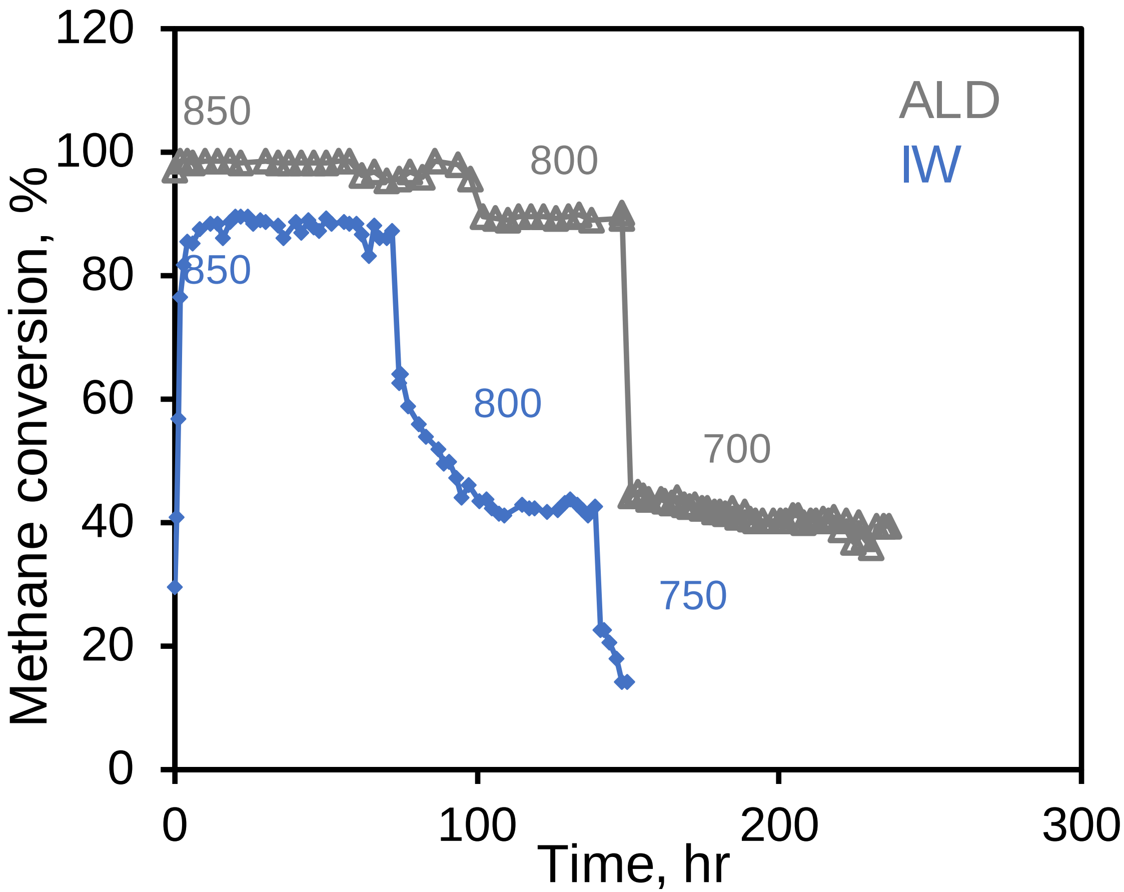
Background of dry reforming of methane using captured CO_2

- **$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$** 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 ($CO + H_2O \rightleftharpoons CO_2 + H_2$)
- **Syngas**: feedstock for fuels and chemicals production
- **H_2/CO ratio** determines the resulting products
  - Dry reforming syngas (H_2/CO ratio = 0.7 - 1) can be used for producing high yield C_{5+} hydrocarbons
  - Higher H_2/CO ratio can be achieved 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

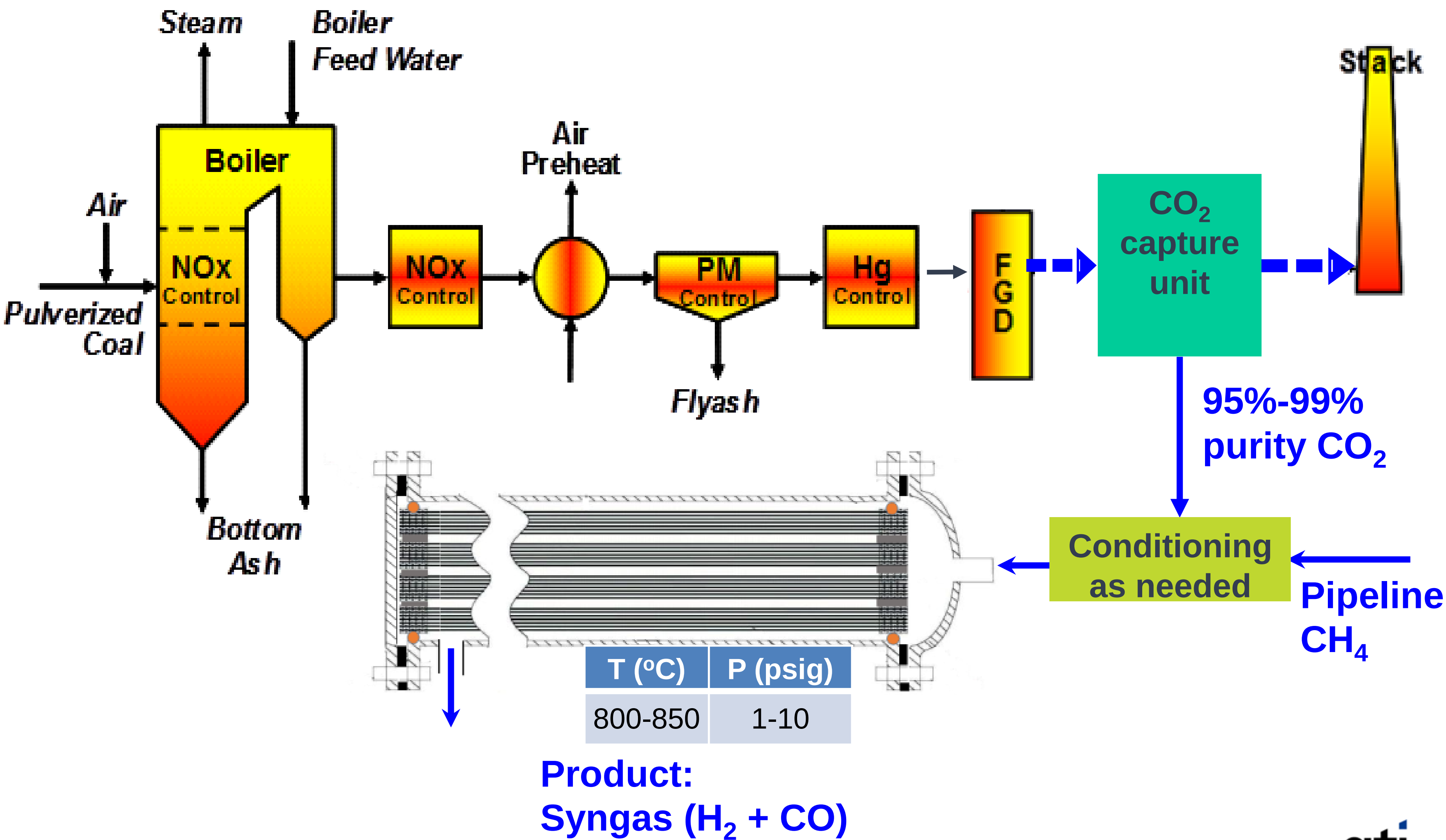
Nano-engineered Ni catalyst prepared by atomic layer deposition (ALD) may resolve sintering issue

- **ALD is a commercial process in semiconductor industry**
- **Advantages over traditional catalysts prepared by incipient wetness (IW)**
  - **Higher activity**
  - **Better stability**

- Ni/γ-Al_2O_3-particle
- CO_2 and CH_4 cylinder gases used in testing



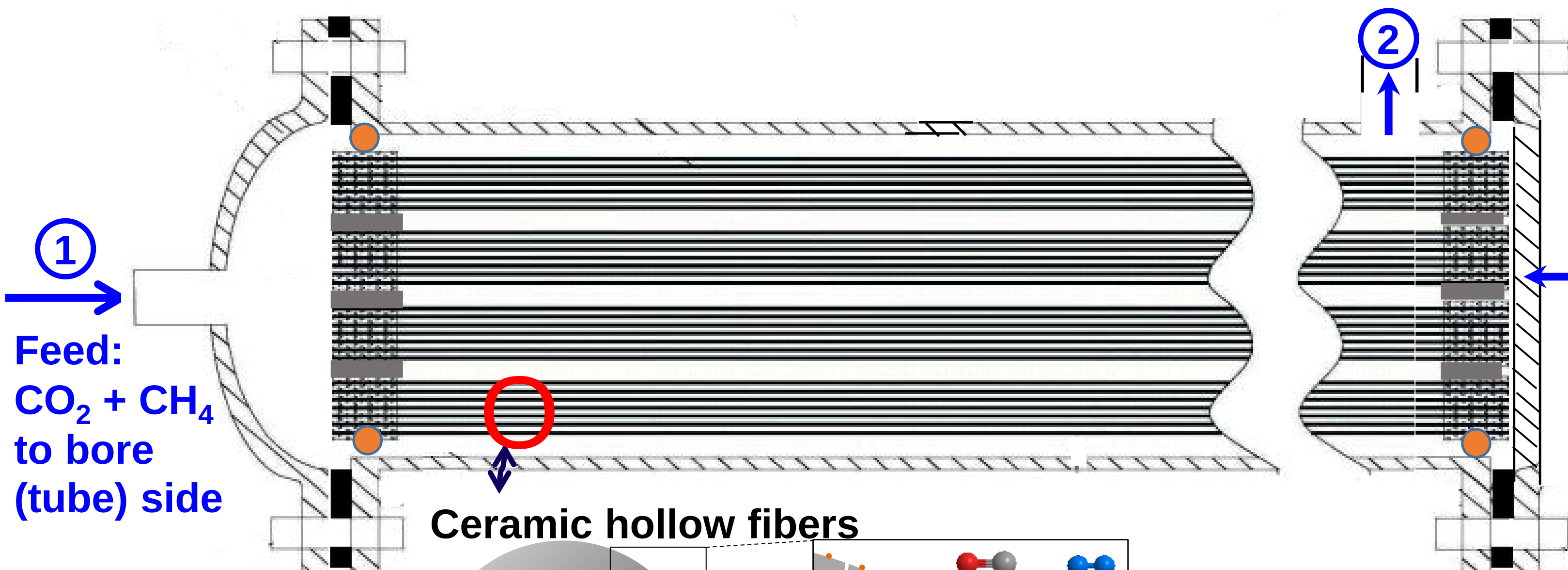
Integration of the technology with coal-fired power plants



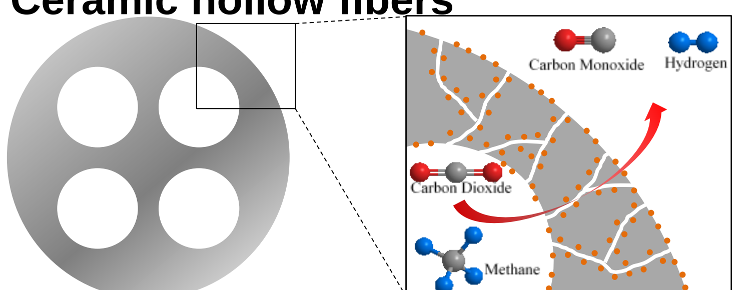
T (ºC)	P (psig)
800-850	1-10

Two conceptual process designs: 1) packed bed reactor, and 2) tube-shell transport reactor

- **<u>Packed bed reactor</u>**: the reactor is filled with nano-engineered catalyst supported on 1-2 cm long hollow fibers
- **<u>Tube-shell transport reactor</u>**:



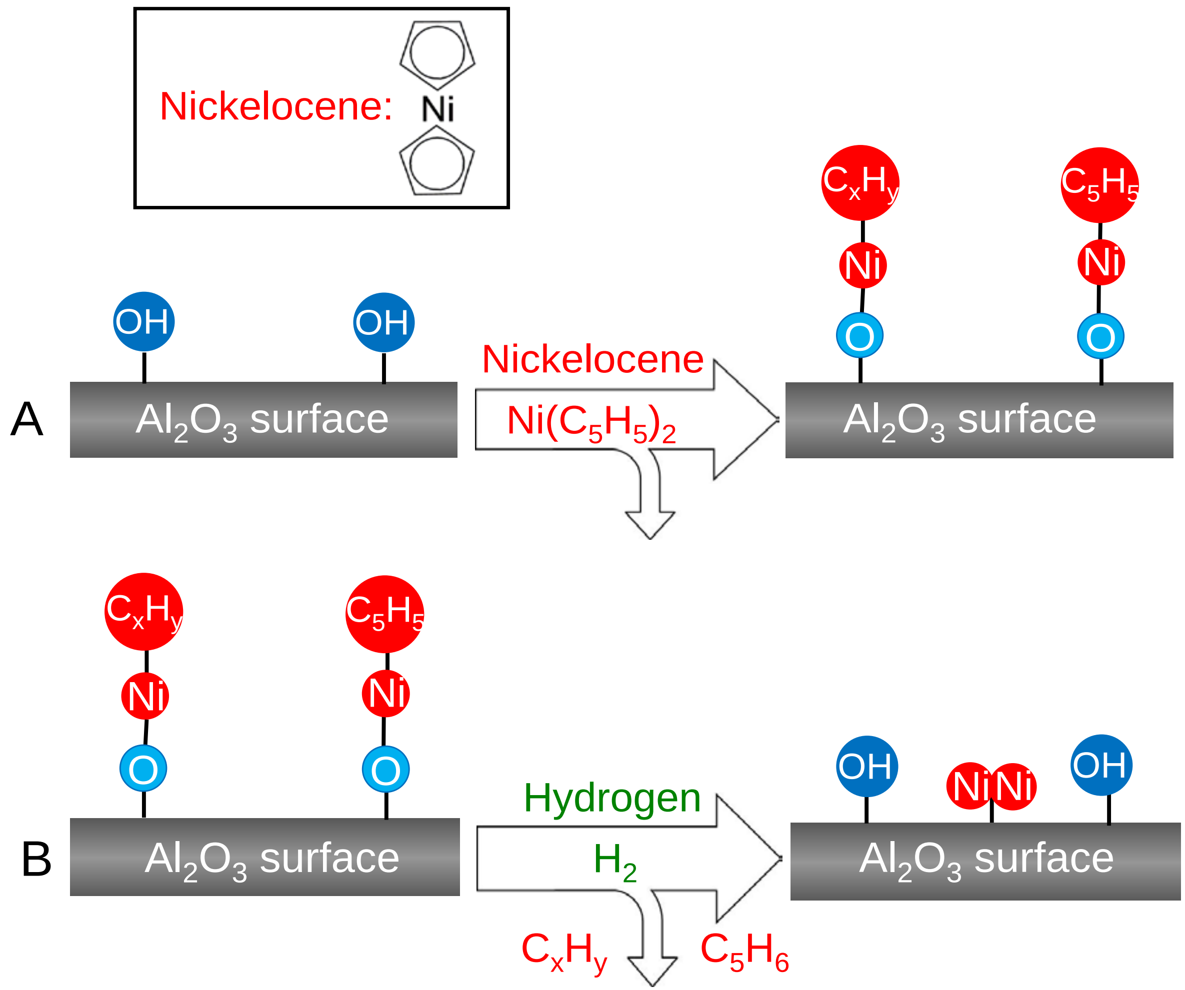
Ceramic hollow fibers



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

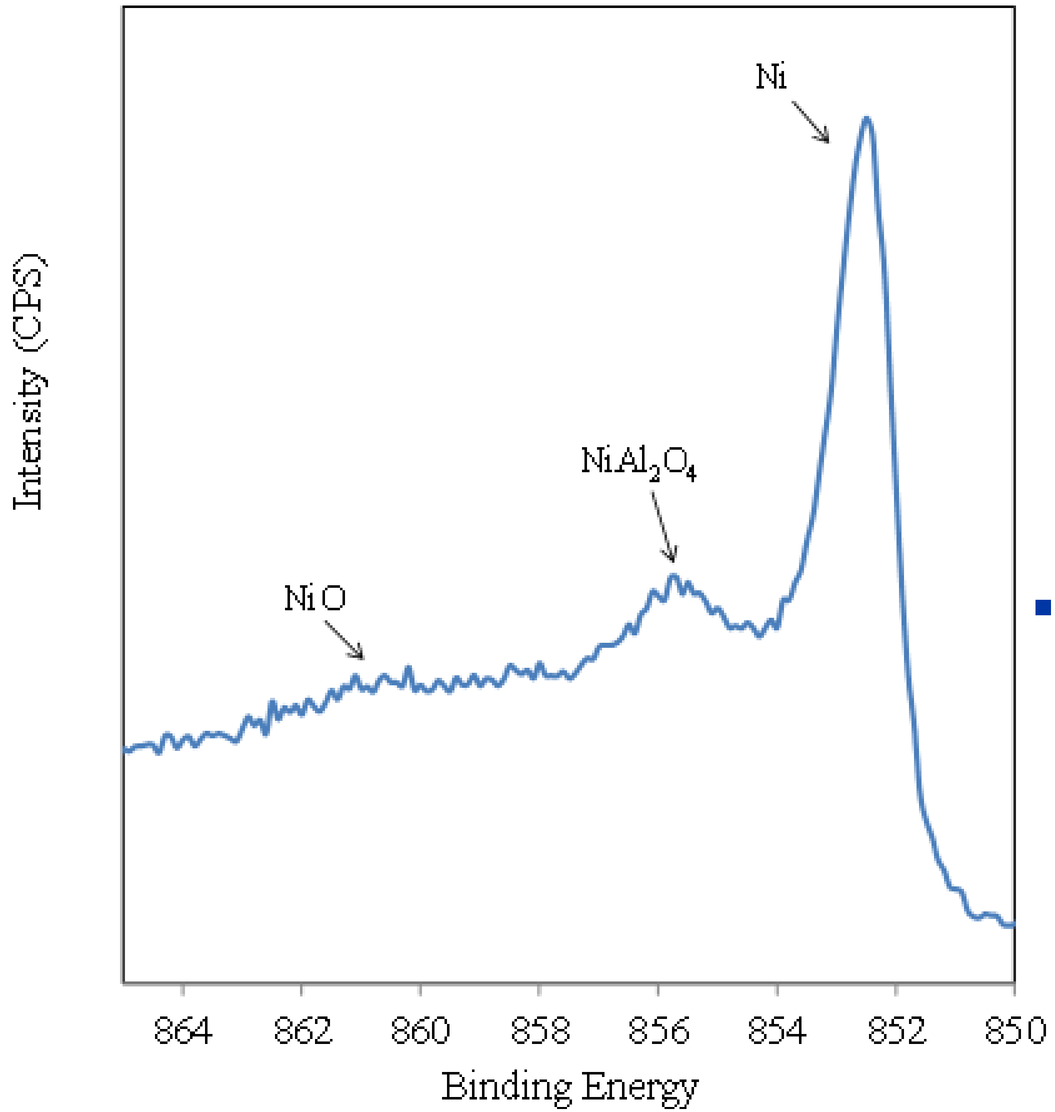
$CO_2 + CH_4 \rightarrow 2\ H_2 + 2\ CO$

Nano-engineered Ni catalyst prepared by ALD



C Catalysts are calcined in air at 550 °C

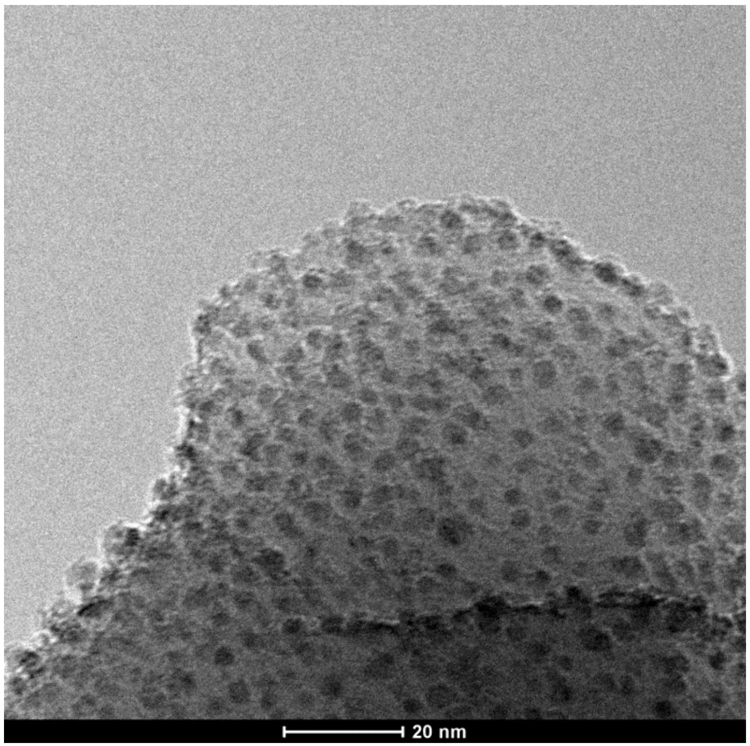
X-ray photoelectron spectroscopy analysis of α-Al_2O_3 nanoparticles supported Ni catalysts

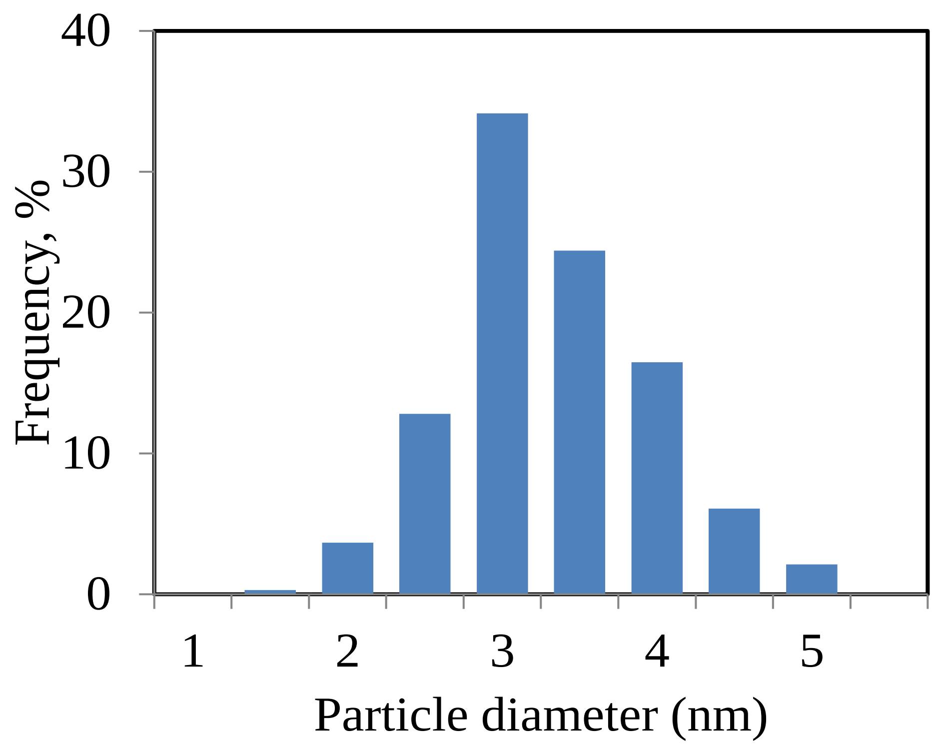


- **In addition to Ni and NiO, $NiAl_2O_4$ formed during Ni ALD, which increases Ni-support interaction**

TEM image of α-Al_2O_3 nanoparticle-supported Ni catalysts

- Particle size: 2-6 nm, average 3.1 nm
  - Particles prepared by traditional methods are ~10-20 nm





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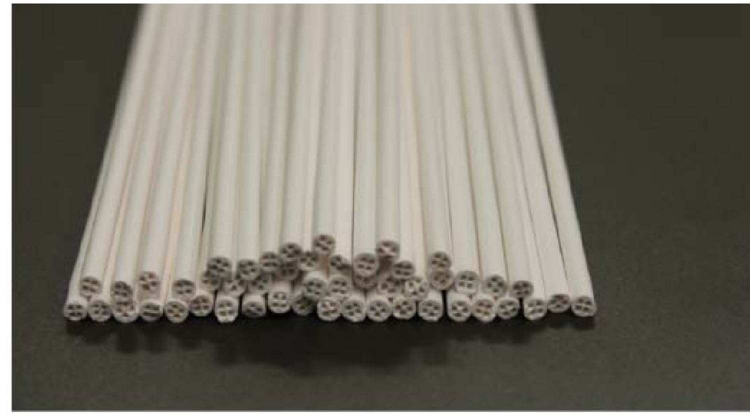
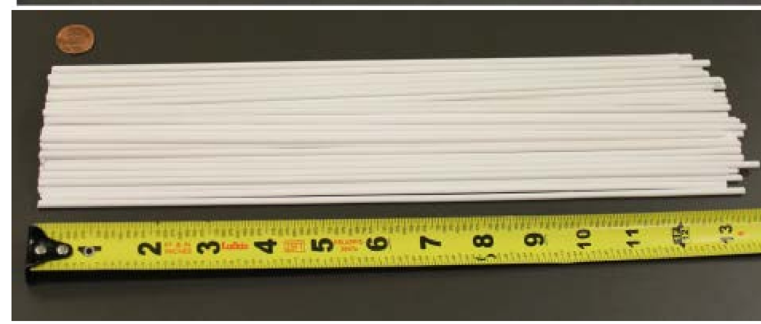
Novel α-Al_2O_3 hollow fiber with high packing density is being used as catalyst substrate in current project

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**

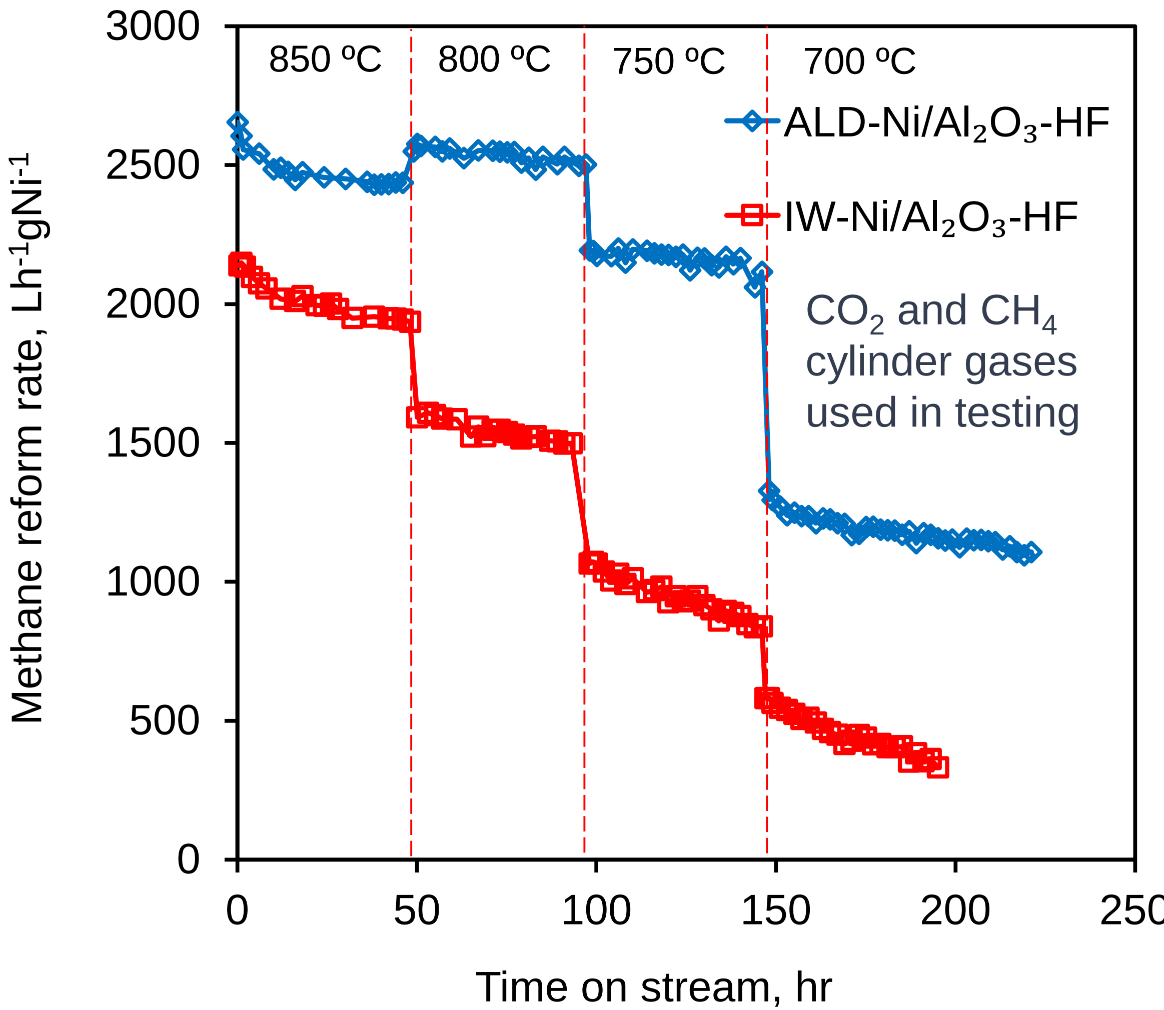




Novel α-Al_2O_3 hollow fibers

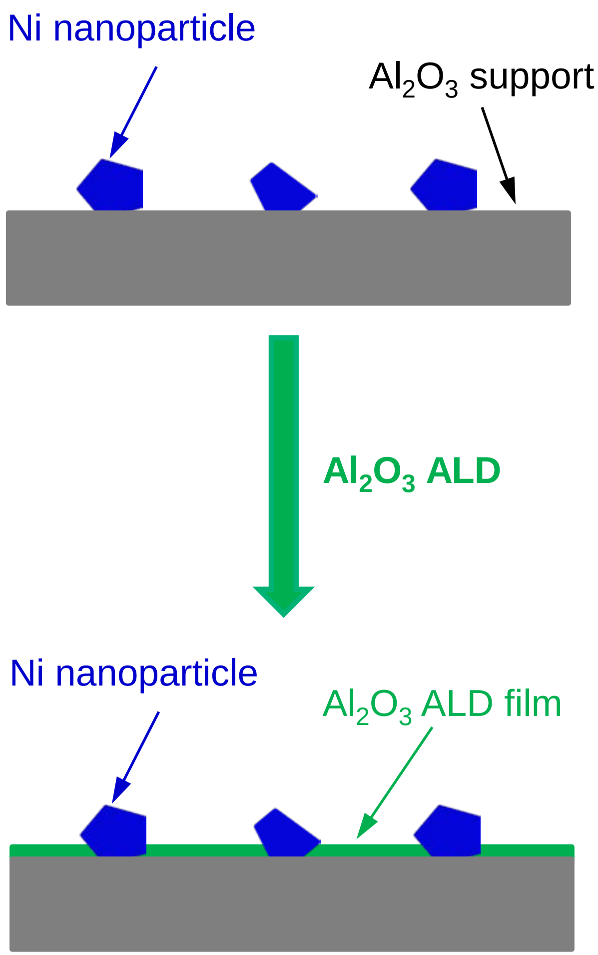
- Four channels, 35 cm long
- OD of 3.2 mm and a channel inner diameter of 1.1 mm
- Geometric surface area to volume as high as 3,000 m^2/m^3

Dry reforming performance of the α-Al_2O_3 hollow fiber supported Ni catalysts (Ni/α-Al_2O_3-HF)



- **<u>Higher activity</u>** due to highly dispersed nanoparticles: ~3.6 nm Ni particles compared to ~10-20 nm particles prepared by traditional method
- **<u>Better stability</u>** due to strong bonding between nanoparticles and substrates since the particles are chemically bonded to the substrate during ALD

Al_2O_3 ALD film increases Ni-support interaction, and thus improves catalytic performance

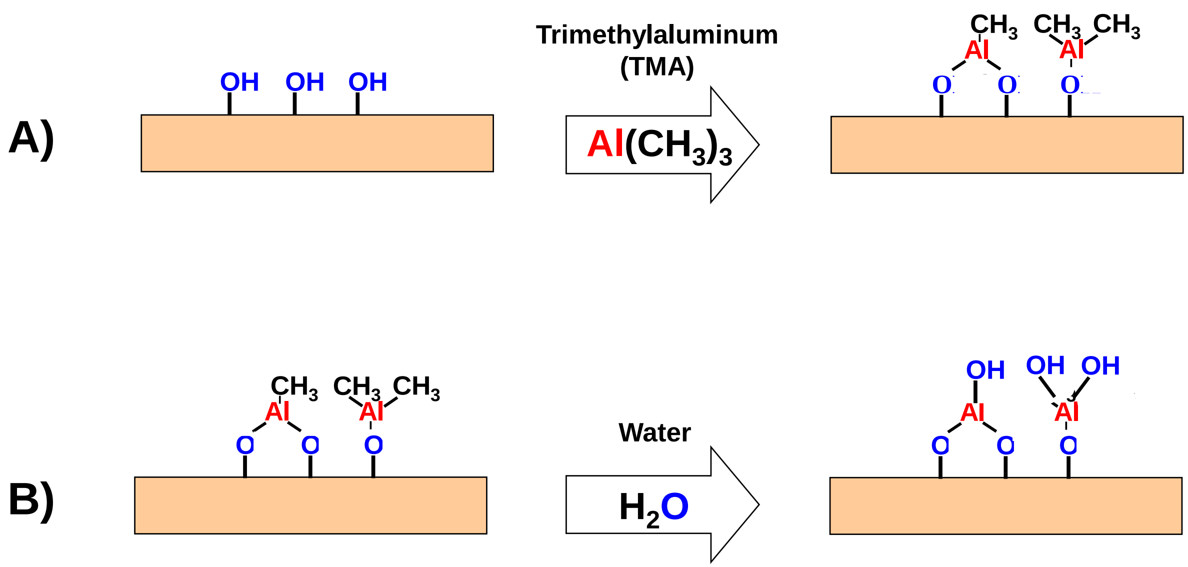


Al_2O_3 ALD Chemistry

Binary reaction: $2Al(CH_3)_3 + 3\ H_2O \rightarrow Al_2O_3 + 6\ CH_4$

A reaction: $2AlOH^* + 2Al(CH_3)_3 \rightarrow 2[Al\text{-}O\text{-}Al(CH_3)_2]^* + 2CH_4$

B reaction: $2[Al\text{-}O\text{-}Al(CH_3)_2]^* + 3H_2O \rightarrow Al_2O_3 + 2AlOH^* + 4CH_4$



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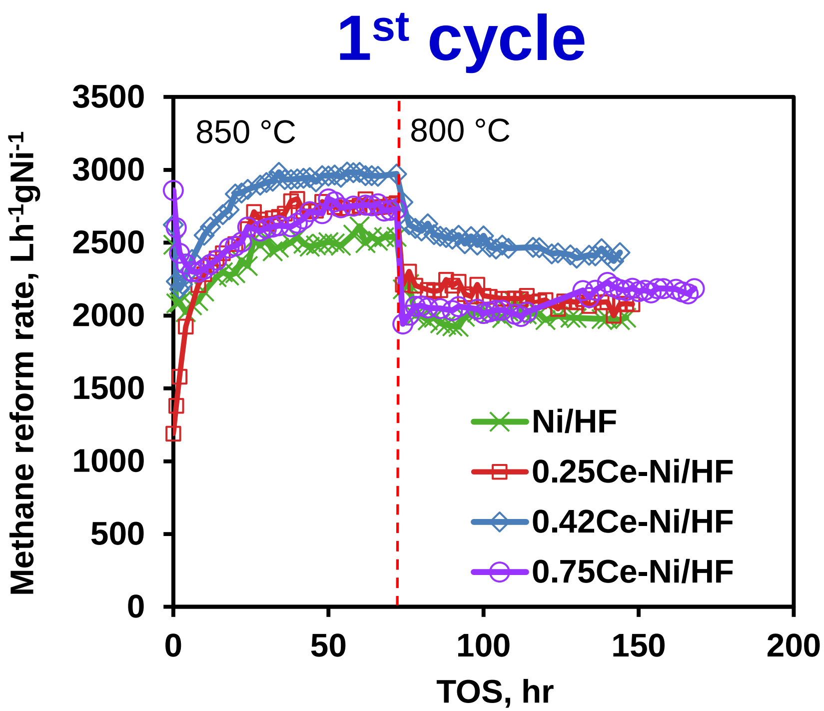
Dry reforming performance of the Al_2O_3 promoted $Ni/\alpha\text{-}Al_2O_3$-HF catalysts

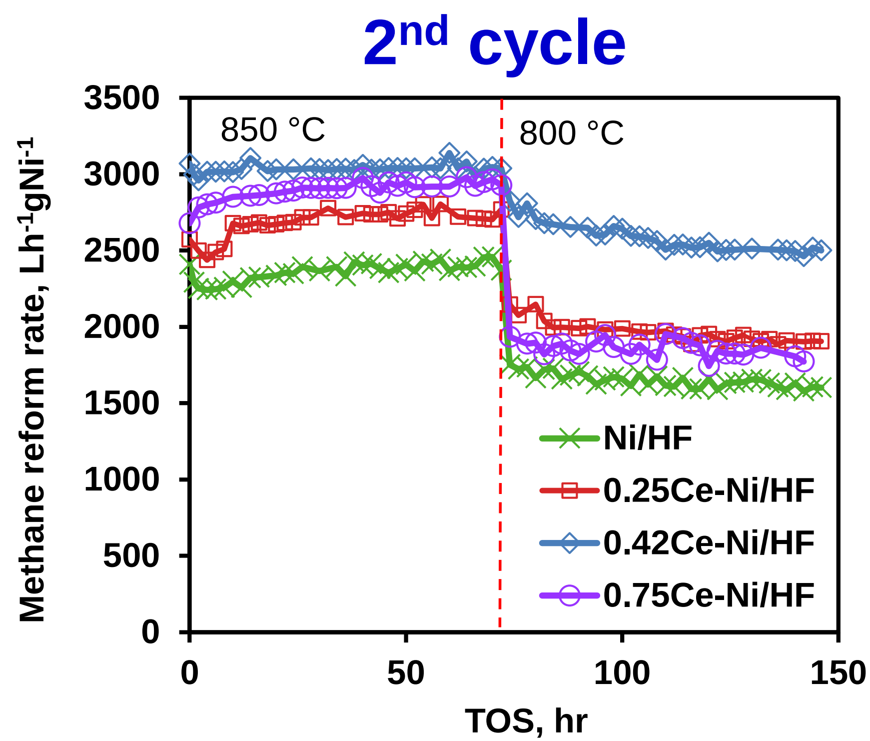
800 °C, 15 psia, CO_2 and CH_4 cylinder gases used in testing

Catalyst	Conversion (%)	H_2/CO ratio	Methane reforming rate ($Lh^{-1}g_{Ni}^{-1}$)
$Ni/\alpha\text{-}Al_2O_3$-HF	88	0.85	2,500
$2Al_2O_3\text{-}Ni/\alpha\text{-}Al_2O_3$-HF	91	0.85	2,600
$5Al_2O_3\text{-}Ni/\alpha\text{-}Al_2O_{3\text{-}}$HF	90	0.84	2,600
$10Al_2O_3\text{-}Ni/\alpha\text{-}Al_2O_3$-HF	88	0.85	2,500

CeO_2 promoted Ni/α-Al_2O_3-HF catalysts

- CeO_2 can potentially increase Ni-support interaction, and provide highly mobile oxygen to inhibit coking of the catalyst
- We improved the catalyst performance by CeO_2 coating prepared by impregnation method





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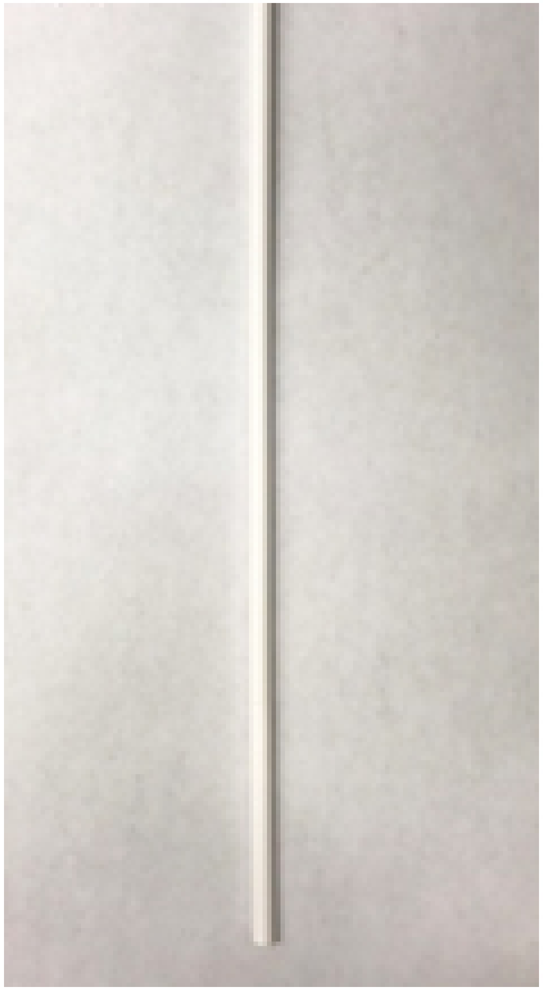
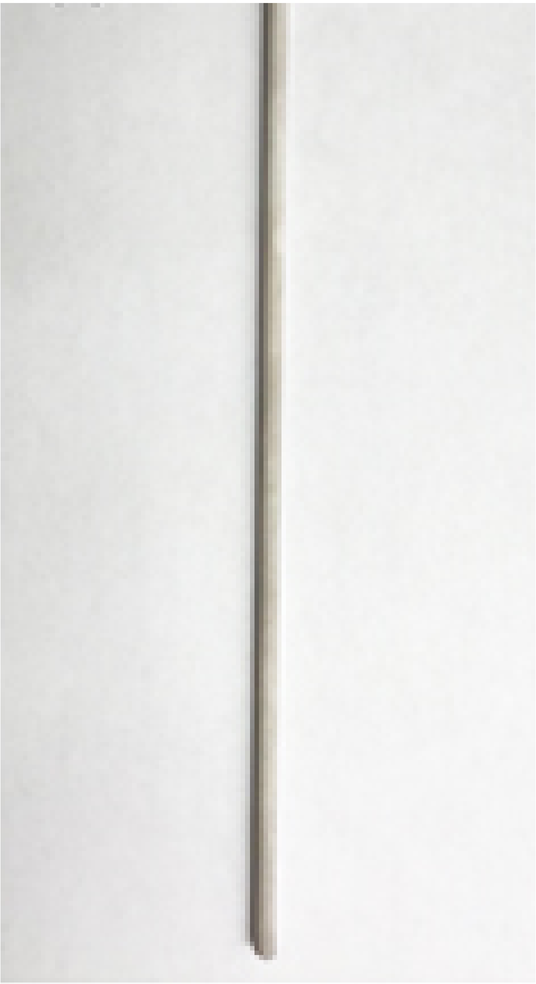
ALD reactor modified for depositing catalysts onto 20-cm-long hollow fibers

Ni nanoparticles successfully deposited on 20-cm-long hollow fibers by ALD



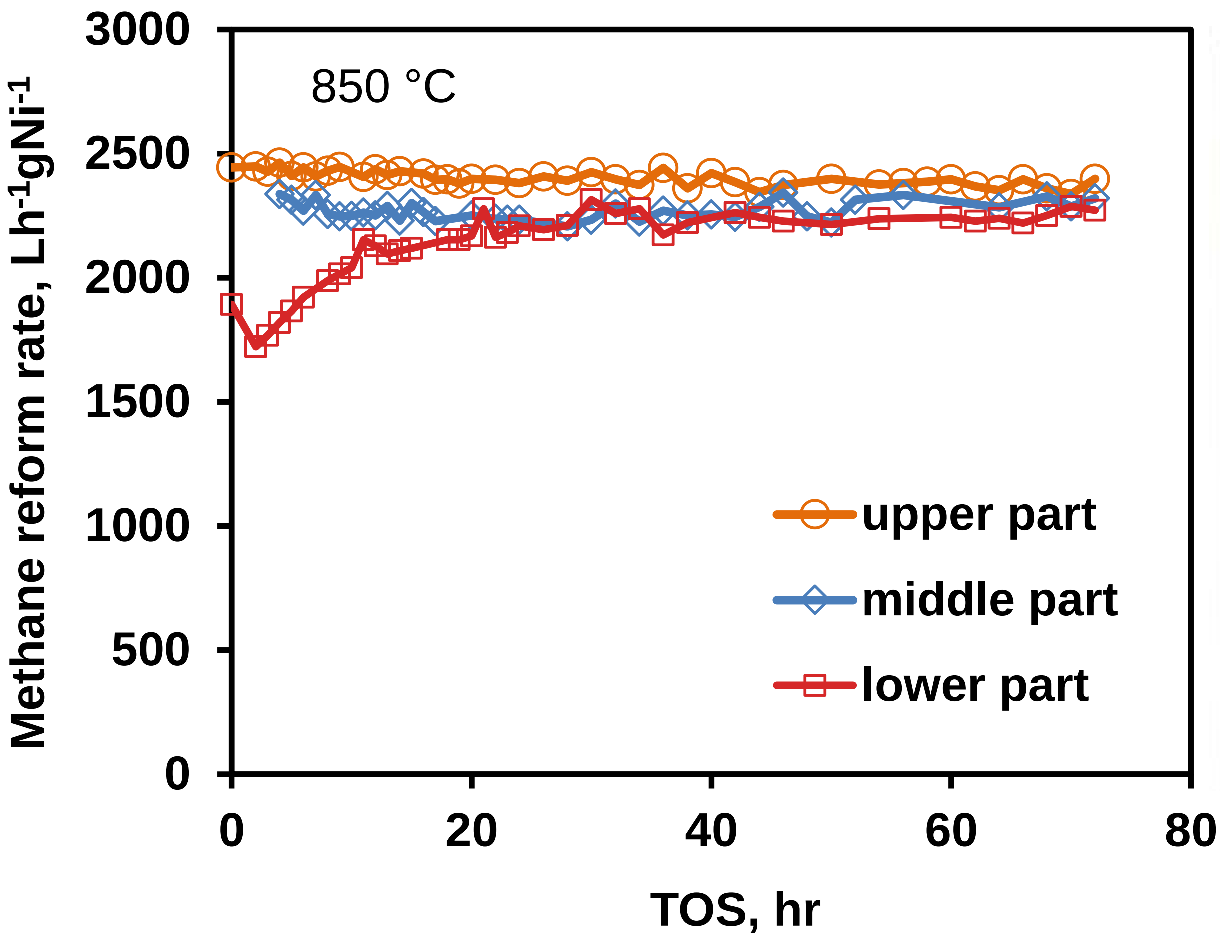
Before Ni ALD

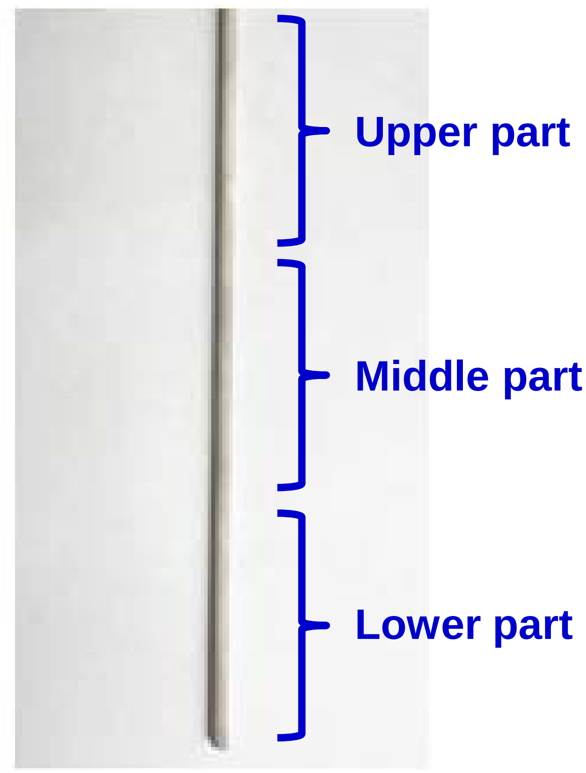


After Ni ALD

Dry reforming performance of the Ni ALD coated 20-cm-long hollow fibers

20-cm-long fibers were broken up into 1-cm-long fibers and tested in a packed bed reactor (CO_2 and CH_4 cylinder gases used in testing)





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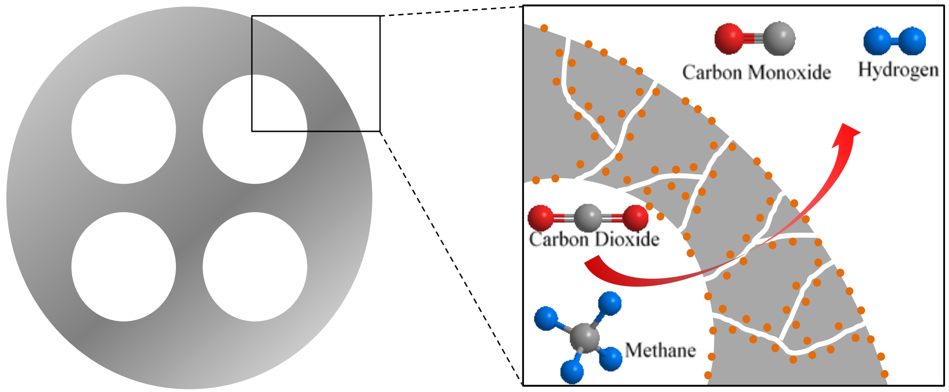
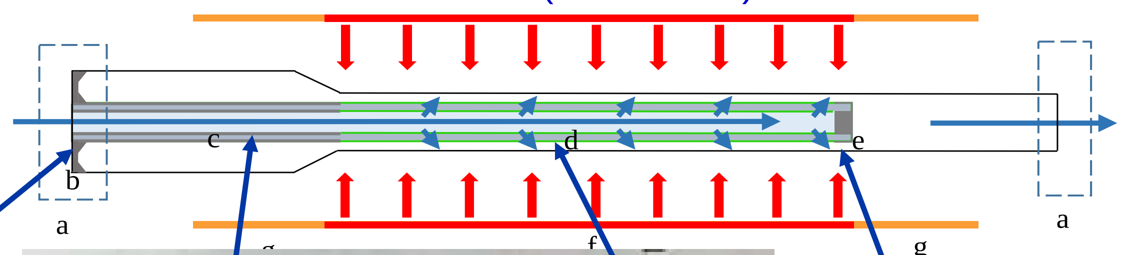
Tube-shell transport reactor designed, Ni coated 20-cm-long hollow fibers to be tested



Low temperature zone

Constant high temperature zone (800-850 °C)



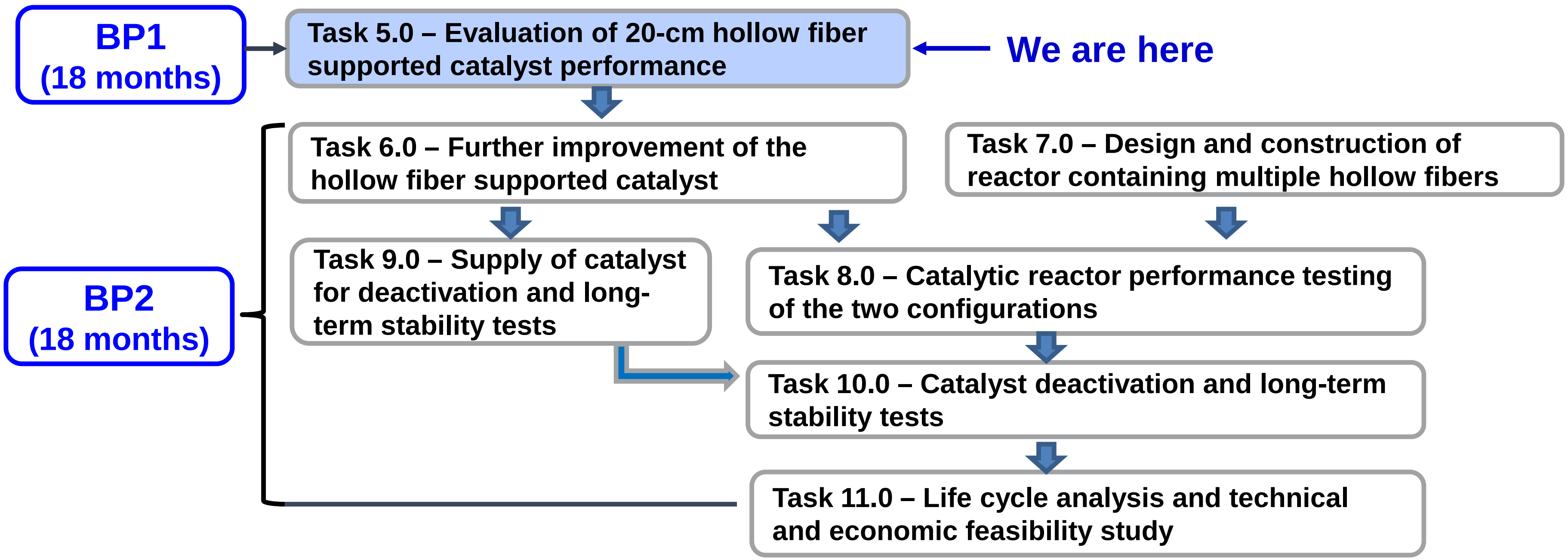
Dead end (sealed)

Glazed part in low temperature zone

Catalytic active part in constant temperature zone

Future plans

- **In this project**



- **After the current project**
  - Test the technology at a larger scale with captured CO_2

Summary

- Novel α-Al_2O_3 hollow fiber increases surface area, and enables tube-shell transport reactor configuration.
- ALD nano-engineered catalyst improves activity and stability for utilization of CO_2 in dry reforming of methane to produce syngas (compared to catalysts prepared by conventional incipient wetness method).
- Coating of Al_2O_3 or CeO_2 on Ni/α-Al_2O_3-HF catalysts further improves dry reforming performance.
- Uniform Ni was successfully coated on 20-cm-long hollow fibers using a modified ALD reactor.

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