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

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Shiguang Li, ***GTI***

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

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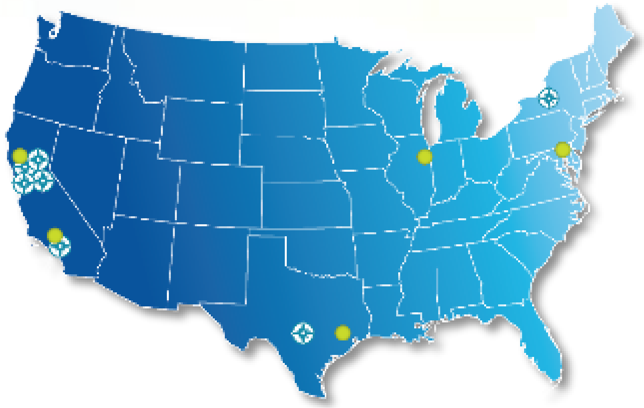
78 History of Turning Raw Technology into Practical Energy Solutions

FOR A BETTER ECONOMY AND A BETTER ENVIRONMENT

SUPPLY	CONVERSION	DELIVERY	UTILIZATION



RESEARCH & DEVELOPMENT

PROGRAM MANAGEMENT

TECHNICAL/ ANALYTICAL

CONSULTING

TRAINING

COMMERCIALIZATION

360+ EMPLOYEES

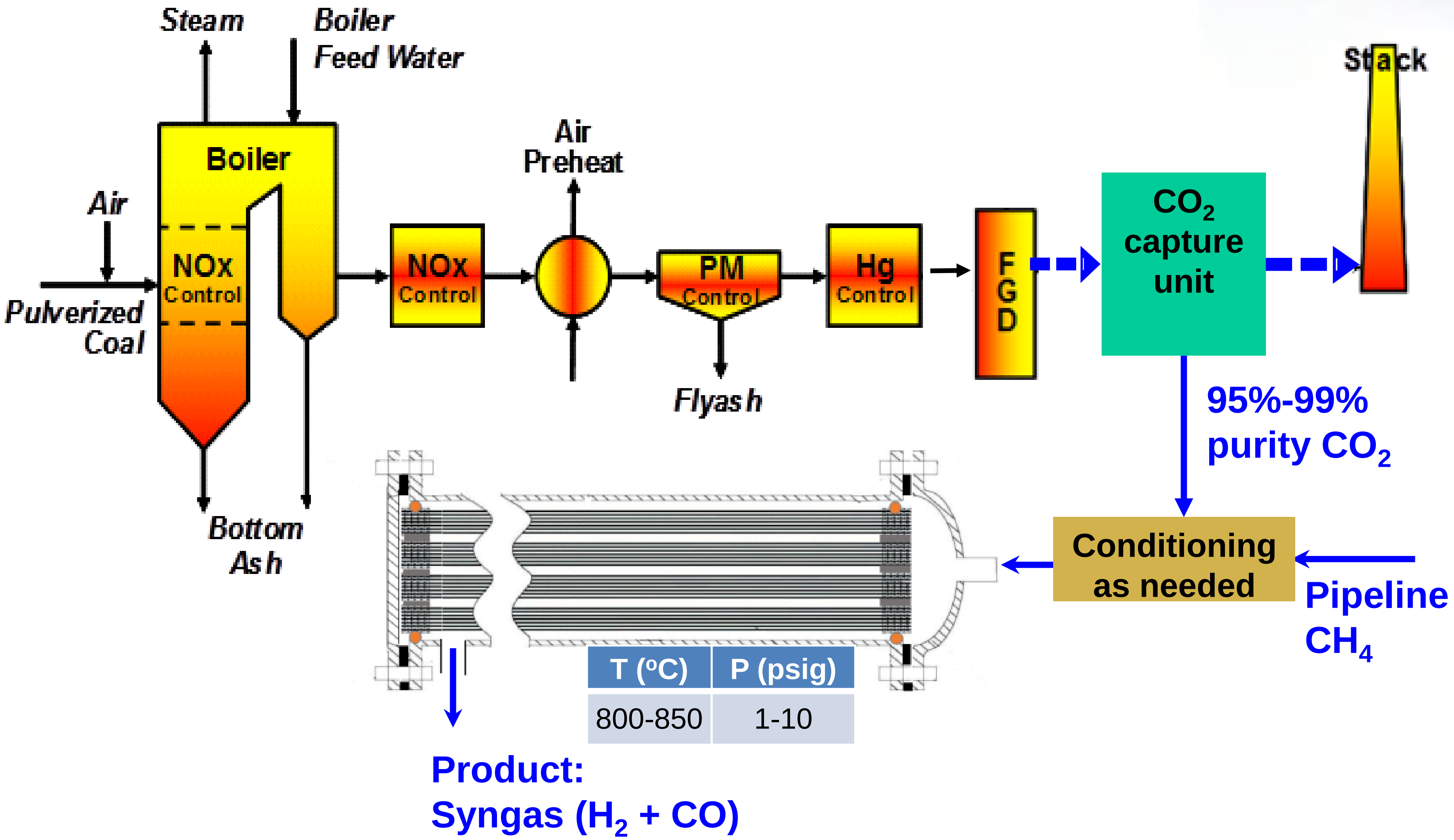
World-class piloting facilities headquartered in Chicago area

Project overview

- **Performance period**: July 1, 2017 – September 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

Integration of the technology with coal-fired power plants



T (ºC)	P (psig)
800-850	1-10

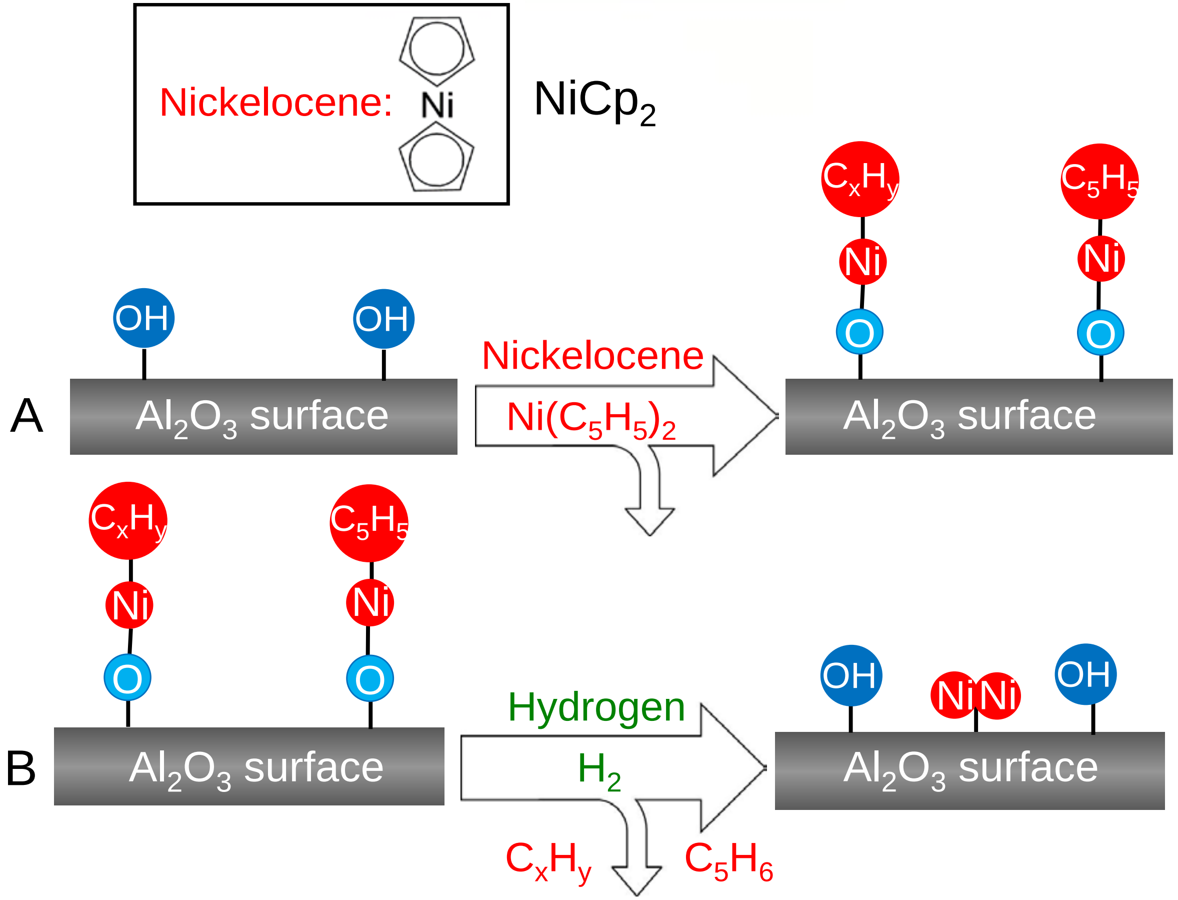
PM: Particulate matter; FGD: Flue-gas desulfurization

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 ($CH_4 + H_2O \rightarrow CO + 3H_2$) 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**

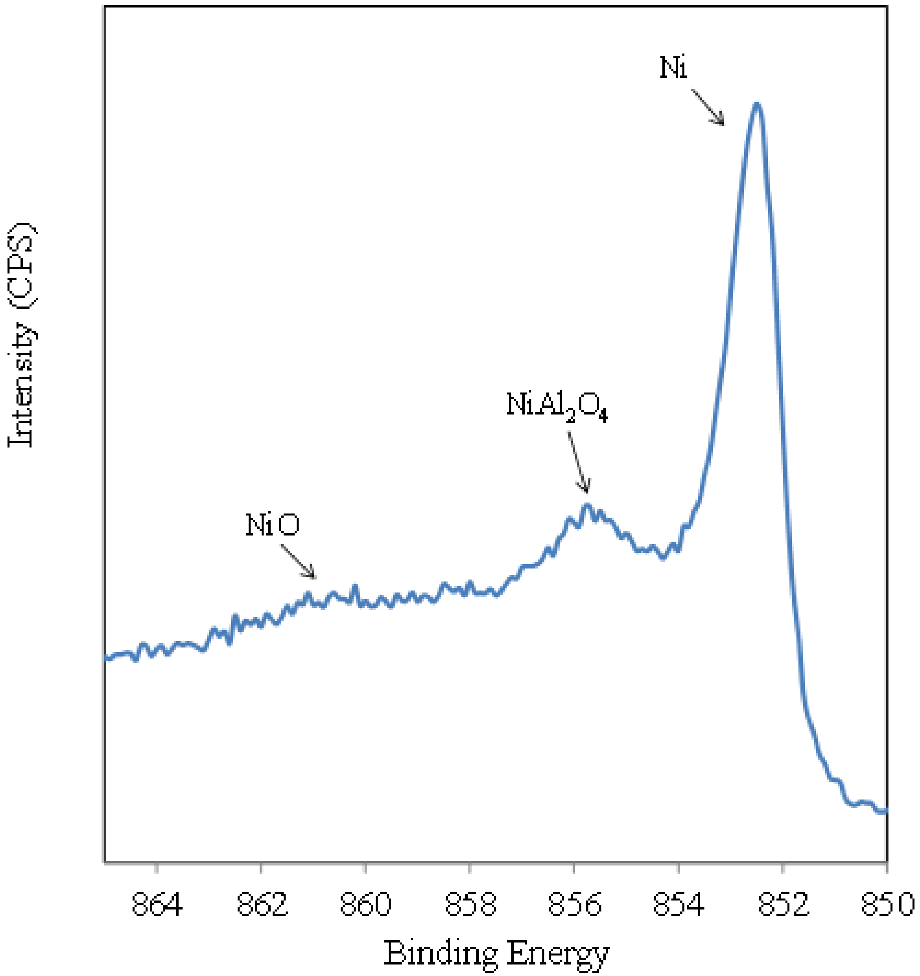


$NiCp_2$ reacts with the surface -OH groups and the Cp ring is removed

Hydrogenate the organic ligands bound to Ni

C Catalysts are calcined in air at 550 °C

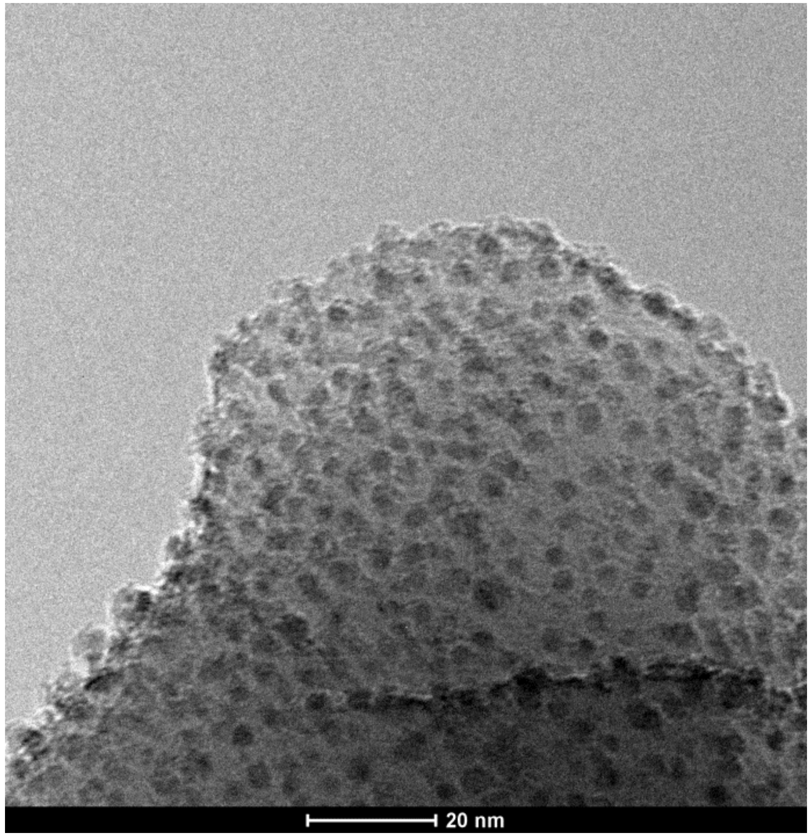
X-ray photoelectron spectroscopy analysis of α-Al_2O_3 nanoparticles supported Ni catalysts

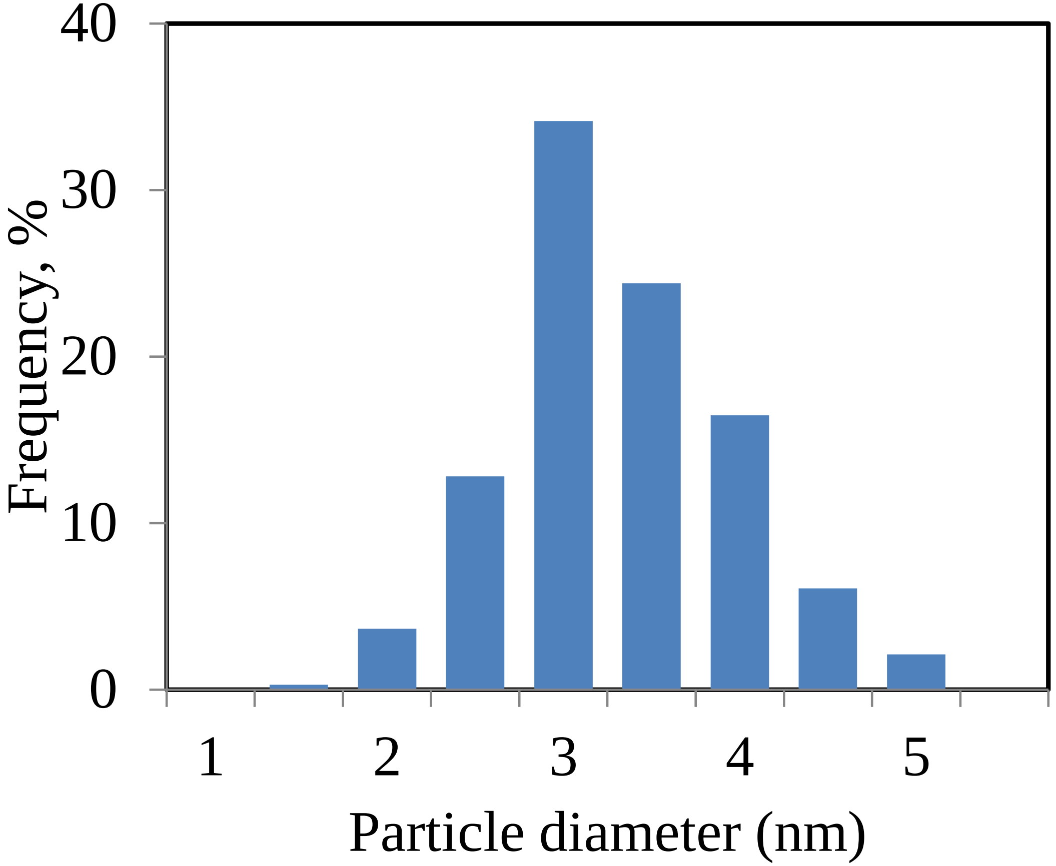


- **In addition to Ni and NiO, $NiAl_2O_4$ spinel formed during Ni ALD, which increases Ni-support interaction**

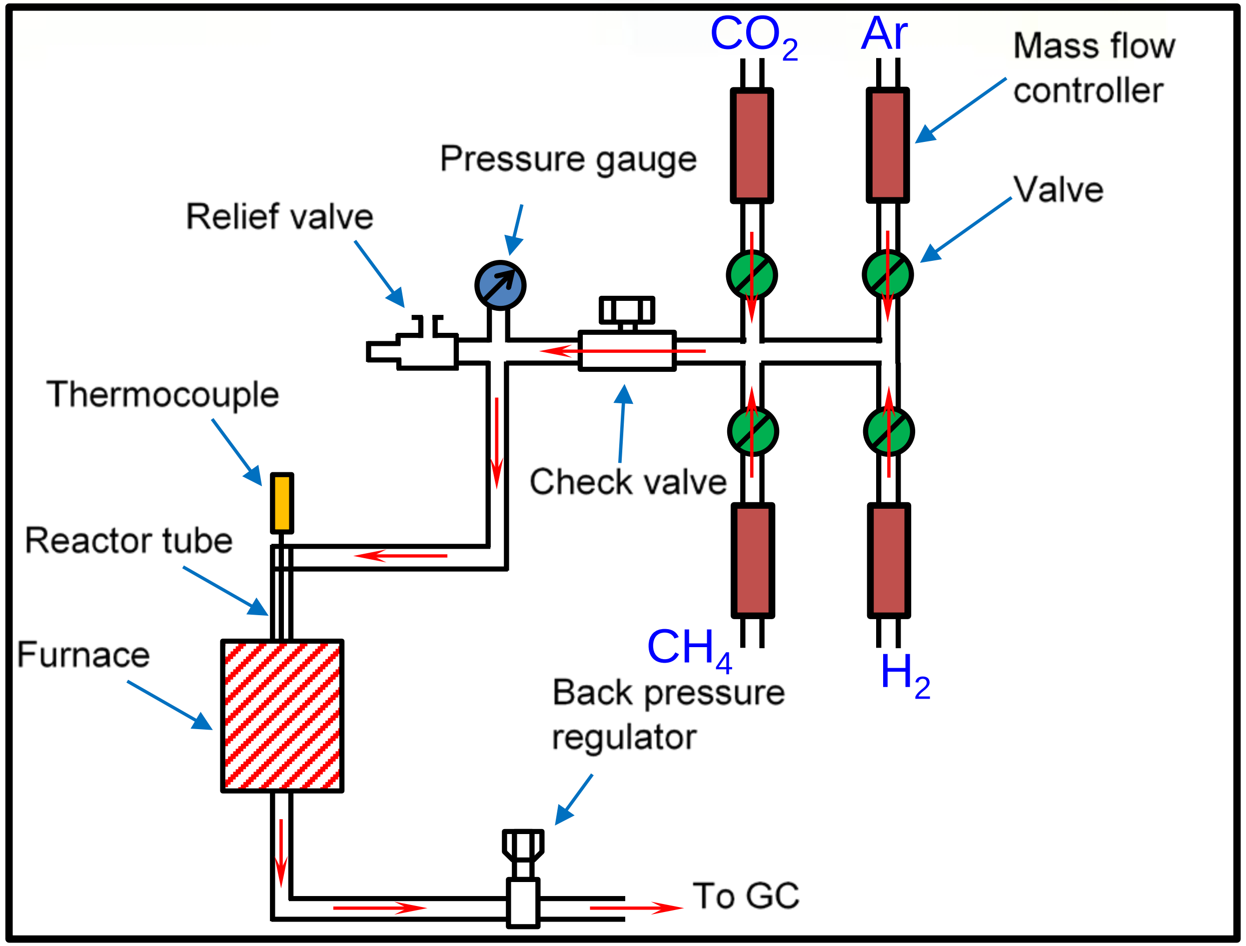
TEM image of α-Al_2O_3 nanoparticle-supported Ni catalysts

- Particle size: 2-6 nm, average 3.1 nm
  - Particles prepared by traditional methods (e.g. incipient wetness) are ~10-20 nm

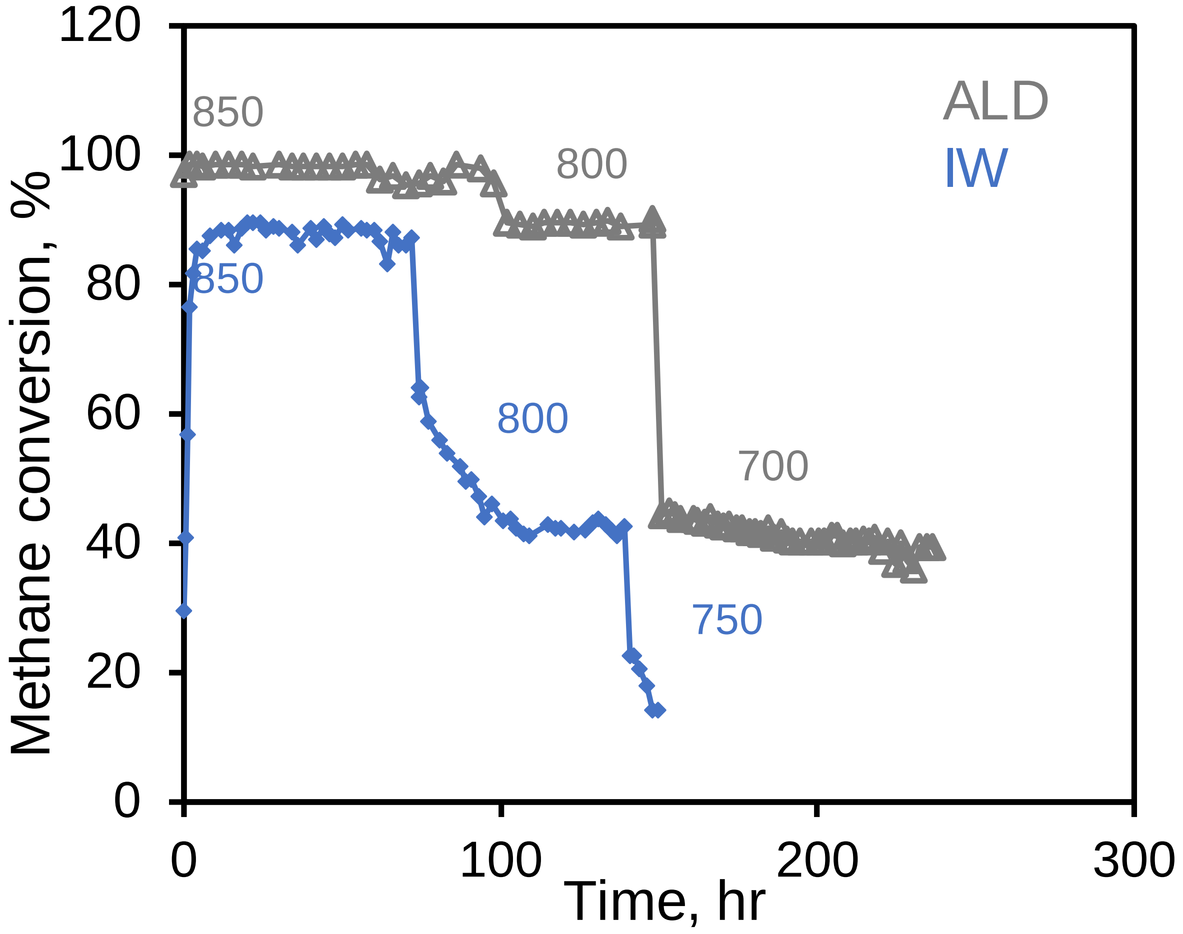




Packed bed catalytic reactor for dry reforming testing



ALD Ni catalyst showed advantages over traditional catalysts prepared by incipient wetness (IW)



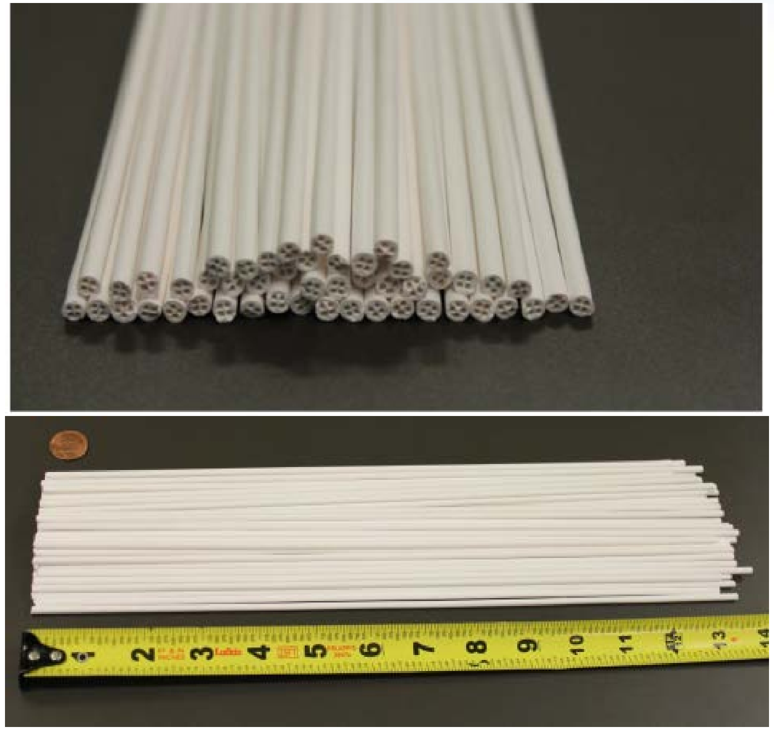
- ALD Ni on γ-Al_2O_3 particles
- CO_2 and CH_4 cylinder gases used in testing

- **<u>Higher activity</u>** due to highly dispersed nanoparticles: ~3.1 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

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**

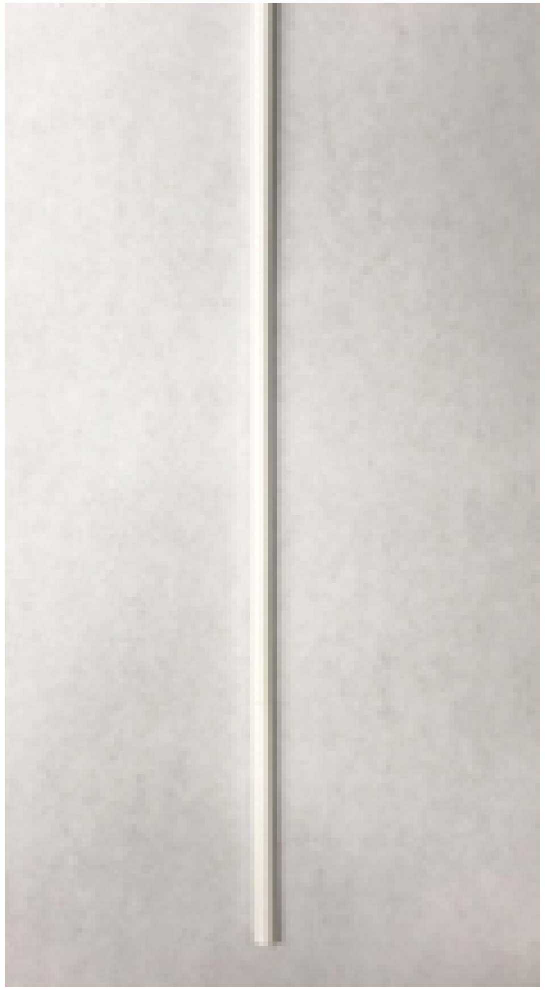


Novel α-Al_2O_3 hollow fibers

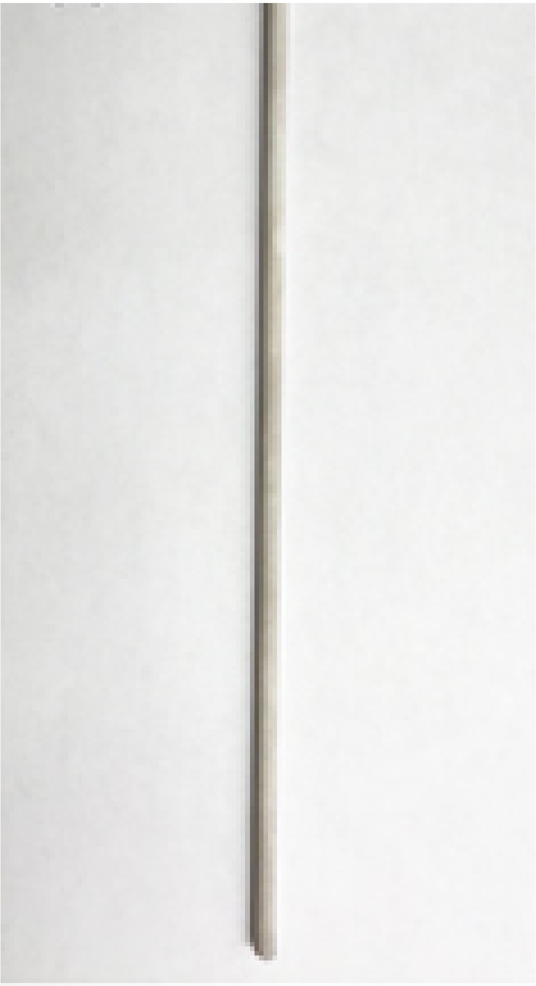
- OD of 3.2 mm and a channel inner diameter of 1.1 mm
- Geometric surface area to volume as high as 3,000 m^2/m^3

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

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



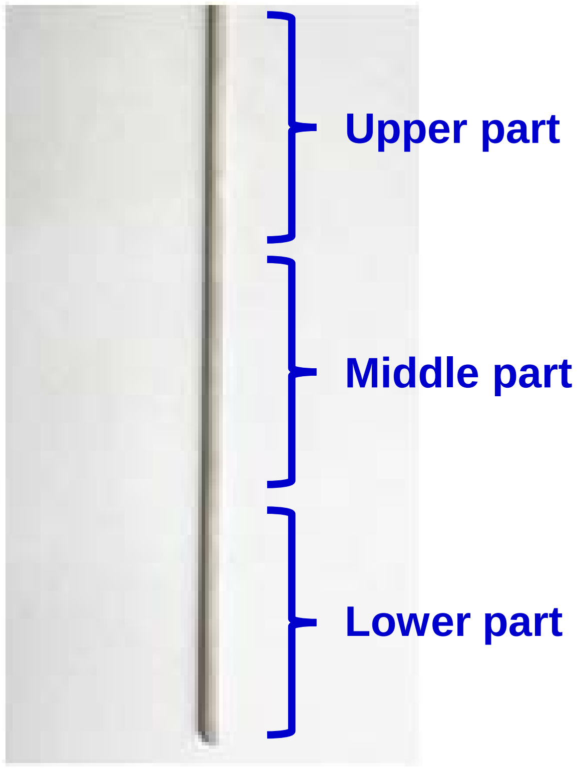
Before Ni ALD

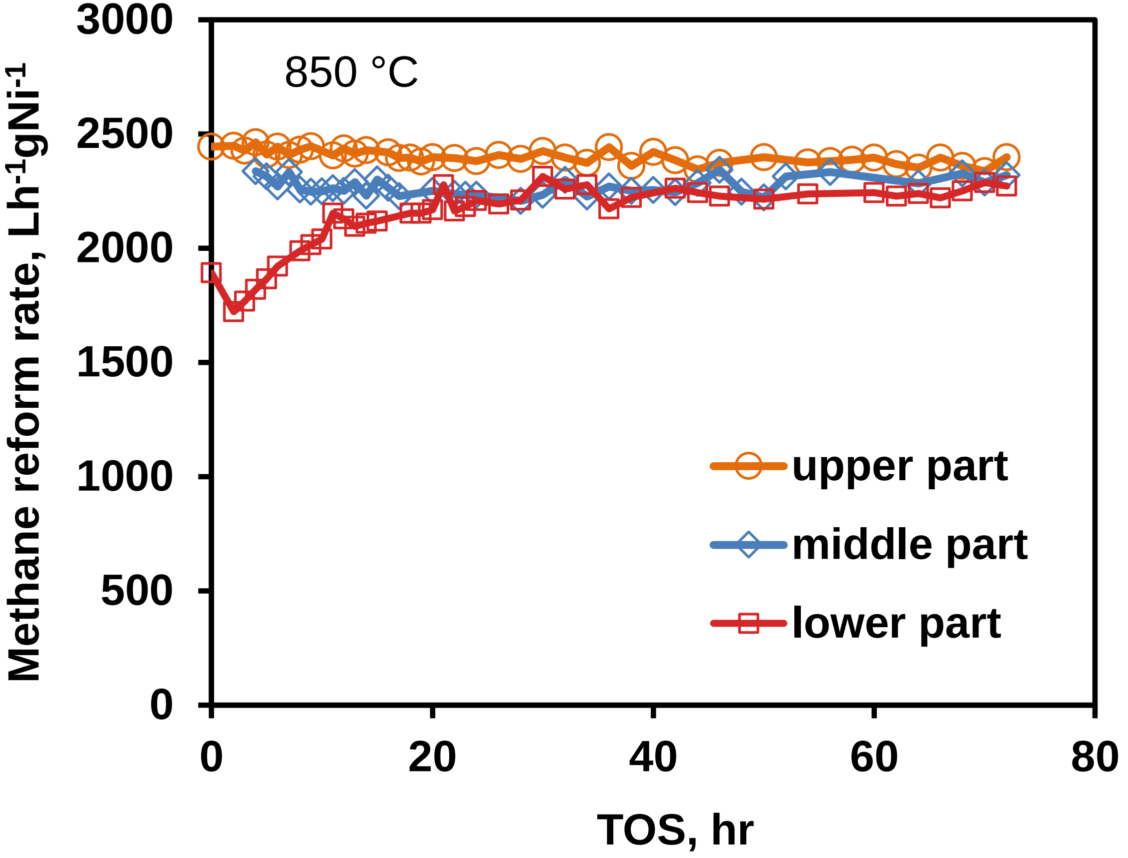


After Ni ALD

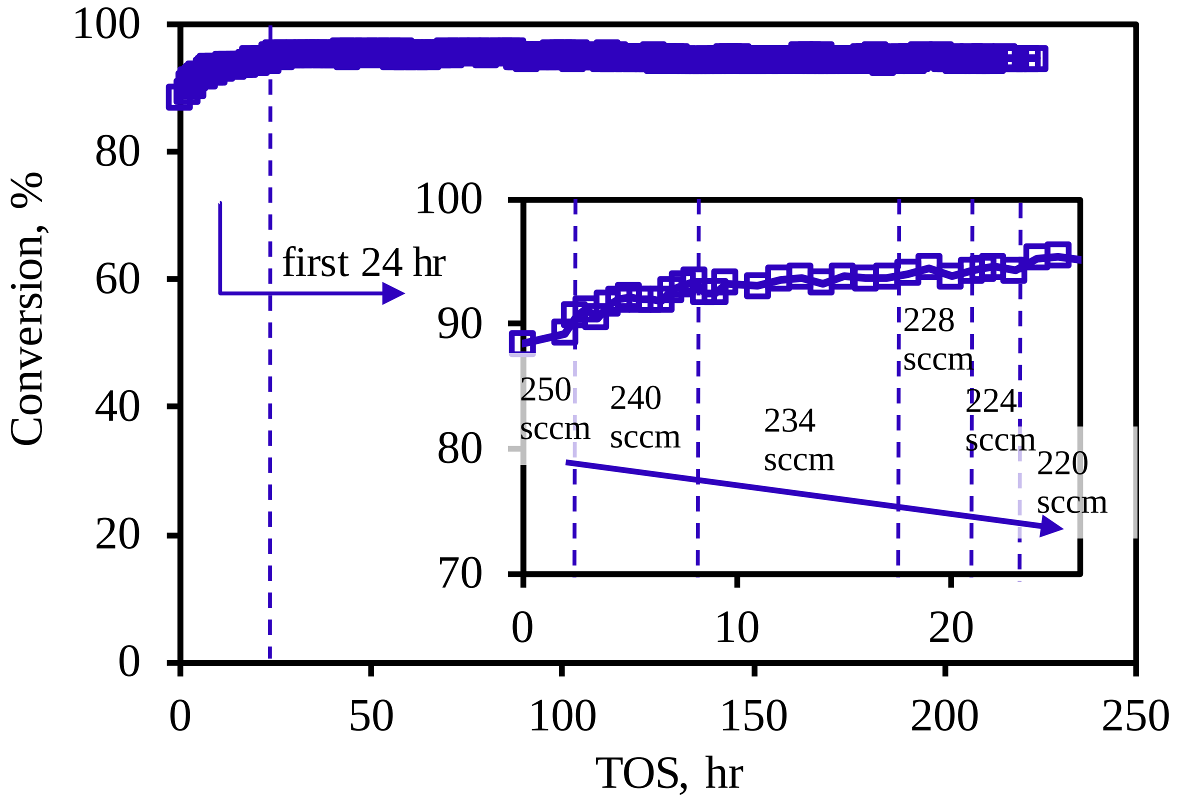
Dry reforming performance of the Ni ALD coated 20-cm-long hollow fibers

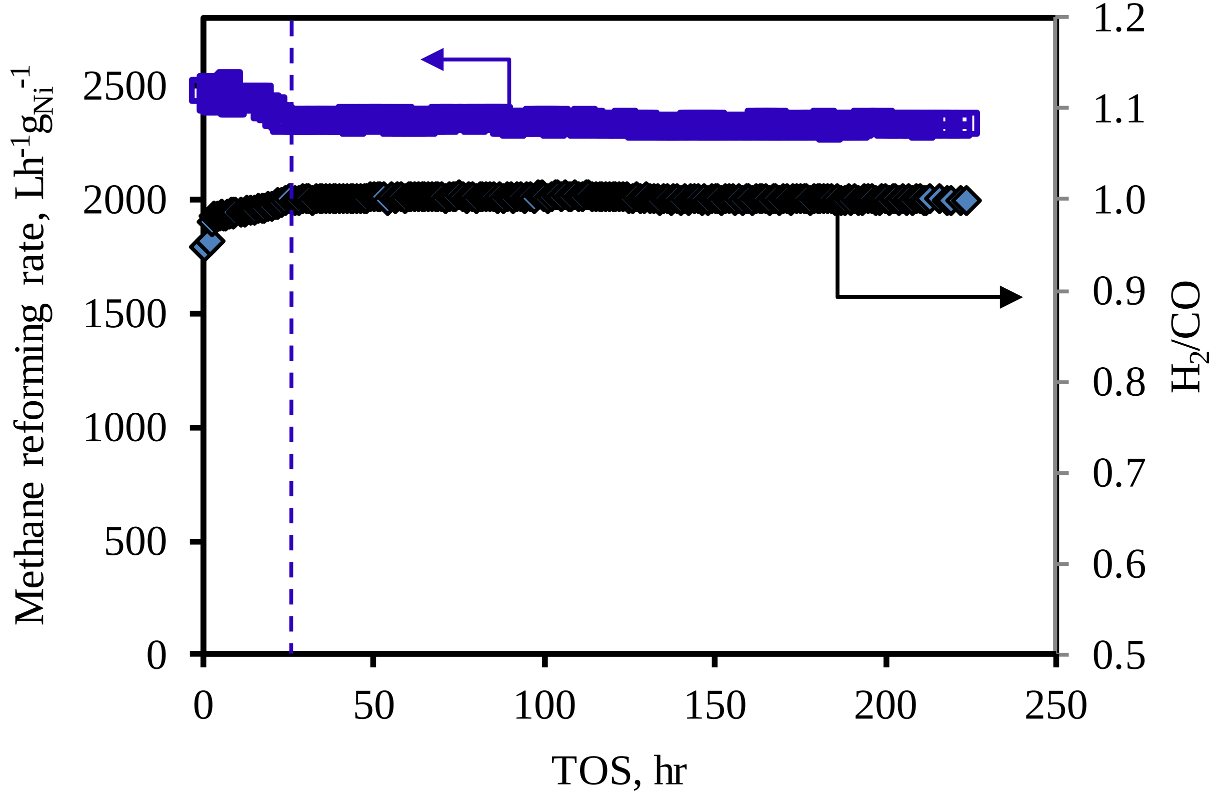
20-cm-long fibers were broken up into 1-cm-long fibers and tested in a packed bed reactor (CO_2 and CH_4 cylinder gases used in testing)





200-h continuous testing of 20-cm long hollow fiber supported Ni ALD catalyst indicated good stability





Designed and constructed reactor system at GTI for performance, deactivation and long-term stability tests

Furnace
(reactor inside)

Future plans

- **In this project**

BP2 (4/1/19-9/30/20)

- Task 6.0 – Further improvement of the hollow fiber supported catalyst
- Task 9.0 – Supply of catalyst for deactivation and long-term stability tests
- Task 7.0 – Design and construction of reactor containing multiple hollow fibers
- Task 8.0 – Catalytic reactor performance testing ← We are here
- Task 10.0 – Catalyst deactivation and long-term stability tests
- Task 11.0 – Life cycle analysis and technical and economic feasibility study

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

Summary

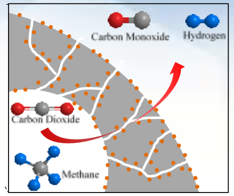
- We are developing ALD nano-engineered catalysts for utilization of CO_2 in dry reforming of methane to produce syngas

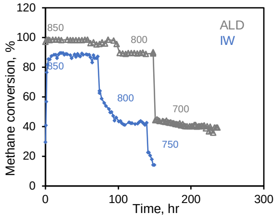
- ALD nano-engineered catalyst improves activity and stability for utilization of CO_2 in dry reforming of methane to produce syngas (compared to catalysts prepared by conventional incipient wetness method)

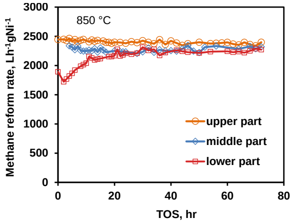
- Uniform nano-engineered Ni nanoparticles were successfully deposited on high packing-density α-Al_2O_3 hollow fiber by ALD

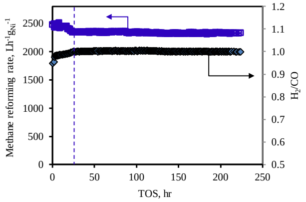
- 200-h continuous testing of 20-cm long hollow fiber supported Ni ALD catalyst indicated good stability

- Designed and constructed reactor system at GTI for performance, deactivation and long-term stability tests









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