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

DOE Contract No. DE-FE0029760

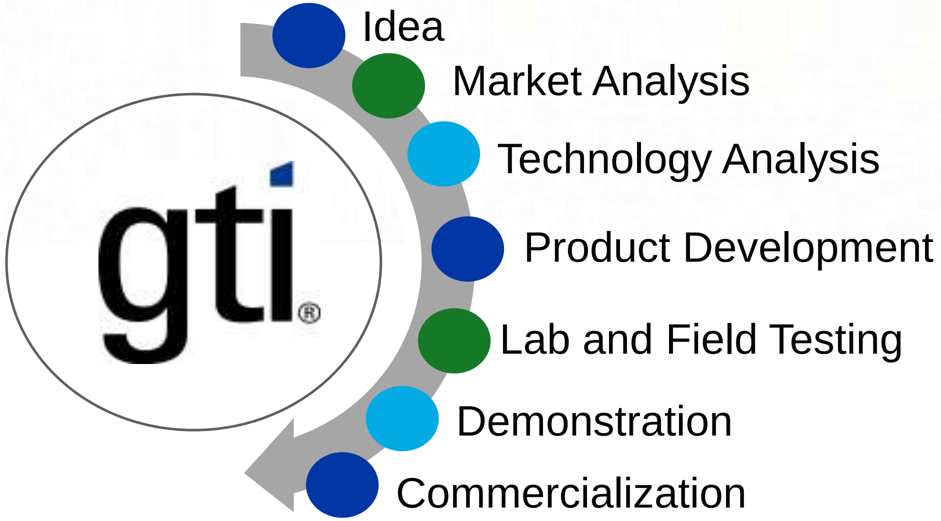
Shiguang Li, *GTI*

Baitang Jin, Zeyu Shang, and Xinhua Liang, *Missouri University of Science and Technology (Missouri S&T)*

CCT 2019

June 3-7, Houston, Texas

Introduction to GTI and Missouri S&T



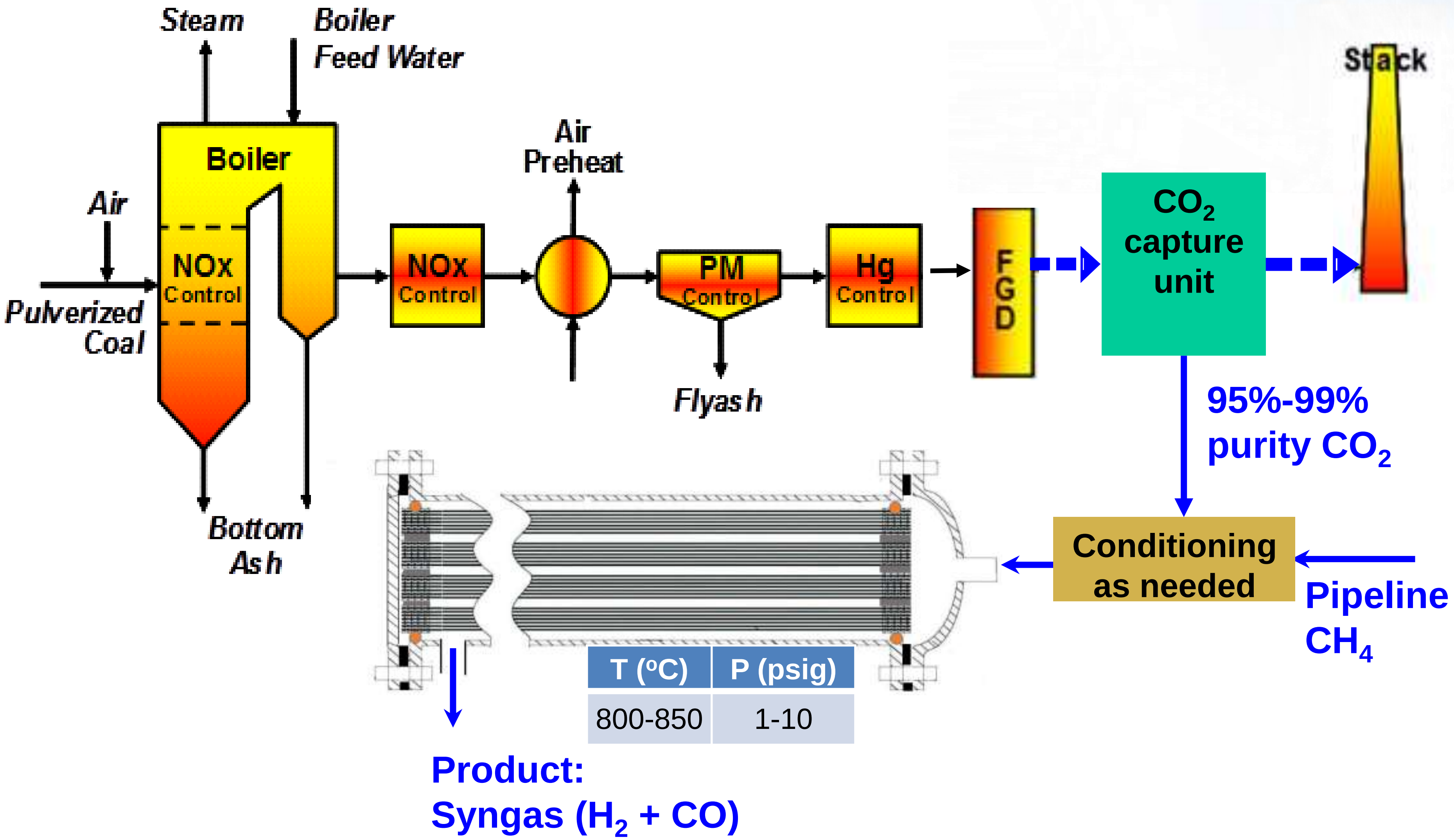
- **<u>Not-for-profit</u>** research company, providing energy and natural gas solutions to government and industry since 1941

OFFICE

SUBSIDIARY

- **<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

Integration of the technology with coal-fired power plants



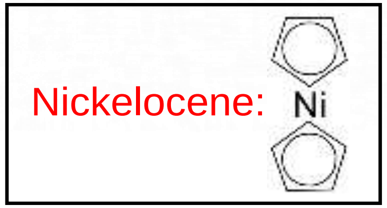
T (°C)	P (psig)
800-850	1-10

Background of dry reforming of methane using captured CO_2

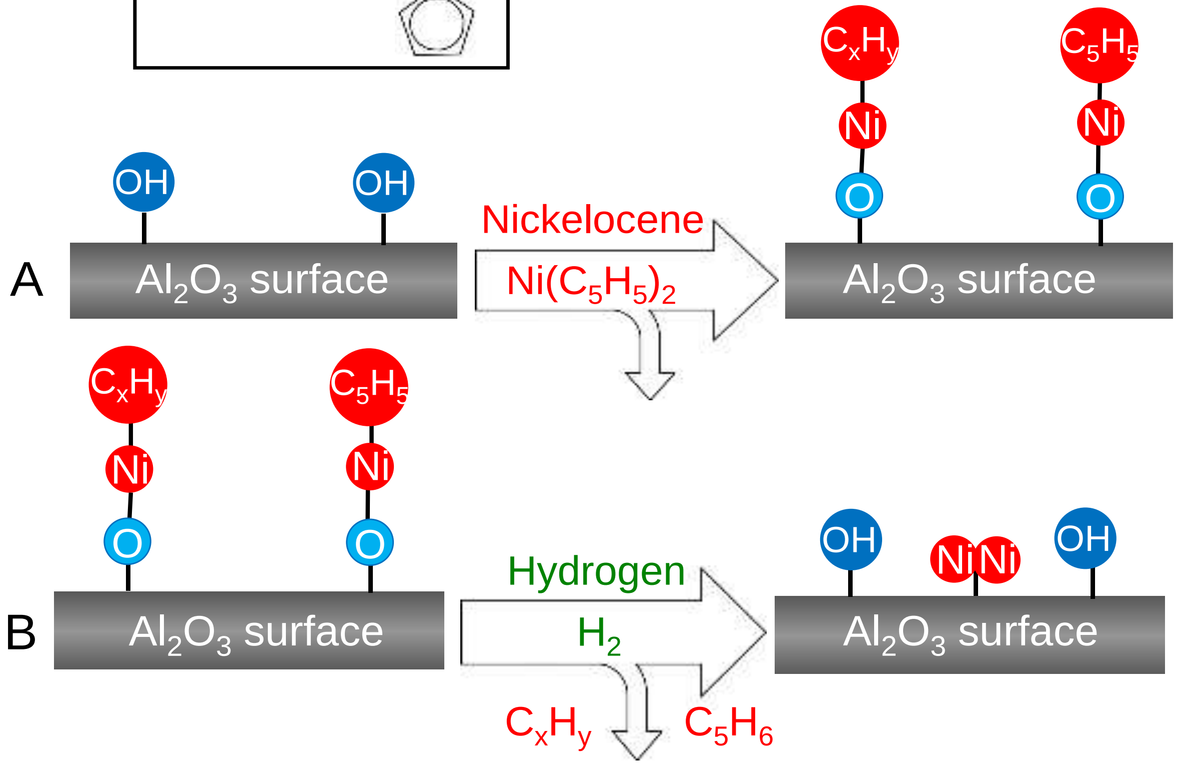
- **$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$** with H_2/CO ratio ≤1 due to the reverse water-gas shift reaction ($CO_2 + H_2 \rightleftharpoons CO + H_2O$)
  - Different from methane steam reforming ($CH_4 + H_2O \rightarrow CO + 3\ H_2$) where H_2/CO ratio >3 due to water-gas shift reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$)
- **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**



$NiCp_2$

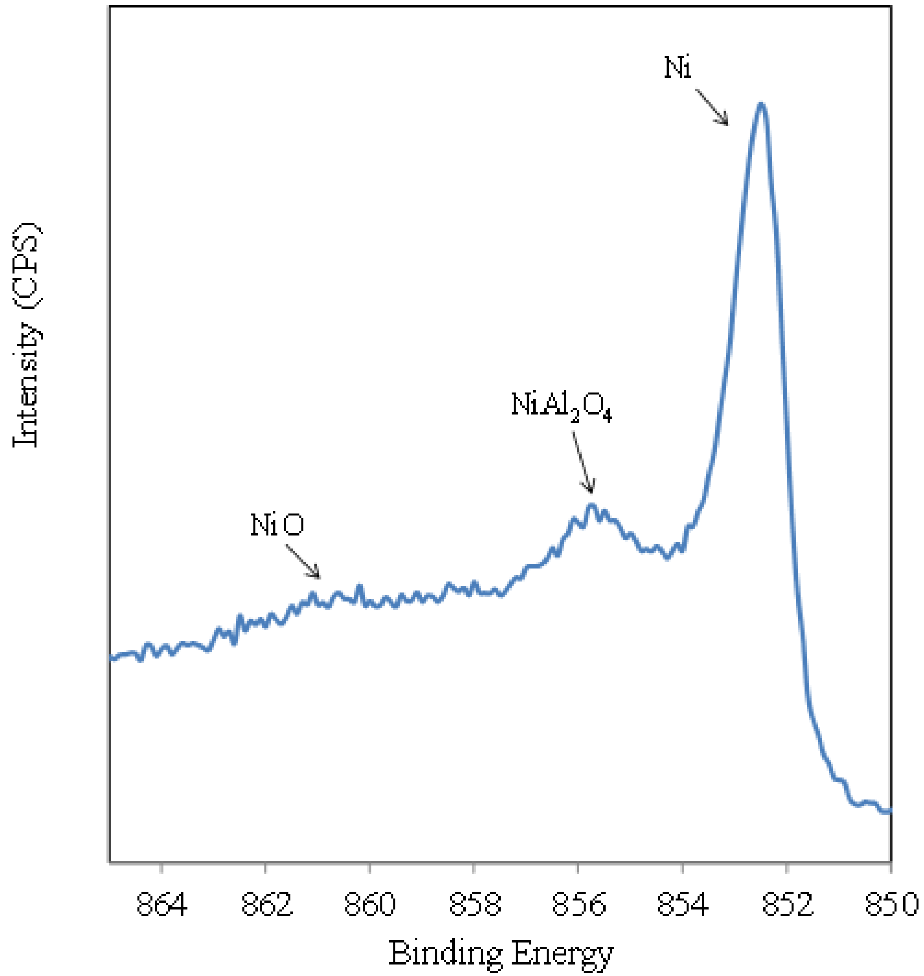


$NiCp_2$ reacts with the surface -OH groups and the Cp ring is removed

Hydrogenate the organic ligands bound to Ni

C Catalysts are calcined in air at 550 °C

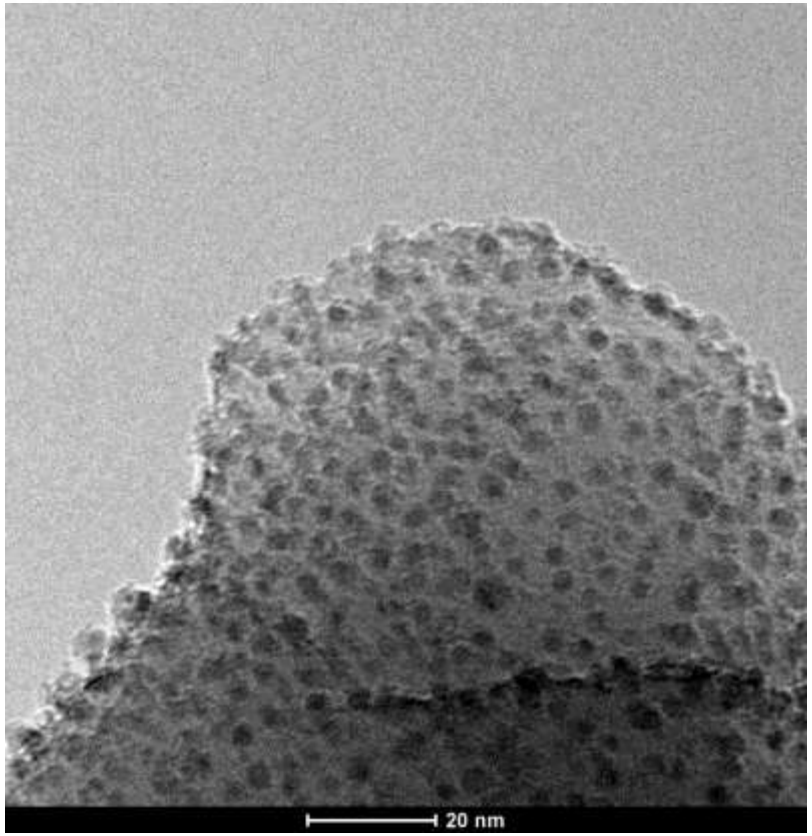
X-ray photoelectron spectroscopy analysis of α-Al_2O_3 nanoparticles supported Ni catalysts

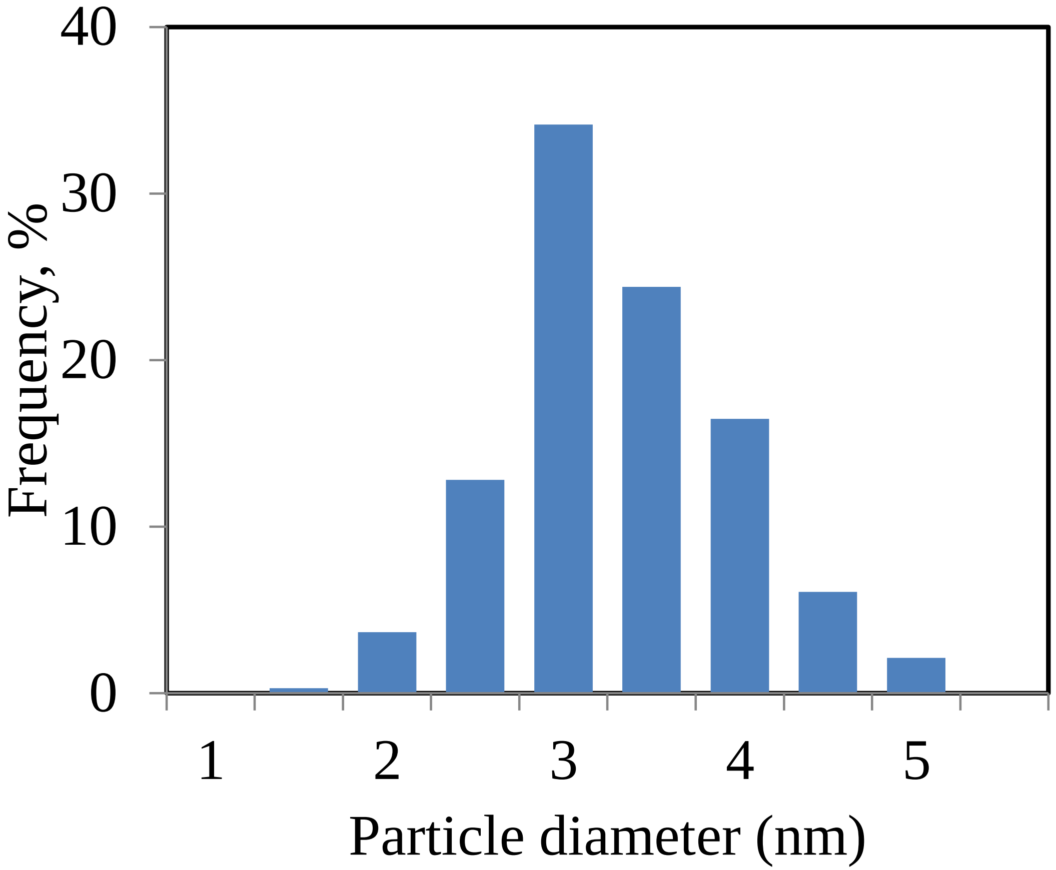


- In addition to Ni and NiO, $NiAl_2O_4$ spinel formed during Ni ALD, which increases Ni-support interaction

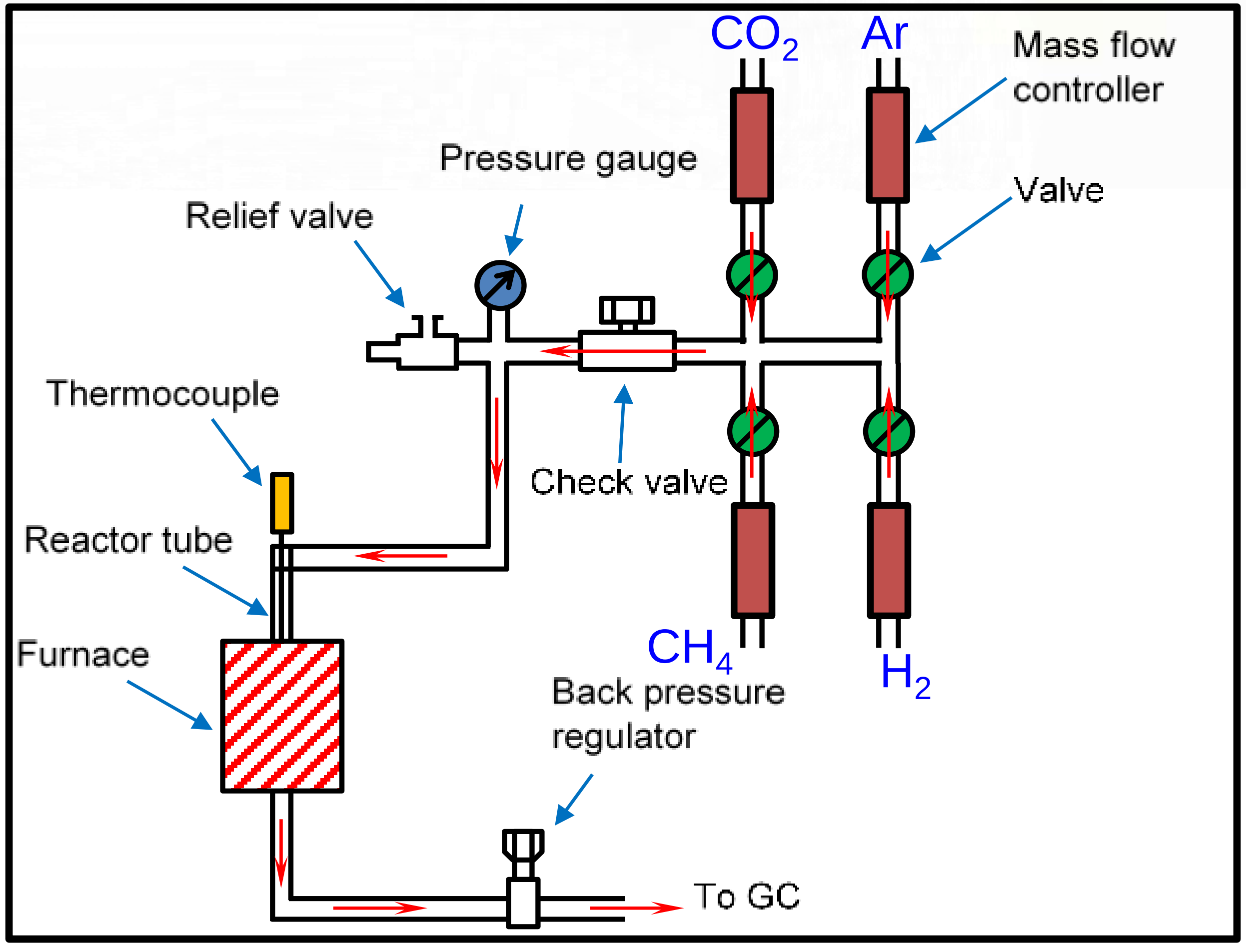
TEM image of α-Al_2O_3 nanoparticle-supported Ni catalysts

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

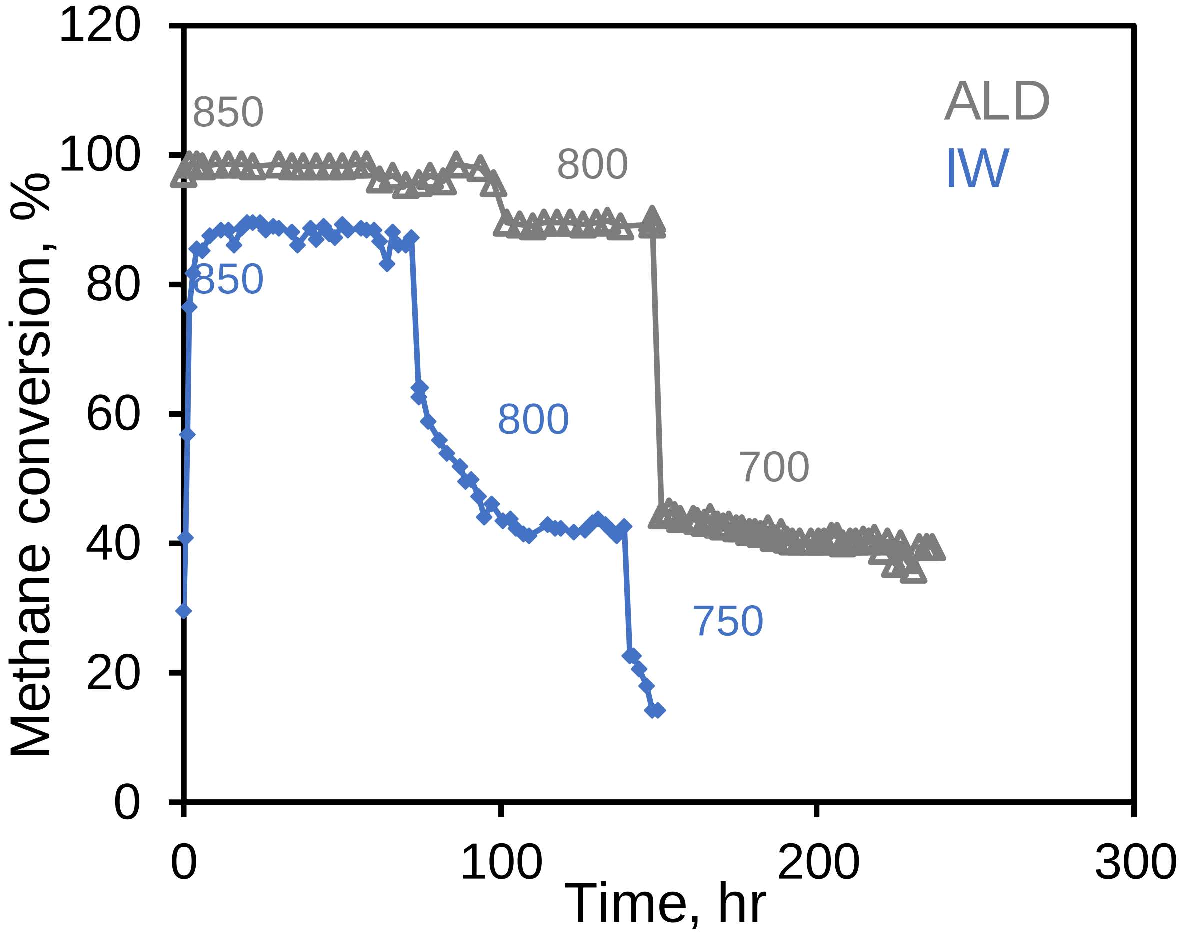




Packed bed catalytic reactor for dry reforming testing



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



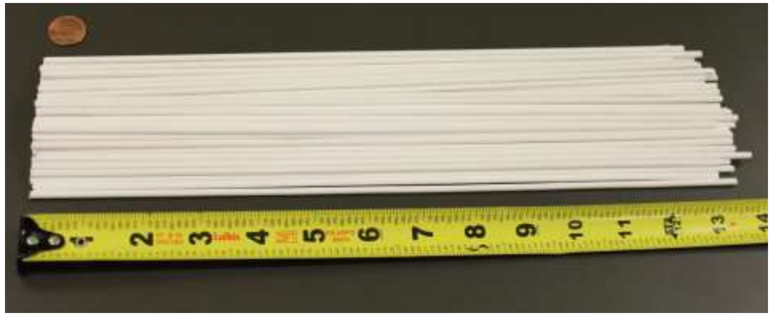
- ALD Ni on γ-Al_2O_3 particles
- CO_2 and CH_4 cylinder gases used in testing

- **<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 also used as catalyst substrate

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
- 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

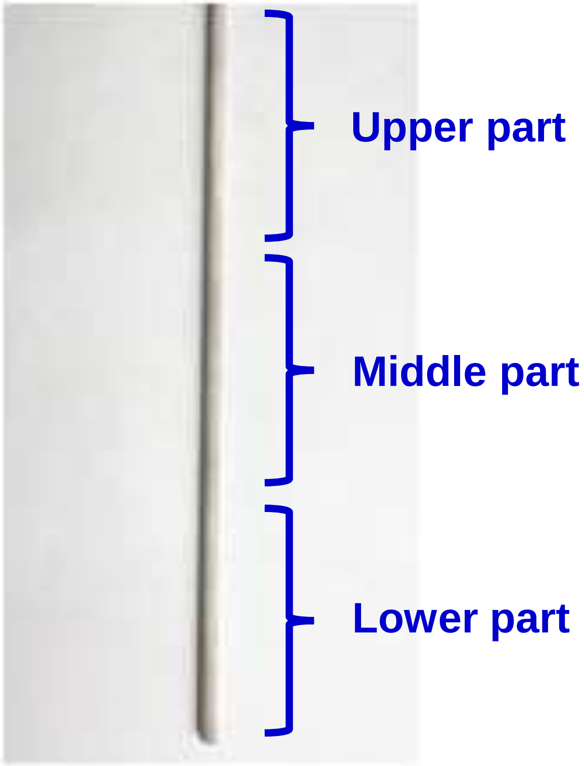
Before Ni ALD

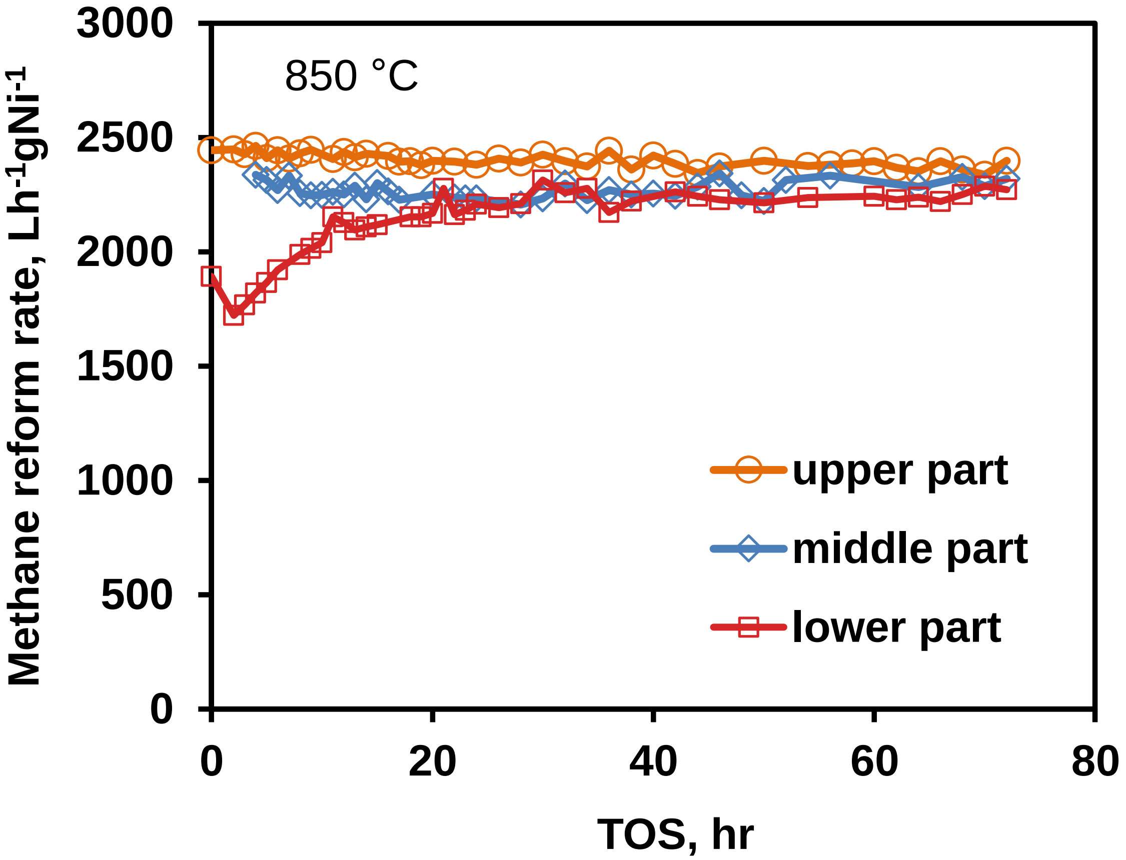
After Ni ALD

gti

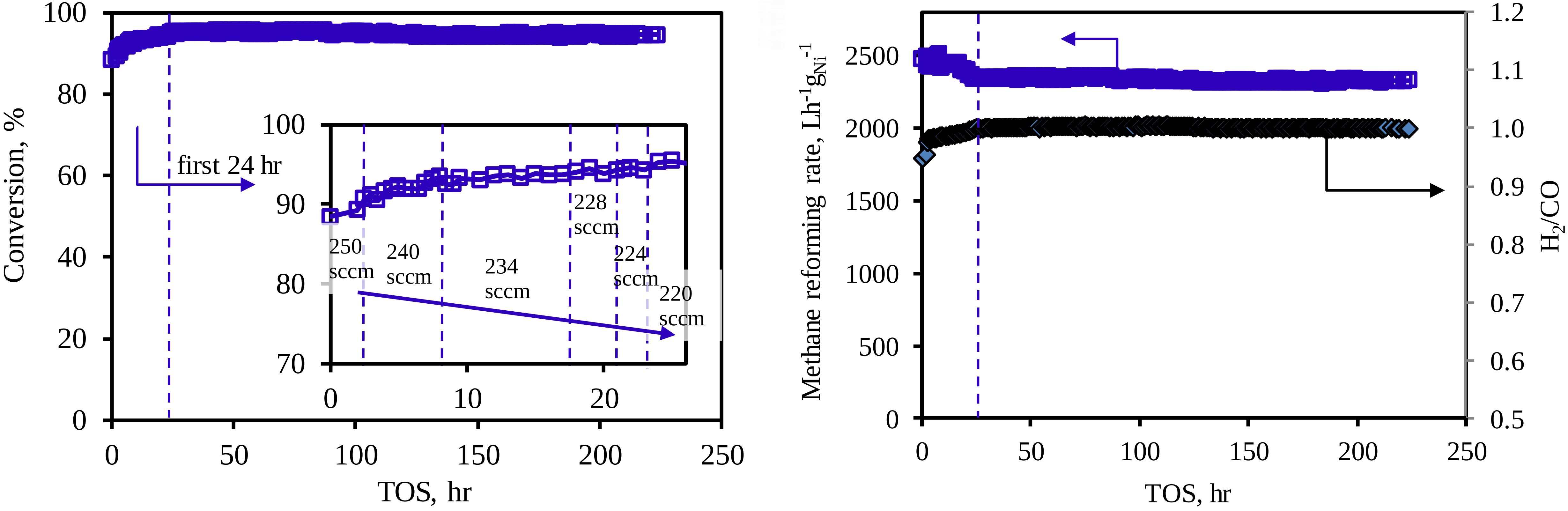
Dry reforming performance of the Ni ALD coated 20-cm-long hollow fibers

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)



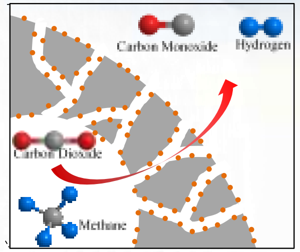


220-h continuous testing of 20-cm long hollow fiber supported Ni ALD catalyst indicated good stability

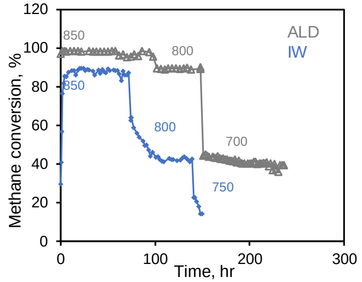


Summary

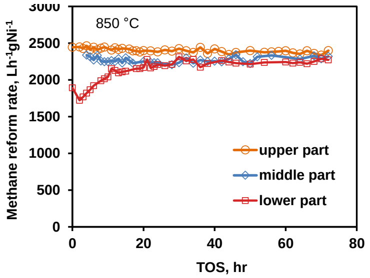
- We are developing ALD nano-engineered catalysts for utilization of CO_2 in dry reforming of methane to produce syngas



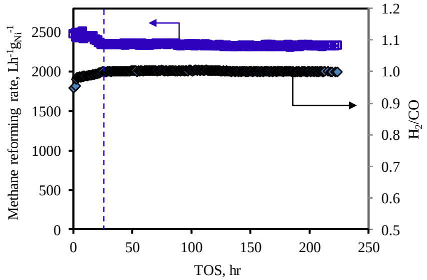
- ALD nano-engineered catalyst improves activity and stability for utilization of CO_2 in dry reforming of methane to produce syngas (compared to catalysts prepared by conventional incipient wetness method)



- Uniform nano-engineered Ni catalyst successfully prepared on high packing-density α-Al_2O_3 hollow fiber by ALD



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



gti

Acknowledgements

- **Financial and technical support**

DE-FE0029760

- **DOE NETL: Bruce Lani and Lynn Brickett**
- **Professor Liang Group**
  - Dr. Xiaofeng Wang
  - Dr. Shoujie Ren

Disclaimer

This presentation was prepared by GTI as an account of work sponsored by an agency of the United States Government. Neither GTI, the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors herein do not necessarily state or reflect those of the United States Government or any agency thereof.