Metal-free Catalyzed Synthesis of Novel Carbon by Carbon Allotrope Seeds

*Muhammad G Salim, Randy L. Vander Wal**

EMS Energy Institute
John and Willie Leone Family Dept. of Energy and Mineral Engineering
Penn State University, University Park, PA 16802
Contact: MS: msalim@psu.edu; *RVW: ruv12@psu.edu

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October 6th, 04-PSU-R2-02: Fuel Cell Technologies, 1:40-2:00 PM

PennState
College of Earth
and Mineral Sciences

Relevance to Research Area : R-2 – Advanced Catalysts and Catalyst Processing for Producing Hydrogen and Value-Added Solid Carbons

- Overview –
  - To overcome catalyst deactivation and address catalyst regeneration
  - Negate the need for separation and recovery of the catalyzed carbon from catalyst

- Problem statement – Necessitated by the high decomposition temperature for natural gas decomposition, a range of traditional metal, metal oxide, and carbon catalysts have been demonstrated in the literature but many of them deactivate because of carbon growth at active sites and the full encapsulation of catalyst particles.

- Objectives –
  - Establish proof-of-concept for carbon allotrope segments as new catalyst systems
  - Obtain data necessary for assessing the scalability and economics of using these carbon catalysts in a hydrogen production facility
  - Optimize the amount/type of high-value carbon produced
  - Improve process economics in thermo-catalytic decomposition of methane

Outline - Metal-free Catalyzed Synthesis of Novel Carbons by Carbon Allotrope Seeds

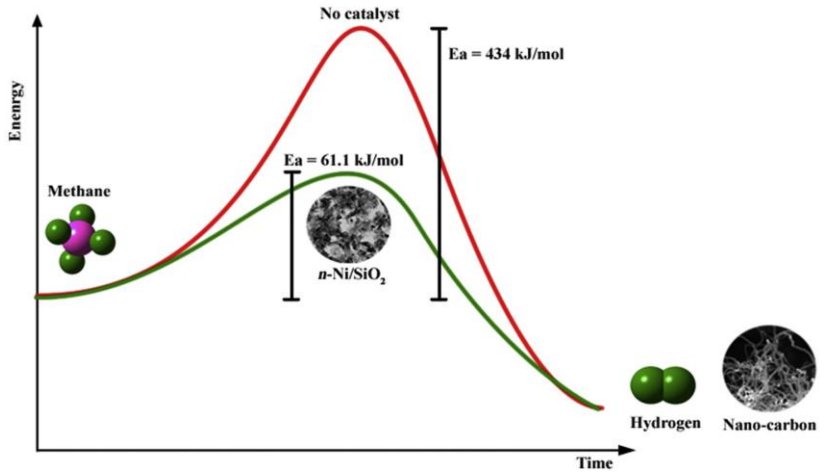
1. **Introduction**
   - Thermo-catalytic decomposition (TCD)
   - Current status of TCD with metal catalysts
   - Advantages of carbon catalysts
2. **Experimental approach and research objectives**
3. **Overview of research progress**
   - Applications and techniques
   - Current results
   - Summary of results
4. **Planned research targets and future work**

Thermo-catalytic Decomposition (TCD) Advantages

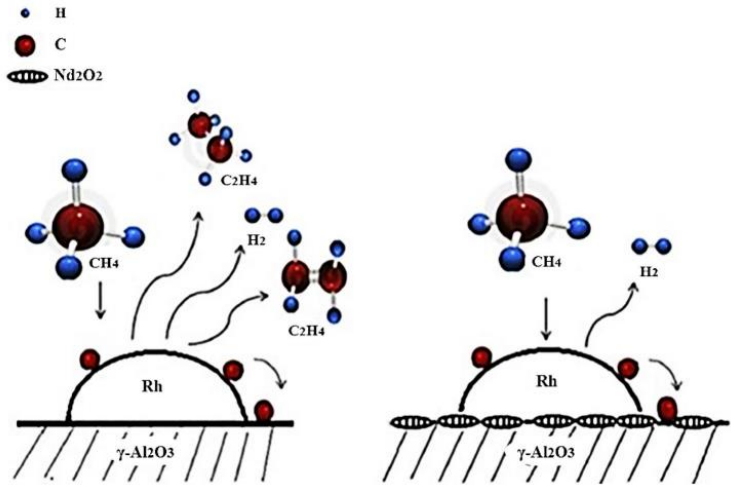
- TCD of methane is an attractive alternative to conventional steam reforming
- The process does not generate CO/CO_2 byproducts nor consume water resources
  - No need for water-gas-shift and CO_2 removal stages
- Stock desulphurization and steam generation are eliminated
- Energy requirement for cracking methane (37.8 kJ/mol of H_2) is less than that for steam reforming (63.3 kJ/mol of H_2)
- TCD life-cycle assessments [1] and techno-economic analyses [2] are positive

1. Environmental feasibility and reduction of greenhouse gases emissions. *International Journal of Hydrogen Energy*, **2009**. *34*(3), 1370-1376.
2. Technoeconomic analysis of the thermo-catalytic decomposition of natural gas. **2001** *Department of Energy, Colorado USA*

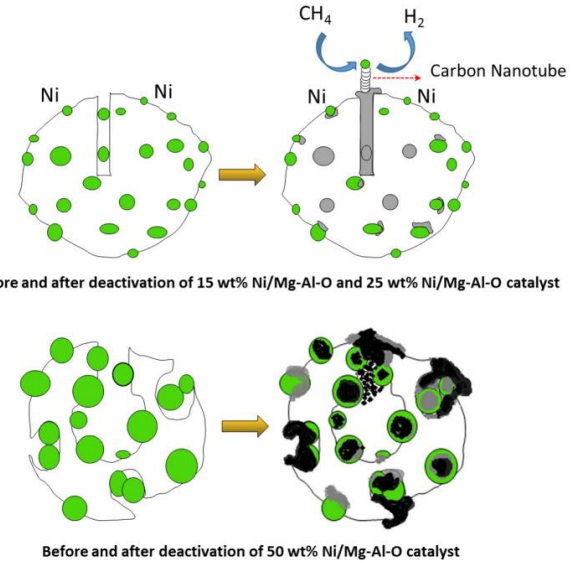
Current Status of Thermo-catalytic Decomposition of Methane – Metal Supported Catalysts



Methane decomposition kinetics[3]

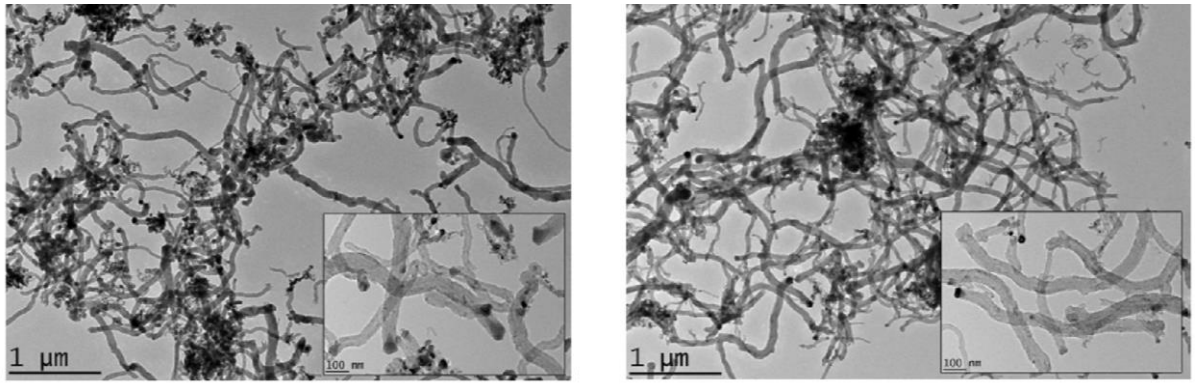


Representation of the behavior of methane decomposition on Rh metallic particles[4]



Catalyst deactivation by coking[4]

Traditional metal catalysts are deactivated during TCD

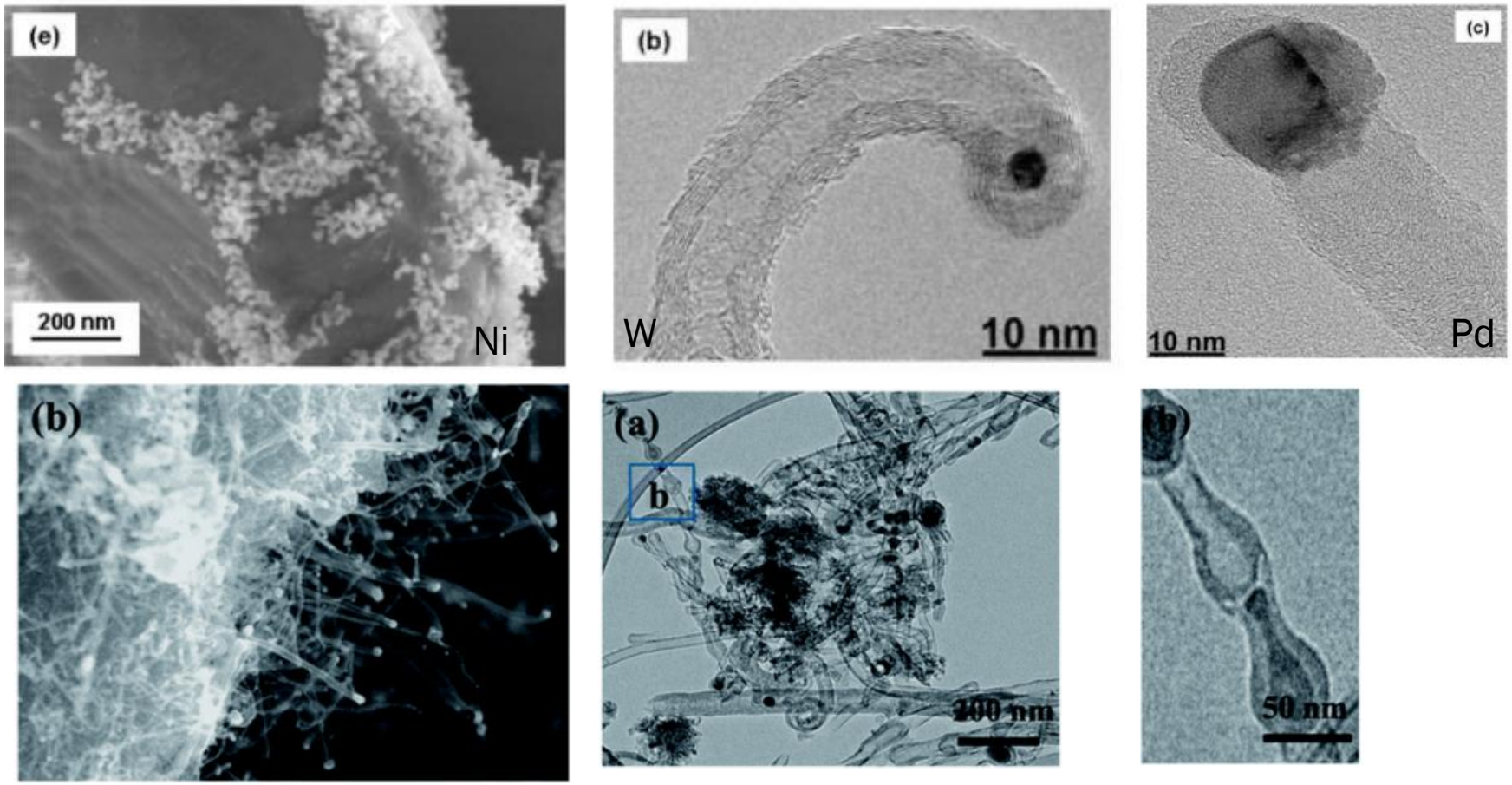


TEM Images of produced nanocarbon after TCD

Metal catalysts imbedded within carbon product – difficult to remove

3. *Int. J. Hydrog.* **2017,** *42* (2), 938-952.
4. *Mater Renew Sustain Energy.* **2020,** *9* (2), 8.

SEM & TEM Images of As-prepared CNTs



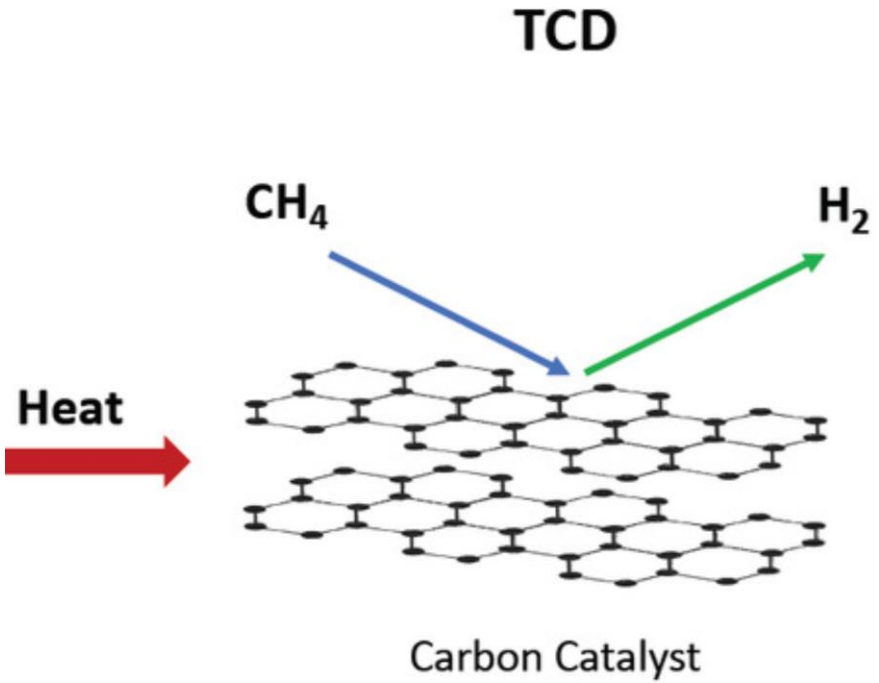
SEM and TEM images of carbon nano-morphologies grown under C_2H_4 or CH_4 flow diluted in inert (N_2) on metal catalyst[5, 6]

5. Carbon **2009,** *47* (3), 659-669
6. RSC Adv., **2018**,8, 12157-12164

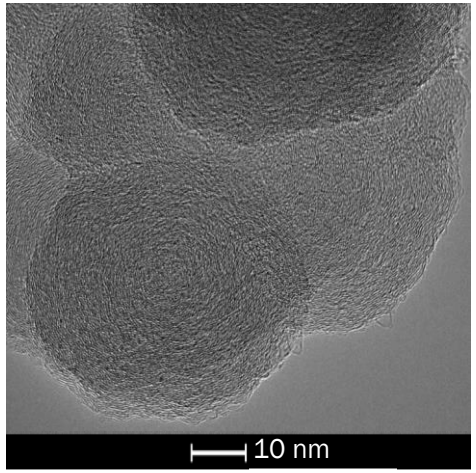
Advantages of Carbon Catalysts

- Stability – immune to coking
- High temperature resistance
- Insensitivity to sulfur poisoning
- Deposited carbon has multiple commercial uses as electrode material, carbon adsorbents, etc.
- Potential to be self-regenerating,

  i.e., **autocatalytic**



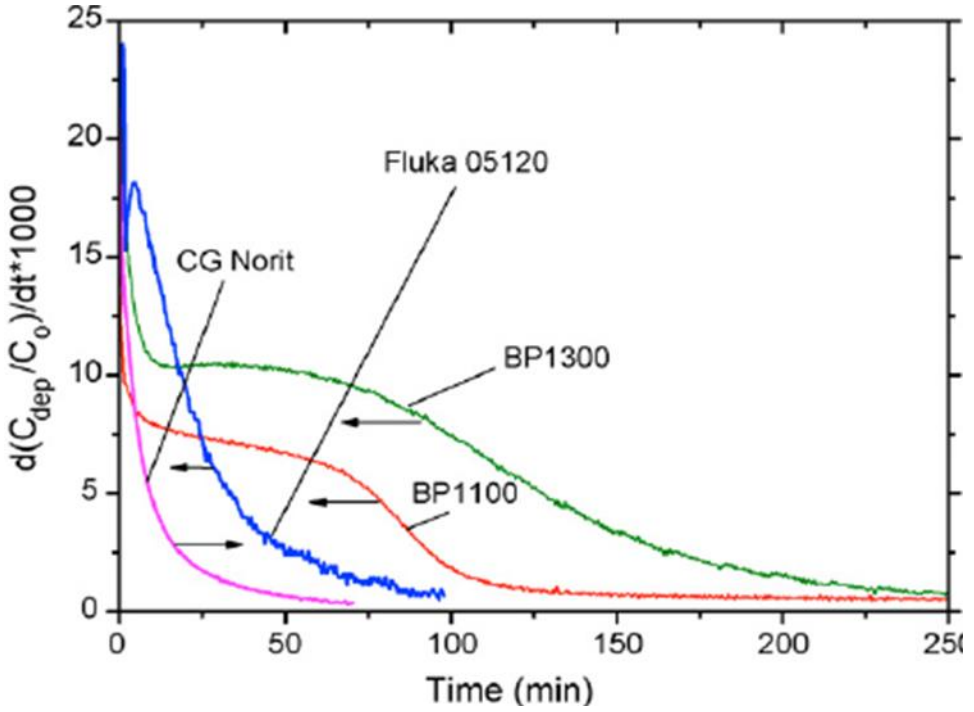
Carbon Black

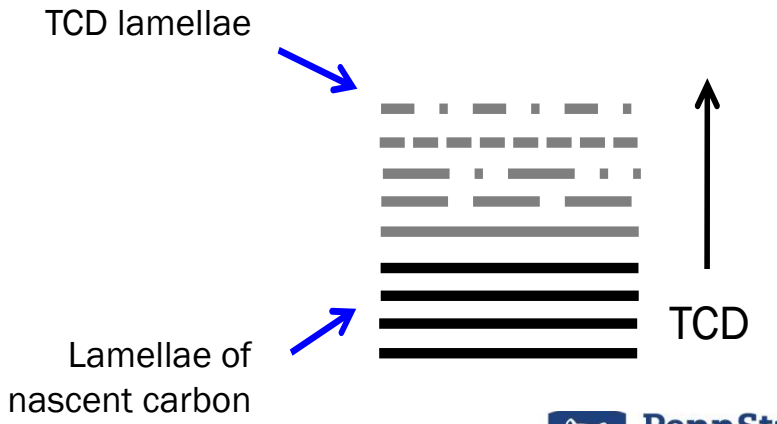


Addressing TCD and Regeneration Research Needs

- Despite advantages, carbon catalysts deactivate
- What is the relation between nanostructure & TCD rates?
- Why do we care?
  1. As carbon deposits, original catalyst is "buried"
  2. Subsequent decomposition is catalyzed by the preceding deposited carbon
  3. If the nanostructure could be controlled by combination of TCD conditions and/or initial catalyst, self-regeneration could occur

➢ **Ideally, the deposited carbon would be auto catalytic**





7. Chem. Eng. J. **2008**, 140, 432–438.

Experimental Approach and Objectives

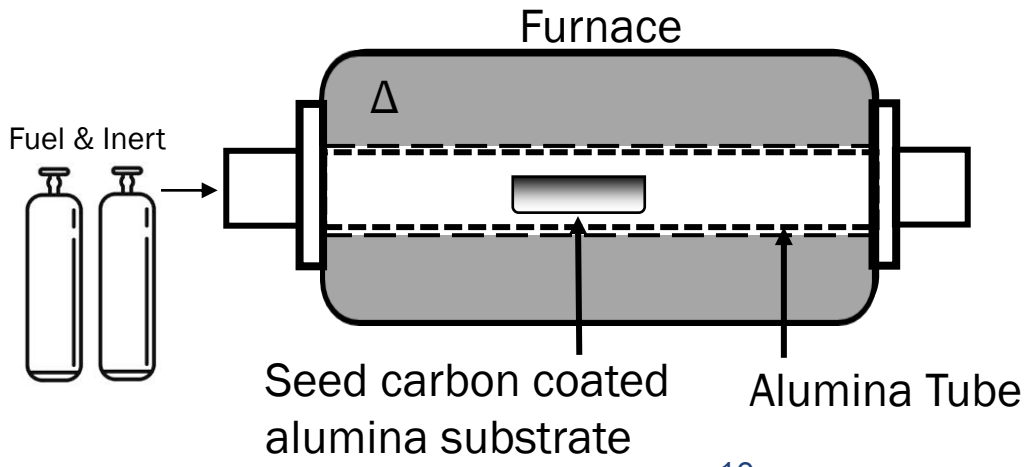
1. Use carbon black as catalysts
   - Integral to the product and compatible with the product structure
   - Experimentally, morphology is easy to distinguish from novel carbon formation
   - Negating the need to separate catalyzed CNTs from a support

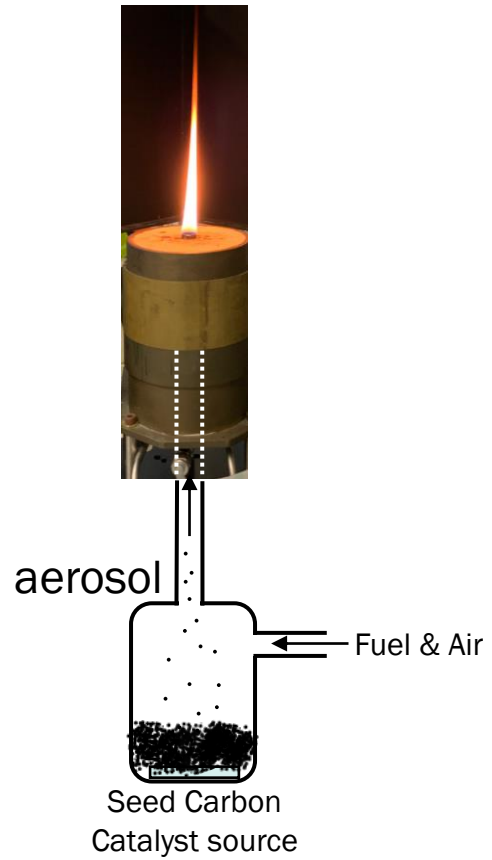
2. Carbon black can be supported or used as an aerosol

3. Evaluate morphologically distinct nanostructure forms
   - Potentially gaining selectivity and control of novel carbon formation

Research Progress Overview

- Application of different techniques and carbon catalysts for TCD with permutations of fuel/inert/air ratios
- Fixed bed reactor and aerosolized carbon seeded flame
  - Furnace: 1000°C, 1200°C, 1500°C
    - Fuels: C_2H_2, C_2H_4, CH_4
    - Fuel/Inert Ratios: 0.05, 0.10, 0.20, 0.25
    - Carbon catalysts: Graphene Oxide, Carbon Black (various)
  - Carbon catalyst-seeded flame
    - Fuels: C_2H_2, C_2H_4, CH_4
    - Fuel/Air ratios: 0.05, 0.07, 0.09, 0.10, 0.12, 0.14, 0.15, 0.20
      - Two-phase burner, with inner Fuel/Inert ratio





Instruments and Equipment

- Sophisticated custom gas-flow controller setup for regulating pre- and post-flow gas mixing for furnace and seeded-flame synthesis

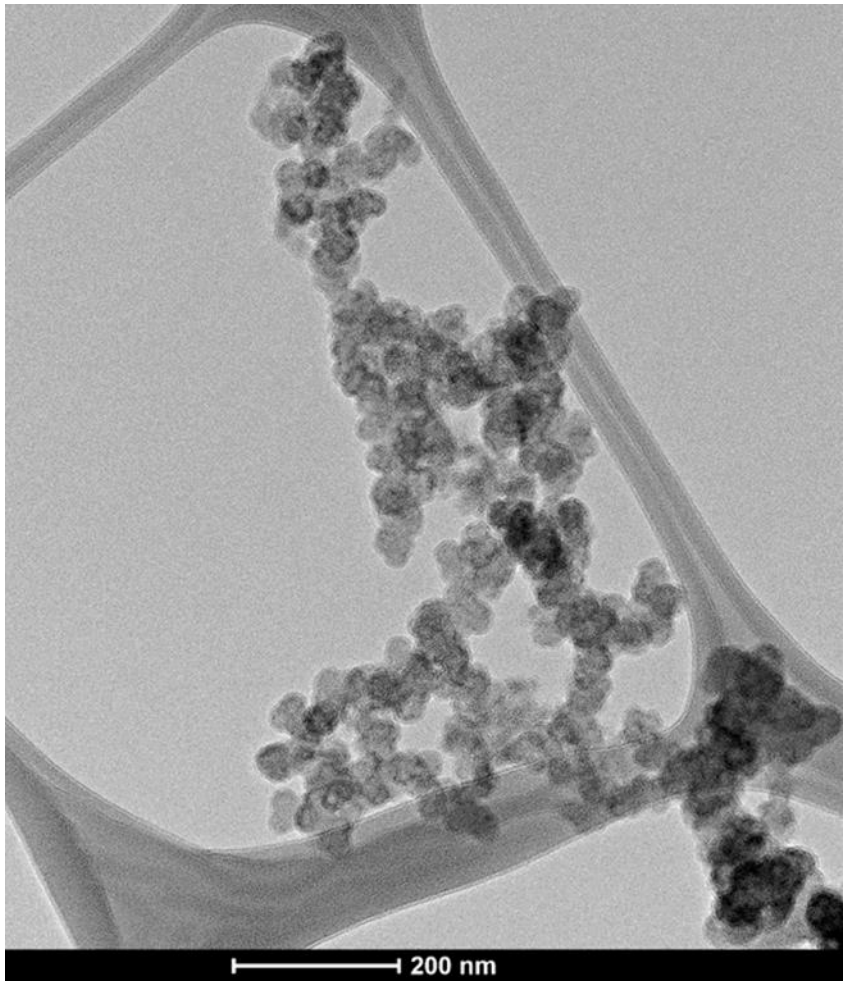
Flow-controlled gas lines for regulating multiple gas mixes

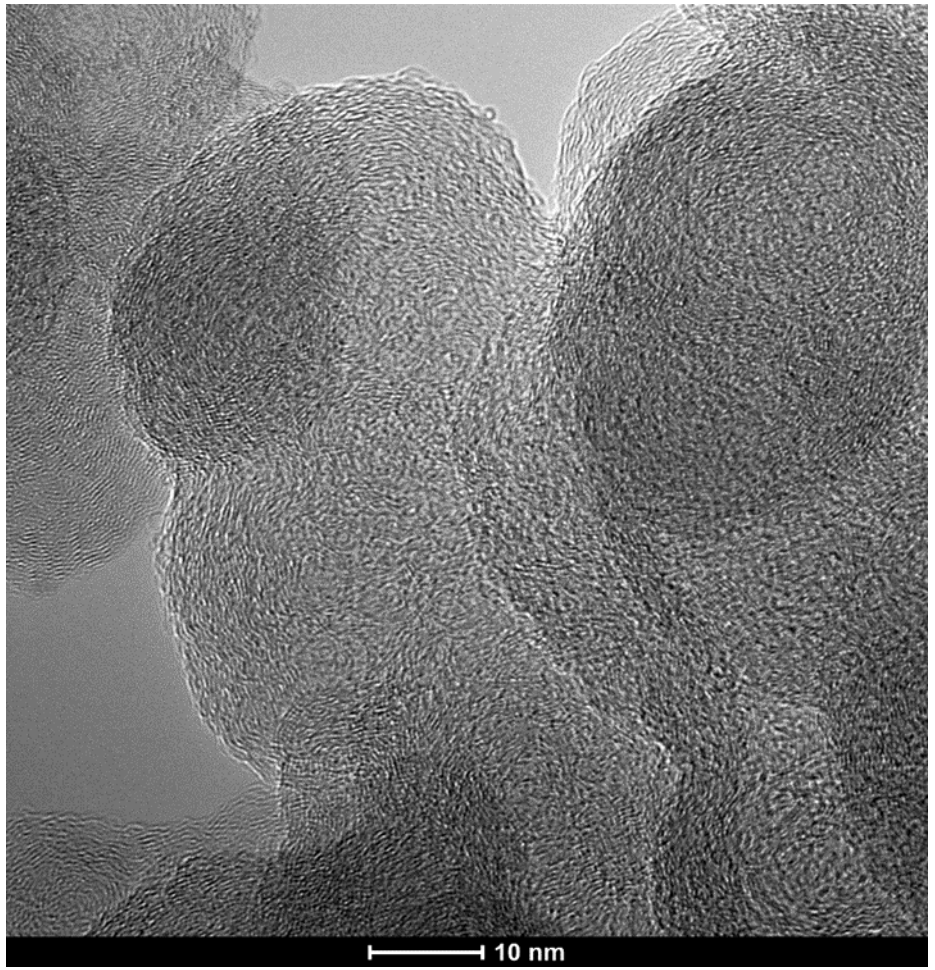
MTI GSL-1700A Tube Furnace
Operation up to 1650°C

Lindberg/Blue M Tube Furnace
Operation up to 1600°C

Results – Nascent Carbon Black as Seed Catalyst

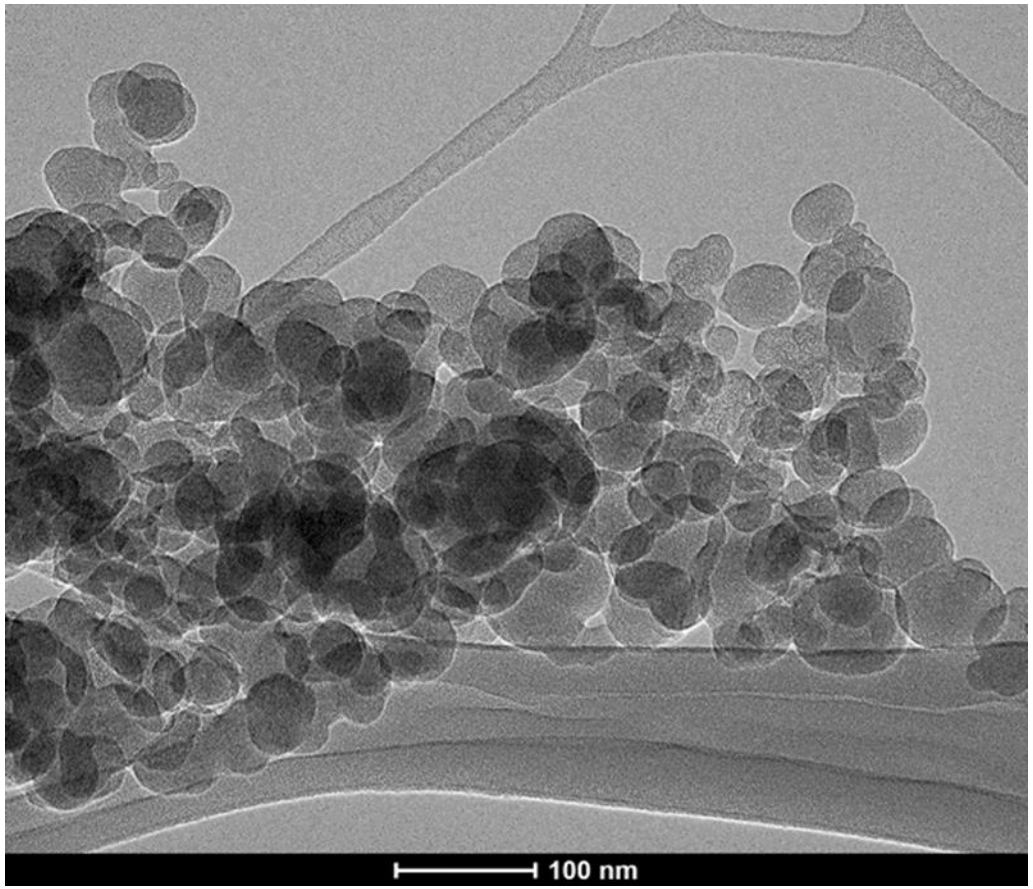
XC72RG - nascent

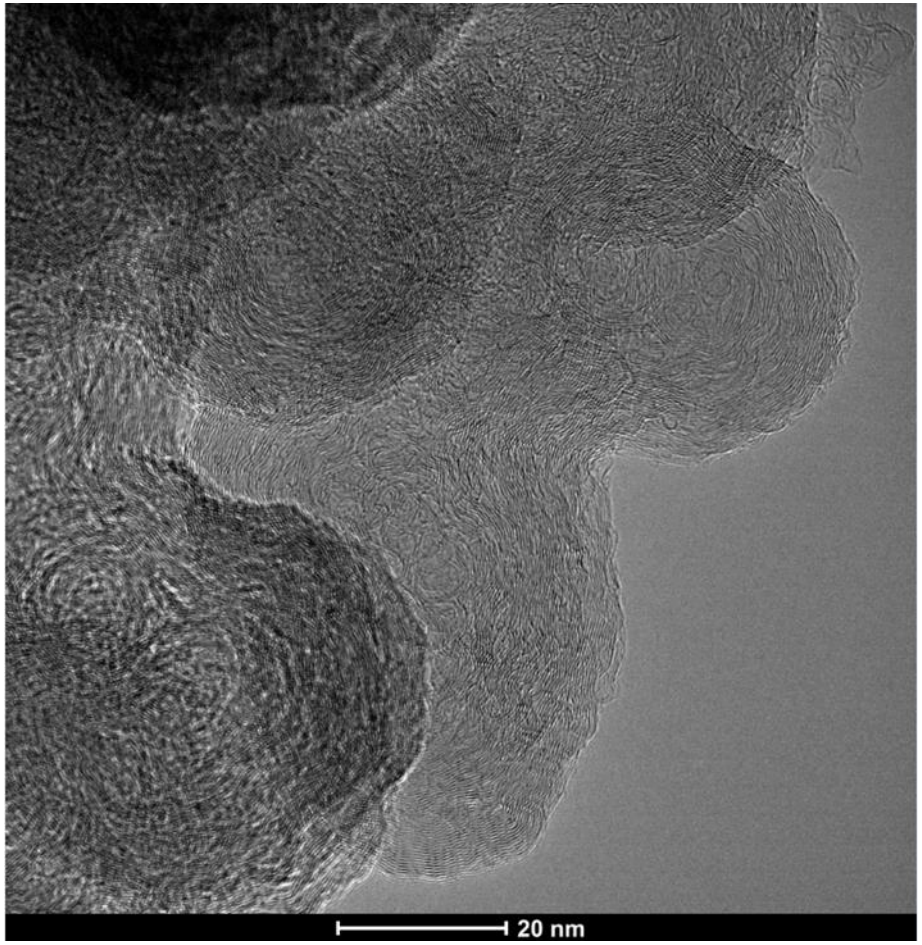




Results – Carbon Black as Seed Catalyst – Inert Environment

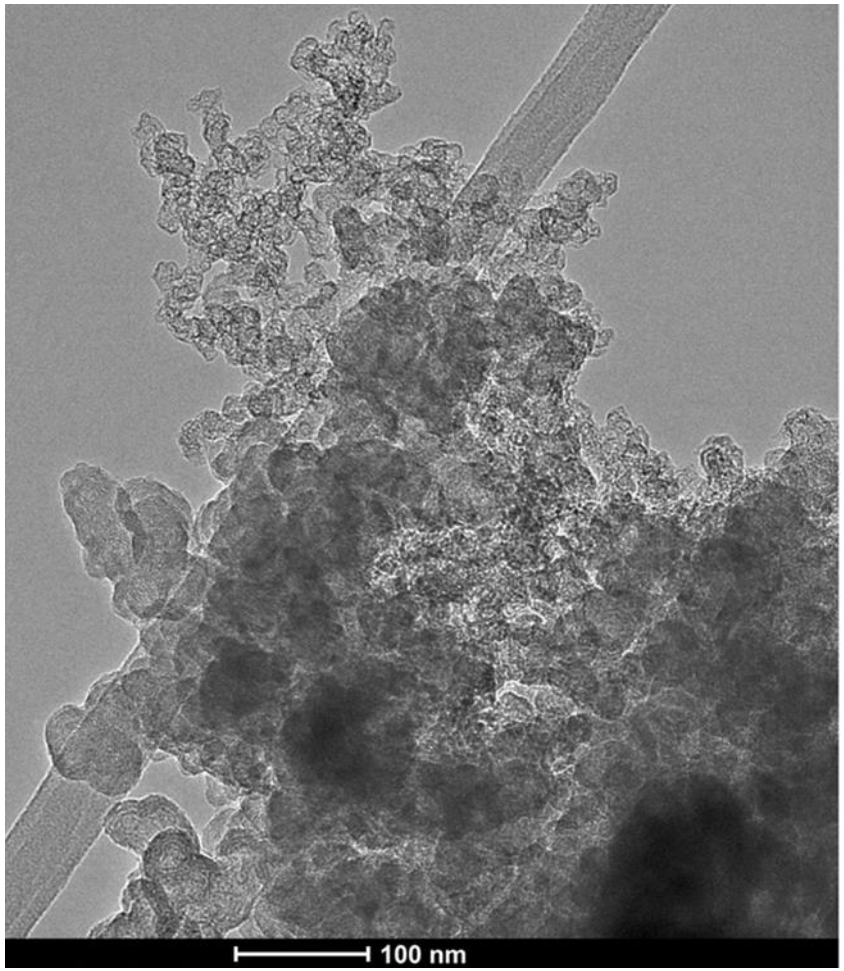
XC72RG – 1500°C – 1 h - Argon

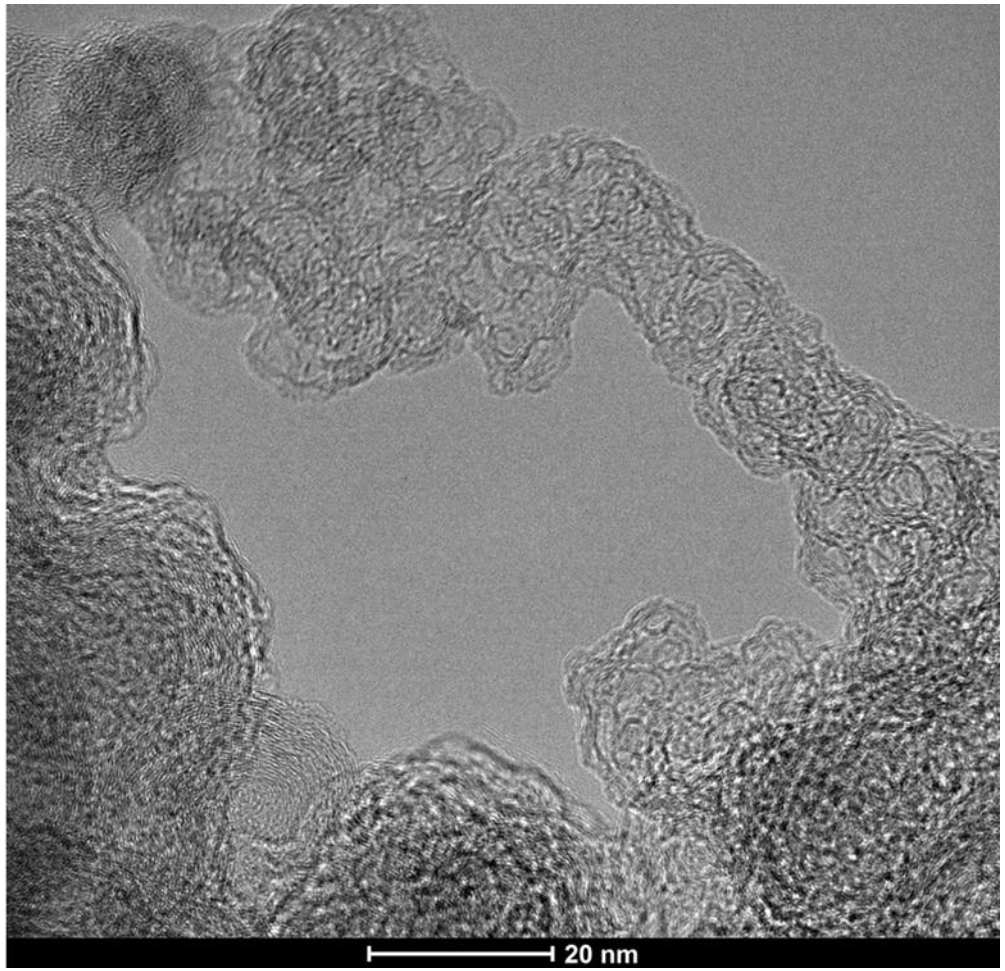




Results – Carbon Black as Seed Catalyst – CH_4 Environment

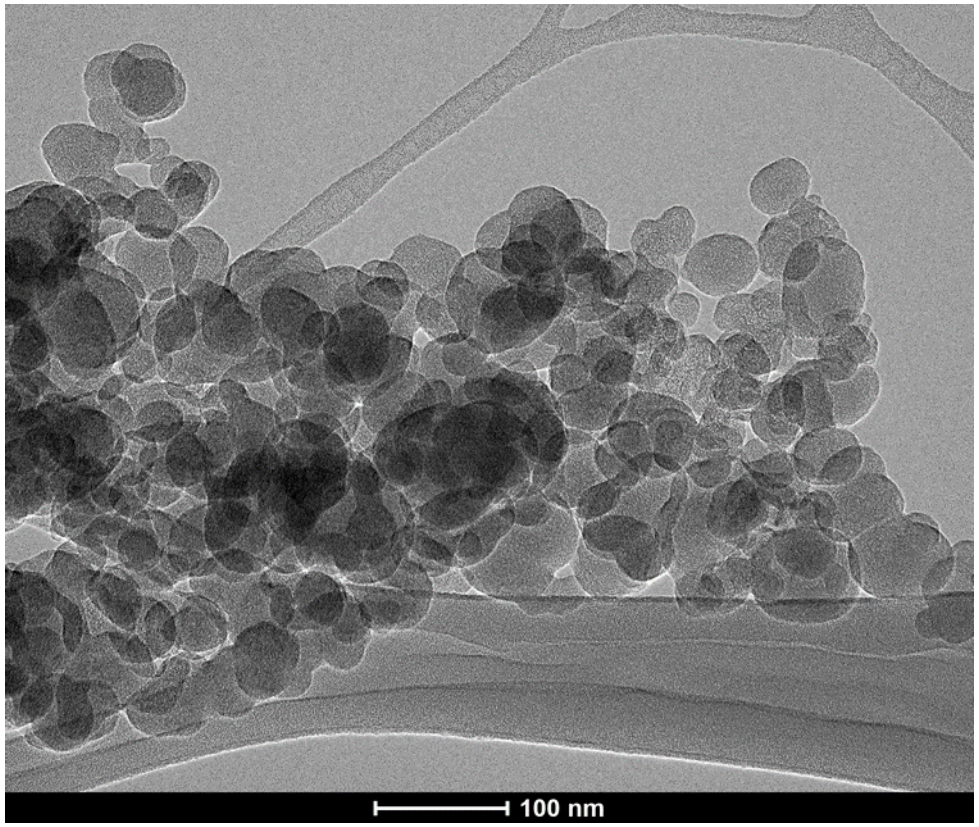
XC72RG – 1500°C – 1 h - CH_4 5%



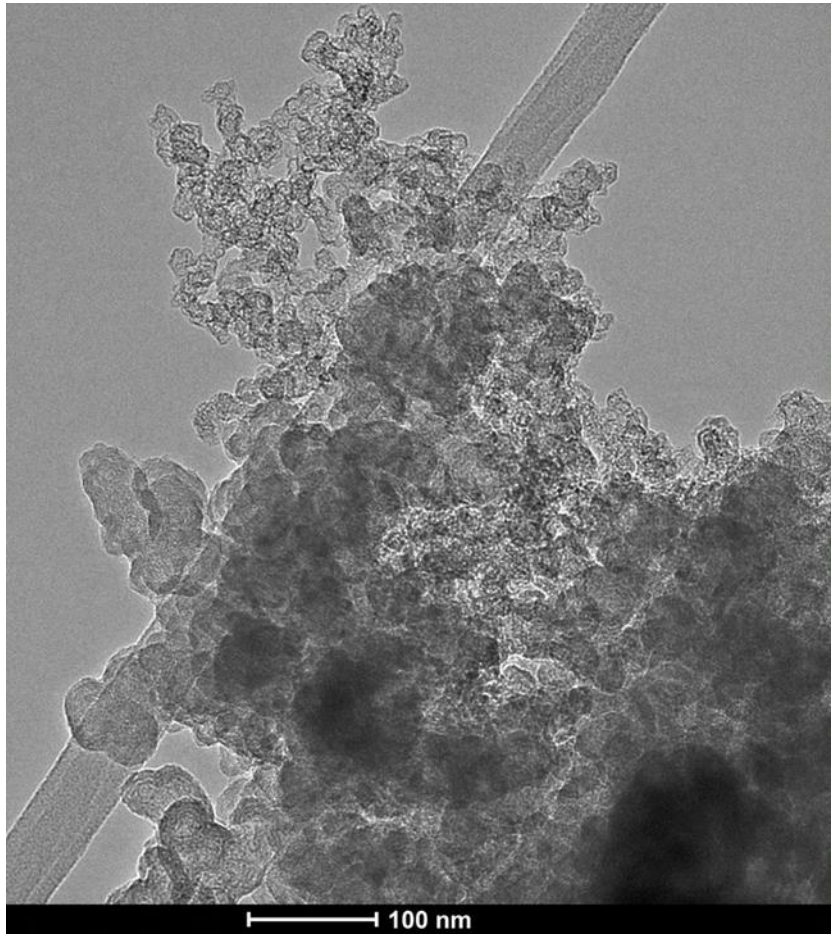


Results – Comparison of Inert vs CH_4 Environments

XC72RG – 1500°C –1 h – Argon

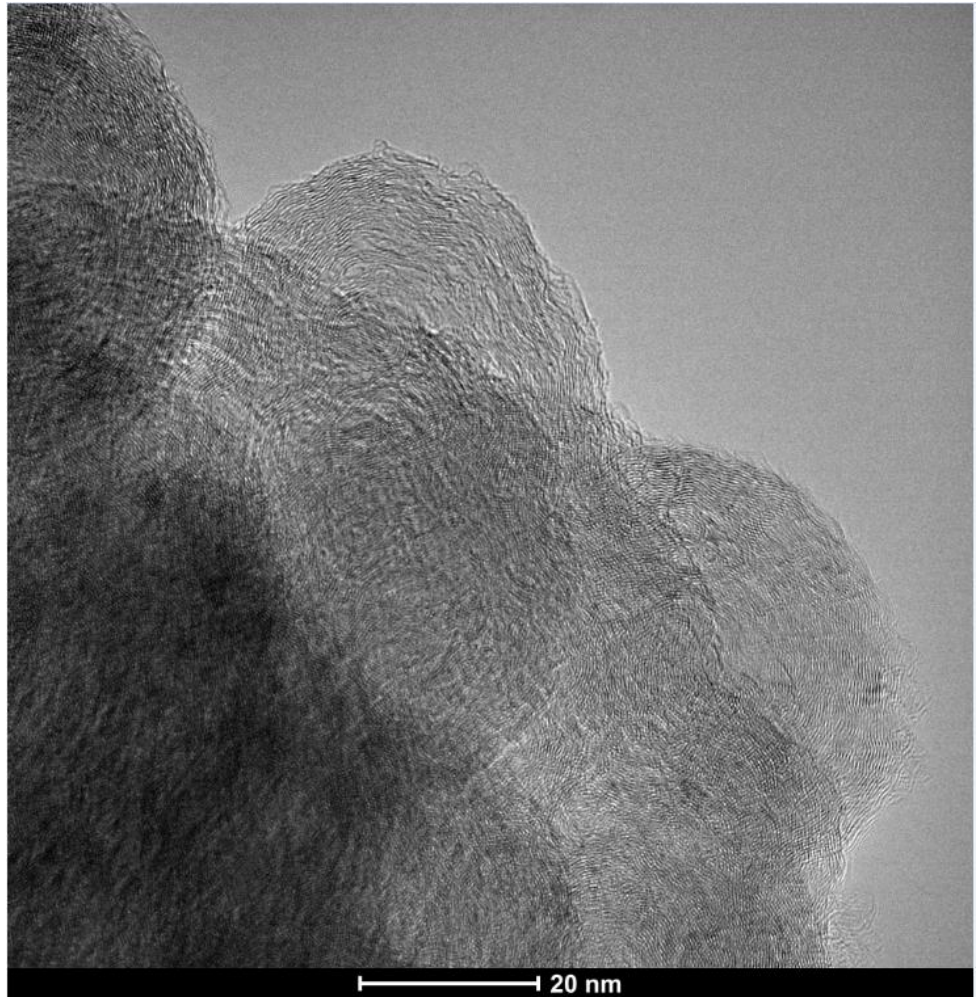


XC72RG – 1500°C – 1 h – CH_4 5%

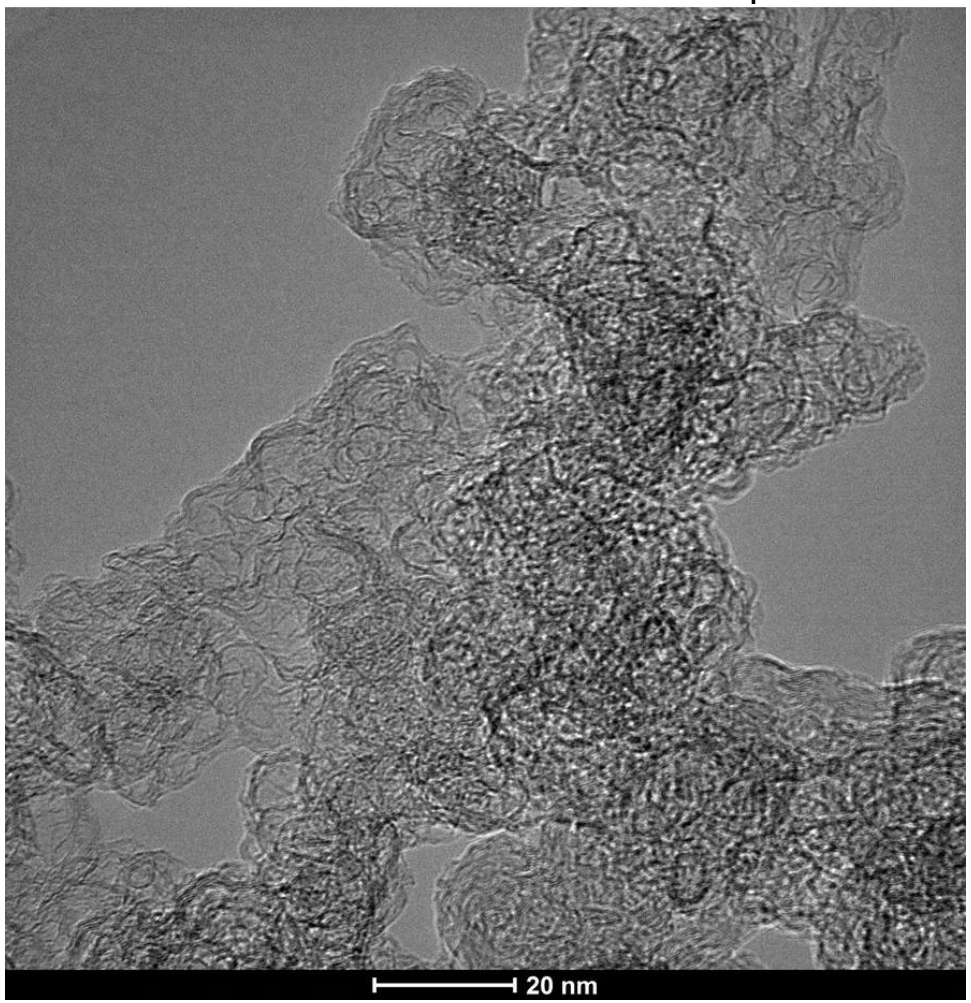


Results – Comparison of Inert vs CH_4 Environments

XC72RG – 1500°C –1 h– Argon

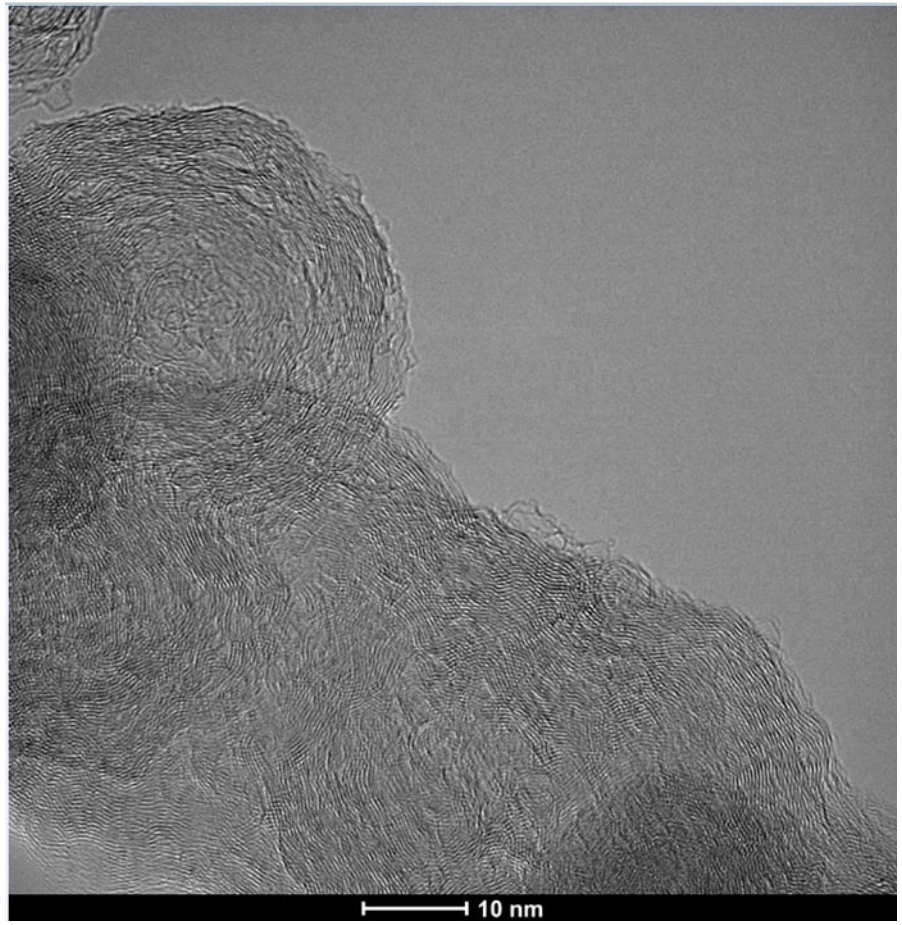


XC72RG – 1500°C – 1 h – CH_4 5%

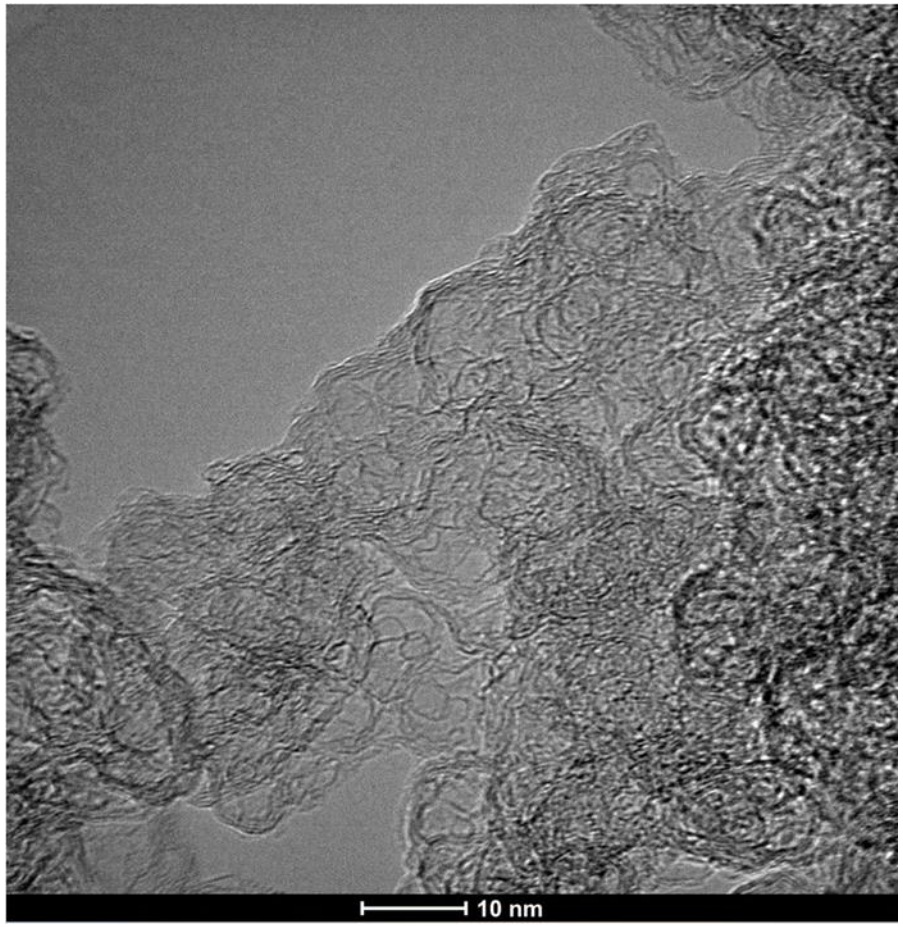


Results – Comparison of Inert vs CH_4 Environments

XC72RG – 1500°C –1 h– Ar



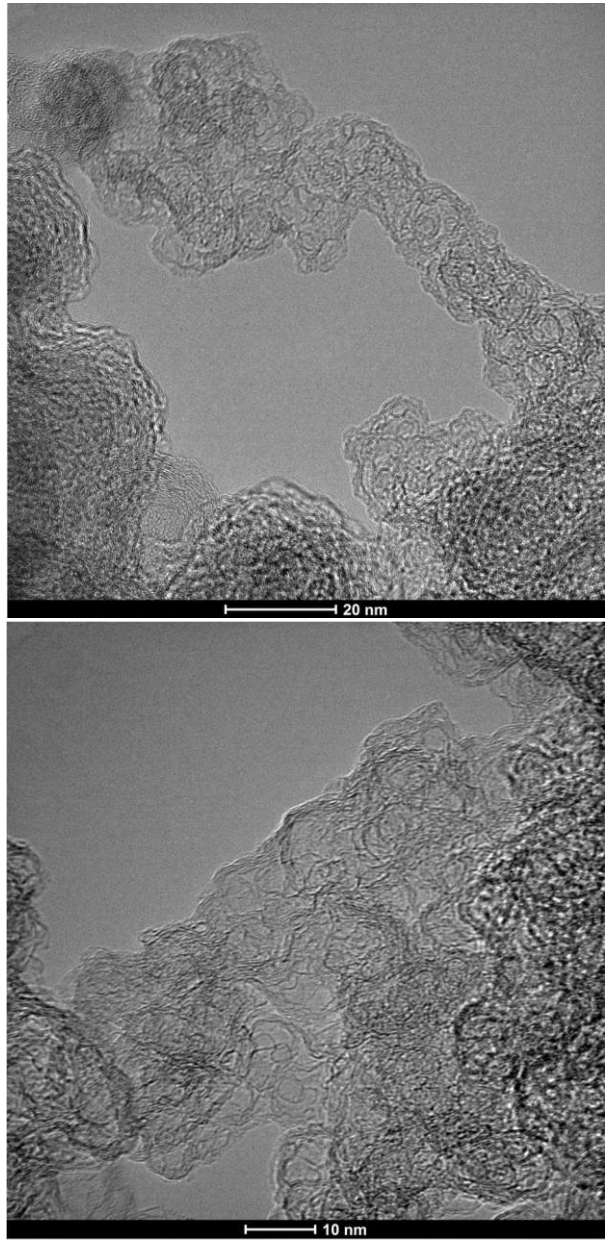
XC72RG – 1500°C – 1 h – CH_4 5%



Summary of Results

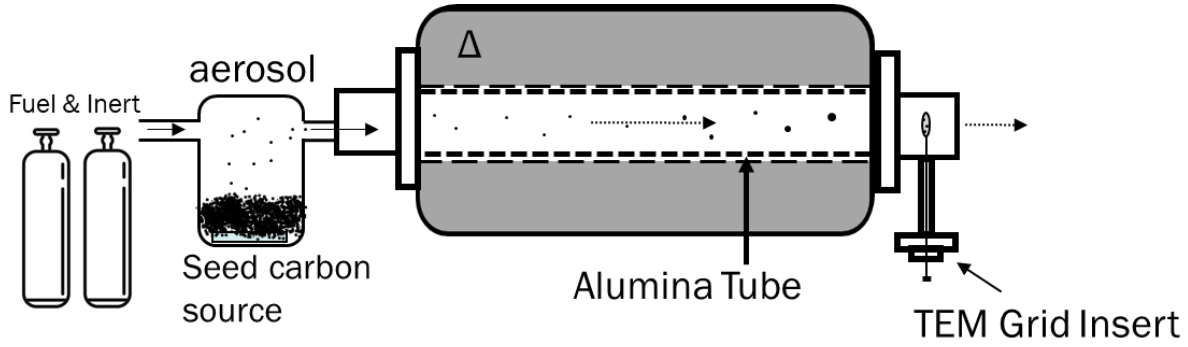
- We have shown TCD using carbon catalysts to be a promising process
- Carbon black as seed catalysts can be self-propagating and rate-maintaining
- Optimization of chaotic nanostructure formation is possible through control of carbon seed catalyst and reaction conditions

XC72RG – 1500°C – 1 h – CH_4 5%



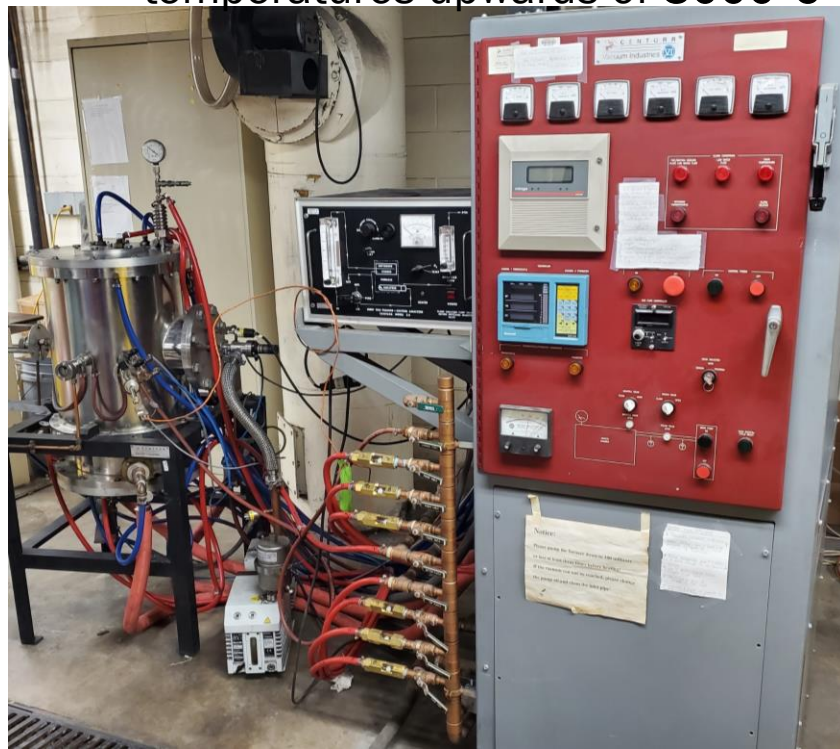
Plans for Research Progression

- Testing under condition of hydrogen and pyrolysis gasses
- Investigation of active site generation and propagation
- Measurement of kinetic rates
  - Microreactor AMI-300 + Gas Chromatograph



Altamira AMI-300 Chemisorption Analyzer with in-tandem Gas Chromatograph

Graphitization Furnace temperatures upwards of **3000°C**

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Thank You!
Muhammad G. Salim, Randy L. Vander Wal*
Contact:
MGS: email – msalim@psu.edu
phone – 724-766-6150
*RVW: email – ruv12@psu.edu
phone – 814 -865-5813
PennState
College of Earth
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