# BIMETALLIC NANOCATALYSTS IN MESOPOROUS SILICA FOR HYDROGEN PRODUCTION FROM COAL-DERIVED FUELS

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# *Outline*

- Steam Reforming and $H_2$ Economy
- Nanocatalysts in Mesoporous Silica

  -Bi-metallic Pd-Co and Pd-Ni in nanoporous Silica
- Characterization – XRD, FT-IR, BET, HRTEM, and Magnetic Studies
- Steam Reforming of MeOH with Bimetallic Nanocatalysts

## HYDROGEN PRODUCTION ( Steam Reforming)

Steam reforming is a favored route to produce $H_2$ from hydrocarbons ($C_nH_{2n+2}$) and low-molecular weight alcohols **with the aid of a catalyst.**

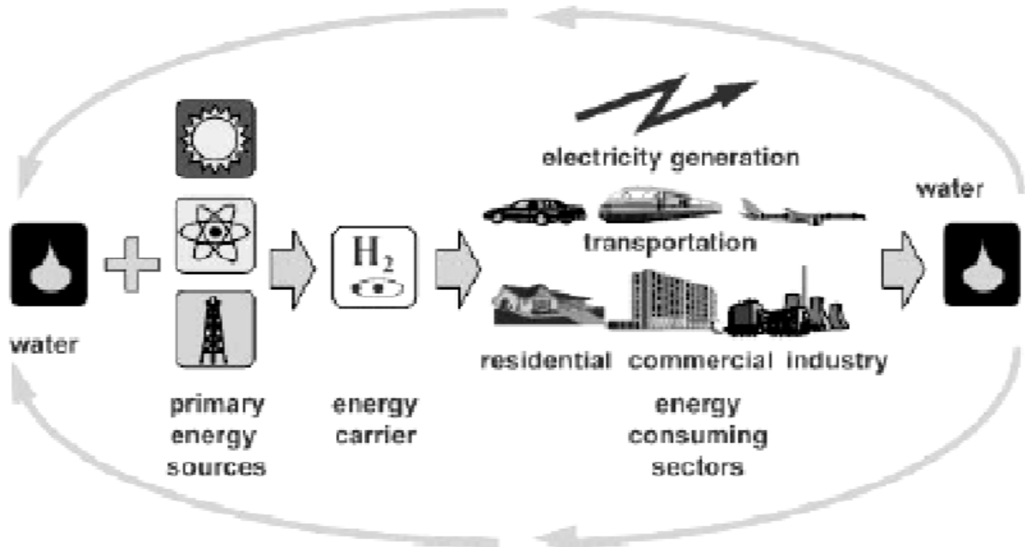
For Example, $CH_3OH + H_2O \leftrightarrow 3H_2 + CO_2$

Methanol decomposition:
$CH_3OH \leftrightarrow 2H_2 + CO$

Water-gas shift reaction:
$CO + H_2O \leftrightarrow H_2 + CO_2$

Steam Reforming of Methanol (SRM) is typically carried out at 200–400$^oC$ using a copper-based catalyst (Cu/Zn/Al).

# HYDROGEN – FUEL OF THE FUTURE




(a) Easy to produce

(b) Versatile; converts easily to other energy forms at the user end

(c) High utilization efficiency

(d) Environmentally compatible (zero- or low-emission)

*Hui-Ming Cheng ,  et.al. Carbon (2001)*

# HYDROGEN PRODUCTION

A number of materials are being developed to replace Cu/Zn/Al catalysts.

Oxide supported Pt group metal catalysts have received a great deal of attention

**These materials are very active; however,**

↓

✓Poor selectivity, yielding primarily CO and $H_2$ during the reforming reaction

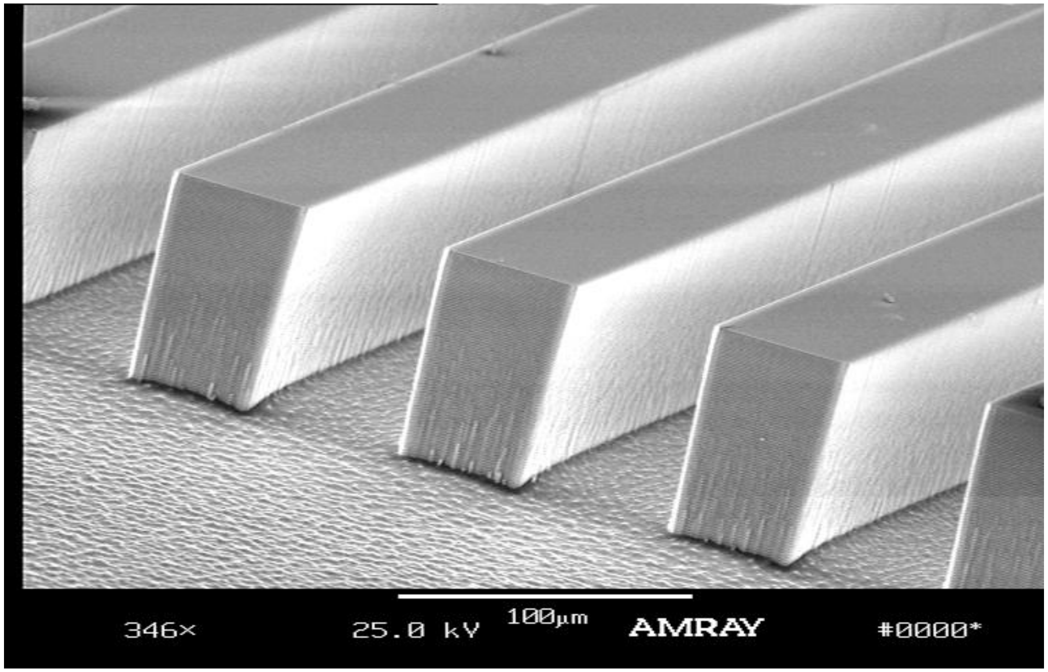
✓High cost

✓Catalyst poisoning by CO

# Goal-Interdisciplinary Research

- **Develop novel nanocatalysts for hydrogen production by steam reforming reactions (SRRs) of fuels/biofuels.**

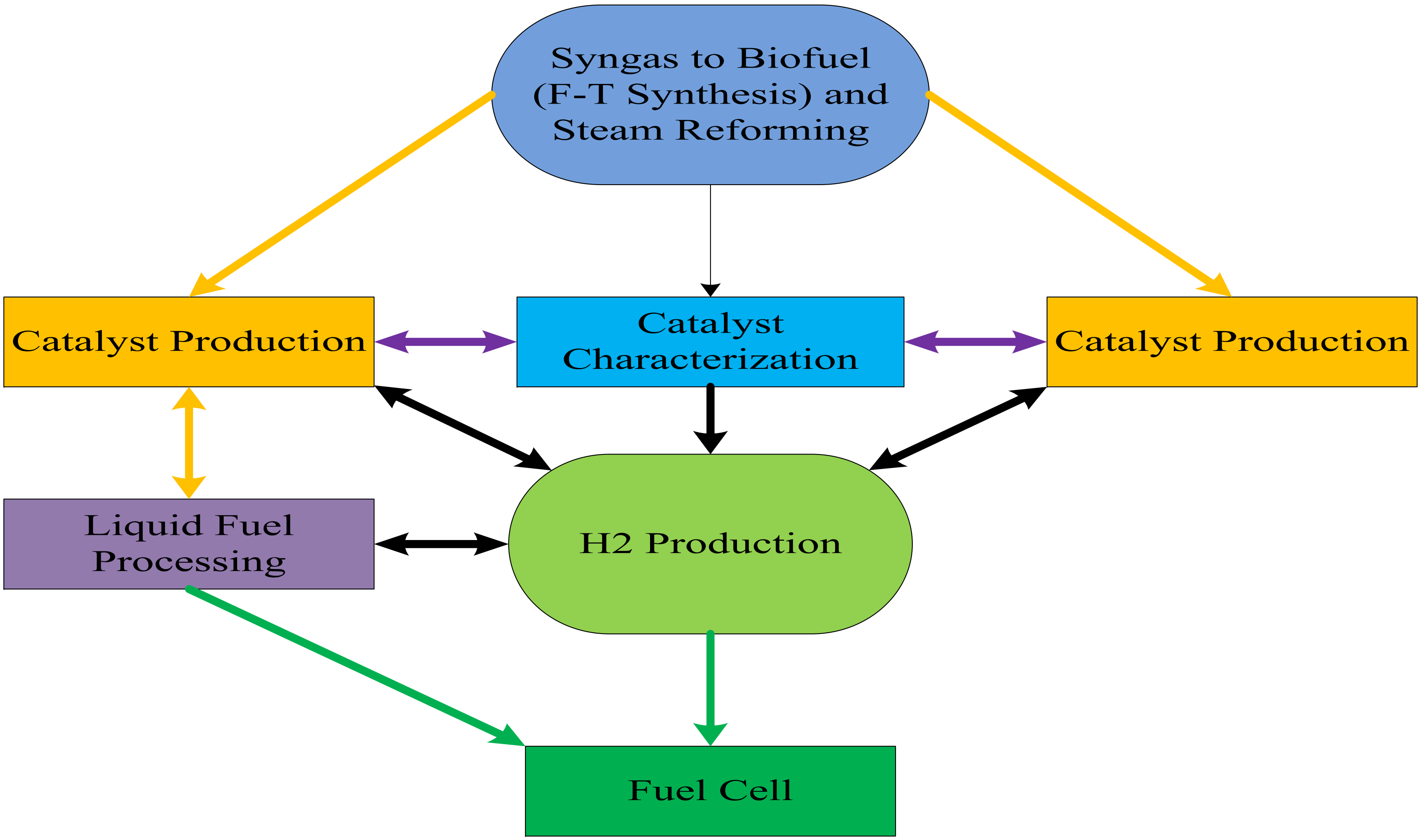
# Si-Microreactors for F-T Synthesis and $H_2$ Production at LA Tech (*Previous Research*)




**Silica Sol-gel Encapsulated Nanocatalysts**

Zhao & Kuila, *Nanocatalysis in Microreactors for Fuels* , **Wiley, 2010**

# Hydrogen Production from Fuels



## Our Strategy

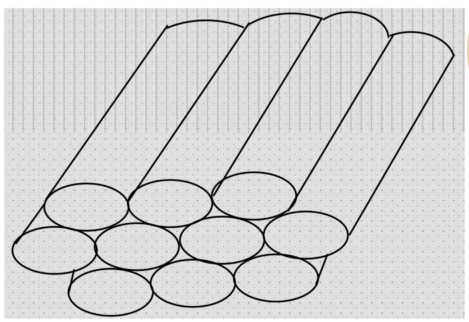
- Optimize structure of a support material to increase the contact area between the catalyst and the reagent
- Alter and optimize the metal catalyst composition to make it CO-tolerant
- Establish a simple synthetic procedure to prepare supported bimetallic nanocatalyst (to investigate synergistic behavior)

# Nanocatalysts for $H_2$ Production

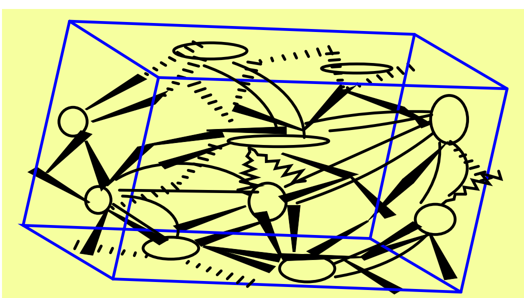
Design, synthesize and characterize novel nanostructured mesoporous silica based catalysts for steam reforming reactions to produce hydrogen

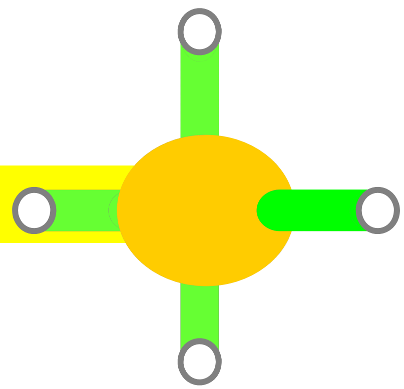
# Mesoporous Silica

- What is Mesoporous Silica?

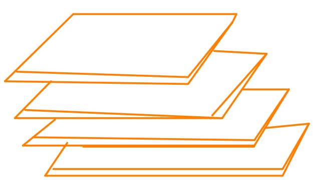


Hexagonal Phase: MCM-41, SBA-15 etc.,

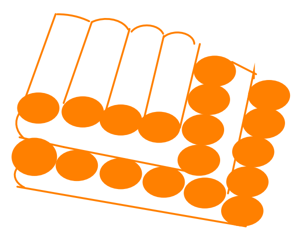




Cubic Phase: MCM-48, SBA-1 etc.,



Lamellar phase



e.g., MCM-50

# Mesoporous Silica

- Hexagonal Structures: SBA-15, MCM-41
- High surface area, Wall thickness- 2 to 7 nm, Pore size- 3 to 15 nm
- Cubic Structure:  SBA-16, MCM-48, SBA-1
- Highly crystalline, High surface area, Wall thickness – 9.6 nm

# Methodologies used previously

- Multi-step synthetic route.

- Disadvantages

# Our approach

- One-pot synthetic route to MCM-41
- Advantages

# Our Methodology

Mix $Pd(NO_3)_2$ or $Ni(NO_3)_2$ with $Pd(NO_3)_2$.

Dissolve Cetyl Trimethyl Ammonium Bromide (CTAB).

Mix CTAB with bimetallic salts.

Add Tetramethoxy Silane and Ammonia.

Stirred vigorously.

Aged in oven.

Filtered and dried.

Calcined and Reduced.

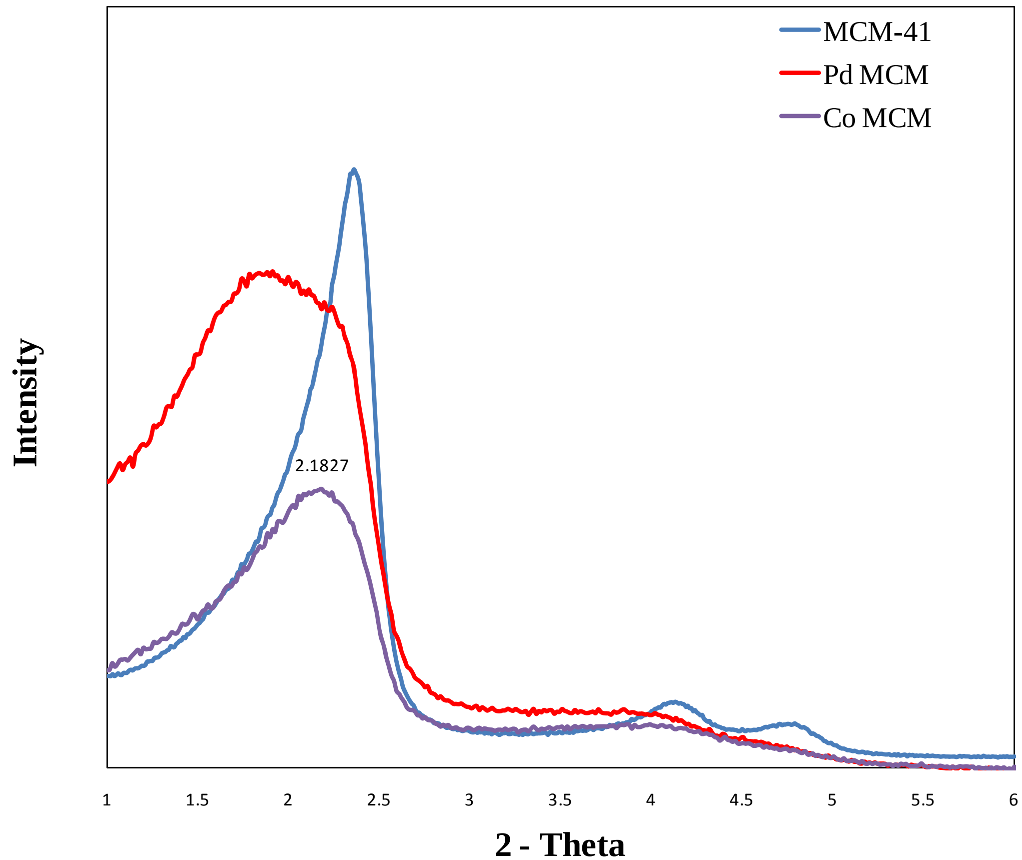
- Synthesized MCM-41 material and compared with bimetallic silica.

# Characterization

- Physical Characterizations: XRD, BET Surface Area, TEM, EDX, and Magnetic measurements.
- Spectroscopy: FTIR

# Low Angle XRD of Mono-metallic MCM-41

- The materials show the characteristic $d_{100}$ peak for MCM-41.
- Co containing materials show low intense peak.

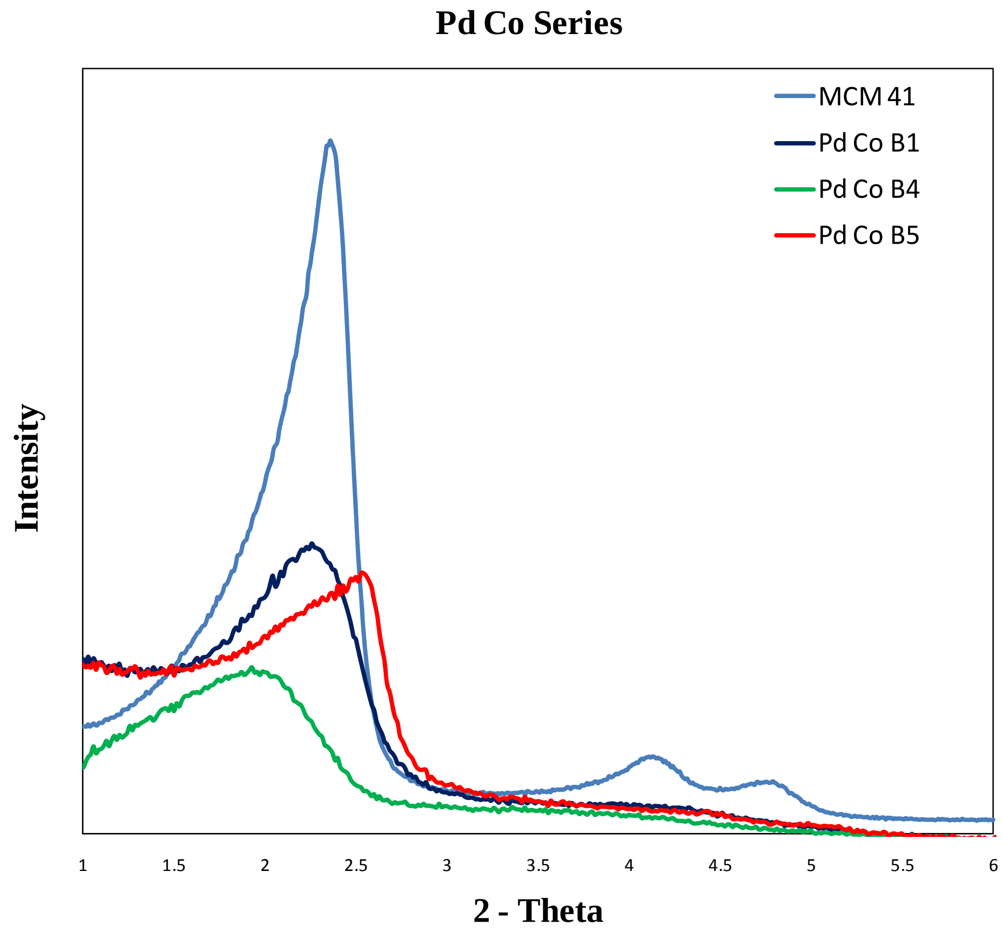


# Low angle XRD of mono and bi-metallic MCM 41 materials

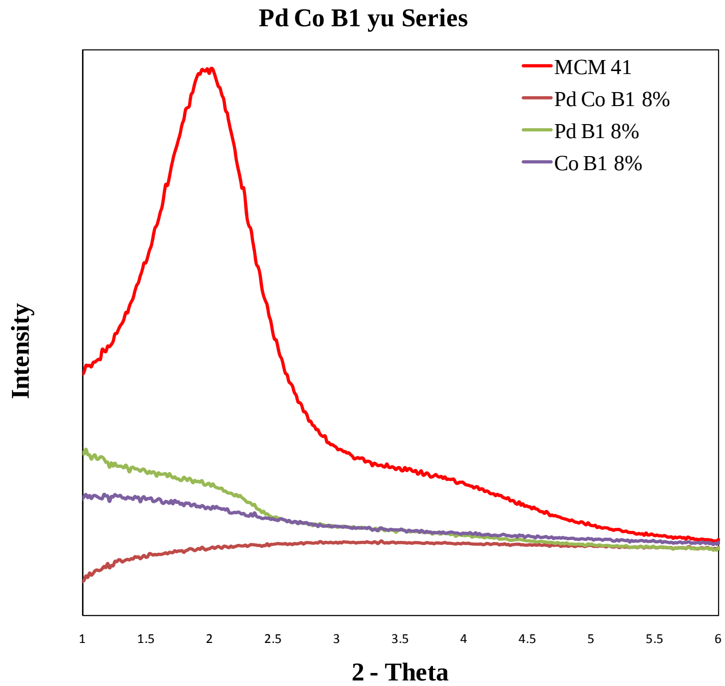
**Observations**

•The $d_{100}$ peak shifts/broadens with the increase in metal content.

• Co MCM shows the peak at $d_{110}$ and $d_{200}$



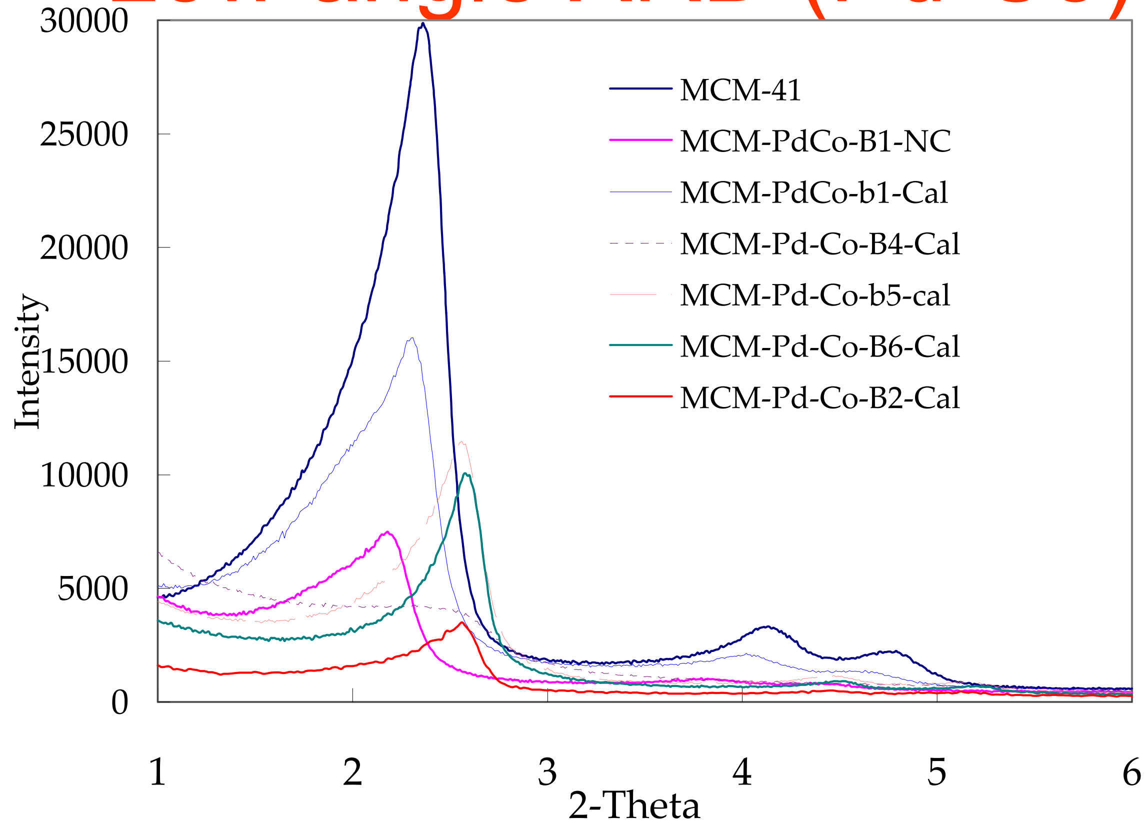
# Effect of Different Metal Loading on Mesoporous Structure for Single and bi-metallic matarials




## Observations

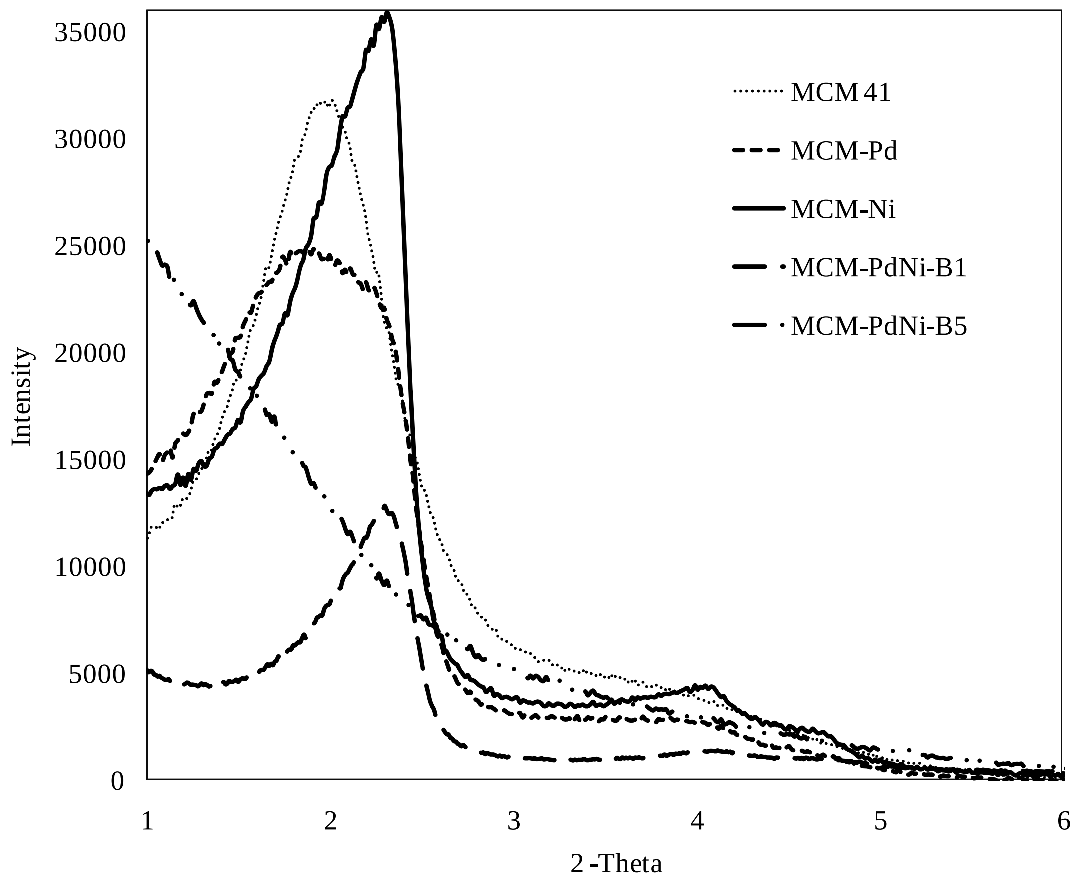
With the increase in metal content, the MCM-41 structure disappears.

# Low angle XRD (Pd-Co)



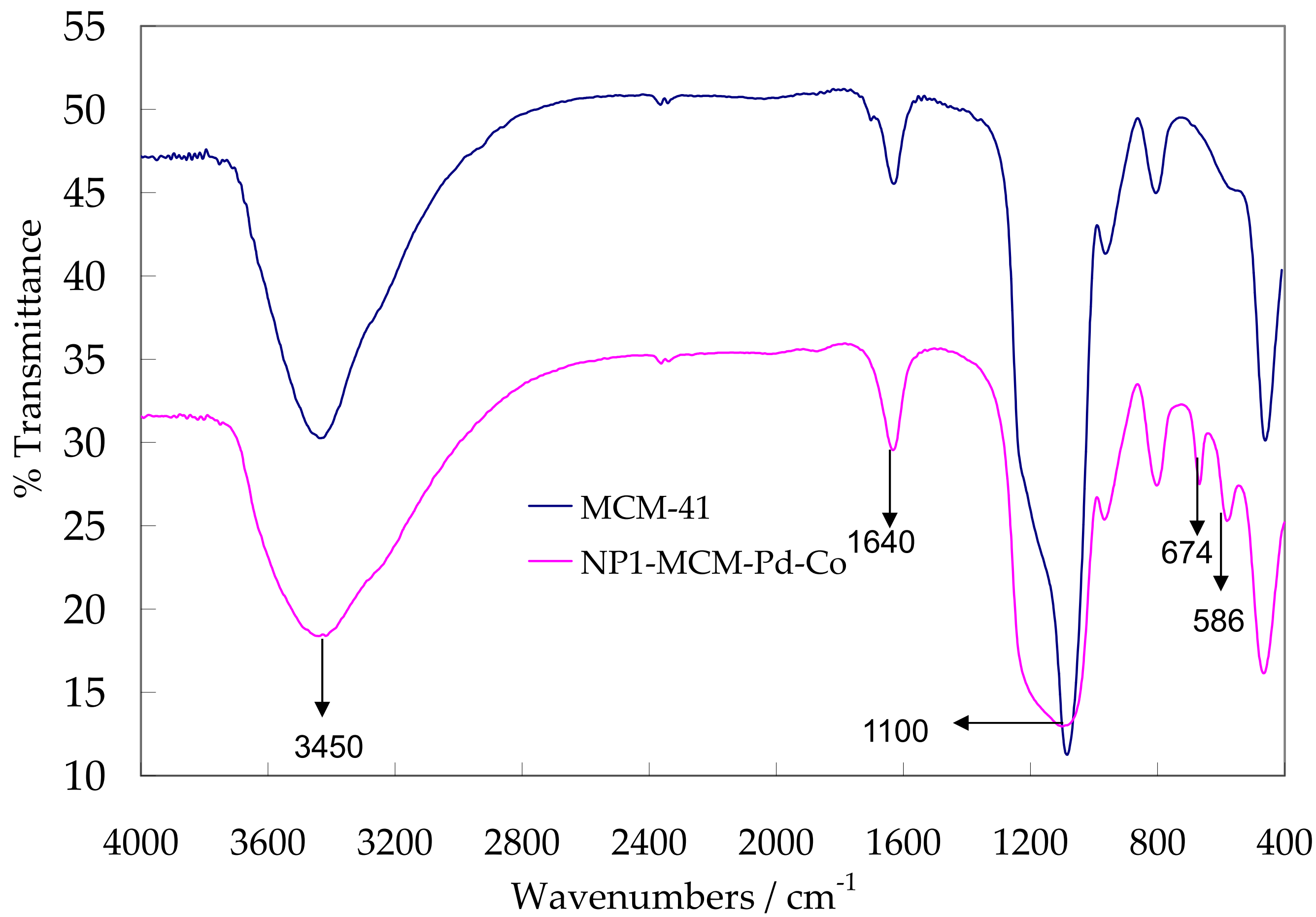

- Peaks at $d_{100}$, $d_{110}$ and $d_{200}$.
- Shift to higher values.
- Decrease in intensity and broadening of the Pd-Co peaks.

# LW XRD of Pd-Ni in Mesoporous Silica




B. Tatineni et al, **2011**

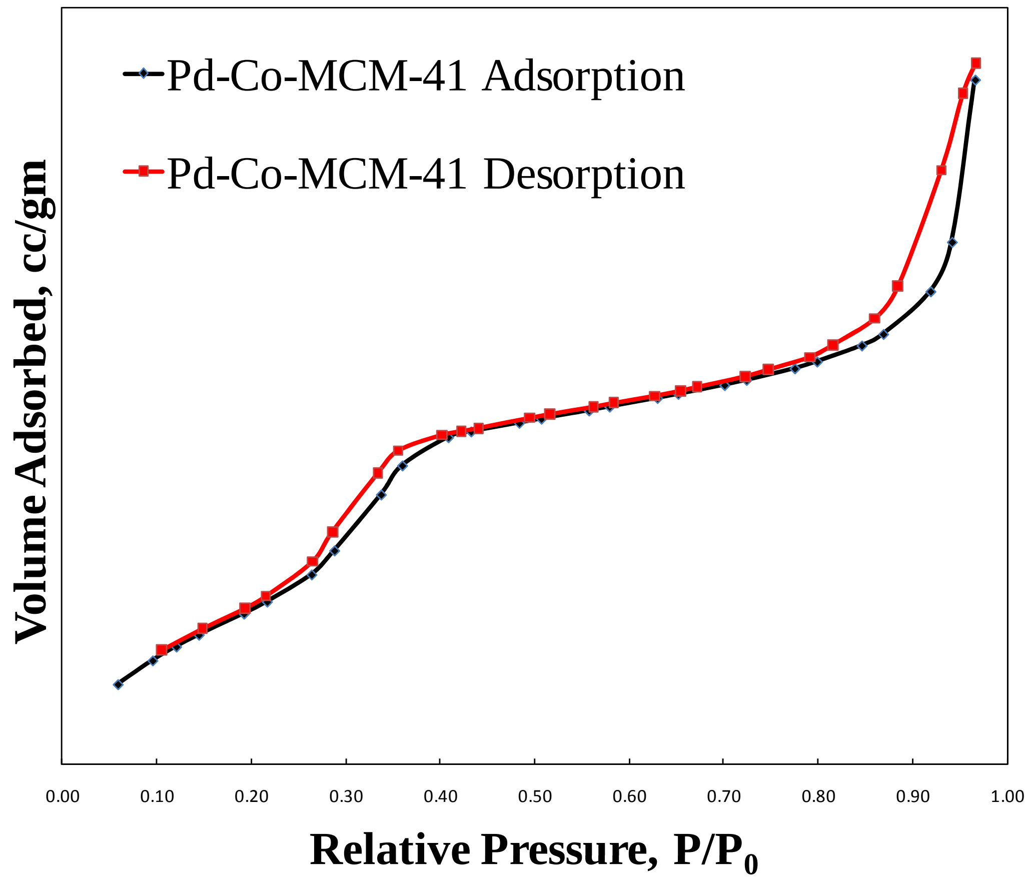
# FTIR Studies




❑Bands at 674 and 586 $cm^{-1}$ - Indicative of strong interaction between heteroatoms and silicon (Si-O-M bonds).

# Isotherms

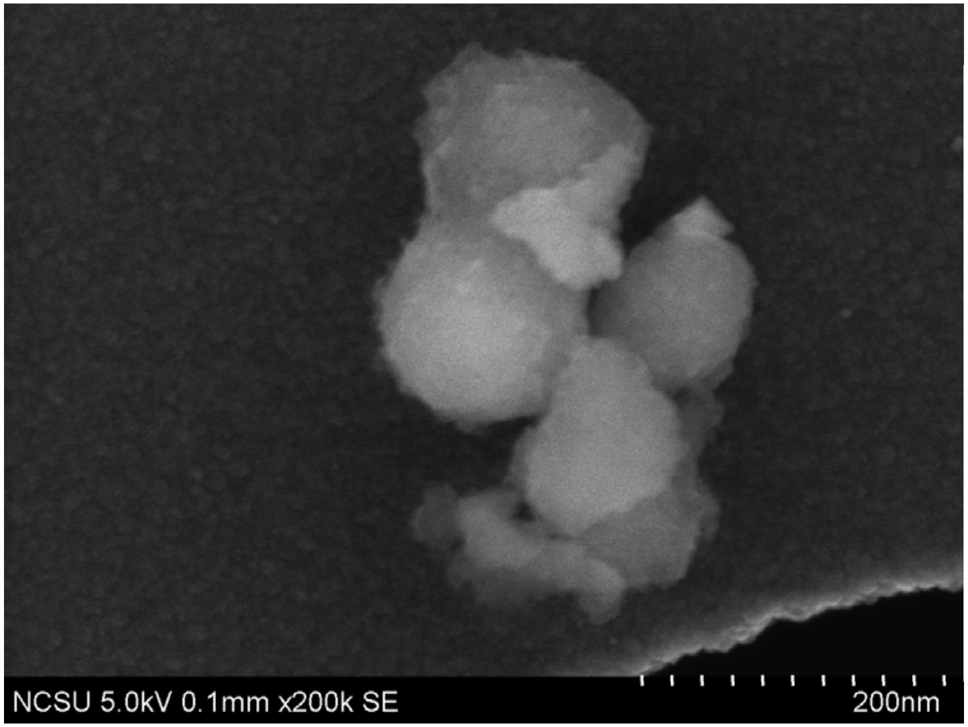
- The synthesized bi-metallic Pd-Co-MCM-41 material shows type IV isotherm, the characteristics of MCM-41 materials.



# Surface Area and Pore Size

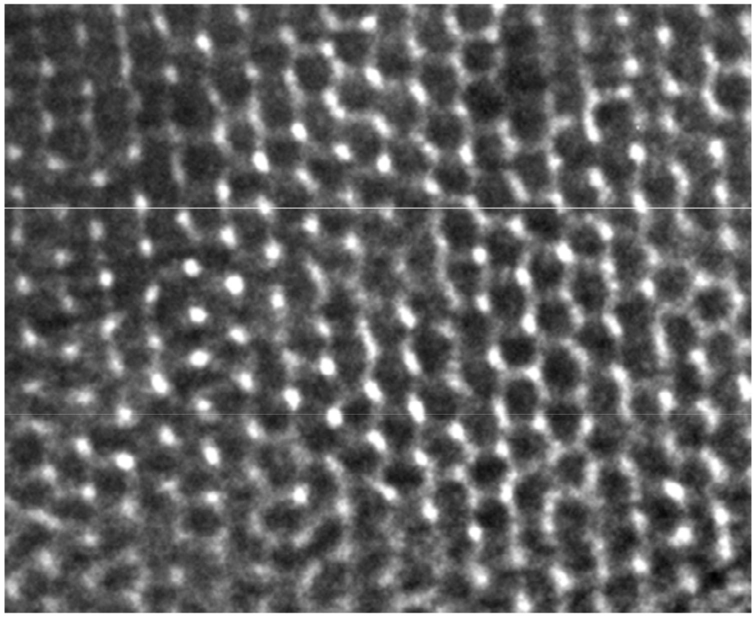
| Sl.No. | Material | BET Surface Area, $m^2/gm$ | Pore Diameter (DFT), Å |
|---|---|---|---|
| 1 | MCM – 41 | 970 | 28.0 |
| 2 | Pd Co B1 | 828 | 29.41 |
| 3 | Pd Co B2 | 845 | 29.41 |
| 4 | Pd Co B5 | 775 | 28.22 |

# SEM IMAGE of Mesoporous Silica

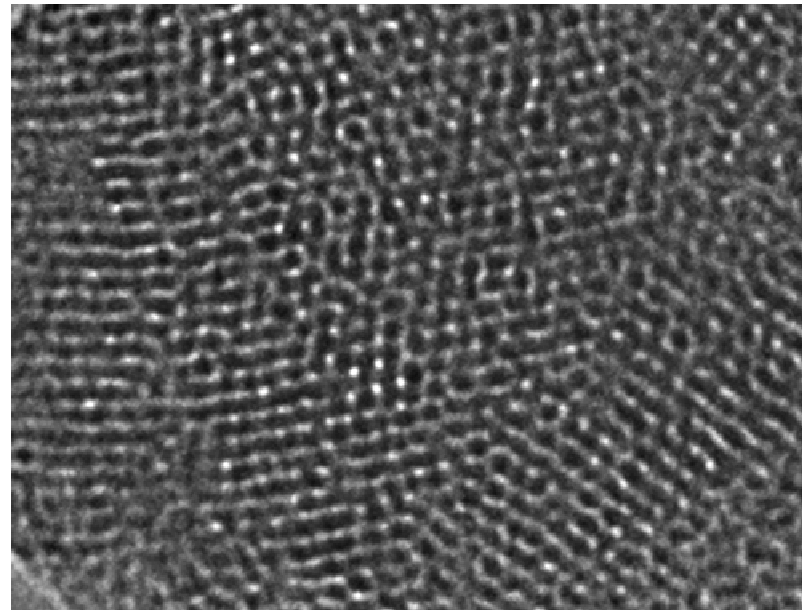



- Particle size - varies from 100 to 300 nm.
- Morphology - hexagonal and winding worm type.
- Small particle size along with worm type structure.
- Supports bimetallic nature.

# TEM



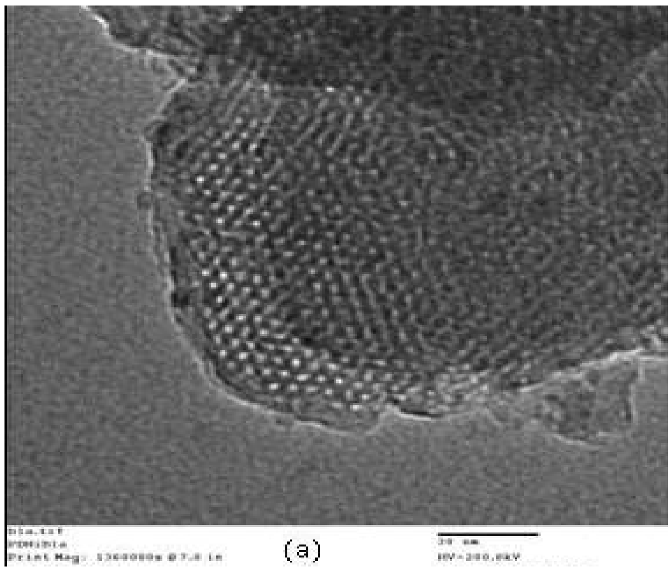
MCM-41



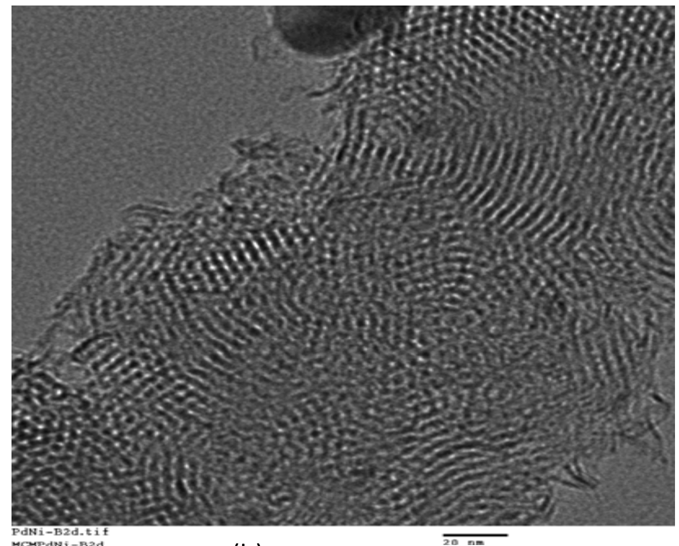
Pd-Co-MCM-41

- Shows the typical hexagonal structure of MCM-41 in Bi-metallic Pd-Co material.
- Indicates uniform size distribution.

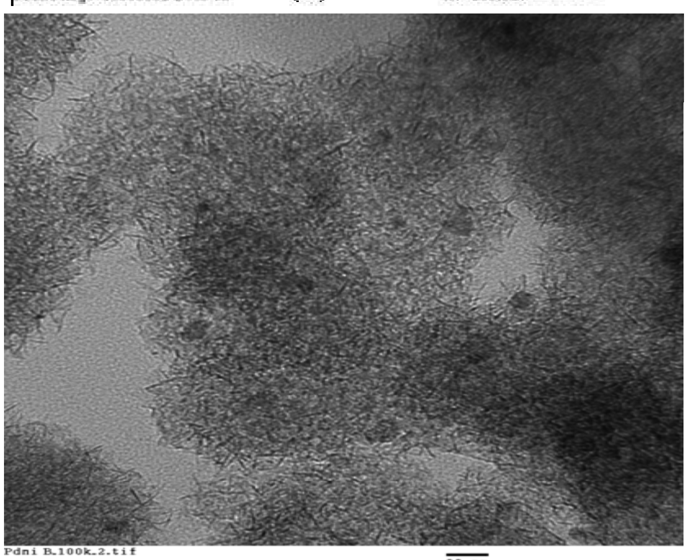
# TEM of Pd-Ni in Mesoporous Silica

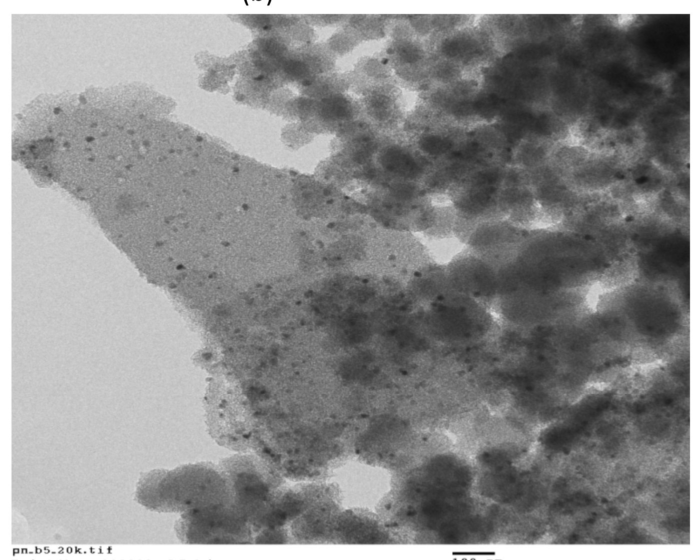


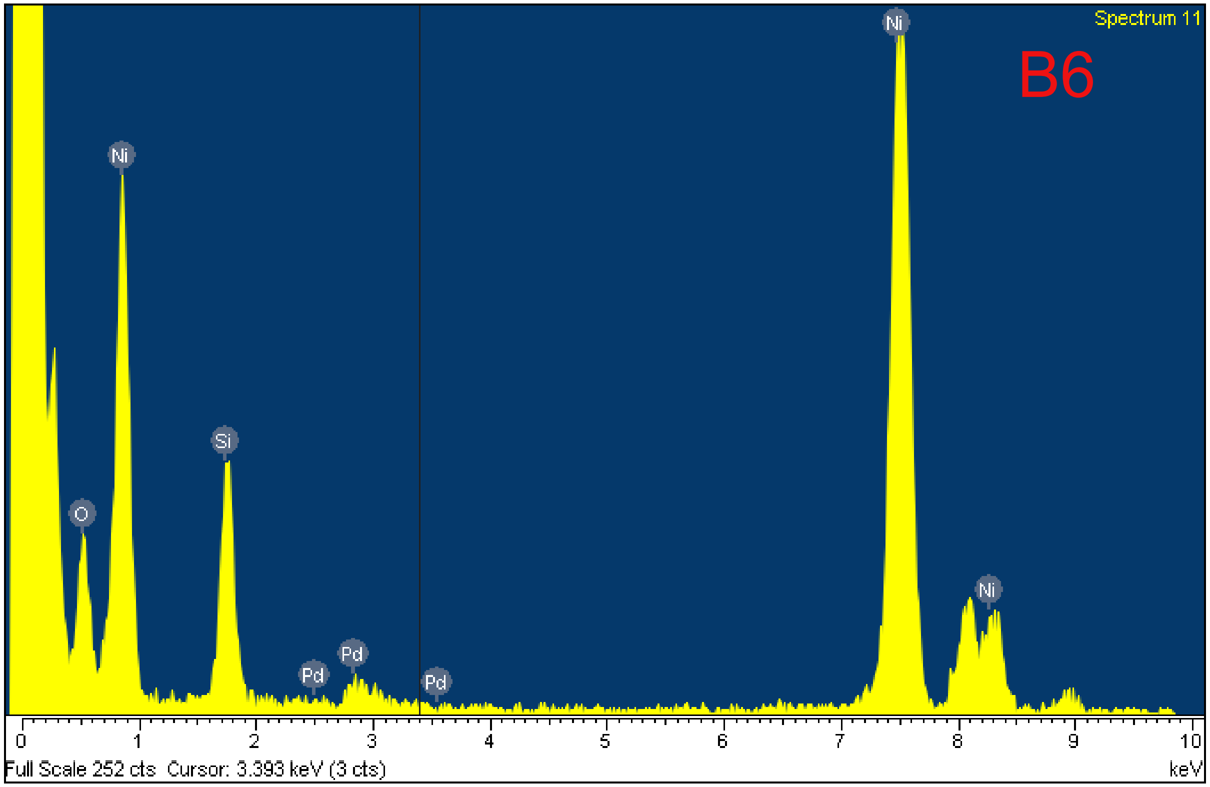
(a)




(b)



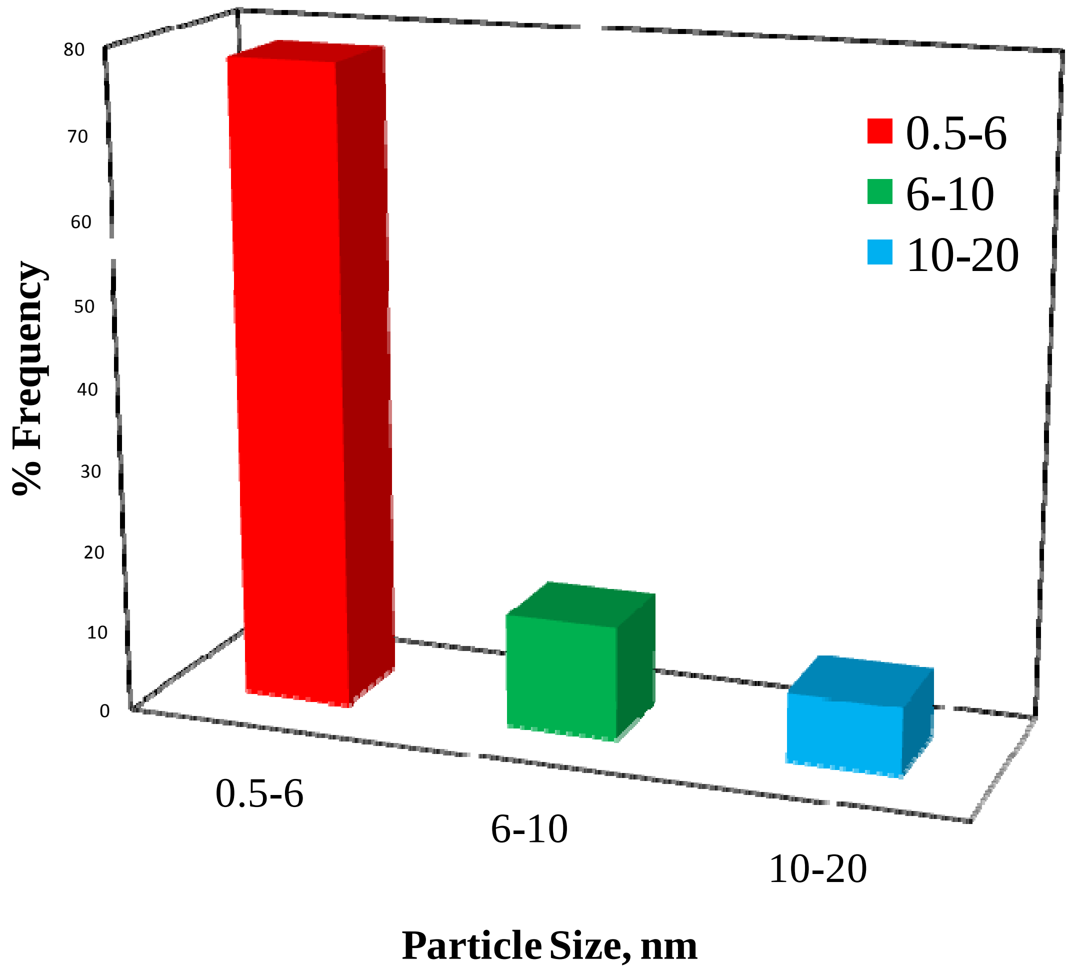





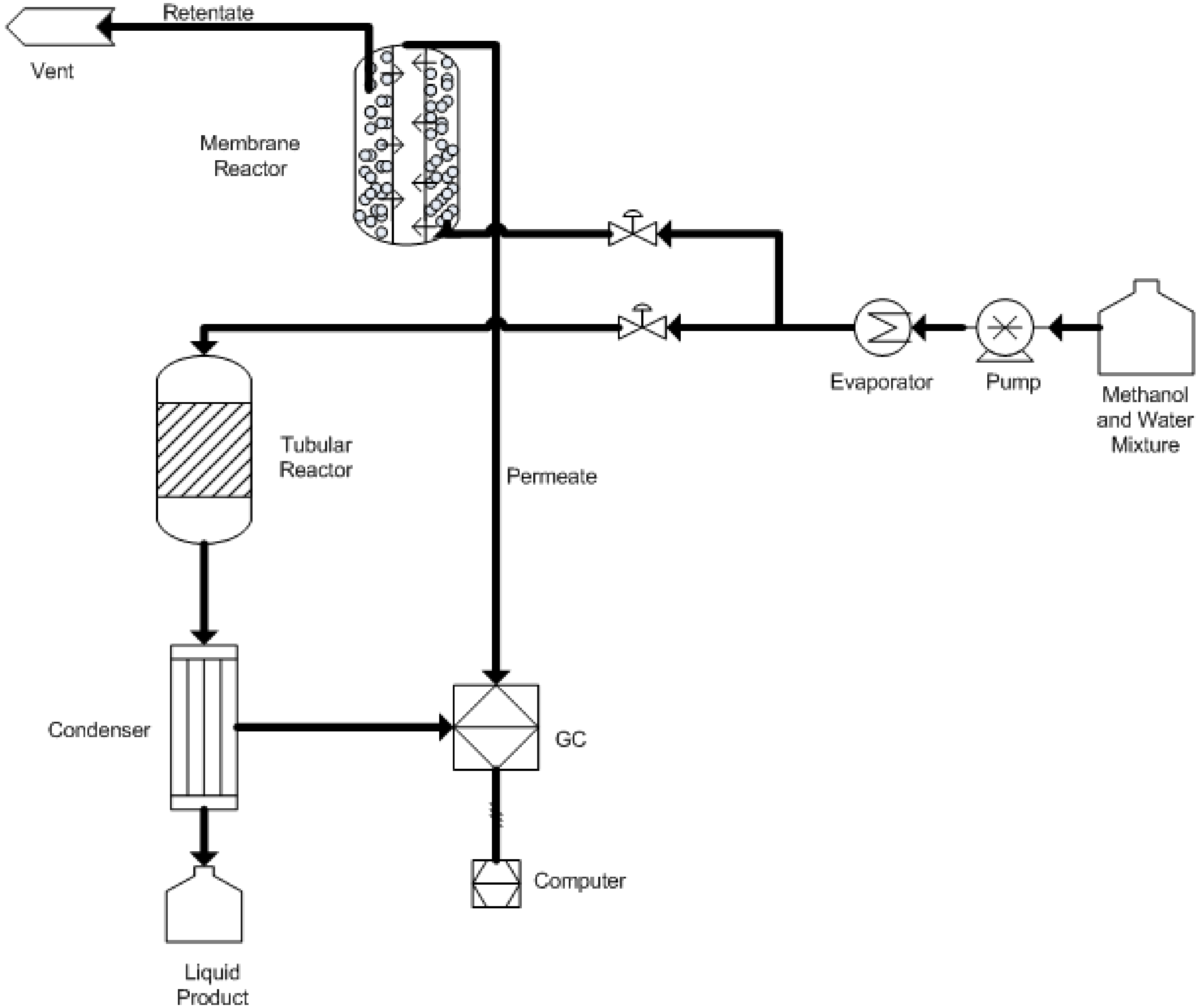

❖ Concentration of PdNi is consistent with the EDX results.

❖ Indicate a homogeneous dispersion of PdNi bimetallic nanoparticles in mesoporous silica.

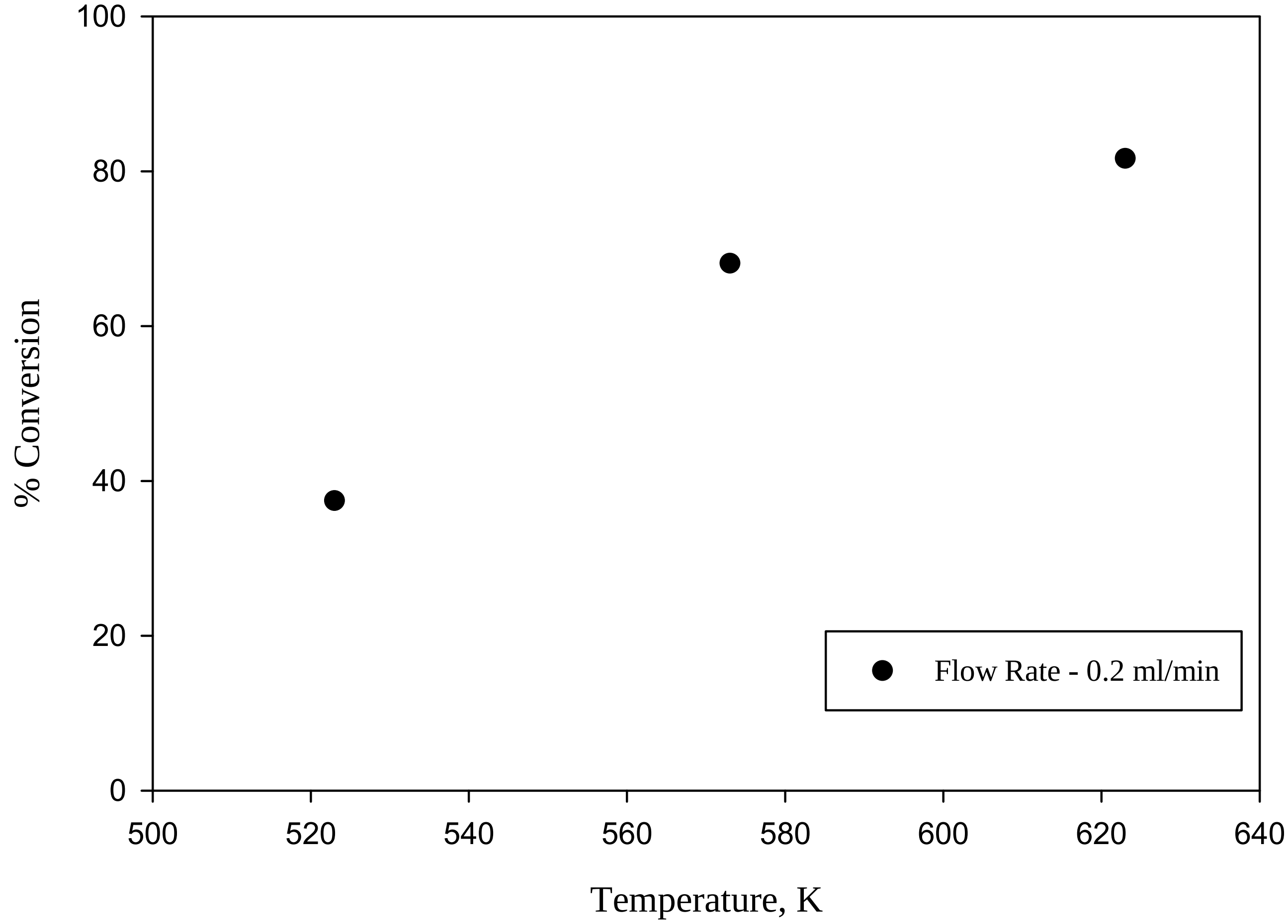
# Particle Size Distribution



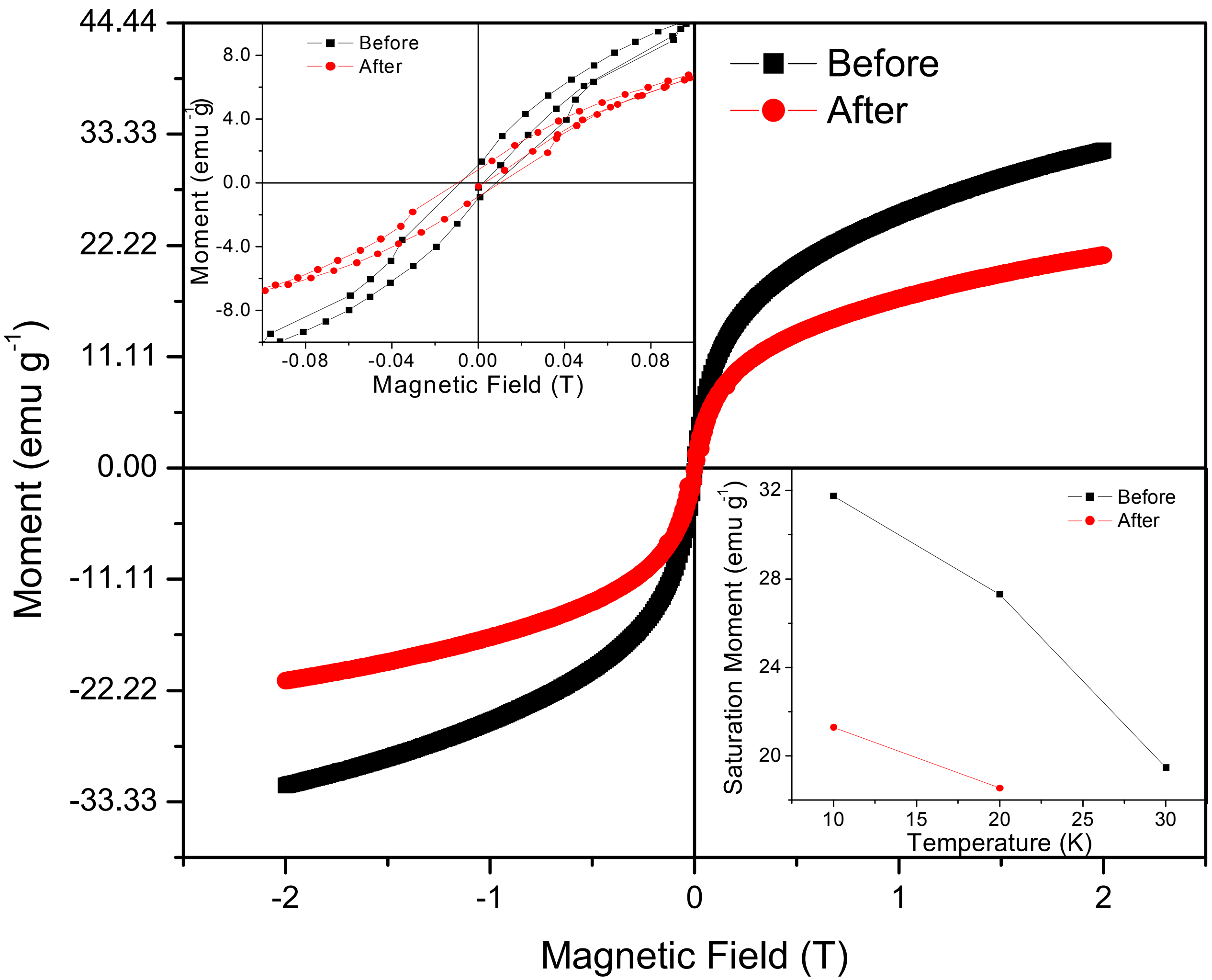
# Our Steam Reforming Set-up



# SRM with Pd-Ni in Mesoporous Silica



# VSM of Pd-Ni before and after SRM reaction



# CONCLUSIONS

- Developed one-pot synthesis of mesoporous silica containing nanometals
- Synthesized ordered mesostructures with uniform distribution of bimetallic nanocrystals.
- Steam Reforming of MeOH with Pd-Ni bimetallic nanocatalysts in mesoporous silica is promising.
- SRM with Pd-Co is currently underway.

# Support (Receiving/Received)

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- Mr. Atikur Rahman (Graduate Student)
- Ms. Jasmine Taylor ( Undergraduate Student)
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- Consultant- Dr. B. Tatineni

- *DOE- NETL*

# Publications/Presentations

- B. Tatineni, Y. Basova, A. Rahman, S. Islam, M. Rahman, A. Islam, J. Perkins, J. King, J. Taylor, D. Kumar, S. Ilias and D. Kuila , "Development of Mesoporous Silica Encapsulated Pd-Ni Nanocatalyst for Hydrogen Production", *In Production and Purification of Ultraclean Transportation Fuels*; Hu, Y., et al.; *ACS Symposium Series;* American Chemical Society: Washington, DC, **2011,** Chapter 9**,** 178-190**.**
- D. Kuila, Development of Nanocatalysts in Silica for Fuels using Si-Micro-channel and Tubular Reactors", International CERT Conference, Greensboro, NC, Invited, **November 7, 2011.**
- D. Kuila et al. Bimetallic Pd-Co Nanocatalysts in Mesoporous Silica for Steam Reforming of Methanol (Fuel-88), ACS National Mtg. Anaheim, CA, March , **2011.**
- S. H. Mohtarami et al, Abstract for ACS National Mtg., **August, 2012,** Philadelphia, Accepted

# Proceedings/Abstracts/Presentations

- D. Kuila, B.Tatineni, M. A. Islam, Y. Basova, M. A. Rahman, M. M. Rahman, S. Islam, S. Ilias, J. Taylor, J. King,"Novel nanocatalysts for hydrogen production" Preprints of Symposia - ACS, Division of Fuel Chemistry 2009, 54(2), 1072-1073; (FUEL-314).

- M. A. Rahman, M. M. Rahman, M. S. Islam, Y. Basova, D. Kuila, S. Ilias, “Ethanol Steam Reforming by Silica Encapsulated Bimetallic Pd_Ni catalyst in a Pd-Composite Membrane Reactor “ 16$^{th}$ Symposium on Separation Science and Technology for Energy Applications, October 18-22, 2009, Gatlinburg, TN, Abstract p.9.
- Y. Basova, M. A. Rahman, M. M. Rahman, S. Ilias, D. Kuila; Novel Bifunctional Nanocatalysts for Aqueous-Phase Reforming”, 238$^{th}$ ACS National Meeting, August 16-20, 2009, CATL – 050.