Lab-Scale Development of a Solid Sorbent for CO_2 Capture Process for Coal-Fired Power Plants

DE-FE0026432

Mustapha Soukri, Luz Minguez Ignacio, John Thompson, Marty Lail,

Kelly Amato, Himanshu Paliwal, Tom Nelson

DOE Project Manager: Steve Mascaro

CO_2 Capture Technology Meeting

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Project Details – DE-FE0026432

Funding: $1,989,415

- $1,591,532 DOE
- $ 397,883 Cost Share

Period: October 2015 – March 2018

Goals/Objective:

- Develop novel 3rd generation fluidizable solid sorbents for RTI's sorbent-based CO_2 capture process:
  - **Fluidizable, hybrid-metal organic frameworks**
  - **Fluidizable hybrid-phosphorus dendrimers**

Project Outline

BP1

- **Design and synthesize two novel fluidizable CO_2 adsorbents.**
- **Demonstrate the superior performance of these advanced CO_2 solid sorbents at the lab scale.**

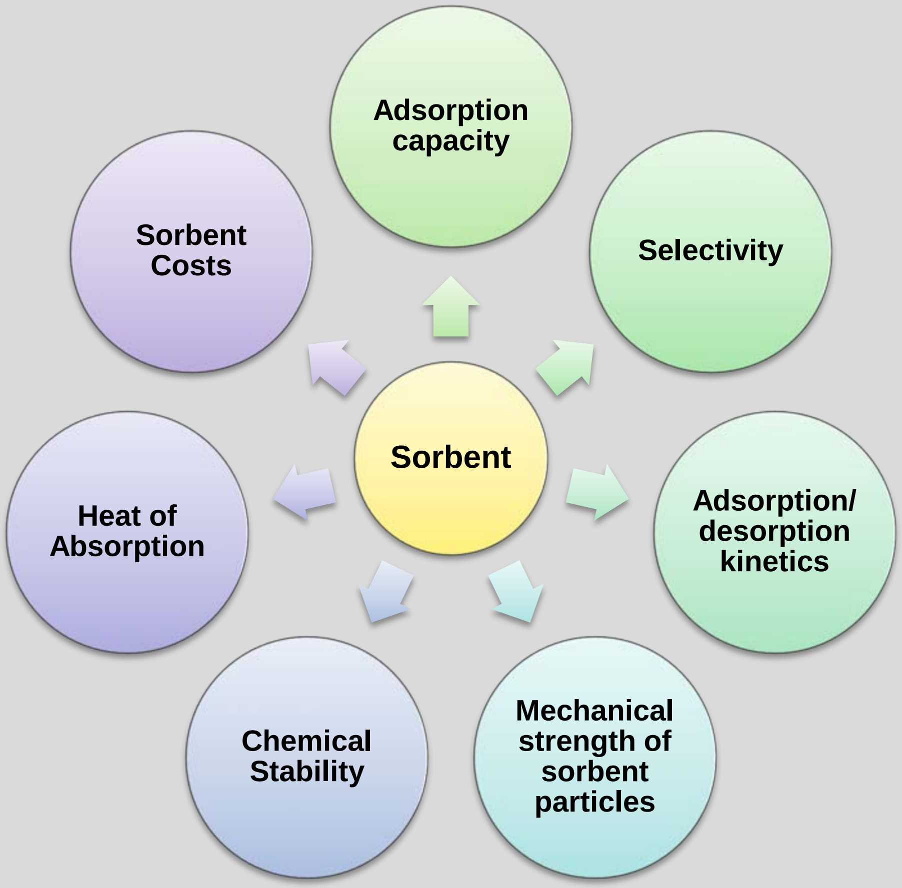
BP2

- **Evaluate the impact of flue gas contaminants such as SOx, NOx, O_2 , and H_2O on these advanced solids sorbents**
- **Conduct a high level techno-economic analysis.**

Selection Criteria for CO_2 Solid Sorbents

Develop and design CO_2 capture solid sorbent that is chemically, thermally, and physically stable over multiple absorption/regeneration cycles and shows significant potential to meet the DOE program targets for CO_2 capture (*>90% CO_2 capture rate with 95% CO_2 purity and <30% increase in cost of electricity*).

- Fluidizable material
- High CO_2 loadings, high selectivity
  - ≥ 12 wt% CO_2 capture
- No PEI leaching or degradation
  - Thermal & Oxidative stability
- Low heat of absorption
- Acceptable density
  - Density ≥ 0.6 to 1 g/cc
- Acceptable attrition resistance
  - Low makeup rate
- Economically practical
  - Low cost and easy scalability

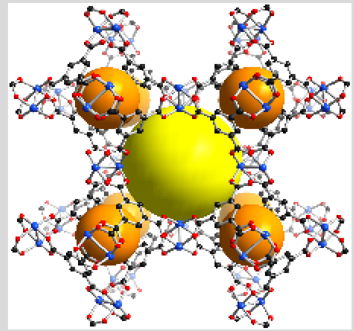


Hybrid MOF-Based CO_2 Adsorbents

Hybrid MOF-Based CO_2 Adsorbents

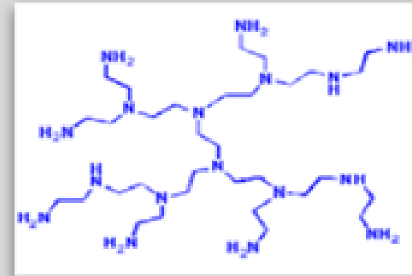
Silica

- Attrition resistance
- Fluidizable
- Low cost
- Acceptable density



MOF (HKUST-1)

- Exceptionally high surface areas
- Tunable pore sizes
- Commercially available linker



PEI

- High amine content
- High CO_2 affinity
- Relatively low cost materials

Silica + MOF + PEI

Table 2. Reported CO_2 Capture Performance Results

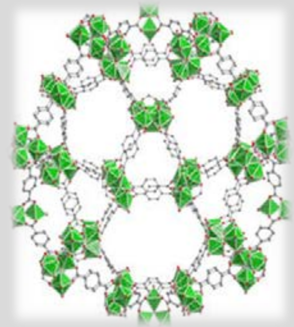
Sample Description	CO_2 Capacity (wt%)
MOF	21.4[a]
MOF-amine	~20
Fluidizable silica (FS)	0
FS-PEI	4.8
MOF-silica	0
MOF-silica-amine	9.3

[a]Final report award # DE-FC26-07NT43092

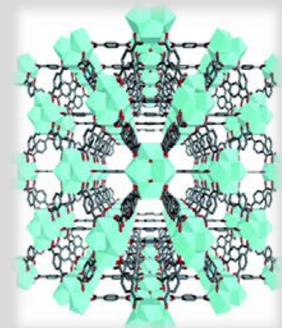
MOFs Selected for Evaluation as **Hybrid MOF-Based CO_2 Adsorbents**

- Air and water stability
- Chemical Stability
- High thermal stability
- High selectivity for CO_2 over other components in flue gas (N_2 and O_2)
- Commercially available linkers

MIL101 (Cr)



UIO-66 (Zr)



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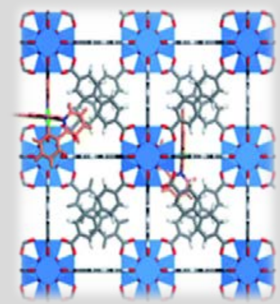
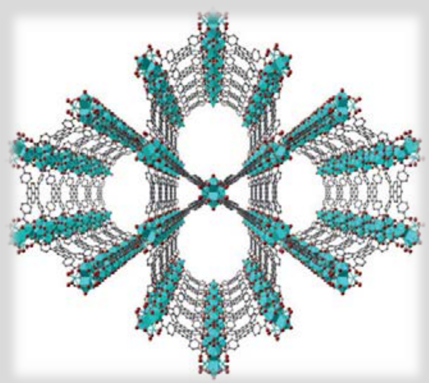
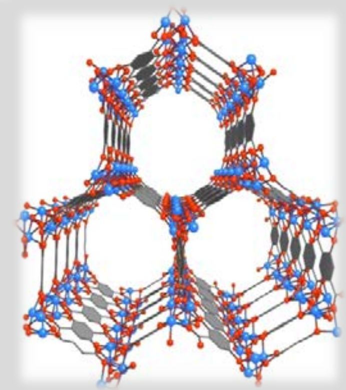




NU-1000 (Zr)

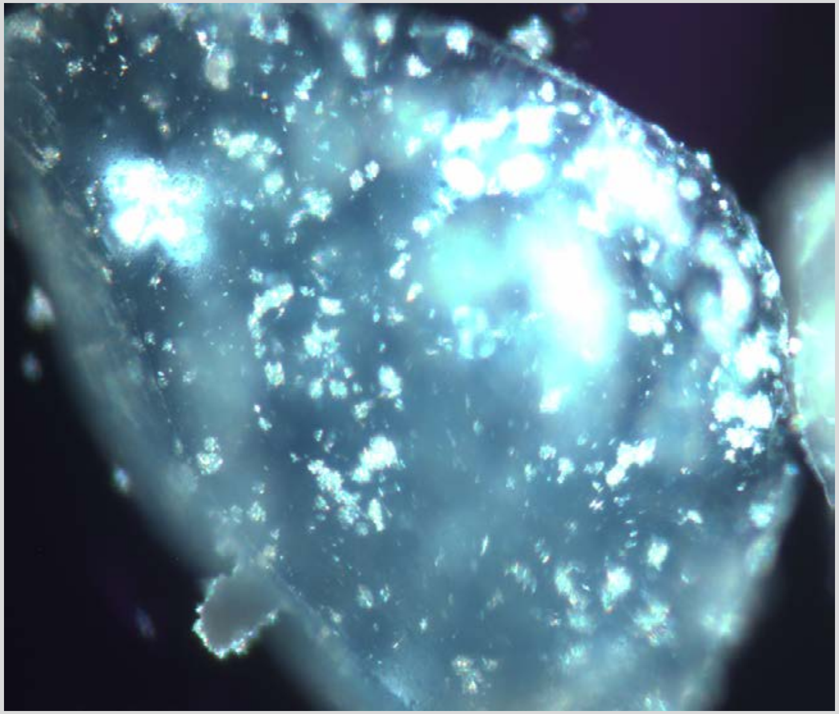


MOF-74 (Mg)

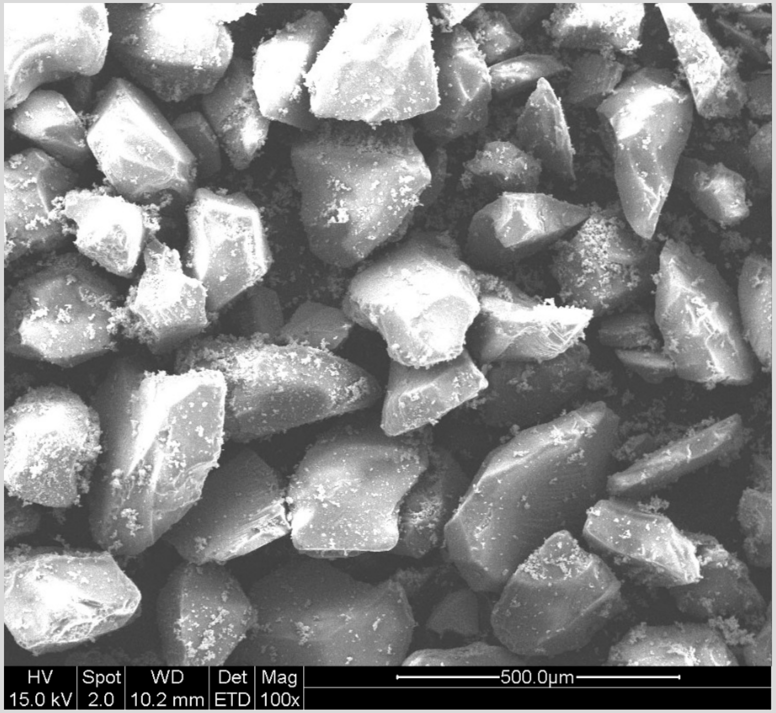
Growing MOF inside the pores of Silica!

Solvothermal Synthesis of MOF-Silica Hybrid

The State-of-Art Solvothermal Synthesis of MOF-Silica Hybrid is non-selective!



Confocal microscope picture



SEM picture

Is the current solvothermal method the best approach for the MOF-Silica hybrid synthesis?

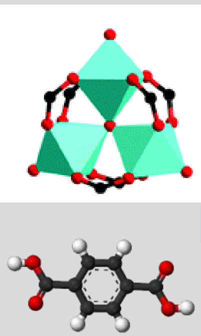
- **Not utilizing the internal pores of the silica**
- **Poor interaction of MOF with Silica → Low yields**
- **Low attrition-resistance**

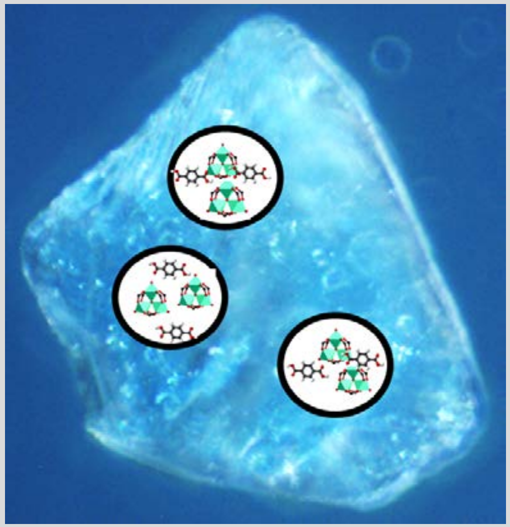
A need for a New Approach!

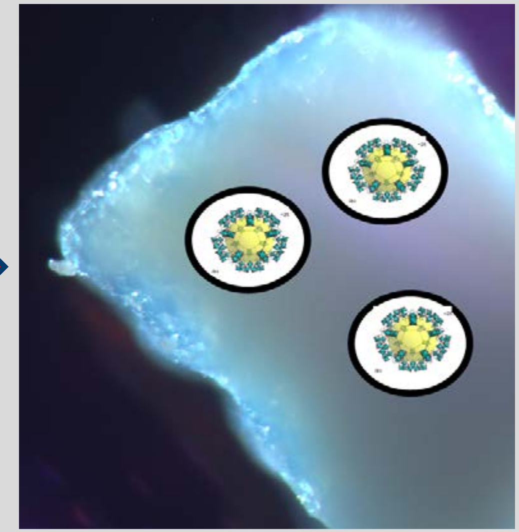
- **Exhibit high MOF loading within the pores of silica (SiO_2)**
- **Excellent MOF dispersion and homogeneity**
- **Elevated surface area as *hybrid MOF-Silica***
- **Nanometric MOF particles**
- **Good Fluidazibility**
- **Good handling**

New Approach for MOF-Silica Hybrid Preparation

Our new approach: Solid State Synthesis



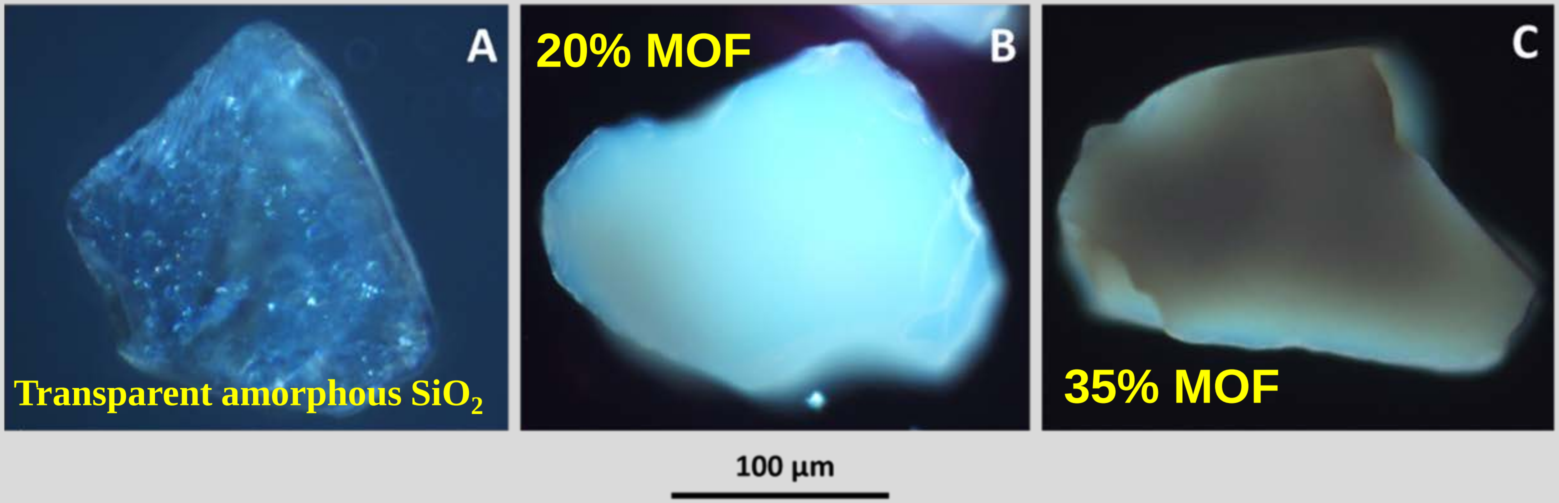


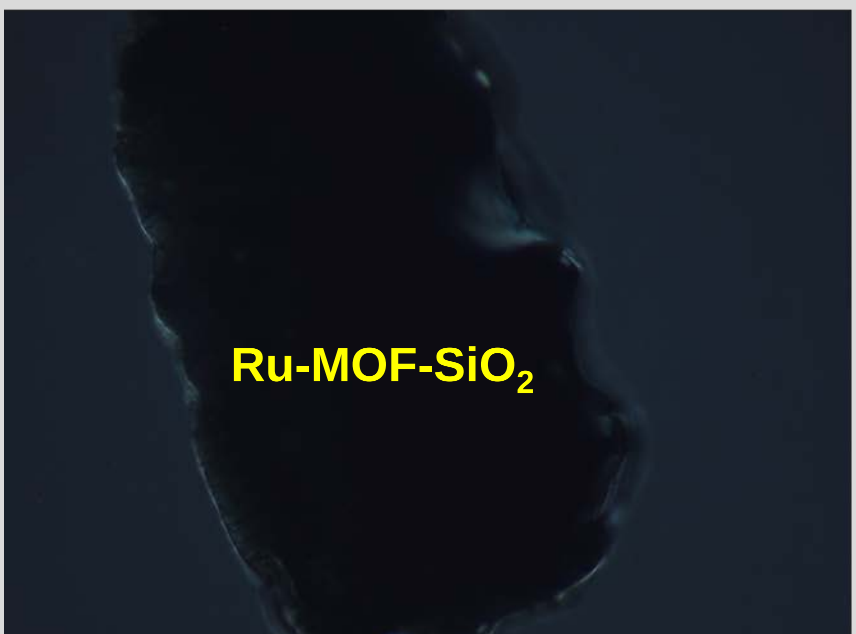


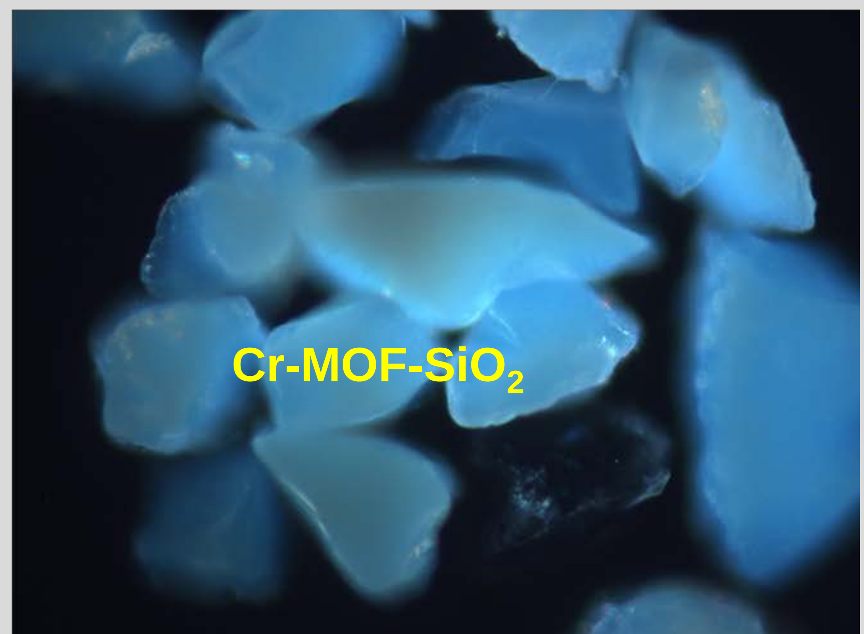
New approach allowed the project to meet the fist goal of the MOF-Silica hybrid Synthesis

Full characterization using the most well known technics such as: Confocal Microscope, SEM, FIB-FESEM, TEM, FTIR, XRD, XRF, N_2 isotherms, TGA, Particle size distribution, Jet-Cut attrition index

Confocal Microscope for the New MOF-Silica Hybrids

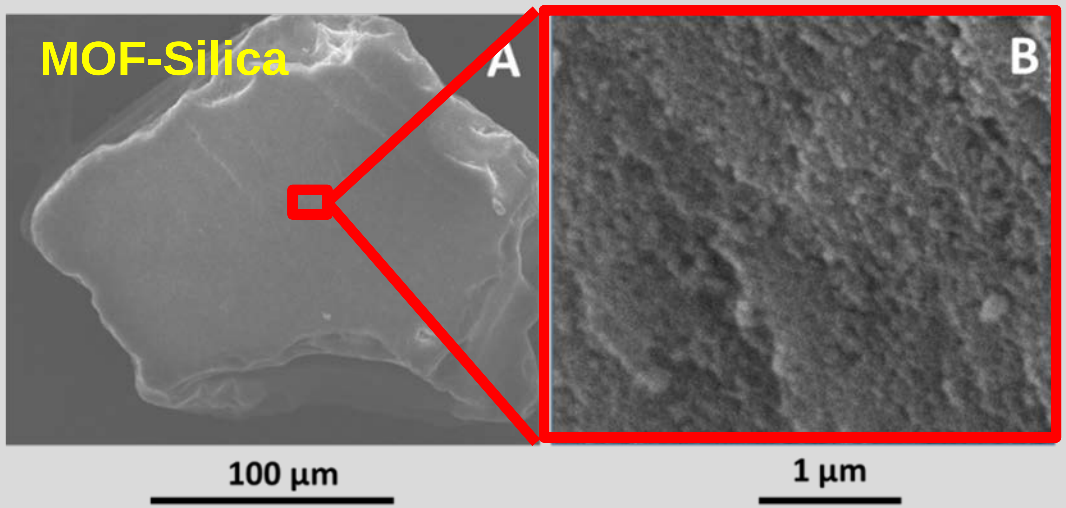




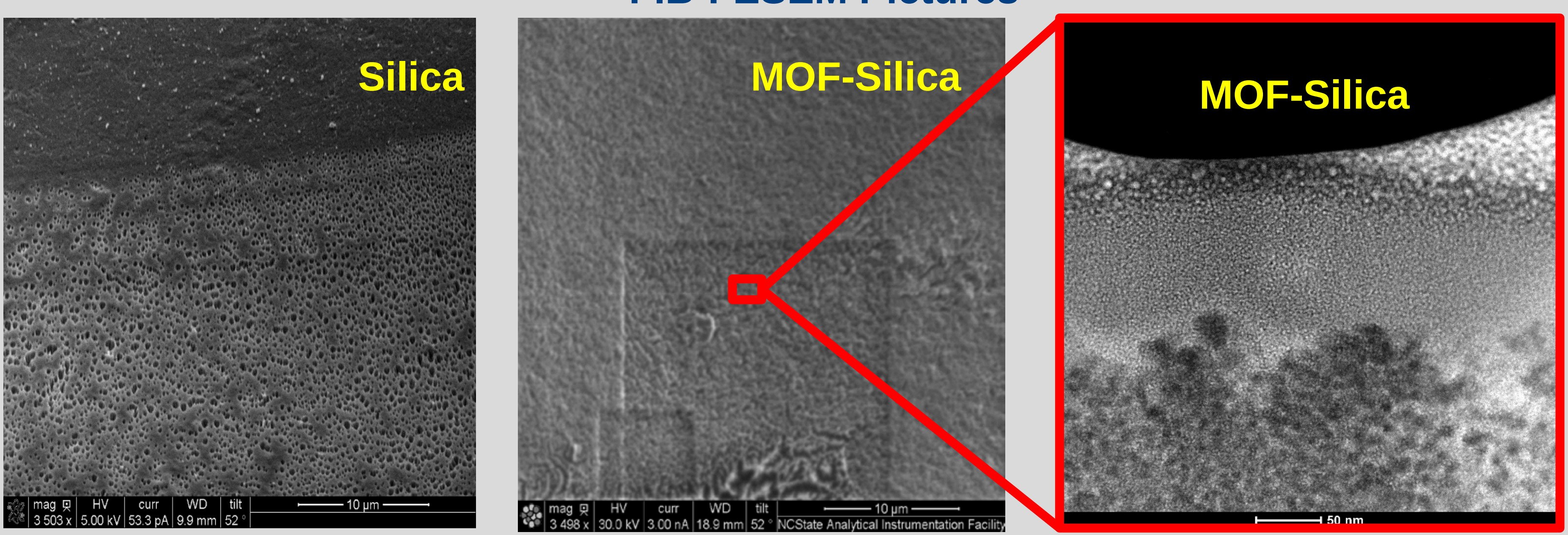


Scanning Electron Microscope (SEM & FIB-FESEM)

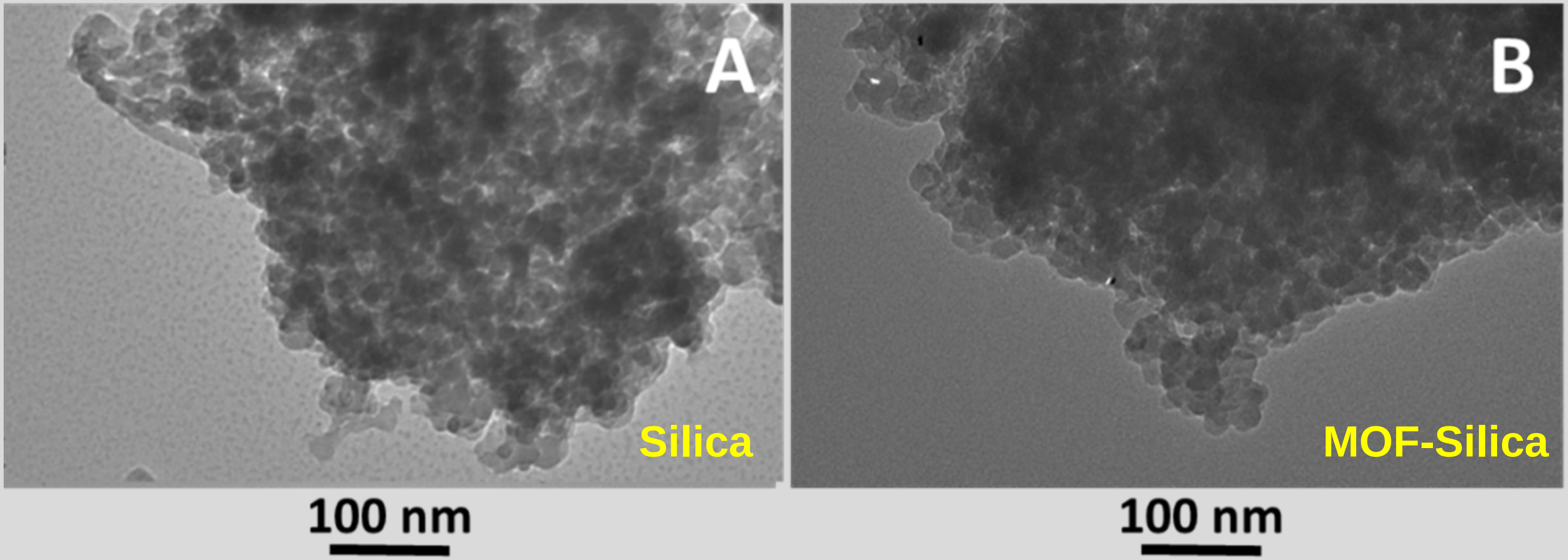
SEM Pictures

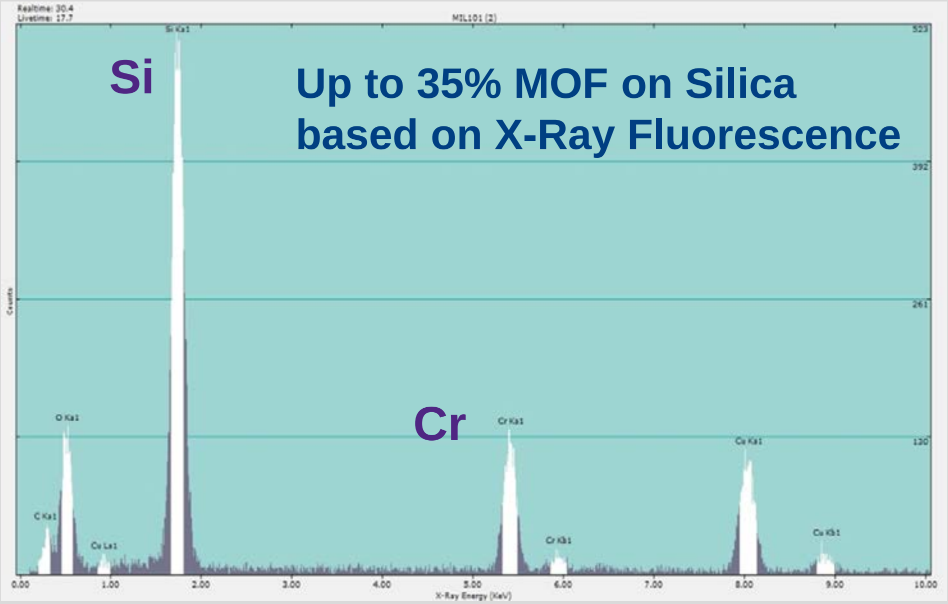


FIB-FESEM Pictures



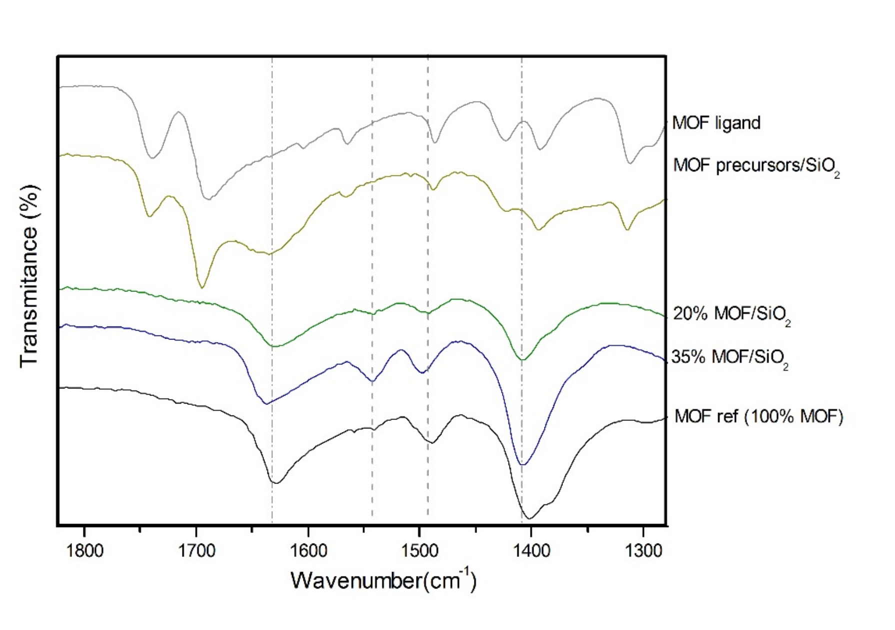
Transmission Electron Microscopy (TEM) & X-Ray Fluorescence (XRF)



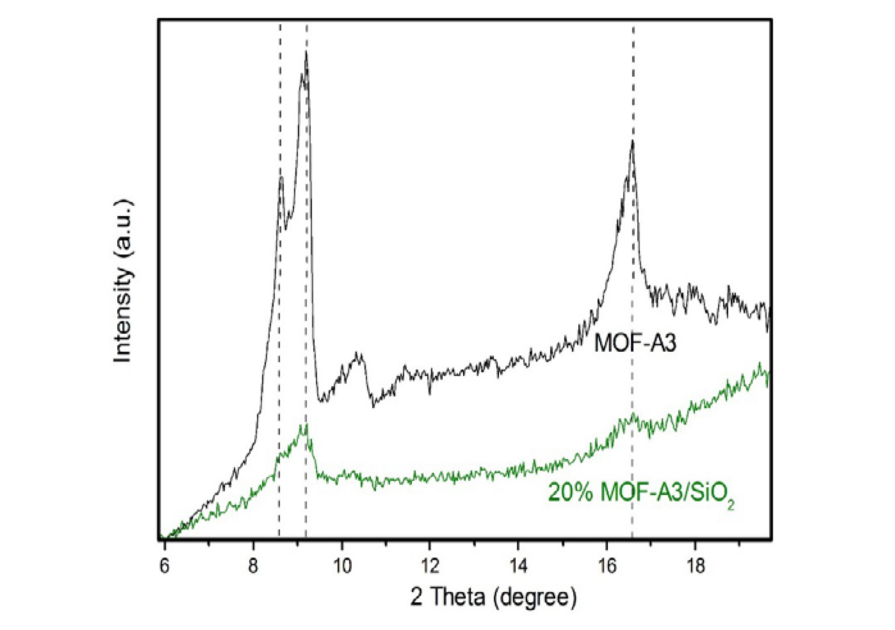


Characterization of The New MOF-Silica Hybrid

FTIR data

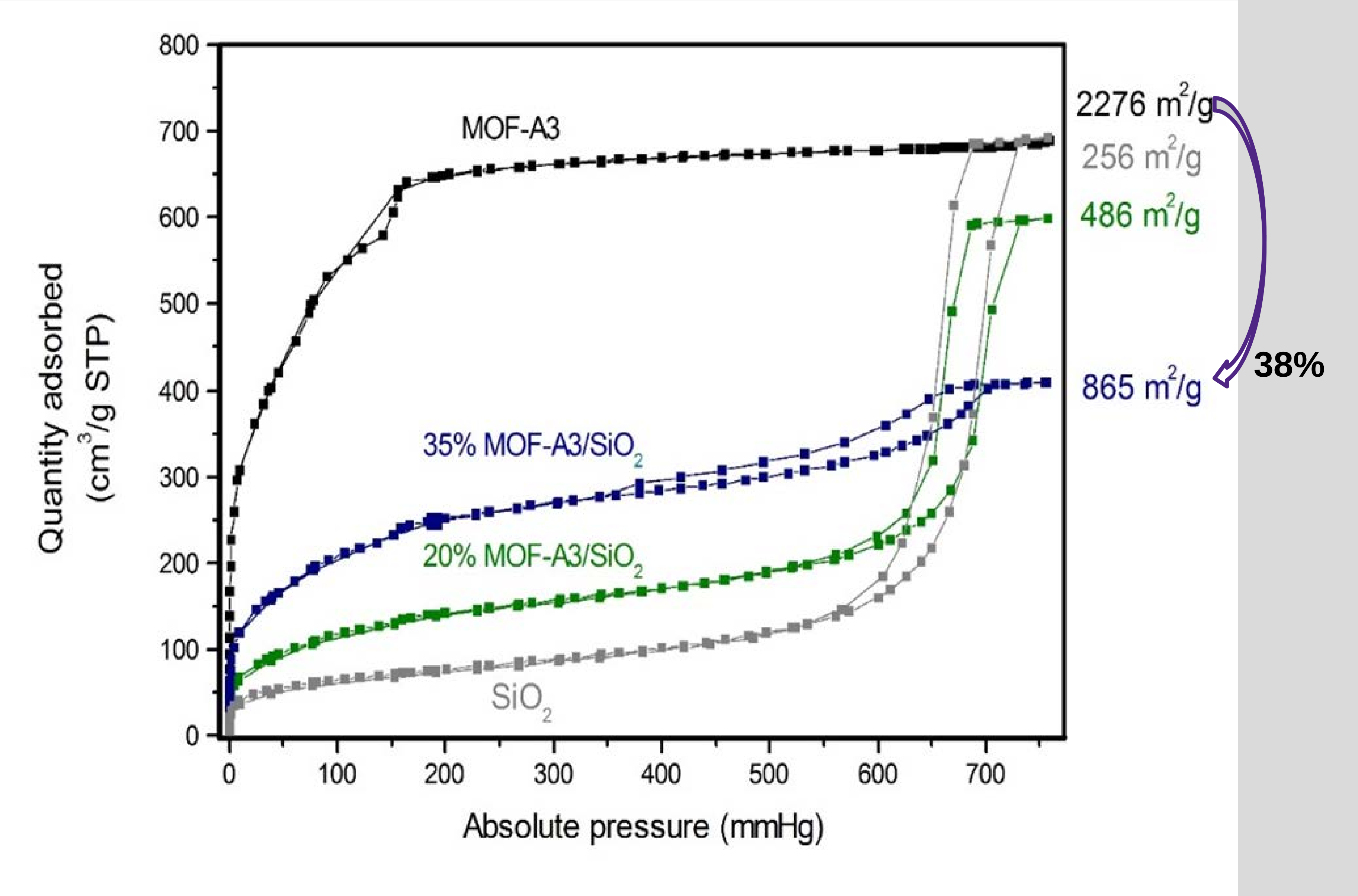


X-Rays diffraction (XRD)



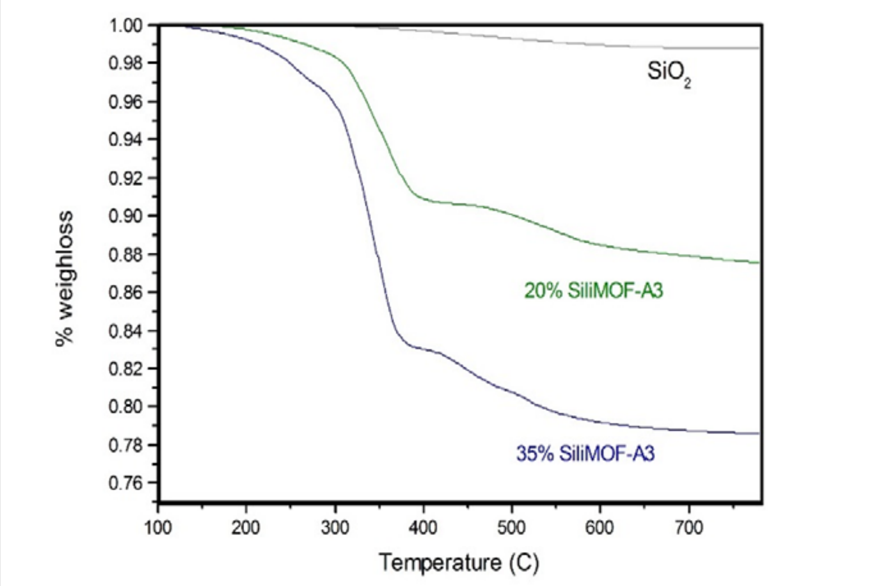
Characterization of The New MOF-Silica Hybrid

N_2 isotherms

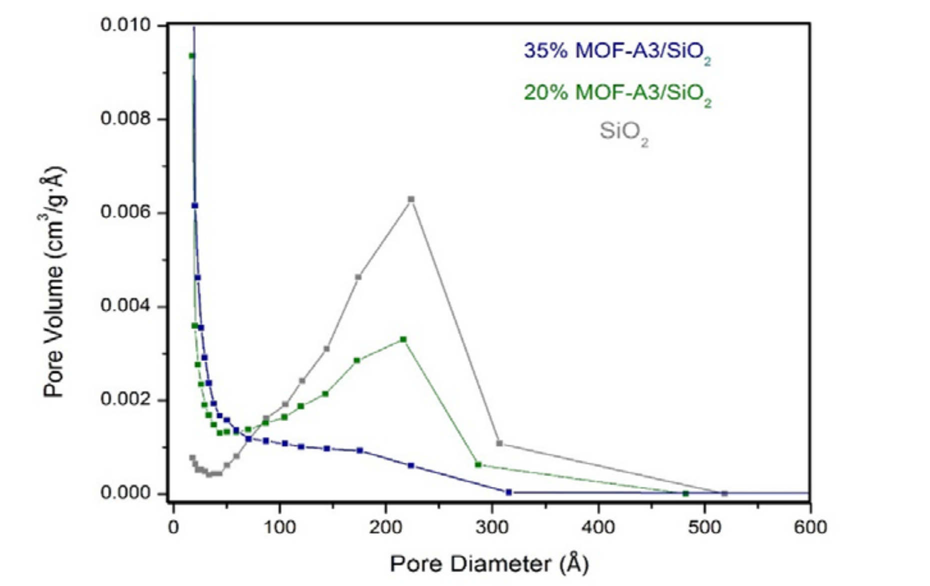


Characterization of The New MOF-Silica Hybrid

Thermogravimetric analysis

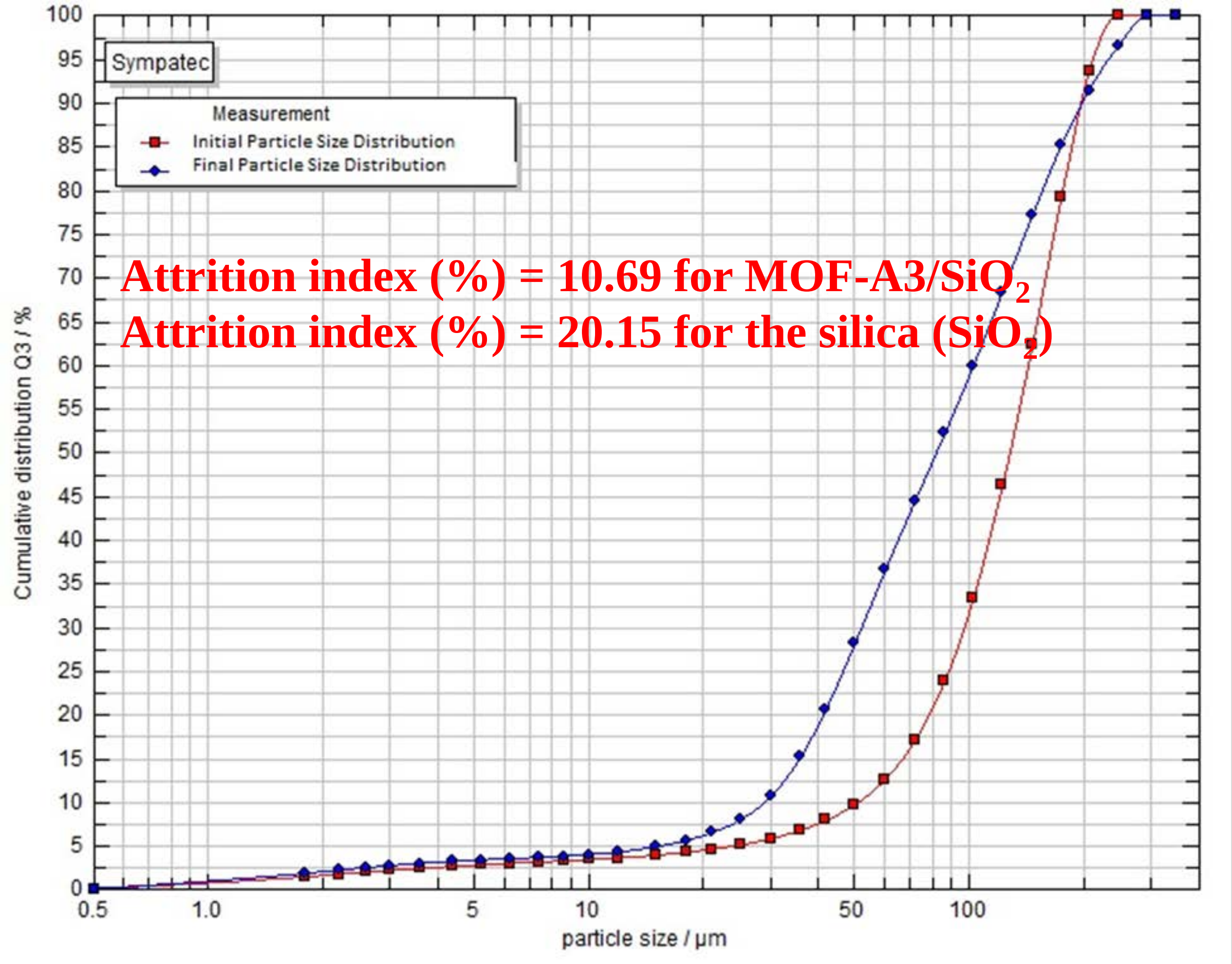


Pore size distribution



Jet Cup attrition index For MOF-Silica Hybrid

Comparison between initial particle size distribution and final particle size distribution for MOF-A3/SiO_2 using Jet Cup attrition index



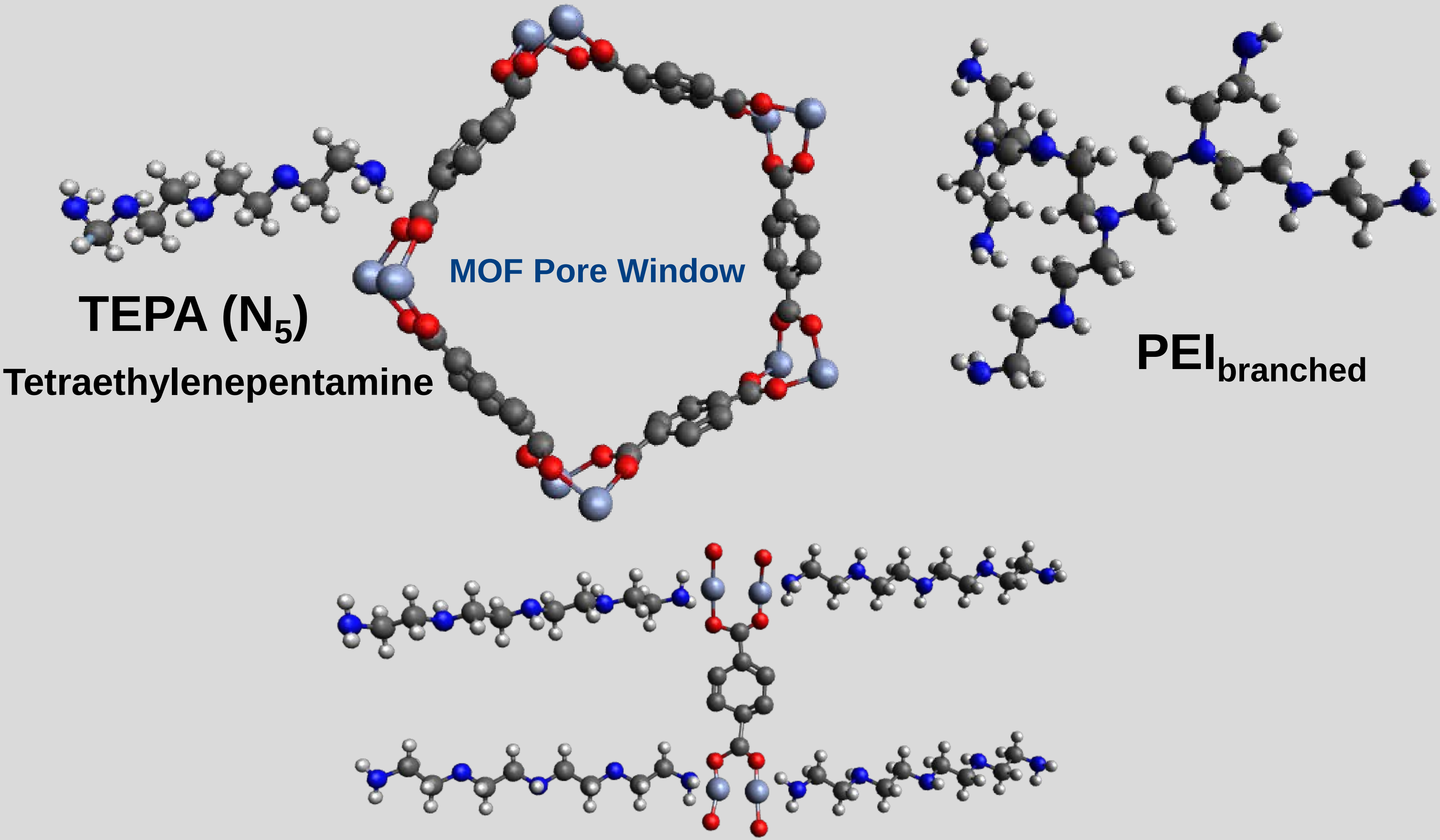
Average Particle size Distribution is *159 µm* for the MOF-A3/SiO_2

Hybrid MOF-Silica Properties

- **Exhibit high MOF loading (up to 35% so far)**
- **Excellent MOF dispersion and homogeneity**
- **Tunable hierarchical micro (MOF)-meso (SiO_2) pore size distribution**
- **Elevated surface areas (up to 900 m^2/g)**
- **Nanometric MOF particles (below 30 nm, enhanced diffusion by shortening the diffusion channels)**
- **Enhanced attrition resistance**
- **Good fluidazibility**
- **Good handling (100-500 microns).**

Hybrid MOF-Silica Sorbent (Amine addition)

Hybrid MOF-Based CO_2 Adsorbents

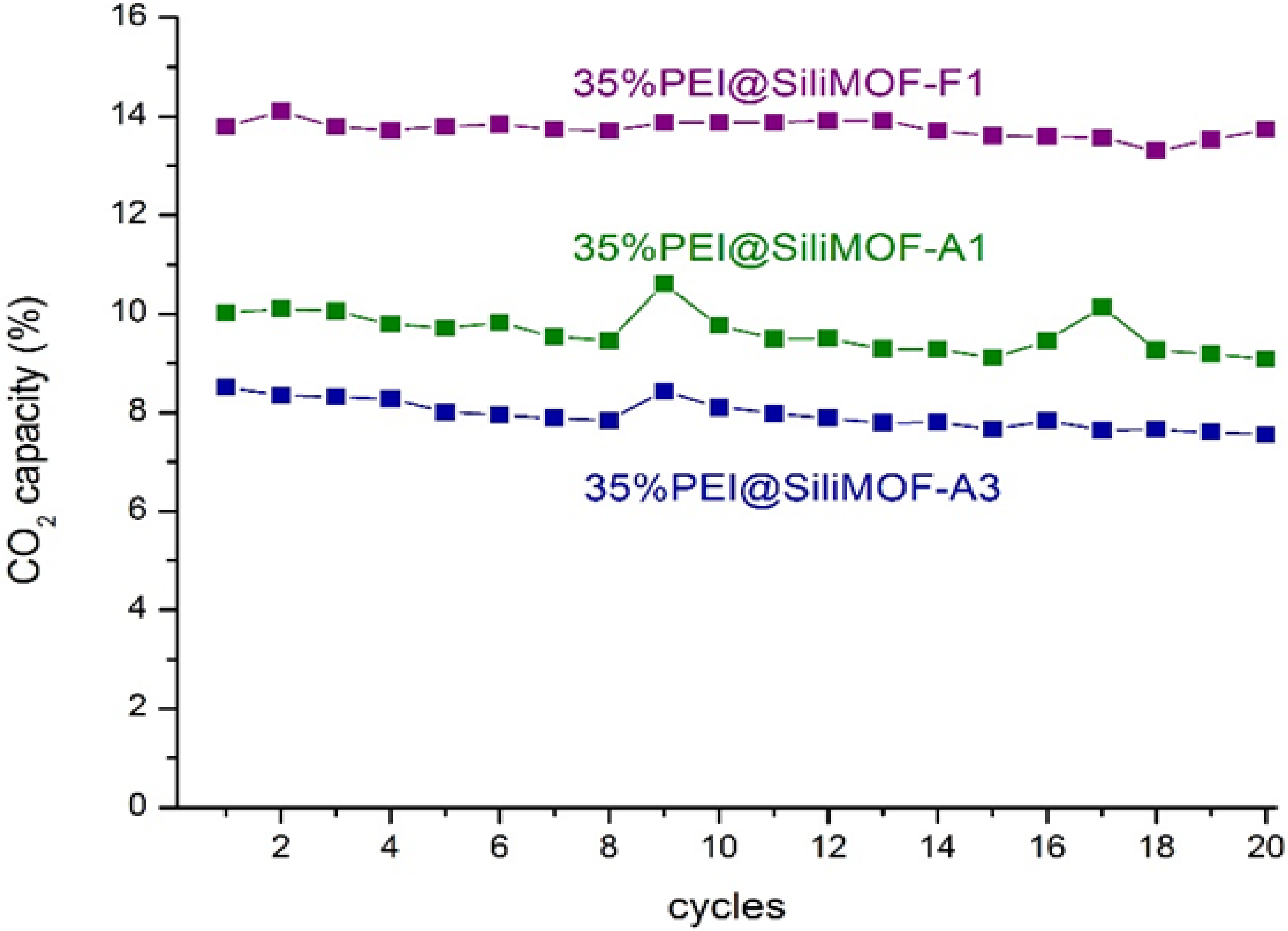


Different amines have been used taking advantage of the coordinatively unsaturated sites (CUS) and demonstrated that the amine stays inside the hybrid material after washing.

Hybrid MOF-Based CO_2 Adsorbents Performance in RTI-PBR

Simulated flue gas composition:

CO_2 = 15 vol%, O_2 = 4.5 vol%, and water = 5.65 vol% balanced with N_2



Hybrid MOF-Based CO_2 Adsorbents

- We have prepared several MOFs based on open-literature synthetic methods

- We have grown MOF inside the pores of silica and collected a clear scientific data that supports MOF@Silica.
  - We developed a very elegant, novel and environmentally friendly way of growing MOF inside the pores of silica that could be extended to other MOFs.

- We have impregnated this hybrid materials (MOF@Silica) with different amines taking advantage of the coordinatively unsaturated sites (CUS) and demonstrated that the amine stays inside the hybrid material after washing.

- We have shown high CO_2 capacity ($\geq$ 14 wt.%) coupled with a good stability of this novel hybrid MOF-based CO_2 adsorbent

- We are in the process of optimizing the synthesis of these hybrid MOF-based CO_2 adsorbents and extending this finding to other hybrid MOF-based CO_2 adsorbents.

Acknowledgements

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Energy Technology Division Team Members

Dr. Mustapha Soukri
msoukri@rti.org
919-541-6560