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

DE-FE0026432

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2017 NETL CO_2 Capture Technology Project Review Meeting

August 21-25, 2017 - Pittsburgh

DOE Program Manager: Steve Mascaro

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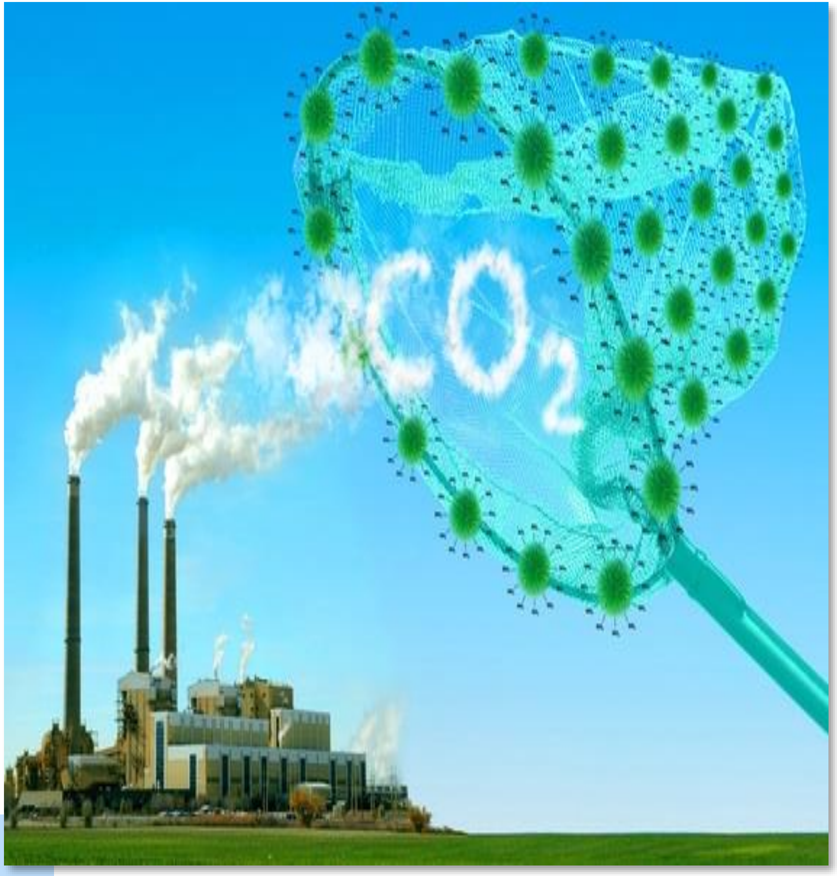


Project Details – DE-FE0026432

- **Funding: $1,989,415**
  - ***$1,591,532 DOE***
  - ***$ 397,883 Cost Share – State of North Carolina***
- **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 SO_x, NO_x, O_2 , and H_2O on these advanced solids sorbents**
- **Conduct a high level techno-economic analysis.**

Project Structure – Budget Period 1

Objective: **Develop several novel hybrid solids sorbent as well as packed-bed reactor testing.**

Timeframe: **10/1/15 to 3/31/17 (18 months)**

Task	Description	Objectives / Activities
1	**Project Management and Planning**	• Coordinate, manage and plan project activities that will include, monitoring and controlling of project scope, technical, budgetary and scheduling activities, project and task planning, asset management, cost tracking, progress reporting and updating Project Management Plan document appropriately.
2	**Hybrid MOF-based CO_2 adsorbents**	• 2.1 – hybrid MOF-based sorbents synthesis and development. • 2.2 – Hybrid MOF-based sorbents evaluation and optimization. • 2.3 – Molecular Modeling of Hybrid MOF-based sorbents.
3	**Hybrid *P*-Dendrimer-based sorbents**	• 3.1 – hybrid *P*-Dendrimer-based sorbents synthesis and development. • 3.2 – Hybrid *P*-Dendrimer-based sorbents evaluation and optimization. • 3.3 – Molecular Modeling of Hybrid *P*-Dendrimer-based sorbents.
4	**Long-term Performance Testing and Technical Merit Comparison**	• 4.1 – Multi-cycle performance testing of most promising *P*-Dendrimer-based and MOF-doped sorbents. • 4.2 – Preliminary sorbent production cost review

Budget Period 1 Milestones

Budget Period 1

	Task	Description	Date
A	1	Update Project Management Plan	10/31/15
B	1	Complete Kick-off meeting	12/17/15
C	2.2	Selection of the first 3 optimized high-potential hybrid MOF solid sorbents for CO_2 capture.	12/31/2016
D	3.3	Selection of the first 3 optimized high-potential hybrid *P*-dendrimer solid sorbents for CO_2 capture.	12/31/2016
E	4.1	Further selection of most-promising hybrid solid sorbent based on long-term performance criteria and cost review.	03/31/2017

Budget Period 1 Milestones Completed

Milestone Description	Budget Period	Planned Completion Date	Actual Completion Date	Verification Method	Comments
A. Updated Project Management Plan	1	10/31/2015	09/23/2015	Project Management Plan file submitted	**Complete.** PMP was updated and approved by DOE/NETL. File was provided to Project Officer and is used as an ACTIVE PMP.
B. Kick-off Meeting	1	12/17/2015	12/17/2015	Presentation file submitted	**Complete.** Presentation given at on-site kick-off meeting on 12/17/2015. Presentation provided for public release to Project Officer on 01/13/2016.
C. Selection of the first 3 optimized high-potential hybrid MOF solid sorbents for CO_2 capture.	1	12/31/2016	11/30/2016	Quarterly Report #5	**Complete.** The project team has produced numerous hybrid MOF sorbents. Several high potential hybrid MOF candidates have exhibited very good CO_2 capture of ≥ 12 wt% and good stability. RTI has selected three hybrid MOF candidates to move forward.
D. Selection of the first 3 optimized high-potential hybrid P-dendrimer solid sorbents for CO_2 capture.	1	12/31/2016	1/31/2017	Quarterly Report #5	**Complete.** The project team has produced over 125 hybrid *P*-dendrimer sorbents. Several high potential *P*-dendrimer candidates have exhibited good physical and performance characteristics, including CO_2 loading capacity ≥ 12 wt.%. RTI has selected three hybrid *P*-Dendrimer sorbent candidates to move forward, including one in particular selected for formulation into a fluidizable form.
E. Further selection of most-promising hybrid solid sorbent based on long-term performance criteria and cost review.	1	03/31/2017	3/31/2017	Quarterly Report #6	**Complete.** Highly promising MOF and *P*-dendrimer sorbent candidates have undergone multi-cycle packed-bed reactor testing. All six highly promising candidates have been tested for at least 250 adsorption/desorption cycles. All sorbent candidates exhibit desirable performance and thermal stability. The P-Dendrimer-based sorbent candidates in particular exhibit little to no degradation in multi-cycle tests.

Project Structure – Budget Period 2

***Objective*:** **Scale-up and testing of preferred sorbent as well as preliminary techno-economic analysis**

***Timeframe*:** **04/01/17 to 3/31/18 (12 months)**

Task	Description	Objectives / Activities
1	**Project Management and Planning**	• Continuation of BP1 project management and planning
5	**Scale-up and Testing of Selected Candidate**	• 5.1 – Scale up production of selected sorbent in fluidizable form. • 5.2 – Performance testing in lab-scale fluidized-bed reactor system. • 5.3 – Contaminant impact testing in packed-bed reactor. • 5.4 – Preliminary review of process requirements relative to conventional equipment. • 5.5 – Optimization of selected candidate and kilogram-scale production.
6	**Preliminary Techno-Economic Analysis**	• 6.1 – Preliminary process design. • 6.2 – Preliminary economic evaluation.

Project Milestones

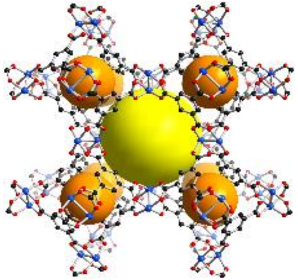
Budget Period 2

	Task	Description	Date
F	5.1	Successful scale-up of preferred hybrid sorbent in fluidized form and experimental data from lab-scale FMBR prototype capable of achieving 90% CO_2 capture from simulated flue gas.	9/30/17
G	6.2	Complete technical and economical evaluation.	3/31/18

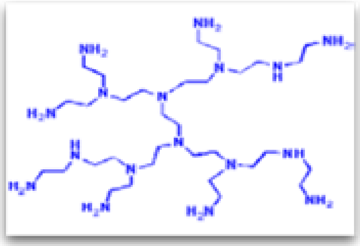
Hybrid MOF-Based CO_2 Adsorbents

Hybrid MOF-Based CO_2 Adsorbents

Silica



MOF (HKUST-1)



PEI

- Attrition resistance
- Fluidizable
- Low cost
- Acceptable density

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

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

Silica + MOF + PEI

Table 2. Reported CO_2 Capture Performance Results

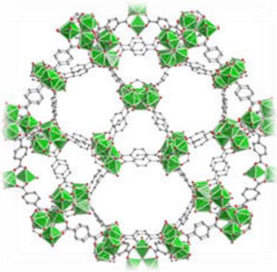
Sample Description	CO_2 Capacity (wt%)
MOF	21.4[a]
MOF-amine	~20
Fluidizable silica (FS)	0
FS-PEI	4.8
MOF-silica	0
MOF-silica-amine	9.3

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

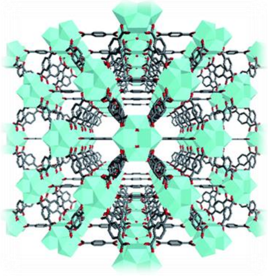
MOFs Selected for Evaluation as Hybrid MOF-Based CO_2 Adsorbents

- 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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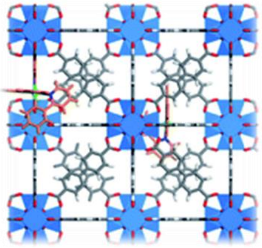
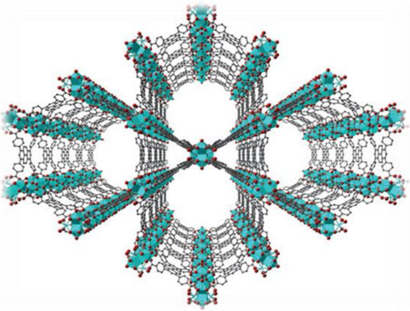
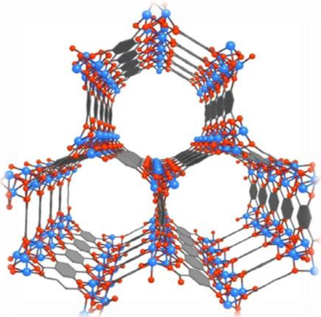




NU-1000 (Zr)

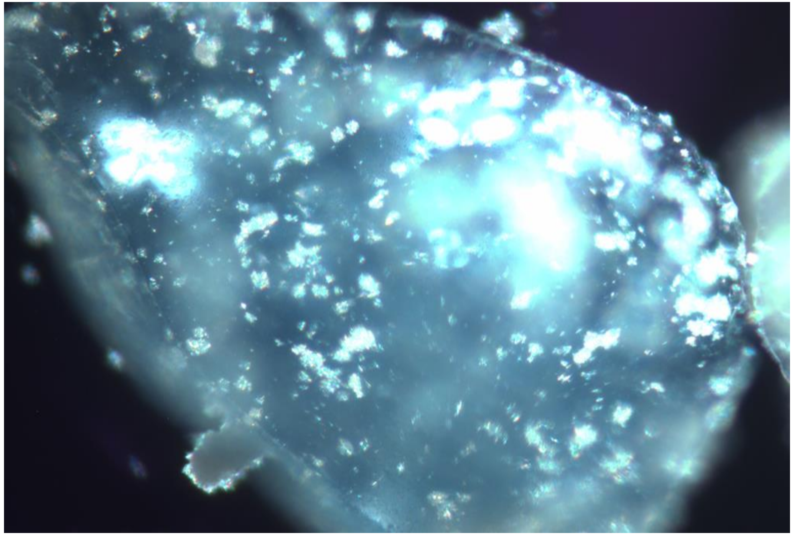


MOF-74 (Mg)

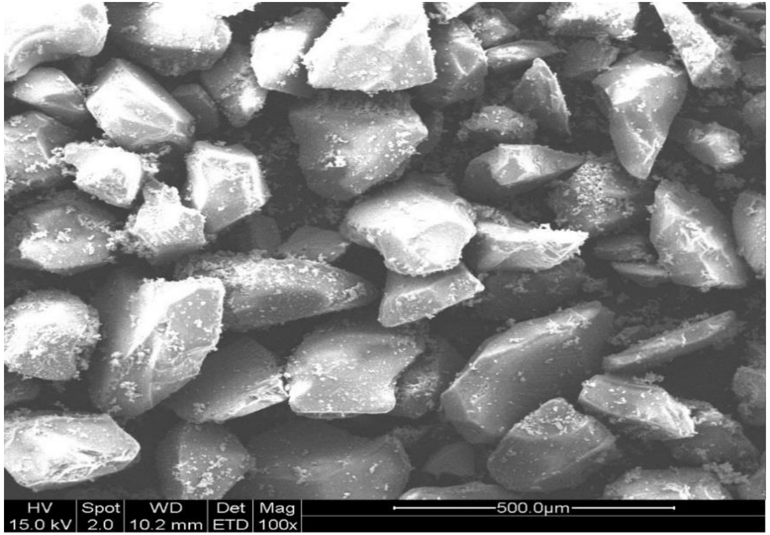
Growing MOF inside the pores of Silica!

Solvo-Thermal Synthesis of MOF-Silica Hybrid

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



Confocal microscope picture



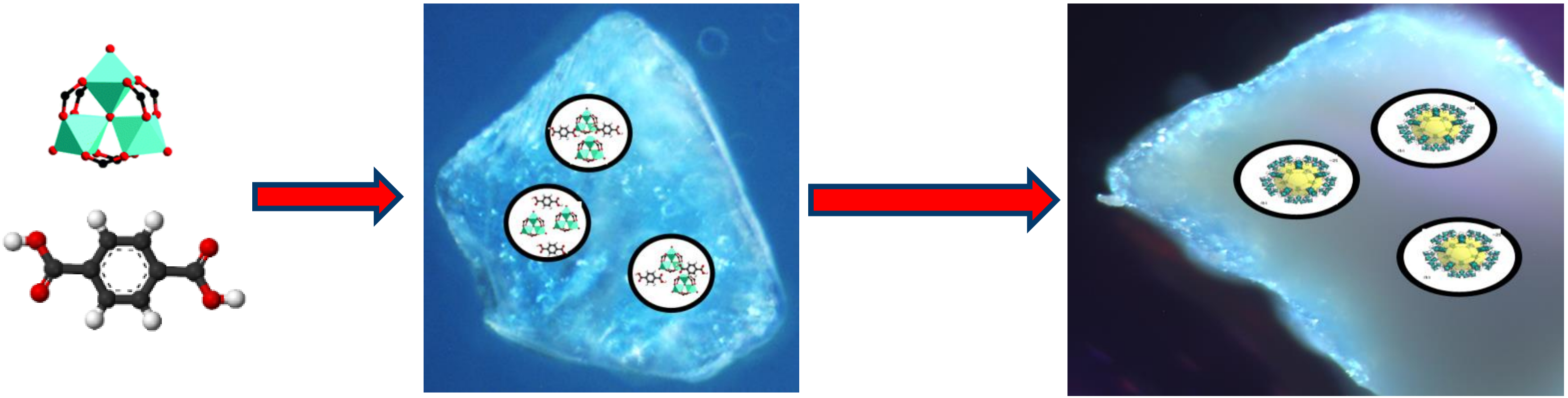
SEM picture

Is the current solvo-thermal 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**

New Approach for MOF-Silica Hybrid Preparation

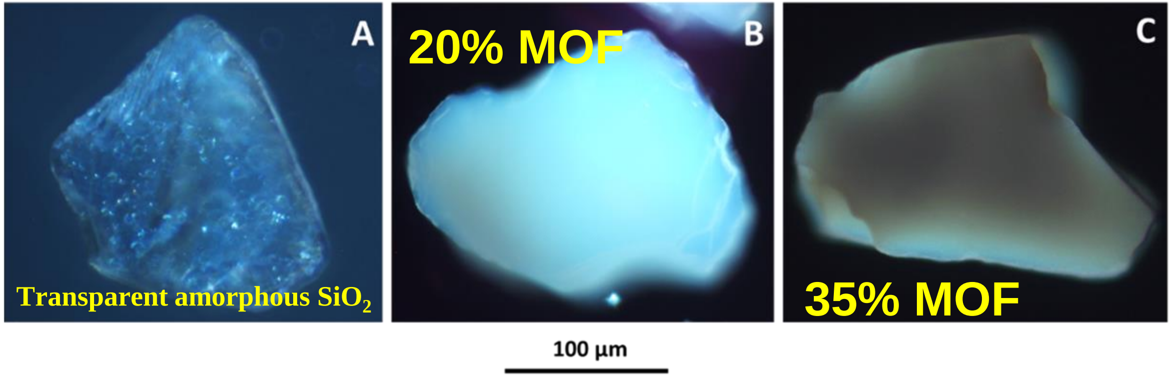
Our new approach: Solid State Synthesis

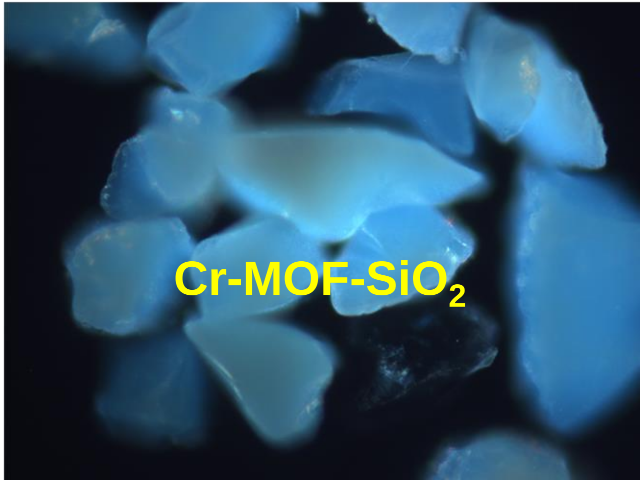


New approach allowed the project to meet the fist goal of the MOF-Silica hybrid Synthesis *via* sequential incipient wetness-impregnation/evacuation

→ **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-Cup attrition index**

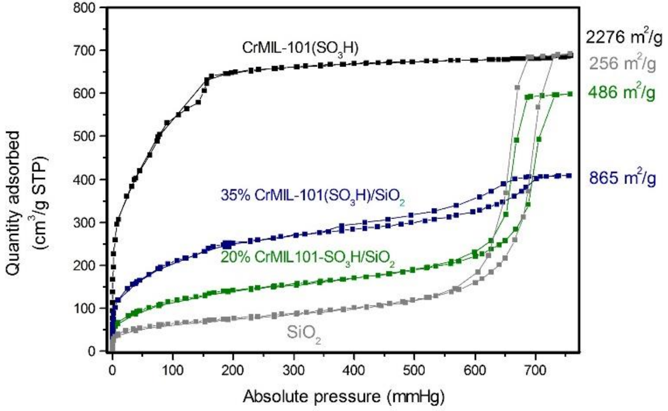
Confocal Microscope for the New MOF-Silica Hybrids



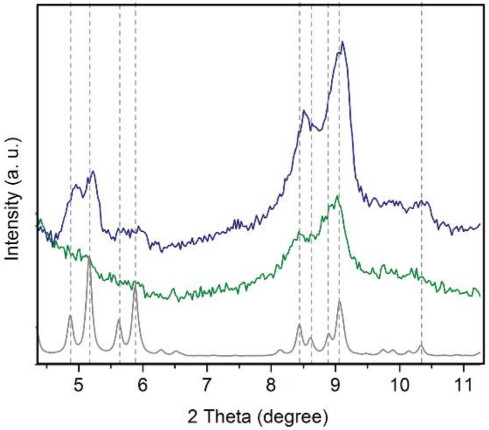


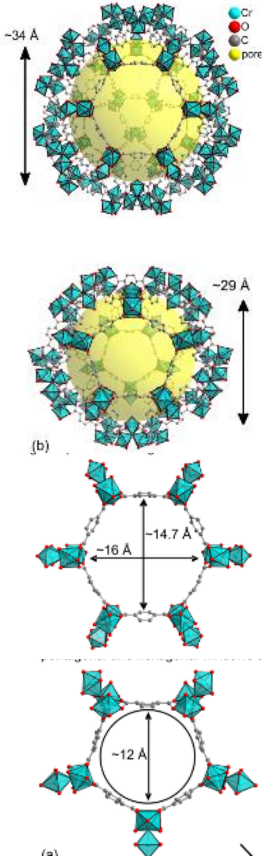
Full characterization for (Cr)MIL-101(SO_3H)/SiO_2

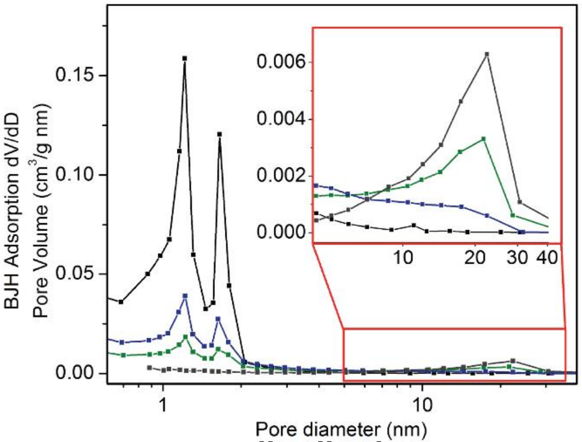
N_2 sorption isotherms



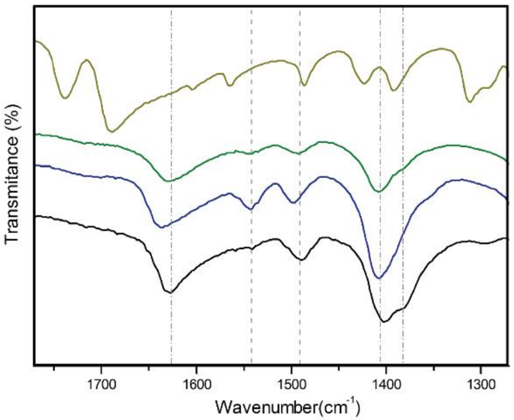
XRD







Pore distribution



FTIR

Confining Metal-Organic Framework Nanocrystals Within Mesoporous Materials: A General Approach via 'Solid-State' Synthesis.

CHEMISTRY OF MATERIALS

Article

Confining Metal-Organic Framework Nanocrystals Within Mesoporous Materials: A General Approach via 'Solid-State' Synthesis.

Ignacio Luz, Mustapha Soukri, and Marty Lail

Chem. Mater., **Just Accepted Manuscript** • Publication Date (Web): 21 Aug 2017

Patent
Atty. Dkt. No. 121-77-PCT

SOLID-STATE CRYSTALLIZATION OF METAL ORGANIC FRAMEWORKS WITHIN MESOPOROUS MATERIALS METHODS AND HYBRID MATERIALS THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

[0010] This application claims the benefit of 62/373,047 filed August 10, 2016, Ignacio Luz, Atty. Dkt. No. 474774US which is hereby incorporated by reference in its entirety.

1. FIELD

[0011] The present disclosure relates to a general method for the solid-state crystallization of metal organic frameworks (MOFs) within the pore spaces of mesoporous materials (MPMs) in the absence of solvent. Additionally, the present disclosure relates to hybrid metal organic framework (MOF) and mesoporous material (MPM) hybrid materials (MOF/MPM) generated therefrom.

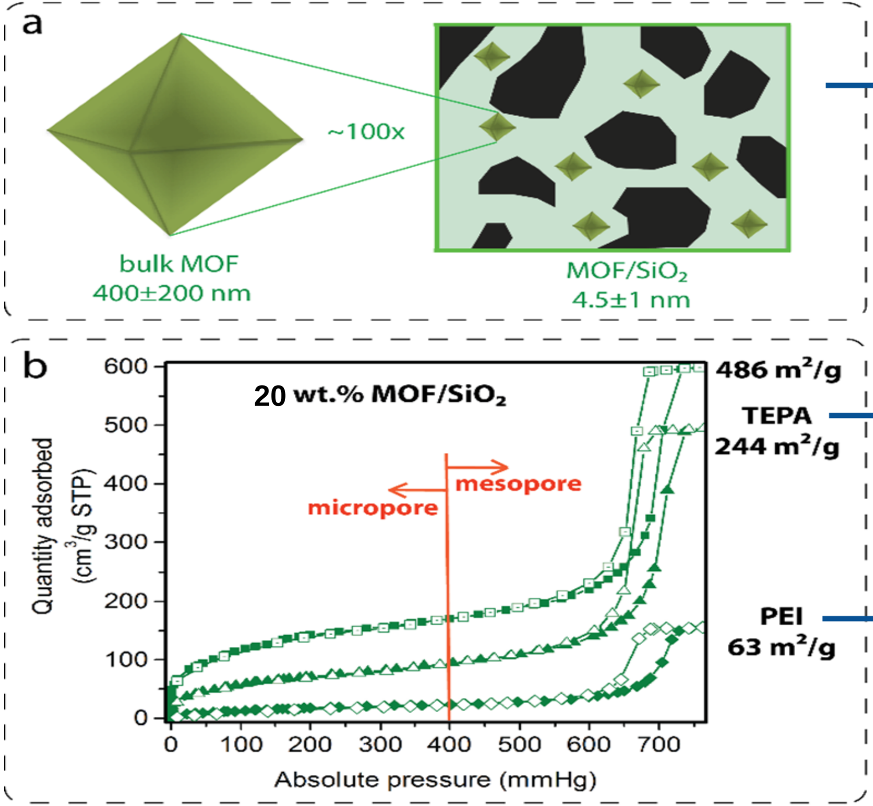
2. BACKGROUND

2.1. Introduction

[0012] The "background" description provided herein is for the purpose of generally presenting the context of the disclosure. Work of the presently named inventors, to the extent it is described in this background section, as well as aspects of the description which may not otherwise qualify as prior art at the time of filing, are neither expressly or impliedly admitted as prior art

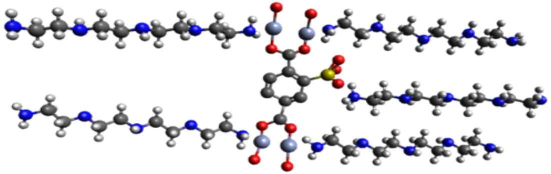
Polyamine-Containing MOF/SiO_2 Fluidized Sorbents

- Adsorption 50°C (15% CO_2, 4.5 O_2, 5.6% H_2O)
- Regeneration 120°C (5.6% H_2O)

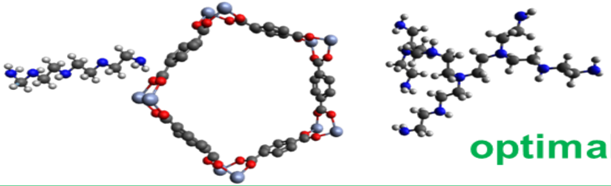


MOF/SiO_2
Hierarchical micro-/mesoporosity

TEPA anchored to MOF/SiO_2

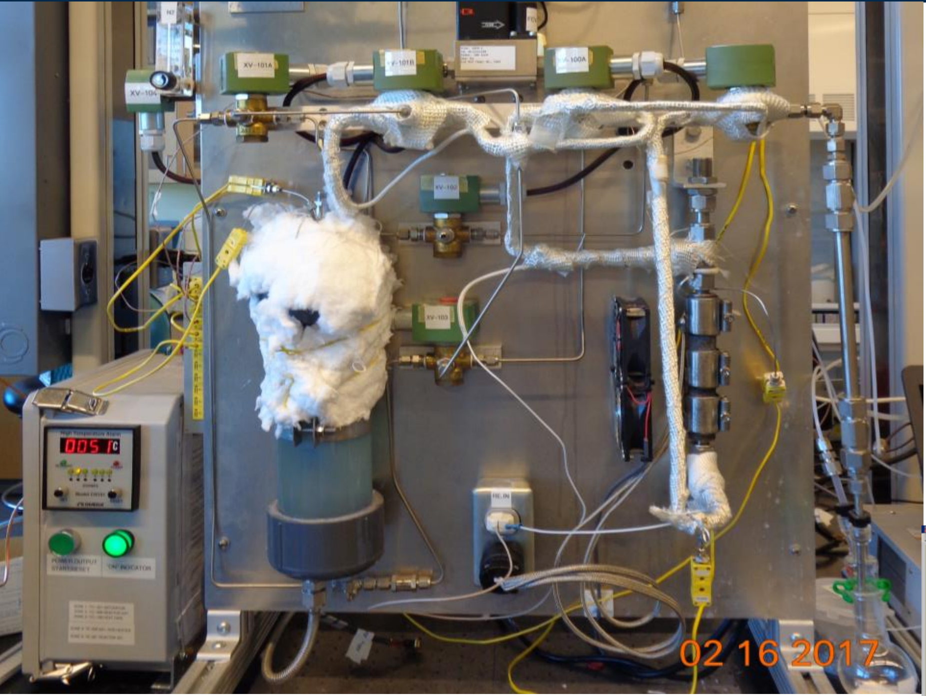


PEI confined on MOF/SiO_2



optimal

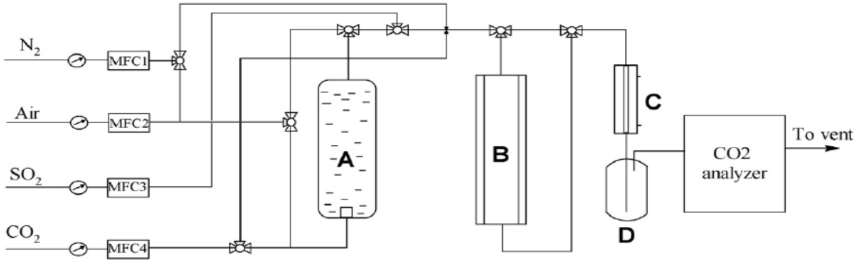
Packed-bed reactor (PBR)

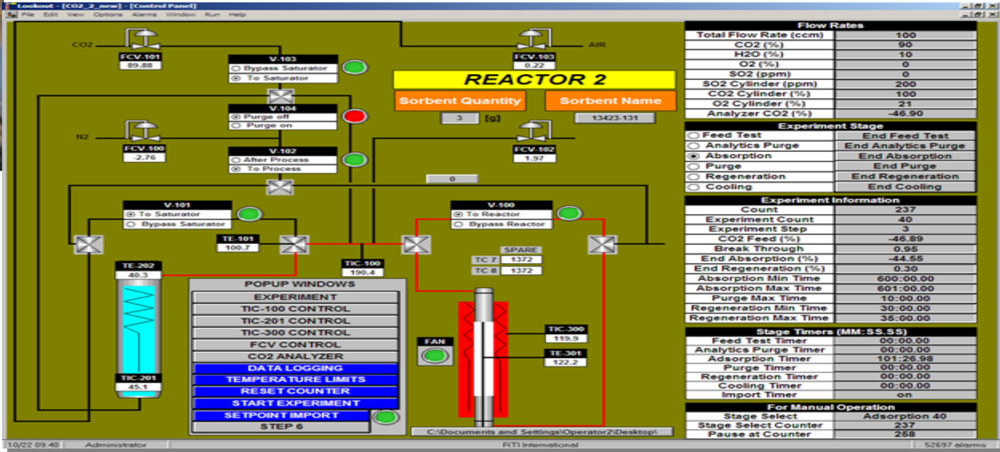


- Fully-automated operation and data analysis; multi-cycle absorption-regeneration
- Rapid sorbent screening experiments
- Measure dynamic CO_2 loading & rate
- Test long-term effect of contaminants

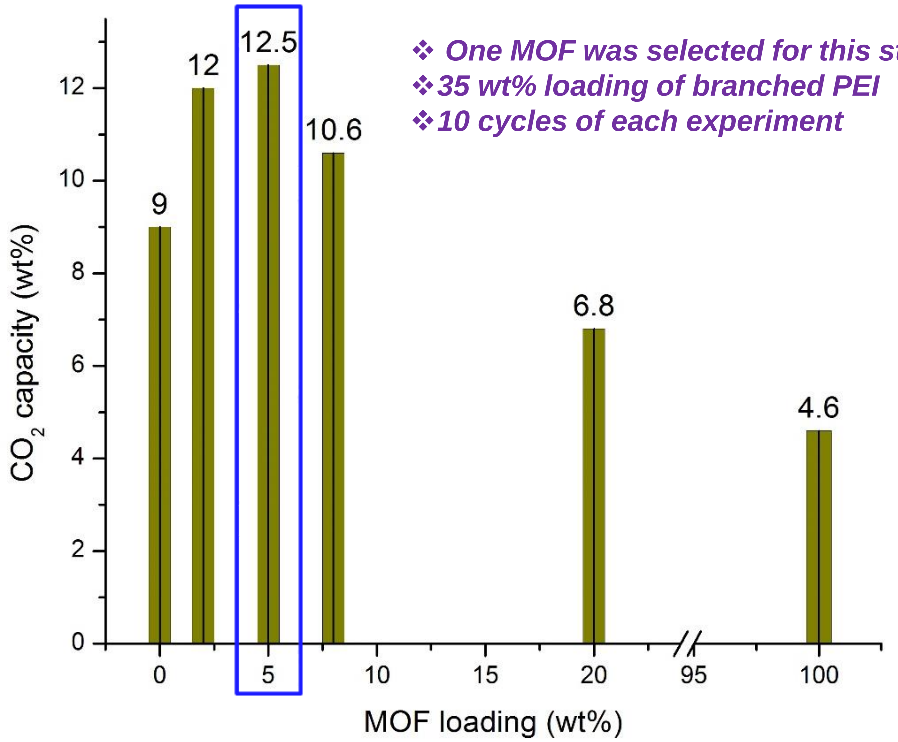
- <u>**2 gram of hybrid CO_2 solid sorbent**</u> is used for testing

<u>**Adsorption**</u>: CO_2=15 vol%, O_2 = 4.5 vol%, H_2O= 5.65 vol% in balance with N_2 at 50 °C
<u>**Regeneration**</u>: H_2O = 5.65 vol% in balance with N_2 at 120 °C





Effect of MOF Loading on CO_2 Capture



❖ *One MOF was selected for this study*
❖ *35 wt% loading of branched PEI*
❖ *10 cycles of each experiment*

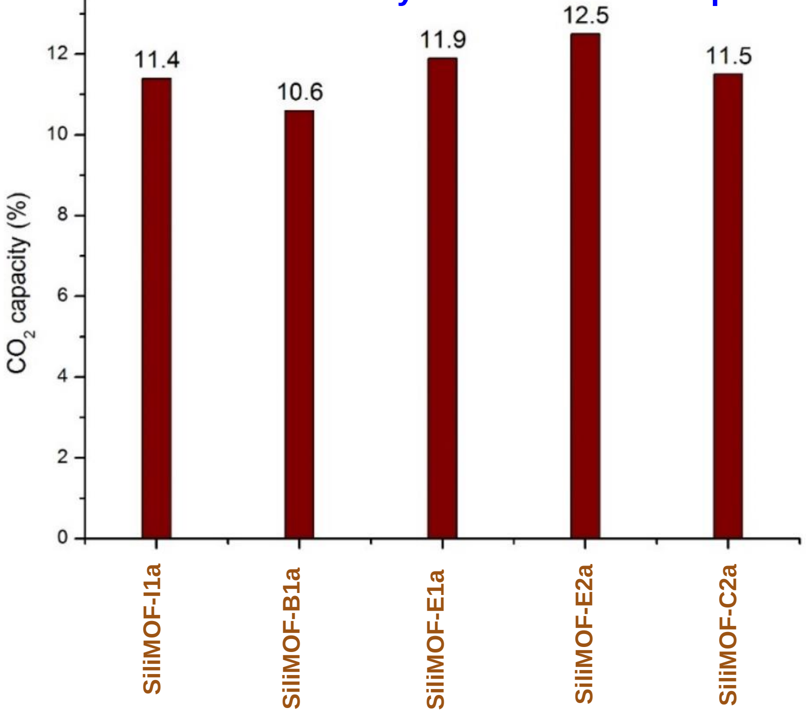
- ➢ 5 wt.% MOF nanocrystals in Silica meso-pores lead to an improvement of CO_2 capture capacity (12.5 wt.% CO_2)
- ➢ Higher MOF loadings undergoes partial inhibition of amine efficiency to capture CO_2
- ➢ This effect has been observed for 10 different hybrid-MOF/SiO_2 exhibiting different features, such as surface area, functional groups, open metal sites and pore size.

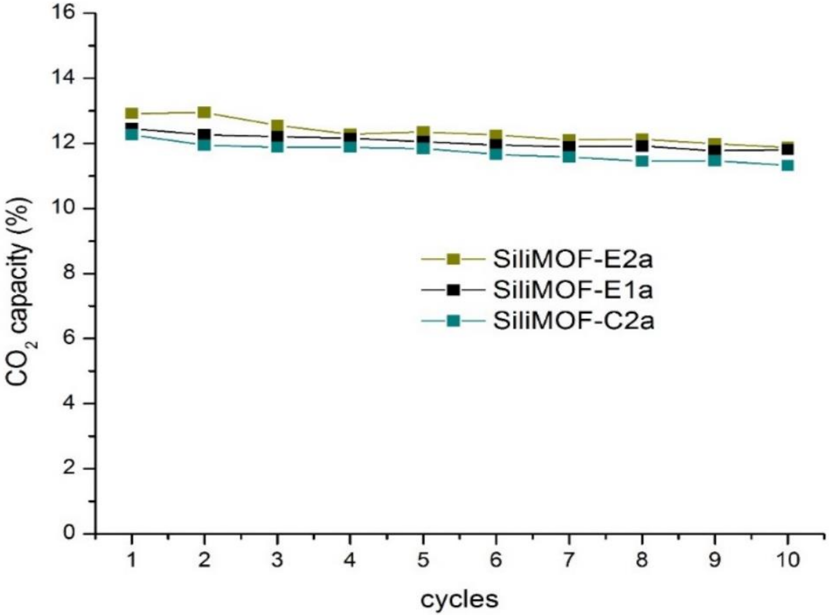
Simulated flue gas composition:

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

Effect of MOFs Structure on CO_2 Capture

5 wt.% MOF nanocrystals in Silica mesopores

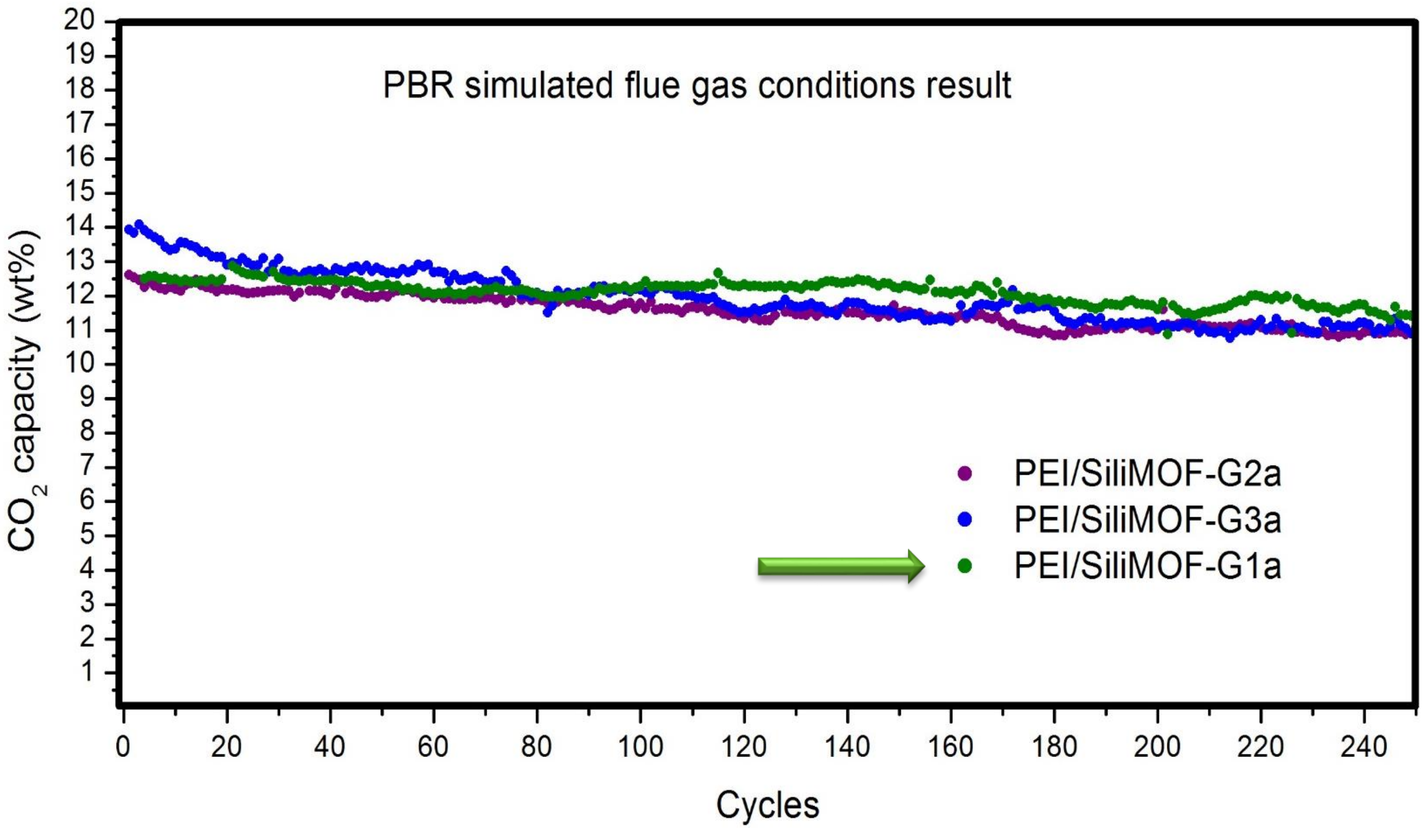




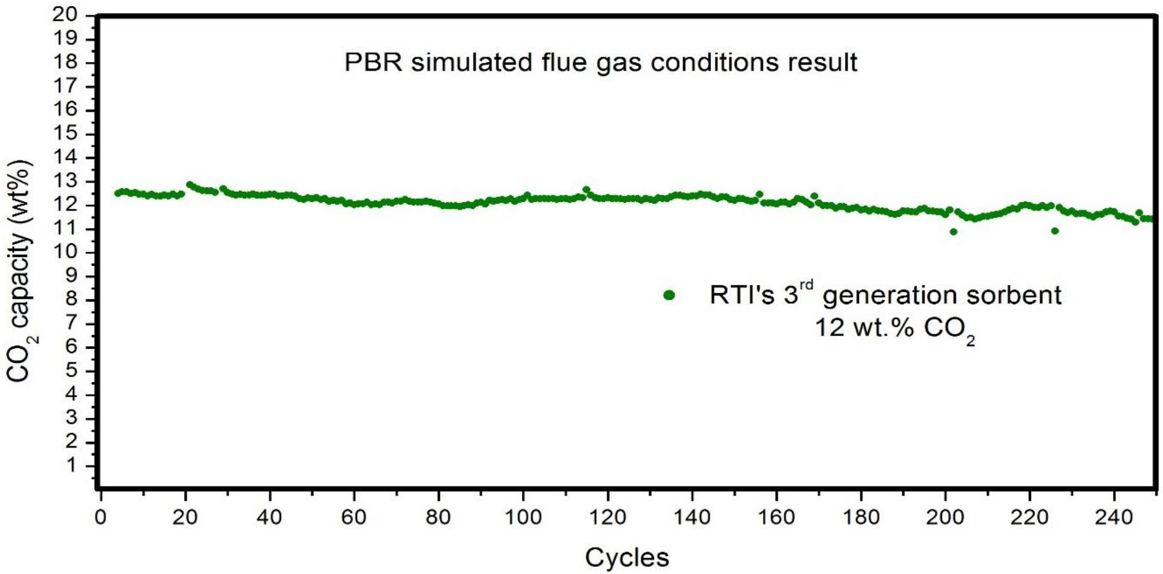
Simulated flue gas composition:

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

Multi-Cycles Testing for 3-Selected Sorbents Candidates



Multi-Cycles Testing for Selected Sorbent Candidate

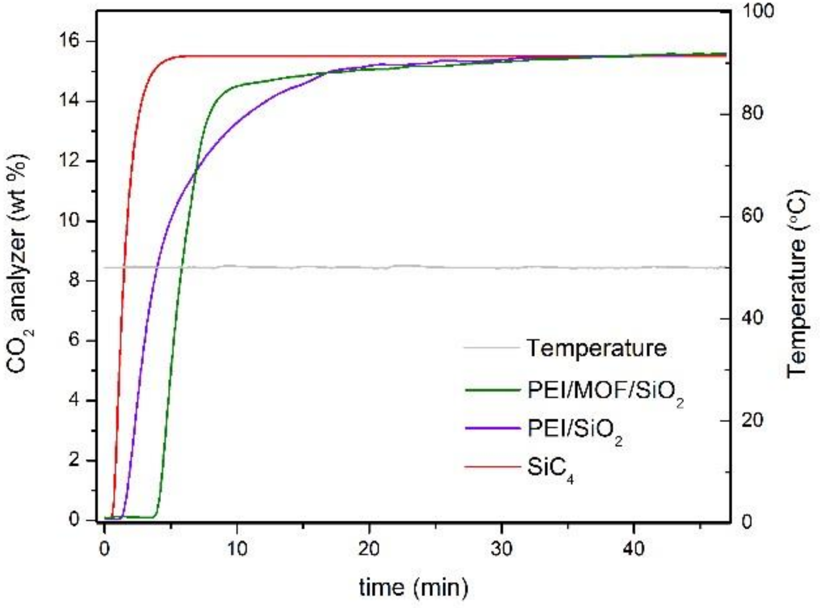


Candidate	Packed bed reactor-CO_2 Capacity (wt%)		Chemical Makeup		Thermal Stability
	Capacity	Cycles	Pre Analysis	Post Analysis	
PEI/HyperMOFG1a	12.5%	250	N: 13.38% C: 22.36% H: 4.84%	N: 12.05% C: 20.57% H: 4.35%	up to 150 °C

CO_2 Capture in Packed-Bed Reactor

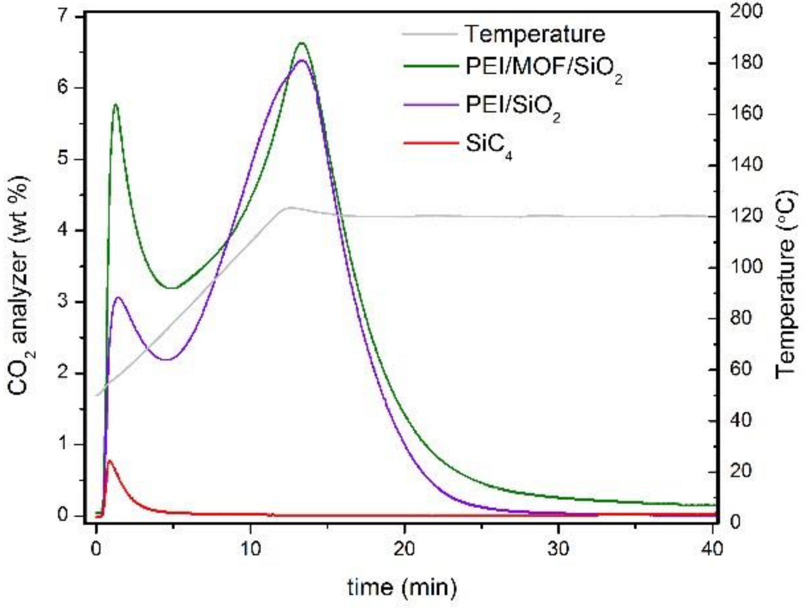
Adsorption

15 vol% CO_2, 4.5 vol% O_2,
5.6 vol% H_2O, N_2 (50 °C)



Regeneration

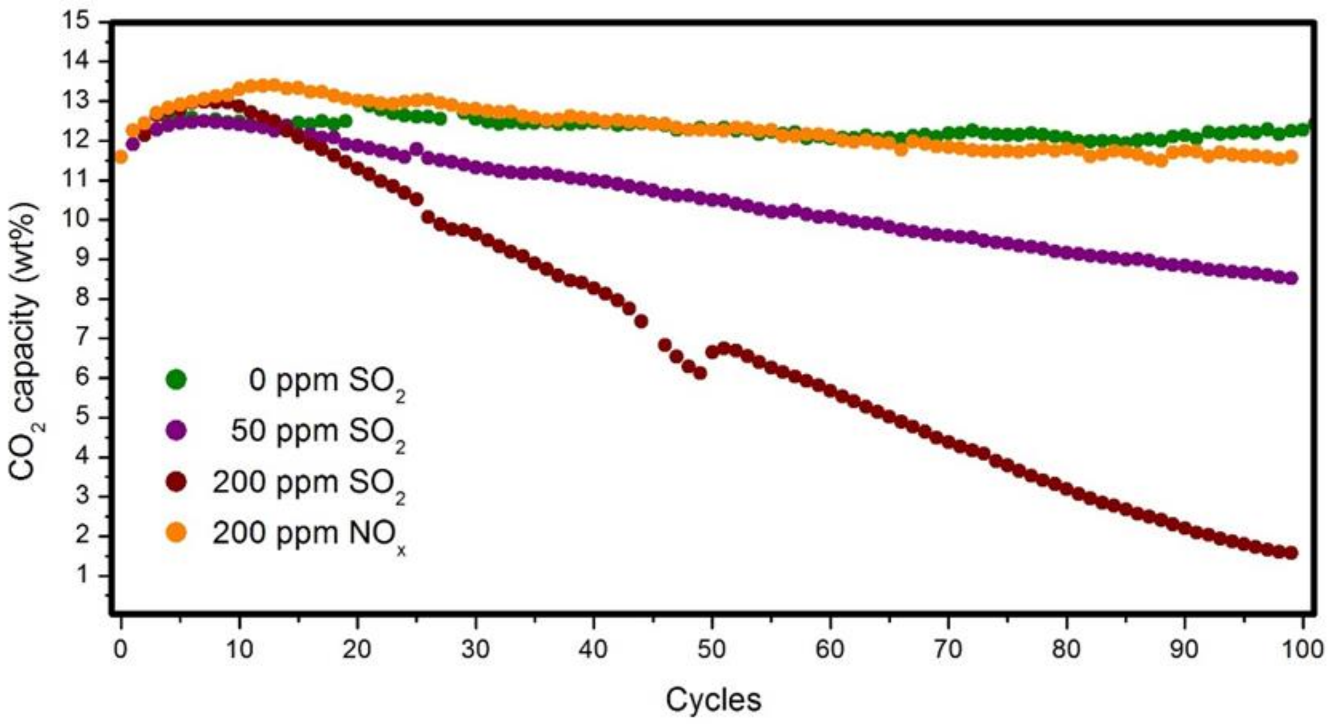
H_2O = 5.6 vol% + N_2 (120 °C)



Unprecedented dual physi-chemisorption

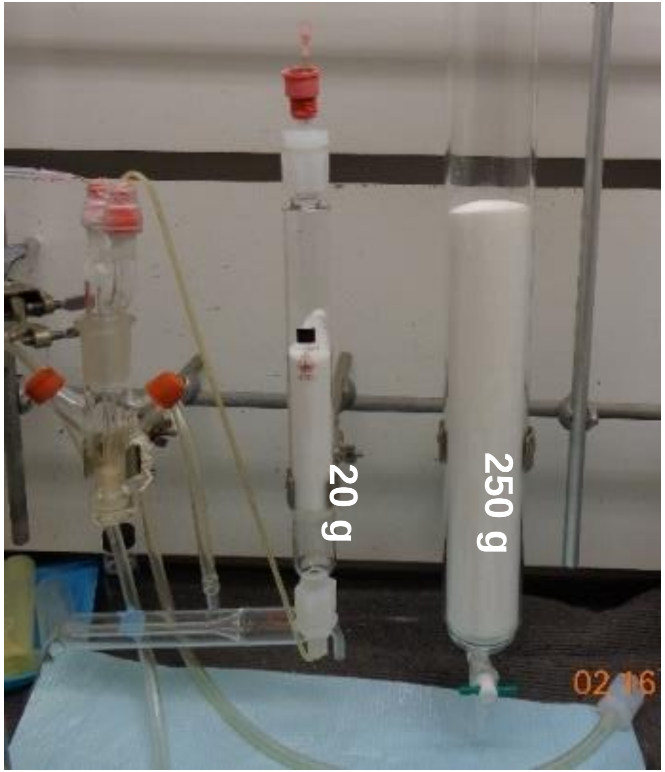
SO_2 and NOx Contaminants Testing for Hybrid *MOF*-Based Sorbent

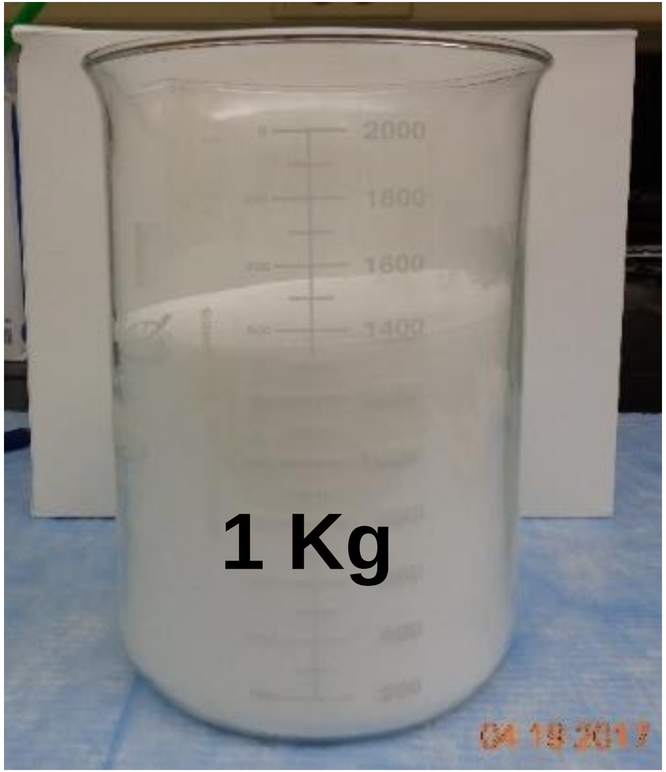
- Completed testing of 50 and 200 ppm SO_2 levels
- 100 cycles testing of NOx (200 ppm) in simulated flue gas streams



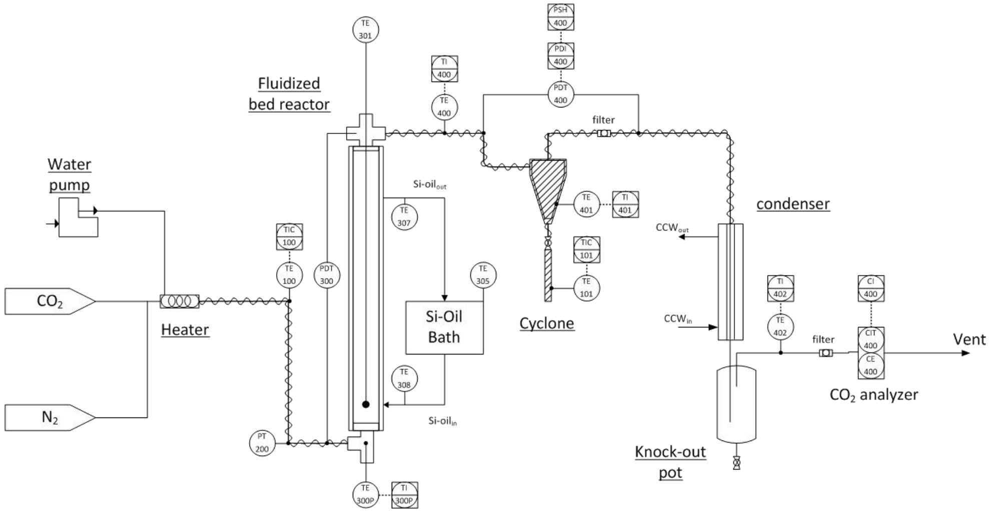
Large scale production of Hybrid *MOF*-Based Sorbent

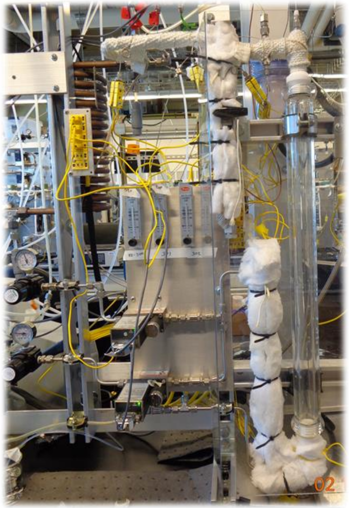
Scale-up from 20 mg up to 1Kg





CO_2 Adsorption in Visual Fluidized-Bed Reactor

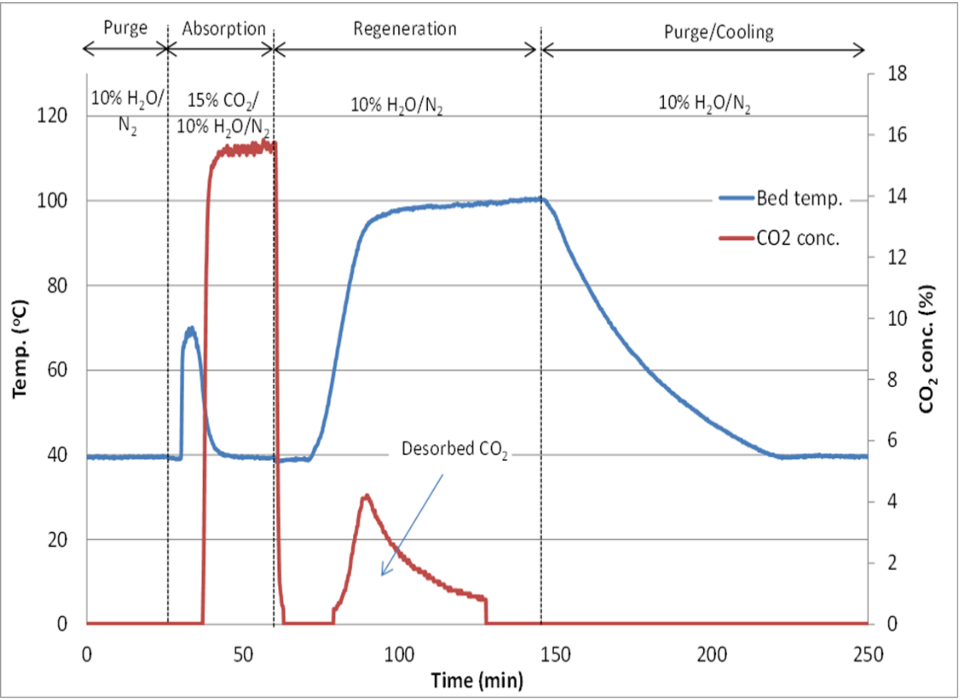




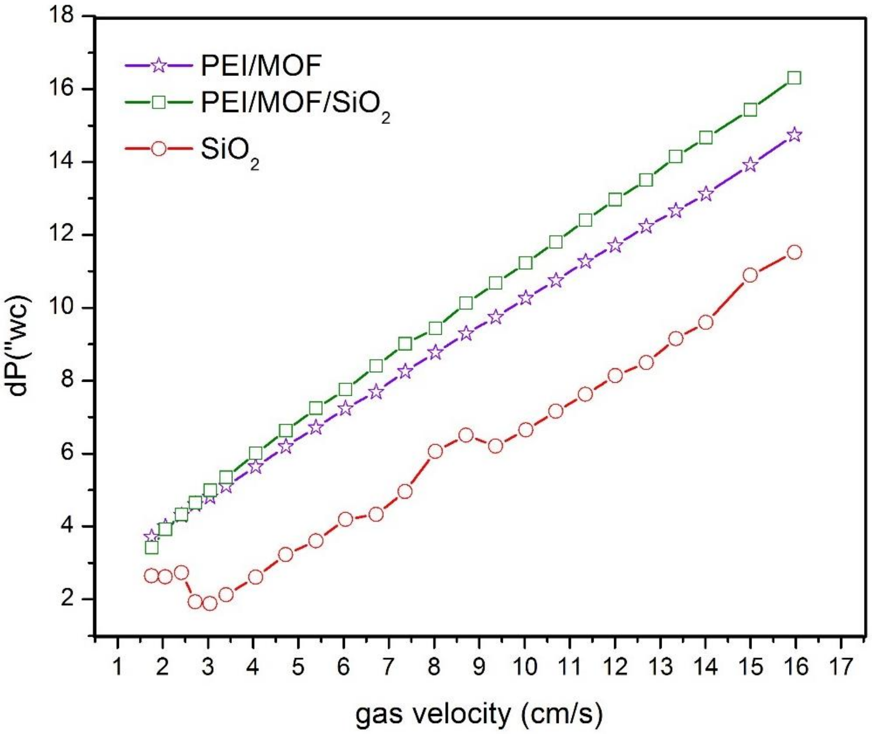
- Verify (visually) the fluidizability of CO_2 capture sorbents
- Operate with realistic process conditions
- Measure △P and temperature gradients
- Test optimal fluidization conditions
- Fluidized bed reactor allows sorbents to be tested under high water content up to 95% in gas stream
- Bed temperature can be as high as 120 °C
- Pressure drop across the bed is measured over the course of experiment

Fluidizability Testing & CO_2 breakthrough

Breakthrough experiment for PEI/MOF/SiO_2

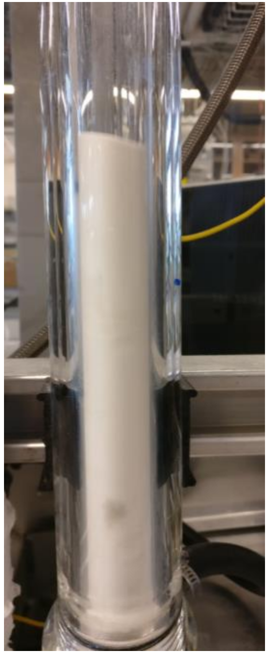


Pressure drop measurement



Fluidizablity Testing Under Humid Stripping Gas

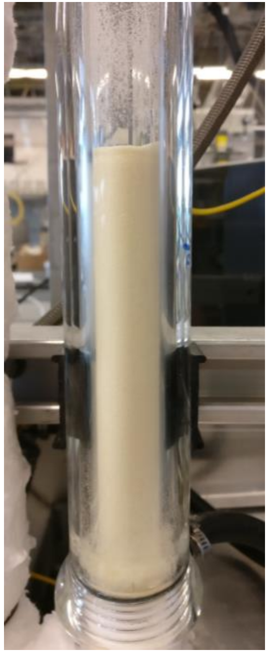
PEI/SiO_2



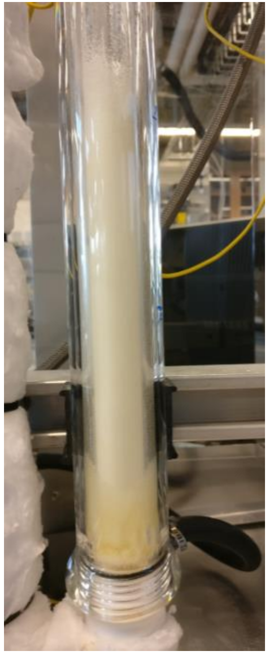
Initial

Under 80% steam for 1 h

MOF/PEI/SiO_2



Initial



Under 80% steam for 1 h

Fluidizability Testing Under Humid Stripping Gas

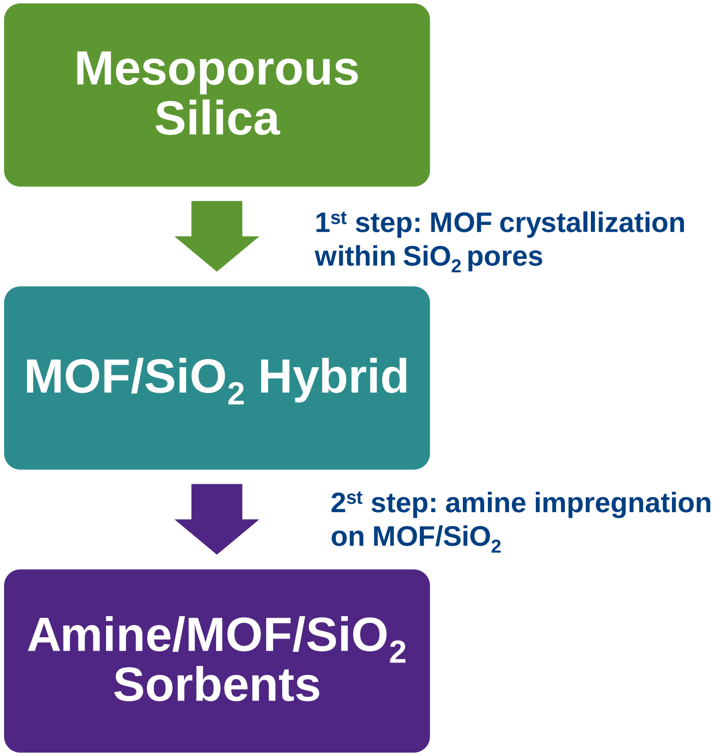
Initial

Regen. under 80% steam for 1 h

Subsequent abs.

RTI's novel CO_2 fluidized solid sorbents exhibit better performance and long term stability in a fluidized configuration

Hybrid MOF-Based CO_2 Adsorbents



- **We developed a very elegant, novel and environmentally friendly way of growing MOF inside the pores of silica that could be extended to other mesoporous supports.**

- **We have shown high CO_2 capacity ($\geq$ 12 wt.%) coupled with:**
  - Excellent MOF dispersion and homogeneity
  - Good water and air stability
  - Good chemical and thermal stability
  - Enhanced attrition resistance
  - Excellent fluidizability and solids handling capability

- **We are in the process of further testing these hybrid MOF-based CO_2 adsorbents to unveil most of their potential as solid sorbent for CO_2 capture.**

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