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

DE-FE0026432

Mustapha Soukri, John Thompson, Ignacio Luz, Marty Lail, Kelly Amato, Jak Tanthana, Himanshu Paliwal and Tom Nelson

April 27, 2017

Budget Period 1 Project Review Meeting

DOE Program Manager: Steve Mascaro

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

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:
  - **Fluidizabke hybrid metal organic frameworks**
  - **Fluidizable hybrid-phosphorous dendrimers**

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)** ***Cost:*** **$1.104 M total**

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

Project 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**

BP1 Milestones Completed

Budget Period 2

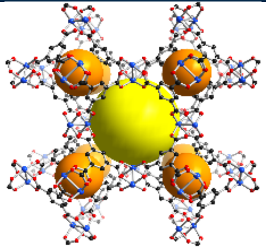
	Task	Description	Date
F	5.1	**Successful scale-up of preferred hybrid sorbent in fluidized form and experimental data from lab-scale FMBR prototype capable of achieving 90% CO_2 capture from simulated flue gas.**	**9/30/17**
G	6.2	**Complete technical and economical evaluation.**	**3/31/18**

Hybrid MOF-Based CO_2 Adsorbents

Hybrid MOF-Based CO_2 Adsorbents

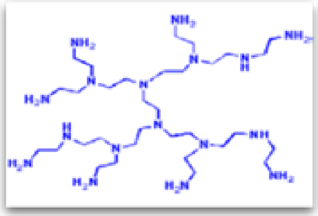
Silica

- 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

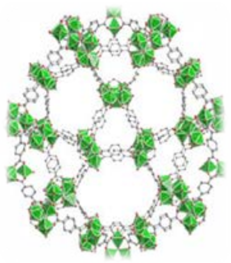
Sample Description	CO_2 Capacity (wt%)
MOF	21.4[a]
MOF-amine	~20
Fluidizable silica (FS)	0
FS-PEI	4.8
MOF-silica	0
MOF-silica-amine	9.3

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

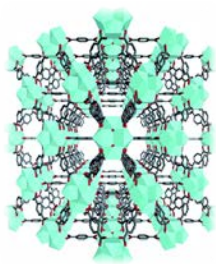
MOFs Selected for Evaluation as **Hybrid MOF-Based CO_2 Adsorbents**

- 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

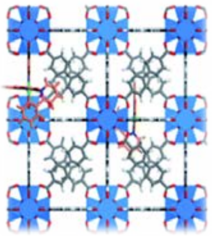
MIL101 (Cr)

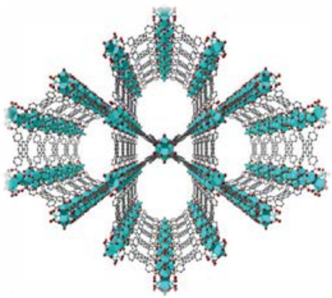


UIO-66 (Zr)

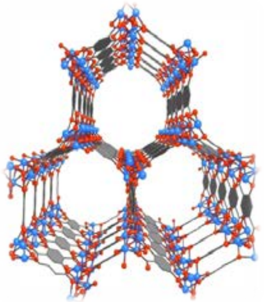


UIO-67 (Zr)





NU-1000 (Zr)

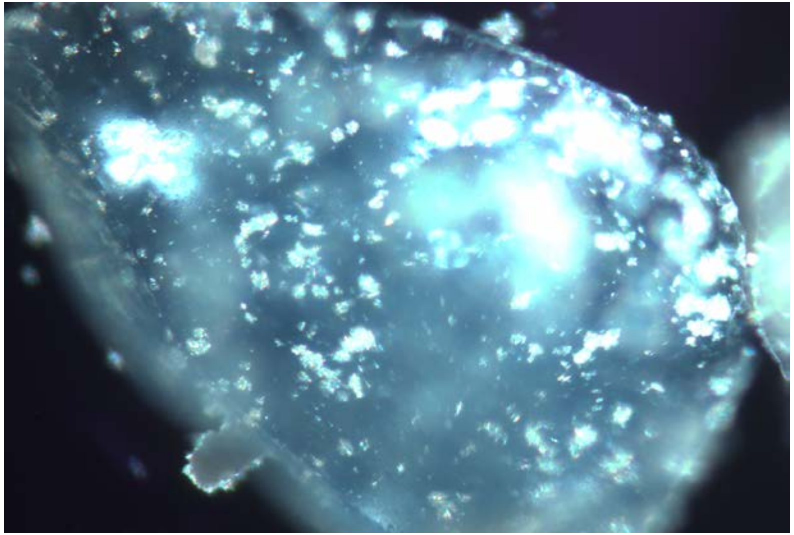


MOF-74 (Mg)

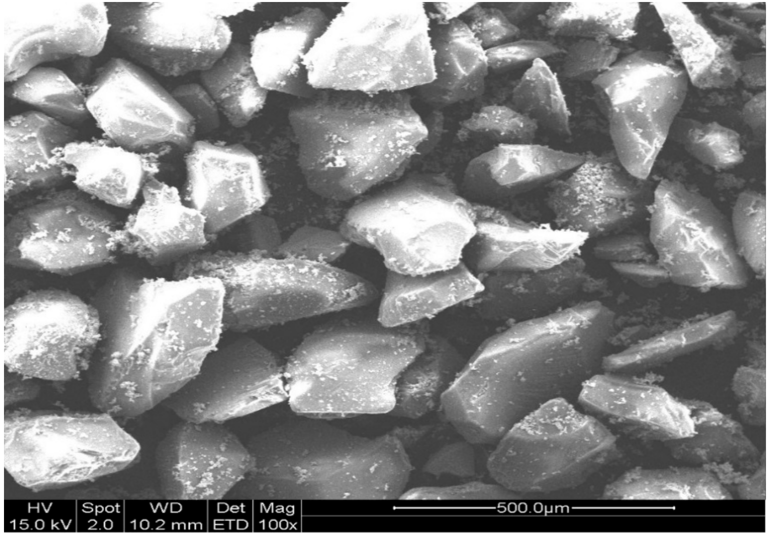
Growing MOF inside the pores of Silica!

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?

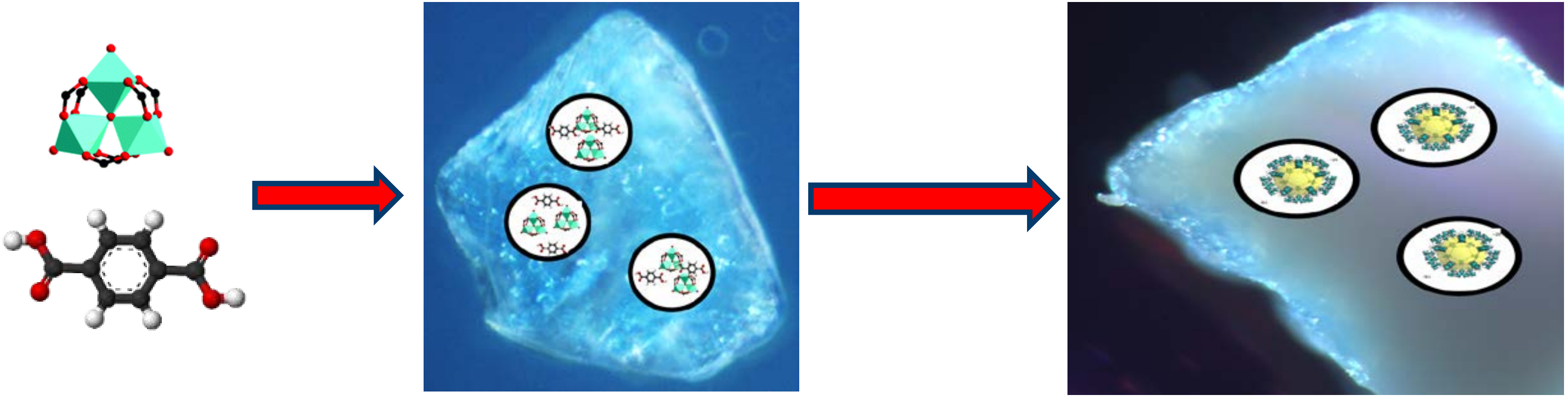
- **Not utilizing the internal pores of the silica**
- **Poor interaction of MOF with Silica → Low yields**
- **Low attrition-resistance**

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

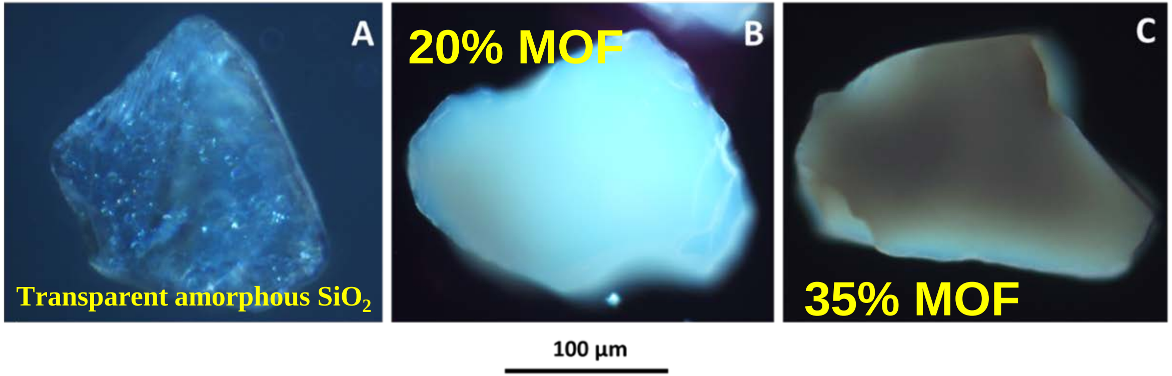
Our new approach: Solid State Synthesis

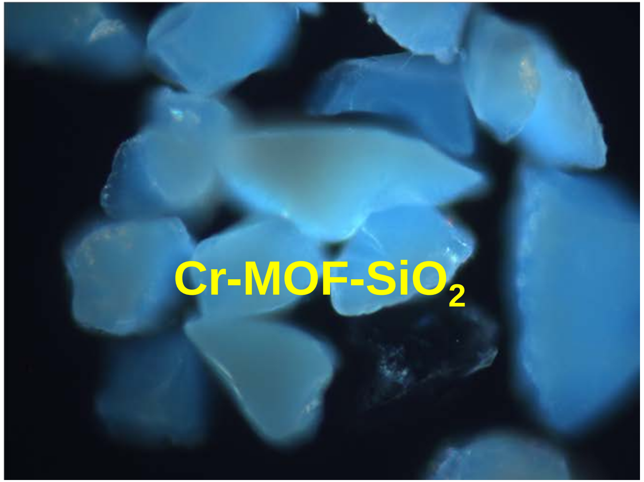


New approach allowed the project to meet the fist goal of the MOF-Silica hybrid Synthesis

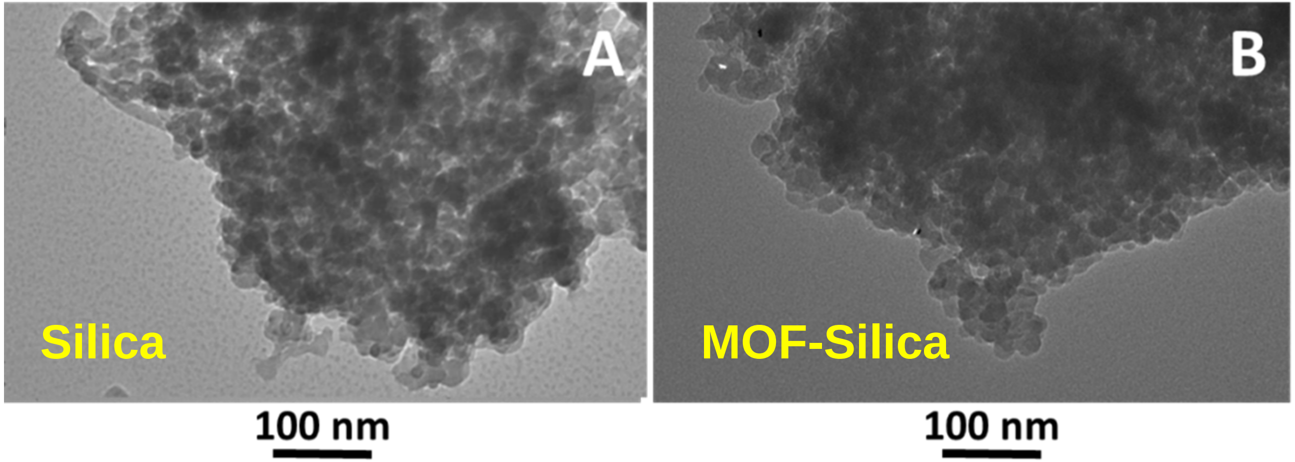
Full characterization using the most well known technics such as: Confocal Microscope, SEM, FIB-FESEM, TEM, FTIR, XRD, XRF, N_2 isotherms, TGA, Particle size distribution, Jet-Cut attrition index

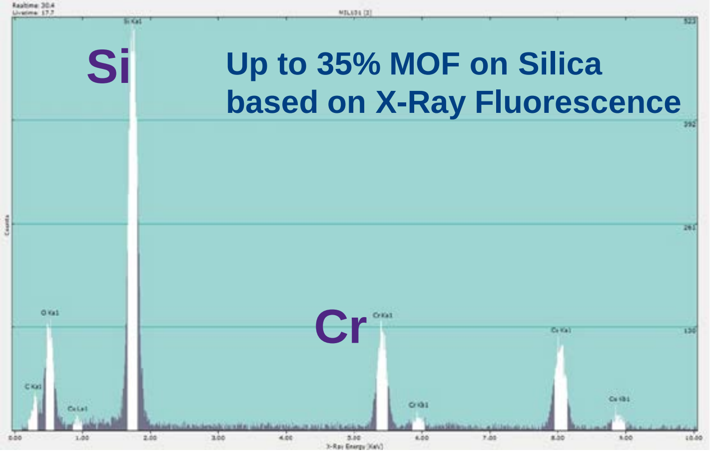
Confocal Microscope for the New MOF-Silica Hybrids





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

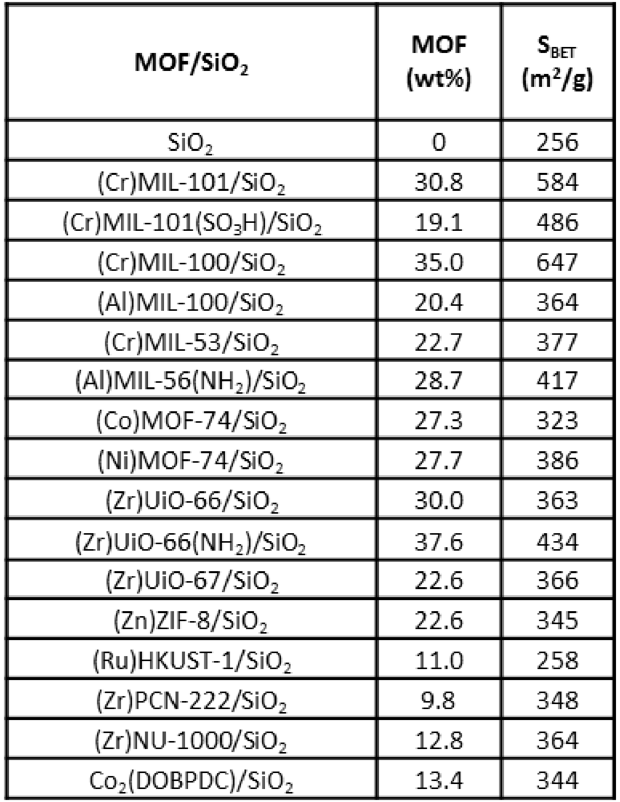




Up to 35% MOF on Silica based on X-Ray Fluorescence

Scope MOF/SiO_2 Hybrid Materials

Scope for MOFs on mesoporous silica

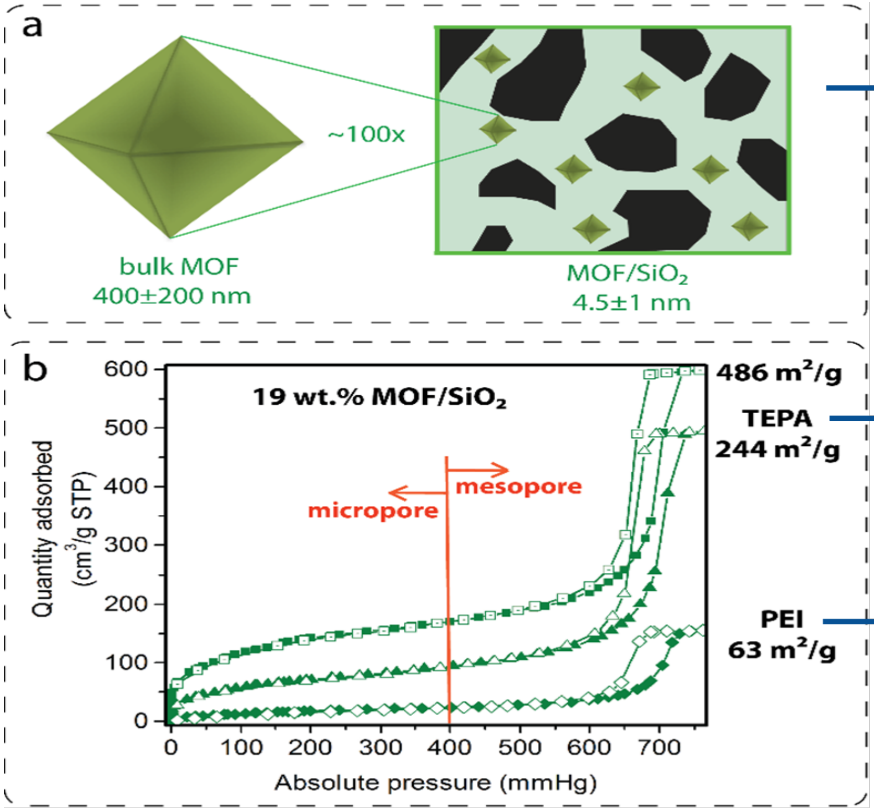


MOF/SiO_2	MOF (wt%)	S_{BET} (m^2/g)
SiO_2	0	256
(Cr)MIL-101/SiO_2	30.8	584
(Cr)MIL-101(SO_3H)/SiO_2	19.1	486
(Cr)MIL-100/SiO_2	35.0	647
(Al)MIL-100/SiO_2	20.4	364
(Cr)MIL-53/SiO_2	22.7	377
(Al)MIL-56(NH_2)/SiO_2	28.7	417
(Co)MOF-74/SiO_2	27.3	323
(Ni)MOF-74/SiO_2	27.7	386
(Zr)UiO-66/SiO_2	30.0	363
(Zr)UiO-66(NH_2)/SiO_2	37.6	434
(Zr)UiO-67/SiO_2	22.6	366
(Zn)ZIF-8/SiO_2	22.6	345
(Ru)HKUST-1/SiO_2	11.0	258
(Zr)PCN-222/SiO_2	9.8	348
(Zr)NU-1000/SiO_2	12.8	364
Co_2(DOBPDC)/SiO_2	13.4	344

Features of Novel MOF/SiO_2 Fluidized Hybrid Materials

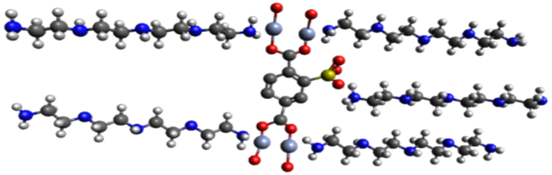
- **Exhibit high MOF loading (up to 40% so far)**
- **Smallest MOF nanocrystals yet reported (4.5 nm)**
- **Excellent MOF dispersion and homogeneity**
- **Tunable hierarchical micro (MOF)-meso (SiO_2) pore size distribution**
- **Elevated surface areas (up to 900 m^2/g)**
- **Higher density (0.65 g/cm^3)**
- **Enhanced attrition resistance (10%)**
- **Good fluidazibility**
- **Good handling (100-500 microns).**

Polyamine-Containing MOF/SiO$_2$ Fluidized Sorbents

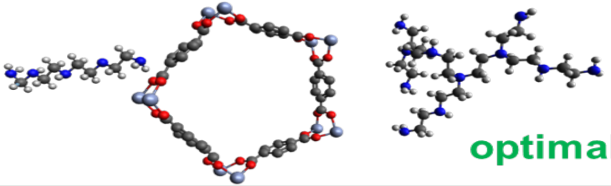


MOF/SiO$_2$
Hierarchical micro-/mesoporosity

TEPA anchored to MOF/SiO$_2$

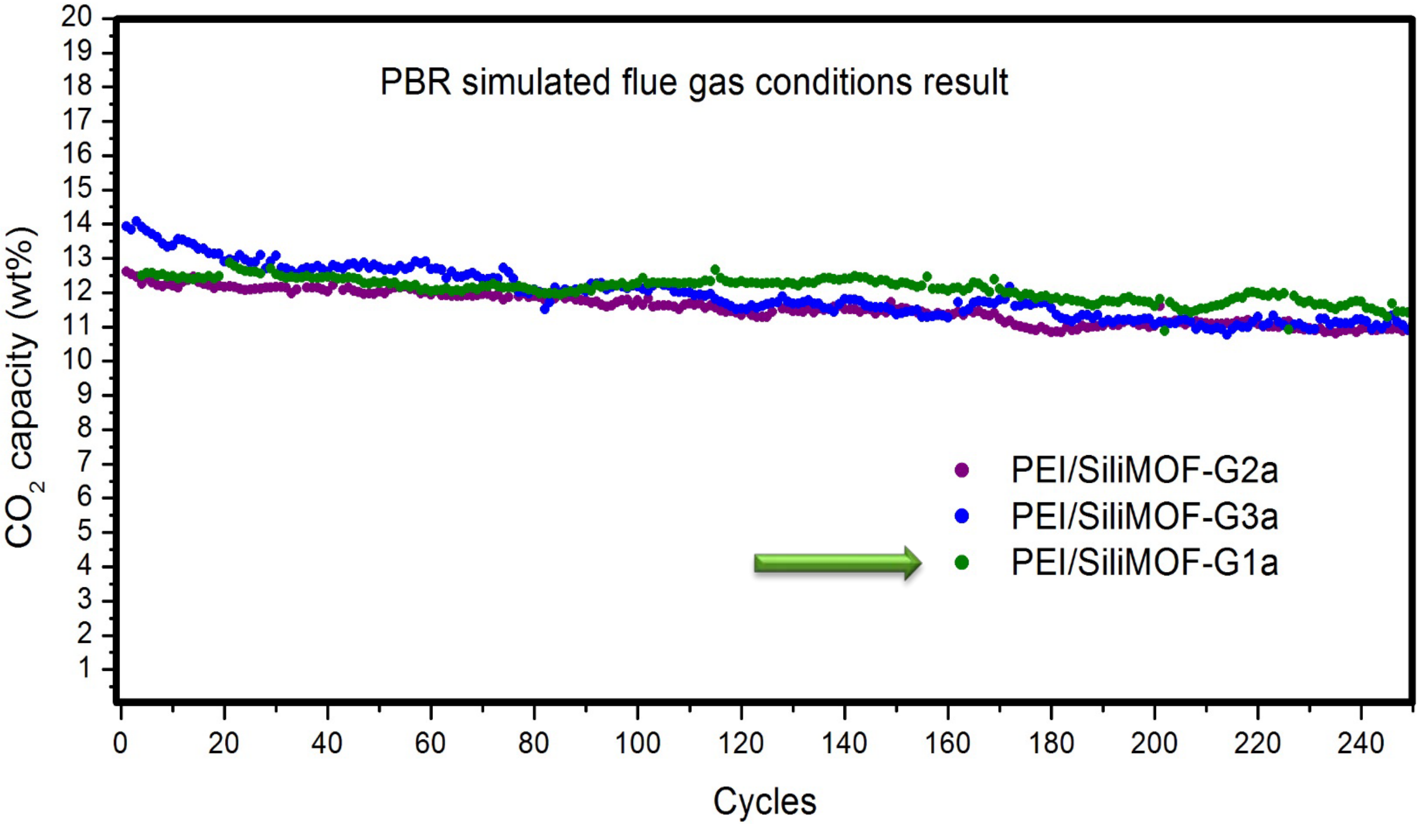


PEI confined on MOF/SiO$_2$



optimal

Multi-Cycles Testing for 3-selected Sorbents Candidates



MOF/SiO_2 hybrid CO_2 Solid Sorbents

***MOF/SiO_2* 3-selected candidates: PEI/$Zn(mIM)_2/SiO_2$, PEI/$Zn(bIM)_2/SiO_2$ and PEI/$Zn(iPrIM)_2/SiO_2$,**

Candidate	Packed bed reactor-CO_2 Capacity (wt%)		Chemical Makeup		Thermal Stability
	Capacity	Cycles	Pre Analysis	Post Analysis	
PEI/SiliMOFG1a	12.5%	250	N: 13.38% C: 22.36% H: 4.84%	N: 12.05% C: 20.57% H: 4.35%	up to 150 ^oC
PEI/SiliMOF-G2a	12.0%	250	N: 13.09% C: 22.24% H: 4.60%	N: 11.87% C: 20.26% H: 4.38%	up to 150 ^oC
PEI/SiliMOF-G3a	12.8%	250	N: 12.14% C: 20.45% H: 4.54%	N: 10.67% C: 18.56% H: 2.01%	up to 150 ^oC

Hybrid MOF-Based CO_2 Adsorbents

Mesoporous Silica

1st step: MOF crystallization within SiO_2 pores

MOF/SiO_2 Hybrid

2st step: amine impregnation on MOF/SiO_2

Amine/MOF/SiO_2 Sorbents

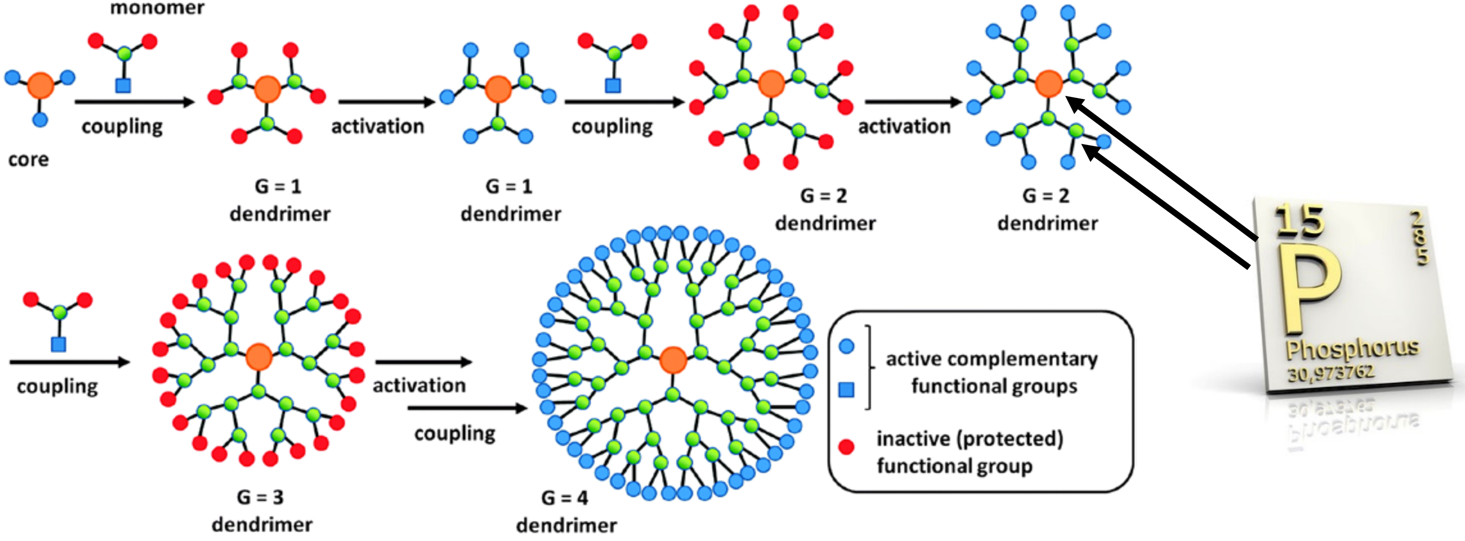
- We developed a very elegant, novel and environmentally friendly way of growing MOF inside the pores of silica that could be extended to other mesoporous supports.
- We have shown high CO_2 capacity ($\geq$ 12 wt.%) coupled with a good stability of these novel hybrid MOF-based CO_2 adsorbents
- We are in the process of scaling up and further testing these hybrid MOF-based CO_2 adsorbents

More than 150 sorbents were tested in packed-bed reactor

Hybrid *P*-Dendrimer-based CO_2 Adsorbents

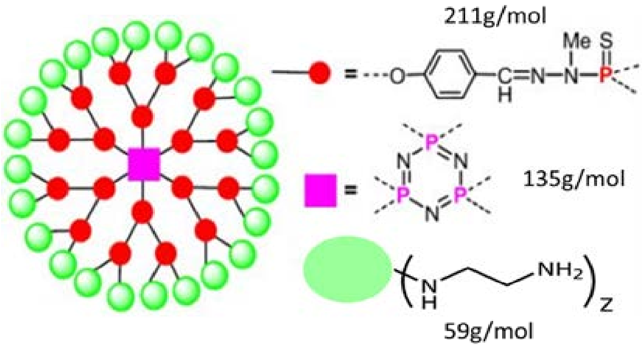
Phosphorous Dendrimer Background

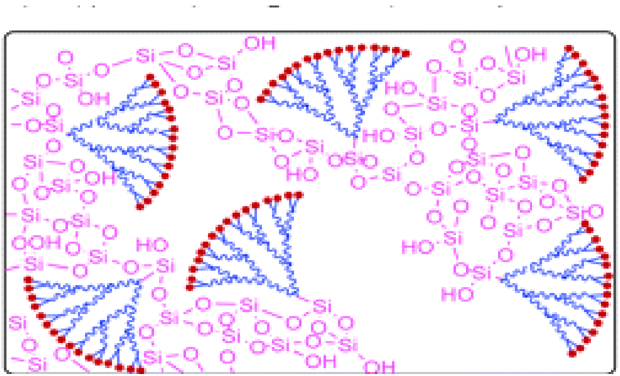
- A **dendrimer** is a symmetrical compound that is built through step-wise symmetrical additions of monomeric units
  - Belongs to the polymer-class of molecules



RTI’s Initial Approach

- ❖ Use a P-dendrimer core to add step-wise ethylenediamine units to build small or large molecules to reach high CO_2 capacity
- ❖ Link amine-functionalized dendrimers to silica for added stability and fluidizability

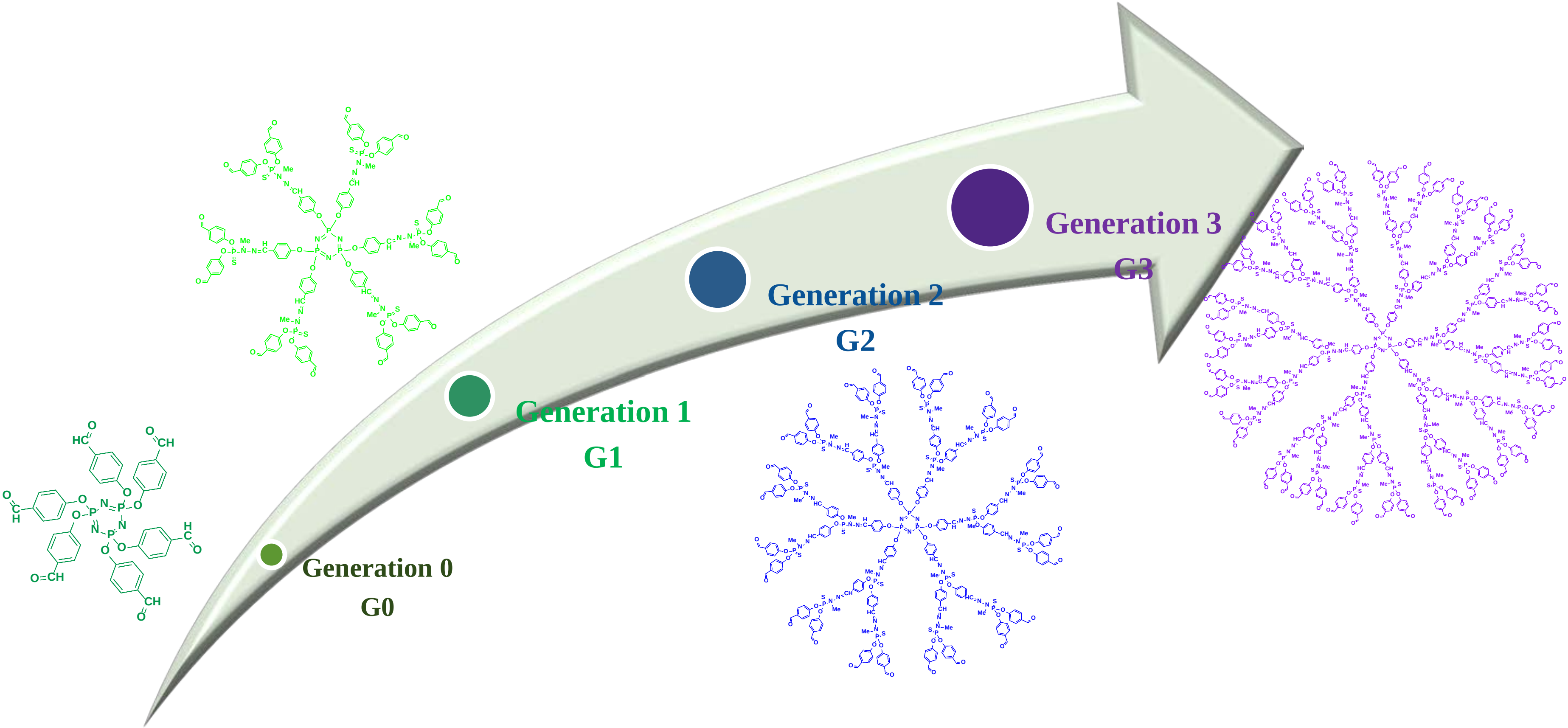




P-Dendrimers	Number of Amines End Groups	Theoretical CO_2 Loading
G1	24	**50 *wt% CO_2***
G2	48	**40 *wt% CO_2***
G3	96	-

***P*-Dendrimers have high theoretical CO_2 Loading**

P-Dendrimers Different Generations structures



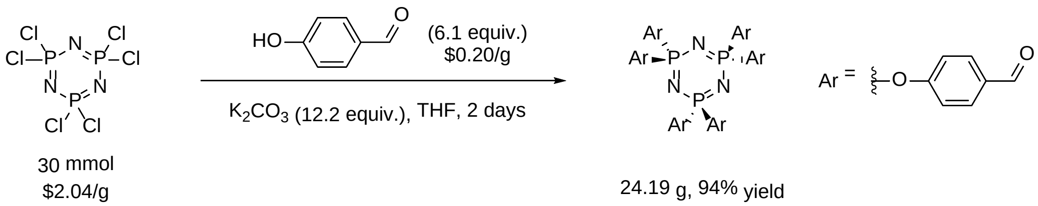
Generation 0
G0

Generation 1
G1

Generation 2
G2

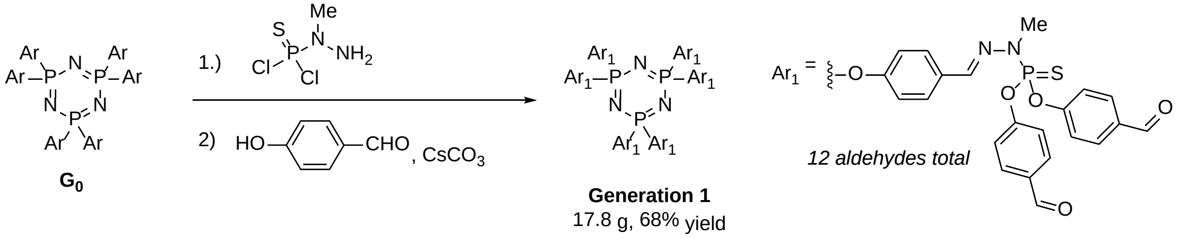
Generation 3
G3

Phosphorous Dendrimer Generations Synthesis



30 mmol
$2.04/g

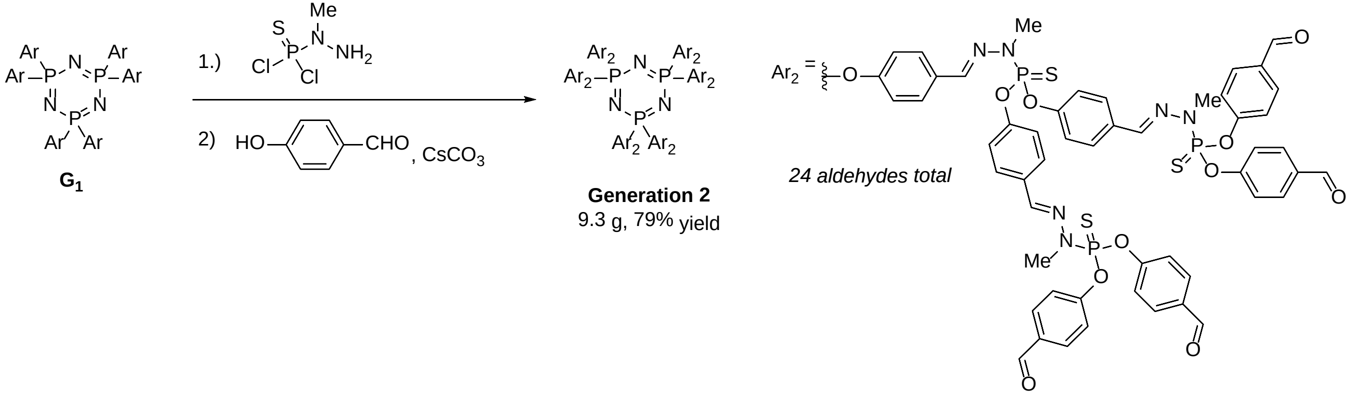
24.19 g, 94% yield



G_0

Generation 1
17.8 g, 68% yield

12 aldehydes total

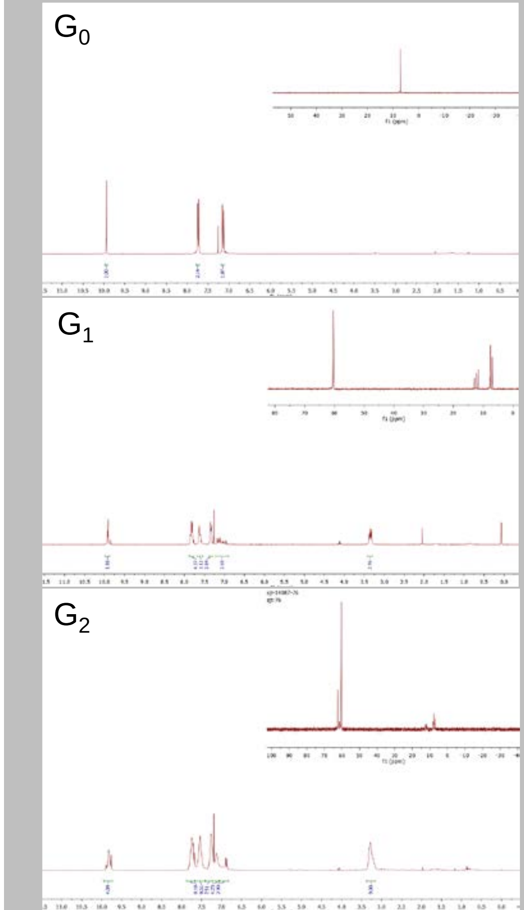


G_1

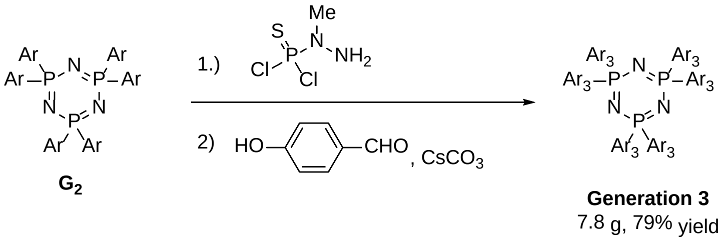
Generation 2
9.3 g, 79% yield

24 aldehydes total

^1H & ^{31}**P** Characterization

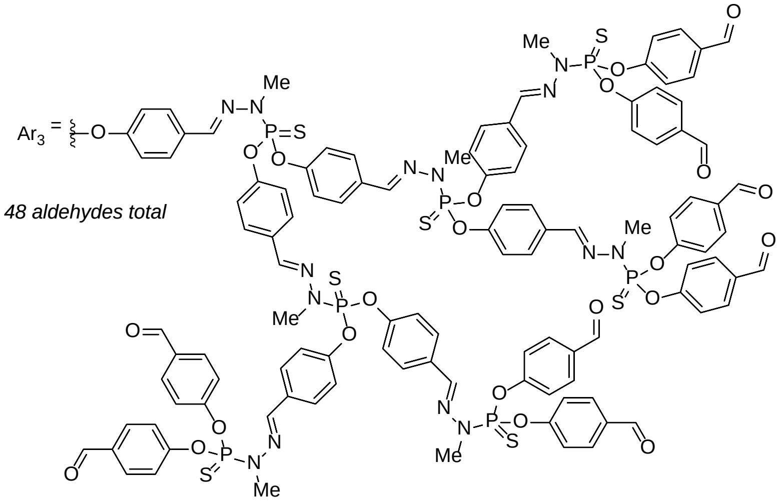


Phosphorous Dendrimer Generations Synthesis

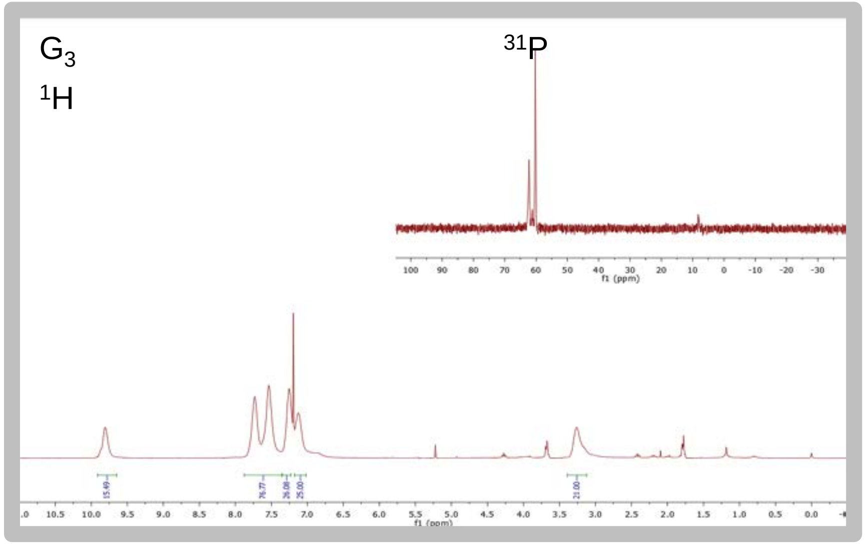


G_2

Generation 3
7.8 g, 79% yield



48 aldehydes total



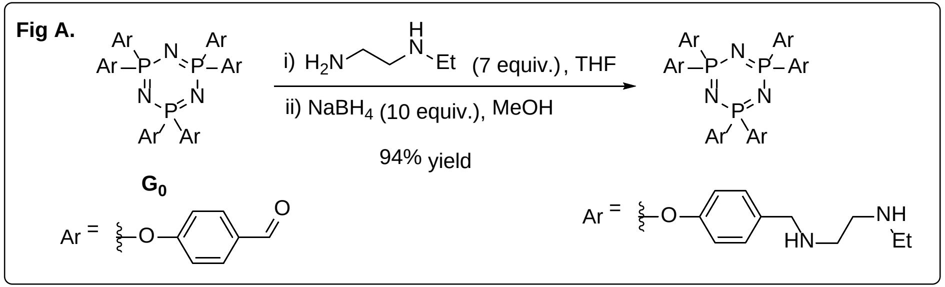
❑ Summary of Generation Growth Strategy

- ➢ 1 Step to synthesize Generation 0
- ➢ 2 Steps required for each additional generation
- ➢ No chromatographic separations required
- ➢ Easily scalable

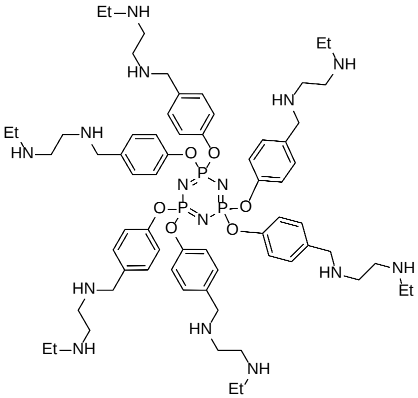
Phosphorous Dendrimer Hybrid Sorbents: *Amine Installation*

- Amines were conveniently installed on the dendrimer scaffold via a reductive amination process.

Fig A.



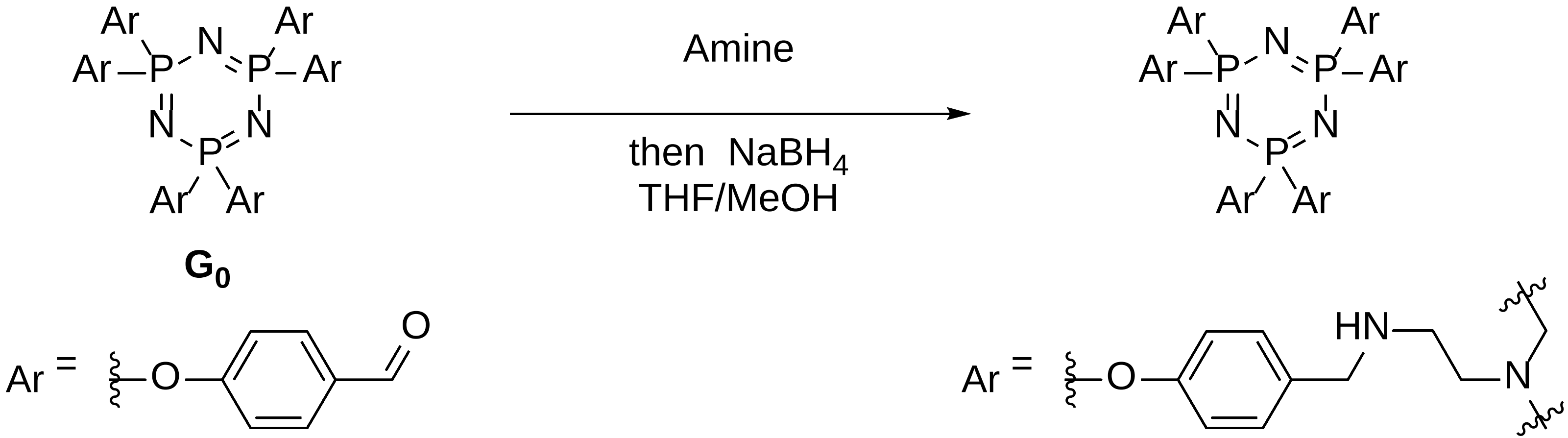
E.g. **N-ethyl Ethylenediamine**



- > 30 amine-functionalized dendrimers were synthesized, however all compounds were inactive towards CO_2 capture

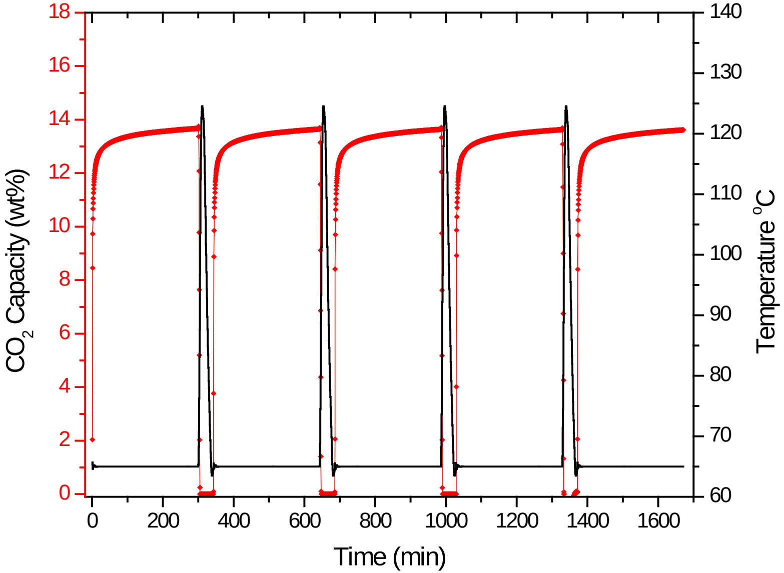
- Through experimental and modeling efforts, it was determined that significant ***intermolecular interactions*** were inhibiting CO_2 binding.

Phosphorous Dendrimer Hybrid Sorbents



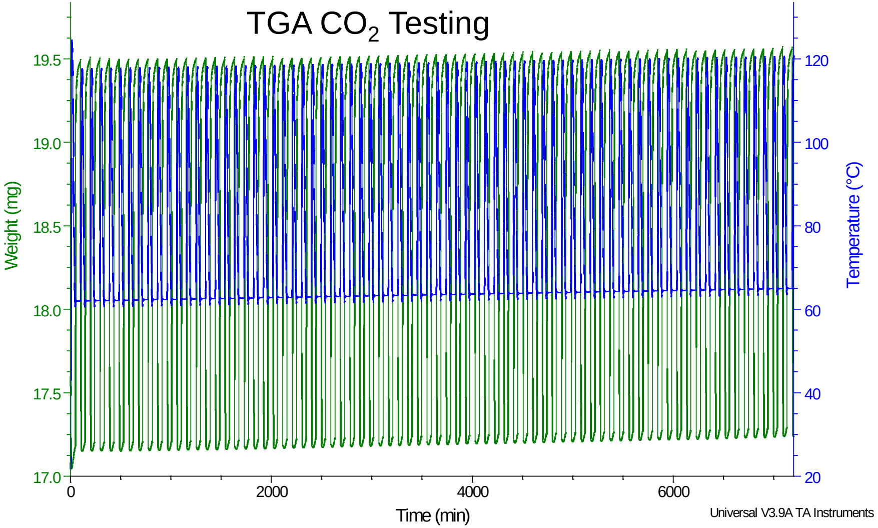
G$_0$

Thermogravimetric Analysis CO_2 Testing

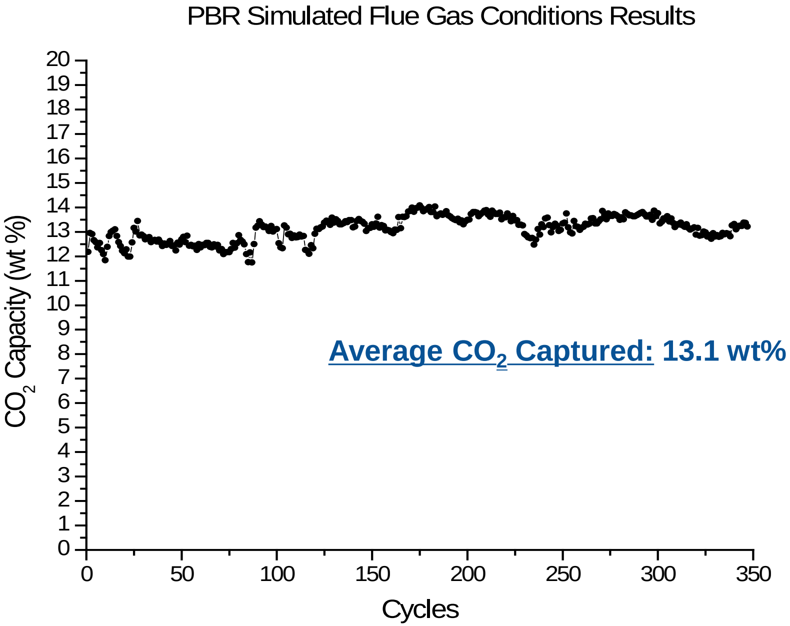


- ***Fast Kinetics:*** 75% wt% CO_2 captured in first 5 min.
- No degradation or loss of CO_2 observed over 5 cycles
- **Average CO_2 Captured: 13.6 wt%**

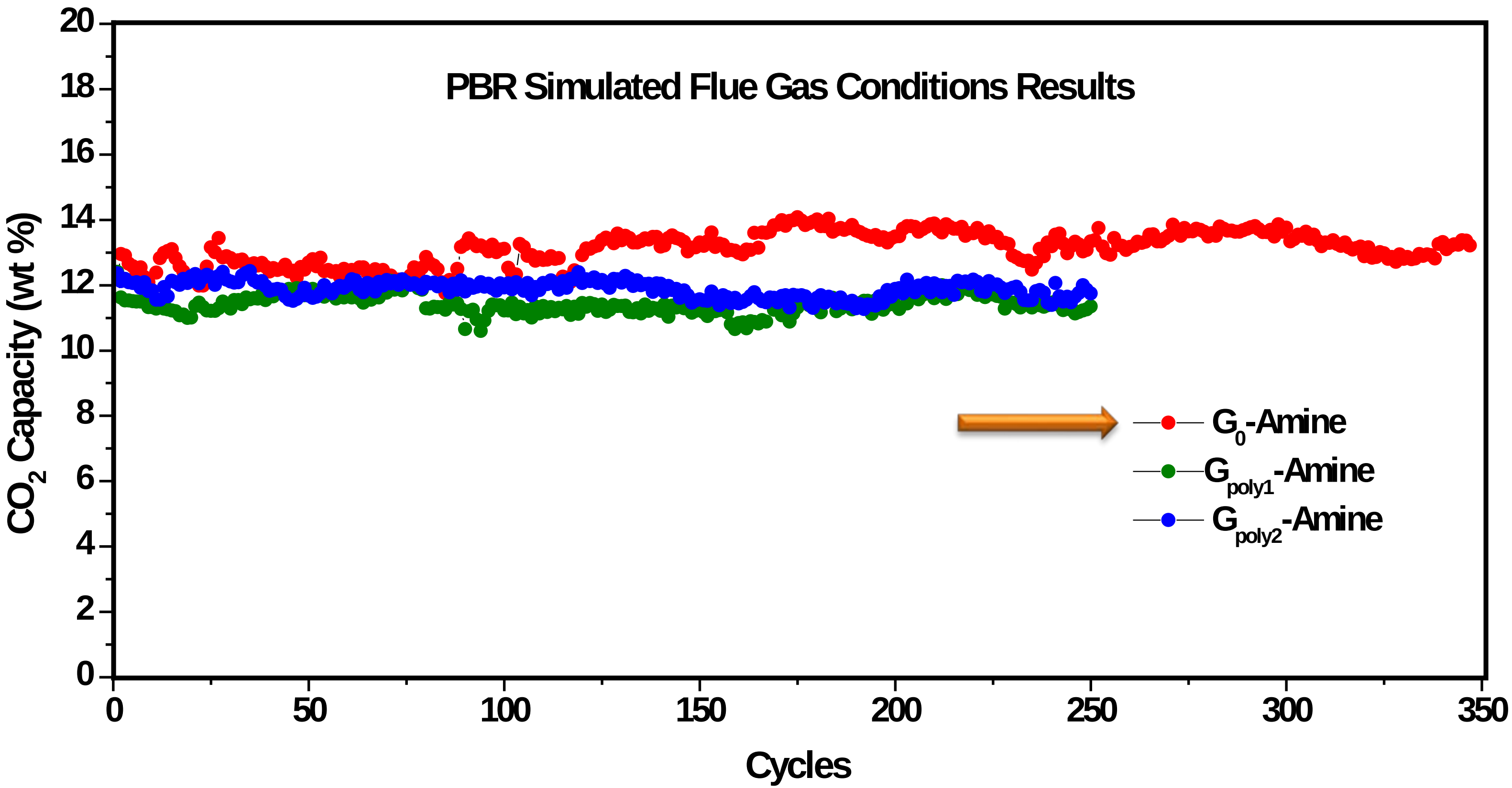
Phosphorous Dendrimer Hybrid Sorbents: Candidate 1



- 75 Cycles of Adsorption/Regeneration
- No degradation or loss of CO_2 observed over entire experiment
- **Average CO_2 Captured: 13.1 wt%**



- 350 Cycles of Adsorption/Regeneration
- 700 Continuous Hours Running
- No degradation or loss of CO_2 observed over entire experiment


PBR Simulated Flue Gas Conditions Results
CO_2 Capacity (wt %)
0
2
4
6
8
10
12
14
16
18
20
Cycles
0
50
100
150
200
250
300
350
G_0-Amine
G_{poly1}-Amine
G_{poly2}-Amine

P-Dendrimer Derived CO_2 Solid Sorbents

_P_-Dendrimer 3-selected candidates: G0-Amine, Gpoly1-Amine and Gpoly2-Amine

Candidate	TGA-CO_2 Capacity (wt%)*		Flue Gas CO_2 Capacity (wt%)*		Chemical Makeup	
	Capacity	Cycles	Capacity	Cycles	Pre Analysis	Post Analysis
G_0-Amine	13.1%	75	13.1%	350	N: 20.0% C: 57.9% H: 8.1%	N: 19.8% C: 58.0% H: 7.8%
G_{poly1}-Amine	10.6%	45	11.4%	250	N: 18.6% C: 53.0% H: 8.0%	N: 18.1% C: 48.6% H: 7.8%
G_{poly2}-Amine	11.2%	25	11.9%	250	N: 12.1% C: 40.7% H: 8.7% S: 0.7%	N: 13.1 % C: 39.3% H: 8.0% S: 0.7%

*Adsorption at 65 ^oC. Regeneration at 120 ^oC.

Sorbent Production Cost Evaluation

Approach: Database created containing multi-scale costs for various price factors that influence sorbent production costs.

Goal is to explore cost factors at four scales: 1) lab-scale (g), 2) bench-scale (kg), 3) pilot scale (ton), and 4) commercial (100+ ton)

Preliminary Results

Sorbent Candidate	CO$_2$ Capacity (wt%)	Lab-scale Cost ($/kg)	Bench-scale Cost ($/kg)	Commercial-scale Cost ($/kg)
PEI/SiliMOFG1a	12.5%	483	194	~ 32
PEI/SiliMOF-G2a	12.0%	505	150	~ 33
PEI/SiliMOF-G3a	12.8%	485	121	~ 27
G_0-Amine	13.1%	870	480	~ 177
G_{poly1}-Amine	11.4%	1052	610	~ 238
G_{poly2}-Amine	11.9%	1,253	748	~ 284

Preliminary Results

- Lab-scale production costs are dominated by labor costs – thus *P*-Dendrimers, with extra steps and time, incur greater lab-scale costs
- MOF candidates costs do not differ widely as production steps are similar with only one step differing based on raw materials used
- At large enough scale, for established manufacturing procedures, production costs are driven down to raw material costs

Sorbent Production Cost Evaluation

Further Refinements to Cost Evaluator

- Additional large-scale quotes are needed for some raw materials used in sorbent production procedures
- Equipment factors are largely tied to burdened labor costs, additional work in developing production-scale process flow diagrams and P&IDs may be needed
- Additional cost factors may need to be addressed in detailed techno-economic analysis of sorbent and process:
  - Competitive demand impacts
  - Safety factors
  - Sorbent stability factors
  - Capacity and yield factors
  - Regulatory factors
- Evaluate cost impact of utilizing continuous synthesis operation at commercial-scale rather than projecting the scale-up of large batch-synthesis operations
- Further engagement with commercial suppliers and commercial materials manufacturers

Commercial-scale Cost Reduction Strategies

- Solvent recycle at commercial-scale will be an absolute necessity to reduce production costs
  - Project team could explore lab-scale solvent recycling techniques
- “Commercial grade” (not analytical grade) chemicals will need to be used
  - Project team could explore lower quality substitutions for various chemicals and materials
- Higher reagent-to-solvent ratios will yield higher solvent usage and smaller equipment sizes at commercial scale
  - Project team could explore this by systematically lowering solvent quantities in lab-scale productions and investigate performance impact
- Improvements in product yield will naturally decrease production costs
- Optimization of production parameters (reaction times, temperatures, reaction gas environments, pressure, etc) is critical as it may yield reduced capital costs (e.g. less equipment tied-up) and operating costs (e.g. lower energy demands)

Project Structure – Budget Period 2

Budget Period 2

Objective: **Lab-scale evaluation of the hybrid solid sorbents for CO_2 Capture.**

Timeframe: **04/1/17 to 03/31/18 (12 months)** *Cost*: **$ 884,999 total**

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.

Acknowledgments

- Financial support provided by DOE NETL under DE-FE0026432

- DOE Project Manager: Steve Mascaro

- State of North Carolina for Cost Share

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