Lab-Scale Development of a Solid Sorbent for CO₂ Capture Process for Coal-Fired Power Plants

DE-FE0026432

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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 3$^{rd}$ 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$_2$O on these advanced solids sorbents.
- Conduct a high level techno-economic analysis.
Selection Criteria for CO₂ Solid Sorbents

Develop and design CO₂ 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 CO₂ capture (>90% CO₂ capture rate with 95% CO₂ purity and <30% increase in cost of electricity).

- Fluidizable material
- High CO₂ loadings, high selectivity
  - ≥ 12 wt% CO₂ 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

- 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

Table 2. Reported CO$_2$ Capture Performance Results

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>CO$_2$ Capacity (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF</td>
<td>21.4$^a$</td>
</tr>
<tr>
<td>MOF-amine</td>
<td>~20</td>
</tr>
<tr>
<td>Fluidizable silica (FS)</td>
<td>0</td>
</tr>
<tr>
<td>FS-PEI</td>
<td>4.8</td>
</tr>
<tr>
<td>MOF-silica</td>
<td>0</td>
</tr>
<tr>
<td>MOF-silica-amine</td>
<td>9.3</td>
</tr>
</tbody>
</table>

$^a$Final report award # DE-FC26-07NT43092
MOFs Selected for Evaluation as Hybrid MOF-Based CO₂ Adsorbents

- Air and water stability
- Chemical Stability
- High thermal stability
- High selectivity for CO₂ over other components in flue gas (N₂ and O₂)
- Commercially available linkers

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!

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 first goal of the MOF-Silica hybrid Synthesis

Full characterization using the most well known techniques such as: Confocal Microscope, SEM, FIB-FESEM, TEM, FTIR, XRD, XRF, N₂ isotherms, TGA, Particle size distribution, Jet-Cut attrition index
Confocal Microscope for the New MOF-Silica Hybrids

Transparent amorphous SiO₂

Ru-MOF-SiO₂

Cr-MOF-SiO₂
Transmission Electron Microscopy (TEM) & X-Ray Fluorescence (XRF)

Silica MOF-Silica

Up to 35% MOF on Silica based on X-Ray Fluorescence
Characterization of The New MOF-Silica Hybrid

FTIR data

X-Rays diffraction (XRD)
Characterization of The New MOF-Silica Hybrid

N₂ isotherms

- MOF-A3: 2276 m²/g
- 35% MOF-A3/SiO₂: 486 m²/g
- 20% MOF-A3/SiO₂: 865 m²/g
- SiO₂: 256 m²/g

38%
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

Attrition index (%) = 10.69 for MOF-A3/SiO$_2$
Attrition index (%) = 20.15 for the silica (SiO$_2$)

Average Particle size Distribution is 159 $\mu$m 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 (SiO₂) pore size distribution
- Elevated surface areas (up to 900 m²/g)
- Nanometric MOF particles (below 30 nm, enhanced diffusion by shortening the diffusion channels)
- Enhanced attrition resistance
- Good fluidizability
- Good handling (100-500 microns).
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.
Simulated flue gas composition:
$\text{CO}_2 = 15 \text{ vol\%}$, $\text{O}_2 = 4.5 \text{ vol\%}$, and $\text{water} = 5.65 \text{ vol\%}$ balanced with $\text{N}_2$
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.
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