Novel Silica Nanostructured Platforms with Engineered Surface Functionality and Spherical Morphology for Low-Cost High-Efficiency Carbon-Capture (FE-0023541)

Nicholas Pizzi, Dr. Cheng-Yu Lai, Dr. Daniela Radu

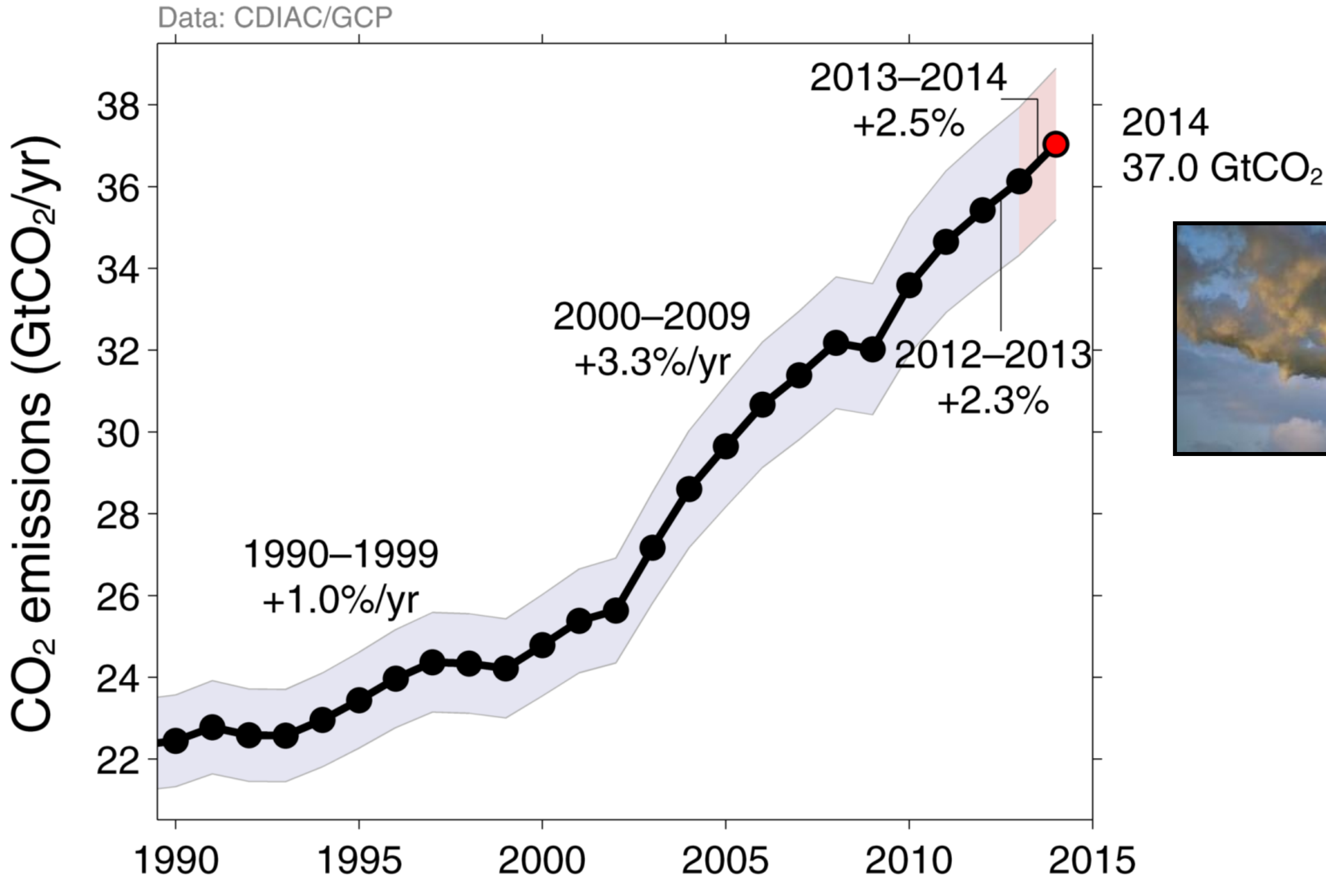
Delaware State University

Motivation for Study

- **Fossil Fuel and Cement Emissions**

Global fossil fuel and cement emissions: 36.1 ± 1.8 $GtCO_2$ in 2013, 61% over 1990

● Projection for 2014 : 37.0 ± 1.9 $GtCO_2$, 65% over 1990



Estimates for 2011, 2012, and 2013 are preliminary

Source: CDIAC; Le Quéré et al 2014; Global Carbon Budget 2014

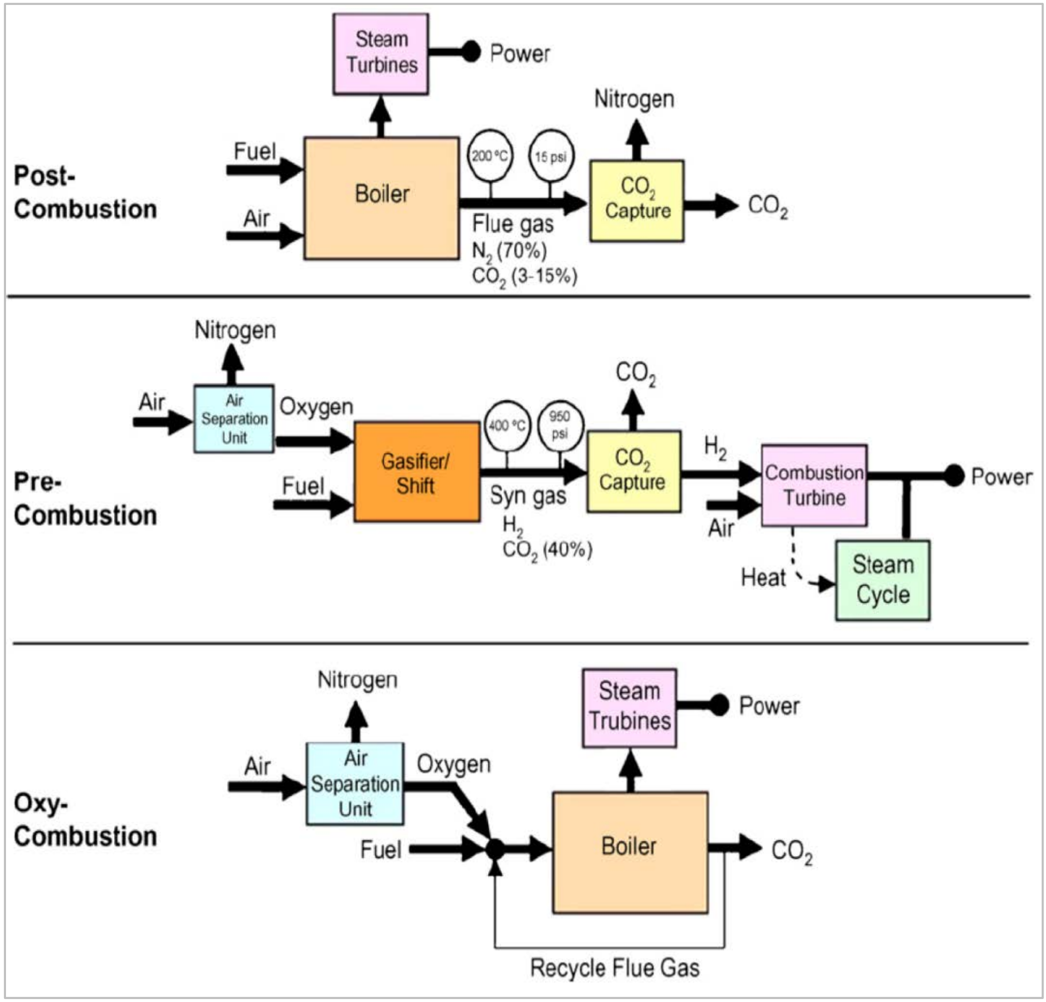
Technical background

Pathways to CO_2 Capture

1. Post-Combustion – CO_2 is separated from other flue gas constituents either originally present in the air or produced by combustion.

2. Pre-Combustion – carbon is removed from the fuel before combustion.

3. Oxy-Combustion – the fuel is burned in an oxygen stream that contains little or no nitrogen



Project Goal and Objectives

Goal

Identify, develop, and optimize engineered sorbent silica nanospheres, with high CO_2 capture capacity at low cost and with high recyclability, and a subsequent coated platform with enhanced nitrogen exclusion.

Objectives

1. Demonstrate a Functionalized stellate macroporous silica (Stellate MSN) platform as solid sorbent with spatial control of CO_2 capture amine functionality and high amine loading at least 7 mmol N/g sorbent, with hybrid sorption–adsorption/absorbtion capacity of at least 5 mmol CO_2 per gram of Stellate MSN sorbent;

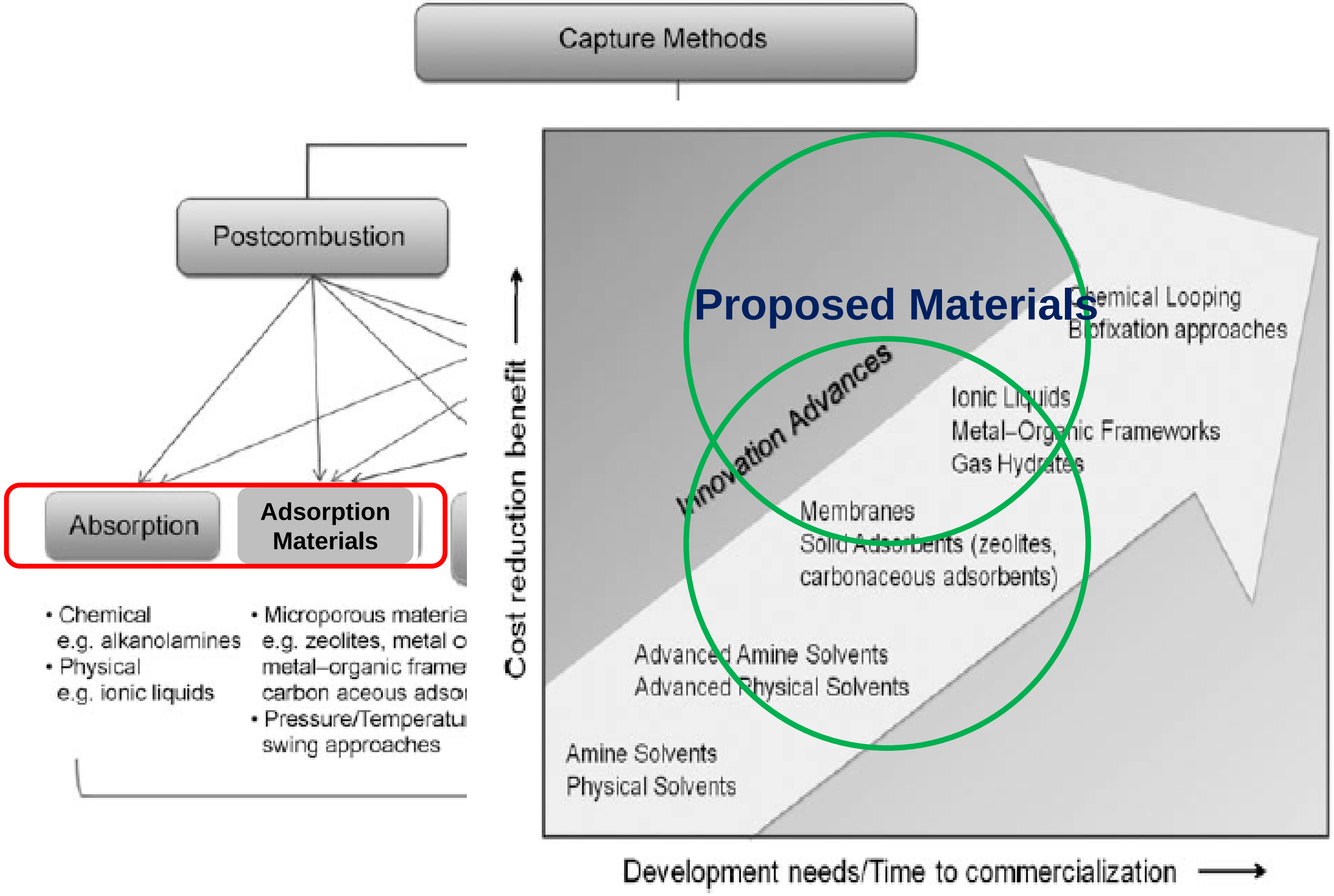
2. Perform parametric and long duration tests to demonstrate performance target of CO_2 capture at >90% of simulated flue gas with 15% CO_2;

3. Engineer a gatekeeping polymeric layer on Stellate MSN surface (PolyMSN), designed to increase CO_2 capture selectivity by excluding N2 from the capture process;

4. Perform parametric and long duration tests to demonstrate proof of concept of nitrogen exclusion in selective CO_2 capture in PolyMSN.

Technical background

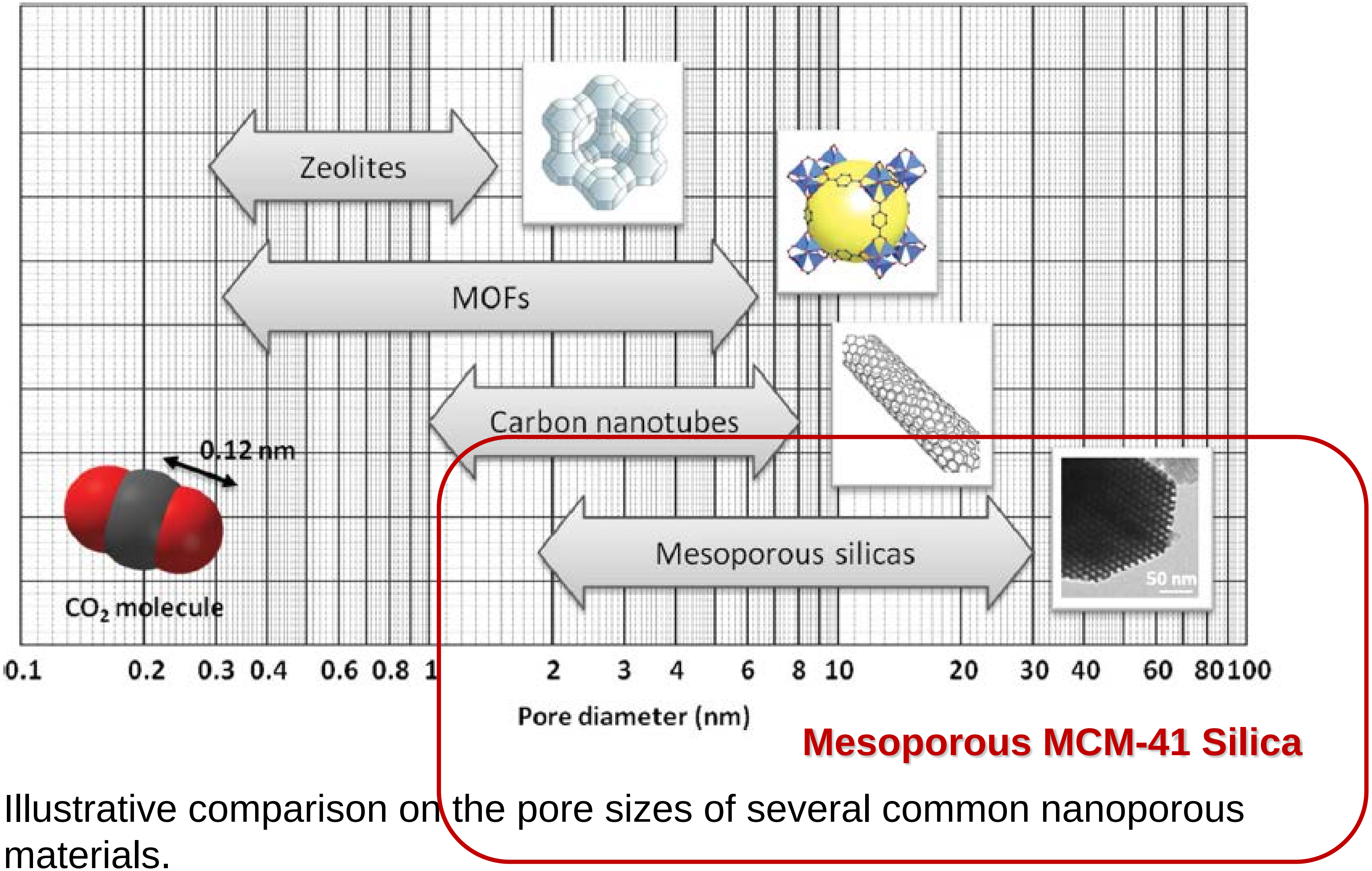
- Separation Technologies for CO_2 Capture



Materials for CO_2 capture in the context of postcombustion, precombustion, and oxyfuel processes.

Technical background

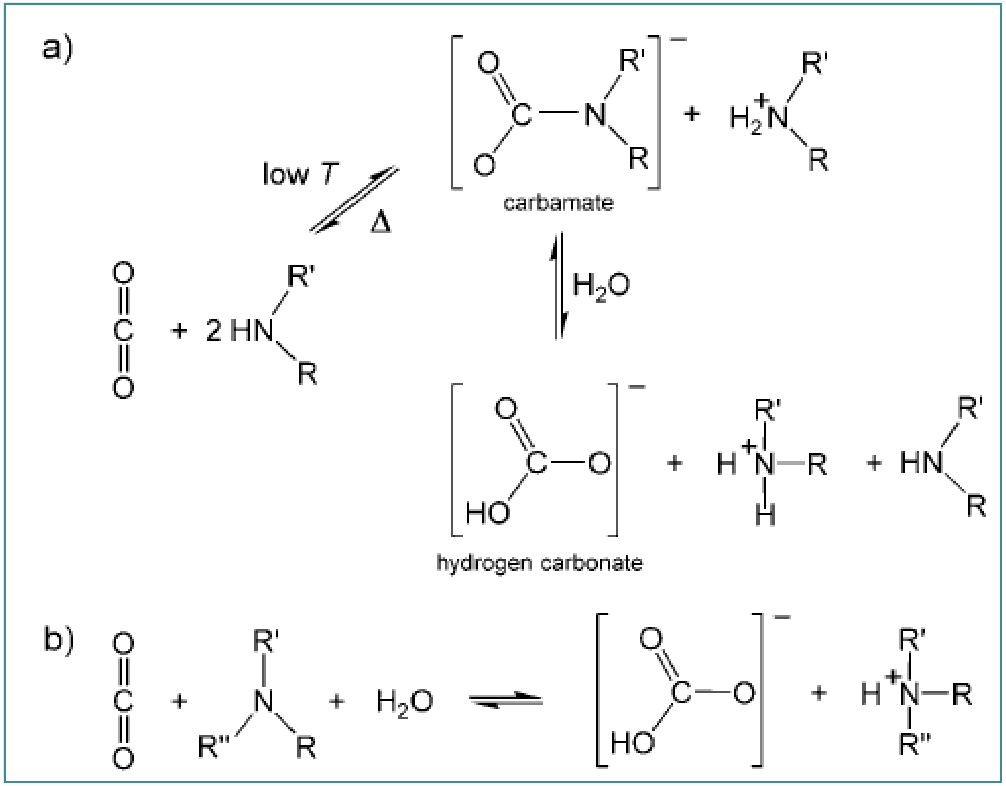
- Emerging Solid Sorbent Materials for CO_2 Capture



Illustrative comparison on the pore sizes of several common nanoporous materials.

Technical background

- Conventional Chemical Absorption for CO_2 Capture



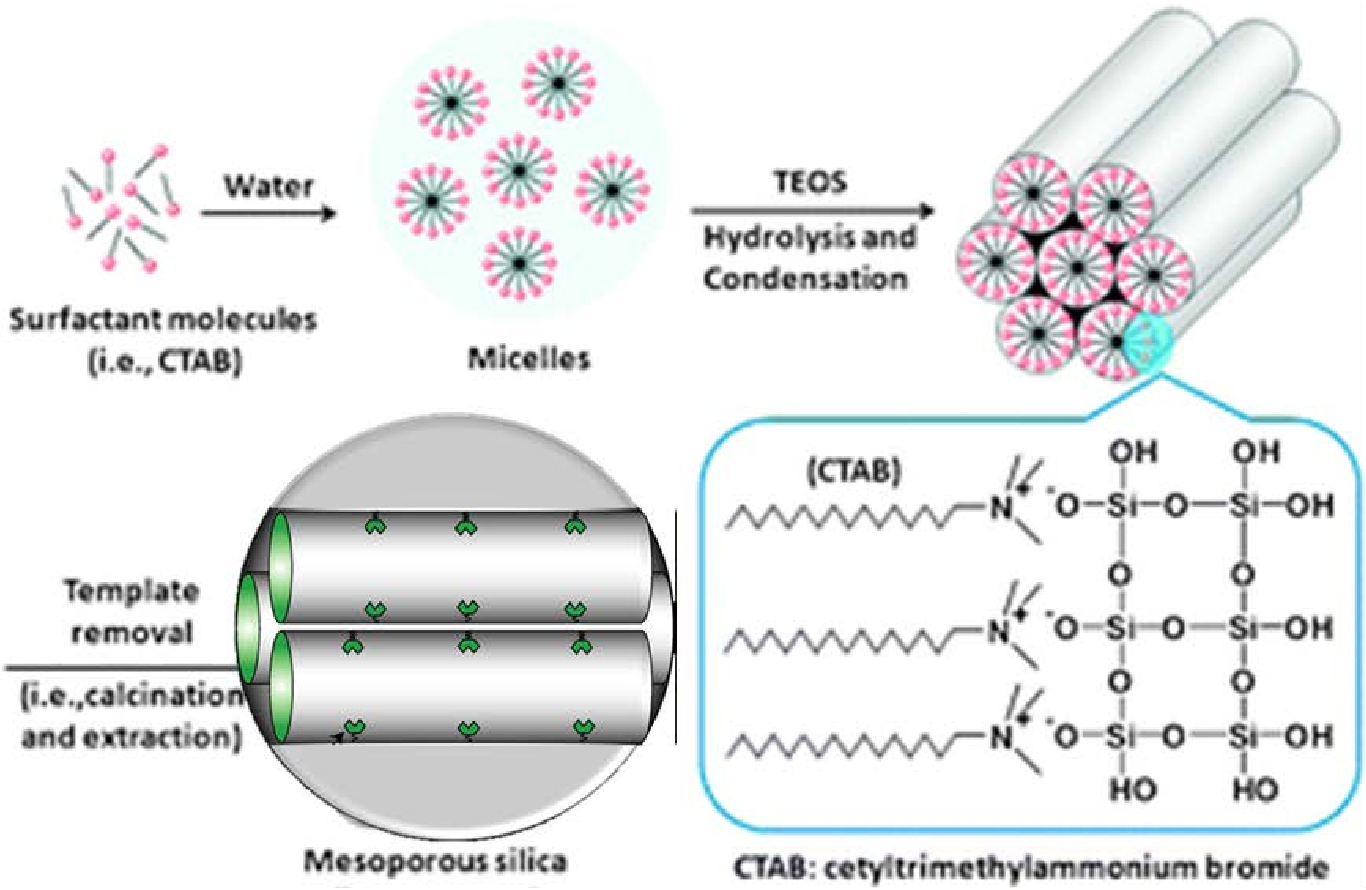
Scheme 1. General reactions for the chemical absorption of CO2 by a) primary or secondary and b) tertiary amine-containing solvents.

Complications associated with the use of *liquid amines*: **corrosion** on equipment, **oxidative degradation** of absorbents, flow problems caused by increasing viscosity relatively **high energy consumption** suggest that this method is far from ideal.

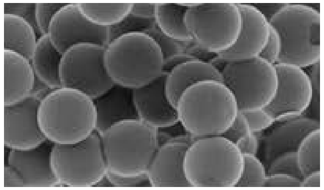
Need for Solid Sorbents

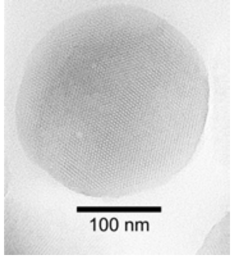
Functionalized Mesoporous Silica Nanospheres

- Multilayer Amino Silane for Enhancing CO_2 adsorption Capacity



SEM/TEM micrographs of functionalized MSN





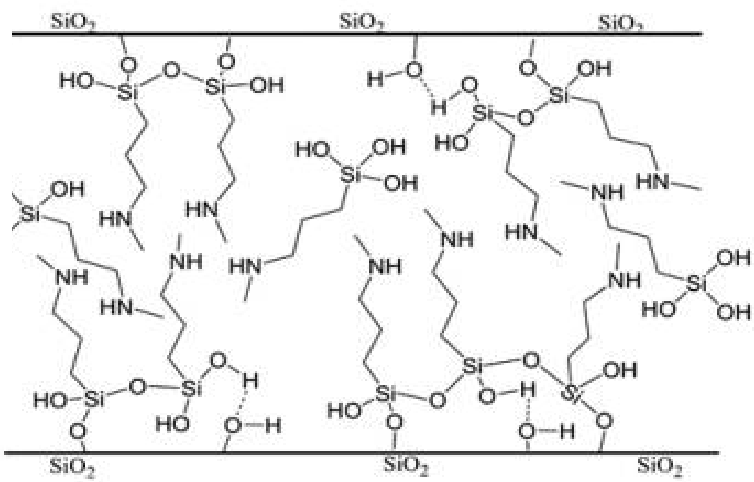
Pitfalls in Designing MCM-41 Type orbent for CO_2 Capture

- **Pitfalls for CO_2 capture:**

-Pore Blocking Hindering Amine Permeability

Typical MSN: cylindrical pores drive close-packing of amine groups and render inner amino groups inaccessible for CO_2 capture

Retard Adsorption Kinetics for CO_2 DIFFUSION



SOLUTION:

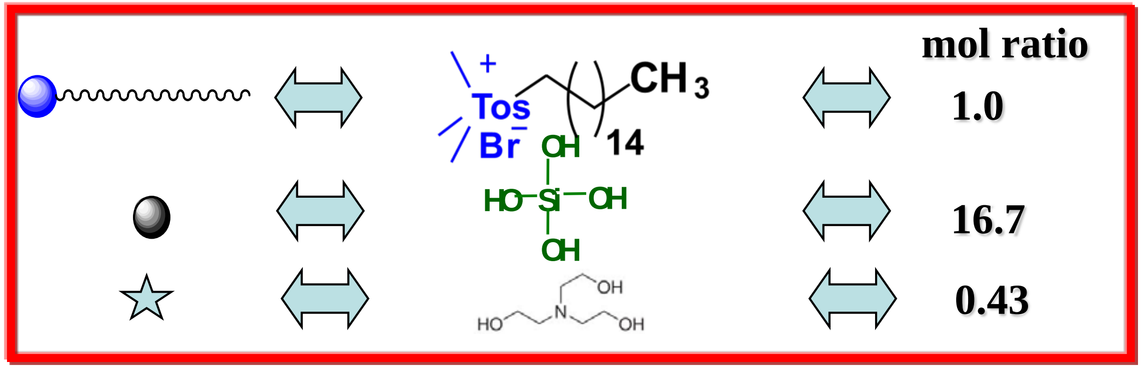
Large Pores–MSN (Hierarchical-pores MSN)

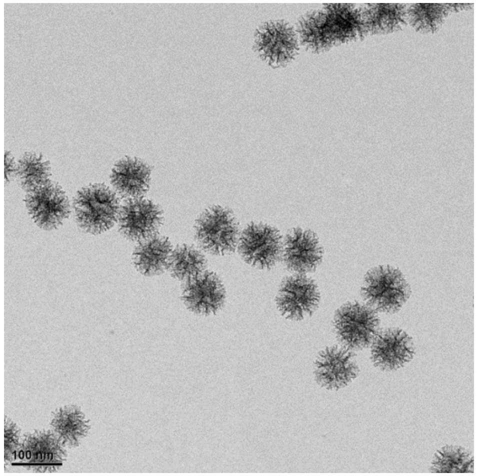
Scheme 2. 3-(Methylamino)-propyltrimethoxysilane (MAP) functionalizated MSN pore

Pedro López-Aranguren, Santiago Builes, Julio Fraile, Lourdes F. Vega, and Concepción Domingo *Ind. Eng. Chem. Res.*, 2014, 53 (40), pp 15611–15619

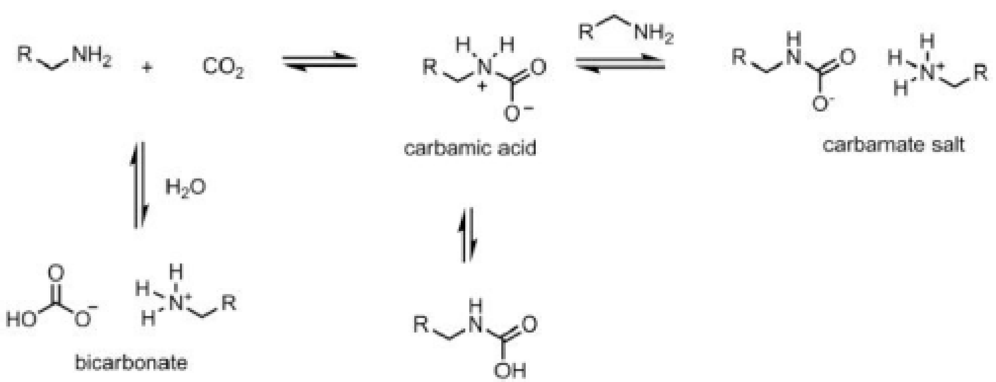
Xin Du, Bingyang Shi, Ji Liang, Jingxu Bi, Sheng Dai and Shi Zhang Qiao. *Advanced Materials, 2013, 25,* 5981–5985,

Our aproach –Hierarchical-Pores Stellate-Macroporous Nanospheres Silica Sorbent



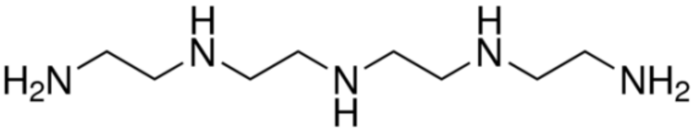


TEM of NSN Nanospheres



Scheme 1. Reaction between primary amines and CO_2

Tetraethylenepentamine-TEPA loaded by wet impregnation



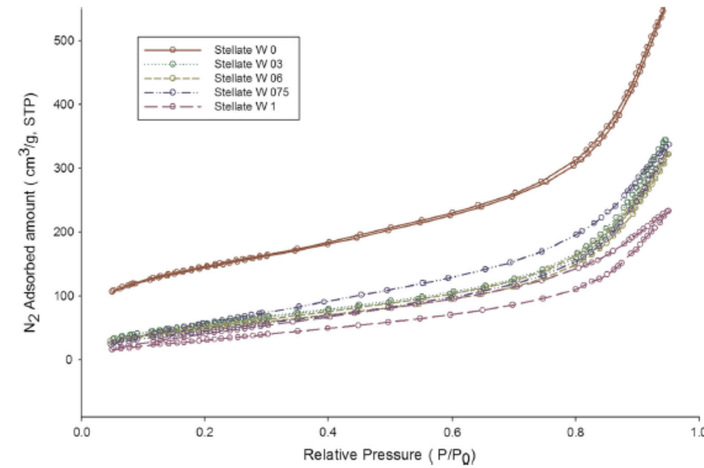
Radu, D.R., Pizzi, N.A. & Lai, CY. *J Mater Sci* (**2016**) 51: 10632.

TEPA – Stellate MSN Sorbent for Carbon Capture

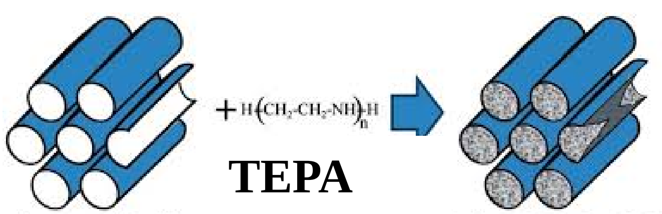
Nanocomposite Sorbents for CO_2 capture materials prepared by **wet impregnation**

Table 1. Amount of TEPA used in the impregnation experiments

Material ID	Stellate MSN (g)	TEPA (g)
W0	0.5	0
W03	0.5	0.15
W06	0.5	0.3
W075	0.5	0.38
W1	0.5	0.5



Material ID	BET surface area (m^2/g)
W0	508.6
W03	220.4
W06	195.4
W075	193.5
W1	139.3



MSN

MSN sorbent

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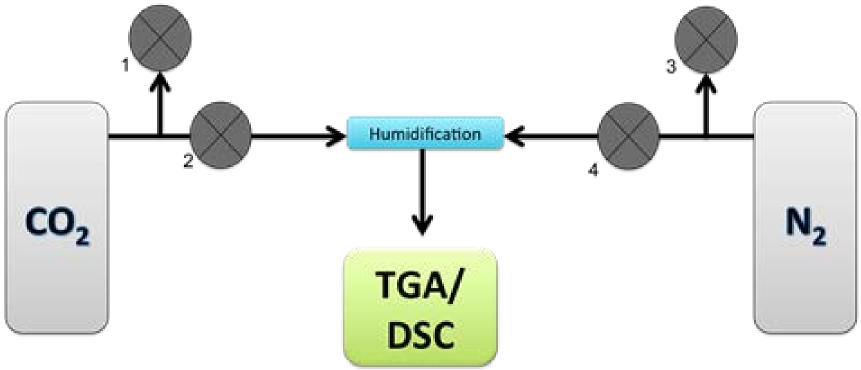
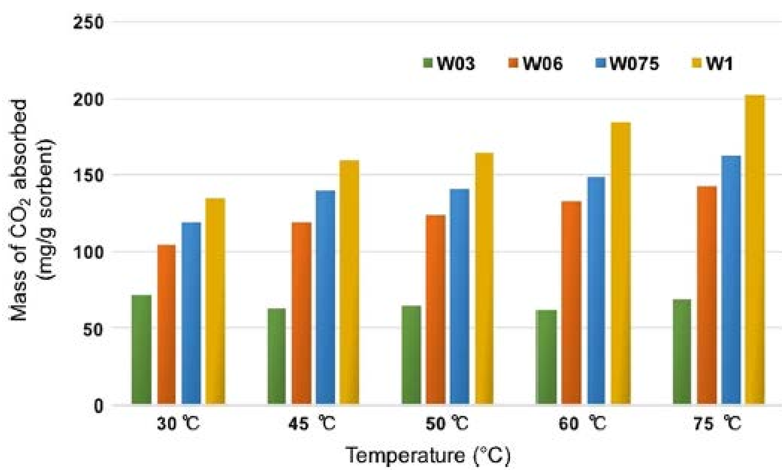
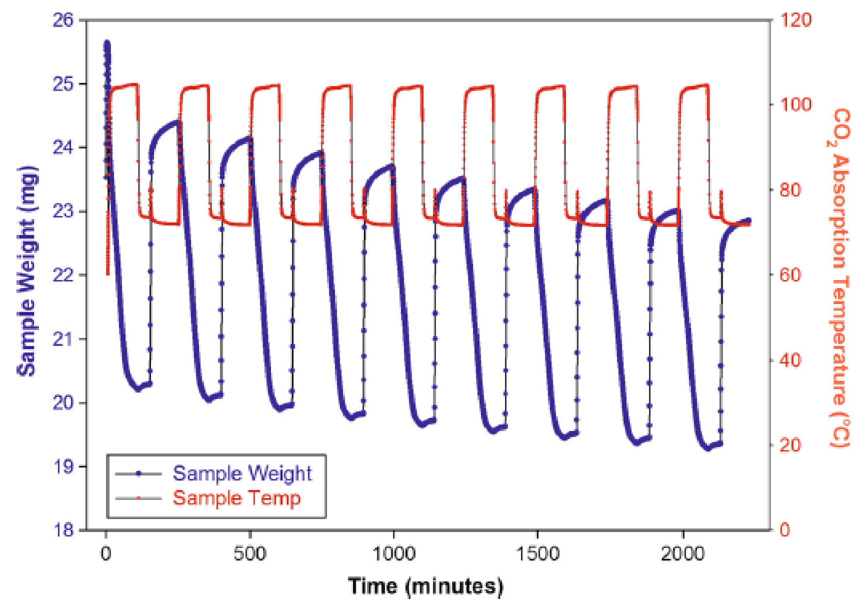
CO_2 Adsorption Analysis for TEPA-Stellate MSN Sorbent



Scheme . TGA setting for CO_2 capture experiments

- High temp Stability
- CO_2 –adsorption capacity of ~ 4.7mmol CO_2 per gram of stellate MSN sorbent
- High amine loading 6.4 mmol N/g sorbent





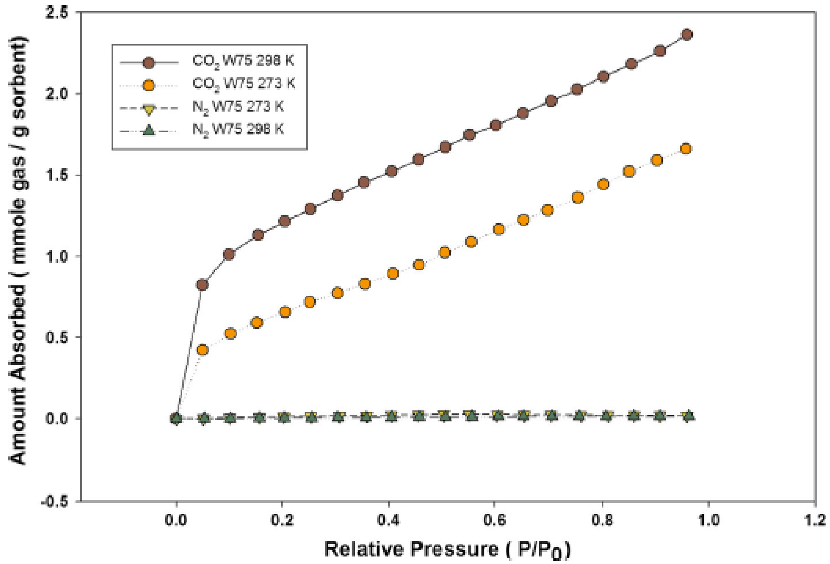
Radu, D.R., Pizzi, N.A. & Lai, CY. *J Mater Sci* (**2016**) 51: 10632.

Project Status

SOPO ID Number	Item Description	Performer	Start Date	End Date
TASK 2.0	Preparation and characterization of NSN-solid sorbents	LAI	**06/01/14**	**02/28/15**
Subtask 2.1	Silica Sorbents Preparation – Synthesis of NSN	LAI	06/01/14	02/28/15
Subtask 2.2	*Silica Sorbents Characterization*	LAI	06/01/14	02/28/15
TASK 3.0	NSN CO_2 capture experiments	RADU	**03/01/15**	**06/31/15**
Subtask 3.1	Determine absorption capacity of NSN via thermogravimetric analysis (TGA)	RADU	03/01/15	06/31/15
Subtask 3.2	Determine the heat of absorption of NSN materials by Differential Scanning Calorimetry (DSC).	RADU	06/01/15	09/30/16
Subtask 3.3	Sorbent Regeneration Experiments	RADU	10/01/15	02/28/16
TASK 4.0	Gate-keeping layer fabrication on NSN surface	LAI	**10/01/15**	**02/28/16**
TASK 5.0	PolyNSN selective CO_2 capture experiments	RADU	**01/01/16**	**05/31/17**
Subtask 5.1	Determine absorption capacity of PolyNSN via thermogravimetric analysis (TGA)	RADU	01/01/16	05/31/17
Subtask 5.2	Sorbent Regeneration Experiments	RADU	01/01/16	05/31/17
TASK 6.0	Conduct long-term tests to determine the chemical and physical stability of the sorbents.	RADU	06/01/15	05/31/17
Final Deliverables	***Final Deliverable 1:*** Demonstrate a high performance NSN platform with at least 5 mmol CO2/g sorbent and high robustness and regeneration capacity (100%). ***Final Deliverable 2:*** Demonstrate a high performance PolyNSN platform with at least 5 mmol CO2/g sorbent, high robustness and regeneration capacity (100%) capability to exclude N2 .	LAI & RADU		**05/31/17**

Task 4 and 5

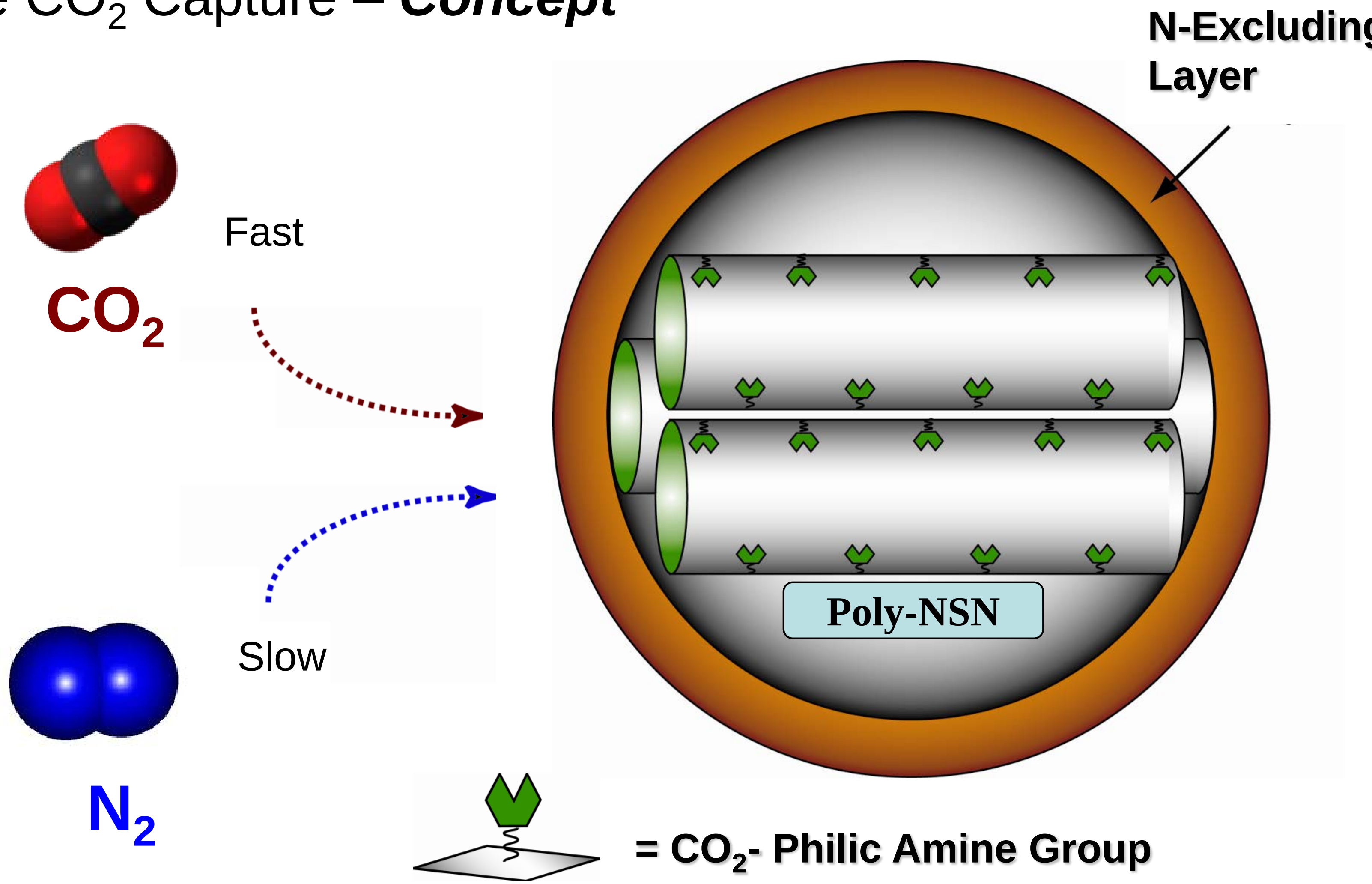
1. Functionalization of Gatekeeping Layer on Stellate-MSN for CO_2 selectivity Capture. (PDL-TEPA Stellate)
2. CO_2 adsorption Capacity of PDL-TEPA Stellate) via TGA
3. CO_2 and N_2 adsorption isotherms – Data collecting



CO_2 versus N_2 sorption selectivity via Nova 4200e

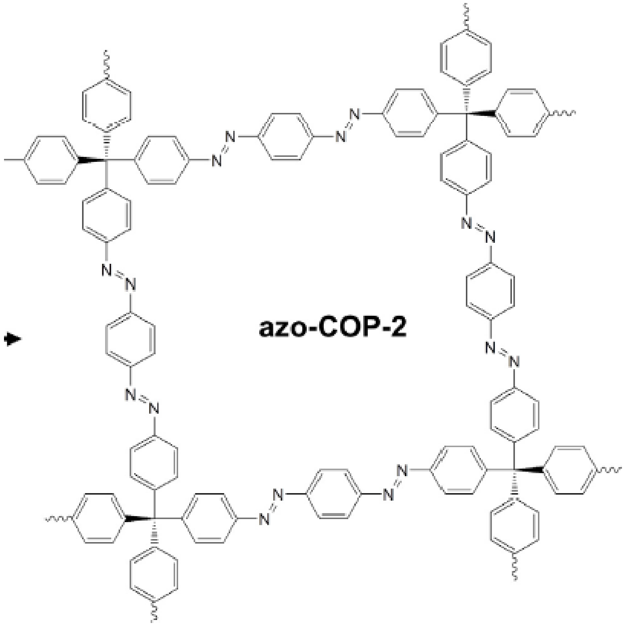
Our Approaches to Final Deliverable

- Incorporation of facile synthesized nitrogen scaffolds for Highly Selective CO_2 Capture – ***Concept***



Increasing CO_2 capture by introducing "Nitrogen-repellent" components

Prior approach[1]: **azo-bridged, nitrogen-rich, aromatic, water stable, nanoporous covalent organic polymer (Azo-COP)** nanoporous covalent organic polymers.
Disadvantage: Cumbersome organic synthesis.

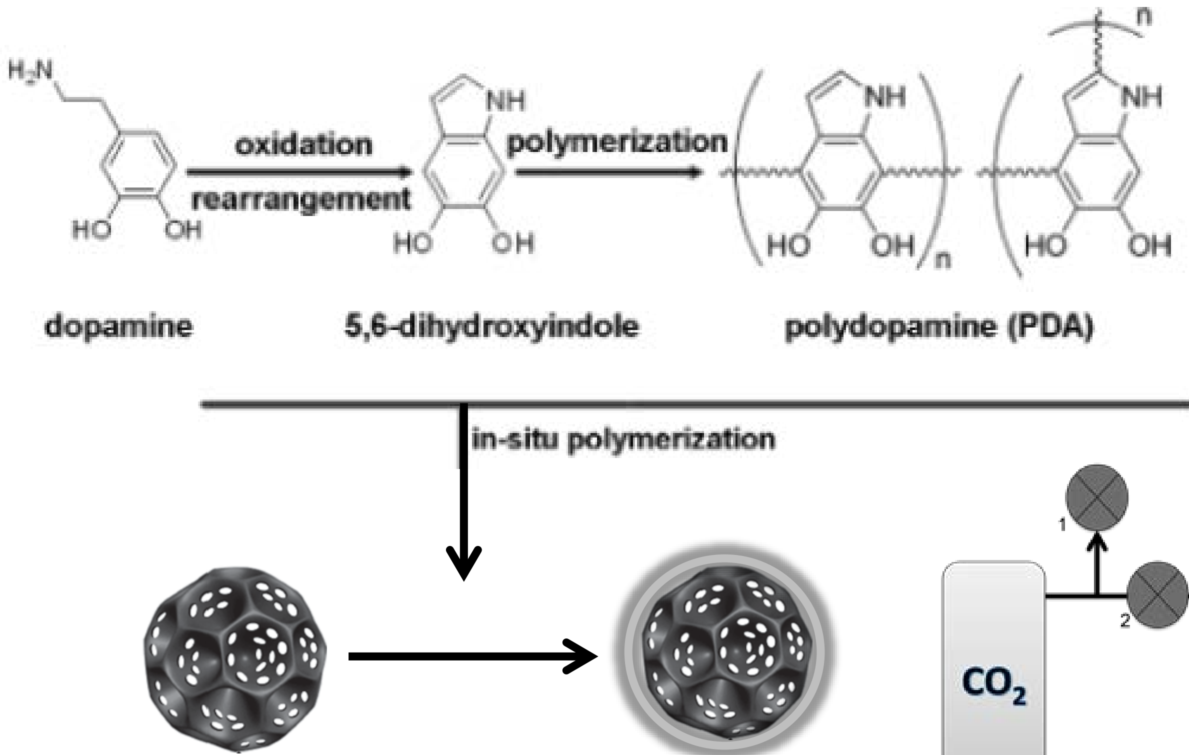


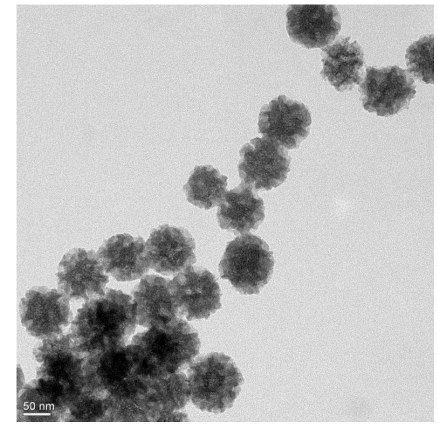
Incorporation of facile synthesized nitrogen scaffolds significantly increases CO_2 adsorption capacities for selective carbon capture.

1. Patel, H. A.; Hyun Je, S.; Park, J.; Chen, D. P.; Jung, Y.; Yavuz, C. T.; Coskun, A., Unprecedented high-temperature CO_2 selectivity in N_2-phobic nanoporous covalent organic polymers. *Nat Commun* **2013,** *4*, 1357.

Stephan Hug, *Linus Stegbauer*, *Hyunchul Oh*, *Michael Hirscher*, and *Bettina V. Lotsch* *Chem. Mater.*, **2015**, *27* (23), pp 8001–8010

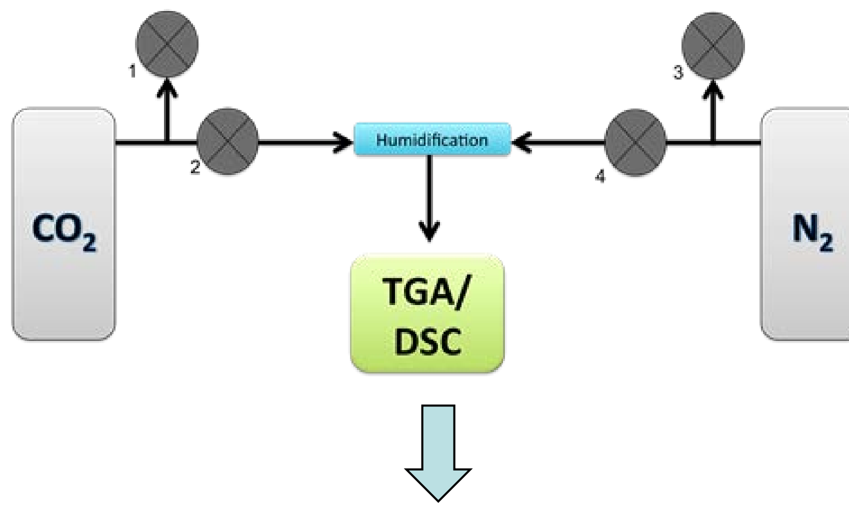
Nitrogen-rich, aromatic, water stable, nanoporous covalent organic polymer for Selective Carbon Capture





TEPA- Stellate

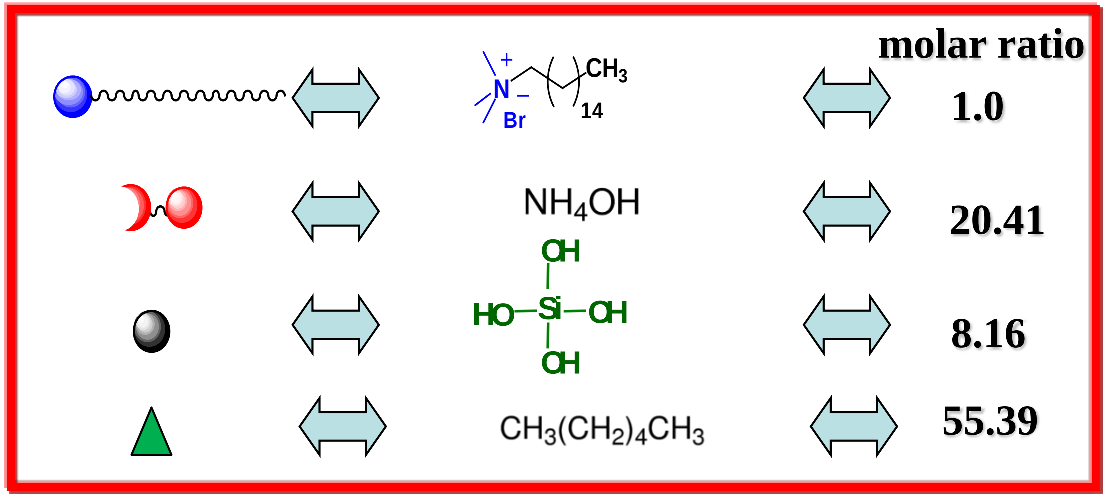
TEPA- Stellate @PDL

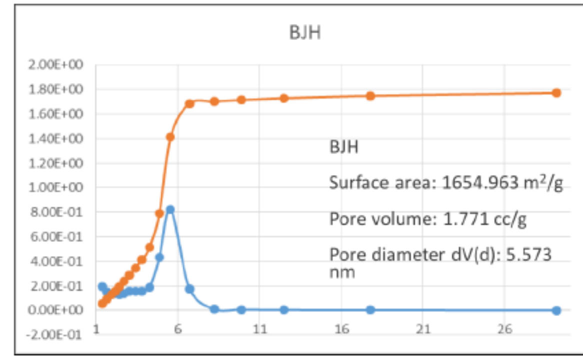


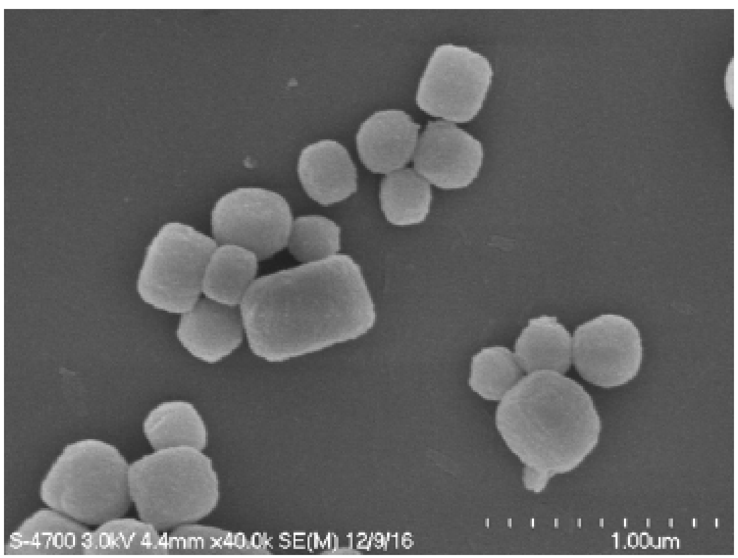
CO_2 absorption in TEPA-stellate MSN@PDL less than TEPA-stellate MSN alone

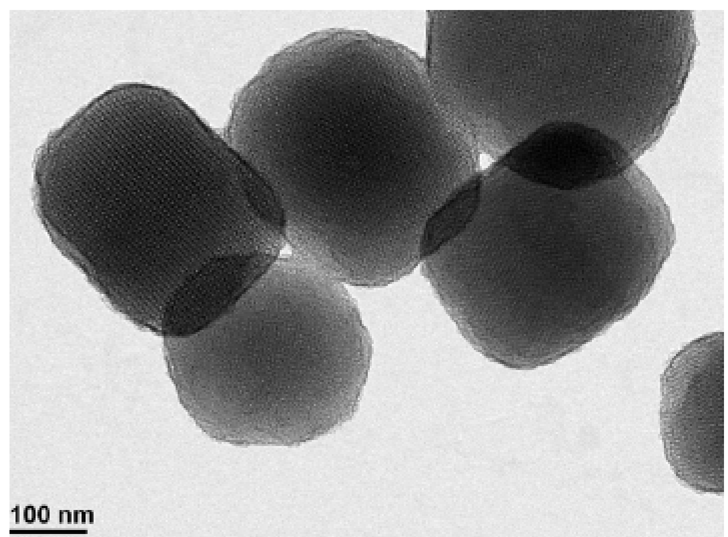
Next Approaches to Final Deliverable

- **Functionalized Mesoporous Silica Nanocubes (MSC)**









N_2 / CO_2 absorption Studies

Chem. Mater., **2016**, *28* (7), pp 2356–2362

Our Approaches to Final Deliverable

- Surface Group Functionalization on the CO_2/N_2 Separation Properties of MSC

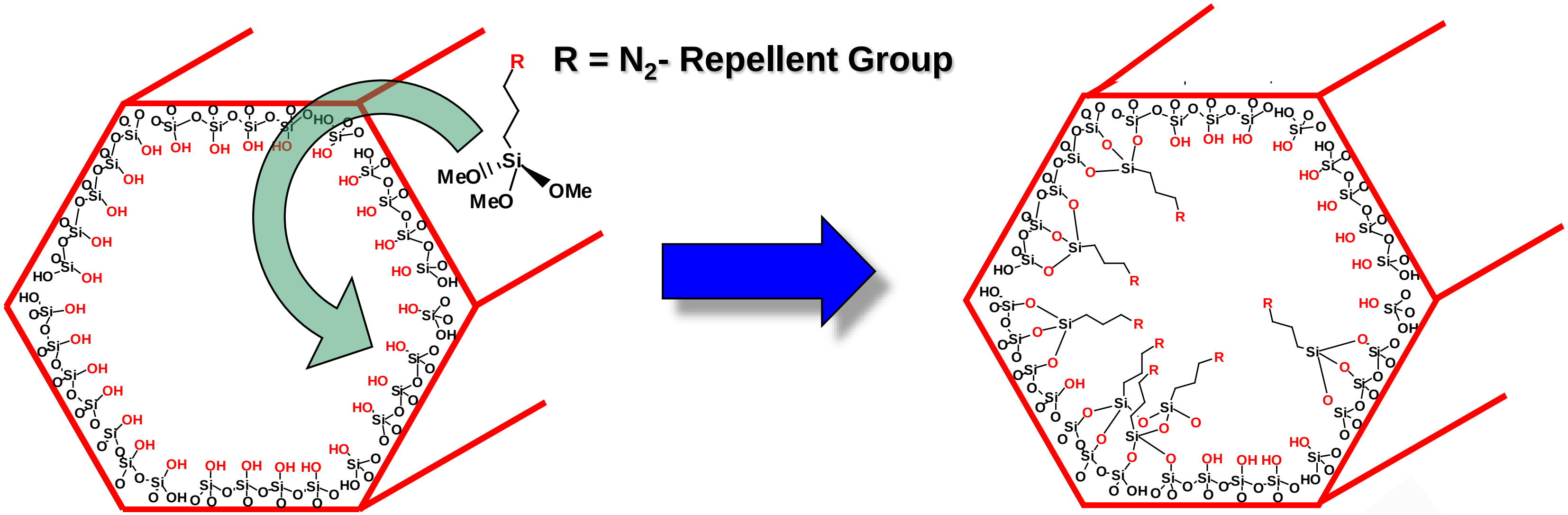
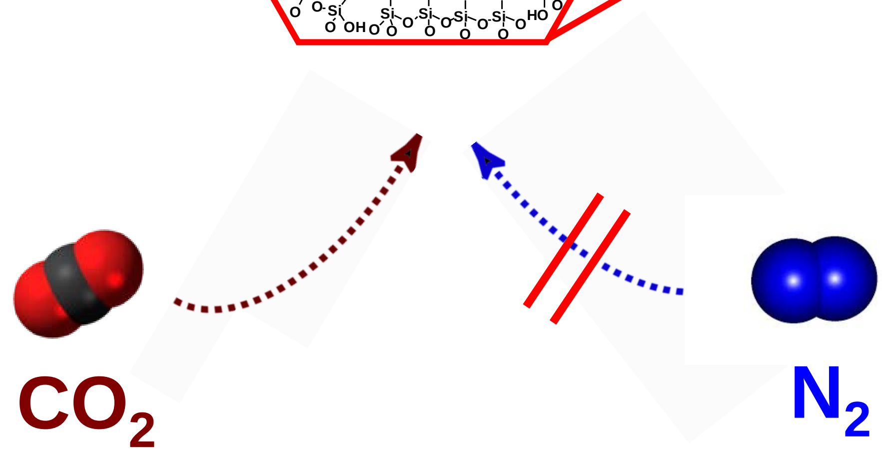


TABLE 1: Selectivities $S(CO_2/N_2)$ at 1 and 10 bar and 298 K for MCM-41 Functionalized with Different Surface Groups[a]

	pore diameter = 42 Å		pore diameter = 19 Å	
	1 bar	10 bar	1 bar	10 bar
unmodified MCM-41	7.0	6.4	9.0	8.5
propylamine	8.7	7.2	10.0	9.3
phenyl	10.9	8.7	12.4	12.1
difluorophenyl	12.3	8.9	12.7	12.8
fluorophenyl	9.9	9.1	12.3	13.4
chlorophenyl	10.8	8.9	13.2	14.6
bromophenyl	9.0	9.7	14.2	14.9
iodophenyl	11.6	9.6	14.3	15.3
diaminophenyl	16.5	13.9	16.9	18.0



Request No Cost Extension to finalize tasks

J. Phys. Chem. C, **2010**, *114* (43), pp 18538–18547

Acknowledgements

- DOE – Dr. Barbara Carney

- **Department of Chemistry,** Delaware State University

Thank you for your attention!

Questions?