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

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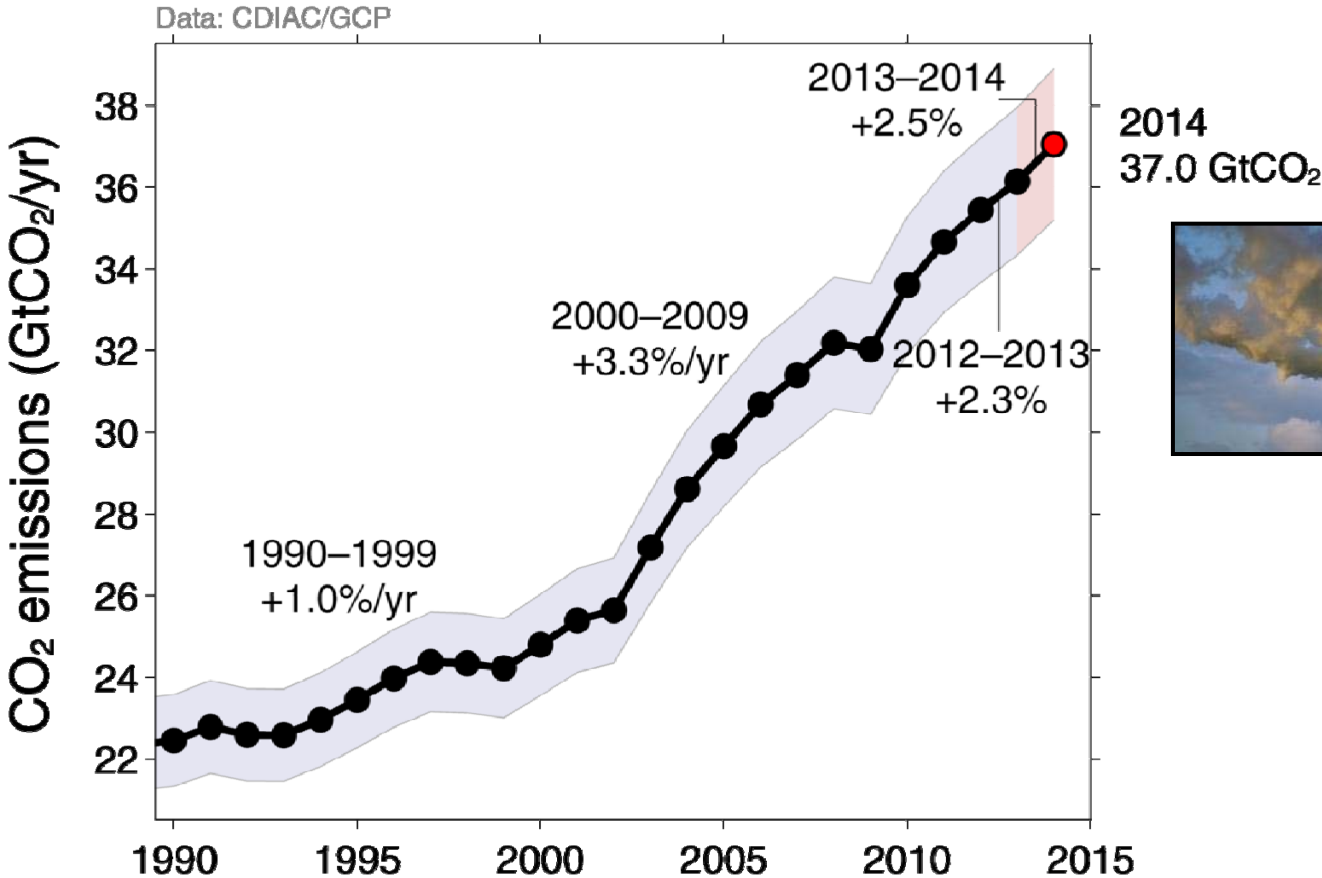
Motivation for Study

- **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

Background and Motivation for the project

At the 2014 Climate Summit, President Obama called for further reductions in greenhouse gas emissions.

1. The implications of the 2014 carbon budget for remaining below two degrees (At the current rate of CO_2 emissions, this 1200-billion-tonne CO_2 'quota' will be used up in around 30 years – or one generation. *Nature Geoscience,* published 22 September)
2. Option to share the remaining **fossil fuel quota** to meet the two degree target (Sharing a quota on cumulative carbon emissions. *Nature Climate Change*, published 22 September)
3. How much societies will need to rely on untried **technologies** to remain below two degrees? (Betting on negative emissions. *Nature Climate Change*, published September 21th, 2014)

CO_2 Reduction and Climate Change

The Paris Agreement will be signed on Earth Day 2016, April 22nd

Over 195 countries reached an historic agreement in Paris at the 2015 United Nations Conference on Climate Change. In short, they agreed to take measurable action, make binding commitments, and work together to reduce greenhouse gas emissions to collectively keep global temperature rise well below 2°C and to pursue efforts to limit it to 1.5°C.

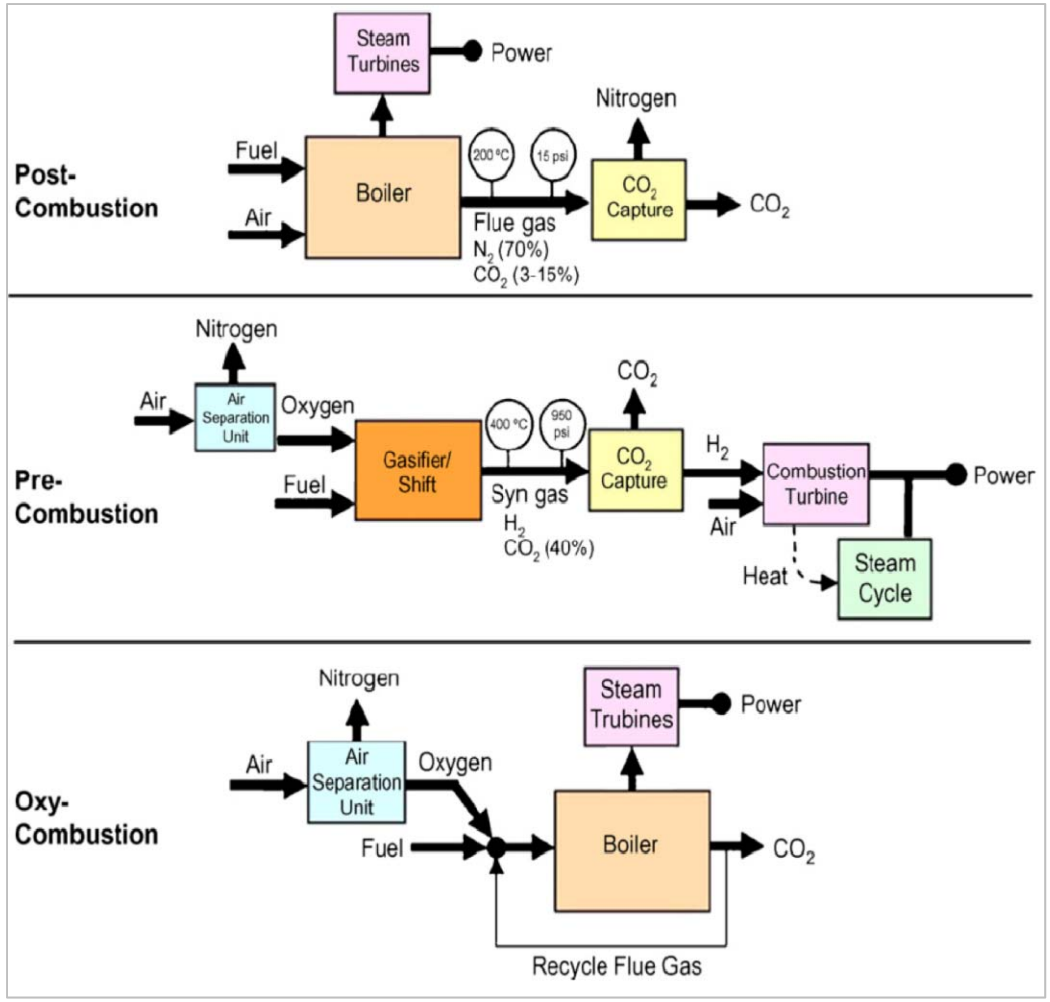
Technical background

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 engineer sorbent silica nanospheres, with high CO_2 capture capacity at low cost and with high recyclability, and a subsequent coated platform with enhanced nitrogen selectivity.

Objectives

1. Demonstrate a nanosheets made silica nanosphere (NSN) 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 NSN sorbent;

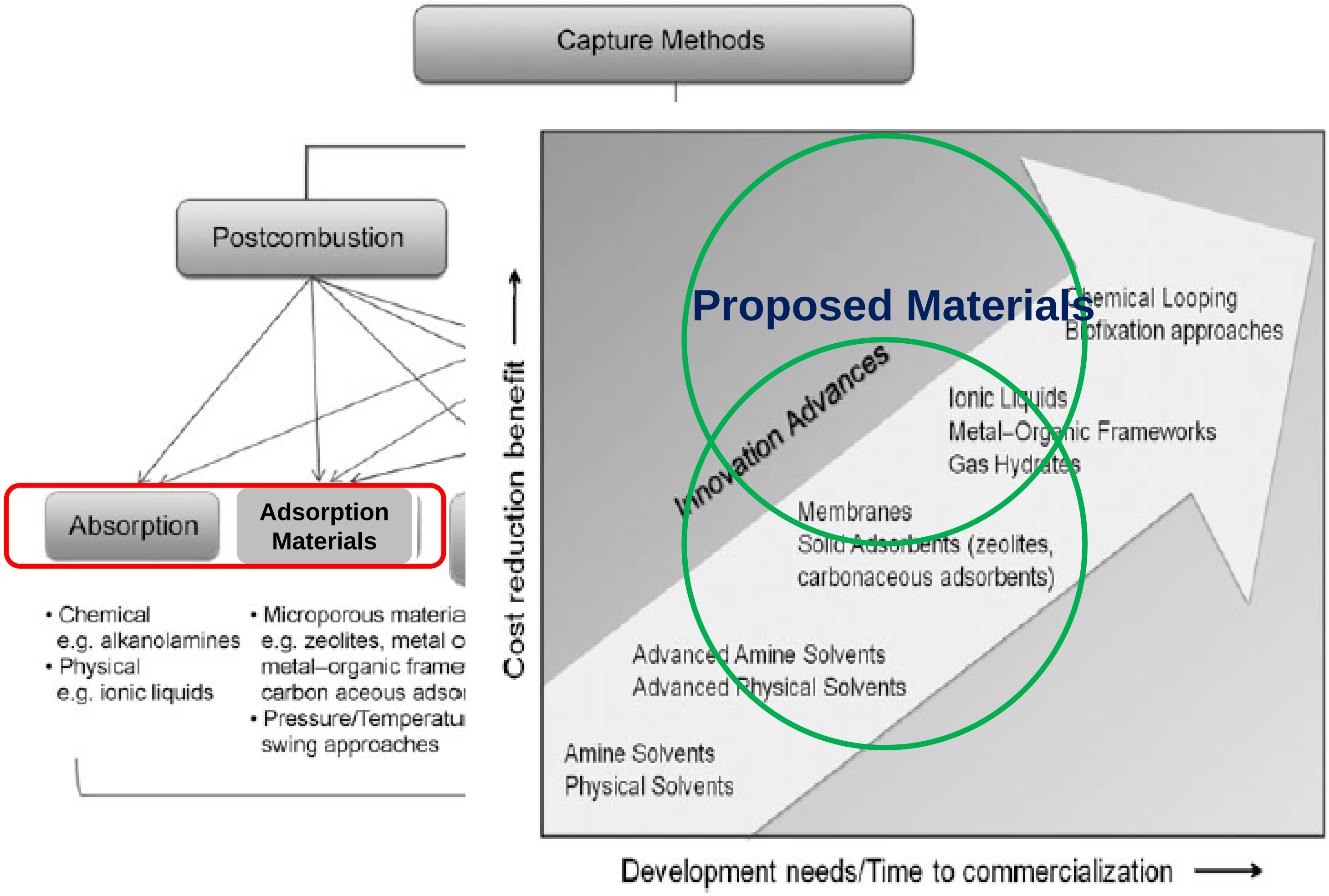
2. Perform parametric and long duration tests to demonstrate performance target of CO_2 capture at >90% of simulated flue gas with 15% CO_2;

3. Engineer a gatekeeping polymeric layer on NSN surface (PolyNSN), designed to increase CO_2 capture selectivity in the capture process;

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

Technical background

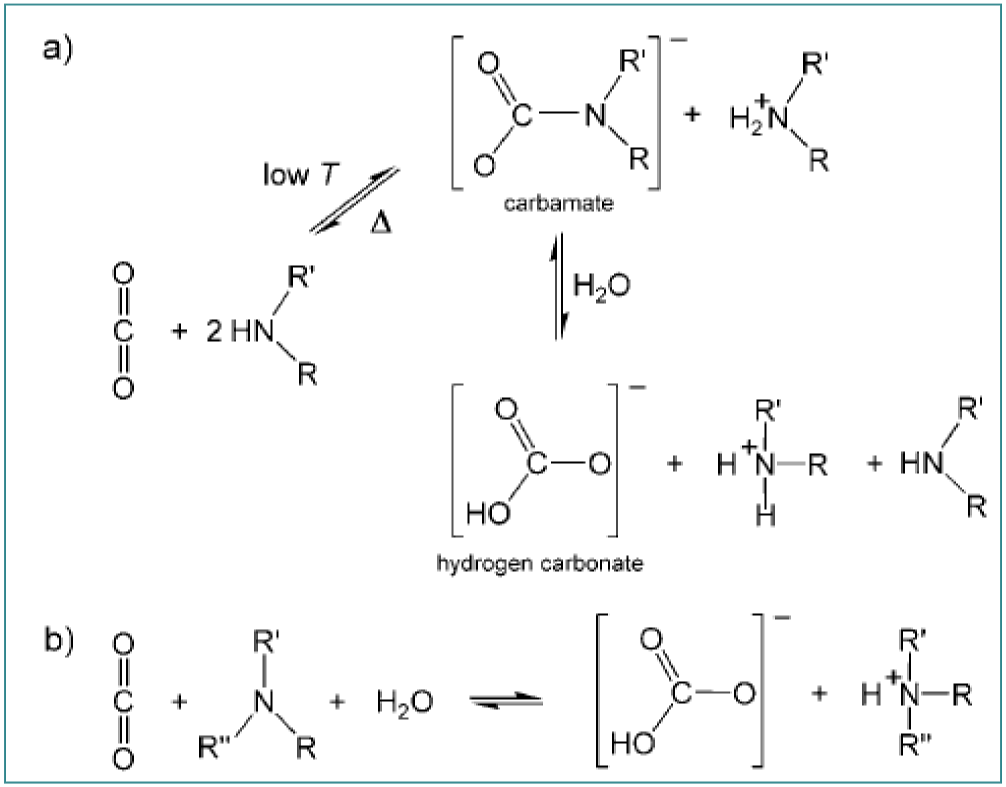
- Separation Technologies for CO_2 Capture



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

Technical background

- Conventional Chemical Absorption for CO_2 Capture



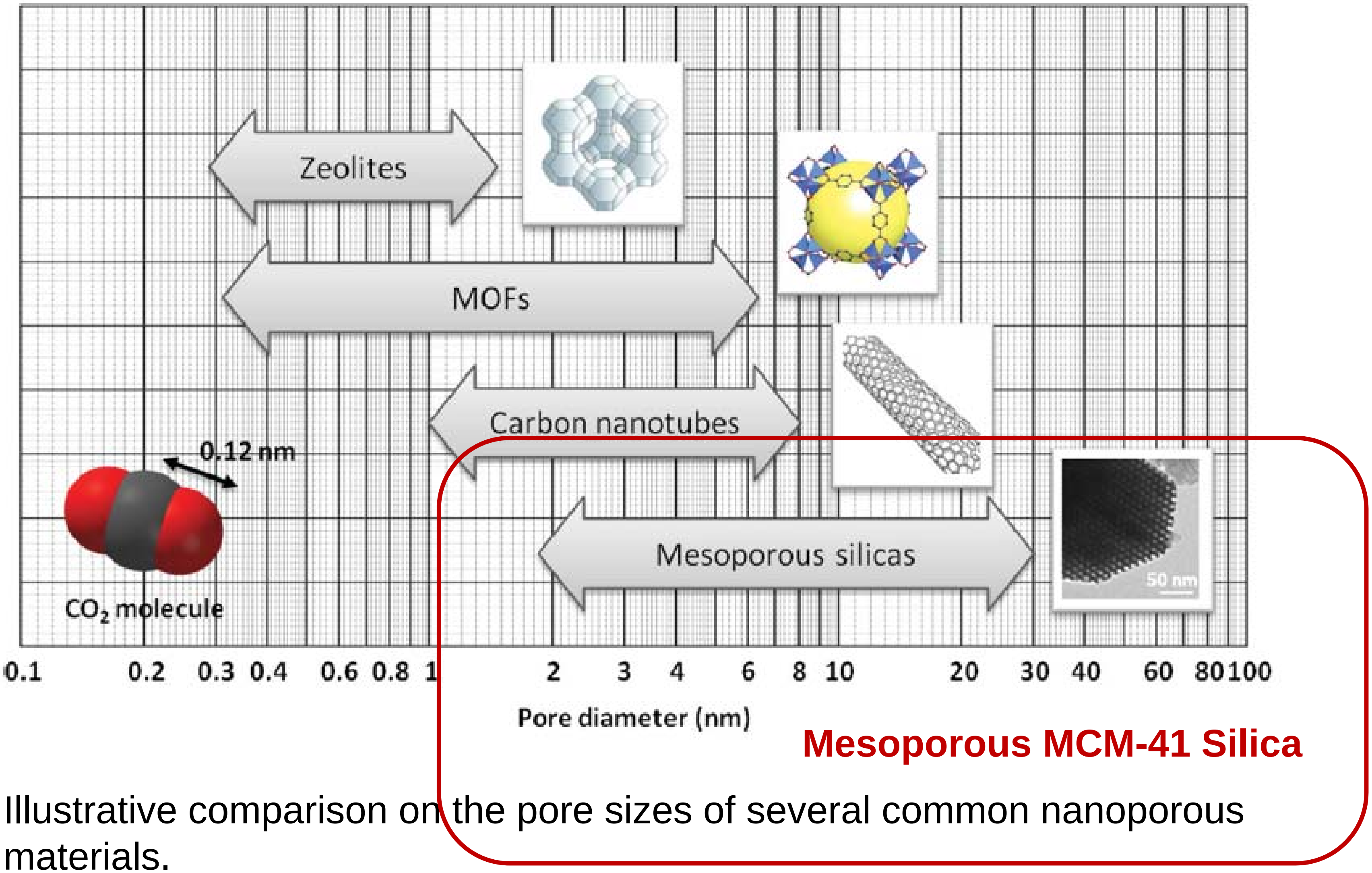
Scheme 1. General reactions for the chemical absorption of CO2 by a) primary or secondary and b) tertiary amine-containing solvents.

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

Technical background

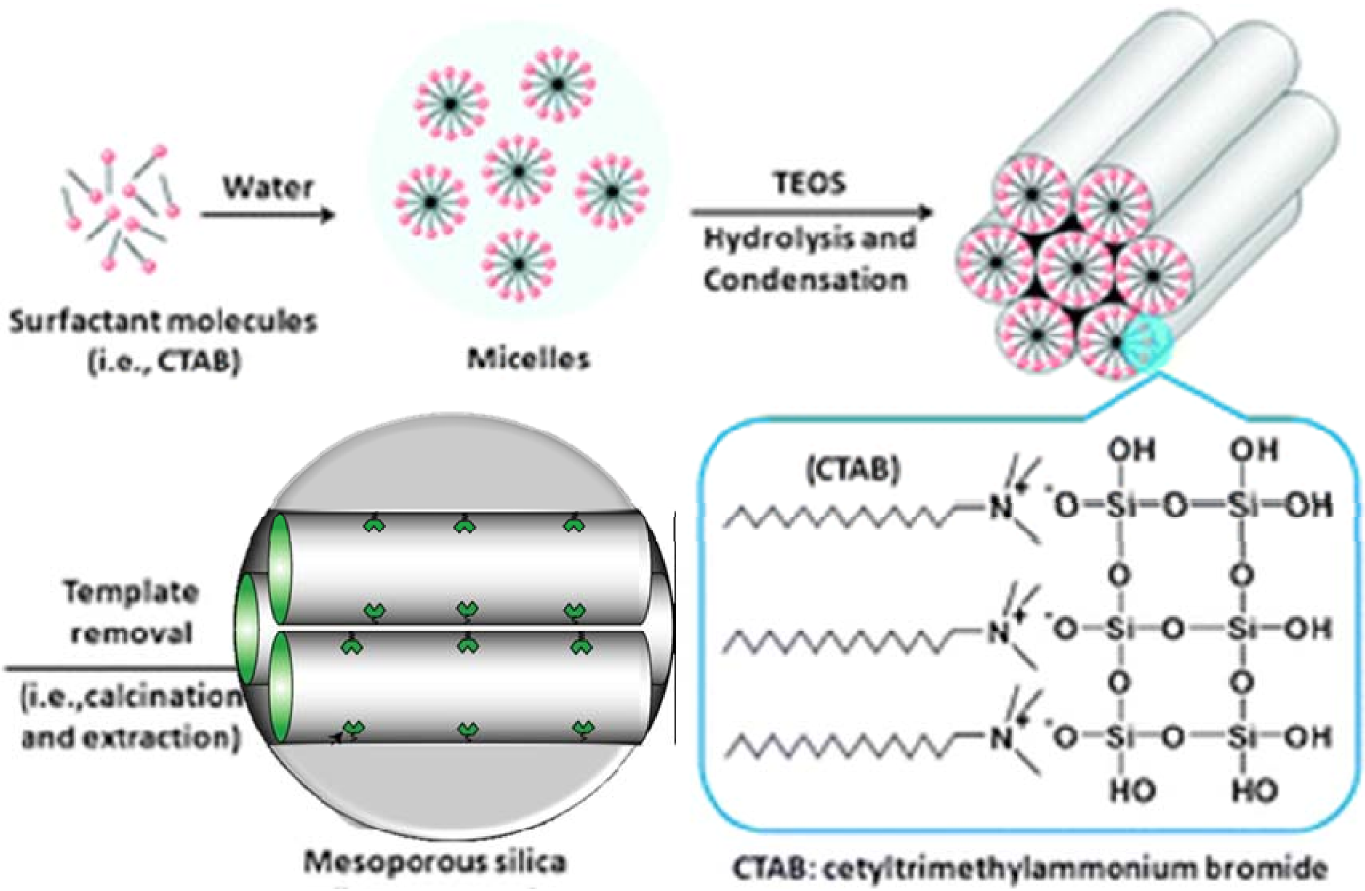
- Emerging Solid Sorbent Materials for CO_2 Capture



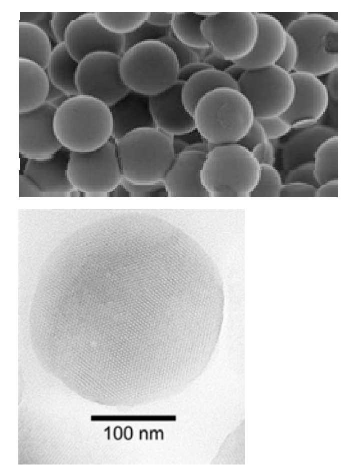
Illustrative comparison on the pore sizes of several common nanoporous materials.

Functionalized Mesoporous Silica Nanospheres

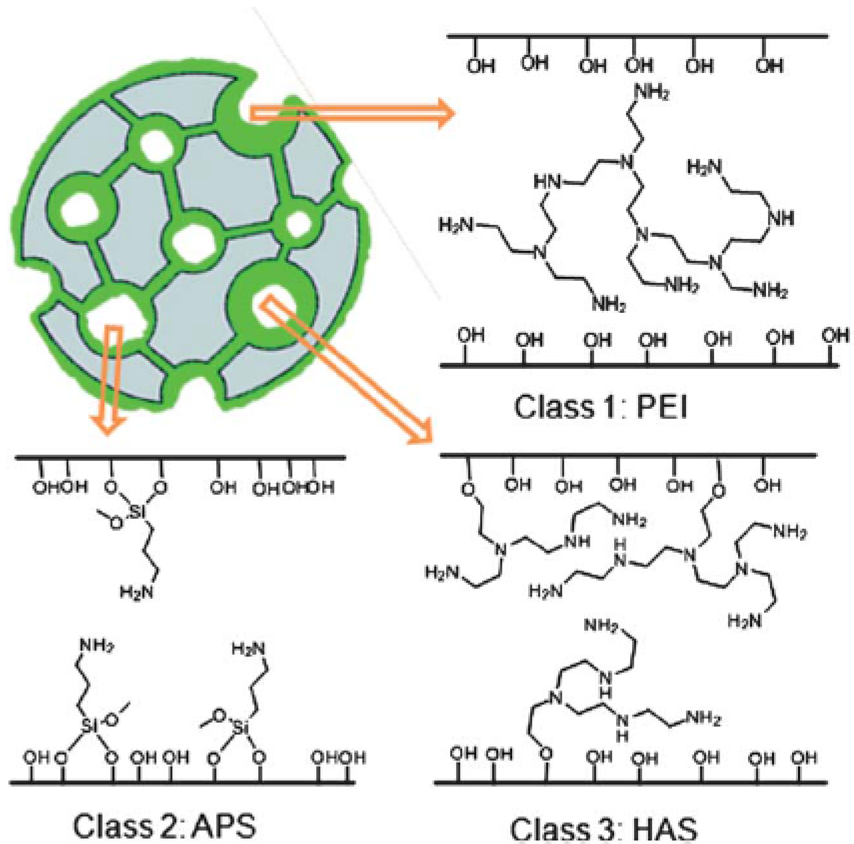
- Multiplayer Amino Silane for Enhancing CO_2 adsorption Capacity



SEM/TEM micrographs of functionalized MSN



Classification of immobilized Amine Mesoporous Silica Sorbents



Porous silica supports have been loaded with CO_2-trapping amine sites using three primary methods: physical impregnation, covalent tethering and in situ polymerization within the pores.

Bollini,P.,Didas,S.A.,and Jones,C.W. 2011. *J.Mater.Chem.* 21, 15100–15120.

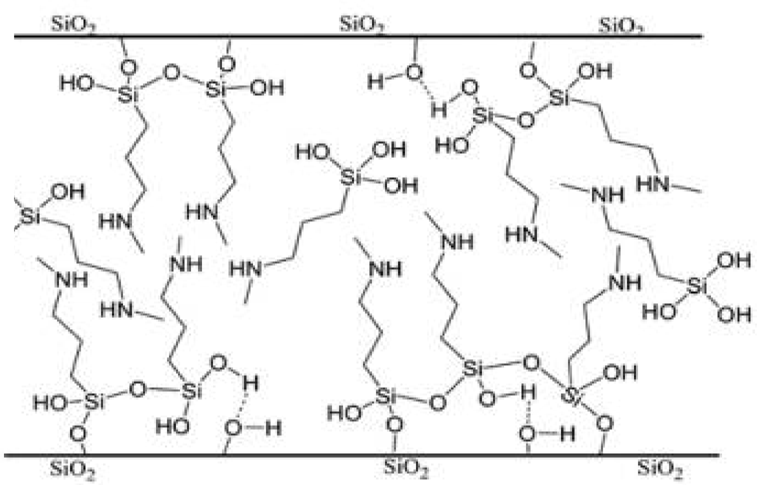
Pitfalls in Designing MCM-41 Type orbent for CO_2 Capture

- **Pitfalls for CO_2 capture:**

-Pore Blocking Hindering Amine Permeability

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

➡ **Retard Adsorption Kinetics for CO_2 DIFFUSION**



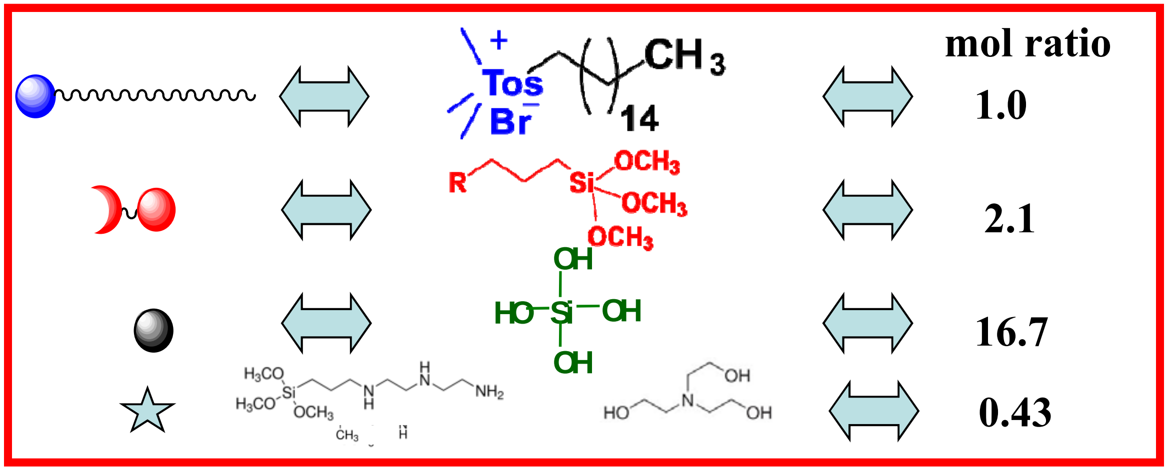
SOLUTION:
Large Pores–MSN (Hierarchical-pores MSN)

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

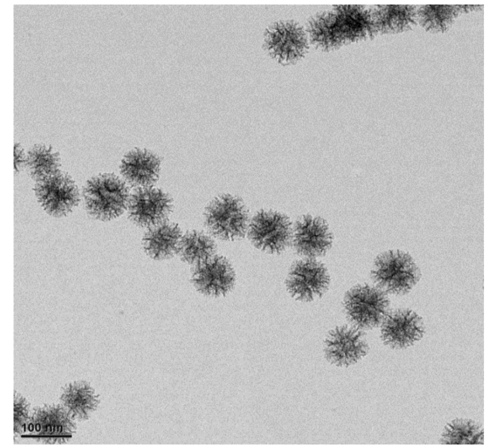
Pedro López-Aranguren, Santiago Builes, Julio Fraile, Lourdes F. Vega, and Concepción Domingo *Ind. Eng. Chem. Res.*, 2014, 53 (40), pp 15611–15619

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

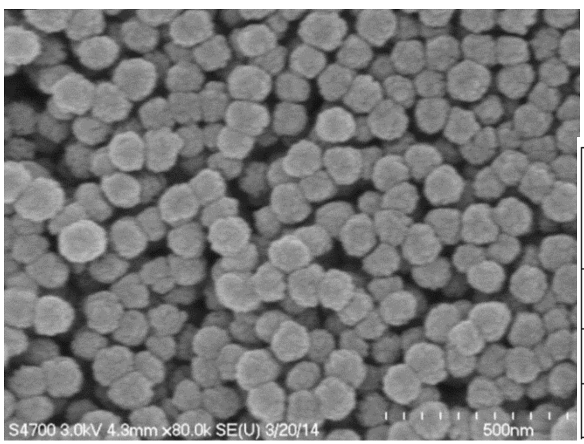
Our 1st Approach – Class II Hierarchical-Pores Stellate-MSN Sorbent



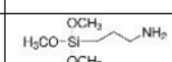
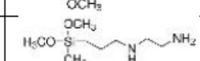
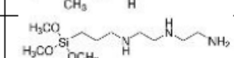
(Grafting of 1 mmol silane precursor)



TEM of Stellate MSN Nanospheres



SEM of Stellate MSN Nanospheres

Name	Molecular Structure	BET Surface Area (m^2/g)	DFT Pore Volume (cm^3/g)	Average BJH Pore Diameter (nm)
(3-Aminopropyl)trimethoxysilane		404.829	0.88	8.95
3-(2-Aminoethylamino)propyldimethoxymethylsilane		422.42	0.795	7.75
N1-(3-Trimethoxysilylpropyl)diethylenetriamine		417.57	0.91	8.34

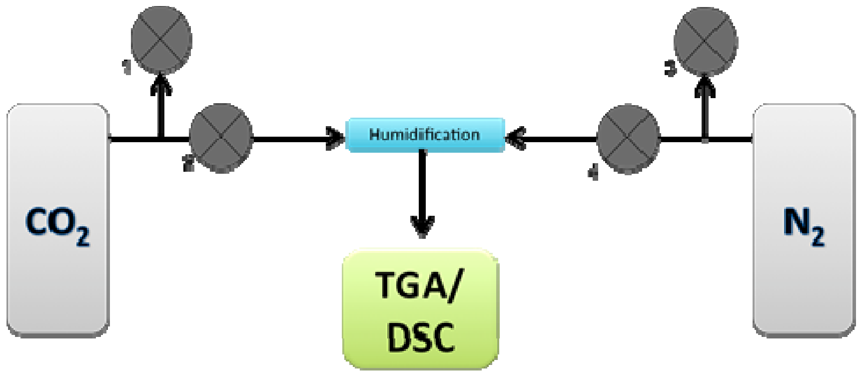
(Grafting 1 mmole silane precursor)

CO_2 Adsorption Analysis for Class II Stella-MSN Sorbent

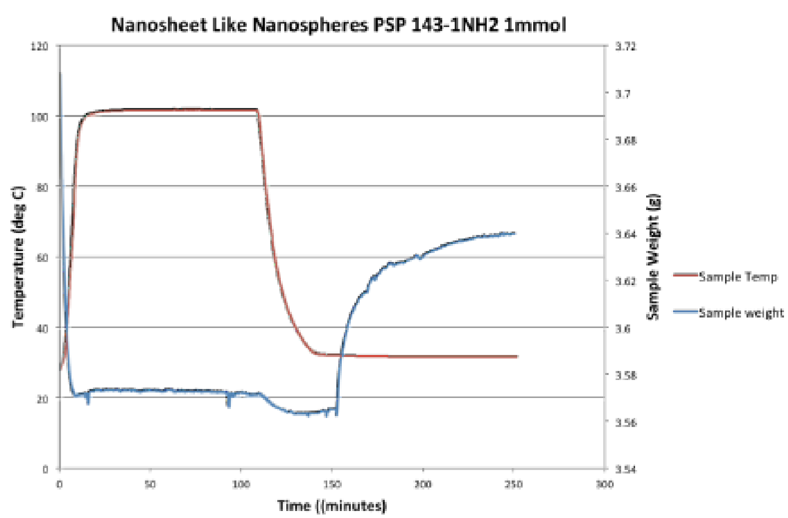
- <u>Carbon dioxide cycling experiments</u> will be performed on TGA Instruments analyzer using:

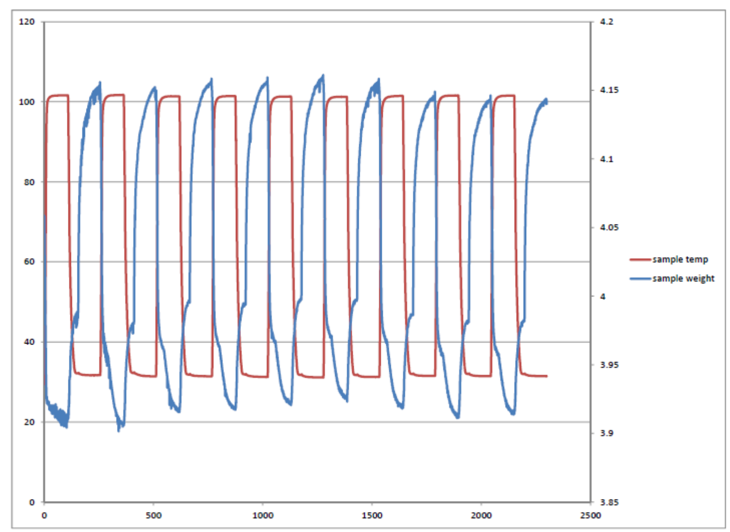
a). CO_2 ;

b). N_2 at a predetermined flow rate for all gases.

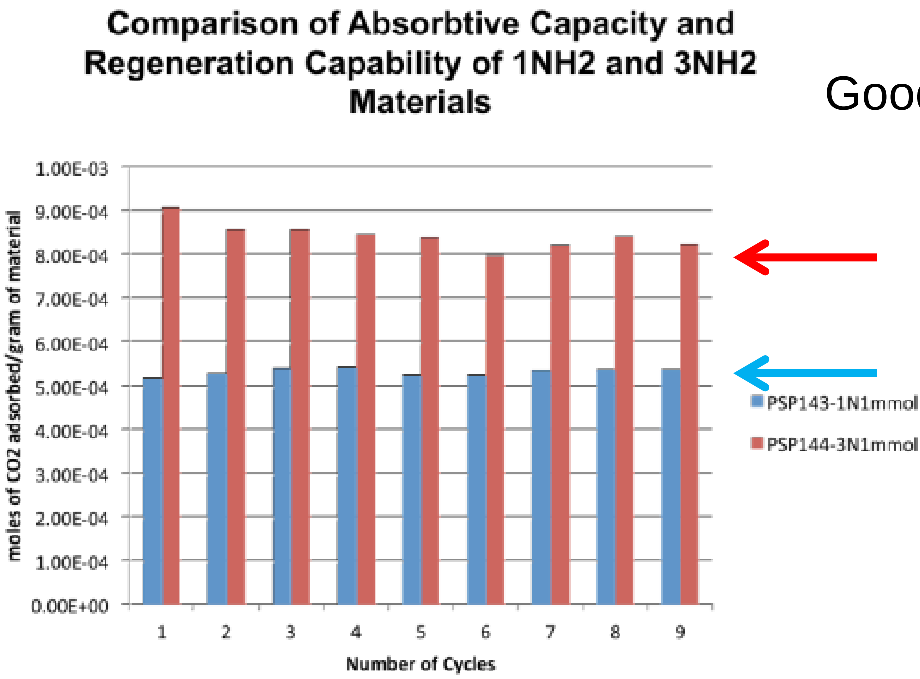


Scheme . TGA setting for CO_2 capture experiments





CO_2 Adsorption Analysis for Stellate- MSN Sorbent



Good Stability BUT low adsorption capacity

3 N amine sorbent
- 4.9 % Adsorption Capacity

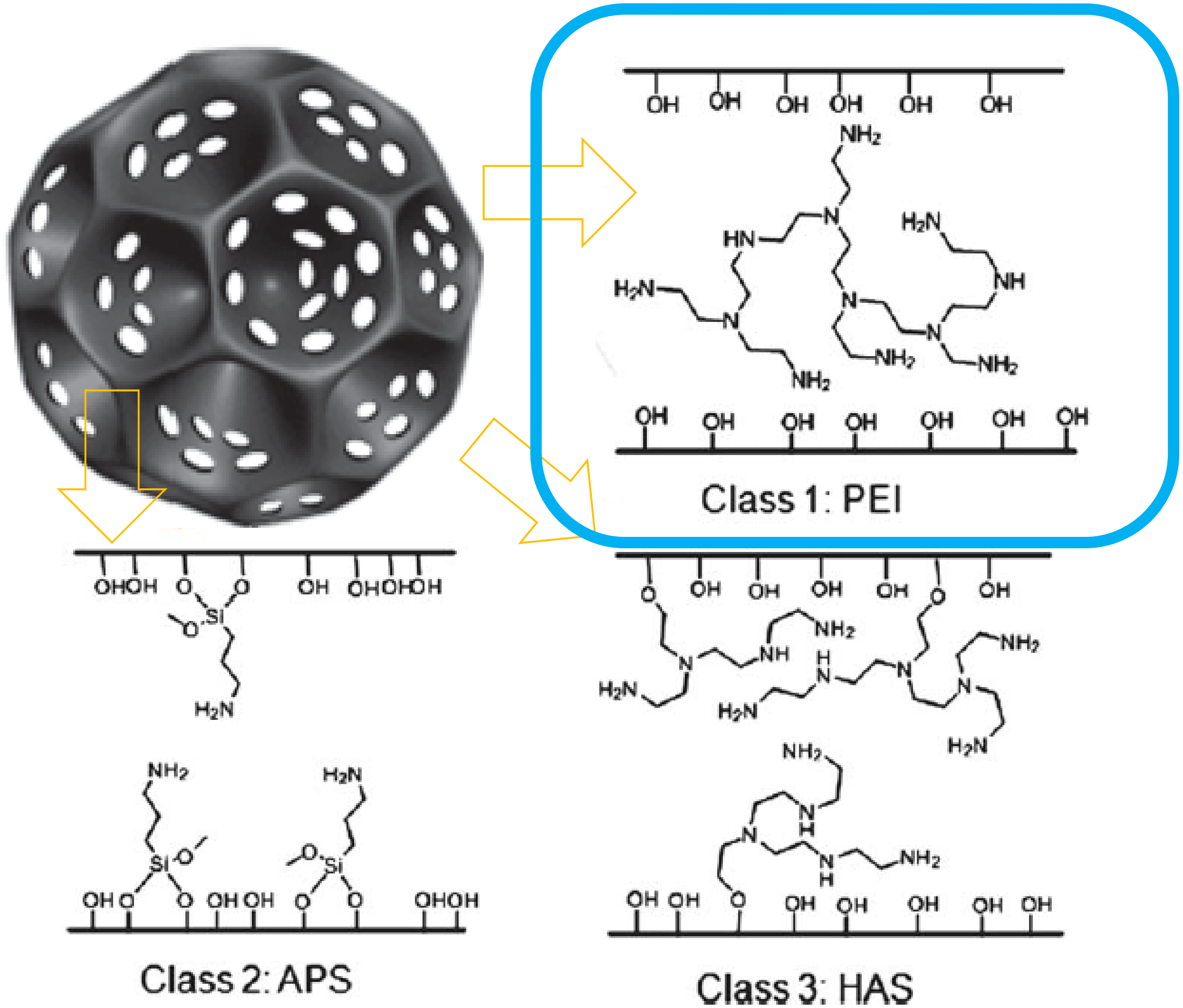
1 N amine sorbent
- 2.2 % Adsorption Capacity

Table 3 | Key parameters for *Class 2* immobilized amine adsorbents.

Reference	Supporting material	Grafted amine	Adsorption temperature (°C)	Adsorption (partial) pressure (bar)	Adsorption capacity (wt. %)
Serna-Guerrero et al. (2010)	Pore-expended MCM-41	Triamine-containing silane	25	0.05	9.0
Zelenak et al. (2008)	MCM-41 SBA-12 SBA-15	3-Aminopropyltriethoxysilane	25	0.1	2.6 4.5 6.7
Zukal et al. (2009)	ITQ-6	3-Aminopropyltrimethoxysilane [3-(Methylamino)propyl]trimethoxysilane [3-(Phenylamino)propyl]trimethoxysilane	20	1	5.3 4.2 2.2
Yang et al. (2012)	MCM-22 MCM-36 ITQ-2	3-Aminopropyltrimethoxysilane	25	1	6.7 5.3 7.6

Front. Energy Res., *Nannan Sun1, ZhiyongTang1,WeiWei , Colin Edward Snape andYuhan Sun* 09 March 2015

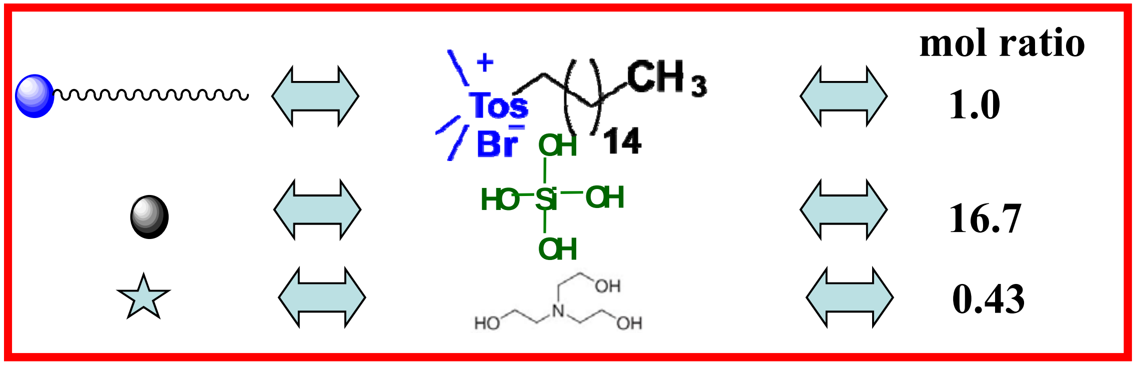
Class I Hierarchical-Pores Stellate-MSN Sorbent

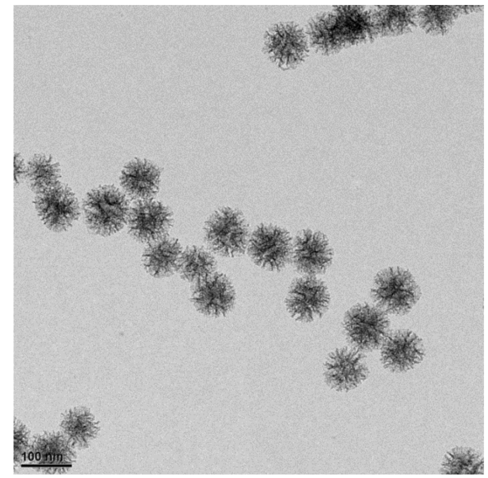


Praveen Bollini, Stephanie A. Didas and Christopher W. Jones *J. Mater. Chem*., 2011, 21, 15100

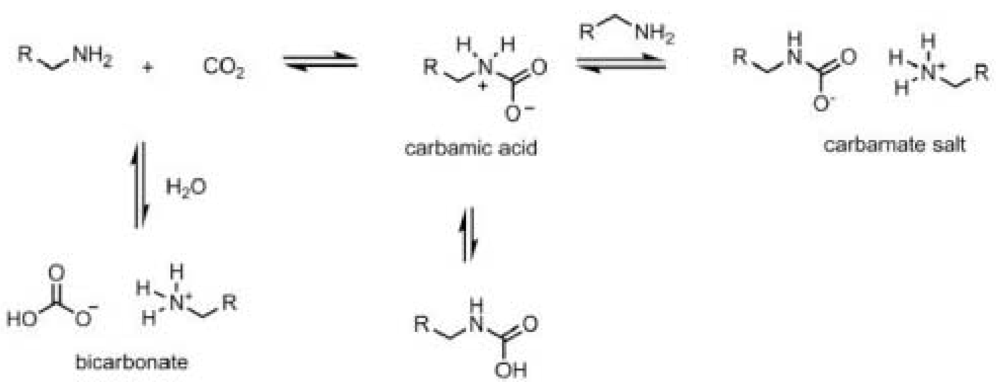
Xin Du, Bingyang Shi, Ji Liang, Jingxu Bi, Sheng Dai and Shi Zhang Qiao. *Advanced Materials, 2013, 25,* 5981–5985,

Our 2nd Approach – Class I Hierarchical-Pores Stellate-Silica Sorbent



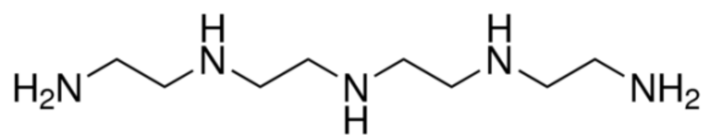


TEM of NSN Nanospheres



Scheme 1. Reaction between primary amines and CO_2

Tetraethylenepentamine-TEPA loaded by wet impregnation

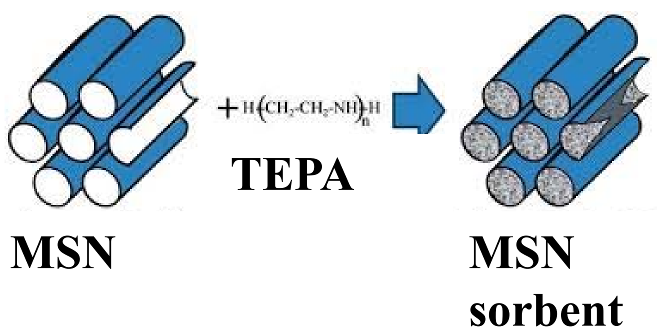


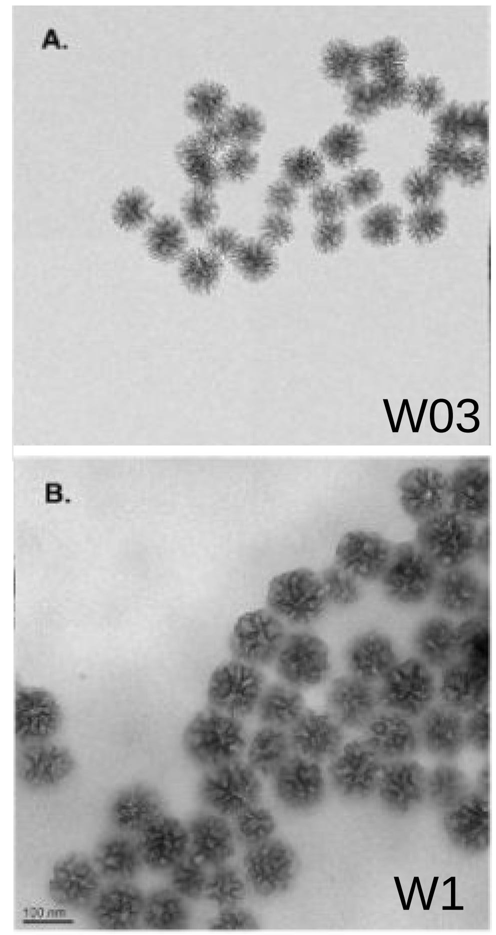
TEPA – Stellate MSN Sorbent for Carbon Capture

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





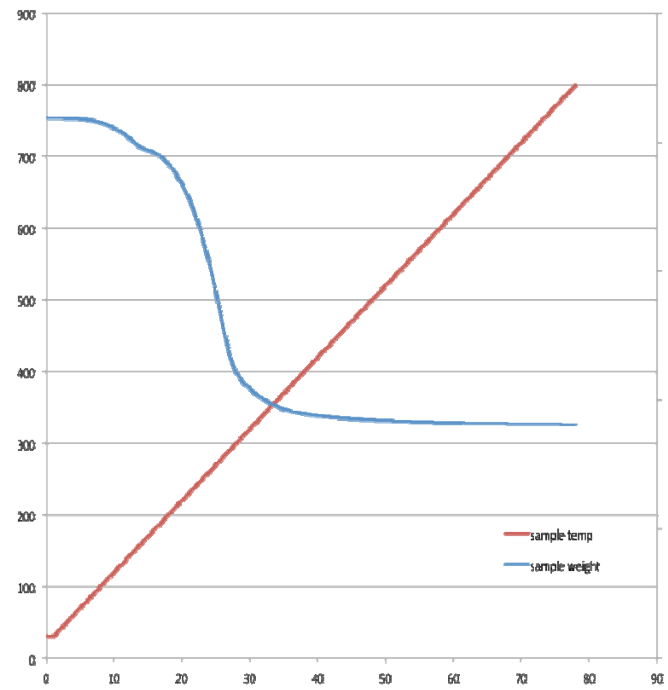
TEM of TEPA treated Stellate MSN

Nichloas Pizzi, Daniela Radu, and Cheng-Yu Lai* , *Chem Comm* submitted

TEPA - Stellate MSN Sorbent for Carbon Capture

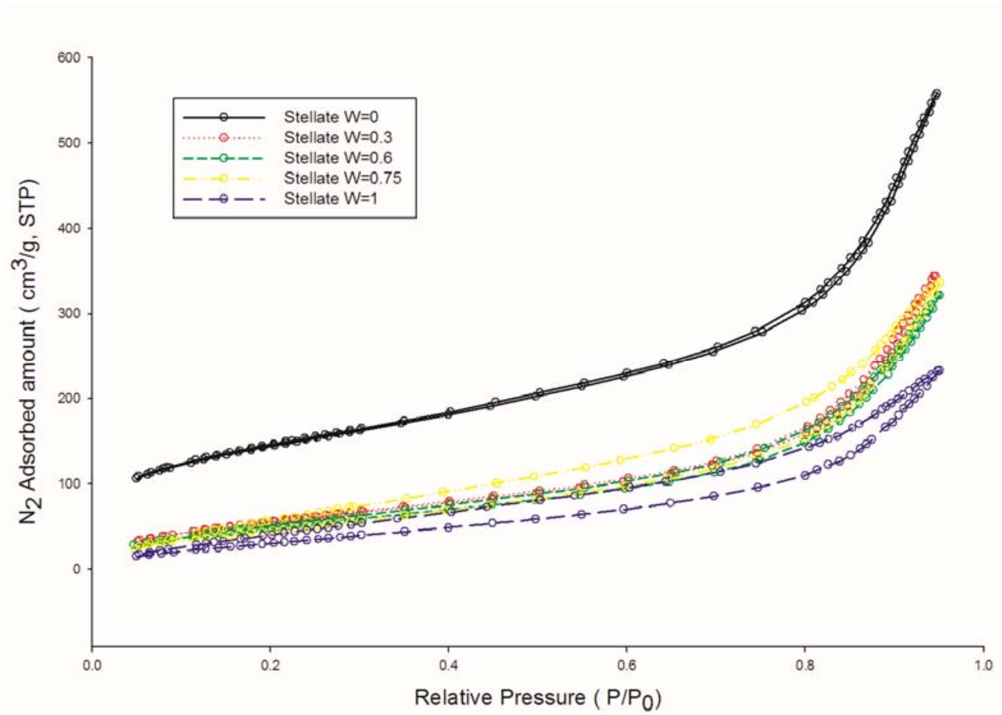
TEPA Loading Study

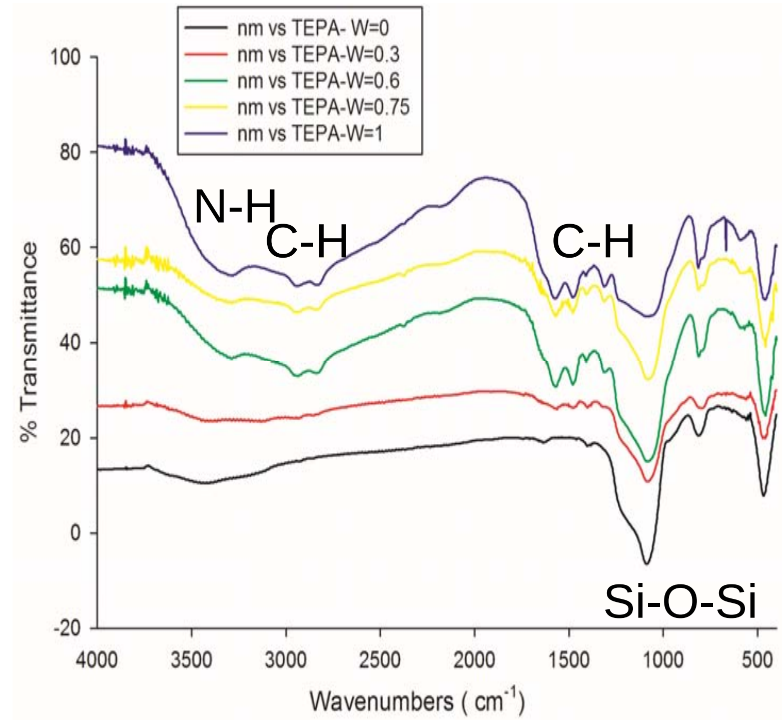
TEPA-Stellate MSN	Amine loading (mmol) by TGA)
W03	2.23
W06	3.93
W075	4.56
W1	6.94



Nichloas Pizzi, Daniela Radu, and Chneg-Yu Lai* , *Chem Comm* submitted

Characterization of TEPA - Stellate MSN





Material ID	BET Surface Area (m^2/g)	Amine Content by TGA (mmol/g)	Amine content/m^2 (μmol/m^2)
W0	508.61	0.00	0.00
W03	220.361	2.23	10.12
W06	195.441	3.93	20.11
W075	193.5	4.56	23.58
W1	139.281	6.94	49.83

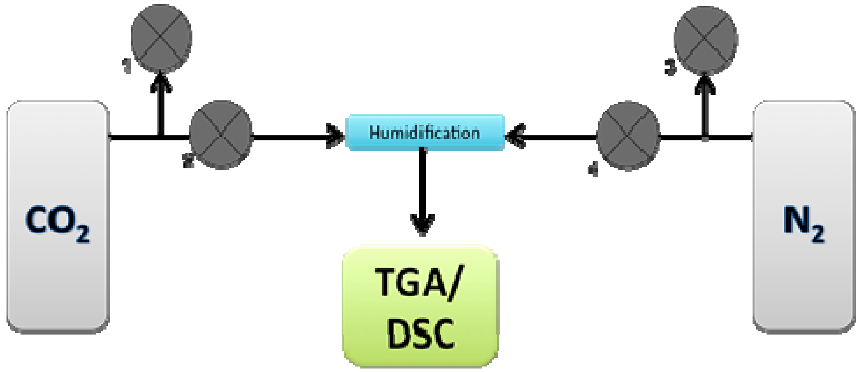
Nichloas Pizzi, Daniela Radu, and Cheng-Yu Lai* , *Chem Comm* submitted

CO_2 Adsorption Analysis for TEPA-Stellate MSN Sorbent

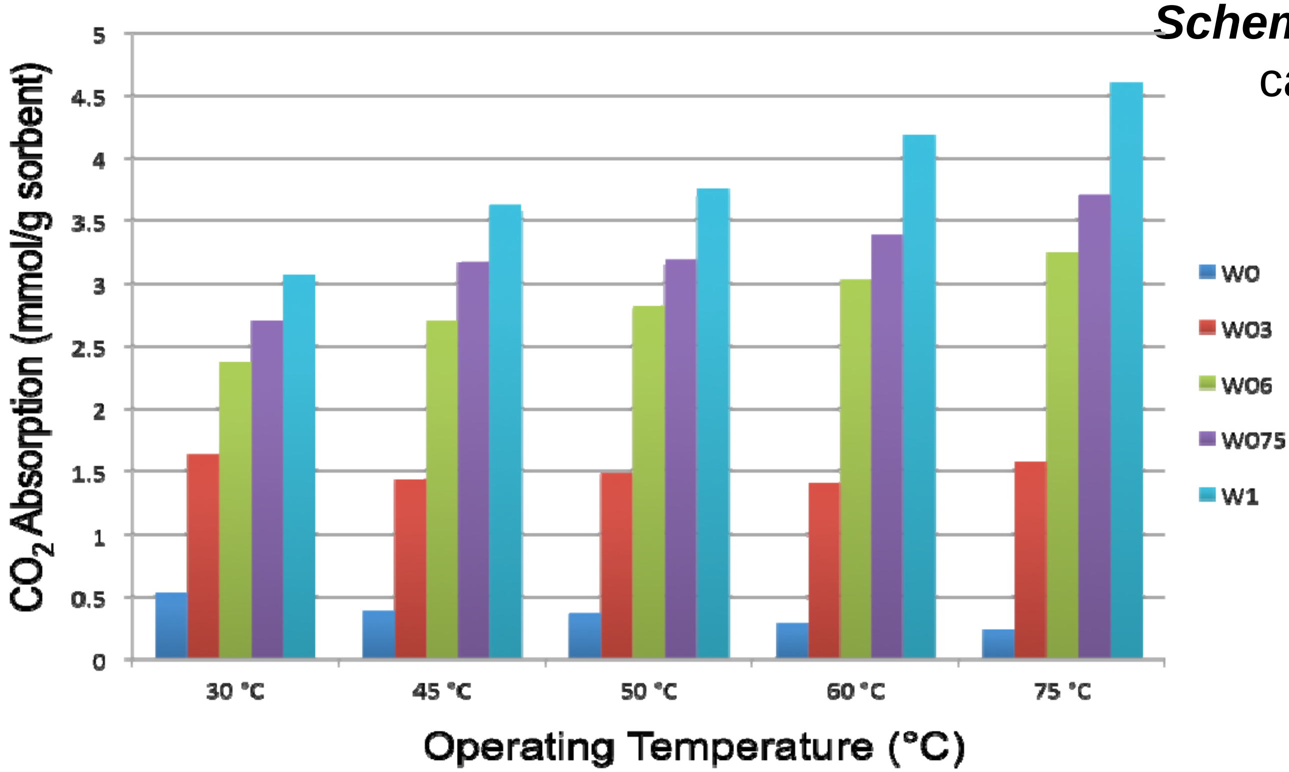
- ***Carbon dioxide cycling experiments*** will be performed on TGA Instruments analyzer using:

a). CO_2 ;

b). N_2 at a predetermined flow rate for all gases.



Scheme . TGA setting for CO_2 capture experiments



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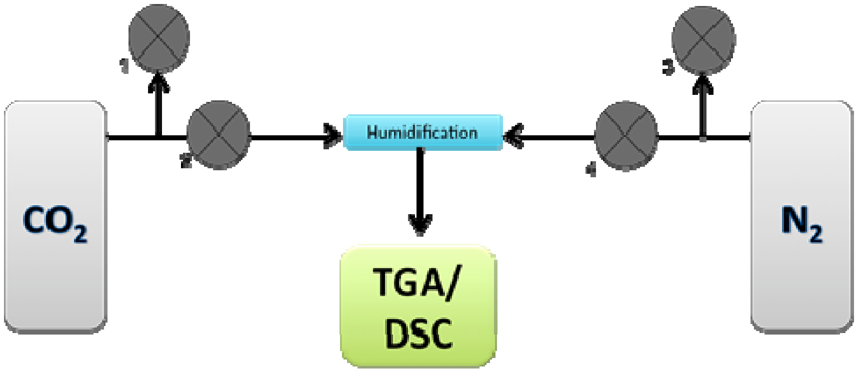

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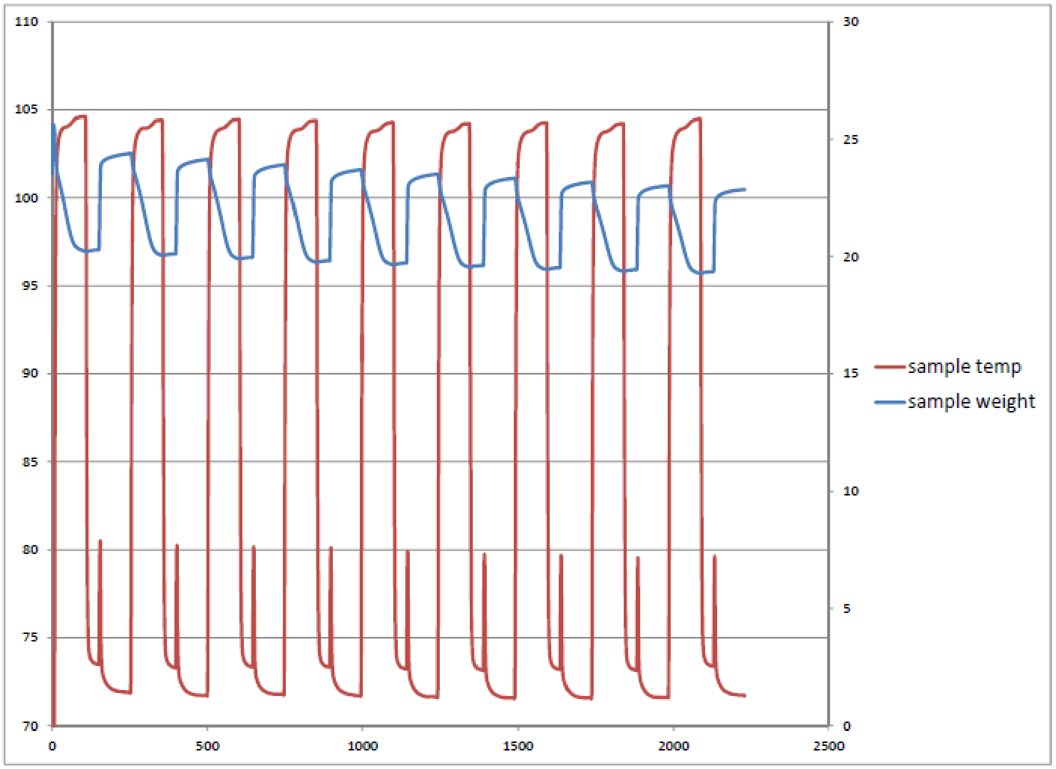


- High temp Stability
- CO_2 –adsorption capacity of ~ 4.7mmol CO_2 per gram of stellate MSN sorbent
- High amine loading 6.4 mmol N/g sorbent

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**

1. **Heat of adsorption**
- **Stellate MSN – 28-32 KJ /mole**
- **Data collection for other sorbents**

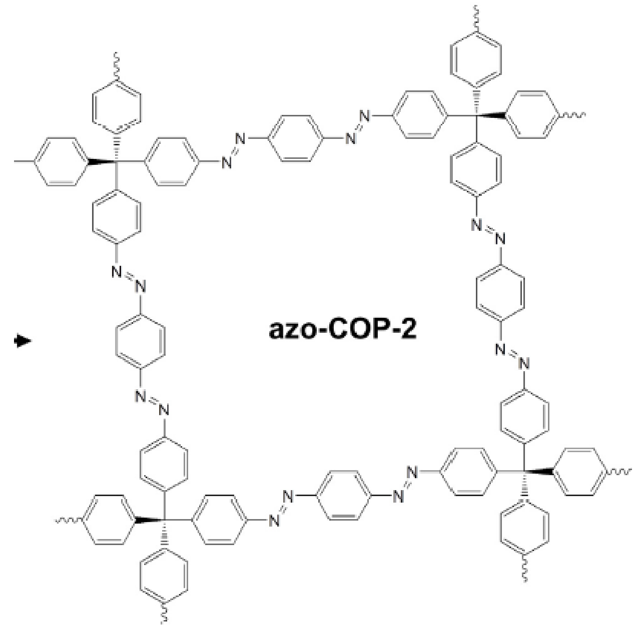
2. **Simulated Flue Gas Testing**
3. **Long Term Stability Test**

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**

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.



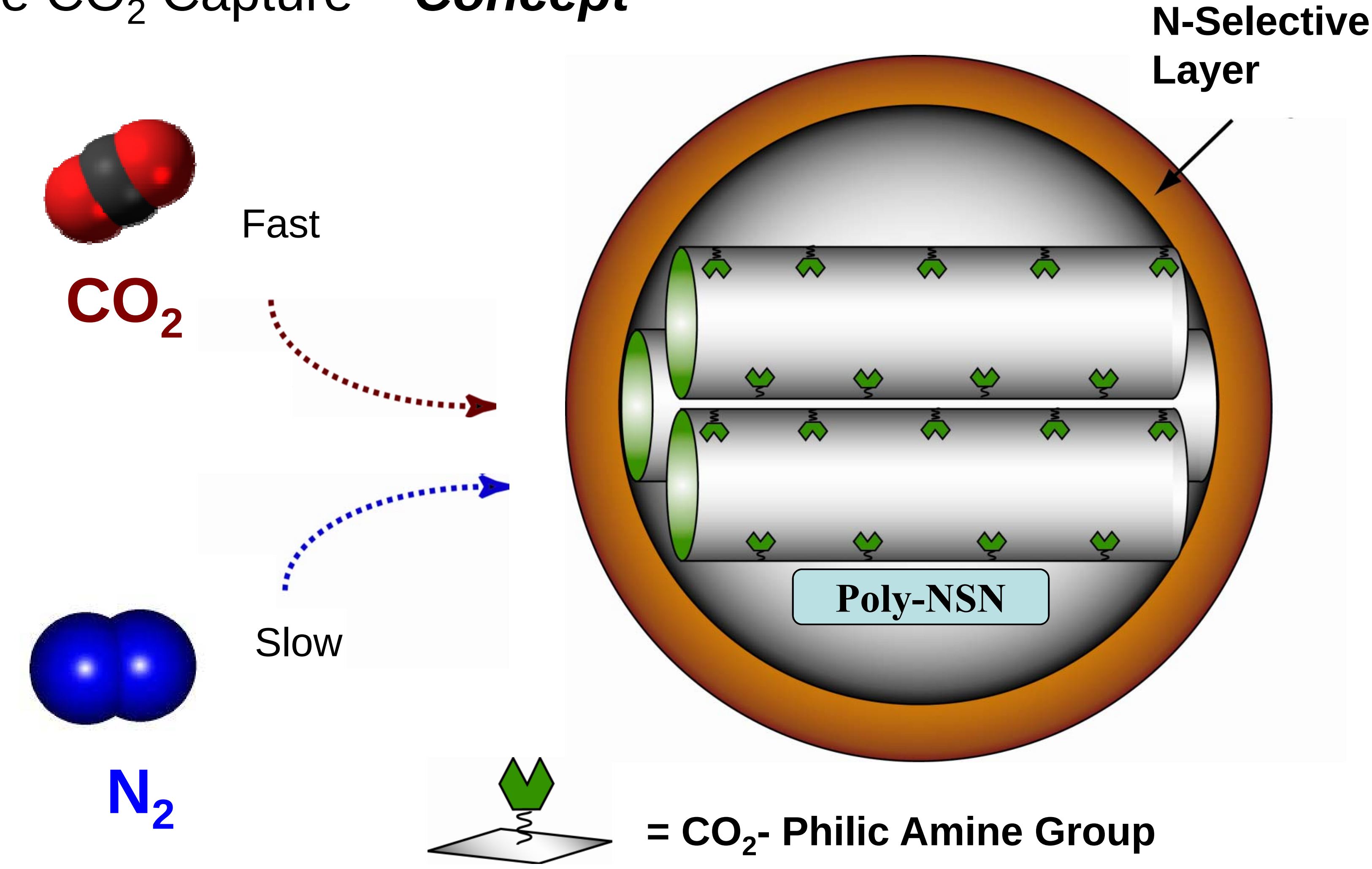
Incorporation of facile synthesized nitrogen scaffolds significantly increases CO_2 adsorption capacities for selective carbon capture.

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.

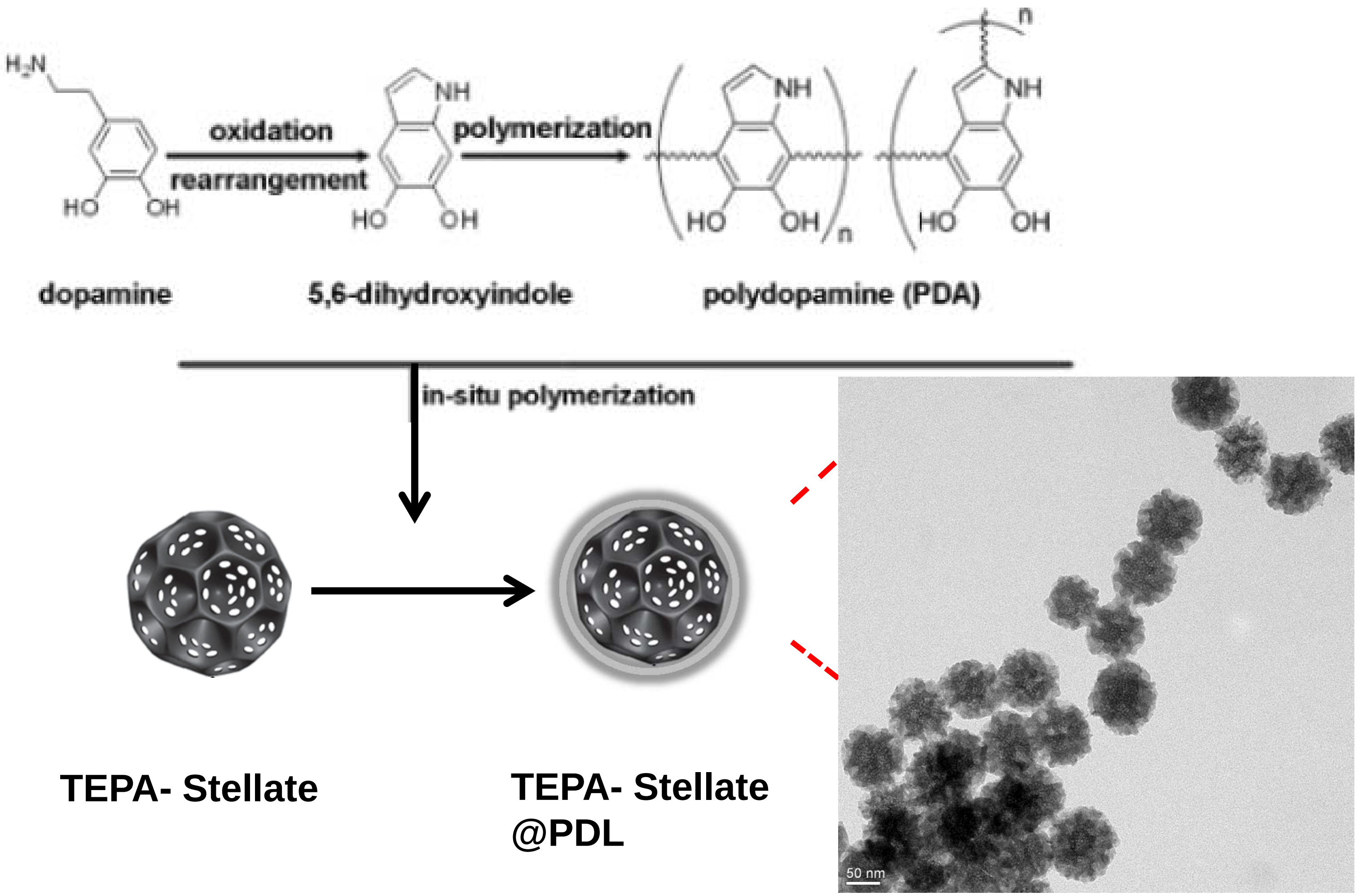
Stephan Hug, *Linus Stegbauer*, *Hyunchul Oh*, *Michael Hirscher*, and *Bettina V. Lotsch Chem. Mater.*, **2015**, *27* (23), pp 8001–8010

Technical background and motivation for the project

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



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



Path forward

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1. **Heat of adsorption for TEPA-Stellate MSN**
2. **Simulated Flue Gas Testing**
3. **Long Term Stability Test**

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**

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Thank you for your attention!

Questions?