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CO_2 Capture from Flue Gas Using Solid Molecular Basket Sorbents

DOE NETL Award No. DE-FE0000458

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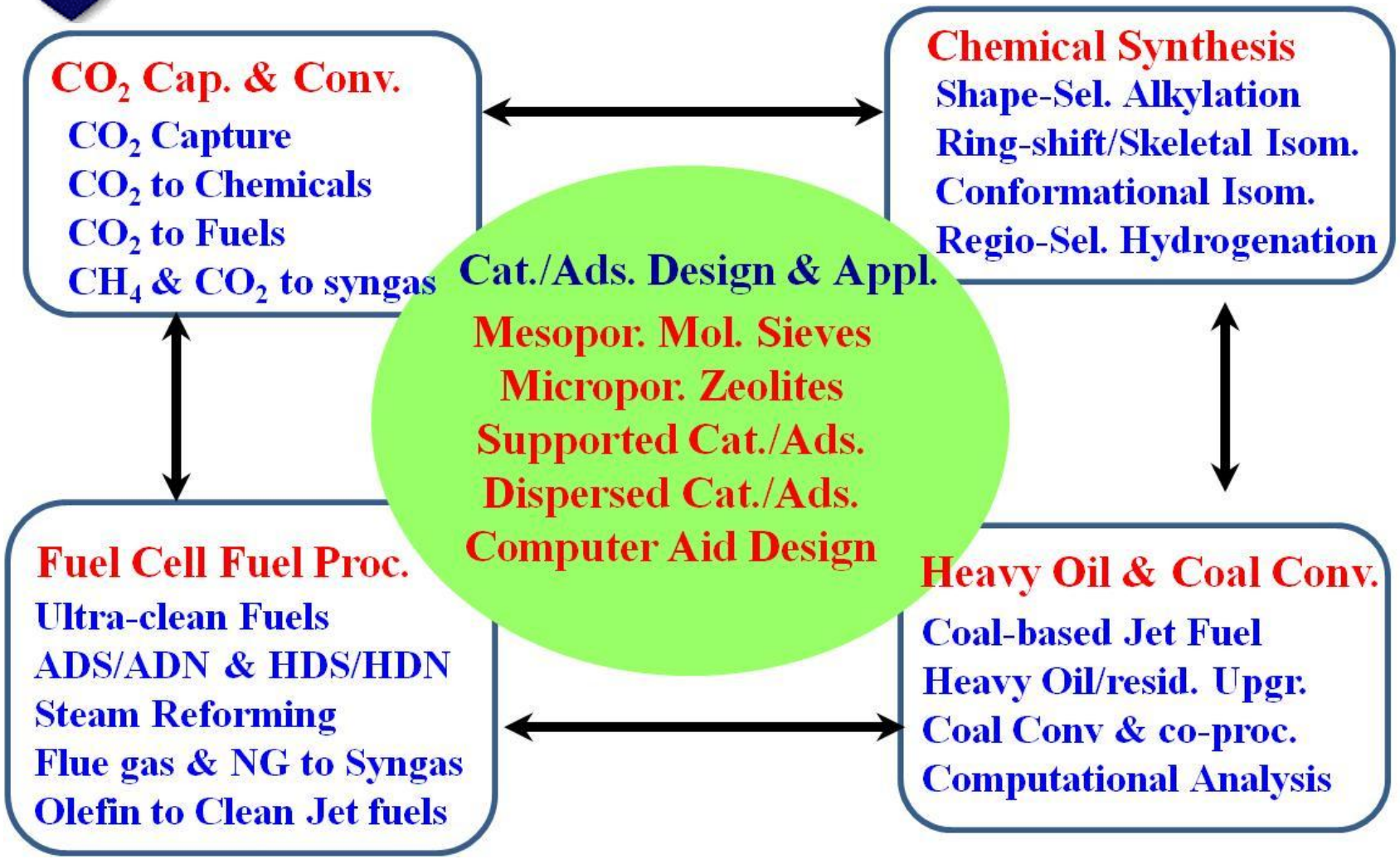
DOE NETL Project Manager: Andrew O'Palko

2011 NETL CO_2 Capture Technology Meeting
Sheraton Station Square, Pittsburgh, August 22-26, 2011

Research at Song's Group



Research Team:

2 Faculties, 4 visiting scholars, 4 Post-doc, and 9 graduate Students

http://www.energy.psu.edu/personnel/CSong.html

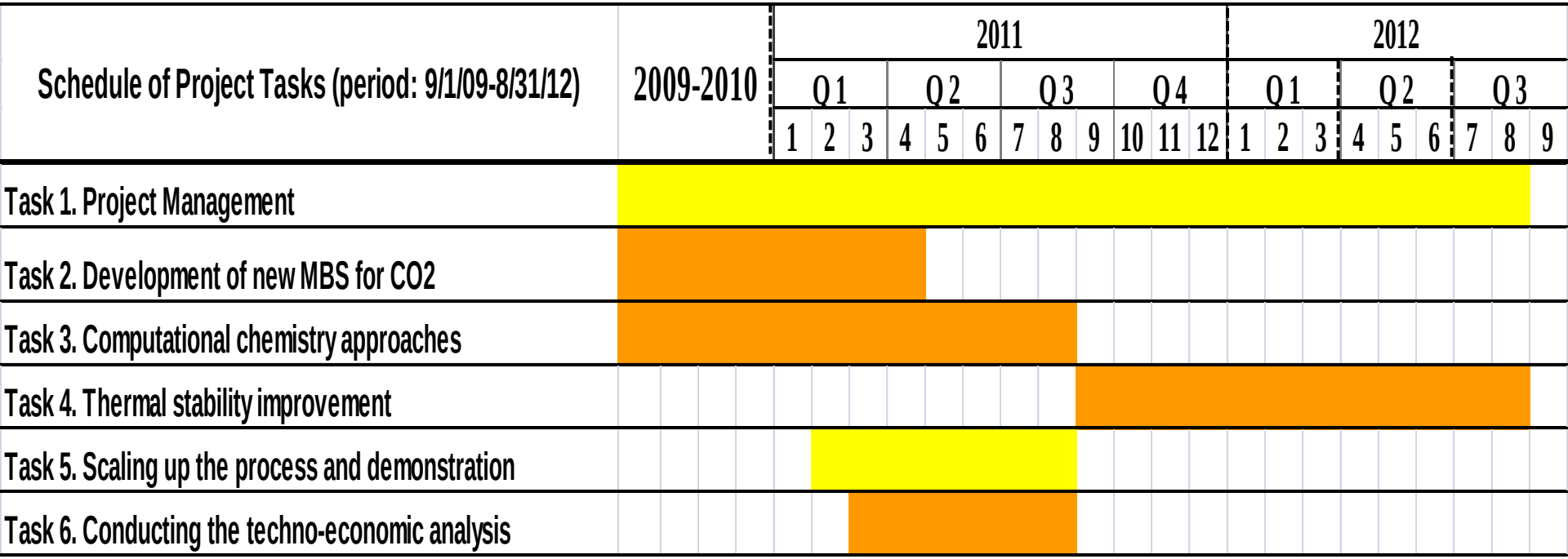
Project Overview

a) Funding (DOE and Cost Share)

Amount requested from DOE: **$456,992**; Non-federal Cost Share: **$114,299**

Total budget: **$571,291**

b) Overall Project Performance Dates (9/1/2009-8/31/2012)*



c) Project Participants

Involving **2 research faculty, 1 post-doctor and 3 graduate students**

*** The non-cost extension period of Sept. 1, 2011 – Aug. 31, 2012**

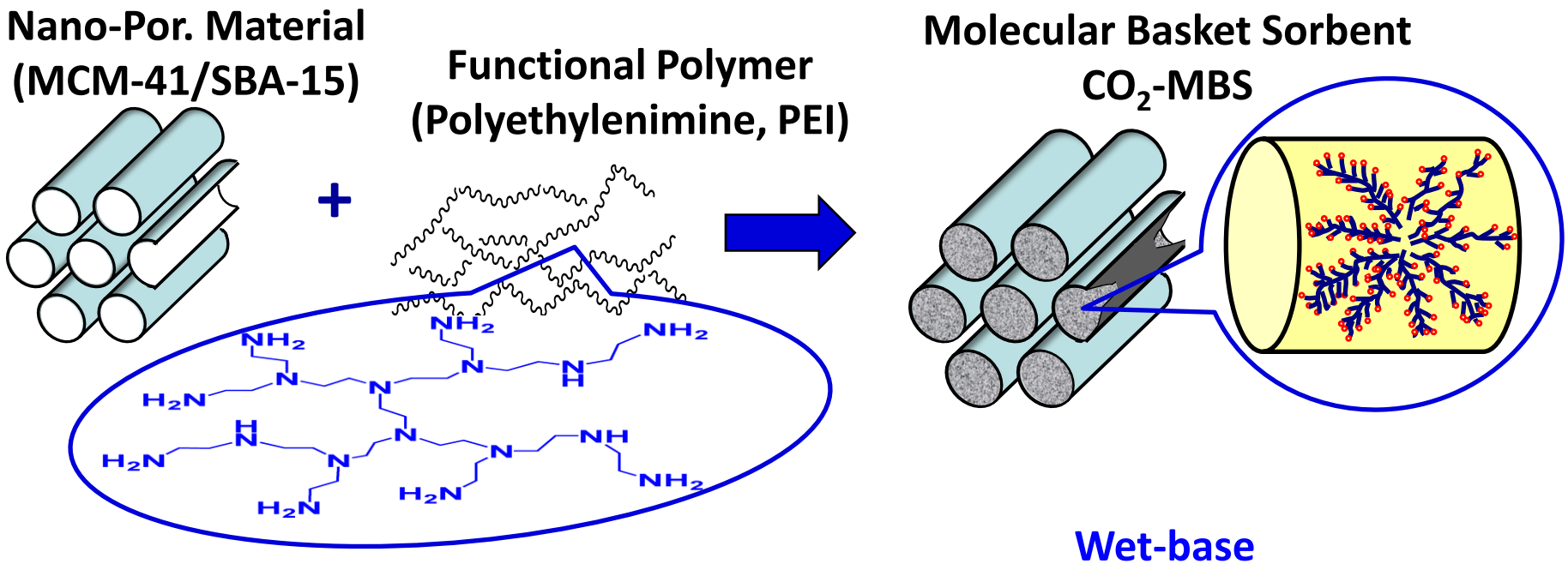
Project Objective

To develop a new generation of solid and regenerable polymeric "molecular basket" sorbent (MBS) for more efficient capture and separation of CO_2 from flue gas of coal-fired power plants.

The new generation of MBS should have:

- **A regenerable working capacity higher than 70 mg-CO_2/g-S**
- **A significantly lower cost compared to the early generations of MBS**

Concept of "Molecular Basket" Sorbent (MBS) – Nano-porous Inorganic Matrix-Polymer Composite



Dry-base

$$CO_2 + 2RNH_2 \rightleftharpoons [RNH_3]^+[O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\overset{\overset{\displaystyle H}{|}}{N}\text{-}R]^-$$

$$CO_2 + 2R_2NH \rightleftharpoons [R_2NH_2]^+[O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\overset{\overset{\displaystyle R}{|}}{N}\text{-}R]^-$$

$$CO_2 + R_3N \not\rightleftharpoons$$

Wet-base

$$CO_2 + RNH_2 + H_2O \rightleftharpoons [RNH_3]^+[HO\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O]^-$$

$$CO_2 + R_2NH + H_2O \rightleftharpoons [R_2NH_2]^+[HO\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O]^-$$

$$CO_2 + R_3N + H_2O \rightleftharpoons [R_3NH]^+[HO\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O]^-$$

Xu et al. *Energy Fuels* 2002, *16*, 1463; *Micropor. Mesopor. Mater.* 2003, *62*, 29; *Fuel Proc. Technol.* 2005, *86*, 1457-72; *Ind. Eng. Chem. Res.* 2005, *44*, 8113-19; Ma et al. *J. Am. Chem. Soc.* 2009, *131*, 5777-83.

Advantages and Challenges of PSU-MBS

Advantages

- High capacity: 140 g-CO_2/kg at CO_2 conc. of 15%
- High selectivity: CO_2/N_2 > 1000
- No corrosion problem
- Suitable operation conditions
- High sorption/desorption rate
- Positive effect of moisture
- Regenerable at mild conditions

Challenges

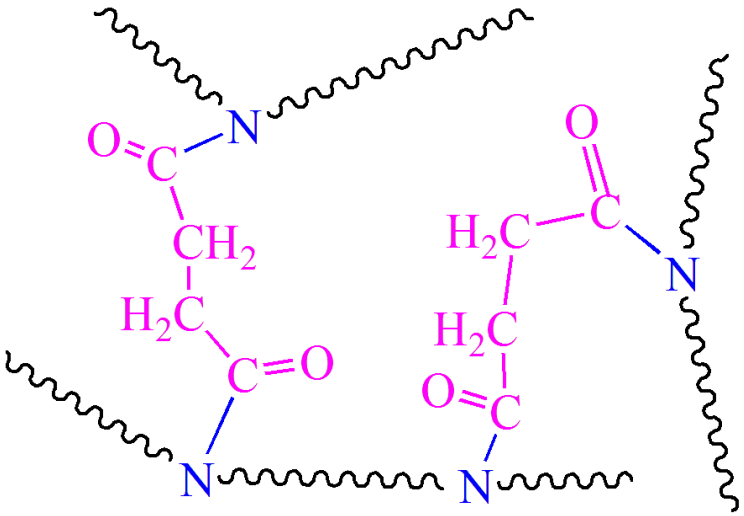
- High Cost of SBA-15 & MCM-41

  Using low-cost support material with high capacity maintained
- Thermal Stability Improvement

  Using cross-linker

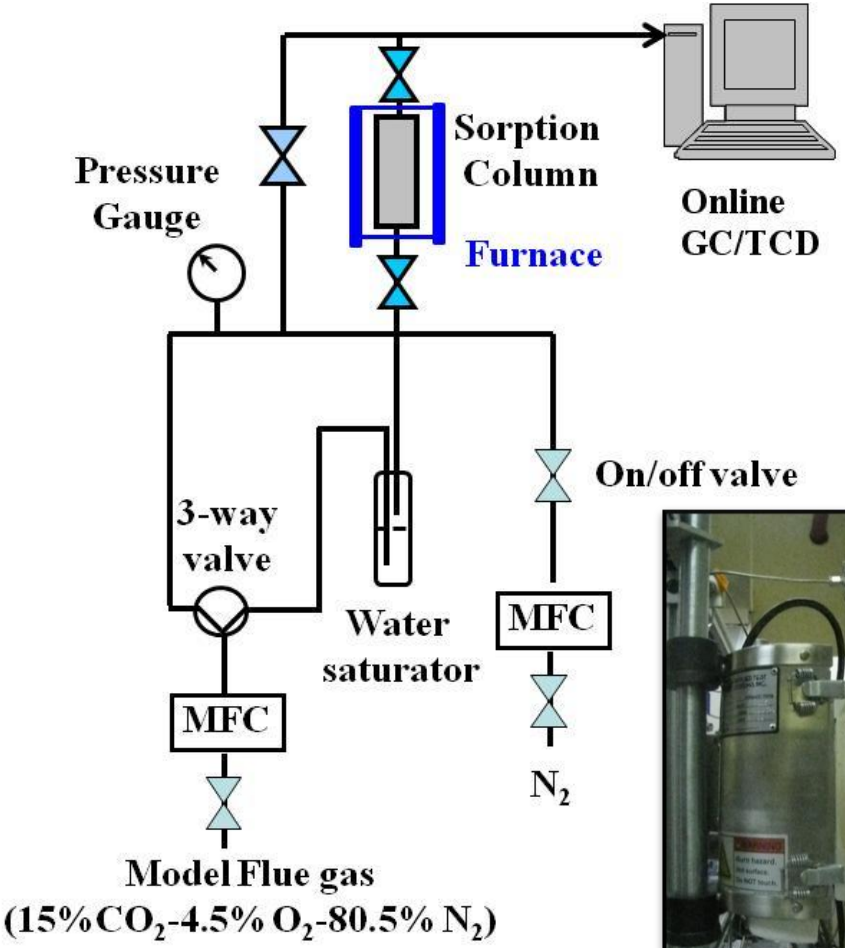
Project Technical Approaches

- Using cheaper nanoporous materials to replace SBA-15 and MCM-41 to reduce the cost for the sorbent
  - Silica-gel
  - Fumed silica
  - Carbon
- Using cross-linkers to improve the thermal stability & regenerability of MBS via chemical bonding



Inter-molecular bonding via cross-linking

CO_2 Sorption Evaluation System

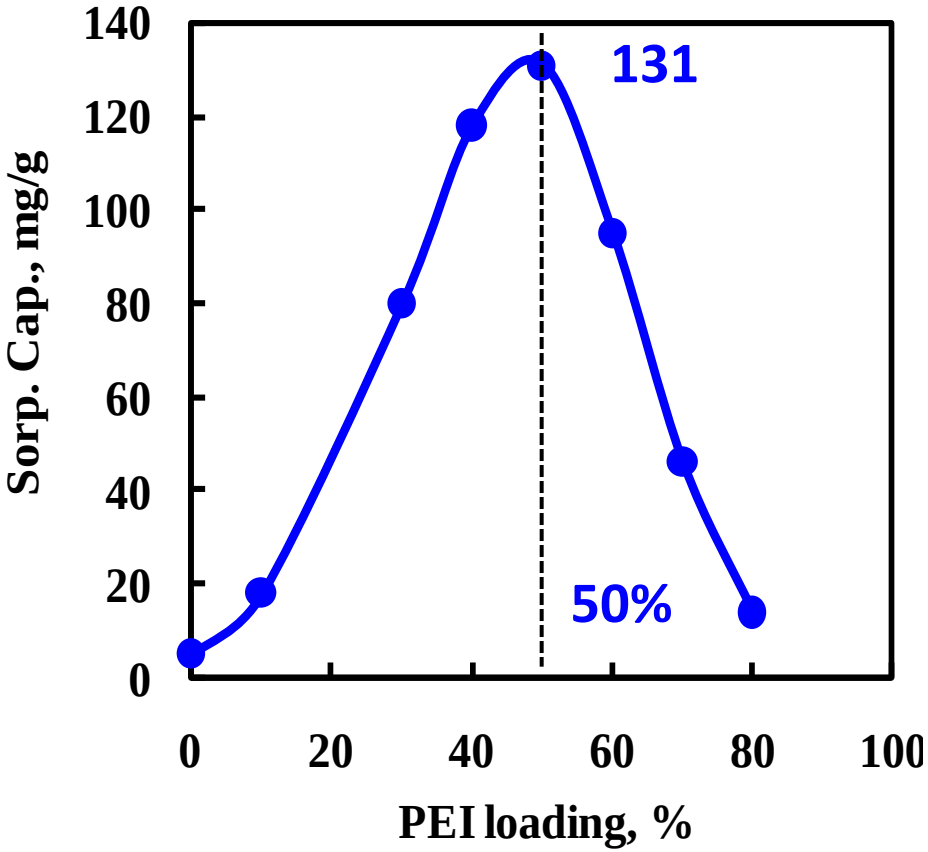


Flow system

TGA system

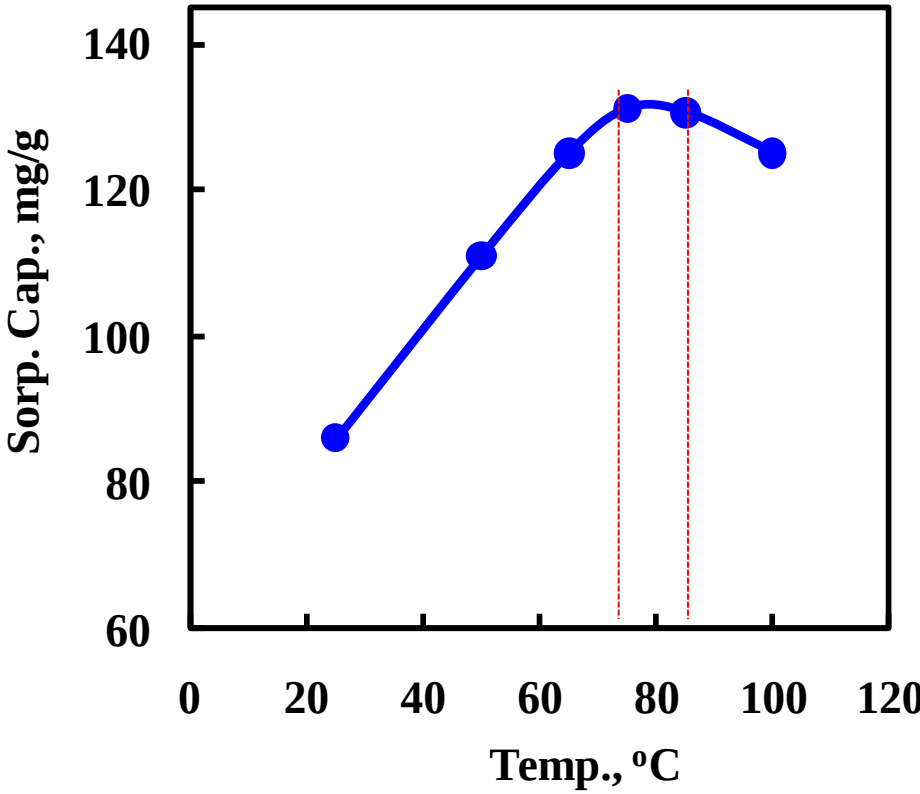
Silica-gel-based MBS

Effect of PEI loading



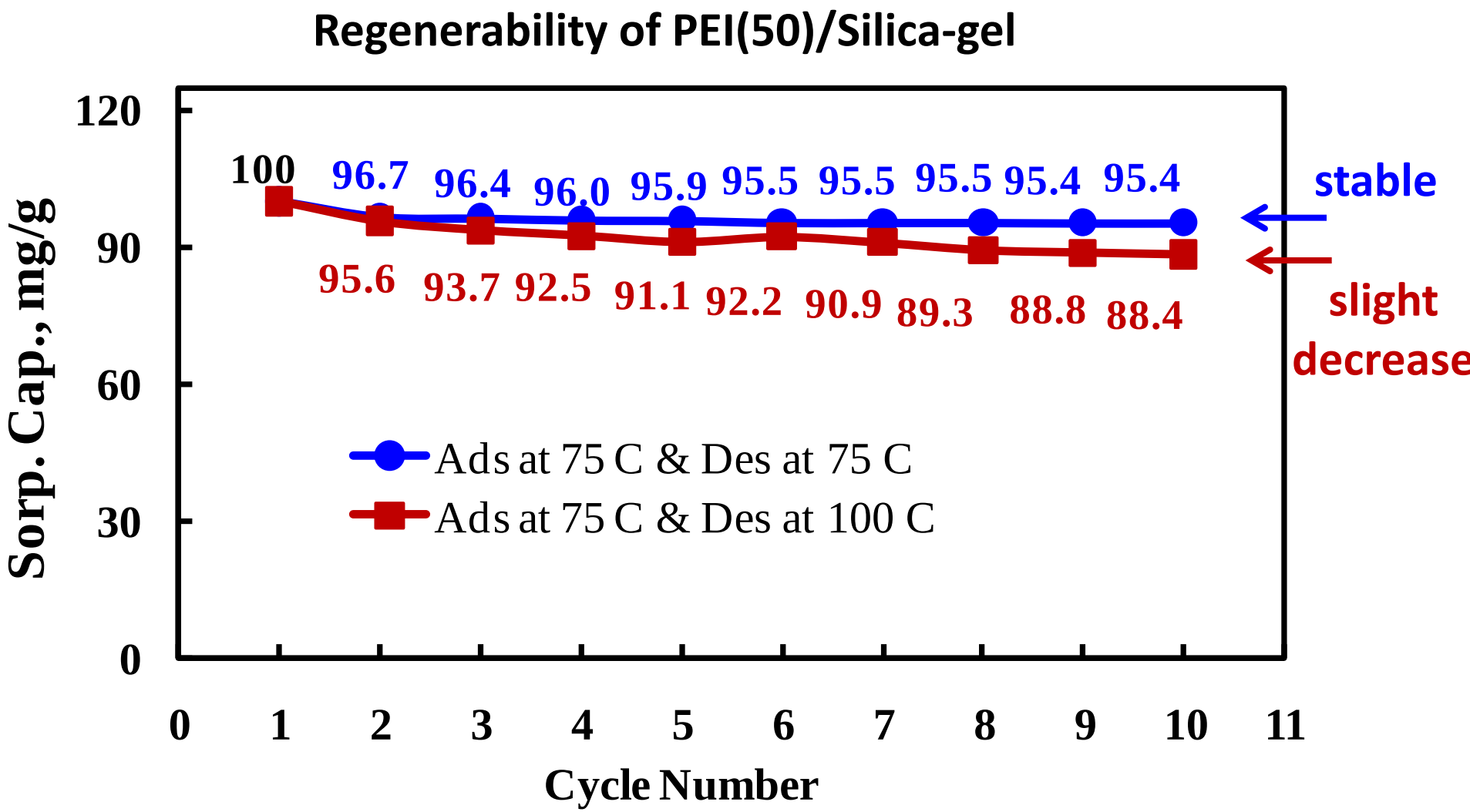
at 75 °C

Effect of Sorp. Temp.



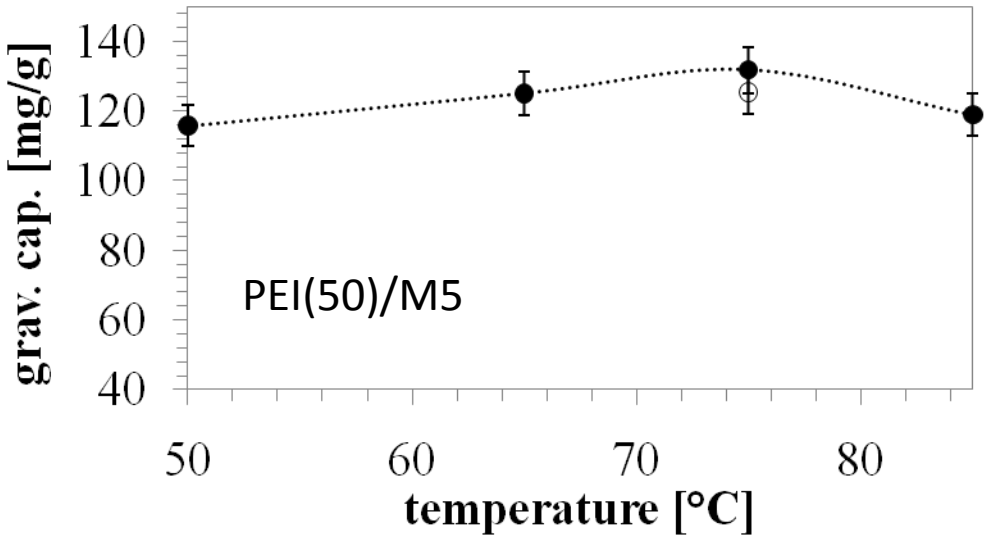
PEI(50)/Silica-gel

Silica-gel-based MBS

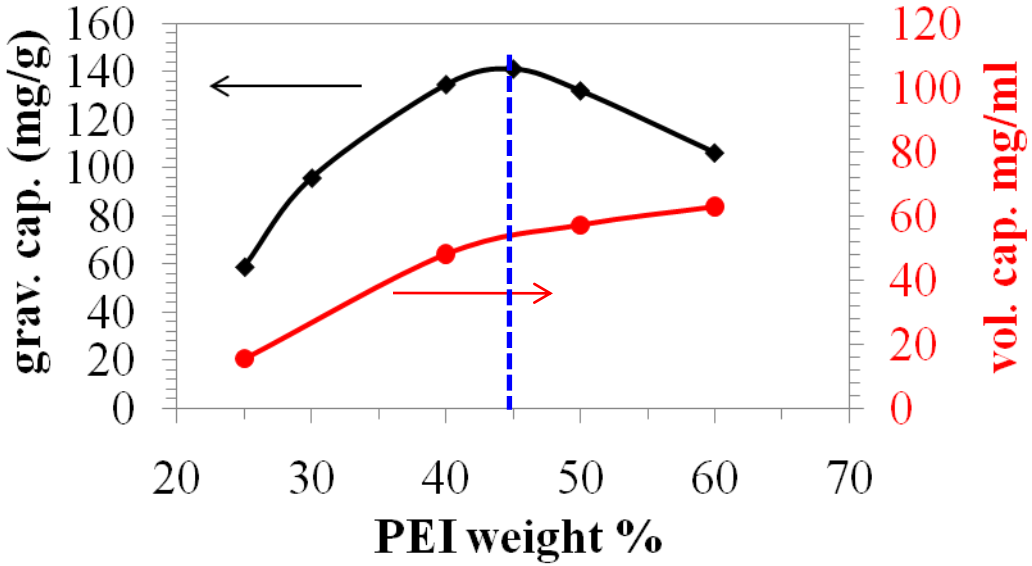


Fumed-silica-based MBS

Effect of Sorption Temperature & PEI loading



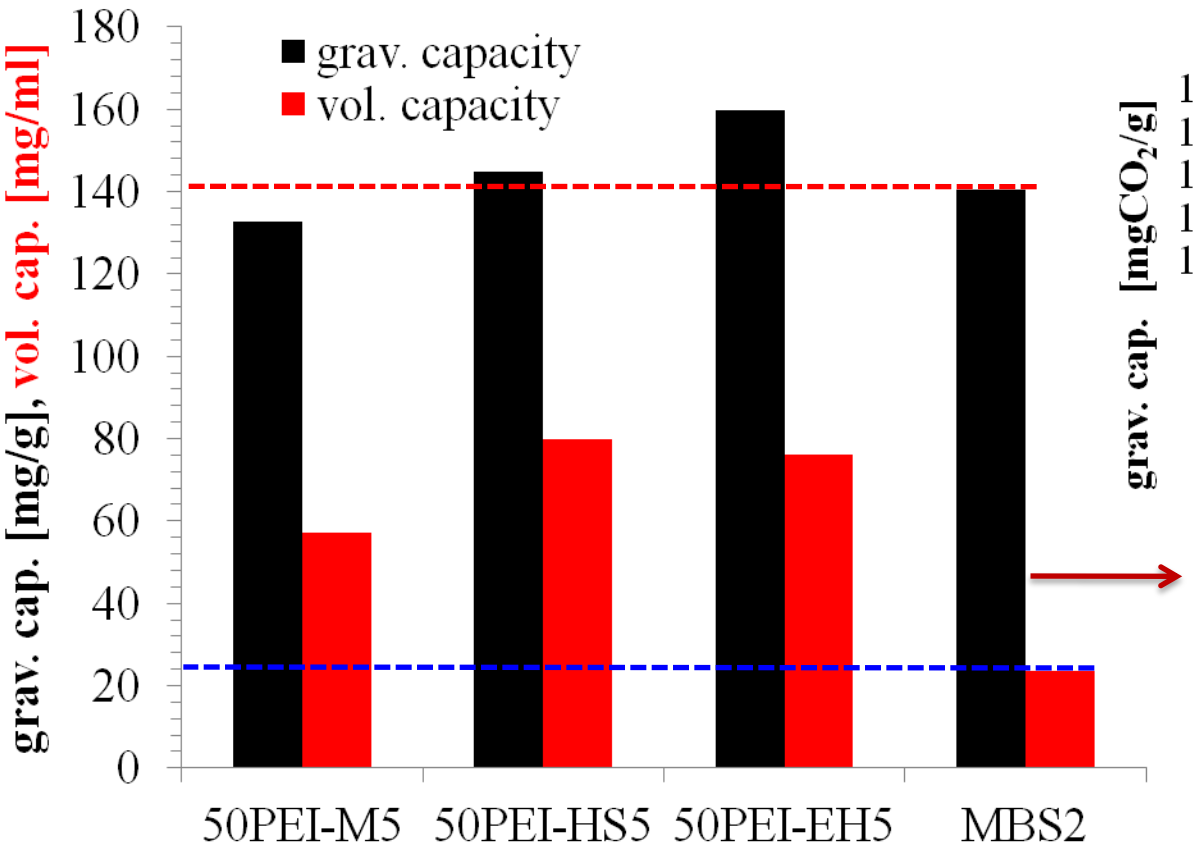
Best Temp Ads ~ 75 °C

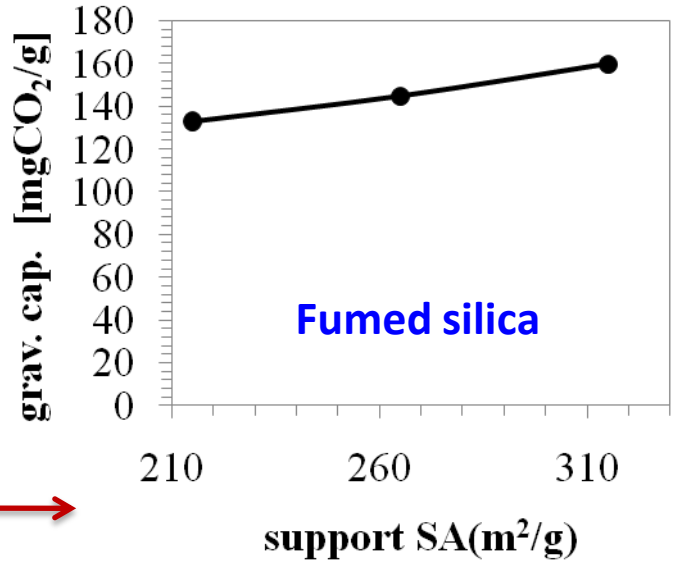


Best Loading ~ 45%

Fumed-silica-based MBS

Effect of Different Fumed Silica Support

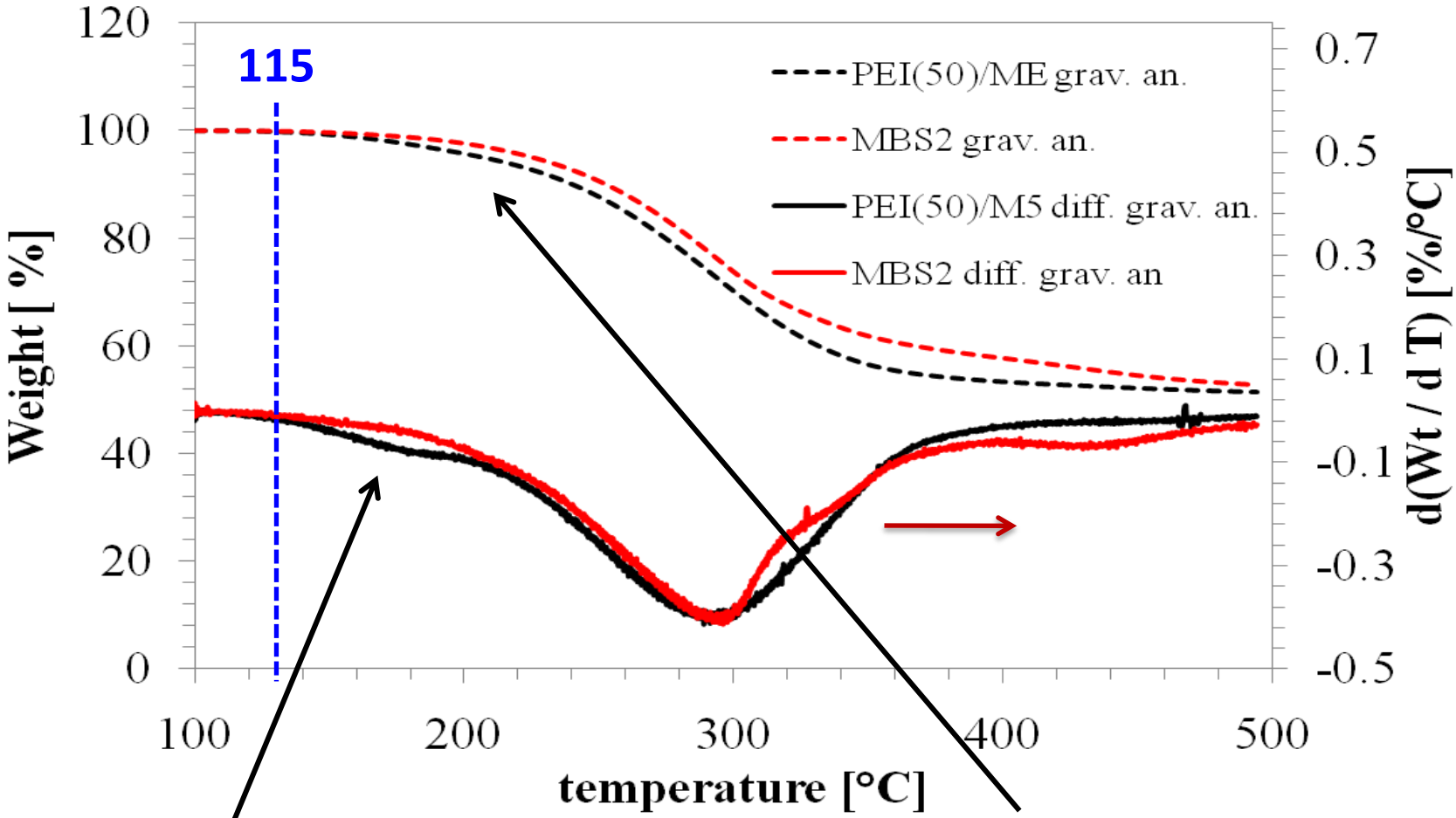




- High gravimetric sorption capacity
- Higher packing density
- Much higher volumetric sorption capacity (2-3 times of MBS-2)

Fumed-silica-based MBS

Thermal Stability by TGA

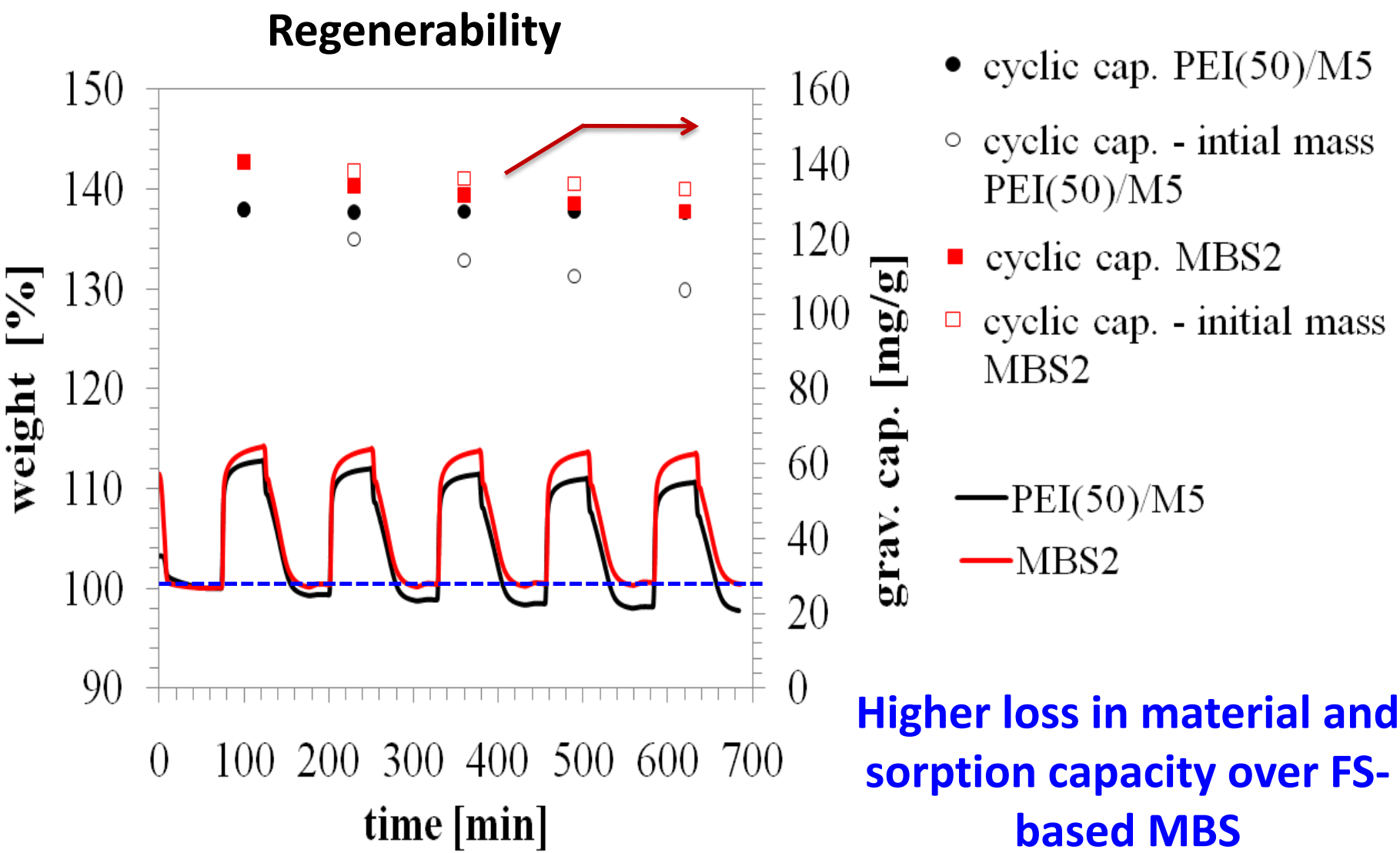


Early on-set of mass loss for PEI(50)/M5

5 wt% mass loss

- 207 C for PEI(50)/M5
- 225 C for MBS2

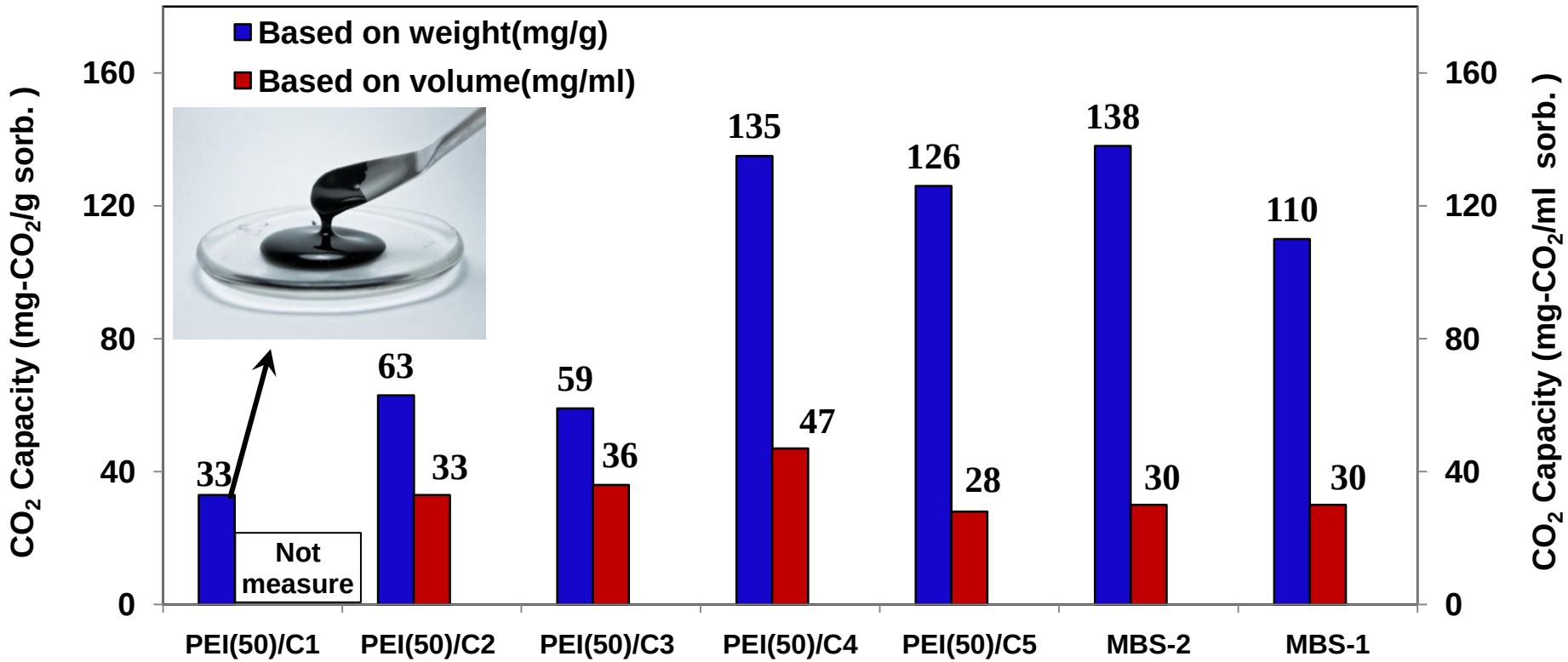
Fumed-silica-based MBS



Higher loss in material and sorption capacity over FS-based MBS

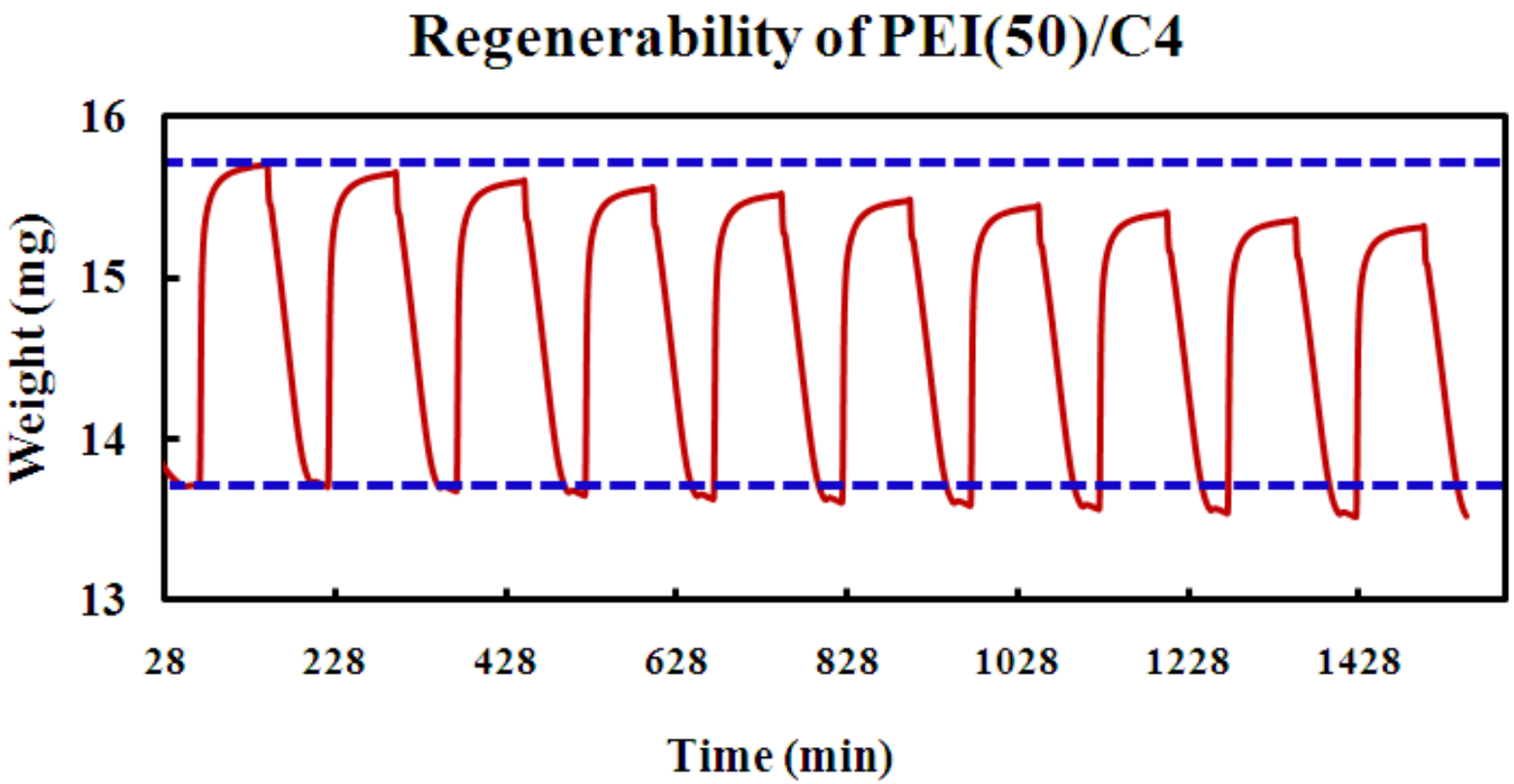
Carbon-based MBS

Effect of different carbon support



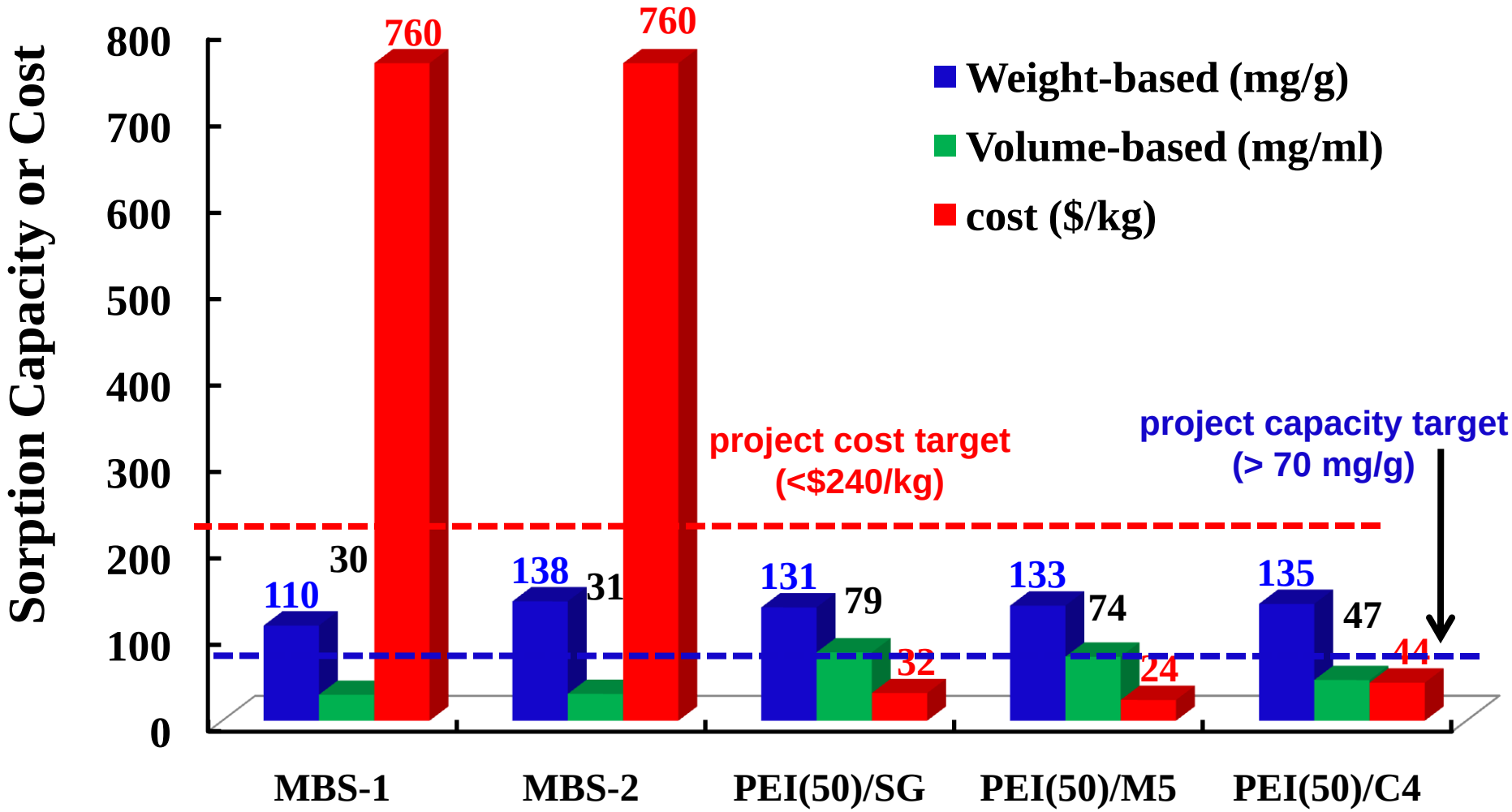
- Type of C material affects the CO_2 sorption capacity
- PEI(50)/C4 gave the highest CO_2 capacity among CB-MBSs and higher volume-based CO_2 capacity than that of MBS-2

Carbon-based MBS



- Slight reduction in material weight and CO_2 sorption capacity during 10 runs is observed
- > 95% sorption capacity of PEI(50)/C4 can be recovered after 10 cycles

Performance and Cost Comparison

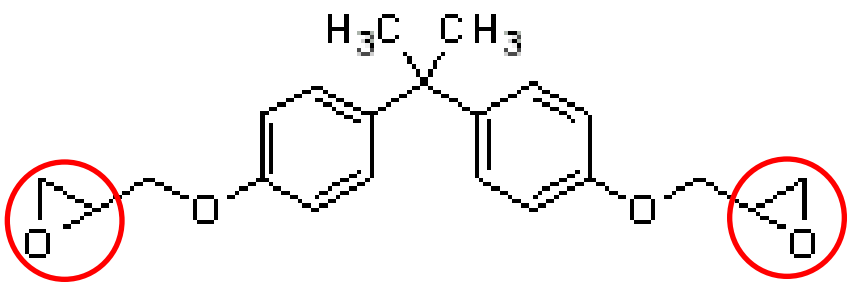


*MCM-41: Sigma-Aldrich, $452.00/25 g (8/2011); PEI: Sigma-Aldrich, $280/kg (8/2011)

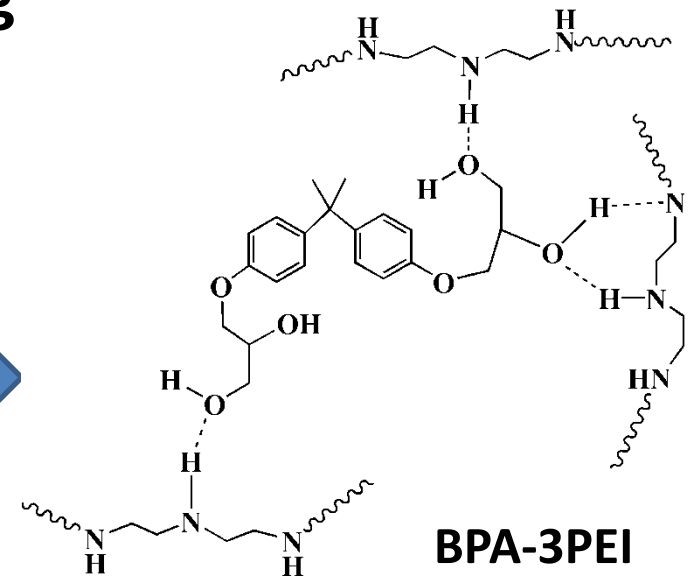
Thermal Stability Improvement

PEI-crosslinking

Bisphenol A Diglycidyl Ether (BPA)

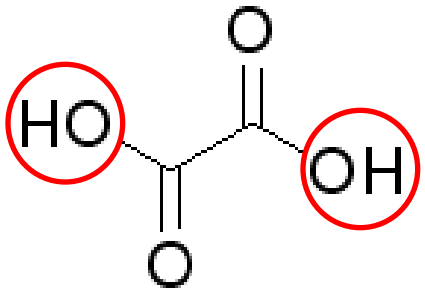


PEI

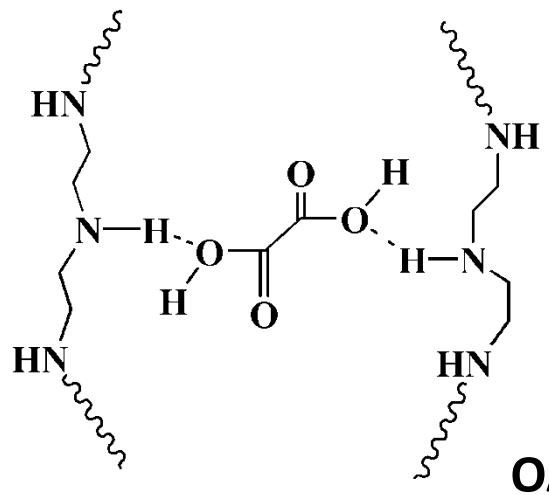


BPA-3PEI

Oxalic acid (OA)



PEI

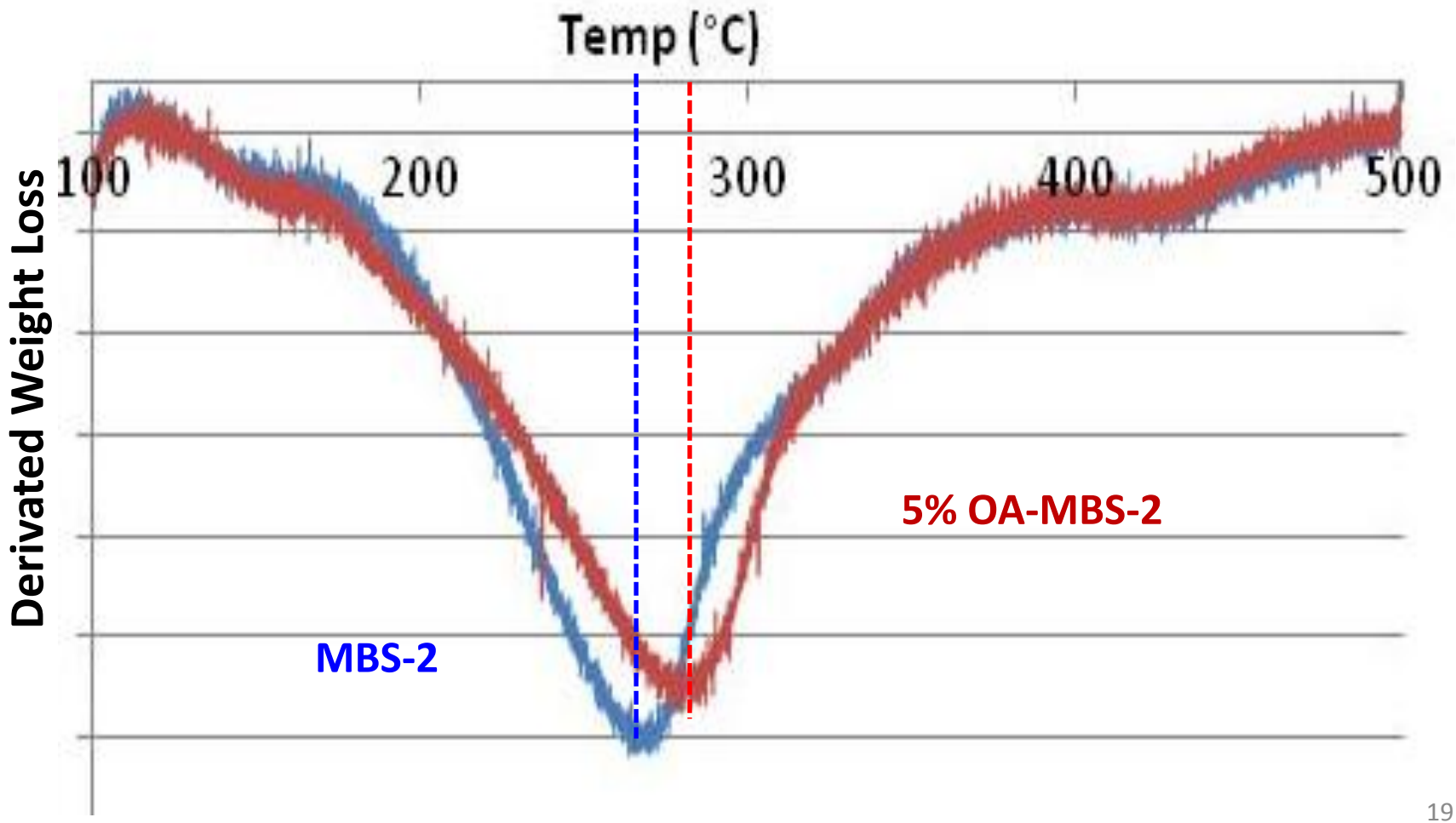


OA-2PEI

Thermal Stability Improvement

OA cross-linked PEI sample

Thermal Stability by TGA

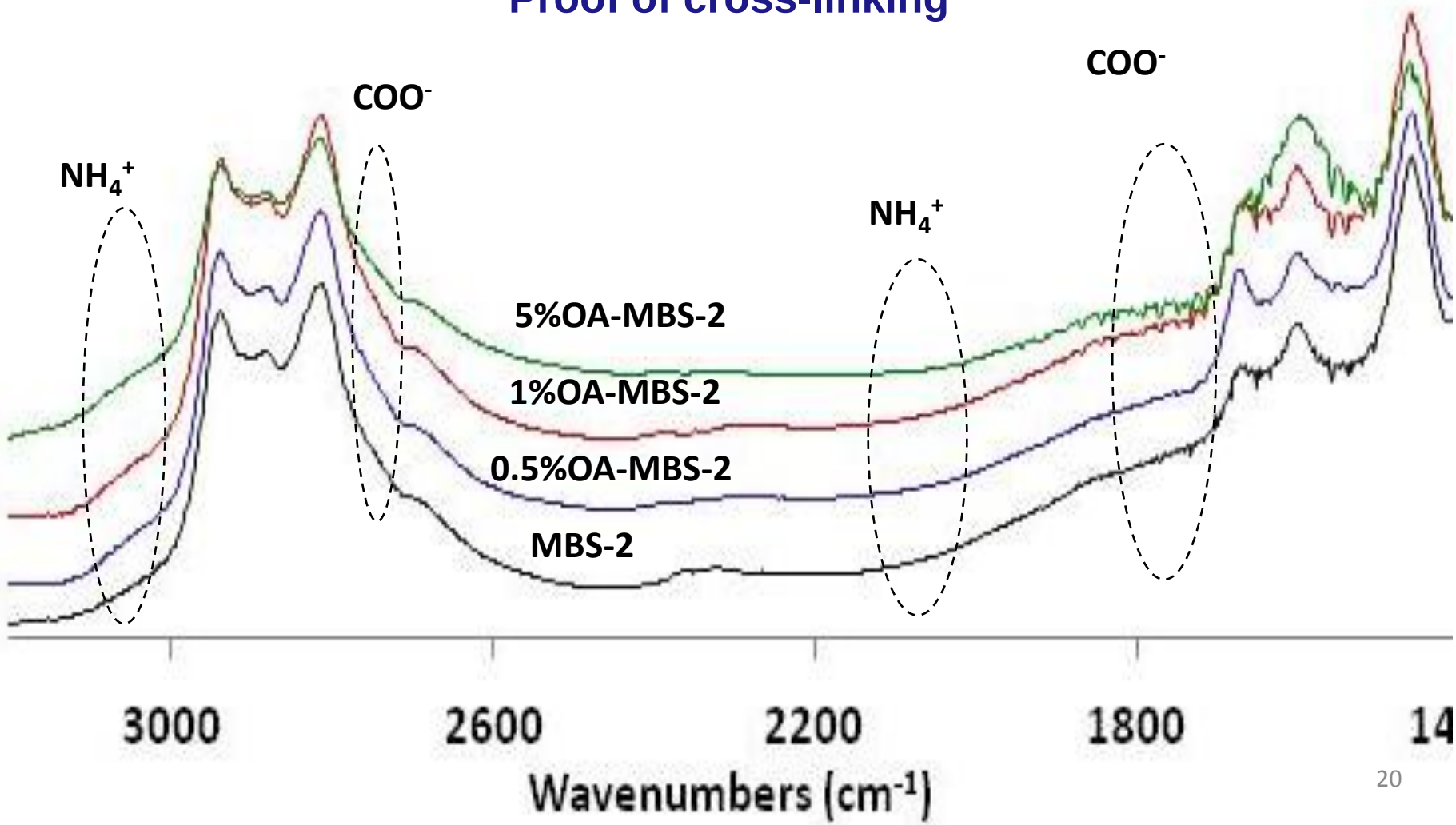


Thermal Stability Improvement

OA cross-linked PEI sample

DRIFTS of OA-MBS-2

Proof of cross-linking

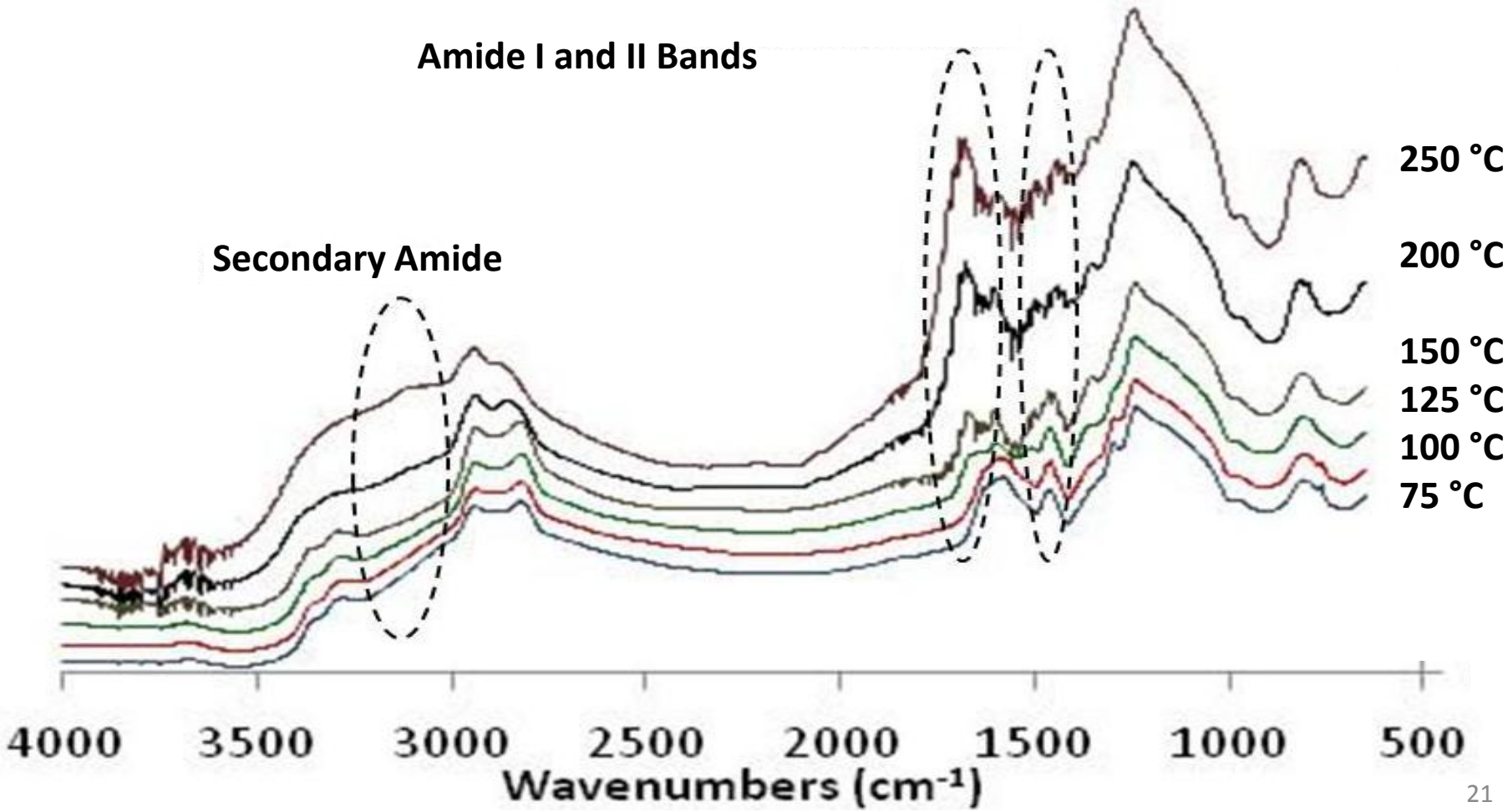


Thermal Stability Improvement

OA cross-linked PEI sample

DRIFTS of 5% OA-MBS-2

Effect of treat temperature



Thermal Stability Improvement

Computational Calculations

- **Method:**

  AM1* method in the module of VAMP in Material Studios

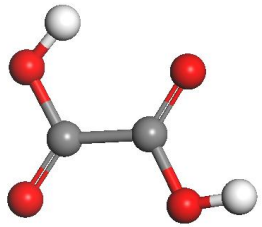
- **The pseudo heat for cross-linking:**

$$\Delta H_{\text{cross-linking}} = \Delta H^{\circ}_{\text{f, diacid-PEI}} - (\Delta H^{\circ}_{\text{f,PEI}} + \Delta H^{\circ}_{\text{f,diacid}})$$

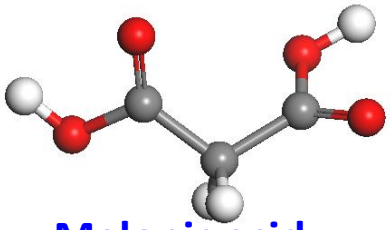
- **The pseudo heat for CO_2 sorption**

$$\Delta H_{\text{sorption}} = \Delta H^{\circ}_{\text{f, CO2-PEI}} - (\Delta H^{\circ}_{\text{f,PEI}} + \Delta H^{\circ}_{\text{f,CO2}})$$

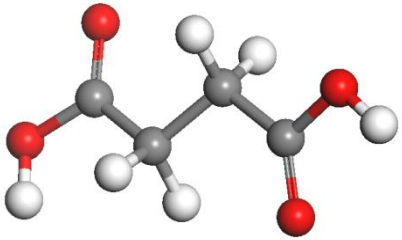
- **Configuration of diacids:**



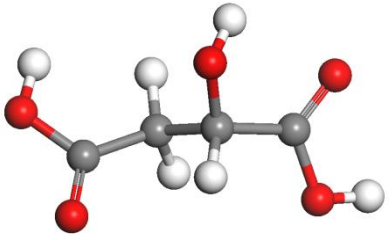
Oxalic acid (OA)



Malonic acid (propanedioic acid)

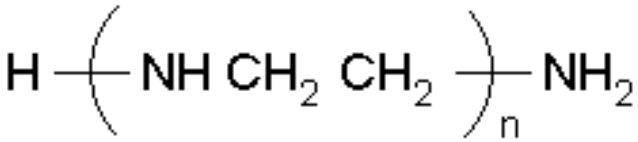


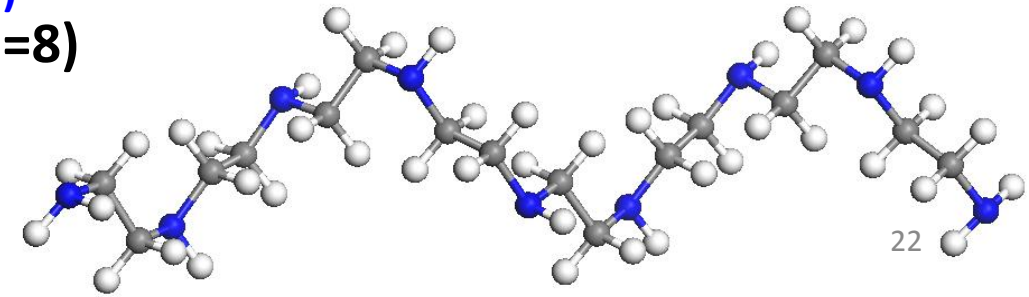
Succinic acid (butanedioic acid)



D/L-Malic acid (hydroxybutanedioic acid)

- **Configuration of linear PEI (n=8)**





Thermal Stability Improvement

Computational Calculations

Effect of diacid structure on cross-linking

	$\Delta H_{\text{cross-linking}}$ (kcal/mol)
Oxalic acid (C2) - 2PEI	-7.66
Malonic acid (C3) - 2PEI	-8.89
Succinic acid (C4) - 2PEI	-7.94
DL-Malic acid (C4-OH) - 2PEI	-5.51

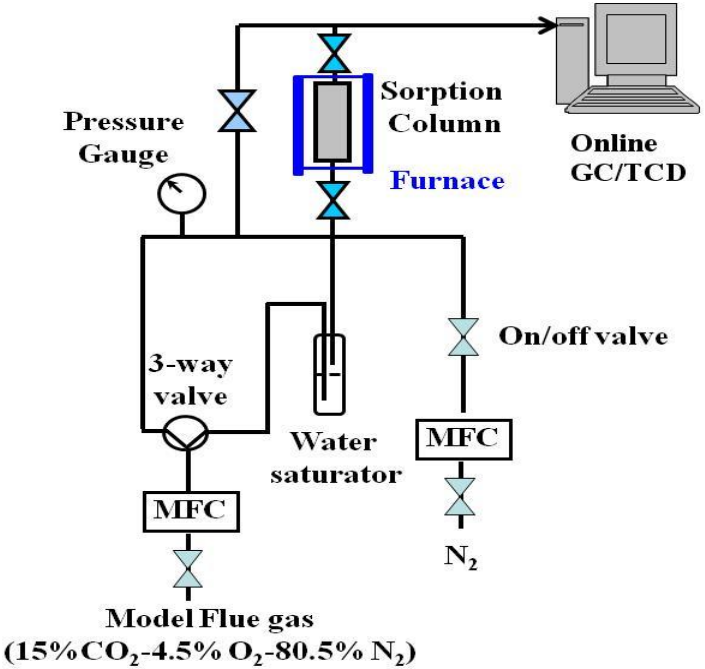
Effect of cross-linking on CO_2 sorption

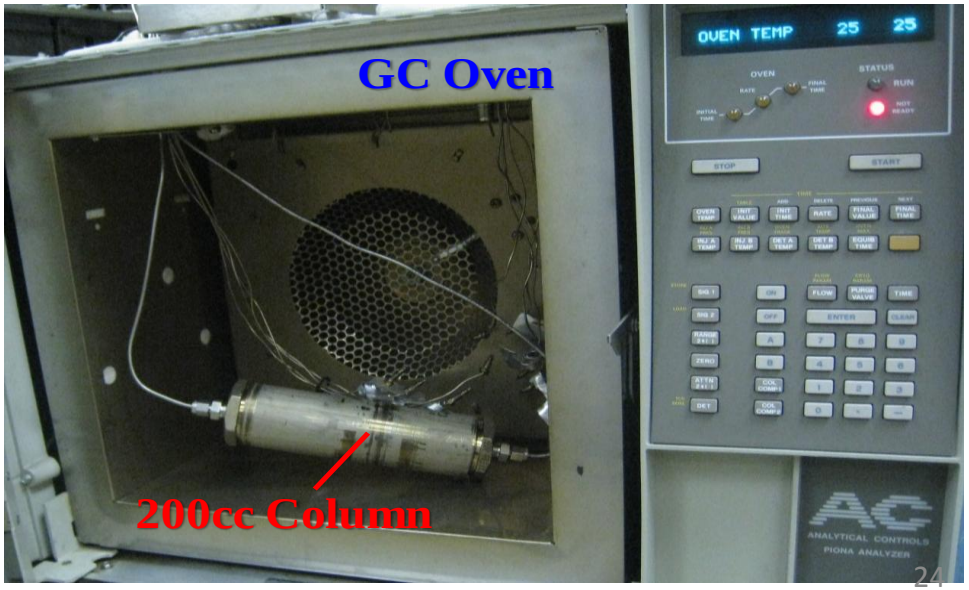
	$\Delta H_{\text{sorption}}$ (kcal/mol)
PEI	-2.83
Oxalic acid - 2PEI – CO_2	-3.10
Malonic acid - 2PEI – CO_2	-3.21
Succinic acid - 2PEI – CO_2	-3.66
DL-malic acid - 2PEI – CO_2	-5.10

Scale-up Test Using MBS-2

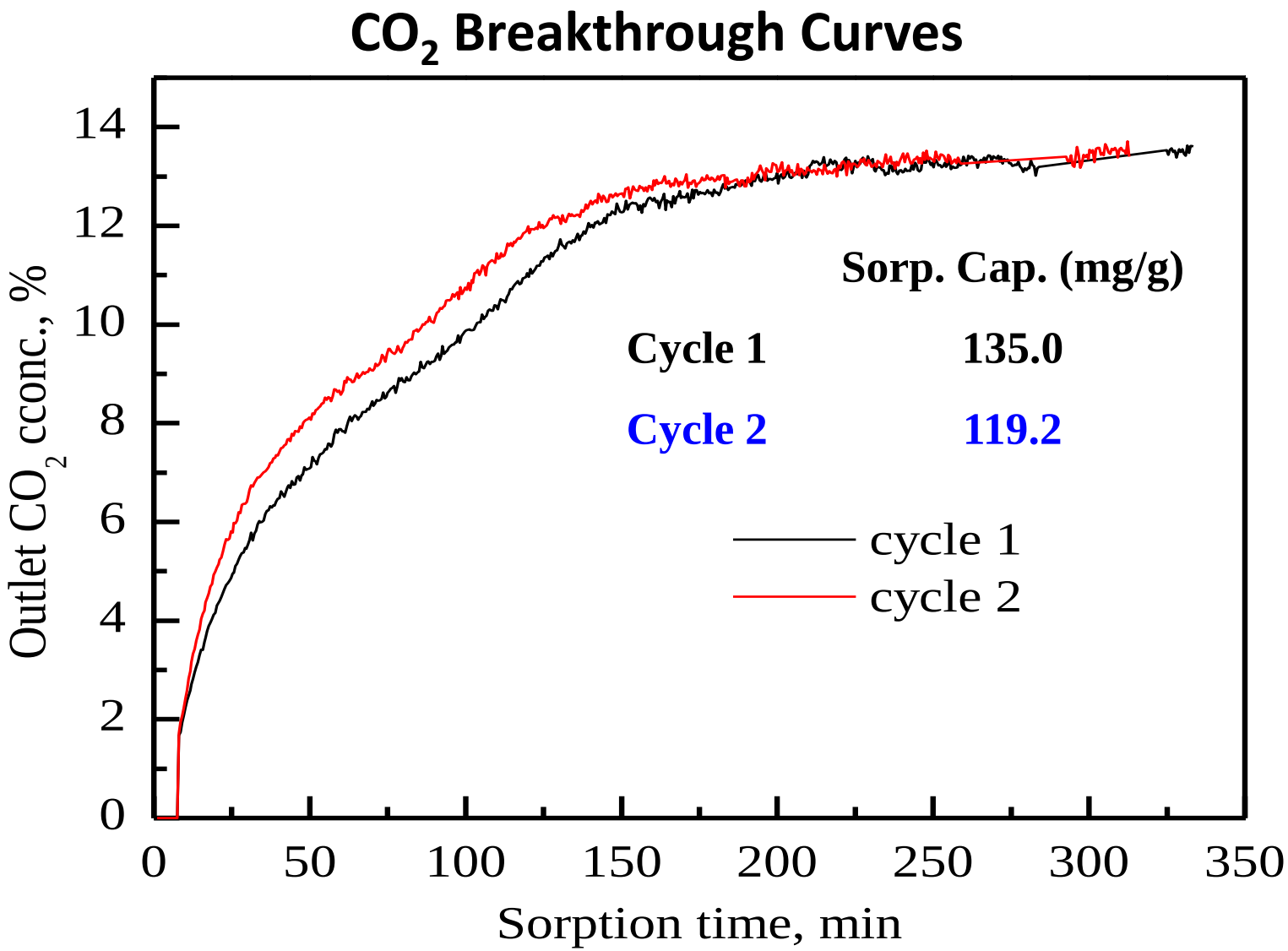
PEI/SBA-15
powder

PEI/SBA-15
10-18 mesh pellets





Scale-up Test



Conditions: V, 200 mL; W, 75 g; T, 75 C; F, 400 ml/min; Flue gas, 15%CO_2-4.5%O_2-80.5%N_2

Summary

- Compared to MBS-2, using silica-gel, fumed silica and carbon to prepare MBS is much cheaper, estimated to < $50/kg, while high sorption capacity can still be maintained at about 13-14wt%. However, the thermal stability of those materials is an issue.
- Primary experimental and computational results show that polymer cross-linking is a possible and promising way to improve the thermal stability of MBS.
- The 200 mL scale-up test has been conducted by using MBS-2, showing a good capacity for CO_2 capture from flue gas. Those cheaper MBSs show much higher volume-based capacity than MBS-2. Thus, better sorption performance may be achieved using these MBSs for scale-up test.

Current Status of Project

Schedule of Project Tasks (period: 9/1/09-8/31/12)	2009-2010	2011												2012									
		Q 1			Q 2			Q 3			Q 4			Q 1			Q 2			Q 3			
		1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10
Task 1. Project Management																							
Task 2. Development of new MBS for CO2	a b				c																		
Task 3. Computational chemistry approaches	b								c														
Task 4. Thermal stability improvement																					h		
Task 5. Scaling up the process and demonstration									d														
Task 6. Conducting the techno-economic analysis																							
Deliverables:																							
1. Formula of new MBS for CO2									e														
2. Process conceptual design									e														
3. Periodical and final reports	f f f f			f			f			f			f			f			f			f	g

Milestones

a: Provide primary results in development of MBS for CO2 capture **Complete**

b: Provide primary results in computational calculations **Complete**

c: Completethe development of MBS for CO2 capture with working capacity of > 70 mg-CO2/g-S **Complete**

d: Complete the scale-up CO2 sorption process using MBS

e: Provide the formulation of MBS and concept process for CO2 capture from flue gas

f: Provide the quarterly technical & budgetary reports

g: Provide the final technical report

On schedule

h: Complete the improvement of the thermal stability of MBS, as measured by 90% reduction in loss of the sorbent capacity after 10 repeated cycles

Future Plans

- Fume-silica based MBS will be prepared in a large quantity for scale up test.
- Conduct 200 ml scale-up test using fumed silica based MBS for CO_2 capture from flue gas.
- Further investigate the improvement of thermal stability of MBS via both experimental and computational approaches.
- On the basis of the data generated from this project, a possible process including sorption and regeneration steps for CO_2 capture from flue gas will be proposed.

Acknowledgment

- The work is supported by DOE through National Energy Technology Laboratory (Award DE-FE0000458)
- DOE Project Manager, Andrew O'Palko for his time, management and valuable discussions and suggestions on this project.
- Support from EMS Energy Institute of the Pennsylvania State University

Thank you for your attention

Question?