Metal Monolithic Amine-grafted Zeolites for CO_2 Capture

Steven S. C. Chuang
Department of Chemical and Biomolecular Engineering
The University of Akron
Akron, OH 44325-3906 USA

Acknowledgment: Project Manager: Tim Fout

Students: J. Fisher and J. Tanthana

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Fuel Cell and Catalysis Lab at The Univ. of Akron

Fuel Cell and Catalysis Lab,
(Pending) First Energy Adv Research Center,
Steven Chuang, PhD '85, University of Pittsburgh
Mary Ann Breslin - Secretary

CO_2 Capture

- Lab - Scale Adsorbant Testing
- Scale - up Adsorbant Testing
- Automated Process Testing
- Mechanical Fabrication

Khalid Almusaiteer, PhD '99 (Chem E),
University of Akron, Visiting Professor
Baodong Wang,PhD '07(Chemistry),Univ.College London
Kamil Gierszal , PhD' 07 (Chemistry), Kent State University
Jak Tanthana , 3rd Year PhD (Chem E) Student (50%)
James Fisher, 4th Year PhD (Chem E) student
Chris Wolfgang, 1st Year MS (Chem E) Student
Matt Isenberg, 1st Year MS (Chem E) Student (50%)
Matt Augustin, Senior (Mech E)

Fuel Cell

- Fuel Cell Fabrication
  - Tape Casting
  - Lamination
  - Screen Printing
- Fuel Cell Testing
- Mechanical Fabrication

Rahul Singh, PhD '08 (Chem E),
University of Akron, Research Scholar
Felipe Guzman, 5th Year PhD (Chem E) Student
Tritti Siengchum, 2nd Year MS (Chem E) Student
Andrew Chien, 2 nd Year PhD (Chem E) Student
Tung Pattanapanishshwat, 1st Year MS (Chem E) Student
Jak Tanthana, 3rd Year PhD (Chem E) Student (50%)
Matt Isenberg, 1 st Year MS (Chem E) Student (50%)
Annie Chen, Sophomore (EE) Student

Brian Mohrman, Senior Year (Mech E)
Jeff Wilson, Senior (Mech E)
Richard Majesi, Freshman (Mech E)
Tim Gulatta, Junior (Mech E)
Dan Lough, Freshman (Mech E)

SO_2 Capture and $DeNO_x$ research

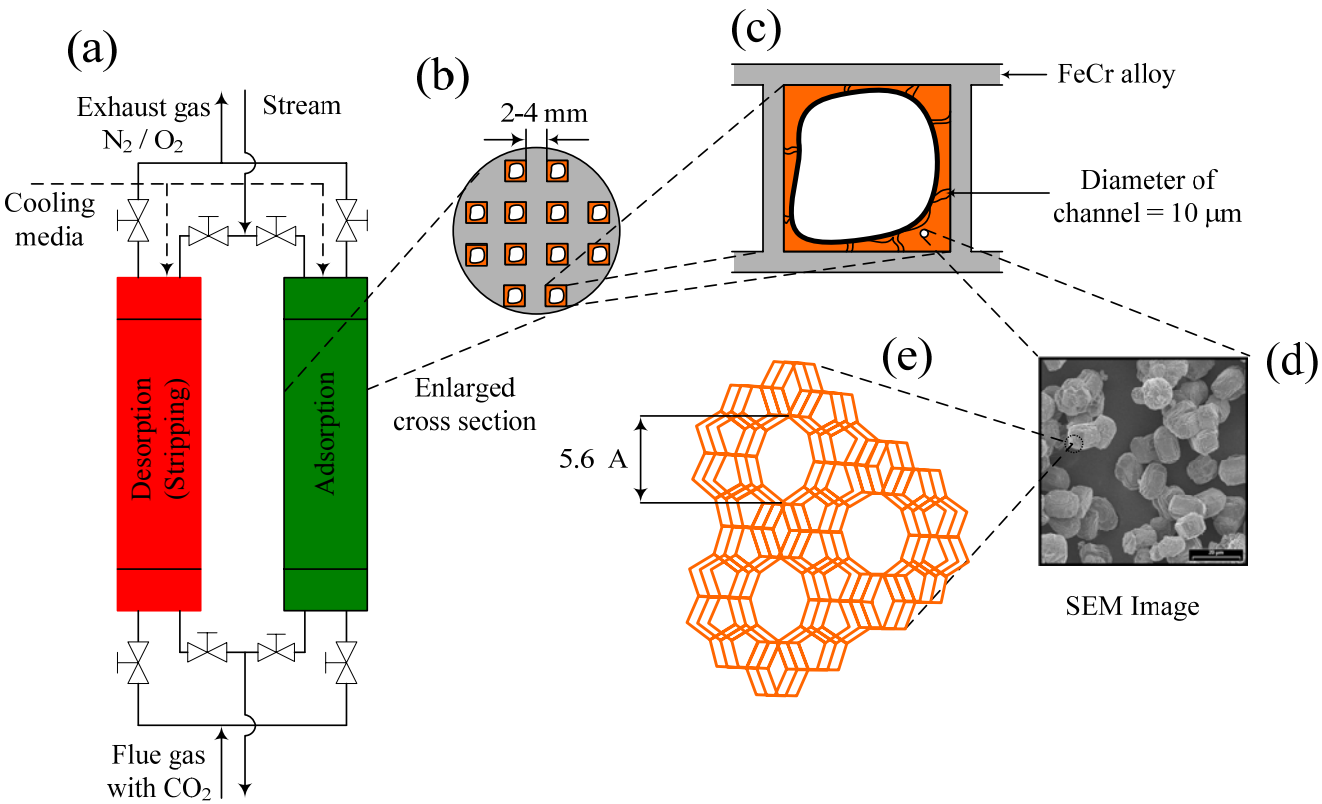
Duane D. Miller, 4th Year PhD (Chem E) Student

Project Overview

- Funding:
  - DOE: $764,964
  - The University of Akron: $192,838
- Date: 2/21/2007 – 2/20/2010
- Project participant: FirstEnergy
- Overall Project Objectives:
  - The objective of this project is to develop a low cost CO_2 capture technology by integration of metal monoliths with grafted amine sorbent.
  - Phase I objective: Develop highly efficient CO_2 absorbents.
    - The performance of the amine-grafted zeolite should be above 1,500 μmol/g for CO_2 capture and above 1,000 μmol/g for SO_2 capture.
  - Phase II objective: Develop a pilot scale CO_2 absorption system.

Technology Fundamentals/Backgrounds

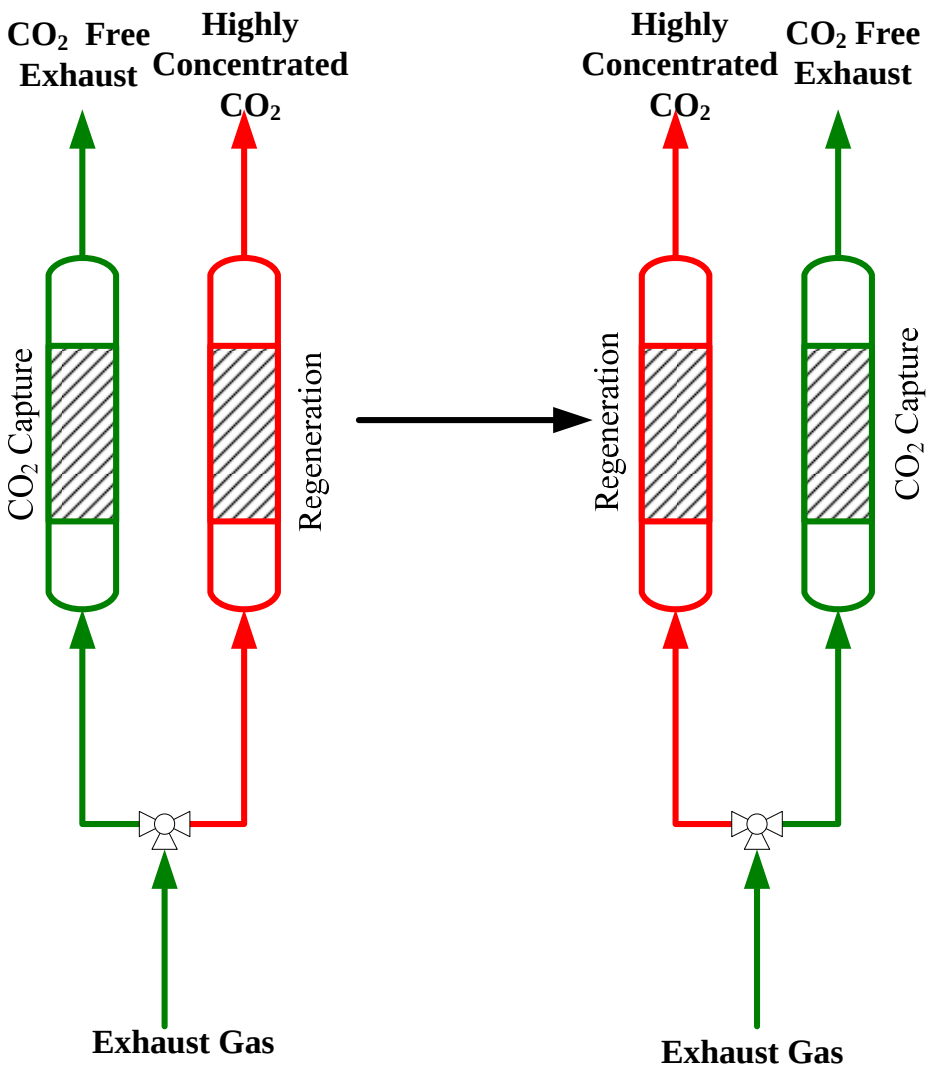
Metal Monolithic Amine-Grafted Zeolites for CO_2 Capture



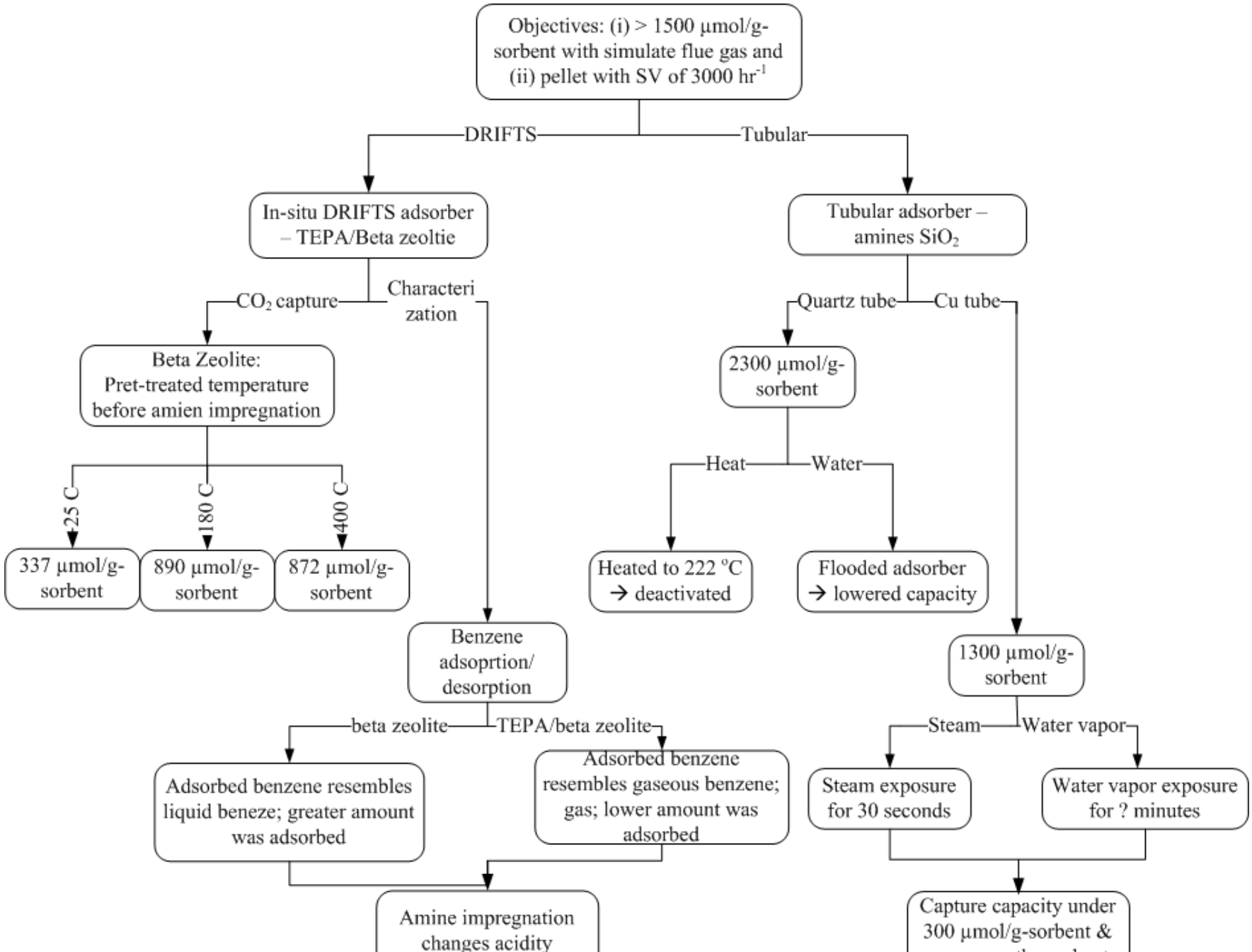
Unique features:

- High CO_2 adsorption capacity.
- Accelerated removal of the heat of adsorption.
- Low regeneration heat duty (i.e., low heat capacity of immobilized amine, zeolite, and metal monolith).
- Low cost immobilized amine sorbent.

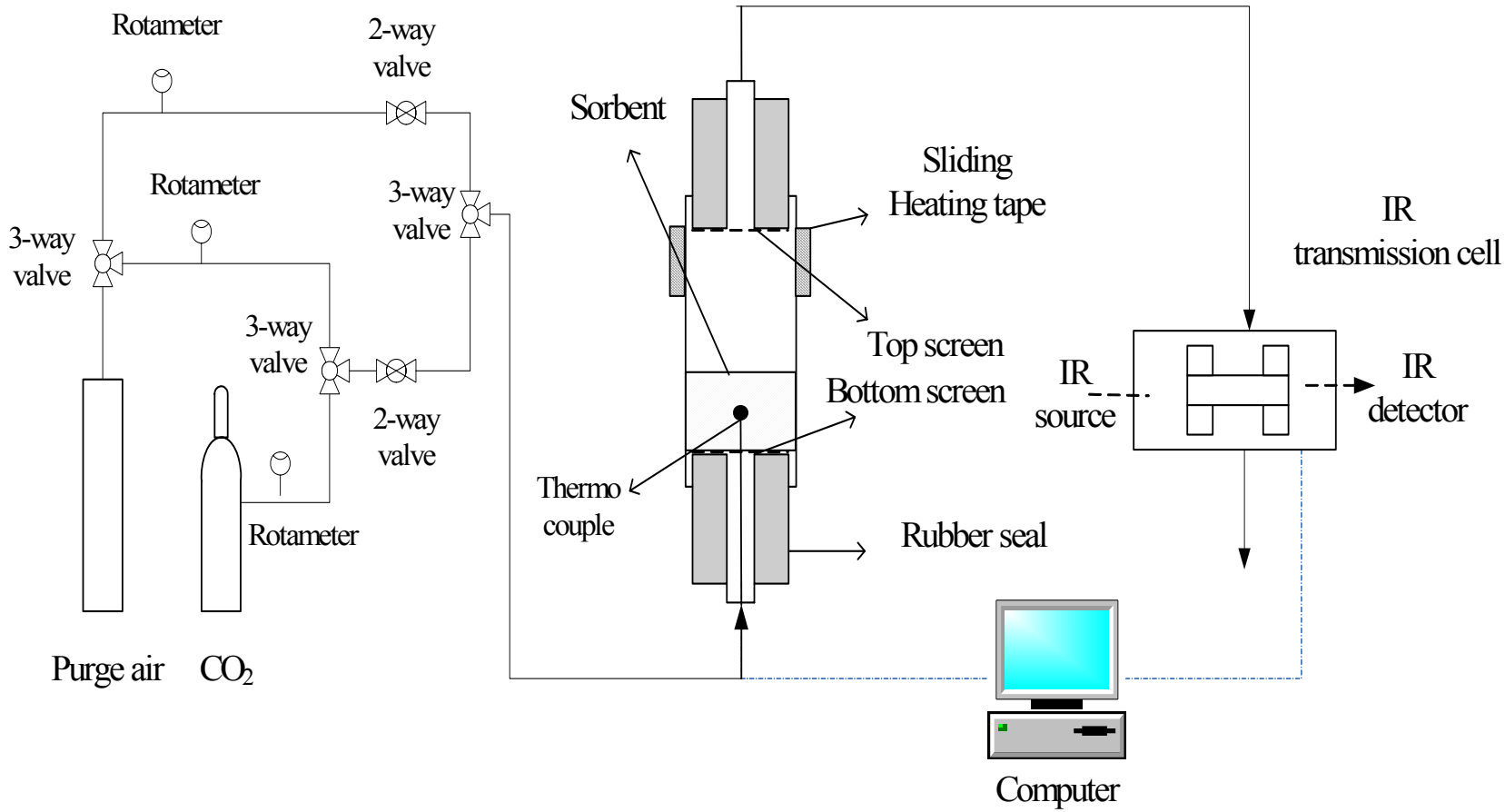
Thermal Cycling



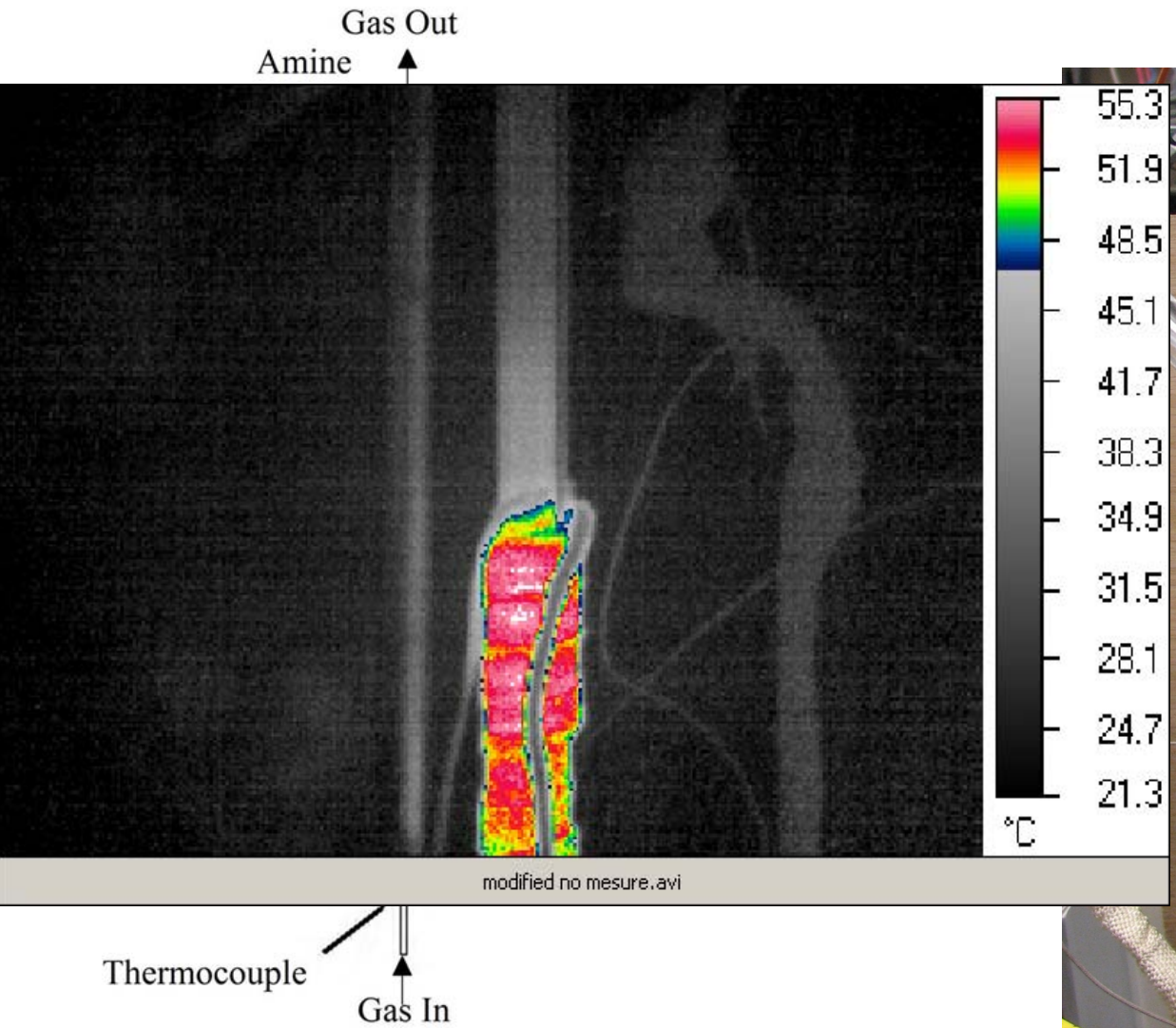
Progress and Current Status

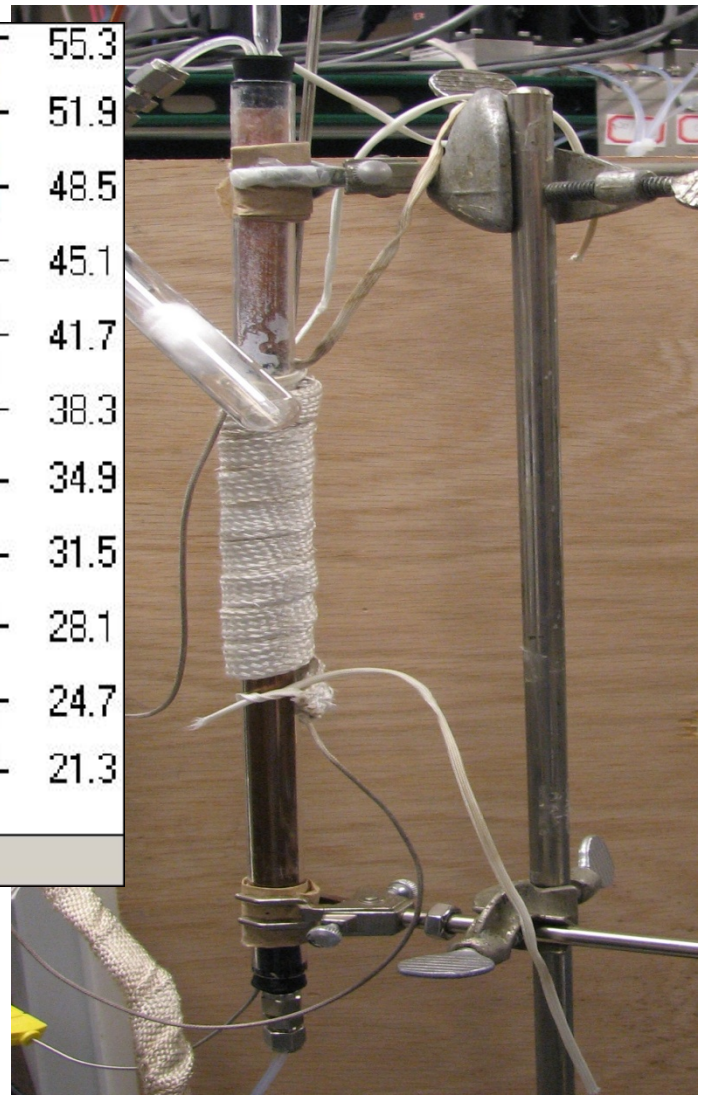


Tubular Testing

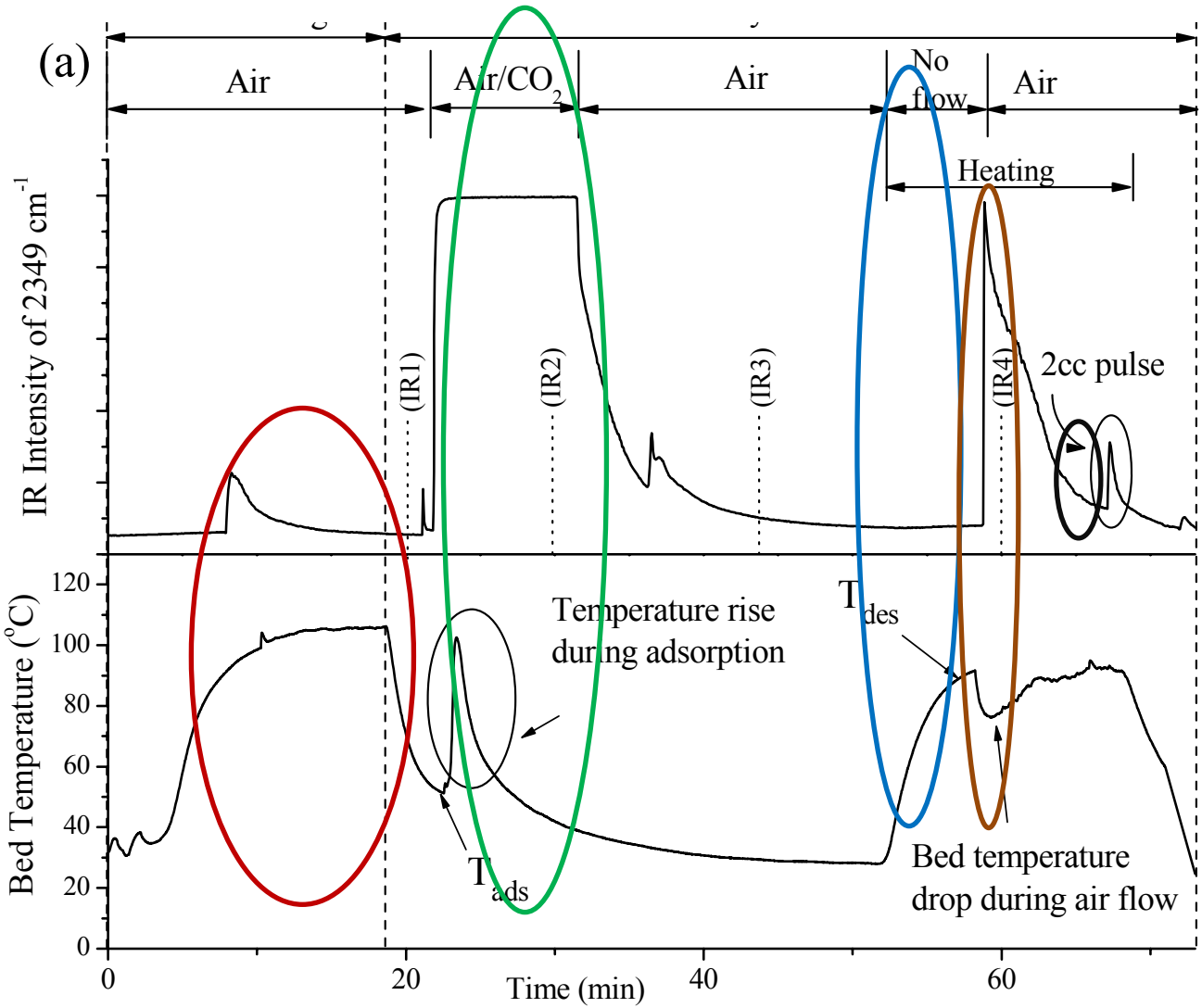


One gram scale tubular adsorber



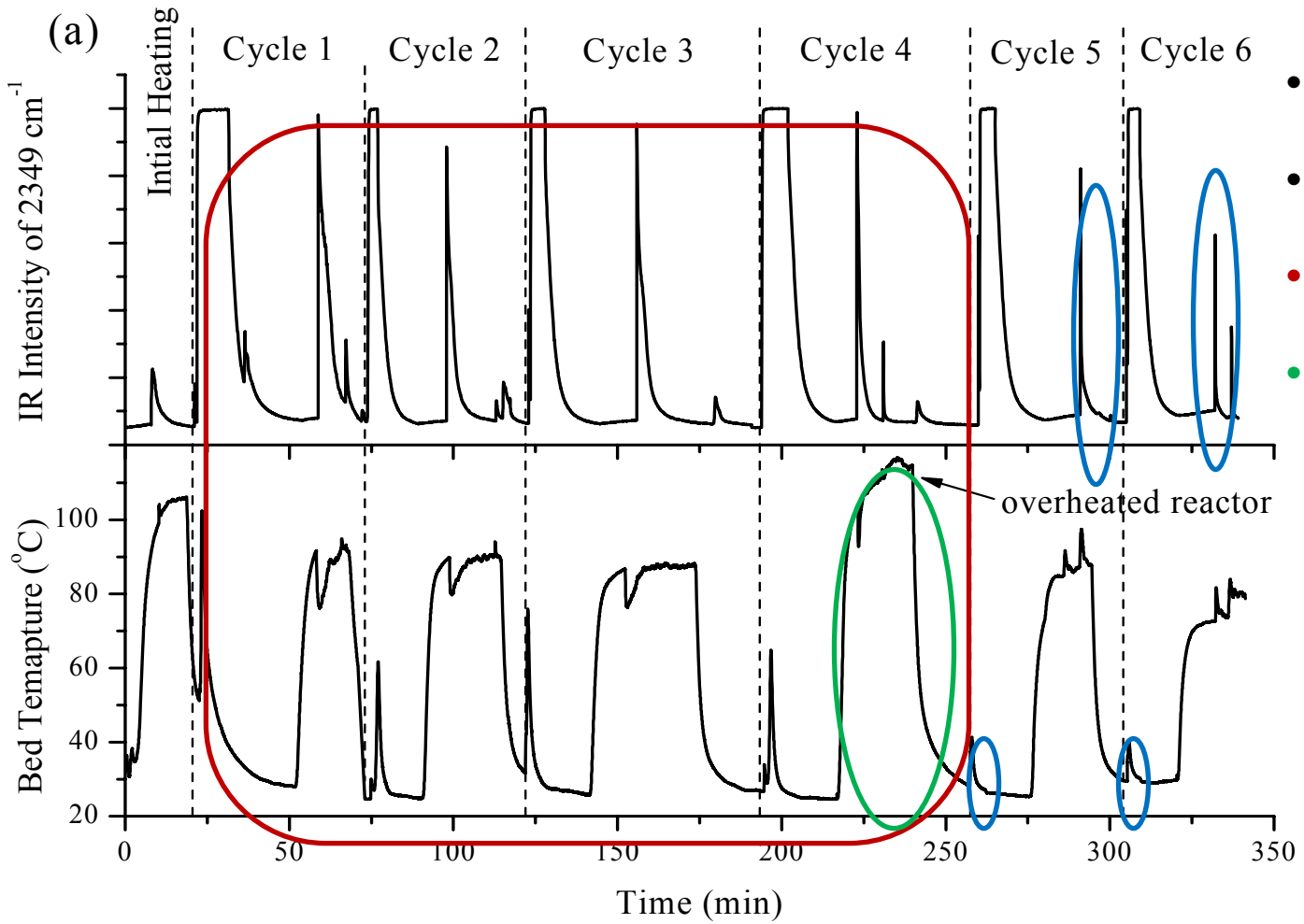


Cycle 1



- IR profile of 2349 cm^{-1}
- Bed temperature profile
- Initial heating released CO_2
- CO_2 adsorption resulted in temperature rise
- Flow was stopped
- External heating applied
- Flow resumed
- CO_2 pulse

Repeated Cycles



- IR profile of 2349 cm^{-1}
- Bed temperature profile
- Consistent desorption
- Cycle 4 – overheating
  - Decreased CO_2 capture capacity
  - Lowered temperature rise

Repeated Cycles

Cycle	μmol CO_2/ g-sorbent	Heat released	T_{ads} (°C)	T_{des} (°C)	T_{max} (°C)
---	2357	---	---	98	104
1	3941	69.4	29	91	91
2	4930	55.7	25	89	91
3	5956	61.7	24	86	88
4	2812	54.0	26	104	116
5	1151	14.4	28	84	97
6	502	15.1	26	72	80

Experimental Section: High Temperature Impregnation

Sample preparation

Start → Silica → (400 °C, 24 hr) → Solution → (150 °C, 8 hr) → Solid powder → (Sieved, 100 screen mesh) → Grafted samples

TEPA /EtOH → Solution: 5,10 and 20 wt%

5,10 and 20 wt% samples → Pre-treatment

CO_2 absorption-desorption study

Pre-treatment → CO_2 absorption → TPD → End

Pre-treatment: Ar; Heating rate = 10 °C/min; 50 → 135 → 50 °C

CO_2 absorption: Ar → CO_2 → Ar; 50 °C

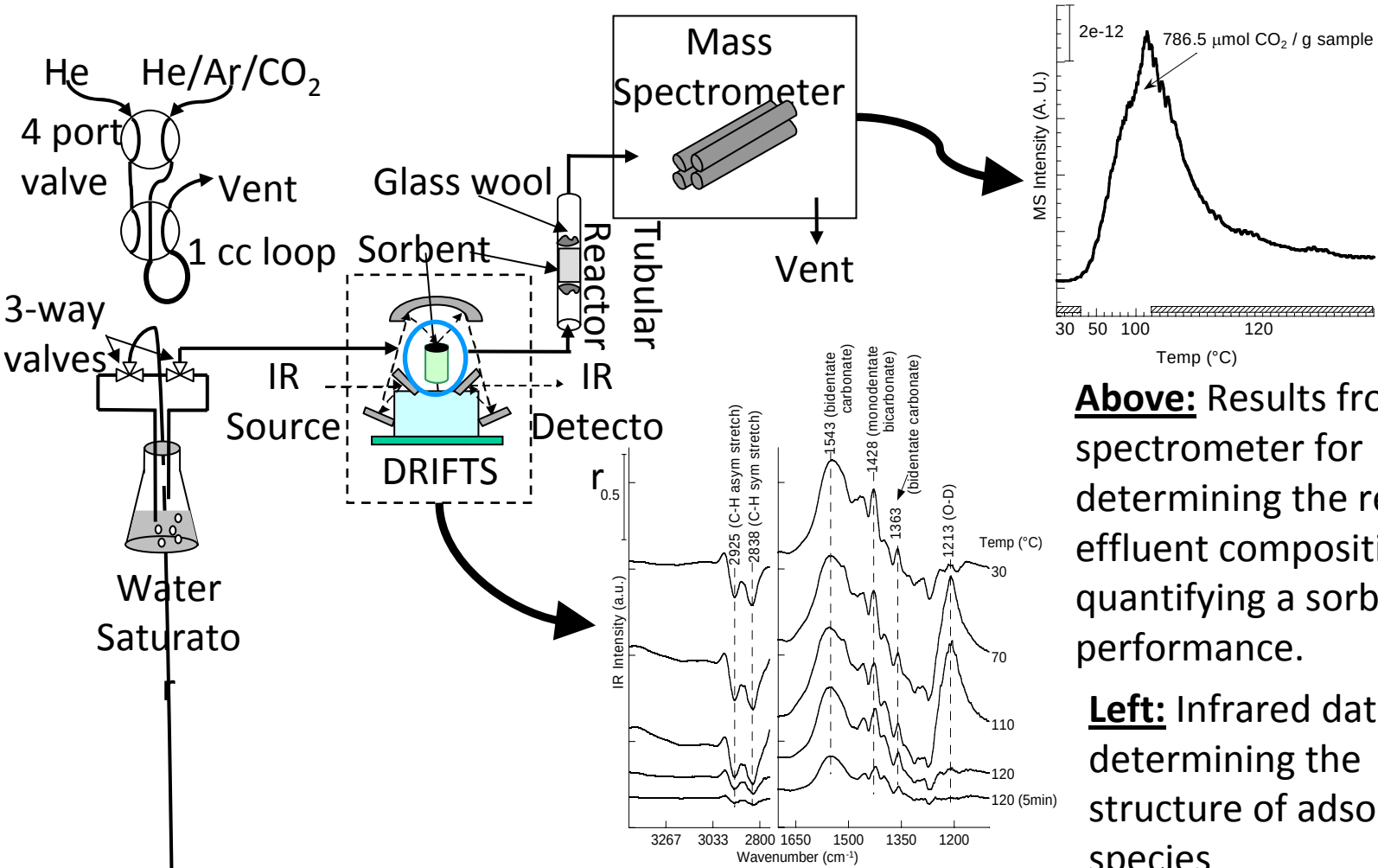
TPD: Ar; Heating rate = 10 °C/min; 50 → 135 → 50 °C

pH study

Acid/base treatment

10 wt% sample; Ar; 30 ul of 0.1 M HCl/ 15 M NH_4OH; 50 °C

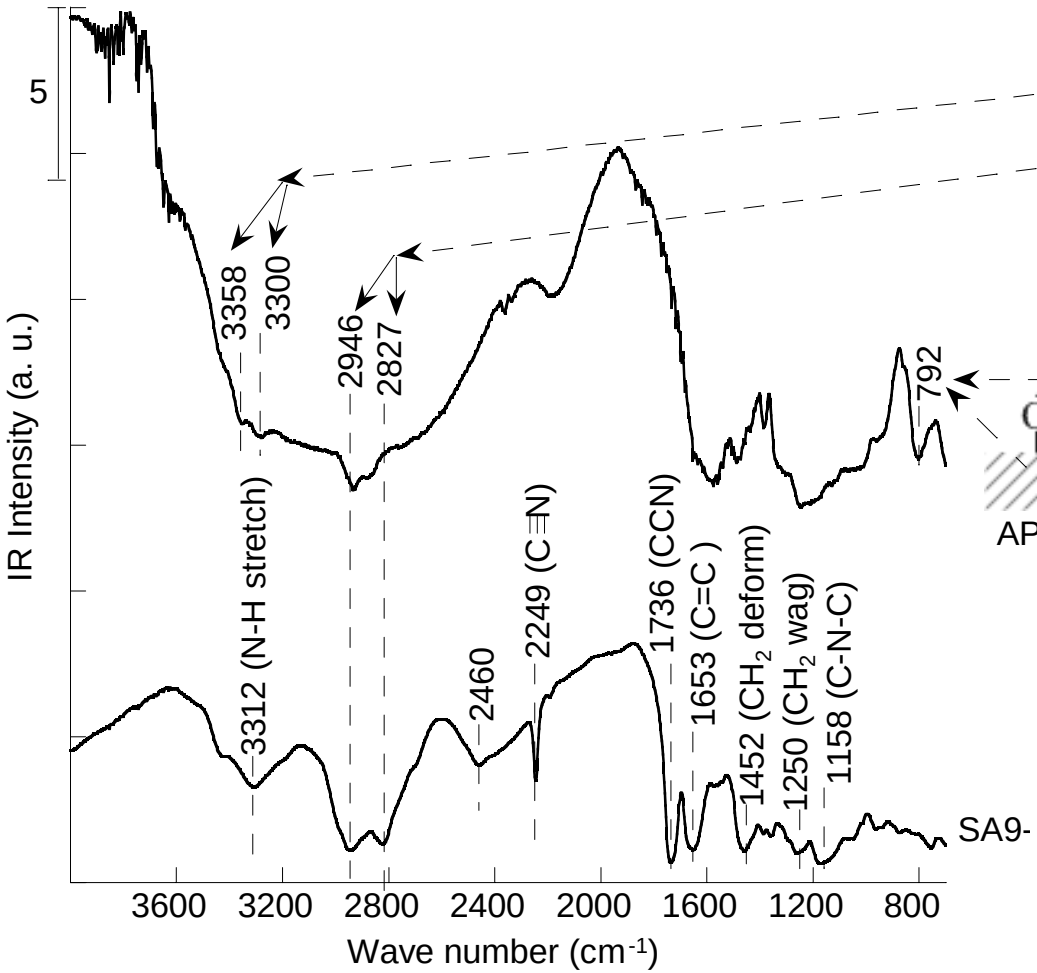
Experimental Setup and Preliminary Results

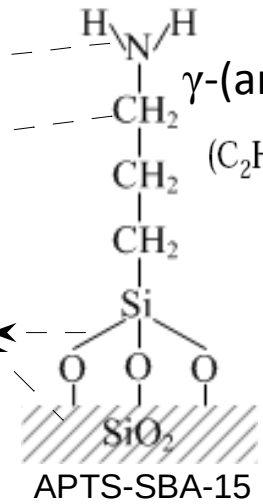


Above: Results from a mass spectrometer for determining the reactor effluent composition, quantifying a sorbent's performance.

Left: Infrared data for determining the structure of adsorbed species

DRIFTS single beam spectra of amine-grafted APTS-SBA-15 sample and commercial SA9-T sample





γ-(aminopropyl)triethoxysilane

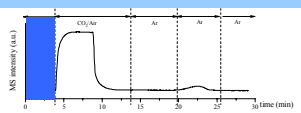
$$(C_2H_5O)_3SiCH_2CH_2CH_2NH_2 + 3Si{-}OH \rightarrow (Si{-}O)_3{-}SiCH_2CH_2CH_2NH_2 + 3C_2H_5OH$$

Table 3. CO_2 Desorption Characteristics

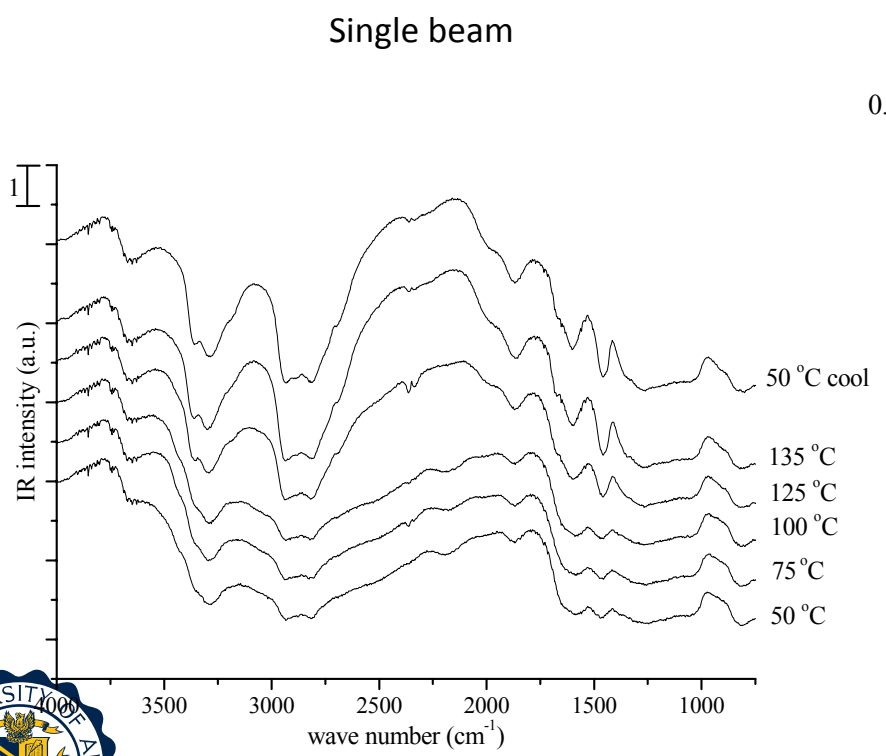
	TPD in He flow			TPD in He/H_2O flow		
	amount of CO_2 des. (μmol/g)	peak temp. (K)	heat of CO_2 desorption (kJ/mol)	amount of CO_2 des. (μmol/g)	peak temp. (K)	Heat of CO_2 desorption (kJ/mol)
Fresh	227	393	6.67	308	375	4.54
1st Reg.	331	393	10.96	357	368	3.90
2nd Reg.	247	370	7.04	406	356	3.22

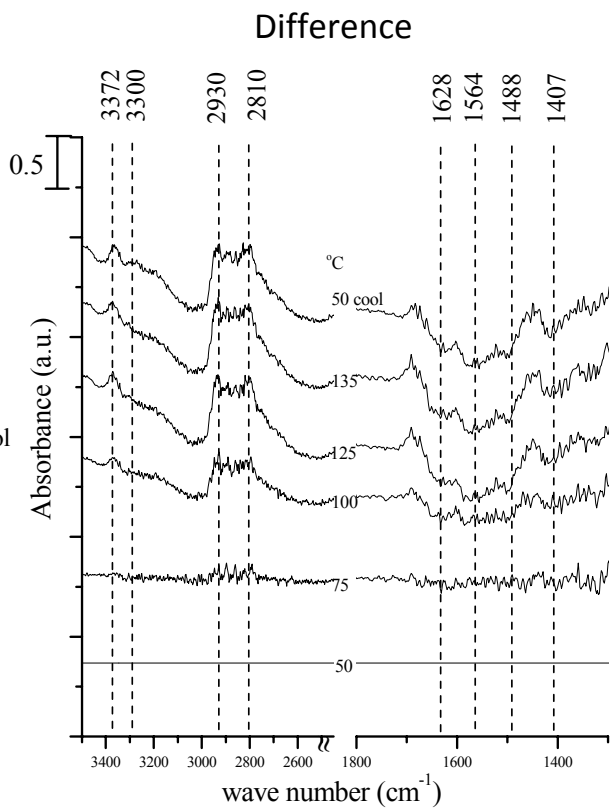
"In-Situ Infrared Study of CO_2 Adsorption on SBA-15 Grafted with -(Aminopropyl)- triethoxysilane", A. C. C. Chang, S. S. C. Chuang, M. Gray, and Y. Soong, Energy&Fuels, 17 (2), 468 -473, 2003.

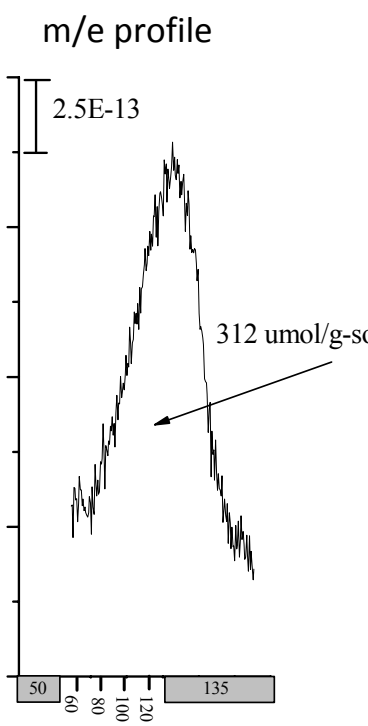
Results and Discussion: Pretreatment



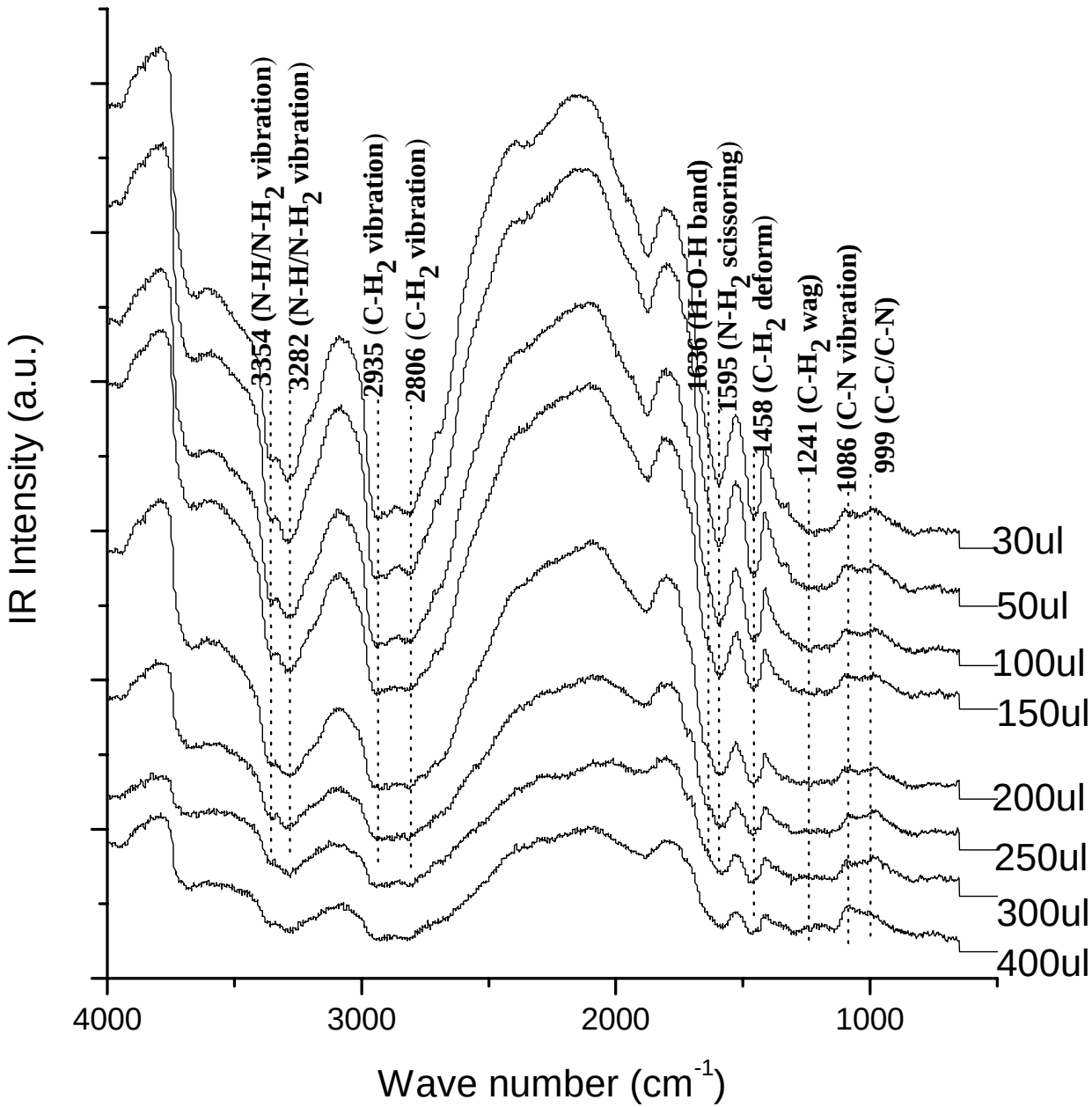
- 20 wt% amine-silica
- Difference plot (right) magnified changes occurred on the sample; amine bands increased while bicarbonate species decreased





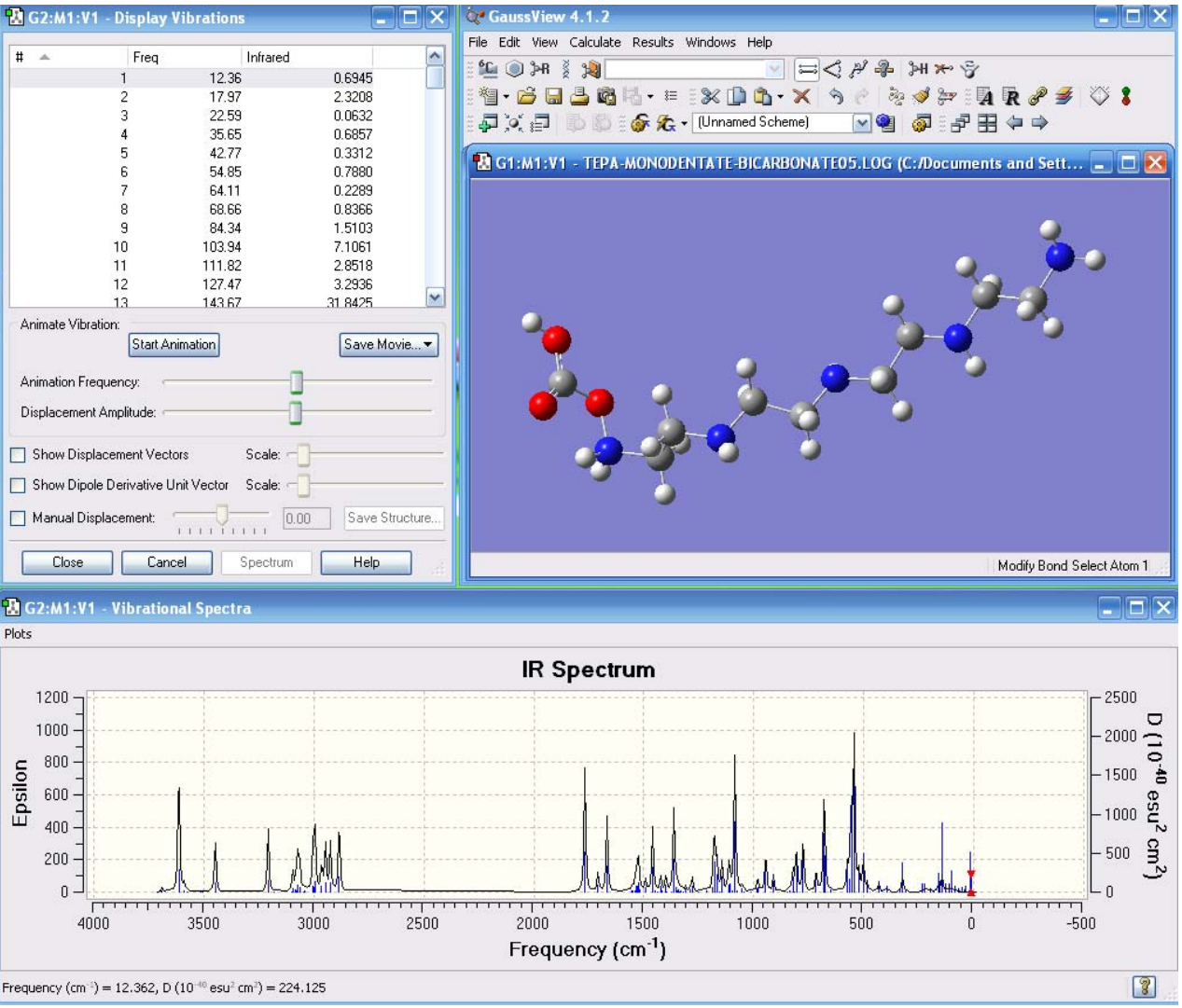


The addition of amines onto SiO_2



Quantum Chemistry

Ab Initio Calculation-Gaussian 03



Monodentate Carbonate Adsorption

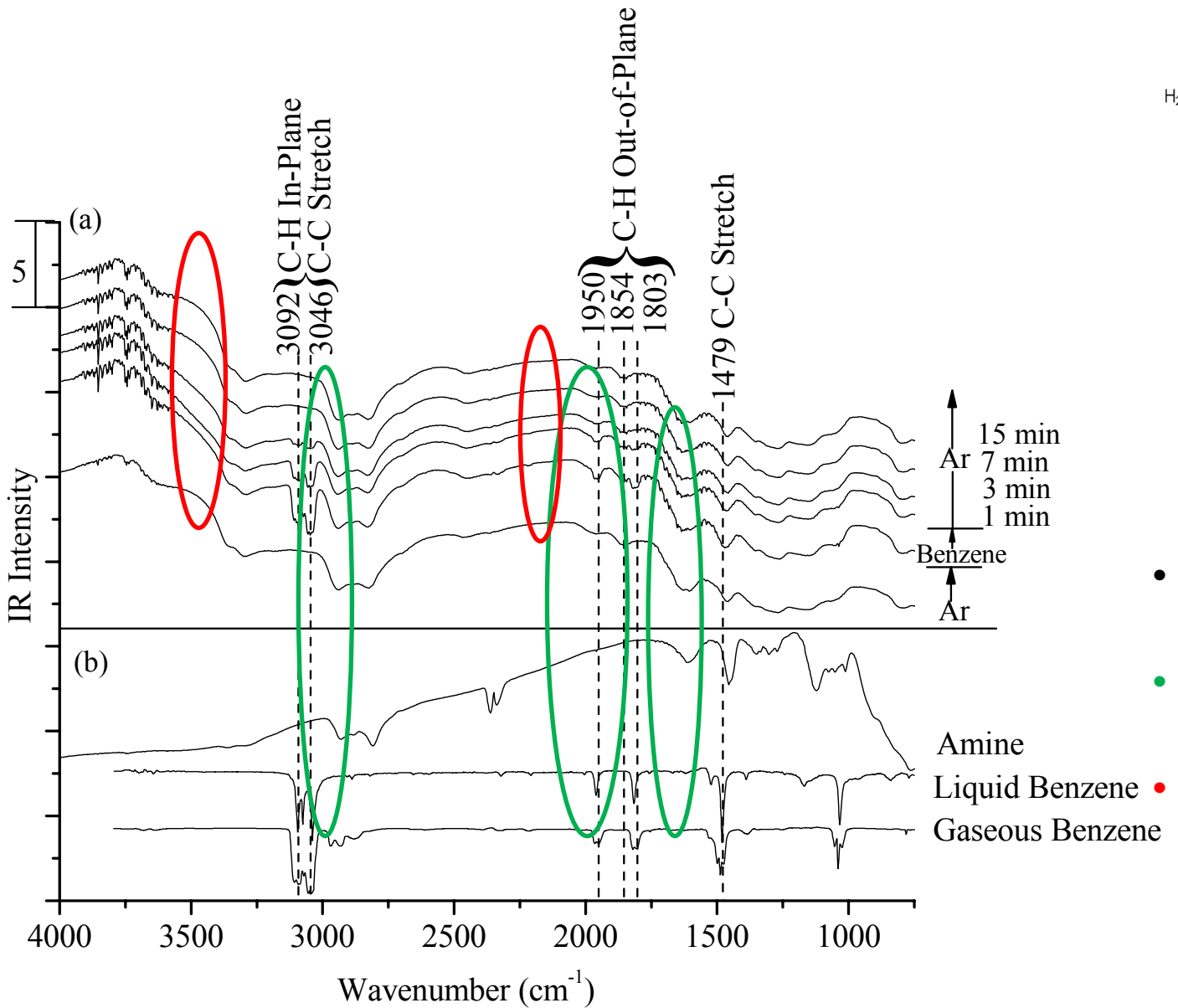
Non-Linear molecule
3N-6 Normal modes
Of vibration.

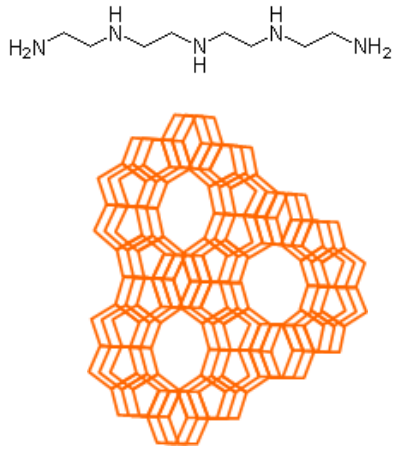
3N-6 = 3(36)-6 = 102

Goal:

fine-tune interaction between CO_2 and sorbents by adjusting amine concentration.

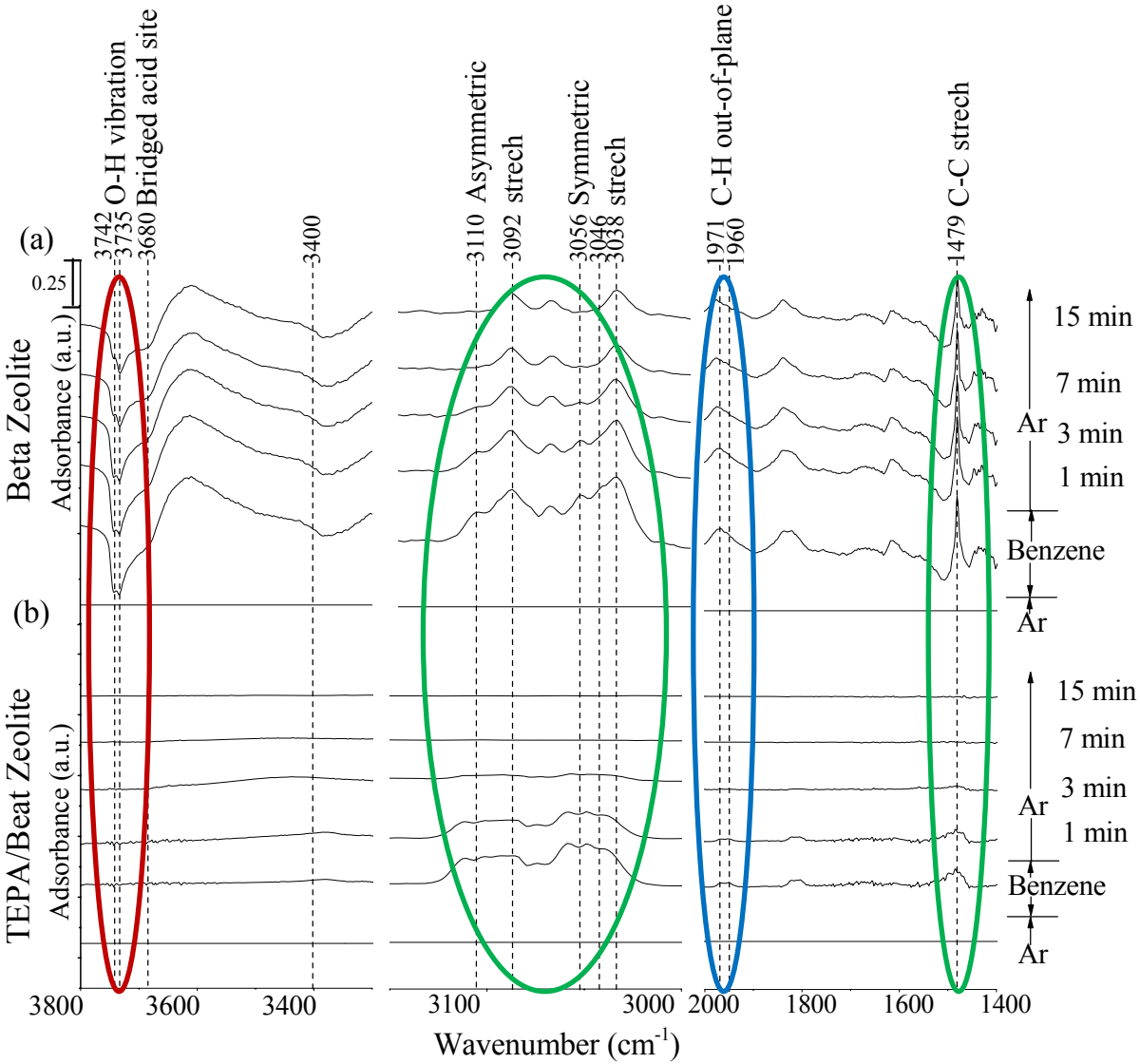
Benzene Absorption/desorption – characterization of amines/beta-zeolite





- Benzene exposure for 2 min
- Gas phase benzene removed by Ar
- Small changes can be observed at 3740 and 1971 cm^{-1}

Benzene absorption/desorption



- The lack of interaction between benzene and TEPA/Beta Zeolite
- Shift in O-H vibration of beta-zeolite shifts (due to its interaction with benzene)
- Benzene did not diffuse into pores due to pore blocking by TEPA.
- Adsorption/desorption at 50, 100, and 135 ^{o}C
  - High rate of decrease in benzene intensity
  - High rate of recovering OH band

Carbon Dioxide Capture from Flue Gas

#Task	Description	Quarters											
		1	2	3	4	5	6	7	8	9	10	11	12
1	Preparation of amine-grafted zeolite												
2	Determination of CO_2 capture capacity and long term stability												
3	Determination of SO_2 capture capacity and long term stability												
4	Fine-tuning of zeolite composition												
5	Fabrication of metal foil structure and CO_2 absorber												
6	Performance test of CO_2 system												
7	Model development economic analysis												

Plan for future testing/development/commercialization

- Testing:
  - Fine-tuning the composition of the amines on the oxide surface.
  - Characterization: elemental analysis, benzene adsorption/desorption.
- Development
  - Build a one-Kg scale CO_2 adsorption/desorption unit.
- Commercialization after successful demonstration of a 10 kg scale unit.