New Diffusive Intermediates for CO_2 Adsorption in Silica-Supported Amine Sorbents

Kuijun Li[*,†], Joel D Kress[§] and David S Mebane[*,†]
[*]National Energy Technology Laboratory
[†]Department of Mechanical and Aerospace Engineering
West Virginia University
[§]Los Alamos National Laboratory

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Overview

- Sorbents, multi-scale model
- Two step zwitterion mechanism
- Water stabilized zwitterion mechanism
- Conclusions and future work

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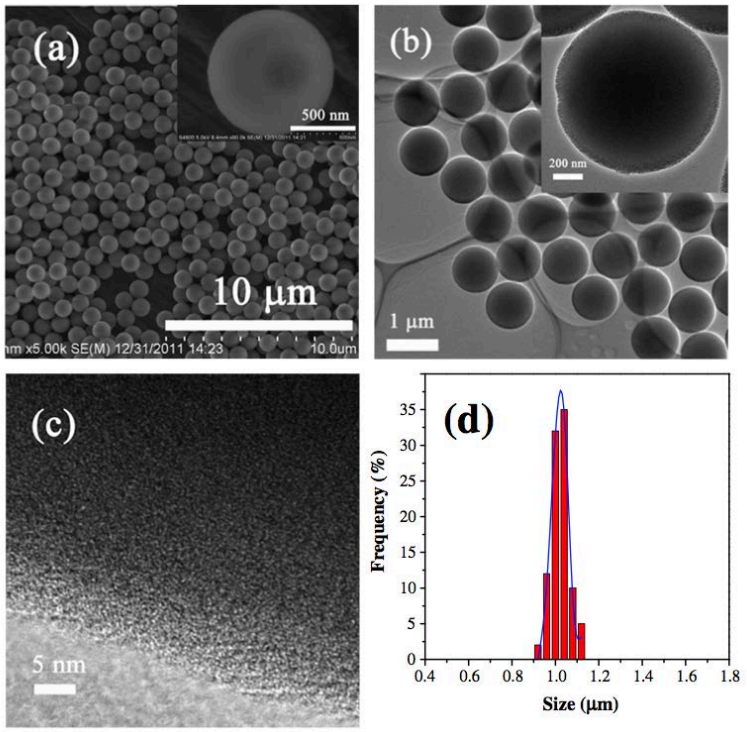
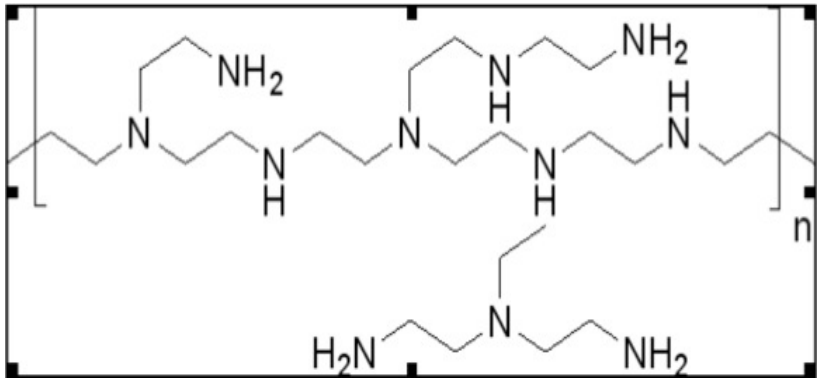
Sorbents

Sorbents: Silica support with PEI loading





PEI structure

SEM (a), TEM (b), and HRTEM (c) images and particle-size distribution histogram (d) of the S600-10 sample

Heydari-Gorji A, et al., Energy & Fuels, 2011, 25(9): 4206-4210.

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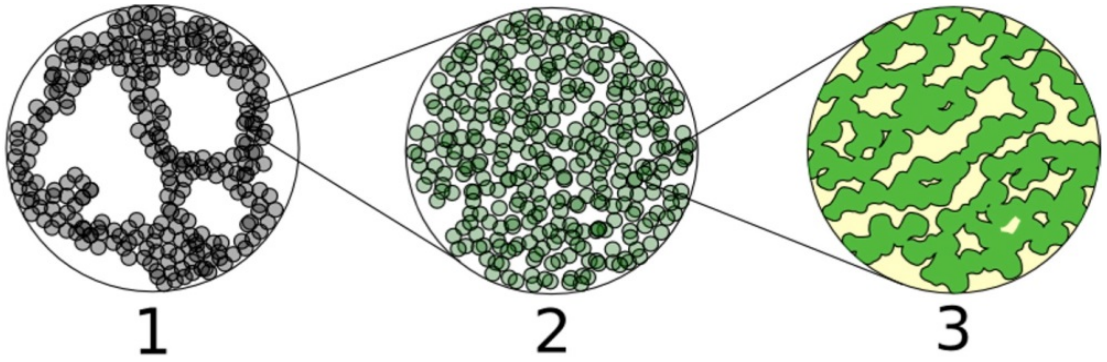
Multi-scale model



Length scale: (1) macroporosity (2)meso-porous particles (3) Silica-PEI composite

Mass transport:

Gas phase diffusion in mesopores;

Solid state diffusion in silica-PEI composites.

DS Mebane, et al., The Journal of Physical Chemistry C 117.50 (2013): 26617-26627.

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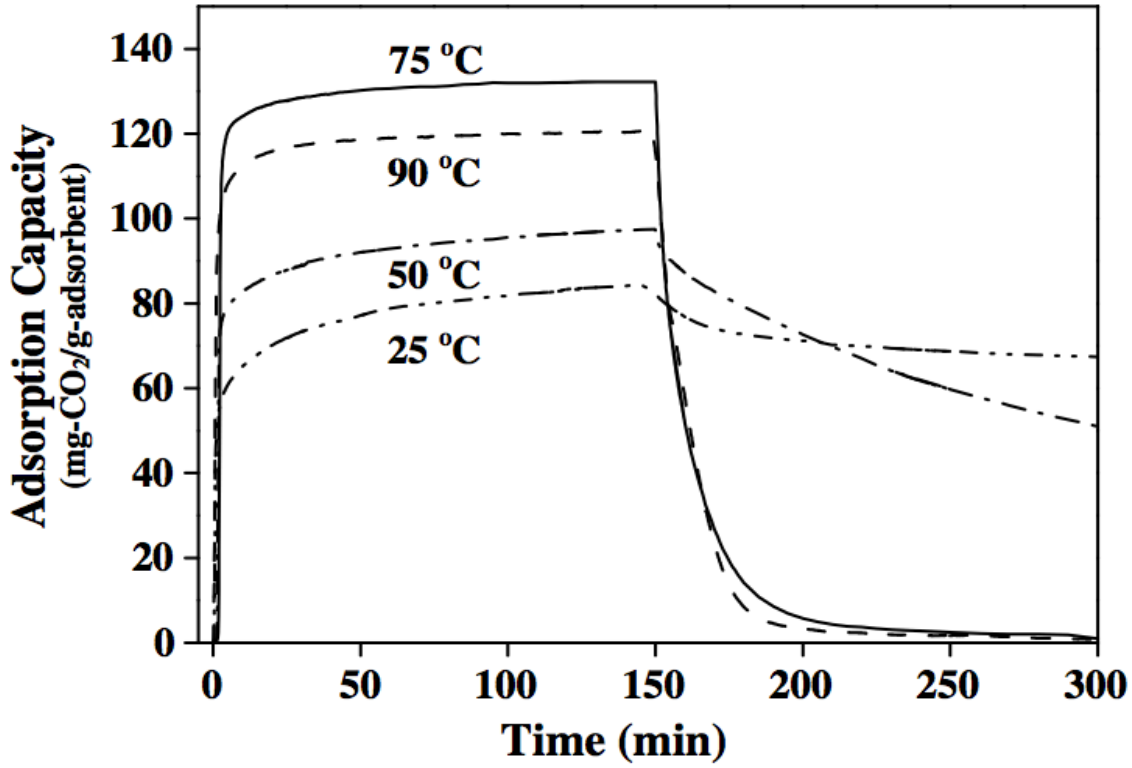
Temperature effect on adsorption capacity



The effect of temperature on the CO_2 adsorption–desorption performance of KIT-6-PEI 50 (150 min adsorption, 150 min desorption)

W.J. Son et al., Microporous and Mesoporous Materials 113 (2008) 31–40

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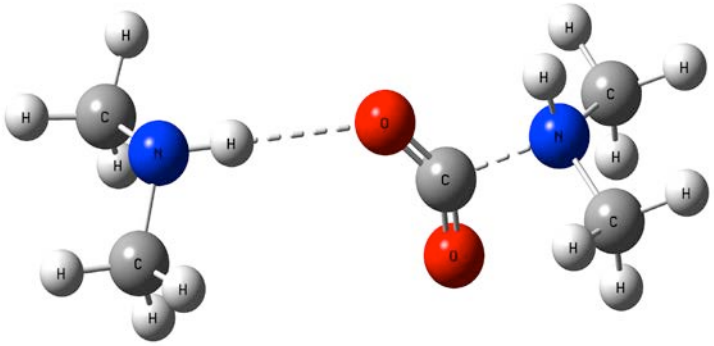
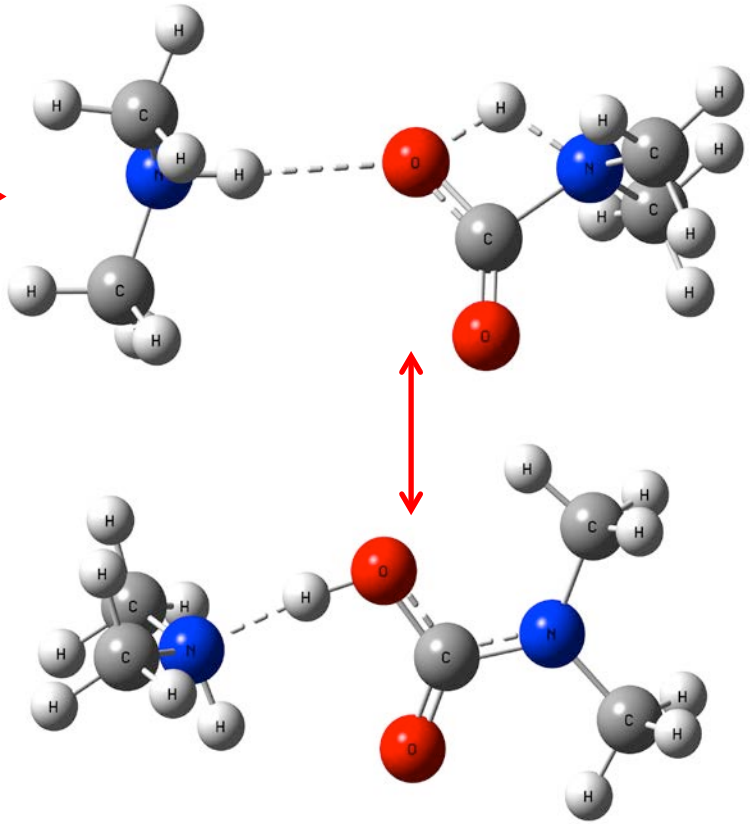
Zwitterion mechanism

Zwitterion, ΔE=+5kJ/mol



Transition state, ΔE=+120kJ/mol



$$R_2NH + CO_2 \underset{}{\overset{kap_1}{\rightleftharpoons}} R_2NH^+COO^- \qquad (1)$$

$$R_2NH^+COO^- + R_2NH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2NH_2^+ : R_2NCOO^- \qquad (2)$$

Ammonium-Carbamate ΔE=-75kJ/mol

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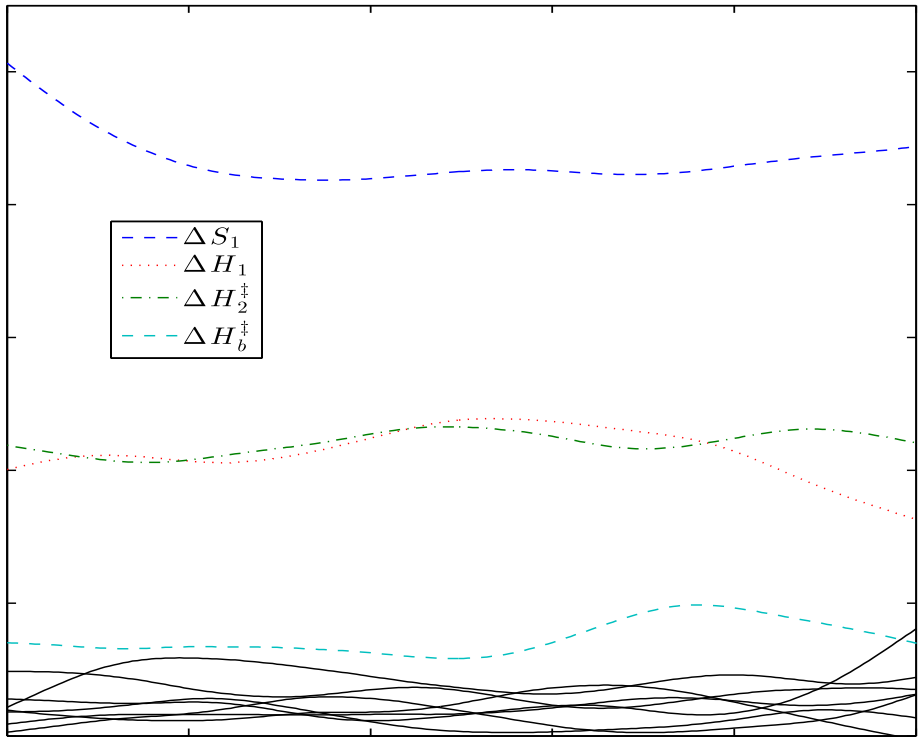
Sensitivity analysis



ΔS_1: entropy of zwitterion formation

ΔH_1: enthalpy of zwitterion formation

$\Delta H^{\ddagger}_2$: activation energy of zwitterion to ammonium-carbamate

$\Delta H^{\ddagger}_b$: activation energy for zwitterion motion

Total variance indices for all parameters plotted at 4% CO_2

DS Mebane, et al., The Journal of Physical Chemistry C 117.50 (2013): 26617-26627.

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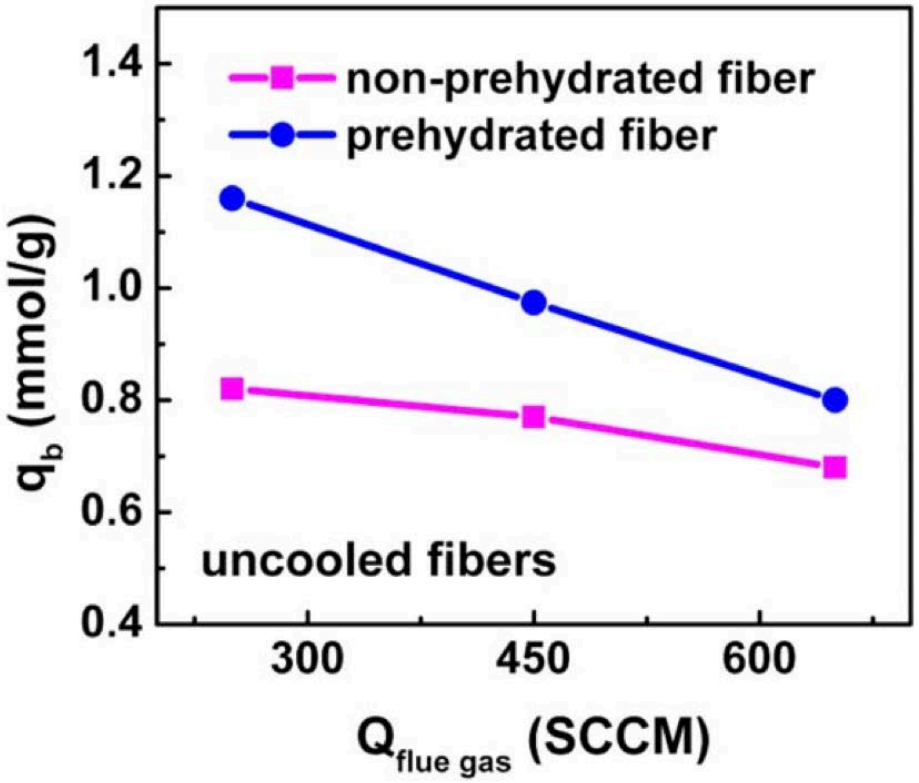
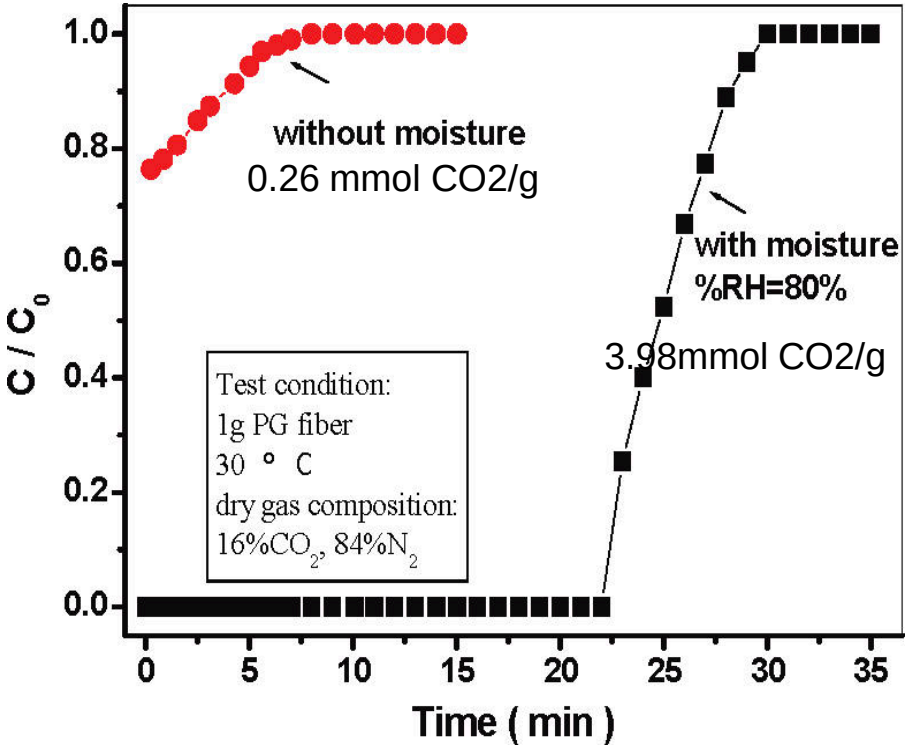
Role of water in CO_2 adsorption



Flow rate effects on adsorption capacity in uncooled, non-prehydrated fibers vs. prehy- drated fibers

Y Fan, et al., AIChE Journal, 2014, 60(11): 3878-3887.



Comparison of the adsorbed volume of CO2 from simulated dry and moist flue gas.

P Li, et al., Langmuir, 2008, 24 (13): 6567-6574

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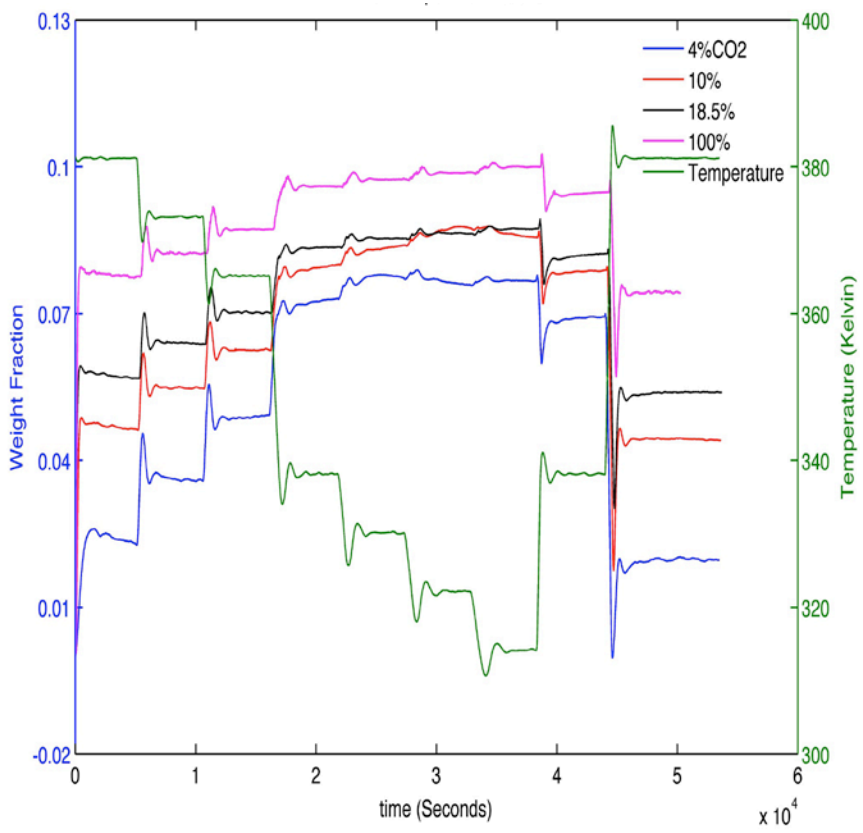
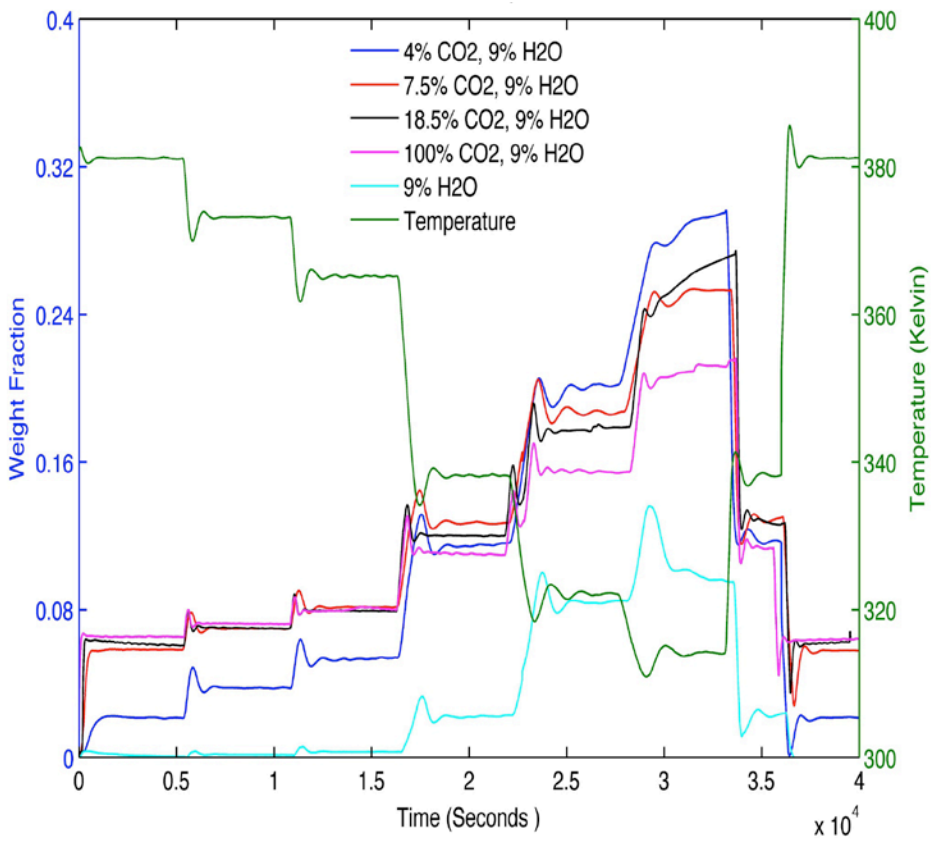
TGA experiment results



Dry Experiment Results



Humid Experiment Results

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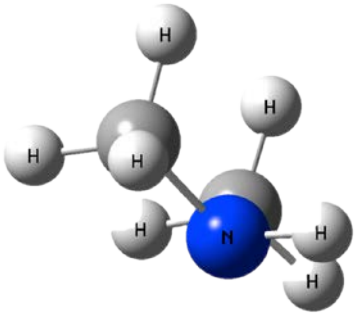
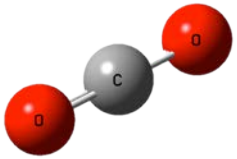
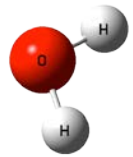
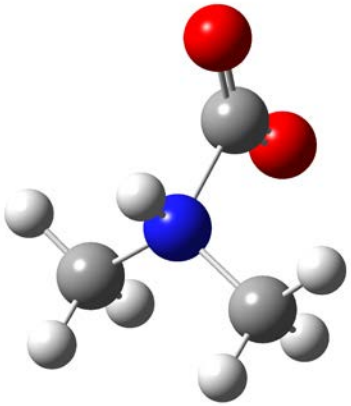
Water effect on stabilizing zwitterion



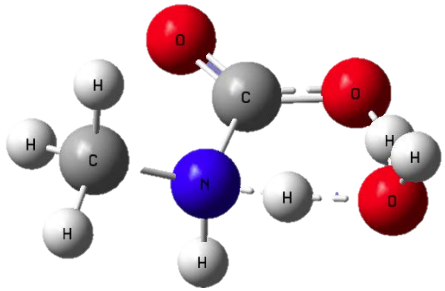




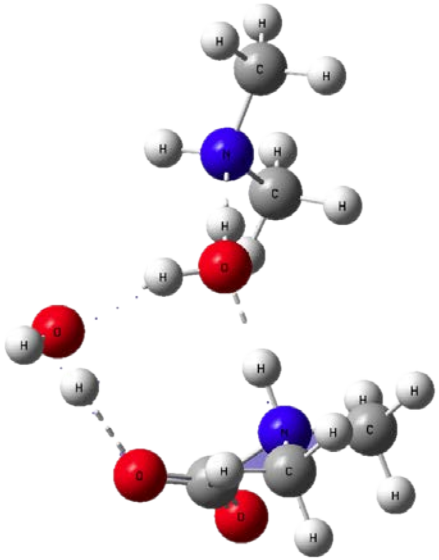
Reactants



ΔE=+5kJ/mol
Zwitterion



ΔE=-18kJ/mol



ΔE=-36kJ/mol

Stabilized zwitterions

DS Mebane, et al., The Journal of Physical Chemistry C 117.50 (2013): 26617-26627.

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Chemical reactions with new diffusive intermediates

New zwitterion, ΔE=-18kJ/mol

Transition state, ΔE=+53kJ/mol

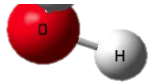
$$\mathrm{R_2NH} + \mathrm{H_2O} \underset{}{\overset{kap_1}{\rightleftharpoons}} \mathrm{R_2NH{-}H_2O} \qquad (1)$$

$$\mathrm{R_2NH{-}H_2O} + \mathrm{CO_2} \overset{kap_2}{\rightleftharpoons} \mathrm{R_2NH^+COO^-{-}H_2O} \qquad (2)$$

$$\mathrm{R_2NH} + \mathrm{CO_2} \overset{kap_3}{\rightleftharpoons} \mathrm{R_2NH^+COO^-} \qquad (3)$$

$$\mathrm{R_2NH^+COO^-} + \mathrm{R_2NH} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{R_2NH_2^+ : R_2NCOO^-} \qquad (4)$$

$$\mathrm{R_2NH^+COO^-{-}H_2O} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \mathrm{R_2NCOO^- : H_3O^+} \qquad (5)$$



Hydronium-Carbamate, ΔE=-34kJ/mol

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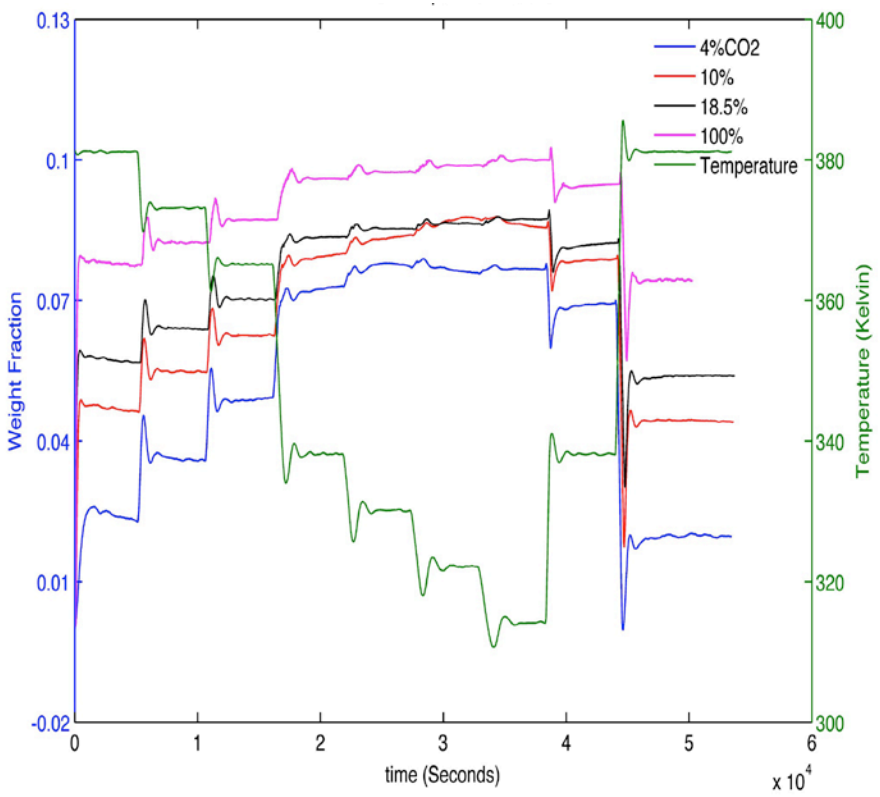
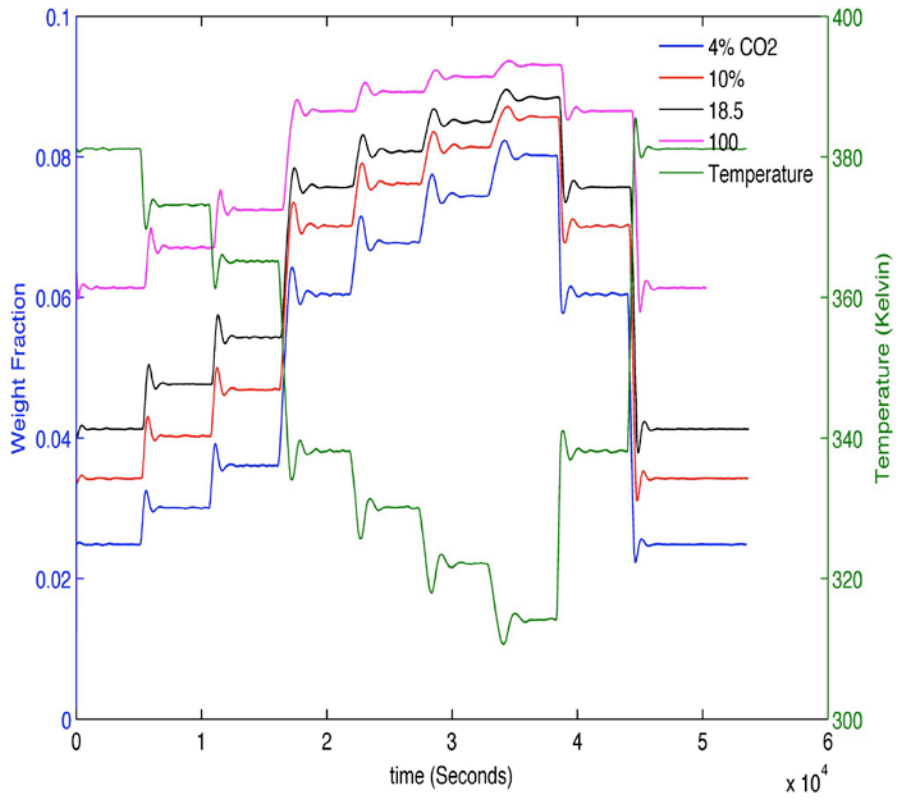
Dry simulation Results



Dry Experiment Results



Dry Simulation Results

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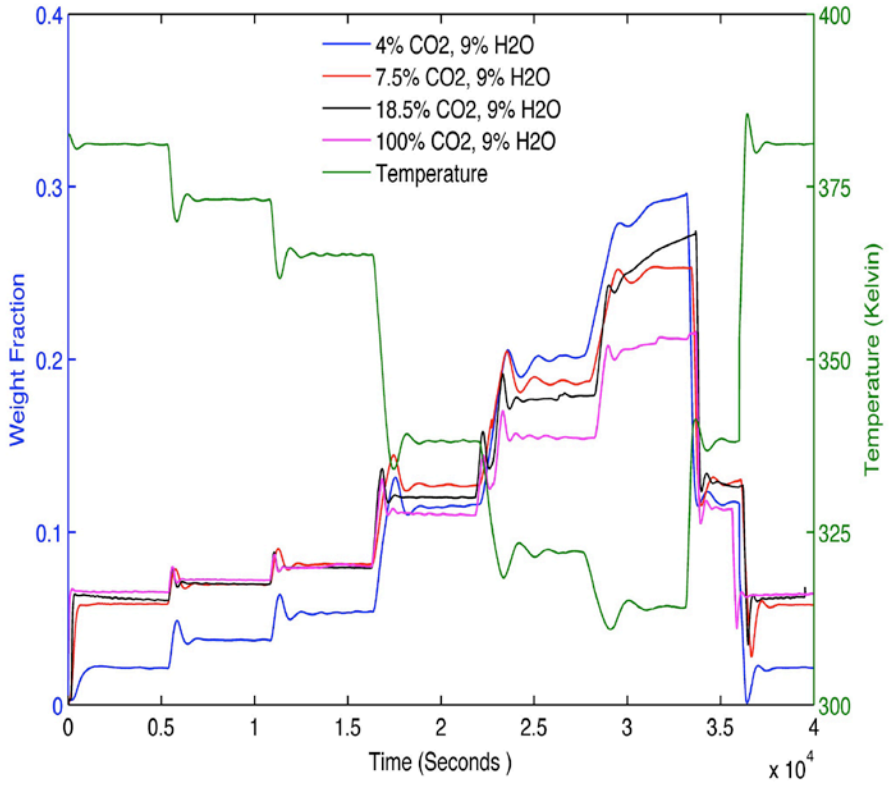
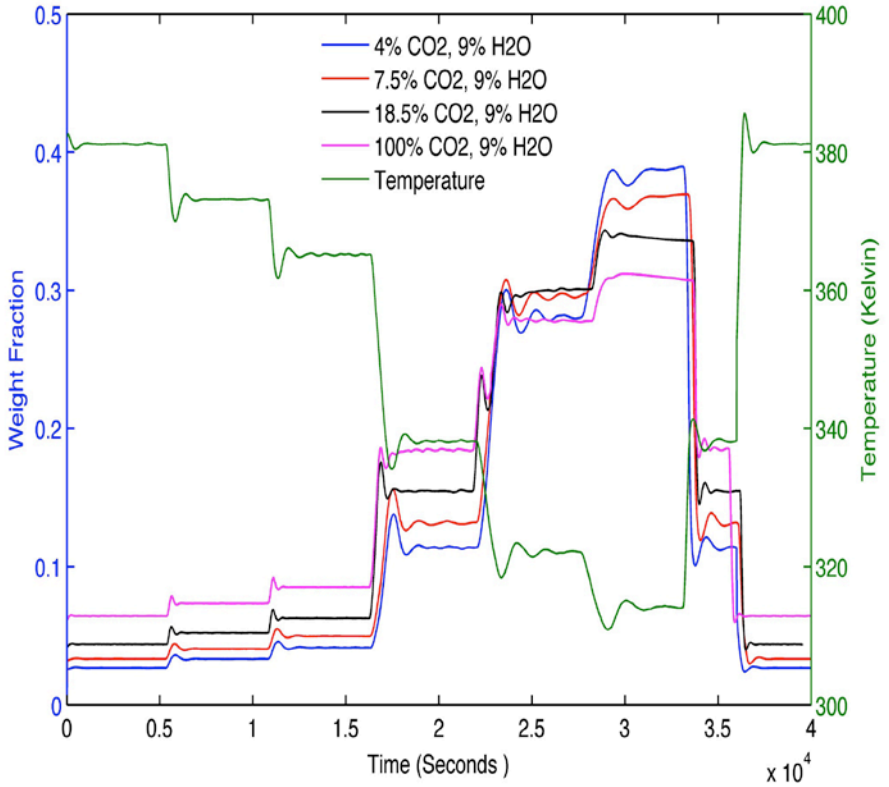
Wet simulation Results



Wet Experiment Results



Wet Simulation Results

Conclusions and future work

- The stability of transport intermediates are important to the capacity of sorbents
- Water increases the capacity of sorbents
- Zwitterion is not stable under dry cases and can be stabilized by water
- CO_2 capacity decrease when increase the CO_2 concentration of humid flue gases

- ➢ Bayesian calibration to quantitative results
- ➢ Dynamic discrepancy for multi-scale process model

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