Integration of high-fidelity CO2 sorbent models at the process scale using dynamic discrepancy

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Integration of High-Fidelity CO$_2$ Sorbent Models at the Process Scale Using Dynamic Discrepancy

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Abstract

A high-fidelity model of a mesoporous silica supported, polyethylenimine (PEI)-impregnated solid sorbent for CO$_2$ capture has been incorporated into a model of a bubbling fluidized bed adsorber using Dynamic Discrepancy Reduced Modeling (DDRM). The sorbent model includes a detailed treatment of transport and amine-CO$_2$-$\text{H}_2\text{O}$ interactions based on quantum chemistry calculations. Using a Bayesian approach, we calibrate the sorbent model to Thermogravimetric (TGA) data. Discrepancy functions are included within the diffusion coefficients for diffusive species within the PEI bulk, enabling a 20-fold reduction in model order. Additional discrepancy functions account for non-ideal behavior in the adsorption of CO$_2$ and H$_2$O. The discrepancy functions are based on a Gaussian process in the Bayesian Smoothing Splines ANOVA framework, which provides a convenient parametric form for calibration and upscaling. The dynamic discrepancy method for scale-bridging produces probabilistic predictions at larger scales, quantifying uncertainty due to model reduction and the extrapolation inherent in model upscaling. The dynamic discrepancy method is demonstrated using TGA data for a PEI-based sorbent and model of a bubbling fluidized bed adsorber. LA-UR-16-23184.
Rapidly synthesize optimized processes to identify promising. Better understand internal behavior to reduce time for troubleshooting. Quantify sources and effects of uncertainty to guide testing & reach larger scales. Stabilize the cost during commercial deployment.

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DOE Carbon Capture Simulation Initiative
Carbon Capture Simulation for Industry Impact

CCS\textsuperscript{2}

- Sept. 2015 – Large Pilot-Scale Post-Combustion
  Six DOE awards for Phase I
- Feb. 1, 2016 – CCS\textsuperscript{2} kick-off
- March, 2016 – Large Pilot-Scale Phase II proposals submitted
- Summer, 2016 – Large Pilot-Scale Phase II awards (1 or 2)

Plan - CCS\textsuperscript{2} to work closely with the Phase II awardees using the CCSI tools developed over the last 5 years
Case Study – Basic Data Submodel

- Polyamine polyethyleneimine (PEI) impregnated mesoporous silica adsorbents

- Motivation and new mechanism for reaction kinetics

- Dynamic discrepancy reduced model and Bayesian calibration

- Conclusions and future work
**Introduction: Polyamine-based Adsorbents**

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

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.


PEI structure
Motivation

• for exothermic adsorption, equilibrium CO$_2$ capacity should increase as operating T decreases

• opposite is observed; not under equilibrium

• kinetic limitation at low T; counter-intuitive, diffusion controlled adsorption

The effect of temperature on the CO$_2$ adsorption–desorption performance of KIT-6-PEI 50

Motivation

- CO₂ capacity in moist conditions much higher compared to dry

- Strongly suggests that moisture has a promoting effect on CO₂ capacity

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

Introduction: Reaction Kinetics

- Zwitterion Mechanism (no direct evidence)

\[
\begin{align*}
R_2NH + CO_2(g) & \rightleftharpoons R_2NH^+CO_2^- \\
R_2NH^+CO_2^- + B & \rightleftharpoons R_2NCO_2^- + BH^+
\end{align*}
\]

1) Intermediate

2) Carbamate

- Termolecular Mechanism (fails, changing rxn. orders w/conc.)

\[
R_2NH \cdots B + CO_2(g) \rightleftharpoons R_2NCO_2^- + BH^+
\]

Carbamate

(B)ase (solvent): amine, water, hydroxide

(B)ase (dry): amine
Quantum Chemistry Calculations

Conclusion
Binding energy with amines: weak dependence wrt alkyl chain length
New Mechanism

Amine

CO₂

H₂O

Zwitterion

Amine Stabilized-Zwitterion

ΔE = -16 kJ/mol

Water Stabilized-Zwitterion
New Mechanism

Transition state of $\Delta E = +120$kJ/mol

Ammonium-carnamate $\Delta E = -75$kJ/mol

$\text{H}_2\text{O}$-zwitterion $\Delta E = -16$kJ/mol

Transition state $\Delta E = +62$kJ/mol

Hydronium-carnamate $\Delta E = -42$kJ/mol

Reactants

Zwitterion $\Delta E = +5$kJ/mol

Transition state of $\Delta E = +120$kJ/mol

Ammonium-carnamate $\Delta E = -75$kJ/mol

$\text{H}_2\text{O}$-zwitterion $\Delta E = -16$kJ/mol

Transition state $\Delta E = +62$kJ/mol

Hydronium-carnamate $\Delta E = -42$kJ/mol

Reactants

$\text{H}_2\text{O}$-zwitterion $\Delta E = -16$kJ/mol

Transition state of bicarbonate $\Delta E = +50$kJ/mol

Bicarbonate $\Delta E = -1$kJ/mol

$\text{H}_2\text{O}$-zwitterion $\Delta E = -16$kJ/mol

Transition state of bicarbonate $\Delta E = +50$kJ/mol

Bicarbonate $\Delta E = -1$kJ/mol

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New Mechanism

\[ R_2NH\cdots NHR_2 + CO_2(g) \xrightleftharpoons[\kappa_1]{\kappa_2} R_2NH^+CO_2^- - R_2NH \] (1)

\[ R_2NH^+CO_2^- - R_2NH \xrightarrow[k_{-2}]{\kappa_2} R_2NCO_2^- : R_2NH^+ \] (2)

\[ R_2NH + H_2O(g) \xrightleftharpoons[\kappa_3]{\kappa_3} R_2NH - H_2O \] (3)

\[ R_2NH - H_2O + CO_2(g) \xrightarrow[\kappa_4]{\kappa_4} R_2NH^+CO_2^- - H_2O \] (4)

\[ R_2NH^+CO_2^- - H_2O \xrightarrow[k_{-5}]{\kappa_5} R_2NCOO^- : H_3O^+ \] (5)

Variables:
\[ z_1 = \text{Amine-Zw (1)} \quad x = \text{Ammonium-Carbamate (2)} \]
\[ z_2 = \text{Amine-H}_2\text{O (3)} \quad z_3 = \text{H}_2\text{O-Zw (4)} \]
\[ y = \text{Hydronium-Carbamate (5)} \]

Solutions:
\[ W_{CO_2} = M_{CO_2} n_v (x + y + z_1 + z_3) / \rho \]
\[ W_{H_2O} = M_{H_2O} n_v (y + z_2 + z_3) / \rho \]
Simulation Results on Temperature Effect

- equilibrium CO₂ capacity should increase as operating T decreases
- opposite is now basically captured with simulation in agreement with expt.
Experiment vs. Simulation Results

Dry Experiment

Humid Experiment

Wet Experiment and Simulation Results

CO₂ Weight Fraction

H₂O Weight Fraction

Adsorption Weight Fraction

Temperature (Kelvin)

Time (Seconds)

Time (Seconds)

Time (Seconds)
**Methods: Bayesian Calibration and Dynamic Discrepancy**

**Bayesian Calibration:**

$$\mathcal{P}(A|B) = \frac{\mathcal{P}(B|A)\mathcal{P}(A)}{\int_{A'} \mathcal{P}(B|A')dA'}$$

$$\mathcal{Z} = Y(\theta) + \delta(\xi) + \epsilon(\psi)$$

$$\Omega(\theta, \xi, \psi|Z) \propto \mathcal{L}(Z|\theta, \xi, \psi)\pi(\theta, \xi, \psi)$$

**Dynamic Discrepancy:**

Discrepancy on Kinetic non-ideality :

$$u_{bi}^* = \zeta_b \exp\left(-\frac{\Delta H_b^+}{RT}\right)$$

$$u_{bi,new}^* = \zeta_b \exp\left(-\frac{\Delta H_b^+}{RT}\right) \exp[\delta(z_{i-1}, z_i, z_{i+1}, \frac{1}{T})]/T$$

$$= u_{bi}^* \exp[\delta(z_{i-1}, z_i, z_{i+1}, \frac{1}{T})]$$

Discrepancy on Thermodynamic Equilibrium :

$$\kappa = \exp\left(-\frac{\Delta H + T\Delta S}{RT}\right)/P$$

$$\kappa_{new} = \kappa \ast \exp[\delta^E(P, T)]$$
Reduced Model

Increase the calculation speed by reducing the control volumes and add discrepancy to diffusivity coefficients.

Normal Model

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Calibration Results

Dry Experiment and Water Experiment and Wet Experiment and Calibration Results
Conclusion

• A new mechanism using amine and water stabilized zwitterions as diffusive intermediates has been proposed
• Model simulation replicated the experiment results qualitatively
• Bayesian calibration and dynamic discrepancy implemented in the model to get quantitatively matched results
• Reduced model is used to improve the calculation speed

Future Work

• Apply this model to bubbling fluidized bed model
• Quantify the uncertainty from model reduction and model upscaling
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