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
Overview

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

Sorbents: Silica support with PEI loading

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

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.

Temperature effect on adsorption capacity

![Graph showing the effect of temperature on CO$_2$ adsorption-desorption performance of KIT-6-PEI 50](image)

The effect of temperature on the CO$_2$ adsorption–desorption performance of KIT-6-PEI 50 (150 min adsorption, 150 min desorption)

Zwitterion mechanism

Zwitterion, $\Delta E=+5\text{kJ/mol}$

Transition state, $\Delta E=+120\text{kJ/mol}$

$$\begin{align*}
R_2\text{NH} + \text{CO}_2 &\xrightleftharpoons[kap_1]{ \text{k}_1} R_2\text{NH}^+\text{COO}^- \\
R_2\text{NH}^+\text{COO}^- + R_2\text{NH} &\xrightleftharpoons[k_2]{ \text{k}_2} R_2\text{NH}_2^+ : R_2\text{NCOO}^- 
\end{align*}$$

Ammonium-Carbamate $\Delta E=-75\text{kJ/mol}$
Sensitivity analysis

Total variance indices for all parameters plotted at 4% CO₂

Role of water in CO$_2$ adsorption

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


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

TGA experiment results

Dry Experiment Results

Humid Experiment Results
Water effect on stabilizing zwitterion

\[ \Delta E = +5 \text{kJ/mol} \]

Zwitterion

\[ \Delta E = -18 \text{kJ/mol} \]

\[ \Delta E = -36 \text{kJ/mol} \]

Stabilized zwitterions

Reactants

Chemical reactions with new diffusive intermediates

New zwitterion, \( \Delta E = -18 \text{kJ/mol} \)

Transition state, \( \Delta E = +53 \text{kJ/mol} \)

\[
\begin{align*}
R_2\text{NH} + H_2O & \rightleftharpoons_R R_2\text{NH}^-H_2O \\
R_2\text{NH}^-H_2O + CO_2 & \rightleftharpoons_R R_2\text{NH}^+COO^- - H_2O \\
R_2\text{NH} + CO_2 & \rightleftharpoons_R R_2\text{NH}^+COO^- \\
R_2\text{NH}^+COO^- + R_2\text{NH} & \rightleftharpoons_R^{k_4} R_2\text{NH}_2^+ : R_2\text{NCOO}^- \\
R_2\text{NH}^+COO^- - H_2O & \rightleftharpoons_R^{k_5} R_2\text{NCOO}^- : H_3O^+
\end{align*}
\]
Dry simulation Results

Dry Experiment Results

Dry Simulation Results
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
Acknowledgements

David C. Miller, NETL
Daniel J. Fauth, NETL
McMahan L. Gray, NETL
Greg Ball, NETL

Disclaimer: This presentation was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency.