Amine-based solid sorbent modeling in the Department of Energy's Carbon Capture Simulation Initiative

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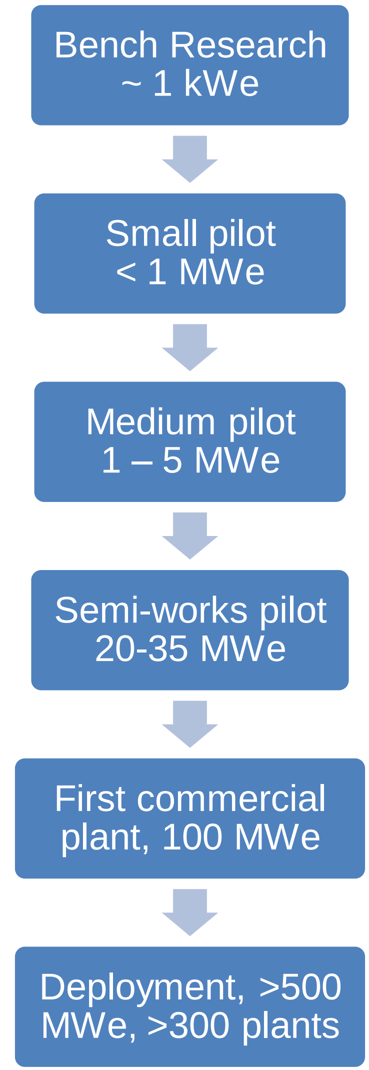
Carbon Capture Challenge

- The traditional pathway from discovery to commercialization of energy technologies can be quite long, i.e., ~ 2-3 decades
- President's plan requires that barriers to the widespread, safe, and cost-effective deployment of CCS be overcome within 10 years
- To help realize the President's objectives, new approaches are needed for taking carbon capture concepts from lab to power plant, quickly, and at low cost and risk
- CCSI will accelerate the development of carbon capture technology, from discovery through deployment, with the help of science-based simulations



Carbon Capture Simulation Initiative

Identify promising concepts → Reduce the time for design & troubleshooting → Quantify the technical risk, to enable reaching larger scales, earlier → Stabilize the cost during commercial deployment

National Labs

- Berkeley Lab
- Pacific Northwest National Laboratory
- NETL
- Los Alamos National Laboratory
- Lawrence Livermore National Laboratory

Academia

- Carnegie Mellon
- Princeton University
- West Virginia University
- Boston University
- Institute for Clean and Secure Energy, The University of Utah

Industry

- Fluor
- B&W
- GE
- EPRI Electric Power Research Institute
- Air Products
- Burns & McDonnell Since 1898
- Duke Energy
- URS
- Alstom
- Southern Company
- Southern California Edison
- Boeing
- Chevron
- ExxonMobil
- WorleyParsons resources & energy
- Eastman

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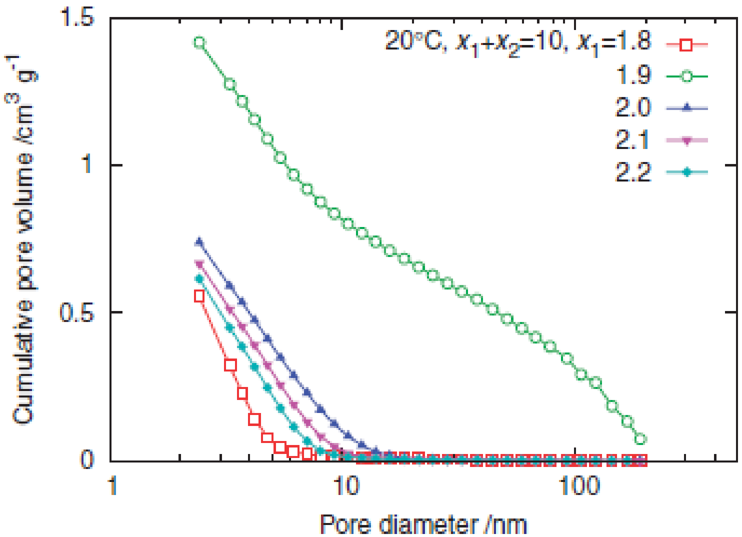
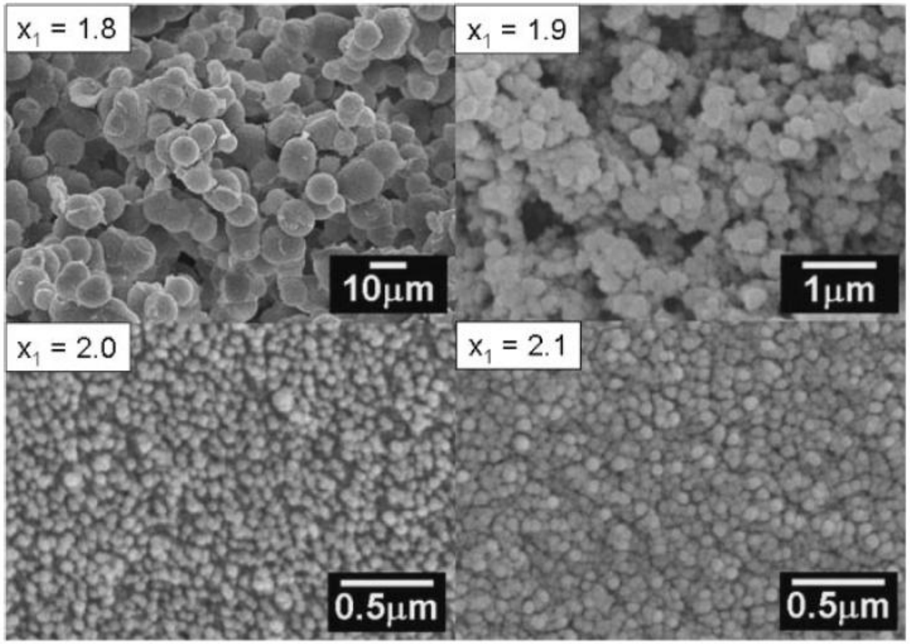
the sorbent: silica support

- mesoporous silica forms the substrate
- silica xerogels (sol-gel process) most economical
- substrate particles agglomerates of micron-sized mesoporous particles





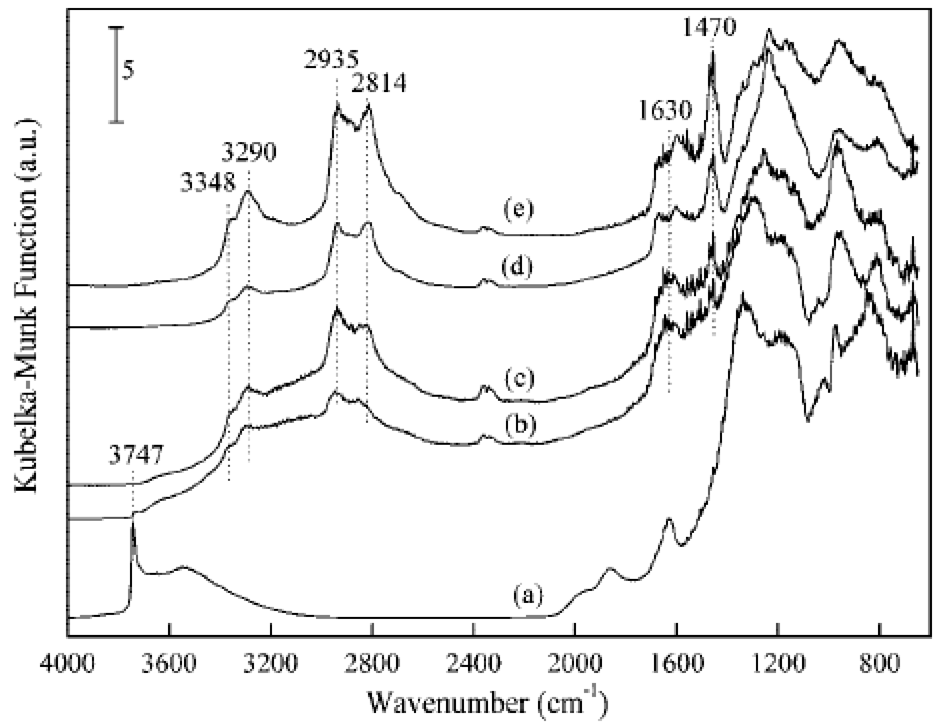
K. Kajihara, et al., Bull. Chem. Soc. Jpn. ***82*** *(2009) 1470.*

the sorbent: PEI loading

- substrate impregnated with polyethyleneimine, or PEI
- PEI tends to fill the mesopores, reducing porosity and internal surface area
- some amines bind with silanol sites that cover the surface of the substrate

An IR peak associated with silanol (3747 cm^{-1}) disappears when PEI is loaded onto the substrate.

X. Wang, et al., J. Phys. Chem. C ***113*** *(2009) 7260.*



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sample	BET surface area (m^2 g^{-1})	pore volume (cm^3 g^{-1})	pore diameter (nm)	CO_2 cap.[a] mg/g of sorb
MCM-41	1229	1.15	2.7	6.3
PEI(50)/MCM-41 (MBS-1)	11	0.03	0	89.2
SBA-15	950	1.31	6.6	5.0
PEI(50)/SBA-15 (MBS-2)	80	0.20	6.1	140

X. Ma, et al., J. Am. Chem. Soc. ***131*** *(2009) 5777.*

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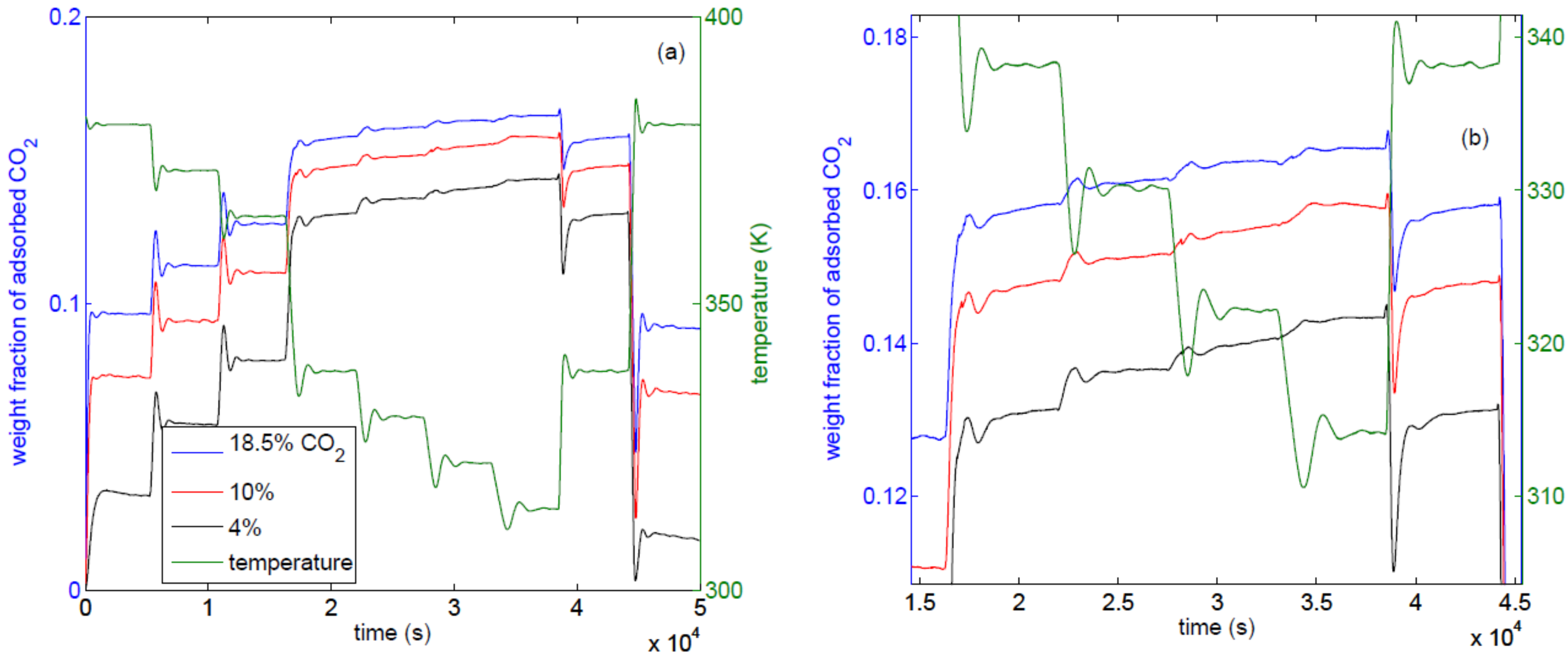
the sorbent: dry TGA behavior



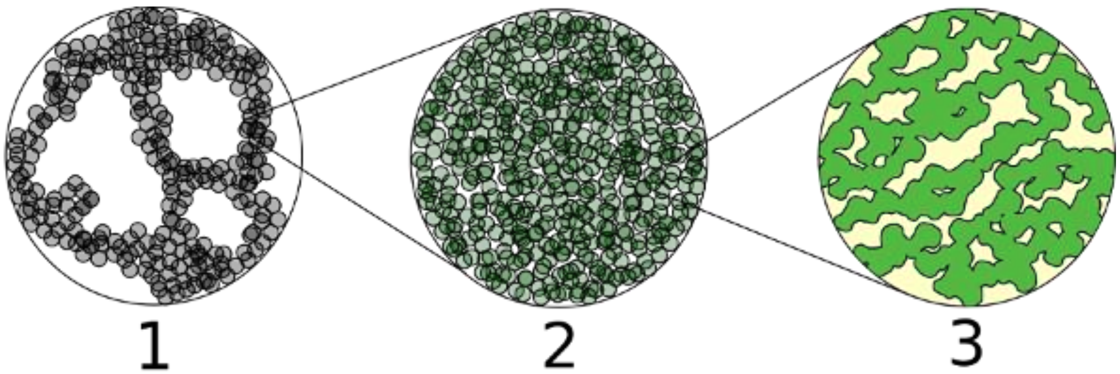
(a)-(b) Sorbent NETL-196C, ~44.1 wt-% PEI, Dry atmosphere. Sorbent synthesis: McMahan Gray, NETL; Sorbent characterization: Daniel Fauth, NETL.

anhydrous model

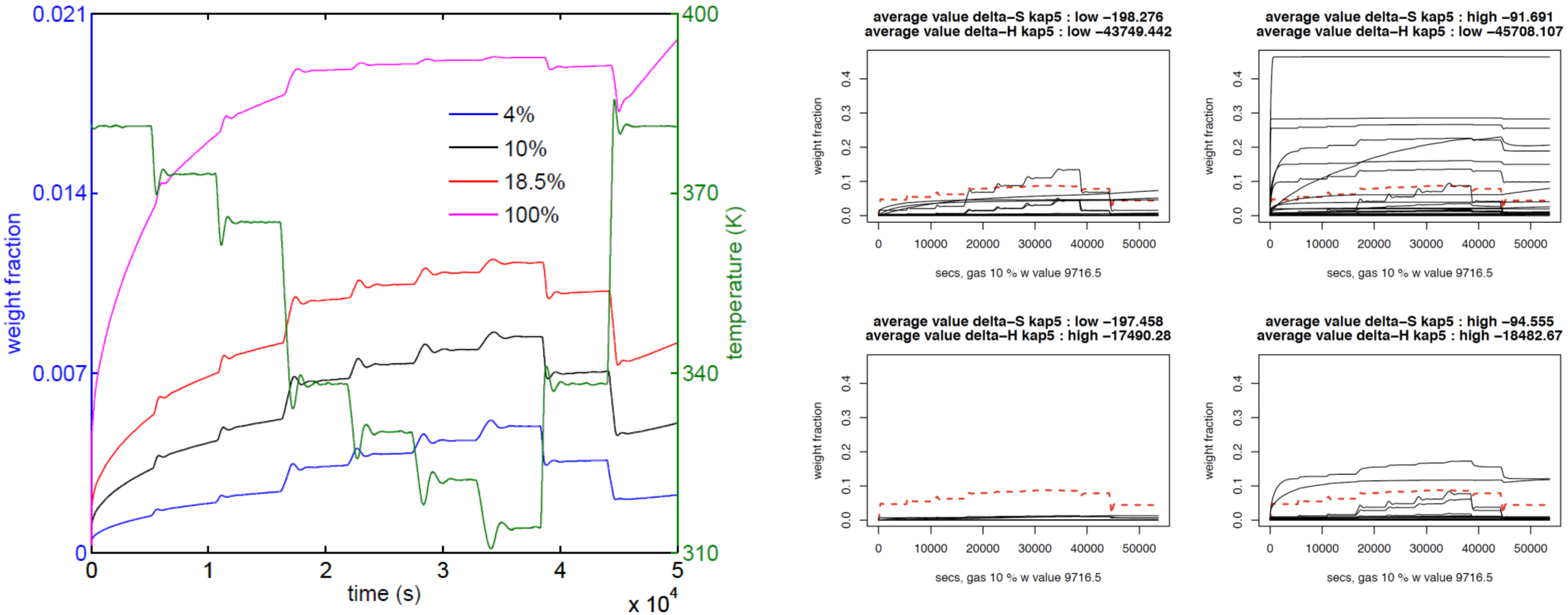
- two-step formation of carbamic acid:

$$R_2NH + CO_2(g) \rightleftharpoons R_2NH^+ - CO_2^-$$
$$R_2NH^+ - CO_2^- + R_2NH \rightleftharpoons R_2NCOOH : R_2NH$$

- three modes of mass transport:
  - gas phase bulk
  - gas phase Knudsen
  - solid state (zwitterion-mediated hopping)



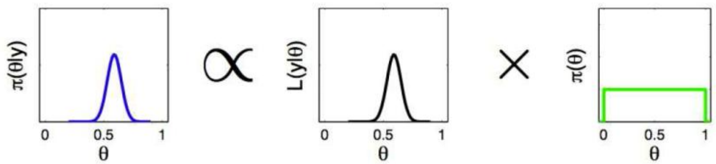
anhydrous model



(left) sample calculated output of the sorbent model showing diffusion effects (right) sensitivity analysis highlighting the importance of zwitterion stability to sorbent working capacity

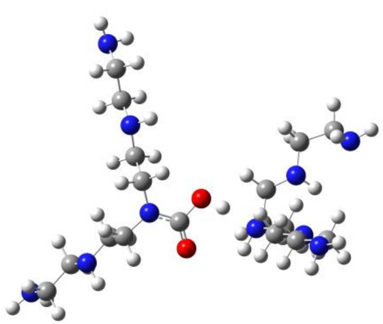
Bayesian methods in parameter estimation

- Bayes' theorem enables the incorporation of prior information in model-based parameter estimates.

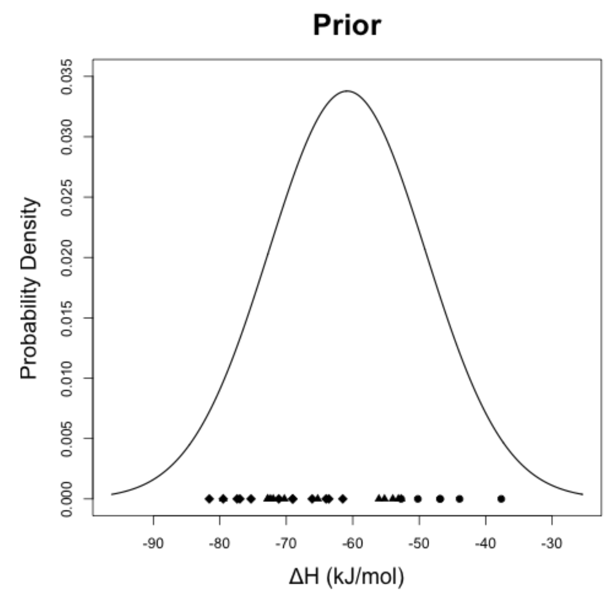


$$\pi(\theta|y) \propto L(y|\theta) \times \pi(\theta)$$

- If model parameters relate to physical quantities, prior information is available through *ab initio* calculations.



rxn	B3LYP	PBE	MP
1	-52.72	-76.36	-62.76
2	-46.86	-70.29	-62.97
3	-50.21	-72.8	-62.76
4	-46.86	-70.71	-64.43
5	-37.66	-69.04	-62.76
6	-43.93	-68.41	-72.38



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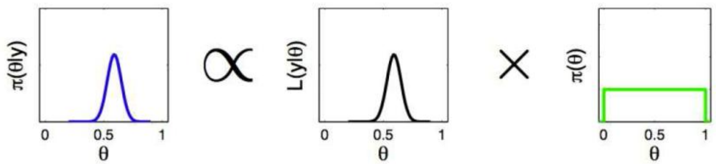
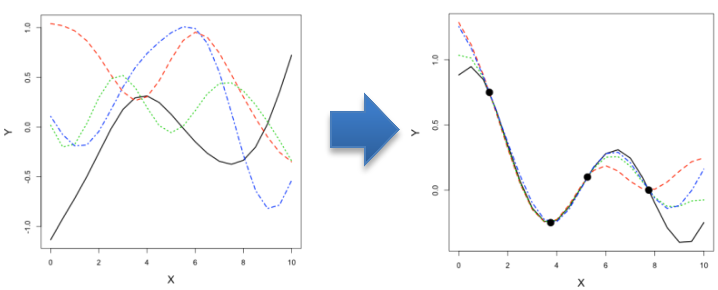


$$\pi(\theta|y) \propto L(y|\theta) \times \pi(\theta)$$

- The error in the form of the model must also be accounted for.
- A Gaussian process generates a stochastic set of curves adhering to certain general properties.

$$\mathbf{Y} = \mathbf{Z}(\boldsymbol{\theta}, \boldsymbol{\zeta}) + \boldsymbol{\delta}(\boldsymbol{\xi}, \boldsymbol{\zeta}) + \boldsymbol{\epsilon}(\boldsymbol{\zeta})$$



$$\mathbf{Y} \sim N\left[\mathbf{Z}(\boldsymbol{\theta}, \boldsymbol{\zeta}), \Sigma(\boldsymbol{\xi}) + \psi \mathbf{I}\right] = \mathcal{L}(\mathbf{Y}|\boldsymbol{\theta}, \boldsymbol{\xi}, \psi)$$

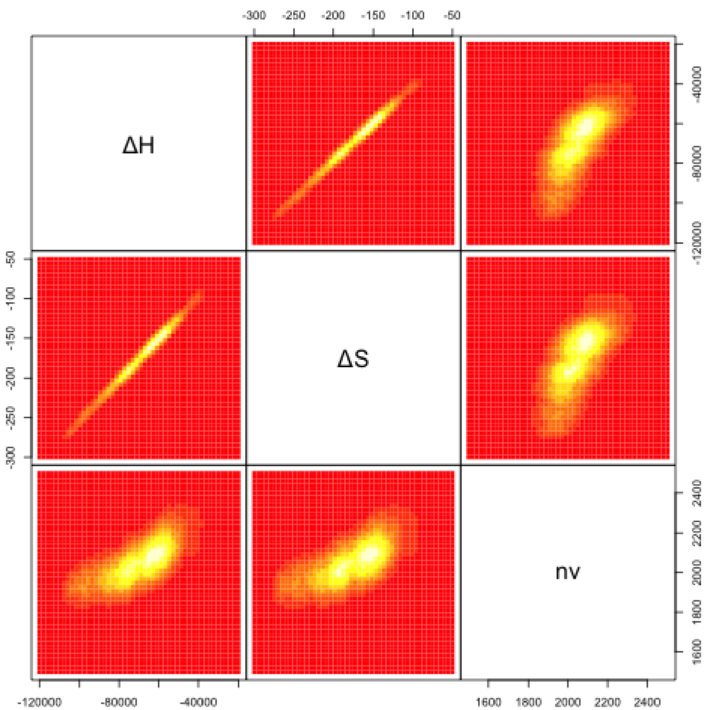
$$\Sigma(i', j'; \boldsymbol{\xi}) = \eta \exp\left[-\frac{(\zeta_{i'} - \zeta_{j'})^2}{\phi^2}\right]$$

Bayesian methods in parameter estimation

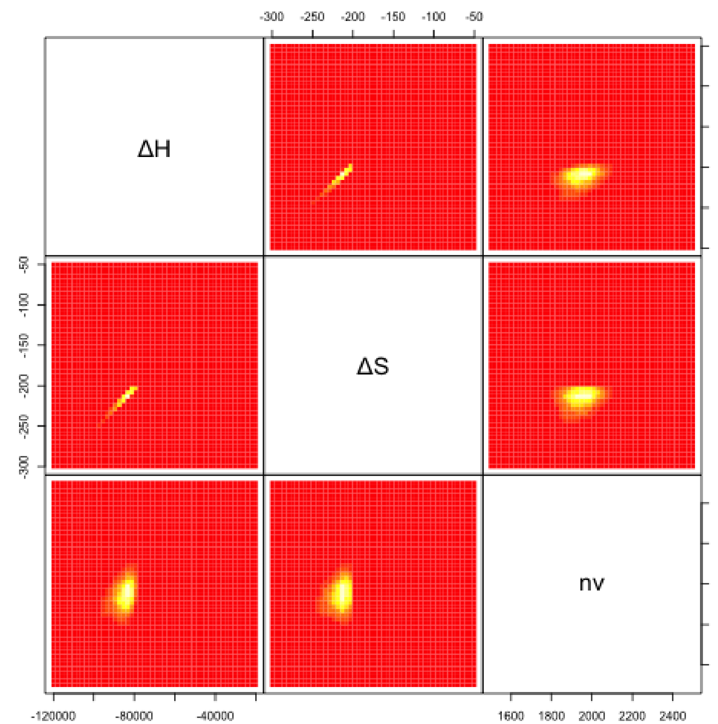
- Equilibrium model for dry uptake of CO_2:

$$2\mathrm{R_2NH} + \mathrm{CO_2(g)} \rightleftharpoons \mathrm{R_2NCOOH} : \mathrm{R_2NH}$$

$$\kappa = \frac{x^2}{(1-2x)^2 p} = \exp\left(\frac{\Delta S}{R}\right)\exp\left(\frac{-\Delta H}{RT}\right)/P \qquad w = M n_{\mathrm{v}} x/\rho$$



posterior distributions (left) without and (right) with informative priors



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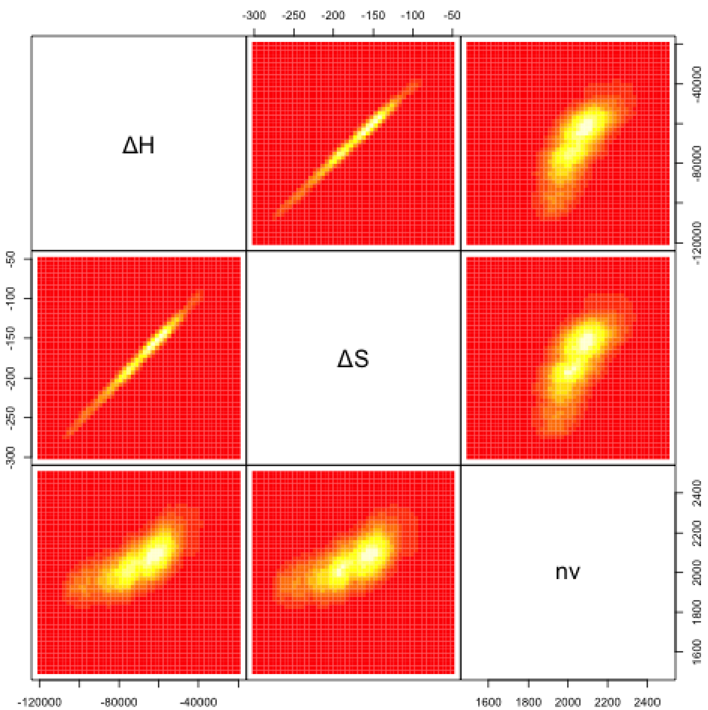

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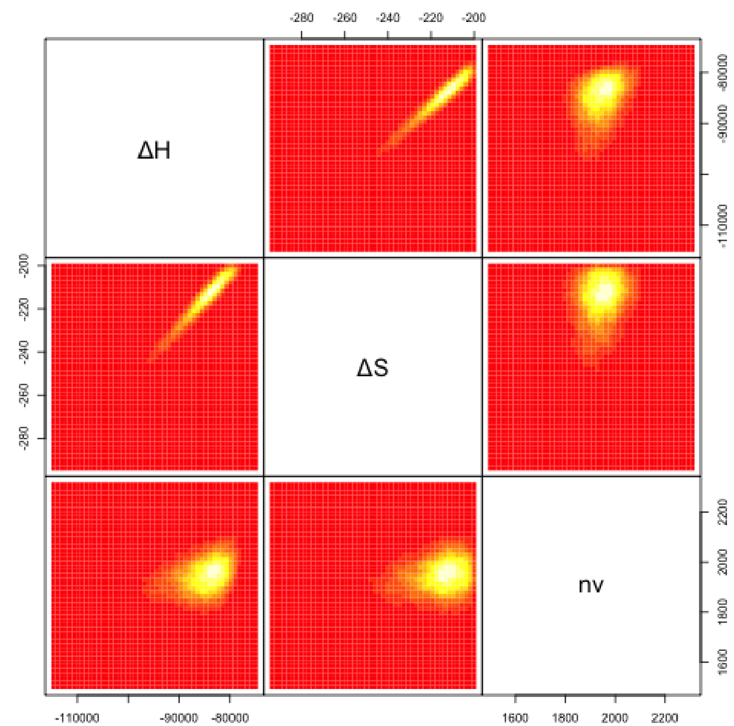

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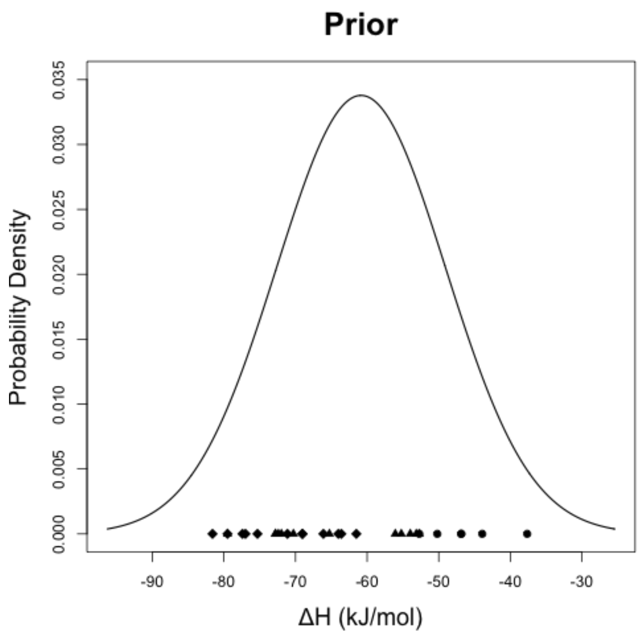
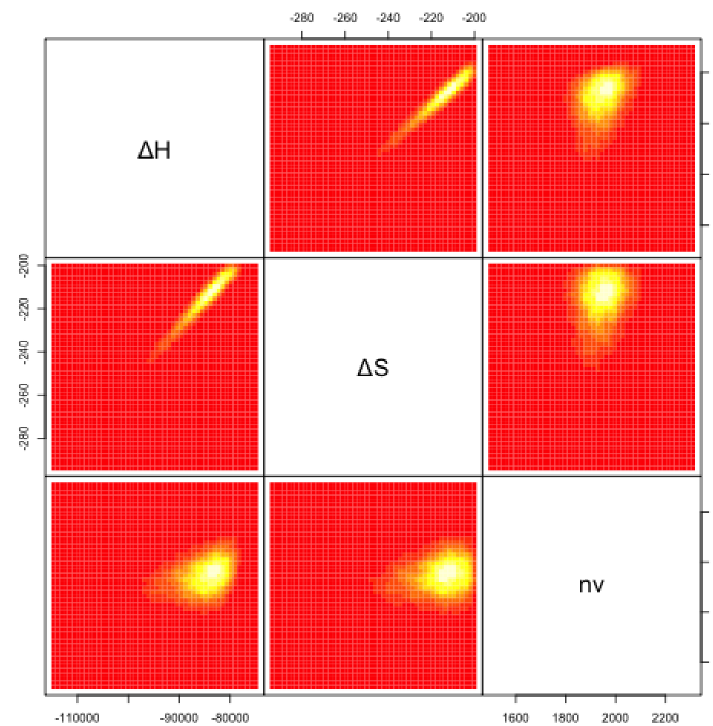
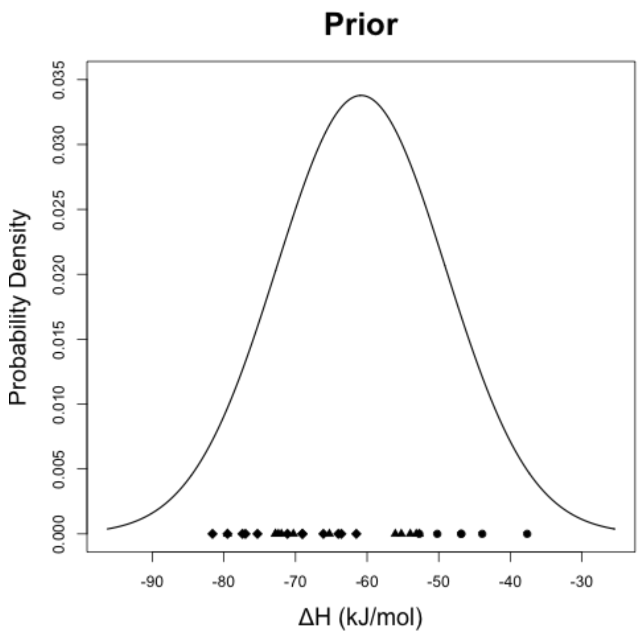


(left) prior distribution for adsorption enthalpy, and (right) posterior distribution



Bayesian methods in parameter estimation

reaction	B3LYP	PBE	PBE0	MP2	MP3
CO_2+2MMA→P-COOH:P	-52.72	-71.13	-81.59	-52.72	-72.8
CO_2+MMA+DMA→S-COOH:P	-46.86	-63.60	-76.99	-53.97	-71.96
CO_2+MMA+DMA→P-COOH:S	-50.21	-66.11	-79.50	-53.14	-72.38
CO_2+2DMA→S-COOH:S	-46.86	-64.02	-77.40	-56.07	-72.80
CO_2+DETA+EDA→P-COOH:S	-37.66	-69.04	-69.04	-55.23	-70.29
CO_2+DETA+EDA→S-COOH:P	-43.93	-61.50	-75.31	-65.27	-79.50



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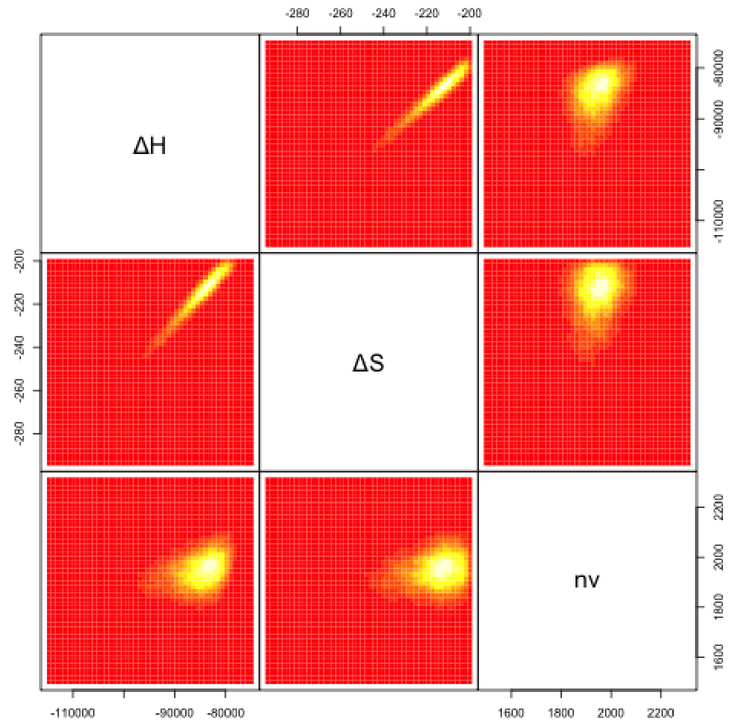

conclusions

- The stability of diffusive intermediates exercise primary control over the working capacity of mesoporous silica-supported, PEI-based CO_2 sorbents.
- *Ab initio* calculations can be used in along with a valid model form discrepancy in a Bayesian framework to influence the experimental calibration of engineering-useful models of complex chemical systems.

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