Anomalous Surface Thermodynamics of Gas Adsorption on Zeolite-Templated Carbon

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The *Next Generation Mesoporous Materials* Project

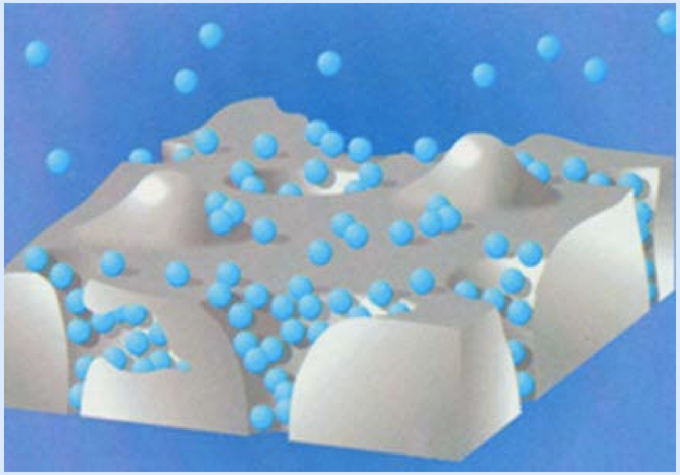
EFree

Goal*: To obtain mesoporous and mesostructured crystalline materials through templated synthetic routes at high pressure for catalysis and related applications.*

Current Research Objective: *To develop gas characterization techniques and novel insight to guide the development of energy relevant materials.*

Physisorption:

$$\frac{H_g(P,T) - H_a(\theta,T)}{T} = S_g(P,T) - S_a(\theta,T)$$



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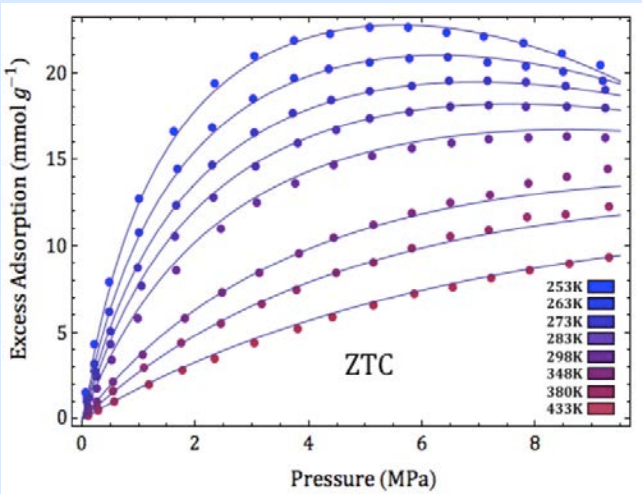
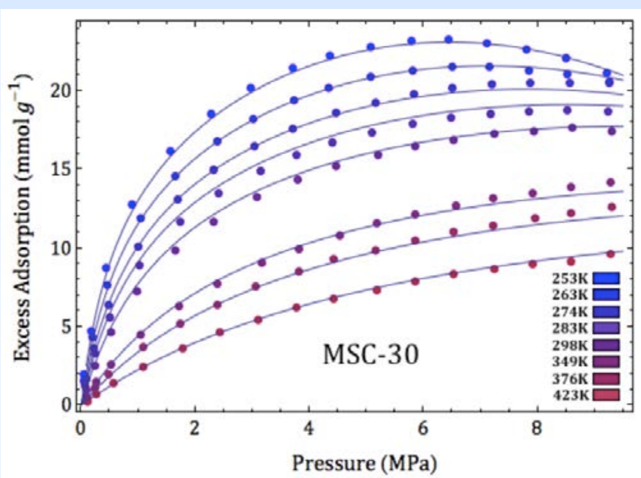
A Superposition of Langmuir Isotherms gives High-Quality Fits





Langmuir

$$\theta = \frac{K_i p}{1 + K_i p}$$

Equilibrium Constant

$$K_i = \frac{A_i}{\sqrt{T}} e^{-E_i/RT}$$

Gibbs Excess

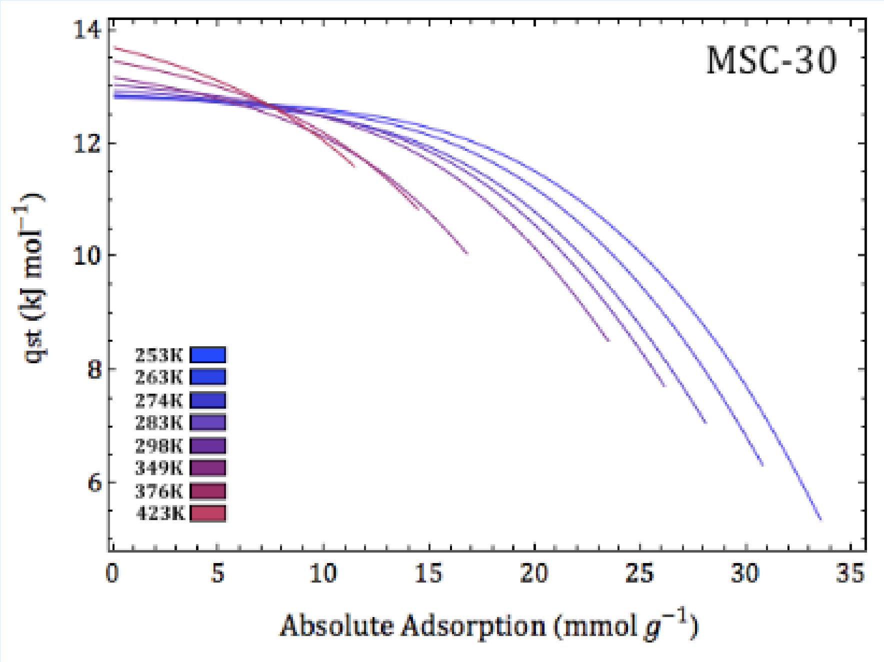
$$n_e = n_a - V_{ads} \rho_g (P, T)$$

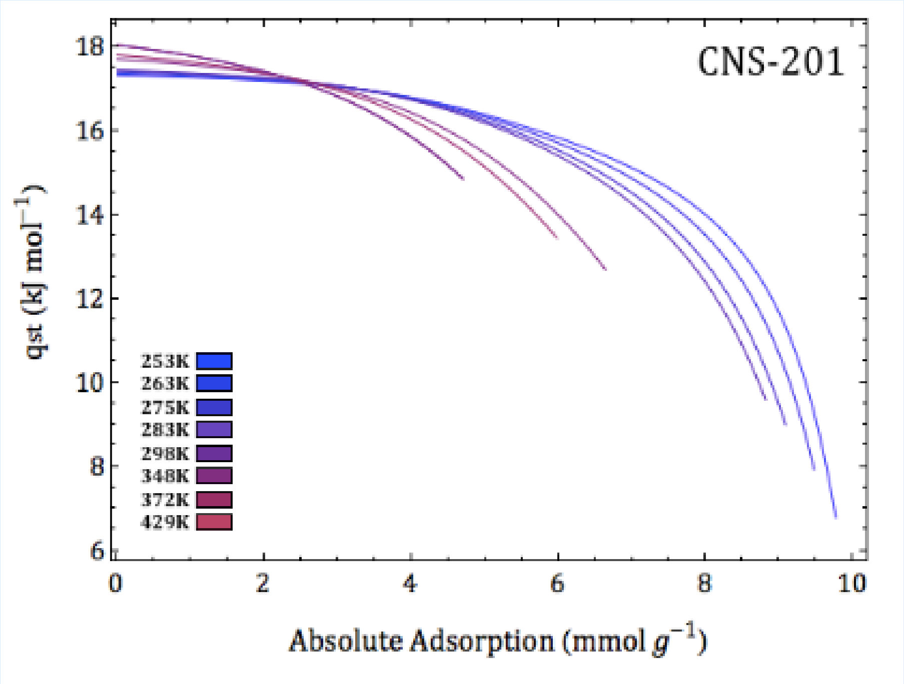
$$n_a(P, T) = n_{max} \sum_i \alpha_i \left(\frac{K_i P}{1 + K_i P}\right)$$

$$V_{ads}(P, T) = V_{max} \sum_i \alpha_i \left(\frac{K_i P}{1 + K_i P}\right)$$

$$n_e(P, T) = (n_{max} - V_{max} \rho_g(P, T)) \left(\sum_i \alpha_i \left(\frac{K_i P}{1 + K_i P}\right)\right)$$

Isosteric Heat Decreases with Loading on Conventional Carbons

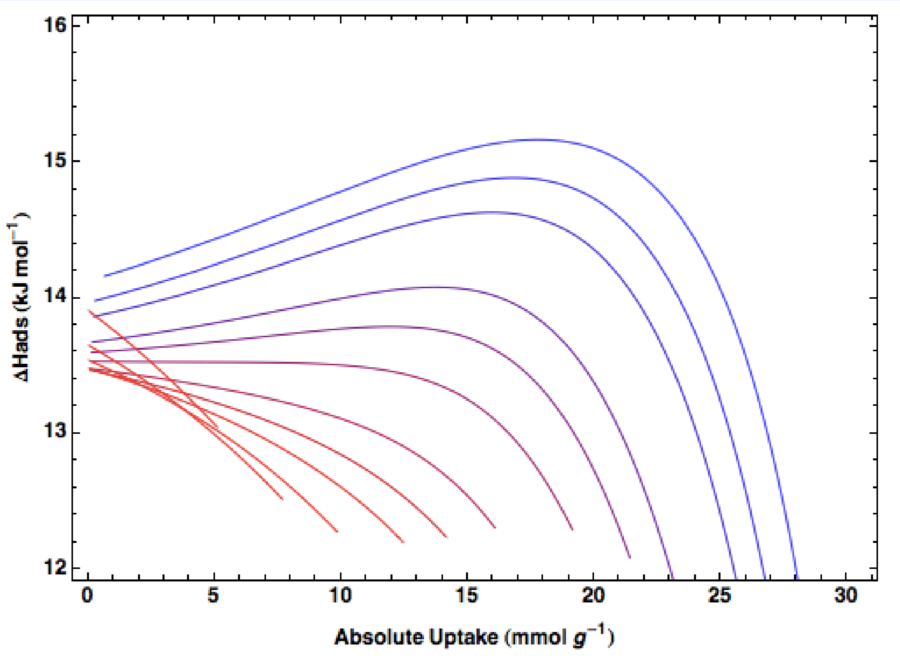




$$q_{st} = -\Delta H_{ads} = -T\left(\frac{\partial P}{\partial T}\right)_{n_a} (\Delta v_{ads})$$

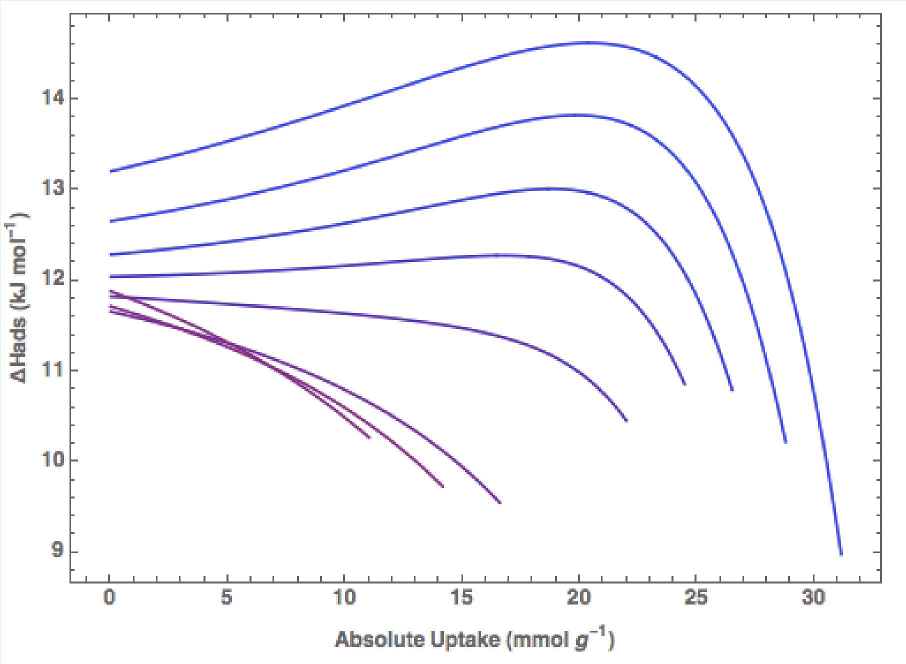
Isosteric Heat on ZTC *Increases* with Loading

Methane on ZTC



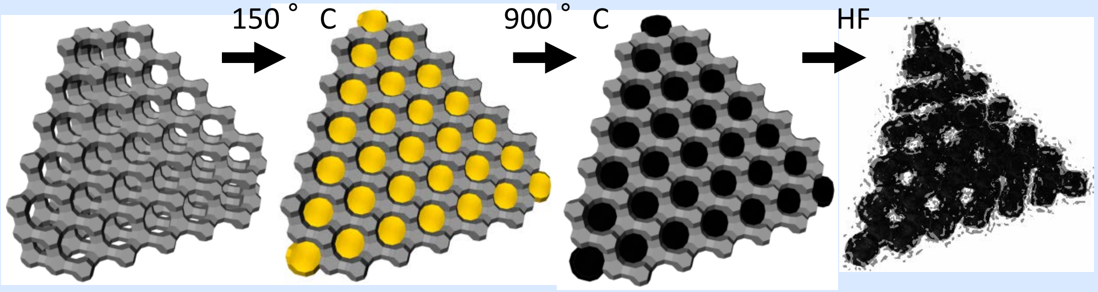
Net Increase: 1.1 kJ/mol

Krypton on ZTC



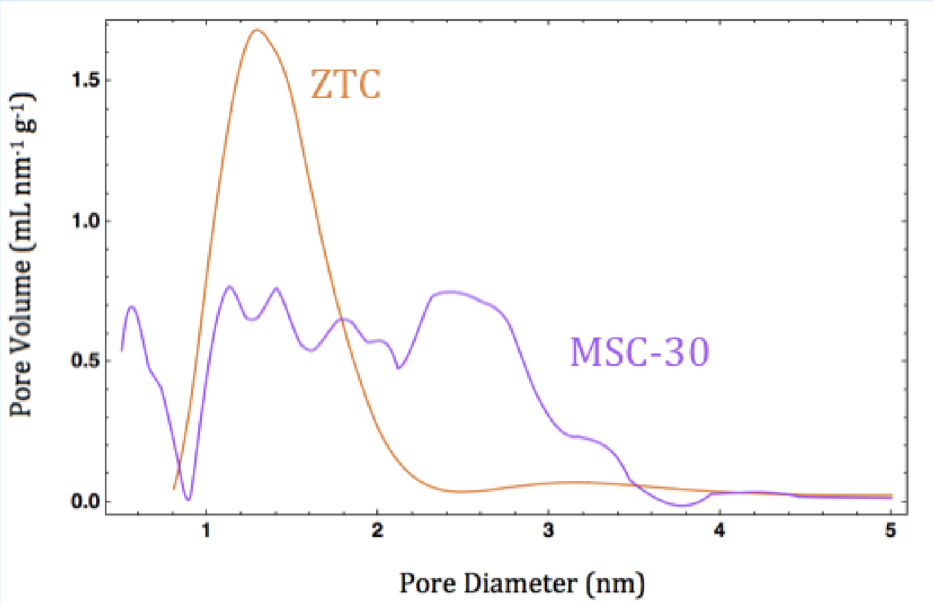
Net Increase: 1.4 kJ/mol

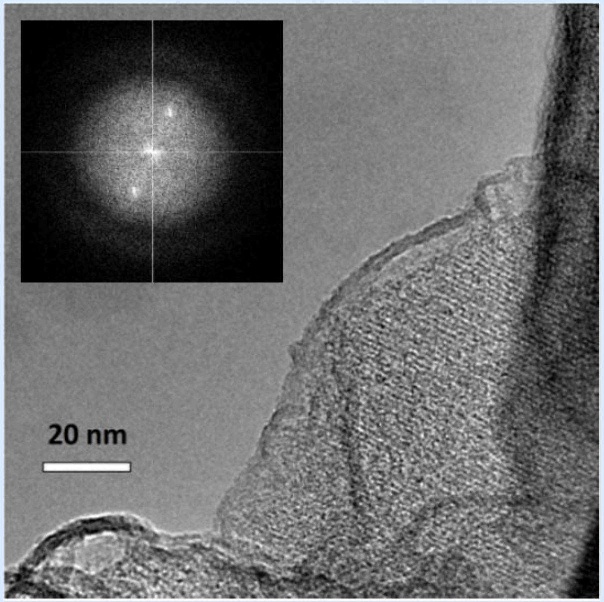
Unlike Activated Carbons ZTC has a Sharp Pore-Size Distribution



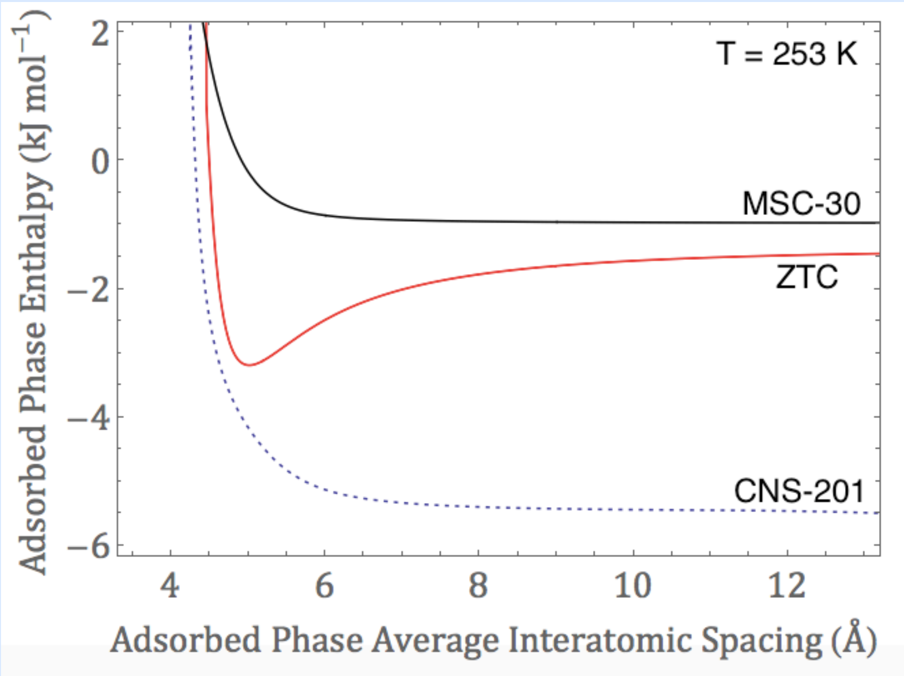
Zeolite NaY NaY-PFA NaY-C ZTC

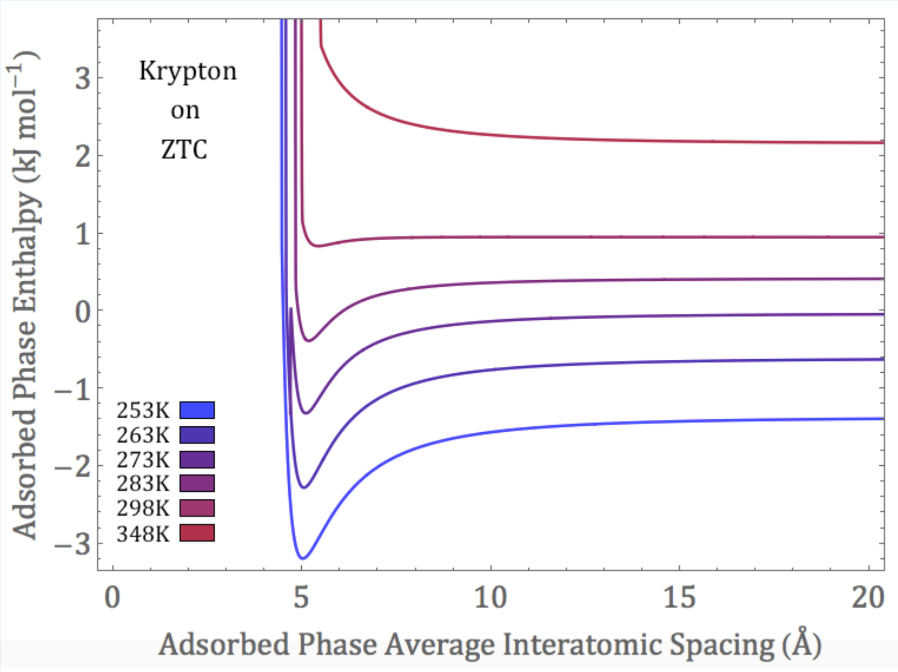
Final Product (ZTC)





The Enthalpy of Adsorbed Phase Kr on ZTC Highlights Atypical Thermodynamics

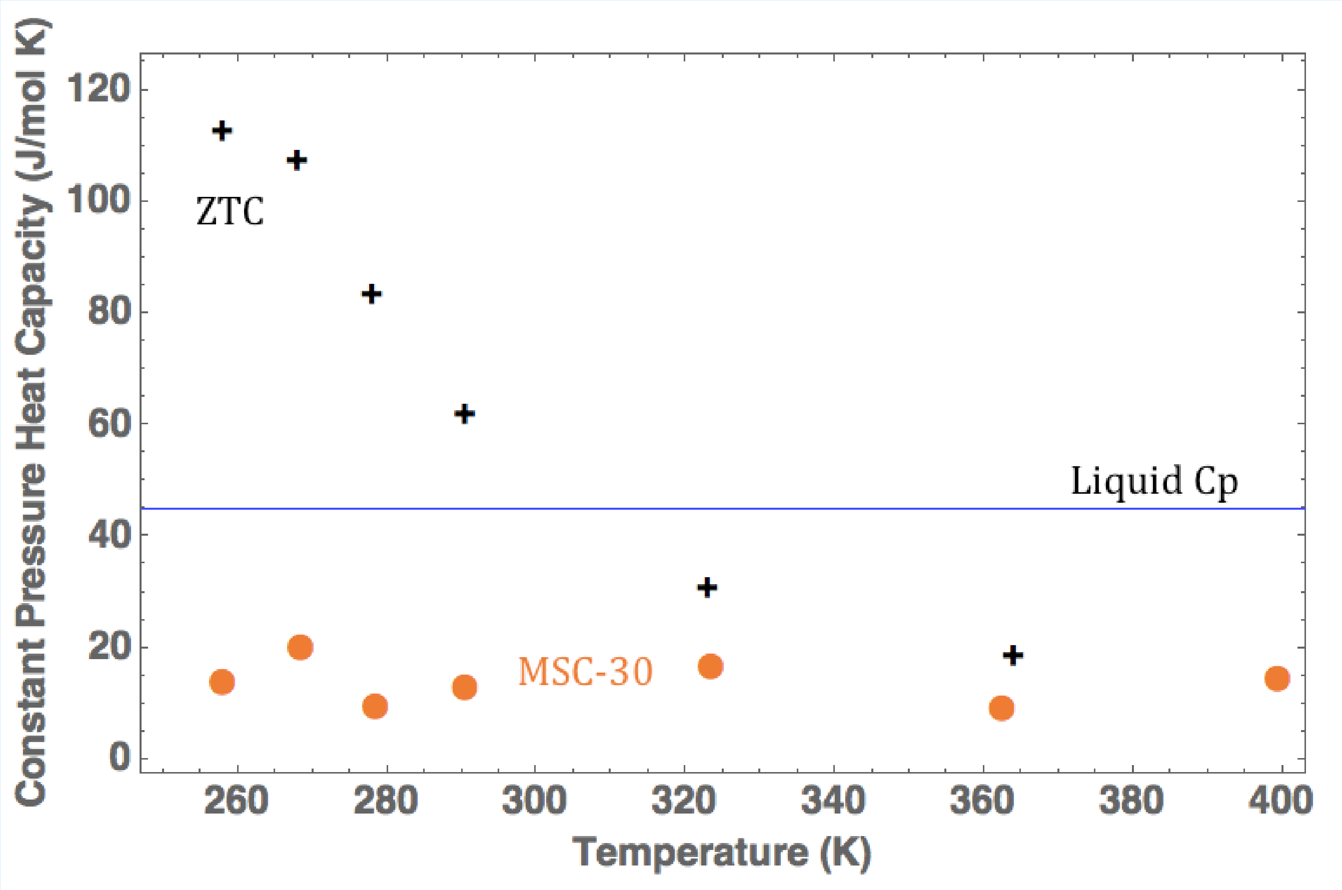




$$H_a = H_g - \Delta H_{ads}$$

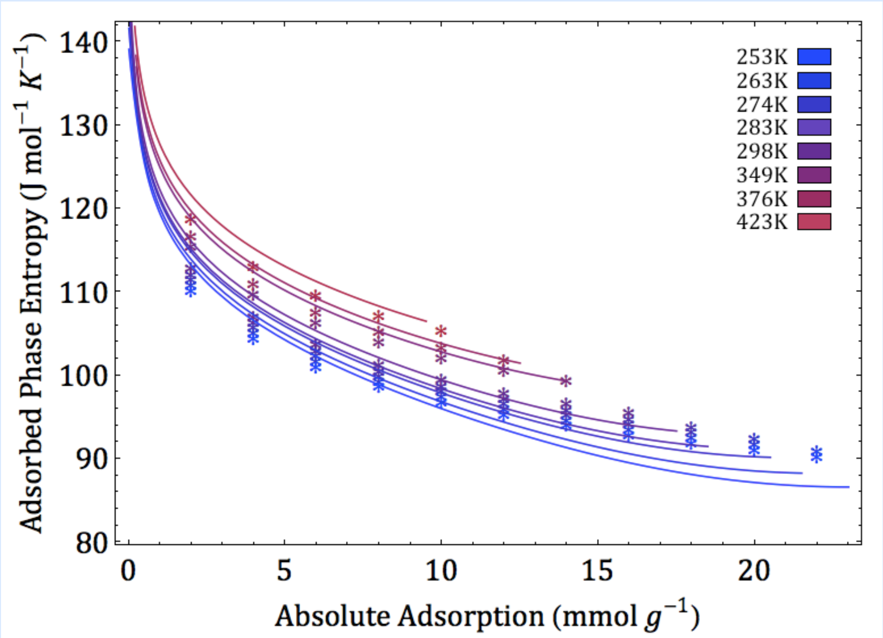
$$x_{avg} = \left(\frac{V_{mic}}{n_a}\right)^{\frac{1}{3}}$$

Adsorbed Phase Molar Heat Capacity (Constant Pressure)

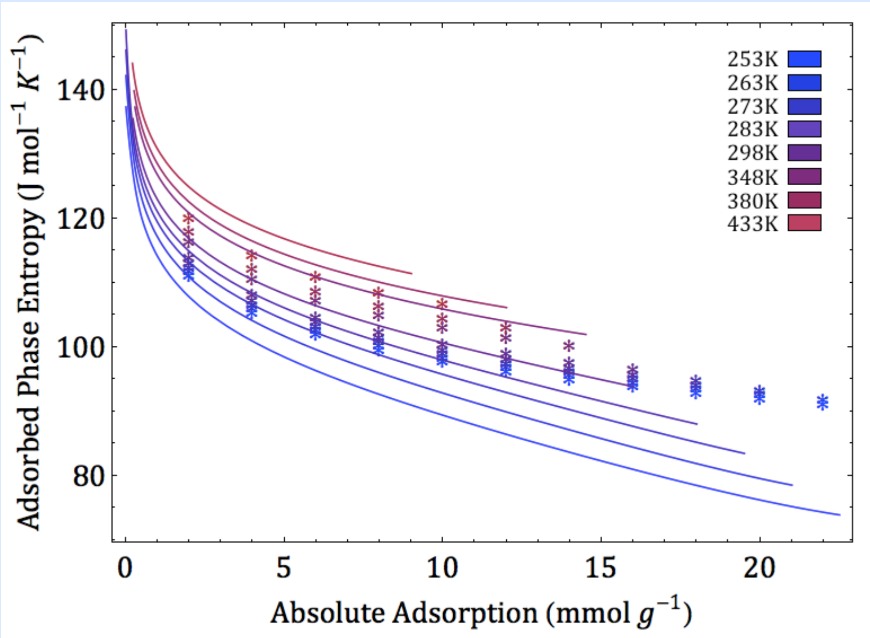


Lower than Expected Adsorbed Phase Entropy on ZTC Suggest Clusters

MSC-30



ZTC

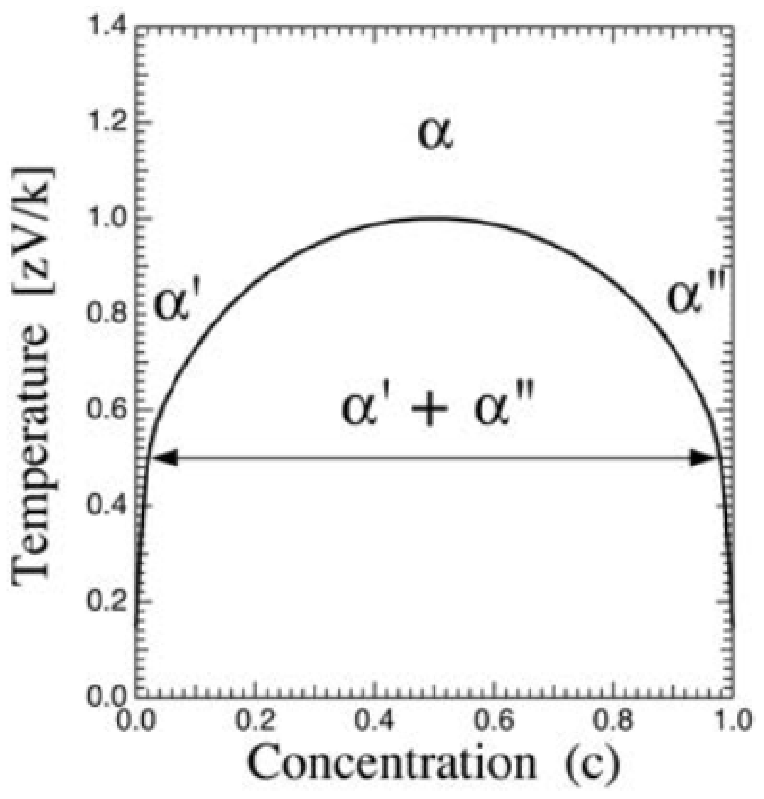


$$\frac{\Delta H}{T} = \Delta S$$

Anomalous Thermodynamics on ZTC may be Explained as Unmixing Transition

-Lower temperatures have more clustered α'' phase and more favorable energetics

-At constant temperature the α'' phase grows linearly with Increased concentration



(Phase Transitions in Materials, Fultz, B., 2013)

Additional Evidence of Cooperative Interactions

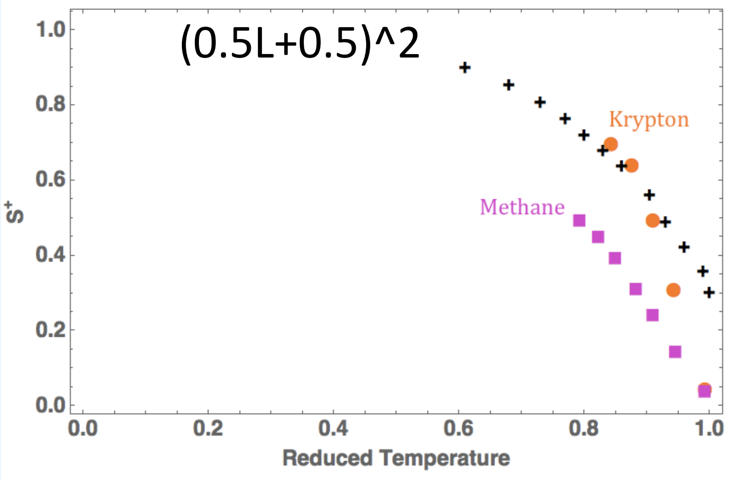
Predictive Model of the Slope
Of the Adsorbed Phase Enthalpy
With Respect to Loading

$$\frac{\partial(\Delta H_{ads})}{\partial\theta} = \frac{z\varepsilon A}{2}$$

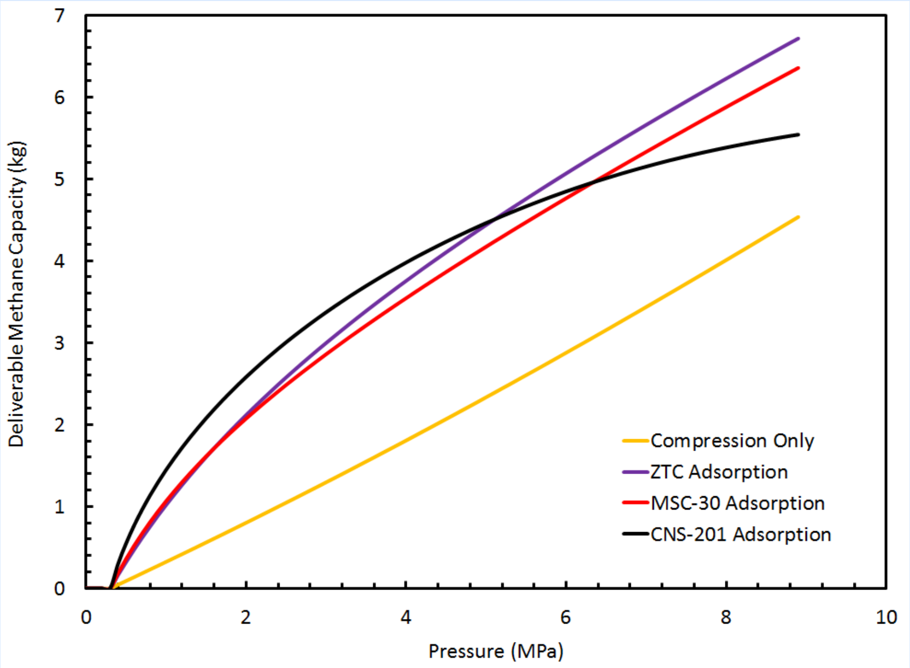
	Estimated Slope (kJ/mol)	Measured Slope (kJ/mol)
Methane	2.4	2.2
Ethane	3.6	3.3
Krypton	2.6	2.7

Critical Temperature for
Square-Lattice Ising Model

$$T_o = \frac{2\varepsilon}{k_B(1+\sqrt{2})}$$



Conclusions



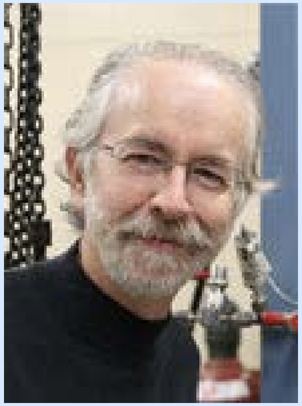
Methane Storage
For 70 L tank
@ 298 K

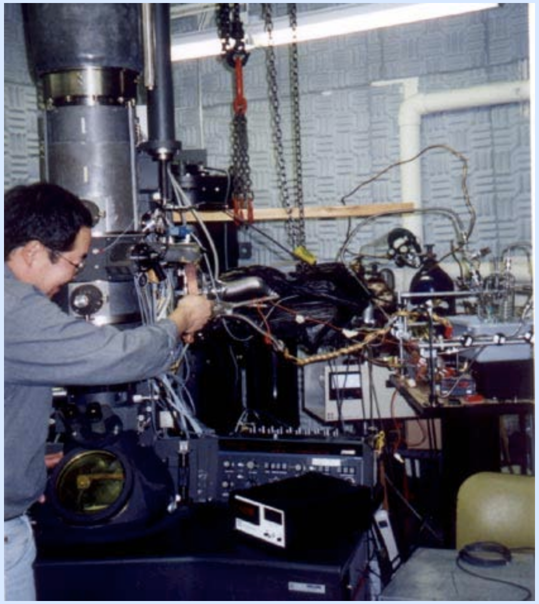
-Control of pore-size distribution enables tuning of adsorption thermodynamics

-Anomalous isosteric heat results from cooperative adsorbate-adsobate interactions enabled by adsorbed-phase clustering only observed on ZTC

-ZTC allows for ~ 50% improvement in deliverable gas capacity (over no adsorbent)

Acknowledgements





Brent Fultz

Nicholas Stadie

Channing Ahn

Conclusions

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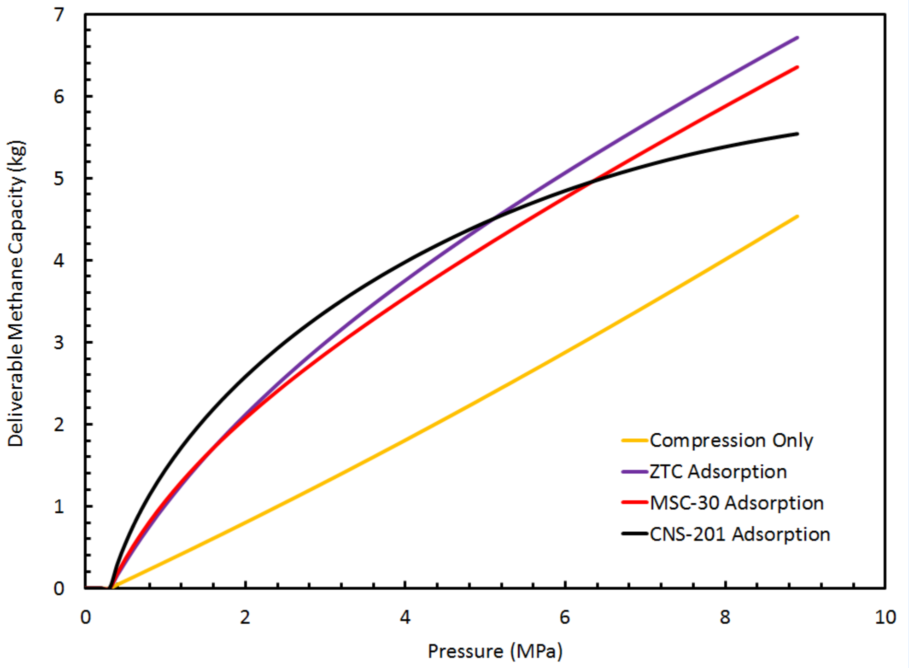

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