Effect of Particle Size on the Adsorption and Desorption Properties of Oxide Nanoparticles

Task 425.023

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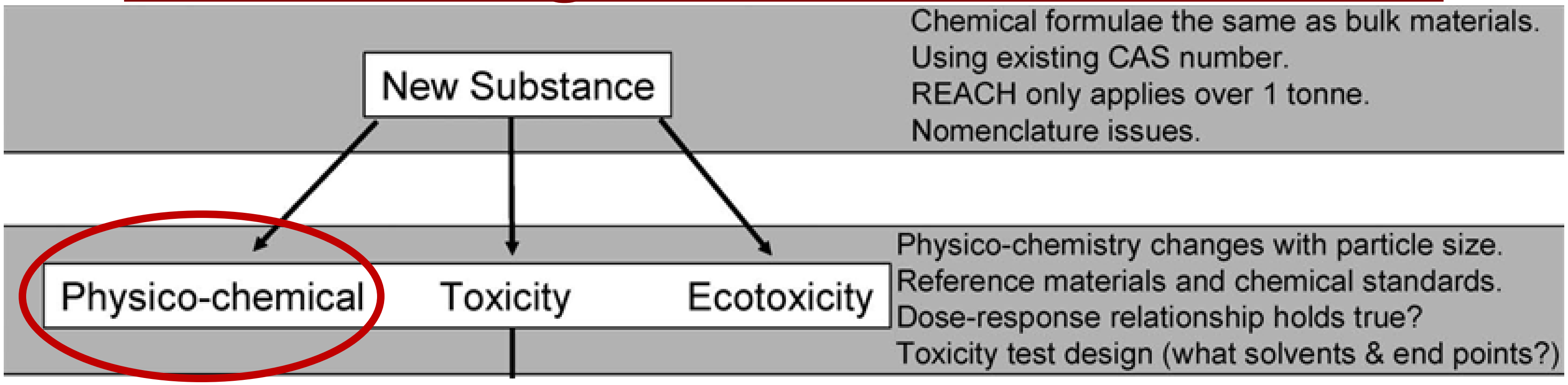
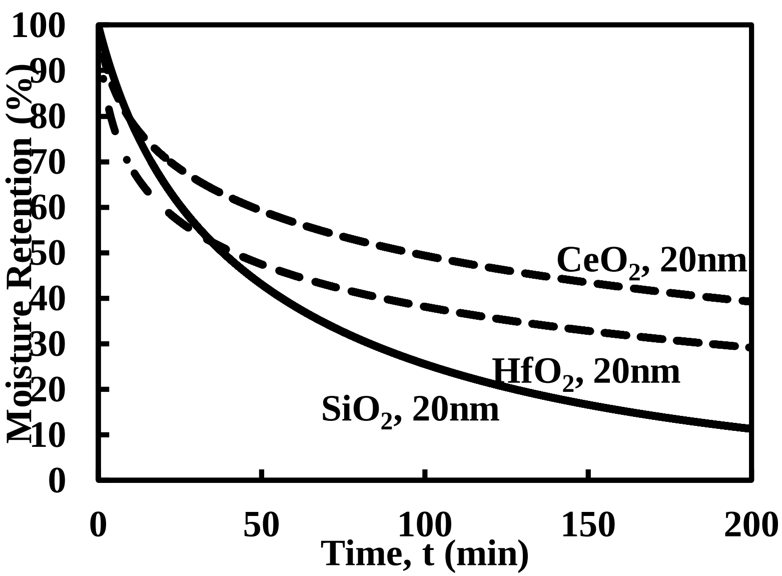
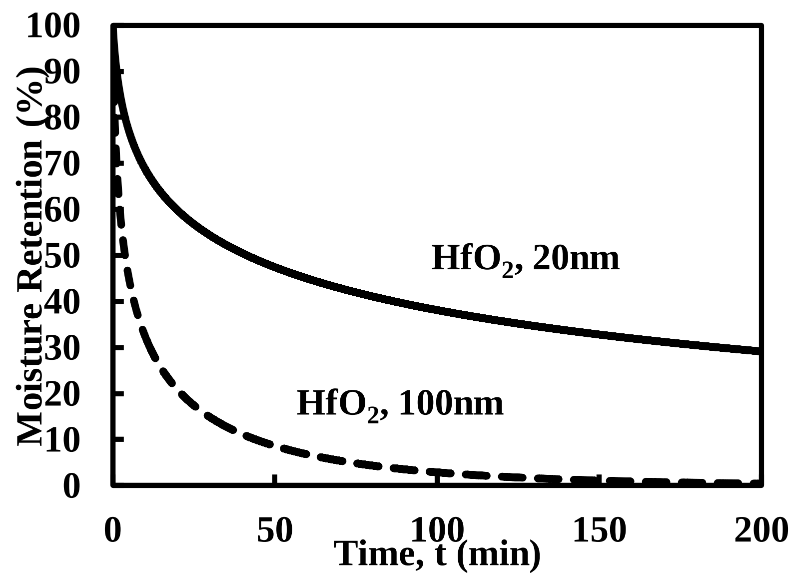
ESH Testing and Evaluation of NPs



Surface Properties: capacity, affinity, and activation energy





Handy, R.D., Shaw, B.J., 2007. Toxic effects of nanoparticles and nanomaterials: Implications for public health, risk assessment and the public perception of nanotechnology. Health Risk Society 9, 125-144.

Objectives and Method Approach

Objective: Characterization of the surface sites on nanoparticles that contribute to concentration, retention, and enhanced transport of toxic chemicals.

Method approach: Surface hydroxylation (adsorption and desorption of contaminants).

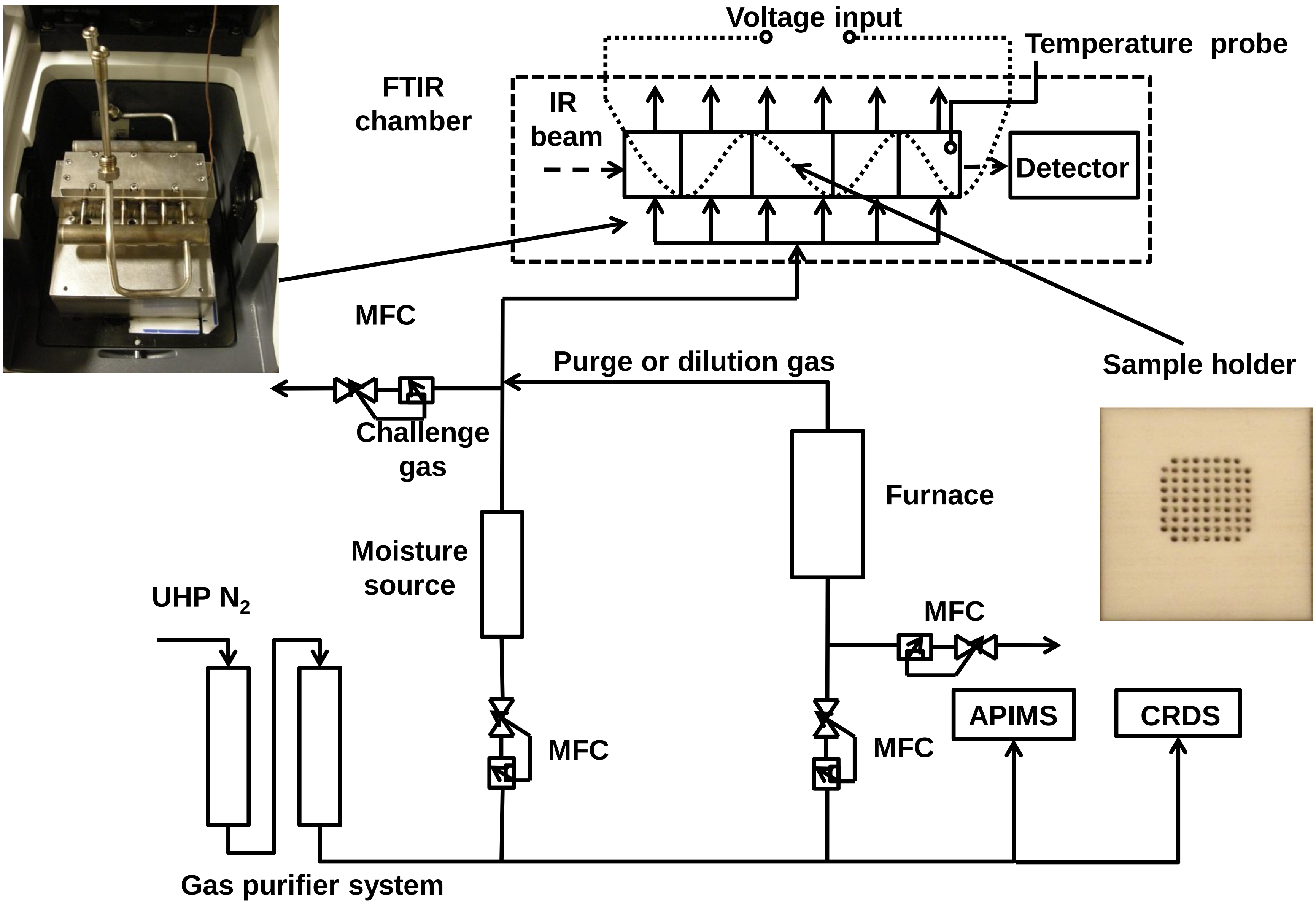
Materials: SiO_2, HfO_2, and CeO_2.

Parameters: Oxide type, particle size, temperature.

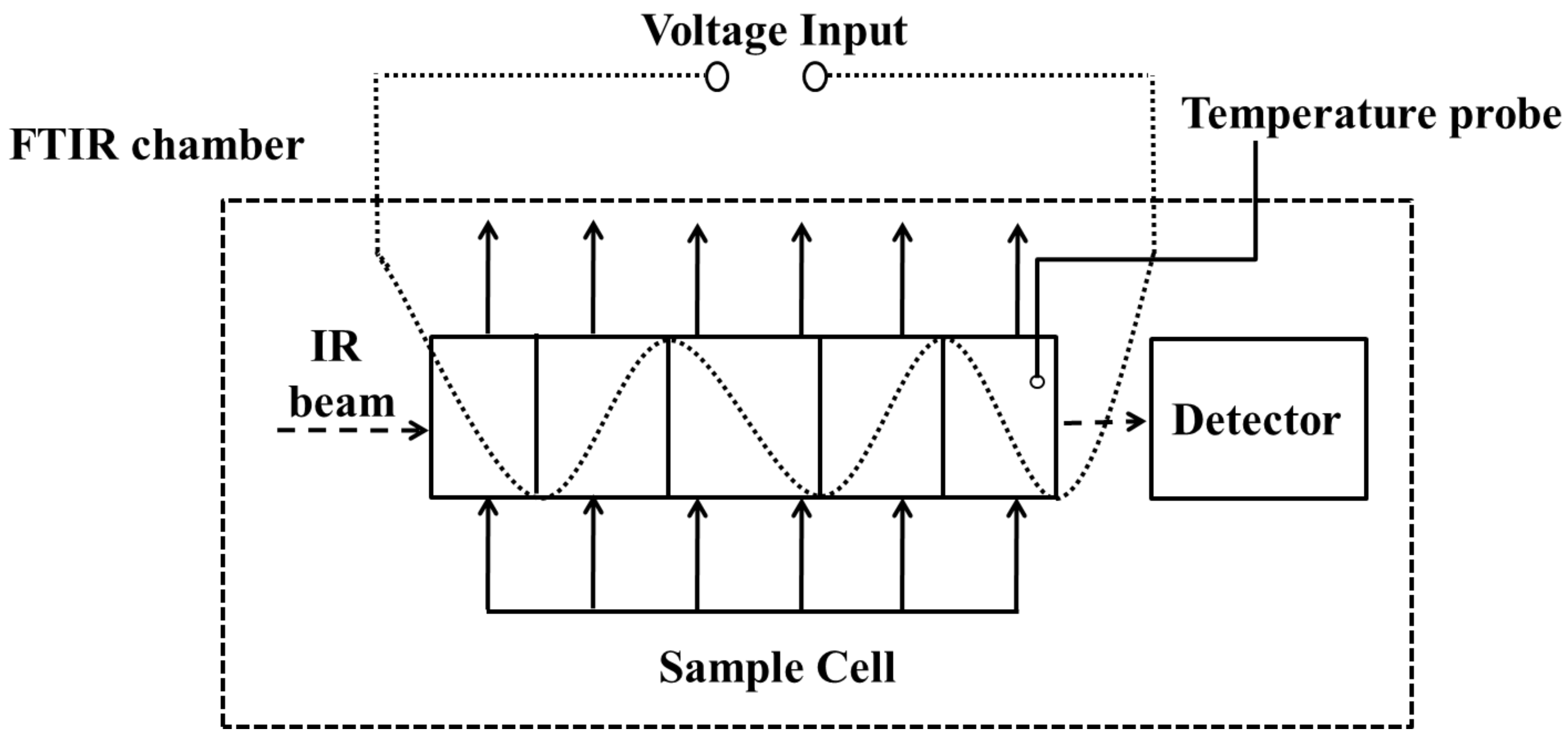
Results: Capacity and energetics of capture and retention of contaminants on active sites.

NPs	Supplier	APS* (reported by supplier) (nm)
CeO_2	Sigma-Aldrich	20 & 50
SiO_2	Sigma-Aldrich	20
SiO_2	Nanostructured & Amorphous Materials	80
HfO_2	Sematech	20
HfO_2	American Elements	100

Schematic Diagram of the Experimental Setup



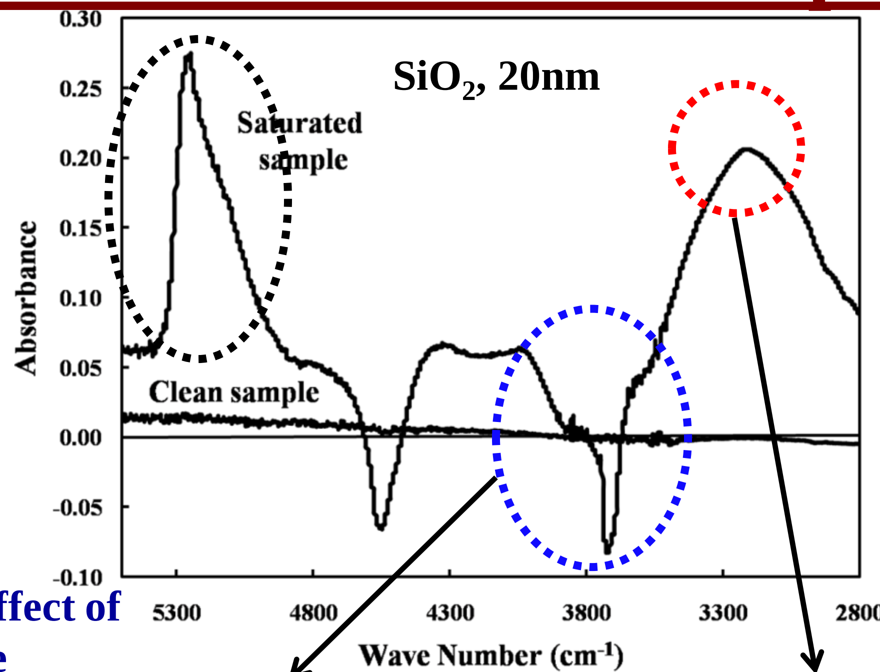
Heating Element Design



Voltage Input	Temperature
0 V	25°C
30 V	55°C
45 V	80°C
60 V	105°C

FTIR Spectra of Moisture Adsorption on NPs

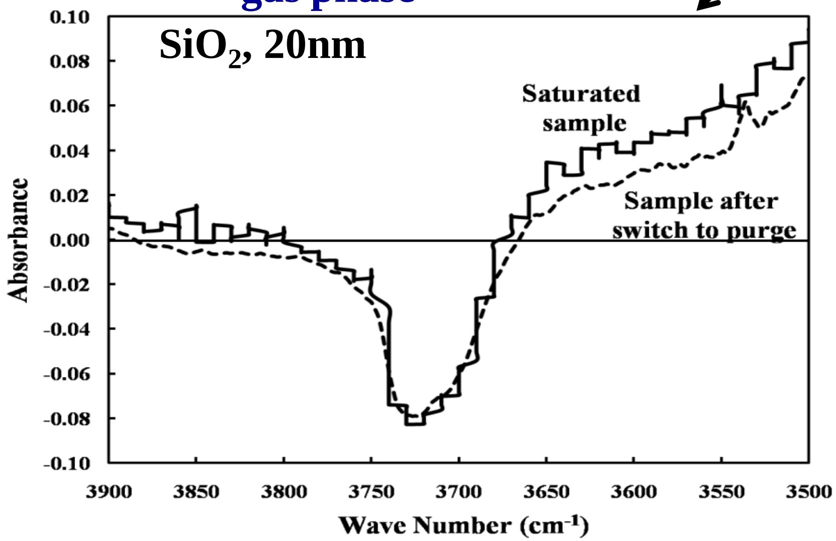
Overtone combination of stretching and bending for water molecules. Wave number: 5200 cm^{-1}



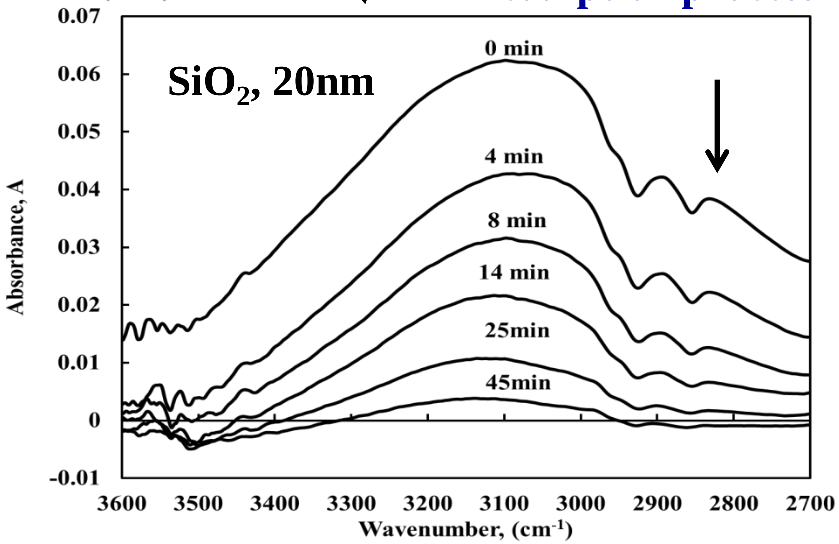
Due to hydrogen bonding, the liquid water stretch vibration is shifted to a lower frequency. Wave number: 3200 cm^{-1}

The main stretching band of water vapor. Wave number: 3800 cm^{-1}

Eliminate the effect of gas phase



Desorption process



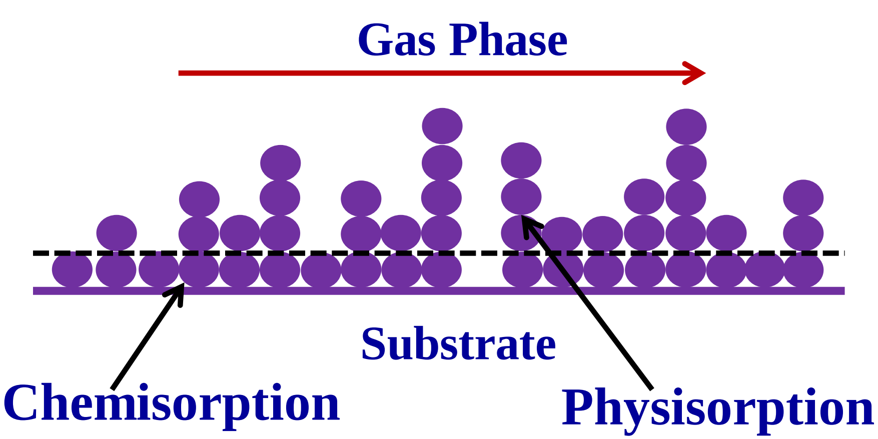
Process Simulation: Single-Particle Domain

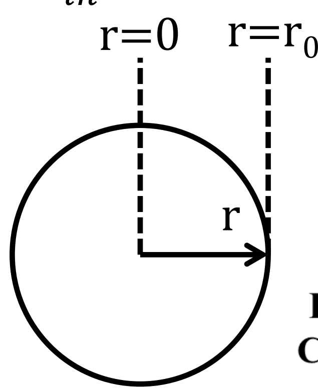
Adsorbent concentration in the gas phase:

$$\frac{\partial C_{g_{in}}}{\partial t} = \underbrace{D_{e_{in}} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_{g_{in}}}{\partial r} \right)}_{\text{Diffusion term}} + \underbrace{\left[k_d C_{s_{in}} - k_a C_{g_{in}} (S_0 - C_{s_{in}}) \right] \frac{A_s}{V}}_{\text{Adsorption and desorption term}}$$

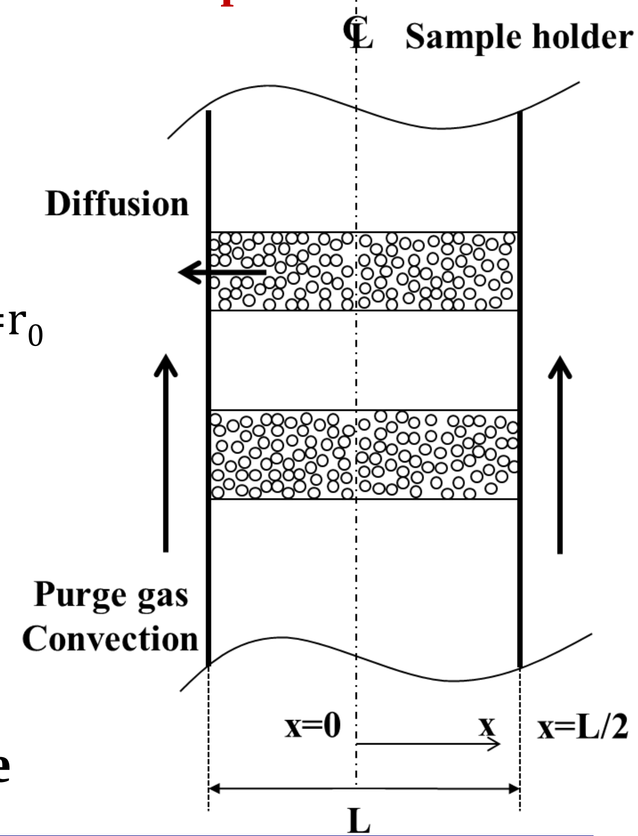
Adsorbent concentration on the surface:

$$\frac{\partial C_{s_{in}}}{\partial t} = k_a C_{g_{in}} (S_0 - C_{s_{in}}) - k_d C_{s_{in}}$$





Nanoparticle



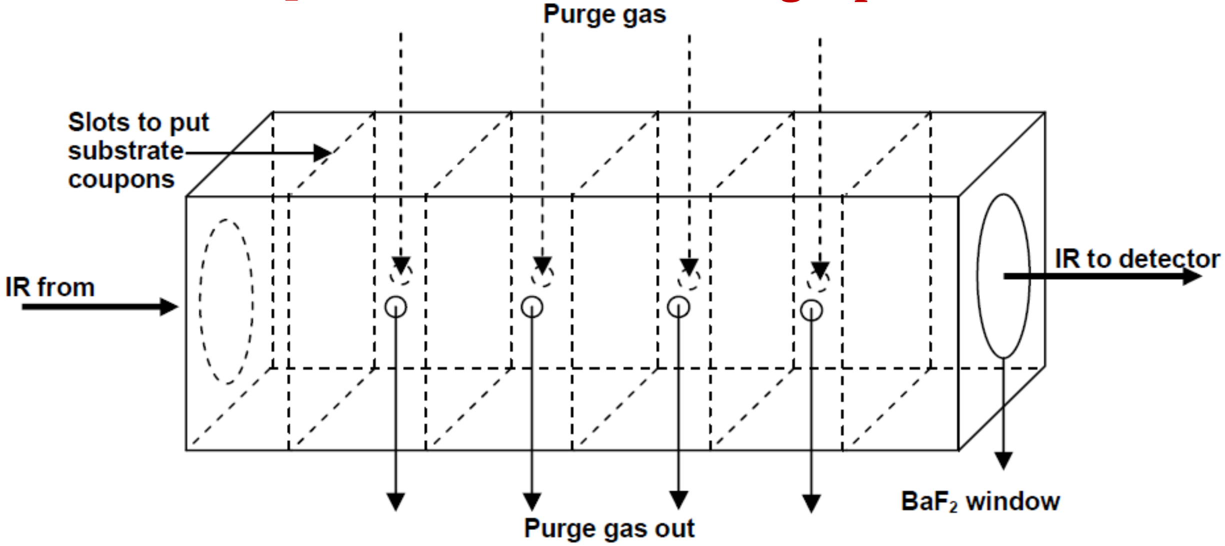
Process Simulation: Packed-bed Domain

Adsorbent concentration in the gas phase:

$$\frac{\partial C_{g_{out}}}{\partial t} = \underbrace{D_{e_{out}} \frac{\partial^2 C_{g_{out}}}{\partial x^2}} - \underbrace{D_{e_{in}} \frac{\partial C_{g_{in}}}{\partial r}|_{r=r_0} 4\pi r_0^2 N_v}$$

Diffusion term in packed-bed domain

Diffusion flux from single-particle domain



Integral of absorbance peak over wavenumber:

$$A_{\text{int}} = \int_{\lambda_1}^{\lambda_2} A d\lambda = \frac{\text{a}}{r_0} \int_{\lambda_1}^{\lambda_2} a d\lambda \int_0^L \int_0^{r_0} C_{s_{in}}(r,x,t) dr dx.$$

Mechanism of Multilayer Model

Adsorption rate coefficients

$$k_a = k_{a_0} exp(\frac{-E_a}{RT})$$

Desorption rate coefficients

$$k_d = k_{d_0} exp(\frac{-E_d}{RT})$$

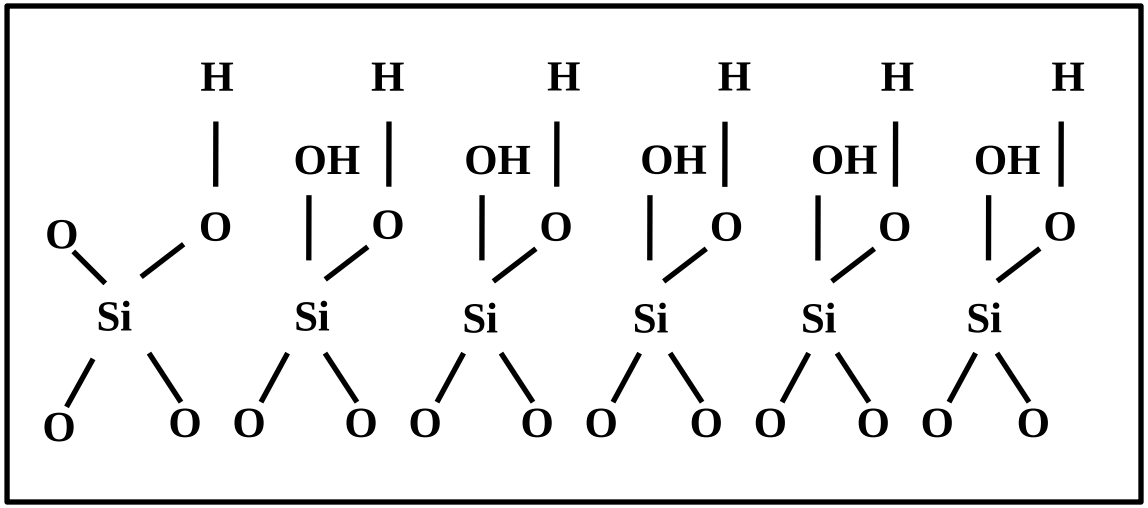
Adsorption activation energies

$$E_a = E_{a_1} \frac{C_{s_0} - C_s}{C_{s_0}} + E_{a_2} \frac{C_s}{C_{s_0}}$$

Desorption activation energies

$$E_d = E_{d_1} \frac{C_{s_0} - C_s}{C_{s_0}} + E_{d_2} \frac{C_s}{C_{s_0}},$$

1: Chemisorption **2: Physisorption**



Numerical Method

Discretization

- Forward Euler Method
- Crank-Nicolson Method

Linearization

- Next Time-step Estimation
- Triangular Matrix Solver

Iteration

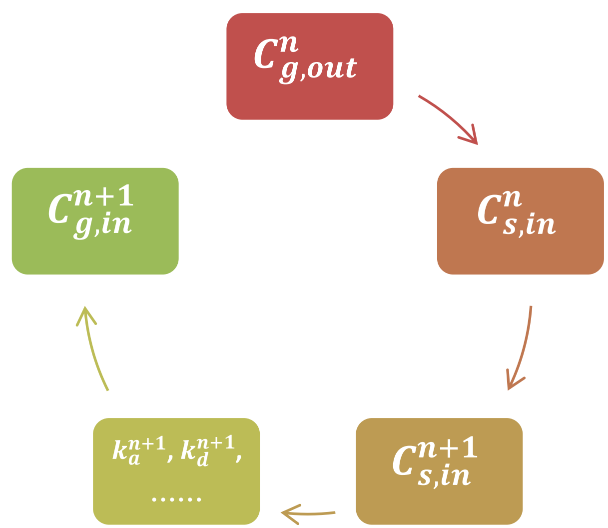
- Update the new value for $C_{s,\,in}$
- Update new value for k_a, k_d and so on

$$\frac{\partial C_g}{\partial t} = \frac{C_{g,i}^{m+1} - C_{g,i}^{m}}{\Delta t}$$

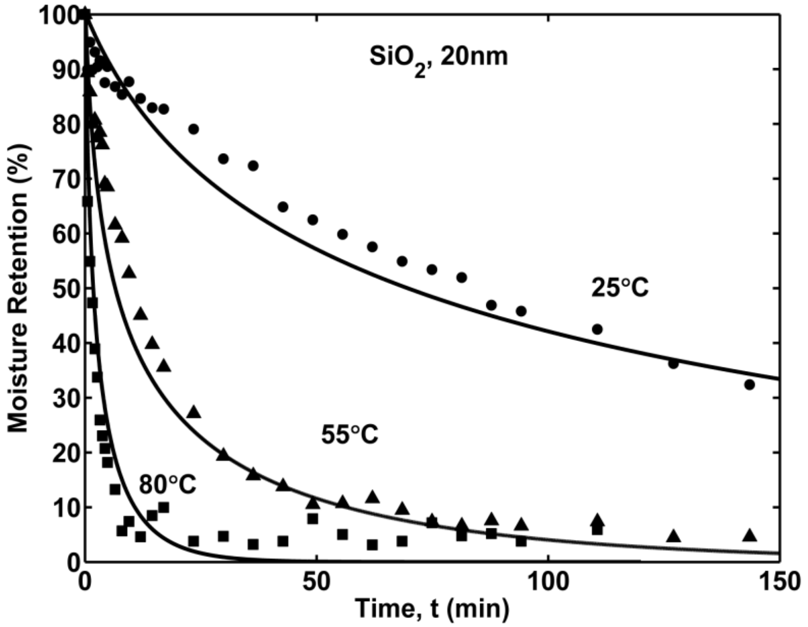
$$\frac{\partial^2 C_g}{\partial x^2} = \frac{1}{2}\left(\frac{C_{g,i+1}^{m+1} - 2C_{g,i}^{m+1} + C_{g,i-1}^{m+1}}{\Delta x^2} + \frac{C_{g,i+1}^{m} - 2C_{g,i}^{m} + C_{g,i-1}^{m}}{\Delta x^2}\right)$$

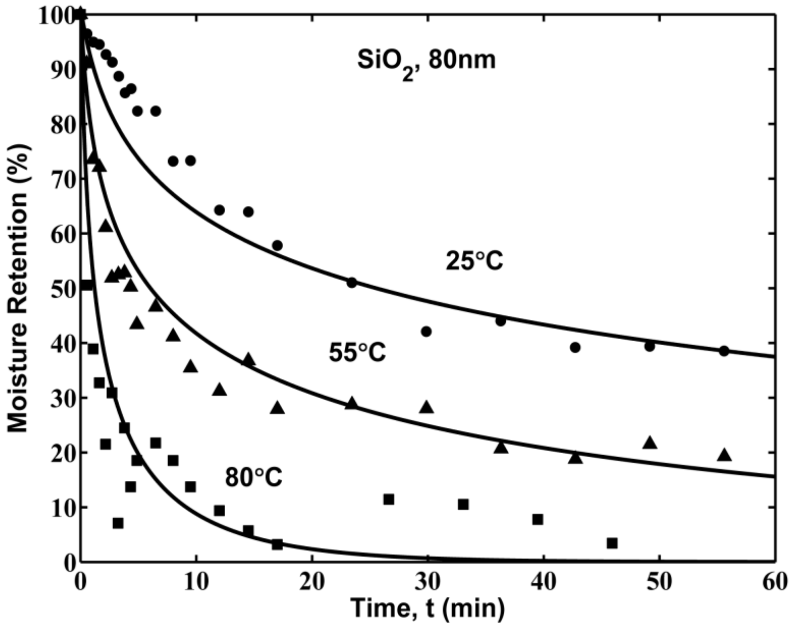
$$C_g = \frac{1}{2}(C_{g,i}^{m+1} + C_{g,i}^{m}),\ C_s = C_{s,i}^{m}.$$

$$\frac{\alpha\Delta\bar{t}}{2\Delta\bar{x}^2}\bar{C}_{g,i+1}^{m+1} + [\frac{1}{2}(\delta\bar{C}_{s,i}^{m} - \gamma)\Delta\bar{t} - \frac{\alpha\Delta\bar{t}}{\Delta\bar{x}^2} - 1]\bar{C}_{g,i}^{m+1} + \frac{\alpha\Delta\bar{t}}{2\Delta\bar{x}^2}\bar{C}_{g,i-1}^{m+1}$$
$$= -\frac{\alpha\Delta\bar{t}}{2\Delta\bar{x}^2}\bar{C}_{g,i+1}^{m} + [-\frac{1}{2}(\delta\bar{C}_{s,i}^{m} - \gamma)\Delta\bar{t} + \frac{\alpha\Delta\bar{t}}{\Delta\bar{x}^2} - 1]\bar{C}_{g,i}^{m}$$
$$- \frac{\alpha\Delta\bar{t}}{2\Delta\bar{x}^2}\bar{C}_{g,i-1}^{m} - \Delta\bar{t}\beta\bar{C}_{s,i}^{m}$$



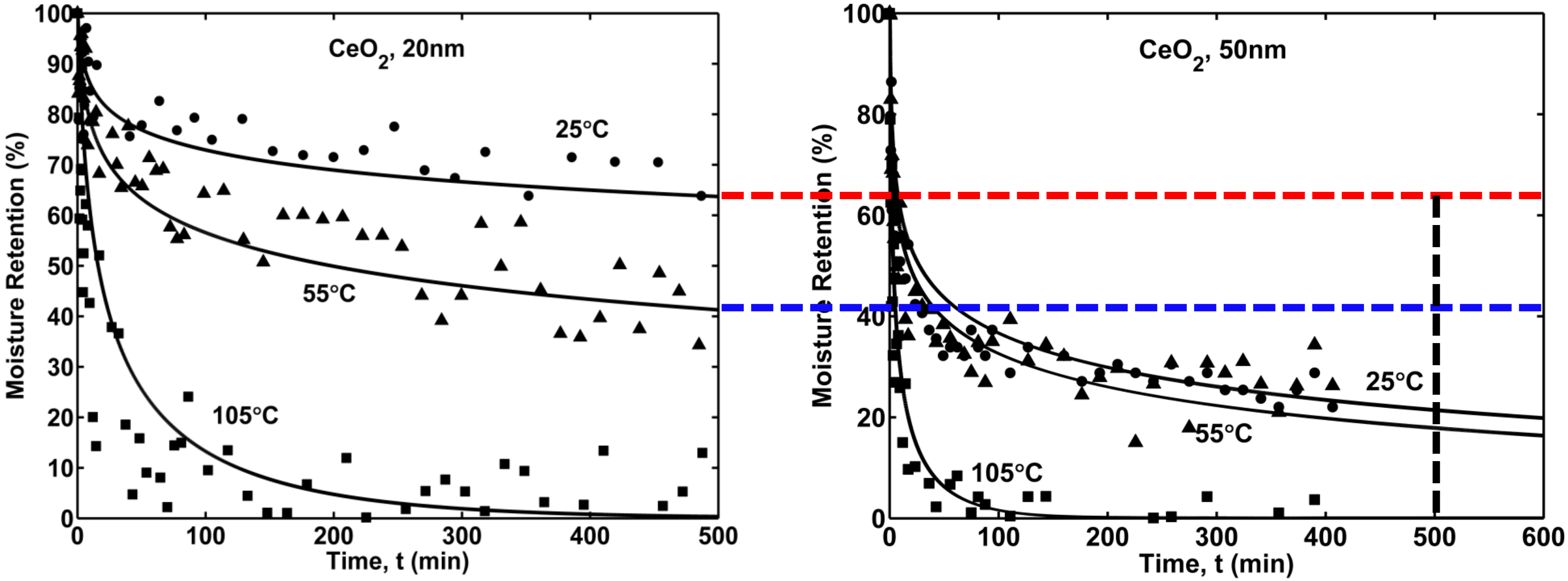
Comparison of Adsorption Profiles of NPs (I)





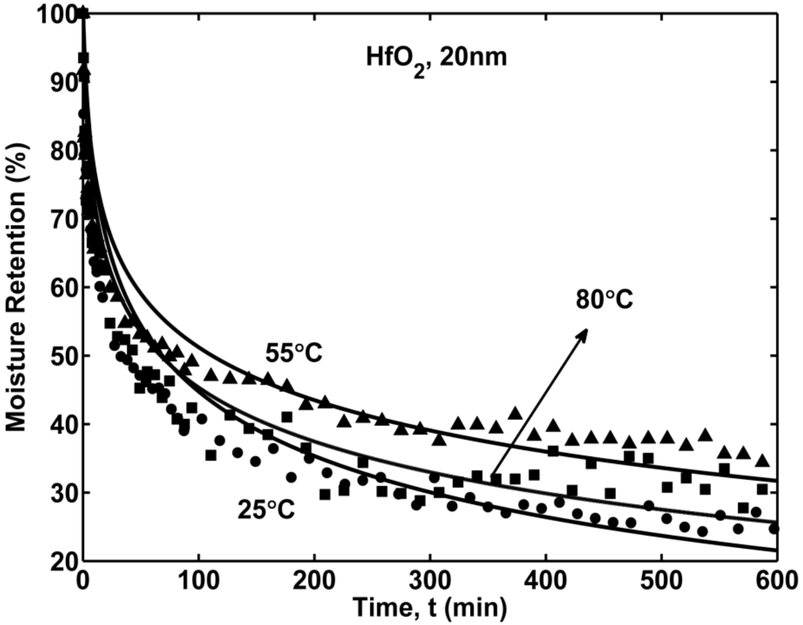
Sample	Saturated surface concentration C_{S_0} (gmol m^{-2})	Fractional coverage θ (%)	E_{a_1} (kJ gmol^{-1})	E_{a_2} (kJ gmol^{-1})	E_{d_1} (kJ gmol^{-1})	E_{d_2} (kJ gmol^{-1})
SiO_2 (20 nm), 25°C	2.0×10^{-6}	67	9.0	6.0	16.0	12.5
SiO_2 (20 nm), 55°C	1.9×10^{-6}	63	9.0	1.2	13.0	8.0
SiO_2 (20 nm), 80°C	1.5×10^{-6}	50	9.0	0.1	7.6	5.7
SiO_2 (80 nm), 25°C	1.1×10^{-6}	37	10.0	6.5	15.5	10.0
SiO_2 (80 nm), 55°C	1.0×10^{-6}	33	10.0	2.0	12.5	5.5
SiO_2 (80 nm), 80°C	5.3×10^{-7}	18	10.0	1.0	7.5	2.2

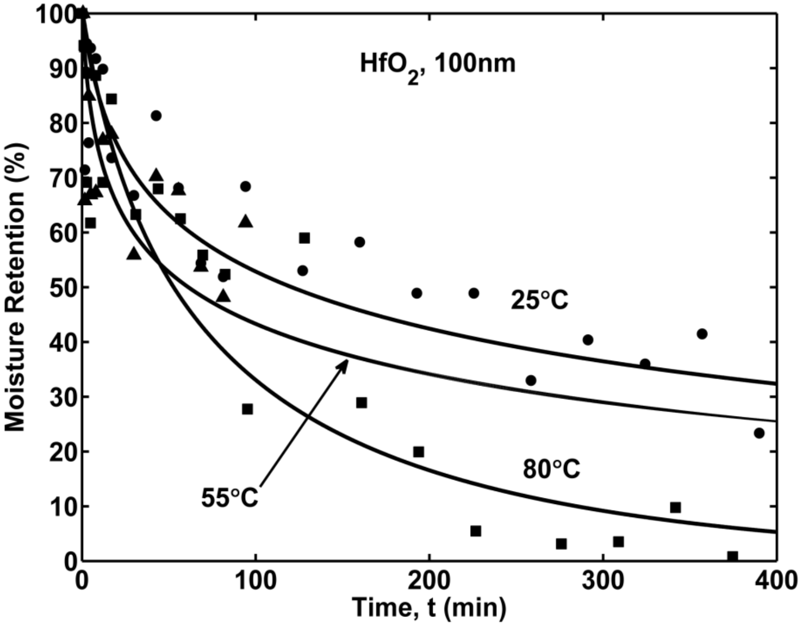
Comparison of Adsorption Profiles of NPs (II)



Sample	Saturated surface concentration C_{S_0} (gmol m^{-2})	Fractiona l coverage θ (%)	E_{a_1} (kJ gmol^{-1})	E_{a_2} (kJ gmol^{-1})	E_{d_1} (kJ gmol^{-1})	E_{d_2} (kJ gmol^{-1})
CeO_2 (20 nm), 25˚C	8.3×10^{-7}	10.4	1.9	1.5	46	7.8
CeO_2 (20 nm), 55˚C	8.2×10^{-7}	10.3	1.9	1.2	30	8.1
CeO_2 (20 nm), 105˚C	8.1×10^{-7}	10.1	1.9	1.0	10	8.9
CeO_2 (50 nm), 25˚C	5.5×10^{-7}	6.9	3.0	0.1	19	5.3
CeO_2 (50 nm), 55˚C	3.7×10^{-7}	4.6	3.0	0.1	20	4.7
CeO_2 (50 nm), 105˚C	3.6×10^{-8}	4.5	3.0	0.1	9	5.0

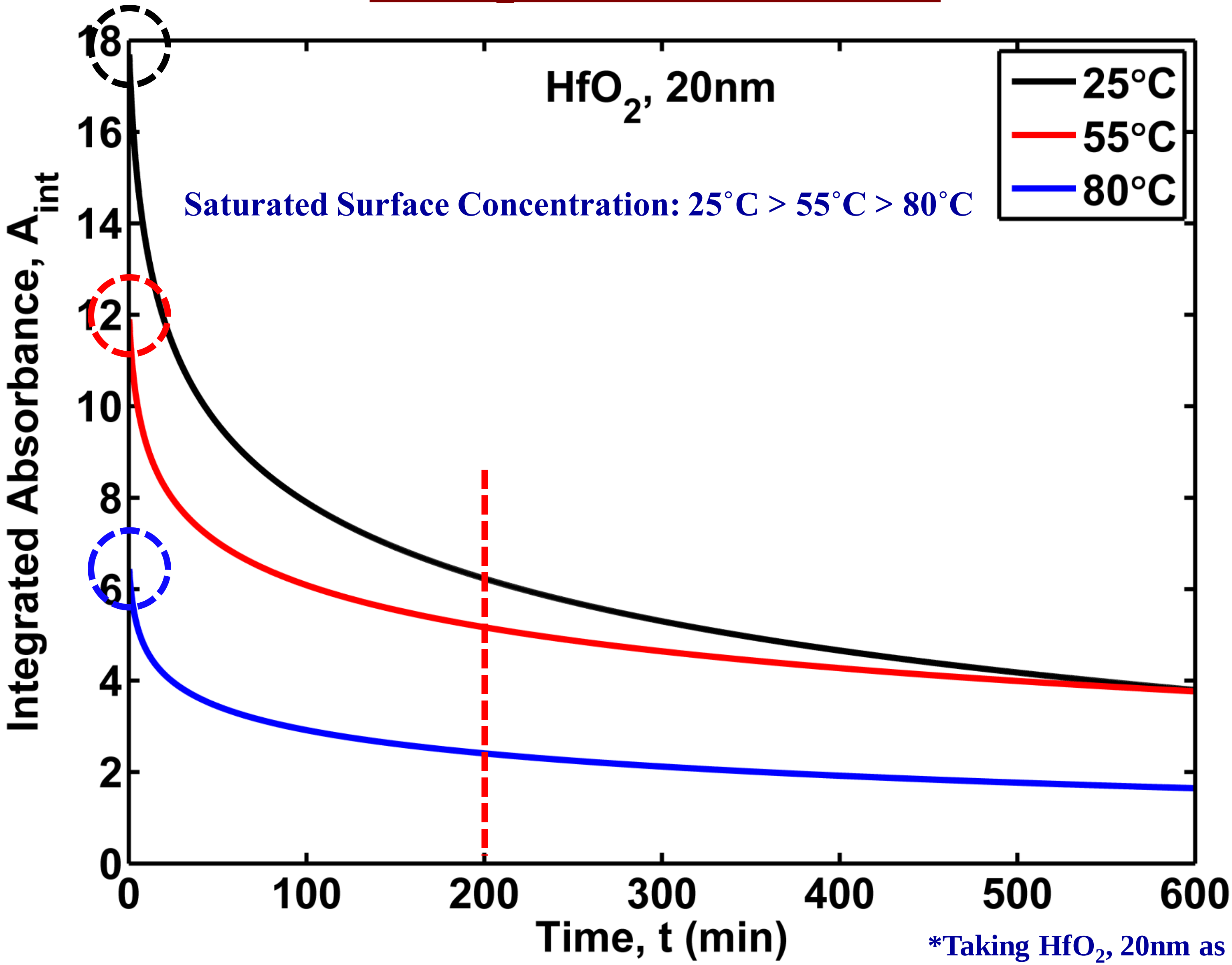
Comparison of Adsorption Profiles of NPs (III)





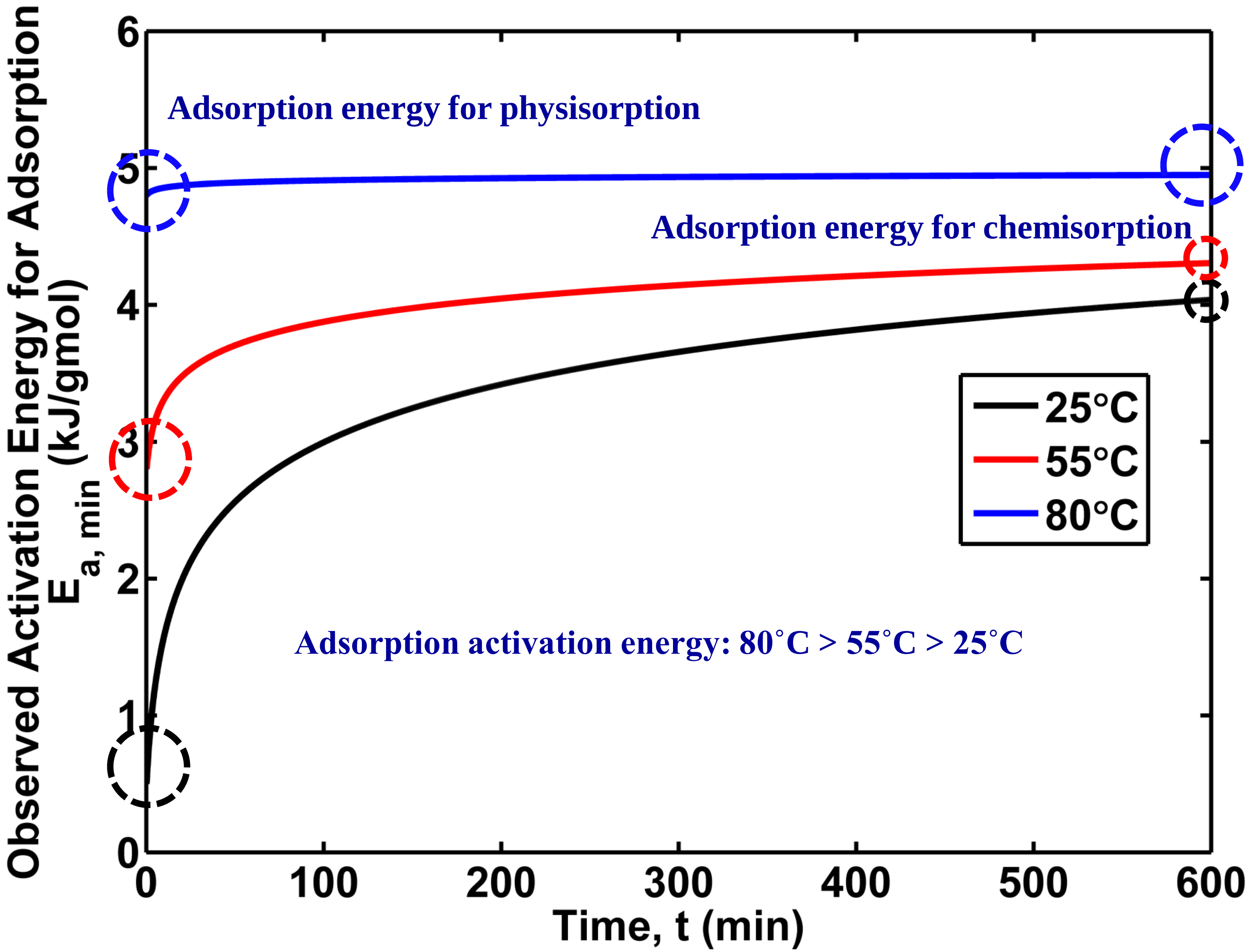
Sample	Saturated surface concentration C_{S_0} (gmol m^{-2})	Fractional coverage θ (%)	Ea_1 (kJ gmol^{-1})	Ea_2 (kJ gmol^{-1})	Ed_1 (kJ gmol^{-1})	Ed_2 (kJ gmol^{-1})
HfO_2 (20 nm), 25˚C	2.2×10^{-6}	55	5.0	0.5	17.0	0.4
HfO_2 (20 nm), 55˚C	1.5×10^{-6}	38	5.0	2.8	23.5	0.7
HfO_2 (20 nm), 80˚C	8.1×10^{-7}	20	5.0	4.8	22.0	0.016
HfO_2 (100 nm), 25˚C	4.4×10^{-7}	11	12.5	10.5	16.5	4.6
HfO_2 (100 nm), 55˚C	3.3×10^{-7}	8.3	12.5	11.0	16.0	3.7
HfO_2 (100 nm), 80˚C	3.1×10^{-7}	7.8	12.5	12.0	11.0	2.6

Temperature Effect

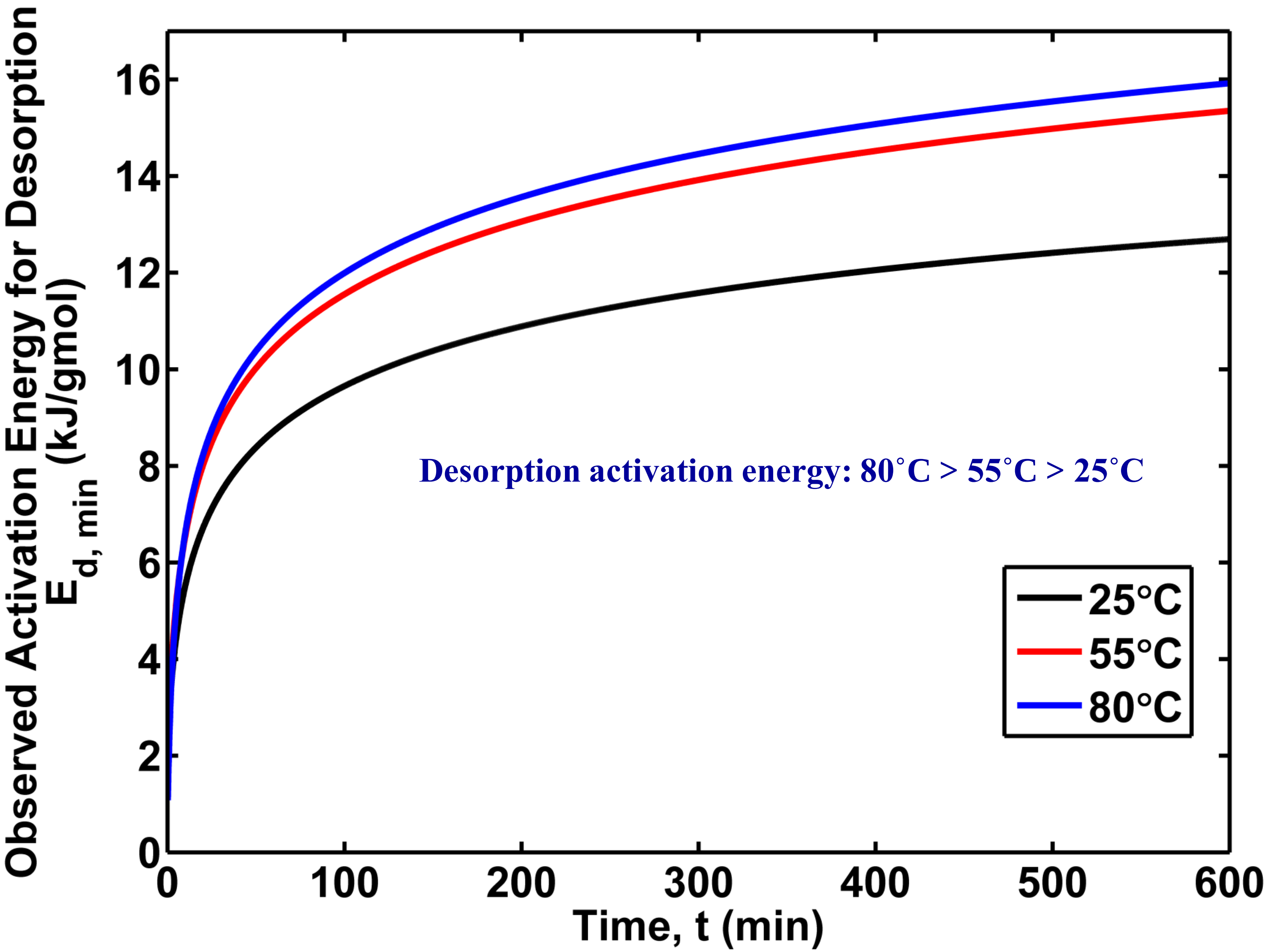


*Taking HfO_2, 20nm as an example

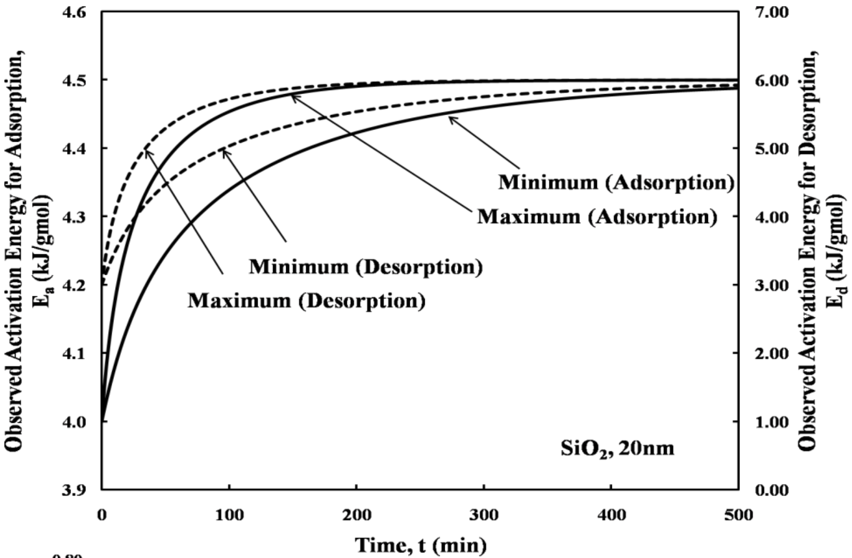
Temperature Effect

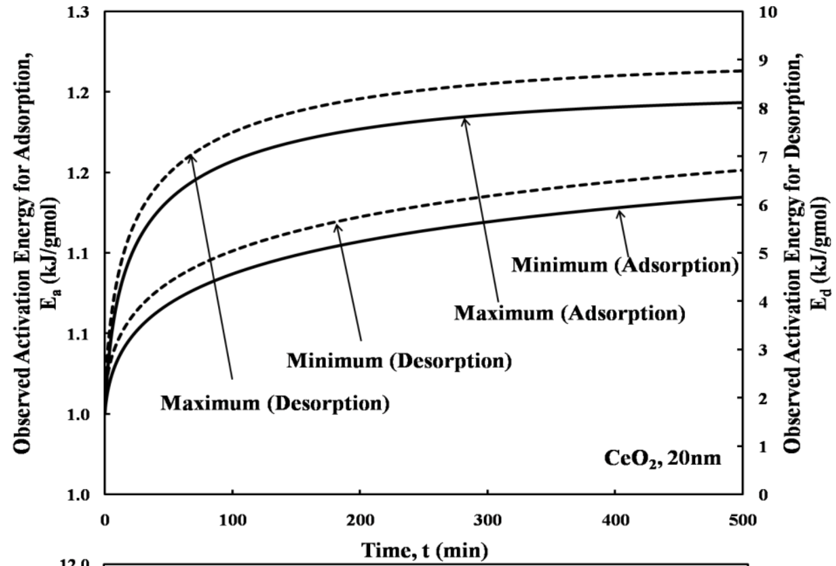


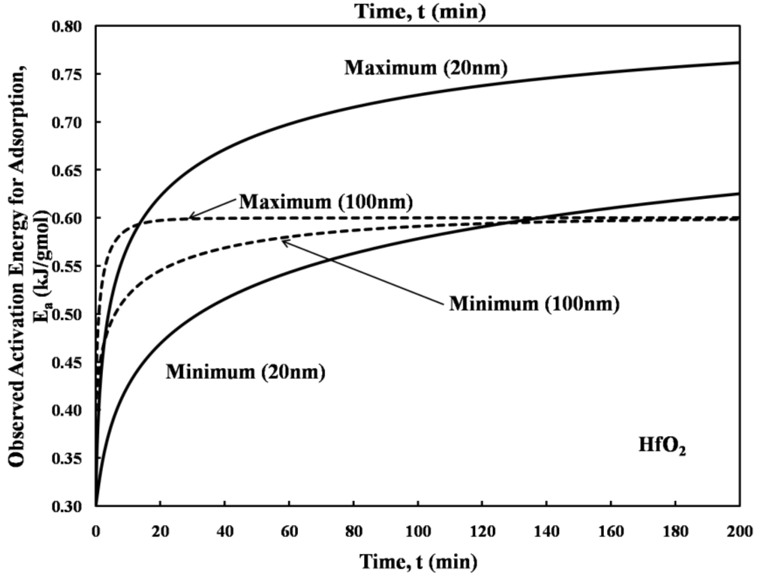
Temperature Effect

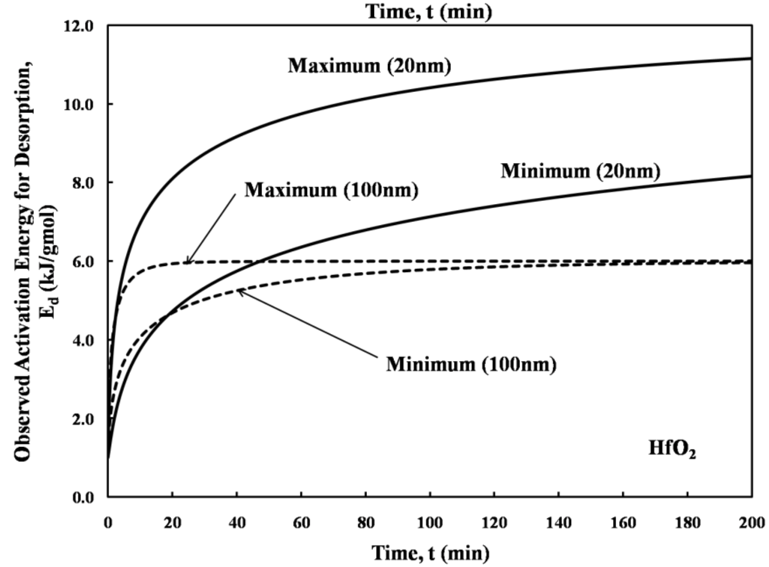


Activation Energy of Surface Processes

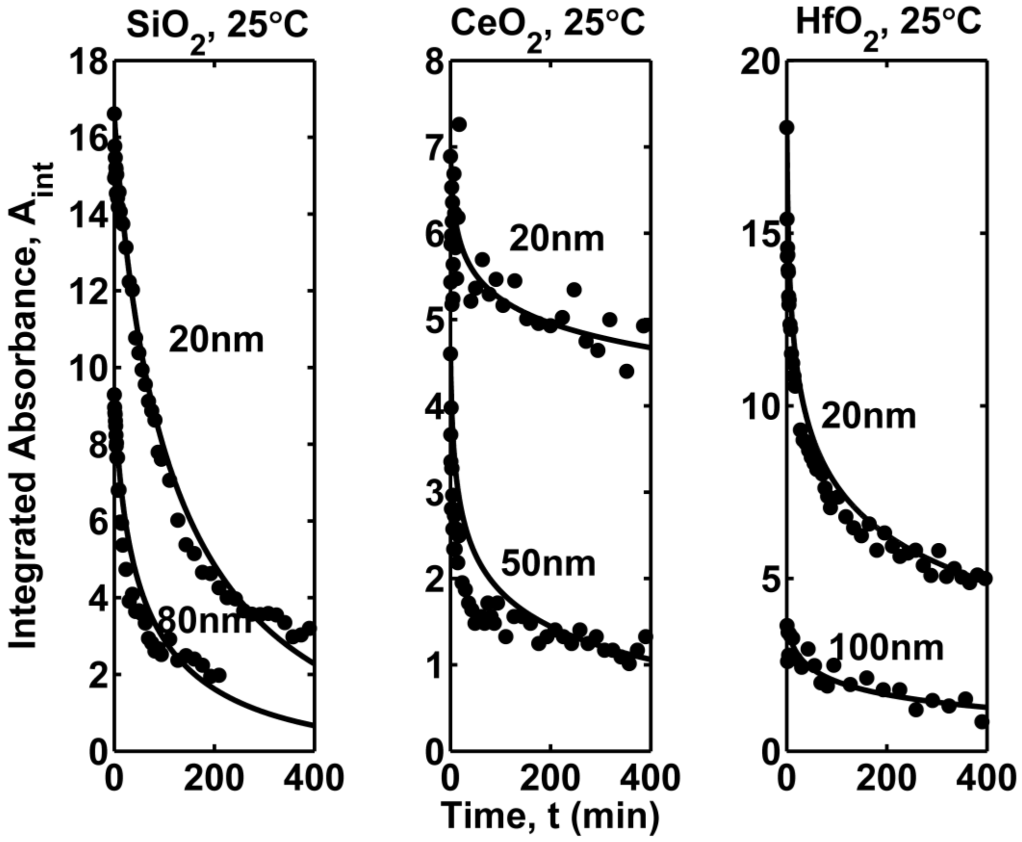






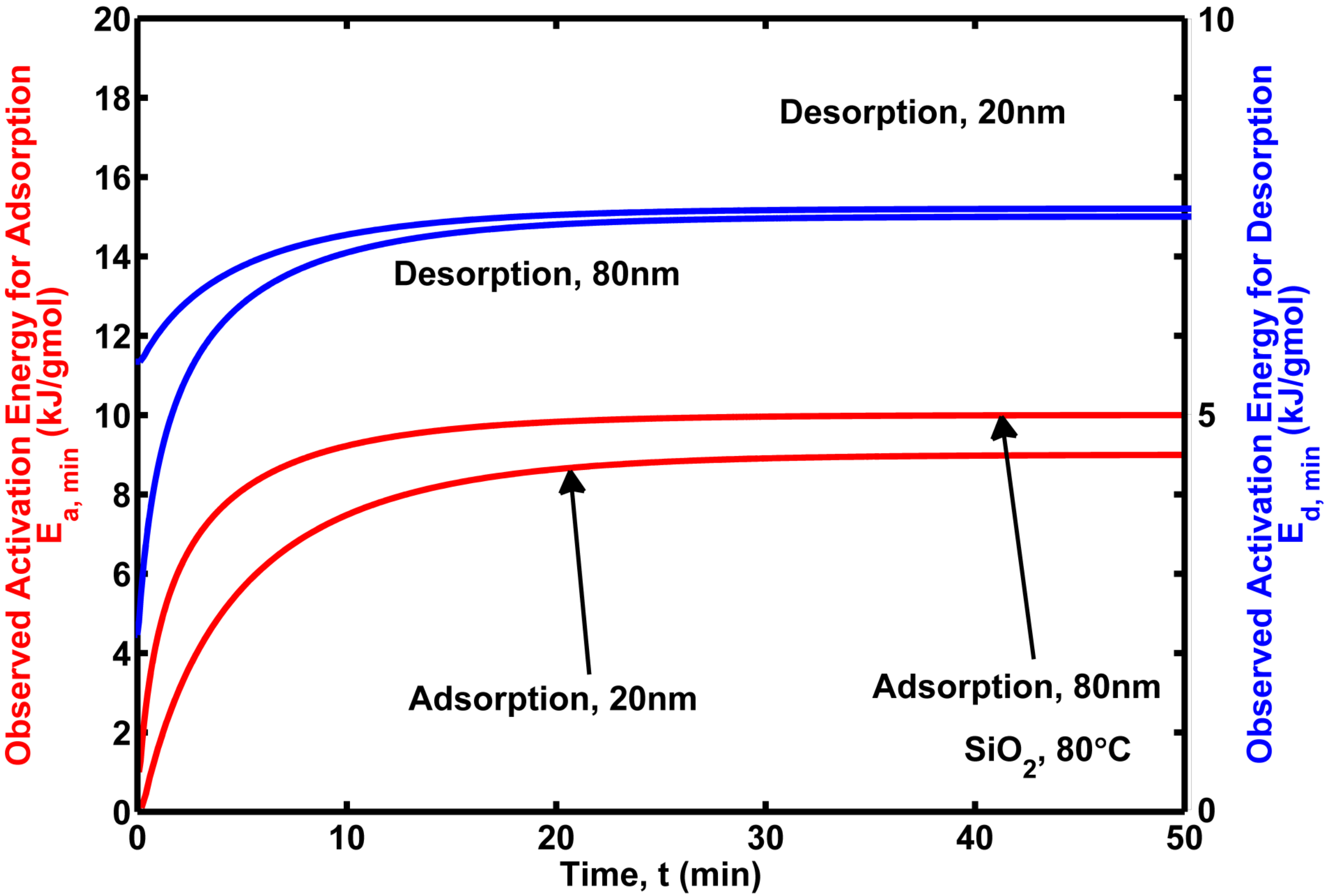


Size Effect on NP Surface Properties

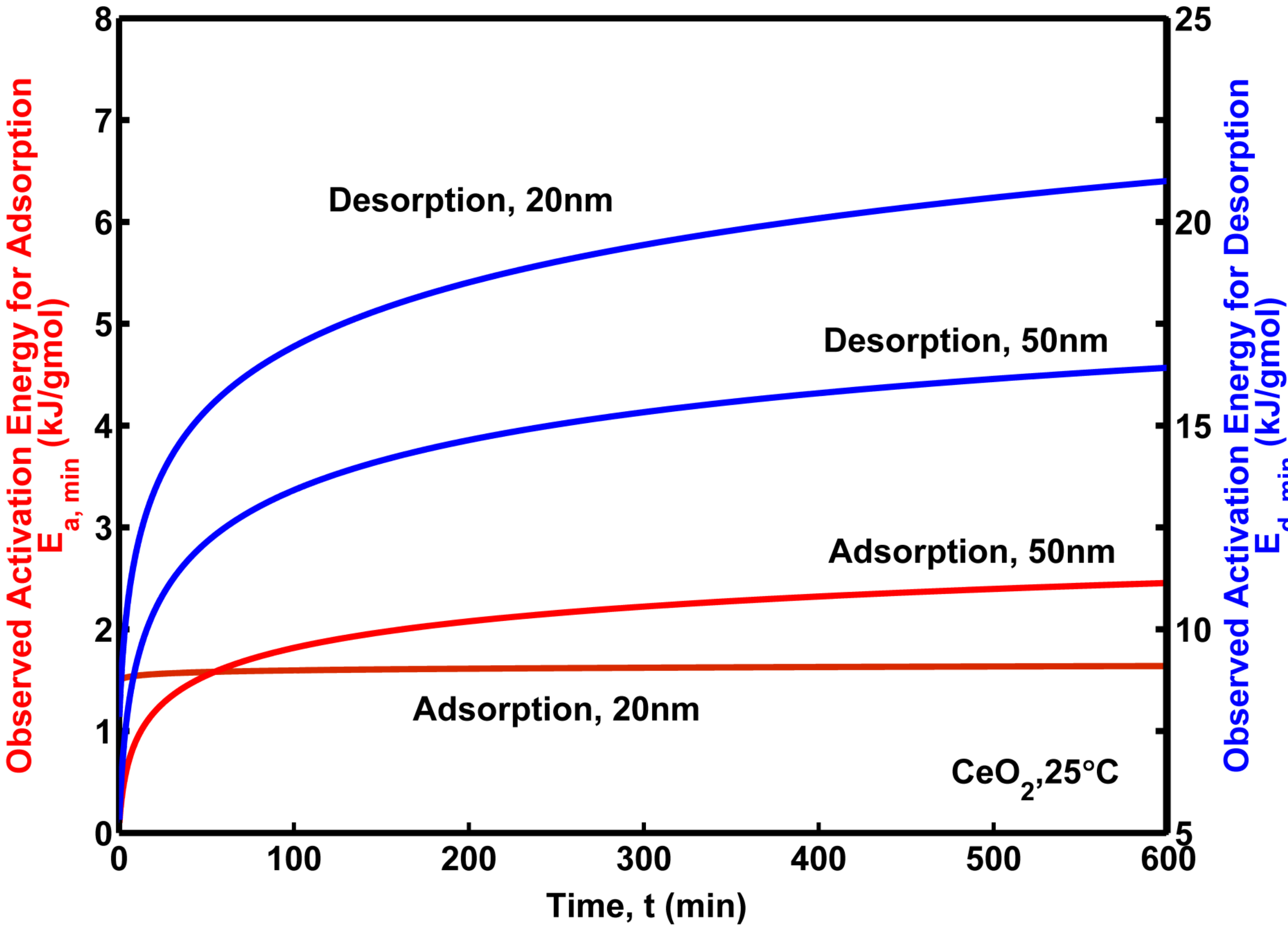


- The surface retention characteristics depend on the particle size.
- Nanoparticles with smaller size will have larger density of surface sites and larger surface retention capacity. They also have higher affinity for retention of contaminants.

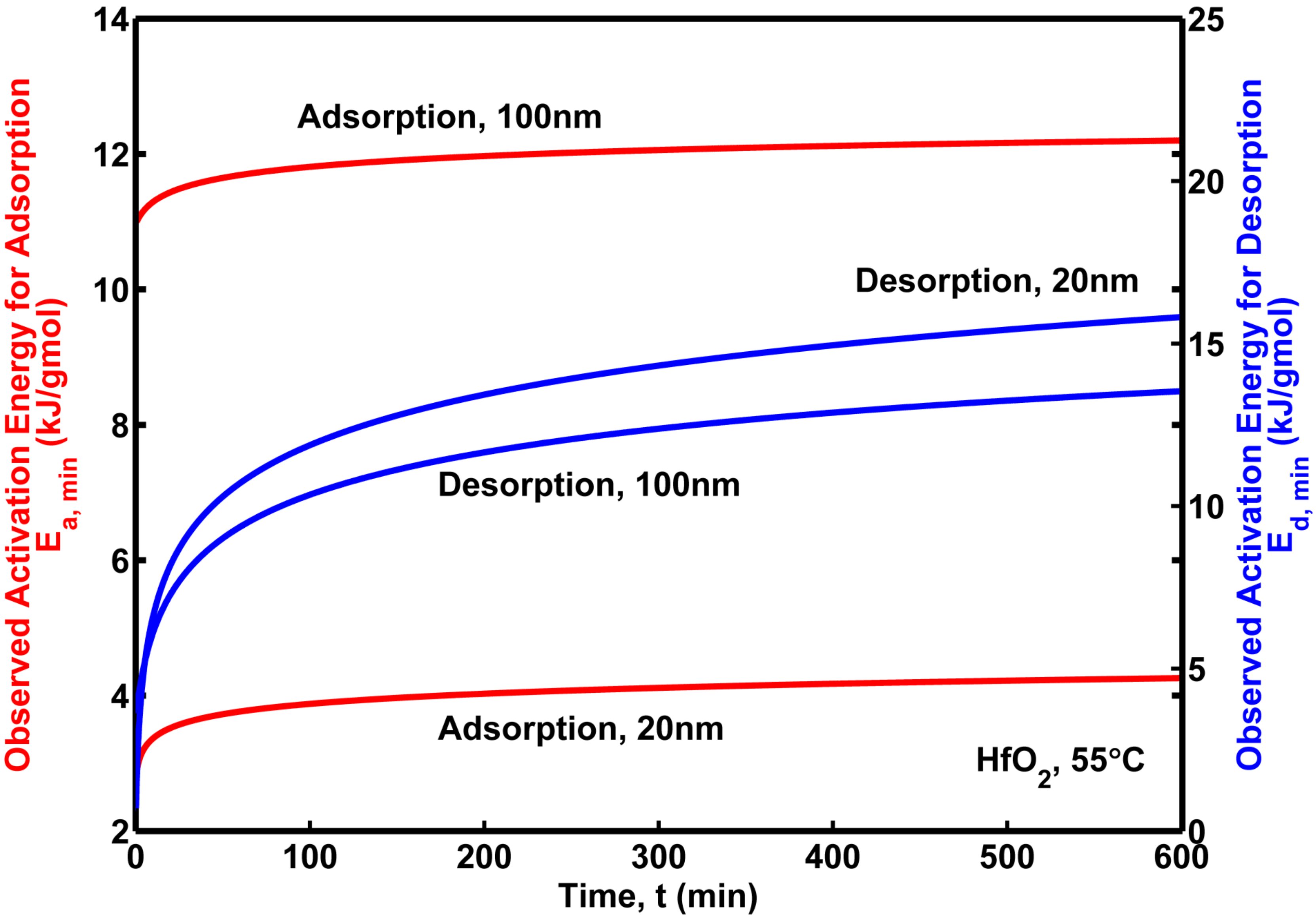
Size Effect on Energy of Surface Processes



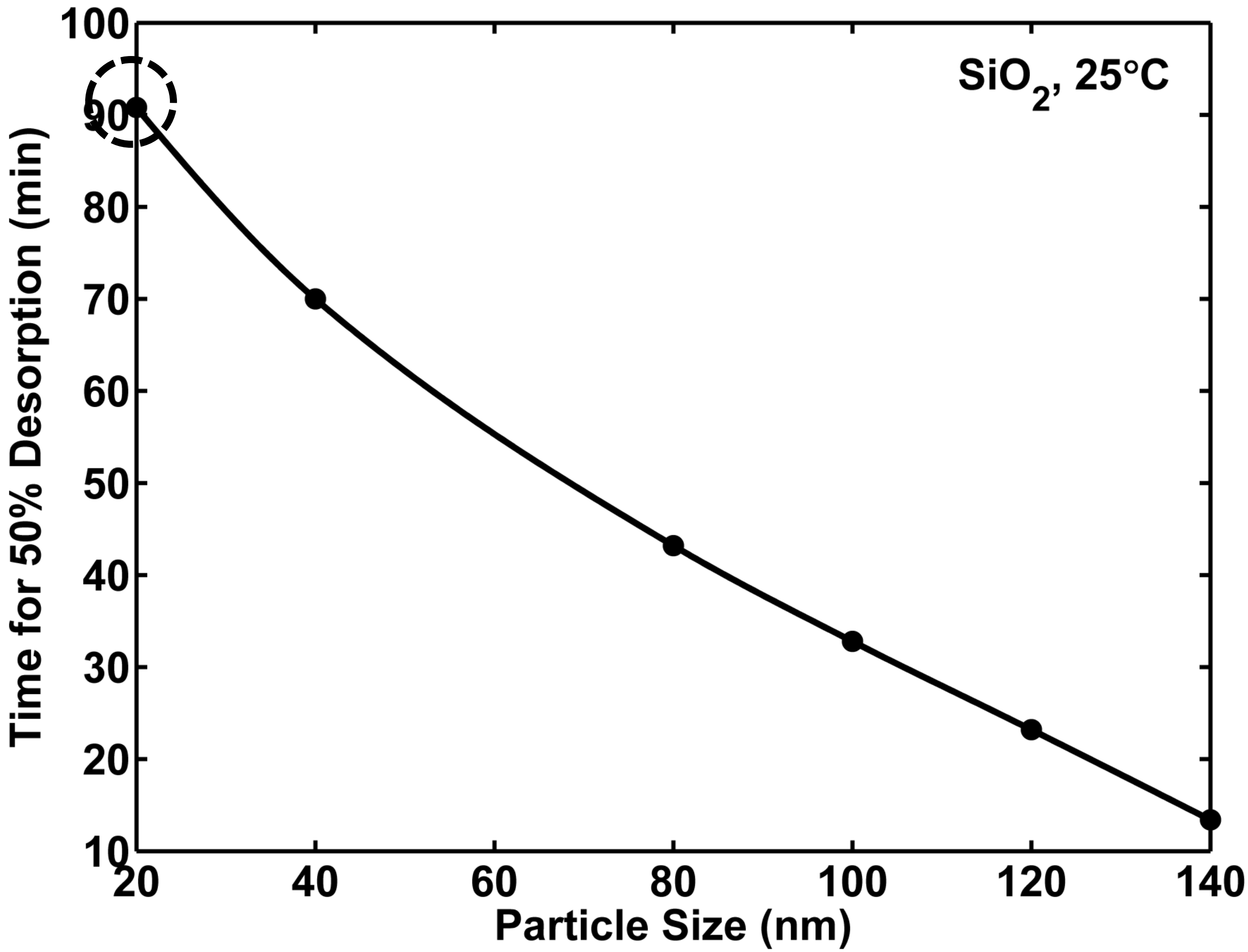
Size Effect on Energy of Surface Processes



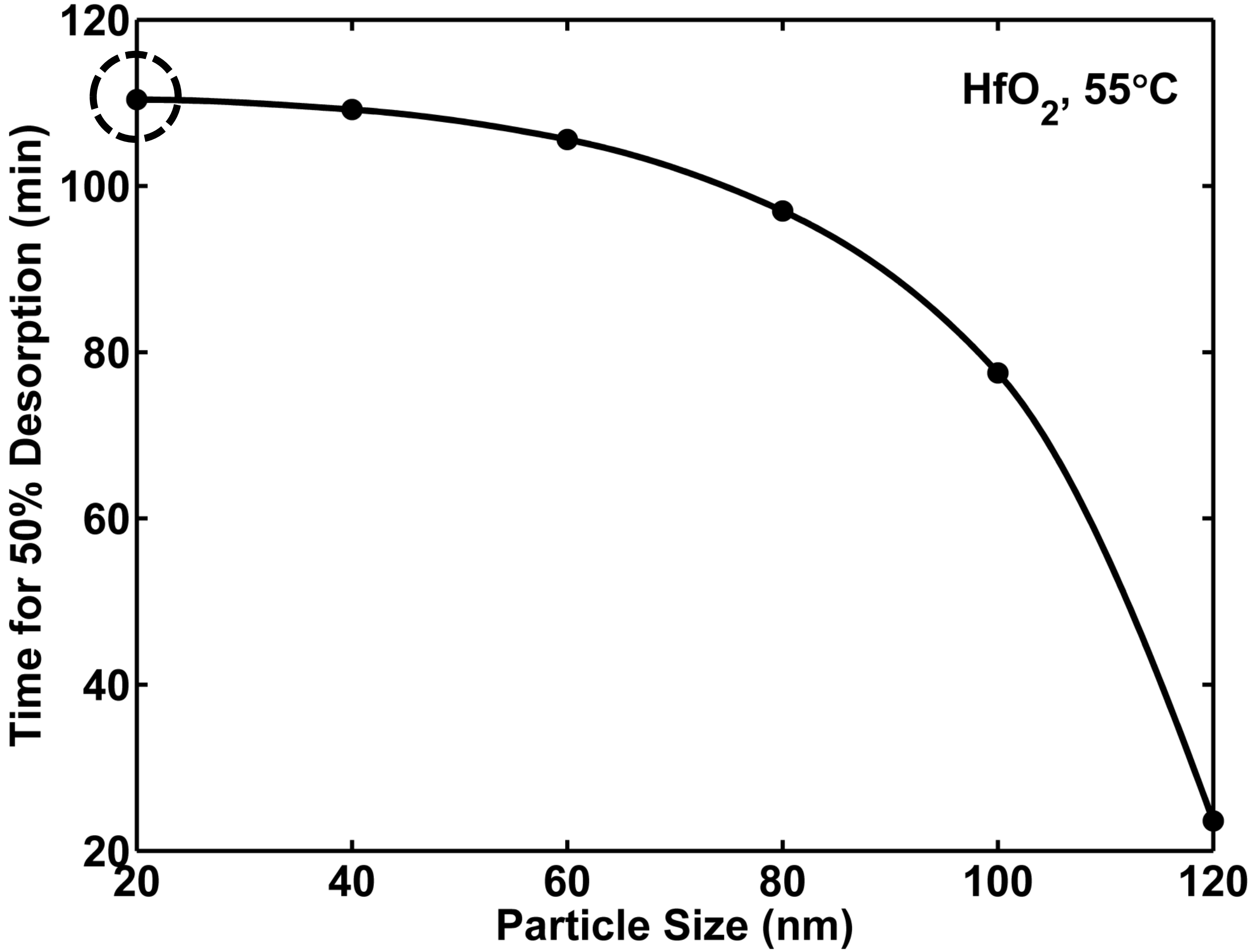
Size Effect on Energy of Surface Processes



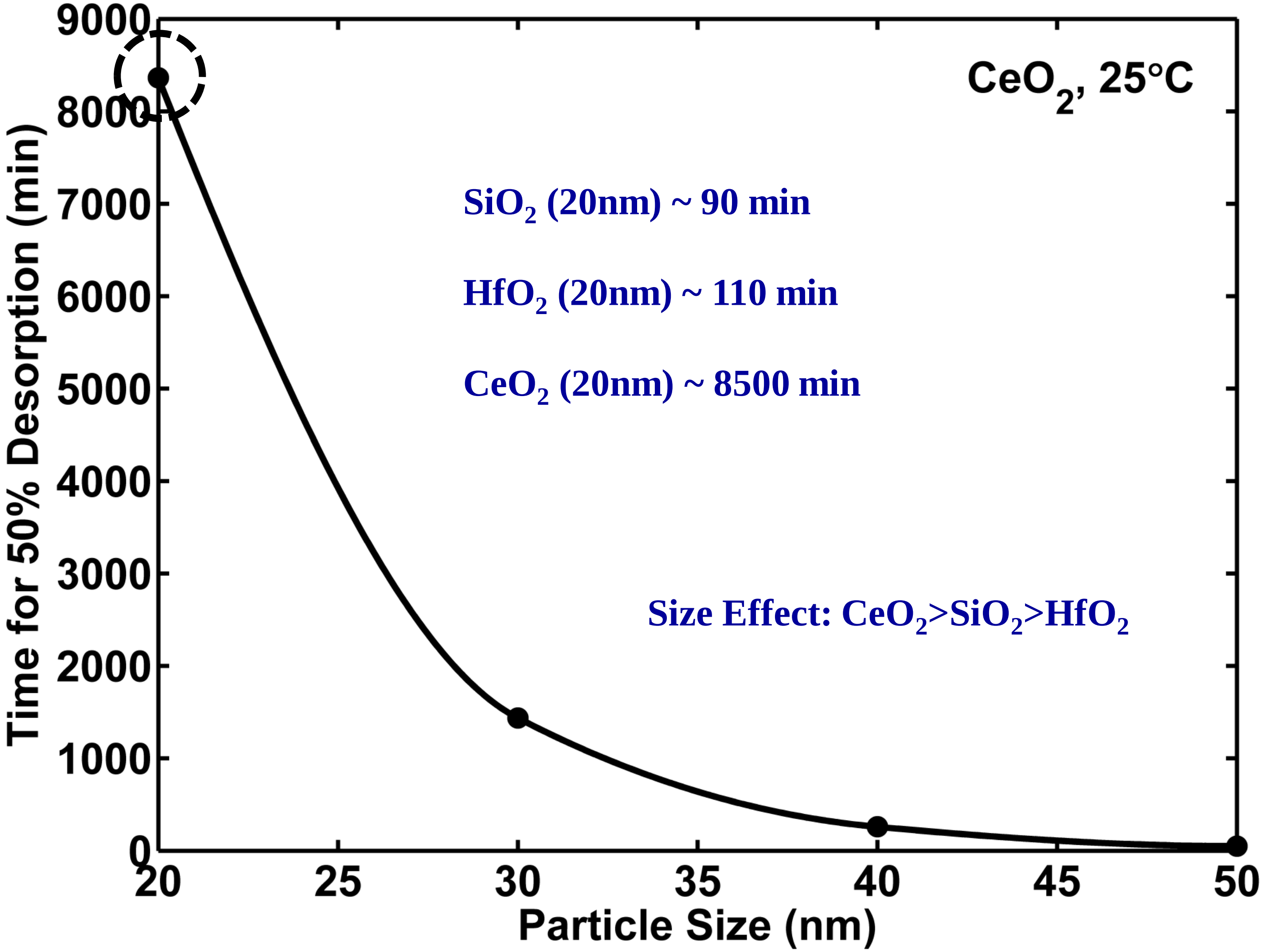
Model Prediction on Desorption Time



Model Prediction on Desorption Time



Model Prediction on Desorption Time



Dimensionless Single NP Model

Dimensionless forms:

$$\bar{C}_{g_{in}} = \frac{C_{g_{in}}}{C_{g_{in,0}}}, \qquad \bar{C}_{s_{in}} = \frac{C_{s_{in}}}{C_{s_{in,0}}}, \qquad \bar{r} = \frac{r}{r_0}, \qquad \bar{t} = \frac{t}{\frac{V}{A_0 k_a S_0}}, \qquad \bar{k}_a = \frac{k_a}{k_{ac}}, \qquad \bar{k}_d = \frac{k_d}{k_{dc}}$$

Dimensionless governing equations:

$$\frac{\partial \bar{C}_{g_{in}}}{\partial \bar{t}} = \frac{D_{e_{in}} V}{r_0^2 A_0 k_{ac} S_0} \frac{1}{\bar{r}^2} \frac{\partial}{\partial \bar{r}} (\bar{r}^2 \frac{\partial \bar{C}_{g_{in}}}{\partial \bar{r}}) + \frac{C_{s_{in,0}} k_{dc}}{C_{g_{in,0}} k_{ac} S_0} \bar{C}_{s_{in}} \bar{k}_d - \bar{k}_a \bar{C}_{g_{in}} + \frac{C_{s_{in,0}}}{S_0} \bar{k}_a \bar{C}_{g_{in}} \bar{C}_{s_{in}}$$

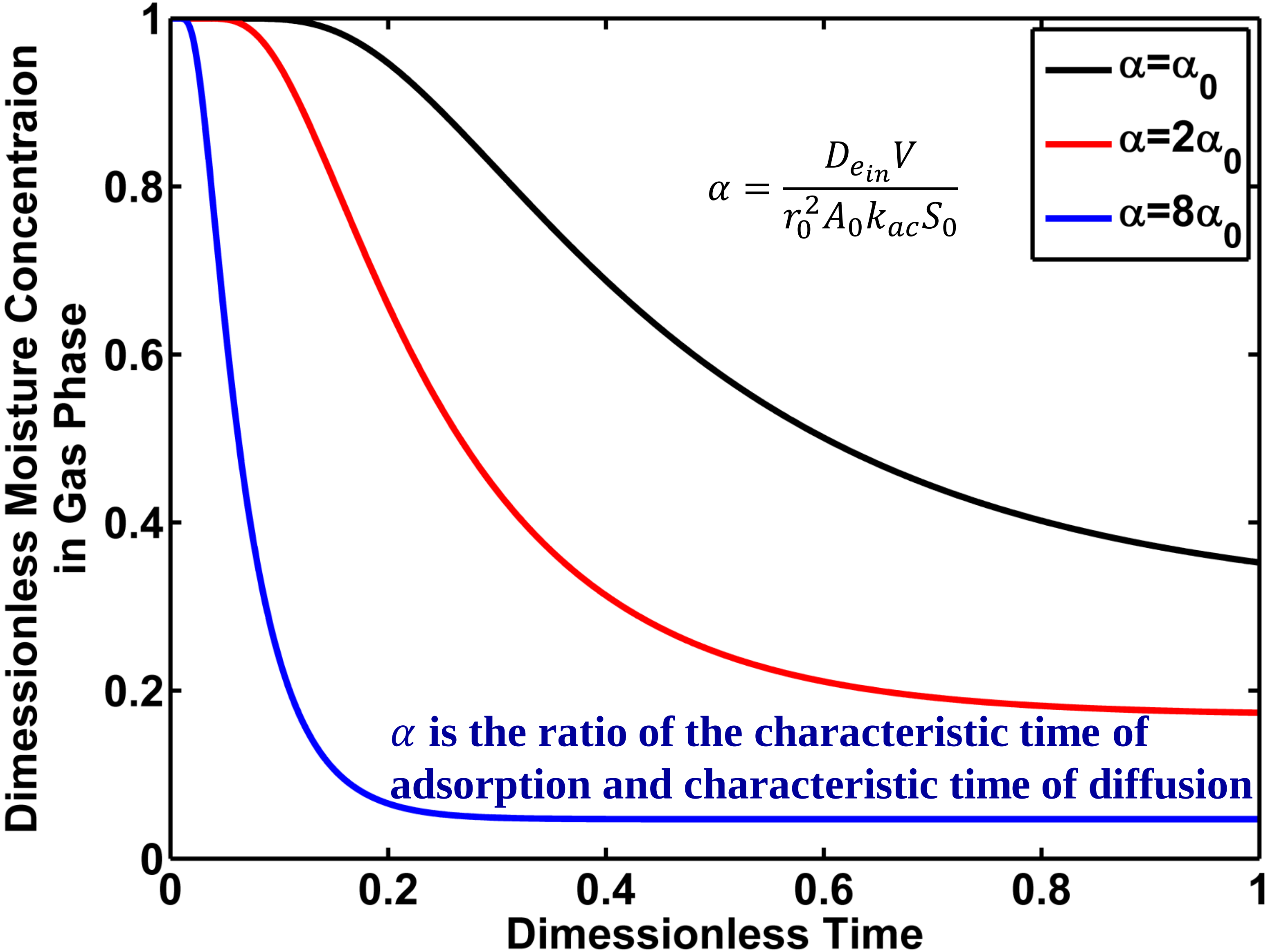
$$\frac{\partial \bar{C}_{s_{in}}}{\partial \bar{t}} = \frac{C_{g_{in,0}} V}{C_{s_{in,0}} A_0} \bar{k}_a \bar{C}_{g_{in}} - \frac{C_{g_{in,0}} V}{A_0 S_0} \bar{k}_a \bar{C}_{g_{in}} \bar{C}_{s_{in}} - \frac{k_{dc} V}{k_{ac} A_0 S_0} \bar{k}_d \bar{C}_{s_{in}}$$

Dimensionless groups:

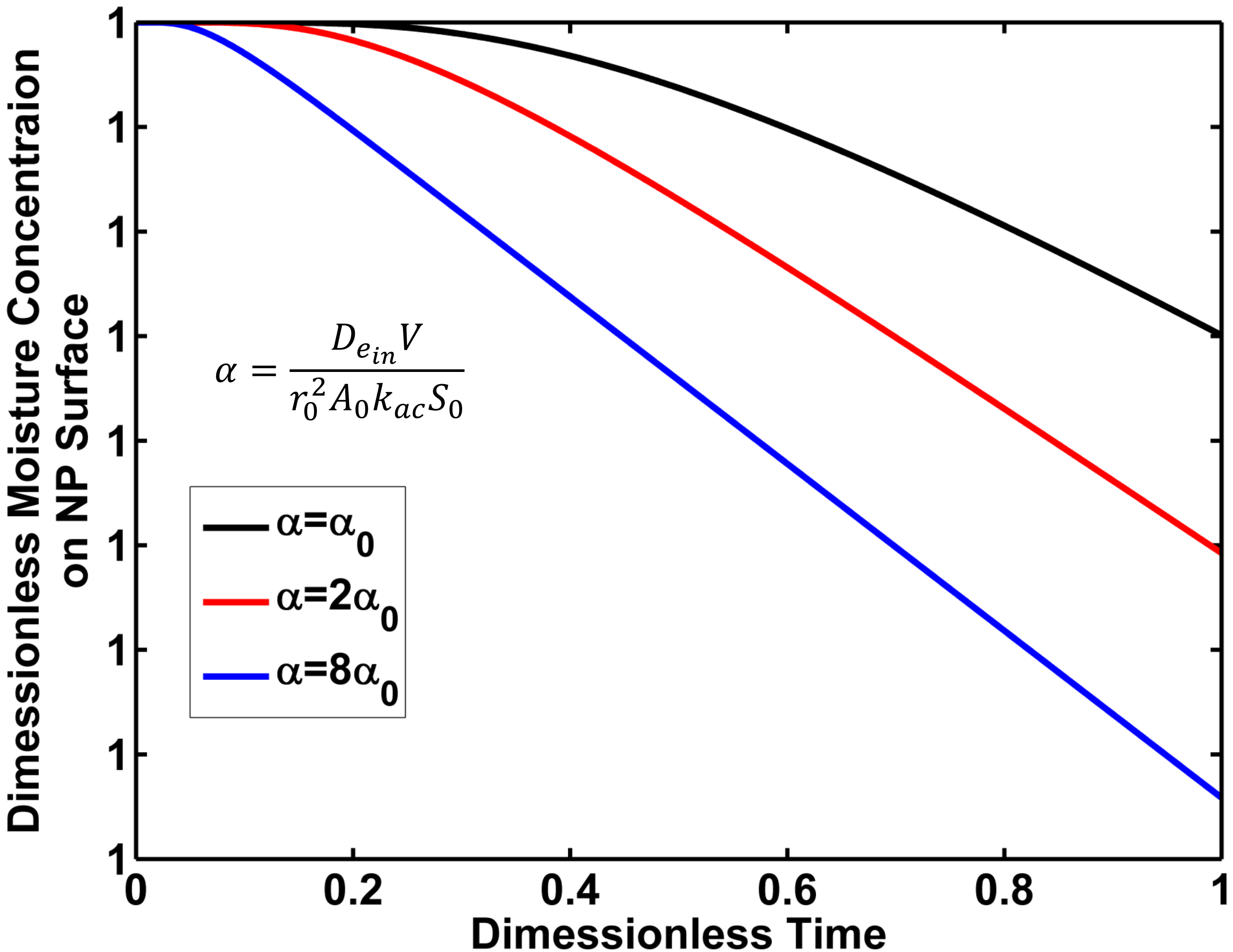
$$\alpha = \frac{D_{e_{in}} V}{r_0^2 A_0 k_{ac} S_0}, \qquad \beta = \frac{C_{s_{in,0}} k_{dc}}{C_{g_{in,0}} k_{ac} S_0}, \qquad \gamma = \frac{C_{s_{in,0}}}{S_0},$$

$$\eta = \frac{C_{g_{in,0}} V}{C_{s_{in,0}} A_0}, \qquad \theta = \frac{C_{g_{in,0}} V}{A_0 S_0}, \qquad \omega = \frac{k_{dc} V}{k_{ac} A_0 S_0},$$

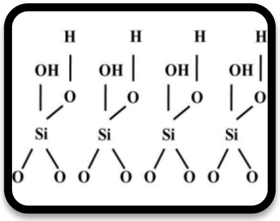
Parametric Study



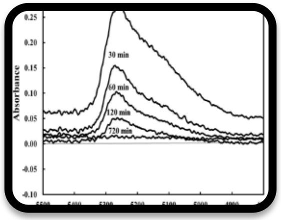
Parametric Study



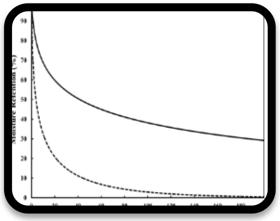
Summary and Conclusions



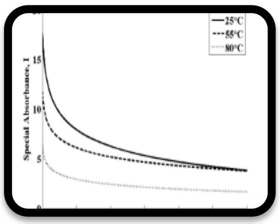
Hydroxylation is a powerful method for characterization of capture and retention (adsorption/desorption) properties of NPs.



The surface retention characteristics depend on the material as well as on the particle size and temperature.



NPs with smaller size will have larger density of surface sites and larger surface retention. They also have higher affinity for retention of contaminants. Based on the size effect on energy, smaller NPs would have higher desorption activation energy and lower adsorption activation energy.



Purge under the higher temperature would benefit the desorption of moisture on the NP surface.

Future Work

- Keep on studying the surface properties of other NPs
- Parametric study based on the dimensionless single NP model
- Upgrade the numerical model and increase the efficiency

Publications and Presentations

- **Hao Wang, F. Shadman, Effect of Particle Size on the Adsorption and Desorption Properties of Oxide Nanoparticles, Submitted to AIChE, April, 2012**
- **Hao Wang, J. Yao, F. Shadman, Characterization of the Surface Properties of Nanoparticles Using Moisture Adsorption Dynamic Profiling, Chemical Engineering Science, June 2011**
- **Hao Wang, Characterization of the Surface Properties of Nanoparticles Using Moisture Adsorption Dynamic Profiling, SRC/SEMATECH Teleconference, July 2011 [PRESENTATION]**
- **Hao Wang, Physicochemical and Surface Characteristics Study of Nanoparticles related to ESH Impact of Emerging Nanoparticles and Byproduct in Semiconductor Manufacturing, SRC/SEMATECH Teleconference, November 2010 [PRESENTATION]**

Acknowledgment

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- **Reyes Sierra, Professor of Chemical &Environmental Engineering, UA.**
- **Buddy Ratner, Professor of Bioengineering, UW.**
- **Junpin Yao, Matheson Tri-Gas Inc.**