Characterization of the Surface Properties of Nanoparticles Using Moisture Adsorption Dynamic Profiling

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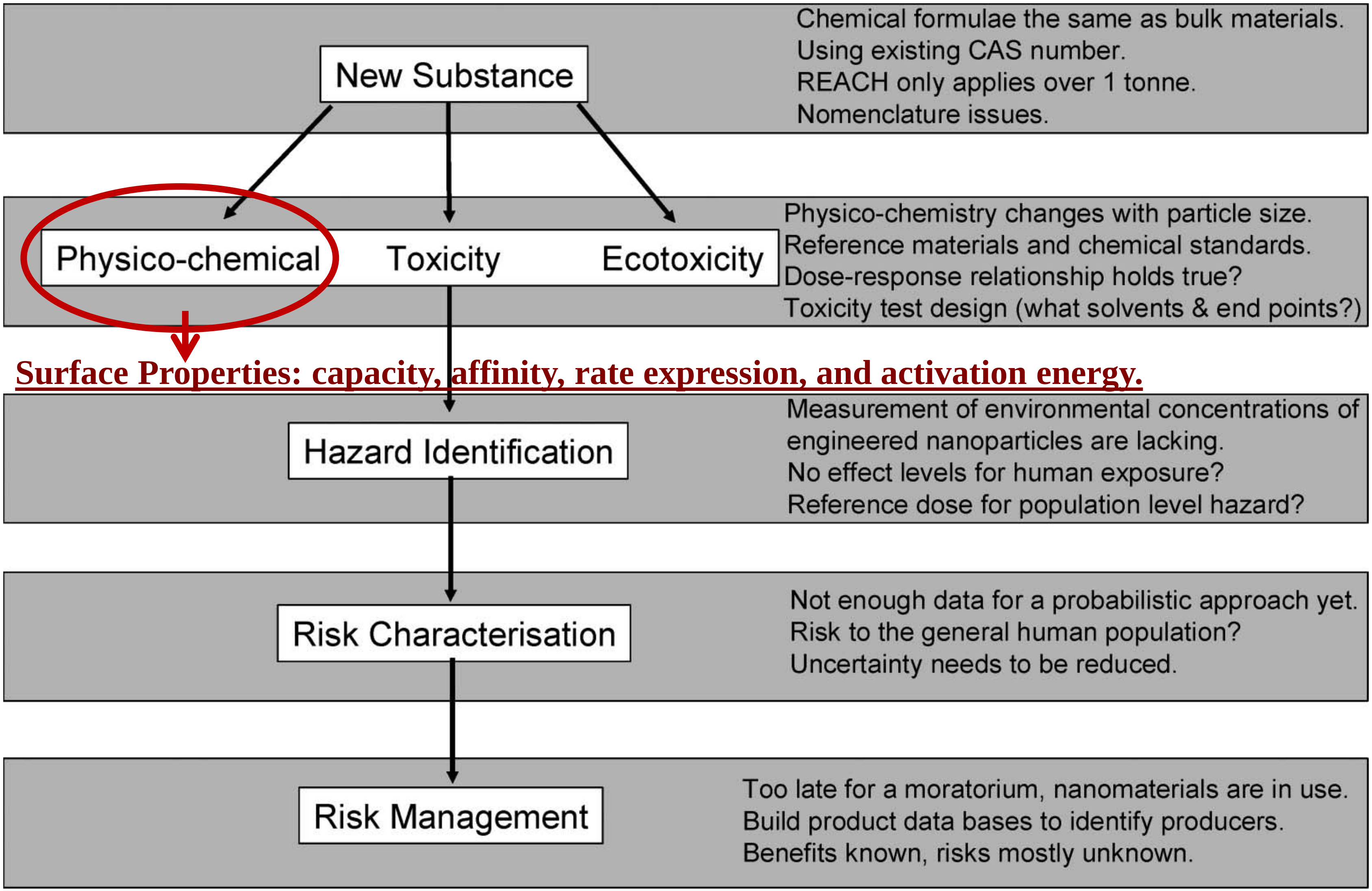
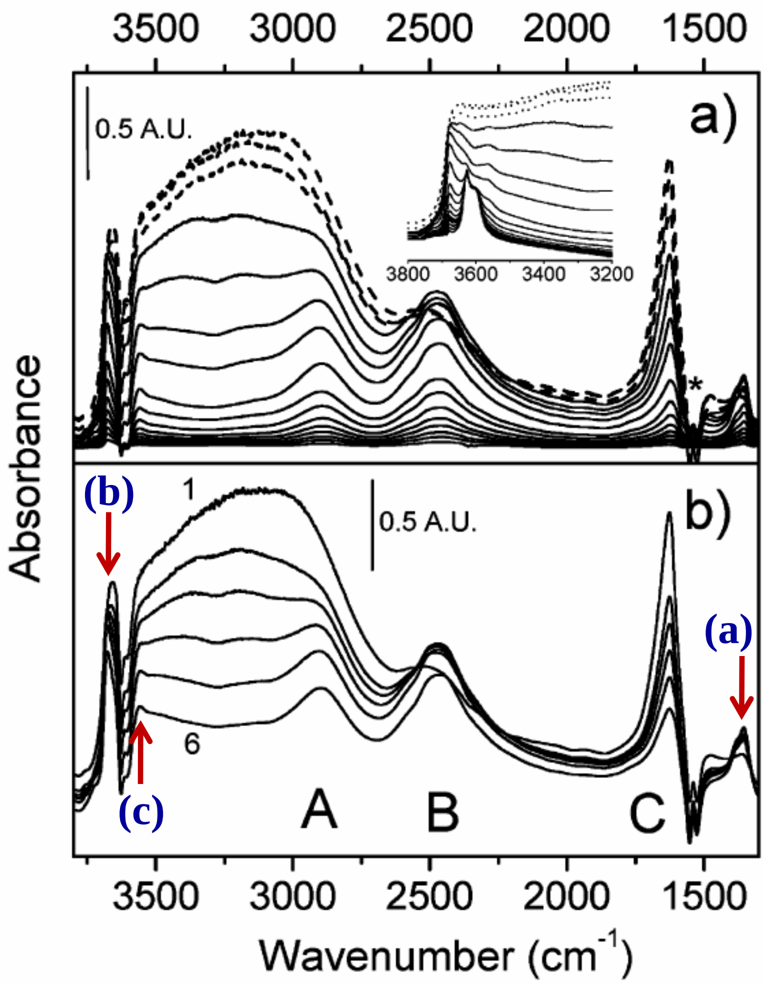
ESH Testing and Evaluation of New Chemicals



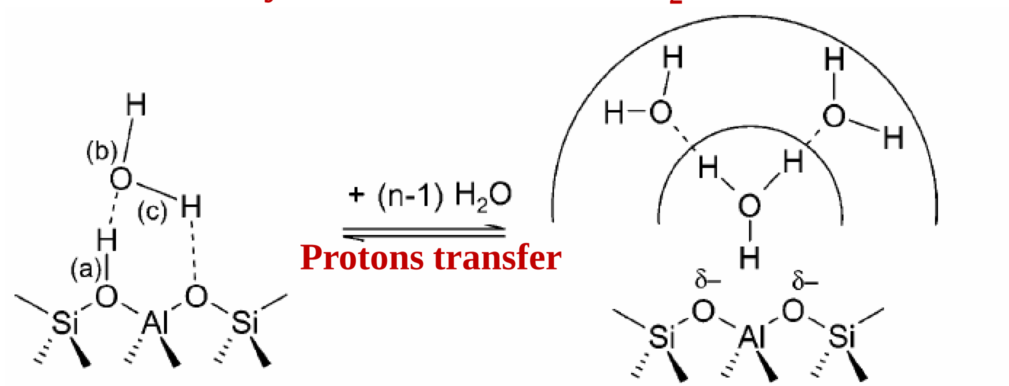
Handy, R.D., Shaw, B.J., 2007. Toxic effects of nanoparticles and nanomaterials: Implications for public health, risk assessment and the public perception of nanotechnology. Health Risk Society 9, 125-144.

FTIR Application on Quantitative Measurements



Zeolite Catalyst

H_2O clusters



- (a) zeolite oxygens O-H bonds, ν (O-$H_{a,\ water}$) : 1355 cm^{-1}.
- (b) unperturbed O-H bonds in H_2O, ν (O-$H_{b,\ water}$) : 3670 cm^{-1}.
- (c) O-H bonds being involved in weak H-bonds to zeolite oxygens, ν (O-$H_{c,\ water}$) : 3560 cm^{-1}.

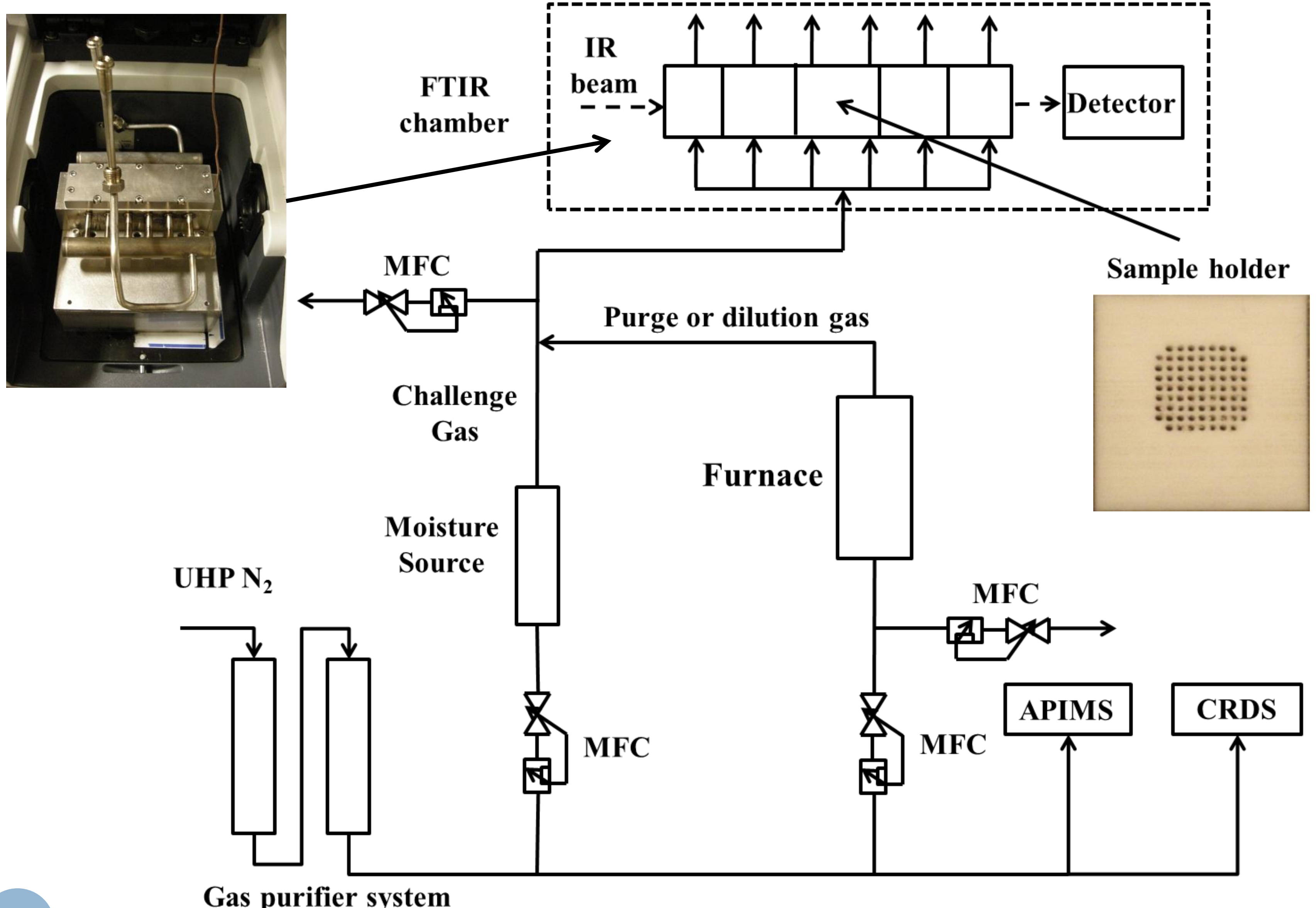
Bordiga, S et al., 2005. FTIR adsorption studies of H_2O and CH_3OH in the isostructural H-SSZ-13 and H-SAPO-34: formation of H-bonded adducts and protonated clusters. J. Phys. Chem. B 109, 7724-7732.

Objectives and Method Approach

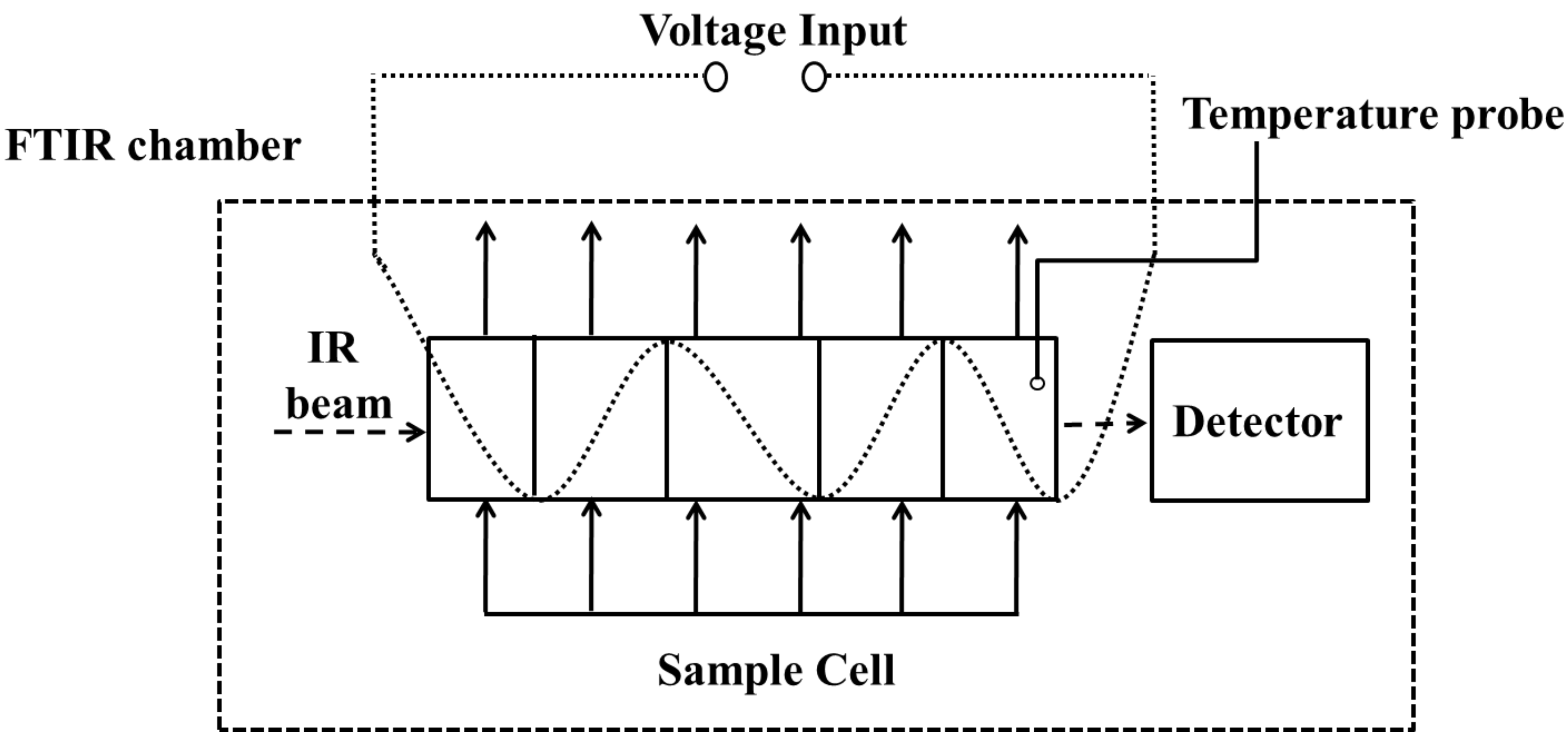
- **Objective**: Characterization of the surface sites on nanoparticles that contribute to concentration, retention, and enhanced transport of toxic chemicals.
- **Method approach**: Surface hydroxylation (adsorption and desorption of contaminants).
- **Materials**: SiO_2, HfO_2, and CeO_2.
- **Parameters**: 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
SiO_2	Sigma-Aldrich	10-20
HfO_2	Sematech	20
HfO_2	American Elements	100

Schematic Diagram of the Experimental Setup

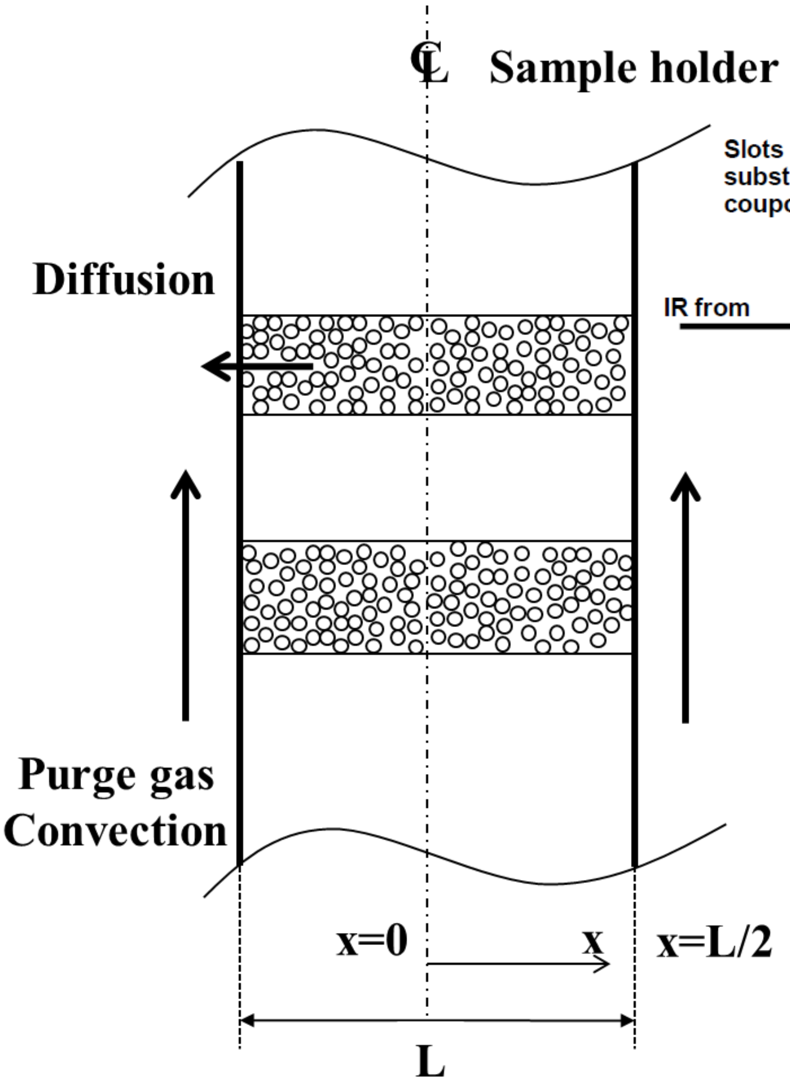


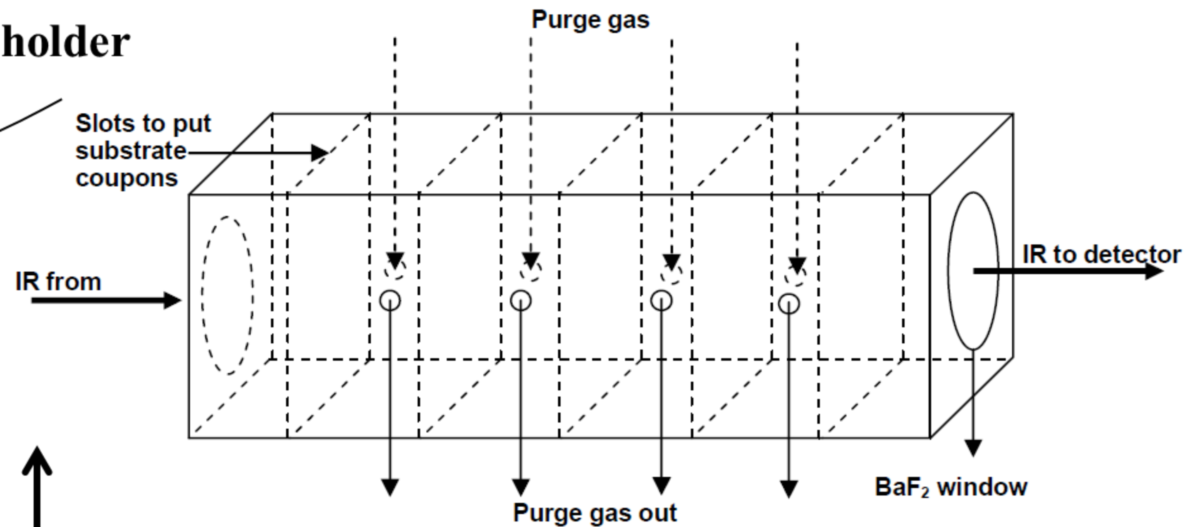
Heating Element Design

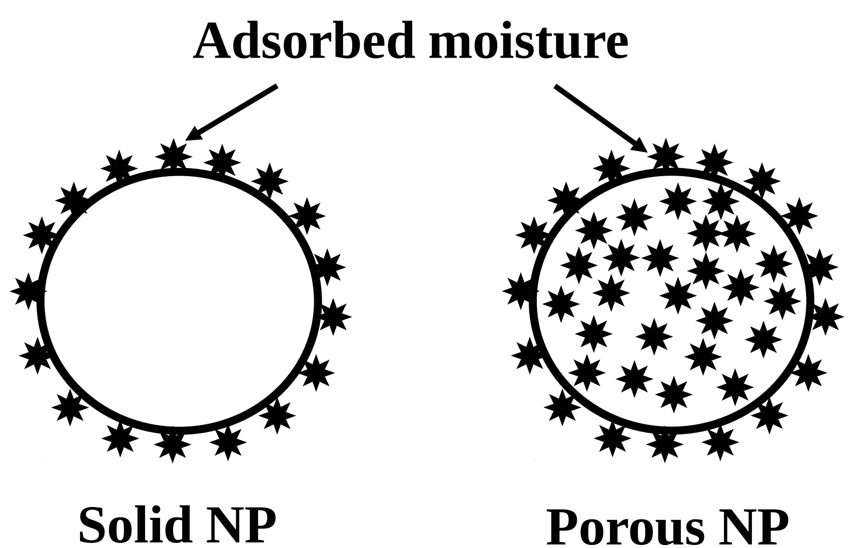


Voltage Input	Temperature
0 V	25°C
30 V	55°C
45 V	80°C

Schematic Diagram of the NP Sample Holder







Mechanism of Multilayer Model

Adsorption rate coefficient

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

Desorption rate coefficient

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

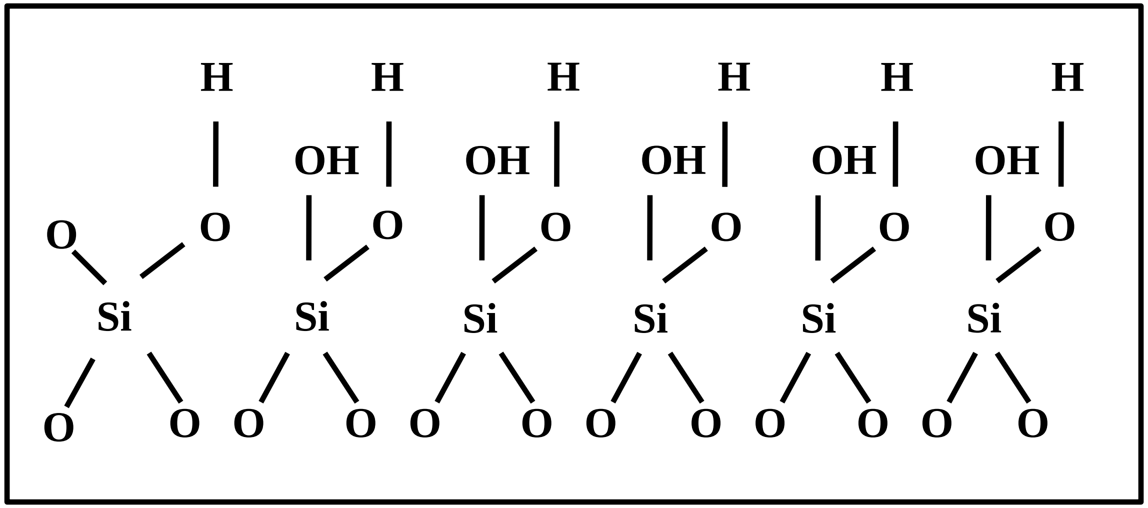
Adsorption activation energy

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

Desorption activation energy

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

1: Chemisorption **2: Physisorption**



Process Simulation for Data Analysis

Adsorbent concentration in the gas phase:

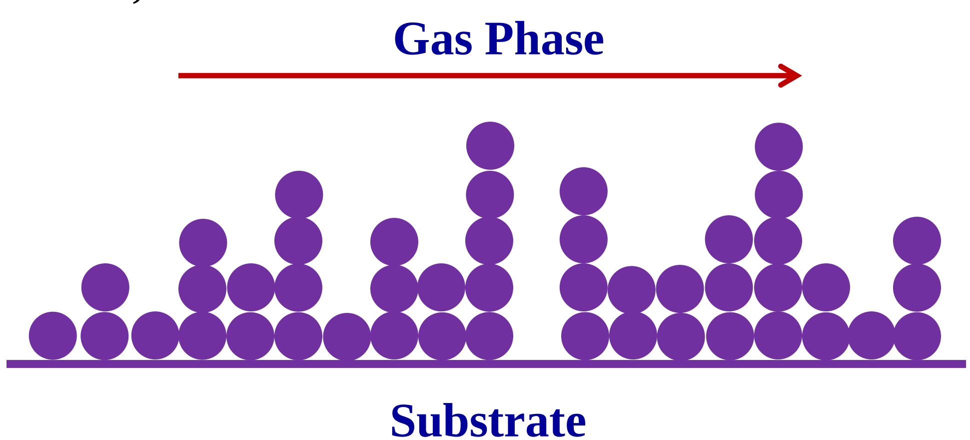
$$\frac{\partial C_g}{\partial t} = \underline{D_e \frac{\partial^2 C_g}{\partial x^2}} + (1-\varepsilon)\frac{3}{r}\underline{[k_d C_s - k_a C_g (S_0 - C_s)]}$$

Diffusion term **Adsorption and desorption term**

Adsorbent concentration on the surface:

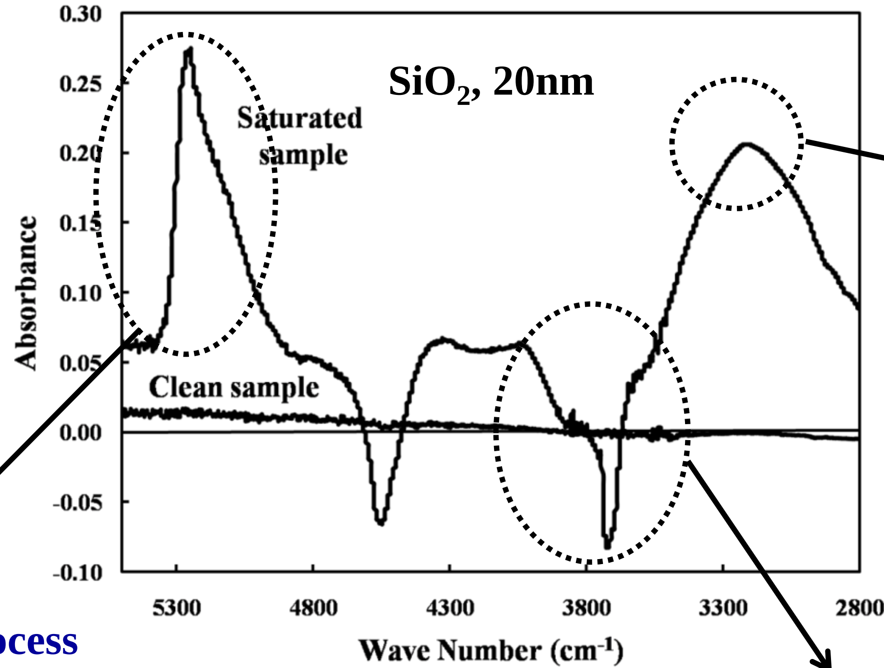
$$\frac{\partial C_s}{\partial t} = k_a C_g (S_0 - C_s) - k_d C_s$$

- C_g concentration in the gas phase, gmol·m^{-3}
- C_s concentration on the surface, gmol·m^{-2}
- k_a adsorption rate coefficient, m^{3}·gmol^{-1}·s^{-1}
- k_d desorption rate coefficient, s^{-1}
- S_0 maximum capacity of the surface, gmol·m^{-2}
- ε packing porosity
- r radius of nanoparticle, m
- D_e effective diffusivity, m^{2}·s^{-1}



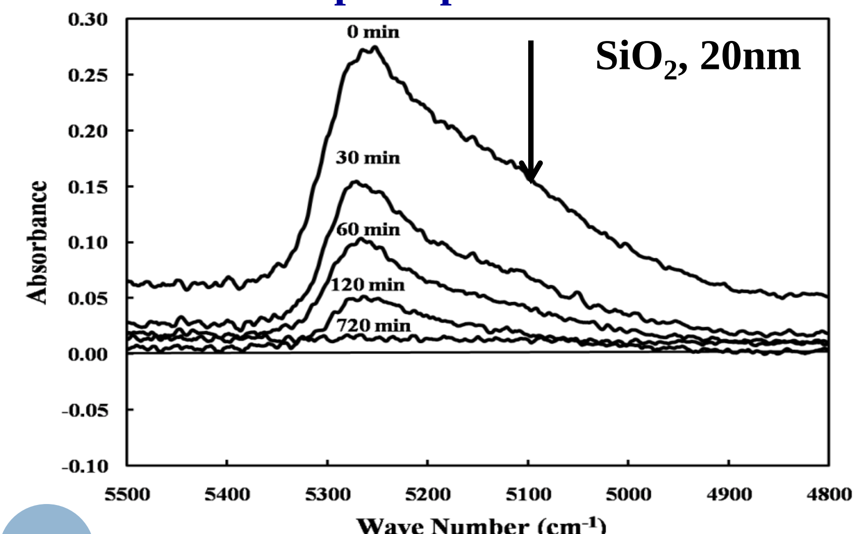
FTIR Spectra of Moisture Adsorption on NPs

Overtone combination of stretching and bending, wave number: 5200 cm^{-1}

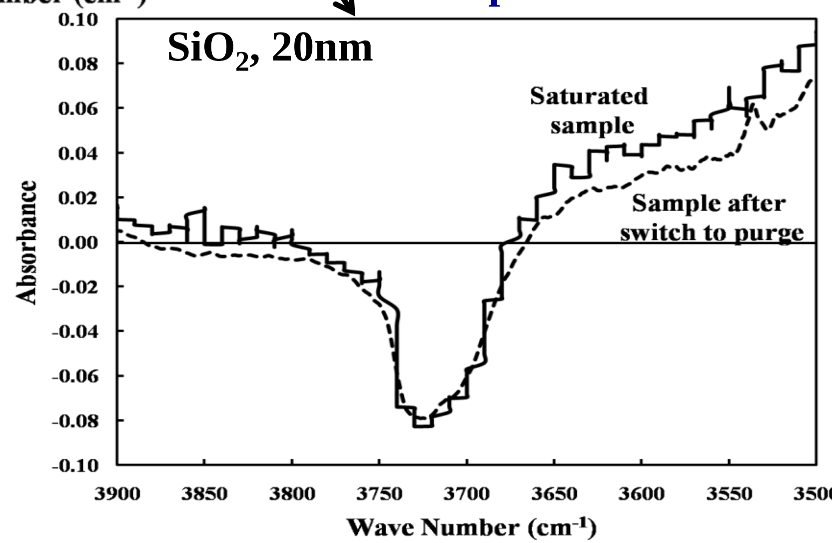


O-H bonds attached to the NPs, wave number: 3200 cm^{-1}

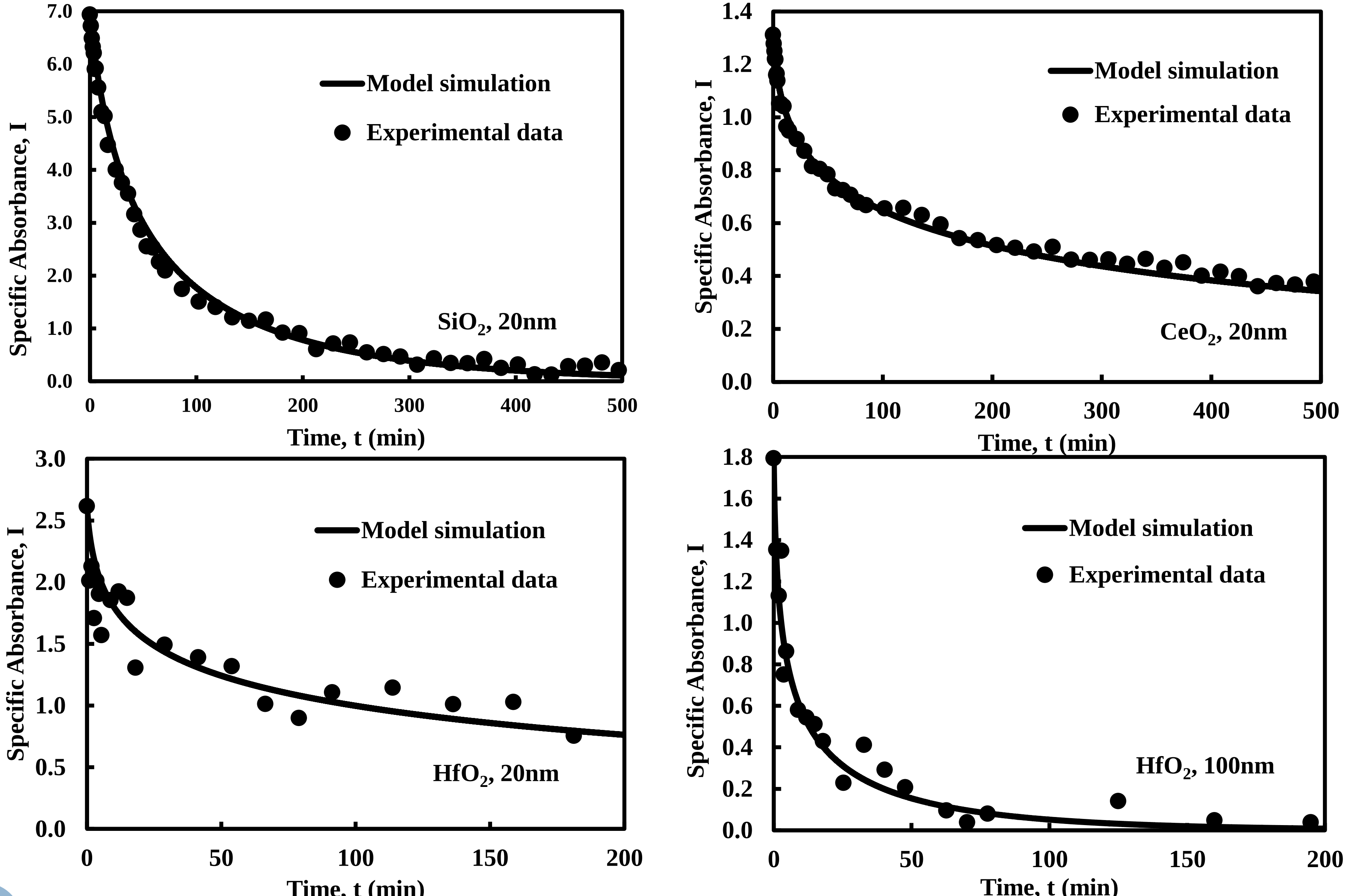
Desorption process



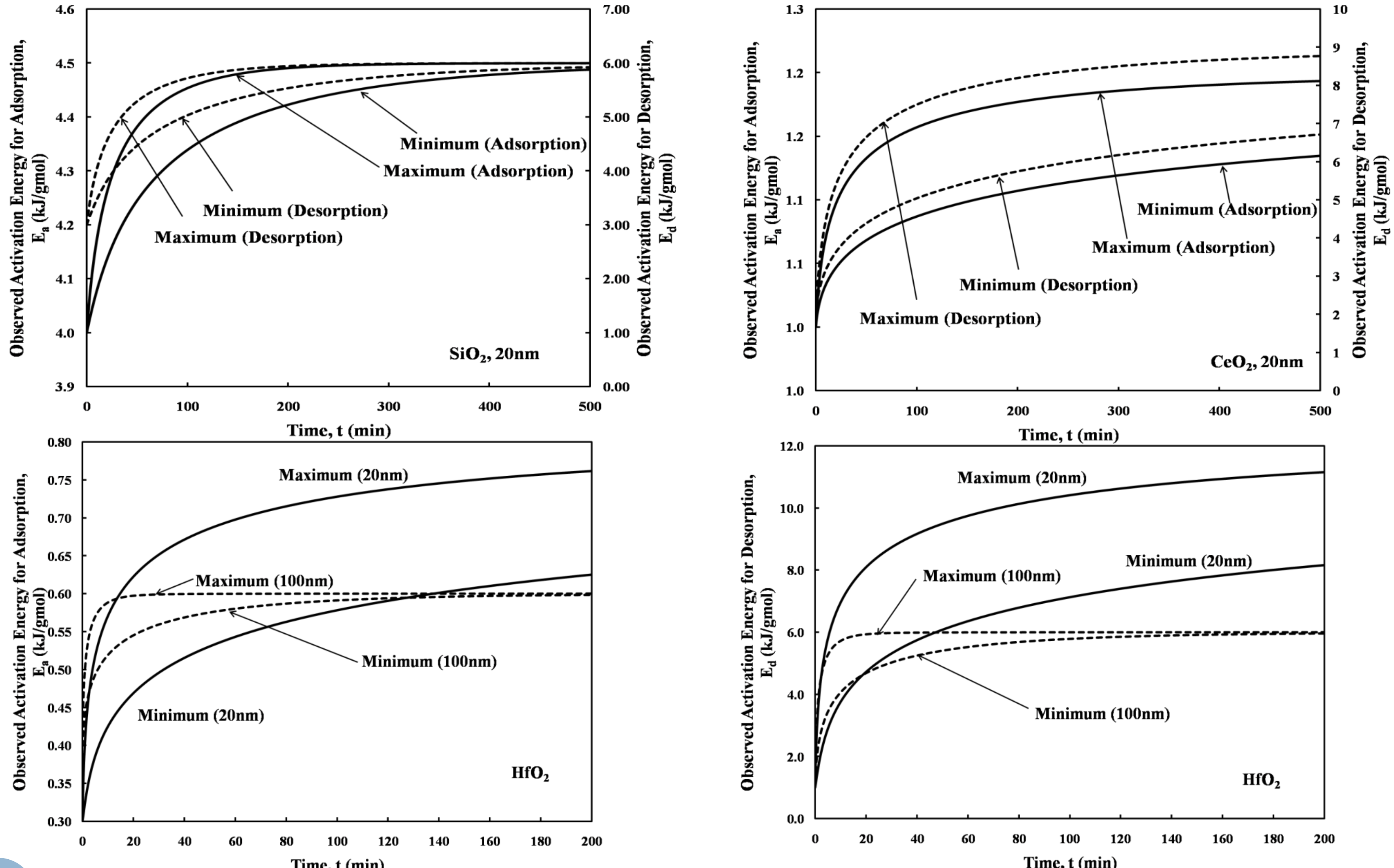
Eliminate gas phase factor



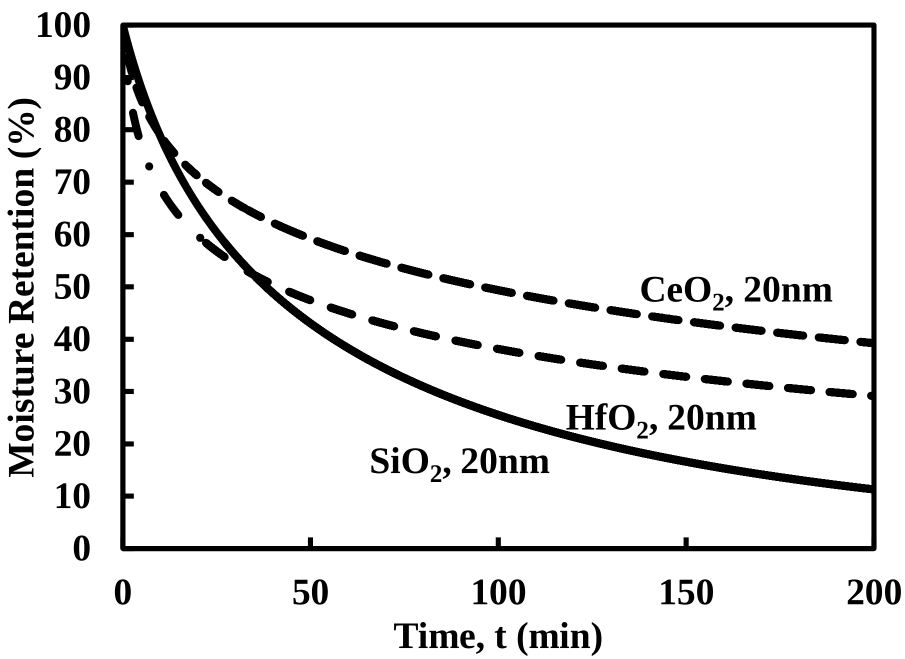
Comparison of Adsorption Profiles of NPs

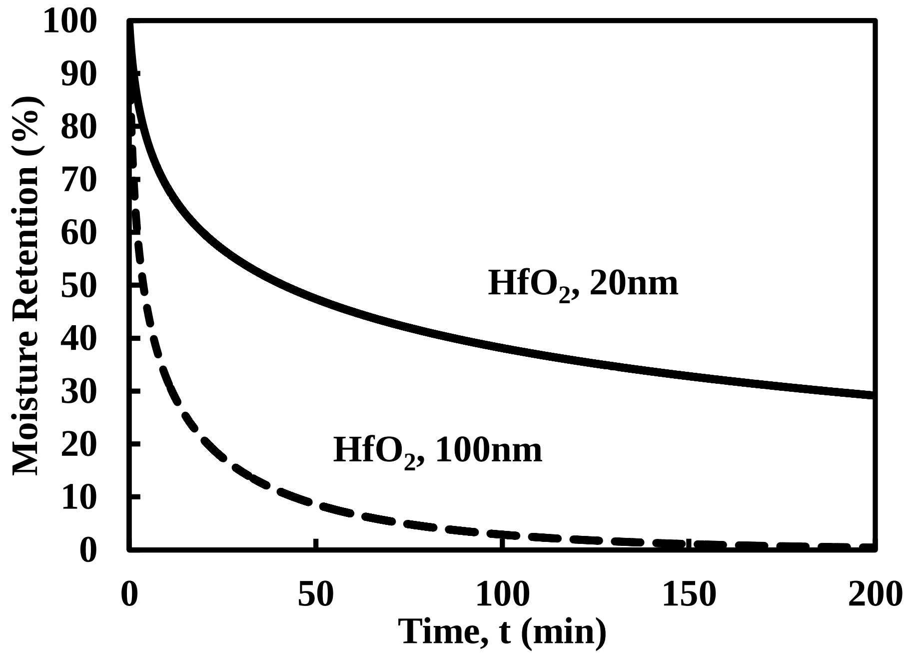


Activation Energy of Surface Processes



Effect of NP Material and Size on Surface Retention





- **The surface retention characteristics depend on the material as well as on the particle size.**
- **The affinity of nanoparticles for adsorption and retention decreases in the order: CeO_2 > HfO_2 > SiO_2. The surface available sites under certain challenge concentrations decreases in the order: SiO_2 > HfO_2 > CeO_2.**
- **Nanoparticles with smaller size will have larger density of surface sites and larger surface retention capacity for most cases. They also have higher affinity for retention of contaminants.**

Parametric study of Species Effect

Sample (20nm)	Maximum capacity S_0 (gmol·m^{-2})	Saturated surface concentration $C_{s,0}$ (gmol·m^{-2})	Fractional coverage θ (%)
SiO_2	7.1×10^{-6}	2.8×10^{-6}	39
HfO_2	1.5×10^{-6}	1.1×10^{-6}	73
CeO_2	5.5×10^{-7}	5.4×10^{-7}	98

Sample (20nm)	$k_{a,0}$ (m^3·gmol^{-1}·s^{-1})	$k_{d,0}$ (s^{-1})	$E_{a,1}$ (kJ·gmol^{-1})	$E_{a,2}$ (kJ·gmol^{-1})	$E_{d,1}$ (kJ·gmol^{-1})	$E_{d,2}$ (kJ·gmol^{-1})
SiO_2	0.028	0.003	4.5	4.0	6.0	3.0
HfO_2	0.200	0.010	0.8	0.3	12.0	1.0
CeO_2	0.800	0.003	1.2	1.0	9.0	2.0

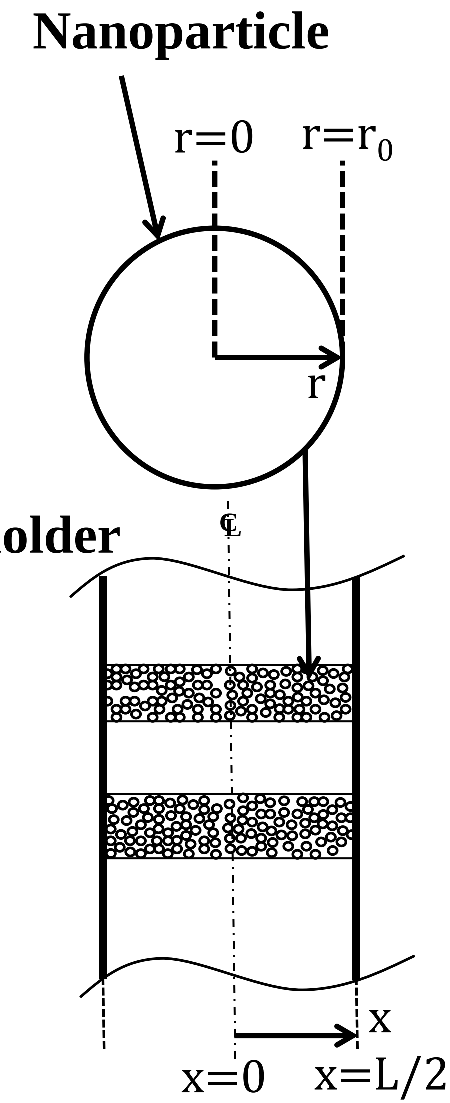
Parametric study of Size Effect

Sample	Maximum capacity S_0 ($gmol \cdot m^{-2}$)	Saturated surface concentration $C_{s,0}$ ($gmol \cdot m^{-2}$)	Fractional coverage θ (%)
HfO_2 (20nm)	1.5×10^{-6} ↑	1.1×10^{-6} ↑	73 ↓
HfO_2 (100nm)	8.7×10^{-7}	7.3×10^{-7}	84

Sample	$k_{a,0}$ ($m^3 \cdot gmol^{-1} \cdot s^{-1}$)	$k_{d,0}$ (s^{-1})	$E_{a,1}$ ($kJ \cdot gmol^{-1}$)	$E_{a,2}$ ($kJ \cdot gmol^{-1}$)	$E_{d,1}$ ($kJ \cdot gmol^{-1}$)	$E_{d,2}$ ($kJ \cdot gmol^{-1}$)
HfO_2 (20nm)	0.20	0.010	0.8	0.3	12.0	1.0
HfO_2 (100nm)	1.29	0.035	0.6	0.4	6.0	1.2

Separate Domain Process Simulation

Nanoparticle Domain



Adsorbent concentration in the gas phase:

$$\frac{\partial C_{g_{in}}}{\partial t} = D_{e_{in}} \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_{g_{in}}}{\partial r}\right) + \left[k_d C_{s_{in}} - k_a C_{g_{in}}(S_0 - C_{s_{in}})\right]\frac{A}{V}$$

Adsorbent concentration on the surface:

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

Sample Holder Domain

Adsorbent concentration in the gas phase:

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

Numerical Method

Discretization

Forward Euler Method	Crank-Nicolson Method

Linearization

Next Time-step Estimation	Triangular Matrix Solver

Iteration

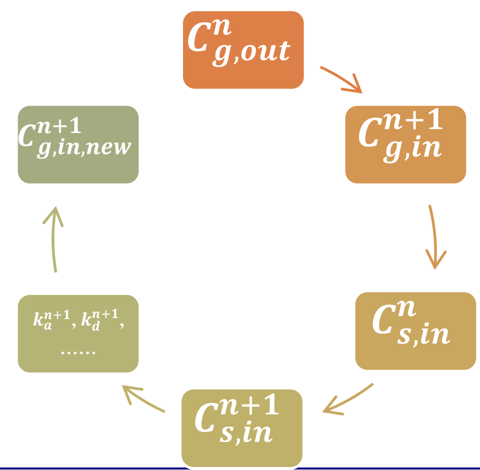
Update the new value for $C_{s,\,in}$	Update new value for k_a, k_d and so on

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

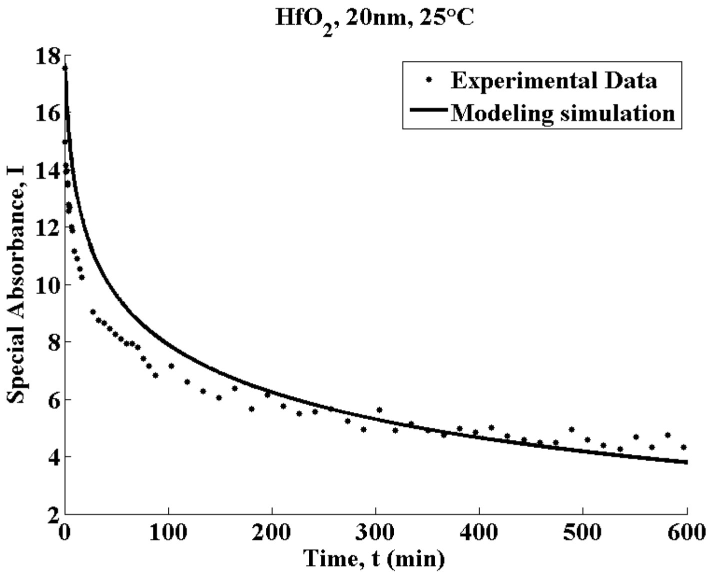
$$\frac{\partial^2 C_g}{\partial x^2} = \frac{1}{2}\left(\frac{C_{g,i+1}^{m+1} - 2C_{g,i}^{m+1} + C_{g,i-1}^{m+1}}{\Delta x^2} + \frac{C_{g,i+1}^{m} - 2C_{g,i}^{m} + C_{g,i-1}^{m}}{\Delta x^2}\right)$$

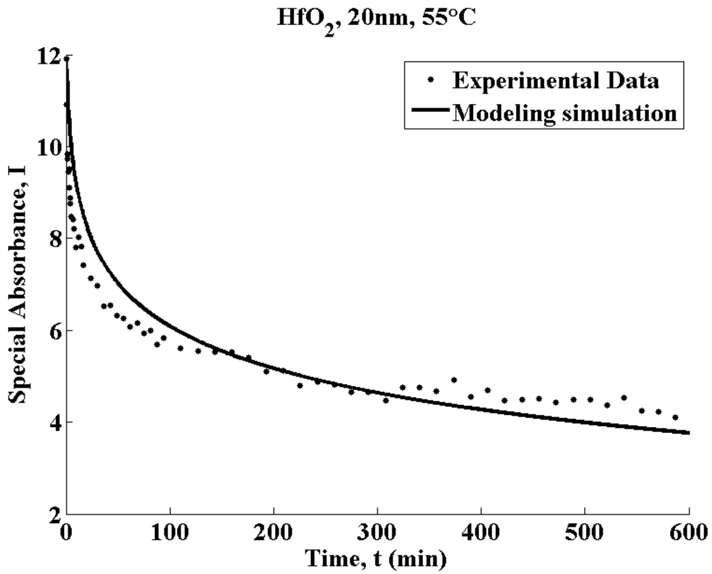
$$C_g = \frac{1}{2}\left(C_{g,i}^{m+1} + C_{g,i}^{m}\right),\ C_s = C_{s,i}^{m}.$$

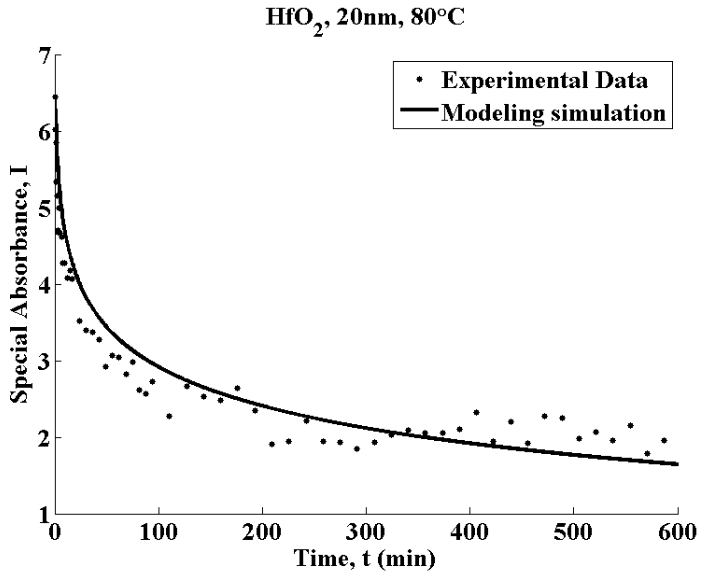
$$\frac{\alpha\Delta\bar{t}}{2\Delta\bar{x}^2}\bar{C}_{g,i+1}^{m+1} + \left[\frac{1}{2}\left(\delta\bar{C}_{s,i}^{m} - \gamma\right)\Delta\bar{t} - \frac{\alpha\Delta\bar{t}}{\Delta\bar{x}^2} - 1\right]\bar{C}_{g,i}^{m+1} + \frac{\alpha\Delta\bar{t}}{2\Delta\bar{x}^2}\bar{C}_{g,i-1}^{m+1} = -\frac{\alpha\Delta\bar{t}}{2\Delta\bar{x}^2}\bar{C}_{g,i+1}^{m}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



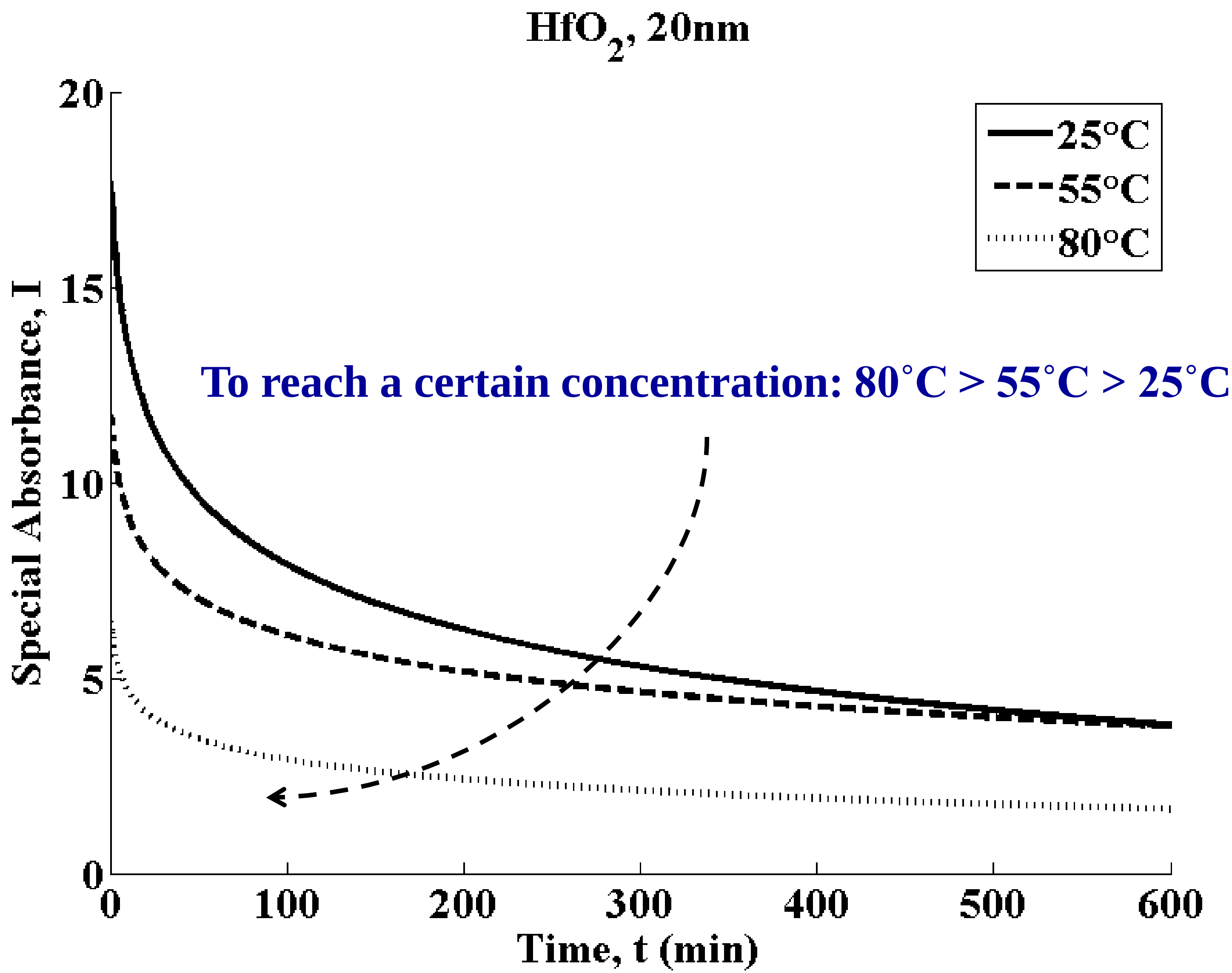
Comparison of Adsorption Profiles of NPs



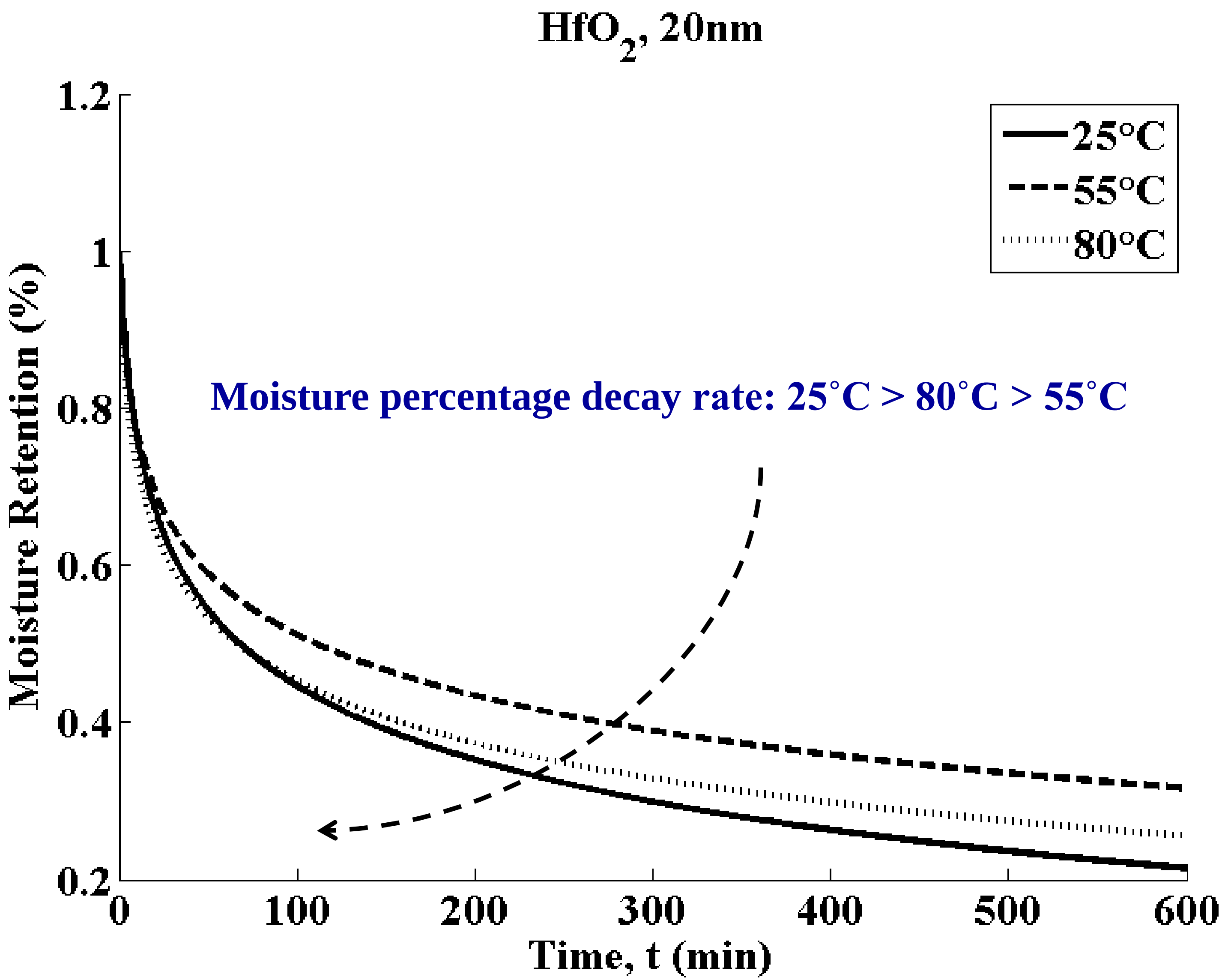




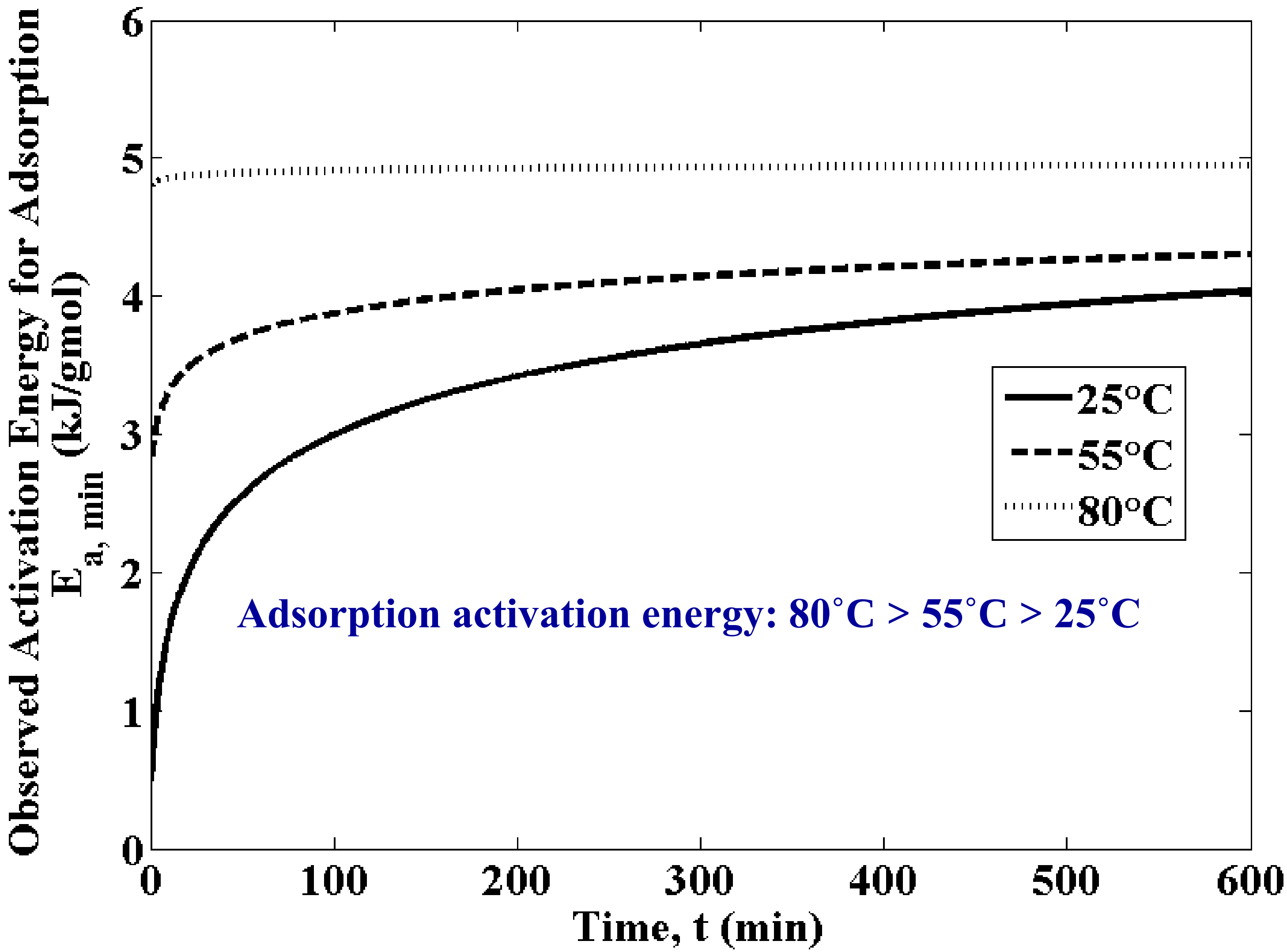
Effect of Temperature on Surface Retention



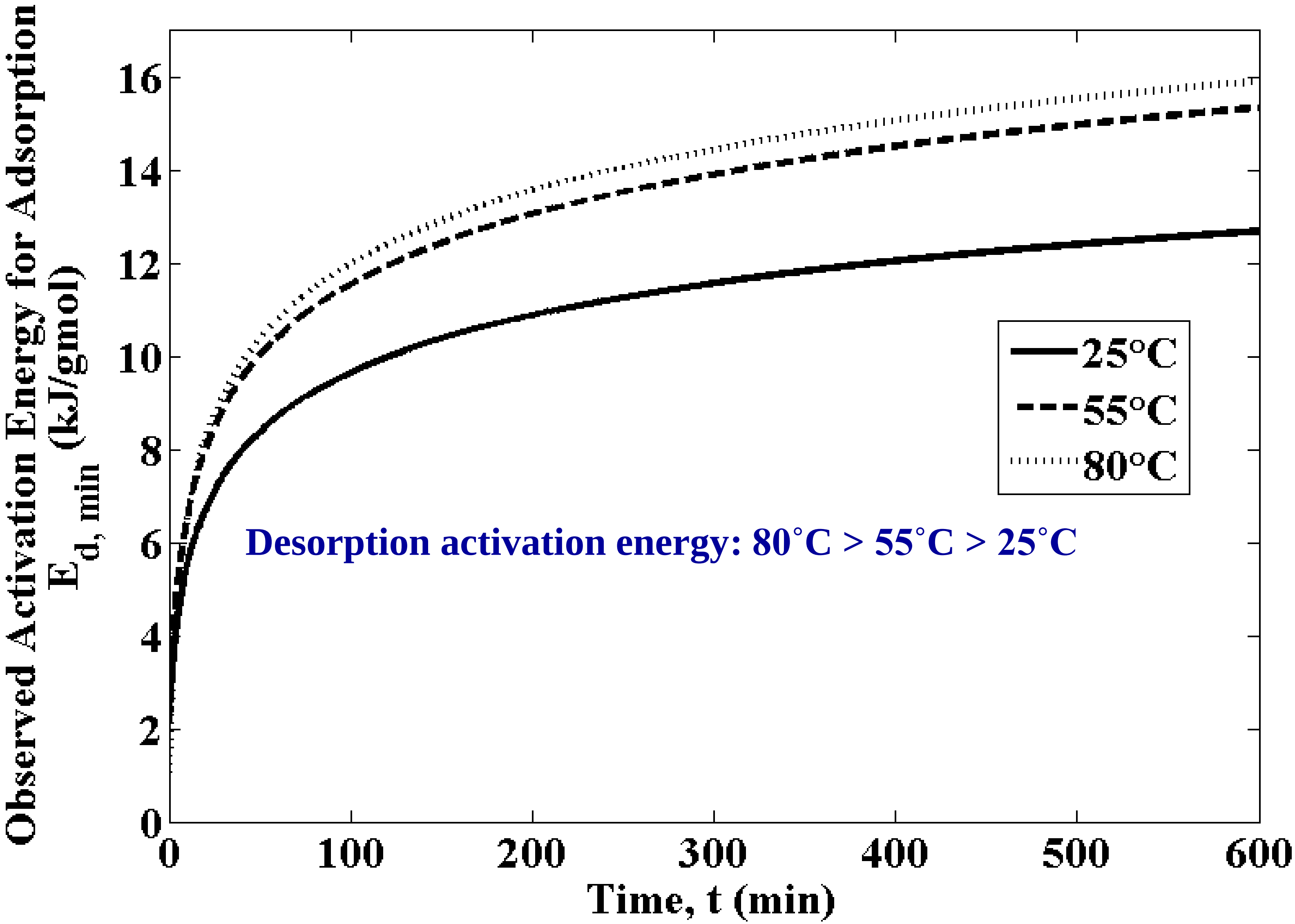
Moisture Retention Percentage



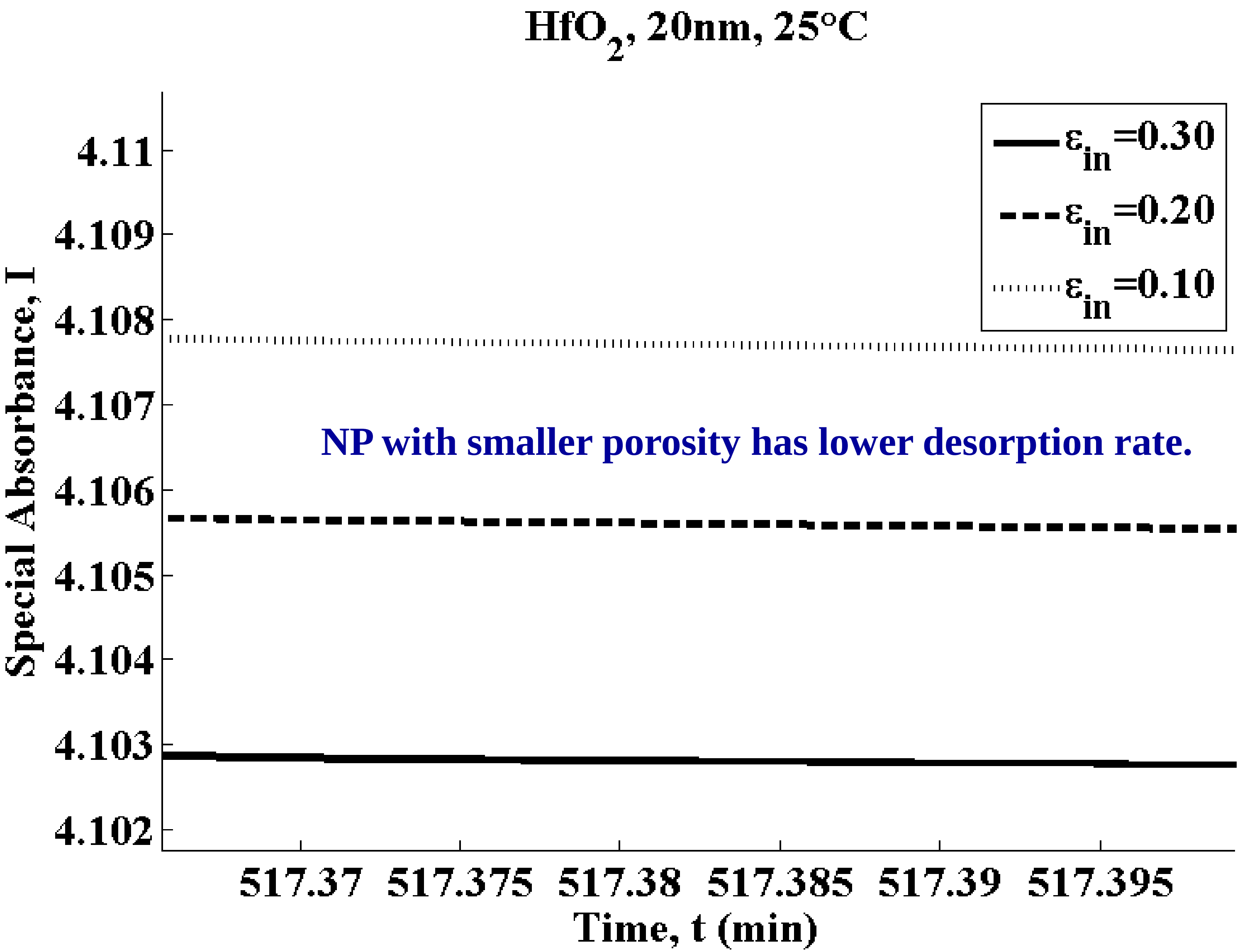
Adsorption Activation Energy of Surface Processes



Desorption Activation Energy of Surface Processes



NP Porosity Study

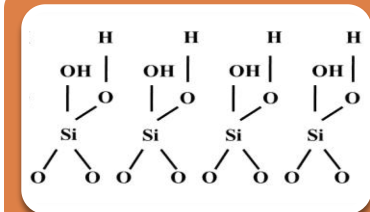


Parametric study of Temperature Effect

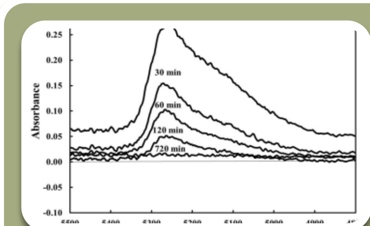
Sample (20nm)	Maximum capacity S_0 ($gmol \cdot m^{-2}$)	Saturated surface concentration $C_{s, 0}$ ($gmol \cdot m^{-2}$)	Fractional coverage θ (%)
HfO_2, 25˚C	1.5×10^{-6}	1.1×10^{-6}	73
HfO_2, 55˚C	1.5×10^{-6}	7.4×10^{-7}	49
HfO_2, 80˚C	1.5×10^{-6}	4.0×10^{-7}	27

Sample (20nm)	$k_{a, 0}$ ($m^3 \cdot gmol^{-1} \cdot s^{-1}$)	$k_{d, 0}$ (s^{-1})	$E_{a, 1}$ ($kJ \cdot gmol^{-1}$)	$E_{a, 2}$ ($kJ \cdot gmol^{-1}$)	$E_{d, 1}$ ($kJ \cdot gmol^{-1}$)	$E_{d, 2}$ ($kJ \cdot gmol^{-1}$)
HfO_2, 25˚C	0.03	0.0025	5.0	0.5	15.0	2.4
HfO_2, 55˚C	0.03	0.0025	5.0	2.8	21.5	2.0
HfO_2, 80˚C	0.03	0.0025	5.0	4.8	21.0	1.1

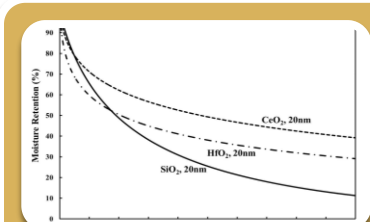
Summary and Conclusions I



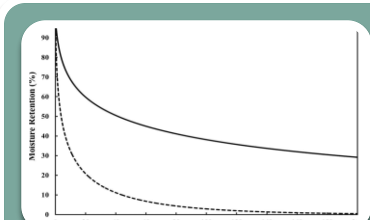
Hydroxylation is a powerful method for characterization of capture and retention (adsorption/desorption) properties of NPs.



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

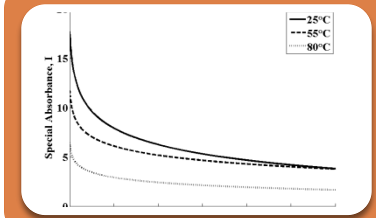


The affinity of nanoparticles for adsorption and retention decreases in the order: CeO_2 > HfO_2 > SiO_2. The surface available sites under certain challenge concentrations decreases in the order: SiO_2 > HfO_2 > CeO_2.

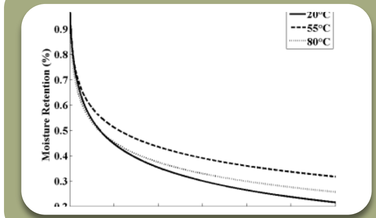


Nanoparticles with smaller size will have larger density of surface sites and larger surface retention capacity for most cases. They also have higher affinity for retention of contaminants.

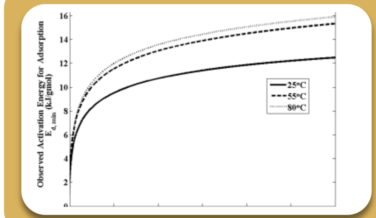
Summary and Conclusions II



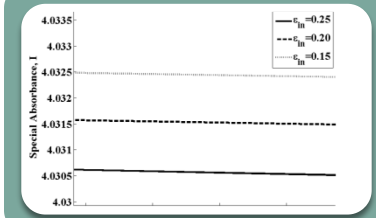
Purge under the higher temperature will reach the same baseline more faster.



The affinity of HfO_2 under different temperatures for moisture retention decreases in the order: 25˚C > 80˚C > 55˚C. The saturated surface concentration under certain challenge concentrations decreases in the order: 25˚C > 55˚C > 80˚C.



The adsorption and desorption activation energy of moisture on HfO_2 decreases in the order: 80˚C > 55˚C > 25˚C.



Higher NP porosity will increase the diffusivity inside of the NP, and it will have higher desorption rate.

Future Work

- Keep on studying the surface properties of different NPs under various temperatures
- Upgrade the experimental setup to increase the energy of the IR light to get more intensity of absorbance
- Upgrade the numerical model for porous NPs and increase the efficiency

Acknowledgements

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