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Adsorption and Coordination Environment of Cations under Nano-scale Confinement

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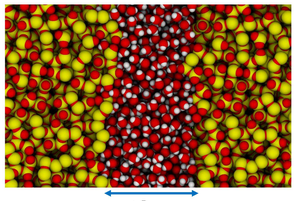
Motivation

Emergent chemical behavior due to nano-scale confinement:

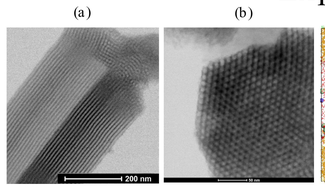
- Decreased dielectric constant[1-2], surface tension[3], and density of water.[3]
- Decreased solvation energies of metal cations.[4]
- Increased inner sphere coordination of metal cations.[4]
- Enhanced metal adsorption.[5-6]
- Modified redox[7] and diffusion.[8,9]



< 5 nm

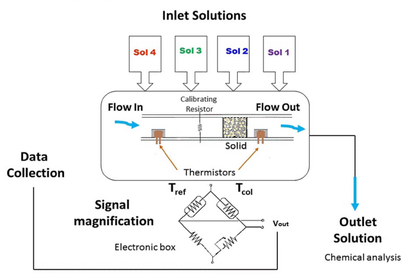
[1] Marti et al., *J. Phys. Chem. B* (2006)
[2] Senapati et al., *J. Phys. Chem. B* (2001)
[3] Takei et al., *Colliod Polym. Sci.* (2000)
[4] Kalluri et al., *J. Phys. Chem. C* (2011)
[5] Wang et al., *Geology* (2003)
[6] Zimmerman et al., *Environ. Sci.Techol* (2004)
[7] Mattia and Calabro, *Microfliud Nanofluid* (2012)
[8] Samsom and Biggin, *Nature* (2001)
[9] Ma et al., *JACS* (2019)

Experiments



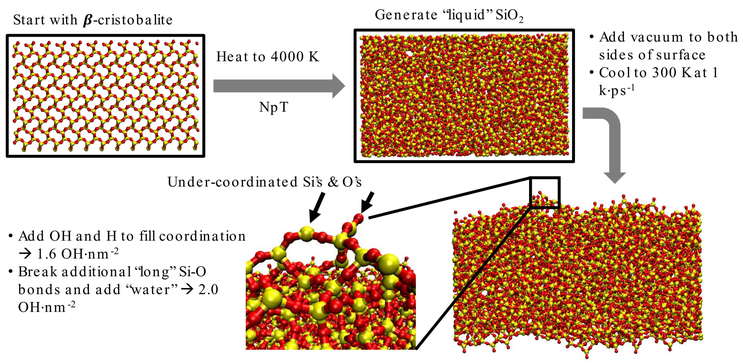
- Transmission electron microscopy images of SBA-15 mesoporous silica (a, b) Molecular dynamics model of silica pore (c).

https://www.aps.anl.gov/

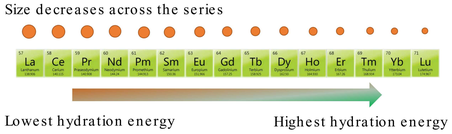


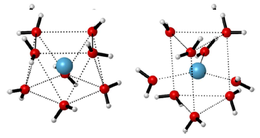
- Approach (1)Batch experiments; (2)Inductively-coupled plasma mass spectrometry; (3)X-ray absorption spectroscopy at Argonne National Lab; (4) Flow microcalorimetry at Georgia State University.

Modeling of Amorphous Silica



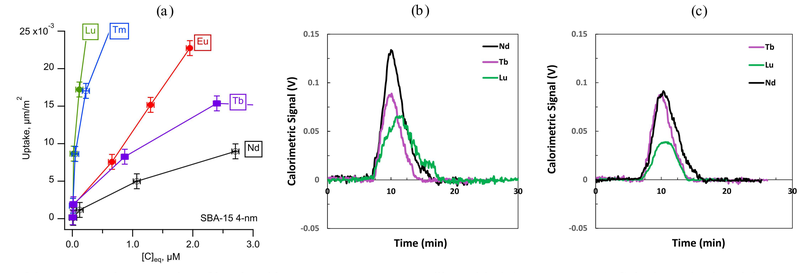
Interfacial Chemistry of Lanthanides (III) under Nano-scale Confinement



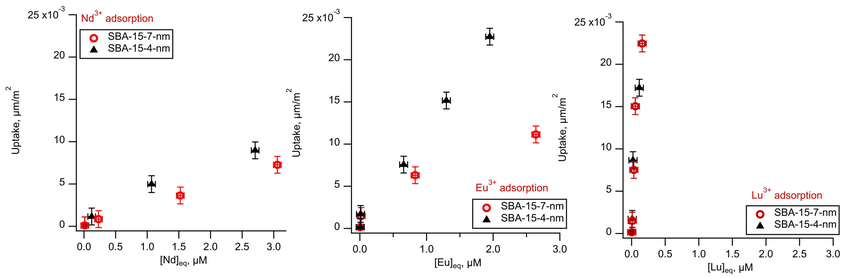


- Hydration shells of lanthanides. From Zhang et al., 2014, Inorg. Chem. 53, 7700.

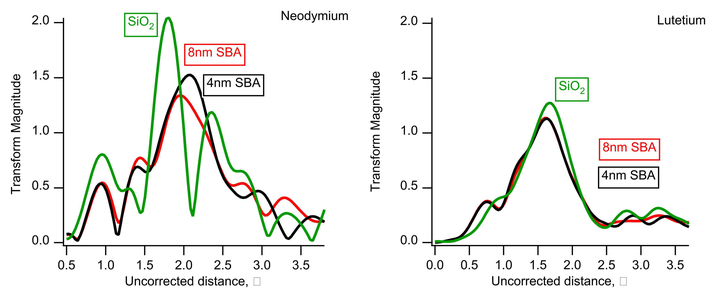
- Lanthanides: large and variable coordination numbers.
- Approach: (1) Single lanthanide adsorption kinetics and isotherms; (2) Mixed lanthanide system - competitive adsorption; (3) XAS for assessing coordination chemistry of lanthanides; (3) *Ab initio* MD for mechanistic insight.



- Mass-dependent uptake of lanthanides onto mesoporous silica with 4.4 nm pores (a). Calorimetric signal during Nd^{3+}, Tb^{3+} and Lu^{3+} adsorption onto mesoporous silica with 4.4 nm pores (b) and 7.0 nm pores (c).



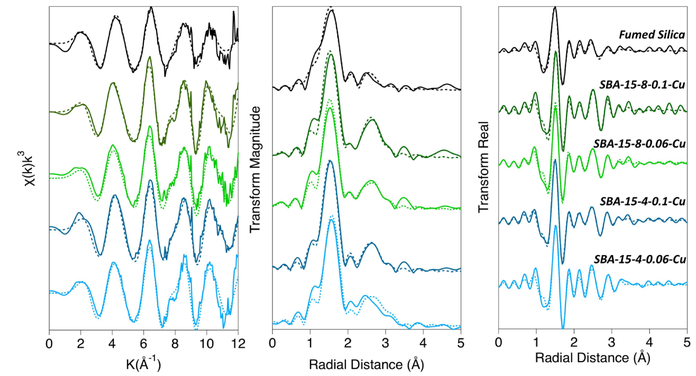
- Pore-size-dependent uptake of lanthanides onto mesoporous silica with 4.4 nm and 7.0 nm pores.



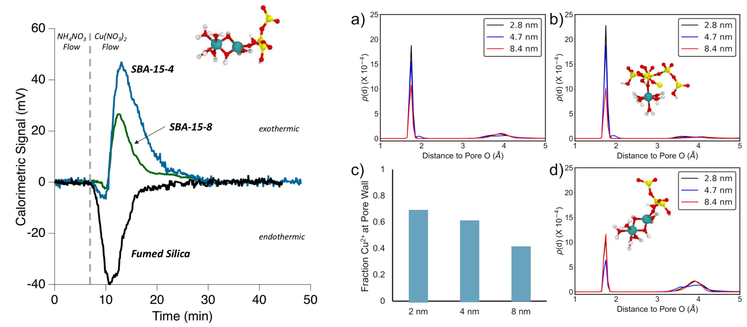
- Neodymium: 1st shell fit with two Nd-O distances; Nd–O bond length: SiO2 < 8nm SBA < 4nm SBA.
- Lutetium: 1st shell fit with one Lu-O distance; Same Lu–O bond length for non-porous SiO_2, and for SBA-15 with 4 nm and 8 nm pores.

Ilgen, et al. In preparation

Copper (II) Adsorption and Hydrolysis Driven by Nano-scale Confinement



- XAFS data and fits shown in k-space, magnitude of the Fourier transform, and the real part of Fourier transform. Solid lines: data, dashed lines: fits.
- More pronounced Cu-Cu backscattering feature observed for Cu^{2+} adsorbed onto porous silica, compared to non-porous.



- Exothermic signal could arise from increased dimerization.
- Cu (blue), O (red), H (white), and Si (yellow).
- Number density of Cu^{2+} as a function of distance to nearest silica pore O for all Cu (a), monomeric Cu (b), and oligomeric Cu (d). Integration of the all Cu densities in the < 2 Å region (c).

- More distorted coordination complexes ($Cu\text{-}O_{ax}$ >> $Cu\text{-}O_{eq}$);
- Increase Cu^{2+} dimerization inside nano-scale pores;
- Weak endothermic signal followed by a strong exothermic signal, suggests that Cu^{2+} undergoes dehydration during the dimerization process;
- The coordination environment of Cu^{2+} on the silica surface depends on pore diameter as well as surface loading;
- On SBA with high surface loadings, in the Cu-Si distances are shorter than for non-porous silica and mesoporous silicas with medium surface loadings.

Knight, et al.
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