Imprinted Organofunctional Sol-Gel Materials for Toxic Metal Separation

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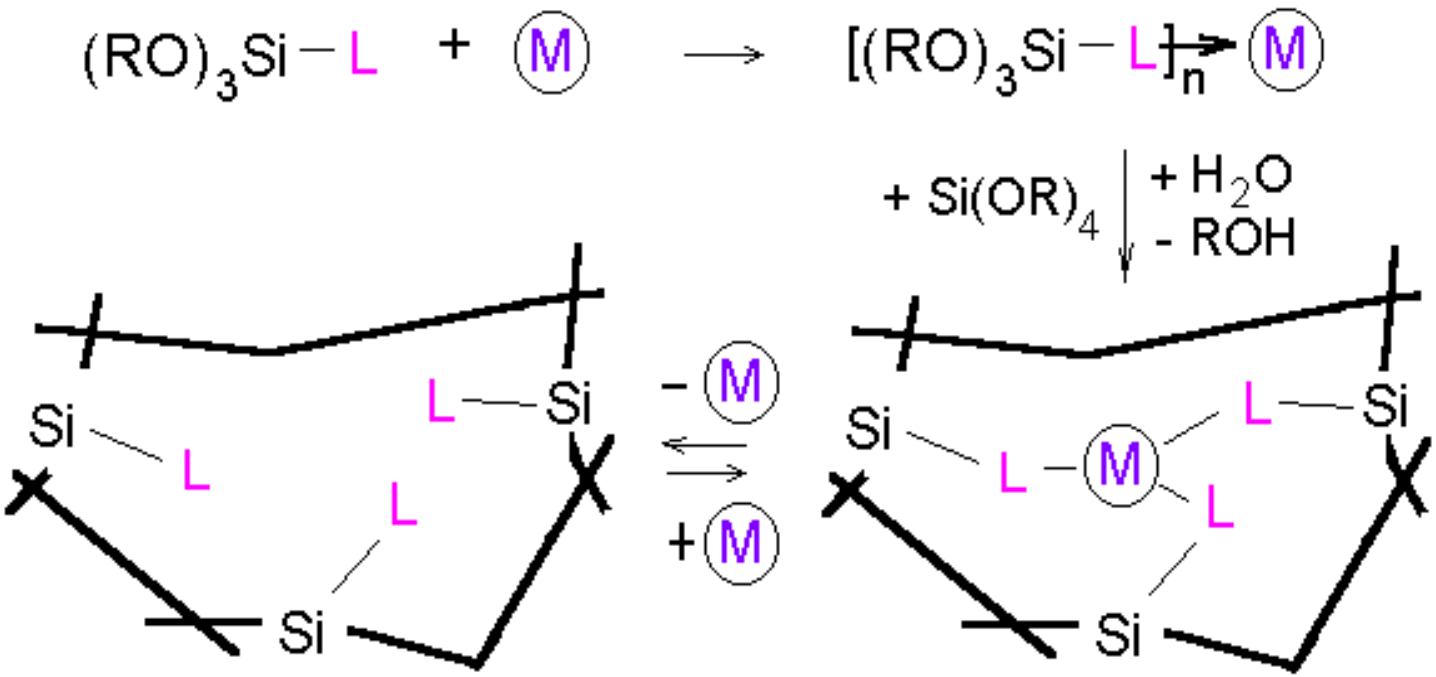
Goals

- Graft ligands (L) on or dope them in *inorganic polymers* (SiO_2 or MO_n) as an alternative to L-containing organic polymer sorbents
- Utilize the *hydrophilic* SiO_2 or MO_n network with *intrinsic* fast metal ion diffusion
- Use template-imprinting process to enhance capacity and selectivity
- Understand the M-L binding in heterogeneous and anisotropic chemical environment in such hybrid sol gels

Background

- Previous studies about inorganic polymers as metal sorbents
  - Grafting ligands on the *external* surface of *preformed* silica gel
  - Self-assembled monolayers of mesoporous supports (SAMMS);[1]
  - Crystalline silicotitanates (CSTs) for Cs^+ removal[2]
- Organofunctional sol-gels[3] from $[(RO)_3Si\text{-}L]_n \rightarrow M$ have been studied as new metal catalysts and materials for metal separation[3]
- Template-imprinting has been used for high-selectivity separation materials, zeolites, and nanoporous silicas[4]

Our approach



Sol-gel (SiO_2) imprinted with target metal

Mesoporous TiO_2-SiO_2 Sorbents for Cs^+ and UO_2^{2+}

- Prepared a series of surfactant ordered, mesoporous mixed TiO_2-SiO_2 oxide (100% -> 0% Si vs. Ti) materials
- Uranyl uptake by mesoporous sorbents is over 200 times faster than observed for comparable microporous materials
- Investigated the use of block copolymers in developing mesoporosity in base-stable, mixed TiO_2-SiO_2 oxide materials for Cs^+ extraction
- Removed >90% Cs^+ selectively within 1 h (Cs^+ capacity: 0.5 mmol/g) in the presence of a 10-fold excess of K^+ and 30-fold excess of Na^+ competitor ions

Hybrid Sol-Gel Sorbents Containing Tethered or Doped Organic Ligands

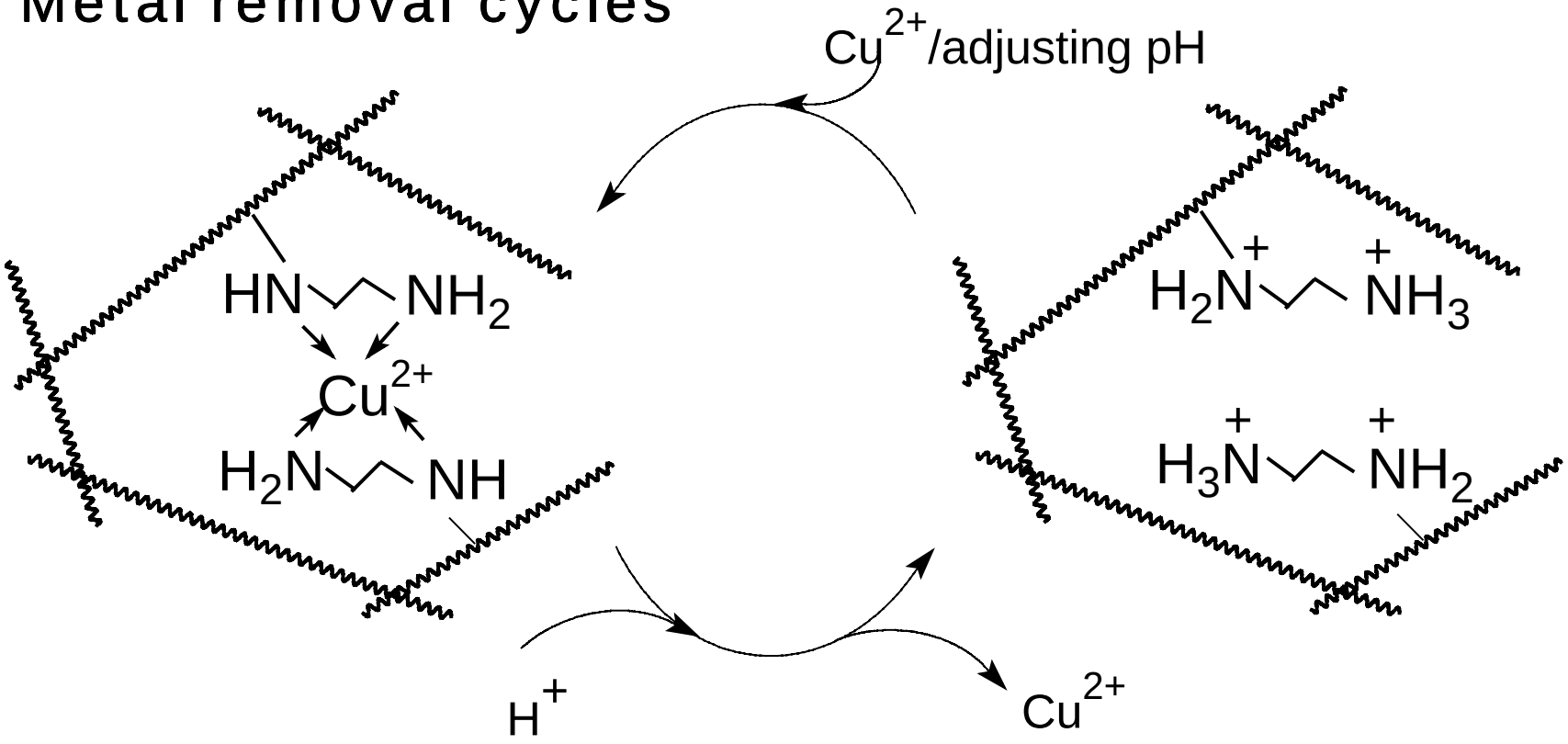
I. Ligand-tethered sol-gels (*Cu^{2+}, Hg^{2+}*)

- Easy gel preparation from off-the-shelf chemicals in 1.5 hr
- Reduce Cu^{2+} from 8.6 → 0.0 ppm (below AA detection limit: 2 ppb) in the presence of competitive Cd^{2+} and Zn^{2+} [5]
- Durable and stable for multiple cycles
- Fast Cu^{2+} binding kinetics
- Regenerate and recycle from Cu^{2+}-loaded gel in 5 min
- No secondary waste during application
- For Hg^{2+}, 10 mg of gels → [Hg^{2+}] at 2 ppm (20 mL) to 0.0 ppm

Table 1. Competitive binding behavior of the ethylene diamine (aapts)-grafted sol-gel solutions (25 mg gel in 2.5 mL of solution buffered at pH = 5.00)

	Initial Conc. (mg/L)	Final Conc. (mg/L)	K_d
1. For a mixture solution of ca. 1 mM of Cu^{2+}, Cd^{2+} and Zn^{2+}			
Cu^{2+}	71.8(0.3)	4.4(0.2)	1.54×10^3
Cd^{2+}	115(2)	108.6(1.5)	5.74
Zn^{2+}	70.3(1.6)	63.8(0.4)	10.15
2. For a mixture solution of ca. 0.1 mM of Cu^{2+}, Cd^{2+} and Zn^{2+}			
Cu^{2+}	6.57(0.05)	0.00	-
Cd^{2+}	11.18(0.10)	no intake of Cd^{2+} was observed	
Zn^{2+}	8.23(0.05)	7.80(0.06)	5.51

Metal removal cycles



II. Ligand-entrapped sol-gels (Sr^{2+})

- Crown ether/sol-gel materials showed high affinities for Sr^{2+}; *Alternative to crown ether/solvent extraction and liquid membranes*
- Removed >99% Sr^{2+} ([Sr^{2+}]: 27.6 ppm → 0.010 ppm) in the presence of a 4-fold excess of Ca^{2+} competitor ions
- Easy gel preparation from off-the-shelf chemicals
- Potentials to work in alkaline solutions
- Avoid the use of organic solvents

Table 2. Sr^{2+} Extraction by Embedded Na_4oddm Ligand

	Initial $[Sr^{2+}]^a$	Final $[Sr^{2+}]^a$	K_d^b	Sr^{2+} Removed (%)
Control[c]	27.600 ± 0.006	24.3 ± 0.7	22	12
Doped gel	27.600 ± 0.006	0.33 ± 0.01	11,000	99
Doped gel[d]	27.900 ± 0.006	0.010 ± 0.003	3.6×10^5	>99

[a]ppm [b]K_d in [mg of Sr^{2+}/g of gel] / [ppm of Sr^{2+} remaining]

[c]Control containing no Na_4oddm ligand [d]Competitive binding in a solution containing 118 ppm Ca^{2+}

Imprinting Studies of Organofuntional Hybrid Sol-Gel Sorbents

I. 1st-Generation Imprinting

- Metal templated ligand assemblies ($[M(L{\sim}{\sim}Si(OR)_3)_n]^{x+}$) are grafted onto the surfaces of preformed mesoporous sol-gel solid
- Removal of the metal template leaves the set of n ligands tethered to pore surfaces
- Organized manner based on the size and electronic signature of template
- Higher capacities for Cu^{2+} in a mixture of Cu^{2+} (1 mM) and Zn^{2+} (5 mM): 99.6% Cu^{2+}/52.6% Zn^{2+} vs. 98.5% Cu^{2+}/70% Zn^{2+} in control[6]

Table 3. Competitive Loading of M_1 (Cu^{2+}) and M_2 (Zn^{2+}) by Cu^{2+}-Imprinted and Control Blank Mesoporous Sorbents at pH 5.0 (Acetic Acid/Acetate Buffer).

Type	Solution (M)	%Cu^{2+} Abs	%Zn^{2+} Abs	Cu^{2+} K_d[a]	Zn^{2+} K_d[a]	k	k'
nonimp-aapts	0.001 Cu^{2+}/0.001 Zn^{2+}	98.5	96.6	6543	2872	2.3	-
imp-aapts	0.001 Cu^{2+}/0.001 Zn^{2+}	99.8	82.9	44045	483	91	40
nonimp-aapts	0.001 Cu^{2+}/0.005 Zn^{2+}	98.5	70	6539	233	28	-
imp-aapts	0.001 Cu^{2+}/0.005 Zn^{2+}	99.6	52.6	23874	111	215	7.7

[a] K_d units: mL/g

aapts: $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OMe)_3$

relative selective coefficients k' ($k' = k_{imprint\text{-}coated}/k_{control}$; $k = K_{d\ (target)}/K_{d\ (competitor)}$)

II. 2nd-Generation Imprinting

- Surface anionic groups ($Si\text{-}O^-$) interact with the charged head groups of cationic surfactants (M_1^+)
- Develop mesoporosity within the gelling, as-synthesized solid
- Second cationic species such as a ligated template complex $M[L\sim\sim Si(OR)_3]_n^{m+}$, is intercalated into pores, exchanging with and removing the surfactant
- >1.0 mmol/g ligand loadings (the highest ligand loadings for the 1st generation was ~0.7 mmol/g)[7]

III. 3rd-Generation Imprinting - Hierarchical or Double Imprinting

- Template complex is associated with the developing pore surface as it is formed
- Molecular architecture on two dimensional scales - mesoporosity with pore radii > 20 Å and microporosity from the point of view of creating a metal ion imprint involving tethered ligands and surface functionality on the order of 1-3 Å
- The highest selectivity in the current literature for Cu^{2+} in a mixture of Cu^{2+} (1 mM) and Zn^{2+} (10 mM): 99.98% Cu^{2+}/2.40% Zn^{2+} vs. 93.37% Cu^{2+}/10.64% Zn^{2+} in control[8]

Table 4 Binding Affinity and Selectivities of Hierarchical Imprinted Sorbents.[a]

Type	Solution (M)[b] $[Cu^{2+}]$	$[Zn^{2+}]$	% Cu^{2+} Abs[d]	% Zn^{2+} Abs[d]	K_d (Cu^{2+}) (mL/g)	K_d (Zn^{2+}) (mL/g)	k	k'
Nonimp-aapts (CTAB)[c]	0.001	0.001	99.66	99.77	29000	44000	0.66	-
Imp-aapts (CTAB)[c]	0.001	0.001	99.17	10.13	11000	67	160	240
Nonimp-aapts (SDS)[e]	0.001	0.001	96.07	44.59	2400	71	34	-
Imp-aapts (SDS)	0.001	0.001	99.56	13.31	23000	15	1500	44
Nonimp-aapts (SDS)	0.001	0.01	93.37	10.64	1400	10	140	-
Imp-aapts (SDS)	0.001	0.01	99.98	2.40	82000	2.5	33000	240

[a]Competitive loading of Cu^{2+} and Zn^{2+} by Cu^{2+}–imprinted and control blank mesoporous sorbents (pH = 5); [b]Initial conc.; [c]aapts imprinted and nonimprinted sorbents prepared with CTAB; [d]percentage metal ion absorbed; [e]SDS: sodium dodecylsulfate

Concluding Remarks

- General feasibility of using hydrophilic, porous metal oxide based materials as sorbents for metal ion extraction
- Simple, one step preparations of new hybrid sol-gel materials which exhibit fast binding kinetics, and high capacities and selectivities for Cu^{2+}, UO_2^{2+}, Sr^{2+} and Cs^{+}
- Development of several different methods for preparing imprinted, hybrid sol-gel sorbents which give the highest distribution coefficients (K_d) and selectivities
- New sol-gel precursors $(RO)_3Si{\sim}{\sim}L$ have been prepared and their abilities to selectively bind target ions are currently under evaluation in hybrid sol-gel sorbents

Acknowledgment

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