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Project Title: **Actinide-Specific Interfacial Chemistry of Monolayer Coated Mesoporous Ceramics**

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# Actinide-Specific Interfacial Chemistry of Monolayer Coated Mesoporous Ceramics

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## Research Objective

The objective of this program is to design, synthesize, and evaluate high-efficiency, high-capacity sorbent materials capable of selectively sequestering actinides from complex aqueous mixtures. One of the central goals of this project is to understand the fundamental interfacial science required to develop novel mesoporous materials coated with organized monolayers of rationally designed ligands, custom-tailored for binding specific actinide cations. This capability addresses waste management by separation of actinides, a central concern of high-level waste (HLW) management at several DOE sites.

PNNL has developed self-assembled monolayers on mesoporous supports (SAMMS) as a superior method of mercury and heavy metal sequestration. SAMMS has proven to be orders of magnitude faster and more effective than existing mercury-scavenging methods. This project builds on the SAMMS concept and extends the interfacial chemistry of monolayer-coated mesoporous materials to study the requirements of selective binding of actinides. The need exists in the management of DOE's HLW to be able to selectively and completely remove the actinides so that HLW volume can be minimized and the nonradioactive components can be segregated and disposed of as low-level waste (LLW). In addition, the short-term risk assessment for tank closure requires a complete and accurate accounting of actinide speciation. These needs dictate the development of selective and efficient separation of actinides from complex waste streams so as to minimize HLW volume, reduce waste management costs, and enhance long-term stability of the HLW form.

## Research Statement

A large fraction of the DOE tank waste is made up of saltcake and liquid wastes containing nitrates and hydroxides as well as an assortment of actinides. If the radionuclides can be removed, this material can be segregated and disposed of as LLW, significantly reducing remediation costs. Selective separation of the actinide fraction thus forms a critical need for this waste management strategy.

There is also a need to determine actinide speciation within the tanks. This can be done either via direct separation or by concentration of low-level actinides and subsequent separation. Isolation of individual actinides such as americium is a key parameter in the risk assessment necessary for tank closure. There are currently no methods available to distinguish or separate americium from plutonium at extremely low concentrations. This is essential information for the short-term risk assessment for HLW tank closure.

The SAMMS concept allows for significant freedom in the design and synthesis of tailored materials for actinide separation. The mesoporous ceramic synthesis is quite general and can be used to prepare a variety of high surface area ceramic oxide supports that are stable in different environments (acidic, corrosive, oxidizing, etc.). The high surface area of the mesoporous support (ca. 1000 m<sup>2</sup>/g) coupled with the high population density of binding groups creates a high loading capacity in the final SAMMS material. The ability to install various different monolayers, along with the ability to manipulate those monolayers post-installation, allows for the creation of a virtually endless list of chemical interfaces within the mesoporous matrix.

## Research Progress

### SCCO<sub>2</sub> Synthesis of SAMMS

The use of supercritical carbon dioxide (SCCO<sub>2</sub>) as the reaction medium for the deposition of self-assembled monolayers in mesoporous ceramic mobil catalytic material #41 (MCM-41) has been found to provide significantly enhanced hydration and silanation kinetics, unprecedented degrees of surface coverage, and the lowest monolayer defect density reported to date. SCCO<sub>2</sub> provides a very fast, effective, and efficient method for derivatizing a range of porous materials and fine powders.

It is well beyond the scope of this report to fully describe criticality and its consequences. However, a brief description of the phenomenon as it pertains to the functionalization of surfaces in small pores may prove useful. Densities similar to that of liquid phases are achievable with a supercritical fluid, given high enough pressures. This allows the fluid to “shield” solute molecules from each other approximately as well as a liquid solvent. However, the elevated temperature prevents the molecules of the supercritical fluid from interacting attractively enough to form long-lived structures, resulting in diffusivities and viscosities similar to those of a gas. The combination of these properties makes supercritical fluids very useful solvents. In particular, supercritical fluids permeate and penetrate small orifices readily.

The kinetics of traditional solution-phase synthesis of SAMMS are restricted by the mass transport of the silane to the inner pore surfaces. This mass transport term is affected by the interfacial wettability of the solvent/silica system, solvent bilayer shear forces, and bulk solvent viscosity. Use of a supercritical fluid as the reaction medium takes advantage of the liquid-like solvating properties and gas-like physical properties of supercritical fluids. Carbon dioxide is an attractive solvent because it is environmentally benign, non-toxic, non-flammable, and inexpensive; the mild critical point conditions for CO<sub>2</sub> ( $T_c = 31.1^\circ\text{C}$ ,  $P_c = 73.8$  bar) are easily attained and are unlikely to cause degradation of either the mesoporous starting material or the SAMMS product. In addition, performing the silanation in SCCO<sub>2</sub> also enhances delivery of the silane to the internal pore surface by direct pressure pumping.

In a hypothetical associative reaction between reagents A and B, increasing pressure can increase reaction rate (an excellent, detailed treatment of this subject is provided by Savage et al. [1995]). Both the transition state and the product will have a smaller molar volume than the starting materials. Therefore, both  $\Delta v^\ddagger$  and  $\Delta v^\circ$  will be negative. Thus, increasing pressure will stabilize the transition state relative to the starting materials, thereby lowering the activation energy of the process and increasing the reaction rate, and any equilibrium will be shifted toward the product.

Thus, exploitation of SCCO<sub>2</sub> as the reaction medium for the synthesis of SAMMS can accelerate monolayer formation both by speeding up delivery of the silanes to the reaction site and by reducing the activation barrier to monolayer formation. The optimized synthetic protocol that we have developed to deposit mercaptopropyl(trimethoxy)silane (MPTMS) monolayers within the pores of MCM-41 involves a one-hour hydration step followed by a six-hour silanation step in refluxing toluene (Feng et al. 1997; Liu et al. 1998). At this stage, the silane coverage is limited to approximately 3.6 to 4.0 silane molecules/nm<sup>2</sup> (this population density is not enhanced by either extending the reaction time or increasing silane concentration). Following the silanation with a two- to three-hour azeotropic distillation helps

to fill in the defects and increases this surface population to 5.0 to 5.2 silanes/nm<sup>2</sup>. This population density is representative of typical silane-based monolayers. In summary, the overall procedure takes about 10 hours of laboratory preparation time and 3 to 10 days of drying time.

Carrying out a similar MPTMS deposition, using SCCO<sub>2</sub> (7500 psi and 150°C) as the reaction medium increased reaction rate considerably. After only five minutes, it was found that this method had deposited a monolayer composed of 6.4 silanes/nm<sup>2</sup>, or approximately 20% higher than our best efforts in liquid-phase solvents (population determined gravimetrically and by <sup>29</sup>Si NMR). To our knowledge, this is the highest documented population density ever reported for a silane-based monolayer.

TEM and BET surface area analyses confirmed that the ordered mesostructure is retained in the monolayer-coated product. The solid-state <sup>29</sup>Si nuclear magnetic resonance (NMR) spectrum of this five-minute sample is shown in [Figure 1](#). The silane demographics of this sample are similar to those found in monolayers prepared under atmospheric pressure and routine solution-phase conditions (8% isolated siloxane, 47% terminal siloxane, and 45% internal siloxane). Maintaining the sample at elevated temperature and pressure resulted in a slow but steady evolution of the silane demographics, with a gradual decrease in the population of the terminal silane with a concomitant increase in the population of the internal silane over 24 hours and complete disappearance of the isolated silane (see [Figure 3](#)). Thermal curing of siloxane monolayers is known (Tripp and Hair 1991; Angst and Simmons 1991; Carson and Granick 1990). However, to our knowledge this is the highest degree of silane monolayer crosslinking documented by <sup>29</sup>Si NMR. Both the unprecedented surface population and the high degree of crosslinking are directly attributable to the use of SCCO<sub>2</sub> as the reaction medium.

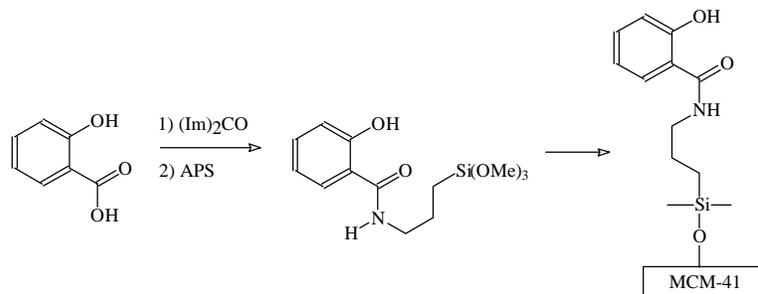
Not only is the monolayer deposition step considerably accelerated relative to standard solution methods, but the final drying phase has been completely eliminated by the use of SCCO<sub>2</sub> as the reaction medium. The SAMMS product emerges from the reaction chamber dry and ready to use, constituting considerable time savings.

## Design and Synthesis of New Classes of SAMMS

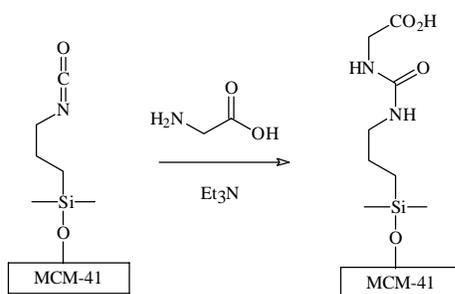
Instead of trying to create monolayers with a homogeneous dispersion of different silanes, we have chosen to design ligand synergy into our fundamental strategy by combining a protic ligand with a synergistic ligand, creating a cross-over, chelating ligand. We have employed three different synthetic pathways, exemplifying the versatility of our convergent SAMMS synthesis.

The first of these strategies is incorporation of the desired ligand via an amide linkage to commercially available aminopropylsiloxane (APS). This is accomplished by activating the carboxylate with carbonyl diimidazole (attempts to effect this amidation via the corresponding esters all failed). This reaction was followed immediately by deposition in freshly prepared MCM-41. This protocol resulted in the deposition of 1.1 silanes/nm<sup>2</sup>, which is the expected level of coverage for a silane of this bulk. A similar strategy is currently being used to make the *p*-NO<sub>2</sub> analog.

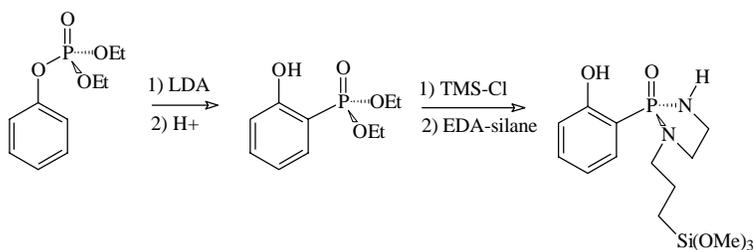
A chelating carboxylic acid function was incorporated by treating isocyanate-SAMMS with a buffered solution of glycine. This approach tethers the acid via a urea linkage. In this fashion, we obtained less than expected surface coverage, presumably due to the steric congestion at the monolayer interface (Fryxell et al. 1996). This problem can be avoided by preforming the silane. This strategy has also been used with other amines (e.g., aminomethylpyridine, aminobenzothiazole).



**Figure 1.**



**Figure 2.**



**Figure 3.**

Preparation of the o-hydroxyphosphonamide (HOPhos) ligand is outlined, as shown below. To date, the adjacent acidic phenolic proton has been problematic in the desired amidation process, but we have side-stepped that issue via protection of that functionality as the TMS ether.

## Lanthanide Testing

Initial testing used lanthanides to mimic actinides to perform preliminary screening more cost-effectively by avoiding radioactive materials. Testing with actinides will begin when we have successfully refined our interface sufficiently to ensure effective scavenging in the desired pH window. To establish a baseline, tests were run using thiol SAMMS to bind the representative lanthanides chosen (lanthanum was

chosen as a light lanthanide, neodymium was chosen as a representative lanthanide, and europium was chosen as an americium(III) mimic).

Two things are apparent from these data. First, the numbers are similar to those obtained in our preliminary tests using thiol SAMMS with plutonium(IV) and americium(III) (Feng et al. 1999), offering support for the decision to start with lanthanide models.

Thiol-SAMMS Binding of Representative Lanthanides

Metal	pH = 6.5	pH = 4.5	pH = 0.5
Lanthanum	4900	1440	41
Neodymium	2670	400	16
Europium	2070	810	8

0.1 M NaNO<sub>3</sub>, 2 ppm solution of the lanthanide as the nitrate  
0.100g SAMMS, 10 mL solution

Secondly, the distribution coefficients fall off with increasing acidity due to protonation of the ligand and release of the metal cation (this is related to the isoelectric point of the ligand). In fact, it is rather surprising that these metals are bound at all at a pH of 0.5.

Sal-SAMMS Binding of Representative Lanthanides

Metal	pH = 6.5	pH = 4.5	pH = 2.5	pH = 0.5
Lanthanum	7870	17	<1	<1
Neodymium	>100,000	18	<1	<1
Europium	>100,000	20	3	6

0.1 M NaNO<sub>3</sub>, 2 ppm solution of the lanthanide as the nitrate  
0.100g SAMMS, 10 mL solution

The sharp demarcation observed in the distribution coefficients determined for the Sal-SAMMS is a direct reflection of the isoelectric point of this ligand. While this is highly encouraging and stands as a validation of our design strategy, we need to create binding capability in a pH window between 2 and 4 because that is the range in which most actinide chemistry is performed (due to solubility and speciation). Thus, we need to lower the isoelectric point of the ligand from 4.5 to 5.0 to 3 or below.

One method of achieving this reduction is to employ the carboxylic acid functionality in conjunction with a suitable electron-withdrawing group (such as an amide or phosphine oxide). A quick test of this concept was explored by looking at the binding affinity of a glycine substituted urea. As the distribution coefficients below show, this material was surprisingly ineffective at scavenging lanthanides. (It should be noted that the surface coverage of this material was less than ideal. This will cause the saturation loading to be lowered but should not significantly affect the K<sub>d</sub> value at sub-saturation loadings).

### Gly-SAMMS Binding of Representative Lanthanides

Metal	pH = 6.5	pH = 4.5	pH = 2.5	pH = 0.5
Lanthanum	112	5	<1	<1
Neodymium	146	25	9	8
Europium	230	14	<1	36

0.1 M NaNO<sub>3</sub>, 2 ppm solution of the lanthanide as the nitrate  
0.100g SAMMS, 10 mL solution

## Summary

Novel synthetic methods employing SCCO<sub>2</sub> have dramatically increased both the quality and production rate of SAMMS. This powerful synthetic strategy has been found to provide significantly enhanced hydration and silanation kinetics, unprecedented degrees of surface coverage, and the lowest monolayer defect density reported to date. New ligands have demonstrated a high affinity for the lanthanide mimics that we have tested so far. However, this affinity doesn't quite coincide with the pH window that we have targeted. Experiments are under way to alleviate this by incorporating ligands of appropriate acidity.

## Planned Activities

We will be incorporating additional synergistic chelating ligands (e.g., the HOPO series, malonamide, phthalamide, and ortho-(phosphine oxide) acids) into the SAMMS interface. The focus will be on increasing the acidity of the protic portion of ligand so as to keep the isoelectric point below 4. We will also explore the amenability of each of these ligands to deposition from SCCO<sub>2</sub> so that we may exploit the desirable attributes that we have discovered inherent in this approach. In addition, we will acquire additional characterization of these lanthanide adducts by extended x-ray absorption fine structure to gain a better understanding of the stereochemistry and stoichiometry of the complexes. Evaluation with actinides (specifically thorium and uranium) will begin later this summer, and we will move on to testing with plutonium and americium this fall.

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## Publications

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## Presentations

Fryxell GE, J Liu, M Gong, SV Mattigod, Y Lin, J Birnbaum, KA Alford, and X Feng. April 1999. "Design and synthesis of mesoporous lanthanide sorbent materials." To be presented at the 101st National Meeting of the American Ceramic Society (invited presentation).

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Fryxell GE, J Liu, TS Zemanian, TA Hauser, JA Franz, K Alford, and LQ Wang. June 1999. "Self-assembled monolayers on mesoporous supports: Synthesis of nanoscale hybrid materials and their applications." To be presented at the Northwestern Regional Meeting of the American Ceramic Society in Portland, Oregon.

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## **Patent Application**

Fryxell GE, TS Zemanian, and J Liu. “Self-Assembled Monolayer and Method of Making.” E-1693, filed March 1999.

## **Press Highlights**

*Popular Science* (March 1999), p. 34, “Metal eaters.”

*Tri-City Herald* (April 11, 1999), p. D1. “PNNL focuses on healthy environment.”