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DOE/ER/14272--T2

Final Progress Report
"New Molecular Precursors for Low-Temperature Routes to New Oxide Materials" (Grant Number ER14272)

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In this grant period, we have explored the "single-source precursor" route to silicate materials containing various main group and transition metals. We have also explored the development of polymeric precursors to zinc silicate materials. In addition, we have begun to examine precursors for phosphate materials, based on the di(*tert*-butyl)phosphate ligand, $^{-}O_2P(O^tBu)_2$. A primary focus of these studies is the development of molecular precursors to homogeneous, ultrapure metal silicates and phosphates. More recently, we have attempted to develop template-assisted network-forming reactions that could lead to micro- or mesoporous materials. Our findings are summarized below.

Zirconium and Hafnium Systems

We previously found that $M[OSi(O^tBu)_3]_4$ (M = Zr (**1**), Hf(**2**)) complexes smoothly decompose quantitatively upon gentle heating (100-140 °C) to homogeneous $MO_2{\cdot}4SiO_2$ materials in the solid state or in solution.[1] In the solid state, this reaction cleanly produces isobutylene and water as the only volatile byproducts detected. Decomposition of **1** in refluxing toluene, xylene or mesitylene gives a transparent gel, which has a high surface area of 520 m^2g^{-1}, and has been shown by electron microscopy to be composed of 30 to 70 nm diameter particles.

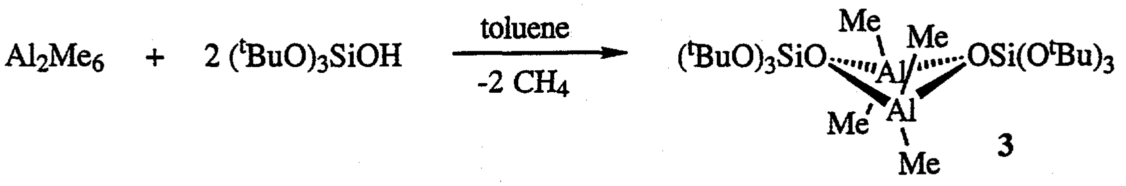
Recent studies on the solution-phase network formation has revealed a somewhat different stoichiometry. Thermolysis in toluene-d_8 shows that *tert*-butanol is also formed, and that a final product ratio of ca. 3:1 isobutylene to butanol is obtained. Furthermore, monitoring this reaction by ^1H NMR spectroscopy has revealed mechanistic information. Early in the transformation, an equivalent of $HOSi(O^tBu)_3$ is released per mol of **1**, and this is accompanied by formation of a new zirconium siloxide cluster complex that probably contains μ-oxo or $\mu\text{-}O_2Si(O^tBu)_2$ bridges. Kinetic and mechanistic studies on elimination reactions of **1** indicate that the decomposition is an autocatalytic process, catalyzed by Brønsted acids. In benzene-d_6, these reactions proceed completely to a freely-flowing solution containing isobutylene, water, *t*-butanol, and *a soluble, zirconia-silica* $Zr_wSi_xO_y(OH)_z$ *sol*. Further heating of this colloidal suspension produces a viscous, transparent gel.

The high-temperature transformations of $MO_2{\cdot}4SiO_2$ (M = Zr, Hf) obtained from both solid state and solution thermolyses have been studied in detail. Eventually, at very high temperatures, segregation into nanosized zirconia particles in a silica matrix occurs. It is clear from

these results that in this system, amorphous and tetragonal zirconia are matrix-stabilized to an inordinate degree. Thermolysis of $ZrO_2 \cdot 4SiO_2$ at 1500 °C for 6 h under argon results in a material that consists of a 9:1 ratio of tetragonal- to monoclinic-zirconia, and cristobalite after cooling to room temperature. Pure tetragonal zirconia is normally stable only over the temperature range of 950 - 2370 °C. We believe that these solid-state effects result from the highly homogeneous network formation that is accomplished with use of the "single source" molecular precursors.

Aluminum Systems

Given the technological importance of aluminosilicates as catalysts, catalyst supports, and structural materials, we have examined the synthesis of $Al\text{-}OSi(O^tBu)_3$ precursors, and the decompositions of these compounds to aluminosilicates.[2] Via additions of $HOSi(O^tBu)_3$ to $(AlMe_3)_2$, we have obtained $\{Me_2Al[\mu\text{-}OSi(O^tBu)_3]\}_2$ (**3**) and $[Me(Bu^tO)Al(\mu\text{-}OSi(O^tBu)_3)]_3$ (**4**). The crystal structure of **3** reveals a dimeric structure with bridging siloxide groups and a surprising bent geometry for the Al_2O_2 core.



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(1)

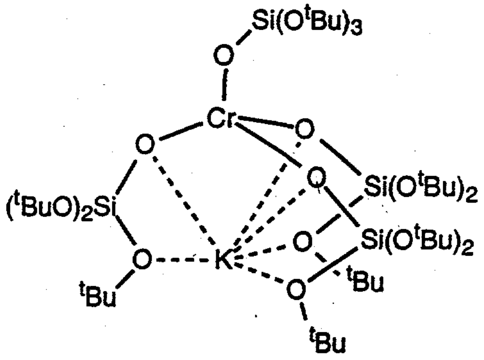
$$\{Me_2Al[\mu\text{-}OSi(O^tBu)_3]\}_2 \xrightarrow{200\,°C} 6\ CH_2{=}CMe_2 + CH_4 + \text{(trace)}\ {}^tBuOH + 2\ AlSiO_a(OH)_b(Me)_c(OH_2)_d \qquad (2)$$

Compounds **3** and **4** undergo thermolyses cleanly at low temperatures (120-150°C) to $Al_2O_3 \cdot 2SiO_2$ materials. Transformations in the solid state and in solution were studied. Also, the physical properties of the materials obtained were examined by BET surface area measurements, X-ray powder diffractometry, and electron microscopy. Surface areas of 200-300 m^2g^{-1} were observed, and it was found that mullite is a major product after extended heating to 1200°C.

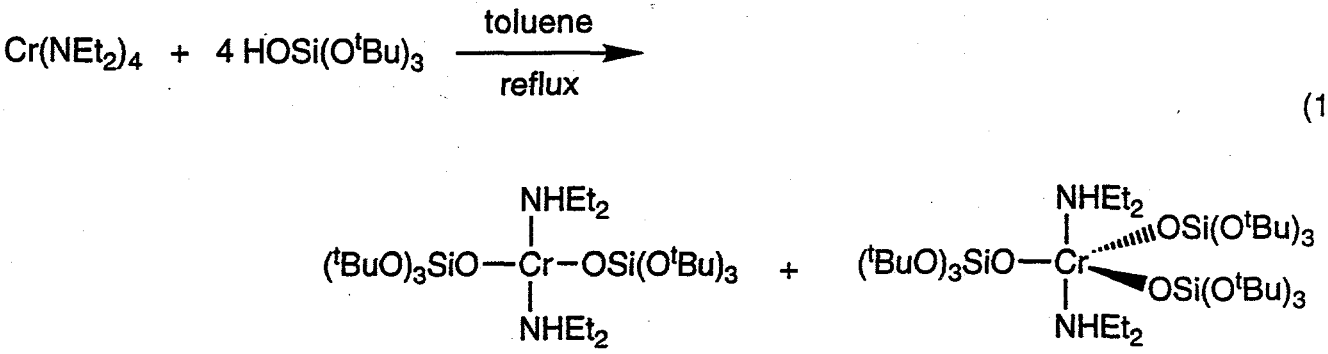
Chromium Systems

Interest in this system stems from the widespread use of $Cr\text{-}SiO_2$ catalysts for the oligomerization of polymerization of olefins. We have begun exploration of convenient synthetic routes to low-temperature precursors for chromium silicates. In summary, we have obtained Cr(II) and Cr(III) complexes $Cr[OSi(O^tBu)_3]_2(NHEt_2)_2$ and $Cr[OSi(O^tBu)_3]_3(NHEt_2)_2$ by the reaction of $Cr(NEt_2)_4$ with $HOSi(O^tBu)_3$. Additionally, high-yield syntheses for

$MCr[OSi(O^tBu)_3]_4$ (M = Na, K) are available via reaction of $CrCl_3$ with $MOSi(O^tBu)_3$.[3] The structure of one of these compounds, determined by X-ray crystallography, is depicted below:



An account of our synthesis and characterization of the Cr(II) and Cr(III) precursors $Cr[OSi(O^tBu)_3]_2(NHEt_2)_2$ and $Cr[OSi(O^tBu)_3]_3(NHEt_2)_2$ (eq 1) has appeared.[4] These complexes



$$Cr(NEt_2)_4 + 4\ HOSi(O^tBu)_3 \xrightarrow[reflux]{toluene} (^tBuO)_3SiO{-}Cr(NHEt_2)_2{-}OSi(O^tBu)_3 + (^tBuO)_3SiO{-}Cr(NHEt_2)_2[OSi(O^tBu)_3]_2 \qquad (1)$$

(1) (2)

have been characterized by X-ray crystallography, and are high spin with magnetic moments of 4.7 μ_B and 3.7 μ_B, respectively. Interest in this system stems from the use of Cr-SiO_2 catalysts for the oligomerization of polymerization of olefins. While this reaction does not provide a high yield of a single product that can be used in a convenient route to chromium silicate materials, it does offer the opportunity to closely compare analogous chromium(II) and chromium(III) siloxide complexes. Given the relatively low yields of these complexes, and the difficulties involved in separating them, we are concentrating our efforts on development of alternative routes to Cr precursor molecules.

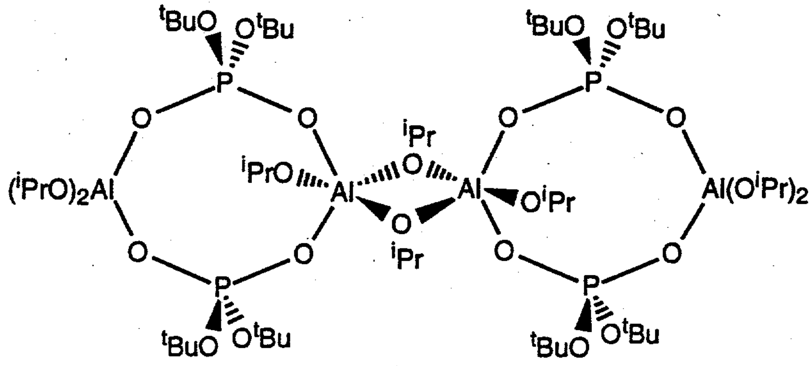
Copper Systems

This system was explored mainly in order to determine: 1) if convenient and/or novel routes to copper-silica composites could be developed using precursors analogous to those explored earlier for electrophilic metals, and 2) if the thermolytic chemistry of a late metal (alkoxy)siloxy precursor would be the same as that observed previously for the electrophilic metal

(Ti, Zr, Hf, Al) precursors. In summary, the Cu(I) precursor $[CuOSi(O^tBu)_3]_4$ was made and crystallographically characterized. It undergoes facile thermolysis at 100-200 °C to give $Cu-SiO_2$, Cu_2O-SiO_2, and $CuO-SiO_2$ materials, depending upon the conditions of the thermolysis.

Metal Phosphate Precursors

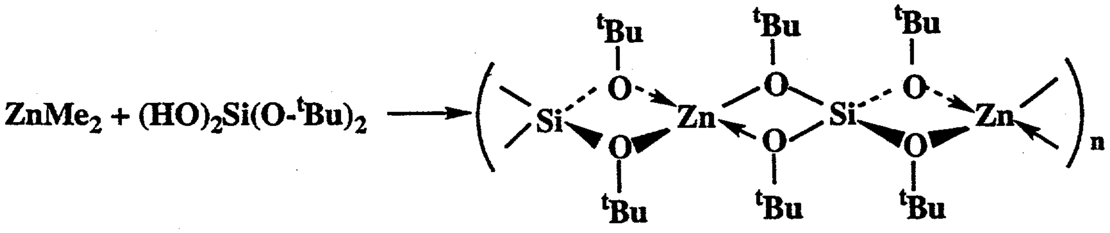
Initial studies indicate that these precursors are most readily prepared using the $HO_2P(O^tBu)_2$ reagent. With this approach, we have obtained $(^tBuO)_2(^tBuOH)Zr[\mu-O_2P(O^tBu)_2]_3Zr(O^tBu)_3$, $Zn_4(\mu_4-O)[O_2P(O^tBu)_2]_6$, and the aluminum compound shown below. Efforts are now underway to examine conversions of these compounds to phosphate networks.[5]



Zinc silicate luminescent materials

Manganese-doped zinc orthosilicate is an important luminescent material which has been widely used as a green phosphor in television tubes and CTR display devices. This material is traditionally synthesized by high temperature methods involving solid state reactions, crushing, grinding and ball milling. Sol-gel processes have also been used recently to generate more homogenous materials which give high emission intensity and high resistance to "burn-in". Based on our previous work with molecular precursors to oxide ceramics, it seemed that the use of a single source, polymeric precursor might allow low-temperature processing methods for the production of thin-film phosphors.

The reaction of $ZnMe_2$ with $(HO)_2Si(Ot-Bu)_2$ proceeded smoothly in toluene with evolution of methane to produce a soluble polymer, which was isolated as a white solid upon vacuum evaporation of the solvent:



The TGA analysis of the polymer showed stepwise decomposition starting at 80°C. The ceramic conversion reaction was complete at 300°C, corresponding to a 52.1% ceramic yield (theor. 52.1% based on the formation of Zn_2SiO_4/SiO_2). An NMR analysis of the volatile materials resulting from the polymer decomposition revealed the presence of both ^tBuOH and isobutylene in nearly a 1:1 ratio. Likewise, bulk pyrolyses of the polymer at 500-1350°C gave ceramics in 44-52% yields.

X-ray powder diffraction (XRD) studies of the ceramic conversion reaction have shown that the product exhibits variations in composition and crystallinity as the processing temperature is increased. Thus, the material annealed at 500°C for 2 h was essentially amorphous. When the sample was heated at 850°C for 2 h, both cristobalite and Zn_2SiO_4 were observed. The materials that were heat treated at temperatures above 1100°C showed highly crystalline cristobalite and Zn_2SiO_4. A decrease in the line widths in the XRD spectra indicate an increase in the average crystal size. Consistent with the XRD results, the crystallization of Zn_2SiO_4 was further supported by an exotherm at 800°C in the DTA curve for the polymer. Similar crystallization temperatures for zinc orthosilicate have previously been observed with sol-gel systems.

Crystalline, manganese-doped zinc orthosilicate was prepared by pyrolysis ($\geq$ 1100°C) of the above polymer precursor containing 1-5% $Mn(CH_2SiMe_3)_2$. The ceramic material thus prepared exhibited intense emissions at 533 nm and 595 nm, similar to those observed in other Zn_2SiO_4:Mn systems.

Because of the excellent processing properties for the starting polymer, we have been able to achieve dense and crack-free ceramic films on microscope slides or quartz plates, for both doped and undoped materials. The luminescent properties of theses films are currently under investigation.[6]

Syntheses of inorganic materials using dendrimeric polymers as templates

The syntheses of inorganic materials with "molecular-level" control of particle size, micro structure, morphology, aggregation and crystallographic orientation of phases has been one of the frontier areas in current materials research. The use of organic compounds and/or macromolecules as templates or active surfaces for the syntheses of microstructures, ceramic composites or for the nucleation of inorganic nanophases has proven to be a promising method for achieving this objective. As an alternative to more conventional templating methods, we have been exploring the use of functionalized starburst dendrimers, based on poly(propylene imine) structures, as molecular templates for the construction of mesoporous silicates and metal oxides, and for generation of nanophases of metal sulfides, oxides or metal clusters.

Preliminary studies show that dendrimer/silicate composite materials can be readily prepared by condensation of silicates on the quaternary ammonium surface of a dendrimer derived from poly(proplyene imine). The TGA analyses show two step weight losses with the second loss corresponding to the thermal decomposition of the dendrimer starting at 150°C. Depending on the dendrimer/silicate ratio, the presence of 15 to 40% dendrimer in the composites was observed. The materials prepared so far are amorphous in nature, however, the synthesis of crystalline phases might be possible by changing the reaction conditions, such as the silicate/template ratio, the reaction temperature, the reaction time, and/or the pH of the reaction medium.[6]

References

(1) K. W. Terry and T. D. Tilley, *Chem. Mater.* **1991**, *3,* 1001.

(2) K. W. Terry, P. K. Gantzel, and T. D. Tilley, *Chem. Mater.* **1992**, *4,* 1290.

(3) K. W. Terry and T. D. Tilley, manuscript in preparation.

(4) K. W. Terry, P. K. Gantzel, and T. D. Tilley, *Inorg. Chem.* **1993**, *32,* 5402.

(5) C. G. Lugmaier, T. D. Tilley, and A. L. Rheingold, work in progress.

(6) K. Su and T. D. Tilley, work in progress.