

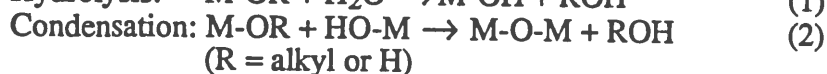
Polyoxotitanates and Their Role in Titania Sol-Gel Polymerization

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Final Seminar

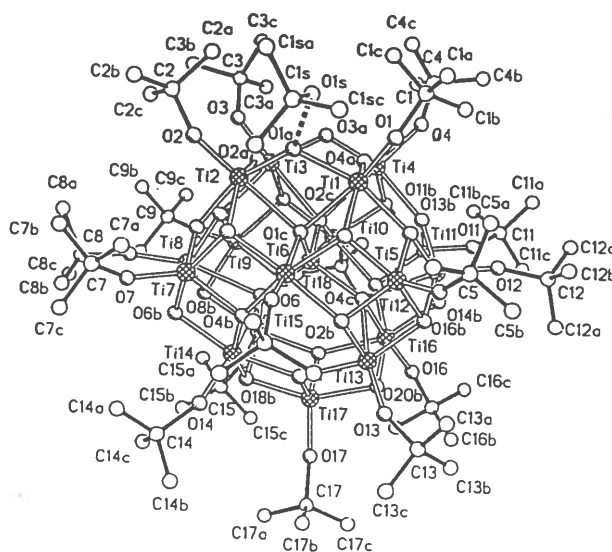
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Sol-gel processing is a viable route to a variety of titania materials that can be used as solar reflective coatings, photocatalysts, catalyst supports, and microporous ultrafiltration membranes [1]. Titania, TiO_2 , is also an important component of several sol-gel derived multicomponent metal oxides that have important electrical and optical properties, including the dielectric BaTiO_3 , the ferroelectric $(\text{Pb}_x\text{La}_{1-x})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ and the piezoelectric $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ [2]. Titania sol-gel polymerization involves hydrolysis and condensation of molecular precursors, usually titanium alkoxides:



The reactions are normally carried out using ≥ 2 equiv of water per titanium and ultimately yield oxide polymers [3]. However, if substoichiometric amounts of water are added to an alkoxide solution under carefully controlled conditions, partially hydrolyzed, molecular polyoxotitanate complexes $[\text{Ti}_x\text{O}_y](\text{OR})_{4x-2y}$, $y/x < 2$, are formed [4-6]. The present study has focused on the chemistry of these polyoxotitanates and their role in titania sol-gel polymerization.

Polyoxotitanates formed upon partial hydrolysis of primary and secondary titanium alkoxides are known [4-6], but no polytitanates derived from tertiary alkoxides have been reported. Hydrolysis of $\text{Ti}(\text{OBu}^t)_4$ was therefore studied in order to isolate and characterize a molecule of this type. Hydrolysis of $\text{Ti}(\text{OBu}^t)_4$ with 1 equiv of water in *t*-BuOH at 100 °C yielded a new polyoxotitanate complex $[\text{Ti}_{18}\text{O}_{28}\text{H}](\text{OBu}^t)_{17}$ [7]. A single crystal X-ray diffraction study of its *t*-BuOH solvate revealed a $\text{Ti}_{18}\text{O}_{45}$ metal-oxygen framework having a pentacapped Keggin structure, where all of the terminal oxygen atoms are alkylated and one of the four doubly-bridging oxygens is protonated:



The hydrogen bond involving hydroxy oxygen O(1a) and *t*-butanol oxygen O(1s) is shown above as a dashed line. This complex is the most highly condensed titanium alkoxide hydrolysis product isolated to date and shows good stability in toluene/*t*-butanol solution. Treatment of the complex with *t*-amyl alcohol led to a partial exchange of *t*-butoxide groups with *t*-amyloxide groups, and the product was identified as $[\text{Ti}_{18}\text{O}_{28}\text{H}](\text{O}i\text{Bu})_{12}(\text{O}i\text{Am})_5$ using NMR spectroscopy. In this molecule, the *t*-amyloxide groups are terminally bonded to the five five-coordinated titanium centers.

Partial hydrolysis and condensation of titanium alkoxides were studied *in situ* by using solution ^{17}O NMR spectroscopy. The ^{17}O NMR spectra of structurally characterized polyoxotitanates served as fingerprints of the species formed in solution [4-6]. The speciation and rates of formation were found to be greatly affected by reaction conditions such as the choice of alkoxide ligand, degree of hydrolysis, solvent, and pH. The low molecular weight species formed did not appear to be intermediates formed under sol-gel polymerization conditions.

It is known that the course of titania sol-gel polymerization is strongly influenced by acidic additives in that hydrolysis of simple alkoxides $\text{Ti}(\text{OR})_4$ yields clear gels, as opposed to precipitates or cloudy gels, only under acidic conditions [3, 8]. Solution ^{17}O NMR and static light scattering techniques were used to examine molecular size distributions in hydrolyzed $\text{Ti}(\text{OEt})_4$ and $[\text{Ti}_{16}\text{O}_{16}](\text{OEt})_{32}$ solutions under acidic and basic (or neutral) conditions as a function of the degree of hydrolysis. Unlike the sol-gel polymerization of $\text{Si}(\text{OR})_4$, in which $\text{Si}(\text{OR})_4$ is the monomer for polymerization [9], sol-gel polymerization of $\text{Ti}(\text{OEt})_4$ was observed to involve the initial formation of stable polyoxotitanates which then serve as monomers for sol-gel polymerization.

A building block approach in titania sol-gel polymerization was explored using two polyoxotitanates, $[\text{Ti}_7\text{O}_4](\text{OEt})_{20}$ [4] and $[\text{Ti}_{16}\text{O}_{16}](\text{OEt})_{32}$ [5], as potential precursors. First, the stability of the $[\text{Ti}_7\text{O}_4](\text{OEt})_{20}$ and $[\text{Ti}_{16}\text{O}_{16}](\text{OEt})_{32}$ core structures toward ethanol was studied. These molecules showed contrasting behavior in that ethanolic solutions of $[\text{Ti}_7\text{O}_4](\text{OEt})_{20}$ showed significant decomposition of the $[\text{Ti}_7\text{O}_4]$ core structure, while solutions of $[\text{Ti}_{16}\text{O}_{16}](\text{OEt})_{32}$ showed no signs of decomposition under the same conditions. However, the peripheral ethoxide groups of the $[\text{Ti}_{16}\text{O}_{16}](\text{OEt})_{32}$ molecule were reactive and could be selectively exchanged by reacting the molecule with other alcohols. Solid state ^{17}O MAS NMR experiments using selective ^{17}O labeling techniques indicated that the $[\text{Ti}_{16}\text{O}_{16}]$ core was largely preserved during sol-gel polymerization [10]. Dynamic light scattering studies comparing kinetics of $[\text{Ti}_7\text{O}_4](\text{OEt})_{20}$, $[\text{Ti}_{16}\text{O}_{16}](\text{OEt})_{32}$ and $\text{Ti}(\text{OEt})_4$ sol-gel polymerization revealed that two different molecular growth pathways were followed. The sol-gel polymerization of $\text{Ti}(\text{OEt})_4$ and $[\text{Ti}_7\text{O}_4](\text{OEt})_{20}$ involved initial formation of stable polyoxotitanates that subsequently polymerized into gels. On the other hand, the sol-gel polymerization of $[\text{Ti}_{16}\text{O}_{16}](\text{OEt})_{32}$ proceeded directly, with $[\text{Ti}_{16}\text{O}_{16}](\text{OEt})_{32}$ acting as the monomer. Nitrogen adsorption studies showed different porosities for $[\text{Ti}_7\text{O}_4](\text{OEt})_{20}$ -, $[\text{Ti}_{16}\text{O}_{16}](\text{OEt})_{32}$ - and $\text{Ti}(\text{OEt})_4$ -derived xerogels arising from the different precursors employed.

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