

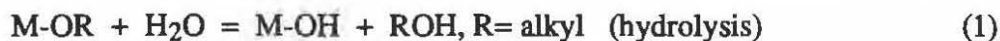
## Investigations of Early Stages of Titania Sol-Gel Processing

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Sol-gel processing is a chemical method for preparing oxide ceramic materials [1]. This technique is based on the inorganic polymerization of metal alkoxide precursors via hydrolysis and condensation:



Partial hydrolysis of metal alkoxide precursors results in the formation of colloidal particles or polymers in a liquid, i.e., a sol. The sol then undergoes polymerization via hydrolysis and condensation to form an oxide network. Subsequent heat treatment of the oxide network yields a dense oxide ceramic. One of the most valuable advantages of sol-gel processing over conventional powder processing is that the viscous solution obtained during sol-gel processing allows the formation of ceramic materials in many different forms such as fibers [2], films [3], monoliths [4], and aerogels [5].

Despite extensive study, relatively little information is available regarding the formulas and structures of polyoxoalkoxides formed in the early stages of sol-gel polymerization [1,6]. As a result, little is known about the principles governing polymerization pathways. The goal of this research was to explore the chemistry behind titania sol-gel processing on the molecular level during the early stages of the polymerization.

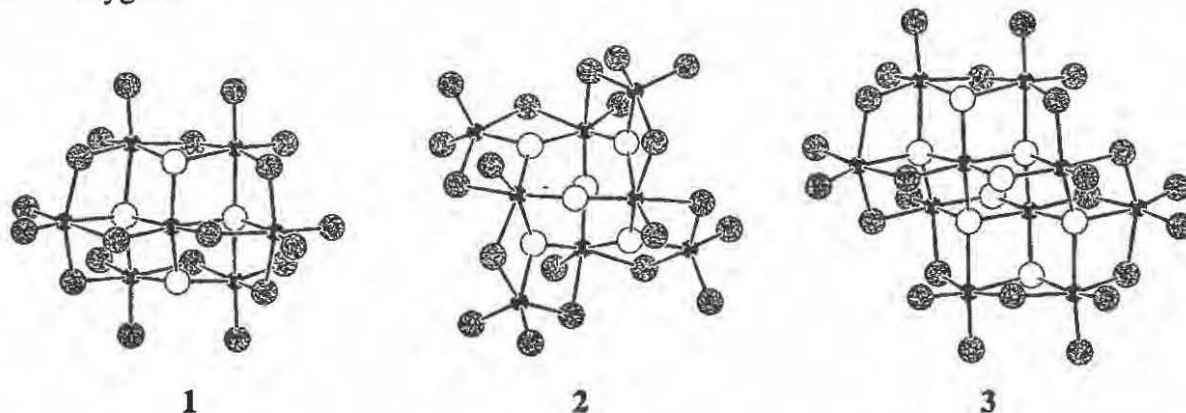
A selective  $^{17}\text{O}$  isotope labeling technique was developed which allowed  $^{17}\text{O}$  NMR spectroscopy to be used to identify the structurally complex titanium oxoalkoxide species formed in titanium alkoxide hydrolysis solution. When a titanium alkoxide is hydrolyzed with  $^{17}\text{O}$ -enriched water, the kinetic inertness of C-O bonds relative to Ti-O bonds generates selectively  $^{17}\text{O}$ -enriched polyoxoalkoxides as indicated in equation (3). Because of this selective enrichment,  $^{17}\text{O}$  NMR spectra of these species show strong resonances for the



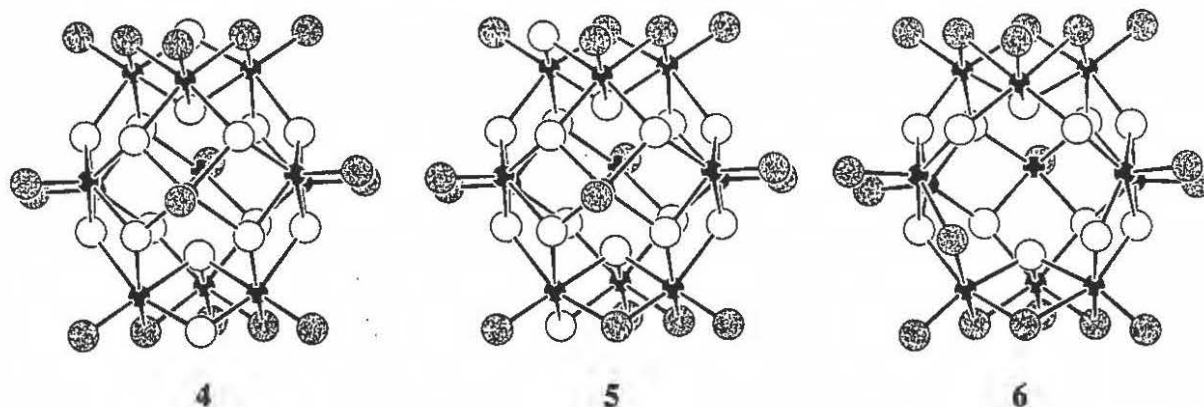
oxide oxygens but not for the alkoxide oxygens. The consequent spectral simplification allows for identification of individual species present in complex mixtures.

Hydrolysis of  $\text{Ti}(\text{OEt})_4$  with  $^{17}\text{O}$ -enriched water resulted in the crystallization of  $[\text{Ti}_7\text{O}^*_4](\text{OEt})_{20}$  (1) which gave  $^{17}\text{O}$  NMR resonances at  $\delta$  537 and  $\delta$  325 [7, 8]. These resonances were among the  $^{17}\text{O}$  NMR resonances observed from  $\text{Ti}(\text{OEt})_4$  hydrolysis mixtures, implying the presence of that compound in the mixture. When compound 1 was hydrolyzed with 1 equivalent of water, new resonances at  $\delta$  725 and 534 appeared together with resonances for 1. The titanium oxoalkoxide responsible for the new resonances could not be isolated, but its benzyl analog,  $[\text{Ti}_8\text{O}_6](\text{OBz})_{20}$  (2), could be obtained in crystalline form and structurally characterized [8]. A new titanium oxoethoxide species was crystallized out from the mixture of 1 and 2 in heptane and this compound was characterized by X-ray crystallography as  $[\text{Ti}_{10}\text{O}_8](\text{OEt})_4$  (3) [8]. However,  $^{17}\text{O}$  resonances of this compound did not appear in the  $^{17}\text{O}$  NMR spectrum of  $\text{Ti}(\text{OEt})_4$  hydrolysis mixture, implying that 3 was not present in

significant concentration. Based on the  $^{17}\text{O}$  NMR chemical shifts observed for several structurally-characterized titanium polyoxoalkoxides,  $^{17}\text{O}$  NMR chemical shift regions were defined as follow:  $\delta$  850 - 650 for  $\text{Ti}_2\text{O}$ ,  $\delta$  650 - 450 for  $\text{Ti}_3\text{O}$  and  $\delta$  450 - 250 for  $\text{Ti}_4\text{O}$  oxide oxygens.



While hydrolysis of  $\text{Ti}(\text{OEt})_4$  yielded a complex mixture of polyoxoalkoxides, reactions of  $\text{Ti}(\text{OPr}^i)_4$  with one equivalent of water in isopropanol solution at  $100\text{ }^\circ\text{C}$  yielded as sole products a 1:1 mixture of two isomeric complexes,  $\alpha_1$ - $[\text{Ti}_{12}\text{O}_{16}](\text{OPr}^i)_{16}$  (4) and  $\alpha_2$ - $[\text{Ti}_{12}\text{O}_{16}](\text{OPr}^i)_{16}$  (5) [9]. Pure 4 and 5 undergo isomerization to 1:1 mixture of both isomers upon heating to  $70\text{ }^\circ\text{C}$  for 24 hours. The X-ray crystallographically determined structure of 4 and structure proposed for the isomeric compound 5 on the basis of spectroscopic evidence are shown below. Hydrolysis of  $\text{Ti}(\text{OPr}^i)_4$  at ambient temperature yielded  $\alpha$ - $[\text{Ti}_{11}\text{O}_{13}](\text{OPr}^i)_{18}$  (6) as a sole product in solution [9]. The structure of this compound was determined from its mixed alkoxide derivative,  $\alpha$ - $[\text{Ti}_{11}\text{O}_{13}](\text{OPr}^i)_{13}(\text{OEt})_5$ , which was structurally characterized using X-ray crystallographic techniques. All three of the compounds form a family of a stable dodecitanates which undergo regioselective ligand exchange reaction upon reacting with alcohols.



The metal oxide framework stabilities of the titanium polyoxoalkoxides was examined in methyl cyclohexane and alcohol solution at ambient and elevated temperatures. The relative stabilities of the titanium polyoxoalkoxides examined was  $[\text{Ti}_7\text{O}_4](\text{OEt})_{20} < [\text{Ti}_8\text{O}_6](\text{OBz})_{20} < \alpha$ - $[\text{Ti}_{11}\text{O}_{13}](\text{OPr}^i)_{18} < \alpha_1$ - $[\text{Ti}_{12}\text{O}_{16}](\text{OPr}^i)_{16}$ . Among the compounds examined,  $\alpha_1$ - $[\text{Ti}_{12}\text{O}_{16}](\text{OPr}^i)_{16}$  showed extremely low moisture sensitivity, failing to react with 4 equivalents of water in 0.035 M isopropanol solution.  $^{17}\text{O}$  NMR studies of hydrolysis and condensation behavior of  $\alpha_1$ - $[\text{Ti}_{12}\text{O}_{16}](\text{OPr}^i)_{16}$  in toluene/acetonitrile solution

showed that the metal oxide framework of the compound was retained during the early stages of sol-gel polymerization.

#### References

1. Brinker, C. J.; Scherer, G. W. *Sol-Gel Science*; Academic Press: San Diego, 1990.
2. Shibata, S.; Kitagawa, T.; Hanawa, F.; Horiguchi, M. *J. Non-Cryst. Solids* **1988**, *88*, 345.
3. Hirano, S.; Kato, K. *Adv. Ceram. Mater.* **1988**, *3*, 503.
4. Wang, S.-H.; Campbell, C.; Hench, L. L. *Ultrastructure Processing of Advanced Ceramics, Glasses, and Composites*; John Wiley & Sons: New York, 1988, p 145.
5. Fricke, J.; Caps, R. *Mater. Res. Soc. Symp. Proc.* **1986**, *88*, 345.
6. Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: New York, 1978.
7. Watenpaugh, K.; Caughlan, C. N. *J. Chem. Soc., Chem. Commun.* **1967**, 76.
8. Day, V. W.; Ebaspacher, T. A.; Klemperer, W. G.; Park, C. W.; Rosenberg, F. S. *J. Am. Chem. Soc.* **1991**, *113*, 8190.
9. Day, V. W.; Ebaspacher, T. A.; Klemperer, W. G.; Park, C. W., submitted for publication.