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Low-Temperature Precursors for Titanium Oxide

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LOW-TEMPERATURE PRECURSORS FOR TITANIUM OXIDE

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Abstract Pyruvic acid oxime (PAO) complexes of metals are promising precursors for metal oxide ceramics. The synthesis of $\text{TiO}(\text{PAO})_2$ and $\text{Ti}_2(\text{PAO-H})_3\text{O}_2(\text{H}_2\text{O})_3$ are reported. Their thermal decomposition allow the preparation of anatase (TiO_2) at temperatures below 300°C .

INTRODUCTION

The development of low temperature routes to ceramic materials is an area of intense interest due to the many technological ramifications. For example, such processes may allow the preparation of high-surface area catalysts (by avoiding sintering), coating of heat-sensitive substrates, or synthesis of novel metastable phases with useful properties. One promising approach for the preparation of ceramics at low temperature is the design of metal complexes whose ligands decompose to small, volatile fragments. An example of such precursors for ceramic oxides is metal complexes of pyruvic acid oxime (PAO). Metal complexes of the mono-anion of PAO decompose to acetonitrile, carbon dioxide, and, initially the metal hydroxide at temperatures that range from 103°C to 240°C (Figure 1). Applications of these precursors for the preparation of zirconia¹ and Synroc² have previously been reported. Herein, we report the synthesis and thermal behavior of PAO complexes of titanium including a complex which contains the PAO dianion.

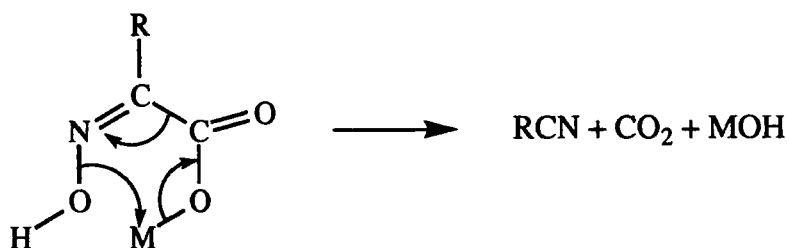


FIGURE 1 Proposed decomposition mechanism of PAO complexes.

RESULTS AND DISCUSSION

NaPAO is readily prepared from sodium pyruvate by treatment with hydroxylamine. The protonated form of pyruvic acid oxime (HPAO) can be obtained by reaction of NaPAO with dilute hydrochloric acid and recrystallization from ethanol. Most metal complexes of the PAO mono-anion may be precipitated from solution by treatment of the metal halide or nitrate salt with an appropriate amount NaPAO in aqueous media. However, aqueous reactions are not suitable for the synthesis of PAO complexes of

titanium due to hydrolysis of the aqua ion of Ti^{4+} . Surprisingly, reactions in non-aqueous media yielded different products depending on the titanium-containing reagent used. $\text{TiO}(\text{PAO})_2$ was obtained quantitatively from the reaction of TiCl_4 with four equivalents of HPAO in methylene chloride. A similar reaction of $\text{Ti}(\text{OEt})_4$ with four equivalents of HPAO produces yellow crystals of $\text{Ti}_2(\text{PAO-H})_3\text{O}_2(\text{H}_2\text{O})_3$ in moderate yield. In both cases, it appears that $\text{Ti}(\text{PAO})_4$ is unstable and immediately one or more ligands decomposed to afford acetonitrile, carbon dioxide, and water (or hydroxide). In fact, when $\text{TiO}(\text{PAO})_2$ is dissolved in dry dimethyl sulfoxide it slowly evolves acetonitrile and carbon dioxide. It is, however, indefinitely stable in the solid state.

The fact that two different products are obtained is likely due to the highly acidic conditions in the TiCl_4 reaction resulting from generation of HCl. The formation of the dianion of pyruvic acid oxime by deprotonation of the oxime is not unexpected since it has been demonstrated that the coordinated oxime is fairly acidic. Thus, treatment of $\text{Cu}(\text{PAO})_2$ with pyridine was reported to give the doubly-deprotonated ligand³.

Both titanium pyruvic acid oxime complexes have a pale yellow color and are highly soluble in water and DMSO. The ^1H and ^{13}C NMR spectra of the complexes in the latter solvent exhibit distinct resonances that are attributable to the monoanion and dianion of pyruvic acid oxime, respectively ;

$\text{Ti}_2(\text{PAO-H})_3\text{O}_2(\text{H}_2\text{O})_3$: $\delta(^1\text{H}, \text{ppm})$; 2.04 (3H, Me) and 3.32 (2H, H_2O) $\delta(^{13}\text{C}, \text{ppm})$; 11.4 (Me), 149.6 ($\text{C}=\text{NO}^-$), and 167.8 (CO_2)

$\text{TiO}(\text{PAO})_2$: $\delta(^1\text{H}, \text{ppm})$; 1.80 (3H, Me) and 10.45 (1H, NOH) $\delta(^{13}\text{C}, \text{ppm})$; 10.4 (Me), 149.6 ($\text{C}=\text{NOH}$), and 165.6 (CO_2)

Notably, the ^1H NMR spectrum of the dianionic complex contains no resonance attributable to the oxime proton.

The thermal behavior of the two complexes varies significantly as well. $\text{TiO}(\text{PAO})_2$ decomposes in a mildly exothermic fashion to TiO_2 , acetonitrile and carbon dioxide at 142°C . The TiO_2 obtained has the anatase structure and a crystallite size of 12 nm as demonstrated by X-ray powder diffraction. The weight loss is gradual and is complete at ca 300°C . The TiO_2 obtained has the anatase structure and a crystallite size of 12 nm as demonstrated by X-ray powder diffraction. On the other hand, the decomposition of $\text{Ti}_2(\text{PAO-H})_3\text{O}(\text{H}_2\text{O})_3$ has a very sharp onset at 170°C and is very exothermic. These differences may prove useful in materials applications since a low-temperature TiO_2 precursor with a gradual, controllable decomposition would be useful for formation of films by metalorganic deposition. Alternatively, violent outgassing of a precursor would be useful for forming fine powders or porous materials.

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