Comments

Comment on "Reaction Pathway to the Synthesis of Anatase via the Chemical Modification of Titanium Isopropoxide with Acetic Acid"

In their report on the synthesis of anatase by sol−gel processing, Parra et al.[1] discuss, inter alia, the reaction of $Ti(O^iPr)_4$ with acetic acid. The reported IR and NMR spectra are consistent with what has been reported by others on reactions of $Ti(OR)_4$ with carboxylic acids, especially the group of J. Livage and C. Sanchez (see Note Added after ASAP Publication at the end of the article). However, the authors interpret the data differently; that is, they propose initial formation of a complex $Ti(acetate)(O^iPr)_2$. Such a complex would be a Ti(III) compound, contrary to the starting compound, $Ti(O^iPr)_4$, and the product, TiO_2, both being Ti(IV) compounds. If this interpretation was correct, $Ti(O^iPr)_4$ would have been reduced by acetic acid, and the intermediates then reoxidized. This is chemically unreasonable, and there is no evidence at all for Ti(III) intermediates or such a complex redox chemistry.

In Figure 7 the authors suggest a different intermediate than in the text of the article, namely, $Ti(acetate)(O^iPr)_2(OH)(H_2O)$. Although this is a Ti(IV) compound, this is also very unlikely. First, in all structurally characterized titanium compounds, carboxylate ligands are bridging rather than chelating. Second, there is ample evidence that reaction of $Ti(OR)_4$ with carboxylic acids results in the rapid formation of polynuclear oxo derivatives, even when a 1:1 ratio is employed. In fact, the authors observe the formation of an ester in their IR and NMR spectra; ester formation provides the water necessary for the formation of the polynuclear compounds.

The chemistry of carboxylate-substituted titanium alkoxide derivatives has been extensively investigated by several groups and was summarized, inter alia, in two recent review articles.[2,3] The results reported in ref 1 do not require a reinterpretation of previous results.

Ulrich Schubert

Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9, A-1060 Wen, Austria

Received March 10, 2008

CM800692T

(1) Parra, R.; Góes, M. S.; Castro, M. S.; Longo, E.; Bueno, P. R.; Varela, J. A. *Chem. Mater.* **2008**, *20*, 143.

(2) Rozes, L.; Stenou, N.; Fornasiera, G.; Sanchez, C. *Monatsh. Chem.* **2006**, *137*, 501.

(3) Schubert, U. *J. Mater. Chem.* **2005**, *15*, 3701.

10.1021/cm800692t CCC: $40.75
Published on Web 04/23/2008