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

In a recent paper we studied the synthesis of anatase using titanium isopropoxide modified with acetic acid as precursor for TiO_2.[1] We wish to thank Prof. Schubert for his comments on our article in which he points out an error that was previously overlooked. The complex Ti(acetate)$(O^iPr)_2$, suggested to form after the reaction of $Ti(O^iPr)_4$ with acetic acid, is indeed incorrect. The reduction of Ti(IV) to Ti(III) would never occur under the experimental conditions reported in our article. On the other hand, the most probable species could be Ti(acetate)$(O^iPr)_3$[2] or $Ti(acetate)_2(O^iPr)_2$.[3] The second structure has been proposed by Birnie III and Bendzko who also concluded that the maximum level of acetate modification is two. In this latter structure, titanium would be octahedrally coordinated only if acetates acted as bidentate ligands, which would be in agreement with our FTIR analysis. Since the $\Delta\nu$ between the signals of the doublet (1542 and 1440 cm^{-1}) corresponding to the stretching vibration modes of the COO group was 102 cm^{-1}, we proposed a preferred bidentate configuration for acetates against unidentate or bridging configurations. According to the literature,[4,5] the occurrence of acetates as bridging ligands is associated with $\Delta\nu$ values greater than 150 cm^{-1}. The acetic acid-modified species mentioned above are supposed to be intermediates toward cluster formation in the presence of water either added or formed in situ due to esterification. Then, although they would rapidly turn into oxo derivatives, species such as Ti(acetate)$(O^iPr)_2(OH)(OH_2)$ may also exist in order for condensation to proceed toward cluster formation. It is clear that the presence of isopropyl acetate would indicate the formation of clusters. However, isopropyl acetate was not detected in the $Ti(O^iPr)_4$/acetic acid 1:1 molar ratio sample after 60 min of being prepared but in those with higher acid contents (1:2 to 1:4). Nevertheless, in our article we did not neglect the formation of oxo-clusters, which certainly takes place after some time. We intended to explain the very first stages of the reactions that ultimately lead to the anatase phase. Finally, we should have referenced the relevant works by Prof. Schubert[6] as well as those by the group of Prof. Sanchez[7,8] in our paper. We regret this omission.

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