

Influence of the synthesis conditions on the anatase-rutile phase transition of TiO₂

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Titania has been the subject of numerous studies because of its many useful optical, electrical and photocatalytic properties, which depend on the crystalline structure of TiO₂. Technological applications have been proposed for both the anatase and the rutile phase of TiO₂ nanoparticles. TiO₂ obtained by sol-gel process is usually amorphous and thermal treatments are necessary to obtain the final desired crystalline materials. The transformation temperature depends on many factors such as impurities present in anatase, oxygen-to-metal coordination in the precursor, oxygen-to-metal bond length in the precursor gel, and on the texture and size of the primary particles^[1,2]. Vioux reports that the crystallization behavior to rutile is most likely influenced by the initial ultrastructure of the amorphous solid^[3,4].

Colloidal TiO₂ particles obtained by addition of polymer or salt in the so-gel process^[5] show a different phase transition behavior, dependent on the synthesis conditions. The addition of polymer favors the phase transition to rutile more strongly than the addition of salt. In order to determine the initial structure of the amorphous as-synthesized TiO₂ particles and the influence on this structure of the phase transition X-ray absorption spectroscopic measurements were carried out. The spectra (Fig. 1) of titania compounds show different pre-edge peaks which are ascribed to the 1s-3d transition of the excited electron and contain information about the coordination of the Ti atom.^[6] Compounds with tetrahedrally coordinated Ti show strong absorption. Octahedral coordination results in less pronounced features, up to three peaks may be observed. With increasing distortion, the central peak gains intensity. The pre-edge peak of the titania beads obtained by addition of salt corresponds to very distorted octahedrally coordinated Ti. The pre-edge peak of titania particles obtained by addition of polymer corresponds to octahedrally

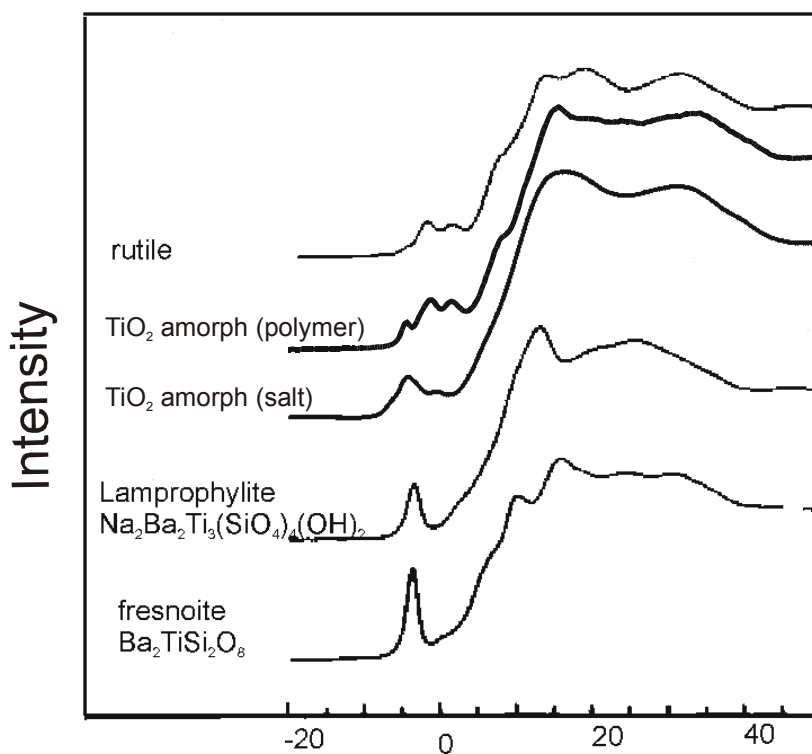


Fig. 1: Normalized Ti K-XANES spectra of the amorphous titania particles and three reference compounds, rutile, lamprophylite and fresnoite.

coordinated Ti. These results indicate that the polymer effects the amorphous structure.

Figure 2 shows that the amorphous structure of the particles obtained by addition of polymer is similar to the anatase structure obtained at 400 °C, so that probably the amorphous structure is a precursor for the phase transition. In contrast to that, the spectrum of the particles obtained by addition of salt and heated up to 400 °C show no feature of anatase although the X-ray diffraction pattern indicates the formation of anatase. Presumably, in the case of the addition of salt, a mixture of anatase and amorphous TiO₂ is obtained at 400°C.

The differences in the anatase-rutile transition phase behavior can be explained with the amorphous precursor phase. In the case of polymer, when the precursor phase is similar to anatase phase, the phase transition needs less energy than in the case of salt, where the amorphous precursor structure is much more different than the anatase structure. Therefore, the total amorphous-anatase phase transition with addition of salt requires higher temperatures than the transition with addition of polymer, so that the anatase-rutile phase transition is also inhibited.

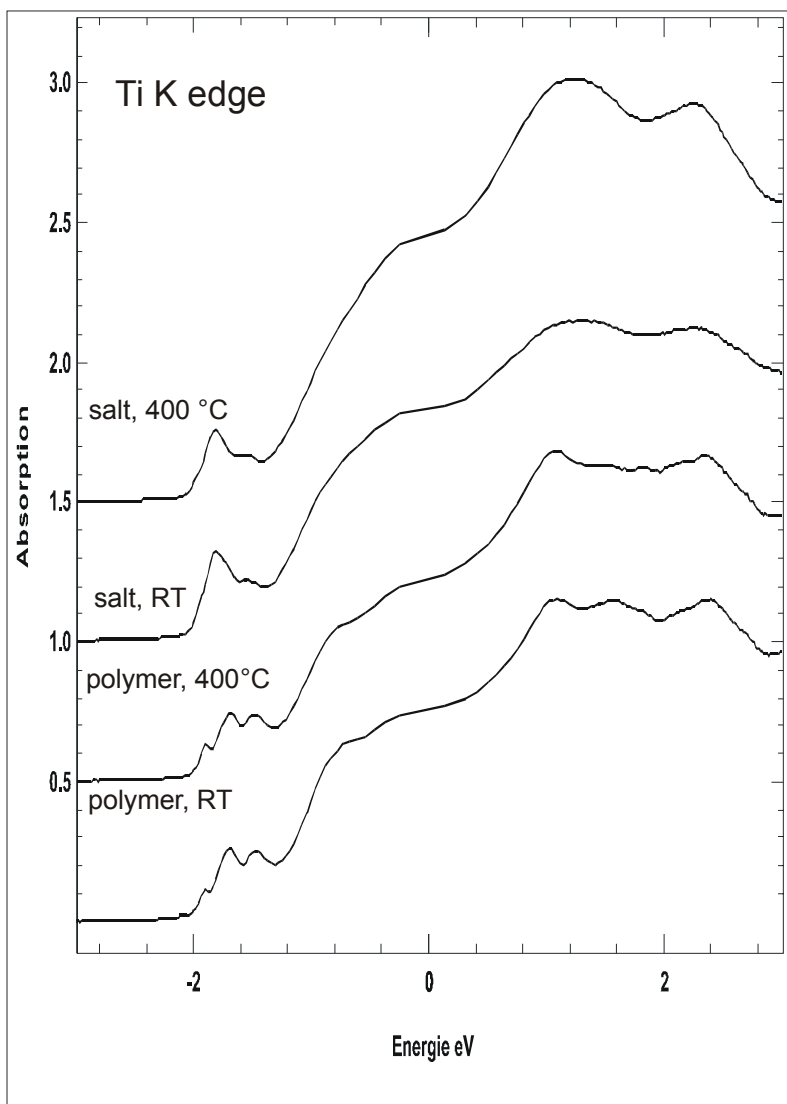


Fig. 2: Normalized Ti K-XANES spectra of the titania particles at different temperatures.

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