Combined *in situ* small and wide angle X-ray scattering studies of TiO_2 nano-particle annealing to 1023 K

Supplementary information

To validate the results obtained from the *in situ* set up, we acquired standard powder diffraction data in a Debye-Scherrer set up using a slit collimated beam from a RU-200 Rigaku rotating anode operated at 50 KV/200 mA, focused and monochromatized (Cu K_α) by a 1D multilayer optic (Xenocs). The detector scan was carried out with a NaI scintillation point detector (Bicron) mounted behind an evacuated flight tube with slit collimation. The sample was loaded in a 0.7 mm quartz capillary with 10μm wall thickness (Hilgenberg GmbH).

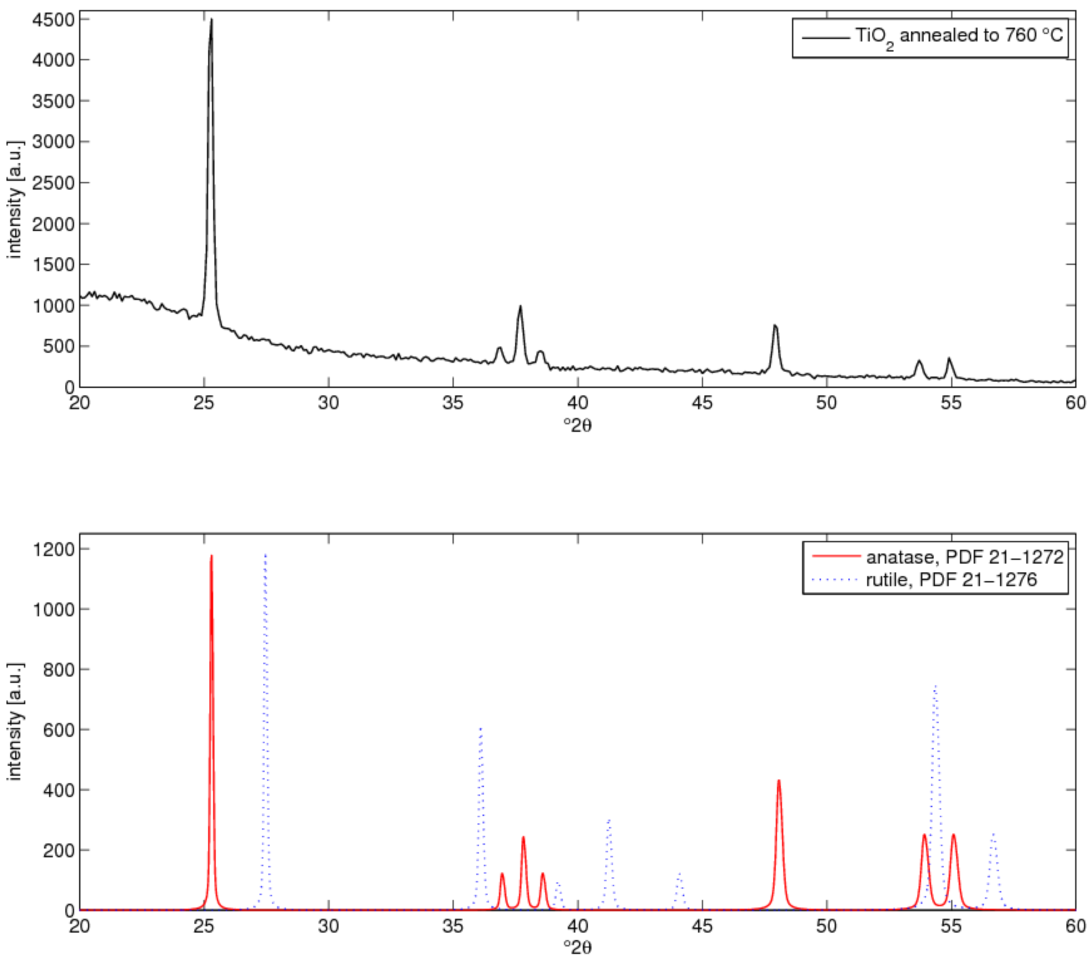

Figure 1 The top panel shows the measured XRD data of the TiO_2 powder annealed to 1023 K. The background scattering at the lowest angles is from the quartz capillary. The panel below shows the simulated patterns of Powder Diffraction File cards 21-1272 (anatase) and 21-1276 (rutile). The only crystalline phase in the powder is clearly anatase.

The standard TiO_2 material, P25 from Degussa (now Evonik), which is used for a large variety of applications, including research in photocatalysis, was measured in the *in situ* setup, loaded in the usual 0.7 mm quartz capillary, to validate the capability for phase distinction and refinement.

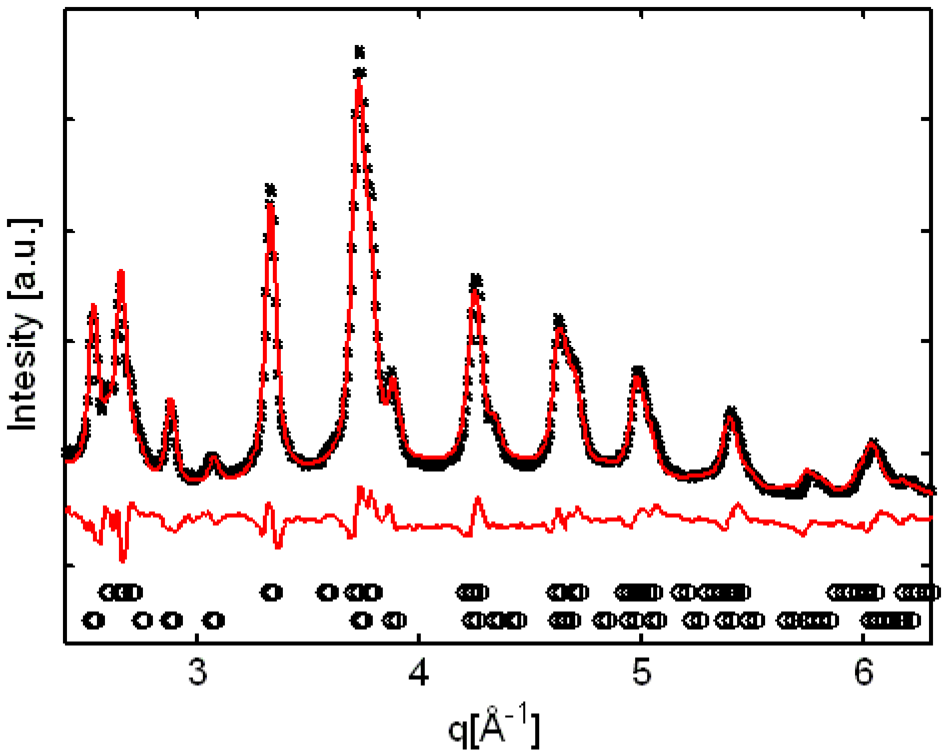

Figure 2 Rietveld refinement of P25 with theoretical peak positions (o) for anatase (top) and rutile (bottom).

The anatase/rutile fractions were determined by Rietveld refinement to 67.4 % ± 0.1 % anatase and 32.6 % ± 0.1 % rutile which is in reasonable agreement with values reported in the literature. Jensen *et al.* (2006) reported the P25 sample to consist of 71 % anatase, 27 % rutile and 2 % amorphous TiO_2 determined from data recorded on a standard powder diffractometer, Porter *et al.* reported the P25 powder consists of 78.8 % anatase[1] and 21.2 % rutile[1] and Bakardjeva *et al.* (2005) 84.7 % anatase[1] and 16.3 % rutile[1]. Ohtani *et al.* (2010) reported different compositions in the same P25 sample from 73 - 85 % anatase, 14 - 17 % rutile and 0 - 18 % amorphous TiO_2 and attributed this to variations in the production.

The crystallite sizes from the Rietveld refinement are for anatase 12.6 ± 0.1 nm and rutile 14.2 nm ± 0.6 nm. However, a wide variety of refined crystallite sizes is reported. Sigma & Aldrich reports on their website a size of ~ 21 nm (Aeroxide® P25), Bakardjeva *et al.* (2005) sizes of 20.8 nm for

[1]Calculated from reported weight fraction with ρ(anatase) = 3.7 g cm^{-3} and ρ(rutile) = 4.3 g cm^{-3}

anatase and 30.5 nm for rutile, Porter *et al.* (1999) reports 20.6 nm for anatase and 14.4 nm for rutile, *Jensen et al.* (2006) determined the crystallite size 19.4 nm and Raj *et al.* (2009) 48 nm for anatase and 51 nm for rutile.

The crystallite sizes we find are clearly in the lowest end of the range of sizes reported. But, considering the large spread in values for phase composition and crystallite sizes reported, it appears that the P25 material shows considerable inhomogeneity, both within and between production batches.

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