HRTEM and EELS Characterization of TiO_2 Nanoparticles in Ti-Doped Zeolite

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TiO_2 nanoparticles grown inside hydrothermally treated Ti-doped zeolite are investigated by high resolution transmission electron microscopy (HRTEM) and electron energy-loss spectroscopy (EELS). The starting material is a dealuminated zeolite with about 4% of Ti^{4+} incorporated into the framework with ZSM-5 structure (orthorhombic unit cell, a = 2.01 nm, b = 1.99 nm, c = 1.34 nm), consisting of single crystalline particles with sizes between 50 and 200 nm. The hydrothermal treatment leads to strong morphological changes: holes and large cavities are formed in the zeolite crystals and TiO_2 nanoparticles of a few nanometer size are produced inside the cavities [1].

The study is performed with a Philips CM200 FEG microscope equipped with a Gatan imaging filter GIF 100, working at 200 keV. The energy resolution for EELS measurements is about 1.2 eV. The spectra were processed via the Gatan EL/P programme.

Typical images of the zeolite material before and after hydrothermal treatment are shown in FIG 1. From a large number of well oriented TiO_2 nanoparticles HRTEM images are taken (FIG 2). Analysis of lattice spacings and angles between lattice planes via calculation of the corresponding power spectra always shows good agreement with the anatase phase of TiO_2.
The TiO_2 phase of particles can also be identified by EELS, even for particles which do not show lattice fringes in HRTEM because of their unfavourable orientation. The Ti $L_{2,3}$ - as well as the O K-edges of the TiO_2 polymorphs rutile, anatase and brookite show clearly recognizable differences in their near-edge structure (ELNES) allowing for distinguishing the different phases [2]. The differences in the Ti $L_{3,2}$-ELNES require a sub 1 eV energy resolution but the O K-ELNES differences are accessible with our energy resolution. EEL spectra for a typical TiO_2 crystal are shown in FIG 3. In order to separate the O K-edge of the TiO_2 particles from the dominating O K-contribution of the zeolite oxygen, Ti $L_{2,3}$/O K-spectra are measured from areas containing a nanoparticle and neighboured areas from the same zeolite crystal (FIG 1c). Subtraction of a suitably scaled spectrum of the pure zeolite gives a difference spectrum corresponding to the Ti $L_{2,3}$/O K-edge of the TiO_2 particle. Comparison of the O K-ELNES with reference spectra from well-characterized anatase-TiO_2 taken under the same experimental conditions in each case shows good agreement.

Analysis of HRTEM images and EELS measurements of the O K-ELNES revealed only nanoparticles of the anatase phase of TiO_2. No other TiO_2 polymorphs could be detected in the sample.

References:
[1] M. Klimenkov et al, Proc. 12th European Congr. on Electron Microscopy (2000),vol.2, p.399
[2] W. Engel and H. Sauer, Proc. 12th Int.Congr. on Electron Microscopy (1990),vol.2,p 70
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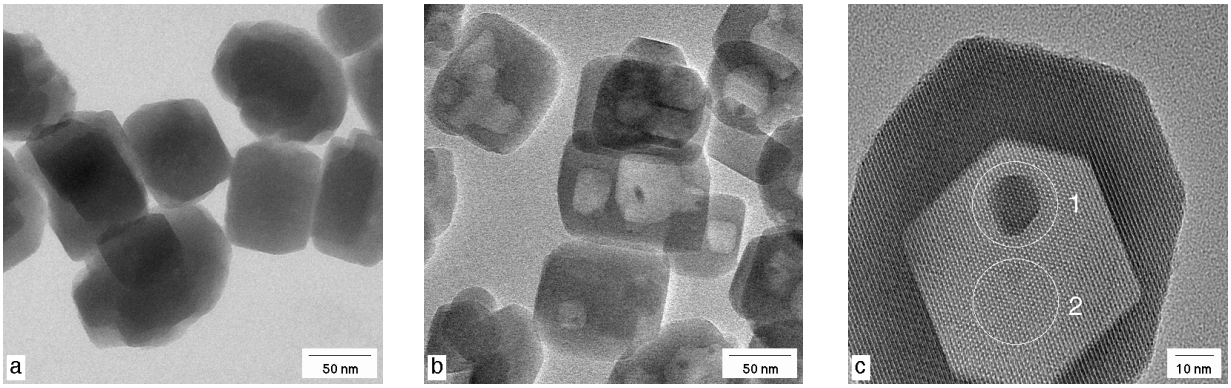

FIG 1: Ti-doped zeolite a) before and b), c) after hydrothermal treatment. c) shows a single crystalline Ti-doped zeolite particle with a large cavity and a precipitated TiO_2 nanoparticle. The circles indicate the different areas for EEL spectrum acquisition.

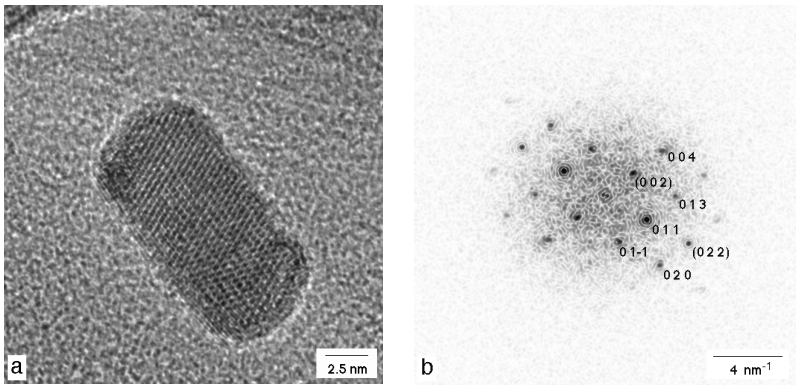

FIG 2: a) HRTEM image and b) power spectrum of an anatase - TiO_2 nanoparticle in [100] orientation

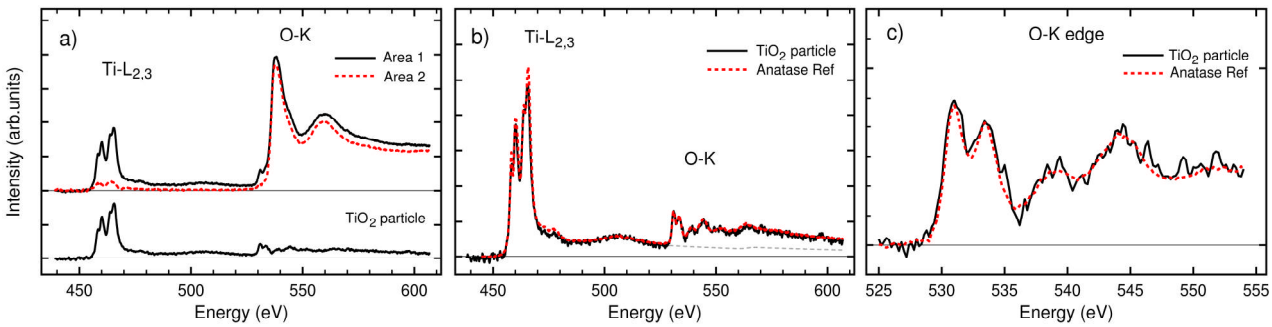

FIG 3: a) Ti $L_{2,3}$/O K-spectra from area 1 and 2 (→ FIG 1c) and the difference spectrum, corresponding to the TiO_2 particle. b) Ti $L_{2,3}$/O K-spectrum of the TiO_2 particle and a reference spectrum of anatase-TiO_2. c) O K-spectra of the TiO_2 particle and anatase-TiO_2.