

**P11.02.77***Acta Cryst.* (2008). A64, C531**Electron density distribution in anatase (TiO<sub>2</sub>) under UV-irradiation: Observation and calculation**

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Anatase-phase TiO<sub>2</sub> is widely recognized as an effective photocatalyst. This photocatalytic activity is ascribed to an excited electron and a hole under UV light. Asahi *et al.* (2000) has reported molecular-orbital bonding structure for anatase using first-principles calculations. Their calculation indicated that the excited electrons occupy Ti 3d t<sub>2g</sub> d<sub>xy</sub> non-bonding orbital, while this has not been confirmed experimentally. Natural single crystal of anatase (Tisey, Norway) was spherically ground in 200 μm in diameter and used for the experiments. A Rigaku AFC-5S four-circle diffractometer with monochromatized MoKα radiation was used for data collections. Three sets of diffraction intensities were collected; set 1 was collected under no light, set 2 under UV (λ = 253.6 nm: 4.9 eV) plus fluorescent light, and set 3, again, under no light. Structural parameters (with harmonic ADP) were preliminarily refined to attain most reliable scale and extinction factors for Fourier summation. Some of ADPs, particularly U<sub>11</sub> at O site showed small but notable increase with UV irradiation. There was no notable difference among electron densities ρ<sub>set1</sub> and ρ<sub>set3</sub>. On the other hand, characteristic differences were found on ρ<sub>set2</sub> - ρ<sub>set3</sub> (ρ<sub>2-3</sub>) in the vicinity of both the Ti and O site positions. Positive densities beside the O site correspond to increase in harmonic ADP by heat with relaxation. On the other hand, appearance of positive density around the Ti site positions could not be explained by change only in harmonic ADP: electron cloud of Ti was deformed in <110>. Maximum in ρ<sub>2-3</sub> (0.24eÅ<sup>-3</sup>) was found at 0.28 Å from the Ti position in <110>. These positions correspond to those of the maxima of wavefunction of Ti 3d t<sub>2g</sub> d<sub>xy</sub> orbital calculated by a DV-Xα method.

Keywords: anatase, UV irradiation, excited electron

**P11.02.78***Acta Cryst.* (2008). A64, C531**Structure determination of metallic nanoparticle catalysts by atomic scale *in-situ* environmental TEM**

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Catalyst chemical vapor deposition (CVD) is now known as the best method for large scale production of carbon nanotubes (CNTs). Metal nanoparticles absorb carbon from a source gas such as acetylene and expel CNTs. Since electronic properties of CNTs can be varied from metal to semiconductor by their atomic structures, there have been a number of theoretical and experimental studies on the role played by nanoparticle catalysts (NPCs). However, actual nucleation and growth process of CNTs from NPCs has never been observed at atomic scale. We show atomic-scale *in-situ* environmental transmission electron microscopy observation of the nucleation of CNTs followed by continuous growth in metal catalyzed CVD with the spatial resolution better 0.2nm. Surprisingly, CNTs grow from solid state NPCs of complex structures. Based on this finding, we succeed in solving long-standing problems on the CVD growth of CNTs.

Keywords: carbon nanotubes, catalyst structure, environmental transmission electron microscopy

**P11.05.79***Acta Cryst.* (2008). A64, C531**Nanocrystalline structure of an active phase in V-Mo-Nb-O catalysts for ethane (amm)oxidation**Tatyana U. Kardash, Ludmila M. Plyasova, Valentina M. Bondareva, Svetlana V. Cherepanova, Dmitry I. Kochubey  
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Development of catalysts based on nanomaterials and characterization of their structure has become the great deal of scientific attention in material science in the last time. The present study is devoted to the investigation of structural features of an active phase in V-Mo-Nb-O catalysts for selective transformations of ethane to ethylene, acetic acid and acetonitrile [1-2]. The catalysts were synthesized by mixing aqueous solutions of ammonium paramolybdate, ammonium metavanadate and niobium oxalate with further drying and calcination in air at 400 °C. Samples were analyzed by XRD, HREM and EXAFS. The active component of these catalysts is a triple compound with Me<sub>5</sub>O<sub>14</sub>-like structure (Me=Mo, V, Nb) and variable composition [1-2]. The active catalyst is XRD amorphous and characterized by the presence of both narrow reflections at d = 4.00, 2.00 Å, and broad reflection at d = 3.40 Å. HREM investigation reveal 1D-ordered nanostructure with block size <5 nm and interlayer distance of 0.40 nm. In perpendicular plane, networks are built by disordered Me<sub>5</sub>O<sub>14</sub>-like subunits, which consist of MeO<sub>7</sub>-bipiramides connected by edge with five octahedra [3]. Model of active nanocrystalline phase was proposed according to HREM data, XRD pattern modeling by DFA method and local structure investigation by EXAFS. Authors acknowledge the financial support of RFBR (project 07-03-00203)

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Keywords: V-Mo-Nb-O catalysts, nanostructure, Mo<sub>5</sub>O<sub>14</sub>**P11.13.80***Acta Cryst.* (2008). A64, C531-532**Structure and ionic conduction in inorganic materials through nuclear/electron density analysis**

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The development of improved electrolyte and electrode materials requires a better understanding of the mechanism of ionic conduction, and crucial to this is a comprehension of the crystal structure at high temperatures. Our group has developed new high-temperature neutron and high-resolution synchrotron diffraction techniques to study the precise crystal structures, nuclear and electron density in inorganic materials up to 1900 K [JAmCeramSoc85(2002)2925,89(2006)1395, JApplCryst37(2004)786, 38(2005)854]. Here we review our recent works on the positional disorder and diffusion path of mobile ions in Bi<sub>2</sub>O<sub>3</sub> [CPL378(2003)395],