Nanocomposites and nanomaterials

The effect of SO_4^{2-} anions on the ultrafine titania nucleation

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Phenomenological model of SO_4^{2-} anions effect on the titania nucleation during titanium tetrachloride hydrolysis was proposed and experimentally tested. For titania synthesis HCl was added to $TiCl_4$ at 0^oC. Sodium hydrocarbonate aqueous solution was added dropwise to $TiOCl_2$ sol up to pH =5.0-5.5 and gel formation. Precipitated TiO_2 was dried at 150 ^oC, obtained xerogels was marked as S1. The S2 material synthesis process was carried out in analogous way was but on the initial stage crystalline Na_2SO_4 was added directly to $TiCl_4$. The material S1 is a mixture of anatase and rutile while the material S2 was close to ultrafine anatase (XRD data). Direct measurements of interplanar distances for S2 sample vary in a range 0.34-0.37 nm which corresponds to (101) plane of anatase (HR TEM data). The specific surface area of S1 and S2 samples are 152 and 328 $m^2 g^{-1}$ (nitrogen absorption data). The presence of chemisorbed OH-groups and molecularly adsorbed water on the particles surface was detected for both samples. (FTIR data). The additional bands on the S2 sample pattern at 1139 and 1060 cm^{-1} correspond to chemisorbed SO_4^{2-} ions (Fig.1). We suggest the next model of Na_2SO_4 impact on titania nucleation on the stage of olation interaction between primary hydrocomplexes based on [1]. Olation interaction between $[Ti(OH)_h(OH_2)_{6-h}]^{(4-h)+}$ monomers leads to the polymer chains formation where monomers are linked by joint edges in octahedrons equatorial planes thus defining the precondition for rutile phase nucleation. The presence of SO_4^{2-} groups in the reaction medium will cause chelating bidentate complexes formation in the octahedrons equatorial planes. As a result the olation between monomers with a common edge outside the octahedron equatorial plane is prevailing. In these conditions polycondensation the zigzag-like or spiral chain of polyhedrons are formed and the conditions for the anatase nucleation are performed.

1. *Kotsyubynsky V.O., Myronyuk I.F., Myronyuk L.I., Chelyadyn V.L., Mizilevska M.H., Hrubiak A.B., Tadeush O.K., Nizamutdinov F.M.* The effect of pH on the nucleation of titania by hydrolysis of $TiCl_4$ // Materialwissenschaft und werkstofftechnik.-2016.-**47**, N 2-3.- P. 288–294.