

Nanochemistry and Nanobiotechnology

Chemical aspects of liquid-phase synthesis of titania nanocrystalline modifications

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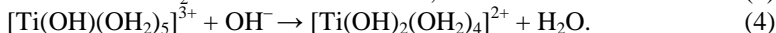
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Crystal modification of powder titania (anatase, rutile, brucite) of nanometer-scale particles have unique properties that are related to their catalytic and photocatalytic activity. A large number of publications and patents relating to new methods for TiO₂ producing based on sol-gel technology.

Recently titanilchloride precursor was used for synthesis of oxide materials. It is obtained by mixing TiCl₄ with water at a temperature close to 0°C. A substance obtained in this way conventionally denoted by the formula TiOCl₂. It does not correspond to real chemical composition of precursor because it does not take into account hydroxility of titanium atoms and the formation it aqua complex cations.

We found out that Ti⁴⁺ cations in the reaction medium formed [Ti(OH₂)₆]³⁺·3Cl⁻ complex compound with water molecules and Cl⁻ anions. The general reaction of titanium aqua complex formation can be written as an equation: TiCl₄ + 6H₂O → [Ti(OH₂)₆]³⁺·3Cl⁻ + ½ Cl₂ (1). However, chemical equilibrium in a solution at temperatures over 40°C is disturbed as a result of the reaction: Ti³⁺ + H₂O → Ti(IV)OH + ½ H₂ (2).

The resulting [Ti(OH)(OH₂)₅]³⁺ cations subsequently change their chemical state, increasing the hydroxility degree of titanium atoms. This process is realized with the participation of water molecules contained in the core of the complex cations and Cl⁻ anions: Cl⁻:



Thermally stimulated process of water dissociation (reaction 3) and increase in the hydroxility degree atoms of titanium precursor (reaction 4) leads to the formation of Ti(OH)₄·2H₂O molecules, which provide the formation of TiO₂ nanoparticles at condensation.

The rod-like rutile particles with diameter of 1 ÷ 3 nm and a length of 10 ÷ 40 nm are formed at a temperature of 40-80°C in the acidic reaction medium (pH = 0,5 ÷ 2,0). For correction of chemical and charge state of precursor K₃PO₄ or Na₂SO₄ was added to its solution. Number of modifying additives in relation to [Ti(OH₂)₆]³⁺ was 5 wt. %. The presence of PO₄³⁻, SO₄²⁻ anions in the reaction medium dramatically changes the crystallization process and provides a formation of ellipsoidal anatase particle with size of 3 ÷ 5 × 4 ÷ 6 nm.