

SURFACE MODIFICATION EFFECT BY Fe IONS ON PHYSICO-CHEMICAL PROPERTIES OF ANATASE AND RUTILE

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Titanium dioxide (TiO₂) in the form of polydisperse rutile or anatase has been considered as one of the best material for photocatalysis, sensors and related technologies. However, the application of pure TiO₂ has inherent limitation due to the band gap in the near-UV spectrum at 3.2 eV for anatase and 3.0 eV for rutile rendering it inactive under visible light. Generally, for shifting the light absorption edge of TiO₂ into the visible range; to improve its photoactivity and facilitate the use of sunlight as an inexpensive, renewable energy source the doping is used. Selective doping of TiO₂ with transition metals ions increases the formation of Ti³⁺ ions, as more Ti³⁺ states may cause more oxygen defects, which contribute the efficient adsorption of oxygen on the titania surface.

The aim of this work is study of the effect of Fe (III) ions on structural, optical and photocatalytic properties of anatase and rutile TiO₂. The polydispersed nanocrystalline pure TiO₂ and surface-modified TiO₂ by Fe³⁺ ions were obtained. The anatase and rutile surfaces were modified by Fe (III) ions by means of the adsorption from diluted solutions of FeCl₃ salts. Pure and Fe-doped TiO₂ samples were characterized using X-ray diffraction (XRD), X-ray fluorescence (XRF), SEM-EDS and TPD analysis, FT-Raman spectroscopy.

The obtained samples have a well crystallized pure-phase structure. The particles of anatase and rutile were aggregates of nanocrystallites. It was established that the adsorption of Fe ions is subject to the Langmuir model for rutile and to Freundlich for anatase. The anatase samples showed the higher sorption capacity than rutile. The atomic percentage of the elements Ti:O:Fe for pure TiO₂ and TiO₂/Fe samples, obtained by EDS technique were 1:2:0 for pure rutile and anatase, 1:2,1:0,07 – anatase/Fe and 1:2,1:0,04 – rutile/Fe. In the process of iron adsorption, we observed a decrease in the pH of solutions, i.e. their acidification, for all studied samples. This acidification of FeCl₃ solutions is explained by the replacement of protons of surface OH groups (≡Ti-OH) by adsorbed iron cations and formation on the sorbent surface of compounds of the type (Fe^{m+}O²⁻Tiⁿ⁺).

According to the data of temperature-programmed desorption of ammonia (TPDA) the Fe-doped anatase possesses significantly higher concentration of acid sites compared to other investigated samples. Medium strength and weak acid sites revealed by TPDA can be ascribed to Lewis acid sites, whereas strong acid sites inherent to anatase-based sample obviously correspond to Brønsted acid sites found using FTIR-spectroscopy.

The effect of Fe ion adsorption on the stoichiometry of synthesized TiO₂ samples was investigated using the method of FT-Raman scattering.

Photocatalytic activity of the samples was evaluated for dye Safranin T destruction. The adsorption-desorption equilibrium for SF-photocatalyst system was achieved within 120 min for all samples. The irradiation of the dye aqueous solution without a photocatalyst showed that 29 % (after 3 h) of SF dye molecules undergo photolysis processes under UV light. Photocatalytic degradation of Safranin T increase twice in the present of photocatalysts.