

Effect of heat treatment on surface acid sites of iron-doped titanium dioxide



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Introduction

Doped titanium dioxide is widely used in photocatalysis because doping causes the change of physico-chemical properties of TiO₂ increasing its photocatalytic activity [1, 2]. The aim of this work was investigate the effect of heat treatment on the surface of titanium oxide modified by iron ions.

Methods

X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), Brunauer-Emmett-Teller (BET) surface area analysis, temperature programmed desorption (TPD) techniques.

Results

The polydisperse nanocrystalline pure samples of anatase (A) and rutile (R) were modified via adsorption of Fe³⁺ ions (A/Fe, R/Fe) from FeCl₃ aqueous solutions with subsequent drying at 150 °C, washing with bi-distilled water and calcination at 300, 600 and 900 °C in air.

From EPR spectra, the signals with a hyperfine structure for TiO₂/Fe (anatase and rutile) samples calcined at 300 °C, 600 °C and 900 °C were observed. Such spectrum indicates surface bound single Fe ions on rutile or anatase TiO₂. EPR spectra of anatase A/Fe-300 °C, A/Fe-600 °C and rutile R/Fe-900 °C show only one paramagnetic intense signal at g = 1.995 and g = 1.998, respectively (Fig. 1). This indicates the presence of oxygen vacancies as a dominant defect in the samples. For A/Fe-900, EPR resonance transitions at g = 8.09, 5.57, 3.47 and 2.65 are observed. Transition at g = 4.22 (4.23) can be ascribed to the Fe (III) ions in orthorhombic sites at the surface of rutile R/Fe-300. The broad peaks detected at g = 2.005 are ascribed to photogenerated holes trapped by lattice oxygen and rich concentration of hole centers such as Ti vacancies in the system.

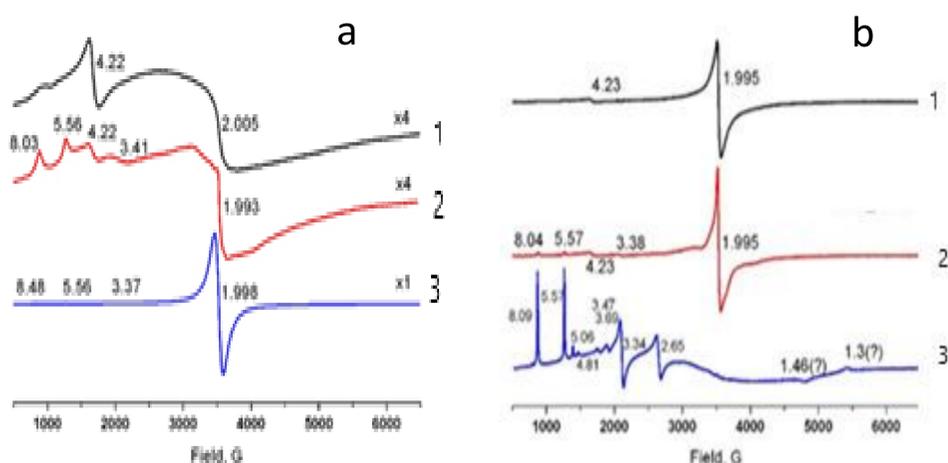


Fig 1. EPR spectra of Fe/TiO₂ rutile (a) and anatase (b) samples calcined at different temperatures (1- 300, 2- 600, 3- 900 °C).

Conclusion

- The effect of Fe (III) ions on the structural, optical and photocatalytic properties of polydisperse anatase and rutile TiO₂ has been investigated.
- TiO₂ surface was modified by Fe (III) ions through the adsorption from the diluted FeCl₃ solutions. The adsorption isotherms of Fe (III) ions from FeCl₃ solutions were investigated. It has been found that adsorption of Fe³⁺ ions on the anatase surface is more than twice effective than on the rutile.
- The influence of various energetically nonequivalent active centers on the surfaces of anatase and rutile on their photoactivity in the reaction of Safranin T destruction is considered. The anatase Fe-doped TiO₂ possesses significantly higher concentration of acid sites compared to Fe-doped rutile. An increase in the calcination temperature from 300 to 900 °C leads to a significant decrease of the concentration of weak acid sites for Fe-doped TiO₂.

According to the data of temperature-programmed desorption of ammonia (TPDA) and pyridine ad(des)orption with IR-spectral control it can be concluded that anatase surface contains active both Lewis and Brønsted acid sites (LAS and BAS) while rutile samples have only LAS regardless of the thermal treatment [3]. The revealed acid sites can be related to weak (the maximum of ammonia desorption < 300 °C) and strong (T_{max} of desorption > 400 °C) ones. The anatase Fe-doped TiO₂ possesses significantly higher concentration of acid sites compared to Fe-doped rutile (Fig. 2, a). An increase in the calcination temperature from 300 to 900 °C leads to a significant decrease of the concentration of weak acid sites for Fe-doped anatase samples (Fig. 2, b).

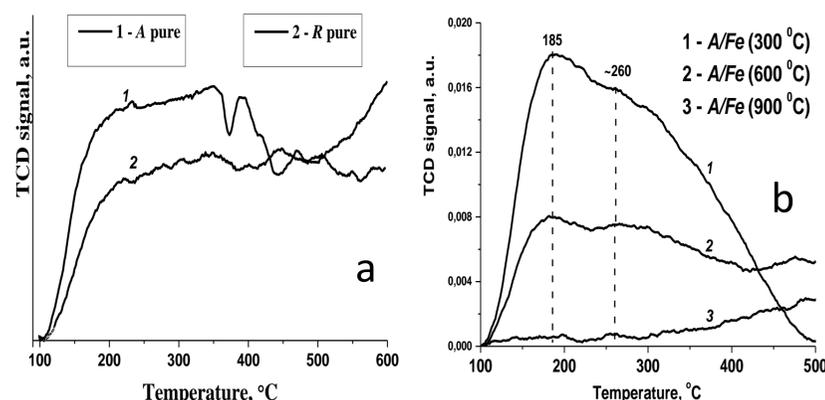


Fig 2. NH₃-TPD profiles for the prepared samples: a: 1 – pure R, 2 – pure A, b: 1 – A/Fe (300 °C), 2 – A/Fe (600 °C), 3 – A/Fe (900 °C).

References

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