# On the Mechanism of Oxalic Acid Oxidation on Iron-doped $TiO_2$ Photocatalysts

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One of the principal problems for practical application of $TiO_2$ materials in photocatalysis and photoelectrochemistry still is the enlarging of its light-absorption area to the visible light wavelengths with the use of surface and volume doping by metal ions [1, 2]. Usually, such doping resulted in the decrease of functional activity of bare $TiO_2$, although the absorption area of doped $TiO_2$ increased noticeably.

Iron-doped $TiO_2$ nanoparticles were prepared using flame spray pyrolysis method, and performed rather high activity in photocatalytic mineralisation of oxalic acid under visible light illumination [3]. Features of Fe-$TiO_2$ photocatalysts (with variation of iron in the range of $0.005 < Fe/Ti < 0.3$) were investigated with CW X-band EPR, XRD and FTIR spectroscopy. Phase composition of the samples is shown in Fig. 1. Several different types of Fe(III) centers were distinguished: isolated paramagnetic centers exist in the samples with $0.005\% < Fe/Ti < 0.05$, which were attributed to high-spin Fe(III) ions ($S = 5/2$) in rhombic ligand fields state [4]. At $Fe/Ti \geq 10$, EPR spectra transformed to a broad single line, typical for Fe(III) ferromagnetic clusters (Fig.2).

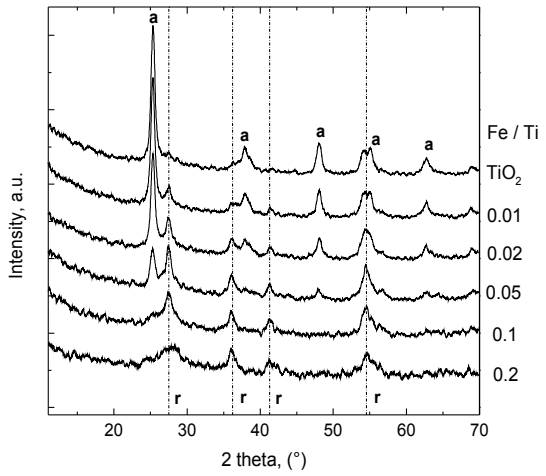
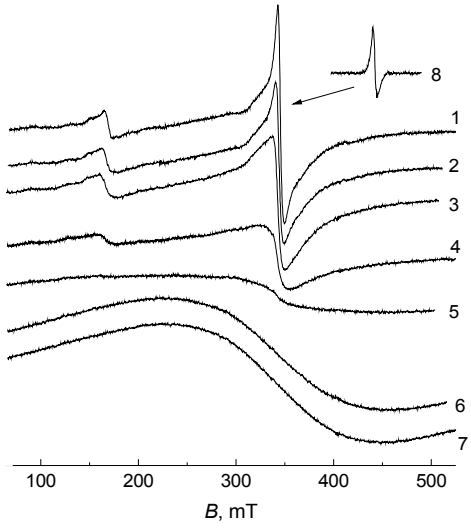



Fig. 1. XRD patterns of bare and Fe-doped $TiO_2$ at different Fe content. The anatase and rutile peaks are marked as (**a**) and (**r**, – – –) respectively.




ESR spectra of Fe-doped $TiO_2$ photocatalysts at different Fe content: *1* – 0.5, *2* – 1.0, *3* – 2.0, *4* – 5.0, *5* – 10.0, *6* – 20.0, *7* – 30.0 at% Fe/$TiO_2$. *8* – obtained by subtraction of *2* from *1*.

Kinetic curves of oxalic acid ($1 \cdot 10^{-4}$ M) decomposition at 25°C and $\lambda > 400$ nm on the bare and Fe-doped $TiO_2$ photocatalysts are given in Fig. 3. Interesting correlations (Fig. 4) were observed in comparison of EPR results with photocatalytic activity and the specific surface area [*S*] data, which allowed us to assume that particularly the isolated Fe(III) centers are responsible for photomineralisation of oxalic acid, while the Fe(III) ferromagnetic aggregates ("clusters") decrease the total efficiency of the system.

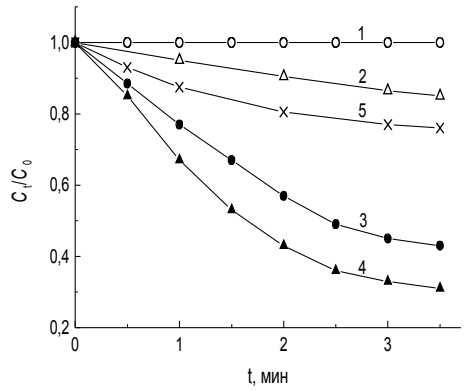



Fig. 3. Decomposition of oxalic acid ($1 \cdot 10^{-4}$ M) at 25°C and $\lambda > 400$ nm at different photocatalysts: *1* – bare $TiO_2$, *2* – Degussa P25, Fe-$TiO_2$ with [Fe]/[Ti] = 0.02 (*3*), 0.05 (*4*), 0.2 (*5*). $C_0$ and $C_t$ are carbon content in the solution at times 0 and t, correspondingly.

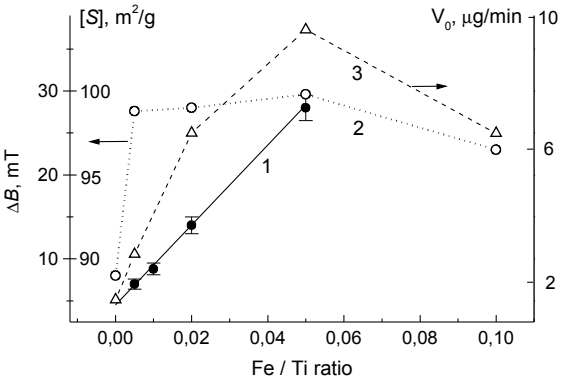



Fig. 4. The line width $\Delta B_{pp}$ (*1*) of paramagnetic $Fe^{3+}$ centers in Fe-doped $TiO_2$, specific surface area [*S*] of the powders (*2*), and initial rates of photocatalytic mineralization of oxalic acid $V_0$ (*3*) *vs*. iron content.

In the paper, we'll report our experimental results on visible light photocatalysis on Fe-doped $TiO_2$ in comparison with the rest published data. The nature of defects and their dynamics under illumination will be also discussed.

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**References:**

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