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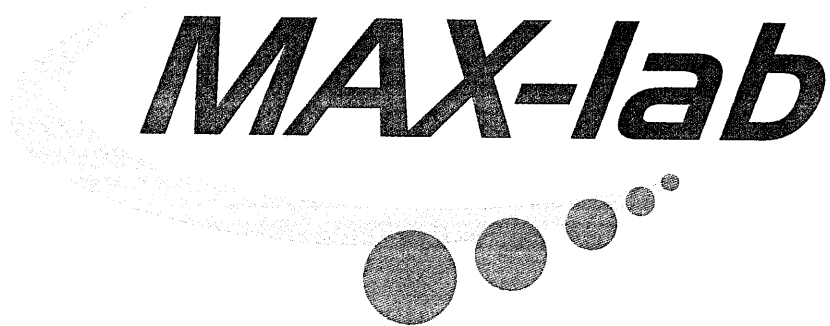
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The local structure of Fe(III) in doped TiO₂ photocatalysts studied with X-Ray absorption spectroscopy

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Since the discovery of photocatalytic water splitting with sunlight[1], the study of titania (TiO₂) based semiconductor photocatalysts is one of the most active areas of materials science, both on fundamental and on applied levels[2-4]. A common way of photosensitizing TiO₂ photocatalyst is doping with metals (*e.g.,* transition metals like Fe(III), V(V), Cr(III), Cu(II), Mn(II), Co(II), *etc.*) or nonmetals (*e.g.,* I in various oxidation states, P(V), N(III), S(VI), *etc.*). Photocatalytic activity of transition metal doped TiO₂ catalysts usually passes through a maximum with increasing dopant concentration, but excessive amount of dopant usually causes a decrease in the photocatalytic activity. In other cases, metal doping was reported to cause detrimental effects on the photocatalytic activity even at the smallest dopant levels. The dopant atoms can be present in various forms: in some cases in separated "islands", either in crystalline or in amorphous forms or dispersed in the atomic level and substitute Ti(IV), either on the surface layer or in the bulk of the semiconductor. The actual form is likely to be related to the photoactivity and associated with the variations of the local structure of the dopant.

Recently, a kind of flame-hydrolytic technique has been established in our laboratories for the preparation TiO₂ photocatalysts with tailor made crystallinity, anatase-to-rutil ratio and surface properties.[5] It is based on the introduction of the vapor of an appropriately chosen volatile Ti(IV) compound into H₂/O₂ flame. The synthesis has been optimized in terms of mechanical settings and we managed to prepare *undoped* TiO₂ catalysts that are almost twice as active in photocatalytic degradation phenol and methanol, as Degussa P-25, which is usually considered to be the most efficient commercial photocatalyst.[5] Fe-doped TiO₂ samples were also prepared by flame-hydrolytic technique[5] (F-series hereafter). We found that doping with iron has a detrimental effect on the photoactivity of flame-synthesized samples. Oxidative hydrolysis of TiCl₃[6] was also utilized for preparing undoped or Fe-doped nanocrystalline TiO₂ (S-series hereafter). Doping enhanced the photoactivity of the samples within the S-series and it was found to pass through a maximum with increasing Fe-content.

First, the bulk properties of the products were characterized by standard analytical techniques which are conventionally used in photocatalysis (*i.e.,* powder X-ray diffraction, various microscopic techniques, UV-Vis diffuse reflectance spectroscopy, N₂ adsorption isotherms). From these measurements no difference was found in the bulk properties of the members of the F- and S-series: their anatase-to-rutile ratio, particle size, band-gap energy, specific surface area and particle morphologies were practically identical. From this we assumed, that the difference in the photoactivity stems from the differences in the chemical state of the doping metal. Therefore we embarked on measurements (including XAFS) to

elucidate the local structure of iron in these samples, X-Ray Absorption Spectra were taken at the beamline I811,MAX II, MaxLab, Lund. The measurements were taken in fluorescence mode, on the iron K-edge.

The pre-edge spectra of the samples in both series show a small octahedral distortion around the iron. The XANES spectra show a significant variation with the increasing iron content in the S series. The main peak at *ca.* 7130 eV gradually sharpens and a shoulder appears at *ca.* 7140 eV, and another shoulder disappear at *ca.* 7200 eV with the increasing iron content. The shoulder at 7140 eV belongs to a forbidden transition in symmetrical geometries, so we can say that the distortion increases with the increasing iron-content. Within the L series, no such variation is seen, therefore there is no change in the distortion.
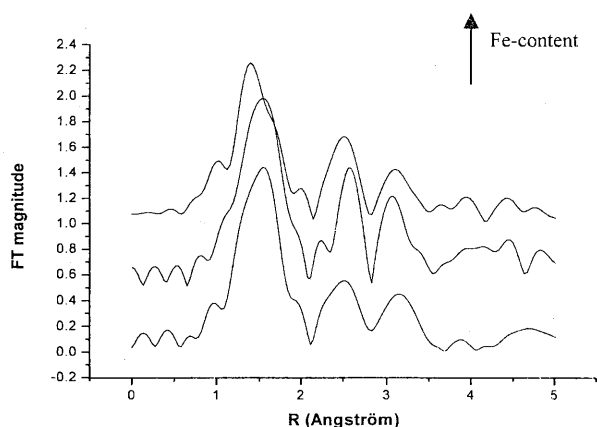

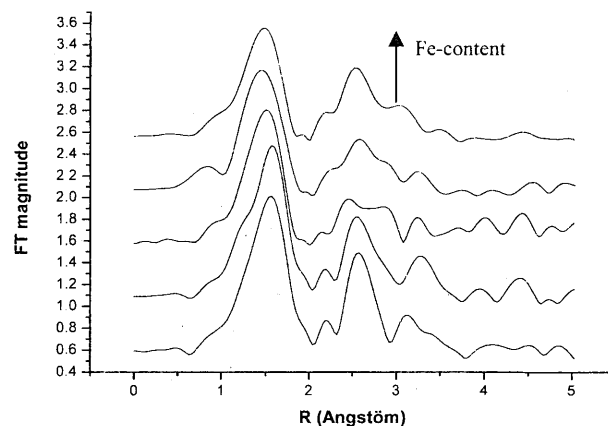**Figure1.** Pseudo-radial distribution function of the S series

Figure 2. Pseudo-radial distribution functions of the L series

The evaluation of the EXAFS data was made by the EXAFSPAK programme. During the analysis spline Victoreen constants were used and the Fourier-transformation was taken between 2.5-14 Å^{-1} without phase correction. Figures 1 and 2 show the pseudo-radial distribution functions for the two series. The second and the third coordination shells are qualitatively different in the two series. Moreover, in the S series the second coordination shell systematically changes with the Fe-content. This can explain why the photocatalytic activity go through a maximum with the increasing iron-content. After modelling the structures we can say that the local structure of the L series is much more regular, than the structure of the S one. In the S series there is a remarkable difference between the structure of the highly concentrated samples and the low concentrated ones. Mössbauer and X-ray photoelectron spectroscopic measurements further confirm the differences existing between the microenvironment of iron within the L- and S-series, corroborating the results from the XAFS measurements.

Based on these results, a clear relationship exists between the local structure of the Fe(III) and the photocatalytic activity of TiO_2 photocatlysts. These results make it possible to optimize the preparative ways of photocatalysts that are able to efficiently utilize the visible region of the solar light for heterogeneous photocatalysis.

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