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Characterization of nanocrystalline TiO_2 powders for heterogenous photocatalytic degradation: surface charge and high surface area

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Abstract – Commercial nanocrystalline TiO_2 (FINNTi -S140) was structurally characterized and used for photodegradation of two differently charged dyes, namely methylene blue and methyl orange. The results show that the degradation process of the dyes depends on the surface charge of the TiO_2 nanopowders. A titanium hydroxide phase involving Ti^{3+} is responsible for the different surface charge that is modified during calcination.

The heterogeneous photocatalytic oxidation of organic pollutants has proved to be a promissing process for removal of dye contaminants and extensive research has been published on nanostructured TiO_2 (anatase form) to promote the degradation and total mineralization of such pollutants in the near UV spectral range. In order to enhance photocatalytic activity most efforts in synthesis are related to the increase in surface area of the nanoparticles. However, it has been shown also that increased crystallinity is important for enhancement of this activity.

In this work commercial nanocrystalline TiO_2 in powder form (FINNTI-S140) supplied by Kemira is used for the photodegradation process of two differently charged dyes, namely methylene blue (MB) and methly orange (MO). For the photodegradation experiments we used as received samples (AK) as well as calcinated samples at 300°C (AK-300), 400°C (AK-400) and 550°C (AK-550) for 1 hour in air. The surface areas of the TiO_2 powders are 310, 155, 110 and 71 m^2/g, respectively, as determined by BET. It is shown that in the photodegradation process using a fixed pH of 5, the nanostructured powders AK-550 are more efficient for MB compared to AK, while for MO the process efficiency is on contrary.

In order to understand such behavior, X-ray diffraction (XRD), electron paramagnetic resonance (EPR) and Raman scattering were used for characterization of the nanocrystalline TiO_2 powders. XRD pattern show that all samples have the anatase form and crystallite sizes increase from about 8 nm to 32 nm for samples AK to AK-550. By EPR it is shown that as received powders contain a magnetic phase which is reduced during calcination (figure 1). Raman scattering detects 5 intense bands ascribed to anatase [1] together with 6 additional bands which we attribute to other forms of TiO_2 (figure 2). During calcination the intensity of the additional bands are strongly reduced.

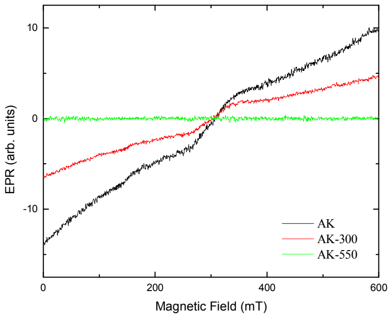

Figure 1: EPR spectra of TiO_2: AK, AK-300 and AK 550.

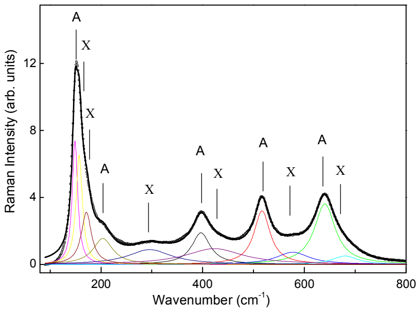

Figure 2: Raman spectra of nanocrystalline TiO_2: AK.

The magnetic phase observed by EPR is attributed to a defective TiO_2 phase involving Ti^{3+} as for example O-Ti^{3+}-OH. The same phase may introduce the additional bands observed by Raman spectroscopy [3]. During the calcination process the defective phase is oxidized and pure anatase is formed. In order to explain the different photodegradation processes for MB and MO we have to assume that the defective TiO_2 phase has a different surface charge compared to fully oxidized TiO_2. This assumption is consistent with the observation of the increase in the isoelectric point (IEP) of 3.7 for AK with that of 4.9 for AK-550. Typical values for IEP for anatase are about 5.5 [3].

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