Photocatalytic oxidation of Acid Black 194 in aqueous medium over an α-Fe_2O_3-TiO_2 composite material

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Introduction

Composite photocatalyst α-Fe_2O_3-TiO_2 has been synthesized by the citrate method, combining the advantages of two semiconductors: a wide band gap one (anatase ΔE_{bg}=3.2 eV) and a narrow band gap one (hematite ΔE_{bg}=2.2 eV). The first one is activated by UV-A light (λ_{max}=388nm), while the second one is activated by visible light (λ_{max}=564nm). So this composite material can utilize a greater share of the solar spectrum, compared to the pure TiO_2 photocatalyst. The composite has been tested for wastewater purification from the azodye Chromium Acidic Black (Color Index Acid Black 194). This dye is used for coloring textiles in BULCOLOR Co. (Kostenetz, Bulgaria), it is contained in the wastewater there and it has been found to be especially stable to UV-light, compared to other dyes [1]. This makes it a suitable model contaminant in water for testing the activity of TiO_2-based photocatalysts. Recently a new application of this azodye has been found: to color anodized alumina films on Al improving the corrosion resistance and decorative properties of such films [2-4].

Experimental

The convenience of using a dye as a model water pollutant lies in the option to observe the course of the photocatalytic reaction spectrophotometrically – in case of Acid Black 194 the absorbance at λ_{max}= 570 nm reveals the degree of discolouring (partial oxidation reaction) over the specific photocatalyst studied. At the same time we measure the total conversion degree by TOC (i.e. the complete oxidation reaction), which is different from the degree of discolouring and in this way both routes of the reaction are monitored. A simple construction open-air batch reactor was used allowing illumination with UV-light or visible light (in separate) or a combination of the two types of irradiation. The UV-C light source was a Philips TUV 4W/G4 T5 lamp, emitting monochromatic light (λ=253.7 nm) giving intensity of illumination 0.007 W/cm^2, while the visible light source was a Tungsram linear halogen lamp 500W, giving intensity of illumination up to 8.9 W/cm^2.

X-ray diffraction (XRD) patterns were recorded on TUR M62 apparatus with PC management and data acquisition, using HZG-4 goniometer and CoK_α radiation. JCPDS database (Powder Diffraction Files, Joint Committee on Powder Diffraction Standards, Philadelphia PA, USA, 1997) was used for the phase identification.

Moessbauer analysis was made using Wissenschaftliche Elektronik GmbH apparatus, working with a constant acceleration mode, ^{57}Co/Cr source and α-Fe standard. The parameters of hyperfine interactions of Moessbauer spectral components were determined by computer fitting: isomer shift (IS), quadrupole splitting (QS), hyperfine effective field (H_{eff}), as well as line widths (FW) and component relative weights (G).

Results/Discussion

The XRD study showed the presence of α-Fe_2O_3 (hematite PDF 33-0664 rhombohedral crystal system) and anatase TiO_2 (PDF 78-2486 tetragonal crystal system) and no rutile, no brookite and no ilmenite. The determined molar ratio TiO_2:α-Fe_2O_3 = 2:1 in the bulk phase, estimated by XRD, coincides with that on the surface, determined by EDS analysis. This method gave another confirmation that there is no ilmenite phase $FeTiO_3$ but two separate phases TiO_2:α-Fe_2O_3.

The Moessbauer data correlated with the XRD data about the hematite crystallite size (34 nm) – a sextet of Fe^{3+} ions only in octahedral coordination. There is also a doublet belonging also to hematite but with extremely small particle size (below 10 nm) with superparamagnetic behaviour.

The specific surface area of the material, determined by single point BET method amounted to 62 cm^2/g, which is higher than the area of TiO_2 Degussa P 25 (50m^2/g) – the standard reference photocatalyst used for comparison with the newly prepared composite material.

The photocatalytic activity testing was carried out at initial concentrations of Acid Black 194 C_o=0.0008 M. This concentration of the dye ensures sufficiently intensive colouring (absorbance 1.394), close to that of the real wastewaters. The photocatalytic activity of the standard reference photocatalyst TiO_2 Degussa P 25 was superior under irradiation with UV light, but it had no activity under visible light irradiation, while the composite material gave 5% partial oxidation degree and 8% complete conversion. Under combined UV-visible light irradiation the composite material exceeds the performance of the TiO_2 Degussa P 25 1.4 times.

References

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