XAS study of oxygen plasma-treated micronized iron oxide pigments

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Abstract

The stability of commercially available yellow (Bayferrox 3920) and red (Bayferrox 140) micronized iron oxide pigments against highly aggressive treatment with oxygen plasma is examined. The red pigment microparticles with hematite crystal structure are stable, while the yellow pigment changes colour during the treatment. Structural analysis with powder X-ray diffraction and X-ray absorption methods, EXAFS and XANES, shows that the yellow pigment microparticles recrystallize from goethite to hematite crystal structure. Larger hematite particles are composed of small highly anisotropic nano-domains. No nanoclusters or amorphous iron oxide phases are detected. The valence state of iron atoms in the pigments is not affected by the strongly oxidative plasma environment.

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1. Introduction

Oxygen plasma treatment of materials has become a technique widely used on both an experimental and industrial scale. It is used in chemistry, biology, medicine, nanotechnology, and in the electronic, and automotive industries [1–8]. The technologies based on the application of an oxygen plasma include non-isotropic plasma etching, selective etching, low-temperature ashing, degreasing, surface activation, and plasma sterilization.

A selective etching of polymer–matrix composite materials by weakly ionized plasma is often used in chemical practice as an excellent method of preparation of samples prior to SEM analysis in order to detect the distribution and orientation of particles in a polymer matrix [8–13]. High etching selectivity can be obtained due to the different probability for oxidation with O atoms for different composite ingredients in the material.
In this process, the mineral pigment particles are often presumed immune to the treatment. In this work, we examine the stability of two commercially available micronized iron oxide pigments (yellow—Bayferrox 3920 and red—Bayferrox 140) to the highly aggressive treatment with oxygen plasma. The structural and chemical changes in the pigments upon exposure to the plasma were analysed by X-ray powder diffraction (XRPD) and X-ray absorption methods—EXAFS and XANES.

2. Experimental

Micronized yellow iron oxide pigment Bayferrox 3920 and red pigment Bayferrox 140 have been exposed to oxygen plasma created in a plasma reactor with a volume of 0.03 m³ with an inductively coupled RF generator with frequency of 27.12 MHz and power of 5000 W. The reactor was pumped with a two-stage oil rotary pump with the pumping speed of 60 m³/h. The base pressure was about 0.3 Pa. Commercially available oxygen (purity 99.99%) was leaked into the plasma reactor so that the working pressure was 75 Pa. Plasma parameters were measured with a Langmuir probe and a catalytic probe [14–16]. The electron temperature was about 6 eV, the plasma density about \(2 \times 10^{16} \text{m}^{-3}\) and the density of neutral oxygen atoms \(6 \times 10^{21} \text{m}^{-3}\). The pigment samples were kept in plasma for 10 min.

The XRPD pattern of the product was collected on a Philips PW 1710 diffractometer using Cu Kα radiation in the 2θ range from 10° to 80° in steps of 0.02° with a sampling time of 1 s per step.

X-ray absorption spectra in the energy region of the Fe K-edge were measured in the transmission mode at the E4 beamline of the HASYLAB synchrotron facility at DESY in Hamburg. The station provided a focused beam from an Au-coated toroidal mirror and a Si(1 1 1) double crystal monochromator with about 1 eV resolution at the Fe K-edge. Higher-order reflections from the monochromator were effectively eliminated by a plane Au-coated mirror, and by a slight detuning of the monochromator crystals, keeping the intensity at 60% of the rocking curve with the beam stabilization feedback control. Samples of the iron oxide pigments and reference compounds (Fe₂O₃, Fe₃O₄, FeSO₄) were prepared as fine powders homogeneously distributed on multiple layers of adhesive tape. The thickness of each sample was chosen to provide optimal absorption of \(\sim 1\) above the Fe K-edge. The exact energy calibration was established with a simultaneous absorption measurement on the Fe metal foil.

3. Results

The two pigments are distinct forms of iron oxides. The XRPD patterns (Fig. 1) confirm that the red pigment is composed of well-crystallized microparticles with hematite (α-Fe₂O₃) crystal structure, while the microparticles of the yellow pigment have goethite (α-FeOOH) crystal structure.

During the plasma treatment no visual changes were observed in the red pigment. In the yellow pigment, a continuous change of colour from yellow through orange to dark red was observed.

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**Fig. 1.** XRPD spectra of the yellow pigment before (top) and after plasma treatment (bottom). Spectrum of the red pigment (α-Fe₂O₃) is shown for comparison (middle).
The XRPD pattern of the dark red product obtained after 10 min exposure to oxygen plasma reveals that the crystal structure of the pigment has changed completely from goethite to hematite. However, the diffraction peaks are much broader than in the case of an untreated red pigment, which clearly indicates a relatively poor crystallinity of the pigment particles after the treatment [17]. The broadening is caused by nano-size perfect-crystal domains, either in the form of separate nanoparticles [18,19] or mosaic domains in relatively large microcrystallites. The width of the lines is inversely proportional to the nanoparticle size. A detailed inspection of the peak widths reveals that there are two subsets of diffraction lines in the spectrum with significantly different broadening, indicating that the microcrystallites are highly anisotropic, i.e. exhibit significantly different sizes in different crystallographic directions [20].

The decisive information on the morphology of the treated pigment is provided by Fe K-edge EXAFS analysis, elucidating the local structure around Fe atoms in the sample. EXAFS analysis is performed with the University of Washington programs using the FEFF6 code for ab initio calculation of scattering paths [21,22]. The comparison of the Fourier transforms of the EXAFS spectra measured on the pigments before and after the exposure to oxygen plasma (Fig. 2) shows that plasma treatment does not change the local structure of the red pigment. The spectra before and after the treatment are identical, exhibiting the characteristic local Fe neighbour shell structure of hematite. The change of crystal structure in the yellow pigment from goethite to hematite after the plasma treatment, identified by XRPD, is also clearly visible in the local neighbourhood of the Fe atoms (Fig. 2).

A detailed comparison of the spectrum of the plasma-treated yellow pigment with the spectrum measured on hematite reveals identical contributions from the first Fe coordination shell and a suppression of the signal of further shells in the treated pigment (Fig. 2). This may indicate either the presence of some amorphous phase which could not be detected by XRPD analysis, or small hematite nanocrystals with diameters of the order of 1 nm, which would result in reduced average neighbour coordination numbers around Fe atoms [18,19]. Another possibility is the poor crystallinity of the hematite microparticles, which would increase the average static disorder in the Fe neighbour shells and, consequently, as witnessed by an increase in Debye–Waller factors, reduce the EXAFS signal.

Quantitative EXAFS analysis was used to determine the type of structural difference. The FEFF model based on crystal structure of hematite (α-Fe₂O₃) [23] was constructed. The Fe atom is octahedrally coordinated to six oxygen atoms (three at 1.94 Å and three at 2.11 Å) in the first coordination shell, followed by alternate shells of iron and oxygen neighbours. The FEFF model comprised all single and multiple scattering paths.
up to 3.9 Å. We calibrated the model by the EXAFS spectrum of the red pigment ($\alpha$-Fe$_2$O$_3$), obtaining a good fit (Fig. 3) for the R region from 1.1 to 4.0 Å with the following set of variable parameters: the amplitude reduction factor ($S^2_0$) and the distances and Debye–Waller factors of individual neighbour shells. The shell coordination numbers were kept fixed at their crystal structure values.

The same model was used to describe the EXAFS spectrum of the plasma-treated yellow pigment. Again, a very good fit is obtained with the same neighbour distances and neighbour coordination numbers as in hematite. The Debye–Waller factors of neighbour shells beyond the nearest one are found to be significantly larger than in hematite. Thus, we may conclude that the crystal structure contains imperfections which produce a large static disorder in the crystal structure of hematite microcrystals. The disorder does not affect the oxygen octahedra around iron atoms, but rather the correlations between the octahedra. There is no evidence for the presence of small hematite nanoparticles or amorphous iron oxide phases.

In addition, we checked for the change of the iron valence state possibly induced in the highly oxidizing atmosphere of the oxygen plasma. The change can be deduced from the energy shift of the Fe absorption edge [24]. The Fe XANES spectra of the pigment samples and reference compounds (FeSO$_4$ and $\alpha$-Fe$_2$O$_3$) with known iron oxidation states are plotted in Fig. 4. The reference spectra

![Fig. 3. Fourier transforms of k$^3$-weighted EXAFS spectra of hematite and of yellow pigment after the plasma treatment (experiment—solid line, EXAFS model—dashed line).](image1)

![Fig. 4. Normalized Fe K-edge XANES spectra of yellow and red pigment before and after the plasma treatment and of reference samples: FeSO$_4$, Fe$_2$O$_3$, Fe$_3$O$_4$ and Fe metal. Zero energy is taken at the 1s ionization threshold in the Fe metal (7112 eV).](image2)
show a K-edge shift of about 3.0 eV per valence state. The edge positions of the treated samples, which are best observed in the derivative spectra (Fig. 5) are evidently identical with that in the standard hematite sample. The shape of the Fe K-edge, which is very sensitive to the changes in local symmetry of the investigated atom site, also confirms that after the plasma treatment of the pigments, iron atoms are located at sites with the same local octahedral symmetry as in hematite.

In conclusion, the change in yellow pigment color during the oxygen plasma treatment can be ascribed to recrystallization of microparticles from goethite to hematite crystal structure. Larger hematite particles are composed of small highly anisotropic nano-domains. No nanoclusters or amorphous iron oxide phase were detected.

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References