Mössbauer study of oxygen adducts in solid Fe(II) phthalocyanines

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Abstract. Beta iron phthalocyanines (β-FePc) oxygenated at low temperatures were investigated with the help of 57Fe Mössbauer spectroscopy and X-ray diffractometry (XRD). The oxygenation of FePc complex is the key step in the pyrolysis of the flat layered molecules that yields acicular iron carbide particles engaged in uniform carbon shells. Mössbauer spectroscopy revealed that upon oxygenation of β-FePc new species were formed which could be associated with FeIIIPc oxygen adducts in high spin and low spin states. The temperature dependent Mössbauer measurements showed the interconversion of the low spin species into high spin species upon raising the temperature.

1. Introduction

Phthalocyanines and metallophthalocyanines have been known for many years as colorants and pigments. Nowadays their use as electrochemical catalysts, gas sensors, and regular heterogeneous catalysts has widely stimulated their research [1]-[3]. Furthermore, it was shown that controlled pyrolysis of flat layered iron phthalocyanine (FePc) can be used for preparing iron carbide nanocrystallites encapsulated in uniform 2.7 nm wide carbon coating [4]. The encapsulation of magnetic carbides by nanotubes enhances their applications since the carbon shells protect the encaged species from the ambient atmosphere where hydrolysis and oxidation could occur. Such carbon-coated magnetic particles have various industrial applications in magnetic data storage or as ferrofluids.

It is essential to know the mechanism of the formation of the nanocapsules in order to be able to control the diameter and thickness of the carbon coatings. Since the oxygenation of the FePc complex is the key step in the synthesis, there is a great interest in the interaction of oxygen with FePc.
Phthalocyanines can acquire several polymorphic forms of which α and β are fairly well characterized. The difference in the α- and β-polymorph lies essentially in the orientation of the flat molecules with respect to the crystallographic axes, where the perpendicular distance between the stacks of molecules is approximately the same. The inclination of the molecular stacks in the α-form is much less than in the β-form. In an FePc molecule, the metal atom is at the centre of a square of nitrogens. In the β-polymorph, there are additional nitrogen atoms of neighbouring molecules present axially above and below the central metal atom whereas in the α-form, the nitrogens of the nearest molecules are not in axial positions and therefore do not form an octahedron about the central metal atom.

In our previous works [5] Mössbauer spectroscopy and X-ray diffractometry were used to investigate the nature of oxygen bonding after the oxygenation of FeIIPc. The results indicated that considerable amount of oxygen can be introduced into the solid β-FeIIPc at relatively low temperatures in the dry state and in aqueous suspensions. A variety of oxygen adducts with β-FeIIPc were shown to be stabilized upon oxygenation, while only a very small amount of oxygen could be introduced into the α-FeIIPc under the same conditions. Here we report cases when an oxygen adduct with β-FeIIPc formed in aqueous suspension exhibits low-spin high-spin transition in the temperature range of 30 K – 293 K.

2. Experimental

Beta forms of FeIIPc were oxygenated under O₂ flow in an aqueous suspension. For the wet oxygenation β-FeIIPc was suspended in distilled water and the oxygenation was accomplished by bubbling O₂ through the aqueous suspension at 50 °C for 75 days.

²⁵⁷Fe Mössbauer measurements of powdered compounds were carried out in transmission geometry between 20 K and 293 K in a closed circuit He refrigerator cryostate (SHI-APD Cryogenics). A ⁵⁷Co/Ph source of 10⁹ Bq activity was used. The Mössbauer spectra were evaluated using the MOSSWIN code [7].

X-ray diffractograms of the pristine and oxygenated β-FeIIPc were recorded by a computer–assisted DRON-2 diffractometer using CoKα radiation and β-filter.

3. Results and discussion

A detail of the powder X-ray diffractogram of the β-FeIIPc oxygenated in aqueous suspension can be seen in figure 1. All lines in the diffractogram can be indexed according to the monoclinic standard β-FeIIPc [5] with lattice parameters of a=14.8148 Å, b=4.7779 Å, c=19.6296 Å and β=121.36°. This reflects that the basic structure is preserved after the long term oxygenation. However, the lattice parameters a and c decreased considerable compared to those of the pristine compound [8], furthermore, significant changes in the relative intensities of the corresponding lines and line broadening can be observed in the diffractogram upon oxygenation. All these changes are well consistent with and indicate the incorporation of oxygen between the molecular layers. The volume of the elementary cell of the oxygenated β-FeIIPc decreased to 1186 Å³ from 1216 Å³ characteristic of pristine compound. This strongly supports the oxygen uptake in good agreement with our earlier result [5].

The temperature dependent Mössbauer spectra of the β-Fe²⁺Pc oxygenated in aqueous suspension are shown in figure 2. There are significant changes in the spectral envelope upon raising the temperature. The spectra of the β-Fe²⁺Pc could be decomposed into three doublets (D1, D2, D3), the data obtained by the computer fit are shown in table 1. The Mössbauer parameters of D1 correspond well with those of the pristine β-Fe²⁺Pc with large quadruple splitting [9]. The doublets D2 and D3 can be associated with Fe²⁺ oxygen adducts in high spin (HS) and low spin (LS) states, respectively.
Although in our previous publication we suggested an assignment of the observed doublets to real oxygen adduct species, in the light of our new experimental findings, it is worthwhile to return to this question and see if alternative models may be possible.

The most remarkable finding in these experiments compared to our previous work is the limited number of species, i.e., actually only one oxygen adduct species is found, which shows up in LS and HS state, depending on the temperature. This species is found now in a sample having the highest oxygen content ever synthesized by us, which is demonstrated by the very low spectral contribution of the doublet of the pristine $\beta$-Fe$^{II}$Pc (7% at room temperature, see table 1).

Table 1. Mössbauer parameters of the oxygen treated $\beta$-Fe$^{II}$Pc. $\delta =$ Chemical Shift$^a$, $\Delta =$ Quadrupole splitting, $A =$ Abundance.

| $T$ (K) | Doublet 1 (D1) | Doublet 2 (D2) | Doublet 3 (D3) |
|---------|----------------|----------------|----------------|
|         | $\delta$ (mms$^{-1}$) | $\Delta$ (mms$^{-1}$) | $A$ (%) | $\delta$ (mms$^{-1}$) | $\Delta$ (mms$^{-1}$) | $A$ (%) | $\delta$ (mms$^{-1}$) | $\Delta$ (mms$^{-1}$) | $A$ (%) |
| 30      | 0.52            | 2.57            | 23             | 0.41            | 0.43             | 24             | 0.31            | 1.24             | 53     |
| 50      | 0.50            | 2.59            | 19             | 0.40            | 0.44             | 31             | 0.30            | 1.24             | 50     |
| 70      | 0.48            | 2.61            | 18             | 0.36            | 0.46             | 35             | 0.29            | 1.26             | 48     |
| 110     | 0.47            | 2.62            | 14             | 0.40            | 0.52             | 46             | 0.28            | 1.24             | 40     |
| 150     | 0.45            | 2.67            | 11             | 0.40            | 0.54             | 54             | 0.27            | 1.25             | 34     |
| 293     | 0.40            | 2.70            | 7              | 0.34            | 0.58             | 77             | 0.24            | 1.07             | 16     |

$^a$relative to $\alpha$-iron

In our previous model [10], where the oxygenation resulted roughly in 60 % oxygen related Fe species, the “spin-crossover” species was assumed to be an Fe atom having a peroxo bridge on one side of the Pc plane, and a dihapto bound O$_2$ on the other side (figure 3 (a), species c, d). Those samples also contained another species (figure 3 (a), species b) in which Fe had one dihapto bound O$_2$ only. Now one can expect that when the oxygen content of the sample increases, the relative contribution of the species (c-d), and also of b would increase at the expense of species a (Fe in pristine Fe$^{II}$Pc). However, as presented in figure 2 and table 1, species b disappears while the pristine FePc is still there.
On the other hand, in case of O₂ type ligands placed in between β-FePc layers in order to form a bridge between iron atoms, the Fe–O distance is around 0.19 nm – almost ideal to form a bond. To reach the regular bond length, found in peroxo bridged complexes of similar type [11], roughly 5 % linear contraction is needed only. Now, considering species (c-d), it is very likely that if the dihapto bound O₂ transforms into end-on bound O₂ by thermal excitation, the rotation of this O₂ molecule would automatically result in the formation of another Fe–O bond with an Fe atom in the neighbouring Pc plane. The final result is the formation of long chains of peroxo bridged irons as presented in figure 3 (b). Note that iron has a strong tendency to form long ...–Fe–O–Fe–O–Fe–O–... chains for example in aqueous Fe³⁺-solutions [12]. In the lattice of FePc, μ-oxo bridges are not, only peroxo bridges are feasible due to the large Fe–Fe distance [5].

In this scenario, the reduction of the number of species is easier to understand: the dominating oxygen adduct species in the high oxygen content sample is the in-chain site (peroxo bridge on both sides of Fe). Chain-terminal species may be five-coordinate Fe atoms with one peroxo bridge only at one side or “quasy” seven-coordinate with an additional dihapto O₂ at the other side of iron.

According to our previous reasoning, a dihapto bound O₂ at the end of the chain can transform into a new bridge easily unless it is on the surface of the crystal lattice and thus another iron is not available. It is difficult to judge which species is favoured energetically, but higher coordination may be preferred by iron (and this is drawn in figure 3). Nevertheless, disregarding the type of the terminal species, the relative number of them is negligible if the chains are long enough, and therefore there is no other doublet found in the Mössbauer spectra, that would represent a single dihapto O₂–Fe oxygen adduct (species b).

The required 5 % bond length contraction upon O₂-bridge formation and the existence of long chains are in perfect agreement with the decreasing lattice parameters found by our XRD measurement. This can also explain why the Mössbauer parameters of doublets D2 and D3 are only close but not identical to those of species c and d found earlier in samples with lower oxygen content.

In our modified model, the species showing spin-crossover is therefore a six-fold coordinated species with two axial oxygens and four equatorial nitrogens, with the O–Fe–O axis being non-perpendicular to the Pc plane. The spin-crossover may be connected with electron-density shift from iron to the O₂ ligands.

Association of the electron density shift with a possible structural deformation is likely because of the non-perpendicular O–Fe–O axis. Taking into consideration that the O–O bond lengths are 0.121 nm, 0.128 nm, and 0.149 nm for neutral dioxygen (O=O), superoxide (O=O⁻), and peroxide (O=O²⁻), respectively, an electron density shift from iron to oxygen (e.g., shift form a formal Fe²⁺ state to a formal Fe³⁺ state with a concomitant shift from O₂ to O₂⁻) can result in lower deformation of the ligand sphere of iron, i.e., the O–Fe–O axis closer to perpendicularity. This simultaneous electronic and structural change can be accompanied by a spin state change, and therefore it is manifested as a spin-crossover process.

Figure 3. Possible distribution of dioxygen in the lattice of β-FePc after oxygenation. (a) Low oxygen content (~60 %) (b) high oxygen content (~93 %)
4. Conclusions
With the help of temperature dependent Mössbauer spectra, a spin-crossover of the six coordinate in-chain Fe-oxygen adduct has been shown. Based on the XRD and Mössbauer spectroscopic data, the formation of long μ-peroxo bridged –Fe–O–O–Fe– chains are suggested upon the introduction of high amount of oxygen into the lattice of β-FePc. The driving force for the high spin to low spin transformation at low temperature is a decreasing distortion of the ligand sphere of iron (toward a regular octahedron) which assumes an electron density shift from iron to the bridging O₂ ligands.

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