Zeolite Included Fe(II)Phthalocyanine

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Abstract. The title compound was prepared by treating iron(0) or pentacarbonyl-iron(0) containing Y zeolite with the appropriate complexant. Because of steric hindrance, the phthalocyanine guest molecule turns out to be encapsulated within the zeolite cavity.

1. Introduction

The use of zeolite molecular sieves as host lattices to include various transition metal complexes has been reported previously [1]. Such zeolite-included complexes are of great interest not only because of their activity in a number of catalytic reactions [1, 2] but also as models of enzyme active centers. In this respect, the iron(II) chelates appear to be very promising models of the reversible binding and activation of molecular oxygen.

Ordinarily, the dimensions of metal chelates are substantially greater than the free diameters of zeolitic cage openings. Therefore, the only way to include such a molecule within the zeolite lattice seems to be an *in situ* synthesis inside a cage using its components, i.e., metal and complexant, to 'assemble' the molecule in the matrix.

This paper reports on the synthesis of Fe(II)phthalocyanine complexes (PcFe(II)) in the Y zeolite lattice. The Fe(II)phthalocyanine complexes are known to be quite analogous to ferroporphyrins which are at the heart of most respiratory enzymes.

The main difficulty in the matrix synthesis of Fe(II)phthalocyanines appears to be the introduction of ferrous ions via conventional ion exchange because of their instability in aqueous solutions. However, given that one could obtain Fe(II)phthalocyanine from metallic iron, an alternative method to ion exchange which may be employed is introducing the metal component into the zeolite in the form of volatile compounds such as pentacarbonyl Fe(0). On heating under an inert gas atmosphere, the $Fe(CO)_5$ adsorbed onto zeolite Y converts into metallic iron species [3].

2. Experimental

The sodium form of Y zeolite (SiO_2/Al_2O_3 molar ratio of 5 : 1) obtained from Leuna Werke (DDR) was used as a starting material. The NaY sample (0.5–1.0 g) was placed into a glass ampoule connected through a 3-way valve with a calibrated capillary tube and vacuum set up. After outgassing the sample at 10^{-4} Torr and 400°C for 2–3 h, dry $Fe(CO)_5$ was trap-distilled into the capillary tube, and then the iron pentacarbonyl vapour was allowed to adsorb onto the zeolite at 20°C. The ampoule with zeolite was shaken periodically to ensure that the $Fe(CO)_5$ was more evenly distributed throughout the sample. The adsorption

completed, the zeolite with iron pentacarbonyl was transferred in a stream of dry He into a metallic reactor. The temperature-programmed decomposition (TPD) of $Fe(CO)_5$ adsorbed on zeolite was then carried out, using He as a carrier gas (30 ml/min); heating rates varied from 4 to $30°$/min. The carbon monoxide evolved was detected by a catharometer, a liquid N_2 trap being set before the detector.

Synthesis of the zeolite-supported PcFe(II) was performed in two ways. (1) The samples obtained by TPD, i.e., decomposed in the He flow by heating up to $400°C$, were used as starting materials.

Such a sample was transferred under a dry He atmosphere into one compartment of a two-chamber ampoule, the second compartment of which was loaded with phthalonitrile (20% in excess of stoichiometry). After being degassed at $20°C$, the ampoule was sealed and then treated at $210-230°C$ for 5–6 h. The reaction finished, washing of the sample with warm acetone was used to remove unreacted complexant.

(2) The synthesis was carried out omitting the step of predecomposition of $Fe(CO)_5$ within the zeolite. The NaY zeolite with adsorbed carbonyl and phthalonitrile was loaded into two separate compartments of a two-chamber ampoule. After degassing the zeolite at $300°C$, carbonyl was adsorbed onto it, and the sealed ampoule was heated at $150°C$ for 10 h.

In both procedures the mass of zeolite and the volume of $Fe(CO)_5$ were such to give 0.05–5.0% by mass of Fe.

Electronic spectra were recorded with a Specord UV–VIS spectrometer.

3. Results and Discussion

3.1. THERMAL DECOMPOSITION OF ADSORBED $Fe(CO)_5$

It was observed that under conditions of temperature-programmed reaction (TPR) at a heating rate up to $30°$/min the thermolysis of adsorbed $Fe(CO)_5$ occurs yielding carbon monoxide and iron as well as CO_2 as a secondary product of CO disproportionation. The thermodesorption of $Fe(CO)_5$ seems not to proceed even at elevated temperatures in agreement with the findings of Jacobs et al. [3]. Hence the TPR traces reflect the specificity of inclusion compound conversion as compared with that of unsupported carbonyl. Typical TPR traces for samples with various contents of iron pentacarbonyl are shown in Figure 1. As pointed out in [3], the $Fe(CO)_5$ adsorption limit on Y type zeolite is 11.4 wt.% of Fe which corresponds to a mean content of about 3 molecules of $Fe(CO)_5$ per supercage. It is evident that a probability of more than one molecule population of a cage increases substantially when the Fe content in the zeolite exceeds ca. 4 wt.%. Correspondingly, as seen from Figure 1, the number of peaks on the TPR curves tends to decrease. In contrast, at small coverages, when almost all the carbonyl entity is present in the zeolite framework as isolated molecules, there are several well resolved peaks in the TPR traces. The first low-temperature peak appears to arise mainly from a release of the first carbonyl group, the relatively stable tetracarbonyl of iron being formed. The activation energy, evaluated using the well-known Amenomiya–Cvetanović equation [4] by varying the heating rates, was about 105 ± 20 kJ/mole. This value is not significantly different from that for photochemical decomposition of iron pentacarbonyl [5].

It is essential for what follows that the maximum rates of CO evolution, i.e., the peak on a TPR curve, occurs at temperatures of $140-180°C$, the first appearance of carbon monoxide being detected even at $70°C$. Hence, it would be quite natural to assume that a substitution of carbonyl ligands of the iron complex for phthalonitrile molecules might be performed at
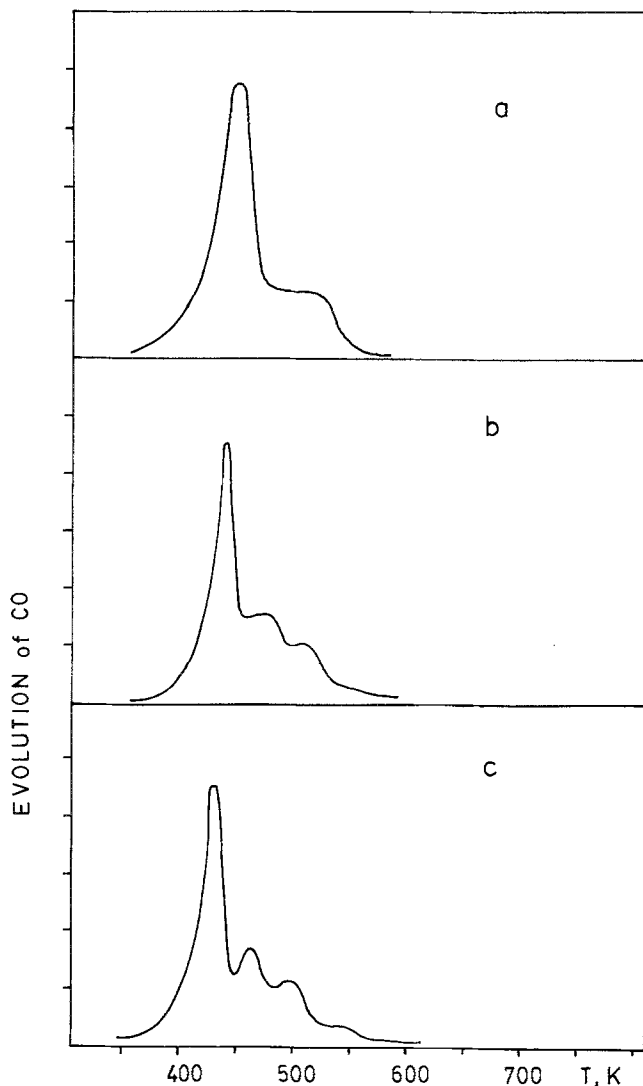
Fig. 1.   The TPR-traces of the decomposition of $Fe(CO)_5$ adsorbed onto Y zeolite. Flow rate of He: 30 ml/min. (a) 5 mass % of Fe, β = 12°/min; (b) 1 mass % of Fe, β = 18°/min; (c) 0.05 mass% of Fe, β = 12°/min.

temperatures which are about 100°C lower than those for 'conventional' synthesis from metallic iron [6]. Lowering the temperature of the PcFe(II) synthesis decreases a superficial mobility of iron atoms and, as a consequence, prevents them from aggregating into clusters.

3.2. *IN SITU* SYNTHESIS OF PcFe(II) IN ZEOLITE

As described above, intracrystalline inclusion of phthalocyanine complexes within a zeolite may be performed by exposing the iron-containing material to phthalonitrile vapour (1). One of the main problems in such a synthesis is to characterize the species formed as a result of this procedure. During the synthesis, one may observe a change in the sample colour from

$$Fe \ + \ 4 \ \text{(benzene-1,2-dicarbonitrile)} \longrightarrow \text{PcFe(II)}$$

(1)
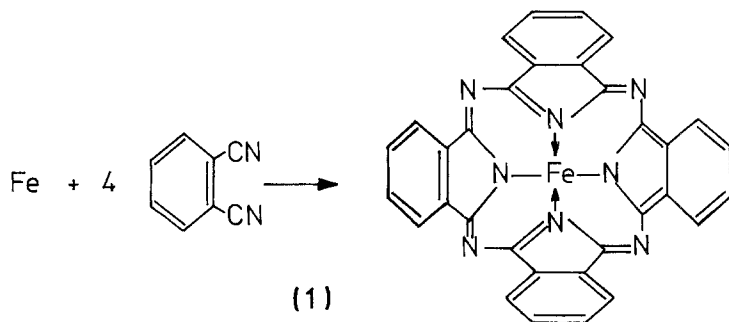
black to greenish blue if, before treating with complexant, the $Fe(CO)_5$ adsorbed was converted into metallic iron (method 1). When the zeolite with adsorbed $Fe(CO)_5$ is used as such (method 2), the colour changes from slightly yellow to greenish blue. Seemingly these observations indicate that the formation of iron complexes might occur at least on the outer surface of the zeolite crystallites (2).

$$Fe(CO)_5 \ + \ 4 \ \text{(benzene-1,2-dicarbonitrile)} \longrightarrow \text{PcFe(II)} \ + 5 \ CO$$

(2)
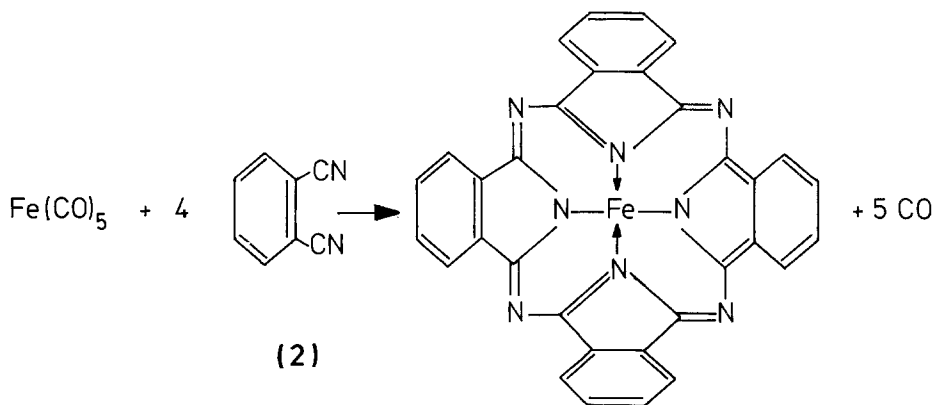
We have attempted to elucidate the problem in the following way. After thorough washing with acetone, the samples were treated firstly with dimethylformamide (DMF) and then with concentrated H_2SO_4. Electronic spectra of the solutions obtained are given in Figure 2 (curves 2a and 2b) along with the spectra of pure iron phthalocyanine in both solvents (curves 1a and 1b). As seen in Figure 2 the characteristic absorption bands for DMF and conc. H_2SO_4 standard solutions of PcFe(II) are at about 680 and 800 nm, respectively. Thus the complexes washed out from the zeolite exhibit spectra which are quite similar to those found for individual PcFe(II) (see Figure 2).

Due to steric hindrance, the PcFe(II) guests cannot leave the zeolite host supercages where they have been formed. Therefore, the DMF removes only the superficial species, whereas the treatment with conc. H_2SO_4 leads to a partial decomposition of the zeolite framework and, as a consequence, to extraction of some internal PcFe(II) guest molecules. All these findings enable us to conclude, at least qualitatively, that the guest phthalocyanine of iron(II) does form in the host lattice of the zeolite. More detailed and quantitative information cannot be obtained in this way because of the incomplete collapse of the zeolite structure after H_2SO_4 treatment. However, further studies will be necessarry to resolve this question quantitatively.
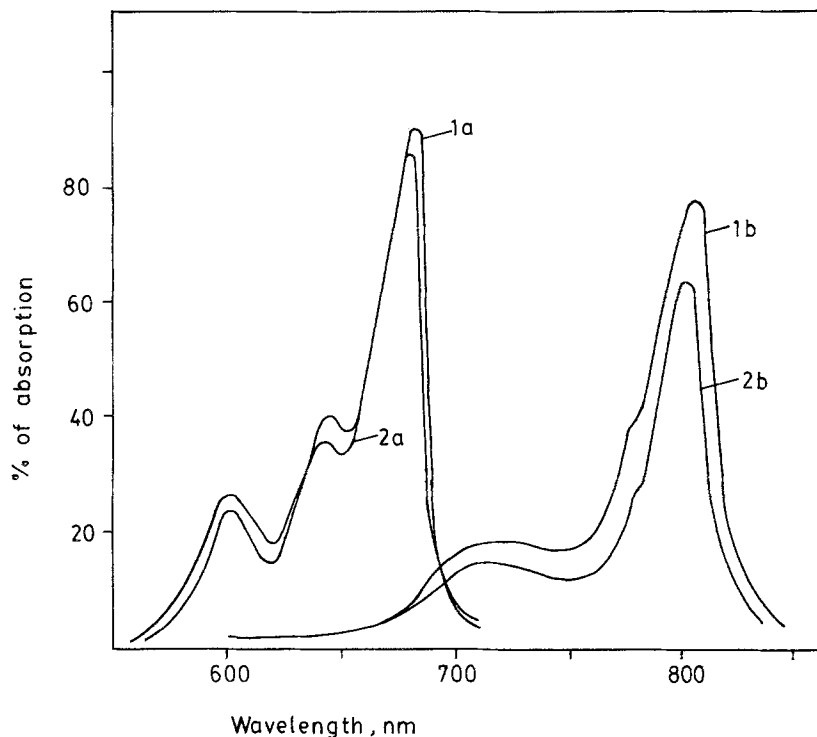
Fig. 2. Electronic spectra of (1) Fe(II)phthalocyanine in DMF (1a), in conc. H_2SO_4 (1b) and (2) solutions obtained by treatment of zeolite with DMF (2a) and with conc. H_2SO_4 (2b) (after being treated with DMF).

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