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The Influence of the Synthesis Temperature on Cobalt Phthalocyanine Encapsulation in Zeolite Y

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Abstract

Several characterization techniques were applied to study the effect of the synthesis temperature on the physicochemical properties of cobalt phthalocyanine incoporated into zeolite Y. The cobalt phthalocyanine was synthesized in the supercages of zeolite Y by the template synthesis method at two different temperatures of 200 and 300 °C and characterized by diffuse reflectance spectroscopy, Fourier transform infrared spectroscopy, pore volume analysis, unit cell dimension calculation, UV-vis spectroscopy, thermogravimetric analysis and X-ray diffraction. The results show that the catalyst synthesized at 200 °C contains 11 wt.% cobalt phthalocyanine and almost all of this complex is encapsulated in the supercages as monomeric species. At higher temperature a considerable amount of the cobalt phthalocyanine is hosted in the mesopores and/or on the external surface of the zeolite as aggregates. The migration of one part of the cobalt cations from the supercages to the small cages at 300 °C decreases the formation of the non-aggregated encapsulated phthalocyanine molecules in the zeolite supercages. The aggregated cobalt phthalocyanine formed at the surface corresponds to the β-polymorph state of the phthalocyanine.

Introduction

The development of molecular engineering and molecular architecture is now reaching a level of sophistication for selective transformation of reactants into products with specific structure. The selectivity arises from the steric effects imposed by the environment of the active site upon substrate approach. By encapsulation of coordination compounds in porous solids like zeolites, some characteristics of the zeolite (pore diameter, main channel and void dimensions and electrostatic field potential) combine with the electronic and stereochemical properties of the complex, lead to the highly selective formation of certain products with precise structure.

The encapsulation of transition metal phthalocyanine complexes (MPcs) inside microporous and mesoporous zeolite molecular sieves has been well established [1–12]. Such materials are called *ship-in-a-bottle* complexes. Owing to their large size (10–14 Å) phthalocyanine complexes cannot be fixed within the microporous structure of zeolites by an ion-exchange process. There are basically three approaches to the preparation of these *ship-in-a-bottle* chelate complexes, namely the flexible ligand method, the template synthesis method and the zeolite synthesis method [1]. The template synthesis method has been widely used for the preparation of intrazeolite metallophthalocyanines. This approach requires four dicyanobenzenes to diffuse into the zeolite matrix where they can cyclize around a resident metal ion (fixed by ion-exchange) to form the tetradentate macrocycle which is too large to exit. Complete characterization of the encapsulated complexes is necessary in order to ensure the feasibility of the intrazeolite synthesis. However, in most of the works concerned with encapsulation, there is little characterization of the real state of the encapsulated coordination compounds and of the support used in encapsulation. Páez-Mozo *et al.* used a systematic program of synthesis and characterization techniques including XPS in order to provide detailed information on the state of cobalt phthalocyanine encapsulated in zeolite Y [13]. They concluded from their data that part of the cobalt phthalocyanine is on the surface of the zeolite. No attempt was made by them to investigate the factors controlling the ratio of the encapsulated to non-encapsulated cobalt phthalocyanines in zeolite Y. Also no data were provided to differentiate the state of deposited cobalt phthalocyanine (i.e., its polymorphism) from the encapsulated ones. They synthesized CoPcNaY at 200 °C, but there are other reports suggesting that a higher temperature is required for encapsulation of metal-phthalocyanine into the zeolite Y supercages. Schulz-Ekloff *et al.* reported the optimum temperature for the synthesis of cobalt phthalocyanine in zeolite X to be 250 °C based on trial and error [14, 15]. Balkus and Ferraris have suggested a temperature of 270 °C as the optimum temperature to prepare cobalt phthalocyanine in zeolite Y, according to differential scanning calorimetry [16]. Bedioui in his review article reported a general procedure for preparation of metallophthalocyanines at 300 °C [5].

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The aim of the present contribution is to show the influence of the synthesis temperature in the formation of aggregated cobalt phthalocyanine complex. We used two different temperatures of 200 and 300 °C, the lowest and highest recommended temperature, respectively, for the synthesis. We will show that the ratio of monomeric to aggregated CoPc molecules is higher when the synthesis is performed at 200 °C. It has been confirmed that the catalytically active sites are indeed monomeric and isolated metal-phthalocyanine molecules are located in the supercages of the zeolite [17].

Experimental

Sample preparation

The synthesis of zeolite NaY was similar to that previously described in the literature [18, 19]. Metallic aluminium (99% pure, Merck, 818531), aluminium sulfate (Fluka, 6421) and fumed silica (Aerosil, Degusa, Switzerland) were used to prepare the final reactant gel. Crystallization was performed by heating the gel in a PTFE vessel inside a stainless-steel autoclave under static conditions. The autoclave was heated at 95 °C for 24 h. After cooling the autoclave, the crystalline product was separated, washed and dried at 110 °C. The cobalt cation was incorporated into the NaY zeolite by an ion-exchange process using a solution of cobalt(II) acetate tetrahydrate (Fluka, 60790) in deionized water. A mixture of 4 g of the NaY zeolite with 100 mL of a 0.025 M cobalt solution was stirred for 48 h at room temperature. The slurry was then centrifuged and the pink solid product washed with deionized water and dried at 250 °C.

Preparation of encapsulated phthalocyanine in the zeolite (CoPcNaY) was performed by mixing 2 g of the dried cobalt-exchanged zeolite (CoNaY) with 2 g of 1,2-dicyanobenzene (Fluka, 80152) introduced in a glass ampule. The ampule was evacuated to 10^{-2} atm for 2 h, and then sealed and heated in an oven at 200 °C (or 300 °C) for 24 h. After heating, the solid color changed from pink to blue. The content of the ampule was removed after cooling and then transfered to a Soxhlet extractor for purification. The product was extracted with acetone, methanol, pyridine, acetone and diethyl ether sequentially. Each extraction step was carried out until the solvent became colorless. Extraction and purification lasted $\approx$ 48 h. The purified CoPcNaY was vacuum dried at 150 °C for 15 h. All the steps following the synthesis were done exactly the same for both cobalt phthalocyanine samples heated at 200 and 300 °C. A free cobalt phthalocyanine sample was also prepared according to the reported procedure [20].

Characterization

X-ray diffraction measurements were performed on a Philips PW 1840 diffractometer with Cu-K$_\alpha$ radiation at room temperature. XRD patterns were recorded using an automatic divergence slit system.

Table 1. Quantitative analysis of the samples[a]

Sample	Al	Si	Co	N
NaY	8.4	22.6	–	–
CoNaY	8.2	22.5	2.4	–
CoPcNaY-200	7.6	20.3	2.1	2.6
CoPcNaY-300	7.4	19.8	2.4	3.3

[a] Si, Al and Co determined by EDX/SEM and N by Kjeldahl methods. Results are in weight percent.

Quantitative analysis of the samples for Si, Al and Co were done by an energy dispersive X-ray analysis (EDX) coupled to a Philips XL30 scanning electron microscope. The concentration of nitrogen in the phthalocyanine containing zeolites (CoPcNaY samples) was determind by the Kjeldahl method.

Diffuse reflectance spectra were recorded by a UV-2100 Shimadzu spectrophotometer equipped with an integrating sphere assembly. A special cell loaded with the solid sample and covered by a quartz window was used in all experiments. All the spectra were recorded at room temperature against barium sulfate as a white reference sample. The spectra were plotted in terms of absorbance. The UV-visible spectra were recorded on the same spectrophotometer in its conventional mode. The cobalt phthalocyanine samples were dissolved in concentrated H_2SO_4 in order to obtain the spectra. The IR spectra were obtained from KBr pellets using a Nicolet 560 FTIR spectrophotometer.

Specific surface area measurements were performed on a Sibata SA-1100 rapid surface area apparatus with nitrogen as the adsorption gas at liquid nitrogen temperature. Samples were first degassed at 250 °C for 1.5 h, prior to gas adsorption.

The values of the unit cell dimensions of the zeolite Y before and after entrapment of phthalocyanine were calculated according to a simple method described in the literature for a face centered cubic lattice [21].

Thermogravimetric analyses were performed on a Polymer Laboratories TG-1500 with a heating rate of 10 °C/min.

Results and discussion

The elemental analyses for the NaY, CoNaY and CoPcNaY samples are listed in Table 1. The CoPcNaY samples were labelled as −200 and −300, representing the temperatures of the synthesis. According to the Si/Al ratio of 2.69 obtained from quantitative analysis of the NaY sample, and by using the table given by Dempsey *et al.* [22], the unit cell formula could be estimated as:

$$Na_{52.5}[(AlO_2)_{52.5}(SiO_2)_{139.5}].$$

The thermogravimetric analysis detected 252 water molecules per unit cell in the fully hydrated NaY sample. In this calculation it was assumed that all the negative charges induced by 52.5 Al/UC is compensated merely by sodium ions. The volume and concentration of the cobalt acetate solution used for the preparation of CoNaY made it possible to exchange not more than 8 sodium ions per unit cell by cobalt cations. The unit cell formula, given below, is close to that expected:

$$Co_{7.2}Na_{38.1}[(AlO_2)_{52.5}(SiO_2)_{139.5}].$$

The quantitative analysis for nitrogen and cobalt content shows that all the cobalt cations are not associated with phthalocyanine. According to the formula of cobalt phthalocyanine ($C_{32}H_{16}CoN_8$) the weight ratio of N to Co in this molecule is equal to 1.9. Using this ratio, 1.37 (200 °C) or 1.74 (300 °C) wt.% cobalt content correspond to the measured nitrogen content. Therefore, 34 (200 °C) or 27 (300 °C) wt.% of the cobalt atoms are not included in the cobalt phthalocyanine molecules, respectively.

Zeolites loaded with cobalt phthalocyanines are blue in color. This color, which arises from ligand $\pi - \pi^*$ transitions, is characteristic of both free and encapsulated complexes [23]. A diffuse reflectance spectroscopic technique was used for characterizing the intrazeolite complexes. The DR spectra for CoPcNaY-200 and CoPcNaY-300 are shown in Figure 1. The maximum at 675 nm is the Q band for CoPcNaY samples [6]. The 640 nm band which is much more pronounced in CoPcNaY-300 belongs to aggregated cobalt phthalocyanine complexes [6, 24, 25]. The shift of the absorption band to higher energy is a direct indication of aggregation and the broadness may reflect the diversity of conformers. Comparison of the two spectra shows that the ratio of the aggregated species to monomeric ones increases with increasing synthesis temperature. At higher temperatures cobalt cations may migrate from supercages toward the sites closer to the lattice oxygens (i.e., the sites in the sodalite cages) [26], therefore less cobalt cations will be left in the supercages to form CoPc complexes. The presence of CoPc as aggregated species may be justified by lattice defects arising from partial dealumination and/or partial destruction due to protons resulting from the hydrolysis of cobalt cations. These processes are more pronounced at 300 °C, therefore a considerably higher amount of aggregated CoPc was detected on CoPcNaY-300 by DRS than on CoPcNaY-200 (Figure 1). The aggregates may be hosted in the mesopores created by zeolite framework fragmentation during CoPc formation [27] or could be deposited on the external surface at partially broken supercages due to enhanced physisorption in a confined geometry [28]. It is not possible to differentiate aggregated species hosted in the mesopores from those deposited at the external surface at the present time.

Uv-vis spectroscopy was used to detect the probable formation of the metal free phthalocyanine during the synthesis [11, 12]. In order to run a UV-vis spectrophotometric experiment, CoPcNaY samples were first dissolved in concentrated H_2SO_4 to destroy the molecular sieve lattice. The spectra of these solutions are shown in Figure 2. The spectrum of free CoPc complex dissolved in 18 M sulfuric acid (not shown in Figure 2) is exactly the same as those of the complexes recovered from the zeolite digested in the acid. This is an indication that none of them show any evidence of metal free phthalocyanine formation. The Q band position in concentrated H_2SO_4 is red shifted, because of protonation of the peripheral nitrogen on the ligand. The band positions from the electronic spectra of our samples match completely with those reported previously [13].

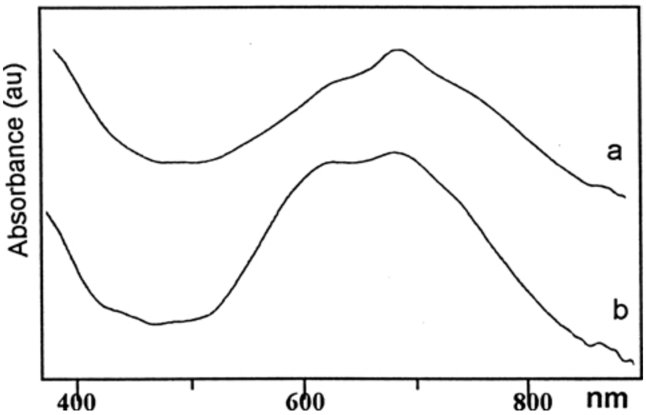

Figure 1. Diffuse reflectance spectra of (a) CoPcNaY-200 and (b) CoPcNaY-300.

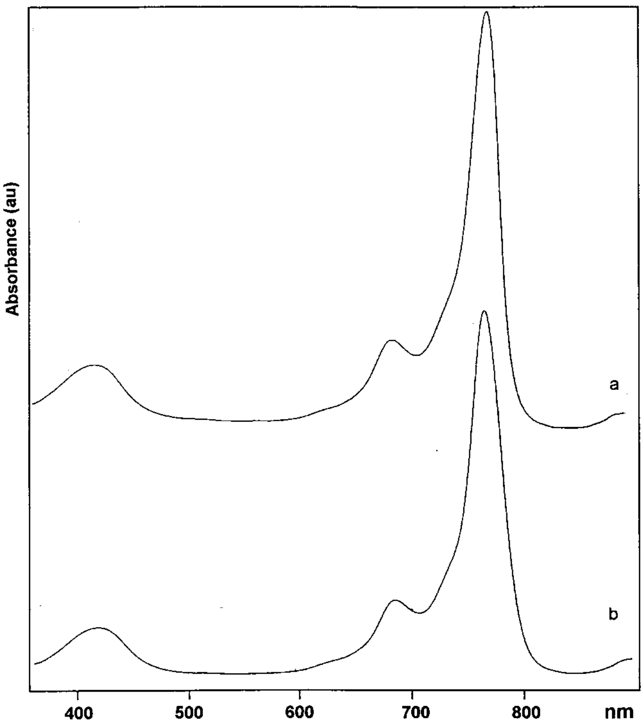

Figure 2. UV-vis spectra of (a) CoPcNaY-200 and (b) CoPcNaY-300 in H_2SO_4 (18 M).

The presence of monomeric and aggregated CoPc can also be verified by the IR spectra. Figure 3 shows the IR spectra for the CoNaY, CoPcNaY-200 , CoPcNaY-300 and CoPc samples. The bands at 1250–1550 cm^{-1} are attributed to C—C stretch vibrations of the phenyl or isoindole rings. The band observed at 1404 cm^{-1} in CoPcNaY-200, is split into two bands at 1404 and 1426 cm^{-1} in CoPcNaY-300. This may well account for the considerable involvement of aggregated CoPc in the CoPcNaY-300 sample. The 1426 cm^{-1} band arises from cobalt phthalocyanine aggregates formed on the external surface or in the mesopores of the zeolite. The IR spectrum of free CoPc shows only the

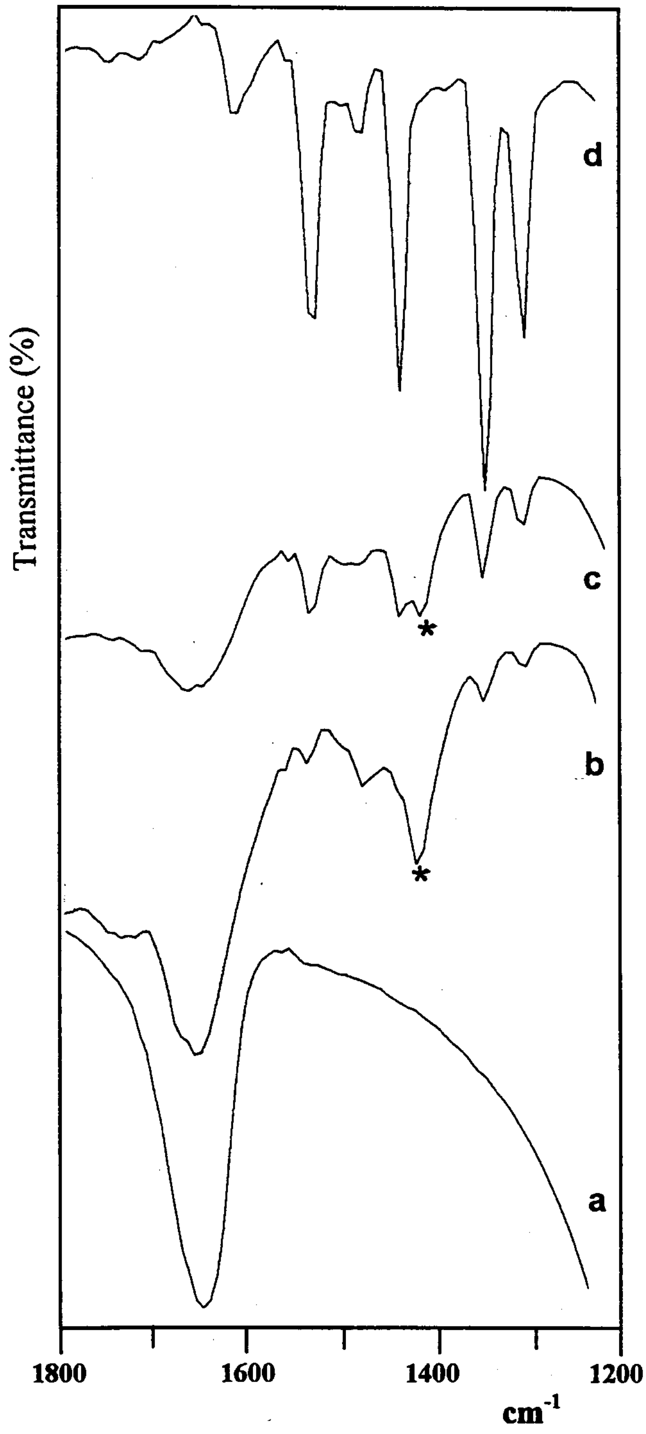

Figure 3. FTIR spectra of (a) CoNaY, (b) CoPcNaY-200, (c) CoPcNaY-300 and (d) CoPc in Kbr. The 1404 cm^{-1} band assigned to monomeric CoPc is indicated by *asterisks* (*).

1426 cm^{-1} band indicating no sign of monomeric cobalt phthalocyanine.

The specific BET surface area and micropore volume of the samples are presented in Table 2. The large reduction in the surface area and micropore volume of CoPcNaY-200 and CoPcNaY-300 compared to CoNaY could be interpreted as the formation of complexes in the pores of the zeolite. The decrease is higher in CoPcNaY-200 than in CoPcNaY-300. This is in accordance with our DRS results and support the idea that in CoPcNaY-300 fewer complexes are entrapped in the supercages of the zeolite.

Table 2. Specific surface area, micropore volume and unit cell dimension of the samples

Sample	Surface area (m^2/g)	Micropore volume (cm^3/g)	Unit cell dimension (Å)
CoNaY	830	0.29	24.78 (± 0.03)
CoPcNaY-200	576	0.20	24.78 (± 0.02)
CoPcNaY-300	707	0.25	24.69 (± 0.02)

Table 2 also contains the unit cell dimensions of the samples. These data are calculated from the 2θ values provided by XRD. CoPcNaY-200 has the same unit cell dimension ($a = 24.78 \pm 0.03$ Å) as CoNaY while a smaller value ($a = 24.69 \pm 0.02$ Å) is found for CoPcNaY-300. This decrease indicates clearly that the higher temperature can change the structure of the sample, probably by dehydration and the migration of cations from supercages to the external surface, since these processes depend on the temperature used [29, 30]. The decrease in the unit cell dimension may also arise from mesopore formation [31].

Figure 4 shows the thermograms for CoNaY, CoPcNaY-200 and CoPcNaY-300. Thermogram b shows an approximately 11% weight loss at about 430 °C which is due to the decomposition of cobalt phthalocyanine. The amount of nitrogen-containing organic compounds remaining in the zeolite after the extraction and purification steps is negligible, according to the thermograms. The weight loss of 11% corresponds to 2.2% nitrogen which is less than the 2.6% N determined by the Kjeldahl method (Table 1). The thermogram for CoPcNaY-300 shows a 16.5% weight loss which according to our BET and DRS results described before is due to the CoPc complexes which are mainly aggregates. These complexes also decompose around 430 °C. We expected to observe a small difference in the decomposition temperature of the monomeric CoPc in the zeolite supercages and the CoPc aggregated species. The CoPc molecules interacting with each other are possibly more stable than those of monomeric species. But this cannot be seen from our thermograms recorded with a heating rate of 10 °C/min.

The number of CoPc molecules present in CoPcNaY-200 was found to be 3.3 CoPc per unit cell (8 supercages) according to the TGA results, assuming that the whole weight decrease (11 wt.%) can be attributed to the thermal decomposition of the encapsulated CoPc. This assumption is not completely correct because our DRS results showed the presence of small quantity of aggregated CoPc in addition to the monomeric species. Therefore the number of CoPc molecules per unit cell is less than that value. We found that the original BET value is restored after burning off the CoPc of the sample of CoPcNaY-200. The specific surface area obtained for this sample following calcination at 450 °C for 5 h (the heating rate was 3 °C/min) was 838 m^2/g.

The thermograms were checked for combustion of H_2Pc which takes place at a temperature higher than 500 °C.

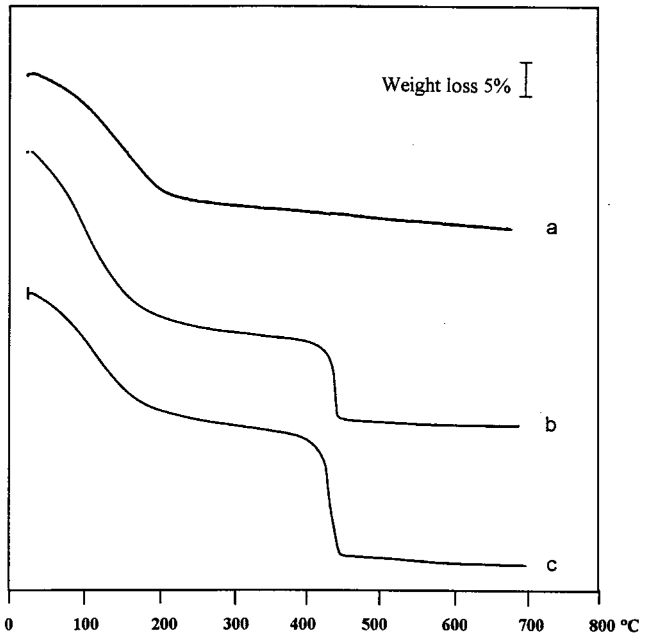

Figure 4. TGA thermograms for (a) CoNaY, (b) CoPcNaY-200 and (c) CoPcNaY-300.

Although the formation of H_2Pc is not expected, some observation in this regard for $CoPcNH_4Y$ has been reported [13]. No evidence of the presence of H_2Pc was found in our TGA results. Although there is a greater weight loss in CoPcNaY-300, the intense 640 nm band in the DR spectrum (Figure 1) and the split 1404 and 1426 cm^{-1} bands (Figure 3) for this sample indicate that a higher amount of aggregated CoPc was formed in CoPcNaY-300. The partial dealumination and/or lattice destruction are probably responsible for producing higher aggregated CoPc in the CoPcNaY-300 sample. The surface deposited species in zeolite encapsulated complexes of the type {Co(salen)}NaY have been reported to be produced from partially broken zeolite supercages [32]. These species cannot be eliminated by prolonged extraction with the sequence of solvents. A more drastic or different purification method may be needed to extract them.

Powder diffraction patterns for CoNaY, CoPcNaY-200 and CoPcNaY-300 are shown in Figure 5. The reason for the increasing background with higher 2θ in the XRD patterns is the fluorescence of cobalt due to the use of a copper X-ray tube. The higher background observed for the X-ray patterns of a and c is correlated to the higher amount of cobalt in these samples. There is a noticeable difference between the XRD patterns of the two cobalt phthalocyanines synthesized at 200 and 300 °C. There are two small reflections at 2θ values of 7.07 and 9.26 in addition to the characteristic reflections of zeolite Y [33]. These two reflections correspond to d-values of 12.50 and 9.55 Å respectively which belong to the β-form of metal phthalocyanines [34, 35]. Also in the XRD of CoPcNaY-200 very small reflections at the same 2θ values are observed. These belong to the very small quantity of surface deposited CoPc complexes formed in CoPcNaY-200. This small quantity was also manifested as a very weak shoulder band at 640 nm in the DR spectrum (Figure 1a). Metal phthalocyanines are known to be polymorphic materials with at least three established polymorphs: α-, β- and x [35]. According to Iwatsu, when the phthalocyanine crystal is small, the α-form is more stable than the β-form. As the crystal grows larger, the situation reverses and the β-form becomes more stable [36]. We believe that in the case of CoPcNaY-300, where many of the CoPc complexes are present as aggregates on the external surface and/or in the mesopores of the zeolite, they could grow larger and therefore be recognized in the XRD pattern (Figure 5c) whereas in the case of CoPcNaY-200, most of the phthalocyanine complexes are formed as monomers in the supercages and are so dispersed that no crystal of appreciable size could be formed.

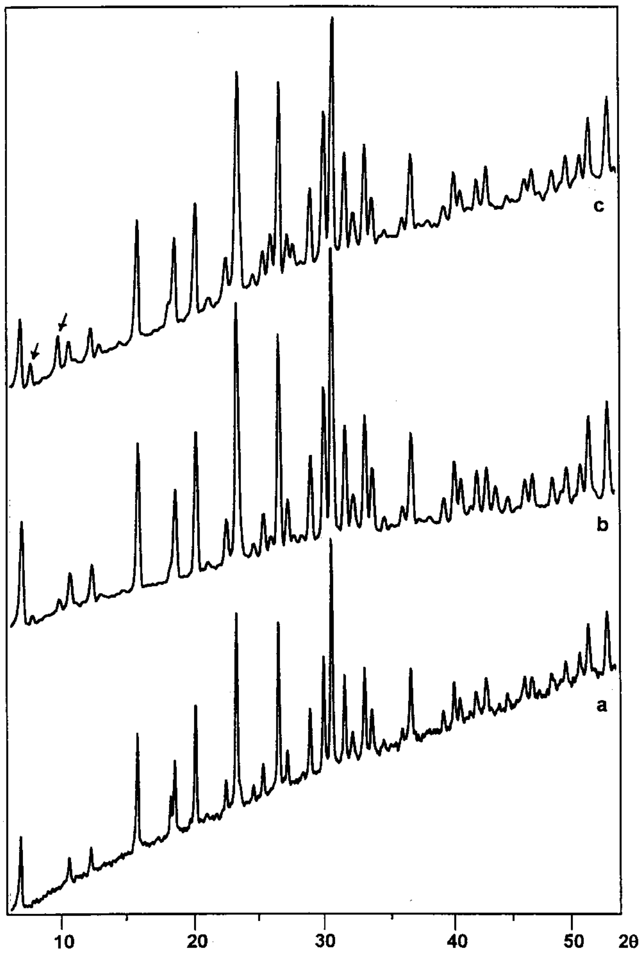

Figure 5. XRD patterns for (a) CoNaY, (b) CoPcNaY-200 and (c) CoPcNaY-300. The arrows in (c) indicate reflections of the β-phthalocyanine formed in CoPcNaY-300.

Conclusions

The examination of the encapsulation process of cobalt phthalocyanine into zeolite Y supercages by the template synthesis method showed that only a very small amount of aggregated CoPc can be detected if the synthesis is performed at 200 °C, the lowest recommended temperature for the synthesis. However, the amount of aggregated CoPc complexes is higher when the encapsulation occurred at the highest recommended temperature (300 °C). Formation of the monomeric encapsulated and aggregated cobalt phthalocyanines were detected by diffuse reflectance spectroscopy, FTIR and XRD. The thermogravimetric analysis confirms that only the CoPc complexes exist in the catalyst as nitrogen-containing compounds. According to the TGA and DRS results there is about one CoPc molecule per three supercages when the synthesis was performed at 200 °C. The 30% decrease of the pore volume also indicates that some of the supercages are occupied by cobalt phthalocyanine complexes. The BET, DRS and XRD data indicate, however, that an appreciable amount of aggregated cobalt phthalocyanine molecules are formed when the sample was synthesized at 300 °C. Aggregated cobalt phthalocyanine molecules may be hosted in the mesopores created by zeolite framework fragmentation during CoPc formation or could be deposited on the external surface at partially broken supercages. It is not possible to differentiate these two aggregated species at the present time. The decrease in the unit cell dimension of the zeolite Y after encapsulation of CoPc at 300 °C is related to the migration of the cobalt cations from the supercages and/or mesopore formation. These processes may motivate formation of aggregated CoPc. The surface deposited or mesopore hosted CoPc species are not eliminated by prolonged extraction with solvent and a different purification technique may be needed in order to remove them. The X-ray diffraction analysis showed that the aggregated cobalt phthalocyanines formed at the surface correspond to the β-polymorph of the phthalocyanine crystals.

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