



# HETEROGENEOUS CATALYSTS BASED ON SULPHONATED PHTHALOCYANINE MACROHETEROCYCLES AND SOLID MATRIXES

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Hybrid materials containing sulfo-substituted cobalt(II) phthalocyanines and various pre-treated solid organic and inorganic matrixes (poly(methyl methacrylate), polypropylene, silicon dioxide) have been obtained. It is shown that the plasma chemical activated polypropylene matrix results 85-90 % attachment of the macrocycles. Attaching the sulphonated cobalt(II) phthalocyanines to silicon dioxide matrix, ~65 % of the macrocycles were found to be bound.

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## Introduction

Water-soluble porphyrins and metallophthalocyanines are of great scientific interest nowadays due to their usage as efficient catalysts and photocatalysts in different oxidation processes<sup>1,2</sup> Recently a number of papers devoted to the use of macroheterocyclic compounds in photodynamic therapy of cancer<sup>3-5</sup> and as antiviral agents have been published<sup>6</sup> However, such compounds have a number of disadvantages restricting their use. Phthalocyanines are prone to self-association in a solution<sup>7</sup> and have a narrow range of photoactivation<sup>8</sup>

One of the promising areas in the chemistry of porphyrins and metallophthalocyanines is their immobilization in a solid matrix of organic and inorganic nature<sup>9,10</sup> eliminating a self-association of macroheterocycles and significantly extending a range of photoactivation. This approach provides additional thermal and morphological properties of a polymer matrix maintaining the desired properties of macrocyclic compounds.

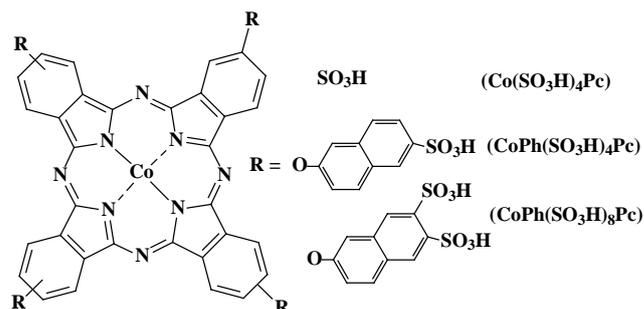
Numerous investigations<sup>11,12</sup> deal with the oxidation processes which are catalyzed by the metal complexes held on the surface of polymers or mineral carriers. The advantage of using a heterogeneous catalyst is the ability of its separation from the oxidation products and its further usage. However deactivation due to the sorption of polar products and a solvent in pores in the case of frequently used zeolite continues to be a serious factor decreasing the effectiveness of a catalyst.

Heterogenization of tetrapyrrol macroheterocyclic compounds on a polymer matrix surface is considered in this article.

## Material

Cobalt complexes of tetra-4-sulphophthalocyanine ( $\text{Co}(\text{SO}_3\text{H})_4\text{Pc}$ ), tetra-4-[(6'-sulfo-2-naphthyl)oxy]-phthalocyanine ( $\text{CoPh}(\text{SO}_3\text{H})_4\text{Pc}$ ) and tetra-4-[(6',8'-disulfo-2-naphthyl)oxy]phthalocyanine ( $\text{CoPh}(\text{SO}_3\text{H})_8\text{Pc}$ ) were prepared from the corresponding phthalonitriles and anhydrous cobalt chloride by template synthesis on heating according to known methods.<sup>13</sup> The structure of the product compounds was characterized by IR and electronic absorption spectroscopy and elemental analysis.<sup>14</sup>

$\text{Co}(\text{SO}_3\text{H})_4\text{Pc}$  (Sigma-Aldrich) were used without additional purification, the purity of reagent being controlled by spectral methods ( $^1\text{H}$  NMR, electron absorption and IR-spectra and elemental analysis).



The organic supports used were commercial nonwovens made from poly(ethylene terephthalate)-poly(methyl methacrylate) (PMMA) and polypropylene (PP). The PMMA has an average molecular mass of 20000 and a density of 203 g m<sup>-2</sup>. The PP has density of 400 g m<sup>-2</sup> and 4 mm thickness.

Cobalt phthalocyanine complexes were immobilized onto the copolymer by deposition from aqueous solutions with a concentration of  $\sim 5 \cdot 10^{-5}$  mol L<sup>-1</sup>. A nonwoven sample of 5×5 cm in size was immersed into 100 ml of a phthalocyanine solution, held for 2–4 h at 298 K, and freed of the solvent by evaporation. The sample was washed by

holding it for 40 min in 100 ml of distilled water and then slowly dried at 313 K. The amount of an immobilized complex was monitored by following electronic absorption spectra of the washing solutions.

An inorganic support used was a silicon dioxide matrix. A modified sol-gel technique was used to synthesize polymeric SiO<sub>2</sub> matrix.<sup>15,16</sup>

Tetraethoxysilane (TEOS) was used as a precursor. The following molar ratio of reactants: TEOS:H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH, 1:4.5:10 was used in the synthesis. Triethylamine was gradually added drop wise to the reaction mixture after its homogenization as a polycondensation catalyst. The resulting hybrid material was dried under vacuum by gradually raising the temperature up to 353 K. Drying was stopped after reaching a constant mass of the sample, the yield of the hybrid material being 22 %. After drying the hybrid material, it was washed 3 times with water: the amount of solvent in each of the washes was 20 ml; the suspension was stirred for 5 min, centrifuged and the solution was separated from the sediment.

## Results and discussion

In holding the macrocycles on the surface of a polymer sample for preliminary preparation of a carrier results in the formation of functional groups on inert materials surface, which is of great importance.

During the immobilization of tetrapyrrol macroheterocyclic compounds the bonding of a macrocycle with a polymer carrier can proceed due to covalent and ionic bonds with active functional groups which are on a polymer matrix surface and due to the coordinative integration of a central metal cation with an electrodonor polymer group.<sup>17,18</sup>

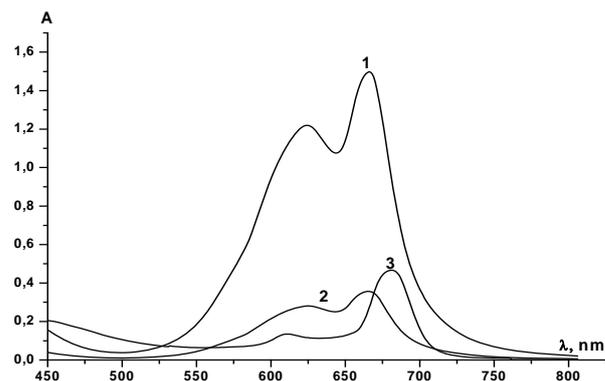
The activation of an organic polymer matrix has been carried out by two methods: 1) by the action of a microwave emission on a PMMA sample, 2) by preliminary treatment in a gas discharge on a PP sample.

In the process of a polymer matrix, the activation of PMMA by a microwave emission equal to 750 W, friability of its structure and the appearance of polarization groups on the surface takes place.<sup>19,20</sup> Changing the time of preliminary activation of a sample it is possible to obtain a hybrid material possessing different degree of phthalocyanine fixation.

The experimental data (Fig. 1, 2) show the possibility of obtaining a hybrid material by the immobilization of phthalocyanines (Co(SO<sub>3</sub>H)<sub>4</sub>Pc, CoPh(SO<sub>3</sub>H)<sub>4</sub>Pc, CoPh(SO<sub>3</sub>H)<sub>8</sub>Pc) onto the activated surface of PMMA. It should be underlined that a definite part of an immobilized macrocycle is connected with the carrier surface by means of weak non-specific interactions. In order to define the immobilization quality the samples of a heterogenic catalyst were washed many times with some portions of a distilled water till the appearance of colorless extracts.

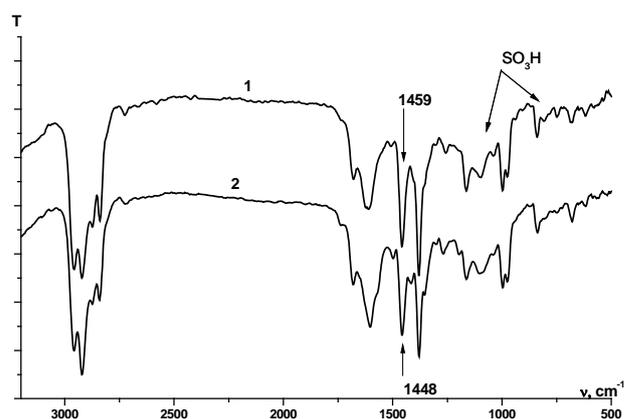
According to UV-Vis (Fig. 1) spectra of aqueous extracts it seems that 65-70 % of a catalyst is fixed on a polymer surface; it corresponds to  $\sim 3.25 \cdot 10^{-6}$  mol g<sup>-1</sup> of phthalocyanines on PMMA. According to the same method phthalocyanines were fixed on PP.

In the following experiments the activation was carried out by the action of a plasma discharge on the polymers. Under the action of a gas discharge on the polymers the oxidation of the surface and the appearance of acid containing functional groups take place.<sup>17,18</sup> This fact can be taken as an initiation stage for the processes of a radical grafting copolymerization on a material surface with an inclusion of a macrocyclic component.



**Figure 1.** UV-VIS spectra of water solution of Co(SO<sub>3</sub>H)<sub>4</sub>Pc – 1, UV-VIS spectra of washing solution – 2, UV-VIS spectra of hybrid material in quinoline – 3.

Firstly a polymer matrix treatment was carried out in a gas discharge excited in a solution volume (“end face” discharge) at pH values of the solutions equal 5-12, the time of discharge burning being changed from 5 to 25 minutes ( $I_{\text{discharge}} = 1$  A).



**Figure 2.** IR-spectra of hybrid material Co(SO<sub>3</sub>H)<sub>4</sub>Pc-Polypropylene obtained by mechanical activation matrix discharge: 1) pH 6, 2) pH 10. The time of discharge 20 minutes.

IR-spectra of hybrid materials obtained at different pH values coincide (Fig. 2). The bands in 1032-1039 cm<sup>-1</sup> region which are responsible for the vibrations of sulpho-groups which are in the structure of a phthalocyanine molecule undergo the process of transformation.

**Table 1.** Effective constants of diethyl dithiocarbamate oxidation rate by the oxygen of air at 298.15 K, pH 8.

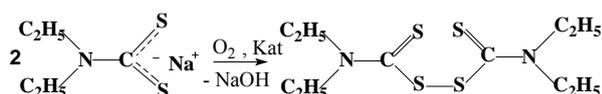
Macrocycle	$k_{\text{eff}} \times 10^4, \text{s}^{-1}$		
	PPMA microwave activation	PP plasma activation	SiO <sub>2</sub>
<b>Co(SO<sub>3</sub>H)<sub>4</sub>Pc</b>	2.3	25 – glow discharge 8 – “end face” discharge	0.88
<b>CoPh(SO<sub>3</sub>H)<sub>4</sub>Pc</b>	3.2	42 – glow discharge 14 – “end face” discharge	1.43
<b>CoPh(SO<sub>3</sub>H)<sub>8</sub>Pc</b>	4.6	28 – glow discharge 12 – “end face” discharge	0.99

A band in 1465 cm<sup>-1</sup> region which characterizes the linking of sulpho-groups with surface polymer groups has different position as well.

During a plasma-chemical treatment of PP surface in an acid solution and further immobilization of a macrocycle the given band is displaced into the region of 1459 cm<sup>-1</sup>. In a similar treatment in an alkaline solution the displacement is greater, it proceeds to the region of 1448 cm<sup>-1</sup>.

In the next working stage the activation of a polymer material was carried out by a glow discharge ( $I_{\text{discharge}} = 10\text{--}50 \text{ mA}$ ). An aqueous – alkaline solution at pH 10 was used as an electrolyte. The control of macrocycles immobilization was done with the help of IR and UV-VIS spectra. The fixation degree is 85–90 %. It was established that the optimum time of discharge burning was 17 min, discharge current being 45 mA.

Polymer samples with metallophthalocyanines on their surface possess catalytic activity in the model reaction of sodium diethyl dithiocarbamate soft oxidation<sup>21</sup> (effective rate constants for the oxidation are presented in Table 1).



Further the macroheterocycles fixation was carried out in an inorganic matrix of silicon dioxide. The degree of a complex fixation in a matrix was established to be 63–65 %. During the combined polymerization of orthosilicic acid and a macrocycle the latter is covalently fixed in the polymer matrix volume and it averts its washing out later.<sup>16,22</sup> A hybrid material on the base of phthalocyanines (Co(SO<sub>3</sub>H)<sub>4</sub>Pc) and polymer matrix of a silicon dioxide possesses as well a catalytic activity during the oxidation of sodium diethyl dithiocarbamate but in this case the activity is increased only two times as compared with homogenic version of catalysis in the presence of Co(SO<sub>3</sub>H)<sub>4</sub>Pc.<sup>16</sup> Hybrid material on the basis of macrocycle displays a photocatalytic activity in the process of oxidation of Rhodamin 6G.<sup>22</sup>

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