Surface Modification of Polypropylene by Water Soluble Co^{II} Phthalocyanine for Preparation of Catalytically Active Materials

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Hybrid materials based on organic polymers and Co^{II} tetrasulfophthalocyanines are obtained. Polymer matrix was previously activated before macrocycle anchoring. Activation was carried out by microwaves and plasma-chemical treatment of polymer surface. The influence of polymer surface pretreatment on the degree of macrocycle anchoring is shown. It is found that pretreatment of polymer matrix by glow discharge gives better anchoring of macrocycle for the most optimal time. Catalytic activity of synthesized materials in reaction of sodium diethyldithiocarbamate mild oxidation is studied. Samples activated by microwaves and face plasma-chemical discharge have shown close catalytic activity. Simultaneously, the catalytic activity of samples activated by pretreatment of polypropylene by glow discharge at the same conditions is in several times higher. Non-linear dependence of sodium diethyldithiocarbamate oxidation rate on temperature for all samples is found.

Keywords: Cobalt(II) tetrasulfophthalocyaninate, polypropylene, hybrid material, sodium diethyldithiocarbamate, oxidation, catalysis.

Поверхностная модификация полипропилена водорастворимым Co^{II} фталоцианином для создания каталитически активных материалов

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На основе органических полимеров и тетрасульфофталоцианина кобальта получены гибридные материалы. Полимерная матрица перед нанесением макроцикла подвергалась предварительной активации. Активацию проводили микроволновым излучением и с помощью плазмохимической обработки поверхности полимера. Показано влияние предварительной обработки поверхности полимера на степень закрепления макроцикла. Установлено, что предварительная активация полимерной матрицы тлеющим разрядом позволяет добиваться наибольшего закрепления макроцикла за наиболее оптимальное время. Для синтезированных материалов изучена каталитическая активность в реакции мягкого окисления диэтилдитиокарбамата натрия. Образцы, активированные микроволновым излучением и торцевым плазмохимическим разрядом, показали близкую каталитическую активность при окислении диэтилдитиокарбамата натрия на воздухе. Одновременно

Polypropylene Modified by Co[II] Phthalocyanine to Obtain Materials for Catalysis

с этим каталитическая активность образцов, полученных после предварительной обработки полипропилена в тлеющем разряде, в несколько раз выше. Для всех образцов установлена нелинейная зависимость скорости окисления диэтилдитиокарбамата натрия от температуры.

Ключевые слова: Тетрасульфофталоцианин кобальта, нетканый полипропилен, гибридный материал, диэтилдитиокарбамат натрия, окисление, катализ.

Introduction

Selective oxidation of mercaptans (RSH) with molecular oxygen to the desired products is topical in the case of complete processing of petroleum products. It supposes using of metal complex catalysts.[1-3] In addition, problems of organic synthesis of practically useful disulfides are solved by mild oxidation of R-SH compounds. As an example, synthesis of thiuram sulfides, that are used as vulcanization accelerators as well as for the preparation of intermediates in the manufacture of dyes and synthetic pharmaceutical products.[4-5] Oxidation of R-SH compounds in air under temperature about 298 K can improve the quality of desired product. It accords to the modern concept of "green chemistry" also.

Water-soluble metallophthalocyanines and their structural analogs are used now as catalysts in oxidation of RSH compounds.[2,6-11] However, there is a significant drawback of using these compounds – propensity to self-association in solution.[12-14]

Processes of self-association of metal phthalocyanines in aqueous and nonaqueous media affect their catalytic properties ambiguously. According to coordination mechanism of catalytic oxidation of RSH, shown in works,[2,15-18] association of phthalocyanine catalyst reduces its activity significantly due to the limitations on access to the central metal cation of the oxygen molecules and the substrate. However, in the case of realization of associative mechanism of catalysis, association of metallophthalocyanines may both increase catalyst's activity due to the interaction of the dimer with the substrate and reduce it.[19-22]

Promising direction of development of the phthalocyanine catalysts chemistry is their heterogenization on various carriers. Oxidation processes catalyzed by metallophthalocyanine complexes, mounted on a surface of mineral carriers (silicas, zeolites, carbon materials, *etc.*), are shown in works of number of laboratories.[23-26] Advantage of heterogeneous catalyst with use of phthalocyanines, mounted on polymer carriers, is the capacity to separate the catalyst from products of oxidation easily. However, deactivation of the catalyst due to the sorption of polar products and solvent in the pores of zeolites or silica remains a serious problem, which reduces the efficiency of the catalyst.

Synthetic organic polymers have no such drawback. They have excellent physical and mechanical properties with high chemical and photochemical stability under a mild oxidation of RSH-compounds. Immobilization of macroheterocyclic tetrapyrrole compounds on activated organic polymers by covalent and coordinative interactions can be applied to regulate catalytic activity of metallophthalocyanines.

Catalytic activity of Co[II] tetrasulfophthalocyaninate (CoPc), mounted on a surface of polypropylene (PP), at model reaction of oxidation of sodium diethyldithiocarbamate (DTC) in air is investigated in this work.

Experimental Section

Commercial (Sigma-Aldrich) cobalt tetrasulfophthalocyanine 99% (CoPc) was used in this work. IR (KBr) ν cm^{-1}: 1720, 1632, 1502, 1452, 1489, 1409, 1379, 1134, 1049, 935, 770, 618. There are intense bands at 770, 1049, 1134 cm^{-1}, caused by presence of sulfonic groups. Oscillations in 930–935 cm^{-1} range are caused by C-H vibrations of 1,2,4-substituted annulated benzene nuclei with porphyrazine ring.[27] ^{1}H NMR (500 MHz, CDCl$_3$, TMS) δ$_H$ ppm: 7.82 (Ar-H); 8.31 (Ar-H); 8.49 (Ar-H).
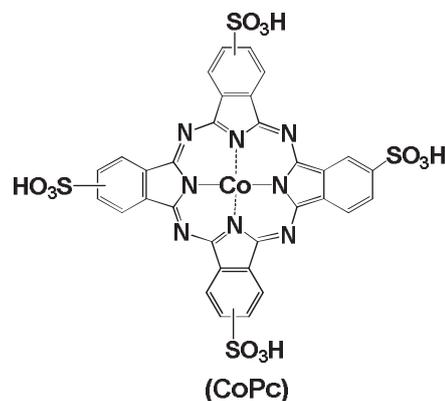
(CoPc)

CoPc immobilization. Non-woven polypropylene is used as solid phase carrier. Specific gravity is 400 g/m², thickness is 4 mm. Immobilization of CoPc on a surface of activated polymer matrix was carried out in CoPc solution with concentration of $5 \cdot 10^{-5}$ mol/l.

A sample of polymer material was previously weighed. Next, it was immersed in 100 ml of CoPc water solution and held for 8 hours under the temperature of 298.15 K. Then the solvent was evaporated and the resulting material was dried at 313 K. After drying, the sample was washed by soaking it in 100 ml of distilled water for 40 minutes and then dried again at 310 K. To determine the quality of immobilization, heterogeneous catalyst samples were repeatedly washed with portions of distilled water until a colorless extract. Amount of immobilized complex was controlled with UV-Vis spectra of washing solution.

Electronic absorption spectra were recorded on a double-beam spectrophotometer Shimadzu UV-1800 in range of 400–900 nm. Investigations were carried out in quartz cuvettes with depth of absorbing layer of 10 mm. IR-spectra were recorded using the FTIR spectrophotometer Avatar 360 FT-IR in frequency range 400–4000 cm^{-1}.

Pretreatment of polymer samples (activation) was carried out in plasma-solution systems with discharge excited in the volume of the electrolyte (so-called "end face") and on its surface (glow). Scheme installations, wiring diagrams, electrical properties of discharges and some chemical effects caused by their actions in solution and on the surfaces of polymeric materials are described in detail.[28-30]

The p*H* was varied in 5–12 range by adding the corresponding amount of nitric acid or sodium hydroxide to distilled water. Time of plasma-solution treatment was 5–30 min, ignition current of the «end face» discharge was 1 A, current of glow - up to 50 mA. Volume of liquid phase while using «end face» discharge was 500 ml, glow – 100 ml.

To activate the sample of polymer by microwaves, it was held in distilled water for 15 min, after this it was dried and then subjected to action of microwaves with power of 750 W.

Catalytic reaction. Experiment to study the kinetics of sodium diethyldithiocarbamate (DTC) oxidation reaction was carried out in special constructed cell with volume of 650 ml. The temperature was maintained 298.15 K with an accuracy of ±0.05 K. The solution with the necessary content of DTC to determine the catalytic activity was prepared based on phosphate buffer solutions. Air was supplied *via* microcompressor with a constant rate of 2 l/min.

With these parameters, the process of the reaction takes place in the kinetic region.[31] After the temperature of the reaction mixture had become constant, solution was mixed, the sample of 2 ml was selected to determine initial concentration and compressor was turned on. The moment of air supply was the beginning of the reaction. Samples of 2 ml were taken at regular intervals during the experiment to determine the current concentration of the DTC.

Method of DTC determination is the following: sample of 2 ml was moved to the flask of 25 ml, and 4 ml of $CuSO_4$ solution with concentration of 0.08 M was added. It has led to the formation of dark-brown precipitate – the complex of copper with DTC. Then mixture was stirred. After this 5 ml of chloroform and 0.05 ml of 50 % acetic acid were added to the resulting solution. Then it was extracted for 1.5 min. The organic layer was moved into a volumetric flask of 25 ml, and the remaining water solution of the Cu-DTC complex was extracted again to improve the accuracy of analysis. Collected solution of copper complex with DTC was diluted to the exact volume. The optical density of the solution was determined at a wavelength of 436 nm. DTC concentration was calculated with help of the known molar extinction coefficient.
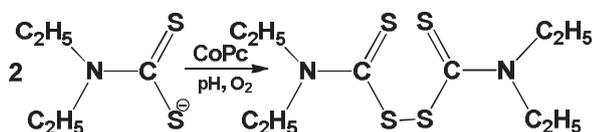
Under condition of constant oxygen and catalyst concentration and p*H* of solution the rate of oxidation reaction of DTC is described by first order kinetic equation:

$$dc/d\tau = -k \cdot c, \qquad (1)$$

where c − DTC concentration (mol/l); τ − time (s), k − effective reaction rate constant (s^{-1})

This is confirmed by the straightforwardness of kinetic dependences $\ln c = f(\tau)$ and the constancy of the rate constants calculated from the equation.

$$k = (1/\tau) \cdot \ln(c_0/c), \qquad (2)$$

where c_0 − initial DTC concentration, c – current (τ) DTC concentration.

It was found in prior experiments, that non-catalytic oxidation of DTC is very slow ($k = 1.7 \cdot 10^{-5}$ s^{-1})

The conversion was calculated from the equation:

$$\chi = (c_0 - c_\tau)/c_0, \qquad (3)$$

where c_0 – initial concentration of DTC, c_τ – DTC concentration at the current time.

Results and Discussion

CoPc Immobilization

It is known that CoPc in water solution at concentration range from $8 \cdot 10^{-3}$ to $8 \cdot 10^{-6}$ mol/l is presented by the associative forms mostly.[32,33] Previously, when using the same materials, we have shown that[34] in the visible region of CoPc's UV-Vis there are two intense absorption bands: corresponding to the associated state of the macrocycle (630 nm) and its monomer form (665 nm) (Figure 1). This fact allows us to control spectrally aggregation of the macrocycle that is important for immobilization. The chosen medium is quinoline. Refractive index of the quinoline is almost equal to the polymer carrier's refractive index that allows us to reduce light scattering to zero.
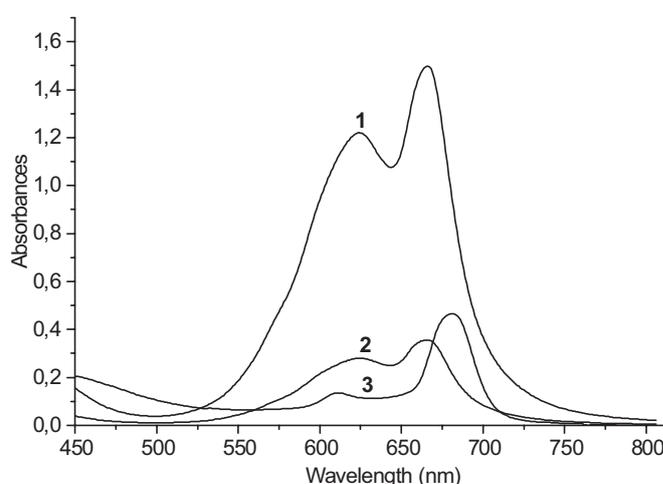
Figure 1. UV-Vis spectra of CoPc aqueous solution ($c = 8 \cdot 10^{-5}$ mol/l, at 298.15 K) (1), UV-Vis spectra of rinsing solution (at 298.15 K) (2), UV-Vis spectra of hybrid material in quinoline (at 298.15 K) (3).

PP Carrier Microwave Activation

When fixing the macrocycle on the surface of organic polymer matrix it is important to create functional groups on the surface of inert material, due to which macrocycle-polymer binding will be.[35,36] Some features of this process were studied in our previous researches.[35]

For example, the attack of polymer surface by various active particles occurs during the treatment of polymer matrix by plasma-chemical discharge. It leads to the fact that plasma-polymer interaction is multi-channel and multi-stage process. It should be noted that the depth of penetration of all active particles into the material is less than hundreds of nanometers. Obviously, the interaction between plasma and polymer is etching, *i.e.* removal of the surface polymer layer of desired thickness, or changing of functional groups composition and polymer structure. It allows to obtain surface of the polymer with desired properties. Meanwhile, it is clear to understand that both types of interaction are occurred during the plasma discharge treating of polymer surface. Such treat-

ment leads to increase of polymer surface energy and hence to increase of hydrophilicity and adhesion.[37,38] Besides, the UV-light generated by discharge plays an important role. Great amount of polar groups, including oxygenate, are formed on the polymer surface under the action of UV-light and fluxes of charged particles and radicals. The action of microwaves represents mainly thermal break of polymer groups and acceleration of polymerization that allows to carry out the insertion into polymer structure.

Upon activation of organic solid carrier by microwaves there are the loosening of its structure and the appearance of polarized groups.[39] During the time changing of sample activation it is possible to get the polymer with different degree of the surface loosening that gets different amount of bonded macrocycle on the surface of polymer.

Based on UV-Vis data it was determined that after repeated washing of obtained samples the catalyst is immobilized on the surface in amount of 65–70 % (Figure 1). It should be noted that the shape of the spectrum (3) (Figure 1) persists after the catalytic process.

Bands in range of 700 cm^{-1} and 1192–1197 cm^{-1} of CoPc-PP IR spectra (Figure 2) corresponding to vibrations of sulfonic groups undergo transformation. At the same time there is a shift to 30–40 cm^{-1} of bands at 1630 cm^{-1}, 1418

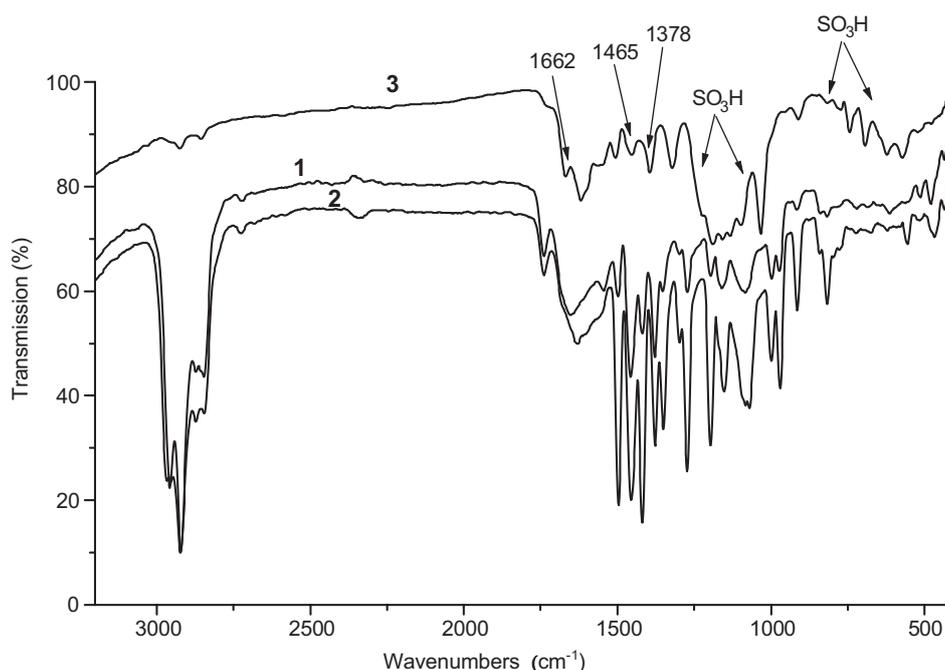cm^{-1} which characterizes the state of the methyl group of polypropylene.

There is no band in range of 970 cm^{-1} and emergence of a new band at 2956 cm^{-1}. It indicates the surface bonding of the CoPc. Obviously, besides covalent bonding, Co-phthalocyanine is linked to the carrier surface by weak nonspecific interactions. Experimental data (Figures 1 and 2) indicate the possibility of phthalocyanine immobilization on an activated organic polymer. Electronic absorption spectrum of the hybrid material immersed in quinoline (Figure 1) (comparison cell – pure quinoline) is characteristic for the unassociated CoPc form. It creates conditions for increase of the catalytic activity of the resulting hybrid material. Thus already 9 minutes of activation result in binding of 65 % of the macrocycle, which corresponds to 3.25·10^{-6} mol of phthalocyanine.

PP Carrier Activation in Plasma-Solution Systems

It is known, that impact of gas discharge on polymer material gives oxidation on its surface and appearance of oxygen-containing functional groups.[39,40] In fact it can be represented as a stage of initiation of radical grafting on the surface of the material with the inclusion of the macrocyclic component.

Table 1. CoPc – PP material.

c_{CoPc}, mol/l	Volume of CoPc solution for immobilization, ml	PP sample area, mm^2	Immobilized CoPc, %	Degree of immobilization g_{PCoPc} / g_{PP}
5·10^{-5}	100	5	65	0.041
5·10^{-5}	100	7	67	0.047
5·10^{-5}	100	5	68	0.042
5·10^{-5}	100	6	70	0.044
5·10^{-5}	100	6	70	0.054

Figure 2. IR spectra of CoPc (1), PP (2), CoPc – PP material (3) in KBr.
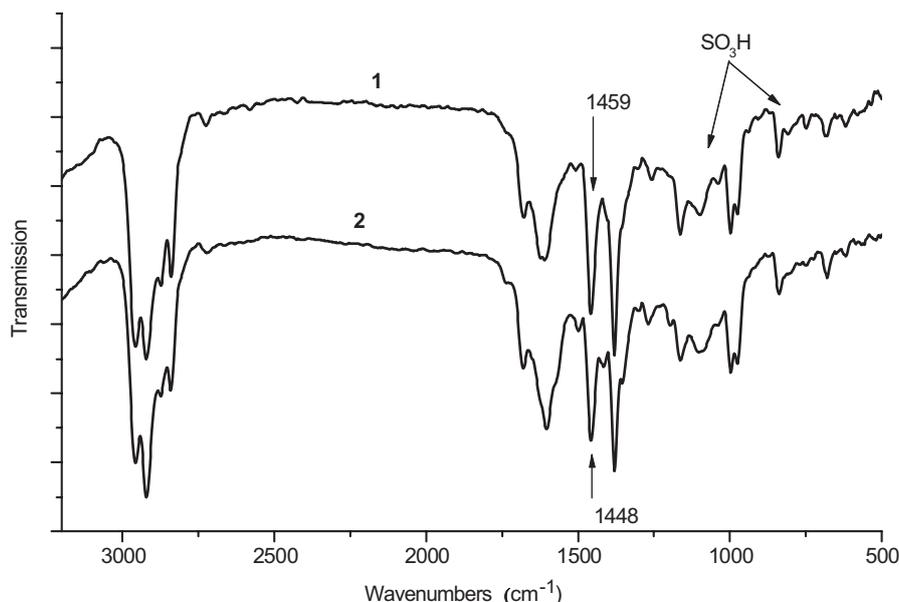
Figure 3. IR spectra of CoPc-PP hybrid material obtained at face discharge activation of polymer carrier: p*H*=6 (1), p*H*=10 (2). (t_{treat}=20 min, c^0_{CoPc}=8·10^{-5} mol/l).

Figure 3 shows IR-spectra of hybrid materials obtained by treatment of polymer matrix by "end face" discharge. Acidity of the liquid phase of plasma-solution system virtually has no effect on the character of the spectrum.

Bands in 1032–1039 cm^{-1} range of IR spectra of obtained materials corresponding to vibrations of sulfonic groups are transformed. A decrease of intensity of the vibrations, indicated lowering the degree of rotational freedom of sulfonic group, is observed. Also band in range of 1465 cm^{-1}, characterized bonding of sulfonic groups with surface groups of the polymer, has different positions. Upon plasma chemical treatment in an acidic solution and subsequent immobilization of CoPc this band is shifted to 1459 cm^{-1}. If the same treatment is in the alkaline solution, shift of this band is much more significant (to 1448 cm^{-1}), these results show the formation of new vibrations -O-O-S-O-, that are linked with covalent interaction between sulfonic group of metallophthalocyanine and the activated polymer surface.

Degree of CoPc binding (up to 80 %) on polymer carrier upon preliminary treatment of polypropylene in basic medium (p*H*=10) using the "end face" discharge was slightly higher than in the case of acidic medium (p*H*=6) (Figure 4).

The plasma-solution activation of the polypropylene by glow discharge, initiated above the surface of the electrolyte solution, also increases degree of catalyst binding up to 85–90 %. Ignition current of discharge was 45 mA, time of treatment was 15–20 min, solution of NaOH with p*H*=10 was used.

Catalytic Activity

It is known, that cobalt tetrasulfophthalocyaninate has a catalytic activity in rather narrow concentration range,[21-22] that is caused by its significant association if concentration is higher than 10^{-5} mol/l. We carried out a preliminary
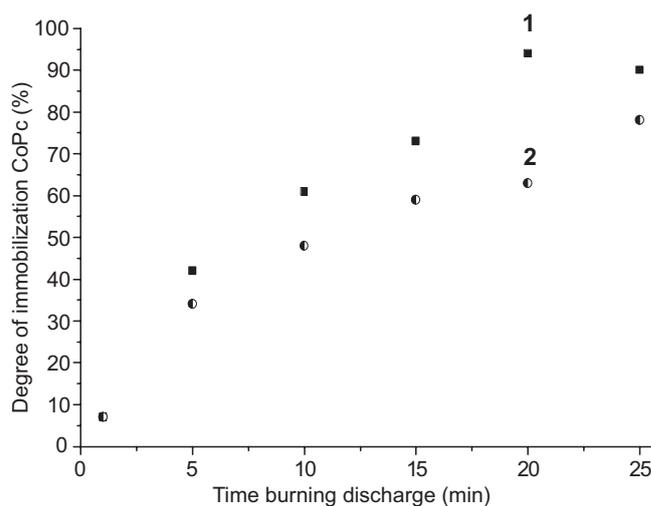
Figure 4. CoPc immobilization (%) on PP at different face discharge treatment time. p*H*=6 (1), p*H*=10 (2). (c^0_{CoPc}=8·10^{-5} mol/l).

experiment of catalytic oxidation of DTC in presence of homogeneous catalyst – solution of CoPc with concentration of 5·10^{-5} mol/l. Value of the effective rate constant k_{ef} was 0.8·10^{-4} s^{-1}. Catalyst based on polypropylene-CoPc activated by microwaves has shown higher catalytic activity. Value of k_{ef} in the presence of the sample of catalyst with mass of 9·10^{-3} g was 4.6·10^{-4} s^{-1}.

Investigation of the kinetics of DTC oxidation at 298.15 K in the presence of catalysts activated by plasma method (Figure 5) has shown that the sample activated by a glow discharge (k=22·10^{-4} s^{-1}) is in 3 times more active than the sample activated in "end face" discharge (k=8·10^{-4} s^{-1}), which is probably caused by the greater degree of loosening of the catalyst surface.
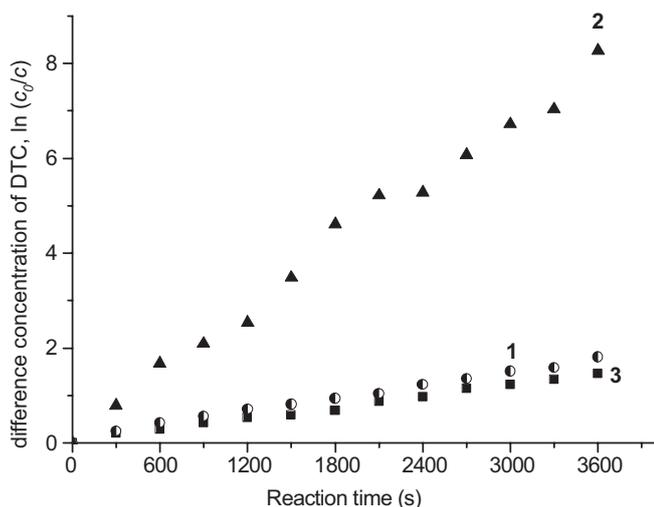
Figure 5. DTC catalytic oxidation (at 298.15 K). PP carrier was activated by "end face" discharge (1); PP carrier was activated by glow discharge (2); PP carrier was activated by microwave radiation action (3) ($c_{DTC}=3 \cdot 10^{-3}$ mol/l, $m_{cat}=7.5 \cdot 10^{-3}$ g, pH=8).

Dependence of catalytic activity of hybrid materials, obtained by activation by plasma chemical discharge, from temperature has non-linear character (Figure 6).
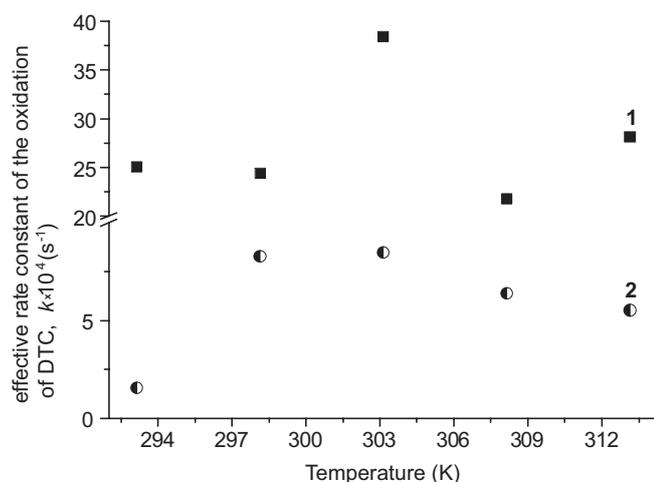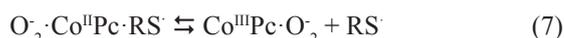

Figure 6. Dependence of DTC oxidation rate on temperature at pH = 8 in the presence of catalyst, obtained by the treatment in plasma-solution systems with glow discharge (1) and face discharge (2).

The highest activity of catalyst in all cases was achieved at 303.15 K, probably due to equilibrium processes occurring in the reaction mixture. This fact is probably caused by the specific coordination interaction between the immobilized phthalocyanine catalyst and DTC. The dependence of the catalytic activity of the obtained materials in the pH range of 4–12 is also not linear, the greatest activity is observed with pH values of 8–9. It is explained by shift of equilibrium (4) towards the existence of thiol as an ion RS$^-$:

$$RSH + OH^- \leftrightarrows RS^- + H_2O \tag{4}$$

The data obtained let us to make conclusion, that oxidation is caused by coordination of oxygen molecule by central cation of metallophthalocyanine from one side and anion of DTC from other side of macrocycle plane and electron transfer from the oxygen to the substrate through the cobalt cation, which is consistent with the literature.[15-20]

This mechanism can be represented by the following scheme of elementary stages known from the literature:[6,7,19,41,42]

$$Co^{II}Pc + RS^- \leftrightarrows Co^{I}Pc \cdot RS \tag{5}$$

$$Co^{I}Pc \cdot RS^- + O_2 \leftrightarrows O_2^- \cdot Co^{II}Pc \cdot RS^- \tag{6}$$

$$O_2^- \cdot Co^{II}Pc \cdot RS^- \leftrightarrows Co^{III}Pc \cdot O_2^- + RS^- \tag{7}$$

$$2RS^- \rightarrow RS\text{-}RS \tag{8}$$

$$Co^{III}Pc \cdot O_2^- \leftrightarrows Co^{II}Pc + O_2 \tag{9}$$

Limiting stage of the oxidation process is formation of free radicals RS$^-$, which then form a chain RS-SR.

Table 2. Catalytic activity of hybrid material CoPc-PP (Activation of PP in a glow discharge within 15 min; I=45 mA, pH=8.5; T=303.15 K).

Sample	Cycles	Reduction catalytic activity, %	χ_{RSSR}, %
1	15	7	95.36
2	17	9	94.91
3	16	8	95.11
4	15	9	95.28
5	16	9	94.56
6	16	8	94.82
7	17	8	95.27
8	15	7	95.04

The obtained samples were tested in a series of catalytic cycles. The results show the possibility of using the catalysts CoPc−PP produced by activation by plasma method in not less than 15 consecutive cycles of oxidation with a degree of the DCT transformation of 95 %. It complies with the requirements to heterogeneous phthalocyanine catalyst for oxidation of mercaptans using molecular oxygen as oxidant.[43]

Conclusions

Thus, the possibility of obtaining an effective heterogeneous catalyst for the oxidation of sodium diethyldithiocarbamate is presented in the work. It is shown, that plasma-chemical pre-treatment of polymer matrix allows high catalytic activity of hybrid material. Based on resulting and literature data the mechanism of obtained catalysts action was supposed.

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