

Sulfonated Co(II) phthalocyanines covalently anchored at organic polymers as catalyst for mild oxidation of mercaptans

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ABSTRACT: Current work is devoted to covalent immobilization of sulfonated derivatives of cobalt phthalocyanines "Merox catalysts" on the surfaces of polypropylene and polyethylene terephthalate. Their catalytic activity in reaction of mild oxidation of sulfur compounds to disulfides with oxygen of the air was studied. Anchoring of the catalyst on this polymer prevents its leaching and promotes its efficient recovering and recycling without significant loss of catalytic activity.

KEYWORDS: sulfonated Co(II) phthalocyanines, polymer, covalent immobilization, materials, catalyst, oxidation of mercaptan.

INTRODUCTION

Oxidation of mercaptans to disulfides is one of the main steps of oil sweetening. This process is important for petrochemical industry, green chemistry and biochemistry [1–3]. Mercaptans and other sulfur compounds, such as thiocarbamates, contained in gasoline and naphtha fractions of refined oil and in liquefied propane-butane mixtures, are extremely dangerous because of their high toxicity, potential threat to the environment of the environment and poisoning of the catalyst that reduces the quality and increases the cost of refining technology [4–6]. It is therefore necessary to remove such compounds from oil. There is the simplest and most common method

among the many methods of mercaptans removing from oil fraction — sweetening that includes mercaptans oxidation in the presence of tetra sulfonic acid of cobalt phthalocyanine [7-10].

The cobalt is interesting as central metal cation because of features of its electronic structure. Cobalt cation (Co²⁺) has electronic configuration [Ar] 3d⁷ 4s⁰ and it is coordinatively unsaturated as a part of the metallophthalocyanine. The cobalt forms stable enough molecular complex and saturates its electronic stucture by taking the ligand (or substrate) into fifth coordination state. Meanwhile, it is possible that ligand (for example molecular oxygen) could be coordinated into sixth coordination state due to transition Co^{II} \rightarrow Co^{III} within metal complex. Biligand complex formed in this case is labile. It is interesting from the point of view of mechanisms of catalytic processes [11, 12] with cobalt

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phthalocyanines, that involve the transfer of electrons from the oxidant to substrate through the macrocycle. Herewith, multistep transitions $Co^{I} \leftrightarrow Co^{II} \leftrightarrow Co^{II}$ are realized. From that point of view phthalocyanine complexes with lanthanides is also interesting. However, the peculiarity of such compounds is formation of multideck structures, in which there are electronic saturation and steric blocking of the complexing metal [13].

Cobalt tetrasulfophthalocyanines are self-assembled in water-alkaline mediums. That is why it is necessary to replace them by less associated in water solutions derivatives or fix at the supports [14–16]. Thus, oxidation of lower mercaptans is easier in case of homogeneous process, but oxidation of high-molecular mercaptans of naphtha and gasoline fractions is easier in case of heterogeneous one [17].

Due to technological features of removing and regeneration of homogeneous phthalocyanine catalyst [18], it is more effective to use cobalt tetrasulfophthalocyanine and its derivatives heterogenized on the surface or in volume of the support. For example, there are works showing anchoring of cobalt tetrasulfophthalocyanine at supports of coal-graphite fabric [19–21], silica [22– 24], zeolites [25, 26]. However, in case of electrostatic anchoring or adsorption of catalyst in pores of substrate there are desorption and leaching of catalyst during the process. That is why covalent immobilization is the most effective method to anchor phthalocyanine molecule at polymer matrix. Besides, this method allows protecting the catalyst from erosion and helps protect the environment [27, 28].

In our previous works [16, 24], catalysts were obtained through covalent immobilization of sulfonated cobalt phthalocyanines on the surface of silica matrix and their catalytic activity was tested in the reaction of sodium diethyldithiocarbamate oxidation. The results showed an adequate effectiveness of the catalyst for oxidation of mercaptans to disulfides. However, there is difficulty in recycling of the catalyst caused by obturation of silica pores.

The authors [29] reported about obtaining of efficient catalyst through covalent anchoring of cobalt tetrasulfophthalocyanine at aminomethylated polystyrene. They used pyridine medium for immobilization of phthalocyanine pretreated with thionyl chloride for the formation of active groups on the surface. Anchoring of macrocycle was due to sulfone-amide bond formation. CoPc-support was reused in oxidation of wide range of mercaptans and showed a good result. There are different methods of polymer matrix pretreatment for immobilization of phthalocyanines, for example chemical halogenation of polymer [30] or joint synthesis of polymers with metallophthalocyanines [31, 32]. In our opinion, chemical methods of polymer pretreatment are technologically more difficult and dangerous for environment.

Previously in our work [33, 34] the polymer treated by microwave with further immobilization.

CoPc-support showed good activity in catalytic oxidation of sodium diethyldithiocarbamate of oil fraction. The main drawback of this method is high initial concentration of macroheterocycle solution to achieve the necessary degree of immobilization on surface of polymer matrix. The catalyst for oil sweetening based on sulfonated derivatives of cobalt phthalocyanine immobilized on the surface of polymer pretreated in plasma-chemical plant is obtained in our work. Main advantages of CoPcsupport are technological simplicity of active component immobilization on the surface of the carrier, high degree of phthalocyanine anchoring, ease of application of the catalyst in oxidation process and its stability in oxidation. The result of plasma-chemical treatment is formation of a large number of active groups (radicals) on the surface giving a desirable degree of phthalocyanine immobilization. Plasma-chemical method is technologically more convenient because it allows activating a large area of polymer without any chemical pollution of environment. CoPc-support was investigated in oxidation of sodium diethyldithiocarbamate and 2-mercaptoethanol by air oxygen. It showed a good result. Disulfide (Thiuram E) was obtained in reaction of sodium diethyldithiocarbamate mild oxidation with high purity. Further obtained Thiuram E was used for organic synthesis by our colleagues.

RESULTS AND DISCUSSION

Preparation and characterization of catalyst

Increasing the size of peripheral substituent promotes distancing of functional group from phthalocyanine macrocycle (Fig. 1) conjugate and increasing its acidity. It leads to a better anchoring of catalyst at the surface of polymer. Increasing the number of sulfonic groups of phthalocyanine molecule promotes increasing the area of interaction of phthalocyanine with polymer matrix.

Covalent immobilization of phthalocyanine on the support is confirmed by IR-spectral analysis (the example of the spectrum is presented in the supplementary material Figs S1 and S2). There are bands of IR-spectra at 700 cm⁻¹ and 1192–1197 cm⁻¹ undergoing transformation, they are responsible for vibrations of sulfonic groups of



Fig. 1. Structure of metallophthalocyanines

CoPc. At the same time there is shift of $30-40 \text{ cm}^{-1}$ of bands at 1630 cm⁻¹, 1418 cm⁻¹ characterizing the state of methyl group of PP. The lack of band at 970 cm⁻¹ and appearance of new band at 2956 cm⁻¹ indicate surface anchoring of CoPc. Obviously, besides cobalt phthalocyanines immobilized covalently there is part of them anchored by weak electrostatic interactions. Simultaneously there is almost no peaks characteristic of the carbonyl groups of polymer molecule. There are characteristic bands of absorption at 630 nm and 685 nm for CoPcI, 640 nm and 700 nm for CoPcII and CoPcIII of UV-vis spectra of anchored phthalocyanines in quinoline analysis (the example of the spectrum is presented in Fig. S3). Degree of anchoring of phthalocyanines was from 0.572 mmol/g to 0.678 mmol/g. It is found that anchoring of CoPcI, CoPcII и CoPcIII on the surface of PP occurs through one fragment of peripheral substituent (Scheme 2a), anchoring on the surface of Lavsan occurs through two fragments of peripheral substituent (Scheme 2b). It should be noted that possibility of anchoring of the phthalocyanine on PP through two sulfonated fragments and in case of CoPcIII through four sulfonated fragments is not excluded.

The investigations of thermal destruction of obtained materials were additionally carried out. Corresponding thermograms are presented in Figs S4-S6. There is a decrease of destruction temperature for nine degrees in case of anchoring of CoPcII on polypropylene. It is obviously reflects the beginning of the material destruction with breaking of polymer-macrocycle bond. In case of CoPcIII immobilization is occurred throug one more adiitional bond (second sulfonic group as part of the naphthalene fragment of phthalocyanine peripheral substituent). It causes insignificant increasing of the temperature of destruction beginning to 423 °C. It is interesting, that the second stage of melting on DSC curve is appeared. The first stage of melting of hybrid material 148-150 °C reflects melting of pure polymer, the second stage 159-160°C is probably connected with melting of surface layer with the phthalocyanine

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Fig. 2. Scheme of heterogeneous aerobic oxidation of mercaptan to disulfide

anchoring on it. Summation of obtained spectral and thermal data suggests primary immobilization of the phthalocyanine on the surface of the polymer. The effects reflected inserting of the macrocycle into the size of the structure (changing of polymer's elementary unit) of polymer are not found.

Catalytic oxidation of RSH

Catalytic experiments were carried out using model reactions proceed according to Fig. 2 in water-alkali mediums in pH range 8–13. Optimal conditions for plasma-solution activation of polymer by glow discharge, initiated on surface of electrolyte solution, are ignition current of 45 mA, time of treatment of 17 min, NaOH solution with pH 10 [35].

Catalytic oxidation of substrates was carried out in presence of phthalocyanine catalysts under aerobic conditions. Investigated compounds were oxidized to corresponding disulfides almost with 100% yield of final product (Table 1). Air was bubbled with rate of 2 L/min through solution of oxidized substrate during catalytic oxidation of RSH. The end of the reaction was controlled by external signs. There were change of solution color from black-green to bluish-green in oxidation of 2-mercaptoethanol and loss of brown-yellow precipitate in oxidation of N,N-diethylcarbamodithioate (DTC). Kinetic curves of DTC oxidation are presented on Fig. 3 and Fig. S7.

Investigation of dependence of oxidation rate and disulfide yields on pH shows that optimal pH values are 9-10 at lower values of pH yield and purity of disulfide are not good enough. At pH > 10, alkali using was increased but the yield and purity were not changed (Table 2).

TOF^a, h⁻¹ Ν Mercaptan Disulfide Time, min Yield, % H_2 H_2 H_2 SH 97 50 62.4 1 OH HO 2 94 72.2 65 C_2H_5 C_2H_5 SН

 Table 1. Aerobic oxidation of RSH to disulfides in water-alkali solution pH 10 in presence of catalyst based on CoPcI and polypropylene matrix

^aTOF: Number of cycles per hour



Fig. 3. Kinetic curves of DTC oxidation in presence of immobilized macrocycles on PP (1) CoPcI; (2) CoPcII (3) CoPcIII (4) H₂PcII (5) H₂PcIII. pH 8 under 25 °C, initial concentration of DTC is 3.62×10^{-3} M

N	pН	CoPcI-PP		CoPcII-PP		CoPcIII-PP	
		Time, min	Yield, %	Time, min	Yield, %	Time, min	Yield, %
1	8	70	88	56	92	52	94
2	8.5	68	92	52	93	49	94
3	9	67	93	52	94	46	95
4	9.5	65	93	50	94	45	95
5	10	65	94	50	94	45	95
6	11	63	94	50	94	45	95
7	12	63	94	49	94	44	95
8	13	62	94	49	94	44	95
N	pН	CoPcI-Lavsan		CoPcII-PP-Lavsan		CoPcIII-PP-Lavsan	
		Time, min	Yield, %	Time, min	Yield, %	Time, min	Yield, %
1	8	69	93	52	95	49	97
2	8.5	67	95	50	95	46	97
3	9	65	95	50	95	44	97
4	9.5	65	95	47	95	44	97
5	10	64	96	43	96	43	98
6	11	63	96	43	96	43	98
7	12	63	96	43	96	42	98
8	13	62	97	43	96	42	98

Table 2. Yield of disulfide and time of DTC oxidation depending on pH of medium, at 25 °C

Results in Table 2 show that catalyst based on CoPcIII has the best catalytic activity. Probably, it may be caused by better stability of macrocycle at surface due to bindings between two sulfonated bridges. Slightly higher activity of catalysts immobilized on the surface of Lavsan probably caused by greater number of interactions of catalyst with polymer. Similar investigations of catalytic activity of polymer materials with anchored metal-free complexes H_2PcII µ H_2PcIII on their surface were carried out for comparison. Kinetic curves of DTC oxidation in

the presence of such catalysts are presented on Fig. 3. Effective constants of the rate are 0.8×10^{-5} s/g and 1.4×10^{-5} s/g for H₂PcII and H₂PcIII respectively that is within the error is similar to the rate of non-catalytic DTC oxidation [36]. It is consistent with the absence of catalytic activity of phthalocyanine-ligands and shows that polymer matrix does not affect the coordination unit of the phthalocyanine macrocycle. Since otherwise the carrier immobilized by metal-free macrocycles should exhibit catalytic activity.

Thus, the obtained data shows the dependence of oxidation reaction on pH of medium (optimal values are 9-10) and size of peripheral substituent of sulfonated phthalocyanine. Increasing the number of sulfonated groups and distancing them from conjugated phthalocyanine system led to better anchoring and catalytic activity of macrocycle. Similar dependences are observed in case of 2-mercaptoethanol oxidation.

Possibility of recycling of heterogeneous catalysts in oxidation processes was investigated on the next step. Oxidation reaction of DTC was used as model (Table S1). After completion of the reaction, the catalyst was mechanically removed from the reaction mixture, washed in 100 mL of distilled water and reused.

All catalysts was used for at least seven cycles without significant loss of catalytic activity and preactivation. In all cycles the time of reaction and yield of disulfides remain almost constant that is a good indicator for heterogeneous catalyst. It should be noted that catalytic activity of heterogenized phthalocyanines CoPcI, CoPcII and CoPcIII is comparable to activity of homogeneous catalyst CoPcI, and in case of CoPcIII-Lavsan catalyst exceeds it. Significant advantage of such catalysts is possibility of recycling without additional activation and easy removal from the reaction mixture. Probably these catalysts are more profitable from the technological and economic point of view due to advantages described above, despite of lower catalytic activity than the homogeneous CoPcI. It let us to suggest that specific activity of these catalysts is somparable with catalysts traditionally used in Merox process [8–10].

EXPERIMENTAL

Polymer materials

Commercial samples of polymers were used in the work. Nonwoven polypropylene (PP), specific density 400 g/m², thickness 4 mm. Nonwoven polyethylene terephthalate (Lavsan), specific density 200 g/m², thickness 3 mm.

Synthesis

Cobalt phthalocyanine tetrasulfonic acid. Cobalt phthalocyanine tetrasulfonic acid (CoPcI) (Fig. 1) was synthesized by a known Weber–Busch method

[37]. Obtained blue-green precipitate was separated by filtrating, washed with ethanol-methanol mixture (3:1) and dried. Structure of complex was confirmed by methods of electronic absorption spectroscopy, IR-spectroscopy, ¹H NMR and elemental analysis. IR spectra (KBr): v, cm⁻¹ 1720, 1632, 1502, 1452, 1489, 1409, 1379, 1134, 1049, 935, 770, 618. Elemental analysis for $C_{32}H_{16}N_8O_{12}S_4Co$, %: C 39.51, H 1.87, N 11.53. Found C 37.82, H 1.79, N 11.18. ¹H NMR (500 MHz): δ_H , ppm 7.91 (Ar-H), 8.29 (Ar-H), 8.53 (Ar-H).

Cobalt tetra-4-[(6'-sulfo-2-naphthyl)oxy]phthalocyaninate. Cobalt tetra-4-[(6'-sulfo-2-naphthyl)oxy]phthalocyanine (CoPcII) (Fig. 1) was synthesized and purified by a known method [38-40]. Mixture of tetra-4[(6'-sulfo-2-naphthyl)oxy]phthalonitrile of potassium (0.78 g, 2 mmol) and anhydrous cobalt chloride (0.065 g, 0.5 mmol) was heated with stirring to a temperature of 190-195 °C and maintained in this state for 1 h. Formed cobalt phthalocyanine was extracted from cooled reaction mixture by dimethyl sulfoxide and precipitated from the extract by absolute ethanol. Obtained precipitate was filtered, washed with ethanol in a Soxhlet apparatus. Final purification was chromatography on silica gel M 60 (eluent DMF/water in volume ratio 1:1). Yield was 0.39 g (54%), blue-green powder, soluble in water, mixture of DMF/water, DMSO, water-alkali solution. IR spectra (KBr): v, cm⁻¹ 1045 (v_s S=O), 1103 (v_{as} S=O), 1205 (v Ar–O–Ar). Elemental analysis for $C_{72}H_{40}N_8S_4O_{16}Co$, %: C 59.22, H 2.74, N 7.68. Found C 58.42, H 2.70, N 7.62. ¹H NMR (500 MHz): δ_H, ppm 7.50 (Ar-H), 7.54 (Ar-H), 7.69 (Ar-H), 7.91 (Ar-H), 8.02 (Ar-H).

Cobalt tetra-4-[6',8'-disulfo-2-naphthyl)oxy]phthalocianinate. Cobalt tetra-4-[6',8'-disulfo-2-naphthyl)oxy] phthalocianinate (CoPcIII) (Fig. 1) was synthesized and purified by described above method [38–40]. 1.01 g (2 mmol) of dipotassium 4-[6',8'-disulfo-2-naphthyl)oxy] phthalonitrile was used for synthesis. Yield was 0.53 g (59%), blue-green powder, soluble in water, mixture of DMF/water, DMSO, water-alkali solution. IR spectra (KBr): v, cm⁻¹ 1039 (v_s S=O), 1103 (v_{as} S=O), 1210 (v Ar–O–Ar). Elemental analysis for C₇₂H₄₀N₈S₈O₂₈Co, %: C 48.57%, H 2.25%, N 6.30%, S 14.39%. Found C 48.32, H 2.20, N 6.23. ¹H NMR (500 MHz): $\delta_{\rm H}$, ppm 7.47 (Ar-H), 7.62 (Ar-H), 7.76 (Ar-H), 7.99 (Ar-H), 8.21 (Ar-H), 8.59 (Ar-H), 8.94 (Ar-H), 9.06 (Ar-H).

Tetra-4-[(6'-sulfo-2-naphthyl)oxy]phthalocyaninate. Mixture of 0.001 mol of potassium salt of 4-[(6'-sulfo-2'-naphtyl)oxy]phthalonitrile and 0.30 g (0.005 mol) of carbamid was heated with stirring to a temperature of 190–195 °C and kept under constant conditions for 1 h [38]. Pre-treatment of the phthalocyanine was carried out by washing of it with 18% solution of hydrochloric acid to a colorless filtrates. Next, the powder war dried. The precipitate was further purified by the extraction with ethanol in Soxhlet apparatus. The final purification was carried out by chromatography with silica gel M60 using mixture DMF:water (1:1) as eluent. The yield was 0.20 g (54%). Elemental analysis for C₇₂H₄₂N₈O₁₆S₄·12H₂O, %: C 53.4, H 4.0, N 6.9, S 7.9. Found C 52.8, H 3.8, N 4.9, S 8.1. UV-vis (DMF): λ_{max}, nm 674, 704, 646_{infl}, 613_{inf}, 336; (H₂O): 606; (NaOH): 677_{infl}, 639; (H₂SO₄): 849, 909, 748. IR spectra (KBr): v, cm⁻¹ 1040 (v_s S=O), 1109 (v_{as} S=O), 1200 (v Ar–O–Ar), 1007 (H₂Pc). Obtained phthalocyanine is a blue-green powder soluble in DMF, concentrated sulfuric acid, water-alkali solutions.

Tetra-4-[6',8'-disulfo-2-naphthyl)oxy]phthalocyaninate. Mixture of 0.001 mol of potassium salt of 4-[(6',8'-disulfo-2'-naphtyl)oxy]phthalonitrile and 0.50 g (0.008 mol) of carbamid was heated with stirring to a temperature of 190-195°C and kept under constant conditions for 1 h [38]. Pre-treatment of the phthalocyanine was carried out by washing of it with 18% solution of hydrochloric acid to a colorless filtrates. Next, the powder war dried. The precipitate was further purified by the extraction with ethanol in Soxhlet apparatus. The final purification was carried out by chromatography with silica gel M60 using mixture DMF:water (1:1) as eluent. The yield was 0.24 g (57%). Elemental analysis for $C_{72}H_{42}N_8O_{28}S_8 \cdot 16H_2O$, %: C 42.9; H 3.6; N 5.5; S 12.7. Found C 41.1; H 3.4; N 6.1; S 12.1. UV-vis (DMF): λ_{max}, nm 701, 674, 645_{inf}, 612_{inf}, 330; (H₂O): 638; (NaOH): 607, (H_2SO_4) : 813, 790, 715. IR spectra (KBr): v, cm⁻¹ 1038 (v, S=O), 1109 (v_{as} S=O), 1228 (v Ar–O–Ar), 1012 (H₂Pc).

Immobilization of metallophthalocyanines on the surface of polymer

Immobilization of metallophthalocyanines was carried out onto the surface pretreated by plasma discharge. The treatment was performed using gas discharge occurring on the surface of electrolyte (glow discharge). The pH value of treating solution was varied in range of 8–12 by adding distilled water and corresponding amount of sodium hydroxide. The time of treatment was 5–30 min, ignition current 50 mA. Samples treated by plasma (size 1×1 cm, 5×5 and 10×10 cm) was immersed in water solution of CoPcI–CoPcIII with concentration of 5×10^{-5} mol/L and held for 8 h under the temperature of 40 °C. Next, the solvent was evaporated and the resulting material dried under the temperature of 60 °C. After drying, the sample was washed with distilled water and ethanol and dried in vacuum at 45 °C for 20 h.

Degree of anchoring was monitored spectrally. IR-spectra of all samples, electronic absorption spectra (UV-vis) of CoPcI-CoPcIII solutions before anchoring at the surface of polymer and UV-vis of solution after washing of the material were registered to control the degree of anchoring. Besides, there was chosen medium with refractive index within the error equal to refractive index of polymer-quinolone. It allowed to register UV-vis spectra of immobilized phthalocyanines.

Coerced peak method was used as quantitative measure of modification degree (the value of optical density of characteristic absorption band T^i related to the optical density of the band of stretching vibrations of characteristic group T^{OTH}). Measurments were carried out on bands 3620, 3415, 2970, 1600 μ 860 cm⁻¹. The most informative measurments were in bands 3620 and 860 cm⁻¹. This method together with electronic spectra allows obtaining of reliable data about degree of macrocycle anchoring on the surface of polymers.

OH ĊH2 ĊH2 plasma treatment CoPc pH 8-12 (NaOH) hydrolysis PF (a) plasma treatment pH 8-12 (NaOH) Lavsan CoPc Ο CoPc hydrolysis (b)

Fig. 4. Immobilization strategy of metallophthalocyanines onto the surface of activated polymer (a) PP, (b) Lavsan

Surface concentration of particles was calculated with equation:

$$N_s = (A/\varepsilon) \cdot N_a \cdot 10^3 [\text{cm}^{-2}] \tag{1}$$

where A — optical density of macrocycle solution, ε — extinction coefficient of monomeric or dimeric form of the solution (depends on association degree of macrocycle). Values ε of investigated macrocycles were taken from works [39, 41]. This calculation assumes tempostabile chromophore system during immobilization.

Elemental analysis for obtained hybrid materials showed containing cobalt in amount of 2.25–3.16% on weight. It is matched with containing of phthalocyanines in samples.

Experiment of catalytic oxidation of mercaptans to disulfides

The experiments to study the kinetics of reaction of sodium diethyldithiocarbamate oxidation were carried out in specially constructed cell with volume of 650 mL in which the solution of N,N-diethylcarbamodithioate (DTC) with concentration of 0.3 mol/L was loaded. At the same time 0.01 g of catalyst was added. The temperature was maintained $25 \,^{\circ}$ C within $\pm 0.05 \,^{\circ}$ C. The air was fed via microcompressor with constant rate of 2 L/min. For these parameters of process, reaction takes place in kinetic region [36]. After establishing a constant temperature the solution was mixed and sample of 2 mL was taken to determine initial concentration of DTC, then compressor was turned on. This moment was taken as the beginning of the reaction. Samples of 2 mL were taken periodically during the experiment to determine current concentration of DTC.

Method of determination of DTC concentration is the following: 4 mL 0.08 mol/L solution of $CuSO_4$ is added to the sample of 2 mL. Herewith the dark-brown precipitate of copper complex with DTC is formed. Mixture is mixed. Then 0.005 mL of 50% acetic acid is added to resulting mixture. Copper complex with DTC is extracted into the chloroform layer. Optical density of solution is determined spectrally at a wavelength of 436 nm. Current concentration of DTC is calculated with help of calibration line. Oxidation of 2-mercaptoethanol was carried out according to the method recommended by [29].

Equipment

Electronic absorption spectra (UV-vis spectra) were registered in spectral range 200–1000 nm on a spectrophotometer «Unico-2800» (USA) in quartz cuvettes with a thickness of 1 mm and 10 mm.

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IR-spectra were registered on FT-IR spectrophotometer Avatar 360 FT-IR ESP in frequency range of 400–4000 cm⁻¹.

Elemental analysis was performed using chromatographic analyzer Flash HCNS-OEA 1112. Helium flow rate was 140 mL/min, oxygen flow rate 250 mL/min, reactor temperature 900 °C.

¹H NMR was registered on spectrometer Bruker-500 (Germany) with frequency of 500 MHz, in $CDCl_3$, D_2O and DMSO internal standard TMS.

The electric circuit of the plasma-chemical setup is presented in Fig. 5. The anode in the gas phase was made of copper wire of diameter 2 mm. The cathode in the solution was made of copper or silver wire of diameter 2 mm, as well as a nickel tube of diameter 1.5 mm.

Thermal investigations were carried out with Synchronous thermal analyzer (DSC/DTA/TG) with the skimmer mass spectrometric analysis system of vapor STA 409 CD/7/G company Netzsch Geraetebau GmbH; In Process Instruments (Germany). Operating temperature range up to 2000 °C. Resolution of thermobalance is 0.1 µg. Measuring range of mass numbers of the mass spectrum up to 1024 a.u.

Reagents and methods for their preparation

Solvents used in the work dimethylsulfoxide were purified and kept in accordance to recommendations [42].

Inorganic salts applied for synthesis were previously recrystallized by methods recommended in [43].

Deuterated solvents, and 2-mercaptoethanol were purchased from Aldrich, and sodium *N*,*N*-diethylcarbamodithioate (99%, ChemMed Synthesis, Russia) was used without additional purification.

CONCLUSION

In summary, heterogeneous catalysts based on nonwoven polymer materials and sulfonated cobalt phthalocyanines with extended periphery have significant



Fig. 5. Scheme of plasma-chemical plant for polymer treatment

prospects as catalysts in oxidation of mercaptans to disulfides. Technological simplicity of polymer activation and catalytic process in presence of heterogeneous catalyst, excellent yield of final product, parameters of activity comparable with already using catalysts, availability to recycling without activation and leaching of catalyst reveal new field of heterogeneous catalytic phthalocyanine systems. Especially noteworthy that the final product of DTC oxidation is thiuram E with purity of 98.5% that let our colleagues to use it without additional purifying in organic synthesis.

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Supporting information

Figures S1–S7 and Table S1 are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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