

# Cobalt phthalocyanine derivatives supported on TiO<sub>2</sub> by sol–gel processing

## Part 2. Activity in sulfide and ethanethiol oxidation

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### Abstract

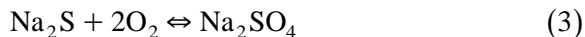
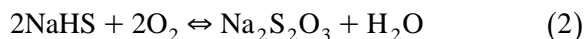
The catalytic activity of cobalt(II) 2,9,16,23-tetrasulphophthalocyanine and cobalt(II) 2,9,16,23-tetra(chlorosulphonyl)phthalocyanine covalently bonded to a TiO<sub>2</sub> matrix by sol–gel processing was investigated for sulfide and ethanethiol (CH<sub>3</sub>CH<sub>2</sub>SH) liquid-phase oxidation. A comparison of the kinetic data as well as the state of active component by using electron spectroscopy in dependence on precursors was carried out. Kinetic data shows that the most stable and active catalysts for ethanethiol oxidation are both CoPc(SO<sub>3</sub>H)<sub>4</sub> and CoPc(SO<sub>2</sub>Cl)<sub>4</sub> in TiO<sub>2</sub> from Ti(O<sup>i</sup>Pr)<sub>4</sub>, whereas in the case of Na<sub>2</sub>S oxidation in neutral medium the activity of the former is higher. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Cobalt phthalocyanines; Supported catalysts; Titanium alkoxides; Sulfide and ethanethiol oxidation; Catalytic activity

### 1. Introduction

In neutral or alkaline media, aqueous sulfide solutions are oxidized by oxygen or air in the presence of sulphonated cobalt phthalocyanines as catalysts. Elemental sulfur, thiosulphate or sulfate are produced depending on the pH, the amount of catalyst, the ionic strength and the

initial concentration of sulfide. The overall oxidation reactions are as follows:



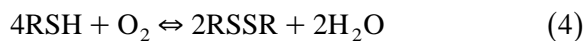
These reactions are interesting models and very important for the purification of oil refinery process gases, liquid hydrocarbon fuels and industrial wastes from hydrogen sulfide [1,2]. The catalytic oxidation of thiols to the corresponding disulfides (Eq. (4)) is technically im-

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portant for the cleaning of gasoline fractions in the Merox process [3,4]:



Efficient catalysts are required to carry out  $\text{HS}^-$  oxidation at low temperatures and for large gas or solution volumes. Catalytically active compounds include transition metal sulfides, transition metal complexes and organic compounds capable of reversible Red-Ox reactions. Metallophthalocyanines, particularly substituted cobalt phthalocyanines (CoPc), are known to be the most effective catalysts for sulfide and mercaptoethanol oxidation in liquid phase both as homogeneous catalysts [5] and immobilized by covalent bonding to the surface of modified silicas [6,7]. It was also found that differently substituted CoPc derivatives coordinately bonded to aminopropyl- or imidazolyl-propyl-modified silica exhibit high catalytic activity in the oxidation of ethanethiol [8]. The substituents influence the catalytic activity: electron-withdrawing enhance, while electron-donating decrease it both for supported [6–8] and homogeneous cobalt phthalocyanines [9].

Polymeric cobalt(II) phthalocyanines exhibit much higher activity in sulfide oxidation than the monomeric counterpart due to disproportionation of Co(II) in solid Co-polyphthalocyanines. A mechanism through simultaneous activation of  $\text{HS}^-$  ion and  $\text{O}_2$  on neighboring Co(III) and Co(I) nuclei was proposed to explain this phenomenon [10]. In homogeneous medium, however, it was shown that an oligomers formation of CoPc tetrasodium sulphonates (CoTSPc) in aqueous solutions [11] and in surfactant reverse micelles [12] leads the activity to decrease. The solvent composition may cause an enhancement in homogeneous CoPc activity up to a factor of 40 by using ammonium salts [13]. It should be noted that  $\text{HS}^-$  oxidation by oxygen proceeds by rather complex mechanisms, and even minor changes in the reaction conditions cause changes both in the product ratio and in the rate of oxidation. Factors such as the aggregation degree of phtha-

locyanines, the type of substituents, the nature of matrix and solvent (in case of homogeneous medium) are important.

We recently reported that  $\text{CoPc}(4\text{-SO}_2\text{X})_4$  ( $\text{X} = \text{Cl}, \text{OH}$ ) react with titanium alkoxides to form derivatives of the type  $\text{CoPc}(4\text{-SO}_2\text{X})_{4-x}\text{-}[4\text{-SO}_3\text{Ti}(\text{OR})_3]_x$ . Upon sol-gel processing of these compounds with an excess of  $\text{Ti}(\text{OR})_4$ , the titanic matrix is built around the CoPc entities. The sulphonate group provide a particularly stable link between the CoPc entity and the titanate matrix [14]. In this paper we report the catalytic activity of these materials for the oxidation of ethanethiol and sodium sulfide. We will compare their activity according to the employed precursors as well as to the structure and oxidation states of cobalt.

## 2. Experimental

### 2.1. Materials

The preparation of the materials by sol-gel processing was described in Ref. [14]. The following combinations of CoPc derivatives and titanium alkoxides were tested:  $\text{CoPc}(4\text{-SO}_2\text{Cl})_4/\text{Ti}(\text{OR})_4$  with  $\text{R} = \text{Et}, \text{Pr}^i, \text{Pr}^n, \text{Bu}^n$ , and  $\text{CoPc}(4\text{-SO}_3\text{H})_4 \cdot 7\text{H}_2\text{O}/\text{Ti}(\text{OR})_4$  with  $\text{R} = \text{Et}, \text{Pr}^i, \text{Pr}^n$ . Cobalt(II) tetrasulphophthalocyanine (CoTSPc) and cobalt(II) tetra(chlorosulphonyl)phthalocyanine (CoTCISPC) were prepared according to the procedure described in Refs. [15,16] with slight modifications. Cobalt(II) tetrasulphophthalocyanine supported on activate charcoal was used for comparison.

### 2.2. Activity in $\text{HS}^-$ oxidation

The weighted amount of the catalyst was placed in a thermostatic glass reactor and filled with a solution of phosphate buffer. A calculated amount of sodium sulfide ( $5 \times 10^{-2}$  M) or ethanethiol ( $7.5 \times 10^{-2}$  M) was put into the reactor, which was closed immediately after being filled with oxygen. The consumption rate of oxygen as the oxidizing agent was measured by a gas burette (ml/min).

The reactor was fixed to a shaker; intensive shaking ensured the process to occur in the kinetic range. Molar ratios  $\text{HS}^-/\text{phthalocyanine} \cong 110$  were used, except for the most active catalysts; a molar ratio  $\cong 300$  was used in this case to avoid the diffusion range.

### 2.3. Stability in the reaction medium

The heterogenized CoPc samples were treated for 24 h with the reaction mixture (0.05 M  $\text{Na}_2\text{S}$  in phosphate buffer,  $\text{pH} = 7.34$ ) and washed with water. All samples are stable in the reaction media, i.e., UV–visible spectrum showed no leaching of the active component during oxidation.

### 2.4. Characterization

Absorption spectra of solutions and diffuse reflection spectra of heterogenized samples were recorded with a Specord UV–VIS M-40 spectrophotometer. Solid samples were pressed into pellets and MgO were used as a reference. Surface area was measured by BET. An amount of sulfur-containing compounds in reaction mixture was controlled by volume analysis.

## 3. Results and discussion

Table 1 summarizes the results of the catalytic activity measurement of the heterogenized

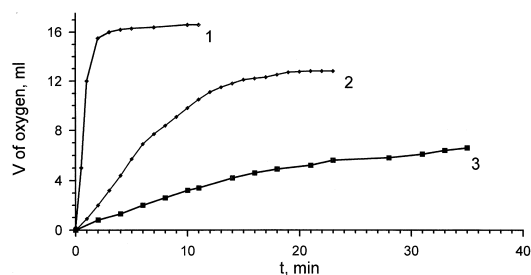


Fig. 1. Oxidation of  $\text{Na}_2\text{S}$ , molar ratio thiol/phthalocyanine  $\sim 110$ . 1— $\text{CoPc}(4\text{-SO}_3\text{H})_4$  on  $\text{TiO}_2$  from  $\text{Ti}(\text{O}^i\text{Pr})_4$ ; 2— $\text{CoPc}(\text{SO}_3\text{H})_2$  on activated charcoal; 3— $\text{TiO}_2$  from  $\text{Ti}(\text{O}^i\text{Pr})_4$ .

CoPc derivatives in the oxidation of  $\text{Na}_2\text{S}$ . The activity was calculated from the linear parts of kinetic curves. The main product of the oxidation is elemental sulfur. The amount of oxygen consumed and the results of the volume analysis showed that 10–15% of initial sulfide was converted to thiosulphate. Sulfate ions were not found in the reaction mixture.

To test the catalytic activity after the first run, the samples 1–7 (Table 1) after use in the catalytic experiment were mixed with fresh catalyst in a 1:1 ratio. Then the catalytic experiment was run again. The results show no decrease in catalytic activity; only the percentage of thiosulphate in the products was slightly higher: 19% of initial sulfide was converted to thiosulphate.

Kinetic curve for  $\text{Na}_2\text{S}$  oxidation in presence of matrix  $\text{TiO}_2$  obtained from  $\text{Ti}(\text{O}^i\text{Pr})_4$  as precursor (curve 3, Fig. 1) closely duplicates the curve obtained for oxidation without any cata-

Table 1

Catalytic activity of heterogenized cobalt(II) phthalocyanines derivatives  $\text{CoPc}(4\text{-SO}_2\text{X})_4$  in  $\text{TiO}_2$  from  $\text{Ti}(\text{OR})_4$  for the oxidation of  $\text{Na}_2\text{S}$

N	Precursors (catalyst)	$t$ for complete oxidation <sup>a</sup> (min)	$V_{\text{O}_2}$ (ml)	Act (mole $\text{S}^{2-}/$ mole kt min)
1	X = OH, R = <sup>i</sup> Pr	9	16.4	35.3
2	R = <sup>n</sup> Pr	16.5	19.9	16.2
3	R = Et	24	19.6	11.3
4	X = Cl, R = <sup>n</sup> Pr	18.5	18.7	10.6
5	R = Et	18	27.1	9.9
6	R = <sup>n</sup> Bu	19	16.2	8.5
7	R = <sup>i</sup> Pr	31	17.8	7.1

$T = 25^\circ\text{C}$ ,  $\text{pH} = 7.3$ ,  $[\text{Na}_2\text{S}]_0 = 5 \times 10^{-2}$  M, molar ratio  $\text{Na}_2\text{S}/\text{CoPc}(4\text{-SO}_2\text{X})_4 = 110$ .

<sup>a</sup>Stopping of the oxygen consumption was the detection limit.

lyst. It was found that the catalyst, prepared from  $\text{CoPc}(4\text{-SO}_3\text{H})_4$  and  $\text{Ti}(\text{O}^i\text{Pr})_4$  as precursors is the most active for sodium sulfide oxidation. It can be seen from Fig. 1 (curve 1) that the activity of this sample is higher than that of  $\text{CoPc}(4\text{-SO}_3\text{H})_4$  supported on activated charcoal (curve 2).

The results of the catalytic activity of the obtained materials in the ethanethiol oxidation are summarized in Table 2. No less than three experiments on the same material was carried out, and the reactivity was the same; average results are given in the table. In this case, the oxidation correspond to Eq. (4), and the consumption of oxygen is the same for all catalysts (12 ml per 25 ml of the reaction mixture) and is close to calculated. To compare the dynamic of oxidation, the maximal oxygen consumption per minute ( $V_m$ , ml/min) are given in Table 2.

Fig. 2 shows the kinetic curves of the catalytic oxidation of ethanethiol (ET) in the presence of the most active catalysts. Experiment 6\*, in which a new portion of ET was added to the filtered solution after N4, was done to control (additionally to the UV–VIS spectrum) whether active component was leached into solution. One can see that the oxidation rate is at the same level as for oxidation without catalyst (curves 3, 4, Fig. 2). We can thus conclude that the catalyst is stable in the reaction media.

The absorbance spectrum of the samples obtained from  $\text{CoPc}(4\text{-SO}_3\text{H})_4$  and  $\text{Ti}(\text{O}^i\text{Pr})_4$  relatively to the standard spectrum of  $\text{CoPc}(4\text{-SO}_3\text{H})_4$  in monomeric and dimeric forms are

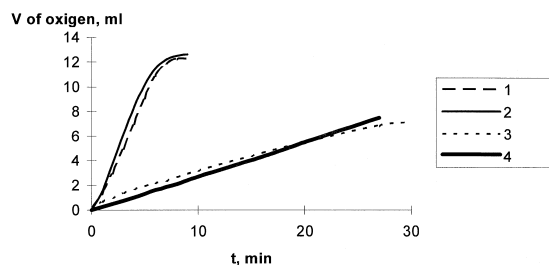


Fig. 2. Oxidation of ethanethiol (ET), molar ratio  $\text{Na}_2\text{S}/\text{CoPc}(4\text{-SO}_2\text{X})_4 \approx 300$ . 1— $\text{CoPc}(4\text{-SO}_3\text{H})_4$  in  $\text{TiO}_2$  from  $\text{Ti}(\text{O}^i\text{Pr})_4$ ; 2— $\text{CoPc}(4\text{-SO}_2\text{Cl})_4$  in  $\text{TiO}_2$  from  $\text{Ti}(\text{O}^i\text{Pr})_4$ ; 3—solution after (2) with new portion of ET; 4—oxidation without catalyst.

presented in Fig. 3. One can see that the complex is mostly dimeric (absorption band at  $1620\text{ cm}^{-1}$ ), and an amount of monomeric forms (absorption band at  $1510\text{ cm}^{-1}$ ) slightly increased after the treatment in reaction media.

The phthalocyanine in  $\text{TiO}_2$ , prepared from the chlorosulphonyl derivative and  $\text{Ti}(\text{O}^i\text{Pr})_4$  (Fig. 4) is mostly monomeric and the amount of associated phthalocyanines slightly increases in a sulfide media.

Specific surface area (by BET) of samples prepared from  $\text{Ti}(\text{O}^i\text{Pr})_4$  and which was measured after treatment in  $\text{HS}^-$  medium are  $42\text{--}46\text{ m}^2/\text{g}$ . Taking into account an amount of active component (1.3 wt.%), molecular area of phthalocyanine ( $\sim 300 \times 10^{-20}\text{ m}^2$ ) and assuming a uniform molecular distribution of  $\text{CoPc}$  in the volume of matrix, one can evaluate that an amount of active component on the surface of materials is near  $0.3\text{ mg}$  (or  $3 \times 10^{-7}\text{ M}$ ) per gram. It mean that used concentration of surface

Table 2

Catalytic activity of cobalt(II) phthalocyanines derivatives  $\text{CoPc}(4\text{-SO}_2\text{X})_4$  in  $\text{TiO}_2$  from  $\text{Ti}(\text{OR})_4$  for the oxidation of ethanethiol (ET)

N	Catalyst (precursors)	$V_m$ (ml/min)	Akt (mole SH/ mole kt min)
1	X = OH, R = $^i\text{Pr}^a$	2.1	80.3
2	X = Cl, R = $^i\text{Pr}^a$	2.2	84
3	X = Cl, R = $^n\text{Bu}$	2.2	31.4
4	X = Cl, R = $^n\text{Pr}$	1.1	15.4
5	without catalyst	0.25	(3.52)
6 <sup>a</sup>	solution after N4	0.25	(3.52)
7	$\text{CoPc}(\text{SO}_3\text{Na})_2$ on act. charcoal	1.7	33.1

$T = 25^\circ\text{C}$ ,  $\text{pH} = 11$ ,  $[\text{ET}]_0 = 7.5 \times 10^{-2}\text{ M}$ , mole ratio  $\text{ET}/\text{CoPc}(4\text{-SO}_2\text{X})_4 = 110$ ; <sup>a</sup>300.

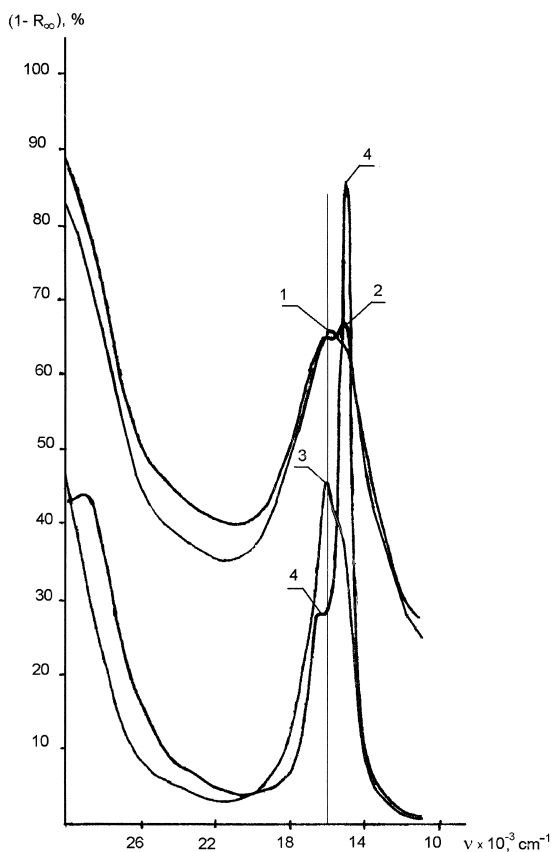
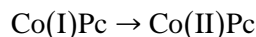
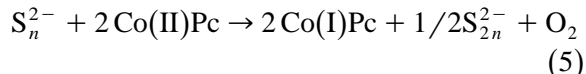


Fig. 3. Absorption spectra of (1)  $\text{CoPc}(4\text{-SO}_3\text{H})_4/\text{TiO}_2$  from  $\text{Ti}(\text{O}^i\text{Pr})_4$  initial; (2)  $\text{CoPc}(4\text{-SO}_3\text{H})_4/\text{TiO}_2$  from  $\text{Ti}(\text{O}^i\text{Pr})_4$  after  $\text{HS}^-$  treatment; (3) homogeneous  $\text{CoPc}(4\text{-SO}_3\text{H})_4$  in dimeric form; (4) homogeneous  $\text{CoPc}(4\text{-SO}_3\text{H})_4$  in monomeric form.

$\text{CoPc}$  was near  $10^{-7}$  M for the most active compounds. This values are in a good correlation between the same amount of homogeneous  $\text{CoTSPc}$  for  $\text{Na}_2\text{S}$  oxidation, whereas for ET-oxidation an activity of surface  $\text{CoPc}$  in solid samples is near to be twice higher than that of their homogeneous analogies.

Contrary to the  $\text{Na}_2\text{S}$  oxidation, both catalysts obtained from  $\text{Ti}(\text{O}^i\text{Pr})_4$  as precursor show the highest activity for ethanethiol oxidation. This phenomenon can be explained by the different mechanism for  $\text{HS}^-$  oxidation in neutral and alkaline media. As it was pointed out before, for  $\text{Na}_2\text{S}$  oxidation in neutral and slightly alkaline media, the polysulfides ( $\text{S}_n^{2-}$ ) are intermediates in the  $\text{CoPc}$ -catalyzed reaction [2,17,18]. In this case a free-radical mechanism

is proposed, involving polysulfides as intermediates. Their reactivity towards oxygen was found to be much higher than for  $\text{S}^{2-}$  or  $\text{HS}^-$  ions [5,19,20] and the rate-determine step is the reduction of  $\text{Co}(\text{II})$  by sulfide, followed by the growth of polysulfide chains (Eq. (5)):



This pathways leads to the formation of elemental sulfur according to Eq. (6):



If the amount of active  $\text{Co}(\text{II})$  catalyst (preferably in the active dimeric form) is not enough,

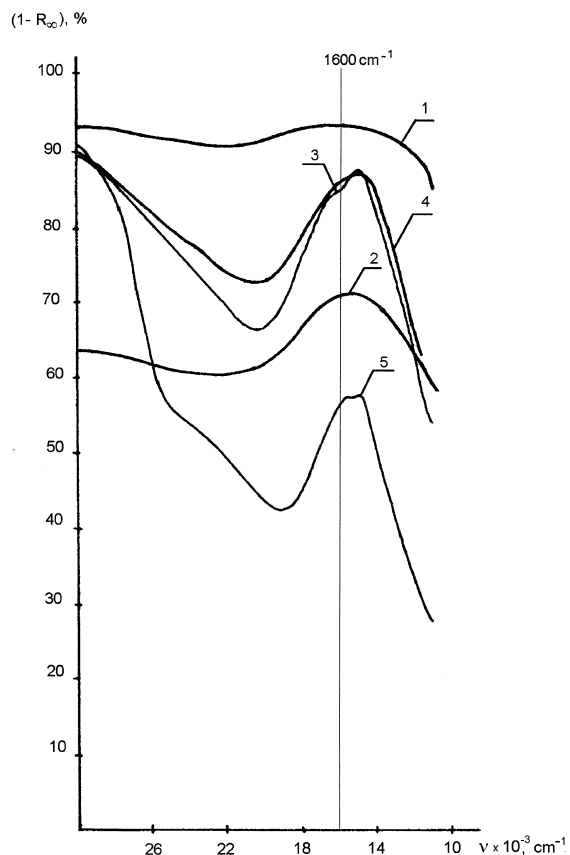
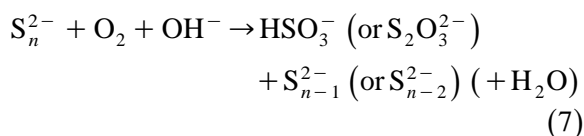


Fig. 4. Absorption spectra of (1) crystalline  $\text{CoPc}(4\text{-SO}_3\text{H})_4$  (without  $\text{MgO}$  as a reference); (2) crystalline  $\text{CoPc}(4\text{-SO}_3\text{H})_4$ ; (3)  $\text{CoPc}(4\text{-SO}_2\text{Cl})_4/\text{TiO}_2$  from  $\text{Ti}(\text{O}^i\text{Pr})_4$  initial; (4)  $\text{CoPc}(4\text{-SO}_2\text{Cl})_4/\text{TiO}_2$  from  $\text{Ti}(\text{O}^i\text{Pr})_4$  after  $\text{HS}^-$  treatment; (5)  $\text{CoPc}(4\text{-SO}_3\text{H})_4/\text{TiO}_2$  from  $\text{Ti}(\text{O}^i\text{Pr})_4$  initial.

polysulfide is destroyed in an uncatalysed way (Eq. (7)):



and the rate of oxidation decreases. The existence of a 'critical' active CoPc concentration was proposed both for homogeneous media [5,20] and for differently substituted CoPc derivatives coordinately bonded to amino-propyl-modified silica [21].

In the case of thiols oxidation there is no evidence for such intermediates, and  $RS^-$  directly react with catalyst. Thus, the way of sulfide oxidation strongly depends on the amount of phthalocyanines catalyst in active form, whereas for the oxidation of ethanethiol the ability to coordinate  $HS^-$  and  $O_2$  is of utmost importance.

#### 4. Conclusion

The new materials obtained by sol-gel processing [14] was investigated for sulfide and mercaptoethanol liquid-phase oxidation. Thus, heterogenized catalysts exhibit high stability in the reaction media due to the anchoring of the CoPc units to the titania matrix; the entrapped CoPc catalyst is monomeric or dimeric, depending on the employed CoPc derivative and  $Ti(OR)_4$ . Kinetic data shows that the most stable and active catalysts for ethanethiol oxidation are both  $CoPc(SO_3H)_4$  and  $CoPc(SO_2Cl)_4$  in  $TiO_2$  from  $Ti(O^iPr)_4$ , whereas in the case of  $Na_2S$  oxidation in neutral medium an activity of the first one is higher. High stability and activity of the materials led us to conclude that the sulphonyl groups can be used for an efficient heterogenization of sulphonated cobalt phthalocyanines catalysts. In a modification of this procedure, the solution containing both substi-

tuted CoPc and alkoxides can be used to coat the surface of solid carriers, such as pellets or honeycomb structures made of metal oxides, followed by hydrolysis and condensation at the solid surface without loss of catalytic activity of the CoPc derivative.

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