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Oxidation and photooxidation of sulfide and thiosulfate ions catalyzed by transition metal chalcogenides and phthalocyanine complexes

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Abstract

The catalytic and photocatalytic activities of supported cobalt or zinc phthalocyanine complexes, bulk MoS_2, MoS_2 deposited on Al_2O_3, potassium intercalated MoS_2 ($K_{0.33}$ $H_2O_{0.66}$ MoS_2), CdS and polycrystalline nickel phosphorus trisulfide ($NiPS_3$) have been investigated in the oxidation of sodium sulfide and $Na_2S_2O_3$. The phthalocyanine complexes and the metal chalcogenides do not catalyze, in the absence of light, the complete oxidation of the sulfide ion to sulfate ion. The final product of the catalytic oxidation is the formed thiosulfate. No oxidation of $Na_2S_2O_3$ has been registered in the dark in the presence of any of the catalytic samples. Their activity was enhanced upon irradiation with visible light. Thiosulfate appears to be the final product also of the photooxidation of the sulfide ion catalyzed by metal chalcogenides. They do not catalyze the further photooxidation of $Na_2S_2O_3$. The only photocatalysts which favour with their presence the oxidation of the sulfide and thiosulfate ions to sulfate ion, are the zinc phthalocyanine complexes. In this case, the photooxidation process involves singlet oxygen. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The sulfide ions are among the most dangerous pollutants in wastewater [1]. The presence of sulfide ions in industrial wastewater (oil-processing industry, paper manufacture, synthetic fiber production), communal wastewater etc. has a mortal effect on the bacterial strains, used for their biological purification [2]. So far, two methods have been utilized for removing sulfide ions from wastewater before discharging them into waterways. According to the first method, the sulfide ion is catalytically or photocatalytically oxidized to elemental sulfur and

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thiosufates [3–14], whereas after the second one it is completely converted into sulfate anion through photocatalytic oxidation [9,15,16]. The complete oxidation of sulfur-containing compounds has been established as the better solution of this environmental pollution problem [17]. Alkali sulfide oxidation, catalyzed by cobalt phthalocyanine complexes (CoPc), has been reported to be incomplete, the end products are mixtures of sulfur, thiosulfates and sulfates [3,13]. The adsorption of HS^- or of O_2 to the cobalt center of the compex is assumed to be the initial elementary step [3,4,6]. Detailed investigations that have been carried out focused on the mechanism of sulfide ion oxidation, catalyzed by cobalt phthalocyanine complexes [6,13]. A free radical pathway of the catalytic redox process has been proposed [4]. The kinetics have been modelled either using a Michaelis–Menten, or Langmuir–Hinshelwood equations [4,13].

Some transition metal oxides and chalcogenides represent another class of catalysts for sulfide ion oxidation to elemental sulfur or thiosulfates [11,12,14]. Metal chalcogenides, such as CdS [7,18–20], are also active photocatalysts in the oxidation of sulfur-containing compounds upon irradiation with visible light, but the oxidation proceeds incompletely. It has been established that upon irradiation with light in the ultraviolet region of the spectrum cobalt phthalocyanine complexes, covalently linked to the surface of titanium dioxide, exhibit high photocatalytic activity in the oxidation of sulfite ions to sulfate ions [21].

Recently, it has been established [9,15,16] that upon irradiation with visible light, including sunlight, closed-shell metal phthalocyanines exhibit high photocatalytic activity in the complete oxidation of sulfide ions to sulfate ions.

The catalytic and photocatalytic properties of phthalocyanine complexes and metal chalcogenides have been studied in the present work in the reaction of sulfide ion or thiosulfate ion oxidation in the presence of oxygen. The thiosulfate anion is, in fact, an intermediate product

in the course of the complete catalytic oxidation of the sulfide anion to sulfate. The aim of this paper is to compare the activities of these two types of catalyst, their photocatalytic properties and the sulfide anion oxidation degree.

2. Experimental

Merck $Na_2S \cdot 9H_2O$ and $Na_2S_2O_3$ were used without further purification. The concentration of $Na_2S \cdot 9H_2O$ solutions, before catalytic oxidation, has been determined in accordance with the method described in Ref. [22] by means of selective precipitation of the sulfide ion with an excess of $CuCl_2$ as CuS and titration of the filtrate with a Titriplex III solution. Cobalt(II)-2,9,16,23-phthalocyanine tetracarboxylic acid $[CoPc(COOH)_4]$ and zinc(II)-2,9,16,23-phthalocyanine tetracarboxylic acid $[ZnPc(COOH)_4]$ were prepared and purified according to the methods described in the literature [23]. Molybdenum(IV) sulfide (Aldrich) and CdS (Merck) were used without further purification. The MoS_2, supported on Al_2O_3 (Merck, 150, Typ T), has been obtained following the procedure described in [24,25]. The support was impregnated with an aqueous solution of $(NH_4)_6$ $Mo_7O_{24} \cdot 4H_2O$, dried for 4 h at 393 K and calcined at 773 K for 8 h in air. The sample was reduced for 1 h with H_2 at 423 K and sulfided thereafter for 3 h in a flow of H_2S at 673 K. After cooling down to 473 K, the sample is purged with H_2 further down to room temperature. The MoS_2 loading on the support amounts to 20 wt.%. K^+ intercalated MoS_2 ($K_{0.33}$ $H_2O_{0.66}$ MoS_2, 1T form) was prepared from K_2MoO_4 by sulfidation with H_2S, subsequent reduction with H2 and hydration [26,27]. X-ray diffraction patterns of MoS_2 and $K_{0.33}$ $H_2O_{0.66}$ MoS_2 powders were measured using Co Kα radiation (Fig. 1a,b).

Polycrystalline nickel phosphorus trisulfide $(NiPS_3)$ was prepared by annealing a mixture of powdered nickel, sulfur and red phosphorus in an evacuated quartz tube [28]. Heating was car-
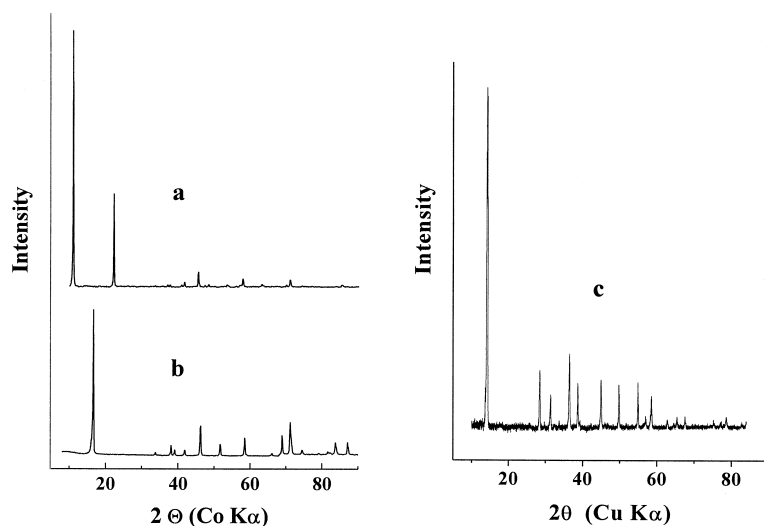
Fig. 1. X-ray powder diffraction patterns of: (a) $K_{0.33}H_2O_{0.66}MoS_2$; (b) bulk MoS_2; (c) $NiPS_3$.

ried out at 973 K for 120 h followed by slow cooling to ambient temperature. Phase purity was monitored through X-ray diffraction (Fig. 1c) [28].

A hydrotalcite-like layered double hydroxide $[Mg_5Al_2(OH)_{14}][CO_3] \cdot yH_2O$ (HT) was prepared by coprecipitation of stoichiometric amounts of Mg^{2+} and Al^{3+} in the presence of carbonate at pH = 12.7 [29]. The double hydroxide was heated in argon at 723 K for 24 h. The BET surface area of HT was ≈ 220 m^2 g^{-1}. $CoPc(COOH)_4$ and $ZnPc(COOH)_4$ were intercalated into HT by means of ion exchange in aqueous medium [30,31]. The distribution of immobilized $CoPc(COOH)_4$ and $ZnPc(COOH)_4$ complexes was studied by ESR and visible reflectance spectroscopy [30,31]. The contents of metal phthalocyanine complexes in the intercalation compounds (40 μmol/g) were determined after decomposition of the hydrotalcite with diluted hydrochloric acid and separation of the insoluble complexes. The amount of $CoPc(COOH)_4$ and $ZnPc(COOH)_4$ complexes was determined by UV–VIS spectroscopy in aqueous alkaline solution [30,31].

Anchored nonsubstituted zinc phthalocyanine complex (ZnPc) was synthesized on silica gel, Davisil (Aldrich, surface area 300 m^2 g^{-1}),

modified by zinc(II) ion, in the presence of 1,2-dicyanobenzene [32]. The amount of ZnPc, deposited on the support (20 μmol/g), was determined photometrically after dissolving the complex in concentrated H_2SO_4.

The rates of sodium sulfide and $Na_2S_2O_3$ catalytic and photocatalytic oxidation were evaluated on the basis of the consumption of oxygen, which was measured using a gas burette. The oxidation process was performed at 293 K, pH = 9 and atmospheric pressure in a static reactor by exposure to a halogen lamp (12 V, 50 W), the illumination being 38 mW/cm^2. The oxidation of sulfide ion to thiosulfate has been confirmed semiquantitavely by means of UV spectroscopy ($\lambda = 205–240$ nm) [13,22]. The amount of sulfate ions formed upon oxidation and photooxidation of Na_2S or $Na_2S_2O_3$ was determined gravimetrically by precipitation with $BaCl_2$. The accuracy of the analysis was ± 7 wt.%.

3. Results and discussion

The oxidation of the sulfide ion in the presence of O_2, catalyzed by cobalt phthalocyanine complexes, is proceeding via a series of parallel

reactions in accordance with the following supposable scheme [22] (Fig. 2).

The ratio between the intermediately formed stable sulfur-containing compounds, such as polysulfides, sulfur, sulfite and thiosulfate, is influenced by the value of pH of the medium [3,13,22]. The final products of the catalytic or noncatalytic oxidation of the sulfide ion at pH $= 9$ are about 70% thiosulfate and $\approx 30\%$ sulfate ions [13]. It is supposed that the sulfate ion is formed upon basic hydrolysis by OH^- groups of unstable polythiosulfite species $S_xO_2^{2-}$. Therefore, the cobalt phthalocyanine complexes catalyze the oxidation of the sulfide ion but they do not influence its selective transformation into sulfate ion (Fig. 2). It was shown in previous studies that the CoPc complexes display catalytic activity during oxidation of SO_3^{2-} ions [9,33] and they do not catalyze the oxidation of sodium thiosulfate [9,31].

The ability of the studied samples to catalyze or photocatalyze the complete oxidation of Na_2S to sulfate ion can be estimated from the oxygen consumption according to the stoichiometry of the following general reaction:

$$HS^- + 2O_2 + OH^- \rightarrow SO_4^{2-} + H_2O \qquad (1)$$

The thiosulfate ion is one of the intermediate products, which is difficult to oxidize catalytically [9,13,31]. The rate of catalytic oxidation of the thiosulfate ion can be determined from the

oxygen consumption according to the stoichiometry of the following reaction:

$$S_2O_3^{2-} + 3O_2 + H_2O \rightarrow 2SO_4^{2-} + 2OH^- \qquad (2)$$
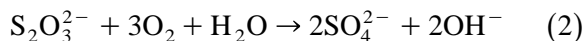
The results from Na_2S and $Na_2S_2O_3$ catalytic and photocatalytic oxidation in the presence of the investigated samples are presented in Table 1. The activities of the investigated samples (Table 1) in the oxidation of Na_2S or $Na_2S_2O_3$ are expressed by r (mol O_2 min^{-1}/ mol of catalyst). The initial rates of the oxidation of the sulfur-containing compounds were determined from the linear part of the plot of the oxygen consumption with time. The results from Na_2S catalytic oxidation in the presence of the investigated catalysts are presented in Fig. 3. A cobalt phthalocyanine complex intercalated into hydrotalcite showed the highest catalytic activity (Table 1). Bulk MoS_2, MoS_2 deposited on Al_2O_3, potassium intercalated MoS_2 ($K_{0.33}$ $H_2O_{0.66}$ MoS_2), CdS and $NiPS_3$ also catalyze the oxidation of Na_2S (Fig. 3). The sulfide ion oxidation, catalyzed by $NiPS_3$, had been studied earlier [14], whereupon some suppositions, regarding the mechanism of the catalytic act, were made. The activities per mol of the investigated catalysts in the dark follow the order (Table 1): $CoPc(COOH)_4/HT > NiPS_3 > K_{0.33}H_2O_{0.66}$ $MoS_2 > CdS > MoS_2/Al_2O_3 > MoS_2$.

The catalytic properties of cobalt phthalocyanine complexes in solution or immobilized
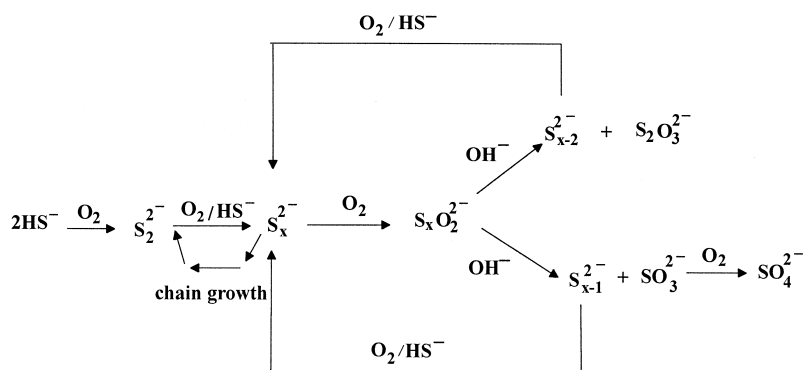

Fig. 2. Reaction scheme of catalytic sulfide ion oxidation.

Table 1

Catalytic and photocatalytic oxidation of Na_2S (4.2 mmol) and $Na_2S_2O_3$ (30 mmol) in an aqueous solution. Temperature 298 K, pH = 9.2, O_2 partial pressure = 1 atm

No.	Sample	Amount (μmol)	Substrate	O_2 consumption (mol min^{-1} $\times 10^5$)	r (mol^{-1}) $\pm 7\%$	Total O_2 consumption (ml)
1	–	–	Na_2S	0.20[a]	–	–
2	$CoPc(COOH)_4$/HT	1.7	Na_2S	18.3[a]	107.6	85
3	$CoPc(COOH)_4$/HT	1.7	Na_2S	18.7[b]	110.0	84
4	$NiPS_3$	17	Na_2S	73.46[a]	43.22	85
5	$NiPS_3$	17	Na_2S	40.6[b]	23.87	87
6	$ZnPc(COOH)_4$	1.7	Na_2S	4.55[a]	26.79	187
7	$ZnPc$/SiO_2	1.7	Na_2S	1.14[a]	6.70	186
8	$ZnPc(COOH)_4$/HT	1.7	Na_2S	0.92[a]	5.40	186
9	$K_{0.33}$ $H_2O_{0.66}$ MoS_2	17	Na_2S	1.35[a]	0.79	86
10	$K_{0.33}$ $H_2O_{0.66}$ MoS_2	17	Na_2S	1.44[b]	0.85	85
11	$K_{0.33}$ $H_2O_{0.66}$ MoS_2	34	Na_2S	2.91[a]	0.56	88
12	$K_{0.33}$ $H_2O_{0.66}$ MoS_2	34	Na_2S	1.87[b]	0.55	88
13	CdS	17	Na_2S	0.92[a]	0.54	88
14	CdS	17	Na_2S	0.85[b]	0.50	85
15	MoS_2/Al_2O_3	17	Na_2S	0.55[a]	0.33	89
16	MoS_2/Al_2O_3	17	Na_2S	0.27[b]	0.16	86
17	MoS_2	17	Na_2S	0.51[a]	0.30	86
18	MoS_2	17	Na_2S	0.24[b]	0.14	87
19	–	–	$Na_2S_2O_3$	0.08[a]	–	–
20	$ZnPc(COOH)_4$	1.7	$Na_2S_2O_3$	1.48[a]	8.70	–
21	$ZnPc$/SiO_2	1.7	$Na_2S_2O_3$	0.29[a]	1.65	–
22	$CoPc(COOH)_4$/HT	1.7	$Na_2S_2O_3$	0.10[b]	[c]	–
23	MoS_2	1.7	$Na_2S_2O_3$	0.09[a,b]	[c]	–
24	MoS_2/Al_2O_3	1.7	$Na_2S_2O_3$	0.07[a,b]	[c]	–
25	$NiPS_3$	1.7	$Na_2S_2O_3$	0.08[a,b]	[c]	–
26	CdS	17	$Na_2S_2O_3$	0.09[a,b]	[c]	–

[a] Upon irradiation.
[b] In the absence of irradiation.
[c] No catalytic oxidation.

on supports and mechanism of thiol and sulfide oxidation have been thoroughly studied [3,4, 6,10,13,34,35]. The cobalt phthalocyanine complexes can reversibly coordinate and activate oxygen in the dark [36,37], which is the basis of the redox mechanism of catalytic oxidation of sulfur containing compounds [3,4,6,10,13, 34,35]. Zinc(II)-phthalocyanine complexes are catalytically inactive in the dark [9,15,16,31], as they are unable to coordinate and activate molecular oxygen [36].

The structure and dispersion of the studied chalcogenide type of catalysts influence essentially their catalytic properties. While the sulfide ion oxidation most probably takes place on edges and defects of the crystal lattice of 2H-MoS_2 and CdS [38], the oxidation of the sub-strate on layered metal chalcogenides $K_{0.33}$ $H_2O_{0.66}MoS_2$ (1T-MoS_2) and $NiPS_3$ can also occur between the catalysts layers [11,14]. The catalytic redox process is accomplished through coordination of the sulfide ion to the bulk or intercalated chalcogenides followed by electron transfer, similar to the processes taking place on CdS microcrystalites [7,18–20]. The oxidation of the catalyst is realized by the oxygen molecule, the catalytic cycle being thus closed.

It is known that the oxidation of the sulfide ion, catalyzed by cobalt phthalocyanine complexes, does not proceed completely [3,13]. The investigated metal chalcogenides do not catalyze in the dark the oxidation of the sulfide ion into sulfate also. This fact is evidenced by the total amount of O_2 ($\approx$ 86 ml), consumed in the
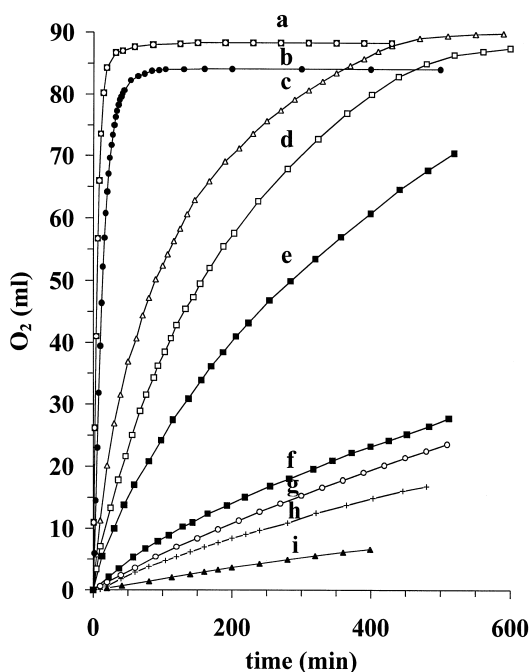
Fig. 3. Oxidation of Na_2S (4.2 mmol) catalyzed by: (a) $NiPS_3$, 17 μmol; (b) $CoPc(COOH)_4$ /HT, 1.7 μmol; (c) $K_{0.33}H_2O_{0.66}MoS_2$, 34 μmol; (d) $K_{0.33}H_2O_{0.66}MoS_2$, 17 μmol; (e) CdS, 17 μmol; (f) MoS_2/Al_2O_3, 17 μmol; (g) MoS_2, 17 μmol; (h) in the absence of catalysts. Oxidation of $Na_2S_2O_3$ (30 mmol): (i) in the absence of catalysts.

redox process (Table 1). The theoretical amount of oxygen, required by the stoichiometry of the oxidation reaction of the sulfide ion (4.2 mmol) into sulfate (Eq. (1)) is ≈ 190 ml.

It has been established that the basic final product of the sulfide ion oxidation in the dark in the presence of chalcogenide type of catalysts is the formed thiosulfate ion. This is proved by the absence of catalytic oxidation of $Na_2S_2O_3$ in the presence of the studied chalcogenides (Table 1), the semiquantitative estimation of the final products by means of UV spectroscopy [13,22] and the consumed quantity of O_2 (≈ 86 ml) (Table 1), while the theoretically needed amount, corresponding to the stoichiometry of the reaction, is 94 ml:

$$2HS^- + 2O_2 \rightarrow S_2O_3^{2-} + H_2O \qquad (3)$$
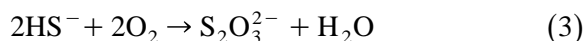
The consumption of O_2 with the time during noncatalytic oxidation of $Na_2S_2O_3$ (30 mmol) is represented in Fig. 3i.

All samples, with the exception of the cobalt phthalocyanine complexes and $K_{0.33}H_2O_{0.66}$ MoS_2, display photocatalytic activity (Table 1). Upon irradiation with visible light the activity of the catalysts changed in the following order (Table 1): $ZnPc(COOH)_4 > NiPS_3 > Zn-Pc/SiO_2 > ZnPc(COOH)_4/HT > K_{0.33}H_2O_{0.66}$ $MoS_2 > MoS_2 > CdS$. Fig. 4 shows typical plots for O_2 consumption vs. time for the catalytic photooxidation of the sulfide ion.

The catalytic activities of cobalt phthalocyanine complexes and of K^+ intercalated MoS_2 ($K_{0.33}H_2O_{0.66}MoS_2$) are one and the same both in the dark and on irradiation with visible light (Table 1). Cobalt phthalocyanine molecules are not photocatalysts [9,15,16,31] due to the very short lifetime of the excited triplet electronic state ($\tau_{T\ CoPc} = 0.065$ μs) [39], thus being unable to convert triplet oxygen ($^3O_2, ^3\Sigma_g$), into singlet oxygen ($^1O_2, ^1\Delta_g$). The absence of photocatalytic activity of the sample $K_{0.33}$-$H_2O_{0.66}MoS_2$ (1T-MoS_2) is owing most probably to the paramagnetic conducting properties of
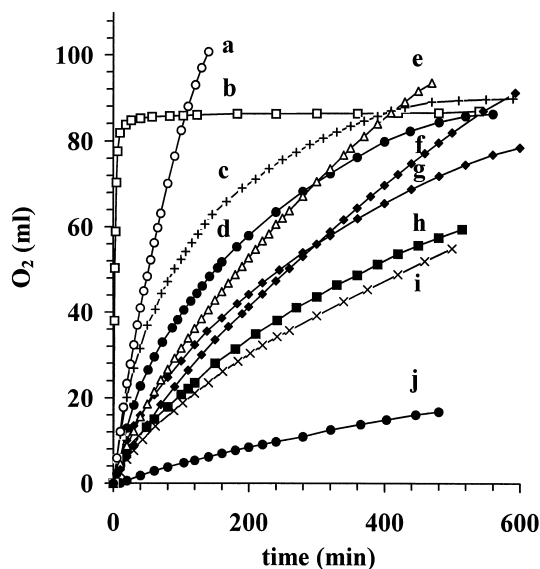
Fig. 4. Photooxidation of Na_2S (4.2 mmol) catalyzed by: (a) $ZnPc(COOH)_4$, 1.7 μmol; (b) $NiPS_3$, 17 μmol; (c) $K_{0.33}$ $H_2O_{0.66}MoS_2$, 34 μmol; (d) $K_{0.33}H_2O_{0.66}MoS_2$, 17 μmol; (e) $ZnPc(COOH)_4/SiO_2$, 1.7 μmol; (f) $ZnPc(COOH)_4/HT$, 1.7 μmol; (g) CdS, 17 μmol; (h) MoS_2, 17 μmol; (i) MoS_2/Al_2O_3, 17 μmol; (j) in the absence of catalysts.

this compound [40]. The properties of the zinc phthalocyanine complexes and CdS as photocatalysts of the sulfide ion oxidation have been studied earlier [7,9,15,16,31].

The catalytic activities of the semiconductors MoS_2, CdS and $NiPS_3$ are enhanced upon irradiation with visible light (Table 1). Similar to oxidation in the dark the total amount of O_2, consumed during photooxidation of Na_2S, catalyzed by semiconductors is ≈ 86 ml (Table 1). Therefore, in the presence of the studied metal chalcogenides, the sulfide ion is not oxidized photocatalytically to sulfate (reaction 1) but the catalytic process is terminated to the accumulation of thiosulfates (reaction 3). This fact is evidenced by the absence of photooxidation of $Na_2S_2O_3$, catalyzed by the investigated chalcogenides (Table 1), the semiquantitative estimation of the final products by UV spectroscopy [13,22] and the consumed quantity of O_2 (≈ 86 ml) (Table 1), while theoretically, the stoichiometrically required amount by reaction 3 is 94 ml.

The reaction mechanism of the first step of photooxidation of the sulfide ion, catalyzed by the semiconductors, is represented schematically in Fig. 5. The bandgap energies of MoS_2, $NiPS_3$ and CdS are respectively 1.75 eV [41], 1.6 eV [42] and 2.4 eV [43], which allows
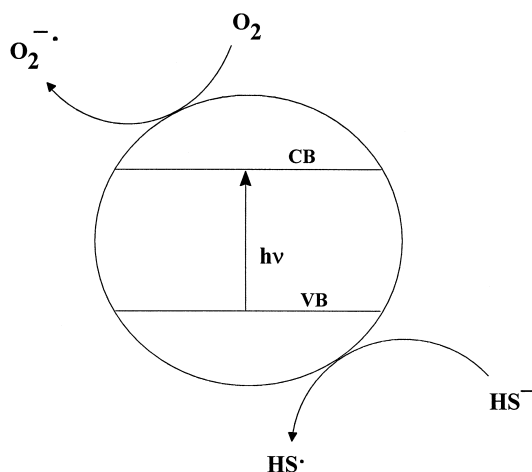

Fig. 5. Schematic representation of the first step of sulfide ion photooxidation, catalyzed by semiconductors.
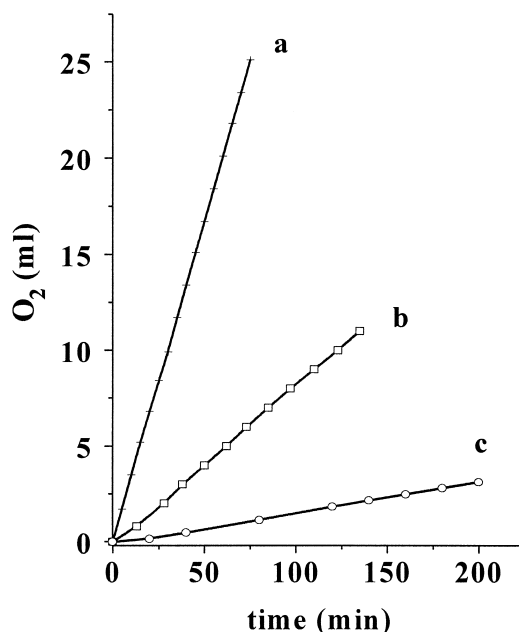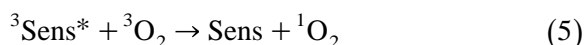

Fig. 6. Photooxidation of $Na_2S_2O_3$ (30 mmol) catalyzed by: (a) ZnPc(COOH)$_4$; (b) ZnPc(COOH)$_4$/HT; (c) in the absence of catalysts.

excitation of semiconductor particles with visible light. Semiconductor particle excitation is followed by charge transfer processes with the participation of adsorbed sulfide ion and oxygen molecules. This reaction mechanism, involving photoinduced electron transfer, explains the formation of disulfides during oxidation of Na_2S.

The zinc phthalocyanine complexes are good photocatalysts of the oxidation of sulfur-containing compounds, and their properties have already been investigated quite well [9,15,16,31]. Upon irradiation with visible light, these complexes (Sens) manifest long lifetimes of the excited triplet electron state ($\tau_{T\ ZnPc} \approx 245$ μs) [39]. The oxygen ($^3O_2$, $^3\Sigma_g$), interacts with the excited triplet electronic state of the complexes and, as a result of energy transfer, it is converted into singlet oxygen ($^1O_2$, $^1\Delta_g$), according to the following equations:

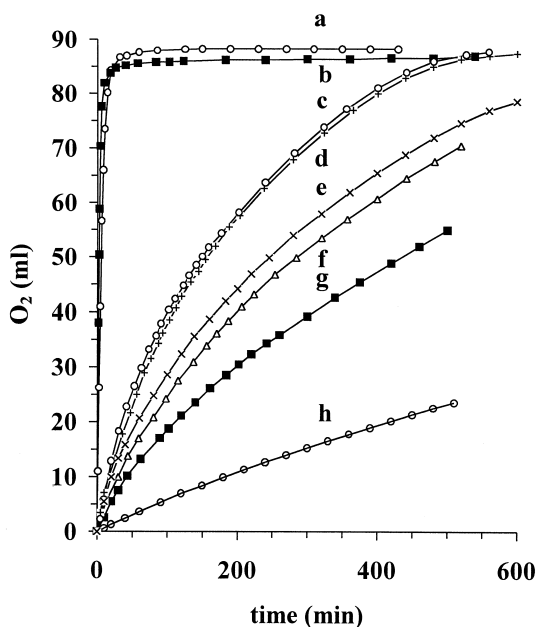$$\text{Sens} + h\nu \rightarrow {}^1\text{Sens}^* \rightarrow {}^3\text{Sens}^* \qquad (4)$$

$$^3\text{Sens}^* + {}^3O_2 \rightarrow \text{Sens} + {}^1O_2 \qquad (5)$$
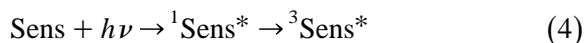
Fig. 7. Oxidation of Na$_2$S (4.2 mmol) catalyzed by: (a) NiPS$_3$, 17 μmol; (d) K$_{0.33}$H$_2$O$_{0.66}$MoS$_2$, 17 μmol; (f) CdS, 17 μmol; (h) MoS$_2$, 17 μmol. Photoxidation of Na$_2$S (4.2 mmol) catalyzed by: (b) NiPS$_3$ 17 μmol; (c) K$_{0.33}$H$_2$O$_{0.66}$MoS$_2$, 17 μmol; (e) CdS, 17 μmol; (g) MoS$_2$, 17 μmol.

The singlet oxygen which is much more reactive than ^{3}O$_2$ is involved in the photooxidation process of the sulfide ion [9,15,16,31]. The consumption of O$_2$ during Na$_2$S oxidation, photocatalyzed by zinc phthalocyanine complexes (Table 1), is ≈ 190 ml, corresponding to complete oxidation of the sulfide ion to sulfate according to Eq. (1).

Polysulfides, elementary sulfur, sulfites, and thiosulfates are intermediate products during the complete oxidation of the sulfide ion to sulfate. The zinc phthalocyanine complexes are the only investigated photocatalysts, capable to oxidise under irradiation the thiosulfate ion to sulfate in accordance with Eq. (2) (Fig. 6).

The changes in the catalytic activity of the investigated metal chalcogenides upon irradiation are presented in Fig. 7. The difference between the catalytic and photocatalytic activity (Table 1) is described by the following order: MoS$_2$ > NiPS$_3$ > CdS. It is known that the quantum yield of photooxidation of sulfur-con-

taining compounds in the presence of bulk or colloidal CdS is low and it is ranging from 0.02 to 0.2 [18–20].

4. Conclusions

The phthalocyanine complexes and metal chalcogenides do not catalyze in the dark the complete oxidation of the sulfide ion to sulfate. The final product of the catalytic oxidation is thiosufate. None of the catalytic samples catalyze in the dark the oxidation of Na$_2$S$_2$O$_3$, which is an intermediate product during the complete catalytic oxidation of the sulfide ion. The activity of the some catalysts was enhanced upon irradiation with visible light. The final product of the sulfide ion photooxidation, catalyzed by metal chalcogenides of semiconductor type, is thiosulfate. The only catalysts in whose presence the photooxidation of the sulfide and of the thiosulfate ions is proceeding to sulfate are the zinc phthalocyanine complexes. In this case, singlet oxygen is involved in the photooxidation process.

Acknowledgements

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