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CATALYSIS

Use of Cobalt(II) Phthalocyanine Sulfonates in Gas Purification To Remove Hydrogen Sulfide

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Abstract—Experiments on liquid-phase oxidation of H_2S with oxygen in the presence of catalysts, cobalt phthalocyanine sulfonates $[CoPc(SO_3Na)_n]$, were performed on a laboratory static installation in order to find conditions under which a stationary oxidation mode can be established at pH ≥ 8. The influence exerted by additional introduction of a soluble salt of Mn^{2+} ($MnSO_4$, $MnCl_2$) into the reaction mixture at various pH values was studied.

Cobalt(II) phthalocyanine sulfonates $[CoPc(SO_3Na)_n]$ are active catalysts for liquid-phase oxidation of H_2S with oxygen [1–3], which can be successfully used in liquid oxidative processes for purification of various gases to remove hydrogen sulfide. Liquid oxidative methods for gas purification include H_2S absorption with an aqueous solution that contains an alkaline agent and a catalyst and catalytic oxidation of the thus caught H_2S with atmospheric oxygen.

In a weakly alkaline medium (pH 7.3–8.0), the absorbed H_2S, which is in the form of HS^- ions, is oxidized in the presence of $CoPc(SO_3H)_n$ at a high rate by the polysulfide mechanism [1]. The main oxidation products are elementary sulfur and thiosulfates [1]. HS^- ions are oxidized via redox transitions $Co(II)Pc(SO_3H)_n + HS^- \rightleftarrows Co(I)Pc(SO_3H)_n$ The oxidation mechanism is described by the scheme

$$Co(II)Pc(SO_3Na)_n + HS_n^- \rightarrow Co(I)Pc(SO_3Na)_n + HS_n^{\bullet} + H^+, \quad (1)$$

$$2HS_n^{\bullet} \rightarrow S_{2n}^{2-} + 2H^+, \quad (2)$$

$$2Co(I)Pc(SO_3Na)_n + 0.5O_2 + 2H^+ \rightarrow 2Co(II)Pc(SO_3Na)_n + H_2O, \quad (3)$$

$$HS^- + S_{2n}^{2-} \rightarrow HS_n^- + S_{(n+1)}^{2-}. \quad (4)$$

In alkaline solutions (pH > 11), HS^- ions are oxidized through oxygen activation via formation of $[Co(III)Pc(SO_3Na)_n \cdot O^{2-}]$ complexes [4], i.e., via the redox transitions [1, 4, 5]

$$Co(II)Pc(SO_3Na)_n \rightleftarrows Co(III)Pc(SO_3Na)_n.$$

In this case, the catalyst activity is more than an order of magnitude lower [1], with sulfites and sulfates formed as a result of oxidation. It should be noted that, in gas purification to remove H_2S, it is important to obtain elementary sulfur, since it is easily separated from the absorbing solution.

At pH 8–11, lower rates of liquid-phase oxidation of H_2S are commonly observed in the presence of $CoPc(SO_3Na)_n$, compared with those at pH 7.3–8.0 and pH > 11. The rate of oxidation and the composition of the oxidation products formed at pH 8–11 are even affected by minor changes in the process parameters {pH value, presence of oxidation (semi)products, such as S^0 and SO_3^{2-} ions [6]}.

In gas purification to remove H_2S, it is necessary to maintain a stationary oxidation mode of oxidation of H_2S being caught. The purification process should be stable in an as wide fluctuation range of the purification process parameters as possible, and, primarily, it should be stable against accumulation of oxidation products and semiproducts.

The aim of this study was to find conditions that make it possible to establish a stationary mode of liquid-phase oxidation of H_2S with oxygen in the presence of catalysts $CoPc(SO_3Na)_n$ at pH 8–11, to select optimal oxidation conditions, and to perform test purification of petroleum gas to remove H_2S on a pilot installation.

EXPERIMENTAL

Experiments on liquid-phase oxidation of H_2S were performed on a static laboratory installation [6].

For the experiments, Na_2S and Na_2SO_3 solutions and solutions of the catalysts $Co(II)Pc(SO_3Na)_2$ and $Co(II)Pc(SO_3Na)_4$ were prepared. The content of Na_2SO_3 and $Na_2S_2O_3$ in the working solutions was determined by iodometry [7], and the concentration of the catalysts, cobalt(II) phthalocyanine sulfonates, by spectrophotometry [6]. The pH value of a solution being oxidized was maintained constant by introducing a phosphate buffer solution.

The rate of NaHS oxidation in the static installation was determined volumetrically from the oxygen absorption, and also from changes in the iodometrically found concentration of NaHS in the reaction mixture [7]. The completion of NaHS oxidation was indicated both by termination of oxygen absorption and by the absence of HS^- ions in the reaction mixture, which was determined using lead indicator paper [8]. The content of oxidation products, Na_2SO_3 and $Na_2S_2O_3$, in the reaction mixture was found iodometrically [7]. The presence of elementary sulfur in the oxidation products in the static installation was determined visually, and the amount of sulfur formed, spectrophotometrically [9]. The overall balance of oxidation products in the static installation correlated with the amounts of oxidized NaHS and oxygen consumed for oxidation.

The concentration of H_2S in an unpurified petroleum gas was found by means of chromatography. The absence of H_2S in a purified gas was established visually, using a lead indicator paper moistened with water and placed in the gas flow [8]. The content of the products formed in oxidation of the H_2S caught, Na_2SO_3 and $Na_2S_2O_3$, was determined iodometrically [7], and the absence of Na_2SO_4 in the absorbing solution was established using $BaCl_2$ [10]. The content of elementary sulfur in the absorbing solution was found spectrophotometrically [9], and the concentration of soda ($NaHCO_3$ + Na_2CO_3), by titration with sulfuric acid [11]. The overall balance of the amount of products formed in oxidation of the H_2S caught in the absorbing solution correlated with the total amount of H_2S caught by the installation for purification of petroleum gas to remove H_2S.

Figures 1a and 1b show the results of experiments on liquid-phase oxidation of H_2S in the presence of catalysts, $CoPc(SO_3Na)_2$ and $CoPc(SO_3Na)_4$, at pH 8.0 and 10.2, performed on the static installation.

As can be seen from Fig. 1a, introduction of already a second portion of the substrate results in that the process becomes steady-state, being characterized by rather high oxidation rate [especially in the presence of $CoPc(SO_3Na)_4$]. In the experiments with the initial concentration of H_2S (curves *1* and *1'*), the main oxidation product was $Na_2S_2O_3$ and, in part, elementary sulfur. The increase in the oxidation rate and sulfur yield upon repeated introduction of the substrate being oxidized into the oxidized reaction mixture (curves *2* and *2'*) is due to the fact that the elementary sulfur formed in the initial experiments maintains a high concentration of polysulfide ions in the reaction mixture through the reaction

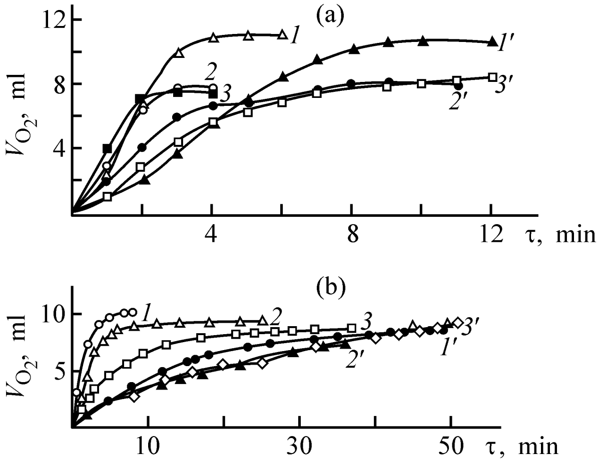

Fig. 1. Kinetics of liquid-phase oxidation of H_2S with oxygen in the presence of a catalyst, (*1*–*3*) $CoPc(SO_3Na)_4$ or (*1'*–*3'*) $CoPc(SO_3Na)_2$ at pH value of (a) 8.0 and (b) 10.2. T = 25°C, P_{O_2} = 101 kPa, V_Σ = 20 ml, $[CoPc(SO_3Na)_n]$ = 5 mg l^{-1}. (V_{O_2}) Oxygen volume and (τ) process duration; the same for Figs. 2–4. Concentration $[H_2S]_0$ (M): (*1*, *1'*) 2.4 × 10^{-2}, (*2*, *2'*) 4.8, and (*3*, *3'*) 7.2.

$$HS^- + (n - 1)S^0 = HS_n^-. \qquad (5)$$

The high running concentration of polysulfide ions in the reaction mixture favors the liquid-phase oxidation of H_2S by the polysulfide mechanism. The yield of S^0 in NaHS oxidation is about 60%, and that of $Na_2S_2O_3$, approximately 40% (curves *2* and *2'*). The kinetic curves *2*, *3* and *2'*, *3'*, which describe liquid-phase oxidation of H_2S, are very close. This is accounted for by the fact that the oxidation products S^0 and $Na_2S_2O_3$, which are accumulated in the solution, have no inhibiting effect on the liquid-phase oxidation of H_2S [6]. Thus, a stationary mode of liquid-phase oxidation of H_2S in the presence of catalysts, cobalt(II) phthalocyanine sulfonates $CoPc(SO_3Na)_n$, is ensured at pH 8.0.

The process of liquid-phase oxidation of H_2S at pH 10.2 (Fig. 1b) does not become steady-state upon repeated charging of the substrate: the time of oxida-

Table 1. Calculated equilibrium compositions of an absorbing solution of soda in purification of an H_2S-containing gas ($[H_2S] = 0.3$, $[CO_2] = 2.5$ vol %; $P_{gas} = 101$ kPa)

pH value	Concentration, M			
	$NaHCO_3$	Na_2CO_3	NaHS	Na_2S
8.0	3.17×10^{-2}	1.47×10^{-4}	2.22×10^{-3}	1.6×10^{-7}
8.5	0.100	1.47×10^{-3}	7×10^{-3}	1.6×10^{-6}
9.0	0.317	1.47×10^{-2}	2.22×10^{-2}	1.6×10^{-5}
9.5	1.00	0.147	0.07	1.6×10^{-4}
10.0	3.17	1.47	2.22×10^{-1}	1.6×10^{-3}

tion increases upon introduction of each subsequent portion of the substrate into the reaction mixture. The elementary sulfur formed in the initial experiment (curve *1*) dissolves afterwards (curves *2* and *3*): in runs with the $CoPc(SO_3Na)_2$ catalyst, no sulfur was formed at all. At pH 10.2, an intermediate oxidation mechanism is operative [4], in which a major part of polysulfide ions formed in reactions (1)–(4) is noncatalytically oxidized to SO_3^{2-} ions. Sulfite ions accumulated in the absorbing solution increasingly disrupt the polysulfide oxidation mechanism by decomposing the sulfide ions:

$$(n - 1)SO_3^{2-} + HS_n^- = (n - 1)S_2O_3^{2-} + HS^-. \quad (6)$$

In the experiments performed at pH 10.2, the liquid-phase oxidation of H_2S did not become steady-state. Therefore, absorbing solutions of this composition cannot be recommended for use in gas purification to remove hydrogen sulfide.

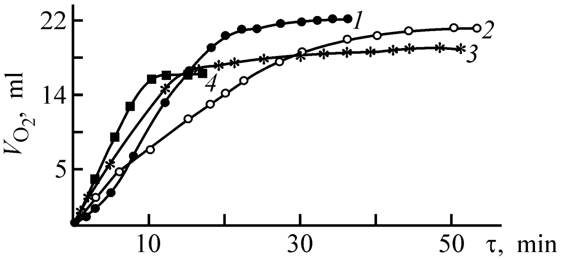

Fig. 2. Kinetics of oxidation with oxygen of alkaline aqueous solutions of NaHS in the presence of catalysts, $CoPc(SO_3Na)_2$, $CoPc(SO_3Na)_4$, and $MnSO_4$. $T = 25°C$, $P_{O_2} = 101$ kPa, pH 11.3, $V_\Sigma = 20$ ml, $[H_2S]_0 = 2.4 \times 10^{-2}$ M. Concentration (M): (*1*) $[MnSO_4] = 0.5 \times 10^{-3}$, (*2*) $[CoPc(SO_3Na)_2] = 10$, (*3*) $[CoPc(SO_3Na)_4] = 10$; (*4*) $[CoPc(SO_3Na)_4] = 10$ mg l^{-1}, $[MnSO_4] = 0.5 \times 10^{-3}$ M.

The disodium salt of disulfonic acid of cobalt phthalocyanine, $CoPc(SO_3Na)_2$, is used in air purification to remove H_2S [12, 13]. In this case, a sufficient capacity of a weakly alkaline absorbing solution for H_2S is ensured both by the alkalinity of the absorbing solution and by the high activity of the catalyst $CoPc(SO_3Na)_2$. In purification of oxygen-free gases, the capacity of the absorbing solution for sulfur depends solely on the alkalinity of the absorbing solution. Table 1 lists calculated equilibrium compositions of a soda solution at various pH values of the solution in purification of a gas containing H_2S.

As follows from the data in Table 1, raising the pH of the absorbing solution from 8.0 to 10.0 leads to an increase in the equilibrium content of H_2S being caught in the absorbing solution by two orders of magnitude (H_2S is present in solutions at pH 8–10 mainly as HS^- and S^{2-} ions). Therefore, it is necessary to use absorbing solutions with the highest possible pH value in purification of oxygen-free gases to remove H_2S with $CoPc(SO_3Na)_n$. Consequently, it is important to select the conditions at which H_2S is oxidized in solutions with the highest possible pH value in the stationary mode by the polysulfide mechanism, to give elementary sulfur as a result of oxidation.

The process of liquid-phase oxidation of H_2S at pH 10.2 (Fig. 1b) does not become steady-state because of the accumulation of the oxidation semiproduct Na_2SO_3 in the absorbing solution. To pass to a stationary oxidation mode, it is necessary to restrict the accumulation of SO_3^{2-} ions in the reaction mixture.

It is known that manganese compounds are active catalysts for liquid-phase oxidation of H_2S and oxidation of sulfite ions to sulfate ions. In this study, it is suggested to introduce soluble Mn^{2+} salts into the reaction mixture in addition to the $CoPc(SO_3Na)_n$ catalyst.

Figure 2 shows data on oxidation of alkaline aqueous solutions of NaHS with oxygen in the presence of the $CoPc(SO_3Na)_2$, $CoPc(SO_3Na)_4$, and $MnSO_4$ catalysts.

Addition of Mn_2^+ salts to the $CoPc(SO_3Na)_4$ catalyst (Fig. 2, curve *4*) makes shorter the time of complete NaHS oxidation, from 48 to 14 min. Also, the composition of the oxidation products is changed: the volume of oxygen consumed for complete oxidation of the reaction mixture decreases from 19.6 to 16.4 ml. In the simultaneous presence of $CoPc(SO_3Na)_4$ and $MnSO_4$, elementary sulfur is formed in NaHS oxidation. In the presence of only one of these catalysts, $MnSO_4$ (Fig. 3, curve *1*) or $CoPc(SO_3Na)_4$ (Fig. 3, curve *3*), no elementary sulfur is formed in NaHS oxidation.

Table 2. Results obtained in purification of petroleum gas on the pilot installation (amount of petroleum gas being purified 0.76 $m^3 h^{-1}$, air flow rate 2.4 $m^3 h^{-1}$, solution circulation rate 47 $l h^{-1}$, time of oxidative regeneration of solution 12.8 min, $MnCl_2$ concentration 80 mg l^{-1}, purified gas contains no H_2S, regenerated solution contains HS^- ions)

τ, min	H_2S content in unpurified gas, vol %	Amount of H_2S caught by 1 l of solution, g	Solution pH		Content of indicated substance in absorbing solution			
			after absorber	after regenerator	$NaHCO_3$, g l^{-1}	Na_2CO_3, g l^{-1}	$Na_2S_2O_3$, g l^{-1}	$CoPc(SO_3Na)_4$, mg l^{-1}
135	2.34	0.57	8.4	8.8	14.9	4.77	111	22
495	1.36	0.38	8.8	9.0	10.8	5.3	102	22
180	1.63	0.4	8.6	9.0	–	–	–	–
505	2.55	0.64	8.5	8.8	6.89	4.62	108	8.0
960	1.99	0.49	8.7	8.9	6.84	3.68	112	8.4

Figures 3 a 4 show the kinetic curves obtained in experiments on NaHS oxidation in the presence of $MnSO_4$ and $CoPc(SO_3Na)_4$ catalysts at pH 11.0 and 11.85, respectively. In these experiments, the stage of oxidative regeneration of the absorbing solution was simulated by multiple introduction of the substrate into an oxidized solution.

At pH 11.0 and 11.85, the process of liquid-phase oxidation of H_2S becomes steady-state already after a second introduction of the substrate. The main oxidation products are elementary sulfur and thiosulfates. Thus, simultaneous use of two catalysts, $CoPc(SO_3Na)_4$ and Mn^{2+}, must ensure a stationary mode of liquid oxidative purification of oxygen-free gases to remove H_2S.

Petroleum gas was purified to remove H_2S by the liquid oxidative method on the pilot installation. The initial absorbing solution contained $CoPc(SO_3Na)_4$ and $MnCl_2$ catalysts, and also sodium thiosulfate, carbonate, and bicarbonate.[1]

The gas to be purified was fed into the bottom part of an absorber packed with iron chips and was washed there in the counterflow mode with the absorbing solution.

The gas purified to remove H_2S was directed from the upper part of the absorber through a spray catcher to the flare, and the absorbing solution saturated with hydrogen sulfide was delivered to the bottom part of the regenerator, an apparatus with a continuous bubbling bed. In the regenerator, air was bubbled through the solution and the H_2S caught was oxidized. The regenerated solution was delivered from the upper part of the regenerator to the upper part of the absorber. The elementary sulfur formed as a a result of oxidation was floated to the solution surface in the regenerator and was removed therefrom as sulfur foam.

Table 2 presents the results obtained in purification of petroleum gas to remove H_2S with $CoPc(SO_3Na)_4$ and $MnCl_2$ catalysts.

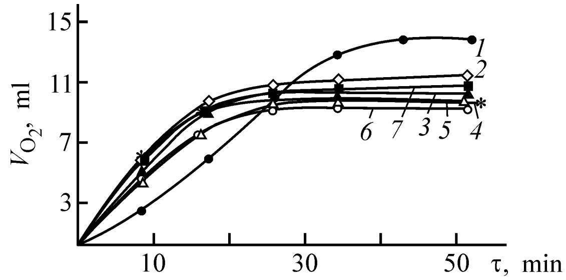

Fig. 3. Kinetics of NaHS oxidation with oxygen in the presence of $CoPc(SO_3Na)_4$ and $MnSO_4$ catalysts. T = 25°C, P_{O_2} = 101 kPa, pH 11.0, V_Σ = 20 ml, $[CoPc(SO_3Na)_4]$ = 10 mg l^{-1}, $[MnSO_4]$ = 0.5 × 10^{-3} M. (*1*) $[NaHS]_0$ = 2.4 × 10^{-2} M, (*2–7*) reaction mixture after the preceding experiment, into which NaHS was introduced in amount equal to its initial content in the reaction mixture.

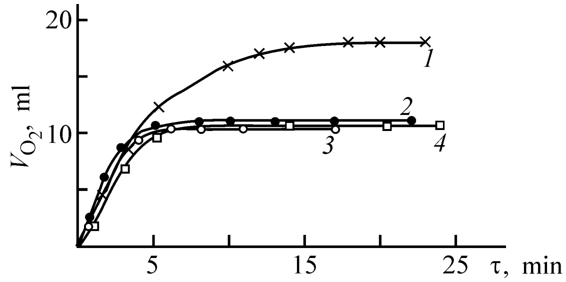

Fig. 4. Kinetics of oxidation of aqueous alkaline solutions of NaHS with oxygen in the presence of $CoPc(SO_3Na)_4$ and $MnSO_4$ catalysts. T = 25°C, P_{O_2} = 101 kPa, pH 11.85, V_Σ = 20 ml, $[CoPc(SO_3Na)_4]$ = 10 mg l^{-1}, $[MnSO_4]$ = 0.5 × 10^{-3} M. (*1*) $[NaHS]_0$ = 2.4 × 10^{-2} M, (*2–4*) reaction mixture after the preceding experiment, into which NaHS was introduced in amount equal to its initial content in the reaction mixture.

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[1] The tests were performed by staff members of the VNIPIgazpererabotka Institute (Krasnodar) with participation of one of the authors of this paper.

It follows from the data in Table 2 that complete gas purification was observed at sufficiently high loads in terms of H_2S to be purified (up to 0.6 g H_2S l^{-1}). At solution pH 8.4–9.0, the purification mode was stable. The yield of sulfur was about 90%.

CONCLUSIONS

(1) It was shown that the process of liquid oxidative purification of oxygen-free gases to remove H_2S with cobalt phthalocyanine sulfonates as catalysts is stable if accumulation of SO_3^{2-} ions in the absorbing solution is prevented.

(2) If manganese chloride $MnCl_2$ was used, together with the $CoPc(SO_3Na)_4$ catalyst, on a pilot installation, petroleum gas containing 1.4 to 2.6 vol % H_2S was completely purified to remove H_2S. In this case, the capacity of the absorbing solution for H_2S was up to 0.6 g l^{-1}, with the yield of elementary sulfur obtained in the process of purification equal to about 90%.

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