=============================== **CATALYSIS** ===============================

Oxidation of Organic Sulfides with Atmospheric Oxygen in the Presence of Phthalocyanine Complexes as Catalysts

I. S. Faizrakhmanov, L. F. Zainullina, R. F. Talipov, and A. Kh. Sharipov

Bashkir State University, Ufa, Bashkortostan, Russia
Institute of Petrochemistry and Catalysis, Ufa Research Center, Russian Academy of Sciences, Bashkortostan, Russia

Abstract—Catalytic oxidation of a mixture of low-molecular-weight sulfides with atmospheric oxygen was studied. The catalytic activity of poly(cobalt phthalocyanine) in this process is higher than that of monomeric cobalt phthalocyanine.

The use of the gas condensate of the Karachagansk deposit in natural gas processing increased the sulfur content in the isopentane and pentane fractions to 0.02 and 0.2 wt %, respectively [1]. The total sulfur content of the isopentane and pentane fractions used in production of synthetic rubbers should not exceed 0.003 and 0.01 wt %, respectively [2].

An analysis of pentanes for sulfur-containing compounds showed the presence of mercaptans and sulfides [1]. The mercaptan fraction consists mainly of ethyl isopropyl, and butyl mercaptans. The sulfide fraction contains dimethyl sulfide as the major component and a minor amount of methyl ethyl sulfide.

One of the procedures for removing sulfur-containing compounds is their catalytic oxidation with atmospheric oxygen [2]. Therefore, a search for effective catalysts for this reaction is a topical problem.

EXPERIMENTAL

The amount of sulfide sulfur in the pentane–isopentane fractions ranges from 35 to 50 wt % relative to the total sulfur content [3]. The efficiency of desulfurization by alkali treatment and demercaptanization in the presence of cobalt disulfophathalocyanine decreases when both sulfides and mercaptan are present in the substrate [4]. We studied comparatively the oxidation of a mixture of sulfur-containing compounds in the presence of cobalt(II) phthalocyanine [PhCo(II)] and its polymer [PPCo(II)] as catalysts. For this purpose, we used isooctane solutions of a mixture of sulfides with a sulfide sulfur content of 0.052–0.059 wt %

and of a sulfide-mercaptan mixture with a mercaptan sulfur content of up to 0.055 wt %. The phthalocyanine complexes were used in the form of a suspension or a solution in aqueous sodium hydroxide. The PPcCo(II) and PcCo(II) concentration in the alkaline solution was 0.025 and 0.033 wt %, respectively. A suspension or a solution (50 ml) of the phthalocyanine complex and a solution of sulfur-containing compounds in isooctane (100 ml) were placed in a 250-ml conical flask. Air was bubbled through a glass tube. The mixture was vigorously stirred for 30 min at 40°C and then the sulfide sulfur content in isooctane was determined.

Sulfur-containing compounds were analyzed by gas chromatography–mass spectrometry on a Finnigan 4021 spectrometer. The total sulfur content of the pentane–isopentane fraction was determined in accordance with GOSTs (State Standards) 22 986–78 and 13 380–81. The experimental results are presented in Table 1. It is seen that PPcCo(II) is a more efficient catalyst for oxidation of low-molecular-weight sulfides that PcCo(II). At the same time, the catalytic activity of poly(metal phthalocyanines) (PPcM) in oxidation may be lower, higher, or equal to that of the monomers (PcM) [5]. The reasons for this phenomenon were not understood. However, the catalytic activity of PPcM was believed to be due to structural features of the intermediates and to the influence of the reaction medium.

Because the PcM–S bond formed by σ electrons of the sulfur atom and donation of d_π-electrons of the metal ion to the unoccupied σ-orbital of the sul-

**Table 1.** Oxidation of sulfides and sulfide–mercaptan mixtures in the presence of cobalt(II) phthalocyanines

Sulfide	Initial S^{2-} content, wt %	PcCo(II)		PPcCo(II)	
		S^{2-} content after oxidation, wt %	conversion of S^{2-}, %	S^{2-} content after oxidation, wt %	conversion of S^{2-}, %
Sulfide					
Dimethyl sulfide	0.0592	0.0370	37.5	0.0105	82.2
Methyl ethyl sulfide	0.0584	0.0382	34.5	0.0126	78.4
Diethyl sulfide	0.0575	0.0387	32.7	0.0132	77.0
Sulfide–mercaptan					
Dimethyl sulfide	0.0592	0.0299	49.5	0.0017	97.1
Methyl ethyl sulfide	0.0584	0.0312	46.5	0.0028	95.2
Diethyl sulfide	0.0575	0.0356	38.0	0.0027	95.3

fur atom is strong [6, 7], the PcM–S(CH$_3$)$_2$ complex should be stable. In the presence of molecular oxygen a PcM–S(CH$_3$)$_2$–O$_2$ complex can be formed. Decomposition of this complex yields the initial catalyst and dimethyl sulfoxide.

The high catalytic activity of PPcCo(II) in oxidation of sulfides by atmospheric oxygen can be due to an undistorted planar structure of the phthalocanine rings in the polymeric chain and, hence to a higher stability of intermolecular complexes of PPcCo(II) as compared to those of PcCo(II) [5]. It should be noted that the degree of sulfide oxidation catalyzed by both PPcCo(II) and PcCo(II) increases in the presence of mercaptans, which can be probably due to involvement of mercaptans and their derivatives in the formation of the intermolecular complexes [7–9].

Based on the experimental results, we developed an industrial installation for removal of sulfur-containing compounds from the pentane–isopentane fraction in the presence of PPcCo(II) (see figure). Raw material, stabilized sulfurous naphtha (C$_5$–C$_6$ fraction), is fed by a pump *2* from receiver *1* to a preliminary washing column *3*. The column is washed with 6% NaOH solution to remove traces of hydrogen sulfide. The prewashed petrol (100 volumes) is mixed with 6–10% NaOH solution (12–15 volumes). The mixture is bubbled with air using a compressor *4* and then is fed into a mixer *6* equipped with nine flow-measuring diaphragms. The turbulence produced in the course of passage of the naphtha, alkali, and air through the diaphragm holes provides a good contact between these components. Mercaptan passes into the alkaline solution and is oxidized to the disulfide [1, 2] which is extracted into the hydrocarbon phase. Sulfides are oxidized mainly to the corresponding sulfoxides. Since low-molecular-weight sulfoxides are readily soluble in water, the major portion of these compounds formed in the system passes into the alkaline solution. The residence time of the system in the mixer is sufficient for the reaction completion. The reaction mixture is fed from the mixer to a settler *7* where the sodium hydroxide solution is separated and recycled with a pump *8* to mixer *6*. The NaOH
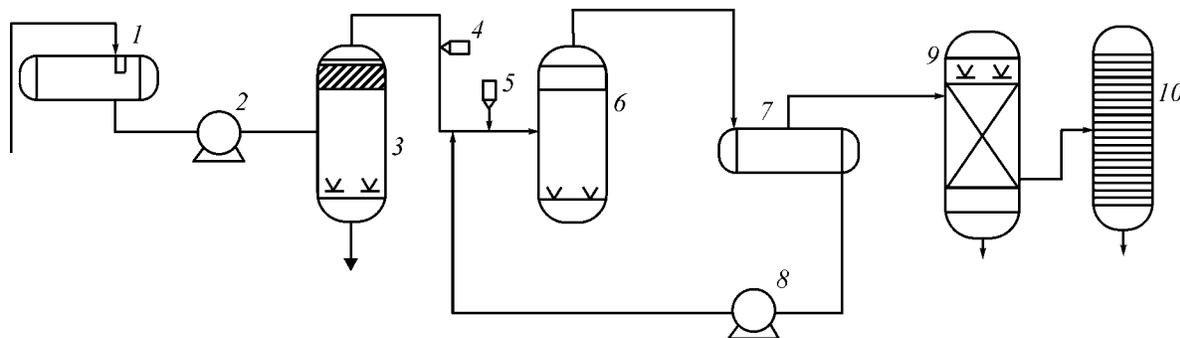
Scheme of an installation for catalytic oxidation of sulfur-containing compounds of the pentane–isopentane fractions with atmospheric oxygen: (*1*) receiver for raw material, (*2*, *8*) pump, (*3*) column for preliminary alkali washing, (*4*) compressed air, (*5*) vessel with catalyst, (*6*) mixer, (*7*) settler for alkali, (*9*) sand filter, and (*10*) distillation column.

Table 2. Distributiion of DMSO between hydrocarbon and aqueous phases (initial aqueous phase: 10% NaOH solution)

DMSO concentration in initial solution, wt %	Hydrocarbon : aqueous solution weight ratio	Hydrocarbon	Total sulfur content of the hydrocarbon phase, wt %
1	1 : 3	n-Hexane	0.0012
25	1 : 3	"	0.0029
50	1 : 3	"	0.0082
5	1.4 : 1	Isopentane	0.0007
9	1.3 : 1	"	0.0016
20	1.2 : 1	"	0.0024
33	1 : 1	"	0.0020
19	1.1 : 1	"	0.0025

solution circulating through the mixer contains 0.01–0.005 wt % PPcCo(II). This complex is added from a vessel *5* at regular intervals.

To remove traces of the alkali emulsion, the hydrocarbon fraction is passed through filter *9*. Then the hydrocarbon fraction containing oxidized sulfur compounds is fed into a distillation column *10* (15 TP, reflux ratio 3). Pentane and isopentane fractions are taken from the top of the column. The total sulfur content in these fraction meets the requirements of TU (Technical Specifications) 38.101 790–79.

The boiling points of the oxidation products, disulfides and sulfoxides, are higher than those of the initial mercaptans and sulfides and, hence, these products can be separated by distillation. Low-boiling sulfoxides (C_5–C_6) are readily soluble in water and are removed by washing.

The main sulfur-containing compound present in the pentane fraction examined, dimethyl sulfide, is oxidized to dimethyl sulfoxide. Dimethyl sulfoxide can be distributed between the aqueous alkali and the hydroxarbon fraction. Dimethyl sulfoxide (DMSO) can be accumulated in the aqueous phase in the course of multiple circulation of the oxidizing agent. Hence, its content in the hydrocarbon fraction should also increase. To determine the maximal DMSO content of the aqueous phase, we studied phase equilibria in the hydrocarbon–DMSO–NaOH solution system. Hydrocarbons were isopentane and n-hexane. The DMSO distribution was estimated from the total sulfur content in the hydrocarbon fraction.

The experimental results listed in Table 2 show that, even at a very high concentration of DMSO in

the aqueous phase, the total sulfur content of the hydrocarbon fraction is not higher than hundredth of a persent. The distribution coefficient of DMSO between the aqueous and hydrocarbon fractions is 100. Thus, isopentane meeting the TU can be obtained at the DMSO content in the aqueous phase lower than 10%.

CONCLUSIONS

(1) It was shown that the catalytic activity of poly(cobalt(II)phthalocyanine) in oxidation of a sulfide mixture by atmospheric oxygen is higher than that of monomeric cobalt(II) phthalocyanine. The conversion of a sulfide mixture increases in the presence of mercaptans.

(2) A flow sheet was developed for removal of sulfur-containing compounds from pentane–isopentane fractions by oxidation with atmospheric oxygen in the presence of poly(cobalt(II) phthalocyanine).

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