Metal complex catalysts for oxidative demercaptanization of sulfur compounds in crude oil*

Yu. A. Gavrilov, I. V. Pletneva, and E. N. Silkina*

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 119991 Moscow, Russian Federation.
E-mail: inna.pletneva1@yandex.ru

Demercaptanization of sulfur compounds in crude oil in the presence of metal complex oxidation catalysts was studied. The adsorption capacities of the catalysts and industrial mercaptane scavengers were compared. The possibility of using these catalysts for the removal of light sulfur impurities in the field oil preparation was shown.

Keywords: catalyst, demercaptanization, hydrogen sulfide, oxidation of mercaptanes, thiols, hydrocarbons.

The presence of hydrogen sulfide, methyl- and ethyl-mercaptanes (H_2S, MeSH, EtSH), and other derivatives of the thiol series in crude oil induces corrosion of apparatus and results in significant exploitation difficulties.[1,2] In addition, high toxicity of light sulfur impurities leads to numerous environmental problems on transport lines and recharging and storage sites. This results in increasingly stringent environmental regulations for oil and oil products. (Table 1).[3,4] It should be taken into account that the fraction of crudes which are high and very high in sulfur content in the total volume of the processed crude continuously increases. Therefore, improvement of refining methods leading to removal of sulfur from petroleum compounds is one of the most important problems in hydrocarbon production and treatment.

Three main methods are presently used for the removal of hydrogen sulfide and sulfur compounds from oil and oil products: hydrodesulfurization, different variants of alkaline oxidative demercaptanization, and use of neutralizing reagents.

Table 1. Normative contents (ppm) of hydrogen sulfide and light hydrocarbons in oil raw materials of different types

Type of oil	Weight fraction of hydrogen sulfide	Total weight fraction of methyl- and ethyl-mercaptanes
1	20	40
2	50	60
3	100	100

* According to the materials of the XXIV Conference "Current Chemical Physics" (September 20—October 1, 2012, Tuapse, Russia).

Hydrodesulfurization (hydrofining) is the catalytic hydrogenation of sulfur compounds to H_2S followed by its catalytic oxidation to elemental sulfur. This method makes it possible to decrease the content of total and mercaptane sulfur in oil distillates to requirements of current standards.[5,6] However, the process is very expensive because of many stages, rigid hydrogenation regimes, and limited service life of the catalysts.

In the cases where a relatively high content of total sulfur in the products is tolerable and the concentration of mercaptanes should be decreased first of all, more economical methods, such as alkaline oxidative demercaptanization and the reagent method, can be applied.

The first method is based on the extraction of sulfhydryl compounds by alkaline solutions followed by extragent recovery using the oxidation of the extraction products (sulfides, mercaptides) with oxygen to di- and polysulfides in the presence of the phthalocyanine catalysts.[7—9] The main drawbacks of this technology are the formation of large volumes of sulfurous alkaline wastes that are needed to be separated and utilized (the last stage is expensive)[10] and a comparatively low stability of alkaline solutions of the phthalocyanine catalysts due to easy oxidation.

The reagent method is the treatment of hydrocarbons with aqueous or aqueous-alcohol solutions of oxygen- or nitrogen-containing compounds (triazines, ethanolamines, formaldehyde, paraformaldehyde, and others), which stoichiometrically interact with H_2S and light mercaptanes (MeSH, EtSH) to form nonvolatile compounds.[1,11,12] A drawback of the reagent method is a fairly low efficiency of RSH absorption causing a large consumption of toxic reagents; in some cases, for example, when using formaldehyde, carcinogenic risk appears.[13]

The activity of neutralizing reagents can substantially be increased by the introduction of transition metal com-

plexes in catalytic concentrations, which makes it possible to oxidize H_2S and light mercaptanes with oxygen to form stable non-toxic di- and polysulfide forms.[1,8,14] For example, there is a method for hydrocarbon purification from hydrogen sulfide impurities including oxidation with oxygen in the presence of aqueous or aqueous-alkaline solutions of transition metal salts and nitrogen-containing basic and/or alkaline reagents.[15] These systems readily absorb H_2S but poorly remove EtSH.

The degree of oxidation of thiols can substantially be increased in the presence of the copper complexes with DMSO.[16] However, a low solubility of DMSO in hydrocarbons restricts possibilities of the method.

The one-component catalysts applicable under industrial conditions for the removal of H_2S, MeSH, and EtSH and, in some cases, heavy mercaptanes are described in this work. These catalysts have high catalytic activity, stability in time, and good compatibility with hydrocarbons, which makes it possible to attain a uniform distribution of the catalysts in the reaction medium.

Experimental

Copper(I) chloride (99+%, Sigma—Aldrich) was used for the preparation of catalysts and additionally purified from traces of copper hydroxychlorides according to a known procedure[17] and stored under deoxygenated argon. 2-Aminoethanol (monoethanolamine (MEA) special purity grade, Laverna) used as a nitrogen-containing ligand was distilled *in vacuo* and the fraction with b.p. 70—71 °C was collected. Diethanolamide of fatty acids from coconut oils (95+%, trade name Awaxan F, OOO "Veresk Co.") served as a surfactant.

Catalytic systems were prepared by the heterogeneous heterophase oxidation of copper(I) chloride with oxygen in a MEA medium with continuous stirring in a cavitation mill at 30 °C under a pressure of 1 atm. The weight and molar ratios $CuCl^1$: MEA were 0.03—0.1 and 0.018—0.062, respectively. The reaction progress was monitored by the change in the oxygen pressure in a calibrated vessel, and the moment when the oxygen uptake had ceased was taken as the time required for the reaction to be completed. A blue labile liquid was formed due to oxidation. To improve compatibility of hydrocarbons with the catalyst, the latter was added with the surfactant in an amount of 0.25—0.5 wt.%.

The activity of the catalysts and kinetics of conversion of H_2S and thiols were determined in stabilized oil and in model mixtures. To prevent the oxidation of sulfur impurities, the oil was stored under an argon pillow for the whole testing period. The model mixtures and crude oil were preliminarily (for 1 h) saturated with air oxygen until the equilibrium solubility of oxygen was attained. The reaction was carried out at 55 °C (typical temperature of oil in preparation processes) and a constant pressure with stirring in glass sealed reactors equipped with samplers for the gas and liquid phases or in sealed glass ampules with samples with periodical stirring. The pressure was controlled with a portable manometer (AZ Instrument, model 8230).

Mixtures of hydrofined Diesel fuel (40.9 wt.%), aviation kerosene (35.7 wt.%), and straight-run gasoline (23.4 wt.%) were used as model hydrocarbons. The mixtures were added with H_2S to a concentration of 100 ppm (from an H_2S+N_2 verifying gas mixture with the hydrogen sulfide content 24.9 vol.%, OOO "Monitoring") and 1-octanethiol (98.5+%, Aldrich) containing from 100 ($2.44 \cdot 10^{-3}$ mol L^{-1}) to 400 ppm ($9.75 \cdot 10^{-3}$ mol L^{-1}) of sulfur.

The petroleum fractions from the Alibekmola (TOO "Kazakhoil-Aktobe"), Ozhginskoe (ZAO "Uralnefteservis"), and Chinarevskoe (TOO "Zhaikmunai") deposits were tested as crude oil.

The contents of hydrogen sulfide and total thiols in the model mixtures and oils were determined by potentiometric titration with silver nitrate ammoniate in ethanol—toluene or isopropanol—toluene solutions according to GOST R 52030-2003.[18] An EVL-1M3.1 silver chloride and an IONIKS 111.050 sulfide-selective electrode were used as reference and measuring electrodes, respectively.

Selective analyses of the contents of H_2S and thiols in the liquid and vapor phases were carried out using GLC on Varian 3800 (capillary column HP-5, Agilent Technologies, 50 m×0.32 mm) and Kristall-4000 (Optima 5 column, Macherey—Nagel, 25 m×0.32 mm) chromatographs. Helium served as a carrier gas. Detection was carried out using a pulsed flame-photometric (S mode) detector (Varian 3800) and a flame-photometric detector (Kristall-4000). The chromatographic analysis was controlled and experimental data were collected and processed using the Galaxie 1.9 (Varian 3800) and Khromatek Analitik (Kristall-4000) programs.

The content of catalysts introduced into the reaction medium and the stability in time of dispersed systems obtained after mixing were evaluated by atomic absorption spectroscopy on a Varian AA240G spectrometer from the content of metals.

The surface tension of the catalysts was measured according to the Rebinder method[19] at 20 °C.

The content of chloride salts in the oil was determined by mercurimetry according to GOST 21534-46 (method A).[20]

Results and Discussion

The catalytic properties on the model hydrocarbon mixtures containing hydrogen sulfide and 1-octanethiol ($C_8H_{17}SH$) were studied to evaluate the possibility of industrial application of the developed systems. This thiol was chosen due to its higher resistance to oxidation compared to MeSH and EtSH. The contents of hydrogen sulfide and 1-octanethiol in the oxidation products of the model systems are given in Table 2. It is seen that the complete conversion of H_2S occurs within the first 2 h and it is nearly independent of its initial concentration. The conversion of $C_8H_{17}SH$ within 6 h does not exceed 30% and achieves 50% in 20 h, which is the characteristic time of residence of raw materials in demercaptanization apparatus and storage reservoirs at units of oil preparation. It can be concluded on the basis of the obtained data that the presence of hydrogen sulfide does not result in a complete loss of activity of the catalyst in the oxidation of $C_8H_{17}SH$. This can be expected if copper sulfide would be formed. The observed decrease in the $C_8H_{17}SH$ concentration is probably due to its interaction with elemental sulfur formed

by the oxidation of hydrogen sulfide in the presence of MEA.[15,21] However, comparative experiments on the influence of MEA on demercaptanization in the model system in the absence of a metal complex showed that the octanethiol concentration changed insignificantly. The activity of the catalyst containing 2% Cu in thiol conversion is low and does not allow one to decrease the concentration of sulfur-containing impurities to a desired value. The conversion of thiol can be increased by increasing the metal content in the initial catalytic system or the MEA concentration in the reaction mixture.[22] The experiments on elucidating the influence of the additional introduction of MEA ($C = 0.2$ g L^{-1}) into the reaction mixture containing Cat-1 ($C = 0.2$ g L^{-1}) showed (see Table 2) that this modification of the system resulted in an insignificant increase in the conversion of $C_8H_{17}SH$ (from 50 to 65%). The further increase in the amino alcohol content makes it possible to enhance the conversion of $C_8H_{17}SH$. However, this way is hardly reasonable in industrial applications since it raises the price of the refining process. A substantial increase in the catalytic activity in 1-octanethiol oxidation in the model mixtures was achieved by an increase in the metal content in the initial catalyst. It follows from the data in Table 2 that an increase in the copper concentration from 2 to 5% results in a decrease in the residual content of $C_8H_{17}SH$ within 20 h to 24 ppm, which corresponds to the norm accepted for oil of type *1* (see Table 1). Since the reactivity of low-molecular-weight mercaptanes is higher than that of 1-octanethiol, it can be assumed that the catalysts will be efficient for the demercaptanization of petroleum.

Crudes of different origin from different deposits vary greatly in the density, group and structural group compositions, contents of hydrogen sulfide and methyl- and ethylmercaptanes, and the general content of mercaptanes. Therefore, it was necessary to study the influence of the crude origin on the ability of the described catalysts to lead the process of oxidation of H_2S and mercaptanes.[23] The results of tests of petroleum from three deposits differed strongly in the contents of H_2S and mercaptanes are presented in Tables 3—5.

As can be seen from the data in Table 3 on the oxidative demercaptanization of the Alibekmola crude, the studied catalysts are efficient in H_2S removal already at low concentrations of the catalyst. According to the chromatographic analysis data, at a catalyst concentration of 0.13 g L^{-1} an almost complete conversion of H_2S is observed already in 3 h, although the oxidation of EtSH, as in the case of the model systems, is considerably slower.

Table 2. Residual contents of hydrogen sulfide and 1-octanethiol after their oxidation in model hydrocarbon mixtures[a]

Catalyst[b] (C(Cat)/g L^{-1})	S/Cat (g g^{-1})	t/h	C, ppm	
			H_2S	$C_8H_{17}SH$
Cat-1	0.63	2	0	—
(0.20)		6	0	84
		20	0	63
Cat-2	0.78	2	0	—
(0.20)		6	0	57
		20	0	24
Cat-2	0.57	2	0	76
(0.30)		6	0	39
		20	0	11
MEA	0.49	2	18	116
(0.20)		6	0	108
		20	0	96

[a] The initial contents of H_2S and $C_8H_{18}S$ are 104 and 120 ppm, respectively; $T = 55$ °C.
[b] Catalysts Cat-1 and Cat-2 contain 2.0 and 5.0 wt.% Cu, respectively.

Table 3. Influence of the concentration of the oxidative demercaptanization catalyst on the conversion of H_2S, MeSH, and EtSH in the Alibekmola crude*

C(Cat-2) /g L^{-1}	H_2S/Cat	S_{total}/Cat	t/h	C, ppm		
	g g^{-1}			H_2S	MeSH	EtSH
0.13	0.93	1.55	3	0	3.5	73.5
			6	0	1.6	56.3
			20	0	0	44.5
0.21	0.60	1.04	3	0	1.5	64.3
			6	0	0	45.0
			20	0	0	34.0
0.36	0.33	0.63	3	0	0	49.3
			6	0	0	7.9
			20	0	0	7.3

* The initial content of H_2S is 150 ppm, that of methylmercaptanes is 14 ppm, that of ethylmercaptanes is 130 ppm, and the initial content of total mercaptanes is 1300 ppm; $T = 55$ °C.

Table 4. Influence of the concentration of the oxidative demercaptanization catalyst on the degree of removal of hydrogen sulfide and thiols in the Ozhginskoe crude*

C(Cat-2) /g L^{-1}	H_2S/Cat	S_{total}/Cat	t/h	C, ppm	
	g g^{-1}			H_2S	RSH
0.23	2.2	3.3	3	120	2600
			6	95	2600
			20	82	2600
0.38	1.3	2.2	3	0	2600
			6	0	2500
			20	0	2500
0.74	0.7	1.4	3	0	2500
			6	0	2400
			20	0	2200

* The initial contents of H_2S and total mercaptanes are 620 and 2800 ppm, respectively; $T = 55$ °C.

Table 5. Influence of the concentration of the oxidative demercaptanization catalyst on the conversion of hydrogen sulfide and thiols in the Chinarevskoe crude*

$C(\text{Cat-2})$ /g L^{-1}	H_2S/Cat	$S_{\text{total}}/\text{Cat}$	t/h	C, ppm	
	g g^{-1}			H_2S	RSH
0.042	1.7	4.0	3	7.8	126.0
			6	3.2	118.0
			20	0	98.0
0.061	1.2	3.0	3	6.2	118.0
			6	0	104.0
			20	0	86.0
0.095	0.8	2.0	3	0	99.3
			6	0	—
			20	0	74.5

* The initial contents of H_2S and total mercaptanes are 88 and 218 ppm, respectively; $T = 55$ °C.

The decrease in the content of light mercaptanes in the oil to the required parameters (40 ppm) is achieved by an increase in the catalyst concentration; however, this decreases the amount of mercaptane sulfur removed per 1 g of catalyst. The results presented show a possibility to obtain stock-tank oil of type *1* (see Table 1).[3]

The results on refining (demercaptanization) of the Ozhginskoe crude with a high initial H_2S content (620 ppm) and the concentration of total mercaptane sulfur is 2800 ppm, are presented in Table 4. The conversion of hydrogen sulfide at a catalyst concentration of 0.23 g L^{-1} within the first 3 h is close to 80% and then remains almost unchanged in time, indicating a nearly complete deactivation of the catalyst. According to the potentiometric titration data, the increase in the catalyst concentration to 0.38 g L^{-1} results in a complete conversion of H_2S. At these concentrations of hydrogen sulfide, the used catalyst is also active in the oxidation of thiols.

For example, at the catalyst concentration 0.74 g L^{-1} the conversion of general mercaptanes is 21%.

It is seen from Tables 3 and 4 that the amount of absorbed H_2S based on 1 g of the catalyst at its complete conversion depends weakly on the initial contents of H_2S and mercaptanes and the origin of the oil. This conclusion is confirmed by the results of refining of the Chinarevskoe crude, which is characterized by relatively low contents of H_2S and total mercaptanes (see Table 5). As shown by the performed tests, the demercaptanization of this oil is possible when the catalyst concentration is 2—2.5 times lower than those used for refining of the Alibekmola crude. In this case, the efficiency of the catalyst for hydrogen sulfide and mercaptane sulfur increases 2—3 times.

By comparing the efficiency of oil demercaptanization for a series of known absorbing reagents with that for the developed catalyst under the same conditions (Table 6), a higher activity of the catalyst in the removal of ethylmercaptane is evident. This component of light sulfur impurities is most difficult to remove. It is also important that the use of such catalytic systems does not result in an increase in the content of chloride salts.

Thus, the obtained results show the possibility to use the metal complex catalysts for oxidative demercaptanization in petroleum industry for field oil refining. The variation of the component composition of the catalysts and conditions of their synthesis and sulfur decontamination will make it possible to attain optimum technical economical parameters for which the use of metal complex catalysts can compete with the traditional methods, such as alkaline oxidative demercaptanization and the reagent method.

Table 6. Comparison of the absorptive capacities of a series o neutralizers and the oxidative demercaptanization catalyst[a]

Reagent	C /g L^{-1}	Content of H_2S/MeSH/EtSH (ppm) in different time intervals/h				S/m^b /g g^{-1}
		1.5	4.5	7.0	20	
Cat-2	0.20	0/5/42	0/2/35	0/0/24	0/0/11	0.840
Absorbent	1.00	0/10/80	0/10/80	0/8/78	0/7/73	0.110
"Koltek PS 1615"	1.50	0/7/72	0/6/64	0/6/56	0/5/52	0.087
MEA/H_2O^c	0.30	20/9/84	11/7/76	0/3/64	0/0/55	0.440
S/MEA^d	0.26	0/10/77	0/7/68	0/2/58	—	0.490

[a] The initial contents of H_2S, methylmercaptanes, and ethylmercaptanes are 110, 14, and 94 ppm, respectively; $T = 55$ °C; the Alibekmola crude TOO "Kazakhoil-Aktobe."
[b] m is the weight of the reagent.
[c] The concentration of MEA is 80 wt.%.
[d] S (12 wt.%) in MEA.[15,21]

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