NEW HETEROGENEOUS CATALYSTS FOR DEMERCAPTANIZATION
OF PETROLEUM AND PETROLEUM PRODUCTS

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New heterogeneous catalytic systems based on Mn–Fe- and Co–Fe-organic cluster compounds deposited on water-free clinoptilolite which manifest high activity in the course of demercaptanization of petroleum and petroleum products have been developed.

Key words*: catalyst, mercaptans, hydrogen sulfide, thiophene, demercaptanization*

The problem of sulfur-containing compounds, mainly hydrogen sulfide and mercaptans with different structure, arises in the commercial preparation of petroleum and gas condensates and in the reprocessing of petroleum fractions and residues in catalytic and thermal cracking. In addition, petroleum contains thiophenes, thiophanes, and other sulfur-containing compounds [1–5].

The need to remove hydrogen sulfides and mercaptans from petroleum and petroleum products is mainly due to the following factors listed below:

- hydrogen sulfide and mercaptan corrode the process equipment and pipelines used in petroleum refining and in storage and transport of petroleum and petroleum products;
- mercaptans and hydrogen sulfide are the nuclei for many catalysts, they are toxic, and they have a very unpleasant odor, so that the presence of these compounds in the petroleum feedstock and petroleum products creates environmental problems in processing and transporting them;
- hydrogen sulfide and mercaptan engender difficulties in purifying sewage water from reservoirs and electric desalinization facilities.

Methods exist for demercaptanization and desulfurization of petroleum feedstock – DMS processes and for removing hydrogen sulfide and mercaptans by means of neutralizers – HCM reagents [6–8].
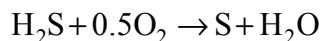
The widely used DMS processes are based on oxidation of low-molecular mercaptans and hydrogen sulfide by atmospheric oxygen in an alkaline medium in the presence of the catalyst IVKAZ. Different modifications of the DMS process are used depending on the concentration of the sulfur-containing compounds present in petroleum. For example, the DMS-1 and -2 technologies are used for commercial refining of petroleum and as condensates with methyl- and ethylmercaptans in the range 260–300 ppm; the DMS-1A process (the facility is in operation at the Oil–Gas Exploration Administration "Nurlatneft') is used to refine feedstock with a higher content of hydrogen

sulfide as well as heavy petroleum; finally, the DMS-3 technology, used at "YuNO" JSC for refining Kazakhstan and Orenburg petroleum ,for deep refinement of petroleum with high mercaptan content C_1–C_4. The residue content of hydrogen sulfide remaining in the feedstock after refinement is up to 10 ppm and mercaptans C_1–C_3 to 20 ppm. In these processes one tonne of feedstock requires 40–150 g sodium hydroxide, 0.20 g catalyst, and 1–5 nm^3 air.

The DMS-3 process is multistage [9, 10]; it is characterized by a high consumption of alkali, which, in turn, determines the need for additional refinement of the product. In addition, the residual content of mercaptans in the refined stock is relatively high.

Heavy petroleum with a high content (450–600 ppm) of hydrogen sulfide is refined using water–ammonia solutions and catalysts. The oxidation of hydrogen sulfide into elemental sulfur proceeds according to the reaction:

$$H_2S + 0.5O_2 \rightarrow S + H_2O$$

.

The consumption of the ammonia solution of the catalyst is 1–1.5 liters/t petroleum.

In the reagent method of neutralization of hydrogen sulfide and mercaptans by the reagent HCM, which is a mixture of the products of reaction of formaldehyde and monoethanolamine with the addition of 0.5 wt. % sodium carbonate, the following reactions occur [11, 12]:
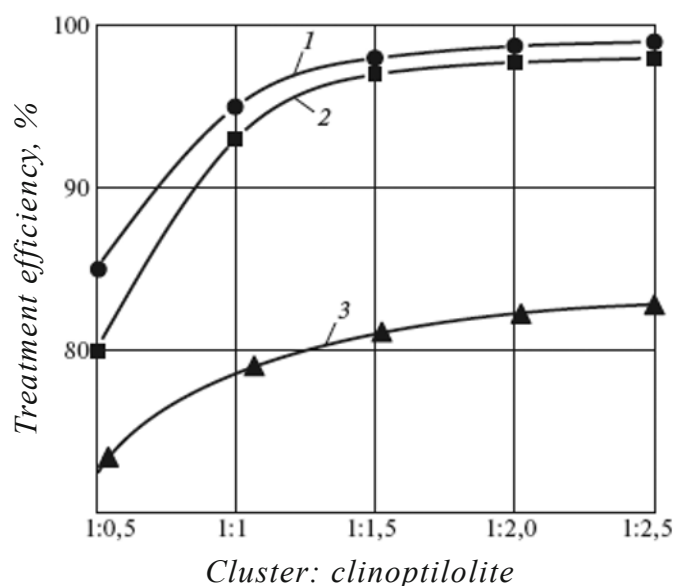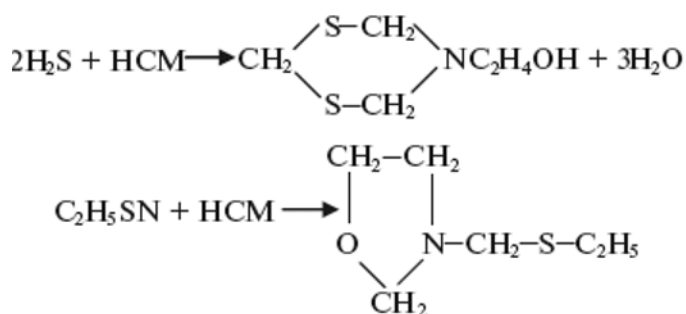

Fig. 1. Effect of the ratio of the active components and clinoptilolite on the activity of catalysts using the clusters: 1 – Co–Fe; 2 – Mn–Fe; 3 – $C_5H_5Mn(CO)_3$.

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The consumption of the reagent HCM per tonne of petroleum is 2–3 liters.

Sulfurous-alkali flows and process condensates are purified of sulfur compounds by the process Serox-W, which consists of liquid-phase oxidation of hydrogen sulfide, sulfides, hydrosulfides, mercaptides, and other compounds. The Serox-W process has been in use since 1990 at "LUKOIL-Neftokhim Burgas" (Burgas, Bulgaria) and since 1996 at the Kuibyshev and Yaroslav Petroleum Refining Plant for purifying process condensate from catalytic cracking facilities. The residual content of sodium sulfide in the drainage water is 20 mg/liter and that of sodium mercaptides is 5 ppm, which does not meet modern requirements.

The Merox process [13] is also used to remove mercaptans from pertroleum fractions. In this process the mercaptans in an alkali medium are converted into the corresponding salts RSNa, which are oxidized into disulfides in the presence of catalysts.

All processes listed above are based on the oxidation of mercaptans into disulfides in an alkaline medium. Their significant drawback is the presence of a stage of separation of the alkali emulsion. In addition, these
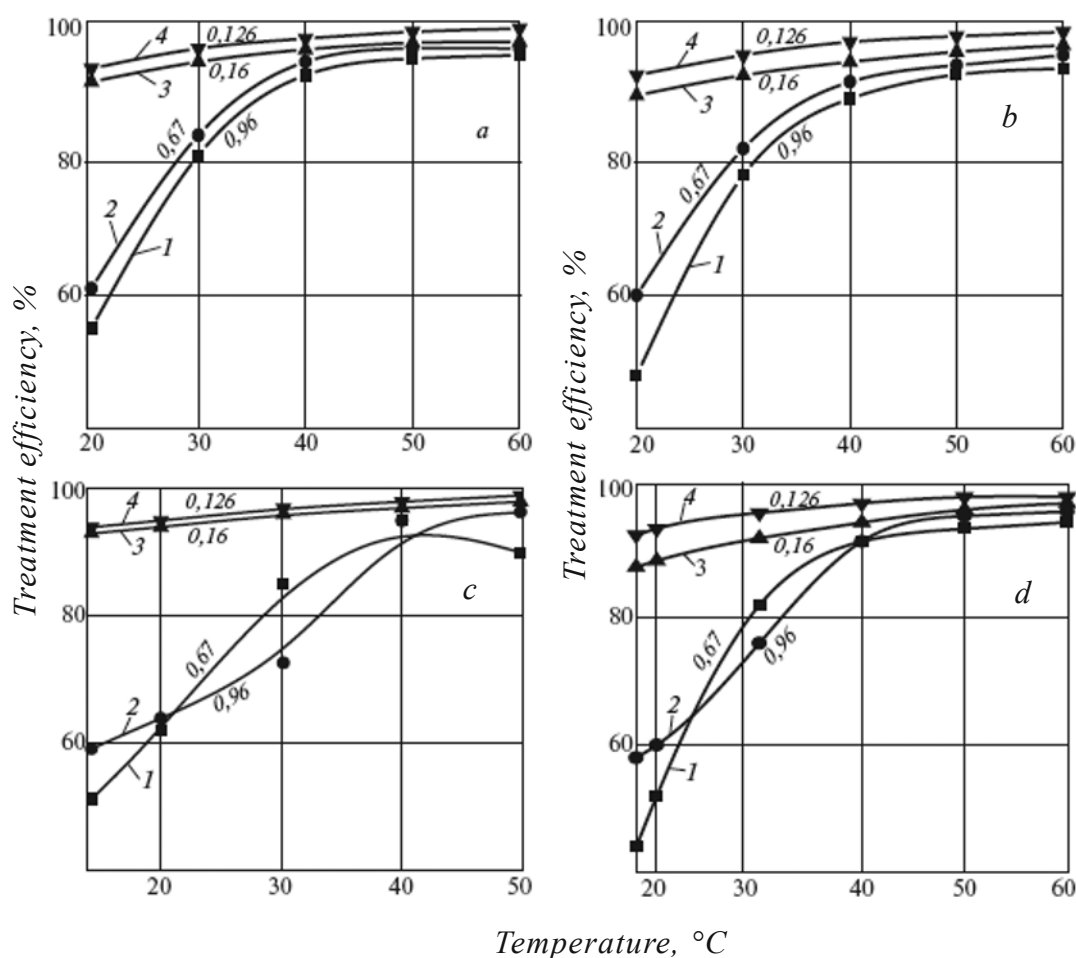

Fig. 2. Effect of the temperature on the treatment efficiency with ratio (Mn–Fe) : clinoptilolite = 1.1 (a) and 1.2 (b), (Co–Fe) : clinoptilolite 1: 1 (c) and 1. 2 (d) in the process of demercaptanization of petroleum products: 1, 2 – Russian straight-run gasoline; 3 – Kazakhstan straight-run gasoline; 4 – Russian stable gaseous gasoline (the numbers on the curves denote the sulfur content in the feedstock before treatment, g/liter).

technologies provide for additional removal of alkali from the product, regeneration of the alkali, and salvaging of the liquid wastes, which makes the processes more expensive.

A relatively new technology of oxidative demercaptanization based on the use of the catalyst MARC [14] is proposed. This technology makes it possible to perform demercaptanization directly in the flow of the petroleum product without introducing an alkali solution. The purification occurs in a tank with an active catalyst, where mercaptans are oxidized into disulfides. The mercaptanization process using the MARC catalyst is used instead of hydrofining and differs by a number of advantages. It is known that hydrofining is conducted at 260–400 °C with the hydrogen-containing gas at high pressure [15]; in addition, the consumption of fuel, energy, and hydrogen is substantial. For example, to decrease the sulfur content by 1% it is necessary to use 10–15 m^3 hydrogen per 1 m^3 sulfur. The sulfur losses as a result of hydrocracking reactions are about 4%. Hydrofining is used to produce low-sulfur automobile fuel.

It is known that in low-boiling petroleum fractions sulfur is present in the form of hydrogen sulfide, mercaptans, carbon disulfide, and dimethyl sulfides. As a result of oxidative demercaptanization in the presence of the catalyst MARC these compounds transform into disulfides at high temperature and low pressure.

Mercaptans of the fraction C_5–C_6 of gasoline from catalytic cracking are represented mainly as ethyl, isopropyl, and propyl mercaptans while other sulfur compounds are represented by carbon disulfide and dimethyl sulfides. For this reason, first, sulfur compounds from the light fraction are subjected to oxidative demercaptanization to raise the boiling temperature of sulfur compounds, and after separation the heavy fraction is subjected to hydrofining. It is well known that during hydro-purification the sulfur compounds break down into hydrocarbons and hydrogen sulfide [16], which must be processed into sulfur or sulfuric acid.

In summary, analysis of the present status of the methods used for reforming sulfur compounds from petroleum and petroleum products shows that these methods employ alkali solutions in large quantities or the processes are conducted at high temperatures and pressures. The processes are multistep and produce large quantities of wastes, salvaging which requires making additional expenditures, which makes these facilities more expensive. The catalysts used are subjected to decontamination, are difficult to regenerate, or cannot be regenerated at all.

We have proposed new catalytic systems, consisting of Co–Fe and Mn–Fe organic ligands – $C_{12}H_{10}FeCoO_2Cl_2$, and $C_{11}H_{10}MnFeOCl_2$ – based on water-free clinoptilolite. The cluster compounds were synthesized in a 0.5-liter hydrate-type autoclave using carbon monoxide as a reducer. First, the carbon monoxide was fed into a buffer tank to create pressure, and then at pressure 1MPa into an autoclave, into which after blowing nitrogen through at room temperature ferrocene $(C_5H_5)_2Fe$, manganese (or cobalt) di-isopropylate dichloride solvate salt $MnCl_2(iso\text{-}C_3H_7OH)_2$, or $CoCl_2(iso\text{-}C_3H_7OH)_2$ and tetrahydrofurane (THF) are loaded in advance. During mixing the reaction temperature was raised by electric heating to 122–130 °C; the mixing continued
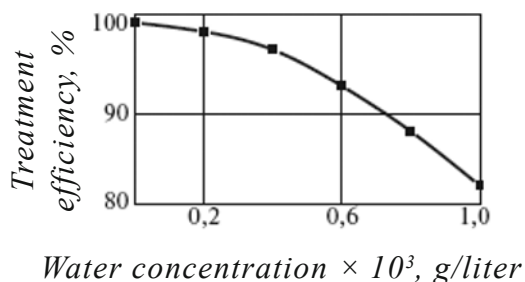

Fig. 3. Effect of the concentration of water in petroleum products on the de-activation of the catalytic system.

for 3–4 h. Then, the mixing was stopped at residual carbon monoxide pressure P_{Co} = 0.4–0.5 MPa, and the carbon monoxide residue was burned.

The solvent was first evaporated from the contents of the autoclave; the residue was washed with petroleum ether and then extracted with stable gas gasoline with distillation range 40–120 °C, after which cluster compounds were obtained. The composition of the products obtained was analyzed and checked by infrared spectroscopy, ^{1}H NMR spectroscopy, and X-ray structural and elemental analysis [17].

The new catalytic systems which we have proposed were obtained by permeating the surface of zeolites of the clinoptilolite type, synthesized by cluster compounds. The critical diameters of the molecules of the synthesized cluster compounds were determined in solvents — acetone and TGF. It was found that the critical diameter is 5.6 Å in acetone and 3.2 Å in TGF. TGF was chosen as the solvent; it dissolves the synthesized cluster compounds well [18, 19].

The activity of the catalytic systems based on the cluster compounds cobalt–iron $C_{12}H_{10}FeCoO_2Cl_2$ and manganese–iron $C_{11}H_{10}MnFeOCl_2$, deposited on water-free clinoptilolite, revealed during purification petroleum and petroleum products containing sulfur compounds. The content of sulfur compounds, mainly hydrogen sulfide and mercaptans, in petroleum products was 0.1–1 g/liter.

The effect of the ratio of clusters and clinoptilolite on the activity of catalysts during refinement of Russian straight-run benzene was investigated first. Catalysts with the ratio Mn–Fe (Co–Fe) : clinoptilolite from 0.5 : 1 to 1 : 3 were synthesized. The results are displayed in Fig. 1.

Evidently, the degree of purification increases with the ratio of the active components and clinoptilolite from 1 : 0.5 to 1 : (1 – 1.5) and reaches 96–99%. Further increase of the reaction to 1 : (2 – 2.5) does not greatly change the degree of purification. Co–Fe clusters on water-free clinoptilolite show somewhat better results, the degree of purification is several percent higher than that characteristic for Mn–Fe clusters, especially for low ratios of the active component : clinoptilolite. No substantial differences are observed for high values of this ratio. For this reason, the ratio Mn–Fe (Co–Fe) : clinoptilolite = 1 : (1–2) can be taken as optimal. The results for $C_5H_5Mn(CO)_3$ deposited on clinoptilolite are worse.

The effect of temperature in the interval 0–60 °C for catalysts with optimal ratios active component : clinoptilolite on the degree of purification of petroleum products containing sulfur, mainly straight-run benzene with sulfur content from 0.116 to 0.961 g/liter, was investigated next. The results are presented in Fig. 2 (a, b) for catalyst (Mn–Fe) – clinoptilolite and in Fig. 2(c, d) for the catalyst (Co–Fe)–clinoptilolite.

Evidently, the treatment efficiency of petroleum products achieved using Mn–Fe-containing catalysts with temperature increasing from 20 to 60 °C increases gradually and reaches 99.8–99.9% with the ratio (Mn–Fe) : clinoptilolite = 1.1 and 1.2. The result is somewhat better when the system (Co–Fe) : clinoptilolite is used. For sulfur content 0.67–0.97 g/liter in the petroleum product the treatment efficiency increases sharply: from ~50% at 20 °C to 96–98% at 50 °C. It should be noted that temperature increasing to 60 °C and higher the activity of the catalyst starts to decrease.

One of the most important parameters affecting the demercaptanization process is the volume rate of feeding of the petroleum products. Conducting the process with volumes rates in the interval 0.1–1 h⁻¹ showed that increasing the volume rate from 0.1 to 0.5 h⁻¹ decreases the treatment efficiency of the petroleum products from sulfur compounds with 99.9% to 90% and a further increase of the volume rate to 1 h⁻¹ results in a substantial decrease of the treatment efficiency.

The effect of pressure on the demercaptanization process was also studied. It was found that increasing pressure from 0.1 to 5 MPa increases the dtreatment efficiency somewhat. However, this increase is not so large,

so that the process should be conducted at atmospheric pressure, which lowers the cost and makes the process more profitable.

It is important to note that catalytic demercaptanization of petroleum products with formation of elemental sulfur in the presence of the catalytic system Mn–Fe (Co–Fe)–clinoptilolite is related with the fact that in the presence of an interaction with acid and base centers of clinoptilolite the Co–Fe- and Mn–Fe-alkali heterocyclic cluster compounds are activated. The active metallic centers promote oxidation of the sulfur compounds to elemental sulfur, and the metallic centers themselves are reduced by the alkali centers of clinoptilolite and return into the initial state. The organic ligands and chlorine atoms present in the cluster compounds are stabilizers during redox processes and protect the clusters from decomposition, which is an advantage of the new catalytic system.

The presence of water in the petroleum products is undesirable for catalysts. For this reason, if water is present in the petroleum products, they should be passed through a desiccator. The effect of the water concentration on the activity of the catalyst is presented in Fig. 3. Evidently, the presence of water in concentrations to $0.6 \cdot 10^{-3}$ g/liter does not especially affect the activity of the catalyst. In its top layer, where petroleum products are fed, approximately 10 % passivation occurs. After a definite period of time this amount of catalyst is replaced by fresh catalyst, and the elemental sulfur released is removed.

The entire catalytic system is subjected to regeneration by period heating – passage of heated inert gas through the catalyst. The optimal regeneration temperature which we determined for the catalyst lies in the range 300–330 °C.

In summary, the new heterogeneous catalysts obtained on the basis of the ligands Mn–Fe and Co–Fe deposited on clinoptilolite show high activity when removing sulfur compounds from petroleum and petroleum products.

REFERENCES

1. V. M. Kurganov, A. I. Vaseiko, and V. P. Fimemota, *Hydropurification of Petroleum Products Using an Aluminum-Nickel-Molybdenum Catalyst*, TsNIITÉneftekhim (1975).
2. O. I. Zakharenko and V. E. Emel'yanov, *Environmental Chemistry and Protection*, Rosneft', Moscow (1999).
3. F. R. Ismagilov, *Ecology and New Technology for Purifying Sulfur-Containing Petroleum Products*, Znanie, Moscow (2000).
4. É. L. Sakharov, *Automobiles and the Environment*, Izd. MISRF, Moscow (2001).
5. Yu. R. Abrakhimov, *Proceedings of VNIINeftekhim* (1998).
6. K. M. Drozdov, A. I. Moiseev, F. A. Bondarev, et al., *Khimichesakaya promyshlennost*, 34, No. 4, 919 (1985).
7. V. L. Kovalev and M. G. Tonikberg, *Ecology and Problems of Hydrogenization Purification of Petroleum Products from Petroleum Refinement of Sulfurous and High-Sulfur Petroleum*, Rosneft', Moscow (2005).
8. G. I. Fuke, T. N. Shabarov, and Kh. G. Sal'nikov, *Zh. Fiz. Khim.*, 38, No. 5, 1136–1147 (2003).
9. A. G. Akhmadullina, B. V. Kizhaeev, I. K. Khrushcheva, et al., *Neftepererabotka i Neftekhimiya*, No. 2, 19 (1993).
10. A. F. Vil'danov, A. I. Lugovskoi, I. A. Arkhireeva, et al., *Khimiya i Tekhnologiya Topliv i Masel*, No. 10, 32 (1991).
11. A. K. Antonovich, T. V. Marganis, and V. B. Gol'dshtein, *Problems of Refining High-Sulfur Petroleum*, Khimiya, Moscow (2006).

12. *Extraction Methods for Removing Mercaptans from Residues of Petroleum Refinement of Sulfurous Petroleum, Kimiya i Khimicheskaya Teckhnologiya, Izd. Vysch. Uchebn. Zaved. RF*, 35, No. 5/6, 1236–1243 (1988).

13. R. M. Masagutov, *Aluminum Silicate Catalysts, Change of their Properties during Refining of Petroleum Products*, Ékologiya, Moscow (2003).

14. A. G. Akhmadullina and R. M. Akhmadullin, *Chemistry and Technology of Fuels and Oils*, 44, No. 6, 371 (2008).

15. L. I. Akhmetov, A. M. Kolbin, F. R. Ismagilov, et al., *Khimiya i Tekhnologiya Topliv i Masel*, No. 3, 8 (1999).

16. B. I. Belinskii, B. M. Berdnikov, Yu. I. V'chnyi, et al., *Ibid.*, No. 3, 8–10 (2002).

17. D. I. Orochko, A. D. Sulimov, and L. I. Osipov, *Hydrogenization Processes in Petroleum Reprocessing*, Khimiya, Moscow (1971).

18. V. M. Kurganov, A. I. Vaseiko, and V. P. Fimemota, *Hydropurification of Petroleum Products Using Aluminum Silicate Molybdenum Catalyst*, TsNIITÉneftekhim, Moscow (1975).

19. *Alkaline Purification of Sulfurous Petroleum and Petroleum Products*, NIITEKhIM Report, No. 4, 210–242 (1977).

20. Patent 0154 (Azerbaidzhan).