

**ТЕОРЕТИЧЕСКОЕ И ЭКСПЕРИМЕНТАЛЬНОЕ ИЗУЧЕНИЕ
АДСОРБЦИОННОЙ СПОСОБНОСТИ АЦЕТАТОВ ПЕРЕХОДНЫХ МЕТАЛЛОВ
В ПРОЦЕССЕ ОБЕССЕРИВАНИЯ МОДЕЛЬНОГО УГЛЕВОДОРОДНОГО ТОПЛИВА**

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В работе исследовано удаление кислых сернистых компонентов (сероводорода, алкантиолов) ацетатами цинка (II), кобальта (II) и меди (II), нанесенными на силикагель при воздействии ультразвука. На примере модельных аналогов бензиновых фракций показана эффективность адсорбционной сероочистки по отношению к сероводороду и алкантиолам. Ацетат кобальта (II) проявляет наибольшее сродство по отношению к сероводороду (90%). Исследуемые адсорбенты проявили одинаковую адсорбционную активность (79-81%) к изопропилтиолу. Для бензиновой фракции (62-180 °С) ацетаты кобальта (II) и цинка (II) показали большую адсорбционную способность по сравнению с ацетатом меди (II). Степень сероочистки, в случае применения ацетата кобальта (II), составляет 90%, что позволяет получить топливо, соответствующее нормативным требованиям. Изучен механизм удерживания рассматриваемых ацетатов на поверхности силикагеля и проведены квантово-химические расчеты, моделирующие адсорбцию ацетатов цинка (II), кобальта (II) и меди (II) на силикагеле. Значения энергии адсорбции ацетатов цинка (II), кобальта (II) и меди (II) достаточно близки и составляют -99,2, -103,3 и -84,1 кДж/моль, соответственно. Приведена оценка энергетики возможных путей превращений серосодержащих соединений в процессе адсорбционной сероочистки. Разложение сероводорода и алкантиолов с образованием сульфида металла, с энергетической точки зрения более вероятно. Значения ΔE реакций взаимодействия ацетата кобальта (II) с метантиолом, этантиолом, пропантиолом составляют 65,3, 57,5, 58,4 кДж/моль, соответственно. Разность между энергиями образования тиолатов и сульфидов металлов составляет 15-20 кДж/моль. Модифицированный ацетатом цинка (II) силикагель, после адсорбции сернистых примесей, может быть рекомендован в качестве средства для обработки дорожек и спортивных площадок, поскольку образующийся сульфид цинка обладает противогрибковым действием.

Ключевые слова: адсорбционная сероочистка, ацетаты цинка (II), меди (II), кобальта (II), силикагель, сероводород, низшие тиолы, квантово-химическое моделирование

**THEORETICAL AND EXPERIMENTAL STUDY OF THE ADSORPTION CAPACITY
OF TRANSITION METAL ACETATES IN THE PROCESS OF DESULFURIZATION
OF A MODEL HYDROCARBON FUEL**

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The removal of acidic sulfur components (hydrogen sulfide, alkanethiols) with zinc (II), cobalt (II) and copper (II) acetates deposited on silica gel under the influence of ultrasound was investigated. The efficiency of adsorption desulfurization in relation to hydrogen sulfide and alkanethiols is shown by the example of model analogues of gasoline fractions. Cobalt acetate shows the greatest affinity for hydrogen sulfide (90%). The studied adsorbents showed the same adsorption activity (79-81%) to isopropylthiol. For the gasoline fraction (62-180 °C) cobalt (II) and zinc (II) acetates showed higher adsorption capacity compared to copper acetate (II). The degree of desulfurization, in the case of the use of cobalt (II) acetate, is 90%, which makes it possible to obtain fuel that meets regulatory requirements. The mechanism of retention of the acetates under consideration on the silica gel surface has been studied and quantum chemical calculations modeling the adsorption of zinc (II), cobalt (II) and copper (II) acetates on silica gel has been performed. The values of the adsorption energy of zinc (II), cobalt (II) and copper (II) acetates are quite close and equal to -99.2, -103.3 and -84.1 kJ/mol, respectively. The estimation of the energy of possible ways of transformations of sulfur-containing compounds in the process of adsorption desulfurization is given. The decomposition of hydrogen sulfide and alkanethiols, with the formation of metal sulfide, is more likely from an energy point of view. The values of ΔE for the reactions of cobalt (II) acetate with methanethiol, ethanethiol, propanethiol are equal to 65.3, 57.5, 58.4 kJ/mol, respectively. The difference between the formation energies of metal thiolates and metal sulfides is 15-20 kJ/mol. Silica gel modified with zinc (II) acetate, after the adsorption of sulfur impurities can be recommended, as a means for treating tracks and sports grounds, since the resulting zinc sulfide has an antifungal effect.

Key words: adsorption desulfurization, zinc (II), copper (II), cobalt (II) acetates, silica gel, hydrogen sulfide, lower thiols, quantum chemical modeling

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INTRODUCTION

The removal of acidic sulfur compounds (H_2S , RSH) is one of the key tasks aimed at improving the characteristics of hydrocarbon fuels. Hydrogen sulfide and alkanethiols are highly toxic and corrosive compounds found in hydrocarbon raw materials. The presence of active sulfur-containing compounds has a negative impact on fuel quality indicators and its compliance with regulatory requirements [1, 2].

Industrial hydrotreating of light distillate fractions from acidic sulfur components, used at modern oil refineries, allows obtaining high-quality oil products that meet regulatory requirements. The negative aspect of the hydrotreating process is the significant consumption of energy and hydrogen-containing gas, the high cost of active and selective catalysts and the strict regime of the process. For small oil refineries that are not equipped with hydrogen production or catalytic

reforming plants, the development of alternative non-hydrogenation methods is important. Among the alternative methods of desulfurization, there are oxidative and extraction desulfurization, biodesulfurization and adsorption [3]. Adsorption desulfurization is an effective method of removing acidic sulfur compounds from hydrocarbon raw materials. The advantages of adsorption desulfurization are low level of capital and operating costs, high efficiency, versatility and relatively easiness of regenerability of adsorbents, as well as the possibility of carrying out the process in mild conditions [3, 4]. The use of adsorption desulfurization as a pre-hydrotreating unit allows to remove the load on the hydrodesulfurization equipment.

The most common desulfurization adsorbents are activated carbon, zeolites, silica, aluminum oxide [5-9]. Recently, special attention has been paid to the targeted synthesis of mesoporous materials and their composites used as adsorbents of sulfur-containing

compounds [3,4,10-13]. However, with all the advantages of mesoporous adsorbents, it is necessary to take into account their low commercial availability, which is due to multi-stage synthesis and high energy costs.

To increase the efficiency of all types of adsorbents, modification of their surface with salts and complexes of transition metals is used.

Adsorption desulfurization using adsorbents modified with inorganic oxygen-containing salts of transition metals, such as copper (II) sulfate, copper (II), iron (II), manganese (II), cobalt (II), zinc (II) nitrates [8, 14] includes a high-temperature calcination stage to obtain metal oxides on the surface of a porous material. The adsorbents modified in this way have a high specific surface area, a smaller particle size and an increased ability to adsorb sulfur compounds.

Salts of organic acids are used to modify adsorbents much less often. The use of various organic absorbers – octoates, dodecanoates or naphthenates of metals (Zn, Fe, Co, Ca, Mn) is described in [15] for the removal of hydrogen sulfide, mercaptans, sulfides and other sulfur-containing compounds from oil and hydrocarbon gases. Despite the high efficiency of the absorbers (up to 98.3%), the disadvantage of this method is the high consumption of carboxylates (from 10 to 100%) and the need to use toxic, expensive aromatic solvents.

Oil-soluble chelated compounds of zinc (II) or iron (III) [15], containing carboxylate groups based on nitrilotriacetic, ethylenediaminetetraacetic and polyaminodisuccinic acids, used as absorbers, allow to achieve a high degree of desulfurization of hydrocarbon raw materials under mild conditions.

In our previous work [16], the removal of acidic sulfur components by Zn (II), Cu (II), Co (II), Ni (II) pivalates deposited on silica gel of different porosity under the influence of ultrasound was investigated. The modified adsorbents actively absorb the lower sulfur compounds of the fuel. The residual content of hydrogen sulfide and mercaptans is 3-5 ppm.

When using both organic and inorganic salts of transition metals as adsorbents, metal sulfides are formed.

The use of zinc (II) complexes for the modification of silicon dioxide as a carrier leads to the transformation of acidic sulfur toxicants into safe compound (ZnS) with anti-tick and antifungal, antioxidant and cytotoxic properties [17,18], which makes it possible to obtain practically useful products. The disadvantages of the method include the fact that transition metal pivalates are not a product of the chemical industry and require, although not complex, a separate synthesis.

Transition metal acetates occupy an intermediate position between the salts of organic and inorganic acids. These compounds are commercially available, but nevertheless, insufficiently studied and little used in the desulfurization process. It should be noted that transition metal acetates can be dissolved in water and ionized to form metal ions and acetate anions, which increases the adsorption capacity during the impregnation of the adsorbent with metal salt.

It was noted [19] that in contrast to unmodified activated carbon the adsorbent impregnated with $Zn(OAc)_2$ exhibits a better adsorption ability to H_2S . Modification of the surface of activated carbon with zinc acetate promotes the growth of active centers on the surface of the adsorbent. It also leads to an increase in the specific surface area due to a decrease in the particle size, which favorably affects the efficiency of adsorption desulfurization.

The search for an alternative, commercially available, water-soluble modifier that does not require heat treatment is an important direction of adsorption desulfurization.

The aim of the work is to study the possibility of modification of the surface of the silica gel with acetates of transition metals (Zn (II), Co (II), Cu (II)) by impregnation, under the influence of ultrasound without heat treatment of the adsorbent, to obtain a highly efficient absorber for the process of adsorption removal of acidic sulfur components of hydrocarbon fuel.

EXPERIMENTAL METHOD

Adsorption desulfurization was carried out on silica gel modified with transition metal acetates (Zn (II), Co (II), Cu (II)), under atmospheric pressure and ambient temperature. A commercial silica gel of Alfa Aesar brand with a pore size of 6 nm was used as a carrier. The modifiers were commercially available reagents: zinc (II) acetate dihydrate $Zn(OAc)_2 \cdot 2H_2O$ («chemically pure», Reachim, Russia); cobalt (II) acetate tetrahydrate $Co(OAc)_2 \cdot 4H_2O$ («pure», ECROS, Russia); copper (II) acetate $Cu(OAc)_2$ («pure for analysis», Neva Reactive, Russia).

Modification of silica gel with Zn (II), Co (II), Cu (II) acetates was carried out by impregnation under the influence of ultrasound according to the previously reported method [16]. The silica gel was dried in a vacuum drying cabinet at 100 °C for 24 h. Aqueous solutions of metal salts (1% by weight) were used to modify the silica gel. To suppress hydrolysis, 0.2 ml of acetic acid was added. The impregnated silica gel was placed in an ultrasonic bath with a generator power of 180 W and an operating frequency of 40 kHz, to intensify the diffusion of a solution of metal acetates into

the porous structure of the carrier. The optimal ultrasonic treatment time was 50, 150 and 180 min for zinc (II), cobalt (II) and copper (II) acetates, respectively. The modified silica gel was kept in a vacuum drying cabinet for 24 h at a temperature of 120 °C.

Experiments on adsorption desulfurization of model mixtures were carried out on a laboratory flow unit consisting of three glass adsorbers arranged in series. 5 g of modified silica gel was placed in a cylindrical type adsorber. Hexane, a model analogue of the gasoline fraction and a real gasoline fraction (62-180 °C) obtained from the Astrakhan gas processing plant of the branch of «Gazprom Pererabotka» LLC (Russia) were used as a hydrocarbon mixture. The hydrocarbon mixture ($V = 60 \text{ cm}^3$), with an initial total sulfur content of 100 ppm, was fed at a rate of 0.9 h^{-1} . The total sulfur content in the initial and purified model mixture was determined by energy dispersion X-ray fluorescence spectrometry on the ASE-1 sulfur analyzer and cyclic voltammetry on the IPC-Pro potentiostat. The registration of the cyclic voltammograms was carried out using a three – electrode, non-diaphragm electrochemical cell with a working volume of 2 cm^3 , the working electrode was Pt ($d = 2 \text{ mm}$), the reference electrode was Ag/AgCl. Tetrabutylammonium perchlorate (0.15 M) was used as a background salt, the working solvent was $\text{CH}_3\text{CN} : \text{CH}_2\text{Cl}_2$ (1 : 1). The concentration of hydrogen sulfide and 2-propanethiol was estimated by the value of the oxidation peak, at their oxidation potential of 1.6-1.7 and 1.8 V, respectively. The experiment was carried out in the same mode for all adsorbents.

The degree of retention of metal acetates on the carrier was controlled by the method of flame atomic absorption spectrometry (novAA 300 atomic absorption spectrometer, Analytical Jena AG).

Quantum-chemical calculations were carried out by the density functional method (B3LYP/6-31++G(d,p)), using the Gaussian 09 program, with full optimization of the geometry of structures. The energy effects (ΔE) of the model reactions, including the adsorption energies, were calculated as the difference in the total energies of the final and initial structures. A fragment of the structure of the silica gel surface was modeled using a cluster of the composition $\text{Si}_3\text{O}_9\text{H}_6$. The structure of considered metal acetates for modeling adsorption complexes and calculating reaction energy effects was taken from the Cambridge Crystallographic Data Center [20].

RESULTS AND DISCUSSION

To clarify the mechanism of retention of the acetates on the silica gel surface, quantum chemical

calculations were performed that simulate the adsorption of zinc (II), cobalt (II) and copper (II) acetates on a silica gel cluster ($\text{Si}_3\text{O}_9\text{H}_6$) and the reactions of acetates with hydrogen sulfide and alkantiols.

The obtained values of the adsorption energy for zinc (II), cobalt (II) and copper (II) acetates are close and equal to -99.2, -103.3 and -84.1 kJ/mol, respectively. The strength of the formed adsorption complexes increases in the series: copper acetate < zinc acetate < cobalt acetate.

According to the results of calculations, zinc (II), cobalt (II) and copper (II) acetates form adsorption complexes of a similar structure, and therefore, the description of the structure of the adsorption complex of cobalt acetate is given as an example. The optimized geometry is shown in Fig. 1.

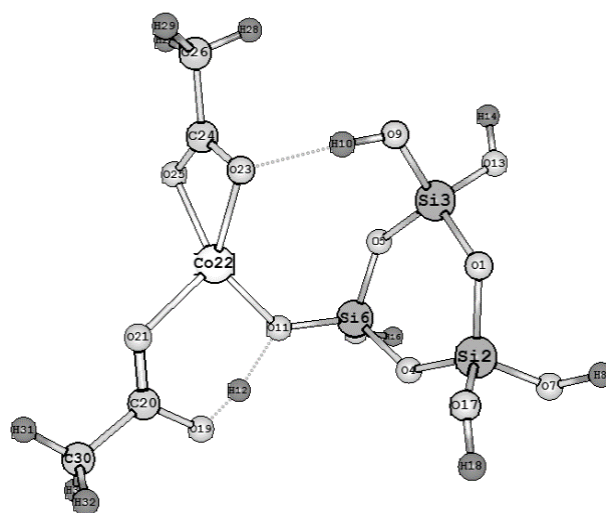


Fig. 1. Optimized geometry of the adsorption complex between a cobalt (II) acetate molecule and a cluster modeling the silica gel surface

Рис. 1. Оптимизированная геометрия адсорбционного комплекса между молекулой ацетата кобальта (II) и кластером, моделирующим поверхность силикагеля

The calculation results show that the adsorption of cobalt (II) acetate on the silanol groups of the silica gel surface can occur by a three-point mechanism, including the formation of hydrogen bonds and bonds between the cobalt atom and the oxygen atom of one of the silanol groups of the silica gel cluster. The cobalt atom in the adsorption complex is in the coordination environment of four oxygen atoms (the geometry of a distorted tetrahedron), three of which belong to acetic acid residues, and the fourth belongs to a silica gel cluster.

The length of the H10–O23 hydrogen bond is 1.852 Å (which is quite a typical value for strong H-bonds involving oxygen atoms). The length of the

H12–O19 bond is 1.048 Å, which is closer to the characteristic values of the lengths of ordinary covalent H–O bonds. At the same time, the length of the O11–H12 bond in the silanol group of silica gel increases sharply - up to 1.465 Å. In fact, there is a transition of the hydrogen atom H12 from the silanol group to the acetic acid residue. The distance between the Co22 and O11 atoms in the adsorption complex is 1.901 Å, which is even less than the length of the Co–O bond in the initial acetate molecule.

During the formation of the adsorption complex, the electron density is transferred from the silica gel cluster to the adsorbate molecule: the sum of the Mulliken charges on the cobalt (II), zinc (II) and copper (II) acetate atoms are negative and equal to -0.054, -0.085 and -0.114, respectively.

The obtained values of the adsorption energy and the parameters of the geometric structure of the adsorption complexes indicate the ability of studied transition metal acetates to be held sufficiently firmly on the surface of the silica gel.

Quantum chemical modeling of the reactions of hydrogen sulfide and alkanethiols (methanethiol, ethanethiol, propanethiol) with zinc (II), cobalt (II) and copper (II) acetates allowed us to evaluate the energy of possible ways of conversion of sulfur-containing compounds in the process of adsorption desulfurization. A fragment of the metal sulfide structure was modeled using the M_6S_6 cluster ($M = Zn, Co, Cu$). The obtained calculation results indicate that the decomposition of hydrogen sulfide and alkanethiols with the formation of metal sulfide is more likely from an energy point of view. The values of ΔE for the reactions of cobalt acetate with methanethiol, ethanethiol, propanethiol are 65.3, 57.5, 58.4 kJ/mol, respectively. The difference between the values of ΔE for the formation of thiolates $M(SR)_2$ and metal sulfides MS is 15–20 kJ/mol.

According to the obtained values of ΔE , the decomposition of hydrogen sulfide is energetically more favorable (34.3 kJ/mol) than the decomposition of alkanethiols (65.3 kJ/mol).

The influence of the nature of transition metal acetates on the efficiency of adsorption of sulfur-containing compounds from a model mixture on modified silica gel was studied during three-stage adsorption (Fig. 2).

The maximum degree of desulfurization is achieved by adsorption of hydrogen sulfide (Fig. 2, 2) from a model mixture on silica gel modified with cobalt acetate (90%). Zinc acetate (75%) and copper acetate (70%) have a lower affinity for H_2S . The ability of modified adsorbents to remove H_2S from the model

mixture is reduced in the following sequence: $Co(OAc)_2/SiO_2 > Zn(OAc)_2/SiO_2 > Cu(OAc)_2/SiO_2$.

The studied adsorbents showed the same adsorption activity with respect to isopropylthiol (Fig. 2, 1).

Adsorption desulfurization was carried out on a model analog of the gasoline fraction with the following component composition: hydrogen sulfide, propyl- and isopropylthiols (the total amount of sulfur is within 100 ppm). The group composition of the fraction (% by weight): *n*-alkanes – 28.73, aromatic hydrocarbons – 26.87, iso-paraffins – 22.50, cycloalkanes – 21.49, alkenes – 0.41. Data on the three-stage adsorption of sulfur-containing components from a model mixture simulating gasoline fraction are shown in Fig. 3.

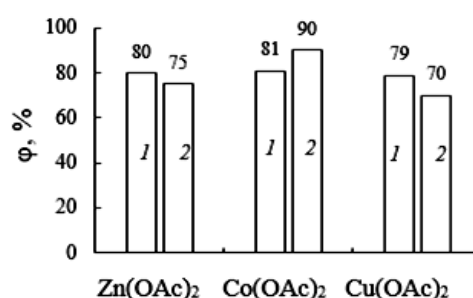


Fig. 2. Degree of desulfurization (ϕ , %) of the model mixture (1 - C_3H_7SH , 2 - H_2S) with the use of silica gel modified with Zn (II), Co (II), Cu (II) acetates

Рис. 2. Степень сероочистки (ϕ , %) модельной смеси (1- C_3H_7SH , 2- H_2S) с применением силикагеля, модифицированного ацетатами переходных металлов Zn (II), Co (II), Cu (II)

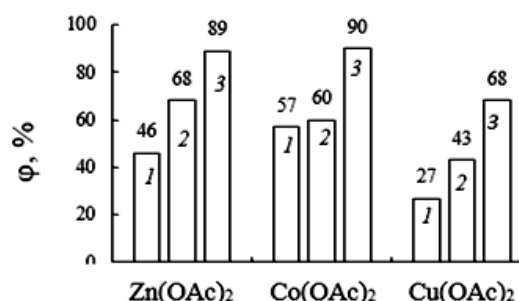


Fig. 3. Degree of desulfurization (ϕ , %) of the model mixture on silica gel modified with transition metal acetates (Zn, Co, Cu)

Рис. 3. Степень сероочистки (ϕ , %) модельной смеси на силикагеле, модифицированном ацетатами переходных металлов (Zn, Co, Cu)

The three-stage adsorption of sulfur components from the model gasoline fraction with silica gel modified with zinc (II), cobalt (II) and copper (II) acetates demonstrates a decrease in the total sulfur content by 89% and 90% for zinc (II) acetate and cobalt (II) acetate, respectively. The lowest efficiency indicators of desulfurization were obtained for copper (II) acetate.

The efficiency of modified adsorbents in the process of removing sulfur components from the gasoline fraction of 62–180 °C was studied. The results of

the three-stage adsorption of acidic sulfur-containing components from real fuel are shown in Fig. 4.

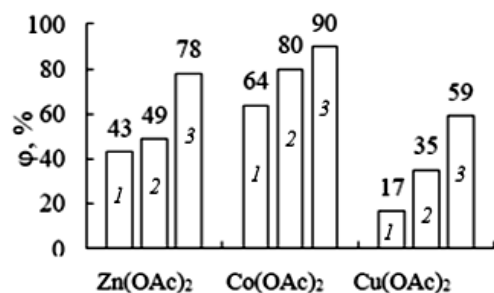


Fig. 4. Degree of desulfurization (ϕ , %) of the gasoline fraction 62-180 °C on silica gel modified with transition metal acetates (Zn, Co, Cu)

Рис. 4. Степень сероочистки (ϕ , %) бензиновой фракции 62-180 °C на силикагеле, модифицированном ацетатами переходных металлов (Zn, Co, Cu)

The adsorption capacity of cobalt (II) and zinc (II) acetate is greater than that of copper acetate. The degree of desulfurization in the case of cobalt (II) acetate is 90%, which is equivalent to the content of sulfur compounds of no more than 10 ppm.

Despite the multicomponent composition of the gasoline fraction, which includes high-molecular sulfur and heteroatomic compounds, the adsorbent modified with cobalt (II) and zinc (II) acetate can be recommended as an absorber of light sulfur compounds of the gasoline fraction.

CONCLUSIONS

The conducted studies have shown the effectiveness of using available zinc (II) and cobalt (II) acetates as silica gel surface modifiers in the process of adsorption desulfurization of hydrocarbon fuels. The adsorbent modified with cobalt (II) acetate exhibits high purification rates (90%), allowing to obtain a hydrocarbon fuel that meets the K-5 (Euro 5) environmental standard. The three-stage adsorption of sulfur components from gasoline fractions made it possible to reduce the content of acidic sulfur compounds by 5-10 times.

The experimental data are in good agreement with the results of quantum-chemical calculations of the formation energies of adsorption complexes. The energy estimation of possible ways of transformations of hydrogen sulfide and alkanethiols in interaction with zinc (II), cobalt (II) and copper (II) acetates is given. From an energy point of view, the decomposition of hydrogen sulfide and alkanethiols with the formation of metal sulfides is more likely. The difference between the formation energies of metal thiolates $M(SR)_2$ and metal sulfides MS is 15-20 kJ/mol.

Despite the small advantages of cobalt (II) acetate in desulfurization, it is advisable to use zinc (II) acetate, since the resulting zinc sulfide exhibits antifungal and antioxidant activity.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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