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ANALYSIS OF THE RESULTS OF EXPERIMENTAL SORBENT FOR CHLORIDE COMPOUNDS REMOVAL

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This research pursues an objective to explore the composition and physicochemical characteristics of the domestic adsorbent obtained through processing alumina waste from the local industry upon completion of testing in the course of purification of hydrogen-containing gas from chlorine-containing compounds. Also, changes in the quantitative ratio of the main chemisorption products of harmful impurities (NaCl, $AlCl_3$, $AlCl_3.6H_2O$ and AlxCly $(OH)_z.nH_2O$) depending on modifiers of various nature were determined. The NaCl content in the adsorbents used rose symbatically in the concentration of main centers due to surface aluminates and sodium carboaluminate in the initial samples. The amount of coke-like deposits with a high hydrogen content $C_nH_{1.75-1.8n}$ satisfactorily correlated with the concentration of strong secondary acid sites arising from the formation of aluminum chlorides and hydroxychlorides. The accumulation of coke-like deposits with graphitic structure during the testing of adsorbents under industrial conditions for gas purification in the regeneration of catalyst reforming did not exceed 1.5% of the mass.

Keywords: *adsorbents, coke-like deposits, aluminum chlorides, aluminum hydrochlorides, acid centers, regeneration gases.*

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Introduction

At the present stage of motor transport development, the improvement of catalytic reforming technology is put in the list of the most relevant high-tech problems of the world oil refining industry [1]. The technical and economic efficiency of high-octane gasoline production relies heavily on properties of the catalyst used and the technological design of this basic process. Semi-regenerative plants are predominant in the world where the process is carried out under a pressure of 1.3-3.0 MPa at a temperature of 480-530 ° C and periodic regeneration of the catalyst is provided [1]. Somewhat less, the most progressive CCR scheme of the reforming process (continuous catalyst regeneration reformer) with continuous regeneration of catalysts in a cyclic version of technological design is implemented. At a temperature of 505-550 ° C, a pressure of 0.9-2.1 MPa, and continuous catalyst regeneration in a regeneration device, are formatted with a high octane number of 95-103 [1, 2].

As is known, more than 90% of all investments in the field of catalysis are spent on resolving problems associated with the deactivation of catalysts, and about 50% of scientific developments are made in the study of coke formation mechanism by the example of individual coxogenic substances [3]. To a lesser extent, patterns of pressure and temperature influence on the formation of coke deposits in the course of processing of hydrocarbon materials of variable composition in industrial reactors have been studied [2,4]. The researchers of Tomsk Polytechnic University carried out work aimed at improving the efficiency of existing plants using computer simulation systems which are especially relevant for semi-regenerative processes where carbonization of catalysts does not determine the stationary state of the targeted chemical reforming reactions [4]. The use of the non-stationary kinetic model proved the feasibility of computer control over industrial processes where coke accumulation during operation of the plant at the current and optimal activity is significantly different for different catalysts [4,5]. When creating the algorithms, the authors took into account the balance of acid and metal functions of Pt-containing catalysts according to the monitoring of the reforming process in industrial reactors of a particular type [6,7].

The mechanism of formation and accumulation of loose and graphitized coke was the object of attention of the developers when choosing the optimal design and operation mode of reactors with a moving layer of Pt-Sn / Al_2O_3 catalysts [6, 8]. Analysis of the work to increase the efficiency of producing high-octane fuel reveals that the main attention of the developers is focused on optimizing the process of gasoline catalytic reforming. At the same time, patents [9-11] mainly limit the number of publications on the auxiliary process - purification of the hydrogen-containing gas from halogen compounds using adsorbents. Therefore, this article considers the results of a study into a new domestic adsorbent Uz-AD-1 and comparative samples of various acid-base properties following the completion of their experimental tests in the process of removing organochlorine compounds from Pt catalyst regeneration gases at the Bukhara Oil Refinery.

Research Methodology

It should be noted that the distribution of the main elements (aluminum, sodium, and chlorine) on the surface of solid used adsorbents was determined using an EVOMA 10 scanning electron microscope (Zeiss). The aluminum content in solutions was determined by complexometric titration, chloride ions by argentometric titration [12], and sodium by flame photometry. To assess the total content of Na and Cl in the initial adsorbents and solid residues after extraction, appropriate samples were dissolved in nitric acid. The absence of carbon dioxide emission during the dissolution procedure indicated the complete removal of carbon from carboaluminate and sodium carbonates in the composition of Uz-AD-1. In order to assess results separately, chlorine in the composition of various chemisorption products, the total amount of Na, Cl, and Al elements in the composition of compounds extracted with water (NaCl, $AlCl_3.xH_2O$ and AlxCly(OH)z. NH_2O) were first determined. Then, in parallel samples, chlorine was determined in aluminum compounds extracted with acetone, where NaCl was almost insoluble [13].

The total carbon content in the composition of coke-like deposits was determined by the classical method through burning a sample of 1g mass in a quartz tube in an oxygen stream at 900 ° C followed by absorption of CO_2 in a column with soda ash [2]. The relative content of chlorinated oligomers in the sediments was estimated by the appearance of the band 1270–1300 cm $^{-1}$ when recording IR spectra in the mode of incomplete internal reflection on a Nicolet S50 spectrometer. The process of removing coke-like deposits at fixed temperatures of 400 and 900°C was studied by calcining 50 g of an average dried sample in a quartz reactor with the registration of reaction products chromatographically [14]. The amount of carbon deposits accumulated in pores and on the surface of adsorbents was determined by the amount of CO_2 and H_2O released during air burning and complete oxidation over heated CuO. To differentiate adsorbed hydrocarbons and amorphous carbon deposits which interfere with reliable and informative analysis of graphitic coke, the material was preliminarily washed with toluene and dried in air [15]. Vapors of hydrocarbons and organochlorine compounds of various classes were identified by gas chromatography [16].

Results and its discussion

As a part of the production localization by alkaline modification of alumina waste from Shurtan GChC OJSC, we developed an import-substituting adsorbent Uz-AD-1 [17] designed to purify process gases from HCl, water and various polar impurities. The target reactions of cyclization, aromatization, etc. at the catalytic reforming unit of the Bukhara oil refinery occur in the presence of a bifunctional chlorinated catalyst CR 401 at a temperature of 500 ° C and a pressure of 5.8 bar. This leads to the appearance of HCl, chlorinated compounds and traces of unsaturated light hydrocarbons in gaseous and liquid effluents which are undesirable in the operation of catalytic reforming, naphtha hydrofining and gas oil hydrofining.

The industrial use of hydrogen reforming effluent gases requires the effective removal of hydrogen halides, since in addition to high corrosivity, halogen-containing substances are catalytic poisons in hydrofining various oil fractions. Tests of the new Uz-AD-1 adsorbent were carried out in a 100-liter experimental adsorber mounted on the bypass line (hydrogen containing gas) immediately before entering the industrial adsorber of the heavy naphtha-reforming unit at the Bukhara oil refinery. It is known that when contacting with alumina, unsaturated hydrocarbons enter into numerous reactions with HCl, including the formation of high molecular weight oligomers “green oils” which reduce the service life of chemisorbents by several times and can lead to blockage of the adsorber [10].

In order to evaluate the effect of the chemical composition of adsorbents seeking to generate chlorinated oligomers, four mesh containers with granules of samples with varied surface properties were placed on a 50 cm layer of Uz-AD-1.

No. 1 - industrial alumina which after calcination at 500 ° C contained 0.18 mEq / g of acid sites with pKa ≤ - 3. No. 2 - alumina-kaolin borate adsorbent with a higher surface acidity - 0.24 mEq / g which does not contain basic centers with pKa ≥ +9 [18]. No. 3 - alumina waste calcined at 550 ° C where weak acid centers with pKa ≈ +3.8 prevailed, the concentration of strong acid centers did not exceed 0.002 mEq / g, and the main centers with pKa ≥ +9 reached 0.013 mEq / g [nineteen]. No. 4-adsorbent Uz-AD-1, mainly with pKa from +8 to +10, due to X-ray amorphous sodium aluminates of the type $Na_7Al_3O_8$ and $NaAlCO_3(OH)_2$.

During the year, gases arising from regeneration of the Pt catalyst CR 401 and containing more than 10 ppm HCl and impurities of unidentified organochlorine and unsaturated compounds were fed into the experimental adsorber. At a flow rate of the purified gas of 28.5-32.5 nm3 / h, a temperature of 4-50 ° C, a pressure of 5.5 bar, there was no breakthrough of chlorine-containing compounds. After the completion of the experimental tests, the selected granules of adsorbents retained their original shape, mechanical strength decreased by an average of 15%. All granules from adsorbents No. 1-4 extracted from containers on the frontal layer were painted black, specific for coke-like deposits. The color of the Uz-AD-1 granules discharged from the experimental adsorber (100 kg) changed from black to light gray, from which an averaged sample was formed to examine changes in the physicochemical and technical properties (sample No. 5). The specific surface of the light granules Uz-AD-1 decreased in the course of operation by 20% and the darkest by 40%. The number of chlorine-containing compounds absorbed during testing by Uz-AD-1 granules of different colors, according to the results of the analysis of six samples taken at random, ranged from 6 to 13% of the mass Cl. A specific feature of some adsorbents spent was revealed, chemisorbing water vapor from atmospheric air, up to the transition to a pasty state. Along with a strong spread of texture characteristics and chemical analysis results, this indicated the formation of the hygroscopic $AlCl_3.6H_2O$ compound, as well as the uneven degree of gaining the Uz-AD-1 sorbent along the layer height.

The data obtained during the study of x-ray phase analysis showed that the weakly crystallized aluminum chloride hexahydrate, $AlCl_3.6H_2O$ is indeed a common product of chemisorption of harmful impurities HCl and H_2O in all analyzed samples. In the diffraction patterns, it corresponds to a set of low-intensity wide lines with d = 6.0, 5.2, 3.89, 3.69, 3.29, 2.57, 2.3, and 2.05 Å (Fig. 1). Three aluminum hydroxide, the second product of the reaction $Al_2O_3 + 3\ HCl + 6\ H_2O \rightarrow Al\ (OH)_3 +$

$AlCl_3.6H_2O$ clearly manifested itself in the diffraction pattern of comparative adsorbent No. 1 in the form of a fairly well crystallized bayerite with lines d = 4.78, 4.38, 3.22, 2.269, 1.722 and 1.452. Å, possibly mixed with gibbsite. The presence of a wide halo in the region of interplanar spacings with d = 11.8–2.31 Å is due to the presence of amorphous hydrate of aluminum hydroxide Al (OH) 3.1.5 H_2O - toucanite and products of partial hydrolysis of $AlCl_3.6H_2O$, as well as subsequent polycondensation with the formation of a mixture of aluminum hydroxochlorides [13].

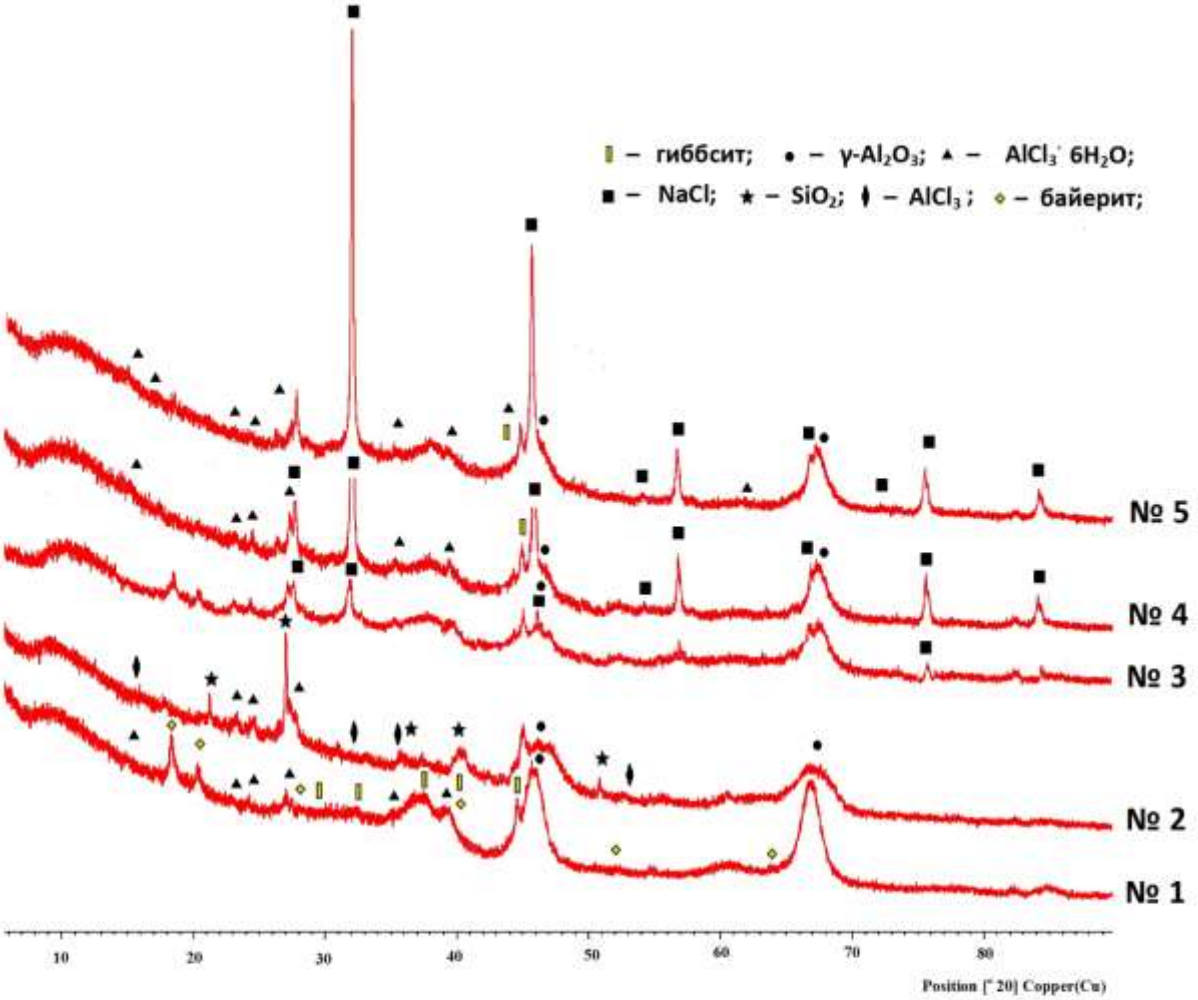

Fig. 1. X-ray diffraction patterns of adsorbents discharged from an experimental BNPZ adsorber.

In this case, a mixture of several hydrolyzed forms of polynuclear hydroxocomplexes of variable composition can be formed which are expressed by the general formula [Al (OH) 3-xCly] n, where x varies between 0-3. The composition of hydroxocomplexes is dependent upon the pH of the medium and the ratio of HCl and H_2O in the gas to be purified. Preservation of distinct quartz lines with d = 4.22, 3.3, 2.46, 2.29, 1.81 Å in the absence of reflections from SiO_2 chlorination products in the diffractograms, together with line broadening with d = 1.98 and 1.39 Å reflects the priority of the interaction of HCl and H_2O with γ-Al_2O_3 in the composition of alumina-kaolin borate sample No.2. Intensive reflections from crystalline NaCl indicate the primary course of deep interaction of chloride compounds in the composition of the regeneration waste gases with surface sodium aluminates characteristic for Uz-AD-1. The diffractogram of adsorbent No. 3, despite the presence of a certain amount of sodium compounds in its composition, differed from the diffraction pattern of adsorbent No. 1 just by more intense lines from aluminum trihydroxides. Although barely noticeable halos are visible in the diffraction patterns of all samples in the region of interplanar distances characteristic of elemental carbon, their overlapping with wide lines in the shape of a halo from aluminum chloride hexahydrate makes it no possible to estimate the nature of coke-like deposits on the granules of spent adsorbents.

The ratio of Na, Cl, and Al elements in the aqueous extract and the insoluble portion of adsorbents No. 3, No. 4, and No. 5 (Table 1) definitely confirms the formation of crystalline NaCl from nearly all sodium ions, as in the composition of fresh Uz-AD-1, and the source material for its preparation. Cubic NaCl crystals are visible against the background of the deposit crusts when considering adsorbent No. 5 on a scanning electron microscope, the area highlighted (marked with an oval) corresponds to spectrum 110 by a rectangle which indicates the formation of a mixture of sodium chloride and aluminum hydroxochlorides (Fig. 2).

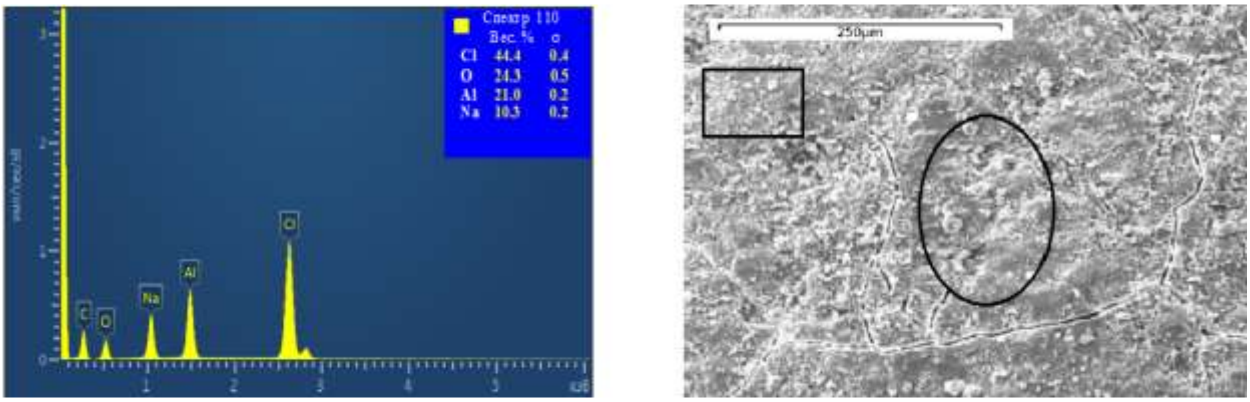

Fig. 2. Results of elemental analysis of the spent Uz-AD-1 on a scanning electron microscope.

All inorganic chemisorption products of HCl and H_2O as a part of the analyzed adsorbents are insoluble in toluene which extracts 99-98% of coke-like deposits of organic origin, practically without affecting the compounds of sodium, chlorine and aluminum. The results of elemental analysis of extracts in acetone from samples of spent adsorbents produced after preliminary treatment with toluene and drying at 100 ° C to remove physically adsorbed water are objectively reflective of the composition of chlorine and aluminum compounds that are readily soluble in acetone, in contrast to NaCl (Table).

Table. Results of elemental analysis of adsorbents used in industrial conditions

Material for analysis	Elements	№1	№2	№3	№4	№5
Content of elements; mg / g spent adsorbent						
Aqueous extract from representative samples of spent adsorbents	Na	missed	missed	7.6	28.1	39.2
	Cl	93.9	98.0	75.0	102.4	114.2
	Al	69.2	23.3	15.9	16.2	13.7
Insoluble residue after extraction with water	Na	missed	missed	missed	0.07	0.03
	Cl	8.9	4.6	3.2	2.7	7.8
Extract in acetone, after removal	Na	missed	missed	missed	0.08	0.05

of deposits by toluene and drying at 100 ° C	Cl	94.3	97.0	63.9	61.42	53.7
	Al	70.4	24.6	24.3	15.6	13.3
Insoluble residue after toluene and acetone extraction procedures	H	10.4	3.59	12.6	6.9	5.91
	Na	missed	missed	missed	0.02	0.03
	Cl	4.5	1.0	1.5	2.0	3.2
	C	0.04	0.06	0.05	0.03	0.01
Gases released from spent samples in the form of CO2 and H2O upon calcination up to 400 ° C	C	3.95	4.51	3.95	3.83	2.48
	∑H и H*	15.8	11.62	19.57	13.60	10.36
Composition of deposits with allowance for water in composition of aluminum chlorides	H*	6.95	8.03	6.99	6.70	4.46
	H*/C	1.76/1	1.78/1	1.77/1	1.75/1	1.80/1
Estimated amount of deposits CHH1.75-1.8n		87.0	93.0	84.0	80.0	51.0
Content of elements; mg / g adsorbent calcined at 400 ° C						
Aqueous extract from calcined representative samples of spent adsorbents	Na	missed	missed	7.3	27.9	39.0
	Cl	0.25	0.12	13.2	42.8	59.4
	Al	0.20	0.23	0.15	0.21	0.18
Insoluble residue after extraction with water	Na	missed	missed	missed	0.06	0.08
	Cl	missed	missed	missed	missed	0.02
Gases emitted in the form of CO2 and H2O upon calcination from 400 ° C to 900 ° C during oxidation of deposits of composition CHH1.10-1.37n	C	0.10	0.09	0.08	0.08	0.05
	H*	0.11	0.11	0.11	0.10	0.06
	H*/C	1.10/1	1.22/1	1.37/1	1.25/1	1.20/1
		1.35	0.44	1.22	1.18	0.71
Solution obtained by dissolving spent adsorbents in nitric acid	Cl	104.6	101.2	78.8	106.8	126.2
	C**	missed	missed	missed	missed	missed

Estimations based on the Table data showed that during the operation of the alumina-kaolin borate adsorbent No. 2, the maximum amount of acid chemisorption products made up 14.6% of the mass based on the weight of the spent sample. 55.5% of the mass is accounted for strong Lewis acid - AlCl$_3$, 27.7% of the mass, by AlCl$_3$.6H$_2$O which has the properties of Brainsted acid and about 16.7% of the mass, poorly soluble aluminum hydroxychloride type Al$_{13}$Cl$_{15}$ (OH) 24. 37.5H$_2$O. Anhydrous aluminum chloride was not detected in spent adsorbents, nor contained additives of kaolin and boric acid. When in contact of alumina in adsorbent No. 1 with exhaust reforming gases, 16.47% of the mass, chemisorption products were formed with 22.1% of the mass. More basic hydrolysis products represented $AlCl_3.6H_2O$ of a pronounced acidic character, the rest - Al_5Cl_3 (OH) $_{12.}$ $7H_2O$ and $Al_{13}Cl_{15}$ (OH) $_{24}$. $37.5H_2O$. Comparative adsorbent No. 3 with a minimum chlorine capacity contained about 8% of the mass soluble in acetone $AlCl_3.6H_2O$, and strongly hydrolyzed forms of aluminum hydrochloride predominated in the insoluble residue. The total amount of chlorine contained in the chemisorption products identified in parallel samples of extracts in water and acetone coincides with the amount of total chlorine detected by dissolving the corresponding weights in concentrated nitric acid.

Analysis of the composition of gases released during the calcination of spent adsorbents according to the method [20] revealed that the amount of carbon included in the composition of organic substances was within 1-2% of the mass. Researchers of coke formation on various catalysts showed that the amount, composition and properties of hydrocarbon deposits, as well as their localization, are determined by the nature of the modifying metal, the acid-base characteristics of the alumina support of the catalysts, and the conditions of industrial processes [21]. During the test and before removing from the experimental adsorber on the bypass line of the Bukhara oil refinery, the adsorbent samples were not subjected to high-temperature treatments, in contrast to the process of unloading the catalysts. But, in the purified regeneration gases, among the limiting hydrocarbons typical for reformate aromatic compounds (xylenes and ethylbenzene) and unsaturated compounds, as well as traces of organochlorine compounds, were identified. These compounds are a potential source for the accumulation and further transformation of compaction products on granules of hydrogen chloride absorbers, including “green oils” [9, 10].

It should be added that high molecular weight deposits of chlorinated oligomers deactivate the surface of adsorbents and significantly limit their service life, since they are not desorbed during the process of purification of reforming gases. The IR spectra of the spent adsorbents differed from the spectra of fresh samples in the greater intensity of wide bands in the regions 3327-3000 and 1630-1580 cm^{-1}, as well as the appearance of new inflection points on the slope of the intense wide band with a maximum of 525-490 cm^{-1} from stretching vibrations of Al bonds -O-Al. This, along with the presence of inflection points at 1170–1200, 1060, 980–960, and 720–660 cm^{-1}, indicates the presence of both olefins and halogenated hydrocarbons in the sediment composition. However, the band 1240–1300 cm^{-1}, specific for the (R) $–CH_2$ (Cl) bonds in chlorine derivatives of hydrocarbons [10], was observed only in the IR spectrum of spent adsorbent No. 2, in which the maximum amount of anhydrous aluminum chloride was detected and coke-like deposits of composition CHH1.78n, extracted with toluene. Similar coke-like deposits with a high hydrogen content were found on alumina (sample No. 1), the acid-base centers of which are capable of converting unsaturated compounds to form oligomers, polymers, and various aromatic structures, especially in the presence of active metals and at elevated temperatures [21, 22]. Among the samples taken from the upper part of the adsorber, the degree of carbonization of adsorbent granules No. 4, with a minimum concentration of acid centers on the surface of the initial Uz-AD-1, proved to be lowest. During the operation, in the experimental adsorber, deposits with a high hydrogen content were formed on all the samples analyzed that burned out at 400 ° C which is typical for light compaction products. High molecular weight hydrogen-depleted compaction products classified as irreversible coke with a pseudo-graphite structure accounted for no more than 0.2% of the total amount of deposits detected. Deposits of the composition CHH1.10-1.37n, fading in the temperature range 400-900 ° C, due to the oxidation of high molecular weight compounds, may also include incompletely oxidized, low molecular weight compounds, settled in the depth of small pores.

The results above can be explained as being due to the fact that in the initial period of operation on Uz-AD-1 samples, the process of absorption of acidic impurities selectively proceeded at the main centers of surface sodium aluminates. During this period, the chemisorption products of NaCl and $AlCl_3.6H_2O$ created an environment unsuitable for oligomerization reactions of trace amounts of olefins (sample No. 5). When the resource of sodium aluminates was exhausted, the process proceeded according to the same scheme as for adsorbents No. 1-No. 3, that is, with the formation of secondary acid centers that accelerate the carbonization of Uz-AD-1 by light oligomers. Primary acid sites on adsorbents No. 1 – No. 3, in combination with chemisorption products — aluminum chlorides — initiated the formation of oligomers already at the initial stage of the industrial experiment. Since no thermal destruction practically occurred in the temperature range from 4 to 50 ° C, coke-like deposits with high hydrogen content were formed.

Conclusions

1. Results of a pilot test of the Uz-AD-1 adsorbent which has surface of major centers, revealed its high chlorine consumption as compared with acidic adsorbents, in the process of removing chlorine-containing compounds from hydrogen-containing gas and the reforming catalyst exhausted during regeneration.
2. It revealed that the reason for the appearance of chlorinated oligomers on the alumina-kaolin borate sample is the increased acidity which stimulates the intensive formation of anhydrous aluminum chloride — a catalyst for oligomerization of olefins and chlorine-containing compounds.
3. Regardless of the strength and concentration of acid-base centers on the surface of the initial adsorbents, during the experimental test, coke-like deposits rich in hydrogen were formed on all spent samples with the general formula $C_nH_{1.75-1.8n.}$ However, the amount of deposits under identical conditions of the frontal layer rose as the concentration of acid sites with $pKa \leq - 3$ increased as well.
4. Modification with sodium cations made it possible to sharply reduce the reactivity of alumina waste in oligomerization reactions of unsaturated hydrocarbons and, therefore, increase the loading cycle of the import-substituting chemisorbent Uz-AD-1.

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HİDROGEN TƏRKİBLİ QAZIN XLORLU BİRLƏŞMƏLƏRDƏN TƏMİZLƏNMƏSİNDƏ TƏCRÜBİ SORBENTİN SINAQ NƏTİCƏLƏRİNİN ANALİZİ

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Tədqiqat işinin məqsədi hidrogen tərkibli qazın xlorlu birləşmələrdən təmizlənməsində istifadə olunan yerli sənayenin gil-torpaq tullantılarının emalından alınmış təcrübi adsorbentin tərkibinin və fiziki-kimyəvi xarakteristikalarının tədqiqi olmuşdur. Modifikatordan asılı olaraq əsas xemosorbsiya məhsullarının (NaCl, $AlCl_3$, $AlCl_3.6H_2O$ and $AlxCly(OH)_z.nH_2O$) miqdar nisbətləri təyin edilib.

Açar sözlər: adsorbent, hidrogen, xlorlu birləşmələr, xemosorbsiya, regenerasiya qazları

АНАЛИЗ РЕЗУЛЬТАТОВ ИСПЫТАНИЯ ОПЫТНОГО СОРБЕНТА ДЛЯ УДАЛЕНИЯ ХЛОРИДНЫХ СОЕДИНЕНИЙ

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Настоящее исследование направлено на изучение состава и физико-химической характеристики отечественного адсорбента, полученного при переработке глиноземистых отходов местной промышленности, после завершения испытаний в процессе очистки водородсодержащего газа от хлорсодержащих соединений. Определено изменение количественного соотношения основных продуктов хемосорбции вредных примесей (NaCl, $AlCl_3$, $AlCl_3.6H_2O$ and AlxCly $(OH)_z.nH_2O$) в зависимости от модификаторов различной природы. Содержание NaCl в отработанных адсорбентах симметрично возрастало с увеличением концентрации основных центров, вызванных поверхностными алюминатом и карбалюминатом натрия в исходных образцах. Количество коксоподобных отложений с высоким содержанием водорода $C_nH_{1.75\text{-}1.8n}$ удовлетворительно соотносится с концентрацией сильных вторичных кислотных участков, возникающих при образовании хлоридов алюминия и гидроксихлоридов. Накопление коксоподобных отложений с графитовой структурой при испытаниях адсорбентов в промышленных условиях очистки газов при регенерации катализатора риформинга не превышало 1.5% масс.

Ключевые слова: адсорбент, коксоподобные отложения, хлориды алюминия, гидроксихлорид алюминия, кислотные центры, регенерационные газы.