_ CHEMICAL KINETICS _____ AND CATALYSIS

Adsorption and Catalytic Properties of Sulfated Aluminum Oxide Modified with Cobalt Ions

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Abstract—The adsorption properties of sulfated aluminum oxide (9% SO_4^{2-}/γ -Al₂O₃) and a cobalt-containing

composite $(0.5\% \text{Co/SO}_4^{2-}/\gamma-\text{Al}_2\text{O}_3)$ based on it are studied via dynamic sorption. The adsorption isotherms of such test adsorbates as *n*-hydrocarbons (C₆-C₈), benzene, ethylbenzene, chloroform, and diethyl ether are measured, and their isosteric heats of adsorption are calculated. It is shown that the surface sulfation of aluminum oxide substantially improves its electron-accepting properties, and so the catalytic activity of $\text{SO}_4^{2-}/\gamma-\text{Al}_2\text{O}_3$ in the liquid-phase alkylation of benzene with octene-1 at temperatures of 25–120°C is one

order of magnitude higher than for the initial aluminum oxide. It is established that additional modification of sulfated aluminum oxide with cobalt ions increases the activity of this catalyst by 2–4 times. It is shown that adsorption sites capable of strong specific adsorption with both donating (aromatics, diethyl ether chemosorption) and accepting molecules (chloroform) form on the surface of sulfated γ -Al₂O₃ promoted by cobalt salt.

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INTRODUCTION

It is known that solid sulfated Periodic Table Group IV metal oxides have a catalytic effect on many electrophilic-type reactions and have in recent years been widely used as catalysts in different processes, including alkylation reactions [1]. Specific features of the formation of such catalysts during thermal treatment and their textural characteristics and composition are considered in the literature. Ways of controlling their acidic properties and catalytic activity, and the mechanisms of Brønsted and Lewis acidity upon the sulfation of different metal oxides, were studied in [2, 3]. Systems based on sulfated aluminum oxides would seem to be promising. They are stable under reaction conditions and can exhibit superacidic properties and activity in acid catalysis reactions [4]. It is known that the efficiency of sulfated oxides grows appreciably upon the introduction of transition metals (Pt, Fe, Ni, Co, Mn) [5, 6]. However, the role of a promoting transition metal additive in the catalytic effect of systems based on anion-modified metal oxides remains poorly understood.

Among the physicochemical ways of studying the nature of active sites of such catalysts, the most widely used techniques are spectral, magnetic resonance and electron microscopy. Inverse gas chromatography is rarely used in studies of catalytic reactions, but its use in studying surface intermolecular interactions seems to be very promising [7-12].

The aims of this work were to synthesize sulfated aluminum oxide $(9\%SO_4^{2-}/\gamma-Al_2O_3)$ and a cobaltcontaining composite $(0.5\%Co/SO_4^{2-}/\gamma-Al_2O_3)$ based on it, and to study their adsorption properties and catalytic activity in the liquid-phase alkylation of benzene with octene-1.

EXPERIMENTAL

Synthesis of Samples

To synthesize sulfated samples, a γ -Al₂O₃ support (AOK-63-11, grade B; specific surface area (S_{sp}), 180 m²/g; average pore volume, 0.29 cm³/g; pore diameter, 8.9 Å) was calcined at 600°C for 8 h, cooled, impregnated with an aqueous sulfuric acid solution (c = 0.5-1.0 mol/L), dried for 16 h at room temperature and then for 8 h at 140°C, and calcined in a dry air flow for 3 h at 450°C.

 $Co/SO_4^{2-}/\gamma$ -Al₂O₃ samples were prepared via incipient wetness impregnation of the sulfated SO_4^{2-}/γ -Al₂O₃ support with an aqueous cobalt nitrate

Table 1. Characteristics of test adsorbates (where *M* is molecular mass, μ is the dipole moment, α is the total polarizability of a molecule, and AN and DN are the electron-accepting and electron-donating energetic characteristics of molecules) [8, 9]

Adsorbate	М	μ, D	α, Å ³	DN, kJ/mol	AN
<i>n</i> -C ₆ H ₁₄	86.2	0	11.9	0	0
$n - C_7 H_{16}$	100.2	0	13.7	0	0
$n - C_8 H_{18}$	114.2	0	15.6	0	0
C ₆ H ₆	78.1	0	10.4	0.4	8.2
$C_6H_5C_2H_5$	106.2	0.59	14.1	—	—
CHCl ₃	119.4	1.15	8.2	0	23.0
$(C_2H_5)_2O$	79.1	1.15	9.0	80.3	3.9

solution, followed by dying for 16 h at room temperature and for 8 h at 140°C. It was then calcinated in a dry air flow for 3 h at 450°C.

The sulfur content in our samples was determined via elemental analysis and the back titration of sulfate groups. In the latter case, weighed samples of the sulfated catalyst were allowed to stand in a 0.05 N sodium hydroxide solution for 4 h, and then the NaOH solution's concentration was determined via titration with a sulfuric acid solution. According to the results from the two independent methods, the content of sulfate groups in the synthesized $SO_4^{2^-}/\gamma$ -Al₂O₃ samples was 9.0 ± 0.5 wt %.

Adsorption Studies

The test adsorbates used to study the surface texture and chemistry of the initial γ -Al₂O₃ and the sulfated samples synthesized on its basis were *n*-hexane, *n*-heptane, *n*-octane, benzene, ethylbenzene, chloroform, and diethyl ether, the properties of which are given in Table 1 [8, 9].

Adsorption properties were studied via dynamic sorption on a Crystallux-4000M chromatograph equipped with a catharometer as a detector. Physico-chemical measurements were made using glass columns 20 cm long with inner diameters of 2 mm. Helium was used as the carrier gas at a flow rate of 30 mL/min. Prior to measurements, the adsorbent was conditioned in the chromatograph's column in a carrier gas flow at 200°C for 3 h. The volumes of the introduced adsorbate samples were varied from 0.5 to 10 μ L.

Adsorption isotherms were measured at temperatures of 100, 110, and 120°C for all of the above adsorbates (except ethylbenzene), and at 150, 160, and 170° C for C₆H₅C₂H₅. Adsorption isotherms were calculated according to Glukauf [10]. The isosteric heats of adsorption (Q_{st}) were determined at different surface coverages, and the contributions from dispersion (Q_{disp}) and specific (Q_{spec}) interactions to Q_{st} were also estimated.

Estimating Catalytic Activity

Prior to each catalytic experiment, catalyst samples were activated in an air flow for 0.5 h at 450°C. The liquid-phase alkylation of benzene with octene-1 was performed in ampoules in the temperature range of 25-120°C with constant stirring. A mixture of benzene, octene-1, and *n*-nonane at a volume ratio of 20:5:1 was used. *n*-Nonane was used as an internal standard. Control experiments demonstrated its inertness under reaction conditions. Octene-1 was subjected to partial isomerization under reaction conditions with a change in the double bond position. In quantitative analysis, the formed isomers of octene-1 were considered as initial octene.

The composition of alkylation reaction products was determined via gas-liquid chromatography on a Crystal 5000 chromatograph equipped with a flame ionization detector and a BP capillary column 25 m long (temperature programming regime, $t_{col} = 85-200^{\circ}$ C).

In addition to gas-liquid chromatography, gas chromatography–mass spectrometry was used in analyzing reaction solutions. Prior to analysis, the reaction solution was separated from the catalyst. Spectra were recorded on a Varian MAT 112S spectrometer. A DB-1 capillary column 60 m long was used in the mode of linear column temperature programming from 40 to 250°C at a rate of 8 K/min. The energy of the ionizing electrons was ~70 eV. The spectra were processed using the MMS Labcom 2 data processing system. The components in the reaction mixture were identified using the NIST/EPA database.

RESULTS AND DISCUSSION

Adsorption Properties

n-Hexane, benzene, ethylbenzene, and chloroform adsorption isotherms, measured on the initial and sulfated γ -Al₂O₃ and the γ -Al₂O₃ based cobaltcontaining composite (0.5%Co/SO₄²⁻/ γ -Al₂O₃) before and after catalytic experiments, are shown in Figs. 1–4. The initial regions of the isotherms are convex with respect to the adsorption axis and belong to type II of the classification in [11]. The isotherms confirm the existence of strong adsorption sites and (probably) residual surface microporosity. The adsorption of the selected test adsorbates on the initial γ -Al₂O₃ samples and all the modified γ -Al₂O₃ based composites falls as the temperature rises at all equilibrium pressures, testifying to the physical character of adsorption.



Fig. 1. *n*-C₆H₁₄ adsorption isotherms at 100°C on composites (1) 0.5%Co/SO₄²⁻/ γ -Al₂O₃, (2) 0.5%Co/SO₄²⁻/ γ -Al₂O₃, after catalysis, (3) SO₄²⁻/ γ -Al₂O₃, and (4) γ -Al₂O₃.



Fig. 3. CHCl₃ adsorption isotherms at 100°C on the composites (1) 0.5%Co/SO₄²⁻/ γ -Al₂O₃, (2) SO₄²⁻/ γ -Al₂O₃, and (3) γ -Al₂O₃.

In contrast to the initial support, diethyl ether was irreversibly chemosorbed both on SO_4^{2-}/γ -Al₂O₃ sulfated aluminum oxide and on the 0.5%Co/SO_4^{2-}/\gamma-Al₂O₃ cobalt-containing composite based on it. The adsorption of all the test adsorbates falls at all temperatures of measurement and the same equilibrium pressures on the composites in the order 0.5%Co/SO_4^{2-}/\gamma-Al₂O₃ > 0.5%Co/SO_4^{2-}/\gamma-Al₂O₃ (after catalysis) > SO_4^{2-}/\gamma-Al₂O₃.



Fig. 2. C_6H_6 adsorption isotherms at 110°C on composites (1) 0.5%Co/SO₄²⁻/ γ -Al₂O₃, (2) 0.5%Co/SO₄²⁻/ γ -Al₂O₃ after catalysis, (3) SO₄²⁻/ γ -Al₂O₃, and (4) γ -Al₂O₃.



Fig. 4. $C_6H_5C_2H_5$ adsorption isotherms at 140°C on composites (1) 0.5%Co/SO₄²⁻/ γ -Al₂O₃, (2) 0.5%Co/SO₄²⁻/ γ -Al₂O₃, after catalysis, (3) SO₄²⁻/ γ -Al₂O₃, and (4) γ -Al₂O₃.

The specific surface areas $(S, m^2/g)$ and monolayer capacity a_m were calculated from the *n*-hexane adsorption isotherms at 100°C by the BET equation, and the parameters of the microporous structure of samples were estimated from the benzene adsorption isotherms using the Dubinin–Radushkevich equation [12]. The micropore radius was calculated from the characteristic adsorption energy (E^0) dependence according to the equation $R = 12/E^0$ [13]. Calculation results are listed in Table 2. From Table 2, we can see

Table 2. Parameters of the microporous structure of the initial γ -Al₂O₃, sulfated γ -Al₂O₃, and 0.5%Co/SO₄²⁻/ γ -Al₂O₃ composite before and after the heterogeneous catalytic alkylation reaction*

Adsorbent	$S, m^2/(g C_6 H_6)$	a _m , µmol∕g	E ⁰ , kJ/mol	<i>R</i> , nm
γ -Al ₂ O ₃	147	276	10.3	1.16
9% SO ₄ ²⁻ / γ -Al ₂ O ₃	73	249	13.3	0.90
0.5% Co/SO ₄ ²⁻ / γ -Al ₂ O ₃	67	227	14.4	0.83
0.5% Co/SO ₄ ²⁻ / γ -Al ₂ O ₃ (after catalysis)	64	218	12.1	0.99

* S is the specific surface area, $a_{\rm m}$ is the monolayer capacity, E^0 is the characteristic energy of adsorption, and R is the pore radius calculated using the Dubinin–Radushkevich equation [12].

that the specific surface area of sulfated γ -Al₂O₃ shrinks after the introduction of 9 wt % of sulfate groups, while additional modification with cobalt salts has virtually no effect on its value. The specific surface area of the sulfated samples is known to strongly depend on the conditions of synthesis, among which the thermal treatment of oxide systems before and after the introduction of sulfate groups can be of crucial importance. In some cases, the specific surface area of sulfated aluminum oxide can grow slightly in comparison to the initial support [4, 5, 14], but the surface modification of γ -Al₂O₃ with sulfate anions usually reduces it [4, 15, 16].

The adsorption isotherms of the test adsorbates are perfectly described by the empirical Freundlich equation [17] for a non-uniform surface:

$$a = kp^n \tag{1}$$

or, in the linear form,

 $\ln a = \ln k + n \ln p. \tag{2}$

The isosteric heats of adsorption (Q_{st}) were calculated from the set of these dependences for three temperatures ($R^2 = 0.999$). The isosteric heats of adsorption at surface coverage $a = 0.35 \,\mu mol/m^2$ were used to determine the contributions from dispersion (Q_{disp}) and specific (Q_{spec}) interactions. The calculation results are given in Table 3.

The dependences of chloroform $Q_{\rm st}$ on the surface coverage in the initial monolayer area of 0.5%Co/SO₄²⁻/ γ -Al₂O₃ and 9%SO₄²⁻/ γ -Al₂O₃ are plotted in Fig. 5 as examples. The data shown in Fig. 5 display the dependence typical of all the studied systems when the highest heats of adsorption correspond to the most active surface sites, which are the first to be occupied by adsorbate molecules. As they are occupied, adsorption occurs on less active sites, and the heats of adsorption gradually fall.

The contribution from the energy of specific interaction (Q_{spec}) was determined as the difference between isosteric heats of adsorption Q_{st} of a polar adsorbate and a hypothetical *n*-alkane with the same total polarizability α . From Table 3 containing isosteric heats of adsorption $Q_{\rm st}$ and specific interaction contributions Q_{spec} for the adsorption of test adsorbates in the region of low coverage at a = $0.35 \,\mu mol/m^2$, it can be seen that the sulfated aluminum oxide and composite surfaces are characterized by high adsorption heats and exhibit stronger specificity in comparison with γ -Al₂O₃. The heats of adsorption of *n*-alkane characterizing nonspecific dispersion interactions on sulfated aluminum oxide and the composite grow slightly, compared to the initial γ -Al₂O₃. The immobilization of both sulfate groups and metal ions reduces the effective diameter of the support's pores, due to the blocking of pore inlet openings. The adsorption potential then grows, due to the imposition

Table 3. Isosteric heats of adsorption (Q_{st} , kJ/mol) of test adsorbates and the contributions of dispersion (Q_{disp} , kJ/mol) and specific (Q_{spec} , kJ/mol) donor-acceptor interactions to them at $a = 0.35 \,\mu mol/m^2$ on initial and sulfated γ -Al₂O₃ and 0.5%Co/SO₄²⁻/ γ -Al₂O₃, before and after the heterogeneous catalytic alkylation reaction

	γ-Al ₂ O ₃		9%SO ₄ ²⁻ /γ-Al ₂ O ₃		$0.5\% Co/SO_4^{2-}/\gamma - Al_2O_3$		$\begin{array}{c} 0.5\% Co/SO_4^{2-}/\gamma \text{-Al}_2O_3\\ \text{(after catalysis)} \end{array}$					
Adsorbate	$Q_{\rm st}$	$Q_{ m disp}$	$Q_{ m spec}$	$Q_{\rm st}$	$Q_{ m disp}$	$Q_{ m spec}$	$Q_{\rm st}$	$Q_{ m disp}$	$Q_{ m spec}$	$Q_{ m st}$	$Q_{ m disp}$	$Q_{ m spec}$
<i>n</i> -C ₆ H ₁₄	39			41			40			40		
$n-C_7H_{16}$	43			46			45			43		
<i>n</i> -C ₈ H ₁₈	47			51			50			46		
C ₆ H ₆	50	36	14	57	37	20	57	36	21	58	38	20
CHCl ₃	57	31	26	47	31	16	79	30	49	47	34	13
$(C_2H_5)_2O$	78	34	44	Chemosorption		Chemosorption		77	36	41		
$C_6H_5C_2H_5$	60	44	16	67	47	20	87	46	41	83	44	39

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of the potential field of closely packed pore walls, thus raising the heat of adsorption.

From Table 3, we can see that diethyl ether, the molecules of which have predominantly electrondonating properties, is irreversibly chemosorbed on the surface of sulfated aluminum oxide. The adsorption of electron-accepting molecules (CHCl₃) is characterized by a drop in $Q_{\rm st}$ values, relative to the initial γ -Al₂O₃. These results point to a considerable increase in the number of electron-accepting (acidic) sites on a surface of aluminum oxide after the introduction of sulfate groups and subsequent calcination, which agrees with the data in [18, 19] on the acidity of sulfated oxides.

However, the immobilization of even small amounts of transition metal cations (less than 0.5 wt %) on a surface of sulfated aluminum oxide changes the adsorption properties of its surface considerably. As can be seen from Table 3, the irreversible chemosorption of diethyl ether on the cobalt-contain-

ing $Co/SO_4^{2-}/\gamma$ -Al₂O₃ samples is similar to the adsorp-

tion on SO_4^{2-}/γ -Al₂O₃, indicating that the acidic properties of surfaces of sulfated oxides not only remain the same after modification with cobalt salts, but are likely to increase. At the same time, the heat of adsorption of chloroform on the Co/SO²⁻/ γ Al O₂ samples considered.

chloroform on the Co/SO₄²⁻/ γ -Al₂O₃ samples considerably exceeds Q_{st} on the sulfated and initial γ -Al₂O₃. The data of Table 3 indicate that the heats of adsorption rise for CHCl₃ due to an increase in the contribution from the energy of specific interaction (Q_{spec}) to the total energy of adsorption, and are 16 and 49 kJ/mol for the sulfated and cobalt modified samples, respectively. The observed adsorption effects on the Co/SO₄²⁻/ γ -Al₂O₃ samples are apparently due to specific interactions between transition metal ions and halogenated hydrocarbon molecules, for which the formation of molecular complexes was determined earlier via IR spectroscopy and confirmed theoretically [20].

An increase in the number of specific adsorption sites after surface modification of sulfated aluminum oxide with cobalt ions is also indicated by a rise in benzene and ethylbenzene adsorption on them, relative to the initial samples (see Table 3). The differences between the isosteric heats of adsorption (ΔQ_{st}) of aromatic hydrocarbons and *n*-alkanes on the surfaces of different adsorbents ($\Delta Q_{spec} = Q_{st}(arom.) - Q_{st}(n$ alkane)) are given in Table 4. $\Delta Q_{spec} = (Q_{C_6H_6} - Q_{n-C_6H_{14}})$ corresponds to the difference between the benzene and *n*-hexane heats of adsorption and characterizes the energy contribution from specific interactions between the π -electron bonds of molecules and active sites on the surfaces of sorbents to the total energy of adsorption of benzene. From Table 4, we can see that the contribution from the specific energy of

Q, kJ/mol



Fig. 5. Isosteric CHCl₃ adsorption heat vs. surface coverage on (1) 0.5%Co/SO₄²⁻/ γ -Al₂O₃ and (2) SO₄²⁻/ γ -Al₂O₃.

interaction grows after the sulfation and subsequent promotion of the γ -Al₂O₃ surface with cobalt, from 11 kJ/mol on the initial sample to 17 kJ/mol on $Co/SO_4^{2-}/\gamma$ -Al₂O₃. In addition, energy contribution $\Delta Q_{\rm spec}$ on the cobalt-modified samples grows appreciably after introducing an alkyl substituent into the benzene ring. ΔQ_{spec} has close values for benzene on different oxide systems (~11–17 kJ/mol), while contribution $\Delta Q_{\text{spec}} = Q_{C_6H_5C_2H_5} - Q_{n-C_8H_{18}}$ for ethylbenzene on $0.5\% Co/SO_4^{2-}/\gamma\text{-}Al_2O_3$ (37 kJ/mol) greatly exceeds the corresponding values obtained on γ -Al₂O₃ and SO_4^{2-}/γ -Al₂O₃ (13 and 16 kJ/mol, respectively). As can be seen from Tables 3 and 4, the heat of adsorption of aromatic compounds in this case grows, due largely to an increase in the energy contribution from specific interactions in which transition metal cations also participate.

In Table 4, contributions $\Delta Q_{\text{spec}} = Q_{\text{st}}(\text{arom.}) Q_{\rm st}(n-{\rm alkane})$ are compared to the data obtained for the adsorption of test molecules on cobalt-containing samples of nonsulfated γ -Al₂O₃, i.e., 5%Co/ γ -Al₂O₃ and 5%CoO/ γ -Al₂O₃, synthesized using the sol-gel method [21]. According to the data in [21], the transition metal contained in such composites is present on the surface of γ -Al₂O₃ predominantly in the form of metallic cobalt nanoparticles (in 5%Co/ γ -Al₂O₃ samples) or cobalt oxide nanoparticles (in 5%CoO/ γ - Al_2O_3 composites). From Table 4, we can see that $\Delta Q_{
m spec}$ for the cobalt-containing composites prepared from nonsulfated γ -Al₂O₃ are low for benzene adsorption (10 and 5 kJ/mol) and 20 and 11 kJ/mol for ethylbenzene adsorption, much lower than on the cobalt-containing sulfated aluminum oxide $(0.5\% Co/SO_4^{2-}/\gamma-Al_2O_3)$. A similar picture is observed for chloroform adsorp-

Adsorbent	$\Delta Q = Q_{\rm C_6H_6}$ $- Q_{n-\rm C_6H_{14}}$	$\Delta Q = Q_{C_6H_5C_2H_5} - Q_{n-C_8H_{18}}$	$\Delta Q_{\rm spec} = Q_{\rm C_6H_5C_2H_5} - Q_{\rm C_6H_6}$	$\Delta Q = Q_{(C_2H_5)_2O}$ $- Q_{n-C_5H_{12}}$	$Q_{\rm spec}(\rm CHCl_3)$
γ-Al ₂ O ₃	11	13	2	43	26
$9\% SO_4^{2-}/\gamma - Al_2O_3$	16	16	10	Chemosorption	16
$0.5\% Co/SO_4^{2-}/\gamma\text{-Al}_2O_3$	17	37	20	Chemosorption	49
$0.5\% Co/SO_4^{2-}/\gamma\text{-Al}_2O_3^*$	18	37	19	40	13
5%CoO/γ-Al ₂ O ₃	5	11	14	28	11
5%Co/γ-Al ₂ O ₃	10	20	18	27	17

Table 4. The differences between the isosteric heats of adsorption (ΔQ_{st}) of aromatic hydrocarbons, diethyl ether, and *n*-alkanes on initial and modified γ -Al₂O₃ at surface coverage $a = 0.35 \,\mu$ mol/m²

* After catalysis.

tion, where specific interaction contribution Q_{spec} is only 17 and 11 kJ/mol for 5%Co/ γ -Al₂O₃ and 5%CoO/ γ -Al₂O₃, respectively, against 49 kJ/mol for 0.5%Co/SO₄²⁻/ γ -Al₂O₃. With respect to diethyl ether, the nonsulfated cobalt-containing samples behave like specific adsorbents instead of chemisorbents ($\Delta Q_{\text{spec}} = 27-28 \text{ kJ/mol}$).

The specific adsorption sites found on the studied sulfated systems could play an important part when exhibiting their catalytic activity in the alkylation reaction. This is confirmed in particular by data obtained for the samples after catalytic reactions in the adsorption of test adsorbate molecules. From Tables 3 and 4, we can see that $Q_{\rm st}$ and contributions $Q_{\rm spec}$ for the test adsorbates on the 0.5%Co/SO₄²⁻/ γ -Al₂O₃ sample fall slightly after catalysis, compared to the initial 0.5%Co/SO₄²⁻/ γ -Al₂O₃ sample, and contribution $\Delta Q_{\text{spec}} (Q_{C_6H_5C_2H_5} - Q_{C_6H_6})$ of 19 kJ/mol is also reduced. In contrast to the chemosorption of diethyl ether on the sulfated composites, the adsorption of diethyl ether is observed both on the surface of the sample after catalysis and on the initial γ -Al₂O₃ (see Table 3), testifying to the participation of the most active electron-accepting surface sites in catalysis.

Considerable changes were also observed in chloroform adsorption. As can be seen from Table 3, a strong reduction in the heat of adsorption is observed after the catalytic reaction on the 0.5%Co/SO₄²⁻/ γ -Al₂O₃ samples, due primarily to a drop in the energy of specific interactions between the chloroform and the adsorption sites based on cobalt atoms.

A surface of sulfated aluminum oxide modified with cobalt cations thus contains different sites capable of the specific adsorption of both donating molecules (adsorption of aromatics, chemosorption of diethyl ether) and accepting molecules (chloroform). It is apparently these sites, which form after the immobilization of transition metal cations on a surface of sulfated oxide, can make a substantial contribution to its catalytic activity. The data given below on the catalytic activity of the studied systems confirm this hypothesis.

Catalytic Properties

The catalytic properties of the synthesized sulfated aluminum oxide and cobalt-containing composite samples were estimated from their catalytic activity in the model reaction of benzene alkylation with olefins at temperatures of 25-120°C. The liquid-phase reaction between benzene and octene-1 barely occurs on the initial aluminum oxide in the studied range of temperatures: the octene-1 conversion does not exceed 3% after 3 h at 120°C. Neither is a catalytic reaction observed under these conditions on the 5%Co/ γ -Al₂O₃ samples obtained via modification of the initial γ -Al₂O₃ with cobalt salts. In contrast, the immobilization of sulfate groups on the surface of γ -Al₂O₃ greatly increases the support's activity: octene-1 conversion on the 9%SO₄²⁻/ γ -Al₂O₃ samples reaches 30–35% in 1 h even at room temperature. The benzene alkylation reaction in this case is selective and produces such linear monoalkyl benzenes (LABs) as 4-phenyl-, 3-phenyl-, and 2-phenyloctane. Their major fraction (more than 50%) is 2-phenyloctane, a target reaction product.

The surface modification of sulfated aluminum oxide with cobalt salts in amounts of 0.5 wt % considerably enhances the activity of these catalysts. Octene-1 conversion on the 0.5%Co/SO₄²⁻/ γ -Al₂O₃ sample was 90% even at room temperature. Our data on process conversion and selectivity on the Co/SO₄²⁻/ γ -Al₂O₃ samples at different temperatures are given in Table 5. It can be seen that octene-1 conversion grew when the reaction temperature was raised to 80°C, but the selectivity to LABs did not change appreciably, and the yield of 2-phenyloctane, the most

Table 5. Conversion (η) and selectivity to LABs (S_1) and 2-phenyloctane (S_2) in the reaction of benzene alkylation with octene-1 on the Co/SO₄²⁻/ γ -Al₂O₃ sample at different temperatures

$T_{\text{react}}, ^{\circ}\text{C}$	η, %	<i>S</i> ₁ , %	<i>S</i> ₂ , %
25	89.8	91	51.7
50	94.8	90	51.1
80	99.3	88	50.9

important product, remained at a level of more than 50%. The content of subsequent products of alkylation, i.e., dioctylbenzenes, did not exceed 8-10%.

It should be noted that the surface modification of

 SO_4^{2-}/γ -Al₂O₃ with transition metal cations not only appreciably increases the yield of alkylation products, but also considerably changes the character of the catalytic reaction. The data on olefin conversion in the liquid-phase benzene alkylation reaction on modified samples of different composition, depending on the mass content of the catalyst in the reaction mixture, are plotted in Fig. 6. It can be seen that the rate of the reaction (alkene conversion over a certain period of time) on the 0.5%Co/SO₄²⁻/\gamma-Al₂O₃ cobalt-containing catalysts grows in an almost linear fashion as the content of the catalyst in the reaction mixture rises. Such dependences are observed for times close to the onset of the reaction and its end (30 and 90 min,



Fig. 6. Octene-1 conversion in the liquid-phase benzene alkylation reaction vs. catalyst content in the reaction mixture at 295 K on samples (*1*, *2*) $Co/SO_4^{2-}/\gamma$ -Al₂O₃ and (*3*, *4*) SO_4^{2-}/γ -Al₂O₃ for (*1*, *3*) 30 and (*2*, *4*) 90 min of the reaction.

At the same time, the character of the reaction on the SO_4^{2-}/γ -Al₂O₃ samples without cobalt differs from the one considered above. From Fig. 5, we can see that alkene-1 conversion on SO_4^{2-}/γ -Al₂O₃ remained nearly the same as the process time was increased (from 30 to 90 min) and grew slightly when the content of catalyst in the reaction mixture was increased. Similar patterns testify to the existence of a limited number of sites that are active in the catalytic process at low temperatures (295–313 K) on sulfated aluminum oxide. In contrast, the nearly linear dependence between the rate of the alkylation reaction and the mass content of the catalyst observed for the 0.5%Co/SO₄²⁻/ γ -Al₂O₃ samples demonstrates the key role of the transition metal, which forms catalytically active sites on the sulfated support surface.

The data obtained in this work on the adsorption of test molecules also indicate that 0.5%Co/SO₄²⁻/ γ -Al₂O₃ contains adsorption sites that greatly increase contributions ΔQ_{spec} to the heat of adsorption of aromatic hydrocarbons and halide-containing molecules (particularly chloroform). The formation of specific adsorption sites on a Co/SO₄²⁻/ γ -Al₂O₃ surface containing sulfate anions is apparently due to the possibility of stabilizing the transition metal in the form of cations on this surface. Preliminary data from the IR spectroscopy of adsorbed carbon monoxide have shown that the electron state of the transition metal on

a $Co/SO_4^{2-}/\gamma$ -Al₂O₃ surface is close to that of ionexchange cations (Co²⁺) on the surfaces of alumosilicate zeolites [22, 23] and differs substantially from the state of cobalt in the oxides (CoO) formed on surfaces of nonmodified γ -Al₂O₃. This agrees with the known literature data for some other sulfated oxides modified with transition metals [15, 24]. The state of a transition metal on a surface of sulfated oxide and its role in alkylation reaction catalysis will be considered in more detail in a separate work.

CONCLUSIONS

Using the dynamic sorption of test molecules of different classes of organic compounds, it was established that the surface sulfation of aluminum oxide leads to the growth of specific intermolecular sorbate sorbent interactions; greatly increases the electronaccepting properties of its surface; and, upon the surface modification of sulfated aluminum oxide with cobalt(II) ions, improves both its electron-accepting and electron-donating properties. The catalytic activity of sulfated aluminum oxide in the liquid-phase alkylation of benzene with long-chain olefins is an order of magnitude higher than for initial aluminum oxide. Additional modification of sulfated aluminum oxide with cobalt ions increases the catalyst's activity

respectively).

by 2–4 times, with the retention of high selectivity toward LABs and 2-phenyloctane.

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