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Adsorption Properties of Aluminum Oxide Modified with Co and CoO Particles

S. N. Lanin^{*}, A. A. Bannykh, E. V. Vlasenko, A. E. Vinogradov, K. S. Lanina, and S. M. Levachev

Department of Chemistry, Moscow State University, Moscow, 119991 Russia *e-mail: SNLanin@phys.chem.msu.ru Received July 21, 2016

Abstract—Adsorption properties of γ -Al₂O₃ modified with Co (5 and 10 wt %) and Co (5 wt %) species are investigated by dynamic adsorption. *N*-hexane, *n*-heptane, *n*-octane, benzene, toluene, ethylbenzene, chloroform, and diethyl ether were used as test adsorbates. Adsorption isotherms were measured, and isosteric adsorption heats were calculated for the indicated sorbates. It was shown that the adsorption isotherms of all the adsorbates and at all the temperatures of measurements on γ -Al₂O₃ modified with Co (5 wt %) and CoO (5 wt %) nanoparticles located above that recorded for the initial γ -Al₂O₃ sample. It was established that the surface of modified γ -Al₂O₃ possessed mainly electron-accepting properties. The 5% Co/ γ -Al₂O₃ and 5% CoO/ γ -Al₂O₃ nanocomposites exhibited the greatest adsorption capacity relative to aromatic hydrocarbons.

Keywords: adsorption, nanoparticles, adsorption isotherms, isosteric adsorption heats, electron-accepting interactions

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INTRODUCTION

Synthesis of nanosized objects, including nanoparticles of a series of chemical elements and compounds, and investigations of their properties are quite promising and rapidly growing fields of modern chemistry and technology. The heightened interest is them is due to new possibilities and trends that are opened up upon the synthesis and investigations of nanoparticles and, often, cannot be described in terms of existing fundamental laws. It is known that metal nanoparticles with sizes of less than 1 nm involve up to 10 atoms and can form a "surface" particle that possesses an extremely high chemical activity [1].

The unique properties of nanosized objects open up great prospects for production of new electrical and computer devices and systems of data storage and transmission, as well as advanced efficient catalysts [2-5].

Nanosized catalysts based on transition metals are studied most intensely. This interest is due to a sharp increase in the adsorption [6] and catalytic activity of metal particles observed in a number of cases when their sizes are reduced to the nanometer-length scale, enabling one to prepare completely different catalysts with qualitatively new and previously unseen properties [1, 7-10].

The catalytic activity of cobalt and cobalt oxide particles is higher by a few orders of magnitude than that exhibited by salt catalysts based on cobalt salts, which is mainly seen in the reactions leading to carbon-chain elongation [11] and methane oxidation [12]. The sharp growth in both the adsorption and catalytic activity is determined by the dimensions, chemical composition, and structure of cobalt nanoparticles, as well as the strength and nature of their interactions with reagents and catalyst support [1, 14, 15]. Catalysts with immobilized bimetal nanoparticles are also promising materials [16, 17].

To understand the mechanisms of catalytic reactions proceeding on immobilized metal nanoparticles (nanocomposites), information on the strength and nature of their interactions with reagents and support is required. For this purpose, data on electron-donating and -accepting behaviors of the surface of supports (γ -Al₂O₃ [18], SiO₂ [19], MN-272 [20], MgO [21], and TiO₂ [22]) are also needed.

The aim of this work is synthesis of γ -Al₂O₃-based nanocomposites modified by Co and CoO nanoparticles and investigation of the adsorption, electron-donating, and electron-accepting properties of their surfaces.

EXPERIMENTAL

Adsorbents. Initial γ -aluminum oxide (SIGMA-ALDRICH) nanoparticles with sizes in the range of 0.16–0.25 mm (specific surface of 110 m²/g, pore volume of 0.29 cm³/g, and pore diameter of 90 Å) and

 Table 1. Mean size of immobilized crystalline nanoparticles Co and CoO

Adsorbent	$2\theta^{\circ}$	β_{hkl} , rad	D, nm
5% Co/γ-Al ₂ O ₃	39.4298	0.7099	13.3
10% Co/γ-Al ₂ O ₃	39.4298	0.5044	18.8
5% CoO/γ-Al ₂ O ₃	39.4298	0.7099	13.3

nanocomposites of γ -Al₂O₃ modified with Co and CoO nanoparticles (5 and 10 wt % Co and 5 wt % CoO) were used as the adsorbents.

Synthesis of γ -Al₂O₃-based nanocomposites modified with Co and CoO nanoparticles [23]. An amount of 1.68 g of CoCl₂ · 6H₂O was diluted in 10 mL of water. The solution was then heated up to 80°C; afterward, 5 g of γ -aluminum oxide and 0.28 g of NaOH were added to it. After the solution was cooled to room temperature (20°C), 0.27 g of a reducing agent, sodium tetrahydroborate (NaBH₄) diluted in 7 g of isopropyl alcohol, was added under constant stirring. During this process, the reaction of synthesis of cobalt nanoparticles proceeds:

$$CoCl_2 \cdot 6H_2O + 2NaBH_4$$

$$\rightarrow Co + 2B(OH)_3 + 2NaCl + 7H_2^{\uparrow}.$$

Having completed the synthesis of Co nanoparticles, we dried the resulting system for 20 min at 80°C in order to remove the "isopropyl alcohol–water" azeotrope mixture and washed it subsequently with water and twice with isopropyl alcohol. After sedimentation, the resulting solid residue was placed into a drying chamber and kept there until alcohol was completely removed from it. The dried sample of Co/ γ -Al₂O₃ nanocomposite was divided into two parts. One part was placed into a desiccator, while the other part was left in the air. One day afterward, the cobalt nanoparticles (0) left in the air oxidized to cobalt oxide(II):

$$\operatorname{Co} + \frac{1}{2}\operatorname{O}_2 \to \operatorname{CoO}.$$

X-ray-diffraction analysis. Samples of nanocomposites were studied by X-ray diffraction on a Rigaku D/MAX 2500 rotating-anode diffractometer (Japan).

Mean diameter D_{hkl} of Co and CoO crystalline particles was evaluated from the recorded X-raydiffraction pattern using the Debye–Scherrer formula [24]:

$$D_{hkl} = \frac{k\lambda}{\beta_{hkl}\cos\theta_{hkl}},\tag{1}$$

where *k* is a dimensionless shape factor (k = 0.89); λ is the wavelength of irradiation, Å; θ_{hkl} is the angle of diffraction; and β_{hkl} is the half-width of the diffraction peak in radians.

Table 1 summarizes the calculated sizes of Co and CoO crystalline particles.

The mean diameters of the Co and CoO crystalline particles with 5 and 10 wt % of metal, upon depositing on the support, amounted to 13.3 and 18.8 nm, respectively.

Adsorbates. *N*-hexane, *n*-heptane, *n*-octane, benzene, toluene, ethylbenzene, chloroform, and diethyl ether were used as test adsorbates to study the chemistry of the surface of initial γ -Al₂O₃ and synthesized γ -Al₂O₃-based nanocomposites. The characteristics of these reagents [25] are given in Table 2.

Adsorption investigations. Adsorption properties of the initial γ -Al₂O₃ support and synthesized nanocomposites were studied by dynamic adsorption on a Crystallux-4000M chromatograph with a thermal-conductivity detector. Glass columns 20 cm long and with an inner diameter of 2 mm were used for the physicochemical measurements. Helium was used as the carrier gas, with the flow rate being 30 mL/min. Before measurements, the sample was conditioned in a carrier gas flow in a chromatograph column at 200°C for 8 h. The volume of injected adsorbate sample was varied from 0.5 to 10 μ L.

Specific retention volumes were determined for $n-C_6H_{14}$, $n-C_7H_{16}$, C_6H_6 , $CHCl_3$, and $(C_2H_5)_2O$ at

Adsorbate	M (amu)	μ, D	α, Å ³	<i>DN</i> , kJ/mol	AN, kJ/mol
<i>n</i> -C ₆ H ₁₄	86.17	0	11.9	0	0
$n - C_7 H_{16}$	100.2	0	13.7	0	0
C ₆ H ₆	78	0	10.4	0.4	8.2
C ₆ H ₅ CH ₃	92.14	0.37	12.4		
$C_6H_5C_2H_5$	106.17	0.59	14.36		
CHCl ₃	119.4	1.15	10.5	0	23
$(C_2H_5)_2O$	79.1	1.70	10.0	80.3	3.9

Table 2. Characteristics of test adsorbates [24] (*M* is the molecular mass, μ is the dipolar moment, α is the total polarizability of the molecule, and *AN* and *DN* are the electron-accepting and -donating energy characteristics of the molecules [35])

Adsorbents	$s, m^2/g$	$a_{\rm m}$, µmol/g	E^0 , kJ/mol	<i>R</i> , nm	$V_{\rm pore},{\rm cm^3/g}$
γ -Al ₂ O ₃	98	275	10.3	1.16	0.25
5% Co/γ-Al ₂ O ₃	78	209	13.2	0.91	0.21
10% Co/γ-Al ₂ O ₃	78	253	10.2	1.20	0.21
5% CoO/ γ -Al ₂ O ₃	71	201	12.1	0.99	0.21

Table 3. Parameters of microporous structure of γ -Al₂O₃ and γ -Al₂O₃-based nanocomposites

100, 110, and 120°C; for $C_6H_5CH_3$ and $n-C_8H_{18}$ at 130, 140, and 150°C; and for $C_6H_5C_2H_5$ at 150, 160, and 170°C for low surface fillings; adsorption isotherms were measured [26, 27] and isosteric adsorption heats were evaluated [28]. The values of adsorption *a* and equilibrium pressure *p* were calculated from the equations

$$a = \frac{mS_{\rm ads}}{gS_{\rm peak}},\tag{2}$$

$$p = \frac{mhRT}{FS_{\text{peak}}},\tag{3}$$

where *m* is the amount of adsorbate injected into a column, *g* is the weight of an adsorbent sample, *h* is the height of a chromatographic peak, *R* is the universal gas constant, *F* is the volumetric flow rate of a gas carrier, *T* is the temperature of column, S_{peak} is the area under a chromatographic peak, and S_{ads} is the area corresponding to the adsorption chromatogram.

The specific pore volumes (V_{pore} , cm³/g) of the initial γ -Al₂O₃ and synthesized nanocomposites were determined from the data on capillary condensation of benzene from saturated vapors (Table 3) using the formula

$$V_{\rm pore} = (\delta/m)d$$
,

where δ is growth in the mass of adsorbent; *d* is the specific density of benzene at 22°C, g/cm³; and *m* is the weight of initial aluminum oxide, g.



Fig. 1. (1) X-ray-diffraction pattern of 5% Co/γ -Al₂O₃ composite; (2) with an imposed theoretical diffraction pattern of Co-phase.

RESULTS AND DISCUSSION

Adsorption isotherms of *n*-hexane, benzene, toluene, and ethyl benzene on the original γ -Al₂O₃ and γ -Al₂O₃-based nanocomposites modified with Co and CoO nanoparticles are shown in Figs. 2–5. The isotherms are convex toward the adsorption axis, indicating that the interactions between the adsorbate and adsorbent are stronger than the adsorbate—adsorbate interactions [29]. At all temperatures of measurements and uniform equilibrium pressures, the adsorption of all adsorbates on the nanocomposites reduced in series: 5% Co/ γ -Al₂O₃ > 5% CoO/ γ -Al₂O₃ > γ -Al₂O₃ > 10% Co/ γ -Al₂O₃.

At all equilibrium pressures, the adsorption of chosen adsorbates on the initial γ -Al₂O₃ and modified samples decreased with a growth in temperature that was indicative of a physical nature of adsorption. Reproducibility of the parameters of elution zones of the adsorbates in repeated measurements confirms this idea; these data indicate the absence of chemosorption and permanence of adsorption properties of



Fig. 2. Adsorption isotherms of n-C₆H₁₄ at 100°C on the composites: (1) 5% Co/ γ -Al₂O₃, (2) 5% CoO/ γ -Al₂O₃, (3) γ -Al₂O₃, and (4) 10% Co/ γ -Al₂O₃.



Fig. 3. Adsorption isotherms of C_6H_6 at 100°C on the composites: (1) 5% Co/ γ -Al₂O₃, (2) 5% CoO/ γ -Al₂O₃, (3) γ -Al₂O₃, and (4) 10% Co/ γ -Al₂O₃.

the studied samples at the specified experimental conditions.

The adsorption isotherms of *n*-hexane at 100°C were used to calculate the specific surface $(s, m^2/g)$ and monolayer capacity a_m following the BET equation [30]. The parameters of the porous structure were evaluated using the Dubinin–Radushkevich equation [31]. The radii of micropores were calculated from the dependence of the characteristic adsorption energy (E^0) from the equation $R = 12/E^0$ [32]. Table 3 summarizes the results of calculations.

Adsorption heats. The surface of aluminum oxide modified by cobalt and cobalt oxide nanoparticles is heterogeneous. Deposition of metal or metal oxide nanoparticles on the surface of aluminum oxide results in the blockage of a part of most active surface sites with these particles. Therefore, the areas of different geometry and chemistry appear on the surface: areas with deposited metal nanoparticles and the remainder of the less active surface of the support.

The adsorption isotherms measured for test adsorbates on heterogeneous surface were best described by the empirical power equation:

$$a = kp^n, \tag{4}$$

where p is the equilibrium pressure and k and n are coefficients.

Dependences of isosteric adsorption heats (Q_{st}) on the filling of adsorbent surface were calculated from the adsorption isotherms measured at various temperatures and presented by power equations (4) expressed in linear form (5) (with coefficient $R^2 = 0.999$):



Fig. 4. Adsorption isotherms of $C_6H_5CH_3$ at 140°C on the composites: (1) 5% Co/ γ -Al₂O₃, (2) 5% CoO/ γ -Al₂O₃, (3) γ -Al₂O₃, and (4) 10% Co/ γ -Al₂O₃.

$$\ln a = \ln k + n \ln p, \tag{5}$$

where k and n are the coefficients.

Isosteric adsorption heats were calculated from these adsorption isotherms using the equation

$$Q_{\rm st} = -R \frac{d\ln p}{d\frac{1}{T}},$$

where p is the equilibrium pressure of adsorbate vapors, mm Hg; R is the universal gas constant, R = 8.314 J/(mol K); and T is the temperature of adsorption equilibrium, K.

Dependences of Q_{st} for test adsorbates $n-C_6H_{14}$, C_6H_6 , $C_6H_5CH_3$, and $C_6H_5C_2H_5$ on surface filling in the area corresponding to a monolayer coverage are given in Table 4. The highest values of adsorption



Fig. 5. Adsorption isotherms of $C_6H_5C_2H_5$ at $T = 150^{\circ}C$ on the composites: (1) 5% Co/ γ -Al₂O₃, (2) 5% CoO/ γ -Al₂O₃, (3) γ -Al₂O₃, and (4) 10% Co/ γ -Al₂O₃.

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1/2	γ-Al ₂ O ₃				5% Co/γ-Al ₂ O ₃			
a, µmol/m ²	C_6H_{14}	C ₆ H ₆	C ₆ H ₅ CH ₃	$C_6H_5C_2H_5$	C_6H_{14}	C ₆ H ₆	C ₆ H ₅ CH ₃	C ₆ H ₅ C ₂ H ₅
0.35	38.8	54.3	61.8	84.0	46.1	56.5	63.8	74.0
0.4	38.4	53.8	60.5	83.3	46.0	54.7	61.2	70.5
0.5	37.8	52.8	58.4	79.5	45.9	53.8	59.7	68.5
0.6	37.2	52.0	56.9	77.1	45.8	52.5	58.0	66.5
0.7	37.0	51.6	56.8	76.2	45.8	51.7	57.0	65.0
0.8	36.6	51.0	54.5	74.5	45.8	51.0	56.0	63.5
0.9	36.4	50.6	53.3	73.4	45.7	50.2	55.2	62.5
1.0	36.1	50.2	52.8	72.8	45.7	49.6	54.4	61.5
······································	5% CoO/γ-Al ₂ O ₃				10% Co/γ-Al ₂ O ₃			
a, µmol/m ⁻	C_6H_{14}	C ₆ H ₆	C ₆ H ₅ CH ₃	$C_6H_5C_2H_5$	C_6H_{14}	C ₆ H ₆	C ₆ H ₅ CH ₃	C ₆ H ₅ C ₂ H ₅
0.3	51.3	55.6	63.3	70.2	47.5	54.5	59.4	67.1
0.4	49.4	54.7	61.5	67.1	46.3	53.3	58.3	65.3
0.5	48.3	54.0	61.0	65.4	45.2	52.3	57.3	63.5
0.6	47.4	53.4	59.2	63.6	44.3	51.6	56.7	62.3
0.7	46.7	52.9	58.3	62.4	43.8	50.7	55.8	61.1
0.8	46.0	52.4	57.4	61.0	43.2	50.2	55.4	60.2
0.9	45.5	52.0	56.8	60.2	42.6	49.7	54.9	59.3
1.0	45.0	51.7	56.2	59.3	42.0	49.1	54.3	58.4

Table 4. Dependence of isosteric heats of adsorption, Q_{st} , kJ/mol, on the filling of surface on the initial γ -Al₂O₃ and γ -Al₂O₃-based nanocomposites

heats are typical for the most active areas of the surface, which are first filled. During this process, adsorption proceeds on the less active sites and the adsorption heats decrease.

Contribution of the specific interaction energy Q_{spec} to the total adsorption energy in the sense of Barrer [33] was determined as the difference between the heat of adsorption of polar molecules and that of the reference molecules with the same polarizability, which are not capable of specific interactions. Kiselev [34] suggested considering molecules of *n*-alkanes as reference molecules. Contribution of the dispersion interaction of a sorbent Q_{disp} was taken equal to that of a hypothetical *n*-alkane Q_v with the same polarizability.

Contribution of the specific interaction energy Q_{spec} was calculated using the following expression:

$$Q_{\rm spec} = Q_{st} - Q_{\rm disp},\tag{6}$$

Table 5 presents isosteric adsorption heats Q_{st} of test adsorbates and the calculated contributions of nonspecific Q_{disp} and specific donor-acceptor interactions Q_{spec} to the total adsorption energy for the low surface filling (at $a = 0.3 \,\mu\text{mol/m}^2$) for test adsorbates on the initial γ -Al₂O₃ and synthesized nanocomposites. As can be seen from Table 5, modification of the original γ -Al₂O₃ surface with nanoparticles leads to a growth (by 5–20%) in the heats of adsorption of *n*-alkanes the molecules of which adsorb only due to non-specific (dispersion) interactions. The values of adsorption heats of polar compounds, which are also capable of specific interactions, decrease below that for the original γ -Al₂O₃, which comes into particular prominence for the 10% Co/ γ -Al₂O₃ nanocomposite.

When the amount of nanoparticles and their mean size increased, the adsorption heats of all polar adsorbates reduced, which can be attributed to the effect of nanoparticle size [20].

The adsorption heats of aromatic hydrocarbons (benzene, toluene, and ethyl benzene), which possess a system of conjugated bonds, on the original γ -Al₂O₃ and γ -Al₂O₃ modified with nanoparticles exceeded that of *n*-alkanes with an equal amounts of carbon atoms due to the formation of π -complexes of these molecules with the active sites on the sorbent surfaces (see Tables 5 and 6).

As can be seen from Table 4, the values of adsorption heats of C_6H_6 and $C_6H_5CH_3$ are slightly change after modifying the γ -Al₂O₃ surface. However, the adsorption heats of ethyl benzene on the initial γ -Al₂O₃ sample, the surface of which possesses a strong acidity, is significantly higher than that on the CoO/ γ -Al₂O₃ and Co/ γ -Al₂O₃ nanocomposites. This fact can likely be explained by a decrease in the acidity

Table 5. Isosteric heats of adsorption Q_{st} , (kJ/mol) of test adsorbates and the contributions to them from dispersion Q_{disp} (kJ/mol) and specific Q_{spec} , (kJ/mol) donor-acceptor interactions at $a = 0.3 \,\mu mol/m^2$ for test adsorbates on the initial γ -Al₂O₃ and synthesized nanocomposites

Adsorbate	$Q_{ m st}$	$Q_{ m disp}$	$Q_{ m spec}$	$Q_{ m st}$	$Q_{ m disp}$	$Q_{ m spec}$	
Ausorbaic		γ -Al ₂ O ₃		5% Co/γ-Al ₂ O ₃			
<i>n</i> -C ₆ H ₁₄	39			46			
$n - C_7 H_{16}$	49			50			
$n - C_8 H_{18}$	58			54			
C ₆ H ₆	54	32	22	56	43	13	
CHCl ₃	58	20	38	55	38	17	
$(C_2H_5)_2O$	83	27	56	69	41	28	
C ₆ H ₅ CH ₃	63	42	21	62	47	15	
$C_6H_5C_2H_5$	85	52	33	72	51	21	
	$Q_{ m st}$	$Q_{ m disp}$	$Q_{ m spec}$	$Q_{ m st}$	$Q_{ m disp}$	$Q_{ m spec}$	
Ausorbaic		5% CoO		10% Co/γ-Al ₂ O ₃			
<i>n</i> -C ₆ H ₁₄	51			47			
$n - C_7 H_{16}$	55			51			
$n - C_8 H_{18}$	59			55			
C ₆ H ₆	56	48	8	54	44	10	
CHCl ₃	54	43	11	56	39	17	
$(C_2H_5)_2O$	75	46	29	68	42	26	
C ₆ H ₅ CH ₃	62	52	10	59	48	11	
$C_6H_5C_2H_5$	70	56	14	66	52	14	

Table 6. Contributions of specific interactions ΔQ_{spec} (kJ/mol) to isosteric heats of adsorption Q_{st} of C₆H₆, C₆H₅CH₃ and C₆H₅C₂H₅ on initial and modified γ -Al₂O₃ at filling $a = 0.30 \,\mu\text{mol/m}^2$

Adsorbent	$\Delta Q_{\rm spec} = Q_{\rm st,C_6H_6} - Q_{\rm st,n-C_6H_{14}}$	$\Delta Q_{\rm spec}$ $Q_{\rm st,C_6H_5CH_3} - Q_{\rm sat,n-C_7H_{16}}$	$\Delta Q_{\text{spec}} = Q_{\text{st,C}_6\text{H}_5\text{C}_2\text{H}_5} - Q_{\text{st,}n\text{-}\text{C}_8\text{H}_{18}}$	$\Delta Q_{\rm spec} = Q_{\rm st, C_6H_5C_2H_5} - Q_{\rm st, C_6H_6}$
γ-Al ₂ O ₃	15	14	27	31
5% Co/γ-Al ₂ O ₃	11	14	20	17
10% Co/γ-Al ₂ O ₃	7	8	12	12
5% CoO/ γ -Al ₂ O ₃	5	8	11	14

of their surface that resulted from a reduction in both the total and local concentrations of acidic Lewis sites on the surface upon its modification (with usage of sodium hydroxide) [35].

The high values of the adsorption heats of $(C_2H_5)_2O$ molecules, which have predominantly electron-donating properties (see Table 1), compared with that of CHCl₃ (electron-acceptor molecules) on the original γ -Al₂O₃ and Co/ γ -Al₂O₃ and Co/ γ -Al₂O₃ and Co/ γ -Al₂O₃ nanocomposites indicate a preliminary electron-accepting (acidic) character of the surfaces of the orig-

inal γ -Al₂O₃ and γ -Al₂O₃ modified with Co and CoO nanoparticles.

Comparison (Tables 5, 6) of contributions Q_{disp} and Q_{spec} of interactions to the total energy of adsorption of polar compounds indicates a significant growth in the contribution of Q_{disp} after the modifications of γ -Al₂O₃ with 5% Co and CoO. Therefore, regardless of the sufficiently high adsorption heats of test molecules on the modified surfaces, the values of contributions of specific interaction energy to the total energy of adsorption on the nanocomposites are less than that of the original γ -Al₂O₃ for both electron-acceptor molecules

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Table 7. Electron-accepting K_A and electron-donating K_D energy characteristics of surface of initial γ -Al₂O₃ and γ -Al₂O₃-based nanocomposites (K_D^0 is the electro-donating number of initial γ -Al₂O₃; K_A^0 is the electron-accepting number of initial γ -Al₂O₃)

Sorbent	K _A	K _D	$K_{\rm A}/K_{\rm D}$	$(K_{\rm D}^0 - K_{\rm D})/K_{\rm D}^0$	$(K_{\rm A}^0-K_{\rm A})/K_{\rm A}^0$
Al ₂ O ₃	0.73	2.33	0.31	1	1
5% Co/Al ₂ O ₃	0.32	0.73	0.44	0.69	0.56
10% Co/Al ₂ O ₃	0.29	0.73	0.40	0.69	0.60
5% CoO/Al ₂ O ₃	0.34	0.47	0.72	0.80	0.53

(CHCl₃) and electron-donor molecules—aromatic compounds and $(C_2H_5)_2O$. For example, the adsorption heats of chloroform remained more or less constant after modification of the surface, but contribution Q_{spec} to the total energy of adsorption decreased from 38 kJ/mol on γ -Al₂O₃ to 17 kJ/mol on the 5 and 10% Co/ γ -Al₂O₃ nanocomposites and 11 kJ/mol on 5% CoO/ γ -Al₂O₃. At the same time, an increase in contribution Q_{disp} from 20 kJ/mol on γ -Al₂O₃ to 38, 39, and 43 kJ/mol was observed for 5 and 10% Co/ γ -Al₂O₃ and 5% CoO/ γ -Al₂O₃ nanocomposites, respectively. Therefore, the dispersion interactions play an essential role in the adsorption process on the surface of modified nanocomposites.

The energy of specific interactions is determined by the electron-donating and -accepting properties of molecules of the adsorbate and the surface of the adsorbent. It can be expressed by the following equation [36–39]:

$$Q_{\rm spec}/\rm{AN} = K_{\rm D} + K_{\rm A}\rm{DN}/\rm{AN}, \qquad (7)$$

where AN and DN denote the electron-accepting and -donating characteristics of molecules of the adsorbate and K_A and K_D are the electron-accepting and -donating energy characteristics of the surface.

Table 7 shows energy characteristics K_D and K_A of the surface of nanocomposites calculated from Eq. (7). As follows from Table 7, the absolute values of electronaccepting and -donating energy characteristics of the surface decreased after modification of alumina surface with Co and CoO nanoparticles compared to that for the initial γ -Al₂O₃ sample, while the relative values of K_A/K_D for the 5% Co/ γ -Al₂O₃, 10% Co/ γ -Al₂O₃, and 5% CoO/ γ -Al₂O₃ nanocomposites exceeded that for γ -Al₂O₃ (0.31): 0.44, 0.40, and 0.72, respectively.

It is evident that the most active sites of the nanocomposites are the Co and CoO nanoparticles. Only hydroxyl groups can be found on the surface of the initial γ -Al₂O₃ sample under the considered conditions. The surface of γ -Al₂O₃ is completely hydroxylated as the initial γ -Al₂O₃ was not heated above 200°C in both the process of deposition of nanoparticles and adsorption experiments (dihydroxylation of the alumina surface starts with temperatures above 200°C [40]). Thus, the thermodynamic characteristics of adsorption were shown to depend on the filling of the surface with adsorbate, mean size of immobilized nanoparticles, and amount of metal species deposited on the support surface.

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