

A.R. Brodskiy, V.P. Grigoriyeva, L.V. Komashko, Y.Y. Nurmakanov,
I.S. Chanysheva, A.A. Shapovalov, I.A. Shlygina, V.I. Yaskevich

"D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis" JSC, Almaty, Kazakhstan.
E-mail: albrod@list.ru

INTERACTION OF THE Fe/ γ -Al₂O₃ CATALYTIC SYSTEM WITH PROBE MOLECULES IV. STUDY OF THE INTERACTION OF HYDROGEN WITH γ -Al₂O₃ OXIDE AND THE Fe/ γ -Al₂O₃ SYSTEM

Abstract. The work is devoted to the study of the interaction of heterogeneous catalytic systems with adsorbed molecules. The results of the interaction with a hydrogen of γ -Al₂O₃ oxide and the Fe/ γ -Al₂O₃ system using IR spectroscopy, methods of temperature programmed desorption and temperature programmed reduction by hydrogen are presented. An ability of the system to adsorb and activate the initial H₂ probe molecule was defined and an assessment of the active (adsorption) centers was made.

Various adsorption centers were detected during their interaction with hydrogen in the temperature range 293-773K on the surface of both γ -Al₂O₃ oxide and the Fe/ γ -Al₂O₃ system using IR spectroscopy. The relative intensity of the absorption bands corresponding to these centers depends on the temperature of interaction with hydrogen.

The adsorbed hydrogen is desorbed in the form of two peaks on the temperature scale from the γ -Al₂O₃ surface and in the form of three peaks from the surface of the Fe/ γ -Al₂O₃ system. The appearance of additional desorption peaks for the Fe/ γ -Al₂O₃ system is associated with iron deposited on alumina. It was concluded that on the surface of γ -Al₂O₃ oxide and the Fe/ γ -Al₂O₃ system, there are adsorption centers that differ in energy characteristics (binding energy). Moreover, these characteristics may also depend on the percentage of the iron-containing component on the surface of aluminum oxide.

Two adsorption peaks are observed on the temperature scale for γ -Al₂O₃ oxide and in the case of the Fe/ γ -Al₂O₃ system, in addition to two adsorption peaks, a desorption peak is also observed using the TPR method of hydrogen. γ -Al₂O₃ oxide and the Fe/ γ -Al₂O₃ system contain different states of metal oxide forms, since several maxima are clearly distinguishable on the TPR curves of hydrogen which indicates the reduction of particles of various compositions.

Key words: heterogeneous catalysis, physicochemical research methods, adsorbed molecules.

Introduction. One of the most common and highly effective methods for studying adsorption centers on the surface of supports and heterogeneous catalysts are infrared spectroscopy [1-5], temperature programmed desorption (TPD) and temperature programmed reduction (TPR) [6-10]. The use of IR spectroscopy to study the donor-acceptor surface properties is based on the spectral probe method. The properties of adsorption centers are judged by the absorption spectra of the adsorbed molecules, as well as by the change in the position of the absorption bands observed during adsorption.

The strength of active sites is judged by the position of the peaks on the temperature scale in the TPR and TPD methods and the activation energy of the probe molecule, and its area can serve as a measure of the quantity of centers of various types.

This work is a continuation of studies on the interaction of a heterogeneous catalytic system with adsorbed molecules [11-13].

Experimental. Fe/ γ -Al₂O₃ system with an iron content of 3; 13 wt.% was prepared by impregnating [10-13] the initial γ -Al₂O₃ oxide with an aqueous solution of iron acetate, followed by drying and calcination in air.

IR spectroscopy

Sample preparation and obtaining IR spectra took place in several stages. At the first stage, the sample (a tablet with KBr filler) was placed in a sealed quartz cell and heated to 523K with simultaneous evacuation for 2 hours. Then, the temperature dropped to 293K. Then, the temperature decreased to 293K. Next, hydrogen purging began at the required temperature (from a given temperature range of 293-773K) for 150 minutes. After that, a temperature of 293K was established then the cell was purged with an inert gas for 30 minutes and after that the IR spectrum was taken.

Equipment - Nicolet iS5 IR spectrometer, Thermo Scientific, USA. Operation mode: resolution 1 cm⁻¹, number of scans - 200.

Temperature programmed desorption (TPD-H₂)

A chromatographic version of temperature programmed desorption was used. The sample with the molecules of the probe substance preliminarily adsorbed on it was subjected to heating at a certain constant speed in the flow of the carrier gas. During desorption, the substance in the gas phase passed through the cell of the thermal conductivity detector (TCD), and the resulting signal was recorded.

Conditions for preparing samples for hydrogen adsorption:

- vacuum treatment 30 minutes;
- sample dehydration in a stream of dry argon (3-5 ml/min) at a temperature of 623K for 120 minutes.

Hydrogen adsorption:

- hydrogen feed rate 5 ml/min;
- adsorption duration one hour; temperature range 293-773K.

Programmed desorption of hydrogen:

- temperature variation range from 293 to 773K;
- speed - 12K/min;
- carrier gas velocity (argon) - 75 ml/min;
- detector sensitivity 1:8.

Desorbed ammonia was detected by chromatograph's TCD and was recorded as a TPD spectrum. At certain temperatures, the TPD spectrum had maxima that characterized the adsorption sites of the sample. The amount of hydrogen desorbed in the corresponding temperature range was determined by peak areas, having previously established how much hydrogen corresponds to the area unit.

Equipment - "CETARAM" thermo analyzer, France.

Hydrogen temperature programmed reduction (H₂-TPR)

Conditions for preparing samples for hydrogen reduction:

- vacuum treatment 30 minutes;
- sample dehydration in a stream of dry argon (5 ml/min) at a temperature of 623K for 120 minutes.

Hydrogen reduction:

- temperature variation range from 293 to 773K;
- speed - 12K/min;
- carrier gas velocity (argon) - 75 ml/min;
- hydrogen concentration 5%;
- detector sensitivity 1:8.

Equipment - "CETARAM" thermo analyzer, France.

Results and discussion. *Investigation of the Fe/ γ -Al₂O₃ system using FTIR spectroscopy during hydrogen adsorption.*

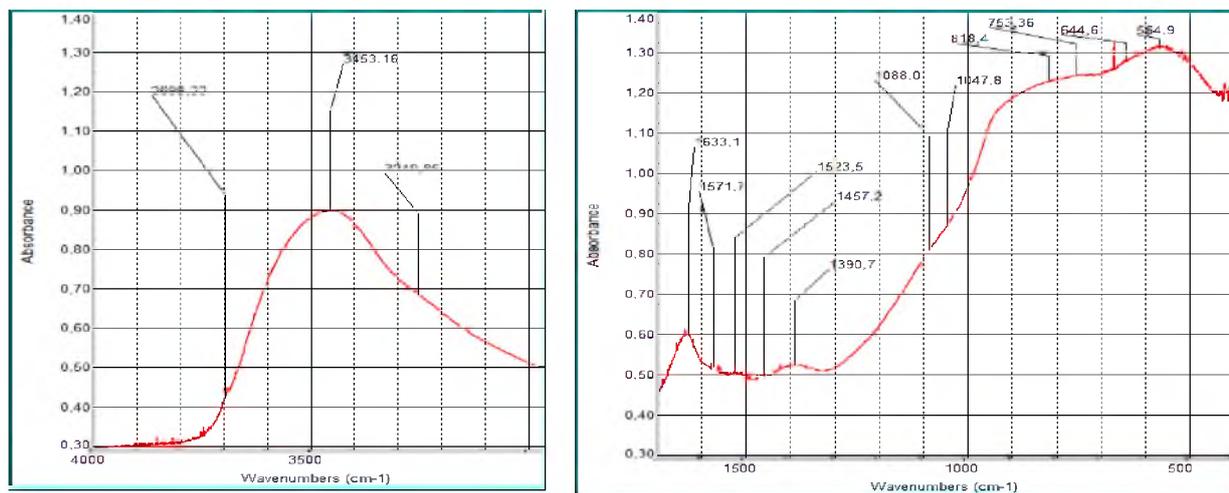
The interaction of γ -Al₂O₃ oxide and the Fe/ γ -Al₂O₃ system with H₂ was studied in the "In Situ" mode in the temperature range 293-773K. The data obtained for γ -Al₂O₃ are necessary as reference points for comparison when studying the Fe/ γ -Al₂O₃ system.

Figures 1-14 show the IR spectra of γ -Al₂O₃ oxide and the Fe/ γ -Al₂O₃ system when interacting with hydrogen at different temperatures and table 3 shows the results of their interpretation.

In the initial γ -Al₂O₃ oxide (Figs. 1-7, Table 1), as well as in its interaction with hydrogen, the IR spectra contain absorption bands corresponding to -OH groups bound on the surface by hydrogen bonds, absorption bands from Al-O bonds, and also vibrations of CH bonds in the -CH, -CH₂, -CH₃ groups (in trace amounts). A small amount of hydrocarbons, apparently, remained in the γ -Al₂O₃ oxide after synthesis.

There is also an absorption band related to -OH bridging groups bound to aluminum ions in octahedral and (or) tetrahedral coordination. However, upon interaction with hydrogen, this absorption band disappears.

Absorption bands appear associated with the Lewis acid sites upon interaction with hydrogen. As temperature increases the relative intensity of the absorption bands corresponding to the Lewis centers decreases noticeably and the band shifts to the long-wavelength region (figures 2-7, table 1).

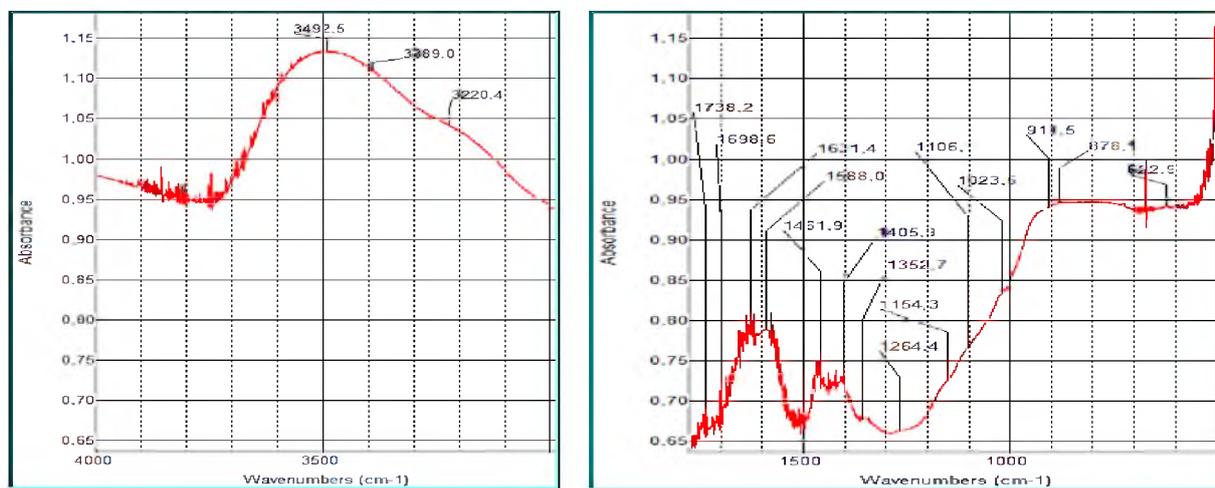


a

b

a - 4000-3000 cm^{-1} range; b - 1700 - 400 cm^{-1} range

Figure 1 - IR spectrum of the initial $\gamma\text{-Al}_2\text{O}_3$ oxide

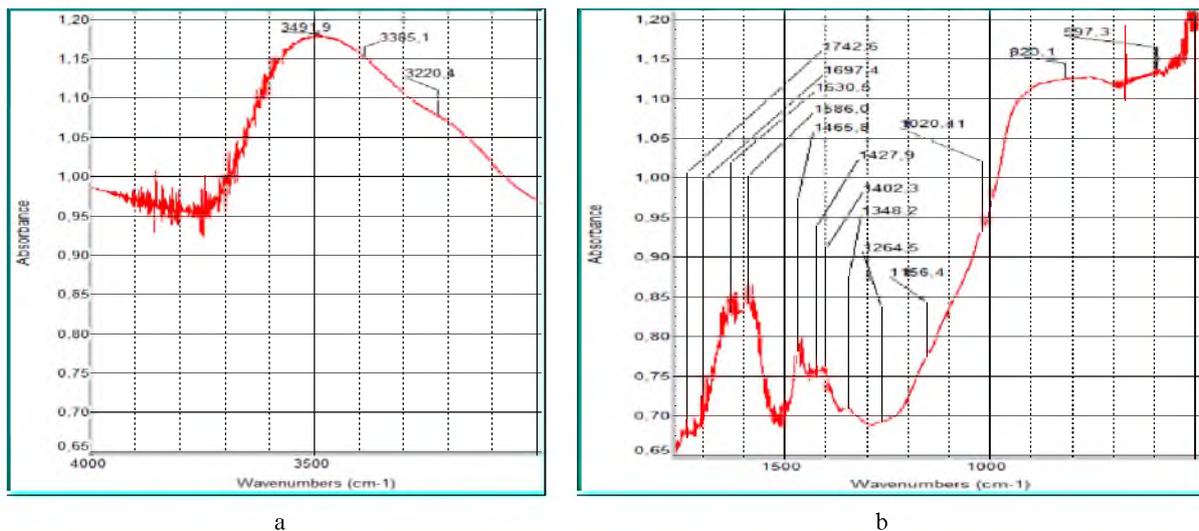


a

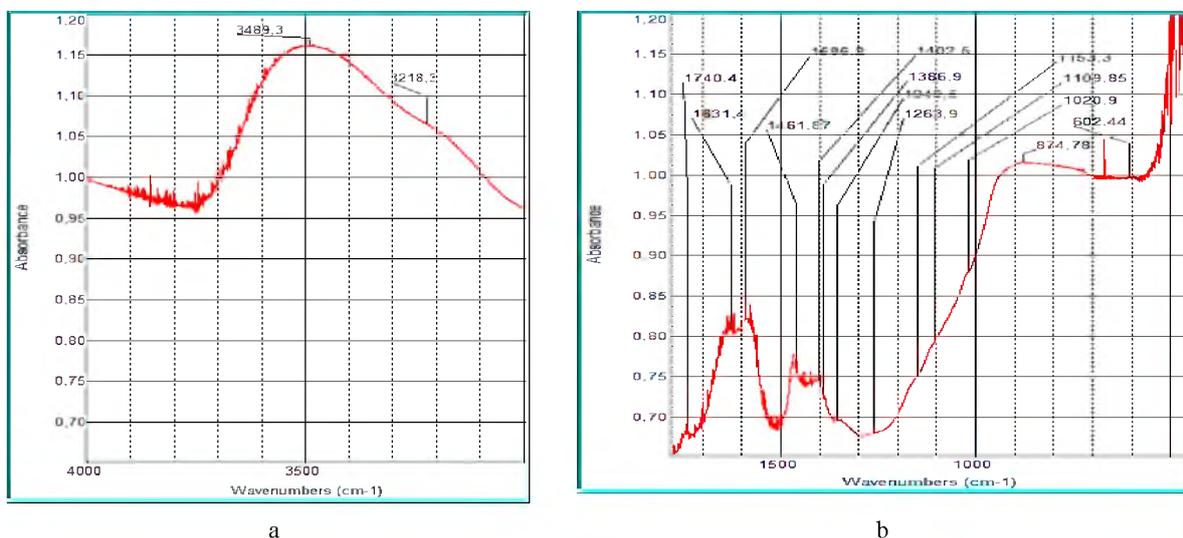
b

a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range

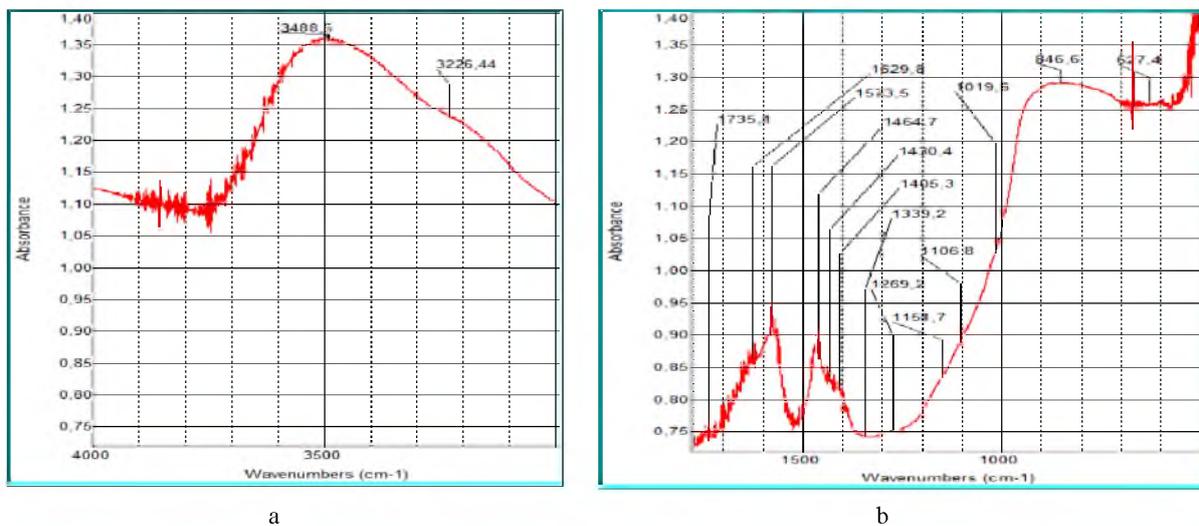
Figure 2 - IR spectrum of $\gamma\text{-Al}_2\text{O}_3$ oxide after hydrogen adsorption at 293K



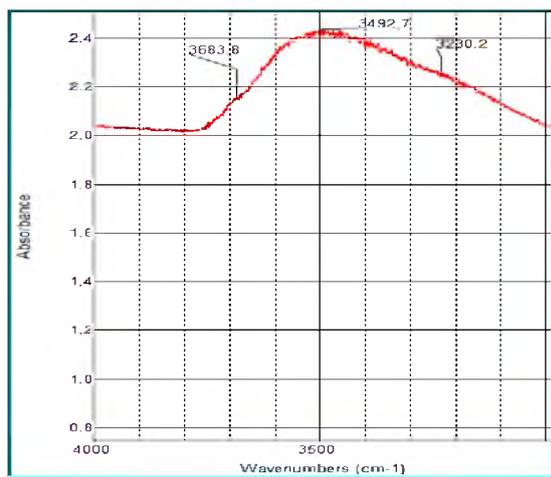
a – 4000-3000 cm⁻¹ range; b – 1750-400 cm⁻¹ range
 Figure 3 - IR spectrum of γ -Al₂O₃ oxide after hydrogen adsorption at 373K



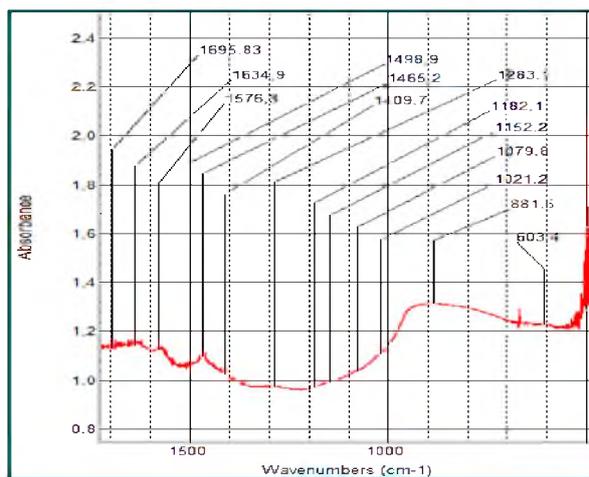
a – 4000-3000 cm⁻¹ range; b – 1750-400 cm⁻¹ range
 Figure 4 - IR spectrum of γ -Al₂O₃ oxide after hydrogen adsorption at 473K



a – 4000-3000 cm⁻¹ range; b – 1750-400 cm⁻¹ range
 Figure 5 - IR spectrum of γ -Al₂O₃ oxide after hydrogen adsorption at 573K

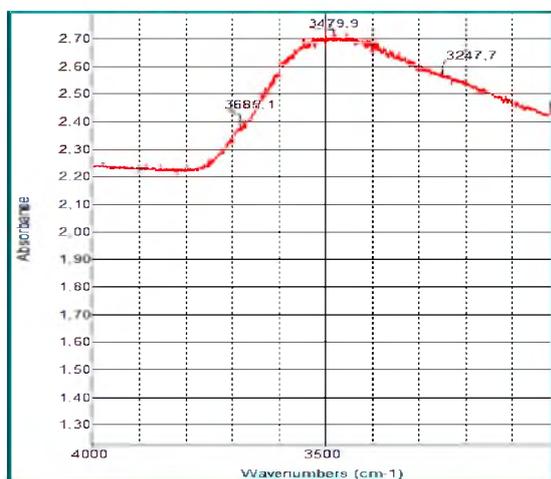


a

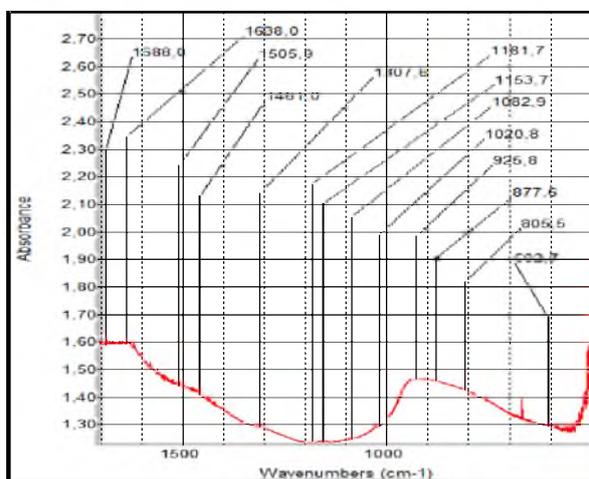


b

a – 4000-3000 cm^{-1} range; b – 1750-400 cm^{-1} range
Figure 6 - IR spectrum of $\gamma\text{-Al}_2\text{O}_3$ oxide after hydrogen adsorption at 673K

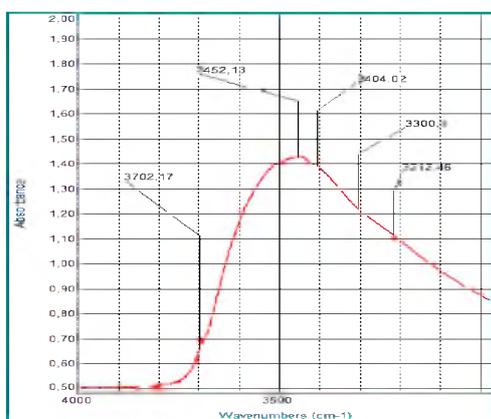


a

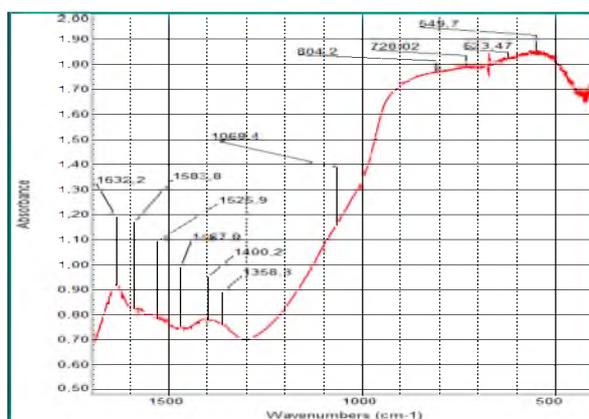


b

a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range
Figure 7 - IR spectrum of $\gamma\text{-Al}_2\text{O}_3$ oxide after hydrogen adsorption at 773K

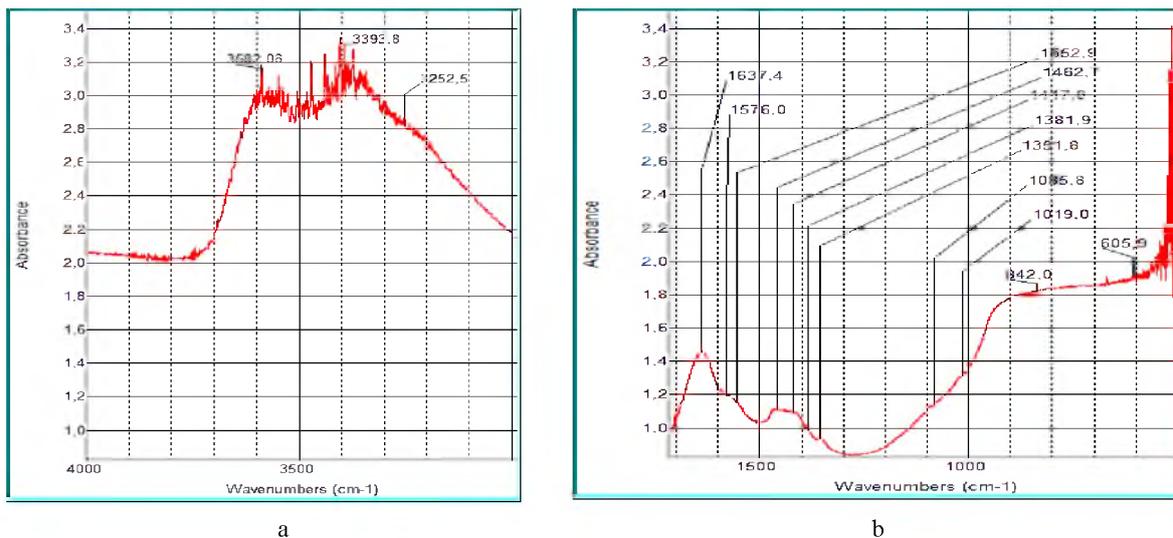


a

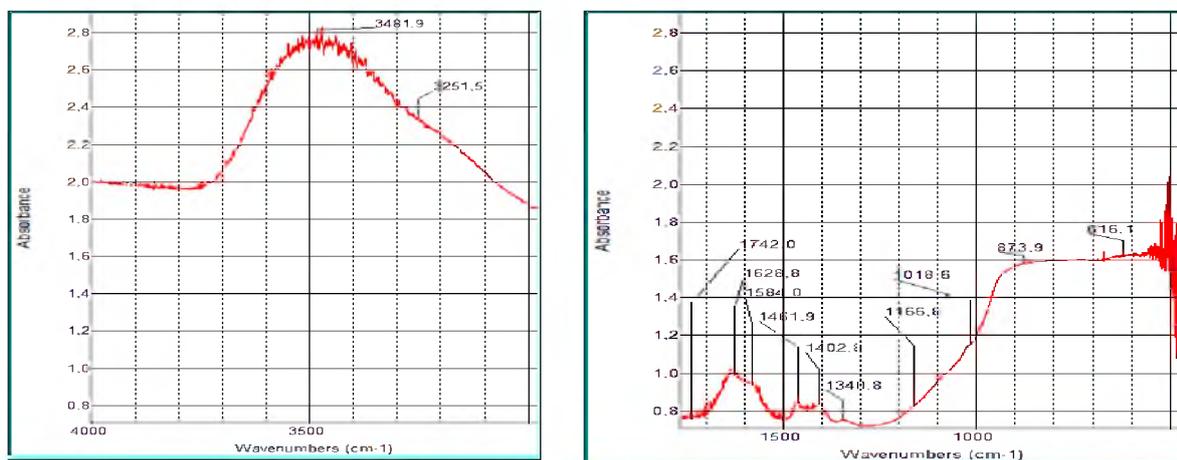


b

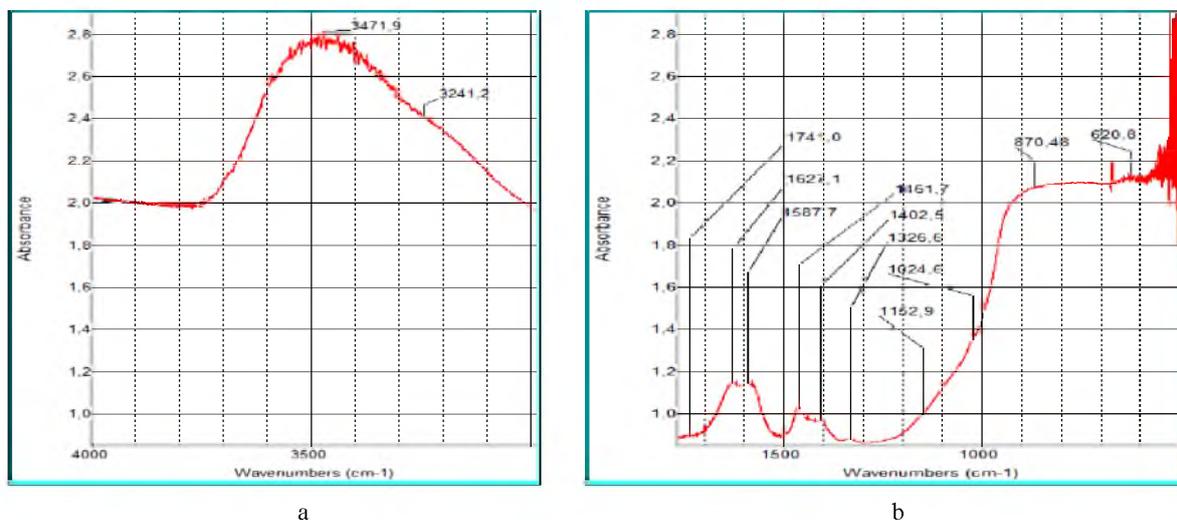
a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range
Figure 8 - IR spectrum of the initial 13%Fe/ $\gamma\text{-Al}_2\text{O}_3$ system



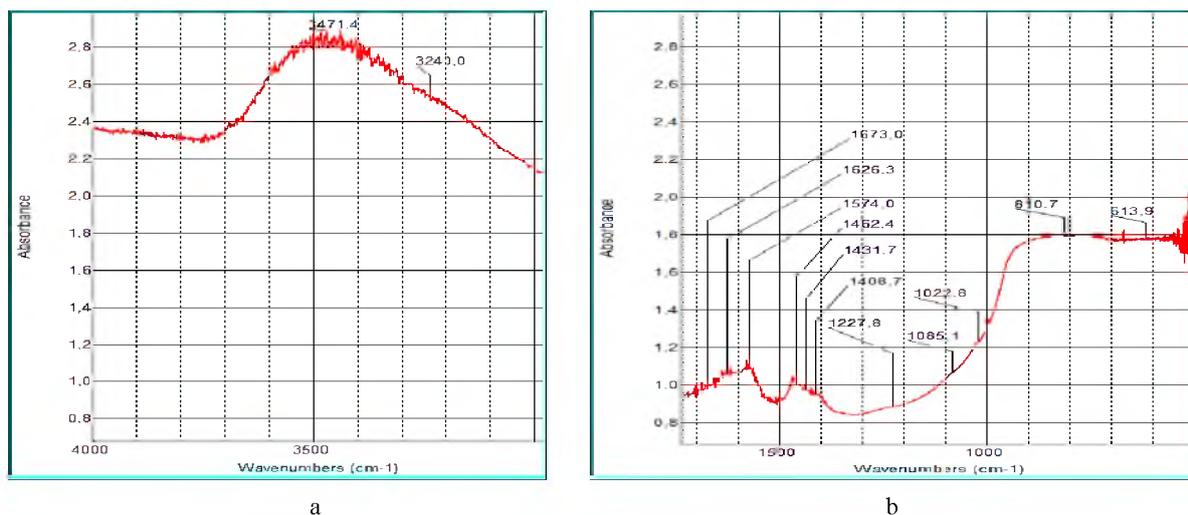
a - 4000-3000 cm⁻¹ range; b - 1750-400 cm⁻¹ range
 Figure 9 - IR spectrum of the 13%Fe/γ-Al₂O₃ system after hydrogen adsorption at 293K



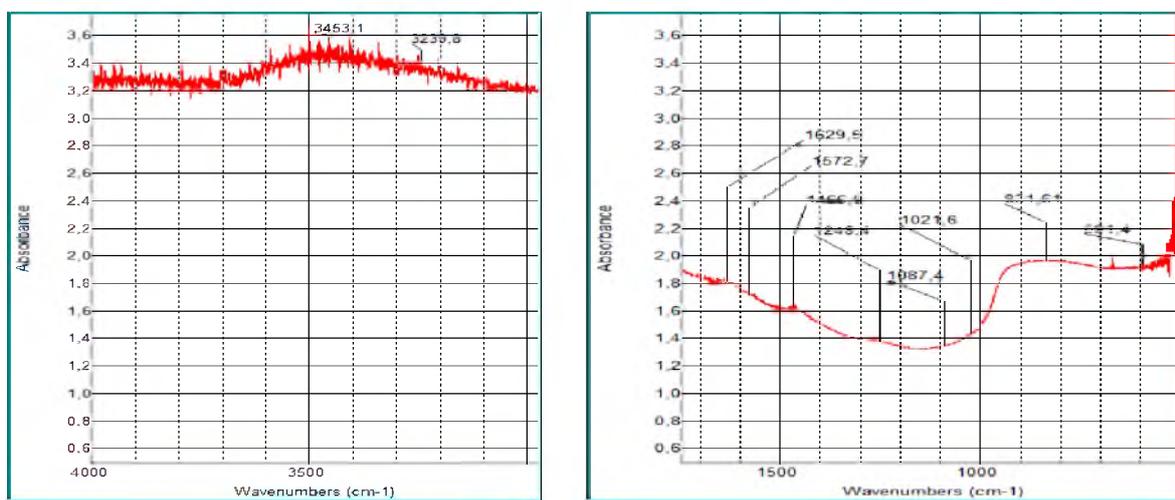
a - 4000-3000 cm⁻¹ range; b - 1750-400 cm⁻¹ range
 Figure 10 - IR spectrum of the 13%Fe/γ-Al₂O₃ system after hydrogen adsorption at 373K



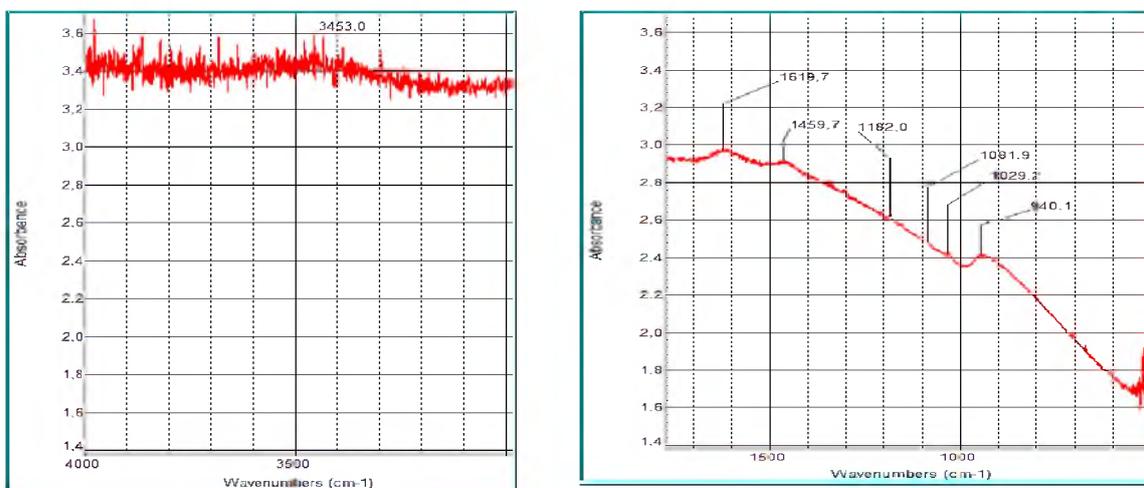
a - 4000-3000 cm⁻¹ range; b - 1750-400 cm⁻¹ range
 Figure 11 - IR spectrum of the 13%Fe/γ-Al₂O₃ system after hydrogen adsorption at 473K



a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range
 Figure 12 - IR spectrum of the 13%Fe/ γ -Al₂O₃ system after hydrogen adsorption at 573K



a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range
 Figure 13 - IR spectrum of the 13%Fe/ γ -Al₂O₃ system after hydrogen adsorption at 673K



a - 4000-3000 cm^{-1} range; b - 1750-400 cm^{-1} range
 Figure 14 - IR spectrum of the 13%Fe/ γ -Al₂O₃ system after hydrogen adsorption upon interaction with H₂ in the range 773K

Table 1 - Interpretation of the data of the IR spectra of γ -Al₂O₃ and Fe/ γ -Al₂O₃ upon interaction with H₂ in the range 293-773K

T, K	Absorption bands, cm ⁻¹		Assignment of absorption bands
	Sample		
	γ -Al ₂ O ₃	Fe/ γ -Al ₂ O ₃	
1	2	3	4
Initial states			
293	3699	3702	Stretching vibrations of bridging -OH groups bound to aluminum ions in octahedral and (or) tetrahedral coordination
	3453, 3250	3452, 3212	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds
		3404, 3301,	Stretching vibrations of -OH groups bound on the surface of alumina by hydrogen bonds
	1633, 1571, 1524, 645	1632, 1584, 1526, 623	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds
	1457, 1391	1468, 1400, 1358	Bending vibrations of C-H bonds in -CH, -CH ₂ , -CH ₃ groups (traces)
	1088, 1048	1068	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination
	818, 753	804, 728	Bending vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination, as well as, possibly, in Al-O-Fe groups in the Fe/ γ -Al ₂ O ₃ system
	565	550	Stretching vibrations of M-O bonds (M = Al; Fe)
Interaction with hydrogen			
293	3493, 3220	3582, 3253	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds, including those on the surface of hydroxides (3582 cm ⁻¹)
	3389	3394,	Stretching vibrations of -OH groups formed upon dissociative adsorption of hydrogen on the surface
	1631, 1588, 623	1637, 1576, 606	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds
	1462, 1406, 1353	1463, 1420, 1382, 1352	Bending vibrations related to -OH groups (against the background of bending vibrations of CH bonds in -CH, -CH ₂ , -CH ₃ groups)
	1264, 1154, 912		Bending vibrations related to -OH groups of different coordination
	1738, 1699		Stretching vibrations related to -AlH ⁺ groups (Lewis acid sites)
	1106, 1024, 878	1086, 1019	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination
	820-700 region	842	The wide unresolved absorption band (820-700 cm ⁻¹) probably refers to bending vibrations in the -Al-O- groups in tetrahedral and (or) octahedral coordination. In this region, bending vibrations belonging to the -AlH ⁺ groups (Lewis acid sites) can also be located. The band at 842 cm ⁻¹ (for the Fe/ γ -Al ₂ O ₃ system), possibly, refers to bonds in the Al-O-Fe groups.
373	3492, 3220	3483, 3252	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds
	3385		Stretching vibrations of -OH groups formed upon dissociative adsorption of hydrogen on the surface
	1631, 1586, 597	1629, 1584, 616	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds
	1466, 1428, 1402, 1348	1462, 1403, 1341	Bending vibrations related to -OH groups (against the background of bending vibrations of CH bonds in -CH, -CH ₂ , -CH ₃ groups)
	1265, 1156	1167	Bending vibrations related to -OH groups of different coordination
	1743, 1697	1742	Stretching vibrations related to -AlH ⁺ groups (Lewis acid sites)
	1020	1019	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination
	820-700 region	874	The wide unresolved absorption band (820-700 cm ⁻¹) probably refers to bending vibrations in the -Al-O- groups in tetrahedral and (or) octahedral coordination. In this region, bending vibrations belonging to the -AlH ⁺ groups (Lewis acid sites) can also be located. The band at 874 cm ⁻¹ (for the Fe/ γ -Al ₂ O ₃ system), possibly, refers to bonds in the Al-O-Fe groups.
473	3489, 3218	3472, 3241	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds
	1631, 1586, 602	1628, 1588, 621	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds

1	2	3	4
	1462, 1403, 1387, 1350	1462, 1327	1403, Bending vibrations related to -OH groups (against the background of bending vibrations of CH bonds in -CH, -CH ₂ , -CH ₃ groups)
	1264, 1153	1153	Bending vibrations related to -OH groups of different coordination
	1740	1741	Stretching vibrations related to -AlH groups (Lewis acid sites)
	1110, 1021, 875	1125	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination.
573	3489, 3226	3471, 3240	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds
	1630, 1574, 627	1626, 1574, 614	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds
	1465, 1430, 1405, 1339	1462, 1409	1432, Bending vibrations related to -OH groups (against the background of bending vibrations of CH bonds in -CH, -CH ₂ , -CH ₃ groups)
	1269, 1152	1228	Bending vibrations related to -OH groups of different coordination
	1735	1673	Stretching vibrations related to the groups -AlH and -FeH (Lewis acid sites)
	1107, 1020, 847	1085, 1023	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination.
	820-700 region	811	The wide unresolved absorption band (820-700 cm ⁻¹) probably refers to bending vibrations in the -Al-O- groups in tetrahedral and (or) octahedral coordination. In this region, bending vibrations belonging to the -AlH groups (Lewis acid sites) can also be located. The band at 811 cm ⁻¹ (for the Fe/γ-Al ₂ O ₃ system), possibly, refers to bonds in the Al-O-Fe groups.
673	3684		Stretching vibrations of terminal -OH groups bonded with aluminum ions
	3493, 3230	3453, 3240	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds
	1635, 1576, 603	1630, 1573, 591	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds
	1499, 1465, 1410	1467	Bending vibrations related to -OH groups (against the background of bending vibrations of CH bonds in -CH, -CH ₂ , -CH ₃ groups)
	1283, 1182, 1152	1248	Bending vibrations related to -OH groups of different coordination
	1696		Stretching vibrations related to -AlH groups (Lewis acid sites)
	1080, 1021, 882	1087, 1022	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination.
	820-700 region	832	The wide unresolved absorption band (820-700 cm ⁻¹) probably refers to bending vibrations in the -Al-O- groups in tetrahedral and (or) octahedral coordination. In this region, bending vibrations belonging to the -AlH groups (Lewis acid sites) can also be located. The band at 832 cm ⁻¹ (for the Fe/γ-Al ₂ O ₃ system), possibly, refers to bonds in the Al-O-Fe groups.
773	3685		Stretching vibrations of terminal -OH groups bonded with aluminum ions
	3480, 3248	3453	Stretching vibrations of -OH groups bound on the surface by hydrogen bonds
	1638, 1506, 603	1620	Bending vibrations of -OH groups bonded on the surface by hydrogen bonds
	1461, 1308	1460	Bending vibrations of -OH groups (against the background of bending vibrations of CH bonds in -CH, -CH ₂ , -CH ₃ groups)
	1162, 1154, 925	1182	Bending vibrations related to -OH groups of different coordination
	1688		Stretching vibrations related to -AlH groups (Lewis acid sites)
	1083, 1021, 878	1082, 1029, 940	Stretching vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination.
	806 (in 820-700 region)		The wide unresolved absorption band (820-700 cm ⁻¹) probably refers to bending vibrations in the -Al-O- groups in tetrahedral and (or) octahedral coordination. In this region, bending vibrations belonging to the -AlH groups (Lewis acid sites) can also be located.

In the initial Fe/γ-Al₂O₃ system (figure 8, table 1), as well as in the initial γ-Al₂O₃ oxide there are absorption bands related to -OH bridging groups associated with aluminum ions in the octahedral and (or)

tetrahedral coordination, absorption bands related to -OH groups bound on the surface by hydrogen bonds, absorption bands related to Al-O bonds. In addition, an absorption band related to Fe-O bonds is observed in the initial Fe/ γ -Al₂O₃ system. This absorption band disappears while interacting with hydrogen. The absorption band associated with the -OH bridging groups also disappears while interacting with hydrogen, similar to what happened in the case of γ -Al₂O₃ oxide.

It should be noted that in the Fe/ γ -Al₂O₃ system (initial state) there are absorption bands belonging to the -OH groups on the surface of aluminum hydroxides. This is in good agreement with the data presented in our works [11, 12]. There were noted that during the synthesis of the Fe/ γ -Al₂O₃ system by impregnation partial hydrolysis of aluminum oxide can occur resulting in the formation of a certain amount of aluminum hydroxide.

Upon interaction with the hydrogen of the Fe/ γ -Al₂O₃ system, as in the case of alumina, absorption bands appear associated with the Lewis acid sites. The relative intensity of the absorption bands corresponding to Lewis centers also decreases as temperature increases similarly to what was observed for γ -Al₂O₃ oxide.

At the same time there are noticeable differences (figures 8-14, table 1), in particular, the absorption bands in the 1283-912 cm⁻¹ region corresponding to the bending vibrations of the -OH groups appear only starting from 373K and this is only one band. The decrease in the number of absorption bands is possibly associated with a partial coating of the hydroxyl surface of the support with an iron-containing component. In addition, in the long-wavelength region of the IR spectra there are absorption bands that can be attributed to bonds in the Al-O-Fe groups.

Absorption bands related to stretching vibrations associated with Lewis centers are present only in a limited 373-573K temperature range. In addition, at 573 K, a significant (more substantial than in the case of γ -Al₂O₃) band shift to the long-wavelength region occurs. Perhaps this is due to the fact that at 573K Lewis centers can be associated with iron. It should be noted that the absorption bands corresponding to the Lewis centers are not recorded at temperatures above 573K, which is in good agreement with the onset of iron reduction in the Fe/ γ -Al₂O₃ system [29]. It follows that the -Fe-H fragments are unstable at higher temperatures. Therefore, we can conclude that the reduction of Fe³⁺ to the Fe²⁺ state occurs upon dissociative adsorption of hydrogen (by a peculiar hydride mechanism) with the formation of hydride states of iron and their subsequent decomposition with the release of hydroxyl groups (water vapor).

3 Study of the Fe/ γ -Al₂O₃ system using temperature programmed desorption during hydrogen adsorption in 293-773K temperature range

The surface properties of γ -Al₂O₃ oxide (as a reference point) and the Fe/ γ -Al₂O₃ system with different iron contents (3% Fe/ γ -Al₂O₃; 13%Fe/ γ -Al₂O₃) were studied. The results of TPD-H₂ for γ -Al₂O₃ oxide are shown in Figure 15 (1) and Table 2.

Adsorbed hydrogen is desorbed from the γ -Al₂O₃ surface on a temperature scale in the form of two peaks (table 2). Over the entire temperature range of adsorption the low-temperature desorption peak A is in 463-443K range. The amount of desorbed gas for peak A is extreme with a maximum position at an adsorption temperature of 373K.

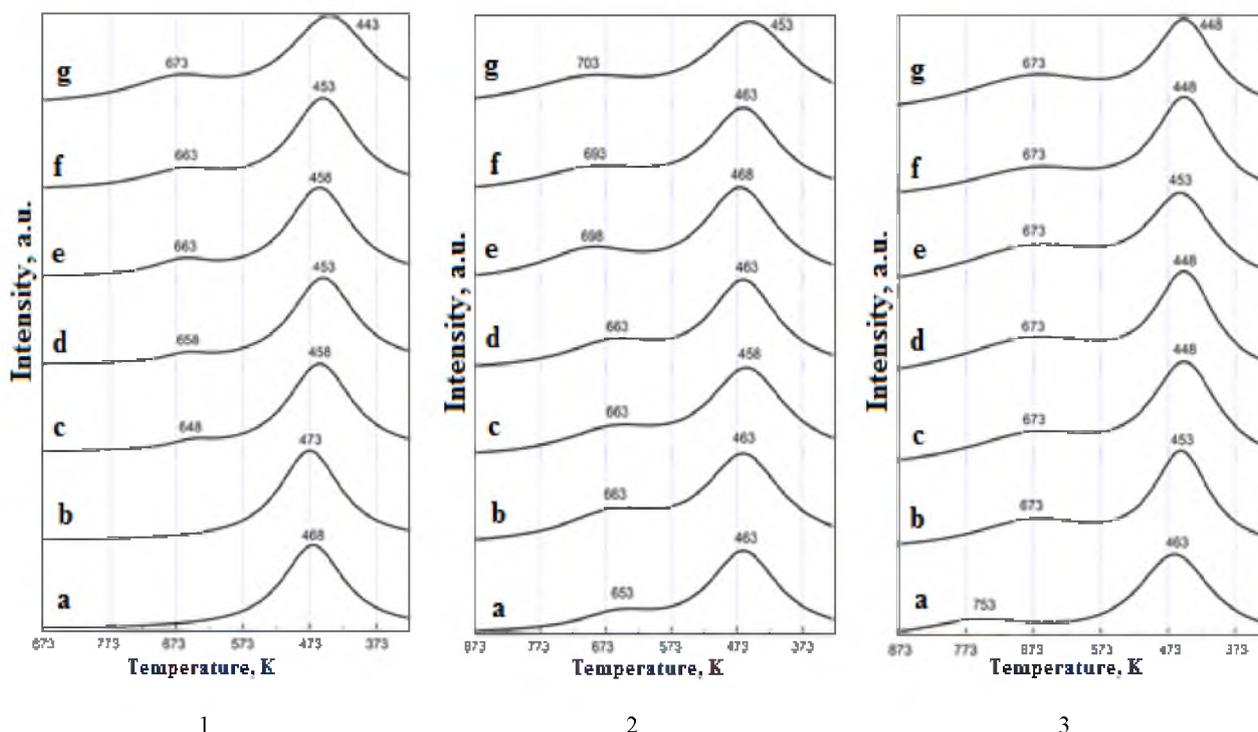
The high-temperature peak B in quantitative terms is much inferior to the lower-temperature peak A. As the adsorption temperature goes up its intensity increases slightly, and the position shifts to the high-temperature region, moreover, peak B appears only at adsorption temperatures above 373K.

It should be noted that the dependence of the total amount of desorbed gas on the adsorption temperature passes through a maximum at 373K.

As follows from Figure 15 (2, 3) and Table 3, in the case of the 3% Fe/ γ -Al₂O₃ system at adsorption temperatures above 473K, the third desorption peak C' appears, and the amount of desorbed gas corresponding to this peak slightly increases with increasing temperature. For the 13%Fe/ γ -Al₂O₃ system, the third desorption peak C'' exists only at an adsorption temperature of 293K. At the same time, the temperature ranges for the existence of peaks A, A', and A'' for γ -Al₂O₃ oxide and Fe/ γ -Al₂O₃ systems are almost identical.

As for the amount of desorbed gas corresponding to these peaks, here the picture is not so clear. As noted above, for γ -Al₂O₃ oxide, the amount of desorbed gas for peak A passes through a maximum at an

adsorption temperature of 373K. The amount of desorbed gas for the A' peak (3%Fe/ γ -Al₂O₃ system) passes through a minimum at an adsorption temperature in the range 473-573K. A similar picture is observed for the A'' peak (13%Fe/ γ -Al₂O₃ system).



H₂ adsorption temperature: a - 293K; b - 373K; c - 423K; d - 473K;
e - 573K; f - 673K; g - 773K

1 - γ -Al₂O₃; 2 - 3%Fe/ γ -Al₂O₃; 3 - 13%Fe/ γ -Al₂O₃

Figure 15 - TPD-H₂ profiles of γ -Al₂O₃ oxide, 3%Fe/ γ -Al₂O₃ and 13%Fe/ γ -Al₂O₃ systems

Table 2 - TPD-H₂ study results for γ -Al₂O₃ oxide

Adsorbent	Adsorption temperature H ₂ , K	The maxima temperature of adsorption peaks, K		The amount of desorbed gas, 10 ⁻⁴ mol/g		The total amount of desorbed gas, 10 ⁻⁴ mol/g
		A	B	A	B	
γ -Al ₂ O ₃	293	458	-	1.96	-	1.96
	373	463	-	3.66	-	3.66
	423	458	648	2.63	0.27	2.90
	473	453	658	2.43	0.43	2.86
	573	458	663	2.35	0.55	2.90
	673	453	663	2.13	0.55	2.68
	773	443	673	1.94	0.55	2.50

The results of TPD-H₂ for the Fe/ γ -Al₂O₃ system are shown in figure 15 (2, 3) and are shown in table 3.

The amount of desorbed gas corresponding to the B'' peak (13%Fe/ γ -Al₂O₃ system) increases slightly with adsorption temperature, as was observed for γ -Al₂O₃ oxide (B peak). In the case of the 3%Fe/ γ -Al₂O₃ system (B' peak), the amount of desorbed gas passes through a maximum at 373K with an increase in the adsorption temperature.

The dependence of the total amount of desorbed gas for 3%Fe/ γ -Al₂O₃ and 13%Fe/ γ -Al₂O₃ systems on the adsorption temperature, unlike γ -Al₂O₃ oxide, passes through a minimum (table 3).

Table 3 - Results of TPD-H₂ studies for Fe/ γ -Al₂O₃ system

Adsorbent	Adsorption temperature H ₂ , K	The maxima temperature of adsorption peaks, K			The amount of desorbed gas, 10 ⁻⁴ mol/g			The total amount of desorbed gas, 10 ⁻⁴ mol/g
		A'	B'	C'	A'	B'	C'	
3%Fe/ γ -Al ₂ O ₃	293	463	653	-	2.98	0.90	-	3.88
	373	463	663	-	3.03	1.03	-	4.06
	423	458	663	-	3.14	0.97	-	4.11
	473	463	663	-	1.84	0.68	-	2.52
	573	468	-	698	1.87	-	0.66	2.53
	673	463	-	693	2.62	-	0.73	3.35
	773	453	-	703	2.61	-	0.76	3.37
13%Fe/ γ -Al ₂ O ₃		A''	B''	C''	A''	B''	C''	
	293	463	-	753	3.07	-	0.81	3.88
	373	453	673	-	2.46	0.66	-	3.12
	423	448	673	-	2.38	0.70	-	3.08
	473	448	673	-	2.17	0.82	-	2.99
	573	453	673	-	2.24	0.84	-	3.08
	673	448	673	-	2.52	0.83	-	3.35
	773	448	673	-	2.50	0.86	-	3.36

The appearance of the third additional desorption peak of C', C'' for the 3%Fe/ γ -Al₂O₃, 13%Fe/ γ -Al₂O₃ systems, respectively, in comparison with γ -Al₂O₃ oxide is associated with the presence of an iron-containing component on the surface of aluminum oxide. The differences between the 3%Fe/ γ -Al₂O₃ and 13%Fe/ γ -Al₂O₃ systems (temperature ranges for the existence of the B', B'' and C', C'' peaks) can be explained by the fact that for the 13%Fe/ γ -Al₂O₃ system coating the surface of alumina with an iron-containing component is multilayer [11, 12].

Summarizing this section, we can conclude that on the surface of γ -Al₂O₃ oxide and the Fe/ γ -Al₂O₃ system there are adsorption centers that differ in energy characteristics (binding energies). Moreover, these characteristics may also depend on the percentage of the iron-containing component on the surface of aluminum oxide.

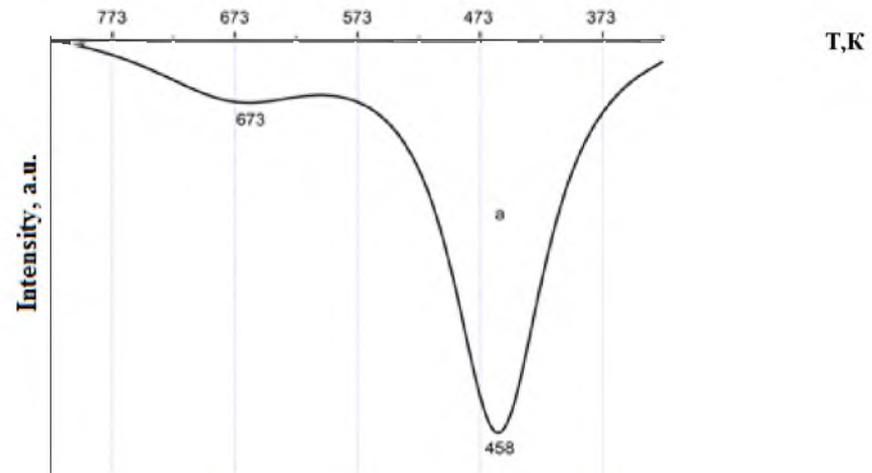
4 Study of the Fe/ γ -Al₂O₃ system using temperature programmed hydrogen reduction in 293 - 773K temperature range

The surface properties of γ -Al₂O₃ oxide (as a reference point) and the Fe/ γ -Al₂O₃ system with different iron contents (3%Fe/ γ -Al₂O₃; 13%Fe/ γ -Al₂O₃) were studied.

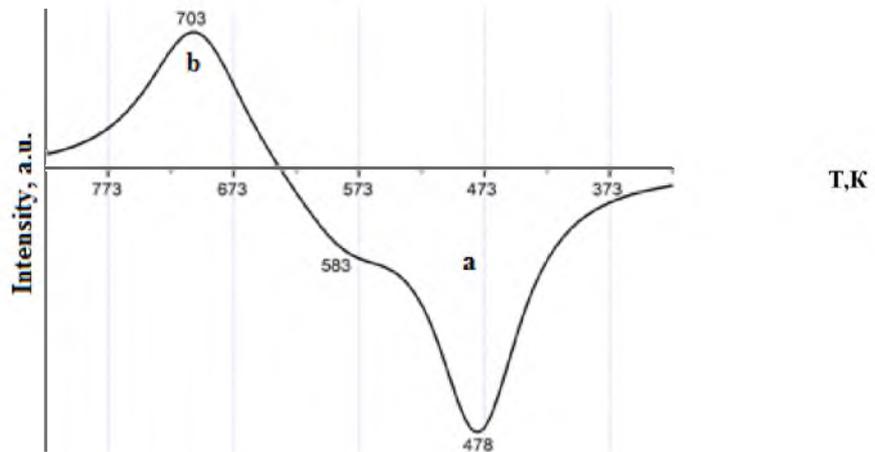
Figure 16 shows the TPR-H₂ curves for γ -Al₂O₃ oxide and the Fe/ γ -Al₂O₃ system. The results are shown in table 4.

The TPR-H₂ profiles for γ -Al₂O₃ oxide (figure 16 (1), table 4) in the adsorption region (a) contain two peaks at temperatures of 458 and 673K, and the second peak is noticeably lower in intensity. In a given temperature range no desorption peaks are observed, which probably indicates the strength of hydrogen bonding with the surface of γ -Al₂O₃ oxide.

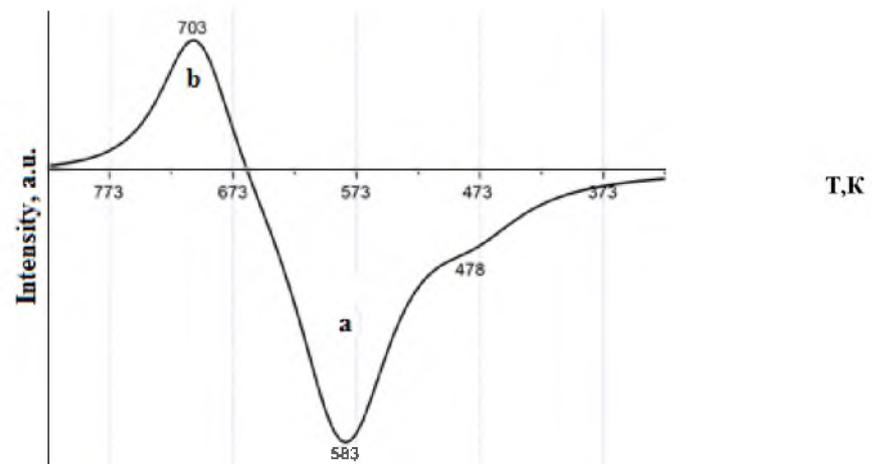
The TPR-H₂ profiles for the 3%Fe/ γ -Al₂O₃ and 13%Fe/ γ -Al₂O₃ systems in the adsorption region (a) also contain two peaks, but at 478 and 583 K (figure 16 (2), (3), table 4). A higher temperature peak is also noticeably lower in intensity.



(1)



(2)



(3)

a – adsorption region; b – desorption region (1) - γ - Al_2O_3 ; (2) - 3%Fe/ γ - Al_2O_3 ; (3) - 13%Fe/ γ - Al_2O_3

Figure 16 - TPR- H_2 profiles for γ - Al_2O_3 oxide and the Fe/ γ - Al_2O_3 system in the temperature range 293-773K

Table 4 - The results of the study using TPR-H₂ for γ -Al₂O₃ oxide and the 3%Fe/ γ -Al₂O₃ system in 293-773K temperature range

Adsorbent	The maxima temperature of adsorption peaks, K		The maxima temperature of adsorption peaks, K	W _{ADS} , 10 ⁻⁴ mol/g		ΣW _{ADS} , 10 ⁻⁴ mol/g	W _{DES} , 10 ⁻⁴ mol/g
	A	B	C	A	B	A + B	C
γ -Al ₂ O ₃	458	673	-	0.94	0.22	1.16	-
3%Fe/ γ -Al ₂ O ₃	478	583	703	0.92	0.33	1.25	0.84
13% Fe/ γ -Al ₂ O ₃	478	583	703	0.35	0.90	1.25	0.70

W_{ADS} - amount of adsorbed substance; ΣW_{ADS} - total amount of adsorbed substance; W_{DES} - amount of desorbed substance.

Noteworthy is the temperature shift of the adsorption peaks for the Fe/ γ -Al₂O₃ system, regardless of the iron content, in comparison with γ -Al₂O₃ oxide. This may be due to the fact that in the case of the Fe/ γ -Al₂O₃ system with 3 and 13% of iron content and is almost completely coated with an iron-containing component, as was shown using scanning electron microscopy in [11, 12] and therefore, adsorption should take place on it.

In addition, (figure 16, table 4), on the TPR-H₂ profile for the Fe/ γ -Al₂O₃ system, regardless of the iron content, there is a desorption region (b) with a peak maximum at 703K. It should be noted that the desorption (from 56 to 67%) of the reagent adsorbed at lower temperatures occurs in the range of ~630-773K. This interval is well superimposed [29] on the temperature interval of the reduction of Fe³⁺ states to Fe²⁺ states.

Since several adsorption peaks are clearly distinguishable on the TPR-H₂ profiles, it can be assumed that γ -Al₂O₃ oxide and 3%Fe/ γ -Al₂O₃, 13%Fe/ γ -Al₂O₃ systems contain different states of metal oxide forms. The presence of a desorption region in the range of 630-773K for 3%Fe/ γ -Al₂O₃, 13%Fe/ γ -Al₂O₃ systems is apparently associated with the reduction of the Fe³⁺ state to Fe²⁺ upon dissociative hydrogen adsorption, for example, by the mechanism:



Conclusion. Studies of the Fe/ γ -Al₂O₃ system in the temperature range 273-773K showed that its surface is heterogeneous and represents a set of adsorption centers with different energy characteristics.

Lewis acid centers were detected using IR spectroscopy on the surface of both γ -Al₂O₃ oxide (support) and the Fe/ γ -Al₂O₃ system, during their interaction with hydrogen in the temperature range 293-773K. The relative intensity of the absorption bands corresponding to these centers depends on the temperature of interaction with hydrogen and decreases with its growth both for γ -Al₂O₃ and for the Fe/ γ -Al₂O₃ system.

For the Fe/ γ -Al₂O₃ system the -OH groups' absorption bands in the region of 1283-912 cm⁻¹ appear only starting from 373 K and this is only one band. The decrease in the number of absorption bands is apparently associated with a partial coating of the hydroxyl surface of the support with an iron-containing component. In addition, in the long-wavelength region of the IR spectra there are absorption bands that can be attributed to bonds in the Al-O-Fe groups.

It was shown that on the surface of γ -Al₂O₃ oxide and the Fe/ γ -Al₂O₃ system, there are adsorption centers that differ in their energy characteristics (binding energies) by TPD-H₂ method. Moreover, these characteristics may also depend on the percentage of the iron-containing component on the surface of aluminum oxide.

Using the TPR-H₂ method, it was found that γ -Al₂O₃ oxide and 3%Fe/ γ -Al₂O₃, 13%Fe/ γ -Al₂O₃ systems contain different states of metal oxide forms, since several extrema are clearly distinguishable on the TPR-H₂ profiles.

This work was financially supported by the State Institution "Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan" under the grant AP05130654.

А.Р. Бродский, В.П. Григорьева, Л.В. Комашко, Е.Е. Нурмаканов,
И.С. Чаньшева, А.А. Шаповалов, И.А. Шлыгина, В.И. Яскевич

«Д.В. Сокольский атындағы жанармай, катализ және электрохимия институты» АҚ, Алматы, Қазақстан

Fe/γ-Al₂O₃ КАТАЛИТИКАЛЫҚ ЖҮЙЕНІҢ ЗОНДТЫ МОЛЕКУЛАЛАРМЕН ӨЗАРА ӘРЕКЕТІ IV. γ-Al₂O₃ ОКСИДІ ЖӘНЕ Fe/γ-Al₂O₃ ЖҮЙЕСІНІҢ СУТЕГІМЕН ӨЗАРА ӘРЕКЕТІН ЗЕРТТЕУ

Аннотация. Жұмыс гетерогенді каталитикалық жүйелердің адсорбталған молекулалармен өзара әрекетін зерттеуге арналған. Мұнда бастапқы γ-Al₂O₃ оксид сутегісімен және ИК-спектроскопия, термобағдарламаланған десорбция, сутегімен термобағдарламаланған түрдегі тотықсыздандыру әдістері арқылы алынған темірдің түрлі құрамды Fe/γ-Al₂O₃ жүйелерінің өзара әрекеттесу нәтижелері келтірілген.

Алюминий оксиді γ-Al₂O₃ және Fe/γ-Al₂O₃ жүйесіне қатысты жүргізілген зерттеулер темір құрамына қарамастан 273 - 773К температуралық интервалында беті біркелкі емес және өз алдына түрлі энергетикалық сипаттамасы бар адсорбциялық орталықтар жиынтығы екендігін көрсетті.

ИК-спектроскопия арқылы γ-Al₂O₃ оксиді (тасымалдаушы) секілді Fe/γ-Al₂O₃ жүйесінде де олардың сутегімен өзара әрекеттесуі кезінде 293-773К температуралық интервалда Льюистің қышқылды орталықтары анықталды. Осы орталықтарға жауап беретін жұтылу жолақтарының салыстырмалы қарқыны сутегімен өзара әрекеттесу температурасына байланысты және ол жоғарылағанда γ-Al₂O₃ сияқты Fe/γ-Al₂O₃ жүйелері үшін де төмендейді.

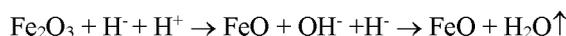
Fe/γ-Al₂O₃ жүйесі үшін жұтылу жолақтары 1283 – 912 см⁻¹ аймағында, ОН-топтар үшін тек қана 373К бастап пайда болады және бұл тек бір ғана жолақ. Жұтылу жолақтары санының азаюы темірқұрамдас компоненттер тасымалдаушысының гидроксильді бетінің жартылай жабылуына байланысты болуы мүмкін. Бұдан басқа ИК-спектрлердің ұзын толқынды аймағында Al-O-Fe топтарындағы байланысқа жатқызуға болатын жұтылу жолақтары бар.

Fe/γ-Al₂O₃ жүйесінде бастапқы күйде Fe-O байланысына жататын жұтылу жолағы байқалады, алайда сутегімен өзара әрекеттескен кезде бұл жұтылу жолағы жоғалады. Fe/γ-Al₂O₃ жүйесінің сутегімен өзара әрекеттесуі кезінде ОН-көпірлік топтарымен байланысты жұтылу жолағы да жоғалады, γ-Al₂O₃ оксиді жағдайында да солай болады.

ТПД-H₂ әдісі көрсеткендей, γ-Al₂O₃ оксидтің бетінде және Fe/γ-Al₂O₃ жүйелерінде өзінің энергетикалық сипаттамалары бойынша (байланыс энергиясы) ерекшеленетін адсорбциялық орталықтар бар. Бұл сипаттамалар алюминий оксидінің бетінде темір құрамды компоненттердің пайыздық мөлшеріне байланысты болуы мүмкін.

ТПВ-H₂ әдісі арқылы γ-Al₂O₃ оксиді және 3% Fe/γ-Al₂O₃, 13% Fe/γ-Al₂O₃ жүйелері металл оксиді қалыптарының түрлі күйі пайда болады, өйткені ТПВ-H₂ қисығында бірнеше экстремумдар анық ажыратылады.

Құрамында темір болғандығына қарамастан 3% Fe/γ-Al₂O₃, 13% Fe/γ-Al₂O₃ жүйесі үшін 630-773К температуралық интервалда 703К кезінде максимум жағдайы бар десорбция аймағы байқалады. 3% Fe/γ-Al₂O₃, 13% Fe/γ-Al₂O₃ жүйесі үшін десорбция аймағының болуы темірқұрамдас компоненттердің, нақтырақ айтқанда, сутегі диссоциативті адсорбциясы кезінде жай-күйінің Fe³⁺-тен Fe²⁺ дейін қалпына келуіне байланысты, мысалы, механизм бойынша:



Түйін сөздер: гетерогенді катализ, физика-химиялық зерттеу әдістері, адсорбцияланған молекулалар.

А.Р. Бродский, В.П. Григорьева, Л.В. Комашко, Е.Е. Нурмаканов,
И.С. Чаньшева, А.А. Шаповалов, И.А. Шлыгина, В.И. Яскевич

АО «Институт топлива, катализа и электрохимии им. Д.В.Сокольского», Алматы, Казахстан

ВЗАИМОДЕЙСТВИЕ КАТАЛИТИЧЕСКОЙ СИСТЕМЫ Fe/γ-Al₂O₃ С МОЛЕКУЛАМИ-ЗОНДАМИ. IV. ИССЛЕДОВАНИЕ ВЗАИМОДЕЙСТВИЯ ВОДОРОДА С ОКСИДОМ γ-Al₂O₃ И СИСТЕМОЙ Fe/γ-Al₂O₃

Аннотация. Работа посвящена исследованию взаимодействия гетерогенных каталитических систем с адсорбированными молекулами. В ней представлены результаты по взаимодействию с водородом исходного оксида γ-Al₂O₃ и систем Fe/γ-Al₂O₃, с различным содержанием железа, полученные с помощью ИК-спектроскопии, методов термопрограммированной десорбции и термопрограммированного восстановления водородом.

Проведённые исследования оксида алюминия $\gamma\text{-Al}_2\text{O}_3$ и систем $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$, независимо от содержания железа, в температурном интервале 273 - 773К показали, что их поверхность неоднородна и представляет собой набор адсорбционных центров с различными энергетическими характеристиками.

С помощью ИК-спектроскопии на поверхности как оксида $\gamma\text{-Al}_2\text{O}_3$ (носитель), так и систем $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ при их взаимодействии с водородом в температурном интервале 293 – 773К были обнаружены кислотные центры Льюиса. Относительная интенсивность полос поглощения, отвечающих этим центрам, зависит от температуры взаимодействия с водородом и с её ростом падает как для $\gamma\text{-Al}_2\text{O}_3$, так и для систем $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$.

Для систем $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ полосы поглощения в области 1283 – 912 cm^{-1} , групп – OH появляются только начиная с 373К, и это только одна полоса. Уменьшение количества полос поглощения, видимо, связано с частичным покрытием гидроксильной поверхности носителя железосодержащей компонентой. Кроме того, в длинноволновой области ИК-спектров присутствуют полосы поглощения, которые можно отнести к связям в группах Al-O-Fe.

В системе $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ в исходном состоянии наблюдается полоса поглощения, относящаяся к связям Fe-O, однако при взаимодействии с водородом эта полоса поглощения пропадает. При взаимодействии с водородом системы $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ исчезает и полоса поглощения, связанная с мостиковыми группами -OH, то же самое происходит и в случае оксида $\gamma\text{-Al}_2\text{O}_3$.

Методом ТПД- H_2 показано, что на поверхности оксида $\gamma\text{-Al}_2\text{O}_3$ и систем $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ присутствуют адсорбционные центры, различающиеся по своим энергетическим характеристикам (энергии связи). Причём, эти характеристики могут зависеть и от процентного содержания железосодержащей компоненты на поверхности оксида алюминия.

Методом ТПВ- H_2 установлено, что оксид $\gamma\text{-Al}_2\text{O}_3$ и системы 3% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$, 13% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ содержат различные состояния оксидных форм металла, поскольку на кривых ТПВ- H_2 четко различимы несколько экстремумов.

В температурном интервале 630 – 773К для систем 3% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$, 13% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ независимо от содержания железа, наблюдается область десорбции с положением максимума при 703К. Наличие области десорбции для систем 3% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$, 13% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$, видимо, связано с восстановлением железосодержащей компоненты, а именно состояния Fe^{3+} до Fe^{2+} при диссоциативной адсорбции водорода, например, по механизму:



Ключевые слова: гетерогенный катализ, физико-химические методы исследования, адсорбированные молекулы.

Information about authors:

Brodskiy A.R., candidate of chemical sciences, assoc. prof., head of the laboratory, “D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis” JSC (Almaty), albrod@list.ru, <https://orcid.org/0000-0001-6216-4738>;

Grigoriyeva V.P., researcher, “D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis” JSC (Almaty), grig1944@inbox.ru, <https://orcid.org/0000-0002-1807-8530>;

Komashko L.V., researcher, “D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis” JSC (Almaty), komashko535@mail.ru, <https://orcid.org/0000-0003-0031-2816>;

Nurmakanov Y.Y., PhD, senior research fellow, “D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis” JSC (Almaty), yerzhan.nurmakanov@gmail.com, <https://orcid.org/0000-0002-0404-1833>;

Chanysheva I.S., researcher, “D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis” JSC (Almaty), chanysheva37@mail.ru, <https://orcid.org/0000-0002-7286-6036>;

Shapovalov A.A., candidate of chemical sciences, assoc. prof., senior research fellow, “D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis” JSC (Almaty), shapov1937@mail.ru, <https://orcid.org/0000-0003-0386-5838>;

Shlygina I.A., candidate of chemical sciences, leading Researcher, “D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis” JSC (Almaty), iashlygina@mail.ru, <https://orcid.org/0000-0002-0883-1007>;

Yaskevich V.I., researcher, “D.V. Sokolsky Institute of Fuel, Electrochemistry and Catalysis” JSC (Almaty), yaskevich46@mail.ru, <https://orcid.org/0000-0001-9342-8337>

REFERENCES

[1] Paukshtis E.A. *Infrakrasnaya spektroskopiya v geterogennom kislotno-osnovnom katalize*. Novosibirsk: Nauka. 1992. 254 s. (in Russian).

[2] Smit A. *Prikladnaya IK-spektroskopiya*. M.: Mir. 1982. 328 s. (in Russian).

[3] Kiselev A.V., Lygin V.I. *Infrakrasnye spektry poverhnostnykh soedinenij i adsorbirovannykh veshchestv*. M.: Nauka. 1972. 459 s. (in Russian).

[4] Shtern E., Timmons K. *Elektronnaya absorbcionnaya spektroskopiya v organicheskoy himii*. M.: Mir. - 1974. - 296 s. (in Russian).

- [5] Paukshtis E.A. Opticheskaya spektroskopiya v adsorbicii i katalize. Primenenie IK spektroskopii. Novosibirsk. Institut kataliza im. G.K. Boreskova. 2010. 55 s. (in Russian).
- [6] Eksperimental'nye metody issledovaniya kataliza. Pod redakciej R. Andersona //M.: izd. Mir. 1972. - 480 s. (in Russian).
- [7] Metody issledovaniya katalizatorov. Pod redakciej Dzh.Tomasa i R.Lemberta // M.: izd. Mir. 1983. - 302 s. (in Russian).
- [8] Klyachko, A.L. Teplota adsorbicii na poverhnosti s diskretnoj neodnorodnost'yu // Kinetika i kataliz. 1978. T.19. № 5. S. 1218-1223. (in Russian).
- [9] Witonska I.A., Walock M.J., Binczarski M., Lesiak M., Stanishevsky A.V., Karski S. Pd-Fe/SiO₂ and Pd-Fe/Al₂O₃ catalysts for selective hydrodechlorination of 2,4-dichlorophenol // J. Mol. Catal. A: Chem. 2014. V. 393. - P. 248-256.
- [10] Dimas-Rivera G.L., Rivera De la Rosa J, Lucio-Ortiz C. J., Martínez-Vargas D. X., Sandoval-Rangel L., García Gutiérrez D.I., Maldonado Bimetallic C.S. Pd-Fe supported on γ -Al₂O₃ catalyst used in the ring opening of 2- methylfuran to selective formation of alcohols // Appl. Catal. A, Gen. 2017. V. 543. P. 133-140.
- [11] A.R. Brodskiy, V.P. Grigor'eva, L.V. Komashko, Y.Y. Nurmakanov, I.S. Chanysheva, A.A. Shapovalov, I.A. Shlygina, V.I. Yaskevich. Interaction of the Fe/ γ -Al₂O₃ catalytic system with probe molecules I. Research of the γ -Al₂O₃ and the Fe/ γ -Al₂O₃ initial system // News of the National Academy of Science of the Republic of Kazakhstan. Chemistry and Technology series. 2018. V. 6. P. 109-119.
- [12] A.R. Brodskiy, V.P. Grigor'eva, L.V. Komashko, Y.Y. Nurmakanov, I.S. Chanysheva, A.A. Shapovalov, I.A. Shlygina, V.I. Yaskevich. Interaction of the Fe/ γ -Al₂O₃ catalytic system with probe molecules II. Study of γ -Al₂O₃ support and Fe/ γ -Al₂O₃ system after interaction with hydrogen and ammonia // News of the National Academy of Science of the Republic of Kazakhstan. Chemistry and Technology series. 2018. V. 6. P. 120-129.
- [13] A.R. Brodskiy, V.P. Grigor'eva, L.V. Komashko, Y.Y. Nurmakanov, I.S. Chanysheva, A.A. Shapovalov, I.A. Shlygina, V.I. Yaskevich. Interaction of the Fe/ γ -Al₂O₃ catalytic system with probe molecules III. Study of the interaction of ammonia with γ -Al₂O₃ oxide and the Fe/ γ -Al₂O₃ system // News of the National Academy of Science of the Republic of Kazakhstan. Chemistry and Technology series. 2020. V. 3. P. 151-167.
- [14] Krylov O.V. Geterogennyj kataliz. M.: IKC «Akademkniga». 2004. 663s. (ISBN 5-94628-141-0) (in Russian).
- [15] Radchenko E.D., Nefyodov B.K., Aliev R.R. Promyshlennyye katalizatory gidrogenizacionnykh processov neftepererabotki. M.: Himiya. 1987. 224 s. (in Russian).
- [16] Ramanovskij B.V. Osnovy kataliza. M.: Binom. 2014. 175 s. (in Russian).
- [17] Goncharuk V.V., Kamalov G.L., Kovtun G.A., Rudakov E.S., Yacimirskij V.K. Kataliz: mekhanizmy gomogenogo i heterogenogo kataliza, klasternye podhody. Kiev, Naukova Dumka. 2002. 543 s. (in Russian).
- [18] Chukin G.D. Stroenie oksida alyuminiya i katalizatorov gidroobesserivaniya. Mekhanizmy reakcij. M.: Tipografiya Paladin, OOO «Printa». - 2010. - 288 s. (in Russian).
- [19] Ingram-Jones V.J., Davies R.C.T., Southern J.C., Salvador S. Dehydroxylation sequences of gibbsite and boehmite: study of differences between soak and flash calcinations and of particle-size effects // J. Mater. Chem. 1996. V.6. P. 73.
- [20] Tsyganenko A. A., Smirnov K. S. Infrared spectroscopic evidence for the structural OH-groups of spinel alumina modifications // Materials Chemistry and Physics. 1990. V. 26. P. 35.
- [21] Radishevskaya N.I., Chapskaya A.Yu., L'vov O.V., Vereshchagin V.I., Korshunov A.V. Sostav i struktura zashchitnoj oksidno-gidroksidnoj obolochki na chasticah na chasticah nanoporoshka // Izvestiya Tomskogo politekhnicheskogo universiteta. 2011. T. 318. № 3 s. 19-23. (in Russian).
- [22] Davydov A.A. IK-spektroskopiya v himii poverhnosti oksidov. Novosibirsk: Nauka. 1984. 240 s.
- [23] Davydov A. A. Molecular spectroscopy of oxide catalyst surfaces; edited by N.T. Sheppard. Wiley, 2003. 684 p.
- [24] Chengshuai L., Kaimin S., Yuanxue G., Fangbai L., Lan W. Dechlorinating transformation of propachlor through nucleophilic substitution by dithionite on the surface of alumina // J Soils Sediments (2012) 12:724-733 DOI 10.1007/s11368-012-0506-0
- [25] Nakamoto K. IK-spektry i spektry KR neorganicheskikh i koordinacionnykh soedinenij. M.: Mir. 1991. 536 s. (in Russian).
- [26] Digne M., Sautet P., Rayband P., Euzen P., Toulhoat H. Hydroxyl Groups on γ -Alumina Surfaces: A DFT Study // J. of Catalysis. 2002. V.211. P.1-5.
- [27] Digne M. Use of DFT to achieve a rational understanding of acid-basic properties of γ -alumina surfaces // J. of Catalysis. 2004. V.226. P.54-68.
- [28] Busca G. The surface of transitional aluminas: A critical review // Catalysis Today. 2014. V.226. P. 2-13.
- [29] Brodskiy A., Yaskevich V., Khussain B., Shapovalov A. Studies of the reduction process of the Fe/ γ -Al₂O₃ catalytic system // EurAsian Journal of BioSciences Eurasia J Biosci 14, 823-828 (2020).