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Д.В. Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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INTERACTION OF THE Fe/γ-Al_2O_3 CATALYTIC SYSTEM WITH PROBE MOLECULES III. STUDY OF THE INTERACTION OF AMMONIA WITH γ-Al_2O_3 OXIDE AND THE Fe/γ-Al_2O_3 SYSTEM

Abstract. The work is devoted to the study of the interaction of heterogeneous catalytic systems with adsorbed molecules. It presents the results of the interaction of the initial γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system with ammonia obtained using IR spectroscopy and the method of temperature programmed desorption.

Lewis and Bronsted acid centers were detected on the surface of both γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system during their interaction with ammonia in the temperature range 293-773K using IR spectroscopy. The relative intensity of the absorption bands corresponding to these centers depends on the temperature of interaction with ammonia.

It was found by ammonia TPD that adsorbed NH_3 is desorbed in the form of five peaks from the γ-Al_2O_3 surface on a temperature scale, and in the form of seven peaks from the surface of the Fe/γ-Al_2O_3 system. It was shown that the total amount of desorbed ammonia decreases markedly with increasing adsorption temperature. Moreover, for individual temperature peaks, the amount of adsorbed ammonia can either decrease, pass through an extremum, or remain approximately constant. The appearance of additional desorption peaks for the Fe/γ-Al_2O_3 system is associated with iron deposited on alumina.

Proceeding from the temperature range of existence of desorption peaks for γ-Al_2O_3 oxide and the Fe/γ-Al_2O_3 system it was established that they contain weak acid centers (desorption temperature up to 523K), acidic centers of medium strength (desorption temperature from 523 to 613K) and strong acid sites (desorption temperature above 613K). The volume of desorbed ammonia in the indicated temperature ranges can serve as a quantitative measure of various types of acid sites.

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

Introduction. One of the most common and highly effective methods for studying acid-base centers on the surfaces of supports and heterogeneous catalysts are infrared spectroscopy [1-5] and temperature programmed desorption of ammonia [6, 7].

The use of IR spectroscopy for studying the donor-acceptor surface properties is based on the spectral probing 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 position of the peak in the TPD method on the temperature scale and activation energy of the probe molecule give the possibility to assess the strength of the center that its area can serve as a measurement of the quantity of the various acid centers of various types.

This work is a continuation of studies on the interaction of a heterogeneous catalytic system with adsorbed molecules [8, 9].

Experimental. Fe/γ-Al_2O_3 system with an iron content of 3; 13 wt.% was prepared by impregnating [10-13] the initial γ-Al_2O_3 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 decreased to 293K. Next, ammonia purging began at the required temperature (from a given temperature range of 293-773 K) 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.

Ammonia TPD

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 ammonia adsorption:

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

Ammonia adsorption:

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

Programmed desorption of ammonia:

- 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 ammonia desorbed in the corresponding temperature range was determined by peak areas, having previously established how much NH_3 corresponds to the area unit.

Equipment - "CETARAM" thermo analyzer, France.

Results and discussion

Investigation of the Fe/γ-Al_2O_3 system by FTIR spectroscopy during NH_3 adsorption.

In the beginning, the interaction of γ-Al_2O_3 with NH_3 was studied in the range of 293-773K. The data obtained for γ-Al_2O_3 oxide were necessary as reference and comparison points when studying the Fe/γ-Al_2O_3 system. Figures 1-7 show the IR spectra of γ-Al_2O_3 oxide when interacting with ammonia at different temperatures and table 1 shows the results of their interpretation. In the initial γ-Al_2O_3 oxide and even after interaction with ammonia, 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, -CH_2, -CH_3 groups (in trace amounts). A small amount of hydrocarbons, apparently, remained in the γ-Al_2O_3 oxide after synthesis.

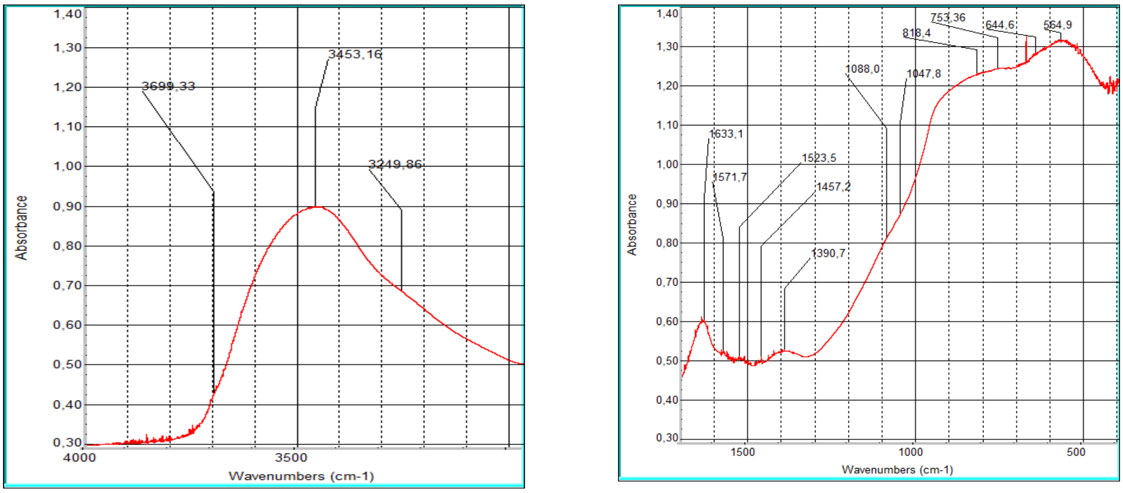


Figure 1 - IR spectrum of the initial γ-Al_2O_3 oxide

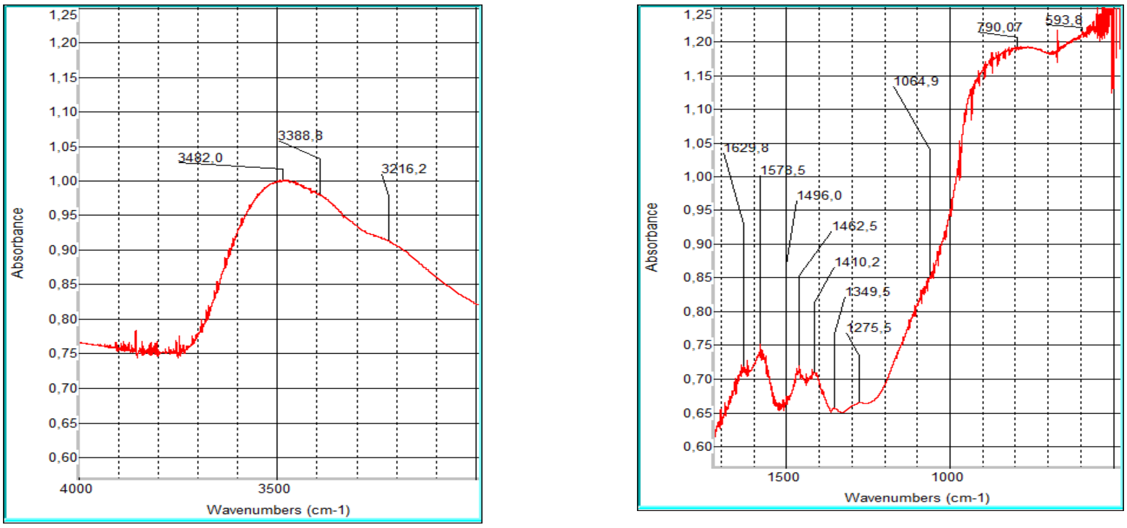


Figure 2 - IR spectrum of γ-Al_2O_3 oxide after adsorption of ammonia at 293K

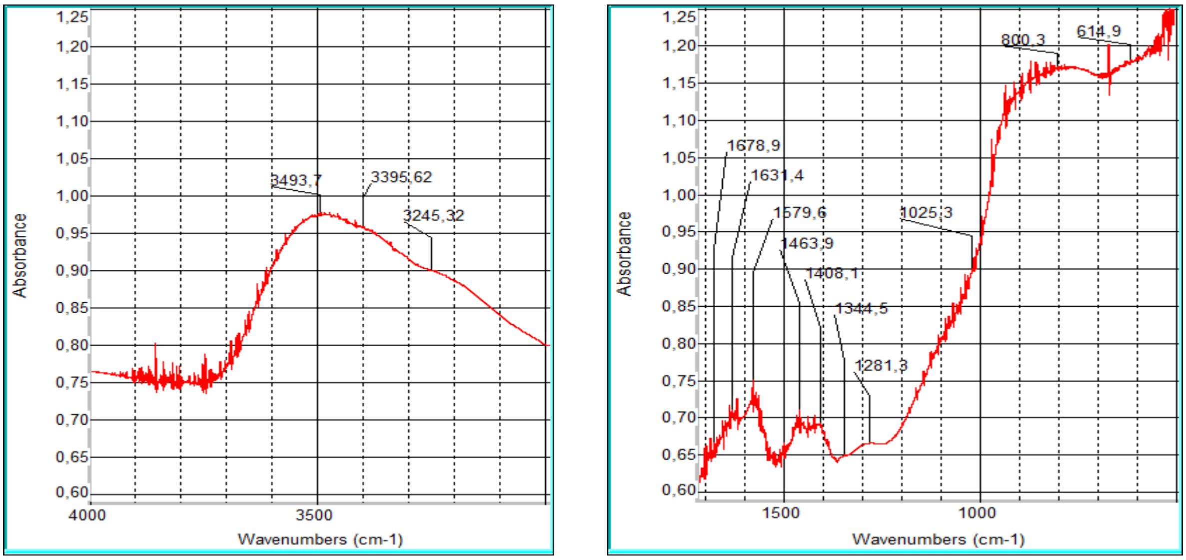


Figure 3 - IR spectrum of γ-Al_2O_3 oxide after adsorption of ammonia at 373K

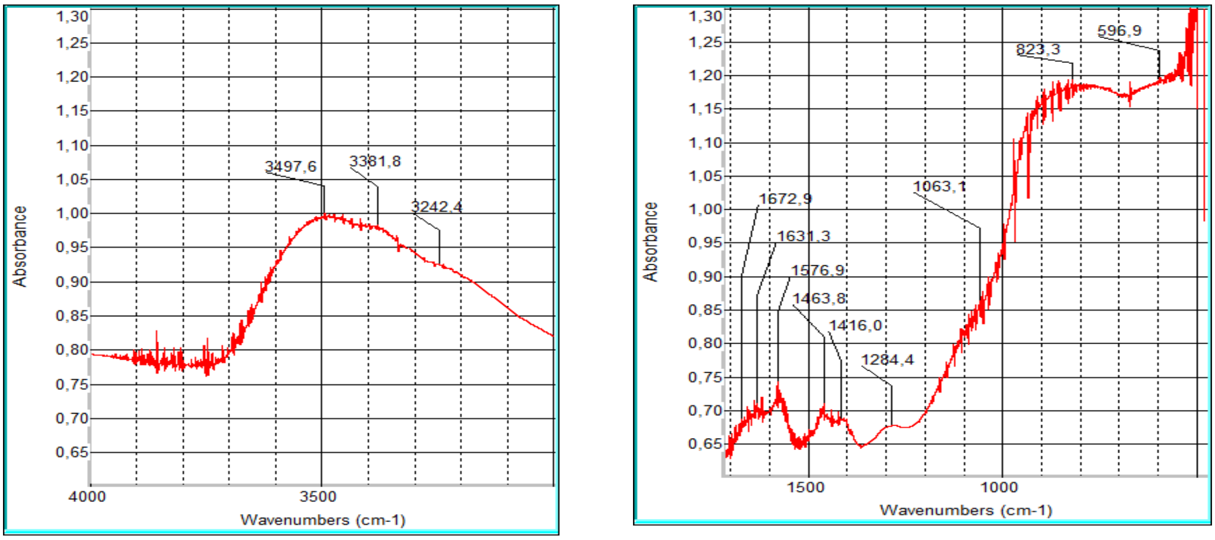


Figure 4 - IR spectrum of γ-Al_2O_3 oxide after ammonia adsorption at 473K

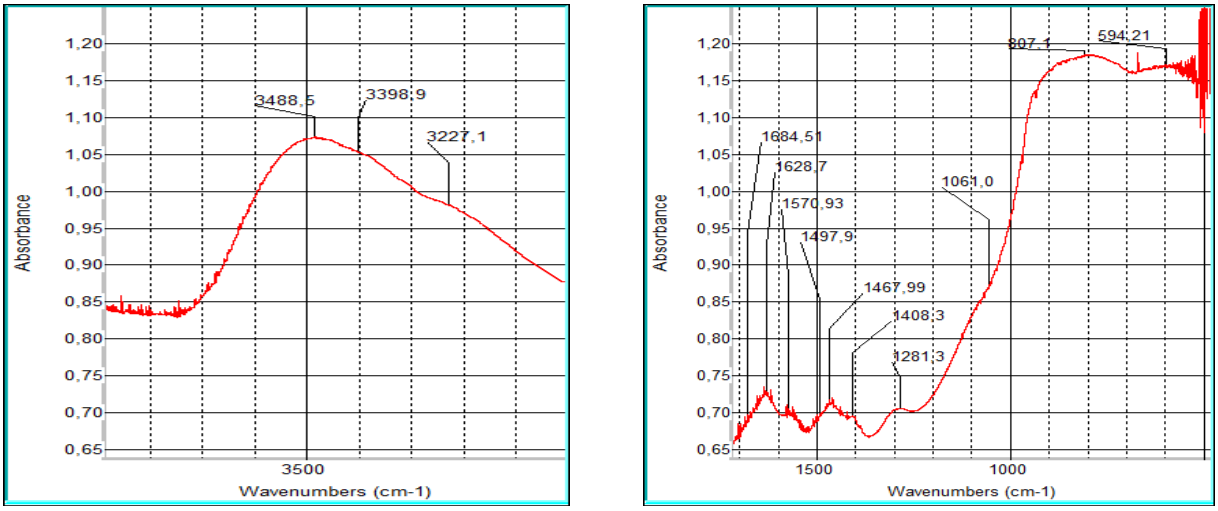


Figure 5 - IR spectrum of γ-Al_2O_3 oxide after adsorption of ammonia at 573K

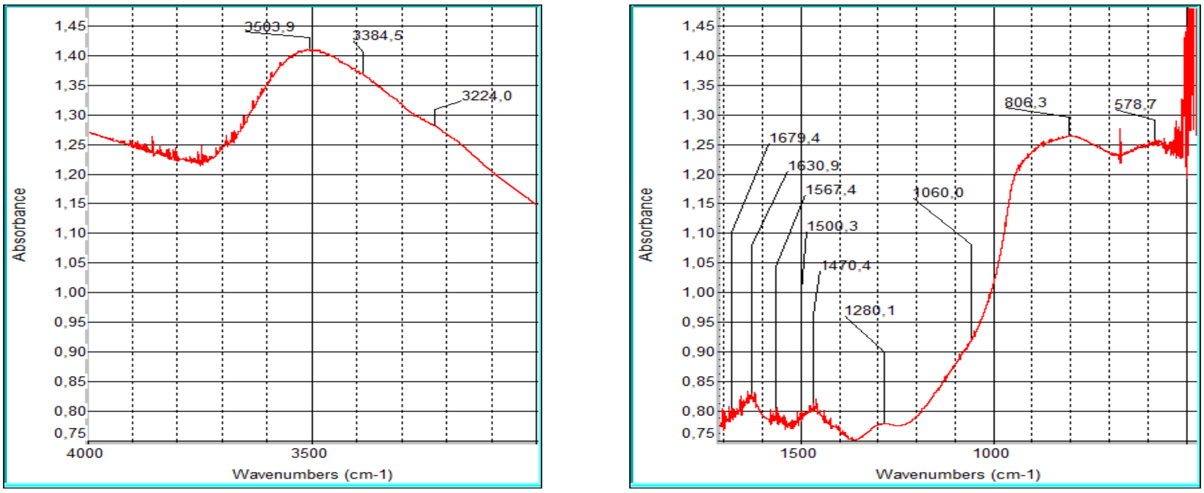


Figure 6 - IR spectrum of γ-Al_2O_3 oxide after ammonia adsorption at 673K

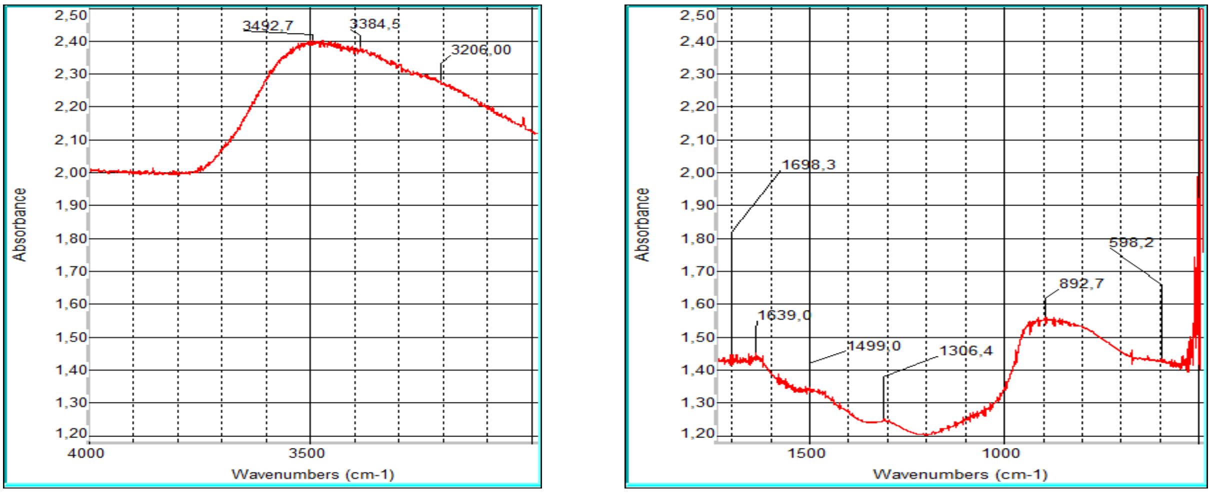


Figure 7 - IR spectrum of γ-Al_2O_3 oxide after ammonia adsorption at 773K

Table 1 - Interpreted data of the IR spectra of γ-Al_2O_3 oxide
and the Fe/γ-Al_2O_3 system in the initial states,
and after their interaction with NH_3 in the range 293-773K

T, K	Absorption bands, cm^{-1}		Assignment of absorption bands
	Sample		
	γ-Al_2O_3	Fe/γ-Al_2O_3	
1	2	3	4
Initial states			
293	3699	3702	Stretching vibrations of bridging groups -OH bound to aluminum ions in octahedral and (or) tetrahedral coordination
	3453, 3250	3452, 3212	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
		3404, 3301,	Stretching vibrations of -OH groups bound on the surface of aluminum hydroxides by hydrogen bonds
	1633, 1571, 1524, 645	1632, 1584, 1526, 623	Bending vibrations of -OH groups bonded to 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 a tetrahedral and (or) octahedral coordination
	818, 753	804, 728	Bending vibrations in -Al-O- groups in tetrahedral and (or) octahedral coordination, possibly, in Al-O-Fe groups in the Fe/γ-Al_2O_3 system
	565	550	The stretching vibrations of the M-O bonds (M = Al; Fe)
Interaction of ammonia			
293	3482, 3216	3475, 3236	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
	1629, 1579, 594	1627, 1585, 631	Bending vibrations of -OH groups bound on the surface by hydrogen bonds
	3389	3389	Stretching vibrations related to -NH groups of ammonia bound to Lewis acid sites
	1276	1692, 1270	Bending vibrations related to -NH groups of ammonia linked by a coordination bond with Lewis acid sites
		3178	Stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers
	1496, 1463, 1410, 1350	1463, 1406	Bending vibrations of N-H groups in NH_4^+ ions - Bronsted centers (on the background of bending vibrations of C-H bonds in -CH, -CH_2, -CH_3 groups)
	1065	1066	Stretching vibrations related to Al-O bonds in -Al-O- groups
	790	834	Bending vibrations of -Al-O bonds in tetrahedra

Continuation of the table 1

1	2	3	4
373	3494, 3245	3479, 3229	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
	1631, 1580, 615	1627, 1584, 611	Bending vibrations of -OH groups bound on the surface by hydrogen bonds
	3386	3383	Stretching vibrations related to -NH groups of ammonia bound to Lewis acid sites
	1679, 1281	1695, 1280	Bending vibrations related to -NH groups of ammonia linked by a coordination bond with Lewis acid sites
		3173	Stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers
	1464, 1408, 1345	1463, 1405, 1351	Bending vibrations of N-H groups in NH_4^+ ions - Bronsted centers (on the background of bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1025	1077	Stretching vibrations related to Al-O bonds in -Al-O- groups
	800	814	Bending vibrations of -Al-O bonds in tetrahedra
473	3498, 3242	3472, 3224	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
	1631, 1577, 597	1626, 1576, 617	Bending vibrations of -OH groups bound on the surface by hydrogen bonds
	3382	3392	Stretching vibrations related to -NH groups of ammonia bound to Lewis acid sites
	1673, 1234	1674, 1273	Bending vibrations related to -NH groups of ammonia linked by a coordination bond with Lewis acid sites
		3163	Stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers
	1464, 1416	1462, 1405	Bending vibrations of N-H groups in NH_4^+ ions - Bronsted centers (on the background of bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1063	1069	Stretching vibrations related to Al-O bonds in -Al-O- groups
	823	813	Bending vibrations of -Al-O bonds in tetrahedra
573	3489, 3227	3472, 3250, 3221	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
	1629, 1571, 594	1619, 1564, 1543, 629	Bending vibrations of -OH groups bound on the surface by hydrogen bonds
	3399	3361, 3310	Stretching vibrations related to -NH groups of ammonia bound to Lewis acid sites
	1685, 1281	1673, 1652, 1269	Bending vibrations related to -NH groups of ammonia linked by a coordination bond with Lewis acid sites
		3154	Stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers
	1498,1468, 1408	1498, 1458, 1408	Bending vibrations of N-H groups in NH_4^+ ions - Bronsted centers (on the background of bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1061	1058	Stretching vibrations related to Al-O bonds in -Al-O- groups
	807	812	Bending vibrations of -Al-O bonds in tetrahedra

Continuation of the table 1

1	2	3	4
673	3504, 3224	3481, 3239	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
	1631, 1567, 579	1620, 1548, 615	Bending vibrations of -OH groups bound on the surface by hydrogen bonds
	3385	3374, 3310	Stretching vibrations related to -NH groups of ammonia bound to Lewis acid sites
	1679, 1280	1699, 1649, 1245	Bending vibrations related to -NH groups of ammonia linked by a coordination bond with Lewis acid sites
		3166	Stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers
	1500, 1470	1490, 1463	Bending vibrations of N-H groups in NH_4^+ ions - Bronsted centers (on the background of bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups)
	1060	1074	Stretching vibrations related to Al-O bonds in -Al-O- groups
	806	856	Bending vibrations of -Al-O bonds in tetrahedra
773	3493, 3206	3472, 3233	Stretching vibrations related to the -OH groups bound on the surface by hydrogen bonds
	1639, 598	1624	Bending vibrations of -OH groups bound on the surface by hydrogen bonds
	3385	3328	Stretching vibrations related to -NH groups of ammonia bound to Lewis acid sites
	1698	1698, 1266	Bending vibrations related to -NH groups of ammonia linked by a coordination bond with Lewis acid sites
		3153	Stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers
	1499, 1306	1479, 1306	Bending vibrations of N-H groups in NH_4^+ ions - Bronsted centers (on the background of bending vibrations of C-H bonds in -CH, $-CH_2$, $-CH_3$ groups)
		1080	Stretching vibrations related to Al-O bonds in -Al-O- groups
	893	924, 853, 804	Bending vibrations of -Al-O bonds in tetrahedra and, possibly, bonds in Al-O-Fe groups (for Fe/γ-Al_2O_3)

Absorption band related to the bridging -OH groups bound to aluminum ions in an octahedral coordination is also observed. However, upon interaction with ammonia, this absorption band disappears.

Absorption bands associated with the Lewis acid sites and with ammonium ions NH_4^+ (Bronsted sites) appear while interacting with ammonia. An increase in temperature causes noticeable decrease in the relative intensity of the absorption bands corresponding to the Lewis and Bronsted centers.

Further, the interaction of the 13%Fe/γ-Al_2O_3 system with NH_3 in the temperature range 293-773K was also studied using the Fourier-transform IR spectroscopy in the “In Situ” mode.

Figures 8-14 show the IR spectra of the Fe/γ-Al_2O_3 system interacting with ammonia and table 1 shows the results of their interpretation.

There are absorption bands related to -OH bridge groups bonded to aluminum ions in octahedral coordination, and absorption bands related to -OH groups bound on the surface by hydrogen bonds , absorption bands related to Al-O bonds in the initial Fe/γ-Al_2O_3 system, as well as in the initial γ-Al_2O_3 oxide. In addition, an absorption band related to Fe-O bonds is observed in the initial Fe/γ-Al_2O_3 system. This band disappears when interacting with ammonia.

It should be noted that in the Fe/γ-Al_2O_3 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 [8, 9]. In that works were noted that during the synthesis of the Fe/γ-Al_2O_3 system by impregnation partial hydrolysis of aluminum oxide can occur as a result of which a certain amount of aluminum hydroxide is formed.

Absorption bands associated with the Lewis acid centers and with ammonium ions NH_4^+ (Bronsted centers) appear when the Fe/γ-Al_2O_3 system interacts with ammonia as in the case of the initial alumina. An increase in temperature, similarly to what was observed for γ-Al_2O_3 oxide, also leads to the decrease of the relative intensity of the absorption bands corresponding to the Lewis and Bronsted centers.

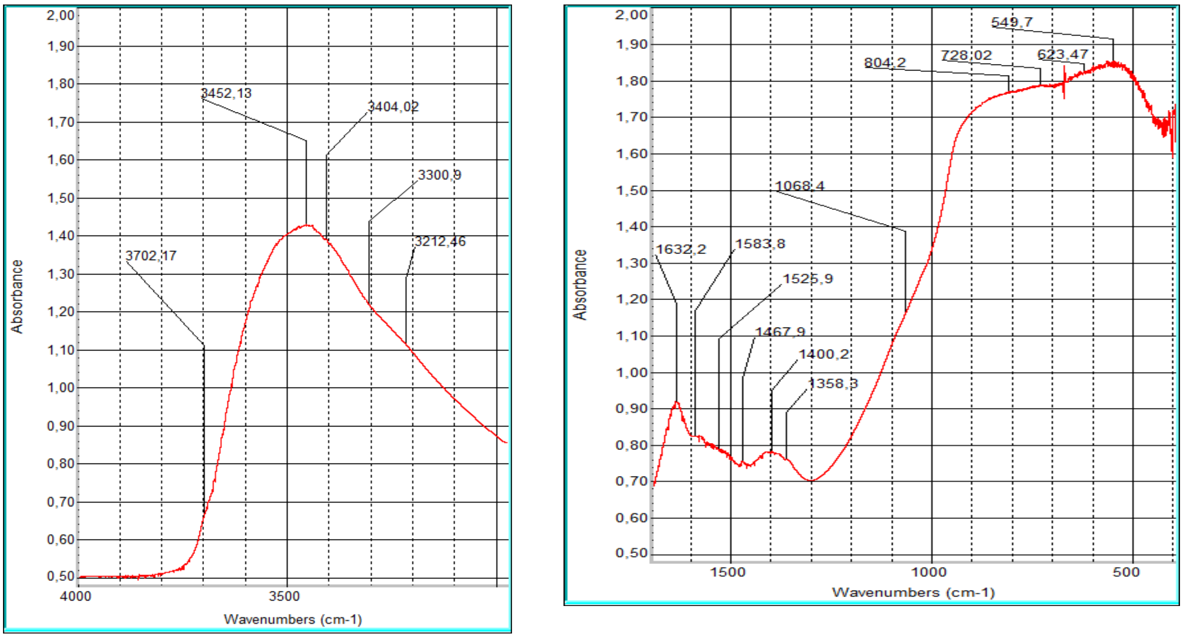


Figure 8 - IR spectrum of the initial 13%Fe/γ-Al_2O_3 system

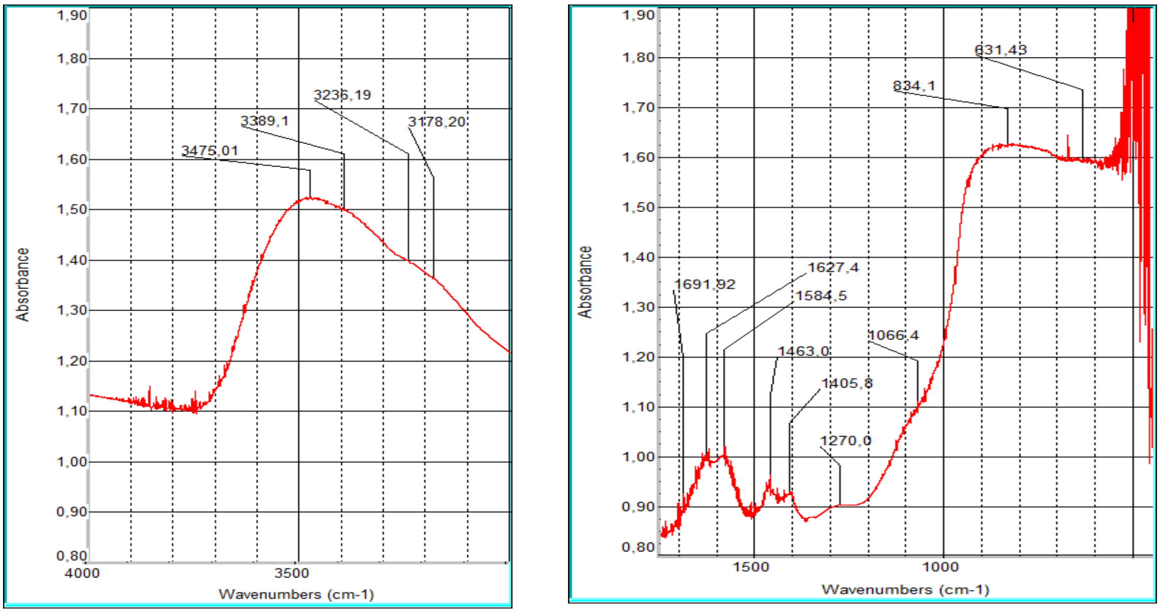


Figure 9 - IR spectrum of 13%Fe/γ-Al_2O_3 system after adsorption of ammonia at 293K

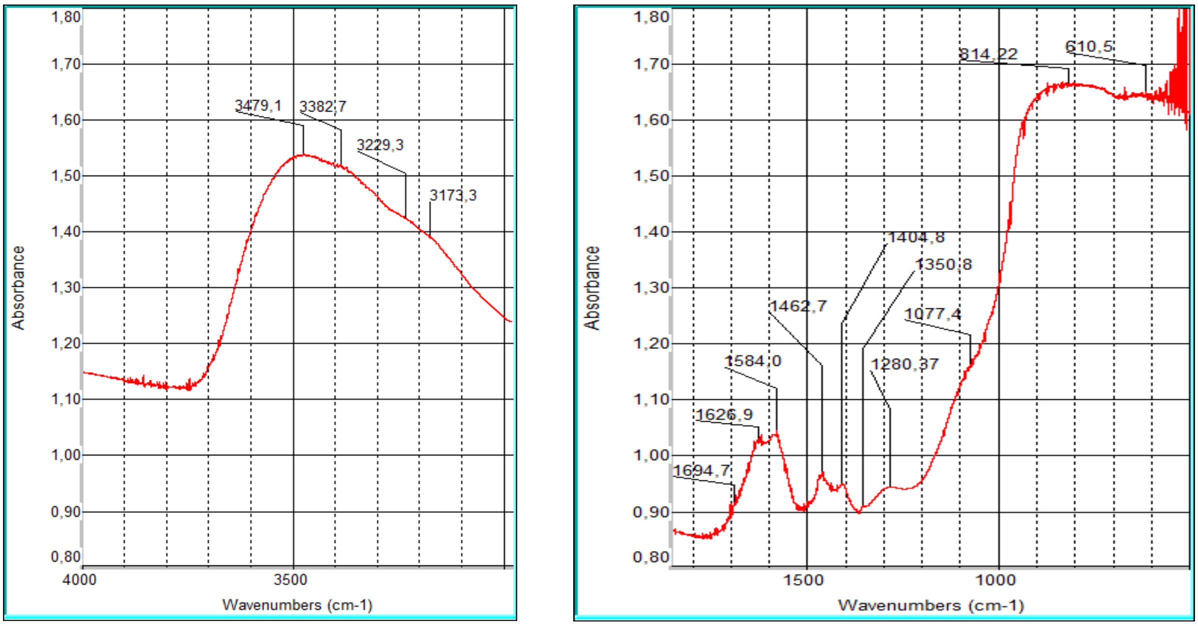


Figure 10 - IR spectrum of 13%Fe/γ-Al_2O_3 system
after adsorption of ammonia at 373K

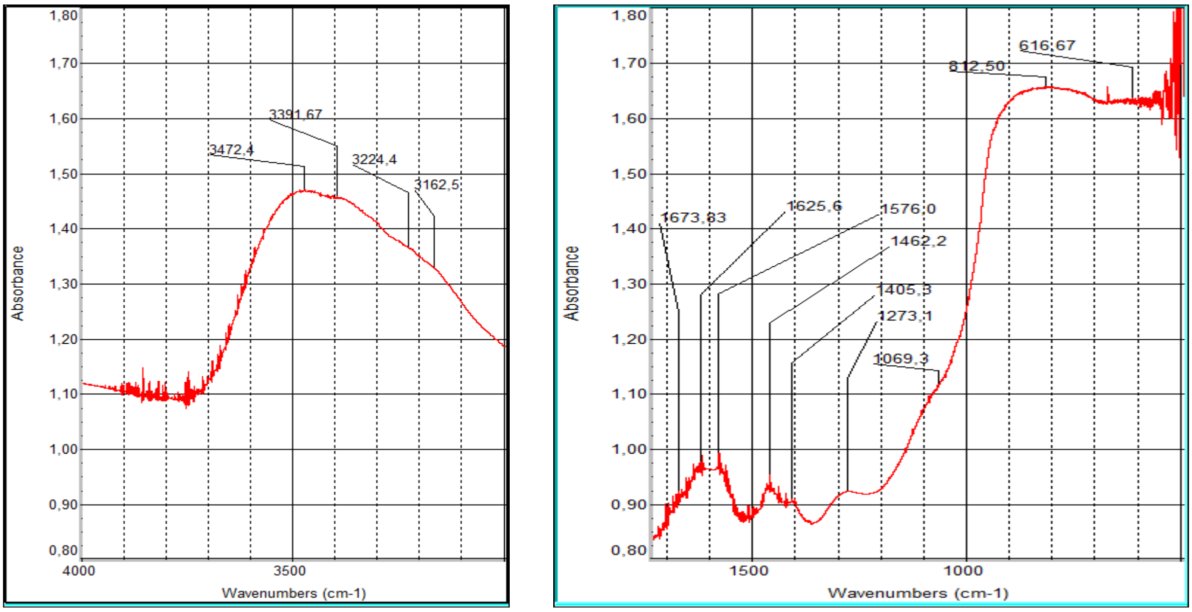


Figure 11 - IR spectrum of 13%Fe/γ-Al_2O_3 system after ammonia adsorption at 473K

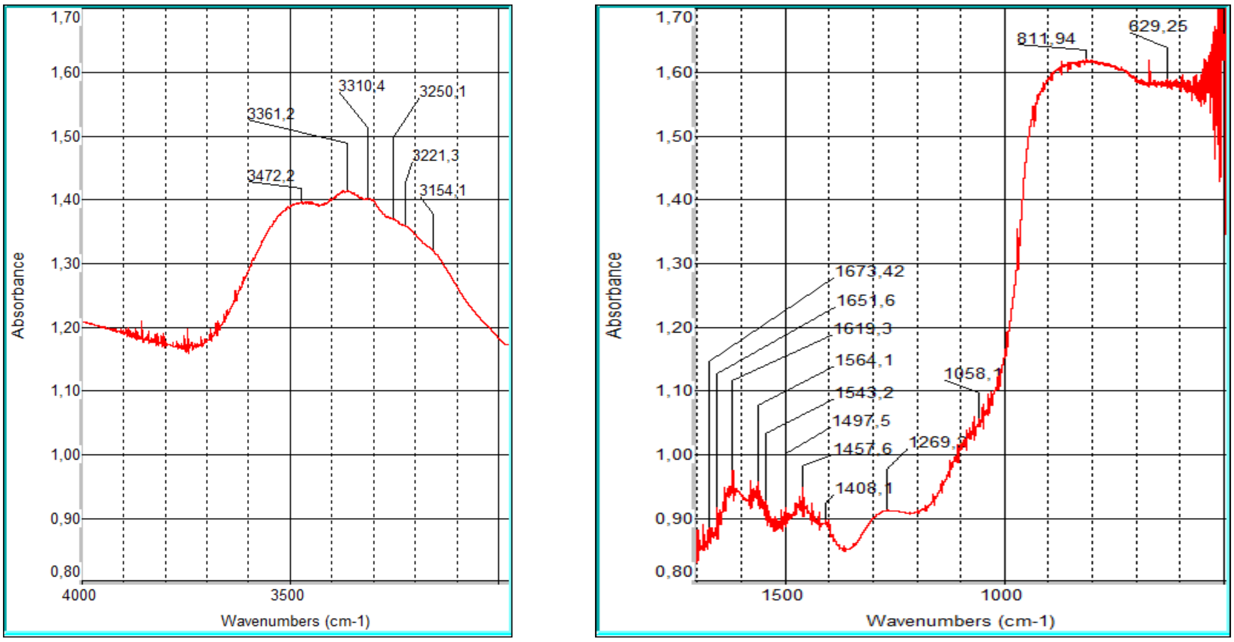


Figure 12 - IR spectrum of 13%Fe/γ-Al_2O_3 system after adsorption of ammonia at 573K

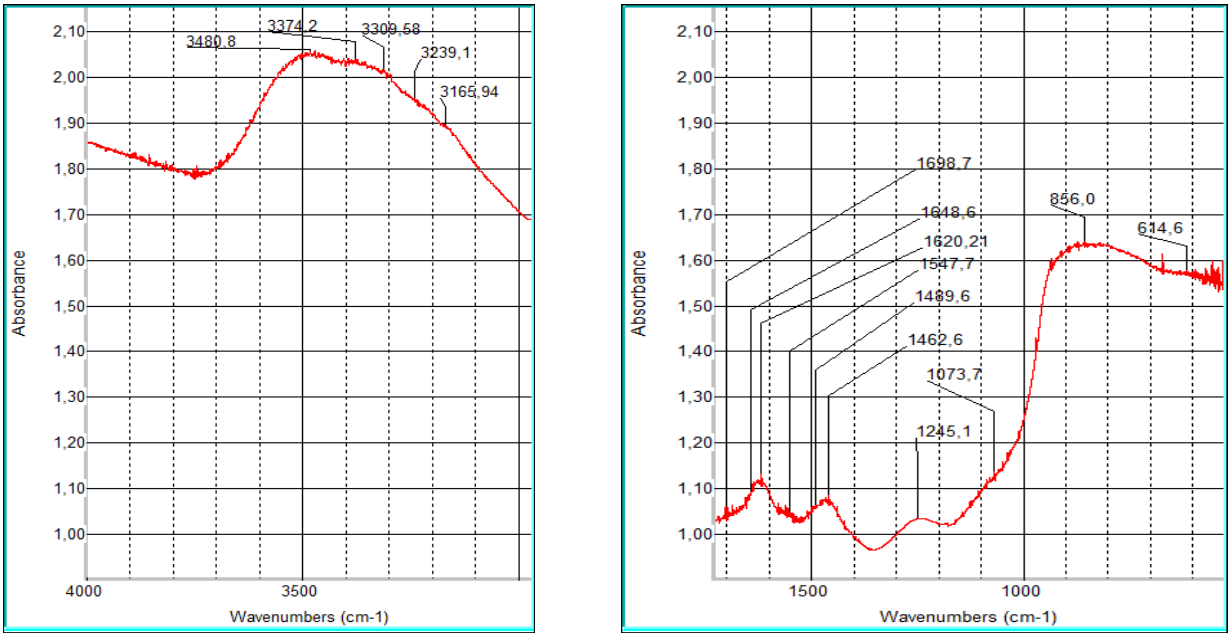


Figure 13 - IR spectrum of 13%Fe/γ-Al_2O_3 system after ammonia adsorption at 673K

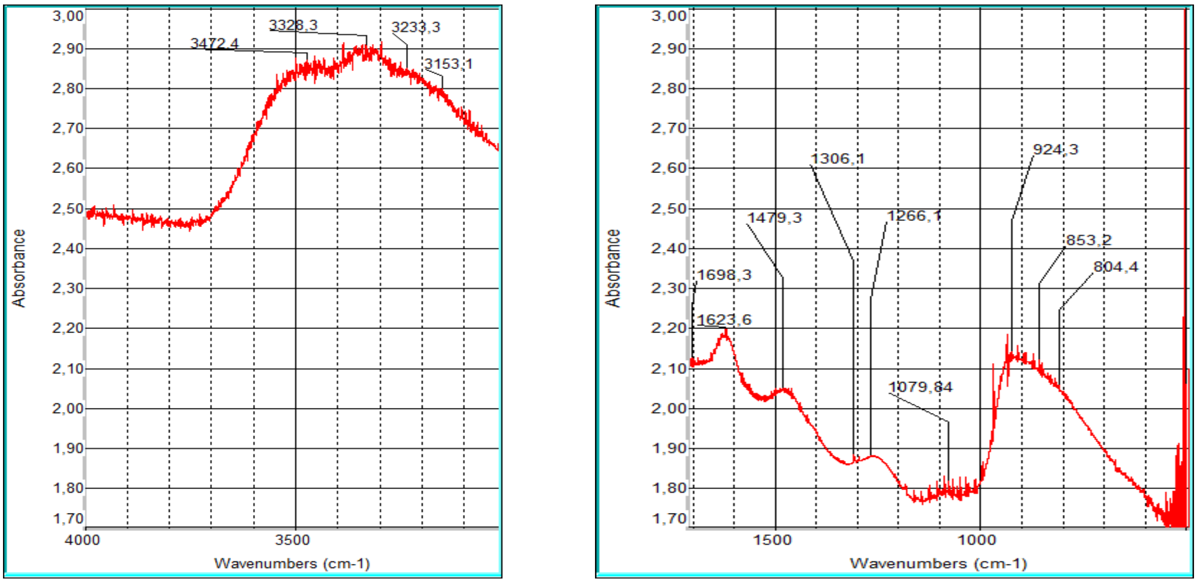


Figure 14 - IR spectrum of 13%Fe/γ-Al_2O_3 system after ammonia adsorption at 773K

At the same time, there are noticeable differences, in particular, the number of absorption bands corresponding to -OH groups bound on the surface by hydrogen bonds and absorption bands corresponding to Lewis centers increases, a band corresponding to stretching vibrations of N-H groups in ammonium ions NH_4^+ appears - Bronsted centers (table 1). In the case of alumina, only bending vibrations were observed. In addition, at 773 K, absorption bands are present in the long-wavelength region of the IR spectra, which can be attributed to bonds in the Al-O-Fe groups.

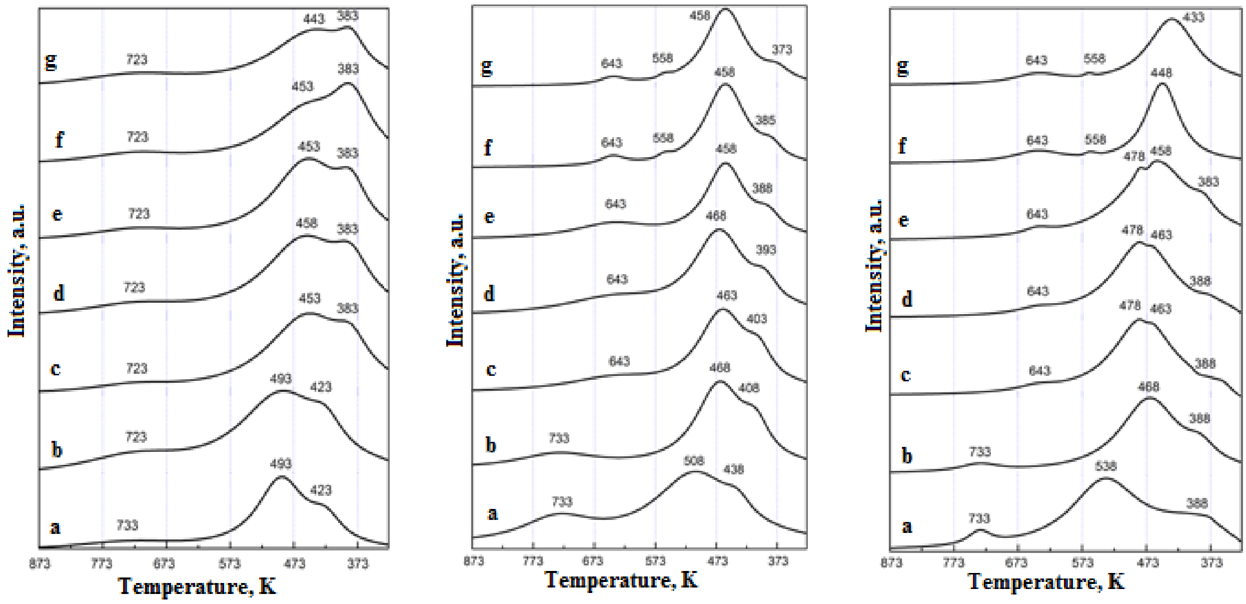
Study of the Fe/γ-Al_2O_3 system using temperature programmed desorption during ammonia adsorption

As it was already noted, the catalytic characteristics of heterogeneous systems correlate with the presence of acid centers of various nature on their surface and an important criterion is the quantity and strength of acid centers.

The properties of the surface of γ-Al_2O_3 oxide (as a reference point) and the Fe/γ-Al_2O_3 system were studied by temperature programmed desorption (TPD) in the temperature range 293-773K using an ammonia as a probe molecule.

The results of ammonia TPD for γ-Al_2O_3 oxide are shown in Figure 15(I) and are shown in table 2.

Adsorbed NH_3 is desorbed from the surface of γ-Al_2O_3 on a temperature scale in the form of five peaks, and the high-temperature peak E is much smaller in quantitative terms than the lower-temperature peak and, as the adsorption temperature rises its position practically does not shift (table 2). Peaks A and C are observed only at ammonia adsorption temperatures of 293, 373K. Peaks B and D appear starting from an adsorption temperature of 423K.



(I) (II) (III)

NH_3 adsorption temperature: a - 293К; b - 373К; c - 423К; d - 473К; e - 573К; f - 673К; g - 773К
Figure 15 - TPD-NH_3 profiles for γ-Al_2O_3 (I), 3%Fe/γ-Al_2O_3 (II) system and 13%Fe/γ-Al_2O_3 (III) system

Table 2 - The results of the study of TPD-NH_3 for γ-Al_2O_3 oxide

Sample	NH_3 adsorption temperature, K	The highest temperatures of the desorption peaks, K					Amount of desorbed NH_3, 10^{-4} mol/g					The total amount of desorbed NH_3, 10^{-4} mol/g
		A	B	C	D	E	A	B	C	D	E	
γ-Al_2O_3	293	423	-	493	-	733	4.82		6.00		0.78	11.60
	373	423	-	493	-	723	4.80		5.47		0.89	11.16
	423	-	383	-	453	723	-	4.03	-	4.71	0.96	9.60
	473	-	383	-	458	723	-	3.79	-	4.06	1.17	9.02
	573	-	383	-	453	723	-	3.71	-	4.02	0.98	8.71
	673	-	383	-	453	723	-	3.47	-	3.04	0.72	7.23
	773	-	383	-	443	723	-	2.73	-	2.67	0.67	6.07

For A, B, C, D peaks the amount of desorbed ammonia decreases with increasing adsorption temperature. For peak E this dependence has an extremal character with a maximum position at an adsorption temperature of 473 K.

It should be noted that with an increase in the adsorption temperature the total amount of desorbed ammonia decreases significantly (table 2).

The results of ammonia TPD for the Fe/γ-Al_2O_3 system with different iron contents are shown in Figure 15 (II, III) and in tables 3-4.

For the 3%Fe/γ-Al_2O_3 system (Figure 15 (II), table 3) the ammonia adsorbed in the temperature range 293-773K is desorbed on the temperature scale in the form of seven peaks (A′, B′, C′, D′, E′, F′, G′). Desorption temperature range for A′, B′, D′, E′ peaks is close to that observed for γ-Al_2O_3 oxide (peaks A, B, D, E) and the amount of desorbed ammonia also decreases with increasing adsorption temperature.

There are some peculiarities, in particular, the peak B′ appears at a higher adsorption temperature, and the peak D′- at a lower temperature, the peak E′ is observed only at adsorption temperatures of 293, 373K. Nevertheless, based on the obtained data, with a high degree of probability, it can be assumed that the adsorption of ammonia (A′, B′, D′, E′ desorption peaks) in the 3%Fe/γ-Al_2O_3 system occurs at the centers which are close in nature to adsorption characteristics of the γ-Al_2O_3 oxide centers.

At the same time, it should be paid attention to significant differences in the TPD spectra of γ-Al_2O_3 oxide and the 3%Fe/γ-Al_2O_3 system. In particular, the adsorption center to which the C′ peak corresponds has a noticeable temperature shift with respect to the C peaks and is present only at an adsorption temperature of 293K. In addition, in the TPD spectrum for the 3%Fe/γ-Al_2O_3 system F′ and G′ peaks appear in the temperature range of ammonia adsorption 423-773K (peak F′) and 673 - 773K (peak G′). Peaks F′ and G′ are located at desorption temperatures of 643 and 558K, respectively. Apparently, these desorption peaks can be associated with iron deposited on alumina.

Ammonia adsorbed in the temperature range 293-773K is also desorbed in the form of seven peaks (A″, B″, C′′, D″, E″, F″, G″) in case of the 13%Fe/γ-Al_2O_3 system (figure 18 (III), table 4). The desorption peaks of B″, D″, E″ are in the same temperature range as the of B, D, E peaks for γ-Al_2O_3 oxide, as well as B′, D′, E′ peaks in the case of the 3% Fe/γ-Al_2O_3 system. The F″, G″ and F′, G′ peaks are identical for the 13%Fe/γ-Al_2O_3 and 3%Fe/γ-Al_2O_3 systems.

The position on the temperature scale of peak A″ is significantly shifted to the high-temperature region. In addition, when ammonia is adsorbed in the range 423-573K the C′′ desorption peak appears at 478K in the 13%Fe/γ-Al_2O_3 system, and the amount of desorbed ammonia for the D″ peak is extreme with a minimum position in the temperature range 473-573K. At the same time, for the 3%Fe/γ-Al_2O_3 system the amount of desorbed ammonia at the D′ peak decreases with increasing adsorption temperature.

Table 3 - TPD-NH_3 study results for γ-Al_2O_3 oxide

Sample	NH_3 adsorption temperature, K	The highest temperatures of the desorption peaks, K					Amount of desorbed NH_3, 10^{-4} mol/g					The total amount of desorbed NH_3, 10^{-4} mol/g
		A	B	C	D	E	A	B	C	D	E	
γ-Al_2O_3	293	423	-	493	-	733	4.82		6.00		0.78	11.60
	373	423	-	493	-	723	4.80		5.47		0.89	11.16
	423	-	383	-	453	723	-	4.03	-	4.71	0.96	9.60
	473	-	383	-	458	723	-	3.79	-	4.06	1.17	9.02
	573	-	383	-	453	723	-	3.71	-	4.02	0.98	8.71
	673	-	383	-	453	723	-	3.47	-	3.04	0.72	7.23
	773	-	383	-	443	723	-	2.73	-	2.67	0.67	6.07

Table 4 - TPD-NH_3 study results for Fe/γ-Al_2O_3 system

Sample	NH_3 adsorption temperature, K	The highest temperatures of the desorption peaks, K							Amount of desorbed NH_3, 10^{-4} mol/g							The total amount of desorbed NH_3, 10^{-4} mol/g
		A′	B′	C′	D′	E′	F′	G′	A′	B′	C′	D′	E′	F′	G′	
3%Fe/γ -Al_2O_3	293	438	-	508		733	-	-	5.20	-	6.59	-	0.80	-	-	12.59
	373	408	-	-	468	733	-	-	3.91	-	-	5.81	0.82	-	-	10.54
	423	403	-	-	463	-	643	-	3.66	-	-	5.71	-	0.81	-	10.18
	473	-	393	-	468	-	643	-	-	2.53	-	5.70	-	1.01	-	9.24
	573	-	389	-	458	-	643	-	-	2.44	-	5.70	-	1.01	-	9.15
	673	-	383	-	458	-	643	558	-	2.00	-	5.30	-	0.96	0.86	9.12
	773	-	373	-	458	-	643	558	-	1.85	-	5.19	-	0.97	0.88	8.79
13%Fe/γ -Al_2O_3		A″	B″	C″	D″	E″	F″	G″	A″	B″	C″	D″	E″	F″	G″	
	293	538	388	-	-	733	-	-	8.10	5.01	-	--	1.62	-	-	14.73
	373		388	-	468	733	-	-	-	2.90	-	7.06	1.20	-	-	11.16
	423		388	478	463	-	643	-	-	1.31	4.37	4.16	-	1.10	-	10.94
	473		388	478	463	-	643	-	-	1.25	3.86	3.38	-	1.15	-	9.64
	573		383	478	458	-	643	-	-	1.25	3.37	3.32	-	1.17	-	9.11
	673	-	-	-	448	-	643	558	-	-	-	6.82	-	1.05	0.88	8.75
	773	-	-	-	433	-	643	558	-	-	-	6.78	-	1.04	0.84	8.66

Conclusion. Investigations of the Fe/γ-Al_2O_3 system in the temperature range 273-773K using IR spectroscopy and the ammonia TPD method showed that its surface is inhomogeneous and represents a set of adsorption centers that differ in their characteristics.

On the surface of both γ-Al_2O_3 oxide (support) and the Fe/γ-Al_2O_3 system Lewis and Bronsted acid centers were detected using IR spectroscopy during their interaction with ammonia in the temperature range 293-773K. The relative intensity of the absorption bands corresponding to these centers depends on the temperature of interaction with ammonia and with its growth decreases both for γ-Al_2O_3 and for the Fe/γ-Al_2O_3 system.

However, significant differences were identified. So, in the case of the Fe/γ-Al_2O_3 system:

- an increase in the number of absorption bands related to -OH groups joined on the surface by hydrogen bonds;
- an increase in the number of absorption bands related to Lewis acid centers;
- the appearance of a band corresponding to stretching vibrations of N-H groups in ammonium ions NH_4^+ - Bronsted centers (no stretching vibrations were observed in the case of alumina).

The observed features can be associated with the presence of an iron-containing component on the surface of the support. This statement is justified because the absorption band related to Fe-O bonds is observed in the initial Fe/γ-Al_2O_3 system, and when the Fe/γ-Al_2O_3 system interacts with ammonia at 773K, absorption bands are present in the long-wavelength region of the IR spectra, which are most likely relate to bonds in Al-O-Fe groups. In addition, the shift of the absorption bands corresponding to the Lewis acid centers in the frequency range also testifies to the effect of the iron-containing component on the adsorption centers.

As a result of studies of γ-Al_2O_3 oxide and 13%Fe/γ-Al_2O_3 systems using ammonia TPD, it was found that adsorbed NH_3 is desorbed in the form of five peaks from the γ-Al_2O_3 surface on a temperature scale, and from the surface of 3%Fe/γ-Al_2O_3 and 13%Fe/γ-Al_2O_3 systems - in the form of seven peaks. For all the samples studied the total amount of adsorbed ammonia decreases markedly with an increase in the adsorption temperature, and for individual temperature peaks the amount of adsorbed ammonia can decrease (peaks B, C, D, A′, B′, D′, B″, C″, E″), and pass through the extremum (peaks E, F′, D″, F″) or remain approximately constant (peaks A, E′, G′, G″).

As the adsorption temperature increases the desorption temperature for some of the peaks of γ-Al_2O_3 oxide and 13%Fe/γ-Al_2O_3 systems remains almost constant (peaks A, B, C, E′, F′, G′, B″, C″, E″, F″, G″) and for the other part of the peaks there is some tendency to lower the desorption temperature.

The appearance of additional desorption peaks (F′, G′, F″, G″) in the 3%Fe/γ-Al_2O_3 and 13%Fe/γ-Al_2O_3 systems, as well as a change in the position on the temperature scale of desorption peaks A″, C′, C″ can be associated with iron deposited on alumina. In particular, C′, F′, F″ peaks, possibly, relate to the adsorption of ammonia on -Al-O-Fe- type fragments, and the C″ peak on -Fe-O-Fe- type fragments, since the last peak is attributed to the 13%Fe/γ-Al_2O_3 system with a significantly higher iron content.

Investigations of the Fe/γ-Al_2O_3 system using Mössbauer spectroscopy [14] showed that the system depending on conditions can contain various forms of iron. The presence of several forms of iron in the system indicates the potential for the formation of catalytically active centers with different electronic characteristics and as a result different catalytic properties. Thus, each form of the iron cation on the support can be a specific active (adsorption) center.

Based on the temperature range for the existence of desorption peaks for γ-Al_2O_3 oxide and 3%Fe/γ-Al_2O_3, 13%Fe/γ-Al_2O_3 systems, it follows that weak acid centers (desorption temperature up to 523K), acidic centers of medium strength (desorption temperature from 523 to 613K) and strong acid sites (desorption temperature above 613K) are present in them [15-17].

The volume of desorbed ammonia in the indicated temperature ranges can serve as a quantitative measure of various types of acid sites.

It should be noted that the total amount of adsorbed ammonia decreases markedly with increasing adsorption temperature and this is in good agreement with the data of IR spectroscopy, according to which the relative intensity of the absorption bands corresponding to the Lewis and Bronsted centers also depends on the temperature of interaction with ammonia and decreases with its growth.

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$Fe/\gamma\text{-}Al_2O_3$ КАТАЛИТИКАЛЫҚ ЖҮЙЕНІҢ ЗОНДТЫ МОЛЕКУЛАЛАРМЕН ӨЗАРА ҚАТЫНАСЫ III. $\gamma\text{-}Al_2O_3$ ОКСИДІ ЖӘНЕ $Fe/\gamma\text{-}Al_2O_3$ ЖҮЙЕСІНІҢ АММИАКПЕН ӨЗАРА ҚАТЫНАСЫН ЗЕРТТЕУ

Аннотация. Жұмыс гетерогенді каталитикалық жүйелердің адсорбцияланған молекулалармен әрекеттесуін зерттеуге арналған. Онда ИҚ спектроскопиясы мен термопрограммалық десорбция әдісімен алынған $\gamma\text{-}Al_2O_3$ оксиді мен $Fe/\gamma\text{-}Al_2O_3$ жүйесінің аммиакпен әрекеттесу нәтижелері келтірілген.

$\gamma\text{-}Al_2O_3$ оксиді мен $Fe/\gamma\text{-}Al_2O_3$ жүйесінің аммиакпен әрекеттесу кезінде екеуінің де бетіндегі ИК спектроскопиясын 293-773К температура аралығында қолдану арқылы Льюис және Бренстед қышқыл орталықтары анықталды. Осы орталықтарға сәйкес келетін сіңіру жолақтарының салыстырмалы қарқындылығы аммиакпен әрекеттесу температурасына байланысты.

Алайда айтарлықтай айырмашылықтар анықталды.

Fe / $\gamma\text{-}Al_2O_3$ жүйесіне қатысты:

– сутегі байланыстарымен біріккен –OH топтарына жататын сіңіру жолақтарының санының өсуі;

– Льюис қышқылы орталықтарына байланысты сіңіру жолақтарының санының артуы;

– NH_4^+ аммоний иондарындағы N-H тобының тербелісіне сәйкес келетін жолақтың пайда болуы – Бренстед орталықтары (алюминий оксиді жағдайында валенттік діріл байқалмады).

Байқалған ерекшеліктер тірек бетінде ($\gamma\text{-}Al_2O_3$) темір кездесетін компоненттің болуына байланысты. Бұл тұжырым негізделген, өйткені Fe-O байланыстарына қарай сіңіру диапазоны $Fe/\gamma\text{-}Al_2O_3$ бастапқы жүйесінде байқалады және $Fe/\gamma\text{-}Al_2O_3$ жүйесі аммиакпен 773К әрекеттескенде сіңіру жолақтары ИК спектрінің ұзын толқындар аймағында болады, олар Al-O-Fe топтарындағы байланыстарға қатысты болып келеді. Сонымен қатар, жиілік диапазонында Льюис қышқылы орталықтарына сәйкес келетін сіңіру жолақтарының ығысуы да құрамында темір бар компоненттің адсорбция орталықтарына әсер етуін дәлелдейді.

Алюминий оксиді $\gamma\text{-}Al_2O_3$ және 3%$Fe/\gamma\text{-}Al_2O_3$, 13%$Fe/\gamma\text{-}Al_2O_3$ жүйелерін зерттеу нәтижесінде температуралық шкала бойынша 293-773К температуралық интервалында аммиактің ТПД көмегімен $\gamma\text{-}Al_2O_3$ бетінен адсорбцияланған NH_3 - беттік шкала бойынша бес шың түрінде десорбацияланатыны анықталды, ал 3% $Fe/\gamma\text{-}Al_2O_3$ және 13%$Fe/\gamma\text{-}Al_2O_3$ жүйе бетінен – жеті шың түрінде десорбацияланатыны анықталды.

Десорбцияланған аммиактың жалпы мөлшері адсорбция температурасының жоғарылауы негізінде айтарлықтай азаятындығы көрсетілді. Сонымен қатар, температураның жекелеген шыңы үшін адсорбцияланған аммиак мөлшері азайып, экстремумнан өтуі немесе шамамен өзгермеуі мүмкін. $Fe/\gamma\text{-}Al_2O_3$ жүйесі үшін қосымша десорбция шыңының пайда болуы алюминий оксидінің бетіндегі темірге байланысты.

$\gamma\text{-}Al_2O_3$ оксиді мен $Fe/\gamma\text{-}Al_2O_3$ жүйесі үшін десорбция шыңының температуралық диапазонын ескере отырып, олардың құрамында әлсіз қышқыл орталықтары (десорбция температурасы 523К дейін), орташа күштік қышқыл орталықтары (десорбция температурасы 523-тен 613К дейін) және күшті қышқыл орталықтары (десорбция температурасы 613К-тан жоғары) бар екені анықталды. Көрсетілген температура диапазонында десорбцияланған аммиактың мөлшері түрлі қышқыл орталықтарының сандық өлшемі ретінде қызмет ете алады.

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

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ВЗАИМОДЕЙСТВИЕ КАТАЛИТИЧЕСКОЙ СИСТЕМЫ $Fe/\gamma\text{-}Al_2O_3$ С МОЛЕКУЛАМИ-ЗОНДАМИ

III. ИССЛЕДОВАНИЕ ВЗАИМОДЕЙСТВИЯ АММИАКА С ОКСИДОМ $\gamma\text{-}Al_2O_3$ И СИСТЕМОЙ $Fe/\gamma\text{-}Al_2O_3$

Аннотация. Работа посвящена исследованию взаимодействия гетерогенных каталитических систем с адсорбированными молекулами. В ней представлены результаты по взаимодействию с аммиаком исходного оксида $\gamma\text{-}Al_2O_3$ и системы $Fe/\gamma\text{-}Al_2O_3$, полученные с помощью ИК-спектроскопии и метода термопрограммированной десорбции.

С помощью ИК-спектроскопии на поверхности как оксида алюминия γ-Al_2O_3 (носитель), так и системы Fe/γ-Al_2O_3 при их взаимодействии с аммиаком в температурном интервале 293–773К были обнаружены кислотные центры Льюиса и Бренстеда. Относительная интенсивность полос поглощения, отвечающих этим центрам, зависит от температуры взаимодействия с аммиаком и с её ростом падает как для оксида γ-Al_2O_3, так и для системы Fe/γ-Al_2O_3.

Вместе с тем, выявлены и существенные различия.

Для системы Fe/γ-Al_2O_3 имеет место:

- увеличение количества полос поглощения, относящихся к группам –OH, объединённых на поверхности водородными связями;

- увеличение количества полос поглощения, относящихся к льюисовским кислотным центрам;

- появление полосы, отвечающей валентным колебаниям групп N-H в ионах аммония NH_4^+, - центры Бренстеда (в случае оксида алюминия валентных колебаний не наблюдалось).

Наблюдающиеся особенности связаны с присутствием на поверхности носителя (оксида алюминия γ-Al_2O_3) железосодержащей компоненты. Такое утверждение обосновано, поскольку в исходной системе Fe/γ-Al_2O_3 наблюдается полоса поглощения, относящаяся к связям Fe-O, а при взаимодействии системы Fe/γ-Al_2O_3 с аммиаком при 773К в длинноволновой области ИК-спектров присутствуют полосы поглощения, которые, вероятней всего, относятся к связям в группах Al-O-Fe. Кроме того, о влиянии железосодержащей компоненты на центры адсорбции свидетельствует и смещение по частотному диапазону полос поглощения, отвечающих льюисовским кислотным центрам.

В результате исследований оксида алюминия γ-Al_2O_3 и систем 3%Fe/γ-Al_2O_3, 13%Fe/γ-Al_2O_3 с помощью ТПД аммиака в температурном интервале 293 – 773К установлено, что с поверхности γ-Al_2O_3 адсорбированный NH_3 по температурной шкале десорбируется в виде пяти пиков, а с поверхности систем 3%Fe/γ-Al_2O_3 и 13%Fe/γ-Al_2O_3 – в виде семи.

Показано, что суммарное количество десорбированного аммиака заметно уменьшается с ростом температуры адсорбции. При этом для отдельных температурных пиков количество адсорбированного аммиака может как уменьшаться, так и проходить через экстремум или оставаться приблизительно постоянным. Появление дополнительных пиков десорбции для системы Fe/γ-Al_2O_3 связано с нанесённой на оксид алюминия железосодержащей компонентой.

Исходя из температурного интервала существования десорбционных пиков для оксида алюминия γ-Al_2O_3 и систем 3%Fe/γ-Al_2O_3, 13%Fe/γ-Al_2O_3 сделан вывод, что в них присутствуют слабые кислотные центры (температура десорбции до 523К), кислотные центры средней силы (температура десорбции от 523 до 613 К) и сильные кислотные центры (температура десорбции свыше 613К). Объем десорбированного аммиака в указанных температурных интервалах может служить количественной мерой кислотных центров различного типа.

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

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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 poverhnostnyh soedinenij i adsorbirovannyh veshchestv. M.: Nauka. 1972, 459 s. (in Russian).

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

[5] Paukshtis E.A. Opticheskaya spektroskopiya v adsorbcii 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] Brodskij A.R., Grigor'eva V.P., Komashko L.V., Nurmakanov Y.Y., Chanysheva I.S., Shapovalov A.A., Shlygina I.A., Yaskevich V.I. Vzaimodejstvie kataliticheskoj sistemy Fe/γ-Al_2O_3 s molekulami-zondami. I. Issledovanie γ-Al_2O_3 i iskhodnoj sistemy Fe/γ-Al_2O_3 // Izvestiya NAN RK, Ser. him. i tekhn. -2018. - № 6, S.109-119. (in Russian).

[9] Brodskij A.R., Grigor'eva V.P., Komashko L.V., Nurmakanov Y.Y., Chanysheva I.S., Shapovalov A.A., Shlygina I.A., Yaskevich V.I. Vzaimodejstvie kataliticheskoj sistemy Fe/γ-Al_2O_3 s molekulami-zondami. II. Issledovanie nositelya γ-Al_2O_3 i sistemy Fe/γ-Al_2O_3 posle vzaimodejstviya s vodorodom i ammiakom // Izvestiya NAN RK, ser. him. i tekhn. 2018. № 6, S. 120-129. (in Russian).

[10] Krylov O.V. Geterogennyj kataliz. M.: IKC «Akademkniga». 2004, 663 s. (ISBN 5-94628-141-0) (in Russian).

[11] Radchenko E.D., Nefyodov B.K., Aliev R.R. Promyshlennye katalizatory gidrogenizacionnyh processov neftepererabotki. M.: Himiya. 1987, 224 s. (in Russian).

[12] Ramanovskij B.V. Osnovy kataliza. M.: Binom. 2014, 175 s. (in Russian).

[13] Goncharuk V.V., Kamalov G.L., Kovtun G.A., Rudakov E.S., Yacimirskij V.K. Kataliz: mekhanizmy gomogennogo i geterogennogo kataliza, klasternye podhody. Kiev, Naukova Dumka. – 2002, 543 s. (in Russian)

[14] Brodskiy A., Yaskevich V, Khussain B. Study of the interaction of the Fe/γ-Al_2O_3 catalytic system with ammonia in the temperature range 293-773K // EurAsian Journal of BioSciences. 2019, V.13, P. 1329-1334.

[15] Yushchenko V. V., Raschet spektrov kislotnosti katalizatorov po dannym TPD ammiaka // Zhurnal fizicheskoj himii. 1997. T. 71, № 4. S. 628-632 (in Russian).

[16] Savickij S.Yu. Opredelenie kislotnyh svojstv ceolitnogo katalizatora, promotirovannogo oksidami skandiya i galliya // Al'manah sovremennoj nauki i obrazovaniya. 2012. T.59, № 4. S. 191-192 (in Russian).

[17] Lamberov A.A., Romanova R.G., Shmelev I.G., Sopin V.F. Vliyanie kislotnogo modificirovaniya na strukturu i kataliticheskuyu aktivnost' oksida alyuminiya // Zhurnal prikladnoj himii. 2002. T.75, № 3. S. 407-412. (in Russian).

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