

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

<https://doi.org/10.32014/2018.2518-1491.33>

Volume 6, Number 432 (2018), 109 – 119

UDC 539.19;541.128.13;544.14;544.46

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

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

**INTERACTION OF THE Fe/ γ -Al₂O₃ CATALYTIC SYSTEM
WITH PROBE MOLECULES I. RESEARCH OF THE γ -Al₂O₃
AND THE Fe/ γ -Al₂O₃ INITIAL SYSTEM**

Abstract. The work is the first part of the studies devoted to the interaction of a heterogeneous catalytic system with adsorbed molecules. It presents the results for the initial oxide γ -Al₂O₃ and Fe/ γ -Al₂O₃ system with an iron content of 0.5; 3; 13% by weight, obtained with a wide range of physicochemical methods. The Fe/ γ -Al₂O₃ system was chosen as the object of the study, since it exhibits catalytic activity in many chemical processes and can later be used as a model.

The performed work showed that during the preparation of the Fe/ γ -Al₂O₃ system by impregnation, the structure of the support can be modified. The nature of the filling of the support surface with the iron-containing phase depends substantially on its percentage and can be multilayered.

It is established that the Fe/ γ -Al₂O₃ system contains iron in the form of Fe³⁺. Depending on the iron content, iron-containing aggregates of various sizes may be present in it, both in the paramagnetic and in the magnetically ordered states.

Key words: heterogeneous catalysis, physicochemical methods of investigation.

Introduction

This work is the beginning of a series of studies devoted to the interaction of a heterogeneous catalytic system with adsorbed molecules. This formulation of the problem is topical, since, in heterogeneous catalysis, the most important stage is the adsorption stage [1, 2].

The iron-containing Fe/ γ -Al₂O₃ (γ -Al₂O₃-support) system was chosen as the object of research because it exhibits catalytic activity in many chemical processes, such as the production of ammonia [3-5] and carbon nanotubes [6, 7], in CO hydrogenation reactions (Fischer-Tropsch synthesis) [8, 9], in the oxidation of hydrogen sulphide to elemental sulfur [1], deep processing of solid fossil and renewable organic raw materials [10], in gasoline reforming reactions [11], and many other reactions [12]. Thus, the catalytic system Fe/ γ -Al₂O₃ being practically multifunctional, in the future, can be used as a model system.

Experimental

The Fe/ γ -Al₂O₃ system with an iron content of 0.5; 3; 13 wt.% was prepared by impregnation [1, 13, 14] of the initial γ -Al₂O₃ oxide with an aqueous solution of iron acetate, followed by drying and calcination in air.

A wide range of physicochemical methods during the research was used.

X-ray diffractometry. The X-ray diffractometer Dron-4-07 with cobalt anode tube was used.

Mode:

- speed 2 deg/min;
- working parameters of the tube: 30 kV, 20 mA.

Transmission electron microscopy. Equipment - EM-125K, accelerating voltage of 75 kV.

Scanning electron microscopy. JSM 6610 LV, JEOL, Japan is a scanning low-vacuum electron microscope. Accelerating voltage 20 kV.

BET method (low-temperature nitrogen adsorption). Equipment -AccuSorb, Micromeritics, USA. The standard procedure. Calcination of the sample at 230-250° C for 3 hours with evacuation. The relative error in determining the specific surface area is $\pm 5\%$.

Mossbauer spectroscopy. Equipment - MS 1104Em, Russia. The source was cobalt 57 in a chromium matrix with an activity of 100 μCi . The spectra were processed on a PC by the "least squares" method. The isomeric shifts are given in terms of $\alpha\text{-Fe}$. The temperature of the spectra is 23°C. The shooting mode is "on the skylight". The error in determining the isomer shift (IS) is $\Delta\text{IS} = \pm 0.03 \text{ mm/s}$; quadrupole splitting (QS) $\Delta\text{QS} = \pm 0.03 \text{ mm/s}$; relative content (S) $\Delta\text{S} = \pm 2\%$.

Results and Discussion

The study of $\gamma\text{-Al}_2\text{O}_3$ oxide and $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system was carried out.

X-ray diffractometry.

X-ray diffraction patterns (Fig. 1) of $\gamma\text{-Al}_2\text{O}_3$ oxide and $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system with various iron contents were obtained.

Following results were obtained:

- Initial $\gamma\text{-Al}_2\text{O}_3$:

Reflexes at 4.5641; 2.7959; 2.3981; 2.2883; 1.9767; 1.5258; 1.3950 Å - $\gamma\text{-Al}_2\text{O}_3$ phase (ASTM 10-424);

- 0.5% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system:

Reflexes at 4.5641; 2.8032; 2.3815; 2.2891; 1.9781; 1.5210; 1.3994 Å - $\gamma\text{-Al}_2\text{O}_3$ phase (ASTM 10-424);

Reflexes at 4.8524; 4.3735; 4.3158; 3.3285; 2.4580; 2.3815; 1.8017; 1.7475 Å - gibbsite phase of $\text{Al}(\text{OH})_3$ (ASTM 33-18);

Reflexes at 4.1784; 2.6891; 2.4580 Å - $\alpha\text{-FeO}(\text{OH})$ (goethite) phase (ASTM 29 - 713);

- 3% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system:

Reflexes at 4.5562; 2.8003; 2.3898; 2.2807; 1.9829; 1.5214; 1.3976 Å - phase $\gamma\text{-Al}_2\text{O}_3$ (ASTM 10-424);

Reflexes at 4.8579; 4.3698; 4.3230; 3.3264; 2.4580; 2.3898; 1.7978; 1.7501 Å - gibbsite phase of $\text{Al}(\text{OH})_3$ (ASTM 33-18);

Reflexes at 4.1784; 2.6904; 2.4580 Å - $\alpha\text{-FeO}(\text{OH})$ (goethite) phase (ASTM 29 - 713)

- 13% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system:

Reflexes at 4.5681; 2.7974; 2.3908; 2.2853; 1.9733; 1.5217; 1.3994 Å - $\gamma\text{-Al}_2\text{O}_3$ phase (ASTM 10-424);

Reflexes at 4.8434; 4.3771; 4.3158; 3.3161; 2.4481; 2.3908 Å - gibbsite phase of $\text{Al}(\text{OH})_3$ (ASTM 33-18);

Reflexes at 4.1817; 2.6837; 2.4481 Å - $\alpha\text{-FeO}(\text{OH})$ (goethite) phase (ASTM 29-713).

The data obtained indicate that the original alumina is indeed $\gamma\text{-Al}_2\text{O}_3$. Partial hydrolysis of aluminum oxide occurs during the synthesis of the $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system, resulting in the formation of aluminum hydroxide in the form of gibbsite. It should be noted that the highest degree of hydrolysis is observed for the $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system with the lowest iron content and it decreases monotonically with its growth (Fig. 1). This is probably due to the fact that as the concentration of iron acetate increases, in the solution there is an ever-decreasing amount of free water capable of causing hydrolysis of aluminum oxide [15].

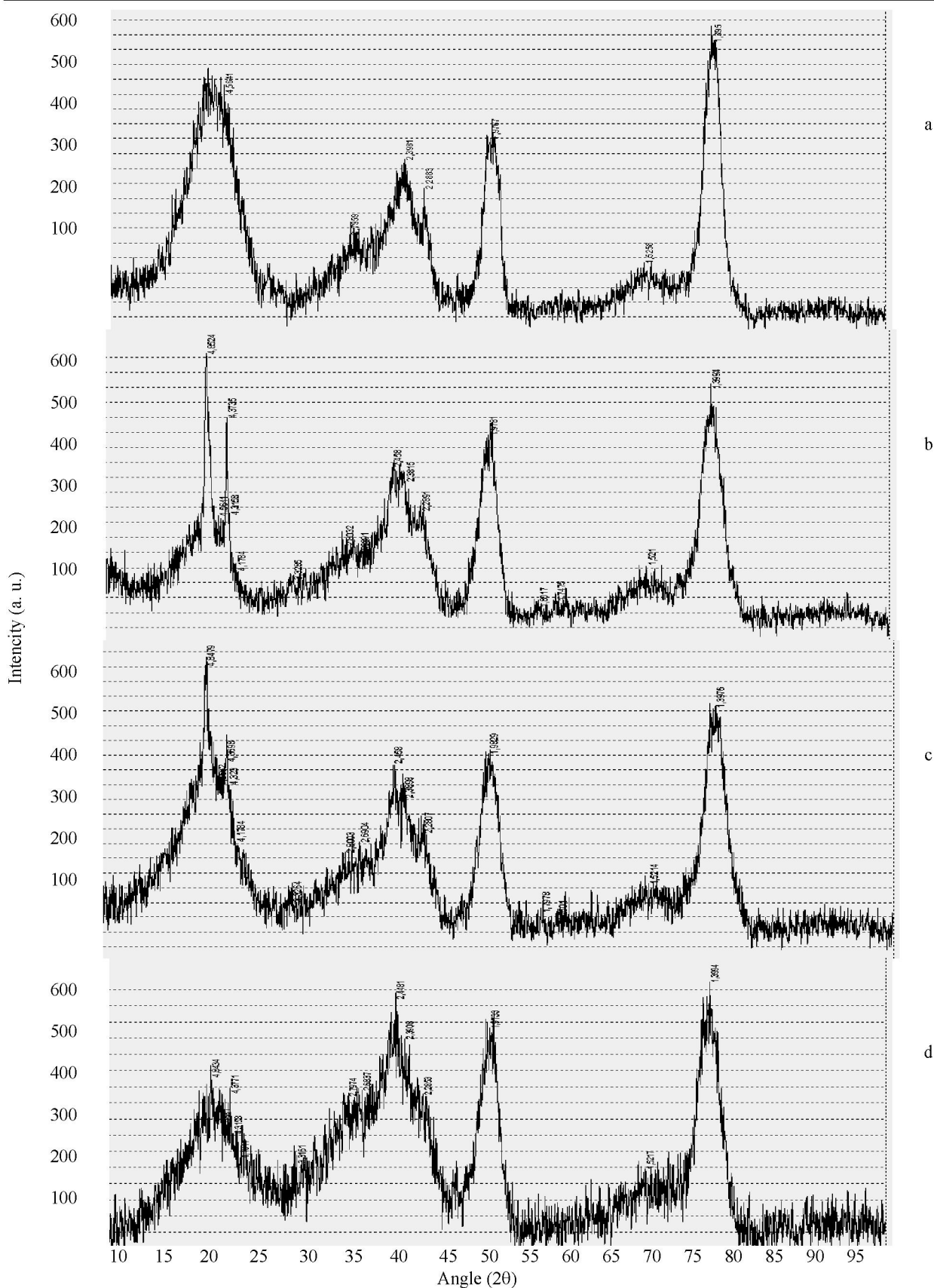


Figure 1 – Diffraction patterns of γ - Al_2O_3 oxide and Fe/ γ - Al_2O_3 system
a - γ - Al_2O_3 ; b - 0.5% Fe/ γ - Al_2O_3 ; c - 3% Fe/ γ - Al_2O_3 ; d - 13% Fe/ γ - Al_2O_3

Transmission electron microscopy.

Microphotographs of the initial aluminum oxide $\gamma\text{-Al}_2\text{O}_3$ and the $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system with different iron contents are shown in Fig. 2.

There are two kinds of particles in $\gamma\text{-Al}_2\text{O}_3$ sample. The first type is characterized by aggregates of large, semitransparent, plate-like particles with a hexagonal facets (the (111) plane of $\alpha\text{-Al}_2\text{O}_3$ crystallites) reaching almost micron sizes (400-800 nm) (Fig. 2a).

The second type of particles is small transparent plates of elongated rectangular shape (planes (001), (111) of $\gamma\text{-Al}_2\text{O}_3$ crystallites) which in the width are 5-10nm (Fig. 2b). Microdiffraction was taken from various parts of the sample. The pictures show reflexes that are located on the rings. They correspond to $\gamma\text{-Al}_2\text{O}_3$ (JCPDS, 10-425). A trace amount of $\delta\text{-Al}_2\text{O}_3$ (JCPDS, 16-394), $\text{Al}(\text{OH})_3$ gibbsite (JCPDS, 7-324) and $\theta\text{-Al}_2\text{O}_3$ (JCPDS, 11-517) also were observed.

Micrograph of the 0.5% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system is shown in Fig. 2c. It has large particles with signs of faceting ranging in size from 200 to 1000 nm. Microdiffraction produces symmetrical and individual reflexes, which correspond to $\gamma\text{-Al}_2\text{O}_3$ (JCPDS, 10-425). A large 200nm in size particle of a pointed shape and small aggregates made up of particles of 10-40 nm in size are shown in Fig. 2d. Microdiffraction gives a large number of symmetrical and individual reflexes, which can be attributed to a mixture of phases: gibbsite (JCPDS, 7-324), $\beta\text{-AlO}(\text{OH})$ Diaspore (JCPDS, 5-355), $\gamma\text{-AlOOH}$ Boehmite (JCPDS, 21-1301), with a significant predominance of the former.

Only phases of aluminum oxides and hydroxides in the sample were found. The low iron content in the system did not allow the detection of iron-containing phases because of a small amount they did not reach the field of view of the microscope.

The microphotographs of the 3% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system have many dense aggregates; also large particles of lamellar type of medium transparency are present in the sample, which is shown in Fig. 2e. A conglomerate of transparent particles of lamellar type of micron size, surrounded by small aggregates of small dense particles 5-10 nm in size is shown in Fig. 2e. Microdiffraction gives a large set of reflexes that are located along a distorted hexagonal view, and individual reflexes, which can be attributed to a mixture of the phases $\gamma\text{-FeO}(\text{OH})$ - goethite (JCPDS, 29-713), FeOOH (JCPDS, 26-792), $\text{Al}(\text{OH})_3$ - gibbsite (JCPDS, 29-41), $\gamma\text{-Al}_2\text{O}_3$ (JCPDS, 10-425).

There is an aggregate of transparent particles of lamellar type ~ 0.5 micron in size for a 13% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system in Fig. 2g. Microdiffraction gives reflexes located on a distorted hexagonal view, which can be referred to $\delta\text{-FeOOH}$ (JCPDS, 13-87). In addition, this micrograph has round-shaped particles with dimensions of 10-30nm. Microdiffraction gives reflexes (rings) related to FeOOH (JCPDS, 26-792). In Fig. 2h, the particles are larger, for them microdiffraction shows a large set of reflections of the following phases: Fe_2O_3 (JCPDS, 32-469) and $\gamma\text{-Al}_2\text{O}_3$ (JCPDS, 10-425).

Scanning electron microscopy

Microphotographs of the initial aluminum oxide $\gamma\text{-Al}_2\text{O}_3$ and the $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system with different iron content are shown in Fig. 3.

From microphotographs it follows that aggregates of various sizes (Fig. 3a, b, c) are present on the surface of the support $\gamma\text{-Al}_2\text{O}_3$, from tens to micrometers. Porous structure of the support surface is clearly visible when the magnification is large (Fig. 3c).

The relief of the support is "smoothed" when the acetate of iron is deposited on $\gamma\text{-Al}_2\text{O}_3$ (Figure 3), and the effect is most pronounced at 13% iron content. It can be assumed that an iron-containing film (crust) is formed on the surface of the support, and this, in fact, leads to a visible "smoothing" effect of the relief. In the case of the $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system with 0.5% iron content (Fig. 3d, e, f), the complete surface coverage of the $\gamma\text{-Al}_2\text{O}_3$ support by the iron-containing component is not noticeable, apparently due to its small amount. On the contrary, it can be assumed that for a system with 13% iron content (Fig. 3 j, k, l), the coating is multilayer.

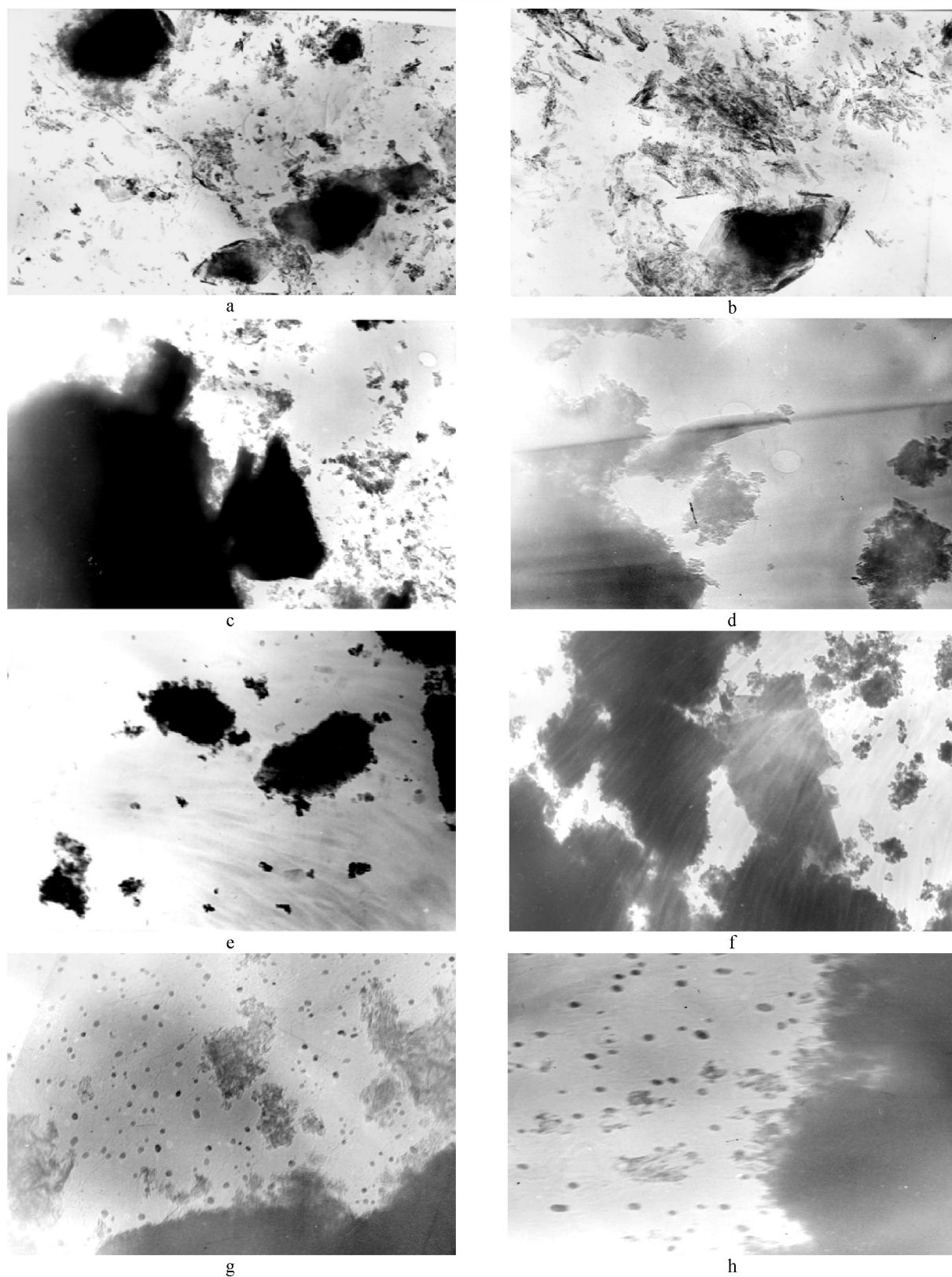


Figure 2 - Micrographs of the initial aluminum oxide $\gamma\text{-Al}_2\text{O}_3$ and the $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system with an iron content of 0.5; 3 and 13%
a, b - initial $\gamma\text{-Al}_2\text{O}_3$ oxide; c, d – 0.5% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system; e, f - 3% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system; g, h 13% $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system.
Magnification: a, c, e, f – 24000 times; b, d, g, h – 50000 times

BET method

Specific surface area and its texture (porosity) for $\gamma\text{-Al}_2\text{O}_3$ oxide and $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system with different iron content are determined. The results are shown in Table 1 and are shown in Fig. 4. The data for $\gamma\text{-Al}_2\text{O}_3$ in agreement with the results of [16].

Table 1 – The specific surface area of the $\gamma\text{-Al}_2\text{O}_3$ oxide and the $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ system

Sample	Parameter		
	SW, m^2/g	V_{ADSmax} , mL/g	V_{true} , mL/g
$\gamma\text{-Al}_2\text{O}_3$	214	180	0,28
0.5%Fe/ $\gamma\text{-Al}_2\text{O}_3$	211	196	0,31
3%Fe/ $\gamma\text{-Al}_2\text{O}_3$	190	115	0,18
13%Fe/ $\gamma\text{-Al}_2\text{O}_3$	173	101	0,16

Note: SW - specific surface area, m^2/g ;
 V_{ADSmax} - total pore volume with gas filling, mL/g;
 V_{true} - total true pore volume, mL/g

From Table 1 it follows that when the iron is precipitated to the support, as the content thereof increases, the value of the specific surface tends to decrease, indicating the filling of the surface.

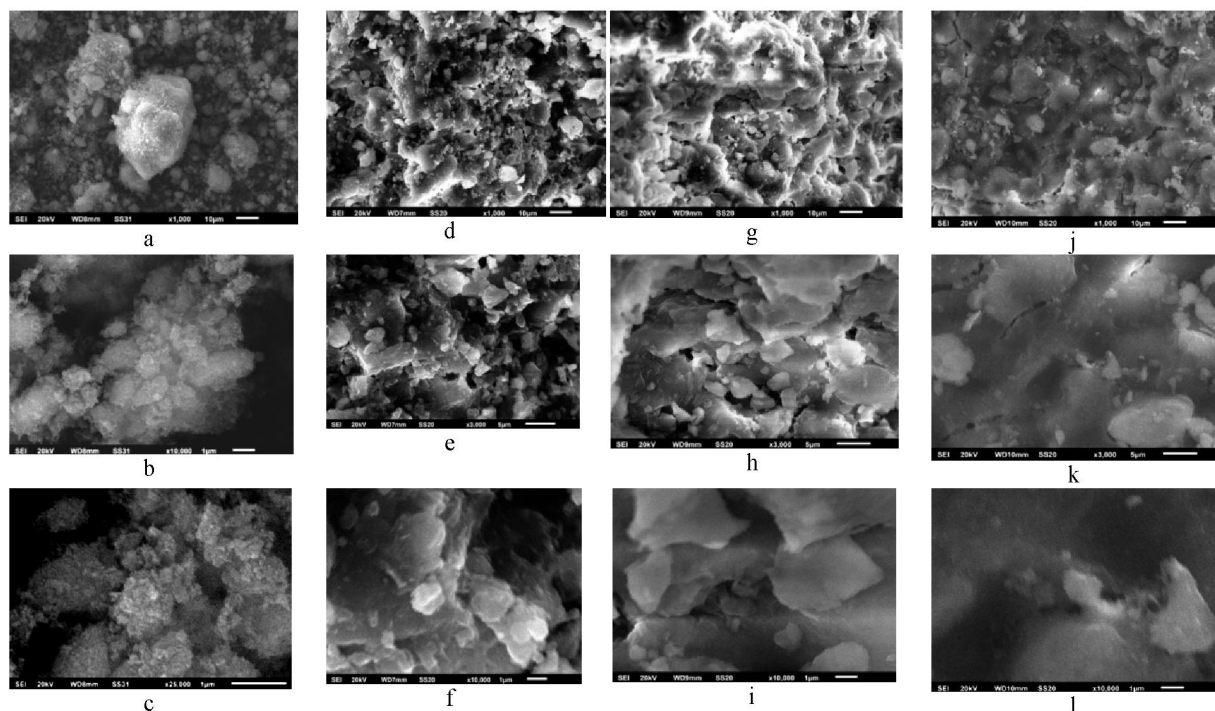


Figure 3 - Microphotographs of aluminum $\gamma\text{-Al}_2\text{O}_3$ and $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ systems with different iron content
 $\gamma\text{-Al}_2\text{O}_3$ - (a, b, c); 0.5%Fe/ $\gamma\text{-Al}_2\text{O}_3$ (d, e, f); 3%Fe/ $\gamma\text{-Al}_2\text{O}_3$ (g, h, i); 13%Fe/ $\gamma\text{-Al}_2\text{O}_3$ (j, k, l).
Magnification: (a, d, g, j) – 1000 times; (e, h, k) – 3000 times; (b, f, i, l) – 10000 times; (c) – 25000 times

At the same time, the pore volume has a maximum at the point for the system of 0.5%Fe/ $\gamma\text{-Al}_2\text{O}_3$. The presence of an extremum can probably be explained by the hydrolysis of $\gamma\text{-Al}_2\text{O}_3$ and the transition of a part of aluminum oxide to the hydroxide, which was discussed above. In aluminum hydroxide, the total pore volume is noticeably higher than that of $\gamma\text{-Al}_2\text{O}_3$ [17]. Since the iron-containing component does not completely cover the support surface in the 0.5%Fe/ $\gamma\text{-Al}_2\text{O}_3$ system (Fig. 3d, e, f), therefore, at least some of the pores of the hydroxide are accessible.

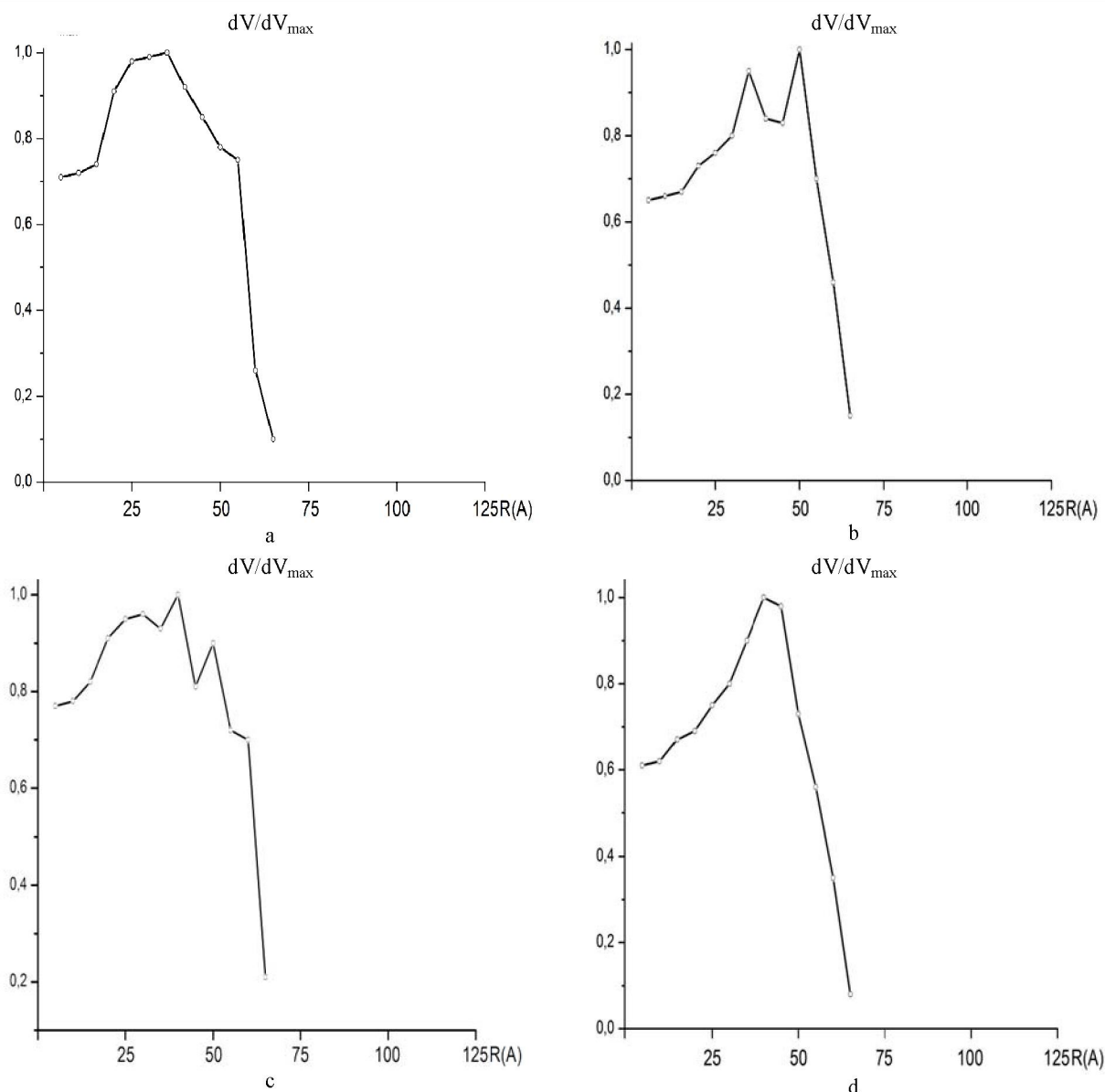


Figure 4 - Pore size distribution in γ - Al_2O_3 and in the Fe/γ - Al_2O_3 system with different iron content

a - γ - Al_2O_3 ; b - 0.5% Fe/γ - Al_2O_3 ; c - 3% Fe/γ - Al_2O_3 ; d - 13% Fe/γ - Al_2O_3

$R(\text{\AA})$ is the pore radius in angstroms (\AA); dV/dV_{max} the ratio of the pore volume of a given radius to the maximum volume

The combination of these factors may lead to an increase in the total pore volume for the 0.5% Fe/γ - Al_2O_3 system.

With an increase in the iron content the total pore volume decreases which on one side may indicate their possible filling, and on the other hand, the difficulty of accessing the probe gas (nitrogen). The latter can be indicated by scanning electron microscopy data (Figure 3), from which it follows that with a high content of iron in the system, the support surface is almost completely closed.

In Fig. 4 - pore size distribution for γ - Al_2O_3 and Fe/γ - Al_2O_3 . The pore size for γ - Al_2O_3 and the Fe/γ - Al_2O_3 system fits within a narrow range of values and their radius does not exceed 65-70 \AA (Fig. 4). When the iron-containing component is applied to alumina, the pore size distribution in comparison with γ - Al_2O_3 (Fig. 4a) varies, for 0.5% Fe/γ - Al_2O_3 , a "dip" is observed in the 40-45 \AA region (Fig. 4b), it follows that in the first place pores of this size are filled. For the 3% Fe/γ - Al_2O_3 system, this "gap" is retained, although the shape of the distribution varies (Fig. 4c), which is apparently related to the filling of the surface with

an iron-containing component. For a system of 13%Fe/ γ -Al₂O₃, due to the filling of the surface, the access of the probe gas to the pores of small size is essentially limited and the pore size distribution shows the presence of basically larger pores (Fig. 4d). All this occurs against the background of a decrease in the total volume of pores (Table 1).

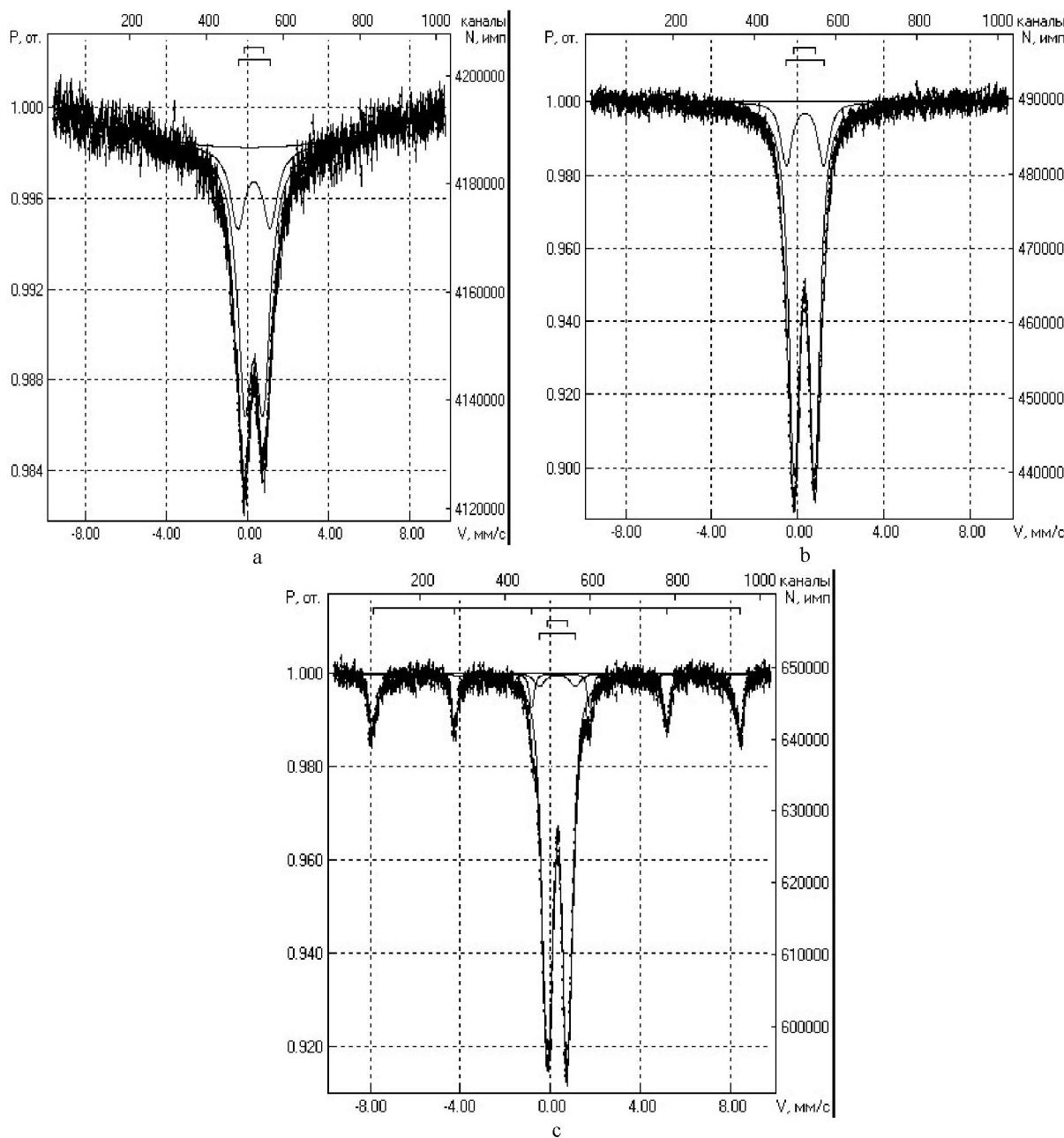


Figure 5 - Mössbauer spectra of the Fe/ γ -Al₂O₃ system with different iron content
a – 0.5%Fe/ γ -Al₂O₃; b – 3%Fe/ γ -Al₂O₃; c – 13%Fe/ γ -Al₂O₃

Mössbauer spectroscopy

Mössbauer spectra of the Fe/ γ -Al₂O₃ system with different iron contents are shown in Figure 5. The spectra showed that the system, based on the values of isomeric shifts, contains various forms of Fe³⁺ both in the paramagnetic state and in the magnetically ordered one.

The following iron forms are present in the system:

0.5%Fe/ γ -Al₂O₃

Fe_i³⁺ form - IS = 0.32 mm•s⁻¹; QS = 0.95 mm•s⁻¹; S = 62%

Fe_2^{3+} form - IS = 0.32 mm•s⁻¹; QS = 1.59 mm•s⁻¹; S = 38%

3%Fe/ γ -Al₂O₃

Fe_1^{3+} form - IS = 0.31 mm•s⁻¹; QS = 0.98 mm•s⁻¹; S = 70%

Fe_2^{3+} form - IS = 0.32 mm•s⁻¹; QS = 1.62 mm•s⁻¹; S = 30%

13%Fe/ γ -Al₂O₃

Fe_1^{3+} form - IS = 0.32 mm•s⁻¹; QS = 0.93 mm•s⁻¹; S = 77%

Fe_2^{3+} form - IS = 0.31 mm•s⁻¹; QS = 1.59 mm•s⁻¹; S = 3%

α -Fe₂O₃ - IS = 0.37 mm•s⁻¹; QS = - 0.21 mm•s⁻¹; H_{eff} = 506 kOe; S = 20%

(H_{eff} is the Zeeman hyperfine magnetic splitting)

The forms of Fe_1^{3+} and Fe_2^{3+} , irrespective of the iron content in the Fe/ γ -Al₂O₃ system, have similar parameters and are paramagnetic. At the same time, having almost identical IS, they differ significantly in QS. The shape of Fe_2^{3+} with a large value of QS can be attributed to iron on the surface of the support, and the form of Fe_1^{3+} with smaller QS - to a more deeply located [18, 19].

It should be noted that with an increase in the iron content in the system, a gradual increase in the relative content of the more deeply located form of Fe_1^{3+} takes place, which agrees with the BET data.

There is also a magnetically ordered phase that corresponds to α -Fe₂O₃ in the 13% Fe/ γ -Al₂O₃ system, in addition to the Fe_1^{3+} and Fe_2^{3+} forms [20]. A somewhat smaller value of H_{eff} (should be 515-517 kOe) indicates that the particles giving in the Mössbauer spectrum of the Zeeman hyperfine magnetic splitting are of the order of 8-12 nm [21]. At such particle sizes, H_{eff} has a smaller value than for bulk samples.

Conclusion

The performed work has shown that during the preparation of the Fe/ γ -Al₂O₃ system by impregnation, the structure of the support can be modified. The nature of the filling of the support surface with the iron-containing phase depends substantially on its percentage and can be multilayered.

It has been established that the Fe/ γ -Al₂O₃ system contains iron in the form of Fe^{3+} . Depending on the iron content, iron-containing aggregates of various sizes can be present in the system, both in the paramagnetic and magnetically ordered states.

Acknowledgments

The work was supported by the Ministry of Education and Science of the Republic of Kazakhstan (AP05130654).

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**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

МОЛЕКУЛА ЗОНДЫ БАР Fe/ γ -Al₂O₃ КАТАЛИЗДІК ЖҮЙЕНІҢ ӨЗАРА ӘРЕКЕТТЕСТІГІ I. γ -Al₂O₃ ЖӘНЕ Fe/ γ -Al₂O₃ БАСТАПҚЫ ЖҮЙЕНІҢ ЗЕРТТЕЛУІ

Бұл жұмыс адсорбцияланған молекулаға ие гетерогенді катализдік жүйенің өзара әрекеттестігіне арналған зерттеудің бірінші бөлігі болып табылады. Оған бастапқы γ -Al₂O₃ тотығы және 0,5; 3; 13 вес.% темір мөлшері бар Fe/ γ -Al₂O₃ жүйесі бойынша кең ауқымды физика-химиялық әдістер жиынтығы көмегімен алынған нәтижелер ұсынылған. Көптеген химиялық процестерде катализдік белсенділік көрсетіп, келешекте модельдік ретінде қолдану мүмкіндігі болғандықтан Fe/ γ -Al₂O₃ жүйесі зерттеу нысаны болып таңдалған болатын.

Жүргізілген жұмыс сіңіру әдісімен Fe/ γ -Al₂O₃ жүйесін дайындау процесінде тасығыш құрылымының модификациясы мүмкін екендігін көрсетті. Темірқұрамды фазамен тасығыш бетінің толтырылу сипаты айтарлықтай оның пайыздық мөлшеріне тәуелді және көп қабатты болуы мүмкін.

Fe/ γ -Al₂O₃ жүйесі Fe³⁺ формалы темір құрайтындығы анықталды. Темірдің мөлшеріне байланысты оған әртүрлі пішіндегі, яғни парамагнитті және магнит тәртіпті күйдегі темірқұрамды агрегаттар қатысуы мүмкін.

УДК 539.19;541.128.13;544.14;544.46

**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 I. ИССЛЕДОВАНИЕ γ -Al₂O₃ И ИСХОДНОЙ СИСТЕМЫ Fe/ γ -Al₂O₃

Аннотация. Работа является первой частью исследований, посвящённых взаимодействию гетерогенной каталитической системы с адсорбированными молекулами. В ней представлены результаты по исходному

оксиду $\gamma\text{-Al}_2\text{O}_3$ и системе $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ с содержанием железа 0,5; 3; 13 вес.%, полученные с помощью широкого набора физико-химических методов. Система $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ была выбрана объектом исследования, поскольку она проявляет каталитическую активность во многих химических процессах и в дальнейшем может быть использована как модельная.

Проведённая работа показала, что в процессе приготовления системы $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ методом пропитки возможна модификация структуры носителя. Характер заполнения поверхности носителя железосодержащей фазой существенно зависит от её процентного содержания и может быть многослойным.

Установлено, что система $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ содержит железо в форме Fe^{3+} . В зависимости от содержания железа, в ней могут присутствовать железосодержащие агрегаты различного размера, как в парамагнитном, так и в магнитоупорядоченном состояниях.

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

Information about authors:

Brodsky Alexander Rafaelevich-Ph. D., Assoc. Professor, head of the laboratory. Institute of fuel, catalysis and electrochemistry. D. In Sokolsky, Almaty. albrod@list.ru, <https://orcid.org/0000-0001-6216-4738>;

Grigorieva Valentina Petrovna - researcher, Institute of fuel, catalysis and electrochemistry. D. In Sokolsky, Almaty. grig1944@inbox.ru, <https://orcid.org/0000-0002-1807-8530>;

Komashko Larisa Vladimirovna - researcher, Institute of fuel, catalysis and electrochemistry. D. In Sokolsky, Almaty. komashko535@mail.ru, <https://orcid.org/0000-0003-0031-2816>;

Nurmakhanov Aslambekovich Yerzhan – PhD, senior researcher, Institute of fuel, catalysis and electrochemistry. D. In Sokolsky, Almaty. yerzhan.nurmakhanov@gmail.com, <https://orcid.org/0000-0002-0404-1833>;

Irina S. Chanysheva - researcher, Institute of fuel, catalysis and electrochemistry. D. In Sokolsky, Almaty. chanysheva37@mail.ru, <https://orcid.org/0000-0002-7286-6036>;

Anatoly Shapovalov-Ph. D., Assoc. Professor, senior researcher, Institute of fuel, catalysis and electrochemistry. D. In Sokolsky, Almaty. shapov1937@mail.ru, <https://orcid.org/0000-0003-0386-5838>;

Slugina Irina artyomovna – Ph. D., leading researcher, Institute of fuel, catalysis and electrochemistry. D. In Sokolsky, Almaty. iashlygina@mail.ru, <https://orcid.org/0000-0002-0883-1007>;

Yaskevich Vladimir Ivanovich - researcher, Institute of fuel, catalysis and electrochemistry. D. In Sokolsky, Almaty. yaskevich46@mail.ru, <https://orcid.org/0000-0001-9342-8337>