

THE INVESTIGATION OF THE STATES OF Cr, Co, Ni, Bi AND K IONS, DEPOSITED ON γ -Al₂O₃ IN THE COMPOSITION OF THE DEHYDROGENATION CATALYST BY ESDO AND RENTGENOGRAPHY METHODS

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The use of the deposited catalysts, which have more high mechanical strength, thermostability and relatively low inputs on their synthesis are the most suitable in the comparison with massive dehydrogenation catalysts. The data on the states of Cr, Ni, Bi, Co and K ions, deposited on γ -Al₂O₃, including in the composition of the catalysts of the paraffin hydrocarbons C₃-C₄ are presented in the given paper. The catalysts prepared in the atmospheric conditions and in the conditions of the low pressure were used. It is established, that valency and coordinative states of ions of transitive metals (Cr, Ni, Co) depend on the conditions of the catalyst preparation. The metal ions in the oxidated form are present in the samples of the catalysts, prepared in the atmospheric conditions. As oxidate forms of metal ions, so the restored ones are presented in the catalysts, prepared in the vacuum conditions. It is supposed, that high activity of the catalysts, obtained in the vacuum conditions, is caused by the presence of the oxidated and restored forms of the active components in the system.

The processes of the catalytic dehydrogenation of the paraffin hydrocarbons are included in the number of most big-volume processes of the world oil-chemical industry. This is connected firstly with the increase of the demand on the olefinic hydrocarbons, which are used for the obtaining: of the synthetic rubbers, plastics, the components of the automotive fuel (meliltretbutyl ether) and other valuable chemical products. The constant high quantity of the investigations, carried out on the perfection already existed and the working of the new dehydrogenation catalysts is caused by this [1-3].

The one of the perspective direction of the perfection of already existed dehydrogenation catalysts is their promotion by the oxides of the rare-earth elements [1-3].

The process of the dehydrogenation of propane on Cr, Co, Ni, Bi and K/ γ -Al₂O₃ catalysts has been worked in the IOCP of NAS of Azerbaijan.

The results of the states of ion metals (Cr, Ni, Bi, Co and K) in the composition of single-, double-, three-component samples of massive catalysts, prepared in the conditions of the lowered and atmospheric pressure were presented in the previous ref [4].

It is established, that catalysts of the samples, prepared in the atmospheric conditions have only oxidated forms of the given metals. In the difference from it, the samples of the catalysts, prepared in the vacuum conditions have as oxidated (Cr⁵⁺, Cr³⁺(O_h), Ni²⁺(O_h) and Co³⁺, Co²⁺), so the restored forms of the given metals (Cr⁰, Ni⁰, Co⁰).

It is established, that the coexistence of the oxidated and restored ions of these metals causes the relatively high catalytic activity of catalyst samples, synthesized in the vacuum conditions.

However, the use of the massive catalysts connects with set of defects, such as: the difficulties at the formation of catalyst granules in the stage of its preparation, relatively low thermal and mechanical stability, high capital inputs, connected with the use of the big quantity of metal salts.

Taking under the consideration the above mentioned, the use of the deposited catalysts on the base of the relatively cheap carrier - γ -Al₂O₃, which supplies the high enough mechanical strength and thermostability, low capital inputs on catalyst synthesis is the more suitable. Moreover, γ -Al₂O₃

is well connecting component, which supplies the quality and easy-to use formation of catalyst granule of its preparation.

Starting from the above mentioned suppositions, the subject of the given paper is the investigation of the states of Cr, Co, Ni, Bi and K, deposited on γ -Al₂O₃.

Experiment system

The definition of the catalyst activity was carried out in quartz reactor with stationary layer of catalyst, at volume advance speed of raw 400h⁻¹ and temperature in reactive band 590°C. The output of propylene on the passed raw was 49,5% at the selectivity 90,03% (mol).

The catalyst was prepared by the way of the marking of nitrates of the salts of corresponding metals on формула, previously treated by the drying at the temperature 400°C, with the aim of the release of catalyst pores from the air and water steams. The calcinations were carried out in the conditions as the lowered, so the atmospheric pressure at the temperature 600-620°C during eight hours.

The electronic spectrums of diffusion reflection (ESDR) have been fixed on the spectrophotometer "Specord M40" in the region 50000-10000 cm⁻¹.

The experiment results

Let's consider the results of spectral investigation of ion states in the composition of studied catalysts (electronic spectroscopy of diffusion reflection).

The oxide systems Ni (5;10;25 and 86,8%)- γ -Al₂O₃ (95;90;75 and 13,2%)

The well-released absorption bands (a.b.) in the region 13000, 15800, 16700 and 27500 cm⁻¹ are observed in the catalyst spectrum, consisting on 5% Ni (fig.1, c.1). The sample has blue color. The observable a.b. can be interpreted by the following way, taking under the consideration from [5, 6]:

- a.b. at 13000 and 27500 cm⁻¹ are registered to the absorption of Ni²⁺ ions, stabilized in the fields of octahedral

coordination (transfers ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ correspondingly);

- a.b. in the regions 15800 and 16700 cm^{-1} show on the existence of the tetrahedrally coordinated ions of $\text{Ni}^{2+}(\text{T}_d)$ in the system [(transfers ${}^3T_1(\text{F}) \rightarrow {}^3T_1(\text{P})$ and ${}^3T_1(\text{F}) \rightarrow {}^3E_1(\text{D})$ correspondingly)].

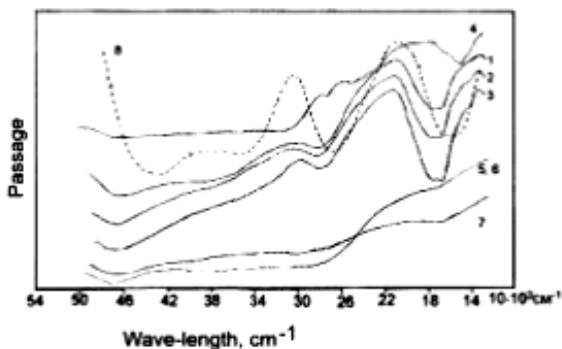


Fig.1. The spectrums of diffusion reflection of catalysts:

1. Ni (5%)- $\gamma\text{-Al}_2\text{O}_3$ (95%) - obtained at the atmospheric pressure
2. Ni (10%)- $\gamma\text{-Al}_2\text{O}_3$ (90%) - obtained at the atmospheric pressure
3. Ni (25%)- $\gamma\text{-Al}_2\text{O}_3$ (75%) - obtained at the atmospheric pressure
4. Ni (86,8%)- $\gamma\text{-Al}_2\text{O}_3$ (13,2%) - obtained at the atmospheric pressure
5. Ni (5%)- $\gamma\text{-Al}_2\text{O}_3$ (95%) - obtained in the vacuum conditions
6. Ni (10%)- $\gamma\text{-Al}_2\text{O}_3$ (90%) - obtained at the vacuum conditions
7. Ni (25%)- $\gamma\text{-Al}_2\text{O}_3$ (75%) - obtained at the vacuum conditions
8. Ni (86,8%)- $\gamma\text{-Al}_2\text{O}_3$ (13,2%) - obtained at the vacuum conditions

It is known, that nickel ions are presented as in octahedral, so in the tetrahedral coordination in the NiAl_2O_4 spinel, which is mixed. The formula of this spinel can be presented as $\text{Ni}_{1/4}\text{Al}_{3/4}[\text{Ni}_{3/4}\text{Al}_{5/4}]\text{O}_4$. It can be proposed, that the surface mixed spinel NiAl_2O_4 creates in our conditions also.

The increase of intensity of a.b. from ions of $\text{Ni}^{2+}(\text{O}_h)$ and $\text{Ni}^{2+}(\text{T}_d)$ is observed with the increase of the nickel concentration till 10 and 25% (fig.1, c. 2 and 3). The spectrum of the sample, consisting 86,8% of Ni significantly differs from the previously spectrums. Thus, the set of a.b. at 14000, 15500, 21700, 23900, 26400 cm^{-1} , characteristic for Ni^{2+} ions is observed in the composition of NiO phase, that explain the green color of the sample (fig.1,c.4).

The given conclusion doesn't exclude the presence of NiAl_2O_4 spinel in the system. From it the another important conclusion is obtained, firstly at the high concentrations of nickel on $\gamma\text{-Al}_2\text{O}_3$ surface the octahedral and tetrahedral vacancies are filled by nickel ions with the creation of NiAl_2O_4 spinel, later the process of formation of NiO phase is carried out.

The spectrums of the samples, consisting 10, 15 and 25% of nickel, obtained in the vacuum conditions significantly differ from the spectrums of the samples of analogical compositions, obtained in the conditions of the air atmosphere. Thus, the strong decrease of the intensity of a.b. from ions of $\text{Ni}^{2+}(\text{O}_h)$ and $\text{Ni}^{2+}(\text{T}_d)$ (fig. 1, c.5, 6 and 7) is

observed. Probably, the process of the partial reconstruction of $\text{Ni}^{2+}(\text{O}_h)$ and $\text{Ni}^{2+}(\text{T}_d)$ ions till Ni^0 carries out in the vacuum conditions.

Thus, at the relative low concentrations (5,10 and 25%) as the oxidated [$\text{Ni}^{2+}(\text{O}_h)$ and $\text{Ni}^{2+}(\text{T}_d)$], so the restored (Ni^0) forms of nickel are stabilized in the system.

The catalyst, consisting 86,8% of Ni and has obtained in the vacuum conditions, has the spectrum, which differs from spectrums of the systems, consisting the relatively less quantity of nickel (fig. 1, c.8). In this case the increase of intensity of a.b. from the ions of Ni^{2+} in NiO phase and their significant expansion is observed. Probably this effect connects with the processes of agglomeration and enlargement of NiO particles, where the strong spin-spin interaction leads to the increase of the intensity and widening of a.b.

The oxide system Cr(10 and 25%)- $\gamma\text{-Al}_2\text{O}_3$ (90 and 75%)

The a.b. are observed in the catalyst spectrum, consisting 10% of Cr and obtained in the atmospheric air in the regions 14400, 17000, 22000, 23000 and 27000 cm^{-1} (fig.2, c.1). The sample has the green-yellow color. The bands in the regions 14400, 22000 and 27000 cm^{-1} can be registered to the Cr^{5+} ions, and at 17000 and 23000 cm^{-1} to the $\text{Cr}^{3+}(\text{O}_h)$ ions (the transfers ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ correspondingly). Probably, the surface of the sample has two types of Cr ions: Cr^{5+} and $\text{Cr}^{3+}(\text{O}_h)$.

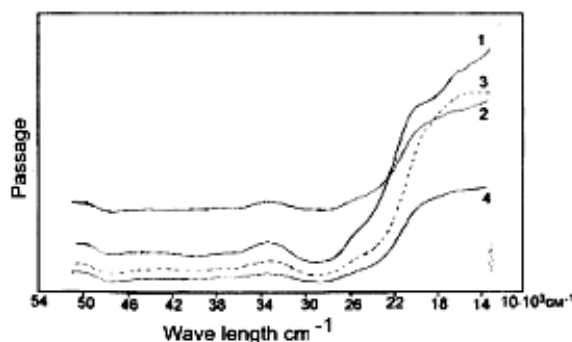


Fig.2. The spectrums of diffusion reflection of catalysts:

1. Cr (5%)- $\gamma\text{-Al}_2\text{O}_3$ (95%) - obtained at the atmospheric pressure
2. Cr (25%)- $\gamma\text{-Al}_2\text{O}_3$ (75%) - obtained at the atmospheric pressure
3. Cr (5%)- $\gamma\text{-Al}_2\text{O}_3$ (95%) - obtained in the vacuum conditions
4. Cr (25%)- $\gamma\text{-Al}_2\text{O}_3$ (75%) - obtained in the vacuum conditions

The increase of the Cr content in the system till 25% leads to the increase of the common absorption background and some degradation of a.b. from Cr^{5+} and $\text{Cr}^{3+}(\text{O}_h)$ ions (fig.2, c.2). The sample has the biscuit color that shows on the increase of the content of Cr_2O_3 phase in the system (in the pure form the Cr_2O_3 phase has the brown color).

The significant decrease of the intensity of a.b. from $\text{Cr}^{3+}(\text{O}_h)$ and Cr^{5+} ions is observed in the catalyst spectrums, obtained in the vacuum conditions. Probably the process of partial reconstruction of $\text{Cr}^{3+}(\text{O}_h)$ and Cr^{5+} ions till Cr^0 carries out in the conditions of the lowered pressure. In the given case the oxidated (Cr^{3+} and Cr^{5+}) and restored forms of Cr (Cr^0) coexist on the catalyst surface.

The oxide systems Cr(50;25;50%)-Ni(16,7;50;25%)- γ -Al₂O₃ (33,3; 25; 25%)

The a.b. in the regions 13000, 14000, 15500, 22000, 23000 and 26000 cm⁻¹ are observed in the sample spectrums, obtained in the air atmosphere (fig.3, c.1).

The observable a.b. can be explained by the following method:

- a.b. at 23000 and 26000 cm⁻¹ can be registered to Cr⁵⁺ ions;

- a.b. at 22000 cm⁻¹ can be registered to Cr³⁺(O_h) ions (transfer ⁴A_{2g}→⁴T_{2g}).

The rest a.b. from Cr³⁺(O_h) ions are masked by the more intensive background absorption.

- a.b. at 13000, 15500 cm⁻¹ are characteristics for Ni²⁺ ions in the composition of NiO phase. The green color of the sample also shows on this fact. The given conclusion also doesn't exclude the presence of NiAl₂O₄ spinel in the system, where probably a.b. from Ni²⁺(O_h) and Ni²⁺(T_d) ions are masked by a.b. from Cr⁵⁺(Cr³⁺)ions and NiO phase.

Thus, Cr⁵⁺, Cr³⁺ ions and NiO, NiAl₂O₄ phases are stabilized on the catalyst surface.

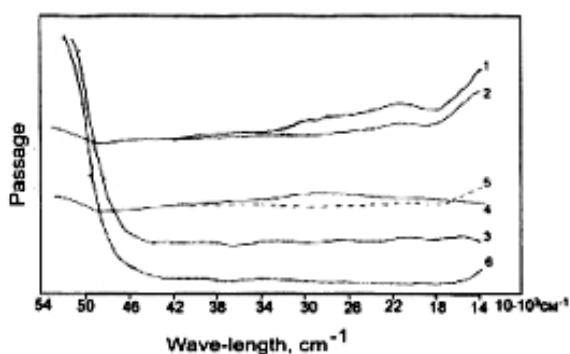


Fig.3. The spectrums of diffusion reflection of catalysts:

1. Cr (25%)-Ni (50%)- γ -Al₂O₃ (25%) – obtained at the atmospheric pressure
2. Cr (50%)-Ni (25%)- γ -Al₂O₃ (25%) – obtained at the atmospheric pressure
3. Cr (50%)-Ni (16,7%)- γ -Al₂O₃ (33,3%) – obtained at the atmospheric pressure
4. Cr (25%)-Ni (50%)- γ -Al₂O₃ (25%) – obtained in the vacuum conditions
5. Cr (50%)-Ni (25%)- γ -Al₂O₃ (25%) – obtained in the vacuum conditions
6. Cr (50%)-Ni (16,7%)- γ -Al₂O₃ (33,3%) – obtained in the vacuum conditions

The disappearance of a.b. at 14000 and 26000 cm⁻¹ is observed in the spectrum at the increase of the Cr concentration till 50% (at the simultaneous decrease of Ni concentration till 25%). Moreover, the intensity of the other a.b. with simultaneous their widening is observed (fig.3, c.2). The sample has brown-green color. Probably the quantity of the surface phase Cr₂O₅ increases at the high concentrations of Cr. The brown constituent of the sample color (in pure form Cr₂O₅ has the brown color) shows on this fact and this leads to the increase of the absorption background and widening of some a.b. Moreover, the part of a.b. from Cr³⁺(O_h) and Ni²⁺(O_h) ions is masked by strong background absorption.

Thus, the catalyst surface is enriched by Cr₂O₅ and NiO phases at relative high Cr concentration.

The decrease of Ni concentration till 16,7% significantly doesn't influence on the spectrum character (at the saving of Cr concentration 50%) (fig.3, c.3). The spectrums of all three catalysts, obtained in the vacuum are characterized by the spectrums, where the total absorption is observed, covering practically all investigated area (fig.3, c.4,5 and 6). Moreover, the samples have gray-black color with bluish shine. The processes of partial reconstruction of Cr⁵⁺, Cr³⁺(O_h) and Ni²⁺(O_h) ions till Cr⁰ and Ni⁰ rather carry out in the samples. It is followed, that the oxidated [Cr⁵⁺, Cr³⁺(O_h) and Ni²⁺(O_h) (in NiO phase)] and restored forms of Cr and Ni (Cr⁰ and Ni⁰) coexist on the surface of the catalyst.

The oxide system Cr(54,1%)-Bi(13,5%)- γ -Al₂O₃ (32,4%)

The total structureless intensive absorption, covering all area is observed in the catalyst spectrum, obtained in the air atmosphere (fig.4, c.1). The sample has black color. On account on this the spectrum interpretation is impossible, but it can be supposed about the presence Cr₂O₅, Cr₂O₃ in the phase system and Bi³⁺ in phase.

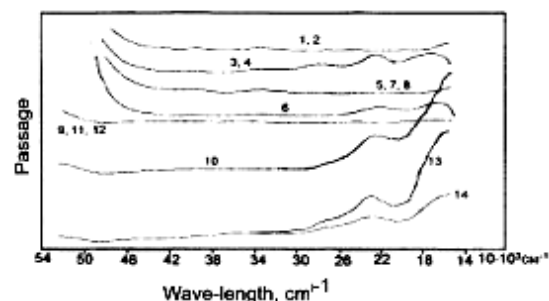


Fig.4. The spectrums of diffusion reflection of catalysts:

1. Cr (54,1%)-Bi (13,5%)- γ -Al₂O₃ (32,4%) – obtained at the atmospheric pressure
2. Cr (54,1%)-Bi (13,5%)- γ -Al₂O₃ (32,4%) – obtained in the vacuum conditions
3. Cr (87,7%)-Bi (7,4%)- γ -Al₂O₃ (4,9%) – obtained at the atmospheric pressure
4. Cr (87,7%)-Bi (7,4%)- γ -Al₂O₃ (4,9%) – obtained in the vacuum conditions
5. Cr (60%)-Bi (20%)- γ -Al₂O₃ (20%) – obtained at the atmospheric pressure
6. Cr (60%)-Bi (20%)- γ -Al₂O₃ (20%) – obtained in the vacuum conditions
7. Cr (67,1%)-Ni (22,4%)-K (5,6%)- γ -Al₂O₃ (4,9%) – obtained at the atmospheric pressure
8. Cr (67,1%)-Ni (22,4%)-K (5,6%)- γ -Al₂O₃ (4,9%) – obtained in the vacuum conditions
9. Cr (57%)-Ni (19%)-Bi (14,3%)- γ -Al₂O₃ (9,7%) – obtained at the atmospheric pressure
10. Cr (10,2%)-Ni (4,3%)-Bi (16%)- γ -Al₂O₃ (69,5%) – obtained at the atmospheric pressure
11. Cr (57%)-Ni (19%)-K (14,3%)- γ -Al₂O₃ (9,7%) – obtained in the vacuum conditions
12. Cr (10,2%)-Ni (4,3%)-Bi (16%)- γ -Al₂O₃ (69,5%) – obtained in the vacuum conditions
13. Cr (10,2%)-Ni (4,3%)-K (1%)-Co(1,6%)- γ -Al₂O₃ - (82,9%) – obtained at the atmospheric pressure
14. Cr (10,2%)-Ni (4,3%)-K (1%)-Co(1,6%)- γ -Al₂O₃ - (82,9%) – obtained in the vacuum conditions.

The quite another picture is observed for the catalyst, obtained in the vacuum. Thus, the wide a.b. are observed in region 17000,22000 and 27000 cm⁻¹ (fig.4, c.2). The bands in

the region 22000 and 27000 cm^{-1} can be registered to the absorption of Cr^{5+} ions, and a.b. at 17000 cm^{-1} can be registered to $\text{Cr}^{3+}(\text{O}_h)$ ions. Probably, Cr^0 particles also present in the system. Probably, bismuth has the doping influence on $\text{Cr}^{3+}(\text{O}_h)$ ions, that leads to their stabilization and stability to the reconstruction processes in the vacuum conditions. In the result of this, the catalyst surface is enriched by Cr_2O_3 phase. The green color of the sample also shows on this fact (in the pure form Cr_2O_3 phase has dark-green color). In the given case mainly Cr^{5+} ions are treated by the reconstruction process. This effect doesn't reveal in the case of the catalyst, prepared in the air atmosphere.

Probably the oxidative medium causes to the enrichment of the surface of Cr_2O_5 and Bi_2O_3 phases that leads to the darkening of the sample and appearance of the wide structureless absorption in the spectrum.

The carried out investigations allow to conclude the set of the important things:

- the surface in the catalyst, obtained in the air atmosphere, is enriched by Cr_2O_5 and Bi_2O_3 oxides in the result of the oxidative processes;
- the Bi^0 particles, having the doping influence on $\text{Cr}^{3+}(\text{O}_h)$ ions stabilize in the result of the reconstruction processes in the catalyst, obtained in the vacuum condition. In the result of this, mainly the Cr_2O_5 phase is treated by the reconstruction. In the given case the Cr^{5+} , $\text{Cr}^{3+}(\text{O}_h)$, Cr^0 and Bi^0 ions coexist in the system.

The oxide system (87,7%)-K(7,4%) - γ - Al_2O_3 (4,9%)

The catalyst spectrums, obtained in the air atmosphere and vacuum are analogical to the spectrums of the system $\text{Cr}(54,1\%)\text{-Bi}(13,5\%)\gamma\text{-Al}_2\text{O}_3$ (fig.4, c.3 and 4) and all conclusions, made on the analysis results of this system can be registered to the system $\text{Cr-K-}\gamma\text{-Al}_2\text{O}_3$.

The oxide system Cr(60%)-Ni(20%)-Bi(15%)- γ - Al_2O_3 (5%)

The catalyst, obtained in the conditions of air atmosphere and vacuum has the spectrum, which is identical to the spectrums of the samples $\text{Cr-Bi-}\gamma\text{-Al}_2\text{O}_3$ and $\text{Cr-K-}\gamma\text{-Al}_2\text{O}_3$ (fig.4, c.5 and 6). It is followed, that introduction of Ni in the catalyst doesn't influence significantly on valency and coordination state of Cr and bismuth ions.

On the assumption of the investigation results of Ni- γ - Al_2O_3 system, it is possible to suppose, that NiO, Cr_2O_5 , Cr_2O_3 , Bi_2O_3 phases form on the catalyst surface, obtained in the air atmosphere.

On the assumption of the investigation results of the previous catalysts, it is possible to suppose, that the surface composition of the catalyst, obtained in the vacuum, consists as on the oxidated forms of Cr (Cr_2O_5 and Cr_2O_3) and Ni (NiO), so on the restored forms Cr^0 and Ni^0 .

The oxide system Cr(67,1%)-Ni(22,4%)-K(5,6%)- γ - Al_2O_3 (4,9%)

The catalyst spectrums, obtained in the air atmosphere and vacuum, are identical and characterized by the total structureless absorption, covering all spectral area (fig.4, c.7 and 8). The both samples have black color. Though spectrum identification in this case is difficult, but it's possible to propose the following:

- the Cr_2O_5 , Cr_2O_3 , NiO, NiAl_2O_4 , K_2O phases are present in the catalysts, obtained in the air atmosphere;
- the phase composition of the catalysts, obtained in the vacuum consists as on oxidated form of Cr (Cr_2O_5 , Cr_2O_3) and Ni (NiAl_2O_4), so on restored forms Cr^0 and Ni^0 . In this case the doping influence of K on Cr ions is absent.

The oxide systems Cr(57 и 10,2%)-Ni(19 и 4,3%)-Bi(14,3 и 16%) and (9,7 и 69,5%)- γ - Al_2O_3

The total structureless absorption, covering practically all area is observed in the catalyst spectrum of $\text{Cr}(57\%)\text{-Ni}(19\%)\text{-Bi}(14,3\%)\text{-K}(9,7\%)\text{-}\gamma\text{-Al}_2\text{O}_3$ composition (fig.4, c9). The decrease of Cr and Ni concentrations till 10,2 and 4,3% leads to the significant changes in the spectrum. Thus, a.b. are observed in the regions 13000, 14000 (weak a.b. in the form of the shoulder), 15900, 16900, 22000, 26000 cm^{-1} and 27300 cm^{-1} (fig.3, c.10). The observable a.b. can be registered to the following way:

- a.b. at 13000 and 27300 cm^{-1} are registered to $\text{Ni}^{2+}(\text{O}_h)$ ions [transfers ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ correspondingly];
- the absorption in the regions 15900 and 16900 cm^{-1} are characteristic for the systems, consisting $\text{Ni}^{2+}(\text{T}_d)$ ions [transfers ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ и ${}^3\text{T}_1(\text{F}) \rightarrow {}^1\text{E}(\text{D})$, correspondingly];
- a.b. at 22000 and 26000 cm^{-1} are characteristic for $\text{Cr}^{3+}(\text{O}_h)$ ions correspondingly (transfer ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$) and Cr^{5+} .
- the presence $\text{Ni}^{2+}(\text{O}_h)$ and $\text{Ni}^{2+}(\text{T}_d)$ simultaneously in the system shows on the creation of the mixed spinel NiAl_2O_4 in the system.

Thus, the catalysts, obtained in the conditions of air atmosphere at relative high Cr and Ni concentrations (57 and 19%) create Cr_2O_5 , Cr_2O_3 , NiAl_2O_4 , NiO phases, probably Bi_2O_3 and K_2O phases, and at relative low concentrations – Cr_2O_5 , Cr_2O_3 , NiAl_2O_4 .

Let's consider the catalysts, obtained in the vacuum conditions:

The both catalysts give total, practically structureless absorption, covering all investigated spectral region (fig.4, c.11 and 12).

In all probability, as in all previous cases, the reconstruction processes, carry out in the vacuum conditions, leading to the appearance of the restored forms of Cr and Ni in the systems (Cr^0 and Ni^0 correspondingly). It is followed the important conclusions:

- as the oxide phases Cr_2O_5 , Cr_2O_3 , NiAl_2O_4 , NiO, so the restored particles Cr^0 and Ni^0 coexist at the high concentrations of Cr and Ni
- the system has the Cr_2O_5 , Cr_2O_3 , NiAl_2O_4 phases and Cr^0 and Ni^0 particles at relative low concentrations.

The oxide system Cr(10,2%)-Ni(4,3%)-K(1%)-Co(1,6%)- γ - Al_2O_3 (82,9%)

The a.b. are observed in the catalyst spectrum, obtained in the air atmosphere in the regions 15800, 17000, 18600, 12000, 23000 and 27500 cm^{-1} (fig. 4, c.13), which can be registered to the following way:

- a.b. in the regions 15800 and 17000 cm^{-1} , as the above mentioned ones can be registered to the absorption of $\text{Ni}^{2+}(\text{T}_d)$ ions [transfers ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ and ${}^3\text{T}_1(\text{F}) \rightarrow {}^1\text{E}(\text{D})$, correspondingly];
- a.b. in the regions 17000 and 18600 cm^{-1} can be registered to Co^{2+} ions, stabilized in the fields of tetrahedral

coordination. It is possible to suppose, that state of Co²⁺(T_d) ion is caused by the creation of the normal surface spinel CoAl₂O₄ [5,6];

- the absorption in the regions 22000 and 23000 cm⁻¹ as in all other cases, is registered to Cr³⁺ and Cr⁵⁺ ions correspondingly.

Thus, the investigated four-component catalyst is the complex multicomponent system, consisting Cr₂O₅, Cr₂O₃, NiAl₂O₄, NiO, CoAl₂O₄ and probably K₂O.

The catalyst, obtained in the vacuum conditions, is characterized by the spectrum, in which the same a.b. are observed, that the above mentioned ones, but with lower intensity (fig.3, c.14). This fact shows on the carrying out of the restored processes, leading to the partial transfer Cr⁵⁺(Cr³⁺), Ni²⁺(O_h,T_d), Co²⁺(T_d)→ till Cr⁰, Ni⁰ and Co⁰ correspondingly.

Thus, on the base of the carried out spectral investigations of valency and coordination state of Cr, Co,

Ni, Bi and K ions, deposited on γ -Al₂O₃ it is possible to make the following conclusions:

1. The conditions of catalyst synthesis (air atmosphere or vacuum) significantly influence on the high energetic state (valency and coordination) of Cr, Co, Ni, Bi and K ions; the catalysts, obtained in the conditions of air atmosphere have only oxidated forms of deposited elements [Cr³⁺(O_h), Cr⁵⁺, Ni²⁺(O_h), Ni²⁺(T_d), Co²⁺(T_d), Bi³⁺, K⁺], whereas, in the systems, obtained in the vacuum conditions, the oxidated and restored forms of deposited elements coexist.

2. The creation processes of chemical compositions by the type of surface compositions NiAl₂O₄ and CoAl₂O₄ carry out at the marking of the given elements γ -Al₂O₃ in the comparison with massive systems.

3. The relative high catalytic activity of four-component systems, obtained in the vacuum conditions is connected by the presence as oxidative, so restored forms of deposited elements in the system.

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DEHİDROGENLƏSMƏ KATALİZATORLARININ TƏRKİBİNDƏKİ γ -AL₂O₃ ÜZƏRİNƏ HOPDURULMUŞ Cr, Co, Ni, Bi VƏ K İONLARININ HALININ DƏES VƏ RENTGENOQRAFİYA METODLARI İLƏ TƏDQIQI

Massiv dehidrogenləşmə katalizatorları ilə müqayisədə daha yüksək mexaniki davamlığa, termostabilliyə malik olan hopdurulmuş katalizatorlara üstünlük verilir. Məqalədə γ -Al₂O₃ üzərinə hopdurulmuş və dehidrogenləşmə katalizatorlarının tərkibinə daxil olan Sr, So, Ni, Bi və K ionlarının hali haqqında məlumat təqdim olunub. Atmosfer və vakuüm şəraitində hazırlanmış katalizatorlar istifadə olunub. Məlum oldu ki, Sr, So, Ni metallarının valent və koordinasiya halı katalizatorun hazırlanma şəraitindən asılıdır. Atmosfer şəraitində hazırlanmış katalizatorların tərkibində metalların oksidləşmiş ion formaları mövcuddur. Vakuüm şəraitində hazırlanmış katalizatorlarda isə həm oksidləşmiş, həm də bərpa olunmuş metalların ion formaları mövcuddur. Ehtimal olunur ki, vakuüm şəraitində hazırlanmış katalizatorun yüksək aktivliyini sistemdə metalların oksidləşmiş və bərpa olunmuş ion formalarının mövcudluğu ilə izah etmək olar.

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ИССЛЕДОВАНИЕ СОСТОЯНИЯ ИОНОВ Cr, Co, Ni, Bi И K, НАНЕСЕННЫХ НА γ -Al₂O₃ В СОСТАВЕ КАТАЛИЗАТОРА ДЕГИДРИРОВАНИЯ, МЕТОДАМИ ЭСДО И РЕНТГЕНОГРАФИИ

По сравнению с массивными катализаторами дегидрирования предпочтительным является использование нанесенных катализаторов, которые обладают более высокой механической прочностью, термостабильностью и относительно низкими затратами на их синтез. В статье представлены данные по состоянию ионов Cr, Ni, Bi, Co и K, нанесенных на γ -Al₂O₃, входящих в состав катализаторов дегидрирования парафиновых углеводородов C₃-C₄. Были использованы катализаторы, приготовленные в атмосферных условиях и в условиях пониженного давления. Установлено, что валентное и координационное состояние ионов переходных металлов (Cr, Ni, Co) зависят от условий приготовления катализатора. В образцах катализаторов, приготовленных в условиях атмосферы, присутствуют ионы металлов в окисленной форме. А в катализаторах, приготовленных в условиях вакуума, сосуществуют как окисленные, так и восстановленные формы ионов металлов. Предполагается, что высокая активность катализаторов, полученных в условиях вакуума, обусловлена присутствием в системе окисленных и восстановленных форм активных компонентов.

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