

THE INVESTIGATION OF STATES OF ION Ni, Cr, Co, Bi AND K IN THE COMPOSITION OF DEHYDRATION CATALYSTS

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The states of ions Ni, Cr, Co, Bi and K, including in the composition of dehydration catalysts of paraffin hydrocarbons C₃-C₄ are considered.

The data on the ion state in the catalyst in the dependence on the preparation method are presented. For the obtaining of the imagination about ion states, the mass catalysts are used.

The catalysts are treated by drying and glowing in the atmosphere conditions and the conditions of low pressure. The conditions of catalyst syntheses influence on the valiant and coordination ion states of transition elements (Cr, Ni, Co), including in the catalyst composition, by the definite way. The catalysts, obtained in the conditions of the low pressure, have as oxidated [(Cr⁵⁺(O_h), N²⁺(O_h) and Co³⁺, Co²⁺], so the reduced Cr⁰, Ni⁰, Co⁰ forms of active components. The conductions of low pressure cause the creation the such components as K₂Cr₂O₇, NiO, Cr₂O₅, Cr₂O₃, Bi₂O₃ in the significant quantities, allowing to carry out the dehydration of paraffin hydrocarbons C₃-C₄.

The catalysts, having ions Ni, Cr, Co, Bi and K are widely used in the industrially-important processes and in a particular, in the processes of dehydration of normal low-molecular hydrocarbons [1-10]. For the optimization of the processes and improvement of exploitation properties of catalysts, it is need to study in detail the contact physico-chemical properties and in a particular, valiant and coordination ion state, including in their composition.

Below of results of spectral (electronic spectroscopy of diffuse reflection) investigation of states of ions Ni, Cr, Co, Bi and K, including in the composition of dehydration catalysts, treated in the IPChP of NAS of Azerbaijan, are given.

The technique of experiment

The electronic spectrums of diffuse reflection (ESDR) in the region 50000-100000cm⁻¹ are taken on the spectrophotometer "Specord M40", which has the ladder for taking of diffuse reflection spectrums.

The catalysts are prepared by the way of the nitrate salt borrowing of corresponding metals. The catalyst samples are treated by drying (100°-120°C) and glowing (600°-620°C) in the conditions of low atmosphere pressure.

The experiment results

The oxide system Cr (80%) – Co (20%)

In the sample spectrum, obtained in the air atmosphere, the absorption bands (a.b.), at 22000 (very weak a.b.) and in the region 12000-18000cm⁻¹ (fig.1, c.1.) are observed. According to the refs [11, 12] absorption bands can be created to the Cr³⁺ ions, stabilized in the octahedron coordination fields (transfer ⁴A_{2g} → ⁴T_{1g}). The observable absorption band at 12000-18000cm⁻¹ is structural and insist on the three components with maximums at 14000, 16100 and 17000cm⁻¹. These maximums can be related to ions Cr⁵⁺ and Co³⁺(O_h) (transfer ¹A_{2g} → ¹T_{1g}), correspondingly.

The presence of ions Co³⁺(O_h) in the system shows on the existence of phase Co₃O₄ in the system [11, 12].

Thus, the given binary system has phases Co₃O₄, Cr₂O₃, Cr₂O₅, i.e. in the given case the ions Co³⁺, Co²⁺, Cr⁵⁺ and Cr³⁺ are exist.

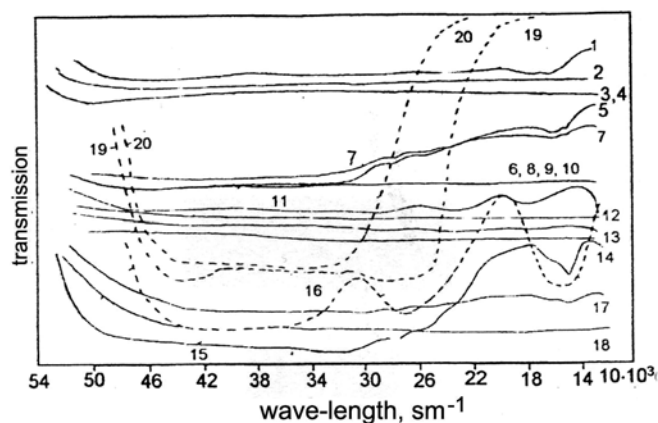


Fig.1. The spectrum of diffuse reflection of catalysts.

- 1 - Cr(80%) - Co(20%) - obtained at the atmosphere pressure
- 2 - Cr(80%) - Co(20%) - obtained in the vacuum conditions
- 3 - Ni(57%) - Co(43%) - obtained at the atmosphere pressure
- 4 - Ni(57%) - Co(43%) - obtained in the vacuum conditions
- 5 - Cr(10%) - Ni(90%) - obtained at the atmosphere pressure
- 6 - Cr(10%) - Ni(90%) - obtained in the vacuum conditions
- 7 - Cr(25%) - Ni(75%) - obtained at the atmosphere pressure
- 8 - Cr(25%) - Ni(75%) - obtained in the vacuum conditions
- 9 - Cr(25%) - Ni(75%) - obtained at the atmosphere pressure
- 10 - Cr(15%) - Ni(75%) - obtained in the vacuum conditions
- 11 - Cr(80%) - Bi(20%) - obtained at the atmosphere pressure
- 12 - Cr(80%) - Bi(20%) - obtained in the vacuum conditions
- 13 - Cr(92%) - K(8%) - obtained at the atmosphere pressure
- 14 - Cr(92%) - K(8%) - obtained in the vacuum conditions
- 15 - Ni(57%) - Bi(43%) - obtained at the atmosphere pressure
- 16 - Ni(57%) - Bi(43%) - obtained in the vacuum conditions
- 17 - Ni(80%) - K(20%) - obtained at the atmosphere pressure
- 18 - Ni(80%) - K(20%) - obtained in the vacuum conditions
- 19 - Bi(75%) - K(25%) - obtained at the atmosphere pressure
- 20 - Bi(75%) - K(25%) - obtained in the vacuum conditions

The wide unstructured absorption band, having almost all area (fig.1, c.2) is observed in the vacuum conditions in the catalyst spectrums. Moreover, the general absorption phone strongly increases. The black color of the sample shows on

this fact. Probably, in the vacuum conditions, the partial reduction process of ions Co^{3+} , Co^{2+} , Cr^{5+} and Cr^{3+} is carried out till the Co^0 , Cr^0 , correspondingly. In the given case, the sample surface has as oxidated (Co^{3+} , Co^{2+} , Cr^{5+} and Cr^{3+}), so the reduced forms of ions of cobalt and chrome (Co^0 , Cr^0).

Oxide system Ni (57%) – Co (43%)

The sample has the black color, and spectrum is characterized by the total absorption, having almost all region (fig.1., c.3). The analogical spectrum has the sample, obtained in the vacuum conditions (fig.1, c.4). Moreover, in the both cases, the general absorption phone strongly increases.

The total unstructured absorption difficults the spectrum interpretation, but taking into consideration the common positions and literature data, it can be proposed, that in the sample, obtained in the vacuum, in the result of partial reduction of ions $\text{Ni}^{2+}(\text{O}_h)$, Co^{3+} and Co^{2+} , the particles Ni^0 and Co^0 should be existed.

Oxide system Cr (10;25 and 75%) – Ni (90;75 and 25%)

The sample spectrum, having 10% Cr and 90% Ni, obtained in the air atmosphere is characterized by absorption band at 13800; 14500; 24000 and 26200 cm^{-1} (fig.1, c.5). Observable absorption bands, according to the refs [11,12], can be interpreted by the following way:

- absorption band at 14500 and 26200 cm^{-1} can be related to Cr^{5+} ions;

- the absorption in the region 24000 cm^{-1} is characterized for Cr^{3+} ions, stabilized in the octahedron coordination fields (transfer ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$).

- the absorption band in the region 13800 cm^{-1} can be related to $\text{Ni}^{2+}(\text{O}_h)$ ions (transfer ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$), including in the phase NiO composition.

Thus, the given catalyst is complex many phase system (Cr_2O_5 ; Cr_2O_3 and NiO).

The catalyst, obtained in the vacuum conditions, is characterized by total absorption, having almost all region (fig.1, c.6). Probably in the vacuum conditions, the ions Cr^{5+} , Cr^{3+} and Ni^{2+} partially reduce till Cr^0 and Ni^0 , correspondingly. In the given case, the oxidated Cr^{5+} , Cr^{3+} and Ni^{2+} and reduced forms of Cr^0 and Ni^0 are coexisted on the catalyst surface.

The increase of chrome quantity in the sample till 25%, insignificantly influence on the place of absorption band on ions Cr^{5+} , Cr^{3+} and Ni^{2+} (fig.1, c.7). The some increase of general phone and intensity decrease of observable absorption bands are observed.

The catalyst, obtained in the vacuum conditions, has the spectrum, identical for the previous catalyst(fig.1, c.8).

The latter increase of chrome concentration till 75%, leads to the strong change of catalyst spectrum, obtained in the air atmosphere. The total absorption, having all region (fig.1, c.9) is observed.

The identical spectrum is observed in the vacuum conditions (fig.1, c.10).

The color of the sample becomes darker at the chrome high concentrations. Probably, the general absorption phone increases and absorption bands, which are character for chrome and nickel ions, are masked. The X-ray-phase analysis of catalyst, prepared in the atmosphere conditions shows the existence of phases NiO, $\text{Ni}_2\text{Cr}_2\text{O}_4$ and in the

catalyst, treated by thermal-vacuum treatment - only phases NiO.

Oxide system Cr (80%) – Bi (20%)

In the sample spectrums, obtained in the air atmosphere, the absorption bands at 16500, 21500 and 27000 cm^{-1} are observed (fig.1, c.11). The bands in the region 16500 and 21500 cm^{-1} can be related to the absorption of ions $\text{Cr}^{3+}(\text{O}_h)$ (transitions ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ correspondingly), and at the 27000 cm^{-1} - to Cr^{5+} .

The Bi^{3+} ions have electron configurations $d^{10}s^2$ and their absorption in the ultraviolet region takes place because of the so-called Ridberg's transitions, i.e. inside the membrane of ions themselves. The Bi^{3+} ion absorption is observed in the region 28500; 32250 and 38460 cm^{-1} [11, 12]. In the given case, probably, the phone absorption masks the absorption bands from Bi^{3+} ions. The stabilization in the system of ions Cr^{5+} , Cr^{3+} and Bi^{3+} can be said.

The catalyst spectrums, obtained in the vacuum, gives the total absorption, having almost all region (fig.1, c.12). Probably, in this case, ions Cr^{5+} and Cr^{3+} , are partially reduced till Cr^0 . The Bi^{3+} ions are more stable [11, 12] and the existence of Bi_2O_3 phase and ions Cr^{5+} , Cr^{3+} and Cr^0 in the sample can be proposed.

The catalyst, prepared in the air atmosphere conditions on RFA shows the existence of phases Cr_2O_3 and Bi_2O_3 in the thermal-vacuum treatment conditions it is amorphous.

Oxide system Cr (92%) – K (8%)

The sample spectrum, obtained in the air atmosphere, is characterized by the weak absorption bands at 16500; 21500 and 27000 cm^{-1} , which can be related to the ions Cr^{5+} and Cr^{3+} (Fig.1, c.13). The absorption from K ions is masked by the phone absorption.

The catalyst, obtained in the vacuum, has the spectrum with the unstructured absorption, having almost all region (Fig.1, c.14).

In the given case, as mentioned above, the oxidated (Cr^{5+} , Cr^{3+}) and reduced (Cr^0) forms of chrome ions are stabilized in the sample.

Oxide system Ni (57%) – Bi (43%)

In the sample spectrum, obtained in the air atmosphere, the absorption bands in the region 13000(arm); 13800; 15500; 21500; 24000; 26300; ~29,000 cm^{-1} (fig.1, c.15), which are character for $\text{Ni}^{2+}(\text{O}_h)$ ions, creating NiO phase, are observed [11, 12]. The grey-green sample color shows on this fact. The absorption from Bi^{3+} ions is masked by the absorption of the phase NiO.

The sample spectrum, obtained in the vacuum condition, significantly differs from the above mentioned case. Thus, the wide intensive absorption bands in the region 13000 - 16000 and ~25500 cm^{-1} (fig.1,c.16) are observed. Besides, in the given case in the difference from all previous binary systems, the disappearance of absorption bands from active component [in the given case absorption bans from $\text{Ni}^{2+}(\text{O}_h)$ in NiO], connected with the partial reduction of transition element under influence of reduction medium, which the vacuum is, doesn't observed. Probably, this effect can be explained by the alloying influence of Bi^{3+} on NiO, that leads

to the stability of nickel oxide, to the reduction processes in vacuum conditions. From this the another important conclusion takes place, i.e. Bi^{3+} ions reveal the alloying properties in the case of binary oxide systems Cr-Bi.

The catalyst, prepared in the atmospheric conditions on RFA shows the existence of phases NiO and Bi_2O_3 .

Oxide system Ni(80%) - K(20%)

The absorption bands from $\text{Ni}^{2+}(\text{O}_h)$ in the phase NiO are observed in the sample spectrum, obtained in the air atmosphere (fig.1,c.17). The dark green sample color also shows on this fact (pure NiO has grey-green color). The significant increase of general absorption phone, connected with the darkness of sample color, is observed.

Thus, the existence of phases NiO and K_2O in the catalyst composition can be said.

The sample, obtained in the vacuum, is characterized by the unstructured absorption (fig.1,c.18). Probably, the part of $\text{Ni}^{2+}(\text{O}_h)$ ions transfers to Ni^0 in the result of reduced processes. The change of sample color from dark-green to black also shows on this fact. Thus, the catalyst includes the phase NiO and Ni^0 particles. The X-ray-phase analysis shows the existence of NiO phase in the both samples, prepared as in the vacuum conditions, so in the atmosphere ones.

Oxide system Bi(75%) - K(25%)

The absorption bands from Bi^{3+} (in Bi_2O_3 phase) at 40800; 31200 and 27000 cm^{-1} are observed in the sample spectrum, obtained in the air atmosphere (fig.1,c.19). The yellow color, which is character for Bi_2O_3 also shows on this fact.

The absorption bands from Bi^{3+} ions are absent in the catalyst spectrums, obtained in the vacuum conditions (fig.1,c.20). Probably, in this case part of Bi^{3+} reduce till Bi^0 .

Thus, in the given case, the catalyst includes Bi^{3+} ions (in Bi_2O_3 phase), the Bi^0 particles, K^+ ions and probably K^0 .

Oxide system Cr(63%) - Ni(21%) - Bi(16%)

The total absorption in all investigated spectral region is observed in the catalyst spectrum, obtained in the air atmosphere (fig.2,c.1). The sample has black color. Probably, in the given case, the absorption bands from ions Cr^{5+} , Cr^{3+} , Cr^{2+} and Bi^{3+} are masked by more phone absorption and don't reveal in the spectrums.

In the difference from this, in the sample spectrums, obtained in the vacuum conditions, the weak, but allowed absorption bands at 16000 and 23000 cm^{-1} , which are accord to Cr^{3+} ions, stabilized in the octahedron coordination fields (transfers ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$ correspondingly), are observed. Besides, the weak-intensive absorption band at 27000 cm^{-1} from Cr^{5+} is observed. Probably, at the catalyst synthesis in the vacuum conditions, part of $\text{Cr}^{3+}(\text{O}_h)$ and ion quantity of trivalent chrome increases in the system. The dark-green color of the sample, which is character for $\text{Cr}^{3+}(\text{O}_h)$ ions shows on this fact. The given conclusion doesn't except the presence of ions Cr^{5+} , Ni^{2+} and Bi^{3+} in the system.

Besides, probably the Bi^{3+} ions or Bi^0 ions influence with the alloying influence on $\text{Cr}^{3+}(\text{O}_h)$ ions, increasing their stability to the reduction processes.

Thus, the given catalyst has the complex composition and includes the ions Cr^{5+} , $\text{Cr}^{3+}(\text{O}_h)$, $\text{Ni}^{2+}(\text{O}_h)$ and Bi^{3+} probably creating the phases Cr_2O_5 , Cr_2O_3 , NiO and Bi_2O_3 , correspondingly.

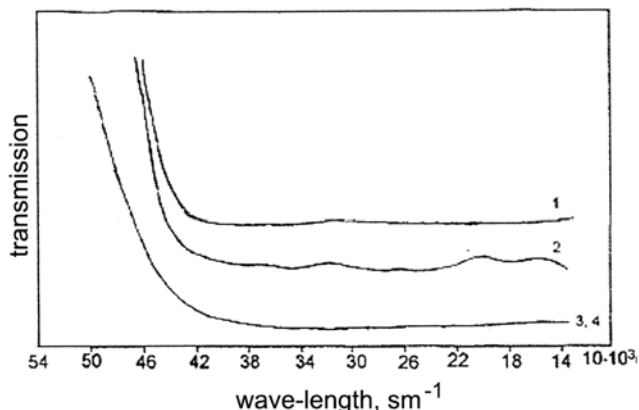


Fig.2. The spectrums of diffuse reflection of catalysts.
 1 - Cr(63%) - Ni(21%) - Bi(16%) - obtained at the atmosphere pressure
 2 - Cr(63%) - Ni(21%) - Bi(16%) - obtained in the vacuum conditions
 3 - Cr(63%) - Ni(21%) - Bi(16%) - obtained in the vacuum conditions

Oxide system Cr (63%) – Ni (21%) – Co (16%)

The sample has the black color and gives the total unstructured absorption, having all region (fig.2,c.3). The catalyst, obtained in the vacuum conditions, has the identical spectrum (fig.2,c.4). In the given case the interpretation of these spectrums is difficulted, but it can be proposed, that oxidated-reduced processes, carrying out with the participation of ions Cr^{5+} , (Cr^{3+}), Ni^{2+} and $\text{Co}^{3+}(\text{Co}^{2+})$ realize in these samples.

Thus, on the base of spectral (ESDR) investigation of massive two- or trivalent component oxide systems, we can make the following conclusions:

- the catalyst synthesis conditions (air or vacuum atmospheres) influence on the valence and coordinate ion states of transition elements (Cr, Ni, Co), including in the catalyst composition, in the definite way;

- the catalyst, obtained in the air atmosphere, include the oxidated forms of ions of chrome, nickel and cobalt Cr^{5+} , $\text{Cr}^{3+}(\text{O}_h)$, $\text{Ni}^{2+}(\text{O}_h)$, $\text{Co}^{3+}(\text{Co}^{2+})$, including in the composition of phases Cr_2O_5 , NiO, Co_3O_4 .

- the catalysts, obtained in the vacuum conditions, have as oxidated [$(\text{Cr}^{5+}$, $\text{Cr}^{3+}(\text{O}_h)$ and $\text{Co}^{3+}(\text{Co}^{2+})$], so the reduced Cr^0 , Ni^0 , Co^0 forms of active components. The fact of coexistence of oxidated and reduced ion forms of transition metals as two- and trivalent oxide systems;

- in the combination with the transition elements, Bi^{3+} ions are more stable to the reduction processes and influence in the case of Ni-Bi system, the alloying influence on $\text{Ni}^{2+}(\text{O}_h)$ ions, that reveals in the stability of nickel ions to the reduction processes.

In the binary systems Bi-K, the Bi^{3+} ions are more influenced to the reduction medium

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DEHİDROGENLƏŞMƏ KATALİZATORLARININ TƏRKİBİNDƏKİ Ni, Cr, Co, Bi VƏ K İONLARININ HALININ TƏDQIQI

Parafin karbohidrogenlərinin dehidrogenləşməsinə təmin edən katalizatorlarına daxil olan Ni, Cr, Co, Bi və K ionlarının halına baxılır.

Hazırlanma üsulundan asılı olaraq katalizatorlarda ionların halı haqqında məlumat təqdim olunur. İonların halının öyrənilməsi üçün massiv katalizatorlardan istifadə olunmuşdur.

Katalizatorlar atmosfer və vakuum şəraitində qurulub və közərdilmişdir. Katalizatorların sintez şəraiti katalizator tərkibindəki Ni, Cr, Co, Bi və K ionlarının valent və koordinasiya halına təsir edir. Vakuum şəraitində hazırlanmış katalizatorun tərkibində həm oksidləşmiş $[(Cr^{5+}, Cr^{3+}(O_h), Ni^{2+}(O_h) və So^{3+}, So^{2+}]$ həm də reduksiya olunmuş (Cr^0, Ni^0, Co^0) aktiv komponentlər mövcuddur. Vakuum şəraiti $K_2Cr_2O_7, NiO, Cr_2O_5, Cr_2O_3, Bi_2O_3$ kimi birləşmələrin əmələ gəlməsinə şərait yaradır və onlar C_3-C_4 parafin karbohidrogenlərinin dehidrogenləşməsinə təmin edir.

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ИССЛЕДОВАНИЕ СОСТОЯНИЯ ИОНОВ Ni, Cr, Co, Bi и K В СОСТАВЕ КАТАЛИЗАТОРОВ ДЕГИДРИРОВАНИЯ

Рассматривается состояние ионов Ni, Cr, Co, Bi и K, входящих в состав катализаторов дегидрирования парафиновых углеводородов $C_3 - C_4$.

Представлены данные по состоянию ионов в катализаторе в зависимости от способа приготовления. Для получения представления о состоянии ионов использованы массивные катализаторы.

Катализаторы подвергали сушке и прокалике в атмосферных условиях и в условиях пониженного давления. Условия синтеза катализаторов определяющим образом влияют на валентное и координационное состояния ионов переходных элементов (Cr, Ni, Co), входящих в состав катализаторов. Катализаторы, полученные в условиях пониженного давления, содержат как окисленные $[(Cr^{5+}, Cr^{3+}(O_h), Ni^{2+}(O_h) и Co^{3+}, Co^{2+}]$, так и восстановленные Cr^0, Ni^0, Co^0 формы активных компонентов. Условия пониженного давления способствуют образованию в значительных количествах таких соединений как $K_2Cr_2O_7, NiO, Cr_2O_5, Cr_2O_3, Bi_2O_3$, позволяющих вести дегидрирование парафиновых углеводородов $C_3 - C_4$.

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