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HYDROGENATION OF ACETYLENE COMPOUNDS ON MULTICOMPONENT RANEY NICKEL (SKELETON CATALYST)

Abstract. This work presents the results of a study of the catalytic activity and selectivity of multicomponent Raney nickel in the hydrogenation of phenylacetylene and hexine-2. Hexin-2 is hydrogenated on Raney nickel selectively and stereospecifically, with the formation of mainly cis-hexene-2. The activity, selectivity and isomerizing ability of modified Raney nickel obtained from Ni-Al-Me and Ni-Al-Me₁-Me₂ alloys (where Me-Cu, Ag, Zn, Ti, Zr, Sn, Pb, Ta, Bi, Cr, Mo, Mn, Fe, and Pd) in the reactions of hydrogenation of phenylacetylene, hexin-2 substantially depend on the nature of the additives introduced into the Ni-Al alloy. In hexin-2 hydrogenation reactions, multicomponent Raney nickel exhibit high stereospecificity. The yield ratio of cis-hexene-2 / trans-hexene-2 is 16-25, depending on the nature of the modifying additive.

Keywords: acetylene compounds, phenylacetylene, hexine, hexane, hydrogenation, Raney nickel, catalytic “bedpan”, modifying additives, activity, selectivity.

Introduction. One of the large-scale processes of petrochemicals and oil refining is the catalytic hydrogenation of unsaturated hydrocarbons. Hydrogenation processes have become urgent due to the presence in the olefin gas molasses of impurities of acetylide and diene hydrocarbons, the removal of which is an important task. Although a number of liquid purification processes using solvents for the selective removal of acetylene hydrocarbons have been developed, their selective catalytic hydrogenation is more economical [1].

Currently, various supported catalysts are used in industry as selective hydrogenation catalysts to increase the surface of the active component, prevent sintering, and save expensive metal. Platinum group metals: Pt, Ph, Ru, Pd supported on carriers are used as active components of supported catalysts for hydrogenation of multiple carbon-to-carbon bonds. In addition to the platinum group metals, copper, cobalt, nickel, applied to various media. Despite the high selectivity of hydrogenation, the use of catalysts containing noble metals increases the cost of the process. The most applicable is a nickel-based hydrogenation catalyst having high activity and relatively low cost compared to noble metal catalysts [2].

Multicomponent Raney nickel successfully used in various hydrogenation processes are recognized as highly effective from an industrial point of view. This is due to: high activity and selectivity; simplicity of preparation and regeneration; stability in work, resistance to poisoning. Intensive studies of recent years have shown that the modification of Raney nickel with various metals makes it possible to control the properties of the catalyst in a wide range [3].

Alloying nickel-aluminum alloys with additives of various (s-, p-, d- and f-) metals makes it possible to control the activity, stability, and specificity of the action of skeletal catalysts obtained from them in the reactions of hydrogenation of organic compounds. For a particular catalytic hydrogenation process, the introduction of additives in a certain ratio of Ni:Al:Me is optimal.

EXPERIMENTAL PART

A portion (0.4-0.8 g) of crushed, powdery alloy, fraction 0.06-0.20 mm (alloy composition is given in table) was treated with a 20% KOH solution at a temperature of 96 C, in boiling water bath for 2 hours. Washing of the water obtained from alkali was carried out by distilled water by decantation 4-5 times, until a negative reaction to OH⁻ ions in the wash water. Then, the catalyst was washed with a solvent in which hydrogenation (ethanol) was carried out.

Hydrogenation of phenylacetylene and hexin-2 on multicomponent Raney nickel in ethanol

Alloy composition	Content of Ni-Al-Me wt. %	phenylacetylene				hexin-2		
		W C≡C	W C=C	ΔE _{in.}	K _s	W C≡C	ΔE _{in.}	K _s
Ni-Al	50-50	68	82	330	0.82	107	270	0.91
Ni-Al-Cu	40-55-5	100	210	180	0.89	140	190	0.96
Ni-Al-Cu	30-60-10	100	240	160	0.89	209	170	0.97
Ni-Al-Ag	48-50-2	82	130	310	0.88	137	280	0.93
Ni-Al-Zn	43-44-13	117	258	170	0.89	160	200	0.96
Ni-Al-Zn	28-36-36	126	290	160	0.90	283	200	0.96
Ni-Al-Ti	47-50-3	97	134	350	0.87	110	310	0.94
Ni-Al-Zr	45-50-5	56	89	300	0.86	94	260	0.90
Ni-Al-Sn	45-50-5	67	95	340	0.89	97	280	0.93
Ni-Al-Pb	40-50-10	63	156	260	0.91	200	230	0.96
Ni-Al-Ta	45-50-5	133	222	330	0.89	189	290	0.95
Ni-Al-Bi	45-50-5	69	128	320	0.90	175	250	0.95
Ni-Al-Cr	47-50-3	70	84	290	0.84	116	300	0.95
Ni-Al-Mo	45-50-5	69	111	350	0.85	118	280	0.91
Ni-Al-Mn	40-50-10	34	50	290	0.83	58	310	0.89
Ni-Al-Fe	45-50-5	25	47	260	0.85	60	280	0.91
Ni-Al-Pd	48-50-2	68	89	360	0.88	90	300	0.93
Ni-Al-Ti-Mo	44-50-3-3	72	100	290	0.87	132	260	0.90
Ni-Al-Mo-Cr	44-50-3-3	75	112	280	0.88	92	270	0.92
Ni-Al-Cr-Cu	42-50-3-5	95	160	310	0.88	152	290	0.96
Ni-Al-Ti-Cu	42-50-3-5	69	110	270	0.86	113	250	0.92
Ni-Al-Ti-Cu	42-50-3-5	72	83	330	0.81	75	280	0.90

*W – activity of the catalyst, cm³/ min.g Ni; ΔE_{in.} – initial shift of the catalyst potential, mV; K_s – selectivity coefficient.

Hydrogenation was carried out in thermostabilized catalytic "bedpan" [4,5] at atmospheric pressure and a temperature of 20 °C. The reaction rate (the amount of absorbed hydrogen per unit time, cm³/min) and the catalyst potential (mV) relative to the calomel reference electrode were recorded simultaneously according to the procedure [4,5]. Before the reaction, the catalyst was saturated with hydrogen in a solvent (volume 25 cm³) until a reversible hydrogen potential was established. Hydrogenation was carried out in kinetic mode (700-800 swings / min).

In this paper we have studied the catalytic activity and selectivity of multi-component Raney nickel in the reactions of hydrogenation of phenylacetylene and hexin-2.

RESULTS AND DISCUSSIONS

The activity of multicomponent Raney nickel during the phenylacetylene hydrogenation (table) depends on the nature of the modifying additives. The introduction of Ta, Zn, Cu, Mo-Cu, Ti and Ag into the alloy leads to an increase in Raney nickel activity ($W_{C=C} = 82-133 \text{ cm}^3 / \text{min.g Ni}$). Additives Zr, Mn and Fe reduce it ($W_{C=C} = 25-56 \text{ cm}^3 / \text{min.g Ni}$). Cr, Pd, Sn and Ti-Cu do not significantly affect the activity of the catalyst ($W_{C=C} = 67-72 \text{ cm}^3 / \text{min.g Ni}$).

The introduction of most modifying additives is associated with an increase in selectivity with the exception of Cr, Mn, and Ti-Cu ($K_s = 0.81-0.84$, $W_{C=C} / W_{C=C} = 1.2-1.4$). The greatest effect falls on Pb, Bi, Zn, Cu, Sn, Ta, Pd, Mo-Cu and Mo-Cr ($K_s = 0.88-0.91$, $W_{C=C} / W_{C=C} = 1.5-2.4$). The potential shift $\Delta E_{C=C}$ depending on the nature of the additive varies between 160-360 mV. On catalysts modified with Cu Zn, $\Delta E_{C=C}$ is 160-180 mV, while Mo, Ti and Pd increase the adsorption strength ($\Delta E = 350-360 \text{ mV}$).

Hydrogenation of phenylacetylene in hexane proceeds at a lower rate and selectivity than in ethanol.

Hexin-2 on Raney nickel is hydrogenated selectively and stereospecifically, with the formation of predominantly cis-hexene-2.

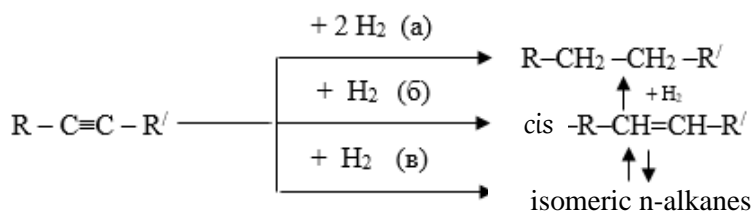
The potentiometric data (table) indicates strong adsorption of hexin-2 on multicomponent Raney nickel ($\Delta E = 230-310 \text{ mV}$), with the exception of Ni-Cu catalysts ($\Delta E = 170-190 \text{ mV}$). The metals Zn, Pb, Cu, Ta, Bi, Mo-Cu, Ag and Ti-Mo are effective additives that increase the activity of the catalyst by 1.3-2.8 times ($W_{C=C} = 132-283 \text{ cm}^3 / \text{min.g Ni}$) / Ti, Zr and Cr-Cu almost do not change it ($W_{C=C} = 94-113 \text{ cm}^3 / \text{min.g Ni}$), while Mn and Fe have a negative effect ($W_{C=C} = 94-113 \text{ cm}^3 / \text{min.g Ni}$). The nature of the modifying additives significantly affects both selectivity ($K_s = 0.89-0.97$ depending on the nature of the element) and the non-isomerizing ability of the catalyst (cis-hexene-2 / trans-hexene-2 = 16-25).

Thus, the activity, selectivity and isomerizing ability of modified Raney nickel obtained from Ni-Al-Me and Ni-Al-Me₁-Me₂ alloys (where, Me-Cu, Ag, Zn, Ti, Zr, Sn, Pb, Ta, Bi, Cr, Mo, Mn, Fe and Pd), in the reactions of phenylacetylene hydrogenation, hexin-2 significantly depend on the nature of the additives introduced into the Ni-Al alloy.

A sharp decrease in the potential shift of the catalysts (ΔE) in the second half of the processes during the hydrogenation of phenylacetylene and hexin-2 on multi-component Raney nickel (table) indicates a higher adsorption of alkynes compared to intermediate alkenes on the surface of the catalysts [4-6]. This is probably due to the high selectivity of hydrogenation of alkynes: $K_{\text{Sphenylacetylene}} = 0.81-0.91$, $K_{\text{Shexin-2}} = 0.89-0.96$, depending on the nature of the modifying additive: solvent-ethanol (table). The observed pattern on the studied catalysts: $K_{\text{Shexin-2}} < K_{\text{Sphenylacetylene}}$, is apparently associated with a different effect of the kinetic factor ($K_{\text{styrene}}/K_{\text{phenylacet.}} > K_{\text{cis-, trans-hexene-2}} / K_{\text{hexin-2}}$) on selectivity processes [6].

Judging by the value of the shift in the catalyst potential ΔE (table), the zero order in acetylene hydrocarbons, we can conclude that these compounds displace both hydrogen and the solvent from the surface of the catalysts [5]. The reaction is limited by the activation of hydrogen. The hydrogenation processes of [4] alkynes can be attributed to those implemented by the III mechanism. Sokolsky.

The process of interaction of alkyn-2 with hydrogen in general terms reflects the scheme proposed in [7, 8]:

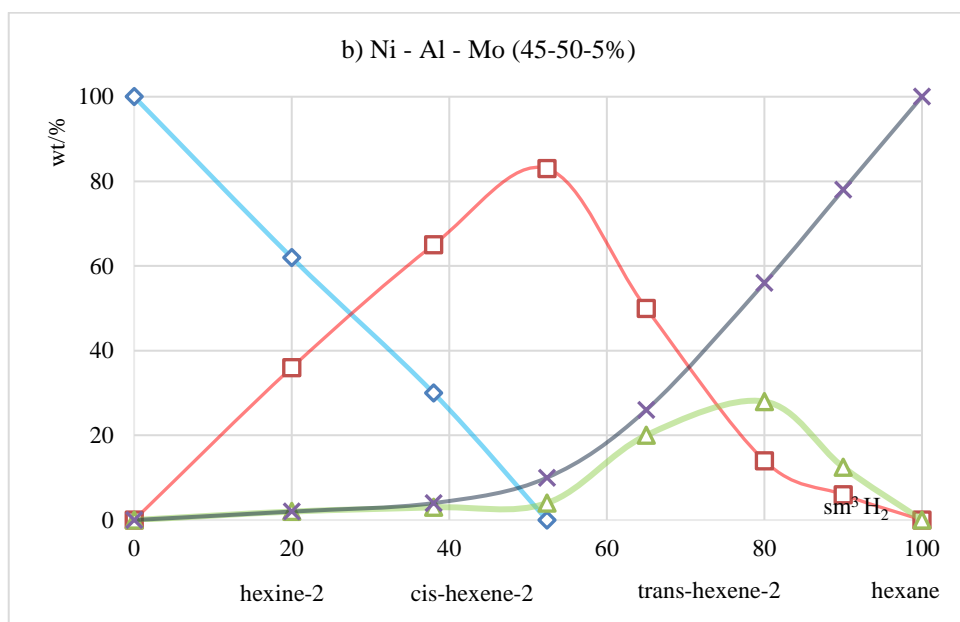
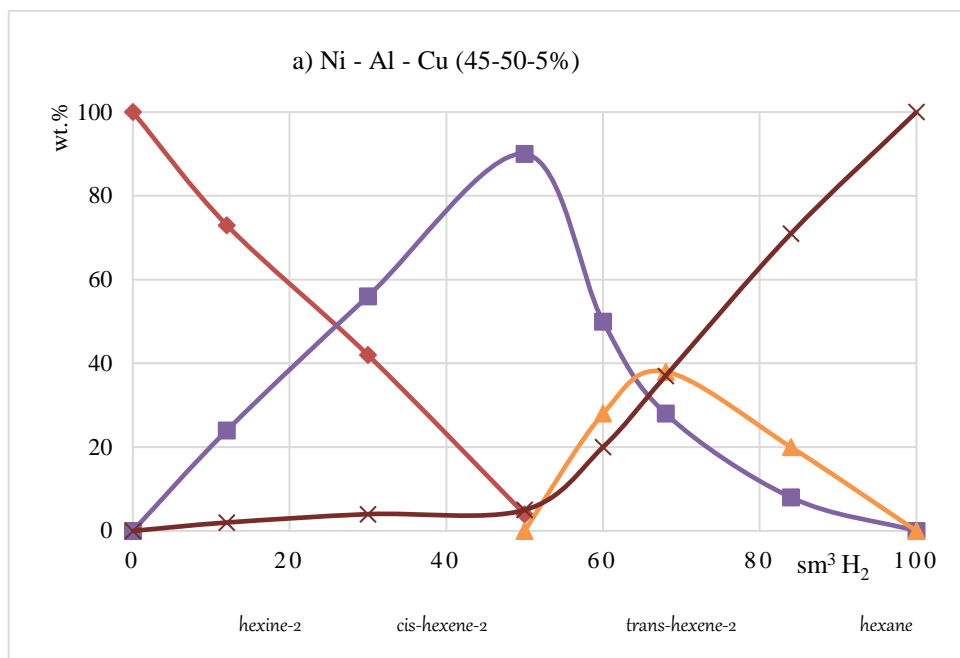


Hydrogenation of hexin-2 on multicomponent Raney nickel proceeds stereospecifically, with the formation of mainly cis-hexene-2 (figure). In the first half of the process, in the presence of hexin-2, trans-hexene-2 and hexane are formed in small quantities (1-2%). By the moment of absorption of 1 mole of hydrogen, the content of cis-hexene-2 reaches a maximum (77-90%, depending on the nature of the modifying additives). Thus, the maximum cis-isomer content on a skeletal catalyst made of Ni-Al-Cu alloy (40-55-5%) is 86%, on Raney nickel – 77%. The stereospecificity, characterized by the ratio of cis-hexene-2 / trans-hexene-2, is 16-25 on catalysts with various modifying additives. The greatest stereospecificity is shown by catalysts containing Cu, Mo-Cu, Pb, Ta, Zn, Bi and Cr.

After the disappearance of hexin-2 from the reaction mixture, the cis-hexene-2 content curve changes sharply, because cis-trans-isomerization proceeds along with saturation. Hexane and trans-hexene-2 accumulate at close rates (figure). The isomerization coefficient of hexene-2 ($K_{\text{isom.}}$) varies from 0.65 to 0.72, depending on the nature of the modifying additive.

According to the reactivity, the starting and intermediate compounds can be arranged as follows: hexin-2 > cis-hexene-2 > trans-hexene-2.

A comparison of the data of chromatographic studies of the hydrogenation of hexin-2 and hexene-1 (table) allows a deeper understanding of the mechanism of cis-trans-isomerization. Hydrogenation of hexene-1 from the very beginning of the



Diagrams of the composition of catalyze

process is accompanied by the formation of cis-hexene-2 and trans-hexene-2, with the amount of trans-isomer prevailing. In the presence of hexene-1, there is no delay in isomerization, in contrast to strongly adsorbed hexin-2 [4, 9]. The conditionality

of isomerization processes by the presence of tightly bound hydrogen is confirmed by the data [10], which indicate a strong decrease in the yield of hexene-2 (and the bond migration coefficient $-C=C-$) with a decrease in the weight of the Raney nickel.

Conclusion. The activity, selectivity and isomerizing ability of modified Raney nickel obtained from Ni-Al-Me and Ni-Al-Me₁-Me₂ alloys (where Me-Cu, Ag, Zn, Ti, Zr, Sn, Pb, Ta, Bi, Cr, Mo, Mn, Fe and Pd), in the reactions of hydrogenation of phenylacetylene, hexin-2 significantly depend on the nature of the additives introduced into the Ni-Al alloy.

In the hydrogenation reaction of hexin-2, multicomponent Raney nickel exhibit high stereociphicity. The yield ratio of cis-hexene-2/trans-hexene-2 is 16-25, depending on the nature of the modifying additive.

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Резюме

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АЦЕТИЛЕН ҚОСЫЛЫСТАРЫН КӨП КОМПОНЕНТТІ ҚАҢҚАЛЫ НИКЕЛЬДІ КАТАЛИЗАТОРЛАРДА ГИДРЛЕУ

Жұмыста фенилацетилен мен гексин-2 гидрлеу реакцияларындағы көп компонентті никельді катализаторлардың каталитикалық белсенділігі мен талғампаз-

дылығын зерттеу нәтижелері келтірілген. Гексин-2 никель Ренейде көбінесе цис-гексен-2 түзе талғампазды және стереоспецификалық гидрленеді. Ni-Al-Me және Ni-Al-Me₁-Me₂ құймаларынан (me-Cu, Ag, Zn, Ti, Zr, Sn, Pb, Ta, Bi, Cr, Mo, Mn, Fe және Pd) алынған түрлендірілген қаңқалы никельді катализаторлардың белсенділігі, талғампаздылығы және изомерлейтін қабілеті Ni-Al құймасына енгізілетін қоспалардың табиғатына байланысты. Гексин-2 гидрлеу реакцияларында көп компонентті қаңқалы никельді катализаторлар жоғары стереоцификалық көрінеді. Цис-гексен-2/транс-гексен-2 шығуының қатынасы түрлендіруші қоспаның табиғатына байланысты 16-25 құрайды.

Түйін сөздер: ацетилен қосылыстары, фенилацетилен, гексин, гексан, гидрлеу, никельді катализаторлар, каталитикалық үйрек, модифицирлейтін қоспалар, белсенділік, талғампаздылық.

Резюме

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ГИДРИРОВАНИЕ АЦЕТИЛЕНОВЫХ СОЕДИНЕНИЙ НА МНОГОКОМПОНЕНТНЫХ СКЕЛЕТНЫХ НИКЕЛЕВЫХ КАТАЛИЗАТОРАХ

В работе приведены результаты исследования каталитической активности и селективности многокомпонентных никелевых катализаторов в реакциях гидрирования фенилацетилена и гексина-2. Гексин-2 на никеле Рене гидрируется селективно и стереоспецифично, с образованием преимущественно цис-гексена-2. Активность, селективность и изомеризующая способность модифицированных скелетных никелевых катализаторов, полученных из Ni-Al-Me и Ni-Al-Me₁-Me₂ сплавов (где Me-Cu, Ag, Zn, Ti, Zr, Sn, Pb, Ta, Bi, Cr, Mo, Mn, Fe и Pd), в реакциях гидрирования фенилацетилена, гексина-2 существенно зависят от природы добавок, вводимых в Ni-Al сплав. В реакциях гидрирования гексина-2 многокомпонентные скелетные никелевые катализаторы проявляют высокую стереоцифичность. Отношение выходов цис-гексен-2/транс-гексен-2 составляет 16-25 в зависимости от природы модифицирующей добавки.

Ключевые слова: ацетиленовые соединения, фенилацетилен, гексин, гексан, гидрирование, никелевые катализаторы, каталитическая утка, модифицирующие добавки, активность, селективность.