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CONTINUOUS HYDROGENATION OF BENZENE ON PROMOTED SKELETARY NICKEL CATALYSTS

Abstract. The aim of this work is to study the physicochemical properties of skeletal nickel catalysts modified by ferroalloys, and to develop a technology for the continuous hydrogenation of benzene. A series of new samples of modified alloyed alumina-nickel catalysts for hydrogenation of benzene to cyclohexane synthesized. Their phase and granulometric compositions, the porous structure of the skeletal nickel catalysts promoted by ferroalloys are studied. Highly active stationary alloy alumina-nickel catalysts with additives as modifiers, technologies for their preparation and activation is developed. The optimal conditions for the process of continuous hydrogenation of benzene under hydrogen pressure are determined. A method developed for the preparation of cyclohexane in the presence of nickel catalysts promoted by ferroalloys, which ensures a high total yield of the desired product.

Keywords: benzol, promoted nickel catalysts, phase composition of the catalyst, porous structure, granulometric composition, cyclohexane, continuous hydrogenation.

Introduction. One of the promising areas of chemical processing of aromatic compounds, which is catalytic hydrogenation, the synthesis products of this process are in great demand in the pharmaceutical, chemical, petrochemical, medicine and other industries. Currently, the world production of caprolactam the volume of production, as well as improving the synthesis of intermediates for the production of various synthetic fibers and resins are very relevant. It is also known [1, 2] that the problem of reducing the content of aromatic hydrocarbons in motor fuels can be solved in many ways, including derivation by adsorption or extraction, and by conversion to other, less harmful compounds. An effective method of improving the operational properties of fuels, in particular gasoline, is their de-aromatization, which consists in the process of hydrogenation of aromatic hydrocarbons in the presence of catalysts. Aromatic hydrocarbons, especially polycyclic, contribute to the formation of carbon deposits in internal combustion engines, which in turn leads to an increase in the NO₂ content of the exhaust gases. In the Republic of Kazakhstan, there are practically no processes for the de-aromatization of light fractions of oil. The reason for this are, firstly, low productivity and a short service life of industrial catalysts used, and secondly, an inadequate range of industrially important contacts and technologies. Catalytic reduction of benzene shows great practical importance, since reaction products have long attracted the attention of researchers as the starting objects for the synthesis of new compounds. Cyclohexane, obtained by catalytic hydrogenation of benzene used for the production of caprolactam, adipic acid and hexamethylenediamine, i.e. is a raw material for the production of synthetic fibers, as well as various resins. Thus, cyclohexane, obtained from local raw materials, creates the opportunity of import substitution in industry, and the products obtained during its processing open up new prospects for the domestic production of synthetic fibers and resins.

A review of the principle technological schemes of hydrogenation of benzene [3-7] shows that in many cases hydrogenation is carried out in the vapor phase at temperatures of 250-325°C and a hydrogen pressure of 10.0-27.0MPa. Platinumoids also used as catalysts. Naturally, under these conditions, isomerization and cleavage products observed in the catalyst, which reduces the quality of the desired product, cyclohexane.

New methods for increasing the activity, stability and mechanical strength of nickel catalysts, adding additives of other metals into the alloy, discovered at the time of their preparation [8-11]. As a result, effective catalysts found to accelerate the hydrogenation reaction of benzene. Hydrogenation of aromatic hydrocarbons carried out in the reactor with a periodic effect at the temperature range 20-200°C and hydrogen pressure 0.1-15.0MPa.

On an industrial scale, co-precipitated copper-chromite oxide catalysts also found wide application in the production of cyclohexane [12, 13], although they are not devoid of significant disadvantages in catalytic and operational properties in hydrogenation processes. In connection with these, the researchers proposed numerous modified Ni, Cu, Co-alloy catalysts [14-18], which have not yet acquired industrial application in these industries. Therefore, it is important to improve these catalysts by modifying them, in order further improve their selectivity, operational and catalytic properties in the hydrogenation of aromatic hydrocarbons in the liquid phase.

Methods. The main reactor is a high-pressure flow column. The process is carried out at the temperature range 473-523⁰K and hydrogen pressures at 10.0-27.0MPa. In the course of the studies, the solution of the unsaturated compound injected at a hydrogen module of 10 and the feed rate of the starting materials is 200-250 ml/h. Initial alloys were prepared according to known technology in a high-frequency melting furnace. The specificity of the preparation of the Ni-Al system is the possibility of using aluminothermy in various furnaces. The temperature of the molten aluminum adjusted to 1000⁰C. When the exothermic reaction (aluminothermy) between nickel (ornickel oxide) and aluminum, the melt temperature increases to 1800⁰C. During the experiments, 100 g of skeletal catalyst with linear dimensions of 3-5 mm are loaded into the column and the leaching process carried out with a solution of NaOH in the reactor. Initially, up to 10% of aluminum removed, after the catalyst rinsed for several hours with distilled water at a high water feed rate and several hours at low.

Activation of the catalyst was carried out directly in the reactor itself. In this case, a granular alloy with linear dimensions of 2-4 mm (100 g) was placed in a special glass attached to the bottom of the reactor and the leaching was carried out with a 10% aqueous solution of sodium hydroxide.

During the leaching with the help of a dosing pump NDV-1000, the reactor initially filled with distilled water, and then an alkali solution fed from the "measuring tank". The degree of aluminum removal controlled by the evolution of hydrogen, the amount of which changed by the gas counter of the GSB-400. After the calculated amount of hydrogen was isolated to the leached catalyst, water supplied from the "measuring tank" to stop the leaching process and wash the catalyst from alkali residues to pH=7. The amount of aluminum removed from the consistency was about 10-15%.

Results and discussion. In this paper, we present the results of a study of the hydrogenation of benzene to cyclohexane on promoted skeletal nickel catalysts modified with ferroalloys (ferroalloys) (ferromanganese), ferrochrome silicon (FCS), and calcium ferrosilicone (CFS).

The granulometric composition of skeleton nickel catalysts with addition of FSH, FSK and ferroalloys studied. The data of microscopic and electron microscopic examination of the granulometric composition of skeleton nickel catalysts are given in table 1. All the catalysts are dominated by particles with $R = 0-2 \mu\text{m}$, which concentration reaches 75-89%. Table 1 shows that, as the amount of additives in alloys increases from 3 to 9% by weight, the concentration of particles with $R = 0-2 \mu\text{m}$ in different catalysts decreases within the limits of 89-75% depending on the nature of the alloying metals. In addition, the modifying additives also increase the concentration of particles with $R=2-4\mu\text{m}$. The results of optical microscopy show that practically all the investigated skeletal nickel catalysts are enriched by 90-99% particles with $R_{\text{max}} = 1-5 \mu\text{m}$.

The results of the granulometric analysis using optical microscopy and electron microscopy confirm the enrichment of skeleton nickel catalysts with particles with $R_{\text{max}} = 1 \mu\text{m}$. Modifying metals increase the proportion of particles with a size of 0-6 μm .

Table 1 – Results of microscopic and electron microscopic examination of skeleton nickel catalysts

Catalyst	Distribution of particles of % on the sizes R, microns					
	0-2	2-4	4-6	6-8	> 8	T ₃
Ni (50%Al)	77	8	6	2	7	0.12
Ni-3-10% FaTi	78	8	8	4	2	0.45
Ni-3-10% FaMo	85	6	5	2	1	0.35
Ni-3-10% FaCr	83	6	6	3	1	0.36

We studied [2] the porous structure of skeletal nickel catalysts with additives of ferroalloys. Argon sorption isotherms show that the forms of hysteresis loops for the majority of modified nickel catalysts are characterized by the parallel arrangement of adsorption and desorption branches in the middle region of relative pressure and according to the de Boer classification are A type, which indicates the predominance of cylindrical pores [3].

Table 2 shows the parameters of the porous structure of skeleton nickel (50% Al) catalysts with addition of ferroalloys. It can be seen that modifying ferroalloys mainly increase S_{BET} , S_{CUM} , respectively, to 110-130.5 and 85-98 m²/g; the volume of pores - in 1.1-1.4 times; the effective radius of the pore R_{EFF} is 1.06-1.5 times. A simultaneous increase in the specific surface area and in the pore volume with relatively high effective radii is apparently due to the dispersion of the nickel phase of the catalysts with modifying metals.

Table 2 – Parameters of the porous structure of skeleton alumino-nickel catalysts with additives of ferroalloys

Catalyst	S_{BET}^* , m ² /g	S_{CUM}^{**} , m ² /g	$\frac{S_{BET}-S_{CUM}}{S_{BET}}$, 100%	V _{of holes} , cm ³ /g	R_{eff} , E***	Isotherm type
Ni (50% Al)	105	75	28.5	0.105	30	A
Ni – 3-10% FaMo	110	85	22.7	0.120	34	A
Ni – 3-10% FaTi	130.5	98	24.9	0.138	36	A
Ni – 3-10% FaCr	123.7	92	23.9	0.148	36	A

*Bayer Emmet Taylor; **cumulative; ***angstrom.

We previously determined the structure and adsorption properties of the obtained alloys and catalysts. Further, these catalysts tested in the process of continuous hydrogenation of benzene in a column-type flow installation. During the experiments, the alloys activated by a 10% solution of sodium hydroxide. At the first leaching, 30% of aluminum removed, the catalyst saturation carried out in a stream of hydrogen for 18 hours at a process temperature of 160⁰C and a pressure of 0.5MPa. The rate of benzene supply varied from 60 to 120 ml/h. An increase in the hydrogen pressure from 5 to 8MPa revealed that with increasing hydrogen pressure up to 6MPa, the degree of conversion of benzene increases, and further increase in pressure does not affect the activity of the catalyst.

Table 4 shows that stationary ferroalloy catalysts exhibit absolute cyclohexane activity and their activity is higher than that of the industrial nickel-titanium catalyst. The values of the contact loads, annealed by 30% in aluminum Ni- FaMo catalysts at 120 ° C and 10MPa, reach respectively 0.70 h-1, which is 2.3 times higher than that of industrial nickel-titanium contacts. The results of the tests showed that the Cu-Al- FaMo catalyst is 1.9 times higher in productivity, and 2.0 times higher in stability than the industrial nickel-titanium contact.

The Ni-Al-FaMo catalyst recommended for the implementation into production of the production of cyclohexane from benzene [3].

Thus, a systematic study of the activity of stationary catalysts with additives of ferroalloys in the reaction of continuous catalytic hydrogenation of benzene with a wide variation in the parameters of the process carried out.

Table 4 – Results of continuous hydrogenation of benzene in a column-type flow installation

Catalyst	T, °C	Composition of catalyst		Wh ⁻¹	Relative duration of process
		cyclohexane	benzene		
Ni –Al	90-100	78-85	15-22	0.12-0.21	210
	110-120	81-92	8-19	0.26-0.28	
	130-140	87-98	-13	0.31-0.35	
Ni -Al- CFS	110-120	94-98	2-6	0.50-0.64	254
	90-100	94-97	3-6	0.42-0.63	
	110-120	96-99.8	0-4	0.53-0.70	
	130-140	98-99.8	0-2	0.69-0.87	
Ni -Al- FSC	90-100	96-99	1-4	0.47-0.72	420
Ni-Al- FaMo	90-100	96-98	4-2	0.48-0.7	
	110-120	99-99.8	1-0.1	0.65-0.82	
	130-140	99.5-99.8	0.5-0.1	0.94-1.2	
Ni-Ti industrial	90-100	84-96	10-16	0.40-0.44	202
	40-120	84-95	5-16	0.47-0.50	
	130-140	98-99.8	0-10	0.50-0.60	

Conclusion. A series of new samples of modified alloy alumina-nickel catalysts for hydrogenation of benzene to cyclohexane synthesized. Their phase and granulometric compositions, the porous structure of the skeletal nickel catalysts promoted by ferroalloys studied. The kinetic regularities of the hydrogenation process on modified nickel catalysts are established. Depending on the temperature and pressure of hydrogen, the optimal conditions for the realization of the technological process for the synthesis of cyclohexane are established. The promoting effects of ferroalloys (FaMo, FMo, FMnMo and FTi), on the physicochemical and adsorption properties of alloyed alumina-nickel catalysts studied. The kinetic regularities of the hydrogenation of benzene on samples of promoted catalysts established. It is experimentally determined that on the developed promoted skeletal catalysts, the rate of selective hydrogenation of benzene increased by a factor of 1.0-1.6 times, than without modifying additives. The optimal compositions of modified alloy catalysts, the conditions for their preparation, activation and hydrogenation processes in their presence identified.

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БЕНЗОЛДЫ ЫНТАЛАНДЫРЫЛҒАН ҚАҢҚАЛЫ НИКЕЛЬ ШАПШАНДАТҚЫШТА ҮЗДІКСІЗ ГИДРЛЕУ

Аннотация. Жұмыстың мақсаты темір балқымаларымен модифицирленген қаңқалы никельді шапшандатқыштардың физика-химиялық қасиеттерін зерттеу, сонымен қатар бензолды осы шапшандатқыштың көмегімен үздіксіз гидрлеу технологиясын жасап шығару болып табылады. Алюмо-никельді балқыма шапшандатқыштардың модифицирленген жана сериялары бензолды циклогексанға дейін гидрлеу үшін синтезделген. Олардың фазалық және гранулометриялық құрамдары, темір балқымаларымен ынталандырылған қаңқалы никельді шапшандатқыштардың борқылдақ құрылымы зерттелген. Жоғары белсенділікке ие стационарлы балқымалы алюмо-никельді үстемелі шапшандатқыштар модификатор ретінде дайындау технологиясы және белсендірілуі жасалып шығарылған. Сутегі қысымы астында бензолды үздіксіз гидрлеу үрдісінің тиімді шарттары анықталған. Мақсатты өнімнің жалпы шығысын қамтамасыз ететін темір балқымаларымен ынталандырылған никельді шапшандатқыш қатысындағы циклогександы алу әдісі жасап шығарылды.

Түйін сөздер: бензол, ынталандырылған никельді шапшандатқыштар, фазалық құрам, шапшандатқышты борқылдақ құрылым, гранулометрлік құрам, циклогексан, үздіксіз гидрлеу.

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НЕПРЕРЫВНОЕ ГИДРИРОВАНИЕ БЕНЗОЛА НА ПРОМОТИРОВАННЫХ СКЕЛЕТНЫХ НИКЕЛЕВЫХ КАТАЛИЗАТОРАХ

Аннотация. Целью данной работы является исследование физико-химических свойств модифицированных ферросплавами скелетных никелевых катализаторов, а также разработка технологии непрерывного гидрирования бензола в их присутствии. Синтезированы серии новых образцов модифицированных сплавных алюмо-никелевых катализаторов для процессов гидрирования бензола до циклогексана. Исследованы их фазовый и гранулометрический составы, пористая структура разработанных промотированных ферросплавами скелетных никелевых катализаторов. Разработаны высокоактивные стационарные сплавные алюмо-никелевые катализаторы с добавками в качестве модификаторов, технологии их приготовления и активации. Определены оптимальные условия осуществления процесса непрерывного гидрирования бензола под давлением водорода. Разработан способ получения циклогексана, в присутствии промотированных ферросплавами скелетных никелевых катализаторов, обеспечивающий высокий суммарный выход целевого продукта.

Ключевые слова: бензол, промотированные никелевые катализаторы, фазовый состав катализатора пористая структура, гранулометрический состав, циклогексан, непрерывное гидрирование.

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