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Synthesis and Research of the Nickel Catalysts of Liquid-Phase Hydrogenation of Benzene Promoted by Ferroalloys

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Abstract

This work develops the technique and technology of modification by ferroalloys of floatable nickel catalysts of hydrogenation of benzene. It in detail studies the influence of the nature of metal of the catalyst, the modifying additives, the size of particles, technological parameters. They worked up reliable data on phase, granulometric and chemical structures, porous structure explaining activity, selectivity and stability of catalysts. The synthesized nickel catalysts are tested in the course of hydrogenation of benzene to cyclohexane in the liquid phase.

Keywords: ferroalloy, nickel catalyst, hydrogenation of benzene, granulometric structures, chemical structures, porous structure, activity of catalysts, selectivity of catalysts, stability of catalysts

Introduction

Development of organic chemistry, petrochemistry and industrial organic synthesis showed that one of the most perspective methods of processing of aromatic connections is its catalytic hydrogenation. The products received thus are in great demand in pharmaceutical, chemical, petrochemical, medicine and in other industries. Cyclohexane and its derivatives got broad application in other industries. Cyclohexane is generally used to produce a caprolactam, adipic acid and hexamethylenediamine, i.e. as a raw material for production of synthetic fibers, and as well as various pitches [1]. Now in the world the output of a caprolactam reaches nearly four million tons per year. Due to the above, the researches directed on improvement of technologies of synthesis of semi-products for production of various synthetic fibers and pitches are very actual [2].

Therefore, despite the increased need of the industry for products of selective hydrogenation of aromatic connections, the problem of development of new highly effective and modifications of the existing catalysts of industrial function remains not solved so far. It is connected with that in literature practically there are no data of systematic researches of the process of hydrogenation of aromatic connections on multicomponent nickel systems of catalysts in the liquid phase.

Experimental part

Experimental studies on receiving the catalysts containing additives were carried out in the high-frequency melting furnace of the OKB-8020 brand. In the quartz crucible was placed the calculated quantity of Al in the form of ingots and gradually lifted temperature to 1000-1100˚ and at these temperatures the calculated amount of nickel in the form of shavings or powder was put into fusion, due to exothermic reaction in the eutectic system the temperature of fusion increased to 1700-1800˚C. The mixing process by an induction field was in limits of 3-5 minutes. The received fusion was merged in graphite molds and the alloy after cooling on air was crushed to grains of 0,25mm size. Activation of alloys is carried out as follows: 1,0 g of the alloy was leached by 20% water solution of caustic sodium taken in the volume of 40 cm^3, in the boiling bain-marie within 1 hour. After that the catalyst was washed from alkali by water till the neutral reaction on phenolphthalein. The catalyst received thus was used for hydrogenation of benzene and physic-chemical researches.

Results and their discussion

Introduction of additives of various metals to Ni–Al alloys is the most effective way to receive the high-productive modified nickel skeletal catalysts possessing high activity, selectivity and stability in hydrogenation processes [3].

We investigated influence of ferrochrome silicon (further FChS), ferromolybdenum (further FMo), ferrotitanium (FTi) and ferrocalcium silicon (further FCS) on the phase structure and the structure of nickel alumina alloys and catalysts. The choice as the modifying components of skeletal catalysts of ferroalloys is caused by their easy availability, low cost and the contents in them of the alloying additives [4] which in the course of leaching of catalysts pass into oxides of various degrees of valency (Mo, Fe). The results are given in table 1. Table 1 shows that the modifying metals have essential impact on qualitative and quantitative structure of initial alloys and catalysts. Additives create except usual for the alloy of Ni-Al (50–50) phases – $NiAl_3$, Ni_2Al_3 and a eutectic ($NiAl_3$+Al) new phases – Fch which are still not deciphered. The sizes of the areas occupied by separate phases were determined by the method of secants.

Table 1
Characteristics of aluminum-nickel alloys and catalysts with the addition of ferroalloys

The modifying additives	Alloys					Catalysts		
	Phases area, %			$Ф_x$	$NiAl_3$ / Ni_2Al_3	Parameter lattice crystal (a), nm	Crystal size (L), nm	Specific surface (S) m^2/g
	$NiAl_3$	Ni_2Al_3	Al+Ni Al_3 eutectic					
Ni – Al = 50 – 50								
-	50	40	10	-	1,25	0,353	5,4	1,5
Ni – 50% Al – FCS								
3-10,0	50	39	7	3	1,28	0,353	4,7	110
Ni – 50% Al – FMo								
3-10,0	48	44	12	6	1,33	0,353	4,6	130
Ni – 50% Al – FTi								
3-10,0	45	33	11	10	1,36	0,353	3,4	112,5
Ni – 50% Al – FChS								
3-10,0	44	39	11	8	1,33	0,353	3,2	122,4

The areas of the phases $NiAl_3$ and Ni_2Al_3 fluctuate within 45-50 and 33-44% and they decrease with growth of concentration of metals in alloys. The content of the eutectic mix and Fch mainly increases respectively to 12% with growth of additives quantity in alloys. $NiAl_3/Ni_2Al_3$ ratio in the promoted alloys is higher (1,28-1,37) than in the alloy of Ni-Al (50-50) without additive (1,25) and decreases with growth of concentration of the alloying metals or increases from the ferrocalcium silicon containing to the ferromolybdenum containing alloys. Catalysts consist of skeletal nickel γ–Al_2O_3, Ni_2Al_3 and Fkh. The modifying additives don't influence on the parameter of nickel crystal lattice, but considerably make small its crystals (from 5,4 to 3,2 nanometers); increase a specific surface of the catalyst to 130,0 sq.m/g.

Thus, input to Al % Ni–50 alloy of ferroalloys additives significantly influences on the phase structure, structure and specific surface of the skeletal nickel catalysts.

Results of the X-ray spectral analysis (tab. 2.) show that the unknown phase of Fch in various catalysts has unequal structure. Only at addition of ferromolybdenum to the skeletal nickel catalyst as a part of leached phases of catalysts and alloys the following making components are found: Fe – 2-4%, Mo – 5-12%. When adding ferrochrome silicon as a part of leached phases of catalysts and alloys Fe is present in amount of 0,5-3,2%, Cr - in amount of 0,1 - 3,3%, Si – 0,9-1,4%, in the structure of the leached silicon wasn't found. In case of adding ferrocalcium silicon to the skeletal nickel catalyst as a part of leached phases of catalysts and alloys Fe is present in amount of 0,4-2,7%, Ca and Si aren't revealed in the structure of phases of catalysts.

Table 2.
Results of the X-ray spectral microanalysis of the unknown phase of Fch found in the modified catalysts

Structure of alloys		Chemical composition		
chemical, mass., in %	Phase	certain phases, mass., in %	catalysts, mass., in %	leached phases, mass., in %
1	2	3	4	5
Ni – Al – FMo				
Ni – 45,0 Al – 46,0 Fe – 2,0 Mo – 3,0	(Ni-0,56 Mo-0,33 Fe-0,11)Al_3	Ni – 43,2 Al – 40,5 Fe – 4,0 Mo – 12	Ni – 88,2 Al – 3,5 Fe – 1,6 Mo – 5	Ni – 78 Al – 3,5 Fe – 2 Mo – 12
Ni – Al – FChS				
Ni – 44,3 Al – 45 Fe – 2,5 Cr – 3,5 Si – 1,0	(Ni-0,51 Cx-0,25 Fe-0,17 Si -0,1)Al_3	Ni – 41,3 Al – 42,7 Fe – 3,2 Cr – 3,3 Si – 1,4	Ni – 87,2 Al – 3,1 Fe – 1,6 Cr – 2,0 Si – 0,9	Ni – 79 Al – 3,0 Fe – 0,5 Cr – 0,1 Si – 0
Ni – Al – FCS				
Ni – 43,5 Al – 44,2 Fe – 2,5 Ca – 0,8 Si – 0,9	(Ni-0,45 Ca-0,1 Fe-0,15 Si – 0,15)Al_3	Ni – 40,5 Al – 42,0 Fe – 2,7 Ca – 0 Si – 0	Ni – 86,7 Al – 3,3 Fe – 1,5 Ca – 0 Si – 0	Ni – 76 Al – 3,1 Fe – 0,4 Ca – 0 Si – 0

Thus, the ferroalloy containing nickel catalysts represent complex system in which additives form the new centers of activation. As show the results of the X-ray spectral analysis in case of the ferromolybdenum additive the number of such centers considerably increases due to inclusions of Fe and Mo that explains their high catalytic activity in reaction of hydrogenation of benzene to cyclohexane.

It is investigated the particle size distribution of skeletal nickel catalysts with additives of FChS, FCh, FCS and FMo ferroalloys. Data of microscopic and electronic-microscopic research of the particle size distribution of skeletal nickel catalysts are provided in table 3. It is shown that nature of distribution of particles on fractions depends on nature and content of the modifying additives in initial nickel alloys. In all catalysts prevail particles with R = 0-2 microns which concentration reaches 75-89%. With growing quantity of additives in alloys from 3 up to 9% of masses, concentration of particles with R = 0-2 microns in catalysts differently decreases within 89-75% depending on the nature of the alloying metals. Besides, the modifying additives also increase concentration of particles with R = 2-4 microns. Results of optical microscopy show that practically all the studied skeletal nickel catalysts are enriched for 90-99% with particles with $R_{макс}$ = 1-5 microns.

Table 3

Results of microscopic and electronic-microscopic research of skeletal nickel (50% Al) catalysts with additives of ferroalloys

Catalyst	Distribution of particles % on R sizes, micron					
	0-2	2-4	4-6	6-8	> 8	T_3
Ni (50%Al)	77	8	6	2	7	0,12
Ni–3-10% FCS	78	8	8	4	2	0,45
Ni–3-10% FTi	82	12	4	1	1	0,41
Ni–3-10% FMo	85	6	5	2	1	0,35
Ni–3-10% FChS	83	6	6	3	1	0,36

We studied the porous structure of skeletal nickel catalysts with ferroalloys additives. Isotherms of sorption of argon show that forms of hysteresis loops for the majority of the modified nickel catalysts are characterized by the parallel arrangement of the adsorptive and desorptive branches in average area of relative pressures and on de Bour's classification they belong to A-type that testifies to prevalence of cylindrical pores. Maxima of pore distribution aren't allocated, but it is possible to notice that they are in close area.

Parameters of porous structure of skeletal nickel (50% of Al) catalysts with ferroalloys additives are specified in table 4. It shows that the ferroalloys generally increase $S_{БЭТ}$, $S_{КУМ}$ respectively to 110-130,5 and 85-98 sq.m/g; the volume of pores – by 1,1-1,4 times; effective radius of pores of Reff – by 1,06-1,5 times. The simultaneous increase of the specific surface and volume of pores with rather high effective radiuses apparently occurs due to dispergation of the nickel phase of catalysts by the modifying metals.

Thus, results of research of phase, chemical, granulometric compositions and structure of nickel alloys and catalysts showed that the modifying metals influence on $NiAl_3/Ni_2Al_3$ ratio in alloys, increase the sizes of particles of catalysts, their specific surface and volume of pores, and also a share of micro- and supermicropores.

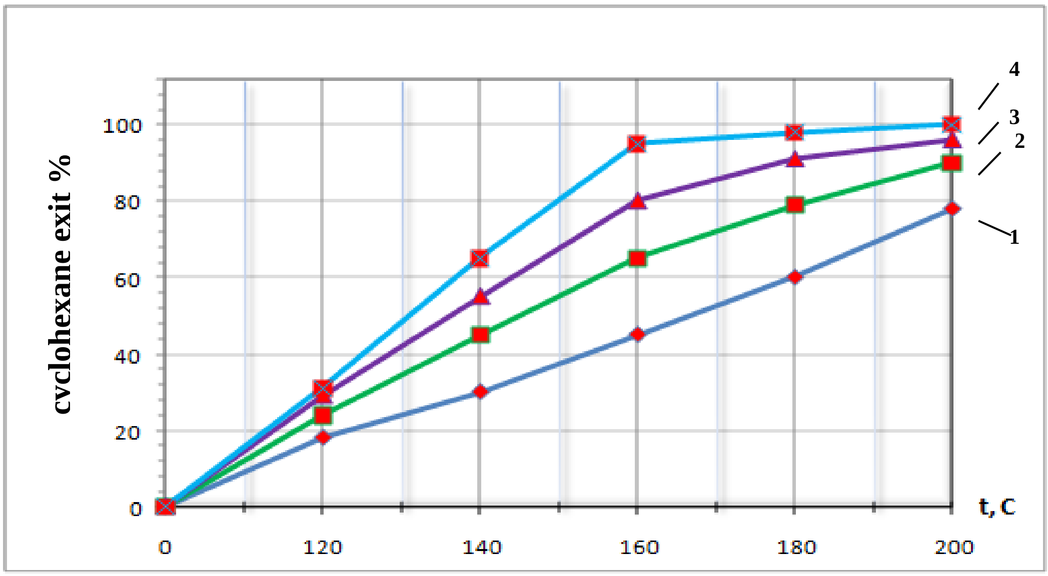
Further, it was experimentally determined that with change of concentration of benzene from 100 to 25% the process speed doesn't practically change, i.e. doesn't depend on concentration of the initial substance. It testifies that heterogeneous reaction proceeds on the zero order concerning benzene the rectilinear course of the received dependence once again confirms the zero order of reaction on benzene.

Table 4
Parameters of porous structure of skeletal nickel (50% of Al) catalysts with ferroalloys additives

Catalyst	$S_{БЭТ}$, m^2/r	$S_{КУМ}$, m^2/r	$\frac{S_{БЭТ} - S_{КУМ}}{S_{БЭТ}}$ 100%	V_{por}, sm^3/r	R_{eff}, Å	Isotherm type
Ni (50%) Al	105	75	28,5	0,105	30	A
Ni – 3-10% FCS	110	85	22,7	0,120	34	A
Ni – 3-10% FMo	130,5	98	24,9	0,138	36	A
Ni – 3-10% FTi	112,5	86	23,5	0,145	37	A
Ni – 3-10% FChS	123,7	92	23,9	0,148	36	A

During researches it was studied catalytic properties and kinetic regularities of reaction of hydrogenation of benzene on the floatable alyumo-nickel catalysts received from multicomponent systems. As additives to the nickel catalyst ferroalloys-ferrochrome silicon (FChS), ferromolybdenum (FMo), ferrotitanium (FTi) and ferrocalcium silicon (FCS) are used.

Data of results on research of hydrogenation of benzene on the skeletal nickel catalysts with additives of optimum composition of ferroalloys (5,0% of FChS, 3,0% of FMo and 5,0% of FCS) at various temperatures are given in fig. 1. The analysis of data shows that temperature increase of the experience from 120 till 200˚C significantly increases the cyclohexane exit on all types of catalysts. However on the most active nickel-ferromolibdenum (3,0 weight. % FMo) catalyst the cyclohexane exit in the range of temperatures 120-200˚C increases from 26,0 till 100%.

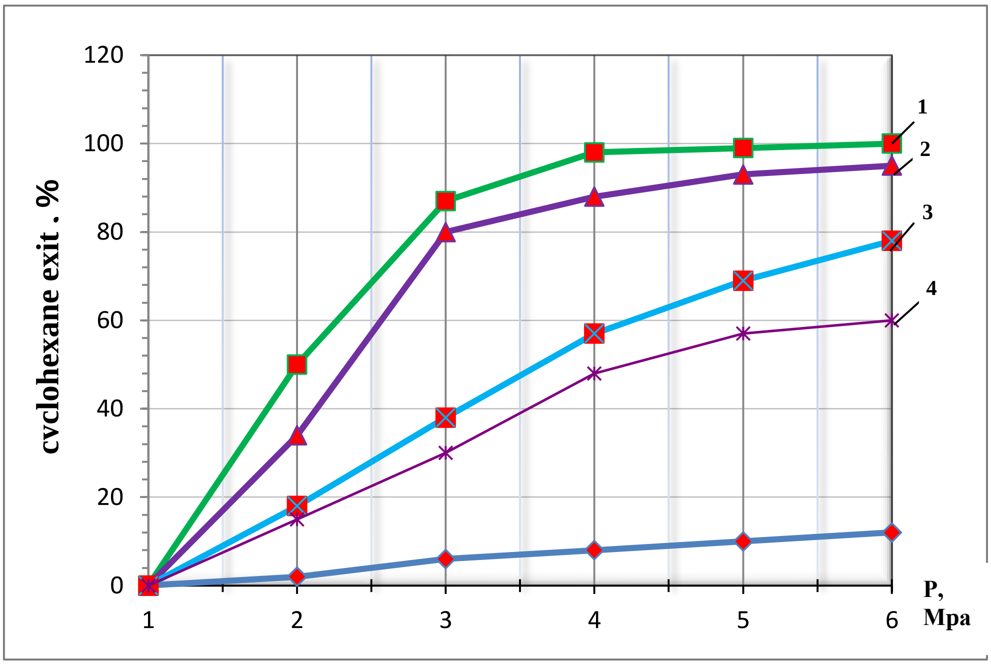


1 - Ni –50% A1; 2 – Ni – FCS- AI; 3 – Ni-FChS –AI; 4 – Ni-FMo –AI

Fig. 1. Dependence of the extent of transformation of benzene on the experience temperature on the skeletal nickel catalysts with additives of Mo, FCS and FChS under pressure of hydrogen of 4 MPas.

It should be noted that low activity is shown by the nickel catalyst containing ferrocalcium silicon additives. The reaction product yield on this catalyst reaches 88,0% at 200˚C while on the skeletal nickel catalyst, at the same temperature, it makes 74,6%. The values seeming activation energy calculated in the range of 120-200˚C on the promotor catalysts make from 6,3 till 9,5 kcal/mol.

Results of researches of influence of hydrogen pressure upon activity of the above mentioned nickel catalysts with ferroalloys additives at 160˚C are shown in fig. 2. The analysis of data shows that the hydrogen pressure variation from 2 to 12 MPas have a positive impact on activity of the promoted nickel catalysts. It is found out that the greatest activity still show nikel ferromolibdenum (3 weight. %) and nikel ferrochrome silikon (5,0 weight. %) catalysts on which the cyclohexane exit sharply raises from 12,4 and 16,0 till 92,0 and 94,2% according to the catalyst type in interval the value of hydrogen pressure is 1,0-6,0 MPas. At value of pressure over 8-12 MPas there is breach of rectilinear dependence. Thus it is revealed changes of the order of reaction on hydrogen from the initial to the fractional. Change of the order of reaction on hydrogen is possible to explain by means of fuller saturation of the catalyst surface by the sorbed hydrogen which quantity corresponds to the stoichiometric ratio of components of reactionary system or transition of one mechanism of reactions to another. Besides, in our opinion the increase in pressure of hydrogen higher than the limit promotes slow increase of its concentration on the active surface and influences on the transition of the order of reaction on hydrogen to the zero value.



1 – Ni:FMo:AI = 47:3:50; 2 – Ni: FChS: AI = 45:5:50;
3 – Ni: FCS: AI=45:5:50 4 – Ni: Al = 50:50

Fig. 2 Dependence of exit of cyclohexane on hydrogen pressure on the skeletal nickel catalysts with additives of ferroalloys at 160˚C.

The promoting influence of ferroalloys can be explained by physical-chemical and adsorptive properties of initial alloys and catalysts, leading to formation of new additional phases and change of quantity of the available. In order to hydrogenate benzene respectively to cyclohexane, among tested by us the catalysts modified by ferroalloys the catalyst of 50% - Al, 47%-Ni and 3% of FMo structure was highly active and selective.

Conclusion

Thus on the basis of results of long-term researches it is possible to make the following conclusions: we for the first time synthesized series of new samples of the modified floatable alumo-nickel catalysts for benzene hydrogenation; their chemical, phase and granulometric structures, porous structure, and also the process of hydrogenation of benzene in the liquid phase were investigated; the complex research of physical-chemical characteristics of the developed catalysts promoted by ferroalloys was conducted. Kinetic consistent patterns of the process of hydrogenation on the modified Ni - catalysts depending on concentration of reagents in solution, temperatures and pressure of hydrogen were determined, optimum conditions of implementation of the technological process of cyclohexane synthesis were established; it was studied the promoting effects of ferroalloys (FMo, FCS, FChS, and FTi) on physical-chemical and adsorptive properties of floatable alumo-nickel catalysts, and also on their catalytic properties in reaction of liquid-phase hydrogenation of benzene. It was revealed that the modifying additives disperse crystals of the skeletal nickel, increase the specific surface, the share of micropores, volume of pores and their effective radius, and also sorption ability of alumo-nickel catalysts of the relatively low adsorptive on their surfaces of forms of hydrogen that promotes increase of catalytic activity of the modified specified ferroalloys of skeletal catalysts. It was revealed the optimum structures of the modified floatable catalysts, conditions of their preparation, activation and carrying out hydrogenation processes at their presence.

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