Obtainment of Sorbitol on Ferroalloy Promoted Nickel Catalysts

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Abstract

The systematic study of the activity of the catalyst suspended with ferroalloys additives in catalytic hydrogenation of glucose over a wide variation of process parameters is given in this article. Since nickel catalysts were studied sufficiently, we limited to the data of the phase composition and structure; specific surface of alloys and catalysts based on aluminum-nickel alloys, modified ferroalloys. Results of the study of phase, chemical, particle size distribution and structure of nickel alloys and catalysts have shown that modifying metals affect to the ratio of $\text{NiAl}_3/\text{Ni}_2\text{Al}_3$ in the alloys, crush crystals, increase catalyst particle size, surface area and large size pore volume and simultaneously increase the micro- and supermicro pore ratio. Highly active, stable and selective catalysts based on nickel for the sorbitol synthesis process was developed.

Keywords: Catalysts; Nickel; Autoclave; Hydrogenation; Glucose; Sorbitol; Physico-chemical properties; Ferroalloys; Kinetics

Introduction

Liquid-phase hydrogenation of unsaturated compounds is a complex process consisting of several successive stages: transport of reactants to the catalyst surface and their subsequent adsorption, catalytic conversion on the surface, and finally desorption of the reaction products from the catalyst surface. The most complex of these is the adsorption stage and acts on the reaction surface, having a chemical nature. At the same time it is impossible to calculate the rate constants of all these stages of the process, so it is assumed that the overall reaction rate should be determined by the speed of the slowest (limiting) of these stages.

As known, hydrogenation of the unsaturated compound can also flow through one or other mechanism depending on the nature of the catalyst, solvent and reaction conditions [1,2]. In this connection, we studied the effect of glucose concentration of the solution, the hydrogen pressure and temperature on the rate of hydrogenation of glucose.

It is known that the initial concentration of the hydrogenated compound in the reaction medium is one of the key factors for ensuring optimal process in the kinetic region. The hydrogenation rate is continuously increased with increasing glucose concentration up to 30% in glucose hydrogenation in the presence of skeletal nickel catalyst was found by Bizhanov [3]. A further increase in the concentration of glucose has practically no effect on the rate of reaction.

Experimental Part

The objects of the study were the following multicomponent alloys and catalysts: skeletal aluminum-nickel catalyst with modifying additives of ferrosilicon (FSi), ferromanganese (FMn) and ferrosiliconmanganese (FSiMn).

In this paper we studied the catalytic properties of alloy copper catalysts, modified with not pure metals, only with ferroalloys. The following ferroalloys were used as additives: ferromanganese (FMn), ferromolybdenum (FMO) and ferromanganesemolybdenum (FMnMo). The alloys were prepared in a high-melting furnace. The quartz crucible was placed a calculated amount of Al in the form of ingots and it was gradually heated up to 1000-1100°C, and then the necessary amount of Ni and ferroalloy additive in the form of chips or powder was added.

As a result of the exothermic reaction, the melting temperature was raised to 1700-1800°C, stirring by the induction field was lasted 3-5 min. The alloy was air-cooled in the graphite molds and was crushed to grains of 0.25 mm. To activate the alloy, 1.0 g of alloy was leached with 20% sodium hydroxide solution (in volume 40 cm³) in a boiling water bath for 1 h, after which the catalyst was washed from alkali with water until neutral reaction to phenolphthalein.

The study of kinetics was carried out in a modified batch reactor system (capacity of 0.5 l). The device was equipped with a hermetic drive capacity of 0.6 kW, the number of turnovers of the agitator was 2800 rev/min. Complete analysis of the reaction products was consisted of determining the reducing sugars by Machen Shoorlya method and polyhydric alcohols by paper chromatography. The experimental results of hydrogenation of different glucose batches on the ferroalloys modified nickel catalysts under a wide variation of process parameters are given in Table 1. It is seen that with increasing the concentrations of an aqueous glucose solution from 5 to 20%, sorbitol yield was decreased due to surface blocking by molecules of hydrogenated substances, and the reaction rate was remained constant or gradually increased. Independence of reaction rate on the concentration of glucose on less active skeletal nickel catalyst is maintained in areas of 80-100°C and 8 MPa and 120°C and 8 MPa and 60-120°C and 6-8 MPa and 100°C and 6 MPa and 40-80°C and 4-6 MPa and a gradual increase was observed for the remaining conditions. The rate constancy in change of the glucose concentration indicates zero order in unsaturated compounds, i.e., in these conditions, the hydrogenation is carried out at full saturation of catalyst surface by molecules of the starting material. Increasing the reaction rate with increasing glucose concentration in a relatively high temperature and hydrogen pressure in investigated catalysts indicates fractional reaction hydrogenated substance. The latter circumstance is due to apparently lack of the unsaturated compound on the surface

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Top, °C	P _{H₂} , MPa	C _{main} , %	Sorbitol yield (%) in time (min)		W·10 ⁴ mol/g _{ct} ·min	n _{kc}
			20	60		
1	2	3	4	5	6	7
Ni-FMn						
80	8	5	70.1	86.9	24.8	0.0
		10	44.0	67.9	25.5	
		20	25.2	39.3	26.0	
100	10	5	74.0	89.1	35.1	0.3
		10	55.9	75.2	38.9	
		20	33.3	58.3	42.6	
120	8	5	92.3	97.3	37.2	0.0
		10	60.7	77.1	36.8	
		20	30.9	52.7	35.8	
Ni-FMnMo						
60	8	5	60.7	80.9	22.0	0.0
		10	35.4	61.3	21.8	
		20	18.5	26.0	21.9	
100	8	5	81.1	96.2	32.4	0.2
		10	57.6	74.5	34.4	
		20	30.5	43.7	37.0	
100	6	5	74.9	96.2	31.8	0.0
		10	58.3	73.8	31.7	
		20	25.3	41.3	31.9	
Ni-FMo						
40	6	5	57.4	78.8	20.4	0.0
		10	34.0	51.3	20.3	
		20	16.3	25.0	20.1	
80	6	5	83.7	97.0	34.8	0.0
		10	52.9	71.4	35.1	
		20	22.7	34.4	34.8	
80	12	5	85.1	98.1	35.6	0.3
		10	63.8	83.8	39.7	
		20	36.1	51.7	43.8	
Note: Conditions: 1.0 g of catalyst (ct)						

Note: Conditions; 1.0 g of catalyst (ct).

Table 1: Effect of concentration of the glucose aqueous solution on the rate of hydrogenation.

resulting in a high process speed with relatively harsh conditions. Bizhanov studied in detail the effect of hydrogen pressure on the kinetics and mechanism of hydrogenation of sugars in the presence of nickel catalysts. It was noted, that the rate of hydrogenation is proportionally increases to a certain limit with increasing hydrogen pressure. The limiting pressure depends on the nature of the hydrogenated compound, solvent, catalyst, and temperature of the experiment. Reaction order with respect to hydrogen is changed from the first to zero, and with respect to hydrogenated substance from zero to fractional depending on the process conditions.

However, the kinetics of the hydrogenation of glucose in the presence of promoted ferroalloys of skeletal nickel catalyst was not investigated. In this connection it is of great interest to track the effect of the simultaneous change of hydrogen pressure and temperature of the experiment on glucose kinetics on promoted nickel catalysts.

The results of our research on the hydrogenation of glucose on nickel catalysts with ferroalloys additives showed that with increasing hydrogen pressure from 2 to 10 MPa and experimental temperatures in the range of 40-120°C, hydrogenation rate of glucose is increased from 5.4 to 54.7 mol/kg min. The most beneficial effect of hydrogen pressure is affected the activity of relatively passive contacts at low temperatures. Raising the test temperature in the range 40-120°C and in 2 and 10 MPa leads to a sharp increase in the process rate. The highest value of the temperature coefficient is occurred in the least active catalysts under

relatively low hydrogen pressures [4,5].

Experiments on the effect of the concentration of glucose and hydrogen show that the order of the reaction of hydrogenated substance is varied from zero to fractional and the order of hydrogen is fractional. Effect of hydrogen pressure on the kinetics and mechanism of monosaccharide hydrogenation in the presence of nickel catalysts was studied in detail by Bizhanov. He showed that the rate of hydrogenation is proportionally increased to a certain limit with increasing hydrogen pressure. The limiting pressure depends on the nature of the compound to be hydrogenated, solvent, catalyst, and the experimental temperature. Reaction order with respect to hydrogen is changed from the first to zero, and with respect to the hydrogenated substance from zero to fractional depending on the conditions of the process [6].

Modifying influence of ferroalloys consistent with the study of physical-chemical and adsorption properties of the starting alloys and catalysts and it is explained due to the formation of new and additional phases and changes in the available phases. Results of the effect of imposed additives on the activity of the multi-component nickel catalyst at a hydrogen pressure of 2-10 MPa are shown in Table 2. The results of our numerous studies carried out earlier [7] showed that the ferroalloys are semi-metallurgical plants, and they may be used as modifiers to increase the activity of alloyed nickel catalysts of xylose hydrogenation.

Top. °C	P _{H₂} , MPa	Xylitol yield (%) in time (min)		W·10 ⁴ mol/g _{cat} ·min	n _{H₂}	n _{main}
		20	60			
1	2	3	4	5	6	7
Ni – FMn						
40	2	4.9	8.5	13.0	1.0	0.0
	6	11.6	20.0	15.9	1.0	0.0
	10	15.0	26.5	17.8	1.0	0.0
80	2	11.1	16.7	20.8	0.9	0.0
	6	21.4	37.9	24.9	0.9	0.0
	10	31.6	53.7	25.8	0.9	0.0
120	2	23.7	31.1	40.9	0.7	0.0
	6	34.4	55.3	48.6	0.7	0.0
	10	48.4	81.5	54.7	0.7	0.3
Ni-FMo						
40	2	5.5	9.3	5.4	1.0	0.0
	6	10.9	21.3	8.8	1.0	0.0
	10	20.8	33.0	11.7	1.0	0.0
80	2	9.1	18.9	8.8	0.9	0.0
	6	22.9	35.7	16.0	0.9	0.0
	10	30.3	53.2	20.2	0.9	0.0
120	2	15.1	28.6	18.8	0.7	0.0
	6	35.0	56.0	29.5	0.7	0.0
	10	49.4	84.8	9.8	0.3	

Note: Conditions: 200 cm³ of 15% glucose solution 1.0 g catalyst.

Table 2: Influence of hydrogen pressure and experimental temperature on the rate of glucose hydrogenation.

This work is a continuation of previous research and devoted to the study of physical and chemical properties of the most active nickel alloys and catalysts modified by ferromanganese, ferromolybdenum and ferromanganese molybdenum (FMn, FMo and FMnMo).

Therefore, we studied the effect of ferroalloys additives on the phase composition, the pore structure and specific surface area of nickel catalysts. It is known that the skeletal nickel Ni- (50% Al) alloy, which consists essentially of aluminides NiAl₃, Ni₂Al₃ is used in the industry for the monosaccharide hydrogenation. Introduction of various additives of metals to Ni-Al alloys is the most effective way to obtain high-modified skeletal nickel catalysts having a high activity, selectivity and stability in the hydrogenation process [2,3]. Introduction of modifying metals to the nickel alloys generates new additional active centers, in particular aluminides changes phase composition of leached alloy, i.e., skeletal catalysts. The majority of the alloying metal (Ti, Mo, Ta, Zr, Fe) in the leaching of the starting alloys are oxidized to form oxides [4]. Studies have shown that in the received catalyst is presented gamma oxides of these metals in various degrees of valency in the stages of the adsorption and activation of reagents. These metal oxides represent refractory phase, which are located at the mouths of the pores and at the boundaries between the grains of a catalyst, which is reflected on its catalytic activity. Despite the fact that the last time a sufficient quantity of studies on the catalytic activity in the recovery of monosaccharide of ferroalloys modified nickel catalysts is presented, but there are insufficient attention is paid to the correlation of activity with physico-chemical characteristics.

It should be also noted that the literature has not matter about influence of ferroalloys additives on the physico-chemical properties of alloyed aluminum-nickel catalyst. Therefore we investigated the influence of FMn, FMo and FMnMo on the phase composition and structure of aluminum-nickel alloys and catalysts.

The results are shown in Table 3, which shows that the modifying

metals have a significant impact on the qualitative and quantitative composition and structure of the starting alloys and catalysts. The test additives of metals form except conventional for Ni-Al (50-50) alloy phases – NiAl₃, Ni₂Al₃ and eutectic (NiAl₃ + Al), a new Fx phase, which is not yet deciphered.

Square of NiAl₃ and Ni₂Al₃ phases are fluctuated within 36-52%, and 29-40%, and it is decreased with increasing concentrations of metals in alloys. The content of the eutectic mixture and Fx is advantageously increased to 18-20% and 12-15% respectively with increasing amounts of additives in the alloys. Ratio of NiAl₃/Ni₂Al₃ in the promoted alloys is more (1.28-1.37) than in the Ni-Al (50-50) alloy without additive (1.25); decreased with increasing concentration of alloying metals or increased from ferromanganese containing alloys to ferromanganese molybdenum containing.

The studies show that the catalysts are consisted of a skeletal nickel, -Al₂O₃, Ni₂Al₃ and Fx. Modifying additives do not affect the crystal lattice parameter of nickel, but it significantly pulverize its crystals (from 5.4 to 3.4 nm); increase the surface area of the catalyst within 100-112.5 m²/g.

We studied the porous skeletal structure of nickel catalysts with ferroalloys additives. Argon adsorption isotherms show that the shape of hysteric loops for most modified nickel catalysts are characterized by a parallel arrangement of the adsorption and desorption branches in the middle region of the relative pressures and belong to the A-type according to De Boer classification, that suggests the predominance of cylindrical pores. The maximum of the pore distribution is not allocated, but you can see that they are in a close area.

Table 4 shows the parameters of a porous structure of skeletal nickel (50% Al) catalysts with additions of ferroalloys. From the data of Table 4, it is shown that the modifier metal generally increases S_{BET}, respectively S_{CUM} to 110-130.5 and 85-98 m²/g; pore volume to 1.14-1.38 times;

Modifying additives	Alloys					Catalysts		
	Phase square, %			F _x	NiAl ₃	Crystal lattice parameter (a), nm	Crystal size (L), nm	Specific surface area (S), m ² /g
	NiAl ₃	Ni ₂ Al ₃	eutectic Al + NiAl ₃					
					Ni ₂ Al ₃			
Ni-Al = 50-50								
-	50	40	10	-	1.25	0.353	5.4	15
Ni-50% Al-FMn								
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-FMnMo								
3-10.0	45	33	11	10	1.36	0.353	3.4	112.5

Table 3: Physicochemical properties of modified nickel alloys and catalysts.

Catalyst	S_{BET}^* , m ² /r	S_{CUM}^{**} , m ² /r	$\frac{S_{BET} - S_{KUM}}{S_{BET}^{90\%}}$	V pore, cm ³ /r	R_{EFF}^{***} , Å	Type of isotherm
Ni (50% Al)	105	75	28.5	0.105	30	A
Ni-3-10% ΦMn	110	85	22.7	0.120	34	A
Ni-3-10% ΦMo	130.5	98	24.9	0.138	36	A
Ni-3-10%ΦMnMo	112.5	86	23.5	0.145	37	A

Note: *Bayer- Emmett-Taylor, **Cumulative, ***Effective.

Table 4: Parameters of the porous structure of skeletal aluminum-nickel (50% Al) catalysts with additions of ferroalloys.

effective pore radius R_{EFF} to 1.13-1.23 times. The simultaneous increase in the specific surface area and pore volume at a relatively high effective radius is occurred apparently due to the nickel phase dispersion of catalyst of modifying metal.

Conclusion

Thus, the introduction of ferroalloys additives to Ni-50% Al alloy significantly effects on the phase structure, the porous structure and the specific surface area of the skeletal nickel catalyst, which ultimately affects the catalytic activity in the reduction of monosaccharide. Results of physico-chemical studies outlined in this article can be successfully used in predicting the catalytic activity of alloyed nickel catalysts modified by ferroalloys in hydrogenation reactions of various unsaturated compounds in nature. The experimental data are corresponds to the certain data by others authors, working in the field of preparation and testing of alloyed catalysts not only based on nickel, but also on copper and cobalt.

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