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Furfural Hydrogenation on Alloyed Copper Catalysts with Additives of Ferromanganese

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ABSTRACT

The present work and is dedicated to the study of influence of ferroalloy-ferromanganese [FMn-alloy containing (% mass): 30.22 Fe: 64.0 Mn;4.3C; 1.28 Si; 0.2 impurities (P,S)] on activity of alloyed copper (50% Al) catalyst in the reaction of furfural hydrogenation under hydrogen pressure. Original alloys were prepared in high-frequency melting furnace by before developed [6] technology. Component content in the alloys varied (% mass): Cu 40...49, aluminum 50, ferromanganese 1.0 ... 10.0. The catalysts were prepared from 10 alloys by leaching with 20% of aqueous solution of caustic soda in a boiling water-bath during 1 hour. The phase composition and structure of the initial alloys and catalysts were investigated by means of roentgenographic and X-ray spectrum methods.

Keywords: furfural, hydrogenation of furfural, high activity and selectivity, additives of ferromanganese

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INTRODUCTION

Previously [1-5], we found that addition of ferroalloys have important influence on physical-chemical and adsorption properties of alloyed copper catalysts, as well as their catalytic activity in reaction of furfural liquid-phase hydrogenation to furfuryl alcohol (FA). The present work is a continuation of previous investigations and is dedicated to the study of influence of ferroalloy-ferromanganese [FMn-alloy containing (% mass): 30.22 Fe; 64.0 Mn; 4.3C; 1.28 Si; 0.2 impurities (P,S)] on activity of alloyed copper (50% Al) catalyst in the reaction of furfural hydrogenation under hydrogen pressure.

Original alloys were prepared in high-frequency melting furnace by before developed [6] technology. Component content in the alloys varied (% mass): Cu 40-49, aluminum 50, ferromanganese 1.0 ... 10.0. The catalysts were prepared from 10 alloys by leaching with 20% of aqueous solution of caustic soda in a boiling water-bath during 1 hour.

The phase composition and structure of the initial alloys and catalysts were investigated by means of roentgen graphic and X-ray spectrum methods.

MATERIALS AND METHODS

Experiments were carried out in the autoclave of Wisniewski with capacity of 250cm³ at intensive mixing [6]. For hydrogenation 200 cm³ of 10%-rated aqueous solution of furfural and 0.5g of the leached catalyst were used. The temperature of experiment was varied from 40 to 120°C, and of hydrogen pressure within 4-12MPa. Hydrogenation products were analyzed in chromatograph "Chrom-4" with flame ionization detector. The activities of suspended catalysts were assessed by (W) rate of hydrogenation, expressed in g of FA 1g of catalyst for 1 hour (W, g/g-h).

The optimum composition of the catalysts was tested in stationary state for continuous hydrogenation of (solvent-free) furfural on the enlarged laboratory installment of column type by method [6]. Industrial catalyst GIPKh-105 was activated by restoring it directly in reactor in a stream of hydrogen at 120°C during 3 hours. The activity of catalysts was assessed by fixed amount of contact loads, expressed in liters of hydrogenated furfural for 1 liter of catalyst per 1 hour (W, l/l-h or h⁻¹), corresponding 98-100% output of FA. Stationary catalyst regeneration was produced with to the extent of decreasing output of FA to 95-96%.

The study results of physical-chemical and adsorption properties of the original alloys and catalysts show that FMn additives form hard leachable inclusions, pulverize crystals of skeletal copper, increase specific surface, pore volume and size of their effective radii, sorption properties by hydrogen. All this has a positive effect on the activity of studying catalysts.

The data on furfuryl hydrogenation at 90°C and 6 MPa in (50% Al) skeletal copper catalysts with additives of FMn are presented in Table 1.

In Table 1 it is evident that furfuryl hydrogenation in studying Cu-FMn catalysts is carried out selectively by FA, formation rate of which is high for 16-20 more times than in (50%Al) skeletal copper without additives. Maximum activity is shown by the catalysts from the alloys with 5.0 and 7.0 % mass of FMn, FA output in which for 60 min. of the process reaches appropriately 58.7 and 56.7 %.

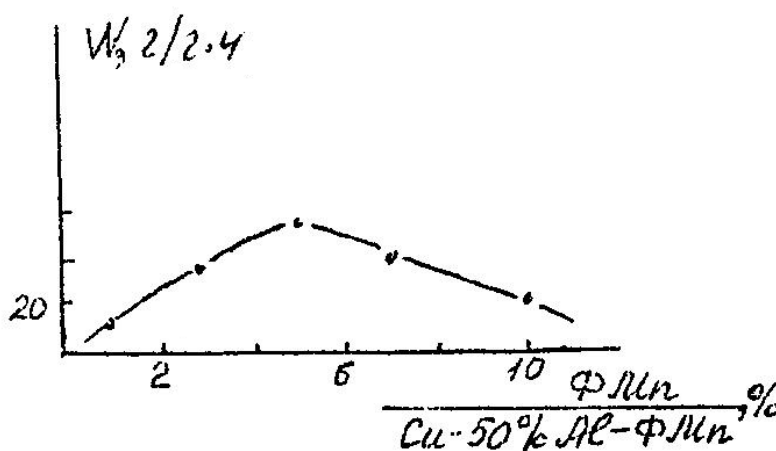
Figure 1 shows the dependence of furfural hydrogenation rate from the content of FMn in copper alloys.

From Figure 1 it is followed that activity curve passes through a maximum, corresponding to the catalyst from alloy with 5.0% mass of FMn.

A promoting effect of the FMn addition is due to the change of phase content, porous structure of catalysts and by increasing of their sorption ability according to the hydrogen. In addition, according to coordination approach [7], the additions of iron and manganese in the form of FMn have an acceptor effect on copper, strengthening the n- coordination of furfural molecules with the surface and Cu^δ-H^δ weakening of bonding strength [6].

Table I- Furfural hydrogenation on alloyed copper catalysts with additives of ferromanganese. Conditions: 200 cm³ of 10%-rated furfural aqueous solution: 90°C and 6 MPa; 0.5 g of the catalyst

Additive of ferromanganese, % mass	FA output (in %) during the time (min.)				W, g/g-h
	10	20	40	60	
Cu (50% Al)	-	-	1.8	3.0	1.2
1.0% FMn	12.3	19.6	34.3	46.7	19.1
3.0	16.0	25.8	39.6	54.0	22.0
5.0	18.1	28.5	46.3	58.7	24.0
7.0	17.4	26.5	44.4	56.7	23.1
10.0	16.0	21.5	37.0	50.5	20.6


Fig.1. Dependence of furfural hydrogenation rate at 90°C and 6 MPa from the content of ferromanganese in copper alloys

The effect of hydrogen pressure and temperature of the experiment on furfural hydrogenation rate in presence of an optimal catalyst Cu-5% FMn (50% Al). The results are given in Table 2.

Conditions: 200 cm³ of 10%-rated furfural aqueous solution: 0.5 catalysts

Table 2 - The influence of experimental temperature and hydrogen pressure on the activity of skeletal Cu-5% FMn (50% Al) catalyst

t, °C	PH ₂ MPa	FA output (in %) during the time (min.)				W, g/g-h	C _{med.} , h ⁻¹	Reaction order by H ²
		10	20	40	60			
40	4	-	1.0	4.0	8.5	3,5	0.8957	1.0
	12	5.0	9.0	17.5	27.4	11,2		1.0
60	4	7.0	11.5	21.5	30.0	12,2	3.1950	0.9
	12	26.0	40.0	60.0	72.0	29,4		0.9
90	4	12.5	21.0	34.8	46.0	18,0	5.2663	0.8
	12	38.8	54.8	76.8	90.6	37,0		0.8
100	4	15.0	24.5	44.5	55.0	22,4	9.0599	0.6
	12	40.5	56.0	78.4	92.5	37,8		0.6
120	4	21.0	33.6	51.0	63.0	25,7	12.3667	0.5
	12	48.6	65.0	89.0	100.0	40,8		0.5

From the data shown in Table 2 it follows that the simultaneous increasing of the hydrogen pressure from 4 to 12 MPa, the temperature of the experiment - in the range of 40-120°C leads to the increased rate of FA formation for 1.8-8.2 more times.

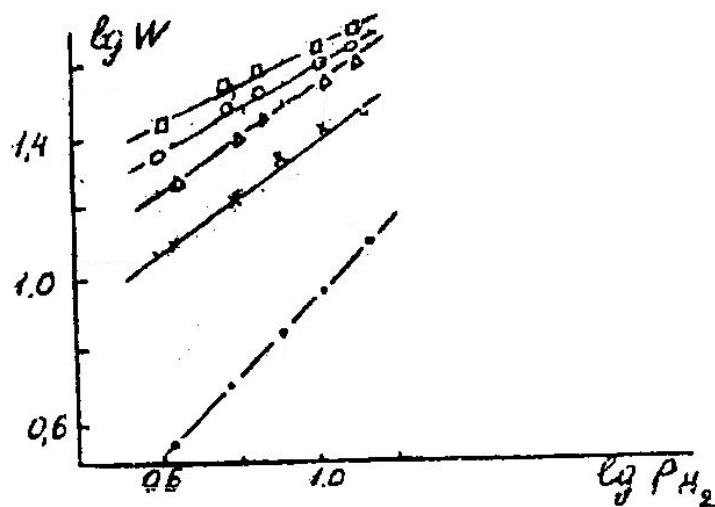


Fig. 2. Dependence of logarithm of furfural hydrogenation rate at 40°C (.), 60 (x), 90 (Δ), 100(o), 120(□) from the hydrogen pressure logarithm on Cu-5% FMn catalyst.

Fig. 2. demonstrates the logarithmic dependence of the furfural hydrogenation rate from the hydrogen pressure. Figure 2 show that this dependence at all temperatures has rectilinear character. The reaction order by hydrogen is reduced from 1 to 0.5 with a simultaneous increase of the pressure and temperature of the process.

Constant logarithm dependence of hydrogenation reaction rate from the reciprocal temperature in Cu-5% FMn (50% Al) catalyst is shown in Figure 3. From Fig.3 it is clear that this dependence follows the Arrhenius equation. Value of the apparent activation energy of the process, which is equal to 24.1 kJ/mol, indicates that furfural hydrogenation on the target catalyst is limited by the activation of both reactants.

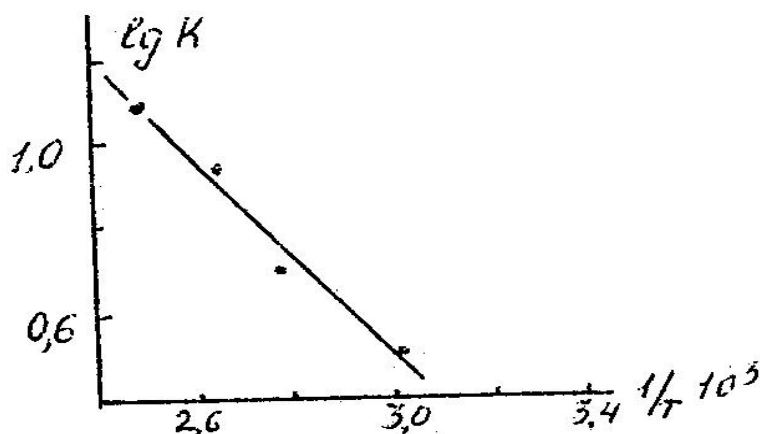


Fig.3. Change of the hydrogenation constant rate of logarithm against the reciprocal temperature on skeletal Cu-5% FMn catalyst

Solvent-free continuous furfural hydrogenation is conducted in Cu-50% Al -5,0FMn stationary catalyst. The results are given in Table 3.

It is evident that the only product of the continuous furfural hydrogenation in the target stationary catalyst is FA, output of which is up to 98.5-100%.

Table 3 - Continuous furfural hydrogenation (solvent-free) in the stationary Cu-50% Al-5% FMn catalyst

Leaching degree of Al, %	V catalyst cm ³	t°C	PH ₂ MPa	WH ₂ h ⁻¹	Wff, h ⁻¹	Product output of reaction, %		Approximate duration of the process, h
						FF	FA	
30	80.0	100-140	1. Cu-Al=50-50 4 180		0.135- -0.277	0.4-8.0	92-99.6	152
30	80.0	80- 140	2. Cu-50%Al-5%FMn 4		180 0.373- -0.490	0.0- 1.0	99- 100	480
35	77.5	120	2...8		180 0.400- -0.520	0.0- 1.5	98.5-100	472
40	75.0		4		10...180 0.415- -0.475	0.0- 1.5	98.5-100	464
Recover. at 120°C during 3 hours	90	90-120	3. Industrial GIPKh-105 4		18 0.200	0.0-15.0	85-100	260

Contact loads intensity of stationary Cu-50% FMn catalyst oscillates in the range of 0.373-0.475 h⁻¹, which is for 1.8-2.3 times higher than that contact of the industrial GIPKh-105. With increasing the depth of aluminum leaching from 30 to 40%, the experience temperature between 80-140°C, hydrogen pressure from 2 to 8 MPa, hydrogen bubbling speed between 10-180 h⁻¹ the contact load of target alloyed catalyst rises in 1.15-1.3 more times. It should be noted that according to the increasing the aluminum leaching depth from the catalyst the decreasing of approximate duration of the process between 480-464 h. are observed. The work stability of copper alloyed catalyst with FMn addition in 1.8-1.84 times higher than in contact of the industrial GIPKh-105 [1-7].

CONCLUSION

- In the article the effect of ferromanganese additives on the activity of copper alloyed catalyst in the reaction of periodic and continuous furfural hydrogenation under hydrogen pressure was investigated.
- It was determined that Cu-FMn catalysts reveal high activity and selectivity by FA, the rate of which is 16-20 more times higher than the corresponding value for non- promotor Cu (50% Al) contact.
- It is shown that with increasing the hydrogen pressure and temperature of the experiment furfural hydrogenation rate on Cu-FMn catalyst are increased. Meanwhile, the reaction order on hydrogen decreases.
- Contact load and stability of stationary copper catalyst work with additives of FMn in 1.8-8.2 more times higher than in the contacts of industrial GIPKh-105.

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