



HYDROGENATION PROCESSING OF RUBBER WASTE USING CATALYSTS BASED ON WASTE OF FERROALLOY PRODUCTION

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ABSTRACT

The work deals with the study of waste Ferroalloy production, stored on the territory of ash-slime storage of Aksu ferroalloy plant (AFP), with a view to their use as promising catalyst for the process of recycling of rubber products to the liquid fuel distillates. The composition and the surface of the studied catalyst were studied by scanning electron microscopy, X-ray phase analysis, the BET method and the IR-spectroscopy. Conditions of process of rubber waste hydrogenation on the catalyst were optimized. Quality characteristics of the produced fuel distillates were defined.

Key words: Waste, Ferroalloy production, Hydrogenation, Catalyst, Surface, Rubber waste, Fuel distillates, Resource saving.

INTRODUCTION

At last time, in the world a large amount of rubber goods and tires waste have gathered. They are of interest in terms of industrial processing as a source of valuable secondary hydrocarbons, fuels, metal cord.

The challenge of recycling of ferroalloy production wastes is also very important because of not only ecological problems but also containing of high amounts of transition metals such as iron, manganese, chromium and some other. These metals, it is known, are used for catalysts producing. Recently, we defined elemental composition of samples obtained from various parts of ash-slime storage territory of Aksu ferroalloy plant (AFP),

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AKSU, Republic of Kazakhstan). These results confirmed abilities of using studied raw materials as catalyst in the process of hydrogenation processing of rubber waste¹.

In connection with the foregoing, in the work a task of search and obtaining of new effective catalyst based on ferroalloy production waste rich in transition metals was set. Also the task of the work is development of new resource saving technology of carbon-containing waste processing in liquid fuel distillates.

EXPERIMENTAL

Electron microscopic study of surface and defining of elemental composition of obtained samples was performed using low vacuum scanning electron microscope JSM-6610LV (JOEL). X-ray analysis was performed using the powder method on diffractometer DRON-4-07 (Russia).

Surface of catalyst was studied by BET method of low temperature nitrogen adsorption using (AccuSorb) device of (Micromeritics) (USA). Sample (0.1 g) set into special ampul, then vacuumized at 200°C for 3-4 hr. Defining of studied catalyst surface was carried out by measuring of nitrogen adsorption at -196°C². Calculation of porosity was carried out by isotherms of nitrogen adsorption and desorption in pores of the sample using computer program of device.

Samples of catalyst were studied by IR-spectrometer Spectrum-65 Perkin-Elmer Fourier at frequencies of 4000-450 cm⁻¹. Crystalline samples were prepared as tablet with KBr.

Research of catalytic activity of thermal treated granulated catalyst in the reaction of hydrogenation was carried out in laboratory flow-type periodically acting device with stationary catalyst bed in argon atmosphere at 400°C and argon pressure of 5 MPa for 1 hr. Sample (15.0 g) of finely divided rubber (0.4-0.6 mm) was mixed with masout (15.0 g) (fraction with boil temperature of 650°C) as thickener and 0.67 g of studied catalyst.

Analysis of fuel distillates composition was carried out on GLC LCM-80M (USSR) with FID in isothermal mode. Stainless steel column 3 m long with diameter of 3 mm, filled with Chromaton N/W-DMCS with 15% Carbowax-20 M as active phase, was used for chromatographic analysis.

RESULTS AND DISCUSSION

We have suggested first time using waste of ferroalloy production as catalysts of process of hydrogenation processing of rubber waste. The part of the studied material was

used in the form of the powder catalyst without preliminary treatment and formation. Other part was formed in granules and was calcinated at high temperature.

Results of the X-ray spectral microanalysis of a sample of the thermal processed granulated catalyst showed significant changing of elemental composition in comparison with the powder catalyst. It is possibly caused by additional formation of oxides of the elements fixed on the device detector under the influence of high temperature. The chlorine and water, which are a part of the catalyst evaporate as a result of calcinating. It, apparently, can promote formation of porous structure and, increase in specific surface area, and more uniform distribution of the active centers (Tables 1 and 2).

Table 1: Results of the X-ray spectral microanalysis of a sample of the powder catalyst

Spectrum	O	Na	Mg	Al	Si	Cl	K	Ca	Ti	Cr	Fe	Total
	wt. %											
Spectrum 1	47.57	1.18	0.38	12.60	25.28	0.65	0.50	4.78	2.32	0.16	4.59	100
Spectrum 2	46.20	0.58	0.44	12.63	23.14	0.73	0.46	7.26	2.07	0.00	6.48	100
Spectrum 3	45.08	0.80	0.59	13.02	23.50	0.86	0.40	5.40	2.04	0.12	8.18	100
Spectrum 4	46.28	0.85	0.47	12.75	23.97	0.75	0.45	5.81	2.14	0.09	6.42	100
Max.	47.57	1.18	0.59	13.02	25.28	0.86	0.50	7.26	2.32	0.16	8.18	
Min.	45.08	0.58	0.38	12.60	23.14	0.65	0.40	4.78	2.04	0.12	4.59	

Table 2: Results of the X-ray spectral microanalysis of a sample of the thermal treated granulated catalyst

Spectrum	O	Mg	Al	Si	S	K	Ca	Cr	Mn	Fe	Zn	Total
	wt. %											
Spectrum 1	42.66	6.41	1.06	34.36	0.47	1.14	2.97	1.64	1.16	1.15	6.98	100
Spectrum 2	42.80	6.70	1.28	34.47	0.56	0.95	3.88	1.15	1.09	0.71	6.40	100
Spectrum 3	44.73	6.13	1.24	33.42	0.82	0.84	5.36	1.10	1.13	0.63	4.62	100
Spectrum 4	43.40	6.41	1.19	34.08	0.62	0.98	4.07	1.30	1.13	0.83	6.00	100
Max.	44.73	6.70	1.28	34.47	0.82	1.14	5.36	1.64	1.16	1.15	6.98	
Min.	42.66	6.13	1.06	33.42	0.47	0.84	2.97	1.10	1.09	0.63	4.62	

Electron microscopic study of a surface of powder and thermal treated granulated catalysts showed increase in dispersion of a metal phase after calcinating at high temperature.

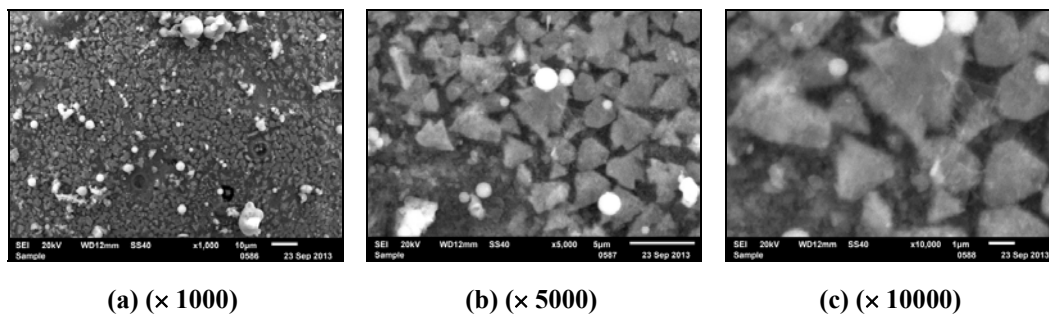


Fig. 1: Micrographs of powder catalyst at various resolutions (not thermal treated)

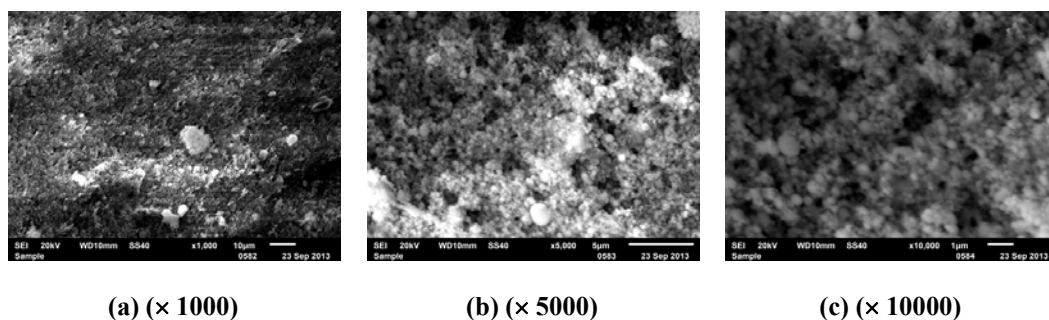


Fig. 2: Micrographs of thermal treated granulated catalyst at various resolutions

As known, increase of specific surface area and dispersity of catalyst metal phase facilitate increase of catalytic activity. So, using the method of electron microscopy, it was defined that preliminary thermal treatment by calcinating facilitates formation of more porous and active surface. It cause of opportunity of using of ferroalloy production waste as active catalysts for the process of rubber waste hydrogenation.

Samples of studied catalyst were analyzed by X-ray on diffractometer DRON-4-07 for defining of phase composition. The results of analysis are shown in Table 3. According to observed reflexes, iron oxide (maghemite), silica (α -quartz) and possible compounds of calcium and aluminium (hydrogrossular) are attended. X-ray phase analysis suggests included metals are finely divided. This indicates the probability of the formation of the catalytic centers of different nature, which is cause of activity and selectivity of catalyst on the whole.

X-ray phase analysis shows relatively high content of iron compounds in surface metal phase. Mössbauer spectroscopy method was used for a more detailed study of iron forms presented on the surface of studied catalysts. On spectrogram of powder catalyst

sample sextet 1, corresponding to form similar by parameters to γ -Fe₂O₃ (maghemite, possible substituted form), and sextet 2, corresponding to form similar by parameters to ϵ -FeOOH (possible substituted form, possible general formula (Fe_{1-x}M_x)OOH, where M – Mg, Al, Si, Ti, Cr etc.), are presented. Moreover, the presence of doublet 1, corresponding to iron in valence condition of Fe²⁺, and doublet 2, corresponding to condition of Fe³⁺, where founded.

Table 3: Phase composition of samples of powder and thermal treated granulated catalysts

Catalyst							
Powder				Thermal treated granulated			
Reflexes (Å)							
5.3	2.95	2.52	2.08	1.60	1.48		2.51
Phase composition							
Fe ₂ O ₃ (maghemite) (ASTM 39 – 1346)				Fe ₂ O ₃ (maghemite) (ASTM 39 – 1346)			
Reflexes (Å)							
3.34	4.22	2.45	2.12	1.81	1.54		-
Phase composition							
SiO ₂ (α -quartz) (ASTM 5 – 490)							
Reflexes (Å)							
2.68	2.20	-	-	-	-		-
Phase composition							
Possible - Ca ₂ Al ₂ (SiO ₄ , CO ₃ , OH) ₃ (hydrogrossular) (ASTM 3 – 801)							

Results of Mössbauer spectroscopy of powder catalyst sample are shown in Table 4.

Table 4: Results of Mössbauer spectroscopy of powder catalyst sample

S. No.	Name	Is (mm/c)	Qs (mm/c)	S rel. (%)
1	Sextet-1	0.36	-0.10	21
2	Sextet-2	0.52	-0.01	9
3	Doublet-1	1.04	2.06	51
4	Doublet-2	0.51	1.00	19

On spectrogram of thermal treated granulated catalyst only two doublets are presented. Doublet 1 is corresponding to iron in valence condition of Fe^{2+} . Doublet 2 is corresponding to iron in valence condition of Fe^{3+} . Results of spectrometric analysis of thermal treated granulated catalyst are shown in Table 5.

Table 5: Results of Mössbauer spectroscopy of thermal treated granular catalyst sample

S. No.	Name	Is (MM/c)	Qs (MM/c)	S rel. (%)
1	Doublet-1	0.28	0.56	64
2	Doublet-2	0.89	1.04	36

So, using of Mössbauer spectroscopy facilitated define that after thermal treating and granulating iron is more homogeneous, mainly in form of Fe^{2+} . Change of iron condition on the surface of catalyst after calcinating was confirmed by IR-spectroscopy.³ This method showed narrowing and shifting of valence oscillations frequency of Fe-O groups from 472 to 483 sm^{-1} (Table 6).

Table 6: IR-spectra of samples of powder and thermal treated granulated catalysts

Catalyst	$\nu \text{H}_2\text{O}$	$\nu \text{C-H}$	$\nu \text{CO}_3^{2-} (\text{CaCO}_3)$	$\nu[\text{Al-O, Si-O}]$	$\nu \text{Fe-O}$
	sm^{-1}				
Powder				1158	
				1096	
	3425	2941	-	914	472
	1625	2848		795	
				561	
Thermal treated granulated	3445	2936	1460	1112	483
	1637	2863	805	1049	

It is known, specific surface area and porosity are important properties of catalysts. Defining of porous structure is informing about value of internal surface of catalyst, and also about diffusion phenomenon, which are characterizing of influence of internal surface on catalytic process. As well as chemical compound, porous structure is important property, which is effect on quality of catalyst.

The surface of catalysts was studied by the BET method. Results showed that maximal specific surface area ($S_w = 116, 5184 \text{ m}^2/\text{g}$) and general volume of porous

($V_{\text{ads max}} = 98.46632 \text{ mL/g}$) observed on granulated catalyst. Powder catalyst showed lower values for these characteristics ($S_{\text{W}} = 7.019654 \text{ m}^2/\text{g}$; $V_{\text{ads max}} = 22.21623 \text{ mL/g}$) (Fig. 3). The dependence of the distribution of pore sizes in the powdered catalyst is shown in Fig. 3a. As it seen, it is characterized by low amount of small pores with diameter of 20 \AA . Unlike powdered, granulated catalyst total pore of similar diameter increases significantly, as evidenced by a large number of adsorbed nitrogen (98.46 mL/g) (Fig. 3b). The increase in the number of pores may be due to the evaporation of some volatile components in the process of preparation of the catalyst at the stage of calcinating. Thus there is an increase in the degree of heterogeneity of the catalyst surface, which was also confirmed by the results of X-ray analysis and electron microscopy.

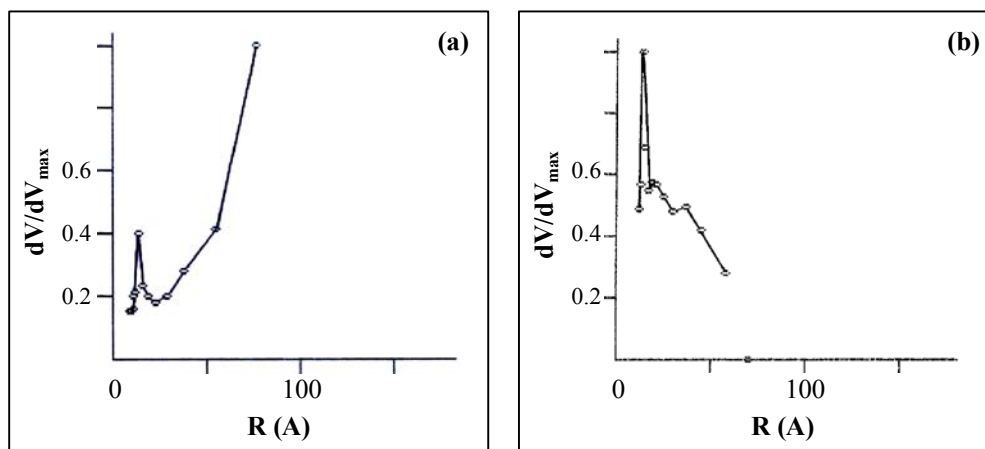


Fig. 3: The pore distribution according to their radii on the powder (a) and heat-treated granular (b) catalysts

Study of activity of heterogeneous catalyst, prepared from ferroalloy production waste, carried out on device for hydrogenation in periodical mode at high pressure⁴. For optimization of rubber waste hydrogenation process conditions thermal treated granular catalyst was used in laboratory flow type device with fixed catalyst bed in argon at temperatures $150\text{-}400^\circ\text{C}$ and under pressure $P_{\text{Ar}} = 5 \text{ MPa}$.

Influence of temperature on rubber waste conversion in set range of temperatures was studied. It was defined, that temperature of 400°C is optimal for the process. At this temperature most high yield of gasoline fraction (24.64 wt. \%), boiled in temperature range of $60\text{-}180^\circ\text{C}$ (Table 7) was obtained. Increasing of process temperature from 150°C to 400°C leads to increase of gas formation due to increased cracking function of catalyst. Therefore, the probability of thermal destructive cleavage of the hydrocarbon component of the original rubber raw materials with the formation of short molecules and their subsequent catalytic

hydrogenation conversion bring significant contribution in the process. The temperature decrease, apparently, reduces the contribution of the thermal destructive transformation of raw materials, resulting in lower selectivity of the catalyst towards the formation of gasoline distillate.

Table 7: Influence of temperature on liquid fuel distillates yield in the process of catalytic hydrogenating conversion of rubber ($m_{\text{catalyst}} = 0.67$, $m_{\text{masoute}} = 15$ g, $m_{\text{rubber}} = 15$ g, $t = 15$ min)

Temp. (°C)	Pressure (MPa)	Gas phase yield (%)	Liquid fuel distillates yield (wt. %)			Slime yield (wt.%)
			60-180°C	180-250°C	250-320°C	
150	5.0	1.2	-	-	28.4	71.60
200	5.0	2.0	-	-	32.2	67.80
250	5.0	2.4	-	1.1	35.1	63.80
300	5.0	3.8	-	10.2	32.0	57.80
350	5.0	11.3	1.78	18.3	21.2	58.72
400	5.0	33.43	24.64	18.38	21.88	35.10

The effect of studied catalyst sample on the yield of liquid fuel distillate of the process of hydrogenation of rubber waste was researched (Table 8). It is established, that the best amount of catalyst is 0.67 g, where the output of the fuel distillate and gasoline fractions corresponded to the maximum values.

Table 8: Influence of sample mass on liquid fuel distillates yield ($T = 400^\circ\text{C}$, $m_{\text{rubber}} = 15$ g, $m_{\text{masoute}} = 15$ g, $t = 15$ min)

Catalyst sample mass (g)	Pressure (MPa)	Gas phase yield (%)	Liquid fuel distillates yield (wt.%)			Slime yield (wt. %)
			60-180°C	180-250°C	250-320°C	
0.50	5.0	38.5	20.0	13.2	15.4	51.4
0.67	5.0	33.43	24.64	18.38	21.88	35.1
1.00	5.0	41.2	18.5	11.4	22.1	48.0
1.50	5.0	42.6	19.0	12.0	18.1	50.9

Liquid fuel distillates obtained after experiment were distilled in temperature range: 0-180°C (yield - 4.92 g); 180-250°C (yield - 3.67 g); 280-320°C (yield - 4.37 g). The hydrogenation rest was, in general, cord and resin in amount of 7.01 g.

The variation of the ratio of rubber and thickener (masoute) from 1:1 to 1:3 showed that it not significantly affects the yield of the liquid phase, but, in general, improves the quality of liquid products. The yield of liquid product at 400°C, 5 MPa, rubber: thickener ratio of 1 : 1 was 19.97 g, and yield of gas phase – 10 g.

Chromatographic analysis of gasoline distillate obtained as a result of hydrogenation processing of rubber waste on thermal treated granular catalyst at optimal conditions showed presence of mainly paraffins, isoparaffins, naphthenes and aromatic hydrocarbons. The mass fractions of product groups were obtained in the following ratio: paraffins (3.374%), isoparaffins (33.280%), aromatic hydrocarbons (8.870%), naphthenes (3.394%). Octane value of distillate, boiled at temperature range of 60-180°C, was 77 by research method.

Thus, it is shown the possibility of using ash-slime storage waste of Aksu ferroalloy plant by additional heat treatment and granulation to prepare an effective catalyst for hydrogenation catalytic processing of rubber goods and tires waste with the aim of implementing the principles of resource saving in industrial production.

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