World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:10, No:10, 2016

Structure and Activity Research of Hydrocarbons Refining Catalysts Based on Wastes of Ferroalloy Production

Zhanat Shomanova, Ruslan Safarov, Yuri Nosenko, Zheneta Tashmuchambetova, Alima Zharmagambetova

***Abstract*—**An effective way of utilization of ferroalloy production wastes is preparing hydrocarbon refining catalysts from them. It is possible due to accordable transition metals containing in the wastes. In the work, we are presenting the results on elemental analysis of sludge samples from Aksu ferroalloy plant (Aksu, Kazakhstan), method of catalysts preparing, results of physical-chemical analysis of obtained catalysts (X-ray analysis, electron microscopy, the BET method etc.), results of using the catalysts in some hydrocarbons refining processes such as hydrocracking of rubber waste, cracking of gasoil, oxidation of cyclohexane. The main results of catalytic activity research are: a) In hydrocracking of rubber waste 64.9% of liquid products were fuel fractions; b) In cracking of gasoil conversion was 51% and selectivity by liquid products was 99%; c) In oxidation of cyclohexane the maximal product yield 87.9% and selectivity by cyclohexanol 93.0% were achieved.

***Keywords*—**Catalyst, cyclohexane oxidation, ferroalloy production waste, gasoil cracking.

I. Introduction

IT is well known that recycling and utilization of industrial wastes is a strongly actual problem [1]-[3]. The wastes from metallurgy industry are of special interest because of content. For example, ash and sludge from ferroalloy plants contain valuable transition metals Fe, Cr, Mn and other significant elements (V, Ti, Al, Mg) [4].

At present time, waste from ferroalloy plant is reused mainly as a component for building mixtures [5]. It is a proper way, but in this case economic effectiveness of reuse is extremely low. The other way for very profitable reuse of the wastes is obtaining some catalysts for refining of hydrocarbon containing raw materials. That is possible because of the wastes are containing catalytically active metals in high disperse condition, which are distributed on the quite porous inorganic surface [6]. The structure of the ferroalloy production wastes is similar to typical heterogeneous catalysts obtained and used in industry.

In this work, we are presenting the structure research of catalysts based on wastes from Aksu ferroalloy plant (AFP, Aksu, Kazakhstan) and their activity in processes of rubber hydrorecycling, gasoil cracking and cyclohexane oxidation.

Z. Shomanova is with Pavlodar State Pedagogical Institute, Pavlodar, Kazakhstan (e-mail: zshoman@yandex.ru).

R. Safarov and Y. Nosenko are with Innovative University of Eurasia, Pavlodar, Kazakhstan (e-mail: ruslanbox@yandex.ru, nosenko1981@yandex.ru).

Z. Tashmuchambetova is with al-Farabi Kazakh National university, Almaty, Kazakhstan (e-mail: zheneta@mail.ru).

A. Zharmagambetova is with D.V. Sokolsky Institute of Fuel, Catalysis and Electro chemistry, Almaty, Kazakhstan (e-mail: zhalima@mail.ru).

II. Experimental

A. Preparing of Catalyst Samples

For research we used waste from ash-sludge storage of AFP. Two types of samples were used for physical-chemical analysis: powder waste sample and calcinated granulated catalyst based on the waste.

The powder waste sample was prepared by washing with distilled water, drying on the air, and then grinding in a mortar.

In order to prepare the calcinated granulated catalyst, the waste was washed with distilled water, then dried on the air and grinded in a mortar. Then, it was moisturized with distilled water and formed in cylindrical granules with a laboratory extruder. The granules were 1.5-2 mm in diameter and 10-15 mm in length. Thereafter the granules were dried at 100-150 °C for 5 hours with the rate of temperature rise of 25-30 °C per hour. Afterwards the granules were calcinated at 200 °C for 1 hour, at 300 °C for 1 hour, at 400 °C for 1 hour, at 500 °C for 5 hours.

B. Elemental Analysis

The analysis was performed using energy dispersive x-ray fluorescence spectroscopy with energy dispersive system for microanalysis INCA Energy 450, set on scanning electron microscope JSM-6610LV ("JOEL", Japan). The samples spectra were three-time obtained. Average containing of element was used as main indicator.

C. X-Ray Diffraction Analysis

The analysis was performed using x-ray diffractometer DRON-4-07 with a tube BSV-27 (Fe). Obtained diffractometric reflexes were interpreted by references ASTM and JCPDS (USA).

D. Scanning Electron Microscopy

The samples were researched with scanning electron microscope equipped with thermionic cathode (LaB6) JSM-6610LV ("JOEL", Japan). The unit is kitted with the system of energy dispersive microanalysis, the system of wave dispersive microanalysis, the system of analysis of diffraction of back-scattered electron with detector of backscattered electrons, the secondary electron detector of Everhart-Thornly, a secondary electron detector for low vacuum mode and

equipment for sample treatment. The unit was used for electron microscopic research of surface and for identification of elemental composition of samples.

E. The Surface Investigation

The surface investigation was performed by low-temperature nitrogen adsorption using the method BET on "AccuSorb" unit ("Micromeritics", USA). A charge of sample (0.1 g) was placed in a special vial, and then vacuumed at 200 °C within 3-4 hours. The definition of the surface of a catalyst was performed with measurement of nitrogen adsorption at the temperature of –196 °C. Calculation of porosity by isotherms of nitrogen adsorption and desorption in the pores of the sample was performed with kit software.

F. Gasoil Cracking

The gasoil fraction of 240 – 350 °C was used. The process was performed in laboratory flow-through installation with a stationary catalyst bed. Volume of catalyst – 75 ml. Temperature – from 450 to 500 °C. Pressure – atmospheric. The volumetric feed rate – 1.5 ml/min. The feedstock amount – 40 g.

G. Rubber Waste Hydrocracking

The worn tires were used as feedstock for hydrocracking process with using of obtained catalyst. The process was performed in laboratory flow-through installation with a stationary catalyst bed. The process was performed in argon atmosphere. Temperature – from 350 to 400 °C. Pressure – 5 MPa. The finely chopped rubber (15 g., 0.4-0.6 mm) was mixed with mazut (heavy fuel oil fraction of 650 °C) for obtain a pasta. The ratio “catalyst:mazut” was 1:3. Thereafter the catalyst (0.67 g) was added. Duration of the process – 1 hour.

H. Cyclohexane Oxidation

Cyclohexane oxidation was performed in thermostatic glass reactor. Oxidant – H_2O_2 (30% aqueous solution). Solvent – acetonitrile. Temperature – from 30 to 60 °C. Pressure – atmospheric. Duration of the process – 4 hours. In the glass reactor acetonitrile (1.2 ml), oxidant (0.9 ml), cyclohexane (0.3 ml) and the catalyst (0.03 g) were placed. The reaction mixture was mixed by magnetic stirrer.

I. Chromatographic Analysis

Results of rubber waste hydrocracking reaction were obtained on Kristall 2000M (Russia) using FID and universal capillary column. Carrier gas – argon.

Results of cyclohexane oxidation reaction were obtained on Chromos GC-1000 (Russia) using FID and universal capillary column. Carrier gas – argon.

III. Results and Discussion

A. Elemental Analysis

Elemental analysis was performed twice. We obtained elemental content of waste samples from AFP ash-sludge storage and prepared catalyst. The results revealed that elements are distributed non-equally on the ash-sludge storage area. We show element concentration meanings as average containing in each specimen. The content of waste sample, wt%: O – 46.18, Si – 34.16, Mg – 5.01, Ca – 4.44, Mn – 2.18, Cr – 1.73, K – 1.41, Zn – 1.38, Al – 1.23, Fe – 1.01, Na – 0.54, S – 0.4, Cl – 0.26, Sn – 0.06.

The results show quite high containing of catalytically active metals such as Cr, Mn, Fe. This fact points to opportunities of obtained material using for making of catalysts for various processes of chemical industry.

The catalyst was prepared from the waste material by the described method. The results of obtained catalyst granules elemental analysis are given as average meanings, wt%: O – 49.67, Si – 33.83, Mg – 5.03, Ca – 1.09, Mn – 1.47, Cr – 1.50, K – 1.63, Zn – 1.31, Al – 1.42, Fe – 1.01, Na – 0.93, S – 0.45, Cl – 0.67.

The certain differences in some elements containing, for example tin, are explained by non-equal distribution of elements on the territory of ash-sludge storage. This fact is a challenge in the research.

B. Electron Microscopy

By the method of electron microscopy, it was established that temperature treatment of catalyst granules lead to changes in surface structure. On Fig. 1, electron micrograph of prepared waste sample is shown.

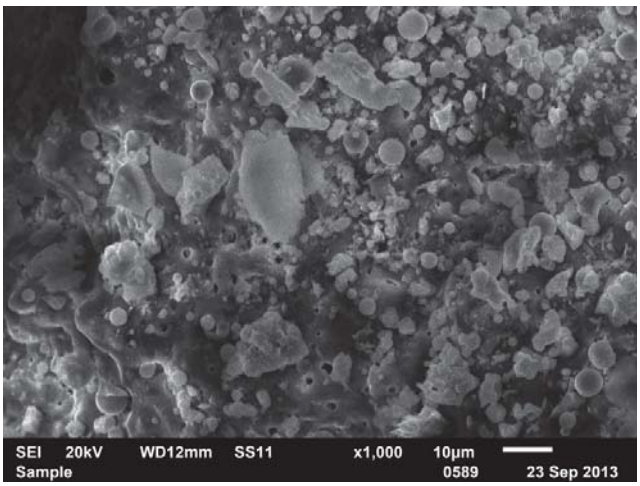

Fig. 1 Electron micrograph of waste sample from ash-sludge storage

Fig. 2 is a micrograph of heat treated catalyst sample. On Fig. 2, particles are more disperse and uniform in comparison to particles shown on Fig. 1. Thus, thermal treatment leads to improve the catalyst surface structure, because it is well known, that catalysts with more disperse and uniform active phase are more active in catalytic processes.

C. X-Ray Diffraction Analysis

The results of electron microscopy are corresponding to data obtained from X-ray diffraction analysis. The radiographs of the waste sample and the catalyst are shown on Figs. 3 and 4. On the radiograph of the waste sample. we can observe presence of sharp peaks. This points more crystalline structure of non-calcinated waste. From the other hand, the radiograph

of the granulated catalyst shows more amorphous structure of the material. However, there is a sharp peak on the radiograph, which points not absolute uniformity of the catalyst surface structure and presence of some crystalline forms.

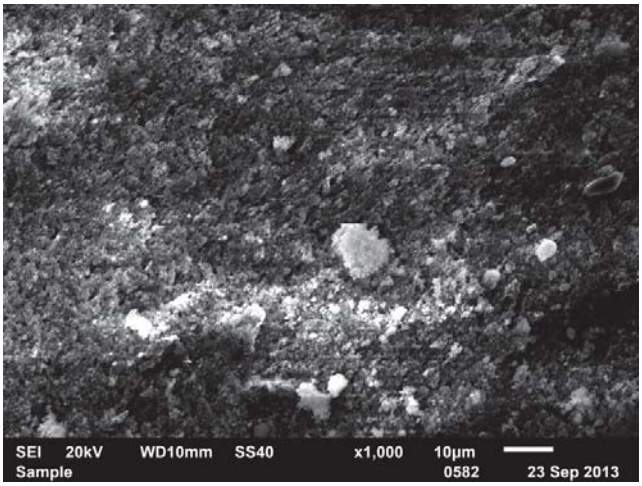

Fig. 2 Electron micrograph of thermal treated catalyst

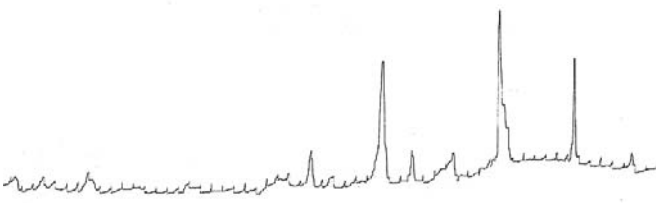

Fig. 3 Radiograph of the waste sample from ash-sludge storage

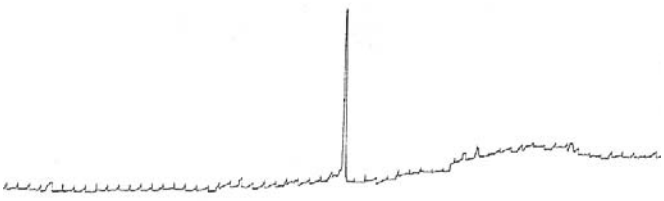

Fig. 4 Radiograph of the thermal treated catalyst

D.The Surface Investigation with the BET Method

Determination of pore structure gives the facts about development of inner surface of a catalyst, and about diffusion effects, which are characterizing involvement of inner surface into the catalytic process. As well as chemical content, the pore structure is an important property, which is contributing the quality of a catalyst.

The results of specimens' research have shown that the maximal specific surface (S_W = 116.52 m^2/g) and total pores volume ($V_{ads\ max}$ = 98.47 ml/g) are reached on the granulated thermal treated catalyst. The powder waste sample has shown lower meanings of the characteristics (S_W = 7.02 m^2/g, $V_{ads\ max}$ = 22.22 ml/g).

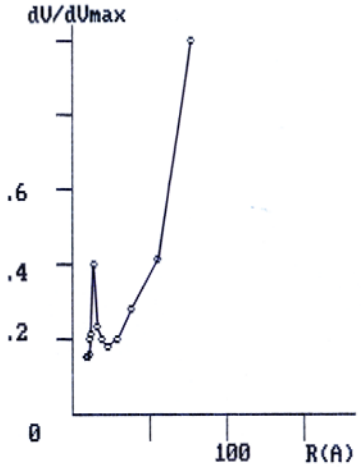

Fig. 5 The pores radii distribution of powder waste sample (the BET method)

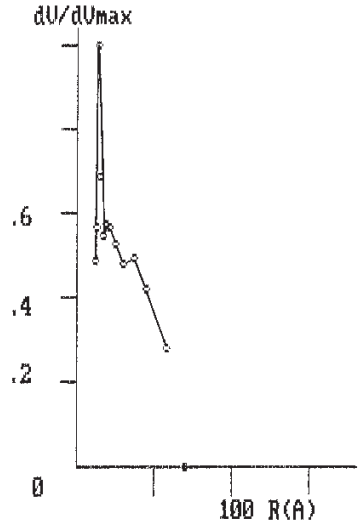

Fig. 6 The pores radii distribution of the granulated catalyst (the BET method)

On Fig. 5, size distribution of catalyst's pores is presented. From the figure it can be observed that powder sample is characterized by small number of small pores about 20 Å in diameter. Unlike the powder sample, the granulated catalyst is characterized by significant increase in total pores (20 Å) volume. This is shown on Fig. 6 and confirmed by more quantity of adsorbed nitrogen (98.46 ml/g). The pores number increase can be related to volatilization of some volatile component at calcination while preparing of catalyst. Herewith amorphousness of the catalyst surface is increased that confirmed by results of x-ray diffraction analysis and electron microscopy.

The results of comprehensive physical-chemical analysis show the better surface structure (more pores number, more total pores volume, more surface uniformity) of the granulated thermal treated catalyst. So the catalyst was used in some processes of hydrocarbon-containing raw materials refining.

E. Gasoil Cracking

The obtained catalyst was used in the process of catalytic cracking of gasoil (240-350 °C) on the stationary laboratory installation. The experiment was performed in comparison of temperature conditions at 450 °C and 500 °C. The results are presented in Table I.

TABLE I
THE CATALYST ACTIVITY IN THE PROCESS OF CATALYTIC CRACKING OF GASOIL

T, °C	Products of cracking, wt%					Conversion, wt%	Liquid product selectivity, %
	Gas	Petrol b.p.–200 °C	Medium distillate 200–270 °C	Gasoil 27 –350 °C	Residue >350 °C		
500	2.00	23.99	29.48	18.28	26.25	55.47	96.39
450	0.43	18.92	32.08	44.98	3.59	51.43	99.16

It was revealed that at higher temperature more conversion is achieved. Higher selectivity by the liquid products is achieved at 450 °C. Thus, ferroalloy production ash-sludge refining allows obtaining of a valuable product – a catalyst of gasoil cracking. That confirms high economic effectiveness of proposed way of utilization of this kind of industrial waste.

F. Rubber Waste Hydrocracking

The main products of worn tires refining are gases (used for afterburning), liquid products (fuel, fuel additions, and oils), and solid residue.

The results of the experiment are presented in Table II.

TABLE II
THE CATALYST ACTIVITY IN THE PROCESS OF RUBBER WASTE HYDROCRACKING

T,C	Gas phase, %	Liquid phase, wt%			Residue, wt%
		Petrol fraction	Kerosene fraction	Diesel fraction	
150	1.20	-	-	28.06	70.74
200	2.00	-	-	31.55	66.45
250	2.40	-	1.07	34.26	62.26
300	3.80	-	9.80	30.78	55.60
350	11.30	1.58	16.23	18.80	52.10
400	33.43	16.40	12.23	14.56	23.36

From Table II, it can be seen that more appropriate condition are the temperature of the process of 400 °C. At this temperature the highest amount of valuable liquid products was obtained. Meanwhile at 400 °C the yield of gas phase products is increased significantly that is point to uselessness of further temperature increase because of diminishing of valuable products yields.

After distillation of obtained liquid fraction petrol fraction (0-180 °C), kerosene fraction (180-250 °C), diesel fraction (250-320 °C) were received as products. By means of chromatographic analysis it was defined that after hydrocracking of rubber waste on the thermal treated catalyst groups of paraffin (3.37%), isoparaffin (33.28%), naphthenic (3.39%) and aromatic (8.87%) hydrocarbons were mostly obtained.

The research octane number of the petrol fraction is 77.

G. Cyclohexane Oxidation

The reaction of cyclohexane oxidation was performed on the granulated thermal treated catalyst in mild conditions with hydrogen peroxide as an oxidant. Only cyclohexanol and cyclohexanone can be products in the reaction. The results of the experiment are presented in Table III.

TABLE III
THE CATALYST ACTIVITY IN THE PROCESS OF CYCLOHEXANE OXIDATION

T, °C	Products, %		Conversion, %	Selectivity, %
	Cyclohexanone	Cyclohexanol		
30	-	-	traces	-
40	2,1	0,2	2,3	$S_{\text{-one}} = 91,3$
50	11,1	5,3	16,4	$S_{\text{-one}} = 67,7$
60	6,1	81,8	87,9	$S_{\text{-ol}} = 93,0$

The catalyst based on the waste of ferroalloy production has shown appropriate properties for reaction of oxidation. It can be explained by elemental content, in particular transition metals Fe, Cr, Mn. These metals are often used as active phases of various catalysts in the processes of oxidation.

IV. CONCLUSION

The catalyst prepared from the ferroalloy production waste after calcination have changed surface properties. That was observed using electron microscopy, the BET method, and X-ray diffraction analysis. The obtained catalyst has shown significant activity in some elected processes of hydrocarbon-containing raw materials refining. Thus, production of a catalyst is a new promising way of high effective utilization of ferroalloy wastes.

ACKNOWLEDGMENT

This work was supported by D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, and the al-Farabi Kazakh National University and was performed under the grant funded by the Ministry of Education and Science of the Republic of Kazakhstan.

REFERENCES

[1] P. N. Bishetti, and L. Pammar, "Experimental study on utilization of industrial waste in concrete," *International Journal of Technical Research and Applications*, vol. 2, pp. 49-52, 2014.

[2] J. R. Rao, P. Thanikaivelan, K. J. Sreeram, and B. U. Nair, "Green route for the utilization of chrome shavings (chromium-containing solid waste) in tanning industry," *Environmental Science & Technology*, vol. 36, pp. 1372-1376, 2002.

[3] S. N. Othman, Z. Z. Noor, A. H. Abba, R. O. Yusuf and M. A. Abu Hassan, "Review on life cycle assessment of integrated solid waste management in some Asian countries," *Journal of Cleaner Production*, vol. 41, pp. 251-262, 2013.

[4] A. V. Zhdanov, V. I. Zhuchkov, V. Ya. Dashevskii, L. I. Leont'ev, "Utilization of ferroalloy-production wastes," *Steel in Translation*, vol. 44, pp. 236–242, 2014.

[5] A. Alhimenko, M. Romanov, "Possibilities of use of industrial waste in road construction on the territory of the Leningrad region," in *Proc. of the International Conference "Innovative Materials, Structures and Technologies"*, Riga, Latvia, 2014, pp. 12-17.

[6] Zh. Du, and Zh. Shao, "Combining transition metal catalysis and organocatalysis – an update," Chemical Society Reviews, vol. 42, pp. 1337-1378, 2013.