*Int. J. Chem. Sci.: 12(4), 2014, 1569-1576*
*ISSN 0972-768X*
*www.sadgurupublications.com*

# INTEGRATED APPROACH FOR RECYCLING OF FERROALLOY PRODUCTION WASTES

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## ABSTRACT

Wastes of Aksu ferroalloy plant (AFP) were used as raw materials for making of perspective catalysts for raw hydrocarbons refining in valuable products. In the article, the results of our research are reported. Supported polymer-containing catalysts for catalytic cyclohexane oxidation were prepared on the basis of the elements, which are a part of wastes. Composition and surface of obtained catalysts were researched with electron microscopy and IR-spectroscopy methods.

**Key words**: Wastes, Ferroalloy, Oxidation, Polymer-supported catalyst, Cyclohexane.

## INTRODUCTION

Industrial development of Republic inevitable leads to increasing of harmful emissions and industrial wastes amounts. It negatively effects on environment condition. Utilization of industrial wastes around the world is carried out in several main directions: minimization at formation source, reuse, processing in raw materials and products, burning and burial. Using of wastes as secondary raw material is the optimal way of utilization if it is impossible to reduce their quantity. With this principles of waste-free and low-waste technology are being developed.

Composition of ferroalloy production wastes, being stored in the territory of ash-slime dump of Aksu ferroalloy plant (AKSU, Republic of Kazakhstan), was studied earlier. Their high quantity of transition metals compounds as well as some other elements were also

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established. That allowed making the assumption of expediency of their extraction or reuse as raw materials for production of catalysts for various organic petrochemical processes.

## EXPERIMENTAL

Heterogenous catalyst, based on AFP production wastes, modified with polymer, was synthesized according to method described earlier[1]. It was made with 3% containing of active phase – Mn : Fe with ratio of 1 : 3. Water solution of polymer was added into suspension of aluminosilicate by stirring at room temperature. For catalyst obtaining sample of polymer was estimated from “metal : polymer element” ratio of 1 : 1.

Obtained mixture was stirred for 2 hours. After that solutions of potassium ferrocyanide and manganese sulfate were added slowly. Obtained mixture was stirred again for 3 hours. Catalyst was settled in mother solution for 15 hours. After that formed sediment carefully washed out with distilled water and dried up in air at the room temperature till obtaining of powdered catalyst of light green color.

Researching of properties of supported onto inorganic carrier polymermodified catalyst was carried out using Transmission electron microscope EMK-125 AK (USSR) at magnification of 24000–120000, Scanning electron microscope Superprobe 773 Joel (Japan) by method Japan Computer Xray Analyser JCXA 733. IR-spectra of polymer-ferrocyanide catalysts were obtained with Fourier transform infrared spectrometer IMPACT 410 (Nicolet, USA) and Specord JR-75 in the frequency interval of 4000-400 $sm^{-1}$.

Oxifunctionalization of cyclohexane was carried out in glass thermostatic reactor joint with reflux condenser and volumetric buret. Catalyst (0.03 g), acetonitrile as solvent (1.2 mL), cyclohexane (0.3 mL) and hydrogen peroxide as oxidant (30% water solution) were sequentially added in reactor. In experiments oxidant was added by single injection of volume of 0.9 mL. Reaction mixture was stirred for 4 hours at 40 °C and atmospheric pressure. Composition of mixture after reaction was analyzed with GLC (LCM-80M, USSR) with flame ionization detector in isothermal mode. Steel column 3 m long with diameter of 3 mm, filled with Chromaton N/W-DMCS with 15% Carbowax-20M as active phase, was used for chromatographic analysis.

## RESULTS AND DISCUSSION

The presence of elements-pollutants (Cr, Zn, Mn, Fe and other) was confirmed as the result of element analysis of AFP wastes samples with using of modern spectral methods (Japan Computer X-ray analyzer JCXA 733). Average containings (wt. %) of oxygen –

46.18, sodium – 0.54, magnesium – 5.01, aluminium – 1.23, silicon – 34.16, sulfur – 0.40, chlorine – 0.26, potassium – 1.41, calcium – 4.44, titanium – 0.01, chromium – 1.73, manganese – 2.18, iron – 1.01, zinc – 1.38, tin – 0.06 were uncovered.

The main elements-pollutants detected in AFP wastes were chromium, manganese, sulfur, iron, zinc[2]. It is well known such elements as chromium, manganese, iron show good catalytic properties in various red-ox processes.

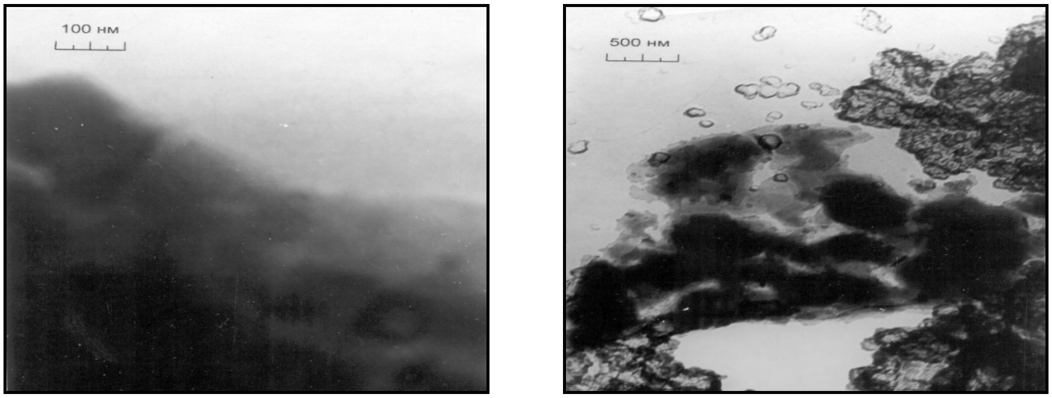
As, it known from literature immobilization of polymer-metallic complexes (PMC) on surfaces of catalytically inactive inorganic supports allows to obtain stable catalysts characterized by high specific surface, activity and selectivity.

Prospects of PMC use consist in possibility of creation enzyme-like catalysts of plain structure, high stability and more available in comparison with enzymatic catalysts and their complicated structure chemical analogs[3]. In the article[4], polymer-ferrocyanide copper complex, supported onto aluminosilicate was described. It has shown high catalytic activity in the process of cyclohexane oxygenation. By analogy, in this work catalyst with manganese hexacyanoferrate as active phase, polyhexamethyleneguanidine hydrochloride (PGMG) as polymer-modificator and middle acid aluminosilicate (Siral-40) as support for active phase was obtained.

Selection of catalytic system was caused by that $Fe^{2+}$ and $Mn^{2+}$ metals are components of active sites of natural enzymes (monooxygenases)[5,6], and PGMG is water soluble and contains active nitrogen-containing group. The last one simply leads to complex with transition metals. Basic character of PGMG promotes its more effective adsorption on middle acid aluminosilicate.

The obtained manganese- and iron-containing catalytic system modified by PGMG and supported by aluminosilicate was researched by electron microscopy. The samples were examined by the method of replicas with extraction and shooting against the light using microdiffraction.

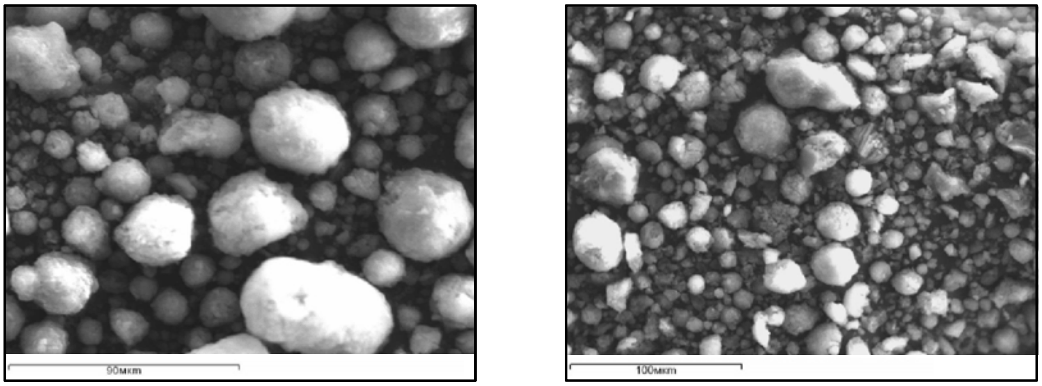
Amorphous structures were found on micrographs of polymermodified supported catalyst (Fig. 1). Edge of fuzzy amorphous formation traced at magnification of 120000 Figure 1a. It is obviously polymeric layer covering the surface of aluminosilicate. Laminar particles coupled with dense non-transparent structures, which are films of polymermetallic complex immobilized onto aluminosilicate, were detected at magnification of 24000 (Fig. 1b). Micro-diffraction analysis showed formation on manganese ferrocyanide at the process of the catalyst obtaining.



**(a) (× 120000)** **(b) (× 24000)**

**Fig. 1: Polymermodified catalyst based on manganese ferrocyanide / PGMG / Siral-40**

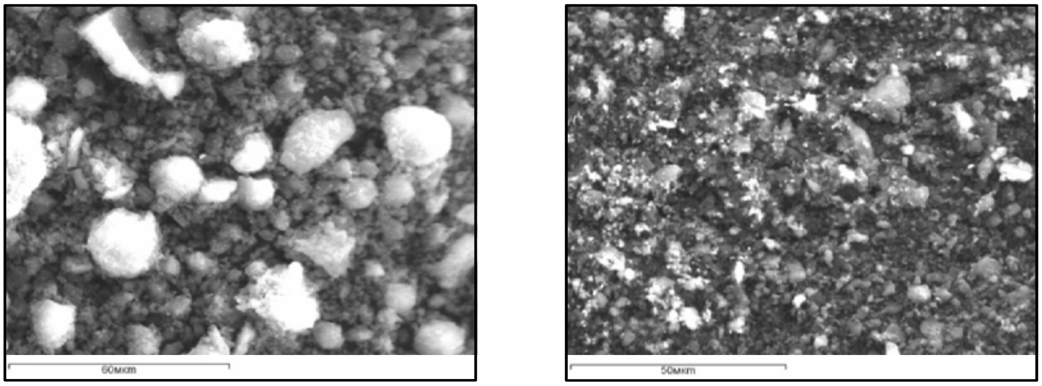
Scanning electron microscopy allows detecting of supporter dispersity increase after modification with polymer. It is well traced on Figure 2.



**(a) Siral-40** **(b) PGMG /Siral-40**

**Fig. 2: Micrographs of supporter (a) before and (b) after modifying with polymer (PGMG)**

More increased dispersion of particles is observed after coating polymer modified surface with metal complex (Fig. 3a). After single carrying out of process of cyclohexane oxidation large crystalline particles did not detected and the surface was more homogeneous (Fig. 3b).



**(a) $Mn_2[Fe(CN)_6]$-PGMG/Siral-40 initial**

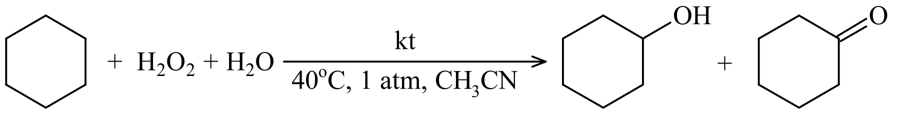
**(b) $Mn_2[Fe(CN)_6]$-PGMG/Siral-40 after oxidation process**

**Fig. 3: Micrographs of polymermodified catalyst $Mn_2[Fe(CN)_6]$- PGMG / Siral-40 (a) before and (b) after the process of cyclohexane oxidation**

IR-spectral analysis of polymer-metallic complex samples revealed, that amide group is a typical functional group of PGMG-containing compounds. Absorption band in the region of wavelengths of 3325 $sm^{-1}$, 3280 $sm^{-1}$, 3177 $sm^{-1}$ are typical for pure polyhexamethylene guanidine. This indicates the presence of bounded and unbounded amide groups. In the $Mn_2[Fe(CN)_6]$/PGMG spectrum NH-group appears as a single peak, shifted out towards the low absorption bands (3173 $sm^{-1}$). This indicates there is only associated amide groups.

So, according to the results of IRS analysis, it was found that in the process of polymer-metallic complex formation interaction of manganese ferrocyanide complex with polyhexamethylene guanidine is realized trough coordination with NH-group. The adsorption process is more efficient due to the formation of hydrogen bonds between polymer-metallic complex and aluminosilicate.

The paper presents the results of the research of activity of polymer-modified, supported onto inorganic supporter, catalyst ($Mn_2[Fe(CN)_6]$-PGMG/Siral-40) in the reaction of cyclohexane oxidation. 30% hydrogen peroxide aqueous solution was used as oxidant. Acetonitrile was used as solvent.



The composition of reaction mixture was identified by comparing with pure individual compounds by gas chromatography (Fig. 4).

The experiment showed that polymermodified supported catalyst based on transition metals from the wastes of AFP is active in the reaction of cyclohexane oxidation with hydrogen peroxide in mild conditions (40°C, atmospheric pressure). In the reaction primary formation of cyclohexanone was observed in comparison with cyclohexanole. The conversion of cyclohexane was 47.3%.

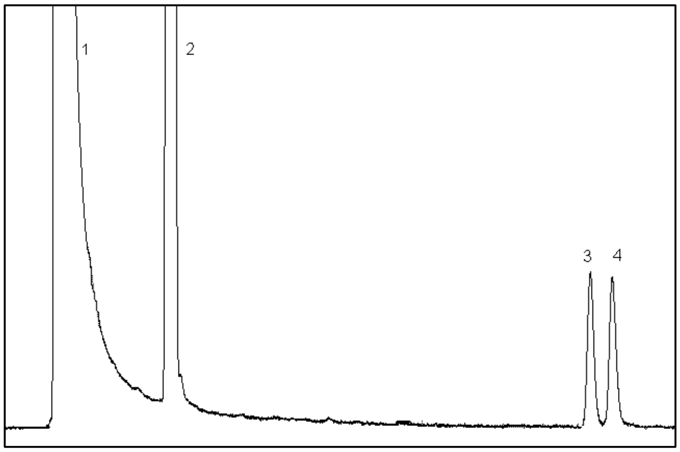


**Fig. 4: Chromatogram of mixture after cyclohexane oxidation reaction with catalyst $Mn_2[Fe(CN)_6]$-PGMG/Siral-40 (40$^o$C, atmospheric pressure)**

1 – Acetonitrile (Solvent); 2 – Cyclohexane; 3 – Cyclohexanole; 4 – Cyclohexanone

Stability of synthesized polymer-containing composite catalyst $Mn_2[Fe(CN)_6]$-PGMG/Siral-40 was researched in a series of consecutive experiments by cyclohexane oxidation. After each experiment reaction mixture was analyzed by gas-liquid chromatography method and after conversion of initial substrate was lower 2% series of experiments was stopped. Stability was defined by turnover number (TON) as the ratio of the total number of moles of reacted in a series of experiments substrate to 1 mole of catalyst metal.

Conversion of substrate was achieved to more than 10% after oxidation of first 10 portions of cyclohexane. Selectivity by ketone was constantly about 80%. Conversion of cyclohexane was gradually decreased after oxidation of following portions of substrate and was decreased to 2% after 18 experiments (Fig. 5). The stability of researched catalyst was of 408 cycles.

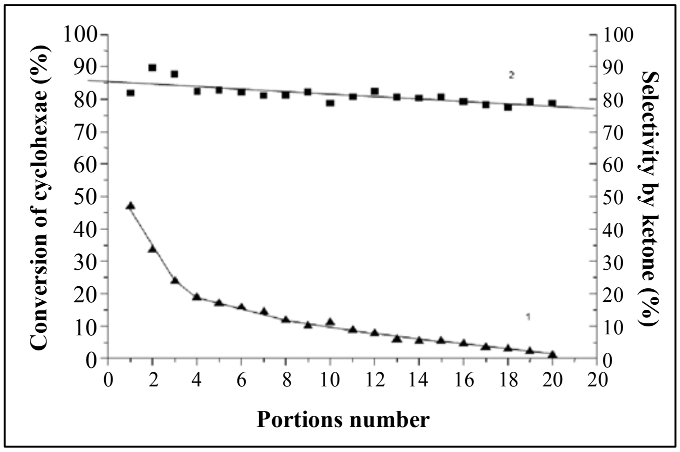


**Fig. 5: Stability of catalyst $Mn_2[Fe(CN)_6]$-PGMG/Siral-40 in the reaction of cyclohexane oxidation with hydrogen peroxide (Solvent – $CH_3CN$, 40°C, atmospheric pressure)**

1 – Conversion of cyclohexane, %; 2 – Selectivity by cyclohexanone, %

So, as a result of developed integrated approach to Aksu ferroalloy plant industrial wastes reuse, selection of composition and synthesis of catalyst by the method of immobilization of polymer-transition metals complex onto aluminosilicate were realized.

It was observed by the methods of electron microscopy and IR-spectroscopy that obtained polymer-modified catalyst is stable and heterogeneous in surface composition. That facts allows to suppose the perspectivity of its using in the processes of catalytic organic synthesis. The effectiveness of using of catalyst based on industrial wastes of AFP in the reaction of cyclohexane oxidation was experimentally showed. After the reaction cyclohexanone and cyclohexanole, intermediates in synthesis of caprolactam and nylon, were obtained.

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*Accepted : 30.09.2014*