

## RESEARCH OF IRON-CONTAINING CONCENTRATES OF BALKHASH DEPOSIT (KAZAKHSTAN) FOR PROCESSING OF LOW-GRADE COAL

Marat Tulepov, Zulkhair Mansurov, Larissa Sassykova, Dauren Baiseitov,  
Orken Dalelhanuly, Zhomart Ualiev, Sholpan Gabdrashova, Zhanar Kudyarova

Al-Farabi Kazakh National University  
71, Al-Farabi str., 050040, Almaty, Kazakhstan  
E-mail: larissa.rav@mail.ru

Received 29 June 2018  
Accepted 20 December 2018

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### ABSTRACT

*The article describes processing of low-grade coal and catalytic hydrogenation of brown coal of Karazhira field (Kazakhstan). The highly dispersed iron-containing concentrates of Balkhash deposit (Kazakhstan) are studied as catalysts of the hydrogenation process in processing of sub-standard coal. The catalysts are prepared by mechanic-chemical activation of the concentrate with subsequent dispergation in the coal in presence of polyethylene. It was found that use of an activated catalyst containing pyrite when coal hydrogenation in tetralin allowed to achieve practically complete decomposition of the organic mass of coal into liquid and gaseous products. Yield of maltens in presence of the activated catalyst was equal to 56.1 % (by wt.). The results show that the effect of mechanic-chemical activation is caused not only increase in specific activity of the ore catalyst, but also probably change of catalytic properties of a surface. These changes can be apparently connected with the defects of crystal structure of a sample as a result of intensive mechanical influence.*

*Keywords:* brown coal, low-grade coal, Balkhash concentrate, Karazhira field, hydrogenation, mechanochemical activation.

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### INTRODUCTION

The iron-containing materials can be used as available catalysts for coal hydrogenation. A high extent of transformation of the organic coal substance is usually reached only under rather severe conditions (high pressure and large amounts of hydrogen and catalysts). For this reason, the use of iron ore materials in synthesis of catalytic systems for coal hydrogenation at processing of sub-standard coal is possible only in case of preliminary effective methods of activation. As a rule, the ore catalysts are used in the form of relatively large particles of a low specific surface. By finely mechanical grinding it is possible to improve the dispersibility of such materials [1 - 4], thereby increasing their specific surface area and very often to change their chemical properties. A change of chalcopyrite reactivity is achieved as a result of its mechanical-chemical activation which disrupts its crystal lattice [5 - 7]. The mechanical-chemical activa-

tion can also lead to decomposition of the substance or affect its interaction with the environment [8 - 11]. The mechanical-chemical processing of the solvent and the coal is one of the perspective directions in the field of obtaining liquid products from coal. The mechanical processing of the coal results in its dispergation which in turn leads to increase of its specific surface. This facilitates the solubility of the mechanically activated coal in organic solvents and increases their reactivity in subsequent chemical reactions [12 - 16].

The aim of the study is to select catalysts providing hydrogen pressure decrease to 1 - 5 MPa during the hydrogenation of low-grade coal. Of most practical interest are cheap iron-based catalysts (for example, iron salts, iron-containing ores and concentrates). Their use excludes the expensive stage of catalyst extraction from the solid sludge of coal hydrogenation process. In this work catalysts based on iron-containing concentrate of the Balkhash deposit (Kazakhstan) are developed and their activity is studied.

## EXPERIMENTAL

Coal of Karazhira field (Kazakhstan) was chosen to study the process of hydrogenation of sub-standard coal and plastics. The concentrate of the Balkhash field of Kazakhstan (BC) was used as a catalyst. It was a mixture of pyrites and chalcopyrites containing 24 % of Fe, 30 % of Cu, Al - 12 % of Al, 12 % of S. The mechanical activation of the natural concentrate of BC and the model iron-containing catalyst (MC) on a base of copper oxide and  $\text{FeCl}_3$  was carried out in a mill-activator of a centrifugal planetary mill. For this aim 15 g of the ore catalyst with a size of the particles less than 0.5 mm and 10 g of steel spheres with a diameter of 8 mm were loaded to the drum of the activator. The processing was carried out at a rotation of 1,820 rev/min, thus a centrifugal acceleration of  $600 \text{ m/s}^2$  was developed. The experiment was carried out in an autoclave of a capacity of 0.25 L at  $430^\circ\text{C}$ . The weight of the dry coal was 15 g, that of BC used as a catalyst was 1.5 g, while that of tetralin - 20 ml.

The iron containing catalysts were prepared and introduced to the reaction mixture in the following way:

(1) The BC powder was subjected to mechanical-chemical treatment in a mixture with water in a centrifugal planetary mill. The activated catalyst was added to a mixture of coal and water (2:10 wt. parts) in an amount of 10 wt. % in respect to the organic mass of the coal (OMC) and was dispersed for 20 min. The mixture was then dried at  $105^\circ\text{C}$ . The final moisture was  $< 1 \text{ wt. \%}$ .

(2) The BC powder was subjected to mechanical-chemical processing in a mixture with water in a mill-activator. Then it was added to tar in an amount of 5% to 45% in respect to OMC and was dispersed with subsequent removal of water from the mixture at  $34^\circ\text{C}$  in a drying box.

The experiments of hydrogenation of coal were carried out in a 0.5 L rotary autoclave. A mixture of coal, a catalyst and tar was charged, sealed and washed with argon to remove the air. After this, hydrogen was pumped to the autoclave to pressure of 5.0 MPa. The temperature was increased to  $430^\circ\text{C}$ . The duration of the experiment was 1 hour from the moment the autoclave

exited the regime, under these conditions the pressure in the autoclave was 8.0-10.5 MPa. After completion of the experiment, the autoclave was cooled and the volume of the gaseous products was determined. Their composition was identified by gas chromatography. The hydrogenation products were divided into the following groups: liquid products (oils), asphaltenes, pre-asphaltenes and a solid residue.

The consumption of the gaseous hydrogen was calculated as a difference between its amount in the autoclave prior to and after the experiment. The condensed portion of the products was recovered from the autoclave and partitioned into maltens through extraction with hexane. The asphaltenes were extracted with benzene. The degree of conversion of OMC to gaseous and liquid products was calculated on the ground of the amount of the solid residue and its ash content.

Thermogravimetric studies were performed under the following experimental conditions: sample weighed - (0.3-0.03 g); grinding is analytical; ceramic crucible with a lid height of 15 mm in diameter 5 mm. Processing of derivatograms included analysis of thermograms. The loss of sample mass at a given temperature was determined according to the thermogravimetry curve. The mass loss rate was determined according to the curve of differential thermogravimetry, the temperature of the maxima of the endo- or exo-effects, according to the differential thermogravimetry curve of adsorption, in accordance with standard procedures. Mass loss curves (TG curves) and mass loss rates (DTG curves) recorded by the instrument were recalculated to 1.0 g of the original sample and expressed as temperature dependences, the nature of which is illustrated by the thermograms.

The X-ray fluorescent and the elemental analysis of a solid sample were carried out on the FOCUS-M2M microanalyzer using Fe-radiation in the range from 2 V to 37 V. The intensity of the diffraction maxima was estimated by an analytical method in a tetragonal singoniya. The coal samples with an introduced catalyst were investigated by a scanning electron microscope NtegraTherma with transmission and reflection lighting modes at an accelerating voltage of 10 kV - 30 kV.

Table 1. The composition of the ore samples before and after mechanical activation.

The samples	Composition, %					
	Fe	Zn	Al	Cu	Cl	S
Elemental analysis						
MC	41.4	-	-	36.5	7.3	-
BC	32.8	6.4	21.11	22.58	-	15.5
The main crystalline phase						
Phase analysis	The initial sample			After mechanical activation		
MC	CuO, FeCl <sub>3</sub>			Fe <sub>2</sub> O <sub>3</sub> , CuO, Cu		
BC	CuFeS <sub>2</sub> , Fe <sub>2</sub> O <sub>3</sub> , FeS <sub>2</sub> ,			Fe <sub>3</sub> O <sub>4</sub> , FeS, CuO, Cu		

## RESULTS AND DISCUSSION

According to the X-ray fluorescence analysis of BC, hematite and chalcopyrite transforming into pyrite (Fig. 1) are the main crystalline phase of the selected ore samples after mechanical activation of the catalyst. Hematite is reduced to magnetite, while pyrites is decomposed to pyrrhotine in the course of the hydrogenation. The elemental and the phase analysis of the ore catalyst prior to the mechanic-chemical activation are presented in the Table 1. The mechanic-chemical activation of the ore catalyst affects not only the extent of conversion of the coal, but also the composition of the liquid products. The processing increases the activity of the BC catalyst

in the reactions of transformation of the high-molecular asfaltens to maltens having a smaller molecular weight, i.e. it increases the cracking properties of the catalyst.

Some general regularities are observed when grinding coal from the Karazhira deposit, and they are well observed in differential thermogravimetric curves after mechanical processing of coals in a mill. The thermogravimetric curves (Figs. 2, 3) have a single minimum indicating dehydration at temperatures of 109°C - 116°C. At mechanical impacts on coal simultaneously with change of total amount of soluble fractions their composition and structure in comparison with fractions from initial coals also changes.

The following transformations of the coal from the

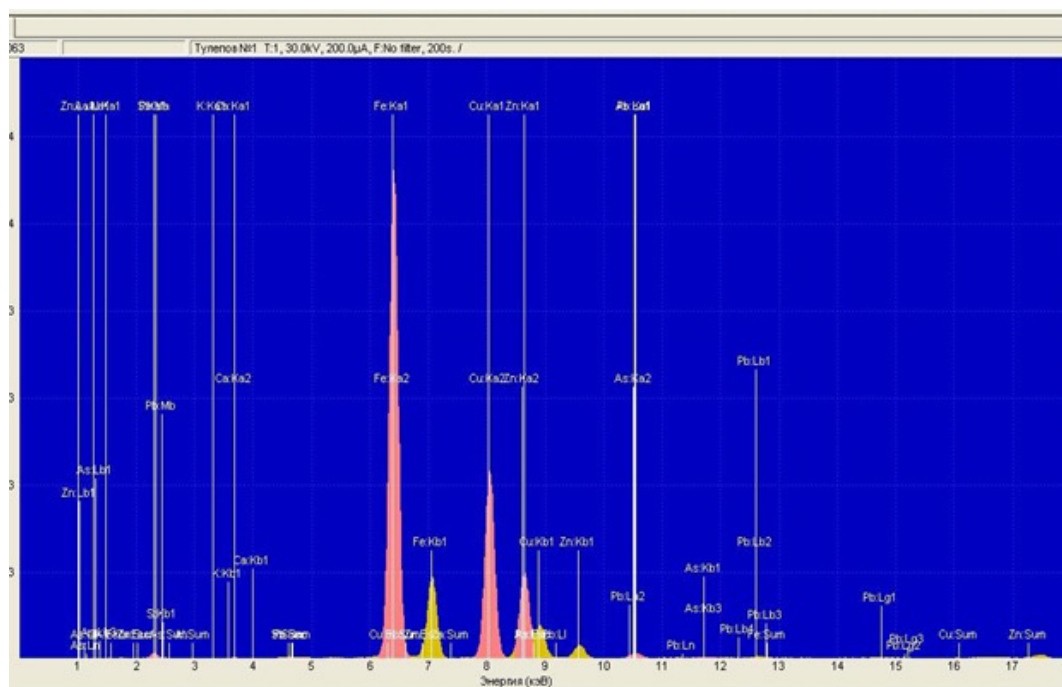


Fig. 1. X-ray fluorescence analysis of mechanically activated Balkhash concentrate (BC).

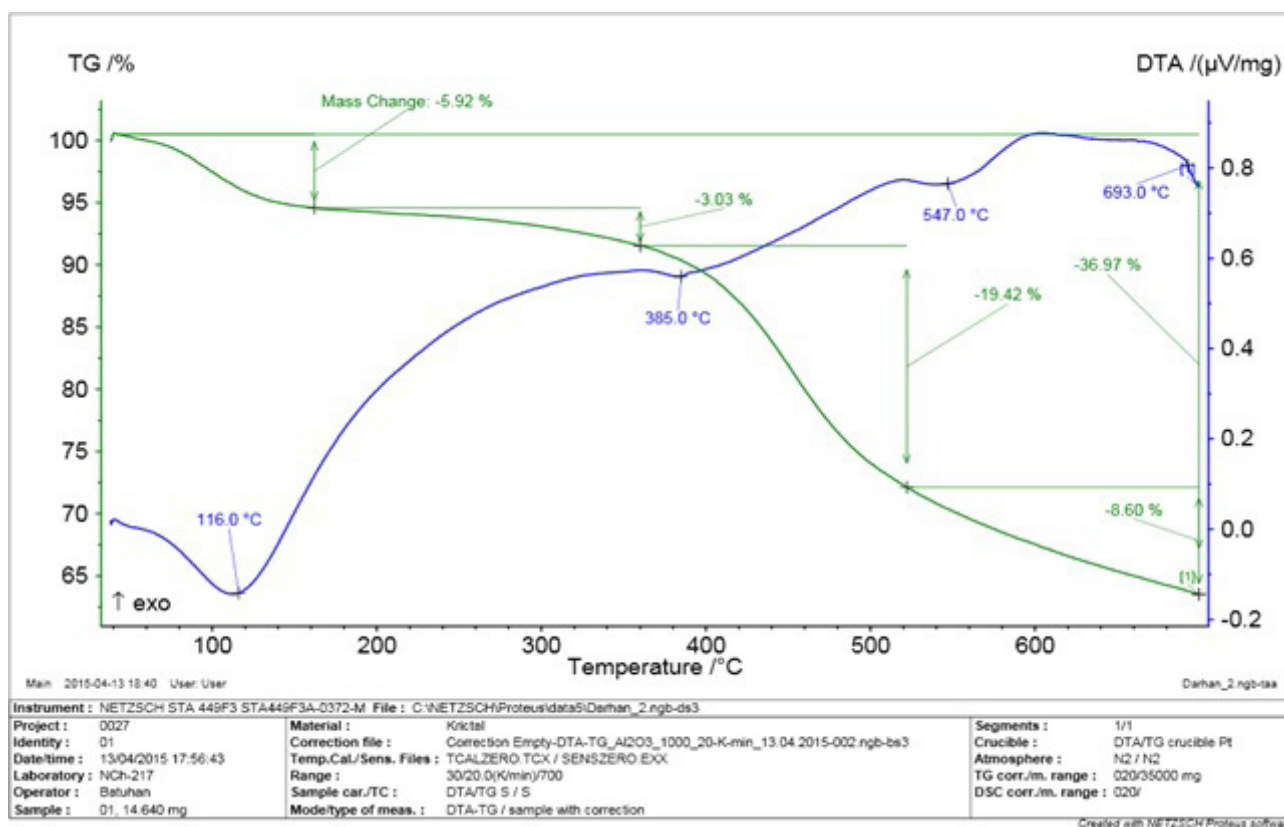


Fig. 2. Thermogravimetric studies of the initial coal.

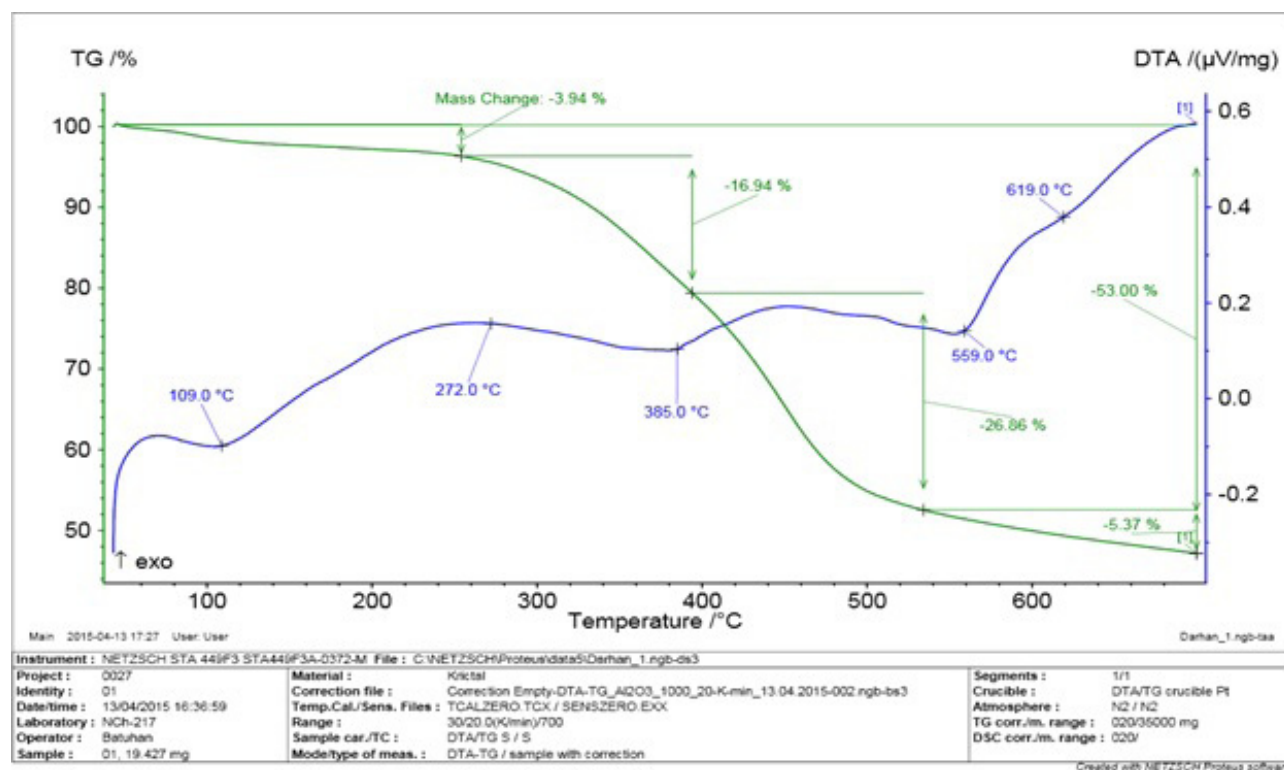


Fig. 3. Thermogravimetric studies of the transformation of coal after mechanoactivation in the presence of a catalyst BC.

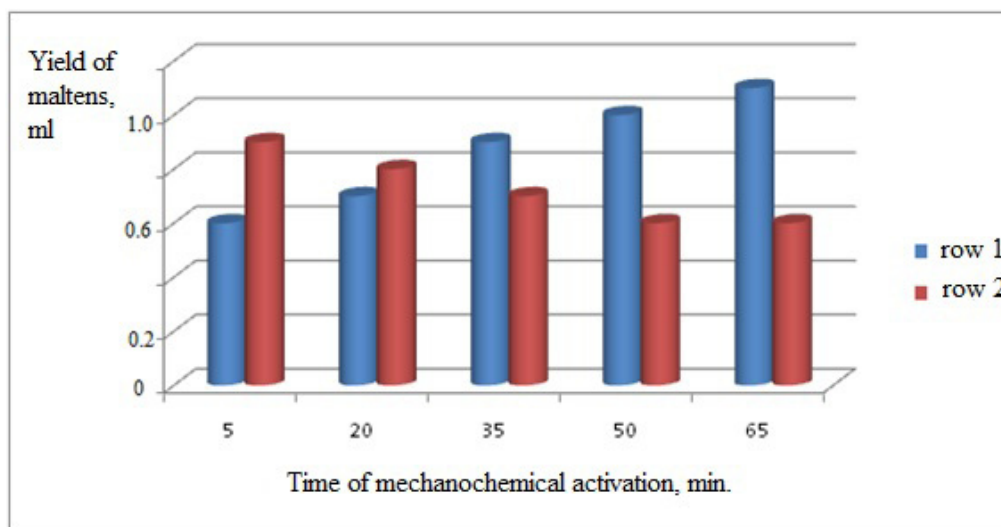


Fig. 4. Dependence of the maltens' yield on duration of the catalysts mechanical activation: 1 – BC, 2 – MC.

Karazhira field after mechanic-chemical activation in presence of BC concentrate (Fig. 3):

- 1) dehydration in the temperature range 109°C;
- 2) thermal destruction of the macromolecular structure of the coal with the formation of radical fragments in the range of 272°C - 385°C;
- 3) recombination of these radicals with the formation of high molecular weight products, saturation of the radicals as a result of the hydrogenation reactions by molecular hydrogen or that of the hydrogen-donor solvent with the formation of low molecular weight products at temperatures of 559°C- 619°C.

The product obtained when coal hydrogenation was divided into maltens (dissolved in hexane) and asphaltens (soluble in benzene, insoluble in hexane) by successive extraction with hexane and benzene, respectively. As the amount of insoluble residue in benzene the conversion extent of OMC was calculated. The yield of maltens was counted as a difference between the extent of transformation of OMC and the yield of asphaltens and gases. By comparing the results of the study of BC catalyst and its model analogue (MC) at the tests by hydrogenation of coal (Fig. 4), it follows that for small mechanical activation time, the conversion of OMC is increased depending on the catalyst on base of BC. At the same time, for further processing (more than 20 min.) a substantial increase in activity of the catalyst does not occur, and the conversion of OMC isn't change. The

activity of the MC is even reduced with a simultaneous decrease in the conversion of OMC with a short activation, but then stabilizes.

These results show that the effect of the mechanic-chemical activation is due not only to the increase of the specific activity of the ore catalyst, but probably to changes of the catalytic properties of the surface. They can evidently be associated with defects in the crystal structure of the sample as a result of the intensive mechanical action [17, 18].

The experiments show that the catalytic activity of BC sample is decreased with increase of the holding time from the moment of activation until its use. Thus, at test of the activated for 60 min. pyrite catalyst after 2 days after treatment the degree of coal conversion was equal to 69 %, after 14 days – 63 % and after 21 days – 59 %. The modification of the iron ore catalysts by mechanical-chemical treatment increases their activity in respect to tetralin. The use of an activated catalyst containing pyrite in the process of coal provides practically complete decomposition of OMC into liquid and gaseous products. The effect observed is probably due to dispergation and destruction of the crystal structure of the ore catalyst whose extent is greater for the sample containing pyrite.

Fig. 5 shows the elemental composition of the brown coal of Karazhira deposit (wt. % in respect to absolutely dry, ashless coal): C - 85,32; O - 14,68. The coal is

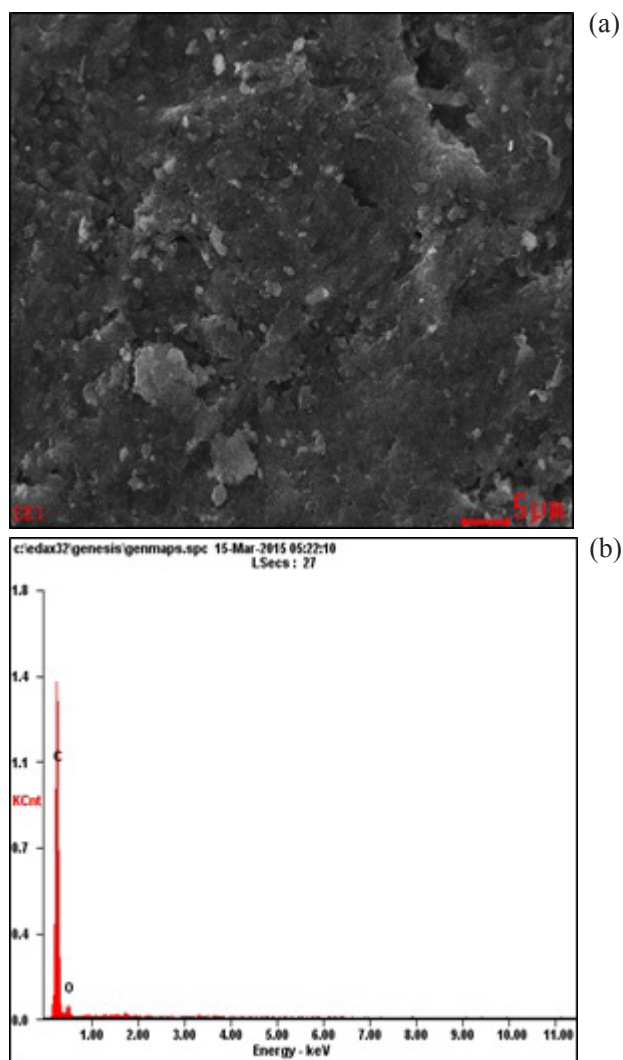


Fig. 5. SEM data analysis (a) and elemental composition (b) of the initial coal.

crushed to particles of a size  $< 0.25$  mm and dried at  $100^{\circ}\text{C} - 105^{\circ}\text{C}$  to content of moisture  $< 1$  wt. %.

There is simultaneous decrease of the particles size and aggregates formation (Fig. 6). The mechanical dispergation of the activated concentrate does not cause destruction of the aggregates (Fig. 6(d)). The dispersing of the activated carbon in the concentrate leads to significant reduction in the size and destruction of the aggregates. A significant part of the catalyst is located on surface of the coal in the form of particles of a size less than 100 nm, preferably in the form of “crust” (Fig. 6(b)). Probably, the greater part of the catalyst is present in a finely divided form on the surface or within the pores of the coal which prevents the reliable recording

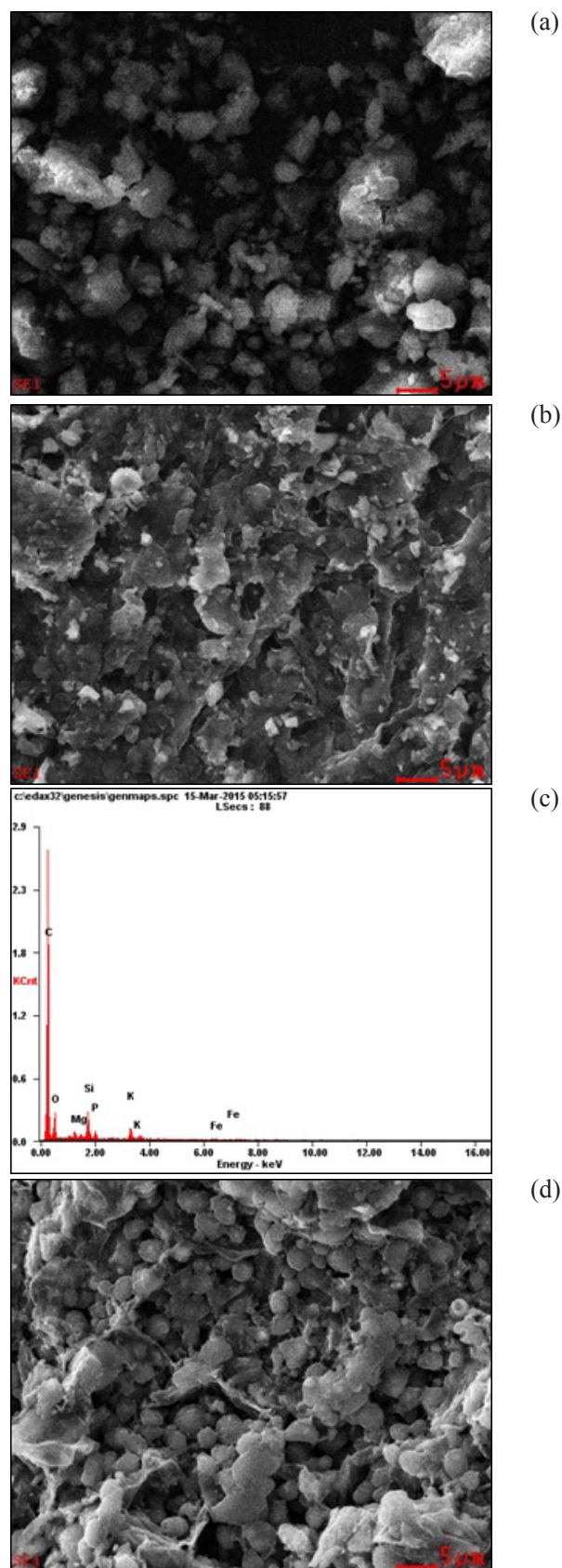


Fig. 6. SEM data analysis (a, b, d) and elemental composition (c) of the coal samples with the introduced catalyst.

by a scanning microscope.

The data of the oscillatory spectroscopy of the initial coal show [19, 20] that the compounds present belong to amorphous formations. In particular, the organic component of the coal is a mixture of various X-ray amorphous components whose presence and quantity changes. The Raman spectrum of the polymer obtained from coal shows that the major product is mainly composed of carbon (at least 90 %). There are additional 10 % of mineral impurities in the polymeric material [16, 17].

## CONCLUSIONS

The paper is devoted to processing of low-grade coal and studying the activity of catalysts based on iron-containing concentrate of the Balkhash deposit (Kazakhstan) in the coal hydrogenation process. It has been found that modifying of iron ore catalysts by method of mechanic-chemical processing increases their activity at a coal hydrogenation in a tetralin. The use of an activated catalyst containing pyrite can result in practically complete decomposition of OMC into liquid and gaseous products. These results show that the mechanic-chemical activation leads not only to increase of the specific activity of the ore catalyst, but probably changes its surface properties. These changes appear to be associated with defects in the crystal structure of the sample as a result of the intensive mechanical action.

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