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HYDROGENATION OF COAL OF "KARAZHIRA" FIELD: OPTIMAL CATALYSTS AND THERMOGRAVIMETRIC RESEARCHES

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ABSTRACT

Hydrogenation of coal of "Karazhira" field (Kazakhstan) was studied at an elevated pressure of hydrogen on various catalysts. As carriers were used Al_2O_3 and carbon, as an active phase (5%): Pd, Co, Mo and Fe. The conducted thermogravimetric researches of coal in the presence of polymers showed that in original composition the content of high-molecular asphalt-resinous components-asfaltens and benzene pitches in the field of temperatures 360-443°C is decreased. As a result of thermal influence the role of components of smaller molecular weight-benzene pitches and oils in bitumen is increased. Optimum catalysts of a hydrogenation of coals are compositions on the basis of Pd/C and Co/C on which the greatest absorption of hydrogen and the maximum speed of hydrogenation is revealed.

Key words: Coal, Catalysts, Hydrogenation, Thermogravimetry.

INTRODUCTION

The efficiency of the process of hydrogenation of coal in industrial conditions is associated with great difficulties. Macrokinetic choice of process conditions: pressure, temperature, process, catalyst composition, and the nature and structure of the original coal are of great importance. The majority of chemical processing of coal (except synthesis of carbon materials) serves for its transformation to low-molecular organic products, which would have sufficiently homogeneous composition[1,2]. Transformation of coal to various organic compounds occurs during heat treatment and exposure of different reagents. Upon heating initially are broken the weakest aliphatic bonds thanks to which the condensed aromatic structures are connected.

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The rupture of communications carbon-oxygen defines the course of process of a depolymerization of brown coals. At selective introduction of metals catalysts to functional groups of coal substance there is an opportunity to operate reactions of a rupture of certain links.

The main disadvantages of well-known techniques of chemical processing of coal compared with oil refining and petrochemical technologies are relatively low productivity and severe reaction conditions (high temperature and pressure). During processing of coals in recent years are more widely used the catalysts and new catalytic processes give the chance to produce various compounds of fuel and chemical appointment[3-8].

The purpose of this research was implementation of process of catalytic hydrogenation of dry brown coal of "Karazhira" (Kazakhstan) field at an elevated pressure of hydrogen, establishment of stages of transformation of coal by various methods, selection of optimum composite of catalysts.

EXPERIMENTAL

In the work, brown coal of "Karazhira" field is used, which elemental composition is presented in Fig. 1 (% for mass of absolutely dry, ashless coal): C-85.32; O-14.68. For studies was taken a sample of 5.0 g of mixture of dry brown coal of field "Karazhira" subjected to mechanical activation (particle size-less than 0.1 mm), and polyethylene with the size of particles of less than 0.5 mm in an amount of 10.0-70.0 wt.% by weight of a mixture of coal-polyethylene.

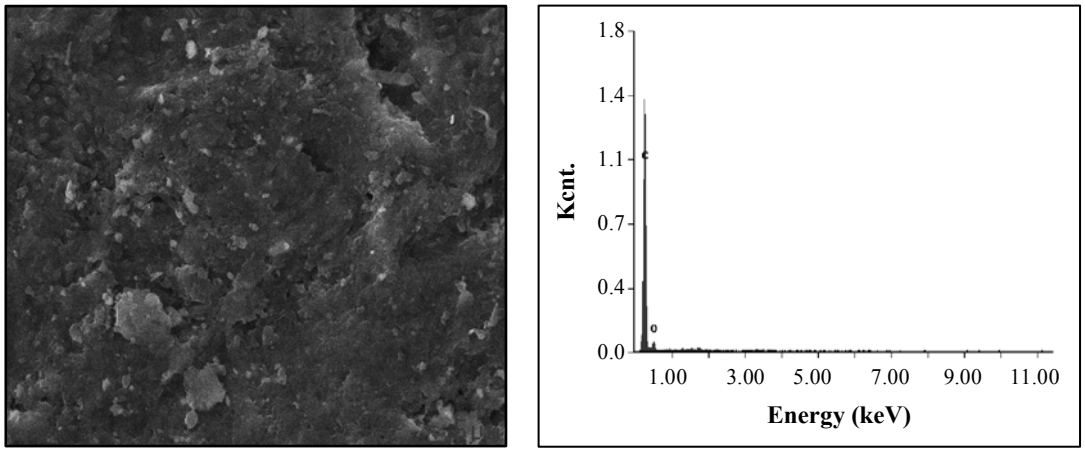

Fig. 1: Data of SEM of the analysis with element composition of initial coal "Karazhira" field

Procedure of mechanoactivation was carried out in a mill activator of the centrifugal and planetary mill. Treatment was carried out at the frequency of rotation of the drum 1820 rev/min that created the centrifugal acceleration developed by the grinding bodies of 600 m/s^2. For hydrogenation is used the steel rotating 0.5 L autoclave (Fig. 2). As catalysts are applied the compositions on the basis of compounds of Pd, Co, Mo and Fe (5%). As carriers are used Al_2O_3 and coal. In the closed autoclave hydrogen was introduced until a pressure of 5.0 MPa. With continuous stirring, the autoclave was performed at heating to 430°C, and this temperature was kept for 60 min., thus the pressure in the autoclave was equal to 6.0 MPa. Then, the autoclave was cooled, and the gaseous products were separated from the autoclave and further fraction boiling up to 200°C was separated by freezing out in a nitrogen trap. The solid product was collected and filtered.

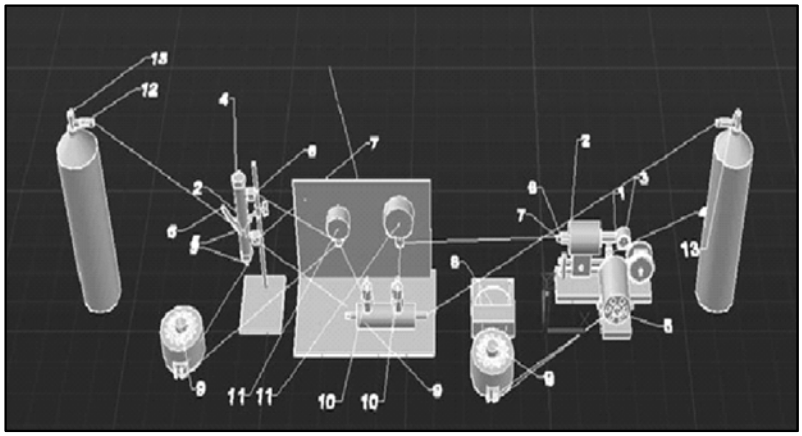

Fig. 2: Installation for hydrogenation in the stationary reactor and in the rotating autoclave

(1) Reactor with the rotating autoclave, (2) The furnace, (3) The manometer of measurement of pressure at the exit, (4) The crane for gases collecting, (5) Stationary reactor, (6) Plug for measurement of temperature in the stationary reactor, (7) Thermocouple for control of temperature in the rotating reactor, (8) Manometers for control of temperature, (9) LATR, (10) Cranes for fixing of pressure in reactors, (11) Manometers for control of pressure in reactors, (12) Reducers for control of a stream of gases, (13) Cylinders with the compressed gases of argon and helium

Thermogravimetric studies were performed under the following experimental conditions: weight of the sample - 0.3 ± 0.03 g; shredding analytical; a ceramic crucible with a lid 15 mm and a diameter of 5 mm was used. Processing of derivatograms included analysis of thermal images. Thermogravimetric analysis was performed for the samples of

raw materials: solid polymeric products and coal material. Weight loss of the sample at a given temperature was determined according to the thermogravimetric curve. The rate of mass loss was determined by curve of differential thermogravimetry, temperature maximums of endo - or exo-effects were set by the differential thermogravimetric adsorption, by standard techniques. The curve losses of the weight (TG-curves) and speeds of loss of the weight (DTA-curves) registered by the device were recalculated for 1.0 g of the initial sample and were expressed them as temperature dependences. On the basis of DTA-curves were determined the temperatures (T_{max}) corresponding to the maximum speeds of loss of weight. It was considered that loss of weight is identical to an yield of volatile products, and the rate of mass loss is equivalent to the rate of release of volatile products when heated. X-ray fluorescent researches and the element analysis of a solid sample were carried out on the microanalyzer FOCUS-M2M with use of Fe-radiation in the range from 2.0 to 37.0 V. Intensity of diffraction maxima was estimated by an analytical method in a tetragonal singoniya. Changes of a surface and structure were defined by the scanning electronic microscope of Ntegra Therma with the lighting modes - "on a gleam" and "on reflection".

RESULTS AND DISCUSSION

When grinding coal of "Karazhira" field were identified some common regularities, which well observed with differential thermogravimetric curves after machining of coal in the mill. Thermogravimetric curves (Fig. 3) have one minimum indicating dehydration at temperatures of 109-116°C. It is found that at mechanical effects on coal at the same time with change of total quantity of soluble fractions their composition and structure in comparison with fractions from the initial coals are changed.

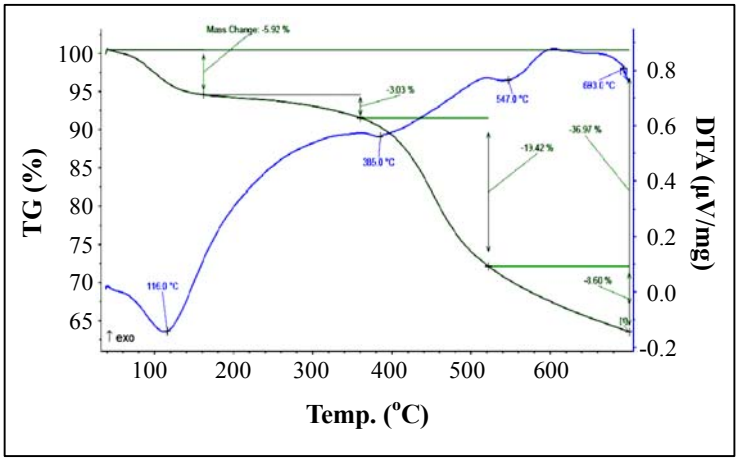

Fig. 3: Thermogravimetric curves of research of the initial coal

Data of oscillatory spectroscopy of initial coal showed (Fig. 4) that compounds in initial coal belong to amorphous formations. In particular, the organic component of coals represents mix of various X-ray amorphous components, presence and quantity of which changes among a metamorphism.

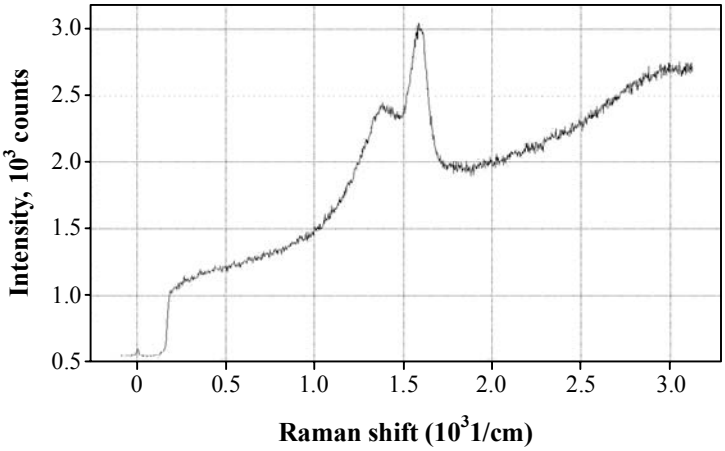

Fig. 4: Raman spectrum of initial carbon materials

It was found that in presence of the polymers in the content of mixture of coal was reduced the content of high polymer asphalt-resinous components - asphaltenes and benzene pitches in the range 360-443°C. As a result of thermal effects in the bitumen was increased role of lower molecular weight components -benzene pitches and oils. In the composition of the oil fraction was increased the content of light petroleum-ether resins and aromatic hydrocarbons in the temperature field 443-527°C.

For selection of optimum composition of the catalyst hydrogenation on catalysts based on Pd, Co, Mo and Fe (5%) supported on Al_2O_3 and carbon, at temperature 325°C and a hydrogen pressure of 5.0 MPa was carried out. It is revealed that at hydrogenation of initial substance on all catalysts direct dependence of absorption of hydrogen on experience duration is observed. The greatest absorption (V_{H2} = 27.4 mmol) is noticed on the Pd-containing catalyst (Fig. 5). By the volume of the absorbed hydrogen catalysts are arranged in the following row:

Pd/C (27.4 mmol) > Co/C (19.6 mmol) > Mo/C (12.6 mmol) > Fe/C (5.3 mmol)

On process duration catalysts settle down in similar sequence. The maximum speed of hydrogenation is observed on the Co-containing catalyst and is equal to 47.2 mmol/min*g of the catalyst. On the Fe/C catalyst hydrogenation takes place with the smallest speed.

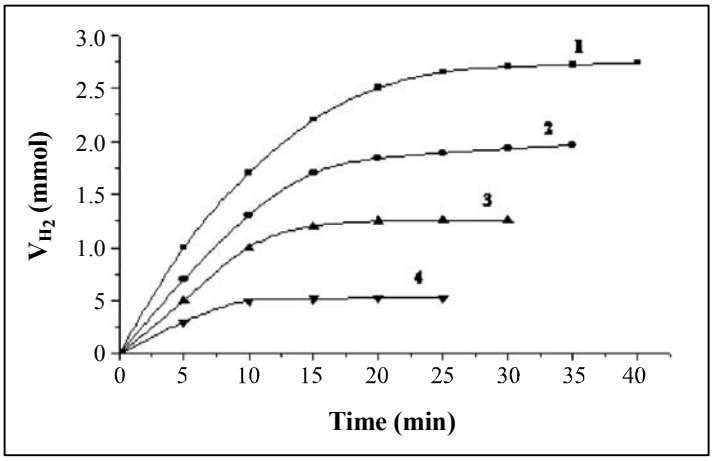

Fig. 5: Dependence of hydrogen absorption on the duration of experience at different catalysts

CONCLUSION

Hydrogenation of coal of "Karazhira" field (Kazakhstan) is studied at an elevated pressure of hydrogen on the catalysts supported on Al_2O_3 and coal on the basis of 5% of metals: Pd, Co, Mo and Fe. The results of studies showed that optimum catalysts of a hydrogenation of coals are compositions on the basis of Pd/C and Co/C on which the greatest absorption of hydrogen (Pd/C) and the maximum speed of hydrogenation (Co/C) is established. The thermogravimetric researches of coal in the presence of polymers showed that in original composition the content of high-molecular asphalt-resinous components-asfaltens and benzene pitches in the field of temperatures 360-443°C is decreased. By the method of gravimetrical studies, the stages of the transformation of coal field "Karazhira" after mechanical activation in the presence of the catalyst based on Fe and hydrogen-donor solvent tetralin were established.

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