

New Supports for Carbon-Metal Catalytic Systems Based on Shungite and Carbonizates of Plant Raw Materials

R.R. Tokpayev*, A.A. Atchabarova, S.A. Abdullayeva, S.V. Nechipurenko,
S.A. Yefremov, M.K. Nauryzbayev

Center of Physical Chemical Methods of Research and Analysis, al-Farabi Kazakh National University,
96A Tole bi str., 050012, Almaty, Kazakhstan

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Abstract

In this paper, new carbon containing materials based on products of shungite ore enrichment and carbonizates of plant raw materials were studied. The phase transformations occurring during the carbonization process were studied. Scanning electron microscopy (SEM) was used to visualize the surface topography. It was established that supports based on plant raw materials have more developed and homogeneous surface. Specific surface area and porosity was studied by BET (Method of Brunauer-Emmet Taylor). It was found that supports based on plant raw materials have developed microporous surface (383–480 m²/g), with predominant micropores on the surface with dimensions of 1.8–2.5 nm. The mechanical strength of the obtained supports is higher than their industrial analogs and it equals 53–91%. Conversion of methylbutynol on active centers of supports was studied. Supports based on plant raw materials have basic active sites whereby they can be used in base catalysis. Supports based on carbon-mineral raw materials possess acid and basic active sites and they can be used to prepare bidirectional type action of catalysts. Conducted research have shown the possibility of using these materials as supports for creating carbon-metal catalyst systems.

1. Introduction

Carbon materials, with their unique properties, are used in various fields of science and technology. They are widely used in processes with aggressive environment: as electrically conducting materials, fillers, composite materials, adsorbents in processes of purification of gases and aqueous media, to extract non-ferrous and rare metals from multicomponent solutions, and also can be realized in production of catalyst systems, wherein they are used as supports.

Currently oxide supports (α-lumina, silica, and others) and carbon supports (activated charcoal, graphite, “sibunite”, graphitized carbon black, etc.) are widely used in catalyst production. Carbon supports have several advantages: they are resistant to acid and alkaline environments and moisture; carbon-based catalysts often have better catalytic properties that catalysts on oxide supports; cost of ex-

traction of precious metals at the disposal of waste carbon catalyst is lower compared to the oxide; also in the disposal of the latter, a large number of acid-alkaline waste are produced that pose serious environmental hazard.

Porous carbon materials have to meet the following requirements that apply to supports of catalysts: inertness, mechanical strength, stability, surface area, porosity [1–4].

In recent years, a number of scientific studies seeking for new, high-performance, cost-effective carbon supports for catalytic systems have increased substantially.

Support based on carbon nanoparticles with a high degree of graphitization to which the active metal (Pt) has been deposited, was studied [5]. The obtained catalyst has high electrochemical activity and stability in oxidation of hydrogen and reduction of oxygen occurring in fuel cells.

* Corresponding author. E-mail: rustamtokpaev@mail.ru

Further investigation of processes taking place in fuel cells [6–7] have shown promising use of graphene and carbon nanotubes as supports of electrocatalysts.

Carbon nanofibers with a predetermined pore size are also successfully used as supports of catalysts. In [8], carbon nanofibers with an average pore diameter 50 nm, to which Pd has been deposited, were obtained. Obtained catalyst was successfully tested in liquid phase for selective hydrogenation of C = C bond.

Carbon nitride, due to its unique structure, can be used in heterogeneous catalytic hydrogenation and oxidation as shown in [9].

Application of carbon directly as supports for catalysts was discussed in detail in the review paper [10] wherein the catalyst system based on carbon have been successfully tested in the process of conversion of methanol, desulfurization of thiophene and the Fischer-Tropsch reactions.

All described catalysts for carbon supports found very limited industrial application for the following reasons:

- high cost;
- microporous structure of some of the supports is not optimal for many catalytic processes;
- low mechanical strength of the granules;
- complexity of reproducibility of porous structure [4].

In this paper, secondary raw materials – shungite rock from “Bakyrchik” deposit of East Kazakhstan (stocks over 30 million tons), as well as walnut shells and apricot pits, which are formed in large quantities in the processing of fruits and nuts in the Southern regions of Kazakhstan and in the neighboring countries of Central Asia, were used as support for the carbon-metal catalyst systems.

Shungite rocks form a natural layer and dumps after extraction and enrichment of polymetallic ores, which resources are sufficient for use on an industrial scale. The presence of carbon in these rocks in an amorphous form and in close contact with silicate raw materials allows considering shungite rocks as a promising carbon-mineral raw materials [11]. A scientific team led by M.K. Naurzybayev and S.A. Yefremov developed technology for shungite processing to obtain the desired products. Shungite processing technology is built on a flexible circuit; it is environmentally friendly and waste-free [12]. Carbon-mineral sorbents for waste and domestic water purification from heavy metal ions [13], fillers of elastomers [14], composite materials for protection against electromagnetic interference [15], etc. were obtained based on products of shungite processing. One of the new directions of research is use of enriched shungite as support for catalytic systems. Us-

ing shungite as raw material in the preparation of the support solves the problem of waste management in polymetallic deposit “Bakyrchik”, while improving whole environmental situation in the region.

The aim of this work was to obtain and study new carbon-metal catalyst systems based on shungite and carbonizates of plant raw materials.

2. Experimental

Preparation of support based on carbon minerals. A necessary requirement for raw materials used in technological conversion is constancy of chemical and particle size distribution. The flotation process was carried out to stabilize the structure of shungite materials. The concentrate with a carbon content $40 \pm 2\%$ by weight was obtained. The obtained concentrate was subjected to heat treatment in an inert atmosphere of argon at $800\text{ }^{\circ}\text{C}$ for 1 h and was then activated with superheated steam at temperature of $850\text{--}900\text{ }^{\circ}\text{C}$ for 40 min, whereby specific surface area increased from 12 to $153\text{ m}^2/\text{g}$. Increase of a specific surface area was due to combustion of amorphous carbon [12].

Preparation of support based on plant raw materials. Plant material was crushed in a rotary-knife mill “RM-120”, Vibrotechnik, Russian Federation. Further material was subjected to heat treatment in an inert atmosphere and activated with superheated steam at conditions similar to those used in preparation of support for carbon-based minerals.

As a result of this work, four types of carbon-containing media were obtained:

- Support No 1 – based on shungite concentrate;
- Support No 2 – based on an activated shungite carbonizate;
- Support No 3 – based on activated walnut shell carbonizate;
- Support No 4 – based on activated apricot pits carbonizate.

Determination of pH of aqueous extract of the support. Weighed portion of 10 g of the support was placed in a flask with 100 mL of water and boiled for 3 min at reflux. Further the flask contents were filtered through a paper filter, discarding the first portion of filtrate. The filtrate was cooled and its pH was determined [16].

Determination of mass fraction of ash of the support. Three powdered samples ($m = 1\text{ g}$) were placed into three pre-calcined crucible. The crucibles with samples were placed in muffle furnace preheated up to $300\text{ }^{\circ}\text{C}$. Crucibles were held in stable temperature zone of $(850 \pm 25)\text{ }^{\circ}\text{C}$ for 3 h. Once the crucible with bottom ash is cooled and weighting procedure was performed [17].

Determination of water mass fraction (moisture) in the support. Sample ($m = 1$ g) was placed into pre-dried glass with weighed cap. The glass was placed into oven pre-heated up to 100–105 °C and dried for 1 h. Then, the glass with sample was removed from the oven, cooled in desiccator and weighed [18].

Determination of iodine adsorption activity. A sample of the support was dried at $T = 100$ – 105 °C in oven. Sample with mass of 1 g was placed into 250 mL conical flask and then 100 mL of iodine solution (0.1 M) in potassium iodide was added. Flask was stoppered and stirred for 30 min at 100–125 rpm. Solution was then allowed to settle, and 10 mL of aliquot were taken from the flask, introduced into 50-mL conical flask and then titrated with sodium thiosulfate. At the end of titration 1 mL of starch solution was added and titration was continued until blue color disappeared. Simultaneously, determination of initial content of iodine in the solution was carried out by titrating 10 mL solution of iodine in potassium iodide with sodium thiosulfate by adding starch solution at the end of the titration.

Determination of strength of the supports. Pre-dried support sample of 50 g (> 0.6 mm) was placed into the apparatus for measuring strength for 10 min, after the end of the experiment sample was removed from the apparatus and dust sifting was carried out using sieve No 10 ($d = 100$ μ m) and strength of support was calculated according to GOST 6217–74 [19].

Study of phase transformations in samples by thermal analysis. Study was performed using analyzer «NETZSCHSTA 449F3», NETZSCH, Germany. Simultaneously two curves were recorded: thermogravimetric (TG) and curves of differential scanning calorimetry (DSC). Powders with particle size of less than 0.1 mm were used for analysis. Weight was 5–20 mg. Calcined alumina (Al_2O_3) was used as an inert material. Steady heating of samples was performed in nitrogen atmosphere up to 800 °C. The rate of temperature rise was selected on the basis of records for collected samples to be analyzed, it was 16 °C/min.

During the thermal analysis, complex method of simultaneous study of weight change curve and differential temperature change at steady increasing temperature was applied to determine the effective kinetic constants of carbon combustion.

Determination of specific surface area and total pore volume of supports. Determination of specific surface area, total pore volume of supports and pore size distribution was carried out by BET method using the instrument of «AccuSorb», Micromeritics, USA. Sample (0.1–0.5 g) was filled in pre-weighed

cell and placed into degassing tank. Degassing was carried out for 2 h at temperature of 200 °C. Adsorption measurements were made at 13 adsorption and 10 desorption points. By changing thermal conductivity of argon gas stream passing through the tube with measured sample, the amount of argon adsorbed to the sample surface from gaseous mixture was determined while cooling by liquid nitrogen and desorbed during subsequent heating of the sample to ambient temperature. By changing concentration of adsorbed gas (argon) in the mixture, multiple values of adsorption were obtained that corresponded to different concentrations of it in the basis. Adsorption isotherms were plotted and specific surface area of the sample was calculated by BET method [20].

Scanning electron microscope analysis (SEM). Surface structure of the support was studied by SEM method using «Quanta 200i 3D», FEI Company, USA. Sample was fixed on a copper holder using conductive adhesive paper. Previously, a thin conductive layer of carbon for better passage of the charges was applied on the surface of the sample in special vacuum system.

Determination of catalytic activity. Catalytic activity of supports was determined by the number of acidic and basic centers on natural and modified samples of supports using test reaction of methylbutynol (MBOH) conversion [21]. Analysis: samples were ground to fraction of $0.200 \div 0.315$ mm. Sample of support (0.15 g) was placed into reaction tube, then into MBOH conversion unit. Activation of samples was carried out for 4 h in the stream of nitrogen gas at flow rate of 50 mL/min at a temperature of 400 °C. Then, the reaction temperature was adjusted up to 250 °C, gas stream saturated with methylbutynol was supplied through the sample. Mixture was sampled periodically in reactor outlet for gas chromatography analysis. The amount of reaction products was calculated by comparing obtained peak area with peak area of toluene, which was used as an internal standard [22].

The reproducibility of experimentally determined parameters of the processes. The total measurement error number of experimentally determined parameters calculated by the known method of estimating errors when we are interested value Z is the sum (or difference) of several independent measured X and Y , to find the total error is not necessary to add the errors themselves, and their squares.

$$Z = (\Delta X)^2 + (\Delta Y)^2$$

Accuracy class of all equipment used in the experiment is 0.25–0.5.

3. Results and Discussion

Obtained derivations of carbon containing materials in nitrogen atmosphere are very diverse, reflecting varying nature of samples (Fig. 1).

The endothermic peak at 100 °C was observed during study of the sample based on shungite concentrate (Fig. 1), due to the removal of adsorbed water molecules. The exothermic peak was observed in the temperature range 382–580 °C, which indicates burnout of unstructured carbon. Further heating of the sample leads to decomposition of chlorite at

temperatures 580–719 °C. Decomposition of carbonate occurs at 719–774 °C, further increasing in temperature leads to dehydration of hydromica [23]. The results of thermal analysis shows smooth decreasing weight during the entire heating time, the total weight loss in this case was 7.91%.

Derivatogram of carbonization process of walnut shell was also characterized by endoeffect and exoeffects (Fig. 2), which are likely to correspond to the decomposition of the main components of walnut shell: cellulose, fats, tanning, coloring, flavoring.

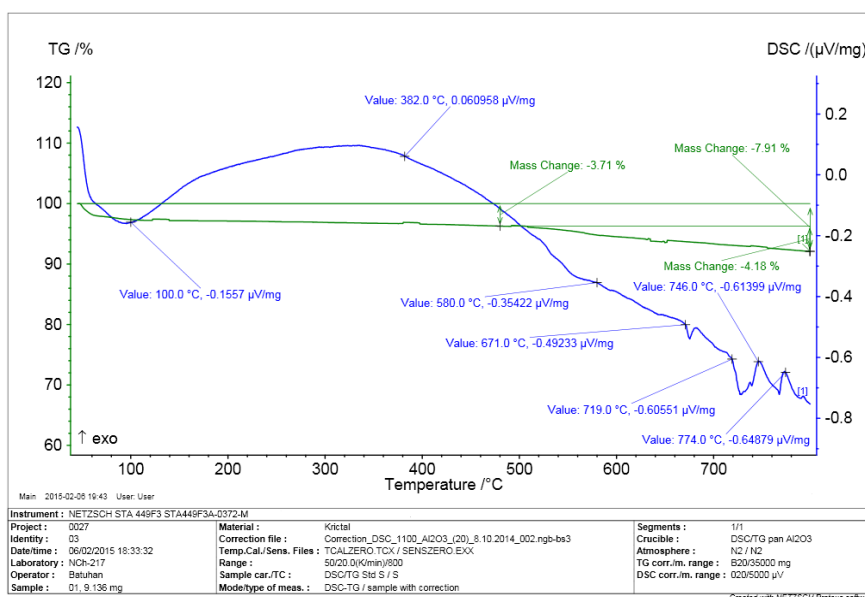


Fig. 1. Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) plots of carbonization process of shungite carbon concentrate.

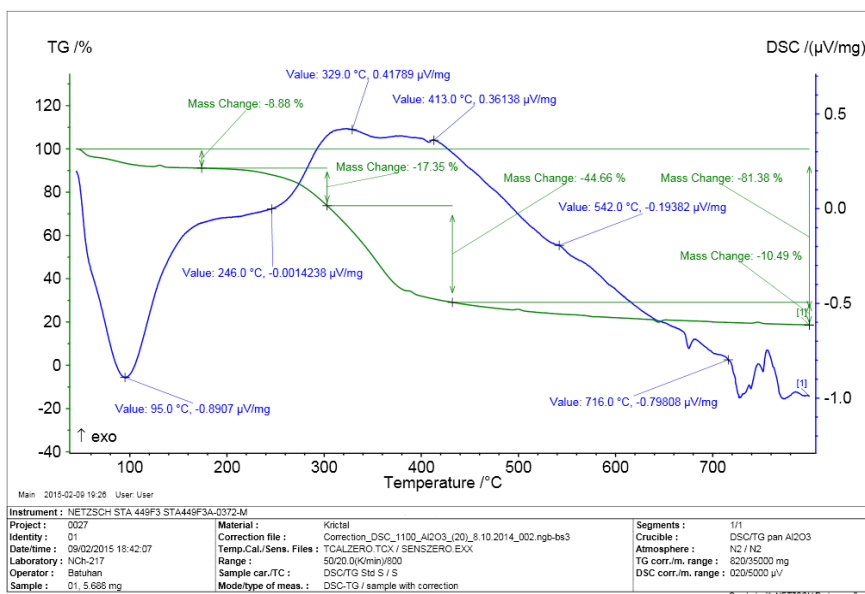


Fig. 2. Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) plots of carbonization process of walnut shell.

The endothermic effect in Fig. 2 is associated with the removal of adsorbed water molecules at 100 °C. The exothermic effect in the temperature range 246–413 °C indicates burnout of unstructured carbon and volatile organic compounds. Burning of lignin and cellulose occurred in the temperature range of 413–542 °C. Gases, resin, liquid and solid com-

pounds are formed as the result of thermal decomposition. Part of the volatile fractions formed liquid and resin during combustion, evaporates, while the other part of the combustion products is converted into carbonized residue. The formation of carbonized residue occurs at the temperature range 542–716 °C. Total mass loss from thermal analysis was 81.38%.

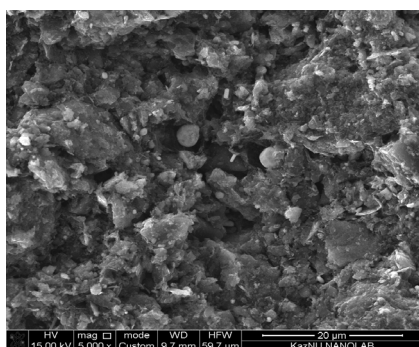
Table 1
Physical and chemical properties of supports

Properties	Support				
	1	2	3	4	5*
Adsorption activity of iodine, %	11.6	24.6	59.5	78.6	60.0
pH of the aqueous extract	7.3	7.5	9.1	9.4	9.3
Moisture, %	1.5	1.7	1.2	1.1	10.0
Ash content, %	55.2	53.7	3.8	3.2	6.0
Mechanical strength, %	60.0	53.0	86.0	91.0	40.0

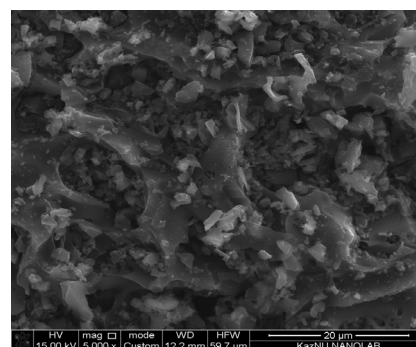
* characteristics of the support on the basis of activated coal of BAU-A in accordance with GOST 6217-74 [16]

Analysis of physical and chemical properties of supports showed that plant-based supports have high iodine value and mechanical strength. pH of aqueous extract of them is shifted to alkaline area, humidity and ash content comply with requirements for this type of support (Table 1). Supports based on minerals have lower iodine value and mechanical strength, pH of aqueous extract is of weakly alkaline character, humidity was within acceptable

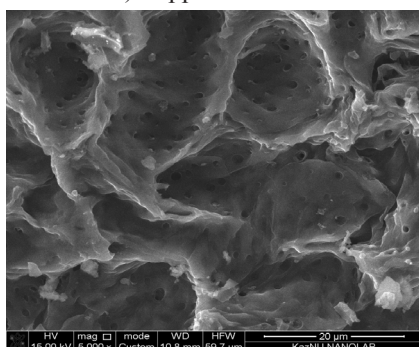
limits. High ash content is due to the nature of shungite origin. As it is known, composition of shungite results in the formation SiO_2 , Al_2O_3 , Fe_2O_3 and other ingredients, which contribute to catalytic activity of the support. Physico-chemical parameters of the studied materials are comparable to the characteristics of the industrial carbon supports (BAU-A). The mechanical strength of the studied samples is higher than BAU-A.



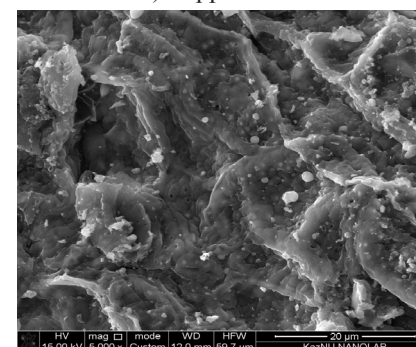
a) Support No 1



b) Support No 2



c) Support No 3



d) Support No 4

Fig. 3. Micrographs of supports.

Results of analysis of the micrographs of supports indicate that the surface of the carbon-based mineral support represented inhomogeneous structure with local accumulations acinar (dendritic) and isometric forms (Fig. 3). The surface of the support based on plant raw material is more homogeneous and smooth. The surface is represented in the form of very characteristic of plant tissue porous

structure with a pore diameter of 1–2 μm .

Supports based on plant raw materials have greater surface area than the supports on the basis of mineral raw materials (Table 2). High values of specific surface area and total pore volume of liquid are due to the presence of micropores and submicropores on the surface of Supports No 3–4 (Fig. 4).

Table 2
Specific surface area and total pore volume of the support liquid

Characteristics	Support				
	1	2	3	4	5*
Specific surface area, m^2/g	12.0	153.2	383.0	480.0	700.0–800.0
Total pore volume, mL/g	0.091	0.122	0.233	0.298	1.600

* characteristics of the support on the basis of activated coal of BAU-A in accordance with GOST 6217-74 [16]

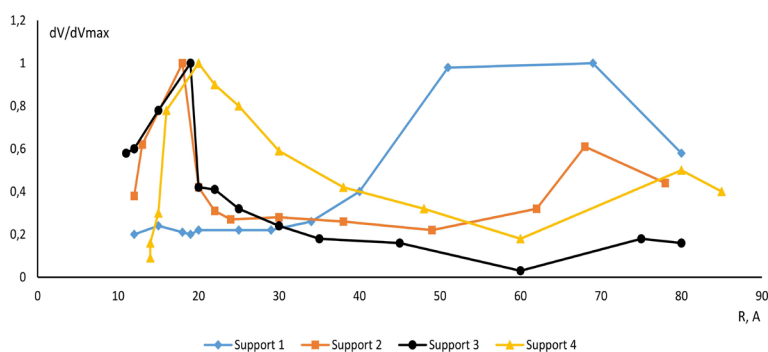


Fig. 4. Micropore size distribution.

The results of analysis showed that the surface of Supports No 2–4 were presented mainly by micropores with dimensions of 1.8–2.5 nm, which explain their large specific surface in relation to the Support No 1, having micropore surface with dimensions of 5.1–8 nm.

Specific surface area and total pore volume of the support liquid of industrial support BAU-A exceed parameters of studied supports, however, this is not a disadvantage, since not all catalytic processes, these indicators are of prime importance [4].

Catalytic activity is determined by the quantity of acidic and basic centers on the supports established using test conversion reaction of methylbutynol. This reaction makes it possible to evaluate acid-base properties of the supports on the basis of distribution of products. Depending on acidity and basicity of surface, it is possible for methylbutynol to participate in three reactions (Fig. 5) [21, 24].

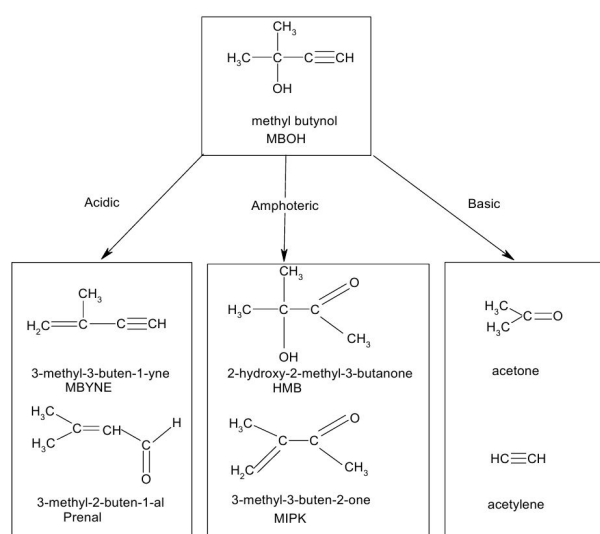


Fig. 5. Diagram of methylbutynol conversion on various active centers of supports.

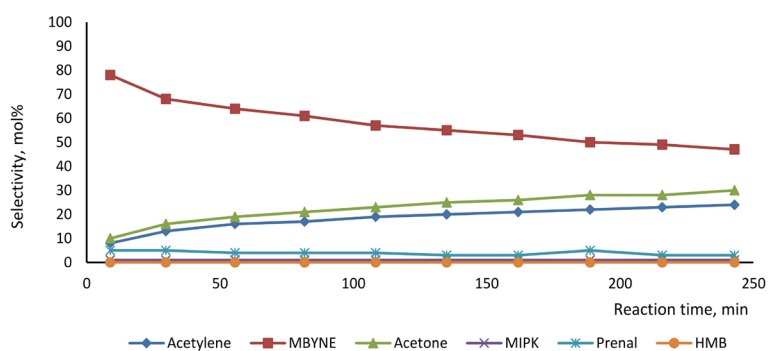


Fig. 6. The selectivity of products formation by methylbutynol conversion on the Support No 2.

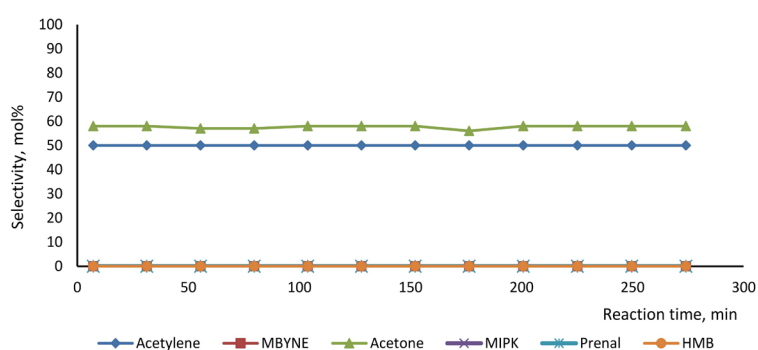


Fig. 7. The selectivity of products formation by methylbutynol conversion on the Support No 3.

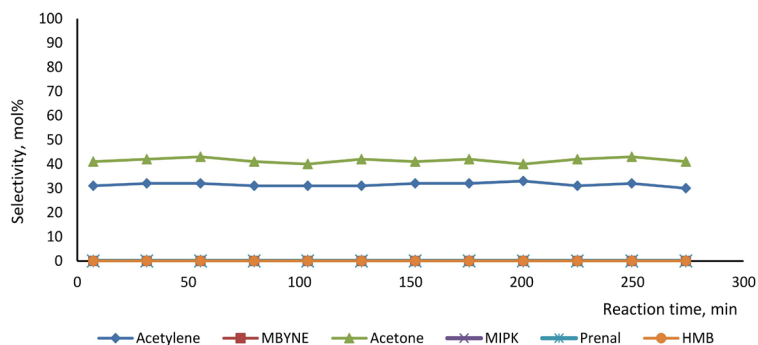


Fig. 8. The selectivity of products formation by methylbutynol conversion on the Support No 5.

Based on obtained results (Fig. 6), it can be concluded that in methylbutynol conversion on the surface of Support No 2, MBYNE is formed with selectivity of 80 molar %; acetone with selectivity of 30 molar %; acetylene with selectivity of 25 molar % and prenal with selectivity 5 molar % indicating the presence of acidic and basic active sites on the surface. Degree of methylbutynol conversion decreased with time and reached to 30%.

The selectivity of acetylene and acetone on the Support 3 was 50 and 60 molar %, respectively (Fig. 7). The degree of MBOH conversion did not

change with time and was 80%. Similar results were observed for industrial support, but with lower selectivity of products – 32 and 41 molar % for acetylene and acetone, respectively (Fig. 8). The degree of methylbutynol conversion was ~ 70%.

4. Conclusions

Thus, new carbon supports for carbon-metal catalyst systems were obtained and studied.

Physical and chemical characteristics of the supports were determined by BET method, SEM,

TG-DSC and others. It was found that supports based on plant raw materials have developed microporous surface (383–480 m²/g), high adsorption characteristics (59.5–78.6%) and high mechanical strength (86–91%). Conversion of methylbutynol on the supports occurred with highly selective formation of the main active centers, which opens the prospect of their use in base catalysis. Degree of methylbutynol conversion did not change with time and was 80%. Study of catalytic activity of the supports based on shungite showed the presence of acidic and basic active sites on the surface with high selectivity, which greatly expands the range of catalytic reactions, and opens possibility for obtaining catalysts with bidirectional action. Degree of methylbutynol conversion over time decreased and reached 30%. An important competitive advantage of the obtained supports is their economic and environmental aspects, due to the fact that all the studied materials are wastes of various industries. Therefore, we think that profitability of production of this type of supports will be higher than their industrial analogs.

Development of new materials based systems on carbonaceous shungite, apricot pits and walnut shell will give a new impulse to the development of carbon-metal catalytic systems.

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