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Targeted Synthesis of Micromesoporous Carbon-Carbon Composites for Making a New Generation Supported Zinc Acetate Catalyst for Synthesizing Vinyl Acetate

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Abstract

A process of modifying the pore structure of mesoporous carbon carrier Sibunit obtained on the basis of technical carbon (soot) *via* introducing furfuryl alcohol into carbon at the stage of granulation was studied. An effect of modification conditions on the textural characteristics of the modified Sibunit was estimated. It was demonstrated that the introduction of furfuryl alcohol into technical carbon at the stage of granulation allows additional developing the Sibunit micropore volume up to 0.17–0.26 cm^3/g. It was found that the percentage of micropores depends strongly on the degree of carbonization, *i. e.*, on the amount of pyrocarbon deposited. When the carbonization level is higher than 60 %, the effect of the modification becomes negligible, which does not allow generating micropores in a great amount within the material. Basing on these results, a model was developed concerning the structure of modified Sibunit.

Key words: carbon, furfuryl alcohol, carbon carrier, pyrocarbon, porous texture, micropores

INTRODUCTION

Porous carbon materials are widely used in catalytic, adsorption and electrochemical processes. The main advantages of carbon-based materials consist in their durability and stability in corrosive environments, high specific surface area and the ability of adjusting the parameters of their porous structure within a wide range. An important advantage of carbon as the catalyst carrier consists in the inertness of the surface, which provides eliminating any undesirable side reactions catalyzed by the carrier to occur.

At present time, the Russian and world industry produces a limited range of porous carbon materials used as adsorbents and catalysts. They are presented mainly by microporous active carbon species of black-coal-based and phytogenous origin [1], the properties and structure of those are determined both by the characteristics of the feedstock, and by the conditions of coal preparation. The use of activated carbon species as carriers for catalysts is restricted by a low mechanical strength and a high content of mineral impurities [2]. For recent years, the list of catalytic processes with the use of carbon materials was extended and, correspondingly, there was an increase observed in the efficiency of these materials [3]. This could be caused by the fact that for each of the catalytic process, mainly synthetic carbon materials are used with specially chosen and optimized morphology, porous structure, geometric shape and grain size.

In the near future zinc acetate catalysts for the synthesis of vinyl acetate from acetylene and acetic acid might become most demanded catalysts, which could be caused by the development of low-cost technologies for the obtaining of acetylene from natural gas. Obtaining vinyl acetate from acetylene and acetic acid in the industry is carried out using zinc acetate applied onto activated carbon as a catalyst at a pressure of about 1.1 atm and at a temperature of 170 °C. The reaction is carried out at 3-4-fold acetylene excess and at the conversion rate of acetic acid amounting to 50-70 % [4]. The catalyst is prepared *via* the impregnation of a grinded carbon carrier by a concentrated solution of zinc acetate (19–20 mass %), then it is subjected to drying in air at 120–170 °C during 12.5 h. [5]. The engineering specifications for the catalyst preparation standardize the content of $Zn(OAc)_2$ within the range of 26–32 mass %, as well as its initial activity (at least 25 g/(L · h) at 170 °C) and the final activity (at least 125 g/(L · h) at 200 °C) [6]. The activity and stability of the catalyst is significantly affected by the texture and nature of the surface of the carrier those determine the modes of zinc acetate application onto the surface of activated carbon species as well as the active component distribution in the pores of the carrier.

As carriers for the zinc acetate catalyst in the industry one traditionally uses activated carbon species those, on the one hand, demonstrate a micro-porosity level necessary for the formation of high activity, and on the other hand, exhibit extremely low mechanical properties and an irregular shape of the particles, which is especially crucial with respect to the synthesis of vinyl acetate in the fluidized bed [7].

For example, for the preparation of catalysts for fixed bed processes one uses charcoal species AGN-1, AGN-2 AGN-3, for the processes in fluidized bed one uses charcoal species ARD, ARD-2. the charcoal species used are characterized by high values of the sorption volume (up to 0.6 cm^3/g) containing about 50 vol. % of micropores and about 10 vol. % of mesopores, with a low abrasion resistance value (~70 %) [8].

Among the carbon materials manufactured today under pilot conditions, composites such as Sibunit could become most suitable for preparing zinc acetate catalysts; they are characterized by a high resistance with respect to abrasion and almost perfect spherical microgranular structure. However, the mesoporous structure of Sibunit [9, 10] is not optimal for the synthesis of vinyl acetate catalyst, which makes difficult its use as a carrier for the zinc acetate catalyst.

In order to increase the fraction of micropores resulting from the synthesis of Sibunit, in this work we proposed to add an aqueous solution of furfuryl alcohol (FA) at the stage of wet carbon granulation. It is known [11] that FA is miscible with water in any proportion resulting in the formation of a homogeneous solution. With increasing the temperature, the FA is involved in the polycondensation reaction to form linear macromolecules. Further increase in temperature as well as the absence of oxidants results in a three-dimensional cross-linking of linear macromolecules to form a cross-linked insoluble and infusible polymer such as polyfurfuryl alcohol. Further the process of Sibunit synthesis on the stage of polyfurfuryl alcohol heat treatment results in the formation of microporous carbon with a narrow pore size distribution and with an average size of micropores amounting to 0.6–0.8 nm. Thus, the introduction of carbon black at the stage of FA granulation could promote an increase in the microporosity of the Sibunit.

The present work was aimed at the investigations concerning the process of the formation of the porous structure of the Sibunit with the introduction of FA into technical carbon at the stage of its granulation as well as the assessment of the synthesis condition influence upon the textural characteristics of the carrier.

EXPERIMENTAL

For the preparation of the microporous carbon carrier we chose P-145 granular technical carbon (TC). Its texture characteristics are presented below:

Average particle size (d_p), nm	18
Specific surface area according to BET, m^2/g	114
Micropore volume according to comparative method, cm^3/g	0.003
Specific pore volume, cm^3/g	0.820
Including the percentage of pores with size, nm:	
<3	0.18
3–5	0.004
5–50	0.250
5–90	0.500
>90	0.066

The choice of the mentioned trademark of the TC we made on the basis of previous studies [12, 13], where it was demonstrated that for Sibunit derived from that P-145 technical carbon, the average pore size amounts to less than 10 nm.

In order to assess the influence of the method of granules preparation, we formed technical carbon granules in two ways as it follows.

1. The use of balling method in a horizontal mixer-granulator of periodic action, 10 dm^3 in volume. Technical carbon black in an amount of 1 kg was filled into a mixer-granulator with adding a 10–16 % aqueous FA solution at a solution/TC ratio equal to 1 : 1. The following characteristics of the granulation process were set: the rotation frequency of the mixer granulator blades amounting to 750 min^{-1}, the granulation time granulation being equal to 3 min.

2. Plunger extrusion method. In this case, we prepared a plastic paste from the technical carbon, the aqueous solution of FA and technological additives in a paddle mixer with stirring for 15 min. Further, the paste was extruded through a die hole with the diameter of 0.6 mm. Extrudates were dried to be grinded into pellets with a length of 0.3–0.6 mm along the generatrix.

After the granulation the product was dried at the temperature of 40–60 °C and graded on sieves with the mesh size of 0.3 and 0.5 mm.

After extrusion and granulation stages the dried and sieved granules were heat-treated in several stages in the air, inert and oxidizing environments.

In order to perform the heat treatment of TC granules we used a laboratory installation which included a cylindrical quartz reactor with the reaction zone volume amounting to 0.5 dm^3 (the rotation frequency ranging within 5–10 min^{-1}). The temperature in the reactor was maintained accurate within ±2 °C *via* using an external heater. The reactor could be with any inorganic (inert) and hydrocarbon gases as well as water vapour, both separately and in a mixture. Water vapour could be supplied to the reactor through an additional heater from an evaporator. Gas supply was controlled by rotameters, whereas the steam supply was monitored by the mass of water entering the evaporator.

The first heat treatment stage such as the polycondensation of FA introduced into the plastic carbon paste was performed *via* holding the granules of TC at 60–80 °C in air during 6–8 h.

The second heat treatment stage such as three-dimensional cross-linking the macromolecules of polyfurfuryl alcohol was carried out in an inert atmosphere within the temperatures range of 160–300 °C during 4–6 h.

The third heat treatment stage such as the pyrolysis of polyfurfuryl alcohol was carried out in an inert atmosphere at the temperature rise from 300 to 800 °C at a rate of 1–2 °C/min with holding at the final temperature within 1–3 h.

The final stages of the heat treatment consisted in the carbonization and activation; those are similar to the stages used in the experimental-industrial technology of obtaining the Sibunit [10]. In this case, the main goal of the carburizing stage consists in the deposition of pyrolytic carbon produced by the thermal pyrolysis of gaseous medium onto the carbon skeleton material. As the result of the pyrolytic carbon deposition onto the surface of the granules their strength increases up to 100–200 kg/cm^2, and the material acquires chemical and thermal stability, whereas its density exhibits a 1.5–2-fold increase. At the same time one observes a decrease in the sorption characteristics: the specific surface area becomes equal to 10–30 m^2/g, whereas the adsorption pore volume is less than 0.2 cm^3/g. The carbonization process was carried out within the temperature range of 800–850 °C, at the volumetric flow rate of feeding hydrocarbon gas equal to 8–10 L/h, with argon used as a carrier gas at volumetric flow rate equal to 50–70 L/h. In the course of this stage of heat treatment we observed the formation of low-porous carbon granules, with a high strength value (100 kg/cm^2). After the process of carburization the sample was cooled in an inert atmosphere to a temperature of 100–120 °C. For each sample we registered an increase in mass, or the carbonization (compaction) level (Δm_1):

$$\Delta m_1 = (m_{\text{carb}} - m_{\text{ini}})/m_{\text{ini}} \cdot 100\ \%$$

Here m_{ini} is the mass of the initial sample, g; m_{carb} is the mass of the sample after carburization, g.

The compacted pyrocarbon samples were activated by steam at a temperature of 850–900 °C and the steam volume flow rate amounting to 0.2–0.8 L/h. After finishing the activation process, the sample under investigation sample was cooled in an inert atmosphere to a temperature of 100–120 °C. For each sample we evaluated the burnout level of the material Δm_2, or the mass loss according to the formula

$\Delta m_2 = (m_{carb} - m_{act})/m_{carb} \cdot 100\ \%$

Here m_{act} is the sample mass after activation, g.

In the course of the experiments, the temperature conditions at all the stages of the heat treatment, the composition and the volume flow rate of the gas mixture (hydrocarbons + inert gas) at the stage of carbonization, as well as the composition and the volume flow rate of the activation mixture at the activation stage remained constant. Changed only while carburizing and activation time.

In order to compare the texture parameters of the unmodified carbon material prepared from P-145 technical carbon we obtained the samples of the carrier using the method of extrusion and the method of balling with no FA introduced.

For analyzing the textural parameters of porous carbon materials we used the adsorption method via comparing the adsorption-desorption isotherms for the standard adsorptive (nitrogen) at −195.7 °C using an ASAP 2020 analyzer (Micromeritics). Before the adsorption measurements the samples were trained in vacuum at 300 °C during 10–12 h. The calculations of the specific BET surface area (S_{BET}) were performed within the range of equilibrium relative values for nitrogen vapour $P/P_0 = 0.05$–0.20 according to the adsorption isotherm. In calculating the value of the specific surface area the nitrogen molecule area in the completed monolayer was assumed to be 0.162 nm^2. The values of the adsorption pore volume (V_s) were determined from the nitrogen adsorption at $P/P_0 = 0.990$. The micropore volume (V_{mi}) was determined *via* comparative α_s method, using the standard nitrogen adsorption isotherm for non-graphitized soot Cabot [14]. The pore size distribution was calculated using a standard BJH method [15].

RESULTS AND DISCUSSION

Table 1 demonstrates the texture characteristics of Sibunit obtained on the basis of P-145 technical carbon. It is seen that the samples under investigation differ from each other in the compaction level by approximately three times (from 60 to 175 %). The level of burnout for the mentioned samples remains at the same value ranging within 25–43 %. The granules with the 60 % compaction level demonstrate the specific pore volume equal to 0.75 cm^3/g. An increase in the compaction level up to 120–175 % results in decreasing the pore volume down to 0.51–0.45 cm^3/g.

The micropore volume in these cases is equal to only about 0.04–0.10 cm^3/g, *i. e.*, the percentage of micropores in the adsorption specific pore volume calculated according to formula

$(V_{mi}/V_s) \cdot 100\ \%$

is not higher than 8–13 %. Thus, the use of P-145 technical carbon does not result in increasing the percentage of micropores in the Sibunit.

Taking into account the mentioned above, the carbon paste at the formation stage was mixed with FA in the amounts ranging within 5–15 % to carry out the stages of the FA polymerization and carbonization with the subsequent stages of carbonization and activation. It should be noted that the rheological behaviour of carbon paste containing the FA was accompanied at the stage of molding the carbon ele-

TABLE 1

Textural characteristics of Sibunit based on P-145 technical carbon

Granulation methods	Compaction level, %	Burnout level, %	S_{BET}, m^2/g	V_s, cm^3/g	V_{mi}, cm^3/g
Balling	60	25	370	0.75	0.10
	120	25	346	0.45	0.06
	120	43	387	0.50	0.04
Extrusion	175	32	437	0.51	0.06

Note. Here and in Tables 2, 3: S_{BET} is specific surface area; V_s is specific pore volume; V_{mi} is specific volume of micropores.

ments by certain peculiarities. Thus, in the course of molding *via* the extrusion through the die hole of 0.6 mm in diameter the carbon paste viscosity gradually increased, which was indicated by a more than twofold increase in the molding pressure value up to 100 kg/cm^2. The increase in the viscosity of a plastic composition under the influence of shear stress is called dilatancy. Such behaviour of carbon compositions was described earlier by the authors of [16]. The authors attribute the presence of dilatancy with the formation of peculiar chain structures in the plastic carbon composition. The presence of FA in the extruded carbon composition enhances this process, whereas the increase in the FA content in the paste results in a more dramatic manifestation of dilatancy at the stage of molding the carbon elements. When the FA content is greater than 15 %, the extrusion of the carbon composition through a die hole with the diameter of 0.6 mm is almost impossible. When forming spherical granules *via* the method of balling during the granulation time of more than 3 min the minimum grain size amounts to 0.5–0.8 mm, whereas at FA content higher than 15 % the carbon composite sticks to the rotating rotor blades, and the formation of spherical granules does not occur.

Table 2 demonstrates the parameters of the porous texture for the samples of Sibunit based on P-145 technical carbon, whose composition was modified by introducing the FA at the stage of molding in the amounts ranging within 5.1–15.4 %. The carbonization level was the same for all the samples ranging within 48–60 %. For comparison, Table 2 demonstrates the texture characteristics of Sibunit obtained with no introduction of FA as well as those corresponding to FA used. One can see that the introduction of the FA in the amounts of 5.1 % results in a slight increase in the specific surface area and specific pore volume. In this case, the volume of micropores is comparable with the pore volume of the sample obtained without FA, with their contribution at a level of 8–12 %. However, increasing the FA concentration in the molding paste up to 6.8–15 % results in a 1.5–3-fold increase in the percentage of micropores in the final carrier, thus their contribution already ranges within 19–28 % of the specific pore volume.

Table 3 presents data concerning the effect of the compaction level of the material its burnout level on the development of micro- and mesoporous component of the modified samples of the activated Sibunit. It can be seen that the increase in the compaction level higher than 100 % results in a drastic decrease in the micropore volume down to the level inherent in the unmodified Sibunit, this level being not dependent on the level of burnout. The total specific pore volume is also reduced. For samples with a compaction level less than 62 %, a significant influence upon the presence of micropores in the texture of the modified Sibunit is exerted by the burnout level of the compacted material at the activation stage. As it can be seen from Table 3, an increase in the level of burnout from 24 to 54 % for the samples with the 48 % compaction level results in

TABLE 2

Effect of the content of furfuryl alcohol (FA) in the molding paste on the texture parameters of modified Sibunit

FA mass fraction, %	Compaction level, %	Burnout level, %	S_{BET}, m^2/g	V_s, cm^3/g	V_{mi}, cm^3/g	Fraction of pores, cm^3/g with size, nm		
						3–5	5–50	50–90
–	60	25	370	0.75	0.09	0.04	0.32	0.36
5.1	59	37	580	1.03	0.08	0.13	0.69	0.04
6.8	48	54	835	1.37	0.26	0.08	0.38	0.48
8.8	48	24	481	0.60	0.17	0.03	0.11	0.22
9.3	62	24	650	0.87	0.23	0.05	0.57	0.01
15.4	60	47	692	0.89	0.25	0.07	0.37	0.19
15.4	60	57	767	1.13	0.21	0.15	0.34	0.32

Note. For design. see Table 1.

TABLE 3

Effect of the compaction level and the burnout level on the texture characteristics of modified Sibunit

Compaction level, %	Burnout level, %	S_{BET}, m^2/g	V_{s}, cm^3/g	V_{mi}, cm^3/g	Fraction of pores, cm^3/g with size, nm		
					3–5	5–50	50–90
48	24	481	0.63	0.15	0.03	0.11	0.22
48	54	835	1.37	0.26	0.08	0.38	0.48
62	24	650	0.87	0.23	0.05	0.57	0.01
62	27	798	1.16	0.21	0.12	0.66	0.10
60	47	692	0.89	0.25	0.07	0.37	0.19
60	57	767	1.13	0.21	0.15	0.34	0.32
109	33	333	0.43	0.06	0.11	0.15	0.10
109	54	579	0.90	0.02	0.22	0.41	0.157
122	25	346	0.45	0.06	0.11	0.17	0.06
175	32	437	0.51	0.06	0.07	0.16	0.07

Note. For design. see Table 1.

an almost 1.7-fold increase in the percentage of micropores. For the sample with the compaction level equal to 60–62 % and the burnout level amounting up to 24–27 %, the specific volume of micropores immediately reaches the value of 0.21–0.23 cm^3/g, whereas further increasing the level of burnout affects their development in an insignificant extent. At the same time, increasing the burnout level results in a substantially (on the average) increased specific total pore volume, which was observed for the synthesis of Sibunit by means of the traditional technology [10]. In addition, with a more than 54 % increase in the level of burnout, regardless of the compaction level, one can observe an increase in the percentage of large mesopores with the size of 50 nm. However, the samples with the compaction level about 48 and >100 % demonstrate an additional increase for mesopores with the size ranging within 5–50 nm. These two factors are likely to cause a sharp increase both in the total pore volume and in the specific surface area.

Figure 1 demonstrates the change in the volume of micropores depending on the compaction level of the modified Sibunit for all the experimental samples, regardless of the method of their formation and the amount of FA introduced. It can be seen that the increase in the level of compaction, *i. e.*, the increase the amount of pyrolytic carbon deposited on the surface of the TC, makes negligible the results of modifying the texture due to the introduction of FA, whereas the textural characteristics of the carbon material in this case are comparable with the textural characteristics of the Sibunit produced using the traditional technology.

The structural model of the modified Sibunit presented in Fig. 2 is in a good agreement with our conclusions.

The furfuryl alcohol introduced into the composition of the dispersion medium is distributed in a uniform manner over the boundaries of particles and the aggregates of technical carbon in the course of preparing the plastic paste and subsequent molding. Further heat treatment stages such as drying, polymeriza-

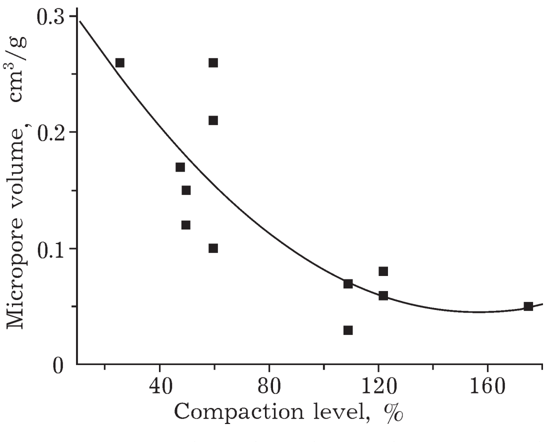

Fig. 1. Micropore volume depending on the compaction level of the modified Sibunit.

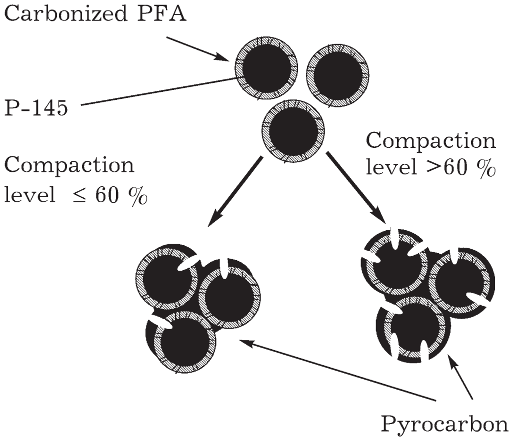

Fig. 2. Model of modified Sibunit structure.

tion and carbonization promote fixing the layer applied, as well as forming a developed system of micropores therein [17, 18]. Performing the compaction stage for the modified Sibunit results in either partial or complete surface coating with pyrocarbon. In this case, the microporous layer formed in the course of polyfurfuryl alcohol carbonization becomes closed in a corresponding manner. The subsequent activation results in developing the mesoporous structure of the material. Thus, the percentage of micropores in the texture of the modified Sibunit with a low compaction level (60–70 %) and the level of burnout equal to 40–50 % amounts to about 18–28 %. The increase in the compaction level up to 80–100 % or more, to all appearance, results in a complete closing the micropores by pyrocarbon. The further activation of these samples even at a high burnout level (*e. g.*, 54 %) does not result in the development of microporosity in the material, since the volume of micropores in this case does not exceed 13 %.

CONCLUSION

The modification the Sibunit preparation technology by introducing furfuryl alcohol at the technical carbon granulation stage in the amounts of 5–15 % of the mass of technical carbon promotes the formation of micropores in the Sibunit exhibiting the volume 0.23–0.26 cm^3/g, or up to 19–28 % of the total pore volume. The traditional technology was improved via an important and prolonged stage of the heat treatment of granulated carbon in an inert atmosphere within the temperature range of 90–500 °C. This stage is necessary in order to form a cross-linked polymer of poly(furfuryl alcohol) on the surface of the technical carbon; no development of micropores in the Sibunit could be possible without formation, carbonization and activation of the polyfurfuryl alcohol. It was found that for the modified technology of obtaining the Sibunit, the formation of a microporous structure and obtaining the maximum percentage of micropores (20–28 vol. %) is possible only at the certain values of the compaction level (~60 mass %) and activation level (~40–50 mass %) of the carbon composite. Any deviation from the optimal parameters for the mode of preparing the carrier at the stages of polymerization of furfuryl alcohol, the compaction of technical carbon and the activation of carbon composite could result in an abrupt decrease in the volume of micropores or the impossibility of developing the microporous structure in the Sibunit. These results demonstrate the technology modification to be promising as well as it is just so concerning the continuation of the research work on modifying the technology of obtaining Sibunit with the use of other organic modifiers, for example, phenol-formaldehyde oligomers.

REFERENCES

1 Kolyshkin D. A., Mikhailov K. K., Aktivnye Ugli, Khimiya, Leningrad, 1972.
2 Van de Sandt, Wiersma A., Makkee M., Beccum H. van, Moulijn J. A., *Appl. Catal. A: Gen.*, 173 (1998)161.
3 Bashkova S., Xianxian Wu F. B., Armstrong T. R., Schwartz V., *Carbon*, 45, 6 (2007) 1354.
4 Romanchuk S. V., Malakhin V. A., *Kinetika i Kataliz*, 36, 2 (1995) 303.
5 Kawaguchi T., Nakagawa J., Wakasugi T., *Appl. Catal. A: Gen.*, 32 (1987) 23.
6 Kawaguchi T., Nakagawa J., Wakasugi T., *Appl. Catal. A: Gen.*, 36 (1988) 67.
7 Mondal K. C., Cele L. M., Witcomb M. J., Coville N. J., *Catal. Commun.*, 8 (2008) 494.
8 Aktivnye Ugli AGN. TU 6-16-2206-77.
9 Likholobov V. A., Fenelonov V. B., Okkel L. G., Avdeeva L. B., Zaikovskii V. I., Kuvshinov G. G., Semikolenov V. A., Duplyakin V. K., Baklanova O. N. and Plaksin G. V., *React. Kinet. Catal. Lett.*, 54, 2 (1995) 381.
10 US Pat. No. 4978649, 1990.
11 Burket C. L., Rajagopalan R., Marencic A. P., Dronvajjala K., Foley H. C., *Carbon*, 44 (2006) 2957.

12 Baklanova O. N., Likholobov V. A., Tsekhanovich M. S., Davydova V. Yu., Chirkova O. A., Drozdov V. A., Surovikin Yu. V., *Kataliz v Prom-sti*, 2 (2009)38.

13 Plaksin G. V., *Khim. Ust. Razv.*, 9, 5 (2001) 609.

14 Kruk M., Jaroniec M., Gadkaree K. P., *J. Colloid Interface Sci.*, 192 (1997)250.

15 Barrett E. P., Joiner L. G., Halenda P. H., *J. Am. Chem. Soc.*, 73 (1951) 373.

16 Baklanova O. N., Plaksin G. V., Duplyakin V. K., *Khim. Ust. Razv.*, 8, 6 (2000) 667.

17 Glover T., Dunne K., Davis R., LeVan M., *Microporous Mesoporous Mater.*, 111 (2008) 1.

18 Ma Z., Kyotani T., Tomita A., *Carbon*, 40 (2002) 2367.