UDC 662.74; 544.723.212

DOI: 10.15372/CSD2019179

Texture Characteristics of the Sorbents Obtained from the Coal of the Kuzbass

I. YU. ZYKOV, YU. N. DUDNIKOVA, V. E. TSVETKOV

Federal Research Centre for Coal and Coal Chemistry, Siberian Branch, Russian Academy of Sciences, Kemerovo, Russia

E-mail: zyak.kot@mail.ru

Abstract

The texture characteristics of carbon sorbents obtained from coal of five different grades from the Kuznetsk Basin (Kuzbass) were studied. The sorbents were prepared by means of alkaline activation using potassium hydroxide. The alkali-coal mixture was homogenized by mechanical mixing at the KOH/coal mass ratio of 1 : 1. It was shown that the sorbents prepared from coal activated with KOH have a developed porous structure and pronounced microporosity. The structure of micropores is practically independent of coal grade. The contribution from mesopores into the porosity of the sorbents is insignificant and is observed only for fat coal. It was established that the specific surface and pore volume of the sorbents increase with a decrease in the degree of coal metamorphism. The sorbent prepared from subbituminous coal has the highest textural characteristics: its specific surface area is 1340 m^2/g, pore volume 0.58 cm^3/g. The minimal values are characteristic of lean coal: 780 m^2/g and 0.33 cm^3/g, respectively.

Keywords: carbon sorbents, coal, alkaline activation, porous structure, texture characteristics

INTRODUCTION

Pollution of water resources is an essential problem encountered by modern society. Most of fresh water sources at the territory of the Russian Federation are polluted [1], so it is necessary to improve the approaches to water purification both at the stage of water intake from water reservoirs and at the stage of water discharge. Sorption involving carbon sorbents is an efficient and not very expensive method of water purification from a broad range of impurities.

Carbon sorbents are prepared from a broad range of carbon-containing natural, synthetic and artificial materials using different methods [2]. Coal may be used as the initial raw material for obtaining carbon sorbents. We demonstrated previously [3–7] that chemical activation of various kinds of coal by potassium hydroxide promotes the formation of a developed porous structure of carbon sorbents.

Solid carbon sorbents are porous materials on the surface and in the pores of which the substances dissolved in water are sorbed. The efficiency of sorption may be determined by the chemical nature of the surface itself, its area and structure of pores. The specific surface area of the sorbent is an essential parameter of sorption properties. Investigation of the physical adsorption of gases by sorbents may give valuable information on their specific surface and porous structure. Nitrogen adsorption is most frequently used at present for this purpose.

The goal of the work was to study the texture characteristics of carbon sorbents obtained by means of the alkaline activation of coal at different stages of metamorphism from the Kuzbass.

EXPERIMENTAL

To obtain carbon sorbents, we used low-ash coal of five grades (D, G, Zh, CC, T) from the deposits of the Kuznetsk Basin (Kuzbass). Commercial coal of each grade was ground and quartered consecutively to obtain the samples with particle size 0.2–0.5 mm, and then the samples were dried in the air. Coal with a particle size less than 0.2 mm was used for analytical investigations.

The characteristics of initial coal were studied according to the standards of ISO 602–74, ISO 562–74 (technical analysis) and ISO 625–75 (elemental composition). The composition of the organic mass of coal was determined by means of elemental analysis with the help of a Thermo-Flash-2000 CHNOS analyzer (Thermo Fisher Scientific, Great Britain).

The sorbents were obtained by means of alkaline activation according to the procedure described in [8]. Coal and KOH were mixed at a mass ratio of 1 : 1 in a Pulverisette 6 ball mill (Fritsch, Germany). The steel cylinder was filled by 1/3 of its volume with a mixture of coal and alkali. Steel balls 8 mm in diameter loaded into the cylinder by 1/3 of its volume were used as milling bodies. The process was carried out until the uniform distribution of coal particles and KOH in the mixture was achieved.

Alkaline activation of coal was carried out under isothermal conditions at a temperature of 800 °C for 60 min. The average rate of heating from the room temperature to the activation temperature was ~9 °C/min. After activation, the sorbents were cooled in the inert medium at room temperature. Coarse agglomerations of sintered particles in the sample were ground to the size less than 1 mm, then washed from residual KOH consecutively with distilled water, 0.1 M HCl solution, and then distilled water to achieve the neutral reaction. The washed sorbents were dried in a drying box at 105±3 °C to the constant mass. Thus prepared carbon sorbents were powders with non-uniform particle sizes. To study the texture characteristics, the size fraction 0.2–0.5 mm was used.

Investigation of the porous structure of carbon sorbents, determination of specific surface (S_{BET}), total pore volume (V_{Σ}), the volume of mesopores (V_{me}) and micropores (V_{mi}), were carried out using an ASAP-2020 analyzer (Micromeritics, USA) by means of low-temperature adsorption of nitrogen. Measurements of nitrogen adsorption-desorption isotherms at 77 K were carried out in the region of the equilibrium relative pressure of nitrogen p/p_0 = 0.001–0.995. Before measurements, sorbent samples were vacuumized at 200 °C for 720 min and the residual pressure of 0.67 Pa for complete removal of sorbed impurities from pores.

To determine the specific surface of sorbents, we used the Brunauer–Emmett–Teller (BET) model. Pore volume was calculated using the t-Plot method using Harkins–Jura equation. Mesopore volume was calculated using the method of Barrett–Joyner–Halenda (BJH). Micropore size distribution was plotted with the help of the density functional theory, DFT. These methods allow calculating the characteristics of the porous structure of carbon sorbents obtained on the basis of fossil coal [9].

RESULTS AND DISCUSSION

The characteristics of initial coal samples used to obtain sorbents are presented in Table 1 in the order of increasing metamorphism degree. It follows from the results of technical analysis that initial coal is characterized by not very high ash content (3.1–8.4 %) and moisture content (up to 4.5 %). The yield of volatile components for coal of SS and T grades does not exceed 20 %, while for coal of D and G grades it is the same and equal to ~43 %. The content of heteroatoms in coal used in the work decreases from 14.2 to 5.6 % per daf with an increase in the degree of metamorphism.

The isotherms of nitrogen adsorption-desorption for the resulting sorbents are shown in Fig. 1. The curves have the appearance typical for microporous samples: there is an initial region of rapid micropore filling, then saturation occurs, which is pronounced as the plateau on the isotherm at p/p_0 > 0.1. The region which is parallel to the axis of relative pressures is at the adsorbed nitrogen volume close to the value of maximal adsorption. A narrow hysteresis loop is observed in the isotherms of sorbents made of D, G and Zh grade coal, which is the evidence of insignificant content of mesopores in the sorbent. For sorbents made of SS and T grade coal, the hysteresis of nitrogen adsorption isotherms is almost completely absent.

With the help of the software built into the ASAP-2020 instrument, a differential micropore volume distribution dV_{mi}/dD was plotted by means of DFT; according to the classification

TABLE 1

Characteristics of initial samples of coal from the Kuzbass

Coal grade	Technical analysis, %			Elemental composition, % per daf			Atomic ratio	
	W^a	A^d	V^{daf}	C	H	(O +N + S)	H/C	O/C
D	4.5	3.4	43.3	80.2	5.6	14.2	0.84	0.13
G	2.2	3.1	43.3	81.8	5.6	12.6	0.82	0.12
Zh	1.4	6.5	34.3	86.3	5.7	8.0	0.79	0.07
CC	1.9	6.0	19.5	87.5	4.5	8.0	0.62	0.07
T	0.5	8.4	14.1	90.3	4.1	5.6	0.54	0.05

Note. W^a is analytical moisture, A^d is ash content, V^{daf} is the yield of volatile substances, daf is the dry ash-free state of the sample.

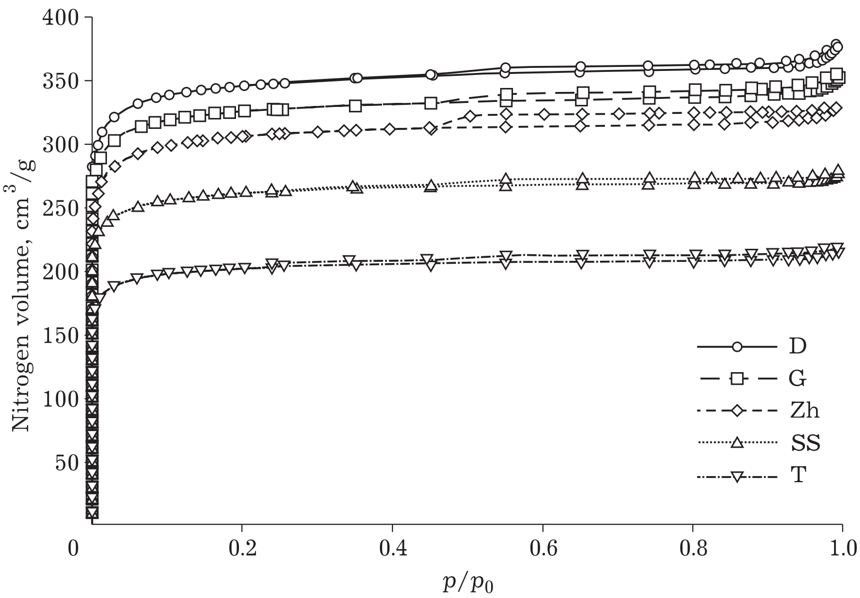

Fig. 1. Isotherms of nitrogen adsorption – desorption at 77 K on the samples of carbon sorbents prepared by the alkaline activation of Kuzbass coal of different grades.

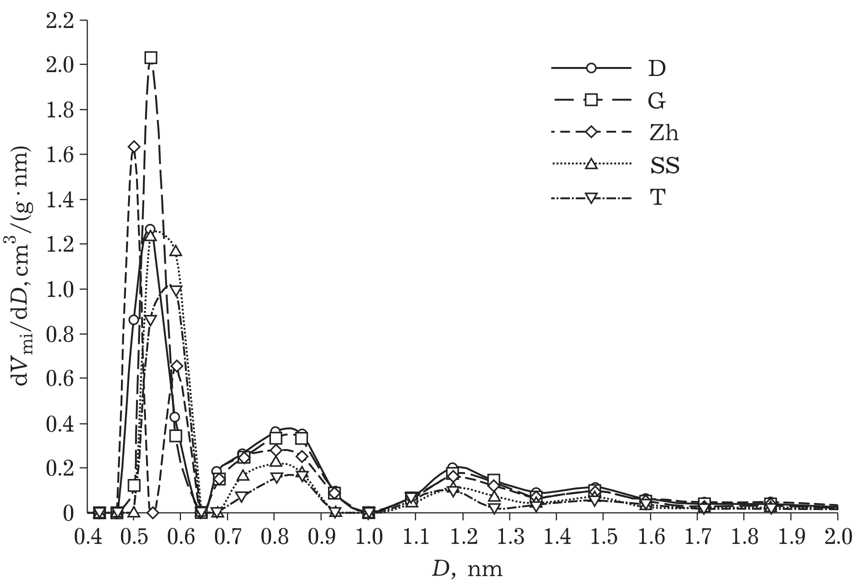

Fig. 2. Differential micropore distribution in the samples of carbon sorbents prepared by alkaline activation of the coal of different grades from the Kuzbass.

TABLE 2

Characteristics of carbon sorbents obtained from the coal of Kuzbass by means of alkaline activation

Coal grade	S_{BET}, m^2/g	V_{Σ}, cm^3/g	V_{mi}, cm^3/g	V_{me}, cm^3/g
D	1340	0.58	0.46	0.07
G	1260	0.54	0.44	0.06
Zh	1180	0.51	0.41	0.07
SS	1010	0.43	0.35	0.03
T	780	0.33	0.27	0.03

adopted by the IUPAC, the upper boundary of micropore diameter is $D = 2$ nm (Fig. 2).

Carbon sorbents have a polymodal micropore size distribution (see Fig. 2). For all carbon sorbents under investigation, three regions of micropores may be distinguished: smaller than 0.65, 0.7–0.9, and 1.0–2.0 nm. Similar micropore distributions are typical for the samples of coal semicoke [10] and the sorbents made of brown coal [11]. The maximum of pore distribution relates to the pores 0.45–0.65 nm in diameter. In this region, one sharp peak with a maximum near 0.54 nm is observed for the sorbents made of D and G grade coal, while there are two maxima of this kind (at 0.50 and 0.59 nm) for the Zh grade coal, and a broad maximum is observed for SS and T grade coal in the region of 0.54–0.59 nm. The medium range 0.7–0.9 nm is represented by a broad peak without a clearly pronounced maximum; the area under it increases when passing from the sorbent made of T grade coal to the sorbent made of D grade coal. A similar situation is observed also in the third region of micropores (1.0–2.0 nm): the distribution curve for the sorbent made of D grade coal passes above all the others. So, the sorbents obtained from coal of different grades possess similar micropore structure in the region of 0.7–2.0 nm, differing only by the volume of micropores. A different picture is observed in the region below 0.65 nm, in which different micropores are prevailing for each sorbent.

The characteristics of the porous structure of the sorbents under investigation are shown in Table 2. Analysis of the data shows that the sorbents possess high texture characteristics. The minimal specific surface of the sorbent made of T grade coal is 780 m^2/g, and the maximal one (for the sorbent made of D grade coal) is 1340 m^2/g. The volume of micropores, similarly to the total pore volume, decreases with an increase in metamorphism stage of initial coal. The volume of mesopores for the sorbents made of low-metamorphism coal is larger than that for the samples made of high-metamorphism coal.

CONCLUSION

Carbon sorbents prepared by means of the alkaline activation of coal from the Kuzbass possess high texture characteristics and clearly pronounced microporous structure. The development of mesopores in the sorbents is insignificant. The isotherms of low-temperature adsorption of nitrogen and the micropore size distributions are similar for the sorbents under investigation. All the studied texture characteristics of the sorbents increase as a sequence of coal grades T < SS < Zh < G < D, which correlates with a decrease in the stage of metamorphism in the row T > SS > Zh > G > D. The sorbent made of D coal grade possesses the maximal characteristics: its specific surface is 1340 m^2/g, pore volume 0.58 cm^3/g. The relative content of mesopores is maximal for the sorbent made of Zh grade coal, however, the number of mesopores is small and they account for only 13.7 % by volume.

Acknowledgements

The work was carried out within the State Assignment (Project No. AAAA-A17-117041910147-2).

The equipment of the Shared Centre at FRC CCC SB RAS was used in the work.

REFERENCES

1 State Report "About the state and conservation of the environment in the Russian Federation in 2017". Moscow: Minprirody Rossii; NPP Kadastr, 2018. P. 87–112.

2 Mukhin V. M., Tarasov A. V., Klushin V. N. Active coal of Russia. Ed. by Prof., Dr. Sci. in Technology A. V. Tarasov. Moscow: Metallurgiya, 2000. 352 p.

3 Zykov I. Yu., Dudnikova Yu. N., Kozlov A. P., Fedorova N. I., Ismagilov Z. R., *Chemistry for Sustainable Development*. 2017. Vol. 25, No. 6. P. 564–568.

4 Kozlov A. P., Zykov I. Yu., Dudnikova Yu. N., Tsvetkov V. E., Fedorova N. I., Ismagilov Z. R., *Vestn. Kuzbas. Gos. Tekhn. Un-ta*. 2018. No. 3 (127). P. 93–101.

5 Fedorova N. I., Dudnikova Yu. N., Zykov I. Yu., Kozlov A. P., Ismagilov Z. R., Koks i Khimiya. 2018. No. 8. P. 19–23.

6 Nikitin A. P., Zykov I. Yu., Kozlov A. P., Ismagilov Z. R., *Koks i Khimiya*. 2018. No. 12. P. 4–10.

7 Kozlov A. P., Zykov I. Yu., Dudnikova Yu. N., Fedorova N. I., Ismagilov Z. R., Vestn. Kuzbas. Gos. Tekhn. Un-ta. 2017. No. 4 (122). P. 170–176.

8 Zvekov A. A., Zykov I. Yu., Dudnikova Yu. N., Mikhailova E. S., Tsetkov V. E., Ismagilov Z. R., Koks i Khimiya. 2019. No. 6. P. 22–27.

9 Kozlov A. P., Dudnikova Yu. N., Zykov I. Yu., Sozinov S. A., Ismagilov Z. R., *Vestn. Kuzbas. Gos. Tekhn. Un-ta*. 2017. No. 6 (124). P. 197–203.

10 Fedorova N. I., Dudnikova Yu. N., Ismagilov Z. R., *Koks i Khimiya.* 2018. No. 4. P. 29–33.
11 Kozlov A. P., Zykov I., Dudnikova Yu., Tsvetkov V., Fedorova N., Ismagilov Z. R. 9th Russian-Chinese Symposium "Coal in the 21st Century: Mining, Intelligent Equipment and Environment Protection" (Proceedings). Qingdao, 18–21 October 2018. P. 328–331.