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## Study of High Porous Carbons Prepared by the Alkaline Activation of Anthracites

Nadezhda M. Mikova<sup>a</sup>, Nikolai V. Chesnokov<sup>a,b\*</sup>  
and Boris N. Kuznetsov<sup>a,b</sup>

<sup>a</sup> Institute of Chemistry and Chemical Technology SB RAS,  
42 K.Marx st., Krasnoyarsk, 660049 Russia  
<sup>b</sup> Siberian Federal University,  
79 Svobodny, Krasnoyarsk, 660041 Russia <sup>1</sup>

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*The influence of alkaline activation on the development of anthracite porous structure under the variation of different factors: anthracite and metal hydroxide origin, their mass ratio in a mixture, activation temperature and duration has been studied. The highest development of anthracite surface area was reached with mass ratio of anthracite/alkali 1:5-7 and the final heating temperature of 800 °C. Under these conditions the maximum value of surface area of carbon material was 2900 m<sup>2</sup>/g in case of KOH activated Siberian anthracite and 2550 m<sup>2</sup>/g for NaOH activated Ilovaisky anthracite.*

*Keywords: porous carbons, preparation, anthracites, alkaline activation, surface area.*

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### Introduction

Chemical activation is now widely used for preparation of porous carbon materials from solid fossil fuel [1]. From the point of view of accessibility and effectivity, the most interesting and promising are alkaline metal hydroxides (NaOH, KOH) used as reagents for chemical activation of carbon raw precursors [2-4]. Treating fossil coals with different in nature alkaline reagents, varying their amount, experimental technique of alkaline hydroxide interaction with coal and the activation process conditions it is possible to vary the final properties and characteristics of the obtained porous carbons. Chemical activation of natural anthracites which have a developed system of the germinal micro

pores by means of alkaline metal compounds can be considered as a promising method, providing the further development of porous structure and preparation of carbon materials with a high surface area [5-8].

In this study the general regularities of the nanoporous carbon structure formation of Siberian and Ilovaisky anthracites in presence of alkaline metal hydroxides have been investigated at various pyrolysis conditions.

### Experimental

The samples of two natural anthracites of Ilovaisky (Ukraine) and Siberian (Kuzbass) deposits were selected as the objects for research. The characteristics of the original coals are

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\* Corresponding author E-mail address: cnv@icct.ru

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Table 1. The characteristics of the original anthracites

№	Sample	Elemental composition, wt. %					Ash content, A, <sup>d</sup> wt. %
		C, <sup>daf</sup>	H, <sup>daf</sup>	N, <sup>daf</sup>	S, <sup>daf</sup>	O, <sup>daf</sup>	
1	Siberian anthracite (SA)	95.69	1.85	1.35	0.27	0.84	3.5
2	Ilovaisky anthracite (IA)	92.06	3.23	1.78	0.48	2.41	3.27

presented in Table 1. The samples of the original materials were crushed and sieved. The fraction with the particles size of 0.5 – 1.0 mm and moisture content 3 – 3.5 wt. % was used.

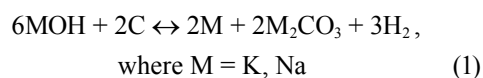
The chemical activation of anthracites was carried out in the mixture with molten alkaline metal hydroxides KOH, NaOH and LiOH. These reagents were used without additional drying. The procedure of porous carbons preparation included the following main stages: mechanical mixing of the anthracite and alkaline hydroxide powders in mass ratio 1:3 – 7, post heating mixture up to the temperature of 600-800 °C, holding definite time under the final temperature and the subsequent cooling to room temperature, followed washing with diluted acid and water, then drying.

In a typical experiment 1 g of fractioned anthracite sample was thoroughly mixed with 5 g of solid alkaline, the mixture was placed in an emery crucible, covered and placed in a stationary electric oven, preheated up to the melting temperature of hydroxide. After 15 min holding the mixture heating was carry out with heating rate of 10 °C/min up to 800 °C and maintained for 15 min at this temperature. After thermal treatment the crucible was taken out and cooled to the room temperature. The pyrolyzed product was sequentially washed from alkaline and inorganic impurities with a distilled water, then with a diluted HCl (pH =5.0 – 5.5), hot water (50-55 °C) until neutral pH and negative reaction on Cl<sup>-</sup> ions. The solid product was firstly dried in the air, then oven dried at 102-105 °C.

The characterization of the porous texture of obtained carbon materials was carry out using physical adsorption of N<sub>2</sub> at 77 K by employing apparatus “Sorbometr-M” Directly before taking measures the samples were treated in the flow of nitrogen under the 300 °C during 4 hours.

### Results and discussion

Coals thermolysis in presence of alkaline metal compounds can be considered as integrated carbonization – gasification process. The general mechanism of chemical activation of carbon-containing materials by alkali has not been completely proved yet, but a number of researchers [7-10] agree in the opinion that this is a complicated process, involving the reactions of alkali hydroxide reduction and carbon oxidation which can be described by the following overall equation:



Under these conditions water releasing is possible as a result of MOH reaction with oxygen-containing groups of coals as well as due to adsorbed H<sub>2</sub>O molecules desorption.

The carrying out of the alkali-anthracite system thermal treatment above hydroxide melting temperature makes it possible to increase the efficiency of anthracite activation. The penetration of alkali into a coal matrix should be considerably facilitated during thermolysis in a melting form. The molten alkali insertion into carbon matrix can result in the porous structure

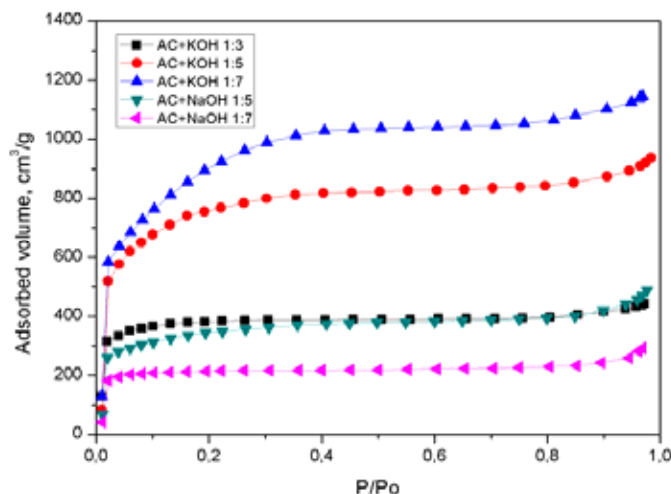


Fig. 1. N<sub>2</sub> adsorption isotherms (77 K) on anthracite samples activated by alkalis at 800 °C

formation along the whole extension of alkali migration [11, 12]. A fast temperature rise under thermolysis of coal generates gas formation, thus promoting the additional development of pores. All these factors lead to formation of carbon products with a high surface area (Table 2).

The surface area of carbon samples and the total volume of pores were calculated from N<sub>2</sub> adsorption isotherms under 77 K. The N<sub>2</sub> adsorption isotherms for some porous carbon materials, prepared by pyrolysis of mixtures SA/KOH and SA/NaOH samples are presented in Fig. 1.

As followed from figure, there are variations in the shape of these isotherms depending on the nature of alkaline hydroxide as well as its content in the mixture.

It is known [13] that depending on the method of moistening and content of water in the initial carbon-alkali mixture, the degree of coal thermal-oxidative degradation can be changed. Though anthracites contain a low quantity of aliphatic and oxygen-containing groups which able to react with alkali, the presence of water enhance the effect of alkaline on hydrolytic transformations of coal organic mass. In this case the water behaves as an active component of the mixture and plays an important role in pore

development of a carbon product. The excess amount of water decreases a melting temperature and alkaline reactive ability in carbon activation.

Thus, it was determined that preliminary moistening of SA raising the water content in a SA/KOH sample (1:5) to 10%, leads to decrease of surface area after its activation at 800 °C from 2500 to 1020 m<sup>2</sup>/g (Table 2). Most probably the water facilitates an alkali penetration into carbon micropores in analogy with the way taking place in coals impregnation by alkaline solutions. The further mixture thermolysis promotes the alkaline solution removal out of pores, and as a result of water evaporation the alkali precipitating in pore entrance happens. This effect results in the decrease of contact area of alkali with anthracite, thus preventing porous structure development of carbon product under alkaline activation process.

The influence of anthracite/alkali ratio variation on the porous structure of carbon products obtained by the pyrolysis of mixture at temperature ≤ 600 °C has been investigated. There are some evidences in the literature on the influence of alkali nature on their ability in carbon activation processes [14]. The similar results were obtained in our study (Fig. 2).

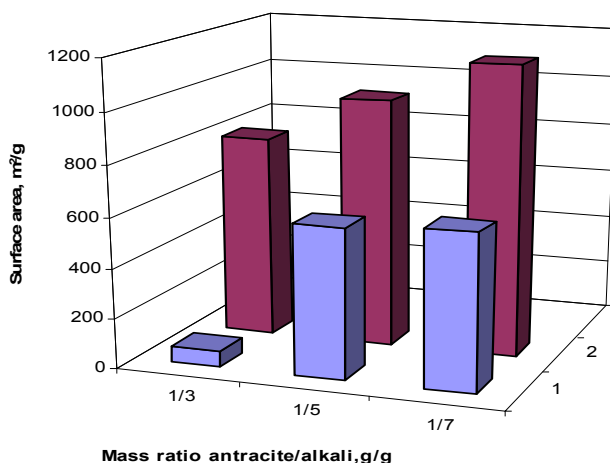


Fig. 2. Influence of anthracite/alkali ratio on the specific surface area of porous carbons, prepared by thermolysis of the mixture at 600 °C: 1 – SA/NaOH, 2 –SA/KOH

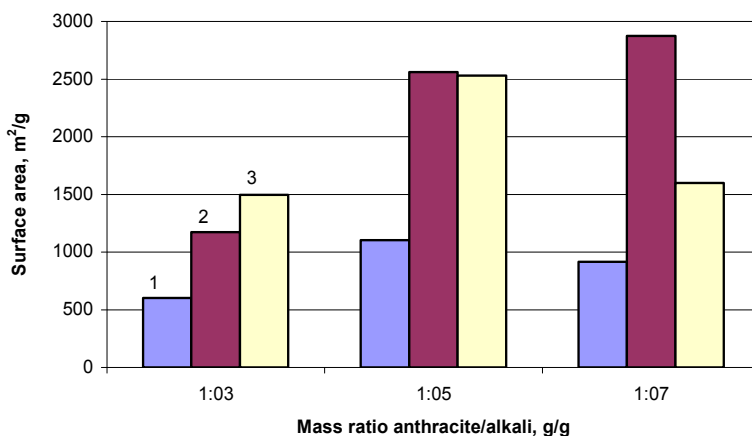


Fig. 3. Influence of anthracite/alkali ratio on specific surface area of porous carbons prepared by thermolysis of the mixture at 800 °C: 1 – SA/ NaOH, 2 –SA/ KOH, 3 – IA/NaOH

Potassium hydroxide is the most effective in the carbon surface area development as compared to Na and Li hydroxides.

The activating influence of KOH increases with the growth of its content in the mixture with anthracite. The sample with the ratio SA/KOH = 1:7 treated at 600 °C has the most developed porous structure. Its surface area value is as large as 1150 m<sup>2</sup>/g.

The increase of anthracite activation temperature up to 800 °C results in the considerably rise of surface area of the obtained carbon materials (Fig. 3). The maximal surface

area (2900 m<sup>2</sup>/g) was observed for SA/KOH sample with anthracite/hydroxide ratio 1:7. At similar activation conditions the surface area of porous carbon prepared from Ilovaisky anthracites reaches only to 1500 m<sup>2</sup>/g.

Anthracite surface can be considerably increased even at low alkali content in the mixture (anthracite/alkali ratio 1:3).

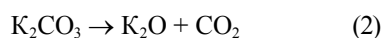
Anthracite samples SA and IA thermolysed at 800 °C in the absence of alkali have surface area only of 162 and 120 m<sup>2</sup>/g accordingly.

Salts of alkaline metals are known to be active catalysts of carbon gasification by such agents

Table 2. Textural characteristics of alkaline activated anthracites (Pore volume was measured at  $P/P_0 = 0-0,25$ )

№	Sample	Mass ratio, anthracite/alkali, $g \times g^{-1}$	Final thermolysis conditions		Surface area, $S_{BET}, m^2/g$	Pore volume, $cm^3/g$
			Temperature, °C	Time, min		
1	SA/KOH	1 : 5	600	60	1050	0.427
2	SA/KOH	1 : 5	800	15	2570	1.126
3	SA/KOH+H <sub>2</sub> O	1 : 5	800	15	1020	0.478
3	SA/KOH	1 : 5	800	60	2400	1.035
4	SA/KOH	1 : 7	800	15	2890	1.254
5	SA/NaOH	1 : 5	800	15	1100	0.495
6	SA/LiOH	1 : 5	600	60	131	0.064
7	SA/LiOH	1 : 5	800	15	235	0.098
8	IA/KOH	1 : 5	800	15	1526	0.700
9	IA/NaOH	1 : 5	800	15	2547	1.178

as O<sub>2</sub>, H<sub>2</sub>O и CO<sub>2</sub> [15, 16]. As it was mentioned earlier, water can be produced during anthracite/alkali mixture thermal treatment. The formation of CO<sub>2</sub> also occurs as a result of decomposition of alkaline metals carbonates:



These carbonates can be produced by means of interaction of molten alkali and carbon [6, 15].

Such gasification agents as H<sub>2</sub>O and CO<sub>2</sub> generated in the process of anthracite/alkali mixture thermolysis stimulate both the formation of new pores in anthracite structure and burning out of micropores till meso- and macropores. But the gasification of same part of carbon during thermal treatment of the mixture reduces the carbon product yield and its surface area.

The results presented in Fig. 2 and Table 2 are evidenced of the significant influence of anthracite and alkali nature on structural characteristics of the obtained porous carbon materials. So, for the mixture of Ilovaisky anthracite and NaOH (1:5 ratio) the growing in  $S_{BET}$  up to 2550 m<sup>2</sup>/g is observed, while in the same experimental conditions the surface area of sample Siberian anthracite/NaOH reached only 1100 m<sup>2</sup>/g.

The variation in surface area values of porous carbons from Siberian and Ilovaisky anthracites, probably, is determined by difference in their chemical composition (Table 1). The higher amount of oxygen-containing functional groups can make the easier fixation of ions of alkaline metals – carbon gasification catalysts – within the anthracite structure due to chemical interaction of alkali with phenolic, acidic and other groups of anthracite. According to literature data the rate of such functional groups decomposition is considerably increased when hydrogen is displaced by an alkaline metal [16].

The reduced content of carbon in Ilovaisky anthracite in comparison with Siberian one (Table 1) indicate on a lower degree of its metamorphism. Therefore, IA has a lower structural ordering than SA and, accordingly, a higher reactive ability in NaOH activation process.

In spite of KOH and NaOH being analogous compounds, their activation effects on carbons differ significantly [17]. It is supposed that KOH activation ability depend on its property to be intercalated between carbon layers in structurally ordered graphite [18]. At the same time NaOH activation is more effective for less structured carbon precursors [19].

Table 3. Elemental composition of carbon products prepared by SA/KOH mixture thermolysis

№	Sample	Final thermolysis conditions		Elemental composition, wt. %				Ash content, wt. %
		Temperature, °C	Time, min	C	H	N	S	
1	SA/KOH = 1:5	600	15 min	92.48	0.69	0	0	2.08
2	SA/KOH =1:3	800	15 min	94.85	0.38	0	0	2,64
3	SA/KOH = 1:5	800	15 min	96.18	0.07	0	0	1.80
4	SA/KOH = 1:5	800	60 min	96.43	0.13	0	0	1.54
5	SA/KOH =1:7	800	15 min	96.91	0.37	0	0	4.24

While exploring the influence of an alkali nature on the porosity development of carbon material, it has been determined that hydroxide activating ability increases in order:  $\text{Li} < \text{Na} < \text{K}$  (Table 2). In the same sequence, catalytic activity of alkaline metals increases in the carbon gasification process [6, 15].

Elemental analysis data (Table 3) show of a certain decrease in C/H atomic ratio in carbon products, produced from mixture with lower alkali content and a moderate treatment temperature.

At increasing the temperature and time of thermal treatment as well as the concentration of alkali in mixture with anthracite the enrichment of products by carbon up to 96-97% takes place. Besides, as a result of thermal treatment the complete elimination of N-, S- heteroatoms occurs and the ash content in carbon products is decreased, except a sample with high alkali content (AC/KOH, 1:7).

It is well known that to prepare high porous carbon materials from anthracites the oxidative pretreatment should be used [20, 21]. The oxidative pretreatment of anthracites provides additional formation of new structural fragments and O-, N-, S-containing functional groups. Their composition and content are depended on the nature of the oxidizing agent [22-24]. This pretreatment can result in considerable reorganization of the original coal structure. The further carbonation with alkali promotes the formation of new bonds between structural

fragments of coal and the creation of a secondary porous structure of carbon product.

The system  $\text{H}_2\text{SO}_4\text{-HNO}_3$  and  $\text{H}_2\text{SO}_4\text{-KNO}_2$  were used in present study as oxidizing reagents for Ilovaisky and Siberian anthracites modification. It was found that preliminary oxidizing treatment of IA and SA samples results in the formation of carbon products with rather low surfaces area, varying between 840 – 1100  $\text{m}^2/\text{g}$  after modified anthracites pyrolysis with KOH. A possible explanation of this fact consists in growth of steric hindrances to alkaline insertion to coal matrix due to introducing of additional functional groups to anthracite.

### Conclusion

Results of the accomplished study show that the use of molten hydroxides of alkaline metals promotes the significant development of anthracite porous structure. Carbon porous materials with high surface area (up to 2500-2900  $\text{m}^2/\text{g}$ ) were produced from mixture of Ilovaisky and Siberian anthracite with molten alkaline hydroxides. The most powerful alkaline activation was observed at anthracite/alkali ratio 1:5 – 7 and final thermolysis temperature of 800 °C. The produced carbon products have a total pore volume up to 1.77  $\text{cm}^3/\text{g}$  and pore size of 2.2 – 2.5 nm.

Prepared from anthracites the mechanically strong nanoporous carbon materials with high surface area can be used as effective sorbents and catalyst carriers.

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