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Thermogravimetric and textural studies of modified carbonaceous materials

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Abstract

Thermoanalytical (TG, DTG) and adsorption methods were applied in investigation of waste agricultural products, e.g. plum stones, which can serve as raw materials for production of active carbon. The study was performed on three series of carbonaceous materials prepared from plum stones. In the first series, the raw material was subjected to ammoxidation by a mixture of NH_3/air, carbonisation and activation by steam. In the second series, the material was carbonised, ammoxidised and activated with steam, whereas in the third series, it was carbonised and finally activated. Modification of carbonaceous material by ammoxidation was used in order to obtain carrier material for catalysts with diverse surface properties. The above procedure allows obtaining an active carbon precursor with high density of surface nitrogen sites of Lewis basic character, which may play an important role as active sites in the catalytic processes.
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Keywords: Waste plum stones; Ammoxidation; Active carbon; TG; Texture

1. Introduction

It has been known for a long time that activated carbons can be prepared from a variety of raw materials [1–3]. The most frequently used precursors are hard coal, brown coal, wood (oak and beech) and some polymers [4]. Moreover, main components of cell membrane (cellulose, hemicellulose and lignin), some waste agricultural products, such as fruit stones (grape seeds plum, cherry, apricot, olive and peaches stones), some leaves (tobacco and eucalyptus), various nutshells (walnut, macadam, hazelnut, coconut, pistachio, peanut and almond) as well as wheat and rye straw can be used as raw material [5–7]. Although coal is the most commonly used precursor, sometimes, agricultural waste is a better choice [6]. The use of activated carbon as adsorbent, catalyst and catalyst support is based on its porous structure and surface chemistry [8,9]. The latter property is determined by the type of carbonaceous material, quantity and bonding of various heteroatoms that combine with car-

bon atoms by chemical bonds different form acidic and basic structures [2,9–15]. Among different heteroatoms possibly introduced into carbonaceous material, nitrogen creates intermediate acidic–basic properties because of its basic properties. The type of nitrogen groups determines the anion- and cation-exchange properties of carbonaceous material [16,17]. It has been established that the efficient method of nitrogen enrichment is ammoxidation, consisting in a simultaneous oxidation of precursor [17–22].

The aim of this work is to investigate and discuss how the mode of active carbon production which involves addition of nitrogen influences on its properties as carrier material with intermediate acidic–basic character, which would improve the efficiency of catalytic system.

2. Experimental

2.1. Starting material

Plum stones (PS) used as starting material in this study were preliminarily cleaned, washed and air-dried at room

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Table 1
Elemental analysis of starting materials (wt.%)

Sample code	C	H	N	(O + S)
PS	48.8	6.1	0.1	45.0
PK	87.4	2.9	0.4	9.3

Key: P, plum stones; S, raw material; K, after carbonisation.

temperature, crushed and sieved to a particle size of ≤3 mm in diameter.

2.2. Preparation of samples

Carbonaceous materials were prepared by three different ways differing in the sequence of processes applied. The first series of samples were subjected to carbonisation, ammoxidation and then activation by steam, the second to ammoxidation, carbonisation and activation by steam and the third to carbonisation and steam activation. Ammoxidation was carried out using a mixture of ammonia and air at a volume ratio of 1:3 (250/750 cm^3/min) in a flow reactor at 523 or 573 K for 5 h [10,18,19]. The samples were carbonised in the gases evolving during the process at temperature increasing at the rate of 5 K/min to the final 973 K, maintained for 1 h. Activation was conducted by steam at 1073 K for 1.5 h [12,16,18–20].

2.3. Elemental analysis

The chemical composition of the samples investigated was performed by an Elementar Vario ELIII microanalyser. The apparatus permits determination of the content of carbon, hydrogen, nitrogen and sulphur, separately from oxygen. After ammoxidation, the samples were washed out with helium till they reached room temperature and then they were subjected to elemental analysis. Results of the elemental analysis are collected in Tables 1–4.

2.4. TG–DTG analysis

Thermoanalytical measurements of the samples were performed on an instrument Setsys TG–DSC 15 made by Setaram. The samples in portions of about 10 mg were heated in the helium atmosphere. The temperature range of the measurement was 293–1173 K, the scanning rate 3 K/min and sensitivity TG 0.04 mg.

Table 3
The influence process of carbonisation on elemental composition of investigated samples (wt.%)

Sample code	C		H		N		(O + S)	
	E	F	E	F	E	F	E	F
PS	48.8	87.4	6.1	2.9	0.1	0.4	45.0	9.3
PN$_1$	72.3	86.1	5.0	2.0	5.3	5.3	17.4	6.6
PN$_2$	69.9	87.2	4.0	1.9	10.8	5.5	15.3	5.4

Key: P, plum stones; S, raw material; N$_1$, ammoxidation in 523 K; N$_2$, ammoxidation in 573 K; E, before carbonisation; F, after carbonisation.

Table 4
The influence process of activation on elemental composition of investigated samples (wt.%)

Sample code	C		H		N		(O + S)	
	I	J	I	J	I	J	I	J
PK	87.4	85.6	2.9	3.1	0.4	0.1	9.3	11.2
PN$_1$	72.3	75.4	5.0	1.1	5.3	0.6	17.4	22.9
PN$_2$	69.9	76.2	4.0	1.2	10.8	0.7	15.3	21.9
PN$_1$K	86.1	76.2	2.0	3.6	5.3	1.1	6.6	19.0
PN$_2$K	87.2	85.4	1.9	3.1	5.5	1.5	5.4	10.0
PKN$_1$	78.2	90.9	2.4	1.3	7.8	1.1	11.6	6.7
PKN$_2$	71.0	91.0	2.1	1.3	15.7	1.3	11.2	6.6

Key: P, plum stones; K, after carbonization; N$_1$, ammoxidation in 523 K; N$_2$, ammoxidation in 573 K; I, before activation; J, after activation.

2.5. Porous structure

The pore structure of the activated carbons was characterised by N$_2$ adsorption method at 77 K. Adsorption isotherms were determined by sorption apparatus Micrometrics ASAP 2010. Prior to measurement, the samples were outgassed under vacuum 1.33×10^{-4} Pa at 623 K until constant weight and then subjected to measurement of nitrogen adsorption and desorption. Calculation of the total pore volume, micropore volume (V_{mic}), mesopore volume (V_{mes}) and their volume distribution from the nitrogen adsorption isotherms was performed using the BJH method. The values of the pore surface area were calculated according to the BET method (S_{BET}).

3. Results and discussion

Results of the elemental analysis of the starting material (PS and PK) given in Table 1 indicate that the raw plum stones

Table 2
The influence process of ammoxidation on elemental composition of investigated samples (wt.%)

Sample code	C		H		N				(O + S)	
	B	D	B	D	B	D (T$_1$)	B	D (T$_2$)	B	D
PS	48.8	72.3	6.1	5.0	0.1	5.3	–	–	45.0	17.4
PS	48.8	69.9	6.1	4.0	–	–	0.1	10.8	45.0	15.3
PK	87.4	78.2	2.9	2.4	0.4	7.8	–	–	9.3	11.6
PK	87.4	71.0	2.9	2.1	–	–	0.4	15.7	9.3	11.2

Key: P, plum stones; S, raw material; K, after carbonization; T$_1$, ammoxidation in 523 K; T$_2$, ammoxidation in 573 K; B, before ammoxidation; D, after ammoxidation.

have relatively low carbon (48.8 wt.%) but high volatile matter (45.0 wt.%) contents, which results from their low degree of coalification.

Carbonisation of the raw material leads to an increase in the carbon content up to 87.4 wt.% accompanied by a decrease in the volatile matter content to 9.3 wt.%. A small increase in the content of nitrogen after carbonisation is a result of a change in the proportion of the weight contribution of particular elements.

Influence of mixture NH_3/air on organic material in rise of temperature leads simultaneously to its oxidation and nitriding. Performance of the process in higher temperature permits the introduction of a greater amount of nitrogen into the sample [16,23].

In the first series of preparations subjected to carbonisation and ammoxidation, significant differences in the amount of nitrogen introduced are noted depending on the temperature of ammoxidation. An increase in temperature from 523 K (sample PKN_1) to 573 K (sample PKN_2) leads to almost twice greater enrichment in nitrogen, i.e. from 7.8 to 15.7 wt.%, accompanied by a decrease in the content of carbon from 87.4 to 78.2 and 71.0 wt.%. This decrease can be explained by a change in the proportion of the other elements as a result of a simultaneous oxidation of the surface of the organic material [16,23].

The samples of the second series were first ammoxidised and then carbonised. Similarly, as for the first series samples, a higher temperature of ammoxidation permits introduction of a greater amount of nitrogen: 5.3 wt.% at 523 K and 10.8 wt.% at 573 K. The alteration of the sequence of the processes applied, i.e. carbonisation followed by ammoxidation, leads significant differences in the content of nitrogen and proportions of the other elements (C, H, S and O) in the samples obtained. The differences can be explained by a different reactivity of the surface functional groups present on the surface of the active carbon precursors in the conditions of the experiment. The ammoxidation of the carbonisate permits an introduction of a greater amount of nitrogen (Table 2).

When ammoxidation is followed by carbonisation, the amount of nitrogen introduced decreases as a result of its release on carbonisation (Table 3). The processes of ammoxidation and carbonisation irrespective of their sequence result in a change in the proportions of the elements in the organic material samples studied. As shown in Table 4, on steam activation of the samples studied, the amount of nitrogen contents drastically decreases and the contents of the other elements also change. This is a consequence of different reactivity of the surface functional groups against the activating agent used, i.e. steam. The process of activation plays an essential role in improving the textural properties of the resulting carbons, as indicated by the data in Table 5. In general, these processes lead to a considerable development of the carbon surface irrespective of the sample history. Carbon preparations subjected to ammoxidation are characterised by much greater surface area than the non-ammoxidised ones. Interestingly, the surface area of the sample first carbonised

Table 5
Basic parameters characterising the porous structure of carbonaceous materials obtained from plum stones

Sample code	V_{micro} (cm^3/g)		V_{meso} (cm^3/g)		S_{BET} (m^2/g)	
	I	J	I	J	I	J
PK	0.185	0.385	0.034	0.162	373	814
PKN$_1$	0.065	0.698	0.022	0.269	123	1260
PKN$_2$	0.029	0.759	0.011	0.269	52	1369
PN$_1$	0.001	0.481	0.002	0.140	1	895
PN$_2$	0.002	0.606	0.004	0.193	2	1090
PN$_1$K	0.001	0.577	0.001	0.156	1	1069
PN$_2$K	0.001	0.434	0.002	0.103	1	813

Key: P, plum stones; K, after carbonization; N$_1$, ammoxidation in 523 K; N$_2$, ammoxidation in 573 K; I, before activation; J, after activation.

and then ammoxidised at 623 K and next activated increases from 52 m^2/g (PKN$_2$) to 1369 m^2/g (PKN$_2$A) that is about 26 times. For the carbons after activation, the volumes of both microspore and mesopores increase relative to those of the non-activated ones.

The DTA curves of the samples studied showed one broad exothermic peak, which is typical of the coal substances. The peak corresponds to a number of superimposed complex thermal effects. Analysis of the TG and DTG curves shown in Figs. 1–4 indicates that the process of the thermal decomposition of the raw material in helium atmosphere comprises mainly three stages. The first one observed for the all the samples studied begins at about 333 K and ends at about 363 K and can be related to dehydratation, whereas the second one in the range 513–553 K is due to release decomposition products of cellulose and the last one, characterised by release decomposition products of lignocelluloses, occurs in the range 593–633 K. The last two stages are not observed in the samples first ammoxidised at 523 and 623 K and then carbonised at 973 K. The TG and DTG curves reveal relatively high loss of mass in the range 953–993 K, which may be ascribed to the oxidation of thermal products of lignite systems and weaker bonded of surface nitrogen groups [24].
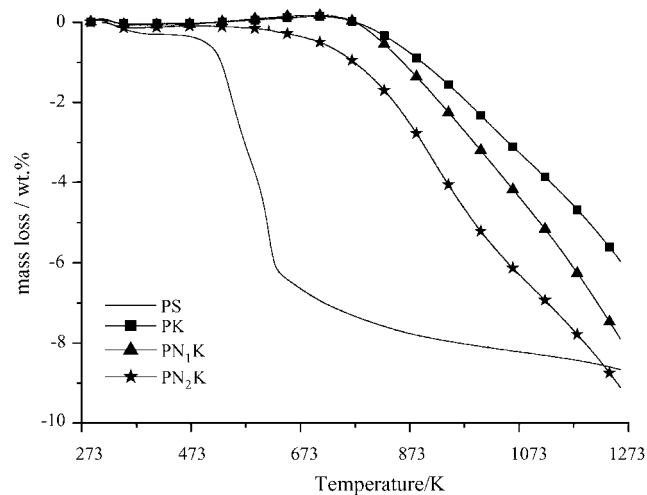

Fig. 1. TG curves of raw plum stones (PS), carbonised (PK), ammoxidised at 423 and 473 K, respectively, and next carbonised (PN$_1$K and PN$_2$K).
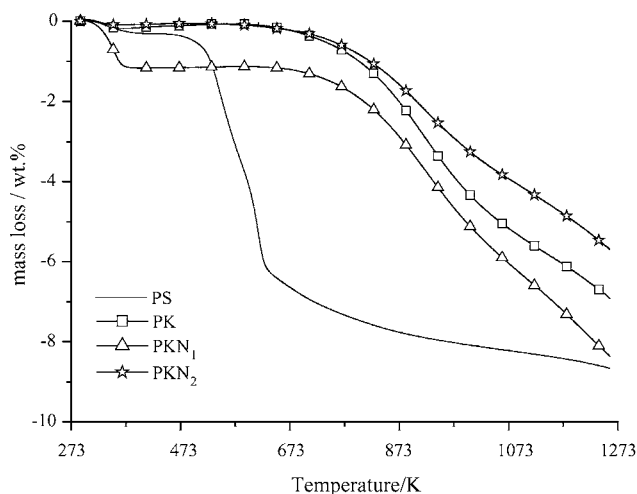
Fig. 2. TG curves of raw plum stones (PS), carbonised (PK), carbonised and ammoxidised at 423 and 473 K, respectively (PKN$_1$ and PKN$_2$).
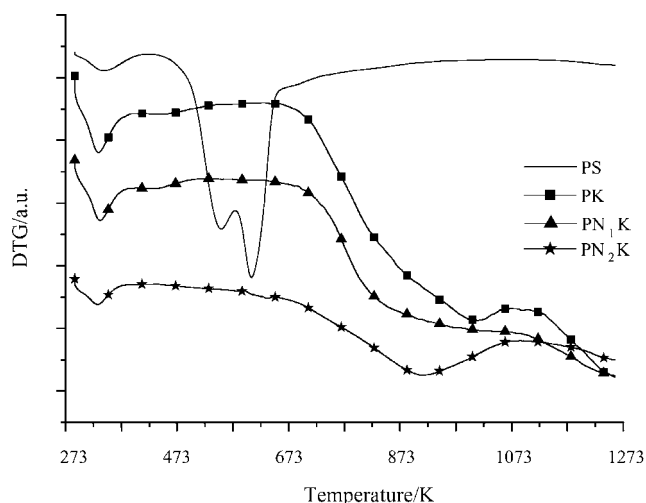

Fig. 3. DTG curves of raw plum stones (PS), carbonised (PK), ammoxidised at 423 and 473 K, respectively, and next carbonised (PN$_1$K and PN$_2$K).
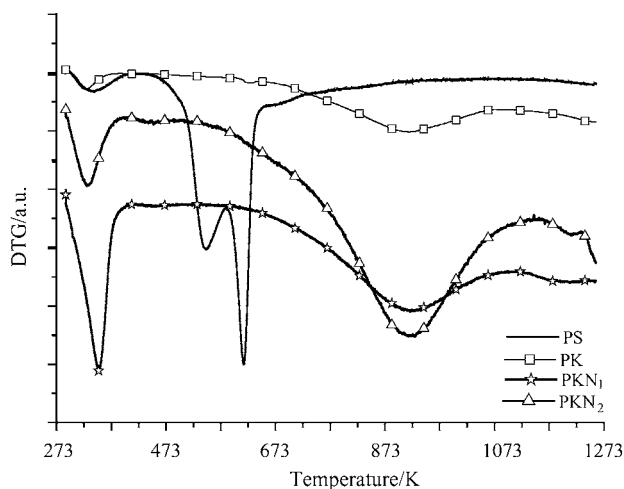

Fig. 4. DTG curves of raw plum stones (PS), carbonised (PK), carbonised and ammoxidised at 423 and 473 K, respectively (PKN$_1$ and PKN$_2$).

The loss is greater in samples subjected first to carbonisation and then to ammoxidation (PKN$_1$ and PKN$_2$), which can be explained by a lower thermal stability of the groups generated in this sequence of processes. Usually, the process of carbonisation leads to increasing degree of condensation of the carbonaceous material, whereas its susceptibility to modification with nitrogen is lower, which is a result of a smaller number of the surface functional groups able to react with a mixture of air with ammonia. Ammoxidation of the material earlier subjected to carbonisation yields precursors of a lower content of nitrogen and lower thermal stability of nitrogen groups. The samples at first ammoxidised and then carbonised are characterised by greater thermal stability acquired in the latter process. Moreover, for the samples subjected to this order of processes, the mass loss indicated in the TG curves and related to the decomposition of the nitric groups in the range 873–973 K is smaller than for the samples at first carbonised and later ammoxidised.

4. Conclusions

The effect of ammoxidation on the nitrogen compounds and on the content of the other elements is diverse and depends on the sequence of processes to which the organic substance studied is subjected. Activation of the earlier ammoxidised material leads to a substantial increase in the surface area accompanied by a drastic decrease in the amount of nitrogen introduced. The study has shown that the temperature ranges of the mass loss maxima in the samples modified and unmodified by nitrogen differ. These changes are manifested by the appearance of a new peak with a maximum at about 923 K, which can be assigned to release of compounds containing nitric group in their structure.

References

[1] B. Roga, L. Wnękowska, A. Ihnatowicz, Chemia Węgla, Wyd. PWT, Warszawa, 1955.
[2] R.C. Bansal, J.B. Donnet, F. Stoeckli, Activated Carbon, Mercel Dekker, New York, Basel, 1988.
[3] A. Volborth, Coal Science and Chemistry, Elsevier, Amsterdam, 1987.
[4] W. Heschel, E. Klose, Fuel 74 (1995) 1786.
[5] A. Ahmadpour, D.D. Do, Carbon 35 (1997) 1723.
[6] T. Lupascu, I. Dranca, V.T. Popa, M. Vass, J. Therm. Anal. Cal. 63 (2001) 855.
[7] F. Rodriguez-Reinoso, Carbon 36 (1998) 159.
[8] B. Viswanathan, S. Sivasanker, A.V. Ramaswamy (Eds.), Catalysis, Principles and Applications, Narosa Pub. House, New Delhi, 2002.
[9] B.R. Puri, Surface complexes of carbons, in: PL. Walker Jr. (Ed.), Chemistry and Physics of Carbon, vol. 6, Marcel Dekker, New York, 1970.
[10] R. Pietrzak, H. Wachowska, Thermochim. Acta 419 (2004) 247.
[11] R.J.J. Jansen, H. van Bekkum, Carbon 32 (1994) 1507.
[12] J. Bimer, P.D. Sałbut, S. Berłożecki, J.P. Boudou, E. Broniek, T. Siemieniewska, Fuel 77 (1998) 519.
[13] J.R. Pels, F. Kapteijn, J.A. Moulin, Q. Zhu, K.M. Thomas, Carbon 33 (1995) 1641.

[14] S.R. Kelemen, M.L. Gorbaty, P.J. Kwiatek, Energy Fuels 8 (1994) 896.
[15] F. Kapteijn, A.J. Moulin, S. Matzner, H.P. Boehm, Carbon 37 (1998) 1143.
[16] K. Jurewicz, K. Babeł, A. Ziółkowski, H. Wachowska, M. Kozłowski, Fuel Process. Technol. 77–78 (2002) 191.
[17] H. Jankowska, A. Świątkowski, L. Starostin, J. Ławrynienko-Omiecyńska, Adsorpcja Jonów na Węglu Aktywnym, Wyd. Naukowe, PWN, Warszawa, 1991.
[18] A. Andrzejak, H. Wachowska, Prace Kom. Mater. Przyr. PTPN 12 (1970) 105.
[19] A. Andrzejak, H. Wachowska, W. Pawlak, Koks Smoła Gaz. 9 (1975) 240.
[20] J. Bimer, P.D. Sałbut, S. Berłożecki, J.P. Boudou, E. Broniek, T. Siemieniewska, Fuel 77 (1998) 519.
[21] J.R. Pels, F. Kapteijn, J.A. Moulin, Q. Zhu, K.M. Thomas, Carbon 33 (1995) 1641.
[22] S.R. Kelemen, M.L. Gorbaty, P.J. Kwiatek, Energy Fuels 8 (1994) 896.
[23] M.A. Wójtowicz, J.R. Pels, J.A. Moulijn, Fuel 74 (1995) 507.
[24] R. Leboda, J. Skubiszewska-Zięba, W. Grzegorczyk, Carbon 36 (1998) 417.