ACTIVATED MONOLITHS BASED ON CARBONACEOUS MESOPHASE

Cristina BANCIU[1], Delia PĂTROI[2], Virgil MARINESCU[3]

Materialele carbonice poroase au un domeniu larg de aplicare în multe domenii precum separarea, purificarea şi stocarea gazelor, ca suport pentru catalizatori sau ca supercapacitori. Această lucrare studiază activarea chimică a monoliţilor pe bază de mezofază carbonică. A fost studiat efectul agentului de activare (NaOH), raportului masic hidroxid de sodiu/mezofază carbonică şi forţei de presare utilizată pentru procesarea monoliţilor asupra caracteristicilor structurale ale monoliţilor de carbon activaţi. Monoliţii pe bază de mezofază carbonică activaţi au fost caracterizaţi prin microscopie optică, microscopie de forţă atomică (AFM), microscopie electronică de baleiaj (SEM) şi difracţie de raze X (XRD).

Porous carbon materials have a wide application in many fields such as gas separation, purification and storage, as catalyst support, or as supercapacitors. This paper studies the chemical activation of monoliths based on carbonaceous mesophase. The effect of the activating agent (NaOH), the sodium hydroxide/carbonaceous mesophase weight ratio, and the compression force used for monoliths processing versus the structural characteristics of activated carbon monoliths, was studied. Activated monoliths based on carbonaceous mesophase have been characterized using optical microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM), and X-ray diffraction (XRD).

Keywords: monoliths, carbonaceous mesophase, chemical activation

1. Introduction

Some solids can be used to separate, to purify or to capture gases from mixtures. These solids can be zeolites or activated carbon, because of their high porosity and controlled dimensions of pores. One of the best materials seems to be

[1] Chem. Eng. PhD Student, National Institute for Research and Development in Electrical Engineering ICPE-CA, Advanced Materials Department, Splaiul Unirii 313, Bucharest, Romania, e-mail: cbanciu@icpe-ca.ro

[2] Phys. Eng., National Institute for Research and Development in Electrical Engineering ICPE-CA, Laboratory for Electrotechnical Materials and Products Characterization, Splaiul Unirii 313, Bucharest, Romania, e-mail: patroidelia@icpe-ca.ro

[3] Phys. Eng., National Institute for Research and Development in Electrical Engineering ICPE-CA, Laboratory for Electrotechnical Materials and Products Characterization, Splaiul Unirii 313, Bucharest, Romania, e-mail: marinescu_v@icpe-ca.ro

carbon composites designed to let gas molecules pass, molecules that are normally attracted by carbon atoms.

Commercial activated carbons with primary micropores played an important role in the removal of small molecules. However, when they are used for catalyst supports, battery electrode, capacitors and greater molecule adsorption, not only the high surface area, but also the mesoporosity are required.

Activated carbons prepared from carbonaceous mesophase usually possess high surface area and micropore volume, making them adequate for adsorption, catalysis and gas or energy storage.

Chemical activation is an interesting method for the production of highly microporous activated carbons. It has been carried out using different activating agents, as phosphoric acid, zinc chloride, sodium or potassium hydroxide, etc. [1-6], and also different carbonaceous precursors.

Chemical activation with KOH or NaOH is one of the most common methods to produce these materials [7, 8], usually as a fine powder [9, 10]. Difficulties in using granular activated carbon can be overcome by incorporating them into a monolith [11, 12]. The manufacture of monoliths normally involves the use of a binder, which implies a reduction of porosity due to partial blocking, the extent of which depends on the kind and proportion of binder used [9, 10]. Because mesophase-based materials have self-sintering ability, these materials are good candidates to produce monoliths of activated carbon of high surface area without using a binder [13, 14].

In this paper we present the effects induced by the chemical activation and the processsing conditions on the structure of activated carbon monoliths based on carbonaceous mesophase.

2. Experimental

The carbonaceous mesophase with max. 0.4% ash content, min. 98% quinoline insoluble and a particles size range of 15-30 μm was used as precursor. Other properties of carbonaceous mesophase are presented in table 1.

Table 1

Physical properties of carbonaceous mesophase

Ash content	max. 0.4%
Size distribution (D50%)	15-30 μm
Fixed carbon	min. 90%
Quinoline insoluble (Q.I.)	min. 98%
Toluene insoluble (T.I.)	min. 98%
Appearance	powder
Softening point	350°C

The carbonaceous mesophase was activated with different quantities of NaOH under the same conditions. The hydroxide was mixed with the precursor at room temperature in a weight ratio of carbon to NaOH of 1:1 and 1:2.

After physical mixing, the mixtures were pressed into a mould at room temperature to produce monoliths (Φ 30 × 15 mm), the pressure used for monoliths processing varying from 14 to 42 MPa (the mixture of the carbon precursors and the activating agent can be consolidated because of its high plasticity).

Using carbonaceous mesophase (CM) and NaOH we obtained six types of monoliths in different processing conditions noted as it can be seen in table 2.

Table 2

Monoliths notation

Notation	CM to NaOH weight ratio	Processing pressure, MPa
P1-1-2	1:1	14
P1-1-3	1:1	28
P1-1-4	1:1	42
P1-2-2	1:2	14
P1-2-3	1:2	28
P1-2-4	1:2	42

The monoliths were carbonized with a heating rate of 5ºC/min up to a maximum temperature of 850°C and held at this temperature for 1 hour in a nitrogen flow of 500 ml/min (Fig. 1).

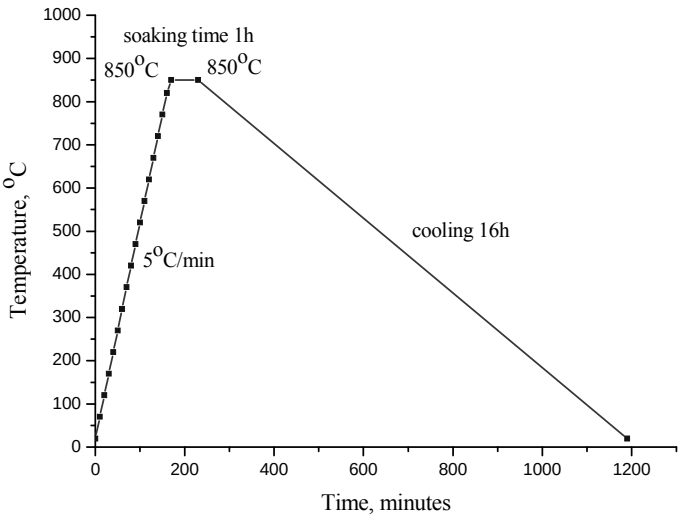


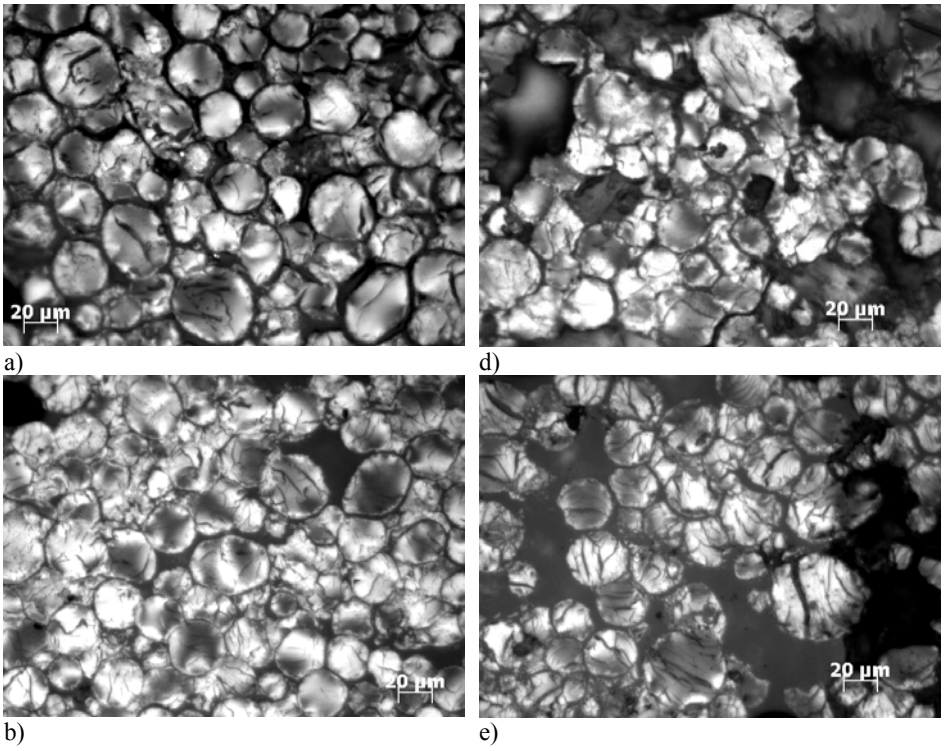
Fig. 1. Thermal treatment diagram for chemical activation of carbonaceous mesophase

After carbonization the obtained monoliths were immersed in a solution of 1M HCl in order to neutralize the sodium compounds results from the heat treatment, washed with distilled water until a pH=7 and then dried at 110°C in a vacuum oven for 16 hours.

The activated carbon monoliths were characterised from a structural point of view using optical microscopy, atomic force microscopy (AFM), scanning electron microscopy (SEM) and X-ray diffraction (XRD). The optical properties were studied by using a Carl Zeiss Jena NU 2 microscope. AFM analyses were performed using a NTEGRA Aura scanning probe microscope. SEM analyses were performed with a Workstation Auriga Carl Zeiss in semicontact mode. X-Ray Diffraction analysis were performed with a D8 ADVANCE type BRUKER-AXS Diffractometer, equipped with a Cu target X-ray tube (λ=1.5406 Å) 40 kV/30 mA and Ni k_β filter, 0.04^o step, measuring time of a point 1 second.

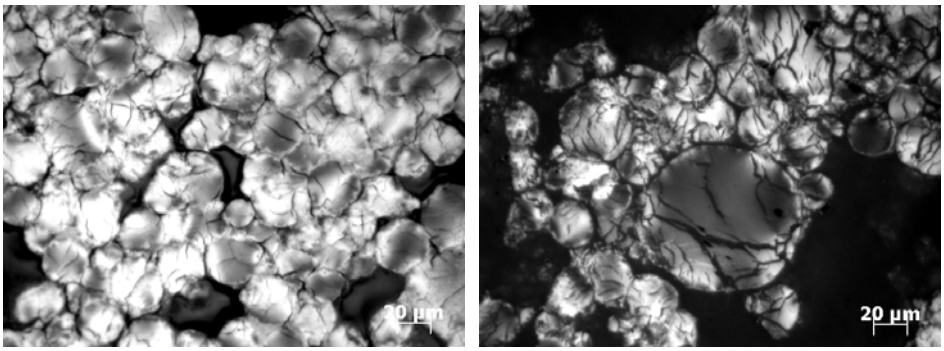
3. Results and discussion

The analysis of microstructure was performed on a transversal cut of the monoliths and the optical micrographs are presented in Fig. 2.



a) d)

b) e)



c) f)

Fig. 2. Optical micrographs of: a) P1-1-2, b) P1-1-3, c) P1-1-4, d) P1-2-2, e) P1-2-3, f) P1-2-4

We can observe that carbonaceous mesophase maintains the same spherical shape at low pressure and the grain boundaries can be distinguished. When we increased the pressure a continuous mass can be observed (P1-1-4 and P1-2-4). At the surface of the activated carbon we can observe pores which appear after carbonization in the presence of sodium hydroxide. During the washing process, the sodium compounds react with HCl and H_2O and the reaction products are removed with water thus creating porosity in the monoliths [15, 16]. CM activated with NaOH in proportion of 1:2 seems to have a higher porosity. According to the previous researches [17], we observe that the powder of CM becames porous after the heat treatement in the presence of NaOH or KOH. BET specific surface area increased to 392.3 m^2/g for CM activated with NaOH, respectively to 1392 m^2/g for CM activated with KOH. Also, total pore volume increased.

Thus, we expect to have the same behavior for the monoliths based on CM.

The CM/NaOH ratio was very important for the monoliths consistency. For instance, the monoliths with CM/NaOH ratio of 1:2 broke down during the washing step or had low consistency, whereas the monoliths with CM/NaOH ratio of 1:1 were hard and did not undergo any weight loss along manipulation.

Fig. 3 shows AFM topography for the six types of monoliths: P1-1-2, P1-1-3, P1-1-4, P1-2-2, P1-2-3 and P1-2-4.

Fig. 4 shows 2D and 3D AFM topography for the sample P1-1-4.

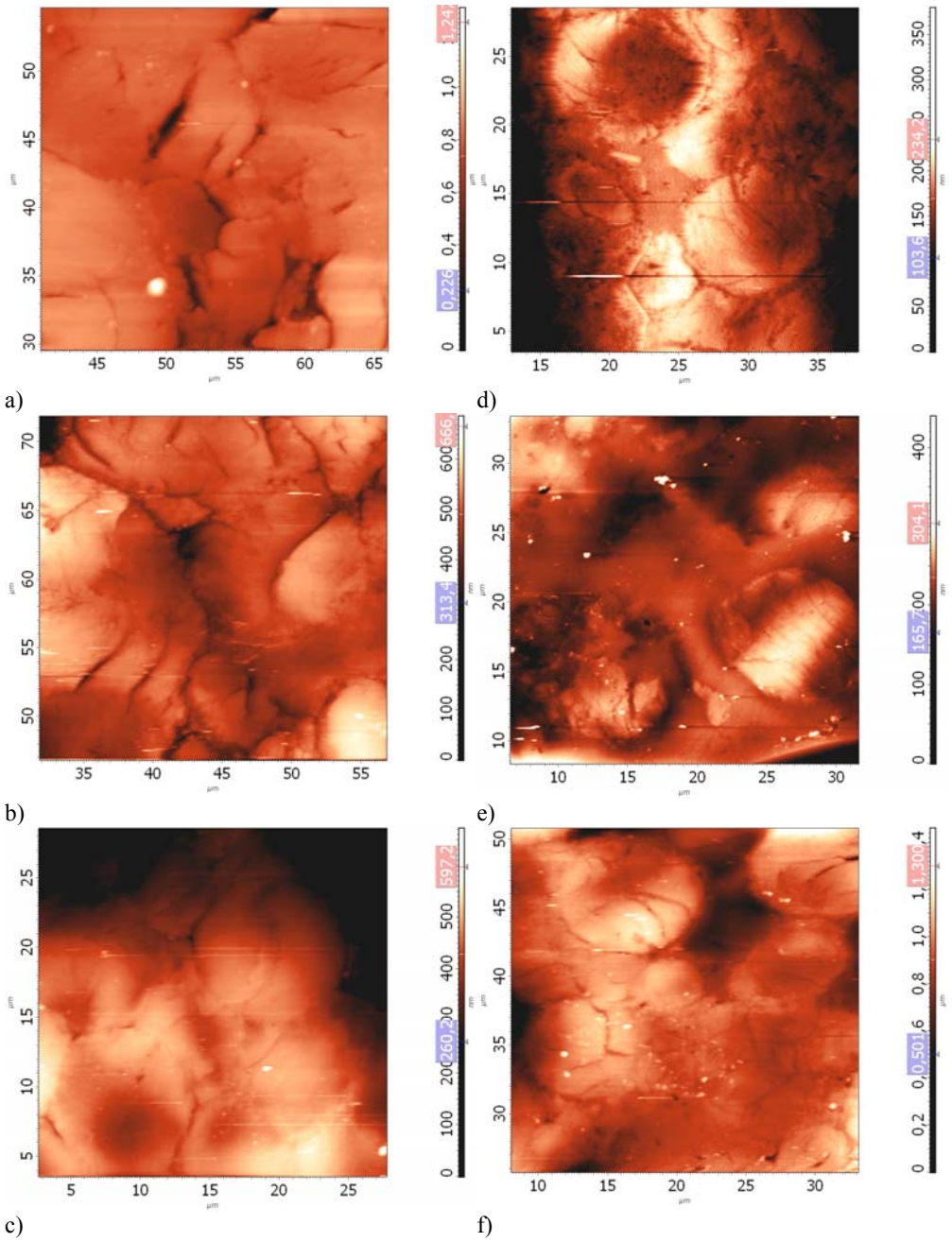


Fig. 3. AFM topography in semicontact mode of: a) P1-1-2, b) P1-1-3, c) P1-1-4, d) P1-2-2, e) P1-2-3, f) P1-2-4

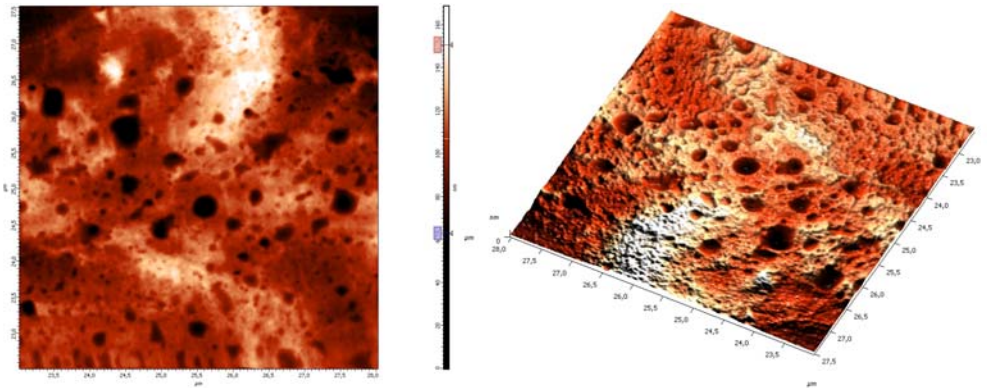


Fig. 4. 2D and 3D AFM topography in semicontact mode of the sample P1-1-4

The topographic images of the samples confirm the observations made by optical microscopy. The monoliths develop a porous structure which is more pronounced with the increasing amount of sodium hydroxide used for activation. We can observe that the porosity is developed on the surface of the CM in the sample P 1-1-4 (Fig. 4).

Fig. 5 presents SEM images for the monoliths type: P1-1-2, P1-1-3, P1-1-4, P1-2-2, P1-2-3 and P1-2-4.

We can observe that the monoliths activated with a greater amount of hydroxide develop a more porous structure. The integrity of the spherical carbonaceous mesophase was affected, the spheres were deformed and present more cracks on the surface. The monoliths still show traces of salt left after the neutralization and washing processes.

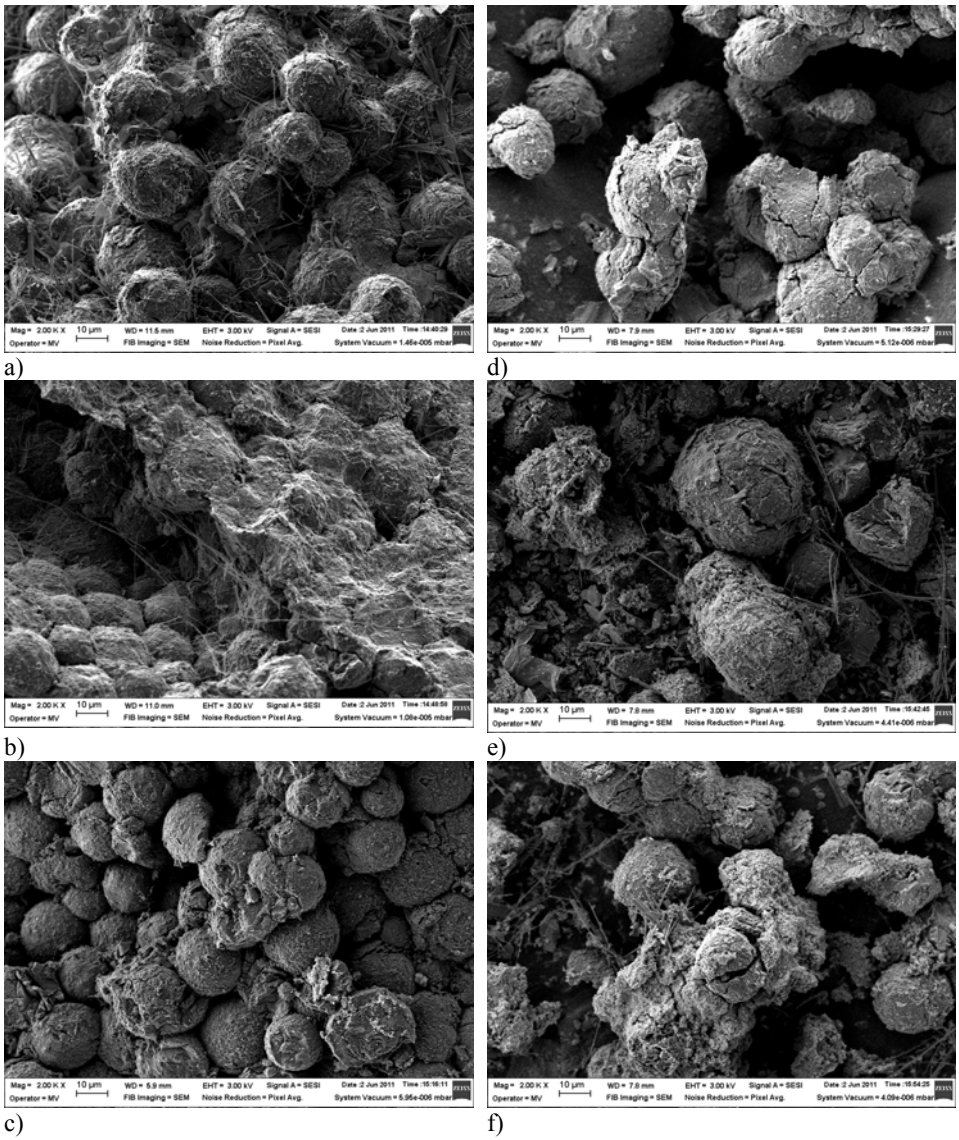


Fig. 5. SEM images of the samples: a) P1-1-2, b) P1-1-3, c) P1-1-4, d) P1-2-2, e) P1-2-3, f) P1-2-4

Figs. 6 and 7 show the XRD patterns of the samples: P1-1-2, P1-1-3, P1-1-4 (Fig. 6) and P1-2-2, P1-2-3, P1-2-4 (Fig. 7).

The patterns for activated monoliths indicate an amorphous structure including a small quantity of crystalline structure. It can be seen from Fig. 6 and 7

that activated CM samples show a typical powder XRD pattern of activated carbon materials.

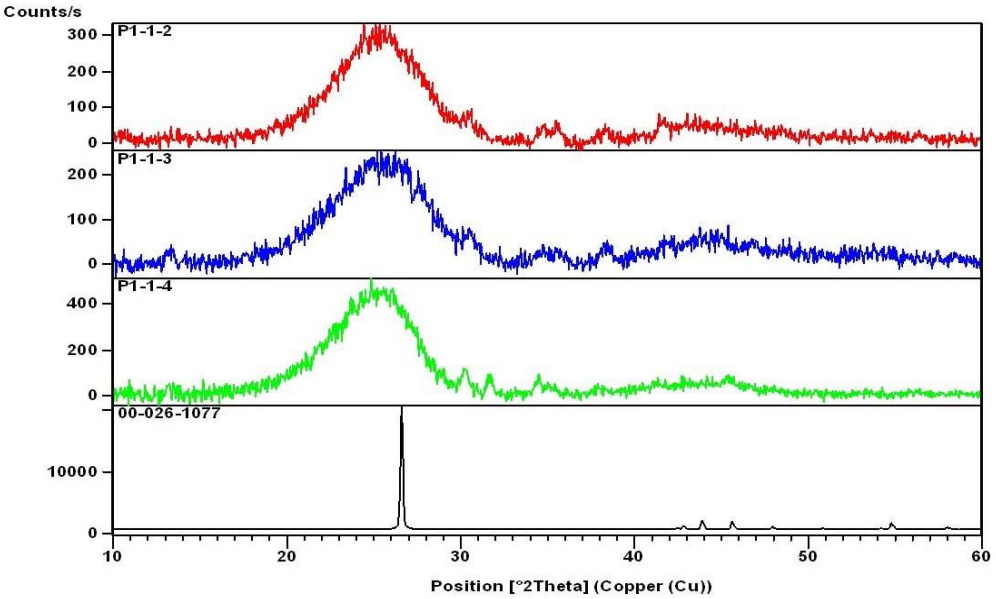


Fig. 6. XRD pattern of the samples: P1-1-2, P1-1-3, P1-1-4 and carbon (ICDD index 00-026-1077)

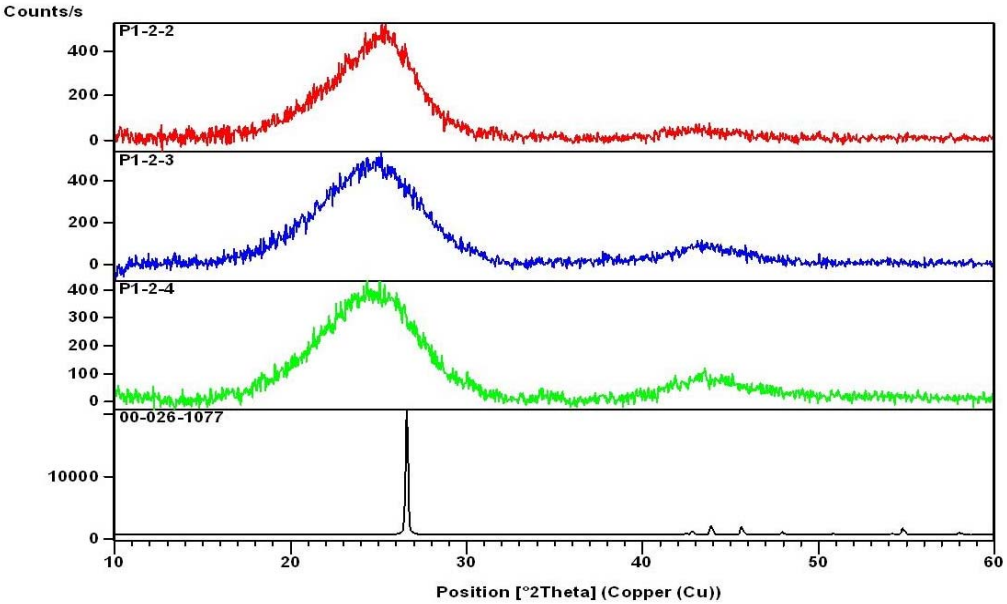


Fig. 7. XRD pattern of the samples: P1-2-2, P1-2-3, P1-2-4 and carbon (ICDD index 00-026-1077)

These results indicates that activated monoliths posses a macrostructure of activated carbon. In the washing process, a great quantity of gas bubbles is produced simultaneous with mass heat releasing. The hydrolysis of sodium compounds is an exothermic reaction, so this intense reaction also affects the porosity by widening of resulted pores in the activated monoliths.

6. Conclusions

In conclusion, a method for preparation of activated carbon monoliths has been established, based on the high self-sinterability of the carbonaceous mesophase.

The chemical activation shows interesting results when applying to pressed carbonaceous mesophase. During the heat-treatment, the crystalline graphitic structure of the carbonaceous mesophase will convert to a porous structure. In the washing process, the reaction products are removed with water and the porosity is created in the mesophase structure.

Also, we observe that the CM/NaOH ratio was very important for the monoliths consistency. Increasing the amount of NaOH leads to an increased porosity, but weakens the strength of the monoliths in spite of the higher compression forces.

The structural analysis of the monoliths indicates that they develop pores, exhibiting additionally some interparticle voids. This porous texture may be important for many advanced applications such as gas separation, purification and storage, as catalyst support, or as supercapacitors.

Acknowledgments

The work has been funded by the financial support of the Romanian National Authority for Scientific Research by Core Programm Project no. PN 09350303/2009.

REFERENCES

[1] *M.J. Illán-Gómez, A. García-García, C. Salinas-Martínez de Lecea, A. Linares-Solano*, Activated Carbons from Spanish Coals. 2. Chemical Activation, Energy and Fuels, **vol. 10**, issue 5, 1996, pp. 1108-1114

[2] *A. Ahmadpour, D.D. Do*, The Preparation of active carbons from coal by chemical and physical activation, Carbon, **vol. 34**, issue 4, 1996, pp. 471-479

[3] *H. Teng, L. Hsu*, High Porosity Carbons Prepared from Bituminous Coal with Potassium Hydroxide Activation, Ind. Eng. Chem. Res., **vol. 38**, issue 8, 1999, pp. 2947-2953

[4] *J. Hayashi, A.P. Watkinson, K.C. Teo, S. Takemoto, K. Muroyama*, Production of activated carbon from Canadian coal by chemical activation, Coal Science and Technology, **vol. 1**, no. 24, 1995, pp. 1121-1124

[5] *D. Lozano-Castelló, M.A. Lillo-Ródenas, D. Cazorla-Amorós, A. Linares-Solano*, Preparation of activated carbons from Spanish anthracite. I. Activation by KOH, Carbon, **vol. 39**, issue 5, April 2001, pp. 741-749

[6] *M.A. Lillo-Ródenas, D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares-Solano*, Preparation of activated carbons from Spanish anthracite. II. Activation by NaOH, Carbon, **vol. 39**, issue 5, April 2001, pp. 751-759

[7] *H. Marsh, D.S. Yan, T.M. O'Grady, A.Wennerberg*, Formation of active carbons from cokes using potassium hydroxide, Carbon, vol. 22, issue 6, 1984, pp. 603-611

[8] *D. Berger, B. Carton, A. Métrot*, Interaction of potassium and sodium with carbons, in Chemistry and Physics of Carbon, vol. 12, Marcel Dekker, New York, 1975, pp. 1-36

[9] *R. Ubago-Pérez, F. Carrasco-Marín, D. Fairén-Jiménez, C. Moreno-Castilla*, Granular and monolithic activated carbons from KOH-activation of olive stone, Microporous and Mesoporous materials, **vol. 92**, issues 1-3, June 2006, pp. 64-70

[10] *D. Lozano-Castelló, D. Cazorla-Amoros, A. Linares-Solano, D.F. Quinn*, Activated carbon monoliths for methane storage: influence of binder, Carbon, **vol. 40**, issue 15, 2002, pp. 2817-2825

[11] *A.B. Fuertes, G. Marban, D.M. Nevskaia*, Adsorption of volatile organic compounds by means of activated carbon fiber-based monoliths, Carbon, vol. 41, issue 1, 2003, pp. 87-96

[12] *Z-G. Shi, F. Chen, J. Xing, Y-Q. Feng*, Carbon monolith: Preparation, characterization and application as microextraction fiber, Journal of Chromatography A, **vol. 1216**, issue 28, 10 July 2009, pp. 5333-5339

[13] *M. Molina-Sabio, F. Rodríguez-Reinoso*, Role of chemical activation in the development of carbon porosity, Colloids and Surfaces A: Physicochemical and Engineering Aspects, **vol. 241**, issue 1-3, July 2004, pp. 15-25

[14] *J.M. Ramos-Fernandez, M. Martinez-Escandell, F. Rodriguez-Reinoso*, Production of binderless activated carbon monoliths by KOH activation of carbon mesophase materials. Carbon, **vol. 46**, issue 2, February 2008, pp. 384-386

[15] *G.H. Oh, C.R. Park*, KOH - Activation Mechanism of Carbon, Proceedings of International Carbon Conference CD, 2003

[16] *R. Xue, Z. Shen*, Investigation of the activation mechanism of mesocarbon microbeads with KOH by XRD, Proceedings of International Carbon Conference CD, 2003

[17] *C. Banciu, A. Băra, I. Ion, D. Pătroi, L. Leonat*, Chemical activation of mesocarbon microbeads, Optoelectronics and Advanced Materials-Rapid Communications, **vol. 4**, nr. 11, 2010, pp. 1717 – 1720