



Synthesis and characterization of carbon cryogel/zeolite composites

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Abstract

A novel method for synthesis of carbon cryogel/zeolite composites was obtained. Method considers forming of carbon cryogel from the sol-gel polycondensation of resorcinol and formaldehyde, followed by freeze drying, and subsequent pyrolysis in presence of different amount of zeolite. Characterization of composite materials by nitrogen adsorption shows that samples are micro- and mesoporous and that specific surface area decrease with increasing the amount of zeolite in samples. XRD method confirms amorphous structure of carbon cryogel and crystalline structure of zeolite, i.e. structure of zeolite has not been destroyed by carbonization process. SEM and EDX analyses reveal homogenous distribution of zeolite through out carbon cryogel and corresponding composition.

Keywords: composite materials, sol-gel process, characterization

I. Introduction

Porous carbon, due to its high surface area and pore accessibility, excellent thermal and chemical stability, as well as, good electrical conductivity is extremely attractive and competitive material for application in separation technologies. Carbon aerogels and cryogels are special class of porous carbon materials [1–5] which are usually formed from the sol-gel polycondensation of resorcinol and formaldehyde, followed by supercritical or freeze drying, and subsequent pyrolysis. These materials have high specific surface area and mesoporous structure and we consider that, in combination with zeolite, separation properties will be approved.

Carbon/zeolite composite is new material which posses properties of both zeolites and carbon. Surface of porous carbon materials is usually hydrophobic and surface of zeolites is hydrophilic and composite material obtained from these precursors combine these properties. Such new material is appropriate for adsorption of both organic substances and metallic ions from aqueous and gaseous phase.

Literature data show that carbon/zeolite composites usually consider dispersion of zeolites on surface of po-

rous carbon [6–11]. Only few studies report simultaneous synthesis of carbon/zeolite composites [12–14]. Preparation of such composites is difficult due to lower stability of zeolites at higher temperatures than carbon.

In this paper we have presented a completely new method for preparation of carbon cryogel/zeolite composite. New composite materials were characterized by low-temperature nitrogen adsorption, X-ray diffraction and scanning electron microscopy.

II. Experimental

2.1. Preparation of RF cryogel with zeolite

In the present work, resorcinol-formaldehyde (RF) gels with zeolite (Z) were synthesized by polycondensation of resorcinol, ($C_6H_4(OH)_2$), with formaldehyde, (HCHO), according to the method proposed by Pekala *et al.* [1]. Sodium carbonate, (Na_2CO_3), was used as a basic catalyst. RF solutions were prepared from resorcinol, 99% purity (E. Merck) and formaldehyde, 36% methanol stabilized (Fluka Chemie), sodium carbonate, p.a. quality (E. Merck), and distilled and deionized water. The sodium form of synthetic zeolite LTA [15], manufactured by Union Carbide Co., was used as starting material. The cation exchange capacity (CEC) of this zeolite was 5.1 meq/g. Cation exchange operation was preformed as follows [16]: 15 g of the Na-LTA ze-

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olite was contacted overnight with 0.3 dm³ of 0.21 M BaCl₂ solution at about 70°C. The solids were separated from liquids with filtration process and afterwards eight times contacted with the exchange solution. The results of atomic absorption spectrophotometer (ASS) by using a Perkin-Elmer 390 spectrophotometer show that the Na⁺ content was less than 0.1 wt.%, so the Na⁺/Ba²⁺ exchange can be considered as nearly complete. After exchange procedure the Ba-LTA zeolite was annealed up to 800°C for 1 h and its structural transformation to amorphous phase was confirmed by X-ray powder diffraction (XRD) analysis.

In all samples concentration of the starting solution was 20 wt.% and R/C molar ratio of resorcinol to catalyst was 100. To study the influence of the zeolite, the amount of zeolite was changed from 5 to 50 wt.%. The synthesis conditions are listed in Table 1. In samples notation zeolite content is used, for instance: CC + 5% Z, means carbon cryogel with 5 wt.% of zeolite. Suspensions with different amount of zeolite were decanted in glass tubes (inner diameter = 10 mm), sealed and placed 2 days at 25°C, 1 day at 50°C and 4 days at 85°C.

Table 1. Synthesis conditions of RF carbon cryogels with zeolite

Sample	R/C [mol/mol]	R/W [wt.%]	Z [wt.%]
CC + 5%Z	100	20	5
CC + 10%Z	100	20	10
CC + 15%Z	100	20	15
CC + 20%Z	100	20	20
CC + 50%Z	100	20	100

R/C - mole ratio of resorcinol to catalyst, R/W - weight ratio of resorcinol to water, Z - zeolite content

RF cryogels with zeolite were prepared by freeze drying according to procedure of Tamon *et al.* [2–5]. RF gels were immersed in a 10-times volume of t-butanol, p.a. quality (Centrohém-Belgrade), for more than one day and rinsed to displace the liquid contained in the gels with t-butanol. The rinsing with t-butanol was repeated twice. The samples were prepared by freeze drying using Modulyo Freeze Dryer System Edwards, England, consisting of freeze dryer unit at High Vacuum Pump E 2 M 8 Edwards. Each of samples was

pre-frozen in deep-freeze refrigerator at –30°C for 24 hours. After that, they were freeze dried in the acrylic chambers with shelves arrangements mounted directly on the top of the condenser of Freeze Dryer. The vacuum during twenty hours of freeze-drying was around 4 mbar.

Carbon cryogels/zeolite composites were prepared by carbonization of the cryogels in a conventional furnace, in nitrogen flow, at 800°C, and after pyrolysis, the furnace was cooled at room temperature.

2.2. Characterization of carbon cryogel/zeolite composites

Adsorption and desorption isotherms of N₂ were measured on carbon cryogels at –196°C using the gravimetric McBain method (laboratory set-up). The specific surface area, S_{BET} , pore size distribution, mesopore including external surface area, S_{meso} , and micropore volume, V_{mic} , for the samples were calculated from the isotherms. Pore size distribution was estimated by applying BJH method [17] to the desorption branch of isotherms and mesopore surface and micropore volume were estimated using the high resolution α_s plot method [18–20]. Micropore surface area, S_{mic} , was calculated by subtracting S_{meso} from S_{BET} . Crystalline phases were identified by X-ray diffraction (XRD) using filtered Cu K α radiation (Siemens D5000). The microstructural study and energy dispersive analysis of X-rays (EDS) were performed on samples with Au coating by JEOL 6300F scanning electron microscope (SEM).

III. Results and discussion

3.1. Adsorption isotherms - BET experiments

Nitrogen adsorption isotherms, as the amount of N₂ adsorbed as function of relative pressure at –196°C, are shown in Fig. 1. According to the IUPAC classification [21] isotherms are of type IV and with a hysteresis loop which is associated with mesoporous materials. Figure 1 shows samples with different wt.% of zeolite. Specific surface areas calculated by BET equation, S_{BET} are listed in Table 2. S_{BET} values, for all samples, lie within 334–593 m²/g. It can be seen that S_{BET} decrease with increasing the amount of zeolite in carbon cryogel sample.

Pore size distribution (PSD) of carbon cryogel samples with different amount of zeolite, shown in Fig. 2,

Table 2. Porous properties of carbon cryogel/zeolite composites

Sample	S_{BET} [m ² /g]	S_{meso} [m ² /g]	S_{mic} [m ² /g]	V_{mic} [cm ³ /g]
CC + 5%Z	593	223	370	0.17
CC + 10%Z	549	227	322	0.15
CC + 15%Z	545	220	325	0.15
CC + 20%Z	513	164	349	0.17
CC + 50%Z	334	88	246	0.12

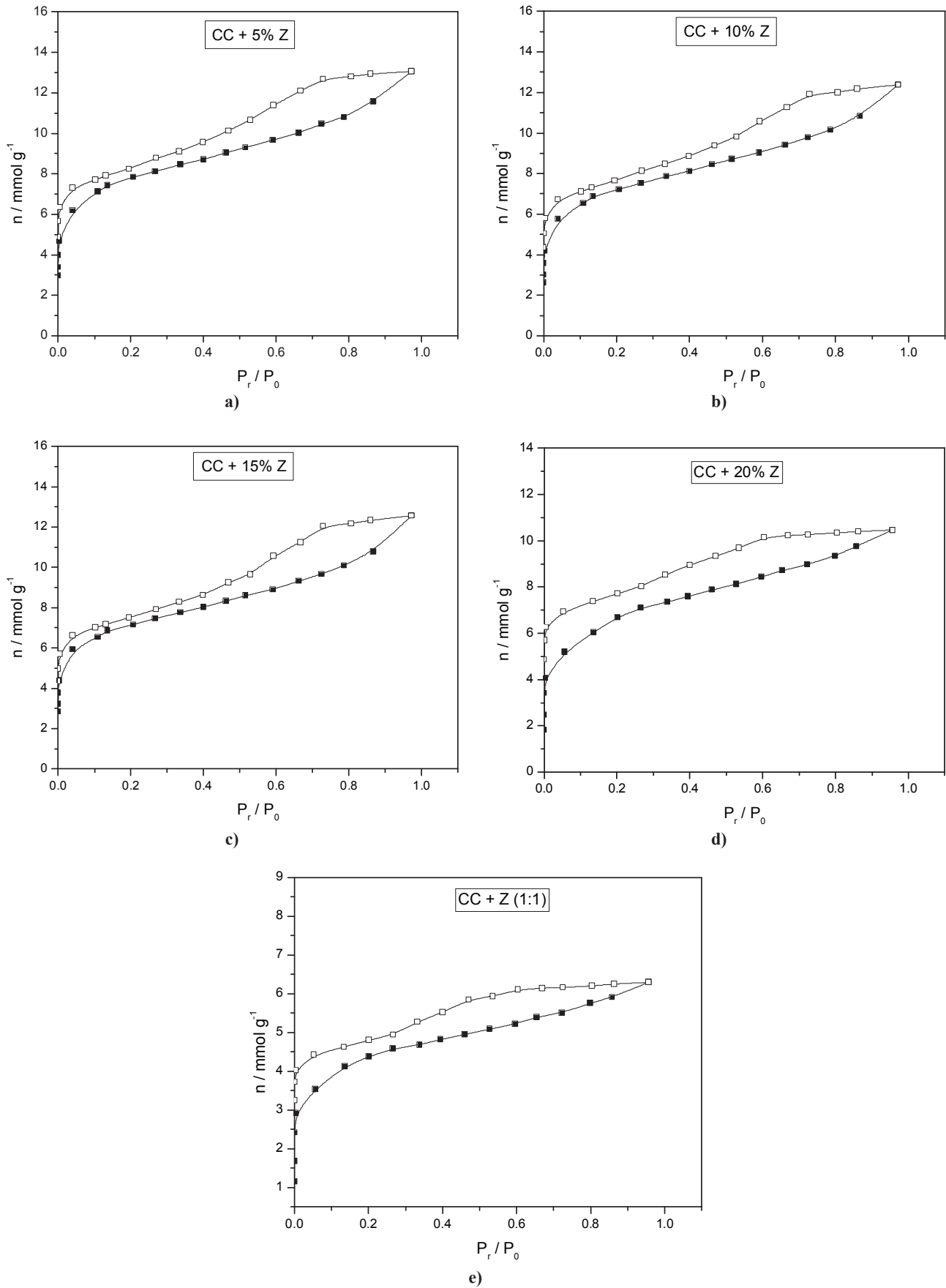


Figure 1. Nitrogen adsorption isotherms, as the amount of N_2 adsorbed as function of relative pressure for carbon cryogel samples with different amount of zeolite: a) 5, b) 10, c) 15, d) 20 and e) 50 wt.% (solid symbols – adsorption data, open symbols – desorption data)

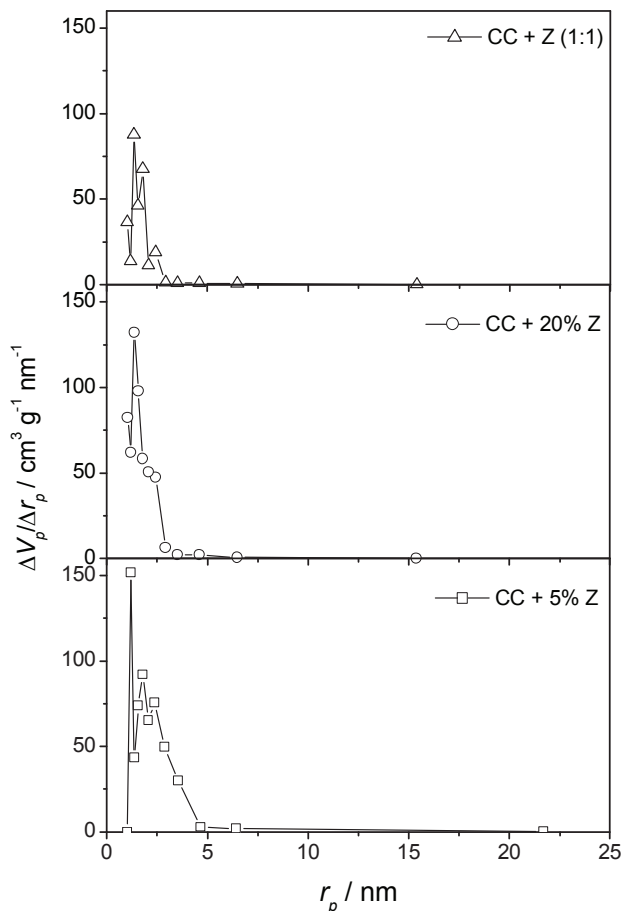


Figure 2. Pore size distribution (PSD) for carbon cryogels with different amount of zeolite (5, 20 and 50 wt.%)

confirm that samples are mesoporous with most of the pores radius between 2 and 5 nm. Samples with 10 and 15 wt.% of zeolite are not presented in Fig. 2 because PSD for these samples is very similar to PSD for CC + 5% Z sample.

α_s plots, obtained on the basis of the standard nitrogen adsorption isotherm, are shown in Fig. 3. The

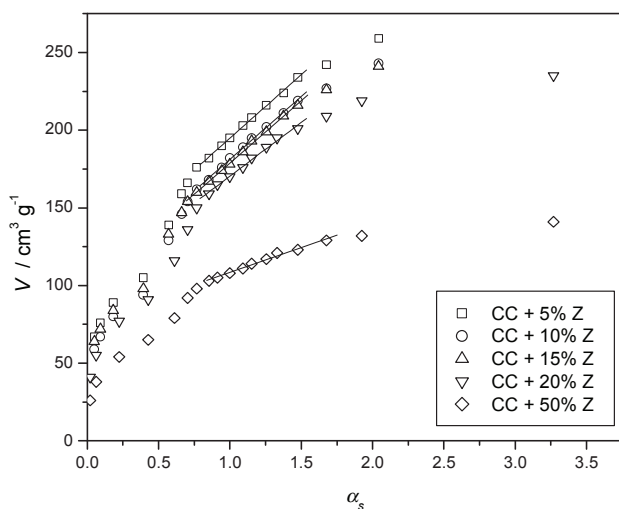


Figure 3. α_s – plots for nitrogen adsorption isotherm of carbon cryogels with different amount of zeolite, based on the standard isotherm of non-porous carbon

straight line in the medium α_s region gives a mesoporous surface area including the contribution of external surface, S_{meso} , determined by its slope, and micropore volume, V_{mic} , is given by the intercept. Calculated porosity parameters (S_{meso} , S_{mic} , V_{mic}) are given in Table 2. For the samples with different weight ratio calculated parameters are the function of the amount of zeolite. Mesopore surface decreases with increasing the amount of zeolite.

From the data in Table 2, and by comparison with data for carbon cryogel without zeolite [22] it can be concluded that addition of zeolite (in lower wt.%) in carbon cryogel does not significantly change the specific surface area and porous structure of carbon cryogel. The higher amount of zeolite leads to decreasing of the specific surface area and the mesoporosity of the samples.

In samples with low zeolite content, the amount of new phase is too small for significant influence on structure of carbon cryogel. As the amount of zeolite increases (material with lower specific surface area), the overall specific surface area decreases. Also, with increasing the amount of zeolite in samples, its particles can penetrate into the structure of carbon cryogel at the moment when that structure is established and close certain number of pores. Decrease in specific surface area is mostly connected with the decrease in mesoporous surface area, Table 2, probably because zeolite easily penetrate in pores with larger dimensions.

3.2. XRD analysis of carbon cryogel/zeolite composites

Figure 4 show the XRD patterns of: a) initial ion exchange BA-LTA zeolite b) Ba-LTA zeolite after heating at 800°C. Figure 5 shows the XRD patterns of carbon cryogel samples with different amount of zeolite. Comparison of XRD patterns in Figs. 4 and 5 showed that characteristic peaks of the Ba exchanged zeolite exist in diffractograms for samples with higher

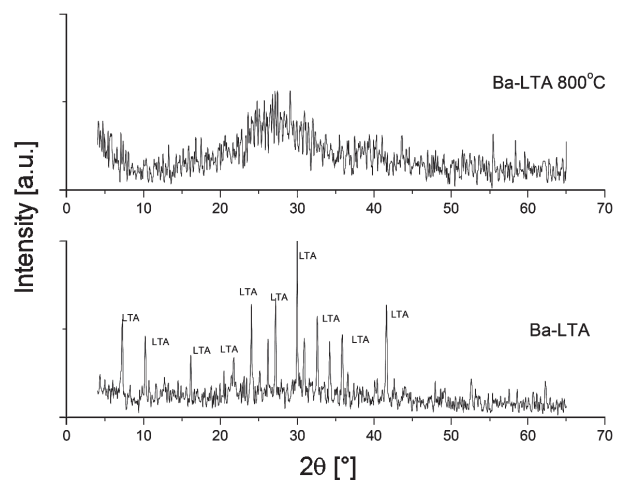


Figure 4. The XRD pattern of a) initial ion exchange BA-LTA zeolite b) Ba-LTA zeolite after heating at 800°C

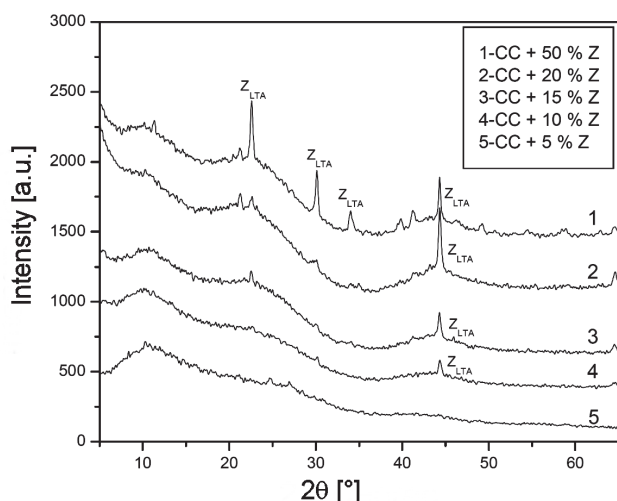


Figure 5. XRD patterns of carbon cryogel samples with different amount of zeolite

amount of zeolite which confirm that zeolite structure was not destroyed during the carbonization process. On the other hand, the XRD patterns show broadening of the diffraction lines in the regions at low 2θ which is associated with the amorphous structure of carbon material (carbon cryogel). The reduction in the peak intensity could be explained by the higher degree of pore filling of the zeolite with the carbon molecules. Increasing carbon/zeolite weight ratio enhances the tight packing of carbon cryogel molecule inside the pore channels of zeolite.

3.3. SEM analysis of carbon cryogel/zeolite composite

SEM image of CC + 20% Z carbon cryogel/zeolite composite is shown in Fig. 6. Typical image shows that zeolite is distributed uniformly throughout the carbon cryogel. The EDS spectrum of CC + 20%Z sample is shown in Fig. 7. It was found that sample mainly consisted of C, O, Al, Si and Ba elements. The mass ratios of C : O : Al : Si : Ba were 84.52 : 12.63

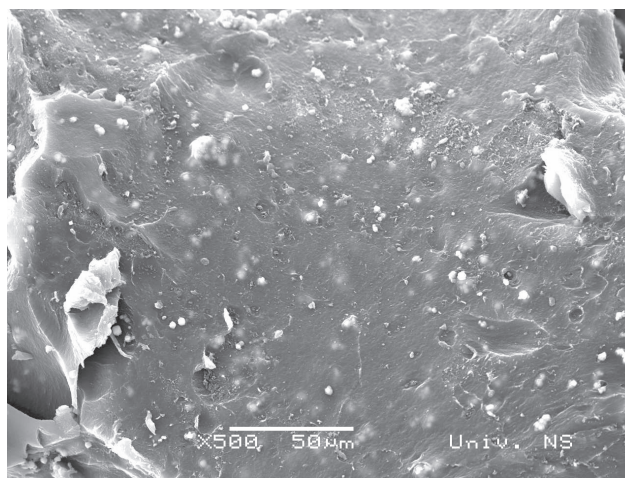


Figure 6. SEM image of CC + 20% Z carbon cryogel/zeolite composite

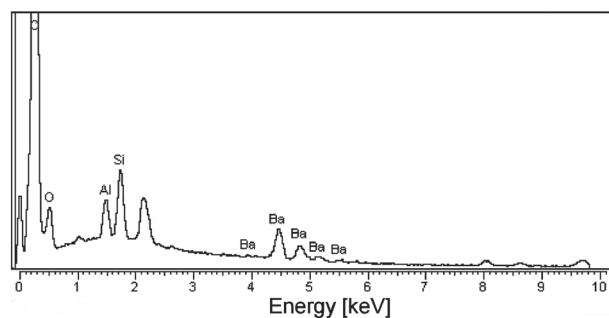


Figure 7. EDS spectrum of CC + 20% Z carbon cryogel/zeolite composite

: 0.46 : 0.74 : 1.65. Indexing of the reflections on the EDS spectrum was compared with literature data [23] and JCPDS card No. 47-0001.

IV. Conclusions

A novel method for synthesis of carbon cryogel/zeolite composites was demonstrated. Samples with different ratio of carbon cryogel and zeolite were obtained. Nitrogen adsorption showed that the structural properties such as specific surface area, mesoporosity and microporosity can be controlled by the amount of zeolite in the sample. XRD analysis confirms that zeolite structure was destroyed during the carbonization process in samples with lower amount of zeolite. With increasing the amount of zeolite in samples, structure of zeolite was kept and dimensions of crystallites increased. This confirms that, with corresponding ratio of carbon and zeolite, we can obtain samples with hydrophobic and hydrophilic properties. With SEM and EDX analyses we have shown that zeolite is uniformly distributed throughout the carbon cryogel and mass ratio between elements corresponds to the desired composition.

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References

1. R.W. Pekala, "Organic aerogels from the polycondensation of resorcinol with formaldehyde", *J. Mater. Sci.*, **24** (1989) 3221–3227.
2. H. Tamon, H. Ishizaka, T. Yamamoto, T. Suzuki, "Preparation of mesoporous carbon by freeze drying", *Carbon*, **37** (1999) 2049–2055.
3. T. Yamamoto, T. Sugimoto, T. Suzuki, S.R. Mukai, H. Tamon, "Preparation and characterization of carbon cryogel microspheres", *Carbon*, **40** (2002) 1345–1351.
4. H. Tamon, H. Ishizaka, T. Yamamoto, T. Suzuki, "Influence of freeze-drying conditions on the mesoporosity of organic gels as carbon precursors" *Carbon*, **38** (2000) 1099–1105.

5. T. Yamamoto, T. Nishimura, T. Suzuki, H. Tamon, "Control of mesoporosity of carbon gels prepared by sol-gel polycondensation and freeze drying", *J. Non-Cryst. Solids*, **288** (2001) 46–55.
6. S.P.J. Smith, V.M. Linkov, R.D. Sanderson, L.F. Petrik, C.T. O'Connor, K. Keiser, "Preparation of hollow-fibre composite carbon-zeolite membranes", *Microporous Mater.*, **4** (1995) 385–390.
7. X. Zhang, W. Zhu, H. Liu, T. Wang, "Novel tubular composite carbon-zeolite membranes", *Mater. Lett.*, **58** (2004) 2223–2226.
8. H. Katsuki, S. Furuta, T. Watari, S. Komarneni, "ZSM-5 zeolite/porous carbon composite: Conventional- and microwave-hydrothermal synthesis from carbonized rice husk", *Micropor. Mesopor. Mater.*, **86** (2005) 145–151.
9. P.S. Tin, T.S. Chung, L. Jiang, S. Kulprathipanja, "The influences of boron on strength and ablation resistance of zirconium-doped graphitised carbons", *Carbon*, **43** (2005) 2013–2032.
10. X. Zhang, H. Liu, T. Wang, A. Wang, K.L. Yeung, "Modification of carbon membranes and preparation of carbon-zeolite composite membranes with zeolite growth", *Carbon*, **44** (2006) 501–507.
11. Z. Zhou, J. Yang, Y. Zhang, L. Chang, W. Sun, J. Wang, "NaA zeolite/carbon nanocomposite thin films with high permeance for CO₂/N₂ separation", *Sep. Purif. Technol.*, **55** (2007) 392–395.
12. N.F. Gao, S. Kume, K. Watari, "Zeolite-carbon composites prepared from industrial wastes: (I) Effects of processing parameters", *Mater. Sci. Eng. A*, **399** (2005) 216–221.
13. N.F. Gao, S. Kume, K. Watari, "Zeolite-carbon composites prepared from industrial wastes: (II) evaluation of the adaptability as environmental materials", *Mater. Sci. Eng. A*, **404** (2005) 274–280.
14. P.R. Shukla, S. Wang, H.M. Ang, M.O. Tade, "Synthesis, characterization and adsorption evaluation of carbon-zeolite composites", *Adv. Powder Technol.*, **20** (2009) 245–250.
15. W. Meier, D. Olson, *Atlas of zeolite structure types*, Structure Commission of the IZA, Juris, Zurich, 1978.
16. A. Dyer, *Verified Syntheses of Zeolitic Materials*, ed. H. Robson, 2001, pp. 67.
17. E.P. Barret, L.G. Joyner, P.P. Halenda, *J. Am. Chem. Soc.*, **73** (1951) 373–380.
18. K. Kaneko, C. Ishii, M. Ruike, H. Kuwabara, "Origin of superhigh surface area and microcrystalline graphitic structures of activated carbons", *Carbon*, **30** (1992) 1075–1088.
19. M. Kruk, M. Jaroniec, K.P. Gadakaree, "Nitrogen adsorption studies of novel synthetic active carbons", *J. Colloid. Interface Sci.*, **192** (1997) 250–256.
20. K. Kaneko, C. Ishii, H. Kanoh, Y. Hanzawa, N. Setoyama, T. Suzuki, "Characterization of porous carbons with high resolution α_s -analysis and low temperature magnetic susceptibility", *Adv. Colloid Interface Sci.*, **76-77** (1998) 295–320.
21. K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, "Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity", *Pure Appl. Chem.*, **57** [4] (1985) 603–619.
22. B. Babić, B. Kaluđerović, Lj. Vračar, N. Krstajić, "Characterization of carbon cryogel synthesized by sol-gel polycondensation and freeze-drying", *Carbon*, **42** (2004) 2617–2624.
23. M.M.J. Treacy, J.B. Higgins, *Collection of Simulated XRD Powder Patterns for Zeolites Published by Structure Commission of the International Zeolite Association*, Fourth revised edition, Elsevier, 2001.