Chemical activation of mesocarbon microbeads

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This paper studies the chemical activation of mesocarbon microbeads in order to obtain activated carbons with controlled porosity. The effect that the activating agent (NaOH and KOH), the alkaline hydroxide/mesophase pitch ratio, and the activation temperature had on the characteristics of activated carbons was studied. Activated mesocarbon microbeads have been characterized using optical microscopy, atomic force microscopy (AFM), X-ray diffraction (XRD) and BET surface area analysis.

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1. Introduction

Some solids can be used to separate CO_2 from gas mixtures. These solids can be zeolites or activated carbon, because of their high porosity and controlled dimensions of pores. The best material seems to be carbon composites designed to let gas molecules pass, molecules that normally are attracted by carbon atoms. That kind of structures can be produced using microbeads structural constituents of mesophase pitch as starting material.

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, potassium hydroxide, etc. [1-6], and also different carbonaceous precursors.

Activated carbon is widely used as adsorbent. Commercial activated carbons with primary micropores played an important role on removal 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 can be produced using microbeads structural constituents of mesophase pitch as starting material. The activating agent (NaOH and KOH), the alkaline hydroxide/pitch ratio, and the activation temperature influence the characteristics of the resultant activated carbons. Activation with NaOH and KOH yielded activated carbons with high pore volumes comparing with precursor. We present in this paper the results obtained by chemical activation of mesocarbon microbeads (MCMB) as starting material with NaOH and KOH.

2. Experimental

The MCMB with max 0.4% ash content, min 98% Q.I. and a particles size range of 15-30 μm was used as precursor. Other properties of MCMB are presented in Table 1.

Table 1. Physical properties of MCMB.

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

The MCMB was activated with NaOH/KOH under the same conditions. The hydroxide was mixed with the precursor at room temperature so as to be 5:1 weight ratio of NaOH/KOH to carbon.

After physical mixing, the mixture was carbonized with a heating rate of 5 ºC/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). After carbonization the obtained material was neutralized with diluted HCl solution, washed with distilled water until a pH=7 and then dried at 110 °C in a vacuum oven for 16 hours.

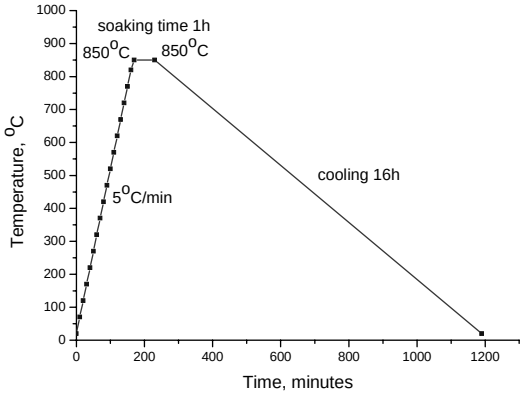
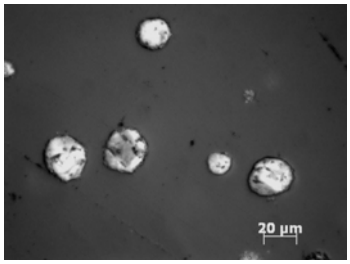


Fig. 1. Thermal treatment diagram for chemical activation of MCMB.

3. Results

The activated carbon and the MCMB were structural characterized using optical microscopy, atomic force microscopy (AFM), X-ray diffraction (XRD) and BET surface area analysis. The optical properties were studied by using a Carl Zeiss Jena NU 2 microscope. AFM analyses were performed with an Atomic Force Microscope model CP-100-10 VEECO. X-Ray Diffraction analyses were performed with a D8 ADVANCE type BRUKER-AXS Diffractometer, equipped with a Cu target X-ray tube (λ=1.5406 Å) and Ni K_β filter. BET surface area analysis was performed with a Quantachrome Autosorb Automated Gas Sorption System, using nitrogen as adsorption gas at the temperature of 77.35 K.



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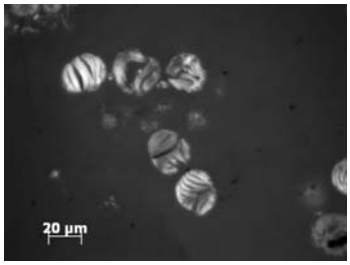

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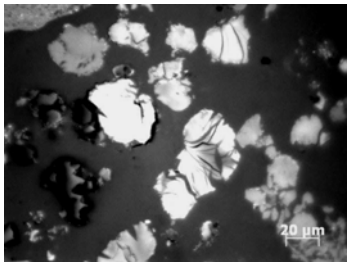


c)

Fig. 2. Optical micrographs of: a) MCMB, b) activated MCMB with NaOH, c) activated MCMB with KOH.

Table 2. Cell parameters obtained from XRD patterns.

Types of carbon	a, [Å]	c, [Å]
MCMB	2.553	6.895
activated MCMB with NaOH	2.453	6.743
activated MCMB with KOH	2.458	6.752

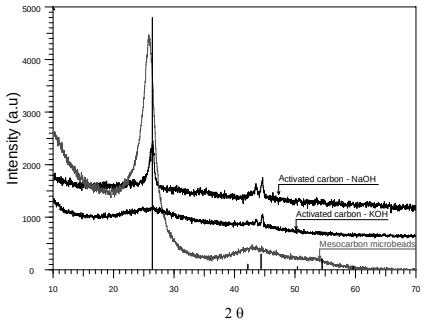
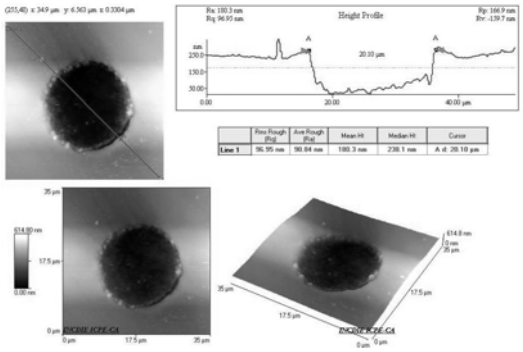
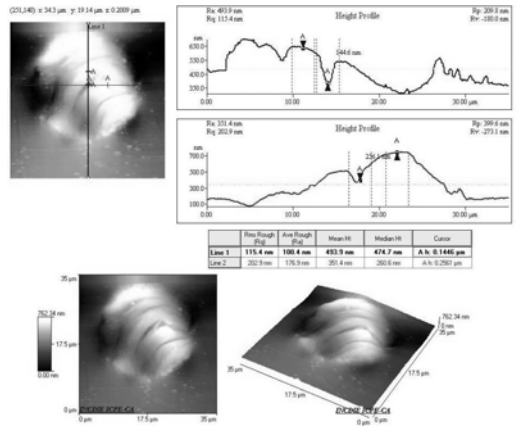


Fig. 3. XRD pattern of: MCMB, activated MCMB with NaOH, activated MCMB with KOH



a)



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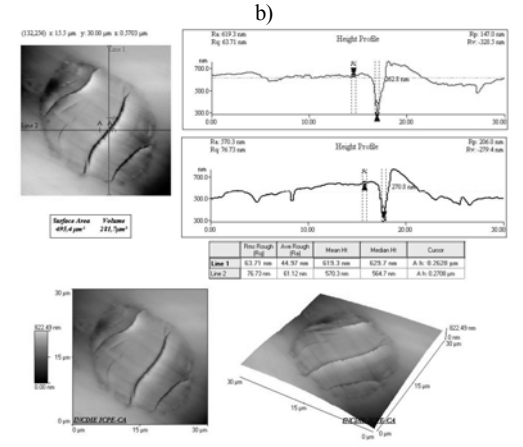

c)

Fig. 4. AFM of: a) MCMB, b) activated MCMB with NaOH, c) activated MCMB with KOH.

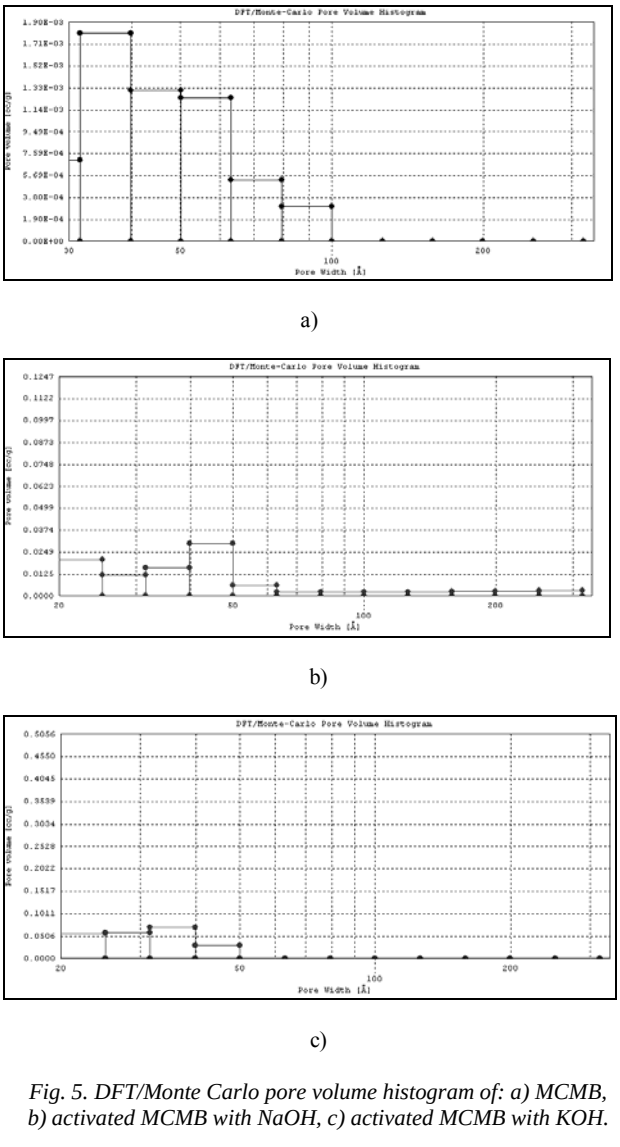

Fig. 5. DFT/Monte Carlo pore volume histogram of: a) MCMB, b) activated MCMB with NaOH, c) activated MCMB with KOH.

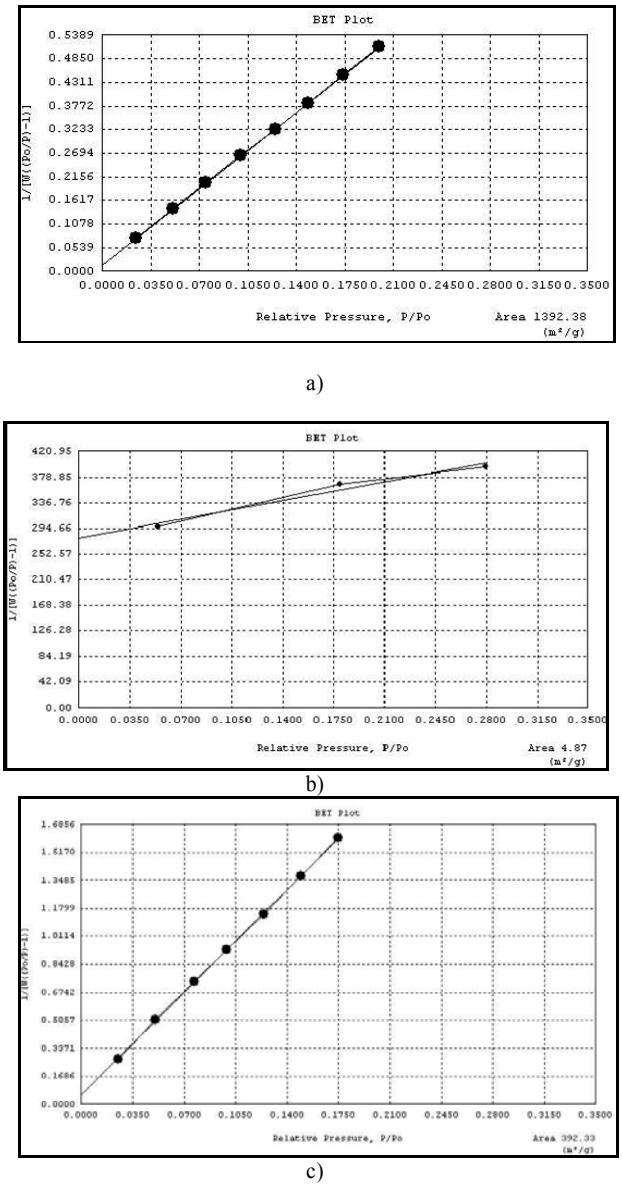

Fig. 6. BET plot of: a) MCMB, b) activated MCMB with NaOH, c) activated MCMB with KOH.

Table 3. BET specific surface area and total pore volume obtained from BET plots.

	MCMB	**Activated MCMB with NaOH**	**Activated MCMB with KOH**
BET specific surface area (m^2/g)	4.865	3.923×10^2	1.392×10^3
Total pore volume at P/P_0=0.995 (cm^3/g)	8.022×10^{-3}	2.903×10^{-1}	7.932×10^{-1}

4. Discussion

Fig. 2 shows optical micrographs of MCMB (a) and activated MCMB with NaOH (b) and KOH (c). We can observe that activated carbon maintains the same spherical shape and roughly the same dimensions like MCMB. The activated carbon presents at the surface pores which appears after carbonization in the presence of hydroxide (NaOH or KOH). During the washing process, the natrium and potassium compounds react with HCl and H_2O and these are removed with water and the porosity in the MCMB is created [7, 8]. MCMB activated with KOH seems to have a higher porosity, fact confirmed by BET analysis, and the appearance of the flakes.

Fig. 3 shows the XRD patterns of MCMB (a) and activated MCMB with NaOH (b) and KOH (c). Table 2 presents cell parameters obtained from XRD patterns. Comparing the XRD patterns for MCMB (Fig. 3a) and activated MCMB with NaOH and KOH (Fig. 3b and 3c) it can be observed that 002 peak becomes shorter and wider. XRD pattern for MCMB indicates a crystalline structure, while the pattern for activated MCMB indicates an amorphous structure including a small quantity of crystalline structure. It can be seen from Fig. 3b and 3c that activated MCMB samples show a typical powder XRD pattern of activated carbon materials. This result indicates that activated MCMB posses a macrostructure of activated carbon. During the washing process, a great quantity of gas bubbles is produces simultaneous with mass heat releasing. The hydrolysis of natrium and potassium compounds is an exothermic reaction, so this intense reaction also affects the porosity by widening of resulted pores in the activated MCMB samples.

Fig. 4 shows AFM for MCMB (a) and activated MCMB with NaOH (b) and KOH (c). It can be seen that the surface structure is different, activated MCMB with NaOH having a porous structure at the surface and being harder than MCMB. The activated MCMB with KOH also develop a porous structure, but the surface of the spheres is soft. The layers of activated MCMB exfoliated because of higher chemical reactivity of the KOH.

Fig. 5 shows DFT/Monte Carlo pore volume histograms for MCMB (a) and activated MCMB with NaOH (b) and KOH (c). Diagrams indicate that the activation with KOH determines the largest pore volume, double that the pore volume of the sample activated with NaOH, for the pores with the width of 20-50 Å (mesopores). MCMB shows the lowest pore volume for the pores with the width of 30-100 Å (mesopores and macropores). Most likely this volume represents the space between the spheres of MCMB.

Fig. 6 shows BET plots for MCMB (a) and activated MCMB with NaOH (b) and KOH (c). BET analysis indicates that after KOH activation, the sample becomes strongly microporous and exhibits a type I Langmuir isotherm [9]. Micropores filling, therefore high gas uptakes, take place at relatively low pressures because of narrow slit pores. The NaOH carbon activation showed a type IV isotherm with a hysteresis loop that indicates narrow slit pores, including pores in the micropore region, mesopores also being present. BET specific surface area increases from 4.865 m^2/g for MCMB to 392.3 m^2/g for MCMB activated with NaOH, respectively to 1392 m^2/g for MCMB activated with KOH (Table 3).

5. Conclusions

The chemical activation shows interesting results when applying to MCMB. During the heat-treatment, the graphitic crystal structure will convert to a porous structure with the activation temperature increasing. During the washing process, the natrium, potassium and other compounds of these react with HCl and H_2O and the products from chemical reaction are removed with water and the porosity is created in the MCMB structure. BET specific surface area increases to 392.3 m^2/g for MCMB activated with NaOH, respectively to 1392 m^2/g for MCMB activated with KOH.

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