Production of binderless activated carbon monoliths by KOH activation of carbon mesophase materials

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Activated carbons (AC) prepared from mesophase-based materials usually possess high surface area and micropore volume, making them adequate for adsorption, catalysis and gas or energy storage. Chemical activation with KOH or NaOH is one of the most common methods to produce these materials [1, 2], usually as a fine powder [3, 4], thus making its conforming to pellets or monoliths an important area of research. 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 [3, 4]. As 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, but no success has been reported up to now [5]. This paper reports the use of mesophase pitch (MP) and mesophase self-sintering carbon (MSC) for the synthesis of activated carbon monoliths (ACM) with high consistency and large porosity, without the need for a binder.

For the preparation of the MP a petroleum residue (ethylene-tar) [6] was pyrolyzed in a laboratory pilot plant at 440°C and a pressure of 1.0 MPa, using a heating rate of 10°C/min and a soak time from 2 to 4 hours. MSC was the solid obtained after extraction of the MP with THF at its boiling point.

The synthesis of the ACMs involved several steps: i) mixture of the MP or MSC with KOH in a ball mill during 30 minutes; ii) uniaxial conforming at room temperature to produce monoliths (25×25×5mm), conforming pressure varying from 100 to 400 MPa (the mixture of the carbon

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precursors and the activating agent can be consolidated because of its high plasticity); iii) heat treatment at 800°C under nitrogen atmosphere, soak time of 2h and heating rate of 2°C/min; and iv) washing of monoliths with a solution of 1M HCl, followed by extensive washing with distilled water until pH=7. The final step consists on drying of the monolith at 100-110°C for 24 hour. Bulk densities of the monoliths were determined by measuring the dimensions of the samples and their dry weight.

Table 1 summarises the characterization of some of the precursors studied in order to achieve ACMs with good mechanical resistance coupled with high surface area. The low ash content of the MP and MPC has to be pointed out, ash being mainly composed by Si, Al, Fe and Ca. For the first screening, the activation was carried out using a KOH/carbon ratio of 2 for all samples. The first activation tests were carried out using MSCs. This kind of material has the highest mesophase and carbon content, coupled with low volatile matter, but it also exhibits the highest softening point and viscosity upon melting of all tested materials. All the monoliths produced with this precursor had low consistency and could not be manipulated without breaking down to a powder, thus indicating that sintering of the grains had not been sufficient. Forming was varied from 100 to 400 MPa but results did not change much. It seems that fusibility of MSC samples is not large enough to allow an extensive reduction of inter-particle space and to impart sufficient mechanical strength to the monoliths.

Table 1: Characterization of some of the mesophase pitches and mesophase self-sintering carbons

Sample	Conditions	TI (%)	NMPI (%)	Mesophase content (%)	C/H _{at}	Carbon Yield (wt%)	Softening point (°C)	Ash content (wt%)
MP-2	440°C-1MPa/2 h	52	33	42	1.68	68	140	0.012
MP-4	440°C-1MPa/4h	62	50	65	1.78	74	200	0.010
MSC-2	MP-2 extracted THF	90	77	60	2.03	87	260	0.017
MSC-4	MP-4 extracted THF	92	82	70	2.05	88	325	0.015

Notes. TI, Toluene insoluble content; NMPI, N-methyl-2pyrrolidone insoluble content; C/H_{at}, C/H atomic ratio;

Softening Point (TMA determination)

The use of MP was not originally considered to be the best option as the carbon yield of the material after pyrolysis was much lower; however, the preliminary results were better than for MSC. It seems that the lower softening point and viscosity of the MP as compared to the MSC is very important to bind the carbon grains, despite the presence of KOH, this being the key of this new process. The results indicate that the carbonization soaking time used to produce the original MP (2-4 h) does not seem to affect the sinterability of their mixtures with KOH, the final ACMs exhibiting similar consistency. One could expect an improvement of the ACM (higher density) when increasing the carbonization soak time to produce the MP, due to the higher mesophase content, C/Hat ratio and carbon content of the MP. However, it seems that there is a compensation effect leading to similar properties, which may be originated by the higher softening point and viscosity of the pitch. On the other hand, the forming pressure was more important for consistency than the carbonization soak time. For instance, the samples conformed at 100-200 MPa, broke down during the washing step or had low consistency, whereas the 400MPa monoliths were hard and did not undergo any weight loss along manipulation. Concerning the range studied here, the best conditions to prepare the monoliths were selected as follows: four hours pyrolysis soaking time, as it gives the highest carbon yield and 400MPa forming pressure, as it yields the largest consistency.

Using these previous optimised conditions to prepare the ACM, the effect of KOH/carbon ratio on the porous texture has also been studied, the nomenclature of ACM indicating the ratio KOH/C (ACM-1, ACM-2, ACM-3 and ACM-4) used. Ash content of the ACMs was lower than 0.01 wt%, lower than in the starting MP. The ACMs were characterised by adsorption of N₂ at 77 K and CO₂ at 273 K. The corresponding N₂ (77K) adsorption isotherms, plotted in Figure 1, are of Type I, with a well defined plateau, thus indicating that these materials are essentially microporous. The shape of the knee between 0 and 0.2 relative pressure indicates that the micropore size distribution becomes broader for the samples with increasing KOH/C ratio.

Figure 1. N₂ Adsorption isotherms at 77°K.

The BET equation was applied to N₂ adsorption isotherms from which an “apparent” or “equivalent” BET area was obtained (the area equivalent to extend the volume adsorbed at the calculated theoretical monolayer) because of the microporous nature of the samples. The apparent surface area increases with KOH activation, reaching values up to 2850 m²/g (Figure 2).

Figure 2. Evolution of bulk density and BET surface with KOH /C ratio

The bulk density is reduced as a result of the increase in the porosity of the materials (Figure 2). This reduction in density is mainly induced by the porosity generated by the activation process itself, but it is also produced by the existence of inter-particle spaces left behind after the removal of the chemicals produced during activation (K₂O, K, K₂CO₃, etc).

The Dubinin-Radushkevich (DR) equation was applied to the N_2 (77K) and CO_2 (273 K) isotherms to obtain the total micropore volume (V_{N_2}) and the volume of narrow micropores (V_{CO_2}) [7]. The mesopore volume was obtained by difference between the volume measured at $P/P_0=0.95$ and the micropore volume (V_{N_2}). The materials are mainly microporous, the micropore volumen increasing with KOH/carbon ratio (Figure 3) and reaching values up to $1 \text{ cm}^3/\text{g}$.

Figure 3. Evolution of the micropore volume deduced from adsorption of N_2 (V_{N_2}) and CO_2 (V_{CO_2}), and mesopore volume (V_{meso}), as a function of KOH/C ratio

Most of this microporosity is narrow, as differences between N_2 and CO_2 curves are only observed for the largest KOH/carbon ratio, when micropores become wider [7]. The volume of mesopores is not large but it increases with the KOH/C ratio up to 24 % of total porosity.

When analysing the microstructure of a transversal cut of the monolith by SEM (Figure 4), a continuous mass can be observed, where no grain boundaries can be distinguished. The existence of voids of several tens of microns, which may have formed in the boundaries of the grains, are responsible for the relatively low density of the monoliths (but this density is large in respect to the typical carbon powders produced by KOH activation).

Figure 4. SEM image of a transversal cut of ACM-3 monolith

In conclusion, a new method for preparation of binderless activated carbon monoliths has been established, in which the high selfsinterability of the mesophase-based material has been used to sinter the powder, yielding consistent monoliths with up to 2800 m²/g apparent surface area. The analysis of the porosity of the monoliths indicates that they are essentially microporous, reaching micropore volumes up to 1 cm³/g, but mesoporosity can be as large as 24 % of the pore volume, exhibiting additionally some interparticle voids. This porous texture (large amount of microporosity with high accessibility due the interparticle voids) may be important for many advanced applications such as supercapacitors.

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