

# Prevention of ordered mesopore structure degradation during microporosity generation in nanocasted carbons

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## Introduction

Emerging applications of porous carbon materials require the development of novel hierarchical carbons with tailored pore sizes. In recent years, a number of reports have been published on the synthesis of ordered mesoporous carbons by “hard templating” with ordered silicas. However, very little knowledge is available to prepare carbons with a controlled bimodal micro-mesopore distribution of pore sizes while avoiding the gradual destruction of the ordered mesostructure. In this work we have investigated the development of microporosity in ordered mesoporous carbons by chemical activation with KOH, comparing the effects of carrying out the activation step in the presence and absence of SBA silica used as template.

## Experimental

CMK3-type ordered mesoporous carbon (CMO) was prepared by gas-phase infiltration of carbon in SBA-15 silica (TG results in air at 1000 °C showed a carbon infiltration degree of 58%) using propylene at 750 °C for 6 h. The resulting composite (SBA-15-CMO) was divided into two parts: one of them was directly activated with KOH, and the other was washed with HF to remove the silica template and obtain the ordered mesoporous carbon (CMO), which was then activated with KOH as well.

Chemical activation was performed in a horizontal furnace. CMO was mixed with powdered KOH in KOH/carbon ratios (X) of 2:1 and 4:1. The impregnated materials were heated in Ar at 5 °C/min to either 750 or 850 °C (T) for 30 min. The resulting activated carbons are denoted as CMMO X:1 T series. SBA-15-CMO composites were activated in the same conditions and are denoted as SiC X:1 T series. The carbons resulting from HF washing the template after activation are denoted as CMMOB X: T series.

## Results and discussion

Figure 1 shows the N<sub>2</sub> adsorption-desorption isotherms measured at 77 K on a selection of representative samples. All the isotherms belong to Type IV in the BDDT classification and they maintain the shape of the isotherm of the starting mesoporous carbon, which indicates the conservation of the mesoporous character, except for CMMO 4:1 850 sample, which becomes type I. The adsorbed volume at low relative pressures increases gradually with increasing both X and T, which evidences microporosity development upon activation. Several pore textural parameters are compiled in Table 1. All of them increase with increasing either X or T. Thus, the micropore volume [ $V_{DR}(N_2)$ ] goes from 0.13 (CMO) to 0.52 cm<sup>3</sup>/g (CMMOB 4:1 850). The BET surface area ( $S_{BET}$ ) increases from 341 (CMO) to a maximum value of 1247 m<sup>2</sup>/g (CMMOB 4:1 850). The mesopore volume ( $V_{meso}$ ) remains almost constant (a slight increase being observed due to collapse of adjacent micropores during activation), with the exception of a drastic decrease to 0.16 cm<sup>3</sup>/g for sample CMMO 4:1 850, which confirms the destruction of the regular mesopore network.

The materials activated after having removed the template with HF exhibit greater N<sub>2</sub> adsorbed amounts at low relative pressures than those activated in the presence of the template. However, as Figure 2 shows, X-ray diffractograms reveal that the solids directly activated with the template (CMMOB series) keep the ordered nanostructure to a much greater extent; note that the characteristic peaks of hexagonal symmetry can be clearly seen in these materials as well as in CMO. However, these diffraction peaks practically disappear following activation in the absence of the template (CMMO series).

Under mild activation conditions (low X and T), microporosity development is greater when the activation is carried out in the absence of the template (Figure 1, Table1), but a slight degradation of the ordered structure occurs upon activation (Figure 2). In the case of strong activation conditions (high X and T) the materials derived from the silica-carbon composite present bigger microporosity development (Figure 1, Table1) along with a substantial preservation of the structural order (Figure 2).

## Conclusions

Hierarchical carbons have been obtained by chemical activation with KOH of ordered mesoporous carbons. Under mild activation conditions, better results are obtained for carbons activated without template as a good compromise is obtained in terms of structure preservation/microporosity development. For strong activation conditions (high X and T), greater micropore volumes are obtained for the activation in the presence of the template, and the destruction of the ordered mesoporous structure is avoided to a larger extent.

## Figures

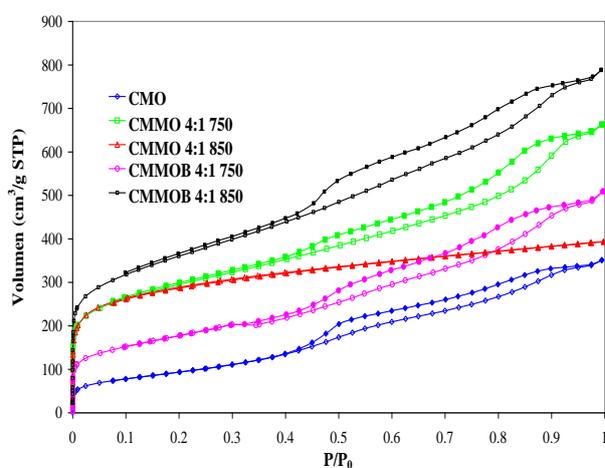


Figure 1. N<sub>2</sub> adsorption-desorption isotherms at 77 K for a selection of activated samples.

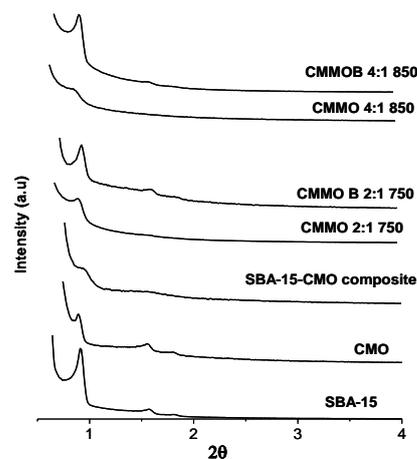


Figure 2. Low-angle X ray diffractograms for a selection of activated samples

Table 1. Porous texture parameters calculated from the N<sub>2</sub> adsorption-desorption isotherms at 77 K.

Sample	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>T</sub> (cm <sup>3</sup> /g)	V <sub>DR(N<sub>2</sub>)</sub> (cm <sup>3</sup> /g)	V <sub>meso</sub> (cm <sup>3</sup> /g)
CMO	341	0.53	0.13	0.40
CMMO 2:1 750	726	0.81	0.30	0.51
CMMOB 2:1 750	393	0.62	0.15	0.46
CMMO 4:1 750	1028	1.00	0.42	0.58
CMMOB 4:1 750	634	0.75	0.25	0.51
CMMO 4:1 850	982	0.60	0.44	0.16
CMMOB 4:1 850	1247	1.19	0.52	0.67