

Surface and pore structures of CMK-5 ordered mesoporous carbons studied by nitrogen adsorption and surface spectroscopic methods

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1. INTRODUCTION

Porous carbons are widely used as absorbents and catalyst supports. In many applications, carbons with mesopores of defined dimensions are desirable. By synthesis in a suitable matrix, ordered mesoporous carbons (OMCs) can be produced in a convenient way [1-4]. In the present work, OMCs were synthesised by polymerisation of furfuryl alcohol in SBA-15 aluminosilicates with different Si/Al ratios. The polymerisation of furfuryl alcohol is normally acid catalysed. The addition of an acid catalyst is required when the synthesis is performed in non-acidic silica [5]. However, this is unnecessary if performed in an acidic aluminosilicate as in the present work. The polymerisation reaction is catalysed by the Brønsted acid sites of the matrix. The introduction of aluminium not only influences the acidity of the matrix, it may also affect its pore structure. Therefore, in the present work, the matrices used for the OMC synthesis were characterised by nitrogen adsorption. The OMCs were studied by X-ray photoelectron spectroscopy (XPS) and by nitrogen adsorption. By XPS, only information on the external surface is obtained. However, it was shown in previous studies on similar OMCs that the surface spectroscopic results are representative for the entire sample [6].

2. EXPERIMENTAL

Aluminum-free SBA-15 silica was synthesised as reported elsewhere [7]. Different amounts of aluminum were introduced by slurring the silica with an aqueous solution of AlCl₃ for approximately 30 min [8]. The Si/Al molar ratio ranged from 5 to 80. For the synthesis of the OMCs the pores of the aluminosilicates were filled at room temperature with furfuryl alcohol by an incipient wetness method. The amount of furfuryl alcohol corresponded to the pore volume of the aluminosilicate. The loaded aluminosilicate was heated to 95 °C in order to polymerise the furfuryl alcohol. Then, the SBA-15 template containing the carbon source was heated with increasing temperature to 900 °C under vacuum. Finally, the OMCs were liberated by treatment with hydrofluoric acid [2].

Elemental analysis of the aluminosilicates for Si/Al ratios was performed with inductively coupled plasma emission spectroscopy (Shimadzu, ICPS-1000III). The powder X-ray diffraction (XRD) spectra were measured for calcined aluminosilicate samples at room temperature using a Rigaku MultiFlex instrument (Cu K_α source, 3 kW). The details of the XPS and nitrogen adsorption experiments have already been described elsewhere [6]. The mesopore size distribution of the aluminosilicates was calculated with a modified BJH

method [9] using desorption data, whereas in spite of its shortcomings, for the OMCs the "traditional" BJH method [10] was used.

3. RESULTS AND DISCUSSION

3.1. Structure of the Al-SBA-15 aluminosilicates

The X-ray diffractograms of the SBA-15 aluminosilicates showed intense narrow diffraction lines, indicating highly ordered structures. The Si/Al ratio only had a minor influence (not shown). It should be considered, however, that extra-framework aluminium species, possibly present in the pores, would not cause new X-ray diffractions to appear. Extra-framework species may narrow the pore diameter or block sections of the pore system. The mesopore volume and surface area of the aluminosilicates decreased indeed significantly with decreasing Si/Al ratio (Table 1). The pore size distribution, however, depended much less on the Si/Al ratio. For the sample with a Si/Al ratio of 80 a narrow pore size distribution with a maximum at widths of 75 to 80 Å was observed. With decreasing Si/Al ratio, the widths of the mesopores changed very little (Table 1). Only for the most aluminium-rich sample (Si/Al ratio of 5), in addition to the above-mentioned pores, a small population of narrower pores with widths of 60 to 75 Å was found.

The differences between the pore widths are too small to explain the differences in the pore volumes. Therefore, the observations discussed above may be attributed mainly to the presence of extra-framework species that occupy the entire cross section of some parts of the mesopores. The presence of extra-framework aluminium species on the external surface could be ruled out. The concentration of aluminium on the surface, as determined by XPS, was smaller (higher Si/Al ratio) or only slightly higher as compared to the bulk (Table 1).

3.2. Chemical nature of the OMC surface

It was discussed in the previous section that the Si/Al ratio of the aluminosilicate had an important influence on the structure of its pore system and its catalytic activity. This in turn should influence the properties of the OMCs formed there. The influence of the aluminosilicate Si/Al ratio on the OMC properties is first presented for the OMC chemistry. The XPS carbon spectra were dominated by an intense asymmetrical so-called graphite peak and by a smaller $\pi \rightarrow \pi^*$ peak (not shown). Such spectra are typical for polyaromatic, "graphite-like" carbonaceous solids as carbon blacks [11] and carbon fibres [12]. The full

Table 1
Properties of the SBA-15 aluminosilicates

Si/Al		Surface area [m ² /g]	Pore width [Å]	Pore volume [cm ³ /g]	
Bulk	Surface ^a			Micro-pores	Meso-pores
5	9.8	619	74	0.01	0.70
10	-	730	74	0.03	0.82
20	23.8	779	75	0.05	0.86
40	-	866	76	0.07	0.93
80	70.6	889	76	0.07	0.94

^a Determined by XPS

Table 2
XPS parameter for the graphitic character of the OMC surface

Sample, Si/Al ratio of matrix in parentheses	FWHM [eV]	Relative area of the $\pi \rightarrow \pi^*$ peak [%]
CMK-5 (5)	1.20	6.3
CMK-5 (10)	1.19	6.8
CMK-5 (20)	1.18	7.2
CMK-5 (40)	1.21	6.1
CMK-5 (80)	1.22	6.0
Graphitised carbon black	0.82	8.9

width at half maximum (FWHM) of the graphite peak depends on the graphitic character of the surface. It becomes narrower with increasing graphitic character [13]. For the OMCs, the FWHM of the graphite peak first decreased with increasing Si/Al ratio of the matrix and then increased again. A minimum value was found for a Si/Al ratio of 20 (Table 2), suggesting that the OMC synthesised in a matrix with a "medium" Si/Al ratio had the highest graphitic character. This finding is supported by the dependence of the $\pi \rightarrow \pi^*$ peak area on the Si/Al ratio. A large $\pi \rightarrow \pi^*$ peak indicates a carbon surface with a high graphitic character [14]. The largest $\pi \rightarrow \pi^*$ peak was found for the OMC synthesised in the matrix with a Si/Al ratio of 20 (Table 2).

The observation that the OMC with the highest graphitic character was formed in the matrix with a medium Si/Al ratio is explained as follows: upon heating, the OMC underwent several reactions (*e.g.* aromatisation and condensation) that increase its graphitic character. At least a portion of these reactions was catalysed by the acid sites of the matrix. Usually, the strength of acid Brønsted sites increases with increasing Si/Al ratio. However, when the Si/Al ratio increases the increasing strength of individual sites is accompanied by a decreased concentration of acid sites. Therefore, the catalytic activity of aluminosilicates can often be described by a volcano curve where the highest activity is observed at medium Si/Al ratios. This is exactly the case for the dependence of the OMC graphitic character on the Si/Al ratio.

3.3. Structure of the ordered mesoporous carbons

If during the OMC synthesis the entire pore system of the matrix is filled with the carbon product, the OMC can be described as a network of carbon rods (*e.g.* CMK-3). However, as in the present work, it is also possible to form the carbon product only on the pore walls of the matrix, without filling the entire pore. The produced CMK-5 OMCs consist of a network of nanopipes. The pore size distribution (PSD) of the CMK-5 OMCs showed the presence of two types of mesopores (Fig. 1). Pore widths and volumes were determined by fitting as shown for one sample (CMK-5 (80)). The pores with widths between 34 and 37 Å were assigned to the voids inside the nanopipes, whereas the pores with width 25 to 30 Å were assigned to the voids in-between the nanopipes [2]. In an earlier study on CMK-3 OMCs it was observed that with increasing graphitic character of the OMCs the carbon rods are shrinking [6]. A similar shrinkage seems to have occurred in the case of the CMK-5 OMCs. The nanopipes have the same initial external diameter (pore diameter of the matrix). However, when the nanopipes shrink the distance between them becomes larger. The largest pore width between the nanopipes was found for the sample with the highest graphitic character (CMK-5 (20)). This sample also had the narrowest pores inside the nanopipes (Table 3).

The extra-framework species present in the pores of the matrix also influenced the OMC structure. As mentioned above, in pore sections where the extra-framework species were present, they blocked the entire cross section of the pores. It is very likely that

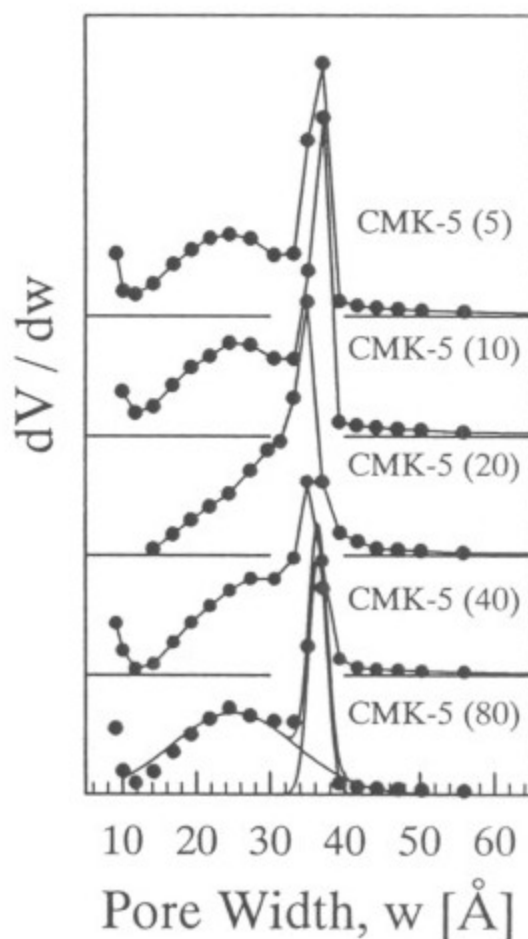


Fig. 1. OMC pore size distribution

