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Formation of SiC via carbothermal reduction of a carbon-containing mesoporous MCM-48 silica phase: a new route to produce high surface area SiC

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Abstract

Infiltration of carbon into mesoporous silica, used as a host structure, was peformed for the preparation of high surface area SiC. Mesopores of MCM-48 silica material were filled with pyrolytic carbon by chemical vapor infiltration using propylene as carbon precursor. Carbothermal reduction of the as-prepared SiO_2/C material in a temperature range 1250–1450 °C and in inert atmosphere led to an almost complete conversion into high surface area SiC material (120 m^2/g). Characterisations were performed by SEM, powder XRD, DRIFT spectroscopy and N_2 adsorption/desorption measurements on the SiC, SiO_2/C and the mesorganized carbon phase.

Keywords: D. Silicon carbide; High surface area; Catalyst support; Mesorganized carbon phase; MCM-48 silica

1. Introduction

The high-thermal conductivity, resistance towards oxidation, mechanical strength and chemical inertness of silicon carbide (SiC) gave to this material numerous applications in the field of biomaterials, high-temperature semi-conducting devices, lightweight/high strength structure and catalysis. In particular, for the latter application, it is a promising candidate for heterogeneous catalysis if it can be obtained with a medium surface area (20–100 m^2/g) and an appropriate pore size distribution. In particular, SiC has shown its efficiency as catalyst support for many reactions such as hydrodesulfurization [1], isomerization reactions [2], automotive exhaust-pipe reactions [3] and in the selective oxidation of H_2S into elemental sulphur [4]. Therefore, considerable attention has been focused on developing various methods for preparing SiC with a high-surface area. Several methods involving different reaction types such as solid–solid, gas–solid and gas-phase reactions have been already described in the literature [1,5–8]. Previous works [9,10] have demonstrated the possibility of preparing SiC materials starting from a C/SiO_2 artefact. In particular, it has been shown that carbon fibres covered with a silica layer produced by a sol-gel method can be a promising route for obtaining fine tubes of SiC after removal of the remaining carbon by gasification [9]. The corresponding overall carbothermal reaction taking place in inert gas may be written as follows:

$$SiO_2 + 3C \rightarrow SiC + 2CO \quad (1)$$

More details about this process are reported in Refs. 9 and 11. Moreover, it has been shown in the case of other types of SiO_2/C materials that the yield, the morphology and the structure of SiC obtained by reaction (1) depend strongly on the carbothermal conditions and the texture of the initial material components (silica, carbon) [9,10]. Within this framework, pyrolytic carbon can be infiltrated in various porous silica matrix used as inorganic templates. Among the investigated templates, zeolites and organized mesoporous silica molecular sieves have been tested. The latter solids display ordered and large pores with a constant diameter ranging from 1.5 to 30 nm and high-surface area up to 1500 m^2/g

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[12,13]. Depending on the synthesis conditions, a hexagonal phase (MCM-41), a cubic phase (MCM-48), or a lamellar phase (MCM-50) was obtained. A survey of the literature shows that various techniques may be investigated to incorporate the carbon species into the porous silica. The most common technique used is the chemical vapor infiltration or the carbonization of various carbon precursors like poly(acrylonitrile), poly(furfuryl alcohol). However, more recently, Ryoo et al. [14] successfully prepared a silica/carbon material using the MCM-48 silica matrix and sucrose as a carbon source. After chemical etching of the inorganic template, carbon with specific surface as high as 1380 m^2/g and with an ordered porous structure was obtained.

The present paper deals with the preparation of mesoporous SiC with high-surface areas. Mesoporous silica in the form of MCM-48 was loaded with pyrolitic carbon by chemical vapour infiltration. The as-made C/SiO_2 material as well as the carbon replica and the obtained SiC were characterised by different techniques. The determining parameters leading to SiC with high-surface area are described.

2. Experimental

2.1. Synthesis

2.1.1. MCM-48

The preparation of organized mesoporous silica was done following the procedure described by Ryoo and coworkers [14]. A colloidal silica (Ludox HS 40) was preheated to 70 °C and mixed to an aqueous sodium hydroxide solution (NaOH pellets, Prolabo 98%) under vigorous stirring. After 1 h, a clear sodium silicate solution was obtained with a molar composition 0.35 Na_2O: 1.4 SiO_2 : 20 H_2O. The latter was then added to an alcoholic solution of hexadecyltrimethylammonium bromide (HTABr) which is the organic template. The resulting gel, with a molar composition of 1.4 SiO_2: 1.0 HTABr: 0.35 Na_2O: 5.0 EtOH: 140 H_2O was transferred into a Teflon-lined stainless steel autoclave and heated under static conditions for 16 h at 140 °C. After filtration, the solid was washed with hot water and then dispersed in a Ethanol/HCl mixture. The as-synthesized solid was turned into mesoporous MCM-48 solid by removal of the organic template by calcination at 540 °C in air.

2.1.2. SiO_2/C material

The SiO_2/C material was prepared by chemical vapour infiltration of pyrolitic carbon within the porosity of the MCM-48 sample at 750 °C. The experiments were carried out in a conventional horizontal tubular furnace. Propylene (2.5 vol.%), in a stream of argon at atmospheric pressure, was used as the pyrolytic carbon precursor. In a typical experiment, the mesoporous ordered silica phase was placed in a fused silica crucible inside the isothermal zone of the furnace. The material was heat-treated at the desired temperature under argon. Once the reaction temperature was reached, the inlet gas was changed from Ar to the propylene/Ar mixture, and the reaction was carried out for ca. 12 h. Several depositions were carried-out and the as-above mentioned conditions are the most satisfactorily for obtaining the highest carbon content. The amount of pyrolytic carbon accumulated on the MCM-48 material was calculated by weighing the mesoporous solid before and after the deposition experiments. Pure carbon samples were obtained by etching of the silica/carbon material with hydrofluoric acid.

2.1.3. SiC material (heat treatment in argon)

The as-prepared SiO_2/C material (0.5 g) was deposited in an alumina crucible which was introduced in an alumina reactor. The system was then heated in an argon flow at atmospheric pressure up to the desired temperature reaction ranging from 1200 to 1450 °C. The sample was held at the final temperature for a time ranging from 5 to 16 h in order to reach an almost quantitative conversion of SiO_2 into SiC. Argon flowed at 20 l/h from the bottom of the reaction tube over the sample up to the top of the reactor where it was evacuated. The reactor was heated up to 1000 °C with a linear rate of 600 °C/h and from 1000 °C to the final temperature with a rate equal to 120 °C/h. The alumina crucible was previously carburized in order to avoid any reaction with the C/SiO_2 material. Moreover, the crucible containing the sample is linked to a microbalance (Mettler AE240) in order to follow the overall weight variation of the material as a function of reaction time. The treated sample was recovered and characterized after cooling down in argon.

2.2. Characterization

The formation of SiC was followed by X-ray powder diffraction (STOE STADI-P diffractometer, Cu $K_{\alpha 1}$ radiation ($\lambda = 0.1506$ nm)) and DRIFT spectroscopy (Brucker JFS 66). The amount of unreacted silica and carbon was determined gravimetrically by selective dissolution in a 40 wt.% HF solution and by gasification in air at 800 °C, respectively. After such treatments, the remaining solid consists essentially of SiC as confirmed by X-ray diffraction and DRIFT spectroscopy.

The nitrogen adsorption-desorption isotherms of the calcined samples were determined at 77 K on a Micromeritics ASAP 2010 apparatus. Prior to the measurments, the samples were outgassed at 250 °C during 16 h. The BET specific surface area (S_{BET}) was calculated using the BET equation [15] for relative pressures in the range $p/p_0 = 0.02$–0.2. The pore size distribution of the

samples were determined using the BHJ method [16] with a cylindrical pore model from the desorption branch of the hysteresis loop of the isotherm. It is worth noting that when these experiments were performed on SiC, the samples were previously oxidized and etched with HF in order to remove remaining carbon and silica respectively.

The morphology of the initial and final materials was observed on a scanning electron microscope (Philip XL 30).

3. Results and discussion

3.1. The starting materials: MCM-48 silica matrix, SiO_2 /C material and the carbon replica

The powder X-ray diffraction pattern of the silica matrix is characteristic of a MCM-48 silica phase [Fig. 1(a)] [17]. From the N_2 adsorption/desorption isotherms [Fig. 2(a)], a specific surface area close to 1240 m^2/g was measured. The obtained BJH pore size distribution confirms the mesoporous character of the material with a narrow pore diameter distribution around 2.5 nm [Fig. 2(b)]. SEM observations are typical for MCM-48 material [Fig. 3(a)]. Particles display a sphere like morphology with a size close to 1 μm. As previously reported [14], some particles with a "crystal shape" were also detected.

After chemical vapor infiltration of the carbon, a SiO_2/C material with a carbon content around 56 wt.% was obtained. Its XRD powder pattern is similar to that of the starting silica material except a small shift towards high *d* value and an intensity loss attributed to the pore filling with carbon [see Fig. 1(b)]. The nitrogen adsorption/desorption isotherms performs on this solid are reported on Fig. 4. A specific surface area close to 50 m^2/g was measured for the SiO_2 /C material which is, as expected, lower than the MCM-48 phase one. Indeed, the pore filling by the carbon species leads to a decrease of both pore volume and specific surface area. Nevertheless, according to the BJH method, it appears a fraction of pores seems not to be filled with carbon, since pores of 2.5 nm in diameter attributed to the starting silica material are still present.

The infiltrated carbon recovered after dissolution of the inorganic template of the SiO_2/C material in a hydrofluoric acid solution, named in this paper C replica, was also characterized. A powder XRD pattern

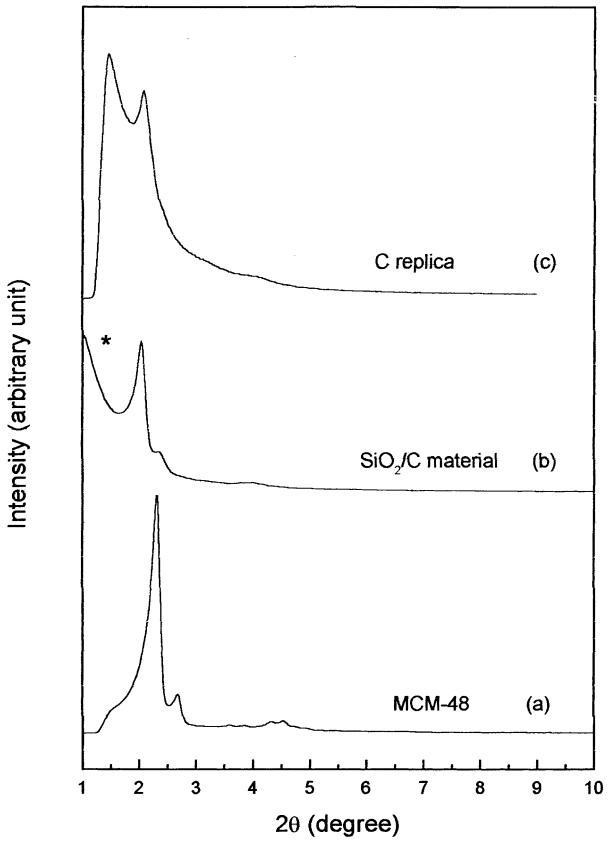

Fig. 1. X-ray diffraction patterns of MCM-48 matrix (a); SiO_2/C material (b) and C-replica (c).*: the drift of the baseline observed at low angle is due to a remaining of the direct X-Ray beam.

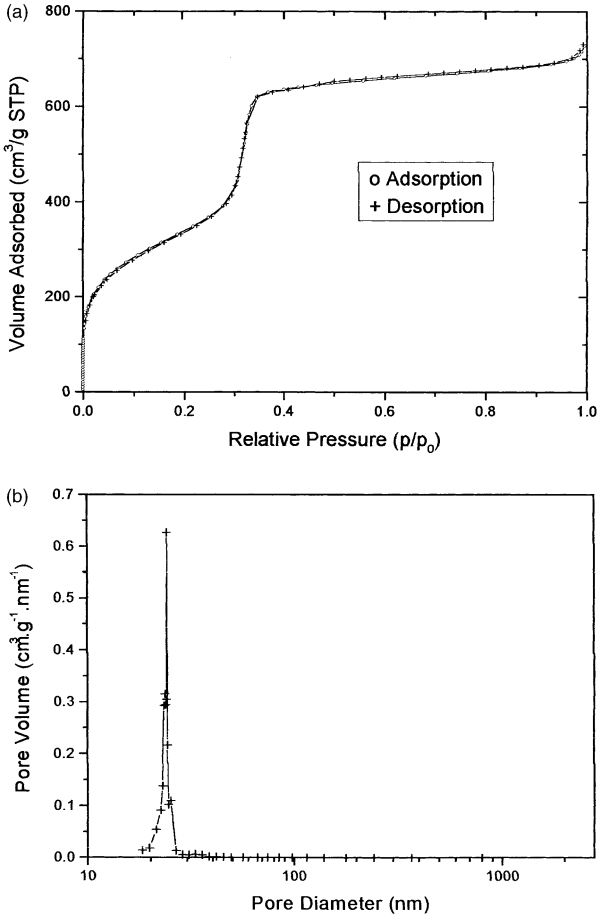

Fig. 2. Nitrogen adsorption/desorption isotherms of the MCM-48 matrix (a) and its BJH pore size distribution (b).

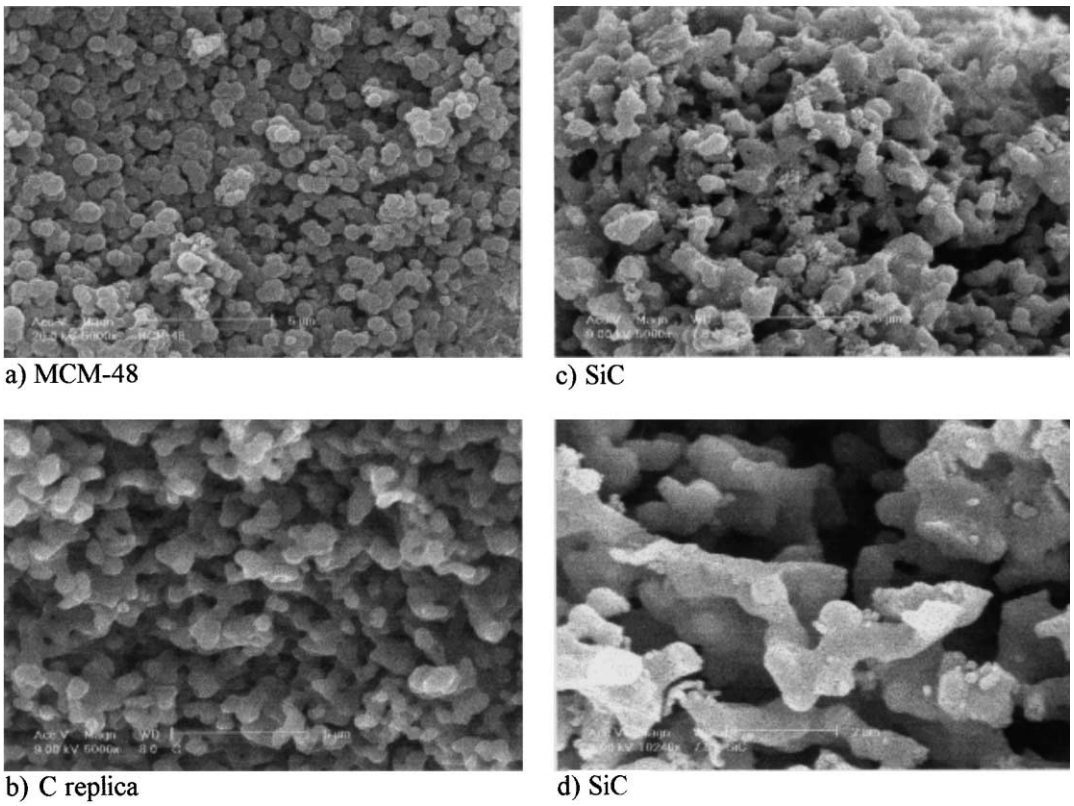

Fig. 3. SEM micrographs of MCM-48 matrix (a); C-replica after HF treatment (b) and SiC-phase (c) and (d).

of this C replica is given in Fig. 1(c). Two characteristic correlation peaks are detected indicating the presence of an ordered structure. N_2 adsorption/desorption isotherms and the corresponding BJH pore diameter distribution of this porous carbon sample are reported in Figs. 5(a) and (b), respectively. The isotherms are rather of type Ib-like [18] and characteristic of the presence of secondary micropores (pore size ranging from 1.5 to 1.8 nm). Moreover, as shown on the desorption curve, mesopores with a pore diameter of 3.2 nm can be detected. The carbon material displays a specific surface area of 980 m^2/g which is not so far from the value of the initial silica matrix. Moreover, the SEM picture indicates that this porous solid exhibits a morphology similar to that of the silica template [Fig. 3 (b)].

3.2. The SiC materials

Whatever the experimental conditions used and reported in Table 1, the as-made SiO_2/C material leads to the formation of crystalline silicon carbide (SiC) as revealed by XRD analysis. Indeed, the XRD pattern (Fig. 6) shows clearly that the cubic form of SiC (β-SiC) is the main product. However, the presence of a shoulder at $d = 0.26$ nm ($2\theta = 33.7°$) indicates that traces of SiC polytypes are also present. DRIFT-measurements (after removal of the unreacted carbon by oxidation) confirms that SiC is formed but reveals also that a small fraction of amorphous SiO_2 is still present after carbothermal reaction. Indeed, as seen in Fig. 7(a), the vibration band wave number at 824 cm^{-1} is characteristic of SiC and the band at 1085 cm^{-1} corresponds to the remaining silica. After treatment of the SiO_2/SiC material in HF solution, no trace of SiO_2 were detected as shown in Fig. 7(b).

The formation of SiC will be referred to the quantity of SiO_2 since silica is the limiting reactant according to reaction (1). The yield of SiC (η), will then be defined as the ratio of the amount of SiC formed to the theoretical amount deduced from complete conversion of SiO_2 into SiC according to Eq. (1). For the selected temperatures, the experiments were conducted up to the overall weight variation was negligible, indicating that the carbothermal reaction was probably ended. This is confirmed by the values of η, reported in Table 1, since an almost complete conversion of SiO_2 into SiC is reached for the

Table 1
SiC materials: experimental conditions and results [Yield (η), specific surface area (S_{BET}) and crystalline phase detected by XRD]

	Temperature (°C)	Duration (h)	Yield (η)	S_{BET} (m^2/g)	XRD results
Sample 1	1450	5	0.86	50	β-SiC
Sample 2	1350	10	0.93	62	β-SiC
Sample 3	1250	16	0.92	120	β-SiC

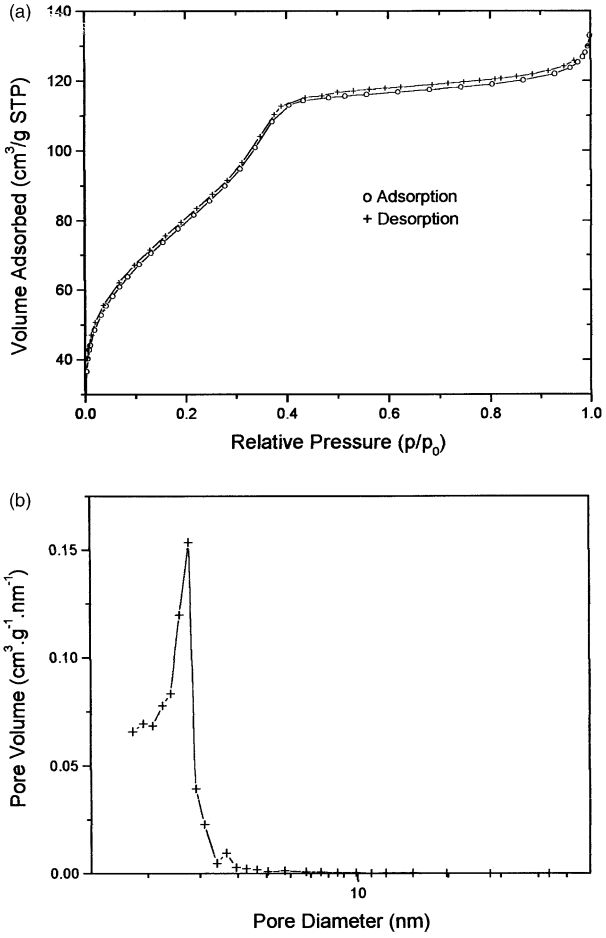

Fig. 4. Nitrogen adsorption/desorption isotherms of SiO_2/C material (a) and its BJH pore size distribution (b).

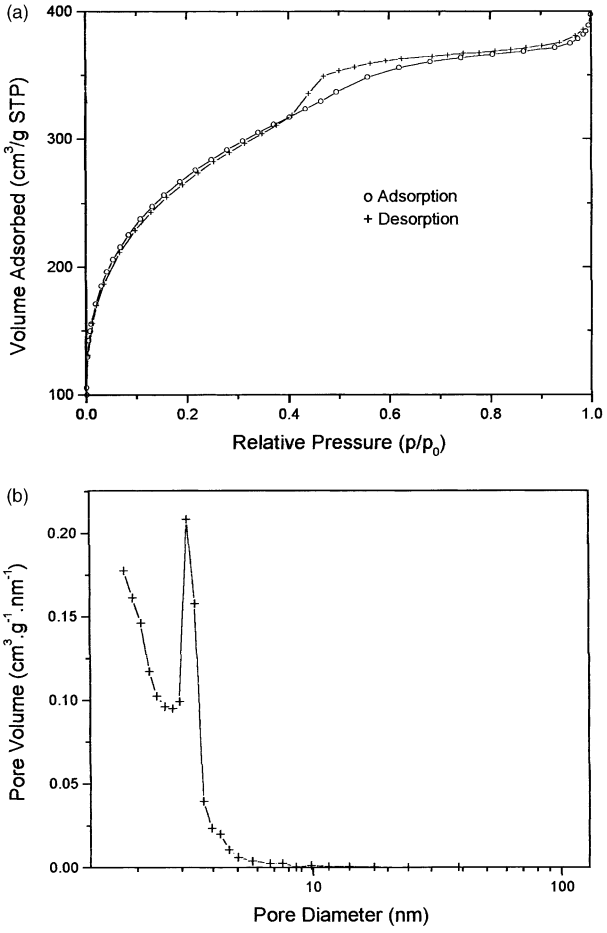

Fig. 5. Nitrogen adsorption/desorption isotherms of the C-replica (a) and its BJH pore size distribution (b).

studied samples. The differences observed between the three samples may be attributed to the experiment time which is shorter above 1250 °C.

For the three different SiC samples, significant specific surface areas, ranging from 50 to 120 m^2/g are reported in Table 1. It can be seen that the value of S_{BET} is noticeably influenced by the temperature of the heat treatment. Indeed, a lowering of the reaction temperature promotes a higher surface area (compare samples 1 and 3). Thus, a SiC material with a S_{BET} close to 120 m^2/g and with an almost complete conversion of SiO_2 to SiC was obtained after a heat-treatment at 1250 °C during 16 h. This value is quite comparable to that published in the literature i.e. 112 m^2/g [19] but in our case the yield is higher, 92% instead of 16%. It is worth noting that in the latter reference, SiC material was obtained starting from microporous carbon whereas in our study mesoporous silica was used.

As an example, the N_2 adsorption/desorption isotherms of Sample 3 are reported in Fig. 8. They correspond to a material with mesopores broadly distributed and could be attributed to an intergranular porosity. This fact means that the particle size of SiC materials is

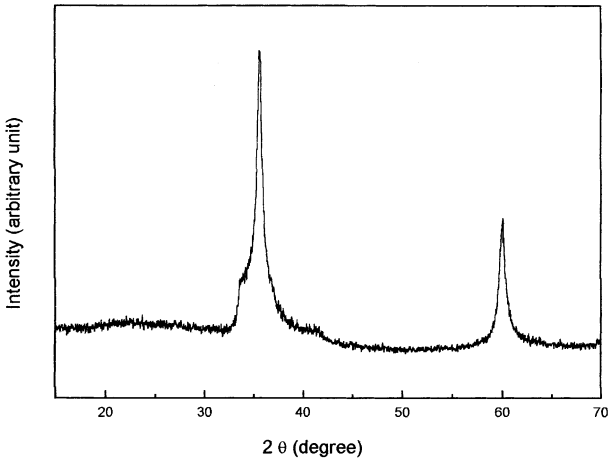

Fig. 6. X-ray diffraction pattern of the SiC-phase (Sample 3).

quite small. Assuming that the SiC particles are spherical with a density of 3.2 and taking into account the surface area determined from the BET analysis (120 m^2/g), a particle size close to 15 nm could be estimated. The pore volume measured is close to 0.4 cm^3/g if extended

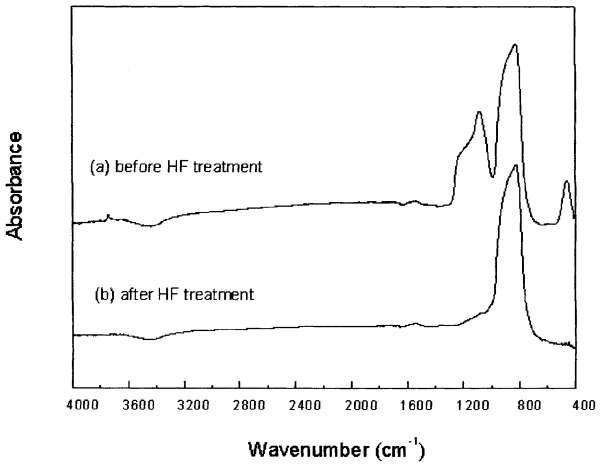

Fig. 7. DRIFT spectra of the SiC-phase, before (a) and after HF etching (b).

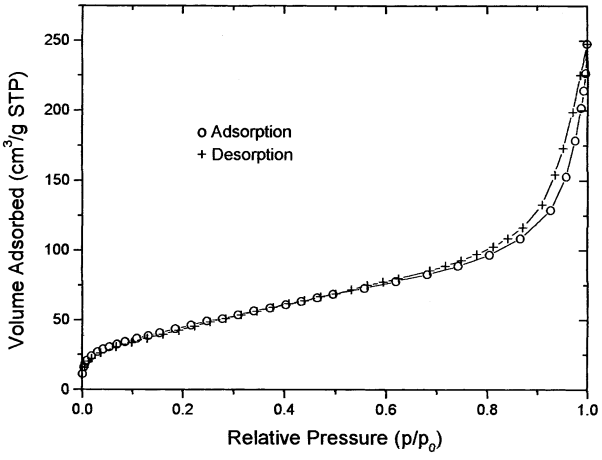

Fig. 8. Nitrogen adsorption/desorption isotherms of the SiC-phase.

to the intergranular porosity. According to t-plot analysis, no microporosity was detected.

The SEM micrographs of the SiC material are given in Fig. 3(c) and (d). It appears clearly that this material consists of aggregates with a size close to 0.25 μm. The smooth surface of the initial silica/C artefact was transformed into a rough surface which is a typical morphology for crystallized SiC.

4. Conclusion

The use of ordered mesoporous MCM-48 silica phase infiltrated with carbon species appears to be a promising route to produce porous SiC with high specific surface area (≈120m^2/g). The important pore volume and the pore connectivity of this type of silica matrix allow a high-carbon loading and a good diffusion of the gaseous carbon species during the chemical vapour infiltration treatment. The resulting high interface between carbon and silica leads to an almost complete conversion into SiC at temperature as low as 1250 °C. However, this original process has to be optimised in order to increase the mesoporosity of the SiC material and to keep the structure of the starting material.

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