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RESEARCH NOTE

The First Preparation of Silicon Carbide Nanotubes by Shape Memory Synthesis and Their Catalytic Potential

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Two main innovations are presented in this article. (1) The first reproducible synthesis of silicon carbide nanotubes of different internal and external diameters. The method used, the shape memory synthesis, is based on the gas–solid reaction between a vapor of SiO and nanotubes of carbon for the high diameters, and nanofibers of carbon for the small diameters. (2) A significant increase in the rate of a catalytic reaction (oxidation of H_2S in S) probably due to a microscopic increase of the partial pressure of H_2S inside the nanotubes, produced by condensation and microcapillarity, while the macroscopic partial pressure outside the tubes remains unchanged. This phenomenon could be extended to many other reactions, with polar gaseous reactants which are prone to condensation by capillarity at the usual temperatures of catalytic reaction, or with liquid phase reaction by an overconcentration of one of the reactants inside the tubes. © 2001 Academic Press

INTRODUCTION: THE SHAPE MEMORY SYNTHESIS

Some years ago we developed (1–4) a new method of preparing carbides that we called shape memory synthesis (SMS), reflecting the fact that the original macrostructural features of a solid (its macroscopic shape) are retained after synthesis. For the preparation of SiC, this method consisted of the generation of SiO vapor by heating a Si/SiO_2 mixture at 1200–1350°C, using a method similar to that developed by Kennedy and North (5); this vapour was then pumped through a shaped carbon or activated charcoal form. The gas–solid reaction between SiO and C occurred at a lower temperature (1000–1250°C) and produced β-SiC material having the same shape as the initial carbon material, as shown in Fig. 1, with a high surface area appropriate for catalytic applications. The CO formed as a coproduct was rapidly pumped out of the reaction zone, pushing the equilibrium toward SiC formation.

For industrial applications as supports for catalysts, many different shapes of SiC have been obtained by a slightly modified method where SiO was generated inside the carbon form (6); it was then possible to prepare big solids in large amounts (see Fig. 2).

It is remarkable that an amorphous material, the activated charcoal, was transformed into a crystalline one, β-SiC, although containing defects, without losing its macroscopic shape. This can be explained only if the reaction was a succession of microscopic steps, where each SiO molecule was reacting one by one with two carbon atoms, exchanging one carbon atom for one Si atom, avoiding the collapse of the macroscopic structure, the carbon leaving as a CO molecule, creating the porosity at the origin of the high specific surface area.

SYNTHESIS OF SiC MICROTUBES FROM C MICROFIBERS

We then decided to exploit this concept of shape memory synthesis to explore the domain of tubes. The microscale was our first aim as it was relatively easy to obtain microfibers of carbon, generally prepared from carburized polymer fibers. Using the same reactor and conditions as those used to obtain the other shapes, carbon microfibers with a mean diameter of 20 μm (Fig. 3a) were reacted with SiO vapor. According to the duration of the reaction the surface of the fibers was more or less deeply transformed into β-SiC and this degree of conversion governed the thickness of the porous SiC layer (7). The remaining unreacted carbon located at the heart of the composite fiber was mildly burnt off, leaving a micropipe or tube of pure β-SiC (Fig. 3b).

These microtubes of SiC were used as a support for a molybdenum-based catalyst for alkane isomerization and compared under the same reaction conditions to the same molybdenum supported on the coarse grains of SiC shown in Fig. 1, also prepared by SMS. The catalytic tests demonstrated that in terms of both activity and selectivity, the two

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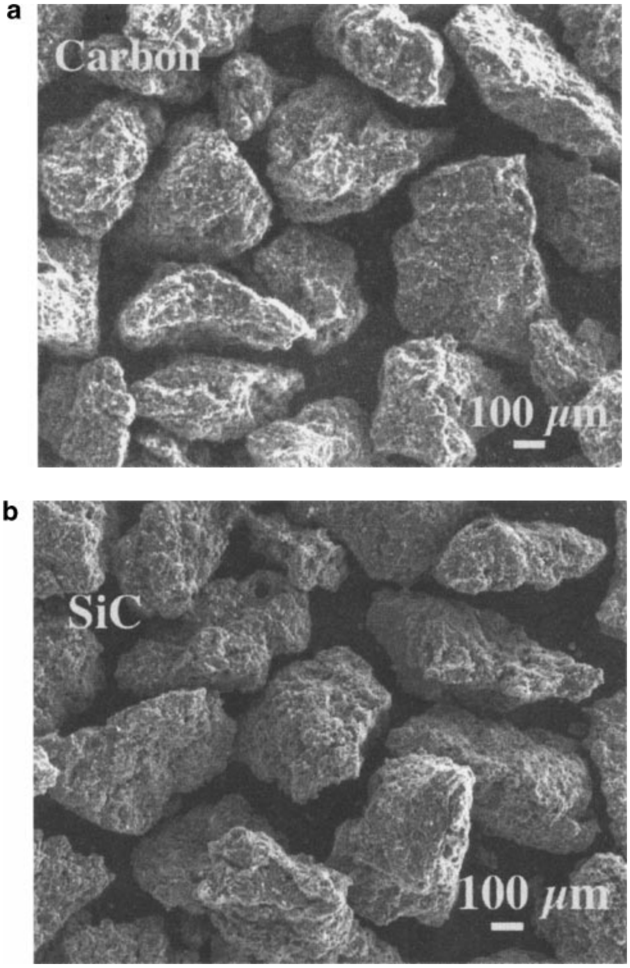

FIG. 1. SEM of (a) starting activated charcoal and (b) equivalent final β-SiC obtained by shape memory synthesis (SMS).

catalysts were identical, meaning that there was no shape selectivity induced by the new support (8). In order to observe such a shape selectivity, we thought that it was probably necessary to decrease the internal diameter of the SiC tubes and consequently to explore the domain of the nanosize instead of the microsize.

SYNTHESIS OF 100-NM-DIAMETER SiC NANOTUBES

A double challenge had to be tackled in order to obtain SiC nanotubes. First it was necessary to have enough carbon nanotubes or nanofibers (at least 1 g) as starting material to obtain a significant amount of SiC to be characterized and tested in a catalytic reaction. Second, the conditions of the reaction between SiO and C had to be fine-tuned because such nanostructures, the starting carbon material and the final SiC structure, were not expected to be as stable as the bigger ones.

Fortunately, it was possible to purchase significant quantities of carbon nanotubes directly from Applied Science in the USA, although these had a relatively large mean diameter of about 100 nm. This material was of good quality, as shown by scanning electron microscopy in Fig. 4, even with differences in tube shapes (open or similar to bamboo), and the presence of bulky carbon particles could be observed by transmission electron microscopy, as shown in Fig. 5. These tubes were submitted as such to the SiO vapor at 1200–1250°C. The product of the reaction, about

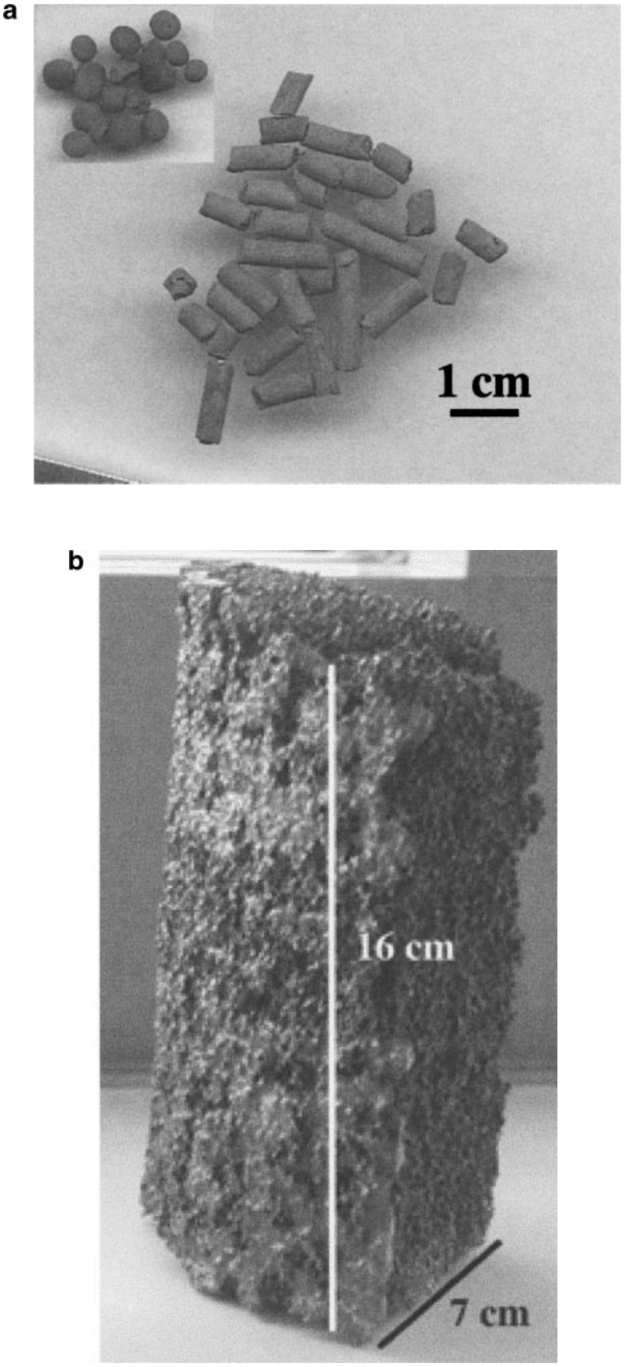

FIG. 2. Different shapes of β-SiC.

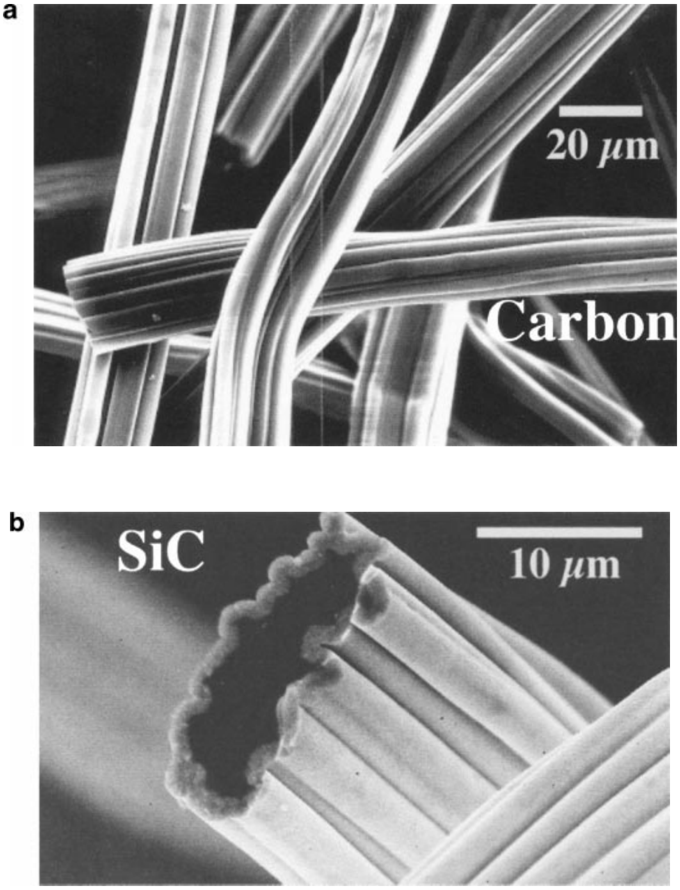

FIG. 3. (a) Starting microfibers of carbon and (b) final microtubes of SiC obtained by SMS.

10 g, was calcined at 600°C in order to eliminate the remaining unreacted carbon, if any, and physical characterizations were performed on this final material. The SEM pictures reproduced in Fig. 6 clearly show that the nanotube shape of carbon in Fig. 4 was preserved and that most of the tubes had an open end. The internal diameter was measured to be between 30 and 100 nm (average 90 nm), which means that the diameter of the starting carbon nanotubes has not been modified by the reaction. X-ray diffraction unambiguously confirmed that this final material was pure β-SiC (Fig. 7), relatively well crystallized. As far as we know, this is the first time that such small tubes of SiC have been produced, since Niu and Moy (9), using our method, have only produced nanofibrils (?) of β-SiC.

CATALYTIC OXYDATION OF H_2S ON NiS_2/SiC NANOTUBES (50–100 nm)

We next decided to check whether such a small diameter could have a specific role in a catalytic reaction that has been well studied by our group, i.e., the direct oxidation of H_2S by O_2 at low temperature (60°C), following the equation:

$$H_2S + 1/2O_2 + \text{steam}\,(25\,\text{vol\%}) \rightarrow S + H_2O.$$

This is an important industrial reaction for the protection of the environment, used to clean the tail gas of sulfur plants (Claus process) containing between 0.2 and 1% of unreacted H_2S, and to avoid its destruction by oxidation into SO_2. The release of SO_2 in the atmosphere is at the origin of acid rain. Many cleaning processes are commercially applied (10), among them those exploited by Elf/Lurgi, Sulfreen, and Doxosulfreen, using supported Ni catalysts working under, or close to, the conditions that we have studied (11, 12).

The use of silicon carbide as a support for the nickel sulfide active catalytic phase has been a great improvement in this process because of the very high activity and selectivity observed when these new catalysts were introduced (100% of H_2S conversion and 100% of selectivity, or 0% of SO_2, an undesired by-product when the oxidation reaction is not selective and partially oxidizes S into SO_2). But more significant was the stability of this new SiC support during the many cycles of reaction–regeneration, where conventional oxidic supports become sulfated or react with Ni, leading to an irreversible deactivation of the catalyst. At these low temperatures, below the sulfur dew point, the elemental sulfur formed by the reaction remains on the catalyst and needs to be evacuated by stopping the reaction after a certain time and heating the reactor above the S boiling point (ca. 220°C). Vapors of sulfur are condensed and recovered outside the reactor. The catalytic bed is then ready to restart for a new cycle. The very high and long activity of the SiC-supported catalyst was explained by the heterogeneity of the SiC surface, hydrophilic zones supporting the active phase and constantly being washed by a water film carrying the elemental sulfur formed on the particles of the active phase toward hydrophobic zones of the surface, where sulfur was stored after the rupture of the water film (13). This mechanical process explained well the capacity for storage of large amounts of solid sulfur, up to 100 wt% without deactivation of the catalyst.

Figure 8 shows the H_2S conversion in percent (dark circles) and the amount of S (open circles) accumulated in the catalyst bed in weight percent (where 60% means 100% of catalyst + 60% of S in the bed) as a function of time on stream. The reaction was carried out at 60°C, on Ni (5 wt%)/SiC grains with 0.2 vol% of H_2S, 0.32% vol% of O_2, 20 vol% of steam, and the balance He to atmospheric pressure. The flow rate was established to maintain a constant weight hour space velocity (WHSV) of H_2S of 0.007 h^{-1}, i.e., WHSV = weight of H_2S per weight of catalyst per hour. These conditions can be observed in a real industrial reactor. The catalyst was immediately highly active, with a total conversion of H_2S and without detectable SO_2 formation (<5 ppm), and these performances

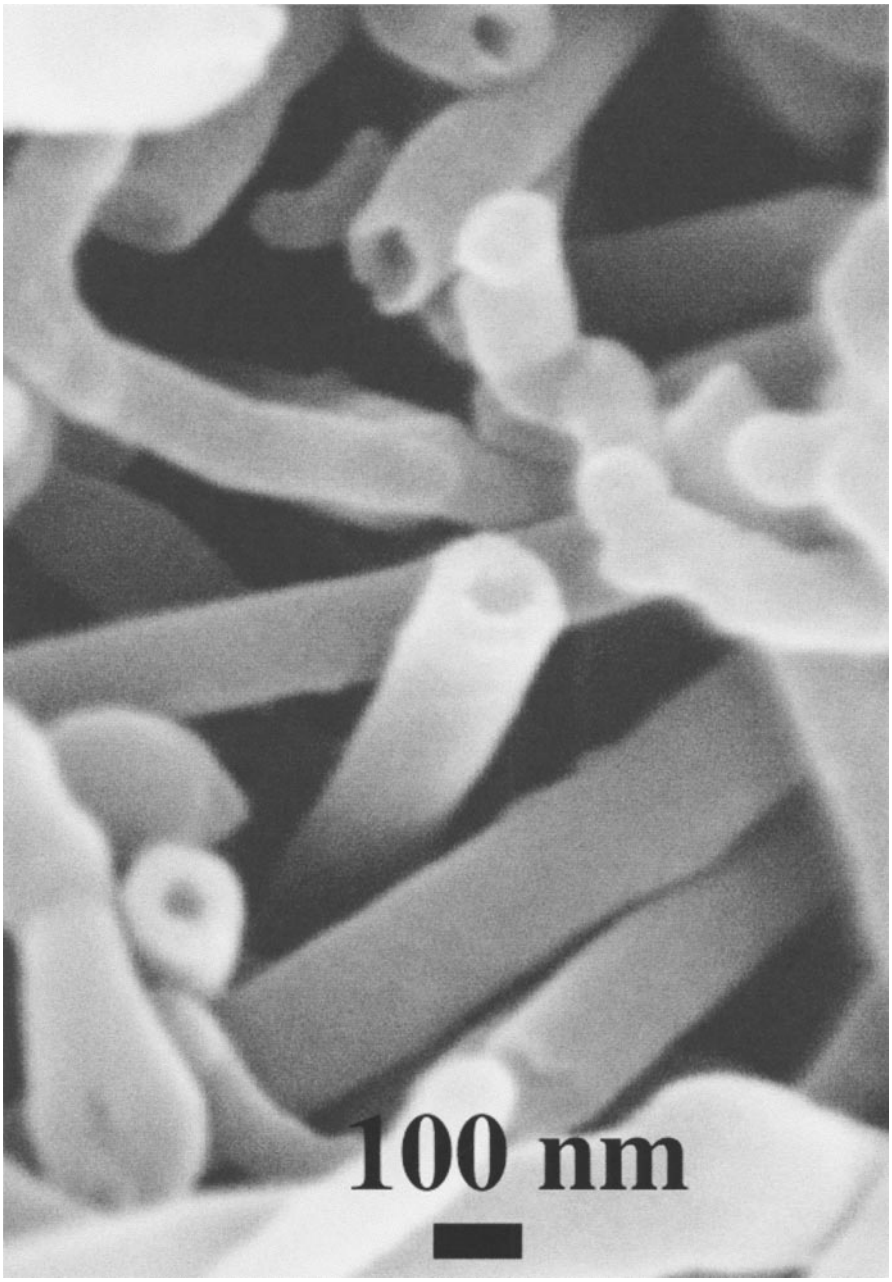

FIG. 4. SEM picture of carbon nanotubes from Applied Science.

remained constant for more than 100 h on stream. This can be compared with results obtained using alumina or silica conventional supports where a similar activity was observed only after 8 h, followed by rapid deactivation due to the burial of the active phase below the accumulated solid sulfur. After 100 h on stream the solid S stored on the surface amounted to 60% of the initial weight of the catalyst.

The same catalyst was then tested at a much higher WHSV, 0.02 h^{-1}; under these conditions the maximum conversion never reached 100%. It was only about 95% for a short time, 5 to 6 h, and then the conversion quickly decreased to zero after 40 h on stream with about 50% of solid S stored on the surface.

A test was then performed under exactly the same conditions (5 wt% Ni and WHSV = 0.02 h^{-1}) on a catalyst supported by the SiC nanotubes which have been described above. There was no difficulty in impregnating the support with a water solution of nickel nitrate. After drying and calcination at 450°C, it appeared that most of the nickel oxide was located inside the tubes as no NiO particles were found outside as evidenced by TEM analyses. It was not possible to look inside the tubes as SiC with such a thickness

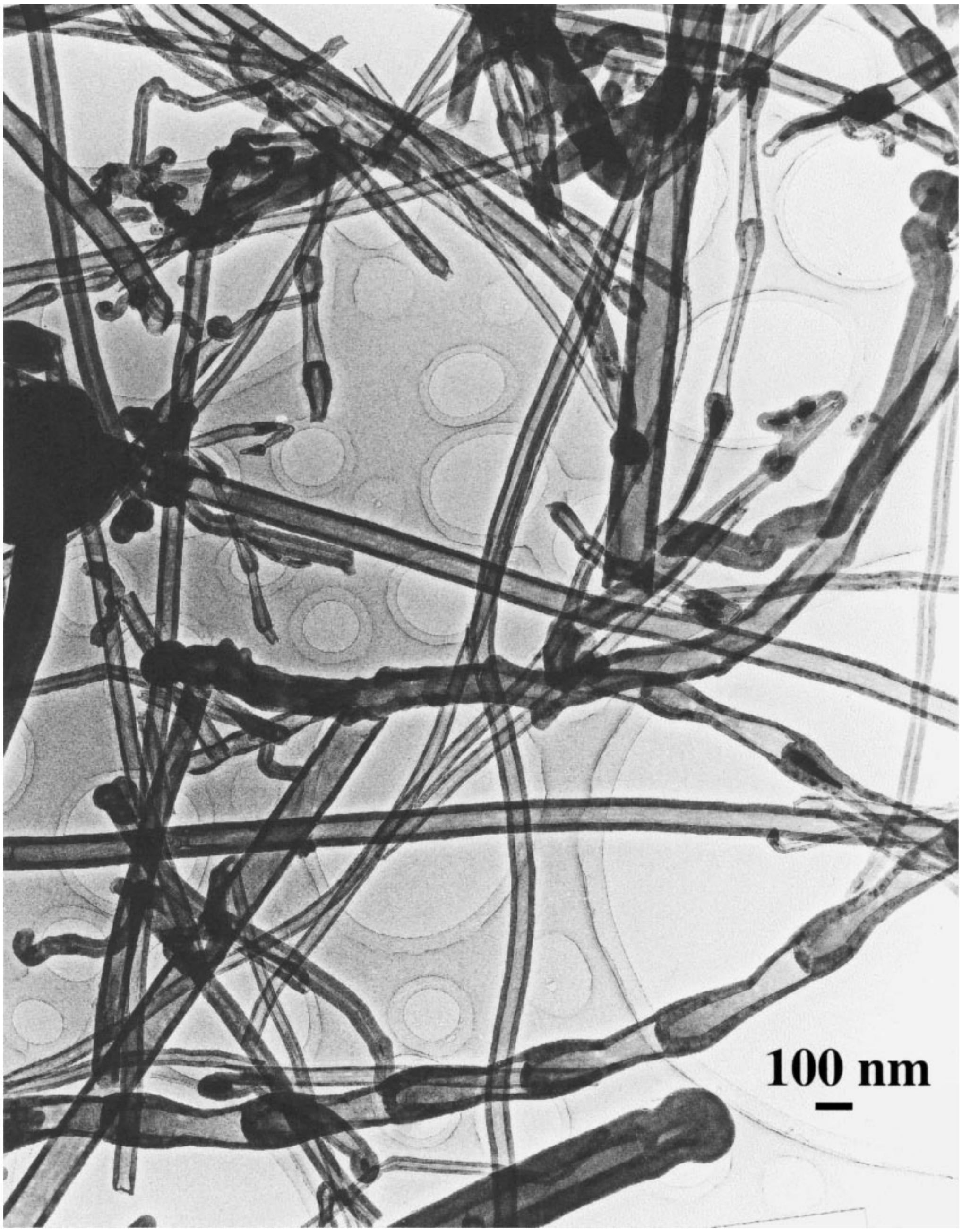

FIG. 5. TEM picture of carbon nanotubes from Applied Science.

is not transparent to electrons. A comparison between the reactivities of the two catalysts is shown in Fig. 9.

The catalyst supported on nanotubes is obviously very active and its capacity for storing solid S is outstanding, more than 200% of the initial weight of the catalyst without loss of any activity. This high storage capacity can easily be understood and does not need new hypotheses. Considering that outside the tubes the void volume is much larger than that outside the pores of a conventional mesoporous material, such as SiC grains, very large amounts of S can be transported outside the tubes by the water film process described above and stored in the void volume before the catalyst becomes loaded with S.

The WHSV was temporarily increased to 0.043 h^{-1} and the conversion dropped to 94%, identical to the conversion observed on the SiC grains but with a WHSV of 0.02 h^{-1}. One could say that the SiC nanotubes as a support were roughly 2 times more efficient than the grains.

At this stage of the study only hypotheses can be brought to explain these results. Baker *et al.* have proposed, when

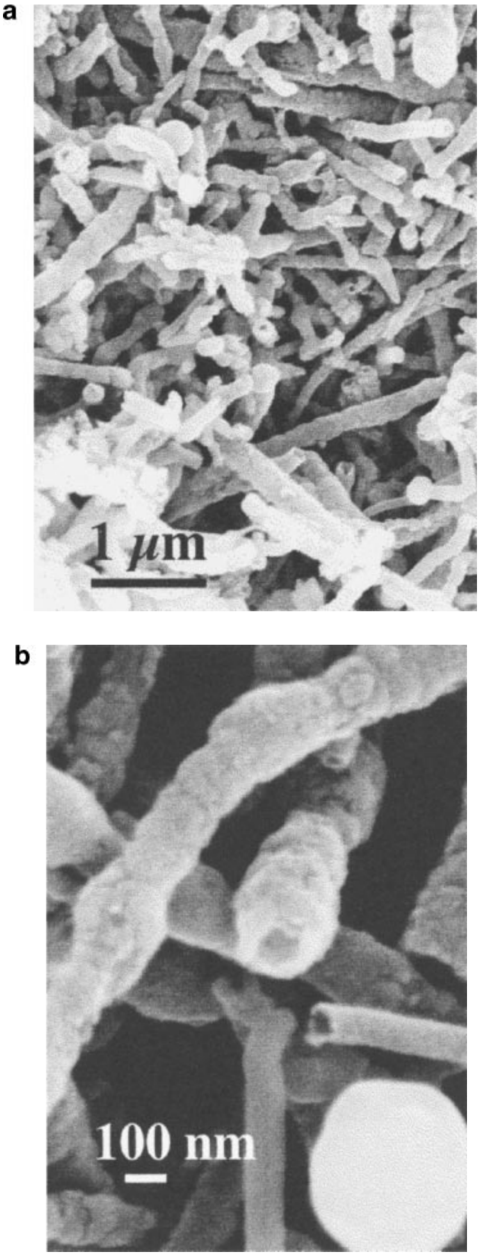

FIG. 6. SEM pictures of SiC nanotubes obtained by SMS.

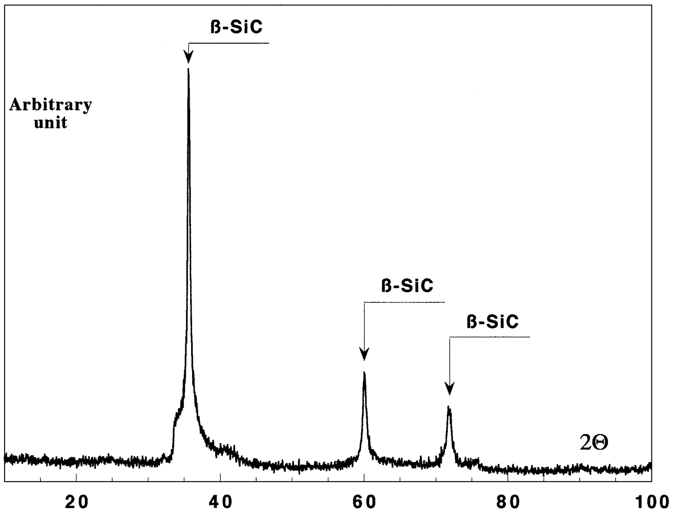

FIG. 7. X-ray diffractogramme of SiC nanotubes obtained by SMS.

studying the catalytic hydrogenation of butadiene (14) or crotonaldehyde (15) on Ni supported on carbon nanofibers, that the extra activity when compared to that of a conventional support was due to the presence of a different crystalline structure of the metal particles induced by the nanofiber surface. This new structure was supposed to be more suitable as a catalytic active phase than the normal structure obtained on a conventional support. As mentioned above, most of the NiS_2 material (particles?) was located inside the non-electron-transparent SiC nanotubes and thus could not be directly observed; only EDAX performed on individual fibers showed that they contained Ni (see later). The very few particles of NiS_2 observed outside the tubes were similar in terms of structure to conventional NiS_2 found on SiC grains (16). If Baker's explanation cannot be rejected in our experiments, no evidence is in favor of it. We prefer to put forward a new idea. The conversion on the catalyst supported on SiC grains was significantly decreased when WHSV was increased; this is a normal kinetic behavior, the contact time becoming too short to allow all the H_2S molecules to adsorb on the active sites and react. Still, very conventionally, such a conversion decrease can be mathematically compensated by an increase in the partial pressure of the reactant, here H_2S, if α is positive in the

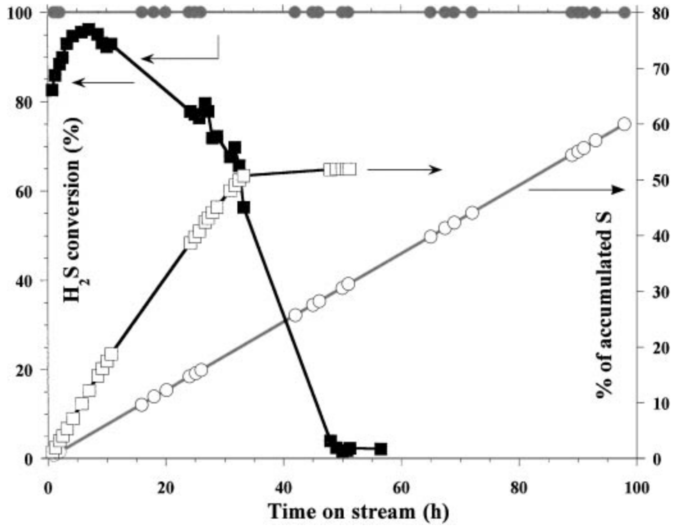

FIG. 8. H_2S oxidation on Ni supported on SiC grains at two different WHSVs, 0.007 (circles) and 0.02 h^{-1} (squares), at 60°C and $H_2S/O_2 = 2.5$.

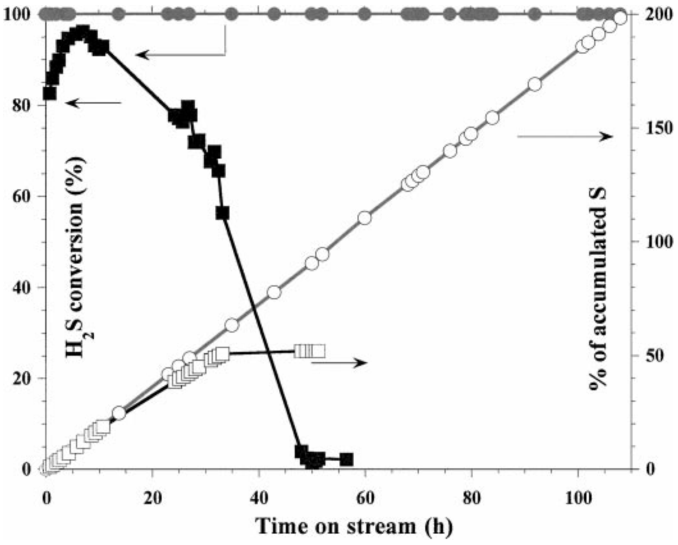

FIG. 9. H_2S oxidation on Ni supported on SiC grains (squares) and SiC nanotubes (circles) at WHSV $= 0.02\ h^{-1}$, at 60°C and $H_2S/O_2 = 2.5$.

equation below as shown by Pieplu *et al.* (17),

$$r = Kp[H_2S]^{\alpha}/\mathrm{WHSV}$$

where r is the rate of the reaction, K a constant including T°, and $p[H_2S]$ the H_2S partial pressure.

Now let us suppose that by microcapillarity the partial pressure of H_2S is greatly increased inside the SiC nanotubes; this would provide a kinetic explanation for the strong increase in conversion observed on the catalyst supported on these tubes. The rate of the reaction would be increased by a microscopic or nanoscopic pressure increase, while at a macroscopic level the apparent partial pressure of H_2S would remain unchanged. This concept is of the same nature as that proposed by different authors using carbon nanotubes as hydrogen storage devices (18, 19), but in nanotubes of a different elemental composition (SiC instead of C), and more importantly, with a molecule containing a permanent dipole, H_2S, which is not the case with H_2. Many new experiments and models should be done to prove this idea. One of them involves preparing new SiC nanotubes of smaller diameter and checking their ability to maintain this interesting property. Complexity can, however, arise due to parasite microdiffusion effects masking the capillarity phenomena.

SYNTHESIS OF 5–10-nm-DIAMETER CARBON NANOTUBES

In order to obtain smaller diameters for the SiC nanotubes, we had to prepare smaller carbon nanotubes or nanofibers as starting material to be reacted with SiO vapors. In a first attempt and according to previous work (20), Fe, supported for the first time on SiC grains, was used as a catalyst. For extensive information on carbon nanostructures see Ref. (21). About 3 g of solid black product was recovered after 5 h of reaction (see conditions in the legend of Fig. 10). We found that under our conditions ethane was the most appropriate gas, probably because it provides the right balance of carbon and hydrogen on the surface of the metal particles. The nature of the gas was important to obtain high yield of product. Jaeger and Behrsing (22) have shown that the nature of the gas does not affect the nature of the nanotubes but can influence the growth rate, which is consistent with our finding. A one-day process of purification (ultrasound, biphasic separation, flotation, and drying), followed by an aqua regia treatment under reflux for one night to dissolve the last traces of Fe, provided 2 g of ultrapure multiwalled nanotubes. The size of these tubes was homogeneous, with an internal diameter ranging from 5 to 10 nm and walls made of 8 to 10 graphene layers separated by a distance of 0.34 ± 0.01 nm. Figure 10 is a good representation of these tubes. Most of them had a open internal void, sometimes closed by an arch of two graphene sheets. These tubes were almost always open at their two ends (not shown in Fig. 10). This material was used as the starting product to be reacted with SiO vapor, but we never managed to obtain SiC nanotubes because the 8 to 10 layers of carbon, attacked externally and internally by the hot SiO vapor, were too fragile to resist this treatment, and

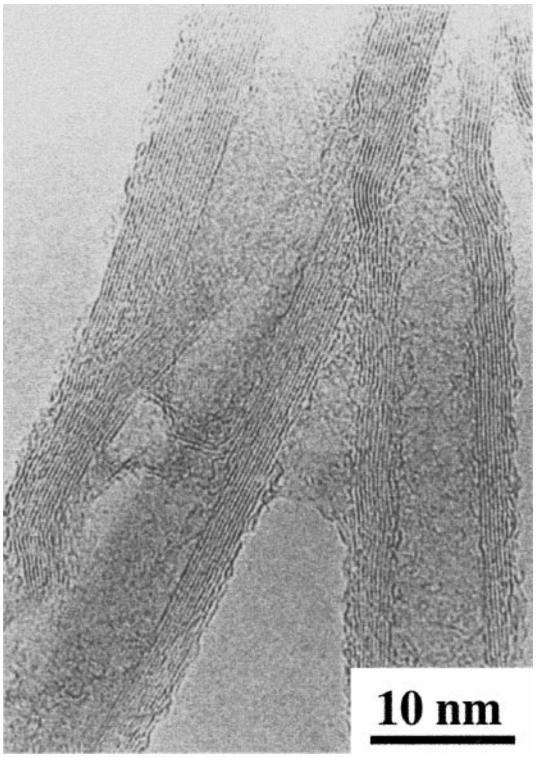

FIG. 10. Carbon nanotubes obtained by reaction of an ethane/H_2 70/50 mixture, on 3 g of Fe/SiC 20 wt%, at 750°C, in a downflow reactor at atmospheric pressure.

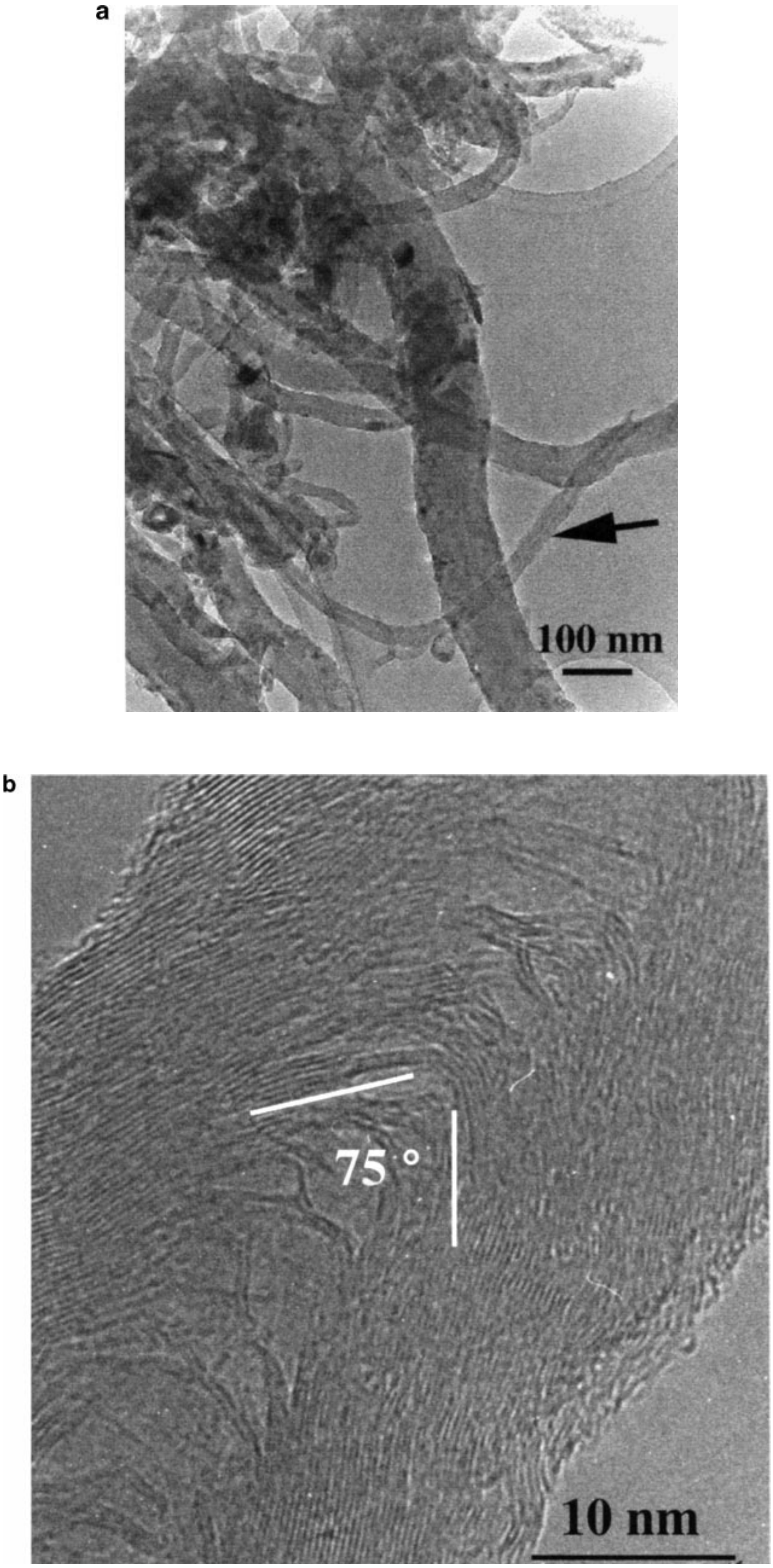

FIG. 11. (a) Carbon nanofibers obtained by reaction of an ethane/H_2 70/50 mixture, on 3 g of Ni/SiO_2 27 wt%, at 650°C, on a flat bed, at atmospheric pressure and (b) higher magnification on the fiber marked by the arrow in (a).

we only obtained very fine SiC powder. Probably, 8 to 10 layers did not provide enough carbon atoms to maintain the solid structure through the step-by-step process of the shape memory synthesis. In order to improve the mechanical resistance of the starting materials, we decided to prepare carbon nanofibers.

SYNTHESIS OF 10–100-nm-DIAMETER CARBON NANOFIBERS

According to the work published by different groups (23, 24), Ni metal seems to be the best catalyst to initiate the synthesis of carbon nanofibers, mainly in a herringbone shape, from gas mixtures of hydrocarbon and hydrogen. Typically 3 g of a highly dispersed Ni/SiO_2 catalyst, containing 27 wt% Ni and prepared by a sol–gel process, was placed as a flat bed in a horizontal reactor. A mixture of 70 cm^3/min of ethane and 50 cm^3/min of H_2 was reacted on this catalyst for 6 h at 650°C. About 4 g of a black powder was recovered from the top of the bed. After separation by flotation, a soda treatment at 80°C for 12 h to dissolve the traces of remaining silica, and an aqua regia attack for another 12 h under reflux, 3.6 g of pure carbon nanofibers was obtained (see Fig. 11a). The diameter of these fibers varied from 10 to 100 nm, with an average of 30 nm. A 30 nm diameter fiber was selected in the TEM picture (see arrow in Fig. 11a) and enlarged 25 × to observe its fine structure at high resolution. The graphene planes in a herringbone pattern were sometimes connected in the middle of the fiber, forming a closed angle of about 75° (Fig. 11b). The distance between the planes was found to be 0.34 ± 0.01 nm. This is consistent with what has been found by other authors (24, 25).

Having obtained large amounts of these fibers, we decided to treat them in the same way as the microfibers from Fig. 4, i.e., reacted with SiO vapor for 7 h at 1250°C.

SYNTHESIS OF 10–80-nm-DIAMETER SiC NANOTUBES

About 10 g of material was obtained after reaction and no further treatment was carried out. A low-magnification TEM picture (Fig. 12) shows that the distribution of diameters, from 10 to 100 nm (mean diameter 30 nm), of the carbon fibers was maintained in the new material, but was accompanied by a non-negligible amount of powder, probably SiC powder resulting from the destruction of some carbon fibers during the reaction. But much more interesting is the fact that the carbon fibers had been transformed into nanotubes open at their ends as also shown in Figs. 13a and 13b. It was confirmed by EDAX (corners in Figs. 12 and 13) that both the big and the small nanotubes were made of SiC (XRD does not give unambiguous proof because of the presence of the powder).

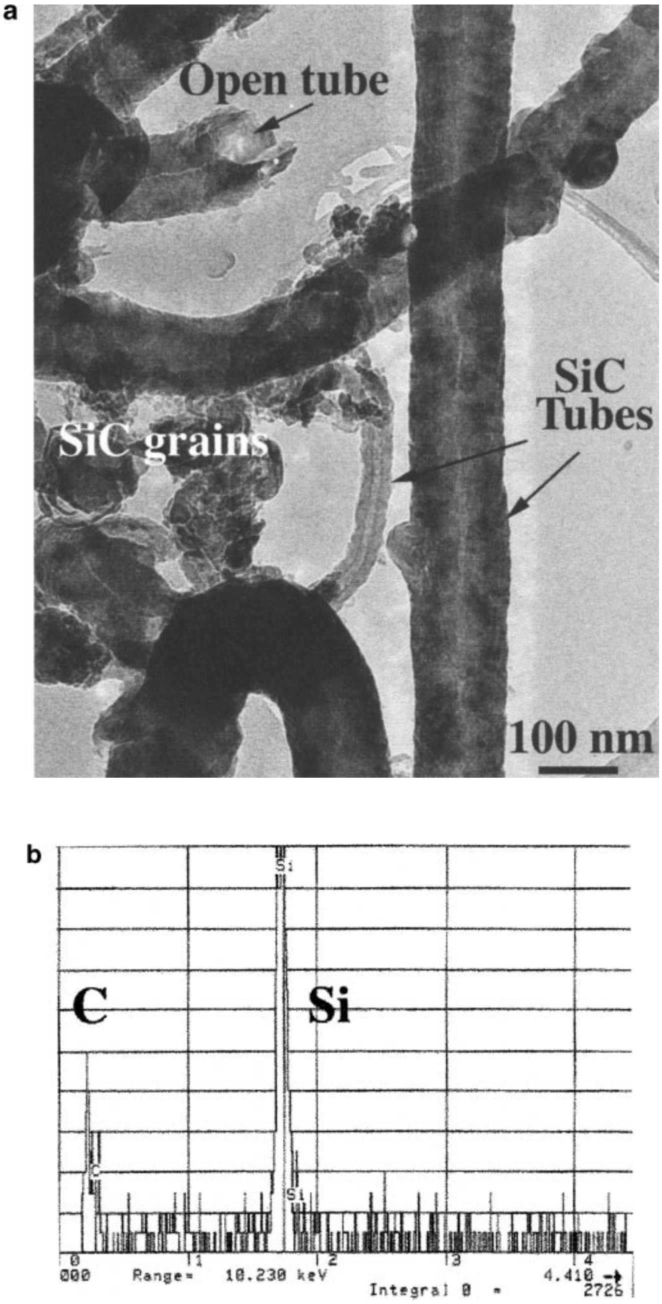

FIG. 12. SiC nanotubes obtained by SMS from carbon nanofibers.

The mechanism of formation of such nanotubes should involve not only an attack on the carbon fibers by SiO vapors but also migration of the internal carbon toward the surface, attracted by the presence of an oxidizing agent, SiO; this phenomenon has already been observed in the preparation of microtubes of Mo and V carbides (8). This explains why calcination was not necessary to open the tubes. The average internal diameter of these nanotubes was 15 nm.

The enlargement in Fig. 13b shows fringes at distances of 0.36 ± 0.01 nm, parallel to the axis of the tubes. If one compares these results to what was observed in Fig. 11b, the transformation of the carbon nanofibers into SiC

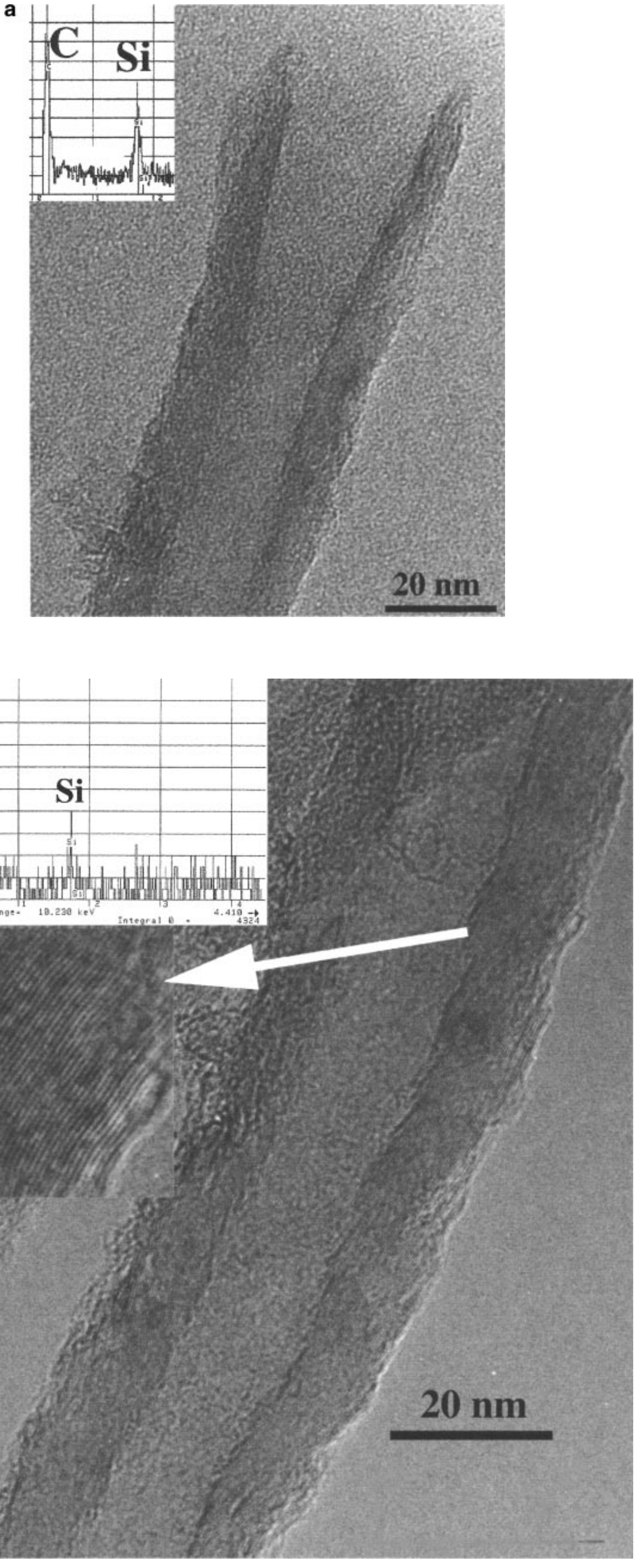

FIG. 13. SiC nanotubes obtained by SMS from carbon nanofibers.

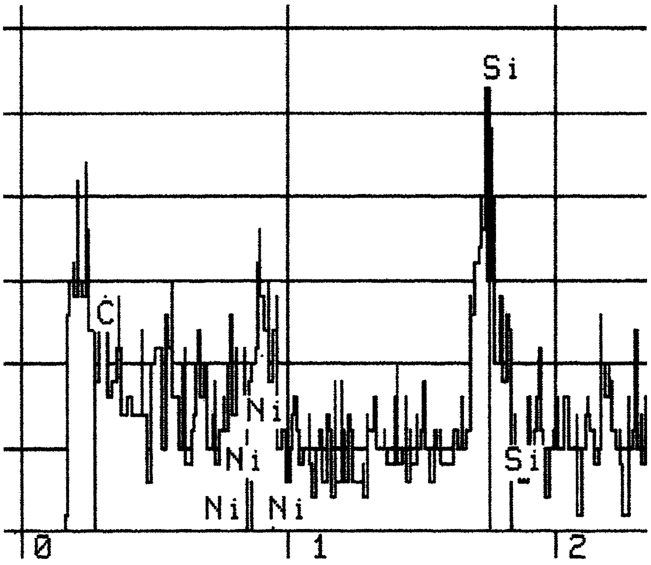

FIG. 14. EDAX obtained in the HRTEM chamber, on an isolated SiC nanotube of 15 nm internal diameter, after impregnation with a water solution of nickel nitrate (5 wt%), activation under H_2S, and 100 h of reaction.

nanotubes, at least for the small diameters, has as a consequence the opening of the 75° angle and the formation of layers of SiC by expansion of the distance between the carbon layers from 0.34 to 0.36 nm, which is consistent with the distance between two planes of C in β-SiC of 0.359 nm.

These SiC nanotubes were impregnated in the same way as the preceeding catalyst with a water solution of nickel nitrate. A catalytic test was then performed under exactly the same conditions as those used previously (5 wt% Ni and WHSV $= 0.02\ \mathrm{h}^{-1}$), showing a total conversion of H_2S, but with a smaller capacity for storing S, due probably to there being a smaller void volume around the nanotubes because of their smaller size. An estimation of the rate by varying the WHSV to obtain 95% conversion showed that this new system was as active as the system made with larger nanotubes.

It was not possible using high-resolution TEM to find any particles of Ni or NiS_2 outside the tube, but the EDAX analysis performed on an isolated microtube (Fig. 14) was unambiguous as to the presence of this metal, very probably inside. If Ni had been found outside, the effect of the microcapillarity would have been inoperative on the catalytic reaction. This new finding on a different sort of SiC nanotubes showed that the first catalytic results obtained on the bigger tubes were not an accident, but were due to the structure of the support. Not only the structure but also the nature of the support were important. The carbon nanotubes, the starting material of the big SiC nanotubes, were also impregnated with Ni and tested for the same reaction. They showed a high activity, but not as high as with SiC nanotubes. This probably meant that the capillarity phenomenon was also acting in the carbon tubes but that the NiS_2 particles, the active phase, were not as well dispersed as on SiC because of the hydrophobic character of carbon, which prevents a good anchoring of the particles during the impregnation step.

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