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A novel necklace like structure assembled with MCM-41 and carbon nanotubes

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Abstract

We report the synthesis of MCM-41 particles which are pierced by carbon nanotubes forming a necklace like structure. We obtained these nanostructures using conventional sol–gel process for mesoporous MCM synthesis, incorporating highly disperse carbon nanotubes. This necklace like structure can be treated to eliminate the surfactant from mesoporous MCM particles obtaining thus a interconnected particles with high surface area ($\sim$1000 $m^2\,g^{-1}$), and calcination treatment under air can also be used to obtain the SiO_2 structure free from carbon, maintaining the necklace structure. Some applications of these nanocomposites are suggested in this work.

Keywords: Nanostructures; Sol–gel synthesis; Scanning and transmission electron microscopy

1. Introduction

MCM-41 is silica based mesoporous material with typical BET surface areas higher than 1000 $m^2\,g^{-1}$ [1] and due to its high surface area MCM-41 has been extensively studied for catalytic applications [2] and as a basis for sensor development [3]. As is known, spherical particle morphology of MCM-41 is tuneable by means of the control of silica source and pH [4], even particles of several microns can be obtained with the use of organic functional groups [5]. In previous studies where we use MCM-41 as catalyst support, we found that the access to internals surface area on MCM particles is only partial, since diffusion restricts the effective use of the whole surface. In the hydrodesulphurization of dibenzothiophene, SiO_2 nanoparticles without porosity and only 200 $m^2\,g^{-1}$ shown higher catalytic activity than the same catalyst on MCM structure with surface area five times higher [5b]. With the original aim to improve the access of molecules to porous system of MCM-41 for catalytic applications, it was considered to form the MCM spheres in the presence of MWCNT, and after MWCNT burning by calcinations in air, we expected to obtain multiple macrochannels in the core of spheres. By this way restrictions of molecules to diffuse to internal mesoporosity (located at core of particles) could be reduced, enhancing thus the MCM-41 performance as catalyst, or as support for catalyst. In this work, we report the synthesis of MCM particles crossed by only one nanotube, conforming thus a necklace like structure.

2. Experimental

Carbon nanotubes (CNT) used for the synthesis of the MCM/CNT composite were synthesized by spray pyrolysis using ferrocene as catalyst and toluene as carbon source [6]. The nanocomposite was obtained by hydrothermal preparation of MCM-41 using the carbon nanotubes to cross through particles. MWCNT were dispersed on isopropyl alcohol and sonicated until complete dispersion was obtained. Silica precursor (TEOS) and the organic template, hexadecyl trimethyl ammonium bromide (HDTMABr) were added to MWCNT suspension and pH was raised by the addition of ammonium hydroxide. Slurry was maintained under stirring at 40 °C during 12 h, and after filtration and washing with distilled water, the MCM-41 interconnected particles were recovered. Calcination treatment was made at 700 °C under airflow. To preserve CNT and remove only organic template, sample was thermally treated at 700 °C under inert gas flow (N_2).

X-ray diffraction (XRD) patterns were obtained in a X-Pert MPD Phillips Diffractometer equipped with a curved graphite monocromator using Cu Kα radiation (k = 1.54056 Å). To evaluate the textural parameters of the samples, physical adsorption of N_2 at 77 K was carried out in an automatic gas sorption

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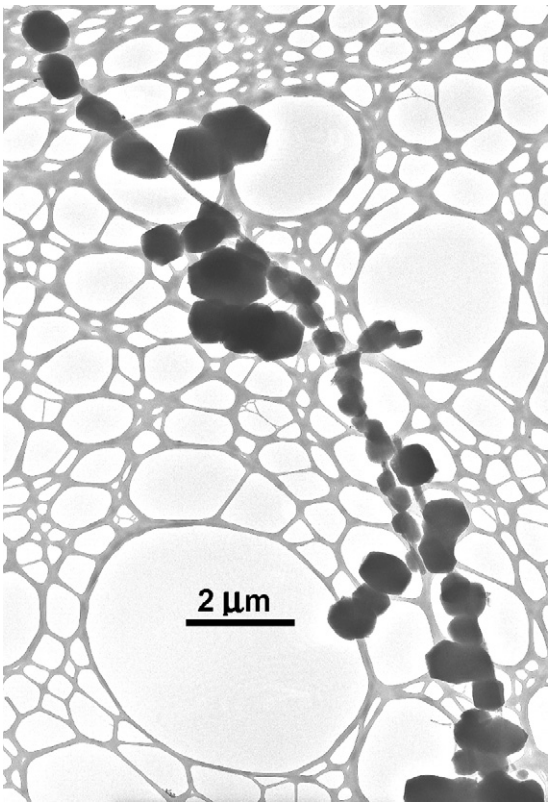

Fig. 1. MCM-41 particles forming a necklace structure by interconnection with carbon nanotubes.

analyzer (Quantachrome Autosorb 1c). Prior to the measurements, the samples were outgassed at 300 °C for 3 h. Surface area was obtained using the multipoint BET method. The study of the morphology of structures was made in a scanning electronic microscopy equipped with an electron dispersive X-ray analyzer in a JEOL SEM, model JSM-5800 LV, additional studies of the obtained materials were made by transmission electron microscopy in a side entry CM-200 equipped with EDX Prime. The specimens for TEM were prepared by dispersing the smple in acetone and ultrasonic for 2 min, the drop of suspension was put onto holey carbon Cu grid, and was allowed to dry.

3. Results and discussions

The synthesis of MCM-41 structure comprises the hydrolysis of TEOS and the condensation of silicate. As can be seen in Fig. 1, the typical spheroid geometry of particles was obtained without the interference of the CNT added during synthesis and the particles surround the carbon nanotubes forming necklace like structure (NLS). Fig. 2 shows XRD of CNT used for NLS and as can be seen, the pattern shows the signal at 26.4, which is associated with the (0 0 2) planes of hexagonal graphite structure of CNT. This signal is also observable in the sample of MCM/CNT (a), which corresponds to sample before calcinations. The small intensity of this peak is due to the low content of carbon nanotubes in the sample (0.007 g CNT/5.4 g of SiO_2). After calcination, several peaks of MCM-41 are enhanced. Fig. 3 shows how after calcination, SiO_2 walls that were formed over CNT external surface, keep the cylindrical form, maintaining thus the necklace like structure even after CNTs were burned and were released from composite as CO_2.

Typical surface area of MCM-41 was maintained according to BET analysis (higher than 1000 $m^2\,g^{-1}$ after calcination at 700 °C). Before calcination treatment, the EDAX analysis shows the carbon distribution as can be seen in Fig. 4a. The carbon in particles is due to organic template, meanwhile the carbon in the cylinders of interconnection correspond to the graphitic structure of CNT. As was mentioned before, after calcination (Fig. 4b), the interconnection of particles is maintained in spite of the burning of CNT, since a SiO_2 wall is formed over nanotubes during MCM formation.

The channels of MCM particles are aligned with CNT, which means that the increase on accessibility was minimal and corresponds only to the access through the channel formed after CNT removal by calcination. Fig. 5 represents the way that according to our results, template and TEOS were organized during synthesis, which is in agreement with the mechanism proposed by Cai et al. [7] for the synthesis of pure MCM-41.

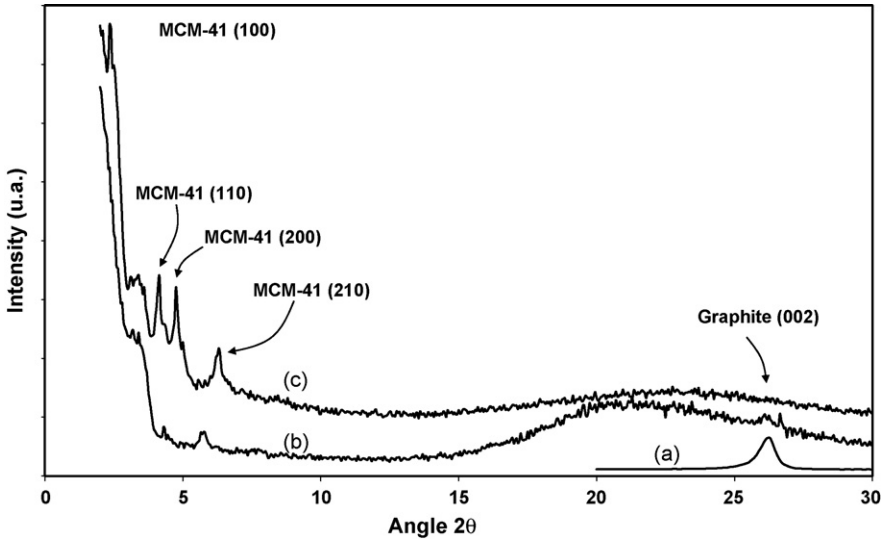

Fig. 2. X-ray diffraction pattern of carbon nanotubes as obtained by spray pyrolysis synthesis (a), MCM-CNT after filtration and washing (b) and MCM after calcination (c).

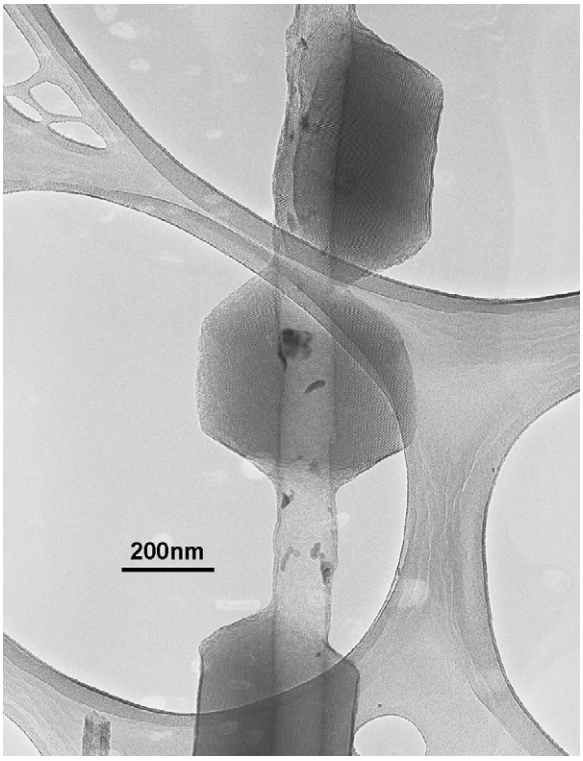

Fig. 3. TEM image of MCM-CNT composite after calcination in air for the elimination of CNT.

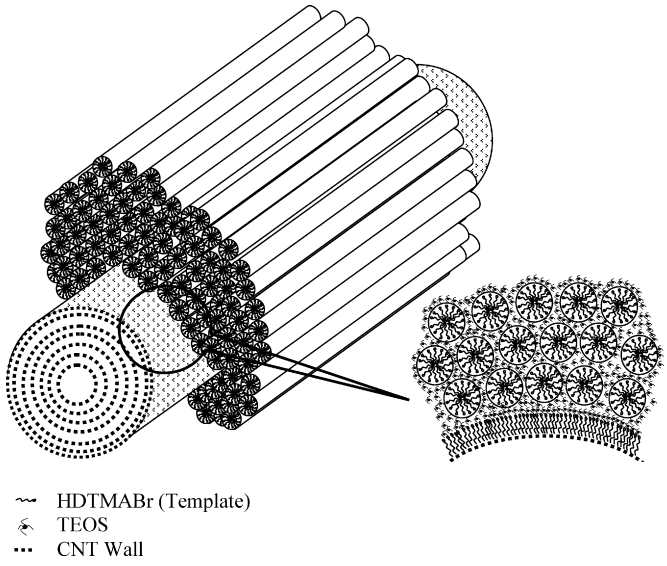

Fig. 5. Schematic representation of the arrangement of reactives during the synthesis of the MCM/CNT composite. Hydrophobic part of template has affinity with the CNT walls, so organization of template on CNT surface becomes similar to the other surface of template micelles. TEOS surrounds the hydrophilic surfaces around covered CNT and rod like micelles. CNT align in the same way of rod micelles.

This finding opens a research field since many applications can be expected from the use of this method of synthesis with small variations. The synthesis of solid sphere particles of oxides interconnected with carbon nanotubes produces an interesting material with potential use for ceramics composites, where sintering under inert atmosphere will permit the maintaining of necklace structure acting thus as reinfocement additive. Instead of MCM-41 also the nanocomposite with MCM-48 structure can be synthesized. This MCM-48/MWCNT can be used for development of nanosensors since porosity of silica matrix is interconnected and after impregnation of SnO_2 a nanocomposite could be obtained with surface area notably high and nanowires (CNT) which can be used as connectors for sensor assembly. The synthesis of MCM-48/CNT structure also solves the problem of the creation of macrochannels to improve the accessibility to internal porosity of MCM particles.

4. Conclusions

A novel structure with a necklace shape was obtained from the synthesis of MCM-41 in the presence of highly disperse multiwalled carbon nanotubes. MCM-41 structure was maintained since the typical surface area of MCM-41 was obtained after thermal treatment to eliminate the organic template. The necklace structure can be maintained after the calcination of CNT since TEOS polymerize over the external wall of CNT, creating thus an external layer of SiO_2 which is not affected by the thermal treatment.

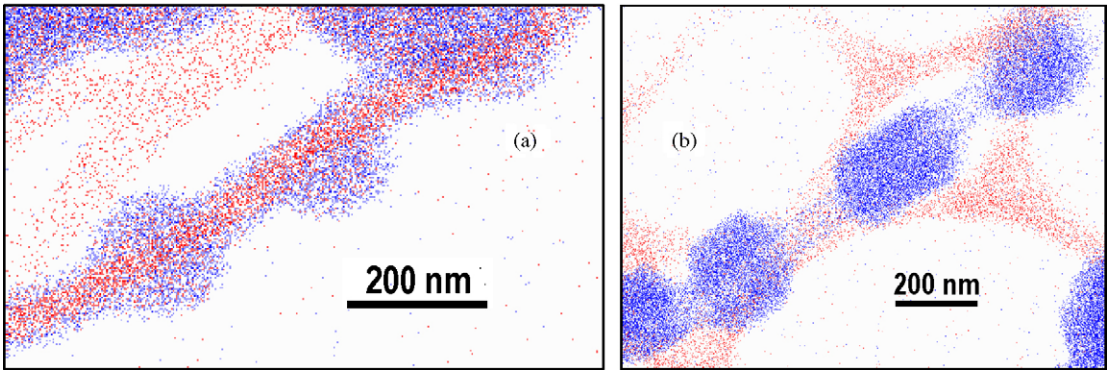

Fig. 4. Micrographs of MCM-41 particles interconnected by carbon nanotubes. (a) STEM mapping image overlay of carbon (red) and silicon (blue) before calcination. (b) STEM mapping image after calcination of nanocomposite in air; since the walls of nanotubes were covered by SiO_2, the structure of interconnected particles remains in spite of the burning of carbon.

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