

Carbon Nanotube Templated Growth of Mesoporous Zeolite Single Crystals

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Several applications of carbon nanotubes have been suggested¹ following their discovery in 1991.² They are specifically used as templating agents for preparing nanostructures, such as oxides^{3,4,5,6} and metals,⁷ with a high aspect ratio similar to that of the carbon nanotubes. These structures are prepared by opening and subsequently filling the carbon nanotubes or by depositing thin layers of material around them. So far, the use of carbon nanotubes as templates for nanostructured materials with low aspect ratios has not been realized. In most heterogeneous catalysts, mass transport occurs primarily in mesopores (2 nm < diameter < 50 nm). Consequently, there has been a continuous search for preparative routes to solid catalysts with pores in this range of diameter. Usually, such mesoporosity arises through the packing of nanosized catalyst crystals. Alternatively, organic templates organized in micelles have been shown to allow synthesis of mesoporous materials (M41S-type) with unique, uniform pore size distributions.⁸ However, the use of these materials as catalysts is hampered by their relatively low thermal stability⁹ and weak acid strength.¹⁰ Zeolites and zeolite types catalyze a wide variety of chemical reactions but have primarily found industrial use in catalytic refinery and petrochemical processes.^{11,12} The limited number of applications is related to the lack of mesopores in the zeolite crystals that only contain intracrystalline mi-

cro pores (<2 nm diameter). Therefore, only a fraction of the active sites in the zeolites is effectively used for catalytic conversions. Additionally, the desired product has a high probability of undergoing secondary reactions during diffusion in the zeolite micropores. The result is low selectivity. Thus, introduction of mesopores in zeolite crystals would be desirable.^{13,14} Thus far, only mesoporous aggregates of nanosized zeolite crystals have been reported.¹⁵ However, it has recently been shown that mesopores can be introduced into zeolite crystals by conducting the hydrothermal crystallization within a carbon black material.^{16,17} Although this leads to mesoporous zeolite single crystals, the resulting pore size distributions are broad. Furthermore, only few useful carbon-black materials are available and careful control of the crystallization conditions is necessary to avoid formation of nanosized, nonmesoporous zeolite crystals.^{18,19}

Here, we show how it is possible to grow mesoporous zeolite single crystals using multiwall carbon nanotubes as mesopore-forming agents. Multiwall carbon nanotubes (MWNT) were supplied by Hyperion Catalysis International, Massachusetts. The nanotubes were purified by reflux with concentrated hydrochloric acid for 24 h. This purification step was repeated until the hydrochloric acid was no longer colored by impurities from the nanotubes (typically 5–6 times). Mesoporous silicalite-1 was prepared by sequential impregnation of MWNT (1.0 g) with a 40 wt % aqueous solution of tetrapropylammonium hydroxide (TPAOH, 1.0 g) and tetraethyl orthosilicate (TEOS, 1.0 g). The sample was digested for 3 h, then transferred to an autoclave, and crystallized at 175 °C for 24 h. After the hydrothermal crystallization, the composite was isolated by filtration, washed with water and ethanol, and dried at 110 °C. The carbon nanotubes were completely removed by calcination in air at 600 °C for 20 h. Transmission electron microscopy (TEM) images and X-ray powder diffraction (XRPD) patterns were obtained as previously described.¹⁶

A representative TEM image of the MWNT starting material is shown in Figure 1. The diameter of the carbon nanotubes varies closely around a 12 nm average with walls consisting of 6–8 graphene layers. Typically, the nanotubes are several micrometers long. Figure 2 schematically illustrates how a zeolite single crystal is grown around the carbon nanotubes. It is essential that nucleation of the zeolite takes place exclusively between the carbon nanotubes. This will not occur if the nanotubes are simply dip-coated with a zeolite synthesis gel

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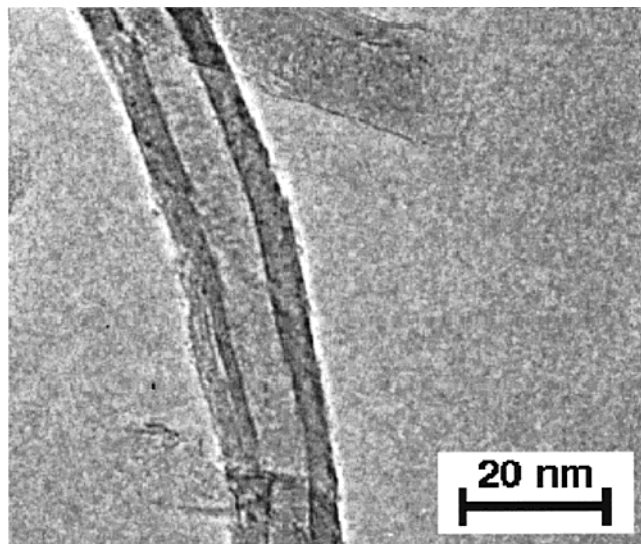


Figure 1. TEM image of the multiwall carbon nanotube starting material. Typically, the carbon nanotubes used have diameters of ≈ 12 nm and the walls contain 6–8 graphene layers.

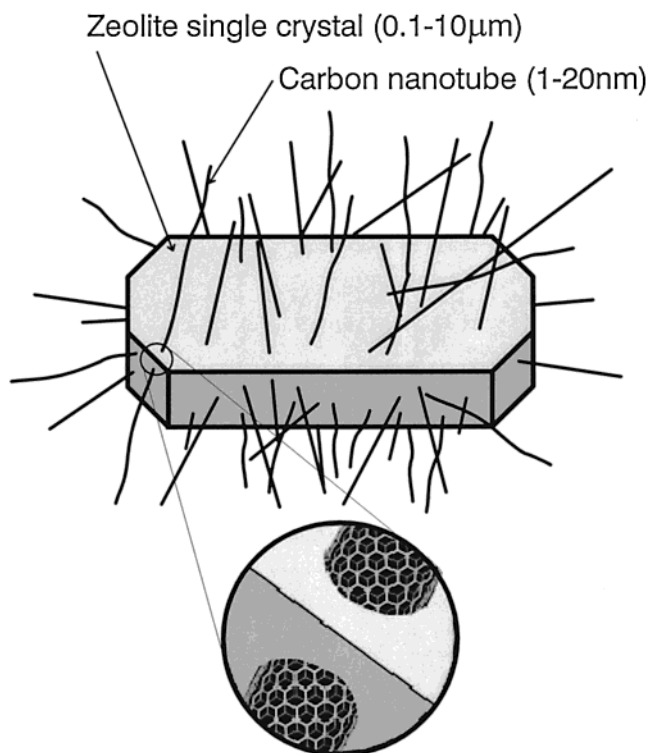


Figure 2. Schematic illustration of the synthesis principle for crystallization of mesoporous zeolite single crystals. The individual zeolite crystals partially encapsulate the nanotubes during growth. Selective removal of the nanotubes by combustion leads to formation of intracrystalline mesopores. When the nanotubes are removed by combustion, a mesopore system with diameters and tortuosity determined by the carbon nanotubes is created.

as has been done with other support materials in previous attempts to produce supported zeolites.^{20,21} Instead, the zeolite gel (0.2:1:17 TPA₂O:SiO₂:H₂O) is synthesized in the void between the nanotubes by sequential impregnations of the individual synthesis gel

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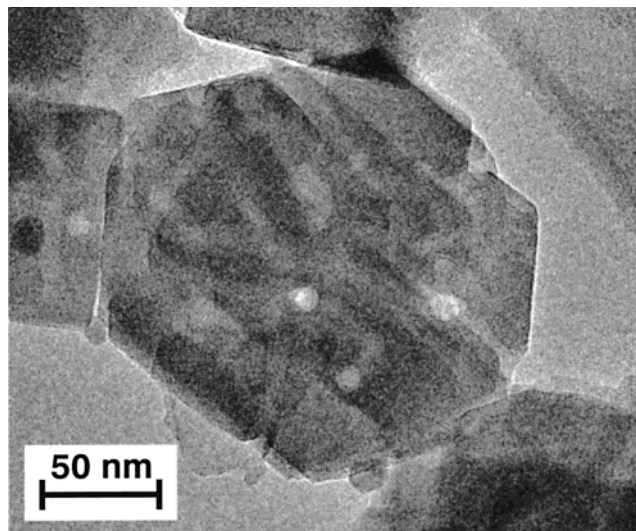


Figure 3. TEM image of a well-crystallized silicalite-1 crystal containing intracrystalline nanopores observed as well-defined channels or brighter “wormholes” extending through the entire crystal. The nanopores are straight channels penetrating the zeolite crystals with random orientation. The pore morphology is completely governed by the parent MWNTs used as the template. Lattice fringes are seen to extend throughout the entire crystal, demonstrating that it is indeed a single crystal.

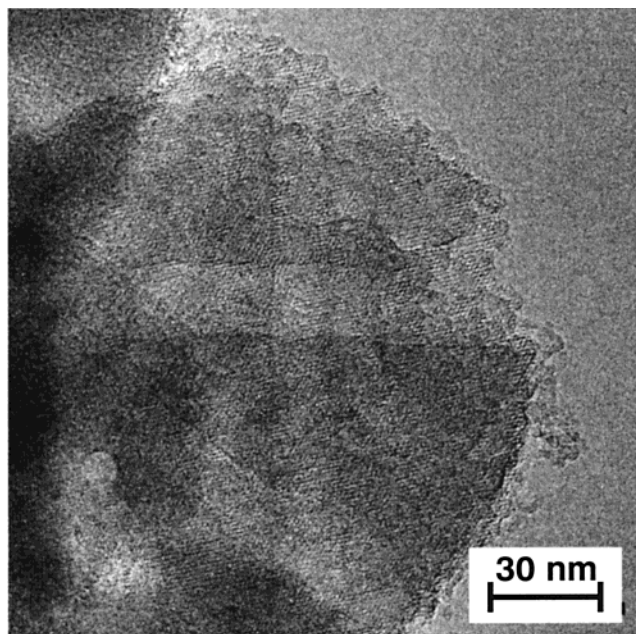


Figure 4. TEM image showing a silicalite-1 single crystal that has grown to encapsulate parts of several carbon nanotubes. Lattice fringes from the silicalite structure are well-resolved and extend through the entire crystal, proving the high crystallinity of the material after introduction of the mesopores.

components. Hydrothermal crystallization is conducted at 175 °C and autogenous pressure, and XRPD shows that only MFI-type silicalite-1 is formed. The TEM image in Figure 3 illustrates a silicalite-1 crystal with mesopores created by combustion of the MWNT templates present during the crystallization. The individual

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zeolite crystals have partly encapsulated the MWNT material during growth in accordance with the schematic representation in Figure 2. It is seen how uniform mesopores penetrate the zeolite crystal. Particularly, straight pores extending along the direction perpendicular to the plane of the TEM image are clearly visible. However, similarly sized pores are also apparent in other directions through the crystal. From the TEM images, crystal sizes in the range of 100–500 nm can be deduced. The amount of mesopores in the zeolite crystals is determined by the ratio of carbon nanotubes to zeolite gel.

Selected area electron diffraction confirms the formation of large silicalite-1 single crystals rather than agglomerates of nanosized crystals. It also verifies that most crystals are actually twins as previously discussed.^{16,17,22} The TEM image in Figure 4 illustrates in more detail the zeolite lattices fringes (compatible with silicalite-1) extending throughout the entire zeolite crystal. This demonstrates that a high crystallinity is

achieved despite the introduction of mesoporosity. Two mesopores orientated perpendicular to each other can easily be seen to penetrate the crystal.

Much effort has been put into developing synthesis methods that will allow tailoring the properties of MWNT materials. It is now possible to control the diameters of the synthesized nanotubes,²³ and when they are grown from small metal particles on a flat support, aligned tubes are in an ordered array obtained in good yield.²⁴ Therefore, the use of MWNTs as templates offers a high degree of control over the diameters and spatial arrangement of mesopores in solid materials. This is a possibility not offered by any other currently available synthesis method.

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