

# Encapsulation of metal particles within the wall structure of mesoporous carbons

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Received (in Cambridge, UK) 22nd December 2004, Accepted 4th February 2005

First published as an Advance Article on the web 16th February 2005

DOI: 10.1039/b419151j

A method for the production of mesoporous carbon, with metal particles encapsulated in the walls to prevent leaching, is demonstrated by the synthesis of a cobalt containing CMK1 structure.

The synthesis of porous carbons has received significant attention due to the various uses in gas separations, catalyst supports and perhaps most significantly in fuel cells.<sup>1</sup> Carbon structures with pore dimensions in the mesoporous region (20–100 Å) have been synthesised using a method involving templating with MCM-48 mesoporous silica material.<sup>2,3</sup> If mesoporous carbon is to be used in fuel cell electrodes, then metal catalyst particles need to be incorporated into the pore structure to provide centres at which the reduction and oxidation of the feed streams can occur. Ryoo *et al.*<sup>4</sup> have successfully incorporated platinum into “nanoporous carbon structures” using the incipient wetness technique with hexachloroplatinic acid to generate nanoparticles of platinum within the pore structure.

Here we report a method for the production of a nanoporous carbon which has the metal particle trapped in the carbon wall. This has the advantage that pore blockage by metal nanoparticles is reduced since the metal is embedded in the carbon wall and not across the pore volume. In addition encapsulation of the metal in the structure will reduce leaching and/or sintering as the particles are fixed.

The basic method for production of these structures is straightforward and is exemplified in Fig. 1. The mesoporous silica structure (MCM-48) is created using the method of Monnier<sup>5</sup>

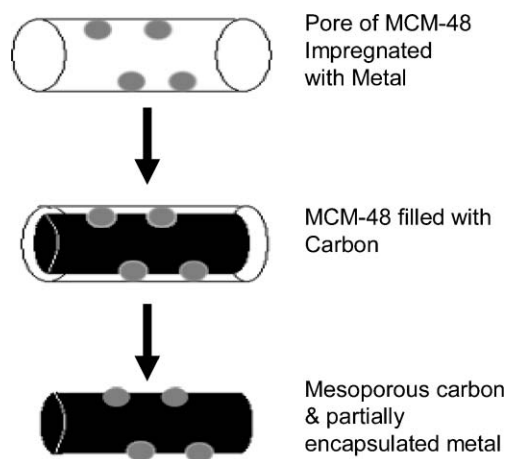


Fig. 1 Schematic of synthesis process.

(0.5 CTACl, 1 TEOS, 0.25 Na<sub>2</sub>O, 97 H<sub>2</sub>O). It is then calcined at 550 °C to remove the surfactant template. After the pore volume has been opened by calcination, the desired metal (Co) is incorporated into the structure using the incipient wetness technique with an ionic solution of 0.05 M cobalt nitrate hexahydrate. The cobalt nitrate was then converted to the oxide in air at 500 °C after which it was reduced to the metal at 400 °C under flowing hydrogen.

The incorporation of the carbon into the structure follows the technique of Ryoo *et al.*<sup>4</sup> who used a sucrose solution to introduce carbon into the pore volume followed by careful reduction to carbonise the sucrose. Dissolution of the silica using 1 M NaOH (2 × 24 h) leads to a negative of the MCM-48 which was named CMK1.

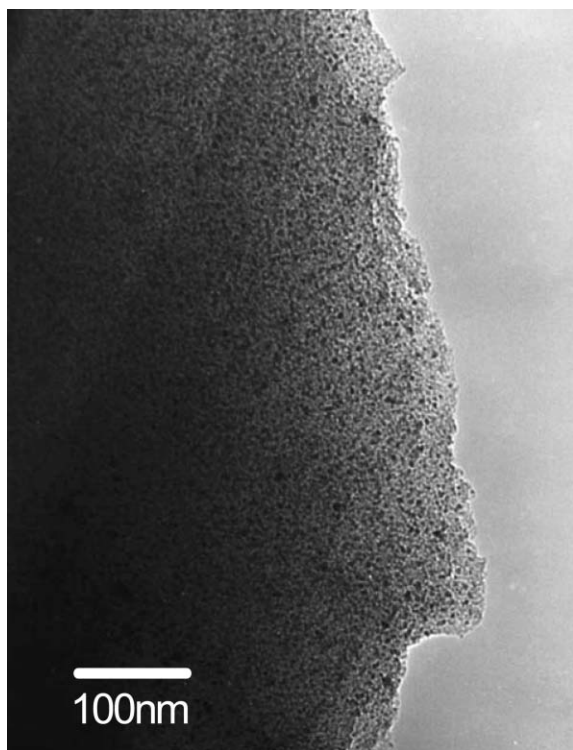
Using this technique we have successfully produced a mesoporous CMK1 material which incorporates metallic cobalt with a target of 4 weight percent. To ensure complete dissolution of the silica, Energy Dispersive X-ray (EDX) analysis was carried out and demonstrated that negligible quantities of silica residue were present in the material. EDX was also used to measure the weight percent of metal in all synthesised samples.

Transmission electron microscopy of the sample (Fig. 2) shows the mesoporous structure of the CMK1 with the metallic cobalt particles incorporated into the carbon framework. The cobalt particles show up as the darker points on the grey carbon background.

The BJH (Barrett, Joyner and Halenda) average pore diameter of Co-CMK1 was found to be 32 Å with a significant peak at around 38 Å corresponding to the pore dimensions of the negative of the MCM-48 (Fig. 3). Clearly some smaller pores are formed due to structural collapse of the carbon. The BET surface area was measured at 630 m<sup>2</sup> g<sup>-1</sup>. The sample in Fig. 2 used a cobalt loading of 4% during the incipient wetness impregnation stage and produced a weight percent of approximately 3 wt.% according to the EDX analysis. Samples between 1 wt.% and 5 wt.% have been synthesised although attempts to produce higher loadings have had limited success as the measured surface area is reduced, probably due to pore blockage by the metal particles which prevents the impregnation of the sucrose solution and consequently inhibits the production of the carbonaceous structure.

The higher the loading of metal, the lower the surface area. CMK1 analogues have also been produced with 1 wt.% copper and cobalt which have BET surface areas of the order of 1000 m<sup>2</sup> g<sup>-1</sup>, while a 35 wt.% nickel containing structure gave a surface area of ~500 m<sup>2</sup> g<sup>-1</sup>. In the latter case, large particles of nickel which were clearly breaking through the walls of the carbon, were apparent up to 300 Å in diameter. In all cases the BJH

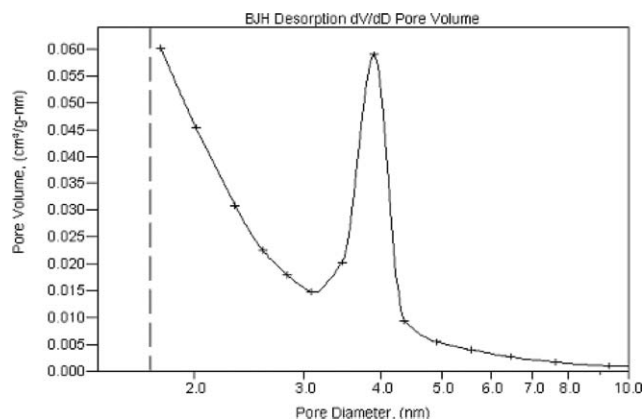
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**Fig. 2** TEM image of (4%)Co-CMK1.

average pore diameter was around 32 Å with a significant peak at 38 Å.

The synthesis method which has been described clearly produces a mesoporous carbon structure which incorporates nanoparticles of metal. Electron microscopy has shown that the cobalt particulates are around 20–30 Å in size which is consistent with particles which have been formed in the pores of MCM-48. The method has also been demonstrated for the incorporation of copper and nickel into CMK1 with similar results. Work is ongoing to synthesise Pt-CMK1. It would appear that if a metal can be incorporated into MCM-48 using incipient wetness or any other technique then the production of the CMK analogue is



**Fig. 3** Pore diameters of the Co containing CMK-1 structure demonstrating the mesoporosity of the material.

straightforward. Nickel and platinum containing mesoporous carbons will be the subject of a forthcoming full paper which will also incorporate leaching studies and metal surface area measurements for these materials.

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