

Imaging the channels in mesoporous molecular sieves with platinum

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Transmission electron micrographic images of platinum wires, incorporated into the channels of mesoporous molecular sieves, show that one-dimensional channels are arranged parallel in MCM-41 while the channels are three-dimensionally interconnected in other types of mesoporous molecular sieves constructed with silica frameworks.

Recently, the templating route using surfactant micelles was a major breakthrough in the synthesis of large-pore molecular sieves such as MCM-41, MCM-48,¹ FSM-16,² SBA-1,2,3,³ MSU-1,⁴ KIT-1,⁵ etc. These new molecular sieves have mesoporous channels with uniform widths that can be tailored in the mesopore range above 1.6 nm, stimulating a great deal of interest in adsorption, catalysis and materials science.^{6,7}

The channel arrangement in MCM-41, MCM-48, SBA-1,2,3 is ordered over a crystallographically long range, and consequently XRD patterns of the materials provide accurate information on the channel arrangement. However, the atomic arrangement in the channel walls of these silica-based materials is disordered, similar to amorphous silica. Such a disordered nature of the channel walls makes it difficult to measure the channel shape and wall thickness using XRD patterns. Furthermore, in the cases of MSU-1 and KIT-1, even the channels are arranged in a disordered way. XRD patterns obtained from the disordered molecular sieves consist of a few diffraction lines, which fail to provide useful information on the structure. Transmission electron micrograph (TEM) images obtained from thin edges of their microparticles or from ultramicrotome cuts also provide no structural information, except that the channels are disordered. These kinds of TEM images do not distinguish between noodle-like disordered arrangements of mesoporous channels and branched network-like disordered structures.

Here, we describe a technique to probe the local structure of the channel arrangement in mesoporous molecular sieves using TEM images of nanosize Pt wires which fill the channels in a locally controlled manner.

An MCM-41 sample was prepared following a hydrothermal crystallization procedure reported previously,^{8,9} using a gel

composition of 4 SiO₂:1 tetradecyltrimethylammonium chloride:1 Na₂O:0.15 (NH₄)₂O:200 H₂O at 370 K using Ludox HS 40 (40 mass% SiO₂ colloidal dispersion in water, Du Pont) as the silica source, following a procedure reported previously.⁹ An MCM-48 sample was crystallized from a gel composition of 1 SiO₂:0.25 Na₂O:0.65 hexadecyltrimethylammonium (HTA) bromide:52 H₂O at 370 K, using the procedure of ref. 10. A fully disordered mesoporous molecular sieve named KIT-1 (Korea Advanced Institute of Science and Technology number 1) has also been prepared using a gel composition of 4 SiO₂:1 HTACl:4 tetrasodium ethylenediaminetetraacetate:1 Na₂O:0.15 (NH₄)₂O:350 H₂O; details of the preparation method are described elsewhere.⁵ The KIT-1 sample exhibits nearly the same BET surface area (1000 m² g⁻¹) and pore size distribution curve (*ca.* 0.3 nm peak width at half the full height, with a maximum at 3.4 nm) as those obtained for MCM-41.⁵

In order to incorporate platinum inside the channels of MCM-41, MCM-48 and KIT-1, calcined samples were slurried in 5 × 10⁻⁵ mol dm⁻³ aqueous solutions of Pt(NH₃)₄(NO₃)₂ (Aldrich) for 1 h at room temperature. The solution to sample ratio was 100 ml g⁻¹. The samples were then filtered, washed with doubly distilled water and dried in a vacuum oven at 320 K. During these treatments, Pt(NH₃)₄²⁺ ions corresponding to 0.1 mass% Pt were incorporated on the molecular sieves by ion exchange. The ion-exchanged platinum species was activated by heating to 593 K in an O₂ flow and subsequently reduced by H₂ flow at 573 K. Hydrogen chemisorption measurements for the resulting samples indicated that the Pt cluster size was *ca.* 1 nm. The samples supporting the small Pt clusters were then immersed in a 2.5 × 10⁻³ mol dm⁻³ aqueous solution of Pt(NH₃)₄(NO₃)₂ and the solution was evaporated in a rotary evaporator, in order to impregnate an additional amount of 5 mass% Pt. After subsequent drying of the samples in a vacuum oven at 320 K, the additionally impregnated Pt species was reduced by H₂ flow. The reduction temperature was increased linearly from room temperature to 673 K over 6 h and maintained for 2 h. The resultant samples are designated Pt/MCM-41, Pt/MCM-48 and Pt/KIT-1.

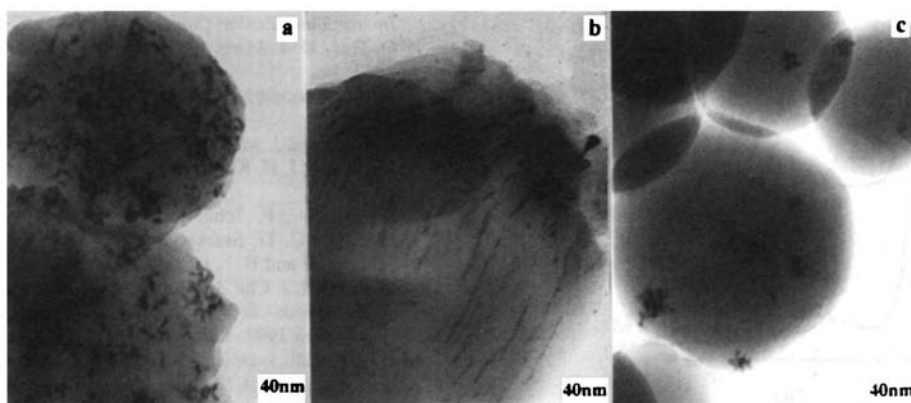


Fig. 1 TEM images of mesoporous molecular sieve MCM-41, (a) KIT-1 (b) and MCM-48 (c) after incorporating Pt wires into the channels. The TEM images were obtained from thin edges of the sample particles (< 1 μm) with a CM20 (Philips) apparatus operating at 100 keV. Dark rod-like images of *ca.* 3 nm diameter apparently arise from the incorporated Pt wires and reveal different local structures of the molecular sieves.

The Pt/MCM-41, Pt/MCM-48 and Pt/KIT-1 samples were suspended in ethanol (99.9 vol%). The suspension was dropped onto a porous carbon grid for TEM measurements and allowed to dry in ambient atmosphere. TEM images were obtained from thin edges of the sample particles (<1 μm) with a CM 20 (Philips) apparatus operating at 100 keV.

The TEM images for the Pt/MCM-41, Pt/KIT-1 and Pt/MCM-48 are shown in Fig. 1(a)–(c). The TEM image for MCM-41 shows dark rod-like objects with a uniform diameter of 3 nm, which is consistent with the width of the mesoporous channel for MCM-41 sample. Apparently, this image arises from agglomeration of electron-opaque Pt atoms to form nanosize wires inside the MCM-41 channel. The image from the supported Pt wires on the MCM-41 shows that the channels are parallel with no branching. Some channels at edges of the MCM-41 particles are bent in a bundle, while others are linear.

The average length of the Pt wires Pt/MCM-41 was controlled by incorporating different amounts of Pt in the two consecutive steps. Small Pt clusters of *ca.* 1 nm were prepared in the first step, deliberately using small amounts of Pt (0.1 mass% Pt) and introducing a calcination process prior to the Pt reduction. In the second Pt-supporting step, a relatively much larger amount of Pt species corresponding to 5 mass% Pt was supported and the calcination process was omitted. Based on our previous work on the formation of metal clusters in zeolite pores,^{11,12} it was reasonable that reduction of the Pt species in a H_2 flow without the calcination process would lead to large agglomeration of Pt atoms onto the small Pt clusters obtained from the first incorporation step. Thus, the small Pt clusters were considered to seed the formation of Pt wires inside the MCM-41 channels. Based on this reasoning, the average length of the supported Pt wires was controlled by increasing the amount of Pt loading in the second step.

The TEM image for Pt/KIT-1 shows Pt wires supported inside mesoporous channels with uniform diameters, similar to Pt/MCM-41, but the Pt/KIT-1 wires are branched and interconnected in a *fully* disordered three-dimensional way. The structure of KIT-1 is characteristic of a new class of molecular sieve exhibiting a *strict* regularity in channel diameter while the channel arrangement is *fully* disordered. Further details of physical properties of the KIT-1 such as the pore size distribution analysed from the N_2 adsorption data, thermal stability, hydrothermal stability and cation exchange upon

aluminium incorporation are reported elsewhere.⁵ The three-dimensional channel network of KIT-1 was reported to show a significant improvement in hydrothermal stability, compared with MCM-41 and MCM-48. The three-dimensional channel network also had a remarkable advantage for catalytic applications, compared with the one-dimensional channel structure of MCM-41.

The XRD pattern for MCM-48 in Fig. 2 is in accord with the cubic $Ia\bar{3}d$ structure known in the literature.^{1,10} The structure of MCM-48 is believed to consist of two independent, left- and right-handed, chiral channel systems. Vartuli *et al.* compared the sorption properties of MCM-41 and MCM-48, and reported that the adsorption of triisopropylbenzene occurred more slowly on MCM-48.¹³ The longer diffusion time for MCM-48 was thought to be consistent with two independent tortuous channels. Recently, the detailed structure was analysed by Alfredsson and Anderson¹⁴ using computer simulation of TEM images, which led to a conclusion of interconnection of the channels belonging exclusively to the same chiral system. While previous work on the structure determination used indirect methods such as sorption measurements and computer simulation, the transmission electron micrograph in Fig. 1(c) of the present study shows a direct image for the channel interconnection.

In conclusion, this study has established a technique to obtain highly resolved TEM images indicating the channel connectivity in mesoporous molecular sieves, using Pt clusters incorporated into the channels. The present technique is very useful for the determination of the local structures of mesoporous molecular sieves. In particular, the TEM imaging technique has been used to prove that the disordered molecular sieve KIT-1 has a three-dimensional network of mesoporous channels interconnected in a *fully* disordered and clearly distinct way from the linear channels of MCM-41.

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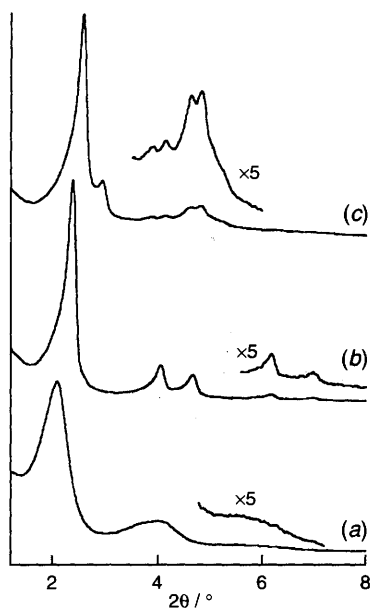


Fig. 2 X-Ray diffraction patterns of mesoporous molecular sieves KIT-1 (a), MCM-41 (b) and MCM-48 (c) after calcination in an O_2 flow at 813 K