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Mesoporous Zeolite Single Crystals

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Zeolites find widespread use in industry as heterogeneous catalysts and particularly in oil refining and petrochemistry as solid acid catalysts.[1] In many applications it is a problem that zeolites have only micropores since it imposes diffusional limitations on the reaction rate. Several different strategies have been pursued to circumvent this problem. One possibility is to increase the pore size of the zeolite, and this approach has led to the discovery of novel zeolites with an unprecedented pore size such as UTD-1.[2,3] Mesoporous molecular sieves, that is, M41S type materials[4,5] appear to offer similar opportunities although they do not possess acidity as high as some zeolites, for example, HZSM-5 or HY. Instead of increasing the pore size, another possibility is to decrease the crystal size of the zeolite. Several synthesis schemes have been reported to reproducibly allow preparation of very small (<50 nm) zeolite crystals.[6] Recently, we described how small crystals of a wide range of zeolites and zeotypes can be prepared by confined space synthesis, that is, by crystallization of the zeolite or zeotype within the pores of an inert mesoporous matrix.[7−9] Removal of the carbon matrix by controlled combustion led to the isolation of very small crystals (∼20 nm) with a high crystallinity. The crystal size was governed by the porous structure of the inert matrix and the maximum crystal size dictated by the pore diameter. Zeolites prepared by this route have large external surface areas and possess the same number of acid sites as the corresponding large zeolite crystals.[9] In confined space synthesis it is essential that the zeolite gel is restricted to the mesopores of the matrix to avoid uncontrolled growth. This was achieved by sequential introduction of the zeolite components in a soluble form and in an amount exactly equal to (or lower than) that necessary to fill the pore volume.

Now, we have found that by using *excess* of a zeolite gel it is possible for the zeolite to grow around the carbon particles of the inert matrix within the whole pore system. This means that zeolite crystals are nucleated within the mesopore system of the carbon matrix. Subsequently, large zeolite single crystals grow and encapsulate the carbon particles when excess gel is present and it is sufficiently concentrated. Removal of the carbon matrix by combustion leads to isolation of large zeolite single crystals with a mesopore system. By proper choice of the carbon matrix it is possible to influence the mesoporous system. The principle in the synthesis scheme is shown schematically in Figure 1.

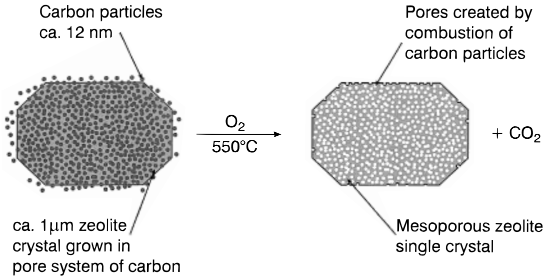

Figure 1. Growth of zeolite crystals around carbon particles. The zeolite is nucleated between the carbon particles; the pores are sufficiently large, and the gel is sufficiently concentrated to allow growth to continue within the pore system.

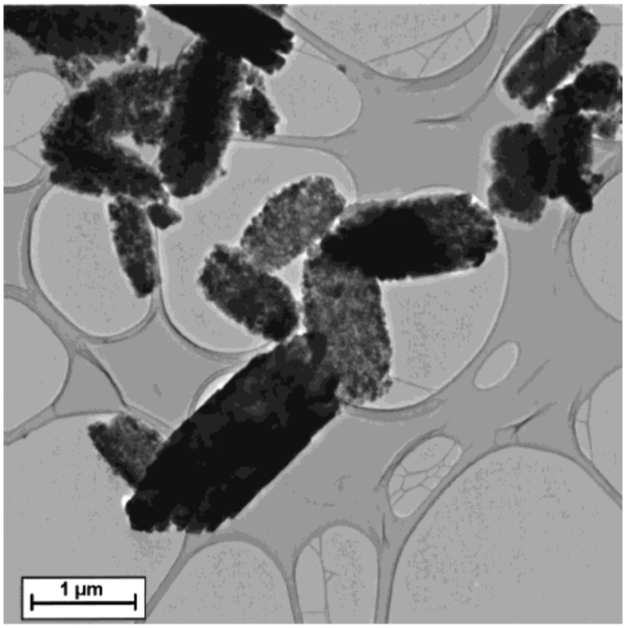

Figure 2. TEM overview of mesoporous ZSM-5 single crystals obtained by controlled combustion of carbon particles. It is seen that the crystals are ∼1 μm and porous due to the removed carbon particles.

Synthesis. In a typical recipe, carbon Black Pearls 2000 (supplied by Carbot Corp.) having an average particle diameter of 12 nm (ASTM D-3249) is impregnated to incipient wetness with a clear solution of tetrapropylammonium hydroxide, sodium hydroxide, sodium aluminate, water, and ethanol. After evaporation of the ethanol, the carbon particles are impregnated to 20% excess (compared to incipient wetness) with tetraethyl orthosilicate (TEOS). The composition of the resulting synthesis gel is 1 Al_2O_3:20 TPA_2O:1 Na_2O:100 SiO_2:200 H_2O and the resulting zeolite concentration ∼40 wt %. After aging for 3 h at room-temperature the impregnated carbon black was introduced into a stainless steel autoclave containing enough water to produce saturated steam and heated very slowly (0.05 °C/min) to 180 °C and kept there for 72 h. After the autoclave was cooled to room-temperature, the product was suspended in water, filtered by suction, resuspended in water, and filtered again. This was repeated four times, and then the product was dried at 110° for 10 h. The carbon black was removed by controlled combustion in air in a muffle furnace at 550 °C for 8 h. In this way a white material is obtained which by chemical analysis is shown to contain less than 0.5 wt % C.

X-ray Powder Diffraction (XRPD). From the XRPD patterns obtained with the setup described previously[7] it is seen that the sample contains only ZSM-5.

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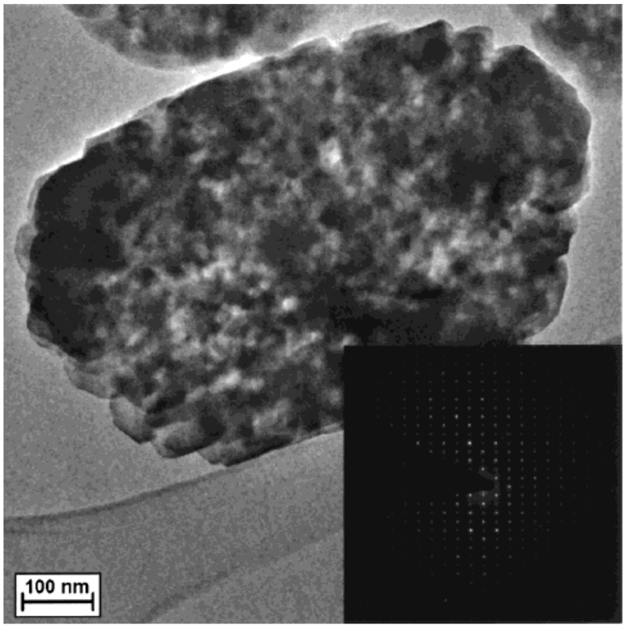

Figure 3. TEM of an isolated single ZSM-5 crystal and the diffraction pattern obtained from the same crystal. The size of the selected area aperture for electron diffraction was ∼1 μm and covered the entire crystal shown in the Figure.

Porosity. Pore size distributions were obtained from isotherms measured with a Quantachrome Autosorb using N_2 as adsorbent at 77 K. Analysis of the desorption isotherm revealed a bimodal pore size distribution with micropores of ∼0.5 nm radius and mesopores in the range of 5−50 nm radius. The pore volumes of the micropores (t-method) and mesopores were 0.09 and 1.01 mL/g, respectively.

Transmission Electron Microscopy (TEM). Transmission electron micrographs were recorded with a Philips CM200 FEG, operating at 200 kV. The sample was suspended in ethanol and dispersed on a copper grid coated with lacey carbon film. Figure 2 shows an overview of the crystals obtained after removal of the carbon matrix. It is seen that relatively large and well-shaped crystals are obtained. Also, the significant mesoporosity of the individual ZSM-5 crystals is indicated in the micrograph. From the micrographs it appears that the crystal sizes vary between ∼0.3−1.2 μm and that the porosity of the individual crystals vary. To demonstrate that the zeolite crystals are actually single crystals rather than just agglomerates of smaller crystals, electron diffraction patterns were obtained from a number of crystals. One crystal, oriented approximately along [100], is shown in Figure 3 together with the corresponding diffraction pattern. Most of the crystals (including that in Figure 3) are actually 90° intergrown or twins as revealed by TEM. This is a typical growth pattern for ZSM-5. Inspection of high-resolution transmission electron micrographs from these single crystals also revealed that lattice fringes extend through the entire crystal.

To produce large mesoporous zeolite crystals rather than nanosized zeolite crystals, it is essential that an excess of a sufficiently concentrated gel is used and that the carbon matrix has pores of a size that allows growth to proceed through the pore system. It is not yet clear exactly which synthesis parameters promote formation of nanosized crystals relative to large mesoporous zeolite crystals. However, it seems reasonable that the nucleation rate relative to the growth rate is of primary importance.

It appears plausible that this synthesis scheme may also be used for the preparation of mesoporous single crystals of other materials. However, it could be of importance that the zeolite contains micropores that allow easy diffusion of oxygen to—and of carbon dioxide from—the carbon particles during combustion to avoid destruction of the zeolite structure.

Previously, Holland et al.[10] have published structures of macroporous zeolites prepared by filling voids in polymer sphere arrays with synthesis gel, and Antonietti et al.[11] have formed meso/macroporous solids by combining polymer sphere templating with gels for MCM-41 materials. Contrary to MCM-41, our mesoporous zeolites do not possess a uniform pore size distribution. Instead, they are highly crystalline zeolites with mesoporosity introduced into the individual crystals by combustion of the carbon matrix. Such mesoporous zeolite single crystals might find applications in heterogeneous catalysis particularly when bulky reactants/products are involved or in bifunctional catalysis when it could be advantageous to locate, for example, an hydrogenating function in the mesopores of the individual zeolite crystals.

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