Microwave synthesis of molecular sieve MCM-41

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Crystalline, thermostable molecular sieve MCM-41 with hexagonal channel porosity is synthesized in a temperature-controlled microwave oven from aged precursor gels within about one hour.

We report here the microwave-assisted formation of well ordered molecular sieve MCM-41 from precursor gels within about one hour. The microwave-assisted synthesis of zeolites is a rather new field of research.[1] Several types of zeolites such as CoAPO-44, CoAPO-5,[2] $AlPO_4$-5,[3] zeolite A,[4] zeolite Y and ZSM-5[5] have been prepared by microwave heating of the precursor gels. Advantages of microwave synthesis include homogeneous heating throughout a reaction vessel, resulting in more homogeneous nucleation and shorter crystallization times compared to conventional autoclave heating. Furthermore, due to the nature of microwave heating the dynamics of the reactants in the liquid, including water, could change the reaction mechanism and offer new means of controlling a resulting zeolite phase.

One of the members of the recently discovered ordered mesoporous aluminosilicates,[6] MCM-41, presents a hexagonal arrangement of unidimensional mesopores with diameters ranging from about 20 to 100 Å. Several preparation methods for this or similar materials have now been reported, including the conventional heating of a precursor gel at about 100 °C for several days,[7] or prolonged reaction at room temperature,[7d] and different reaction mechanisms have been proposed.[8]

Microwave MCM-41 was synthesized by dissolving 0.083 g of $NaAlO_2$ (Pfaltz & Bauer) in 9 ml of bulk solution of $C_{16}H_{33}NMe_3Cl/OH$ [60% of OH^- anion; the bulk solution was prepared by mixing 58 g of 25% $C_{16}H_{33}NMe_3Cl$ with 30 g of Amberlite IRA-400(OH) ion-exchange resin (Aldrich)], stirring for 1 h, followed by filtration. Then 2.0 g of 10% tetramethylammonium silicate (SACHEM Inc., Austin, Texas) was added followed by 1.0 g of silica (Hi-Sil T600 Lot No. 1-350). The mixture was stirred well at room temperature for 12 h, then heated in a Teflon autoclave in a Questron microwave oven at 160 °C for 1 min, followed by heating at 150 °C for 80 min. The microwave power was controlled with temperature feedback in an autoclave.

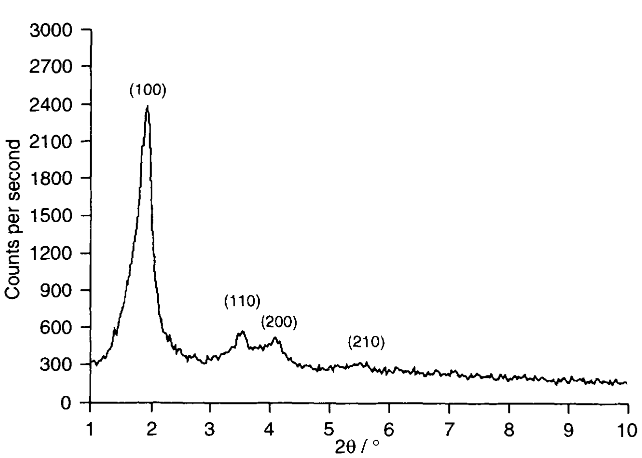

Fig. 1 X-Ray diffractogram of MCM-41 molecular sieve prepared in a microwave field (copper radiation). Synthetic conditions: see text.

The resulting solid was isolated by filtration, washed with warm water, then calcined at 550 °C in air for 12 h. The X-ray powder pattern of the product, Fig. 1, shows four well defined peaks which can be indexed with 100, 110, 200 and 210 in hexagonal symmetry. The corresponding *d*-spacing is 42 Å, similar to that of products obtained with conventional oven heating. The ordered hexagonal pore structure of this sample was further confirmed with transmission electron microscopy (Fig. 2). The calcined particles have a rather uniform size of about 100 nm, which is comparable to the coherence length (42 nm) calculated from the X-ray powder pattern using the Scherrer equation. The homogeneous and rather small crystal size of the product is probably the result of the fast and homogeneous condensation reactions occurring during microwave heating. This is consistent with previous observations regarding the microwave synthesis of zeolites.[4,5] The nitrogen sorption isotherm, Fig. 3, of the material shows the typical type IV mesopore sorption behaviour of MCM-41,[9] with the initial steep increase in sorption, inflection at about P/P_0 = 0.3, and

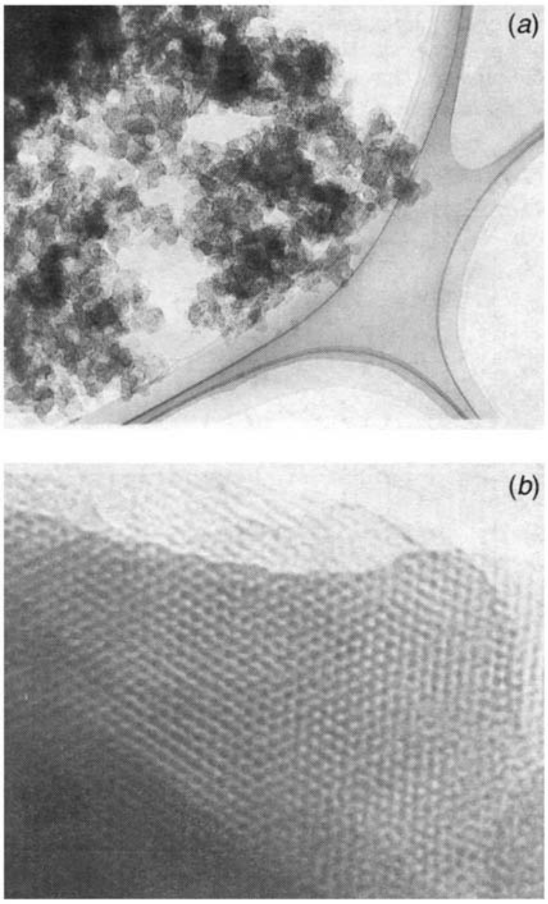

Fig. 2 Transmission electron micrographs of MCM-41 prepared in a microwave field. (*a*) View of crystallites (scale: 5.4 mm = 100 nm). (*b*) View of hexagonal channel system (scale: 9.6 mm = 20 nm).

saturation of the mesopores at about $P/P_0 = 0.4$. Typical surface areas of these materials are 900–1000 $m^2 g^{-1}$. The absence of hysteresis in the desorption branch suggests that no interparticle mesoporosity is present.

Several synthesis parameters such as the microwave reaction temperature, time, concentration of surfactant, and Si : Al ratio were investigated in order to optimize the crystallinity of the product and to gain insight into the crystallization mechanism. Using the above gel composition, the best temperature in the microwave oven for preparing MCM-41 is between 140 and 160 °C. Above 170 °C or below 130 °C, poorly ordered materials are obtained after heating for 60 min. Apparently, the condensation rate is not sufficient at the lower temperature to result in a stable aluminosilicate framework. When the temperature is too high (or the heating time is too long), continued heating results in decomposition of the already formed structure. A hexagonal phase is already formed after heating the gel at 150 °C for 20 min. Increasing the heating time will first increase the crystallinity, then decrease it after heating for 3 h. Continued microwave action may cause the metastable MCM-41 material to collapse into a denser, amorphous phase in the reactive solution, for example by destroying the surfactant. Nevertheless, after calcination the materials preserve their initial hexagonal pore structure, while showing a small shrinkage of the *d*-spacing, in agreement with previous reports.

The surfactant concentration also affects the order of the materials obtained. Although all the surfactant concentrations used in our experiments are above the critical concentration for micelle formation[10] of both $C_{16}H_{33}NMe_3Cl$ and $C_{16}H_{33}NMe_3OH$ in water, they are below the concentration for the hexagonal liquid-crystal phase.[11] The products obtained with different amounts of surfactant in the gel between 0.66 and 2.65 mmol all reveal the hexagonal MCM-41 phase, but have higher crystallinity at the highest surfactant concentration.

The presence of aluminate has an adverse effect on crystallinity. We have compared the crystallinity of phases obtained with Si : Al = 4.2, 8.4 and 16.7 : 1 at fixed Si : surfactant ratio. The highest Si : Al ratio gives the best crystallinity. One could speculate that the hexagonal surfactant : inorganic structure is formed by the interaction of silicate and surfactant, and that aluminate destroys this biphasic array.

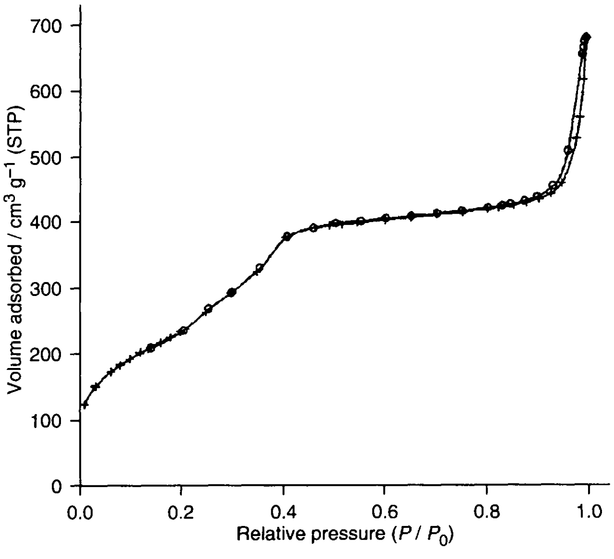

Fig. 3 Nitrogen sorption isotherm of MCM-41 prepared according to text (+, adsorption; O, desorption)

In conclusion, this study establishes the profound effect of microwave radiation on the synthesis of molecular sieve MCM-41. High quality hexagonal mesoporous materials of good thermal stability can be obtained by heating precursor gels to about 150 °C for an hour or even less. The variation of crystallinity with various reaction conditions suggests that the formation mechanism of MCM-41 under microwave heating is similar to that observed with conventional oven heating. Apparently, the effect of the microwave heating is to accelerate the condensation reactions of the silicate network. Further mechanistic studies of this system are underway in this laboratory.

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Footnote

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