Nanosized zeolite crystals—convenient control of crystal size distribution by confined space synthesis

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Confined space synthesis is a novel method in zeolite synthesis, which allows preparation of nanosized ZSM-5 crystals with a controlled crystal size distribution.

Traditional methods of zeolite synthesis typically involve crystallization from a gel or a clear solution under hydrothermal conditions.[1] Much work has been focused on preparation of large zeolite crystals suitable, *e.g.* for single crystal X-ray diffraction studies. Key factors in controlling the crystal size and morphology have been systematically studied.[2] In shape-selective zeolite catalysis improved selectivity is often found with larger crystals.[3] However, in many other catalytic reactions it appears favourable to use very small zeolite crystals since mass transfer limitations are of less importance. Furthermore, deactivation has in several cases been shown to proceed slower on small crystals due to their larger specific external area.[4] In the literature, some synthesis methods yielding small zeolite crystals have been reported.[5] However, none of these methods allow an easy control of the crystal size and the resulting crystal size distributions appear to be very dependent on the exact experimental conditions. Furthermore, isolation of the small zeolite crystals is not simple due to the colloidal properties of these materials. Therefore, we have attempted a novel method for the preparation of nanosized zeolite crystals. In contrast to other methods, it is possible to tailor-make zeolite crystal size distribution and recovery of the zeolite is simple. The synthesis method involves crystallization of the zeolite within the mesopore system of an inert support material. By use of carbon as the inert support material easy recovery of the zeolite is possible by controlled pyrolysis of the carbon.

Two different carbon black materials, Black Pearls 700 (BP700) and Black Pearls 2000 (BP2000) (supplied by Carbot Corp.) were used in the experiments. The carbon black was dried at 150 °C for 24 h prior to use. All other reagents, tetraethylorthosilicate (TEOS, 98 wt%), tetrapropylammonium hydroxide (TPAOH, 40 wt%), ethanol (EtOH, 99 wt%), sodium hydroxide (NaOH, 97 wt%), aluminium isopropoxide [Al(OPr^i)$_3$, 98 wt%] and distilled water, were used as received.

In a typical recipe, 20 g of carbon black was impregnated to incipient wetness with a clear solution of TPAOH, H_2O, NaOH, EtOH and optionally aluminium isopropoxide. Ethanol was evaporated at room-temperature and subsequently the carbon black was impregnated with TEOS yielding *ca.* 10 and 38 wt% SiO_2 in BP700 and BP2000, respectively. The composition of the synthesis gel (molar basis) was

$$x\ Al_2O_3 : 9\ TPA_2O : 0.15\ Na_2O : 50\ SiO_2 : 390\ H_2O : 200\ EtOH,$$
$$0 \leqslant x \leqslant \tfrac{1}{2}$$

After ageing for 3 h at room temperature the impregnated carbon black was transferred to a porcelain cup, introduced into a stainless steel autoclave containing enough water to produce saturated steam and heated in an oven at 180 °C for 48 h.

After cooling the autoclave to room temperature the product was suspended in water, filtered by suction, resuspended in water, and filtered again. This was repeated four times and finally the product was washed with 99% ethanol and dried at 110 °C for 3 h. The carbon black was removed by pyrolysis in a muffle furnace at 550 °C for 6 h. Three different zeolite samples were prepared using the reported method.

X-Ray powder diagrams were recorded by slow scanning on a Phillips vertical goniometer equipped with a θ-compensating divergence slit and a diffracted beam graphite monochromator utilizing Cu-Kα radiation. Crystal sizes were calculated from the two most intense diffraction peaks (2θ at 23.1 and 23.72° corresponding to the 501 and 151 reflections, respectively) by XRPD line broadening using the Scherrer equation. Transmission electron micrographs were obtained with a Philips EM430 (300 kV).

The ZSM-5 crystals are grown inside the pore structure of the carbon black support materials. Table 1 gives details of the pore structure of the two carbon blacks obtained from N_2 adsorption and desorption isotherms. The significantly larger pore volume of BP2000 compared with BP700 accounts for the higher SiO_2 content after impregnation. It is also seen that the average pore radius of the BP2000 is about twice as large as for BP700.

Fig. 1 illustrates the X-ray powder diagrams obtained after the zeolite synthesis and pyrolysis of the carbon black. It is seen that the sample contains highly crystalline ZSM-5 with an apparently small crystal size as judged from the diffraction line width. Table 2 gives details of crystal sizes determined using the Scherrer equation where crystal sizes of the ZSM-5 prior to and after removal of the carbon support by pyrolysis are provided. Apparently, some growth results from the removal of the carbon black, but this is within within the experimental uncertainty of the crystal size determination using the Scherrer equation.

The transmission electron micrograph of SZ† shown in Fig. 2 provides independent support for the formation of very small

Table 1 Selected properties of carbon black material

Support	d_{pore}[a]/nm	Pore volume[a]/mg g^{-1}	Surface area[a]/m^2 g^{-1}
Carbon Black Pearls, BP700	21.2	0.73	170
Carbon Black Pearls, BP2000	45.6	4.5	520

[a] BJH method (desorption).

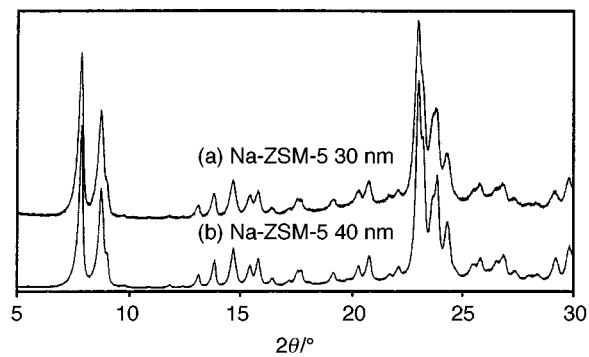

Fig. 1 XRPD of (a) SZ50† and (b) LZ100†. Carbon black removed by pyrolysis at 550 °C.

Table 2 Crystal sizes L_{501} and L_{151} determined by the Scherrer equation of ZSM-5 zeolites prepared by confined space synthesis. Calcination of ZSM-5 causes a phase transition[6,7]

Sample	Support	Si/Al	L_{501}/nm	L_{151}/nm
SZ	BP700	∞	20.3	16.0
SZ†[a]			37.4	25.8
SZ50	BP700	50	19.1	15.5
SZ50†[a]			29.4	31.2
LZ100	BP2000	100	48.4	67.1
LZ100†[a]			45.0	33.9

[a] Carbon black removed by pyrolysis at 550 °C.

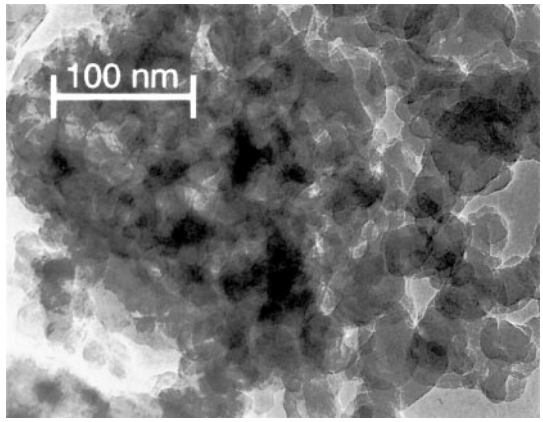

Fig. 2 Transmission electron micrograph of ZSM-5 crystals (SZ†) prepared by confined space synthesis.

zeolite crystals. From this figure it can also be seen that most crystals are in the range 8–30 nm and very little intergrowth is observed.

Sample SZ† has a total BET surface area of 412.4 $m^2\ g^{-1}$ with an external surface area of 185.0 $m^2\ g^{-1}$. The t-plot method (de Boer) of the SZ material revealed a bimodal pore size distribution. In addition to the pore volume inside the ZSM-5 crystals the material had an additional pore volume of 0.58 ml g^{-1} with an average pore radius of 15 nm. This mesopore system resulting from the packing of nanosized ZSM-5 crystals seems to provide excellent possibilities for diffusion of reactants and products, which is of significant importance in heterogeneous catalysis.

The ZSM-5 crystals synthesised using the confined space synthesis have sizes as low as 8 nm. To our knowledge this is the smallest crystal size of highly crystalline ZSM-5 reported so far. Jacobs *et al*.[8] reported the existence of X-ray amorphous ZSM-5, which contained crystals of <8 nm size in an amorphous matrix of silica. Camblor *et al*.[9] were able to synthesize zeolite beta with a crystal size as low as 10 nm determined by TEM. However, the crystal sizes depended strongly on the content of aluminium in the synthesis gel.

By use of the confined space synthesis it is possible to tailor-make zeolites with a given crystal size distribution and also to prepare very small zeolite crystals. Currently, studies are in progress to determine the minimum size of crystalline ZSM-5 crystals that can be prepared by the reported method. Furthermore, other zeolites and zeotypes are being prepared by confined space synthesis.

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Notes and references

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