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Confined Space Synthesis. A Novel Route to Nanosized Zeolites

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Confined space synthesis is a novel method in zeolite synthesis. It involves crystallization of the zeolite inside the pore system of an inert mesoporous matrix. In this way it is possible to prepare nanosized zeolites with a controlled size distribution by proper choice of the inert matrix. Here, confined space synthesis was adopted to prepare nanosized ZSM-5, zeolite Beta, zeolite X, and zeolite A with tailored crystal size distributions using mesoporous carbon blacks as inert matrices. All zeolites were characterized by X-ray powder diffraction, transmission electron microscopy, and nitrogen adsorption/desorption prior to and after removal of the carbon matrix. ZSM-5 with Si/Al ratios of 50, 100, and ∞ (silicalite-1) were synthesized with controlled average crystal sizes in the range 20−75 nm. Nanosized zeolite Beta (7−30 nm), zeolite X (22−60 nm), and zeolite A (25−37 nm) were prepared similarly. Removal of the carbon matrix by controlled combustion allows a convenient method for isolation of the pure and highly crystalline zeolites. Therefore, confined space synthesis appears to be an attractive method for preparation of zeolites with a controlled size distribution.

Introduction

Recently, we described the synthesis of tailor-made crystal size distributions (CSD) of nanosized ZSM-5 zeolites.[1−3] Here, we report the synthesis and characterization of various nanosized zeolites, including ZSM-5.

Numerous reports of zeolite crystallization exist in the literature, and key factors in controlling the crystal size and the morphology of zeolites during synthesis have been studied systematically. Lately, nanosized zeolites have attracted considerable attention. Schoeman and co-workers synthesized zeolites A, Y, and silicalite-1 with narrow crystal size distributions around 80−100 nm.[4,5] Sodalite was size-tailored with a crystal size of 37 nm by adjusting the content of aluminum in the synthesis gel, which is one of the growth-limiting nutrients.[6] Zeolite Y was synthesized with a crystal size as low as 23 nm by increasing the amount of seeds.[7] Corkery et al. synthesized 55 nm silicalite-1 crystals by crystallization for 40 months at 35 °C.[8] Synthesis of ZSM-5 with a crystal size of 30−50 nm determined by scanning electron microscopy (SEM) (13 nm as determined by X-ray diffraction) has also been reported.[9] X-ray amorphous crystals of ZSM-5 smaller than 8 nm were synthesized by interrupting the crystallization during synthesis.[10,11] Meng et al. synthesized zeolite L with an average crystal size of 30 nm by preconditioning the raw materials.[12] Zeolite Beta with a crystal size of 10 nm was obtained by reducing the Si/Al ratio to 8.[13] Reported sizes of small zeolite crystals are summarized in Table 1.

Table 1. Nanosized Zeolites Reported in the Literature

zeolite type	method of characterization	ave cryst size/nm	ref
ZSM-5	XRPD/SEM	13/30	7
silicalite-1	TEM/SEM	55/63	6
silicalite-1	XRPD/DLS	70 ± 20/95	3
zeolite Beta			10
Si/Al = 8	XRPD/TEM	10/5−15	
Si/Al = 12.5	TEM	20	
zeolite Y	XRPD/DLS	100/100	2
zeolite Y	XRPD	23	5
zeolite A	XRPD/DLS	230/240	2
sodalite	DLS/TEM	37/<50	4
zeolite L	XRPD	30	9

Most of the above-mentioned synthesis methods are based on controlling the crystal size distributions by adjusting the synthesis gel composition or the crystallization temperature/time. This reduces the degrees of compositional freedom, and only zeolites with specific compositions can be synthesized. Furthermore, the recovery of nanosized zeolite crystals from the resulting stable colloidal suspensions requires high-speed centrifugation.

Lately, catalytic applications of nanosized zeolites have received much attention because of their large external surface areas and reduced diffusion limitations compared to ordinary zeolite crystals of micrometer size. Fluid catalytic cracking (FCC),[14,15] hydrocracking of gasoil,[16] hydroxylation of phenol

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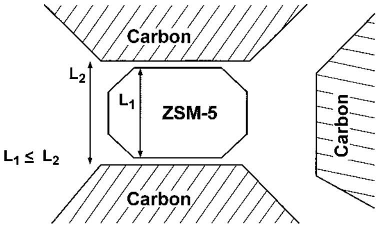

Figure 1. Schematic illustration of confined space synthesis.

with H_2O_2,[17] and hydration of cyclohexene to cyclohexanol[18] are examples of important commercial zeolite-catalyzed processes where small zeolite crystals have been claimed to possess special advantages. Reducing the crystal size of zeolite Y resulted in an increased activity and selectivity in FCC due to improved diffusion of reactants and products.[14,15] Reducing the crystal size of titanium silicalite-1 from 10 to 0.2 μm enhanced the activity for hydroxylation of phenol to dihydroxybenzenes (hydroquinone and catechol), an effect attributed to reduced diffusion limitations.[19] ZSM-5 crystals smaller than 50 nm are preferred for the hydration of cyclohexene to cyclohexanol.[18] Using ZSM-5 with a crystal size of 30 nm for the aromatization of ethylene reduced deactivation caused by coking of the external surface.[9] Recently, Camblor et al. found that higher activity and selectivity to middle distillates in hydrocracking of vacuum gasoil over NiMo/zeolite Beta was achieved with 8 nm zeolite Beta.[16]

We present a novel method in zeolite synthesis, confined space synthesis, which allows preparation of nanosized zeolite crystals with a controlled crystal size distribution. The principle of confined space synthesis is to synthesize the zeolite inside the mesopores of an inert matrix. The maximum crystal size is limited by the diameter of the mesopores as shown schematically in Figure 1.

In this study, we have used mesoporous carbons as the inert matrices and recovery of the zeolite is easily achieved by controlled combustion of the carbon matrix. In principle, the confined space synthesis is not limited to size-tailoring of zeolites but might be applicable to many other materials. In heterogeneous catalysis it might occasionally be desirable not to remove the matrix but use it as a support material for the zeolite catalyst.

Experimental Section

Materials. Two different carbon blacks, Black Pearls 700 (BP700) and Black Pearls 2000 (BP2000) (supplied by Carbot Corp.), were used as inert matrices in all syntheses. Some details of the pore structure of the two carbon blacks obtained from the N_2 adsorption and desorption isotherms are summarized in Table 2. The carbon blacks were dried at 150 °C for 24 h prior to use.

All other reagents were of reagent grade and used without further purification: tetraethyl orthosilicate (TEOS, 98 wt %, Aldrich), sodium silicate solution (29% SiO_2 and 9% Na_2O, Merck), tetrapropylammonium hydroxide (TPAOH, 40 wt %, Aldrich), tetraethylammonium hydroxide (TEAOH, 35 wt %, Aldrich), ethanol (EtOH, 99 wt %, Bie & Berntsen A/S), ammonia (NH_3, 25 wt %, Riedel-de Haën), sodium hydroxide (NaOH, 97 wt %, Riedel-de Haën), aluminum isopropoxide ($Al(^iOPr)_3$, 98 wt %, Struers), aluminum nitrate nonahydrate ($Al(NO_3)_3\cdot 9\ H_2O$, 98%, Aldrich), sodium aluminate ($NaAlO_2$, 54 wt % Al_2O_3 and 41 wt % Na_2O, Riedel-de Haën), and distilled water.

Table 2. Properties of Carbon Matrices Used in Confined Space Synthesis

matrix	d_{pore}, nm[a]	pore vol, ml g^{-1} [a]	surface area $m^2\ g^{-1}$ [a]
carbon Black Pearls, BP700	31.6	1.4	264
carbon Black Pearls, BP2000	45.6	3.6	520

[a] Average pore diameter calculated by BJH method (desorption).

Table 3. Recipes (in gram) for ZSM-5 Syntheses Based on 20.00 g of Carbon Matrix

carbon	TPAOH	H_2O	NaOH	$Al(^iOPr)_3$	EtOH	TEOS
BP700	11.18	1.64	0.022	0.00	10.88	12.67
	11.18	1.64	0.022	0.24	10.88	12.67
BP2000	11.72	1.71	0.023	0.126	65.40	13.27
	11.72	1.71	0.023	0.252	65.40	13.27

Synthesis of Nanosized ZSM-5. A clear solution of TPAOH, H_2O, NaOH, EtOH, and optionally $Al(^iOPr)_3$, with a composition according to Table 3, was prepared. The calculated amount of carbon black (based on the pore volume) was impregnated to incipient wetness with the clear solution. Ethanol was evaporated at room temperature, and subsequently, the carbon black was impregnated with pure TEOS or an ethanol solution of TEOS (according to Table 3) corresponding to 10 and 12 wt % SiO_2 in BP700 and BP2000, respectively.

The composition of the synthesis gel (molar basis) was

$$x\mathrm{Al_2O_3/9TPA_2O/0.15Na_2O/50SiO_2/390H_2O} \qquad x = \{0, {}^1/_4, {}^1/_2\}$$

The impregnated carbon black was transferred to a porcelain cup and placed in a stainless steel autoclave with sufficient water to produce saturated steam at 180 °C. After aging for 3 h at room temperature, the autoclave was heated in an oven at 180 °C for 48 h. After cooling 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 dried at 110 °C for 3 h.

Synthesis of Nanosized Zeolite Beta. Predried (at 150 °C) carbon black BP2000 (20.0 g) was impregnated with a clear solution of TEAOH (16.2 g), H_2O (0.65 g), $NaAlO_2$ (0.37 g), and EtOH (71.4 g). The procedure for evaporation of EtOH, impregnation with TEOS (12.7 g), and aging used in the synthesis of nanosized ZSM-5 was followed. The composition of the synthesis gel (molar basis) was

$$\mathrm{1.6Al_2O_3/15.7TEA_2O/2.3Na_2O/50SiO_2/510H_2O}$$

After aging for 3 h at room temperature, the autoclave was heated in an oven at 140 °C for 5 days. The washing and drying procedure used for the synthesis of nanosized ZSM-5 was followed.

Synthesis of Nanosized Zeolite X. Predried (at 150 °C) carbon black BP2000 (20.0 g) was impregnated with a clear solution of $Al(NO_3)_3\cdot 9H_2O$ (5.7 g), H_2O (5.7 g), and EtOH (56.2 g). After evaporation of EtOH and a subsequent impregnation with a clear solution of sodium silicate (6.9 g), NaOH (4.2 g). and H_2O (58.5 g), the composition of the synthesis gel (molar basis) was

$$\mathrm{1Al_2O_3/8Na_2O/4.5SiO_2/180H_2O}$$

After aging for 24 h at room temperature, the autoclave was heated in an oven at 110 °C for 8 h. The washing and drying procedure used for the synthesis of nanosized ZSM-5 was followed.

Synthesis of Nanosized Zeolite A. In the synthesis of zeolite A, amorphous silica was synthesized in the carbon black prior to synthesis of the zeolite. Carbon black BP700 (20.0 g) was impregnated to incipient wetness with a solution of aqueous NH_3 (3.60 g), H_2O (3.60 g), and EtOH (5.80 g). EtOH was evaporated at room temperature, and subsequently, the carbon black was impregnated with TEOS (6.80

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g), yielding approximately 10 wt % SiO_2 in BP700. After aging for 3 h at room temperature, the impregnated carbon black was transferred to a porcelain cup, introduced into a stainless steel autoclave containing sufficient water to produce saturated steam, and heated in an oven at 180 °C for 15 h. The autoclave was cooled to room temperature, and the carbon black was suspended in water, filtered by suction, resuspended in water, and filtered again. This was repeated four times, and finally, the product was dried at 110 °C for 3 h. To remove NH_3, the carbon black was heated to 180 °C for 24 h, resulting in carbon black with amorphous silica (SiO_2−BP700). NaOH (0.70 g) and $NaAlO_2$ (0.62 g) were dissolved in water (9.70 g) at 80 °C and cooled to room temperature. The solution was impregnated into the SiO_2−BP700 by incipient wetness impregnation and aged for 24 h at room temperature, giving the following composition of the synthesis gel (molar basis):

$$1Al_2O_3/4Na_2O/10SiO_2/162H_2O$$

The impregnated carbon black was transferred to a porcelain cup, introduced into a stainless steel autoclave containing sufficient water to produce saturated steam, and heated in an oven at 110 °C for 72 h. Cooling, rinsing, and drying procedures used in the synthesis of nanosized ZSM-5 were followed.

Synthesis of Large Crystal Zeolites. Large crystals of the zeolites used as reference materials were synthesized according to literature recipes. ZSM-5 (Si/Al = 50) with an average crystal size of ca. 8 μm was synthesized according to Jacobs et al.[20] Zeolite Beta (Si/Al = 15) with a crystal size of approximately 1 μm was prepared according to recipes reported by Jacobs et al.[21] LTA with a crystal size of 1−2 μm was synthesized according to L. D. Rollmann et al.[22]

Removal of Carbon Black. The carbon black was removed by combustion in air in a muffle furnace at 550 °C for 6 h. To remove the carbon black completely, it was crucial that the sample was distributed in a thin layer of a few millimeters thickness.

X-ray Powder Diffraction (XRPD). X-ray powder patterns 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 by XRPD line broadening (full width at half-height) corrected for the instrument broadening using the Scherrer equation. Because of the Bragg−Brentano parafocusing geometry used in the XRPD setup, reflections at low 2θ ($<15°$) were avoided in calculation of crystals sizes. The following reflections were used for the crystal size determinations: for ZSM-5, [501], [151] (prior to removal of carbon matrix); [051], [−511] (after removal of carbon matrix); for zeolite Beta, [004], [300], [302], [304], [008], [306]; for zeolite A, [442]/[600], [444]; for zeolite X, [440], [733], [662]. Usually, the crystal sizes determined from different reflections vary significantly. This can be due to, for example, crystal size anisotropy and stacking faults. The crystal sizes based on XRPD reported below are given as intervals estimated from the different reflections or for simplicity as an approximate average value.

Transmission Electron Microscopy (TEM). Transmission electron micrographs were obtained with a Philips EM430 (300 kV).

N_2 Adsorption/Desorption. The adsorption/desorption isotherms were measured with a Quantachrome Autosorb using N_2 as adsorbant at 77 K. Samples were outgassed at 350 °C for 18 h prior to measurements. Total surface area and external surface area were calculated according to BET and *t*-plot (DeBoer) methods, respectively. Meso- and micropore volumes were calculated by the *t*-plot (DeBoer) method, and pore size distributions were calculated by the BJH method (desorption).

Results and Discussion

Carbon Matrix. The average mesopore radii of BP2000 and BP700 are approximately 23 and 16 nm, respectively. The mesopore volumes of both carbon matrices are sufficient to contain an amount of synthesis gel resulting in more than 10 wt % of zeolite in the final product. The carbon matrix was completely removed by combustion in air in a muffle furnace at 550 °C for 6 h. Removal of the carbon matrix at 500 °C in air required 16 h. The absence of ignition of the carbon matrix at temperatures below 550 °C prevented thermal decomposition of the zeolite, resulting in highly crystalline samples of the pure zeolites. The carbon blacks used as matrices in these preparations were virtually ash-free, which prevented contamination of the zeolite products during and after combustion.

Synthesis. A crucial factor in confined space synthesis is to restrict crystallization of the zeolite gel to the mesopore system of the inert matrix and to maintain sufficiently low concentrations to avoid uncontrolled growth in the pore system. Applying incipient wetness impregnations of the mesopores with the zeolite gel precursor solutions ensure this. The precursor solutions have to be clear solutions with a low viscosity, which enable them to enter the mesopores of the matrix instead of blocking the pore entrances and/or deposit on the external surface of the carbon grains. Sequential impregnations of the mesopores are necessary because zeolite gels usually are turbid, unstable, and high-viscosity gels. The first impregnation solution contains a volatile compound in addition to some of the zeolite precursor(s). After evaporation of the volatile compound the matrix is impregnated with the next precursor solution. Special care has to be taken when the precursors must decompose in order to free pore volume for the subsequent impregnations. Hydrolysis of TEOS in the pores of the carbon matrix is catalyzed by the aqueous alkaline solution that has been introduced in advance. Because of the volatility of TEOS, complete hydrolysis has to be ensured prior to drying or autoclaving of the impregnated sample. The ethanol formed by hydrolysis of TEOS is allowed to evaporate before subsequent impregnations or hydrothermal crystallization. Oligomers in the zeolite gel precursor solutions must be sufficiently small to enter the mesopores of the matrix.

The sodium silicate solution used for the preparation of zeolite X was mixed with additional NaOH and diluted with water before impregnation in order to favor the existence of small silica species. The other low-silica zeolite LTA was prepared using TEOS, a monomeric silicon source. Nanosized LTA could also be prepared by the procedure used for zeolite X, i.e., using a sodium silicate solution instead of TEOS. After sequential impregnations with all the precursors the zeolite gel can be crystallized under hydrothermal conditions. This is done by transferring the impregnated matrix to a porcelain cup, which is placed in an autoclave together with sufficient water to ensure a saturated steam atmosphere at the desired crystallization temperature.

To prevent diffusion of the zeolite gel components from the mesopores, it is necessary to avoid the presence of excess liquid water. The excess water at the bottom of the autoclave should not be in direct contact with the contents of the porcelain cup. The crystallized samples are washed with demineralized water, filtered on a Büchner filter, and dried at 110 °C. In this study, the zeolites are not ion-exchanged. However, we have shown for ZSM-5 that ion exchange is facilitated when the nanosized zeolites remain in the matrix during the ion-exchange processes. First, the organic templates were decomposed by calcination of the dry zeolite, still contained within the carbon matrix, at 500 °C in N_2. Then the zeolite was ion-exchanged with NH_4NO_3 and the carbon matrix and NH_4^+ was removed by subsequent controlled combustion as described above. This

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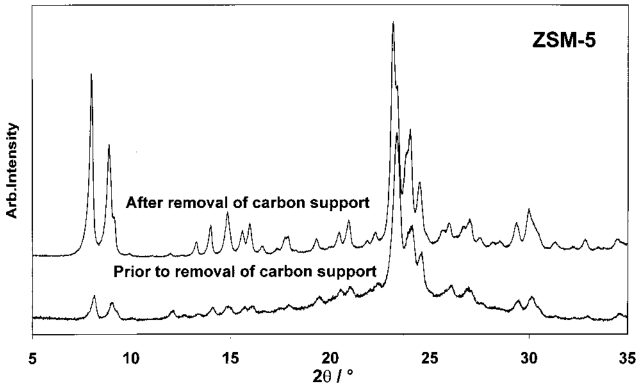

Figure 2. XRPD patterns of ZSM-5 before and after controlled combustion of carbon matrix.

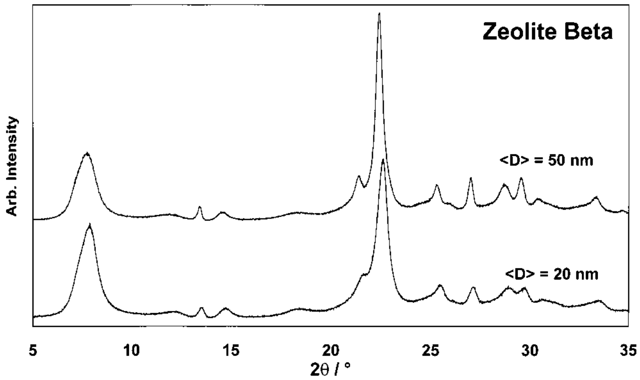

Figure 3. XRPD patterns of zeolite Beta after combustion of carbon matrix.

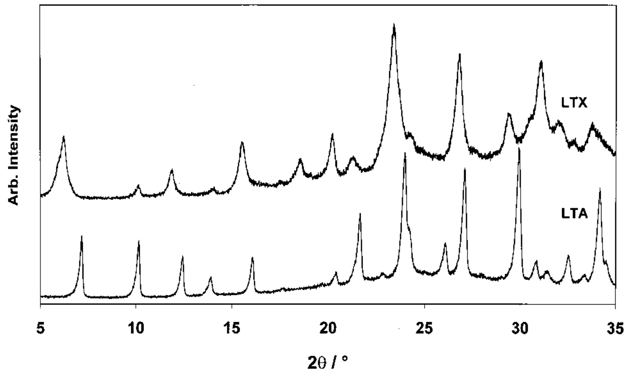

Figure 4. XRPD patterns of zeolites A and X in carbon matrices.

resulted in pure high-crystalline samples of nanosized ZSM-5 in the acidic form.[2]

XRPD. In Figure 2, the XRPD patterns of ZSM-5 (Si/Al = 50), synthesized in BP2000, before and after controlled combustion of the carbon matrix are shown. The reflections from the crystalline nanosized zeolite are seen superimposed on the amorphous background from the carbon matrix. It is possible to check the structure and crystallinity and to estimate the average crystal size of the nanosized zeolite synthesized by confined space synthesis prior to removal of the matrix. Comparison of the patterns before and after combustion of the carbon matrix suggests that neither sintering nor loss of crystallinity of the nanosized zeolite is observed. The XRPD patterns of zeolite Beta prepared by confined space synthesis are shown in Figure 3. Here, significantly broadened diffraction lines are noted. XRPD patterns of LTA and zeolite X in the carbon matrices are shown in Figure 4. The diffraction lines for these zeolites are also broadened significantly. Crystal sizes calculated by the Scherrer equation of the zeolites before and after removal of the carbon by combustion are listed in Table 4.

Table 4. Crystal Sizes of Zeolites before and after Combustion of Carbon Matrix

zeolite	carbon	Si/Al[a]	d_{carbon}, nm[b]	*L*, nm[c]
ZSM-5	BP700	∞	31.6	22−25/(26−37)[d]
ZSM-5	BP700	50	31.6	20−37/(22−30)[d]
ZSM-5	BP2000	100	45.6	27−45/(34−75)[d]
ZSM-5	BP2000	50	45.6	23−41/(37−45)[d]
Beta	BP2000	15	45.6	7−14/(9−30)[d]
LTA	BP700	5	31.6	25−31/(33−37)[d]
LTX	BP2000	2	45.6	22−53/(25−60)[d]

[a] Si/Al ratio in synthesis gel. [b] Average pore diameter of carbon matrix. [c] Determined by XRPD. [d] Carbon matrix removed by calcination at 550 °C for 6 h.

The small differences in crystal sizes before and after removal of the matrix might be due to sintering caused by the exothermic decomposition of the carbon. However, it is more likely related to uncertainty in the calculated crystal size before combustion caused by the necessary deconvolutions of the XRPD patterns of carbon black and the zeolite. Therefore, it is concluded that the crystal sizes of the zeolites do not change significantly by combustion of the carbon matrix. Precautions in estimating crystal size of nanosized zeolite Beta have previously been reported.[23] This is due to the polymorphous structure of zeolite Beta consisting of two polymorphs A and B.[24] Zeolite Beta in the microscale range has broad and sharp peaks related to (3*n*,3*n*,*l*) reflections and faulting by *a*/3 and *b*/3 displacements on (001) planes, respectively. As a consequence, only the sharp reflections were used in the calculation of crystal size. The crystal size of zeolite Beta in the carbon matrix BP2000 based on the (302) and (600) reflections were 14 and 7 nm, respectively, and after removal of the carbon the crystal size was similarly determined to be 9−30 nm. The average pore diameters of the carbon matrices used in the syntheses are included in Table 4. It is evident that the calculated crystal sizes of all the zeolites corresponded reasonably to the average mesopore diameter of the carbon matrix. The crystal sizes determined by XRPD of ZSM-5 synthesized in the two different carbon matrix materials corresponded reasonably well to the average pore diameter of the carbon matrices.

TEM. Figure 5 illustrates the transmission electron micrograph of zeolite Beta after controlled combustion of the carbon matrix. It is observed that only a little intergrowth of the zeolite crystals has occurred. The crystal sizes of zeolite Beta synthesized in BP2000 are in the range 8−22 nm as determined from the micrograph, which compares well with the 7−14 nm determined from XRPD.

Lattice fringes and sharp edges of the nanosized crystals are seen in Figure 5, indicating a high degree of crystallinity. The nanosized crystals in Figure 5 exhibit a narrow crystal size distribution. Differences in average crystal sizes determined by TEM and XRPD are probably due to fact that the average crystal size calculated by the Scherrer equation is a ratio of the width of the size distribution, $\langle L^2\rangle/\langle L\rangle$.[25] Therefore, in relative terms, the largest crystals will contribute more to the average crystal size determined by XRPD than the small crystals. Generally,

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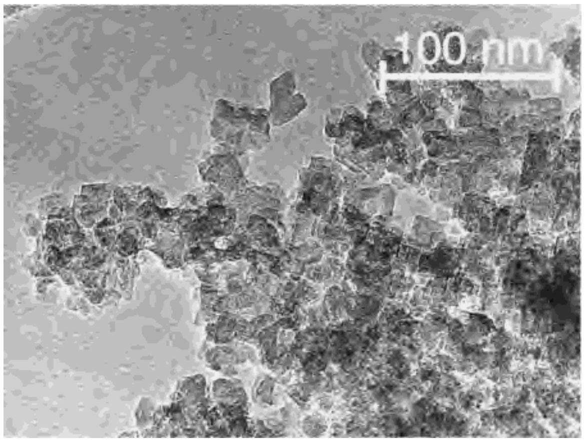

Figure 5. TEM of zeolite Beta after combustion of carbon matrix.

Table 5. Surface Areas and Pore Volumes of Zeolites after Combustion of Carbon Matrix at 550 °C for 6 h

zeolite	BET area,[a] $m^2\ g^{-1}$	external area,[a] $m^2\ g^{-1}$	micropore,[b] mL g^{-1}	mesopore,[b] mL g^{-1}	r_{mesopore},[b] nm
ZSM-5	412.4	185.0	0.12	0.52	17.4
ZSM-5	434.0	250.9	0.09	0.97	17.6
Beta	651.4	167.5	0.25	2.42	>50

[a] Calculated by BET and *t*-plot method. [b] Calculated by BJH method (desorption).

crystal sizes determined from XRPD of very small zeolite crystals are not very accurate and should be taken only as first approximations to the true crystal size.

N_2 Adsorption/Desorption. The nanosized zeolites were also characterized by nitrogen adsorption and desorption after combustion of the carbon matrix, and the results are summarized in Table 5. The external surface areas of ZSM-5 and zeolite Beta were remarkably high, indicating very little intergrowth of the small crystals. On the other hand, the surface area of LTA was very low and no evidence for micropores was found. This is probably caused by the zeolite crystals being embedded in a small amount of amorphous material. The amorphous material might either be a result of incomplete crystallization or of a slight thermal decomposition of the low-silica zeolite during combustion of the carbon matrix.

All samples of high-silica zeolites (ZSM-5 and Beta) contained micropores, indicating a high crystallinity. The external surface areas of ZSM-5 were larger than 180 m^2/g and accounting for approximately half the total surface area. Yamamura et al.[9] reported an external surface area of only 41.6 m^2/g for ZSM-5 (Si/Al = 12.5) with a crystal size of 30 nm determined by SEM (13 nm as determined by XRPD). This suggests a higher crystallinity of nanosized zeolites prepared by confined space synthesis compared to other methods. A mesopore system with a radius of 17.5 nm and specific volumes of 0.5−1.0 mL g^{-1} could be calculated for ZSM-5 by the *t*-plot (DeBoer) method. The pore size distribution is shown in Figure 6.

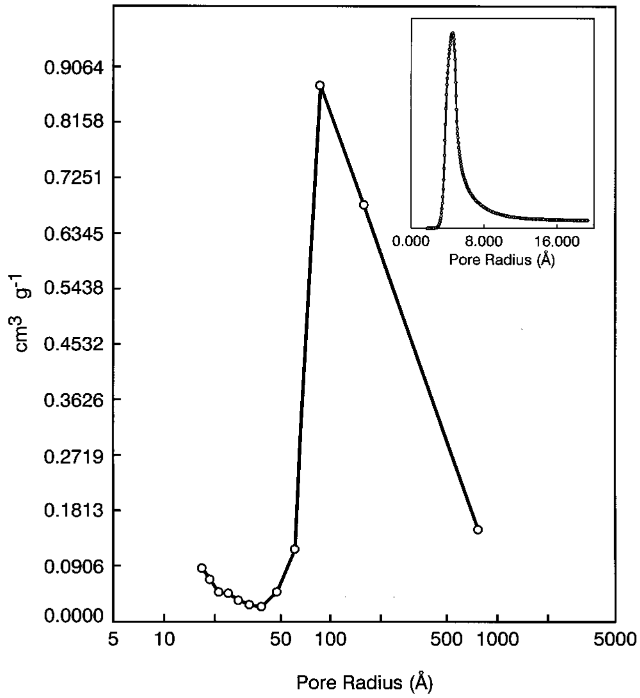

Figure 6. Micro- and mesoporosity of ZSM-5 after combustion of carbon matrix.

The external surface area of zeolite Beta was in the same range as that of zeolite Beta synthesized by Camblor et al.[23] who reported that zeolite Beta (Si/Al = 8) with a crystal size of 5−10 nm had an external area of 265.5−288.5 m^2/g. The mesopore system of our zeolite Beta had a radius larger than 50 nm and a specific volume of 2.4 mL g^{-1} calculated by the *t*-plot (DeBoer) method. This mesopore system, which Camblor also reported, is assigned to the packing of the small zeolite crystals and is of significance in heterogeneous catalysis because of its influence on the diffusion of products and reactants.

Conclusion

Confined space synthesis involves crystallization of the zeolite gel inside the mesopore system of an inert matrix. The crystal size of the zeolite is controlled by the size distribution of the inert mesopore system and does not depend on the gel composition. The zeolite gel is introduced into the mesopores of the matrix by sequential incipient wetness impregnations of the matrix with zeolite gel precursor solutions. A low viscosity of the impregnation solutions limits the zeolite gel to the mesopores of the matrix. Using carbon black as the inert matrix enables easy recovery of the zeolite by controlled combustion of the carbon matrix. Recovery, washing, and ion exchange of nanosized zeolites in the matrices are facile compared to conventional methods for isolation (e.g., high-speed centrifugation) and handling of nanosized zeolites. Synthesis of zeolites with a preferred gel composition, which would have been difficult, if not impossible, in a conventional synthesis, is possible by confined space synthesis. ZSM-5, zeolite Beta, zeolite X, and zeolite A are synthesized with size-tailored crystal sizes in the range 7−75 nm and with very little intergrowth of the individual crystals. The zeolites have an additional intercrystalline mesopore volume. Catalytic applications of these materials are currently being investigated.

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