DOI: 10.1002/chem.201101401

Hierarchical Mesoporous Zeolites: Direct Self-Assembly Synthesis in a Conventional Surfactant Solution by Kinetic Control over the Zeolite Seed Formation

Yan Zhu,^[a] Zile Hua,^[a] Jian Zhou,^[a] Lijun Wang,^[a] Jinjin Zhao,^[b] Yun Gong,^[a] Wei Wu,^[a] Meiling Ruan,^[a] and Jianlin Shi^{*[a]}

Abstract: By kinetic control over the zeolite seed formation, we report the direct fabrication of hierarchical mesoporous zeolites using hexadecyl trimethyl ammonium bromide (CTAB) as the soft template in a conventional solution route. Nanometer-sized, subnanocrystal-type zeolite seeds with a high degree of polymerization are essential to prevent the formation of a separate amorphous mesoporous phase and the

phase separation between the mesophase and zeolite crystals in the presence of CTAB and a certain amount of ethanol. The mechanisms for the formation of hierarchically porous zeolites

Keywords: aldol condensations • heterogeneous catalysis • kinetics • surface chemistry • surfactants • zeolites

in the solution process, including the effect of mother liquid aging, formation of subnanocrystal zeolite seeds and their self-assembly effect with CTAB, and the role of ethanol are proposed and discussed in detail. The prepared mesoporous ZSM-5 zeolite showed much higher catalytic activity than conventional counterparts for aldol condensations involving large molecules, especially in the synthesis of vesidryl.

Introduction

As important heterogeneous catalysts, ZSM-5 type zeolites are widely used in petrochemistry and the fine chemical industry for a series of reactions involving cracking,^[1] alkylation,^[2] acylation,^[3] isomerization,^[4] aromatization,^[5] and aldol condensation.^[6] The penetrating and intersecting micropore networks, composed of straight channels along the *b* axis (0.53 nm × 0.56 nm) and zigzag channels along the *a* axis (0.51 nm × 0.55 nm), endow the catalyst high shape and size selectivity towards reactant and/or product molecules. The enhanced selectivity of ZSM-5 zeolites was evidenced in the separation of xylene isomers, especially for highly pure *p*-xylene. In toluene disproportionation reactions or the alkylation of toluene with methanol, ZSM-5 catalysts

[a] Dr. Y. Zhu, Dr. Z. Hua, Dr. J. Zhou, Dr. L. Wang, Dr. Y. Gong, W. Wu, M. Ruan, Prof. J. Shi State Key Laboratory of High Performance Ceramics and Superfine Microstructures Shanghai Institute of Ceramics, Chinese Academy of Science No.1295 Ding-xi Road Shanghai 200050 (P.R. China) Fax: (+86)21-5241-3122 E-mail: jlshi@mail.sic.ac.cn
[b] Dr. J. Zhao

School of Material Science and Engineering Shijiazhuang Tiedao University 17 Northeast, Second Inner Ring Shijiazhuang, Hebei (P.R. China)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201101401.

offer a higher para selectivity for para-xylene over metaxvlene.^[4,7] On the other hand, the adjustable acidity promotes the formation of carbocations, which are reactive and can accelerate reactions like isomerization. However, ZSM-5 zeolites fail to catalyze larger molecules or reactions involving macromolecules due to their diffusion limitations in the micropore channels, and carbon deposition in the pore system during the reaction would consequently lead to severe catalyst deactivation.^[8] To solve the diffusion problem, aluminum-substituted mesoporous silicates have been synthesized by using hexadecyl trimethyl ammonium bromide (CTAB) as a soft template since 1992.^[9] Although the ordered mesopores (around 2 nm in diameter) could easily be used in diffusion restricted reactions, the poor hydrothermal stability and weak acidity, resulting from the noncrystalline frameworks, greatly limited practical applications.^[10] Alternatively, the diffusion limitation of reagents through zeolite micropores can be solved when nanozeolites (particles no bigger than 100 nm) are employed. Within the past few decades, nanozeolites have been successfully synthesized by the hydrothermal treatment of colloid solutions at relatively low temperatures with or without the addition of a growth inhibitor or nucleation promoter.^[11] However, zeolite crystals smaller than 100 nm might be thermodynamically unstable due to high surface energy and vast amounts of surface defects. Meanwhile, nanocrystals are difficult to handle and have low yields during synthesis, in which the majority of the building units are left unused in the mother liquid. Consequently, the synthesis of hierarchical and microsized zeolites, which combines the acidic activity and shape selectivity of micropores and the free diffusion properties of mesopores, has attracted great attention among researchers in chemical and material sciences in the last few years.

To date, the synthesis of hierarchical mesoporous zeolites falls into three categories: 1) the selective etching of presynthesized zeolites to create mesopores in zeolite crystals,^[12] including selective acid etching for framework dealumination and alkali etching for framework desilication; 2) crystallization of the framework of presynthesized mesoporous aluminosilicates, keeping the mesopores unaffected during zeolite formation, which includes traditional hydrothermal treatment and steam-assisted crystallization methods;^[13] and 3) the assembly of nanosized zeolite crystallites, in which the mesopores are formed among the crystallites. Generally, in the framework crystallization approach, mesoporogens and microporogens are used simultaneously in one system. Tetrapropylammonium (TPAOH) is a commonly used micropore structure-directing agent (SDA) for ZSM-5 zeolites. A number of hard or soft templates have been used as mesoporogens. Compared with soft templates, most of the hard templates serve as scaffolds, either through endo- or exotemplating,^[14] such as carbon particles,^[6a,15] carbon aerogel,^[16] and 3DOM carbon.^[17] Also monodisperse polystyrene (PS) spheres^[18] and poly(methylmethacrylate) (PMMA) nanospheres^[19] have been used as hard templates for generating mesopores in zeolites with unique morphologies. Nevertheless, most of the mesoporous materials with isolated secondary porosity so far are unsuitable for the diffusion of large molecules, because of the rigidity of the hard templates. Combined with the high cost and complexity in the fabrication of hard templates, soft templates may offer a more promising alternative approach for the preparation of hierarchical mesoporous zeolites.

Soft templates can be distinguished from hard templates by diverse interactions with zeolite precursors, such as covalent bonds, van der Waals forces, hydrogen bonds, and electrostatic forces. They can be classified as organosilanes, cationic polymers, silylated polymers, general surfactants, and other agents with unique molecular structures. Organosilane soft templates, which were proposed by Ryoo et al., prevent phase separation during crystallization by using specially designed bifunctional coupling agents.^[6b] On the other hand, Xiao et al. synthesized hierarchical zeolite beta and ZSM-5 by using the cationic polymers polydiallyldimethylammonium chloride (PDADMAC) and the dimethyldiallyl ammonium chloride acrylamide copolymer (PDDAM) as mesoporogens, and the mesopore size could be tuned by the amount of polymers used.^[20] Also, Park et al. prepared MSU-MFI, with intracrystal mesopores of 2.2 and 5.2 nm, using silylated polypropylene oxide diamine and polyethylenimine polymers as templates.^[21] Furthermore, stable single-unit-cell nanosheets of zeolite MFI were successfully fabricated with the specially designed and synthesized bifunctionalized agent $C_{22}H_{45}$ -N(CH₃)₂-C₆H₁₂-N(CH₃)₂-C₆H₁₃ (C₂₂₋₆₋₆), which possesses two quaternary ammonium groups spaced by a C₆ alkyl linkage and a long chain alkyl group (C_{22}) on the end.^[6c] Based on the strong interactions between the zeolite precursor and mesoporogen, either by chemical bonding or

enlargement of charge densities, the hierarchical structures listed above could be created without phase separation between the mesophase and crystalline zeolite. At the same time, unfortunately, the synthesis of these unique templates is very complex, leading to a high cost for the synthesized mesoporous zeolite materials.

Using ordinary surfactants, such as CTAB, to prepare hierarchical zeolites has been of great interest since the discovery of MCM-41. Several years ago, Pinnavaia et al. synthesized steam-stable aluminosilicate mesostructures using zeolite precursors. MSU-S (MFI) and MSU-S (BEA) type mesostructures were prepared by assembling the respective zeolite seeds with CTAB under hydrothermal conditions.^[22] Nevertheless, diffraction peaks were not present in the XRD patterns, indicating a noncrystalline framework, although infrared (IR) spectroscopy with a band in the 550-600 cm⁻¹ region confirmed the presence of five-membered ring subunits. Then in 2006, Bagshaw et al. synthesized an intimate composite material, composed of highly ordered mesoporous MSU-S (BEA) and a well-crystallized zeolite Beta over microscale domains, which displayed Beta-type XRD diffraction pattern.^[23] However, this material was still a mixture of ordered mesophase and zeolite crystals with inferior catalytic activity and stability, and phase separation could not be avoided when using traditional surfactants in reactions with the zeolite precursors. To solve this problem, Zhu et al. proposed a new strategy to prepare hierarchical zeolites, which used CTAB coupled with tert-butyl alcohol (TBA) and 1,3,5-trimethylbenzene (TMB) as a cosolvent and additive, respectively, enhancing the stability of the surfactant micelles.^[24] This coincided with the strong interactions required between zeolite precursors and templates.

All of the above reports focused on designing and/or choosing different types of surfactants, yet little attention has been paid to modulation of the zeolite building blocks, or zeolite seeds, during the production of hierarchical mesoporous zeolites. The crystallization process of zeolites, which can be distinguished in a chronological sequence as the induction period, nucleation, and crystal growth, is a heterogeneous process with constituents typical of different polymerization degrees, even in the same period, such as induction.^[11c,25] Due to the important effect of the zeolite precursor in the induction period on the nucleation, great efforts have been made to characterize the primary units, oligomers, and nanoparticles.^{[26] 29}Si NMR spectroscopy combined with other techniques clearly quantified the distribution of the Q^n bands in the zeolite precursor at an early stage, and the latest results by Petry et al. proved the presence of oligomers and their evolution into aggregated nanoparticles, which demonstrated the connectivity in nanoparticles is about 0.3 units above oligomers.^[26b] At the same time, techniques such as XRD, SEM, and TEM could be used to characterize crystal growth.^[25a,d] However, the in situ detection of nucleation at relatively high temperatures is still challenging. By aging the zeolite precursor of silicalite-1 at 90°C, Kirschhock et al. and Bals et al. proposed the presence of nanoslabs and tablets, the structures of which are still unclear, and prepared ordered mesoporous materials by altering the reaction conditions to be unfavorable for zeolite growth.^[25e,27] Hence, the bond making and cleavage of Si-O-Si and subsequent rearrangement of the subunits into small nuclei centers with high regularity are still obscure and further work is necessary.

Although there is no clear definition and demarcation due to the uniqueness and complexity of different reaction systems, zeolite precursors can be approximately classified into primary units of either oligomers (composed of different subunits) and nanoparticles or subnanocrystals and nanocrystals, according to the polymerization degree or framework regularity. Therefore, most of the above zeolite seeds before interaction with mesoporogen should be oligomers and nanoparticles, and few of them contain subnanocrystals or nanocrystals. Nevertheless, the crystallization of zeolites is a rather slow process compared with the rapid formation of the mesoporous phase even at low temperatures.^[25a-d] Based on the kinetic priority for the formation of the mesophase and the small energy differences in the thermodynamics between microporous zeolite frameworks and ordered mesophases,^[25c] constituents with low polymerization degrees would redissolve, or rearrangement could occur under the directing effect of mesotemplates. Hence, zeolite nucleation and/or growth can be largely interrupted accordingly. Finally, an amorphous silicate mesophase results, or a mixture of zeolite and mesophase is obtained for prolonged hydrothermal treatment processes, as demonstrated by Pinnavaia et al.^[22] In the end, this paradox results in separate mesostructures and zeolite crystals with mesoporosity apart from the microporous zeolite lattice.

Fortunately, the constituents of the zeolite precursor, which is kinetically controlled, can be tuned by heat treatments for different time periods. Therefore, to diminish a mismatch between kinetics and thermodynamics in the fabrication of mesoporous zeolites, further efforts are needed in the design of experiments, from the perspective of kinetic control, to synthesize mesoporous zeolites without phase separation in solution.

Herein, the kinetic control for the zeolite seed formation was first attempted in the direct fabrication of hierarchically mesoporous ZSM-5 zeolites by controlling the zeolite seed formation and using CTAB as a soft template in our experiments, in which the key was to produce a large number of subnanocrystal-type zeolite seeds in a heating process. They were then allowed to interact with the surfactant for mesostructure assembly. These unique subnanocrystal-type zeolite seeds were fabricated by aging a water solution of tetraethylorthosilicate (TEOS), aluminum isopropoxide (Al- $(iPrO)_3$) and tetrapropylammonium (TPAOH) in sealed Schott Duran bottles at 100°C for two to three days. Such zeolite seed solutions are believed to contain mostly subnanocrystals, which have much higher polymerization degrees than the corresponding oligomers and nanoparticles before aging, and tend to crystallize upon subsequent treatment. This nearly clear solution was then mixed with CTAB in an ethanol/water solution with subsequent hydrothermal treat-

ment at 150 °C. Finally, the zeolites with mesopores penetrating through the micropore system were formed. This strategy differs from the soft templating approach proposed by Ryoo et al,^[6b] in which specially designed bifunctional surfactants were employed but zeolite seed formation was not necessary, and differs from the early reports,^[22] in which zeolite subunits were used directly as the building blocks but a crystallized zeolite phase was not obtained as evidenced by XRD. Moreover, the present work is also different form our steam-assisted crystallization approach recently reported, in which phase separation was prevented by avoiding the liquid phase during the framework crystallization.^[13b,c] The present approach is based on the principle that the formation of discrete mesophases, separate from zeolite crystals, can be effectively prevented by generating a large amount of subnanocrystals with relatively high polymerization degree combined with the use of ethanol.

In addition, the catalytic conversions involving large organic molecules were tested using the prepared mesoporous zeolites in the aldol condensation between 2-hydroxyacetophenone and benzaldehyde and between 2',4'-dimethoxyacetophenone and 4-methoxybenzaldehyde. Results indicate that the presence of mesoporosity in the zeolite particles can lead to enhanced catalytic activities for aldol condensation reactions.

Results and Discussion

Synthesis of hierarchical ZSM-5 zeolites with mesoporous structures: ZSM-5 zeolites with different hierarchical porous structures were prepared with different amounts of CTAB (C) and ethanol (E) and designated as HMZ-xC-yE, in which x and y represent the molar ratio of CTAB to H_2O times 10^{-3} and of ethanol to H₂O, respectively. For comparison, ZSM-5 zeolites without using CTAB were synthesized, while keeping the other conditions unchanged, and labeled as HMZ-0C-yE. The yield of the zeolites without CTAB was very low, as described in detail in the Experimental Section, about 10% compared with yields higher than 85% for samples assembled with CTAB. This means that CTAB plays an important role in the mesostructure assembly process with subnanocrystals. Table 1 lists the textual properties of HMZ-xC-yE. The relative percentages of microporous volume $(V_{\text{mic}}/V_{\text{tot}})$ and the external surface area $(S_{\text{ext}}/S_{\text{BET}})$ were calculated and are listed for comparison (Table 1) along with the data for conventional ZSM-5 zeolite, which has a small external surface area of about $43 \text{ m}^2\text{g}^{-1}$ because of the absence of mesostructures. Small differences in the total BET surface area between HMZ-0.28C-0E and HMZ-0C-0E were found, but the external surface area increased from $103 \text{ m}^2 \text{g}^{-1}$ (HMZ-0C-0E) to $172 \text{ m}^2 \text{g}^{-1}$ (HMZ-0.28C-0E), as clearly indicated by the S_{ext}/S_{BET} ratios. For the sample HMZ-0C-0E, the jump at $P/P_0 > 0.9$ in the nitrogen sorption isotherms belongs to the intercrystal porosity due to the aggregation of small zeolite crystals. However, for the sample HMZ-0.28 C-0E, the slow rise at $P/P_0 < 0.4$ contrib-

14620 -

Table 1. Textual properties of hierarchical ZSM-5 zeolites.^[a]

	$\frac{S_{\rm BET}}{[m^2g^{-1}]}$	$\frac{S_{\rm ext}}{[\rm m^2 g^{-1}]}$	$\frac{S_{\rm mic}}{[{\rm m}^2{\rm g}^{-1}]}$	V_{tot} [cm ³ g ⁻¹]	$V_{\rm ext}$ [cm ³ g ⁻¹]	$V_{ m mic}$ [cm ³ g ⁻¹]	$V_{\rm mic}/V_{\rm tot}$	$S_{\rm ext}/S_{\rm BET}$
HMZ-0.28 C-0 E	357	172	185	0.200	0.116	0.084	0.42	0.48
HMZ-0.28 C-0.012 E	379	185	194	0.213	0.125	0.088	0.41	0.49
HMZ-0.28 C-0.024 E ^[b]	416	229	187	0.257	0.172	0.085	0.33	0.55
HMZ-0.28 C-0.035 E	431	272	159	0.273	0.201	0.072	0.26	0.63
HMZ-0.28 C-0.047 E	440	289	151	0.289	0.221	0.068	0.24	0.66
HMZ-0.56 C-0.035 E	412	309	103	0.256	0.21	0.046	0.18	0.75
HMZ-0.21 C-0.035 E ^[b]	450	240	210	0.294	0.197	0.097	0.33	0.53
HMZ-0.14 C-0.035 E	384	178	206	0.265	0.171	0.094	0.35	0.46
HMZ-0C-0.035E	367	133	234	0.244	0.136	0.108	0.44	0.36
HMZ-0C-0E	349	103	246	0.232	0.118	0.114	0.49	0.29
HMZ-0.28 C-0.035 E (3d HT)	398	225	173	0.263	0.176	0.083	0.32	0.67
HMZ-0.28 C-0.035 E (12h ST)	402	241	161	0.270	0.162	0.108	0.40	0.60
conventional ZSM-5	370	43	327	0.192	-	-	-	0.12

[a] S_{BET} is the BET surface area; S_{mic} and V_{mic} are values calculated from t-plot analyses; V_{tot} is the single-point adsorption total pore volume at $P/P_0 = 0.984$; $S_{\text{ext}} = S_{\text{BET}} - S_{\text{mic}}$ and $V_{\text{ext}} = V_{\text{tot}} - V_{\text{mic}}$. In our experiments, the external surface areas and external pore volumes were the calculated results for the secondary porosity except the intrinsic micropores. S_{ext} and V_{ext} are effective parameters to evaluate diffusion limitations in zeolites, which are negligible for the conventional ZSM-5 zeolite. The samples labeled HMZ-0.28 C-0.035 E (3d HT) and HMZ-0.28 C-0.035 E (12h ST) are the treated HMZ-0.28 C-0.035 E samples after aging for 3 days at 100 °C for the hydrothermal stability test and after a steam treatment for 12 h at 700 °C, respectively. The textual properties for conventional ZSM-5 zeolite are listed for comparison. [b] Values of sample HMZ-0.28C-0.024E and HMZ-0.21C-0.035E, were given by Micromeritics ASAP 2020, while others were calculated by Micromeritics Tristar 3000.

utes evenly to the external surface area compared with the contribution of intercrystal pores. Adding ethanol into the mixture, the BET surface area increases from $357 \text{ m}^2\text{g}^{-1}$ (HMZ-0.28C-0E) to $431 \text{ m}^2\text{g}^{-1}$ (HMZ-0.28C-0.035E), and the corresponding external surface area increases to 272 m²g⁻¹, and the micropore volume remains almost unchanged. Even for the zeolite preparation without CTAB, the BET surface area increased slowly at increased ethanol amounts. This is because a certain amount of ethanol hinders the overgrowth of zeolite crystals and slows down the crystallization process,^[11b] which favors the self-assembly of zeolite subnanocrystals or nanocrystals under the direction by micro- and/or mesopore directing agents. However, high amounts of ethanol (sample HMZ-0.28C-0.047E) prevent the formation of CTAB micelles and subsequent self assembly with the zeolite seeds, resulting in phase separation between the mesophase and zeolite crystals. Consequently, to synthesize zeolites with mesopores penetrating through the micropore framework, the molar ratio of ethanol to H₂O needs to be smaller than 0.035, under these conditions.

Furthermore, different amounts of CTAB were tested and the results are listed in Table 1. A clear relationship between the BET surface area and the amount of CTAB was not found. With increasing CTAB amounts, the BET surface area first increases from 384 (HMZ-0.14C-0.035E) to $450 \text{ m}^2 \text{g}^{-1}$ for HMZ-0.21C-0.035E then decreases slightly for samples HMZ-0.28C-0.035E and HMZ-0.56C-0.035E. The mesopore and micropore surface areas change accordingly. This means the meso- and microporosity can be tuned, to a certain extent, by changing the using amount of the surfactant and ethanol in the preparation of hierarchical zeolites.

Figure 1 shows SEM images of HMZ with different amounts of CTAB. Sample HMZ-0.14 C-0.035 E (Figure 1 A) was composed of ellipsoidal particles with a rough surface and a particle size of about 150 nm. Compared with HMZ-0.14 C-0.035 E, HMZ-0.28 C-0.035 E, synthesized with a higher amount of CTAB, shows a larger particle size and a more regular, cubic morphology simi-

lar to conventional ZSM-5 zeolites (Figure 1). An enlarged SEM image in Figure 1D shows the typical rough surface of the mesoporous zeolite. All of the particles in these samples show rough surfaces and mesoporous structures in the high resolution



Figure 1. SEM images of hierarchical zeolites: A) HMZ-0.14C-0.035E; B) HMZ-0.21C-0.035E; C) and D) HMZ-0.28C-0.035E; E) TEM image and F) HR-TEM image and SAED patterns (inset) of HMZ-0.28C-0.035E.

field emission scanning electron microscopic (FE-SEM) images demonstrating the presence of mesoporosity in the zeolite particles. Therefore, by choosing the right type of

Chem. Eur. J. 2011, 17, 14618-14627

www.chemeurj.org

FULL PAPER

CHEMISTRY A EUROPEAN JOURNAL

zeolite seed precursor, hierarchical ZSM-5 with regular microporosity and a co-existing mesoporosity of about 2.5 nm can be synthesized.

The nitrogen adsorption and desorption isotherms (Figure 2a) of some samples give more detailed information on the pore structures. The sharp increase at $P/P_0 < 0.05$ in all of the samples indicates the presence of micropores, but the gradual increase in the P/P_0 range of 0.05–0.3 is observed in most of the samples except HMZ-0C-0E. Even for HMZ-0.28 C-0 E, without ethanol, there is a slow uptake before the appearance of a distinct plateau. Combined with pore size distribution in Figure 2b, the results for HMZ-0.28C-0.035E and HMZ-0.28C-0.024E clearly indicate the presence of mesopores of about 2-3 nm co-existing with micropores. Only microporosity is present in HMZ-0C-0E (Figure 2); however, mesopores of about 2.5 nm are formed in HMZ-0.28 C-0E, to which CTAB was added. Mesoporosity becomes more and more apparent with increased ethanol content from sample HMZ-0.28C-0.024E to HMZ-0.28C-0.035 E. All of the above results demonstrate that the formation of mesoporous zeolites is a result of self-assembly between the subnanocrystal zeolite seeds and the mesostructure directing agent, CTAB, with synergetic assistance by a certain amount of ethanol.



Figure 2. a) Nitrogen adsorption and desorption isotherms of HMZ-xCyE and b) the corresponding pore size distribution calculated by the BJH method using the desorption branch of the isotherms. The isotherms in a) are shifted by 0, 80, 120 and 160 cm³g⁻¹, respectively, along the *y* axis to avoid overlapping. The isotherms in b) are shifted by -0.01, 0.01, 0.03and 0.05 cm³g⁻¹ respectively, along the *y* axis.

For HMZ-0.28 C-0.035 E, the total BET surface area was $431 \text{ m}^2 \text{g}^{-1}$, and the external surface area and pore volume reach 272 m²g⁻¹ and 0.201 cm³g⁻¹, respectively, with microporosity comparable to other samples. Therefore, further characterization and catalytic reactions were made using this sample. Figure 3a shows the X-ray diffraction pattern of



Figure 3. a) Wide-angle XRD patterns of HMZ-0.28 C-0.035 E and b) the corresponding sample after 3 days of hydrothermal treatment, labeled as HMZ-0.28 C-0.035 E (3d HT), to test its hydrothermal stability.

HMZ-0.28C-0.035E, which exhibits typical and sharp diffraction peaks for the ZSM-5 lattice structure. Moreover, the high-resolution TEM (HR-TEM) image of the sample and the selected area electron diffraction (SAED) patterns (Figure 1F) prove that this domain is a single crystal with mesopores (about 3 nm) penetrating through the micropore framework. Even for small particles with irregular shape, TEM images (Figure S1, Supporting Information) show the crystal structure.

The hydrothermal stability of HMZ-0.28C-0.035E was tested by subjecting the calcined sample (0.2 g) in water (50 mL) to 100 °C for three days under vigorously stirring. This sample is labeled as HMZ-0.28C-0.035E (3d HT). A further test for the steam stability of HMZ-0.28C-0.035E was carried out by exposing the calcined sample (0.2 g) to a flow of N₂ (50 mL min⁻¹) saturated with about 40% water vapor at 700 °C for 12 h. This sample is designated as HMZ-0.28C-0.035E (12h ST). The samples showed a BET surface area loss of only around 10% (Table 1), which, compared with the severe destruction of ordered mesoporous materials MCM-41(Al) (Table S1, Supporting Information), proves the as prepared hierarchical ZSM-5 zeolites to be enough stable for applications in catalytic reactions. Furthermore, SEM images (Figure S2, Supporting Information) and X-ray diffraction patterns (Figure 3b) also demonstrate that this material possesses high hydrothermal and steam stability.

The catalytic properties of hierarchical ZSM-5 zeolites and other counterparts: Chalconoids and flavanoids have attracted increasing attention in pharmaceutical fields due to their antitumor, anti-inflammatory and antifungal properties. They are commonly catalyzed by acids or bases under ho-

FULL PAPER

mogeneous conditions using the Claisen–Schmidt condensation and subsequent isomerization. However, the difficulties in the separation and recovery of the catalysts makes heterogeneous catalysis by solid acids or bases a much more attractive and environmental friendly alternative. Thus, in our experiments, H-ZSM-5 zeolites (HMZ-0.28 C-0.035 E and conventional ZSM-5), and ordered mesoporous materials (MCM-41) with the same Si/Al ratio (50:1) were used as the catalysts for aldol reactions between 2-hydroxyacetophenone and benzaldehyde and between 2', 4'-dimethoxyacetophenone and 4-methoxybenzaldehyde without any solvents. For the reaction between 2-hydroxyacetophenone and benzaldehyde, conventional ZSM-5 zeolite showed a moderate conversion rate (19.1 %), significantly lower than for HMZ-0.28 C-0.035 E (41.6 %, Table 2). In spite of the relatively

Table 2. Catalytic data of aldol condensations using hierarchical zeolites and their counterparts. $\!\!^{[a]}$



[a] Catalytic properties were compared on the basis of the same weight of the catalyst (see the Experimental Section for details). The BET surface areas were 431 $m^2 g^{-1}$ for HMZ-0.28C-0.035E, 370 $m^2 g^{-1}$ for the conventional ZSM-5, and 987 $m^2 g^{-1}$ for MCM-41(Al). [b] These data indicate percentage selectivity of flavanone/chalcone/others, and the other data indicate the reactant conversion [%].

small molecular size of the reactants and products in the catalytic synthesis of flavanone and 2'-hydroxychalcone, the difference in the catalytic activities between HMZ-0.28 C-0.035 E and the conventional ZSM-5 zeolite was significant. Furthermore, HMZ-0.28 C-0.035 E exhibits a much more enhanced catalytic activity in the synthesis of vesidryl (2', 4, 4'trimethoxychalone) compared with the conventional ZSM-5 zeolite (Table 2), which shows less than 2% conversion. Therefore, the presence of mesoporosity in HMZ-0.28C-0.035E can greatly enhance the catalytic activity in the reactions, especially involving large organic molecules. Moreover, the MCM-41(Al) catalyst without diffusion limitations displayed very low catalytic activities in aldol condensations. This can be attributed to the lack of strong acid sites because of the short-range atomic order in MCM-41 compared with highly crystalline zeolites. Therefore, the enhanced catalytic activity by hierarchical zeolites in aldol condensations was from the combined effect of framework acidity and mesoporosity.

Mechanism for the formation of mesoporous zeolites through kinetic control of zeolite seed formation: To test the influence of the zeolite precursor on the synthesis of hierarchical mesoporous zeolites, the precursor was aged at 100 °C for different time periods. The samples are designated as HMZ-*n*d, in which *n* represents the number of days the zeolite precursor was aged at 100 °C. All of the other conditions were the same as for sample HMZ-0.28 C-0.035 E, which was aged for 2 days at 100 °C. According to the experimental results, four interaction models between CTAB and the zeolite precursor at different stages are proposed and illustrated in Scheme 1–4. These are as follows.



Scheme 1. The primary units are $[SiO_4]$ and/or $[AIO_4]$ tetrahedrons. Selfassembly synthesis of ordered mesoporous materials under structure direction by CTAB.

- For zeolite precursors only with primary units of [Si–O] tetrahedrons, ordered mesoporous materials such as MCM-41 can be prepared by a standard self-assembly synthesis under hydrothermal conditions.
- 2) When the zeolite precursor is mainly composed of silicate oligomers and nanoparticles of low polymerization degree, the self-assembly of TPA+ around these lowpolymerized species can be destructed by strong interactions between the highly hydrophilic species and the hydrophilic ends of the CTAB molecules. This is a result of the competition between self-assembly (between the mesoporogens and the oligomers and/or nanoparticles) and crystallization of these species under the direction of the microporogens. Therefore, either mesophase or large zeolites or a mixture of the two are formed, depending on the experimental parameters. For example, Kirschhock et al. and Bals et al. prepared ordered mesoporous materials using much higher polymerized species, such as nanoslabs or tablets, by lowering either the hydrothermal treatment temperature or the pH value of the reaction system to avoid the nucleation of the zeolite.^[25e,27] More generalized rules are: 1) oligomers larger in size (by several nanometers, see below) than the primary units may not be as well structure-directed by the mesopore structure directing agent (surfactant) for self-assembly as the primary units, which always leads to the formation of the mesophase with less ordered mesostructure and 2) the polymerized species and nanoparticles propagate into nuclei centers and quickly grow into large zeolite crystals by hydrothermal treatment at elevated temperatures.

www.chemeurj.org

- 14623



Scheme 2. Oligomers and/or nanoparticles leading to amorphous and not well-ordered mesoporous phases or a mixture of the mesophase and pure zeolite crystals. Silicate oligomers are aggregated subunits such as threemembered rings, four-membered rings or five-membered rings with relatively low degrees of polymerization. Nanoparticles are aggregated oligomers with connectivity above oligomers. The final products depend on the competition between mesoporogens (CTAB) and microporogens (TPAOH). TEM (top) and SEM (bottom) images are for the HMZ-0d sample prepared from this type of zeolite seed.

Therefore, the most common results (Scheme 2) are the formation of large zeolite crystals accompanied by considerable amounts of amorphous mesoporous silica. A SEM image of sample HMZ-0d, without having been aged at 100 °C (Scheme 2) shows the presence of micrometer-sized zeolites with smooth surfaces surrounded by a large amount of disordered mesophase (TEM image, Scheme 2). Small-angle XRD patterns (Figure S3, Supporting Information) showed a small, broadened diffraction peak around 2° (2θ), which demonstrates the partially but much less ordered mesoporous structure compared with traditional MCM-41, which has three distinct peaks. This result of phase separation does not differ from earlier reports by Pinnavaia et al.^[22]

A EUROPEAN JOURNAL

3) In the literature, subnanocrystals (ca. 2-10 nm) are regarded as species with the typical, regular atomic arrangement of the MFI structure and are easy to crystallize. However, the crystal structure could not be detected by XRD. In the present study, these subnanocrystals were formed in mother liquids by aging at 100°C with the concentrations tunable by varying the heating time. However, different from sample HMZ-0d without aging, the aged zeolite seeds should have experienced some kind of structure alteration into a more ordered atomic arrangement, and the subsequent interaction between the aged seeds and CTAB at this stage led to the formation of mesoporous zeolites. The SEM image of the HMZ-1d sample (Scheme 3A) shows the zeolite particles with mesoporous structure, together with a few mesophase particles (circled), and the corresponding TEM images (Scheme 3B and C) clearly show the zeolite lattice structure. Zeolite precursors aged at 100°C for 2-3 days formed hierarchical mesoporous zeolites without detectable isolated mesophase particles. The SEM and TEM images (Scheme 3D-F) indicate that the particles from sample HMZ-3d are regularly shaped, similar to the HMZ-0.28C-0.035E sample aged for 2 days (Figure 1 C-F). Therefore, aging zeolite precursors at 100 °C

for 2-3 days is key for the creation of hierarchical porous zeolite in a conventional solution process. All of the oligomers and/or nanoparticles or other lowpolymerized species, which are responsible for the formation of amorphous mesophases, except for pure zeolite crystals (HMZ-0d, Scheme 2) and for mesoporous zeolite particles (HMZ-1d, Scheme 3A), could be eliminated and were converted to subnanocrystals in the mother liquid by aging



Scheme 3. Subnanocrystals in the self-assembly synthesis of hierarchical mesoporous zeolites (HMZ) resulting in a low ordered mesoporous network penetrating through the zeolite microporous framework. Subnanocrystals are of much higher polymerization degree and atomic arrangement ordering than oligomers and/or nanoparticles and are obtained by properly aging the seed solution at relative high temperatures. A) SEM and B) TEM images of the structure of HMZ-1d for zeolite precursors aged for 1 day at 100 °C. The circled area (A) shows the mesophase. C) The enlarged image of the dotted square in B which shows the crystalline structure. D) The SEM and E) TEM images for HMZ-3d (the zeolite precursor aged at 100 °C for 3 days), and F) is a HR-TEM image of the zeolite crystals in E.

for enough time. As a result, the strong interaction between subnanocrystals and CTAB micelles, similar to the case between the oligomers and CTAB, led to the creation of less ordered mesostructures among the zeolite subnanocrystals, and the subsequent crystallization of the subnanocrystal framework resulted in the regularly shaped hierarchical zeolites with penetrating mesoporous network in the particles. 4) In the case of sufficient zeolite seed crystallization, the mother liquids contained mainly small zeolite nanocrystals tens or hundreds of nanometers in size. The presence of such nanocrystals of about 100 nm was verified in TEM images (Figure S4, Supporting Information) after aging the zeolite precursor at 100 °C for 4 days. However, due to the size mismatch between the CTAB micelles and the zeolite precursor at this stage, only aggregates of the nanocrystals were obtained (HMZ-4d, SEM image, Scheme 4).



Scheme 4. Nanocrystals and their aggregates of about 100 nm.

The above results demonstrate that a kinetic control over the zeolite seed formation is vitally important for the preparation of mesoporous zeolites. In the present case, the formation of zeolite subnanocrystals of several nanometers in size by aging the mother liquids at 100 °C for 2 or 3 days is key. The presence of the surfactant, CTAB, played an important role in mesostructure formation; however, well-ordered mesostructures could not be created in cooperative self-assembly with subnanocrystals.

An essential piece of evidence to further support the above conclusion would be to characterize the structures and sizes of the silicate oligomers and/or nanoparticles, subnanocrystals, and nanocrystals. Unfortunately, however, the structures of most zeolite seeds cannot be directly detected by TEM or SEM characterization due to the quick structure destruction of the seeds under high-power electron beams. Hence, dynamic light scattering (DLS) was employed to roughly measure the sizes of the seeds during the aging process of the mother liquid (Figure 4). In all the cases, seeds of around 10 nm are present, which could be ascribed to the presence of silicate oligomers and/or nanoparticles and/or subnanocrystals. It is worth noting that the real seed size is remarkably smaller, especially for small size particles, than those detected by DLS, which gives the hydrated particle size. The aging did not alter the seed size significantly; however, structure change, such as polymerization and atomic arrangement, must have occurred within the seeds during aging, leading to significantly different material structures, which, unfortunately, could not be directly detected in the present study. Aging for 2 or 3 days resulted in a significantly sharpened size distribution of subnanocrystals; however,



FULL PAPER

Figure 4. Particle size distributions of zeolite seeds measured using dynamic light scattering (DLS) without or after aging at 100 °C for different time periods: a) 0 h, b) 24 h, c) 72 h, and d) 96 h.

over-aging (4 days, for example) led to decreased numbers of subnanocrystals.

The presence of a size peak at about 400 nm before aging was attributed to the aggregation of the oligomers and/or nanoparticles, which is similar to the ordered liquid phases (OLP) proposed by Kirschhock et al.^[25e] The peak shifts to about 130 nm after 24 h of aging (Figure 4b), implying the de-aggregation and transformation of some oligomers and/or nanoparticles into subnanocrystals, corresponding to the sharpening of the size distribution peak for subnanocrystals. Aging for 3 and 4 days led to much larger particles about 800 nm in size, which is believed to be the aggregates of nanocrystals of about 100 nm (TEM image, Figure S4, Supporting Information).

Conclusion

In summary, by kinetic control of zeolite seed formation instead of by changing surfactants, CTAB can be used directly for the synthesis of hierarchical mesoporous ZSM-5 zeolites through the self-assembly with subnanocrystal-type zeolite seeds in the presence of a certain amount of ethanol. The resultant materials showed a typical cubic, regularly-shaped morphology with mesopores penetrating through the micropore system. Catalytic results showed significantly higher activities for the prepared mesoporous zeolites than for common zeolites and amorphous mesoporous silica for reactions involving bulky molecules in aldol condensations. This is due to the 2.5 nm mesoporous structure and crystalline nature of the prepared catalysts.

A detailed investigation showed that the dominant presence of subnanocrystals typical of a high degree of polymerization and several nanometer in size, in a nearly transparent zeolite seed solution, was the prerequisite for the direct self-assembly synthesis of the mesoporous zeolite when using CTAB as the mesoporogen and ethanol as a self-assembly modulator. Subnanocrystals can be prepared by aging the mother liquid at 100 °C for 2–3 days, but the direct

www.chemeurj.org

assembly of the silicate oligomer seeds without aging with CTAB led to a phase separated mixture of amorphous mesoporous silica and pure zeolite crystals. Over-aging the seed solution resulted in nanocrystals of about one 100 nm in size and large aggregates of the zeolite. This study presented the first example for the preparation of mesoporous zeolites in an ordinary solution route using conventional surfactants.

Experimental Section

Synthesis of hierarchical mesoporous ZSM-5 zeolites (HMZ): First, Al-(*i*PrO)₃ (0.3066 g, 1.50 mol) and TEOS (15.624 g, 0.075 mol) were mixed with deionized water (25.92 g) at room temperature. After stirring for 2 h, TPAOH (aqueous, 25%, 21.963 g, 0.027 mol) was added dropwise into the resultant emulsion, which became a clear solution after stirring at 40°C for 2–3 h. Finally, the clear solution was transferred to an oil bath at 100°C and aged for 2 days under continuous stirring. The molar ratio in the precursor was Al(*i*PrO)₃:TPAOH:TEOS:H₂O = 1:18:50:1570, and the entire reaction was carried out in a sealed 250 mL Schott–Duran bottle.

After cooling the precursor solution to room temperature, the nearly transparent solution was mixed with an aqueous (90 g of water) solution of CTAB (0.3825-1.53 g, 1.05-4.20 mol) at 80 °C. After 2-3 h at this temperature, absolute ethanol (EtOH, 4-16 g, 0.3-1.2 mol) was added to the mixture. The mixture was stirred for 3 h at 80 °C. At last, the mixtures described above were hydrothermally treated at 150°C in Teflon-lined stainless steel autoclaves under autogenous pressure for 24 h. The final products were filtered, washed repeatedly with deionized water, dried overnight at 100 °C and calcined at 550 °C for 7 h. However, for samples synthesized without CTAB, the zeolite crystals were separated from reaction mixture by centrifugation at 12000 rpm for 30 min, then washed three times with deionized water. All of the other conditions were unchanged. The final molar composition was Al-(*i*PrO)₃:TPAOH:SiO₂:CTAB:EtOH:H₂O = 1.00:18.00:50.00:0.7-2.8:200-432:4903. This series of materials was designated as HMZ-xC-yE for hierarchical mesoporous ZSM-5 zeolites with different amounts of CTAB (C) and ethanol (E) in the reaction system, in which x and y represent the molar ratio of CTAB to H_2O times 10^{-3} and of ethanol to H_2O , respectively.

Characterization: Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a JEOL-2010F electron microscope operated at 200 kV, and field emission scanning electron microscopic (FE-SEM) images were obtained on a Hitachi S-4800. X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2200PC diffractometer using $Cu_{K\alpha}$ radiation (40 kV and 40 mA) with a scanning rate of 4° min⁻¹ for high-angle tests, and 0.4° min⁻¹ for smallangle tests. The nitrogen sorption measurements were performed using Micromeritics Tristar 3000 and Micromeritics ASAP 2020 porosimeters at 77 K. Samples HMZ-0.28C-0.024E and HMZ-0.21C-0.035E were measured using Micromeritics ASAP 2020 for more accurate microposity, and the others were characterized using Micromeritics Tristar 3000. The mesoporous specific surface area and the pore size distribution were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The micropore volumes were calculated by the t plot method. The particle size distribution of the zeolite precursor was characterized by dynamic light scattering (DLS)

Catalytic reactions: For the catalytic reactions, conventional ZSM-5 zeolites with Si/Al=50 were bought for comparison. The MCM-41 zeolites (Si/Al=50) were prepared according to the procedure by Kresge et al.^[9a] All of the materials were ion-exchanged three times with NH₄⁺ (1 M NH₄NO₃), followed by calcination at 550 °C to convert the materials to the H⁺ form. Before the catalytic reactions, the catalysts were pre-activated at 150 °C for at least 2 h.

The aldol condensations were carried out under N_2 atmosphere, using a three-neck flask equipped with a reflux condenser. Condensation of 2-hy-

droxyacetophenone with benzaldehyde was performed by heating a mixture of 2-hydroxyacetophenone (1.36 g, 10 mmol), benzaldehyde (1.59 g, 15 mmol), and the catalyst (150 mg) at 150 °C for 12 h. In the synthesis of vesidryl, 2',4'-dimethoxyacetophenone (1.80 g, 10 mmol), 4-methoxybenzaldehyde (1.36 g, 10 mmol), and the catalyst (70 mg) were mixed, and the reaction was conducted at 140 °C for 24 h. After the reaction, the samples were diluted and analyzed by GC-MS (Agilent, 6890/5973N). The conversion rate and selectivity were given by drawing a standard curve to determine the concentration of corresponding substances.

Acknowledgements

The authors thank the National Natural Science Foundation of China (Nos. 20633090, 20703055, 50872140, and 50702072) for financial support.

- a) J. Čejka, S. Mintova, *Catal. Rev. Sci. Eng.* 2007, *49*, 457–509; b) J. Qi, T. Zhao, F. Li, G. Sun, X. Xu, C. Miao, H. Wang, X. Zhang, *J. Porous Mater.* 2010, *17*, 177–184; c) S. Bao, G. Liu, X. Zhang, L. Wang, Z. Mi, *Ind. Eng. Chem. Res.* 2010, *49*, 3972–3975; d) D. P. Serrano, J. Aguado, G. Morales, J. M. Rodriguez, A. Peral, M. Thommes, J. D. Epping, B. F. Chmelka, *Chem. Mater.* 2009, *21*, 641–654.
- [2] a) D. Wang, X. Li, Z. Liu, Y. Zhang, Z. Xie, Y. Tang, J. Colloid Interface Sci. 2010, 350, 290–294; b) N. R. Shiju, V. V. Guliants, Appl. Catal. A 2009, 356, 1–17.
- [3] M. Bejblová, D. Procházková, J. í. C?ejka, *ChemSusChem* 2009, 2, 486–499.
- [4] L. B. Young, S. A. Butter, W. W. Kaeding, J. Catal. 1982, 76, 418– 432.
- [5] N. Chu, J. Yang, C. Li, J. Cui, Q. Zhao, X. Yin, J. Lu, J. Wang, Microporous Mesoporous Mater. 2009, 118, 169–175.
- [6] a) J.-B. Koo, N. Jiang, S. Saravanamurugan, M. Bejblová, Z. Musilová, J. Cejka, S.-E. Park, J. Catal. 2010, 276, 327–334; b) M. Choi, H. S. Cho, R. Srivastava, C. Venkatesan, D.-H. Choi, R. Ryoo, Nat. Mater. 2006, 5, 718–723; c) M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki, R. Ryoo, Nature 2009, 461, 246–249; d) S. Saravanamurugan, M. Palanichamy, B. Arabindoo, V. Murugesan, J. Mol. Catal. A: Chem. 2004, 218, 101–106.
- [7] J. Čejka, B. Wichterlová, Catal. Rev. Sci. Eng. 2002, 44, 375-421.
- [8] K. Egeblad, C. H. Christensen, M. Kustova, Chem. Mater. 2008, 20, 946–960.
- [9] a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710–712; b) K. R. Kloetstra, H. W. Zandbergen, H. Bekkum, *Catal. Lett.* **1995**, *33*, 157–163.
- [10] A. Taguchi, F. Schüth, Microporous Mesoporous Mater. 2005, 77, 1– 45.
- [11] a) C. Madsen, C. J. H. Jacobsen, Chem. Commun. 1999, 673–674;
 b) W. Song, R. E. Justice, C. A. Jones, V. H. Grassian, S. C. Larsen, Langmuir 2004, 20, 8301–8306; c) S. C. Larsen, J. Phys. Chem. C 2007, 111, 18464–18474; d) Y. Hu, Y. Zhang, Y. Tang, Chem. Commun. 2010, 46, 3875; e) A. Petushkov, S. Yoon, S. C. Larsen, Microporous Mesoporous Mater. 2011, 137, 92–100.
- [12] a) C. Mei, P. Wen, Z. Liu, H. Liu, Y. Wang, W. Yang, Z. Xie, W. Hua, Z. Gao, J. Catal. 2008, 258, 243–249; b) J. Pérez-Ramírez, D. Verboekend, A. Bonilla, S. N. Abelló, Adv. Funct. Mater. 2009, 19, 3972–3979; c) A. Jia, L.-L. Lou, C. Zhang, Y. Zhang, S. Liu, J. Mol. Catal. A: Chem. 2009, 306, 123–129; d) Y. Tao, H. Kanoh, L. Abrams, K. Kaneko, Chem. Rev. 2006, 106, 896–910.
- [13] a) J. Wang, J. C. Groen, W. Yue, W. Zhou, M. O. Coppens, *Chem. Commun.* 2007, 4653–4655; b) J. Zhou, Z. Hua, J. Shi, Q. He, L. Guo, M. Ruan, *Chem. Eur. J.* 2009, *15*, 12949–12954; c) J. Zhou, Z. Hua, X. Cui, Z. Ye, F. Cui, J. Shi, *Chem. Commun.* 2010, *46*, 4994–4996.
- [14] F. Schüth, Angew. Chem. 2003, 115, 3730–3750; Angew. Chem. Int. Ed. 2003, 42, 3604–3622.

14626 -

© 2011 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

FULL PAPER

- [15] C. J. H. Jacobsen, C. Madsen, J. Houzvicka, I. Schmidt, A. Carlsson, J. Am. Chem. Soc. 2000, 122, 7116–7117.
- [16] Y. Tao, H. Kanoh, K. Kaneko, J. Am. Chem. Soc. 2003, 125, 6044– 6045.
- [17] a) W. Fan, M. A. Snyder, S. Kumar, P. S. Lee, W. C. Yoo, A. V. Mc-Cormick, R. L. Penn, A. Stein, M. Tsapatsis, *Nat. Mater.* 2008, 7, 984–991; b) Y. Wang, G. Jin, X. Guo, *Microporous Mesoporous Mater.* 2009, 118, 302–306.
- [18] B. T. Holland, L. Abrams, A. Stein, J. Am. Chem. Soc. 1999, 121, 4308–4309.
- [19] J. Zhao, J. Zhou, Y. Chen, Q. He, M. Ruan, L. Guo, J. Shi, H. Chen, J. Mater. Chem. 2009, 19, 7614–7616.
- [20] L. Wang, Z. Zhang, C. Yin, Z. Shan, F.-S. Xiao, Microporous Mesoporous Mater. 2010, 131, 58–67.
- [21] D. H. Park, S. S. Kim, H. Wang, T. J. Pinnavaia, M. C. Papapetrou, A. A. Lappas, K. S. Triantafyllidis, *Angew. Chem.* 2009, 121, 7781– 7784; *Angew. Chem. Int. Ed.* 2009, 48, 7645–7648.
- [22] a) Y. Liu, W. Zhang, T. J. Pinnavaia, Angew. Chem. 2001, 113, 1295–1298; Angew. Chem. Int. Ed. 2001, 40, 1255–1258; lib > K. Triantafyllidis, E. Iliopoulou, E. Antonakou, A. Lappas, H. Wang, T. Pinnavaia, Microporous Mesoporous Mater. 2007, 99, 132–139.
- [23] S. A. Bagshaw, N. I. Baxter, D. R. M. Brew, C. F. Hosie, N. Yuntong, S. Jaenicke, C. G. Khuan, J. Mater. Chem. 2006, 16, 2235.

- [24] D. H. Pan, P. Yuan, L. Z. Zhao, N. A. Liu, L. Zhou, G. F. Wei, J. Zhang, Y. C. Ling, Y. Fan, B. Y. Wei, H. Y. Liu, C. Z. Yu, X. J. Bao, *Chem. Mater.* 2009, 21, 5413–5425.
- [25] a) N. N. Feoktistova, S. P. Zhdanov, W. Lutz, M. Büllow, Zeolites 1989, 9, 136–139; b) B. J. Schoeman, J. Sterte, J. E. Otterstedt, Zeolites 1994, 14, 568–575; c) A. Corma, M. E. Davis, Chemphyschem 2004, 5, 304–313; d) C. S. Cundy, P. A. Cox, ChemInform 2005, 36, 1–78; e) C. E. A. Kirschhock, S. P. B. Kremer, J. Vermant, G. Van Tendeloo, P. A. Jacobs, J. A. Martens, Chem. Eur. J. 2005, 11, 4306–4313.
- [26] a) A. Aerts, L. R. A. Follens, M. Haouas, T. P. Caremans, M.-A. Delsuc, B. Loppinet, J. Vermant, B. Goderis, F. Taulelle, J. A. Martens, C. E. A. Kirschhock, *Chem. Mater.* 2007, *19*, 3448–3454; b) D. P. Petry, M. Haouas, S. C. C. Wong, A. Aerts, C. E. A. Kirschhock, J. A. Martens, S. J. Gaskell, M. W. Anderson, F. Taulelle, *J. Phys. Chem. C* 2009, *113*, 20827–20836; c) M. Haouas, D. P. Petry, M. W. Anderson, F. Taulelle, *J. Phys. Chem. C* 2009, *113*, 10838–10841.
- [27] a) S. P. B. Kremer, C. E. A. Kirschhock, A. Aerts, K. Villani, J. A. Martens, O. I. Lebedev, G. Van Tendeloo, *Adv. Mater.* 2003, *15*, 1705–1707; b) S. Bals, K. J. Batenburg, D. Liang, O. Lebedev, G. Van Tendeloo, A. Aerts, J. A. Martens, C. E. A. Kirschhock, *J. Am. Chem. Soc.* 2009, *131*, 4769–4773.

Received: May 8, 2011 Revised: August 8, 2011 Published online: November 14, 2011