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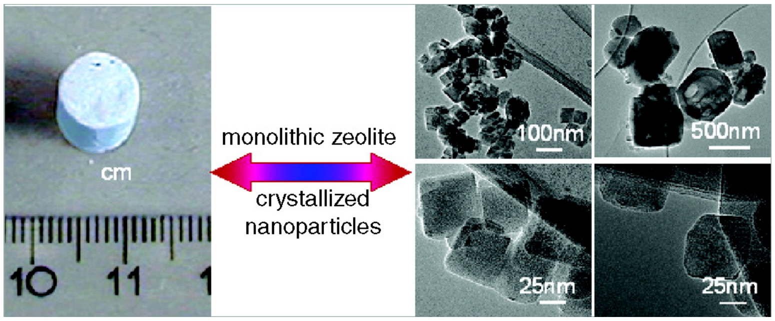

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Hierarchically Structured Monolithic Silicalite-1 Consisting of Crystallized Nanoparticles and Its Performance in the Beckmann Rearrangement of Cyclohexanone Oxime

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Abstract: In this study, we present a synthetic pathway for the fabrication of self-supporting zeolite monoliths consisting of crystallized nanoparticles. A resorcinol-formaldehyde-based organic aerogel is used as a template, and silicalite-1 is used as the zeolite example. The silicalite-1 monoliths obtained consist of individual well-defined zeolite nanocrystals with sizes of 30−40 nm. The monoliths exhibit a high mechanical stability and have hierarchical porosity, with micropores within the zeolite particles, a mesopore system formed by the packing of the nanoparticles, and a macropore system on the monolith level. Such monolithic zeolites show high selectivity typically above 80% to ϵ-caprolactam combined with a high rate of reaction of 0.46 $g_{caprolactame}/(g_{catalyst} \cdot h)$ in the Beckmann rearrangement of cyclohexanone oxime.

1. Introduction

Zeolites as the most well-known microporous crystalline materials are widely used as shape-selective catalysts in the petrochemical industry, or as adsorbent and ion exchanger in industrial separations or purification of fluids, and are also considered to be promising materials for various applications in sensors, electronic devices, and other advanced materials.[1] However, the structural micropores in zeolites are often disadvantageous with respect to mass transfer of bulkier molecules because they cause diffusion limitations of reagents and products. The mass transfer to and from the active sites located within the micropores can be slow, depending on diffusivities.[2] Thus, the particle sizes and the shapes of zeolitic catalysts have to be optimized for a given reaction. In past years, substantial efforts have been directed to the synthesis of zeolite materials with controlled shapes and porosities to minimize diffusion limitations. One possibility is to decrease the zeolite crystal size down to the nanometer scale, and thus to increase the external surface area of the crystallites and reduce the diffusion path length.[3] Nevertheless, the crystals often easily agglomerate without leaving transport pores and/or are difficult to isolate. It is thus advantageous to introduce meso- and even macropores into the zeolitic materials. The introduction of mesopores or macropores into zeolites has recently been achieved using new strategies that go beyond the traditional methods of steaming, leaching, or chemical treatment. Much attention has been focused on the endo- and exotemplating[4] route with various templates, such as porous carbon, silica, or wood cells, to prepare zeolites with desired pore structure.[5−8] As illustrative examples, Jacobsen et al. have used carbon blacks[9] or carbon nanotubes[10] as templates to synthesize zeolites with an additional mesopore system. Mesoporous ZSM-5 zeolite has also been synthesized using colloid-imprinted carbon as template in Pinnavaia's group.[11] The crystal size of the zeolite can be flexibly tailored through a rational choice of the pore size of the template.

Conventionally, as-synthesized zeolites are obtained in the form of a powder. To make them suitable for practical applications, that is, to avoid excessive pressure drops in fixed bed reactors or dusting problems, zeolites are usually extruded with inorganic binders. However, the addition of binders may result in partial blocking of the pore system of the zeolite and leads to dilution of the active species. It could therefore be interesting to develop a mechanically stable and self-supporting monolithic zeolite. Many attempts have already been made in this field.[12,13] Gao et al. suggested a strategy for synthesizing macroporous monolithic silicalite-1, in which the transformation of mesoporous silica spheres by hydrothermal treatment was involved. The monoliths obtained have a high mechanical strength and readily controllable sizes and shapes.[14] Kaneko et al. reported the synthesis of ZSM-5 having uniform mesopores

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by using carbon aerogel as template.[15] In that case, the carbon aerogel template was prepared using a supercritical drying procedure, which often leads to monoliths that break down to small pieces after impregnating with aqueous solutions. This is due to the pressures developed by the capillary forces (the reason supercritical drying after the synthesis is used in the first place) as well as the flimsy skeleton of these carbon aerogels. Thus, it is hard to control the morphology of the obtained ZSM-5, which is usually obtained as small grains with irregular shapes.[15]

These problems are even more severe if the zeolitic crystals are colloidal particles with sizes below 100 nm, which are, in addition to the necessary shaping, difficult to remove from the synthesis solutions. We therefore here present a study on the fabrication of monolithic zeolites consisting of individual particles in the size range of several tens of nanometers, with silicalite-1 used as a model. The monoliths obtained exhibit high mechanical stability and have hierarchical porosity, with micropores within the zeolite particles, a mesopore system formed by the packing of the nanoparticles, and a macropore system on the monolith level.

The Beckmann rearrangement of cyclohexanone oxime is a reaction for which the location of the reaction site in MFI type materials is controversial. It proceeds either on the external surface of MFI-type zeolites[16,17] or is at least severely diffusion-limited and thus benefits from small particles and a pronounced transport pore system.[18] Irrespective of the actual localization of the reaction site, a catalyst should benefit from nanosized zeolite particles in any case, and it was thus expected that such monolithic zeolites would show high selectivity to ϵ-caprolactam combined with a high rate of reaction, which was indeed observed in this study.

2. Experimental Section

(A) Synthesis of Organic Aerogel Templates. Organic aerogels were prepared on the basis of the polymerization of resorcinol (R) and formaldehyde (F) in a saturated aqueous solution of magnesium hydroxide, where the Mg^{2+} concentration was determined as 0.0018 M. Typically, the molar ratio of resorcinol to formaldehyde was 1:2, and the weight percentage of R and F in a solution was 25 wt %. Resorcinol (Fluka 99%) and formaldehyde (Fluka 36.5% in water, methanol stabilized) were dissolved in the Mg^{2+}-containing solution under magnetic stirring. Subsequently, the solution was transferred into a glass mold and then polymerized at room temperature for 1 day, at 50 °C for 1 day, and at 90 °C for 3 days to form a cross-linked framework. The formed wet gels were immersed into acetone to exchange the water inside the framework. The organic aerogel monoliths were then obtained after drying at ambient conditions. The monolith size and shape of the organic aerogel can be tuned by varying the corresponding glass mold.

(B) Synthesis of Monolithic Zeolites. The organic aerogel monolith was impregnated with a solution of tetrapropylammonium hydroxide (TPAOH, 40 wt % solution) and tetraethyl orthosilicate (TEOS) via incipient wetness, where the composition of the solution was fixed at 1TPAOH:2.8TEOS. After aging at room temperature for 1 day and hydrothermal treatment at 120 °C or 180 °C for 96 h, the obtained silicalite-1/organic aerogel was divided into two parts. One part was directly calcined at 550 °C for 8 h to produce silicalite-1, which was named S-*x* °C-1, where S indicates silicalite-1, *x* indicates the hydrothermal temperature, and 1 indicates single impregnation with zeolite synthesis solution. Another part was heated to 800 °C with a heating rate of 2 °C/min under argon atmosphere. The obtained composite was then impregnated with silicalite-1 precursor solution again, followed by hydrothermal treatment. Finally, the silicalite-1 monolith was obtained after calcination at 550 °C for 8 h to remove the endotemplate TPAOH and the carbon exotemplate. These samples were labeled S-*x* °C-2, where S and *x* have the same meaning as indicated above, and 2 indicates double impregnation with zeolite synthesis solution.

(C) Characterization. The powder X-ray diffraction (XRD) patterns of the samples were recorded with a Stoe STADI P transmission diffractometer in Debye−Scherrer geometry (Cu $K\alpha_1$: 0.154060 nm) with a primary monochromator (curved germanium crystal (111)) and a 40° position-sensitive detector. The monoliths were crushed and ground, and then placed in a quartz glass capillary for analysis. Nitrogen adsorption isotherms were recorded with an ASAP2010 adsorption analyzer (Micromeritics) at 77 K. Prior to the sorption measurements, all samples were degassed at 200 °C for at least 6 h. Micropore surface areas (S_{mic}) and micropore surface volumes (V_{mic}) were calculated by the *t*-plot method. Total pore volume (V) was estimated from the amount adsorbed at $p/p_0 = 0.99$. Scanning electron microscopy (SEM) investigations were carried out with a Hitachi S-3500N instrument. High-resolution transmission electron microscopy (TEM) measurements were carried out on a Hitachi HF2000 microscope equipped with a cold field emission gun at a beam energy of 200 kV. Monolithic zeolites were ground into fine powder, and then were prepared dry on a lacey carbon grid.

Mechanical strength was tested by smoothing the opposing surface of the monolith with sand paper and then placing an increasing load (using a water-filled container placed on a metal plate on top of the sample) on the monolith until it crushed. Because we could not produce geometries required for standardized crushing strength determination, the values reported should be taken only as indicative.

(D) Measurement of Catalytic Activity. The catalytic activity was tested in the Beckmann rearrangement reaction of cyclohexanone oxime to ϵ-caprolactam. The continuous flow reactor was packed with a known amount of catalyst together with 2 g of quartz sand. The monoliths were tested as prepared in monolithic form without grinding or, alternatively, ground and sieved to particle sizes between 250 and 125 μm, respectively, and tested under the same reaction conditions. The samples were activated overnight in airflow at 300 °C. Before reaction, the reactor was cooled to 280 °C. Cyclohexanone oxime was dissolved in toluene as reactant, at a molar ratio of toluene to cyclohexanone oxime of 26.5. This reactant was fed to the reactor by a HPLC-pump along with N_2 as carrier gas. The reaction ran under atmospheric pressure with WHSV = 1.95 $g_{oxime}/(g_{catalyst}\cdot h)$, thus adjusting the vapor pressure of oxime to 2.2 kPa. The product was recovered by condensation of the effluent, collecting fractions for 5 min each. For analysis, three samples collected after 1 h (55, 60, 65 min) were chosen. The condensate was analyzed by gas chromatography using a flame ionization detector, Agilent Technology 6890N.

3. Results and Discussion

The synthetic route for monolithic silicalite-1 is schematically shown in Figure 1. The organic aerogel was impregnated with clear zeolite synthesis solution. After aging at room temperature, the sample was loaded in an autoclave to perform the hydrothermal treatment. It is noteworthy to point out that the impregnated carbon aerogel sample was suspended above the liquid phase (water) in the autoclave, similar to some approaches for a “dry zeolite synthesis”.[19] After the hydrothermal treatment step, the composite was carbonized at 800 °C. At this stage,

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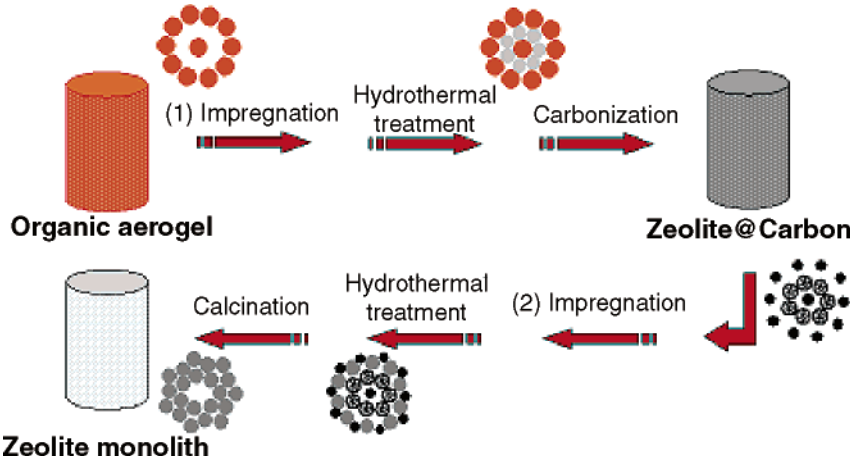

Figure 1. Schematic illustration for the synthesis pathway to monolithic silicalite-1.

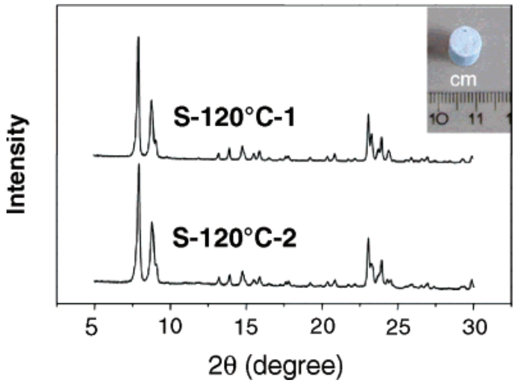

Figure 2. Representative XRD patterns of monolithic silicalite-1 (S-120 °C-1 and S-120 °C-2 mean that samples were hydrothermally treated at 120 °C, via a single step templating and two-step templating, respectively). The inset is an optical photograph of the obtained S-120 °C-2.

the product shows ~40% linear shrinkage as compared to the starting organic aerogel, which is mainly due to framework shrinkage of the organic aerogel. During this high temperature treatment, the template (TPAOH) is decomposed. To ensure that the final monolithic product is mechanically stable, a high loading level of zeolite was achieved by a second impregnation step with zeolite solution. After a second aging and hydrothermal treatment, the composite was calcined to remove the TPAOH and the carbon template to produce very stable zeolite monoliths. A crushing strength on the order of 50 kPa was determined for such monolithic samples, which is several times higher than that of typical tablets produced with a binder. As shown in the inset in Figure 2, the zeolite monolith maintains the cylindrical shape of the original organic template after the sequential treatments. Depending on the exact conditions, 1 g of organic aerogel template produces about 1.5−2 g of zeolite, indicating a high yield based on this proposed synthetic strategy.

For comparison, single step impregnation of the organic aerogel was also carried out to explore this simpler pathway of fabricating monolithic zeolite. That is, the organic aerogel was impregnated with zeolite precursor, followed by hydrothermal treatment and direct calcination to remove both templates, organic aerogel and TPAOH. The obtained samples are white in color and can maintain the monolithic shape. However, any extra force leads to fragmentation of the monolith into small pieces, probably due to the low degree of interconnectivity between individual zeolite crystals, which results from the low loading of zeolite precursor caused by the single step impregnation process. The second impregnation and hydrothermal treatment step results in more densely packed crystals, which allows the formation of more solid−solid bridges, overall leading to improved stability of the monolith.

The possibility of directly using a carbon aerogel (produced from an organic aerogel) as template to synthesize monolithic zeolite has also been investigated. The carbon aerogel was impregnated with zeolite precursor. However, in this case, the carbon aerogel easily breaks into small pieces during the aging and hydrothermal crystallization steps. Thus, it is hardly possible to obtain monolithic zeolite following this pathway. Two reasons could explain why no monolithic zeolite was formed in this case: On one hand, the stress caused by the growth of zeolite crystals in the confined space of the carbon aerogel framework may lead to a cracking of the carbon aerogel monolith. Essentially, the growth of zeolite crystal is restricted by the pore spaces of the hard template. The first units observed in the synthesis of Si-TPA-MFI type are estimated to have a size of ca. 2.8 nm.[20] If zeolite formation in the pore system follows the same pathways as in clear solution, the hard template should provide pores with a size at least in the mesopore range to allow the formation of such zeolite seeds. In contrast to that requirement, a carbon aerogel contains abundant micropores and has a rigid framework as compared to the organic aerogel.[21] The starting growth of the zeolite crystal in the micropores might then cause strong stress on the carbon aerogel framework, resulting in fragmentation of the monolithic shapes. As an alternative explanation, the absorption in and the removal of water from the carbon aerogel during impregnation with the zeolite precursor gel may cause capillary force sufficiently strong to break the carbon aerogel framework. In contrast to this, organic aerogels, having larger textual pores without any detected microporosity,[22] may allow much easier growth of zeolite crystals. Moreover, the framework of the organic aerogel consists of polymeric chains produced from resorcinol-formaldehyde polymerization. Such a framework can elastically swell to release the stress generated from either the growing

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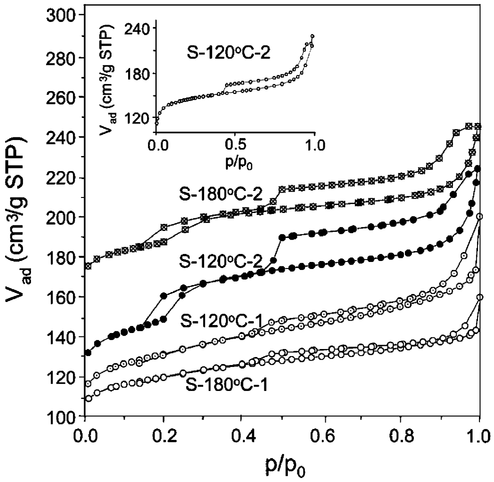

Figure 3. Nitrogen sorption isotherms of monolithic silicalite-1 samples. The isotherms of S-120 °C-2 and S-180 °C-2 are offset vertically by 20 and 70 cm^3 (STP) g^{-1}, respectively. The inset is the argon sorption isotherm of S-120 °C-2.

crystals and/or the capillary forces during the templating process. Thus, using an organic aerogel as exotemplate for the two-step impregnation is highly advantageous to produce monolithic zeolite.

To produce a self-supporting, stable monolithic sample, the organic aerogel used as template needs to have a continuous, well-connected pore system. This requirement limits presently the possibilities to strongly vary the pore sizes and solid fraction of the resulting zeolite monolith. For the synthesis of an organic aerogel (as well as a carbon aerogel derived from it) with the desired properties, only a limited window of synthesis parameters is available. Replication from aerogels with other textural properties is in principle possible, but the monoliths become very unstable or easily break at even small loads.

The monolithic samples obtained by the two-step and single step templating from organic aerogels were characterized by XRD to identify the crystal phases. As shown in Figure 2, representative XRD patterns of these monolithic samples clearly show characteristic reflections, which can be assigned to phase pure silicalite-1, regardless of whether a single or two-step templating process had been used.

N_2 sorption experiments were performed to determine the textural properties of the monolithic zeolite samples. The nitrogen sorption isotherms (in Figure 3) of the corresponding zeolite monoliths show a high uptake at the very initial stage of the isotherms, which is associated with the presence of micropores in zeolites. Two additional adsorption steps with associated hysteresis loops can clearly be identified in the isotherms of silicalite-1 prepared by the two-step templating. The high-pressure adsorption step at $p/p_0 > 0.4$ is caused by the capillary condensation in the textural mesopores. The other step occurring at $p/p_0 \approx 0.2$ may on first sight also be interpreted as an adsorption in pores of the material. This was the interpretation in a recent report on sorption in ZSM-5 synthesized using mesoporous carbon (CMK-3) as a template.[23] However, it is known that such a step can occur for nitrogen adsorption in MFI-type samples due to a structural rearrangement of the adsorbed nitrogen phase.[24,25] To clarify the origin of this hysteresis loop, a monolithic silicalite-1(S-120 °C-2), hydrothermally treated at 120 °C and prepared by the two-step templating, was additionally characterized by argon (Ar) sorption. Ar is often preferred for acquisition of low-pressure isotherm data, because the presence of the quadrupolar moment in N_2 results in enhanced interaction with the zeolite framework.[26] The obtained argon isotherm is shown as an inset in Figure 3. As can clearly be seen, a step with hysteresis is present at $p/p_0 > 0.4$, similar to the one in the nitrogen isotherms. However, the step at $p/p_0 \approx 0.2$, which is present in the nitrogen isotherm, has completely vanished with argon as adsorptive. This proves the absence of real porosity in this relative pressure range. As proven by previous reports,[24,25] the hysteresis loop at $p/p_0 \approx 0.2$ can be explained by a fluid-to-crystal-like phase transition of nitrogen molecules in the micropores. Consequently, it does not indicate any real porosity. From another point of view, the existence of this hysteresis loop indicates that well-crystallized zeolite crystals form by the present two-step templating strategy, as this step is only observable in high-quality crystals. For silicalite-1 obtained by a single step templating process, the nitrogen sorption isotherms do not exhibit the hysteresis loops presented around $p/p_0 \approx 0.2$. This demonstrates the difference in crystal perfection of the monolithic zeolite produced from the single step templating and the two-step templating.

Table 1. Texture Parameters of Silicalite-1 Monoliths and Organic Aerogel[a]

sample	S_{BET} m²/g	V_{mic} cm³/g	V_{tot} cm³/g	V_{mic}/V_{tot}
organic aerogel	17		0.02	
S-120 °C-2	408	0.12	0.25	0.48
S-180 °C-2	395	0.12	0.24	0.50
S-120 °C-1	443	0.15	0.26	0.58
S-180 °C-1	402	0.15	0.22	0.68

[a] Note: S_{BET}, specific surface area calculated on the basis of the BET theory, should only be considered as indicative, because the algorithm is not valid for microporous materials; V_{mic}, micropore volume calculated by the *t*-plot method; V_{tot}, single point total pore volume.

The textural parameters calculated from the nitrogen sorption isotherms are compiled in Table 1. The micropore volume (V_{mic}) of the silicalite-1 through two-step templating is slightly lower than those of the samples synthesized via single step templating. Total pore volumes of thses samples, however, are roughly identical. As compared to the typical silicalite-1, which has a micropore volume of 0.14 cm^3/g, but negligible meso- or macropore volume,[27] the textural porosity of monolithic silicalite-1 is improved by the repeated templating process, as reflected by the ratio of the micropore volume to the total pore volume, V_{mic}/V_{tot}.

Figure 4 shows the TEM images of silicalite-1 hydrothermally treated at 120 and 180 °C. The sample shown in Figure 4a (S-120 °C-2 obtained via twice repeated impregnation and hydrothermal treatment at 120 °C) consists of well-defined, cube-shaped crystals. Under high resolution (Figure 4b), well-crystallized small crystals with sizes of 30−40 nm, occasionally up to 100 nm, are visible, which corresponds to the sizes

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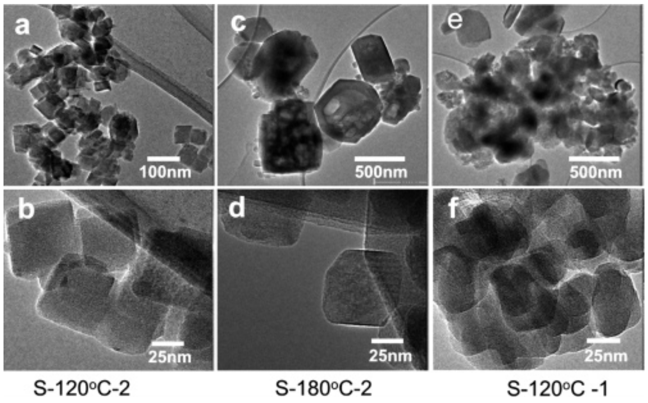

Figure 4. TEM images of silicalite-1 monoliths (S-120 °C-2 (a and b), S-180 °C-2 (c and d), and S-120 °C-1 (e and f)).

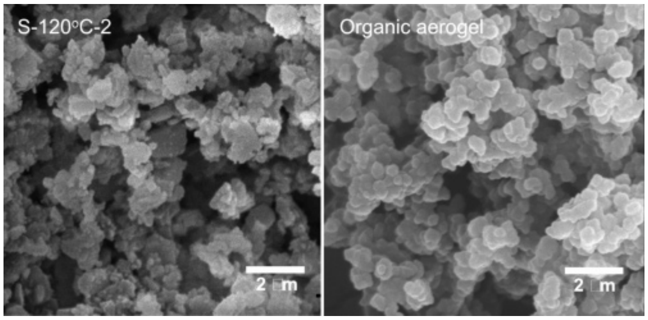

Figure 5. SEM images of silicalite-1 monolith S-120 °C-2 (left) and organic aerogel template (right).

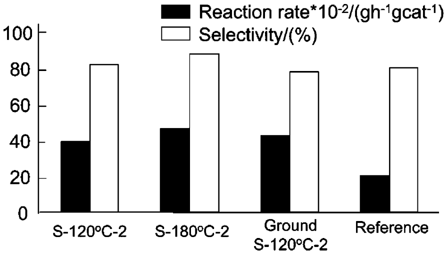

Figure 6. Catalytic activity to Beckmann rearrangement of cyclohexanone oxime for monolithic silicalite-1 and reference (reference data cited from ref 28).

determined from the line broadening analysis of the XRD reflections using the Scherrer formula. The random packing of these nanosized crystals creates the mesopores in these samples. Hydrothermal treatment at 180 °C instead of 120 °C preferentially leads to formation of large crystals (Figure 4c). In addition, small nanosized crystals similar to those observed in the sample obtained at low hydrothermal treatment temperature still can be found (Figure 4d) due to the restricted growth of the crystals in the confined space of the carbon matrix. In this case, a nonhomogeneous distribution of crystal sizes, which cover a wide range from 30 to 300 nm, is obvious. Interestingly, many clearly discernible open holes in these large crystals can be observed, which are probably caused by growth of the crystal around parts of the carbon aerogel and then opened during removal of the aerogel hard template, in a manner similar to that of the mesopores observed in the work of the group of Jacobsen.[9] With respect to improved mass transfer, these holes are certainly advantageous. Furthermore, TEM images of silicalite-1 obtained through the single step templating process (S-120 °C-1, Figure 4e and f) show that less well-defined particles with not as distinctive morphologies are formed, which have sizes similar to the ones obtained through two-step templating.

Figure 5 shows scanning electron microscopy (SEM) images of the silicalite-1 (S-120 °C-2) and the organic aerogel template. The morphology of S-120 °C-2 (Figure 5 left) shows that the nanosized crystals tend to form clusters with sizes of 2−3 μm, which construct the framework and the macropores of the silicalite-1 monolith. The presence of macropores is also reflected in the additional uptake close to relative pressures of 1 in the nitrogen sorption isotherms. Moreover, it is hard to find any larger silicalite-1 crystals in the SEM survey, which again confirms that the framework of the monoliths consists of nanosized crystals. The particle morphologies found in the silicalite-1 monolith, both in size and in shape, are quite similar to those of the original organic template (Figure 5, right). This is due to the fact that both the pore structure and the solid structure of the organic aerogel are quite similar. The zeolite monolith reproduces the pore structure of the organic gel and thus is the negative replica of the gel structure. Because the macropore sizes of the silicalite correspond to the particle sizes of the organic aerogel, in principle, the macropore size of the silicalite-1 monolith should be controllable by variation of the particle size of the organic aerogel template. However, this is at present still difficult to change substantially, because it is also necessary that a continuous pore system is present in the organic aerogel for the production of a stable monolith. The pore connectivity of the organic aerogel is decreased, if the particle size of the organic aerogel is appreciably changed.

The successful negative replication of the organic aerogel monolith to the zeolite monolith reflects pronounced interconnectivity between the pores of the organic aerogel template. The pronounced pore system and the small size of the zeolite crystallites, together with the good mechanical stability of the monolithic particles, should make them suitable for catalytic applications, in which mass transfer limitations can be expected. Therefore, the silicalite-1 monoliths (S-120 °C-2 and S-180 °C-2) were tested as catalysts in the vapor phase Beckmann rearrangement reaction of cyclohexanone oxime to ϵ-caprolactam (CPL).

Figure 6 shows the results of the catalytic experiments. The reaction rate is as high as 0.46 $(g_{CPL})/(g_{catalyst}\cdot h)$ with selectivities typically above 80%. For comparison, nanosized silicalite-1 prepared according to the method described by Martens et al.[28] gave a similar selectivity, but the reaction rate did not exceed 0.2 $(g_{CPL})/(g_{catalyst}\cdot h)$. Due to the substantial differences in reaction conditions in published papers, our data are difficult to compare with literature data. However, the performance of our catalyst seems to be superior to those reported in most papers. Höldrich et al.[29] quote rates of 0.3 $(g_{CPL})/(g_{catalyst}\cdot h)$ (calculated from given conversions and reaction conditions) with ammonia treated silicalite-1 at 300 °C, while Tatsumi reports 0.65 $(g_{CPL})/(g_{catalyst}\cdot h)$ for the silicalite-1 system with benzene as solvent.[30] Higher rates of up to 2.25 $(g_{CPL})/(g_{catalyst}\cdot h)$ with benzene as solvent are quoted by the Sumitono group,[31] who,

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however, worked at 350 °C. This rate has to be considered as a lower bound because the conversion in this study was reported to be 100%. Thus, rates of 0.46 (g_{CPL})/($g_{catalyst}$·h) we have observed are very satisfactory, considering the reaction temperature of only 280 °C, because the rate increases substantially between 280 and 350 °C.

Moreover, to investigate if there is a diffusion limitation of such monoliths, the samples were also measured after grinding and sieving to particle sizes between 250 and 125 μm. The results show that the reactivity is nearly identical to that of the monolith, proving the absence of diffusion limitations on the particle level. Additionally, selectivity, which is the more sensitive factor with respect to diffusion limitations, is also almost unchanged. Thus, the advantage of the monolith with hierarchical pore structure as compared to an unstructured catalyst is obvious. After the catalytic reaction, the monoliths still maintain their original shapes, and no fragmentation takes place, confirming a high mechanical and thermal stability of the monolithic silicalite-1. The catalytic reactions were repeated several times by using S-120 °C-2 monoliths synthesized from different batches. The results are reproducible within ±5%, confirming the reliable synthesis of the monolithic zeolite by the present synthetic strategy.

4. Conclusions

We have established a synthetic pathway for the fabrication of monolithic silicalite-1 with hierarchical pore systems. The monolith consists of well-defined nanosized crystals aggregated in such a way that macropores, mesopores, and micropores are formed. The silicalite-1 monolith shows high catalytic activity and selectivity in the Beckmann rearrangement of cyclohexanone oxime. A disadvantage is the still rather complex synthetic procedure, but improvements seem possible. We are currently also expanding the methodology to prepare other monolithic zeolites with hierarchical pore systems.

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Note Added after ASAP Publication. After this article was published ASAP on August 20, 2005, a production error in Table 1, column 1, entries 2 and 4, was corrected. The corrected version was published ASAP on August 24, 2005.

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