Origin of Morphology Change and Effect of Crystallization Time and Si/Al Ratio during Synthesis of Zeolite ZSM-5

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Hydrothermal synthesis of ZSM-5 is an often applied but incompletely understood procedure. In comparison to current research efforts that aim to produce complex micro-mesoporous catalysts for the conversion of biogenic and bulky hydrocarbons, this work focuses on the dependency between Si/Al ratio and zeolite morphology of microporous ZSM-5 to understand and control the crystallization process. In two series of time dependent crystallization, kinetics were analyzed at Si/Al ratio 20 and 100 to optimize the crystallization time. Subsequently, zeolites with different Si/Al ratio were obtained and characterized. The results show a transition from a slow dissolution-recrystallization process to a fast solid-state-transformation with increasing Si/Al ratio. This is followed by a switching morphology from clusters of small agglomerates to bigger spherical particles. Respective acid site density and zeolite morphology determine local residence time, hydride transfer behavior and finally selectivity towards aromatics and higher hydrocarbons during methanol conversion. This background should provide control of even more complex syntheses of porous catalysts.

Introduction

Although Argauer and Landolt patented the synthesis procedure of the ZSM-5 zeolite already in 1972,[1] it is still ongoing research to vary synthesis parameters and the applied template molecules in order to purposefully change the catalyst properties. This is evident by the steady numbers of publications, which address different aspects from different perspectives in the synthetic procedures.[2–7] The production of ZSM-5 generally follows three steps that are divided into the formation of a primary gel, the subsequent hydrothermal conversion to a secondary gel with the final crystallization step. The complex interdependency of a variety of parameters does not allow an easy general conclusion. It is therefore important to examine all individual steps in order to develop a targeted, reproducible synthesis of tailor-made zeolite materials for various applications. Especially primary nucleation and crystal growth are affected by the type and nature of the Si and Al sources,[8–9] the Al content,[10] the ratio of organic template to Si,[10] the structure of the organic and inorganic cations,[11,12] the pH value,[13] the crystallization temperature,[14] the use of crystal seeds,[15] the water content in the synthesis gel[16] and the use of other pore builders.[17–19] In order to use ZSM-5 as a catalyst in hydrocarbon conversion processes, its properties must be adjusted carefully. In particular, the ratio of silicon to aluminum (Si/Al) is important since it determines the acidic properties of the catalyst after ion-exchange to H-ZSM-5 and, thus, influences the dominant reactions in hydrocarbon conversion.[20] Crystal size and morphology affect the local residence time and product formation behavior.[21]

A deeper look into the formation process of zeolite ZSM-5 by two-step hydrothermal synthesis reveals a complex mechanism of initial gelation and subsequent hydrothermal crystallization.[22] The induction period, which produces the SBU (secondary building unit), strongly depends on the structure directing agents present, e.g. sodium (Na+) and tetrapropylammonium (TPA+) cations[23] and also their interactions, which have a significant influence on the morphology of the zeolite phase that forms.[24] Both should be present in high and almost constant concentration by typically using Na2SiO3 as Si source and TPABr as template in the gel. The location of incorporated aluminum in the framework is directed by organic and inorganic cations and it is known that Al ions slow down the crystallization process.[22] TPA+ cations, if applied as organic template, play a prominent role compared to Na+ or K+ cations, which mainly determine the rate of initiation.[25,26] The mineralizing agent OH− modifies the rate of the re-organization processes of the gel during hydrothermal treatment.

With the aim of a controlled synthesis protocol, this work focuses on the origin of the interdependence between the Si/Al ratio, the crystallization time, the crystal morphology, the acidic properties of ZSM-5 zeolites and their different performances in methanol to hydrocarbons processes. For this purpose, two time resolved synthesis series at different Si/Al ratios show respective changes in morphology and crystallinity which allows to estimate a sufficient crystallization time. Furthermore, five ZSM-5 samples are synthesized and converted into H-ZSM-5...
5 by ion-exchange. The obtained zeolites are fully characterized by solid-state analysis including their morphology as well as initial catalytic tests for methanol conversion reaction.

Results and Discussion

This work demonstrates a fast and simple procedure for the reproducible synthesis of ZSM-5 with varying Si/Al ratios (20 to 100) at high quality. This was based on the optimization of reproducible synthesis routes for ZSM-5 developed in the research group.\(^\text{[27]}\) The synthesis was carried out under hydrothermal conditions in an autoclave. The samples were then extensively characterized and investigated for their catalytic properties in the conversion of methanol.

Results of the synthesis for morphology studies: variation of synthesis time

The time resolved synthesis series of ZSM-5 with Si/Al ratio of 100 confirmed the characteristic reflections of the MFI type for all samples (Figure 1). Consequently, ZSM-5 had already been formed after a crystallization time of 12 h at 150 °C. This was not the case for the samples with a Si/Al ratio of 20 since after 12 h and 24 h no characteristic reflections of the MFI type were observed. This can be explained by a much slower nucleation process for samples with an increased aluminum content in agreement with reports by Cundy and Cox.\(^\text{[28]}\)

In order to examine the change in the morphology of the two synthesis series over time, scanning electron microscopic (SEM) images were taken for each of the samples and for the dried synthesis gel (Figure 2). The SEM images show that the original morphology of the synthesis gel of the two ZSM-5 samples (Si/Al 100 and 20) were similar (Figure 2a, e). After 96 h of crystallization time (Figure 2c, g) the morphologies differ significantly from those of the respective gels. This also indicates the transformation of the amorphous gel into a crystalline solid. Moreover, the SEM images of the two crystalline ZSM-5 samples after 96 h show different crystal morphologies (Figure 2d, h). More images of samples after 12 h to 96 h are illustrated in the supported information (Figures S1 and S2). The particle surface changed with increasing crystallization time. After 48 h, a crystalline phase formed which caused defined reflections in the XRD pattern and after 96 h defined edges and faces appeared in the SEM images. The resulting particles were small and showed defined, faceted edges and faces in the SEM images.

![Figure 1](image1.png)

**Figure 1.** X-ray powder diffractograms of the time resolved synthesis series of Na-ZSM-5 with a Si/Al ratio of 100 and 20.

![Figure 2](image2.png)

**Figure 2.** SEM images of Na-ZSM-5 with Si/Al ratio of 20 and 100 at different crystallization time: (a to d) Si/Al ratio of 20 after gel formation and after 96 h hydrothermal crystallization, (e to h) Si/Al ratio of 100 after gel formation and after 96 h crystallization (magnification a x700; b x2,000 c x10,000; d x15,000; e x600; f x2,500; g x8,000; h x15,000).
surfaces. In contrast, for the ZSM-5 samples with a Si/Al ratio of 100, a clear change in the morphology to the dried synthetic gel was visible after 12 h (Figure S1 and S2). Spherical particles had formed which were slightly bigger than those from samples with a Si/Al ratio of 20 (Figures 2d, h). More uniform crystalline structures were visible on the particle surface after 24 h and 48 h. Afterwards, the morphology of the particles did not change any further.

The trend from XRD, which confirms first crystalline structures for Si/Al 20 after 48 h (Figure 1), is also reflected in the surface measurements via dynamic gas physisorption (Table 1). The samples with the Si/Al ratio of 100 already showed a surface area of 400 m$^2$/g after 12 h of crystallization time. In contrast, the samples with a Si/Al ratio of 20 after 12 h and 24 h had significantly lower surface areas. After 48 h, the surface area started to increase up to 300 m$^2$/g and after 72 h up to 400 m$^2$/g. This further indicates that the formation of ZSM-5 proceeds more slowly with a Si/Al ratio of 20, i.e. with increased aluminum content. A direct comparison of the two samples with different Si/Al ratios indicates, that a zeolite with Si/Al = 100 was already formed within 12 h, while a sample with Si/Al = 20 formed after 72 h. Hence, drawbacks in crystallinity because of a reduced crystallization rate from high aluminum contents can be compensated by an extended crystallization time.

For comparability, the samples Si/Al = 100; 48 h and Si/Al = 20; 96 h are examined in more detail and Table 2 displays the Si/Al ratios determined by ICP-OES and the results of the B.E.T. surface measurements of the static volumetric gas sorption. The Si/Al ratio of the final zeolites matches that of the initial gel composition. Whereas crystallinity and surface area were optimized by Si/Al ratio and crystallization time, the synthesis series of the ZSM-5 with a Si/Al ratio of 20 seemed to produce particles with a different morphology compared to Si/Al ratio of 100. As reported by Cundy and Cox, aluminum has an influence on the nucleation and crystal formation mechanism.

An increasing aluminum content inhibits the nucleation and growth of ZSM-5 and a competing dissolution of the starting material takes place. If the crystallization is not disturbed, the direct solid phase transformation of the gel to the MFI structure is favored. The aluminum-dependent change of dominance of these two processes leads to the formation of different product morphologies as demonstrated in Figure 2. The sample with the high aluminum content (Figure 2b to d, Si/Al = 20) shows significantly smaller, but strongly overgrown agglomerates, whereas the sample with the low aluminum content (Figure 2f to h, Si/Al = 100) shows larger spherical particles. A deeper look into formation kinetics in the next paragraph reveals the reason for this behavior.

### Kinetic consideration of the crystallization process of ZSM-5 zeolite

From B.E.T. surface analysis a crystallization yield is defined which helps to determine the crystallization kinetics for ZSM-5.

Many groups have already discussed the role of nucleation and crystal growth as well as the dynamics of both from simple numerical models over fundamental approaches by Avrami-Johnson equation up to more complex approaches including accelerated nucleation. Even in the 90s, there has been a controversial discussion on the reliability of constant (Avrami-Johnson) or autocatalytic nucleation in hydrothermal zeolite synthesis, which ended in a case analysis depending on the shape of the crystallization curve.

Due to a smooth alignment of the graphs to the maximum value of B.E.T. surface area in our experiments, there is no dominance of an accelerated nucleation process. (Figure 3)

Therefore, an approach by Avrami-Johnson has been applied to approximate kinetic data. The Avrami-Johnson equation is used under the side conditions of a steady-state

| Sample | Surface area $A_{area}$ [m$^2$/g] | Sample | Surface area $A_{area}$ [m$^2$/g] |
|--------|----------------------------------|--------|----------------------------------|
| Si/Al = 100; 12 h | 410 | Si/Al = 20; 12 h | 37 |
| Si/Al = 100; 24 h | 380 | Si/Al = 20; 24 h | 29 |
| Si/Al = 100; 48 h | 390 | Si/Al = 20; 48 h | 300 |
| Si/Al = 100; 72 h | 470 | Si/Al = 20; 72 h | 370 |
| Si/Al = 100; 96 h | 410 | Si/Al = 20; 96 h | 400 |

| Si/Al | Si/Al$_{ICP-OES}$ | Surface area $A_{area}$ [m$^2$/g] | Monolayer volume [cm$^3$/g] | Cumulative pore area [m$^2$/g] |
|-------|------------------|----------------------------------|---------------------------|-----------------------------|
| Si/Al = 100; 48 h | 90 | 441 | 101 | 29 |
| Si/Al = 20; 96 h | 20 | 361 | 90 | 32 |

**Figure 3.** Kinetics of the hydrothermal synthesis of ZSM-5 zeolite; Avrami-Johnson approach for constant nucleation rate to estimate crystallization time and quality with increasing Si/Al ratio from B.E.T. surface area.
concentration of silica and alumina in solution during a dissolution-recrystallization process. Consequently, the nucleation rate stays constant. A similar approach for constant or almost zero nucleation rate could be used for direct solid-state transformations.\textsuperscript{(12)}

We finally come to an expression for the B.E.T. surface area [Eq. (1)]:

\[
AJ(t) = \text{BET}_{Al}(t) = a \cdot \left(1 - e^{-kt}\right)
\]  

(1)

The parameter \(a\) describes the maximum B.E.T. surface area for an infinitely long crystallization. With \(k\), the approach describes the shape of the graph. The boundary condition of the starting point is fulfilled for almost non-porous gels [Eq. (2)].

\[
\text{BET}_{Al}(t=0) = 0 \text{ m}^2/\text{g}
\]  

(2)

From this, a parameter \(t_{99}\) is calculated, which defines the time to reach 99% of maximum crystallinity [Eq. (3)].

\[
t_{99} = \sqrt{\frac{2}{k}} \ln(10)
\]  

(3)

With increasing content of Al there is a deceleration of the crystallization process. Consequently, a linear interpolation between \(t_{99}\) and the number \(n_{Al}\) of Al per unit cell of ZSM-5 leads to a model-based formula to estimate an appropriate (minimum) crystallization time [Eq. (4)].

\[
t_{99}[h] = 13.722 \cdot n_{Al} + 0.852
\]  

(4)

Transformation between Si/Al ratio and \(n_{Al}\) leads to the model description in Figure 3 [Eq. (5) and (6)].

\[
\frac{Si}{Al} = \frac{96 - n_{Al}}{n_{Al}} \quad \text{for } H_{4}Al_{n}Si_{96-n}O_{192}
\]  

(5)

\[
t_{99}[h] = 13.722 \cdot \left(\frac{96}{\frac{Si}{Al}}\right) + 0.852
\]  

(6)

The influences of aluminum may be summarized with:

(i) The constant and sufficiently high amount of Na\textsuperscript{+} promotes the growth of formed nuclei\textsuperscript{(26)} at comparably low and almost constant nucleation rate, which leads to an Avrami-Johnson type crystallization behavior.\textsuperscript{(32)}

(ii) Higher concentration of Al leads to locally higher concentration of OH\textsuperscript{−} via a Lewis-acid-base adduct and locally higher concentration of charge-compensating cations. A locally high concentration of OH\textsuperscript{−} itself promotes the re-dissolution, which hampers the crystallization process.\textsuperscript{(33)}

(iii) A local increase of OH\textsuperscript{−} increases the negative surface charge of the SBUs within the gel. This is a barrier for secondary condensation processes after SBU re-organization, which depends on the initial removal of the layer of solvent and ions from the particle surface.

A new mechanistic explanation for the interdependency of Si/Al ratio and morphology includes the consideration of aluminum species during gel preparation, which complicates the condensation process. Additional OH\textsuperscript{−} and charge-compensating cations (Na\textsuperscript{+}, TPA\textsuperscript{+}) are needed to force the Al into a tetragonal environment\textsuperscript{(30)} (Scheme 1). Thus, aluminum species promote the dissolution of nuclei (by OH\textsuperscript{−} spots) and hinder the interconnection within the gel by formation of charged, separating subunits during gelation and aging.

Consequently, the re-dissolution of the particles and a secondary nucleation on the external surface of gel particles with slow particle growth become more dominant (dissolution-recrystallization process).\textsuperscript{(34)} Low Al containing ZSM-5 therefore shows larger spherical particles (Figure 2f to h), whereas high Al containing ZSM-5 is characterized by smaller particles with a strongly overgrown surface (Figure 2b to d).

### Results of synthesis for catalytic investigations: variation of Si/Al ratio at high crystallinity

These investigations on synthesized H-ZSM-5 samples focus on varying Si/Al ratio at sufficient crystallization time for respective synthesis gel composition (summarized in Table S1 in the supporting information). The zeolites were synthesized and post-synthetically converted to H-ZSM-5 for catalytic investigations. The phase purity of the samples was determined by X-ray diffraction referenced to a sample with a Si/Al ratio of 20. The
X-ray diffraction patterns show that only reflections of the MFI structure are visible (Figure 4). A deeper look reveals changing intensity ratios of the reflections with decreasing Si/Al ratio, i.e. an increasing aluminum content. The main group of reflections was determined between 8.0 and 9.2° 2θ and the second group between 23.2 and 24.5° 2θ. The synthesized H-ZSM-5 samples show an increasing intensity of the MFI-typical second group of reflections with increasing aluminum content. One reason for this is the increased aluminum content, which leads to a higher hydrophilicity of the zeolite. That is why more water adsorbs in the zeolite framework on contact with air. The total water content of the saturated samples was determined via thermogravimetry (Figure S3 and Table S3, supporting information). To confirm this, H-ZSM-5 samples with Si/Al ratio of 20 and 100 were dried under vacuum and a second set of samples was saturated over a saturated sodium sulfate solution. Powder diffractograms were recorded from these samples and the dried sample with a Si/Al ratio of 20 had a significantly reduced intensity of the second group of reflections compared to the saturated sample (Figure S4). For Si/Al ratio of 100 the effect is not visible since there is less water in the sample due to the lower aluminum content. Furthermore, an increase in the half-width of the reflections can also be seen in the diffractograms with increasing aluminum content, which is related to increased structural deformation and cracks of the framework by incorporation of aluminum into the crystal structure.[35,36]

As the content of aluminum increases, the crystallization time rises roughly beyond the value $t_{95}$ of the model description in the previous section to ensure good quality ZSM-5. For a deeper view on the short-range order, another crystallinity parameter was determined via ATR-FTIR measurements with a method of Shukla and Pandya.[30] The parameter was calculated from the absorption ratio of the bands at 550 cm$^{-1}$ and 450 cm$^{-1}$ which were standardized to the reference sample Si/Al = 20 with a crystallinity of 100%. The spectra are illustrated in the supporting information (Figure S5). Table 3 shows the values for the determined crystallinity using ATR-FTIR and powder XRD. It can be seen that with increasing aluminum content of the H-ZSM-5 samples, the crystallinity increases for both ATR-FTIR and XRD. One reason for this could be the adjustment of crystallization times, which is necessary because the crystallization is hindered by larger amounts of aluminum.[22] The incorporation of aluminum in the tetrahedral position of the silicate framework can also have a slight influence on the XRD as well as ATR-FTIR measurements, for example, by intensifying, weakening or broadening signals during measurements, which can lead to an over- or under-estimation of the respective crystallinities. To clarify this incident, the micro-pore volume was measured, which confirms almost similar values for all samples. Thus, the real quality of the samples after optimization of the crystallization time is similarly high. A deeper view on nature and position of the incorporated aluminum atoms follows from solid-state $^{27}$Al-MAS-NMR.

The solid-state $^{27}$Al-MAS-NMR spectra of the synthesized H-ZSM-5 samples with varying Si/Al ratio show two resonances. The first resonance appears at $\delta = 0.3$ ppm with a low intensity which is caused by octahedrally coordinated aluminum and the second at $\delta = 54$ ppm which is mainly caused by tetrahedrally coordinated framework aluminum.[36-38] The results of the $^{27}$Al-MAS-NMR measurements confirm a successful incorporation of aluminum into the framework. A spectrum of a sample with Si/Al = 20 is displayed in Figure S6 in the supporting information. Especially framework aluminum is strongly connected to framework-bonded cations, mainly protons after ion-exchange. For the characterization and determination of acidic properties, the synthesized H-ZSM-5 samples were analyzed by temperature-programmed ammonia desorption analysis (Table 4). It appears that the number and the strength of the acid sites increases with the aluminum content of the sample. This applies to both weak ($S_1$, 750 s / 250–300°C) and strong acid sites ($S_2$, 1800 s / 600–800°C) as shown in Table 4.

![Figure 4. X-ray diffraction patterns of synthesized H-ZSM-5 samples with varying Si/Al ratio between 100 and 20 and their molecular formula.](image)

### Table 3. Material properties of the ZSM-5 samples from XRD, ATR-FTIR and ICP-OES.

| Sample Si/Al | rel. crystallinity XRD [%] | rel. crystallinity ATR-FTIR [%] | micro-pore volume [cm$^3$/g] | $t_{95}$ [h] | $t_{exp.}$ [h] |
|-------------|---------------------------|--------------------------------|-----------------------------|----------|-------------|
| Si/Al = 100 | 87 | 58 | 94 | 0.149 | 14 | 48 |
| Si/Al = 80 | 72 | 71 | 97 | 0.154 | 17 | 48 |
| Si/Al = 60 | 57 | 71 | 97 | 0.154 | 23 | 48 |
| Si/Al = 40 | 37 | 94 | 93 | 0.151 | 33 | 72 |
| Si/Al = 20 | 19 | 100 | 100 | 0.151 | 64 | 96 |

[a] Si/Al ratio determined via dissolution and ICP-OES measurement of the H-ZSM-5 samples, [b] crystallinity (long-range order) determined according to ASTM D5758-01, [c] crystallinity (short-range order) determined according to Shukla and Pandya,[35,36] [d] with standard isotherm (ASTM Standards Designation: D4641-87)

### Table 4. Results of the temperature-programmed ammonia desorption analysis of the synthesized H-ZSM-5 samples with a Si/Al ratio between 100 and 20.

| Sample Si/Al | Al atom per pore intersection $S_{total}$ [mmol/g] | $S_1$ [mmol/g] | $S_2$ [mmol/g] | $S_1/S_2$ |
|-------------|---------------------------------|----------------|----------------|------------|
| Si/Al = 100 | 87 | 0.27 | 0.05 | 0.36 | 0.14 |
| Si/Al = 80 | 72 | 0.33 | 0.53 | 0.08 | 0.45 | 0.18 |
| Si/Al = 60 | 57 | 0.41 | 0.55 | 0.11 | 0.47 | 0.23 |
| Si/Al = 40 | 37 | 0.41 | 1.04 | 0.25 | 0.79 | 0.32 |
| Si/Al = 20 | 19 | 1.19 | 1.51 | 0.50 | 1.01 | 0.50 |

[a] Si/Al ratio determined via dissolution and ICP-OES measurement of the H-ZSM-5 samples.
550–600 °C) denoted as S1 and S2. For TPAD profiles, please consult Figure S7 in the supporting information.

The results of surface analysis by physisorption of nitrogen were evaluated using B.E.T. theory and the B.J.H. method (Table 5).\[20,46\] They correspond to the isotherm type I according to Thommes et al.,\[41\] which is characteristic to the physisorption of gas molecules on microporous solids with a small external surface in relation to the total surface area (Figure 5 and S8 in the supporting information).

In addition to the characteristics of the Type Ia isotherm, there are some minor characteristics of Type II. This is attributed to macropores and inter-particle volume of the crystallites. Especially the shape of the desorption curve of the H-ZSM-5 sample with a Si/Al ratio of 20 differs from the other samples because of larger macropores (range p/p0 > 0.8). However, all isotherms show hysteresis type H4 according to Thommes et al.,\[41\] which is characteristic for aggregates of zeolite crystals. The synthesis was successful since the results show similar specific surface area of synthesized H-ZSM-5 according to B.E.T. theory (A_{spe}) ranging between 400–440 m²/g.

A confirmation of different crystal morphology and inter-particle volume comes from scanning electron microscopy.

The sample H-ZSM-5 Si/Al = 100 (Figure 6a) shows small spherical to ellipsoidal particles with diameters between 4–6 µm. Upon closer inspection, the particles have some smaller crystals attached to their surface and regular steps on the surfaces of the spherical grains. With increasing aluminum content (falling Si/Al ratio) the morphology of the catalyst samples changed from spherical particles to smaller and fully broken ellipsoids (Figure 6b to d), as formerly concluded from the kinetic considerations.

The intact spherical particles or their larger fragments also showed a defined, edged surface. An explanation is the longer crystallization time of the samples with a higher aluminum content.

The dissolution process (dissolution-recrystallization process) takes more time with lower aluminum content and less time with higher aluminum content than the conversion of the solid (solid-to-solid transformation). According to this concept, the sample H-ZSM-5 Si/Al = 20 should have little to no large spherical particles and should consist only of small crystallites (Figure 6e, f), which agglomerate randomly as consequence of a higher external crystallite surface area.

This is also visible in the particle size distribution of the respective samples (Figure S9 and Table S4 in the supporting information).

With an increasing aluminum content, the particle size distribution becomes broader. This becomes visible in the cumulative distribution and in the individual distribution of the particle sizes. For the samples with a Si/Al ratio of 40 to 100, the D50 value is between 4 and 6 µm. With a Si/Al ratio of 20, the D50 value is already 8.9 µm. From a Si/Al ratio of 60 onwards to 20, there is a significant broadening of the distribution. This is illustrated in Figure S9 in the supporting information.

The properties of the material, especially number and strength of acid sites, morphology, structural and textural properties mainly determine the catalytic behavior of H-ZSM-5 in catalytic test reactions. Catalytic conversion of methanol shows almost complete conversion for all samples at 350 °C and consequently high activity. Different from the conversion turnover, the composition of the product stream changes significantly with decreasing Si/Al ratio (Figure 7).

As the Si/Al ratio decreases, the olefin content decreases and the percentage of paraffin and aromatic components increase. The aromatics were formed from the olefins by hydride transfer reactions with increasing aluminum content and increasing acid site concentration. Here, olefins were converted into aromatics and paraffins in a ratio of 1:3. This coincides with the work of Madeira et al.,[42,43]

The effect described above can also be explained by the change in morphology. Small particles lead to the formation of aromatics, since deactivation was pushed back due to the lower formation of coke precursor species. By examining the catalytic conversion of methanol on the H-ZSM-5 samples, it is concluded that the synthesis was successful and that all

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**Table 5. Results of the static volumetric nitrogen physisorption studies of the synthesized H-ZSM-5 samples with Si/Al ratios between 100 and 20.**

| Sample Si/Al | Surface area A_{spe} [m²/g] | Monolayer volume [m³/g] | Cumulative pore surface area [m²/g] |
|--------------|-----------------------------|-------------------------|-----------------------------------|
| Si/Al = 100  | 399                         | 0.16                    | 22.9                              |
| Si/Al = 80   | 416                         | 0.17                    | 27.3                              |
| Si/Al = 60   | 428                         | 0.17                    | 22.8                              |
| Si/Al = 40   | 439                         | 0.18                    | 67.1                              |
| Si/Al = 20   | 436                         | 0.18                    | 38.5                              |

[a] B.E.T. Parameters linear regression between p/p0 0.001 to 0.04, [b] B.J.H. Calculations used desorption branch from p/p0 0.3 to 0.95 (ASTM Standards Designation: D4641–87).

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**Figure S5. Exemplary nitrogen physisorption isotherms of samples with (a) Si/Al ratio of 60 and (b) Si/Al ratio of 20.**

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samples were catalytically active. Figure 8 shows the composition of the gas phase over time on stream of the H-ZSM-5 samples with a Si/Al ratio of 20 and 100 during the conversion of methanol. The sample with a Si/Al ratio of 20 showed a high selectivity for C\textsubscript{3} compounds (up to 40\%) as well as for olefins (>50\%) and paraffins (>45\%) at one hour ToS. From the second hour onwards, the selectivity for C\textsubscript{4} and C\textsubscript{5}+ compounds rose and the proportion of olefins decreased while the amounts of paraffins and aromatics increased. For the remaining observed time, the composition of the gas phase remained almost constant.

The sample with a Si/Al ratio of 100 showed a high selectivity for C\textsubscript{4} and C\textsubscript{5}+ compounds as well as for olefins. In contrast to the sample with a Si/Al ratio of 20, the composition of the products did not change over the entire ToS. A comparison of the two samples shows that with the higher aluminum content of the catalyst (lower Si/Al), more long-chain products from C\textsubscript{3}+ and more paraffins were formed.

The amount of aromatics also increased significantly with rising aluminum content of the H-ZSM-5 sample. This is not only due to the rising activity of the catalyst samples but also due to an increased acid site density and the associated change in selectivity at different site multiplicities for certain products. Moreover, an increased site density leads to an increased probability of subsequent reaction steps, i.e. an increased intrinsic contact time, which is crucial for all HCP processes.\textsuperscript{[43]}

During the conversion of methanol on H-ZSM-5, a selective deactivation during the formation of the individual products takes place, which is typical for this kind of reaction network.\textsuperscript{[44]}

The intrinsic contact time also depends on the morphology and the particle size and not only on the acid site density. The smaller crystals of sample with Si/Al ratio of 20 showed lower coking and deactivation for 5 hours ToS than it would have been expected for increased hydrocarbon build-up compared to the sample with Si/Al ratio of 100 (Figure 8). Therefore, the conversion path in the HCP reaction network depends on the density, number and distribution of centers (roughly the Si/Al ratio),\textsuperscript{[45]} as well as the morphology and intrinsic contact time which all determine the final product selectivities.

**Conclusion**

Current reports to produce complex micro-/mesoporous H-ZSM-5 catalyst materials reveal complex structures with good performances in bio-feed conversion and cracking of long-chained hydrocarbons. Due to a gap in control of the zeolite synthesis process, this work focuses on the dependency between Si/Al ratio and zeolite morphology of microporous H-ZSM-5 to understand and control the procedure. The synthesis of a high-quality H-ZSM-5 with varying Si/Al ratio is a result of an optimization of B.E.T. surface area by simultaneous adaption of the aluminum content in the synthesis gel and the crystallization time. The production of high-quality H-ZSM-5
was confirmed by extensive characterization including catalytic performance in methanol to hydrocarbons process (MTH). With increasing aluminum content (decreasing Si/Al ratio) the ZSM-5 particles change from individual spherical particles to small, edged agglomerates. Thereof increased amounts of aluminum slow down the formation of ZSM-5. While low aluminum content leads to a dominant and fast phase-transformation process of larger gel particles by charge-density matching of silica with TPA$^+$ to form ZSM-5 crystals, higher amounts of aluminum tend to produce charged and repulsive gel subunits, which inhibit this process. Consequently, a base-catalyzed dissolution-recrystallization process known as Oswald-ripening becomes dominant, which leads to smaller, slow growing crystallites from secondary nucleation.

The conversion of methanol to hydrocarbons shows that the selectivity of the products strongly depends on the Si/Al ratio (acid site density and distribution) and the morphology of the catalyst samples. As the aluminum content increases, the number of catalytically active centers increases, but at the same time the morphology changes to smaller crystals with increased external surface, which also shifts the local residence time and thus the selectivity towards aromatics. In contrast, a small amount of aluminum leads to the preferential formation of olefins and small hydrocarbons on slightly bigger zeolite crystals, which is beneficial in the MTO process.

The special novelty of this work compared to classic and current reports$^{[3,5,6,22,26]}$ is a deeper look into the mechanism of ZSM-5 formation with focus on the mechanistic reason for resulting particle morphology. Furthermore, an Avrami-Johnson approach$^{[30,32]}$ helps to use the knowledge on the crystallization behavior to control the synthesis of a high quality ZSM-5 zeolite.

**Experimental Section**

**Chemicals**

The chemicals used for this investigation include sodium trisilicate (Na$_3$Si$_3$O$_7$, Si as SiO$_2$ ≥ 60% and Na as Na$_2$O ≥ 18%, Fluka), sodium aluminate (NaAlO$_2$ technical, Al as Al$_2$O$_3$ 50–56% and Na as Na$_2$O 37–45%, Sigma-Aldrich), tetrapropylammonium bromide (TPAB, C$_{12}$H$_{28}$BrN > 98.0%, TCI), sulfuric acid (H$_2$SO$_4$ 95–97%, VWR), ammonium nitrate (NH$_4$NO$_3$ 99%, Grüssing), hydrofluoric acid (HF 40%, Merck Millipore), nitric acid (HNO$_3$ 69%, Supra-quality, Carl Roth), hydrochloric acid (HCl 37%, VWR), boric acid (H$_3$BO$_3$ 99.9995%, Alfa Aesar), and methanol (CH$_3$OH 99.9%, TCI). All chemicals were used as received.

**Synthesis procedures**

**Hydrothermal synthesis of Na-ZSM-5:**$^{[27]}$ One liter of ultrapure water was mixed with 60 g template tetrapropylammonium bromide (TPAB). After 10 min a mixture of 100 g sodium trisilicate and varying amounts of sodium aluminate (Table 6) were gradually added to the slurry within 30–45 min under continuous stirring. After completion, the slurry was stirred for another 10–15 min. At moderate mixing, the pH value was adjusted carefully with a 50 wt.% sulfuric acid to pH = 10 without reaching pH = 9. It is crucial to adjust the pH for the second process step because at lower pH an uncontrollable peptization of silica occurs.$^{[46]}$ A higher pH promotes hydrolysis of the silica-based gel and crystals, which slows down or inhibits the reconnection of silica species.$^{[26]}$
resulting gel was transferred into a PTFE (polytetrafluoroethylene) inlet of an autoclave (Berghof). Hydrothermal synthesis was performed at 150 °C under autogenous pressure, applying reaction times between 2 h and 96 h. The product separated from the liquid phase after cooling to 80 °C and the solid product filtered and washed with 2 L of ultrapure water and 0.5 L of ethanol. The obtained material was dried over night at 65 °C. The synthesis of the time dependent series proceeds as described above. Three gels were prepared, two with a Si/Al ratio of 100 and a third with a Si/Al ratio of 20. The resulting gels were divided into five equal portions and transferred into the PTFE inlets of autoclaves (Berghof). The crystallization time varied between 12–96 h for the samples with a Si/Al ratio of 20 and between 2–96 h for the samples with a Si/Al ratio of 100 (Table 6).

Post-synthetic ion exchange to H-ZSM-5: In order to remove the organic template, the solid material was heated to 120 °C in an air stream at a heating rate of 1.1 K/min. After a dwelling time of 1 h, the temperature was increased to 540 °C (1.1 K/min) and calcined for 12 h. For the ion exchange, 20–25 g of calcined zeolite and 200–250 mL of a 0.1 M NH₄NO₃ solution was used and the suspension stirred at 80 °C for 3 h. The still hot suspension was then filtered and the filter cake washed with 1 L of deionized water. After drying overnight at 80 °C, the entire process was repeated two times. The conversion into the acidic H-form (H-ZSM-5) was achieved in a further calcination step by first heating the sample to 120 °C (1 h dwelling time) and then to 450 °C (6 h dwelling time) under air. The heating rate for deammonization was again 1.1 K/min.

Characterization of materials

Table 6. Parameters for the synthesis of H-ZSM-5 at 150 °C, with 100 g Na₂SiO₃, 60 g TPABr and 1,000 g H₂O.

| Sample           | NaAlO₂ (g) | t_postthermal (h) |
|------------------|------------|-------------------|
| H-ZSM-5 SiAl = 100 | 1.02       | 2–96; 48          |
| H-ZSM-5 SiAl = 80  | 1.30       | 48                |
| H-ZSM-5 SiAl = 60  | 1.70       | 48                |
| H-ZSM-5 SiAl = 40  | 2.55       | 72                |
| H-ZSM-5 SiAl = 20  | 5.02       | 12–96; 96         |

TPAD: The acidic properties of the samples were investigated via temperature-programmed desorption of ammonia (TPAD). All measurements were carried out on a Thermo Scientific TPDRO 1100 instrument equipped with a thermal conductivity detector (TCD). Before ammonia adsorption, 150 mg of catalyst sample was dried in an argon flow at 550 °C and cooled down to the adsorption temperature of 100 °C. Ammonia adsorption was performed for 30 min and desorption was investigated under helium flow for 30 min and subsequent heating to 700 °C (10 K/min heating rate and 1 h dwelling time).

N₂ physisorption: To determine the specific surface areas of the zeolitic samples, dynamic nitrogen physisorption measurements were carried out on a Horiba Scientific’s SA-9600 Series. For this, the samples were pre-dried at 200 °C for at least 20 h before starting the three-point measurement. For a detailed investigation of the textural properties, static nitrogen physisorption measurements were carried out and the isotherms were recorded. For this the Thermo Scientific Surfer Gas Adsorption Porosimeter was used and the samples were pre-treated at 250 °C in a vacuum for 8 h to remove all adsorbed molecules before the measurement. The results of the surface analysis by physisorption of nitrogen were evaluated using the B.E.T. theory and the B.J.H. method.[26,41] Therefore, specific surface area of micropores was calculated from B.E.T. theory[47] in the range p/p₀ = 0.001…0.04 and the specific surface area of meso-/macropores was calculated from B.J.H. theory[48] with p/p₀ = 0.30…0.95.

XRD: The powder diffraction experiments to investigate changes in the long-range crystalline order were carried out with the X-ray powder diffractometer STADI P from STOE. The diffractograms were recorded by transmission measurement of the solid samples with Cu-Kα radiation (1.5406 Å) at room temperature in the range between 5° and 2θ 25°. Two different methods were used to record the diffractograms. For the majority of the samples, the material was fixed between two x-ray amorphous adhesive strips. A capillary measurement was carried out with dried as well as saturated samples. For this purpose, the samples were dried overnight in a vacuum at 200 °C under Schlenk conditions. The samples were then transferred to a glove box under argon. The filled capillaries were closed with highly viscous fat and PTFE-tape. The other samples were saturated over an aqueous sodium sulfate solution in a desiccator for 24 h and then filled into a capillary. The crystallinity of the zeolites was determined by comparing the reflection maxima at 23.2 and 24.3° 2θ in accordance with ASTM D5758-01.[49] As reference standard, the sample with the highest crystallinity (Si/Al = 100) was set to 100% crystallinity.

ICP-OES: Elementary analysis started with the dissolution of zeolite powder via microwave assisted solution with MARS 6 from CEM. For the digestion process, 25 mg of the zeolitic sample were suspended in a mixture of 3 mL of nitric acid (69%), 2 mL of hydrochloric acid (37%) and 1 mL of hydrofluoric acid (40%). The digestion was performed for 15 min in the microwave under autogenous pressure (170 °C, 1,800 W). After a dwelling time of 10 minutes, the solution was cooled to room temperature and quenched with 10 mL saturated boric acid solution. The amounts of silicon, aluminum and sodium were quantified by ICP-OES on an Optima 2000 DV (PerkinElmer) and calibrated to two wave numbers for Si (212.4 and 251.6 nm), Al (237.3 and 396.2 nm) and Na (589.0 and 589.6 nm). For the calibration, defined solutions were prepared from ICP-OES standards (1,000 mg/L; PerkinElmer) by dilution with ultrapure water.

Scanning electron microscopy (SEM): The morphology of the synthesized H-ZSM-5 samples was analyzed on a scanning electron microscope SU8020 from Hitachi HTE. For this purpose, the zeolite samples were mounted on carbon pads, which were fixed on an aluminum sample holder and coated with gold with the rotary-pump coating system Q150R ES from Quorum. The accelerating voltage was 2 kV and the magnification varies between x250 and x15,000.

ss-MAS-NMR: Characteristics of aluminum species on solid samples were investigated by ²⁷Al-MAS-NMR with a Bruker Ascend 300 MHz NMR spectrometer. At a resonance frequency of 78.2 MHz and a rotation frequency of 16 kHz at the magic angle, 2000 scans were accumulated for each sample with a rate of 0.5 pulse per second. As an external standard, an aqueous solution of aluminum nitrate was used.

Particle size analysis: Dynamic laser scattering was used to determine particle size distribution with a Bettersizer S3 Plus by 3P Instruments. The wet dispersion procedure was performed with 2,000 rpm stirring and 200 W (26 kHz) ultrasound for 2 min. Data acquisition and processing were done in accordance with ISO 13320:2009. Calculation of particle size distribution was realized by using the Mie theory.[50]

ATR-FTIR: The attenuated total reflection Fourier-transform infrared measurements were performed to investigate the short-range order of the produced zeolites. For this purpose, the dried H-ZSM-5 samples were pressed on the sample holder of the ATR-FTIR spectrometer Vertex 70 from Bruker with a KBr beam splitter, a
diamond as ATR-crystal and a globar as a radiation source. A separate background was recorded for each sample and the measurement was carried out with 32 scans between 350 cm\(^{-1}\) and 1,600 cm\(^{-1}\) (resolution 1 cm\(^{-1}\)).

**Thermogravimetric analysis:** The TG50 (Mettler Toledo) was used to determine the water content of the saturated H-ZSM-5 samples. For this purpose, 20 to 40 mg of sample were heated from 35 °C to 850 °C in a nitrogen stream at a heating rate of 10 K/min.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** Kinetics · Mechanism of crystallization · Zeolite morphology · Zeolite synthesis · ZSM-5

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