Ethanol to Aromatics on Modified H-ZSM-5
Part I: Interdependent Dealumination Actions

Markus Seifert,[a] Mathias S. Marschall,[a] Torsten Gille,[a] Clemens Jonscher,[a] Oliver Busse,[a]
Silvia Paasch,[b] Eike Brunner,[b] Wladimir Reschetilowski,[c] and Jan J. Weigand*[a]

In this study a H-ZSM-5 zeolite (Si/Al = 11) was modified by a stepwise treatment with steam, sodium hydroxide and hydrochloric acid. During progressing dealumination by various treatment methods, the drawbacks of initial post-synthetic steps, e.g. pore-filling by steam dealumination, are compensated by subsequent steps, e.g. washing by acid, which leads to a scientifically based preparation of required ZSM-5 zeolite. Solid-state properties of as-synthesized and modified zeolites are determined by structural (XRD, ICP-OES, NMR), textural (physisorption, laser scattering) and acid sites analysis (TPAD). Consequently, extended dealumination without structural damage is demonstrated. Its origin by framework dealumination and pore cleaning is verified in ethanol to hydrocarbon process (ETH) by shape-selective formation of coke and aromatics, characterized by “aromatics index” (AI).

Introduction

Zeolite H-ZSM-5 is a well-known and frequently used catalytically active material for conversion of methanol and ethanol to hydrocarbons since its invention by Mobil Oil Corporation in 1972.[1] Because of its wide use as additive to FCC (fluid catalytic cracking) catalysts or in hydrocracking, a huge variety of different options for post-synthetic modification are known.[2–5] In addition to the broad variability in Si/Al ratio from synthesis, post-synthetic methods help to tune its activity and selectivity, as well as catalyst stability or regeneration.[6–8] However, it is known, that aluminum rich, acidic zeolite H-ZSM-5 shows less stability against hydrothermal or thermal treatment due to a facilitated framework dealumination, which leads to long-term deactivation effects.[9] Coke is formed by hydrocarbon species produced during conversion of small alcohols, which blocks the active sites as well as the pores and causes short-term deactivation.[10]

Initiably little influence of EFSPE (extra-framework species) on ethanol conversion in H-ZSM-5 is detected by use of chelating agents avoiding overabundant dealumination of the zeolite framework.[11] The main goal of this work is to improve the short-term durability of commercial H-ZSM-5 zeolite during the conversion of ethanol to aromatics by a targeted framework dealumination. Based on the assessment of positive and negative effects of each post-synthetic procedure, a combination of treatment methods is proposed and tested.

Reaction mechanism and catalyst deactivation in the conversion of ethanol to aromatics

Conversion of ethanol to hydrocarbons (ETH process) on acidic H-ZSM-5 reveals a complex network of different kinds of chemical reactions. Current work discusses Lewis and Bronsted acid site catalyzed reactions.[12,13] After fast and almost complete dehydration of ethanol to ethene and diethyl ether mainly carbocation based reactions such as oligomerization, cracking, cyclization, isomerization and hydride transfer reactions lead to a formation of so-called “hydrocarbon pool”[13,14] This hydrocarbon pool of homologating compounds may be considered as the result of competing reaction pathways from hydrocarbon species on different acid sites in the active surface of the porous catalyst material.

According to the principle of continuous homologation[12,15–19] reactive hydrocarbon species, mainly carocations, are formed after a short initiation period, which support an autocatalytic growth of olefins, paraffins and aromatics from small olefins, such as propene or butenes. The steady-state production of hydrocarbons up to branched monocyclic aromatics leaving the size-limiting pores of ZSM-5 zeolite shifts to an undesired growth towards
naphthenes and bigger molecules blocking the pores and the external surface.\textsuperscript{18–20}

Furthermore, consecutive growth beyond monocyclic molecules towards naphthenes and other coke precursors on ZSM-5 is described\textsuperscript{19,20} because of side-chain growth and further cyclization. Consequently, dehydration becomes dominant, which leads to increasing amounts of ethene (C2) with ongoing deactivation by coke.\textsuperscript{10}

**Impact and chemical nature of intra- and extra-framework species**

EFSPE are in general all species not belonging to the ideal crystal structure on the external and internal surface of catalyst samples. EFAL (extra-framework aluminum) and EFSI (extra-framework silicon) are generated as residuals or byproducts during the synthesis or pretreatment of zeolites. Especially in the case of dealumination processes, it may happen that transformations between framework and non-framework species take place.\textsuperscript{21,22}

Depending on the type of reaction, catalytic activity is mainly attributed to strong Brønsted and Lewis acid sites in the framework and weak Brønsted or Lewis acid sites as well as weak adsorption sites at the non-framework positions, respectively.\textsuperscript{23}

Their steric influence can lead to pore blocking and diffusion limitations of reactant molecules. However, the chemical impact of such sites on the zeolite is in most cases much more severe. For example, EFAL often represents Lewis acid sites, which are able to promote ethanol dehydration and associated rapid coke deposition, but not the formation of desired hydrocarbons. The removal of most of all undesirable EFSPE, i.e. the cleaning of the pore system, might help to facilitate mass transport and to reduce coke formation.

**Exemplary methods for framework dealumination**

Different methods of dealumination and/or desilication of framework species as well as removal or transformation of EFSPE are state of the art.\textsuperscript{21,24}\textsuperscript{26} In most cases the dealumination of zeolites in the liquid phase, e.g. by use of mineral acids leads to non-negligible structural damages.\textsuperscript{11} Gas phase dealumination as in the case of hydrothermal treatment or by use of volatile SiCl\textsubscript{4} improves efficiency of dealumination processes.

Also within these processes, structural damages of zeolitic materials occur depending on post-synthetic preparation conditions such as temperature, pressure or treatment duration. Formation of sticky species, e.g. aluminohydrate-oxo-species, that are hard to remove by washing procedures afterwards, is often inevitable and complicates the dealumination process.\textsuperscript{21,24}

**Results and Discussion**

To illustrate the experimental procedure, an overview of post-synthetic methods to modify a commercial H-ZSM-5 is given in Figure 1. Dealumination and desilication were performed by a combination of the treatment with base and acid\textsuperscript{21} and a following hydrothermal dealumination and acid washing.\textsuperscript{21} Changing materials properties during post-synthetic modification is correlated to catalytic properties concerning yield of aromatics and deactivation by coke from a total mass balance in ethanol conversion. For results of state-of-the-art single-step treatment by base (NaOH), steam (St) or acid (HCl) please consult the supporting information (S2), Table S2. We found no improvement for batches with an additional acid pre-leaching.

**Properties of original H-ZSM-5 zeolite**

A reference material from Clariant is used and further denoted as original H-ZSM-5. The reference zeolite has a Si/Al ratio of 11, a surface area of 390 m\textsuperscript{2}/g (BET) and particle size of 1–3 \textmu m. The particles show uniform morphology of non-typical sheeted zeolite crystallites. The commonly found pinacoid-shaped particles are replaced by 1 × 1 × 3 \textmu m stretched and stacked crystals with smaller nanocrystalline adducts on the external surface. (see Figure 2) XRD pattern shows no additional phases apart from ZSM-5. This shape is typical for a redissolution and recrystallization of gel particles by a decreased crystallization due to high aluminium content.\textsuperscript{26}

The solid-state NMR spectra reveal a variety of species inside and outside the zeolite framework due to high aluminum content. (see Figure 3) The samples are saturated by water vapor under 80 % humidity to ensure a reproducible hydration state of aluminum species. The signals are divided into a quadrupolar framework pattern with octahedrally (0 ppm) and tetrahedrally coordinated (35–60 ppm) framework aluminum (FAL) and a quadrupolar line of EFAL (30–40 ppm), which is narrowed or broadened by geometric shear and quadrupolar interaction to counter-ions and water molecules.\textsuperscript{21} Especially

![Figure 1. Procedure for post-synthetic modification of original H-ZSM-5 zeolite to increase yield of aromatics in ethanol to hydrocarbons process (ETH): 1st single-step treatments with steam (St), hydrochloric acid (HCl) and sodium hydroxide (NaOH); 2nd combination of two steps to overcome drawbacks from the first treatment; 3rd procedure to increase dealumination extent.](image-url)
the original H-ZSM-5 material exhibits a relatively high amount of octahedrally coordinated FAL (0 ppm) and visible tetrahedrally coordinated EFAL (30–40 ppm), which indicates adhesive residuals from synthesis inside and outside the pore system. Original H-ZSM-5 zeolite consists of small crystallites with high crystallinity but unusual shale-like morphology and non-uniform EFAL and framework species. Aluminum zoning seems non-reliable due to low particle sizes.

Catalytic results from ethanol conversion reveal approximately full conversion for all samples, despite NaOH treatment (see Figure 4, furthermore see Figure S5 in the supplementary). Increased amounts of ethylene with ToS and reduced selectivity towards C3+ products indicate catalyst decay, which correlates to coke formation as reported earlier. A deactivation model is used to simplify the comparison of the deactivation tendency by a two-parameter plot (initial C2 fraction, exponential factor) as described in the experimental part.

Properties after washing with base and acid

Combined desilication by base and dealumination by acid is a promising method to step up the degree of overall dealumination. Especially for ZSM-5 with Si/Al < 15 additional formation of mesopores is limited (see Table 1). Aluminum hinders the formation of additional hierarchical channel systems within different zeolite material.

The efficiency of the dealumination process increases by combined treatment compared to acid caused dealumination (Si/Al = 12). Crystallinity as determined by XRD is not affected significantly, but strong acidity is generated. Consequently, a removal of non-crystalline or extra-framework material enhances the overall acidity. HCl compensates unfavorable ion-

---

**Table 1.** Solid-state properties of original H-ZSM-5 zeolite before and after base and acid washing (15 g batch are denoted with (1)) with 0.5 M NaOH and 0.5 M HCl at 90 °C during 24 h or 4 days.

| Sample     | XRD cryst. [%] | Sorption\[^{[a]}\] BET (BJH) [m^2/g] | ICP-OES Si/Al (Na/Al) | Acidity strong [mmol/g] |
|------------|----------------|-------------------------------------|-----------------------|------------------------|
| original   | 100            | 390 (61)                            | 11 (0.0)              | 0.56                   |
| H-ZSM-5    |                |                                     |                       |                        |
| NaOH24h(1) | 128\[^{[b]}\]  | 410 (19)                            | 10 (1.1)              | - \[^{[c]}\]          |
| HCl24h(1)  | 100            | 350 (44)                            | 12 (0.0)              | 0.52                   |
| HCl4d(1)   | 103            | 390 (10)                            | 15 (0.0)              | 0.51                   |
| NaOH24h-HCl24h(1) | 141\[^{[b]}\] | 430 (11)                            | 17 (0.3)              | 0.66                   |

\[^{[a]}\] Physisorption of nitrogen, BET and BJH surface for micro- and mesopore surface analysis. \[^{[b]}\] Crystallinity > 100 % as a sign to reduction of crystalline silica structures, see supporting information for further explanation. \[^{[c]}\] Desorption profile of ammonia changes significantly due to Na\(^+\) ion-exchange.
Properties after steam and acid treatment

Combined dealumination by steam with subsequent acid treatment is a suitable method to enhance dealumination.[21,25] Adaption of this method to the original H-ZSM-5 shows framework dealumination by steam and further dealumination by acidic washing. Temperatures for steam treatment should not exceed 400 °C to ensure framework stability and high crystallinity. From DFT calculations,[21] framework dealumination of ZSM-5 is preferred due to its favored pore geometry to coordinate and stabilize EFAL. The increase of Si/Al up to 16 at 400 °C and subsequent acid washing for 24 h (St400-HCl24h) is more effective than the simple acid leaching (HCl24h), which leads only to Si/Al = 12. Higher temperature of steam (500 °C) concludes to structural damage. (see Table 2)

Concentration of strong acid sites from TPAD is reduced continuously with increasing temperature of steam from 300 °C, 400 °C up to 500 °C. Meanwhile the concentration of weak acid sites remains constant. Consequently, a local framework dealumination and removal seems plausible without formation of bigger pores (see BJH surface). Therefore, the framework conserving mechanism of dealumination differs from the framework leaching dealumination by base and acid. The combination of both methods to enhance its efficiency becomes obvious. Catalytic results from ethanol conversion show good durability and only slight reduction of initial build-up activity with steam treatment at 400 °C and subsequent washing with HCl. (see Figure 6) Higher temperatures result in reduced coking due to less activity, but structural damages are known from XRD.

Properties after combined treatment (NaOH-HCl-St-HCl)

Direct combination of dealumination by steam and acid with prior treatment by base and acid result in further enhanced dealumination (Si/Al = 20). Meanwhile, there is only a slight fragmentation of the sheeted zeolite crystals. (Figure 7)

There is a species selective change of NMR signals of tetrahedrally coordinated EFAL (30–40 ppm) and octahedrally coordinated FAL (0 ppm) by introduction of Na⁺ by base and H⁺ by acid treatment.[27] Complete Na⁺ exchange to Na-ZSM-5 by NaOH forces EFAL and octahedrally coordinated FAL into a tetrahedral anionic environment, whose signals are broadened and known as “invisible Al”. (see Figure 8) By ion-re-exchange with acid, octahedrally coordinated FAL re-occurs due to missing quadrupolar broadening by Na⁺. The re-appearance of the FAL NMR signal seems to be faster than the EFAL NMR signal, i.e. counter-ion re-exchange on framework seems to be facilitated due to higher polarity or simply higher number and accessibility of the framework species.

Table 2. Solid-state properties of original H-ZSM-5 zeolite before and after steaming (St) and acid washing with 0.5 M HCl at 90 °C during 24 h.

| Sample | XRD cryst. [%] | Sorption(II) BET (BJH) [m²/g] | ICP-OES Si/Al | Acidity strong [mmol/g] |
|--------|----------------|-------------------------------|----------------|-------------------------|
| original | 100 | 390 (61) | 11 | 0.56 |
| H-ZSM-5 | | | | |
| St300-HCl24h(1) | 101 | 370 (30) | 14 | 0.50 |
| St400-HCl24h(1) | 100 | 390 (42) | 16 | 0.43 |
| St500-HCl24h(1) | 87 | 400 (42) | 16 | 0.30 |

[a] Physisorption of nitrogen, BET and BJH surface for micro- and mesopore surface analysis.

Figure 5. Deactivation and activity plot (incl. coke in wt.-% after 10 h ToS) for combined treatments with NaOH and HCl after different durations from underlying kinetic deactivation model.

Figure 6. Deactivation and activity plot (incl. coke in wt.-% after 10 h ToS) for combined treatments with steam (St) and HCl from underlying kinetic deactivation model.
By mild steam treatment and further acid washing the signals of tetrahedrally coordinated EFAL (30–40 ppm) re-occure. Partial framework dealumination by steam leads to an annealing and unification of tetrahedrally coordinated EFAL with less quadrupolar broadening.\(^{[27]}\) Finally, last acid treatment step removes residual Na\(^+\) completely, which is related to an increase in the signal at 0 ppm. (see (Na/Al) in Table 3) These processes confirm a strong impact of the post-synthetic methods to the chemical environment of FAL and EFAL.

Consequently, deactivation rate connects directly to strong surface acidity (S2) originating from aluminum species. Moreover, fast washing with hot water after acid treatment and high ratio of solution to solid material avoid precipitation of solved silica and alumina onto the external crystallite surface. Additionally, a bigger amount of solution helps to intensify the dealumination procedure, which results in lower total acidity. Catalytic results from ethanol conversion show a decrease of coke formation with increasing dealumination extent. (see Figure 9) The deactivation rate drops by dealumination, mainly after the first washing with acid. Meanwhile only steaming reduces the initial build-up activity for ethene significantly. Ammonia desorption experiments confirm a slight increase in strong surface acidity after steaming.

Comparison to synthesized ZSM-5 with varying Si/Al ratio

Direct comparison of original H-ZSM-5 zeolite to as-synthesized ZSM-5 reveals differences in acid site distribution. Whereas commercial H-ZSM-5 with Si/Al = 11 shows small crystals of 1–3 μm and high amounts of weak acid sites compared to the strong sites, a ZSM-5 with Si/Al = 40 from lab-scale hydrothermal synthesis consists on crystals of 3–5 μm. The amount of acid sites compared to absolute content of aluminum is higher for lab-scale synthesis. (see Table 4) The performances of different ZSM-5 zeolites in their H-form differ significantly. A plot with deactivation rate, initial build-up activity of C2 gas phase fraction.

(1) Increasing Al content leads to increased initial build-up activity of C2 gas phase fraction.

(2) Increasing Al content correlates with an increasing deactivation rate.

(3) The amount of coke deposited on the zeolite material after 10 h ToS is proportional to the model deactivation rate.

In combination with a complete regenerability of the fresh and modified zeolite material short-term deactivation should mainly originate by coke formation. (cf. Däumer et al.\(^{[10]}\))

Table 3. Solid-state properties of original H-ZSM-5 zeolite before and after combined treatment (100 g batch are denoted with (2)) with steaming (St), acid washing with 0.5 M HCl at 90 °C and washing with 0.5 M NaOH at 90 °C, each for 24 h.

| Sample                | XRD cryst. [%] | Sorption\(^{[a]}\) BET (BJH) [m\(^2\)/g] | ICP-OES Si/Al (Na/Al) | Acidity strong [mmol/g] |
|-----------------------|----------------|------------------------------------------|-----------------------|-------------------------|
| original H-ZSM-5      | 100            | 390 (61)                                 | 11 (0.0)              | 0.56                    |
| NaOH24h-HCl24h(2)     | 141 \(^{[a]}\) | 430 (59)                                 | 17 (0.4)              | 0.66                    |
| Si400-HCl24 h(1)      | 100            | 390 (42)                                 | 16 (0.0)              | 0.43                    |
| NaOH24h-HCl24h-Si400-HCl24h(2) | 123 \(^{[a]}\) | 410 (89)                                 | 20 (0.0)              | 0.41                    |

[a] Physisorption of nitrogen, BET and BJH surface for micro- and mesopore surface analysis, [b] Crystallinity > 100% as a sign to reduction of crystalline silica structures, see Supporting Information for further explanation.
Impact of combined dealumination and desilication

Preliminary investigations focused the necessity to distinguish between the dealumination of extra-framework and framework aluminum as well as between the dealumination and the final process of removal.\(^{[1]}\) The procedure confirms, that the initial desilication by base with the undesirable ion-exchange to sodium form of ZSM-5 and the framework dealumination by steam must be followed by an acid washing. This ensures a re-exchange to the H-form of the zeolite and the physical removal of mobilized aluminum and silicon species. Especially the washing with hot water directly after desilication and acid washing without cooling is important to avoid fast precipitation on the surface. (see supporting information, Table S1, S2)

Mechanistic explanation of pore cleaning efficiency from aromatics yield in ethanol conversion reaction

Surface reaction from ethanol to hydrocarbons and coke is considered on the external grain and internal pore surface of H-ZSM-5. Shape selective transport of monocyclic aromatic species is dominant to para-substituted aromatics within pore channels.\(^{[31]}\) Secondary alkylation, transalkylation and formation of bicyclic product molecules is limited to the external surface and pore entrance region\(^{[32]}\) as for methanol conversion. (see Figure 11) Pore cleaning leads to facilitated product transport from the pores to the gas phase. Especially EFSPE lead to limited flush of aromatics out of the pore system, which increases the probability for secondary alkylation and cyclization reaction. Finally, cleaned pores are indicated by increased amounts of small aromatics on the cost of coke formation.

These reaction events of different reaction types are in permanent competition at the active sites, whereas the geometric constellation and strength of the sites within the multiplet defines the dominance of each individual reaction type.\(^{[13]}\) (see Figure 11 and Table 6) Therefore, hydride transfer and cyclization events are identified as key steps to formation of aromatics.\(^{[23,32]}\) Higher site density leads to growth within the pores. Optimized site density and dominance of cyclization and hydride transfer compared to oligomerization and cracking is managed by framework dealumination as well as removal of EFSPE.

Table 4. Solid-state properties of original H-ZSM-5 zeolite and samples after hydrothermal synthesis, ion-exchange with NH\(_4\)NO\(_3\) and deammonization.

| Sample | ICP-OES Si/Al (Na/Al) | TPAD (acidity)\(^{[1]}\) | TPAD (acidity)\(^{[1]}\) | S1/S2 |
|--------|----------------------|-------------------------|-------------------------|-------|
|        | weak (S1) [mmol/g]   | strong (S2) [mmol/g]    |                          |       |
| original | 11 (0.0)          | 0.77                    | 0.56                    | 1.38  |
| H-ZSM-5 |                       |                         |                         |       |
| SiAl-40 | 32 (0.2)           | 0.44                    | 0.37                    | 1.18  |
| SiAl-60 | 49 (0.1)           | 0.38                    | 0.28                    | 1.37  |
| SiAl-80 | 63 (0.3)           | 0.24                    | 0.22                    | 1.08  |
| SiAl-150 | 113 (0.8)          | 0.15                    | 0.13                    | 1.16  |
By this consideration of shape selective conversion a high (AI) quantifies the pore cleaning and optimization of site density within the final dealumination procedure. (see Table 5) Preliminary work by use of chelating agents confirms, that only pore cleaning in combination with framework dealumination leads to changes in shape selective transport and formation.[11] Thus, coking behavior, durability and formation of aromatics in ETH process are suitable indicators for shape and site-multiplet selective restrictions within aromatics formation in the H-ZSM-5 pores. They are summarized as “aromatics index” (AI). (see equation)

The obtained data confirm efficient pore cleaning especially after combination of desilication and dealumination as well as additional steaming and acid washing. A single combination of steaming and acid washing leads to efficient dealumination, but not necessarily to a facilitated access of hydrocarbons within the pore system. The removal of EFAL after framework dealumination by acid is facilitated especially after prior desilication by base.

**Reasonable Si/Al ratio to formation of aromatics**

Consideration of framework aluminum as main origin for acid catalyzed activity from strong Brønsted acid sites results in a model, which connects good (AI) and Si/Al ratio within ZSM-5.

As the key reactions to coking and aromatics formation within hydrocarbon pool of methanol and ethanol conversion the cyclization and hydride transfer are accepted. Both mechanisms benefit from neighboring Brønsted acid sites, i.e. for the model: Pre-coordination and re-adsorption is facilitated by site multiplets consisting of two sites (doublets). On the other hand, overabundant sites increase the probability of corresponding

### Table 5. Comparison of catalytic results by model parameters aromatics index (AI) and durability (ToS), after combined treatment with steaming (St), acid washing with 0.5 M HCl at 90 °C and washing with 0.5 M NaOH at 90 °C during 24 h.

| Sample            | Sorption\(^\text{H}\) BET (BJH) [m\(^2\)/g] | ICP-OES Si/Al (Na/Al) | Model yield (AI) [%] | Model deactivation (ToS)\(^\text{h}\) |
|-------------------|------------------------------------------|-----------------------|----------------------|-----------------------------------|
| original          | 390 (61)                                 | 11 (0.0)              | 8                    | 9                                 |
| H-ZSM-5           |                                          |                       |                      |                                   |
| NaOH24h-HC24h(2)  | 430 (59)                                 | 17 (0.4)              | 16                   | 43                                |
| St400-HC24h(1)    | 390 (42)                                 | 16 (0.0)              | 6                    | 6                                 |
| NaOH24h-HC24h-SI400-HC24h(2) | 410 (89) | 20 (0.0) | 23                   | 80                                |

[a] Physisorption of nitrogen, BET for micro-pore surface analysis, [b] (ToS); model parameter at 50 % deactivation, see supporting information.

### Table 6. Results of a geometric consideration of homogeneous and statistical distribution of framework aluminium in ZSM-5. EFAL not considered: correlation between Si/Al ratio and framework acid site multiplets in adaption to model of isolated ensembles by Nikolaj I. Kobozev.[33,34]

| Si/Al ratio | Al per unit cell | Al per pore intersection | Most common acid site multiplet per pore intersection |
|-------------|------------------|--------------------------|------------------------------------------------------|
| 1.91        | 33\(^\text{H}\)    | 8                        | -                                                    |
| 6.4–7.0     | 13–12            | 3                        | triplet                                              |
| 9.7–11      | 9–8              | 2                        | doublet (+ triplets)                                 |
| 18–23       | 5–4              | 1                        | singlet (+ doublets)                                 |
| 31–47       | 3–2              | 0.5                      | singlet                                              |
| 95          | 1                | 0.25                     | singlet (isolated pore intersection)                 |

[a] Estimation of aluminium distribution according to Löwenstein's rule, i.e. no [AlO\(_4\)]\(^-\) tetrahedron is directly connected to another one.[35]
Coke formation through pore channels beyond more than one site multiplet. A fast formation of small aromatics and moderate formation of coke needs a few isolated acid site doublets, but not too much to avoid a multiplet based hydrocarbon growth. (Si/Al = 18–23)

Including amounts of EFAL and slight inhomogeneities in aluminum distribution[37] into consideration, the most promising Si/Al ratio might increase slightly. (Si/Al ≈ 20–25) With the post-synthetic strategy described in this work the limit is almost reached (Si/Al = 20).

**Conclusion**

Improved dealumination of original H-ZSM-5 zeolite (Si/Al = 11) is demonstrated by a strategic combination of desilication (NaOH), acid washing and ion re-exchange (HCl), framework dealumination by steam (St) and acidic removal of extra-framework species (HCl). Consecutive washing with sodium hydroxide and hydrochloric acid enhances the dealumination process and compensates the drawback of NaOH by an ion-re-exchange to H-form. In case of steaming the additional washing with hydrochloric acid increases dealumination efficiency as well as removal of extra-framework species from the pores.

Framework dealumination as well as pore and bulk cleaning by consecutive washing tend to reduce coke formation. Especially with initial desilication by base, there is a facilitated access of the pores for small aromatics, which increases aromatics production. The novelty of the mentioned procedure for extended dealumination is the strategic combination to overcome drawbacks of the former by the subsequent treatment step.

The use of shape selective conversions is a suitable method to characterize zeolite pore systems and their textural properties known from “constraint index” (CI),[38] “extended constraint index” (CI*)[39] or “spaciousness index” (SI).[40] The use of aromatics formation and durability in “aromatics index” (AI) is a new method to describe pore cleaning and site isolation efficiency.

**Experimental Section**

**Hydrothermal synthesis of Na-ZSM-5**: Zeolite samples were prepared in accordance to a synthesis route established by the research group. The first step represents the preparation of a synthesis gel. Ultrapure water is mixed with the template tetrapropylammonium bromide (TPAB) after grinding. After 10 min a grinded mixture of sodium trimisicate and sodium aluminate in sufficient ratio are added stepwise to the aqueous slurry within a period of 30–45 min under continuous mixing. After completion the slurry is mixed again for 10–15 min. Under moderate mixing pH value is adjusted carefully by a 50 wt.% sulfuric acid to pH = 10 without reaching pH = 9. The resulting gel is transferred into the stainless steel autoclave (PTFE inlet, Berghof, 2.5 L). Hydrothermal synthesis is performed at 150 °C and autogenous pressure. Synthesis time varies between 48–72 h and starts with reaching the final temperature. The product is separated from the liquid phase after cooling down to 80 °C and opening of the autoclave. The solid product is filtered and washed by 2 L of water and 0.5 L of ethanol. The sample is dried over night at 60 °C.

**Post-synthetic activation to H-ZSM-5**: To remove organic templates the solid material is heated to 120 °C with 1.1 K/min in air flow. After a holding time of 1 h temperature is increase by 1.1 K/min up to 540 °C. Cooling down to 40 °C starts after 12 h. In a next step ion exchange is realized with a ratio of 1 g zeolite and 10 mL of 0.1 M NH₄NO₃ solution. The procedure takes 3 h under stirring at 80 °C under reflux. The hot product is filtered and washed with 1 L of water. The material is dried over night at 80 °C. The entire procedure is repeated two times. The conversion of the ammonium zeolite to its protonated form is done by heating the sample stepwise to 120 °C and 450 °C with 1.1 K/min under air flow. The temperature program includes holding steps of 1 h and 6 h at 120 °C and 450 °C, respectively.

**Procedures for dealumination and desilication**: Steaming (St) was carried out in a vertical glass tube reactor in nitrogen with 15 L/h and water with 2 g/h. Temperature was increased with 2 K/min to 400 °C without water flow and held for 12 h under atmospheric pressure. Basic washing (NaOH) of 15 g (dry) zeolite samples was carried out for 24 h with 0.5 M NaOH (99 %) from Grüssing GmbH. Samples are washed with hot water (85–90 °C) afterwards in portions of 10 × 300 mL. Acidic washing (HCl) of 15 g (dry) samples was performed over 24 h/96 h with 0.5 M hydrochloric acid (37 %) from Sigma Aldrich. Samples of 15 g batches are denoted with (1) in the Tables. For scale-up, a 6.6-fold amount of sample was used and denoted as (2) in the Tables. Each step was followed by drying at 60 °C for 12 h and water vapour saturation over saturated (NH₄)₂SO₄ for reproducible weighting. During post-synthetic treatment of original ZSM-5 with base and acid subsequent washing with hot, boiling water over a glass filter (Por4/G4) was necessary to remove leached silica and alumina. The treatment with base or acid leads after 24 h to first precipitation at the surface of the round flask. The effect is well-known as Ostwald ripening or re-crystallization of silica and alumina.[41] The hot solution was transferred to the filter and was separated from mother liquor within 10 min avoiding cooling as good as possible. An electric kettle was used to speed-up the process of washing. Especially during scale-up of the procedure from 15 g to 100 g the importance of high amounts of solution (10:1) and a speed-up of the washing process become decisive to avoid unwanted precipitation on the zeolite surface. (see Table S3)

**Solid-state and surface characterization**

TPAD: The acidic properties of the samples were investigated by temperature-programmed desorption of ammonia (TPAD). All measurements were carried out on a ThermoScientific TPDRO 1100 instrument equipped with a thermal conductivity detector (TCD). Typically, about 300 mg of catalyst sample were used. Before ammonia adsorption, the samples were dried under flowing argon at 550 °C and cooled down to the adsorption temperature of 100 °C. Ammonia adsorption was performed for 30 min. Ammonia desorption was investigated under helium flow by purging the sample chamber for 30 min and subsequent heating up to 550 °C/700 °C for 1 h with a heating rate of 10 K/min. For calculation of weak (S1) and strong (S2) acidity from TPAD profile a rough division of the integral at 1800 s (417 °C) was used due to a similar TPAD profile of each sample. For calculation of mmol(NH₃) per gram zeolite from the TCD signal (thermal conductivity detector) a calibration factor was used (k = 7.353347×10⁻⁷ mmol/(mW*°C)). A more complex curve fitting with asymmetric Gauss function neither enhanced the accuracy nor changed any trends. (temperature profiles see supplemental information Figure S6). Despite the
sodium form, we always observe a high temperature peak (S2) as discussed in the literature.[8,20] 

\( N_2 \) physisorption: All samples were calcined under vacuum. The standard procedure was a calcination at 250 °C for 8 h. After calcination all samples were cooled in liquid nitrogen and physisorption isotherms were collected. The measurements were carried out on a Sorptomatic 1900 from Carlo Erba Instruments and fitted according to BET theory.[41] To distinguish between changes in external and internal surface, isotherms from nitrogen physisorption experiments are analyzed in the micropore \((p/p_0 = 0.001 – 0.05)\) and meso-/macropore region \((p/p_0 = 0.35 – 0.95)\). Two models BET-2-parameter \( f(\theta) \) and BJH model[41] are used to calculate specific surface parameters to observe trends in porosity by synthesis and post-synthesis procedures.

XRD: Powder diffraction experiments to investigate changes in crystalline long-range order were performed with a SuperNova from Rigaku Oxford Diffraction by accumulation over 10 min with Cu–Kα radiation at 100 K. For calculation of crystallinity by XRD, a modified method of ASTM D5758-01 was used.[40] Within this standardized method the total area of the reflex group near 24.3 ° 20 or the relative heights of the biggest and smallest reflex at the group at about 24 ° 20 are used. In accordance to the second method the height of the biggest reflex at 24 ° 20 is used for calculation. Related to the first method the absolute height of this reflex is used, but in relation to the reflex at about 8 ° 20, which is not only sensitive to ZSM-5. As reference the original H-ZSM-5 was used and set to 100 %. There is an artifact of crystallinity > 100%, which occurs if organic templates are inside the zeolite structure (24 ° 20 increased) or if silica-rich crystalline material is removed (8 ° 20 decreased).

\[
\text{cryst.} = \frac{\text{max}(22.2, 24.0 \text{ ° 20})}{\text{max}(22.2, 24.0 \text{ ° 20})} \cdot 100 \%
\]

For calculation a refinement of the diffractogram was done by a curve fitting. A device and angle dependent underground signal was subtracted by a degenerative exponential function. The sample preparation with a nylon loop and a viscous oil showed an almost polynomial (2nd order) underground signal with migrating maximum at about 20 to 30 ° 20. The correction was done by 3 different 2nd order polynomial functions, which were subtracted prior to calculation of the crystallinity. (original diffraction patterns see supplementary information)

TGA: Thermogravimetric analysis was performed with a TG50 from Mettler Toledo under nitrogen flow (200 mL/min) to evaluate dry mass of each sample and under synthetic air (200 mL/min) for coke mass determination after catalytic tests. Temperature program consists of a ramp between 35–850 °C at a rate of 10 K/min each run.

ICP-OES: Elementary analysis was performed by dissolution of zeolite powder by microwave-assisted solvation with a mixture of 3 mL nitric, 2 mL hydrochloric and 1 mL hydrofluoric acid. Quenching with boric acid was followed by quantitative determination of silicon, aluminum and sodium by inductively coupled plasma combined with optical emission spectroscopy. For analysis of solutions a Optima 2000 DV by PerkinElmer was calibrated to Si at 212.4 nm, Al at 396.2 nm and Na at 589.0 nm. Calibration was done by defined solutions of 1000 mg/L standards by PerkinElmer and deionized water.

MAS-NMR: Characteristics of aluminium species on solid samples were investigated by \(^{27}\text{Al-MAS-NMR}\). Spectra are acquired on a Bruker Ascend 300 MHz NMR spectrometer at a resonance frequency of 78.19 MHz and with a sample spinning rate of 16 kHz at the magic angle. For each sample 1000 scans were accumulated with a repetition time of 1 s. As external standard an aqueous solution of aluminium nitrate was used. All samples are stored under water vapor atmosphere (80% humidity with saturated \((\text{NH}_4)_2\text{SO}_4\) solution).

Particle size analysis: Dynamic laser scattering was used to determine particle size distribution with a Bettersizer S3 Plus by 3P Instruments. Wet dispersion procedure was performed with 2000 rpm stirring and 200 W (26 kHz) ultrasonic for 2 min. Data acquisition and proceeding are in accordance to ISO 13320:2009 with calculation of particle size distribution from scattering data by Mie theory.[41]

Catalytic measurement: All zeolite powder materials were pressed at 1.5–2 MPa, crushed and sieved in a range of 315–400 μm. The conversion was carried out in a vertical fixed-bed steel tubular reactor. For each run 500 mg catalyst sample (dry mass) was used. Reaction temperature for catalytic testing was 350 °C controlled by a thermocouple directed heating. Ethanol (2.5 g/h) and nitrogen carrier gas (15 L/h) were fed into the reactor via heated pipes (WHSV of 5 h

\( ^\text{-1} \)). During 10 h ToS and 2.5 bar (absolute pressure) condensable products were trapped in a liquid separator. In all cases, a mass balance was defined including yield of coke, liquid condensable and gas-phase products with regard to ethene. The resulting gaseous and liquid reaction mixtures were analysed by gas chromatography using an HP 5890 Series GC System equipped with an FID (flame ionization detector) and a non-polar 100 m HP-1 column. Pre-tests showed no or only traces of ethanol or diethyl ether at above 300 °C. Prior to catalytic testing all samples were dried at 120 °C for 1 h in nitrogen (5 L/h) following a calcination step (rate 3 K/min) at 450 °C for 0.5 h. (temperature program, see supplementary information Table S1)

Catalyst regeneration by burning of coke: Prior to further runs with spent catalyst samples residual coke is burnt in an external oven in air up to 550 °C. Sieved material is coked during catalytic test, cooled down to room temperature and pre-dried again at 120 °C for 1 h in an air flow (10 L/h). Coke is burnt afterwards in air up to 550 °C (rate 1.1 K/min) for 24 h. For the next reaction cycle two regenerated samples are mixed to ensure 500 mg dry mass after sieving to 315–400 μm and to ensure residual regenerated material for analytics, e.g. XRD and physisorption of \( N_2 \).

Product analysis and mass balance: Product analysis was standardized by DHA method for determination of hydrocarbons including response factor analysis. Single experiments were performed for additional oxygenates, e.g. ethanol. Chromatograms were collected from a HP 5890 Series GC System. Mass balance was calculated from gas and liquid phase analysis by GC and balancing of liquid phase products and coke analysis by TGA. Data analysis was done for each individual compound and summarized in fractions such as olefins, paraffins and aromatics. Chemical composition of coke was neglected due to its low amount below 1 wt. % of full mass balance. Compound determination in gas phase was compared to results from gas chromatography and mass spectrometry (GC/MS) with a Clarus 680 GC and a Clarus SQ 8 S MS from PerkinElmer with an extended DHA method. Further details concerning mass balance and deactivation plot model are listed at the end of the supplementary information. (Supplementary Experimental Section)
Acknowledgements

The authors acknowledge support by apl. Prof. Dr.-Ing. habil. Michael Stintz, Dipl.-Ing. Petra Fiola and Mr. Andre Kupka from Chair of Mechanical Process Engineering (TU Dresden) for SEM and EDX measurements. This research was funded by the German Research Foundation (DFG), funding number 269574272. The authors also thank the German Federal Ministry for Education and Research (BMBF) for financial funding of this research within the directive Client-II “International Partnerships for Sustainable Innovation” by FONA. Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: aromatics index · ETH process · heterogeneous catalysis · post-synthesis · structure-activity relationships · synthesis design · zeolites

[1] R. J. Argauer, G. R. Landold, Patent US3,702,886, 1972.
[2] R. M. Lago, W. O. Haag, R. J. Mikovsky, D. H. Olson, S. D. Hellring, K. D. Schmitt, G. T. Kerr, Stud. Surf. Sci. Catal. 1986, 28, 677–684.
[3] M. Göhlich, W. Reschetilowski, S. Paasch, Microporous Mater. 2011, 142, 179–183.
[4] L. H. Öng, M. Dömkö, R. Olindo, A. C. van Veen, J. A. Lercher, Microporous Mater. 2012, 164, 9–20.
[5] E. T. C. Vogt, B. M. Weckhuysen, Chem. Soc. Rev. 2015, 44, 7342–7370.
[6] E. Brunner, H. Ernst, D. Freude, M. Hunger, C. B. Krause, D. Prager, W. Reschetilowski, W. Schwierger, K.-H. Bergk, Zeolites 1989, 9, 282–286.
[7] T. Masuda, K. Hashimoto in: ACS Symposium – Deactivation and testing of Hydrocarbon-Processing Catalysts, Series 634, (Eds.: P. O’Connor, T. Takatsuka, G. L. Woolery), American Chemical Society, Chicago – Illinois, 1995, pp. 62–76.
[8] Z. B. Sousa, D. V. Cesar, C. A. Henriques, V. T. Silva, Catal. Today 2014, 234, 182–191.
[9] M.-C. Silaghi, C. Chizallet, J. Sauer, P. Raybaud, J. Catal. 2016, 339, 242–255.
[10] D. Dauner, K. Räuchle, W. Reschetilowski, ChemCatChem 2012, 4, 802–814.
[11] D. Dauner, M. Seifert, W. Reschetilowski, Microporous Mater. 2016, 219, 66–70.
[12] A. D. Chowdhury, A. L. Paioni, G. T. Whiting, D. Fu, M. Baldus, B. M. Weckhuysen, Angew. Chem. Int. Ed. 2019, 58, 3908–3912.
[13] K. A. Cumming, B. W. Wojciechowski, Catal. Rev. 1996, 38, 101–157.
[14] K. Borgh, R. Batchu, V. V. Galvita, K. Alexopoulos, M.-F. Reyniers, J. W. Thybaut, G. B. Marin, Angew. Chem. 2016, 128, 13009–13013; Angew. Chem. Int. Ed. 2016, 55, 12817–12821.
[15] U. Olsbye, S. Svelle, M. Bjørgen, P. Beato, T. V. W. Janssens, F. Joensen, S. Bordiga, K. P. Lillerud, Angew. Chem. 2012, 124, 5910–5933; Angew. Chem. Int. Ed. 2012, 51, 5810–5831.
[16] S. Hamieh, C. Canaff, K. B. Tayeb, M. Tanighi, S. Maury, H. Vezin, Y. Pouilloux, L. Pinard, Eur. Phys. J. Special Topics 2015, 224, 1817–1830.
[17] J. F. Haw, W. Song, D. M. Marcus, J. B. Nicholas, Acc. Chem. Res. 2003, 36, 317–326.
[18] R. Johansson, S. L. Hruby, J. Rass-Hansen, C. H. Christensen, Catal. Lett. 2009, 127, 1–6.
[19] F. F. Madera, N. S. Gnep, P. Magnoux, H. Vezin, S. Maury, N. Cadrain, Chem. Eng. J. 2010, 161, 403–408.
[20] F. F. Madera, K. B. Tayeb, L. Pinard, H. Vezin, S. Maury, N. Cardran, Appl. Catal. A 2012, 443, 171–180.
[21] H. K. Beyer in: Post-Synthesis Modification I, Vol. 3 (Eds.: H. G. Karge, J. Weitkamp), Springer, Berlin Heidelberg, 2002, pp. 203–255.
[22] R. Srivastava, N. Iwasa, T. Fujita, M. Arai, Catal. Lett. 2009, 130, 655–663.
[23] S. Schallmoser, T. Ikuno, M. F. Wagenhofer, R. Kolvenbach, G. L. Haller, M. Sanchez-Sanchez, J. A. Lercher, J. Catal. 2014, 316, 93–102.
[24] J. Weitkamp, S. Ernst, H. Dauns, E. Gallei, Chem. Ing. Tech. 1986, 58, 623–632.
[25] C. S. Triantafillidou, A. G. Vissidiis, L. Nalbandian, N. P. Evmiridis, Microporous Mater. 2001, 47, 369–388.
[26] C. S. Triantafillidou, A. G. Vissidiis, M. Sanchez-Sanchez, J. A. Lercher, J. Catal. 2016, 330, 59–63.
[27] H. Bremer, N. Michael, W. Reschetilowski, K.-P. Wendlandt, Wiss. Z. TH Leuna-Merseburg 1983, 25, 205–213.
[28] C. S. Triantafillidou, M. N. Vissidiis, J. Catal. 2015, 341, 107–117.
[29] H. Schulz, Catal. Lett. 2018, 145, 1263–1280.
[30] W. Reschetilowski in: Einführung in die Heterogene Katalyse, Vol. 1, (Eds. W. Reschetilowski), Springer-Spektrum, Berlin Heidelberg, 2015, pp. 138–150.
[31] J. C. Green, J. C. Jansen, J. A. Moulijn, J. Pérez-Ramírez, J. Phys. Chem. B 2004, 108, 13062–13065.
[32] C. S. Triantafillidou, A. G. Vissidiis, N. P. Evmiridis, Ind. Eng. Chem. Res. 2000, 39, 307–319.
[33] H. Bremer, N. Michael, W. Reschetilowski, K.-P. Wendlandt, Wiss. Z. TH Leuna-Merseburg 1983, 25, 205–213.
[34] S. Brunauer, P. H. Emmett, E. Teller, J. Am. Chem. Soc. 1938, 60, 30–39.
[35] N. M. Emanuel, Russ. Chem. Rev. 1974, 43, 317–362.
[36] W. Löwenstein, Am. Mineral. 1954, 39, 92–96.
[37] D. E. Perea, I. Arslan, J. Liu, Z. Ristanovic, L. Kovarik, B. W. Arey, J. A. Lercher, S. R. Bare, B. M. Weckhuysen, Nature 2015, 6, 7589.
[38] D. S. Shihabi, Patent US5,549,314, 1985.
[39] J. A. Martens, M. Tielen, P. A. Jacobs, J. Weitkamp, Zeolites 1984, 4, 98–107.
[40] I. Zones, T. V. Harris, Microporous Mater. 2000, 35, 31–46.
[41] G. S. Shiralkar, P. N. Joshi, M. J. Eapen, B. S. Rao, Zeolites 1991, 11, 511–516.
[42] S. Brunauer, P. H. Emmett, E. Teller, J. Am. Chem. Soc. 1938, 60, 309–319.
[43] E. P. Barrett, L. G. Joyner, P. P. Halenda, J. Am. Chem. Soc. 1951, 73(1), 373–380.
[44] ASTM International, Standard test Method for Determination of Relative Crystallinity of Zeolite ZSM-5 by X-ray Diffraction, 2015, Beuth Verlag GmbH, (Berlin; ASTM D5758-01).
[45] International Organization for Standardization, Particle size analysis – Laser diffraction methods, 2009, Beuth Verlag GmbH, (Berlin; ISO 13320:2009).

Manuscript received: August 18, 2020
Revised manuscript received: September 10, 2020
Accepted manuscript online: September 14, 2020
Version of record online: October 19, 2020