

Structure-performance descriptors and the role of Lewis acidity in the methanol-to-propylene process

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Abstract

The combination of well-defined acid sites, shape selective properties and outstanding stability place zeolites among the heterogeneous catalysts of the greatest practical relevance. The development of structure-performance descriptors for processes catalysed by these solids has been a matter of intense debate, both in industry and academia. The direct conversion of methanol-to-olefins is a prototype where various catalytic functions contribute to the overall performance. Propylene selectivity and resistance to coking are the two most important parameters in developing new MTO catalysts. Here, we present a systematic investigation on the effect of acidity on the performance of ZSM-5 for the production of propylene. Our results demonstrate that isolation of Brønsted acid sites is key to selectively form propylene. Simultaneously, the introduction of Lewis acid sites prevents the formation of coke, hence drastically increasing catalyst lifetime. Our insights provide conceptually new information into the tunability of active sites in zeolite acid-catalysed reactions.

The methanol-to-olefins (MTO) process is a prototype case study of zeolite catalysis with the potential to alleviate the progressively growing demand for olefins.¹ Zeolites containing Brønsted acidity are the catalysts of choice,² with ZSM-5 and SAPO-34 being the two materials industrially applied.³ Zeolite topology is an important⁴ yet not the sole parameter in defining catalyst performance in MTO.⁵ Accessibility,⁶ strength, distribution,⁷ amount⁸ and nature⁹ of acid sites are also of high importance.

Brønsted acid sites (BAS) are believed to be the active sites for olefin production,^{5, 10} however there is currently a consensus that the production of olefins proceeds *via* an autocatalytic reaction. Accordingly, adsorbed hydrocarbon species in the micropores of a zeolitic catalyst, typically alkenes and arenes, act as “co-catalyst pool species” (Figure 1a). Both species participate in two competitive reaction pathways, mechanistically described by the dual-cycle concept: reaction products may either be formed through an alkene or aromatic based cycle *via* methylation/cracking reactions, depending on the nature of the hydrocarbon pool (HP) species.^{5, 11 12}

Optimization of the active site has primarily focused on the nature of the BAS and the hydrocarbon pool species. Herein, we show that the active site has an even higher degree of complexity: the combined presence of BAS and Lewis acid sites (LAS) may drastically improve the overall performance of the catalyst. Olefin selectivity and resistance to coking are the two most important parameters in developing new catalysts for this process. In the last few decades, modification of ZSM-5 zeolites with different elements like phosphorus, boron or alkaline-earth metals¹³ has been shown to strongly improve the selectivity to propylene and, simultaneously, improve catalyst lifetime. This sets up the grounds for the Methanol-to-Propylene (MTP) process: carried out over mildly Brønsted acidic ZSM-5 catalysts at slightly higher temperatures than classical MTO chemistry ($T \geq 500$ °C). The improved propylene yields have been rationalized on the basis of the lower density of BAS and, in some cases, spatial constraints due to post-synthetic modifications,¹⁴ however no clear structure-performance descriptors have been developed.

Here we present a systematic investigation on the effect of acid site isolation and Brønsted and Lewis acidity on the performance of ZSM-5 zeolites in the MTO process. By establishing a correlation between the type and concentration of acid sites with lifetime and selectivity to ethylene and propylene, we decouple the effect of Brønsted from the effect of Lewis acidity, further determining the respective contributions of BAS and LAS. Next, by combining theory with operando UV-Vis and ¹H NMR we are able to understand the role of Lewis acidity and to demonstrate that these sites are not spectators. Indeed, LAS become an integral part of the active site and influence the reactivity of intermediates in the hydrocarbon pool cycle. The established structure-performance relationships may be applied to other high temperature zeolite catalysed reactions.

Results

Assessing textural and acidic properties of the catalysts.

We prepared three series of ZSM-5 zeolites with different amounts and types of acid sites. We followed two main approaches: (i) controlling amount of acid sites and their location during zeolite synthesis, and (ii) modifying the acidity of already synthesized zeolites (Figure 1b). The first series of pre-synthetically modified zeolites (**Z**) was prepared by varying the amount of Al in the synthesis gel and/or utilizing different structure-directing agents (SDA). Another two series of catalysts were obtained following different protocols of post-synthetic modification using commercial Z1 as starting material. **M**-series was obtained by Z1 demetalation with various desilicating and dealuminating agents, while **AE**-series was prepared by incorporation of different amount and type of alkaline-earth metal (AE1-AE5 are Ca-, AE6 – Sr-, AE7 – Mg-modified).

All synthesized zeolites from Z-series have the expected MFI topology, comparable morphology and crystal size (Supplementary Fig. 1, 2). Variation of Al during the synthesis resulted in zeolites with different Si/Al ratio (300 and 650 for Z2 and Z3 respectively), while variation in SDA affected textural properties. N₂ adsorption reveals the existence of a hysteresis loop in the pre-capillary condensation region of microporous Z2 and Z3 (Supplementary Fig. 3, 4) attributed to the phase transition from a disordered phase to a lattice-like fluid phase.¹⁵ This becomes less evident with increasing the Al content and completely disappears for Z1 sample with Si/Al=40. Z4, synthesized using a di-quaternary ammonium-type surfactant as described by Ryoo and co-workers,¹⁶ additionally exhibits a hysteresis loop at high relative pressures indicative of mesoporosity between stacked sheets.¹⁷

FT-IR spectroscopy of pyridine adsorbed (Supplementary Fig. 5) indicates a decrease in Brønsted acidity¹⁸ (absorbance at 1546 cm⁻¹) in the Z1-Z4 series, in line with the increasing Si/Al ratio. For M-series, treatment with various demetalating agents caused a decrease of BAS in comparison to Z1 (Table 1) and resulted in an increased amount of Lewis acid sites (LAS). Lewis acidity is due to the presence of extraframework Al and/or perturbed Al species.¹⁹ Another side-effect of this post-synthetic modification was the generation of mesopores, which are generally held responsible for lifetime improvement in methanol conversion.^{20, 21} For all samples except M4, demetalation caused a significant increase in the mesoporous surface area (Table 1). Oppositely, incorporation of alkaline-earth metals resulted in a significant decrease of both surface area (S_{BET}) and pore-volume (V_p), both gradually reduced with an increase of alkaline-earth loading (Supplementary Fig. 3). Besides, the modification also caused almost a tenfold decrease in BAS concentration (from 232 $\mu\text{mol g}^{-1}$ to 27 $\mu\text{mol g}^{-1}$ for Z1 and AE4). Another clear difference between the Z1 sample and the AE series is the appearance of a significantly higher concentration of Lewis acid sites (Supplementary Fig. 5).

Comparison of the acidic properties of the studied catalysts reveals that Z3 possesses the same concentration of Brønsted acid sites as AE4 and AE5. The only difference between these samples is the presence of a notable amount of Lewis sites resulting from Ca incorporation. To gain insight into the

proximity between these two acid functionalities, two-dimensional ^1H - ^1H DQ (DQ=double-quantum) and ^1H - ^1H RFDR (RFDR=radiofrequency-driven recoupling) MAS NMR was carried out (Figure 2). These two methods are particularly powerful when combined: RFDR gives a self-correlation peak, whereas DQ does not.²² The cross-peaks in the horizontal frequency span of 1-2 ppm belong to both terminal Si-OH protons and bridging Ca-OH protons (Figure 2).^{22, 23} When AE3 is fully dehydrated at 450 °C (Supplementary Fig. 6), the DQ correlation vanishes, but the RFDR correlation does not. This indicates that, under reaction conditions, the acidic protons behave as isolated entities.

Effect of pre-synthetic and post-synthetic modification. The impact of acidic properties was evaluated under conditions relevant for the MTO process. Z1 exhibits the shortest lifetime in comparison to the other samples, it deactivates after 16.5 h on stream, which corresponds to an integral throughput of $132 \text{ g}_{\text{MeOH}} \cdot \text{g}_{\text{catalyst}}^{-1}$ (Figures 3a and 3b). The lower concentration of Brønsted acidity in Z3 extends the catalyst lifetime up to 28 h (Figure 3b, Supplementary Fig. 7).²⁴ According to Mores *et al.*,²⁴ the lower the Si/Al, the faster the formation rate of methylated aromatic species, in turn leading to faster coking rates. Z3 is characterized by steady formation of all products, propylene being the dominant one (up to 48%) (Supplementary Fig. 7). Another striking difference is the much lower fraction of paraffins, ethylene and aromatics in comparison with Z1 (Supplementary Fig. 10). Bjørgen *et al.*¹¹ demonstrated that the formation of ethylene is mechanistically separated from other olefins, being mostly formed *via* xylenes and/or trimethylbenzenes, whereas propylene is selectively formed *via* methylation and cracking reactions within the alkene cycle (Figure 4b). The formation of paraffins is a result of hydrogen transfer to olefins, where methanol can act as hydrogen donor. Proton transfer occurs on both BAS²⁵ and extraframework aluminium species.²⁶ The sharp decrease in formation of ethylene and aromatics in sample Z3 suggests the almost full suppression of the aromatic cycle.^{3, 20, 26} As hypothesized by Guisnet *et al.*,²⁷ the aromatic cycle dominates when zeolites with high acid site densities are used. In this line, isolation of Brønsted acid sites by decreasing the Al content leads to higher propylene yields.¹ Further comparison of Z3 with AE5 confirms that the concentration of Brønsted acid sites is indeed the main descriptor for the observed selectivity (Supplementary Fig. 8). These two catalysts, having a very similar concentration of acid sites, exhibit almost identical selectivity to paraffins, ethylene and propylene. In contrast, AE5, prepared by post-synthetic modification with Ca, displays two times longer lifetime (Figure 3b). The only obvious difference between these two catalysts is the presence of Lewis acidity in AE5 arising from the Ca incorporation.

Demetalated mesoporous M1-M4 show a longer lifetime and higher selectivity to propylene in comparison with the parent Z1 (Supplementary Fig. 9). The improved stability towards deactivation of mesoporous zeolites is generally explained by a facilitated molecular transport,²⁸ along with a higher external surface area that provides more space for coke deposition.^{29, 30} On the other hand an increased selectivity to propylene can be explained by the decreased concentration of acid sites, the latter being also responsible for the improved lifetimes.^{20, 30} Further examination of the textural and catalytic

properties reveals a linear correlation between mesopore surface area and catalyst lifetime (Supplementary Fig.11). Analysis of the spent catalyst indicates a significantly higher amount of coke deposited in micro- and mesopores for the M-series of zeolites in comparison with Z1. Another striking observation is the significantly longer lifetime of M4, having the lowest surface area in comparison with other samples from the M-series. In the same manner, Z2 and M4 are rather similar both in porosity and concentration of BAS, but differ in concentration of Lewis acid sites.

Establishing acidity-performance relationship. The integral propylene selectivity was related to changes in BAS concentration. To account for changes in textural properties, we normalized the concentration of BAS (n_{BAS}) by the BET area (S_{BET}) to yield an acid site surface density (c_{BAS}). During the normalization procedure, we assumed an even distribution of Al within zeolite framework. This assumption was later validated by UV-Vis spectroscopy (*vide infra*) and ^{27}Al NMR experiments (Supplementary Fig.12-14).

Figures 3c and 3d show the integral propylene and ethylene selectivity as a function of Brønsted acid site density. These figures clearly demonstrate a linear correlation between c_{BAS} and selectivity to propylene and ethylene for all samples. At high BAS densities, acid sites are in closer proximity. As a consequence, successive reactions can occur at these sites along the diffusion pathway, promoting the aromatic cycle.²⁷ Low Brønsted acid site densities prevent consecutive reactions leading to aromatization and coking, thus favouring methylation and cracking reactions. Altogether, these results confirm that Brønsted acid site isolation is instrumental to attain a high propylene selectivity. Opposite trends obtained for ethylene and propylene also confirm that these two products are formed through two competitive routes. To decrease the impact of the “secondary reactions” we also plotted ethylene and propylene selectivity taken at 98% of oxygenates conversion (Supplementary Fig. 15), i.e. when almost the entire catalytic bed is deactivated and only the lower part participates in MTO. As it can be observed, similar correlations are obtained.

The relationship between c_{BAS} and methanol throughput is more complex. Although high Brønsted site densities result in faster deactivation due to faster coking rates, not only Brønsted acid site density but also distribution play an important role. Wang *et al.*⁷ showed that the same concentration of Brønsted acid sites can still lead to different lifetime due to an uneven Al distribution and formation of Al pairs. Analysis of Al distribution assessed by UV-Vis of Co-exchanged zeolites shows that this distribution within α -, β - and γ -sites is rather similar (Supplementary Fig. 12), excluding the effect of Al location. Therefore, the different resistance to deactivation of AE5 and Z3 with similar c_{BAS} is a strong argument to claim that c_{BAS} is not the only descriptor for catalyst lifetime. The same discussion holds for Z2 and M4, the latter being stable for at least 3 times longer. Considering that demetalation of M4 did not result in significant development of the external surface area, the potential effect of mesopores on catalyst lifetime can be ruled out. Preparation of M4 involved extraction of framework Al by steaming, leading to

the formation of “inefficient” occluded mesopores barely impacting intracrystalline diffusion.^{31, 32, 33} Milina *et al.*⁶ have shown that interconnectivity of mesopores in hierarchical ZSM-5 has the largest impact on lifetime. This catalyst however showed the longest lifetime among the M-series. As the only obvious difference between these catalysts (AE5 vs Z3 and M4 vs Z3) is the presence of Lewis acid sites, it seems logical to study the effect of c_{LAS} . Figure 3e shows the methanol throughput plotted as a ratio of Lewis and Brønsted acid sites. The obtained “volcano” plot yields an optimum LAS/BAS ratio between 2 and 6. Interestingly, the two optimal catalysts are AE3 and AE7, samples prepared by Ca and Mg incorporation, respectively, both with an AE to Al molar ratio of 1.8.

On the role of Lewis acidity. The impact of Lewis acidity on MTO is not yet fully understood. There are only a few works dealing with this topic and often reporting a rather negative influence on performance.²⁶ The majority of those works focuses on the presence of extraframework Al (EFAl). Here, we investigate the beneficial effect of alkaline-earth metal modification at the molecular level by performing a series of Density Functional Theory (DFT) based simulations. Earlier, we proposed $[Ca(\mu-O)(\mu-OH)Ca]^+$ moieties as possible active sites in the Ca-modified ZSM-5 catalyst,³⁴ inspired by the experimentally defined optimal Ca:Al ratio of 2 and the literature reports that divalent extraframework cations tend to self-organize into binuclear complexes in zeolites.³⁵ We studied the stability of various Ca binuclear complexes when incorporated in a ZSM-5 structure containing two Brønsted acid sites per unit cell. The $[Ca(\mu-O)_2Ca]$ has a very high basicity and quickly deprotonates the vicinal Brønsted acidic sites. An alternative stabilizing interaction for the singly protonated $[Ca(\mu-O)(\mu-OH)Ca]^+$ is to bind to the zeolite framework, but this is by far less stabilizing than the formation of $[Ca(\mu-OH)_2Ca]^{2+}$ (Figure 5). This analysis clearly shows the capacity of alkaline earth modification to reduce the number of BAS sites in the catalyst.

Further, we investigated the reactivity and stability of some key hydrocarbon pool (HP) species at Lewis and Brønsted acid sites. Figure 4a shows that the free energies of activation for the methylation reactions of propene and 1,2,3,5-tetramethylbenzene (tetraMB) significantly increase upon Ca incorporation. The obtained transition states are shown in Supplementary Fig. 26 and 27. These two reactions are crucial for the alkene and aromatics catalytic cycles.^{36, 37, 38} When the reaction is catalysed by a BAS near a Ca moiety ($BAS/[Ca(\mu-OH)_2Ca]^{2+}$) or by a LAS formed by the $[Ca(\mu-OH)_2Ca]^{2+}$ moiety, the free energy barriers increase by 54-67 kJ/mol for propene and 101-129 kJ/mol for tetraMB compared to the reactions catalyzed by an isolated BAS. Thus, alkene and aromatics methylation are slowed down to a different extent in Ca-ZSM-5. These results show that the growth of aromatics by methylation, and thus the propagation of the aromatics based HP cycle, is strongly suppressed by Ca incorporation while alkene methylation and the propagation of the autocatalytic cycle can still take place. These calculations were experimentally verified by co-feeding benzene with DME over sample Z3 and AE5. The apparent activation energy of benzene methylation increased from 64 kJ/mol over Z3 to 85 kJ/mol over AE5 (Supplementary Fig. 21). In line with this observation, higher selectivity to secondary products was

observed over Z3 than over AE5 (Supplementary Fig. 20). At 500 °C, alkaline earth modification was found to decrease the rate of benzene conversion by a factor of 4.1. Similar co-feeding experiments with isobutene also indicate a decrease of the rate of isobutene conversion by a factor of 2.4 at 500 °C, which is smaller than for benzene conversion. We further investigated the stability of carbocations, which are known to be key intermediates in the aromatic cycle.³⁹ Proton enthalpies for a series of MTO intermediates were studied in ZSM-5 samples with an isolated BAS and samples with a BAS nearby a $[\text{Ca}(\mu\text{-OH})_2\text{Ca}]^{2+}$ or $[\text{Mg}(\mu\text{-OH})_2\text{Mg}]^{2+}$ site. The selection of HP species is inspired by the proposed intermediates in the alkene and aromatic based cycle.⁴⁰ We found that the stability of carbenium ions is largely reduced in LAS modified zeolites, e.g. the protonation enthalpy of 1,2,2,3,5-pentamethylbenzenium ion reduces from -120 kJ/mol to -75 and -65 in Mg and Ca modified zeolites (Figure 4c). The difference in protonation enthalpies may be ascribed to the stabilizing interaction of the double bonds of the neutral cyclic species with the $[\text{Ca}(\mu\text{-OH})_2\text{Ca}]^{2+}$ sites. Our findings show that cyclic HP intermediates formed in LAS-modified zeolites would be much less reactive in the aromatic based cycles. The influence on alkenes is far less pronounced, which is an indication that this cycle is less affected by incorporating LAS. These conclusions are fully in line with the free energy profiles for methylation of propene and tetraMB shown in Figure 4a. We also investigated the lifetimes of neutral species at realistic working condition of 500 °C (Supplementary Fig. 41). We performed molecular dynamics simulations on the neutral species and investigated the tendency of the zeolite framework to protonate the HP compounds. In accordance with our static simulations, systematically longer lifetimes are found for the neutral species in LAS modified zeolites. We observe similar features for extraframework aluminum (EFAI) species with a $[\text{HOAl}(\mu\text{-OH})_2\text{AlOH}]^{2+}$ structure, indicating similarities between EFAs and Ca species (see Supporting Figures S34-S38).

Operando UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) is an insightful technique to follow the evolution of HP formed in zeolitic microenvironment,^{41, 42, 43} able to distinguish between different neutral and protonated species. To identify experimentally whether the presence of Lewis acidity affects the nature of HP species, we monitored the formation of hydrocarbons produced during MTO *via* UV-Vis DRS for Ca-containing AE3 and compared the obtained spectra with Z1 and Z2. The spectra of Z1 and Z2 taken during the first minutes of MTO are characterized by similar absorption bands but different intensities (Figure 6 and Supplementary Fig.16). This points to the fact that hydrocarbon species are of the same nature but form in different amounts, the nature of hydrocarbon species is independent from the amount of BAS. In UV-Vis, the region above 35000 cm^{-1} corresponds to neutral aromatic species, while protonated aromatics and neutral polyaromatics absorb light at lower wavenumbers. For samples Z1 and Z2, the first minutes of MTO are characterized by the appearance of a band around 35000 cm^{-1} corresponding to neutral benzene and a broad component composed by a combination of bands around 23600, 20600 and 17000 cm^{-1} (Supplementary Fig. 16), corresponding to methyl-substituted benzenium cations.^{41, 42} With time-on-stream, the appearance of the absorption band below 15000 cm^{-1} (Supplementary Fig. 16) indicates an accumulation of polyaromatic species in Z1 and Z2. The early

appearance of this band indicates that formation of polyaromatics starts at the beginning of reaction (Supplementary Fig. 16). In sharp contrast, the UV-Vis DRS of AE3 reveal neither neutral nor charged aromatic species. The spectra are characterized by a wide band around 30000 cm^{-1} becoming much broader with increasing time-on-stream. Attribution of this region is rather controversial in literature but it is generally agreed that these bands are indicative for monoenylic and dienylic cations.⁴⁴ After 5 h on stream, the absorption bands below 15000 cm^{-1} display the highest intensity for samples Z1 and Z2 pointing at the prevalence of naphthalene and its homologs; they are still not observable for AE3. These observations support the theoretical calculations (vide supra) and suggest that indeed LAS prevent further reactions involving aromatic moieties.

Finally, ^1H and ^1H - ^1H double-quantum (DQ) MAS NMR experiments at very high spinning speed were performed to validate the nature of trapped species in fully deactivated AE5, Z1 and Z3. The ^1H (MAS) NMR spectra of the analysed samples clearly show a difference, especially for the resonance at 7 ppm (Figures 6b). The signals at 7.8 and 7.1 ppm with a strong autocorrelation in DQ experiments (Figures 6c and 6d) are assigned to aromatic hydrogen. In line with UV-Vis, MAS NMR also demonstrates that aromatic species do not accumulate in Ca-containing zeolites and play a minor role in catalyst deactivation. The trapped species in Ca-containing AE5 are mainly of aliphatic nature, as confirmed by the resonances appearing in the range between 4.3 - 0 ppm.⁴⁵

Discussion

In pursuit of a long-living MTP catalyst, a great number of zeolite-based catalysts with ZSM-5 topology have been engineered.¹³ Herein, we identified the main descriptors governing selectivity and lifetime by rationalizing catalytic results of samples prepared by different synthetic protocols. Normalization of acidity by surface area helped elucidate catalytic behavior not only of microporous but also of mesoporous zeolites, which are generally more stable towards deactivation due to the combination of improved mass-transfer properties and ability to hold more coke. We have demonstrated that BAS isolation and Lewis acidity are the most important parameters in defining catalyst selectivity and lifetime.

First of all, we have confirmed that propylene selectivity is controlled by BAS density (C_{BAS}). Acid site isolation is the key to maximize propylene selectivity by preventing secondary reactions leading to the formation of aromatics. Thus, BAS is the first descriptor of catalytic performance, and its influence on product distribution is generally confirmed in the literature.¹ BAS isolation may be achieved using various approaches. Herein, we showed that, apart from decreasing of Al content, incorporation of alkaline-earth metals also results in generation of isolated BAS. Taking Ca species as an example, we showed that alkaline-earth metals tend to deprotonate BAS thus neutralizing inherent zeolite acidity, forming $[\text{Ca}(\mu\text{-OH})_2\text{Ca}]^{2+}$ species of Lewis acidic nature and isolated BAS, as demonstrated by ^1H - ^1H DQ and ^1H - ^1H RFDR MAS NMR. The generation of a new type of LAS turned out to be critical to obtain long-living

catalysts. Catalyst lifetime may be optimized by tuning the LAS/BAS ratio according to a typical volcano plot. We found that $[\text{Ca}(\mu\text{-OH})_2\text{Ca}]^{2+}$ LAS species have the tendency to suppress aromatics growth by methylation and destabilize crucial carbenium ions for the aromatic cycle, thereby blocking this reaction pathway. Hand in glove, UV-Vis DRS showed that 'LAS-containing' catalysts do not form polyaromatic species - notorious for catalyst deactivation - in contrast to 'LAS-free' catalysts. For the latter, the formation and evolution of aromatic species was witnessed during the first minutes of MTO independently on the amount of BAS. Finally, the destabilizing effect of LAS presence on aromatic cycle was confirmed by ^1H MAS NMR performed on fully deactivated catalysts. The trapped hydrocarbons in case of Ca-containing samples were mainly aliphatic of nature, while non-modified catalyst materials had a large amount of aromatic species.

With this information in hand, we can now formulate clear design rules to achieve ideal MTO catalysts maximizing propylene selectivity and lifetime. The presented case shows that a subtle interplay between various functions in the catalyst – in this case incorporation of LAS and BAS sites – may be used to obtain an optimally performing catalyst. Given the fact that zeolite catalysis often encounters similar reaction intermediates, we expect that the trends here discovered will be of high relevance also for many other zeolite catalyzed processes, such as catalytic cracking or isomerization. We conceptually showed the potential for tuning active sites in zeolite acid-catalysed reactions to a greater degree of complexity.

Methods

Synthesis of the Z-series catalysts. **Z1** is calcined at 550 °C commercially available ZSM-5 zeolite (CBV 8014, Zeolyst International). **Z2** and **Z3** were hydrothermally synthesized following the procedure described by Fan *et al.*⁴⁶ **Z4** was synthesized according to protocol of Na *et al.*⁴⁷ The as-synthesized **Z2**, **Z3** and **Z4** were calcined in air at 550 °C to remove the template, and ion-exchanged with NH_4NO_3 (1 M, 80 °C, 2 h) followed by calcination in air at 500 °C for 5 h.

Synthesis of the M-series catalysts. **M1** was obtained from **Z1** by desilication and acid leaching. Desilication was carried out in 1 M NaOH at 70°C for 1 h. **M2** and **M3** were obtained by treatment of **Z1** in 0.1 and 0.2 M NaOH at 65°C for 30 min. In the preparation of **M3**, the treatment solution also contained 0.2 M tetrapropylammonium bromide. Both samples were converted into protonic form by ion exchange in NH_4NO_3 solution (0.1 M, 25 °C, 8 h) and calcined at 550 °C for 5 h. **M4** was obtained from microporous **Z1** by *in-situ* dealumination in two consecutive MTO runs.

Synthesis of the AE-series catalysts. **AE1** was prepared by solid-state ion-exchange with $\text{Ca}(\text{CH}_3\text{COO})_2$. **AE2** was prepared by triple ion-exchange with 1 M $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ at 80 °C. **AE3**, **AE4**, **AE5** were prepared by incipient wetness impregnation (IWI) with an aqueous solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.4 M, 4.0 M and 6.0 M, respectively). **AE6** and **AE7** were prepared by IWI with 2.4 M $\text{Sr}(\text{NO}_3)_2$ and 2.4 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. After the modification, all AE samples were calcined at 550°C. Detailed information is further provided in Supplementary Experimental Section

Characterization. N_2 adsorption at -196°C was carried out using a Tristar II 3020 analyzer (Micromeritics). Microscopy images were recorded using a JEOL JSM-6010LA with a standard beam potential of 10 kV and an Everhart-Thornley detector. The XRD patterns of the powders were recorded with a Bruker D8 Advance X-ray diffractometer equipped with a LynxEye position-sensitive detector and monochromatic $\text{CoK}\alpha$ ($\lambda = 1.788970 \text{ \AA}$).

Transmission FT-IR spectroscopy using pyridine as a probe molecule was performed using a Nicolet 6700 spectrometer with a MCT/B detector. For the wafer preparation, 50 mg of catalyst was used without any dilution. The amount of Brønsted (BAS) and Lewis (LAS) acid sites was derived from the bands at 1545 and 1456 cm^{-1} using extinction coefficients of 1.67 and 2.22, respectively.¹⁸ Assuming that one molecule of pyridine is adsorbed on one acid site, the following expressions were used to calculate C_{BAS} and C_{LAS} . ^1H MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance) measurements were performed on a 11.7 Tesla Bruker DMX500 NMR spectrometer operating at a ^1H Larmor frequency of 500 MHz. A Bruker triple resonance 4 mm MAS probe head with a sample rotation rate of 10 kHz was used. ^1H NMR spectra were recorded with a 90° pulse of 5 μs duration and 3 s interscan delay. Double Quantum (DQ) experiments were performed using the back-to-back (BABA) recoupling sequence for excitation and reconversion of the DQ coherences with a 100 μs duration. The 2D RFDR (Radio Frequency-Driven Recoupling) experiments were implemented *via* the application of rotor-synchronised 180-degree pulses (one inversion pulse per rotor period) for homonuclear dipolar recoupling. A total mixing time duration of 1.6 ms was used. Deactivated zeolite materials were analysed by one-dimensional ^1H MAS SS NMR and ^1H - ^1H Multiple-Quantum Spectroscopy. One-dimensional ^1H MAS SS NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 600 MHz resonance frequencies for ^1H . The sample spinning frequency was 30 KHz for ^1H . Two-dimensional double-quantum (DQ) experiments were recorded on a Bruker AVANCE III spectrometer operating at 600 MHz with a conventional double-resonance 2.5 mm CP/MAS probe. The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were collected on a Perkin–Elmer Lambda 900 spectrophotometer equipped with an integrating sphere (“Labsphere”) in the 200–800 nm range. The absorption intensity was expressed by the Schuster-Kubelka-Munk (SKM) equation. Quantification of A_{pairs} and determination of their location is reported by Dědecěk et. al.⁴⁸ Operando UV-Vis diffuse reflectance spectra were obtained using an AvaSpec 2048L spectrometer connected to a high temperature UV-Vis optical fiber probe. The measurements were performed in the wavenumber range 11 000 - 50 000 cm^{-1} .

Catalyst Testing. Catalytic experiments were carried out in a Microactivity Reference unit (PID Eng&Tech) at 500 °C and ambient pressure. The catalyst (pressed, crushed and sieved to particle sizes 250-420 μm) was mixed with SiC (6:1 wt.%) and placed in a fixed-bed with an internal diameter of 9 mm for standard experiments. An ISCO pump was used to feed methanol to the reactor system. A weight-hourly space velocity (*WHSV*) of 8 $\text{g}_{\text{MeOH}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$, a $\text{N}_2 : \text{MeOH} = 1:1$ molar feed composition and atmospheric pressure were utilized. Conversion, selectivities and yields were calculated on a molar carbon basis. The performance results are presented in graphs as a function of the methanol mass throughput per amount of catalyst used ($\text{g}_{\text{MeOH}} \text{g}_{\text{cat}}^{-1}$) and defined as the overall amount MeOH fed through the catalytic bed before the conversion of oxygenates drops below 80 %. Presented selectivities are integral values. In each case, the catalyst was operated in a fixed bed reactor until methanol conversion dropped below 50 %.

Static calculations. Periodic Density Functional Theory (DFT) calculations are performed using the Vienna Ab Initio Simulation Package (VASP 5.3) with the PBE functional and using Grimme D3 dispersion corrections.^{49, 50, 51, 52} During the calculations, the projector augmented wave (PAW) method is used. Furthermore, a plane-wave cutoff of 600 eV is used during the calculations and the self-consistent field (SCF) convergence criterion is set to 10^{-5} eV. The sampling of the Brillouin zone is restricted to the Γ -point. The static calculations are performed in a ZSM-5 unit cell consisting of 96 T atoms. More information on the introduction of Al substitutions and unit cell parameters can be found in the Supplementary Computational Section. For a comprehensive overview of the state-of-the-art in modeling zeolite catalysis refer to Ref. 38.

Dynamic calculations. The ab initio MD simulations are performed using the CP2K software package.^{53, 54} To account for the flexibility of the catalyst framework at realistic reaction conditions the NPT ensemble at 673 K and 773 K and 1 bar is used. During the ab initio MD simulations, the temperature is controlled by a chain of five Nosé-Hoover thermostats and the pressure by an MTK barostat. To represent the ZSM-5 zeolite, the same unit cell is used as during the static calculations, so extra information can be found in the Supporting Computational Section.

Data availability. Data supporting the findings of this study are available within this paper and its Supplementary Information, and are available from the corresponding author upon reasonable request.

Code availability. The applied DFT codes (VASP and CP2K) are commercially available. Analysis of static calculations was performed with the TAMkin toolkit, which is freely available from <https://molmod.ugent.be/software>. Molecular dynamics runs were analysed using the freely available VMD software (<http://www.ks.uiuc.edu/Research/vmd/>).

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Author Contributions

I.Y. and J.G. conceived, coordinated the research and designed the experiments in close collaboration with V.V.S. I.Y. synthesized and characterized most catalysts and performed all catalytic tests with support from M. R. and I. V. S. M. and J.P.R. provided several demetalated zeolite catalysts and J.S.M.E. and M.M. provided the ZSM-5 nano-sheets and performed the methylation reactions. S.B., K.D.W. and V.V.S. performed the DFT and ab initio MD calculations. B.M. and E.A.H. performed NMR characterization and J. Go. performed the *in-situ* UV-VIS analysis. All authors contributed to analysis and discussion on the data. The manuscript was primarily written by I.Y, K.D. W., V. V. S. and J.G. with input from all authors.

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Figure Captions.

Figure 1 | Schematic illustrations of the hydrocarbon pool concept for the methanol-to-olefins reaction and the synthesis of pre- and post-synthetically modified zeolites. (a) Representation of a ZSM-5 catalyst having Brønsted acid sites (*blue*) located at the intersection of straight and sinusoidal channels and Lewis acid sites appearing due to the incorporation of extraframework species (*green and red*). During MTO reaction, ZSM-5 channels are “inhabited” by olefins and aromatics, which act as “co-catalysts pool species”. (b) Series **Z** was prepared by varying Si/Al ratio and/or SDA during the ZSM-5 zeolite synthesis, series **M** was prepared by post-synthetic demetalation of microporous ZSM-5 zeolite, while series **AE** was prepared by post-synthetic incorporation of alkaline-earth metals into microporous ZSM-5 zeolite.

Figure 2 | Evaluation of Brønsted and Lewis acid sites interactions. ^1H - ^1H RFDR (a, c) and ^1H - ^1H DQ (b, d) MAS NMR spectra of AE3 modified with Ca (a, b) and Z3 with the same amount of BAS (c, d). Both samples are dehydrated at 200°C (1 °C min⁻¹).

Figure 3 | Catalytic behaviour of pre- and post-synthetically modified catalysts. (a) The modification with Ca (AE3) and Mg (AE7) leads to significant prolongation of catalyst lifetime (■), increases yield of propylene (★) and decreases yield of ethylene (▲). (b) Methanol throughput and catalyst lifetime over catalysts under study. Reaction conditions: $T = 500\text{ °C}$, $WHSV = 8\text{ g}_{\text{MeOH}}\text{ g}_{\text{catalyst}}^{-1}\text{ h}^{-1}$. (c, d, e) Descriptors of ZSM-5 acidity in MTO. Z (*black*) – pre-synthetically modified ZSM-5 with different Si/Al ratio; M (*green*) - post-synthetically demetalated ZSM-5; AE (*orange*) – zeolites modified by post-synthetic incorporation of alkaline-earth metals. Acidity-performance relationship clearly shows that the density of Brønsted acid (C_{BAS}) sites determines (c) propylene and (d) ethylene selectivity, while the ratio of Lewis and Brønsted acid sites ($C_{\text{BAS}}C_{\text{LAS}}^{-1}$) governs catalyst lifetime (e). Error bars represent standard deviation of the catalytic performance results performed at least two times for each sample. Dashed lines in (c) and (d) represent linear fit to the provided data, while dashed line in (e) is to guide the eye.

Figure 4 | Modified zeolites decrease the stability and growth rate of aromatic MTO intermediates. (a) Free energy profiles at 500 °C (kJ/mol) for propene and 1,2,3,5-tetramethylbenzene methylation by methanol catalysed by an isolated BAS (-), a BAS near a $[\text{Ca}(\mu\text{-OH})_2\text{Ca}]^{2+}$ moiety (-) and a LAS formed by the $[\text{Ca}(\mu\text{-OH})_2\text{Ca}]^{2+}$ site (-). (b) The dual cycle mechanism for the MTO process with indication of intermediates that are unaffected by the alkaline earth modification (*green*) and destabilized by the modification (*red*). (c) Calculated protonation enthalpies at 500 °C (kJ/mol) for the various MTO intermediates at an isolated BAS (◆) in the presence of a $[\text{Mg}(\mu\text{-OH})_2\text{Mg}]^{2+}$ (■) or a $[\text{Ca}(\mu\text{-OH})_2\text{Ca}]^{2+}$ (▲) moiety.

Figure 5 | DFT based enthalpy calculations at 500 °C reveal the most stable structure of binuclear Ca species in ZSM-5. (a) reference state, (b) $[\text{Ca}(\mu\text{-O})(\mu\text{-OH})\text{Ca}]^+$ compound in ZSM-5 (c) $[\text{Ca}(\mu\text{-O})(\mu\text{-OH})\text{Ca}]$ bound to the framework, (d) $[\text{Ca}(\mu\text{-OH})_2\text{Ca}]^{2+}$ in ZSM-5 (e) snapshot of $[\text{Ca}(\mu\text{-O})(\mu\text{-OH})\text{Ca}]$ bound to the framework (f) snapshot of $[\text{Ca}(\mu\text{-OH})_2\text{Ca}]^{2+}$ in ZSM-5.

Figure 6 | Visualisation of the trapped hydrocarbon species in Z- and AE-series. (a) operando UV-vis diffuse reflectance spectra collected during methanol conversion over Z1 and Z2 zeolites with different Si/Al ratio and Ca-modified AE3 at 500°C indicates that aromatic species do not accumulate in Ca-modified samples. For Z1 and Z2 zeolites, formation of polyaromatic species (naphthalene and homologues) is observed during the first seconds of MTO, indicating that catalyst deactivation starts at the beginning of the reaction. UV-vis diffuse reflectance spectra were taken every 20 s. (b) Analysis of the spent catalyst by ^1H NMR indicates further that aromatic species are the

minor components in completely deactivated Ca-modified catalysts, which is characterized by the predominant presence of aliphatic protons. (c) ^1H - ^1H DQ MAS NMR spectra of Z3 shows that aliphatic protons are correlating with aromatic protons, suggesting that trapped species are mainly represented by alkylated aromatics; (d) in AE5, aliphatic protons are mainly autocorrelated. Black lines indicate peaks in single quantum space, while red dashed lines show the (auto-)correlation in double quantum space.

Table 1.

Table 1 | Textural and acidic properties of the ZSM-5 zeolites under study.

Catalyst	Si/Al ^a	Cation ^b	V _{total} ^c	V _{micro} ^c	S _{BET} ^d	S _{meso} ^b	S _{micro} ^e	n _{BAS} ^f	n _{LAS} ^f
	(mol mol ⁻¹)	(%)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(m ² g ⁻¹)	(m ² g ⁻¹)	(m ² g ⁻¹)	(μmol g ⁻¹)	(μmol g ⁻¹)
Z1	39	-	0.26	0.15	448	85	363	232	35
Z2	260	-	0.22	0.15	425	85	340	50	12
Z3	1280	-	0.21	0.17	429	74	355	28	11
Z4	61	-	0.67	0.09	535	328	207	96	74
M1	65	-	1.20	0.12	575	314	261	149	77
M2	36	-	0.35	0.14	456	142	314	188	53
M3	31	-	0.43	0.14	584	276	308	154	108
M4	41	-	0.28	0.11	347	127	220	49	50
AE1	42	Ca (6.1)	0.21	0.11	323	56	267	128	1
AE2	45	Ca (0.2)	0.27	0.15	429	85	344	138	108
AE3	47	Ca (2.4)	0.24	0.13	392	77	315	40	228
AE4	46	Ca (3.8)	0.22	0.13	387	74	313	27	240
AE5	46	Ca (4.6)	0.23	0.12	385	75	310	29	240
AE6	45	Sr (5.2)	0.20	0.13	379	106	273	85	108
AE7	44	Mg(1.4)	0.22	0.14	417	95	322	76	217

^a Molar ratio determined by ICP-OES.

^b **AE1** was prepared by solid-state ion-exchange with Ca(CH₃COO)₂. **AE2** was prepared by ion-exchange with 1 M Ca(NO₃)₂·4H₂O. **AE3**, **AE4**, **AE5** were prepared by incipient wetness impregnation with an aqueous solution of Ca(NO₃)₂·4H₂O of different concentrations. **AE6** and **AE7** were prepared by incipient wetness impregnation with Sr(NO₃)₂ and Mg(NO₃)₂·6H₂O respectively. Further details are provided in the Methods section.

^c From N₂ adsorption isotherm using t-plot method.

^d From N₂ adsorption isotherm using BET method.

^e From N₂ adsorption isotherm. S_{micro}=S_{BET}-S_{meso}.

^f Concentration of Brønsted (BAS) and Lewis (LAS) acid sites derived from FT-IR spectroscopy with pyridine as a probe molecule.