

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

Irina Yarulina^{1,2}, Kristof De Wispelaere³, Simon Bailleul³, Joris Goetze⁴, Mike Radersma¹, Edy Abou-Hamad², Ina Vollmer¹, Maarten Goesten⁵, Brahim Mezari⁵, Emiel J.M. Hensen⁵, Juan S. Martínez-Espín⁶, Magnus Morten⁶, Sharon Mitchell⁷, Javier Perez-Ramirez⁷, Unni Olsbye⁶, Bert M. Weckhuysen⁴, Veronique Van Speybroeck³, Freek Kapteijn¹ and Jorge Gascon^{1,2}

¹ Catalysis Engineering, Chemical Engineering Department, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands

² King Abdullah University of Science and Technology, KAUST Catalysis Center, Advanced Catalytic Materials. Thuwal 23955-6900, Saudi Arabia

³ Center for Molecular Modeling, Ghent University, Technologiepark 903, B-9052 Zwijnaarde, Belgium

⁴ Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

⁵ Schuit Institute of Catalysis, Laboratory of Inorganic Materials Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

⁶ Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway

⁷ Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland.

*Correspondence to: jorge.gascon@kaust.edu.sa

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” (Scheme 1). 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 1). 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 Figures 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 Figures 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 Figure 5A) 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 Figure 3C). 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 Z1 sample and the AE series is the appearance of a significantly higher concentration of Lewis acid sites (Supplementary Figure 5C).

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 in 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 Figure 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 Figure 7).²⁴ According to Mores *et al.*,²⁴ the lower the acidity, 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 Figure 7). Another striking difference is the much lower fraction of paraffins, ethylene and aromatics in comparison with Z1 (Supplementary Figure 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 4). 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 Figure 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 Figure 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 Figure 11A). 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 Figures 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 Figure 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 Figure 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. The top panel of Figure 4 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 Figure 26 and 27. These two reactions are crucial for the alkene and aromatics catalytic cycles.^{36, 37} 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 Figure S21). In line with this observation, higher selectivity to secondary products was observed over Z3 than over AE5 (Supplementary Figure S20). 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 ± 0.3 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.³⁸ 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.³⁹ 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 4, bottom panel). 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 (Figure 4). These conclusions are fully in line with the free energy profiles for methylation of propene and tetraMB shown in Figure 4. We also investigated the lifetimes of neutral species at realistic working condition of 500 °C (Supplementary Figure 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 EFALs 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,^{40, 41} 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 Figure 16A). 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 Figure 16A-C), corresponding to methyl-substituted benzenium cations.^{40, 41} With time-on-stream, the appearance of the absorption band below 15000 cm^{-1} (Supplementary Figure 16B) 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 Figure 16C and 16D). 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.⁴² 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.⁴³

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. Catalysts denoted as Z (Z1, Z2, Z3) are microporous ZSM-5 zeolite. Z1 was obtained by calcination at 550 °C of commercially available ZSM-5 zeolite (CBV 8014, Zeolyst International) to obtain its protonic form. **Z2** and **Z3** were hydrothermally synthesized following the procedure described by Fan *et al.*⁴⁴ In a typical synthesis, NaAlO_2 (0.025 and 0.010 g for Z2 and Z3 respectively), 16.8 mL 1M tetrapropylammonium hydroxide, and 8.4 mL tetraethyl orthosilicate were mixed in 15.6 mL water, aged at 100 °C for 2 h and subsequently left for stirring for 16 h. The synthesis solutions were subjected to hydrothermal synthesis at 180 °C for 24 h. The as-synthesized material was calcined at 550 °C for 10 h in a static oven to remove the template. The calcined material was converted to the protonic form by triple ion-exchange with NH_4NO_3 (1 M, 80 °C, 2 h, 100 mL per gram of zeolite) followed by calcination at 550 °C. **Z4** is zeolite with nanosheet morphology and was synthesized reproducing the protocol from Na *et al.*⁴⁵ The synthesis was carried out by adding dropwise a solution of 2 g sodium aluminate (53 wt% Al_2O_3 , 43 wt% Na_2O) in 42.7 g water to a previously homogenized 64.0 g aqueous solution containing $\text{C}_{22-6-6}\text{Br}_{12}$ (14.5 wt% in water) in 38.0 g of water glass (27 wt% SiO_2 , 8 wt% Na_2O). The gel was then aged in an autoclave at 60 °C for 6 h before hydrothermal synthesis at 150 °C for 7 days. The as-synthesized sample was calcined in air at 550 °C to remove the template, and ion-exchange with NH_4NO_3 (1 M, 80 °C, 2 h) followed by calcination in air at 500 °C for 5 h yielded **Z4**.

Synthesis of the M-series catalysts. **M1** is a mesoporous ZSM-5 zeolite obtained from **Z1** by desilication and acid leaching. Desilication of **Z1** was carried out in a 1 M NaOH aqueous solution in a capped vessel ($\text{volume}_{\text{base solution}}/\text{mass}_{\text{Z1}} = 8.0 \text{ mL g}^{-1}$) and under stirring at 70 °C for 1 h in an oil bath. This treatment was followed by immediate quenching in a water-ice bath and centrifugation to separate the zeolite powder from the solution. The residue of the desilicating agent was removed from the zeolite crystallites by subsequent redispersion in deionized water and centrifugation cycles until neutral pH was reached. Desilicated ZSM-5 was dried overnight at 120 °C for 12 h and calcined at 550 °C for 5 h ($5 \text{ }^\circ\text{C min}^{-1}$). The yield of the desilication procedure was 25% (average of four experiments starting from ca. 20 g H-ZSM-5). **M2** and **M3** were also obtained by alkaline treatment performed in stirred 0.1 and 0.2 M NaOH aqueous solutions ($30 \text{ cm}^3 \text{ g}_{\text{zeolite}}^{-1}$) at 65 °C in an EasyMax™ 102 (Mettler Toledo) reactor. After 30 min, the slurries were quenched in an ice-water bath and the solids collected by filtration, washed, and dried for 10 h at 25 °C. In the preparation of M3, the treatment solution also contained 0.2 M tetrapropylammonium bromide. Both samples were converted into protonic form by three consecutive ion exchanges in an aqueous NH_4NO_3 solution (0.1 M, 25 °C, 8 h, $100 \text{ cm}^3 \text{ g}_{\text{zeolite}}^{-1}$) and calcined at 550 °C ($5 \text{ }^\circ\text{C min}^{-1}$) for 5 h prior to characterization and catalytic evaluation. The treatment yields were 85 and 78%, respectively. **M4** was obtained from microporous **Z1** by *in-situ* dealumination in two consecutive runs in MTO reaction ($T = 500 \text{ }^\circ\text{C}$, $WHSV = 8 \text{ h}^{-1}$) with regeneration step in between.

Synthesis of the AE-series catalysts. Catalyst materials denoted as AE were obtained by modification of **Z1** with alkaline-earth metals. **AE1** was prepared by solid-state ion-exchange with $\text{Ca}(\text{CH}_3\text{COO})_2$. The required amount of calcium acetate (to achieve 6 wt.% of Ca) was ground with **Z1** for 30 min followed by calcination at 550 °C. **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 for 2 h followed by calcination at 550 °C. **AE3**, **AE4**, **AE5** were prepared by incipient wetness impregnation 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). The samples were subsequently dried in a desiccator followed by drying for 12 h at 80 °C and calcination at 550 °C. **AE6** and **AE7** were prepared by incipient wetness impregnation with 2.4 M $\text{Sr}(\text{NO}_3)_2$ and 2.4 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ respectively and post-treated following a similar procedure as that for sample **AE3**.

Characterization. N_2 adsorption at -196 °C was carried out using a Tristar II 3020 analyzer (Micromeritics). Prior to the experiment, samples were outgassed under vacuum at 350 °C for 16 h. Microscopy images were recorded using a JEOL JSM-6010LA with a standard beam potential of 10 kV and an Everhart-Thornley detector. X-ray microanalysis (SEM/EDX) confirmed the elemental composition in the sample by scanning microscopy (SEM) coupled with a dispersive X-ray microanalysis system (EDX) with a Silicon-drift detector. The XRD patterns of the powders were recorded in Bragg–Brentano geometry with a Bruker D8 Advance X-ray diffractometer equipped with a LynxEye position-sensitive detector. Measurements were performed at RT by using monochromatic $\text{CoK}\alpha$ ($\lambda = 1.788970 \text{ \AA}$) radiation between $2\theta = 5^\circ$ and 50° . Transmission FT-IR spectroscopy using pyridine as a probe molecule was performed using a Nicolet 6700 spectrometer equipped with a MCT/B detector. For the wafer preparation, 50 mg of catalyst was used without any dilution. The specimen was activated in vacuum at 400 °C for 16 h to remove adsorbed species. After activation, wafers were saturated with pyridine vapor and further evacuated at 160 °C for 2 h. Spectra were recorded in 1000-4000 cm^{-1} range at 4 cm^{-1} resolution and co-addition of 128 scans. The amount of Brønsted (BAS) and Lewis (LAS) acid sites was derived from the bands at 1545 and 1456 cm^{-1} as described elsewhere 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} .

$$C_{\text{BAS}} = 1.88 \cdot IA(B) \cdot R^2 / W \quad (1)$$

$$C_{\text{LAS}} = 1.42 \cdot IA(L) \cdot R^2 / W \quad (2)$$

where IA (BAS, LAS) is the integrated absorbance of the BAS or LAS band (cm^{-1}), R – radius of catalyst disk (cm), while W – mass of catalyst sample (mg). ^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. The dehydration of the samples was performed under high vacuum (10^{-5} mbar) at two temperatures. Moderated dehydration was done at 200 °C for 1 h and the complete dehydration was done at 450 °C for 17 h. The dehydrated zeolites were placed into the 4 mm MAS NMR zirconia rotor under inert conditions and transferred to the NMR probe head. ^1H chemical shift was calibrated using tetramethylsilane (TMS). 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 . Experiments at 600 MHz utilized a 2.5 mm double-resonance probe. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. NMR chemical shifts are reported with respect to the external references TMS. 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, according to the following general scheme: excitation of DQ coherences, t_1 evolution, z filter, and detection. The spectra were recorded in a rotor synchronized fashion in t_1 by setting the t_1 increment equal to one rotor period. One cycle of the standard back-to-back (BABA) recoupling sequences was used for the excitation and reconversion period. Quadrature detection in w_1 was achieved using the States-TPPI method. An MAS frequency of 29762 kHz

was used. The 90° proton pulse length was 2.5 μs, while a recycle delay of 5 s was used. A total of 96 t_1 increments with 32 scans per each increment were recorded. The DQ frequency in the w_1 dimension corresponds to the sum of two single-quantum (SQ) frequencies of the two coupled protons and correlates in the w_2 dimension with the two corresponding proton resonances. 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. BaSO₄ was used as a white standard for CoHZ and the bare zeolite for MoHZ. Before measurement, the samples were degassed at 400 °C under N₂ flow for 12 hours and then transferred to the sample holders in the glovebox. The absorption intensity was expressed by the Schuster-Kubelka-Munk (SKM) equation $F(R_\infty) = (1 - R_\infty)^2 / 2R_\infty$. Quantification of $A_{l\text{pairs}}$ and determination of their location is reported by Dědeček et. al.⁴⁶ 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 g_{MeOH} g_{cat}⁻¹ h⁻¹, a N₂ : MeOH = 1:1 molar feed composition and atmospheric pressure were utilized. The product mixture was analyzed online with an Interscience CompactGC equipped with a 15 m capillary RTX-1 (1% diphenyl-, 99% dimethylpolysiloxane) column and a flame ionization detector. Conversion, selectivities and yields were calculated on a molar carbon basis. Thus, conversion was defined as the carbon-based fraction of light oxygenates (methanol and dimethyl ether) consumed during the reaction:

$$X = \frac{n_{C,MeOH_{in}} - n_{C,MeOH_{out}} - 2 \cdot n_{C,DME_{out}}}{n_{C,MeOH_{in}}} \cdot 100\% \quad (3)$$

The selectivity towards ethylene (4) and propylene (5) was calculated based on the carbon number as follows:

$$S_{ethylene} = \frac{2 \cdot n_{C_2H_4}}{n_{C,MeOH_{in}} - n_{C,oxy_{out}}} \cdot 100\% \quad (4)$$

$$S_{propylene} = \frac{3 \cdot n_{C_3H_6}}{n_{C,MeOH_{in}} - n_{C,oxy_{out}}} \cdot 100\% \quad (5)$$

and the yield of a component i was defined from its selectivity and methanol conversion:

$$Y_i = \frac{S_i \cdot X}{100} \% \quad (6)$$

The performance results are presented in graphs as a function of the methanol mass throughput per amount of catalyst used (g_{MeOH} g_{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. 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 Brioullin 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 Information. Transition states were initially optimized with the improved dimer method and then refined with a quasi-Newton algorithm. Geometries were slightly displaced along the normal mode corresponding to

the motion that leads the system over the barrier to generate starting geometries for the optimization of reactant and product states. For these calculations a conjugate gradient algorithm was applied. For the normal mode analysis, a partial Hessian vibrational analysis (PHVA) is performed using VASP and TAMkin.⁴⁷ This means that not the entire system, but only the guest molecule, the extraframework species and certain framework atoms are taken into account during the NMA. More information on the performed PHVA can be found in the Supplementary Information. For the analyzed hydrocarbon pool species, the stability of its protonated form in H-ZSM-5, Mg-ZSM-5, Ca-ZSM-5 and EFAI containing ZSM-5 zeolites was studied statically by defining the protonation enthalpy as:

$$H_{\text{prot}} = H(\text{H-X}^+_{\text{ads}}) - H(\text{X}_{\text{ads}})$$

The resulting protonation energies, are depicted in Figure 4 (a more detailed overview can be found in Supplementary Table 9).

Dynamic calculations. The ab initio MD simulations are performed using the CP2K software package.^{48, 49} 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 be consistent with the static simulations, the PBE functional is also used for the MD simulations. Furthermore, the combined Gaussian and Plane Wave (GPW) basis sets approach is used. The DZVP-GTH basis set and pseudopotentials is used for all atoms except Ca, for which a MOLOPT basis set is used, and Grimme D3 dispersion corrections⁵⁰ were added. The time step for integration of the equations of motion is set to 0.5 fs. 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 information.

Acknowledgements

This research received funding from the Netherlands Organization for Scientific Research (NWO) in the framework of the TASC Technology Area “Syngas, a Switch to Flexible New Feedstock for the Chemical Industry (TA-Syngas).” SB, KDW and VVS acknowledge the Fund for Scientific Research - Flanders (FWO), the Belgian American Educational Foundation, the Research Board of Ghent University (BOF), BELSPO in the frame of IAP/7/05 and funding from the European Union’s Horizon 2020 research and innovation program (consolidator ERC grant agreement No 647755 – DYNPOR (2015-2020)). The computational resources and services used were provided by Ghent University (Stevin Supercomputer Infrastructure) and the VSC (Flemish Supercomputer Center), funded by the Research Foundation - Flanders (FWO).

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.

References

1. Bleken, F.L., *et al.* Conversion of methanol into light olefins over ZSM-5 zeolite: Strategy to enhance propene selectivity. *Appl. Catal., A* **447**, 178-185 (2012).
2. Keil, F.J. Methanol-to-hydrocarbons: process technology. *Microporous Mesoporous Mater.* **29**, 49-66 (1999).
3. Sun, X.Y., *et al.* On reaction pathways in the conversion of methanol to hydrocarbons on HZSM-5. *J. Catal.* **317**, 185-197 (2014).
4. Teketel, S., *et al.* Morphology-induced shape selectivity in zeolite catalysis. *J. Catal.* **327**, 22-32 (2015).
5. Olsbye, U., *et al.* Conversion of methanol to hydrocarbons: how zeolite cavity and pore size controls product selectivity. *Angew. Chem. Int. Ed.* **51**, 5810-5831 (2012).
6. Milina, M., Mitchell, S., Crivelli, P., Cooke, D. & Perez-Ramirez, J. Mesopore quality determines the lifetime of hierarchically structured zeolite catalysts. *Nat. Commun.* **5**, 1591-1594 (2014).
7. Liang, T., *et al.* Conversion of methanol to olefins over H-ZSM-5 zeolite: reaction pathway is related to the framework aluminum siting. *ACS Catal.* **6**, 7311-7325 (2016).
8. Yarulina, I., *et al.* Methanol-to-olefins process over zeolite catalysts with DDR topology: effect of composition and structural defects on catalytic performance. *Catal. Sci. Technol.* **6**, 2663-2678 (2016).
9. Deimund, M.A., *et al.* Effect of heteroatom concentration in SSZ-13 on the methanol-to-olefins reaction. *ACS Catal.* **6**, 542-550 (2016).
10. Hemelsoet, K., Van der Mynsbrugge, J., De Wispelaere, K., Waroquier, M. & Van Speybroeck, V. Unraveling the reaction mechanisms governing methanol-to-olefins catalysis by theory and experiment. *ChemPhysChem* **14**, 1526-1545 (2013).
11. Svelle, S., *et al.* Conversion of methanol into hydrocarbons over zeolite H-ZSM-5: ethene formation is mechanistically separated from the formation of higher alkenes. *J. Am. Chem. Soc.* **128**, 14770-14771 (2006).
12. Haw, J.F., Song, W.G., Marcus, D.M. & Nicholas, J.B. The mechanism of methanol to hydrocarbon catalysis. *Acc. Chem. Res.* **36**, 317-326 (2003).
13. Stöcker, M. Methanol-to-hydrocarbons: catalytic materials and their behavior. *Microporous Mesoporous Mater.* **29**, 3-48 (1999).
14. Janardhan, H.L., Shanbhag, G.V. & Halgeri, A.B. Shape-selective catalysis by phosphate modified ZSM-5: Generation of new acid sites with pore narrowing. *Appl. Catal., A* **471**, 12-18 (2014).
15. Llewellyn, P.L., *et al.* Adsorption by MFI-type zeolites examined by isothermal microcalorimetry and neutron-diffraction. 2. Nitrogen and Carbon-Monoxide. *Langmuir* **9**, 1852-1856 (1993).
16. Choi, M., *et al.* Stable single-unit-cell nanosheets of zeolite MFI as active and long-lived catalysts. *Nature* **461**, 246-249 (2009).
17. Cychosz, K.A., Guillet-Nicolas, R., Garcia-Martinez, J. & Thommes, M. Recent advances in the textural characterization of hierarchically structured nanoporous materials. *Chem. Soc. Rev.* **46**, 389-414 (2017).
18. Emeis, C.A. Determination of integrated molar extinction coefficients for infrared-absorption bands of pyridine adsorbed on solid acid catalysts. *J. Catal.* **141**, 347-354 (1993).
19. Brus, J., *et al.* Structure of framework aluminum Lewis sites and perturbed aluminum atoms in zeolites as determined by Al-27{H-1} REDOR (3Q) MAS NMR spectroscopy and DFT/Molecular mechanics. *Angew. Chem. Int. Ed.* **54**, 541-545 (2015).

20. Mei, C.S., *et al.* Selective production of propylene from methanol: Mesoporosity development in high silica HZSM-5. *J. Catal.* **258**, 243-249 (2008).
21. Milina, M., Mitchell, S., Michels, N.L., Kevlin, J. & Perez-Ramirez, J. Interdependence between porosity, acidity, and catalytic performance in hierarchical ZSM-5 zeolites prepared by post-synthetic modification. *J. Catal.* **308**, 398-407 (2013).
22. Volkringer, C., *et al.* The Kagome topology of the Gallium and Indium Metal-Organic Framework types with a MIL-68 structure: synthesis, XRD, solid-state NMR characterizations, and hydrogen adsorption. *Inorg. Chem.* **47**, 11892-11901 (2008).
23. Ruspic, C., *et al.* A well-defined hydrocarbon-soluble calcium hydroxide: Synthesis, structure, and reactivity. *J. Am. Chem. Soc.* **128**, 15000-15004 (2006).
24. Mores, D., Kornatowski, J., Olsbye, U. & Weckhuysen, B.M. Coke formation during the methanol-to-olefin conversion: in situ microspectroscopy on individual H-ZSM-5 crystals with different Bronsted acidity. *Chemistry-a European Journal* **17**, 2874-2884 (2011).
25. Martínez-Espín, J.S., *et al.* Hydrogen transfer versus methylation: on the genesis of aromatics formation in the methanol-to-hydrocarbons reaction over H-ZSM-5. *ACS Catal.* **7**, 5773-5780 (2017).
26. Müller, S., *et al.* Hydrogen transfer pathways during zeolite catalyzed methanol conversion to hydrocarbons. *J. Am. Chem. Soc.* **138**, 15994-16003 (2016).
27. Guisnet, M., Costa, L. & Ribeiro, F.R. Prevention of zeolite deactivation by coking. *J. Mol. Catal. A: Chem.* **305**, 69-83 (2009).
28. Mitchell, S., *et al.* Structural analysis of hierarchically organized zeolites. *Nat. Commun.* **6**, 8633-8647 (2015).
29. Schmidt, F., *et al.* Coke location in microporous and hierarchical ZSM-5 and the impact on the MTH reaction. *J. Catal.* **307**, 238-245 (2013).
30. Bleken, F.L., *et al.* Catalyst deactivation by coke formation in microporous and desilicated zeolite H-ZSM-5 during the conversion of methanol to hydrocarbons. *J. Catal.* **307**, 62-73 (2013).
31. Kortunov, P., *et al.* The role of mesopores in intracrystalline transport in USY zeolite: PFG NMR diffusion study on various length scales. *J. Am. Chem. Soc.* **127**, 13055-13059 (2005).
32. Karger, J. & Valiullin, R. Mass transfer in mesoporous materials: the benefit of microscopic diffusion measurement. *Chem. Soc. Rev.* **42**, 4172-4197 (2013).
33. Karger, J. Transport Phenomena in Nanoporous Materials. *ChemPhysChem* **16**, 24-51 (2015).
34. Yarulina, I., *et al.* Suppression of the Aromatic Cycle in Methanol-to-Olefins Reaction over ZSM-5 by Post-Synthetic Modification Using Calcium. *ChemCatChem* **8**, 3057-3063 (2016).
35. Pidko, E.A., Hensen, E.J.M. & van Santen, R.A. Self-organization of extraframework cations in zeolites. *Proc. R. Soc. A* **468**, 2070-2086 (2012).
36. De Wispelaere, K., Bailleul, S. & Van Speybroeck, V. Towards molecular control of elementary reactions in zeolite catalysis by advanced molecular simulations mimicking operating conditions. *Catal. Sci. Technol.* **6**, 2686-2705 (2016).
37. Van Speybroeck, V., *et al.* First principle kinetic studies of zeolite-catalyzed methylation reactions. *J. Am. Chem. Soc.* **133**, 888-899 (2011).
38. Nicholas, J.B. & Haw, J.F. The prediction of persistent carbenium ions in zeolites. *J. Am. Chem. Soc.* **120**, 11804-11805 (1998).

39. Fang, H., *et al.* Theoretical investigation of the effects of the zeolite framework on the stability of carbenium ions. *The Journal of Physical Chemistry C* **115**, 7429-7439 (2011).
40. Goetze, J., *et al.* Insights into the Activity and Deactivation of the Methanol-to-Olefins Process over Different Small-Pore Zeolites As Studied with Operando UV-vis Spectroscopy. *ACS Catal.* **7**, 4033-4046 (2017).
41. Hemelsoet, K., *et al.* Identification of intermediates in zeolite-catalyzed reactions by in situ UV/Vis microspectroscopy and a complementary set of molecular simulations. *Chem. Eur. J.* **19**, 16595-16606 (2013).
42. Wulfers, M.J. & Jentoft, F.C. The role of cyclopentadienium ions in methanol-to-hydrocarbons chemistry. *ACS Catal.* **4**, 3521-3532 (2014).
43. Behera, B., Ray, S.S. & Singh, I.D. NMR Studies of FCC Feeds, Catalysts and Coke. *Fluid Catalytic Cracking VII Materials: Methods and Process Innovations* **166**, 163-200 (2007).
44. Hong, Y., *et al.* Platinum nanoparticles supported on Ca(Mg)-zeolites for efficient room-temperature alcohol oxidation under aqueous conditions. *Chem. Commun.* **50**, 9679-9682 (2014).
45. Na, K., *et al.* Pillared MFI Zeolite Nanosheets of a Single-Unit-Cell Thickness. *J. Am. Chem. Soc.* **132**, 4169-4177 (2010).
46. Dedecek, J., Balgová, V., Pashkova, V., Klein, P. & Wichterlová, B. Synthesis of ZSM-5 zeolites with defined distribution of Al atoms in the framework and multinuclear MAS NMR analysis of the control of Al distribution. *Chem. Mater.* **24**, 3231-3239 (2012).
47. Ghysels, A., Verstraelen, T., Hemelsoet, K., Waroquier, M. & Van Speybroeck, V. TAMkin: A Versatile Package for Vibrational Analysis and Chemical Kinetics. *J. Chem. Inf. Model.* **50**, 1736-1750 (2010).
48. Hutter, J., Iannuzzi, M., Schiffmann, F. & VandeVondele, J. CP2K: atomistic simulations of condensed matter systems. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **4**, 15-25 (2014).
49. VandeVondele, J., *et al.* Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Comput. Phys. Commun.* **167**, 103-128 (2005).
50. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, (2010).