Systematic Catalyst Screening of Zeolites with Various Frameworks and Si/Al Ratios to Identify Optimum Acid Strength in OME Synthesis

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Oxymethylene dimethyl ethers (OME, oligomers with the chain length x) present a promising emission reducing diesel additive, which can potentially be produced based on renewable resources. In this work, the OME synthesis catalysed by zeolites was investigated starting from paraformaldehyde and methanol. The catalytic performance of zeolites with different framework types (BEA, FAU, MFI, MOR) and various Si/Al ratios was comparatively studied. The zeolites were characterised by means of NH\textsubscript{3}-TPD, ICP-OES, XRD and N\textsubscript{2} physisorption. A relationship between catalytic activity and Si/Al ratio was established demonstrating the highest turnover frequency for zeolites with high Si/Al ratios. HZSM-5 114 with a TOF of 3375 mol\textsubscript{OME}/mol\textsubscript{AcidSite} \times \text{s}^{-1} \text{h}^{-1} was determined as the best-performing zeolite which indicates that the OME\textsubscript{x} synthesis requires a moderately strong acid strength.

Introduction

One of the defining challenges of the 21\textsuperscript{st} century is the development of alternatives to fossil fuels. An increasing population and closely linked economy rely heavily on mobility and transport. Especially for combustion engines the reduction of harmful emissions such as particulate matter (soot) and nitrogen oxide (NO\textsubscript{x}) gases is of paramount importance. Here, oxymethylene dimethyl ethers (OME\textsubscript{x}) as diesel additives present a promising solution based on renewable resources. OME\textsubscript{x} oligomers with the structure H\textsubscript{2}C=O-(CH\textsubscript{2}O)\textsubscript{x}-CH\textsubscript{3} and the chain length of x=3–5 exhibit diesel-like properties with regards to e.g. cetane number, boiling point and viscosity.\textsuperscript{[2]} Due to their high oxygen content and lack of C–C bonds OME\textsubscript{x} produce significantly less soot particles upon combustion avoiding the typical soot-NO\textsubscript{x} trade-off. Already a blend ratio of 35\% OME\textsubscript{x} independently of the chain length, reduces soot emissions by 90\%.\textsuperscript{[3]} OME\textsubscript{x} can be produced from methanol (MeOH) and a formaldehyde (FA) source such as aqueous formaldehyde solution, the oligomer paraformaldehyde (pFA) or trioxane (Tri), a cyclic trimer of formaldehyde (Scheme 1, route A).

The OME\textsubscript{x} synthesis proceeds in an acid-catalysed equilibrium reaction obtaining OME\textsubscript{x} in a chain length distribution which can be described by the Schulz-Flory distribution.\textsuperscript{[5]} The side product methyl formate is formed in the reaction of two molecules of formaldehyde. Water is produced as co-product if methanol is used as endcapping agent in the reaction. Alternatively, the reaction can be conducted via an anhydrous approach proceeding from OME\textsubscript{x} and a formaldehyde source (gaseous FA or Tri).

For this research the OME\textsubscript{x} synthesis was based on pFA and methanol since these substrates are less energy- and cost-intensive than OME\textsubscript{x} and particularly trioxane.\textsuperscript{[5]} Based on preliminary experiments, the usage of ion-exchange resins as solid acid catalysts in the OME\textsubscript{x} synthesis was discarded since the leaching of SO\textsubscript{3}H groups was detected leading to significant sulfur concentrations in the reaction mixture. This concurs with literature, as acidic ion-exchange resins have reportedly shown leaching of sulfonic groups reducing their suitability for the production of fuel additives.\textsuperscript{[3–4]} Hence, zeolites were selected as solid acid catalysts due to their reported catalytic activity in the

Scheme 1. Synthesis routes for the production of OME\textsubscript{x} based on the platform molecule methanol; route A: starting from methanol and a formaldehyde source (FA or Tri) with water as co-product, route B: anhydrous approach from OME\textsubscript{x} and a formaldehyde source (gaseous FA or Tri).
OME$_x$ synthesis$^{[3b]}$ as well as the tunability of their acid properties.$^{[2]}$

Numerous hypotheses have been proposed in literature with regards to the correlation between structure and catalytic activity of solid catalysts in the liquid phase OME$_x$ synthesis. However, the correlations are often contradictory, and comparison is complicated by the use of various catalyst materials and different substrate systems. For instance, aqueous and anhydrous systems exhibit significantly different properties. In zeolites and ordered mesoporous silica, such as SBA-15, the acid strength and acid density can be determined by variation of the Si/Al ratio which may also influence whether the acid functionalities manifest as Brønsted or Lewis acidity. A systematic investigation of the influence of the Si/Al ratio in HZSM-5 zeolites based on OME$_x$ and trioxane was conducted by Wu et al. with molar ratios ranging from 56 to 4500.$^{[3c]}$ An increase of the zeolite’s Si/Al ratio led to higher TOF values in the OME$_x$ synthesis with the highest OME$_{2.8}$ selectivity for HZSM-5 580. The authors concluded that the Si/Al ratio has a significant influence on the catalytic activity which requires a medium Si/Al ratio for a sufficient number of predominantly Brønsted acid sites with medium strength in the OME$_x$ synthesis. Similar experiments were conducted by Xue et al. using Al-SBA-15 with different Si/Al ratios between 2.5 and 200 in the OME$_x$ synthesis, also based on OME$_x$ and trioxane.$^{[6]}$ However, here the catalyst with the highest OME$_{2.8}$ selectivity was Al-SBA-15 150 which possessed a fairly low acid density and only weak acid sites. Xue et al. deduced that a higher acid strength and higher acid density in low Si/Al catalysts caused a faster dissociation of trioxane to FA overtaking the OME$_x$ formation, which leads to the increased conversion of FA to the side product methyl formate.

Contrary to Wu et al.$^{[3b]}$ and Xue et al.$^{[8]}$ who each explored different Si/Al ratios within the same material, Lautenschütz et al. employed different zeolite frameworks (FAU, BEA, MFI, MOR) while maintaining a similar SiO$_2$/AlO$_2$ ratio of around 30 (Si/Al in the range of 13–17).$^{[10]}$ In the OME$_x$ synthesis, based on OME$_x$ and trioxane the catalytic activity showed the trend HBEA 25 > HY 30 while HMOR 30 was catalytically inactive.$^{[9]}$ HZSM-5 27 exhibited only a low activity which agrees with results by Wu et al. who also found a low catalytic activity for HZSM-5 zeolites with a high Al content.$^{[3c]}$ Lautenschütz et al. did not observe a correlation between catalytic activity and acid density of either, weak or strong acid sites, although, interestingly, the two most active zeolites featured very similar amounts of weak and strong acid sites, respectively. Instead, it was concluded that the accessibility of active sites was critical for catalytic activity since zeolites with a large external surface area displayed the highest activity. The influence of the pore diameter was described as a necessary but not sufficient condition for catalytic activity since the large-pore zeolite HMOR 30 was catalytically inactive. In order to explore the same effect, Xue et al. employed Al-SBA-15 with three different pore sizes in the mesoporous range between 5 and 8 nm.$^{[8]}$ For catalysts with low Si/Al ratios larger pore sizes showed a beneficial influence on OME$_{2.8}$ selectivity. The authors attributed the influence of the pore diameter to a favourable diffusion of FA monomers. The improved diffusion prevents the building of methyl formate provided that the formation of FA from trioxane is faster than the incorporation into OME$_x$. The influence of the specific external surface and internal diffusion limitations in catalysts was also investigated by Baranowski et al. who modified the external surface of HZSM-5 zeolites.$^{[10]}$ Zeolites with a passivated external surface exhibited a decreased reaction rate. In contrast, for hierarchical zeolites with mesopores, the group reported a doubled reaction rate and a 10% increase in OME$_{2.8}$ selectivity based on OME$_x$ and trioxane which was assigned to a better accessibility of active sites. For the substrate system OME$_x$ and pFA, Zheng et al. observed similar results in a comparison of different ion-exchange resins, where NKC-9 with the highest specific surface area and the largest pore size exhibited the highest catalytic activity.$^{[11]}$ The impact of the specific surface was also recognised by Oestreich et al. who examined the OME$_x$ synthesis based on methanol and pFA in the presence of ion-exchange resins.$^{[10]}$ Here, an increase of the resin’s crosslinking reduced the catalyst activity which was associated with a decreased accessibility of active sites. The influence of the catalyst porosity in the OME$_x$ synthesis starting from OME$_x$ and trioxane was investigated by Fu et al. who modified the pore diameter of aluminosilicates using zeolites and specifically synthesized materials.$^{[12]}$ In the presence of catalysts with pores in the range of 2 nm, the authors reported a shift in the chain length distribution leading to a higher equilibrium yield of OME$_{2.8}$ of 53.5% compared to 49% for a microporous Y zeolite which they assigned to shape selectivity. Additionally, the influence of the catalyst’s acid strength in the OME$_x$ synthesis has been investigated for further materials such as Zr-alumina (ZrO$_2$/$\gamma$-Al$_2$O$_3$),$^{[13]}$ PVP-stabilised heteropolyacids,$^{[14]}$ sulfated oxides (SO$_4$/$\gamma$-Fe$_2$O$_3$/SiO$_2$),$^{[15]}$ SO$_4$/$\gamma$-TiO$_2$ and SO$_4$/$\gamma$-ZrO$_2$,$^{[16]}$ as well as the combination of a Lewis acid catalyst ($\gamma$-Al$_2$O$_3$) and a Brønsted acid catalyst in the form of ion-exchange resin NKC-9.$^{[17]}$

In conclusion, the combinatory effect of the two interacting zeolite parameters Si/Al ratio and framework type has to, at the best knowledge of the authors, not yet been explored in the OME$_x$ synthesis. For this reason, a systematic catalyst screening was conducted for the OME$_x$ production employing four different zeolite framework types (BEA, FAU, MFI, MOR) with varying Si/Al ratios. The aim of this work is the development of an in-depth understanding of zeolite catalyst performance and a rationalised approach to structure-activity relations in the OME$_x$ synthesis.

**Results and Discussion**

**Catalyst Characterisation**

In this study commercial zeolites of different zeolite framework types (BEA, FAU, MFI, MOR) with varying Si/Al ratios were employed. The crystal structure of all zeolites was confirmed via X-ray diffraction. The powder XRD patterns of all samples are consistent with simulated reference diffractograms (Fig-
Nitrogen sorption measurements were conducted for all zeolites to investigate the pore structure. The adsorption isotherms (Figure S1) display for all zeolites a steep \( N_2 \) uptake at low relative pressures ensued by a plateau which is characteristic for microporous material (type I isotherm). Several zeolites additionally exhibit a hysteresis loop at higher relative pressures that is associated with pore condensation in mesopores, which can also be caused by cavities between zeolite particles forming interparticular spaces in the range of mesopores. Typically, Si-rich HZSM-5 zeolites exhibit a hysteretic step in the range of \( p/p_0 = 0.1-0.2 \). It is discussed that this type of hysteresis is caused by a phase transition of the adsorbate from a disordered liquid-like state to a more ordered solid-like state.

The results of the \( N_2 \) physisorption regarding textural properties are listed in Table 1. Comparing the different framework types, an overall trend can be detected with the specific properties are listed in Table 1. Comparing the different framework types, an overall trend can be detected with the specific

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**Table 1. Textural properties of the investigated zeolites derived from \( N_2 \) physisorption.**

| Zeolite | \( S_{\text{meso}} \) \( [m^2 g^{-1}] \) | \( S_{\text{micro}} \) \( [m^2 g^{-1}] \) | \( S_{\text{total}} \) \( [m^2 g^{-1}] \) | \( V_{\text{total}} \) \( [cm^3 g^{-1}] \) | \( V_{\text{micro}} \) \( [cm^3 g^{-1}] \) | \( V_{\text{meso}} \) \( [cm^3 g^{-1}] \) |
|---------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| H\( 13 \) | 508 | 376 | 132 | 0.46 | 0.17 | 0.28 |
| H\( 18 \) | 624 | 498 | 126 | 0.36 | 0.23 | 0.13 |
| H\( 81 \) | 611 | 473 | 138 | 0.47 | 0.22 | 0.25 |
| HY 3 | 698 | 633 | 65 | 0.37 | 0.29 | 0.08 |
| HY 15 | 815 | 674 | 141 | 0.54 | 0.31 | 0.23 |
| HY 35 | 833 | 678 | 154 | 0.55 | 0.31 | 0.24 |
| HY 49 | 807 | 622 | 185 | 0.52 | 0.29 | 0.23 |
| HZSM-5 14 | 352 | 290 | 62 | 0.20 | 0.13 | 0.06 |
| HZSM-5 34 | 410 | 292 | 118 | 0.33 | 0.13 | 0.20 |
| HZSM-5 114 | 371 | 176 | 194 | 0.23 | 0.09 | 0.14 |
| HZSM-5 4716 | 372 | 236 | 136 | 0.21 | 0.11 | 0.09 |
| HMOR 6 | 446 | 416 | 30 | 0.26 | 0.19 | 0.07 |
| HMOR 10 | 476 | 442 | 34 | 0.27 | 0.20 | 0.07 |
| HMOR 16 | 422 | 372 | 50 | 0.24 | 0.17 | 0.07 |

[a] Specific surface area \( (S_{\text{meso}}) \) determined via BET method, [b] t-plot method used to obtain values for micropore surface area \( (S_{\text{micro}}) \), also given are mesopore volume \( (V_{\text{micro}}) \) and total pore volume \( (V_{\text{meso}}) \).
strength of the acid sites (see Chapter Catalytic Activity). For very high Al contents this correlation is especially pronounced, as can be seen for HY 3 holding the highest density of weak acid sites. In contrast, almost equal values for the density of weak and strong acid sites are displayed by zeolites with low Al contents.

When comparing the different zeolite frameworks, however, the Si/Al ratio, at which the proportion of weak and strong acid sites changes, is not consistent. In HZSM-5 34 there are twice as many weak as strong acid sites, while HY 35 exhibits a balanced density for weak and strong acid sites. Moreover, for Hβ zeolites this equilibration of weak and strong acid densities cannot be observed in the employed range of Si/Al ratios. Even at the lowest Al content, in the case of Hβ 81, the zeolite still discloses a higher density of weak than of strong acid sites. This could be an indication of how the different framework structures and, hence, differences in site locations and arrangements, influence the acid strength of the active sites.

### Catalytic Activity

In order to identify highly active catalysts for the production of OME, and elucidate structure-activity relations, a catalyst screening was conducted. For a systematic investigation of
zeolites four different zeolite frameworks in H-form (BEA, FAU, MFI and MOR) with varying ratios of Si/Al were employed in the OME synthesis. The Si/Al ratio is known to influence the acid properties of zeolites and is often used as a measure for the intrinsic acid strength. The formation and composition of acid sites in zeolites has been described in numerous publications. In short, it can be said that each Al which is introduced into the zeolite lattice creates an acid site. Hence, the Al content determines the amount of acid sites in the zeolite. However, an increase in Al, and therefore acid site density, leads to the decrease of the intrinsic acid strength of each site due to charge compensation. The overall acid strength of a zeolite is the product of both factors, acid site density and intrinsic acid strength.

Following the optimisation of reaction conditions and exclusion of mass transport limitations, the OME synthesis was performed at 65 °C starting from a molar FA/MeOH ratio of 1.3 and 1.6, respectively. Generally, an increase in FA concentration shifts the OME distribution towards longer OME chain lengths and, hence, increases the OME yield. However, a higher FA concentration leads to precipitation in the product mixture due to the increased formation of longer OME chains which has also been observed by Oestreich et al. In comparison, the influence of rising temperature is subordinate leading to a minor shift of the OME chain lengths distribution towards shorter chains due to the slightly negative reaction enthalpy of −25.3 kJ mol⁻¹. Oestreich et al. reported that a decrease of temperature from 120 °C to 40 °C increases OME yields only by approximately 8 %. In this study, a reaction temperature of 65 °C was selected to achieve an equilibrium within 2–3 hours. In order to measure and compare the catalytic activity of all investigated zeolites prior to the thermodynamic equilibrium, the product yields were compared at a methanol conversion of 20%.

Figure 2 exemplary shows the OME formation over time in the presence of two highly active catalysts Hβ 81 and HY 35. The corresponding results for the catalyst performance are listed in Table 4 displaying equilibrium OME concentrations after 180 min (entry 3 and 4). The OME distribution at the thermodynamic equilibrium can be described by the Schulz-Flory distribution. It was found that even during chain growth prior to the equilibrium the OME chains exist in the Schulz-Flory distribution. This leads to a simultaneous formation of all OME chains which has been discussed in several publications.

Table 4. Catalytic performance of Hβ 81 and HY 35 at a low substrate conversion (Xsub=20%) and at thermodynamic equilibrium specifying reactant conversions X, product yields Y, selectivity S for all OME and OME5 as well as mass balance. 

| Entry | Catalyst | t [min] | XFA [%] | XMeOH [%] | YOME1 [%] | YOME2 [%] | YOME3 [%] | YOME4 [%] | YOME5 [%] | SOME1 [%] | SOME2 [%] | SOME3 [%] | SOME4 [%] | SOME5 [%] | SOME6 [%] | Mass balance [%] |
|-------|----------|--------|---------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------------|
| 1     | Hβ 81    | 12b    | 10.8    | 20.0      | 3.2       | 2.1       | 1.4       | 5.1       | 5.8       | 2.9       | 1.8       | 1.1       | 0.6       | 5.8       | 94.6     |
| 2     | HY 35    | 37b    | 10.7    | 20.0      | 4.0       | 2.4       | 1.1       | 7.5       | 6.7       | 3.7       | 2.0       | 0.9       | 0.4       | 6.7       | 99.2     |
| 3     | Hβ 81    | 180c   | 29.0    | 55.5      | 7.3       | 4.6       | 2.6       | 13.5      | 11.2      | 6.7       | 3.8       | 2.1       | 1.1       | 12.7      | 93.6     |
| 4     | HY 35    | 180c   | 31.6    | 53.2      | 7.4       | 4.7       | 2.7       | 13.4      | 11.1      | 6.8       | 3.9       | 2.2       | 1.1       | 12.9      | 92.6     |
| 5     | zeolites, ion-exch. resinsb | n.a. | n.a.     | n.a.      | n.a.      | n.a.      | n.a.      | n.a.      | n.a.      | n.a.      | 5.6       | 3.1       | 1.6       | 0.8       | 10.3     |

[a] Reaction conditions: (1)–(4)Starting from a substrate mixture of pFA and MeOH, n(FA)/n(MeOH) = 1.6, 65 °C, 0.4 wt% catalyst, (5) Oestreich et al.: 80 °C, n(FA)/n(MeOH) = 1.6, 1 wt% catalyst using zeolites (BEA, FAU, MFI, MOR) and ion-exchange resins (Amberlyst 36, IR 120, Dowex50W crosslinked with 2%, 4% and 8% divinylbenzene, respectively); n.a. = not available. [b] at conversion Xsub=20%, [c] at thermodynamic equilibrium; yields referring to FA.
Comparing Hβ 81 and HY 35 at low substrate conversions, the catalysed OME synthesis proceeds with a significantly different reaction velocity illustrating the different catalytic activity of the two zeolites. The methanol conversion of 20% for each reaction is indicated by the dashed line (Figure 2) which occurs in the presence of Hβ 81 at 12 min and for HY 35 at 37 min revealing Hβ 81 as the catalyst with the higher activity (Table 4 entry 1 and 2). All active catalysts exhibit a high selectivity for the formation of OME with OME, and OME as main products (Table 4 and Figure S3–Figure S7), and only minor formation of the side product methyl formate.

For comparison, in Table 4 entry 5 experimental results by Oestreich et al. are displayed who conducted the OME synthesis using various zeolites and ion-exchange resins under similar reaction conditions as applied in this work.[24,27] Due to equal substrate ratios, comparison of the OME selectivities published by Oestreich et al. and in this work is viable and shows a high agreement at the thermodynamic equilibrium (Eq. 5) in the OME synthesis revealing that the zeolite’s activity for an Hβ zeolite, albeit with a Si/Al ratio of 13 (denominated BEA25 based on SiO/AlO), followed by a HY zeolite with a Si/Al ratio of 17 (Y30) while the MOR zeolite was catalytically inactive.[9] However, in the experiments by Lautenschütz et al. the HZSM-5 zeolite with a Si/Al ratio of 13 (MFI27) showed no considerable catalytic activity[8] while in this study HZSM-5 34 possessed the second highest catalytic productivity. The different results for the MFI framework demonstrate that the catalytic activity of a zeolite framework cannot be judged solely by testing one Si/Al ratio. Here, too, it needs to be considered that Lautenschütz et al. employed an anhydrous system by using OME and trioxane which impedes comparison. Likewise starting from OME and trioxane, Xue et al. concluded that the trioxane dissociation to FA requires a higher strength of acidity.[8] For the MFI framework only HZSM-5 4716 exhibits no catalytic productivity, presumably due to its extremely low Al content, which is reflected in the absence of acid sites in NH-TPD (Table 3). Additionally, HY 3 discloses only a very low catalytic productivity which underlines that a high Al content is not advantageous to the catalytic productivity. Unsurprisingly, NH-TPD measurements revealed mainly weak acid sites for HY 3 (Table 3) which concurs with charge compensation effects and indicates that a low acid strength is not sufficient for the OME synthesis.

As described above, it needs to be considered that the catalytic productivity is determined by the intrinsic acid strength of each acid site as well as the acid site density, both of which are influenced by the Si/Al ratio of the zeolite. For this reason, in the following the catalytic productivity is normalised to the total number of weak and strong acid sites n(AS) determined via NH-TPD to obtain the turnover frequency (TOF) as shown in Eq. (6). By means of normalisation the influence of the acid site density, which varies significantly between the employed zeolites due to the different Si/Al ratios, is eliminated. As a result, the TOF quantifies the influence of the average acid strength of an active site and can be used as a measure for the catalytic activity of a single acid site of the zeolite. This enables a better understanding of the required acid strength in the OME synthesis and the identification of the catalyst with the highest performing active sites.

The influence of the normalisation to the acid site density is shown in Figure 4 displaying both, the catalytic productivity CP (Figure 4a) and the turnover frequency TOF (Figure 4b). Figure 4 (a) presents the same data as Figure 3, only now sorted by overall Si/Al ratio rather than framework category. Exemplarily, the normalisation manifests in the different values of CP and TOF for HZSM-5 114 which possesses a low acid density due to its low Al content but demonstrates a high TOF. This means that the zeolite’s individual acid site holds a high catalytic activity. For all other zeolites the same trend can be deduced, with CP>TOF indicating few but highly active acid sites and CP<TOF representing zeolites with many acid sites of lower strength.
activity. Consequently, the normalisation reveals a different order for the turnover frequency with the highest-performing zeolite HZSM-5 114 displaying a TOF of 3375 mol$_{\text{OME3-5}}$ mol$_{\text{AS}}^{-1}$ h$^{-1}$. The next level of turnover frequency of around 1400 mol$_{\text{OME3-5}}$ mol$_{\text{AS}}^{-1}$ h$^{-1}$ is displayed by three zeolites of different frameworks, namely Hβ 81, HY 35 and HZSM-5 34. Generally, a high TOF $\geq$ 970 mol$_{\text{OME3-5}}$ mol$_{\text{AS}}^{-1}$ h$^{-1}$ is demonstrated by zeolites possessing medium to high Si/Al ratios between 34 and 114, amongst which HY 49 exhibited the lowest TOF of 970 mol$_{\text{OME3-5}}$ mol$_{\text{AS}}^{-1}$ h$^{-1}$. All other zeolites with higher Al concentrations display a TOF $<$ 970 mol$_{\text{OME3-5}}$ mol$_{\text{AS}}^{-1}$ h$^{-1}$. Since the Si/Al ratio is a measure for the intrinsic acid strength, this could be an indication that a threshold acid strength is favourable for the OME$_x$ production. Overall, Figure 4(b) reveals a clear correlation between Si/Al and the TOF compared to Figure 4(a) which supports the validity of the normalisation and indicates that the TOF is significantly influenced by the intrinsic acid strength. However, it is not only the Si/Al ratio which affects the catalytic activity as can be seen for zeolites with almost identical Si/Al ratios such as Hβ 13, HZSM-5 14, HY 15 and HMOR 16. While Hβ 13 and HZSM-5 14 exhibit a comparable TOF, HY 15 and HMOR 16 differ significantly which substantiates that the framework and its inherent parameters influence the intrinsic catalytic activity of the zeolites.

In addition to the amount of acid sites, which has been incorporated via normalisation, it is also important to consider that zeolites possess acid sites of different acid strength as determined by NH$_3$-TPD (Table 3). However, it has been established in this work that the Si/Al ratio does not suffice as a sole measure of acid properties across framework types and further investigations are necessary. However, it has been established in this work that the Si/Al ratio has a significant influence on the TOF suggesting that a
moderately high intrinsic acid strength is required for the OME synthesis which agrees with results in literature.\textsuperscript{[5c,10]}

**Conclusion**

In this work a systematic screening of zeolite catalysts for the OME synthesis was conducted with four different frameworks (BEA, FAU, MFI, MOR) and varying Si/Al ratios for each framework. So far in literature, the optimisation of solid catalysts for the OME synthesis via variation of Al content has only been performed within a structure type e.g. MFI zeolites and Al-SBA-15. The Si/Al ratio is known to influence the acid properties of zeolites by determining the acid site density as well as the intrinsic acid strength of a single site. The aim was to identify the optimum acid strength for the OME synthesis and to build an understanding for structure-activity relations by identifying the influencing factors. This was achieved by normalising the catalytic productivity to the amount of acid sites which introduced the turnover frequency (TOF). The TOF quantifies the influence of the average acid strength of an active site and can, hence, be used as a measure for the catalytic activity of a single acid site of a zeolite. Overall, the best-performing zeolite was HZSM-5 114 with a TOF of 3375 mol\textsubscript{OME3-5} mol\textsubscript{AS} h\textsuperscript{-1} followed by HY 35 (1444 mol\textsubscript{OME3-5} mol\textsubscript{AS} h\textsuperscript{-1}), HZSM-5 34 (1430 mol\textsubscript{OME3-5} mol\textsubscript{AS} h\textsuperscript{-1}) and Hβ 81 (1420 mol\textsubscript{OME3-5} mol\textsubscript{AS} h\textsuperscript{-1}). A high catalytic activity with a TOF $\geq$ 970 mol\textsubscript{OME3-5} mol\textsubscript{AS} h\textsuperscript{-1} was demonstrated by zeolites possessing medium to high Si/Al ratios between 34 and 114, amongst which HY 49 exhibited the lowest TOF of 970 mol\textsubscript{OME3-5} mol\textsubscript{AS} h\textsuperscript{-1}. All zeolites with higher Al concentrations display lower TOF values in the range of 4–524 mol\textsubscript{OME3-5} mol\textsubscript{AS} h\textsuperscript{-1}. Since the Si/Al ratio is a measure for the intrinsic acid strength this could be an indication that an acid strength above a certain threshold is favourable for the catalysis of the OME synthesis. By comparison of zeolites with similar Si/Al ratios but varying frameworks, which exhibited different TOF values, it could also be observed that the zeolite framework, and its inherent properties, affect the catalytic activity underlining the complexity of structure-activity relations in zeolites. Nonetheless, the results demonstrate that the Si/Al ratio has a significant influence on the catalytic activity of zeolites and corroborate that the OME formation requires a moderately high intrinsic acid strength. For future investigations, the best-performing zeolites could be examined further to gain understanding regarding the influence of zeolite framework and textural properties.

**Experimental Section**

**Chemicals and Materials**

The reagent paraformaldehyde (99.9%) was purchased from Sigma-Aldrich and methanol (99.9%) from Merck, both were used without further purification. For GC calibrations OME (99%) and methyl formate (anhydrous, 99%) were acquired from Sigma Aldrich. OME to OME$_2$ (each $>0.97$ g/g) were kindly provided by the Institute of Catalysis Research and Technology at the KIT as part of the collaboration in the project Kopernikus P2X by the German Federal Ministry of Education and Research (BMBF). An overview of all employed zeolites is given in Table 2 including material specifications. The zeolites Beta (BEA) and Mordenite (MOR) were kindly provided by Clariant in proton form and different SiO$_2$/Al$_2$O$_3$ ratios, as specified by the manufacturer, namely Hβ (25, 30, 150), and HMOR (14, 20, 40). MFI zeolites were equally provided by Clariant, however, in ammonium (NH$_4^+$) form which were calcined at 500 °C for 5 h in static air with a heating rate of 5 °C min$^{-1}$ to obtain the proton form HZSM-5 (30, 90, 200, 800). Faujasite (FAU) zeolites were purchased in proton form HY (5, 30, 60, 80) from Alfa Aesar. Hβ, HY and HMOR were also calcined prior to usage at 550 °C for 4 h in static air with a heating rate of 2 °C min$^{-1}$ to remove any contamination and stored under Ar thereafter. All zeolites were acquired in powder form and used as such.

**Catalytic Experiments**

The catalyst screening in the OME synthesis was conducted in 8 mL stirred reactor flasks sealed with septum at 65 °C in a water bath and a stirrer speed of 300 rpm. The substrate mixture of methanol and formaldehyde was prepared in advance in large quantity to ensure an equal substrate ratio in all experiments since this had a strong influence on the distribution of OME. For this purpose, paraformaldehyde was dissolved in methanol at 80 °C under reflux for 48 h. Subsequently, any remaining solid paraformaldehyde was filtered off and the substrate mixture was stored under Ar. For a series of long-term experiments, a molar substrate ratio of 1.6 for FA/MeOH was employed. For the screening a molar ratio of FA/MeOH = 1.3 was utilised. To prevent a difference in catalyst concentration after sampling, caused by withdrawal of a heterogeneous mixture of liquid phase and solid catalyst, a separate experiment was conducted for each reaction time and the catalyst was weighed in subsequent to the substrate mixture according to 0.4 wt%. The reaction was started upon setting of the reactor flask into the preheated water bath since the small cross-section of the reactor allowed a quick heat transfer. After completion of the reaction time, the sample was quenched in an ice bath for 1 min to reduce OME, loss in the gas phase. Using a syringe, the sample was extracted through the septum and the catalyst was filtered off by means of a syringe filter (0.45 μm pore size, medium polarity). The samples were analysed via gas chromatography (GC) using a Focus GC system by Thermo Scientific equipped with an Agilent VF-WAXms column (60 m, 0.25 mm i.d., 0.25 μm) coupled with a flame ionisation detector (FID). For the calibration 1-heptanol as internal standard and pure OME fractions of OME$_3$-$5$ were purchased in proton form HY (5, 30, 60, 80) from Alfa Aesar. Hβ, HY and HMOR were also calcined prior to usage at 550 °C for 4 h in static air with a heating rate of 2 °C min$^{-1}$ to remove any contamination and stored under Ar thereafter. All zeolites were acquired in powder form and used as such.
thermodynamic equilibrium and compared for all catalysts at the same methanol conversion of \( X_{\text{reactant}} = 20\% \) which was achieved by interpolation of the experimentally determined values. For this, the reaction rate of the desired products \( \text{OME}_x \) was normalised to the catalyst mass \( m(\text{cat}) \) to obtain the catalytic productivity \( CP \) as shown in Eq. (5) and normalised to the amount of acid sites \( n(\text{AS}) \) of the deployed catalyst which was determined via NH\(_3\) temperature-programmed desorption (TPD) to obtain the turnover frequency TOF as shown in Eq. (6).

\[
X(\text{reactant}) = \frac{n(\text{reactant})}{n(\text{reactant}) - n(\text{reactant})}
\]

\[
Y(\text{OME}_x) = \frac{n(\text{OME}_x)}{n(\text{FA})}
\]

\[
S(\text{OME}_x)_{\text{ads}/\text{des}} = \frac{m(\text{OME}_x)}{m(\text{sample})}
\]

\[
\text{MB} = \frac{m(\text{products}) + m(\text{reactants}) + m(\text{H}_2\text{O})}{m(\text{sample})}
\]

\[
\text{CP} = \frac{n_{\text{mol}}(\text{OME}_x)}{t_{\text{obs}} \cdot m(\text{cat})}
\]

\[
\text{TOF} = \frac{n_{\text{mol}}(\text{OME}_x)}{t_{\text{obs}} \cdot n(\text{AS})}
\]

Catalyst Characterisation

The examination of the zeolites via X-ray diffraction (XRD) was conducted by means of a D-5000 (Siemens) using a Cu-K\(_\alpha\) radiation tube (\( \lambda = 0.154056 \) nm). The tube voltage and current were 45 kV and 40 mA, respectively. Diffraction patterns were collected in the 3–90 2\( \theta \) range with 0.02 intervals and a step time of 1 s. MOR zeolites were measured using a STADIP (STOE & Cie) with Cu-K\(_\alpha\) radiation (\( \lambda = 0.15406 \) nm) at 40 kV and 30 mA. The N\(_2\) adsorption and desorption isotherms of the zeolites were measured using a Quadrasorb SI (3P Instruments) at 77 K. Prior to measurement, the samples were degassed under vacuum (FloVac Degasser) for 12 h at 120 °C and subsequently for 3 h at 300 °C. Analysis of the data was conducted with the software QuadraWin provided by 3P Instruments. The specific surface area was ascertained using the Brunauer-Emmett-Teller (BET) method in the range of \( p/p_0 = 0.05–0.2 \). The total pore volume was derived from the adsorbed volume of nitrogen at \( p/p_0 = 0.95–0.98 \). For the determination of micropore surface area and micropore volume the t-pplot analysis was applied. For quantification of the acid density of each zeolite, ammonia temperature-programmed desorption (NH\(_3\)-TPD) was conducted at ZetA Partikelanalytik GmbH, Mainz, Germany. First, the samples were heated with 10 °C/min to 650 °C while flushing with He which was held for 15 min at 650 °C to free the surface from contamination. After cooling to 60 °C, NH\(_3\) was dosed onto the samples at a flow rate of 10 mL/min while heating to 120 °C which was held for another 20 min at 120 °C. Prior to measurement, the samples were flushed with He for 60 min and cooled down to room temperature. The spectra were recorded during heating of the samples to 650 °C with a heating rate of 10 °C/min. The content of Si and Al in all employed zeolites was determined by means of inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Spectroblue by Spectro Analytical Instruments. Prior to analysis, 30 mg of the solid sample was dissolved in 10 mL of an aqueous solution of sulfonic and hydrofluoric acid (800 mL\( \text{H}_2\text{SO}_4\), 40 mL \( \text{H}_2\text{SO}_4\), 160 mLHF) by treatment in a microwave (10 min at 600 W to 120 °C, holding for 20 min). For the injection the solution was diluted with water to 50 mL.

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Conflict of Interest

The authors declare no conflict of interest.

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