From Catalytic Test Reaction to Modern Chemical Descriptors in Zeolite Catalysis Research

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In Memory of Prof. Dr.-Ing. Jens Weitkamp

For the successful implementation of catalysts in industrial processes, three overall goals are optimized: activity, selectivity, and stability. This review will address the role of chemical descriptors in aiding and guiding the development of optimal zeolite catalyst designs with the above performance criteria in mind. It will focus on both gas-phase and liquid-phase catalysis with a special focus on methanol to hydrocarbon, and biomass valorization reactions. By way of preface, the research on constraint and spaciousness indices is discussed. These indices can be considered the original chemical descriptors of catalysis research.

Keywords: Biomass, Constraint Index, Descriptors, Methanol to Hydrocarbons, Zeolite Catalysis

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1 Introduction

Zeolite catalysis research has evolved tremendously over the last century. One of the most important advancements in catalytic transformations came with the development of synthetic zeolites (i.e., zeolite Y) [1] that exhibited activities several orders of magnitude higher than non-porous amorphous silica-alumina (ASA) when employed in fluid catalytic cracking (FCC) as shown in Fig. 1 [2, 3]. Contributions by Prof. Weitkamp have advanced, in no small part, the understanding of how these microporous materials transform and valorize crude oil feed into useful commodity and specialty chemicals. His name is intimately linked to the field of hydrocracking where saturated, long-chain hydrocarbons found in heavy vacuum gas oil (VGO) are converted into smaller jet, diesel and gasoline fraction alkanes. This can be achieved with the use of bi-functional zeolite catalysts and a significant contribution by Prof. Weitkamp was the establishment of a correlation between product distribution and the zeolite spaciousness, owed to the peculiar cracking behavior of cyclic alkenes (see below) [4, 5].

Prof. Weitkamp’s research and efforts have had far-reaching impacts on the general chemistry community in Norway, and zeolite catalysis research at the University of Oslo in particular. In 1997, Prof. Weitkamp chaired a committee that carried out an evaluation of chemistry research at Norwegian universities and colleges on the national level. Based on this report, a strategy for chemistry research in Norway was devised. In 2010, Prof. Weitkamp was involved in the mid-term evaluation of the inGAP (innovative natural gas processes and products) center for research-based innovation. This center was established by the Research Council of Norway and was designed to increase innovation and the competitiveness of Norwegian chemical industry through coordinated research efforts. Clearly, Prof. Weitkamp was uniquely qualified for the evaluation of such a center. On a more personal note, it is clear that the heterogeneous catalysis and zeolite research carried out by Prof. Weitkamp is thematically closely related to the activities that have been ongoing within the Catalysis group at the University of Oslo for several decades. The work of Prof. Weitkamp has been highly inspirational, in particular his ability and drive to combine applied and industry relevant research with fundamental science.

Zeolites are crystalline aluminosilicates formed by the connecting of shared oxygen atoms of AlO₄ and SiO₄ tetrahedra [3, 6]. This generates a well-defined, periodic and uniquely porous structure that can be accessed solely by molecules of size equal to, or smaller than the pore diameter. The zeolite becomes a molecular sieve, able to screen a range of compounds, adsorbing only those small enough to enter the pores. Within the pore structure, the largely periodic alternation of Al and Si tetrahedra, with differing
valence electron shells (\(\text{Al}^{3+}\) and \(\text{Si}^{4+}\)) generates a negative framework charge, which when substituted with protons allows for the creation of Bronsted acidic adsorption sites (\(=\text{Al}-\text{O}^\text{H}^+\)-\(\text{Si}\)), capable of catalytically transforming molecules [7]. Thus, the zeolite is not only screening for molecules entering the pore network, but also selective towards which products are formed, via limiting the formation of certain transition states, and which products are desorbed and released from the porous network. This gives zeolites their intrinsic shape selectivity [8, 9]. For example, it has been observed that conversion of n-hexane and 3-methylpentane does not proceed at equal rates over a medium-pore zeolite such as H-ZSM-5 [10]. Instead, the linear alkane is cracked more readily (Scheme 1).

The intrinsic nature of shape selectivity results in zeolites exhibiting unique behavior compared to non-porous and/or amorphous materials and with the number of newly discovered zeolite frameworks continuously increasing (currently 252 unique frameworks) [11], it is desirable to establish concrete structure/performance relationships. These relationships can often be represented by chemical descriptors, some of which we will discuss in this review. A typical example is the Si/Al ratio where a high ratio corresponds to a small amount of Al in the framework and thus implies the presence of only a few Bronsted acid sites resulting in a slow conversion of the substrate in acid catalyzed reactions. It should be noted that industrial applications often employ promising catalysts that are not yet fully understood mechanistically. This is exemplified by continuing research on FCC and methanol to hydrocarbons (MTH) process and catalyst development despite their early industrial adoption in the 1960s and 1980s, respectively [2, 12, 13]. However, through extensive – and increasingly better and more accessible – characterization, academia and industrial R&D are able to elucidate which catalyst parameters are most crucial and subsequently design superior materials in iterative improvement cycles.

2 Catalytic Test Reactions as the First Descriptors

Some of the earliest descriptors were pioneered by researchers at Mobil (constraint index, CI), as well as Weitkamp, Martens and co-workers (modified constraint index, CI* & spaciousness index, SI) [5, 10, 14]. At the time, the lack of advanced characterization techniques limited the scope of determining pore openings in newly discovered zeolites. Therefore, the above-mentioned researchers developed descriptors via the use of specific test reactions to exploit the varying degrees of shape selectivity in zeolites and classify the pore opening accordingly. While these descriptors are nowadays considered outdated, their origin and how they relate to the development of novel descriptors is still worth revisiting. The original constraint index (CI) was initially proposed in 1981 by Frillette, Haag and Lago at Mobil [10]. It describes the comparison between the logarithmic cracking rates of a linear n-hexane molecule compared to that of its bulky isomer 3-methylpentane (3-MP) fed in equal molar ratios (Scheme 1 and Eq. (1)).

\[
\text{CI} = \frac{\log(1 - X_{n\text{-C}_6})}{\log(1 - X_{3\text{-MP}})}
\] (1)

The bulkiness of the branched isomer requires a larger pore environment with less steric constraints for appreciable cracking rates to occur. These two extremes of cracking possibilities provided a neat tool to easily screen and differentiate between small- (8-ring), medium- (10-ring) and large-pore (≥12-ring) zeolites. In the small-pore zeolites (CHA, ERI, LTA) only the linear alkane is cracked whereas the large-pore variants (such as 12-ring FAU and BEA frameworks) exhibit an exceedingly fast cracking rate of the branched isomer leading to CI values below unity. With CI values closer to unity (2-12), the medium-pore zeolites naturally fall between the extremes reflecting the possibility, although sterically constrained, of 3-MP cracking (Fig. 2). However, some anomalies do exist such as the observation that ZSM-12 (MTW framework) a one-dimensional 12-ring system with a CI value of 3.0 behaves more like a medium-pore zeolite than a corresponding large-pore BEA (CI 2.0) or FAU (0.2) system [15]. This anomalous behavior is now associated with a lack of pore intersections typical for three-dimensional systems as well as a constrained 12-ring of diminished pore aperture (6 Å) [16]. Another facet that affects the outcome of the constraint index is the reaction temperature. As the temperature increases from 300 to

![Figure 1. Improvement in product selectivity for the FCC process during the 20th century as new process designs and catalysts designs were developed. The use of porous aluminosilicates starting in the 60s led to an increase in the gasoline fraction replacing the use of ASA previously established in the 1940s. Figure reproduced from Ref. [2], published by The Royal Society of Chemistry.](image-url)
510 °C, the relative rate of 3-MP cracking compared to n-hexane increases leading to a reduction in the constraint index for medium pore zeolites such as ZSM-5 from 11 to 1.5 [10, 15]. Finally, these test reactions should be performed at low conversions and partial pressures of the alkanes. This minimizes bimolecular side reactions such as the formation of coke leading to a loss of active sites either via adsorption on acid sites or blocking of accessibility to the pore network, which can affect product distributions. Thus, these test reactions need to be performed at similar temperatures and low conversions for fair comparisons to be derived.

In response to some of these shortcomings Weitkamp and colleagues from KU Leuven developed the modified constraint index (CI*) involving bifunctional catalysts (Pd/Zeolite) used in hydrocracking reactions (Scheme 1) [9, 14, 17]. It assesses the product distribution derived from the hydroisomerization of n-decane at low yields (5%). n-Decane is first isomerized on metal sites to monobranch isomers such as 2-, 3-, 4-, and 5-methyl-nonane, 3- and 4-ethyldecan, and 4-propylheptane. These isomers are subsequently cracked over acid sites resulting in a range of distinctive isomerized and hydrocracked products. The product distribution will be characteristic of the zeolite’s pore size. For example, on ZSM-5, the longer branched isomers are no longer observed. Instead, 2-methyl-nonane is the most pronounced isomer formed when using ZSM-5. Therefore the ratio of the monobranch isomers 2-methyl-nonane and 5-methyl-nonane was elucidated as a convenient descriptor for the pore size [14]. The use of small amounts of noble metal (e.g., 0.27 wt % Pd) and operating at low conversions enables to shift the focus away from acid-catalyzed reactions towards the isomerization step. This, in addition to the presence of H₂, prevents the buildup of coke highlighting some of the advantages over the original constraint index.

The spaciousness index (SI) is a descriptor used to identify large-pore zeolites (Scheme 1) [5]. Similarly to the modified constraint index the SI probes the conversion of a large alkane (C₁₀), in this case a bulky butylcyclohexane. The SI also utilizes a bifunctional catalyst, thus avoiding the rapid catalyst deactivation prone to occur in CI studies. However, unlike the CI*, here the focus lies on the cracking of the cycloalkane rather than the isomerization. The reaction has been observed to be extremely selective in non-constrained environments (e.g., Ni/SiO₂-Al₂O₃) [18] yielding predominantly an isoalkane, isobutane, and a larger cycloalkane, methylcyclopentane. This effect originates in the paring reaction where the carbocation, the protonated substrate adsorbed on the acid site, undergoes skeletal rearrangement to form a tri-branched intermediate (Scheme 1). Subsequent facile beta scission followed by hydrogenation over the metal sites ultimately yields, with high selectivity, isobutane and methylcyclopentane. The crucial step, however, is the bulky tri-branched intermediate, which is readily accommodated in the supercage of FAU, yet cannot be formed in the 10-ring channels and intersections of MFI [4]. Thus, studying a range of zeolites with varying pore size, the shift in product distribution is evident. Large-pore FAU tends to yield a symmetric distribution of C₄ isoalkanes and C₆ cycloalkanes, whereas smaller pore sizes favor C₃ and C₇ fragments in addition to more linear C₄ and C₅ fragments. The molar product ratio of isobutane to n-butane was found to be a descriptor for...
the pore size, called the spaciousness index. Due to the difficulty of forming the bulky intermediate in 10-ring pores, these zeolites tend to have very low SI values (Pd/HZSM-5 SI = 0.8) and it is recommended to use the SI descriptor mainly for larger ring structures where it becomes significantly more sensitive. For example, the SI allows to differentiate between a one dimensional 12-ring (Pd/HZSM-12) and a cage-type 12-ring (Pd/HY) zeolite. The lack of intersections and cage structures in ZSM-12 results in only a small surplus of isobutane being formed (SI = 3) compared to FAU facilitating the formation of the bulky intermediate (SI = 21) [15]. Another advantage over the constraint index lies in the SI being independent of the reaction temperature across a range from 200–350 °C and as a consequence independent of the conversion and product yields of the reaction, making this a very user-friendly descriptor to use when identifying unknown structures [19].

It has been suggested by Ernst et al. that the routine analysis of an unknown material would involve first the determination of the spaciousness index, which if the descriptor value is larger than 2, indicates a large-pore zeolite. If the value is smaller than 2, the material should subsequently be investigated via the modified constraint index which would allow to further differentiate between systems containing intersections (e.g., ZSM-5) and unidimensional systems (ZSM-22) [15].

Over the years these descriptors have found extensive use, however, with the discovery of new zeolite materials of increasing complexity (and ring size), the applicability of these early descriptors has been challenged [16]. Zones and Harris tested the CI on a number of newly discovered materials focusing on an extended number of high-silica cage systems with 8-, 9-, or 10-ring window systems (e.g., DDR, STT, MWW) as well as extra-large-pore zeolites with 14-ring channels, UTD-1 and CIT-5 [16]. For the latter group of materials they find that the CI is insufficient to differentiate between a 12-ring and 14-ring as they both readily convert 3-MP as well as the linear n-hexane. We surmise that the spaciousness index could be a more sensitive alternative. Furthermore, they also identify that the nominal ring size is inadequate to fully assess whether facile 3-MP cracking occurs. Instead, the shape of the 12-ring is a more crucial descriptor; SSZ-31 (*STO) exhibits a CI value close to unity (characteristic for medium-pore zeolites) due to the ellipsoidal 12-ring constricted in one axis (5.5 Å x 8.8 Å). A similar observation was made by Haag et al. in the original work for large-pore ZSM-12 (CI = 3), which also contains a constricted 12-ring with an accessible pore diameter of 6 Å (rather than 7 Å in regular 12-ring systems) [10].

The biggest challenge to the constraint index (and likely to the modified constraint index and spaciousness index as well), however, lies in the anomalous behavior of small-pore and medium-pore zeolites with large internal cage structures [16, 20]. CI values suggesting a large-pore 12-ring system for MWW (MCM-22, SSZ-25) and STF (SSZ-35) frameworks did not align with the structural analysis of 10-ring pore windows opening into larger cavities [20]. While cracking on the external surface (e.g., in lattice terminating 12-ring “half cups” in MWW) was not found to be a major contributor, the lack of constraint at the active site in the large internal cage results in the lower than expected CI values [20]. For the 8-ring systems in SSZ-36 and SSZ-28 8-ring, despite having small-pore access windows, cracking selectivity for 3-MP over n-hexane was higher (CI = 3.2–4.0) than for some medium-pore zeolites (ZSM-5 CI= 6) [16]. This results in lower than expected CI values, although it should be noted that the molecules’ conversion is lower than in 10-ring systems. They arrive at several possible explanations for this behavior such as diffusion limitations resulting in the overall low conversion of n-hexane, lattice vibrations at elevated temperatures leading to more accessibility, as well as distorted 8-ring pores (e.g., in SSZ-28) [16].

3 Chemical Descriptors for Selectivity

The advent of zeolite catalysis research was related to society’s heavy reliance on oil as a feedstock. Consequently,
the early catalyst descriptors mentioned above are intimately related to chemical reactions (e.g., cracking, hydroisomerization) relevant to the transformation of oil-based feedstock. However, zeolites, owing to their high thermal stability and wide topological variety, spurred by the discovery of high-silica variants employing structure-directing agents [21], were also increasingly utilized in novel processes such as exhaust gas treatments [22–24], small molecule activation for natural gas upgrading [12,25,26], as well as chemical production from biomass feedstock [27,28]. This has resulted in a plethora of chemical descriptors aimed at establishing structure/activity relationships for the design of improved catalysts, some of which will be discussed hereafter.

In the late 1970s, a field of catalysis research arose focusing on the transformation of methanol to hydrocarbons (MTH and variations thereof such as methanol to olefins (MTO), methanol to gasoline (MTG) and methanol to aromatics (MTA)) [29]. It was commercialized early on with the first plant being operated by Mobil in 1986, however, fundamental research continues to this day. This continued interest on MTH is related to the fact that methanol, the substrate in the formation of longer chain hydrocarbons (C1–C11), can be obtained from a variety of more sustainable sources such as carbon dioxide, biomass, waste and natural gas [13]. This enables the production of high-demand chemicals without relying extensively on oil. The following section will delineate which parameters need to be varied to affect the product distribution, acting as a chemical descriptor for selectivity.

It is worthwhile to compare this conceptual strategy of influencing the product distribution in MTH with the test reactions discussed above. While the latter established structure/activity relationships originating from some form of shape selectivity to identify new frameworks, the early insight from MTH extrapolated this knowledge to identify and link potential frameworks with desired product ranges (e.g., olefins, hydrocarbons, aromatics). Using ZSM-5 the product distribution was heavily shifted towards C5+ and aromatic fractions [12,30]. If, however, a small-pore CHA type zeolite/zeotype (isostructural to an aluminosilicate framework but consists of different elemental tetrahedrons such as silicates, phosphates and aluminate – SAPO) is used [31,32] then the presence of light olefins (propene & ethene) in the effluent product stream at the expense of larger aromatics suggests a dependence of the product distribution on the pore size. Indeed, Zones and Harris remarked that the erroneous structural identification of some zeolites using the constraint index (e.g., SSZ-23 with a 9-ring system) could have been avoided when studying instead their MTH product distribution, where SSZ-28 falls between small-pore (8-ring) CHA materials and the medium-pore (10-ring) ZSM-5 system [16].

Over the years, more insight has been gained into the MTH reaction mechanism, and thus a better understanding over product selectivity. MTH is considered an autocatalytic reaction where methanol is first adsorbed onto the zeolite to form a surface methoxy species, which can then initiate the first C-C bond [33,34]. Once enough of these C2 fragments are formed during the induction period, the reaction transitions to its autocatalytic nature, which can best be described by a dual cycle concept of competing aromatics and olefin cycle (Fig. 3).

In the olefin cycle consecutive methylation and cracking reactions take place as envisioned by Dessau [34], whereas in the aromatic cycle one first forms benzene molecules which are subsequently methylated and undergo elimination reactions to yield olefins and possibly aromatics. While the olefin cycle can yield a range of alkenes, the aromatic cycle was shown, using 13C/12C switching experiments, to result primarily in ethylene, in addition to aromatic compounds [35,36]. This mechanistic stage is the origin for the perceived dependence of product selectivity on pore size: In the case of cage-type structures such as CHA (e.g., SAPO-34 or SSZ-13), the high fraction of synthesized light olefins was related to the formation of a hydrocarbon pool of larger aromatics (hexa/hepta-methylenebenzene ions) inside the CHA cage [37,38]. These bulky molecules can no longer diffuse through the 8-ring pore window, and instead undergo further methylation reactions and subsequent elimination steps yielding smaller alkenes that are able to leave while restoring the initial hydrocarbon pool. In the ZSM-5 case, these species also exist, albeit at a much lower concentration, and based on the incorporation rates of 13C they exhibit a lower reactivity. Instead, 13C enriched solid-state NMR identified cyclopentadienium ions as the dominant hydrocarbon species [12,13]. This is associated with the more constrained environment in the 10-ring pores compared to the large 18 Å CHA cage. The topological differ-

![Figure 3](image-url)  
Figure 3. Concept for the olefin (left) and aromatic (right) dual cycle believed to occur in the micropores during the autocatalytic stage (following the initial C-C formation of MeOH) of the MTH reaction. Depending on pore topology the relative propagation of each cycle and thus the product distribution (olefin or aromatics) can be affected. Reproduced with permission from Ref. [12] Copyright (2012), Wiley.
ences in ZSM-5 compared to CHA, namely the lack of small-pore windows, allows for the olefin- (consecutive methylation/cracking) and aromatic-cycle (paring/elimination reaction of aromatic intermediates) to operate in parallel, yielding primarily ethylene and aromatics. As the product distribution appears to be linked to the available space in the zeolite pore network and diffusional limitations of the products through pore windows it was envisioned that a one-dimensional 10-ring system without any intersections would be able to affect the propagation of the aromatics cycle [39]. The direct comparison with ZSM-5, SAPO-34, and H-BEA of comparable Si/Al shown in Fig. 4 highlights that ZSM-22, a one-dimensional 10-ring zeolite, largely suppresses the aromatics cycle [39]. Furthermore, the high propylene/ethylene ratio is further evidence for the origin of ethylene from the aromatics cycle. Thus, the formation of cyclopentadienyl and benzenium species is only feasible in the intersections of ZSM-5 as well as the larger pores of H-BEA. Another useful descriptor for assessing the relative propagation of olefin and aromatic cycle, and thus the product distribution, was identified by Bhan et al. as the ratio of ethylene to 2-methylbutane and 2-methyl-2-butene [40]. They also showed how co-feeding alkenes or aromatics could help to drive the product selectivity towards the olefin or aromatic cycle, respectively.

It should be noted here, that the early use of MTH reactions as a descriptor for pore size (as suggested by Harris and Zones) did not consider the full picture as the more recent insight actually suggests bulkier intermediates to be present in small-pore zeolites than in medium-pore zeolites. Zones and Davis revisited this by investigating a range of cage-type zeolites and zeotypes and establishing instead the cage-defining ring size (Fig. 4) as the crucial descriptor for the olefin distribution obtained during methanol upgrading [41]. Similar to the differences in hydrocarbon pool species observed for CHA and ZSM-5, the different cage geometries studied here impact the nature of the reactive intermediates formed. Thus, the cage-defining ring size, roughly corresponding to the cage size and geometry, is a descriptor for which intermediates are formed and how they are arranged, thus influencing the ultimate product distribution. This allowed for the proposal of zeolite structures that favor ethylene over propylene (e.g., 12-cage ring size ERI and LEV), propylene over ethylene (e.g., 14-cage ring size AEI, RTH), butylene preferred (16-cage ring size, LTA, RHO) and the classical CHA structure (12-cage ring size) which favors equal amounts of ethylene and propylene.

4 Descriptors Used for the Activity in Solid Acid Catalysts

4.1 Acid Site Density

As mentioned above, zeolites are considered the main conduit for the transformation of oil-based feedstock and it was their implementation in FCC applications, where their superior activity compared to amorphous aluminosilicates (ASA) [2], led to their proliferation in refineries and other fields of catalysis. As such, the catalytic activity of zeolites is an important descriptor class and the following section will highlight some of the structural properties influencing it. We primarily attribute their activity in acid-catalyzed reactions to the presence of a charge imbalance resulting from the periodic substitution of Si$^{4+}$ with Al$^{3+}$ in the framework that generates a negative framework charge needing to be

![Figure 4. a) MTH product distribution for different zeolite frameworks based on pore size. Ethylene peaks marked by 0 and propylene by *. Reproduced with permission from Ref. [39]. Copyright (2010) Elsevier. b) The product distribution for cage-type zeolites can be further discriminated based on the cage-defining ring size. Reproduced with permission from Ref. [41]. Copyright (2019) American Chemical Society.](image-url)
balanced by a positive cation [7, 42]. In the case of a proton being the charge balancing cation, the material becomes a Brønsted acid, able to catalyze reactions involving the protonation of adsorbed substrates. As such, most activity descriptors for zeolites in acid-catalyzed reactions must be intrinsically linked to the number, strength and accessibility of these Brønsted acid sites (BAS). As the BAS concentration is a function of the framework Al, one of the most straightforward activity descriptors for zeolites is the material’s chemical composition, more specifically the Si/Al ratio (or in the case of zeotypes, the M⁴⁺/M³⁺ ratio). However, it is possible for some of the framework Al to become dislodged during post-synthetic treatment steps leading to extra-framework Al that no longer generates the Brønsted acidic bridging hydroxyls [43, 44]. Thus, an extensive number of tools exist to characterize and quantify these well-defined active sites, such as infrared and Raman spectroscopy [6, 45], solid state NMR [46, 47], or temperature programmed desorption measurements involving base probe molecules [7, 42]. A larger number of Brønsted acid sites (BAS) corresponds to a more rapid conversion of the substrate and higher activity. Nonetheless, for MTH chemistry it is generally observed that zeolites of intermediate acidity with Si/Al between 30–50 are preferred [39]. More acidic zeolites lead to a more rapid deactivation with the mode of deactivation being also affected (see below) [48, 49].

### 4.3 Acid Site Accessibility

4.3 Acid Site Accessibility

In addition to the number and strength of the acid sites, the accessibility of these sites plays another important role. Owing to the large internal surface area of zeolites, the majority of the acid sites are generated within the porous environment and accessibility to these pores will determine, in addition to the product selectivity (see above), also the activity of the material. We have already noted how differences in diffusion rates of the substrate can seemingly affect the interpretation of the constraint index for small-pore zeolites [16], and here we want to instead focus on the effects of confinement on the activity of zeolites. Once the molecule diffuses into the pore it starts to interact with the curved pore walls, primarily via attractive and repulsive van der Waals interactions [60, 61]. Depending on how closely the molecule size and pore width are matched, the molecule essentially becomes solvated by the framework [56, 62]. In the work of Iglesia and co-workers this confinement effect has been quantified by studying the oligomerization of light alkenes over different zeolite frameworks [55]. They observed that the smaller the framework pore structure became (TON < MFI < BEA < FAU < ASA), the higher the measured intrinsic rate constants were. This trend was also observed with alkane cracking [58], dimethyl ether homologation and methanol dehydration [53, 57], suggesting that the bimolecular transition states (larger than the individual reactants) experience a better fit in the constrained environment. Indeed, when plotting the rate constants against the void diameter, defined as the largest sphere that can be placed into the framework, the frameworks including the non-porous ASA fall on a line (Fig. 5a). To quantify this
correlation, they were able to use DFT calculated dispersive energies for interactions between organic substrates and inorganic hosts (frameworks). As the dispersive energy becomes more negative, indicating a stronger interaction between the transition state and the pore walls, the rate constants increase.

The concept of confinement also extends to catalysis performed in the liquid phase. This is especially important for reactions involving biomass-derived feedstock, owed to the high concentration of water in this feedstock. In addition to the high-water content in the feed, the large amount of oxygenates requires several hydrotreating and acid-catalyzed dehydration steps in order to generate the desired product molecules (typically furanics, aromatics, and/or cycloalkanes) used in fuel and as fine chemicals [27, 28]. Consequently, these reactions typically take place under relatively mild conditions (temperatures < 200 °C). In this state, the constraints of zeolite pores and the resulting confinement of substrates also leads to a significant impact on the catalytic activity. For acid catalyzed dehydration and alkylation reactions, zeolites tend to exhibit superior activity in this milieu compared to homogeneous acids [66–66]. This was attributed to the confined spaces, where the active sites, solvated hydronium ions, H₃O⁺(H₂O)ₙ, have an improved association with the substrate molecule due to the hydronium ions being less mobile than in homogeneous acids. Consequently, significantly higher rate constants were achieved (Fig. 5b). The stronger association with the substrate led to a higher gain in the entropy of activation, while the enthalpy of activation was the same as with non-constrained homogeneous acids. Analogous to how Iglesia et al. varied the framework for gas phase reaction, Lercher et al. studied the framework variation for alcohol dehydration in the liquid phase [64]. As the framework became larger (MFI < BEA < FAU < H₃PO₄), the transition state of the alcohol dehydration was more poorly solvated resulting in lower turnover rates (Fig. 5).

5 Zeolite Stability Descriptors

The previous section established the parameters that influence the catalytic activity of zeolites. However, zeolites that facilitate a rapid conversion of the substrate by containing a large number of acid sites tend to deactivate significantly faster. This appears to be the case in methanol to hydrocarbon reactions as well as several dehydration reactions related to the valorization of biomass feedstock [31, 65, 67]. Therefore, the following section will highlight the importance of the final class of catalyst descriptors, namely stability. Albeit that zeolites are known for their high (hydro)thermal stability, adverse conditions such as unselective side reactions, interactions between solvent and zeolite in combination with high temperatures and pressures can lead to a myriad of deactivation behaviors. Some of these are reversible, meaning the original activity can be recovered typically via high temperature regeneration processes; others tend to be irreversible, limiting the scope of application.

5.1 Zeolite Stability in the Gas Phase

In the field of MTH, stability is generally a function of the relative rates of coke and product formation. The deactivation mode follows a burning cigar model, with the active front moving through the catalyst bed leaving the deactivated part behind [68]. It can subsequently be regenerated by burning off the coke. Utilizing high-resolution X-ray diffraction data, the MTH process (including the deactivation) can be visualized. For SAPO-34, Wragg et al. followed the reaction by observing changes in the crystallographic c-axis that expands and contracts as reaction intermediates are formed and consumed [69, 70]. Applying the same methodology of tracing unit cell deformations with X-ray diffraction it was also possible to obtain a diagnostic descriptor for the extent of deactivation. For ZSM-5, the amount of coke deposited on/in the zeolite, was directly correlated with the difference between the refined unit cell vectors of a and b, (a-b) [71]. As more coke is deposited, the unit cell is deformed due to the formation of primarily tetramethyl-
benzene, a bulky intermediate of the MTH's aromatic cycle. Scanning along the axial length of a capillary fixed-bed reactor Svelle et al. were then also able to observe deactivation of the catalyst bed in action, following the typical burning cigar model [72]. Coking is closely related to the density of acid sites as well as their strength. Ideal material compositions are of intermediate acidity (e.g., Si/Al 30-50) as these limit the extent to which reactant molecules can interact with each other forming coke precursors. The acid strength is also crucial as shown for SAPO-34 over SSZ-13 (both CHA) as well as for the AFI framework (SAPO-5 versus SSZ-24), with the weaker acidity in the SAPO suppressing hydride transfer and cyclization reactions that lead to the rapid formation of aromatic coke molecules in the zeolite [59,73]. Furthermore, the void environment in different zeolite topologies also has a profound impact on the species generated that can lead to further deactivation. The larger the void space, the heavier the reaction intermediates. This applies to both cavity size in cage type zeolites (e.g., CHA, ERI, LTA, UFI) and intersection size in 3D zeolites (MFI, IMF) [74,75]. The heavier intermediates were correlated with a faster deactivation rate. In MTH it is also important to consider diffusional limitations as a contributor to catalyst deactivation as the long diffusional pathways in large crystallites can increase the extent of undesirable secondary reactions forming more coke. Consequently, the development of nanosized as well as hierarchical structures, containing both micropores and less restricted mesopores, has found increasing interest in this field [76,77]. The latter can be typically accomplished via desilication as a post-synthetic method [78,79], or via the use of surfactants and other templating agents (such as carbons) in the synthesis gel [77]. Improved accessibility to acid sites has been observed in hierarchical systems and this effect can be quantified using sterically hindered base molecules, known as the accessibility index [80]. These modifications facilitate a longer lifetime for zeolites during the MTH reaction [81]. It was noted that the formation of hierarchical systems can also increase the number of framework defects present in the system, which appeared to have an impact on the conversion capacity [82]. Strikingly, it was observed that these non-acidic silanols, typically associated with incompletely condensed Si-O bonds and/or removed T-atoms, seemingly initiate the formation of coke [83]. Studying a large set of ZSM-5 materials of different provenance, Barbera et al. established that active site concentration and crystal size had no direct correlation with catalyst deactivation (although catalyst activity was directly linked to these parameters) [84]. Instead, the deactivation rate was linked to the ratio of internal/external SiOH as quantified by the OH stretching bands at 3726 and 3745 cm$^{-1}$, respectively (Fig. 6a). It was proposed that the ideal ZSM-5 catalyst for MTH would have small amounts of internal defects, a large external surface area or both those aspects. The latter aspect of a larger external surface area (i.e., smaller crystal sizes) once more points toward diffusional limitations in large crystallites being an important driver of catalyst deactivation in the MTH reaction. Recently it has been shown by Losch et al. that smaller crystallite size (<1μm) does improve the lifetime, however, more strikingly it was the absence of defects that tremendously boosted the lifetime for the conversion of methanol in micron sized ZSM-5 [85]. This counter-intuitive behavior was explained by the high Si/Al preventing propylene from reacting further and by the possibility of the absence of diffusion limitations for these small molecules (methanol and propylene). However, the reported conditions favored the formation of propylene (MTP) and whether the same counter-intuitive correlation between crystal size and lifetime holds for MTH, where the absence of diffusion limitations for larger hydrocarbons cannot be ascertained, remains to be seen. Nonetheless, the significance of structural defects is clear.

5.2 Zeolite Stability in the Liquid Phase

The role of structural defects on zeolite stability has also been studied extensively in the field of aqueous phase catalysis as part of biomass transformations [65,87,88]. Especially in low-density zeolite frameworks (e.g., FAU, BEA) extensive deactivation was observed when the zeolite was immersed in hot liquid water. Unlike the formation of coke, this deactivation was irreversible as indicated by the loss of microporosity and crystallinity [89]. While the lability of the framework was initially associated with the Si/Al (less Al rich FAU deactivated more extensively) it was later found that the extent of deactivation was instead correlated with the number of structural defects [89–91]. This is an

![Figure 6. Zeolite stability in the gas phase (for MTH) as a function of internal SiOH (a) and zeolite stability in the liquid phase (aqueous cyclohexanol dehydration) as a function of Bronsted acid site concentration (b). In the latter, internal SiOH groups lead to a more detrimental zeolite performance in samples with low acidity. a) Reprinted with permission from Ref. [86], Copyright (2011) Elsevier. b) Reprinted with permission from Ref. [45], Copyright (2018), Elsevier.](image)
excellent example of the limitations and possible pitfalls that descriptors pose, as the correlation between higher Si/Al and the larger extent of deactivation does not necessarily imply causation. The Si/Al ratio in the investigated FAU system varied from 5 to 41, however, at such high Si/Al ratios the role of defect formation in highly dealuminated FAU cannot be neglected and its impact on zeolite stability was not considered at the time [90]. Instead, later studies on FAU and BEA established the more accurate correlation between stability and internal defect concentration [89, 92]. Indeed, removal of these defects led to an improved stability providing the necessary causation for their impact on stability [92, 93]. These structural defects allow for the condensation of water molecules that can hydrolyze Si from the framework leading to a loss of long-range order. While the presence of hot liquid water as a solvent is necessary due to the economic constraints placed upon biomass transformations, its adversarial behavior on zeolite stability can be partially mitigated by either eliminating the presence of defects or by limiting the concentration of water within the zeolite pores (Fig. 6b) [65]. The former is exceedingly difficult to achieve as even the use of fluoride anions in the synthesis does not prevent the formation of some residual SiOH [45]. This is likely owed to the polymorphism in BEA zeolite leading to extensive intergrowth areas. Minimizing the concentration of intraporous water, on the other hand, is more readily achieved by decreasing the acidity of the materials rendering them more hydrophobic [45, 88]. It should also be noted that crystal size has a beneficial role to play in stabilizing zeolites in hot liquid water, as indicated by a comparison in the lifetime between micrometer sized BEA zeolite and a sub-micron counterpart, despite a larger defect concentration in the former zeolite [94]. Likely, the dissolution of silica during the framework hydrolysis and transport out of the zeolite pores is hindered by the long diffusional pathways, thus preventing further hydrolysis. Similar stabilizing effects of zeolite particle size are also observed for steaming treatments [95].

While the above-mentioned behavior results in irreversible damage to zeolites, most biomass transformations also have to address the formation of carbonaceous deposits known as humins [96]. These species are typically polymeric structures that block access to, as well as potentially alter, active sites. Their formation is facilitated by the low stability of furanic substrates (derived from sugar molecules) when present in acidic condition leading to ring opening, self-condensation and subsequent polymerization. The relative propagation of these non-selective side reactions depends on factors such as acid strength, diffusional pathways (i.e., particle size) and acid site density [67]. For example, Prodinger et al. recently showed that the dehydration of furylethanol to vinylfuran is hampered by the competing formation of humins. Using a weak acid such as solid phosphoric acid, the selectivity towards vinylfuran was significantly lower compared to the outcome using microporous H-ZSM-5 [97]. This indicates that a sufficiently strong acid site is required to ensure a facile alcohol dehydration and minimize the acid-catalyzed humin formation. As such, descriptors used for gas phase MTH chemistry (DPE & Si/Al) should also be applicable here.

6 Conclusion

This brief review aims to capture the evolution of chemical descriptors starting with the early contributions by Prof. Weitkamp. In those early days, the main goal of Weitkamp as well as researchers at Mobil was the development of suitable test reactions to identify the pore size of novel zeolites. While there were certain limitations for these descriptors, their sensitivity towards shape selectivity in zeolites was nonetheless crucial for the further development and understanding of zeolite catalysis. For example, the concept of shape selectivity, has allowed the development of descriptors that define the product distribution in MTH chemistry. However, these modern chemical descriptors tend to increasingly address the intricacies of zeolite catalysts. This is in response to some of the early correlations, established with rudimentary descriptors, being found to be incomplete: Correlation does not necessarily equal causation. The refinement of our understanding for the MTH product selectivity with regard to the importance of the void space geometry within zeolites as opposed to simply pore window size is one such example. The achievement of these insights goes hand in hand with the development of more advanced characterization. Yet delving deeper into the workings of a zeolite catalyst also comes with trade-offs such as requiring special test conditions (e.g., pressure gap). This makes it difficult to propose descriptors that are generally applicable under industrially relevant conditions. We can summarize some of the more general descriptors discussed in this contribution as follows: Pore size and more specifically the void space in the channel intersections and cavities of microporous materials is one of the most important selectivity descriptors in MTH to date. All of this is facilitated by the activity of acid sites generated in aluminosilicates and SAPOs via the substitution of heteroatoms of varying valence charge. Their concentration (Si/Al), strength (DPE) and accessibility (dispersive VdW interactions as well as enthalpic and entropic values defining confinement) provide the necessary propensity for the activation and conversion of small molecules as well as the cracking of large substrates derived from oil-based or alternative renewable feedstock. Lastly, we discuss here stability descriptors with respect to reversible deactivation due to the formation of carbonaceous species in gas phase MTH reactions and liquid phase biomass transformations. In addition, adverse conditions such as hot liquid water promote irreversible deactivation such as the amorphization of zeolite frameworks leading to a loss of intrinsic catalytic activity. In both the gas phase and liquid phase, the presence of structural defects as well as the number and strength of acid sites.
appears to be closely linked to deactivation rates. This highlights the close relationship between Selectivity, Activity and Stability and the need for the careful design of zeolite catalysts based on a prior understanding of the chemistry facilitated by the use of descriptive structure/activity relationships, i.e., chemical descriptors.

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