Small-Pore Zeolites: Synthesis and Catalysis

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ABSTRACT: In the past decade or so, small-pore zeolites have received greater attention than large- and medium-pore molecular sieves that have historically dominated the literature. This is primarily due to the commercialization of two major catalytic processes, NO_x exhaust removal and methanol conversion to light olefins, that take advantage of the properties of these materials with smaller apertures. Small-pore zeolites possess pores that are constructed of eight tetrahedral atoms (Si⁴⁺ and Al³⁺), each time linked by a shared oxygen. These eight-member ring pores (8MR) provide small molecules access to the intracrystalline void space, e.g., to NO_x during car exhaust cleaning (NO_x removal) or to methanol en route to its conversion into light olefins, while restricting larger molecule entrance and departure that is critical to overall catalyst performance. In total, there are forty-four structurally different small-pore zeolites. Forty-one of these zeolites can be synthesized, and the first synthetic zeolite (KFI, 1948) was in fact a small-pore material. Although the field of 8MR zeolite chemistry has expanded in many directions, the progress in synthesis is framework-specific, leaving insights and generalizations difficult to realize. This review first focuses on the relevant synthesis details of all 8MR zeolites and provides some generalized findings and related insights. Next, catalytic applications where 8MR zeolites either have been commercialized or have dominated investigations are presented, with the aim of providing structure–activity relationships. The review ends with a summary that discusses (i) both synthetic and catalytic progress, (ii) a list of opportunities in the 8MR zeolite field, and (iii) a brief future outlook.

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1. INTRODUCTION

1.1. General Introduction to Zeolite Catalysts

Zeolites are a group of crystalline, microporous materials that are constructed from regular networks of alumina and silica tetrahedra (TO_4 – oxygen atoms bridge the tetrahedral atoms).^{1,2} These oxide networks, technically also known as tectoaluminosilicates, are often relatively open, through the presence of specific sub-2-nanometer pores and cages. Besides zeolites, that in the strict sense only have Si^{4+} and Al^{3+} in T atom positions, porous oxides with other elements that allow tetrahedral coordination, e.g., P^{5+} , Ti^{4+} , Ge^{4+} , Ga^{3+} , Co^{2+} , or Zn^{2+} , are known. The channels and voids allow for the intracrystalline transport, adsorption, and reaction of molecules and explain the use of the term molecular sieves for this broad class of inorganic materials. Currently, the diversity of existing crystalline molecular sieve topologies is documented in 235 frameworks.³ While some of these topologies are represented by vastly diverse compositions in the type of T atoms involved and their molar ratios, others are only represented by a single material. The former is illustrated by CHA (each unique framework topology is given a three letter code³), a framework encountered in the zeolite mineral chabazite, but also in synthetic silicoaluminophosphate (SAPO-34), aluminosilicate (synthetic zeolite SSZ-13)^{4,5} and more exotic versions (e.g., AlCoPO_4 ⁶). An example of the latter is EEI, so far, only found as a high-silica zeolite (Figure 1).^{7,8}

The focus in the present work is placed solely on zeolite compositions. There, the generation of a negative charge, when Al^{3+} is isomorphically substituted for Si^{4+} in the oxide framework, dictates the need for a balancing cation such as H^+ , Na^+ , or NH_4^+ , or even divalent cations when two charges

are in close proximity. This exchange capacity can be used to create catalytic sites inside the pores, leading to active site confinement.⁹ Zeolites are commercially employed in catalysis, adsorption (separation), and ion-exchange applications. Most catalytic uses are found in hydrocarbon (petrochemistry, refining) and environmental technology,¹⁰ while ion-exchange and sorption properties are respectively exploited in laundry detergent powders and adsorbents/desiccants. It is obvious that the size of the pores and the possible presence of additional cages or larger intersections influence the (organic) chemistry and catalytic applications that can result within. Typically, small-pore zeolites have pore sizes in the range of 0.30–0.45 nm, while medium-pore zeolite openings range from 0.45–0.60 nm and large pore materials have their largest pores in the range from 0.60–0.80 nm.¹¹

Although the first synthetic zeolite was a small-pore material (*vide infra*), the catalytic application of zeolites was initially heavily focused on large-pore zeolites. Since the discovery of the synthetic form of faujasite in the 1960s, the large-pore zeolite Y (FAU), with supercages, has been exploited in the fluid catalytic cracking of oil, a large scale catalytic operation producing gasoline.¹² Later the discovery of zeolite BEA and the introduction of MOR in catalytic processes fortified the role of large pore zeolites in petrochemistry, i.e., the catalytic upgrading of platform molecules from the refinery (e.g., transalkylation). With the advent of ferrierite (FER), MCM-22 (MWW), and ZSM-5 (MFI), medium-pore zeolites found commercial application as well, e.g., in olefin isomerization (FER), refinery dewaxing or xylene isomerization (MFI), and ethylbenzene synthesis (MWW).¹⁰ Many of these classic hydrocarbon processes rely on shape-selective effects inside the specific voids.¹³ In the 1990s, a push for extra-large pore materials resulted in the synthesis of zeolites UTD-1 (DON)¹⁴ and CIT-5 (CFI),¹⁵ with pore sizes close to 1 and 0.8 nm, respectively, as well as the generation of series of ordered mesoporous (alumino)silicates such as MCM-41.¹⁶ The new millennium brought about the search for catalytic processes dealing with alternative feedstocks and environmental remediation. Alternatives to crude oil have since been studied, with the goal of finding more sustainable (if efficient) routes to chemicals and materials, notably, from lignocellulosic biomass or (natural) gas. Dealing with biopolymer feedstock and its rather large sugar constituents¹⁷ has pushed zeolite development into mesopore-generation (e.g., hierarchical materials) as well as fueled the rise of Lewis acidic silicates such as Sn-BEA.^{18–22} Thus, far, new zeolite structures have not been targeted in biomass conversion, but rather the goal has been to adapt commercial zeolite catalysts to new processes.^{9,23,24} On the other hand, the prospect of upgrading small-molecule feedstocks such as natural gas (CH_4 ,²⁵ C_2H_6), syngas (CO/H_2),²⁶ and CO_2 ²⁷ and thereof derived platform molecules such as methanol and ethylene *did* stimulate the use and synthesis of small-pore zeolites in recent years. Together with the fast progress in catalytic environmental remediation, i.e., the use of Cu-zeolites for the reduction of vehicle NO_x emissions, these small-molecule conversions have triggered new synthetic strategies and allowed improved materials and even new zeolites to emerge.

1.2. 8MR Zeolites: Definitions and Scope of the Review

The 235 documented framework types thus present a diverse range of different pore and cavity systems with different potential uses. Considering only aluminosilicates (zeolites) and

Figure 1. EEI and CHA frameworks with isolated cage and an exemplary 8MR-window (blue) and the GIS framework without cage. O atoms are represented by straight lines, and every corner is a T atom position (EEI is an example of the three letter codes designated by the International Zeolite Association (IZA)³).

Table 1. Complete List of All Known Forty-Four 8MR Zeolite Frameworks and Four 8MR Silicates^a

IZA code	Material name ^b	Pore ^c	Cage ^d	ref	IZA code	Material name	Pore	Cage ^d	ref
ABW	Li-A(BW)	8	×	34	LEV	Levyne, ZK-20, SSZ-17, Nu-3	8 × 8	✓	35
AEI	SSZ-39	8 × 8 × 8	✓	36	LTA	Linde type A, ITQ-29	8 × 8 × 8	✓	37
AFX	SSZ-16	8 × 8 × 8	✓	38,39	LTJ	Linde type J	8 × 8 × 8	×	40
ANA	Analcim(t)e	irreg.	×	41	LTN	Linde type N	- ^e	×	42
ATT	RMA-3	8 × 8	×	43	MER	merlinoite, Linde type W	8 × 8 × 8	✓	44
BCT	Svyatoslavite	8	×	45	MON	Montesommaite	8 × 8 × 8	×	
BIK	Bikitaite	8	×	46	MTF	MCM-35, UTM-1	8	✓	47
BRE	Brewsterite, CIT-4	8 × 8	×	48	MWF	MCM-25	8 × 8 × 8	✓	51
CAS		8	×	50	NSI	Nu-6-(2)	8 8	×	49
CDO	UZM-25, MCM-65, RUB-37	8 × 8	×	52,53	PAU	Paulingite, ECR-18	8 × 8 × 8	✓	54
CHA	Chabazite, K-G, SSZ-13, SSZ-62	8 × 8 × 8	✓	4,55	PHI	Phillipsite, ZK-19	8 × 8 × 8	×	56
DDR	ZSM-58, Sigma-1	8 × 8	✓	57,58	RHO	Rho	8 × 8 × 8	✓	59
EAB	TMA-E, Bellbergite (later)	8 × 8	✓	60,61	RTH	SSZ-50	8 × 8	✓	62
EDI	Edingtonite, K-F	8 × 8 × 8	×	44,63,64	SAS	SSZ-73	8	✓	65
EEI	ERS-18, SSZ-45	8	✓	7,8	SFW	SSZ-52	8 × 8 × 8	✓	66
EPI	Epistilbite	8 × 8	×	67,68	THO	Thomsonite	8 × 8 × 8	×	63
ERI	Erionite, UZM-12	8 × 8 × 8	✓	69,70	TSC	Tschörtnerite	8 × 8 × 8	✓	
ESV	ERS-7	8	✓	71	UFI	UZM-5	8 × 8	✓	72,73
GIS	Gismondine, (Na-) P1	8 × 8 × 8	×	74	YUG	Yugawaralite, Sr-Q	8 × 8	×	68,75,76
GOO	Goosecreekite	8 × 8 × 8	×		ETL ^f	EU-12	8 × 8 8	×	77
IHW	ITQ-32	8 × 8	×	78	IFY ^g	ITQ-50	8 × 8 × 8	✓	79
ITE	ITQ-3, Mu-14	8 × 8	✓	80,81	ITW ^g	ITQ-12	8 × 8	✓	82,83
JBW	nepheline hydr. I	8	×	41	RTE ^g	RUB-3	8	✓	84–86
KFI	ZK-5	8 × 8 × 8	✓	87,88	RWR ^g	RUB-24	8 8	×	89,90

^aThis list is based on a refined search, using data from the Structure Commission of the International Zeolite Association (IZA) as a starting point.

^bMost prominent or first reported *aluminosilicate* members of the topology. Better-known, pure-silica representatives might exist (e.g., for DDR). Natural zeolites are recognized by their full name, and references for such zeolites are only given in case a synthetic route exists. “×” indicates intersecting channels, “|” indicates a parallel pore system, and “||” indicates nonintersecting channels in multiple directions (considered a 1-dimensional material). 8 × 8 × 8 does not necessarily mean these channels run in perpendicular directions (i.e., along *a*, *b*, and *c*). ^cCage (Present: ✓. Not-present: ×.) is defined here as an accessible void larger than the intersections of pores and being of sufficient size to allow for small organic molecule, e.g., methanol, adsorption. ^eLTN only has 6MR apertures and inaccessible cages. ^fRecently approved code by the IZA. ^gOnly reported in pure silica. IFY is obtained from all-silica LTA ITQ-29 by pressure-induced transformation. ITW is made in F-media using 1,3,4-trimethylimidazolium cation. RTE and RWR come from topotactic transformation.

direct synthesis methods, rings of T atoms containing as few as 3 (MEI²⁸) and as much as (excluding larger ones where T-atoms are not 4-connected) 14 members (CFI, SFH,

SFN)^{15,29,30} have been identified (the number of T atoms in the ring equals the number of oxygen atoms in the ring). In light of the above definitions and different catalytic scopes of

small and large pore materials, the entrance to and exit from the intracrystalline void spaces have been defined. As such, 8-membered ring (8MR, referring to T atoms, in fact 16 atoms are in the ring) structures are considered small-pore zeolites, while materials with openings limited by 10- and 12-membered rings are defined as medium and large-pore zeolites, respectively.³¹ Often, rings larger than 12 are denoted as extra-large pore materials. Medium, large, and extra-large pore materials can also contain smaller pores: LTL, *e.g.*, has its 1-dimensional 12MR channels intersected by 8MR openings.

Even though some large-pore zeolites behave like small-pore 8MR systems through intergrowth faulting of the main pore (*e.g.*, 12MR GME,³² note that a fault-free version has just been reported³³), this review will only focus on the synthesis and applications of pure 8MR zeolites (8 being the largest ring size) for reasons provided below. Besides the T atom definition of pores, the pore connectivity as well as the occurrence of larger cavities is of major importance for applications. For example, EEI has a very large cage ($5.6 \times 19.8 \text{ \AA}$), that is only accessible through 8MR windows (Figure 1), as is the case for another 8MR zeolite, SFW.⁸ 8MR zeolites without cages also exist: a commercially used example is GIS, seen in Figure 1. Table 1 lists the forty-four known 8MR zeolites. Additionally, the list contains four pure-silicate 8MR molecular sieves. When expanding this list to other T atoms (*e.g.*, common PO_4), a total of seventy-six 8MR microporous materials can be found.³

Given the importance of the fit between molecules and pores, it is fairly obvious that 8MR zeolites will excel in applications dealing with smaller molecules and ions.⁹¹ Perhaps it is no coincidence that the discovery of the “molecular sieving” effect itself was done with an 8MR zeolite, *cfr.* Weigel and Steinhoff in 1924. They discovered the rapid adsorption of water, methanol, formic acid, and ethanol vapors on natural chabazite (CHA), while acetone, ether, or benzene vapors were not adsorbed.⁹² Today, over 90 years later, synthetic versions of CHA are produced at the kiloton-scale for use as methanol-to-olefins (SAPO-34, mainly in China)⁹³ or NO_x reduction catalysts (Cu-SSZ-13).^{94,95} Even though 8MR zeolites have been known for quite some time, it is only recently that the two significant commercial catalyst uses mentioned have occurred. These technologies have stimulated recent research into 8MR zeolites and molecular sieves. Given these events, the objective of this review is to provide a critical and comprehensive overview of the chemistry, synthesis, and catalytic applications of 8MR zeolites (strictly only aluminosilicates) from the early days (1940s) to the present. A classic historic and general account of hydrothermal zeolite synthesis (up to 2003) was presented by Cox and Cundy.⁹⁶ Other comprehensive reviews in the field focus on one particular aspect of zeolite chemistry, such as more sustainable synthesis routes,⁹⁷ new frameworks since 2007 (focused on structural information),⁹⁸ catalytic applications for a specific group of substrates such as biomass,²⁴ C–H activation,⁹⁹ or nitrogen containing exhaust gases.^{100,101} At this time, there is a brief overview on synthesis strategies for small pore molecular sieves by Moliner *et al.*³¹ Thus, our goal in the present review is to provide in-depth discussions on both the synthesis and catalytic applications of 8MR zeolites in order to highlight structure–property relationships for this increasingly important class of materials.

1.3. Introduction to the Use of 8MR Zeolites as Catalysts

From the early days of applied zeolite science, 8MR zeolites have been investigated for sorption and separation applica-

tions.⁹² However, 8MR materials largely have been neglected as catalysts until recently (large and medium pore materials dominate in petrochemical applications). Since the discovery of the excellent olefin selectivities and yields using certain acidic 8MR molecular sieves during methanol conversion in the 1980s¹⁰² and the remarkable stability and activity during redox reactions of transition metal-exchanged 8MR zeolites for NO_x reduction in the 2000s, these zeolites have been extensively explored for catalytic conversions of small, often gaseous, molecules. Lately, there has been an increase in interest due to changes in cost/availability of gaseous feedstocks and emission legislation.¹⁰³ An overview of prominent reactions where 8MR zeolites have been used is found in Figure 2.

Commercial applications (current and previous) of 8MR zeolites include materials that have the following topologies: CHA, EDI, ERI, GIS, LTA, MER, and RHO.¹⁰ Most of these materials are used for separations and sorption, while ERI, CHA, and RHO also are exploited in catalytic applications. ERI was used as a hydrocracking catalyst in refineries, before its replacement by ZSM-5 (a 10MR-zeolite of the MFI topology). Specifically, ERI was used in the Selectoforming process, aimed at increasing the octane number of light naphtha by the shape-selective cracking of short linear alkanes while preserving the branched ones (section 3.6.1).¹⁰⁴ Besides MTO, the reaction that is industrialized with SAPO-34 (CHA), the selective catalytic reduction (SCR) of NO_x with Cu-SSZ-13 is now being exploited worldwide. The catalytic synthesis of methylamines (at one point, commercial based on large pore-zeolite MOR) has been performed with 8MR zeolite Rho (RHO) at the pilot stage. RHO was useful in order to exploit shape-selectivity and avoid the formation of trimethylamine, but it never reached the commercial stage. Two reactions related to MTO are the ethanol dehydration and the ethylene oligomerization-cracking processes (Figure 2). The former is not to be mistaken for the MTO-analogous ethanol-to-olefins route, as it can be performed through somewhat different reaction routes and conditions, as C–C coupling is not per se needed (unless propylene is formed). Lastly, there is the partial oxidation of methane-to-methanol, with the use of O₂ (or N₂O) as oxidant. This reaction, discovered on Cu-exchanged ZSM-5^{105,106} and later observed from other larger-pore materials,¹⁰⁷ has recently also been reported with Cu-exchanged 8MR zeolites by Lobo and co-workers.²⁵ The similar nature of these catalysts with those used in SCR research warrants discussion that is provided below.

Although the CHA-materials dominate the industrial catalytic applications, numerous other 8MR materials have been explored for SCR, MTO, and methylamine synthesis, and sometimes, they yield better results with respect to the industrial standards. Here, after we thoroughly discuss the synthetic details of 8MR zeolites in the next section, this review will focus on selected catalytic data in order to demonstrate structure/activity relations of 8MR zeolites (section 3). Other applications, summarized below (provided for completeness), will not be discussed in detail.

While we limit our presentations to catalytic applications of 8MR zeolites, we mention the largest commercial applications of 8MR zeolites (volumetric scale) to inform readers that catalysis remains a growth area for these types of zeolites. The largest commercial applications for 8MR zeolites are still found in ion-exchange and sorption/separation. The use of zeolites P and A (GIS and LTA, respectively) in detergent-builders, *e.g.*, to remove Ca^{2+} ions from aqueous solutions, is well-known.

Figure 2. Reported important reactions with 8MR zeolites. Methanol to olefins and NO_x reduction (solid lines) are commercially applied, at this time, using 8MR materials. The dashed boxes have only been investigated at small or pilot plant scale (amines) or have been shut down (Selectoforming). MMA, DMA, and TrMA, respectively, are mono-, di-, and trimethylamine. Methane oxidation can also use N₂O as an oxidant.

Other common detergent-builders are the large pore materials zeolite X and Y.¹⁰⁸ Also, 8MR zeolites (LTA) are often used as dessicants. Furthermore, in gas sorption and separation, 8MR zeolites are of major importance, due to their ability to discern between short chain alkanes and olefins,¹⁰⁹ different light hydrocarbons,^{110,111} CO₂/CH₄,¹¹² H₂/N₂, and CO₂/N₂.¹¹³ Often zeolite membranes are constructed in this context (LTA).^{114–116} Aside from these common applications, small-pore zeolites have been explored in all kinds of specialty devices and materials.¹¹⁷ Thin films of pure-silica CHA have been assessed in low-dielectric constant applications,¹¹⁸ while aluminous LTA has been applied in films for humidity sensors¹¹⁹ and Ag-LTA in photoluminescent materials.¹²⁰

2. SYNTHESIS OF 8MR ZEOLITES

2.1. Introduction to Different Strategies for Making 8MR Zeolites

Of the forty-four 8MR zeolites listed in Table 1, three are found as natural minerals only and no route for their synthesis exists to date (these lack an entry in the reference column in Table 1). For the remaining forty-one zeolites, a dedicated synthesis route, usually leading to a pure-phase product, exists. When analyzing the different routes to these 8MR aluminosilicates, a set of distinct synthetic approaches can be identified (Table 2). These methods will be explained one by one, from A to G, in the following paragraphs. Then, in section 2.2, an overview of all synthetic 8MR zeolites is presented, with an indication of which methods have been reported for each framework. Specific examples and mechanistic insights of the use of these methods (other than those in the next paragraph) are found

Table 2. Distinguishable Routes for the Synthesis of 8MR Zeolites^a

Code	Method	Typical example
A	Geothermal mimicking/high T approaches	synthetic epistilbite (EPI)/CAS
B	Hydroxide media, alkali cation SDA ^b	Linde type A (LTA)
C	Hydroxide media, OSDA (often with alkali)	SSZ-13 (CHA)
D	Interzeolite conversion (IZC) ^c	SSZ-39 (AEI)
E	Charge density mismatch (CDM) ^d	UZM-5 (UFI)
F	Fluoride media, OSDA	ITQ-32 (IHW)
G	Topotactic condensation	CDS-1 (CDO)

^aSDA: (inorganic) structure directing agent; OSDA: organic structure directing agent. ^bOSDA-free, seed-assisted hydroxide methods are also included here, as these are mostly reported for 8MR zeolites that can be made in the absence of OSDA with strong alkali, e.g., CHA, RTH, not known from unseeded hydroxide media OSDA-free synthesis, is the exception to this.¹²¹ (This contrasts with a lot of high-silica, large-pore zeolites (BEA, MFI), whose syntheses without OSDA were reported long after their discovery through the use of OSDAs.) ^cAlways with inorganic cations and/or OSDAs. ^dAlways with OSDAs.

throughout section 2.3, where all synthetic progress of the relevant 8MR zeolites is detailed per topology.

The first forays into zeolite synthesis were conducted by geothermal mimicking (Method A, Table 2), in an attempt to simulate the mineralization process found in the Earth's crust. This is mostly done by bringing mixtures of alkali, silica, and alumina (often glasses), with compositions close to that of the natural zeolites, to high pressures and temperatures. The pioneer of (classic) zeolite synthesis was Richard M. Barrer, who meticulously explored crystallization fields with different

alkali cations and Si/Al ratios.¹²² Soon, new zeolite recipes began emerging from his school in the 1940–50s and from research at Union Carbide (Linde type materials). Early on, several attempts were made to obtain synthetic chabazite, but the first synthetic 8MR zeolite prepared was likely analcite (ANA), a dense zeolite with little use for molecular sieving, dating back to 1882.^{123,124} In 1948, while looking for synthetic chabazite, Barrer discovered the first synthetic zeolite with no natural counterpart, and he documented its chabazite-like behavior.¹²⁵ The zeolite later turned out to be an 8MR material with the KFI topology¹²⁶ and thus analogous to the ZK-5 zeolite (in the meantime reported) and its structure (Mobil).^{88,127} Another 8MR milestone came in 1956, when R. M. Milton (later joined by Breck and co-workers) at Union Carbide demonstrated the synthesis of LTA (also not found in nature), with excellent ion-exchange properties.^{128–130} To this day, the production of this so-called zeolite A is one of the largest scale manufacturing processes of all synthetic zeolites, mainly due to its use as a detergent-builder. Several 8MR zeolites were discovered by these pioneers and others in their wake, by using different alkali as structure-directing agents in hydroxide media (Method B, Table 2): lithium-ABW (1951), potassium-EDI (K–F, 1956), rubidium-ATT (RMA-3, 2005), cesium-BIK (at Mobil, 1989), sodium-cesium-RHO (Rho, 1973), etc.

In 1961, Barrer introduced a new method to prepare zeolites by adding charged organic ammonium and alkylammonium species in the gels.^{131,96} This breakthrough effectively pioneered the use of organic structure directing agents (OSDAs) in zeolite synthesis (Method C, Table 2). LTA, for instance, was soon thereafter made in the presence of tetramethylammonium (TMA).¹³² The use of organic cations, typically bulkier per charge than classic alkali cations, revolutionized the synthesis field. Important was the realization that the larger organic cations required less aluminum to be built-in in the zeolite framework (countercharge), thus opening up the possibility of high-silica materials. Initially, only larger pore materials were discovered using OSDAs, such as the 10MR MFI and the 12MR-zeolites MWW and BEA. The first OSDA-directed 8MR zeolite was EAB (1970), containing a medium-large cage, made by using a combination of TMA and sodium cations.⁶⁰ An excellent example of this strategy (Method C, Table 2) for 8MR zeolites is the synthesis of CHA-type zeolites that can now be prepared over a very wide range of Si/Al ratios by using the large *N,N,N*-trimethyl-1-adamantyl-ammonium cation (ADAM) as OSDA.⁴ This method, invented by Zones and based upon stabilization of the large CHA cage by the organic, is industrially used to make the 8MR zeolite (SSZ-13) for exhaust cleaning.¹³³ Up to today, the use of new and complex OSDAs continues to lead to new zeolites¹³⁴ or new recipes for known zeolites, the latter often with access to higher Si/Al ratios.^{135,136} By means of illustration, the two OSDAs that can be used to prepare the EEI zeolite (Figure 1) are illustrated in Figure 3, along with the organic initially reported for SFW, an interesting zeolite related to CHA, with a very large cage. The most recent example of Method C (OSDA/hydroxide media) is the synthesis of EU-12 by using choline (*N,N,N*-trimethyl-ethanolammonium), Rb^+ , and Na^+ (8MR-zeolite ETL, 2016).⁷⁷

Barrer also introduced the use of a zeolite as sole source for making another zeolite, by studying the hydrothermal transformations of analcime in the presence of metal salts (yielding KFI with barium halides for instance).¹³⁹ Dwyer and Chu presented the transformation of FAU, still in its growth

Figure 3. OSDAs for making EEI (Figure 1) or SFW (Figure 10) zeolites in hydroxide media. The charged quaternary nitrogen atoms are marked in red. For SFW, more practical organics have been found recently, through computational OSDA design. The work of Deem et al. is a good example of this strategy.^{137,138}

medium and considered metastable, into a MAZ-zeolite (ZSM-4, or Omega) in the presence of TMA at 100 °C. Normally, the more dense zeolite P (GIS) is expected in the absence of TMA. Also, the MAZ zeolite appeared to nucleate on the surface of the dissolving FAU-crystal.^{140,141} Later, Zones reported an interesting series of experiments that involved the transformation of zeolite P (GIS) and Y (FAU) into a range of high-silica 8MR zeolites (LEV, CHA, AFX) by the addition of organocations, e.g., ADAM, and by starting from actual dry zeolites.^{142–144} Davis and co-workers later used (diluted) alkaline earths and successfully synthesized CIT-4⁴⁸ (synthetic BRE, use of seeds) and epistilbite (EPI) from zeolites P1 (GIS) and L (LTL).⁶⁸ Due to peculiar differences between this method of interzeolite conversion (IZC) and classic hydroxide media reactions that use separate (and different) silica and alumina sources, we consider this a distinct method (Table 2, Method D). The Sano group reported a number of interesting IZC-based studies that yielded relevant 8MR zeolites such as AEI, CHA, and LEV, often from FAU precursors (see section 2.3, with the respective frameworks).^{145,146} The observations that IZC often gives faster syntheses than identical recipes with traditional inorganic sources and that, sometimes, only IZC leads to a particular zeolite, e.g., AEI, have led to the idea that structural similarities (composite building units, cages, specific membered rings or other less-defined structures, e.g., ladders; collectively sometimes referred to as “nanoparts”) between starting and product zeolites play, under the right conditions, a decisive role in the nucleation/growth of the new material (exemplified in Figure 4 for FAU to CHA).^{145,146} This is similarly asserted in seeded-synthesis.¹⁴⁷

A new, creative approach to zeolite synthesis emerged from researchers at UOP in the 2000s, when Lewis et al. introduced the concept of charge density mismatch (CDM, Method E, Table 2).¹⁴⁸ This approach (technically a variation on method C) is based on the creation of an initial mixture that is not able to crystallize because of a mismatch between the low charge density of the used OSDA and the high charge density of the potential aluminosilicate network (at low hydroxide content, often only sourced from the OSDA). Often, the inorganic-cation free, mismatched mixture is a solution, rather than a gel in the case of alkali cations. Then, a second, crystallization-inducing, high charge density OSDA (often TMA or alkali cations) is added, but only in minute amounts. This OSDA cannot effectively dominate structure formation nor balance all Al present but triggers condensation. This forces the SDAs to work together. The classic example is the synthesis of 8MR UZM-5 (UFI, 2003) using tetraethylammonium (TEA) initially and TMA and Na^+ in a later stage.^{73,148}

A game-changer in molecular sieve synthesis was the introduction of fluoride ions as mineralizing agent, traced

Figure 4. Cartoon illustrating the hypothesis that *nanoparts* are involved in the FAU-to-CHA IZC. Adapted from ref 145.

back to Flanigen and Patton in 1978.¹⁴⁹ Typically, the more neutral synthesis media, often based on equimolar HF to OSDA(OH[−]) addition, in the absence of alkali, prove successful to make less dense, high-silica zeolites and pure-silicates (Method F, Table 2, Caution: HF is extremely corrosive). For several known 8MR zeolites, fluoride routes have been successfully explored as alternatives to hydroxide protocols: some with minor adaptations (e.g., CHA), some with largely different OSDAs (LEV).¹²² A few new 8MR zeolites, discovered and exclusively found in fluoride media, are ITQ-32⁷⁸ (IHW) and SSZ-73⁶⁵ (SAS). Their OSDAs and structures are seen in Figure 5. IHW is somewhat of a special

Figure 5. OSDAs used for SAS, IHW, or ITE (ITQ-3) zeolites in fluoride media. Mu-14 OSDA is shown for comparison, but not used in F[−]-media. For IHW, the double-charged OSDA promotes a large Al incorporation and yields ITQ-32 with Si/Al ratios between 13 and 32, while the piperazine-derived OSDA (upper) leads to a higher Si/Al (>300) material.⁷⁸

case, as it has 12-ring connections between the [100] channels, but there are no 12-ring channels, classifying it as an 8MR zeolite. A final example is zeolite ITE, originally discovered in pure-silica form, in low water fluoride media, but Al was also said to incorporate.¹⁵⁰ Later, Valtchev et al. found a procedure to prepare Al-rich ITE in classic hydroxide gels, and their OSDA is remarkably different (Figure 5).^{80,81}

It has been discovered that 2D-layered precursors could transform into 3D-frameworks upon high-temperature treatment (calcination) by the condensation of silanol groups in the layers that release water (topotactic condensation, Method G, Table 2). Marler and co-workers performed pioneering efforts in this synthetic area. Among the first zeolites prepared this way was FER, from the PREFER layer.¹⁵¹ Certain zeolites can (so far) only be made through the topotactic mechanism. The classic 8MR example is the synthesis of the CDO framework from the PLS-1 or RUB-36 or UZM-13 layers. In the case of CDO, the layers also have a FER structure, but they are arranged in a different way due to the organic.¹⁵² These layers are synthesized hydrothermally and thus come stacked with organic moieties. PLS-1 is, for instance, made with TMA and K⁺ cations in a silica,¹⁵³ water, and dioxane mixture, while RUB-36 and UZM-13 are made with diethyldimethylammonium cations.^{52,154} The latter two layers have been reported with Al incorporated, thus leading to zeolite versions of the CDO topology.¹⁵⁵ Aluminosilicate CDO is also found in the isostructural MCM-65 zeolite.^{53,156,157} The topotactic conversion of RUB-36 to a silicate version of CDO is shown in Figure 6. A recent trend in material design is to take the layered precursors and pillar them with additional reagents, such as e.g. dimethyldichlorosilane, to obtain interlayer expanded materials. The connecting atoms are (mostly) not 4-fold coordinated in the framework (not strictly zeolites), but it can be an interesting route to introduce heteroatoms in the material for certain applications.¹⁵⁸ In the context of creating 8MR, the expansion concept is less useful, as the condensation of the classic layers (without expansion) usually creates at least an 8MR.

Figure 6. Topotactic conversion of RUB-36 layers to the CDO framework. Aluminum T atoms can be present in this conversion. Purple = Si; red = O; blue = terminal oxygens. The OSDA here (green center = quaternary N) is diethyldimethylammonium. The light blue arrow corresponds to 11.1 Å. Left part adapted from Marler et al., ref 152, with permission of The Royal Society of Chemistry.

Table 3. Reported Methods and Si/Al Ranges for the Forty-One 8MR Synthetic Zeolites^f

IZA code	Si/Al range of the materials ^a	METHOD ^b	IZA code	Si/Al range of the materials	METHOD
ABW	1	B, D	ITE	17 - 35 ⁸⁰ , 33 - ∞ ⁸¹	C, F
AEI	5 - 25.5 and 266 (Table 4)	C, D, F	JBW	1	B
AFX	3.7 - 16.7 ¹⁵⁹	C, D	KFI	1.7 - 4.2	B, C, D
ANA	1.5 - 5	A, B, D	LEV	1.9 - 49.0 (Table 6)	B, C, D, F
ATT	3.5 - 3.9	B	LTA	1-5.5, 8.3 - ∞ (Table 7)	B, C, E, F
BCT	1	A	LTJ	1.08	B
BIK	8.9 - 25	B	LTN	1	B
BRE	2.9 - 3.0	D	MER	1.5 - 3.6	B, C, D
CAS	5	A	MTF	20.8 ⁴⁷ - ∞ ¹⁶⁰	C, G
CDO	19-78 ⁵² , 102-∞ ¹⁵⁵	G	NSI	12 - ∞ ¹⁶¹	G
CHA	1.15 ⁴⁴ - ∞ ¹⁶² (Table 5)	B, C, D, F	MWF	3.4 ⁵¹ - 4.3 ¹⁶³	C
DDR	16 ¹⁶⁴ - ∞	C	PAU	2.9- 3.7 ^{54,165}	C
EAB	2.7-2.9	C	PHI	2 ¹⁶⁶ , 2.6 ¹⁶⁷ , 1.5-3.1 ⁵⁶	B
EDI	1.32 ¹⁶⁸ -1.5 ⁶³	A,B,C ^d	RHO	2.8 - 8	B, C, F
EEI	70.3 ⁷ and >250 ⁸	C	RTH ^c	6 - 59 ¹⁶⁹ , 15 - 100 ⁶²	C, D, F, G
EPI	3	A	SAS	254 (s)	F
ERI	2.8 - 5.5 ^{60,170} , 4.7 - 7.4 ⁷⁰	C, D, E	SFW	8 ^e	C
ESV	8.1 - 8.4	C	THO	1	A
ETL	9.6	C	UFI	6-11 ¹⁷¹⁻¹⁷²	E
GIS	1-3	A, B, C, D	YUG	± 3	A, B, D
IHW	13 - 32, >300	F			

^fFrameworks highlighted in blue are discussed in detail in section 2.3. ^aMolar range over different methods and reports (not all referenced): can be incomplete as this is a tentative attempt/estimate. When no continuous range is reported, or methods diverge too much, two ranges are given. (s) indicates that no Si/Al was reported and that the Si/Al ratio of the synthesis recipe is given. ^bSee Table 2: Method A = geothermal mimic or high T approaches (e.g., up to 1200 °C for CAS⁵⁰); B = hydroxide media + alkali; C = hydroxide media + OSDA; D = interzeolite conversion; E = charge density mismatch; F = Fluoride media + OSDA; G = topotactic condensation. ^cRTH can also be made by seeding borosilicate, yielding products in the Si/Al 35–57 range¹²¹ and in pure-silica forms.^{173,174} ^dFor EDI: metal–amine complex used alongside OSDA. ^eClaimed: 6–25¹⁷⁵

Figure 7. Largest cages of the ten most relevant 8MR frameworks with their pore descriptors. Adapted from parts of the IZA Web site.³ Colors for LEV cage are discussed in section 2.3.8.

Now that a concise overview of the generalized strategies for 8MR syntheses has been presented, we elaborate further on details for specific 8MR zeolites. Reviews on more generalized mechanisms of zeolite synthesis, applicable for all types of zeolites, can be found elsewhere and are focused on more classic zeolite synthesis (OH^- , OSDA, alkali, F^-), e.g., see Cundy and Cox.¹⁴¹

2.2. Overview of Si/Al Ratios and Methods per Framework

Table 1 lists all 8MR zeolites, while section 2.1 (Table 2) identifies a set of distinct routes for their synthesis. Table 3 shows which methods have been reported for each 8MR aluminosilicate. Additionally, the reported ranges of Si/Al ratios that can be obtained by direct synthesis are shown (tentative). The Si/Al range is often method-specific: for example, when a zeolite can be made in both OH^- and F^- media, Si/Al ranges of materials made in the latter are often higher.

2.3. Synthesis Details of 11 Significant Frameworks

Based on the openness of topologies (2D-3D, cages), the amount of synthesis and application studies reported, and their (potential) catalytic relevance, we have selected the 11 most important 8MR zeolite frameworks and have detailed the progress on their synthesis. The aim is to (i) highlight interesting synthetic strategies or unique features of the synthetic approaches by concrete examples and (ii) develop links between topologies. These 11 topologies are highlighted in Table 3. Unsurprisingly, these are the ones where multiple methods of synthesis have been explored. Second, ten of these topologies have large cages, explaining their usefulness in catalysis and sorption (Figure 7). This review has no intention to draw or explain the structure of every topology in detail, and it refers the reader to the IZA³ and Zeomics resources.¹⁷⁶ However, some structural features and important building units will be shown when useful to the discussion of the synthetic method. Zeolite P (GIS) is the only framework in the selected series without large voids, but this zeolite is often used in ion-exchange to soften water.

2.3.1. AEI. 2.3.1.1. *Structure and Implications.* The AEI topology, as many others, was first encountered in aluminophosphate (AlPO-18) and SAPO-type compositions.¹⁷⁷ The framework can be described entirely of d6r-building blocks (d6r = double 6MR = hexagonal prism) without the need for any other composite building unit. Herein, we refer to such topologies as part of the “d6r-only” family. In AEI, these building units are linked by 4MRs, to form chains and eventually planes, with the d6r units all aligned in the same way (Figure 8). These planes are stacked along the *c*-axis, each with a 180° rotation, and this leads to the asymmetric, pear-like cage with a sort of side-pocket (Figure 7). The cage has also been described as basket-shaped, although that expression fits the cage of 8MR zeolite ESV better.⁷¹ If the planes in Figure 8 are not rotated, but just stacked, the CHA-structure is obtained (vide infra).

Figure 8. Building the AEI framework from linking d6r in chains to form planes, and stacking those planes.

Zones et al. discovered a recipe yielding the aluminosilicate version of AEI and named it SSZ-39.³⁶ Wagner et al. noted that the zeolite formed with a range of organics (examples in Table 4) in mixtures with a medium Si/Al ratio (15) and a lot of

Table 4. Chronologic Overview of Reported AEI-Zeolite Syntheses (Entry 1 = Oldest)^c

E	sources	OSDA	synthesis mixtures composition relative to Si				Product		ref
			Al	OSDA	Na ⁺	H ₂ O	μm	Si/Al	
1	NH ₄ -FAU (Si/Al 2.6) + sodium silicate		0.067	0.14	0.52	30	-	7.4	36,178
2			0.02	0.14	0.52	30	-	25.5	36
3 ^a	Al(NO ₃) ₃ + TEOS ^a	DEDMP	0.0017	0.5	0.6 (HF)	4.9	1.5-2.5	266	180
4	steamed NH ₄ -FAU (Si/Al 2.6) + sodium silicate		0.067; 0.033	0.17	0.40	40	0.5-1.0	7.4; 9.1	181
5	H-FAU _{s,a} ^b		0.09; 0.063	0.2	0.05	5	0.4-0.6	11.1; 14.9	182
6	H-FAU _{s,a} ^c	TEP	0.033	0.3	0.1	5	0.5	20.6	183
7	H-FAU _{s,a}	DEDMP	0.063	0.2	0.2	7.5	0.2-0.6	12.0	183
8		cis/trans-3,5 = 48/52	0.067	0.14	0.51	28	0.5-1	6.2	184
9	steamed NH ₄ -FAU (Si/Al 2.6) + sodium silicate		0.033	0.14	0.57	28	-	9.5	184
10		cis-3,5/cis-2,6 = 50/50	0.033	0.14	0.57	28	0.5-1.0	8.7	184
11	NH ₄ -FAU + sodium silicate ^d		0.056	0.14	0.54	19	-	13.0	185
12	H-FAU _{s,a}	cis/trans-3,5 (?)	0.094	0.2	0.2	15	0.3-0.4	8.2	186
13	H-FAU _{s,a}	DEDMP + TEP	0.059	0.14 + 0.06	0.1	5	0.2	14	187
14	H-FAU _{s,a}	TEP	0.090	0.1	0.1	5	0.04-0.05	8.5	188
15	H-FAU _{s,a} + silica sol	cis/trans-3,5 (?)	0.033	0.17	0.18	3.3	0.2-0.3	16.4	189

^aE = entry, DEDMP = *N,N*-diethyl-2,6-dimethylpiperidinium, TEOS = tetraethylorthosilicate, TEP = tetraethylphosphonium. Product crystal sizes are given in μm, mostly from electron microscopy. ^bFluoride-media synthesis (F/Si ratio is found in Na⁺-column) with addition of SSZ-39 seeds, made according to the Zones patent (first entry). DEDMP was also tested by Zones et al. in similar gels, yielding only zeolite SFF.¹⁹⁰ ^cs,a = steamed + acid-leached. ^d0.1 NH₄F/Si was added, as well as 10 wt % of AEI-seeds. ^e(NH₄)₂SiF₆-treated, dealuminated FAU, LZ-210.¹⁴⁴

hydroxide; the latter needed to solubilize the aluminum.^{36,178} They noted that in these cases, the inorganic gel composition can dominate over the organic/inorganic interactions and lead to cage-containing zeolites with even-membered ring constructions and small portals (e.g., AEI, AFX, CHA, SFW, ... vide infra). The even-membered rings (8MR, 6MR, 4MR) are hypothesized to form more readily at high Al-substitution (than 5MR), because the strict alteration of Si and Al (Löwenstein's rule) can more easily avoid the unfavorable Coulombic interactions when two negatively charged alumina tetrahedra are close to each other (i.e., in the extreme case, Si/Al = 1 can be obtained in a 6MR but never in a 5MR).

2.3.1.2. AEI Zeolite Synthesis. Since this zeolite has proven merits in catalysis,^{179,181} a detailed discussion of its synthesis is warranted. Table 4 presents an overview of most of the reported AEI syntheses.

Figure 9. Competition from the ratios of reflections measured in PXRD between small-pore AEI and large pore GME zeolites as a function of the concentration of the *N,N*-dimethyl-*cis*-3,5-dimethylpiperidinium OSDA. The modeling energy and OSDA position for GME are accurate and found in ref 33. The energy for AEI is found in earlier work,¹⁹² without the optimal OSDA position documented: A simple cartoon showing one per cage (confirmed from various techniques) was made.

The original patent on SSZ-39 claims a set of different organics. Ten of these are effectively based on piperidine, with different, often methyl, substitutions on the ring and with the nitrogen quaternized by methyl or ethyl groups. The foremost examples are *N,N*-diethyl-2,6-dimethyl-, *N,N*-dimethyl-3,5-dimethyl-, and *N,N*-dimethyl-2,6-dimethylpiperidinium (Table 4, entries 1, 4, and 9). Typically, these OSDAs, e.g., DEDMP in entry 1, lead to SSZ-39 with a Si/Al ratio around 7.5, in synthesis mixtures with Si/Al ratios of 15, with the help of a FAU zeolite as aluminum (and partial Si) source. Evidently, the different Si/Al ratios in the product and synthesis mixture reveal a low yield, as part of the silica remains unused. Another patented OSDA was based on an azoniabicyclononane (Table 4, Entry 2), and when tested in a Si/Al 50 mixture, a material was produced with a Si/Al ratio of 25 (a value so far not attained for piperidinium-OSDAs in OH-media). This is still the lowest Al-substitution reported in AEI zeolites made in hydroxide media. Later, Cao et al. claimed a route for AEI (with Si/Al > 200) also using DEDMP in Al-deficient fluoride gels, based on using SSZ-39 seeds made in hydroxide media (Table 4, entry 3). However, Zones et al. published a thorough study investigating the role of a range of piperidinium-based OSDAs, also DEDMP, in fluoride media, but never obtained AEI.¹⁹⁰

Moliner et al. reproduced the original synthesis of SSZ-39, in the context of deNO_x catalysis, with the use of *N,N*-dimethyl-3,5-dimethylpiperidinium (*cis*- and *trans*-3,5; unspecified isomer ratio, Table 4, entry 4).¹⁸¹ They noted the large impact of different sources on the success of making SSZ-39 in hydroxide media, and they showed that only a specific combination of a FAU zeolite precursor, also a member of the d6r-only family, and sodium silicate (as in Zones' patent) yielded SSZ-39. Later, Dusselier et al. showed that sodium silicate was replaceable, e.g., by using TEOS or colloidal silica, as long as the FAU-zeolite Al-source was used, and the relatively high OH⁻ and Na⁺ contents remained.¹⁸⁴ Dusselier et al. also investigated the influence of diastereo- and structural isomers of the tetramethylated-piperidinium OSDAs by using different *cis*/*trans*-3,5 mixtures (ranging from 48/52 to 98/2) and mixtures of these with *N,N*-dimethyl-*cis*-2,6-dimethylpiperidinium (*cis*-2,6). From an economic point of view, these 3,5- and 2,6-dimethylpiperidine-based molecules are important, since their precursor dimethylpyridines are among the most common commercially produced alkylated pyridines.¹⁸⁴ The *cis* and *trans* isomers of the 3,5-form both arise during the hydrogenation of the aromatic ring, while for the 2,6-form, the *cis*-

isomer dominates due to steric hindrance. Dusselier and co-workers showed specific conditions where SSZ-39 could be made, with *cis*-3,5, *trans*-3,5, or *cis*-2,6 isomers and, even tertiary, mixtures thereof (Table 4, entries 8–10). As the OSDA is often one of the decisive cost factors in commercial zeolite synthesis, these results are thus important, as mixtures (in line with the organic production) could be used instead of more expensive pure isomers. Although mixtures worked, the authors noted remarkable isomer-dependent trends for the AEI zeolite synthesis. A relative rate of formation trend was documented (in the studied conditions: *trans*-3,5 > *cis*-3,5 > *cis*-2,6). Second, it was shown that preferential incorporation existed (visible in ¹³C MAS NMR and confirmed by zeolite dissolution), when isomers were presented in competition (*trans*-3,5 > *cis*-3,5 and *cis*-2,6 > *cis*-3,5 isomer). Recently, Shantz and co-workers deepened the isomer-study, confirming most of the findings and the *trans*-induced faster rate of formation, while also carefully analyzing the solid yields. Additionally, in Si/Al 45 synthesis suspensions, a small but clear increase in the Si/Al ratio of the material is found when increasing the *trans*-isomer content.¹⁹¹ On a side note, recently it was found that when the concentration of water content of syntheses with pure *cis*-3,5 was lowered (in fact only going from H₂O:Si 35 to 20, in conditions like those of Table 4 entry 8), another zeolite formed. This zeolite, CIT-9, proved to be a fault-free GME. The concentrated *cis*-3,5 route thus ended a 40-year search for a simple recipe to a porous version of this 12 × 8 × 8 topology.³³ Although not a small-pore zeolite, this is informative in the light of targeting cage-based 8MR zeolites. The selectivity of the *cis*-OSDA for both GME and AEI, respectively in concentrated and dilute conditions, visualized in Figure 9, was suggested to be linked to the concentration of the OSDA in the syntheses. The *cis*-OSDAs were found in the 12MR channel of GME from molecular modeling, while for AEI, one OSDA per cage is found (Figure 9, left). The calculated energies for GME are most favorable when using two organics per unit cell, instead of less, implying OSDAs closely line up in the 12MR pore (Figure 9, right). It is likely that this type of structure-direction only occurs when the concentration in the synthesis suspension is high, while dilute conditions lead to AEI, with occlusion of one OSDA per cage.

In this context, the work of Schmidt et al. is intriguing, as it documented a computational search for the optimal OSDA for SSZ-39. Besides proposing a new OSDA from computation and successfully obtaining AEI aluminosilicate with that heavily

substituted, asymmetrically quaternized piperidine (Table 4, entry 11), they reported the calculated stabilization energies of all reported N-based OSDAs for SSZ-39.¹⁸⁵ In decreasing order, the values for DEDMP, azoniabicyclononane, *N,N*-dimethyl-2,6-dimethylpiperidinium, and *N,N*-dimethyl-3,5-dimethylpiperidinium (structures in Table 4) were -16.2 , -14.9 , -14.0 , and -13.3 kJ/mol_{Si}. Their new OSDA scored the highest value of -16.9 kJ/mol_{Si}. SSZ-39 synthesis with this organic led to a material with relatively high Si/Al ratio of 13. The energy difference between the 3,5- and the 2,6-isomer OSDAs is not deemed significant enough to explain the differences in rates and incorporation noted by Dusselier et al. Moreover, the calculations did not take into account cis/trans-isomerism. Usually, for a given framework, stabilization energy differences among OSDAs on the order of 2 kJ/mol are significant to corroborate synthesis trends.

A new OSDA and set of conditions for AEI materials was reported by the Sano group, using tetraethylphosphonium hydroxide (TEP) and a FAU-zeolite as both Si and Al-source (Table 4, entry 5). This route, effectively an interzeolite conversion (method D in Tables 2 and 3), only worked well when a small amount of NaOH and specific dealuminated FAU zeolites (Si/Al ratios 11 and 17) were used. Remarkably, these synthesis-Si/Al ratios are similar to those used earlier in the mixtures with sodium silicate and an aluminous FAU zeolite. An issue with quaternized P-based organics is that during calcination, to remove the organic and empty the voids for application, often monomeric and condensed phosphorus species (e.g., oxides) remain in the solid. These P-species can alter the zeolite's properties. A P/Al ratio of 1.2 was indeed found after calcination of these AEI zeolites. Later, the group revisited their procedure, to investigate the P-species in the zeolite, and demonstrated deNO_x activity after Cu-exchange. Using an excessive amount of seeds and by adding NH₄F, a pure-phase material with Si/Al = 21 was obtained using TEP (Table 4, entry 6). In the same work, the authors also successfully prepared SSZ-39 from interzeolite conversion with DEDMP (Table 4, entry 7). Although not highlighted in their work, this methodology is an easy route for SSZ-39, using classic (easy-to-remove) N-based organics.¹⁸³ The Si/Al ratio of the starting and product zeolite in this IZC were 16 and 12, respectively, suggesting a solid conversion yield near 75% (considering all Al incorporated in the new phase). Interestingly, the crystal sizes of the IZC-materials (entries 5–7) are somewhat smaller than those of the classic SSZ-39 zeolites, around 200–600 nm (vs 0.5–1.0 μm).¹⁸³ The materials prepared by TEP also seemed significantly more thermally stable, likely by phosphorus-modification. In a more recent report, the authors even proposed a mixed-OSDA strategy, using DEDMP and TEP together (Table 4, entry 13) to take advantage of an optimal, small amount of phosphorus-modification, to increase the hydrothermal stability.¹⁸⁷

Martín et al. further studied IZC-methods for preparing SSZ-39 from FAU (actual USY-zeolites, Table 4, entry 12).¹⁸⁶ Notably, instead of DEDMP,¹⁸³ they used the cis/trans-3,5 OSDA (ratio unknown). This improvement could be relevant, as a diethyl-quaternization step in OSDA synthesis (e.g., for DEDMP) is usually harder than a dimethyl one. The Si/Al ratio of the starting and product zeolite were 10.5 and 8.2, respectively, indicating a high solid conversion yield. Interestingly, the authors also reported the addition of Cu-tetraethylenepentamine to this synthesis, yielding Cu-SSZ-39 for SCR directly (without Cu-exchange afterward).¹⁸⁶ The

same authors also reported a modification of the TEP-procedure, using the Si/Al = 10.5 FAU-zeolite as source (Table 4, entry 14).¹⁸⁸ They noted, compared to their work above in a similar synthesis with cis/trans-3,5, that the crystal sizes of the resulting zeolites were very small and in the range of 50 nm. These zeolites are about an order of magnitude smaller than the TEP-zeolites reported earlier. The reason for this result is uncertain, although a faster nucleation rate, originating from an unknown interplay between the specific starting FAU zeolite and TEP is likely. Crystal sizes can be crucial to the performance in certain catalytic applications (see section 3.4.3.3). A recent AEI synthesis was also reported in this context, when Kubota and co-workers found medium-small crystallites (Table 4, entry 15) when using colloidal silica, an appropriate FAU-zeolite, and the cis/trans-3,5 OSDA (isomer ratio unknown). The concept in this report was to work with very low water content (H₂O/Si = 3.3), and with specific alkaline ratios. The result, 300 nm small SSZ-39 particles, with a high Si/Al of 16, is remarkable and could be of use in catalysis. Additionally, an interesting and informative set of experiments was shown that involved different FAU precursors. For instance to obtain AEI in the conditions of entry 15, but with a more aluminous FAU (Si/Al = 5.3 instead of 10.3), the NaOH addition had to be increased to 0.24 (and the dilution, H₂O:Si to 5), to avoid MTW and FAU competition.¹⁸⁹

2.3.1.3. AEI-Zeolite Conclusions. AEI presents an important set of materials due to the excellent performance in both SCR and MTO catalysis (sections 3.2, 3.4). In the last 3 years, remarkable progress in its hydrothermal synthesis has been reported. Some interesting observations, insights, and comments can be made:

- (1) The Si/Al ratios of the zeolite prepared in hydroxide media still have not risen above 20 (except for one patent entry). The question is whether this derives (i) from structure-specific limitations of the AEI framework itself, favoring more Al-incorporation or (ii) due to the lack of an OSDA that fits very well. The latter could be plausible, given that the patent entry made use of the relatively large azonia-OSDA.
- (2) Since AEI and CHA are very similar structures and both are “d6r-only” members, it is worthwhile to note that the latter can be made in OH[−]-media up to Si/Al = 55 by using the very well fitting ADAM OSDA (section 2.3.3), and that there is no structural limitation to even pure-siliceous CHA materials (F[−]-media). This argument is in favor of the possibility of creating AEI with higher ratios. On the other hand, creating highly siliceous cage-containing zeolites in hydroxide media should also be approached from a charge balance perspective: in the ideal case, one OSDA occupies every large cage. AEI has 36 T atoms surrounding the cage (Figure 7), with each T atom shared over 3 cages, rendering the amount of T atoms per cage at 12 (the unit cell, having 48 T atoms and 4 full cages, confirms this count).¹⁸⁴ This implies that the ideal AEI structure made with one OSDA per cage should include one aluminum for charge balancing, or thus have a Si/Al ratio of 11. The reported ratios in Table 4 seem to be centered around this value. Higher Si/Al values in OH[−]-media entail the incorporation of charge-balancing siliceous defects (although these can anneal in calcination). Perhaps the structure of AEI does not allow the incorporation of such defects to the same

extent as CHA, considering for instance that AEI has three crystallographically different (although very similar) T atoms, while CHA has one.

- (3) A multitude of OSDAs for aluminosilicate AEI have been reported. Notably, the heavily substituted piperidinium published by Schmidt et al. (entry 11, Table 4), with the largest stabilization energy for the cage, has not been tested in a range of conditions intended for creating higher silica materials.¹⁸⁵ It should be.
- (4) Not one AEI zeolite has been made without the presence of a FAU-zeolite. The FAU is used either as source for alumina, with silica added separately, or as only source in IZC. An exception here would be the fluoride-based method described in the patent, but there, AEI-seeds are used. To the best of our knowledge, aluminosilicate AEI is a unique case in this respect, certainly in the realm of 8MR zeolites. Since the source of alumina has so far always been a zeolite, there are indications that this influences the Al-incorporation into the new zeolite and thus its Si/Al ratio. Insights from the numerous IZC routes reported for CHA (see below, section 2.3.3.4) could be of use. Strikingly, CHA can be made without FAU-sources, but it seems to go faster if they are present (again pointing to the need for a good fitting OSDA for AEI). Both FAU and AEI are members of the d6r-only family (the only other 8MR-zeolite members are CHA, AFX, KFI, SAS, SFW, and TSC). It is likely that this structural similarity helps in forming the new zeolite during IZC (e.g., along the line of Figure 4, with 6MR-nanoparts) or partial IZC. The hypothesis, preeminent in IZC literature,¹⁴⁶ is that the new zeolite is formed faster (and selectively) through the reassembly of (nano)parts from the dissolving mother zeolite. It is also interesting to note the similarities to seeding and its benefits in classic synthesis. There, seeds sometimes completely disappear in the X-ray diffractogram in the first hours of the synthesis but still direct the crystallization to be faster or more selective, indicating that they do not completely dissolve to monomolecular T atoms.¹⁹³
- (5) Although the AEI zeolite can thus be made with a different range of organics (Table 4, Zones patent), the inorganic conditions are thought to predominate over the organic/inorganic interactions. Zones noted this, because these zeolites are formed in the presence of high OH⁻ contents (i.e., 0.7 OH⁻/Si).¹⁷⁸ This is thought to favor the occurrence of even-membered rings (AEI is built from 4, 6, and 8MR), as well as being needed to solubilize the aluminum. In Table 4, the OH⁻ content can be calculated by simply adding the OSDA/Si and Na/Si columns.¹⁷⁸ Interestingly, most syntheses where FAU was used and another silica source was added indeed feature a high OH/Si, while the IZC routes use remarkably less hydroxide. Given the fact that a FAU zeolite is built from 4MR and 6MR (d6r), there is a good chance that the complete breakdown of the structure to monomolecular Al- and Si-precursors is not occurring, but rather to some (not necessarily well-defined) nanoparts.^{145,146} A possible reason why IZC routes need considerably less hydroxide for success (i.e., to inhibit other phases or amorphous solids) could be that the precursors-derived nanoparts with even-membered rings replace the role of a high-in-hydroxide medium favoring even-membered rings. Note that in the case of

using FAU with additional silica, the Si/Al of the product is more than doubled with respect to the starting zeolite (entries 1, 4, 8–10). Considering a d6r (with 12 T atoms) in a FAU precursor with three aluminums (Si/Al = 9/3 = 3), this entails theoretically replacing one (or two) aluminums by external silicons to obtain a Si/Al = 5 (or 11). The use of a high hydroxide content in these FAU+silica syntheses is thus needed to mobilize aluminum, at least locally. The use of high hydroxide entails the coaddition of alkali (Na) that does not help in creating high-silica materials (Na⁺ can easily balance charge in d6r cages). On the contrary, in the case of pure IZC, the Si/Al ratios of the product are always lower than that of the starting FAU (entries 5–7, 12–14), meaning that silica is being selectively dissolved during the transformation, and part of it stays in solution. There is thus less of a need for hydroxide-rich conditions since the aluminum does not need to be solubilized. These two types of synthesis, although leading to the same product and seemingly similar, are thus very different (!). There is of course a middle path, and in our opinion, this is embodied in the last entry in Table 4. Kubota and co-workers used an appropriate FAU source and a silica sol (instead of Na-silicate) and noted the crucial selection of both NaOH and water contents depending on the FAU used. Using less of a more aluminous FAU warranted higher hydroxide addition, but in a higher dilution, while using more of a siliceous FAU allowed the authors to use a lesser NaOH content in the gel. The latter also entailed heavily concentrating the solution to H₂O/Si = 3.3.¹⁸⁹ We believe this is necessary to let the OSDA interact better with the FAU (note how these conditions start to resemble those of IZC, as these often rely on low water contents).

- (6) Dusselier et al. found remarkable organic-sensitive trends in the isomer-study, although the inorganic conditions in these OH⁻ rich syntheses are thought to dominate (comment 5).¹⁸⁴ A likely explanation for these results is that the relative occurrence of kinetically competing phases (e.g., MOR) is altered by the different isomers. For instance in Si/Al = 15 mixtures, the 2,6-isomer did not produce AEI, while the 3,5-isomers did (in Si/Al = 30 mixtures, both isomers did produce AEI). Similarly, cis-3,5 leads to GME in concentrated conditions. The kinetic competition of other phases clearly differs with the Al-content of the synthesis. The reason why IZC (could) overcomes this, is perhaps that the aluminum is not substantially solubilized, as is the case in the isomer studies using additional silica (corroborating comment 5).
- (7) Crystal sizes could offer insights into the mechanisms governing AEI synthesis, as they are determined by the interplay between nucleation and crystal growth. The interaction of FAU precursors with the OSDA and the added Na⁺ should mainly effect the former (e.g., nanosized synthesis by Martín et al).¹⁸⁸
- (8) The most recent synthesis by Kubota and co-workers seems relevant for catalytic purposes (also see comment 5), as Al-incorporation this low had never been reported for the perhaps most accessible *N,N*-dimethyl-3,5-dimethylpiperidinium OSDA.

2.3.2. AFX. The first material reported with the AFX structure had a SAPO-composition. AFX is a member of the

ABC-6 stacking family of structures. The ABC-6 pattern consists of planar hexagonal arrays of nonconnected 6MR that are translated horizontally and connected (stacked) vertically. Each planar layer is in an A, B, or C position, yielding repeating descriptions, e.g., ...AABBCCBB... for AFX (Figure 10). The

Figure 10. Structures of CHA, AFX, and SFW along [001] (top) and [110] (bottom). Adapted with permission from ref 66. Copyright 2013, American Chemical Society. Note how the “d6r-only” nature in ABC-6 zeolites is visible in the double repeat of each layer (e.g., AA). Yellow = very large SFW cage.

other ABC-6 members in the 8MR zeolite family are CHA, EAB, ERI, LEV, and SFW. The ABC-6 pattern for AFX generates a large cage (*aft* composite building unit), resembling an extended version of the cage of CHA (Figure 7). Another way to build the AFX structure is by translating and connecting d6r units. As with AEI, AFX is a member of the d6r-only family. The only two other structures that belong to both the d6r-only and the ABC-6 families are CHA and SFW. The structural link between these three materials with expanding cages (Xie et al.⁶⁶) provides an interesting case for relating synthesis and structure (Figure 10).

The zeolite version of AFX, named SSZ-16, was discovered by Zones using a 1,4-bis(1-azoniabicyclo[2.2.2]octane)butyl dibromide OSDA in hydroxide media, in the presence of Na⁺.^{39,142} This OSDA consists of two quinuclidine units connected by their quaternary nitrogen atoms through a four-carbon polymethylene bridge (Figure 11). The quinuclidine unit resembles 1,4-diazabicyclo[2.2.2]octane, better known as DABCO (structure in Figure 18, without the R-group of ERI OSDAs), but does not have a second N atom in the 4-position.

Figure 11. OSDA for CHA, AFX, and SFW (cages and structures in Figures 7 and 10) Only for SFW, two OSDAs per cage were found. ADAM = N,N,N-trimethyl-1-adamantylammonium.

A couple of other diquaternary OSDA (diquat) with four-carbon bridges were also found to work and are based on connecting two ADAM, two DABCO, or even two triethylammonium units.³⁸ Archer et al. used 1,3-imidazolium linked ADAMs for synthesizing SSZ-16 (not a diquat),¹⁹⁴ while Lee et al. reported C5-bridged triethylammoniums (Et₃-diquat-5).¹⁹⁵ Figure 11 shows three of these SSZ-16 organics, along with the common OSDAs for CHA and SFW. The Si/Al range reported for AFX is narrow, from 3.7 to 17, suggesting that the d6r units in this zeolite have a preference for a specific amount of aluminum incorporation in OH[−] media: from 1 to 3 aluminums per 12 T atoms (=d6r unit). The Si/Al ratio for the commonly used DABCO-, quinuclidine-, and triethylammonium-based diquats seems to be closer to 5 (or 2 Al per d6r).^{38,164,195,196} The simplified T atom count per cage for charge balance estimates (as for AEI above and CHA below) is harder for AFX due to the presence of a second type of smaller cage (*gme*-unit, Figure 10), in spite of the structural similarity of the AFX cage and CHA-cage (1.5× expansion).

The most siliceous AFX Si/Al (17) was reported using the monoquaternary bis-ADAM-imidazolium linked OSDA (Figure 11),¹⁵⁹ likely due to the lower charge-over-size ratio of this organic. Aiming at lower Si/Al ratios in the syntheses mixtures often gives competition with other Na⁺-rich phases that do not need to include organic. Given the d6r-only feature of AFX and the fact that the CHA zeolite, with structural similarity, can be made over the full range of Si/Al ratios, there does not appear to be a thermodynamically-induced lower limit to Al-incorporation. An all silica version of AFX should thus be able to form. The likely reason why no higher-silica versions of AFX have been made is that the stabilization energies of the reported OSDAs are not low enough, and perhaps most of these organics are too flexible. Considering that ADAM provides a very high stabilization of −16.7 kJ per mole of T atoms in CHA, its synthesis over a wider range of Si/Al is less surprising. The trends in AFX and SFW (for the latter, −11.1 kJ/mol is the lowest framework-OSDA stabilization encountered¹³⁷) seem to indicate that higher silica materials need to have a more specific OSDA–inorganic interaction, to be successfully synthesized in hydroxide media, or, in reverse, that these types of structures (ABC-6, d6r-only, cages) have a preferred Si/Al compositional range, tentatively estimated from 2.6 (close to natural CHA) to 11. An interesting and detailed synthesis study using the bis-triethylammonium diquat was reported by Hrabanek et al., showing the importance of aging and inorganic sources for SSZ-16. The authors noted a strong influence of nucleation on particle size and, interestingly, isolated core–shell structures with amorphous silica inside an SSZ-16 shell, when fumed silica was used.¹⁹⁷

Recently Martín et al. reported a new, IZC-based, route to AFX, with a large multicyclic Diels–Alder derived OSDA that also led to ERI in slightly different conditions (OSDA: see Figure 18). A very small synthetic window and the use of the right FAU (Si/Al = 6) zeolite precursor led to AFX (i.e., OSDA/Si = 0.2, NaOH/Si = 0.1, H₂O/Si = 15). The Si/Al range of the product, 5.2, is in line with previous SSZ-16 materials. The same conditions, save for changing Na⁺ for K⁺, lead to ERI.¹⁹⁸

2.3.3. CHA. 2.3.3.1. Synthetic Chabazite, SSZ-13, and Pure Silicas. As mentioned above and illustrated in Figures 7 and 10, the structure of CHA consists of symmetric, medium-sized cages obtained by stacking planes of nonconnected 6MR rings along an AABBCC sequence, or from d6r units. The latter

Figure 12. Crystallinity from PXRD (relative to the most crystalline sample from tumbling) and zeolite particle sizes from DLS, as a function of the synthesis time at 160 °C. Si/Al = 50, H₂O/Si = 31, ADAM/Si = 0.6 ratios. Gels from TEOS and Al-hydroxide. Prepared with data from ref 206.

description resembles that of AEI (Figure 8), but for CHA, the planes of d6r units are stacked on top of each other along the *c*-axis, without prior rotation. CHA has only one unique T atom position. Since the early days, attempts were made to synthetically access CHA-zeolites, given the interesting sorption and sieving properties, discovered as early as 1924 on chabazite minerals. Barrer and Baynham obtained species K-G from potassium aluminosilicate gels.⁴⁴ A standard recipe is now available to obtain this zeolite with Si/Al ratio between 2 and 3 in classic hydroxide media (*cfr.* Synthesis Commission of IZA).¹⁶⁷ This recipe uses Na⁺/K⁺ and M⁺/Al ratio of 0.085, and 2.2, respectively, at 95 °C, in a Si/Al 2.6 gel with a FAU-type zeolite as T atom source (in fact an organic-free IZC).¹⁹⁹ Recipes with more classic sources are also known. A low-silica recipe using only K⁺ with addition of NH₄F was reported recently.²⁰⁰

A breakthrough in CHA zeolite synthesis was realized by Zones in 1985, who demonstrated Si/Al ratios well above those of the organic-free synthesis by using the large ADAM OSDA (Figure 11) in common hydroxide media.⁴ Zeolites with Si/Al ratios higher than 10 are often required for catalytic applications, as they are more stable than their more aluminous counterparts at high temperatures or in steam-rich conditions. In synthesis mixtures with Si/Al ratios below 55, the zeolite can now readily be made with the according Si/Al ratio in the material. Above that ratio, the hydroxide syntheses also starts to produce MWW, STT, and AFI-type zeolites.^{162,201,202} The large cages are ideally occupied by one ADAM molecule. By switching to fluoride media, Cambor and co-workers showed the possibility of making pure-silica CHA with ADAM.¹⁶² Typically, such a synthesis works in the absence of inorganic cations, and the amount of HF added neutralizes the amount of base generated by the addition of the OSDA in its hydroxide form (ADAM(OH⁻)). Furthermore, F⁻ anions associate closely with the ADAM cation and counterbalance its charge so that the framework can be neutral, and pure-silica CHA can form.²⁰³ Zones' SSZ-13 discovery was very important for the application-relevant CHA topology,⁴ and it generally can be seen as a breakthrough for large cage-containing 8MR zeolites. Many materials, with useful Si/Al ratios, followed it: SSZ-16 (AFX), SSZ-45 (EEI), SSZ-50 (RTH), SSZ-52 (SFW), SSZ-73 (SAS), *cfr.* Table 3.

2.3.3.2. Alterations to the ADAM Recipe. Many variations to the Zones recipe have been reported. Eilertsen et al. detailed a recipe using ADAM, NaOH, and NaF (in a 2:3:1 OSDA:Na:F molar ratio), from aluminum(hydr)oxide and fumed silica sources.²⁰² This recipe appears to be a combination of fluoride and hydroxide-media and yields materials with Si/Al ratios

between 15 and 133 (in agreement with similar values in the gels). The particle sizes were generally in the 20 μm range for the Si/Al ratios under 40 and were much smaller, close to 4 μm, for the higher Si/Al mixtures. In this context, Zones also patented a small crystallite aluminosilicate CHA, named SSZ-62, specifically with zeolite particles sizing between 0.05–0.1 μm, in the Si/Al = 10–25 range.⁵⁵ Common crystal sizes are 1 μm or larger for SSZ-13. The small crystals were obtained with classic ADAM and NaOH synthesis, but with a specific Al-hydroxide gel (from easily soluble Al₂O₃) and precipitated amorphous silica, at a precise H₂O:Si ratio of 16.

Usually, the unit cell of a zeolite contracts with decreasing Al incorporation, due to the larger bond length of Al–O vs Si–O. The unit cell parameters of Eilertsen's SSZ-13 series with Si/Al ranging from 15–133 were measured for both as-made and calcined materials.²⁰² For as-made materials, the authors found an anisotropic contraction, with most unit cell shrinkage along the *a*-axis, while the *c*-axis parameter remained more or less constant. In the calcined materials, there was a large relaxation of strain (or expansion of the unit cell with increasing Al content) along the *c*-axis as well. Likely, the trend in the as-made materials can be linked to the orientation of the OSDA in the zeolite: the ADAM cation sits either parallel or antiparallel to the *c*-axis, as determined on pure-silica forms by Villaescusa et al.²⁰⁴ This arrangement could sterically prevent large shrinkages along the *c*-axis parameter of the unit cell in as-made higher silica materials. Interestingly, this would suggest that the structure direction with ADAM for CHA (and thus crystal growth) is more favorable at lower Si/Al ratios; as for more siliceous materials the ADAM-cavity fit is less good. This could be one of the reasons why the competition of other zeolites is more profound at Si/Al ratios >55 in OH⁻-media, although charge balancing is also key (*vide infra*).

In search for a single-parameter variation synthesis, Eilertsen et al. reported another series of CHA-zeolites made in fluoride media (ADAM:HF = 1) and with Si/Al ratios ranging from 20 to infinity. The particle sizes of the zeolites in this series (at 2–4 μm), as well as the surface areas, are more or less constant. For Si/Al ratios larger than 100, Si/F ratios were around 12, confirming the incorporation of about one F⁻-anion per OSDA in the materials, likely in the d6r unit, as in pure-silica CHA.^{204,205} Such series are very useful in application studies, as the impact of purely Si/Al-variation on, e.g., catalysis or sorption, can be studied, while every other property remains more or less constant. Structure–activity relations in such cases are more unambiguous.

Lillerud and co-workers also investigated the formation of SSZ-13, with a focus on the particle size (through the crystal

Figure 13. Size-tailored SSZ-13 zeolites by using polymer additives. Figure based on photographs by Kumar et al. in ref 207. The average reported crystal size is given.

growth mechanism) in Si/Al = 50 syntheses from TEOS and aluminum hydroxide.²⁰⁶ This Si/Al ratio is close to the upper limit for hydroxide media syntheses. The influence of stirring versus tumbling versus static syntheses on particle size and crystallinity was tracked in time (Figure 12). It is important to note that the starting point for particle size from dynamic light scattering (DLS, right curve) at time zero corresponds to aggregates of clusters of silicon/aluminum/ADAM, sizing about one micron, obtained by aging the precursor solution under stirring for 24 h at room temperature. The final particle sizes for static synthesis were larger (as expected), but for stirring, no growth of the particles was seen. The growth of particles under tumbling or static conditions was not behaving in a linear manner, but rather with an induction period (sigmoidal) and mostly, the particles grew after reaching full crystallinity (compare left to right plots). The crystallization is also slower in the case of the strongest agitation (stirring). The crystallization process can hence be partly controlled, as is particle size.

The authors further noted a sigmoidal relation between the particle size and synthesis temperature for static conditions, a strange observation, since Arrhenius type behavior is to be expected for crystal growth rate. A third interesting series unexpectedly showed that diluting the synthesis mixtures led to increased particle sizes. Normally, the sizes are expected to be smaller because the growth rate depends on the concentration of reagents. A possible explanation could be a decreased nucleation rate due to the decreased alkalinity of the medium (giving less crystals growing larger). A final trend showed smaller particles when increasing the ADAM content. By combining parameter insights, the authors were able to prepare SSZ-13 particles sizing around 200–300 nm (DLS). The difference with small-crystal SSZ-62 zeolites is thus the more siliceous nature.²⁰⁶

Rimer and co-workers reported an insightful study where remarkable control of the particle sizes was established (ranging from 0.1 to 20 μm) using zeolite growth-modifiers, and these results provided insights into the crystallization pathways.²⁰⁷ The systems of study were gels made from fumed silica and aluminum hydroxide with Si/Al at 19, and Na/Si, ADAM/Si, and H₂O/Si ratios at 0.2, 0.1, and 44, respectively. This control (6 days at 180 °C) yields particles of around 2 μm (in line with other reports discussed above), although a small fraction of 200 nm large cubic particles was always encountered. In a temporal analysis of their tumbling synthesis, they tracked the amorphous to crystalline transformation and noted a long induction period (where no crystals appear) of 40 h (compare

to black curve in Figure 12) followed by a fast complete crystallization in under 10 h. The induction period showed amorphous wormlike particles. The latter do not seem to decrease in size, indicating their consumption occurs by direct attachment rather than dissolution to soluble precursor species, and the reaction of those species with growing crystals. The latter is the classical mechanism for crystal growth, in layers, fitting to crystal habit and unit cell dimensions. Evidence for the attachment of larger amorphous precursors to growing crystals was mainly found from atomic force and electron microscopy, where features resembling the former amorphous particles were seen. On top, cryo-TEM showed the presence of tiny (<10 nm) particles near the growing crystals that were not found in solution. These surface-attached mini particles are hypothesized to be an intermediate stage during the structural rearrangement of the attached amorphous particles. Classical growth was also observed in AFM, but to a lesser extent and in a later stage, when the attachable particles become depleted. Based on these insights, the addition of several growth modifiers was tested. Remarkably, the addition of 1.6 wt % of polyethylenimine (PEIM, Figure 13) resulted in 130 nm large zeolite particles. Likely the neutral polymer prevents the attachment of the amorphous particles and aggregation. Similar effects were found for hexadecyl trimethyl ammonium bromide (CTAB). In reverse, adding cationic poly(diallyldimethylammonium chloride) or PDDAC (Figure 13) seemed to decrease nucleation time and enhance crystal growth, leading to crystals of 20 μm in size (with some mesopores), likely by speeding up attachment. Combining the polymers gave access to crystal size control (overview, Figure 13).

The motivation to access smaller crystal sizes from synthesis derives from the higher external surface area such particles have and the shortening of the diffusion paths for reagent and product molecules. This sometimes ameliorates the performance of a zeolite in catalytic applications by overcoming diffusional limitations, coke formation, or low selectivities. The Corma and Yu groups further explored the merits of CTAB (growth modifier) addition, in a different way:²⁰⁸ after a classic SSZ-13 synthesis mixture (Si/Al 20, Na/Si 0.2, ADAM/Si 0.2; H₂O/Si 44) had been in the oven at 160 °C for 1 day, CTAB was added, at a CTAB/Si ratio of 0.12. After 9 more days, this resulted in aggregated SSZ-13, with a bulk Si/Al ratio of 17, sizing in the 50–200 nm range. This material displayed interparticle mesoporosity in N₂-adsorption in addition to its 0.2 cm³/g of microporosity. Leaving the classic gel uninterrupted for 6 days instead, gave classic SSZ-13 with Si/Al = 15 and particles sizing 1.5–2.5 μm, with 0.25 cm³/g of

microporosity. More defect sites and a lower framework incorporation of Al were however noted for the nano-SSZ-13. Lastly, the Sano group also reported control over the particle sizes in their interzeolite conversions (section 2.3.3.4).

In analogy to Eilertsen's 15-133 series, Hensen and co-workers also added NaF in hydroxide media, but in a 4:3:2 OSDA:Na:F molar ratio, for a Si/Al 20 synthesis (and 0.2 ADAM/Si).²⁰⁹ Remarkably, a bimodal distribution in the micropore range was observed for the material, as next to the cage-average micropore calculated at 0.54 nm, a micropore in the range of 4.6–7 Å seemed present. Additional evidence was found in the occurrence of tiophene diffusion in the bimodal samples, as well as by a much faster uptake of *n*-butanol and isobutanol in sorption experiments. It was hypothesized that F-addition favors the particle attachment mechanism of non-classical growth, as described above by Rimer and co-workers,²⁰⁷ and results in additional micropores at the boundaries of the particles attached to the growing zeolites.

Another technical alteration used to obtain SSZ-13 consists of a fast continuous-flow synthesis, as presented by Okubo and co-workers.²¹⁰ The method consists of adding seeds, hence avoiding the slow nucleation phase, which then grow without thermal lag while quickly moving in a tubular reactor heated at 210 °C (in e.g., a 10 min synthesis). The crystal growth rate was enhanced by selecting the right Al-source, which proved to be Al(OH)₃. This solid has a low solubility and was hypothesized to hamper the formation of an amorphous aluminosilicate with the colloidal silica. The amorphous aluminosilicate phase is thought to decrease crystal growth rates. In such systems, the clogging of the tubular reactor is to be overcome.

2.3.3.3. Other OSDAs for CHA and Mesoporous Recipes.

Since the synthesis of ADAM is expensive, alternative OSDAs have been highly sought after. Cao et al. reported the use of *N,N,N*-dimethylethylcyclohexylammonium hydroxide as OSDA for high silica CHA (Figure 14).²¹¹ Using very low water

Figure 14. Alternative OSDAs for CHA. BTMA = *N,N,N*-trimethylbenzylammonium, TEPA = tetraethylenepentamine.

content ($\text{H}_2\text{O}/\text{Si} = 6.4$) and keeping the ratios of Na^+ and OSDA/Si at 0.1 and 0.2, this method yields CHA-zeolites (in competition with MTW) at 150 °C with Si/Al ratios around 54. Wang et al. further explored this recipe in a solvent-free approach using the bromide form of this OSDA (Figure 14).²¹² After grinding the solid precursors (sodium metasilicate, aluminum sulphate, solid silica gel, OSDA), the mixture was reacted at 180 °C. The ratios of Na^+ and OSDA to Si were 0.4 and 0.1 here, and the obtained CHA-zeolites, in high yield, had limited Si/Al ratios, ranging from 5 to 10.²¹²

Ren et al. reported the use of a metal complex for directing CHA-synthesis.²¹³ They noted that a Cu^{2+} -amine complex (TEPA, Figure 14) had similar size properties as the CHA-cage. Using dilute gels ($\text{H}_2\text{O}/\text{Si} = 200$) from silica sol and sodium aluminate, with both Na/Si and Cu-TEPA/Si ratios around 0.1,

Cu-CHA-zeolites were obtained at 140 °C, with Si/Al ratios in the range of 4 to 7.5. After calcination, the Cu-containing material could directly be used for SCR of NO_x with NH₃. Corma and co-workers later reported a one-pot recipe for Cu-SSZ-13 based on using both Cu-TEPA and ADAM, in both hydroxide and fluoride media.²¹⁴ Using mixtures allows one to obtain higher Si/Al ratios in the solids and a better control of the Cu loadings.

Another synthesis using the addition of a second organic to ADAM was reported by Zones, with *N,N,N*-trimethylbenzylammonium (BTMA, Figure 14). He showed that combinations of 1:1 up to 1:7 (ADAM:BTMA) could direct to the SSZ-13 structure from fumed silica and Al₂O₃, as well as combinations of ADAM and *N,N,N*-triethylbenzylammonium (up to 1:3). No characterization of the products was given.²¹⁵ Sano and co-workers later succeeded in making CHA-zeolites by only using BTMA hydroxide by making use of the IZC method (Table 2, method D).²¹⁶ IZC has been thoroughly investigated for CHA, in both the presence and absence of organic cations or seeds (see section 2.3.3.4).

Rather unexpected, Xu et al. were able to use choline chloride (Figure 14) in gels from sodium aluminate and colloidal silica and obtain CHA-zeolites.²¹⁷ These gels had 0.2 choline/Si ratios and importantly, unknown amounts of seeds of SSZ-13, made with ADAM. The claimed materials had limited Si/Al ratios between 3.3 and 8.7. The authors assumed that 2 choline (chloride) units clustered in the large CHA cage, although the thermogravimetric analysis showed a weight loss of only 9.6% linked to the organic (choline = 104 g·mol⁻¹). In classic SSZ-13 synthesis using ADAM, the weight loss equals around 20%, due to one organic cation, weighing 194 g·mol⁻¹, decomposing per cage.

Hensen and co-workers reported on the direct synthesis of mesoporous SSZ-13 by using, in addition to ADAM, a mesoporegen with two cationic heads (Figure 14).^{218,219} The same molecule was also used by Ryoo et al. for creating nanosheet MFI.²²⁰ This meso-SSZ-13, with Si/Al = 17, had 0.21 cm³/g of mesoporosity on top of a normal amount of microporosity. A combination of this strategy with the F-assisted bimodal microporous SSZ-13 synthesis (above) was recently demonstrated, resulting in trimodal hierarchical SSZ-13.²²¹

Tatsumi and co-workers reported the synthesis of CHA zeolites without organic nor starting zeolite sources, but with the addition of large amounts (20 wt %) of classically prepared (using ADAM) seeds. In this manner, they were able to synthesize CHA from amorphous gels (fumed silica, sodium aluminate, or Al-isopropoxide) using Na⁺ with K⁺ or Cs⁺ alkali. The K⁺ materials had Si/Al ratios below 4 (a bit higher than the classic OSDA-free recipe from FAU zeolite¹⁹⁹) but interestingly, with Cs, a ratio of 5.2 could be attained. A time series at 170 °C indicated at least partial dissolution of the seeds, as a fully amorphous diffractogram appeared after 1 h. The synthesis was complete in 24 h, and longer times led to other phases appearing.¹⁹³

2.3.3.4. Interzeolite Conversions (IZC). The IZC of FAU to CHA was already schematized in Figure 4. Table 5 lists most of the IZC routes that have led to CHA zeolites. As mentioned, the standard recipe for OSDA-free, high-alumina CHA is based on the transformation of a FAU-zeolite at 95 °C with Si/Al = 2.6 (Table 5, entry 1).¹⁹⁹ The FAU in this procedure, as described by the Synthesis Commission¹⁶⁷ contained a little bit of Na⁺, but the main element needed for CHA is K⁺. Ji et al.

Table 5. Overview of CHA-Zeolite Syntheses by Interzeolite Conversion^a

E	starting zeolite ^b	Si/Al reag.	synthesis mixtures composition relative to Si			T, t (°C, h)	Si/Al prod.	ref
			M ⁺ (OH ⁻)	OSDA(OH ⁻)	H ₂ O			
1	(Na,H)-FAU	2.6	0.84 (K ⁺ /Na ⁺ : 12)		43	95, 96	2.16	167
2	NH ₄ -FAU ^c	6.0	1.1 (K ⁺)		44	100, 96	2.4	222
3	NH ₄ -FAU ^d	2.7	1.37 (K ⁺ /Na ⁺ : 18)		58	95, 96	2.1	223
4	Na-FAU	2.7	1.67 (K ⁺ /Na ⁺ : 3.5)		58	95, 96	1.6	223
5	Na-GIS ^e	3.0 ^e	0.68 (Na ⁺)	0.11 ADAM(I ⁻)	25	130, 144	7.5 ^e	143
6	H-FAU _{s,a}	21	0.1 (NaCl)	0.2 BTMA	5	120, 504	16.9	216
7	H-FAU _{s,a} CHA-seeds 2%	22	0.1 (NaCl)	0.2 BTMA	5	125, 168	18.2	224
8	H-FAU _{s,a} CHA-seeds 2%	16	0.1 (Na ⁺)	0.2 BTMA	5	125, 168	14.7	224
9	H-FAU _{s,a} CHA-seeds 2%	81	0.1 (NaCl)	0.2 BTMA	5	125, 168	21.3	224
10	H-FAU _{s,a} CHA-seeds 10%	97		0.3 BTMA	5	125, 168	18.6	224
11	H-FAU _{s,a} CHA-seeds 2%	23	0.1 (Na ⁺)	0.2 ADAM	5	125, 48	19	225
12	H-FAU _{s,a} CHA-seeds 2%	114	0.1 (Na ⁺)	0.2 ADAM	5	125, 48	67	225
13	H-FAU _{s,a}	10.5	0.2 (Na ⁺)	0.2 TEA	5	160, 72	8.5	226
14	H-LEV	9	3 (Na ⁺)		80	125, 1.5	2.8	227

^aE = entry. M⁺(OH⁻) refers to alkali added and can be more than one (added with ratio given). If another anion is used instead of OH⁻, this is mentioned in brackets. The same is valid for the OSDA column. ^bMostly, if FAU is mentioned, this is either zeolite Y or a treated version of Y. _{s,a} = steamed and acid washed, for leaching out aluminum. If this is in the case of FAU, these zeolites are better known as USY (ultrastable Y). ^cCBV 712 of Zeolyst. ^dCBV 300: contains some Na. ^eNot strictly an IZC, as sodium silicate is added, rendering the Si/Al synthesis ratio +/- 16. These conditions resemble a lot of those in Table 4 for AEI.

recently confirmed this result, albeit with a more siliceous starting zeolite (Table 5, entry 2).²²² Both products were very similar. Van Tendeloo et al. reported a similar conversion from NH₄⁺-FAU (entry 3).²²³ Interestingly, these authors also exchanged the starting FAU with Na⁺, K, or H⁺ prior to the conversions in the KOH solution, and they noted similar CHA formation, albeit with a little variation in the Si/Al ratios (e.g., Table 5, entry 4). In the same report, Van Tendeloo demonstrated the synthesis of three other 8MR zeolites from the same NH₄-FAU: ABW, MER, and ANA. They did this by respectively using LiOH, RbOH, or CsOH, instead of KOH for CHA, all at mild conditions.²²³

Groundbreaking work in the context of IZC with organics was published by Zones and Van Nordstrand in the late 1980s. Following the success of using ADAM for SSZ-13, they explored different zeolites as alumina source for making different (higher silica) zeolites with the addition of OSDA.^{142–144} The work began when they noticed the intermediate production of zeolite P (GIS) in the hydrothermal synthesis of SSZ-13. The ADAM organic seemed not to interfere with the first transformation of sodium silicate and Al₂(SO₄)₃ into GIS, via aluminosilicate oligomerization and gel formation. Then, as witnessed by monitoring both the pH and the relative mass of solids formed in time (compared to reactions without organic, only forming GIS), the uptake of ADAM by the solid phase and its gradual transformation to SSZ-13 occurred.¹⁴³ The CHA-phase was also more siliceous than the GIS-phase, indicating that all alumina was already in the solid GIS-phase, while silica was added from solution. No Al³⁺ was thus detected in solution at any point. The authors then made Na-GIS (Si/Al = 3) and dried it prior to reacting it with added sodium silicate, NaOH, and ADAM. This successfully led to SSZ-13, and while the Si/Al ratio went up to 7.5, the weight of zeolite more than doubled (Table 5, entry 5). Zones later reported a study using the same ingredients, but zeolite FAU instead of GIS, again with sodium silicate.¹⁴⁴ A range of effects originating from modifications on the starting FAU was shown. They noted that the surface chemistry of FAU had a profound impact on its conversion. For instance, steamed

FAU samples were much slower in reacting, but if the aluminum at the surface after steaming was acid-removed, they reacted much faster. Silylation also inhibited the reactivity of certain FAU zeolites. Importantly, in all these conversion, there is no new product formation without an increase in mass for the solid phase. Given the additional silica source, these first reports cannot be considered pure IZC, but they provided valuable insights into the use of different FAU zeolites and the dynamics of converting the zeolite in the high hydroxide crystallization field. Another important insight was that no amorphous phase was produced during the process, and SSZ-13 formed during the breakdown of the parent FAU.

The Sano group has reported excellent results using real IZC (without added silica) for non-8MR frameworks (such as BEA, RUT, ...; for an overview see ref 145), but they also managed to demonstrate some for CHA. They were able to transform FAU zeolite into high-silica CHA-materials using BTMA (Figure 14) as the OSDA (Table 5, entry 6).²¹⁶ Typically, this IZC is conducted in low water conditions, similar to the IZC results reported for AEI (Table 4). The CHA-zeolite could only be made from FAU precursors with Si/Al ratios in the 21–23 range, and, as expected, it could not form from amorphous (gel) precursors with this OSDA. This latter result is in line with data from the Zones patent that combined ADAM and BTMA to get SSZ-13 from fumed silica and Al₂O₃, while noticing that the presence of (at least one-seventh) ADAM was unconditional.²¹⁵ The solid yield of this IZC was not reported, and it could be a bottleneck, although, considering the Al-content in starting and product zeolite, a maximum yield of about 80% can be derived. This preliminary calculation assumes the full consumption of the AlO₄⁵⁻ tetrahedra and, thus, no leftover dissolved aluminum in the synthesis mixture. The studies from Zones and Van Nordstrand suggest this to be correct.¹⁴³ The Sano group later added CHA-seeds to their IZC methods and widened their good results: the synthesis could be reduced to 7 days (Table 5, entry 7), and the synthesis reported a solid yield of 92%.²²⁴ Using NaOH instead of NaCl with seeds allowed a wider set of starting FAU zeolites (Si/Al wise) to be used. However, the Si/Al ratio in the products varied only

Figure 15. Crystallization curves for CHA-zeolites from Si/Al = 35 mixtures at 125 °C, in the case of IZC (from FAU) and from an amorphous hydrogel (from fumed SiO₂ and Al(OH)₃). Figure adapted with permission from Takata et al. ref 225. Copyright 2016 Elsevier.

within a limited range, up to a maximum of 21.3 (Table 5, entries 8–9). Although Na⁺ was not essential, it required more organic and more seeds without its presence (viz. Table 5 entry 10). The unseeded IZC materials sized in the 1 μm range, while for the seeded materials, in the presence of Na⁺, crystallites were much smaller, around 100–200 nm. Those prepared with more seeds and without Na⁺ were even smaller.

The Sano group also explored their IZC reactions using ADAM. Significant differences with the previous BTMA route were the shorter time needed for complete crystallization and the possibility of obtaining higher Si/Al ratios in the resulting materials (Table 5, entries 11 and 12, compared to 7 and 10). CHA crystal sizes were in the 100 nm range (compare for instance to the nanosized SSZ-13s described in section 2.3.3.2). Interestingly, the rates of crystallization were compared from use of classic amorphous gels and IZC, in both the absence and presence of seeds (Figure 15). Without seeds (left curves), IZC was remarkably faster than the more classic synthesis from amorphous precursors. However, one should note that the crystallization times for the amorphous gels are excessive here, even for a classic synthesis and much longer than those listed in Figure 12 (also from amorphous precursors). The reason for this could be the low organic content, low temperature, and unusually high concentration (lower water content) for these kinds of amorphous gels (ADAM:Si = 0.2, H₂O/Si = 5). These features however do not diminish the remarkably fast performance of IZC under these conditions with less organic. With seeds, the differences are smaller, although IZC reaches full crystallinity at only 6 h, versus 24 h for the amorphous gel (Figure 15). The authors suggest that the enhanced crystallization rate of IZC derives from locally ordered aluminosilicate species (*nanoparts*) formed by the partial decomposition of the starting FAU zeolite (Figure 4). As mentioned earlier, both FAU and CHA are d6r-only members, so there definitely exists a structural similarity between the IZC starting and product zeolite in this case (same as AEI above). In a way, the often positive effect of adding seed crystals in more classic syntheses also partially relies on this phenomenon. How seeds interact with the zeolite precursor during IZC remains a good research question. A second question is the role of the starting zeolite's Al-content, in all of the above, as this is often a decisive factor in IZC, whether or not a phase can form.

Recently, Corma and co-workers discovered that the common OSDA TEA, in its hydroxide form, could also lead to CHA-zeolites when starting from a FAU zeolite (Table 5,

entry 13). These conditions closely resemble those reported by the same group for AEI-zeolite (Table 4, entry 12) and the product materials had similar Si/Al (8.5). The reflections of this CHA in the diffractogram had somewhat different intensities (relative to each other) and broader widths than those known for classic SSZ-13. The yield from this synthesis is high, micropore volumes were normal, and the zeolites sized 0.1–0.2 μm. Moreover, TEA is a commercial and cheap OSDA, available at the large scale, due to, among other applications, its use for zeolite BEA synthesis. Zeolite BEA was logically the main competing phase, but the combination of TEA and the zeolitic source of Si and Al, with its structural similarity to the product, favored CHA in a narrow range of conditions.²²⁶ The findings of Martín et al. should be further investigated to see whether they can lead to CHA zeolites with larger Si/Al ratios (as, e.g., up to 20 was attained for IZC using BTMA).

Often, IZC series progress from more open structures with lower framework densities (say FAU) to more dense structures (CHA). The use of OSDA can of course reverse this trend and create more open structures, even in IZC. Large inorganic cations can effect such transformations as well, and the first IZC ever (Barrer) was that of dense ANA to more open KFI (see section 2.1). Sano and co-workers discovered a way to synthesize CHA from the more dense LEV structure without OSDA (Table 5, entry 14).²²⁷ LEV, similar to CHA, is also an ABC-6 zeolite (section 2.3.8 vs Figure 10 for CHA). In the mixtures (rich in NaOH), the authors witnessed the transformation of LEV to amorphous to CHA to ANA. In analogous amorphous starting gels, such intermediate (and thus kinetically controlled) growth of a CHA phase was never found. The CHA zeolite produced, however, had a low pore volume and too much aluminum to be of practical use. Additionally, LEV-zeolites are not commercially accessible.

Finally, Goel et al. also demonstrated IZC of FAU to CHA without OSDA, through the use of seeds and NaOH.²²⁸ Tatsumi and co-workers have previously demonstrated seeding for CHA in amorphous gels.¹⁹³ The product CHA in the seeded-IZC report had amorphous phase cocrystallized next to it. This phase influences the Si/Al ratio of the measured bulk sample and likely explains the low micropore volume (<0.1 cm³/g).

The above IZC syntheses for making CHA (specifically Table 5, entries 6–13) present significant results, especially if an alternative to the use of ADAM is desired. FAU (and USY) zeolites are among the cheapest available due to their large-

scale use in catalytic cracking processes. Given a high-value application for the CHA-materials and considering that the aluminum content and pore volume are adequate for application (respectively 15–20 and $0.29 \text{ cm}^3 \cdot \text{g}^{-1}$), the IZC recipe using BTMA has the potential to be commercially feasible, next to the ADAM recipe. Moreover, a comparative study suggested that the acid-stability of the IZC BTMA materials was higher than that of the classic ADAM zeolites from amorphous gels with Si/Al ratios around 15.²²⁹ The CHA-zeolites made with TEA seem promising as well, although the Si/Al product range is a bit limited.

2.3.3.5. Insights into the Al-Distribution in CHA Zeolites. The CHA topology is d6r-only, so the distribution of Al in d6r units (constructing the entire framework; or the distribution in 6MR even) is representative of the entire framework. Second, it is important to note that, as proposed by Barthomeuf, there is a maximum density of Al atoms in a zeolite beyond which the formation of $-\text{Al}-\text{O}-\text{Si}-\text{O}-\text{Al}-$ (next nearest neighbor (NNR) aluminums) becomes a certainty. For CHA, based on the topological density, this limit is near a Si/Al ratio of 7.²³⁰ When such NNR-pairs are found in one face of a flat 6MR, or two Al-atoms are across of each other in that ring (both shown in the inset of Figure 16, left), they are known to exchange

Figure 16. Control over Al-distribution in terms of pairs/isolation in CHA. Left: the theoretical abundance (in fraction of the Al-atoms) of the two types of Al-pairs (inset) in 6MRs in a random distribution, varying with the framework Si/Al ratio. Right: the fraction of Al in pairs measured by Co^{2+} titration for a set of Si/Al 15 materials made with different Na/ADAM ratios in the synthesis gels, at fixed total cationic charge $[(\text{Na}^+ + \text{ADAM})/\text{Al}] = 7.5$. The random distribution value can be attained through synthesis (red square), as can the 100% isolated case (green square). Higher Na/ADAM ratios give MOR-zeolite competition. Adapted with permission from ref 233. Copyright 2016 American Chemical Society.

divalent ions very well.¹⁹⁶ Bates et al. showed that the energy difference for divalent cation exchange (of relevance to redox catalysis, e.g., Cu^{2+} in SCR, see section 3.2) on two framework Al-atoms in a 6MR (e.g., Figure 28) was much more favorable than in the 4MR or 8MR of CHA.²³¹ Bates et al. then theoretically calculated the number of such 6MRs (with exactly two aluminums) occurring per framework aluminum, based on a random Al-distribution and Löwenstein's rule in an ideal CHA framework, for a given Si/Al ratio (Figure 16, left). Their

curve predicted a density of 22% of these 6MR Al-pairs for a Si/Al = 5 CHA-zeolite (normalized on total Al-content) or, translated, a fraction of 44% of the Al occurring in such pairs. By extension, this random distribution relation should be valid for all other d6r-only members, since the way these d6r-units connect in space should not matter for the statistical model.²³¹ Earlier, Akporiaye et al. attempted to model experimental ^{29}Si NMR spectra of different CHA-zeolites (with maximum Si/Al at 7.6) by specific ordered Al distributions as well as by random distributions. They found the random distribution to fit best for their two highest Si/Al materials (5.2–7.6). Although this result does not prove randomness, the inadequate description by several ordered configurations is suggestive.²³²

A groundbreaking insight in Al-distribution in CHA-zeolites was recently reported by Di Iorio and Gounder, who studied the distribution in terms of isolation or pairing in relation to synthesis methods.²³³ They focused on the Al-pairs mentioned above (inset Figure 16, left), while using $\text{Al}(\text{OH})_3$ and colloidal silica in hydroxide media and developed an accurate method to quantitate these pairs (known to stabilize extra-framework divalent cations).²³³ The method is based on taking twice the saturation capacity from the Co^{2+} -ion exchange isotherm, with verification by diffuse reflectance UV-vis spectroscopy, Cu^{2+} -exchange, and selective titration of the remaining H^+ . The Co-exchange work of Dědeček and co-workers for other frameworks (MFI, BEA, ...) is instrumental in this context.^{234–236} Di Iorio et al. thus conducted a series of syntheses to study the influence of the organic ADAM vs inorganic Na^+ cations. One of the striking conclusions was that when Si/Al = 15 materials were made in the absence of Na^+ (and the specific inorganic sources) no pairs occurred (green square, Figure 16, right). This perfect isolation of each aluminum is likely related to the incorporation of one charged ADAM cation per cage. As each cage has 36 T atoms shared over 3 cages, or thus 12 full T atoms, a Si/Al ratio of 11 would then equal one aluminum incorporated (negative framework charge) per OSDA per cage. Thus, it would present the ideal case of charge neutrality in the absence of inorganic cations and fluoride anions. Although one ADAM per cage is often analyzed in SSZ-13 syntheses, framework anionic defects (e.g., deprotonated silanols) likely interfere with this ideal ratio, allowing less Al to be incorporated in hydroxide media or thus higher Si/Al ratios, when only ADAM is used. Di Iorio et al. obtained CHA (with Si/Al = 26) from a Si/Al = 30 synthesis, and even hydroxide materials in the Si/Al = 50 regions are feasible. Attempts to crystallize CHA from higher Si/Al synthesis mixtures in OH^- media, as mentioned above, do not succeed. In contrast to the isolated Al case when only ADAM was used (green square, Figure 16), the use of both Na^+ and ADAM in a 1/1 ratio led to a number of Al-pairs (red square, Figure 16, right) in line with the statistically predicted number for random distribution (red dot, Figure 16, left). Intermediate values (between 0–1) of the Na^+/ADAM ratio (or thus cationic charge density) confirmed this observation and offer one a limited control over the desired amount of pairing (up to the statistical random occurrence) for a given Si/Al ratio. The authors demonstrated this for Si/Al = 15 and 25 materials. At ratios higher than 1, the number of pairs again decreased. Explaining these results is difficult, although it was noted that above a certain ratio, competing zeolites occurred (dashed line in Figure 16). A likely explanation for the influence of the cationic charge density on the number of pairs (maximal when $\text{Na}^+/\text{ADAM} = 1$) was given, based on the more favorable stabilization of an Al-

(charge)-pair by both the quaternary ammonium head of the OSDA and a Na^+ cation in close vicinity (of the same 6MR), compared to when they are further apart (not balancing a pair). The case where they are further apart would entail a larger disruption of the nonpolar contacts between the apolar adamantyl group of ADAM and the siliceous network, on the other side of the OSDA. This would be in line with the reported orientation of ADAM in CHA, i.e., along the *c*-axis or length of the cage. This result suggests that the polar head of ADAM points up to a 6MR, while an additional Na^+ resides in the d6r that 6MR is part of. A recent update by Gounder and co-workers showed that the use of Al-isopropoxide in the synthesis was able to yield up to 44% of Al in pairs, for a Si/Al = 14 material (contrary to 20% in the theoretical curve, Figure 16, left), indicating that statistical pairing is exceeded.²³⁷ The pairing series was also used in catalytic test reactions (section 3.6).

As reported above, Corma and co-workers used ADAM in combination with Cu-TEPA to obtain Cu-SSZ-13 in one pot.²¹⁴ Interestingly, they noted different deNO_x activities for materials from the F^- and OH^- -preparation routes, in spite of similar heteroatom substitution, Cu loading, and particle sizes. This suggests a strong influence of the preparation on the materials. Perhaps, this is related to differences in the Al-pairing or siting, influencing the Cu-speciation. The Co-titration method could thus be of use here, in case Cu can be fully removed before Co-exchange.

2.3.3.6. CHA-Zeolite Conclusions. CHA is, arguably, the most interesting 8MR zeolite from a synthesis point of view, due to its industrial relevance, the vast body of literature, its structure with large cages, and its compositional flexibility (from highly aluminous to pure-silica). Some insights/observations are

- (1) CHA is a member of both the d6r-only and ABC-6 families. The only other two members of both structural families are AFX and SFW, and they present a series with expanding, structurally related cages and similar synthesis conditions.
- (2) CHA can be made without organic, using K^+/Na^+ mixtures in very aluminous compositions or with the help of OSDAs, most commonly ADAM, in more siliceous to even pure-silica forms. Unlike for AEI, there is a great flexibility for different kinds of T atom sources in the ADAM-route.
- (3) It is clear that the ADAM/CHA-cage pair has a highly favorable host/guest interaction. This is evidenced from molecular modeling, the large conditional flexibility (F^- , OH^- , IZC, ...) and the high structural specificity, certainly when compared to, e.g., tetra-alkylated ammonium or piperidinium-based OSDAs. Few other molecular sieves are stabilized well by ADAM, the large-pore silicate AFI being a known exception.²³⁸ The competition with other phases in OH^- -media, for instance, only occurs in mixtures with Si/Al > 55. Strong-structure direction is, however, still not the same as true templating.^{91,192}
- (4) Based on the charge balance and counting cages, the ideal Si/Al ratio of a defect-free SSZ-13 is 11, assuming one ADAM per cage and no sodium in the synthesis (cfr. AEI). The same calculation for AFX and SFW networks is more difficult due to the additional presence of other smaller cages (Figure 10).

- (5) The demonstrated control over particle size in CHA syntheses is rather exceptional in the 8MR zeolite literature. The use of growth-modifiers and insights into the particle attachment mechanism should be further explored for different Si/Al ratios within CHA (e.g., lower ratios are used in SCR, higher in MTO, viz. sections 3.2 and 3.4) and for other frameworks. Lessons learned for CHA could be transferable to zeolites with structural similarity based on 6MR (ABC-6: LEV, ERI, EAB, ...) or d6r (AEI, AFX, KFI, SFW, SAS).
- (6) IZC is a successful method for CHA-synthesis, and materials with Si/Al ratios ranging from 2 to 67 have been reported (Table 5). This upper limit is even higher than in common hydroxide media synthesis. The role of structural similarity between starting (FAU) and product zeolite can assist in the construction of the latter and possibly plays a structure-directing role. Recall that even the OSDA-free standard recipe relies on using an aluminous FAU-zeolite. Hard proof of the *nanoparts* hypothesis is still lacking, but due to ample reports focusing on CHA, the FAU-to-CHA IZC presents an ideal case for deeper investigation. The role of Al mobility/solubility should however not be forgotten.
- (7) The work of Gounder and coauthors in preparing and characterizing the amount of Al-pairs (potentially of use as divalent cation exchange sites) is instructive. It shows that the random Al-distribution, e.g., entailing 16% of the Al-atoms occurring in pairs for Si/Al = 15, is obtained if the Na/ADAM ratio in the synthesis is fixed at 1 for specific amorphous inorganic sources. Lower ratios lead to less pairs, and sodium-free synthesis leads to fully isolated Al-centers in the zeolite. This presents a first proof of a degree of control over the pairing from synthesis in 8MR literature. It is imperative that the Al-distributions resulting from other CHA-synthesis protocols (detailed in this review) are characterized (Co-titration). Equally so, the protocol could be easily verified for other “d6r-only” materials, given that the statistical model for random pairing is based on the Al-occurrence in 6MRs (Figure 16, left).

2.3.4. DDR. The framework DDR is known since its pure-silica form (deca-dodecasil 3R) was prepared by Gies using 1-adamantylamine.²³⁹ In addition to RTH, it is one of the few “relevant” 8MR zeolites that contain 5MR. Since the pioneering effort of Gies, a great deal of work has been performed on pure-silica DDR, especially in the context of sorption and gas-separation (i.e., CH_4/CO_2 ,²⁴⁰ propylene/propane²⁴¹). These pure-silica (nonzeolite) syntheses are out of the scope of this review. The first aluminosilicate DDR, ZSM-58, was patented by Valyocsik,⁵⁸ while Stewart et al. reported the similar Sigma-1 zeolite.⁵⁷

ZSM-58 is made using so-called methyltropinium (Figure 17) in classic gels containing Na^+ , and it typically has high Si/Al ratios; originally from 31 to 111.⁵⁸ Several groups later reported samples with higher and lower Si/Al ratios (178 and 18).^{242,243} In similar gels, with Si/Al ratios specifically at 30 and OH/Si ratios around 0.1–0.17, Stewart et al. found that using the free amine, 1-adamantylamine (Figure 17), also worked for DDR formation, giving the zeolite Sigma-1. Competing zeolites in OH^- -richer media were mordenite and ZSM-5 (both also containing 5MR). Interestingly, using Si/Al ratios lower than 30 gave a competitive formation of LEV zeolite (Nu-3, see section 2.3.8), while less alumina favored Sigma-2 formation

Figure 17. Reported OSDAs for aluminosilicate DDR synthesis and the DDR structure.

(SGT). The material produced by Stewart and co-workers had a Si/Al ratio near 50, but later, Lobo and co-workers and Jeon et al. managed to obtain Sigma-1 zeolite with Si/Al ratios of 16.^{244,164} Given that the all-silica version of DDR exists, the Si/Al ratios of reported DDR-zeolites thus range from 16 to infinity.

Recently, Yarulina et al. studied Sigma-1 and ZSM-58 in close comparison, while assessing the impact of seeding on defect formation and MTO performance (for in depth catalytic discussion, see section 3.4.3).^{245,246} The authors conveniently showed how the use of seeds with specific sizes (0.08, 0.5, and 2.5 μm , respectively, from ball-milling) can produce Sigma-1 zeolites with controlled and uniform sizes (0.5, 2.5, and 4.6 μm , respectively). The particle size of ZSM-58 in this study, made for comparison, was ca. 1 μm .

2.3.5. ERI (and EAB). Erionite is a naturally occurring zeolite with Si/Al ratios close to 3. This zeolite is a member of the ABC-6 family, as is the closely related EAB zeolite (Table 3,

stacking sequences in Figure 18). Interestingly, EAB, with the cage in Figure 18 and also a Si/Al ratio near 3, was first discovered using TMA and only later found in a mineral composition (see Table 1). Natural erionite was used as a shape-selective cracking catalyst in the past (section 1.2, and 3.6.1), and this fueled the need for synthetic recipes. Aiello and Barrer reported the first synthetic ERI, with a similar composition to that of natural erionite using Na^+ and TMA cations. They noted that the TMA cations had to be residing in the large cage of the structure (Figure 7), since the other voids (the *d6r* and *can*-units, Figure 18) are too small to host TMA. Likely, more than 1 TMA was found per cage. The large cages are connected and construct an open 3D-network of 8MR-pores, unlike in EAB, where *gme*-cavities connect the larger cages, and a 2D-network results. Meier reported that in EAB synthesis, the TMA cation occupies the *gme*-cavities (previously shown to be a good fit).⁶¹ The framework densities of EAB and ERI are 16 and 16.1 T atoms/1000 $\text{\AA}^3$, respectively.

While EAB forms in mixtures with the Si/Al ratio at 6.8 and the Na^+ and TMA⁺ to Si ratios at about 0.5,⁶¹ making pure ERI with TMA is more difficult. Often, intergrowths with the closely related OFF zeolite (large pore material) are obtained.²⁴⁷ Rubin and Rosinski patented a method for synthetic ERI, with Si/Al ratios around 4, based on adding BTMA (also used for making CHA through IZC, Figure 14) to Na^+ - and K^+ -containing Si/Al = 14 mixtures.²⁴⁸ Later, OFF intergrowths were also detected in this material.²⁴⁹ Occelli et al. reported an interesting synthesis based on DABCO derivatives (Figure 18).¹⁷⁰ Ironically these authors first labeled their material as an ERI/OFF mixture, but later, through electron diffraction, they showed that it was in fact phase-pure ERI after all, with the Si/Al ratio around 5.²⁴⁹

A breakthrough for synthetic ERI was presented in the 2000s, by using the charge density mismatch approach (method E, Table 2).^{69,148,250} This route offers access to more siliceous ERI, known as UZM-12, so far, up to Si/Al 7.4. The CDM approach is often seen as a two-step procedure. For ERI, first, a mix of SiO_2 , Al-butoxide, and $\text{TEA}(\text{OH}^-)$ is made, with a Si/Al ratio of 16 and a high TEA/Si of 0.8. This mixture does not induce crystallization or solid formation, not even after 28 days.⁷⁰ After digestion overnight, Miller et al. added the crystallization-inducing solution, consisting of a large diquat (e.g., Me_6 -diquat-6, Figure 18) and some KCl (diquat/Al = 2 and K/Al = 4), and incubated at 125 $^\circ\text{C}$ for 7 days. This leads to a pure ERI-zeolite with Si/Al at 5.7. Hong and co-workers incubated similar solutions, but with the diquat and KCl added right from the start, with similar ERI formation results.⁷⁰ They

Figure 18. ABC-6 stacking sequence of ERI and EAB. Middle figures adapted from Meier and Groner.⁶¹ Note that both structures have *d6r* (where two layers are repeated), but they cannot be exclusively formed by that composite building unit. Reported classic DABCO-derived OSDAs for ERI on the left (for DABCO, remove R-groups and the charge), the large Diels-Alder derived OSDA in the middle, and the cooperative CDM OSDAs on the right. Diquats are the crystallization-inducing organics for UZM-12.

Figure 19. Left: the structure of KFI as built from chains of d6r units (blue), with its pau (yellow) and lta cages (green). Right: OSDAs reported for KFI: methyl-di-quaternized DABCO (up) and crown-ether (down). Left: 2D-network adapted from the IZA;³ 3D-network adapted with permission from Remy et al.¹¹² Copyright 2013 American Chemical Society. Compare left to Figure 8 for AEI and CHA.

also noted that diquats (with 6 different kinds of end-groups) that were either too short or long ($n = 3$ or 7) did not yield ERI. These authors also computed the stabilization energies of the diquats in the large ERI cage. They found that the differences between TEA and the diquats were sufficiently large to assume that TEA only acted as a CDM OSDA (preventing the initial mixture from condensing). Strikingly, since a large range of diquats worked in this approach, it is safe to suggest the structurally nonspecific role of these organics, thus as crystallization OSDAs, rather than fitting perfectly. The cation incorporation for the Me₆-diquat-6 ERI for instance, was estimated at (diquat_{1.6}TEA_{0.1}K_{2.1}H_{0.9}H₂O_{10.3})-[Al_{6.3}Si_{29.7}O₇₂], clearly in excess for the diquat with respect to TEA.⁷⁰ It is interesting to note that the recipes from Ocelli et al, using DABCO derivatives (Figure 18), are not far off from the CDM recipes in terms of gel composition, with the exception that, instead of TEA, Na⁺ was used.

Finally, in 2017, Martín et al. reported a new IZC route to ERI, based on a large multicyclic Diels–Alder derived OSDA (Figure 18, middle of OSDAs) and the use of the right FAU (Si/Al = 6) zeolite precursor (OSDA/Si: 0.2, KOH/Si: 0.1, H₂O/Si: 5–15). The same OSDA also led to AFX zeolite (section 2.3.2).¹⁹⁸ An intergrowth of ERI and LEV is also known in the patent literature, i.e., SSZ-105.²⁵¹

2.3.6. GIS. Zeolite P is the synthetic analogue of gismondine (and some other very related mineral structures). It was discovered as Na–P by Barrer and his colleagues.²⁵² The cageless zeolite presents a medium-dense structure (i.e., 16.4 T atoms per 1000 Å³ compared to 19.2 for dense ANA, and 15.1 for CHA), with channels running in three dimensions. The structure is (unusually) flexible and has good inorganic ion-exchange properties.²⁵³ The latter is the reason for its commercial application at the kiloton scale, in a form also known as maximum aluminum P or MAP.^{108,254} Its ion-exchange performance is sometimes attributed to the small crystallite sizes with large external surface areas.²⁵⁵

Barrer and co-workers discovered this zeolite using inorganic components alone. It is a common phase observed in sodium-rich, highly alkaline aluminosilicate gels heated to around 100 °C, and therefore, it is often encountered as an impurity in zeolite synthesis containing both sodium and OSDA. An example of this is the synthesis of AEI, where relatively high OH/Si and Na/Si ratios prevail. GIS-zeolite impurities can often easily be removed via acid-washing, e.g., with HCl, while the OSDA-filled AEI zeolite is acid-stable.¹⁸⁴ Structural elucidation of GIS was performed by Baerlocher and Meier,⁷⁴

and even a TMA-directed, so-called high-silica P, was documented by them. TMA appeared to be occluded, and the Si/Al was 3.²⁵⁶ In the early days of zeolite synthesis, obtaining highly crystalline samples with Si/Al ratios of 1 was difficult. Moreover, different types of zeolite P were found, with different crystal habits. Hansen et al. clarified these issues (discerning between zeolite P1 (Si/Al ± 1.6), P2 (Si/Al ± 2.2), and high-silica P) and investigated the relation between chemical composition and crystal structure.²⁵³ Albert et al. managed to obtain well-crystallized Na–P-zeolites with Si/Al ratio at unity (MAP), from equimolar sodium aluminate and silicate mixtures, with added NaOH at 100 °C for 5 days (likely, the commercial recipe is similar, but with shorter crystallization times). They refined the structure of their aluminous NaP, as well as its Ca-exchanged form (CaP), hereby confirming the GIS net and discussing the close structural relationship between synthetic P-zeolites and gismondine.^{257,258}

The IZA recipe for zeolite P (Si/Al = 1.2) is based on a long 60 day procedure at 85 °C using kaolinite clay as the source of both T atoms in a NaF-rich medium (F/Si = 2.4).²⁵⁹ Gismondine type zeolites have also been prepared via hydrothermal, high-pressure (geomimicking) conditions by Ghobarkar and Schaf. These authors synthesized a lot of 8MR zeolite in this way (e.g., EDI, EPI, ANA, THO, see method A in Table 3). At 1000 bar, and temperatures near 250 °C, gismondine type minerals could be prepared from the glass 4CaO–4Al₂O₃–8SiO₂.⁶⁷

As mentioned (sections 2.3.3.4), zeolite P has been used as an Al-source in partial interzeolite conversions, leading to CHA (and LEV, see later). The opposite direction, i.e., IZC leading to GIS, is also known. Subotic and co-workers studied the transformation of zeolite A (LTA) into P (GIS).²⁶⁰ In this transformation, the authors thought it was more likely that the P-nucleation happened in the solution, rather than on the zeolite A's surface and thus that zeolite A and P existed as discrete particle systems during all stages of the transformation. IZC in this case clearly contrasts with that of other more siliceous zeolites (e.g., CHA or LEV), probably due to the highly alkaline (NaOH) conditions.

The more recent zeolite P work focuses on morphology control (Si/Al dependent),²⁶¹ the use of different, cheaper, T atom sources (e.g., fly ash), or alternative methods (e.g., microwave, sonochemistry).^{262,263} Sharma et al. noted a Na–P1 synthesis where the zeolite seemingly exhibits spherical morphologies, composed of a large number of nanocrystalline particles (40–100 nm), rendering the zeolite mesoporous.²⁶⁴

Table 6. Overview of Notable LEV-Zeolite Synthesis Conditions

E	Sources ^a	OSDA	synthesis mixtures composition relative to Si				T, t °C, h	Si/Al prod.	ref
			Al	OSDA	Na ⁺	H ₂ O			
1	Si, NaAlO ₂		0.19	0.95	0.27	13	95, 120	2.1	35
2	Si, NaAlO ₂		0.02	0.20	0.20	12	180, 72	49	272
3	Si, NaAlO ₂ (seeds)	MeQ(OH ⁺)	0.033	0.29	0.40	27	180, 180	26.5	273
4			0.067	0.29	0.39	11	150, 96	11.2	273
5	Si + Al(OH) ₃	MeQ(I ⁺)	0.20	0.20	0.30	17	170, 360	5.0	275
6	Na-GIS + Na-silicate	MeQ(I ⁺)	0.063	0.13	0.94	34	135, 168	6.0	142
7	Si, pseudo-boehmite		0.2	2	2 F ^b	16	170, 360	8.2	279
8			0.1	1 + 1 ^c	2 F ^b	16	170, 360	10.7	279
9	Si, NaAlO ₂		0.033	0.52	0.08	15	130, 552	13.5	280
10	Si, NaAlO ₂	DEDMA	0.08	0.50	0.08	10	150, 336	11.5	281
11	colloidal SiO ₂ , Al(OH) ₃		0.04	0.12	0.12	8	150, 240	7.4	282
12	Si, Al(NO ₃) ₃		0.033	0.10	1.13	40	160, 72	7.9	283
13	H-FAU _{s,a}		0.063	0.50	0.2 NaCl	5	125, 168	8.8	284
14	H-FAU _{s,a}		0.045	0.50	0.2 NaF	5	125, 168	10.7	285
15	H-FAU _{s,a}		0.045	0.30	0.05 ^d NH ₄ F	10	150, 168	21.3	285
16	H-FAU _{s,a} + seeds (E13)	-	0.040	0 ^e	0.6	15	125, 72	5.3	286
17	Si, NaAlO ₂ + seeds (E10)	ethanol	0.047	1.5 ^f	0.73	35	120, 72	4.1	287
18	H-FAU _{s,a}		0.056	0.2	0.3	5	170, 24	10	288

^aSi indicates silica sol or fumed silica. Quaternary amines (OSDA) and Na⁺ in/from hydroxide form unless otherwise mentioned. s.a. = steamed and acid-leached. ^bNear neutral fluoride media synthesis without Na⁺, with HF (F/amine = 1). ^cMethylamine and seeds added. ^dNo Na⁺ used. ^eNote that the seeds (17%) contained choline, as they were made according to entry 13. ^f1-2 ethanol to Si used, on top of 5% seeds made according to reference from entry 10, with Si/Al 9.8, calcination unsure.

Goel et al. have looked into incorporating metal clusters in the small-pore zeolite, by blending (organic amine or ammonia ligated) metal precursors into the synthesis. Interestingly, metal-containing zeolite ANA (dense 8MR zeolite) was obtained by the IZC of a metal-containing GIS.²⁶⁵

The relevance of MAP is evident, given its industrial application. However, pure-phase syntheses of GIS zeolites with Si/Al ratios higher than 3 have not been encountered in our search. It might however be important to look for highly siliceous or even pure silica GIS phases, as these could have beneficial properties for small-molecule separation (CO₂/CH₄/H₂ e.g.). The synthesis of such GIS materials will be especially challenging, as it does not resemble the high-silica approaches for cage-based 8MR zeolites, e.g., applied to CHA or LEV, where organics are incorporated easily. Even lessons from LTA synthesis (section 2.3.9), that for a long time had the same limitations to its Si/Al range (max. 3), do not seem relevant here.

2.3.7. KFI. Barrer encountered the first KFI zeolite using Basalts and synthetic analcime (also other minerals and gels) as T atom source at around 200 °C.¹²⁵ He recognized it as being the first synthetic zeolite with no natural counterpart and noticed its 8MR behavior by comparing it to chabazite. Structure elucidation and the first presentation of the very relevant framework were presented by Meier and Kokotailo, with Mobil's ZK-5 zeolite (different synthesis). ZK-5 was among the first zeolites prepared with an OSDA in hydroxide media.^{88,127,266} The structure of KFI can be built from the large (α -cage) *lta*-composite building unit, a large cuboctahedron, also found in LTA and RHO (Figure 7). These large cages are linked to each other by their 6MR, effectively forming d6r units (Figure 19). In contrast, to obtain LTA, the large cages are linked by their 4MR (in d4r), and by sharing their 8MR, while in RHO, they are exclusively linked by their 8MR (via d8r, Figure 23 below).¹²⁷ Given the KFI description based on *lta*-cages, linked by d6r, the remaining space is filled by *pau*-cages (2 projections of this building unit in Figure 19). In the

Figure 20. Left: crystallization curves for LEV with MeQ(I[−]) in the conditions of Table 6, entry 5 at different temperatures. Using induction time (t_{ind} , in hours) as a measure for nucleation rate and the linear slope of the relative crystallinity (R , in change/day) for the crystallization rates, the plot on the right can be constructed for Si/Al = 5. Right: logarithmic nucleation and growth rate as a function of the Al-content. The nucleation curve is translated to fit both plots in one frame. Based on data and figures from Tuoto et al.²⁷⁵

light of 8MRs, the latter is an interesting unit, as it is composed of two types of 8-rings, one set of these being near planar. Interestingly, the entire KFI structure can also be constructed from only d6r units. As with AEI and CHA, the d6r units can be visualized ordered in chains that form planes (Figure 19, left), which lead to the large cavities by stacking.

Given the clear structural links between KFI, RHO, and LTA, based on the large cage and with KFI being a member of the “d6r-only” family, the synthesis of KFI presents an interesting case. Kerr reported ZK-5 using the methylated diquat of DABCO (Figure 19) in the presence of Na⁺, and these materials had Si/Al ratios between 2.0–2.5. Later, ZK-5 was produced by Robson, in a more straightforward, organic-free way, using K⁺ as principal cation and Cs⁺ as cocation (with or without Na⁺). Robson’s KFI zeolites had Si/Al ratios below 3.5.⁸⁷ The latter recipe was recently confirmed by Ji et al. yielding Si/Al = 3.1, in an attempt to evaluate dealuminated KFI in methanol conversion.²⁶⁷ A higher-silica KFI was claimed by Verduijn, using a mix of Sr²⁺ and K⁺, typically in gels with Si/Al ratios near 5. The actual ratios of the materials were often close to 3.5.²⁶⁸ When insufficient Sr²⁺ is added (Sr²⁺/Si < 0.0025), the gels typically lead to the one-dimensional 12MR zeolite LTL. Interestingly, Verduijn noticed that decreasing the alkalinity was found to slightly increase the Si/Al ratios and also that the addition of trace Ba²⁺ helped as well: a gel containing K⁺/Si, Sr²⁺/Si, and Ba²⁺/Si ratios of 0.36, 0.01, and 0.0005, respectively, yielded KFI with Si/Al = 4.2, at 150 °C. Chatelain et al. reported an interesting variation of the Sr²⁺ recipe, by using an additional organic crown-ether (Figure 19) in the gel and the same amounts of K⁺ and Sr²⁺. The crown ether was found to speed up the crystallization of KFI, slightly decreasing the Al incorporation (Si/Al = 4.0). One crown-ether was incorporated per unit cell in the product, in the *lta*-cage. In a reverse strategy for aluminum and in the context of CO₂ adsorption, Remy et al. proposed a recipe for low-silica KFI, achieving Si/Al ratios near 1.7, based on using Li⁺, Na⁺, K⁺, and TMA cations.¹¹² This recipe somewhat resembles another entry by Barrer, who combined Li⁺, Cs⁺, and TMA to obtain KFI.²⁶⁹

The structure of KFI, the first synthetic zeolite and also the first example of interzeolite conversion, is a promising one: as Meier pointed out, the zeolite has two independent 3D-pore systems based on 8MRs and large, useful cages.¹²⁷ For gas-separation and adsorption, KFI has been reported to some extent, but its use as a catalyst is largely unexplored. The latter is explained by the fact that, strikingly, a zeolite version of the framework with Si/Al > 5 has never been reported. Methods to postsynthetically remove Al have been evaluated, but a

synthetic recipe leading to more stable KFI zeolites with Si/Al ratios in the range of 10–50 would be a game-changer. Given the recent progress in making high-silica and even pure-silica LTA in fluoride media, based on stabilizing the large α -cages (see below^{37,135,172}), the synthesis of the KFI framework could be revisited in high-silica gels, using similar OSDAs. A second approach to KFI could focus on IZC methods starting from FAU, as reported for CHA and AEI. Given the systematic relationship between KFI and the structures of these two d6r-only frameworks (planes of d6r), as pointed out by Lillerud,²⁷⁰ new synthesis routes to KFI might be found in modified CHA or AEI-conditions. The most difficult part will be to stabilize the larger *lta*-cages. In this context, the SAV-topology deserves mention: this framework, also constructed from d6r planes and chains and with a relatively large cage, has only been reported in metalloaluminophosphate composition (not a zeolite), using azamacrocycles. The latter are similar to crown-ethers (Figure 19), but with nitrogen instead of oxygen and with additional methyl groups on the nitrogens.²⁷¹ Exploring these or similar OSDAs in conditions known to crystallize zeolites CHA or AEI (LTA, KFI) could be an option.

2.3.8. LEV. LEV, known from minerals (Table 1-3), is another member of the ABC-6 family, with stacking sequence AABCCABBC. LEV has some d6r units, but cannot exclusively be built from them. LEV has one of the smaller cages of the 8MR zeolites (Figure 7).

Kerr claimed the first synthetic LEV by using monomethylated DABCO (Table 6, entry 1), and he obtained highly aluminous products (Si/Al from 1.9 to 2.7) that closely resemble the natural levyne. Short and Whittam patented Nu-3, a more siliceous form of LEV, with Si/Al ratios ranging up to 50 by using *N*-methylquinuclidium as OSDA (MeQ, Table 6, entry 2).²⁷² Casci et al. further investigated Nu-3 formation (Table 6, entry 3–4) with MeQ. Although structurally similar to DABCO, the MeQ molecule is not able to lead to LEV in the conditions of Kerr, and vice versa, the DABCO OSDA did not lead to Nu-3 in Casci’s conditions.²⁷³ Later, Stewart also patented Nu-3 made from 1-adamantylamine (not in table).²⁷⁴ Adamantylamine is known from DDR synthesis (section 2.3.4).

Tuoto et al. presented a thorough study on the crystallization of LEV from classic gels, with the MeQ OSDA in its iodide form.²⁷⁵ They studied nucleation and crystallization rates for different Si/Al starting ratios ranging from 5 to 25 (e.g., Table 6, entry 5), as well as for different temperatures. This range is more aluminous than that in Casci’s work,²⁷³ and the Al-incorporation matched the content in the synthesis mixtures well. The crystallization curves for Nu-3 at Si/Al = 5 (Figure

20, left) allowed for the calculation of an (apparent) activation energy that is around 21 kJ/mol for both nucleation and crystal growth (thermally activated, Arrhenius). This energy for the crystallization is on the low side, as for example Thompson's review showed a range of 45–80 kJ mol⁻¹ to be common for a variety of molecular sieves.²⁷⁶ Values in the latter range would be indicative of control (limitation of rate) by the surface reaction rather than by diffusion from precursors of the gel or solution to the crystal surface. Given the low value for LEV found by Tuoto et al., the question arises whether their data shows diffusion-limited growth rates. Such low values could suggest that larger condensed particles (amorphous precursors) have to transport to the surface and attach to the growing crystal, rather than monomolecular T atom precursors or small oligomeric species.^{167,207} Next, these authors investigated the influence of the amount of aluminum on both rates, and they expressed this in linear plots with logarithmic variables (Figure 20, right). The higher Al-content of the gel or the process of incorporating more Al in the frameworks, had a strong negative effect on the rates of crystallization and nucleation (i.e., longer induction times).

The authors also performed a thermogravimetric analysis (TGA) to find proof that MeQ associated with negatively charged silica defects, i.e., Si–O⁻ or siloxy groups,²⁷⁷ at high Si/Al ratios (next to compensating Al-framework charge). For Si/Al = 5, a uniform decomposition zone for the organic was found in TGA, but for lower Al-incorporations, a second decomposition temperature emerged, in conjunction with an improper charge balance indicating the formation of SiOM or Si(OM)₂ (with M being MeQ⁺, Na⁺ or H⁺). The latter was confirmed by ²⁹Si NMR and mass spectrometry, as well as by calcination, where the defect groups disappeared upon dehydration.²⁷⁵ The authors also analyzed the MeQ, Na, and Al contents per unit cell, but no calculation related to MeQ occlusion in cages was given. We performed a count of the number of (individual) T atoms per cage for LEV in two ways. The unit cell possesses 6 full cages for 54 T atoms or on average 9 “full” T atoms per cage.¹⁷⁶ This value is also possible to obtain from counting the T atoms surrounding the cage and taking into account their degree of sharing over cages: 30 T atoms form the *lev*-cage, but by viewing a 3D-model, one can discriminate between T atoms that are part of the d6r units (red in Figure 7) and those that are part of singular 6MR (the ABC-6 sequence can be useful here). The latter (blue in Figure 7, 12/30 T atoms) are shared over 4 cages, while the remaining 18 d6r-T atoms are shared over 3 cages, thus adding up to 9 full T atoms per cage. Considering one MeQ per cage, this would indicate that Si/Al = 8 ratios (8Si + 1Al) are ideal for not having defects. Interestingly, Tuoto et al. analyzed 5.8 MeQ molecules per unit cell, perfectly matching the 5.8 aluminums per unit cell for their material with Si/Al ratio of 7.5. More aluminous materials incorporated more Na⁺ (no defects), while less aluminous ones had more or less the same amount of Na⁺ (but with increasing defect sites). The balance MeQ/Al was only 1 in the Si/Al = 7.5 case. Taking into account our analysis and those for AEI and CHA above, it appears that there is an ideal Si/Al ratio for the MeQ (Nu-3) LEV-type material. An interesting open question is whether this influences or causes the slower rates of nucleation and growth in the more aluminous case (e.g., Figure 20, right, Si/Al = 7.5), considering, e.g., that building defects entail less condensation reactions and less strain. This analysis is illustrated in Figure 27 in section 2.4.

Using MeQ as well, Zones and co-workers reported the formation of Nu-3 starting from zeolite P (GIS) and soluble sodium silicate (Table 6, entry 6).¹⁴² Recall that these authors also used this type of gel-free system to obtain 8MR zeolites CHA (Table 5, entry 5) and AFX from the same GIS. Interestingly, Chan et al. presented a follow-up study where the GIS-to-LEV transformation was monitored by electron microscopy, as all changes take place without GIS transforming into an amorphous phase.²⁷⁸ The nucleation of the LEV was found to occur at the surface of the disappearing GIS crystals (solution/solid interface), but no evidence of phase-intergrowth was found in electron diffraction. The authors suggested a role for the organic as a phase-transfer reagent at this interface due to the rate-enhancement effect of the organic. Keeping Tuoto's low activation energies for LEV crystal growth in mind, this role could be plausible. The resulting zeolites' Si/Al values are quite low, i.e., doubled versus the starting GIS (additional sodium silicate is added). Whether this is limited by the high solubility of silica in these hydroxide rich systems (Table 6, entry 6) or our above hypothesis that the MeQ-zeolite has a tendency for low Si/Al ratios around 8 (or lower based on Na⁺) remains to be seen.

Caullet et al. prepared LEV in fluoride media by using the free amine quinuclidine (Table 6, entry 7, drawn with proton as the pK_a is 11, and the synthesis neutral).²⁷⁹ They noted that the obtainable Si/Al ratio in the materials was very limited (between 8 and 11) and that only 0.6–1.3 F⁻-anions were incorporated per unit cell (along with 6 quinuclidiniums (ammonium)). Pure-silica LEV, with coincorporation of one F⁻-anion per OSDA, can thus not be made in this manner. The authors also added methylamine to some synthesis and noted that, in its presence, a part of the OSDA incorporated was in situ formed MeQ (entry 8).

Researchers from Mobil reported zeolite ZSM-45, also of the LEV-topology, by using choline chloride, metal–organic complexes²⁸⁹ such as [Co(C₅H₅)₂]⁺ or, notably, diethyldimethylammonium as organic additive (DEDMA, Table 6, entry 9). The latter organic was claimed to lead to LEV in mixtures with Si/Al ratios between 5 and 40, while lower or higher values led to formation of FAU or MTW-type zeolites, respectively.²⁸⁰ Yamamoto et al. confirmed this recipe and presented a structural analysis of this LEV-analogue in a synthesis where product and gel roughly had the same Si/Al ratio (Table 6, entry 10).²⁸¹ Notably, they found that the ethyl groups of the occluded OSDA were allocated to build a 5-membered organic ring (4-carbon, 1 nitrogen). They then briefly also demonstrated successful LEV syntheses with the *N,N*-dimethylpyrrolidinium, and *N,N*-dimethylpiperidinium cations (i.e., respectively using the 5-membered ring and an organic with one additional carbon in the ring). The latter had already been reported for LEV, by Xu et al., who showed Si/Al ratios ranging from 3.4 to 10.6 in the materials, even though some gels had much higher ratios (Table 6, entry 11, chloride form).²⁸²

Hong and co-workers discovered that the aliphatic diquat (or protonated di-tertiary amine in this case) Me₄-diquat-5 (bromide form, Table 6, entry 12) could lead to LEV in a very narrow range (Si/Al in gel = 20–30).²⁸³ This group had already successfully used other diquats for 8MR zeolites (see AFX and ERI). The narrow range of conditions and the high OH⁻ and Na⁺ contents demonstrate the inorganic domination in this synthesis. Strikingly, the Si/Al of this aluminosilicate LEV, again, is close to 8. Moreover, elemental analysis showed around 3 diquats per unit cell, which seemed plausible from ¹³C

NMR and stabilization energy calculations considering one organic spanning 2 cages. The authors rightfully noted that the diquat in this case plays a structurally nonspecific space-filling role, as it is also known to lead to NON, MTW, and MOR in similar inorganic-dominated gels. This is similar to the role of such diquats in ERI synthesis (CDM).

Besides the partial IZC mentioned above for LEV from GIS (added silica, entry 6), the Sano group reported the synthesis of LEV from FAU-zeolites, in both hydroxide and fluoride media. They found that choline hydroxide as organic worked well, and they noticed highly microporous LEV forming from zeolites with Si/Al ratios of 16–22 (not higher, Table 6, entry 13).²⁸⁴ From TGA, seven decomposing cholines per unit cell were counted and the Si/Al ratio was (again) close to 8. Amorphous precursor syntheses did not lead to LEV-crystallization. FAU belongs to the d6r-only family, while LEV contains a decent number of d6r, on top of free 6MR connected through 4MR and 8MR. A time-resolved PXRD study showed the disappearance of all FAU reflections, before LEV reflections appeared from the X-ray-amorphous mixtures. Later, the same group investigated this transition in fluoride (-containing) media, using 1-adamantylamine or choline hydroxide (Table 6, entry 14–15).²⁸⁵ Using choline hydroxide, Na⁺ was necessary to obtain crystalline LEV and it should be noted that these syntheses contain more OH⁻ (from OSDA) than F⁻ anions. From adamantylamine (no hydroxide), the conditions were more flexible, were Na⁺-free, and worked over a larger Si/Al range. Recall that Stewart patented this OSDA for Nu-3 in classic hydrothermal systems.²⁷⁴ The 1-adamantylamine products were in close relation to the starting FAU, i.e., 13–29 in the obtained zeolites (Table 6, compare entries 14–15). The 1-adamantylamine-containing synthesis thus inferred high yields. Another striking difference with the choline catalyzed IZC was that the FAU zeolite did not disappear with 1-adamantylamine before LEV reflections were seen. A very recent IZC details the use of *N,N*-dimethylpiperidinium hydroxide as OSDA for obtaining nanosized LEV particles (e.g., 35 nm in entry 18). Comparable synthesis from amorphous sources yielded 80 nm crystals, while a similar recipe with choline hydroxide (cfr, entry 13–14) led to larger 220 nm sized zeolites. Nanosized LEV materials in the range of Si/Al = 10–30 can be accessed with this new IZC route.²⁸⁸

Finally, two organic-free, seed-assisted methods for LEV synthesis have been reported (Method B, Table 2). First, the Sano group succeeded in transforming FAU (Si/Al = 25) in the presence of a large amount, 17 wt % based on silica, of uncalcined, choline hydroxide containing seeds (Si/Al = 10.7, made according to entry 13).²⁸⁶ The resulting zeolite had a low Si/Al, and the yield was around 20% (entry 16). Interestingly, the authors note that the LEV had a silica enriched core and Al-enriched shells. Likely, the core stems from partially dissolved, more siliceous seeds onto which the new zeolite has grown. All choline in the seeds was recovered in the final zeolite. When calcined seeds were used, no LEV was formed, indicating that the seeds are more stable when containing the organic.²⁸⁶ A second OSDA-free method was reported by Zhang et al., using 5 wt % of LEV-seeds from a DEDMA synthesis (likely calcined) and ethanol (Table 6, entry 17). The ethanol suppressed the competing MOR-zeolites, and the resulting LEV had a low Si/Al ratio of 4. Solid yields were not mentioned and the pore volume of the Na-containing zeolite was very low.²⁸⁷

In conclusion, LEV is an appealing 8MR zeolite, and even though the structure is known from aluminous natural minerals

(Si/Al = 2), its synthetic aluminosilicate counterparts are always synthesized with the use of an OSDA (despite of some OSDA-derived seeded synthesis). When comparing all representative entries in Table 6, it is clear that a lot of syntheses lead to LEV with Si/Al ratio around 8, and a link with the cage-based organic incorporation has been suggested. The best OSDA for making these zeolites over the broadest Al-content range is the methyl-quinuclidinium cation. So far, the highest Si/Al ratio reported still dates back to the first patent using said organic.²⁷² The abundance of 6MR in the structure could matter in the IZC conversion routes starting from FAU but is yet to be proven. Recent mechanistic studies concerning the crystallization mechanisms of LEV and other cage-containing zeolites (CHA, LTA, and UFI) are discussed in section 2.4.

2.3.9. LTA. 2.3.9.1. *Introduction and Pioneering Syntheses.* LTA is the best-known 8MR zeolite. Its use as a universal drying agent (desiccant) in gases and polar or nonpolar liquids and an ion exchanger and adsorbent for organics is widespread (domestic, industrial, academic). Consider for instance that zeolites 3A, 4A, and 5A are all commercially available LTA varieties, that effectively have different practical pore openings of 3, 4, and 5 Å, because they are exchanged with either K⁺, Na⁺, or Ca²⁺, respectively. The cubic structure of the zeolite is easily recognizable and harbors the large *lta* (or α)-cage (Figure 7). These cages partially connect with each other through d4r units, as well as by sharing their 8MR. The common building unit arising from this organization is the sodalite (*sod*-) cage, and the structure is more easily visualized by connecting *sod*-cages through d4r (Figure 21). Recall that in KFI and RHO, the *lta*-cages connect through d6r and d8r units, respectively (Figures 19, 23, and 24).

Figure 21. Structure of LTA with its three composite building blocks (red). Adapted from Conato et al., ref 290 with permission of The Royal Society of Chemistry. (Compare to Figure 23, section 2.3.10). The blue structure shows LTA built from eight *lta* (or α)-cages.

The pioneering synthesis of LTA led to the zeolite called “Linde type A”. A standard procedure is now available for this material that has a Si/Al ratio of 1 (Table 7, entry 1). Since the discovery, researchers have attempted to make LTA type materials with higher Si/Al ratios. As reported by Kerr, Si/Al ratios near 1.5 were attained by using the TMA cation in conjunction with Na⁺ (ZK-4 material, Table 7, entry 2). Entry 3 presents the very similar IZA-recipe for ZK-4. Later, Mobil researchers also reported zeolite alpha, with Si/Al ratios near 3.²⁹¹ The standard IZA recipe for that form of LTA differs from the original one. Essentially, the OSDA added per Si is much lower in the IZA-recipe for a strikingly higher Al-content, while the gels are richer in sodium (compare Entries 4 and 5 in Table 7). Kühl et al. also reported a method leading to LTA with Si/

Table 7. Overview of Notable LTA-Zeolite Synthesis Conditions

E	material name / approach	OSDA	synthesis mixtures composition relative to Si				T, t °C, h	Si/Al prod.	ref
			Al	OSDA	Na ^a	H ₂ O			
1	Linde type A	-	1.03	-	3.29	66	99, 4	1	167
2	ZK-4		0.49	2.03	0.72	75	100, 24	1.4	132
3	ZK-4	TMA	0.51	2.11	0.79	82	100, 32	1.4	167
4 ^b	zeolite alpha	TMA	0.09	0.89	0.09	15	78, 144	3	291
5	zeolite alpha	TMA	0.20	0.48	0.21	12	90, 30	3	167
6	UZM-9	TEA + DEDMA + TMA	0.12	0.4 + 0.1 + 0.06	0.06	14	98, 240	5.5	148
7	ITQ-29 ^c		0.02 ^e	0.25 + 0.25	0.5 F ⁻	3	135, 120	47	37
8	as entry 7, different seed	TMA + π - π -complex	^d	0.25 + 0.25	0.5 F ⁻	4.5	135, 168	110 - 440	294
9	as entry 7, FAU + seeds	TMA + π - π -complex	0.02 ^e	0.25 + 0.25	0.5 F ⁻	2	135, 120	63	295
10	pure Si-LTA seeds		0.05	0.05 + 0.45	0.5 F ⁻	5	125, 216	12	135
11		TMA +	0.01	0.05 + 0.45	0.5 F ⁻	5	125, 168	42	135
12	no seeds	TMA + DM3(4MB)	0.02	0.02 + 0.50	0.49 F ⁻	5	175, 72	56	172
13	seeds	TMA + DM3(4MB)	0.13	0.10 + 0.50	0.49 F ⁻	5	175, 11	8.3	172
14	no seeds		0.01	0.01 + 0.50	0.49 F ⁻	5	175, 72	-	172
15	HOU-2	-	0.43	-	0.56	10	65, 24	2.1	290
16 ^f	metal/LTA		1.18	0.12	3.76	65	100, 12	1	296

^aNa/Si, unless other element is explicitly mentioned; then element/Si ratio is tabulated, e.g., F/Si. ^bCalculated from example 1 of the original patent, assuming use of pure NaAl₂O₃ where stated sodium aluminate. ^cSeeded with 10 wt % pure-silica LTA. Two such OSDAs can form a π - π -complex; see Figure 22. ^d1, 5, or 10 wt % of LTA (Si/Al = 2) seeds added, giving Si/Al of 110, 267, or 440. ^e10 wt % of FAU (Si/Al = 2.5) added, and 5 wt % of ITQ-29 seeds. ^f0.011 Pt/Si was also added. The organic is said to lose its methyl groups by hydrolysis, associate with 3 Na⁺ cations, and complex with the metal giving Pt(Na₃-OSDA-SH)₄.

Al ratios ranging between 1 and 2.25 using (eventually intercalated) phosphates (claimed to complex Al-atoms during the synthesis).²⁹²

2.3.9.2. Toward Higher Si/Al Ratios. The Si/Al ratios of classic LTA zeolites (<3) are not high enough to ensure a good performance in acid-catalyzed reactions. This is due to the low hydrothermal stability and low hydrophobicity. Given the large voids and highly open 3D structure, LTA should be an interesting catalytic sieve, if Si/Al ratios higher than 10 are achievable.

Moscoso et al. filed a patent in 2002 for the synthesis of LTA through the CDM approach.²⁹³ The charge density mismatch approach seems to work well for small pore-zeolite synthesis, since next to LTA, ERI and UFI zeolites can be made that way (Tables 2 and 3: method E).

The first CDM paper describes how to find the right, frustrated (CDM) precrystallization mixtures.¹⁴⁸ These mixtures stay solutions even after long times at higher temperatures, due to the charge density mismatch between the

relatively high Al-content (high charge density potential framework) and the (low charge density) CDM OSDA (ideally tetrapropylammonium or TEA, in mixtures with Si/Al $\leq$ 10 at OH/Si $\geq$ 0.8). Then, by adding the right amount of TMA or Na (higher charge density), matching occurs and the crystallization is induced. LTA was encountered in a TEA-mismatched mixture (Si/Al = 8, TEA/Si = 1) upon adding TMA and Na (both 0.5 per Al) and 8 days at 125 °C. The conditions closely resembled that to make UZM-5 (at 150 °C, 4d), the new zeolite topology discovered via CDM (UFI, Table 3). Further optimization led to a mismatch mixture containing both TEA and DEDMA (this OSDA was encountered in Table 6 as well for LEV), crystallized by adding Na and TMA ([Na + TMA]/Al = 1, Table 7, entry 6). The material had a high Si/Al ratio of 5.5 (high for a OH⁻-media derived LTA), and all three organics were found to be incorporated.¹⁴⁸ A detailed charge density model was recently proposed, focusing on UFI and LTA. The authors noted that the crystallization inducing cations (and heat) attack the CDM barrier, while the driving

Figure 22. Formation of ITQ-29 (LTA) from the supramolecular self-assembly of 4-methyl-2,3,6,7-tetrahydro-1H,5H-pyrido [3.2.1-ij] quinolinium iodide. Atom colors: green = N, red = C, blue = T atoms, yellow = O, white = H. For aluminosilicate, TMA needs to be added, that presumably occupies the sod-cage in the center (not shown). Note how the *lta*-cages are connected in this view, compared to that in Figures 21 and 23. Reproduced with permission from ref 37. Copyright 2004 Nature Publishing Group.

force for solid formation from a frustrated mixture is the Coulombic stabilization associated with the charged zeolite framework.²⁹⁷ The mechanism of LTA formation via this route, in comparison to UFI, was studied in detail by Hong and co-workers, as discussed in section 2.4.^{297,298}

A second breakthrough for LTA was presented by Corma et al. in 2004, when they prepared so-called ITQ-29, in fluoride media syntheses. Although mostly pointing to germanosilicate and pure-silicate versions of LTA, the authors also showed an aluminosilicate LTA by using TMA in conjunction with a large supramolecular OSDA complex of two identical large aromatic π - π -stacked cations (Figure 22). That moiety self-assembles in solution and incorporates in the large cage.³⁷ The synthesis was heavily seeded (Table 7, entry 7) and yielded a material with a Si/Al ratio of 47.

Valtchev and co-workers further investigated the self-assembly approach, focusing on aluminosilicates.²⁹⁴ They proposed a reproducible recipe for high-silica LTA by adding nanocrystalline aluminous LTA seeds (Si/Al = 2, made according to ref 299)—still containing TMA—to the fluoride media synthesis (Table 7, entry 8). The seeds dissolved, and the aluminum was incorporated into the growing crystals. Highly siliceous LTA's thus obtained could be used for new seeded synthesis (1 wt % being enough). The lowest Si/Al ratio in this approach was 110. Very recently, Moteki and Lobo expanded this approach by using FAU crystals as Al-source in fluoride media, still with the self-assembled complex OSDAs leading to LTA zeolites with Si/Al ratios ranging from 63 to 420 (Table 7, entry 9).²⁹⁵ As with the aluminous LTA seeds, it was shown that the FAU-crystals dissolved in the early stages, prior to LTA formation. It should be mentioned that germanosilicate ITQ-29 seeds were added there. This method of using FAU crystals as Al-source in low-water fluoride media gels was also demonstrated for CHA.²⁹⁵ Note that (i) the synthesis of aluminosilicate LTA with the self-assembling OSDAs has never succeeded without seeds (Entries 7–9); (ii) the use of Kryptofix K222 ($C_{18}H_{36}O_6N_2$), a large crown-ether, for (germano)silicate ITQ-29 has also been reported, but not for aluminosilicate³⁰⁰ and; (iii) many recipes with other organics are known for other LTA sieve compositions (e.g., $AlPO_4$).^{301,302}

A third breakthrough in widening the Si/Al ratios of LTA was reported by Davis and co-workers.¹³⁵ The use of 1,2-dimethyl-3-(4-methylbenzyl)imidazolium (DM3(4MB)) and a small amount of TMA in fluoride media offers an LTA-recipe with flexibility in the aluminum incorporation (Table 7, entries 10–11). As such, Boal et al. demonstrated seeded syntheses yielding LTA with Si/Al ratios ranging from 12 to 42. This almost closes the gap in the prior Si/Al range, as up until then, no aluminosilicate LTA had been reported with ratios in the range between 5.5 (CDM method) and 47 (self-assembled OSDA). It was also possible to obtain pure-silica LTA, with either seeds or TMA added. The robustness of the method was shown by germanosilicate and titanosilicate LTA syntheses. TGA showed two OSDA molecules in the *lta*-cage, and this was supported by molecular modeling. A stabilization energy of -16.9 kJ per mol Si, for 2 OSDAs per unit cell, was found. The energies for the supramolecular stacked OSDA were also calculated and averaged at -13.03 kJ/(mol Si). A bit later, Jo et al. reported the same OSDA for LTA synthesis (entries 12–13), as well as a modified version with a fluoro group (entry 14).¹⁷² The syntheses with the same OSDA were conducted at higher temperature, and no seeds were needed for similar results as the earlier report (compare to entries 11–12). Using seeds, a material with intermediate Al-content was obtained (Si/Al = 8.3, entry 13).

2.3.9.3. Other LTA Syntheses. The Rimer group interestingly reinvestigated the synthesis of LTA without organic with the help of kinetic (ternary) phase diagrams, as often used in the early days of zeolite discovery.²⁹⁰ Remarkably, they found a region in the diagram, using classically composed mixtures of colloidal silica, NaOH, and sodium aluminate, where LTA zeolites with Si/Al ratios near 2 formed. The narrow region dictated a Si/Al ratio in the mixtures between 2.3 and 4.0 and a Si/OH ratio between 1.8 and 2.5 (e.g., Table 7, entry 15). When compared to the classic OSDA-free LTA synthesis (entry 1), the Si/Al ratio of the product is doubled. When compared to the ZK-4 syntheses (entries 2–3), one can see that the conditions are not greatly different, but—while ignoring the presence of TMA and its OH^- —the NaOH-derived Si/OH ratios are crucially lower, at 1.4 and 1.3, respectively, for entries 2 and 3 in Table 7. The authors also noted that the size of the

Si-precursor colloids greatly mattered, as smaller ones produced FAU and fumed silica produced amorphous materials in the same conditions. The (right type of) colloids are said to lead to the assembly of amorphous core–shell precursors with silica-rich insides and alumina-rich shells.³⁰³ The authors recently investigated the role of heterogeneous aluminosilicate precursors in the sol–gel system during LTA nucleation. They put forward some interesting observations pointing to the role of core–shell particles containing entrained solvent, in a seemingly macroscopic homogeneous “gel”. The particles give rise to microscopic domains with very different spatial Si and Al distributions. The degree of heterogeneity influences the nucleation via the rate of silica release into the Al-rich environments (e.g., shell). Confinement effects, indicating that zeolite formation inside the amorphous precursor particles is energetically less favored than on the outside, were hypothesized.³⁰⁴ The synthesis of nanocrystal LTA has also been reported.³⁰⁵

There have been a lot of developments in the direct synthesis of mesoporous zeolites (opposed to popular postsynthetic methods^{306,307}), for overcoming mass-transfer limitations. Xiao et al. showed the use of mesoscale cationic polymers for this purpose,³⁰⁸ while Ryoo and co-workers reported the concept by using organosilane surfactants as mesopore-generating agents (mesoporegen, also see section 2.3.3.3 for CHA) in hydrothermal zeolite synthesis. Interestingly, the cationic polymer used by Xiao is the same as that used by Rimer and co-workers as growth-modifier to control the crystal sizes of CHA-zeolites (PDDAC). LTA was included in the pioneering effort by Ryoo.³⁰⁹ In follow-up work focusing on LTA (classic NaA), it was shown that mesopore generation happened fully disordered, for instance evidenced by generating Pt-nanowires in the mesopores and visualizing these with TEM. The openness of the mesopores was probed with ¹²⁹Xe-NMR. The additional use of triblock copolymers for mesopore-expanding was also shown.³¹⁰ Hasan et al. demonstrated the use of (nonsilane) surfactant CTAB to obtain mesopores in NaA (again, also used in the CHA growth-modifier study).³¹¹ A different approach to LTA mesoporosity was shown by the Tsapatsis team, hydrothermally growing LTA zeolite inside 3D-ordered carbon templates with imprinted mesopores.³¹² Another entry in the literature expanded the concept of using organofunctionalized silica precursors (or seeds)³¹³ to obtain an ordered mesoporous LTA.³¹⁴ Even the synthesis of hollow core–shell LTA zeolite crystals has been reported.³¹⁵ The reader is referred to recent reviews^{316–318} on the topic of synthesizing hierarchical zeolites, a large and active field, with many entries for LTA.

Finally, an interesting synthesis of LTA was reported by Iglesia and co-workers, who showed a strategy to encapsulate metal particles in the zeolite during their hydrothermal synthesis. The added metal precursor was stabilized by mercaptosilane ligands, preventing metal (hydr)oxide precipitation. Meanwhile, it was suggested that the trialkoxysilane side of the organic, thought to be balanced by 3 Na⁺ cations after hydrolysis, promoted T atom condensation.²⁹⁶ The precursor to the encapsulated metal–sulfur complex is seen in Table 7 (entry 16) along with the gel composition, that shows a quite high Al-content. The authors focused on the properties of the encapsulated metal particles in the zeolite, but not on the synthesis. The amount of organic incorporated per unit cell from TGA would for instance be a good measure to see the degree of complex incorporated and to verify if it has a

structure-directing role rather than being encapsulated during a classic zeolite A synthesis. The cluster sizes also indicate that the migration of metal atoms had to have occurred, if the metal–sulfur complexes were encapsulated in a 1 per cage fashion, as schematized in the work.²⁹⁶ The authors further explored this context, replacing mercaptosilanes with amines.³¹⁹ For instance, LTA synthesis was shown by adding NH₃-complexed Pt or ethylenediamine-complexed Pd to an aging gel. At this point, these results are in line with the pioneering work of Davis and co-workers in the 1980s that effectively demonstrated Rh- and Ru-containing LTA zeolites.^{320–322} Even earlier, the need for metal precursors to be present during zeolite crystallization was recognized, e.g. in FAU zeolite synthesis.³²³

2.3.9.4. LTA-Zeolite Conclusions.

- (1) LTA is a valuable topology, and its high-alumina zeolite members are commercially available and implemented at a large scale.
- (2) So far, hydroxide media syntheses have not produced LTA with Si/Al ratios above 5.5. The latter was obtained by a clever tuning of the charge densities (cation addition sequence) to obtain cooperative OSDA behavior (CDM). The mechanism of this synthesis is discussed later (part 2.4).
- (3) TMA is an important organic for LTA: it is the main OSDA for ZK-4 and zeolite alpha, but it is also added in the CDM method, as well as in the fluoride routes accompanying more complex OSDAs. TMA is known to stabilize *sod*-cages.
- (4) LTA can be built entirely from d4r-units. It has been noted that pure-silica 4MRs in d4r units are traditionally hard to obtain due to reasons of strain (Si–O–Si < Si–O–Al). It can thus be hypothesized that every 4MR needs at least one Al-atom to be energetically more stable and thus form more readily (than pure-silica 4MR). This dictates a minimum of 2 aluminums per d4r (per 8 T atoms) to obtain the minimal strain relief for every 4MR of the cube. Knowing that LTA can be built from only d4r units and that this unit is the most demanding one from a structural point of view, this implies that the Si/Al ratio to just minimally relieve strain is at most 3. Maximal strain relief would entail the incorporation of 2 Al atoms per 4MR, as is the case in Linde type A (Si/Al = 1) material. The highest reported value of Si/Al that one can attain in OH[−] media without organics is 2, lending credibility to this structure/charge/strain perspective. The relation between d4r strain and (in)organic charge balancing in more siliceous CDM-zeolites should be informative for future syntheses in OH[−]-media.
- (5) The new organic proposed by the Davis group gives access to LTA zeolites with Si/Al ratios of 8.3 to infinity, but only in F[−]-media. The success is due to the stabilization of the large *lta*-cage by two OSDAs, in combination with the fluoride ion incorporating in the d4r, aiding in its stabilization.¹³⁵ It has been concluded that the d4r units are virtually impossible to make in pure-silica composition in the absence of F[−]-ions.^{203,324} The need for seeds and some TMA still reflects the challenging nature of constructing LTA with less aluminum, even in fluoride media.

- (6) It is interesting that no IZC conversions have been reported with LTA as the product. This is even more remarkable considering that the common FAU source can be entirely constructed from *sod*-cages. That no FAU-to-LTA IZC has been noted could be an argument in favor of the (partial) d6r (6MR) *nanopart* hypotheses in other reported FAU IZC syntheses (to AEI, CHA, LEV, ...).

2.3.10. RHO and Its New Family (PAU, MWF). Zeolite Rho was discovered by Robson et al. and reported in 1973.³²⁵ This zeolite contains the large *lta* (or α)-cages (Figure 7), and these cages are connected by the 8MR portals to form d8r units and by sharing a 6MR. The structure, built from the *lta* and d8r tiles, was predicted by Meier and Kokotailo while figuring out the structure of KFI (ZK-5).¹²⁷ Figure 23 (and Figure 24 below) shows the connection mode of the *lta*-cages in RHO, along with that for zeolites LTA and KFI.

Figure 23. Connection mode of the *lta*-cages in the RHO, KFI and LTA structures. Adapted from ref 127. The *lta*-cages in LTA also connect via sharing 8MRs (not shown, see e.g., Figure 22).

Rho was discovered by replacing part of the NaOH in a typical LTA synthesis with CsOH, at about 0.12 Cs⁺/(Cs⁺+Na⁺). This ratio needs to be somewhat precise as trace Cs⁺ leads to FAU contaminations, and too much Cs⁺ to CHA. The Cs⁺ is believed to direct the formation of the d8r units and thus the linking mode of the α -cages. The classic Rho recipes lead to Si/Al ratios near 2.9.^{59,267} This recipe was recently confirmed as a starting point (Si/Al = 2.8) for a steaming study.²⁶⁷ Burkett and Davis were the first to try 18-crown-6 ether (and 15-crown-5) in gels with Cs⁺ present and the Si/Al ratio at 5.³²⁶ They noticed RHO formation and a small incorporation of the ether from weight analysis. Chatelain and co-workers systematically investigated this synthesis and noted excellent RHO formation in the presence of the ether, obtaining Si/Al ratios of around 4 (instead of <3 without) in gels with 0.36 Na/Si, 0.06 Cs/Si, and Si/Al 5 at 110 °C.³²⁷ The ether is occluded in about half of the *lta*-cages of RHO (two

cages per unit cell). A perspective summarizes the use of macrocycles (oxa-, oxa-aza-, as well as pure aza- (N-containing) macrocycles) in the synthesis of microporous materials.³²⁸ From an application point-of-view, it is interesting to note that OSDA-free Rho is known to be flexible and undergoes phase-changes with temperature, owing to the deformation of the 8MR windows, which diminishes the sorption capacity. The crown-ether-RHO had an increased sorption capacity, and no structural changes were noted. Typically, protonated Rho shrinks upon heating, and a gradual decrease of the unit cell's *a*-parameter was recorded while heating from 30 to 250 °C. The different behavior of the crown-ether RHO zeolite seems a direct consequence of the lower Al content. Recently, a new synthesis for RHO was presented by Liu et al. using the PDDAC cationic polymer, remarkably, in the absence of Cs⁺.³²⁹ The polymer, already encountered here as growth-modifier for CHA (Figure 13) and mesoporegen for LTA, led to zeolite Rho, but with the classic Si/Al ratios of 2.8.³²⁹

In 2017, Ke et al. reported a breakthrough synthesis for RHO-zeolites, as Si/Al ratios up to 8 were achieved.³³⁰ The synthesis strategy consists of using a presynthesized complex made from a mixture with well-balanced Na⁺, Cs⁺, and 18-crown-6 ether ratios. This complex is said to be a supramolecular sandwich, where two ethers interact with one Cs⁺. The complex is hypothesized to stabilize the large α -cage of RHO during synthesis, and this was corroborated by TGA analysis, from which 2 ethers per cage were calculated. It is interesting to compare the Cs/ether ratios of this approach, around 0.45, to those in the work of Chatelain et al. where a value of 1.2, thus in excess of Cs⁺, is used. Clearly, this is crucial in the formation of the complex and the structure direction. Ke et al. also performed SCR with the new high-silica RHO zeolites (section 3.2).

In 2015, the Hong, Zou, and Wright groups reported on a complex family of related zeolites with embedded isorecticular structures and expanding unit cells, based on RHO, and in a further expansion PAU.⁵¹ While elucidating the structure of zeolite ZSM-25, patented back in 1981, they noticed the structural similarity of its strong reflections to those of PAU (Table 1) and RHO. ZSM-25, now framework code MWF, is an 1× expanded version of PAU, constructed from the same 7 tiles (colored tiles, see Figure 24), but with its *a*-parameter of the unit cell expanded by 10 Å. PAU itself is a doubly expanded version of RHO and the 1× expansion of a (so far not-synthesized) theoretical member of the family (RHO-G2, already predicted by Vaughan et al. in 1999⁵⁴). The first synthetic PAU, named ECR-18, was reported by Vaughan as well. PAU is a very intriguing structure, and it has a very high

Figure 24. Four first members of the RHO family and the tiles to construct them. Figure adapted with permission, from ref 51. Copyright 2015, Nature Publishing group.

free volume of almost 50%. This derives from the fact that there are no smaller inaccessible cages (such as e.g., *d6r*) in the structure. The introduction of TEA (0.29/Si) in the K^+/Na^+ gel with Si/Al = 4.5 is essential, and the crystallization field is narrow. The product, having Si/Al of 3.6, shows interesting thermogravimetric analysis, as a distinction could be made between TEA degrading from *pau*-cages (also note *pau*-cages in KFI, Figure 19) and TEA from α -cages. The distinction was based on profiles of TEA-Rho and TEA-MER (merloinite), another 8MR zeolite built from *pau*-cages and *d8r*.⁵⁴ In an interesting side note, Cambor and co-workers reported a recipe for synthetic MER with increased Si/Al ratios (from 2 up to 3.8), by adding TEA to the K^+ -rich (Si/Al = 5) gels (the principle Barrer and Denny first put forward¹³¹).

Guo et al. clearly represented the expansion relation between RHO, PAU, and MWF (Figure 24), and based on this, they calculated even more complex members, PST-20 and PST-25 (not shown). The classic recipes for synthetic PAU and MWF both use a combination of TEA and Na^+ , while additionally K^+ is used for PAU. Based on the increasing numbers of *t-oto*, *t-gsm*, and *t-phi* cages in the expanding series (Figure 24) and the fact that these cages are found in certain zeolites made with bivalent cations, the authors added alkaline earth cations to the mix. With Sr^{2+} , a more complex member of the series was synthesized (PST-20, not shown).⁵¹ Although rationalizing the needs of the different (secondary building units) cages/tiles in the structure in terms of stabilizing cations can thus be rewarding, one may not underestimate the role of trial and error in synthetic experimentation. The synthesis mechanism of PAU, MWF, and PST-20, in this isorecticular expansion series, was recently investigated. This leads to a hypothesis where nucleation starts with the construction of *lta*-cages and *plg*-tiles, that connect via shared 8MRs along the diagonals of the cubic unit cell. This is then followed by the stepwise construction of the remaining tiles in Figure 24 (right), with the exception of *pau* and *d8r*, which form in the end, along the edges of the cubic cell.³³¹

In conclusion, given the interest in high-silica RHO from a catalysis point-of-view (section 3.2, i.e., methylamine synthesis, SCR,³³⁰ MTO²⁶⁷), its synthesis should be revisited, in the search for zeolites with Si/Al ratios in excess of 8. Although this upper barrier has only recently been moved, further progress, e.g., along the lines of stabilizing the *lta*-cage in high-silica LTA materials, seems plausible, especially considering the absence of *d4r* units in the structure.

2.3.11. RTH. The RTH framework was discovered as a borosilicate (RUB-13) by Gies and co-workers using polymethylated piperidine and ethylenediamine. Lee and Zones reported a complex OSDA that directed the synthesis toward aluminosilicate RTH zeolites in a range of gels with large Si/Al variation (15 to pure-silica). The organic cation *N*-ethyl-*N*-methyl-5,7,7-trimethylazoniumbicyclo-[4.1.1]octane (Figure 25, left) showed a high specificity for RTH, and subtle changes to the substitutions on the ring altered the product selectivity. The resulting Si/Al ratios of the materials, named SSZ-50, were not divulged but likely evolved in trend with the gels.⁶² Tatsumi and co-workers later reported an organic-free method for zeolitic RTH, by seeding deboronated RUB-13 and carefully tuning water and NaOH content.^{121,332} This route is quite unique in the fact that high-silica materials were obtained (Si/Al = 37–57), an uncommon result for this kind of organic-free, seeding synthesis (e.g., see 12MR BEA literature).

Figure 25. Reported OSDAs for RTH zeolites. Molecular modeling data adapted from ref 136. The right modeling result involves 2 OSDAs per cage.

Schmidt et al. recently reported a new OSDA-route for RTH, in both hydroxide and fluoride media in 2014 (method C and F, Table 3).¹⁶⁹ The relatively simple OSDA is pentamethylimidazolium (Figure 25), known previously to lead to pure-silica STW in fluoride media.³³³ The organic leads to RTH materials with Si/Al ratios varying between 6 and 59 in hydroxide gels and 7–27 in fluoride media. Quite uncommonly, the most siliceous materials were obtained in hydroxide media. In a further expansion of the work, Schmidt reported a range of imidazolium cations (Figure 25) that also lead to RTH.¹³⁶ Although no widening of the Si/Al range with this library was reported, some synthesis recipes were interesting, as they use an ultrastable Y (USY) zeolite as the only source of T atoms (a FAU IZC). A FAU zeolite with a Si/Al ratio of 15 led to different RTH-zeolites (Si/Al = 9–14) in the presence or absence of seeds, with some of the imidazoliums, and exclusively either with or without seeding for others. The library of cations could be useful, as some of these are certainly cheaper to produce than others. From a synthesis point of view, the pentamethylated one proved the most versatile in terms of inorganic conditions. This was also confirmed by calculating and comparing the interaction energies of the organics with RTH (based on 4 OSDAs per unit cell, or two per cage): the pentamethylimidazolium attained the most favorable, lowest value of $-20 \text{ kJ mol}^{-1}_{\text{T atom}}$. This compared positively to the original SSZ-50 OSDA, that attained values of only $-11 \text{ kJ mol}^{-1}_{\text{T atom}}$. Figure 25 shows the modeled positions of both OSDAs in the cage of RTH (cage also seen in Figure 7).

Very recently, Jo et al. also reported on the use of the 1,2,3-trimethylimidazolium OSDA for RTH synthesis (included in Figure 25), in somewhat different conditions and in the context of $deNO_x$ and CO_2 sorption.³²⁴ The material only formed in gels with Si/Al ratio of 10 (or somewhat lower) and, in contrast to the Schmidt data, did not form when seeds were added to higher silica syntheses. This difference could derive from the use of different sources, as Schmidt used mesoporous FAU zeolites at higher Si/Al ratios.¹³⁶ The authors also presented evidence in favor of 2 OSDAs per cage, and they even

investigated the arrangement of the cations through Rietveld refinement. It was concluded that the rings of both ions reside in the cage parallel to each other, with the three methyl groups pointing to opposite directions of the parallel axis.³²⁴ It should be noted however that the pentamethylated version (Figure 25) also easily incorporates (likely) in a pair, not to say there can be no favored arrangement when two trimethylated imidazoliums are present.

Finally, the Davis group reported an unexpected discovery, when Schmidt et al. noticed a layered precursor during a pure-silica attempt at HEU synthesis in fluoride media using a diquatery OSDA (Figure 26).³³⁴ They discovered the pure-

Figure 26. Topotactic conversion of the RTH layer to pure silica RTH. Based on work of Schmidt et al.¹⁷⁴

silica RTH-layer: the first 2D-layer with small pores (8MR) perpendicular to the surface of the layer (Figure 26). The layers are only half a unit cell thick, and since the 8MR pore-system is already present before topotactic condensation, the layered material could be interesting on its own for application. The

distance between the layers is 11.8 Å, similar to the RUB-36 materials (Figures 6 and 26).

The synthesis of RTH is a case worth studying, not only because of its interesting features for application (unique cage), but especially because it is a zeolite with a wide compositional flexibility in terms of Al-incorporation, perhaps related to its 5MRs. The fact that it can be made with Si/Al ratios in the sub-10 range as well as in pure-silica form is encouraging.¹⁶⁹ This indicates that there might be opportunities for new zeolite formation in gels with Si/Al ratios between 5 and 30, given that the structural influence of Al-cations is diminished in that range relative to the low silica-gels (that easily favor e.g., LTA, RHO, KFI). Moreover, since the unveiling of the easy pentamethylimidazolium route to RTH and the unique RTH-layer, the opportunities to tailor RTH to application, with heteroatoms for example, are ample.¹⁷⁴

2.4. Summary Points of Zeolite Synthesis and Its Mechanisms

From the survey of 8MR syntheses presented, there are a number of points that merit discussion:

- (1) It is remarkable that certain zeolites have not yet been synthesized over a wider range of Si/Al ratios (cf. ranges in Table 3), particularly given their interesting cage structure for applications, e.g., MTO (section 3.4). Especially high Si/Al ratios seem to be elusive for a lot of 8MR zeolites (e.g., >8 for RHO, >5 for KFI), although the four pure-silica sieves from Table 1 have not yet been reported with aluminum either. Obviously, there are multiple explanations for this observation including the argument that not enough trials were conducted or no suitable OSDA has been identified. Another main reason is probably due to a structure-induced lower limit to Al-incorporation (i.e., a maximum Si/Al), dictated by strain

Figure 27. Summary of synthesis considerations for cage-containing small-pore zeolites in terms of product Si/Al ratios, illustrated here for LEV, tentatively shown here defect-free with MeQ incorporated in each of its cages and Al represented by a green dot. (A) OSDAs are always crucial to attaining high Si/Al ratios. (B) Energy analysis for LEV: the bold bar inside the box indicates the median, while the diamond indicates the mean. Plot reproduced with permission from ref 335. Copyright 2016, American Chemical Society. (C) Calculation of optimal Si/Al for a given zeolite in OH⁻-media synthesis with quaternary ammoniums based on the number of OSDAs per cage (TGA, elemental analysis), T atoms per cage, and cages per unit cell. (D) Some experimental Si/Al ratios for LEV. (E) Role of IZC to LEV and its Si/Al ratios.

in small cages, composite building blocks, or simply 4MR, 5MR, and 6MRs. The role of d4r in LTA synthesis is a good example (see 2.3.9.4). It is very likely that on top of structure-direction by alkali and cage-stabilization effects, this strain, and similar structure-related effects, have a real contribution in the overall thermodynamics or kinetics of phase-formation.

In this context, the computational energy analysis of aluminosilicate zeolites across a wide range of frameworks and Si/Al ratios, by Okubo and co-workers, is highly relevant.³³⁵ First, the work found similar linear relationships between framework energies and their T atom density, compared to previous pure-silica computation. More interesting in this context was the comparison of relative framework energies of different Si/Al ratios (1, 3, 7, 15, 31, ∞) within one zeolite topology (as well as 10 different Al-distributions, i.e. where does Al sit, for Si/Al 3, 7, 15 and 31). The data set suggests that the relative thermodynamic stability and the existence of preferential Al-sites rely not only on topology but also on composition (Al-content). For a given framework, an energetically favorable Si/Al ratio, e.g., 3 for LEV (see Figure 27B), is calculated. Note that these calculations assume proton counteractions, rendering it more likely that these energy differences arise intrinsically from the structure. Other examples include MFI, where Si/Al = 31 and pure-silica were most favorable, while for FAU, Si/Al = 3 was lowest in energy. For 8MR zeolites CHA, KFI, LTA, RHO, and RTH minima (the means) were found at Si/Al = 1, 31, 3, 1, and 31, respectively. Comparing CHA and KFI, both can be exclusively built from d6r units, revealing that the energy analysis is very different. LTA, RHO, and KFI, all containing α -cages, also differ substantially. The Al-deficient optimum for RTH can be rationalized from its 5MR-content, as such zeolites are often more siliceous and the lowest Si/Al for RTH found synthetically is indeed 6. It is difficult to link the analysis for KFI to synthesis results, as the highest Si/Al ratio accessible is around 4. The use of OSDAs and/or small alkali cations that direct zeolite formation in real syntheses, where metastable intermediates or end-products are often kinetically controlled, renders comparison of synthesis outcomes to the calculations with H^+ counteractions difficult. However, the data can suggest an equilibrium zeolite product and provide some energetic clues into a zeolite's formation with certain Al-content. Of course, for those topologies for which they exist, the Al-content of natural minerals could be used in the same manner, i.e. thermodynamic minima in the presence of inorganic cations and time. Synthetic zeolites with high content of OSDA, such as SSZ-13, and most cage-containing small-pore zeolites are stabilized differently.

- (2) It is clear that the synthesis of most, if not all, catalysis-relevant 8MR zeolites proceeds through the use of an OSDA to access higher Si/Al ratios, e.g., Figure 27A in OH^- media for LEV (Method C in Table 2). Properties of good OSDAs have been documented.^{336,337} The Si/Al ratio via geomimicking and alkali-cation approaches in hydroxide media is always limited (method A, B). OSDAs are also crucial in the CDM approach, in F-media (method E, F), as well as in all relevant IZC

syntheses (i.e., not highly alkaline IZC, method D). The rare cases where OSDA-free syntheses lead to products with intermediate Si/Al ratios (e.g., 5–10) always rely on large additions of seeds made via OSDA-routes.

It is obvious that the synthesis of a zeolite with an OSDA relies on the space-filling interaction between the organic and the framework, which translates to fitting in the cage for most small-pore zeolites (Figure 7). Furthermore, the OSDAs for 8MR zeolites are mostly charged (quaternary ammonium, phosphonium), with the exception of a couple of pH-dependent amines, and this positive charge needs to be balanced, during synthesis, either with framework charge based on isomorphic Al-substitution or a siloxy-defect, or a free F^- -anion. The Si/Al range of the product is thus influenced by the OSDA in two ways: (i) the OSDA/framework energy and (ii) the overall charge balance that needs to be neutral. The first, experimentally, shows that OSDAs with a really good space-fit (often confirmed from pure-silica molecular modeling) allow for a broad range of Si/Al products within one topology. Two examples here are ADAM for CHA and pentamethylimidazolium for RTH (two per cage); the latter e.g. allows for Si/Al = 6–59 products in hydroxide media. Whether or not these molecules are true templates is up to the reader,³³⁸ but bear in mind that ADAM can also lead to AFI and STT, e.g. when inorganic conditions change or overrule the organic stabilization. Generally, excellent fits between OSDAs and cages can be identified if the organic can direct to a given topology in both OH^- and F^- -media. The charge balance (ii) entails that if a charged OSDA is occluded in a cage, in OH^- -media, at least one aluminum should result in the unit cell, per (organic-capable) cage. Lower Al-incorporation should not be possible unless silicon based defects are built-in, while lower Si/Al ratios are possible only when other smaller cations (TMA or Na^+) are coinorporated.

- (3) Based on charge balancing and counting the atoms surrounding a cage, it should be possible to predict an ideal (maximum) Si/Al ratio for which no siloxy defects are needed, for every cage-based zeolite-framework made in hydroxide media and with organic cations occluded in the cages. This defect-free ratio has been calculated for CHA, AEI, and LEV above and is illustrated in Figure 27C for LEV. To what extent the formation of a zeolite and more specifically its Al-content is influenced by the absence or presence of defects in a given OSDA/zeolite/Si/Al system remains unknown. The effect could be both thermodynamically, e.g., certain defects produce less or more strain on the lattice, or kinetically driven; that is, their rate of formation could be different as for example defect-sites require less condensation reactions, or it could be driven by both. It is interesting to note that certain zeolites have ordered defects, e.g., pure silica ITQ-39 (-ITN).³³⁹
- (4) The prior analysis, predicting an optimal Si/Al in the absence of smaller cations and defects, and the properties of an excellent OSDA, able to lead to high Si/Al ratios, imply that syntheses direction by a well-fitting organic overrule constraints by defect formation. OSDAs that fit less well, e.g. *N,N*,3,5-tetramethylpiperidinium for AEI (Figure 9) or MeQ for LEV (Figure 27), do not allow free choice of the Al-content in the product. Strikingly,

the Si/Al ratios of different syntheses along these lines end up near the one predicted from cage-counts (e.g., Table 4, Table 6). This infers that defect formation in the synthesis of cage-containing zeolites with organics is indeed further away from the equilibrium. In these kinds of synthesis, the inorganic constituents and external conditions play a larger role, such as for instance the starting inorganic T atom sources, temperature, and agitation. Interzeolite conversion and the CDM approach (Table 2, method D, E), often leading to new recipes for existing zeolites with organics that do not perfectly fit a given cage, fortify this point. Examples of IZC in this case are the use of TEA for CHA, choline for LEV, and most AEI syntheses, while CDM examples include LTA and ERI. Effectively, this means that it can still be rewarding to explore common or reported OSDAs in unusual conditions. Unusual here could be related to the content and stoichiometry of the recipe, e.g., two cations cooperating (CDM); the source of T atoms (e.g., zeolite), or the external conditions (flow, ...).²¹⁰ Exemplary here is the discovery of 12MR-zeolite GME with the same OSDA as that for AEI with conditions only differing in water content (Figure 9).³³

- (5) In light of constructing 8MR zeolites, the work by Hong and co-workers on the mechanism of formation of LTA,^{297,298} UFI,⁷² LEV, and CHA³⁴⁰ sheds an interesting perspective. Through the use of time-resolved multinuclear liquid and solid-state NMR, and other techniques, the authors propose that the large cages of these structures form first, with OSDA incorporated (e.g., α -cage for UFI and LTA; *cha*-cage; *lev*-cage), before they connect through smaller units, e.g. d6r or shared 8MRs. For LEV, the linking of *lev*-cages is hypothesized to occur in pairs by sharing an 8MR, before these pairs in turn link together forming the d6r and the LEV framework (center in Figure 27). Although plausible, these studies focus on one composition and fixed conditions. The influence of the starting Si/Al ratio on these mechanisms would be interesting in light of the predicted optimal Si/Al ratios deduced from charge/cage counts (e.g., 8 for LEV). If the synthesis of cage-based small-pore zeolites begins with the construction of the large OSDA-precluded cages, rather than smaller building blocks, focus should be put on the charge balance. We surmise here that such a scenario would favor the incorporation of one Al-per cage, maximum Al-dispersion (isolation rather than pairing), and Si/Al ratios near or below the optimum from cage-counts. Extending these studies with Si/Al variation, as well as different inorganic sources, might yield clues into the Si/Al question.
- (6) Interzeolite conversion is a relatively unexplored route for zeolite synthesis. Many aspects of IZC remain unclear, because the crystalline source material can interact with all constituents of the synthesis mixture in more than one way. The sol-gel mechanisms likely do not occur in a lot of IZCs. Even though poorly understood, the trial and error approach has yielded good results, and the benefits of the IZC route should be generally accepted by now. The *nanoparts* idea remains a hypothesis, and if proven, will likely be very conditional and framework specific. Two major types of IZC can be distinguished, those with very high alkaline cation concentrations (OSDA-free) and those with OSDA, and a lot less mineralizing power. The latter are considered true IZC, since in the case of the former (e.g., FAU to ABW, CHA, MER, ANA),²²³ the zeolite likely only functions as T atom source that completely breaks down, and no clear benefits of using the zeolite in terms of phase selectivity exist. True IZC, and everything in between, uses lower OH/Si ratios and OSDAs, often to yield surprising results.
- (7) Fluoride media syntheses (Route F, Table 2) are not really on the forefront in 8MR zeolites, except in a couple of cases where pure silica or very high Si/Al ratios are desired (Table 3). The exception is LTA, where two breakthroughs, leading to catalytic innovation (see section 3.2), rely on F^- : the supramolecular complex and the DM3(4MB) syntheses. F^- is needed to stabilize the siliceous d4r units. Few 8MR zeolites have a high hydrophobicity, since few have been made in the very high Si/Al range (e.g., 100+) and/or can be made according to a fluoride route. Striking counterexamples are the synthesis of EEI, DDR, and CHA, possible in high Si/Al ratios, in OH^- -media (Figure 1, Table 3). The not-straightforward translation of OSDA effects from OH^- to F^- -media, and vice versa, can be partially explained by the charge/cage perspective. Since F^- anions can neutralize the OSDA charge locally, pure silica nets can be formed defect-free (and more hydrophobic). Therefore, the (perceived) drive toward the “ideal” Al-content per unit cell from cage-counts is absent in fluoride media, and the space-filling role (i) of the OSDA is much more important. OSDAs with less tight fits (see above) often do not produce the zeolite in fluoride media. Although F^- -mediated syntheses are more challenging at the large scale, innovation surrounding Lewis acidic Sn-BEA zeolites is lowering industrial barriers for zeolites to come.³⁴¹
- (8) Next to the Al-content discussion, a second important observation is the nonexistence of aluminosilicate versions of certain 8MR molecular sieves with interesting structures. The ABC-6 molecular sieves AFT and SAT or the d6r-only SAV-structure are examples. For germanosilicates, the reason is often the increased stability of structural units (4MR) due to Ge-inclusion in the ring (in fluoride media). These positive effects do not occur in aluminosilicate formation. Why certain $AlPO_4$ and SAPO-sieves have not translated to aluminosilicate versions is more difficult to understand. Why do OSDAs for many (M)A(1)PO syntheses never direct the corresponding zeolite? Differences in mechanisms of structure-direction at acidic (AlPO) vs basic (zeolite) synthesis conditions could be one reason. For one, the use of charged amines (due to neutral/acidic pH and amine pK_a values near 10) in AlPO synthesis does not translate easily to zeolitic OH^- -media, since the highly basic mineralizing environment renders the amines neutral. It thus seems that the charge of the OSDA outweighs its space-filling role in a lot of (M)A(1)PO syntheses.

3. CATALYSIS WITH 8MR ZEOLITES

3.1. Introduction

As outlined in section 1.3, small-pore zeolites have been commercialized for a number of applications. Here, a concise overview of the key catalytic reactions where small-pore zeolites show promise or have been commercialized is presented. These applications are exhaust cleaning, partial oxidation of methane, olefin generation (MTO and ethylene/ethanol conversion), and methylamine synthesis. Additionally, a brief overview of a few other reactions is provided at the end of this section. Unlike section 2, this section does not provide an exhaustive discussion for every reaction and its mechanism but rather highlights the specific issues when using different small-pore zeolites and pinpoints recognized, structure–activity relations. For more details on each topic, the reader is referred to reaction-specific and detailed existing reviews in every subsection. Note that zeotypes such as SAPOs are often also used for these reactions but are deliberately not discussed here, in order to keep the focus on aluminosilicates.

3.2. Selective Catalytic Reduction (SCR or deNO_x) for Exhaust Cleaning

3.2.1. Introduction to SCR and General Features of SCR with Zeolites. In the 1980s, Iwamoto et al. discovered the high activity and stable performance of Cu²⁺-exchanged ZSM-5 (medium-pore MFI zeolite) for NO decomposition.³⁴² Since then, zeolite catalysts have been prominently featured in emission control literature, and the SCR of NO_x with ammonia (or urea) is now one of the dominant technologies. The term deNO_x, often used to refer to SCR, suggests that both NO and NO₂ can be present in exhaust gases, and both need remediation. The largest fraction in diesel exhaust is NO, thus leading to the most standard chemical reaction of SCR (seen in Figure 2), converting NO into N₂ and H₂O, with the aid of the ammonia reductant and O₂.³⁴³ Oxygen-gas free versions can also be written, e.g., when NO₂ is present in significant amounts and “4NO + O₂” is replaced with “2NO + 2NO₂” in Figure 2. This is also known as the fast SCR reaction.³⁴⁴

Cu-ZSM-5 (MFI) has been at the forefront since the beginning, although its low hydrothermal stability above 700 °C (in the presence of steam), its lower activity in the lower temperature region, as well as its tendency to hydrocarbon adsorption (fouling), has motivated the search for more stable zeolite hosts. Small-pore zeolites^{4,55} provide an answer here, as they inhibit larger hydrocarbons from entering the cages. Bull et al. reported SCR with Cu-SSZ-13, and they noted a comparably high SCR activity, a better hydrothermal stability, and less hydrocarbon poisoning than other Cu-zeolites tested before (large pore BEA, medium-pore MFI).³⁴⁵ Others were also on this approach,³⁴⁶ e.g., researchers at Ford.^{103,347} Peden and co-workers demonstrated early on that the hydrothermally aged version of this catalyst outperforms BEA, MFI, and Y-zeolites.³⁴⁸ A swift commercialization followed, and in 2010, Cu-SSZ-13 could be found as an emission control catalyst in on-road diesel automotive exhaust aftertreatment systems.³⁴⁴ Cu-SSZ-13 based SCR is a genuine and inspiring success story of small-pore zeolite chemistry. Note that the classic gasoline engine aftertreatment system is based on the “three-way catalysts” in catalytic converters and has been commercial for over 30 years (reducing CO, NO, and hydrocarbons).¹⁰⁰ This type of system does not work well on lean-burn engine operation, as is the case when oxygen/fuel ratios are high, e.g.,

in diesel vehicle engines, hence the need for Cu-zeolites or other catalytic systems for these situations. Cu-zeolites were preferred over V/Ti systems or Fe-zeolites, due to their lower dependence on feed gas NO₂ for low temperature deNO_x (fast vs standard SCR mentioned above).¹⁰³

The literature on SCR with Cu-SSZ-13 and Cu-SAPO-34 has grown large since 2010. A couple of recent review articles^{95,100,344} clearly describe the state-of-the-art in this field. The mechanism of SCR, at the level of the active Cu-site, is not completely known. For the standard SCR, the role of the redox chemistry of copper is still under scrutiny. Paolucci et al. demonstrated that zeolites exchanged with isolated Cu²⁺, contain both Cu⁺ and Cu²⁺ ions during 200 °C SCR.³⁴⁹ A catalytic cycle based on their work is found in Figure 28, showing the 6MR (half of the d6r) of the CHA framework with two aluminum atoms across from each other (e.g., Figure 16).

Figure 28. Suggested cycle for Cu-SSZ-13 at 473 K in the standard SCR. The dotted line separates oxidized Cu (top) from reduced (bottom) halves of the redox cycle. Reproduced with permission from ref 349. Copyright 2014 Wiley.

Details of the mechanistic, kinetic, and cation-siting aspects of SCR based on Cu-SSZ-13 catalysts are not presented here, and the reader is referred to the above-mentioned reviews, as well as expert contributions.^{133,350–355} A recent review in this journal also focuses on converting N-containing exhaust gases with zeolites.¹⁰¹ The next section provides an overview of the different 8MR zeolite hosts reported for SCR and compares the impact of topology vs CHA (Table 8). After that, selected synthesis–structure–activity relations are detailed.

3.2.2. Overview of Small-Pore Zeolite Catalysts for SCR of NO_x. Assessing SCR activity often seeks to find the range of temperature where conversion is close to 100% (Table 8), and working conditions resemble those of an exhaust (wet). Generally, a N₂-balance stream, rich in O₂ (e.g., 5–14%) containing some water (e.g., 2–10%, labeled as W, “wet conditions”, vs D, dry) and a couple of 100 ppm’s of NO and NH₃, is used as reactants (often 500 ppm of both). Selectivity is also important, as NO₂ and N₂O have to be avoided in favor of N₂. Cu-SSZ-13 leads to significantly less N₂O and NO₂ (e.g., less than 5 and 10 ppm, respectively, over the entire

Table 8. List of the 8MR-Framework Zeolites Tested in SCR of NO_x with NH₃

Top. ^a	Material	Practical numerical example ^b				T-range	90% NO conv. (°C) ^d	R ^b	Performance ^e	remarks
		Si/Al	M	M/Al	NO/NH ₃ /H ₂ O ^c (ppm/D,W)					
CHA	SSZ-13	9.0	Cu	0.18	500/500/D	F: 200–500 A: 200–500		244	++++	Commercial. Many reports. Excellent catalyst.
		12	Cu	0.20	350/350/W	F: 175–550 A ^d : - (Figure 31)		356		A ^d : above 80%, Figure 31.
		12	Fe	0.20	350/350/W	F: 360–500 A: -		357	+++	See Figure 31.
AEI	SSZ-39	9.1	Cu	0.32	500/530/W	F: 270–550 A: 220–450		181	++++	A Cu-SSZ-13 under same aging, was less stable
		8.0	Fe	0.1	50/60/W	F: 350–550 F: 400–500		358	+++	one-pot synth has good aged activity
AFX	SSZ-16	4.5	Cu	0.23	500/500/D	F: 200–500 A: 200–400		244	+++	Good SCR, decent aging
		5.2	Fe	0.1	50/60/W	F: 550 A: n.r.		198	++	Removal of Na ⁺ needed
DDR	Sigma-1	16	Cu	0.14	500/500/D	F,A: 300–350		244	+	A worse than F, but max =
		5.2	Cu	0.3 ^h	500/530/W	F: 500–550 A: -		198	+	A: max 45% at 300 °C
		5.2	Fe	0.1	50/60/W	F: - A: n.r.			+	F: max 65% at 500 °C
KFI	ZK-5	4 ^g	Cu	0.38	500/500/W	F: 250–500 A: 300–450		359	+++	Cu/Al in aging important
LEV	Nu-3	8	Cu	0.08	500/500/D	F: 250–400 A: 250–300		244	++	A worse than F, but max =
LTA		16	Cu	0.58	500/500/W	F: 260–475 A: 275–500		172	++++	Aged at 750 °C
RHO		7	Cu	0.1 ⁱ	500/500/W	F: 250–500 A: n.r.		330	/	Too few data to judge
RTH	SSZ-50	10	Cu	n.r.	500/500/W	F: 200–430 A: -		324	++	A: max 70% at 360 °C
UFI	PST-7	11	Cu	0.44	500/500/W	F: 260–500 A: -		172	++	A condition same as LTA. 70% at 330 °C

^aTop. = topology. ^bR = reference. The table is by no means complete and entries were selected for allowing the broadest, most accurate comparison. ^cD points to dry reactant flows, W, points to deliberately adding H₂O to the SCR feedstock (wet, realistic). O₂ is also present. ^dRange where NO conversion in standard SCR is still ≥90%, often estimated from graphs with connected data points. F indicates fresh catalyst, while A means after hydrothermal aging (high T steaming, often different conditions). - indicates that conversion was always below 90%, see remarks column. n.r.: not reported. ^ePerformance relative vs all entries and benchmark SSZ-13. ^fERI/OFF intergrowth known as ZSM-34 also patented for SCR; see ref 360. Erionite would not be an accurate material name here. ^g3.7 from synthesis, after Cu procedure and calcination, 4.2. ^hEstimated for 2.8 wt %. ⁱEstimate.

temperature range (T-range), on 350 ppm of NO feedstock) than Cu-beta and Cu-ZSM-5.³⁴⁸

3.2.3. Cu-Zeolite Catalyzed SCR: The Impact of Topology. After performing a Cu-cation siting study for both zeolites,¹⁹⁶ CHA and AFX were investigated thoroughly by Fickel et al., noting that both were excellent catalysts when compared to ZSM-5.²⁴⁴ Different behavior for SCR is mostly found after a hydrothermal treatment (e.g., 750 °C, 5% water feed). There, Cu-SSZ-13 and Cu-SSZ-16 excelled versus Cu-ZSM-5, but also between them, differences were notable: while the CHA zeolite still performed near identical SCR, the AFX material loses its activity at temperatures over 350 °C. In the same study, LEV and DDR-zeolites were assessed, but these had lower activity (especially DDR), evidenced from the operation window in Table 8. The authors concluded that the dimensionality of DDR and LEV (2D) was likely to blame for the reduced SCR activity. Furthermore, it was suggested that during the dealumination process, under hydrothermal aging, Al(OH)₃, with an estimated 0.5 nm diameter, needs to exit the framework in order to cause structural trouble. Small-pore

windows, such as those constricting CHA and AFX cages, prevent this, and thus Al-species stay inside the pore where they were originally dislocated. At lower temperatures, realumination could occur.²⁴⁴ A further finding by Chen and co-workers noted that for large pore BEA, a destructive Cu/Al₂O₃ interaction induces framework collapse above 800 °C, but this interaction is minimized by pore-size in CHA.^{2,361} Evidenced from the fact that since 2010 about 200 publications have been reported containing the term “Cu-SSZ-13” in a topic search (Web of Science, 10/10/2017), remarkable focus has been placed in the catalytic community on SCR with the CHA-zeolite. It is worth noting that a typical commercial sample has a Si/Al ratio around 17 and a Cu loading of 2.8 wt % (BASF), corresponding to a Cu/Al ratio of 0.5, or, charge-based at least, stoichiometric exchange.³⁶²

A truly excellent SCR topology was identified by Moliner et al.; AEI. SSZ-39 proved to have a good activity over a broad T-range and a very high hydrothermal stability.¹⁸¹ In their study, a comparison to a SSZ-13 with higher Si/Al = 12 and similar Cu-loading clearly showed the benefit of SSZ-39. The

stability of SSZ-39 in hydrothermal steaming conditions was also verified later by Dusselier et al. in an MTO study (section 3.4) where dealumination by steaming was pursued (and in the presence of Cu^{2+} , the framework held up well).¹⁷⁹ The second SCR study for AEI was conducted on IZC materials made with the tetraethylphosphonium OSDA from the Sano group, compared to the N-based DEDMP cation (Table 4 entries 6–7). Although NO conversion was lower for the P-zeolites, the thermal stability of the Cu-free hosts in calcination was a bit better for the P-containing materials. After hydrothermal steaming, the P-based zeolite also seemed to have an increased NO-conversion (for P/Al = 0.2, e.g.), while that of the more classic material decreased a little, although these steaming times were short (1 and 4 h at 900 °C). The NO conversion however decreased with increasing P/Al ratio, suggesting that only a small amount of P-modification could be beneficial.¹⁸³ A similar effect (small amount of P-modification from synthesis, not postsynthesis) was observed for the dual-template AEI (Table 4 entry 13).¹⁸⁷ Martín et al. reported SCR on their SSZ-39 made with their efficient IZC synthesis method using *N,N*-dimethyl-3,5-dimethylpiperidinium (Table 4, entry 12) and compared them to the P-containing OSDA materials and an SSZ-39 prepared with both the piperidinium and Cu-tetraethylenepentamine (Cu-TEPA) present.¹⁸⁶ The latter is known as a one-pot-approach that allows the loading of Cu in situ during synthesis. Here, the P-containing material underperformed versus the others, and a lower hydrothermal stability was noted for the P-based material after steaming at 750 °C. The P-content of the material here however was not reported. The two other Cu-SSZ-39 materials were stable during steaming (from PXRD) and behaved similarly, i.e., excellent SCR (e.g., at 500/500/W, F: 250–490 °C and A: 260–450 °C, for the postsynthetic *N,N*-dimethyl-3,5-dimethylpiperidinium based zeolite, compared to Table 8).

RTH, assessed by Jo et al., showed a good fresh performance, but this activity did not stay after hydrothermal aging.³²⁴ Gounder and co-workers investigated the kinetic and structural changes after SCR on AEI, CHA, and RTH zeolites.³⁶³ When comparing rates, in standard SCR (Cu, 250 °C), AEI and CHA performed similarly, before and after aging. RTH, however, had 2–3× lower rates and zero activity after hydrothermal aging. After aging, the RTH framework is still intact (XRD) and porous (physisorption), inferring that the structural changes for the worse happen to the Cu-sites. The study thus confirms the positive role of d6r containing zeolites in terms of protecting the active Cu species during hydrothermal aging. Furthermore, the lower “fresh” activity for SCR in RTH is likely caused by the 2D nature of its pore system with constrained, asymmetric 8MR windows. These likely limit access, rendering the RTH framework to behave as a 1D SCR catalyst.

Martín et al. tested new IZC routes to ERI and AFX based on large dicationic OSDAs, in both Cu and Fe-forms. Notably, ERI was not a good SCR catalyst, as high-temperatures were needed for the fresh catalyst and aging deteriorated the performance heavily.¹⁹⁸ AFX had already been studied by Fickel et al., but not in wet conditions. At 500/530/W (compared to Table 8), the fresh Cu-SSZ-16 catalyst achieved over 90% NO conversion in a temperature range from 350 to 550 °C, while the aged zeolite only went up to 80% at 300–350 °C. The difference with the dry SCR data from Table 8 logically suggests that deNO_x under more realistic, wet conditions is more difficult for AFX, although comparing across reports is difficult (Cu-loading, GHSV, ...).

Zeolites containing the large *lta*-cavity were also studied for SCR, by different groups (KFI, RHO, UFI, LTA). The team of Hong and co-workers assessed both UFI and LTA frameworks, made with benzylimidazolium-based cations (e.g., Table 7, Entries 10–13 for synthesis and Table 8 for SCR data).¹⁷² Especially LTA stood out, and high activity was found initially and retained after hydrothermal aging tests up to 750 °C. At 850 °C, activity was mostly gone, but this was true for benchmark CHA and MFI as well. A direct comparison to SSZ-13 with the same Si/Al ratio, after 750 °C aging, showed a clear pattern of LTA outperforming CHA. The authors continued their work and found that for a perfectly exchanged LTA-zeolite, even better stability and SCR activity after aging occurred. Figure 29 compares data from different LTA and CHA zeolites, before and after a severe 900 °C aging. The severity of the aging is known to destroy a lot of the SSZ-13 activity. Yet, LTA, with the right amount of Cu, is highly stable. This is likely the best hydrothermal aged SCR catalyst reported to date. Figure 29, part a, shows that having an overexchange,

Figure 29. Performance in SCR for Cu-LTA, compared to Cu-SSZ-13. NO conversion as a function of temperature over the (left) fresh and (right) 900 °C-aged forms of: (a) Cu-LTA-16-0.14 (square), Cu-LTA-16-0.32 (dot), Cu-LTA-16-0.48 (triangle) and Cu-LTA-16-0.65 (rhombus). (b) Cu-SSZ-13-16-0.15 (green), Cu-SSZ-13-16-0.34 (brown), and Cu-SSZ-13-16-0.49 (red). (c) Again Cu-LTA-16-0.48 (red triangle), this time with Cu-LTA-11-0.48 (green), Cu-LTA-23-0.50 (blue). Reaction conditions: 500/500/W, (as in Table 8), while hydrothermal aging was performed under flowing air containing 10% H₂O at 900 °C for 12 h. The last two values of the catalyst identification correspond to the Si/Al and Cu/Al ratios of the catalysts, respectively. Adapted with permission from ref 364. Copyright 2017 Wiley.

Figure 30. Cu-LTA SCR site proposal and catalytic conversions after aging (a) Structure of the fresh, dry Cu-LTA-23-0.50 catalyst with 2 different sites labeled as Cu(1) and Cu(2). Colors: red, O; blue, Cu; yellow, Si; Al is not represented in this figure. (b) Numbers of Cu ions at single-6MR (●) and Cu ions inside sod-cages (■) per unit cell of Cu-LTA-23-0.50 vs hydrothermal aging temperature. The NO conversions at 320 °C (viz. dip in Figure 29c) of fresh and aged catalysts are given as a bar diagram. Reproduced with permission from ref 365. Copyright 2017 American Chemical Society.

Figure 31. Comparing Cu and Fe-SSZ-13 in standard, wet SCR before (fresh) and after hydrothermal aging. Conditions in inset. Adapted with permission from ref 356. Copyright 2015 Elsevier.

e.g., Cu/Al of 0.65, is deleterious for the SCR performance of the LTA after the high-temperature aging. Yet, values close to 0.4–0.5 Cu/Al, render LTA zeolites stable against aging and still highly performing from 250 to 550 °C. The most stable SSZ-13 material tested (series b, Figure, 29) has a lower Cu/Al ratio (of 0.15), rather than a higher. For SSZ-13, it was already known that higher Cu/Al ratios are not always optimal for surviving the aging, as for example Cu/Al 0.28 vs 0.35 already caused a large difference after aging in the dry SCR runs by Fickel et al. on Si/Al = 6 materials.²⁴⁴ The optimal SSZ-13 catalyst fails to attain even 50% of NO conversion after high temperature aging. Finally, three different Si/Al ratios of LTA, with optimal exchange near 0.5 were tested as well, clearly

showing that the improved SCR effect only holds true for the least aluminous materials (Si/Al = 16 and 23, Figure 29c). Rietveld refinement indicated that Cu²⁺ ions were located only at the center of single-6MR, and it was surmised that they serve not only as active center but also as a dealumination suppressor.³⁶⁴

Interestingly, the low temperature SCR with Si/Al = 23 materials (thus with the least amount of Cu, see Figure 29 part c, blue, from left to right) improved upon aging, hinting at stabilization or relocation of low-temperature active sites during the aging, rendering them more active. The same authors studied this phenomenon in-depth, and they demonstrated that it originates from the migration of Cu⁺ ions present inside the

sod-cages (against d4r windows) to vacant single-6MR during the hydrothermal aging (Figure 30). The sod-cages could be seen as a useful catalyst reservoir releasing active sites during SCR.

Cu-KFI for SCR was patented by Reichinger et al.,³⁶⁶ while recently, a thorough study was published by Kim et al.³⁵⁹ Low temperature activity and decent performance are two excellent features of Cu-KFI. The aged performance was tested for two Cu-loadings, and the highest one prevailed (shown in Table 8). The report directly compared to SSZ-13, with the latter yielding a slightly better performance. However, one should keep in mind that this KFI-zeolite is made without OSDA and thus, potentially, very cheap.³⁵⁹ Further testing in more stringent conditions, longer aging, and repeated cycles is due. The other lta-cage containing zeolite, RHO, has not been tested adequately. Cu-RHO was briefly tested for SCR by Ke et al., in the light of their new synthesis with the Cs-crown-ether complex leading to rho materials with higher Si/Al ratios. However, no aging experiments were given, rendering SCR assessment rather difficult.³³⁰ Given the interesting findings of the Hong group for LTA, high Si/Al RHO zeolites could yield surprising results. Finally, of note is that a few of the small-pore zeolites, i.e., ERI, LEV, CHA, and DDR, were already included in the list of tested materials featured in a patent by Andersen et al.^{2,346}

3.2.4. Fe-Zeolite Catalyzed SCR. The above discussion clearly highlights the extraordinary performance of CHA, AEI, LTA, and KFI-zeolites in copper-based SCR. A few of the 8MR zeolite materials have also been investigated using Fe cations as active centers, i.e., CHA, AEI, AFX, and ERI. Fe-SSZ-13 was assessed by Peden and co-workers.³⁵⁷ Later, a comparison of reaction kinetics with Fe- and Cu-based zeolite was made.³⁵⁶ Fresh Fe-SSZ-13 was on average less active than the Cu-version in standard SCR under wet conditions (see Figure 31 comparing both zeolites, in fresh and aged conditions). Although a serious drop in activity ensued for the Fe-version after aging, it interestingly retained more activity than the Cu-material above 500 °C. A full discussion of Fe-species, their loading effects, and transformation, in SSZ-13, is found in further work by the Peden group.^{367,368}

Fe-SSZ-39 was assessed by Martín et al. (entry in Table 8), and a one-pot method for introducing Fe into the small-pore material was presented. Ferric nitrate was added to the *N,N*-dimethyl-3,5-dimethylpiperidinium OSDA-based IZC synthesis.³⁵⁸ The classic SSZ-39, postsynthetically exchanged via ferrous sulfate, was also compared, but it performed worse than the one-pot zeolite after aging. Clearly, the way of introducing Fe matters, especially since Fe needs to be carefully ion-exchanged. Fe-ERI and Fe-AFX were briefly looked into by Martín et al. as well (Table 8), but no aging was performed, and the feedstock ppm concentration of NO was low, compared to the work with Fe-SSZ-13.¹⁹⁸

3.2.5. Synthesis–Structure–Activity Observations. Since the detailed study of SCR entails testing many different conditions (e.g., aging and hydrothermal stability), and the dynamic nature of the active site of the classic catalyst is still under elucidation, it is understandable that few true synthesis–structure–activity relations have been reported (opposed to for example MTO, see section 3.4). The greatest number of structure–activity relations has been detailed for Cu-SSZ-13, and the reader is referred to the above-mentioned reviews in this context. Not often do these studies rely on synthetic variation other than Si/Al ratios, that is easily varied in SSZ-13,

and Cu-content (Cu/Al).³⁶⁹ On the other hand, CHA zeolites made via new synthetic routes (e.g., see Table 5 or Figure 14), such as Corma and co-workers' TEA-based (Si/Al = 8) material,²²⁶ or the solvent-free CHA zeolite (Si/Al = 5) made with *N,N,N*-dimethylethylcyclohexylammonium (Figure 14) of the Xiao group,²¹² are often tested in SCR, to see if the material can match the activity of a classic SSZ-13.

Interestingly, the way Cu (or Fe) is introduced into the zeolite can offer a synthetic challenge.

Beale and co-workers compared the classic ion-exchange route versus a chemical vapor deposition (CVD) based ion-exchange.³⁷⁰ The latter is performed using a setup where precursor salt and zeolite are in close contact (glass-wool) and heated in an inert flow at 250 °C. The CVD method yielded only half the Cu-loading as the classic wet exchange, and its SCR was abysmal. While the copper sites were found for the CVD material and they were like those obtained from ion exchange—i.e., the Cu²⁺ center on the outside of the d6r subunits of the CHA structure (e.g., see Fickel et al.,¹⁹⁶ but note that these are dry, nonworking condition coordinated species)—a secondary inactive CuAlO₂-like phase was present. Another solid-state ion-exchange method at higher temperature did yield active SCR catalysts.³⁷¹

The approach by Ren et al., concerning the use of a Cu-TEPA complex for directing CHA-synthesis, delivers Cu as active SCR site to the cages.²¹³ The SCR activity of the fresh sample on a 1000/1000/D feedstock was above 90% NO conversion in the zone of 175–450 °C, for a Si/Al ratio of 4 and, concomitantly, a high Cu-loading (9.5 wt %). The coupling between Cu loading and Si/Al through synthesis, in the first report, shows a reduced degree of freedom in choosing Cu and Al content separately. However, later, the group reported Cu-content control and better SCR features.³⁷² Martínez-Franco et al. followed in this path but combined ADAM with Cu-TEPA, that allowed more control over Si/Al and Cu/(Si+Al) ratios and obtained decent SCR performance and good hydrothermal stability.³⁷² Martín followed the same strategy for AEI, yielding “one-pot” Cu-SSZ-39, mentioned above.¹⁸⁶ In an interesting side-note, Yamada et al. focused on bead-milling SSZ-16 zeolites and then subjecting them to postmilling crystallization, rendering <100 nm large crystals. These showed faster and more homogeneous (in the crystal) ion-exchange, due to accessibility, when subjected to Cu²⁺, but no SCR was reported.³⁷³

The effect of morphology and particle sizes in SSZ-13 was investigated, following three modified synthesis procedures, based on ADAM as OSDA.³⁶² More classic >1 μm zeolites were compared to 450 and 260 nm sized particles. The latter, based on longer aging in the synthesis, already show mesoporosity in physisorption, deriving from interparticle adsorption. The SCR performance of the different-sized zeolites, with similar Si/Al and Cu/Al (0.15) ratios, was very similar. This is attributed to the extraordinary stability of the Cu ion–framework Al pairs, against steaming, independent of particle size. This method could however help in depositing more Cu-SSZ-13 active species, on SCR setups based on wash-coated layers of zeolite upon a support. Access to thinner (from smaller zeolite particles), more active layers there could improve mass and heat transport.

Finally, a mesoporous SSZ-13 was studied, that was based on desilication by base leaching. Using the mildest leaching conditions (0.1 M NaOH), microporosity was somewhat reduced (0.36 to 0.23 cm³·g^{−1}), and mesopores were created

($0.23 \text{ cm}^3 \text{ g}^{-1}$). Si/Al and Cu/Al ratios of this material and the parent (nondesilicated) were similar, but the treated materials showed a remarkable improvement in the low temperature SCR regime (1000/1000/D), e.g. a 2-fold increase in NO conversion at 150 and 250 °C (said to derive from improved accessibility).³⁷⁴

3.2.6. Conclusions from NH_3 -SCR of NO_x with 8MR Zeolites. Small-pore zeolites are essential to lean-burn diesel engine exhaust cleaning catalyst technology. Cu-SSZ-13 is already commercial, and its performance is linked to its excellent stability under hydrothermal conditions. Detailed studies to understand the full mechanistic aspects and catalytic cycle of this system are still published regularly. The discovery of the SSZ-13 zeolite⁴ thus led to great progress in exhaust cleaning technology. The CHA zeolite is however made with ADAM, and this OSDA is quite costly. The excellent SCR performance has thus motivated researchers to look for alternative CHA synthesis recipes, and in turn brought great innovation in the synthesis field.

Apart from CHA, AEI is an excellent topology for SCR as well, and studies unraveling its performance are underway. Similarities in CHA and AEI performance and stability have led many to hypothesize that desirable properties are derived from the d6r-only nature of the frameworks. For the AFX zeolite, also d6r-only, decent SCR performance was noted. The effect of the size of the cavity, large in AFX, could be a topic of future research (this is for instance crucial in MTO chemistry, section 3.4.3). When considering the other d6r-only topology with related but even larger cavities (see Figure 10), i.e., SFW, interesting structure–activity relations could be unraveled. Synthetic access to SFW-zeolites is not straightforward, but recently a new route has been detailed.^{66,137} At this time, an SCR study on SFW is lacking.

Finally, a very recent breakthrough in small-pore zeolite based SCR warrants a highlight. New synthetic access to LTA-zeolites with Si/Al ratios in the range of 11–50^{135,172} has led to the discovery of an unprecedentedly active and stable SCR catalyst, based on full Cu exchange (Cu/Al 0.5) and a remarkable stability in steaming up to 900 °C (Figure 29). The LTA framework lacks d6r units, but single-6MR are present, e.g., the faces of the sod-cavity, and these were found to be active cation hosting sites (centered in the single-6MR, inside the large *lta*-cavity). Furthermore, time will tell if the synthesis of this material is cost-effective (fluoride route) and a potential competitor for Cu-SSZ-13. It is worth noting that KFI, also constructed using only d6r building blocks, has *lta*-cages as well. A first SCR assessment proved to be promising, but synthetic access to KFI with Si/Al ratios significantly larger than 4 is lacking. This is remarkable given the fact that KFI (ZK-5) was the first synthetic zeolite (Barrer).

3.3. Partial Oxidation of Methane to Methanol

3.3.1. Introduction to Methane-to-Methanol with Transition Metal-Exchanged Zeolites. Panov et al. reported the decomposition of N_2O at low temperature using Fe-exchanged ZSM-5 in 1990 with release of N_2 . The oxygen was deposited onto the catalyst to form a highly reactive oxygen-Fe. Subsequently contacting the oxidized material with methane at room temperature resulted in the production of an adsorbed methanol precursor.³⁷⁵ Recently, the active Fe-site for this reaction was reported in the form of an $\alpha\text{-Fe}^{\text{II}}$ against a single-6-ring of for example BEA.³⁷⁶

In 2005, Groothaert et al. documented the first activity for methane partial oxidation to methanol with O_2 on Cu-zeolites.¹⁰⁶ The structure of the Cu-active complex was supposedly elucidated in 2009 by researchers in Stanford and Leuven.³⁷⁷ The accepted catalytic cycle, featuring a dimeric copper species (mono($-\mu\text{-oxo-}$)-dicopper), is seen in Figure 32.

Figure 32. Proposed reaction cycle on Cu-ZSM-5 for O_2 activation and CH_4 hydroxylation. Reproduced with permission from ref 378. Copyright 2010 American Chemical Society.

After activation in O_2 , the active site is formed, which can then react with a subsequent feed of CH_4 . After stoichiometric reaction, a strongly adsorbed partially oxidized methane product is formed and the site is deactivated, requiring reactivation with O_2 . The adsorbed product can be recovered as methanol by liquid extraction or steaming.³⁷⁸ A review by Vanelderen et al. points out the biomimetic links between such Cu-zeolites and Cu-methane monooxygenases.¹⁰⁵

Besides MFI, a plethora of medium and large pore Cu-zeolites have been proposed for this reaction, notably MOR.^{107,379} An overview on the coordination chemistry of copper in zeolite shows that Cu^{2+} preferentially coordinates in 6MR (as in some SCR-zeolites), with 1, 2, or 3 Al T atoms.³⁸⁰ Some of these species then autoreduce under inert atmosphere at high temperature, to Cu^+ , before the reaction with O_2 to form the active dimer (Figure 32).

In the context of feedstock shifts in the chemical industry (e.g., shale gas) and a general revival in C–H activation,³⁸¹ the field of methane oxidation with transition metal ion-exchanged zeolites has expanded rapidly in the last three years. Not only have breakthroughs been reported in terms of methanol extraction³⁸² or even reactivation with steam,³⁸³ efforts have also been directed to turn the stepwise stoichiometric reaction into a catalytic one.³⁸⁴ The latter report for instance details a gas-phase process for continuous methanol production, flowing a mixture of CH_4 , H_2O , and O_2 over Cu-ZSM-5 at 210 °C, with good selectivity, and (a still very low) CH_3OH production rate of $0.88 \mu\text{mol g cat}^{-1} \text{ h}^{-1}$. Note that a catalytic liquid phase methane oxidation process using Fe-ZSM-5 with H_2O_2 as oxidant has been known for a longer time, but so far, no small-pore zeolites have been reported for this case.³⁸⁵

It was only in 2015 that the first small-pore zeolites (Table 9) exchanged with Cu were reported for gas-phase methane oxidation, as pioneered by the Lobo group.²⁵ Several reports have surfaced since, but still only a select number of topologies have been tested (Table 9). For a comparative series of medium- and large pore zeolites, the reader is referred to a recent critical assessment,³⁸⁶ as well as an in-depth review in this journal.⁹⁹

Table 9. List of 8MR-Framework Zeolites Tested in Partial Oxidation of Methane

Top. ^a	Material	Si/Al ^b	M	M/Al	Oxidant	MeOH production ($\mu\text{mol/g cat}$) ^c	ref	Activity remarks
MFI	ZSM-5	11.5	Cu	0.34	O ₂	16	25	Benchmark
CHA	SAPO-34	6 ^b	Cu	0.6	O ₂	15	25	Low vs zeolite
AEI	SSZ-39	10	Cu	0.26	O ₂	36	25	High, 0.09 MeOH/Cu
AFX	SSZ-16	6.5	Cu	0.34	O ₂	39	25	Low, 0.05 MeOH/Cu
CHA	SSZ-13	12	Cu	0.35	O ₂	31	25	Medium, 0.06 MeOH/Cu
CHA	SSZ-13	15.8	Cu	0.84	O ₂	30	387	
CHA	SSZ-13	12	Cu	0.4	O ₂	45	388	
CHA	SSZ-13	12	Cu	0.4	N ₂ O	35	388	
CHA	SSZ-13	12	Cu	0.5	O ₂	107 ^d	389	Very high: 0.2 MeOH/Cu
CHA ^e	SSZ-13	13.8	Cu	0.5	O ₂	16 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	384	catalytic
CHA ^f	SSZ-13	12	Cu	0.4	N ₂ O	55 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	388	catalytic

^aTop. = topology. ^b(Al + P)/Si in the case of silicoaluminophosphate. ^cThree-step cycle reaction, with oxidation temperature at 450 °C and reaction temperature (CH₄ step) at 200 °C. ^dOxidation temperature of 500 °C. ^eFlow mode at 260 °C with activation at 550 °C. ^fFlow mode at 300 °C. Here, rates are reported.

Figure 33. Three different structures of possible active sites in Cu-SSZ-13 within 5 kJ mol^{−1} of a [CuOH]⁺ site in the zeolite: A and C are peroxo [Cu₂O₂]²⁺ species while B is a mono-(μ-oxo) dicopper(II). Colors: red, O; blue, Cu; yellow, Si; marine, Al; H, white. Bond distances are given in Å. Reproduced with permission from ref 390. Copyright 2017 American Chemical Society.

3.3.2. Small-Pore Cu-Zeolites for Methane Oxidation.

Wulfers et al. assessed AEI, AFX, and CHA versus MFI and SAPO-34 for methane oxidation following the three-step activation, reaction, extraction cycle. The three small pore, d6r-based zeolites performed similarly, and about 30–40 μmol methanol per gram of catalyst was obtained, as compared to only 16 $\mu\text{mol}\cdot\text{g}^{-1}$ for a ZSM-5. The small-pore zeolite results give methanol per Cu ratios between 0.03 (an aluminous CHA, not in Table 3) and 0.09 (AEI). It has been noted that the active sites of these copper-containing small-pore zeolites could be the same as those active for the decomposition of NO in SCR.²⁵ Park et al. confirmed the value for CHA, but higher Si/Al and Cu/Al ratios were used (Table 9).³⁸⁷ Later, the Lobo group also found the system to work with N₂O instead of O₂.³⁸⁸ Moving from a consecutive to a real catalytic system is clearly a necessity if this process is ever to be viable. Roman-Leshkov and co-workers broke ground in that respect, using O₂ in flow conditions, and with several types of zeolites. The rates with Na-Cu-SSZ-13 attained 16 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$.³⁸⁴ Ipek et al. investigated expanding the N₂O-activated cycle into a catalytic process for Cu-SSZ-13 as well, noting similar rates at 260 °C (19 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), and up to 55 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ at 300 °C (Table 9).³⁸⁸ Ipek et al. also launched a full scale investigation into the nature of the Cu-sites in SSZ-13 and SSZ-39 and showed that trans-μ-1,2-peroxo dicopper(II), that is, [Cu₂O₂]²⁺, and mono-(μ-oxo) dicopper(II), that is, [Cu₂O]²⁺, likely form on these Cu-zeolites (with Cu/Al = 0.4–0.48, Si/Al = 10–12), as seen in Figure 33.

The thermodynamically optimized structures need at least one Cu-cation on the 8MR of SSZ-13 (Figure 33). Aluminous SSZ-13 zeolites have a higher percentage of bare Cu²⁺ on d6r 6MR windows, containing two Al-atoms (e.g., see Figure 16). These bare sites seem inactive for methanol formation, while Cu²⁺ ions on 8MR windows are believed to lead to Cu_xO_y active species.³⁹⁰ Studt and co-workers recently performed a DFT study, suggesting that monocopper species are also active sites for partial methane oxidation in 8MR zeolites. The suggested [Cu^{II}OH]⁺ active site was said to provide an additional route for methane activation in zeolites in addition to the known multicopper sites.³⁹¹ Pappas et al. studied the Cu-SSZ-13 in great detail, uncovering structure–activity relations and allowing them to optimize methanol formation: up to 107 $\mu\text{mol}\cdot\text{g}^{-1}$ was found using a long high temperature O₂-activation (Table 9). After four cycles, 125 $\mu\text{mol}\cdot\text{g}^{-1}$ was even obtained, related to the water-assisted movement of the metal during the extractions, to (more) active positions. Bare Cu^{II} species on 6MRs were indeed excluded as active sites, while [Cu^{II}OH]⁺ species, also inactive, are identified as precursors to the methane converting site. A positive linear structure–activity correlation was found between activity and the reducibility of the Cu center.³⁸⁹

3.3.3. Conclusions on Small-Pore Zeolites for Methane Oxidation. While Cu- and Fe-zeolites have been known for quite some time to possess activity for methane oxidation after activation with O₂ or N₂O, the use of the first small-pore zeolites in these types of reactions was reported in 2015 and, thus far, only with Cu. Only a few topologies have been tested,

Figure 34. Dual-cycle mechanism in MTO. Reprinted with permission from ref 403. Copyright 2016 Elsevier.

and most of the focus has been placed on CHA, where the active sites have now been more clearly defined. There is a large opportunity for improvement in this area, especially when considering that the Si/Al ratios needed for this reaction are similar to the ones in SCR where hosting the same transition metals plays a crucial role. However, the active site requirements to the zeolite framework seem to be different (e.g., Al in 6MR, 8MR, ...). Drawing parallels between the SCR literature, large-pore methane oxidation reports, and the identity of the active site (precursors) in SSZ-13 will undoubtedly lead to new insights and active small-pore zeolite catalysts for this reaction (and likely new types of active sites).

3.4. Olefin Generation: Methanol-to-Olefins (MTO) and Ethanol/Ethylene Conversion

3.4.1. History and General Chemistry of MTO. The MTO reaction is an industrially viable way to produce light olefins (C2–C3–C4) at temperatures around 350 °C. Typically, MTO requires a solid acid catalyst such as a zeolite or a silicoaluminophosphate (zeotypes). The MTO reaction evolved from the methanol-to-gasoline process, as discovered in the 1970s by the Mobil researchers Chang and Silvestri.^{392,393} Serendipity was involved, as the researchers were looking for routes to make highly branched alkanes from methanol and isobutane. The latter molecule did not convert, but methanol did and gave a mixture of aromatics and isoalkanes with C-numbers not larger than C11.³⁹⁴ In the 1980s, the first plant was commissioned in New Zealand, to produce gasoline from natural gas, through intermediate methanol production. The selectivity to light olefins (MTO) was remarkably improved when UOP researchers discovered SAPO-34, the silicoaluminophosphate of the small-pore CHA topology. Nowadays, MTO, focused on making ethylene and propylene, offers an industrially viable alternative route to olefins from non-petroleum sources, such as biomass, natural gas, and coal. The intermediate methanol is often produced via syngas through Cu/ZnO/Al₂O₃ catalyst technology.^{395,396} A large number of industrial and academic research groups have contributed to the understanding and advancement of MTO over the years, and informative reviews on the subject are available.^{93,102,394,397–399} In recent years, several large scale

commercial units have been built in China, mainly based on SAPO-34,⁹³ but also a ZSM-5-based (medium sized pore-zeolite MFI) operation is reported.³⁹⁴

MTO can be considered in four consecutive steps.⁴⁰⁰ First, the dehydration of methanol yields dimethyl ether (DME), methanol, and water in equilibrium. Second, an induction time is present, on fresh catalysts, and only few olefins are produced. Internally, intermediate species start to accumulate, and the first C–C bond formation occurs. The third step involves high yield production of olefins, i.e., actual MTO, and a so-called hydrocarbon pool mechanism is dominant in most of the materials. The fourth step describes the deactivation by coking inside the zeolite.

In SAPO-34 a hydrocarbon pool of alkylbenzenes is present, and these intermediates dominate the pathway of olefin formation.⁴⁰¹ An active pool can consist of benzene and naphthalene aromatics that are substituted with methyl groups (mostly more than one). The organic pool together with the inorganic acid forms a hybrid reaction hub for adding C1 species (methanol, dimethyl ether, ...) that then transform, forming ethyl and propyl side groups that lead to olefin expulsion. Other mechanisms can also lead to olefin generation during the third phase, such as the methylation of olefins, with chain lengths increasing, followed by cracking of the longer olefins into ethylene and propylene. This route can be considered independent of the pool pathway and is often thought to be present to some extent as the minor reaction path. Dual-cycle mechanisms combining the methylation and hydrocarbon pool have also been proposed.⁴⁰² Figure 34 shows the dual-cycle, as it conveniently displays both major paths.⁴⁰³

A lot of mechanistic research has recently focused on elucidating the first C–C bond formation, either on ZSM-5 or SAPO-34.^{404–406} MTO is a very interesting reaction to study since it involves a whole range of classic (as well as less common) hydrocarbon chemistries: isomerization, alkylation, hydrogen transfer,⁴⁰⁷ cracking, (de)protonation, homology and oligomerization, and cyclization and aromatization. The study of MTO has certainly helped to understand other vital hydrocarbon conversions. Overviews of MTO chemistry, often centered on SAPOs, are available.^{93,394,408}

Table 10. Complete List of 8MR-Framework Zeolites Tested in MTO and General Assessment

Top. ^a	Typical behavior ^b and advantages	Practical numerical example ^c						Per- formance ^f	Drawbacks
		Material ^d	Si/Al	T (°C)	WHSV (h ⁻¹)	S _{alkenes} ^e C2/3/4 (%)	R ^e		
CHA	Benchmark, cheap, tunable C2/C3.	SAPO-34	n.r.	450	1.5	40/40/- ^g	93	++++	Hydrothermal stability
			0.12 ^g	400	1.3	42/37/15	179		
CHA	High activity, commercial in SCR ^h	SSZ-13	50	475	0.5	61/25/-	415	++++	Heavy and fast coke formation
			55	400	1.3	48/37/11	416		
			67	325	0.5	39/49/-	201		
AEI	selective for C3+C4. High activity, long lifetime	SSZ-39	62 ⁱ	400	1.3	17/48/20	179,188	++++	Steaming was needed ^j
AFX	Low activity vs CHA	SSZ-16	16.7	400	1.3	23/31/-	159	++	Large coke species, short lifetime
CDO	Main product DME	RUB-37	204	400	1.3	2/4/-	413	+	Alkanes, few olefins
DDR	90% yield of C2+C3 few paraffins	ZSM-58	55	400	2.0	30/38/12	417	++++	Fast coking of strongest acid sites
		Sigma-1	50	400	1.0	27/47/11	418		
ERI	Initial high selectivity to olefins	UZM-12	6.5	350	0.67	29/41/10	70	++	Fast deactivation
ESV	Low activity, some DME	ERS-7	8.1	400	1.3	none	413	n.a.	No olefins
ITE	Selective to C3	ITQ-3 type	18.1	400	1.3	18/40/17	419	++	Short lifetime
KFI	Interesting C3+C4 selectivity	ZK-5	17 ⁱ	400	1.3	21/34/21	267	++	Steaming needed
LEV	C2 as main olefin.	SSZ-17	16.8	400	1.3	43/31/-	159	++	C5 olefins and DME
		Nu-3	30 ⁱ	400	1.0	37/24/7	418		
LTA	Interesting C4 selectivity	ITQ-29	42	400	1.3	24/25/24	135	++	Fast deactivation
		UZM-9	5.1	350	0.7	20/45/18	420		
MTF	Main product DME	UTM-1	45	475	0.5	4/3/-	415	n.a.	No olefins
		MCM-35	31.7	400	1.3	none	413		
SFW	Low activity vs CHA	SSZ-52	6.1	400	1.3	35/35/8	419	++	Similar to AFX
RHO	Interesting C3+C4 selectivity	Rho	23 ⁱ	400	1.3	21/40/21	267	+	Fast deactivation, needs steaming
		Rho	3.5	400	1.0	31/29/-	421		
RTH	Selective to C3+C4. Medium-high activ.	SSZ-50	17	400	1.3	15/47/21	169	+++	Medium lifetime
		Al-TTZ-1	41	400	1.0	23/45/-	121		
UFI	Initial high selectivity to olefins	UZM-5	6.9	350	0.7	30/45/18	420	+	Very fast deactivation

^aTop. = topology. ^bTypical MTO result in terms of products and activity. ^cThe example is found in the first reference (R) listed, while others mentioned are illustrative works of MTO with this framework. The table is by no means complete, and different behaviors can be encountered in different conditions. ^dAlways in Brønsted acidic H⁺ form. ^eSelectivity for individual alkenes, from chosen reference, at one point in time, where the sum of alkenes is highest and at full (or highest reported) conversion. - indicates C4 was not reported separately. ^fPerformance relative vs all entries, ranked from n.a. (no MTO activity) over + (few olefins, fast deactivation) to ++++ (excellent MTO). Material synthesis drawbacks (or ease) not taken into account. ^gFor this industrial benchmark, a range of different olefin ratios can be achieved, depending on conditions, and the value shown is not binding. Propylene selectivities of over 80% are claimed. The Si/Al of this catalyst is in fact the Si/(Si + P + Al) ratio. ^hA lower Si/Al is needed there. ⁱSteamed materials: their Si/Al ratio considering only framework-Al obtained by correcting low bulk ratio with the Al-tetrahedral fraction in MAS NMR. ^jTheoretical value.

3.4.2. Overview and Specifics of Small-Pore Zeolite

MTO. Aside from ZSM-5, most of the MTO research has focused on small-pore SAPO-34. Here, we limit our discussion to small-pore aluminosilicates, where the MTO literature is less abundant. SSZ-13 (CHA) was one of the first zeolites tested in this category, as patented by Santilli and Zones.^{409,410} On average, compared to SAPOs, zeolites are more strongly acidic and have a higher hydrothermal stability. Katada et al. published a detailed comparison of the acidic properties of small-pore cage-based zeolites with different topologies in comparison to SAPO's (not in an MTO study, but still informative).⁴¹¹ Bleken et al. studied the effect of acid strength for this reaction, comparing SAPO-34 and SSZ-13 (Si/Al = 11).⁴¹² Keeping acid density and crystal size constant, and probing strength with CO-IR, a more active MTO chemistry (olefin production but also aromatics production and thus deactivation) was found for the aluminosilicate at the same temperature. Reaction paths and intermediates were similar, demonstrating topology matters more in this respect, although ethylene to propylene ratios were a bit higher for SSZ-13. Due to the higher activity, aluminosilicates can work at lower (optimal) temperature.

Ethylene to propylene ratios usually also increase with temperature, and this is understood from the prevalent dual-cycle mechanism and the kinetic competition between (and activation barriers of) aromatic and olefinic cycles (C2/C3 olefin ratios are said to be also influenced by shape-selectivity originating from differences in diffusivity¹⁰²). For MTO, the stronger acidity of aluminosilicates is thus not needed per se. The hydrothermal stability can be important for having longer catalysts lifetimes and an overall lower solid use per olefin generated. Given the industrial mode of MTO, often in fluidized bed with regeneration loops at low to intermediate coking levels, this could be important.

The MTO reaction on small-pore cage containing zeolites is a prime example of reaction intermediate confinement, as the cage traps the large hydrocarbon pool's polymethylbenzene intermediates, allowing only the escape of C1–C4 compounds (and a limited fraction of longer linear alkanes/alkenes) and mostly ethylene, propylene, and some butylenes (incl. butadiene). The ratio of ethylene:propylene:butylenes (aside from the mentioned condition dependence) can thus depend on topology-specific changes as well as on the size and shape of

the cage that can allow different hydrocarbon pool species. Care should be taken, when interpreting topology-dependent selectivities, that the conditions used are comparable (i.e., particle size, T, methanol turnover level, coking level, conversion). 8MR zeolites without cages have also been assessed, generally without success.⁴¹³ Table 10 lists a comprehensive overview of (all) tested 8MR aluminosilicate zeolite frameworks for the MTO reaction. Typical catalytic data for each framework are supplemented both with relative grading and (dis)advantages. Note that Table 10 does not intend to credit first results reported for a given framework but aims to compile data with the most similar operating conditions.

Aside from the following comparison between small-pore zeolites and their structure–activity relations, work dedicated to understanding the mechanism of MTO in SSZ-13 (using one material with fixed properties) and other aluminosilicates has been reported. Such conditional (e.g., cofeeding, water addition, ...) and kinetic studies⁴¹⁴ are not detailed here.

3.4.3. Key Structure–Activity Relations in Zeolite-Catalyzed MTO. **3.4.3.1. Topology and the Presence of Cages.** From the body of MTO literature, it is obvious that topology is the decisive factor for both activity (selectivity) and deactivation. Based on the information provided in Table 10 and comparing across different reports, it is clear that sufficiently sized-cages are needed when MTO is targeted in small-pore zeolites. Zero MTO activity was found for the 1D ESV and MTF zeolites (very small cage) in a recent study, and the main product in these dense materials is DME. Although MTF showed no olefins, a minor amount, possibly due to impurities, was detected in earlier work (both in Table 10). In comparison to small-pore SAPO zeotypes,^{422,423} and large pore zeolites (ZSM-5: MFI, MEL, TON, BEA, ...),⁴²⁴ relatively few studies have narrowed in on the role of cage dimensions in comparative studies for small-pore zeolites. Although parallels between SAPOs and zeolites with the same structure in terms of product distribution have been drawn (e.g., SSZ-13 above, or for AEI: SSZ-39¹⁷⁹ and SAPO-18⁴²⁵), direct zeolite-zeotype comparisons remain difficult.

The size and the shape of the cage, as well as their connectivity, are decisive in MTO as they:

- (i) determine the nature (size and reactivity) of the hydrocarbon pool species that can be included and, derived thereof, MTO activity and C2/C3/C4 olefin product distribution;
- (ii) are linked to acid site density (protons per cage);
- (iii) determine deactivation routes through the molecular sizes of accumulating carbonaceous deposits, a.k.a. coke. These originate from species in the pool that are not active toward olefin expulsion anymore (or from reactions at external surface areas).

It is clear that confinement effects and the number of acid sites confined within one cage are crucial in this complex chemistry. With a focus on cage dimensions, CHA, AFX, and LEV (SSZ-17) zeolites were compared by Bhawe et al. at similar Si/Al ratios (16) and crystal sizes. The selectivity toward ethylene increased with a decrease in cage size (LEV being the smallest and largest ethylene producer). AFX, with huge *aft*-cavity (Figure 7, 15.1 T/1000 Å³), showed the worst performance in terms of both activity (53% of conversion at WHSV = 1.3) and lifetime. Studying the organic species on partially and fully coked AFX samples showed that initially large

organic species (phenanthrenes, anthracenes) form on the zeolite, while smaller species later occupy the remaining free cage volume. In contrast, for LEV and CHA zeolites (density of 15.9 and 15.1 T/1000 Å³, respectively) at partial coking, the size of the organics at maximum propylene selectivity correlated with the cages size (C2-benzenes for LEV, C3-C4-benzenes for CHA), while heavier carbonaceous species are only encountered later, at full coking. The average molecular weight of the hydrocarbon pool in this case continues to increase. For AFX, the average weight stayed more or less constant during deactivation. This suggests that materials with too large cages can deactivate faster and differently, based on the initial formation of large species right from the start, which could cause pore blockages. Recently, SFW was used for the first time in MTO, and compared to CHA and AFX because of their structural relation (see Figure 10, the SFW-cage is a *c*-axis expanded version of the AFX-cage).⁴¹⁹ SFW produced equal amounts of C2 and C3 olefins and little butylenes (Table 10), as did AFX in this study (33/33/8 for AFX with Si/Al = 14.7, similar to the tabulated value from another study). Product selectivity and deactivation for the elongated cages are very similar, as is the cage diameter and 8MR windows. Compared to CHA, larger cages more readily produce organics that lead to faster deactivation.

Park et al. compared LTA (UZM-9, 14.2 T/1000 Å³), UFI (15.2 T/1000 Å³), and ERI (UZM-12, (16.2 T/1000 Å³) zeolites at 350 °C (Table 10) vs SAPO-34.⁴²⁰ UFI and LTA (*lta*-cage) showed propylene as main product, supplemented with both ethylene and medium amounts of butylenes, while ERI produced more or less 1/1 C2/C3 and a few C4 olefins. The ERI-zeolite tested by Kang et al. showed a somewhat higher ethylene/propylene ratio at peak olefin yield (50/23/5 for a Si/Al = 5.7).⁴¹⁹ These materials with high Al-content (Si/Al = 5–7) gave a fast deactivation by coking, as evidenced from anthracene and phenanthrene molecules (quickly) present in the LTA and UFI cage and alkylated naphthalenes in ERI. These large polycyclic aromatics are typical dead-end coke species for this reaction and lead to pore-filling and cage blocking and thus active site and catalyst deactivation. CHA, on the other hand, with a smaller cage (Figure 7), allows the formation of multialkylbenzenes (active hydrocarbon pool species) but suppresses the formation of polycyclic aromatics, at least initially. However, since the UFI, ERI, and LTA materials tested all had very high acid site densities, deactivation paths could be different for Al-deficient materials. Since Boal et al. recently discovered an easy route to high-silica LTA (14.2 T/1000 Å³) zeolites, the MTO performance of these materials was especially interesting. As seen in Table 10, a Si/Al = 42 LTA-zeolite (synthesis: Table 7, entry 11) showed low C2 + C3 olefin selectivities but a large fraction of butylenes and C5–C6 molecules. Also, as a fast deactivation was noticed, it seems clear that the large *lta*-cavity of LTA favors the formation of higher-carbon number products and thus also likely easy deactivation by larger carbonaceous coking species (rather than being caused (only) by high Al-content in UZM-9). The selectivity toward butylenes was also clear in the SAPO version of LTA.⁴²² Table 10 suggests that zeolites UFI, KFI, and RHO, all containing the same *lta*-cage (although little differences exist, caused by the different connection mode), also show olefin distributions in favor of larger products, like LTA, although, comparing across different conditions and Si/Al ratios is difficult.

Figure 35. Coke analysis via GC-MS of soluble species in dichloromethane after HF-mediated breakdown of the zeolite in left: CHA (SSZ-13, Si/Al 60); middle: DDR (Sigma-1, Si/Al 50); and right: LEV (Si/Al 30). Reproduced with permission from Goetze et al.⁴¹⁸ (ACS Author Choice open access).

An interesting case is the dense zeolite DDR with relatively small cages (17.9 T/1000 Å³), accessible only in 2D by ellipsoidal windows (3.6 Å × 4.4 Å). Compared to CHA (15.1 T/1000 Å³), for instance, this is a dense material, as CHA has 3.8 Å × 3.8 Å pores, accessing the cage in 3D. Olson et al. indeed noticed a much faster diffusion of propane and propylene in CHA than in DDR-zeolites.¹¹⁰ Thus, apart from the size and shape of the cavity, the accessibility, determined by the dimensionality (1D-2D-3D) of the pore system and the shape of the 8MR windows, may matter as well. DDR produces virtually no saturated alkanes, as well as high amounts of C2 and C3 olefins (Table 10).^{246,417} In light of costly separation of alkanes from alkenes (e.g., propane from propylene), this could be interesting. Gascon and co-workers studied DDR by looking at the two different methods of making this zeolite (Sigma-1 and ZSM-58). ZSM-58 produced up to 80% of olefins at 400 °C (Table 10), while for Sigma-1, up to 90% of C2 + C3 olefins can be yielded at 450 °C (not in table). As commonly encountered, the ethylene-to-propylene ratio depends on the temperature, e.g., for Sigma-1, going from 0.5 at 380 °C to 1.6 at 475 °C (Si/Al = 58). The ratio also partially depends on catalyst morphology and composition.

A detailed study on the deactivation of zeolite using three different topologies, CHA, LEV (Nu-3), and DDR (Sigma-1), has been published by Goetze et al.⁴¹⁸ As seen in Figure 35, CHA coke species exist of methylated benzenes, methylated naphthalenes, and pyrene, while for DDR, 1-methylnaphthalene is mainly found, supplemented with diamantane after the 350 °C reaction. This molecule resembles the OSDA used for Sigma-1 (1-adamantlyamine, see section 2.3.4) but was confirmed to not come from the remains of the synthesis. LEV coke species consist mainly of naphthalene (and methylbenzenes at low T), since larger species likely do not fit. An operando-UV-vis study further tried to distinguish the different species between the induction, active, and deactivation periods and at different temperatures. For an in-depth study of deactivation in MTO, with a focus on active intermediate, the reader is referred to the review by Olsbye et al., where SSZ-13 is also covered.⁴²⁶

Dusselier et al. studied MTO with SSZ-39 (AEI) noting high C3 and C4 selectivities and about 85% of olefins at full conversion.¹⁷⁹ Schmidt et al. reported a new route to RTH, assessing MTO performance in the process, and documenting around 70% of C3 + C4 olefins (Table 10).¹⁶⁹ Given the fact that the cage of RTH (16.6 T atoms/1000 Å³) is somewhat smaller than that of AEI (15.1 T/1000 Å³), these selectivities are intriguing, as they are not straightforwardly explained by the “large cage, large products” observations over for instance LTA (14.2 T/1000 Å³). A more detailed study on the origin of this selectivity is due, although parallels to SAPO-18 (AEI) vs SAPO-34 suggest that indeed the shape of the cage is important, the AEI cage being more basket-shaped and wider at the bottom than the more symmetric CHA cavity.^{425,427,428} SSZ-39 is a very interesting catalyst for MTO, but steaming was needed for optimal performance (section 3.4.3.2). No SAPO versions of RTH exist. Computational chemistry could be useful in this regard but so far has mainly focused on ZSM-5 and SAPO-34.

Sastre computationally screened a series of relevant cages (all found in Table 10), for the methylation of hexamethylbenzene (HMB), as a model reaction for successive methylation of a hydrocarbon pool species (before olefin expulsion), and for reactions leading to the formation of coke.⁴²⁹ In RTH, LEV, and AEI cavities it was found that it is impossible to host a linear O–C(H₃)...C(HMB) angle, required by the planar methyl group of methanol interacting with HMB (Figure 36). In other cavities, larger O–C–C angles (more linear) can be achieved, indicating this reaction to be more likely there. Whether this can be linked to active behavior or deactivation kinetics remains an open question.

Additional discussion on the impact of cavities (in light of the recent work of Kang et al.) taking in consideration other parameters such as Si/Al ratio, is found in section 3.4.4 (also featuring zeolite ITE, found in Table 10).

3.4.3.2. Si/Al Ratio and the Presence of Paired Al. It seems that the inherent selectivity in terms of C2/C3/C4 ratio of a cage-containing MTO-active zeolite, at a fixed temperature and assessed at maximum C3 + C2 olefins production, is not

Figure 36. Cages of small-pore zeolites filled with the HMB-methylation transition state (green = C, red = O, white = H, purple = Si). For AEI, LEV, and RTH, the O–C–C angle is 150°, 125°, and 156°, respectively, while larger values, closer to linear, are found for others. The Al-atom close to the Brønsted acid site where methanol interacts is highlighted in blue. Reproduced with permission from ref 429. Copyright 2016 Springer.

strongly dependent on the Si/Al ratio (for example: double entries in Table 10 for RHO, LEV, RTH at the same temperature, or for CHA in Figure 37). However, this does not mean transient behavior in olefin selectivities is absent, and often ethylene yields tend to rise during the time on stream. The Si/Al dependent behavior in MTO can be described for a couple of small-pore zeolites, where synthetic access to a diverse range of Si/Al ratios exists (cf. Table 3) or from dealumination studies based on steaming.

Synthetic access has allowed for the investigation of the effects of Si/Al ratio with CHA (from 2.3 up to 67),²⁰¹ RTH (Si/Al = 17, 29, 59),¹⁶⁹ LTA (Si/Al = 12, 33, 38, and 42; although it is more difficult to draw conclusions here),¹³⁵ and DDR (Si/Al = 32, 55, 107, 198),⁴¹⁷ all made via the use of OSDA in hydroxide media, with the exception LTA (HF). Deimund et al. studied CHA thoroughly, concluding that lower Si/Al ratios lead to drastically shorter catalytic lifetimes (e.g., less than 2 h for Si/Al = 17 to more than 5 h for Si/Al = 55) as well as significant transient ethylene selectivity and high light alkane initial selectivities (see A in Figure 37). The higher Si/Al ratio materials resembled the output of SAPO-34. The lifetime effect was also noticed before by Tatsumi and co-workers,²⁰¹ but not the alkanes (perhaps also reaction condition related). The effects of the Si/Al (transient nature, alkane production initially) were ascribed to the paired Al site content, that is increasingly present as the Si/Al ratio drops. Cu²⁺ titration confirmed the paired Al-site content along a theoretical line for

“d6r only” zeolites (section 2.3.3.5 and Figure 16)⁴³⁰ and was plotted with the initial propane selectivity (B in Figure 37). In light of Al-site density per cage, a Si/Al ratio of 11 would translate to approximately 1 acid site per cage. Given that one cage consists of 36 T atoms, each shared over three cages in CHA, and that pairing, inducing alkanes, assumes at least 2 per cage locally, it is clear that the optimal acid site density for MTO is less than 1 per cage for CHA. In the RTH series, higher initial alkane production was also encountered for lower Si/Al materials.

Kumita et al. found an optimum MTO performance at Si/Al = 55 (400 °C) for ZSM-58 of the DDR topology, more or less corresponding to 1 acid site per cage. Less aluminum resulted in prompt deactivation, while more aluminum did not help either.⁴¹⁷ However, Sigma-1, the other DDR zeolite made with a different organic (Figure 17), showed a reverse trend at 450 °C. There, more methanol converted over the materials with the least amount of Al (Si/Al = 158 and 208 vs 60, for similar crystal sizes), and also the yield to ethylene increased, while propylene decreased. Interestingly, the C2/C3 olefin ratio changes from 0.7 to 1.3 for Si/Al ratios varying from 60 to 208, thus demonstrating a zeolite where acid site density influences olefin ratios. Also, for Sigma-1, the acid strength was varying with the Al content and, with that, the nature of some coke species. Truly exceptional in this series of DDR-zeolites is the very low Al-content (e.g., Si/Al = 158) that was able to still perform MTO. The differences between Sigma-1 and ZSM-58 are likely explained by the not-so constant particle sizes in the ZSM-58 series (section 3.4.3.3). What remains puzzling is why for the same Si/Al ratio, ZSM-58 converts up to 3× more methanol before deactivation than Sigma-1.²⁴⁶

For some small-pore zeolite (Table 3), synthetic access to a wide range of Si/Al ratios is not possible. However, using organic-free methods of zeolite production, CHA, RHO, and KFI materials with low Si/Al ratios were subjected to steaming studies by Ji et al.^{222,267} For CHA (OSDA-free: Si/Al = 2.4, Table 5, Entry 2) remarkable improvements were obtained. When steaming temperature and partial pressure are optimized and an additional acid washing step is incorporated, the time to deactivation at 400 °C MTO for instance increased from 1.3 g of methanol per g of catalyst to 5.0 (for a sample steamed at 600 °C and acid washed with a 0.1 M HCl solution). The same sample was able to produce 71% of olefins at full conversion at 450 °C with a time to deactivation of 9 g·g^{−1}. The Si/Al ratio only considering the framework Al (MAS NMR) of this treated CHA increased to 12. For RHO and KFI, the steamed samples

Figure 37. (A) MTO behavior for different Si/Al in SSZ-13; (B) paired Al site content (fraction of framework Al) and initial propane selectivity as a function of Si/Al ratio. Based on data and plots in ref 416. Copyright 2016 American Chemical Society. WHSV: 1.3 h^{−1}, 400 °C.

Figure 38. MTO performance of SSZ-39 (AEI) before and after steaming at 750 °C in its NH_4 -form. WHSV: 1.3 h^{-1} , 400 °C. Red: alkanes, green: propylene, blue: butylene. Based on data and plots in ref 179. Copyright 2015 American Chemical Society.

showed increased lifetimes and olefin selectivities, but the conversion over the materials was never prolonged beyond 2 h on stream. Interestingly, steaming also created some mesoporosity, also thought to contribute to the increase in lifetime, by allowing better access to the micropores. Phosphite treatment of the external surfaces, to block acid sites locally, was found not to influence the inherent C2/C3/C4 olefin ratios, but it prolonged the lifetime further of steamed RHO and KFI zeolites. Likely, acid sites in mesopores made by steaming can also serve as sites for coke deposition.

Remarkable steaming improvements were also noted for SSZ-39.¹⁷⁹ This zeolite is difficult to access in high Si/Al ratios from synthesis (section 2.3.1, most materials around Si/Al = 5–10). The Si/Al = 8.5 material (easily accessed) shows quite mediocre MTO performance, characterized by fast deactivation, transient olefin selectivities, and high initial alkane production (Figure 38, left). After steaming at 750 °C, however, a superior MTO catalyst was obtained, showing extraordinary lifetime, few alkanes, and a stable, high olefin production (85%, Figure 38, right). Extra-framework Al in this case is still present inside the zeolite particles, but no lowering of the micropore volumes was found in N_2 -physisorption. The tetrahedral Si/Al_T ratio based on combining the bulk value and tetrahedral Al-fraction from Al-MAS NMR was calculated to be 62 (or lower if the steaming temperature was lower). This result is consistent with the crucial role of acid site density in the cages. The steamed SSZ-39 catalyst converted over 11 $\text{g}\cdot\text{g}^{-1}$, and the experiment was halted before full deactivation.

3.4.3.3. Crystal Size. Crystal sizes can vary a lot from synthesis, and as documented in section 2, numerous researchers have targeted smaller crystals in their protocols with the aim of improving mass transport issues and, perhaps, coking problems in catalytic applications.

Li et al. compared the nanosized CHA zeolites obtained by CTAB addition (section 2.3.3) and noticed a remarkable conversion capacity increase from 4.2 to 10.4 $\text{g}\cdot\text{g}^{-1}$ when going from the standard, 1.5–2.5 μm crystals, to the 50–200 nm nanocrystals (WHSV 0.8 h^{-1} , 350 °C).²⁰⁸ Interestingly, the C2/C3 ratio also increased for the nanosized samples. This was explained by the lower contribution of hydrogen transfer reactions, causing lower deactivation in the aromatic pool.

Yarulina et al., in their DDR study, also reported on the effect of crystal sizes for Sigma-1 (DDR) with Si/Al ratio of 158, i.e., 0.4, 2.4, and 4.6 μm . Again, smaller crystals were able to convert more methanol, up to 3.6 g of methanol per g of catalysts, more than medium (2.3 $\text{g}\cdot\text{g}^{-1}$) or large-size crystals (1.6 $\text{g}\cdot\text{g}^{-1}$).²⁴⁶

The ethylene yield also dropped with increasing crystal sizes, while C3 and C4-olefins remained constant.

Finally, Martin et al. compared the small SSZ-39 crystals of about 40–50 nm, obtained from IZC (section 2.3.1, Table 4), to a larger SSZ-39 catalyst of 0.2–0.4 μm ; both with Si/Al around 8.5.¹⁸⁸ The latter value is similar to the one shown in Figure 38, while the particle sizes are clearly smaller: around 0.5–1 μm was used in the work of Dusselier et al., and these values were apparently unaffected by steaming. Methanol conversion dipped below 50% after 540 and 940 min on stream, for the large and nanocrystals, respectively (after a throughput of 7.2 $\text{g}\cdot\text{g}^{-1}$ and 12.5 $\text{g}\cdot\text{g}^{-1}$). Comparing throughputs with data in Figure 38 is difficult, as a different WHSV and temperature (0.8 h^{-1} and 350 °C) were used for the nano-SSZ-39 study (although selectivities were in good agreement).^{179,188}

3.4.3.4. Other Parameters: Seeding and Defects, Mesopores and Hierarchy. Gascon and co-workers reported an interesting comparison between DDR zeolites, Sigma-1 and ZSM-58, made with and without seeding syntheses.²⁴⁵ Seeding is known to speed up zeolite synthesis, either by speeding up nucleation or by core-shell growth around the seed crystals. Faster zeolite crystallization leads to framework imperfections, and this possibly affects MTO performance. Seeding ZSM-58 and Sigma-1 gave nanoparticles with average sizes of 100 nm in DLS, while direct hydrothermal synthesis yielded disks (12–15 μm , Sigma-1) or spheres (0.5–1.6 μm , ZSM-58). The lifetime at 450 °C was not linked to sizes in this case, in contrast to the discussion in the above section, and the larger crystals, made without seeds, often performed better. An SSZ-13 benchmark confirmed this. Characterization showed that the main difference between the seeded and the nonseeded zeolites was the large amount of defects, i.e., internal silanols and silanol nests, in seeded materials. It appears that one reason why seeded zeolites deactivate much faster is that the defects accelerate the formation of internal coke and that the positive effect on lifetime of particle size can thus be overridden in seeded small crystals. Finally, confirmation was found in an SSZ-13 zeolite with improved lifetime, after it was subjected to a postsynthetic defect-healing with NH_4F , a method reported by Valtchev et al.⁴³¹ This defect-induced impact on MTO is a crucial observation, as too often seeded zeolite catalysts are used without benchmarking the effect of their defects.

A large subfield of zeolite catalysis involves material hierarchy, aiming at enhanced mass transport via mesoporous access to microporous active sites.^{24,307,432} Olsbye and co-

workers reported a desilication study of SSZ-13 with Si/Al = 14, with NaOH, for MTO. Mesopores were created at the expense of micropores. The methanol throughput significantly decreased for the mesoporous version and was said to originate from lower surface areas and acidity, while no evidence for larger coke species was found. Possibly, Lewis acidity, created in the mesoporous zeolite also catalyzed the aging of the hydrocarbon pool.⁴³³

Interestingly, the dual-template SSZ-13 reported by Hensen et al. (section 2.3.3), with micropores similar to the classic SSZ-13 ($0.21 \text{ cm}^{-3} \cdot \text{g}^{-1}$) and containing about the same amount of mesopore volume, outperformed the nonmesoporous version in MTO: the lifetime, at WHSV of 0.8 h^{-1} and 350°C , more than doubled.²¹⁸ This was said to come from a more efficient use of the micropore space, by an increase of the surface to volume ratio. These observations are in line with those of the Corma group regarding nanosized SSZ-13. A detailed follow-up study by the Hensen group showed that the increase of access needs to be balanced by an increase in the rate of coke formation.²¹⁹

The interesting bimodal microporous SSZ-13 derived from adding NaF in hydroxide media was tested in MTO and also gave a longer lifetime. The effect was more pronounced if the F/Si ratio in the synthesis was higher (0.1 vs 0.05 F:Si).⁴³⁴ The spatial coke distribution was visualized and showed that throughout the entire spent crystal, aromatics were found, versus mainly at the outer rim for the classic SSZ-13. Access again improved performance here, clearly, although the effects of defects in the F-rich conditions (given for example healing with NH_4F in the work of Yarulina et al. for DDR and CHA) should be investigated as well. The Hensen group further combined the mesopore approach with the bimodal micropores, and the trimodal material outperformed both other approaches.²²¹ Confocal microscopy of spent catalysts, in the middle of single crystals, shows the much higher degree of utilization of the crystal, when the bimodal micropores or, in addition to that, mesopores are present (Figure 39). The trimodal catalyst does not light up with exposure from the 488 nm laser (Figure 39c), which is indicative of polymethylated naphthalenes. Likely for this faster catalyst, these species have already converted into bulkier multiring aromatics. The additional porosity clearly enhances the utilization of the crystals, said to originate from faster transport of methanol. The total methanol conversion capacity for the trimodal SSZ-13 resides in the range of $16\text{--}20 \text{ g} \cdot \text{g}^{-1}$, versus only $6.8 \text{ g} \cdot \text{g}^{-1}$ for the classic or $12.5 \text{ g} \cdot \text{g}^{-1}$ for the bimodal microporous version.²²¹

Selzer et al. investigated hierarchical DDR zeolites for MTO, made by desilication of a ZSM-58 material with Si/Al = 48 using NaOH in the presence of TEA. Higher product yields and longer lifetimes were noted for the mesopore-containing zeolites, which also featured lower Si/Al ratios. The benign effect of the mesopores was attributed to the increased acidity (although previous DDR work above found less Al to work better) and faster adsorption/desorption kinetics, the latter retarding coke formation.⁴³⁵

3.4.4. Overarching Analysis of Small-Pore Zeolite Cavities for MTO. Very recently, Kang et al. presented an interesting MTO study, arguably the most comprehensive set to date, comparing 11 framework topologies, as well as some interesting intergrowths (LEV/ERI: SSZ-105 and CHA/GME: SSZ-99) and an 8MR-zeolite with an unreported topology and an interesting, large cage (SSZ-27).⁴¹⁹ The testing of ITE (cage

Figure 39. Confocal fluorescence microscopy images of different modal porous crystals collected after the MTO reaction. Images were taken in the middle plane of single crystals and are shown in false colors. The visualization of the coke species is done with different lasers. Adapted with permission from ref 221. Copyright 2016 American Chemical Society.

in Figure 5) and SSZ-27 (both having pentasil subunits as is also the case for DDR) shows that ITE produces double the amount of propylene versus ethylene (Table 10), while SSZ-27 deactivates quickly, likely due to its tortuous nature (not in IZA database so far).

This study visually confirms (Figure 40, left) and generalizes the correlation that the initial alkane production—higher at low Si/Al—noticed for CHA (Figure 37 above) is present for numerous structures. It also appears that the longer a single cage dimension, the more propane is formed, and this is linked to faster deactivation. Implications from these results are that more symmetrical cages are better, as one longer dimension diminishes lifetime. Also, the number of frameworks tested at the same conditions allows for the identification of four classes of behavior in terms of olefins selectivity (Figure 40, right):

- (I) equal C2 and C3 olefins with low C4 olefins (CHA, AFX, SFW)
- (II) more C2 than C3 olefins with low C4 olefins (LEV, ERI)
- (III) less C2 than C3 olefins with C4 olefins equal to C2 olefins (AEI, RTH, DDR, ITE)
- (IV) equal C2, C3, and C4 olefins (LTA, RHO)

The fact that pentasil units are found in DDR versus only d6r units in AEI but that they, sort of, behave the same indicates that such structural features are not the dominant reason for high propylene selectivities. The IV class, with very large but symmetrical cages, compared to cages that are only large in one dimension (SFW and AFX) reveals that not only size but also shape is crucial.⁴¹⁹

3.4.5. Conclusions of Small-Pore Cage-Based Zeolite-Catalyzed MTO. When designing small-pore, cage-based zeolites for MTO, the following should be considered:

Figure 40. Left: initial propane selectivity after <10 min on stream as a function of the tetrahedral Si/Al ratio as measured by energy-dispersive X-ray spectroscopy for a number of zeolites and intergrowths. Right: averaged product selectivities for conversions in the range of 98–100% for a range of zeolites compared to SAPO-34. Four classes I–IV of behavior are indicated and explained in the text. Both plots reproduced with permission from Kang et al., ref 419 Copyright 2018 Wiley. Conditions of MTO reaction: 400 °C, WHSV 1.3 h⁻¹, 10% methanol in inerts. SSZ-28 (DDR type); SSZ-98 (ERI-type), SSZ-99, 104, and 105 are intergrowths or with stacking faults.

- have large enough cages to allow hydrocarbon pool species to form (e.g., not MTF)
- do not have too large of a cage (even a single dimension of the cage) for fast coking or accumulation of “dead” hydrocarbon pool species (e.g., too large: AFX), and if large, it seems better to have a symmetric one.
- there are four types of behavior in terms of olefin selectivity observed thus far, for different cages
- have a high number of cages per nm³ of solid (low T-site density is an indicator here, although large cages also lower this)
- have a 3D channel structure for optimal diffusion of reactants and products
- have at most one active site per cage
- avoid low Si/Al ratios, as these element ratios favor high alkane production (Figure 40)
- minimize particle size and avoiding silanol defects

Thus, a conceptualized, ideal cage would be one that just barely can host the right hydrocarbon pool species needed, but not the coke precursors or e.g. bicyclic aromatics. At this time, although trends are increasingly unraveled, it is not yet clear how to design a crystalline structure to purposefully control the light olefin selectivities to any of the desired products (cf. AEI vs RTH vs DDR). A unifying concept to link the nature of light olefin production to the structure is thus still at large.

3.4.6. Olefin Generation from Ethanol or Ethylene Conversions: ETO and ETP. In addition to MTO, the ethanol-to-olefins process (ETO) is also well-known. Ethylene can be formed via simple dehydration, e.g. shown with 8MR-zeolite ETL at 200 °C,⁷⁷ but the mechanisms of olefin generation in ETO are more complex as higher olefins are also formed and multiple routes can be at work, e.g., identified in ZSM-5 by Galvita and co-workers.⁴³⁶ Also, the often considered crucial first C–C bond’s formation present in MTO is absent with ETO. ETO could be interesting when considering biobased ethanol, if sustainably sourced availability arises. Another common reaction in this context is the ethanol to butadiene conversion,⁴³⁷ requiring different chemistries, e.g., combining dehydrogenation and aldol condensation, often performed on nonporous oxides, or Lewis acidic large pore zeolites.⁴³⁸ ETO has been investigated mainly with ZSM-5 and SAPO-34,⁴³⁹ but also with zeolites SSZ-13 and MTF.

Tatsumi and co-workers studied the conversion of ethanol at 350 °C on H-SSZ-13 and H-MTF. While the CHA-type material yielded 25% of ethylene, 40% of propylene as well as some alkanes, MTF only led to 90% of ethylene, likely due to the small cage, and some diethyl ether.⁴⁴⁰ Itakura et al. assessed their SSZ-13 sample made via IZC using BTMA (Table 5, Figure 14), in ETO chemistry, at 400 °C. At their conditions and full conversion, initial yields of 55, 35, and 3% of ethylene, propylene, and butylenes were obtained.²¹⁶ Itakura went on to study ETO on their materials in greater depth, and they found an interesting relation for the Si/Al of the SSZ-13 zeolites, showing a maximum of 47% of propylene for Si/Al = 15 (Figure 41).²²⁴ This behavior is related to the oligomerization ability of ethylene on acid sites.⁴³⁹

Inoue et al. also tested their LEV-zeolite made by IZC with choline hydroxide (Table 6, Entry 13) in the conversion of ethanol to olefins, at 400 °C, with 36% of ethylene and 35% of propylene obtained initially (resembling those values in Table

Figure 41. ETO at 400 °C on H-SSZ-13 showing different propylene and ethylene yields in function of different Si/Al ratios obtained from IZC with BTMA. Reproduced with permission from ref 224. Copyright 2011 Elsevier.

Figure 42. ETP on different 8MR topologies, with a focus on propylene selectivity, plotted as a function of D_i , diameter of the maximum included sphere in the framework (Foster et al.⁴⁴⁴) D_i is proportional to pore volume. Adapted from Koyama et al., ref 442 with permission of the PCCP Owner Societies.

10 for MTO). When coke starts forming, the selectivity to ethylene goes to 100%.²⁸⁴

Another reaction of interest, especially in the light of cheap ethylene from gas-fired steam crackers, e.g., in the US,⁴⁴¹ is the conversion of ethylene to propylene (ETP, see Figure 2). Tatsumi and co-workers assessed ethylene feedstocks in their MTF-CHA comparison and found that while MTF was largely inactive, CHA converted 68% of ethylene into mainly propylene, with a 34% yield, and with some propane.⁴⁴⁰ When the coke content increased, the activity decreased, but the selectivity to C3 olefin increased. This is explained by the decreased hydrogen transfer reaction at high coking levels. Baba and co-workers reported a thorough study on the conversion of ethylene to propylene,⁴⁴² as well as the conversion of butylene,⁴⁴³ with a focus on the effects of pore volume and topology. The study is a nice example of a dedicated effort to find topology-effects in catalysis. They suggested that in ETP, the propylene selectivity depends on the pore volume of the zeolite, rather than on classic pore size-sieving effects.⁴⁴² Excellent propylene selectivities from, for example ethylene and pentene cracking, can be obtained based on selecting the right pore volume, that can accommodate the volume of an olefin and/or its carbenium ion. Figure 42 shows data that demonstrate a clear maximum for 8MR zeolites tested (also includes SAPO-data) for D_i values (diameter of the maximum included sphere) around 7–7.6 Å.

Interpretation aside (D_i , cage size, sieving, hydrocarbon pool?, ...), the screening showed that CHA, DDR, ERI, and LEV (the usual suspects in MTO, viz. Table 10) attained propylene selectivities over 60% and clear superiority versus large-cage LTA, KFI, and RHO (although Si/Al values did not always allow fair comparison).

Finally, Hunger and co-workers investigated the mechanism of ETP in detail over SSZ-13, and they noted a longer lifetime after dealumination, caused by a reduced coke formation at lower acid density.⁴⁴⁵ Also, the nanosized LEV zeolites by IZC, made with *N,N*-dimethylpiperidinium, were briefly assessed for the ethylene conversion at 400 °C. The 35 nm crystals (Si/Al = 10) displayed a better lifetime than a zeolite with 220 nm sized

crystals. ETP was also studied in the case of IZC-derived CHA zeolites.⁴⁴⁶

3.5. Methylamine Synthesis

3.5.1. Introduction to Zeolite-Catalyzed Methylamine Synthesis. Methylamines are crucial chemicals in many industrial processes. They are not only intermediates for amine-functionalized chemicals (pesticides, solvents, ...) but also have their own uses (water treatment). The Bronsted acid-catalyzed amination of methanol yields a thermodynamically controlled product profile, with trimethylamines (TrMA) being most abundant, followed by dimethylamine (DMA) and monomethylamine (MMA, structures, see Figure 2). For example, at the relevant 400 °C and for a 1/1 MeOH/NH₃ feed, 62% of TrMA is predicted, versus only 17 and 21% of MMA and DMA, respectively, at 99% MeOH conversion. From an application point-of-view, however, DMA and then MMA are the most important.⁴⁴⁷ Typically, a gas-phase process contacts methanol and ammonia at elevated temperature over a dehydrating catalyst, mostly run in an adiabatic plug flow reactor containing a fixed catalyst bed. In order to avoid TrMA formation (favored), H-MOR zeolites have been applied commercially for a while.⁴⁴⁸ The reader is referred to a thorough review in the field (dated, but the field does not expand during the last years), listing a large number of zeolites tested, and even individual data tables for small-pore RHO, CHA, KFI, and LTA.⁴⁴⁷

3.5.2. Small-Pore Zeolites for Methylamine Synthesis from Methanol and Ammonia. Generally, the acidic zeolite should hinder (the formation or) escape of TrMA (3.9 × 5.4 × 6.1 Å) from the pores, while still allowing DMA (3.9 × 4.7 × 6.0 Å) and MMA (3.7 × 3.9 × 4.4 Å) to form.¹⁶⁴ Hong et al. tested a range of different small-pore zeolites in identical conditions, i.e., H-form at 400 °C. Similar and high conversions were attained for UFI, CHA, AFX, and RHO (Table 11), allowing fair comparison of the selectivities. For LEV, MTF, and DDR, however, lower conversions were found. The selectivity of UFI-zeolite is clearly the worst, and >60% of TrMA is formed, versus for example only 8% for the Rho benchmark. The results can be rationalized on pore size effects given the larger diameter of the 8MR in UFI (the reader is

Table 11. A List of the Different 8MR-Framework Zeolites Tested for Methanol Conversion in the Presence of Ammonia with Conversion (X), Selectivities (S), and Conditions

Top. ^a	Material ^b	Si/Al	T/WHSV (°C/h ⁻¹)	X _{MeOH} (%)	D _{MMA} ^f (%)	D _{DMA} ^f (%)	D _{TrMA} ^f (%)	Ref
RHO	Rho	n.r. ^d	400/4.0	90	34	53	13	450
		3.9	400/4.3	88	31	61	8	164
AFX	SSZ-16	6.1	400/4.3	89	27	63	11	164
CHA	SSZ-13	5.1	400/1.7	93	39	49	13	164
	chabazite	2.4	340/- ^c	89	46	49	4	451
DDR	Sigma-1	16	400/0.34	64	37	31	31	164
ERI	erionite	n.r. ^e	380/2.71	87	26	32	42	447
KFI	ZK-5	3	400/2.0	90	26	63	11	450
LEV	levyne	7.9	400/0.34	39	63	22	15	164
LTA	SA	1	380/0.35	99	31	51	19	447
MTF	MCM-35	29	400/0.34	70	9	13	78	164
UFI	UZM-5	6.9	400/4.3	93	17	21	61	164

^aTop. = topology. ^bOften other cations than H⁺ also present. ^cW/F: 67 g·h·mol⁻¹. ^dLikely standard Si/Al for Rho around 3–4. ^eNatural mineral, often around 3. ^fDistribution of methylamine products (C%). Often, minute amounts of dimethylether are also formed: e.g. for LEV, 27% of MeOH conversion is to methylamine products, while for SSZ-13, this is 90%.

referred to the online database of the IZA).³ Furthermore, the cage volume, and the dimensionality were also suggested to matter, as these could be at the origin of the suboptimal MTF, LEV, and DDR performance. CHA, AFX, and LEV were also compared in both zeolite and SAPO versions, to assess acid strength and densities. However, a Si/Al variation within one optimal zeolite has not been performed. Overall, AFX and RHO were found to be the most selective zeolites in that study, and the data in Table 11 show that higher selectivities, with the exception of KFI, are not encountered. KFI was studied thoroughly, by Shannon and co-workers, but found to be less active and stable than RHO.⁴⁴⁹

3.6. Other Relevant Reactions

3.6.1. Cracking. Since the beginnings of shape-selectivity (Weisz)^{452,453} all types of zeolites have been tested in reactions involving the cracking of hydrocarbons. In the early days, the focus was mainly placed on natural 8MR zeolites and LTA, since few synthetic small-pore materials existed. Aside from chabazite,⁴⁵⁴ natural mineral erionite (ERI) was investigated.⁴⁵⁵ Small-pore zeolites offer the advantage in cracking that the intracrystalline 8MR pores allow discriminating between paraffins (*n*-alkanes) and larger isoparaffins (branched), e.g., valid in hexane cracking, as the branched isomers do not easily enter (reactant type shape-selectivity). On top of that, Chen et al. noted the cage effect for the first time, when cracking *n*-alkane C₂₂H₄₆ over erionite and found odd product distributions. Remarkably absent were products with C1–C2, C7–C9 and >C12 carbon numbers indicating additional effects in addition to classic cracking mechanisms. The missing products undergo secondary cracking, while e.g., C10–C12, fragments were said to be able to cross the cage of ERI (bridging across two 8MR windows), while diffusing along an 8MR pore.¹⁰⁴ C7–C9 fragments were indeed found to have very low diffusivities in ERI, compared to longer or shorted alkanes and are trapped in the zeolite (cages), allowing further cracking to C3–C4 products.⁴⁵⁶ It is worth noting that Barrer had already in the 1950s studied the geometric factors involved in diffusion, by looking at the channels of small-pore natural mineral zeolites of the LEV, CHA, and ERI type.⁴⁵⁷ A detailed cracking study by Weitkamp and co-workers focused on small-pore zeolites and *n*-octane (allowing β -scission) as the substrate.²⁴³ LTA, CHA (chabazite), LEV (Nu-3), RHO (Rho), the two types of DDR, and KFI (ZK-5) were used in

a fixed-bed setup. Haag-Dessau monomolecular cracking (C1–C3 products, few branching) was found to be dominant and more prominent as the pores narrow. Bimolecular cracking products (branched) were also detected, such as isobutane and isobutene. Bimolecular hydrogen transfer is hindered in 8MR zeolites, leading to more olefins than paraffins, but no pure monomolecular cracking was observed. Selectivities to C1 and C2 products increased with decreasing pore-window size (e.g., RHO < LTA) and increasing spatial constraint (LEV, DDR). The selectivities of LEV, DDR, and RHO were over 30% for C1–2 products, versus only 15–21% for CHA, KFI, and LTA with larger 8MR windows (than RHO).

Aside from cracking with ERI-zeolites and the zeolite series mentioned above, the hydrocracking of *n*-decane has been reported on Nu-6 zeolite (NSI topology) with Si/Al = 45. It was shown to be an active and selective dewaxing catalyst yielding 76% of cracking products at 79% conversion.⁴⁹ Santilli and Zones reported on SSZ-16 (AFX) with Si/Al = 6 for the cracking of hexane and hexadecane in the light of studying shape-selectivity.⁴⁵⁸ While hexane and hexadecane both cracked when fed separately, hexadecane ceased to convert in a 50/50 feedstock mixture. Due to the steric nature of this effect, caused by both the small pore and the presence of hexane, this behavior was denoted as an example of “secondary shape-selectivity”.

Yun and Lobo reported propane cracking on H-SSZ-13, and they unearthed a structure–activity relation based on thermal treatment for Si/Al = 6 and 12 materials.⁴⁵⁹ Without treatment, both propane cracking and dehydrogenation reaction rates were similar. Interestingly, after a mild thermal treatment (500 °C), the zeolites started to crack more selectively (2×), while the high temperature treatment (550–800 °C) enhanced their dehydrogenation behavior. The authors hinted to the formation of another, new type of active site (not Brønsted) in SSZ-13 after the harsh treatment.

3.6.2. Structure–Activity Relation of Al-Pairing in CHA for Dimethyl Ether Formation. The paired Al series (Figure 16 and the updated work by Gounder et al.) were used to elaborate an elegant synthesis–structure–activity relation for the Brønsted catalyzed dehydration of methanol to DME. It was seen that the rates were 1 order of magnitude smaller on isolated protons, versus those on acid sites in paired arrangements. Evidence was presented to state that such paired

protons can access alternate reactions paths that are inaccessible to isolated acid sites.²³⁷

4. SUMMARY—OPPORTUNITIES—OUTLOOK

4.1. General Summary

- (1) Cundy and Cox disagreed with the tendency that many researchers have to label the hydrothermal synthesis of zeolites as poorly understood or as a kind of alchemical mystery.⁹⁶ The synthesis of new frameworks in the 1960s, especially LTA in the 8MR group, sparked fundamental studies and revealed a lot about hydrothermal synthesis mechanisms when alkali are used in hydrothermally treated gels. Although some aspects of inorganic cation-directed zeolite synthesis in hydrothermal media remain unexplained, like the effect of concentration (water content) on phase competition and relative growth rates, a great deal of these crystallization pathways have been elucidated to some extent. However, the introduction of OSDAs complicates and expands the conceptual view of zeolite synthesis, as has the use of zeolites as source materials (interzeolite conversion) and the roles of seeding. A proof of this complication is found in the charge density mismatch approach, leading to new 8MR zeolite UFI with common TEA, TMA, and Na combinations. Also, the same OSDA can lead to (a range of) completely different zeolites (e.g., Figure 9: AEI vs GME). This is especially the case when the organics are on the smaller side relative to the intrazeolite pore space, and when the OSDA has numerous conformations in solution. OSDA-based syntheses in fluoride media without aluminum and alkali are simpler systems to rationalize how the OSDA leads to a particular topology. Smaller OSDAs and alkali can also stabilize smaller cages, composite building blocks, or tiles of the framework, besides residing in the main cage of the small-pore zeolite. What structural unit they stabilize at what time in the synthesis process depends on the conditions and inorganics used, and an overarching explanation for these interactions is missing. The most useful 8MR zeolites from a catalytic point of view feature larger cages with 8MR access. The larger cage is useful in structure prediction or when optimizing synthetic strategies, as they are the voids mostly filled with OSDA. In the case where OSDAs have a decent but not very tight fit with such cages, the Si/Al ratio of the product is hard to control. In that situation, it appears that cage-based, small-pore zeolites are driven toward an optimal Si/Al ratio, depending on the overall charge balance (e.g., 1 OSDA cation per cage) and the ease (or difficulty) of building in siloxy defects in the material (section 2.4).
- (2) The last 15 years have seen remarkable progress in the synthesis of 8MR zeolites, and a few are highlighted: the pentamethylimidazolium route to RTH; the IZC route to CHA with TEA; the DM3(4MB) or supramolecular assembly route to LTA; the IZC routes to AEI and LEV; control over the Al-pairing in CHA via the Na/ADAM ratio or its particle size via growth-modifiers; the isorecticular series based on RHO; the synthesis of ERI and UFI through charge density mismatch; and last but not least the discoveries of the first 2D 8MR zeolite layer (RTH) and SFW, a zeolite with an 18-layer structure.
- (3) The use of OSDAs in hydroxide media is the main route in the synthesis of 8MR zeolites, although for some zeolites, the use of HF is beneficial, e.g., when d4r need stabilization in high-silica composition. In some synthesis, NaF or NH₄F is added to hydroxide-rich synthesis media with interesting results (e.g., IZC of FAU to LEV, Table 6; or the trimodal porous CHA). Interzeolite conversion (not the highly alkaline versions) and charge density mismatch approaches are two successful routes, also with OSDAs, to diversify synthesis routes toward existing frameworks (e.g., TEA for CHA), to attain new Si/Al ratios for a given framework (e.g., AEI) or even yield new zeolites (e.g., UFI by OSDA cooperation).
- (4) Small-pore zeolites have been used in a range of fundamentally interesting or commercially relevant catalytic reactions. Cu-SSZ-13 catalysts are now the commercial standard in certain diesel-exhaust cleaning systems, and excellent selectivities, activity, and times-on-stream stability have been documented in methanol-to-olefins catalysis, e.g., with CHA, AEI, and DDR-zeolites. The higher stability of aluminosilicates versus SAPOs or other zeotypes may be beneficial in the light of longer catalyst's lifetime, especially in repeated reaction/regeneration catalytic processes, as is the case in commercial MTO (now with SAPO). However, the cost of the aluminosilicate should be competitive. Specifically, for the case of MTO, zeolites seem able to compete in terms of performance, with SAPO-34 but the latter are made with cheap amines, instead of (often) quaternary ammonium OSDAs. The cost of a zeolite is largely determined by the cost of the organic and the synthesis time in a given reactor unit. Some of the OSDAs needed for 8MR zeolite synthesis are not currently available (e.g., the new benzyl-imidazolium for LTA), while others are commercially accessible at the large scale (TEA, TMA, choline) or in close alignment with industrial precursors (e.g., dimethylpiperidines for AEI). Useful benchmarks for OSDA-cost assessment are the commercial ADAM used in SSZ-13 synthesis for SCR, estimated to cost around 20–30 USD·kg^{−1} and TEA, at 3–5 USD·kg^{−1}.
- (5) The progress in synthesis has led to a more widespread exploration of 8MR zeolites in heterogeneous catalyzed gas-phase processes. The new routes to AEI, RTH, LTA, and RHO, for example, now give synthetic access to a wider range of Si/Al ratios, allowing catalytic tests to be run with a more appropriate acid or active site density. An important example here is the new synthesis route to LTA using DM3(4MB), leading to the discovery of a very efficient SCR catalyst, that at certain conditions, is outperforming Cu-SSZ-13. Apart from improvements in controlling the Al-content, for selected zeolites, the fine-tuning of particle sizes, hierarchy, and even some control over the pairing or isolation of Al has been reported (CHA, Figure 16). This synthetic control over the zeolite properties has led to improvements in catalytic performance of certain 8MR-topologies.
- (6) New reactivities for small-pore zeolites can still be found. The partial oxidation of methane to methanol on Cu centers in SSZ-39 and SSZ-13 was for instance first reported in 2015 (Table 9). The reaction is now mostly performed in a cycle involving methanol extraction and reactivation after every reaction, although catalytic

processes have been documented, for the first time, in recent years. For this reaction, catalytic development will need to focus on increasing the productivities drastically while synthesis efforts could be directed toward increasing the numbers of active sites per gram of zeolite support.

4.2. Opportunities in Synthesis and Catalysis

In no particular order, some opportunities in the synthesis and catalysis with 8MR zeolites are as follows:

- For some 8MR frameworks with catalysis-relevant features, access to higher Si/Al ratios is lacking. Table 3 provides an extensive overview, although the Si/Al limits of AEI (max 25 (OH^-)), EAB (max. 3), ERI (max. 8), KFI (max. 4), and RHO (max. 8) come to mind. This challenge becomes even more formidable if one is to consider a cost-effective synthesis route.
- In this context—e.g., KFI with less Al, or more cost-effective routes—the computational prediction of suitable OSDAs for a given lattice, as successfully demonstrated by Deem and co-workers for SFW, STW, and AEI,^{137,138,185,333} should be further explored.
- Given the new OSDA for high-silica LTA, i.e., DM3-(4MB), and the proposed mechanism for LTA-synthesis starting with the construction of the large cage; the synthesis of KFI and RHO, with the same α -cage differently connected, could be explored with DM3-(4MB) in conditions resembling that of RHO and KFI. A second OSDA to consider for LTA and KFI syntheses is the Cs^+ -18-crown-6-ether complex reported for RHO.
- The forty-four existing 8MR zeolites (Table 1) are part of the 8MR molecular sieve family totaling seventy-six zeotypes. There are thus thirty-two small-pore frameworks that are, so far, unattainable in zeolite composition. Four of these are pure-silicates (Table 2), while the remaining ones usually are (metallo)-aluminophosphates. Some of these structures could be highly unique catalysts when access to their zeolite counterpart is found. One such example is the SAV topology (MgAlPO_4),²⁷¹ a 3D framework with large, unusual cages, that can be exclusively built from d6r units, and that is closely related to KFI.
- The control of the pairing or isolation of Al sites in CHA could be expanded to other frameworks relevant in catalysis with an abundance in 6MR (LEV, AEI, KFI) and perhaps even 8MR zeolites with 5MR (RTH, DDR). Such control can undoubtedly lead to catalytic insights and new synthesis-structure–activity relationships.
- The cage-count approach, detailed for AEI, CHA, and LEV, and discussed in section 2.4, should be applied to other cage-containing zeolites.
- Tables 1 and 3 present more zeolite materials than those used in catalysis, i.e., Table 8, 9, 10 or 11. Given the structure–activity relations detailed above, some candidates could be worthy of investigation, e.g., EAB or PAU for SCR or MTO (provided they can be made with less aluminum or dealuminated) or RHO for the partial oxidation of methane. For the latter, the SCR overview can be useful, as the same metal precursor to the respective active sites is used. SFW and ETL, recent additions to the 8MR zeolite group, are also relatively unexplored in catalysis.

- The search for alternative MTO catalysts is still ongoing, and significant advantages could be achieved for zeolites that would be more selective to a single olefin, i.e., specific to propylene or ethylene.
- The performance of the steamed AEI in MTO is highly promising, especially when C4 olefins are valued more than ethylene. The recent improvements in synthetic access to AEI with larger Si/Al ratios (Table 3) would be helpful.
- A detailed study of the effects of seeding on defect formation in zeolite synthesis is needed. The work on DDR showed that secondary growth from seeds can lead to materials rife with defects and deteriorated MTO performance.²⁴⁵ Although seeding is used a lot as a synthetic tool to enhance nucleation/crystallization rates and phase selectivity, the consequences of their use on catalysis are rarely investigated in comparison to nonseeded materials.
- Fe-containing small-pore zeolites could be more broadly assessed in SCR, and for the low-temperature partial oxidation of methane (with N_2O activation).
- Although not within the scope of this review, the recent development of siliceous 8MR zeolites containing Lewis acid framework atoms (e.g., Sn⁴⁶⁰ and Ti⁴⁶¹ in CHA, Ti in LTA,¹³⁵ Zn in AEI⁴⁶²) is worth noting. In the context of catalysis (e.g., MTO or methylamine synthesis) such Lewis acidic sites could display unexpected selectivities.^{18,463,464}

4.3. Outlook

Changes in global energy, carbon (feedstock) and environmental challenges (point-source pollution control) are demanding innovative solutions. Material science and catalytic technology have a large role to play in dealing with the key issues. For instance, feedstocks in the (petro)chemical industry are shifting to a more gaseous nature and with them, the required specifications of catalytic and porous materials. Small-pore zeolites have proven potential in the MTO reactions, as well as in engine pollution control based on NO_x removal. The catalytic potential of cage-containing, small-pore 8MR aluminosilicates is obviously large and growing. Engineering small-pore zeolites to this end and tailoring them to applications is clearly an active component of modern catalytic technology.

The recently increasing interest in using 8MR zeolites has sparked innovation in the synthesis of these types of materials (small pore zeolites have been ignored for several decades due to the emphasis on medium pore materials like ZSM-5), and a large number of new strategies have been reported recently. In years to come, control over the Al-substitution, both in content and exact location in the framework, will be a topic of research and debate. Structure–activity relations based on active site elucidation (e.g., Cu in SCR or partial methane oxidation) under working catalytic conditions (operando) will spark further interest in controlling the porous host and the location of its framework charge. The search for a 100% selective MTO catalyst based on the shape of the cage and its Al-distribution is another example. In SCR, the question of how structure leads to stability remains to be elucidated, and the role of the shape of the cage and the mechanisms of framework protection by active divalent cations are not completely understood. The relation between starting and product zeolite in IZC is puzzling, and the mechanism of these syntheses is clearly different from standard hydrothermal syntheses starting from amorphous

reagents. The exploitation of IZC for different purposes, not only the synthesis of a given zeolite with Si/Al control, but also active-site control (e.g., Cu in situ) or metal encapsulation is in its early stages of development. Finally, computation has shown that likely, there are framework-dependent, preferred Al-contents and locations for proton-balanced zeolite (Si,Al) systems. In future work, such computation will include OSDAs and all other cations present, in order to simulate not only the energetic minima of the framework but also those of the OSDA-framework hybrid (the true product of a synthesis) and its Al-location. In reverse, computation will also play an increasingly larger role in synthesis, via the prediction of feasible OSDAs for a given lattice (e.g., the success with SFW). The charge density mismatch approach as well as the tuning of Al pairing in CHA clearly shows that the role of charged cations, i.e., their nature, quantity, density, and interactions with other charged species (both cations and anionic Al-incorporations), is crucial to the synthesis path followed and, therefore, the end-product, the kinetic construct that is a zeolite. It is expected that the role of the OSDA as a charge center, and not only a space-filler, will be better understood.

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Notes

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ABBREVIATIONS

Abbreviations not found in this list = topology-designating three-letter codes (e.g., AEI), material names (e.g., CIT-9), or specific composite building units (e.g., *can* (-cage))
8MR = eight-member(ed) ring, with members being T atoms, technically, 16 atoms are in the ring
 $\mu\text{mol} \cdot \text{g} \text{ cat}^{-1}$ = μmol per gram of catalyst
ADAM = *N,N,N*-trimethyl-1-adamantyl-ammonium
BTMA = *N,N,N*-trimethylbenzylammonium
CDM = charge density mismatch
CTAB = hexadecyl trimethylammonium bromide
CVD = chemical vapor deposition
d6r = double six-ring (also d4r, d8r exists)
DABCO = 1,4-diazabicyclo[2.2.2]octane
DEDMA = diethyldimethylammonium
Diquat = diquateryary OSDA
DLS = dynamic light scattering
DM3(4MB) = 1,2-dimethyl-3-(4-methylbenzyl)imidazolium
DME = dimethyl ether
IZA = International Zeolite Association
IZC = interzeolite conversion
MeQ = *N*-methylquinuclidium
MMA, DMA, TrMA = mono-, di-, trimethylamine
NMR = nuclear magnetic resonance spectroscopy
OSDA = organic structure directing agent
PDDAC = poly(diallyldimethylammonium chloride)
PEIM = polyethylenimine
PXRD = powder X-ray diffraction
Si/Al = molar silicon to aluminum ratio
TEA = tetraethylammonium
TEOS = tetraethylorthosilicate
TEP = tetraethylphosphonium
TGA = thermogravimetric analysis
TMA = tetramethylammonium
T-range = temperature range

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