

UNIVERZITA KARLOVA
Přírodovědecká fakulta

Studijní program: Chemie

Studijní obor: Chemie



Alica Seidlová

Syntéza tvarově selektivních katalyzátorů pro izomerizaci *m*-xylenů v plynné fázi

Typ závěrečné práce:

Bakalářská práce

Vedoucí práce: Mariya Shamzhy, Ph.D.

Konzultanti: Jan Přech, Ph.D.

M.Sc. Emadeldin H. Shamma

Praha, 2025

CHARLES UNIVERSITY
Faculty of Science

Study program: Chemistry
Branch of study: Chemistry



Alica Seidlová

Synthesis of shape-selective catalysts for gas-phase *m*-xylene isomerization

Type of thesis:

Bachelor thesis

Supervisor: Mariya Shamzhy, Ph.D.

Consultants: Jan Přech, Ph.D.

M.Sc. Emadeldin H. Shamma

Prague, 2025

Vyhlásenie:

Vyhlasujem, že som záverečnú prácu spracovala samostatne, a že som uviedla všetky použité informačné zdroje a literatúru. Táto práca ani jej podstatná časť nebola predložená k získaniu iného alebo rovnakého akademického titulu.

V Prahe 16.5.2025

Alica Seidlová

Acknowledgement

I would like to thank my supervisor Mariya Shamzhy, Ph.D. for her guidance, invaluable feedback, dedication and time during my research. Likewise, I would like to thank the consultants of this thesis Jan Přeč, Ph.D. for his help with the catalytic experiments and M.Sc. Emad H. Shamma for his assistance with synthesis, SEM and EDS measurements, and his generosity. Furthermore, I would like to thank prof. Jiří Čejka and Maksym Opanasenko, Ph.D. for their insightful advice, and my colleagues for their help with measurements, namely Subhajyoti Samanta, Ph.D. and M.Sc. Yuqi Zhang (*in situ* FTIR), Martin Kubů, Ph.D. (N₂ physisorption), Michal Mazur, Ph.D. (STEM). Finally, I would like to thank my family and friends for their endless support.

Abstract

This bachelor thesis investigates the effect of zeolite pore size and crystal morphology in gas-phase *m*-xylene isomerization, that ranks among the most important zeolite-catalysed reactions in the petrochemical industry. Monomolecular *m*-xylene isomerization produces targeted *p*-xylene, a key precursor to terephthalic acid and polyethylene terephthalate. In contrast, competing bimolecular side-reactions such as disproportionation and transalkylation yield undesirable byproducts, indicating the critical role of shape selectivity governed by both pore size and crystal morphology of a zeolite catalyst.

To understand the relationship between zeolite pore architecture and catalytic performance, a series of zeolites with unimodal one-dimensional (1D) and three-dimensional (3D) pore systems were synthesised, characterized and tested in gas-phase *m*-xylene isomerization. The zeolites included 8-ring ESV and CHA, 10-ring TON and MFI and 12-ring AFI and BEA. Among them, the 10-ring zeolites TON and MFI showed the highest *p*-xylene selectivity, as they favour monomolecular isomerization of *m*-xylene and suppress bimolecular side-reactions.

To investigate the combined effects of zeolite pore size and crystal morphology, zeolite IWW with its complex multimodal 3D pore network, comprising of 8-, 10- and 12-ring pores was synthesized as a germanosilicate in two distinct morphologies (platelets and needles), post-synthetically functionalized and tested in gas-phase *m*-xylene isomerization. Following Ge-for-Al substitution, IWW zeolite samples of both crystal shapes showed high concentration of Brønsted acid sites and were highly active in *m*-xylene isomerization. Morphology-related differences were evident with the needle-like IWW catalysts displaying higher *p*-xylene selectivity, which approached that of commercial MFI zeolite.

Key words: zeolites, acid sites, pore size, crystal morphology, heterogeneous catalysis

Abstrakt

Táto bakalárska práca skúma vplyv veľkosti pórov a morfológie kryštálov zeolitov na izomerizáciu *m*-xylénu v plynnej fáze, ktorá patrí medzi najvýznamnejšie reakcie katalyzované zeolitmi v petrochemickom priemysle. Monomolekulárnou izomerizáciou *m*-xylénu vzniká cieľový *p*-xylén, ktorý je kľúčovým prekursorom výroby kyseliny tereftalovej a polyetyléntereftalátu. Naopak, konkurenčné bimolekulárne vedľajšie reakcie, ako disproportionácia a transalkylácia, vedú k vzniku nežiadúcich vedľajších produktov, čo zdôrazňuje kľúčovú úlohu tvarovej selektivity, ktorá je riadená veľkosťou pórov a morfológiou kryštálov zeolitového katalyzátora.

Aby sme pochopili, ako architektúra pórov zeolitu ovplyvňuje ich katalytický výkon, bol syntetizovaný a charakterizovaný súbor unimodálnych zeolitov s jednorozmernými (1D) a trojrozmernými (3D) pórovými systémami, ktorý bol následne otestovaný v izomerizácii *m*-xylénu v plynnej fáze. Medzi skúmané materiály boli zaradené zeolity s 8-člennými pórmami ESV a CHA, 10-člennými pórmami TON a MFI, a 12-člennými pórmami AFI a BEA. Zeolity s 10-člennými pórmami TON a MFI, ktoré uprednostňujú monomolekulárnu izomerizáciu *m*-xylénu a potláčajú bimolekulárne vedľajšie reakcie, boli najviac selektívne voči *p*-xylénu.

Pre štúdium vplyvu veľkosti pórov v kombinácii s vplyvom morfológie kryštálov zeolitov, bol syntetizovaný zeolit IWW s komplexnou multimodálnou 3D sieťou 8-, 10- a 12-členných pórov vo forme germanosilikátu s dvoma odlišnými morfológiami (doštičkové a ihlicové kryštály), ktorý bol post-synteticky funkcionalizovaný a otestovaný v izomerizácii *m*-xylénu v plynnej fáze. Po substitúcii germánia za hliník vykazovali vzorky IWW s oboma tvarmi kryštálov vysokú koncentráciu Brønstedových kyslých centier a vysokú katalytickú aktivitu. Rozdiely spojené s morfológiou sa prejavili vyššou selektivitou voči *p*-xylénu v prípade ihlicovitých kryštálov IWW, ktoré dosiahli hodnoty selektivity blízke komerčnému zeolitu MFI.

Kľúčové slová: zeolity, kyslé miesta, veľkosť pórov, morfológia kryštálov, heterogénna katalýza

Table of contents

List of abbreviations	7
1. Introduction.....	9
2. Goals of the thesis	11
3. Theoretical part.....	12
3.1. Zeolites.....	12
3.1.1. Structure	12
3.1.2. Important properties: acidity and porosity	17
3.1.3. Preparation	20
3.2. Characterization of zeolites.....	22
3.2.1. X-ray diffraction	23
3.2.2. Physisorption.....	24
3.2.3. Scanning electron microscopy	26
3.2.4. FTIR Spectroscopy	28
3.3. Application of zeolites in catalysis	33
3.3.1. <i>m</i> -Xylene isomerization	36
4. Experimental part.....	40
4.1. List of used chemicals.....	40
4.2. Synthesis of zeolite catalysts.....	41
4.2.1. 1D 8-ring ESV aluminosilicate	41
4.2.2. 1D 10-ring TON aluminosilicate	41
4.2.3. 1D 12-ring AFI aluminosilicate	42
4.2.4. 3D 8-ring CHA aluminosilicate	42
4.3. Post-synthesis Ge-for-Al substitution in IWW zeolites	43
4.4. Characterization of zeolite catalysts	43
4.5. <i>m</i> -Xylene isomerization	44
5. Results and discussion	47

5.1. Structural, textural and acidic properties of zeolite catalysts.....	47
5.2. Catalytic properties of zeolite catalysts in <i>m</i> -xylene isomerization.....	58
5.2.1. <i>m</i> -Xylene isomerization: the effect of pore system in zeolite catalysis	58
5.2.2. <i>m</i> -Xylene isomerization: the effect of crystal morphology in IWW zeolite catalyst.....	63
6. Conclusion	71
7. References	73

List of abbreviations

Abbreviation	Full name
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
BAS	Brønsted acid site
BSE	Backscattered electron
BTX	Benzene, toluene and xylenes
D ₃ -AN	Deuterated acetonitrile
<i>d4r</i>	Double-4-ring
DEB	Diethylbenzene
DIB	Diisopropylbenzene
Dis/Iso	Disproportionation to isomerization
Dis/Trans	Disproportionation and transalkylation
DTBPy	2,6-di-tert-butylpyridine
EB	Ethylbenzene
EDS	Energy dispersive X-ray spectrometer
FCC	Fluid catalytic cracking
FID	Flame ionization detector
FTIR	Fourier-transform infrared
GC	Gas chromatograph
HPLC	High Performance Liquid Chromatography
IUPAC	International Union of Pure and Applied Chemistry
IZA	International Zeolite Association
LAS	Lewis acid site
MTH	Methanol-to-hydrocarbons
MTO	Methanol-to-olefins
NMR	Nuclear magnetic resonance

Abbreviation	Full name
OSDA	Organic structure directing agent
PE	Primary electron
PET	Polyethylene terephthalate
Py	Pyridine
SDA	Structure directing agent
SE	Secondary electron
SEM	Scanning electron microscopy
STEM	Scanning transmission electron microscopy
TEOS	Tetraethylorthosilicate
TMB	Trimethylbenzene
T-O-S	Time on stream
TS	Transition state
WHSV	Weight hour space velocity
XRD	X-ray diffraction

1. Introduction

Zeolites are microporous crystalline materials characterized by a network of channels and cavities with molecular-scale dimensions, that are widely applied as heterogeneous catalysts. One of the most important properties of zeolite catalysts is their shape selectivity, which arises from steric hindrance of reactants, transition states or products in their voids. The size of pores in zeolites is determined by the number of tetrahedral atoms forming the ring at the pore entrance, classifying them into 8-ring, 10-ring, 12-ring, and 14-ring pore systems. Variations in pore size and geometry directly influence molecular diffusion, allowing control over reactant accessibility and product selectivity.

The isomerization of *m*-xylene is a key zeolite-catalysed industrial process, primarily driven by the high demand for *p*-xylene, a crucial precursor for terephthalic acid, that is essential in the production of polyethylene terephthalate (PET). Shape selectivity is a determining factor in *m*-xylene transformation, as it involves a complex reaction network, including:

(1) monomolecular or bimolecular **isomerization**, that leads to the interconversion of xylene isomer and is influenced by the size and geometry of the zeolite pores, that can preferentially allow the formation of the smallest *p*-xylene;

(2) bimolecular **disproportionation**, that produces a mixture of toluene and trimethylbenzenes (TMBs) through methyl group transfer between two aromatic molecules;

(3) monomolecular **dealkylation**, that results in the removal of a methyl group from *m*-xylene and yields toluene and light hydrocarbons.

Currently, zeolite MFI with 10-ring channels, is the most used industrial catalyst for *m*-xylene isomerization. However, recent research has focused on zeolites with multiple pore sizes within the same catalyst.^{1,2}

Beyond its industrial significance, *m*-xylene isomerization is commonly used as a benchmark test to evaluate newly synthesized zeolites featuring diverse pore systems or novel crystal morphologies. The ultimate aim of such research is to understand the relationship between zeolite structure and catalytic performance, thereby guiding the optimization of catalyst design to increase the economic viability of the process.

Recent advancements in IWW zeolite synthesis have demonstrated the ability to control its crystal morphology towards platelet- or needle-like crystals by modifying the crystallization conditions.³ This zeolite possesses a complex pore system, consisting of interconnected 8-, 10- and 12-ring pores. The presence of pores with different sizes within IWW zeolite is a

particularly promising feature for *m*-xylene isomerization.⁴ The 10-ring pores are well suited for hosting the isomerization reaction, as they can accommodate xylene molecules while still imposing steric constraints that lead to transition states and product shape selectivity. Apart from containing the active acid centres, the larger 12-ring pores are expected to facilitate easy diffusion of reactants and products, enhancing overall mass transport. In turn, the smaller 8-ring pores are generally inaccessible to xylene due to steric hindrance but may play a regulatory role by modulating access to the larger channels and influencing the spatial distribution of acid sites, thereby indirectly affecting the catalytic performance. This unique combination of pore sizes has the potential to enhance catalytic performance and product selectivity beyond that of conventional catalysts and therefore will be explored in detail in this thesis.

2. Goals of the thesis

The aim of this B.Sc. thesis is to address whether and how the multi-size pore system and crystal morphology of IWW zeolite catalyst influence its activity and selectivity in acid-catalysed *m*-xylene transformation.

To achieve this general goal, the following tasks have been solved in this study:

- 1) To functionalize IWW germanosilicate zeolites with platelet and needle-like crystals by post-synthesis Ge-for-Al substitution.
- 2) To prepare reference aluminosilicate zeolite catalysts characterized by
 - one-dimensional (1D) and three-dimensional (3D) 8-ring pore systems, such as ESV and CHA;
 - 1D and 3D 10-ring pore systems, such as TON and MFI;
 - 1D and 3D 12-ring pore systems, such as AFI and BEA.
- 3) To characterize the physicochemical properties of prepared zeolites using X-ray diffraction (XRD), chemical analysis, nitrogen physisorption, scanning electron microscopy (SEM) and *in situ* Fourier-transform infrared (FTIR) spectroscopy.
- 4) To evaluate activity and selectivity of prepared zeolite catalysts in *m*-xylene isomerization and relate it to the structure of zeolites investigated.

3. Theoretical part

3.1. Zeolites

Zeolites are crystalline microporous aluminosilicates widely applied as industrial solid acid catalysts. Earning their name by connecting the Greek words *zeo* = to boil and *lithos* = stone, zeolites have been thoroughly studied for years. Their history dates to 1756, when they were first discovered by Alex F. Cronstedt, a Swedish mineralogist, who had observed steam upon heating the aluminosilicate mineral stilbite, thus naming it a *boiling stone*. It was later explained that water molecules are present in zeolites due to their unique organized porous structure with channels and/or cages all throughout.⁵

3.1.1. Structure

Zeolites are framework materials composed of corner-sharing $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedra (TO_4). Neighbouring TO_4 units are interconnected by bridging oxygen atoms. The connection results in the formation of common finite (containing up to 16 T-atoms) or infinite structural units such as cages, chains and layers. These building units are not inherent to one zeolite, but present in many different ones. What makes a particular framework type unique is the way of stacking, connecting and overlaying of building units in relation to each other.^{6,7} However, the real framework structure of a zeolite does not match the predicted zeolite topology perfectly. Topology refers to a geometric model considering the highest symmetry, but in reality, the arrangement of TO_4 units is imperfect and prone to defects, as shown in Figure 1.⁸

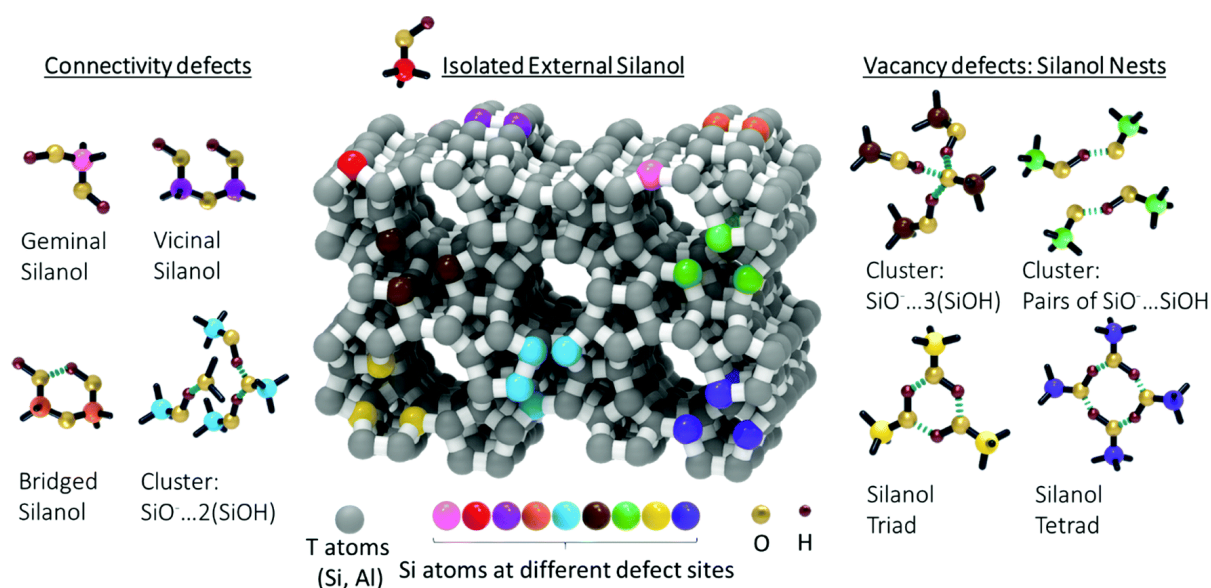


Figure 1: Schematic representation of different types of silanols grouped into three main categories: isolated external silanols, connectivity defects and vacancy defects. Green dotted lines indicate hydrogen bonding.⁸

Today, more than 250 unique zeolite frameworks have been discovered ranging from naturally occurring aluminosilicates to synthetic elementosilicates. In addition, many zeolite types are yet unattainable, but theoretically predicted.^{9,10} Three-letter codes are assigned to a confirmed framework type by the Structure Commission of International Zeolite Association (IZA). The IZA database facilitates pertinent information about all known zeolite framework types such as their XRD patterns and ²⁹Si nuclear magnetic resonance (NMR) spectra. This information is published at <https://www.iza-structure.org/databases/>.¹⁰

Zeolites are materials with uniform pore sizes, which are directly dependent on framework structure. Pore opening is designated as a n -ring, where n represents the number of T-atoms (alternatively also bridging O-atoms) limiting the pore entrance. Sizes of pores determine the performance of a particular zeolite when functioning as a catalyst. The variation in the arrangement of atoms depending on the framework can provide pores of uniform sizes (we designate such materials as *unimodal* zeolites) or of various sizes (*bi*-, *three*-, or generally *multimodal* zeolites). Based on the value of n , according to the largest pore present in the structure, zeolites are sorted into four groups (Table 1).¹¹

Table 1: Classification of zeolites based on pore size

Classification	n	Pore diameter	Examples
Small-pore	8	~4.1 Å	ESV, CHA
Medium-pore	10	~5.5 Å	TON, MFI
Large-pore	12	~7.4 Å	AFI, FAU
Extra-large pore	> 12	> 7.4 Å	CFI, DON

Another classification of zeolites is based on the dimensionality of the pore system. The pore system can be either one-, two- or three-dimensional (i.e., 1D, 2D, 3D). While 2D and 3D pore systems contain channels intersecting in two and three dimensions, 1D-pore zeolites have no intersecting channels, which may result in limited diffusion of reacting molecules when these zeolites are utilized as catalysts.

3.1.1.1. Multimodal zeolite IWW

IWW germanosilicate zeolite (Figure 2 and 3) was the first synthetic zeolite containing interconnected 8-, 10- and 12-ring channels.⁴ The presence of Ge favours the formation of cubic *d4r* structural units (Figure 2, highlighted in red), that make up columns along the *c*-axis.^{10,12}

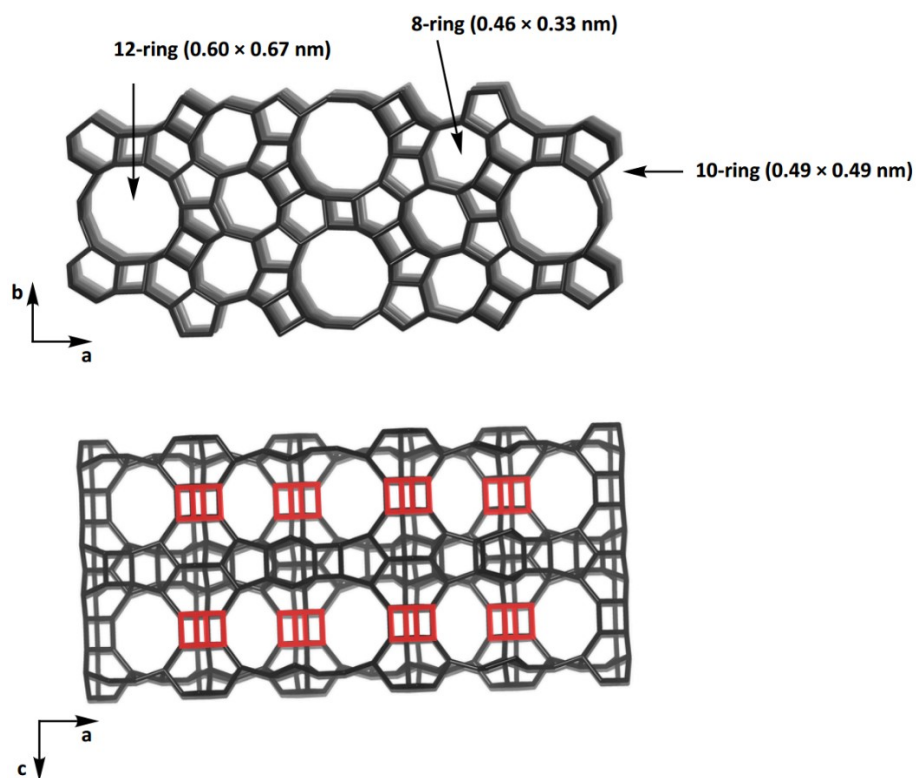


Figure 2: IWW framework type.

The multimodal channels create a complex 3D pore system in IWW zeolite. Straight 8- and 12-ring channels run parallel to each other (Figure 3, highlighted in blue), while the sinusoidal 10-ring pores intersect them perpendicularly (Figure 3, highlighted in red).^{4,12}

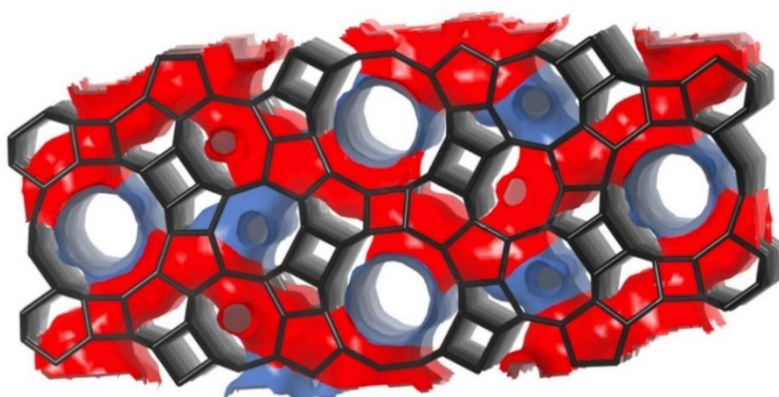


Figure 3: The pore system of IWW.

3.1.1.2. Unimodal zeolites with 1D and 3D pore systems under study

ESV zeolite (Figure 4) has a 1D pore system formed by 8-ring channels with large side-pockets along them. This structure can be described as consisting of 17-sided picnic-basket-shaped cages, where channels run through the “basket handles” and side-pockets form the “basket bottom”.^{12–14}

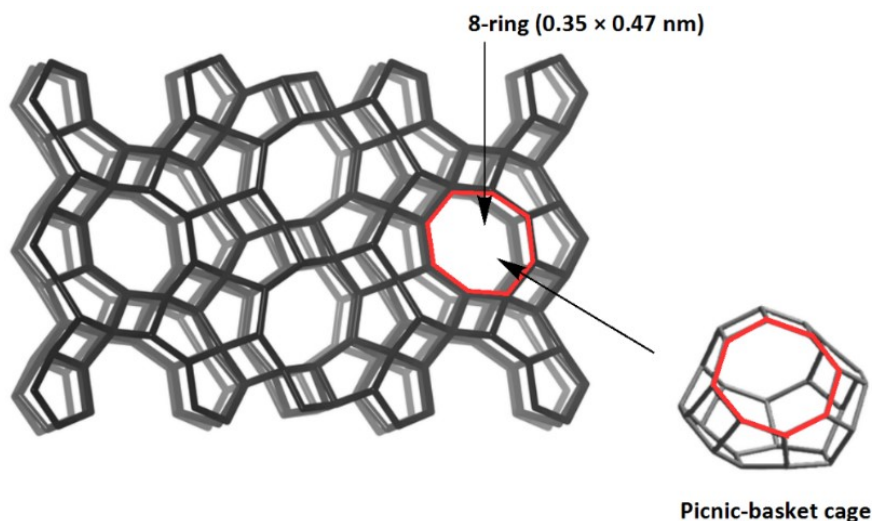


Figure 4: ESV framework type.

TON zeolite (Figure 5) has a 1D pore system formed by 10-ring channels. The framework comprises of zig-zag pentasil chains formed by structural units composed of 5 T-atoms (highlighted in red).^{12,13,15}

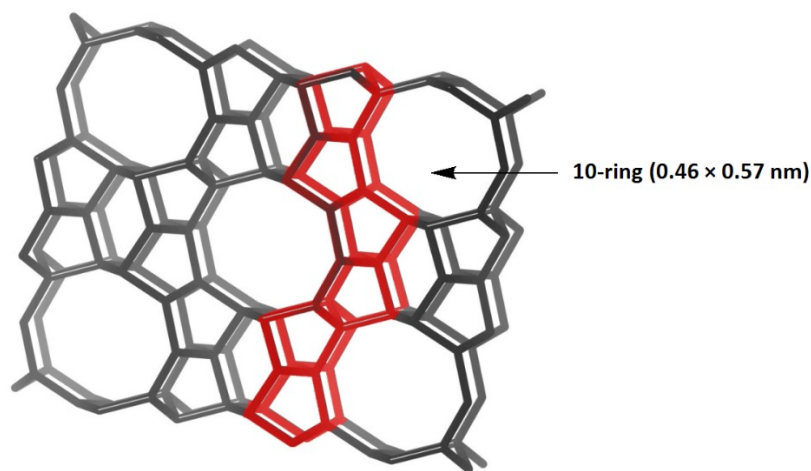


Figure 5: TON framework type.

AFI zeolite (Figure 6) has a 1D pore system formed by 12-ring channels. These circular pores are outlined by alternating structural units composed of 4 and 6 T-atoms.^{12,13,16}

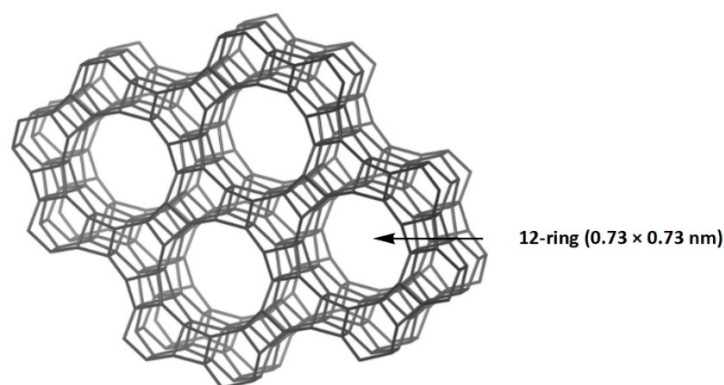


Figure 6: AFI framework type.

Chabazite (CHA) type zeolites (Figure 7) have a 3D pore system formed by 8-ring channels. This framework contains large, elongated cavities (highlighted in red), that are interconnected *via* six 8-rings with adjacent cavities.^{6,12,13}

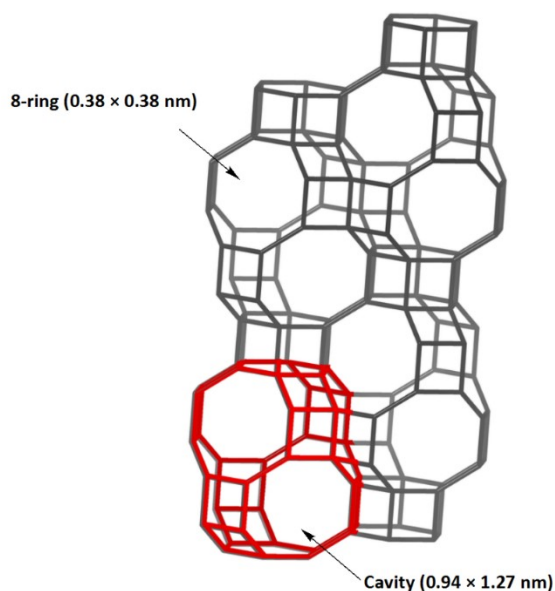


Figure 7: CHA framework type.

MFI zeolite (Figure 8) has a 3D pore system formed by interconnected straight and sinusoidal 10-ring channels. Similarly to TON, the framework consists of pentasil chains (highlighted in red).¹¹⁻¹³

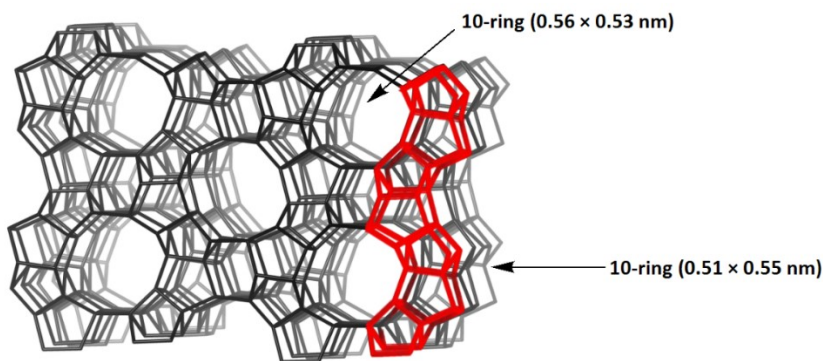


Figure 8: MFI framework type.

Zeolite BEA features a 3D pore system composed of interconnected saddle-shaped 12-ring channels. The framework is built from periodic layers (Figure 9) stacked along a crystallographic axis using specific symmetry operations and translations. This gives rise to polymorphs A, B, and C. The intergrowth of polymorphs A and B forms a disordered yet continuous framework while preserving the unobstructed 3D 12-ring channel system characteristic of all BEA polymorphs. In contrast, polymorph C has an ordered structure containing *d4r* units and an assigned code BEC.^{6,12,13}

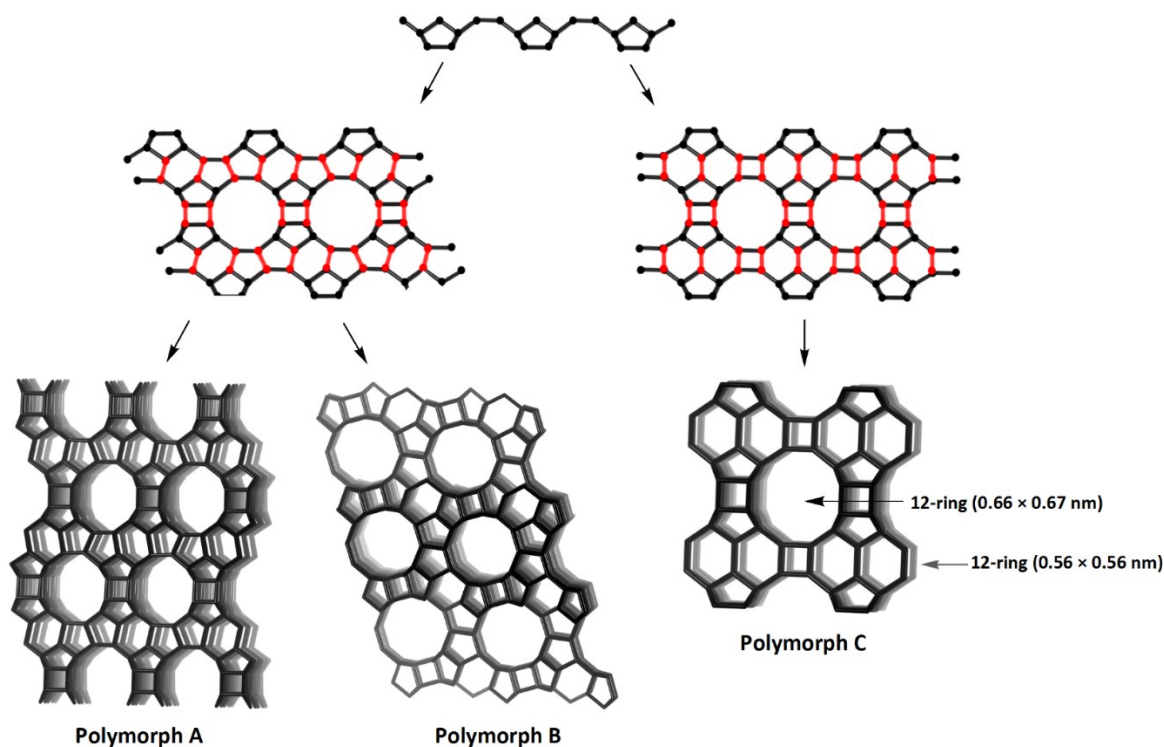


Figure 9: BEA framework type.

3.1.2. Important properties: acidity and porosity

Zeolites can display both Brønsted and Lewis acidity, earning them the name *solid acids*. The possibility to tune the nature of acid sites along with high thermal stability makes zeolites environmentally friendly replacements of harmful mineral acid catalysts such as H₂SO₄, HF, AlCl₃ for different industrial processes.¹⁷

Through isomorphous substitution, meaning the replacement of a framework T-atom in a crystalline structure for another element other than Si without altering the type of crystal structure, elements of similar size and electronegativity to Si have been introduced into zeolite frameworks.^{17,18} In the case of three-valent elements (B, Al, Ga, Fe), a local negative charge -1 is present in each TO₄ tetrahedron. This charge is compensated by out-of-framework interchangeable cations. The most common cations are alkali or alkaline-earth metal such as

Na^+ , K^+ , Ca^{2+} and Mg^{2+} , organic tetraalkylammonium or tetraalkylphosphonium cations and protons.¹⁹

In the last case, bridging hydroxyl groups ($\equiv\text{Si}(\text{OH})\text{T}^{3+}\equiv$) are generated and act as Brønsted acid sites (BAS) - proton donors (Figure 10).¹⁷ When interacting with basic molecules, the proton is donated or at least partially transferred to the base. The BASs of zeolite catalysts play a key role in industrially relevant transformation of hydrocarbons. For example, when a hydrocarbon reactant comes into contact with a BAS, it may be protonated to form a carbocation or a related highly reactive positively charged intermediate. Such mechanisms are fundamental in industrially significant applications, notably in fluid catalytic cracking (FCC), where complex hydrocarbons are converted into lighter, more valuable products such as gasoline and olefins, as discussed in Section 3.3.

The type of T^{3+} -atom determines the strength of BAS, which usually decreases in the sequence: $\text{Al} > \text{Ga} > \text{Fe} \gg \text{B}$.²⁰ Besides T^{3+} -associated BAS, very weak BAS in zeolites can be attributed to terminal silanols.

Lewis acid sites (LAS), electron pair acceptors, are found in zeolites containing four-valent T-atoms (T^{4+}), most commonly Sn or Ti with unoccupied electron orbitals (Figure 10). Also, LASs are formed upon dehydroxylation of Al^{3+} -associated BAS during the synthesis of a zeolite or its post-synthesis handling at high temperatures (e.g., for removal of organics or water from the internal voids). High-temperature treatment can further lead to the formation of extra-framework species, which act as LASs. Other less common examples of LAS include extra framework metal ions, which compensate for the negative charge of aluminosilicate framework.¹⁷

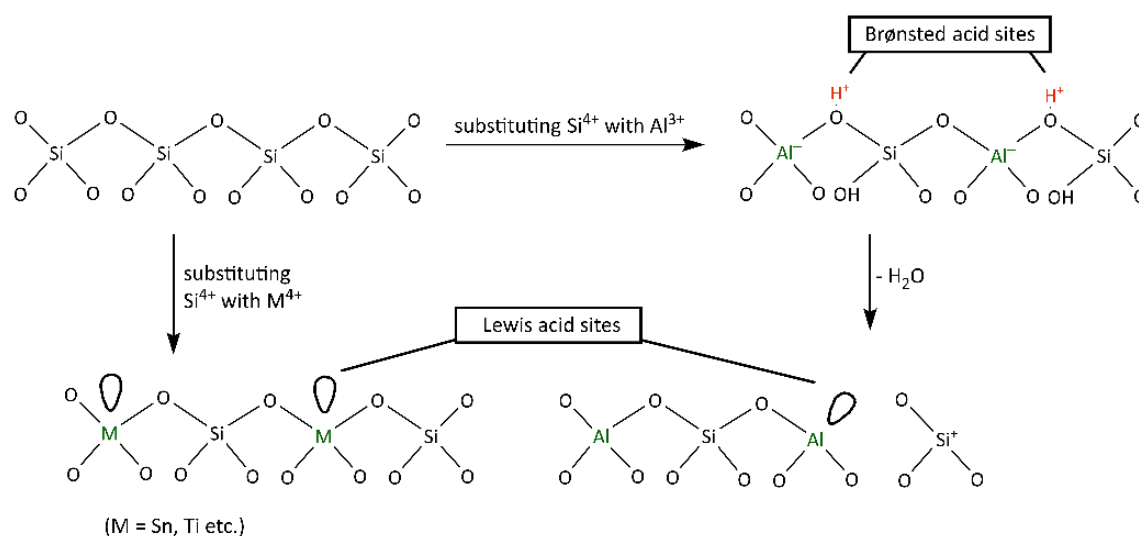


Figure 10: Formation of Brønsted and Lewis acid sites in zeolites.

Both BAS and LAS can act as catalytically active sites when accessible for reacting molecules either on external surface or internally (in pores).²¹

Pore architecture of a zeolite, the size and shape of pore openings and internal voids, determines the outcome of competing catalytic reactions, the phenomenon known as shape selectivity. Shape selectivity can be divided into three categories:

- A) *Reactant shape selectivity* (Figure 11) restricts catalytic reactions involving reactants, which are too bulky to diffuse through the pores of a zeolite and to reach the active sites.

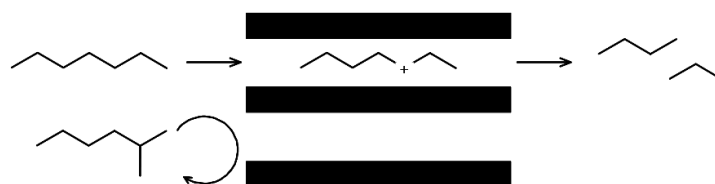


Figure 11: Reactant shape selectivity.

- B) *Transition state (TS) shape selectivity* (Figure 12) restricts the formation of certain TS in the internal voids of a zeolite, potentially hindering energetically favourable products. Unlike reactant shape selectivity, both the reactant and product can easily diffuse through the pores, however, steric constraints limit the formation of specific intermediates.

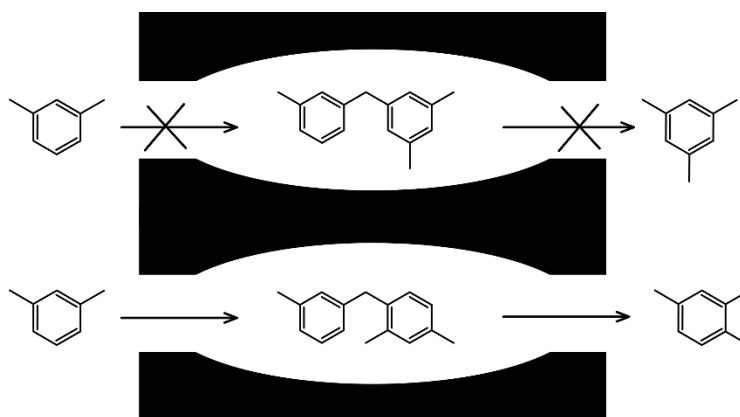


Figure 12: TS shape selectivity.

- C) *Product shape selectivity* (Figure 13) restricts desorption and diffusion of products that are too bulky to exit through the narrow zeolite pores. As a result, only smaller products can leave the pore system, which influences the overall product distribution.^{21,22}

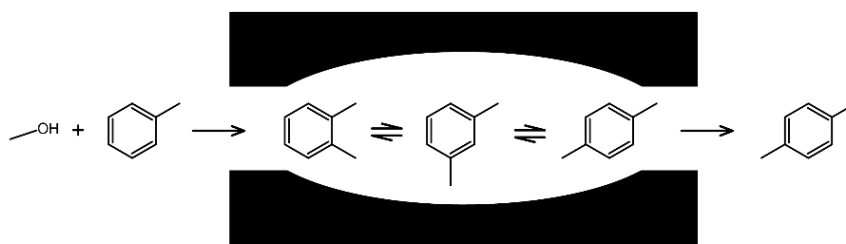


Figure 13: Product shape selectivity.

3.1.3. Preparation

Hydrothermal synthesis in aqueous media is a conventional method for zeolite preparation. Zeolites crystallize at temperatures $>100\text{ }^{\circ}\text{C}$ and pressures up to 2 MPa for different periods (hours to months). Due to these harsh conditions, synthesis must be performed in highly durable sealed metal autoclaves. Autoclaves house a sealed Teflon insert, that contains the reaction mixture. Hydrothermal synthesis is performed in ovens either under static conditions or under rotation.²³

The reaction mixture consists of (i) a source of framework-building elements (Si, Al, Ge, etc.), (ii) mineralizer facilitating mass transfer during zeolite crystallization (OH^- or F^- ions), (iii) inorganic and/or organic cations as structure directing agents (SDA) driving the formation of target structure and (iv) a solvent, typically water.

(i) Common Si sources are colloidal silica sol, fumed silica, alkali metal silicates and tetraethylorthosilicate (TEOS). Al sources include aluminium hydroxide, nitrate, sulphate and alkoxides, while oxides and hydroxides are the most typical sources of metals such as B, Ga and Ge. Typically, silica (SiO_2) and alumina (Al_2O_3) are soluble under very basic conditions (silica at pH 10.5), however, with the addition of mineralizing agents (OH^- or F^-), many zeolites have been prepared at lower pH values.²⁴

(ii) Mineralizing agents increase the solubility of the silicate and aluminate species and facilitate the formation/breaking of Si-O-Al bonds upon dissolution/precipitation processes. Hence, the concentration and type of mineralizing agents, OH^- or F^- , affects the rate of different crystallization steps, crystal size and Si/Al ratio in the final zeolite product.²⁵

(iii) Inorganic and/or organic cations serve as SDAs, that drive the formation of the target structure due to their specific shape, charge, polarizability, hydrophobicity and other intrinsic properties.²⁶ Commonly used SDAs include Na^+ , K^+ or tetraalkylammonium cations. These cations stabilize the forming framework through hydrogen bonding, van der Waals and Coulombic interactions.²³ Organic SDAs (OSDAs) can act as templates, around which the Si and Al species organize and then condense to form cages and channels of a size related to the

used OSDA. A specific zeolite can be prepared using different SDAs. Nevertheless, one SDA can be used for preparation of several zeolites.²⁷ The interaction between an SDA and other reagents is governed by the solvent.^{21,25}

(iv) The most common solvent in zeolite synthesis is water. It acts as a medium for the dissolution, diffusion, and interaction of reactants. Other examples of solvents used for zeolite synthesis include alcohols, diols and ammonia.^{24,25}

Upon mixing at room temperature, silicate and aluminate ions in alkaline solution produce a precursor mixture containing amorphous colloidal aluminosilicates, coagulated silica and alumina. The subsequent hydrothermal treatment initiates a series of dissolution-precipitation and equilibrium reactions, that convert these amorphous species into well-defined zeolite crystals.²⁵

The mechanism of zeolite crystallization comprises of four subsequent stages. During pre-nucleation (1), reagents depolymerize and form anionic oligomers. Primary nucleation (2) involves an assembly of anionic oligomers and SDA molecules into primary units. These units aggregate and form nucleation centres (3), which presuppose the last stage, crystal growth of formed nuclei by their aggregation or by consumption of low-molecular anionic species (4).^{23,25,28} Crystal size and morphology stem from the composition of the reaction mixture, more specifically the ratios of Si/T ($T = \text{Ge, Al}$). In the case of germanosilicate zeolites, increasing the Si/Ge results in decelerated nucleation and prolonged crystallization period. For aluminosilicate zeolites, the situation is the opposite – higher Si/Al leads to faster crystallization due to fewer repulsive anionic oligomers, that serve as building units upon nucleation and crystal growth. Change in the reaction mixture composition can also affect the morphology of resulting zeolite particles, their shape and size. For example, increasing the Si/Ge in the synthesis of IWW germanosilicate zeolite (one of the subject of this B.Sc. thesis) impedes the crystal growth along the *a*- and *b*-axis, changing the crystal morphology.³

If the desired composition and catalytic properties cannot be obtained by direct synthesis, zeolites are usually modified post-synthetically. For example, dealumination by steaming or by acid treatments as well as desilication in alkaline medium followed by isomorphous substitution of framework elements for alternative elements can help improve not only composition and related acidity (type, concentration, strength of acid sites), but also generate additional porosity. Isomorphous substitution is particularly effective in Ge-containing zeolites, such as IWW, being studied in this thesis. Substituting framework Ge for Si, Al or Ti promotes their hydrolytic and thermal stability.^{17,24}

3.2. Characterization of zeolites

Thorough characterization of a zeolite precedes its utilization as a catalyst. Detailed information about the structural, textural and acidic properties not only verifies successful synthesis of the material but can also help rationalize its catalytic performance. Structural properties and crystal morphology are studied using diffraction methods such as XRD and SEM, respectively. Furthermore, SEM instruments often employ an energy dispersive X-ray spectrometer (EDS), that provides information about the chemical composition of a sample. Textural properties such as the pore volume and surface area are investigated using physisorption methods and acidic properties such as concentration of acid sites are studied using *in situ* FTIR spectroscopy. An overview of zeolite characterization methods is shown in Table 2.

Table 2: Overview of characterization methods utilized in this thesis.

Method	Analysed phenomenon	Information obtained	Ref.
XRD	Interference of scattered X-rays	• Structure of a zeolite • Size of the crystallites • The fraction of crystalline and amorphous phases	11,29
Physisorption	Physisorption of adsorbate on surface and within pores	• Type of pores (e.g., micro- vs. mesopores) • Total pore volume, micropore volume • Surface area • Pore size distribution	21,23,28,30
SEM	Interaction of a focused electron beam with the surface atoms of a sample	• Crystal morphology • Particle size distribution	31–33
Chemical analysis	Emission of characteristic X-rays	• Chemical composition	33
<i>In situ</i> FTIR spectroscopy	Absorption of infrared light	• Concentration, nature and relative strength of acid sites • Presence of functional groups	17,21,34–40

3.2.1. X-ray diffraction

Powder XRD uses monochromatic X-rays to study the structure of a zeolite (verifying the structural type, detecting new zeolite structures and determining the type and size of their unit cells). X-rays are utilized because of their wavelength, that is in the same order of magnitude as the distance between atoms in the zeolite framework (approximately 1 Å – 2 Å).¹¹

The result of an XRD measurement is a diffractogram, that displays the relation between intensity of scattered X-rays (y -axis) and the scattering angle θ (x -axis, usually expressed as 2θ). Examining individual features of the diffractogram (position, intensity and width of peaks, background) provides important information on zeolite structure. The *peak position* (expressed in $^\circ 2\theta$) is determined by the geometry of the zeolite unit cell and meets the Bragg's law (Eq. 1):

$$n \cdot \lambda = 2d \cdot \sin \theta \quad (1)$$

where n is the diffraction order, λ is the wavelength of the X-ray beam, d is the spacing of diffraction planes and θ is the scattering angle (Figure 14).²⁹

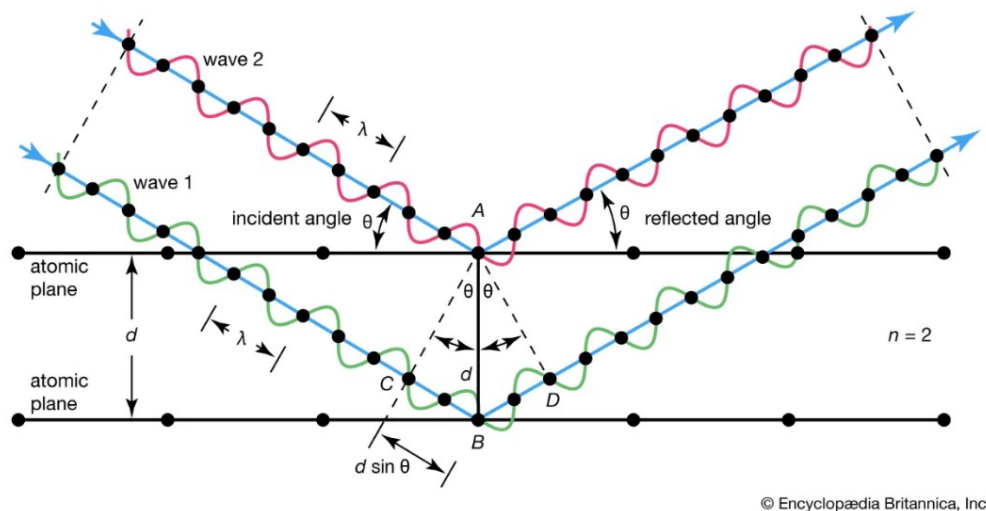


Figure 14: Bragg diffraction.⁴²

Relative *peak intensity* correlates to the type and concentration of atoms present in a particular position of the unit cell. *Widths of peaks* are indicative of the size of crystallites in the zeolite sample. The thinner (sharper) the peak, the larger the crystalline (diffracting) domains. The *background* of a diffraction pattern provides information about amorphous phase in the sample (Figure 15).^{11,29}

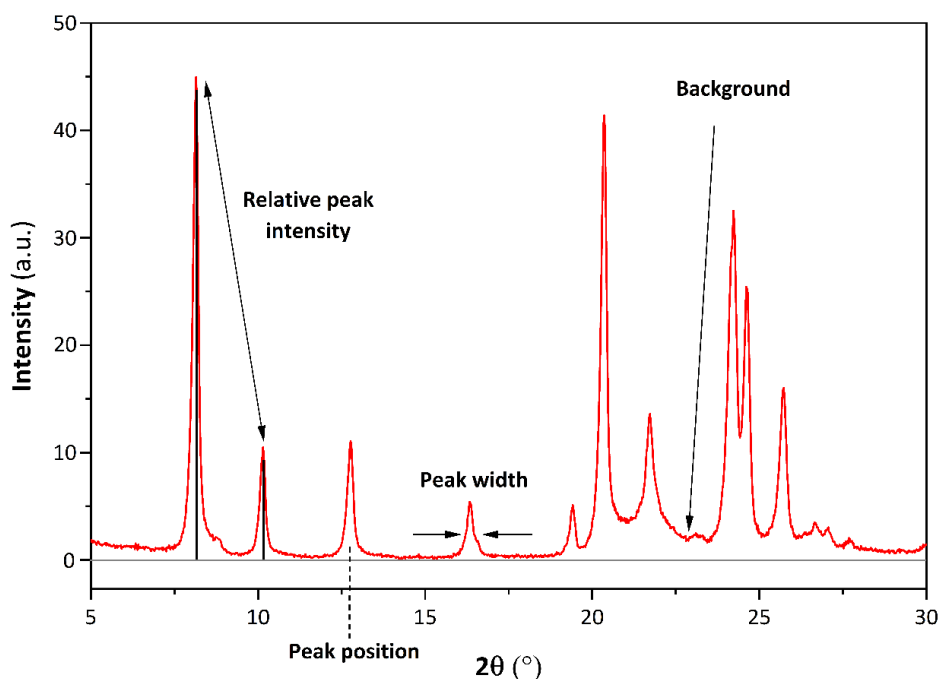


Figure 15: Schematic representation of an XRD pattern.

3.2.2. Physisorption

Adsorption is the enrichment of the surface of a solid or a liquid (adsorbent) with gas molecules or atoms (adsorbate). Depending on the type of interaction between the adsorbent and adsorbate, we distinguish two types of adsorption: chemisorption and physisorption. In chemisorption, strong chemical bonds are formed between the adsorbent and the adsorbate. These bonds significantly change the electronic structure of the adsorbed species, due to which chemisorption is often either irreversible or the desorption of the adsorbed species requires high energies. In physisorption, the interactions between the adsorbent and the adsorbate include van der Waals forces, such as attractive dispersion interactions and short-range repulsive interactions. The electronic structure of the adsorbate is not significantly changed, which ensures that the adsorbed species can be easily desorbed under mild conditions. Physisorption typically occurs at low to moderate temperatures and is usually reversible.^{23,30}

In zeolites, physisorption of inert gases, such as nitrogen and argon, is used for the characterization of porosity. Physisorption measurements provide information about the specific surface area, pore volume and pore size. The result of a physisorption measurement is an adsorption/desorption isotherm – the relation between the amount of adsorbed gas, n (y -axis), and relative pressure, p/p° (x -axis), where p is the equilibrium and p° is the saturation vapor pressure at a constant adsorption temperature below the critical point of the adsorptive. IUPAC recognizes six types of isotherms depending on their shape (Figure 16). Each of them

is characteristic of a particular pore structure and depends on the interaction between adsorbate and adsorbent.³⁰

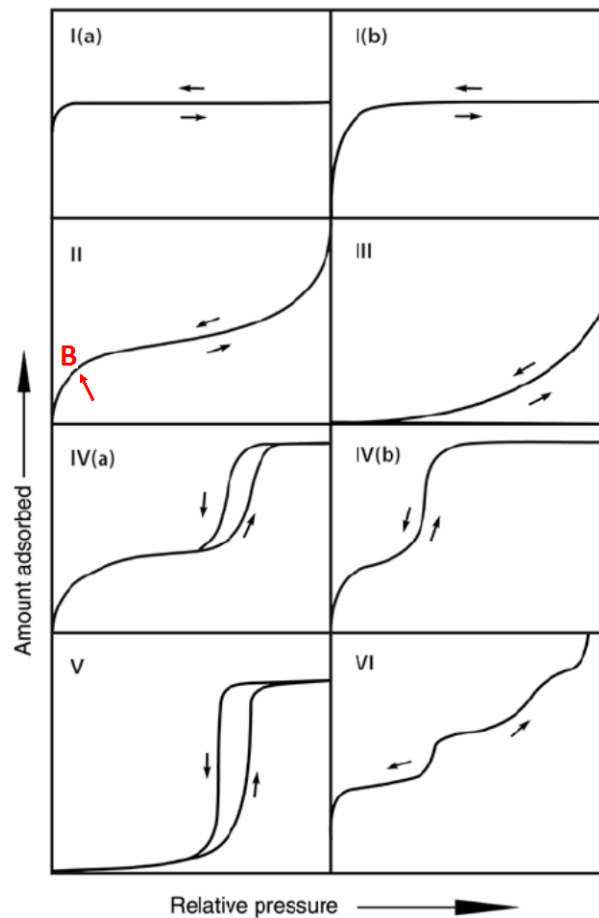


Figure 16: Classification of physisorption isotherms.

Reversible type I isotherms, I(a) and I(b), are characteristic of microporous solids, such as zeolites, with pore width below 2 nm and small external surface.⁴³ The increase in the value of n is rapid. It reaches the limiting value at low $p/p^\circ < 0.1$ and then plateaus. Type I(a) isotherm is typical for microporous materials having predominantly narrow pores < 1 nm. Type I(b) isotherm is given by materials with larger micropores of 1 - 2 nm.³⁰

Reversible type II and type III isotherms are characteristic of nonporous or macroporous materials with pore width above 50 nm. Type II isotherm shape displays multilayer adsorption, where point B corresponds to the completion of monolayer coverage. Type III isotherm displays no point B, hence no identifiable monolayer formation, and is typical for weak interactions between the adsorbent and adsorbate.³⁰

Type IV isotherms, IV(a) and IV(b), are given by purely mesoporous materials with pore width between 2 and 50 nm.⁴³

Type V isotherms indicate very weak adsorbent-adsorbate interactions and molecular clustering followed by pore filling. They are typically observed for water adsorption on hydrophobic adsorbents.³⁰

Type VI isotherms are characteristic of highly uniform nonporous surfaces, where each step represents the formation of a new adsorbed layer. They are most commonly obtained by physisorption measurements of graphitized carbon blacks.³⁰

Nitrogen, argon and carbon dioxide are the common adsorbates. Physisorption measurements are performed at a constant temperature – at -196 °C (77 K) for N₂, -186 °C (87 K) for Ar and 0 °C (273 K) for CO₂.²¹ Nitrogen is the most widely used for several reasons – it is readily available, non-reactive and cheap. However, due to its quadrupole moment, the molecule may interact with the surface groups or extra framework cations of the adsorbate. This leads to uncertainties, particularly in determining the micropore size distribution.²³ Argon is less reactive than nitrogen and therefore widely used for evaluation of micropore size.³⁰

The total adsorption volume is usually measured at the relative pressure $p/p^\circ = 0.95$ from the adsorption branch of the isotherm. The micropore volume of zeolites, V_{mic} , is calculated using an empirical t -plot method. This method compares the adsorption isotherm of a porous zeolite sample with a nonporous sample of identical chemical composition. The t -plot is a graph displaying the relation between the volume of adsorbate adsorbed, V_{ads} (y-axis) and the thickness of the adsorption layer, t (x-axis). In the case of a nonporous material, this relation is linear with no intercept. However, the presence of micropores and mesopores generates horizontal and vertical deviations (Figure 17). The micropore volume is obtained by extrapolating the horizontal line to a positive intercept on the y-axis (Figure 17 red line), whereas the specific external surface of a sample, $S_{\text{ext.}}$, is given by the slope of the curve.⁴³

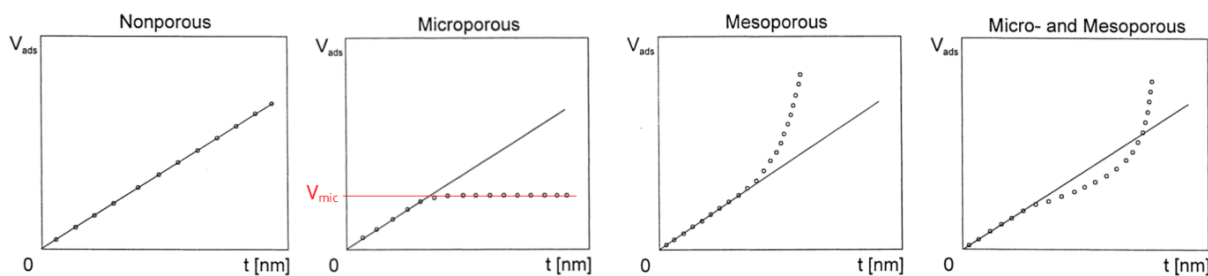


Figure 17: t -Plots for nonporous, microporous, mesoporous and micro-mesoporous solids.

3.2.3. Scanning electron microscopy

Microscopy, a fundamental characterization technique for materials, is based on the interaction of a beam of photons or electrons with the surface. The collection and the analysis

of the resulting beam (e.g., reflected photons, secondary and backscattered electrons) generates the image. The most available and widely used microscope is a simple optical microscope. Although cheap, it has a limited resolution of 200 nm as it uses visible light radiation with wavelengths of 400 - 700 nm. Zeolites are nanomaterials with complex surfaces and structural features in the magnitude of nanometers and angstroms. To properly characterize these materials, an electron beam with shorter wavelengths, that produces higher resolution images is employed.^{31,32}

Electron microscopy uses a beam of highly accelerated electrons with wavelengths of 1 - 40 pm. As electrons carry a negative charge, they interact strongly with atoms. This results in a wide range of produced signals. The key signals emitted from a sample are scattered primary electrons (PEs), secondary electrons (SEs) and X-rays. PEs can undergo elastic scattering and emerge back out of the surface as backscattered electrons (BSEs). SEs are ejected valence electrons generated through inelastic scattering of PEs. Characteristic X-rays are produced when a PE ejects an inner-shell electron, creating a vacancy. This vacancy is filled by a higher-energy electron, releasing an X-ray with energy specific to the electron levels of atoms. BSEs and SEs are utilized for imaging, while characteristic X-rays are utilized for chemical analysis, making electron microscopy multifunctional as both a spectroscopy and nanoscale imaging tool.^{31,32}

SEM is a class of electron microscopy utilized in the examination of material surface. Pressure inside the chamber of scanning electron microscope is usually $10^{-1} - 10^{-4}$ Pa, i.e., high vacuum. Figure 18 shows the typical layout of SEM microscope. The electron gun accelerates electrons through 1 – 30 kV accelerating voltage. With the use of electromagnetic lenses, the electron beam is focused on a spot and scanned across the specimen in a sequence. Emitted SEs, BSEs and X-rays are collected by the corresponding detector. These detectors convert the signal into an electrical pulse, that is processed and displayed as an image or an energy dispersive X-ray spectrum.³¹ The X-ray spectrum is measured with an EDS and is composed of peaks characteristic to specific element. The position of the peaks provides information about the nature of elements present in the sample, while their intensity is related to their concentration.³³ On top of EDS analysis, SEM is typically utilized in examining crystal morphology and size.³¹

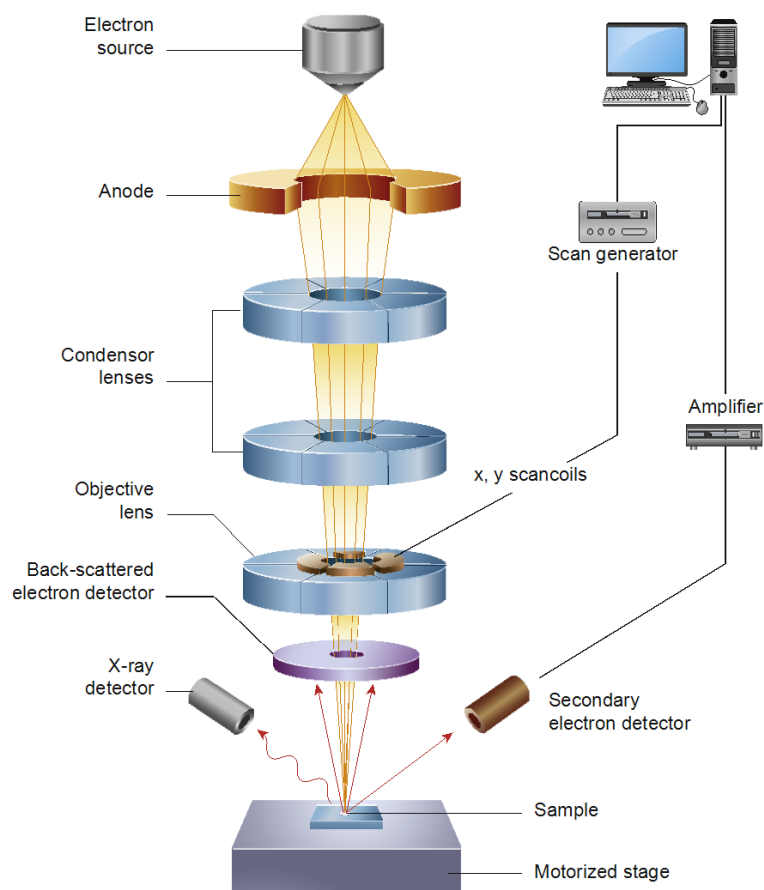


Figure 18: Schematic diagram of core components of an SEM microscope.

3.2.4. FTIR Spectroscopy

IR spectroscopy studies the interaction of IR radiation and matter, specifically how the matter absorbs energy, that corresponds to its vibrational modes. The IR spectrum is divided into three regions: near-IR ($14000\text{ cm}^{-1} - 4000\text{ cm}^{-1}$ or $1.6 - 0.5\text{ eV}$), mid-IR ($4000\text{ cm}^{-1} - 400\text{ cm}^{-1}$ or $0.5 - 0.05\text{ eV}$) and far-IR ($400\text{ cm}^{-1} - 10\text{ cm}^{-1}$ or $0.05 - 0.0012\text{ eV}$).³⁴

Modern IR spectroscopy utilizes a high-performance Fourier Transform IR mode, that applies a Michelson interferometer. In contrast to a dispersive spectrophotometer, that analyses IR radiation one wavenumber at a time, the FTIR spectroscopy setup allows all the frequencies of the IR beam to reach the detector at the same time, enabling faster and more accurate multi-scan measurements and achieving a signal-to-noise ratio as high as $65000 : 1$.³⁴ The outcome of FTIR spectroscopy measurement is a spectrum, that displays the relation between the absorbance (y -axis) and the wave-number (x -axis). The position of absorption bands is characteristic to vibrations of certain functional groups, while their intensity is proportional to the number of these groups, meaning FTIR provides both qualitative and quantitative analysis of materials.

In zeolite characterization with FTIR spectroscopy, the mid-IR region is the most informative, while the experiments are usually performed *in situ*.³⁴ *In situ* IR spectroscopy enables us to study the surface of zeolite catalysts under various conditions and in diverse media. For instance, by monitoring the IR spectra of a zeolite in the OH vibration region (*vide infra*) during thermal treatment, we can identify the most effective temperature range for achieving complete dehydration of a catalyst. Additionally, this technique is commonly employed to investigate the type, strength, distribution, and quantity of acid sites within zeolites, typically through the adsorption and desorption of probe molecules, tracked *via* spectral changes.

The OH vibration region ($3800\text{ cm}^{-1} - 3500\text{ cm}^{-1}$) is used to identify the nature of the surface functional groups in an activated zeolite. Terminal silanol O-H bond stretching vibrations ($3747\text{ cm}^{-1} - 3744\text{ cm}^{-1}$) are independent of zeolite topology and Si/Al.³⁶ Other distinct bands include O-H vibrations of internal silanol groups ($\sim 3720\text{ cm}^{-1}$) and bridging hydroxyl groups ($3650\text{ cm}^{-1} - 3600\text{ cm}^{-1}$), that display strong Brønsted acidity (Figure 19).³⁵

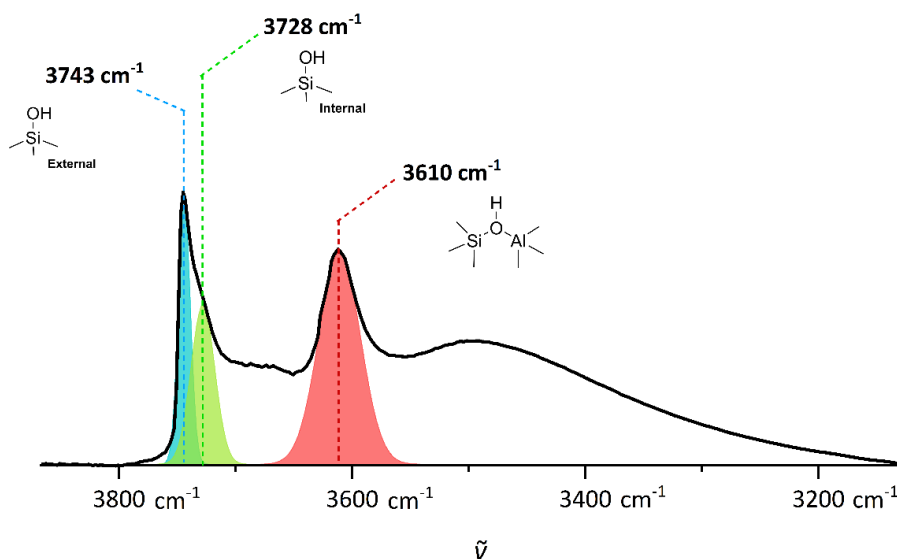


Figure 19: Typical FTIR spectrum in the OH-region of an activated aluminosilicate zeolite.

As only limited information can be directly extracted from the FTIR spectra of a pristine zeolite, the properties of acid sites (type, concentration, relative strength) are investigated by chemisorption of basic probe molecules, that interact with the acid site. Qualitatively, the differentiation between BAS and LAS is apparent from characteristic bands positions related to either physisorption, protonation or coordination of the probe molecule. Commonly used probe molecules include deuterated acetonitrile (D_3 -AN), pyridine (Py) and 2,6-di-*tert*-butylpyridine (DTBPy). These probe molecules vary in size and can therefore provide information about

concentration of acid centres accessible for reacting molecules of different sizes, used in zeolite-catalysed reactions.

D₃-AN, with the smallest kinetic diameter of 0.38 nm, penetrates most of the pores, including 8-ring channels, and, therefore, is commonly used to quantify the total concentration of acid sites in zeolites. Adsorption of D₃-AN results in characteristic bands in the FTIR spectrum corresponding to physisorbed D₃-AN (~2265 cm⁻¹), D₃-AN adsorbed on silanol groups (~2275 cm⁻¹), on BAS (~2297 cm⁻¹), on weak Al LAS (~2315 cm⁻¹) and on strong Al LAS (~2325 cm⁻¹).^{21,36,38} These peaks are overlapping, as shown in Figure 20.

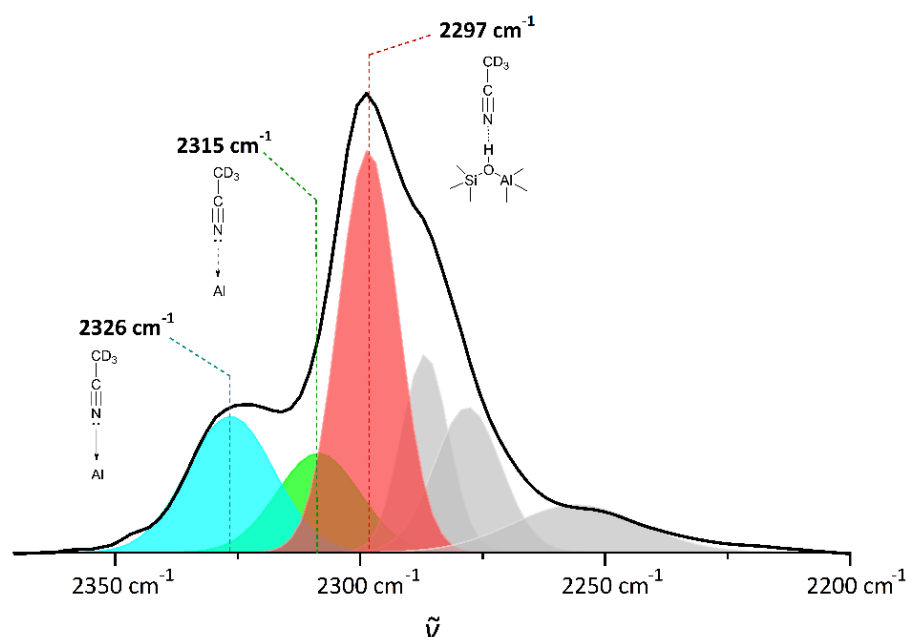


Figure 20: Typical FTIR spectrum of D₃-AN adsorbed in an aluminosilicate zeolite.

Py, with the kinetic diameter of 0.54 nm, does not penetrate small 8-ring pores.³⁹ Adsorption of Py results in characteristic bands (Figure 21) corresponding to the pyridinium ion vibration, indicating BAS (~1545 cm⁻¹, ~1637 cm⁻¹), Py adsorbed on BAS and LAS (~1491 cm⁻¹), on silanol groups (~1445 cm⁻¹, ~1595 cm⁻¹) and Py coordinatively bonded to Al, indicating LASs (~1455 cm⁻¹, ~1620 cm⁻¹). Furthermore, physisorbed Py characteristic band (~1580 cm⁻¹), that is lower in intensity is observed. Apart from assessing the concentration of BASs and LASs, we can determine the relative strength of these sites by thermodesorption of Py, that shows a stepwise decrease in area of characteristic bands with increasing temperature.^{17,37}

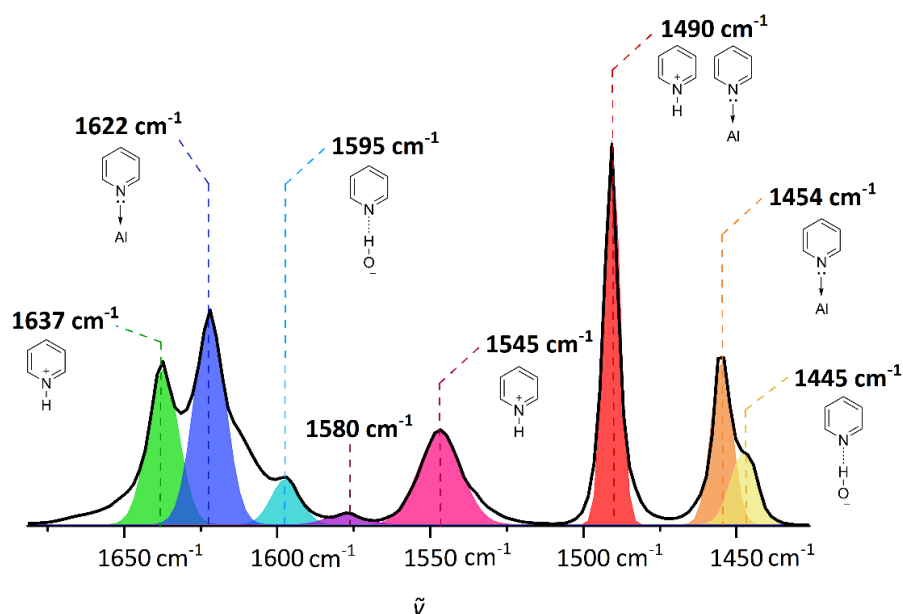


Figure 21: Typical FTIR spectrum of Py adsorbed in an aluminosilicate zeolite.

DTBPy, with the kinetic diameter of 0.79 nm, does not penetrate 8- and 10-ring pores of a zeolite and only comes in contact with acid sites on the external surface and those accessible through large (12-ring) and extra-large pores (>12-ring).³⁹ Adsorption of this probe molecule is thus used for the characterization of surface acidity.³⁶ Presence of surface BASs is verified by characteristic band of protonated DTBPy (~ 1530 and ~ 1615 cm^{-1} , the latter used for quantitative analysis) (Figure 22).⁴⁰

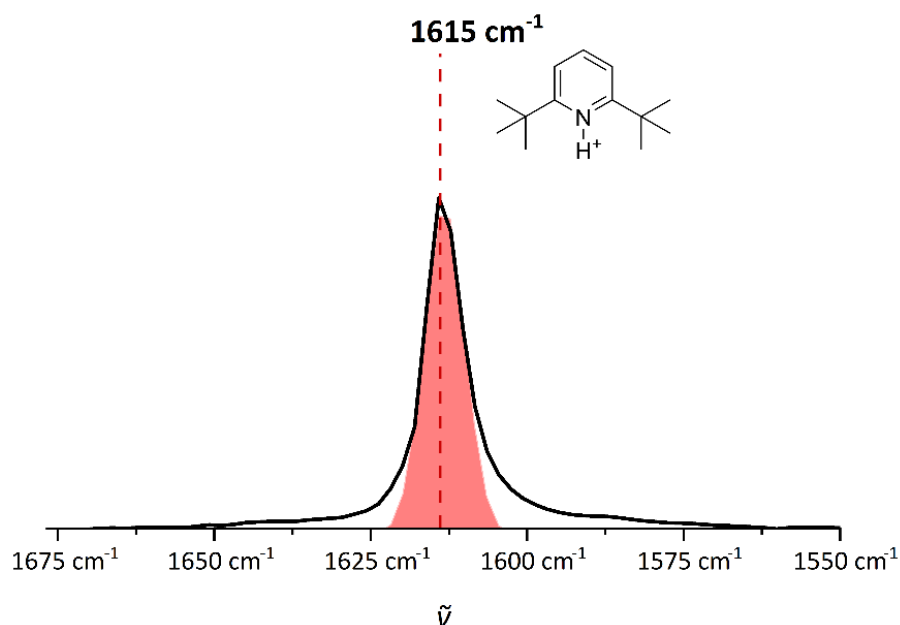


Figure 22: Typical FTIR spectrum of DTBPy adsorbed in an aluminosilicate zeolite.

Quantitatively, the concentration of acid sites is calculated using the Lambert-Beer's law, adjusted for analytes adsorbed on the solid surfaces:

$$A = \varepsilon \cdot c \cdot \frac{m}{S} \quad (2)$$

where A is the integral intensity of a band, [cm^{-1}]; ε is the molar absorption coefficient, [$\text{cm} \cdot \mu\text{mol}^{-1}$]; c is the concentration of acid sites, [$\text{mmol} \cdot \text{g}^{-1}$]; m is the mass of the self-supported zeolite wafer, [mg]; and S is the surface area of the wafer, [cm^2]. Whereas obtaining values of A , c , m and S is straightforward, the values of ε are either unknown or exhibit significant variations across the reported data.^{36,39} The difficulty in determining ε arises from its dependence on experimental factors (e.g., the choice of probe molecules and temperature) and material properties, such as the nature of acid sites, zeolite topology and chemical composition. For example, the values of $\varepsilon(\text{Py-BAS})$ increase in the order $\text{MFI} \approx \text{BEA} < \text{MOR} < \text{FAU}$, which can be correlated to factors such as strength of BASs, Si/Al and confinement effects.³⁷

3.3. Application of zeolites in catalysis

Controlled acidity, narrow pore size distribution and thermal stability are the main reasons aluminosilicate zeolites act as highly active, selective and reusable catalysts in many industrial processes including oil refinery and petrochemistry (Table 3). Tunability of zeolite's properties such the porous structure, acidity and chemical composition is a gateway to designing catalysts, that have enabled performing previously inaccessible reactions such as the formation of gasoline range liquids from natural gas.^{44,45} Additionally, using zeolite catalysts enables many industrially important reactions to proceed under milder conditions, resulting in less energy-intensive processes.⁴⁶

Zeolites catalyse industrial processes such as FCC, methanol-to hydrocarbons (MTH) and alkylation of aromatics to produce liquid fuels and bulk chemicals such as ethylbenzene (EB) and cumene, that are commodities on the petrochemical market (Table 3).⁴⁷

FCC is an industrial process, that produces most of the world's gasoline and accounts for over 95% of synthetic zeolite consumption.⁴⁶ During FCC, heavy hydrocarbons of natural oil are broken down into lighter, more valuable gasoline-range hydrocarbons or short-chain olefins depending on the catalyst composition.⁴⁵ Micro-mesoporous 3D 12-ring zeolite FAU ultrastabilized by steaming (USY) and 3D 10-ring zeolite MFI (ZSM-5) are the most used catalysts in this process.^{1,48}

MTH reactions yield olefins, alkanes and aromatics. Methanol-to-olefins (MTO) are catalysed by CHA-type materials with a 3D network of 8-ring channels and cavities, such as SAPO-34 and SSZ-13. These catalysts have shown superior TS and product shape selectivity towards light olefins, especially to ethylene and propylene.^{49,50}

Alkane aromatization is a petroleum refining process, that aims at increasing the octane number of gasoline and producing valuable aromatics such as benzene, toluene and xylene (BTX). Unlike conventional platinum-on-alumina reforming catalysts, platinum-on-zeolite catalysts used in alkane aromatization offer intrinsic acidity and shape-selectivity, enabling them to efficiently promote reactions such as dehydrocyclization of alkanes as well as disproportionation, transalkylation, and isomerization of aromatics.⁵¹ Among zeolites, MFI has been extensively studied for its ability to convert light alkanes such as methane and ethane into aromatics under suitable conditions. In particular the CyclarTM process utilizes Ga-substituted MFI zeolites, with moderate acid strength, that outperform traditional Al-containing MFI in catalytic activity, selectivity, and stability for the aromatization of propane.^{52,53} Furthermore,

MFI zeolites catalyse the conversion of toluene, which is the most abundant yet the least valuable component of BTX.

Toluene undergoes disproportionation/transalkylation (Dis/Trans) with equally less valuable C₉₊ aromatics to produce benzene and xylenes. The unimodal 3D 10-ring pore system of MFI supports efficient disproportionation, while minimizing heavy by-products and coke formation, and displaying high *p*-xylene selectivity. Apart from toluene Dis/Trans, commercially valuable *p*-xylene is typically obtained *via* isomerization of C₈-alkylaromatics.⁵³

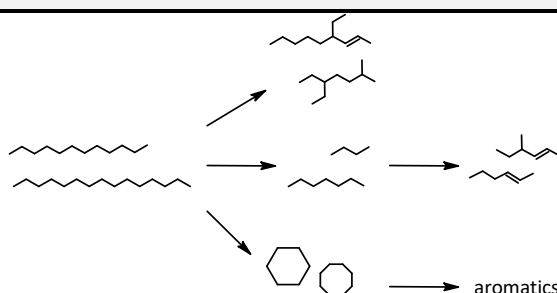
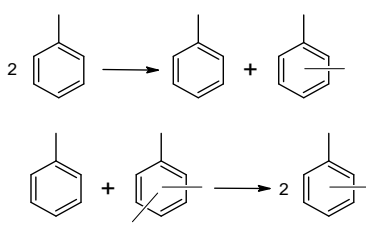
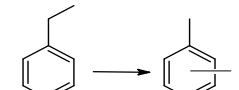
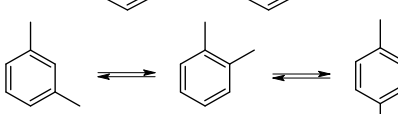
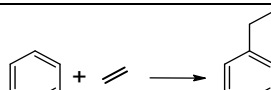
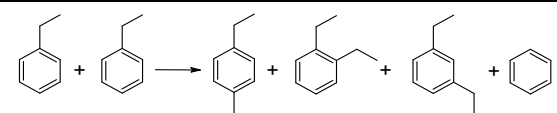
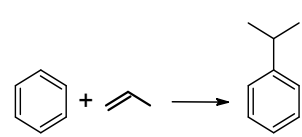
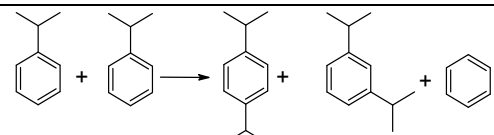
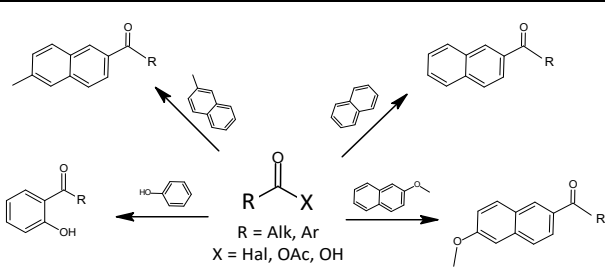
C₈-alkylaromatics isomerization encompasses EB and xylene isomerization, where the latter is a particularly important reaction within BTX production, especially the conversion of *meta*- and *ortho*-xylenes to *para*-xylene (the focus of this work and discussed in detail in Section 3.3.1.). BTX can undergo alkylations, transalkylations and disproportionations, that yield bulk chemicals such as EB, diethylbenzene (DEB) and cumene.

EB, a precursor to styrene and polystyrene, is produced by alkylation of benzene with ethylene. This reaction is catalysed by MWW-type zeolites with a 2D 10-ring pore system such as MCM-22, that contains large 12-ring cavities.⁵⁴ MWW catalysts are very selective towards EB as the formation of diethylbenzenes (DEBs) and triethylbenzenes is reduced. EB can be further alkylated by ethylene over MFI catalysts yielding DEBs. Selectivity towards the preferred *para*-isomer (*p*-DEB) is enhanced through post-synthetic narrowing the MFI pore openings.⁵⁵

Cumene, a phenol and acetone production intermediate, is produced by alkylation of benzene with propylene or C₃ alcohols. Zeolite catalysts with wide 12-ring pores BEA, FAU and mesoporous MOR are among the most effective in the formation of cumene. However, large supercages of FAU zeolite favour the formation of heavy products, which decreases its selectivity and stability. Transalkylation reactions of cumene occur parallel to alkylation reactions and yield benzene and diisopropylbenzene (DIB). Mesoporous MOR has shown great shape selectivity favouring *p*-DIB formation.⁵⁶

Fine chemistry reactions such as Friedel-Crafts acylation utilize acidic zeolite catalysts, that have become replacements of traditional homogeneous catalysts such as HF, H₂SO₄, AlCl₃, ZnCl₂.¹⁷ The main objective of Friedel-Crafts acylation is to prepare valuable ketones, which are further used in pharmaceuticals and fragrances. Zeolites used in Friedel-Crafts reactions include BEA, FAU and MOR, where large-pore zeolites show higher yields in acylation of polycyclic aromatic molecules.⁵⁷

Table 3: Industrially significant processes, that utilize zeolite catalysts.

Process	Reaction scheme	Catalyst	Pore architecture
FCC		USY	3D 12-ring
		MFI	3D 10-ring
MTO	$\text{CH}_3\text{OH} \rightarrow \text{C}_2^- - \text{C}_4^-$	CHA	3D 8-ring
BTX production			
Alkane aromatization	$\text{C}_n\text{H}_{2n+2} \rightarrow \text{aromatics}$		
Toluene Dis/Trans		MFI	3D 10-ring
EB isomerization		MOR	2D 8-, 12-ring
m-Xylene isomerization		MFI	3D 10-ring
EB production via alkylation		MWW	2D 10-ring
DEB production via disproportionation		MFI	3D 10-ring
Cumene production via alkylation		BEA	3D 12-ring
		FAU	3D 12-ring
		MOR	2D 8-, 12-ring
DIB production via disproportionation		MOR	2D 8-, 12-ring
Friedel-Crafts acylation		BEA	3D 12-ring
		FAU	3D 12-ring
		MFI	3D 10-ring
		MOR	2D 8-, 12-ring

3.3.1. *m*-Xylene isomerization

Xylene isomerization is among the most prevalent zeolite-catalysed reactions in the petrochemical industry. The most valuable product of *m*-xylene isomerization is *p*-xylene, which is a precursor for terephthalic acid, PET, resins and plasticizers.

The nature of the catalyst determines the outcome of xylene isomerization. When using mineral acids as catalysts, the reaction is governed by the thermodynamic equilibrium and yields a mixture of xylenes close to the thermodynamic ratio of approximately 24% *p*-xylene, 54% *m*-xylene and 22% *o*-xylene at 250 - 450 °C. In contrast, shape selective zeolite catalysts direct *m*-xylene isomerization towards the production of the most demanded, but least thermodynamically favourable *p*-xylene. Unimodal MFI-type zeolites impose diffusional constraints that hinder the migration of bulkier *m*- and *o*-xylenes. This effect increases the selectivity for *p*-xylene far beyond its thermodynamic equilibrium concentration.^{55,58}

m-Xylene isomerization, whether catalysed by liquid or solid acids, can occur *via* two pathways – monomolecularly or bimolecularly. Monomolecular (intramolecular) mechanism leads to the rapid reversible addition of a proton to the benzene ring, followed by a 1,2-methyl shift in the xylene molecule (Figure 23).^{58,59}

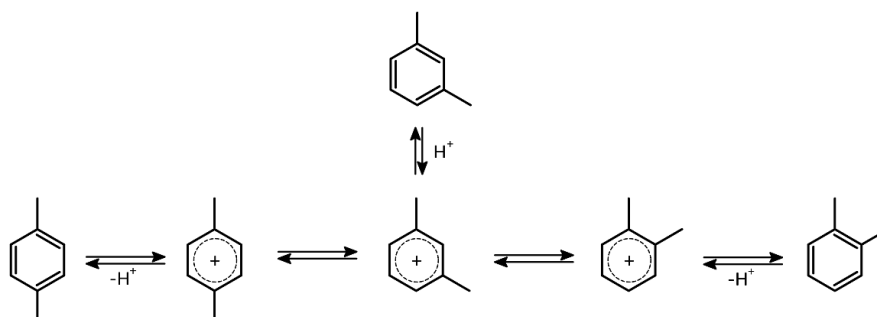


Figure 23: Monomolecular mechanism of *m*-xylene isomerization.

Bimolecular (intermolecular) mechanism leads to a cascade of multiple reactions, such as disproportionation of xylenes (I) and toluene (II); transalkylation of TMB and xylenes (III) or toluene (IV); dealkylation of xylenes (V) and toluene (VI), which may lead not only to the targeted *p*-xylene formation in reactions II - IV but also to various side-products (Figure 24).⁶⁰

Whether the reaction occurs *via* monomolecular or bimolecular mechanism depends on the reaction conditions and on the pore architecture of a zeolite catalyst meaning the pore size, channel system and presence of structural features such as supercages and cups. In small-pore zeolites, monomolecular mechanism is preferred due to space confinement. Alternatively, in larger-pore zeolites with bigger voids, bimolecular reactions occur preferably due to the lower

activation energy compared to monomolecular *m*-xylene isomerization and appropriate space available to form bulky intermediates.^{55,58,59,61}

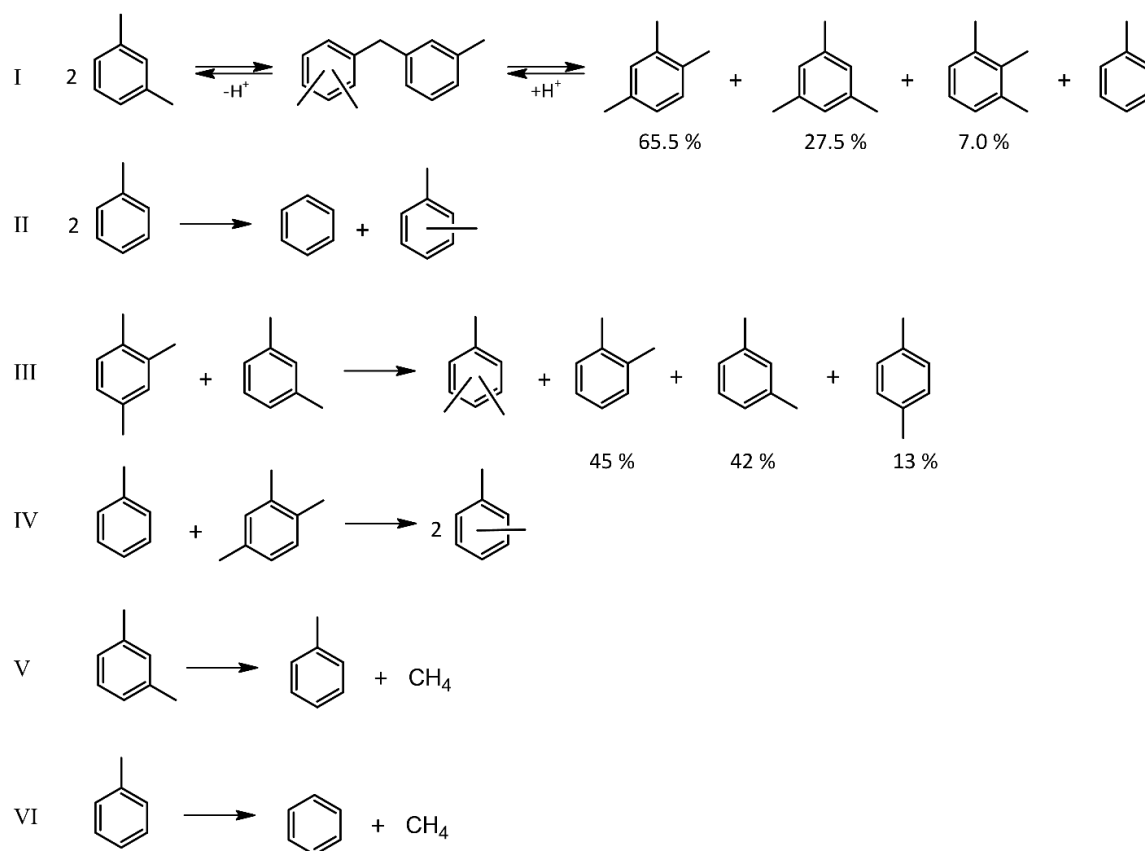


Figure 24: Bimolecular mechanism of *m*-xylene isomerization (I) and possible consequent reactions (II-VI).

Unimodal zeolite MFI containing a 3D pore system has shown high *para*-selectivity in *m*-xylene isomerization and is the most utilized industrially. MFI consists of two types of intersecting medium 10-ring channels – straight, with pore diameters of 0.53×0.56 nm, and sinusoidal with pore diameters of 0.51×0.55 nm, with a channel intersection of 0.86 nm.⁶² Product and TS shape selectivity towards *p*-xylene is controlled by these channels, as the kinetic diameter of *p*-xylene (~ 0.58 nm) is smaller than the kinetic diameters of *m*- and *o*-xylene (~ 0.68 nm).⁶² In addition, the diffusivity of xylene isomers within the MFI pores follows the order: *p*-xylene > *o*-xylene > *m*-xylene, according to previously calculated diffusion coefficients, D . *p*-Xylene has the highest value of D (4.7×10^{-17} m²/s), measured at 100 °C (373 K) and 1 mbar, and thus diffuses throughout the MFI pores easily.^{63,64} This results in yields of *p*-xylene/*o*-xylene above 2 and a disproportionation/isomerization ratio (Dis/Iso) of 0.01.⁶⁰ *para*-Selectivity of MFI catalysts in *m*-xylene isomerization can be further increased by tailoring its crystal morphology. For example, synthesising MFI with chain-like crystals parallel to the straight channels increases the selectivity towards *p*-xylene by approximately 10% compared to the bulk zeolite.⁶² Although the narrow pores of MFI strongly inhibit

transalkylation reactions, they promote undesired dealkylation reactions. Moreover, limited accessibility to active sites and diffusion hindrance cause slow mass transfer in the MFI channels.¹ For these reasons, efforts in developing a new catalyst for *m*-xylene isomerization continue.

Unimodal zeolite EUO with a 1D pore system, formed by 10-ring channels with 12-ring side pockets, has been recently utilized by industrial plants as a *m*-xylene isomerization catalyst.¹ Under similar reaction conditions, EUO shows xylene conversion comparable to MFI as well as high selectivity towards *p*-xylene. EUO catalysts show Dis/Iso comparable to MFI (~0.02 for EUO and 0.01 for MFI), while a significantly higher *p*-xylene/*o*-xylene (4.9 for EUO and 2 for MFI).⁶⁵ The 1D pore system promotes overall higher product shape selectivity towards *p*-xylene.^{1,66} Moreover, the *para*-selectivity of 1D unimodal 10-ring zeolites MTT, SFF and 12-ring zeolites AFI, IFR were studied in comparison to MFI. The effect of pore size is apparent, as medium-pore zeolites show *p*-xylene/*o*-xylene higher (3.4 for MTT) and comparable (2.3 for SFF) to that of MFI (2). Alternatively, large-pore zeolites AFI and IFR display a 2-fold lower *p*-xylene/*o*-xylene than MFI close to 1. The Dis/Iso is lower for more selective MTT and SFF compared to AFI and IFR, meaning pronounced restriction of bimolecular reactions within the 10-ring pores.^{65,67}

Bimodal zeolite MOR with a 2D pore system of 8- and 12-ring channels shows higher *m*-xylene conversion compared to MFI.⁶⁰ Large 12-ring pores guarantee facile diffusion, however, these pores also facilitate bimolecular disproportionation and transalkylation reactions that yield a significant amount of toluene and TMBs.¹ High Dis/Iso (0.33) highlights the significant contribution of disproportionation reactions, which leads to low selectivity towards the desired *para* isomer. In contrast, zeolite MFS with a similar bimodal structure exhibits a Dis/Iso of ~0.005, that is approximately two times lower than MFI (0.01). MFS contains smaller 8- and 10-ring pores, that hinder the formation of bulky byproducts and promote *p*-xylene formation.⁶⁵ Upon optimal selection, multimodal zeolites can decrease the diffusion barrier while also being highly selective.

As demonstrated above, zeolite pore size and architecture greatly affect the reaction pathways and therefore the selectivity towards *p*-xylene in *m*-xylene isomerization. Small- to medium-pore 8- and 10-ring catalysts show higher selectivity towards *p*-xylene but restrict diffusion. Large-pore 12-ring catalysts increase diffusion of reacting molecules but promote the formation of undesirable side-products such as toluene and TMBs *via* disproportionation and transalkylation reactions. Besides pore size, product and TS shape selectivity is induced by the

shape, size and structure of zeolite crystals i.e. crystal morphology. Crystal morphology-induced shape selectivity is observed not only in *m*-xylene isomerization, but also confirmed in MTH reaction.⁶⁸

Three-modal germanosilicate zeolite IWW has a 3D pore network of parallel 8- and 12-ring pores, perpendicularly intersected by 10-ring channels.⁴ Post-synthetic substitution of Ge for Al generates BASs making IWW catalytically active in *m*-xylene isomerization. In theory, the 10-ring pores would promote monomolecular isomerization and high selectivity towards *p*-xylene while overall, the 3D channel network of 8-, 10- and 12-ring channels enables molecular traffic control and can selectively direct diffusion of molecules based on their shape and size. Moreover, recent studies show, that by adjusting the Si/Ge ratio, different crystal morphologies of IWW can be obtained, most notably platelets (Si/Ge ~ 4) and needles (Si/Ge ~ 10).³ Similarly to MFI, by tailoring the morphology of IWW, the catalytic performance can be improved.

4. Experimental part

4.1. List of used chemicals

Table 4: List of used chemicals

Chemical	Purity	Supplier
1,6-Diaminohexane	98%	Alfa Aesar
2,6-Di-tert-butylpyridine	97%	Sigma Aldrich
Aluminium hydroxide	Extra pure	Acros Organic
Aluminium nitrate nonahydrate	99%	VWR CHEMICALS
Aluminium sulfate hexadecahydrate	P.A.	Fluka
Ammonium nitrate	≥99%	Sigma Aldrich
CAB-O-SIL M-5	-	Acros Organic
Carborundum 500 µm	-	VWR CHEMICALS
D ₃ -acetonitrile	100 %	Sigma Aldrich
LUDOX AS-40 colloidal silica (aq.)	40 wt. %	Sigma Aldrich
LUDOX HS-40 colloidal silica (aq.)	40 wt. %	Sigma Aldrich
<i>m</i> -Xylene	99%	Thermo Scientific
<i>N,N,N</i> -trimethyl-1-adamantammonium hydroxide	25%	TCI
Potassium hydroxide, pellets	≥85%	Sigma Aldrich
Pyridine anhydrous	99.8%	Sigma Aldrich
Sodium hydroxide	99.2%	VWR CHEMICALS
Sodium metasilicate (aq.)	29.5 wt. % Si 7.9 wt. % Na	Sigma Aldrich
Tetraethoxysilane (TEOS)	98%	Thermo Scientific

4.2. Synthesis of zeolite catalysts

3D 10-ring MFI zeolite (CBV8014, Si/Al = 40) and 3D 12-ring BEA zeolite (CP811E-75, Si/Al = 40) were purchased from Zeolyst in ammonium form. Hydrogen-form (H-form) of BEA and MFI samples, which was used in catalytic tests, was obtained by calcination at 350 °C for 4 hours. Germanosilicate zeolites IWW with platelet and needle-like crystals (designated as IWW-platelets and IWW-needles) were provided by MSc. E. Shamma and used for post-synthesis Ge-for-Al substitution.

4.2.1. 1D 8-ring ESV aluminosilicate

Zeolite ESV was synthesised following the procedure reported in Ref.¹⁴, using a reaction mixture with the molar composition of 1.0 SiO₂ : 0.3 Na₂O : 0.04 Al₂O₃ : 0.2 *N,N*-dimethylpiperidinium hydroxide : 40 H₂O. Aqueous *N,N*-dimethylpiperidinium hydroxide, the SDA for ESV synthesis, was synthesized and provided by MSc. E. Shamma. In a Teflon beaker under stirring, 22.48 g of *N,N*-dimethylpiperidinium hydroxide was dissolved in 7.04 g of distilled water. After the complete dissolution of the SDA, 1.03 g of aluminium sulfate hexadecahydrate was added to the solution. The mixture was left to stir for 30 minutes. Then, 18.80 g of sodium metasilicate was added dropwise and the reaction mixture was left to stir for 1 hour at room temperature. Lastly, 0.10 g of previously synthesised ESV zeolite was added into the mixture as seeds before transferring the mixture into a Teflon-lined 90ml autoclave. The mixture crystallized for 14 days in an oven under rotation (60 rpm) at 170 °C. The solid product was isolated by filtration, washed with distilled water and dried at 60 °C. The zeolite was calcined at 680 °C for 5 hours with a heating rate of 1 °C/min under airflow.

4.2.2. 1D 10-ring TON aluminosilicate

Zeolite TON was synthesised following a modified synthesis reported in Ref.⁶⁹, using a reaction mixture with the molar composition of 112 SiO₂ : 10 K₂O : 1 Al₂O₃ : 24.5 1,6-Diaminohexane : 3265 H₂O. In a Teflon beaker under stirring, 0.69 g of 1,6-Diaminohexane was dissolved in 11.50 g of distilled water. After a complete dissolution of the SDA, 0.33 g of potassium hydroxide and 0.15 g of aluminium sulfate hexadecahydrate was added and the mixture was left to stir for 30 minutes. Subsequently, 4.00 g of LUDOX AS-40 colloidal silica (aq.) was added dropwise. The reaction mixture was left to stir for 90 minutes at room temperature. Afterwards, 0.10 g of previously synthesised TON was added to the mixture as seeds before transferring the mixture into a Teflon-lined 25ml autoclave. The mixture crystallized for 5 days in an oven under rotation (60 rpm) at 160 °C. The solid product was

isolated *via* repeated centrifugation at 2000 rpm for 4 minutes, washed with distilled water and dried at 60 °C. The zeolite was calcined at 550 °C for 5 hours with a heating rate of 1 °C/min under airflow.

4.2.3. 1D 12-ring AFI aluminosilicate

Zeolite AFI was synthesised using a reaction mixture with the molar composition of 30 SiO₂ : 3 NaOH : 1 Al(OH)₃ : 3 *N,N,N*-trimethyl-1-adamantammonium hydroxide : 954 H₂O. In a Teflon beaker under stirring, 7.78 g of *N,N,N*-trimethyl-1-adamantammonium hydroxide was dissolved in 47.00 g of distilled water. After the complete dissolution of the SDA, 0.38 g of sodium hydroxide and 0.24 g of aluminium hydroxide was added. The mixture was left to stir for 30 minutes. Lastly, 5.50 g of CAB-O-SIL M-5 was added dropwise. The reaction mixture was left to stir for 90 minutes at room temperature. Subsequently, the reaction mixture was transferred into a 90ml Teflon-lined autoclave and left to crystallize for 8 days in an oven under rotation (60 rpm) at 160 °C. The solid product was isolated by repeated centrifugation at 2000 rpm for 4 minutes, washed with distilled water and dried at 60 °C. The zeolite was calcined at 550 °C with a heating rate of 1 °C/min under airflow for 5 hours.

4.2.4. 3D 8-ring CHA aluminosilicate

Zeolite CHA was synthesised following the procedure reported in Ref.⁷⁰, using a reaction mixture with the molar composition of 1 SiO₂ : 0.35 Na₂O : 0.025 Al₂O₃ : 0.35 *N,N,N*-trimethyl-1-adamantammonium hydroxide : 18 H₂O. In a Teflon beaker under stirring, 32.96 g of *N,N,N*-trimethyl-1-adamantammonium hydroxide was dissolved in 0.77 g of distilled water. After the complete dissolution of the SDA, 1.60 g of sodium hydroxide was added. Subsequently, 0.22 g of aluminium hydroxide was added, and the mixture was left to stir for 30 minutes. Lastly, 16.67 g of LUDOX HS-40 was added dropwise. The reaction mixture was left to stir for 90 minutes at room temperature. 0.10 g of previously synthesised CHA was added to the mixture as seeds. The reaction mixture was transferred into a 90ml Teflon-lined autoclave and left to crystallize for 12 days in an oven under rotation (60 rpm) at 160 °C. The solid product was isolated by filtration, washed with distilled water and dried at 60 °C. The zeolite was calcined at 550 °C for 5 hours with a heating rate of 1 °C/min under airflow.

The H-forms form of ESV, TON, AFI and CHA aluminosilicates were obtained by ion-exchange with ammonium nitrate. The zeolite powders were mixed with 1M ammonium nitrate solution in a plastic cup (100 ml of the solution per 1 g of zeolite). This mixture was stirred for 8 hours at room temperature. Then, the zeolite was isolated by filtration. The ion-exchange

process was repeated five times. Afterwards, the sample was dried at 60 °C and calcined at 350 °C for 3 hours with a heating rate of 1 °C/min under airflow.

4.3. Post-synthesis Ge-for-Al substitution in IWW zeolites

0.1 g of IWW-platelets or IWW-needles sample was subjected to treatment with 10 ml of a 1M aluminium nitrate at 95 °C for four days. Following the treatment, the solid was isolated by filtration, rinsed with distilled water, and subsequently dried. Finally, the zeolite was calcined at 450°C for 4 hours with a heating rate of 1 °C/min.

4.4. Characterization of zeolite catalysts

XRD measurements were performed on Bruker D8 Advance diffractometer equipped with LYNXEYE XE-T detector and CuK α radiation generator. Zeolite samples were homogenized using a mortar and pestle and loaded into plastic holders. Diffractograms were obtained in the 2 θ range between 3° and 40°.

Physisorption measurements were performed on Micrometrics 3Flex volumetric Surface Area Analyzer using nitrogen as the adsorptive. A sample was outgassed at 110 °C for 1 hour, with a heating rate of 1 °C/min, using the Micrometrics Smart Vac Prep system. Subsequently, the sample was activated at 250 °C for 8 hours with the same heating rate. Nitrogen adsorption and desorption isotherms were measured at -196 °C (77 K) in the p/p° range between 0 and 0.95. The micropore volume and external surface area were obtained using the *t*-plot method. The total micropore volume was calculated at $p/p^\circ = 0.95$.

SEM images were obtained using JEOL JSM-IT800 and a Thermo Fisher Scientific Scios 2 DualBeam FIB-SEM microscopes using secondary and backscattered electron detectors. The sample was ground and spread over carbon tape. Images were acquired at an accelerating voltage of 1 - 3 kV, a beam current of 10 – 50 pA, and a working distance up to 10 mm. The size of crystals was estimated by measuring and averaging the dimensions of at least seven crystals using the ImageJ software.

Elemental composition analysis was conducted by EDS using the FEI Quanta 200F X-ray detector integrated into the SEM system. Data collection was performed at an accelerating voltage of 15 kV, a beam current of 10 nA, and a working distance of 10 mm.

In situ FTIR spectroscopic measurements were performed using a Nicolet iS50 spectrometer equipped with an MCT/B detector. Spectra were collected in the range between 4000 cm⁻¹ and 400 cm⁻¹ with a resolution of 4 cm⁻¹. The sample was homogenized by grinding and formed into a self-supported wafer with a density between 8 to 12 mg/cm². The wafers were

activated under high vacuum at 450 °C for 4 hours with a heating rate of 5 °C/min. D₃-AN, Py and DTBPy were used as probe molecules. These probe molecules were firstly degassed, then adsorbed. D₃-AN was adsorbed at room temperature at a partial pressure of 3.5 Torr for 20 minutes. Subsequently, it was desorbed at room temperature for 20 minutes. Py was adsorbed at 150 °C at a partial pressure of 3.5 Torr for 20 minutes. Afterwards, it was desorbed at 150 °C, 250 °C, 350 °C and 450 °C for 20 minutes. DTBPy was adsorbed at 150 °C at equilibrium pressure of the probe molecule for 20 minutes and then desorbed at the same temperature for 60 minutes. Spectra were obtained (i) before activation, (ii) after activation, (iii) after adsorption of the probe molecule and (iv) after desorption of physisorbed probe molecule.

Concentrations of BAS and LAS were calculated by integrating the intensities of specific IR bands. For D₃-AN, bands at 2298 cm⁻¹, 2310 cm⁻¹ and 2326 cm⁻¹ were analysed. The acid site concentrations were calculated using molar absorption coefficients, $\epsilon(2298\text{ cm}^{-1}) = 2.05\text{ cm}/\mu\text{mol}$ and $\epsilon(2310, 2326\text{ cm}^{-1}) = 3.60\text{ cm}/\mu\text{mol}$.⁷¹ For Py, bands at 1445 cm⁻¹, 1455 cm⁻¹ and 1546 cm⁻¹ were analysed and the following molar absorption coefficients were used: $\epsilon(1445\text{ cm}^{-1}, 1455\text{ cm}^{-1}) = 1.71\text{ cm}/\mu\text{mol}$; $\epsilon(1546\text{ cm}^{-1}, 10\text{-ring}) = 1.09\text{ cm}/\mu\text{mol}$ and $\epsilon(1546\text{ cm}^{-1}, 12\text{-ring}) = 1.12\text{ cm}/\mu\text{mol}$.³⁷ For DTBPy, the band at 1615 cm⁻¹ was analysed with the corresponding molar absorption coefficient $\epsilon(1615\text{ cm}^{-1}) = 5.3\text{ cm}/\mu\text{mol}$.⁷²

4.5. *m*-Xylene isomerization

Gas-phase *m*-xylene isomerization experiments were carried out on a Micromeritics Microactivity Effi microflow experimental unit equipped with a stainless-steel fixed-bed reactor (internal diameter 11 mm). Prior to the experiment, zeolite powders were pressed, grained and sieved to obtain particle sizes between 200 μm and 500 μm . This granulated zeolite catalyst was diluted with Carborundum (particle size 500 μm) to reach consistent reactor bed volume across all samples. The reaction was performed under atmospheric pressure and at 350 °C using N₂ as the carrier gas.

The catalyst was activated at 450 °C for 90 minutes under an airflow of 200 ml/min. Subsequently, the reactor was flushed with N₂ and cooled down to the reaction temperature. Liquid *m*-xylene was pumped from a reservoir to an evaporator, with a flow between 0.2 and 0.7 ml/min, using an HPLC pump. Gaseous *m*-xylene was blended with N₂ and this mixture was fed to the catalyst bed. To prevent condensation of the reactant and products, the reactor system, connecting lines and valves were heated to approximately 145 °C. The duration of the experiment was 215 minutes time-on-stream (T-O-S).

Sampling occurred in 30-minute intervals, with the zero-sample taken at 5 minutes T-O-S. These samples, containing the reaction mixture, were analysed using an online-connected Agilent 8890 Gas Chromatograph (GC) equipped with a heated 6-port sampling valve, VF-WAXms column (30 m $\times$ 0.25 mm $\times$ 1.00 μ m) and an FID detector. Signals from the FID detector were used for the evaluation.

The values of weight hour space velocity (WHSV), which is a measure of the contact time between the reagent and catalyst, were adjusted by varying either the amount of the zeolite catalyst or the flow of *m*-xylene and calculated using Eq. (3):

$$\text{WHSV} = \frac{\rho_{m\text{-xylene}} \cdot F_{m\text{-xylene}}}{m_{\text{zeolite}}} \quad (3)$$

where $\rho_{m\text{-xylene}}$ is the density of *m*-xylene, [g/ml]; $F_{m\text{-xylene}}$ is the flow of *m*-xylene, [ml/h]; and m_{zeolite} is the mass of the zeolite catalyst in the reactor bed, [g].

Conversion of *m*-xylene, $X_{m\text{-xylene}}$, was calculated using Eq. (4):

$$X_{m\text{-xylene}} = 1 - \frac{A_{m\text{-xylene}}}{\sum A_{i, \text{norm.}}} \cdot 100 \% \quad (4)$$

where $A_{m\text{-xylene}}$ is the integrated area of the GC signal for *m*-xylene and $A_{i, \text{norm.}}$ is the integrated area of the GC signal of every compound in the reaction mixture normalized to the molar response of *m*-xylene based on product carbon number.

Yield of a product, Y_p , was determined using Eq. (5):

$$Y_p = \frac{A_{p, \text{norm.}}}{\sum A_{i, \text{norm.}}} \cdot 100 \% \quad (5)$$

where $A_{p, \text{norm.}}$ is the integrated area of the GC signal for a product and $A_{i, \text{norm.}}$ is the integrated area of the GC signal of every compound in the reaction mixture normalized to the molar response of *m*-xylene based on product carbon number.

Selectivity towards *p*-xylene, $S_{p\text{-xylene}}$, was determined using Eq. (6):

$$S_{p\text{-xylene}} = \frac{Y_{p\text{-xylene}}}{X_{m\text{-xylene}}} \cdot 100 \% \quad (6)$$

where $Y_{p\text{-xylene}}$ is the yield of *p*-xylene and $X_{m\text{-xylene}}$ is the conversion of *m*-xylene.

Ratio of disproportionation to isomerization was determined using Eq. (7):

$$\text{Dis/Iso} = \frac{Y_{\text{Dis.}}}{Y_{\text{Iso.}}} = \frac{Y_{\text{toluene}} + Y_{\text{TMB}}}{Y_{p\text{-xylene}} + Y_{o\text{-xylene}}} \quad (7)$$

where Y_{toluene} is the yield of toluene, Y_{TMB} is the yield of TMB, $Y_{p\text{-xylene}}$ is the yield of *p*-xylene and $Y_{o\text{-xylene}}$ is the yield of *o*-xylene.²

The deactivation rate of zeolite catalysts, $k_{\text{Deac.}}$, was determined using Eq. (8):

$$k_{\text{Deac.}} = \frac{X_i - X_f}{X_i} \quad (8)$$

where X_i is the initial conversion of *m*-xylene at the start of the reaction and X_f is the conversion of *m*-xylene at the end of the reaction.

5. Results and discussion

5.1. Structural, textural and acidic properties of zeolite catalysts

Structural identity and phase purity of studied zeolites were evaluated by powder XRD. The XRD patterns of commercial and synthesised 3D (CHA, MFI, BEA) and 1D (ESV, TON, AFI) unimodal zeolites were measured and compared with reference diffractograms from the IZA database (Figure 25, 26).¹⁰ For example, the structural identity of as-synthesised germanosilicate IWW-platelets and IWW-needles samples with different crystal morphologies was evident from reflections at 6.98° , 8.00° , 8.34° , 9.30° and 10.64° 2θ (CuK α radiation), that are characteristic for IWW. Moreover, the crystal structure of the IWW samples was preserved upon alumination, as confirmed by unchanged characteristic diffraction lines in Al-IWW-platelets and Al-IWW-needles samples (Figure 25, A). The broader diffraction lines in both as-synthesised and aluminated IWW-needles samples reflect smaller size of crystallites compared to the IWW-platelets samples. All unimodal zeolites under study showed identical peak position to their respective reference materials, confirming their structural identity. Furthermore, all diffractograms displayed no additional signals, indicating phase purity of all samples.

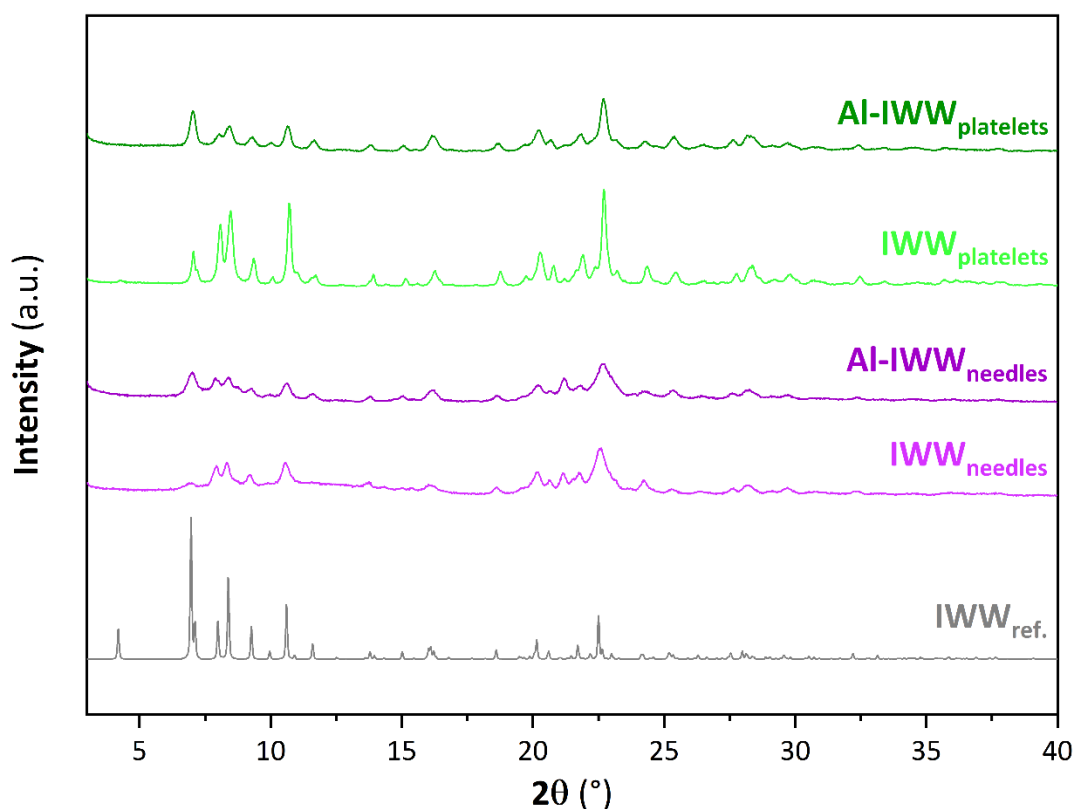


Figure 25: XRD patterns of multimodal IWW-platelets and IWW-needles samples before and after alumination (Al-IWW-platelets and Al-IWW-needles).

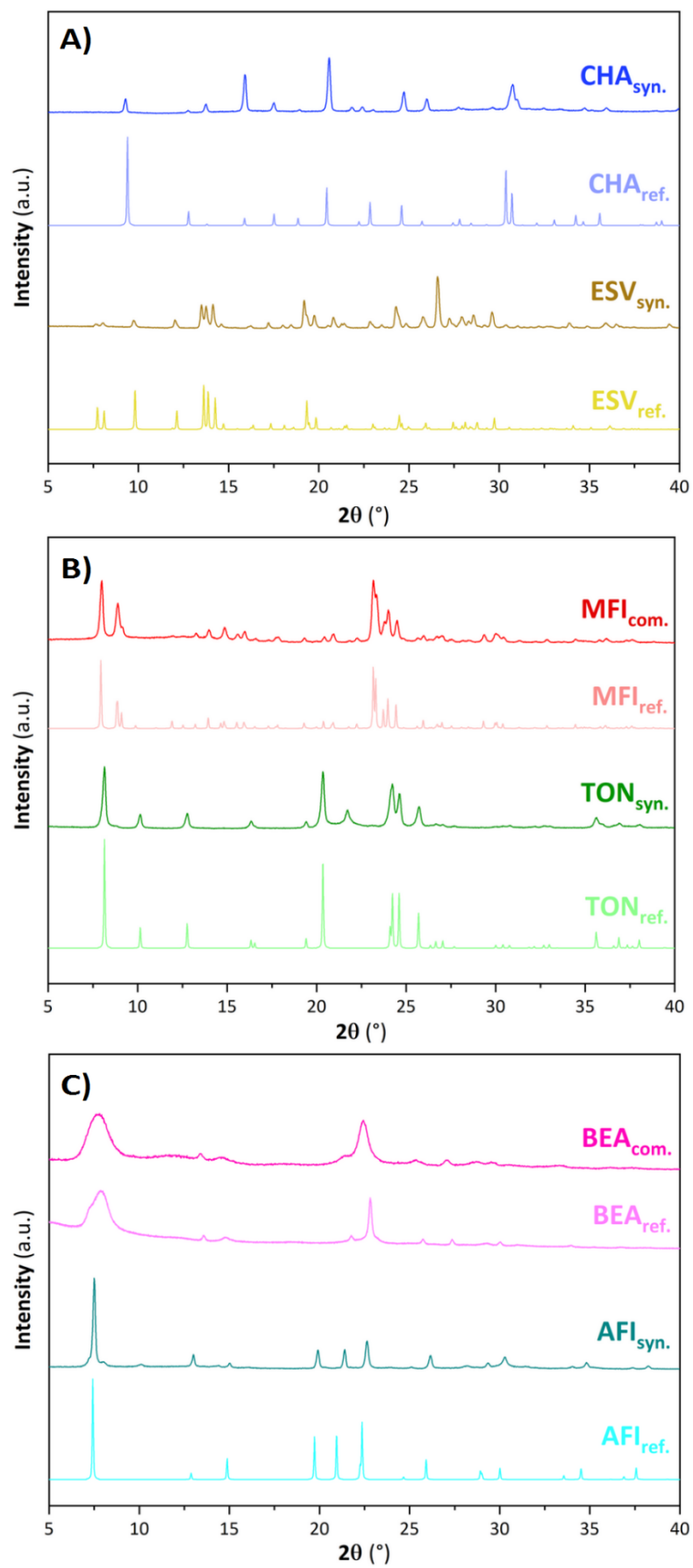


Figure 26: XRD patterns of unimodal zeolites A) 8-ring ESV and CHA; B) 10-ring TON and MFI; C) 12-ring AFI and BEA.

Crystal morphology of studied zeolites was examined by SEM imaging. Depending on the Si/Ge ratio in the reaction mixture, zeolite IWW was prepared in two crystal morphologies. While the sample IWW-platelets synthesized from a reaction mixture with Si/Ge = 4 consists of small platelet-shaped crystals ($0.43 \times 0.21 \times < 0.10 \mu\text{m}$, Table 5) stacked on top of each other, the sample IWW-needles obtained from a reaction mixture with Si/Ge = 10 consist of very thin needle-shaped crystals ($0.48 \times < 0.01 \times < 0.10 \mu\text{m}$, Table 5). Furthermore, we observed preserved crystal morphology upon Ge-for-Al substitution of the IWW zeolites, with small impurities of amorphous phase in Al-IWW-needles (Figure 27). Overall, SEM imaging confirmed successful synthesis of IWW-platelets and -needles, phase purity and high crystallinity of all samples.

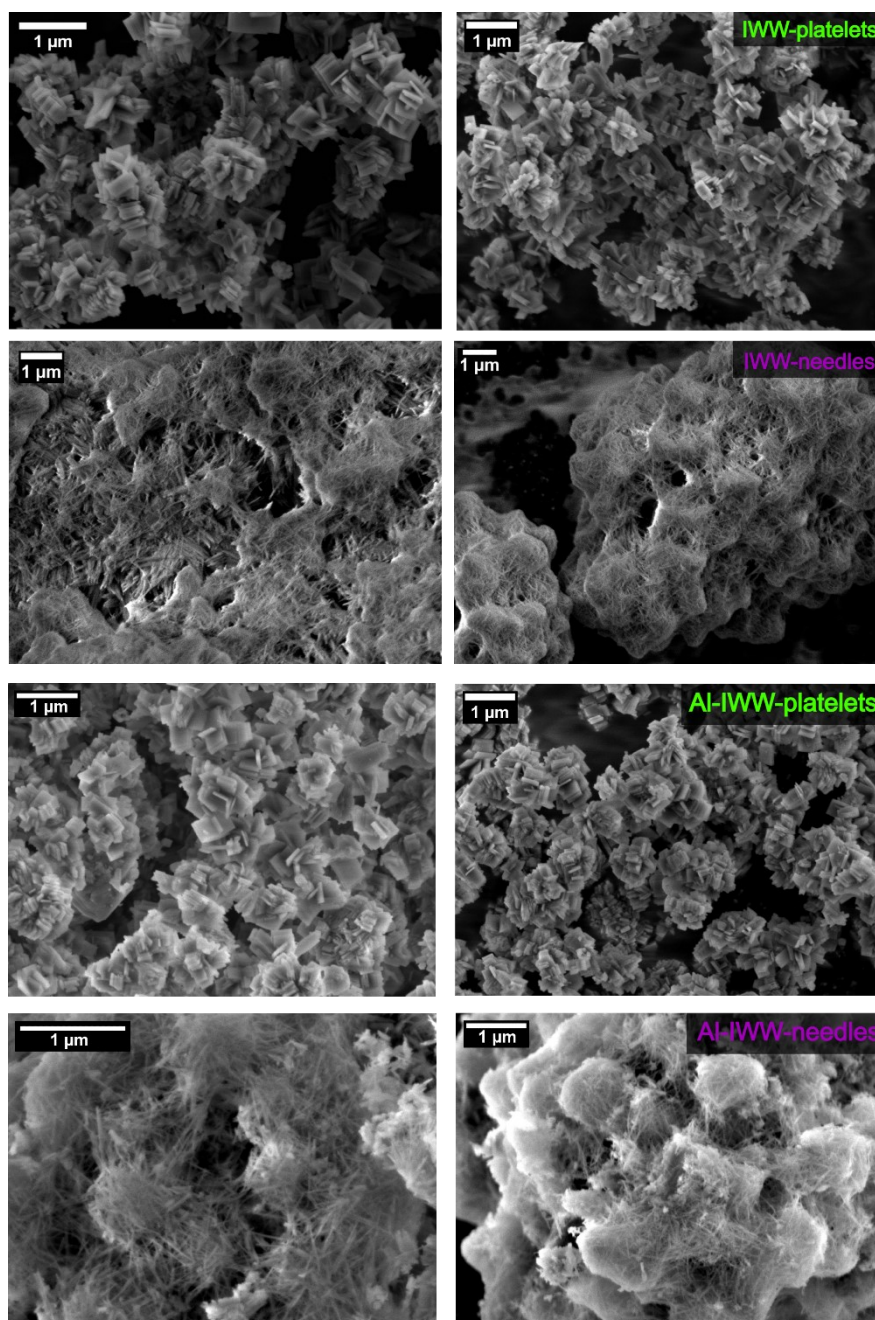


Figure 27: SEM images of IWW-platelets and IWW-needles before and after alumination.

Further analysis of IWW-needles using scanning transmission electron microscopy (STEM) revealed the spatial arrangement of perpendicular 12- and 10-ring channels within one needle crystal (Figure 28). The top view shows the 12-ring channels, indicating smaller dimension of the crystal being perpendicular to [010] crystallographic direction, while the 10-ring channels are parallel to the direction of the crystal growth. The side view also confirms this presumption. Although the side view did not show the 10-ring channels, it displayed characteristic crystalline IWW layers with a characteristic d -spacing of 1.2 nm as reported in Ref.⁷³. Therefore, one needle crystal is oriented along 10-ring channels, while short 12-ring channels penetrate the crystal from the top and the bottom. This finding is essential when evaluating the role of pore size and crystal morphology in *m*-xylene isomerization (Section 5.2.).

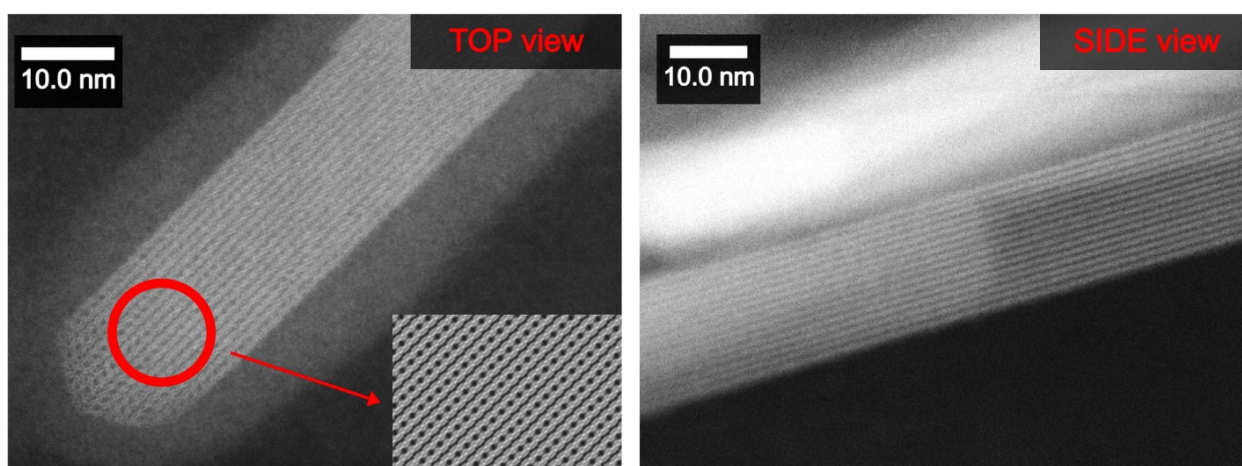


Figure 28: STEM images of the IWW-needles crystal from the top and from the side.

SEM images of 1D and 3D unimodal zeolites (Figure 29) show distinct crystal shapes and sizes, consistent with previous reports.^{70,74–78} The 8-ring ESV zeolite exhibits the largest crystals ($1.3 \times 1.0 \times 0.42 \mu\text{m}$, Table 5) with octahedral morphology, while CHA zeolite forms uniform cubic crystals with $0.1 \mu\text{m}$ edges.^{70,74} The 10-ring TON zeolite shows needles; while MFI zeolite features spheroids of rectangular prisms of $0.25 \times 0.16 \times < 0.1 \mu\text{m}$.^{75,76} The 12-ring AFI zeolite shows conical rod-like crystals ($0.40 \times 0.10 \times < 0.1 \mu\text{m}$), and BEA crystals appear as small spherical particles ($0.16 \times 0.11 \times < 0.1 \mu\text{m}$).^{77,78}

EDS was used to evaluate the elemental composition of all samples, specifically the Si/Al (Table 5) and the concentration of Al (Table 6). SEM imaging confirmed successful synthesis of IWW in two distinct morphologies and phase purity of all samples.

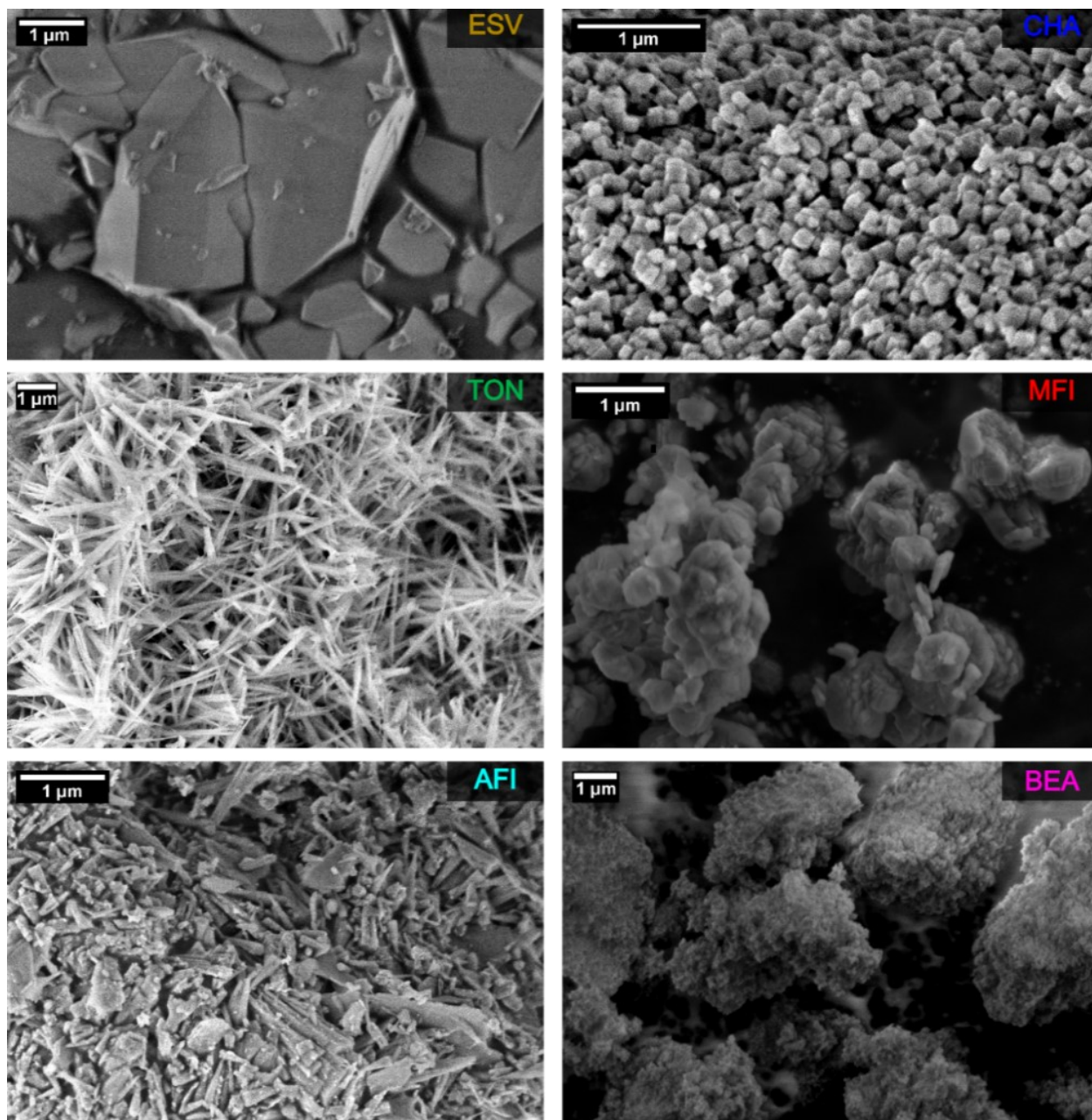


Figure 29: SEM images of unimodal zeolites ESV, CHA, TON, MFI, AFI and BEA.

Textural properties such as micropore volume and external surface area of multimodal IWW and unimodal zeolite samples were determined by N₂ physisorption. IWW samples display the type I isotherm (according to the IUPAC classification), with a significant uptake at low pressure ($p/p^\circ < 0.1$) and nearly flat region in the range of $p/p^\circ = 0.1 - 0.9$, which confirms their microporous nature (Figure 30, A). A steep increase in adsorbed volume at $p/p^\circ > 0.8$ reflects intercrystalline adsorption due to the loosely packed, small needle-like crystals of IWW-needles samples. In contrast, this feature is absent in the IWW-platelets sample, which consists of larger, more densely packed crystals that minimize interparticle voids. We could notice 1.1-1.4-fold increase in the micropore volume for IWW samples upon the Ge-for-Al

substitution, independently of crystal morphology (Table 5). This increase, consistent with previous reports, is attributed to the non-equivalent replacement of Ge by Al, which slightly increases the framework void volume.⁷⁹ Chemical analysis shows that parent IWW zeolites have a Si/Ge ratio of 4.7 (IWW-platelets) and 12.5 (IWW-needles), while aluminated samples exhibit Si/Ge = 21 (Al-IWW-platelets) and 31 (Al-IWW-needles) and Si/Al = 12 (Al-IWW-platelets) and 14 (Al-IWW-needles) supporting this interpretation. Despite substitution, the structure and crystallinity was preserved after the alumination treatment, as is apparent from the XRD patterns and SEM images.

Table 5: Crystal size, elemental composition and textural properties of studied zeolite catalysts.

Catalyst	Si/Al	Si/Ge	Crystal size μm				V_{mic} cm ³ /g	V_{tot} cm ³ /g	S_{ext} m ² /g	
ESV	10	n.d.	1.3	×	1.0	×	0.42	<0.01	<0.01	1
CHA	13	n.d.	<0.10	×	<0.10	×	<0.10	0.30	0.35	25
TON	27	n.d.	1.5	×	<0.10	×	<0.10	0.10	0.10	1
MFI	35	n.d.	0.25	×	0.16	×	<0.10	0.14	0.24	107
AFI	25	n.d.	0.40	×	<0.10	×	<0.10	0.07	0.14	37
BEA	38	n.d.	0.16	×	0.11	×	<0.10	0.15	0.66	193
IWW-platelets	n.d.	4.7	0.43	×	0.21	×	<0.10	0.17	0.24	81
IWW-needles	n.d.	12.5	0.48	×	<0.10	×	<0.10	0.16	0.39	107
Al-IWW-platelets	12	21	0.43	×	0.21	×	<0.10	0.24	0.32	70
Al-IWW-needles	14	31	0.48	×	<0.10	×	<0.10	0.17	0.41	110

Similarly to the IWW samples, majority of unimodal zeolites, apart from BEA and ESV, displayed the type I isotherm characteristic of microporous materials. Negligible adsorption of N_2 was observed for the 1D 8-ring ESV zeolite (external surface area, S_{ext} , of $1 \text{ m}^2/\text{g}$ and the micropore pore volume, V_{mic} , of less than $0.01 \text{ cm}^3/\text{g}$). The measured values were very low and did not match with those previously reported in Ref.⁷⁴ This discrepancy is likely due to the inability of N_2 molecules, with a kinetic diameter of 0.364 nm , to penetrate in depth of the 8-ring pores of ESV ($0.35 \times 0.47 \text{ nm}$), particularly in the case of large zeolite crystals, such as those synthesized in this study (Table 5). Zeolite BEA displays an isotherm with a steep increase in adsorption volume at $p/p^\circ < 0.1$ and a slope in the range of $p/p^\circ = 0.1 - 0.9$ with a hysteresis loop, which resulted from capillary condensation. These features are characteristic of a

combination of type I and type IV isotherms and result from interparticle porosity, as previously reported for small BEA crystals.⁷⁷

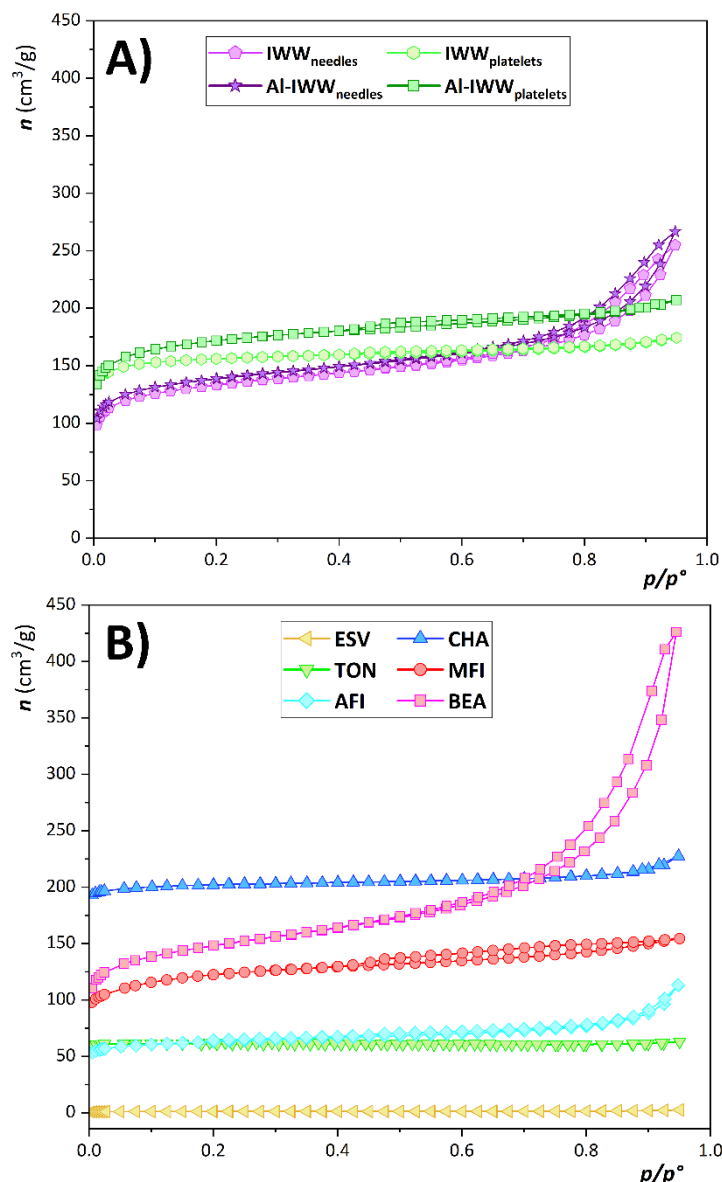


Figure 30: The N₂ physisorption isotherms of A) IWW-platelets and IWW-needles before and after alumination; B) unimodal zeolites.

A clear distinction in textural properties between 1D and 3D unimodal zeolites is observed (Table 5). The external surface area correlates with zeolite crystal size and is higher for materials with smaller crystals (Table 5). N₂ adsorption in 1D 8-ring ESV showed very small pore volume (<0.01 cm³/g) compared to 3D 8-ring CHA, where CHA exhibits the largest micropore volume (0.30 cm³/g) among all studied zeolites. This was previously attributed to the presence of spacious cavities within the CHA structure.⁷⁰ Consistently to the literature reports, 1D 10-ring TON exhibits a micropore volume approximately 1.4-fold as small as 3D 10-ring MFI, while 1D 12-ring AFI and 3D 12-ring BEA follow a similar trend.^{77,80,81} Notably,

the micropore volume values determined for the zeolites under the study (except ESV with large crystals) fall within the range previously reported in the literature, supporting not only the successful synthesis and post-synthesis modification of studied zeolites but also the accessibility of micropores, which is crucial for catalytic application.

The concentrations of acid sites, both Brønsted and Lewis, were assessed by FTIR spectroscopy by utilizing basic probe molecules of varying sizes. D₃-AN (kinetic diameter ~0.38 nm) was used to quantify the total acid site concentration, as this probe molecule can access the acid centres in all 8-, 10- and 12-ring pores. Py (0.54 nm) has a size comparable to that of the targeted product in xylene isomerization reaction, *p*-xylene (see Section 5.2.), and was used to probe acid sites relevant to catalysis. DTBPy (0.79 nm) was employed to assess acid sites located on the external surface of 8- and 10-ring unimodal zeolites as its size prevents diffusion into <12-ring micropores. The concentration of acid sites accessible to each probe molecule is considered as an indicator allowing to rationalize the performance of studied zeolites in *m*-xylene isomerization.

Figure 31, A shows the OH-region of the FTIR spectra (3800 cm⁻¹ – 3400 cm⁻¹) for all activated zeolite samples. Characteristic bands at 3743 cm⁻¹ for external silanol vibration and at 3728 cm⁻¹ for internal silanol O-H vibration are present in all spectra. In the case of ESV, the low intensity of the band at 3743 cm⁻¹ can be attributed to the large size of the ESV crystals (1.3×1.0×0.42 μm, Table 5), that results in a lower concentration of external silanol groups, whereas the broad band at 3500 cm⁻¹ indicates incomplete activation of the zeolite. Apart from the ESV spectrum, the absence of the O-H stretching band around 3650 cm⁻¹, typical of adsorbed water, indicates successful removal of physisorbed water during the thermal pretreatment prior to probe molecule adsorption analysis. The characteristic band at 3610 cm⁻¹ is attributed to O-H vibration in bridging hydroxyl groups (i.e., BAS). For the IWW samples, this band appears after alumination (Al-IWW-platelets and Al-IWW-needles) and thus confirms the formation of BASs upon incorporation of Al into the IWW framework. The intensity of the band is generally expected to increase with higher Al concentration in the samples as follows: BEA (0.43 mmol/g, Table 7) = MFI (0.46 mmol/g) < TON (0.60 mmol/g) < AFI (0.64 mmol/g) < Al-IWW-needles (1.12 mmol/g) < Al-IWW-platelets (1.20 mmol/g) = CHA (1.20 mmol/g) < ESV (1.54 mmol/g). However, this correlation is not clearly observed in the spectra of the studied zeolites, suggesting that a significant portion of the acid sites are Lewis-type and not detectable without adsorption of a probe molecule.

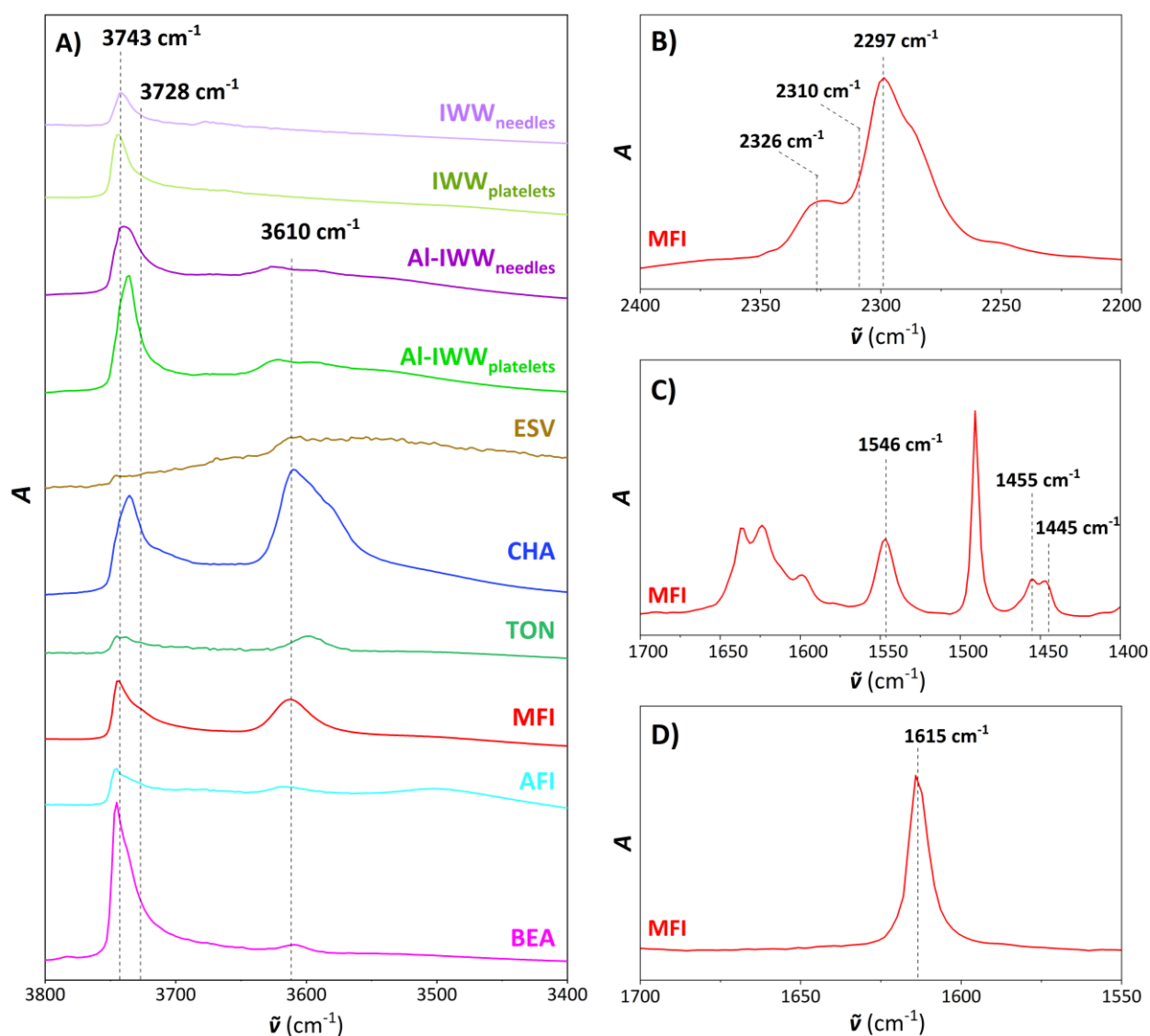


Figure 31: FTIR spectra depicting A) characteristic bands in the OH-region after the activation of the studied zeolites; and characteristic bands after adsorption of probe molecules in the activated MFI zeolite: B) D₃-AN; C) Py and D) DTBPy.

The overall concentration of acid sites was measured by adsorbing D₃-AN as the probe molecule and evaluating characteristic bands shown in Figure 31, B: BAS at 2297 cm⁻¹, weak LAS at 2310 cm⁻¹ and strong LAS at 2326 cm⁻¹. Based on the calculated values, the concentration of acid sites accessible for D₃-AN ranges from 0.06 to 0.70 mmol/g across the samples, with BAS fractions between 39% and 88%. Notably, the number of acid sites accessible for D₃-AN was lower than the total Al content, as reflected by the Σ_{AN}/Al (Table 6), that ranges from 0.04 to 0.80. This discrepancy is commonly observed in the literature. For instance, the results of Zholobenko et al. suggest (BAS + LAS)/Al ratios between 0.47 and 0.82 for various zeolites.³⁷ For the studied zeolites, this ratio was significantly lower in the case of 1D unimodal zeolites (0.04 for ESV, 0.28 for TON, 0.16 for AFI) compared to 3D unimodal

zeolites (0.58 for CHA, 0.80 for MFI, 0.72 for BEA) and multimodal IWW catalysts (0.51 for both Al-IWW-needles and Al-IWW-platelets). As we can exclude the inaccessibility of BAS for D₃-AN (disappearance of 3610 cm⁻¹ band of bridging ≡Si-(OH)-Al≡ groups after D₃-AN adsorption is observed for all the samples), the result is most probably related to variations in the spatial distribution and coordination environment of aluminium, that affect the strength and accessibility of LASs, rendering some, that inactive or undetectable by D₃-AN under the applied conditions.

Concentration of acid sites accessible for Py was evaluated based on the characteristic bands shown in Figure 31, C: 1546 cm⁻¹ for BAS, 1445 cm⁻¹ and 1455 cm⁻¹ for LAS. No acid sites were accessible to Py in unimodal 8-ring zeolites ESV and CHA. In contrast, Py accessed the same number of acid sites as D₃-AN in the unimodal 12-ring zeolites AFI and BEA, and in the multimodal Al-IWW samples of both morphologies, as is apparent from the Σ_{Py}/Al values (Table 6).

Table 6: Concentration of BASs and LASs in multimodal IWW and in unimodal zeolites, determined by FTIR spectroscopy of adsorbed probe molecules of variable sizes.

Catalyst	$c(\text{Al})^a$ mmol/g	$c(\text{D}_3\text{-AN})^b$ mmol/g				$c(\text{Py})^b$ mmol/g				$c(\text{DTBPy})^b$ mmol/g	
		BAS	LAS	Σ	Σ _{AN} /Al	BAS	LAS	Σ	Σ _{Py} /Al	BAS	BAS _{DTBPy} / Σ _{BAS}
ESV	1.54	0.04	0.02	0.06	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CHA	1.20	0.47	0.23	0.70	0.58	n.d.	n.d.	n.d.	n.d.	0.03	0.06
TON	0.60	0.15	0.02	0.17	0.28	0.29	0.02	0.31	0.52	0.01	0.02
MFI	0.46	0.25	0.12	0.37	0.80	0.26	0.11	0.36	0.78	0.03	0.12
AFI	0.64	0.05	0.06	0.11	0.17	0.08	0.07	0.15	0.23	0.04	0.67
BEA	0.43	0.14	0.17	0.31	0.72	0.20	0.15	0.35	0.81	0.19	1
Al-IWW- platelets	1.20	0.30	0.31	0.61	0.51	0.29	0.23	0.53	0.44	0.30	1
Al-IWW- needles	1.12	0.22	0.36	0.57	0.51	0.32	0.27	0.59	0.53	0.23	1

^a – based on EDS results

^b – based on *in situ* FTIR spectroscopic results

Concentration of BAS accessible for DTBPy was evaluated based on the characteristic band at 1615 cm^{-1} shown in Figure 31, D. DTBPy cannot access and therefore detect LAS due to steric hindrance from the bulky tert-butyl groups at the 2 and 6 positions of the aromatic ring, that limit the access of the nitrogen donor to the coordinatively unsaturated Al sites acting as electron acceptors. Based on the calculated values, all 8- and 10-ring unimodal zeolites showed negligible concentration of external BASs ($0.01 - 0.03\text{ mmol/g}$), representing $< 12\%$ of the total Brønsted acidity determined with $\text{D}_3\text{-AN}$. In contrast, all BAS detected by smaller probe molecules were also accessible to DTBPy in the 3D 12-ring BEA zeolite and the multimodal Al-IWW zeolites. A clear difference in acid site accessibility to DTBPy was observed between 12-ring zeolites with 1D and 3D pore systems: only 67 % of BAS were accessible to DTBPy in 1D AFI compared to 100% in 3D BEA.

The comprehensive acidity characterization of the synthesized zeolites reveals two important trends:

- 1) The total BAS concentrations vary widely across the zeolites ($0.04 - 0.47\text{ mmol/g}$, Table 6). Multimodal Al-IWW catalysts exhibit BAS concentrations comparable to the benchmark MFI zeolite ($0.22 - 0.30\text{ mmol/g}$), while unimodal 1D zeolites such as ESV and AFI showed much lower values ($0.04 - 0.05\text{ mmol/g}$). This variation in active sites number, along with differences in pore size and dimensionality, is expected to strongly influence *m*-xylene conversion in the isomerization reaction.
- 2) The concentration of external BAS is negligible in 8- and 10-ring unimodal zeolites ($<0.03\text{ mmol/g}$; $<12\%$ of total BAS), suggesting a minimal role in catalysis.

Overall, as will be shown in the following section of this thesis, the synthesized zeolites characterized in detail for their structural, textural, and acidic properties, provided a comprehensive set of catalysts for investigating the influence of pore architecture on *p*-xylene selectivity in *m*-xylene isomerization under optimized conditions of the catalytic experiment.

5.2. Catalytic properties of zeolite catalysts in *m*-xylene isomerization

The catalytic performance of studied zeolites was analysed based on *m*-xylene conversion, *p*-xylene selectivity, Dis/Iso, *p*-xylene/*o*-xylene and *p*-xylene yield. The unimodal 3D 10-ring zeolite MFI was used as the reference catalyst because of its industrial significance in *m*-xylene isomerization, but also due to its medium 10-ring channel system. Its 10-ring channel system is known to promote high *p*-xylene selectivity, while its 3D network supports a steady conversion and minimizes deactivation. Under reaction conditions of 350 °C and WHSV = 4.4 h⁻¹, the MFI catalyst achieved a conversion of 48% and a *p*-xylene selectivity of 63%, with no noticeable deactivation over 215 min on-stream (Figures 32 and 33). In line with prior reports showing minimal contribution of the bimolecular mechanism in 10-ring channels and their intersections, MFI exhibited a near-zero Dis/Iso ratio (0.01) and a *p*-xylene/*o*-xylene of 1.8, both characteristic of a monomolecular isomerization pathway.⁶⁰

A direct comparison between unimodal zeolites, with variable dimensionality and pore sizes, and multimodal IWW zeolites at similar WHSVs does not clearly reveal the effect of pore size or channel architecture on key catalytic performance characteristics in *m*-xylene isomerization such as *p*-xylene selectivity, *p*-xylene/*o*-xylene and Dis/Iso. Mentioned parameters are strongly dependent on the conversion and vary widely among the studied catalysts due to significant differences in BAS concentrations (0.03–0.47 mmol/g, Table 6).⁵⁸

5.2.1. *m*-Xylene isomerization: the effect of pore system in zeolite catalysis

At comparable WHSVs (4.4 – 8.8 h⁻¹), *m*-xylene conversion influenced by both pore architecture and acid site concentration ranged from 0 to 48% (Figure 32, A). To isolate the effect of pore structure, the values of WHSV were tuned by changing the amount of catalyst or the flow of *m*-xylene (4.4 – 40 h⁻¹), yielding a narrower range of conversion between 20% and 35%, for better comparison (Figure 32, B).

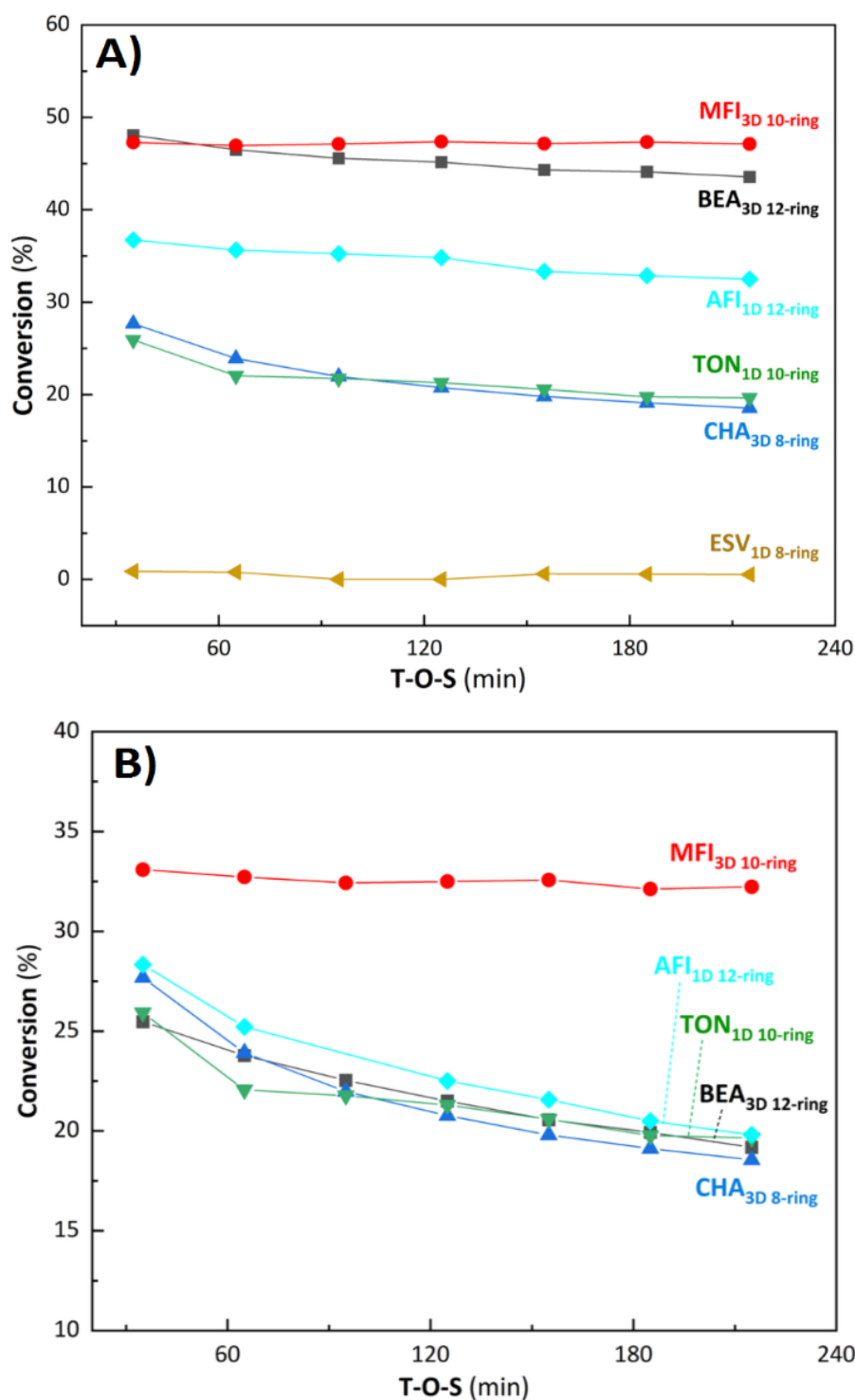


Figure 32: Conversion of *m*-xylene vs. T-O-S over unimodal zeolites at 350 °C ESV (1D 8-ring), TON (1D 10-ring), AFI (1D 12-ring), CHA (3D 8-ring), MFI (3D 10-ring) and BEA (3D 12-ring) at A) WHSV 4.4 – 8.8 h⁻¹; B) WHSV 4.4 – 40 h⁻¹.

The 8-ring pores of unimodal zeolites ESV and CHA are virtually inaccessible to *m*-xylene, whose molecular diameter exceeds the dimensions of the pore opening. *m*-Xylene has a median diameter of 0.73 nm and enters pores with diameters of at least 0.584 nm, according to Ref.⁶⁵ The inability of *m*-xylene to penetrate small 8-ring channels of ESV is evident from

the low *m*-xylene conversion over ESV (Figure 32, A), that reaches only 1-2%. In contrast, CHA demonstrates high *p*-xylene selectivity of 58% at 20% *m*-xylene conversion. Considering the marginal concentration of BAS on the external surface of CHA crystals detected by DTBPy (Table 6), which are unlikely to contribute to shape-selective *m*-xylene isomerization, this exceptional catalytic performance can be attributed to the dynamic alterations in both the zeolite framework and the reacting molecules under reaction conditions, that facilitate the movement through the 8-ring pores.^{82,83}

We suggest that the combination of dynamic flexibility and high acidity of CHA promotes monomolecular isomerization of *m*-xylene to *p*-xylene as indicated by Dis/Iso of 0.04 and a *p*-xylene/*o*-xylene of 1.5 (Figure 33, B), both comparable to those of MFI. In contrast, the poor activity of the ESV catalyst can be explained by less pronounced dynamic flexibility of its picnic-basket shaped pores (Figure 4) and very low concentration of acid sites accessible for the molecules, as evidenced by *in situ* FTIR spectroscopic studies (Table 6).

Among the studied zeolites, the 10-ring unimodal zeolites TON and MFI are the most selective towards *p*-xylene. Both zeolites initially display a starting of 63%, with TON increasing to 68% and surpassing MFI after 1 hour onstream. Increasing selectivity towards *p*-xylene with time can be explained by partial blockage of the 1D pore system in TON by deposition of coke, that narrows the pore opening and thus limits the formation of larger *o*- and *m*- isomers. This is supported by an increasing *p*-xylene/*o*-xylene from ~1.8 to 2.0 after 3 hours on-stream.

Furthermore, both TON and MFI display the lowest Dis/Iso of 0.01, which confirms that monomolecular isomerization of *m*-xylene is favoured by the 10-ring pore. No deactivation was observed for 3D MFI, that showed steady catalytic performance throughout the entire catalytic experiment.

The unimodal 3D 12-ring zeolite BEA displays similar *m*-xylene conversion to MFI, despite having lower BAS concentration (0.14 mmol/g for BEA vs. 0.25 mmol/g for MFI, Table 6) and 1.4-fold shorter contact time (WHSV = 6.0 h⁻¹ for BEA and 4.4 h⁻¹ for MFI, Figure 31 A). However, BEA catalyst exhibits the lowest *p*-xylene selectivity (44%) among all studied zeolites. This can be attributed to the large 12-ring pores and their intersections, that promote the bimolecular mechanism and facilitate the formation of biphenyl intermediates, that are subsequently transformed to TMBs, as indicated by the highest Dis/Iso value of ~0.30 (Figure 33, B). These findings agree with the previous reports on large-pore zeolites, Ref.⁸⁴⁻⁸⁶

In contrast, the 1D 12-ring zeolite AFI achieved higher selectivity than BEA after 35 minutes on-stream (51% and 44%, respectively), despite having a similar 12-ring size along with a larger pore diameter. Over time, *p*-xylene selectivity increased up to 60%, while the Dis/Iso decreased from 0.18 to 0.11 after 215 minutes on-stream. This trend likely results from partial pore blockage due to the formation of coke, which restrict the formation of larger intermediates and favour monomolecular isomerization.

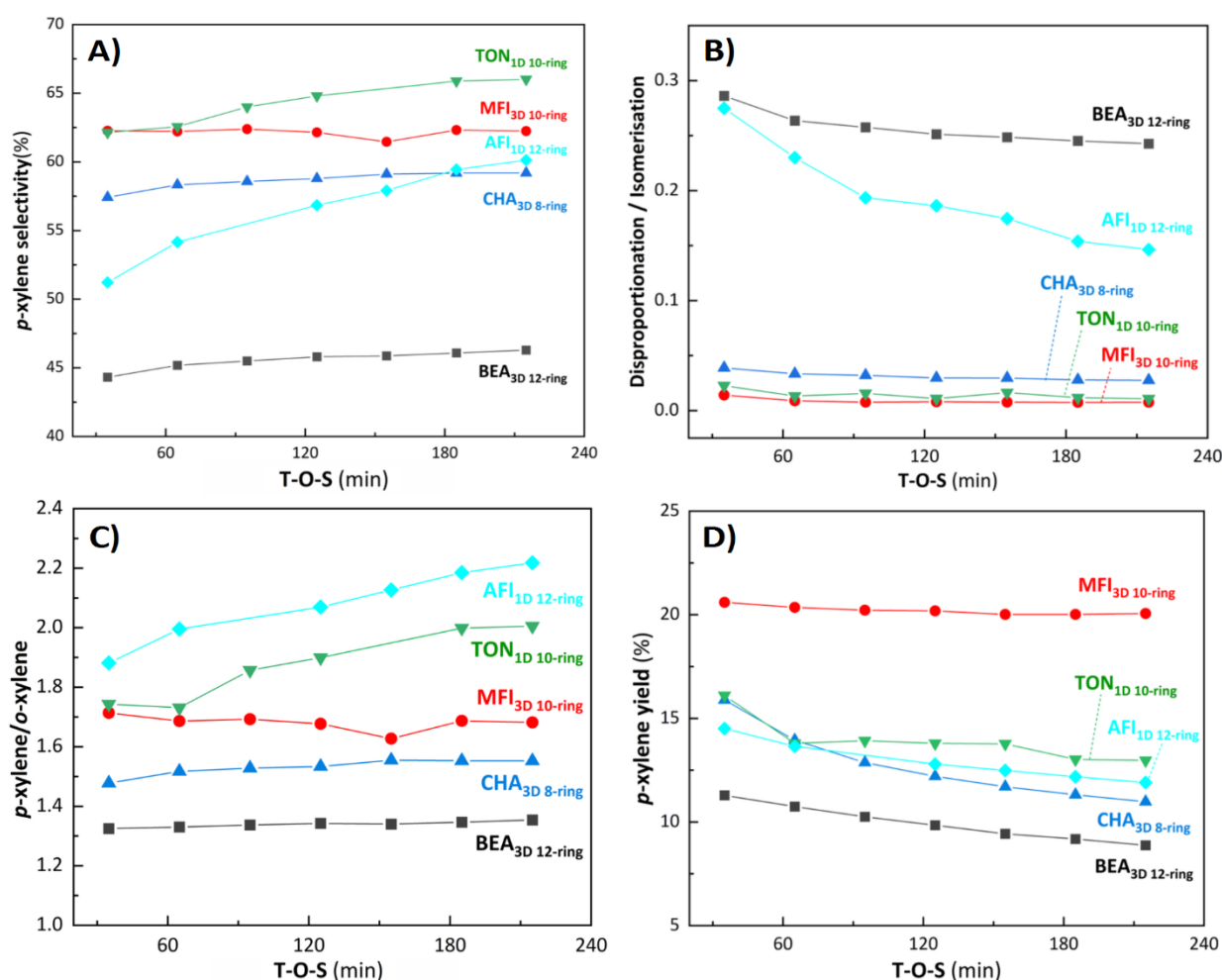


Figure 33: T-O-S dependence of A) *p*-xylene selectivity, B) Dis/Iso; C) *p*-xylene/*o*-xylene; D) *p*-xylene yield over unimodal zeolites at variable WHSV values of 4.4 – 40 h⁻¹.

The difference between 1D and 3D unimodal zeolites is notable when comparing not only *m*-xylene conversion, but also their deactivation behaviour after 215 minutes onstream. On one hand, the 1D 10-ring TON displays the deactivation rate of 24% compared to a minute 2.5% drop for 3D 10-ring MFI. On the other hand, the 1D 12-ring AFI and 3D 12-ring BEA show higher deactivation rates of 30% and 25%, respectively, likely due to the accumulation of coke deposits in their larger pores.

The *p*-xylene selectivity among unimodal zeolites decreases in the order: TON (1D 10-ring) > MFI (3D 10-ring) > AFI (1D 12-ring) ~ CHA (3D 8-ring) >> BEA (3D 12-ring). This trend reflects an increasing contribution of bimolecular disproportionation with either larger pore size (e.g., 1D 10-ring TON vs. 1D 12-ring AFI) or increased pore dimensionality (e.g., 1D 10-ring TON vs. 3D 8-ring CHA).

All in all, the 8-ring pore zeolites can be active in *m*-xylene isomerization and achieve *p*-xylene selectivity comparable to the industrially relevant MFI. The 10-ring pore zeolites, either with 1D or 3D pore system, favour monomolecular isomerization of *m*-xylene, suppress bimolecular side-reactions and exhibit high *p*-xylene selectivity. The 12-ring pore zeolites promotes bimolecular side-reactions, such as xylene disproportionation, and although partial deactivation by coke can enhance *p*-xylene selectivity, it remains lower than that achieved with 10-ring zeolites.

5.2.2. *m*-Xylene isomerization: the effect of crystal morphology in IWW zeolite catalyst

A comparison between the catalytic behaviour of multimodal Al-IWW zeolites with platelet- and needle-like crystals and unimodal zeolites enabled us to address the impact of IWW pore architecture and crystal morphology on *m*-xylene isomerization. Catalytic performance was referenced against MFI, while the WHSV values were varied in the range 4.4 - 40 h⁻¹. Across all tested WHSVs, both Al-IWW samples consistently showed greater *m*-xylene conversion than MFI and other unimodal zeolites (Figure 34).

At long contact time (WHSV 4.4 h⁻¹), Al-IWW-platelets and Al-IWW-needles exhibited similar conversions (~65%), notably exceeding that of MFI zeolite (~47 %). Given their comparable BAS concentrations (0.26 - 0.32 mmol/g, Table 6), the higher conversion of Al-IWW catalysts is attributed to enhanced molecular transport through their 12-ring pore system. With decreasing contact time (increase in WHSV from 4.4 to 20 and 40 h⁻¹), *m*-xylene conversion steadily decreased in MFI (47 → 35 → 32%) and Al-IWW-needles (65 → 55 → 44%), consistent with common explanations: (i) shorter residence time limits the extent of the reaction, (ii) diffusion constraints hinder access to active sites, and (iii) insufficient time to reach equilibrium lowers observed conversion. In contrast, Al-IWW-platelets maintained more stable conversion (65 → 60% → 55%) across the same WHSV range, suggesting more efficient catalytic performance under reduced contact time. This stability may theoretically originate from (i) higher intrinsic activity of BASs in Al-IWW-platelets leading to faster reaction rates; (ii) higher accessibility of BASs leading to their better utilization at high throughput; or (iii) more favourable pore arrangement, minimizing internal diffusion limitations. However, hypothesis (i) was ruled out by pyridine-FTIR thermodesorption results, which showed similar acid strength distributions in both IWW morphologies. Hypothesis (ii) was also excluded based on FTIR-DTBPY results, which showed lower concentrations of accessible BASs in Al-IWW-platelets (Table 6), despite their more stable performance. Thus, the superior *m*-xylene conversion achieved over Al-IWW-platelets is most likely due to more efficient mass transport. We assume that platelet-shaped crystals (0.43 × 0.21 × <0.10 μm) offer more balanced pore orientation and diffusion paths compared to the needle-shaped Al-IWW crystals, where 10-ring channels run along the long edge of a crystal (~0.48 μm), and 12- and 8-ring pores are confined to much shorter dimensions (<0.1 μm). This anisotropy in the needle morphology likely restricts diffusion and contributes to the observed decline in conversion at higher WHSVs.

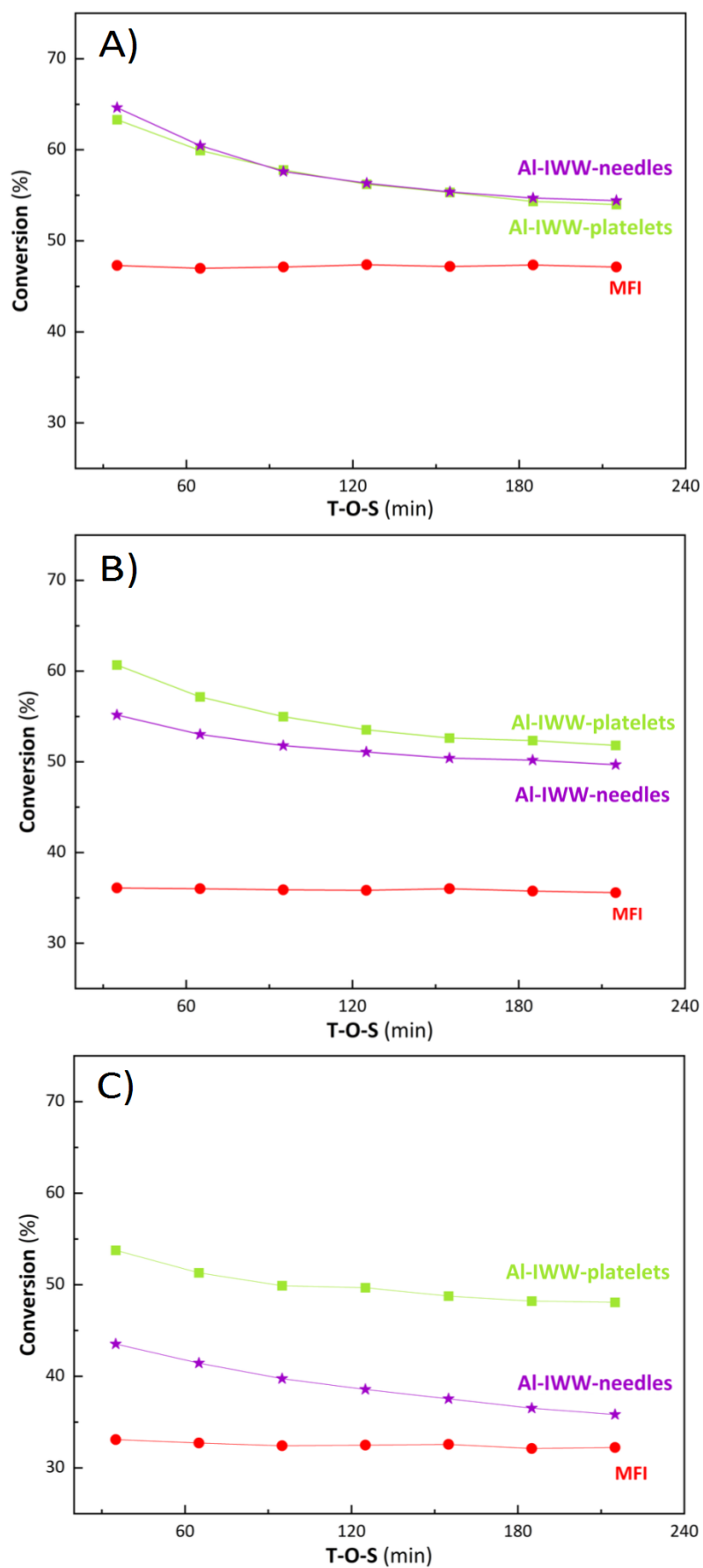


Figure 34: Conversion of *m*-xylene vs. T-O-S over MFI and Al-IWW zeolites at 350 °C and at WHSV of A) 4.4 h⁻¹; B) 20 h⁻¹; C) 40 h⁻¹.

To evaluate the selectivity of the Al-IWW zeolite catalysts, we tuned the values of WHSV by changing either the amount of catalyst or the flow of *m*-xylene, narrowing the range of conversion to 44 - 60%. This minimized the influence of variable BAS concentration throughout the samples. Morphology-related differences in *p*-xylene selectivity between the Al-IWW-platelets and -needles are apparent from Figure 35 A. While MFI, with 50% *p*-xylene selectivity under the tested conditions, outperforms both Al-IWW catalysts, the needle-shaped sample Al-IWW-needles (45%) is more selective than Al-IWW-platelets (41%). The superior selectivity of MFI can be attributed to its unimodal 10-ring pore system, that sterically hinders bulkier *m*- and *o*-xylenes. In the case of Al-IWW samples, the contribution of the active sites within the 12-ring channels is non-negligible and lowers the selectivity towards the targeted isomer. This is further confirmed by *in situ* FTIR-DTBPY adsorption measurements, which showed that ~100% and ~72% of BASs (measured with Py) are located either in the 12-ring pores or on the surface of Al-IWW-platelets and Al-IWW-needles, respectively. The higher *p*-xylene selectivity in Al-IWW-needles can be thus attributed to its crystal morphology – long 10-ring channels, aligned along the needle axis, akin to selective environment of unimodal TON and MFI. Furthermore, a significant fraction of BASs in these 10-ring channels drive the formation of *p*-xylene through monomolecular isomerization, as verified by lower Dis/Iso (Figure 33, B) of Al-IWW-needles (decreasing from 0.43 to 0.15 over time) than Al-IWW-platelets (0.77 to 0.25). MFI outperforms both samples with a Dis/Iso of 0.03, underscoring the role of 12-ring channels in Al-IWWs in facilitating side reactions. The increase in *p*-xylene selectivity and decrease in Dis/Iso over time for both Al-IWW samples may result from partial blockage of the larger 12-ring pores, as previously observed in unimodal AFI and BEA.

While MFI outperforms Al-IWW catalysts in both *p*-xylene selectivity and Dis/Iso, all samples show a similar *p*-xylene/*o*-xylene of ~1.05 (Figure 35, C). At similar conversions, this trend outlines that Al-IWW samples yield a larger variety of side-products, such as TMBs, while maintaining a consistent distribution of xylene isomers.

Overall, at similar *m*-xylene conversion, MFI with its unimodal 10-ring pore system demonstrates the highest *p*-xylene selectivity and promotes the monomolecular isomerization pathway (Dis/Iso = 0.03). Clear differences are observed between the multimodal Al-IWW catalysts with platelet- and needle-like crystals: the long 10-ring channels of Al-IWW-needles act similarly to those of MFI and show higher *p*-xylene selectivity than Al-IWW-platelets, where the contribution of the 12-ring channel lowers the *p*-xylene selectivity.

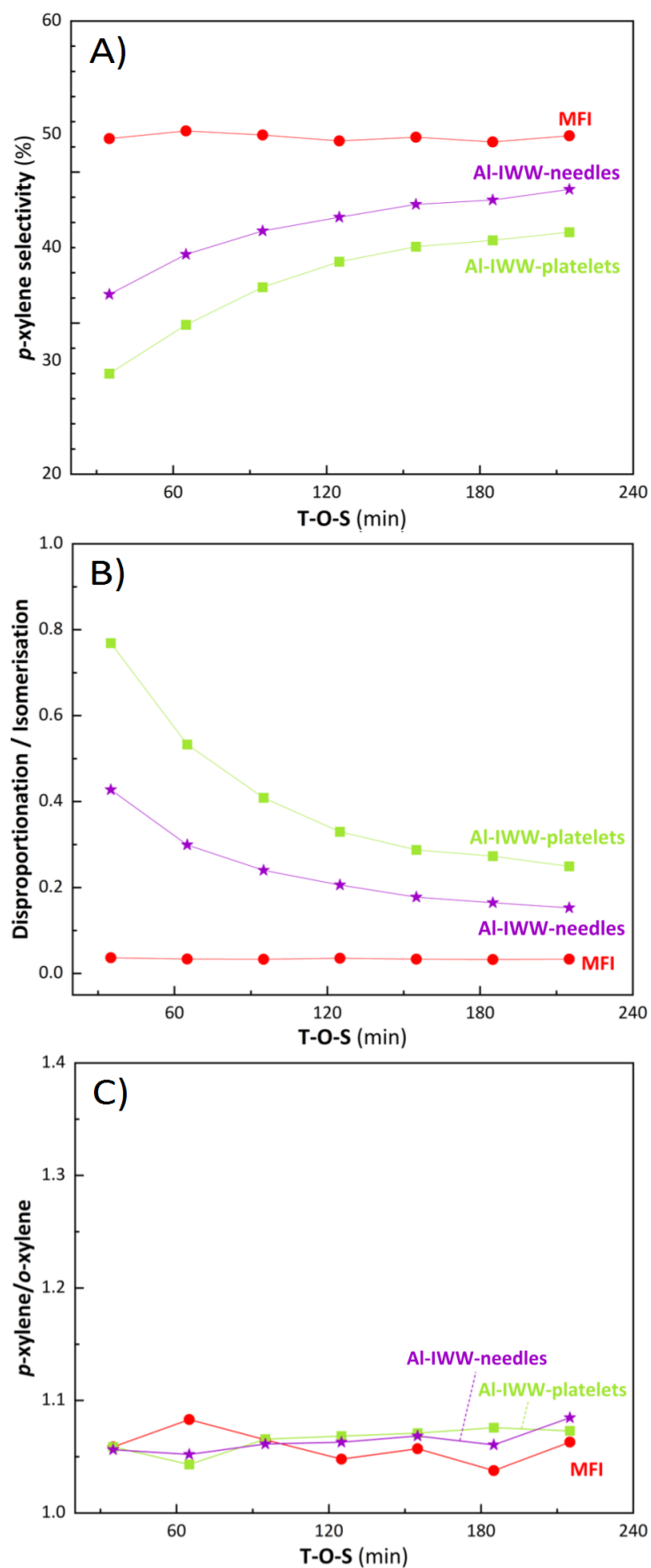


Figure 35: T-O-S dependence of A) *p*-xylene selectivity, B) Dis/Iso; C) *p*-xylene/*o*-xylene; over zeolites MFI, Al-IWW-platelets and -needles at variable WHSV values of 4.4 – 40 h⁻¹.

At similar *m*-xylene conversion, *p*-xylene yield follows the same trend as *p*-xylene selectivity: MFI displays the highest *p*-xylene yield (24%), followed by Al-IWW-needles (23%) and Al-IWW-platelets (20%) (Figure 36). The effect of contact time on the *p*-xylene yield was further investigated by performing the experiment at low (4.4 h^{-1}), medium (20 h^{-1}) and high (40 h^{-1}) WHSV.

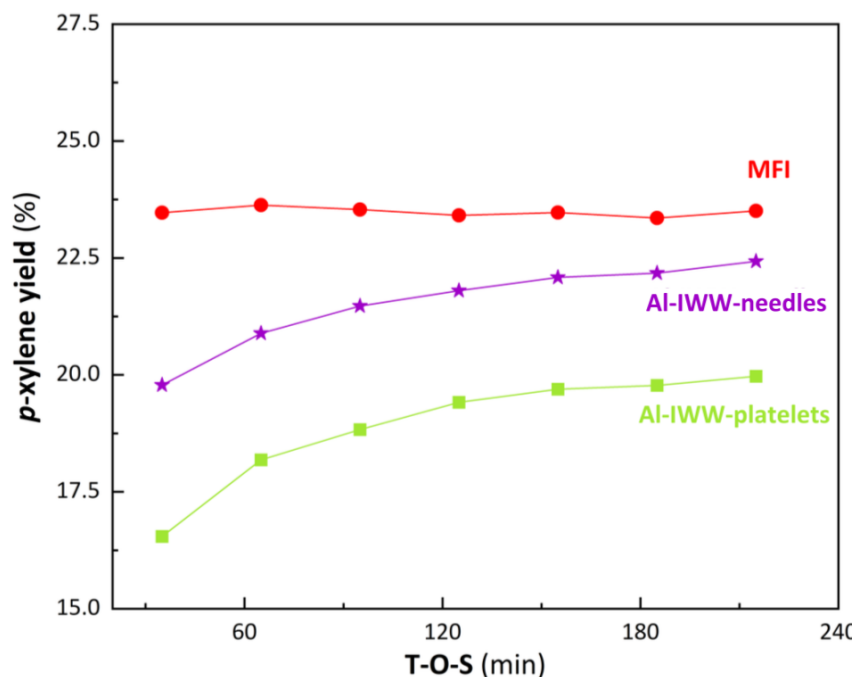


Figure 36: *p*-Xylene yield vs. T-O-S over MFI and Al-IWW zeolites at $350 \text{ }^{\circ}\text{C}$ and at WHSV $4.4 - 20 \text{ h}^{-1}$.

At low WHSV = 4.4 h^{-1} , no crystal morphology-related differences in *p*-xylene yield are observed between Al-IWW-needles and -platelets. MFI displays the highest yield (24%), while both Al-IWW samples reach ~20% after 215 minutes on-stream (Figure 37, A). With increasing WHSV from 4.4 to 20 h^{-1} , *p*-xylene yield decreases for MFI ($24\% \rightarrow 22\%$), but remains unchanged for Al-IWW-platelets (20%) and increases for Al-IWW-needles ($20\% \rightarrow 23\%$).

Further increase in WHSV from 20 to 40 h^{-1} results in decreased *p*-xylene yield over MFI ($22\% \rightarrow 20\%$) and an increased *p*-xylene yield over Al-IWW-platelets (23%), that corresponds to their high conversion under these conditions. Al-IWW-needles show a *p*-xylene yield of 20%, similar to MFI (Figure 37, C). The distinct dependence of *p*-xylene yield on WHSV for IWW zeolites with different morphologies and a superior behaviour of Al-IWW-platelets compared to Al-IWW-needles at shorter contact times can be attributed to several factors, such as differences in diffusion pathways, pore accessibility, and the spatial distribution of BASs.

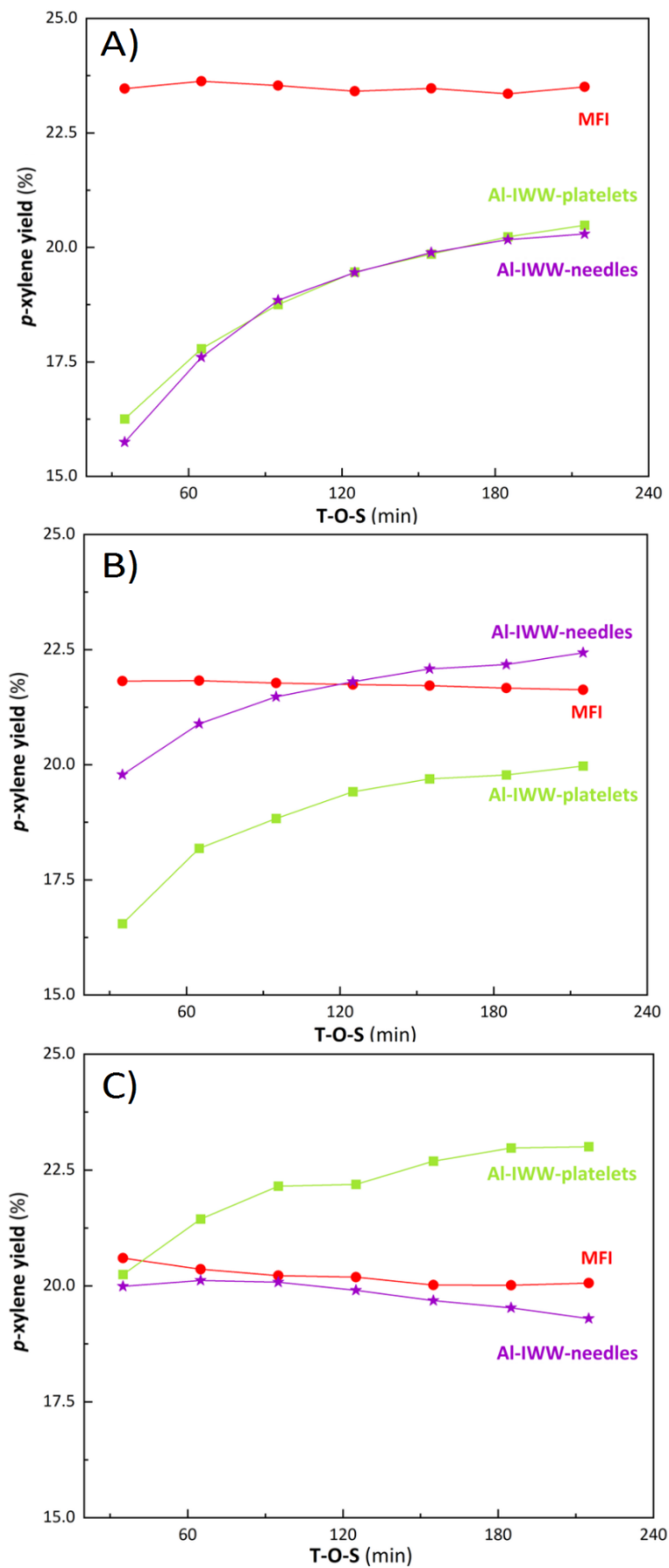


Figure 37: *p*-Xylene yield vs. T-O-S over MFI and Al-IWW zeolites at 350°C at WHSV of A) 4.4 h⁻¹; B) 20 h⁻¹; C) 40 h⁻¹.

We assume that unimodal 3D MFI with narrow 10-ring channels suffers from significant diffusion limitations at higher WHSVs, that restrict the access of *m*-xylene to internal active sites and thereby lower *m*-xylene conversion (Figure 34) and *p*-xylene yield (Figure 37). In contrast, the multimodal pore system of Al-IWW of both crystal morphologies allows for more efficient diffusion, likely through their larger 12-ring channels. Al-IWW-needles, featuring long 10-ring channels aligned with the crystal axis, exhibit enhanced selectivity at intermediate WHSV = 20 h⁻¹, where diffusion is likely still sufficient to reach internal BASs. However, at high WHSV = 40 h⁻¹, the short contact time may not allow *m*-xylene to fully access the internal sites, which leads to a decline in *p*-xylene yield. Alternatively, Al-IWW-platelets with platelet-like crystals (0.43 × 0.21 × <0.10 μm, Table 5) offer shorter diffusion paths compared to Al-IWW-needles, that become advantageous under high WHSV. In addition, the relatively high concentration of BASs located in the 12-ring pores or on the external surface in Al-IWW-platelets may be more catalytically relevant at high WHSV, where diffusion is limited and reactions primarily occur at or near the external surface of the zeolite catalyst. This leads to increased activity and higher *p*-xylene yields. For Al-IWW-needles, we assume the BASs are embedded deeper in the 10-ring channels, which requires longer residence times of reagents for effective catalysis.

Similarly to the trend observed in *p*-xylene selectivity, the *p*-xylene yield for the Al-IWW samples gradually increases over time on-stream, which is attributed to the partial pore blockage due to coke formation (Figure 37, A). No deactivation is observed for the MFI catalyst across the studied WHSV values. However, for the Al-IWW catalysts, the deactivation is evident and varies with WHSV values (Figure 34). At low WHSV = 4.4. h⁻¹, both Al-IWW-platelets and -needles display a deactivation rate of ~16%. At a WHSV of 20 h⁻¹, the deactivation rate for Al-IWW-platelets remains practically unchanged (~15%), while it decreases to 10% for Al-IWW-needles, showing a similar behaviour to MFI. The trend reverses at high WHSV = 40 h⁻¹: Al-IWW-platelets display a lower deactivation rate (11%) than Al-IWW-needles (18%) after 215 minutes on-stream. Faster deactivation of Al-IWW-needles at high WHSV can be attributed to smaller crystal size and their elongated shape, which may enhance coke deposition and block internal pores more rapidly. In contrast, shorter diffusion paths in Al-IWW-platelets help suppresses fast deactivation by facilitating better mass transport and limiting coke accumulation.

All in all, the combination of 10- and 12-ring channels in a 3D interconnected pore system positions Al-IWW as a competitive alternative to the benchmark MFI zeolite for gas-

phase *m*-xylene isomerization, especially at short contact times. Clear crystal morphology-related differences in catalytic behaviour were observed between the Al-IWW-platelets and Al-IWW-needles, particularly in terms of *p*-xylene selectivity. Al-IWW-needles catalyst, featuring long 10-ring channels aligned with the direction of crystal growth, promoted monomolecular *m*-xylene isomerization, suppressed side-reactions such as *m*-xylene disproportionation and yielded more *p*-xylene at similar conversions. On the other hand, Al-IWW-platelets catalyst characterized by shorter diffusion paths allows facile access to BASs, that becomes particularly advantageous at shorter contact time. This contributes to the relatively high *p*-xylene yield, that can be achieved over Al-IWW-platelets at short residence times, despite lower intrinsic selectivity compared to the needle-shaped counterpart. These findings highlight the critical role of crystal morphology along with pore architecture in governing the catalytic behaviour of IWW zeolites in *m*-xylene isomerisation, and suggest possible strategies for optimizing their performance, particularly with respect to *p*-xylene selectivity.

6. Conclusion

This thesis investigated the catalytic behaviour of IWW zeolite in *m*-xylene isomerization in relation to the features of its pore architecture and crystal morphology. A systematic study was first conducted using unimodal 1D and 3D zeolite catalysts ESV, CHA, TON, MFI, AFI and BEA with 8-, 10-, and 12-ring pores. Each of these unimodal zeolites exhibited catalytic behaviour specific to its pore size and channel connectivity. Insights gained from these model systems were then applied to the multimodal IWW zeolite, that contains isolated 8- and 12-ring channels, intersected perpendicularly by 10-ring channels. Furthermore, by preparing IWW catalysts in two crystal morphologies (as platelet- and as needle-like crystals), we could evaluate the effect of IWW zeolite crystal size and shape on catalytic performance in *m*-xylene isomerization.

Unimodal aluminosilicate zeolite catalysts and multimodal IWW germanosilicate zeolites were prepared *via* hydrothermal synthesis. Furthermore, post-synthesis Ge-for-Al substitution was employed to introduce Brønsted acidity into the IWW zeolite, with successful incorporation confirmed by *in situ* FTIR spectroscopy. Thorough characterization of crystal morphology, structural, textural and acidic properties of all zeolite catalysts under study was performed using SEM, STEM, XRD, N₂ physisorption and *in situ* FTIR spectroscopy. Catalytic testing was carried out in gas-phase *m*-xylene isomerization in a flow reactor with experimental conditions (e.g., WHSV values) carefully adjusted to enable accurate comparison of *p*-xylene selectivity, Dis/Iso, and *p*-xylene yield across the set of zeolites.

Commercial zeolite MFI was used as the reference catalyst due to its industrial significance. The MFI catalyst achieved the highest *p*-xylene selectivity (63%) and restricted undesirable side-reactions, as evidenced by the lowest Dis/Iso (0.03), with no noticeable deactivation after 215 min on-stream.

The pore size of zeolite catalysts was shown to influence the selectivity in *m*-xylene isomerization as follows:

- **8-ring zeolites** (e.g., CHA) were unexpectedly active and selective, achieving up to 58% *p*-xylene selectivity with negligible side-reactions (Dis/Iso ~0.05) - the behaviour attributed to dynamic flexibility of CHA framework promoting monomolecular isomerization of *m*-xylene to *p*-xylene.
- **10-ring zeolites** (e.g., TON and MFI) show the highest *p*-xylene selectivity (68% for TON, 63% for MFI) and minimal side-reactions (Dis/Iso 0.03) - the behaviour

attributed to their ability of suppressing bimolecular transformations of reacting aromatics.

- **12-ring zeolites** (e.g., BEA) showed the lowest *p*-xylene selectivity (45%) and a high Dis/Iso (~ 0.3) due to the prevalence of bimolecular side-reactions, such as disproportionation.

These results demonstrate that larger pore sizes and higher pore dimensionality increase the likelihood of undesired bimolecular pathways of *m*-xylene transformation.

IWW zeolite catalysts with multimodal pore system of isolated 8- and 12-ring channels, intersected perpendicularly by 10-ring channels, exceeded the reference MFI catalyst in *m*-xylene conversion across all tested conditions, despite comparable BAS concentrations (0.26 - 0.32 mmol/g). This outperformance of MFI by IWW catalysts was attributed to enhanced mass transport through their larger 12-ring channels.

Comparative analysis of the catalytic performance of multimodal IWW zeolite catalysts with distinct crystal morphologies, either platelet- or needle-like, further revealed pronounced morphology-related effects in *m*-xylene isomerization:

- **IWW catalyst with needle-like crystals**, containing long 10-ring channels aligned along the direction of crystal growth, promoted *p*-xylene formation through monomolecular isomerization (Dis/Iso = 0.15) and achieved *p*-xylene selectivity, approaching that of MFI.
- **IWW catalyst with platelet-like crystals** showed lower selectivity (Dis/Iso = 0.30) but outperformed both benchmarking MFI catalyst and IWW zeolite with needle-like crystals in terms of *p*-xylene yields, especially at shorter contact times (WHSV 20 h⁻¹ and 40 h⁻¹). This enhanced performance has been attributed to more efficient molecular transport within the platelet-shaped crystals, that offer a more balanced pore orientation and shorter diffusion paths than the elongated, needle-like IWW crystals.

In conclusion, the combination of 10- and 12-ring pores in the IWW zeolite catalyst, along with its tuneable crystal morphology, presents a promising approach to achieving an optimal balance between selectivity and activity in the industrially important *p*-xylene synthesis. However, further optimization, such as selective passivation of acid sites in the 12-ring channels or targeted placement of active sites within the 10-ring channels, may be required to suppress non-selective pathways and enhance overall *p*-xylene selectivity over IWW catalysts.

7. References

1. Shi, J., Wang, Y., Yang, W., Tang, Y. & Xie, Z. Recent advances of pore system construction in zeolite-catalyzed chemical industry processes. *Chem. Soc. Rev.* **44**, 8877–8903 (2015).
2. Remperová, N., Přech, J., Kubů, M., Gołabek, K., Miñambres, J. F., Hsieh, M.-F., Turrina, A. & Mazur, M. Gas-phase isomerisation of m-xylene on isorecticular zeolites with tuneable porosity. *Catal. Today* **390–391**, 78–91 (2022).
3. Veselý, O., Shamzhy, M., Roth, W. J., Morris, R. E. & Čejka, J. Controlling Crystal Morphology of Anisotropic Zeolites with Elemental Composition. *Cryst. Growth Des.* **24**, 2406–2414 (2024).
4. Corma, A., Rey, F., Valencia, S., Jordá, J. L. & Rius, J. A zeolite with interconnected 8-, 10- and 12-ring pores and its unique catalytic selectivity. *Nat. Mater.* **2**, 493–497 (2003).
5. Millini, R. & Bellussi, G. Zeolite Science and Perspectives. in *Zeolites in Catalysis: Properties and Applications* (eds. Čejka, J., Morris, R. E. & Nachtigall, P.) 0 (The Royal Society of Chemistry, 2017).
6. Smeets, S. & Zou, X. Zeolite Structures. in *Zeolites in Catalysis: Properties and Applications* (eds. Čejka, J., Morris, R. E. & Nachtigall, P.) 0 (The Royal Society of Chemistry, 2017).
7. McCusker, L. B. & Baerlocher, C. Chapter 2 - Zeolite Structures. in *Studies in Surface Science and Catalysis* (eds. Čejka, J., van Bekkum, H., Corma, A. & Schüth, F.) vol. 168 13–37 (Elsevier, 2007).
8. C. Medeiros-Costa, I., Dib, E., Nesterenko, N., Dath, J.-P., Gilson, J.-P. & Mintova, S. Silanol defect engineering and healing in zeolites: opportunities to fine-tune their properties and performances. *Chem. Soc. Rev.* **50**, 11156–11179 (2021).
9. Pophale, R., Cheeseman, P. A. & Deem, M. W. A database of new zeolite-like materials. *Phys. Chem. Chem. Phys.* **13**, 12407–12412 (2011).
10. IZA. https://europe.iza-structure.org/IZA-SC/ftc_table.php.
11. McCusker, L. B. & Baerlocher, C. Zeolite structures. in *Studies in Surface Science and Catalysis* (eds. Čejka, J. & van Bekkum, H.) vol. 157 41–64 (Elsevier, 2005).
12. Baerlocher, C., Meier, W. M. & Olson, D. *Atlas of Zeolite Framework Types*. (Elsevier, Amsterdam New York, 2001).
13. Auerbach, S. M., Carrado, K. A. & Dutta, P. K. Handbook of Zeolite Science and Technology.
14. Campbell, B. J., Cheetham, A. K., Bellussi, G., Carluccio, L., Perego, G., Millini, R. & Cox, D. E. The synthesis of the new zeolite, ERS-7, and the determination of its structure by simulated annealing and synchrotron X-ray powder diffraction. *Chem. Commun.* 1725–1726 (1998)
15. Marler, B. Silica-ZSM-22: synthesis and single crystal structure refinement. *Zeolites* **7**, 393–397 (1987).
16. Khoo, D. Y., Awala, H., Mintova, S. & Ng, E.-P. Synthesis of AlPO-5 with diol-substituted imidazolium-based organic template. *Microporous Mesoporous Mater.* **194**, 200–207 (2014).

17. Shamzhy, Mariya, Opanasenko, M., Concepción, P. & Martínez, A. New trends in tailoring active sites in zeolite-based catalysts. *Chem. Soc. Rev.* **48**, 1095–1149 (2019).
18. Yu, J. Chapter 3 - Synthesis of Zeolites. in *Studies in Surface Science and Catalysis* (eds. Čejka, J., van Bekkum, H., Corma, A. & Schüth, F.) vol. 168 39–103 (Elsevier, 2007).
19. Cundy, C. S. Synthesis of zeolites and zeotypes. in *Studies in Surface Science and Catalysis* (eds. Čejka, J. & van Bekkum, H.) vol. 157 65–90 (Elsevier, 2005).
20. Shamzhy, M. & Ramos, F. S. de O. Tuning of acidic and catalytic properties of IWR zeolite by post-synthesis incorporation of three-valent elements. *Catal. Today* **243**, 76–84 (2015).
21. Čejka, J., Bekkum, H. van, Corma, A. & Schueth, F. *Introduction to Zeolite Science and Practice, Volume 168, Third Edition*. (Elsevier Science, Amsterdam ; Boston, 2007).
22. Weitkamp, J. Zeolites and catalysis. *Solid State Ion.* **131**, 175–188 (2000).
23. Shamzhy, M. & Čejka, J. Zeolites as Solid Acid Catalysts. in *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering* B9780443157424000806 (Elsevier, 2024).
24. Strohmaier, K. G. Synthesis of Zeolites. in *Zeolites in Catalysis: Properties and Applications* (eds. Čejka, J., Morris, R. E. & Nachtigall, P.) 0 (The Royal Society of Chemistry, 2017).
25. Grand, J., Awala, H. & Mintova, S. Mechanism of zeolites crystal growth: new findings and open questions. *CrystEngComm* **18**, 650–664 (2016).
26. Gómez-Hortigüela, L. & Cambor, M. Á. Introduction to the Zeolite Structure-Directing Phenomenon by Organic Species: General Aspects. in *Insights into the Chemistry of Organic Structure-Directing Agents in the Synthesis of Zeolitic Materials* (ed. Gómez-Hortigüela, L.) 1–41 (Springer International Publishing, Cham, 2018).
27. Vinaches, P., Bernardo-Gusmão, K. & Pergher, S. B. C. An Introduction to Zeolite Synthesis Using Imidazolium-Based Cations as Organic Structure-Directing Agents. *Molecules* **22**, 1307 (2017).
28. Cundy, C. S. & Cox, P. A. The Hydrothermal Synthesis of Zeolites: History and Development from the Earliest Days to the Present Time. *Chem. Rev.* **103**, 663–702 (2003).
29. The Powder Diffraction Pattern. in *Fundamentals of Powder Diffraction and Structural Characterization of Materials* (eds. Pecharsky, V. K. & Zavalij, P. Y.) 151–202 (Springer US, Boston, MA, 2009).
30. Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquerol, J. & Sing, K. S. W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **87**, 1051–1069 (2015).
31. Inkson, B. J. 2 - Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for materials characterization. in *Materials Characterization Using Nondestructive Evaluation (NDE) Methods* (eds. Hübschen, G., Altpeter, I., Tschuncky, R. & Herrmann, H.-G.) 17–43 (Woodhead Publishing, 2016).
32. Ul-Hamid, A. *A Beginners' Guide to Scanning Electron Microscopy*. (Springer International Publishing, Cham, 2018).

33. Goldstein, J. I., Newbury, D. E., Michael, J. R., Ritchie, N. W. M., Scott, J. H. J. & Joy, D. C. *Scanning Electron Microscopy and X-Ray Microanalysis*. (Springer, New York, NY, 2018).
34. Theophanides, T. *Infrared Spectroscopy - Materials Science, Engineering and Technology*. (2012).
35. Karge, H. G. Characterization by IR spectroscopy. in *Verified Syntheses of Zeolitic Materials* 69–71 (Elsevier, 2001).
36. Bordiga, S., Lamberti, C., Bonino, F., Travert, A. & Thibault-Starzyk, F. Probing zeolites by vibrational spectroscopies. *Chem. Soc. Rev.* **44**, 7262–7341 (2015).
37. Zholobenko, V., Freitas, C., Jendrlin, M., Bazin, P., Travert, A. & Thibault-Starzyk, F. Probing the acid sites of zeolites with pyridine: Quantitative AGIR measurements of the molar absorption coefficients. *J. Catal.* **385**, 52–60 (2020).
38. Shamzhy, M., Přech, J., Zhang, J., Ruaux, V., El-Siblani, H. & Mintova, S. Quantification of Lewis acid sites in 3D and 2D TS-1 zeolites: FTIR spectroscopic study. *Catal. Today* **345**, 80–87 (2020).
39. Shamzhy, M., Gil, B., Opanasenko, M., Roth, W. J. & Čejka, J. MWW and MFI Frameworks as Model Layered Zeolites: Structures, Transformations, Properties, and Activity. *ACS Catal.* **11**, 2366–2396 (2021).
40. Gołabek, K., Shamzhy, M., Kubů, M., Soták, T., Magyarová, Z., Hronec, M. & Čejka, J. Adsorption and catalytic study of cyclopentyl methyl ether formation: structure-activity interplay in medium-pore zeolites. *Appl. Mater. Today* **28**, 101505 (2022).
42. X-ray tube | X-ray imaging, radiation, medical imaging | Britannica. <https://www.britannica.com/technology/X-ray-tube> (2025).
43. Storck, S., Bretinger, H. & Maier, W. F. Characterization of micro- and mesoporous solids by physisorption methods and pore-size analysis. *Appl. Catal. Gen.* **174**, 137–146 (1998).
44. Chen, N. Y. *Shape Selective Catalysis in Industrial Applications, Second Edition*,. (CRC Press, Boca Raton, 2023).
45. Li, Y. & Yu, J. Emerging applications of zeolites in catalysis, separation and host–guest assembly. *Nat. Rev. Mater.* **6**, 1156–1174 (2021).
46. Vermeiren, W. & Gilson, J.-P. Impact of Zeolites on the Petroleum and Petrochemical Industry. *Top. Catal.* **52**, 1131–1161 (2009).
47. Weitkamp, J. & Hunger, M. Chapter 22 - Acid and Base Catalysis on Zeolites. in *Studies in Surface Science and Catalysis* (eds. Čejka, J., van Bekkum, H., Corma, A. & Schüth, F.) vol. 168 787–835 (Elsevier, 2007).
48. Badienezhad, M., Sohrabnezhad, S. & Samiei, A. Synergetic Effects of Hierarchical Porosity, Chemical, Acidic, and Hydrothermal Modification of the NaY Zeolite and Its Simultaneous Use in the Technology of the Fluid Catalytic Cracking (FCC). *Iran. J. Chem. Chem. Eng.* **43**, 2996–3006 (2024).
49. Yang, M., Fan, D., Wei, Y., Tian, P. & Liu, Z. Recent Progress in Methanol-to-Olefins (MTO) Catalysts. *Adv. Mater.* **31**, 1902181 (2019).

50. Goetze, J., Meirer, F., Yarulina, I., Gascon, J., Kapteijn, F., Ruiz-Martínez, J. & Weckhuysen, B. M. Insights into the Activity and Deactivation of the Methanol-to-Olefins Process over Different Small-Pore Zeolites As Studied with Operando UV–vis Spectroscopy. *ACS Catal.* **7**, 4033–4046 (2017).
51. MÉRIAUDEAU, P. & NACCACHE, C. Dehydrocyclization of Alkanes Over Zeolite-Supported Metal Catalysts: Monofunctional or Bifunctional Route. *Catal. Rev.* **39**, 5–48 (1997).
52. Guisnet, M., Gnep, N. S. & Alario, F. Aromatization of short chain alkanes on zeolite catalysts. *Appl. Catal. Gen.* **89**, 1–30 (1992).
53. Martínez, A., Arribas, M. A. & Moussa, S. Application of Zeolites in the Production of Light Olefins and BTX Petrochemical Intermediates. in *Zeolites in Catalysis: Properties and Applications* (eds. Čejka, J., Morris, R. E. & Nachtigall, P.) 0 (The Royal Society of Chemistry, 2017).
54. Perego, C. & Pollesel, P. Advances in Aromatics Processing Using Zeolite Catalysts. in *Advances in Nanoporous Materials* vol. 1 97–149 (Elsevier, 2010).
55. Al-Khattaf, S., Ali, Syed A., Aitani, Abdullah M., Žilková, Naděžda, Kubička, David & Čejka, J. Recent Advances in Reactions of Alkylbenzenes Over Novel Zeolites: The Effects of Zeolite Structure and Morphology. *Catal. Rev.* **56**, 333–402 (2014).
56. Marcilly, C. R. Where and how shape selectivity of molecular sieves operates in refining and petrochemistry catalytic processes. *Top. Catal.* **13**, 357–366 (2000).
57. Opanasenko, M. Zeolites for Fine Chemistry. in *Zeolites in Catalysis: Properties and Applications* (eds. Čejka, J., Morris, R. E. & Nachtigall, P.) 0 (The Royal Society of Chemistry, 2017).
58. Guisnet, M., Gnep, N. S. & Morin, S. Mechanisms of xylene isomerization over acidic solid catalysts. *Microporous Mesoporous Mater.* **35–36**, 47–59 (2000).
59. Byun, Y., Jo, D., Shin, D. N. & Hong, S. B. Theoretical Investigation of the Isomerization and Disproportionation of *m*-Xylene over Medium-Pore Zeolites with Different Framework Topologies. *ACS Catal.* **4**, 1764–1776 (2014).
60. Demikhova, N. R., Rubtsova, M. I., Vinokurov, V. A. & Glotov, A. P. Isomerization of Xylenes (a Review). *Pet. Chem.* **61**, 1158–1177 (2021).
61. Gonçalves, J. C. & Rodrigues, A. E. Xylene Isomerization in the Liquid Phase Using Large-Pore Zeolites. *Chem. Eng. Technol.* **39**, 225–232 (2016).
62. Liu, Y., Zhou, X., Pang, X., Jin, Y., Meng, X., Zheng, X., Gao, X. & Xiao, F.-S. Improved para-Xylene Selectivity in meta-Xylene Isomerization Over ZSM-5 Crystals with Relatively Long b-Axis Length. *ChemCatChem* **5**, 1517–1523 (2013).
63. Mirth, G., Čejka, J. & Lercher, J. A. Transport and Isomerization of Xylenes over HZSM-5 Zeolites. *J. Catal.* **139**, 24–33 (1993).
64. Zheng, S., Jentys, A. & Lercher, J. A. Xylene isomerization with surface-modified HZSM-5 zeolite catalysts: An in situ IR study. *J. Catal.* **241**, 304–311 (2006).

65. Min, H.-K., Cha, S. H. & Hong, S. B. Mechanistic Insights into the Zeolite-Catalyzed Isomerization and Disproportionation of *m*-Xylene. *ACS Catal.* **2**, 971–981 (2012).
66. Rao, G. N., Kumar, R. & Ratnasamy, P. Shape selectivity of zeolite EU-1 in reactions of aromatic hydrocarbons. *Appl. Catal.* **49**, 307–318 (1989).
67. Jones, C. W., Zones, S. I. & E. Davis, M. *m*-Xylene reactions over zeolites with unidimensional pore systems. *Appl. Catal. Gen.* **181**, 289–303 (1999).
68. Teketel, S., Lundegaard, L. F., Skistad, W., Chavan, S. M., Olsbye, U., Lillerud, K. P., Beato, P. & Svelle, S. Morphology-induced shape selectivity in zeolite catalysis. *J. Catal.* **327**, 22–32 (2015).
69. Hayasaka, K., Liang, D., Huybrechts, W., De Waele, B. R., Houthoofd, K. J., Eloy, P., Gaigneaux, E. M., van Tendeloo, G., Thybaut, J. W., Marin, G. B., Denayer, J. F. M., Baron, G. V., Jacobs, P. A., Kirschhock, C. E. A. & Martens, J. A. Formation of ZSM-22 Zeolite Catalytic Particles by Fusion of Elementary Nanorods. *Chem. – Eur. J.* **13**, 10070–10077 (2007).
70. Devos, J., Bols, M. L., Plessers, D., Goethem, C. V., Seo, J. W., Hwang, S.-J., Sels, B. F. & Dusselier, M. Synthesis–Structure–Activity Relations in Fe-CHA for C–H Activation: Control of Al Distribution by Interzeolite Conversion. *Chem. Mater.* **32**, 273–285 (2020).
71. Wichterlová, B., Tvarůžková, Z., Sobalík, Z. & Sarv, P. Determination and properties of acid sites in H-ferrierite: A comparison of ferrierite and MFI structures. *Microporous Mesoporous Mater.* **24**, 223–233 (1998).
72. Góra-Marek, K., Tarach, K. & Choi, M. 2,6-Di-*tert*-butylpyridine Sorption Approach to Quantify the External Acidity in Hierarchical Zeolites. *J. Phys. Chem. C* **118**, 12266–12274 (2014).
73. Kasneryk, V., Shamzhy, M., Zhou, J., Yue, Q., Mazur, M., Mayoral, A., Luo, Z., Morris, R. E., Čejka, J. & Opanasenko, M. Vapour-phase-transport rearrangement technique for the synthesis of new zeolites. *Nat. Commun.* **10**, 5129 (2019).
74. Bae, J. & Hong, S. B. Choline-mediated synthesis of zeolite ERS-7 via an excess fluoride approach. *Chem. Commun.* **54**, 10997–11000 (2018).
75. Okamoto, M., Nishimura, Y., Takahashi, M. & Chen, W.-H. Synthesis of Short, Needle-Shaped Crystals of TON-Type Zeolite by Addition of Inhibitors of Crystal Growth along the [001] Direction. *Cryst. Growth Des.* **18**, 6573–6580 (2018).
76. Zhao, J., Yu, H., Xu, H., He, Z., Shao, F., Lu, P. & Valtchev, V. Empowering catalysis and separation: morphology control of MFI zeolites using organic additives. *Sustain. Energy Fuels* **9**, 323–337 (2025).
77. Bok, T. O., Andriako, E. P., Knyazeva, E. E. & Ivanova, I. I. Engineering of zeolite BEA crystal size and morphology via seed-directed steam assisted conversion. *RSC Adv.* **10**, 38505–38514 (2020).
78. Hu, E., Huang, Y. L. W., Yan, Q., Liu, D. & Lai, Z. Synthesis of highly *c*-oriented AFI membranes by epitaxial growth. *Microporous Mesoporous Mater.* **126**, 81–86 (2009).

79. Shamzhy, M. V., Eliašová, P., Vitvarová, D., Opanasenko, M. V., Firth, D. S. & Morris, R. E. Post-Synthesis Stabilization of Germanosilicate Zeolites ITH, IWW, and UTL by Substitution of Ge for Al. *Chem. – Eur. J.* **22**, 17377–17386 (2016).
80. Tzanis, L., Trzpit, M., Soulard, M. & Patarin, J. High pressure water intrusion investigation of pure silica 1D channel AFI, MTW and TON-type zeolites. *Microporous Mesoporous Mater.* **146**, 119–126 (2011).
81. Li, X., Tsai, S.-T., Wu, K. C.-W., Curnow, O. J., Choi, J. & Yip, A. C. K. Morphology control of ionic-liquid-templated ZSM-22 and ZSM-5 zeolites using a two-step process and its effect on toluene methylation. *Microporous Mesoporous Mater.* **328**, 111475 (2021).
82. Hu, Z.-P., Han, J., Wei, Y. & Liu, Z. Dynamic Evolution of Zeolite Framework and Metal-Zeolite Interface. *ACS Catal.* **12**, 5060–5076 (2022).
83. Ghojavand, S., Dib, E. & Mintova, S. Flexibility in zeolites: origin, limits, and evaluation. *Chem. Sci.* **14**, 12430–12446 (2023).
84. Adair, B., Chen, C.-Y., Wan, K.-T. & Davis, M. E. Reactions of *meta*-xylene on zeolites with intersecting medium and large pores I. Basic studies. *Microporous Mater.* **7**, 261–270 (1996).
85. Kulikov, L. A., Ostroumova, V. A., Naranov, E. R., Egazar'yants, S. V., Maximov, A. L. & Karakhanov, E. A. Effects of MTW Zeolite Crystallite Morphology on Product Formation in Isomerization of m-Xylene. *Pet. Chem.* **62**, 914–923 (2022).
86. Pérez-Pariente, J., Sastre, E., Fornés, V., Martens, J. A., Jacobs, P. A. & Corma, A. Isomerization and disproportionation of m-xylene over zeolite β . *Appl. Catal.* **69**, 125–137 (1991).