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A Review of the Chemistry, Structure, Properties and Applications of Zeolites

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Abstract This review article describes the structure of zeolites starting from atomic level to the complex networks of channels and voids that permeate the material. The chemistry within the material is outlined relating it to its crystal structure. The resulting properties are described relating them to the crystal structure and the chemistry. Finally, the applications of the material are summarised relating them to the material crystal structure, chemistry and properties.

Keywords Zeolites, Zeolite crystal structure, Zeolite applications, Zeolite properties

1. General Introduction

1.1. Background

1.1.1. Introduction

Most natural zeolites are formed as a result of volcanic activity. When volcanoes erupt, magma (molten rock within the earth) breaks through the earth's crust and flows out in form of lava accompanied by gases, dust and thick ash. Volcanoes normally occur where tectonic plates are diverging or converging. In cases where such locations are on an island or near an ocean, the ejected lava and ash often flow into the sea. Upon reaching the sea, the hot lava, water and the salt from the sea undergo reactions which, over the course of thousands of years, have led to the production of crystalline solids known as zeolites [1-3].

The word zeolite is formed from two Greek words "zeo" = boil & "lithos" = stone; to mean boiling stones [4]. It was given to this type of substances in 1756, by a Swedish mineralogist named Axel Fredrik Cronstedt, who discovered them and their trait of intumescence. He observed that upon heating this mineral steam was released, as water evaporated and the zeolite seemed to be boiling because of the rapid water loss [3-6].

The water molecules that are lost on heating have been adsorbed in the pores and cavities (of dimensions ranging from 0.3 nm to 1.0 nm) present in the zeolites' crystalline structure [7]. These cavities result from the structural composition of zeolites, which is characterized by a framework of linked tetrahedra, each consisting of four O atoms surrounding a cation – usually Si. These Si-O bonds are arranged in a three-dimensional structure of silicate tetrahedra, leading to the presence of open cavities in the form of channels and cages, which are usually occupied by H_2O molecules and extra-framework cations that are commonly exchangeable. [4, 8, 9].

Heating or dehydrating zeolites results in high void volumes, which impart to the zeolite the so called ''molecular sieve'' and adsorbent properties. Molecular sieves only allow molecules of a certain size (equal to, or less than the pore size) to pass through entry channels, whereas molecules larger than the pore size are excluded. Once dehydrated, gas or liquid molecules that are small enough to pass through the channel openings may be sorbed to the inner zeolite structure, whereas larger molecules are excluded [5].

1.1.2. Chemical Composition

All zeolites are composed of an elementary structure of an aluminosilicate framework which comprises of a tetrahedral arrangement of silicon cations (Si^{4+}) and aluminium cations (Al^{3+}) that are surrounded by four oxygen anions (O^{2-}). Each oxygen ion within the Si-O and Al-O bonds connects two cations and is shared between two tetrahedrons (as shown in figure 1.1), thus yielding a macromolecular three-dimensional framework of SiO_2 and AlO_2 tetrahedral building blocks. In this arrangement of atoms, each tetrahedron consists of four O atoms surrounding a Si or Al cation, resulting in a three-dimensional structure of silicate tetrahedra with a Si:O ratio of 1:2 [10].

Some Si^{4+} ions are substituted by Al^{3+} ions, resulting in a net negative charge in the tectosilicate framework (Figures 1.2 and 1.3). This charge arises from the difference in formal valency between the $(AlO_4)^{5-}$ and $(SiO_4)^{4-}$ tetrahedrons and is normally located on one of the oxygen

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anions connected to an aluminium cation. The resulting negative sites are balanced by counterions which are usually alkaline or alkaline earth metals, such as Na^+, K^+ or Ca^{2+} in most cases. Li^+, Mg^{2+}, Sr^{2+} and Ba^{2+} are also found in some zeolites [10]. These ions are found on the external surface of zeolite, bound with the aluminosilicate structure by weaker electrostatic bonds [11, 12].

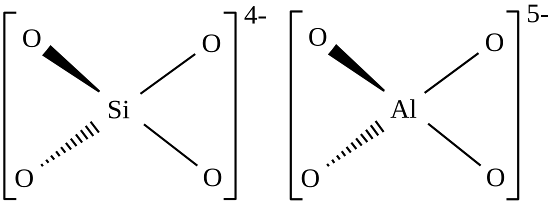


Figure 1.1. Tetrahedral arrangement of the SiO_4 and AlO_4 molecules forming unit blocks of a zeolite

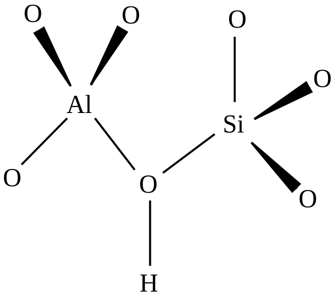


Figure 1.2. Tetrahedral arrangement of the Si-O and Al-O bonds forming a unit block of a zeolite

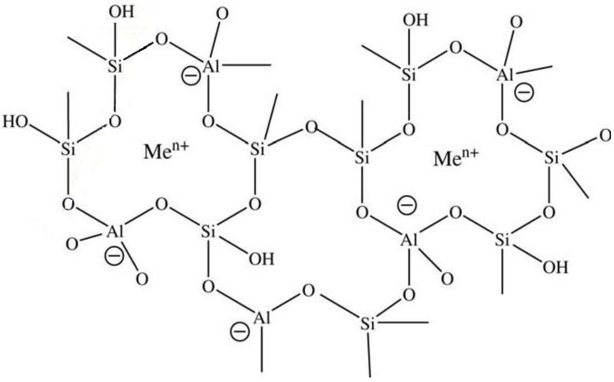


Figure 1.3. A two-dimensional representation of the framework structure of zeolites [9]. Me^{n+} signify extraframework cations

These mobile non-framework counterions – which are commonly exchangeable – are situated in cavities which result from the 3-dimenisonal Si-O/Al-O bond tetrahedra framework. H_2O molecules are also found in these cavities (which, when aligned, become channels) and are the reason why zeolites can be hydrated at low temperatures. The general chemical formula for natural zeolites is $[(Li, Na, K)_a(Mg, Ca, Sr, Ba)_d(Al_{(a+2d)}Si_{n-(a+2d)}O_{2n}]\cdot mH_2O$ [4, 8, 9, 10, 13, 14].

1.1.3. Formation of Zeolites

Many zeolites occur naturally as minerals, and are extensively mined in many parts of the world. Others are synthetic, and are made commercially for specific uses, or produced by research scientists trying to understand more about their chemistry. Almost all natural zeolites occur in cavities of volcanic lava flows [15] and therefore have to be mined. Murata *et al.,* [16] have suggested that zeolites are formed through diagenetic rock-water reactions – reactions through which the change of sediments or existing sedimentary rocks results in a different sedimentary rock during and after rock formation. These reactions also result in the production of other secondary minerals. This metamorphosis of volcanic debris leads to production of zeolites in layers or "zeolite zones" called facies [17]. The type of the zeolite formed is determined by various factors. Chief among these is the form of volcanic matter which reaches the water – whether lava or ash. The type of water involved (whether marine, fresh water lakes, ground waters or saline shallow lakes), together with the alkalinity of the water and the type and concentration of ions it contains also play a crucial part [18].

Zeolites are formed in the hardened lava either during diagenesis resulting from active geothermal systems in areas of high heat flow, during burial metamorphism of the lava pile or during hydrothermal alteration of continental basalts [19]. Zeolites form in these locations as a result of very low grade metamorphism [20, 21]. While others are formed in metamorphic regions, others form under subtle amounts of heat and pressure – conditions which can just barely be called metamorphic. Pe-piper [22] has suggested that mordenite – a zeolite named after the small community of Morden, in Canada, where it was first found – is formed through hydrothermal circulation of alkaline lake waters instead of metamorphic processes as was previously believed. Furthermore, Hay [23] has shown that zeolite formation may occur under any or a combination of the following conditions: saline, alkaline lakes or soils; deep-sea sediments; low-temperature open hydrologic systems; burial diagenesis; and hydrothermal-geothermal systems. Saline, alkaline lakes cause volcanic ash layers to alter rapidly to zeolites, resulting in the formation of relatively pure deposits.

Most of the zeolites formed during diagenetic processes in sedimentary rocks can be grouped into several types of geological environments or hydrological systems such as hydrologically open systems, hydrologically closed systems, soil and surficial deposits, deep marine sediments and marine sediments from arc-source terrains [19]. Natural zeolite ores are found in many parts of the world among rocks near active or extinct volcanoes. Most of the world's supply is obtained in Asia, Australia and Europe; with the United States contributing about one percent [24].

Zeolites are used in a variety of applications worldwide due to their unique porous properties. Their applications comprise different areas of industry inclusive of technology and environmental remediation such as pollution control and disposal of hazardous materials.

This review intends to look at the role of zeolites in modern industrial applications. These roles will be classified as (a) industrial applications (water purification); (b) medicinal applications; and (c) catalysis.

2. Crystal Structure

2.1. Structures of Zeolites

Zeolites are not an easily definable family of crystalline solids and are similarly not simple to categorise [25]. In 1997, the subcommittee on zeolites of the International Mineralogical Association, Commission on New Minerals and Mineral Names agreed that any substance with a topologically equivalent structure, also possessing essential zeolitic characteristics (i.e. a framework structure with cavities occupied by ions and water molecules which have considerable freedom of movement, permitting ion exchange, molecular "sieving", absorption, diffusion, dehydration, reversible dehydration and catalysis) be classified as a zeolite irrespective of its Si and Al content in tetrahedral sites [4, 26]. Subsequently, a revised definition of a zeolite was proposed as follows:

> *A zeolite mineral is a crystalline substance with a structure characterized by a framework of linked tetrahedra, each consisting of four O atoms surrounding a cation. This framework contains open cavities in the form of channels and cages. These are usually occupied by H_2O molecules and extra-framework cations that are commonly exchangeable. The channels are large enough to allow the passage of guest species. In the hydrated phases, dehydration occurs at temperatures mostly below about 400 °C and is largely reversible. The framework may be interrupted by (OH, F) groups; these occupy a tetrahedron apex that is not shared with adjacent tetrahedra. [4].*

2.1.1. Primary and Secondary Building Units

The crystal structures of zeolites are normally categorized into primary building units (PBUs) and secondary building units (SBUs). The PBUs are the $(SiO_4)^{4+}$ and $(AlO_4)^{5+}$ tetrahedra. These combine by sharing oxygens with adjacent tetrahedra to form a spacial arrangement of simple geometric forms – the SBUs. The SBUs come in a variety of forms – some being single rings, double rings, polyhedra or even more complex units which are linked together in a variety of ways to produce a unique system of channels and cages. A zeolite's unit cell always contains an integral number of SBUs. At present, 23 different types of SBUs are known to exist. These are shown in Figure 2.1 [25].

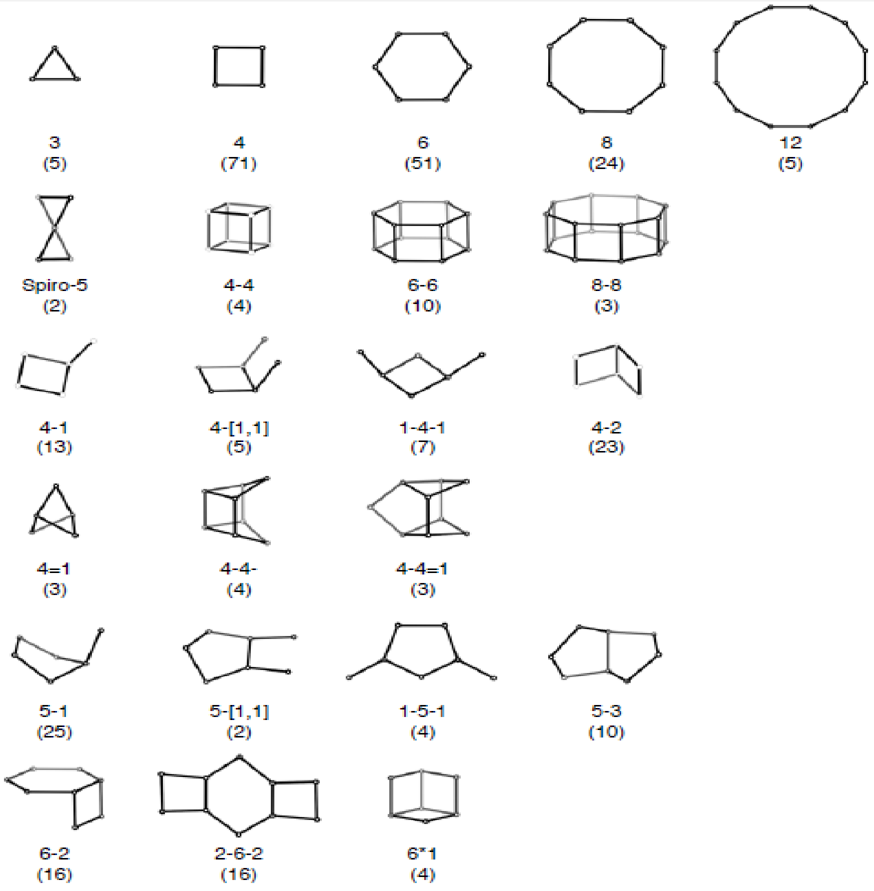


Figure 2.1. Secondary Building Units and their Symbols. Number in parentheses indicates frequency of occurrence

Figures 2.2 and 2.3 show how PBUs join together to form SBUs and different forms of SBUs, respectively. An example of how SBUs are linked together to produce a unique zeolite structure is shown in Figure 2.4 and Figure 2.5 [27, 28].

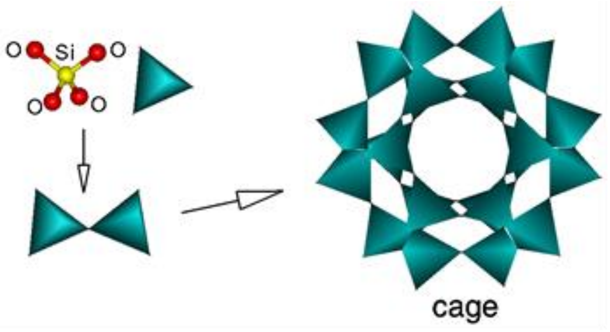


Figure 2.2. A Combination of $(SiO_4)^{4+}$ PBUs to form SBUs, alignment of which results in a cage

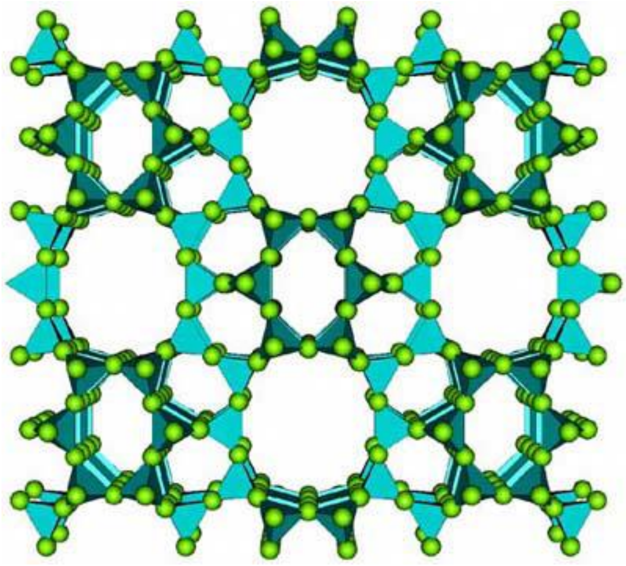


Figure 2.3. A chemical model of a complex zeolite structure. The differently sized holes represent channels and cages. Image courtesy of Geoffrey Price, University of Tulsa [29]

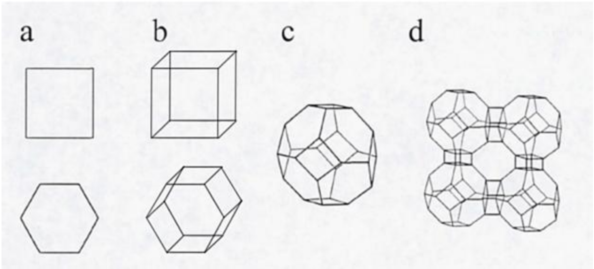


Figure 2.4. Different orientations of Secondary building units (SBUs). The intersections of lines represent the centres of tetrahedral cations (Al or Si). a) Single 4- and 6- rings; b) Double 4- and 6- rings; c) Truncated cubo-octahedrons composed of 4- and 6- rings; d) Four truncated cubo-octahedrons linked together by four double 4- rings

This special arrangement of SBUs contributes to the crystalline structure, hence the type and morphology of different species of zeolites (Fig 2.5 & 2.6).

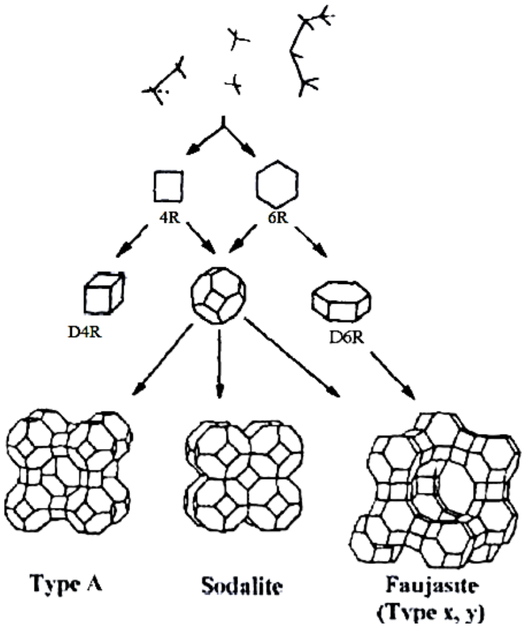


Figure 2.5. Structures of three different zeolites and their micropore systems [5]

Secondary building units are non-chiral and may contain up to 16 T-atoms. Since a unit cell always contains an integral number of them, they are derived assuming that the entire framework is made up of one type of SBU only.

2.1.2. Composite Building Units

In addition to the PBUs and SBUs described above, zeolites may contain other components such as double rings, cancrinite cages and alpha cavities. These are called composite building units CBUs. They appear in several different framework structures, and can be useful in identifying relationships between framework types. Unlike SBUs, CBUs are not necessarily achiral, and cannot be used to build the entire framework [25]. The most common example of CBUs is the rings, whose sizes are decided by the number of tetrahedrons in a ring. A ring is therefore characterised by, and named after the number of tetrahedrons it consists of. A ring consisting of n tetrahedrons is called an n-ring. Zeolite rings frequently comprise of 4, 5, 6, 8, 10, or 12 tetrahedrons. Frameworks with rings of 14, 18, and 20 tetrahedrons have been reported [30-34] while 3-, 7-, or 9-ring frameworks are rare [35-37]. As shown in Figure 2.6, the size of the rings in the framework determines the pore size in different zeolites. The entrance to the pore is known as a window [38].

Rings may be joined to form more complex CBU structures such as prisms and cages. Cages are defined as polyhedrons whose largest rings are not big enough to allow the passage of molecules larger than water [39, 38]. They can be viewed as channels of limited or fixed length. They are however bigger in diameter than normal channels and are only accessible via the channels themselves. Cages are usually formed at the crossing of two channel systems. These typically trap those molecules which are bigger than the channel systems, molecules which may have been formed within the cages or during synthesis.

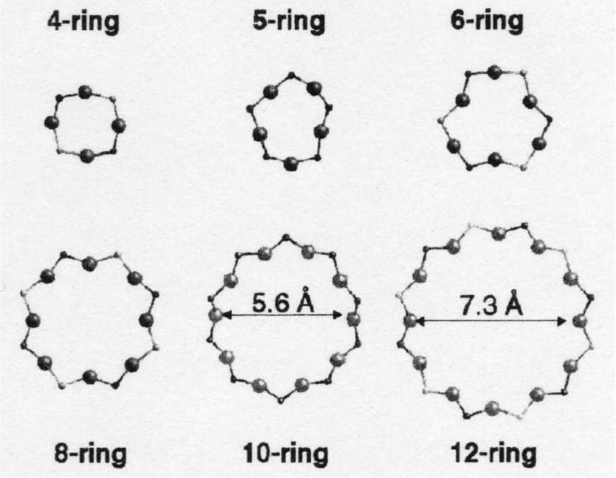
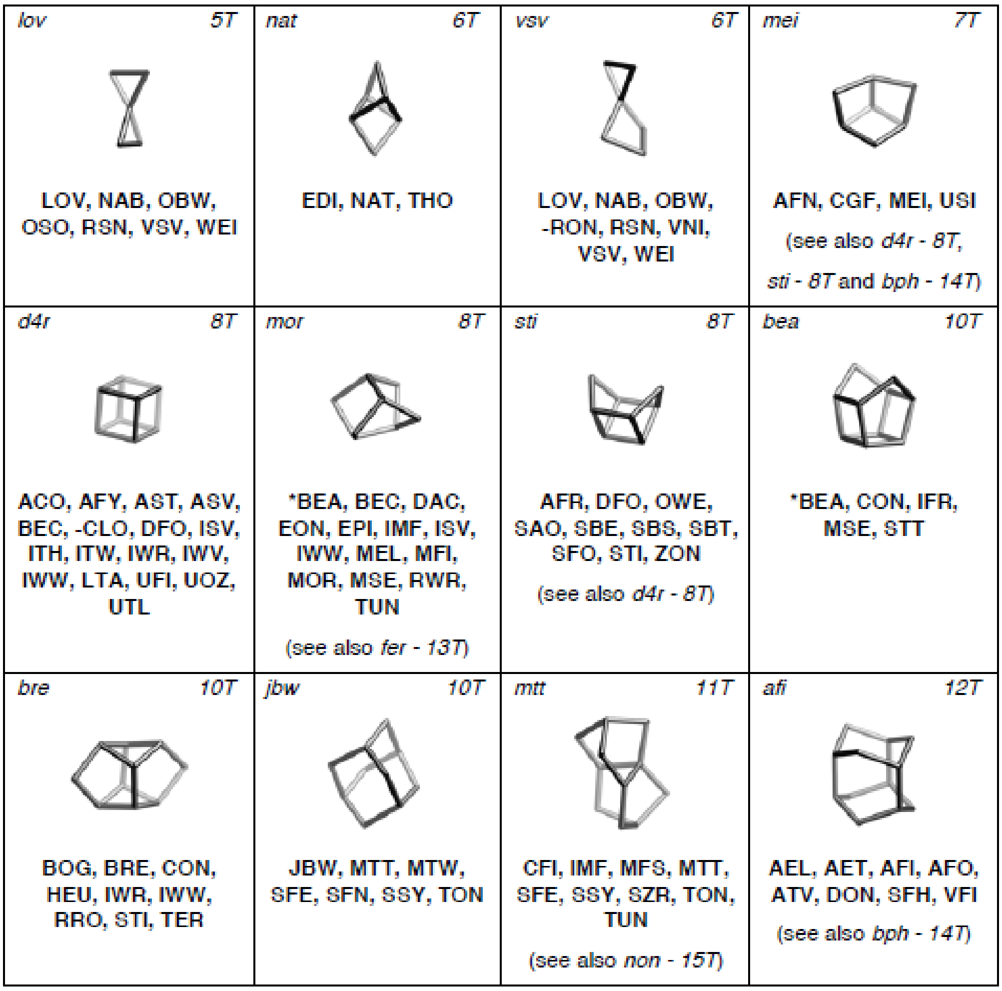


Figure 2.6. Composition and size of rings in the zeolitic framework. The pore size of a specific zeolite is determined by the ring type [39]

Together, these rings, channels and cages form composite building units of zeolites. Examples of composite building units are given in Figure 2.7 and Appendix 1.

According to Bedioui [40], the structure of zeolites may be summarized as follows: the PBU $(SiO_4)^{4-}$ or $(AlO_4)^{5-}$ tetrahedra (Fig. 2.8 a) are connected through their corners of shared oxygen atoms to form a wide range of small SBUs (Fig. 2.8 b). These are interconnected to form a wide range of polyhedra – the CBUs (Fig. 2.8 c), which in turn connect to form the infinitely extended frameworks of the various specific zeolite crystal structures. This summary is depicted in Figures 2.8 (a-d) and 2.9. The corners of the polyhedra represent Si or Al atoms and the connecting lines represent the shared oxygen atoms [5].

Different types of zeolites (e.g. clinoptilolite, mordenite, erionite etc.) naturally occur with dissimilar morphology. Clinoptilolite and heulandites are isostructural and both generally occur as plates or laths with tabular form. Mordenite usually occurs as fine fibers or as thin laths and needles. Chabazite has a cube-like appearance due to its rhombohedal SBUs (Figure 2.10).



lov 5T LOV, NAB, OBW, OSO, RSN, VSV, WEI	*nat* 6T EDI, NAT, THO	*vsv* 6T LOV, NAB, OBW, -RON, RSN, VNI, VSV, WEI	*mei* 7T AFN, CGF, MEI, USI (see also *d4r* - *8T*, *sti* - *8T* and *bph* - *14T*)
d4r 8T ACO, AFY, AST, ASV, BEC, -CLO, DFO, ISV, ITH, ITW, IWR, IWV, IWW, LTA, UFI, UOZ, UTL	*mor* 8T *BEA, BEC, DAC, EON, EPI, IMF, ISV, IWW, MEL, MFI, MOR, MSE, RWR, TUN (see also *fer* - *13T*)	*sti* 8T AFR, DFO, OWE, SAO, SBE, SBS, SBT, SFO, STI, ZON (see also *d4r* - *8T*)	*bea* 10T *BEA, CON, IFR, MSE, STT
bre 10T BOG, BRE, CON, HEU, IWR, IWW, RRO, STI, TER	*jbw* 10T JBW, MTT, MTW, SFE, SFN, SSY, TON	*mtt* 11T CFI, IMF, MFS, MTT, SFE, SSY, SZR, TON, TUN (see also *non* - *15T*)	*afi* 12T AEL, AET, AFI, AFO, ATV, DON, SFH, VFI (see also *bph* - *14T*)

Figure 2.7. Examples of CBUs. Each unit is identified with a lower-case three-character code in italics and the number of T-atoms in the unit. Framework types containing the unit are listed below each unit

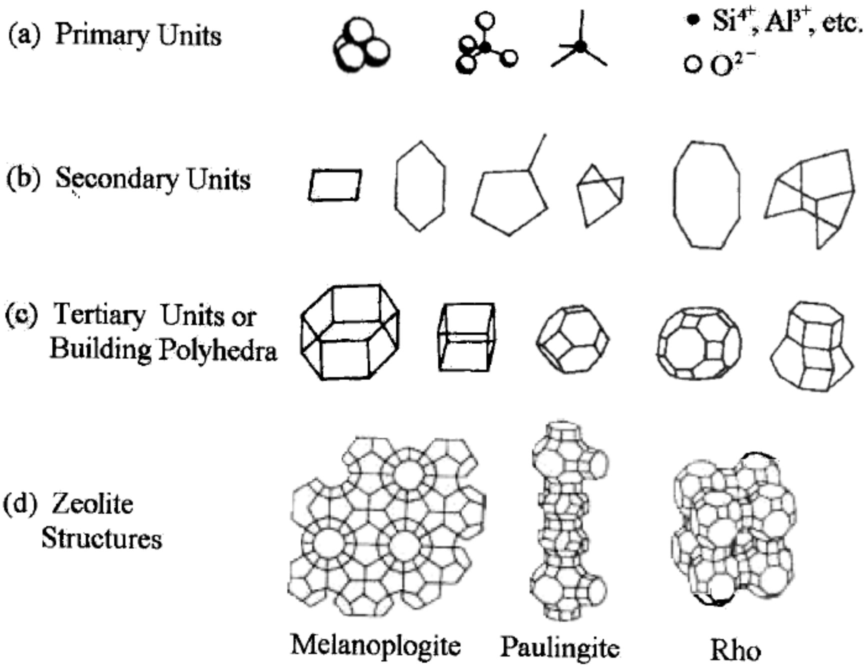


Figure 2.8. Development of a zeolite from (a) the framework PBU – the $(SiO_4)^{4-}$ or $(AlO_4)^{5-}$ – through (b) the SBUs and (c) CBUs to (d) a zeolite structure

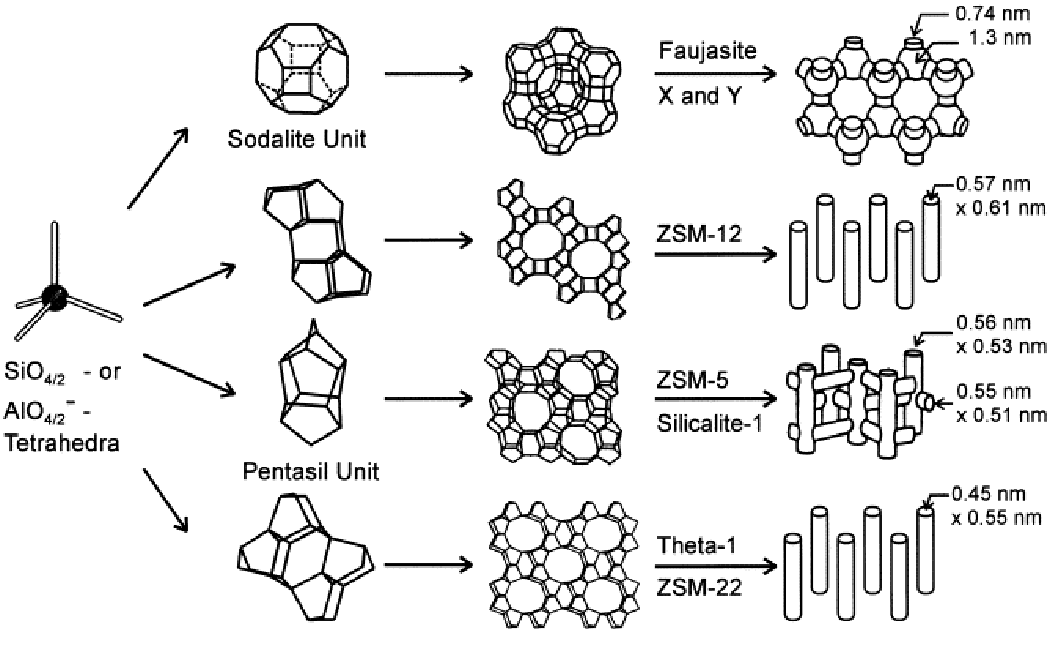


Figure 2.9. Structures of four selected zeolites and their micropore systems and dimensions [42]

Because of the crystalline structure consisting of a three-dimensional tetrahedral network of silicon and aluminium linked together by common oxygen atoms, zeolites are naturally porous. These pores are a product of interlinked cages, resulting from the tetrahedral structural arrangement of atoms and they are normally of sizes less than 2nm, hence zeolites belong to a group of microporous materials [43]. According to the IUPAC definition [44], microporous materials are those materials having pore sizes less than 2nm. Materials with pore sizes between 2nm and 50nm are classified as mesoporous, while those with pore diameters greater than 50 nm belong to the macroporous category.

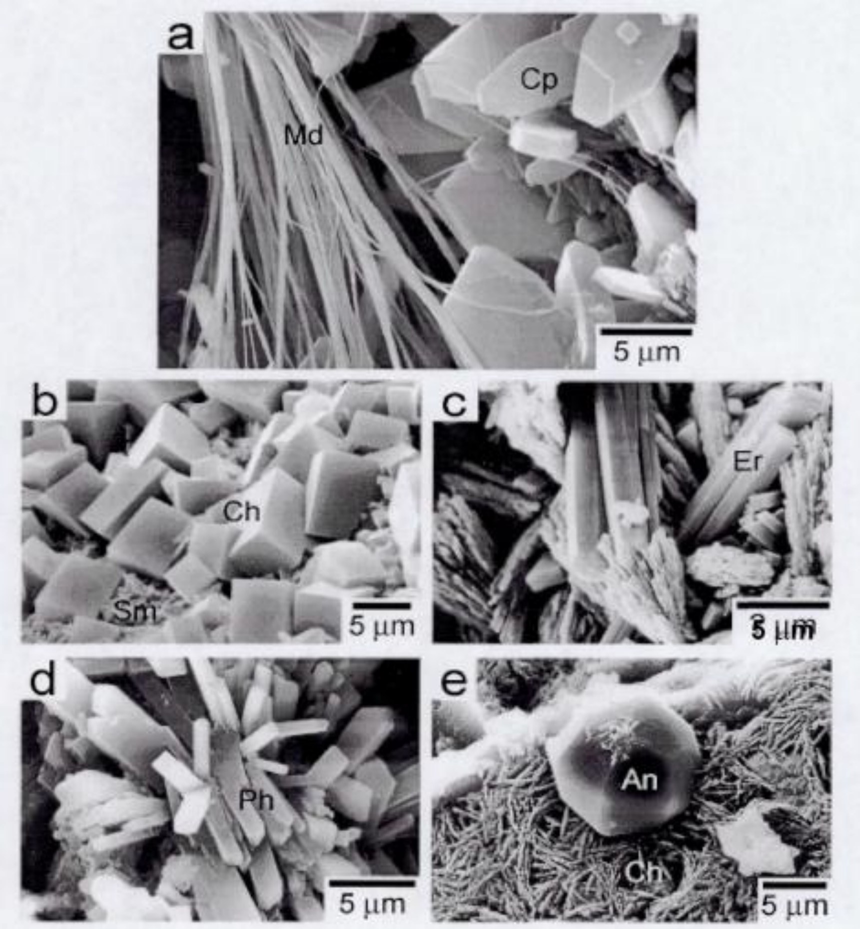


Figure 2.10. Scanning electron micrographs of common natural zeolites. a) Clinoptilolite (Cp) and modernite (Md); b) Chabazite (Ch) and smectite (Sm); c) Erionite; d) Phistlistine and e) Analzime (An) and Chabazite (Ch) [40]

3. Properties and Applications

3.1. Applications of Zeolites

Over the years zeolites have attracted a great deal of attention among researchers and scientists due to their flexibility and adaptability. Following their discovery in 1756 by Axel Fredrik Cronstedt, zeolites were found to be good adsorbents, ion exchangers and molecular sieves. The molecular sieve properties of zeolites in particular are extensively employed in industry. Zeolites have been used in the separation of straight-chain hydrocarbons from branched-chain hydrocarbons [27], chemical sensors [45] in industrial process control, environmental and indoor air-quality monitoring, effluent and auto-exhaust control, medical monitoring [5], air separation [46] and removal of heavy metals [47] to mention but a few.

Zeolites continue to find various applications in solving environmental, scientific, industrial and day to day problems. Their usefulness and their applications in chemistry (and day-to-day life) is addressed in this section.

3.2. Purification of Water

The earliest use of zeolites was in their application as adsorbents in 1777 by Fontana and Scheele. Since then, their adsorbance properties have enabled them to be applied in a variety of processes used to solve environmental issues. Zeolites were subsequently found to be good adsorbents for molecules such as H_2O, NH_3, H_2S, NO, NO_2, SO_2, and CO_2 to mention but a few [48].

3.2.1. Treatment of Industrial Wastewater

Increasing demands for high quality drinking water has led to a worldwide need to purify water from various sources including natural, industrial, agricultural and municipal waste waters. Consequently, the use of natural zeolites as agents in the removal of wastewater contaminants has gathered tremendous interest culminating in extensive studies.

Wastewater streams resulting from industrial processes (such as mining and manufacturing) have different physical-chemical characteristics. They may contain ions of metals like Sb, Cr, Cu, Pb, Zn, Co, and Ni, together with waste liquids which are generated by metal finishing or the mineral processing industries [49, 50]. These metals, which are toxic even at trace levels, may exist in these waters at very high concentrations. Such waters should not be discharged directly into natural waters as they pose a great risk for the aquatic ecosystem, resulting in several types of health problems into animals, plants and human beings. Furthermore, these waters should not be discharged directly into the sewerage system as they interfere with the biological wastewater treatment processes. Additionally, these biological processes may not be capable of fully removing toxic metals from these waters [51-53].

3.2.2. Treatment of Municipal Wastewater

Treatment of municipal wastewaters by the use of zeolites is aimed at enhancing the efficiency of the pollutant reduction process. One of the significant contaminants of greywater (wastewater originated from kitchen, bathroom and laundry in households) is the ammonium ion (NH_4^+). Sources of ammonium in household water include ammonium salts, which function as acidity regulators, thickeners and stabilisers in kitchen detergents. Bathroom ammonia is mainly from urine, whereas laundry wastewater contains ammonium ion from the use of fabric softeners and laundry disinfectant agents. These normally contain quartenary ammonium salts, dialkyldimethylammonium chlorides, distearyldimethylammonium chloride and/or alkyldimethylbenzylammonium chlorides, which function as cationic surfactants [54, 55].

3.2.3. Treatment of Drinking Water

After it was discovered that the presence of clinoptilolite can enhance nitrification of sewage sludge, natural zeolites have been used in various places for the treatment of municipal wastewater for drinking purposes. The addition of powdered clinoptilolite to sewage before aeration has been reported to lead to increases in O_2 consumption and sedimentation. This results in a sludge that can be more easily dewatered and, hence, used as a fertilizer [56]. Mixing sludge with natural zeolites for the purpose of treatment has been reported to lead to production of clear water with improved quality parameters such as color (by 92%), suspended particles (by 94%), chemical oxygen demand (by 95%), dissolved oxygen (by 950%), P_2O_5 (by 96%), NH_4 (by 99%), SO_4 (by 97%), NO_3 (by 92%), NO_2 (by 82%), total Cr (by 90%), Mn (by 94%) and Ni contents (by 93%). Additionally, production of an odourless and cohesive zeo-sewage sludge was reported [57].

In other studies, zeolites have been used to reduce levels of heavy metals – such as lead and chromium – which are found in sewage sludge from municipal wastewater treatment plants. Kosobucki *et al*., (2008) [58] have demonstrated that through the use of zeolites, up to 68% of heavy metals can be removed from sludge by addition of zeolites to sludge at a ratio of 2:98 (zeolite:sludge). Application of ultrasonic energy appeared to improve the process of heavy metal removal from sludge. According to Kosobucki and co-workers [58], the ultrasonic energy serves to influence both the structure and physicochemical properties of the zeolite, hence leading to improvements in the immobilization process of heavy metals from the sewage sludge.

Treatment of well groundwater with natural zeolites was shown to remove 55 % of NO_3, 74% of Pb, 79% of Ag and improved pH from 9.6 to 7.3. Quality parameters were improved by 93% for the color and 96% for the chemical oxygen demand. In addition, the zeolite removed 51% of colonial *Mycrocystis* cyanobacteria, 75% of *Filamentous* cyanobacteria as well as 92% *Chroococcus* cyanobacteria from their culture. The natural zeolites' ability to remove inorganic, organic, and organometallic compounds, as well as gas species, metals and radionuclides from their aqueous solutions can be attributed to absorption (mainly ion exchange), adsorption and surface precipitation processes [57].

3.2.4. Properties of Zeolites Enabling Water Purification

3.2.4.1. Cation Exchange Capacity

Most of the methods in which natural zeolites are used, for the purification of water are based on their cation-exchange behaviour. In this process, the exchangeable zeolite surface ions are replaced at the sites by ions from the solution. The dissolved cations are removed from water by being exchanged with the cations on a zeolite's extra-framework exchange sites. According to Kalló [59], many natural zeolites (e.g. clinoptilotite, mordenite, philtipsite, chabasite) are selective on several toxic metals which are often present in industrial waters (e.g. Cu^{2+}, Ag^+, Zn^{2+} Cd^{2+}, Hg^{2+}, Pb^{2+}, Cr^{3+}, Mo^{2+}, Mn^{2+}, Co^{2+} and Ni^{2+}). In addition to these metals, these zeolites are highly selective on the NH_4^+ ion and exchange it preferably even in the presence of competing cations. These ions are removed from the water and replaced with biologically acceptable cations such as Na^+, K^+, Mg^{2+}, Ca^{2+} or H^+ from the zeolite exchange sites. Smical (2011) [28] has shown that the ion exchange process may be presented by the following equation:

$$z_A B_{(z)}^{Z_B^+} + z_B A_{(s)}^{z_A^+} \Leftrightarrow z_A B_{(s)}^{z_B^+} + z_B A_{(z)}^{z_A^+}$$

Reaction 3.1

Where: z_A and z_B represent the A & B exchangeable ion charges and the coefficients (z) and (aq) refer to zeolite and to aqueous solution, respectively. The reaction proceeds until equilibrium is attained. The point of equilibrium is defined largely by the theoretical cation exchange capacity (TCEC) of the zeolite, which in turn, is given by the sum of free extra-framework cations of the zeolite. This number of free extra-framework cations of the zeolite is directly related to the amount of aluminum present in the framework and hence the amount of Al^{3+} that replaces Si^{4+} in the structure. Cation exchange capacity is usually expressed in milliequivalents (meq) metal per 100g of zeolite. Since the exchangeable cations of natural zeolites are usually represented by: Na^+, K^+, Mg^{2+}, and Ca^{2+}, for a particular natural zeolite, TCEC = Σ (*Na*, *K*, *Mg*, *Ca*) as is shown on Table 3.1 [60-63].

Table 3.1. Cation exchange capacity (CEC) of zeolites [60, 64]

Zeolite Name	**FTC**	**Formula**	**Si/Al Ratio**	**Main cation**	**CEC (meq/g)**
Analcime	ANA	$Na_{16}(Al_{16}Si_{32}O_{96}) \bullet 16H_2O$	1.5 – 2.8	Na	3.6 – 5.3
Chabazite	CHA	$Ca_2(Al_4Si_8O_{24}) \bullet 12H_2O$	1.4 – 4.0	Na, K, Ca	2.5 – 4.7
Clinoptilolite	HEU	$(Na,K)_6(Si_{30}Al_6O_{72}) \bullet 20H_2O$	4.0 – 5.7	Na, K, Ca	2.0 – 2.6
Heulandite	HEU	$Ca_4(Si_{28}Al_8O_{72}) \bullet 24H_2O$	4.0 – 6.2	Na, K, Ca, Sr	2.2 – 2.5
Mordenite	MOR	$Na_2KCa_2(Al_8Si_{40}O_{96}) \bullet 28H_2O$	4.0 – 5.7	Na, K, Ca	2.0 – 2.4
Philipsite	PHI	$K_2(Ca_{0.5}Na)_4(Al_6Si_{10}O_{32}) \bullet 12H_2O$	1.1 – 3.3	Na, K, Ca	2.9 – 5.6
Laumontite	LAU	$Ca_4(Al_8Si_{16}O_{48}) \bullet 16H_2O$	1.9 – 2.4	Na, K, Mg	3.8 – 4.3
Natrolite	NAT	$Na_{16}(Al_{16}Si_{24}O_{80}) \bullet 16H_2O$	1.2 – 1.7	Na	2.9 – 3.2
Erionite	ERI	$(Na_2K_2Ca)_2(Al_4Si_{14}O_{36}) \bullet 15H_2O$	2.6 – 3.8	Na, K, Ca	2.7 – 3.4
Faujasite	FAU	$(Na_2,Ca,Mg)_{3.5}(Al_7Si_{17}O_{48}) \bullet 32(H_2O)$	2.1 – 2.8	Na, K, Mg	3.0 – 3.4
Ferrierite	FER	$(Na,K)_2Mg(Si,Al)_{18}O_{36}(OH) \bullet 9H_2O$	4.9 – 5.7	Ca	2.1 – 2.3

The total CEC given in the table below differs from the ideal cationic exchange capacity, which is defined based on the chemical formula of a pure zeolite. According to Perego *et al.*, [64] there are several factors which determine the actual / operating cation exchange. These include (a) the zeolite's framework structure; (b) the zeolite's framework electrostatic field strength; (c) the nature of the cation and its charge density; (d) the composition of the contacting solution; (e) the pH of the contacting solution (pH is a measure of protons, which are also cations and are exchangeable); (f) the composition and work-up of the raw mineral used as a zeolite and; (g) the process apparatus and operating conditions (e.g. continuous stirred tank vs. fixed bed column).

Due to these, literature result comparison is extremely difficult and often contradictory. This fact is also supported by a report by Castaldi *et al.*, [43], who have shown that the sorption capacity of a particular zeolite is not fully given by the total cation exchange capacity due to the fact that the specific crystal structure and the distribution and accessibility of the exchange sites for cations play the greatest roles in determining the extent at which cations in the zeolite will be exchanged.

Compared to other ion exchange materials such as organic resins, the use of natural zeolites is expedient in that they provide low-cost treatment, exhibit excellent selectivity at low temperatures, release non-toxic exchangeable cations (e.g. K^+, Na^+, Ca^{2+} and Mg^{2+}) to the environment, provide simple operation as well as easy maintenance of the full-scale applications, are compact in size and can be used in relatively little space [12, 65, 66].

Natural zeolites are however rarely obtained in pure form. They are normally contaminated to varying degrees with other minerals such as quartz, amorphous glass and other feldspars [67, 68]. Consequently, natural zeolites are excluded from many important commercial applications which require uniformity and purity [69].

3.2.4.2. Adsorption Kinetics

A series of studies undertaken by Widiastuti *et al.*, [12] have shown that the efficiency of a zeolite to remove ammonia from greywater is influenced by several parameters, among which are initial ammonium concentration, contact time and pH. Adsorption kinetics can be used to investigate the process of adsorption of contaminants onto the adsorbents. This helps to clarify the mechanism of adsorption (which depends on the physical and/or chemical characteristics of the adsorbent as well as the mass transport process). Five different kinetic models (pseudo first order, pseudo second order, Bangham, intra-particle diffusion and Elovich models) have been used to try and elucidate the mechanism of ammonium adsorption onto zeolite particles [6, 12, 70]. The pseudo first order is determined by equation 3.1 below:

$$\frac{dq_t}{dt} = k_f(q_e - q_t) \tag{3.1}$$

where q_t (mg/g) is the amount of adsorbate adsorbed at time t (min), q_e (mg/g) is the equilibrium adsorption capacity, and k_f (min^{-1}) is the rate constant of pseudo first order model (min^{-1}). The pseudo second order is determined by equation 3.2 below:

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2 \tag{3.2}$$

Where all the terms retain their definition as per Eq 3.1 and k_s is the rate constant of pseudo second order model (in $g \bullet (mg/min)^{-1}$).

The Bangham model is represented by the following equation (Eq 3.3):

$$log\ log\left[\frac{C_o}{C_o - q_t m}\right] = log\left[\frac{k_o m}{2.303V}\right] + \alpha\ logt \qquad (3.3)$$

where C_o is the initial concentration of adsorbate in solution (mg/L), V is the volume of solution (mL), m is the mass of adsorbent per liter of solution (g/L), q_t (mg/g) is the amount of adsorbate retained at time t, and α (<1) and k_o are constants.

The intra-particle diffusion model is given by Eq 3.4:

$$q_t = k_{id} t^{1/2} + C \qquad (3.4)$$

where k_{id} is the intra-particle diffusion rate constant. If adsorption follows the intra-particle diffusion mechanism, then plot of q_t versus $t^{1/2}$ will be a straight line with a slope = k_{id} and intercept = C. The values of the intercepts give an indication about the thickness of the double layer – the larger the intercept the greater is the double layer effect. This effect can be minimised by working in salt solution.

The Elovich equation is given by

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \qquad (3.5)$$

Integrating Eq 3.5 and applying the initial conditions q_t=0 at t=0 and q_t=q_t at t=t, yields the Elovich model (Eq 3.6)

$$q_t = (1/\beta)\ ln(\alpha\beta) + (1/\beta)\ lnt \qquad (3.6)$$

where α is the initial adsorption rate (mg/(g min)) and the parameter β is related to the extent of surface coverage (g/mg) and activation energy.

Figure 3.1 shows that the pseudo second order fits the kinetics data best for 5 and 50 mg/L ammonium concentrations with an R^2 value of 0.99.

With this understanding of the reaction pathway and mechanism acquired, it is possible to predict the rate at which pollutants are removed from aqueous solutions, thus enabling the design of appropriate sorption treatment plants. The formula for a pseudo second order reaction rate is given by equation 3.2 above. Integrating this for the boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t, Eq 3.2 may be rearranged as shown by Eq 3.7:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t \qquad (3.7)$$

A plot of t/q_t against t is linear with slope = 1/q_e and intercept = 1/$k_s q_e^2$, where q_e is the equilibrium adsorption capacity and k_s is the pseudo second order constant. The expression $k_s q_e^2$ may be used to define the initial sorption rate, h (mg/g min) as t→0. Consequently, h, q_e and k_s can be determined experimentally from the slope and intercept [72-74].

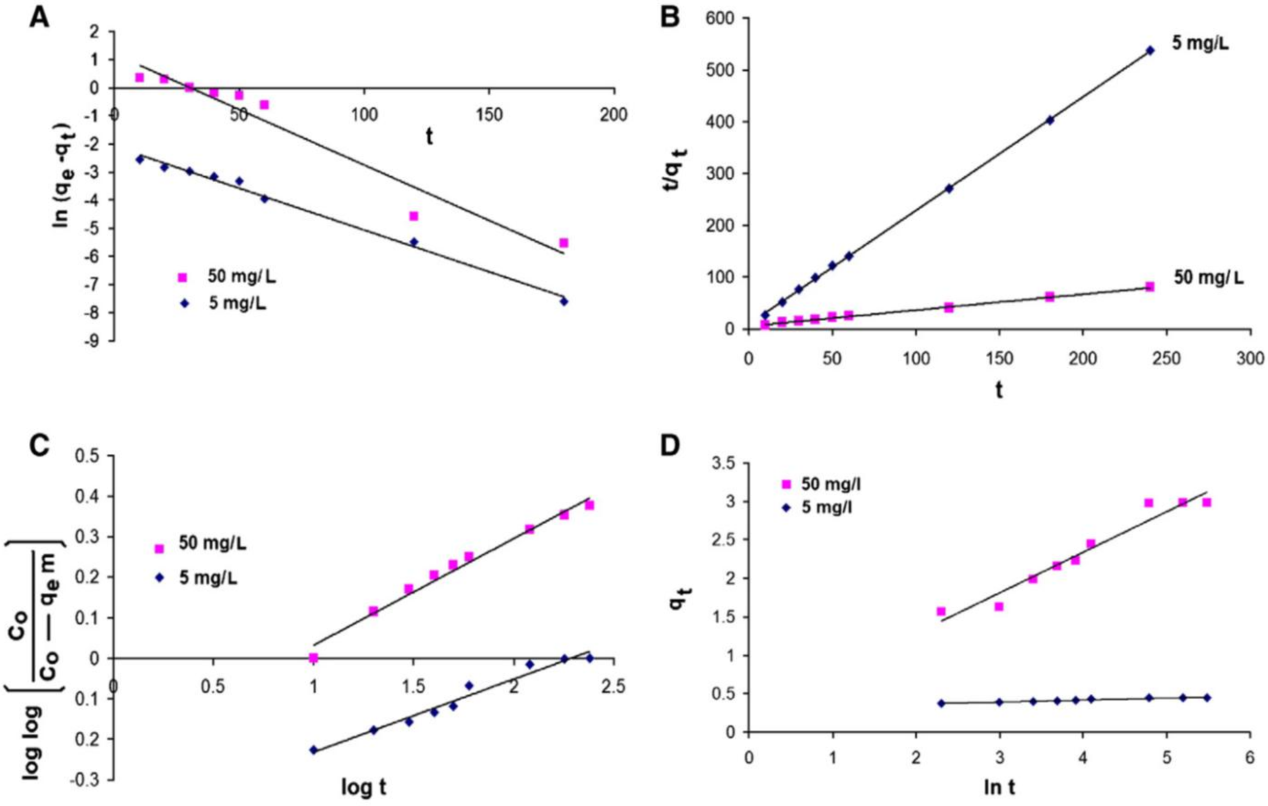


Figure 3.1. (A) Pseudo first order, (B) Pseudo second order, (C) Bangham, and (D) Elovich kinetic plots for ammonia removal by the zeolite at initial concentrations 5 mg/L and 50 mg/L, contact time 8 h, temperature 25℃ and ratio of solid/liquid 1 g/100 mL [12]

3.2.4.3. Adsorption Isotherms

In order to design efficient adsorption systems, adsorption isotherms are used in the determination of surface properties such as affinity of the adsorbent and the adsorption capacity of the adsorbent. This helps in designing efficient adsorption systems. Various isotherms (e.g. Langmuir, Freundlich and Tempkin models) have been used to fit data for the removal of ammonium in wastewater using natural zeolites by various countries [12, 75]. Du *et al.*, [67] have suggested that the Freundlich model presents the best fit as evidenced by the high R^2 value in Table 3.2 and Figure 3.2 below.

According to other authors [59, 76, 77], the adsorption isotherm of ammonium removal from aqueous solution using natural zeolites from various origins could be more generally approximated by the Langmuir model. These results suggest differences in zeolite characteristics such as purity, mineral content and chemical composition. It has therefore been concluded that these zeolites have heterogeneous surfaces with a non-uniform distribution of heat of adsorption over the surface [65, 66, 75, 77].

Table 3.2. Adsorption isotherms tested [12]

Isotherm models	**Parameters**		
Langmuir	**q_{max} (mg/g)**	**k (L/mg)**	**R^2**
	6.3012	**0.049**	**0.8892**
Freundlich	**K_F (mg/g)/(mg/L)$^{i/n}$**	**$1/n$**	**R^2**
	0.6555	**0.480**	**0.9523**
Tempkin	**k_t (L/mg)**	**B_1**	**R^2**
	1.7449	**0.8997**	**0.7891**

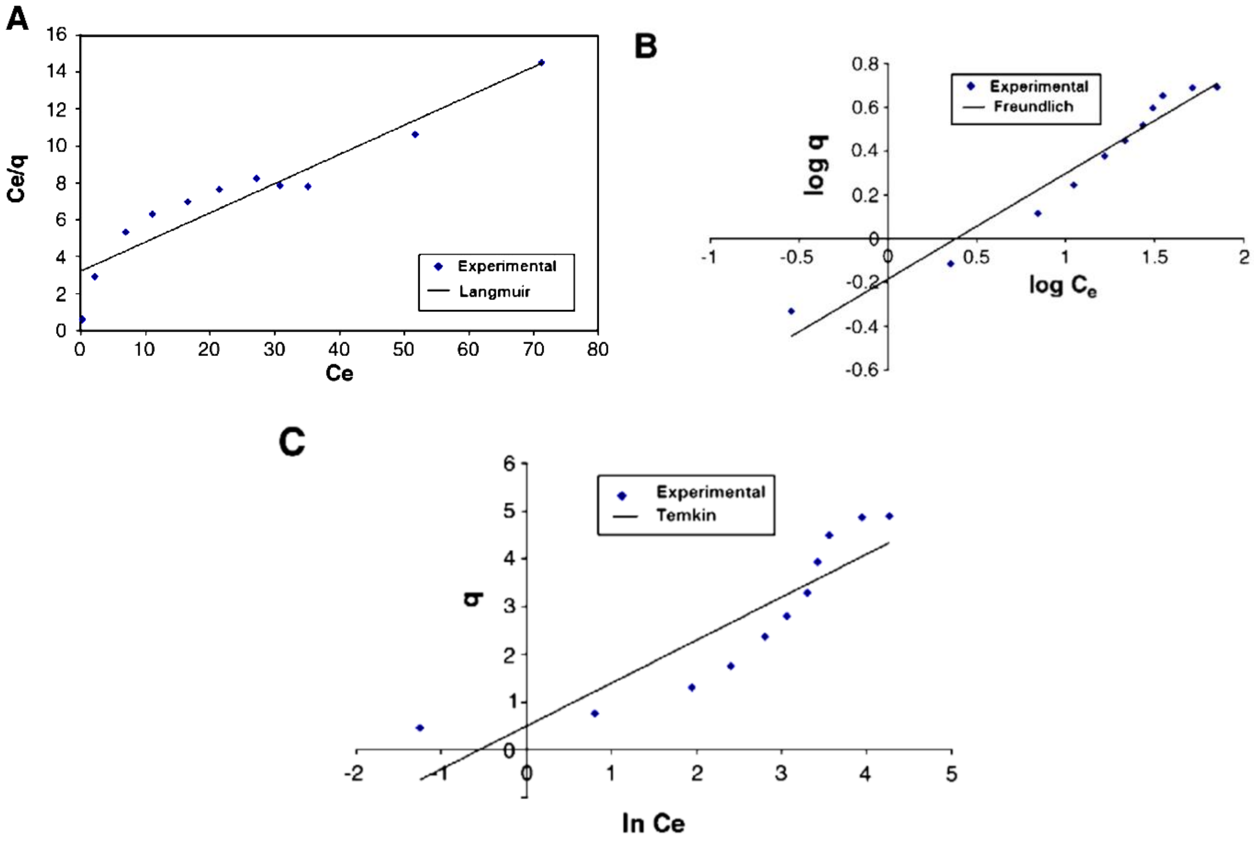


Figure 3.2. The linearised Langmuir (A), Freundlich (B), and Tempkin (C) adsorption isotherm of ammonium curve [12]

3.3. Formation of Sludge

The excellent adsorption properties of zeolites are also exploited in the enhancement of the formation of sludge. During the biological treatment stage, an increase of biological activity (which is brought about by the oxygen consumption by the living sludge) can be achieved, based on the adherence of bacteria to small zeolite rock grains. According to Zita and Hermansson [78], bacteria are able to enhance contact between surfaces by use of hydrophobic interactions which are due to bacterial surface structures. During flocculation, bacteria which have adhered reversibly to surfaces bring these surfaces closer, thus mediating a direct contact between the surfaces. When the bacteria required for sludge formation adsorb on the zeolite surface, they result in an increased rate of settling, hence speeding up sludge-formation activity [79].

Kubota *et al.*, [80] have shown that adsorption of bacteria onto zeolites is pH dependent. According to the DLVO (Derjaguin, Landau, Vervey, Overbeek) theory, the interaction of zeolites with bacteria is governed by two independent interactions: long-range repulsive electrostatic forces on the particle surface and attractive van der Waals forces due to the solid particle cores. Since the electrostatic double-layer forces and the van der Waals forces are independent and additive, whether adsorption occurs or not is a result of the magnitude of both forces [81, 83].

Zeta potential measurements of several bacterial species and zeolites have shown that surface charges of both zeolites and bacteria increase with decreases in pH. Under most physiological conditions, bacterial cell surfaces carry a net negative charge as shown by negative values of their measured zeta potentials [80]. This value becomes more negative with increasing pH. Zeolite zeta potentials are also negative and are further decreased by more basic conditions – signifying an increase in zeolite surface charges. The electric double layer interaction therefore has the properties of pH dependence since it is a function of the surface charge of the colloids (Figure 3.3). The van der Waals interaction, on the other hand, is independent of the pH value of the medium as it is inversely proportional to the sixth power of the distance between two substances.

A combination of increases in both zeolite and bacterial surface charges result in increased electric repulsion, hence reduced adsorption at higher pH values. In general, low pH (more acidic) conditions favour adsorption more than higher pH (more basic) conditions [80, 82, 83].

In the case of NH_4^+ adsorption however, the opposite is found to be true. As can be seen in Figure 3.4, at any given solution concentration an increase in the solution pH results in greater amounts of NH_4^+ being adsorbed [77].

The NH_4^+ adsorption capacities of the zeolite, calculated using the one-surface Langmuir model, have been shown to increase linearly with pH (Figure 3.5).

According to Widiastuti *et al.*, [12], the relationship between NH_4^+ adsorption and pH is not as simplistic. In aqueous solutions, ammonium behaviour changes with the change in pH. This change in behaviour of ammonia has an effect upon the zeolite's performance and its efficiency at various pH levels. In aqueous solution, the ammonium species can be found in a dissociated ammonium (NH_4^+) form or in a non-dissociated ammonia (NH_3) form. The formation of any of the forms depends upon the pH of the solution. As shown in Figure 3.6, the ammonium ion exists predominantly at a pH lower than 7, whereas at pH higher than 10, the ammonia (NH_3) exists as the chief species.

Rožić *et al.*, [84] identified ion exchange as another major mechanism of ammonium removal from aqueous solutions by natural zeolite in addition to adsorption. This being the case, a natural zeolite's efficiency to remove ammonium tends to be high at pH 5-7. It is at this pH where the ammonium ion (NH_4^+), can ion-exchange with the cations in the zeolite, the predominant species at this pH. For these reasons, the optimum ammonium removal efficiency is achieved in the pH range 5-6.

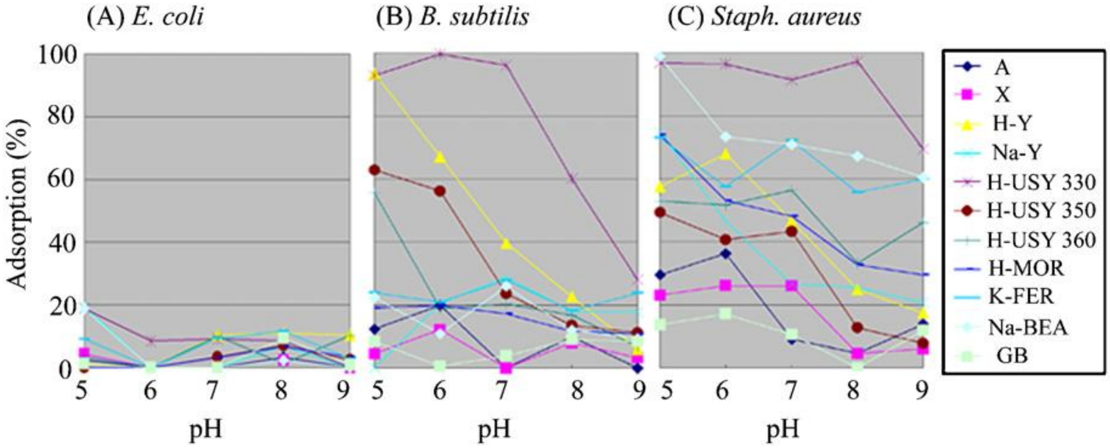


Figure 3.3. Adsorption of the three bacteria species: (A) *E. coli*, (B) *B. subtilis* and (C) *Staph. aureus* under different pH conditions (pH 5, 6, 7, 8 and 9, 150mM NaCl). The amount of adsorption was calculated by determining the absorbance of their supernatants at $\lambda = 600$ nm

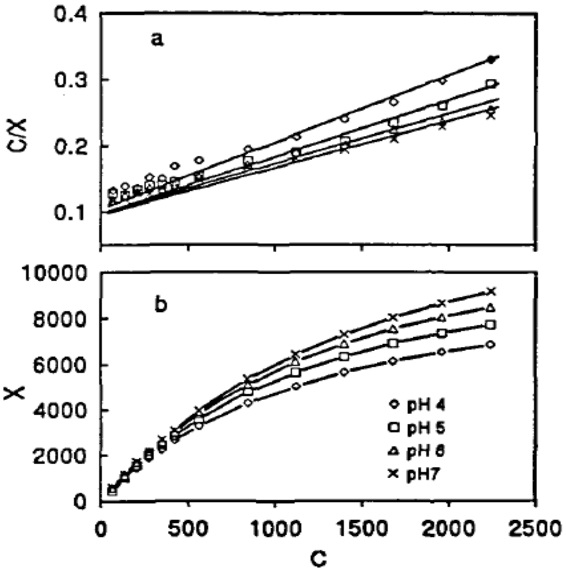


Figure 3.4. (a) One-surface and (b) two-surface Langmuir isotherms for NH_4^+ adsorption on the natural zeolite (clinoptilolite) at pH values 4, 5, 6, and 7. X=mg N kg^{-1} zeolite and C=mg N L^{-1} solution [83]

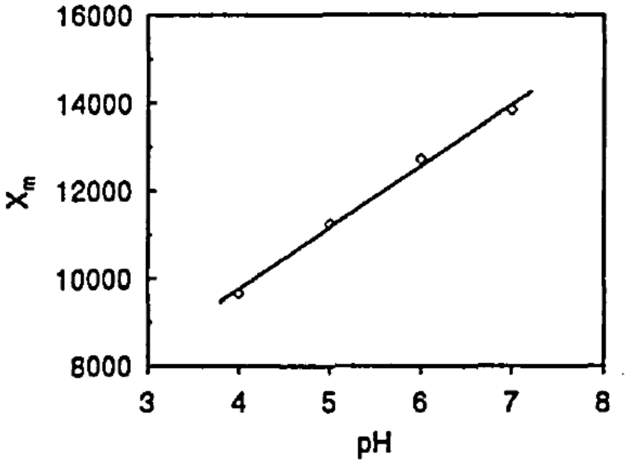


Figure 3.5. Maximum NH_4^+ adsorption capacity (X_m) of the natural zeolite as a function of pH calculated using the one-surface Langmuir model. X_m= mg N kg^{-1} of zeolite

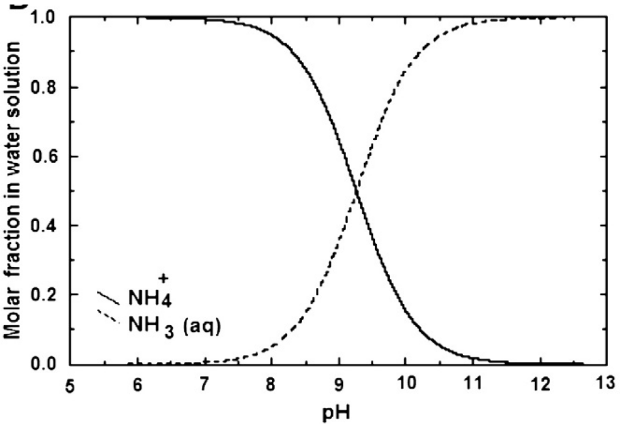


Figure 3.6. Behaviour of ammonia in aqueous solution at 25°C

3.4. Medicinal Uses of Zeolites

Natural silicate materials have been shown to exhibit diverse biological activities. By virtue of being aluminosilicates, zeolites also possess biological activity which may either be positive or negative. This biological activity arises as a result of the fact that most – if not all – of biochemical processes occur through ion exchange, adsorption, catalysis or processes which are closely related to the aforementioned. For this reason, zeolites have been used in various medicinal processes, some of which are discussed below.

3.4.1. Treatment of Cancer

Cancer is generally defined as an uncontrolled growth of abnormal body cells, which tend to spread and kill normal cells, often causing death. Cancer is mostly attributed to an alteration (mutation) of the DNA in the genes that produce proteins responsible for controlling the processes of cell growth and division. Such mutations lead to production of faulty proteins causing the affected cells to become abnormal and grow and divide in an uncontrollable manner, leading to production of malignant tumors.

In a study carried out by Pavelić *et al.*, [85] on the effect of natural clinoptilolite zeolite particles on development of several cancer models in vivo and in vitro, it was discovered that mechanically activated clinoptilolite zeolites act as anticancer therapeutic agents in vivo animal studies and in tissue culture cell models. Clinoptilolite applied orally in mice and dogs suffering from a variety of tumor types led to an improvement in overall health status, prolongation of life span, and decrease in tumors size in most animals. Local application of clinoptilolite to dogs suffering from skin cancers effectively reduced formation and growth of cancerous tumors on the dogs' skins.

Clinoptilolite acts as an adjuvant by enhancing the body's immune response to cancerous cells. Additional tissue culture studies showed that clinoptilolite's anticancerous mechanism of action includes inhibiting protein kinase B. This protein has been shown to have the ability of inactivating an important cyclin inhibitor and tumor suppressor molecule – $p27^{KIP1}$, and is also responsible for the ability of transformed epithelial cells to survive without cell attachment. Furthermore, clinoptilolite induces the expression of tumor suppressor proteins ($p21^{WAF1/CIP1}$ and $p27^{KIP1}$), and blocks cell growth in several cancer cell lines. It is therefore suggested that clinoptilolite treatment might affect cancer growth by attenuating survival signals, inducing tumor suppressor genes and apoptosis (programmed cell death) of treated cells. In a separate study, clinoptilolite was found to induce activation of macrophages – large phagocytic white blood cells – the purpose of which is to destroy cancerous cells. Toxicology studies carried out on mice and rats demonstrated that clinoptilolite treatment does not have negative effects on healthy cells. The mechanisms of action of clinoptilolite in vivo, however, remain largely unknown [85, 86, 87].

3.5. Catalysis

Since the 1960s [88] zeolites have been applied as catalysts in a variety of industrial chemical reactions (e.g. petroleum cracking, isomerization and alkylation reactions) which are used for production of fine chemicals, dyestuffs, detergents, and scents [83-85]. In many industrial processes, these alkylations are traditionally performed in the presence of toxic and corrosive liquid acids (e.g. fluoric and sulphuric acids), the disadvantage being that the resulting products then need to be separated from the acid with difficult and energy consuming processes.

3.5.1. Properties of Zeolites Enabling Catalysis

Catalysis of most reactions is achievable due to the desirable zeolite properties such as their large surface areas, unique pore size, crystallinity, and their thermal stability, together with the possibility of tuning the zeolite pore size in synthetic zeolites. In addition, zeolites are by nature ion exchangers – a property that enables them to function as Brønsted acids in catalytic reactions [92].

3.5.1.1. Proton Transfer

One of the most prominent catalytic reaction in which zeolites are utilized is Fluid catalytic cracking (FCC) – a reaction process used in the cracking of petroleum. In this process, high-molecular weight hydrocarbon fractions of petroleum crude oils are converted to more valuable gasoline, olefinic gases, and other products. Though originally carried out by thermal means, it has been almost completely supplanted by catalytic cracking since the latter produces more gasoline with a higher octane rating, together with byproduct gases that are more olefinic, and hence more valuable, than those produced by thermal cracking.

Petroleum cracking reactions that are catalyzed through the use of zeolites are based on hydrocarbon proton-transfer initiated reactions. According to Farneth and Gorte [93], proton transfer "is only the initiation step of a complex matrix of competitive and consecutive reactions that ultimately lead to product". Being centered on the formation of carbocations, these reactions are therefore dependent on the surface acidity and the crystalline structure of the catalysts. Due to their ability to exchange protons, zeolites are able to catalyze these reactions by acting like Bronsted acids (species with a tendency to give up a proton) [94] in the reaction sequence.

The processes occurring in alkane cracking, though complex, have been studied for a while and are now established. Farneth and Gorte [93] have proposed two mechanisms according to which cracking may occur. In line with the first mechanism, the process involves the formation of carbenium ions and transfer of hydride ions. It is a chain-like reaction which can be depicted in the following manner:

$$R'–CH_2–CH_2–R + R^+ \longrightarrow RH + R'–CH^+–CH_2–R \quad (3.8a)$$

$$R'–CH^+–CH_2–R \longrightarrow R'–CH=CH_2 + R^+ \quad (3.8b)$$

This mechanism is followed by those zeolites whose extra-framework exchangeable cations (depicted by R^+) possess catalytic properties.

In cases where the zeolite extra-framework cations are exchanged to H^+, a huge number of very strong acid sites ensues. In this case the cracking process occurs according to the following mechanism:

$$R'–CH_2–CH_2–R + H^+ \longrightarrow R'–CH_3^+–CH_2–R \quad (3.9a)$$

$$R'–CH_3^+–CH_2–R \longrightarrow H_2 + R–CH^+–CH_2–R \quad (3.9b)$$

or

$$R'–CH_3^+–CH_2–R \longrightarrow R'–CH_3 + CH_2^+–R \quad (3.9c)$$

Farneth and Gorte [93] have shown significant evidence that Brønsted acid sites are primarily responsible for alkane cracking. This includes the observed reaction products – methane and H_2 – which are in agreement with the second mechanism.

3.5.1.2. Zeolite Pore Size

The size of pores in a zeolite is a result of the number of tetrahedrals in a ring [5], together with the type of cation present in the zeolite under question [67]. This is due to the fact that cations occupy positions which tend to block part of the pores. Monovalent cations occupy every cationic site and lead to lesser pore sizes than in those zeolites with divalent cations, which occupy only every other cationic position, thus leaving bigger spaces on the zeolite pores.

According to Zhu *et al.*, [95], interaction between adsorbed carbenium ions and zeolite surfaces is much stronger in those zeolites with small pore diameters. The fact that catalysis occurs in the zeolite pores as shown by Derouane [96] proves that the size of a zeolite's pores has a direct bearing on the catalytic process.

For a simple first order reaction, the correct expression for the reaction rate is described by the Langmuir–Hinshelwood kinetics:

$$r = k \bullet \theta_A \quad (3.10a)$$

$$= k \bullet K_A(\mathrm{A}) / (1 + K_A(\mathrm{A}) + K_B(\mathrm{B})) \quad (3.10b)$$

where the rate constant is depicted by k and the adsorption equilibrium constants for the reactant and product by K_A and K_B, respectively. In cases where $K_A(\mathrm{A}) + K_B(\mathrm{B})$ is much smaller than 1 (as is often the case for gas phase reactions at rather high temperatures), equation 3.10b is reduced to

$$r = k \bullet K_A(\mathrm{A}) \quad (3.11)$$

For gas phase reactions, expanding equation 3.11 yields

$$r = A \bullet \exp(\Delta S_A R) \bullet \exp(-(E_A + \Delta H_A)\,RT) \quad (3.12)$$

Given that $\Delta H_A = -Q_A$, where Q_A is the heat of adsorption of the reactant A, it can be deduced therefore that the reaction rate is dependent upon the pore size since Q_A is a function of pore size and hence, confinement. This can be used to explain the observation that zeolites with a larger pore size tend to have very high conversion rates (above 95%), whereas those zeolites with relatively smaller pore sizes tend to exhibit lower conversion [95].

In addition, zeolites with large pore sizes have been found to suffer from poor stability as catalysts. Guisnet and Magnoux [97] reported a phenomenon in which large pore zeolites – due to their large pores and supercages – lead to an enhancement of the formation of hydrogen-deficient condensed-ring aromatics. These undesired by-products adsorb strongly on the acidic sites of the zeolite, thus leading to a reduction in the available catalyst sides, hence the degradation and subsequent deactivation of the catalyst.

3.5.1.3. Shape Selective Catalysis

In addition to the pore size, the structure of a zeolite also determines its capacity to catalyse some reactions and not others. This structure-activity relation of zeolites was named *Shape-Selective Catalysis* by Weisz and Frilette in 1960 [98, 99].

Shape selective reactions have been categorized into three types according to their mechanism of action. The first type is reactant selectivity – in which some reactant molecules are too bulky to enter the zeolite pores and are therefore excluded from the reaction. An example is seen in the dehydration of butanols by Ca-A (i.e. zeolite A, exchanged with calcium). N-butanol is readily dehydrated as it can easily penetrate the crystals, whereas isobutanol (which does not penetrate) does not undergo chemical dehydration. This can be used to explain why some zeolites such as Ca-A zeolite and ZSM-5 (used by Mobil company) selectively cracks only straight chain paraffins from a mixture of paraffinic and aromatic hydrocarbons to straight chain products, whereas cycloparaffins, branched and aromatic hydrocarbons which may be present in the mixture are not affected [5]. Figure 3.7 is a schematic of reactant selectivity [100].

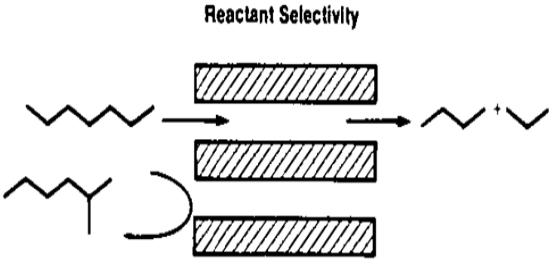


Figure 3.7. Schematic diagram depicting the process of reactant selectivity through pores of a zeolite catalyst. Bulky molecules cannot diffuse through the zeolite pores

The second category – product selectivity – results when the reaction products formed within the pores are restricted from diffusing through the zeolite pores due to incompatibilities caused by their size and / or shape. Product molecules which are sterically less hindered are able to diffuse out of the zeolite microporous framework, whereas the bulky products are hindered from moving throughout the zeolite's cavities. These products may be converted to less bulky molecules (through equilibration) or ultimately accumulate and block all the zeolite's pores, leading to poisoning and ultimate deactivation of the catalyst. The effects of product selectivity are much the same with those of reactant selectivity [100, 101]. An example of product selectivity is depicted in Figure 3.8.

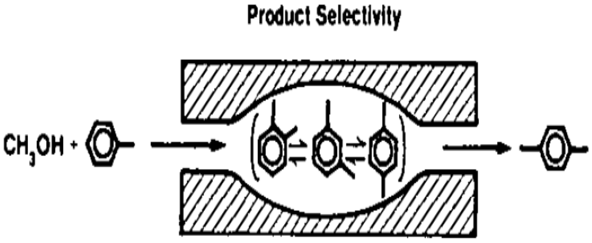


Figure 3.8. A schematic diagram depicting an example of product selectivity through the microporous framework of a zeolite catalyst

The third category of shape-selective reactions is called restricted transition-state selectivity. This category occurs when certain reactions are prevented due to the hindrance of the formation of certain reaction intermediates and/or transition states in the reaction pathway, due to a limitation in the shape and/or size of the microporous lattice. Those intermediate states which tend to require more space than that available in the intracrystalline void volume are most likely not to be formed as a result of the shape and size of the microporous lattice allowing the access of the species formed to interact with the active sites [98, 101]. This is depicted in Figure 3.9.

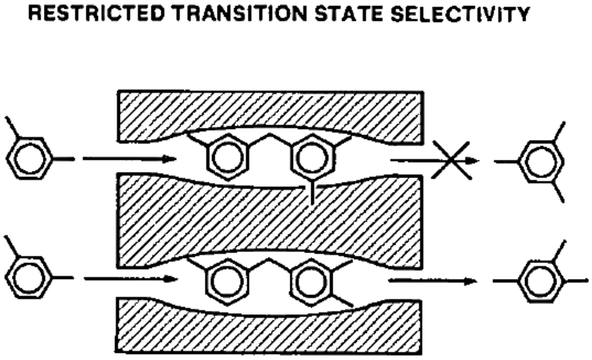


Figure 3.9. A schematic of an example of restricted transition-state selectivity through the microporous framework of a zeolite catalyst

Shape selectivity in zeolites increases with the decrease in pore size, leading to those zeolites with relatively smaller pore sizes being able to suppress reactions which include formation of bulky intermediates, hence allowing only certain products to be formed. This shape-selective character of zeolites is a direct consequence of the strong interaction existing between the adsorbed carbenium ions and the zeolite surface. This interaction is stronger in those zeolites with smaller pore diameter, leading to higher selectivity of product in the cracking process. For this reason, butene cracking in zeolites of small pore-size results in the formation of preferably propene and ethene [95, 98].

3.5.1.4. Ion Exchange

Ion exchange plays a very prominent role in zeolite catalysts. The presence of Al^{3+} ions in zeolite framework atoms leads to anionic lattice sites which have to be charge balanced by cations. If the cations in question are protons or ammonium ions, these lattice sites then act as Brønsted acid sites. Zeolites with such acidic sites can be used in processes which require high hydrogen pressure (e.g. hydrocracking of heavy petroleum distillates) [42, 90]. Most zeolites may also operate as bi-functional catalysts – containing both Brønsted acid sites and a component which activates hydrogen (such as a noble metal like palladium or platinum). Such zeolites are applicable in industrial processes such as the isomerization of light gasoline.

In the manufacture of zeolite catalysts, ion exchange plays an outstanding role as well. For many catalytic applications, a Brønsted acid form of a zeolite is required. Brønsted acid sites in zeolites can be readily generated by introducing ammonium ions followed by a heat treatment or by introducing multivalent metal cations, typically cations of the rare-earths, again followed by heat treatment. In processes which work under hydrogen pressure, such as hydrocracking of heavy petroleum distillates or the isomerization of light gasoline, bifunctional catalysts are needed which contain both Brønsted acid sites and a component which activates hydrogen, typically a noble metal like palladium or platinum. These noble metals can again be easily introduced into the zeolite pores by ion exchange with cationic forms of such metals, e.g. $[Pd(NH_3)_4]^{2+}$ or $[Pt(NH_3)_4]^{2+}$, followed by thermal removal of the ammine ligands. More recently, the use of metal-containing zeolite catalysts for the selective reduction of nitrogen oxides with light hydrocarbons, e.g. in exhaust gases from diesel has become a topic of worldwide research [102, 103].

3.6. Natural Zeolites vs. Synthetic Zeolites

Most of the natural zeolites which are industrially useful are abundant minerals, present in large natural deposits which can be procured at very low costs, making them an economical alternative to synthetic zeolites. Examples of these are clinoptilolite and chabazite. These zeolites can break down heavy molecules (e.g. asphaltenes) within oilsands bitumen into lighter fractions more effectively than alternative processes such as thermal breaking or cracking with zeolite Y (an expensive, synthetic zeolite catalyst). After treatment with natural zeolites, hydrocarbons such as pentane and hexane can then be used to fully extract the lighter petroleum fractions from the oilsands. This combination of efficient, natural zeolite catalyzed cracking and light hydrocarbon extraction has been defined as a step towards waterless liquid hydrocarbon extraction [104].

Although appearing in distinct facies, natural zeolite ores are normally not pure. Due to the vastly differing conditions under which zeolites can form, their ore is normally contaminated by other elements such as metals and crystals. For this reason, isolation processes such as crushing and pellet formation are usually used to obtain zeolites in pure, usable form. These isolation processes also involve different procedures due to the fact that zeolites are obtained from volcanic or sedimentary rocks of dissimilar types, structure and hardness; formed under different conditions. Further complications arise due to there being more than 60 different types of naturally occurring zeolites, each being formed under certain varying conditions [9, 47, 105].

The benefits of synthetic zeolites are that they can be specifically manufactured to favor certain reactions over others. The control of N_2O emissions [67] and the removal of radioactive waste from the environment by use of synthetic zeolites [106-108] are some of the few examples which have demonstrated the benefits of synthetic zeolites over their natural counterparts. The efficiency of natural zeolites in the remediation of wastewater polluted with Cs and Sr radionuclides was found to be lower than that of synthetic zeolites when such waters also contains organic cations [109]. Similar results were obtained in the adsorption of radon by natural and synthetic zeolites [110] and also in the adsorption of various toxic metal ions (Cr^{3+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, and Cd^{2+}) using natural and synthetic zeolite, where the synthetic zeolite showed much higher adsorption capacity for all the ions than did the natural zeolite [111].

The polarities of synthetic zeolites can be easily manipulated as it depends on the zeolite's Al content. Zeolites with high Al content (i.e. low Si:Al ratio) are much more polar than those with higher Si:Al ratio. High polarity zeolites are exhibit stronger sorption capacities due to the presence of stronger (chemisorption) forces and high TCEC values [46, 112]. The polarities of zeolites can be employed to favour applications which may require hydrophilic/ hydrophobic environments. Natural zeolites are normally hydrophilic due to the interaction of the dipole of the H_2O molecule with the electrostatic fields of the anionic aluminosilicate framework. Non-polar zeolites (with higher Si:Al ratio) lack this anionic property and are therefore hydrophobic.

These "high silica zeolites" have a more homogeneous surface characteristic and exhibit high hydrophobic selectivities. They have been used in applications which would otherwise have failed in the presence of water. An example is in the direct esterification of acetic acid with n-, iso-, and tert-butyl alcohol. One of the intermediate products of this reaction is water, whose presence poisons the acid sites of the catalysts. However, the poisoning is lower in the presence of the more hydrophobic high-Si/Al-ratio ZSM-5 catalysts [113].

Yet another advantage of synthetic zeolites is the ability to adjust their pore sizes. According to Bandura *et al.*, [114] synthetic zeolites have significantly larger pore volumes than their natural counterparts. Koshy and Singh [115] have shown that the increased pore sizes of synthetic zeolites places them in a more favorable position as economically viable sorbent minerals for trapping various contaminants from air and water. Furthermore, zeolites with smaller pore sizes normally suffer from pore blockage and ultimately poisoning and deactivation when used as catalysts [116]. In contrast, zeolites having large interconnected channels allow for both shape selectivity and fast diffusion of large molecules through the channels and remain stable much longer in reactions [117, 118].

4. Conclusions

Zeolites have been classified into two major types depending on their source: natural zeolites – which are mined from the earth, and synthetic zeolites – which can be made in the laboratory.

Natural zeolites are mostly found in volcanogenic sedimentary rocks [50], having been formed by chemical reactions of the volcanic ash and alkaline water a few thousand millennia ago. At least 60 species of natural zeolites are known to exist, occurring naturally in soils, sediments, and rocks [44], predominantly concentrated in those rocks and soils of volcanic origin. The most common natural zeolites are analcime, chabazite, clinoptilolite, erionite, mordenite and phillipsite. Natural zeolites have strong adsorptive properties which can be exploited for the removal of contaminants such as heavy metals, nitrogen and sulfur from the extracted petroleum products.

Since the current applications of zeolites require more zeolites than can be mined worldwide, together with the fact that natural zeolites contain impurities (such as quartz which is found in most of the clinoptilolite deposits) often leading to a decrease in the zeolites’ adsorption and ion exchange efficiency [119], a need for artificial production has arisen, resulting in synthetic zeolites. More than 200 synthetic zeolites have been reported [9] and shown to have a more uniform composition than natural zeolites [44]. Synthetic zeolites have higher surface areas, higher micropore volumes, lack impurities and can be specially manufactured for a specific task [61]. A large number of different zeolites with varying functional groups have been synthetically produced for specific purposes. The most common synthetic zeolites are zeolites A, X, Y and ZSM-5.

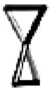
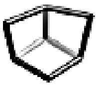
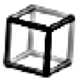
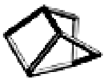
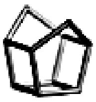
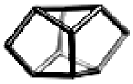
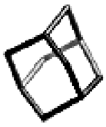
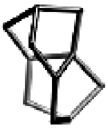
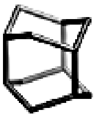
Further research is necessary to tackle the yet undetermined parameters such as the exact behaviour and mechanisms in zeolite-catalysed reactions. Additional comprehension of mechanistic properties of contaminant-surfactant-zeolite interactions will allow advances in applicability of zeolites in providing new low cost, eco-friendly (green) solutions to industrial, agricultural, medicinal to mention but a few challenges.

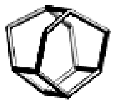
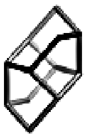
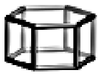
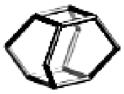
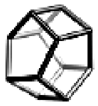
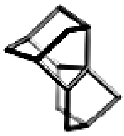
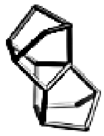
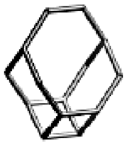
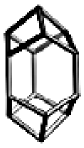
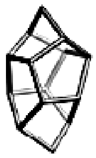
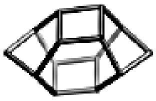
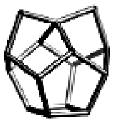
Appendices

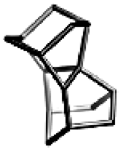
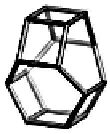
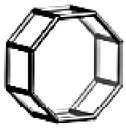
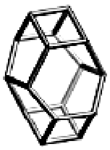
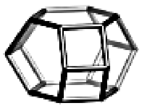
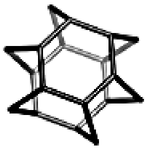
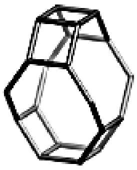
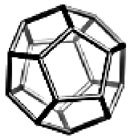
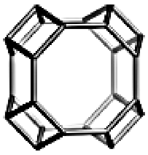
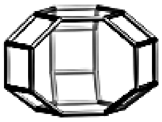
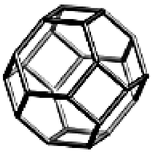
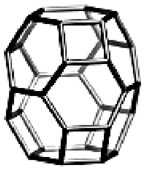
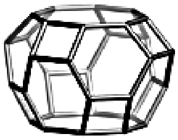
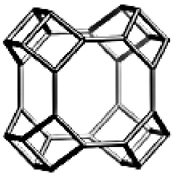
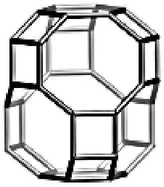
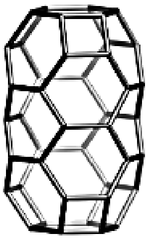
A1. Appendix 1 Selected Composite Building Units

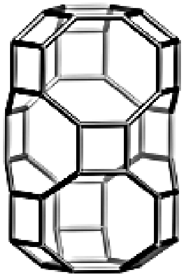
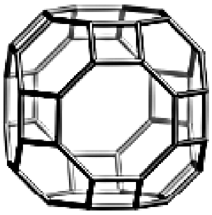
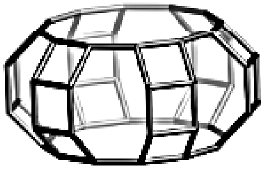
Arranged in order of number of T-atoms in the unit.

Each unit is identified with a lower-case three-character code in italics and the number of T-atoms in the unit. Framework types containing the unit are listed below each unit [25].

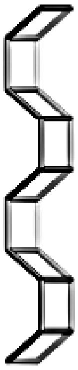
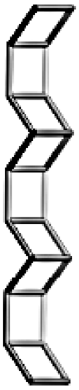
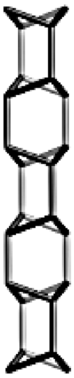
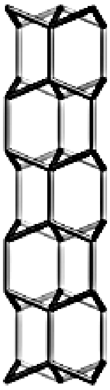
lov *5T*  **LOV, NAB, OBW, OSO, RSN, VSV, WEI**	*nat* *6T*  **EDI, NAT, THO**	*vsv* *6T*  **LOV, NAB, OBW, -RON, RSN, VNI, VSV, WEI**	*mei* *7T*  **AFN, CGF, MEI, USI** (see also *d4r - 8T*, *sti - 8T* and *bph - 14T*)
d4r *8T*  **ACO, AFY, AST, ASV, BEC, -CLO, DFO, ISV, ITH, ITW, IWR, IWV, IWW, LTA, UFI, UOZ, UTL**	*mor* *8T*  ***BEA, BEC, DAC, EON, EPI, IMF, ISV, IWW, MEL, MFI, MOR, MSE, RWR, TUN** (see also *fer - 13T*)	*sti* *8T*  **AFR, DFO, OWE, SAO, SBE, SBS, SBT, SFO, STI, ZON** (see also *d4r - 8T*)	*bea* *10T*  ***BEA, CON, IFR, MSE, STT**
bre *10T*  **BOG, BRE, CON, HEU, IWR, IWW, RRO, STI, TER**	*jbw* *10T*  **JBW, MTT, MTW, SFE, SFN, SSY, TON**	*mtt* *11T*  **CFI, IMF, MFS, MTT, SFE, SSY, SZR, TON, TUN** (see also *non - 15T*)	*afi* *12T*  **AEL, AET, AFI, AFO, ATV, DON, SFH, VFI** (see also *bph - 14T*)

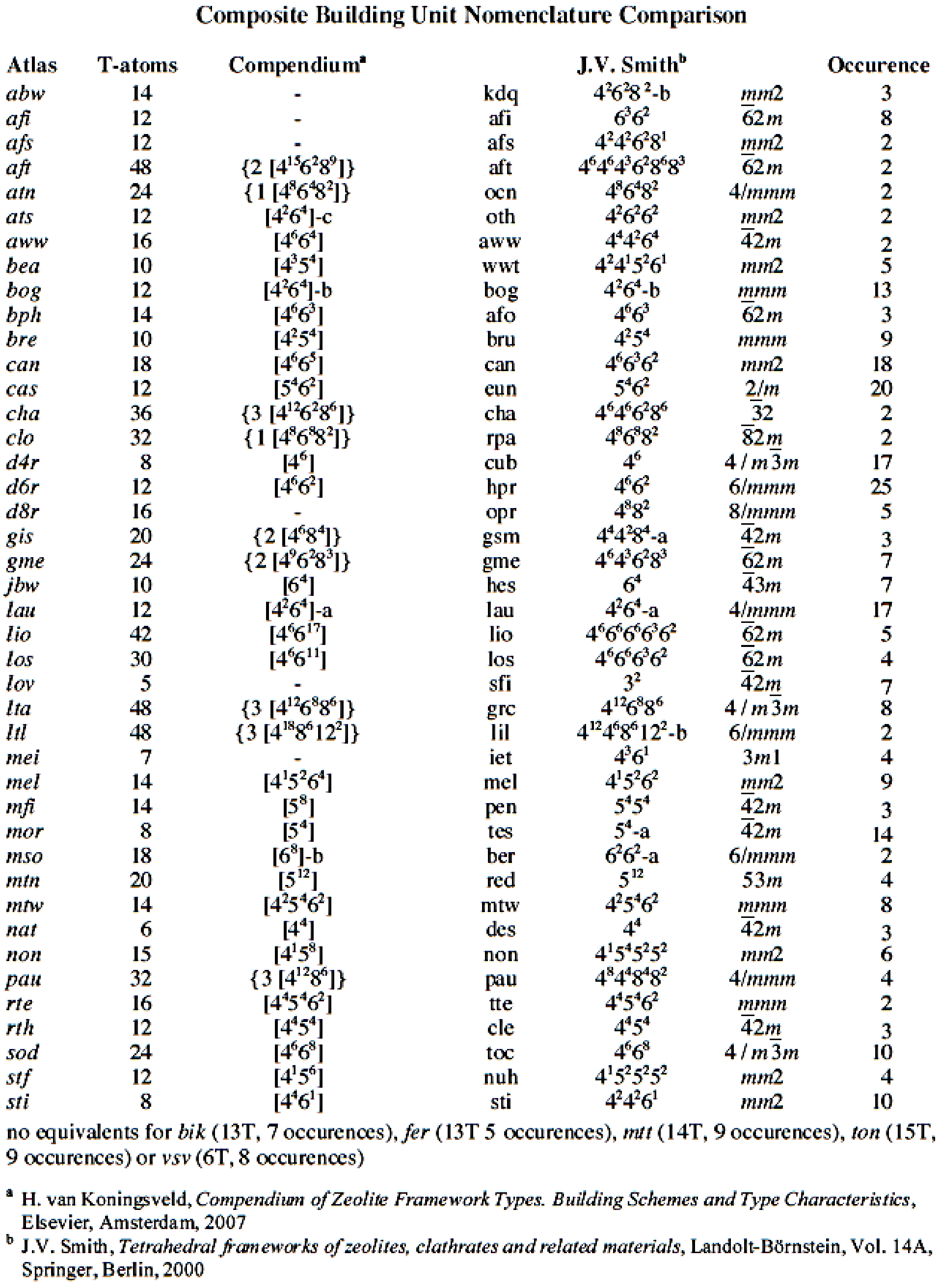
afs *12T*  **AFS, BPH** (see also *aww - 16T*)	*ats* *12T*  **ATS, IMF, OSI**	*bog* *12T*  **AEL, AET, AFI, AFO, AHT, ATV, BOG, CGF, DFO, LAU, TER, USI, VFI**	*cas* *12T*  **BOG, CAS, CFI, EUO, GON, IHW, IWV, MFI, MTW, NES, NSI, SFF, SFH, SFN, STF, STT, TER, TUN, UTL, VET**
d6r *12T*  **AEI, AFT, AFX, CHA, EAB, EMT, ERI, FAU, GME, KFI, LEV, LTL, LTN, MOZ, MSO, MWW, OFF, SAS, SAT, SAV, SBS, SBT, SZR, TSC, -WEN**	*lau* *12T*  **ASV, ATO, BCT, CON, DFO, EZT, IFR, ITH, IWR, IWW, LAU, MSO, OSI, -RON, SAO, TUN, UOZ** *(see also mtw - 14T)*	*rth* *12T*  **ITE, RTH, UFI**	*stf* *12T*  **SFF, STF, TUN, IMF, IWW**
bik *13T*  **BIK, CAS, MTT, MTW, NSI, SFE, TON**	*fer* *13T*  **CDO, FER, IMF, MFS, UTL**	*abw* *14T*  **ABW, ATT, JBW**	*bph* *14T*  **AFS, BPH, EZT**
mel *14T*  **CON, DON, ITH, IWR, IWW, MEL, MFI, MWW, SFG**	*mfi* *14T*  **MEL, MFI, MTF**	*mtw* *14T*  ***BEA, BEC, GON, ISV, MSE, MTW, SFH, SFN**	*non* *15T*  **EUO, IHW, IWV, NES, NON, UTL**

ton 15*T*  CFI, IHW, IWV, MTT, NES, SFE, SSY, TON, UTL	*aww* 16*T*  AWW, SAO	*d8r* 16*T*  MER, PAU, RHO, SBE, TSC	*rte* 16*T*  RTE, RUT
can 18*T*  AFG, CAN, ERI, FAR, FRA, GIU, LIO, LOS, LTL, LTN, MAR, MOZ, OFF, SAT, SBS, SBT, TOL, -WEN	*mso* 18*T*  MSO, SZR	*gis* 20*T*  ATT, GIS, SIV	*mtn* 20*T*  DDR, DOH, MEP, MTN
atn 24*T*  ATN, SBE	*gme* 24*T*  AFT, AFX, EAB, EON, GME, MAZ, OFF	*sod* 24*T*  EMT, FAR, FAU, FRA, GIU, LTA, LTN, MAR, SOD, TSC	*los* 30*T*  FRA, LIO, LOS, TOL
clo 32*T*  AWW, -CLO	*pau* 32*T*  KFI, MER, MOZ, PAU	*cha* 36*T*  AFT, CHA	*lio* 42*T*  AFG, FAR, LIO, MAR, TOL

aft *48T*	*lta* *48T*	*ltl* *48T*
		
AFT, AFX	**-CLO, KFI, LTA, LTN, PAU, RHO, TSC, UFI**	**LTL, MOZ**

Selected Chains

double zigzag chain	*double crankshaft chain*	*double sawtooth chain*	*narsarsukite chain*	*double narsarsukite chain*
dzc	*dcc*	*dsc*	*nsc*	*dnc*
				
ABW, ATN, ATS, CAN, JBW, OSI, SFE, SFH, SFN, SSY, USI	**APC, ATT, AWO, DON, GIS, GME, MER, PHI, SIV, UEI**	**ATT, EON, LTL, MAZ, MOZ, OFF, OWE, SAO, -WEN**	**AEL, AET, AFI, AFO, APD, ATV, DFT**	**AET, AHT, VFI**



Composite Building Unit Nomenclature Comparison

Atlas	T-atoms	Compendium[a]	J.V. Smith[b]			Occurence
abw	14	-	kdq	$4^2 6^2 8^2$-b	$mm2$	3
afi	12	-	afi	$6^3 6^2$	$\bar{6}2m$	8
afs	12	-	afs	$4^2 4^2 6^2 8^1$	$mm2$	2
aft	48	$\{2\ [4^{15} 6^2 8^9]\}$	aft	$4^6 4^6 4^3 6^2 8^6 8^3$	$\bar{6}2m$	2
atn	24	$\{1\ [4^8 6^4 8^2]\}$	ocn	$4^8 6^4 8^2$	$4/mmm$	2
ats	12	$[4^2 6^4]$-c	oth	$4^2 6^2 6^2$	$mm2$	2
aww	16	$[4^6 6^4]$	aww	$4^4 4^2 6^4$	$\bar{4}2m$	2
bea	10	$[4^3 5^4]$	wwt	$4^2 4^1 5^2 6^1$	$mm2$	5
bog	12	$[4^2 6^4]$-b	bog	$4^2 6^4$-b	mmm	13
bph	14	$[4^6 6^3]$	afo	$4^6 6^3$	$\bar{6}2m$	3
bre	10	$[4^2 5^4]$	bru	$4^2 5^4$	mmm	9
can	18	$[4^6 6^5]$	can	$4^6 6^3 6^2$	$mm2$	18
cas	12	$[5^4 6^2]$	eun	$5^4 6^2$	$2/m$	20
cha	36	$\{3\ [4^{12} 6^2 8^6]\}$	cha	$4^6 4^6 6^2 8^6$	$\bar{3}2$	2
clo	32	$\{1\ [4^8 6^8 8^2]\}$	rpa	$4^8 6^8 8^2$	$\bar{8}2m$	2
d4r	8	$[4^6]$	cub	4^6	$4/m\bar{3}m$	17
d6r	12	$[4^6 6^2]$	hpr	$4^6 6^2$	$6/mmm$	25
d8r	16	-	opr	$4^8 8^2$	$8/mmm$	5
gis	20	$\{2\ [4^6 8^4]\}$	gsm	$4^4 4^2 8^4$-a	$\bar{4}2m$	3
gme	24	$\{2\ [4^9 6^2 8^3]\}$	gme	$4^6 4^3 6^2 8^3$	$\bar{6}2m$	7
jbw	10	$[6^4]$	hes	6^4	$\bar{4}3m$	7
lau	12	$[4^2 6^4]$-a	lau	$4^2 6^4$-a	$4/mmm$	17
lio	42	$[4^6 6^{17}]$	lio	$4^6 6^6 6^6 6^3 6^2$	$\bar{6}2m$	5
los	30	$[4^6 6^{11}]$	los	$4^6 6^6 6^3 6^2$	$\bar{6}2m$	4
lov	5	-	sfi	3^2	$\bar{4}2m$	7
lta	48	$\{3\ [4^{12} 6^8 8^6]\}$	grc	$4^{12} 6^8 8^6$	$4/m\bar{3}m$	8
ltl	48	$\{3\ [4^{18} 8^6 12^2]\}$	lil	$4^{12} 4^6 8^6 12^2$-b	$6/mmm$	2
mei	7	-	iet	$4^3 6^1$	$3m1$	4
mel	14	$[4^1 5^2 6^4]$	mel	$4^1 5^2 6^2$	$mm2$	9
mfi	14	$[5^8]$	pen	$5^4 5^4$	$\bar{4}2m$	3
mor	8	$[5^4]$	tes	5^4-a	$\bar{4}2m$	14
mso	18	$[6^8]$-b	ber	$6^2 6^2$-a	$6/mmm$	2
mtn	20	$[5^{12}]$	red	5^{12}	$53m$	4
mtw	14	$[4^2 5^4 6^2]$	mtw	$4^2 5^4 6^2$	mmm	8
nat	6	$[4^4]$	des	4^4	$\bar{4}2m$	3
non	15	$[4^1 5^8]$	non	$4^1 5^4 5^2 5^2$	$mm2$	6
pau	32	$\{3\ [4^{12} 8^6]\}$	pau	$4^8 4^4 8^4 8^2$	$4/mmm$	4
rte	16	$[4^4 5^4 6^2]$	tte	$4^4 5^4 6^2$	mmm	2
rth	12	$[4^4 5^4]$	cle	$4^4 5^4$	$\bar{4}2m$	3
sod	24	$[4^6 6^8]$	toc	$4^6 6^8$	$4/m\bar{3}m$	10
stf	12	$[4^1 5^6]$	nuh	$4^1 5^2 5^2 5^2$	$mm2$	4
sti	8	$[4^4 6^1]$	sti	$4^2 4^2 6^1$	$mm2$	10

no equivalents for *bik* (13T, 7 occurences), *fer* (13T 5 occurences), *mtt* (14T, 9 occurences), *ton* (15T, 9 occurences) or *vsv* (6T, 8 occurences)

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