

Chapter 2

Basics of Zeolites

Abstract Tectosilicates have been commonly established as zeolites, which are found in nature as well as synthesized artificially. Depending upon the type of source (read raw) materials used and the method(s) of synthesis adopted, properties of the zeolites would vary and hence their application as adsorbents could be different. Keeping this in view, an in-depth description of the zeolites, their types and properties are presented in the following.

Keywords Zeolites · Fly ash zeolites · Properties of zeolites · Application of zeolites

2.1 Zeolites

Zeolites represent a group of more than 50 soft, white aluminosilicate minerals of tectosilicate type, i.e., a three dimensional framework (refer Fig. 2.1a, b) of interconnected tetrahedra, comprising (mostly) of aluminum, silicon and oxygen atoms [1]. They consist of a crystalline structure built from $[\text{AlO}_4]^{5-}$ and $[\text{SiO}_4]^{4-}$, bonded together in such a way that all four oxygen atoms located at corners of each tetrahedron are shared with adjacent tetrahedral crystals as shown in Fig. 2.1c–e [1–7]. As presented in Fig. 2.1f, if each tetrahedron in the framework contains silicon as its central atom, the overall structure becomes electrically neutral (as in Quartz, SiO_2). In zeolite structures, some of the quadri-charged silicon cations are replaced by triply-charged aluminum, giving rise to a deficiency of positive charge. The so developed charge is balanced by the presence of singly- and/or doubly-charged cations, such as sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}), elsewhere in the structure, featuring spacious pores or rings [2, 5, 6, 8, 9].

The general formula of a zeolite is $\text{M}_{e2/n} \text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ [2, 10], where, M_e is any alkali or alkaline earth atom, n is the charge on that atom, x is the number of Si tetrahedron varying from 2 to 10, and y is the number of water molecules varying from 2 to 7. The Si and Al tetrahedra combinedly form a structural framework in zeolites with centrally located Si or Al atoms and corners

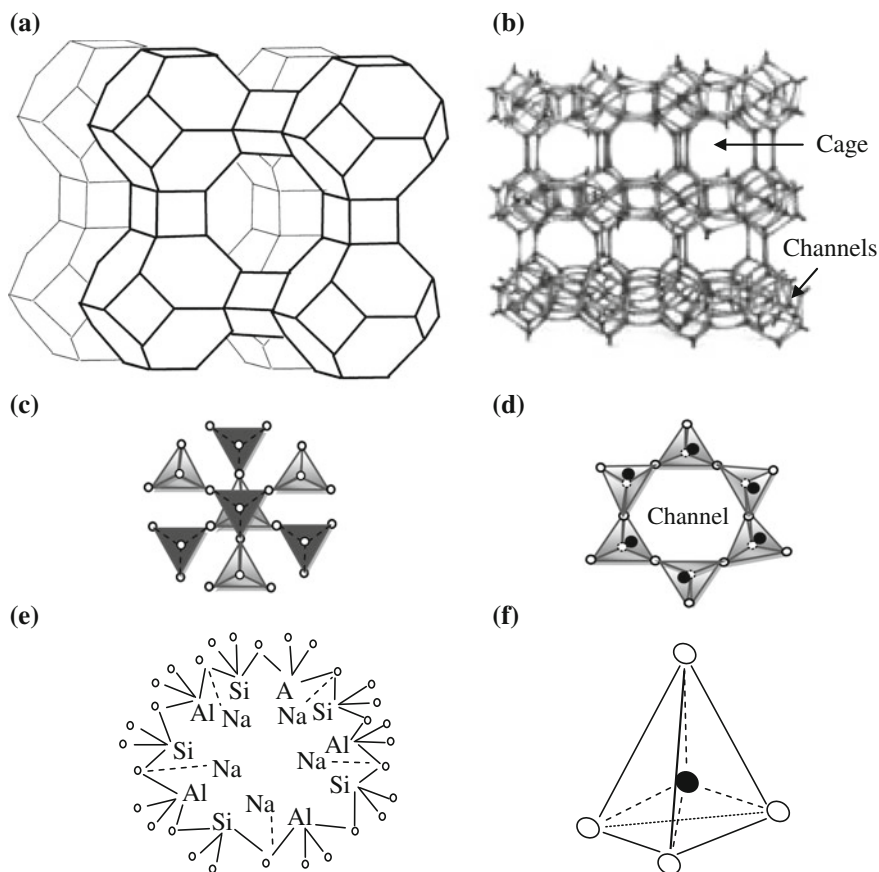


Fig. 2.1 **a** The schematic view of the crystal structure of zeolite 4A and **b** typical zeolite structure showing three dimensional cages and channels [8]. **c** Basic tectosilicate structure of zeolite where *dark* (i.e., vertex in) and *light* (i.e., vertex out) *shades* to add 3-dimensional (3-D) effect and upside down orientation of the tetrahedra for vertex sharing between two rings of the zeolite structure in its 2-D view on a picture plane. **d** Single ring tetrahedron structure and framework of a zeolitic mineral and **e** $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ in a ring of sodium zeolite and **f** Pictorial representation of a 3-D view of a tetrahedral with centrally located Si or Al atoms, exhibited by *dotted lines* drawn to represent the portion within the body of the mineral [8]

occupied by oxygen atoms. The oxygen atom being common between $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra, remains oriented in such a way that the framework develops voids or pores in the form of cages and channels between the tetrahedra, as depicted in Fig. 2.1a, b [11, 12]. The structural formula of the zeolite based on its crystal unit cell (assuming both the SiO_2 and AlO_2 as variables) can be represented by $\text{M}_{a/n}(\text{AlO}_2)_a(\text{SiO}_2)_b \cdot w\text{H}_2\text{O}$, where, w is the number of water molecules per unit cell, and a and b are total numbers of tetrahedra of Al and Si, respectively per unit cell. The ratio of b/a usually varies from 1 to 5, for Mordenite [i.e., $\text{Na}_8(\text{AlO}_2)_8$

(SiO_2)₄₀, where a is 8, b is 40 and hence b/a is 5] and zeolite 4A [i.e., $\text{Na}_{96}(\text{AlO}_2)_{96}(\text{SiO}_2)_{96}$, where a is 96, b is 96 and b/a is 1]. Exceptionally, some zeolites are having b/a varying from 10 to 100 or even higher than 100 for ZSM -5 type zeolites [6, 8, 10, 13].

As depicted in Fig. 2.1e, a low silica sodium zeolite ($\text{Si}/\text{Al} = 1$, $\text{Na}/\text{Al} = 1$, i.e., zeolite 4A) possess an open cage within the lattice and a vast network of negatively charged open channels (accommodating Na^+ cation) due to presence of the common oxygen atom between Si and Al tetrahedra [12]. In addition, the pores or channels (refer to Fig. 2.1a–c) are of microscopically small size as of molecular dimensions and hence they are also called as the “molecular sieves” which facilitate cation exchange in adsorption process. Based on these attributes, zeolites find applications in separation and filtration processes.

The crystalline lattice structure of zeolites consists of exceptional lattice stability by virtue of which they facilitate considerable freedom of ion-exchange and reversible dehydration. Zeolites can accommodate new cations (mainly sodium, potassium, magnesium and calcium), water molecules and even small organic molecules. Furthermore, ions and molecules in the cages are loosely bound so that they can be removed or exchanged without destroying the zeolitic framework. However, this depends on the chemical composition and the crystalline structures of a specified zeolite. In general, zeolite minerals have been classified into various families as presented in Table 2.1 [2, 7, 8, 14, 15].

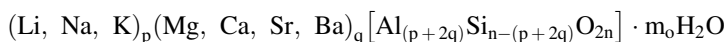
Though, zeolites were first identified by Cronsted in 1756 their molecular sieve properties remained untouched until mid 1920s and a lack of development for commercial use of natural zeolites remained for some time more [2, 15]. With this in view, researchers’ attention turned to the synthesis of zeolites, popularly known as synthetic zeolites, by employing pure chemicals [15] and/or minerals present in natural resources or their by-products like coal fly ash [3, 4, 16–29].

Table 2.1 Minerals of the zeolite family [8]

Family of zeolites	Minerals	Shape
Analcime	Analcime, pollucite, wairakite, bellbergite, bikitaite, boggsite, brewsterite	Cubic/tetrahedral
Chabazite	Chabazite, willhendersonite, cowlesite, dachiardite, edingtonite, epistilbite, erionite, faujasite, ferrierite	Rhombohedral
Gismondine	Amicite, garronite, gismondine, gobbinsite, gmelinite, gonnardite, goosecreekite	Monoclinic/orthogonal
Harmotome	Harmotome, phillipsite, wellsit	Monoclinic
Heulandite	Clinoptilolite, heulandite, laumontite, levyne, mazzite, merlinoite, montesommaite, mordenite	Monoclinic/orthogonal
Natrolite	Mesolite, natrolite, scolecite, offretite, paranatrolite, paulingite, perialite	Orthogonal/tetrahedral
Stilbite	Barrerite, stilbite, stellerite, thomsonite, tschernichite, yugawaralite	Monoclinic

2.1.1 Natural Zeolites

Zeolites in nature often, formed as crystals in small cavities of basaltic rocks over the years or as volcanic tuffs or glass altered by the interaction with saline water. These natural zeolites are formed in a number of geological environments such as alkaline deserts, lake sediments, ash ponds and marine sediments at relatively low temperature, under natural conditions. They also get crystallized in geologically young metamorphic rocks in mountainous regions. In the 1950s, geologists discovered that million-ton deposits of volcanic tuff consisting mostly of zeolitic materials are not uncommon [5, 7, 15]. Such zeolitic crystals, by virtue of their unique structures, get filled up with water which can be driven off by heating. As such, the dried up crystals possess a honeycomb-like structure consisting of openings or pores of the order of a few atoms in width ($\sim 2\text{--}10 \text{ \AA}$) [30–32]. The most general formula of natural zeolites is as depicted below [8, 22, 33]:



where, p is the number of monovalent metal ion, q is the number of divalent metal ions, n is the half of the number of oxygen atom and m_o is the number of water molecules.

Natural zeolites such as Clinoptilolite (i.e., popularly known as Clino zeolites) and Chabazite have applications in various diversified fields such as water treatment, fertilizer application for soil amendment and plant growth by establishing better retention of nutrients. The Clinoptilolite has been broadly accepted for its usage in agriculture, soil amendment and feed additives because of its higher acid resistant silica content (viz., $\text{Si/Al} = 1\text{--}5$) [14]. However, such zeolites are contaminated by other minerals (e.g., Fe^{2+} , SO_4^{2-} , Quartz, other zeolites, and amorphous glass) and hence they may not be suitable for several important commercial applications where uniformity and purity are essential [8].

2.1.2 Synthetic Zeolites

These zeolites are synthesized by chemical processes, which result in a more uniform and purer state as compared to the natural types in terms of their lattice structures, sizes of pores and cages in their frameworks. The principal raw materials useful for synthesis of synthetic zeolites can be pure chemicals rich in silica and alumina, minerals available on the earth or by-products of industries. Fly ash being an abundantly and cheaply available industrial by-product, rich in minerals containing silica and alumina can be an alternative material for synthesis of synthetic zeolites [20, 34–39]. The type of zeolites formed is a function of the temperature, pressure, concentration of the reagent solutions, pH, process of activation and ageing period, SiO_2 and Al_2O_3 contents of the raw materials [1, 8]. Based on the

Table 2.2 Grades of zeolites [8]

Zeolite grade	Si/Al molar ratio	Some of the common mineral names and their framework codes
Low silica	≤ 2	Analcime (ANA), cancrinite (CAN), Na-X (FAU), natrolite (NAT), phillipsite (PHI), sodalite (SOD)
Intermediate silica	2–5	Chabazite (CHA), faujasite (FAU), mordenite (MOR), Na-Y (FAU)
High silica	>5	ZSM-5 (MFI), zeolite- β (BEA)

Si/Al molar ratio in the activated fly ash, zeolites can be classified/graded as “low silica zeolites”, “intermediate silica zeolites” and “high silica zeolites”, as listed in Table 2.2. In general, for zeolites, an increase in this parameter (i.e., Si/Al from 0.5 to infinity) [5] can significantly result in the increase in various other parameters (viz., acid resistivity, thermal stability and hydrophobicity) except few parameters (viz., hydrophilicity, acid site density and cation concentration) which get decreased [5, 8, 10, 40, 41]. In general, synthetic zeolites hold some key advantages over their counterparts’ i.e. natural zeolites. Zeolites type A, X, Y, P and Na-P1 are well known synthetic zeolites synthesized from fly ash which have a wider range of industrial applications than the natural zeolites [1, 8, 20, 22, 36, 42, 43].

2.1.3 Properties of Zeolites

A comprehensive discussion on various properties of zeolites viz., physical, chemical, ion exchange and adsorption properties, mineralogical and morphological characteristics, thermal characteristics, characteristics of zeolites in acidic medium, crystal structure, framework of zeolitic crystals and surface properties is presented in the following.

2.1.4 Physical Properties

The most general physical properties of the zeolites are bulk density and specific gravity (i.e., somewhere in between 2 and 2.4), which can correlate with their porosity (i.e., the measure of the pore volume in zeolite) and the cation exchange capacity (CEC) [15, 35, 41, 42].

For example, the observed trends of variations such as one between porosity and CEC and another between porosity and specific gravity are exhibited by Fig. 2.2a. It can be noticed that there is negligible change in specific gravity with increase in porosity of zeolites (viz., Analcime, Mordenite, Phillipsite, Clinoptilolite, Erionite, Heulandite and Chabazite), whereas, the trend of variation in CEC is initially decreasing with increasing porosity up to 34 %. Beyond this, there is reversion in

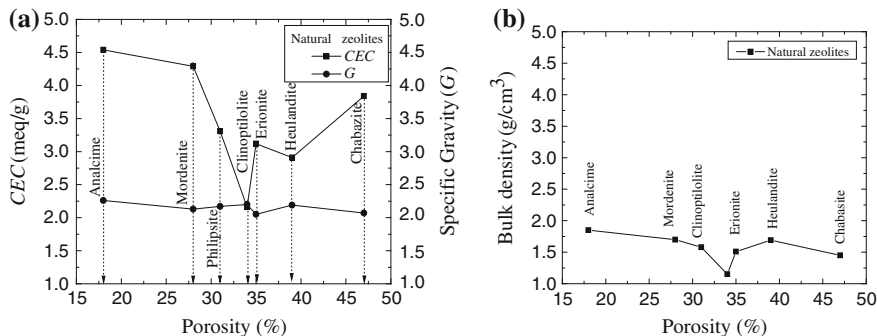


Fig. 2.2 Variation of porosity of natural zeolites **a** with CEC and G , **b** with bulk density [8]

the trend which can be attributed to the corresponding extreme variations in the purity (i.e., higher grade) of zeolites.

In addition, the surface hardness of zeolite is of the order of 3–5 kg which can be indirectly correlated with its specific gravity [15, 34, 35, 41, 42].

The most common physical property of the ash zeolites is its specific surface area, which is dependent on the extent of dissolution of fly ash particles in alkaline solvents [19, 22, 31]. In line with this, another important physical property of zeolites is their void volume which can directly be correlated with the CEC of the synthesized product (e.g., fly ash zeolites, Na-P1) and which in turn depends upon the specific area as depicted in Fig. 2.3a, b [1, 22]. Moreover, both CEC and the surface area of the ash zeolites are found to undergo significant variations with increase in molarity and the reaction time, as depicted in Fig. 2.3c, d [22, 29]. From the trends depicted in Fig. 2.3c, it can be observed that the CEC increases, marginally, with an increase in concentration, however, the same is noticed to be fluctuating, randomly, with an increase in reaction time. This can be attributed to the variations in the pore size and volume, as depicted in Fig. 2.3a. On the contrary, the surface area maintains an increasing trend with increase in concentration and the reaction time, as depicted in Fig. 2.3d, which can be attributed to increase in dissolution of fly ash ingredients (viz., glass, Quartz and Mullite).

Another important physical property of the ash zeolites is their pore radius R_p . This parameter helps in studying the adsorption properties of zeolites as an adsorbent. R_p can be correlated with the specific surface area SSA_{BET} , which can be determined by nitrogen adsorption technique (i.e., by employing BET method and the relationship, $R_p = 2 \cdot V_p / SSA_{BET}$, where V_p is the pore volume) [44]. The pores are assumed to be cylindrical in shape for natural zeolites; Clinoptilolite and Mordenite, for which SSA_{BET} generally lies between 11–16 m² and 115–120 m²/g, respectively. The trend depicted in Fig. 2.4 exhibits an initial increase in R_p with an increase in SSA_{BET} , up to 20 m²/g, beyond which it decreases sharply [8]. This trend violates the inverse relationship between the two parameters as mentioned above.

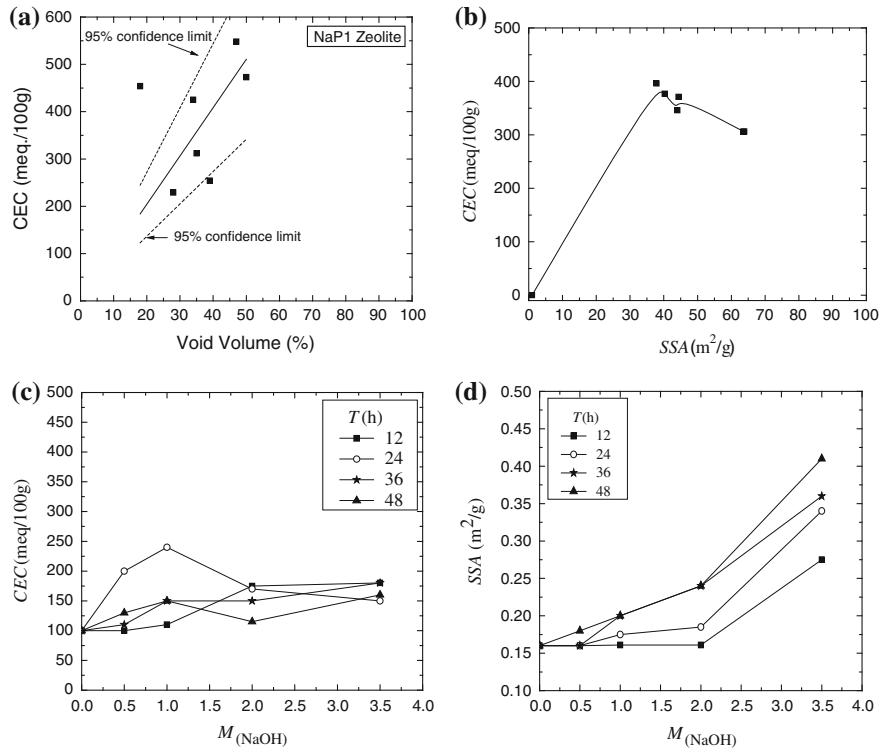


Fig. 2.3 Variation of CEC with **a** void volume, **b** specific surface area of the activated fly ash, **c** with concentration of NaOH and **d** variation of specific surface area with concentration of NaOH [8]

Fig. 2.4 The observed relation between specific surface area and pore radius of zeolite [8]

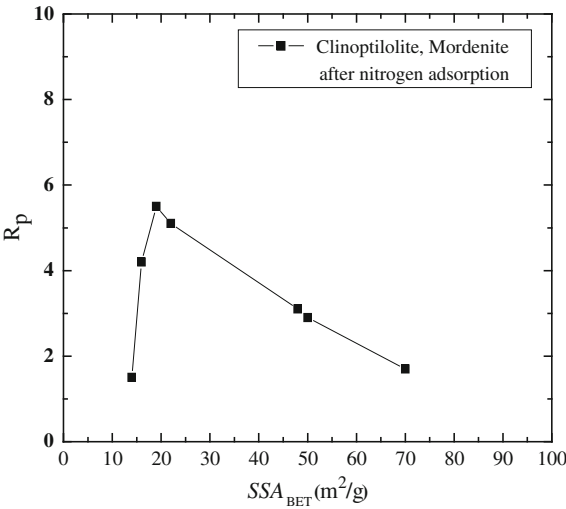


Table 2.3 Physical properties of the zeolite–clinoptilolite [8]

Bulk density (g/cc)	Clinoptilolite content (%)	CEC (meq./g)	Surface charge density (meq./Å ²)	Si/Al	Pore size diameter (Å)	Pore volume (%)	Total surface area (m ² /g)
2.38–2.81	75–85	0.8–1.2	10×10^{-23}	1–5	4–7	≤ 52	≤ 800

The most general physical property of common zeolites (e.g., Na-X also called zeolite X or Linde X or molecular sieve 13X which is an analogue of natural zeolite popularly known as Faujasite) is their particle size, which has been reported to vary from 2 μm (for bulk-Na-X) to 800 nm (for micro-Na-X) and from 20 to 100 nm for nano-Na-X zeolite [45]. Incidentally, a wide range of variation in the particle size, the effective particle size (i.e., the sieve size which allows passing of 10 % of the material by weight) and the uniformity co-efficient (i.e., the ratio of the sieve size that can permit passage of 60 % of the material by weight to the sieve size corresponding to the passage of 10 % of the material by weight) are quite commonly associated with the zeolites. An example of a commercial grade of the natural zeolite, popularly known as Clinoptilolite, which is used in fertilizers manufactured by St. Cloud, USA, is being cited in Table 2.3 to exhibit a wide range of variations in various physical properties of zeolites [8, 46].

2.1.5 Chemical Properties

Zeolites consist of aluminium oxide, calcium oxide, iron oxide, magnesium oxide, potassium oxide, silicon oxide and sodium oxide within their structure with water molecules and/or cations in the pores and the cages [10, 20, 27, 46–48]. A certain fraction of the mass of the zeolites is lost on ignition because of loss of water. Researchers have suggested that, for a material to get zeolited, the ratio of (Si + Al)/O in it should be equal to 0.5 [16, 46–48]. The cation exchange capacity (CEC), adsorption properties, pH, and loss on acid immersion of zeolites are some of the chemical properties which are reported to depend on the chemical composition of the synthesized products. Table 2.4 presents typical chemical composition of a fly ash, its crystalline constituents (viz., Quartz and Mullite), one commercial grade synthetic zeolite, a fly ash zeolite and their comparison with a natural zeolite [47, 48].

It can be noticed from the data presented in Table 2.4 that the chemical composition of the fly ash zeolites (i.e., synthesized by Ojha et al. [48] and Park et al. [47]) is very close to the commercial grade synthetic zeolite 13X with Si/Al ratio equal to 1.5 [12, 47, 48], whereas, natural zeolite is comparatively rich in silica with Si/Al ratio equal to 4 [12, 21]. Hence, it can be opined that a wide range of chemical

Table 2.4 Chemical composition of fly ash, its minerals and zeolites of natural and synthetic types (by weight%) [8]

Material	Oxide (%)						
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	Na ₂ O	K ₂ O
Fly ash	52.1	32.1	5.5	2.1	0.75	1.9	1.3
Mullite	27.8	71.5	–	–	–	–	–
Quartz	>99	–	–	–	–	–	–
Fly ash zeolite	43.6	29.5	3.6	1.9	0.7	20.5	0.91
Zeolite-13X (commercial grade)	48.26	31.85	3.2	0.08	0.38	15.7	0.07
Natural zeolites	64.0	16.1	2.8	0.3	0.2	3.5	3.7

– not applicable

transformation takes place from mineral phase of the fly ash to the corresponding fly ash zeolite phase.

2.1.6 Ion Exchange and Adsorption Properties

Zeolites usually gain cations (viz., Na⁺, K⁺ and NH₄⁺) during the synthesis process or by interaction with the surrounding medium by virtue of their ion exchange or adsorption characteristics [1, 11, 17, 29, 31, 39, 49]. In fact, the cations are accommodated to balance the negative charge developed on the surfaces of pores in zeolites. This can be attributed to the replacement of Si atom by Al atom in some of the [SiO₄]^{4–} tetrahedra and its conversion into the [AlO₄]^{5–} tetrahedron which is interconnected to other [SiO₄]^{4–} tetrahedron by common oxygen atom as depicted above in Fig. 2.1e, f. As for example, ion exchange process can be described by exposing a sodium zeolite to a waste water sample or a fresh solution containing other metal cations (e.g. NH₄⁺). In fact, the sodium ions of the zeolite can be exchanged by ammonium ions provided they are not excluded from the zeolite pores due to higher molecular size. Based on the findings of the previous researchers, a typical ion exchange process of waste water treatment by zeolite application at room temperature is simulated below by allowing ammonium chloride solution to pass through a zeolite sample, as depicted in Fig. 2.5. It can be noticed that the Na⁺ of the zeolite can easily be exchanged with the NH₄⁺ by this process of ion exchange.

The heavy metal cations such as Rb, Cs, Ag, Cd, Pb, Zn, Ba, Sr, Cu, Hg, Co, and Cr have affinity towards zeolites, although, their selectivity by the zeolites for exchange depends on the hydrated molecular size of the cations, their relative concentrations in the medium associated with the process and the Si/Al molar ratio of the zeolite framework [3, 25, 37, 38, 43, 50, 51].

Based on these properties, the zeolites have been also found to adsorb gases and separate them for useful industrial applications. The most common gases being CO,

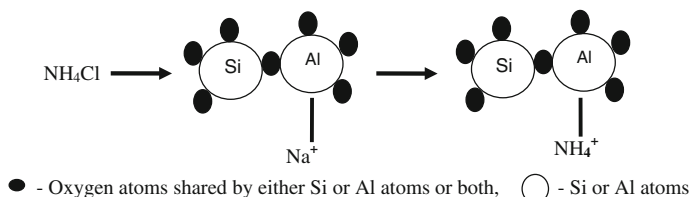


Fig. 2.5 Typical ion exchange process in a mixture of ammonium chloride and any sodium zeolites [8]

CO_2 , SO_2 , H_2S , NH_3 , HCHO , Ar, O_2 , N_2 , H_2O , He, H_2 , Kr, Xe, CH_2OH , Freon and Formaldehyde [38, 43, 51, 52].

2.1.7 Mineralogical Properties

X-ray diffraction (XRD) analysis has been a useful tool to check the presence of minerals (viz., Mullite, Hematite, Magnetite and α -Quartz) as the main crystalline phase in the fly ash and its zeolites, in addition to the presence of amorphous glassy phase [16, 38]. Furthermore, micrographs obtained by scanning electron microscopy (SEM) of the fly ash and its zeolites, as depicted in Fig. 2.6a, have been found to be a useful tool for demonstrating the shape and grain size of constituent minerals (refer Table 2.5 [8, 24]).

However, after crystallization, only the new peaks detected in the XRD pattern can depict the presence of zeolite crystals, of varying intensity corresponding to different reaction times for treatment with NaOH, as depicted in Table 2.6 [4, 8, 20, 37]. It can be noticed that the XRD intensities reduce significantly, corresponding to an increase in the reaction time from 2.5 to 3.0 h. This can be attributed to an increase in dissolution of crystals of zeolite P and Quartz, which is an indication of their less stable forms as compared to Mullite. Further, based on the location of peaks, the maximum intensities for some common zeolites are presented in Table 2.7. From the data presented in the table, it can be noted that most commonly occurring ash zeolites (viz., zeolite P, Na-A and Na-X) can easily be identified by the appearance of new peaks in the XRD diffractogram.

Similarly, XRD of naturally available zeolitic minerals do exhibit variations in their mineralogical features, and hence their properties (viz., structure type, pore size dimensions, channel dimensions, surface charge density and electro-negativity), which are the decisive factors related to zeolites and their industrial applications [16, 23, 53, 54].

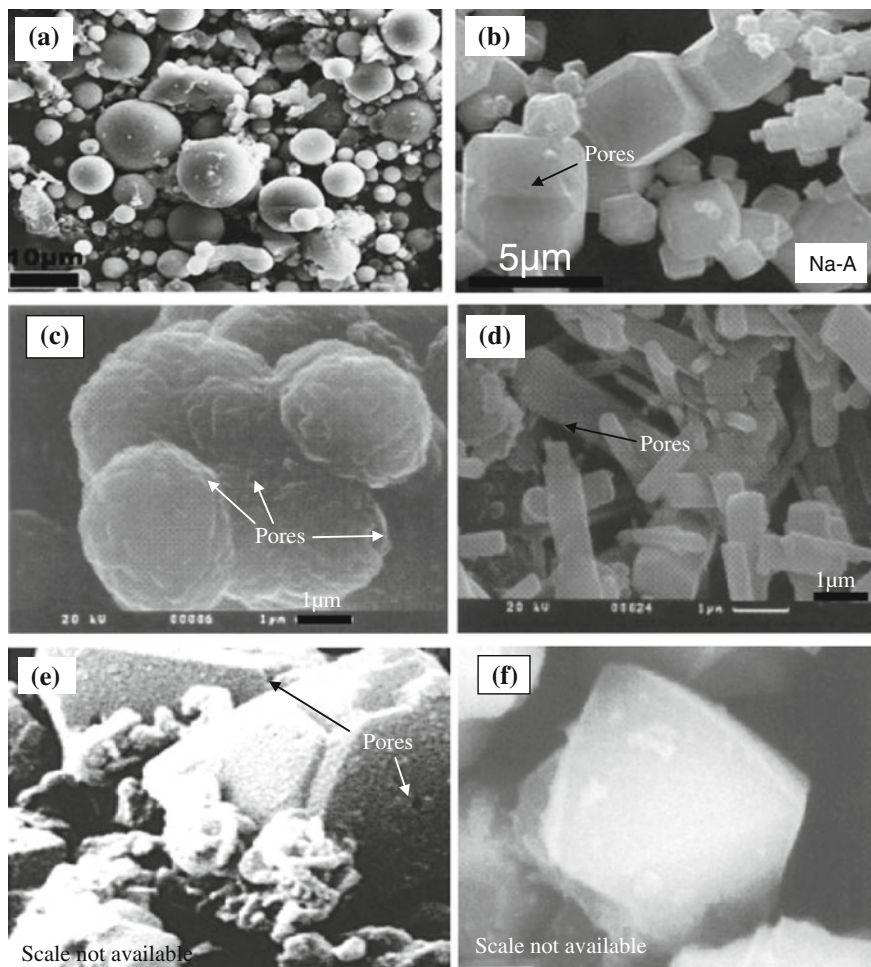


Fig. 2.6 SEM micrographs of the **a** Fly ash (spherical morphology), **b** Na-A (cubic morphology), **c** Sodalite (ball shaped morphology), **d** Cancrinite (Hexagonal, prismatic, needle like morphology), **e** Zeolite Y (cubic morphology), **f** Zeolite Na-X (octahedral morphology) [8]. **g** Mordenite (acicular or prismatic crystals) and Analcime (spherical crystals), **h** Clinoptilolite (hexagonal) and NaP1 (ball shaped), **i** Fibrous Na-P1, **j** Na-P1 (polycrystalline), **k** Na-A with emerging agglomerates and **l** Na-X (Cubic) [8]

2.1.8 Morphological Properties

The size and shape of crystals of minerals can be ascertained by interpreting the SEM micrographs of the raw materials (viz., fly ash) and the end products obtained from the zeolitization process [8]. The SEM micrographs of fly ash reveal the presence of spherical particles of size 50–80 μm along with broken hollow spheres,

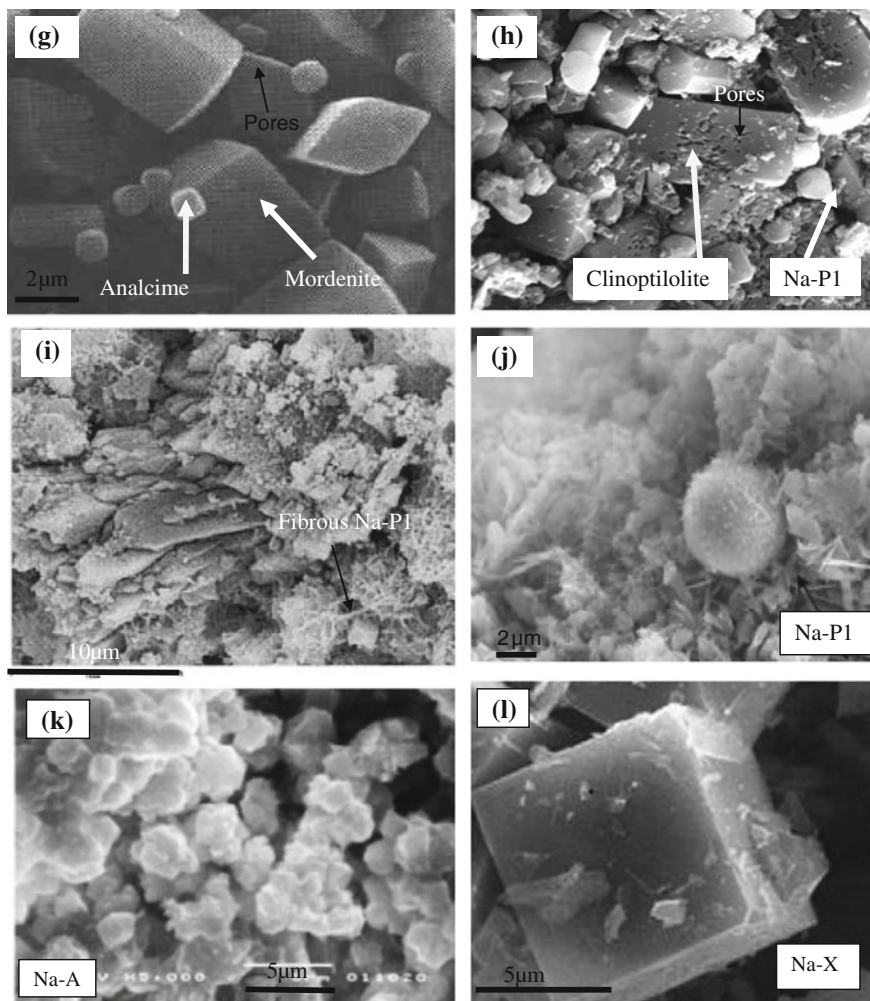


Fig. 2.6 (continued)

as depicted in Fig. 2.6a. However, after zeolitization, most of the products retain the initial spherical morphology of the fly ash, except some surface alterations leading to roughness due to chemical action as shown in Fig. 2.6b, c. In addition, needle-like crystals of different sizes can be observed on the grain surface, which can be attributed to the growth of Cancrinite crystals (refer Fig. 2.6d). Such characteristic hollow structures of zeolitic minerals facilitate their application in several industrial processes and products [8, 54].

Three dimensional surface pores of small crystals of zeolites A, X and Y can be observed in the SEM images, as depicted by black spots in Fig. 2.6b, e, f [3, 8], whereas; one dimensional large crystals can be seen in the zeolites, Mordenite, as

Table 2.5 Particle shapes and size of minerals present in fly ash and its zeolites [8]

Minerals		Particle shapes	Size (μm)
Source	Type		
Fly ash	Hematite	Spheroidal aggregates	5–10
	Magnetite	Spherical form	5–15
	Glass	Spherical form, spheroidal mode, yellowish and greenish	10–400
	Quartz	Sharp edged, elongated, oval and spherical	20–250
	Carbon	Irregular and jagged form	22–150
	Mullite	Pillar like, single form with cleavage and colorless	60–420
Zeolites	Na-P1	Fibrous	–
	Analcime	Tetrahedral	10–20
	Na-X	Octahedral	20
	Cancrinite sodalite	Hexagonal Hexagonal	20–30
	Na-A	Cubic	40–50

– not applicable

Table 2.6 Effect of reaction time on the XRD intensity of the minerals [8]

Reaction time (h)	XRD peak intensity (counts per second)		
	Zeolite P	Quartz	Mullite
0	325	260	85
0.5	425	215	82
1.0	515	240	78
1.5	500	190	75
2.0	550	165	70
2.5	570	160	65
3.0	550	140	60

Table 2.7 Maximum peak intensities and their location in the X-ray diffract gram for common ash zeolites [8]

Zeolite	2θ (°, Cu Kα)	Peak XRD intensity (counts per second)
P	28	650
Na-A	7	650
X	6	1800

depicted in Fig. 2.6g [8, 34, 55]. It has been reported that the initial ball-shaped morphology as seen in Fig. 2.6c, h of zeolite Na-P1 get transformed to star-shaped grains or other crystal shapes after continuous dissolution and crystallization as depicted in Figs. 2.6h, j, k, l, p [8, 30].

Natural zeolites which consist of fibrous morphology include Natrolite, Tetranatrolite, Paranatrolite, Mesolite, Scolecite, Thomsonite, Erionite and

Mordenite are also depicted in Fig. 2.6i. Clinoptilolite has been reported to occur as idiomorphic plates and laths, which are several micrometers in length and 1–2 μm in thickness, whereas, most of the crystals display characteristic monoclinic symmetry and many are coffin-shaped. Some zeolites appear as fibrous aggregates as depicted in Fig. 2.6i, whereas, others as robust, non-fibrous crystals as seen in Fig. 2.6b, d, h, m, n [8, 34, 42, 54, 56, 57].

2.1.9 Thermal Characteristics of Zeolites

The thermal properties (viz., temperature resistance, thermal stability, thermal conductivity and heat capacity of zeolites have been studied to investigate the loss of water or thermally induced cracking at higher temperatures [46]. The thermal stability of zeolites has been noticed to increase with their crystallinity. A higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and CEC of the zeolites can directly add to their temperature resistance. The synthesized Na-X zeolite has been found to lose its crystallinity between 973 and 1073 K [27]. High-silica zeolites (HSZ) are thermally and chemically stable up to about 1000 $^\circ\text{C}$ whereas; pure-silica zeolites are stable in all mineral acids except hydrofluoric acid. HSZs have been found to have Si/Al ratios greater than 50, while the ratio for low-silica zeolite (LSZ) is less than 2–5. The variation of the degree of thermal stability of fly ash zeolites, has been found to follow the trend Na-P1, < Na-X < Sodalite. Moreover, Na-P1, Na-X and Sodalite, have been opined to maintain their crystalline structure for temperatures below 300, 700 and 900 $^\circ\text{C}$, respectively [58].

The thermal conductivity and heat capacity of zeolite 4A ($\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}$, popularly identified as Linde A, or Na zeolite) have been reported by earlier researchers [58], for the temperature range 35–300 K, who have demonstrated that the thermodynamic stability of zeolites depends on the strength of the Si-O and Al-O bonds in their structural framework [11]. It has also been observed that such stability of zeolites gets enhanced by an increase in its Al content. Further thermal conductivity of the zeolite Na-X, can be affected by its particle size (2 μm to 800 nm), the temperature range (5–390 K), and the degree of packing and the distribution of voids. The inter relationship between thermal conductivity (k) of zeolite Na-X and the temperature is presented in Fig. 2.7 [8, 45].

Fig. 2.7 Effect of temperature on thermal conductivity of Na-X zeolite [8]

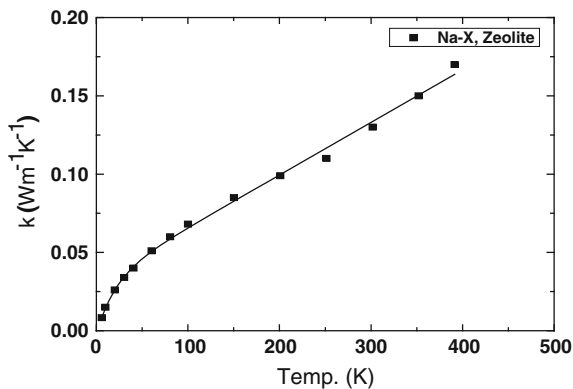
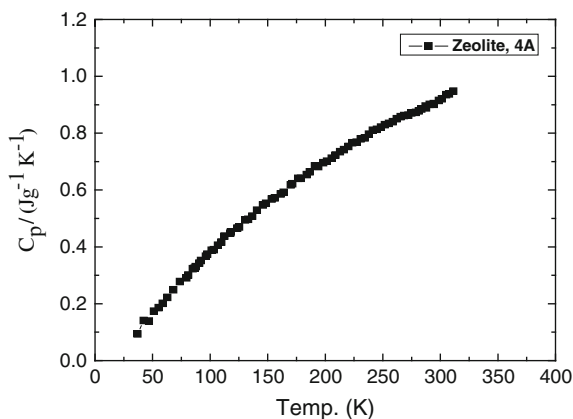


Fig. 2.8 Effect of temperature on heat capacity of zeolite 4A [8]



Incidentally, the heat capacity of zeolites has been reported to be a useful tool to demonstrate the interdependency of their thermodynamic stability and phase transition with their structure, under varying temperature, as depicted in Fig. 2.8 [8, 11].

2.1.10 Stability of Zeolites in Acidic Medium

Zeolites are composed of various atoms of different electronegativity (refer to Table 2.8). However, their intermediate electronegativity (i.e., geometric mean of the component atoms after redistribution of the electrons in the compound) is reported to be established as demonstrated by Sanderson's principle of electronegativity equalization (i.e., when two or more atoms initially different in electronegativity combine chemically, they become adjusted to the same electronegativity within the compound). The intermediate electronegativity can be determined for a compound, P_u , Q_v , R_z by Eq. (2.1) [59]:

Table 2.8 Electronegativity (E) of elements [8, 59]

Element	E	Element	E
H	3.55	K	0.42
C	3.79	Ca	1.22
N	4.49	Zn	2.98
O	5.21	Rb	0.36
F	5.75	Sr	1.06
Na	0.70	Cd	2.59
Mg	1.56	Cs	0.28
Al	2.22	Ba	0.78
Si	2.84	Ag	2.57
Ge	3.59	—	—

— not detected

$$E_i = [(E_P)^u \cdot (E_Q)^v \cdot (E_R)^z]^{1/(u+v+z)} \quad (2.1)$$

The change in electronegativity undergone by each atom can be obtained by Eq. (2.2).

$$\Delta E_P = 2.08 \cdot \sqrt{E_P} \quad (2.2)$$

The partial charge on the atom P can be obtained by Eq. (2.3).

$$[E_i - E_P] / \Delta E_P \quad (2.3)$$

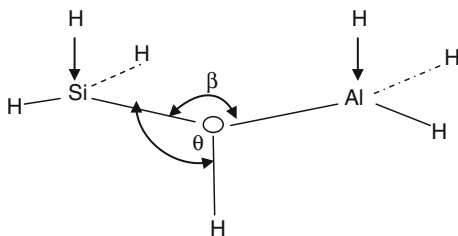
where, E is the electronegativity of the atom (refer Table 2.8); P , Q and R are the atoms in the mineral, and, u , v , and z are their numbers in one mole of their compound, respectively.

With this in view, the acidic strength of zeolites with reference to the stability of their framework and the presence of H^+ proton sites in the crystal structure of zeolites can be directly correlated with their intermediate electronegativity.

With the intention of establishing the effect of the variation in bonding and structure of zeolitic mineral on its acidic strength, a model applicable for the bond angles between various elements is being depicted in Fig. 2.9 [8, 60]. In fact, the angle β (refer Fig. 2.9) between Si-O-Al bonds in the zeolite crystal structure can play an important role against its surface corrosion in acidic medium. The high T-O-T (i.e., T stands for Si and Al atoms, and O stands for oxygen atom) bond strength has been noticed in high silica zeolites, whereas, it has been demonstrated to be low in case of low silica zeolite, e.g., Faujasite. In addition, the O-H bond might become unstable due to infra-red radiations, at lower bending frequency, in a zeolite structure. The probability of instability of the bond -[Si-O-Al]- has been found to be more corresponding to higher value of angle, β ($\approx 127^\circ$) between the bond, as depicted in Fig. 2.9 [8, 59].

Similarly, the Si-O and Al-O bond lengths are also reported to be dependent on -[Si-O-Al]- bond angle. With this in view, it can be opined that an increase in β results in decrease in θ and hence lowering of the acidic strength. It has been demonstrated [8, 59] that lower the required frequency for stretching the OH bond, the greater would be the acidic strength of zeolites. For an example, it has been

Fig. 2.9 A model of bond angle Si-O-Al and Si-O-H in the zeolite framework [8, 59]



reported that the bending frequency of Mordenite is higher than that of Faujasite zeolites [8, 59].

2.1.11 Crystal Structure of the Zeolite

Zeolites, as minerals of the tectosilicate group, i.e., three dimensional arrays of interconnected SiO_4 tetrahedra, have basically three different structural variations [8, 15]:

- (a) Chain like structures: the crystals appear as acicular or needle like prismatic crystals as of Natrolite ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$). Such zeolite (specific gravity, $G = 2.2$; hardness $H = 5.5$) can appear as compact fibrous aggregates with fibers of divergent radial arrangement as depicted in Fig. 2.10a, b. In Fig. 2.10b, $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra have been depicted as shaded and non-shaded triangles (white in color), respectively, while the shaded small circles depict the vertex of the triangles, i.e., the oxygen atom. Moreover, small sized circles between the vertexes denote Na^+ , as external linkage to the tetrahedral and exhibited in Fig. 2.10b [8].

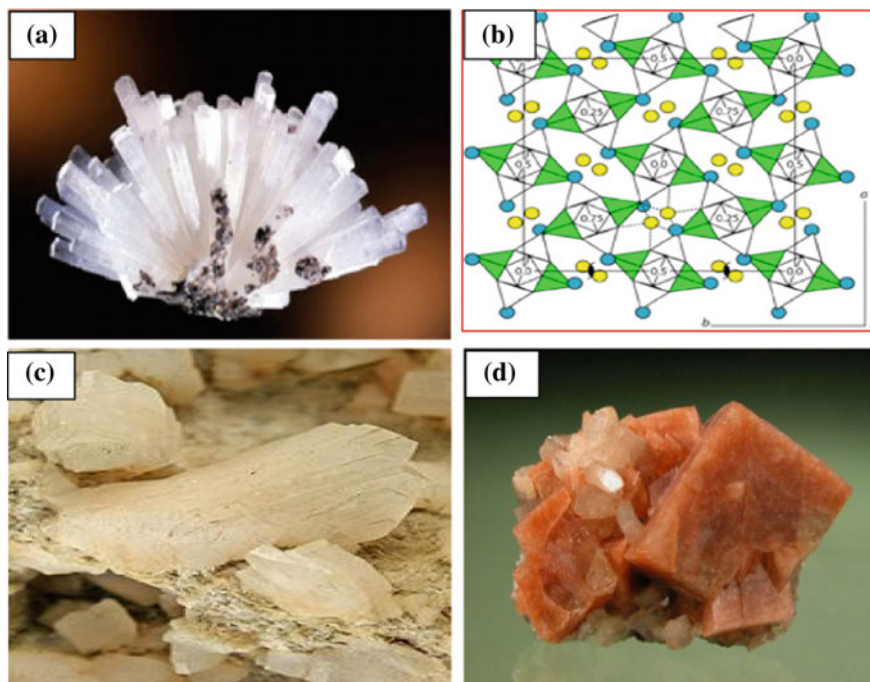


Fig. 2.10 Crystal structures of common zeolites **a, b** Natrolite, **c** Heulandite and **d** Chabazite [8]

- (b) Sheet like structures: the crystals appear as flattened, platy or tubular usually with good basal cleavages of Heulandites $[(\text{Ca}, \text{Na})_{2-3}, \text{Al}_3(\text{Al}, \text{Si})_2 \text{Si}_{13} \text{O}_{36} \cdot 12\text{H}_2\text{O}]$ with ends like wedges. The crust of such crystals ($G = 2.2$, $H = 3-4$ kg) has appearance like rhombic prisms as depicted in Fig. 2.10c [8].
- (c) Framework structures: the crystals appear more equal in dimensions as that for Chabazite $[(\text{Ca} \text{ Na}_2 \text{ K}_2 \text{ Mg}) \text{Al}_2 \text{Si}_4 \text{O}_{12} \cdot 6\text{H}_2\text{O}]$, which has rhombohedral/cubic shaped crystals ($G = 2.0$ to 2.2 , $H = 3-5$ kg), as depicted in Fig. 2.10d [8].

Keeping the above structures in view, the natural zeolites have a unique three-dimensional honeycomb structure (Fig. 2.6i), which creates an open and negatively charged framework through which liquid and gases can be exchanged or absorbed.

2.1.12 Framework Structure of Zeolitic Crystals

Each of the silicon and aluminium tetrahedra (refer Fig. 2.11), present in a zeolite, is popularly known as its primary building unit (PBU). Whereas, the simple geometrical shapes (i.e., ring shapes, designated by R in Fig. 2.11) are created by inter linkage between two or more tetrahedra. Hence, the formed linkages are called secondary building units (SBU). To clarify this fact, such units depicted in Fig. 2.11a–g) have been picturized as single and double rings, respectively. It can be noticed from these figures that each ring is composed of four-, five-, six- or eight-numbers of inter-linked several Si and/or Al tetrahedra, represented by small circles (refer Fig. 2.1c, d, f, where these tetrahedra have been represented by actual tetrahedral shapes) [5, 8].

It can be noticed that, each SBU consists of the lines representing oxygen bridges (-O-), whereas intersection points of these lines represent the positions of silicon or aluminium atoms. As a result, -[Si-O-Al]- linkages are formed which can develop a specific geometry of the surface pores in the zeolite framework. Further, regular cavities of discrete shape and size can get enclosed in between the linkages of various SBUs, which can accommodate different cations (viz., Na, K, Ca, Li and Mg) as an ion exchange or a molecular sieve [5].

For example, the shape and dimension of channels and/or pores of some common zeolites are being depicted in Fig. 2.11h, i, j [8]. It has been established that Si/Al ratios have considerable effect on other properties (viz., CEC, channel dimension, void volume and specific gravity). Figure 2.11h represents the zeolite, Analcime (ANA)-distorted 8-ring, viewed along [110], which has cubic shaped irregular channels of size (Å): 4.2×1.6 [8].

Figure 2.11i depicts Heulandite (Clinoptilolite group: HEU), 8 membered ring, along [001], which has monoclinic crystals and 2-dimensional channels of size (Å) 4.6×3.6 , 4.7×2.8 and 7.5×3.1 , which is variable due to considerable

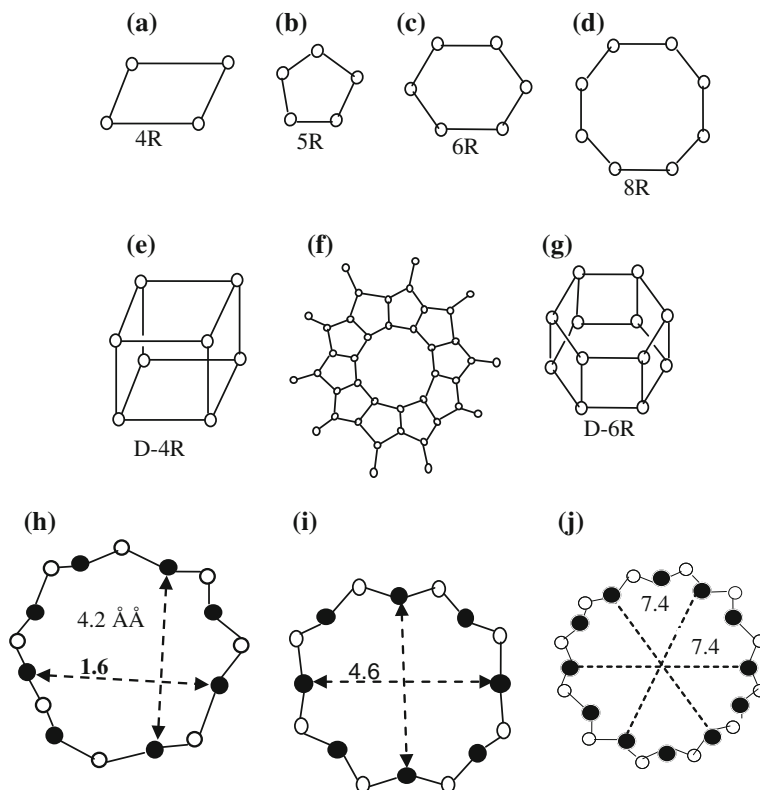


Fig. 2.11 Different types of linkages of tetrahedra in the secondary building units of framework structures of zeolite groups. **a, c, d** Analcime group, **b** Heulandite and Mordenite groups, **e** Phillipsite group, **f** Pentasil and **g** Chabazite group [8]. Variation in channel shapes and dimensions of common zeolites. **h** Analcime—8R, **i** Clinoptilolite—8R and **j** Faujasite—12R [8]

flexibility of the framework. Figure 2.11j depicts the zeolite Faujasite: FAU-12 ring, viewed along [111], which has 3-dimensional channels of size 7.4 Å [8, 12, 47].

Based on such variations in the framework of zeolites, a ‘structure code’ has been assigned to each one of them, for the sake of simplicity in their identification. In fact, as many as 191 types of structure codes (i.e., Framework Type Code, FTC) have been proposed by the Structure Commission of the International Zeolite Association (IZA-SC) [5]. It is notable that several zeolites exhibit similarities in their structures which can be grouped together to form an iso-structural group of zeolites. Table 2.9 represents details of the common groups based on the type of structure of zeolites [8].

Further, the framework structure of zeolite can be correlated with its Si/Al ratio. It has been observed that, in general, with an increase in the Si/Al ratio, the zeolite structure gets transformed from 4-, 6- and 8-membered rings to 5-membered rings

Table 2.9 Different types of framework structure and their iso-structural species [8]

Zeolite	Structure	Main species	FTC	Isostructural species
Analcime	4R and 6R	Analcime	ANA	Ca-D, Kehoeite, Leucite, Na-B, Pollucite, Viscite, Wairakite
Natrolite	Chain of PBU	Natrolite Edingtonite Thomsonite	NAT EDI THO	Laubanite, Mesolite, Metanatrolite, Scolecite K-F Gonnardite
Chabazite	D-6R	Chabazite Cancrinite Erionite Gmelinite Levyne Losod Linde L Mazzite Offretite Offretite Sodalite	CHA CAN ERI GME LEV LOS LTL MAX MAX OFF SOD	Linde D, Herschelite, Linde R Basic Cancrinite – Linde S, Na-S Levynite, ZK-20, LZ-132, NU-3 – – Omega, ZSM-4 Zeolite O Basic Sodalite, Danalite, Nosean Hydroxysodalite, Sodalite hydrate,
Phillipsite	D-4R	Phillipsite Li-A Gismondine Merlinoite	PHI ABW GIS MER	Harmotone, Wellsite, ZK-19 CsAlSiO ₄ , RbAlSiO ₄ Amicte, Garronite, Linde B, Na-P1, P, P _c , P _t , Na-P K-M, Linde W
Heulandite	4R or 5R	Heulandite Brewsterite Stilbite	HEU BRE STI	Clinoptilolite – –
Mordenite	5R	Mordenite Ferrierite Bikitaite Dachiardite Epistilbite	MOR FER BIK DAC EPI	Na-D, Ptilolite, Zeolon Sr-D, ZSM-21, ZSM-35, ZSM-38 – – –
Faujasite	Cubic	Faujasite ZK-5 Linde A	FAU KFI LTA	Linde X, Y, ZSM-20, Ba-P, Ba-Q, P-[Cl], Q-[Br], ZK-4, ZK-21, ZK-22, Alpha, N-A

LTA Na-A or Linde A zeolite (with Si/Al = 1 and SBU $\approx$ D-4R)

FAU Na-X and Na-Y zeolites (with Si/Al = 1.23 and 2.5, respectively and SBU $\approx$ D-4R)

CHA zeolite Chabazite (with Si/Al = 2 and SBU $\approx$ D-6R)

HEU zeolite Clinoptilolite (with Si/Al = 5 and SBU $\approx$ 5R)

ERI zeolite Erionite (with Si/Al = 3 and SBU $\approx$ D-6R)

ANA zeolite Analcime (with Si/Al = 2, SBU $\approx$ 4R-6R)

MOR zeolite Mordenite (with Si/Al = 5 and SBU $\approx$ 5R)

– not available

[5]. For example, a series of ash zeolites with their structure code, corresponding to their Si/Al ratio, and SBU (shown in paranthesis) have been listed, in the footnote of Table 2.9.

2.1.13 Surface Properties

The surface properties (viz., hydrophobicity, hydrophilicity and binding to reactant molecules) of zeolites bearing negative surface charge can be varied by organic functionalization of their internal and external surfaces, which can improve their affinity to absorb water and other cations. The zeolites of a particular pore size on their external surface can allow penetration of molecules of smaller size or shape to their internal pores by diffusion. The organic cations have been found too large in size to enter the internal pores and hence they are adsorbed in the surface pores of zeolites. Furthermore, Si/Al ratio is an important parameter, which can influence such adsorption by zeolites. This is based on the fact that more the number of aluminium atoms, more will be the electronegativity of the zeolite pore surfaces which correspond to less Si/Al ratio. For example, zeolites Na-A possesses lower Si/Al (~ 1) molar ratio as compared to zeolites X and Y. As such, it can compensate the exchange of Si by Al atoms in the framework to avoid formation of Al-O-Al linkage, with extra framework cations on its internal and external surfaces both, to maintain its uniform acidic strength and intermediate electronegativity [8, 59].

In order to modify the surface features, the zeolites can be treated with long chain type surfactants, such as hexa-decyl-tri-methyl-ammonium chloride (HDTMA), stearyl-dimethyl-benzyl-ammonium chloride (SDMBA) and distearyl-dimethyl-ammonium chloride (DSDMA). As a result, they have been found to replace inorganic cations like Na^+ and Ca^{2+} from the external surface of zeolites [8, 61]. Moreover, surface modification of synthetic zeolites: A, X, Y and the natural zeolite, Clinoptilolite has been reported to occur by action of cationic surfactants (viz., HDTMA chloride, SDMBA chloride and DSDMA chloride) on the surface of the zeolites [8, 43, 62].

Such modification results in an alteration in the surface properties so much that the hydrophilic zeolites (i.e., with $\text{Si/Al} < 10$) are converted into hydrophobic zeolites (i.e., with $\text{Si/Al} > 10$) which can absorb molecular diameters (e.g., organic cations) larger than water [5, 8]. With this in view, it has been reported that the adsorption capacities of different surface modified zeolites can increase with the increase in their Si/Al ratio [8]. This can be attributed to the corresponding increase in their uniform pore size and their adsorption capacities which can follow the increasing order such as $\text{CLI} > \text{Ca-Y} > \text{Ca-X} > \text{Ca-A} > \text{Na-Y} > \text{Na-X} > \text{Na-A}$ as presented in Table 2.10 [8, 62]. The adsorption capacity of zeolites can become a tool for proving the superiority of one zeolite over another for application point of view e.g., removal of pesticides from the environment [8, 62].

Table 2.10 Maximum adsorption capacity of common zeolites for organic cations [8]

Zeolite	Si/Al	Pore size (Å)	Adsorption capacity of the organic cations (μmol/g)			
			MB	HDTMA	SDMBA	DSDMA
Na-A	1.00	4.2	14	61	50	29
Ca-A	1.00	4.9	27	160	91	61
Na-X	1.23	7.4	24	84	70	55
Ca-X	1.23	7.6	63	192	101	72
Na-Y	2.50	7.9	52	116	70	60
Ca-Y	2.50	8.0	86	208	115	77
CLI	5.00	4.4	148	388	288	158

2.1.14 Critical Evaluation of Properties of Some Commonly Available Zeolites

Zeolites are identified by their most critical and valuable property, known as the cation exchange capacity (*CEC*), which defines its suitability for various industrial applications. Apart from this, various attributing characteristics (viz., pore diameter and pore volume) of pores or channels, specific gravity and particle compositions (viz., chemical and mineralogical), particle shapes and size (i.e., morphology) of the zeolites need to be critically evaluated for fixing their suitability for a specific application. The pores in the zeolite add to their values as molecular sieve for separation of particular type of fluids and gases. Moreover, the particle shapes and sizes, mineralogy and morphology of the zeolites can vary a lot depending up on the complexities involved in the chemistry of their synthesis. As such, the particle sizes can be grouped separately as meso-porous sizes (10–60 μm) and micro-porous sizes (<10 μm) [24], which can have direct and/or indirect correlations with *CEC*, specific gravity and other properties of zeolites. In general, the specific gravity of zeolites has been reported to vary from 2 to 3 [20]. In order to present a simplified picture of some zeolites, their comparison with respect to others, and to fix the superiority of a particular zeolite over other, Table 2.11 presents various properties of fly ash zeolites which can be useful for the readers [2, 8, 20, 24, 25, 29, 51, 52, 59].

Table 2.11 Properties of some commonly available fly ash zeolites [8]

Zeolite	CEC (meq./g)	Channel/pore diameter (Å)	Pore volume (%)	Specific gravity	Chemical formula
X/Linde X	5	7.3	50	1.93	$\text{NaAlSi}_{1.23}\text{O}_{4.46} \cdot 3.07 \text{H}_2\text{O}$
Clinoptilolite-8R	2.54	3.9–5.4	39	2.16	$(\text{Na}, \text{K}) \text{Al}_3 \text{Si}_5 \text{O}_{12} \cdot 3 \text{H}_2\text{O}$
Laumontite	4.25	4.6–6.	34	2.20–2.30	$\text{CaAl}_2 \text{Si}_4 \text{O}_{12} \cdot 4 \text{H}_2\text{O}$
Erionite	3.12	3.6–5.2	35	2.02–2.08	$(\text{Na}_2, \text{Ca}_6, \text{K})_9 \text{Al}_6 \text{Si}_{27} \text{O}_{27} \cdot 27 \text{H}_2\text{O}$
Mordenite 8R	2.29	2.6–5.7	28	2.12–2.15	$\text{Na}_8 (\text{Al}_8 \text{Si}_{40} \text{O}_{96}) \cdot 24 \text{H}_2\text{O}$
Hydroxysodalite	0.3	2.3	–	–	$\text{Na}_4 \text{Al}_3 \text{Si}_3 \text{O}_{12} \cdot \text{OH}$
A/Linde A	4.7	4.1	47	1.99	$\text{Na}_{12} \text{Al}_{12} \text{Si}_{12} \text{O}_{48} \cdot 27 \text{H}_2\text{O}$
Y	3.12	7.3	–	–	$\text{Na}_{1.88} \text{Al}_2 \text{Si}_{4.8} \text{O}_{13.54} \cdot 9 \text{H}_2\text{O}$
Na-PI	2.7	$3.1 \times 4.5 /$ 2.8×4.8	–	–	$\text{Na}_6 \text{Al}_6 \text{Si}_{10} \text{O}_{32} \cdot 12 \text{H}_2\text{O}$
Analcime	0.6–4.54	2.3–2.6	18	2.24–2.29	$\text{NaAlSi}_2 \text{O}_6 \cdot \text{H}_2\text{O}$
Chabazite	3.81	3.7–4.2	47	2.05–2.10	$\text{CaAl}_2 \text{Si}_4 \text{O}_{12} \cdot 6 \text{H}_2\text{O}$
Herschelite	2.1	3.5	NA	NA	$\text{Na}_{1.08} \text{Al}_2 \text{Si}_{1.68} \text{O}_{7.44} \cdot 1.8 \text{H}_2\text{O}$
KM- zeolite	1.9	4.5	NA	NA	$\text{K}_2 \text{Al}_2 \text{Si}_3 \text{O}_{10} \cdot \text{H}_2\text{O}$
Faujasite	1.41	7.4	–	1.98	$\text{Na}_2 \text{Al}_2 \text{Si}_{13.3} \text{O}_{88} \cdot 6.7 \text{H}_2\text{O}$
Hydroxycancrinite	–	–	–	–	$\text{Na}_{14} \text{Al}_{12} \text{Si}_{13} \text{O}_{51} \cdot 6 \text{H}_2\text{O}$
Tobermorite	–	–	–	–	$\text{Ca}_5 (\text{OH})_2 \text{Si}_6 \text{O}_{16} \cdot 4 \text{H}_2\text{O}$
Linde F	1.9	–	–	–	$\text{KAl SiO}_4 \cdot 1.5 \text{H}_2\text{O}$
Parialite	–	–	–	–	$\text{K}_9 \text{NaCaAl}_{12} \text{Si}_{24} \text{O}_{72} \cdot 15 \text{H}_2\text{O}$
Kaslite	–	–	–	–	KAlSiO_4
Phillipsite-8R	–	4.2–4.4	–	2.2	$(\text{CaNa}_2 \text{K}_2)_3 \cdot \text{Al}_6 \text{Si}_{10} \text{O}_{32} \cdot 12 \text{H}_2\text{O}$
Sodalite	0.3	2.3	–	2.27–2.33	$\text{Na}_4 \text{Al}_3 (\text{SiO}_4)_3 \text{Cl}$

– not available

2.2 Conclusions

Zeolites are tetrahedral crystalline aluminosilicate minerals with a general chemical formula (i.e., in terms of oxides of Si and Al), represented as $M_{e/2/n} O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$. Moreover, a generalized structural formula (i.e., in terms of AlO_2 and SiO_2 both assumed as variable parameter) of a crystal unit cell of zeolites correspond to $M_{a/n} [(AlO_2)_a (SiO_2)_b] \cdot wH_2O$. The ratio of b/a usually varies from 1 to 5, for common zeolites, Mordenite and zeolite 4A, respectively. Zeolites have also been synthesized when b/a varies from 10 to 100 or even higher, as in case of ZSM-5 type of zeolites. Most important properties of zeolites are their CEC, channel or pore diameters and volume, specific gravity, chemical composition, mineralogical and morphological characteristics. The presence of negatively charged microscopically small sized surface and/or internal pores of zeolites adds to their values as absorbent and/or adsorbent. They are also called as the “molecular sieves” as cation exchange materials. Based on these attributes, zeolites find applications in separation and filtration processes.

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