
Quadrupolar Interaction with Zeolite and Pressure Swing Adsorption in Portable Medical Oxygen Concentrators for Breathing of Covid-19 and COPD Patients*

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Pressure swing adsorption (PSA) technology is used in medical oxygen concentrators for selective adsorption of nitrogen under pressure from air to produce oxygen-enriched air for breathing. The functional material in oxygen concentrators is aluminosilicate zeolite like Li-13X, 5A (LTA) with a relatively high Al-content. It selectively adsorbs nitrogen from the air into their molecular sieves due to the strong quadrupolar interaction between the adsorbed nitrogen and the electrical field of the charge balancing non-framework exchangeable cations of aluminosilicate zeolites. In an oxygen concentrator, two adsorbent vessels packed with the zeolite working alternately in a cyclic process are used for a near-continuous production of the oxygen-enriched air.

1 Introduction

In the Covid-19 pandemic situation, the necessity and importance of portable oxygen concentrators have been realised throughout the globe, especially in our country, India. Oxygen concentrators are based on the principle of pressure swing adsorption (PSA) [1, 2], which leads to selective adsorption of a particular gas under a high pressure followed by its desorption under a reduced pressure to reactivate the adsorbent bed for the next cycle. The functional material—zeolite (aluminosilicate)—in the oxygen concentrators is widely known for its porous structure. Zeolites are charac-



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Keywords

Pressure swing adsorption (PSA), oxygen concentrators, covid-19, aluminosilicate zeolite, Li-13X, molecular sieves, non-framework cations, quadrupole moment, quadrupolar interaction.

terised by their molecular sieves of well-defined dimensions and shape for different types of zeolites. The pore size of these channels acting as the molecular sieves can also be tailored. The size and shape selectivity (i.e. stereokinetic factor) of zeolites have been extensively exploited for industrial purposes like separation of different substances and catalytic activity [3, 4]. For catalytic activity, besides the stereokinetic factor, its acidic character (both Brønsted and Lewis acidity) is also essentially required. But oxygen concentrators use a totally different property involving the quadrupolar interaction between the adsorbate and adsorbent zeolite [5–7]. It removes nitrogen from the air (approximate composition by volume: 78% nitrogen, 21% oxygen, 1% argon and other gases) not based on size selectivity but through quadrupolar interaction between the more quadrupolar nitrogen (*cf.* nitrogen is of higher quadrupole moment than that of oxygen and argon is nonquadrupolar) and the cationic surface charge of non-framework exchangeable cations. This is why, zeolites having higher Al-content and, consequently, higher surface electrical field due to the more charge balancing non-framework cations are used to adsorb nitrogen selectively from air under high pressure.

2 Structural Features and Properties of Microporous Aluminosilicate Zeolites [3, 8, 9]

The term ‘zeolite’ (boiling stone in Greek) was coined by the Swedish mineralogist A. F. Cronstedt in 1756 because the mineral appeared to boil when heated, producing a large amount of steam and other gases.

The term ‘zeolite’ (boiling stone, in Greek *zeo* meaning ‘to boil’ and *lithos* meaning ‘stone’) was coined by the Swedish mineralogist A. F. Cronstedt in 1756 because the mineral appeared to boil when heated, producing a large amount of steam and other gases. These byproducts are absorbed into the well-defined intersecting 3D channels (described as the molecular sieves) running through the mineral lattice. As the cavity diameter ranges from 200–2000 pm, zeolites are classified as microporous substances.

Zeolites are examples of negatively charged framework (3D) of aluminosilicates where Si^{4+} and Al^{3+} having comparable ionic radii undergo isomorphous substitution. This isomorphous substitution of Si^{4+} by Al^{3+} produces a charge imbalance, forming



an anionic framework that requires an additional positive charge (say M^+ or $\frac{1}{2}M^{2+}$) for each replacement. These additional charge balancing cations (generally hard cations of Group 1 and 2, or H^+ ion) are described as the non-framework cations, and these are exchangeable. These charge balancing non-framework cations introduce unique properties to aluminosilicates. If these are H^+ ions (i.e. H^+ – form zeolite), then the aluminosilicates can act as the Brønsted acids, and their acidity may be even higher than that of concentrated H_2SO_4 [3, 4]. The H^+ -form of zeolite on being dehydrated produces the coordinatively unsaturated Si-centres that can act as the strong Lewis acids [3, 4]. These charge balancing extra non-framework cations make the aluminosilicates hydrophilic and are also responsible for attracting the polar molecules strongly like water, ammonia, etc., into the molecular sieves of zeolites. The unique properties of aluminosilicate zeolites are:

- (i) Highly porous, providing a huge surface area.
- (ii) Molecular sieves of different well-defined diameters (window diameter, i.e. bottleneck diameter, to determine the size and shape selectivity; may be tailored by changing the exchangeable cations) and shapes to selectively adsorb the gases, liquids and other adsorbates based on the size and shape selectivity (i.e. stereokinetic effect).
- (iii) Electrostatic interaction between the surface cationic charge of the exchanged non-framework cations and the polar and quadrupolar adsorbates.

In fact, because of their unique properties, both naturally occurring and synthetic zeolites find versatile industrial uses [3, 4]. There are about 80 naturally occurring and more than 200 synthetic zeolites (LTA, ZSM-5, etc.). The natrolite, commonly called Na-Zeolite, is used as Permutit water softener.

By contrast, in pure silica, there are no such non-framework cations to attract the polar molecules into their molecular sieves that are nonpolar and mildly hydrophobic. Similarly, uncharged aluminophosphate (ALPO) framework based zeolite is hydrophobic because $AlPO_4$ is isoelectronic with Si_2O_4 . In other words, structurally

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and electronically, two SiO_4 tetrahedra, i.e. $(\text{SiO}_4)_2$, in polymeric SiO_2 and aluminophosphate units (AlO_4PO_4) in polymeric AlPO_4 are equivalent [10].

In aluminosilicates, all the vertices of the primary building blocks, SiO_4 and AlO_4 tetrahedra are shared between the two adjacent tetrahedra. According to Lowensteins' rule [11], the Al–O–Al linkages in the zeolitic frameworks are not stable. In fact, the $[\text{O}_3\text{Si–O–AlO}_3]$ unit is stabilised better than the $[\text{O}_3\text{Al–O–AlO}_3]$ unit because of the higher formal charge of Si^{4+} . Thus each aluminate tetrahedron must be linked to four silicate tetrahedra. However, non-Lowenstein zeolitic materials can be synthesised at high temperatures [10].

The primary building units (PBUs) of zeolites are the vertex-shared $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra with the flexible Si/Al–O–Si/Al linkages ($120\text{--}180^\circ$). The basic structural unit of zeolite can also be represented by $(\text{Si}, \text{Al})\text{O}_2^{x-}$ (where Si^{4+} and Al^{3+} having comparable ionic radii undergo isomorphous substitution). In terms of these basic structural units, zeolites can be represented as: $\text{M}_{p/n}[(\text{AlO}_2)_p(\text{SiO}_2)_q].m\text{H}_2\text{O}$, where n denotes the valence of the non-framework cation to neutralise the negative charge of the framework $[(\text{AlO}_2)_p(\text{SiO}_2)_q]^{p-}$. These basic structural units may undergo oligomerisation to produce the 6-membered $[(\text{Si}, \text{Al})\text{O}_2]_6$ and 4-membered $[(\text{Si}, \text{Al})\text{O}_2]_4$ rings. These rings may interlink to give the larger polyhedral clusters $[(\text{Si}, \text{Al})_{24}\text{O}_{48}]$ known as the sodalite β -cage ($[4^66^8]$) (i.e. 6 square faces and 8 hexagonal faces) or simply sodalite cage (truncated octahedron, i.e. expanded form of cuboctahedron) (*Figure 1*) of internal diameter about 600 pm as the secondary building units (SBUs) of many zeolites.

A truncated octahedron is produced by slicing off each vertex of an octahedron ($[3^8]$). It generates a square face in place of each vertex and a hexagonal face in place of each triangular face of the octahedron. Each of the 24 vertices of the truncated octahedron is occupied by either Si or Al with a bridging O^{2-} along each edge. This truncated octahedron ($[4^66^8]$) has been very often utilised as the space-filling polyhedron to construct the zeolitic structure.



The 3-dimensional zeolitic structure is attained through the interlinking of these truncated octahedra by the 24 bridging oxygens exo to the surface of the polyhedron, i.e. truncated octahedron. In other words, these sodalite cages interlink in different ways using the square and hexagonal faces to generate the 3-dimensional structure of zeolite with open channels.

The diameter of the open channels depends on the mode of combination of the sodalite cages. The open channels are known as molecular sieves that can selectively trap or absorb different small molecules of appropriate size. These channels can also produce clathrate-type compounds involving guest-host supramolecular interaction.

The two most symmetric ways of interlinking the sodalite cages can produce two well-known zeolite structures: zeolite A (Linde Type A, LTA) and faujasite (FAU) (*Figure 1*). Sodalite mineral (a naturally occurring material), itself comprises sodalite cages in a different way.

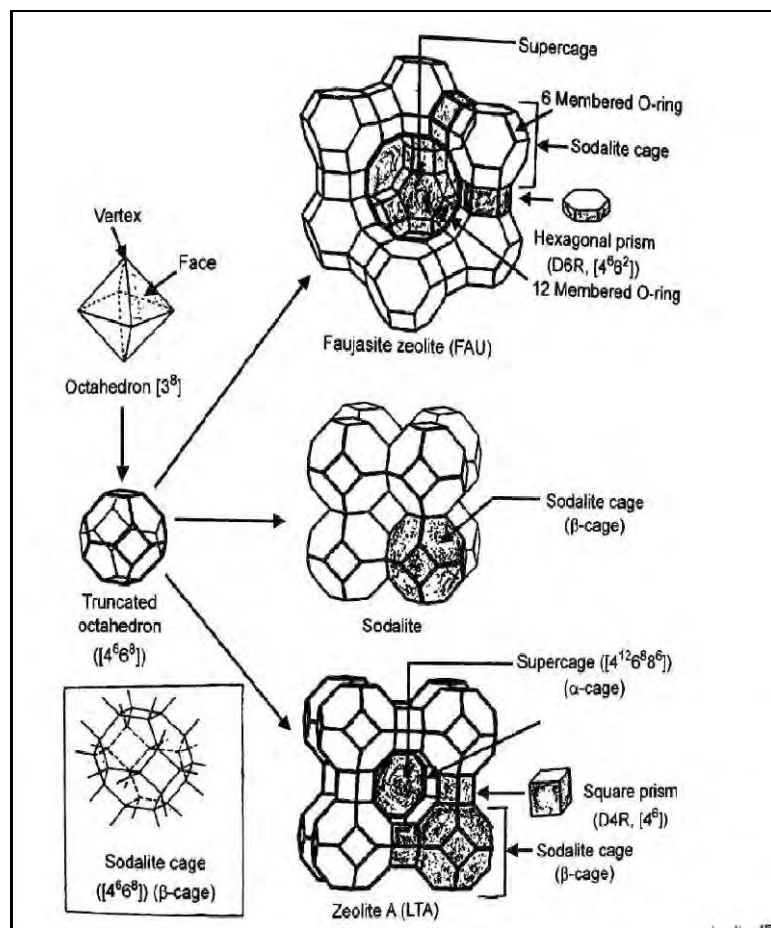
3 LTA (Zeolite A) [3, 8, 10–14]

The structure of synthetic zeolite A (Linde Type A, LTA, idealised composition for Type 4A: $[\text{Na}_{12}(\text{Al}_{12}\text{Si}_{12}\text{O}_{48})\cdot 27\text{H}_2\text{O}]$, Si/Al = 1) is produced by bridging (not sharing or fusing) the square faces (i.e. O bridges the square faces) through the oxygen of the truncated octahedrons (i.e. sodalite cages). In other words, the sodalite cages are connected through the square prisms constructed by double 4-membered rings (D4R, $[4^6]$). In this mode of interlinking, the 24 bridging oxygens of the sodalite cages are grouped into 6 octahedrally disposed squares. Eight sodalite cages are bridged in a cubic pattern to constitute a large cavity called α -cage (to distinct from the smaller β -cage of sodalite unit) called supercage ($[4^{12}6^88^6]$) of diameter about 1140 pm. This large cavity is connected to 6 identical cavities in the adjacent unit cells by the 8-membered O-rings (8MRs) (i.e. 8 Si/Al–O–Si/Al edges to construct the ring) of diameter about 410 pm. Besides this, the large central cavity is connected to 8 smaller cavities with a di-

Sodalite cages interlink in different ways using the square and hexagonal faces to generate the 3-dimensional structure of zeolite with open channels.



Figure 1. Structural features of sodalite cage and zeolites: sodalite, zeolite A (LTA) and faujasite (FAU) constituted using the sodalite cage as the basic structural unit.



ameter of about 660 pm by 6-membered O-rings (6MRs) (i.e. 6 Si/Al–O–Si/Al edges to construct the ring) with a ring opening diameter of about 220 pm. The 8-membered O-rings (8MRs) (i.e. octagonal faces) give the measure of the window size (i.e. bottleneck diameter, about 410 pm) of LTA.

It may be noted that the internal cavity diameter is about 1140 pm, but the window size (i.e. bottleneck diameter) will determine whether a particular guest molecule will be absorbed or not into the cavity. The water (H_2O) and other small molecules, including the straight chain hydrocarbons (not the branched hydrocarbons and aromatic hydrocarbons), can enter the channel and diffuse

through the octagonal faces. Obviously, the molecules with a van der Waals diameter larger than 410 pm cannot enter the cavity through these octagonal faces. In the hydrated form, all the cavities are occupied by the water molecules, but in the anhydrous state, the cavities may be occupied by other molecules of the appropriate size to pass through the octagonal apertures connecting the cavities.

4 Different Types of Zeolite A (LTA) [3, 8, 10–14]

Type 3A, 4A and 5A are named according to their window pore size in the angstrom unit. Type 3A having the composition $0.6\text{K}_2\text{O} : 0.4\text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 2.0 \pm 0.1\text{SiO}_2 : x\text{H}_2\text{O}$ offers the pore opening diameter $\approx 3\text{\AA}$ (i.e. 300 pm). The 3A form is produced by partially substituting the inherent sodium ions of the 4A structure with the larger potassium ions. Consequently, the effective ring opening pore size is reduced to $\approx 3\text{\AA}$ from 4\AA . Type 4A (very often described as zeolite A or LTA) having the composition $1.0\text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 2.0 \pm 0.1\text{SiO}_2 : x\text{H}_2\text{O}$ offers the pore opening diameter $\approx 4\text{\AA}$ (i.e. 400 pm). Type 5A having the composition $0.8\text{CaO} : 0.2\text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 2.0 \pm 0.1\text{SiO}_2 : x\text{H}_2\text{O}$ offers the pore opening diameter $\approx 5\text{\AA}$ (i.e. 500 pm). The 5A form is produced by partially substituting the inherent sodium ions of the 4A structure with the smaller divalent calcium ions. Consequently, it increases the effective ring opening pore size to $\approx 5\text{\AA}$ from 4\AA . In the type A zeolites, the monovalent exchangeable cations like Na^+ and K^+ are located near the 8-ring opening to reduce the pore opening diameter, while the divalent cations like Ca^{2+} tend to populate the sites that do not partially block the 8-ring opening. It shows that the nature of the exchangeable non-framework cation can control the ring opening pore size of the molecular sieves of the zeolites.

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By fusing together the four-membered rings of sodalite cages, sodalite (a naturally occurring material) is formed, and by bridging the 4-membered rings, the synthetic zeolite A is formed.

5 Sodalite [3, 8, 10]

Here it may be noted that by fusing together the four-membered rings of sodalite cages, sodalite (a naturally occurring material) is formed. It possesses 4- and 6-membered (6MR, 220 pm diameter) O-rings. It may be noted that by bridging (not fusing) the 4-membered rings, the synthetic zeolite A is formed. Sodalite $[\text{Na}_8\text{Cl}_2(\text{Al}_6\text{Si}_6\text{O}_{24})]$ is colourless, but the partial replacement of the supernumerary chloride anions by the disulphide ion (S_2^{2-}) gives the brilliant blue mineral lapis lazuli (*cf.* ultramarine blue $[\text{Na}_8(\text{S}_2)(\text{Al}_6\text{Si}_6\text{O}_{24})]$ where the disulfide S_2^{2-} ions participates in charge transfer (LMCT) transitions giving rise to the characteristic colour).

6 FAU (Faujasite Zeolite) [3, 8, 10, 13]

In the naturally occurring faujasite (FAU) zeolite (named to honour B. Faujas de Saint-Fond, French geologist and volcanologist) (synthetic counterparts: X and Y type depending on the Si/Al ratio), the sodalite cages are interconnected by bridging the 6-membered rings (6MRs) of sodalite cages (*cf.* in LTA structure, the sodalite units are bridged by the 4-membered rings), i.e. the sodalite cages are connected through the hexagonal prisms constructed by the double 6-membered rings (D6R, $([4^6 6^2])$). In other words, the 24 bridging exo oxygens of sodalite cages are grouped into 4 mutually tetrahedrally disposed hexagons to give the faujasite structure having the idealised formula $[\text{NaCa}_{0.5}(\text{Al}_2\text{Si}_5\text{O}_{14}) \cdot 10\text{H}_2\text{O}]$. In the faujasite structure, the sodalite cages adopt a diamond-like structure. In faujasite, the 12-membered oxygen rings (12MRs) form the larger channels extended in three dimensions.

In faujasite, a three-dimensional pore network provides the roughly spherical geometry of a supercage of about 1200 pm diameter connected via windows to four others in a tetrahedral arrangement. The window pore formed by a 12-membered O-ring (12MR) is of a larger diameter of about 740 pm than that of the 8-membered O-ring (8MR) window of zeolite A. Thus the window pore size



(i.e. bottleneck diameter of about 740 pm) is much smaller than the internal cavity diameter (1200 pm), and the window pore size will determine whether a particular guest molecule will be absorbed or not into the cavity.

7 Different Types of FAU Zeolites [3, 8, 10, 13]

Synthetic faujasite zeolites are divided into X and Y zeolites (also known as Linde X and Linde Y) depending on the Si/Al ratios, which are approximately 1.0–1.5 and 1.5–3.0, respectively for the zeolites X and Y. Both X and Y type zeolites have the similar structural features. Type 13X having the composition $1.0\text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 2.8 \pm 0.2\text{SiO}_2 : x\text{H}_2\text{O}$ possesses the window pore size $\approx 9\text{\AA}$ larger than those of type A zeolites.

8 Silicalite Zeolite (ZSM-5, MFI Framework) [3,8,10,13,15]

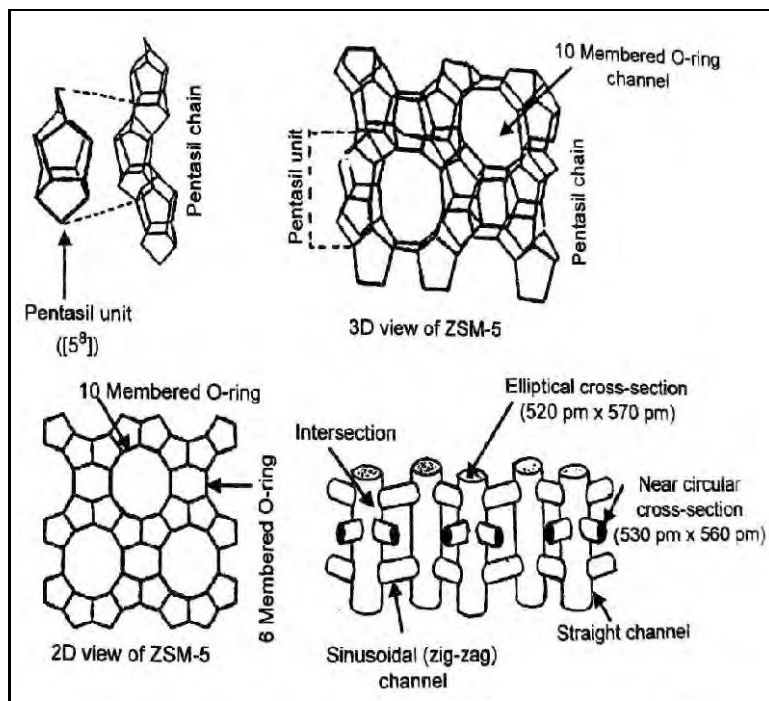
Synthetic zeolite silicalite (ZSM-5) with a high Si/Al ratio is composed of several pentasil units ($[5^8]$) as the secondary building units (SBUs). A pentasil unit is constructed by a combination of 14 MO_4 ($\text{M} = \text{Si/Al}$) tetrahedra with 8 five-membered O-rings (i.e. 8 pentagonal faces, ($[5^8]$)) where the vertices of the tetrahedra are occupied by either Al or Si obeying the Lowensteins' rule [11] and an oxygen connects the vertices. The pentasil units are linked together by the oxygen bridges to produce the pentasil chains that run parallel and are interconnected by the oxygen bridges to produce the corrugated sheets with 10-membered O-rings (10MRs) (i.e. 10 Si/Al–O–Si/Al edges to construct the ring). Adjacent layers of the sheets are related to one another by an inversion centre.

The ZSM-5 framework possesses two sets of intersecting 10-membered O-ring (10MR) channels running perpendicular to one another. One set of straight channels is running parallel to the corrugation with a slightly elliptical cross-section $520\text{ pm} \times 570\text{ pm}$, while the other perpendicular set of channels runs in a zig-zag (sinusoidal) way with a near circular cross-section $530\text{ pm} \times 560\text{ pm}$

Synthetic zeolite silicalite (ZSM-5) with a high Si/Al ratio is composed of several pentasil units as the secondary building units.



Figure 2. Structural features of silicalite (ZSM-5) zeolite.



(Figure 2). The straight and sinusoidal channels are linked to one another to form a 3-dimensional 10-membered O-ring (10MR) channel system, and these 3-dimensional channels intersect with about 900 pm diameter at intersections.

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The catalyst ZSM-5 (an aluminosilicate) with a high Si-content characterised by the presence of more hydrophobic channels to accommodate the nonpolar hydrocarbons was developed in the research laboratories of Mobil Oil for the synthesis of hydrocarbon fuel (synthetic petroleum fuel) from methanol [3, 4]. Besides its catalytic use in the petroleum industry, it is also used as a heterogeneous catalyst for hydrocarbon isomerisation. The molecular sieves of ZSM-5 can be exploited to synthesise exclusively *ortho*-xylene that finds a potential use as an octane buster in gasoline. The other *meta*- and *para*-isomers of xylene are not produced in this catalytic path as they cannot be sterically accommodated into the ZSM-5 channels, and the process is controlled by the shape and size of the ZSM channels. The initials stand for



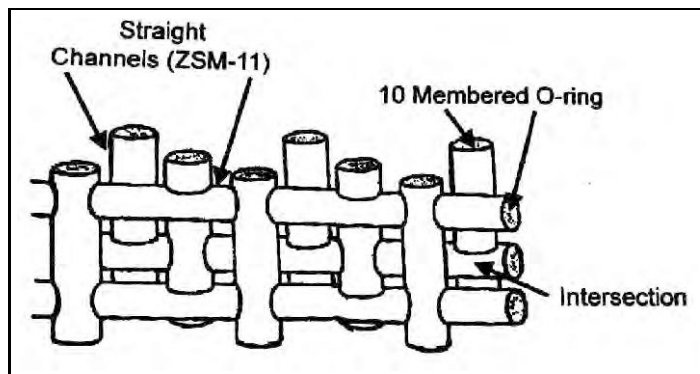


Figure 3. Structural features of ZSM-11 zeolite.

Zeolite Socony Mobil, and 5 denotes that these are constructed by 5-membered O-rings (5MRs).

9 ZSM-11 (MEL Framework) [13, 16]

The synthetic zeolite ZSM-11 is structurally similar to ZSM-5. Both have two sets of 3-dimensional intersecting 10-membered O-ring (10MR) channels. In ZSM-5 (MFI), one set of channels is straight, and the other perpendicular set of channels is sinusoidal (zig-zagged), while in ZSM-11 (MEL), both sets of channels are straight and are almost circular (530 pm × 540 pm) (*Figure 3*).

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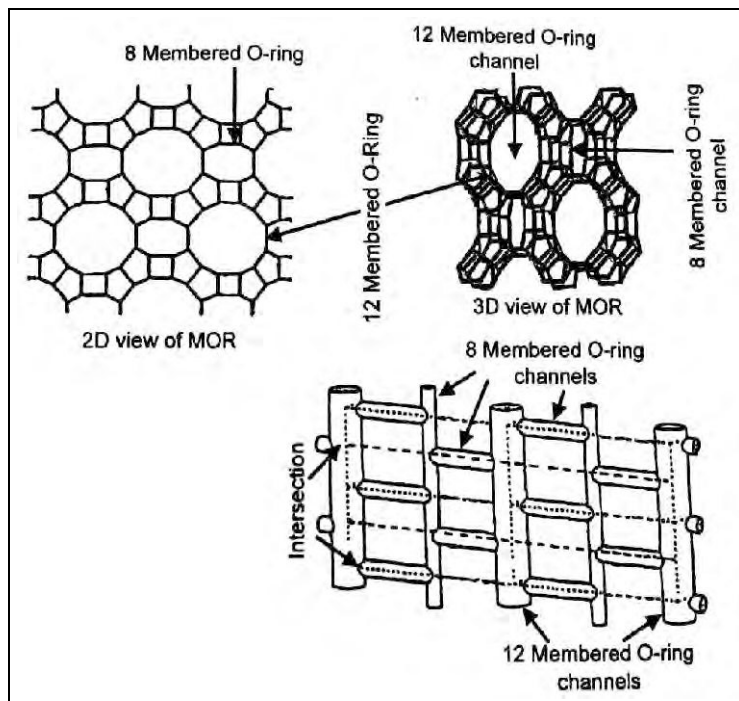
10 Mordenite (MOR) [3, 8, 10, 13, 17]

MOR with the idealised chemical composition $\text{Na}_8[\text{Al}_8\text{Si}_{40}\text{O}_{96}] \cdot 24 \text{H}_2\text{O}$ is one of the most abundant natural zeolites. Because of its high Si/Al ratio (= 5), it is highly resistant to acid attack, and its molecular sieves are relatively more nonpolar. This mineral is named after the small community Morden, living by the side of the Bay of Fundy (Canada), where the mineral was first found. Both the natural and synthetic mordenites find versatile industrial uses. Mordenite (MOR) zeolite structure is based on the 5-membered O-rings linked together into a series to produce the major channels, as in the case of ZSM-5 and ZSM-11.

MOR possesses two sets of intersecting 12- and 8-membered O-



Figure 4. Structural features of mordenite (MOR) zeolite.



ring (12MR and 8MR) channels. The 12-membered O-ring (12MR) channels (670 pm × 700 pm) run parallel, while the 8-membered O-ring (8MR) channels (260 pm × 570 pm) run both perpendicular and parallel to connect the major 12-membered ring (12MR) channels (*Figure 4*).

11 Zeolites Used in Commercial Oxygen Concentrators

Different types of aluminosilicate zeolites with relatively high Al-content like, A Type (Si/Al = 1) called Linde Type A (LTA), faujasite X-type (Si/Al = 1.0–1.5), etc., can selectively adsorb N₂ over O₂ and Ar (argon) from the air.

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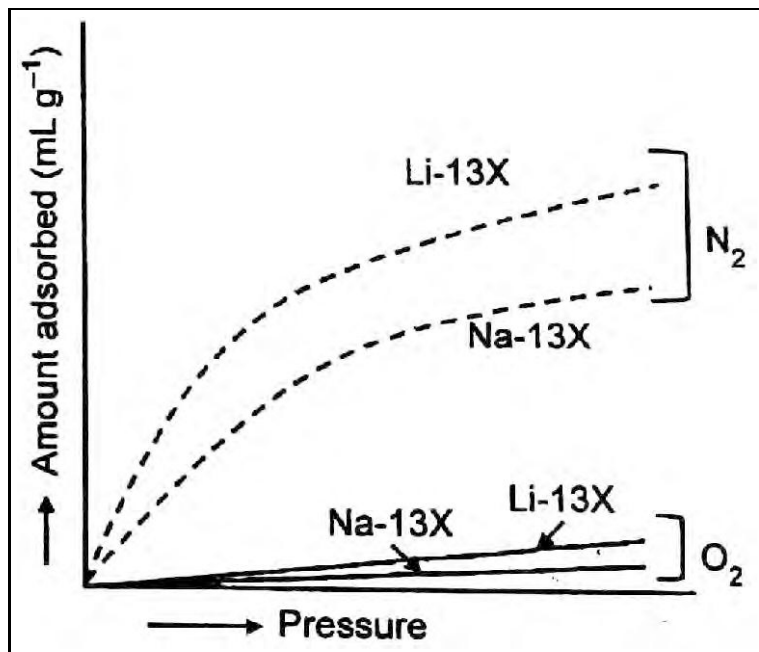


Figure 5. Qualitative representation of adsorption isotherms for N_2 and O_2 on Na-13X and Li-13X zeolites at a particular temperature.

der high pressure (*Figure 5*).

The air we breathe approximately consists of 78% nitrogen, 21% oxygen, 1% argon and other gases by volume. Pressure swing adsorption (PSA) technology in oxygen concentrators produces oxygen-enriched air by selectively eliminating nitrogen from the air.

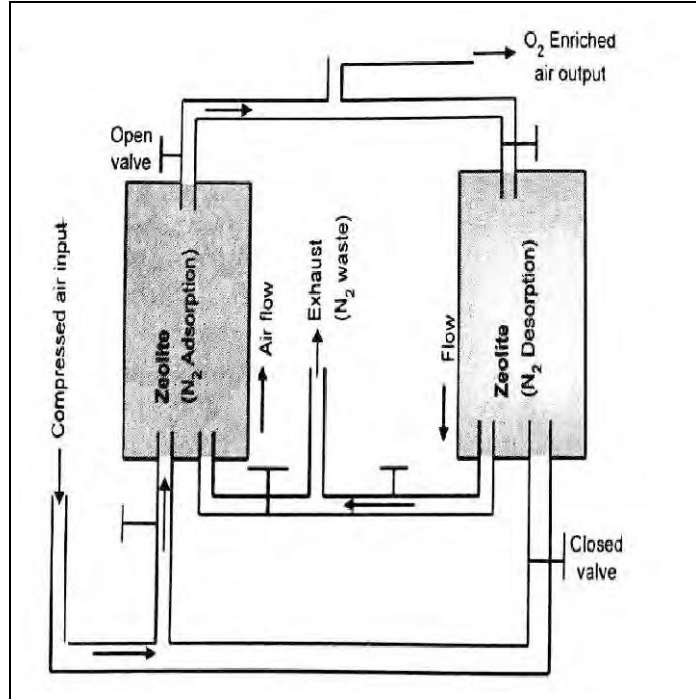
12 Pressure Swing Adsorption (PSA) [1, 2]

Pressure swing adsorption process leads to the adsorption of a gas under high pressure by an adsorbent. The adsorbed gas is released (desorbed) when the pressure is reduced. PSA in oxygen concentrators is based on the principle that under high pressure, a zeolite (most commonly used Li^+ exchanged 13X zeolite) selectively adsorbs the nitrogen gas from the ambient air to increase the oxygen concentration in the output flow of the air. The efficiency of the process is higher at high pressure and low temperature. When the zeolite bed gets saturated by adsorbing the nitrogen gas, the

Pressure swing adsorption process leads to the adsorption of a gas under high pressure by an adsorbent. The adsorbed gas is released (desorbed) when the pressure is reduced.



Figure 6. Flow diagram of pressure swing adsorption (PSA) technology in oxygen concentrator.



bed can be regenerated for the next cycle by reducing the pressure causing the desorption of the adsorbed nitrogen gas.

In medical oxygen concentrators used for the covid-19 and COPD (chronic obstructive pulmonary disease) patients and others requiring oxygen-enriched air for breathing, two adsorbent vessels packed with zeolite are used for a near-continuous production of oxygen-enriched air (Figure 6). When one vessel gets exhausted (i.e. adsorbent bed is saturated with the adsorbed N_2), the compressed air is transferred to the second vessel that starts to operate by adsorbing nitrogen, and the exhausted first vessel starts to regenerate through desorption of N_2 (released or vented to atmosphere) under the reduced pressure. When the second vessel gets exhausted, the compressed air is again fed into the reactivated first vessel, and the process is thus alternately repeated continuously to maintain a constant flow of oxygen.



13 Quadrupolar Interaction Between the Adsorbed Gas and Electrical Field of the Non-framework Cations of Zeolites

The kinetic diameter (that gives the measure of molecular size, *Table 1*) of oxygen, nitrogen, and argon are very much comparable, and these are 3.46, 3.64 and 3.40 Å respectively. These values are different for different sources, but the order is the same. From the values of kinetic diameter and van de Waals diameter of the main component gases (*Table 1*) in air, it is evident that the pore size (*Table 2*) in zeolite 5A (5Å) and 13X zeolite (about 9Å) can accommodate all these gas molecules from the air. Thus here, the size selectivity (i.e. stereokinetic factor) by the molecular sieves of zeolites is not the crucial factor.

N₂ molecule having a higher quadrupole moment than that of O₂ and Ar molecules experiences a stronger electrostatic attraction with the extraframework zeolite cation. Thus the nitrogen selectivity over the oxygen and argon selectivity arises from the difference in electrostatic attraction between the adsorbate molecules and the adsorbent surface [5–7]. This is why, in oxygen concentrators, the zeolites having the high Al/Si ratio to produce the stronger surface electrostatic field by the charge balancing non-framework cations are selectively used. In Li⁺ exchanged 13X zeolite (i.e. Li-13X), this electrostatic interaction for the adsorbed N₂ molecule having a higher quadrupole moment (about 3 times higher than that of O₂ molecule) with the exchanged non-framework smaller Li⁺ cation with a much higher charge density (compared to that of Na⁺) measured by charge/radius ratio causes the higher selectivity (compared to that of Na-13X) for nitrogen gas adsorption from the air [5–7] (*Figure 5*).

Experimental data indicate that the heats of adsorption of N₂, O₂ and Ar on the non-ionic solid surface are quite similar, whereas, on the ionic solid surface, the heat of adsorption of N₂ is unexpectedly higher than that of O₂ and Ar. It is because of the stronger electrostatic interaction between N₂ having the highest quadrupole moment among the given gases and the electrical field of the ionic surface [5]. A similar observation has been noted for



Molecule	Kinetic diameter (Å) [18]	Van der Waals diameter (Å) [19]	Polarizability (10^{-40} C m ² /V) [20,21]	Quadrupole moment (Q/e)(Å ²) [5]
Ar	3.40	3.76	1.81	0.0
N ₂	3.64	3.10	1.91	0.27
O ₂	3.46	3.04	1.72	<0.09
CO ₂	3.40		2.93	0.65

Table 1. Some gas molecules with their kinetic diameter, van der Waals diameter, polarizability and quadrupole moment.

Zeolite [#]	Si/Al	Window Ring Size	Window (Bottle-neck) diameter (pm)	Cavity Diameter (pm)
Sodalite	1	4MR	260	600
Zeolite A (LTA)	1	8MR	410	1140
Faujasite (FAU)	2.5	12MR	740	1200
ZSM-5 (MFI)	30	10MR	520 × 570 (Elliptical, straight channels)	
	(very high)		530 × 560 (Near circular, sinusoidal channels)	
ZSM-11 (MEL)	Very high	10MR	530 × 540 (Near circular, straight channels)	
Mordenite (MOR)	5	12MR	670 × 700	
		8MR	260 × 570	
AIPO-5		12MR	800	

In pure silica, the hydrophobic channels are associated with bottleneck diameter of 600 pm

Table 2. Some common zeolites with their window (bottleneck) diameters.



Extraframe cation	Zeolite	-ΔH (in kJ mol ⁻¹)		
		N ₂	O ₂	Ar
Li ⁺	FAU (X)	27.0	13.4	12.4
Na ⁺	FAU (X)	18.5	12.0	11.2
Li ⁺	MOR	34.0	19.9	22.1
Na ⁺	MOR	26.7	18.5	18.3
Na ⁺	LTA	19.6	13.8	11.9
Ca ²⁺	MOR	37.9	23.6	23.2
Sr ²⁺	MOR	33.0	21.7	23.6
Ca ²⁺	FAU (X)	28.8	15.3	13.5
Sr ²⁺	FAU (X)	25.2	13.9	13.5
Ca ²⁺	LTA	25.1	14.1	

Table 3. Comparison of heats of adsorption (-ΔH) of N₂, O₂ and Ar on different types of zeolites [7].

the preferential adsorption of nitrogen over that of oxygen and argon by different types of zeolites (Table 3). The experimental data reveal that the heat of adsorption of nitrogen by the zeolite increases with the increase in charge density of the non-framework cation for a particular zeolite. In fact, the heat of adsorption of nitrogen on the zeolite surface increases in the following order of non-framework cations as expected from their charge density [7]:

$$\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+; \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}.$$

14 Understanding Quadrupole Moment and Quadrupolar Interaction

An elementary quadrupole system comprises two dipoles of equal magnitude, oriented antiparallel to produce a net charge zero and zero net dipole moment [22–25]. An ellipsoidal (prolate or oblate) charge distribution can be considered as a sum of a spherical charge and a quadrupole. Spherical charge distribution leads to zero dipole moment and zero quadrupole moment. It may be

An elementary quadrupole system comprises two dipoles of equal magnitude, oriented antiparallel to produce a net charge zero and zero net dipole moment



Figure 7. Illustration of a dipole, molecular charge distribution and dipolar behaviour of the angular H_2O molecule.

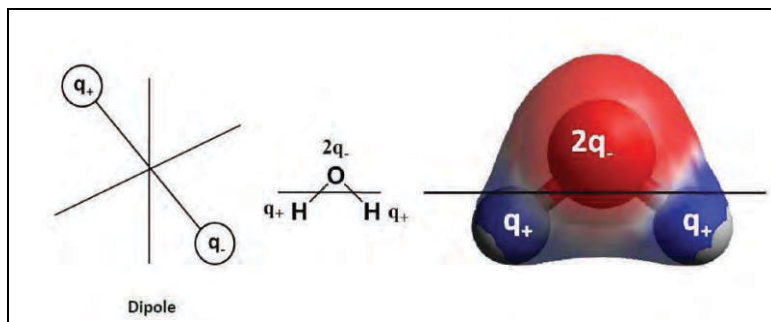
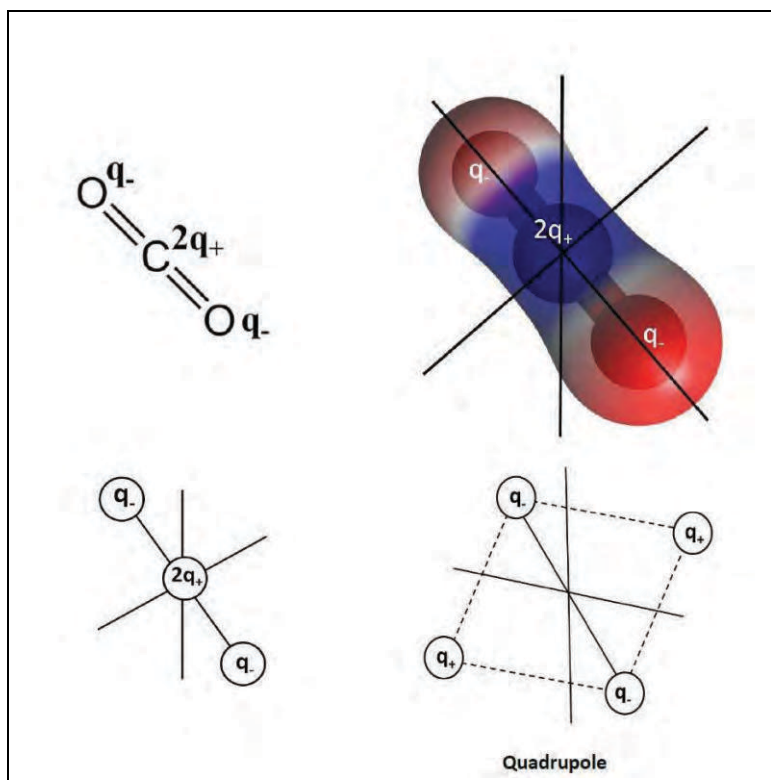


Figure 8. Illustration of molecular charge distribution and quadrupole behaviour of linear CO_2 molecule.



noted that dipole moment is a vector quantity while quadrupole moment is a tensor quantity.

For the monopoles, the sum of all charges is nonzero, and these are definitely the ions. The net charge is zero for both the dipo-



lar and quadrupolar molecules. For dipolar molecules like HCl, H₂O, etc., a straight line can be drawn through the molecule such that the more negative partial charges reside on one side of the line while the more positive partial charges reside on the other side of the line (*Figure 7*).

For a quadrupolar molecule, an 'X' can be drawn through the molecule such that the more negative partial charges reside in the opposite quadrants while the more positive partial charges reside in the other two quadrants. In the model of a nonpolar linear CO₂ molecule, it can be rotated in the presence of such an 'X'. For its diagonal orientation (*Figure 8*), the negative partial charges of oxygen are located in the two opposite quadrants, while the positive partial charge on carbon can be imagined to be located in the other two quadrants. This is why the linear CO₂ molecule does not possess the dipole moment but has a quadrupole moment.

The homonuclear diatomic molecules like N₂ or O₂ do not possess any permanent dipole moment, but they may have the quadrupole moment depending on the nature of molecular charge distribution [5, 22, 25]. If the charge is spherically or symmetrically distributed in a molecule, then the molecule possesses quadrupole moment zero, while the ellipsoidal charge distribution leads to the quadrupole moment. Thus quadrupole moment gives the measure of deviation from the spherical charge distribution. The higher quadrupole moment of N₂ compared to that of O₂ indicates that the charge distribution of the O₂ molecule is more symmetrical than that of the N₂ molecule. In fact, the quadrupole moment of N₂ is about three times higher than that of O₂ (*Table 1*). It simply means that the charge distribution of N₂ is three times more asymmetric than that of O₂. The zero quadrupole moment of the monoatomic argon (Ar) gas molecule indicates that the charge distribution in the Ar molecule is spherically symmetrical.

The quadrupole moment of the molecules is of no importance in intermolecular interaction in the gas phase or when they are adsorbed on the nonionic solid surface, but when these are adsorbed on the ionic solid surface having an electrical field, the interaction between the quadrupole moment of the adsorbed molecule

The homonuclear diatomic molecules like N₂ or O₂ do not possess any permanent dipole moment, but they may have the quadrupole moment depending on the nature of molecular charge distribution.



and the surface electric field of the adsorbent like zeolite possessing an electric field of the exchangeable non-framework cations is quite important [5–7].

It has been experimentally verified that when nitrogen, oxygen and argon are adsorbed on the non-ionic solid surface, their heats of adsorption are more or less similar because the weak van der Waals interaction between the adsorbate and adsorbent surface is comparable for the given gas molecules [5]. In fact, they have comparable sizes and comparable polarizabilities (*Table 1*) responsible for the van der Waals interaction. But when these gas molecules are adsorbed on the ionic solid surface, nitrogen is more strongly adsorbed (*Figure 4*) than oxygen or argon because of the higher quadrupole moment of nitrogen.

15 Future Outlook

It is established that the selectivity of nitrogen adsorption over that of oxygen by zeolites mainly depends on the degree of electrostatic interaction between the adsorbed gas and the electrical field of the non-framework exchangeable cations of zeolites.

It is established that the selectivity of nitrogen adsorption over that of oxygen by zeolites mainly depends on the degree of electrostatic interaction (i.e. quadrupolar interaction) between the adsorbed gas and the electrical field of the non-framework exchangeable cations of zeolites. This interaction can obviously be increased by using the zeolites having the relatively high Al/Si ratio bearing the more non-framework charge balancing cations. As the interaction largely depends on the charge density and on the nature of non-framework cations of zeolites (*Table 3*), by varying the non-framework cations for a particular zeolite, the efficiency of the selectivity ratio (N_2/O_2) of adsorption by the zeolites can be monitored. Thus effects of the nature, number and locations of the charge balancing non-framework cations can be explored to increase the selectivity ratio (N_2/O_2) of adsorption by the zeolites to develop the better oxygen concentrators.

16 Conclusion

Oxygen concentrators work based on the principle of pressure swing adsorption (PSA) [1, 2], leading to selective adsorption



of a particular gas under a high pressure followed by its desorption under a reduced pressure to reactivate the adsorbent bed for the next cycle. In an oxygen concentrator, two adsorbent vessels packed with zeolite (most commonly, Li-13X) are used for a near-continuous production of the oxygen-enriched air.

The functional material zeolite (aluminosilicate) in the oxygen concentrators is widely known for its porous structure characterised by its molecular sieves of well-defined dimensions and shapes. In oxygen concentrators, zeolites like zeolite 5A and Li-13X with a relatively high Al-content selectively absorb nitrogen into their molecular sieves from the air, not because of size and shape selectivity. It occurs due to the stronger quadrupolar interaction between the adsorbed nitrogen (*cf.* nitrogen is of higher quadrupole moment than oxygen and argon is nonquadrupolar) and the electrical field of the charge balancing non-framework exchangeable cations of aluminosilicate zeolites [5–7].

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