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Separation of oxygen and nitrogen from air by molecular sieve adsorbents

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Oxygen and nitrogen gases, which find commercial applications in many industries, are totally produced from air. During the last two decades, pressure swing adsorption based processes for separating these gases from air are being increasingly used and have become competitive to conventional low temperature fractionation processes. In the present review, brief idea about the adsorption principle, and adsorption process employed for separation of these gases from air is given. Microporous solids like zeolites and carbon molecular sieves used as adsorbents are central to this separation. The intrinsic equilibrium and kinetic properties of these solids can strongly influence the efficiency and economics of a particular separation process. Therefore, review has mainly focused on the developments on the adsorbents used for oxygen and nitrogen separation. Zeolites, carbon molecular sieves and inorganic metal complexes that show adsorption selectivity towards oxygen or nitrogen are discussed at length.

Introduction

Air is rich in nitrogen (78.084 mol%) and oxygen (20.946 mol%), and is the only source for the production of these gases ever since Linde achieved large-scale liquefaction of air in 1895[1]. This development gave rise to a large cryogenic industry for the separation of oxygen. World over, oxygen is mainly used for steel making, ethylene oxide production, coal gasification etc. (Table 1). The oxidation process for ethylene-to-ethylene oxide production consumes the largest amount of oxygen among petrochemicals. The largest single site oxygen facility is in South Africa for coal gasification at SASOL II consuming 1560 tons per day of oxygen. A substantial quantity of oxygen or oxygen-enriched air is used for the treatment of municipal wastes.

During the last 40 years, the demand for oxygen-free nitrogen for inert gas atmosphere led to the development of nitrogen generation plants. The use of N_2 as an inert gas for blanketing started gaining ground in the 1950s. The use for purging the tanks and vessels that store hydrocarbons and corrosive liquids gave an impetus to N_2 applications in chemical industries. The hydrocarbon vapors accumulate in the residual space at the top of the containers storing hydrocarbons. The atmospheric air is drawn into the tank during emptying of these containers. The practice of nitrogen blanketing in these containers has become prevalent in hydrocarbon industries to prevent hazardous air-hydrocarbon mixtures. Nitrogen blanketing while storing corrosive liquids like sulfuric acid minimizes the corrosion of vessels by avoiding oxygen. Similarly, in metal industries nitrogen blanketing is used to prevent metal oxidation during smelting. Another growing application for nitrogen is for maintaining

Table 1. Commercial applications of oxygen and nitrogen gases

Application	% Share	Process
	Oxygen	
Metal industry : Steel manufacturing, metal fabrication Welding	60	Cryogenics & PSA
Chemical industry : Production of ethylene oxide, acetylene, titanium oxide, propylene oxide, vinyl acetate	20	Cryogenics
Partial oxidation processes : Coal gasification	10	Cryogenics
Others :	10	PSA/Cryogenics
Pollution control : Industrial & municipal waste water treatment Fish farming		
Paper industry : Bleaching & treatment of pulp		Cryogenics
Medical uses : Breathing gas for patients suffering from Pulmonary disorder		PSA/Cryogenics
Glass industry :		PSA/Cryogenics
	Nitrogen	
Chemical industry : Blanketing of vessels having flammable or toxic chemicals	25	Cryogenics/PSA
Oil industry : Well fracturing, enhanced oil recovery	25	Cryogenics/PSA/ Comubstion
Electronic industry : For inert dust free atmosphere	15	Cryogenics
Metal industry : Cooling mould, blanket gas	15	Cryogenics/PSA
Food industry : Food preservation, soft drinks	10	Cryogenics/PSA

dust-free and inert atmosphere in the electronic industry. Nitrogen gas production, during last 40-50 years, has become[2] a major industry as a consequence of these diverse applications (Table 1).

Adsorption separation of oxygen and nitrogen

Theoretically, both oxygen and nitrogen can be obtained both from the air and water. Because water-electrolysis is expensive, virtually all oxygen is produced from air. The various physical properties of oxygen and nitrogen, the two main constituents of air, are given in Table 2, and form the basis of separation of these gases from air. Gaseous oxygen

Table 2. Physical properties of oxygen and nitrogen gas

Property	Oxygen	Nitrogen
Atomic weight	32.00	28.01
Boiling point, °C at 101.31 kPa	−182.97	−195.8
Specific volume, $m^3\ kg^{-1}20°$ at 101.31 kPa	0.755	0.855
Quadrupole moment, $Å^2$	< 0.11	0.31
Polarizability, $cm^{-1} \times 10^{24}$	1.60	1.76
Lennerad-Jones force constant, σ, Å	3.5	3.7
Lennerad-Jones force constant, ε / k, K	118	95
Kinetic diameter, Å	3.46	3.64
Molecular length, Å	2.0	2.1
Molecular width, Å	1.4	1.5

required for commercial applications is obtained predominantly using cryogenic fractionation due to difference in boiling points of nitrogen (−195.8°) and oxygen (−182.97°). In the 1950s and 1960s, combustion of hydrocarbons in air to produce nitrogen was an accepted method. This gave relatively pure nitrogen, the only impurities being carbon dioxide and moisture. Later, cryogenics based processes came into practice for production of highly pure and dry nitrogen. Cryogenic industries, today, has become the predominant source for nitrogen supply to many industries. The late 1970s and early 1980s saw the advent of adsorption and membrane technology for air separation and made their niche in many industries for the separation of oxygen and nitrogen from air[2–6].

In the present review, we shall briefly discuss the adsorption principle, adsorption processes used for oxygen and nitrogen recovery from air. However, the developments in the area of the adsorbents that are central to adsorption processes will be discussed at length.

Principle of adsorption separation

Separation of these gases is based on the selective physical adsorption of one or more components of a gas mixture on the surface of a microporous solid. When a gaseous mixture is exposed to an adsorbent for a sufficient time, equilibrium is established between the adsorbed and gas phase. Adsorbed phase often has a composition different from that of bulk phase. The gas phase becomes richer in the less selectively adsorbed component. The attractive forces responsible for adsorption are of the van der Waals type. Desorption can be achieved either by increasing the temperature of the system (Temperature Swing) or by reducing the adsorbate pressure (Pressure Swing). Desorption step also regenerates the adsorbent surface for reuse during the subsequent adsorption step. Therefore, the adsorption separation process consists of a cyclic sequence of adsorption and desorption steps.

In a typical adsorption isotherm (Fig. 1), the amount of gas adsorbed for a component gas decreases along the curve from point-A to point-B with a decrease in the partial pressure of that component. The adsorption capacity available for separation in pressure swing adsorption (PSA) is the difference in the capacities for the given component at the two pressures. However, in actual practice, due to the heat of adsorption, there is an associated change in the temperature of the system and working adsorption capacity is slightly different as shown in Fig. 1.

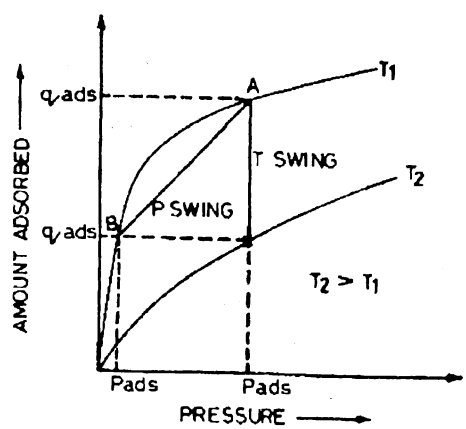


Fig. 1. Adsorption isotherms showing pressure and temperature swings.

Adsorption selectivity for a component A over B in a gaseous mixture is defined as

$$\alpha_{A/B} = x_A y_B / y_A x_B$$

where x and y are the adsorbed and the gas phase concentrations. There are three following factors used singly or in

combination for achieving the desired selectivity : (i) steric factors, such as difference in the shape and the size of the adsorbate molecules, (ii) equilibrium effect, i.e. when the adsorption isotherms of the components of the gas mixture differ appreciably, and (iii) kinetic effect, when the components have substantially different adsorption rates.

Adsorption processes :

Adsorption processes commercially used for the separation of oxygen and nitrogen from air are pressure swing adsorption (PSA) type processes. This process, in its simplest form consists of two adsorption beds (Fig. 2a), which are alternately pressurized and depressurized. The basic steps involved[5,6] in the process shown in the Fig. 2b are described below.

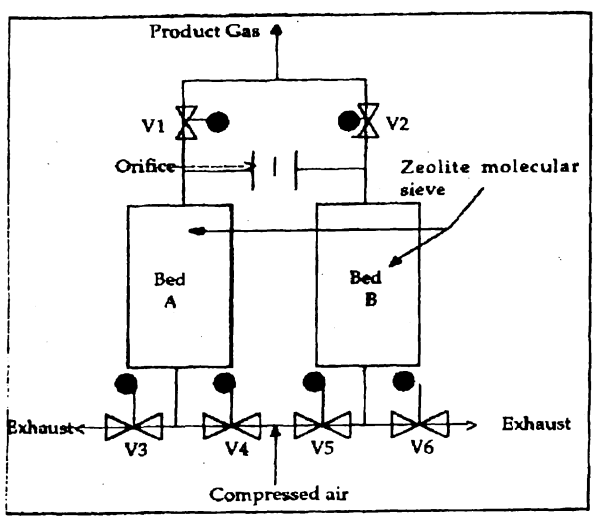


Fig. 2a. Schematic diagram of a two-bed pressure swing adsorption process.

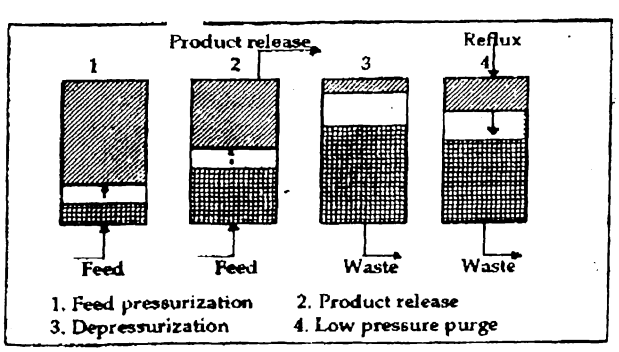


Fig. 2b. Basic steps indicating mass transfer zones in a PSA process.

Feed pressurization : The feed gas, i.e. air is compressed into an adsorbent bed at a pressure of 5–7 atm from one end with the other bed-end being closed. The gas freed from the adsorbed gas, for example, nitrogen in case of oxygen-enrichment process, is accumulated at the closed end.

Product release : At the higher pressure, the adsorbate-free gas, for example, oxygen in case of oxygen enrichment process, is withdrawn from the far end of the bed while airflow is maintained. The distinct regions as shown in Figure and described below develop inside adsorbent bed. (a) At the air inlet end, adsorbent bed is saturated with the adsorbate and the gas phase will have the composition of the air. (b) At the outlet end, adsorbent bed is still adsorbate free and the gas phase is enriched in oxygen. (c) The adsorbent bed region in between is known as mass transfer zone and it is in this zone the adsorption is occurring and air composition changes rapidly along the axial position. Adsorption front moves along the bed as more air is introduced and eventually the adsorbent is completely saturated with nitrogen and bed is said to be to 'breakthrough' into enriched oxygen stream.

Depressurization : This involves reducing the air pressure from 5–7 to 1 atm. During this step, adsorbed nitrogen is largely desorbed into the gas phase and gets released as a waste stream.

Low pressure purge : To complete the regeneration, adsorbent bed is further purged with product quality oxygen from the product-end at a low pressure usually in the countercurrent to the feed airflow.

A typical PSA unit consists of 2–4 adsorbent beds, solenoid valves, piping and an electronic timer for automatic valve switching. The steps of adsorption and desorption are repeated in each bed and finally the production of a continuous stream of enriched oxygen results at the product-end. The total cycle time may vary from a few seconds to a few minutes.

Adsorbents

Microporous solids like zeolites and carbon molecular sieves are employed as adsorbent for oxygen and nitrogen separation from air, respectively. Adsorbent is central to the separation process as adsorption selectivity and capacity determines the product purity as well as adsorbent bed size design. From the process simulation studies[7], it is reported that the minimum adsorption selectivity for a desired component of 3 is required for a separation process to be economical. It is well known that the intrinsic equilibrium and kinetic properties of the adsorbent can strongly influence the efficiency of a particular separation process. Still, most of the focus in the literature is on process innovation and relatively little on new adsorbent development. Effect of adsorbent development on the process economics of an ad-

sorption process for oxygen enrichment can be clearly signified from the data in Table 3. Therefore, developments in the area of adsorbents used for oxygen and nitrogen separation are described in details in the following sections.

Table 3. Impact of improved adsorbent on PSA process for oxygen enrichment from air

Property	NaCaA	LiX
α_{N_2/O_2}	3.3	10
Adsorbent beds	4	2
Valves	28	6
Pressure, atm	3.3/10	1.1/0.2
O_2 recovery, %	38	68
Power, kJ mol^{-1} product	48	68
Cycle time, min	6	4
Working capacity of adsorbent, moles product/kg of adsorbent	0.018	0.06
Adsorbent inventory in tones for 200 Nm^3 h^{-1} product	50	10

Nitrogen selective adsorbents :

As observed from Table 2, nitrogen molecule possesses a quadrupole moment (0.31 $Å^2$) higher than oxygen molecule (<0.11 $Å^2$) and is expected to interact strongly with polar surfaces. This difference in adsorption affinities with polar surface forms the basis for separation of these gases from air wherein nitrogen is retained on the adsorbent surface and oxygen-enriched air is recovered as a product. In principle, all polar adsorbents such as alumina, silica gel and zeolite molecular sieve can be used for O_2 enrichment of air by PSA. However, zeolite based adsorbents are the most prominently used adsorbents for this separation. The different zeolites used for O_2 enrichment of air include[2,8] NaA, CaA, NaX, CaX and other cation exchanged X, CaY, mordenite, chabazite, erionite. To have a better insight, a brief introduction of zeolite structure, type of interactions involved between nitrogen and oxygen with zeolite surface and the total energy of physical adsorption are discussed below.

Zeolite molecular sieves : Zeolites are crystalline aluminosilicates[9] with a framework based on extensive three-dimensional network of AlO_4 and SiO_4 tetrahedral. The AlO_4 in the structure gives rise to anionic charge for the framework, which is balanced by cations that occupy non-framework positions. A general chemical formula of zeolite is represented as $M_{n/2}O.Al_2O_3.xSiO_2.yH_2O$, where M is the exchangeable cation and n its valence. The value of x is equal to or greater than 2 because Al^{3+} does not occupy adjacent tetrahedral sites. Mainly alkali and alkaline earth metal-cations form the exchangable cations. The structure of the crystal framework contains voids (cavities, pores) and channels of molecular dimensions. The pore or channel openings range from 3 to 10 Å, depending on the structure. Framework structure of zeolite A and X, the most widely used adsorbents, are shown in Fig. 3.

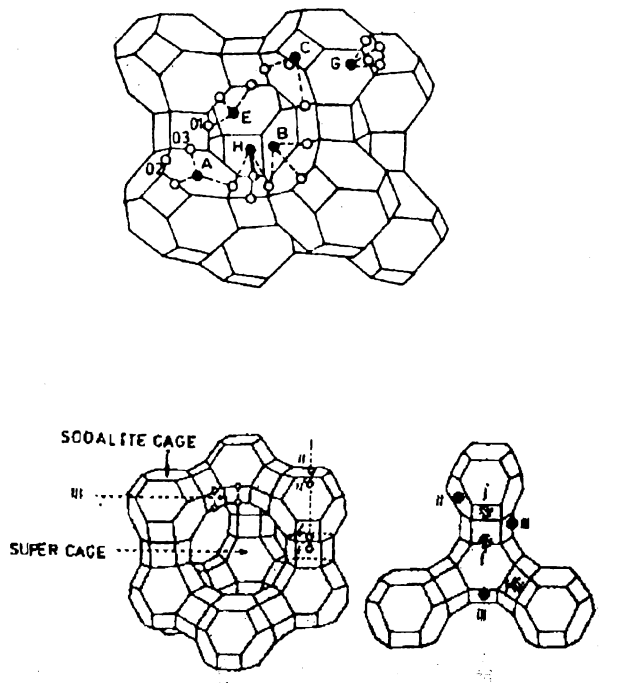


Fig. 3. Framework structures of zeolite A (above) and Faujasite (X and Y).

Energetic of physical adsorption of N_2/O_2 in zeolite :
The total energy of physical adsorption between nitrogen/oxygen molecules and zeolite surface is comprised of dispersion Φ_D, polarization Φ_P, field-dipole interactions $\Phi_{F\mu}$, field-quadrupole interactions Φ_{FQ}, close-range repulsion Φ_R, and sorbate-sorbate interactions Φ_{SP}. Thus, Φ is given as

$$\Phi = -(\Phi_D - \Phi_R) - \Phi_P - \Phi_{F\mu} - \Phi_{FQ} - \Phi_{SP}$$

The adsorbate nitrogen and oxygen being nonpolar and also adsorption coverage being small, the term $\Phi_{F\mu}$ and Φ_{SP} can be ignored while calculating interaction energy. Hence the above equation for total energy becomes

$$\Phi = -(\Phi_D - \Phi_R) - \Phi_P - \Phi_{FQ}$$

Substituting the terms for various interactions[10], the equation becomes

$$\Phi = -1/4Q(\delta F/\delta R) - 1/2(\alpha_s/k)F^2 - \Sigma_A / r^6 + \Sigma_B / r^{12}$$

where Q is the quadrupole moment, k a constant (in SI units, $k = 9 \times 10^9$), F the field, and α_s the polarizability of a ad-

sorbate molecule. The values of the constants A and B are calculated by the method described by Barrer[11].

As, in zeolites, Al and Si atoms are buried inside the center of the tetrahedral and are not directly exposed to nitrogen/oxygen molecules and also possess small polarizability values, their interactions with the adsorbates molecules can be ignored. Therefore, the principal interactions of oxygen and nitrogen molecules with the zeolite structure are through the lattice oxygen atoms and accessible extra-framework cations.

Reasonable idea of these interactions can be had from the heats of adsorption data at zero coverage for N_2, O_2 and Ar in zeolite mordenite, A and X, shown in Table 4. In

Table 4. Heats of adsorption of N_2, O_2 and Ar at zero coverage in various zeolites

Zeolite	ΔH kJ mol^{-1}			$-[\Delta H_0(N_2) - \Delta H_0(Ar)]$ kJ mol^{-1}
	N_2	O_2	Ar	
Mordenite				
ZM-060 (Si/Al = 5.5)	25.6	17.0	15.7	9.9
ZM-210 (Si/Al = 5.5)	18.8	16.7	17.4	1.4
ZM-510 (Si/Al = 5.5)	18.9	16.8	17.7	1.2
NaA	19.6	13.8	11.9	7.5
NaX	18.5	12.0	11.2	7.3

mordenite, ZM-060, there is electrostatic and polarization interactions between extra-framework Na^+ cations and the adsorbate molecules. Lattice oxygen interacts with the adsorbates molecules through dispersion forces. As in ZM-210 and ZM-510, there are no extra-framework Na^+ cations, heats of adsorption reflect only dispersion interactions between zeolite oxygens and adsorbate molecules. Furthermore, argon (3.7 Å) molecule having zero quadrupole moment can be presumed to interact through dispersion and polarization forces only with the zeolite oxygens. Therefore, the difference in the heat of adsorption of nitrogen and argon will give an idea about electrostatic contribution to the total N_2 interaction energy.This difference for N_2 (Table 4) is 9.9 kJ mol^{-1} for ZM-060, compared to 1.4 and 1.2 kJ mol^{-1} for ZM-210 and ZM-510 respectively. The higher interaction energy for ZM-060 is clearly arising because of electrostatic interaction of Na^+ ions with N_2 molecules. The contribution of the quadrupole interaction energy for N_2 with an isolated Na^+ ion has been theoretically calculated as 13.9 kJ mol^{-1}. Lower value for this interaction when Na^+ ions are inside zeolite cavity is expected due to screening effect of framework oxygens on Na^+ ions. The values for ZM-210 and ZM-510 reflect that dispersion interactions for argon are marginally higher than those for oxygen.

Heats of adsorption data for NaA, NaX and Na-mordenite, ZM-060 (Table 4) show that these values for the three adsorbates do not differ much for zeolite A and X. However, ZM-060 shows substantially higher value because contributions from electrostatic as well as dispersion and polarization interactions are higher for zeolite mordenite. Higher interactions of adsorbate molecules in mordenite have been attributed[12] to restricted rotational freedom of adsorbed molecules inside mordenite side pockets.

Factors on which adsorption capacity and selectivity depend : The following are the major factors that influence the nitrogen capacity and selectivity of a given zeolite molecular sieve.

(i) Type of zeolite and Si/Al ratio : Both natural and synthetic zeolites have been reportedly used for oxygen generation using adsorption. Most of adsorbent development research has been confined to post-synthesis modification particularly of zeolites A and X. Other zeolites and zeolite-type microporous solids also hold potential for new adsorbent for this application.

Natural zeolite reported[8] suitable for this includes chabazite, mordenite, clinoptilolite etc. For example, Itado mordenite from Japan adsorbes about 30 cm^3 N_2/g at room temperature and atmospheric pressure. Oxygen generator using this zeolite has also been reported[8]. However, natural zeolites have problems of purity and availability. Coe *et al.*[13] reported that synthetic lithium exchanged chabazite (Si/Al = 2.6) exhibits 26.5 and 6.7 cm^3 STP/g N_2 and O_2 adsorption capacity, respectively, and α_{N_2/O_2} = 5.9. With suitable isotherm shape at ambient conditions to increase the working adsorption productivity beyond the standard zeolites used for air separation, this adsorbent is reported to hold potential for oxygen generation. Most of the present commercial PSA units employ synthetic zeolites with NaCaA, NaX, CaX and mordenite for oxygen generation.

The adsorption capacity of an adsorbent depends on the number of cations. However, the strength of the cation/sorbate interaction is relatively independent of the number of the cations present[14]. Hence, the adsorption capacity for weakly interacting adsorbates such as nitrogen is directly related to the number of sorbate-accessible cations in a zeolite. Therefore, it can be increased if the numbers of cations are increased in a given zeolite. Further, the number of cations in a zeolite depends on its Si/Al ratio. Coe *et al.*[15] developed a unique way of increasing Al content in the form of low silica X zeolite (LSX) with Si/Al ratio equal to 1

(the typical value being 1.25). CaLSX contains about 18.5% more accessible cations over CaX having Si/Al as 1.25. This results in a 20% increase in the nitrogen adsorption capacity. It is claimed that LSX possesses air separation properties superior to any other pelletized nitrogen selective adsorbent[15]. In a similar manner, a low silica zeolite X in which more than 95% of cations can be exchanged with lithium is patented[16], which exhibits an extraordinarily high adsorption capacity and selectivity towards nitrogen from its mixture with oxygen. For example, at 700 torr, the nitrogen adsorption capacity of 99% Li-exchanged LiX (Si/Al = 1) is 32% higher than the 94% Li-exchanged LiX (Si/Al = 1.25). The adsorption data for binary mixtures of oxygen and nitrogen[16] also show that LiX (Si/Al = 2.0) has higher nitrogen selectivity than LiX (Si/Al = 2.5) with the same exchange level. It has been shown[16] that at room temperature and at 1 atm, N_2/O_2 separation factor of 11 for LiX (Si/Al = 1.0) compared to 6.4 of LiX (Si/Al = 1.25) and 3.2 of NaX.

(ii) Nature and locations of cations : In general, in a given zeolite, the interaction energy and the adsorption capacity for nitrogen are expected to increase with the charge density of the cation[17-20]. However, adsorption data given in Figs. 4 and 5 show that there are factors other than cation charge density, which play significant role in adsorbate-adsorbent interactions. For example, among monovalent cations, lithium shows abnormally high values for heats of adsorption, specific retention volume and adsorption selectivity. Furthermore, bivalent cations show values lower than that expected by extending the heats of adsorption versus cation charge density plot for monovalent cations. These observations have been explained in terms of different sites, these cations occupy inside zeolite structure (Fig. 3).

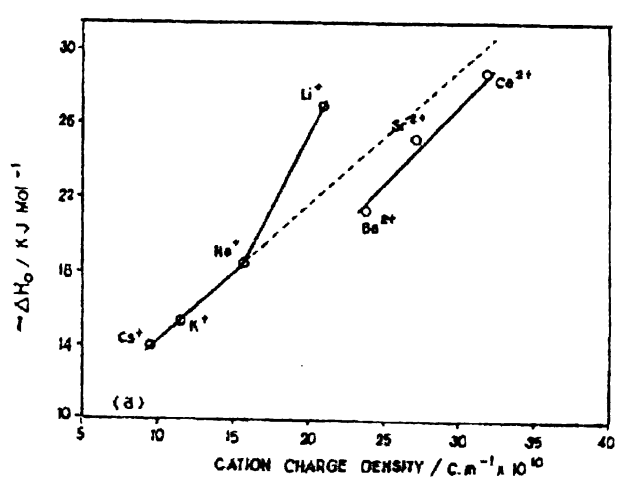


Fig. 4. Dependence of heats of adsorption (ΔH_0) at zero coverage with extra-framework cation charge density.

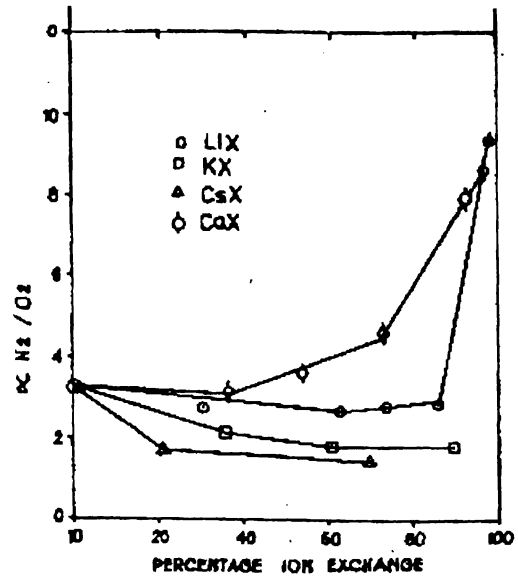


Fig. 5. Dependence of nitrogen adsorption selectivity, α_{N_2/O_2} with percentage cation exchange.

The distribution of cations in NaX is of 4 type I sites, 32 type I′ sites, 31 type II sites and 8 type III sites with 6 ions unlocated. However, the cations, which are accessible and interact with the adsorbate nitrogen/oxygen molecules are site II and site III cations only. Lithium is reported[21,22] to preferentially occupy sites I′ and II in zeolite X. Li^+ ion due to its smaller size (0.68 Å) resides almost in the plane of the six-member ring, while the larger Na^+ cation (0.95 Å) is held above the plane in trigonal-pyramidal coordination to the O_2 molecules. As a result, site II Li^+ cations are less accessible to adsorbates than site II Na^+ ions, and show weaker interactions and heats of adsorption. Once the entire Na^+ cations of site II are replaced, Na^+ ions from site III or unlocated positions are replaced by Li^+ ions and increase in heats of adsorption is observed. It has been reported[23] that the sharp rise in the heat value observed above 90% Li exchange is due to Li^+ ions occupying accessible site III at the expense of Na^+ ions from site I or unlocated position.

The lower heats of adsorption observed for bivalent Ca, Ba and Sr cation in zeolite X compared to values extrapolated from monovalent cations is also resulting from the fact that bivalent cations occupy site II only[9,24] where monovalent cations occupy sites II and III. Site III is more accessible to adsorbate molecules and show higher interaction. Similar conclusions have been made about the effect of cation locations on the adsorption of nitrogen/oxygen in zeolite A[25], particularly in calcium exchanged zeolite A where abnormally high adsorption capacity and selectivity was observed with calcium exchange of >90% (Fig. 6 and

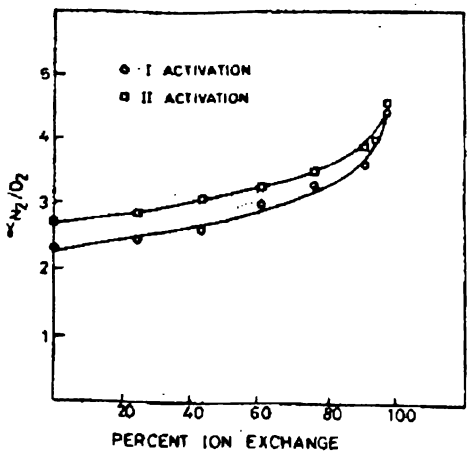


Fig. 6. Dependence of nitrogen adsorption selectivity on calcium exchange in NaCaA zeolite at 300 K.

Table 5). This has been attributed to the highly accessible site near the pore opening of the zeolite A occupied by calcium cations at this exchange level. Far-IR studies[26,27] have shown that at higher than 90% calcium exchange in zeolite A, a major part of Ca^{2+} ions are located at site B, i.e. in the six-ring but displaced into the α-cage and hence more accessible to adsorbate molecules. The remaining cations are located at the inaccessible site C, in the six-ring displaced in the β-cage. However, at less than 75% calcium exchange level, Ca^{2+} ions are located at site A, i.e. in the plane of the six-ring and less accessible than cations at site B.

Therefore, it is highly significant to understand cation locations in the zeolite structure to develop the desired adsorbent. The commercial implications of having high selectivity adsorbent can be seen from the data given in Table 3 wherein the commercial performance comparison of LiX and NaCaA adsorbent is given. Choudary *et al.*[28] extended the study of N_2/O_2 adsorption to rare earth exchanged zeolite X and the adsorption selectivity and capacity values are shown in Table 6. However, it has been demonstrated[25,29–31] that the adsorption capcaity for zeolites having multivalent cations are more sensitive to the activation procedure followed.

Table 5. Effect of presorbed water on ΔH_0 of nitrogen and oxygen in different adsorbent samples

Adsorbate	ΔH_0, kJ mol^{-1} presorbed water, mmol g^{-1} of zeolite			
	0.0	0.9	1.6	3.5
		NaA		
N_2	19.6	11.7		
O_2	13.8	8.5		
		NaCaA-24		
N_2	20.0	19.7	19.5	16.5
O_2	14.3	14.0	13.4	13.1
		NaCaA-43		
N_2	20.5	20.0	19.7	16.6
O_2	14.3	13.5	13.4	13.0
		NaCaA-60		
N_2	21.0	20.6	20.4	19.8
O_2	14.0	14.4	13.5	14.1
		NaCaA-75		
N_2	21.8	21.5	21.1	20.0
O_2	14.0	13.8	13.8	14.5
		NaCaA-90		
N_2	23.7	21.9	21.7	19.3
O_2	14.0	13.7	14.1	14.3
		NaCaA-97		
N_2	25.1	23.7	21.8	21.3
O_2	14.1	14.8	13.9	14.6

Table 6. Adsorption data for oxygen/nitrogen gaseous mixture on different adsorbents at 30°

Adsorbent	Henry constant, K/mmol g k Pa^{-1}		Adsorption selectivity α_{O_2/N_2}	Heats of adsorption, kJ mol^{-1}	
	O_2	N_2		O_2	N_2
NaX	1.60	4.78	0.3	11.9	16.5
NaY	0.97	2.19	0.4	11.4	15.5
CeY	1.25	1.20	1.0	13.4	13.5
CeX	4.25	2.16	2.0	33.1	20.7
CaX	1.49	12.63	0.1	15.3	28.8
LiX	1.28	11.93	0.1	13.4	27.0

(iii) Degree of cation exchange : In general, nitrogen adsorption capacity and selectivity increase with the increase in the degree of bivalent ion exchange[30,31] as shown in Figs. 5 and 6[25]. For example, Henry constant for N_2, which is indicative of adsorption capacity, increases with calcium exchange with steep rise at 90% exchange level. However, Henry constant for oxygen is not affected significantly by calcium exchange. Similarly, heat of adsorption (Table 5) for N_2 increases form 20 to 25 kJ mol^{-1} as the percent calcium exchange increase to 97 whereas that for O_2 remains at 14–15 kJ mol^{-1}. In the case of zeolite X, the effect of Ca-exchange on N_2 adsorption capacity and selectivity is more pronounced[18], than in zeolite A as shown in Fig. 5. We have observed three-fold increase in nitrogen selectivity as calcium exchange increase from 0 to 95% level.

(iv) Activation of the adsorbent and presorbed moisture : In any application of zeolites for adsorption purposes, the first step is to activate/regenerate the adsorbent in order to drive off the residual water. This is generally carried out by heating the adsorbent at an elevated temperature (upto 450°).

Both for zeolite A[25] and X[29–31], it has been shown that an activation procedure has an influence on the adsorption behavior of Ca-exchanged zeolites. It has further been emphasized that in the case of polyvalent cation exchanged zeolites, thermal activation step should be carefully controlled failing which zeolite undergoes substantial degree of hydroxylation. Our studies[25] in zeolite A has demonstrated that the presence of moisture and CO_2 in the air from which nitrogen is adsorbed has also negative effect on the adsorption capacity and selectivity. This effect is more pronounced even with less than 1 mmol/g of adsorbed water for highly calcium-exchanged zeolite A (Table 5). Effect of CO_2 is more pronounced than moisture. CO_2 may be physiosorbed or chemisorbed in NaCaA zeolites, thus effecting the adsorption behavior. Effect of presorbed water can be explained in terms of hydroxylation of the bivalent cations. Hydration is an equilibrium reaction,

$$M^{n+} + xH_2O \rightleftarrows M(OH)^{+}\ (n-e) + eH^{+} + (x-e)\ H_2O$$

where M is a cation having valency n (usually 2 or 3), x is 1 to 6 and e is 1 or 2. Products on the right-hand-side of the equation are detrimental to the zeolite capacity and stability. Hydroxylated multivalent cations, such as $Ca(OH)^{+}$, are known to be ineffective sites for the selective adsorption especially for nitrogen. Additionally, the zeolite framework is unstable towards H^{+}. The equilibrium may be shifted towards left by minimizing the amount of water present at any given temperature particularly above 150° during activation.

Oxygen selective adsorbents :

Carbon molecular sieves : The production of nitrogen from air by PSA is largely based on the kinetic separation for oxygen due to the faster diffusion of the latter in carbon molecular sieve. From the sorption uptake curves for oxygen and nitrogen, as given in Fig. 7, it is observed that oxygen is adsorbed to its equilibrium value much faster than nitrogen[6,32]. This is because oxygen molecule that is smaller in size (kinetic diameter 3.46 Å) diffuses much faster in carbon molecular sieve than nitrogen (kinetic diameter 3.64 Å). The diffusion time constant (D/r^2) for oxygen and nitrogen in carbon molecular sieve, as calculated from sorption uptake, is reported[33] to be 1.7×10^{-4} and 7×10^{-6} s^{-1}, respectively. Hence, oxygen gets selectively adsorbed in carbon molecular sieve adsorbent and nitrogen is collected as the high-pressure product.

Carbon molecular sieves used for air separation are made from activated carbon by post-treatment that narrows the pore size distribution so that predominant pores are 3–4 Å. These sieves are able to distinguish the 0.2 Å difference between O_2 and N_2. Unlike zeolites, there are no cations present in carbon molecular sieves. Adsorption mainly occurs on defect sites and/or along the edges of basal planes of graphitic arrays. Carbon molecular sieves differ from activated carbon not only in terms of narrower and precise pore size distribution but also in actual surface compositions. Surface functionality like ketonic, carboxylic, phenolic groups normally observed on activated carbon surfaces are not detectable in carbon molcular sieves.

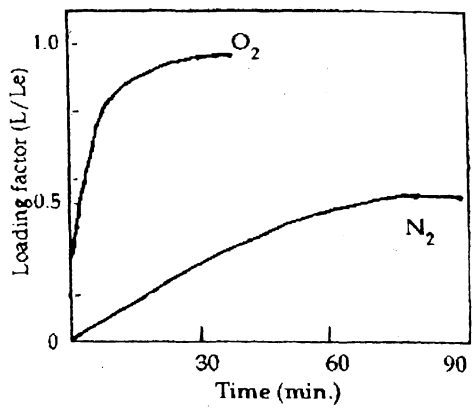


Fig. 7. Adsorption isotherm of N_2 and O_2 in carbon molecular sieves at 300 K.

General methods of manufacturing carbon molecular sieves involve[34–37] carbonization of coal or nut hulls in inert atmosphere. Carbonized solids are activated in a reactive atmosphere like air or steam to generate porosity. Controlled depositing of carbonaceous material on pore entrance does further control the pore size of thus produced porous material. This is the key step in production of carbon molecular sieves and is mainly done by pyrolysis of benzene or furfuryl alcohol or olefins near the pore mouth. The two principal producers of carbon molecular sieves for nitrogen recovery are Bergbau Forschung Gmbh, Germany and Calgon Carbon Corporation, U.S.A.

Carbon molecular sieves based adsorption process has established[37] itself in the nitrogen separation area with more than 1500 commercial units operating world wide for producing nitrogen from a few liters per minute to 3000 Nm^3 per hour with a purity range of 95–99.999% by volume. Especially for uses requiring moderately pure nitrogen (>99.9%), PSA is most competitive. Presently, 46% application is in inerting of storage tanks, process lines and vessels etc. as seen in Table 1. It is also being increasingly used in creating modified atmosphere to prolong storage life in food storage area. In fact, it can be an environmentally accepted replacement for food grain fumigants such as ethylene bromide. The nitrogen purity achieved with PSA is of 99.9%. To obtain a higher purity, the residual oxygen

is reacted with hydrogen on a palladium catalyst.

Zeolite molecular sieves : In the recent years, attempts are in progress to develop an alternative to earlier molecular sieves by synthesizing oxygen selective zeolite through molecular engineering of the starting zeolites[38]. Zeolite 4A is modified[39] by incorporating divalent iron and further by partly exchanging sodium with potassium cations. The Fe in the NaA forms terminal bonding such as –Si–O–Fe–, –Al–O–Fe–, etc. This type of bonding leads to a partial pore closure, which in turn results in a slower diffusion of nitrogen. It has been observed that incorporation of 0.5% of Fe as Fe^{II} ion decreases the rate of nitrogen adsorption, simultaneously increasing the capacity of oxygen adsorption from 2.2 to 3 and to 3.8 ml g^{-1} in the case of 1% Fe containing NaA. The difference in the rates of adsorption increases with lowering of temperature. If the Na^+ ions are replaced by K^+ ions, the oxygen selectivity is further enhanced. Efforts are being made to improve the processes for air separation[38,40] using oxygen selective zeolites based on the different diffusivities for N_2 and O_2.

Efforts are also being made to develop molecular sieves, which are more selective to nitrogen than the conventional zeolites. Chao[41] observed that highly exchanged form of zeolite X exhibits extraordinary capacity and selectivity to nitrogen molecule. These are considered useful for separating nitrogen from its mixtures with oxygen or with other gases, such as hydrogen, methane, argon etc.

As seen above, the only kinetic processes, which are commercialized, are for nitrogen separation from air using carbon molecular sieve adsorbent. Zeolites, despite their enormous potential have not been used commercially for kinetic separation. Recently, interesting developments are taking place in this area with some studies[38–46] being done to use zeolite 4A molecular sieve for nitrogen separation. In the sodium form of zeolite A (4A), the 8-membered windows of the zeolite are partially blocked by Na^+ cation, which reduces the free diameter to about 3.9 Å. At ambient temperature, both nitrogen and oxygen are able to penetrate the 4A lattice at a rate, which is controlled by the intracrystalline diffusion. Intracrystalline diffusion in 4A is an activated process. Correlation of the diffusion energies of the small molecules in molecular sieve adsorbents with the van der Waals radius shows that the diffusion kinetics is largely controlled by the repulsive energy involved during the passing of the molecules through the pores. Nitrogen and oxygen molecules have difference of 0.2 Å in their van der Waals radii. It is interesting to observe that such a small difference in size is sufficient to cause as appreciable difference in the activation energies (23 and 18.5 kJ mol^{-1} for N_2 and O_2, respectively)[46] and thus in diffusion coefficients. The diffusivities for nitrogen, oxygen and argon in 4A at 30° as reported[43] are 3.6×10^{-9}, 3.8×10^{-11} and 8×10^{-11} cm^2 s^{-1}, respectively. The characteristic diffusion time for nitrogen, and argon is 2–3 orders of magnitude longer than that of oxygen. In zeolite crystals, the diffusion time is in seconds for oxygen and in minutes for nitrogen. The characteristic diffusion time for oxygen in crystals is also much shorter than that of oxygen in pellets. This shows that the diffusion of oxygen in crystals is the dominant step in the kinetic separation cycle. The equilibrium isotherms for nitrogen and oxygen in 4A zeolite at 25° show that the thermodynamic equilibrium is not favorable for kinetic separation because nitrogen, which is strongly adsorbed, has a lower diffusivity. Nitrogen gas can be produced by PSA by choosing a cycle-time lying between the diffusion time of oxygen and nitrogen. Nitrogen separation from air using molecular sieve of the type 4Å has been successfully demonstrated[46] in the laboratory using a four-step PSA cycle.

Encapsulated inorganic metal complexes : A new class of oxygen selective adsorbents based on inorganic metal complexes can be used for the purification and separation of oxygen from air. The synthesis of these adsorbents employs ship-in-a-bottle concept wherein oxygen selective metal complexes are synthesized inside the cavities/pores of microporous solids like zeolites.

It is known[47] that certain metal complexes with appropriate ligands reversibly bind oxygen in solution or solid form at or above room temperature as shown in equation below :

$$n\,M(L) + O_2 \rightleftarrows [M(L)]_n\,(O_2)$$

where $n = 1$ or 2. To make use of such complexes for oxygen separation, metal complex-oxygen adduct reaction needs to be reversed by heating the adduct or by lowering the partial pressure of oxygen or by the addition of a ligand capable of replacing the bound oxygen.

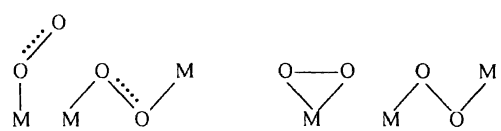
There are several metal complexes of certain transition metals[48–52] like Co^{II}, Fe^{II}, Mn^{II}, Cr^{II} and Cu^{II}, known to reversibly bind oxygen in solution or solid form. Some of these are shown in Table 7. However, Co^{II} complexes are the most extensively studied metal complexes both in solution and solid state. It is pertinent to discuss the nature of metal complex-oxygen interactions here. It has been observed[53] that to synthesize reversible oxygen adduct, it is necessary to have metal ions that have oxidation potential lying in a certain range so that there is some donation of electron to the oxygen molecules but not enough to cause irreversible oxidation of the metal. This shows that the metal

Table 7. Oxygen adduct of some metal complexes

Complex	Type of complex	M : O
Co(bzacen)(py)(O_2)	Superoxide - like	1 : 1
Fe(TpivPP)(1-Melm)(O_2)	Superoxide - like	1 : 1
Cr(TPP)(py)(O_2)	Superoxide - like	1 : 1
$[Co_2(NH_3)_{10}(O_2)]^{5+}$	Superoxide - like	2 : 1
$[Co_2(CN)_{10}(O_2)]^{5-}$	Superoxide - like	2 : 1
Ir(CO)(PPh_3)$_2$(Cl)(O_2)	Peroxide - like	1 : 1
Ti(OEP)(O_2)	Peroxide - like	1 : 1
$[Co_2(NH_3)_{10}(O_2)]^{4+}$	Peroxide - like	2 : 1
$[Co_2(CN)_{10}(O_2)]^{6-}$	Peroxide - like	2 : 1

like Cr^{II} that are readily oxidized react with oxygen irreversibly and the metal like Ni^{II} that are difficult to oxides do not react with oxygen. However, metal like Co^{II} having redox potential lying between the two limiting redox potentials react reversibly with oxygen. This is the reason that cobalt(II) complexes are most studied for reversible oxygen binding. Four-coordinate Co^{II} complexes are poor oxygen absorbers whereas five-coordinate chelates readily bind oxygen at ambient pressure of oxygen[54].

Binding of oxygen molecule to metal center may form two types of species, namely, superoxo (**I**) and peroxo (**II**). Monomeric (1 : 1) and dimeric (2 : 1) metal-oxygen adduct may form with both superoxo and peroxo binding. However, monomeric adducts are found to be more active for reversible binding of oxygen.



(1 : 1) (2 : 1) (1 : 1) (2 : 1)

(I) (II)

The reversible uptake of oxygen by cobalt complexes in solutions, aqueous as well as non-aqueous, has been extensively studied with a view to understanding the binding and activation of oxygen. However, the synthesis of these complexes in the porous cavities of microporous solids like zeolites and the use of such systems for air separation is an area of recent interest. The three-dimensional pore structure of zeolites provides the possibility of site isolation, stabilizes complexes by anchoring them to the lattice by coordination to framework oxygen. Synthesizing these complex inside the cavities of a zeolite inhibits the dimerization and irreversible oxidation of the complex, which occur in the solutions.

Several studies[55–62] have been carried out for modifying oxygen-binding capacity of Co^{II} complexes by attaching suitable ligands (Fig. 8) to the metal inside the zeolite. Five-coordinated Co^{II}-amine complexes $[Co^{II}Lx]$-Y with L = ammonia, methylamine, and *n*-propylamine in zeolite-Y

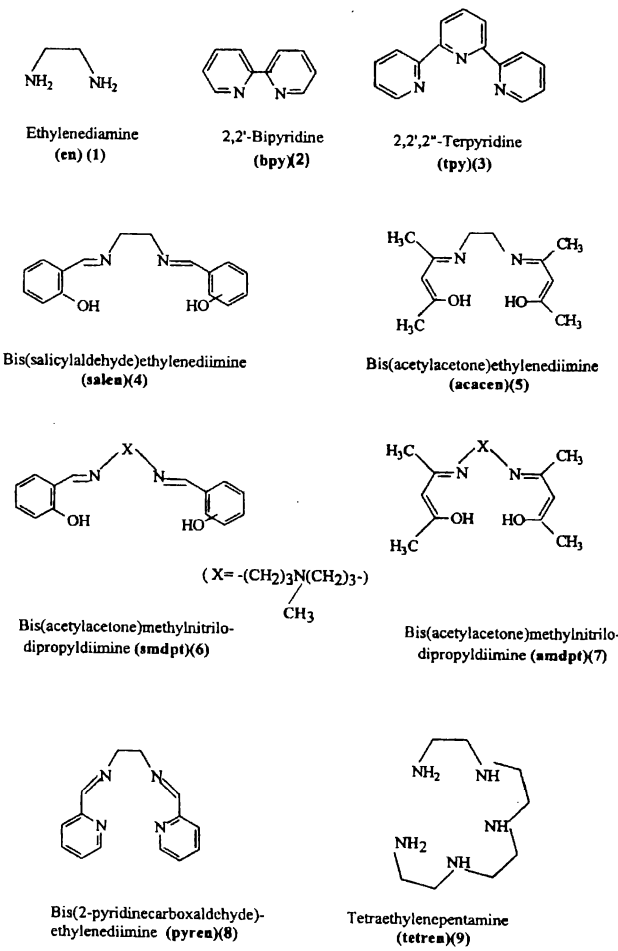


Fig. 8. Bi-, tri-, tetra- and pentadentate ligands used for Co^{II} complexation in various zeolites.

formed six-coordinated oxygen adducts $[Co^{III}LxO_2^-]^{2+}$. Both with ammonia and methylamine, monomeric (1 : 1) and also dimeric (2 : 1) Co-oxygen adduct can be formed, whereas with *n*-propylamine only 1 : 1 adduct is observed[55,56]. With ethylenediamine (en) monomeric 1 : 1 oxygen adducts $[Co^{III}(en)_2O_2^-]^{2+}$ formed are found sufficiently stable in the presence of O_2 up to 70° in zeolite X and Y[57]. The mixed-ligand bipyridine-terpyridine complex in zeolite Y formed the oxygen adduct $[Co^{III}(bpy)(tpy)O_2^-]^{2+}$ in the presence of 30 torr of O_2 which was found to be completely reversible at 298 K and was thermally stable in the presence of O_2 up to 343 K[58]. In partially Co-exchanged LiY, this mixed com-

plex can be obtained in higher concentration[59]. All these complexes have been characterized by EPR spectroscopy. The close similarity between the EPR parameters of 1 : 1 adducts of CoY and in frozen solution or the solid state suggests that the structure is the same. The monomeric 1 : 1 oxygen adducts are superoxo species where the unpaired electron is largely localized on the oxygen molecule[55,56].

All these Co^{II} complexes involve neutral ligands and though effective for separating oxygen from air, coordination of water as a sixth ligand or oxidation of the ligand limits their utility[59]. Drago *et al.*[60,61] overcame these problems by reporting an anionic, oxygen-selective Co-cyanide complex, $[Co(CN)_5]^{3-}$ within zeolite Y. This adsorbent is stable to repeated cycling in air. Even at low concentration of complex loading in the zeolite, the adsorbent was observed to increase the amount of oxygen adsorbed by more than twice over argon at 100 torr. It has been shown that by exchanging Cs^+ ion into Co–Na–Y prior to the addition of cyanide, the active $Co(CN)_5^{3-}$ complex is formed inside the zeolite at higher concentration. An equilibrium constant for oxygen binding of 18 ± 2 $torr^{-1}$, with an oxygen binding cobalt species concentration of 43 ± 4 micromol g^{-1} material was reported[62]. Large oxygen affinity of this complex results in highly oxygen-selective adsorbent with α_{O_2/N_2} of 5000 (Fig. 9). Air products Inc. has reported[63] the synthesis of lithium cyanocobaltate which when used as such has highest reported oxygen capacity (55 Std cm^3 g^{-1}) for any solid at ambient temperature. Polymeric cyanocobaltate, $Li_3Co(CN)_5.4DMF$ was observed to bind O_2 reversibly at ambient temperature. This complex loses two DMF molecules on heating upto 160° to produce a complex $Li_3Co(CN)_5.2DMF$. This complex was found to have higher capacity for oxygen than the one with four DMF molecules and was also reported to bind O_2 at a faster rate. For example, $Li_3Co(CN)_5.2DMF$ sorbs about 7 wt% O_2 in 10 min and purging with N_2 releases more than 90% of the adsorbed oxygen in 30 min. However, there are two drawbacks of this material which do not make these complexes attractive for commercial application. For example, its capacity is sensitive to moisture and on repeated cycling use there is a loss in its activity.

The use of Co^{II} metal complexes with ligands like amines, cyanide and bi- or terpyridine dispersed in zeolites has been encouraging and has led to some perspective on metal complexes based oxygen-selective adsorbent development. These complexes have enhanced reversible oxygen binding as the active species are monodispersed in the zeolite cavities and thus retarding binuclear complexes formation. However, these systems have a major disadvantage, as the number of mono- or bidentate ligands surrounding the Co^{II} cation is not easily controlled. The use of polydentate ligands like salen (**4**)[64] and tetren (**9**)[65] was reported to overcome this problem. De Vos *et al.*[66–68] studied tetravalent as well pentavalent ligands in zeolite Y (faujasite with cubic symmetry) and in EMT (faujasite with hexagonal symmetry). With the use of tetradentate salen (**4**) and acacen (**5**) ligands in zeolites CoNaY, low concentration of oxygen binding Co^{II} species is reported. Incorporation of nitrogen base into these Schiff bases results in the pentadentate ligands smdpt (**6**) and amdpt (**7**), which has enhanced concentration of oxygen binding Co^{II} species.

Co^{II} Schiff base complexes have also been immobilized

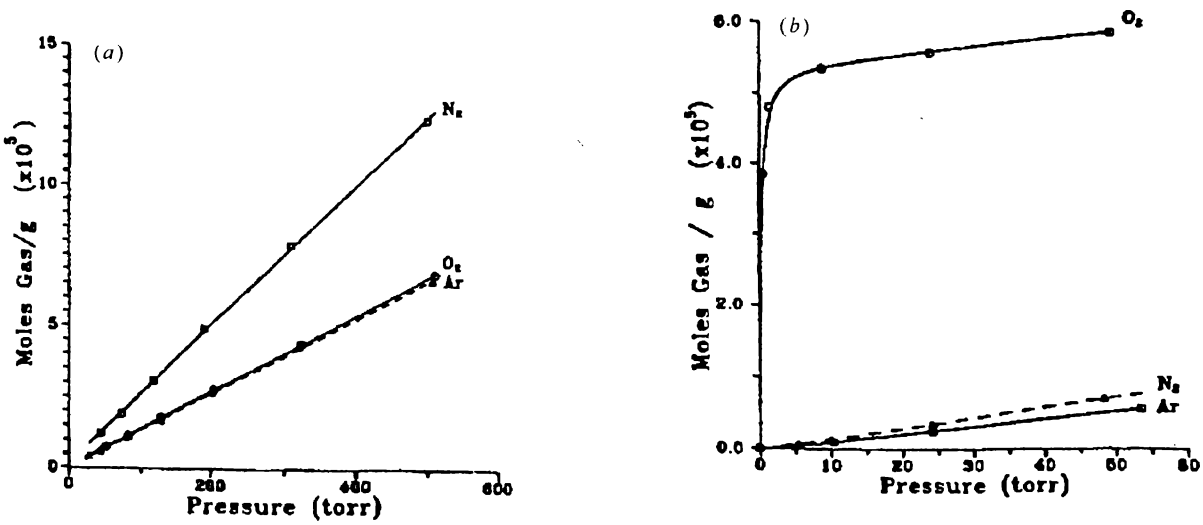


Fig. 9. Adsorption isotherm of N_2, O_2, Ar for (a) zeolite NaY and (b) CsClCo(CN)-Y, at 298 K.

in porous organic hosts[69] and have been found to bind oxygen at room temperature. Beside the above stated Schiff base ligands there are other ligands also like porphyrin and phthalocyanin which may have potential for oxygen adsorption with Fe^{II} and Mn^{II}; however, no adsorption study has been done using these ligands in micro/mesoporous solids like zeolites and silica. The following three basic techniques used for encapsulating metal complexes inside microporous solids cavities are explained in details in the literature[70,71]. (a) Flexible ligand method : reacting the performed ligand with the metal cations previously introduced into the zeolite cages. (b) Ship-in-the-bottle technique : assembling the ligand from smaller species inside the zeolite cavities. (c) Zeolite synthesis method : synthesis of the zeolite structure around the performed transition metal complex.

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