Review

Application of natural zeolites in the purification and separation of gases

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Abstract

There are many natural zeolites of which a small number including clinoptilolite, chabazite, mordenite, erionite, ferrierite and phillipsite offer the greatest promise for gas separation. Patents and other literature have been surveyed to identify the bulk separation and purification processes for which these zeolites have potential. The abundance and low raw material cost of natural zeolites have rarely offset such disadvantages as variable composition, low purity and often poorer separation performance compared to the more-favored synthetic zeolites. The results of the present study indicate that these natural zeolites are particularly well suited for trace-gas removal. In contrast, they are less likely to provide competitive performance in bulk separations. Clinoptilolite and chabazite are judged the most versatile, while also offering unique adsorption characteristics. Effective and efficient methods for screening all types of adsorbents are presented for various gas separations. Natural zeolites must demonstrate unique or superior performance to be serious contenders in commercial separations. Use of these methods should enhance such opportunities. The importance of including relevant process considerations in the analyses is demonstrated through application to processes for a bulk separation (O_2 production from air) and purification (removal of trace levels of N_2O from air). The results are not encouraging for the use of natural zeolites in air separation. Conversely, clinoptilolite and chabazite outperform commercially available synthetics in N_2O removal from air.
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Keywords: Gas separation; Clinoptilolite; Chabazite; PSA; Natural zeolite

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1. Introduction

Zeolites, because of their inherent ability to adsorb polar compounds, have long been considered as excellent candidate materials for separation and purification of gases. Moreover, certain zeolites are known to occur abundantly in nature. These attributes notwithstanding, the use of natural zeolites has been small in comparison to that of synthetic zeolites and other adsorbents in commercial gas separations utilizing adsorption. The object of this review is to explore why natural zeolites have not found a more prominent role in gas separations and to suggest strategies and methodologies that might lead to the increased use of natural zeolites.

Adsorption processes became commercially significant in the mid-1960s and the 1970s for H_2 purification, O_2 production, air purification and drying of various process streams. Historically, natural zeolites have been suggested for drying, acid gas removal, natural gas purification and air separation. The first International Conference on the Occurrence, Properties and Utilization of Natural Zeolites, held in Tucson, Arizona in 1976, contained numerous papers on the application of natural zeolites to gas separations [1]. By contrast, only a few such application studies appeared in the subsequent International Conferences on Natural Zeolites (1985, 1991, 1993, 1997) and the International Symposium in Sophia, Bulgaria, 1995. In seeking to understand this situation, the gas separation application-oriented technical literature has been surveyed (emphasis given to the last 30 years).

Although natural zeolites are abundant and inexpensive, these attributes may not offset the effects of impurities and inconsistency of properties relative to the more uniform synthetic zeolites. The effects of these advantages and disadvantages upon the application of natural zeolites in gas separations are explored in this study. Modification of the adsorptive properties of natural zeolites by ion-exchange, thermal treatment and structural changes to improve separation potential is also discussed.

The routine characterization of the adsorption properties of natural zeolites is often insufficient for judging effectiveness in a gas separation. Typically adsorbents have been suggested and ranked for particular separations on the basis of isotherms or

Henry's law constants alone. Not only are the characteristics of the adsorbent important, but the process conditions and dynamics are also critical to the separation performance and economics. Simple methods utilizing working capacity and selectivity are presented for comparing and selecting adsorbents for various types of gas separations. Finally, the application of these methods is demonstrated through the commercial industrial processes of bulk separation of air to produce oxygen and purification of air to remove nitrous oxide.

2. Commercial gas separations by adsorption: an overview

Adsorption may provide an advantage over costly, energy-intensive alternative separation processes such as distillation, absorption or other methods, particularly at low to moderate throughput. The economic viability of adsorptive processes is largely due to the versatility of zeolites. Important industrial gas separations are summarized below [2].

2.1. Air separation

Oxygen can be enriched from air to a purity of 90–95% by pressure swing adsorption (PSA). This mature technology is economical for plants producing up to 250 t/d O_2 using advanced synthetic zeolites such as LiX (Si/Al = 1.0).

2.2. Natural gas upgrading

Energy resources such as natural gas, coal gas, landfill gas (CH_4, C_2H_6, C_2H_4, etc.) are typically found diluted with N_2 and/or CO_2. Adsorption can often be applied to upgrade these low-calorific fuels through bulk separation to remove N_2, CO_2, and H_2O and through purification to eliminate undesirable trace contaminants such as H_2S, mercaptans, etc.

2.3. Hydrocarbon separation

Hydrocarbons from refinery, petrochemical and organic synthesis processes often require separation, e.g. olefins from paraffins, n-paraffins from iso-paraffins, cyclic paraffins from aromatics. Several adsorptive processes have been commercialized for such applications (UOP's SORBEX and PAREX and BOC's Petrofin processes), and there is a continuing need to develop new processes for hydrocarbon separations [3,4].

2.4. Oxygen/argon purification

Oxygen obtained from cryogenic distillation or PSA may contain up to 5% Ar impurity. Subsequent purification in a distillation column side arm is difficult due to the close boiling points of these two liquids. Adsorptive methods for enriching both oxygen and argon products are known but are usually not competitive with alternative technologies.

2.5. Pre-purification of air

Atmospheric air supplied to a cryogenic air separation unit (ASU) contains up to 3 vol% moisture, 400 ppm CO_2 and traces of hydrocarbons, NO_x, SO_x, etc. These contaminants must be removed to avoid the fouling of heat exchangers and distillation column components and for safety reasons. Thermal swing adsorption (TSA) and PSA processes utilizing zeolites are common in this application.

2.6. Flue gas/exhaust gas cleanup

Stack gases from fossil-fuel power plants and fuel–gas combustion processes contain substantial amounts of atmospheric pollutants such as CO_2, SO_x, NO_x, H_2S, NH_3, etc. Such contaminants can be removed and/or recovered by adsorption.

2.7. Hydrogen and rare gas purification

Hydrogen obtained from steam reforming or from petrochemical streams contains several of the following impurities: CO_2, CO, N_2, CH_4, C_2–C_8 hydrocarbons, H_2O and H_2S. Bulk separation and purification are combined to recover high purity H_2 and/or CO_2. Similar adsorption processes may be used to purify and recover helium or other rare gases.

3. Gas separations using natural zeolites: a survey

Synthetic zeolites have served a prominent role in shaping the development of adsorptive process technologies for many of the separations discussed above. While frequently suggested for a variety of gas separations, natural zeolites are seldom used in commercial adsorption processes. Nevertheless, adsorption characteristics of natural zeolites have been studied broadly from which a significant body of literature has emerged. Two excellent reviews, covering both the properties and the applications of natural zeolites, have been provided by Sand and Mumpton [1] and by Tsitsishvili et al. [5].

Considering both properties and availability, six natural zeolites (clinoptilolite (CLI), chabazite (CHA), mordenite (MOR), erionite (ERI), ferrie-rite (FER) and phillipsite (PHI)) appear to have the greatest potential for industrial gas separations [5–7]. The patent and application-oriented literature was surveyed to identify gas separations that used any of these six adsorbents. Literature from any era was considered if it was directed at a particular separation. Literature containing only adsorption data was also included if a gas separation could be inferred, i.e. by the present authors. In this latter regard, preference was given to the most recent literature. Of course, anyone interested in a particular separation is wise to consult the entire body of literature covering the adsorption characteristics of any pertinent gas component and the natural zeolite of interest. A good starting point is the text by Barrer [8].

Patents claiming natural zeolites as primary adsorbents for a particular gas separation application have been compiled in Table 1. As a group, patents provide some indication of the technical, economic and commercial viability of a separation. The number of patents is relatively few compared to the academic interest generated by these adsorbents. Open literature (non-patent) oriented to gas separations using the six natural zeolites cited above have been compiled in Table 2. The literature references usually contain more details of fundamental adsorption characteristics and less information regarding process feasibility than patents. Clinoptilolite appears to be the most favored natural zeolite for gas separations, followed by chabazite

and mordenite. Erionite, ferrierite, and phillipsite project a much smaller application base for gas separations. Applications for natural zeolites are more prevalent in purification than in bulk separation. Synthetic zeolites having both large pores and large pore volume are well suited to equilibrium bulk separations. Natural zeolites having small pores and small pore volumes (including chabazite, having a high pore volume) display strong adsorption at low concentrations, resulting in high potential for purification applications. Small pore zeolites are also well suited for kinetic bulk separations of permanent gases.

Upgrading and purification of natural gas, coal gas and landfill gas are promising kinetic bulk separation applications for these natural zeolites. Clinoptilolite has a unique pore structure that allows smaller molecules such as CO_2 and N_2 to diffuse in quickly while hindering the diffusion of slightly larger molecules such as CH_4 [9–18]. The ability to engineer the pore size by ion-exchange extends the application potential of the adsorbent. Commercially available synthetic zeolites generally provide poor rate selectivity for separating permanent gases.

Reviewing Tables 1 and 2, it appears that natural zeolites have their greatest potential in gas purification. Purification of light gases such as air, natural gas, hydrogen, helium, etc. are of particular interest [19–25]. The unique pore structure and chemical composition of the small pore natural zeolites such as clinoptilolite and chabazite are well suited for the removal of contaminant molecules—especially at trace concentrations. The good thermal stability and acid resistance of clinoptilolite and mordenite are attractive in flue gas cleanup applications [5,26–30].

4. Modifying natural zeolites to improve separation capability

The adsorption characteristics of any zeolite are dependent upon the detailed chemical/structural makeup of the adsorbent. The Si/Al ratio and the cation type, number and location are particularly influential in adsorption. The thermal treatment and the resulting level of dehydration may also

Table 1
Survey of patents related to the use of natural zeolites in gas separations

	Application	Gas 1 (less adsorbing)	gas 2 (more adsorbing)	Materials	Ref #	Patent
(A) Bulk separation						
1	Air separation	O_2	N_2	Li-CHA	[62]	US 4,925,460
				Li,Sr,Ni-CHA, Ca,Ni-ERI	[68]	GB 1,443,197
				ERI, CHA (ion-exchanged)	[80]	JPA 49-70,877
2	Natural gas upgrading	CH_4, C_2's, etc.	N_2	CLI	[81]	JPA 61-255,994
				Ca^{2+}-CLI	[82]	JPA 62-132,542
				Mg^{2+}-CLI	[18]	EPA 90312177.0
				Na-CLI	[17,83]	US 5,993,516 and GB 2,296,712 A
		CH_4	CO_2	Na-CLI	[84]	US 5,938,819
				Na-CLI	[23]	US 4,935,580
(B) Purification						
3	Ar/O_2 enrichment	Ar	O_2	CLI	[85]	EPA 84850131.8
		O_2	Ar	Ag-MOR	[86]	US 5,226,933
4	Air pre-purification	Air (N_2, O_2)	CO_2	Ca-CLI	[19]	US 5,587,003
			N_2O	CLI	[20]	Patent pending
5	H_2 and rare gas purification	H_2, He, Ne, Kr, Xe	H_2O, CO, CO_2, CH_4	MOR	[87]	US 4,425,143
		H_2, He, Ne, Kr, Xe	N_2, CH_4	Li-CHA	[62]	US 4,925,460
		H_2, He, Ne, Kr, Xe	N_2, CO, CH_4, O_2	CHA	[21]	US 4,732,584
		H_2, He, Ne, Kr, Xe	N_2, CO, CH_4, O_2	Ca,Sr-CHA	[22]	US 4,943,304
		H_2, He, Ne, Kr, Xe	N_2, O_2, Ar, Kr	Ca,Na-CHA	[88]	US 4,713,362
6	Natural gas purification	CH_4, C_2's, C_3's	CO_2	Na-CLI	[23]	US 4,935,580
		CH_4, C_2's, C_3's	NH_3	Li,Na-CLI	[33]	US 5,019,667
		CH_4, C_2's, C_3's	NH_3	Na-CLI	[34]	US 5,116,793
7	Hydrocarbon desulfurization	C_6–C_{10}	H_2S	Ba-CLI	[16]	US 5,164,076
8	Exhaust gas cleanup	Auto exhaust	C_2H_4, etc.	Ag-FER	[51]	US 6,309,616
		Exhaust gas	SO_x, NO_x	NH_4-CLI	[39]	US 4,059,543
		Exhaust gas	NO_x	CLI, MOR (acid-treated)	[40]	US 4,367,204

affect the final properties of the adsorbent. Many of these factors have been extensively studied for synthetic zeolites. Indeed, the breadth of applications presented above is partly due to the ability to tailor zeolites through structural and chemical modifications to affect the desired gas separation. This flexibility is derived primarily from modifying the Si/Al ratio and from exchanging cations.

The Si/Al ratio of synthetic zeolites is determined by the synthesis chemistry. The Si/Al ratio of natural zeolites (see Table 3) cannot be modified except by acid treatment to dealuminate the structure. Different deposits of the same natural zeolite may have different Si/Al ratios, created according to nature's chemistry. The same Si/Al ratio does not dictate a unique set of cation locations as cation location can be affected by the Al ordering or distribution, thus resulting in different adsorption characteristics [31]. As a group, the natural zeolites in Table 3 have a higher Si/Al ratio

Table 2
Survey of open literature related to the use of natural zeolites in gas separations

	Application	Gas 1 (less adsorbing)	Gas 2 (more adsorbing)	Materials	Ref #
(A) Bulk separation					
1	Air separation	O_2	N_2	K,Ca-CLI	[11]
				Ag-MOR	[67]
				K,Mg,Ba-CLI	[9]
				CLI, CHA, MOR	[65]
				K-CLI, CHA, ERI, MOR	[69–71]
				MOR	[64]
				CLI, MOR, CHA	[5]
				Li-CHA	[63]
2	Natural gas upgrading	CH_4, C_2's, etc.	N_2	CLI, Na,Ca-CLI	[12,13,15]
				K,Ca-CLI	[11]
				Ca,Mg-CLI	[9]
				Ca,K-CLI	[10]
		CH_4	CO_2	K,Na,Ca-CLI	[11]
				CLI, MOR, ERI	[14]
3	Refinery gas separation	Iso-paraffin	*n*-Paraffin	CHA	[89,90]
		Cyclohexane, benzene	*n*-Hexane	ERI	[91]
(B) Purification					
4	Ar/O_2 enrichment	Ar	O_2	CLI	[67]
				Ca-CHA	[92]
		O_2	Ar	Ag-MOR	[67]
5	Air pre-purification	Air (N_2, O_2)	CO_2	CHA	[93]
			CO_2, C_1–C_2's	Na,K-CLI, CHA	[24,94]
			CO_2, CO, NO	CLI	[25]
			CO	H-MOR	[95]
				CLI	[41,96,97]
			CH_4	H,Mg,K-CLI	[12,13]
			H_2S, SO_2	CLI	[26]
6	Gas drying	Air, hydrocarbons, H_2, etc.	H_2O	Na,K-CLI, CHA	[24,94]
				CHA, PHI, CLI	[98,99]
				Ca,K-CLI	[100]
				CHA	[29]
				CLI, MOR	[5,69]
				K,H,NH$_4$-CLI	[101]
7	H_2, N_2, and rare gas purification	H_2, He, Ne, Kr, Xe	N_2, CO, O_2, Ar, CH_4	Ca-CHA	[88,92]
		H_2	HCl, CO_2, H_2S	CHA	[29]
		N_2	Kr	H-MOR	[102,103]
		N_2	Ar	Ag-MOR	[67]
8	Natural gas, coal gas, biogas, etc. purification	CH_4, C_2's, C_3's	H_2S, SO_2	CLI	[26]
			SO_x	CLI, MOR, CHA	[5]
			NH_3	PHI	[5]
			NH_3	PHI, MOR, CHA, CLI, FER	[7]
			NH_3	CLI	[104]
			CO	H-MOR	[95]

Table 2 (*continued*)

	Application	Gas 1 (less adsorbing)	Gas 2 (more adsorbing)	Materials	Ref #
9	Flue gas cleanup	Flue gas	SO_2	CLI	[27,105]
				MOR	[28]
			SO_2, H_2S	CLI	[26]
			SO_x, NO_x	CHA	[29]
				CLI, MOR	[5]
			CO_2, NO_x, SO_2	MOR, Na,H-MOR	[30]
			SO_2, CO_2	H-MOR	[106]

Table 3
Summary of key structural properties of selected natural zeolites

Natural zeolite	Si/Al [5]	Major cations [5,36,107]	Channel geometry [108] (no. ring), nm {dim.}	Kinetic pore diameter[a] [7,109], nm	Max. H_2O capacity [37], kg/kg	Total pore volume[b] [107], %
Chabazite	1.5–4.0	Na, Ca, K	(8) 0.38×0.38 {3D}	0.43	0.28	48
Clinoptilolite	4.0–5.2	Na, Ca, K	(8) 0.26×0.47 (10) 0.3×0.76 (8) 0.33×0.46 {2D}	0.35	0.14	34
Erionite	3.0–4.0	Na, K, Ca	(8) 0.36×0.51 {2D}	0.43	0.20	36
Ferrierite	4.3–6.2	K, Mg, Na	(10) 0.42×0.54 (8) 0.35×0.48 {2D}	0.39	0.12	24
Mordenite	4.4–5.5	Ca, Na	(12) 0.65×0.70 (8) 0.26×0.57 (8) 0.48×0.34 {2D}	0.39	0.15	26
Phillipsite	1.3–3.4	K, Na, Ca	(8) 0.38×0.38 (8) 0.30×0.43 (8) 0.32×0.33 {3D}	0.26	0.22	30

[a] Based upon the minimum kinetic diameter of adsorbate molecules.
[b] [$cm^3 H_2O$/cm^3 crystal]×100.

than that of the Types A and X commercial zeolites. Table 3 also contains a summary of important structural properties of the six natural zeolites of interest.

The adsorption characteristics of zeolites are strongly dependent upon their cation composition. Both the equilibrium and kinetic adsorption properties can be altered by ion-exchange. Some researchers advocate ion-exchanging natural zeolites to manipulate these properties and/or to in-sure consistent chemical composition [32–35]. The effective pore opening in ion-exchanged forms of clinoptilolite is not inversely proportional to the cation radius as expected for some other zeolites, e.g. the pore openings of exchanged clinoptilolites increase in the following order according to Chao and Rastelli [34]: Ca < Na < Li < Mg < Zn < K < Sr < Ba. Pore size is not a simple matter of pore blocking [12,13,35]. Cation type, location and number can completely alter adsorption behavior

as evidenced by the reversal of the equilibrium selectivity of CH_4/N_2 in Mg^{2+} and Ca^{2+} exchanged clinoptilolites [13].

Acid washing of small pore natural zeolites may remove impurities that block the pores, progressively eliminate cations and finally dealuminate the structure as the strength and duration of the treatment increases [27,36–38]. In clinoptilolite, acid treatment can increase both porosity and adsorption capacity, improve adsorption of acid gases and extend adsorbent life [5,39,40]. Alkali washing has been shown to modify both the pore size and pore volume of clinoptilolite [41]. Treatment with neutral compounds, such as copper to weaken strong acidic sites, was suggested to reduce irreversible adsorption [42].

The method and extent of dehydration is important in determining the adsorption properties and structural stability of activated zeolites [23,33, 43,44]. Dehydration and thermal treatment can result in cation migration, thereby influencing cation location and pore openings. Both equilibrium and kinetic adsorption properties may be effected. O'Connor et al. [10] have suggested the creation of a "hydration-controlled nano-valve" in clinoptilolite using a systematic dehydration procedure to force the cations to migrate to pre-determined locations. The specially dehydrated zeolite has improved kinetic selectivity for the separation of N_2 from CH_4. Arcoya et al. [9] have correlated chromatographic O_2/N_2 separation efficiency of clinoptilolite with activation temperature.

"Pore engineering" is a popular term given to methods of modifying zeolites to manipulate the kinetic separation properties of the adsorbent. However, these methods may alter the equilibrium adsorption characteristics as well. Such tailoring can be qualitatively appreciated from the channel geometry, kinetic pore opening and total (H_2O accessible) pore volume summarized in Table 3. Structural differences resulting from Si/Al ratio or from the method of dehydration and cation exchange can be utilized to exclude molecules from the zeolite framework, hinder diffusion, alter pore volume and change the adsorbate equilibrium capacity. The cation type, size, charge density, location and the extent to which it is exposed to the adsorbate molecules have a strong effect

upon both adsorption capacity and selectivity [45,46]. Clearly, modifications and the resulting induced structural/chemical changes greatly extend the gas separation potential of natural zeolites.

5. Advantages and disadvantages of natural zeolites

Quality is important in the manufacture of synthetic zeolites and good product consistency is realistically attainable with modern production technology. Such reproducibility is important to attaining acceptable and sustainable levels of performance in gas separations. Natural zeolites, however, are inherently variable in chemical composition and purity. Natural zeolites obtained from the different areas of the same mine can also vary in chemical composition. A poor mineral deposit may have as low as 15–20% zeolite content while a high purity deposit can have 90–95% zeolite content [7,38,47,48]. Impurities such as soluble silicates can inhibit aggregation of natural zeolites and removing such impurities can be economically prohibitive [33]. The matrix in which the zeolite is bound may be so dense that it impedes diffusion into the zeolite granule. Chabazite (AW500 supplied by UOP) is an example of combining fine particle natural zeolite with a binder to achieve a more consistent macropore geometry. Finally, the potential human health risk from the inhalation of fibrous erionite and mordenite may discourage their use as adsorbents [49,50].

Natural zeolites, especially some included in Table 3, generally have greater thermal stability and better resistance to acid environments than many common commercial synthetic adsorbents [16,37,51]. Thermal stability tends to be higher for higher Si/Al and for those zeolites containing alkali cations, e.g. high silica Na,K-PHI is stable at 725 K, while low silica Ca-PHI degrades at temperatures as low as 575 K [5,45]. More importantly, the small pore natural zeolites of Table 3 can only adsorb gases and vapors having a kinetic diameter of less than about 0.5 nm. Coupled with the ability to adsorb more strongly at low gas partial pressures, this small pore characteristic provides unique separation potential (kinetic,

equilibrium and steric) only partially fulfilled in Type A and other commercially available synthetic zeolites.

The low cost of natural zeolites is often cited as a major incentive for their use. Although the raw material cost is "low," the adsorbent is shipped to a processing site where it must be at least calcined, sized and packaged prior to use in any gas separation application. The useable adsorbent yield from the mined material may be only 50–75% due to water evaporation and over/under-sized waste. The incremental costs of this minimal processing of clinoptilolite, in quantities greater than 10 000 kg, has been normalized to the cost of a commercial zeolite 13X and illustrated in Fig. 1. The final cost of the natural zeolite adsorbent is 60% higher than 13X and more than 10 times higher than the original raw material cost. Although each application must be judged on its own merits, this example shows that the "low" cost of natural zeolites does not necessarily result in a lower adsorbent cost for a gas separation.

The use of natural zeolites is not likely to be determined by either the low cost of the raw mineral or its inconsistency in chemical composi-

tion, but rather by the fulfillment of a unique or superior ability to separate gases of interest.

6. Finding the best adsorbent for the desired separation

There are numerous different structural types of zeolites and molecular sieves. Considering all possible cation variations within each type of zeolite results in an unmanageable number of potential candidate adsorbents for any particular separation. Thus, efficient and effective methods for screening adsorbents are necessary. Conditions of the feed to be separated, the purity and value of the desired product, competing processes and other important constraints will vary widely across the many gas separations of interest. In air separation, the raw feed is free and product recovery may be secondary in adsorption processes. The price of the O_2 product, however, is dictated by a demand that is largely supplied by cryogenic distillation. In H_2 purification, the feed to the purifier has substantial value due to processing in the reformer and the shift reactor. The H_2 feed pressure is determined in the upstream processes and high product recovery in the purifier is critical. Such factors must be considered in the adsorbent selection process.

The size and electrostatic characteristics of the adsorbate molecules are important. For example, many zeolites with a pore opening $\geqslant 0.4$ nm will separate air simply due to the difference in the quadrupole moments of N_2 and O_2. Although isotherms confirm this fact, they are hardly necessary to conclude the applicability of almost any medium to low silica zeolite for such a separation [37]. The size, dipole and/or quadrupole moments and polarizability of molecules often point to the most appropriate mechanism for the separation in polar zeolites, i.e. equilibrium, kinetic or steric. Equilibrium and kinetic separations are based upon the differences in capacity and diffusion rates, respectively, while steric separation results from the exclusion of one or more of the gases in the mixture from the zeolite pores. Methods for evaluating adsorbent effectiveness for a given separation vary from the measurement of a few
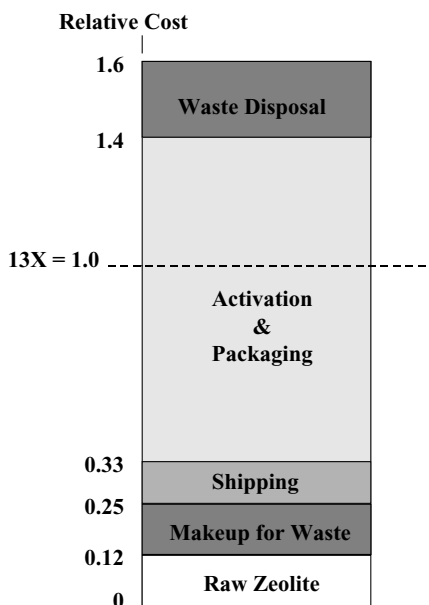

Fig. 1. Relative costs of processing a natural zeolite for use in gas separation.

isotherms to execution of detailed process models. Isotherms alone would confirm an adsorbent's ability to affect steric separations, but would not be sufficient to select the best adsorbent for either kinetic or equilibrium separations. Detailed process modelling requires accurate and extensive adsorbent characteristic input data. Obtaining such data for a large number of candidate adsorbents can be prohibitive. As a result, simple methods are required for ranking adsorbents for a particular separation by relating adsorbent characteristics to process performance.

The two most important characteristics of adsorbent effectiveness in a gas separation are the working or dynamic capacity and the working selectivity. The term "working" is used to indicate that the evaluation is to be performed at conditions representative of the actual process. The most common gas separation processes are TSA and PSA. Such cyclic processes may be applied in bulk separation or purification of gases or vapors. The working parameters are defined according to the type of separation, i.e. bulk equilibrium, bulk kinetic, TSA purification, etc. In the discussions below, a binary mixture of adsorbates A and B is considered. The concepts may be extended to additional components, although multicomponent separations can often be characterized as a series of binary separations. The definition of working capacity is given in Eq. (1) [52]:

$$\Delta X_A = X_A(y, P, T)_{ADS} - X_A(y, P, T)_{DES} \quad (1)$$

where $X_A(y, P, T)_{ADS}$ and $X_A(y, P, T)_{DES}$ are the equilibrium loadings of A (kmol/kg) corresponding to the gas phase mole fraction (y), total pressure (P) and temperature (T) at the end of the adsorption and desorption steps, respectively. The working capacity physically represents the net amount of adsorbate transacted on and off of the adsorbent for each complete cycle, providing a good indication of the amount of adsorbent required for the separation. An adiabatic separation factor, or working selectivity of component A relative to component B, has been defined in Eq. (2) as follows [52]:

$$\alpha = \frac{\Delta X_A}{\Delta X_B} = \frac{X_A(y, P, T)_{ADS} - X_A(y, P, T)_{DES}}{X_B(y, P, T)_{ADS} - X_B(y, P, T)_{DES}} \quad (2)$$

The adiabatic separation factor is simply the ratio of the component working capacities and represents the separation capability of the adsorbent at process conditions. This parameter is closely related to the product recovery in bulk separations, where a successful separation requires $\alpha > 1$. The loadings X_i defined in Eqs. (1) and (2) are determined by applying a multicomponent isotherm model to the pure component isotherm data and evaluating at the conditions in the adsorbent bed at the end of the adsorption and desorption steps of the process. Such multicomponent isotherm models are described by Yang [3]. The temperature of the adsorbent at the end of the adsorption step, T_{ADS}, may be chosen arbitrarily or in relation to the feed temperature. T_{DES} is defined using Eqs. (3) and (4):

$$T_{DES} = T_{ADS} - \Delta T \quad (3)$$

$$\Delta T \approx \frac{-\Delta X_A \Delta H_A}{C_{ps}} \quad (4)$$

where ΔT represents the difference in temperature of the adsorbent between the adsorption and desorption steps, ΔH is the heat of adsorption of the most strongly adsorbed component and C_{ps} is the specific heat of the adsorbent. An iterative calculation is required, starting with a guess for ΔT and followed by the calculation of T_{DES} and ΔX_A using Eqs. (3) and (1). A corrected ΔT is then calculated from Eq. (4). The procedure is repeated with the new value of ΔT until the difference in ΔX_A from the last two calculations is negligible.

Adsorbents may be simply screened by this method for their potential in separating bulk components in a PSA process. The optimum adsorbent may be one for which the product of working capacity and selectivity is maximized. These techniques may be applied regardless of whether the heavy (most strongly adsorbed) adsorbate is the major [52] or the minor component [53] in the mixture. Alternative methods have also been suggested [54].

Eqs. (1) and (2) apply directly to PSA equilibrium bulk separations. Mass transfer resistance can significantly influence an equilibrium separation. It is important to supplement the equilibrium-based

evaluations above with adsorption rate characteristics, i.e. such as determined from breakthrough tests representative of at least the adsorption step in the process [3]. Additionally, activated diffusion may impose a kinetic selectivity on the process. While it is common to characterize kinetic selectivity as a ratio of diffusivities or a ratio of diffusion coefficients determined from fractional uptake measurements, the variation of the ratio of molar uptake rates with time provides the most direct measure of the kinetic separation potential [35].

Purification must be treated differently from bulk separation, although Eqs. (1) and (2) may still apply in a modified form. Purification and bulk separation have often been distinguished by the concentration of the contaminant to be removed from the mixture. An upper limit concentration of 3.0–5.0 vol% for the contaminant is selected for the purpose of the discussion below. This definition is arbitrary, however, and it should be recognized that completely different adsorbent properties might be required for purifying a feed stream containing parts-per-billion (ppb) level contamination than a feed stream containing 3.0 vol% of the same adsorbate. The kinetic separation mechanism may apply to purification processes, although it becomes less favorable as the ratio of concentration of the major to minor gas components in the feed increases. The discussion below concerning purification is limited to those cases dominated by equilibrium separation.

TSA processes with relatively large bed depth and long cycle times are common, e.g. pre-purification of air prior to cryogenic separation. When the thermal regeneration results in complete desorption of the components, Eq. (2) may be simplified:

$$\alpha = \frac{\Delta X_A}{\Delta X_B} = \frac{X_A(y, P, T)_{\text{ADS}}}{X_B(y, P, T)_{\text{ADS}}} \tag{5}$$

(α = separation factor).

When the major component in the feed is not substantially adsorbed, the minor component equilibrium loading is a direct indicator of working capacity, i.e. provided the mass transfer resistance is negligible. Examples include PSA or TSA processes with weakly adsorbed major components like He or H_2, or in steric separations. In

such cases the denominator of Eq. (5) approaches zero and selectivity should be viewed with caution. For very low impurity concentrations, the Henry's law constant becomes the dominant factor in ranking adsorbents.

When a contaminant is removed in a shallow adsorbent layer in TSA and significant resistance to mass transfer exists, the selectivity is redefined according to Eq. (6):

$$\alpha = \frac{\Delta X_A}{\Delta X_B} = \frac{\frac{m_{\text{in}}}{w_s} \int_0^{t_b} (y_{\text{in}} - y_{\text{out}})\, dt}{X_B(y, P, T)_{\text{ADS}}} \tag{6}$$

The numerator in Eq. (6) represents the working capacity of the adsorbent for the contaminant. m_{in} represents the molar feed flow into the bed, y_{in} and y_{out} are the inlet and outlet mole fractions of the minor component, respectively, w_s is the mass of adsorbent and t_b is the breakthrough time corresponding to a predetermined concentration. The denominator is the equilibrium capacity of the major component at the conditions at the end of the adsorption step, i.e. assuming complete desorption of all components. This situation may result when using small pore zeolites at conditions where the depth of the adsorbent layer is shorter than the mass transfer zone length.

When the bulk component is adsorbed to a significant degree, Eqs. (5) and (6) may yield $\alpha \ll 1$. Such low values of α do not necessarily indicate poor separation, only that the working capacity of the trace component is quite low compared to that of the bulk component. The higher value of α is usually an indication of the best adsorbent, provided that working capacity is sufficient for the purification using a reasonable size of adsorber.

In the case of PSA purification with relatively short cycles and significant residual loading at the end of desorption, i.e. incomplete desorption, there are no simple means to evaluate candidate adsorbents. In this case the local working capacities are quite low and can be predicted from Eq. (1) only if the local conditions in the bed are accurately known. The best method for evaluation of adsorbents in this case is by process modelling.

Adsorbent/adsorbate characteristic data are required in applying the methods described above.

Pure component isotherms must be measured for at least two temperatures, preferably four temperatures. Special attention must be given to low pressure data when purification of low concentration components is of interest. The pure component isotherm data are then used in a multicomponent model such as the loading ratio correlation [3]. Kinetic effects are determined either through uptake and/or breakthrough experiments. Porosimetry measurements to determine particle density, pore size distribution and intraparticle void fraction are also useful. Minimal data according to each of the evaluation methods described above are required to rank and select adsorbents for a particular separation. These simple techniques offer greater incentive for including natural zeolites in gas separation studies. Application of these methods is demonstrated below.

7. Gas separation case studies

The production of O_2 from air and the removal of nitrous oxide (N_2O) from air prior to cryogenic air separation are used to demonstrate the importance of combining process conditions with adsorbent characteristics as an integral part of selecting the most appropriate adsorbent for the gas separation of interest.

7.1. O_2 production

From medical oxygen concentrators to steel production, the separation of air by PSA for O_2 (90–95% purity) production represents a very important commercial application of adsorptive gas separation [55]. The process has been one of the most widely studied bulk separations as evidenced by the number of patents and publications beginning with the work of Skarstrom [56] and continuing today with contributions from many others. The years of searching for better N_2-selective adsorbents and improving the process offer many lessons. The larger quadrupole moment of N_2 relative to O_2 was recognized early as being responsible for the N_2-selective characteristic of many zeolites [57]. Adsorbent investigations by chemists/material scientists occurred concurrently with process studies by engineers. Curiously, these two groups did not communicate well for a long time. Selecting process conditions according to isotherm shape and the introduction of vacuum cycles grew out of process studies, but attention was seldom given to structure and chemistry details of the zeolite adsorbents. Material scientists showed the importance of exchange level, Si/Al ratio and methods of preparation of zeolites, but often failed to relate adsorbent characteristics to relevant process conditions. As a result, the use of 13X, 5A and Na-mordenite dominated commercial applications of PSA air separation for more than 25 years [58]. Gaffney [59], Kumar [60] and Coe [61] have given good reviews of the more recent developments in both adsorbents and processes for O_2 production.

Development of either adsorbents without a clear sense of the process requirements or processes without an understanding of adsorbent characteristics is unlikely to lead to an optimum separation. The cost of oxygen is the driving force in O_2 production [2]. Although O_2 recovery, power consumption, O_2 purity and adsorbent productivity are all important process performance parameters, the optimization of one or even two of these does not guarantee the lowest O_2 product cost. Similarly, maximizing the capacity or the selectivity of the adsorbent does not insure optimum process performance—particularly if these characteristics are determined in a manner that is not relevant to the process conditions of the separation.

While the literature is filled with studies of N_2-selective adsorbents aimed at air separation, the proportion of these studies involving natural zeolites is small. Furthermore, only a few of these investigations relate the adsorbent properties to conditions representative of practical air separation processes. Lithium-exchanged synthetic and natural chabazites (Li-CHA) have been investigated [62,63]. The working capacity and selectivity of Li-CHA exceeded that of CaA and CaX adsorbents, but selectivity was significantly lower than that of CaLSX (Si/Al = 1.0). These studies showed that a narrow range of Si/Al and at least 65% Li-exchange resulted in the most promising Li-CHA adsorbents. Mordenite, clinoptilolite and chabazite from various locations were compared

to commercial 3A, 4A and 5A adsorbents by measuring the breakthrough of N_2 using an air feed at 101.3 kPa [64]. Mordenite from Itado, Japan showed the highest O_2 generating capacity. Commercial PSA O_2 generators of various O_2 output capacities were constructed using natural zeolites. Clinoptilolite, mordenite, chabazite, erionite and ferrierite have all been investigated for O_2 enrichment potential [9,36,65–71].

Ranking the equilibrium adsorption potential of various adsorbents for air separation can be efficiently and effectively accomplished using Eqs. (1) and (2) above. The N_2 working capacity and the adiabatic separation factor are compared for NaX, CaA, LiX and clinoptilolite as a function of the adsorbent temperature (end of the adsorption step) in Figs. 2 and 3. This comparison is made at a process pressure ratio $P_r = P_{ADS}/P_{DES} = 5.0$, where P_{ADS} and P_{DES} are the pressures at the end of the adsorption and desorption steps, respectively. The higher working capacity of LiX for temperatures above 265 K is clearly evident in Fig. 2. The smaller micropore volume of clinoptilolite is reflected in its relatively lower N_2 working capacity. The working capacity is directly related to the
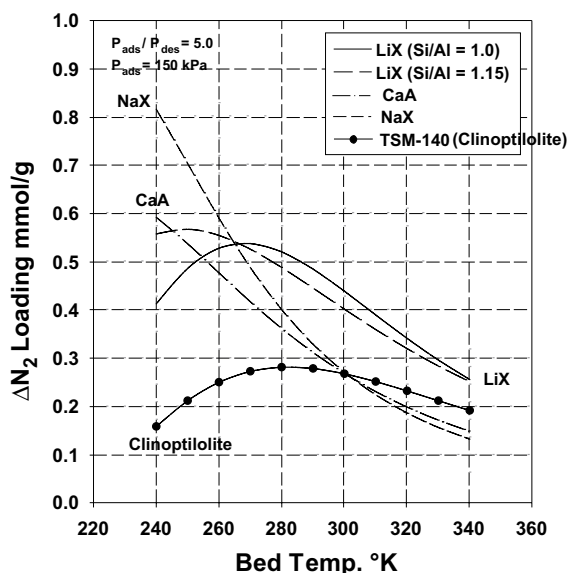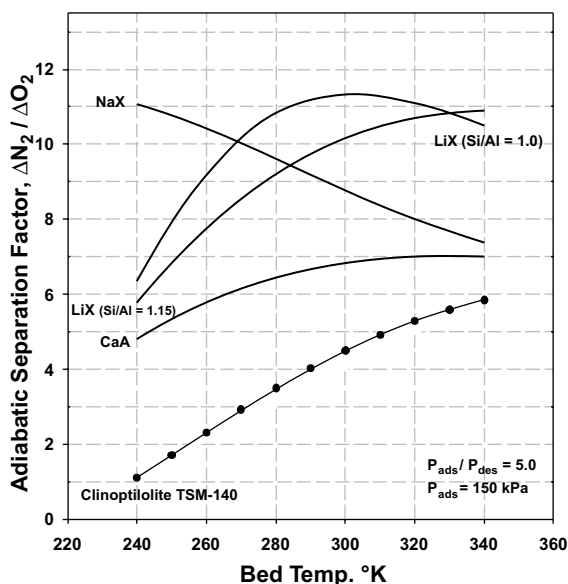

Fig. 3. Variation of adiabatic separation factor ($\Delta N_2/\Delta O_2$) with bed temperature.

amount of adsorbent required to produce a unit amount of product O_2 at the desired purity of 90%. The characteristics in Fig. 3 reveal not only the strong temperature dependence of the adiabatic separation factor for these adsorbents, but also the distinctly different selectivity behavior of NaX. Compared to LiX, the N_2/O_2 separation factor for clinoptilolite is not attractive. Similar results can be shown at other values of P_r [52].

A thorough evaluation of adsorption characteristics must include adsorption rate. The mass transfer resistance may vary greatly between adsorbents as shown in the comparison of breakthrough characteristics for 13X, LiX and clinoptilolite in Fig. 4. The results were obtained by introducing a continuous flow of air at 150 kPa into a column of adsorbent saturated with pure O_2 while measuring the O_2 content of the effluent as N_2 begins to breakthrough the bed. The test method has been described elsewhere [72]. Resistance in the macropores of the adsorbent particles is the rate controlling mechanism for adsorption in 13X and LiX. The pore diffusivity is similar in these two adsorbents, although LiX has a slightly sharper mass transfer front and a noticeably longer breakthrough time compared to 13X, i.e.

Fig. 2. Variation of adiabatic N_2 working capacity with bed temperature.
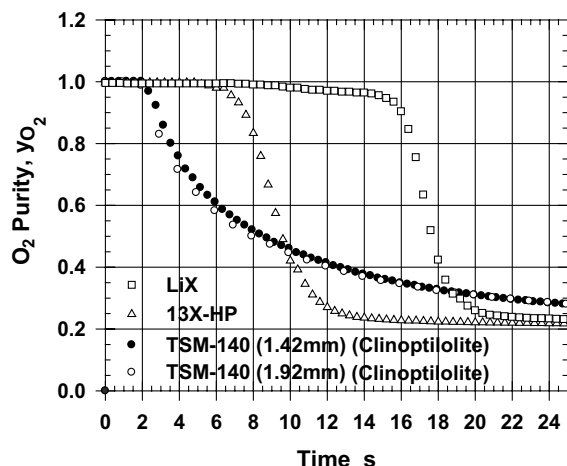
Fig. 4. Breakthrough characteristics for air separation.

the latter reflecting the higher working capacity of LiX. The contrasting behavior of clinoptilolite is largely due to its micropore resistance to mass transfer. This conclusion derives from the fact that the use of different average particle sizes of the same adsorbent had no impact upon the clinoptilolite breakthrough curve in Fig. 4. The slow kinetics arise out of the small micropore size of clinoptilolite, comparable to the size of the O_2 and N_2 molecules. This property of clinoptilolite represents a serious barrier to its use in air separation.

Both the adsorbents and processes for production of O_2 by PSA are well developed. Natural zeolites have not yet been competitive with the LiX adsorbent [73] used in commercial air separation. Chabazite, with its higher micropore volume, is the most likely natural zeolite to attain the high N_2 working capacities required in O_2 production. Li-CHA, although demonstrating some promise, suffers from unfavorable ion-exchange thermodynamics and the requirement of a narrow range of Si/Al ratios (perhaps requiring a synthetic analog) [63]. As a result, the production of O_2 from air does not appear to be a promising application for natural zeolites.

7.2. Removal of N_2O from air

Nitrous oxide (N_2O) is present in air at concentrations of 300–350 ppb and represents an increasing problem in the cryogenic separation of air [74]. The presence of N_2O is most troublesome in facilities designed primarily to supply gaseous O_2, as well as in those plants equipped to additionally recover the rare gases Kr and Xe. Although periodic liquid O_2 draining or the use of silica gel traps can limit the accumulation of N_2O, removing N_2O before it enters the cryogenic ASU is desirable. Cryogenic air separation plants are usually equipped with adsorbent pre-purifiers to remove H_2O, CO_2, C_2H_2 and other hydrocarbon contaminants from air. Pre-purifiers containing a zeolite (13X) adsorb some N_2O, but as much as 40% or more of this contaminant typically breaks through the adsorbent bed. Retrofitting of existing pre-purifiers to remove 90% or more N_2O is quite attractive relative to alternative means of N_2O control.

CO_2 is generally the first primary contaminant to breakthrough a TSA pre-purifier. As a result, the adsorber effectiveness can be monitored continuously by sensing the CO_2 concentration of the clean air effluent before it enters the ASU. Since N_2O breaks through the bed before CO_2 in conventional pre-purifiers, effective design for CO_2 does not guarantee the removal of N_2O to the desired efficiency. To reverse this effect, adsorbents selective for N_2O over CO_2 have been sought [75]. The highest selectivity, determined by the ratio of Henry's law constants, was found for CaX, Na mordenite and BaX. Other similar work [76,77] concluded that CaX and its mixed cation varieties or CaLSX were preferred for the removal of N_2O. These results suggest zeolites with high cation charge density and low Si/Al ratio for N_2O removal. The typical configuration is a three-layer adsorbent bed in which H_2O is removed in the first layer, CO_2 is removed in the second layer and the combination of CO_2 and N_2O are removed in the third layer.

A review of the electrostatic characteristics of N_2O and CO_2 suggest similar adsorptive strength for both gases in polar adsorbents. The higher quadrupole moment of CO_2 may be partially compensated by the presence of a weak dipole moment in N_2O. Both molecules would be adsorbed more strongly than N_2, which has a substantially weaker quadrupole moment and lower

polarizability. Both CO_2 and N_2O have a kinetic diameter of 0.33 nm. Adsorption studies of 5A adsorbent with CO_2 and N_2O [78] at relatively high concentrations (1800–24 000 ppm) suggest that CO_2 is the more strongly adsorbed molecule, although co-adsorption was significant. In view of these observations, it is doubtful that N_2O/CO_2 selectivity >1.0 can be achieved in low Si/Al ratio zeolites.

Since pre-purifiers are designed to remove CO_2 (present in air at about 400 ppm) to less than 0.1 ppm, the selection of an adsorbent for the removal of N_2O in a post-treatment layer can be viewed as N_2O competing with N_2 rather than CO_2. Although zeolites would be expected to selectively adsorb N_2O over N_2, such selectivity may be diminished by the large concentration advantage of N_2 (790 000 ppm) over N_2O (0.35 ppm) in the gas mixture. Thus, the problem becomes one of finding an appropriate adsorbent that has high $\Delta N_2O/\Delta N_2$ separation factor, high ΔN_2O capacity and low ΔN_2 loading.

Working capacity and working selectivity as defined in either Eq. (5) or (6) above can be applied for adsorbent screening. The co-adsorption effect of N_2O upon N_2 at these concentrations is negligible and the denominator of Eq. (5) or (6) may be obtained directly from the pure-component N_2 isotherm. Conversely, the co-adsorption of N_2 has a very significant effect upon the adsorption of N_2O and the working capacity for N_2O is best determined directly from a breakthrough test. Both the N_2O saturation and breakthrough capacities can be obtained from such a test.

Different types of adsorbents were selected for evaluation. Silicalite (HISIV 3000), 4A, NaY, NaKX, 13X APG-I (NaX, Si/Al = 1.25), 13X APG-II (NaX, Si/Al = 1.15), LiX (Si/Al = 1.15) and LiX (Si/Al = 1.0) were obtained from UOP (Des Plaines, IL). Barnebey-Sutcliffe (Columbus, OH) supplied the activated carbon (207C), Alcoa provided the composite CDX, CaX was provided by Zeochem (Louisville, KY) and Süd-Chemie (Meigs, GA) supplied Na-MFI-20. Na-mordenite and H-ZSM5 were obtained from Zeolyst (Valley Forge, PA). H-ZSM5 was exchanged to Na-ZSM5. ZSM-5 was included because of its reported N_2O removal effectiveness [79]. Clinoptilolite (TSM140

and CS400) and Chabazite were supplied by Steelhead Specialty Minerals (Spokane, WA).

Breakthrough tests were conducted using the following feed gas mixtures: 1.0 ppm N_2O in N_2 and 1.0 ppm N_2O in He. The N_2O feed concentration of 1.0 ppm is close to ambient levels and was selected as a compromise between the length of breakthrough tests and the usable concentration range of the N_2O analyzer. All of the breakthrough tests were performed at 600 kPa, 300 K and an inlet gas flow rate of approximately 0.08 kmol/(m² s) (21.3 slpm) using an adsorption column length of either 22.9 or 5.6 cm. These feed conditions are representative of air pre-purifiers for cryogenic ASU. Initial breakthrough was established at 50.0 ppb N_2O, from which an initial breakthrough loading (IBL) was determined as the average amount of N_2O adsorbed per unit adsorbent mass, i.e. from the numerator in Eq. (6). The results from these tests were used to determine N_2O separation factor and working capacity. Breakthroughs were continued to saturation, i.e. until the effluent N_2O concentration reached the feed concentration. Nitrogen isotherms, as shown in Fig. 5, were determined gravimetrically. The denominator in Eq. (6) was determined directly from these isotherm results.
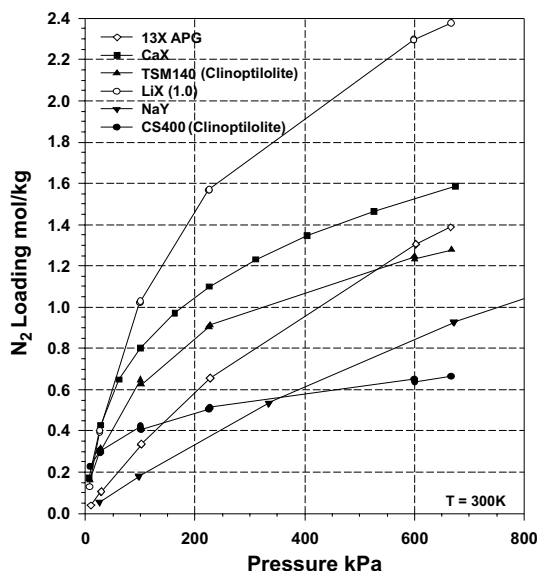

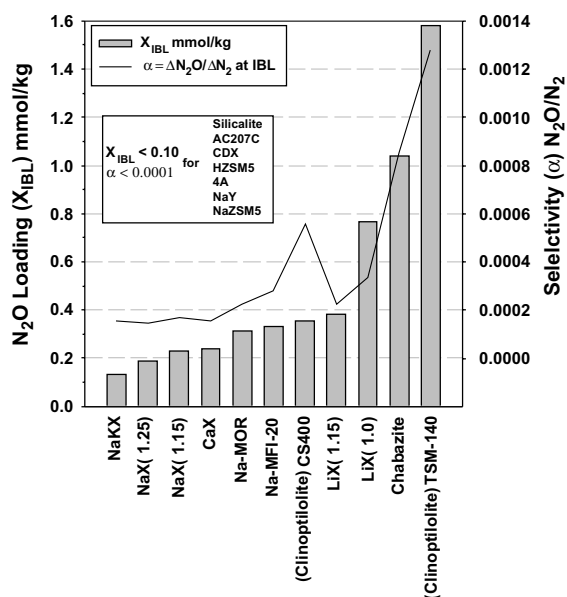Fig. 5. Nitrogen isotherms for synthetic and natural zeolites.

Fig. 6. Loading of N_2O and N_2O/N_2 selectivity at initial breakthrough for candidate adsorbents.

The effective N_2O working capacities determined as IBL are compared in Fig. 6. There is nearly a two-order of magnitude difference in the working capacities of these adsorbents. In comparing the saturation loading of N_2O for 1.0 ppm in He and N_2, respectively, the co-adsorption of N_2 was clearly important as the N_2O saturation capacity was reduced by more than a factor of 10 for some adsorbents. The separation factor (α) as determined from Eq. (6) is also shown in Fig. 6. These values were obtained by dividing the IBL (ΔX_A) by the pure-component N_2 capacity (ΔX_B) at the feed N_2 partial pressure ($P_{N_2} = 600$ kPa). Many of the adsorbents have similar working characteristics, but chabazite and clinoptilolite (TSM140) are clearly superior in both working capacity and selectivity. It is interesting that the present strategy of maximizing N_2O/N_2 selectivity results in adsorbents with a somewhat higher Si/Al ratio than resulted from previous approaches that emphasized high N_2O/CO_2 selectivity. Also note that Na-ZSM5 shows poor performance for this application, contrary to expectations derived from prior studies [79]. However, those studies were performed at higher temperatures and N_2O concen-

trations and in He compared to the present work where adsorbents were evaluated at near-process conditions. The adsorbent screening methods described above for N_2O removal resulted in a new commercial application for clinoptilolite [20].

The examples above demonstrate an effective means for screening adsorbents for both a bulk gas separation and purification. Working characteristics of the adsorbents are determined using relevant process conditions while factoring key process constraints into the analysis. A cross-section of adsorbent types, including natural zeolites, can be evaluated efficiently by these methods.

8. Concluding remarks

Natural zeolites need greater advantages than low initial cost and abundance if they are to compete with other adsorbents in gas separation processes, i.e. they must demonstrate superior performance in specific separations. The results of the present study suggest that clinoptilolite and chabazite possess unique adsorption properties which may be unmatched by synthetic zeolites for some gas separations. The greatest application potential appears to be in gas purification, particularly trace-gas removal.

Whether or not a natural zeolite is useful for a separation depends upon its adsorption characteristics for the gas components in the mixture and the particular conditions of the feed. In other words, the pursuit must be process or separation-centered, not adsorbent-centered. Adsorbent characteristics must be determined beyond simple isotherms and must be obtained at conditions relevant to practical processes. Much can be learned by comparing the differing behaviors of well-characterized synthetic zeolites with those of natural zeolites. Material scientists and process engineers working together are likely to be more productive than either working alone. Cost and performance are always factors. Finding the match between a natural zeolite and a gas separation is a difficult challenge. Meeting this challenge requires a change in the way gas separations have been approached by all of us working in the field of natural zeolites.

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