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Adsorption of N_2, O_2, and Ar in Potassium Chabazite

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Abstract. Chabazite with Si/Al of 2.4 ratio was synthesized and exchanged with cations viz. K^+, Li^+ and Ca^{2+}. N_2, O_2 and Ar adsorption isotherms were measured in the pressure range 0–1000 torr and temperatures viz. 0, 30 and 50°C. K-CHA showed better O_2/Ar selectivity than Ca-CHA although adsorption capacity was larger for Ca-CHA. Zero loading isosteric heat of adsorption values for K-CHA, were considerably lower than Ca-CHA which reflect diminished charge density of the K cation. The high O_2/Ar selectivity is possibly due to partial pore blockage as a result of the large potassium cation located near the 8-member ring leading to the 20-hedron cage. The O_2/Ar selectivity may be exploited to produce high purity oxygen (>99%) from a two stage PSA system employing K-CHA in the second stage.

Keywords: K-CHA, Li-CHA, Ca-CHA, adsorption

1. Introduction

Pressure swing adsorption processes are being increasingly used for separation of gases such as air as an alternative method to cryogenic distillation because of the large energetic costs involved in the latter. Adsorbents such as carbon molecular sieves (Yang, 1987), zeolites (Murakami et al., 1991) and titanosilicates (Kuznicki et al., 2001) are well known for selective separation of N_2 and O_2. Synthetic zeolites A, X, mordenite and natural/synthetic chabazite having alkali and alkaline earth metals as the extra framework cations are used for the separation based on the difference in the interactions of O_2 and N_2 molecules with zeolite cations. The effects of cations are more readily revealed when zeolites with identical structure but different cation size, charge and concentration are used in adsorption studies. Bezus et al. (1972) demonstrated that the gas adsorption and heat of adsorption on zeolites depend on the density and localization of the cations in zeolite lattice. Among the cations, Li^+ is known to significantly increase N_2 adsorption and LiX (>95% Li) is the best adsorbent known for O_2 production. Recently, Sebastian and Jasra (2003) demonstrated that AgA has high adsorption capacity, with N_2/O_2 selectivity in the range 5–14.6 and the material showed higher selectivity for Ar over oxygen.

Zeolite chabazite, is useful for separation of nitrogen from oxygen or argon streams. Polyvalent chabazite is especially found to be useful for removing trace nitrogen from argon, for purifying methane and for oxygen/argon separation in chromatographic applications. The adsorption of a variety of permanent gases and simple hydrocarbon gases has been examined on natural chabazite (Barrer et al., 1972; Garden et al., 1956; Barrer and Papadopoulos, 1972), Ca, Na form (Garden et al., 1956; Coe and Roberts, 1988; Maroulis et al., 1988; An and Joye, 1997), H-form (Barrer and Davies, 1970, 1971); mixed cation form (Ca, Mg, Na, Ni) (Maroulis et al., 1988), Li form (Coe et al., 1990) and Sr form (Coe et al., 1990b).

The chabazite structure consists of double 6-ring (D6R) building units arranged in layers in the sequence AABBCC and linked by tilted 4-rings. The framework contains large ellipsoidal cavities each approximately 6.7 × 10 Å. Each cavity can be accessed by 6 openings each of which consists of 8-rings of somewhat variable dimension depending on extent and type of ion

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exchange and adsorption. The Si/Al ratio and ordering in chabazite controls the charge-balancing cation quantity and siting which in turn controls the adsorption characteristics of the zeolite. There are three general types of cation sites in chabazite: SI at the center of the D6R, SII in the 6-ring projecting into the cavity, and SIII in the 8-ring window (either off-center or centered depending on cation radius) (Mortier et al., 1977). The distribution of cations on these sites depends on Si/Al ratio, cation type and exchange level, and extent of dehydration. Synthesis of chabazite with different Si/Al ratios is well known in the literature. Gaffney and Coe (1991) report synthesis of chabazite with Si/Al ratio in range 1.8 to 2.3 and demonstrate that Ca and Sr exchanged chabazites are better for separation of N_2 and Ar. In the present study, we have synthesized chabazite following the Gaffney and Coe (1991) procedure, and ion-exchanged to K^+, Li^+ and Ca^{2+} forms. The adsorption isotherms of nitrogen, oxygen and argon were measured and pure-component selectivity ratios and heats of adsorption were calculated.

2. Experimental

2.1. Materials

Materials used for synthesis were aluminum hydroxide (BDH), tetramethylammonium hydroxide pentahydrate (97% Aldrich), potassium hydroxide (85%, Ajax chemicals), sodium hydroxide (97%, Ajax chemicals), and silica sol (Ludox LS 30 wt% in water). Sodium chloride (99.8%, Proanalysis), potassium chloride (99.8%, Ajax chemicals), lithium chloride (99%, Ajax Chemicals) and calcium chloride dihydrate (98%, Ajax chemicals), lithium hydroxide (98%, Ajax chemicals) and deionized water were used for ion exchange. Nitrogen (99.99%), Oxygen (99.9 %) Helium (99.9%) and Argon (dried 99.9%) were all procured from the Linde gas company.

2.2. Synthesis of Chabazite

Chabazite was synthesized following the procedure reported by Gaffney and Coe (1991) with gel composition $0.16\,(TMA)_2O{:}6.67\,Na_2O{:}2.2\,K_2O{:}17.5\,SiO_2{:}Al_2O_3{:}276\,H_2O$. A typical procedure involved dissolution of aluminum hydroxide, sodium hydroxide, potassium hydroxide and tetra methyl ammonium hydroxide pentahydrate in deionized water. This solution was then added to silica sol (Ludox LS, 30 wt% in water, Aldrich) and the thick gel formed was stirred for 15 minutes. The gel was then transferred to a polypropylene bottle (125 ml, FEP, Nalgene) and heated in an oven for 4 days at 85°C. The polypropylene bottle was quenched with cold water, the product obtained (TMA-Chabazite or TMA-CHA) was filtered, washed with water, and dried in an oven at 100°C.

2.3. Cation Exchange

Cation exchange reactions of chabazite are well known and have been reported in previous studies (Torracca et al., 1998, Dyer and Zubair, 1998). In our study, TMA-CHA obtained as described above was first converted into its sodium form (Na-CHA) by three consecutive ion exchanges with 1 M NaCl. Typically, 300 ml 1 M NaCl at pH 9 (adjusted by addition of 0.01 M NaOH) was added to 5 g of zeolite, and the solution was heated to 90°C and stirred for 12 hours. The solution was decanted and fresh solution was added. This procedure was repeated three times. After the final exchange the solution was vacuum filtered and washed with copious amount of de-ionized water until the solution showed absence of chloride (i.e., no precipitation upon treatment with $AgNO_3$). The resulting sodium chabazite was dried at 100°C overnight. The potassium form of chabazite (K-CHA) was prepared from Na-CHA by three consecutive ion exchanges using 1 M KCl and using a similar procedure as that used for prepataion of Na-CHA.

The calcium form of chabazite (Ca-CHA) was prepared from Na-CHA by five consecutive ion exchanges of Na-CHA with 1 M $CaCl_2$ (5 g zeolite:300 ml $CaCl_2$). The solution was heated at 80°C for 12 hours, decanted and fresh solution was added. This procedure was repeated five times. Finally, the Ca-CHA formed was filtered off washed with copious amount of de-ionized water and dried at 100°C overnight.

Lithium chabazite was prepared from Na-CHA, by five consecutive ion exchanges of Na-CHA with 2M LiCl (3 g zeolite:100 ml LiCl) at pH 9 (adjusted by addition of 0.01 M LiOH) following the same procedure as used in Ca-CHA preparation.

3. Characterization and Adsorption Measurements

The degree of crystallinity and confirmation of the chabazite phase was determined by powdered X-ray diffraction patterns of the samples performed with a Rigaku, Geiger-flex diffractometer employing CuKα radiation ($\lambda = 1.542$). Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was used for determining the elemental composition. Helium density pycnometry (Micromeritics AccuPyc 1330) was used to determine sample skeletal volumes. Adsorption isotherms were measured using a purpose-built conventional static volumetric apparatus with a working pressure range of 0–1000 torr and temperature range 0–90°C. This unit had previously been validated against a commercial adsorption apparatus (Micromeritics ASAP 2010). All the samples were thoroughly dehydrated and degassed on a Micromeritics ASAP 2010 gas adsorption analyzer at 350°C under high vacuum for 18 hours prior to measurement. Adsorption data for N_2, O_2, and Ar were measured over the temperature range 0–90°C and the zero loading isosteric heats of adsorption determined by the Clausius-Clapeyron equation.

$$\Delta H^{\text{o}}_{\text{ad}} = R\{[\partial \ln p]/[\partial(1/T)]\}_{\theta}$$

Where R is the universal gas constant, θ is the fraction of the adsorbed sites at a pressure p and temperature T. A plot of ln$p$ against 1/T gives a straight line with slope of $\Delta H^{\text{o}}_{\text{ad}}/R$. Two MKS pressures transducers were used: 0–100 torr and 0–1000 torr. Good agreement was found between them and the 0–100 torr transducer was used to calculate zero loading heats of adsorption.

4. Results and Discussion

Three samples of chabazite, viz. K-CHA, Li-CHA and Ca-CHA were used in this study. X-ray data of as-synthesized sample (TMA-CHA) and exchanged samples showed the presence of pure chabazite phase and the diffraction pattern is in agreement with reported data (Gaffney and Coe, 1991). The results of elemental analysis are shown in Table 1.

Table 1. Results of elemental analysis for different cation forms of chabazite.

Sample name	Si/Al	Unit cell formula
K-CHA	2.4	$K_{8.3}Na_{2.3}[Al_{10.6}Si_{25.4}O_{72}]$
Li-CHA	2.1	$Li_{11.7}[Al_{11.7}Si_{24.3}O_{72}]$
Ca-CHA	2.1	$Ca_{5.8}[Al_{11.5}Si_{24.5}O_{72}]$

As evident from the data in Table 1, 100% exchange for K-CHA was not achieved. This is in agreement with the observation of Torracca et al. (1998) who obtained a maximum of 85% exchange of Na for K but not in agreement with Dyer and Zubair (1998) who obtained complete exchange. However, it should be noted that the work of Dyer and Zubair (1998) used Bowie chabazite (obtained from Bowie, Arizona), which is a silica-rich chabazite (Si/Al ∼ 4) compared to that of Torracca et al. (1998) who used an aluminum-rich chabazite (Si/Al∼1.5). There are four possible exchange sites: one in the D6R hexagonal prism, which must be entered through the 6-ring ("free" aperture 0.26 nm), and three in the ellipsoidal 20-hedron cage which can be accessed through the 8-membered rings ("free aperture" of 0.38 nm). The ionic diameter of the K^+ ion is 0.28 nm, which is comparable to the free diameter of the 6-ring window. However, it appears that K^+ can only access this site in silica-rich chabazite (as in Dyer's work) probably due to the lower framework charge density and K^+ hydration sphere. The output Si/Al ratio is significantly lower than the input (gel composition) Si/Al as it is very difficult to synthesize chabazite with Si/Al > 3 (Gaffney and Coe, 1991).

Although isotherms were measured over a range of temperatures for all of the zeolite samples, for the sake of clarity we show the N_2, O_2 and Ar adsorption isotherms at 0°C for K-CHA sample only in Fig. 1. The N_2 adsorption capacity on K-CHA is higher than both O_2 and Ar as expected since the quadrupole moment of N_2 (0.31 A^3) is much larger than either O_2 (0.1 A^3) or Ar (0 A^3) and interacts strongly with the electric field generated by K^+. Although not shown, the adsorption capacity of K-CHA for N_2 is lower than for Ca-CHA and Li-CHA consistent with the much higher charge density of the Li and Ca cations (4.6 and 2.1 for Li^+ and Ca^{+2} versus 0.43 for K^+). This same trend is also seen in the zero-loading heats of adsorption shown in Table 2. The exact adsorption behaviour however depends on not only the cation charge density

Table 2. Heats of adsorption and adsorption selectivity of N_2, O_2, and Ar over different cation forms of chabazite.

	Isosteric Heats of adsorption, kJ mol^{-1}			Adsorption selectivity at 1 bar, 0°C	
Sample	Nitrogen	Oxygen	Argon	N_2/O_2	O_2/Ar
K-CHA	−16.0	−9.6	−7.2	1.8	1.8
Li-CHA	−24.3	−19.8	−11.7	1.9	1.6
Ca-CHA	−31.9	−21.7	−17.6	2.0	1.4

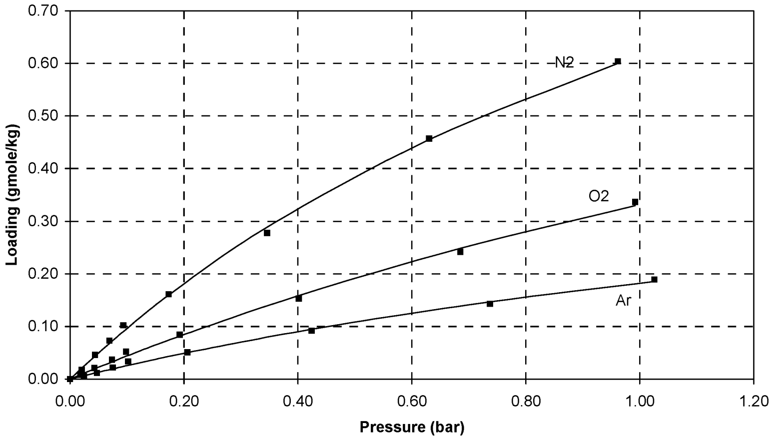

Figure 1. Adsorption isotherms of N_2, O_2 and Ar at 0°C in K-CHA.

but also the cation siting and hence accessibility. These in turn are functions of Si/Al ratio and Al distribution. Coe and Roberts (1990b) have shown that competing effects of cation crowding in alumina-rich chabazites and cation dilution in silica-rich chabazites leads to optimal Si/Al ratios for maximal adsorption interaction. Recent molecular simulation studies (Civalleri et al., 2003) have shown that Li cations are more stable at SII sites (hexagonal face of the D6R unit) whereas K prefers the SIII site no doubt as a consequence of the much larger cation radius. In contrast to the lower adsorption capacities, our samples of K-CHA showed improved oxygen/argon pure component selectivities relative to Li-CHA and Ca-CHA. The reason for this is not clear but it is likely related to the large K^+ ionic radius and the partial pore blockage as a result of potassium cations in site SIII. Access of the argon molecule to the 20-hedron cage may be more difficult than the smaller oxygen molecule in the presence of the potassium cation.

Data for heats of adsorption of N_2, O_2 and Ar on samples of Ca-CHA prepared and dehydrated under a variety of conditions were reported by Maroulis et al. (1988). For argon, isosteric heats of −18 to −20 kJ/mol were reported, while oxygen isosteric heats of −18 to −24 kJ/mol were reported. These are slightly larger than those measured here. These small differences can readily be attributed to small differences in synthesis and dehydration conditions (Maroulis et al. dehydrated their samples to 400°C).

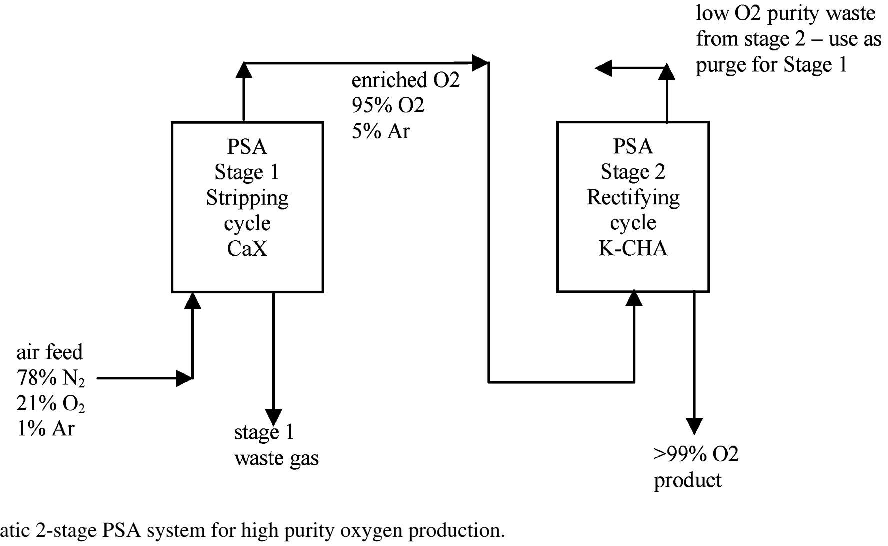

Figure 2. Schematic 2-stage PSA system for high purity oxygen production.

The high oxygen/argon selectivity shown by K-CHA can be exploited to permit production of high purity oxygen in a simple two-stage PSA system without the need for expensive AgX based zeolite (eg. Chiang et al., 2002), as demonstrated in Fig. 2. In a first stage traditional O_2PSA (or O_2VSA) run as a stripping cycle, a nitrogen selective zeolite (such as CaX) is used to produce an oxygen-enriched product of 95%O_2, 5%Ar. This stream is then sent to a second stage (much smaller) PSA using K-CHA adsorbent operated with a rectifying cycle (incorporating product purge) producing high purity oxygen (>99%) in the blowdown gas and an argon enriched waste gas. Alternatively, the 95%O_2/5%Ar stream may be sent to a dual-reflux PSA to produce a pure O_2 and pure argon stream.

5. Conclusion

The adsorption properties of N_2, O_2, and Ar have been measured on samples of potassium exchanged chabazite and show good O_2/Ar selectivity although the adsorption capacity of nitrogen is reduced relative to that of Li-CHA and Ca-CHA. The enhanced O_2/Ar selectivity relative to the Ca and Li forms of chabazite is probably due to enhanced pore blockage as a result of the larger potassium cation. Since the potassium form of chabazite is relatively easy and cheap to synthesize, its potential as an O_2/Ar molecular sieve should be explored further. In addition, the effect of variations in Si/Al ratio should be further investigated to determine the optimum range for air separation applications. Recently developed novel PSA cycles should be considered in conjunction with existing Skarstrom type cycles to produce high purity oxygen (>99%) in multiple stage PSA systems.

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