Adsorption of Nitrogen, Oxygen and Argon on Na-CeX Zeolites

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Abstract. Commercial type X zeolites (Linde 13X) are nitrogen selective. Oxygen is the less abundant component in air; hence oxygen selective sorbents are desired for air separation. Mixed Na-Ce type X zeolites containing different ratios of Ce^{3+}/Na^+ ions are prepared by partial ion exchange of commercial X zeolite. The adsorption isotherms of nitrogen, oxygen and argon are measured and the pure-component selectivity ratios are compared and analyzed against commercial zeolites (13X) for air separation. Oxygen selectivity over nitrogen ($\sim$1.5) and argon ($\sim$4.0) are seen for mixed Na-Ce type X zeolite (Si/Al $= 1.25$; $Ce^{3+}/Na^+ < 4.0$) from Henry's constant determined from low pressure adsorption measurements. The oxygen and nitrogen isotherms cross over for mixed Na-Ce type X zeolite (Si/Al $= 1.25$; $Ce^{3+}/Na^+ < 4.0$), and the pressure at which cross they over increases as Ce^{3+}/Na^+ approaches 1. The oxygen selectivity as claimed in the patent by N.V. Choudary, R.V. Jasra, and S.G.T. Bhat (US Patent no. 6,087,289, 2000) is seen only at very low pressures in the volumetric adsorption measurement and the hydrogen treatment of the Ce-exchanged samples have no effect on the adsorption characteristics.

Keywords: Ce-X zeolite, nitrogen sorbent, sorbent for air separation, Ce-ion exchange

Introduction

Nitrogen and Oxygen are two of the most widely produced chemicals in the world, ranked the second and third in quantities of production. Cryogenic distillation of air is the primary technology used for the production of these gases. There are other processes now being employed successfully. Among them adsorption based systems have improved by leaps over the last two decades and have been an alternative technology for industrial production of nitrogen and oxygen (Yang, 1997). Approximately 20% of air separation is

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presently through adsorption based separation systems (Rege and Yang, 1997).

Synthetic zeolites (A, X and Y) have been used in commercial pressure swing adsorption (PSA) systems for air separation. These zeolites are nitrogen selective, i.e., adsorbing N_2 more strongly than O_2 at a ratio of approximately 4:1 due to the interaction between the N_2 and the charge compensating cation present in the zeolites. Among the cations, Li^+ gives strong interactions with N_2 (McKee, 1964), and its use was greatly increased in recent years with the following advances in LiX sorbents: (1) Li^+ ion exchange must exceed 70% occupancy threshold to have any effect on the N_2 adsorption (Chao, 1989; Chao et al., 1992; Coe et al.,

1992), and (2) there is a significant increase in N_2 adsorption for Li^+ ion-exchanged low silica X-type zeolites over commercial LiX zeolite. The best N_2 selective zeolite now used commercially is the Li-LSX (Si/Al = 1.0) (Rege and Yang, 1997; Yang, 1997). It is also known that the addition of small amounts of Ag^+ (e.g., 1–3 cations/cavity) can further improve both the sorbent selectivity and N_2 capacity (Yang and Hutson, 1998; Hutson et al., 1999).

Separation of air by adsorption of the less abundant component (O_2) is more desirable, and active research is being carried out to produce a material that adsorbs oxygen preferentially to nitrogen for use in industrial adsorption systems. Carbon molecular sieves (CMS) are oxygen selective in the case of kinetic separation of air in a PSA system (Juntgen et al., 1981; Chen et al., 1994). 4A zeolite has also been used for kinetic separation of air (Yang, 1997). Oxygen binding complexes of cobalt remain the only possible oxygen selective sorbents (based on equilibrium) with a potential for air separation (Li and Govind, 1994; Ramprasad et al., 1995; Jones et al., 1979; Niederhoffer et al., 1994; Hutson and Yang, 2000).

Air contains 0.94 mole% argon which serves as a limiting factor for the maximum oxygen purity achieved (∼95%). Some applications like welding and cutting processes, plasma chemistry, Ozone generator, breathing oxygen at high altitudes in pressurized space suits and laboratory applications require oxygen purity greater than 99%. This necessitates argon-oxygen separation through cryogenic distillation (Egoshi et al., 1999, 2000) or kinetic separation using molecular sieves (Miller and Theise, 1989). The crude argon produced during cryogenic distillation of air contains nitrogen and oxygen (3–5%). The argon purity can be enriched by catalytic hydrogen combustion or low temperature oxygen adsorption in an oxygen selective synthetic zeolite (Choudary et al., 2000). Some Ag-zeolites have been shown to have a selectivity for Ar over O_2 (Hutson et al., 1999; Knaebel and Kandybin, 1993), hence can be used for this separation (Knaebel and Kandybin, 1993). Several hybrid membrane-PSA systems have also been considered for producing high purity O_2 by using the higher permeability of Ar.

Choudary et al. (2000) disclosed interesting air separation properties of CeX zeolites based on first-moment analyses of chromatography data.

In this work, mixed Na-Ce type X zeolites containing different ratios of Ce^{3+}/Na^+ ions were prepared by partial ion exchange of a commercial X zeolite. The

adsorption isotherms of nitrogen, oxygen and argon were measured and the pure-component selectivity ratios (KN_2/KO_2) were compared and analyzed against commercial zeolites for air separation.

Experimental Details

Materials

Commercial X-type zeolite with a Si/Al ratio of 1.25 (Linde 13X, lot 945084060002) in the form of binder less, hydrated powders was used. Helium (99.995%, prepurified, Cryogenic Gases), oxygen (99.6%, extra dry, Cryogenic Gases), nitrogen (99.998%, prepurified, Cryogenic Gases) and argon (99.998%, prepurified) were used as obtained. Cerium chloride hydrate ($CeCl_3 \cdot 6H_2O$, 99%, Strem Chemicals) and deionized water were used for the preparation of cerium (III) chloride solution for ion exchange. Deionized water were was used for sample washing and silver nitrate ($AgNO_3$), 99.9% Strem Chemicals) was used to confirm the absence of Cl^- ions in the washings.

Preparation of Sorbents

The mixed Na-Ce zeolites were prepared by conventional batch ion-exchange of X type zeolite using 0.085 M (2.1 wt%) aqueous solution of cerium (III) chloride at 95°C for 24 h. Three different samples of Na-CeX zeolites were prepared each using 10X (Na-CeX#10), 5X (Na-CeX#5) and 1X (Na-CeX#1) the theoretical (100%) Ce^{3+} needed for ion exchange. The samples were filtered and washed with hot deionized water until the solution showed the absence of chloride (i.e., no precipitation upon treatment with $AgNO_3$). The adsorbents were dried overnight at 100°C in air. For comparison against the oxygen selective cerium exchanged X type zeolites produced by Choudary et al. (2000), a sample of Na-CeX zeolite (sample id. CeXP-1) containing Ce^{3+}/Na^+ ratio of 3.3 was prepared following similar procedure.

Composition of Na-CeX Zeolites

The zeolite samples were compositionally analyzed using neutron activation analysis (NAA) in the research nuclear reactor of the Phoenix Memorial Laboratory at the University of Michigan. The samples were exposed sequentially to 1-minute coreface irradiation delivered

via pneumatic tube to a location with an average thermal neutron flux of 2.13×10^{12} n/cm^2/s. Two separate counts of the resulting gamma ray activity were made, one after a 13-minute decay and a second count after 1 h and 56 min decay; both were for 500 s. Element concentrations for Al and Na were determined based on comparison with three replicates of the standard reference material NIST1633A (coal fly ash) while CeO_2 was used as basis for determining Ce content. A fourth replicate of each material was included as a check standard.

Hydrogen Treatment

The absorbent samples were loaded into reaction tubes (TPR tubes) and heated from ambient to 400°C and held at 400°C for 12 h with 60 cc/min of hydrogen. The sample was cooled to room temperature and the samples were quickly transferred to the Micromeritics analysis glass tubes and sealed for isotherm measurements.

Adsorption Isotherms

The adsorption isotherms were measured using a static volumetric system (Micromeritics ASAP-2010) (Hutson et al., 2000). Prior to measurement of isotherms, the samples were treated with hydrogen and then activated in a vacuum at 300–400°C for a minimum of 4 h.

Results and Discussion

Chemical Analyses

As mentioned in the experimental section, the samples were analyzed for their composition using neutron activation analysis (NAA). In this analysis the Si concentration were pre-specified. Results of these analyses are given Table 1. The unit cell composition for those analyzed samples are calculated using a basis of 86 Al/u.c. and the results are tabulated in Table 2. The ratios of Ce^{3+}/Na^+ ions for the samples are listed in Table 3. As seen from the results it could be said that the extent of Ce exchange accomplished depends on the amount of excess cerium (III) chloride solution used and 100% Ce-exchange is difficult to achieve and needs consecutive exchanges.

Table 1. Elemental composition of Na-CeX (Si/Al = 1.25) zeolite samples.

	CeX#10		CeX#5		CeX#1	
Comp.	wt%	+/−	wt%	+/−	wt%	+/−
Al	12.577	0.086	12.208	0.081	12.372	0.081
Ce	22.126	0.429	22.452	0.470	17.347	0.458
Na	0.627	0.016	0.885	0.022	2.488	0.056

Table 2. Unit cell composition for the Na-CeX (Si/Al = 1.25) zeolite samples.

Comp.	CeX#10 (atm/uc)	CeX#5 (atm/uc)	CeX#1 (atm/uc)
Al	86.0	86.0	86.0
Si	107.5	107.5	107.5
Ce	27.0	26.5	22.0
Na	5.0	6.5	20.0
O	387.0	387.0	387.0

Adsorption Isotherms

The Na-CeX sorbent samples after the hydrogen treatment are degassed in vacuum at 400°C for 4 hours. The equilibrium isotherms of nitrogen and oxygen on the various sorbent samples prepared in this study were measured using Micromeritics ASAP2010 unit as mentioned earlier. Figure 1 shows the nitrogen and oxygen isotherms measured at 22°C for NaX (commercial type X zeolite). Figures 2 through 4 show the adsorption isotherms of nitrogen and oxygen for various samples prepared in this study. The isotherms are fitted with both Langmuir equation (Yang, 1997) and Virial equation (Reid et al., 1998; Sun et al., 1998). Langmuir equation:

$$q = \frac{KP}{1 + BP} \qquad (1)$$

Virial equation:

$$\ln\left(\frac{P}{q}\right) = A_0 + A_1 q + A_2 q^2 + \cdots \qquad (2)$$

and

$$K = \exp(-A_0) \qquad (3)$$

where q is the amount adsorbed per unit weight of the sorbent and K is the Henry's constant. Both Langmuir equation (1) and Virial expansion (2) reduce to Henry's

Table 3. Langmuir isotherm parameters for N_2/O_2 on Na-CeX from volumetric measurement.

Sorbent[a]	Ce^{3+}/Na^+	Degas temp (°C)	Nitrogen		Oxygen		Pure-component adsorption selectivity O_2/N_2
			K (mmol g^{-1} atm^{-1})	B (atm^{-1})	K (mmol g^{-1} atm^{-1})	B (atm^{-1})	
NaX	0	400	0.590	0.281	0.162	0.257	0.27
CeX#10	5.8	400	0.231	0.458	0.156	0.426	0.68
CeX#5	4.2	400	0.220	0.531	0.187	0.394	0.85
CeX#1	1.1	400	0.237	0.297	0.299	0.753	1.26

[a]Refer to text for preparation condition for the sorbents.
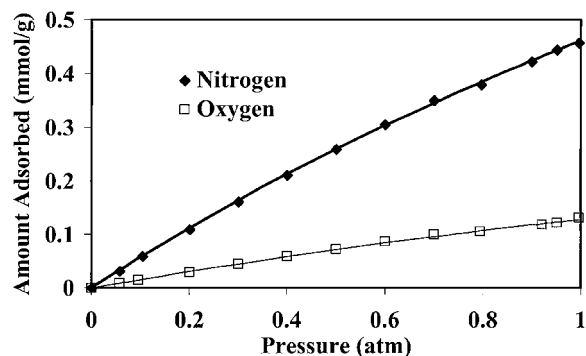
Figure 1. Nitrogen and oxygen adsorption isotherms on NaX (Linde—13X) zeolite at 22°C after degassing at 400°C for 4 hours.
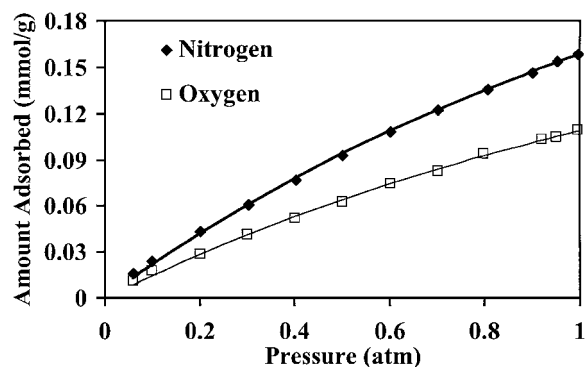

Figure 2. Nitrogen and oxygen adsorption isotherms on CeX#10 (Na-CeX; Si/Al = 1.25; Ce^{3+}/Na^+ = 5.8) zeolite at 22°C after degassing at 400°C for 4 hours.

Law ($q = KP$) in the low pressure region. The fitted Langmuir and Virial parameters are provided in Tables 3 and 4, respectively. The adsorption isotherms were also measured without hydrogen treatment of the samples and found to give identical results to those measured after hydrogen treatment within the limits of experimental error. With hydrogen treatment we expect the Ce^{3+} to be reduced and the adsorption results

show that either the reduction of Ce^{3+} is minimal or did not have any effect on both N_2 and O_2 adsorption isotherms.

Figures 2 and 3 show equilibrium selectivity (qN_2/qO_2) towards nitrogen while Fig. 4 has a crossover point and the equilibrium selectivity changes
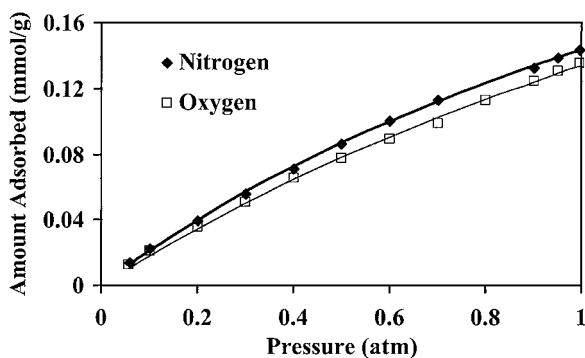

Figure 3. Nitrogen and oxygen adsorption isotherms on CeX#5 (Na-CeX; Si/Al = 1.25; Ce^{3+}/Na^+ = 4.2) zeolite at 22°C after degassing at 400°C for 4 hours.
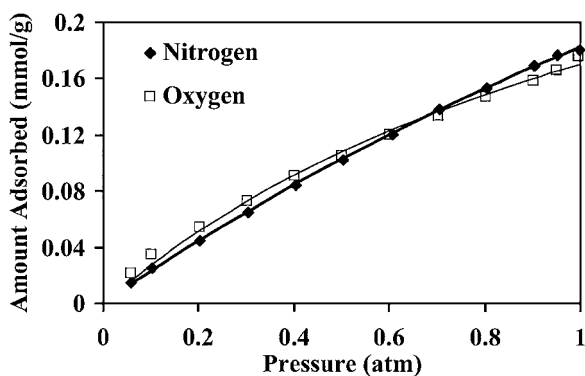

Figure 4. Nitrogen and oxygen adsorption isotherms on CeX#1 (Na-CeX; Si/Al = 1.25; Ce^{3+}/Na^+ = 1.1) zeolite at 22°C after degassing at 400°C for 4 hours.

Table 4. Virial parameters for N_2/O_2 adsorption isotherms on Na-CeX (Si/Al = 1.25) from volumetric measurement.

Sorbent[a]	Virial parameters						K (mmol g^{-1} atm^{-1})		Pure-component adsorption selectivity O_2/N_2
	N_2			O_2					
	A_0	A_1	A_2	A_0	A_1	A_2	N_2	O_2	
NaX	0.554	0.302	0.397	1.772	3.113	−8.284	0.575	0.170	0.30
CeX#10	1.243	6.564	−18.482	1.540	12.262	−58.789	0.288	0.214	0.74
CeX#5	1.366	5.888	−13.861	1.408	8.415	−30.748	0.255	0.245	0.95
CeX#1	1.329	3.351	−7.575	0.748	10.810	−29.512	0.265	0.474	1.79

[a]Refer to text for preparation condition for the sorbents.

Table 5. $N_2/O_2/Ar$ adsorption on Na-CeX from gas chromatography data (Choudary et al., 2000).

Adsorbent[a]	Ce^{3+}/Na^+	Henry constant K (mmol g^{-1} atm^{-1})			Pure-component adsorption selectivity ratios		
		O_2	N_2	Ar	O_2/Ar	O_2/N_2	N_2/Ar
NaXP	0	0.1621	0.4843	0.1510	1.1	0.3	3.2
CeXP-1	3.3	0.3212	0.2178	0.0780	4.1	1.5	2.8
CeXP-3	8.0	0.1520	0.2665	0.0730	2.1	0.6	3.6
CeXP-4	16.5	0.2685	0.2634	0.0719	3.8	1.0	3.7
CeXP-1[b]	3.3	0.2158	0.1814	0.0567	3.8	1.2	3.2

[a]Refer to Choudary et al. (2000) for detail sample preparation conditions.
[b]Low pressure adsorption isotherm measured in a volumetric apparatus in this study using the sample prepared similar to CeXP-1 sample of Choudary et al. (2000). Henry constant determined using Virial equation.

from oxygen to nitrogen as the pressure increases. Choudary et al. (2000) have prepared oxygen selective cerium exchanged X zeolites. Table 5 gives a summary of nitrogen, oxygen and argon adsorption on mixed Na-Ce type X zeolite measured by gas chromatography by Choudary et al. (2000). The best oxygen selective X zeolite from the work of Choudary et al. (2000) is prepared in this study and low pressure adsorption isotherms of nitrogen, oxygen and argon are measured. The Henry's constants determined from virial expansion along with adsorption selectivity are provided in Table 5. The values of Henry's constant obtained from volumetric adsorption data are slightly lower than the values from Choudary et al. (2000) These selectivity ratios are comparable to gas chromatography data (Choudary et al., 2000). Figure 5 shows the adsorption isotherms of nitrogen, oxygen and argon on mixed Na-Ce type X zeolite ($Na^+:Ce^{3+} = 1:3.3$). Figure 6 shows the very low pressure region of the isotherms shown in Fig. 5. From these figures it is seen that the equilibrium adsorption selectivity changes from oxygen to nitrogen and there is a cross over point seen
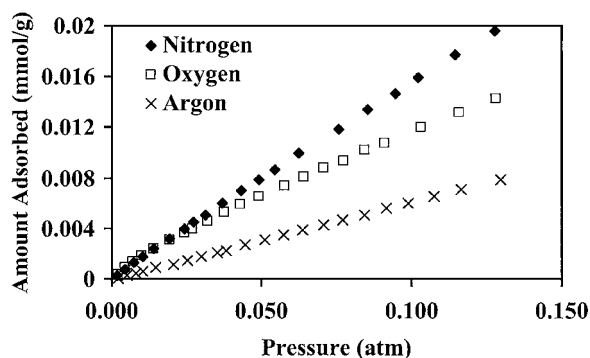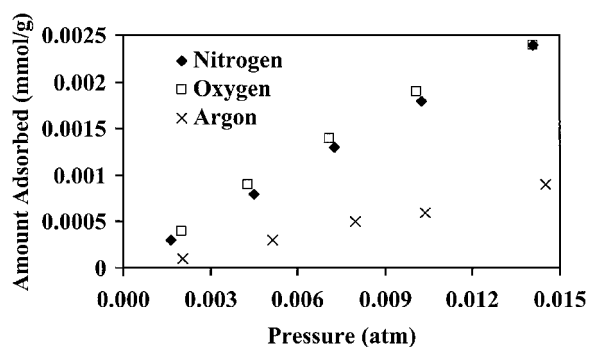
Figure 5. Nitrogen, oxygen and argon adsorption isotherms on CeXP-1* ($Ce^{3+}/Na^+ = 3.3$) zeolite at 30°C after degassing at 300°C for several hours. (*sample preparation condition refer to Choudary et al., 2000).

in the oxygen, nitrogen isotherms (Fig. 6). Similar effect is also seen in the volumetric adsorption data of nitrogen and oxygen on mixed Na-Ce type X zeolite ($Na^+:Ce^{3+} = 1:1.1$) shown in Fig. 4. Quantitative comparisons of the O_2/N_2 selectivity ratios for the

Figure 6. Nitrogen, oxygen and argon adsorption isotherms on CeXP-1* ($Ce^{3+}/Na^+ = 3.3$) zeolite at $30°C$ after degassing at $300°C$ for several hours (low pressure data from Fig. 5).

various samples used in this study are given in Tables 3 and 4. The selectivity ratios from Langmuir equation and Virial expansion are comparable except for the sample—CeX#1 (i.e., low Ce) because of the reversal in selectivity seen at higher pressure. The equilibrium adsorption selectivity (O_2/N_2) decreases as the cerium exchange increases and it is greater than one for mixed Na-Ce type X zeolites with $Ce^{3+}/Na^+ < 4$. The commercial X zeolite which has $Ce^{3+}/Na^+ = 0$ is nitrogen selective. This implies that very small Ce^{3+}/Na^+ ratio per unit cell is needed for the oxygen nitrogen isotherms to cross over. Figure 7 shows the variations of the Henry constant and pure-component adsorption selectivity ratios as a function of Ce^{3+}/Na^+ ratio per unit cell. The Henry constant for N_2 adsorption decreases as the Ce^{3+}

increases while that of O_2 adsorption increases and then decreases towards higher Ce^{3+}/Na^+ ratio.

The commercial X zeolite has 86 Al^- ions thereby 86 charge compensating Na^+ ions on the extra-framework sites. Sixteen Na^+ ions are located in the hexagonal prism or in the sodalite cage, thirty-two of the Na^+ are located in the large cavities, almost in the plane of the 6MR rings, which connect the supercages and the sodalite cages. The remaining thirty-eight are in constant motion in the large cavities (Sherry, 1966). The N_2—Na^+ interactions are stronger than O_2—Na^+ interactions giving rise to nitrogen selectivity. Ce^{3+} are trivalent ions hence exchanging Na^+ with Ce^{3+} reduces the number of charge compensating cations and thereby reducing the adsorption amount for nitrogen and bringing it to the levels of oxygen. Ce^{3+} being trivalent will take up different site locations compared Na^+ hence bringing about the changes in adsorption characteristic. In a fully exchanged Ce-X zeolite four Ce^{3+} cations are found to be in the center of the hexagonal prism, twenty-four are found to be within the sodalite cage near the 6 MR comprising the hexagonal prism and at most one in the center of the 12-membered ring (Hunter and Scherzer, 1971). The presence of mixed cations on extra-framework sites may result in partial occupancy of sites and these will change as the Ce^{3+}/Na^+ ratio changes. With partial Cerium exchange there could be more Ce^{3+} ions occupying the 12-membered ring sites there by exposing themselves for adsorption. This could be due to Na^+ ions occupying the inner sites in the hexagonal prism and
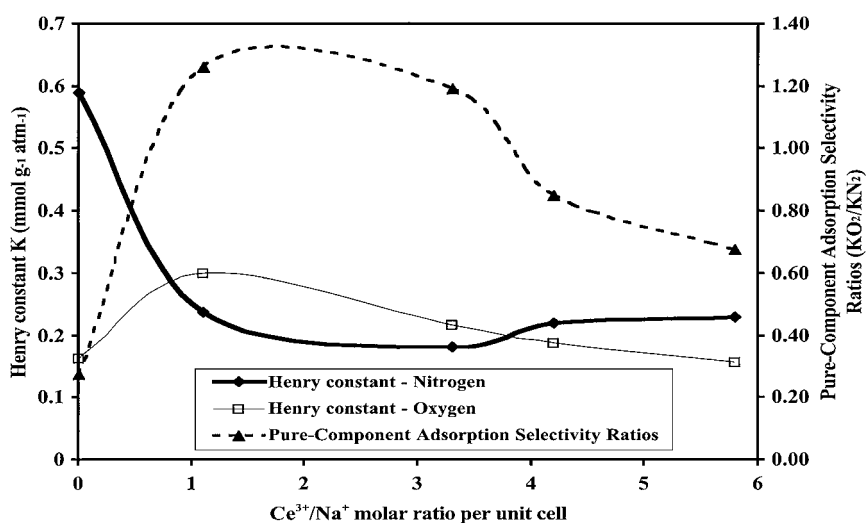

Figure 7. Pure-component adsorption selectivity ratios and Henry constant plotted against Ce^{3+}/Na^+ ratio per unit cell.

the sodalite cages (Barrer, 1978). From the adsorption data measured on the samples prepared here we find a threshold ratio of Ce^{3+}/Na^+ per unit cell to be 3.3 below which we see oxygen selectivity in the low pressure region. There is also a lower limit to this ratio since NaX zeolite with $Ce^{3+}/Na^+ = 0$ does not show oxygen selectivity and it is obvious that as the ratio goes down so does the absolute number of Ce^{3+} ions present per unit cell and there by bringing down the Ce^{3+} number in the main cavity too. In this study a lower limit to Ce^{3+}/Na^+ ratio of 1.1 was located.

Conclusions

Adsorption characteristics of nitrogen, oxygen and argon on mixed Na-Ce type X zeolites are studied. The hydrogen treatment of Ce-exchanged samples is found to have no effect on the adsorption characteristics of nitrogen and oxygen. Oxygen selectivity is seen for mixed Na-Ce type X zeolite ($Si/Al = 1.25$; $Ce^{3+}/Na^+ < 4.0$) from Henry's constant determined from low pressure adsorption measurements. Oxygen and nitrogen isotherms cross over for mixed Na-Ce type X zeolite ($Si/Al = 1.25$; $Ce^{3+}/Na^+ < 4.0$) and the pressure at which they cross over increases as Ce^{3+}/Na^+ approaches 1. The oxygen selectivity described by Choudary et al. (2000) is seen only at very low pressures in the volumetric adsorption measurement.

Nomenclature

A_0, A_1, A_2	Virial parameters
K	Henry's constant (mmol g^{-1} atm^{-1})
P	Pressure (atm)
q	Molar adsorbed amount (mmol/g)

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