

Anomalous adsorption of nitrogen and argon in silver exchanged zeolite A[†]

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A new adsorbent based on zeolite AgA having N₂ adsorption capacity of 22.3 cc g⁻¹ at 101.3 kPa and N₂/O₂ selectivity in the range of 5 to 14.6 at 303 K, the highest known so far for any zeolite A type of adsorbent, is reported; furthermore, this adsorbent also shows argon selectivity over oxygen.

Pressure swing adsorption (PSA) processes are being increasingly used for the separation of O₂ and N₂ from air.^{1,2} Adsorbents namely carbon molecular sieves,³ pore engineered zeolites⁴ and titanosilicates with adjustable pores⁵ are reported for the size/shape selective separation of air. Synthetic zeolites A, X and mordenite having alkali and alkaline earth metals as the extra framework cations are used for the separation based on the difference in the interactions of O₂ and N₂ molecules with the zeolite surface.^{2,3} N₂ selective zeolites NaCaA, CaX and LiX are the widely used adsorbents for the O₂ enrichment of air. However, LiX adsorbent with >95% Li⁺ exchange and zeolite Si/Al ratio of one is the best adsorbent known⁶ for O₂ production due to its high N₂ adsorption capacity (~30 cc g⁻¹ at 101.3 kPa & 303 K and N₂/O₂ selectivity of 10). Among the zeolite A based adsorbents, NaCaA displays the highest N₂ adsorption capacity of around 15 cc g⁻¹ at 101.3 kPa & 303 K and N₂/O₂ selectivity of 3 to 5 depending on the extent of Ca²⁺ exchange and is used in commercial PSA processes for O₂ production. To have favorable process economics, it is desirable to have adsorbents with higher N₂ adsorption capacity and selectivity. In the present study, we report a new adsorbent, AgA based on zeolite A, which shows adsorption capacity 1.5 times higher than that of NaCaA. The adsorbent also shows N₂/O₂ in the range of 5 to 14.6 at 303 K. This is the highest N₂ adsorption capacity and selectivity for any zeolite A type adsorbents reported so far. Furthermore, this adsorbent also shows Ar selectivity over O₂.

Ag⁺ forms a mononuclear species with appreciable stability in water and was introduced into the zeolite cavities by a single step cation exchange from its aqueous solution. A commercially available molecular sieve 4A powder and 1.5 mm diameter beads from *Zeolites and Allied Products, Bombay, India* was used as the starting material without further purification. The zeolite was refluxed with aqueous AgNO₃ solution in the ratio 1:80 at 353 K in the absence of direct contact with light. The residue was filtered, washed with hot distilled water until the

washings were free from Ag⁺ and dried at 353 K. Exchange of Ag⁺ into zeolite NaA is highly facile and can occur even at ambient conditions due to the high exchange selectivity⁷ of Ag⁺ over Na⁺ (88%) in zeolite A. This provides an additional advantage⁸ for AgA adsorbent over commercially used CaA and LiX, in which the adsorbent preparation comprises multi-stage and involved Ca²⁺/Li⁺ exchange.⁶ However, silver salts being expensive add to the cost of the adsorbent and direct exposure of the adsorbent to light needs to be avoided due to its light sensitivity. Furthermore, the recovery of silver from the spent adsorbent will need to be done to bring down the over all cost of the adsorbent. X-Ray powder diffraction of the Ag⁺ exchanged zeolite collected using PHILIPS X^{pert} MPD system in the 2θ range of 5–65 using CuKα1 (λ = 1.54056 Å) shows that the structure of the zeolite A is retained after Ag⁺ exchange.

N₂, O₂ and Ar adsorption at different temperatures was measured using a static volumetric system (Micromeritics ASAP 2010), after activating the sample under vacuum for 8 h with programmed heating (1 K min⁻¹) from 298 to 653 K (Table 1). Ag⁺ exchanged zeolite was air dried at ambient temperature prior to activation. The sample dried in an oven (383 K) and later activated under vacuum at 653 K with rapid heating showed poor N₂ adsorption capacity.

The N₂ adsorption isotherm on fully Ag⁺ exchanged zeolite A at 303 K is compared with that of NaA and CaA (Fig. 1a). The adsorption capacity of N₂ is much higher than CaA in the pressure range studied. AgA shows equilibrium adsorption capacity of 22.3 cc g⁻¹, 4.36 cc g⁻¹ and 6.25 cc g⁻¹ respectively for N₂, O₂ and Ar at 303 K & 101.3 kPa. The N₂ adsorption capacity and N₂/O₂ selectivity is nearly same as that commercially used LiX (19.8 cc g⁻¹ at 303 K & 101.3 kPa). A distinctly high isosteric heat of adsorption, † Δ*H*_{ad}, for N₂ in AgA (36.55 kJ mol⁻¹) compared to that in NaA (20.38 kJ mol⁻¹), CaA (22.23 kJ mol⁻¹) and LiX (25.82 kJ mol⁻¹) reflects the stronger interaction between N₂ molecules and the Ag⁺ exchanged zeolite surface. Adsorption of N₂ in AgA was confirmed by measuring FTIR (Perkin Elmer Spectrum GX) spectra of zeolite samples having adsorbed N₂ at 303 K. IR band at 2091 cm⁻¹ was observed. N₂ molecules being totally symmetric do not absorb IR radiation. However, N₂ molecules adsorbed in zeolites experience induced dipole moment which varies during vibration and induced band is observed.⁹

The adsorption behavior of alkali and alkaline earth metal ion exchanged zeolites for O₂, N₂ and Ar were explained by

† Electronic supplementary information (ESI) available: Clausius–Clapeyron equation. See <http://www.rsc.org/suppdata/cc/b2/b209929b/>

Table 1 Isosteric heat of adsorption and adsorption selectivity

Sample	Heat of adsorption in kJ mol ⁻¹ at equilibrium adsorption 0.21 mmol g ⁻¹			Adsorption selectivity					
				N ₂ /O ₂		N ₂ /Ar		Ar/O ₂	
	Nitrogen	Oxygen	Argon	6.66 kPa	101.99 kPa	6.66 kPa	101.99 kPa	6.66 kPa	101.99 kPa
NaA	20.38	15.24	12.97	3.02	2.99	3.36	3.18	0.90	0.93
CaA	22.23	16.09	12.19	5.57	3.23	6.84	3.51	0.82	0.82
AgA	36.55	15.44	16.42	14.60	5.09	8.52	3.90	1.48	1.63
LiX	25.82	16.82	13.56	9.40	5.13	11.23	6.11	0.82	0.83

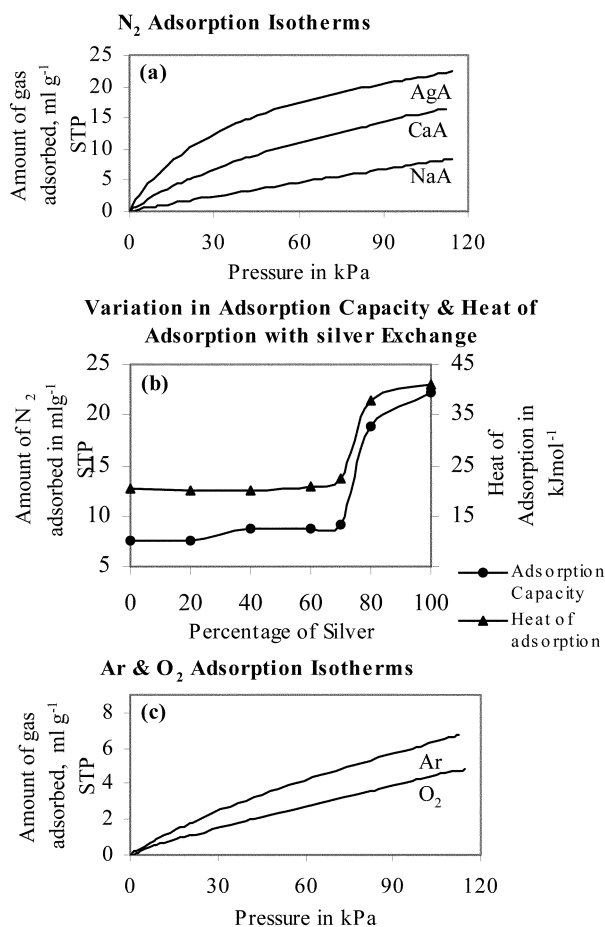


Fig. 1 (a) N₂ adsorption isotherms measured on various adsorbents at 303 K. (b) Variation in adsorption capacity and isosteric heat of adsorption with the percentage of Ag⁺ exchange. (c) Ar and O₂ adsorption isotherms on AgA measured at 303 K.

considering the difference in the quadrupole moment of the adsorbate molecules and the size and charge density of the cation. Even though Na⁺ and Ag⁺ have the same charge and similar size, the adsorption behavior of zeolites having these cations inside their cavities are different. The N₂ adsorption capacity is almost three times higher for silver zeolite A compared to NaA. This anomalous adsorption of N₂ in AgA could be attributed to the reported^{10–15} formation of silver clusters inside zeolite A cavities. Silver cations in AgA zeolite on vacuum dehydration at higher temperature are reported to form Ag_n^{x+} clusters in sodalite cages. Though, the exact mechanism by which Ag_n^{x+} clusters influence N₂ adsorption is under investigation, there are two possible ways by which N₂ adsorption might be affected. It is reported^{10–15} that under prolonged evacuation at higher temperature, Ag⁺ cations present inside main zeolite cage undergo intrazeolite auto reduction to Ag⁰ by interacting with framework oxygens. Ag⁰ then migrates to sodalite cage and forms clusters by interacting with Ag⁺ cation present therein. However, this will result in positively charged structural defects on the zeolite surface, which will have higher electrostatic interactions with N₂ molecules. With fully exchanged AgA, formations of four weakly interacting Ag₃^{x+} clusters are reported¹² inside sodalite cage. Two Ag⁺ cations of the clusters are present¹² in the six-ring of sodalite cage with Ag⁰ at the center. These Ag⁺ cations are accessible to N₂ molecules as six-ring is also a part of the main cage. N₂ molecules having a higher quadrupole moment (0.31 Å²) will have higher interactions compared to O₂ and Ar molecules having values of <0.11 Å² and zero respectively.

Zeolite A having varied silver content shows nonlinear dependence both for adsorption capacity and heats of adsorption for N₂ (Fig. 1b). Both ΔH_{ad} and N₂ adsorption capacity of the

AgA sharply increase after exchanging around 70% of the extra framework Na⁺ with Ag⁺ cations. N₂ adsorption isotherm data measured at 77.35 K also showed an increase in micropore area (Radushkevich) from 2.20 to 19.22 m² g⁻¹ as the Ag content increased from 0 to 100% indicating enhanced ingress of nitrogen inside zeolite A cavity at higher silver content. This is explained in terms of different locations Na and Ag cations occupy inside zeolite cavity. Three Na⁺ cations present¹⁶ at site II in the 8-ring partially block the pore aperture and thus restrict the ingress of N₂ inside the pores of NaA. From our adsorption data, it is apparent that up to the level of 70% Na⁺ exchange, Ag⁺ exchanges those Na⁺ ions which are present at sites I (inside 6-ring) and III (4-ring inside main cage) only. It is only after 70% exchange that Na⁺ ions located at site II in the 8-ring are replaced. In fully exchanged AgA, activation induces¹² intrazeolitic auto-reduction of main cage Ag⁺ ions, which migrate and form Ag₃^{x+} clusters in sodalite cage.

Ar and O₂ adsorption isotherms on AgA, (Fig. 1c) show Ar selectivity over O₂. Equilibrium adsorption capacity for Ar and O₂ at 303 K and 101.3 kPa are 6.25 and 4.36 ml g⁻¹ of zeolite indicating Ar selectivity over O₂. This is also confirmed from ΔH_{ad} for Ar and O₂ at equilibrium adsorption of 0.21 mmol g⁻¹, which are 16.42 and 15.44 kJ mol⁻¹ respectively.

These studies show that AgA zeolite has a potential to be a superior N₂ selective adsorbent for O₂ enrichment of air due to high adsorption capacity and selectivity. The observed Ar selectivity over O₂ show that it may be useful for O₂ production with purity higher than the O₂ purity limit of 95% in present adsorption processes. Furthermore, Ag⁺ exchange in zeolite A is more facile than Ca²⁺ and could be completed in a single stage. A brick red/orange red colour of activated adsorbent which changes in the presence of moisture in the feed gas mixture can be used a visual indicator on the activated state of the adsorbent.

Notes and references

- S. Sircar, *Ind. Eng. Chem. Res.*, 2002, **41**, 1389–1392.
- R. V. Jasra, N. V. Choudary and S. G. T. Bhatt, *Separation Science and Technology*, 1991, **26**, 885–930.
- R. T. Yang, *Gas Separation by Adsorption Process*, Butterworths, Boston, 1987.
- M. Niwa, K. Yamazaki and Y. Murakami, *Ind. Eng. Chem. Res.*, 1991, **30**, 38–42.
- S. M. Kuznicki, V. A. Bell, S. Nair, H. W. Hillhouse, R. M. Jacobinas, C. M. Braunbarth, B. M. Toby and M. Tsapatsis, *Nature*, 2001, **412**, 720–724.
- C. C. Chao, *US Patent*, 4,859,217, 1999; C. C. Chao, J. D. Sherman, J. T. Mullhaupt and C. M. Bolinger, *US Patent*, 5,174,979, 1992; C. G. Coe, J. F. Kirner, R. Pierantozzi and T. R. White, *US Patent*, 5,152,813, 1992; S. U. Rege and R. T. Yang, *Ind. Eng. Chem. Res.*, 1997, **36**, 5358–5365.
- D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, *J. Am. Chem. Soc.*, 1956, **78**, 5963–5971.
- J. Sebastian and R. V. Jasra, *PCT International Application No. 10/105,876*, 2002.
- E. C. De Lara and Y. Delaval, *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 790–797; F. Geobaldo, C. Lamberti, G. Ricchiardi, S. Bordiga, A. Zecchina, G. T. Palomino and C. O. Aren, *J. Phys. Chem.*, 1995, **99**, 11167–11177.
- T. Sun and K. Seff, *Chem. Rev.*, 1994, **94**, 857–870.
- V. S. Gurin, N. E. Bogdanchikova and V. P. Petranovskii, *J. Phys. Chem. B*, 2000, **104**, 12105–12110.
- M. D. Baker, J. Godber and G. A. Ozin, *J. Phys. Chem.*, 1985, **89**, 2299–2304; M. D. Baker, G. A. Ozin and J. Godber, *J. Phys. Chem.*, 1985, **89**, 305–311; M. D. Baker, G. A. Ozin and J. Godber, *Catal. Rev. Sci. Eng.*, 1985, **27**, 591–651.
- Y. Kim and K. Seff, *J. Phys. Chem.*, 1987, **91**, 671–674; Y. Kim and K. Seff, *J. Am. Chem. Soc.*, 1978, **100**, 175–180.
- P. A. Jacobs and J. B. Uytterhoeven, *J. Chem. Soc., Faraday Trans. 1*, 1979, **75**, 56–64.
- L. R. Gellens, W. J. Mortier, R. A. Schoonheydt and J. B. Uytterhoeven, *J. Phys. Chem.*, 1981, **85**, 2783–2788; R. A. Schoonheydt and H. Leeman, *J. Phys. Chem.*, 1989, **93**, 2048–2053.
- D. W. Breck, *Zeolites Molecular Sieves*, Wiley, New York, 1974.