# Efficient methane/nitrogen separation with low-sodium clinoptilolite

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**The presence of sodium is shown to have a highly detrimental effect on the gas separation ability of clinoptilolite towards methane and nitrogen.**

Much of the world's natural gas reserves are impure, one of the principal contaminants being nitrogen. Non-burning components reduce the thermal value of the gas, making it unsuitable for use as it is found. Currently, nitrogen is removed from natural gas by cryogenic processing, which is a very costly and energy-hungry procedure. Because of high processing costs, many easily accessible gas fields are being neglected in favour of those with lower natural nitrogen concentrations, even though these fields may lie in remote, inaccessible regions, or conservation areas. Gas separation using clinoptilolite potentially offers a much more cost-effective and environmentally friendly solution.

Clinoptilolite is a naturally occurring zeolite mineral, with an open aluminosilicate framework structure, and a high internal surface area. The clinoptilolite structure consists of a 2-dimensional network of interconnecting channels, formed by 10- and 8-membered tetrahedral rings (Fig. 1). The channel dimensions are approximately A $7.2 \times 4.4$ Å, B $4.7 \times 4.1$ Å and C $5.5 \times 4.0$ Å.[1] Small molecules can penetrate these pores, where they become adsorbed onto the internal surface. Nitrogen diffuses into the pores of clinoptilolite around $10^3$ to $10^4$ times faster than methane due to the smaller size of nitrogen (critical dimensions $N_2$ $4.0 \times 3.0$ Å, $CH_4$ 4.4 Å), and nitrogen is more strongly adsorbed on the channel wall.[1,2] Therefore, clinoptilolite can be used for the kinetic separation of these two gases. The channels are occupied by charge-balancing cations such as $Na^+$, $K^+$ and $Ca^{2+}$ (Fig. 1) plus adsorbed water. By controlling the cation content, it is possible to fine-tune the effective channel dimensions and electrostatic properties, to optimise the separation capacity.
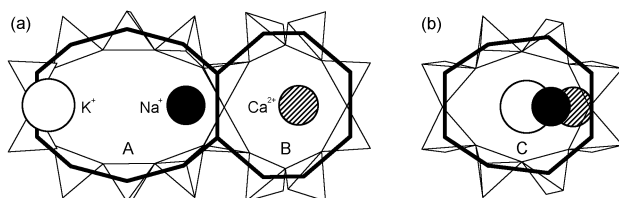


**Fig. 1** Cation locations in the clinoptilolite channel system.[3] (a) Channels A and B viewed down [001] (b) C viewed down [101].

Natural clinoptilolite samples of differing compositions from Semnan, Iran; Anaconda, Death Valley Junction, California; Nižný Hrabovec, Slovakia; and Beliplast, Bulgaria were used (Table 1). Samples were ground, and soluble impurities were removed by washing with hot ultra-pure water, prior to use.

Gas separation experiments were performed using a Perkin-Elmer Sigma 4B gas chromatograph with thermal conductivity detector and integrator. Helium carrier gas was used at a flow rate of 30 cm³ min⁻¹. Clinoptilolite samples were pressed into 710–1000 µm pellets and loaded into a 1 m by ¼″ OD stainless steel column. Columns were activated at 395 °C for 8 h under flow of carrier gas before use, to dehydrate the zeolite. 1 ml samples of a mixture of 25% $N_2$ and 75% $CH_4$ were introduced to the column by syringe. Retention times were measured with respect to hydrogen at temperatures in the range 0 to 90 °C. Specific retention volume ($V_g$) was calculated according to eqn. (1), where $t_r$ is relative retention time, $F$ is flow rate, $w$ is mass

$$\ln V_g = t_r \ (F/w)(273/T) \tag{1}$$

of zeolite in the column and $T$ is temperature.[2] Adsorption enthalpy ($-\Delta H$) was calculated using the slope of Fig. 2, from eqn. (2), where $R$ is the gas constant.[2] Calculated values are

$$V_g = (-\Delta H/RT) + C \tag{2}$$

shown in Table 2.

The high-sodium zeolite from Semnan showed no separation behaviour towards the methane/nitrogen mixture, with both components eluting as a single peak. The sodium-containing Anaconda clinoptilolite gave moderate separation. By contrast, the sodium-free samples from Beliplast and Nižný Hrabovec showed excellent separation ability, with nitrogen being strongly retained while methane is only weakly held (Table 2).

To confirm the detrimental effect of sodium suggested by the above results, two Na-loaded samples were prepared. 25 g Beliplast zeolite was mixed with 250 ml 1 M NaCl solution at 80 °C for 4 h, then filtered, washed and dried. This exchange was performed either once or twice, to give Na1-Beliplast and Na2-Beliplast samples with differing levels of sodium (Table 1). The single-exchanged sample Na1-Beliplast showed a significant reduction in retention of nitrogen when compared with the Na-free Beliplast, with resulting $V_g$ and $\Delta H$ values being very similar to the natural Na-containing Anaconda sample (Table 2, Fig. 2). The further increased sodium loading of Na2-Beliplast caused a dramatic drop in the separation capacity, resulting in the co-elution of methane and nitrogen.

**Table 1** Unit cells (from XRF/TGA) and relative crystallinity (from XRD) of clinoptilolite samples used

| Clinoptilolite | Si | Al | Na | Ca | K | Fe | P | Mg | Ti | O | H₂O | Crystallinity (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Semnan | 28.25 | 7.53 | 2.68 | 0.26 | 1.24 | 0.54 | 0.29 | 0.34 | 0.05 | 72 | 14.48 | 83.2 |
| Anaconda | 28.02 | 7.74 | 2.25 | 0.66 | 2.24 | 0.22 | 0.22 | 0.42 | — | 72 | 19.29 | 83.7 |
| Nižný Hrabovec | 28.51 | 6.78 | — | 1.53 | 1.99 | 0.53 | 0.27 | — | 0.27 | 72 | 15.48 | 81.8 |
| Beliplast | 30.02 | 5.14 | — | 1.58 | 2.35 | 0.44 | 0.18 | 0.28 | 0.06 | 72 | 17.98 | 96.8 |
| Na1-Beliplast | 30.47 | 4.97 | 1.74 | 0.61 | 1.97 | 0.45 | 0.11 | 0.36 | 0.04 | 72 | 17.75 | 100.0 |
| Na2-Beliplast | 30.46 | 5.00 | 2.91 | 0.34 | 1.67 | 0.24 | 0.20 | — | 0.04 | 72 | 17.75 | 96.9 |
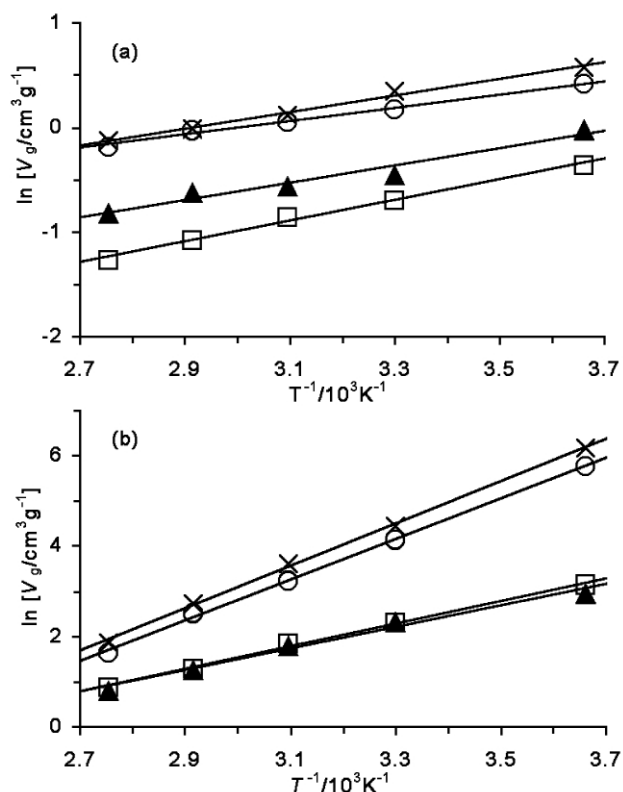
**Fig. 2** Retention of (a) methane and (b) nitrogen on clinoptilolites. [○ Nižný Hrabovec; □ Anaconda; × Beliplast; ▲ Na1-Beliplast].

This confirms that sodium is highly detrimental to methane/nitrogen separation using clinoptilolite. This could be attributed to the fact that sodium (ionic radius 0.95 Å) is located towards the centre of the 10-membered A channel, effectively blocking

**Table 2** Specific retention volume ($V_g$) at 30 °C and adsorption enthalpy ($-\Delta H$) for methane and nitrogen on different clinoptilolite samples

| | Methane | | Nitrogen | |
|---|---|---|---|---|
| Clinoptilolite | $V_g/cm^3g^{-1}$ | $-\Delta H/kJ$ $mol^{-1}$ | $V_g/cm^3g^{-1}$ | $-\Delta H/kJ$ $mol^{-1}$ |
| Anaconda | 0.50 | 8.23 | 10.2 | 19.8 |
| Nižný Hrabovec | 1.13 | 5.24 | 62.4 | 37.3 |
| Beliplast | 1.41 | 6.62 | 84.9 | 38.9 |
| Na1-Beliplast | 0.64 | 6.86 | 10.4 | 20.8 |

it at high concentrations (Fig. 1). In contrast, potassium (1.33 Å) sits at the outer edge of this channel, while calcium (0.99 Å) occupies the B channel, although the precise location of the cation sites varies with temperature.[3] Since the smaller 8-ring B and C channels are blocked by $Ca^{2+}$ and $K^+$ respectively, and their effective dimensions will not be affected by sodium concentration, channel A would appear to be the main separation-active site.

These zeolites also showed marked temperature dependence, with nitrogen adsorption increasing exponentially with the inverse of temperature (Fig. 2), while methane retention is influenced much less by temperature. This suggests that such adsorbents would be suitable for use in a temperature-swing separation process.

## Notes and references

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