



## Novel low energy hydrogen–deuterium isotope breakthrough separation using a trapdoor zeolite



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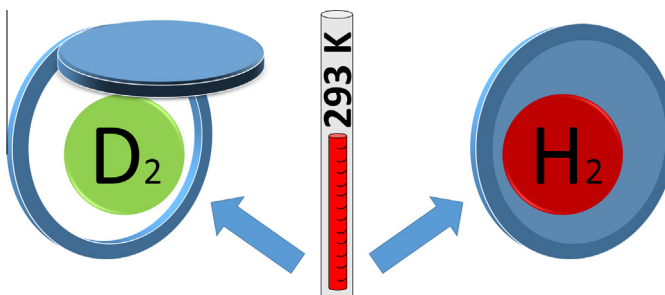
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### HIGHLIGHTS

- Packed beds of “trapdoor zeolite” result in breakthrough separation of H<sub>2</sub> isotopes.
- Breakthrough separation of <sup>1</sup>H and <sup>2</sup>H occurs at ~293 K.
- Interactions with trapdoor cations result in differences in breakthrough times.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Cs-chabazite, a type of zeolite with caesium counter-cations, possesses interesting gas separation properties due to a highly selective molecular “trapdoor” effect. Herein the use of this material for H<sub>2</sub>/D<sub>2</sub> isotope separation is demonstrated. Isotope separation was achieved using breakthrough separation with a single pass through a packed bed at moderate temperatures (293 K) and pressures (0.17 MPa) when one species was in a sufficiently low concentration. The breakthrough separation curves were successfully modelled using the Thomas kinetic breakthrough model and the Yoon and Nelson kinetic breakthrough model, where working transferable kinetic rate constants were developed. Use of this material for hydrogen isotope separation would significantly lower the total energy demand compared with current hydrogen isotope separation techniques such as cryogenic distillation and is applicable to separating out low concentrations of D<sub>2</sub> (0.0156%) present in standard grade H<sub>2</sub>.

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## 1. Introduction

Over the last two decades, there has been a clear change in trend across the global community towards sustainable sourcing and more efficient use of fuels and chemical feedstocks, specifically concerning reductions in the use of finite fossil fuels. This has been most apparent at the governmental level, with policies such as the

UK Low Carbon Transition Plan [1] and international legally binding agreements such as the Kyoto Protocol 2020 [2], which focus on reducing CO<sub>2</sub> emissions. These are significant drivers for developing and implementing alternative, low carbon energy sources. In line with this global trend, there has been major financial and resource investment into large international collaborative projects (totalling over £17 billion) for unconventional energy generation, such as the Joint European Torus (JET) [3], Canadian Deuterium Uranium Reactors (CANDU) [4], the International Thermonuclear Experimental Reactor (ITER) [5] and the Tokamak Fusion Test Reactor (TFTR) [6]. These projects use large quantities of the hydrogen

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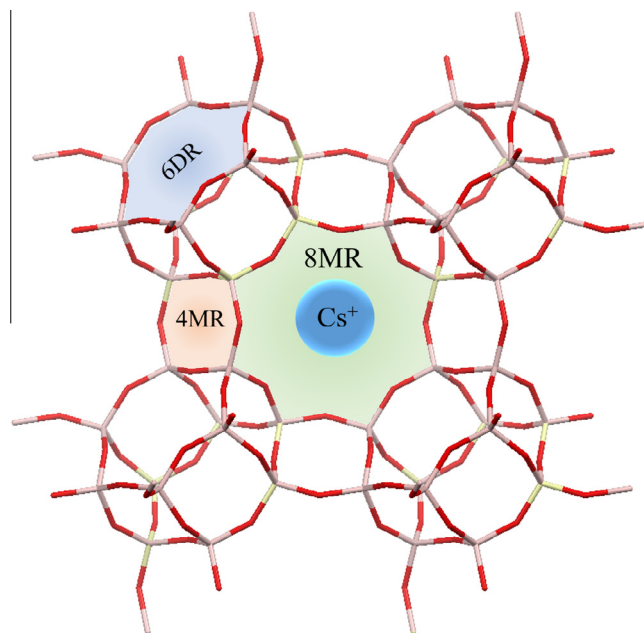
isotope deuterium ( $^2\text{H}$  or  $\text{D}$ ) as a feedstock fuel, which can cost up to €4000 per kg [7]. The demand for  $\text{D}_2$  would increase dramatically if any of these three technologies were implemented on a wider scale in the future. Aside from such projects, ultrapure hydrogen ( $\text{H}_2$ ) and deuterium ( $\text{D}_2$ ) are already in high demand for application as deuterated chemical tracers, deuterated research grade chemicals and nuclear reactor heavy water moderators [8–10], driving the need for reductions in production costs for both chemical feedstocks, even at current production levels.

The most common method of producing ultrapure  $\text{H}_2$  and  $\text{D}_2$  is through separation of the isotopes from standard grade  $\text{H}_2$  feedstock (standard grade  $\text{H}_2$  composition:  $\text{H} > 99.98\%$  and  $\text{D} < 0.0156\%$  [11]), which is generated from steam reforming of natural gas by means of the water–gas shift reaction [12]. However, this fossil fuel-based method is ultimately unsustainable. Thus, alternative sources and methods for producing large-scale standard-grade  $\text{H}_2$  and  $\text{D}_2$  are being researched [13–15]. The liquid-based Girdler-Sulfide enrichment process can be used for initial  $\text{D}_2$  enrichment of seawater up to  $\sim 20$  wt%, but this is used exclusively for heavy water production for the nuclear power industry and its use is in sharp decline due to the large financial cost of operation and large quantities of poisonous  $\text{H}_2\text{S}$  produced [16]. The gas phase separation of hydrogen isotopes can be achieved either by cryogenic distillation at  $\sim 33$  K [17,18], or through an absorption/chemisorption method using palladium (Pd) or vanadium (V) packed beds [19,20], both of which have extreme energy and financial cost penalties [21–22]. Other methods of hydrogen isotope separation have been investigated, but are uncommon due to the energy and financial costs [23–26].

There has been recent interest, by Hirscher et al. [27], in using nanoporous materials in a swing adsorption configuration (pressure, vacuum and temperature driven) for separating  $\text{H}_2$  and  $\text{D}_2$ . The research has focused on the use of metal-organic frameworks (MOFs) [28,29] which have achieved highly pure separations, but only with low working pressures (0.001 MPa), low mass throughputs and small sample sizes due to the difficulty and expense of MOF synthesis and the degradation of MOFs with cycling. Another family of nanoporous materials that holds promise for isotope separations are zeolites, due to their low cost of production, widespread availability and mechanical and chemical stability [30]. However, little research has been done to date on the use of zeolites for hydrogen isotope separation [31,32]. The common, naturally-occurring chabazite branch of the zeolite family is of special interest for isotope separations due to an unusual selective trapdoor phenomenon reported by Webley et al. [33].

Caesium ( $\text{Cs}^+$ ) chabazite ( $\text{Cs-CHA}$ ) has a three-dimensional structure that consists of double six-ring prisms (6DR) arranged in layers linked by tilted four-membered rings (4MR) – see Fig. 1. Although large supercavities ( $6.7 \times 10 \text{ \AA}$ ) exist in the structure, eight-membered rings (8MR) that are  $3.8 \text{ \AA}$  by  $3.8 \text{ \AA}$  in diameter function as highly selective doorways, providing the only access to the crystal interior (Fig. 1). A  $\text{Cs}^+$  cation is positioned energetically favourably in the centre of each of the 8MRs, balancing the charge of the framework and acting as selective aperture ‘trapdoors’ [34,35]. These trapdoors have a critical admission temperature ( $T_c$ ) that is different for every gas (e.g.  $T_c$  for  $\text{H}_2 = 333 \text{ K}$ ) [36], above which the trapdoor is considered ‘open’ and below which it is considered ‘closed’. However, some gases, such as  $\text{CO}_2$ , have been reported to either not have a  $T_c$ , or for the  $T_c$  to be so low as for the trapdoor to be deemed permanently open, allowing for free gas access to the internal microporous supercavities.

A material allowing selective  $\text{H/D}$  separation without the need for cryogenic temperatures would vastly reduce the energy cost of hydrogen isotope separation, in comparison with the cryogenic distillation method currently used.



**Fig. 1.** Framework diagram of the Cs-chabazite structure, showing the 4MR (peach), 6DR (light blue) and 8MRs (light green) overlaid in bold, created using a crystallographic information file (cif) from Mazzi et al. [37] and Mercury (v3.5.1) software. Red = O, pink = Si, yellow = Al. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Studies into the selective trapdoor phenomenon of the chabazite structure [34,36,37] have thus far not investigated the effect that the  $\text{H}_2$  and  $\text{D}_2$  may have on the cation trapdoor. However, differences in the interactions of  $\text{H}_2$  and  $\text{D}_2$  with the cation trapdoor are predicted, based upon research into hydrogen isotope interactions with beryllium cations by Artiukhin et al. [38] and lithium cations by Czerwiński [39]. Based on this hypothesis, we aimed to test whether the selective trapdoor could be used to separate  $\text{H}_2$  and  $\text{D}_2$  at moderate temperatures (293–343 K) and pressures (0.17–1.00 MPa).

## 2. Materials and methods

Caesium ( $\text{Cs}^+$ ) cation-exchanged chabazite zeolite material was synthesised in the Webley lab in accordance with previous reports [33]. Powder X-ray diffraction (PXRD) confirmed phase purity, thermogravimetric analysis (TGA) confirmed thermal stability up to 1173 K and  $\text{N}_2$  sorption isotherms at 77 K showed low  $\text{N}_2$  uptake, suggesting the pore-blockage for  $\text{N}_2$  access due to the molecular trapdoor effect. Note that the presence of a small proportion of pores of  $10 \text{ \AA}$  in width implies the existence of pore apertures not containing  $\text{Cs}^+$  cations due to localised  $\text{Al}^{3+}$  deficiencies [40] (see Figs. S1–4 in Supplementary Information).

Breakthrough isotope separation experiments were conducted on a bespoke Hiden Isochema Isotope Exchange (IsoEx) rig. This rig consisted of a tubular reactor (0.6  $\text{m}$   $\text{d}$  by 20 cm) held within a UniTemp BTZ-175E environmental chamber for precise reactor temperature control between 273 and 343 K, with an external reactor jacket heating coil for temperatures of 293–453 K (see Fig. 2). Hydrogen ( $\text{H}_2$ ), deuterium ( $\text{D}_2$ ) and argon (Ar) inlet pressures were controlled by three pressure transducers (GE Measurements and Control, PDCR 4020, 20 MPa) and gas flow was controlled by in-line mass flow controllers (Bronkhorst High Tech, M9208158C). A vacuum pump was used for in-line pre- and post-reactor degassing of the sample. A dynamic sampling mass spectrometer (Hiden Isochema, HPR-20 QCI) downstream of the reactor was used for exhaust gas detection.

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