Novel protium-deuterium isotope trapping and breakthrough separation using a molecular trapdoor

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**H₂: Haber-Bosch**
Ammonia for synthetic fertilisers

**H₂: Fischer-Tropsch**
Liquid hydrocarbon fuels

**H₂: Fuel cells**
Mobile clean power generation

**D₂: Research purposes**
Deuterated chemicals
Neutron facilities

**D₂: Nuclear power industry**
Heavy water moderators

**D₂: Fusion power fuel?**
(50 years away as always?)
Isotope separation

CH₄ → Steam reforming and separating

H₂O → Girdler Sulfide Process: 15-20% HDO

Breakthrough
relatively simple
breakthrough crossover
can have low purity
low throughput
can suffer from material degradation

Cryogenic distillation
good purity
energy intensive
difficult temp regulation
large initial capital investment

Electrolysis
simple
energy intensive
time consuming

→ Pure H₂ and D₂
Isotope separation

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  - breakthrough crossover
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- **Cryogenic distillation**
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  - energy intensive
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- **Electrolysis**
  - simple
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- **Molecular trapdoor?**

CH$_4$ → Steam reforming and separating

H$_2$O → Girdler Sulfide Process 15-20% HDO

→ Pure H$_2$ and D$_2$
Isotope separation

Is a molecular trapdoor material not just a molecular sieve?

Molecular trapdoor?
What is a molecular sieve?

Molecular sieve
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Kinetic diameter dependent
What is a molecular trapdoor?

Molecular trapdoor
What is a molecular trapdoor?

Molecular trapdoor

+ + + +

gas mix

A

B
What is a molecular trapdoor?

Molecular trapdoor

gas mix
What is a molecular trapdoor?

Kinetic diameter dependence

and

Cation interaction dependant
Chabazite (Cs)

A microporous zeolite material, with a 2.5 Si:Al ratio

3D framework made up of double 6 ringed prism layers connected by tilted 4 membered rings. Contains super cavities within the interior (6.7 x 10 Å)

8 membered rings have an unoccupied kinetic diameter of 3.8 Å (Cs kinetic diameter is 3.34 Å), which are the only accessible channels to the porous interior

Cs trapdoor has different critical open/closed temperatures for different gases

Shang, J. et al. JACS, 2012 134 (46), 19246-19253
To separate the hydrogen isotopes of protium and deuterium by complete packed bed breakthrough curve separation

To separate the hydrogen isotopes of protium and deuterium by manipulating the occupancy/state of the Cs trapdoors as an adsorptive-trapping method

To determine the specific mechanism responsible for the trap door characteristics of chabazite (Cs)
Project aims

1. Trapdoor characterisation
2. Breakthrough isotope separation
3. Trapping isotope separation
Characterisation

Trapdoor characterisation

Breakthrough isotope separation

Trapping isotope separation
Characterisation

HTP-1
Varying temperature He pycnometry

ASAP 2020
Volumetric sorption

IGA
Gravimetric sorption
CO$_2$ kinetic diameter: 3.30 Å
CH$_4$ kinetic diameter: 3.80 Å

Open pore aperture: 3.80 Å

May be down to maximum equilibration time ($t_{\text{max}} = 120$ min) being insufficient.
CO₂ kinetic diameter: 3.30 Å
CH₄ kinetic diameter: 3.80 Å

Open pore aperture: 3.80 Å

CO₂ desorption would not decrease below 2.4 wt% uptake under vacuum alone at 273 K. Heating to 343 K was required to release the trapped CO₂.
N\textsubscript{2} kinetic diameter: 3.64 Å
H\textsubscript{2} kinetic diameter: 2.89 Å
Ar kinetic diameter: 3.40 Å

Open pore aperture: 3.80 Å

No observable trapping, like what was seen with CO\textsubscript{2}, but difficult to observe volumetrically.

No H\textsubscript{2} adsorbed at 77 K and 1 bar, despite having the smallest kinetic diameter.
Characterisation – He pycnometry

One would expect the skeletal volume to decrease as the trapdoors open.

Volume at 360 and 373 K is approximately 25 times higher, so seems anomalous, although are within a similar range to other porous materials.

Future investigation is planned using a proton cation to remove the trapdoor properties, and varying temperature He isotherms.
Project aims

- Trapdoor characterisation
- Breakthrough isotope separation
- Trapping isotope separation
Breakthrough separation

Hiden Isochema IsoEx with a mass spec
D$_2$ takes much longer to breakthrough. Suggests that only the D$_2$ is passing through the caesium cation trapdoor (despite being closed) and is being slowed by a chromatographic effect (adsorbing/desorbing from pore to pore) in the porous interior of the chabazite.

The H$_2$ does not have access to the porous interior so is saved from the chromatographic effect.
Breakthrough separation

H$_2$ now taking longer to breakthrough. Suggests that the H$_2$ can now pass through the caesium cation trapdoor and is also being slowed by a chromatographic effect.

The breakthrough time of the D$_2$ did not change, which suggests that there is no critical open/closed temperature between 298-343 K and is independent of the occupancy.
For a $1 \times 1$ cm packed bed of chabazite (Cs) with the trapdoors closed, there was a possible 22 minute complete breakthrough separation, and a possible 140 minute partial breakthrough separation.

Further breakthrough isotope separation experiments have been planned using a 50:50 gas mixture of $H_2:D_2$. 
Project aims

1. Trapdoor characterisation
2. Breakthrough isotope separation
3. Trapping isotope separation
Trapping separation

Full H$_2$ breakthrough with trapdoors open (343 K), then the trapdoors closed (298 K) before H$_2$ flow stopped.
Trapping separation

Full H$_2$ breakthrough with trapdoors open (343 K), then the trapdoors closed (298 K) before H$_2$ flow stopped.

Outgassed for 4 hours
Trapping separation

Full H₂ breakthrough with trapdoors open (343 K), then the trapdoors closed (298 K) before H₂ flow stopped.

Outgassed for 4 hours

Full Ar breakthrough with trapdoors closed (Ar used as a carrier gas).

Shows D₂ flowing from the chabazite despite no D₂ used in the experiment.
Trapping separation

Full H₂ breakthrough with trapdoors open (343 K), then the trapdoors closed (298 K) before H₂ flow stopped.

Outgassed for 4 hours

Full Ar breakthrough with trapdoors closed (Ar used as a carrier gas).

Shows D₂ flowing from chabazite despite no D₂ used in the experiment.
Trapping separation

Full H₂ breakthrough with trapdoors open (343 K), then the trapdoors closed (298 K) before H₂ flow stopped.

Outgassed for 4 hours

Trapdoors opened, releasing the trapped H₂.

Shows that D₂ and H₂ can be separated from an ultrapure hydrogen gas stream.
Trapping separation

Full $\text{H}_2$ breakthrough with trapdoors open (343 K), then the trapdoors closed (298 K) before $\text{H}_2$ flow stopped.

Outgassed for 4 hours

Trapdoors opened, releasing the trapped $\text{H}_2$.

Shows that $\text{D}_2$ and $\text{H}_2$ can be separated from an ultrapure hydrogen gas stream.
Trapping separation

Shows not only that H\textsubscript{2} has been trapped from the initial pure H\textsubscript{2} feed and controllably released by the manipulation of the caesium trapdoor/occupancy, but that some D\textsubscript{2} has also been trapped.

The D\textsubscript{2} concentration in the H\textsubscript{2} stream was $<0.0034\%$ (ultrapure H\textsubscript{2}), so this could possibly represent a significant mass percentage capturing of the residual D\textsubscript{2}.

Further breakthrough isotope separation experiments have been planned using a 50:50 gas mixture of H\textsubscript{2}:D\textsubscript{2}, and standard (non-ultrapure) hydrogen.
Conclusions

• Interesting He-Pyc results showing a large skeletal volume increase at elevated temperatures, which is the inverse of what was expected. Further work is planned on refining the exact critical open/closed conditions for a range of gases.

• D₂ is largely independent of the Cs trapdoor occupancy/position, whereas H₂ is highly dependent. Thus, complete breakthrough isotope separation seems possible.

• Determined that D₂ can be captured and separated from an ultrapure H₂ gas stream by the manipulation of the Cs trapdoor.
Thank you for listening

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AWE
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