Supporting Information

Chemical Affinity of Ag Exchanged Zeolite for Efficient Hydrogen Isotope Separation

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**Thermal desorption spectroscopy (TDS)**

*TDS Procedure details for pure H\textsubscript{2} or D\textsubscript{2} desorption study.* Firstly, the sample is activated in an ultrahigh vacuum (UHV) at 500 K, and then cool to RT. The sample is exposed to D\textsubscript{2} or H\textsubscript{2} atmosphere (10 mbar). Afterwards, the sample is rapidly cooled to the boiling temperature of the adsorbed gas, and the gas molecules that had not been adsorbed were pumped out. Finally, a linear heating ramp (0.1 K·s\textsuperscript{-1}) is applied. The desorbing gas is continuously detected using a quadrupole mass spectrometer, recognizing a pressure increase in the sample chamber when gas desorbs. The area under the desorption peak is proportional to the desorbing amount of gas, which can be quantified after careful calibration (by Pd\textsubscript{95}Ce\textsubscript{5} alloy) of the TDS apparatus.
**TDS Procedure details for hydrogen isotope separation.** The sample chamber is in an ultrahigh vacuum (UHV) at RT, and cool down to aimed temperature at 25 K, 40 K, 60 K, 77 K and 90 K, respectively. Then, the sample is exposed to a defined 1:1 D₂/H₂ mixture atmosphere (3, 10, 30 and 60 mbar) for 10 min. After 1:1 D₂/H₂ mixture loading at the given exposure temperature and pressure, the gas molecules that had not been adsorbed were pumped out. Afterwards, the sample is rapidly cooled to the boiling temperature of the adsorbed gas. Finally, a linear heating ramp (0.1 K·s⁻¹) is applied in order to thermally activate desorption. The desorbing gas is continuously detected using a quadrupole mass spectrometer, recognizing a pressure increase in the sample chamber when gas desorbs. The area under the desorption peak is proportional to the desorbing amount of gas.

**Calibration of the mass spectrometer signal.** A solid piece of a diluted Pd alloy Pd₀₉₅Ce₅ (~0.5 g) was used for calibration. Before the calibration, the oxide layer of the alloy was removed by etching with aqua regia. Then the alloy was heated up to 600 K under high vacuum to remove any hydrogen that might be absorbed during the etching procedure. Afterwards, it was exposed to 40 mbar pure H₂ or pure D₂ for 1.5–2.5 h at 350 K after the mass had been collected. As H and D were bound preferentially to the Cerium atoms at low exposure pressures, the alloy could be
handled under ambient conditions for a short time. The alloy was weighed after being cooled down to room temperature. The mass difference between unloaded state and loaded state was equal to the mass uptake of hydrogen or deuterium, respectively. After weighing, the alloy was loaded in the chamber again, and then a 0.1 K·s⁻¹ heating ramp (RT to 600 K) was applied for a subsequent desorption spectrum. The obtained mass of gas is directly corresponded to the area under the desorption peak.
Evaluation of the desorption energy

Desorption energy can be determined via *Kissinger* method\(^1\) by employing desorption spectra recorded with different heating rates. After exposure to a 10mbar H\(_2\) or D\(_2\) pure gas at 60K the thermal desorption spectra have been recorded applying different heating rates of 0.01, 0.05, 0.1 and 0.2 K·s\(^{-1}\). The desorption maxima for both H\(_2\) and D\(_2\) show a clear shift to lower temperatures for slower heating rates indicating a thermally activated desorption process.

For an adsorbed gas molecule, the desorption process can be described by the Polanyi-Wigner equation for first order with the assumption that the pre-exponential factor and the desorption energy are independent of coverage:

\[
-\frac{d\theta}{dT} = \nu \cdot \exp\left(-\frac{E_{des}}{RT}\right) \cdot \theta
\]  
(Equation S1)

where \(\theta\) is the referred to as the surface coverage, \(\nu\) is the frequency factor, \(E_{des}\) is the activation energy for desorption, \(R\) is referred to the gas constant and \(T\) the measured temperature.

Considering the assumption that the surface coverage at the maximum temperature is independent of the heating rate, the temperature of the maximum desorption rate \(T_{max} = T\) \((max \ r_{des})\) is determined. The activation energy derivated from a plot \(ln(T_{max}^2/\beta)\) vs. \(1/T_{max}\) is described as follows.
For \( T = T_{\text{max}} \), the following condition must be fulfilled,

\[
\left. \frac{dr_{\text{des}}}{dT} \right|_{T_{\text{max}}} = 0 \quad \text{(Equation S2)}
\]

Because of,

\[
r_{\text{des}} = -\frac{d\theta}{dT} = -\beta \cdot \frac{d\theta}{dT} \quad \text{(Equation S3)}
\]

The equation 1 can be rewritten as

\[
0 = \left. \frac{dr_{\text{des}}}{dT} \right|_{T_{\text{max}}} = n \cdot \Theta^n - 1 \cdot \frac{d\theta}{dT} + \Theta^n \cdot \frac{E_{\text{des}}}{RT_{\text{max}}^2} \quad \text{(Equation S4)}
\]

For the first-order desorption process (\( n = 1 \)), substituting \( d\theta/dT \) by equation 1, and solving for

\[
\frac{E_{\text{des}}}{RT_{\text{max}}^2} \text{ obtains}
\]

\[
\frac{E_{\text{des}}}{RT_{\text{max}}^2} = \frac{v_1}{\beta} \cdot \exp \left( -\frac{E_{\text{des}}}{RT_{\text{max}}} \right) \quad \text{(Equation S5)}
\]

Desorption energy can be obtained from the slope by plotting \( \ln \left( \frac{\beta}{RT_{\text{max}}^2} \right) \) vs. \( 1/T_{\text{max}} \) for a series of heating constant.
Figure S1. (Top) TG/DSC measurement of fully exchanged Ag-Y measured in argon flow.

(Bottom) QMS signal of O₂ recorded simultaneously with the TG/DSC data.
Figure S2. (Top) Nitrogen sorption isotherm of exchanged Ag-Y at 77K. (Bottom) Argon sorption isotherm of exchanged Ag-Y at 87K. Closed and open symbols represent the absorption and desorption of the sample.
Figure S3. H$_2$ (black) and D$_2$ (red) desorption spectra of 1:1 D$_2$/H$_2$ mixture exposure on zeolite AgY at T$_{\text{exp}}$ of 60 K for various exposure pressure (1, 10, and 100 mbar).
Figure S4. a) The adsorbed amount of isotope gases (H\textsubscript{2} black, D\textsubscript{2} red) and their total amount (blue) as function of exposure pressure obtained at T\textsubscript{exp} of 60 K. b) The D\textsubscript{2}/H\textsubscript{2} selectivity as function of exposure pressure.
Figure S5. a) Hydrogen and b) deuterium desorption spectra of a 10 mbar 1:1 D$_2$/H$_2$ mixture exposure on zeolite AgY at exposure temperature of 60 K for various exposure time, 1 (green), 5 (orange), 10 (red), 30 (navy), and 120 (blue) min.
Figure S6. a) The adsorbed amount of isotope gases (H$_2$ black, D$_2$ red) and their total amount (blue) as function of exposure time obtained at $T_{\text{exp}}$ of 60 K. b) The D$_2$/H$_2$ selectivity as function of exposure time.
Figure S7. Thermal desorption curves for $\text{H}_2$ (left, square) and $\text{D}_2$ (right, circle) recorded at heating rates: 0.2 (olive), 0.1 (red), 0.05 (blue), 0.02 (green) K/s for zeolite AgY exposed to a 10 mbar gas atmosphere at 60 K. The minute shoulders/peaks on the low temperature side of the signals are likely caused by hydrogen/deuterium molecules adsorbed physically in cages of the zeolite Y framework at cryogenic temperature.
Figure S8. Kissinger plots for the desorption of H$_2$ (left, red) and D$_2$ (right, black) from AgY loaded at 60K.
Table S1. Summary of experimentally measured hydrogen isotope separation performance on various porous materials.

| Compound         | $T_{exp}$(K) | Selectivity (D$_2$/H$_2$) (1:1 Mixture) | Adsorbed D$_2$ amount (mmol/g) | Ref. |
|------------------|--------------|-----------------------------------------|--------------------------------|------|
| MFU-4 (Zn, Cl)   | 40           | 6.9                                     | 0.02                           |      |
|                  | 50           | 5.8                                     | 0.40                           | 2    |
|                  | 60           | 7.5                                     | 1.24                           |      |
| Py@COF-1         | 22           | 9.7                                     | 0.50                           | 3    |
|                  | 30           | 7.9                                     | 0.60                           |      |
| Cu(I)-MFU-4I     | 90           | 7.1                                     | 1.5                            | 4    |
| Fe-MOF-74        | 77           | 2.5                                     | /                              | 5    |
| Co-MOF-74        | 77           | 3.2                                     | /                              |      |
| Ni-MOF-74        | 77           | 5                                       | /                              |      |
| ZIF-7            | 20           | -                                       | /                              | 6    |
| ZIF-8            | 20           | 11                                      | /                              |      |
| COF-1            | 20           | 7                                       | /                              |      |
| COF-102          | 20           | 1                                       | /                              |      |
| CPO-27-Co        | 60           | 11.8                                    | 2.7                            | 7    |
| IFP-1            | 30           | 2.0                                     | 9.30                           |      |
| IFP-3            | 30           | 2.8                                     | 2.49                           | 8    |
| IFP-7            | 77           | 1.5                                     | 0.05                           |      |
| IFP-4            | 77           | 2.1                                     | 0.01                           |      |
| Zeolite 5A       | 30           | 2.7                                     | 4                              | 9    |
| CC3              | 30           | 1.7                                     | 3.67                           | 10   |
|                  | 50           | 1.8                                     | 1.20                           |      |
| 6FT-RCC3         | 30           | 2.2                                     | 2.81                           |      |
|                  | 50           | 3.0                                     | 0.78                           |      |
| Material          | 20 | 40 | 60 |
|------------------|----|----|----|
| 6ET-RCC3         | 30 | 3.9| 0.39|
|                  | 50 | 1.8| 0.32|
| Cocyst1          | 30 | 8.0| 4.72|
| MIL-53(Al)       | 40 | 10.5| 2.3 |
| MOF-74           | 77 | 19 | 3.5 |
| MOF-74-IM-10     | 77 | 26 | 4   |
| MOF-74-IM-38     | 40 | 12.5| 1   |
| 5A/GE2           | 77 | 1.07| 5.40|
| CoFA             | 25 | 16.6| 5.5 |
| ZIF-67@NH₂-SiO₂  | 77 | 1.52| /   |
| FMOFCu           | 25 | 14 | 0.1 |
|                  | 77 | 4  | 0.05|
| Ag(I)-ZSM-5      | 77 | 8.7 | 0.06|
| Cu(I)-ZSM-5      | 100| 24.9| 0.05|
| SIF SIX-1-Cu     | 20 | 7.1 | 0.1 |
| SIF SIX-3-Zn     | 20 | 5.0 | 0.9 |
| SIF SIX-3-Cu     | 20 | 3.5 | 0.06|
| SIF SIX-3-Ni     | 20 | 1.9 | 0.8 |
| HKUST-1          | 20 | 17 | 17.9|
| FCTF-1-400       | 20 | 12.8| 19.5|
| STAM-1           | 20 | 9.9 | 2.8 |
| Cu-PYC           | 20 | 2.2 | 10.3|
| CPO-27(Co)       | 20 | 3.0 | 13.8|
| KAUST-7          | 20 | 9.8 | 0.37|
| FJI-Y11          | 77 | 1.76| /   |
| Ni₂Cl₂BBTA       | 77 | 4.5 | 1.7 |
| Ag(I)-Zeolite Y  | 90 | 10 | 3   |

This work
Figure S9. Cutout from zeolite Y framework showing main motifs including two sodalite cages (sod), a hexagonal prism (hpr) and a supercage (spr). Vertices signify T sites of the framework (Si or Al atoms); oxygen atoms omitted for clarity. Green spheres show extra framework cation sites I, I’ and II.
Computational errors

**Treatment of vibrational modes.** For the calculation of the thermodynamic properties, we use the harmonic approximation and only allow motion of the six degrees of freedom of the H$_2$ molecule. To validate this minimal approach, we compare it with a reference where only the terminal O–H groups are frozen in space and the rest of the cluster is allowed to vibrate. For these calculations, we use the generic models we have introduced in a previous publication$^{22}$ as well as versions of the generic model with one water molecule adsorbed at Ag$^+$. 

A comparison of both approaches shows that the modes from the minimal approach have almost perfectly matching counterparts in the reference approach. The vibrational frequencies of corresponding modes agree within 20 cm$^{-1}$ and the total error of the zero-point energy is less than 0.2 kJ·mol$^{-1}$. The zero-point energy of the six modes of D$_2$ is underestimated, both in absolute terms and with respect to those of H$_2$, leading to a slight overestimation of the D$_2$/H$_2$ selectivity.

In the reference model, the remaining vibrational modes are almost identical irrespective of whether H$_2$ or D$_2$ is adsorbed at the Ag$^+$ site. Overall, these modes slightly favor the adsorption of D$_2$ over that of H$_2$, thereby cancelling out some of the above overestimation.
We conclude that the additional error incurred by the minimal vibrational treatment on the quantities relevant for the calculation of the selectivities, namely the *differences* between the adsorption energies of $\text{D}_2$ and $\text{H}_2$ should be very low and on the order of 0.1 kJ·mol$^{-1}$.

**Computational level for single-point calculations.** Previous experience$^4$, $^{23}$ shows that PBE0-D3(BJ) combined with typical triple- or quadruple-zeta basis sets is a robust method to estimate $\text{H}_2$ adsorption energies when the interaction is dominated by charge transfer effects. Ag-Y with an adsorption energy in the 30…40 kJ·mol$^{-1}$ range would be considered to be such a system. However, the introduction of water leads to a considerable reduction of the $\text{H}_2$ adsorption energy for some structures and dispersion interactions make up a larger share of the total interaction energy. A correlated wavefunction approach, which natively includes dispersion interactions therefore becomes desirable and this is our rationale for resorting to the DLPNO-CCSD(T) method. While TightPNO cutoffs would be desirable for very weak interactions, these cutoffs are prohibitively resource-consuming for the systems at hand and the accuracy afforded by NormalPNO should be sufficient given the strength of the interaction.
Figure S10. Comparison of DLPNO-CCSD(T) single-point energies for the adsorption of H₂ calculated with def2-TZVPP (x axis) and def2-QZVPP (y axis).

With NormalPNO cutoffs, the generous def2-QZVPP basis is still within reach for the systems with up to one molecule of water. Where possible, we compare this larger basis set with the more economical def2-TZVPP basis set. Like in prior studies we note that the differences between the reaction energies are small and def2-TZVPP predicts slightly weaker binding with a maximum deviation of +3.0 kJ·mol⁻¹, a minimum deviation of -0.6 kJ·mol⁻¹ and average and root-mean-square deviations being -1.6 and 1.9 kJ·mol⁻¹, respectively (see Figure S10). We explain this effect with a comprehensive error cancellation between basis set superposition error (overestimating the
strength of the interaction) and basis set incompleteness error (underestimating the strength of the dispersion interaction), the latter apparently being slightly dominant. From a practical point of view, this justifies the use of def2-TZVPP.

**Figure S11.** Comparison of single-point energies for the adsorption of H$_2$ calculated with DLPNO-CCSD(T)/def2-TZVPP (x axis) and PBE0-D3(BJ)/def2-QZVP (y axis).

Figure S11 shows the correlation between PBE0-D3(BJ)/def2-QZVP and DLPNO-CCSD(T)/def2-TZVPP single-point energies. It is apparent that the former overestimates the interaction by 5…10 kJ·mol$^{-1}$ with respect to the latter. The error appears to be rather systematic,
so we expect this DFT method to be a robust predictor of trends for the system at hand where DLPNO-CCSD(T) becomes too expensive.

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