

Structural insight into hydrogen isotope separation mechanism in a ultramicroporous material

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Separating H₂/D₂ mixtures is one of the most challenging issues in modern separation science and technology since the isotopes have identical size, shape and thermodynamic properties. Current technologies using through cryogenic distillation or Girdler-sulfide process are energy intensive and inefficient (selectivity is often less than 2.5). A promising alternative is the use of porous materials to separate directly gaseous mixture of isotopes based on kinetic quantum sieving (KQS),¹ in which D₂, which has a shorter de Broglie wavelength than H₂, can diffuse faster through the confined pore at a cryogenic temperature. Various porous materials have demonstrated the quantum separation mechanism, including metal-organic frameworks²⁻⁴, covalent organic frameworks⁵, and organic porous molecules⁶. Consequently, the best separation factor of .6 at 40 K was reported by utilizing the KQS effect⁸. However, due to weak binding energies of hydrogen isotopes on the surface of porous media, the separation approach based on KQS exhibits significant selectivity only at cryogenic temperatures, which still requires huge energy consumption, limiting its practical applications. To overcome this limitation, the chemical affinity quantum sieving (CAQS) effect has been developed⁷, where the heavier isotope has a stronger interaction with strong adsorption sites due to its lower zero-point energy. Our group has reported an outstanding experimental value of D₂/H₂ selectivity of 11.8 at 60 K in CPO-27-Co⁹ and a selectivity of 11 at the enhanced temperature of 100 K in Cu(I)-MFU-4l¹⁰. Recently, hydrogen isotope separation has been investigated on a porous crystal MTZ by the in-house designed cryogenic thermal desorption spectroscopy after exposure to hydrogen isotope mixtures. By exploiting controllable parameters such as temperature and pressure, the thermal desorption spectrum shows a single desorption peak with a temperature shift of 6 K between H₂ and D₂. The D₂/H₂ selectivity is increasing with temperature and pressure, reaching its maximum of 32 at 60 K from an equimolar isotope mixture, which is the highest ever recorded. Since the natural abundance of deuterium is much lower than in a 1:1 isotope mixture, we also prepared a mixture containing only 5% D₂. After exposing to the sample, D₂ is enriched to 75% after only one cycle, demonstrating the capacity of MTZ for a practical application of hydrogen isotope separation. To better study the potential adsorption sites of hydrogen isotopes within the cavities of MOF and to address the structural confinement for the possible pore condensation. Neutron diffraction experiment under conditions relevant for the isotope separation process was carried out at the POWGEN instrument at SNS, shedding light to the isotope separation mechanism.

References

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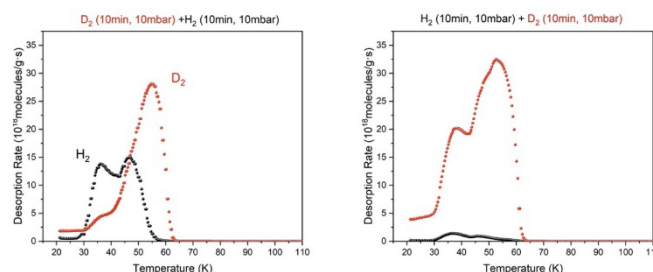


Figure 1