

Kinetics & thermodynamics of CH₄ storage in porous solid aided clathrates

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Clathrate hydrates are inclusion compounds consisting of a host lattice, formed by hydrogen bonded water molecules, in which gas molecules, such as CH₄, CO₂ and H₂ can reside by attractive van der Waal's forces with the host. Typically, these structures are formed at elevated pressures and temperatures around or below the freezing point of water. In the past, clathrates were merely regarded an obstacle in gas and oil transportation due to spontaneous formation in pipelines leading to flow assurance problems. Recently, however, they have received increased attention as medium to store gases, given their non-explosivity, environmentally benign nature, moderate storage conditions, low production cost, low risk of handling and high volumetric storage capacity, i.e. up to 160 m³ CH₄ (at 0 °C and 1 bar) is stored in 1 m³ CH₄ clathrate [1].

Clathrate formation in bulk water is hampered by low water to hydrate conversions, high pressures to initiate formation and slow nucleation and growth kinetics. A promising solution is the use of nanoporous materials to confine the water phase (Figure 1). Under nanoconfinement the gas-liquid interface is increased compared to bulk water, allowing clathrate formation to occur at milder conditions, with improved kinetics and with increased gas storage [2]. However, while plenty of research has been devoted to identifying moderately hydrophobic mesoporous materials as optimal clathrate formation promoters in terms of formation pressure and gas uptake, quantitative kinetic data of confined clathrate nucleation, growth and reformation is greatly underrepresented. Yet this is crucial for the potential of clathrates as a future energy storage medium.

Two high-pressure experimental setups were developed in-house to quantitatively monitor the kinetics and thermodynamics of solid aided clathrate formation. A gravimetric system was constructed by changing the electronics and software of a magnetic suspension balance, allowing the highly accurate and direct monitoring of gas uptake/release kinetics during clathrate formation/dissociation, respectively. A robust volumetric system was built to mimic the future gas uptake/release process in a storage vessel. Hence, the poster will cover results of nucleation, growth and reformation of methane clathrates aided by mesoporous silicas (hydrophobized SBA-15) showing the effect of temperature, pressure, water loading and multiple reformations on the kinetics and thermodynamics of methane clathrate formation.

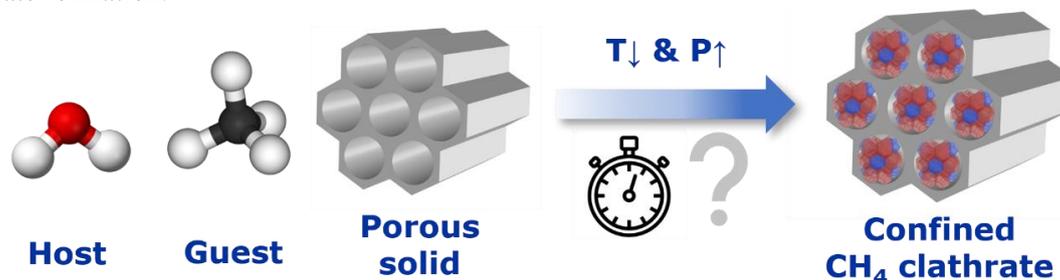


Figure 1: Graphical representation of porous solid aided (confined) CH₄ clathrate formation, highlighting the need for quantitative kinetic data. Crystal cages of CH₄ clathrate are depicted in partially transparent red & blue.

References

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