

Characterization of methane and CO₂ hydrates intercalated on smectites by means of atomistic calculations.

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Gas hydrates are crystalline compounds consisting of gas molecules encaged in cavities of a hydrogen-bonded network of water molecules. Gas hydrates are characterized by the general formula $X \cdot n\text{H}_2\text{O}$, where X is the guest molecule within a water cage, and n is the hydration number per guest molecule. Three different gas hydrate structures can be found: sI, sII and sH (Sloan, 1998). Cubic sI structure consists of 46 water molecules per unit cell, forming two dodecahedron (small 5^{12}) and six tetradecahedron (large $5^{12}6^2$) cages and is formed when small guest molecules such as methane or carbon dioxide are trapped.

Methane hydrates are found in permafrost regions and sediments of the ocean floor in outer continental margin regions where medium pressures and low temperatures can be reached. Gas Hydrates are important on Earth's system because hydrate decomposition would cause the methane release into atmosphere (high greenhouse gas) causing great impact on Earth's climate. On the other hand, these natural gas hydrates are seen as a potential major energy resource. Hence, the knowledge of stability and physical-chemical properties of methane hydrate crystal structure is important for evaluating some new green becoming technologies such as, strategies to produce natural gas from marine methane hydrates and simultaneously store CO₂ as hydrates.

Clay minerals like smectites are major constituents of ocean sediments, the study of interactions between these minerals with hydrates on the seafloor can be useful to determine variations on hydrate stability field, and to know the properties and behavior of hydrate-smectite complex. Characterization and better understanding of those deposits are necessary to develop CO₂ storage as hydrates by methane replacement, and to explore these chlatrates in other planets.

Swelling clays such as montmorillonite usually contains multiple planes of weakly bonded H₂O in the interlayer between the 2:1 (silicate) layers. Koster van Groos et al. (2009) synthesized a smectite–methane hydrate intercalate with $d(001)=2.2$ nm indicating the presence of one unit cell of methane hydrate crystal intercalated between the 2:1 layers of smectite. Probably the presence of phyllosilicates stabilizes the methane hydrates.

Due to the complexity of experimental studies with hydrates, Computational Mineralogy can be very helpful. In this study we compare the behavior of CO₂ and methane hydrates intercalated in montmorillonite and beidellite. We have reproduced the crystal lattice structure of methane and CO₂ hydrates and their spectroscopic properties. Our results are in agreement with the appearance of a $d(001)$ value of ~ 2.2 nm in both types of hydrates intercalated as crystal lattice in beidellite and montmorillonite. However, comparing mean square displacement (MSD) profiles from molecular dynamics simulations of H₂O molecules in the hydrates, we found that hydrate crystal MSD show a typical solid profile without diffusion, while in the intercalates there is more diffusion of water molecules, indicating that CO₂ and methane hydrate structure is more flexible and stable in the smectite-hydrate complex. The aim of this work is to contribute to a better understanding of the crystalline structure of CO₂ hydrates and study the liability of the smectite-hydrate complex by theoretical approaches.