

CH₄-CO₂ Replacement Mechanism and Kinetics in Zeolitic Ice: Revealing the Double Occupation Mechanism

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Summary: The CH₄-CO₂ replacement in the nonporous “zeolitic ice” or gas hydrates is a promising approach for not only combined carbon capture and sequestration (CCS) but also for energy extraction, but its industrial application is limited by the lack of a clear understanding of the diffusion mechanism and kinetics ^[1] . Reliable data on the amount of recoverable methane and CO₂ storage capacity in hydrates are also missing. In this study, DFT calculations using the vdW-DF2 method were used to investigate the adsorption interactions of CH₄ and CO₂ in sl clathrate hydrates, and the thermodynamic stability of the system was evaluated. The maximum storage capacity of CH₄ and CO₂ in sl clathrate cages was calculated to be 12.3 and up to 42.9 wt%, respectively. The replacement mechanism was found to occur mainly in the large cage (5¹²6²) via a “double occupation mechanism,” which facilitates both CO₂ and CH₄ diffusion through the large cage channel. The diffusion energy barrier of CH₄ and CO₂ was found to be significantly lower using this mechanism, at 0.525 and 0.307 eV, respectively, compared to 1.066 and 0.416 eV using the traditional “hole-in-cage-wall” scenario which proposes the dislocation of a water molecule in the solid crystal ^[2]. However, the replacement process was found to be less probable in small cages in the case of pure CH₄-CO₂ exchange due to the high energy barrier of methane diffusion. The estimated diffusion energy barrier of methane between empty small and large cages was 1.156 eV, while that of replacing CO₂ was 0.725 eV. Finally, the viability of the replacement process was confirmed under realistic pressure and temperature conditions from Gibbs free energies and equilibrium constant value obtained via quasi-harmonic approximation approach. The proposed mechanism overcome the drawbacks of the “hole-in-cage-wall” scenario and the results agrees well with experimental observations and can be a basis of diffusion kinetics studies and estimation the economic feasibility of the replacement process.

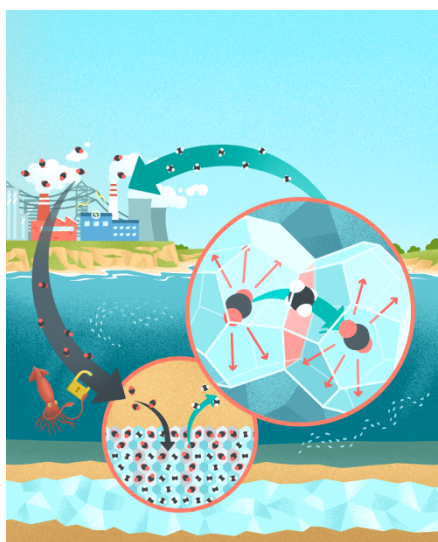


Fig. 1 Graphical Abstract of Simultaneous CCS and Energy Recovery in Zeolitic Ice

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