Hydrate thermal dissociation behavior and dissociation enthalpies in methane-carbon dioxide swapping process - DTU Orbit (03/04/2019)

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The swapping of methane with carbon dioxide in hydrate has been proposed as a potential strategy for geologic sequestration of carbon dioxide and production of methane from natural hydrate deposits. However, this strategy requires a better understanding of the thermodynamic characteristics of CH₄ and CO₂ hydrate as well as (CH₄ + CO₂) or (CH₄ + CO₂ + N₂) mixed hydrates (since (CO₂ + N₂) gas mixture is often used as the swapping gas), along with the thermal physics property changes during gas exchange. In this study, a high pressure micro-differential scanning calorimetry (HP μ-DSC) was performed on synthesized gas hydrates to investigate the dissociation behavior of various hydrates. The hydrate dissociation enthalpies were determined by both μ-DSC measurement and Clapeyron equation. For the single guest molecule hydrate system, the average dissociation enthalpies of CH₄ hydrate and CO₂ hydrate measured by integrating the endothermic peak area are 55.01 kJ·mol⁻¹ and 58.96 kJ·mol⁻¹, respectively, which are very close to the values calculated by Clapeyron equation. However, in the multicomponent guest hydrates system, the μ-DSC measured dissociation enthalpies of the (CH₄ + CO₂) binary hydrates and (CH₄ + CO₂ + N₂) ternary hydrates are a little higher than that of Clapeyron equation, it was found that their dissociation enthalpies are located between the limiting values of pure CH₄ hydrate and CO₂ hydrate, increasing with the mole fraction of CO₂ in hydrate phase. By monitoring the heat flow changes with the μ-DSC apparatus, it was observed that there was no noticeable dissociation or reformation process of hydrate occurring in the CH₄ − CO₂/(CO₂ + N₂) swapping, which indicates that most CH₄ hydrate forms (CH₄ + CO₂) or (CH₄ + CO₂ + N₂) mixed hydrates directly instead of dissociating into liquid water or ice first. The dissociation equilibrium data obtained from the endothermic thermograms of the mixed hydrates after CO₂ and (CO₂ + N₂) swapping demonstrates that about 66% and 85% of CH₄ in hydrate phase are replaced, respectively.

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