

# Calorimetric studies on the dissociation characteristics of methane hydrates in porous media

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Methane as main component of natural gas is currently considered one of the most important alternative fuels. However, one major drawback is its low volumetric energy storage density. Thus, an efficient solution for mobile storage is urgently needed. A promising approach is the storage of gas in hierarchically ordered porous media by combining gas adsorption in intra-particle pores and hydrate formation in the wetted inter-particle spaces. This technique is assumed to be a promising alternative to conventional storage methods, e. g. compressed or liquefied gas at moderate pressures and temperatures.

Here, we will present our recent research work that focusses on the dissociation characteristics of methane hydrates in different porous media using calorimetric methods. A high-pressure Setaram microDSC7 evo is used to measure dissociation enthalpies ( $\Delta H$ ) and phase equilibria data. Since the calorimeter cells do not have a stirrer, a multi-cycle method is adopted [1]. Each cycle is composed of a deep cooling phase followed by a heating phase to a temperature above the freezing point of water but lower than the temperature of dissociation of methane hydrates. Thus, the free water is crystallized and then liquefied during each cycle, while the hydrate quantity gradually increases during the process overall. Hereafter, we determined the dissociation profiles as well as the equilibrium temperature and equilibrium pressure of methane hydrates during melting in porous media [2]. The results demonstrate that the developed calorimetric procedure is suitable for the characterization of dissociating methane hydrates in porous media. The enthalpy determined by baseline integration of the peak for pure CH<sub>4</sub>-hydrates matched literature values [3] very well (deviations < 2 %). Additionally, a new kind of filling aid was developed to place wetted porous samples inside the cell. Based on the experimental results it can be shown that the methane storage capacity of wet adsorbent material is significantly enhanced by gas hydrate formation. In comparison to dry adsorbent material, the excess storage capacity could be increased by up to 150 %.

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