Experimental report

16/12/2022

Proposal:	**7-04-173**	**Council:**	4/2019
Title:	Methane hydrate formation in hydrophilic and hydrophobic porous modelcarbons		
Research area:	Other...		

This proposal is a resubmission of 7-04-170

Main proposer:	**Mirian CASCO**
Experimental team:	Mirian CASCO Sven GRAETZ
Local contacts:	Monica JIMENEZ RUIZ

Samples:
Hydrophilic ordered mesoporous carbon (HOMC)
Hydrophobic ordered mesoporous carbon (OMC)
Hydrophobic ordered mesoporous carbon + D2O (OMC+D2O)
Hydrophilic ordered mesoporous carbon + D2O (HOMC+D2O)

Instrument	Requested days	Allocated days	From	To
IN1 LAG	5	4	27/09/2021	01/10/2021

Abstract:

The proposal aims to evaluate the formation of methane hydrate in the cavities of hydrophobic and hydrophilic porous model carbons. Traditionally, methane hydrates are formed in nature under demanding conditions of low temperature and high pressure. However, by taking advantage of the confinement effects, these structures can be synthesized under milder conditions, faster kinetics and with a stoichiometry that mimics nature. The surface chemistry of the pore wall affects considerable the state of the confined water which, at the same time, may have an influence in the formation of methane hydrates. In order to gain knowledge on this process, we propose the use of two different model carbons exhibiting equal textural properties but different hydrophilicity to grow methane hydrate nanocrystals. Although the formation of these methane hydrate structures in nanopores has been already anticipated from our conventional methane adsorption measurements, Inelastic Neutron Scattering is the most suitable technique to identify the water confined structure and its effect on the methane hydrate formation process.

Report-7-04-173

Methane hydrate formation in hydrophilic and hydrophobic porous model carbons

Introduction

Natural methane hydrate is considered the largest reservoir for fossil fuels on earth. Typically, methane hydrate is formed deep under sea or in the permafrost under demanding conditions of temperature and pressure.[1] Although methane hydrate has been postulated as a novel energy storage system, it is known from literature that its synthesis from methane and bulk water suffers from kinetic limitations (days or even longer). However, this drawback can be overcome by taking advantage of the confinement effect in the inner cavities of nanoporous carbons (Fig.1a).[2] Experimental results have shown that methane hydrate can be synthesized below 2ºC and moderate pressures (3-4 MPa), with a stoichiometry that mimics nature and, more importantly, with faster kinetics (within minutes).[3] Inelastic neutron scattering experiments clearly described the free rotational modes of isolated methane molecules (Fig.1b), thus confirming the presence of methane molecules entrapped in the ice cavities, and synchrotron X-ray powder diffraction showed the formation of the sI crystal structure of methane hydrate.[2,4] We have recently proved a pore size in the order of 10-20 nm as optimal to store methane via methane hydrate formation in pre-humidified pores of model carbons.[5] Despite these interesting findings, there are key questions that remain unanswered. For instance, we observed that the chemistry of the carbon wall strongly impacts the confined water state which in turn affects the confined methane hydrate formation process. As a result, the total methane uptake capacity is profoundly affected.

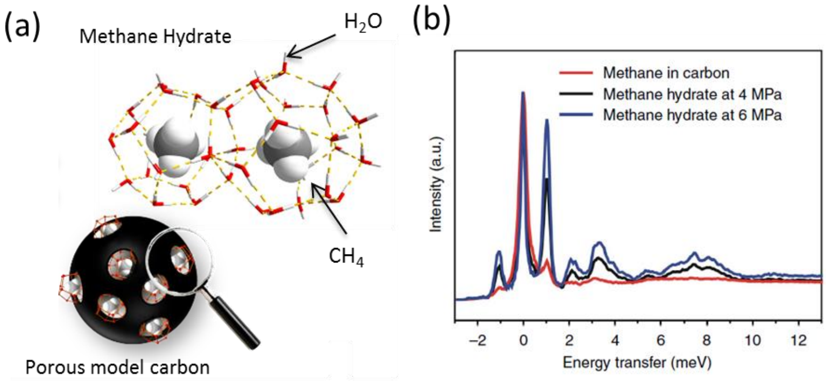

Figure 1. (a) Scheme of confined methane hydrate in porous model carbon. (b) Rotational spectra of hydrogen coming from the methane molecule in wet (deuterated)-activated carbon at different pressures[3].

In this experiment we propose to utilize two porous model carbons with identical textural properties but differing surface properties, i.e. hydrophobic vs. hydrophilic. Inelastic Neutron Scattering (INS) will allow to elucidate unique features on confined water properties and the methane hydrate formation in these different environments. INS is the most suitable technique to track the hydrogen atoms that allows to i) identify the nature of the confined water in the pores as a function of the surface chemistry and, in particular, to obtain information about the strength of the hydrogen bond interaction[6], ii) identify the methane hydrate crystals in both samples, and iii) correlate the nature of the confined water with the water-to-hydrate conversion.

Results

We divided the experiment into two steps. In the first one, we aimed to study the water molecule vibrational modes in the hydrophilic (HOMC) porous model carbons at 5K. In the second one, we aimed to observe the water molecule vibrational modes in the wet sample upon pressurization with 30bar of CH4 at 5K. The pores of the HOMC were loaded with different water content to reach two different scenarios: unsaturated pores (i.e., 60 and 80% of the pore volume) and oversaturated pores (i.e., 150% of the pore volume). The hydrophobic sample (OMC) was loaded with water to reach 60% of the pore volume so that we could compare the performance of the confined water in a hydrophobic environment. The measurements were performed in the vibrational neutron spectrometer Lagrange. This instrument allows access to the vibrational and intramolecular modes of water. In addition, the low energy range of the spectrum provides the possibility to measure the rotational modes of methane. Therefore, we used the Si111, Si311, and Cu220 monochromators to cover the energy range from 0 – 500 meV.

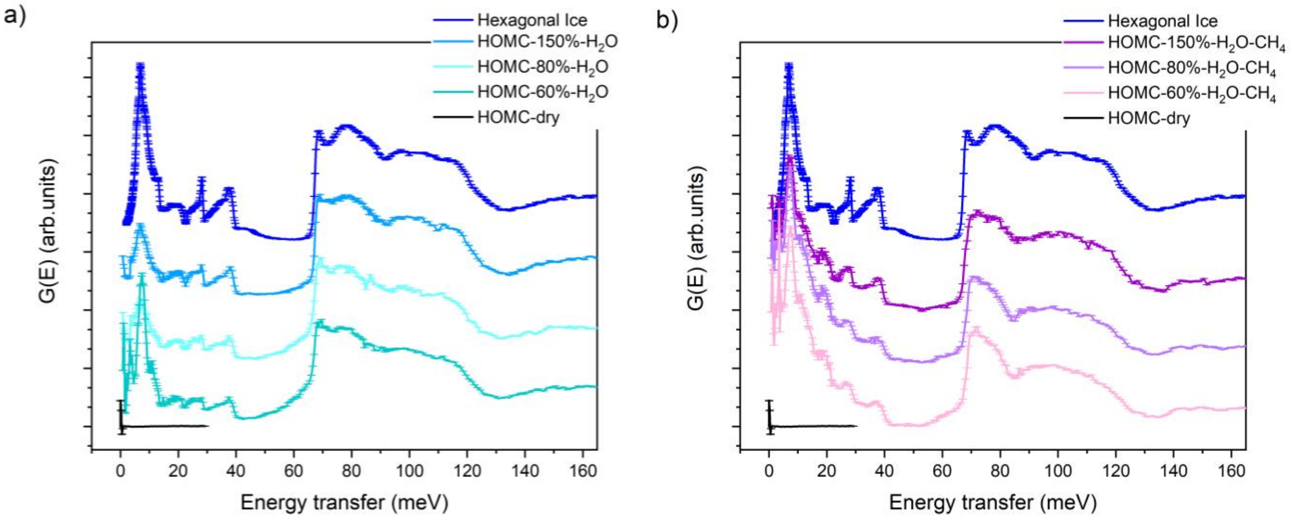

Figure 2. a) INS spectra measured in Lagrange for samples dry-HOMC and wet HOMC with different pore filling (10, 60, 80 and 150%).The spectrum for hexagonal ice is also included for comparison. (not published data) b) same samples pressurized with CH4

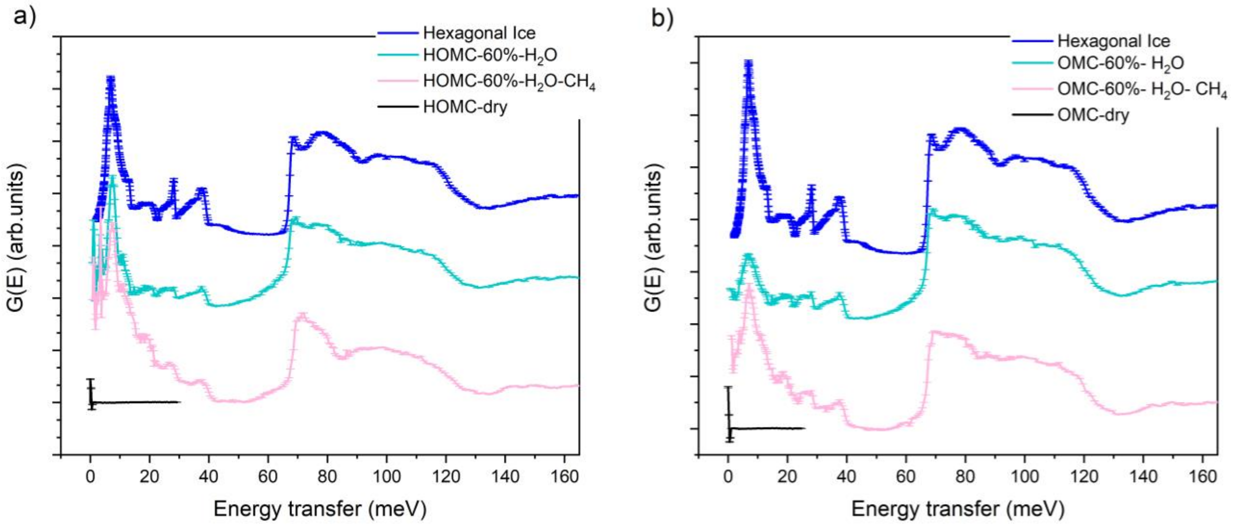

Figure 3. INS spectra measured in Lagrange for samples (a) dry-HOMC, wet HOMC with pore filling 60, and wet HOMC with pore filling 60 upon pressurized with CH_4, (b) dry-OMC, wet OMC with pore filling 60, and wet OMC with pore filling 60 upon pressurized with CH_4. The spectrum for hexagonal ice is also included for comparison. (not published data)

References [1] Dendy Sloan *et al*. **Clathrate Hydrates of Natural Gases**, *3rd Ed.*, (CRC Press, 2007). [2] Borchardt, L., *et al*. **ChemPhysChem** 1–18 (2018). [3] Casco, M.E., *et al*. **Nature Commun**. 6, 6432, (2015). [4] Casco, M.E., *et al*. **Chemical Science** 7, 3658-3666, (2016). [5] Borchardt, L., *et al*. **Phys. Chem. Chem. Phys**. 18, 20607–20614 (2016