

Experimental report

25/01/2023

Proposal: 7-05-538

Council: 10/2020

Title: Methane hydrate formation in periodic mesoporous organic silicas

Research area: Engineering

This proposal is a new proposal

Main proposer: Mirian CASCO

Experimental team: Mirian CASCO
Sven GRAETZ

Local contacts: Monica JIMENEZ RUIZ

Samples: MCM-41
B-PMO

Instrument	Requested days	Allocated days	From	To
IN1 LAG	6	3	04/10/2021	07/10/2021

Abstract:

The proposal aims to evaluate the formation of methane hydrate in the cavities of periodic mesoporous organic silica. 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 walls affects considerably the wettability, which in turn has an influence in the location of the methane hydrates crystals. In order to gain knowledge on this process, we propose the use of two different periodic organic silica exhibiting equal textural properties but different wettability 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.

Methane hydrate formation in periodic mesoporous silica

In recent studies, we have shown that the physical properties of confined water, such as mobility and phase state, have a tremendous impact on the water-to-hydrate conversion in ordered mesoporous carbons¹. Silica, however, is the basic component of rock where most hydrate is found. Therefore, we aim to study by inelastic neutron scattering the impact of silica polarity on the phase properties of confined water. To this end, we selected benzene mesoporous organosilica (BPMO) because it is a model material that combines highly ordered pore structure with well-defined surface chemistry within cylindrical pores offering an ideal scenario to investigate confined fluids.²⁻⁴ The water partially wets BPMO due to the alternation between silanol and benzene groups on its surface. This particular feature dramatically changes the water behavior compared to the well-known MCM-41 that exhibits merely silanol groups (uniform wetting). Therefore, we have proposed to measure in the vibrational neutron spectrometer Lagrange: dry BPMO and dry MCM-41, and BPMO and MCM-41 loaded with different amounts of water. In the second part, we pressurized the wet sample using 30bar of CH₄ to form methane hydrates at 223K. Lagrange allows access to the vibrational modes and the 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 whole energy range needed for the experiments (from 0 – 500 meV). The INS spectra results from 0 to 180meV are shown in **Figure 1(a-d)**. They were measured with a resolution in the energy of 2% E_i. Not published data.

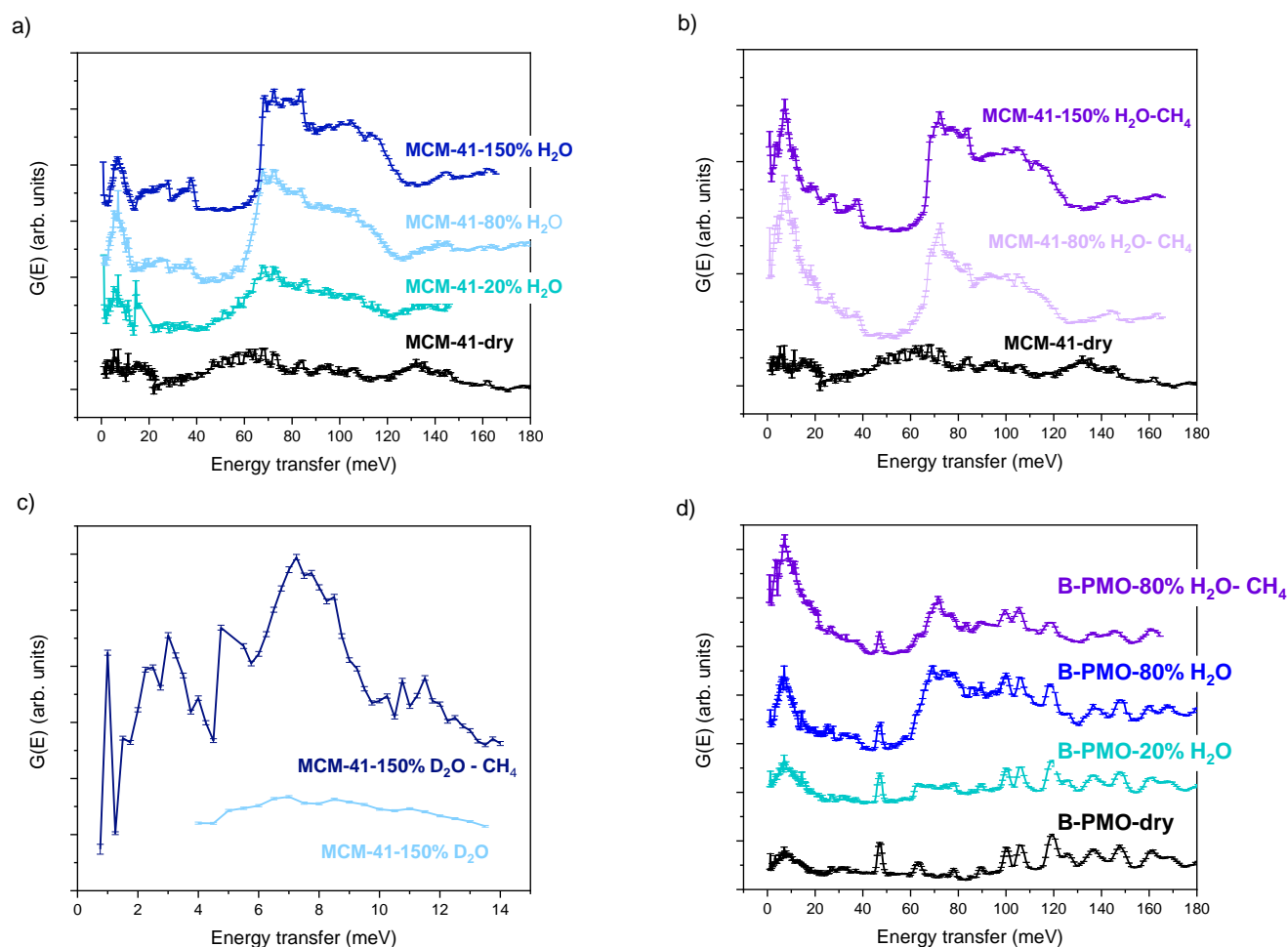


Figure 1. INS spectra at 4K of (a) dry and wet MCM-41, (b) wet MCM-41 pressurized with methane, (c) wet MCM-41 using heavy water before and after pressurizing with methane (low energy range), (d) dry and wet B-PMO before and after pressurizing with methane. Not published results.

References ¹M. E. Casco, et al. *J. Phys. Chem. C*, 2019, **123**, 24071. ²M. Thommes, et al. *Langmuir*, 2013, **29**, 14893. ³J. B. Mietner, et al. *Angew. Chemie - Int. Ed.*, 2017, **56**, 12348. ⁴M.E. Casco, et al. *Chem.Eng.J.*, 2021, **405**, 126955.