EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

Experiment title: Enhanced formation of CH_4 clathrate hydrates in hydrophobic confinement		**Experiment number**: 26-02-868
Beamline: BM26B	**Date of experiment**: from: 05/04/2018 to: 09/04/2018	**Date of report**: 26/04/2018
Shifts: 12	**Local contact(s)**: Daniel Hermida Merino	*Received at ESRF:*

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Report:

Over the past decade, considerable scientific effort has been devoted to the formation of CH_4 clathrate hydrates. Clathrate hydrates can crystallize when non-polar gases and water are equilibrated under high pressure at low temperature. . Van der Waals interactions between gas molecules and the water force the latter to reorganize its hydrogen bonding network into ice-like materials with cavities large enough to store a variety of gas molecules such as CH_4 and CO_2. As 1 m^3 of CH_4 hydrate can store up to 160 m^3 of gas, clathrate hydrates offer a safe and sustainable way of storing large amounts of non-polar gaseous energy carriers such as CH_4 and are expected to play a key role in the energy economy of the future.[1]

During this stay at the DUBBLE beamline, CH_4 clathrate hydrate crystallization was monitored with *in situ* SAXS/WAXS to investigate the kinetics of clathrate hydrate formation. X-ray diffraction has been applied to study CH_4 clathrate hydrate formation in the micropores of carbonaceous host materials, but the effect of different pore sizes (1-20 nm) and surface chemistry (siliceous materials with varying hydrophobicity) remains poorly understood.[2-4] Reverse phase microporous silica gels (pore Ø6nm) hydrophobized with C_8 and C_{18} alkyl groups and POSISil materials, a specific type of porous silicone materials with general formula $(R_2SiO)_n$ combining micro-, meso- and macropores, were used as host material. Experiments were carried out in 1 mm quartz capillaries containing defined amounts of the nanoporous host materials and water. Using our unique high-pressure set-up, which allows leak-proof connection between a capillary and virtually any instrument having Swagelok fittings (Figure 1), the capillaries were pressurized with CH_4 up to pressures of 60 bar and the SAXS/WAXS profile was measured as function of temperature. The results with C_8 silica gels look promising, already evidencing the formation of CH_4 clathrate hydrate from hypercooled water (Figure 2). The remaining data is still being analyzed.

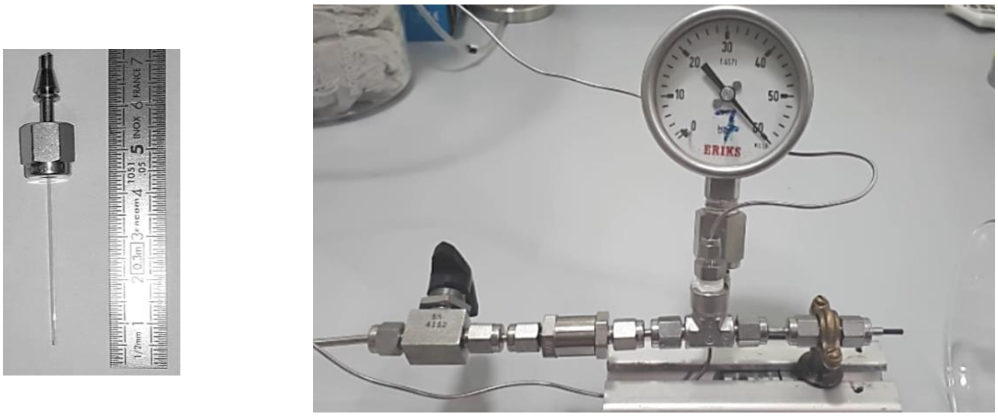

Figure 1. Left: 1 mm quartz capillary which has been modified to allow connection to a pressure regulating system with standard Swagelok components. Right: Pressurization of the capillary with 60 bar of CH_4.

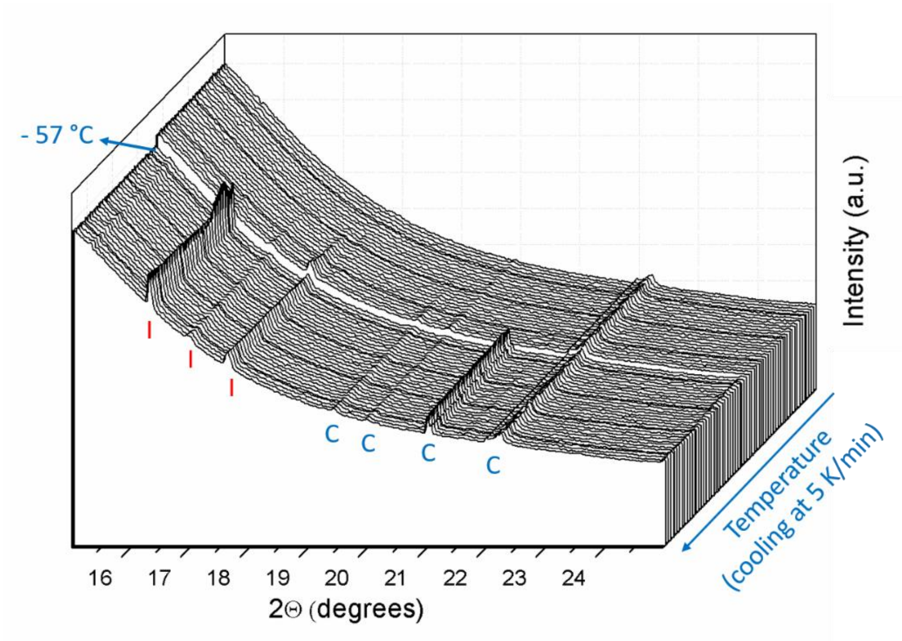

Figure 2. WAXS diffractogram showcasing the formation of CH_4 clathrate hydrate inside the pores of a hydrated microporous silica grafted with C_8 alkyl groups. Reflections characteristic of CH_4 hydrate structures are denoted by 'C', whereas reflections attributed to the presence of hexagonal ice are indicated with 'I'. The onset of clathrate formation is clearly visible at -57 °C.

(1) Casco, M. E.; Silvestre-Albero, J.; Ramirez-Cuesta, A. J.; Rey, F.; Jorda, J. L.; Bansode, A.; Urakawa, A.; Peral, I.; Martinez-Escandell, M.; Kaneko, K.; Rodriguez-Reinoso, F. *Nat Commun* **2015**, *6*, 6432.
(2) Iiyama, T.; Nishikawa, K.; Suzuki, T.; Kaneko, K. *Chemical Physics Letters* **1997**, *274*, 152-158.
(3) Futamura, R.; Ozeki, S.; Iiyama, T. *Carbon* **2015**, *85*, 8-15.
(4) Liu, X.; Zhou, L.; Li, J.; Sun, Y.; Su, W.; Zhou, Y. *Carbon* **2006**, *44*, 1386-1392.