# Experimental report

06/09/2022

**Proposal:** **6-07-92**

**Council:** 4/2021

**Title:** Localization, structure and dynamics of physisorbed H2 on the surfaceand in pores of gels used as precursor for smectite clay synthesis

**Research area:** Materials

**This proposal is a new proposal**

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**Samples:** Laponite clay mineral

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| PANTHER | 7 | 3 | 28/09/2021 | 01/10/2021 |

## Abstract:

Up to now all the research on H2 adsorption have been focused on crystalline materials having well define pore structure closely matching the H2 kinetic diameter (e.g. MOFs, zeolite, nanotubes and carbon nanofibers). We have recently revealed a surprisingly high H2 uptake by gels used as precursors for hydrothermal synthesis of smectites: hectorite and saponite. The gels are by definition amorphous, but they display a high surface area (about 4 to 5 times higher than their well crystallized clay equivalent), and high volume of micropores. This proposal aims at understanding how H2 behave in the nanostructure of these gels, what is its localization and dynamic in the structure. Based on this understanding, we hope to improve the sorption properties of the gels, in order to make them a low-cost material for large-scale, land-based H2 storage applications.

# Hydrogen Storage in Clay Materials

Experiments #6-07-92 and 6-07-98 were done by same teams, between 28/09/2021 and 04/10/2021. We thus present here a report for both experiments.

## 1. Laponite material

Ni_Laponite precursor was used in this study because of its high hydrogen adsorption. It was first assumed to be a gel and we will keep the name 'Gel-Ni-laponique' in the following for simplicity, but we have shown by X-ray diffraction that it consists in nanocrystals of laponite (a trioctahedral material (2:1) falling into the hectorite subgroup).

The results presented lie on the neutron energy loss side (the Stoke's side) of the spectrum.

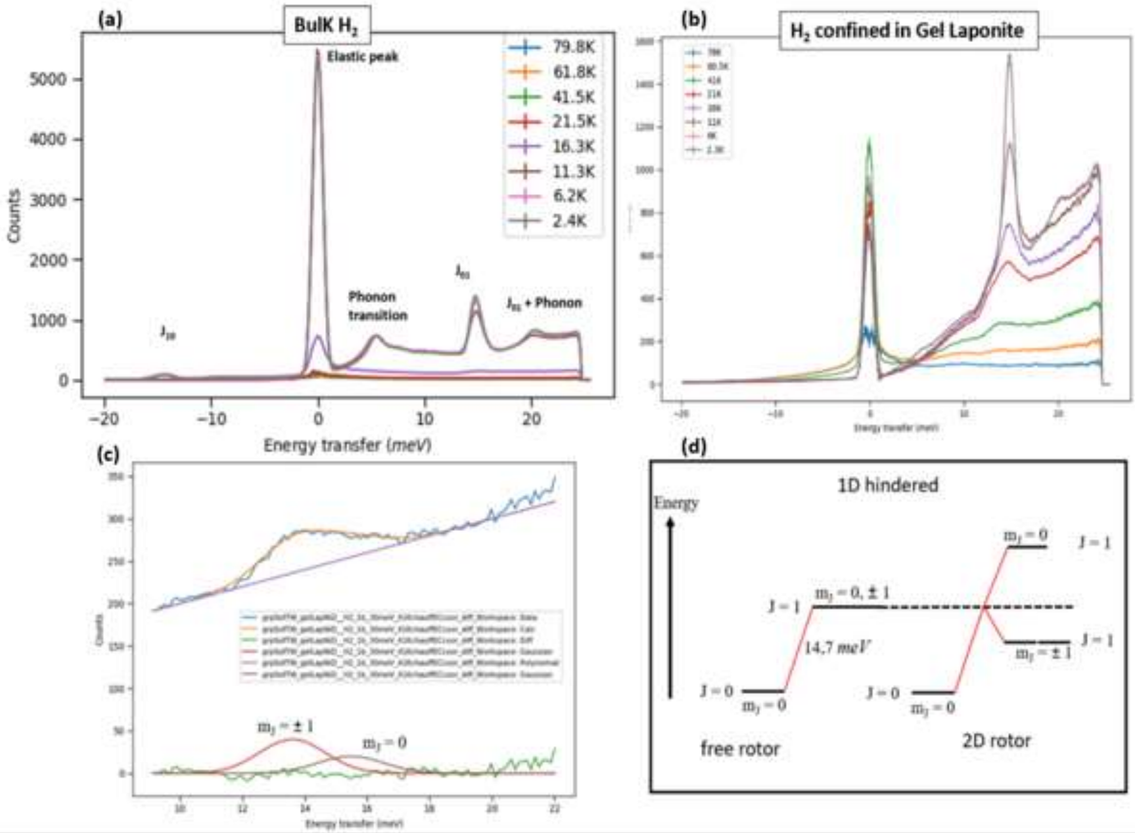

Figure1. (a) and (b) shows INS spectra of bulk and confined $H_2$respectively, (c) fiited $J_{01}$ rotational line at 41K (Data: blue, caculated: orange, difference: green, Guassian lines: red & brown, background baseline: purple)
(d) The para-ortho transition for a free rotor and for a 2D rotor

When $H_2$ is free to rotate isotropically, a transition line characterized by sharp and well-defined peak centered at 14.74 meV is observed (Figure 1(a)), corresponding to the transition of $H_2$ from para (S=0, J=0) to ortho state (S=1, J=1). Moreover, the first excited state (ortho state) is composed of three energy levels associated with quantum number $m_J$. They are degenerate in the case of free rotor $H_2$. This three-fold degeneracy is lifted as a function of the local symmetry of the adsorption site, with line-shifts that are dependent on the interaction between the $H_2$ molecules and the host surface.

Data obtained from a ‘Gel_Ni_Laponite’ after injection of 1 bar of $H_2$ at 78K followed by cooling are shown in Fig. 1(b) and (c). The spectra clearly show that $J_{01}$ exhibits a structure which can be fitted by two gaussian lines with an intensity ratio of 2:1 (Fig. 1(c)). It implies (Fig. 1(d)) that $H_2$ is bounded in such a way that one dimension is hindered ($H_2$ axis lying parallel to a surface). Upon cooling, the intensities of the transition to $m_J = 0$ and to $\pm 1$ increase with decreasing temperature but their ratio remains approximately constant at 2:1 (Fig. 2) showing that the bound geometry does not change. Slight shifts of the peak positions may be explained by hydrogen-hydrogen interactions. Finally, signature for a new binding site appears at 21K as a a single peak, which reveals an isotropic environment.

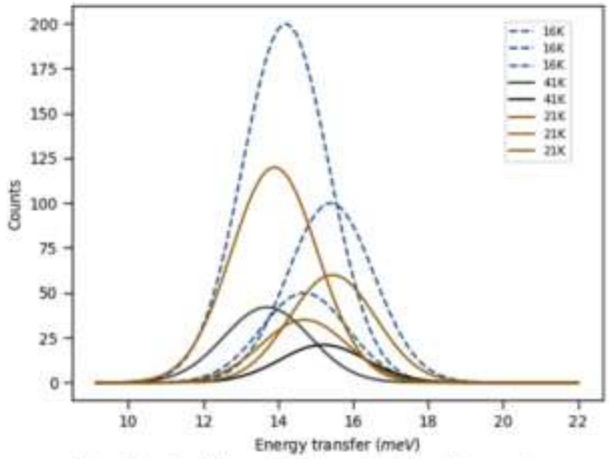

Figure2. $J_{01}$ transition region fitting as function of temperatue

To improve the adsorption properties of the ‘gel’, and thus to develop better clay-based materials for hydrogen storage, it is important to understand what are the attractive sites. It can be hypothesized that (at least part of) $H_2$ molecules are stored between the layers of the material (fig.3 inset). We show in fig. 3 the behavior in temperature of the intensity at the small Q values reachable in the experiment, in the region of the (001) peak characteristic of the interlayer spacing, around 0.5 Å$^{-1}$. At Q=0.4Å$^{-1}$, the intensity increases with decreasing temperatures from 77.5K to 21K while the intensity is the strongest at T=41K for Q=0.55 Å$^{-1}$. This peculiar behavior points towards the need for further elastic experiments to study the amount of $H_2$ in the interlayer spacing or possibly in other nanopores of the gel material, depending on temperature or $H_2$ pressure.

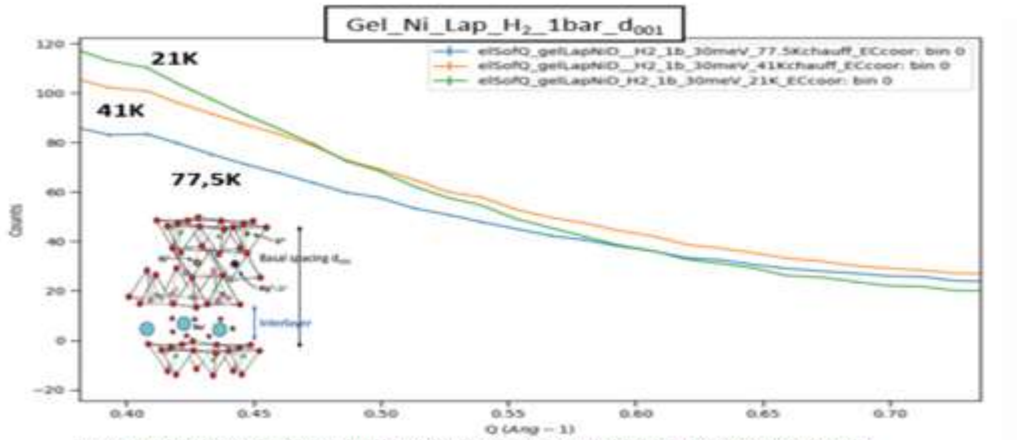

Fig.3. Intensity integrated from -1.5 to 1.5meV as a function of the wave-vector; inset: the laponite structure

## 2. Kaolinite material

Kaolinite material is made of a 1:1 uncharged dioctahedral layer, consisting in a single silica tetrahedral sheet and a single alumina octahedral sheet. Contrary to laponite, it is a non-swelling clay material. Here, our aim was to investigate if pore anisotropy between kaolinite sheets forming the macroscopic material could favor $H_2$ adsorption.

Two samples were used in this investigation:

- an oriented sample. The anisotropy of the first two rings, corresponding to (001) and (11) with (02) Miller indices, is shown in Fig. 4(a)
- an isotropic sample: no anisotropy shown in Fig.4(c)

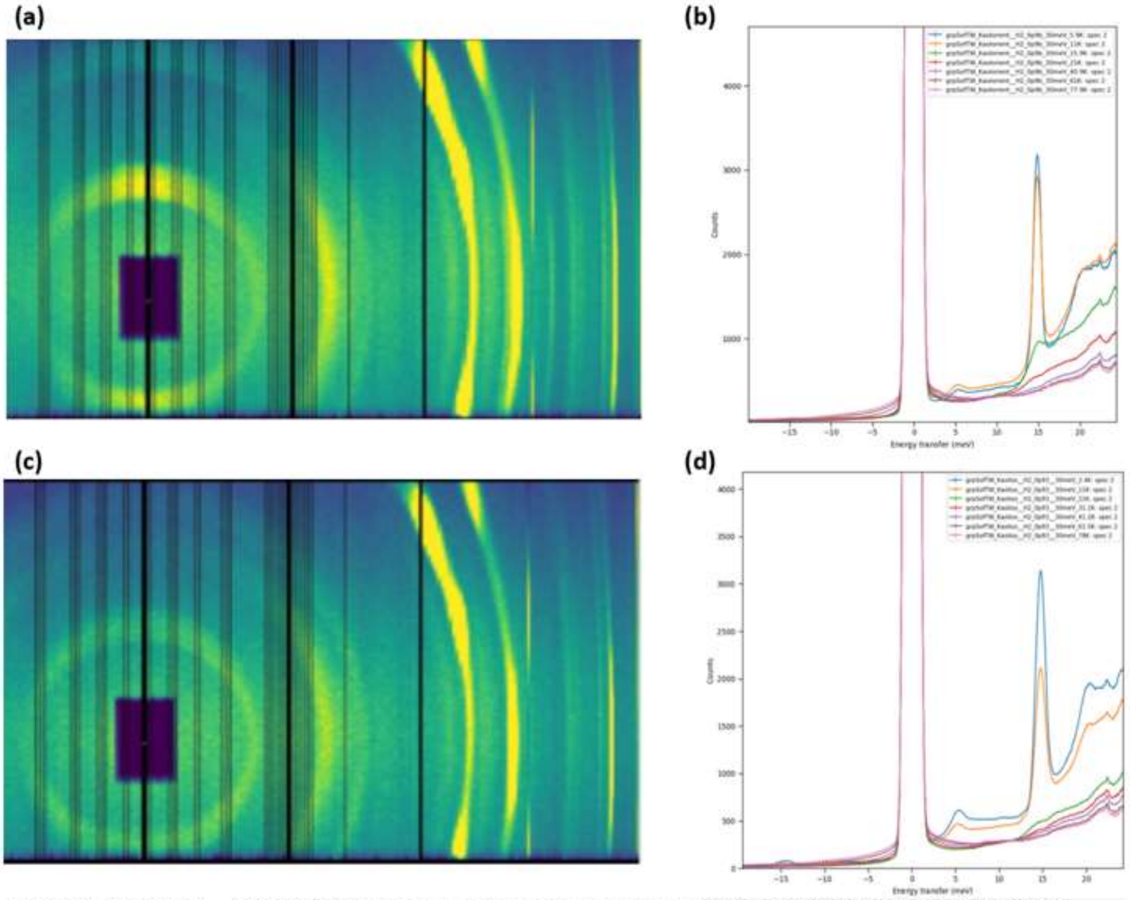

Figure 4. (a) and (c) 2D scattering from oriented and isotropic kaolinite at 78 K respectively, (b) and (d) showing INS spectra of kaolinite samples after 0.9 bar of H2 injection at 78K and cooling down to 5.9K in (b) and 2.4K in (d).

Figure 4(b) and (d) do not show any sign of strong binding sites in both samples (kaolinite oriented and isotropic), which rules out our hypothesis that pore anisotropy may be favorable for $H_2$ adsorption. It is probably due to too large pore sizes.