Experimental report

13/04/2017

Proposal:	**7-05-460**	**Council:**	4/2016
Title:	Hydrogen diffusion in MoS2		
Research area:	Materials		

This proposal is a new proposal

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Samples:	MoS2 powder MoS2

Instrument	Requested days	Allocated days	From	To
IN11	10	6	06/09/2016	12/09/2016

Abstract:

Molybdenum disulfide, MoS2, is a well-known catalyst for hydrogenation reactions and a promising candidate for the reduction of production costs in proton exchange membrane fuel cells (PEM), which still rely on noble metal catalysts. A large number of recent studies have focused, therefore, on the preparation and characterization of MoS2 materials for electrolysis and fuel cell applications. The preparation of electrochemically active MoS2 is not straightforward though, since different reaction pathways on amorphous and crystalline nanoparticles have been observed. Therefore, a fundamental understanding of reaction and transport mechanisms is needed for further development.

Hydrogen transport is the most important step for many reactions. Hence, we want to use the unique dynamic range of neutron spin-echo to survey the diffusivity of atomic and molecular hydrogen on single crystal and polycrystalline MoS2 samples.

1. Introduction

Molybdenum disulfide, MoS_2, is a well-known catalyst for hydrogenation reactions. Recently it has also been considered for water splitting for fuel cell applications, and as catalyst in PEM fuel cell electrodes [1-4]. Catalytic activity has been observed to be much stronger in nanocrystalline samples and to be absent in single crystal samples. The aim of this study is to understand the hydrogen dynamics, which is a first step for explaining catalytic activity and also the dependence on crystal size.

In fact, in earlier models [5,6] the catalytic activity of MoS_2 has been related to the formation of a reservoir for atomic hydrogen on the (0001) surface after dissociation of H_2 molecules on grain boundaries or point defects related to sulfur vacancies. Transport to and from the grain boundaries or defects is a prerequisite of this model. Interestingly, theoretical studies (DFT) have shown that diffusion of H_2 through hydrogen covered (0001) planes is hindered and that accomodation of an H atom in the middle of a sulfur ring is accompanied by severe lattice deformation [7]. On the contrary, other DFT studies show intercalation of H atoms and metallization of the surface [8]. Experiments reveal considerable H atom diffusion into the bulk, even for MoS_2 single crystals [9,10]. Experimental evidence for diffusion pathways are lacking.

2. Samples

Two samples have been analyzed by spin-echo neutron scattering at the IN11 instrument:

a) **A set of several single-crystalline MoS_2 samples of 0,2 mm thickness, in the following denoted as “single crystal sample”.** In fact, in electron diffraction these crystals reveal slight mosaic structure with tilt angles of a few degrees in the plane perpendicular to the c-axis of the crystal structure (in the surface plane). The single crystal sample has been analyzed in two scattering geometries: with the surface parallel and perpendicular to the scattering vector Q, respectively. Four days prior to the experiment the sample had been electrochemically loaded with hydrogen at room temperature. From nuclear reaction analysis measurements on samples of the same supplier we know, that under these conditions strongly bound hydrogen is stored down to several-10 nm below the surface.

b) **MoS_2 nanopowder with an average particle size of 90 nm, in the following denoted as “powder sample”.** The powder sample had been activated, ex situ, by heating in a vacuum oven at 400°C and was then, in situ, exposed to hydrogen gas at 20 K.

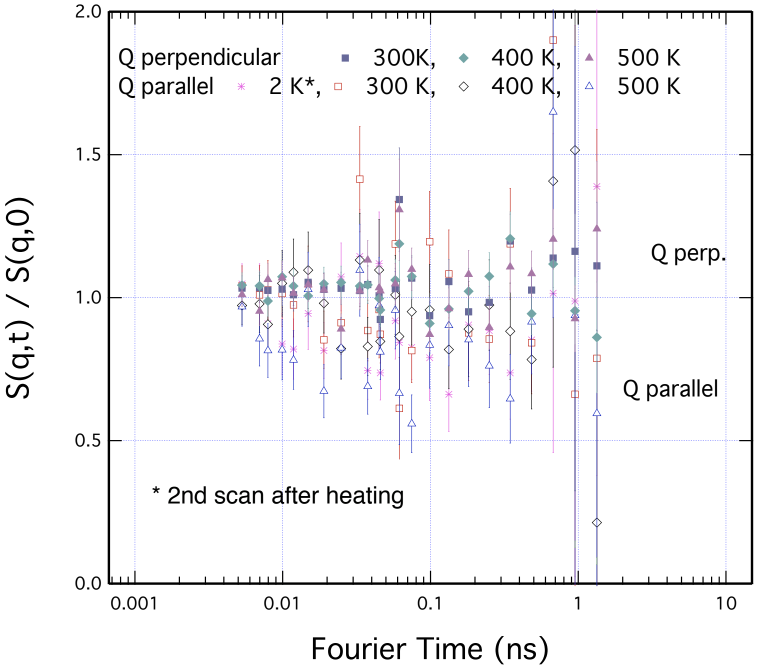

Fig. 1: Normalized intermediate scattering function from IN11 as a function of Fourier time for sample temperatures between 2 and 500 K, Q perp. und Q parallel denotes the scattering vector being parallel or perpendicular to the crystal surface. Data have been normalized to the first scan at 2 K(5 K).

3. IN11 experiments

The single crystal sample has been analyzed along two directions: with the surface parallel and perpendicular with respect to the scattering vector, respectively. In Fig. 1 the spin-echo signal is plotted as a function of Fourier time for both orientations and several sample temperatures. All data are referenced to the first spectra recorded at sample temperatures of 2 and 5 K, respectively. With Q being oriented parallel to the surface a decay of the intermediate scattering function is observed at higher temperatures. Upon re-cooling to 2 K, the signal is not recovered completely, which is due to partial desorption above 300 K.

In the other sample orientation, where Q is perpendicular to the crystal surface we find no significant deviation from the elastic line and, hence, no indication of diffusive dynamics within the dynamic window of IN11, i.e., from 1 ps to 5 ns.

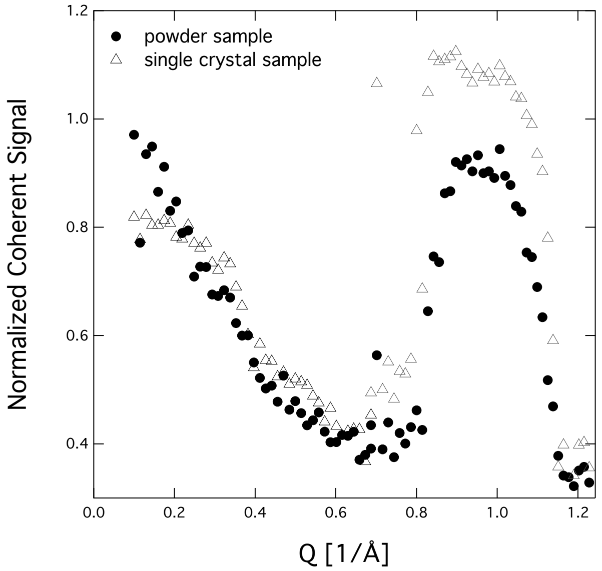

Fig.2: Coherent Signal as a function of momentum transfer Q. The curve for the hydrogen-free powder sample (black symbols) is similar to the single crystal sample (open symbols). Differences are discussed in the text.

In Fig. 2 the coherent signals for the freshly activated, i.e. hydrogen-free, powder sample and the single crystal sample with Q perpendicular to the surface are compared.

For both samples elastic diffraction is found with a peak at around 0.95 $Å^{-1}$, which stems from diffraction in the direction along the c-axis of the crystal structure, i.e., perpendicular to the MoS_2-layers. This diffraction signal is also found in the single crystal samples and the similarity clearly indicates that the particles are crystalline and, therefore, rather comparable to exfoliated material than to amorphous powder.

However, there are slight differences: For the powder sample the small angle scattering is strongly enhanced, whereas for the hydrogen loaded single crystals the amount of coherent scattering is reduced by 20% due to incoherent scattering from hydrogen. On the diffraction peak at 0.95 $Å^{-1}$, therefore, incoherent signal is superimposed resulting in higher signal compared to the powder.

Upon exposure of the powder sample to hydrogen gas at 20 K physisorption is observed. As shown in Fig. 3, a subsequent increase in coherent scattering indicates conversion of ortho- to para-hydrogen, with a characteristic time of 6 min. Thus, the conversion is by about a factor of 10 faster than on the surface of carbon aerogel, which has been studied previously in the same setup [13]. As the MoS_2 surface is catalytically active, this is in line with predictions.

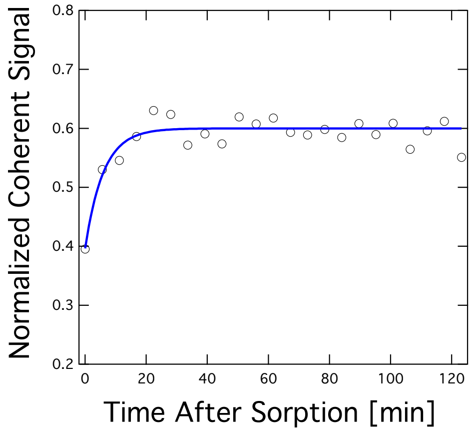

Fig. 3: Change in coherent signal with time, indicating conversion from ortho- to para-hydrogen.

At a sample temperature of 20 K, the spin-echo spectra show fast dynamical processes with a slight dependence on the scattering vector Q and on Fourier time.

Upon heating in a closed system, partial desorption of H_2 is observed at a temperature of 100 K and a stronger desorption at around room temperature. These processes are reversible; upon cooling a pressure drop is reproduced and also the dynamic behaviour at 20 K is recovered. The hydrogen species, which is present at 20 K after the first adsorption, is likely to be molecularly physisorbed H_2.

At 500 K a reaction of the surface with hydrogen is observed. The pressure in the closed sorption system drops and preliminary analysis suggest that 80% of the hydrogen in the system was absorbed.

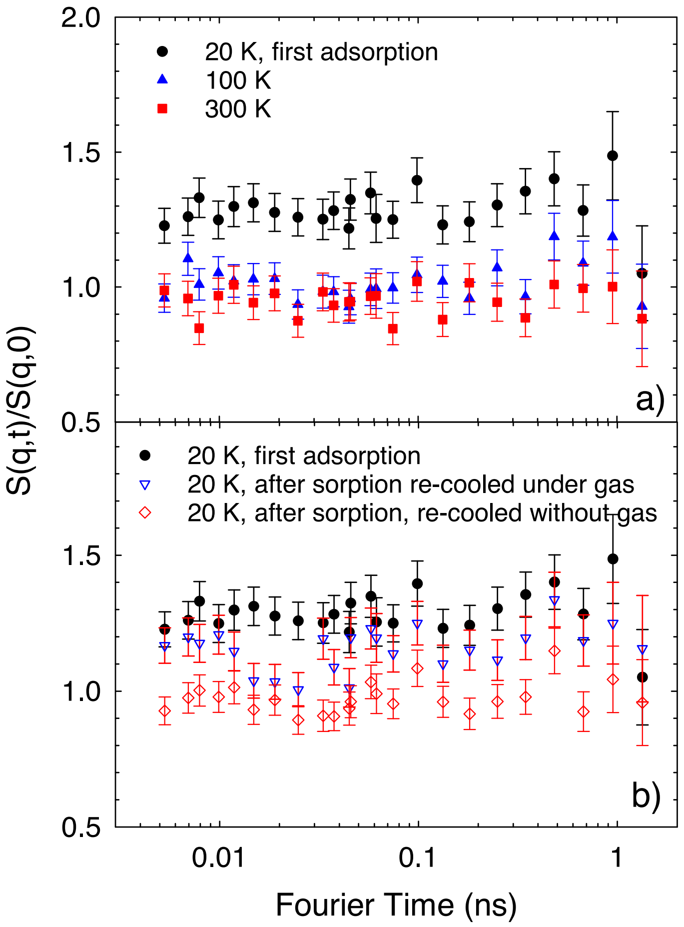

Fig.4: Spin-echo spectra for the loaded powder sample, normalized by the empty sample signal. a) After first adsorption we find clear indication of fast incoherent motion (polarization above 1), which disappears upon desorbing hydrogen at 100 K. b) After a cycle of treatment at 500 K (sorption of 80% of the hydrogen), the dynamic signal at 20 K has strongly decayed if adsorption is avoided.

Then the sample was cooled to 20 K and NSE spectra were recorded. Finally, to distinguish the absorbed species from re-adsorbed hydrogen, the hydrogen gas was removed from the system at 300 K sample temperature and again spin-echo spectra were recorded at 20 K. It can be concluded that the observed species is surface hydrogen rather than incorporated hydrogen. Fig. 4 compares spectra at 20 K for the various steps.

We can draw several preliminary conclusions from these experiments:

- The samples show strong signal from the hydrogen adsorbate.
- Fast dynamics are observed for the powder.
- For the single crystal samples, we mostly find movement parallel to the crystal planes within the dynamic range of IN11.
- The single crystal and powder samples show a similar structural scattering pattern on the IN11 length scales.
- We find H_2 physisorption at low temperatures and reaction at elevated temperatures.
- The MoS_2 powder sample shows very fast ortho-para-conversion.

4. References

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