Experimental report

22/06/2020

Proposal:	**7-05-501**	**Council:**	10/2018
Title:	Hydrogen dynamics in Mo2C catalyst		
Research area:	Chemistry		

This proposal is a new proposal

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Samples: H/Mo2C

Instrument	Requested days	Allocated days	From	To
IN11	8	2	13/06/2019	15/06/2019

Abstract:

MoS2 and Mo2C are intensely studied catalyst candidates for the hydrogen evolution reaction (HER) in water electrolyzers. We have recently initiated a project to elucidate the structural and dynamic foundations for the reactivity of these molybdenum compounds by use of neutron scattering. A first NSE experiment on MoS2 powders (7-05-460) revealed considerable reactivity and very fast diffusion within the layers of this 2D material. Now we want to concentrate on the new material molybdenum carbide Mo2C: We propose a first set of experiments on the dynamics of hydrogen in Mo2C powders to establish the time scales of the diffusivity at temperatures up to 550 K.

This experiment is part of an ILL PhD student project that will commence in the autumn of 2018 and that will join neutron diffraction and spectroscopy with MD simulations and additional techniques such as X-ray diffraction, nuclear reaction analysis and electrochemistry.

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Scientific background and aims of the proposed experiment:

Recently, there has been immense progress in technologies related to the production of renewable energy, however storage concepts have not yet reached the same maturity. ‘Power-to-gas’ is one of the most promising concepts: Hydrogen gas is produced from water when energy is available and reconverted when energy is in demand. Each conversion process needs to be carried out as efficiently as possible using optimized materials.

In the frame of this technology the molybdenum compounds MoS_2 and Mo_2C are intensely studied catalyst candidates for the hydrogen evolution reaction (HER) in water electrolyzers [1,2]. Recent electrochemical studies on MoS_2 allow detailed conclusions about its catalytic activity [3-9], which is much more governed by dynamics than the original explanations of reactivity solely in terms of defect sites suggested. A drawback of MoS_2 for electrochemical application, however, is its poor electrical conductivity of only $2{,}17 \cdot 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ [10], which is five orders of magnitude lower than the conductivity of graphite. From this point of view, Mo_2C and MoC are very promising due to their good electrochemical performance combined with good conductivity [11-14]. Similar to some oxidic catalysts they reveal a large flexibility in structures and stoichiometry and have favourably low work functions for their active surface (e.g., 3.4 eV for the (111) surface of Mo_2C) [15]. For both substances, the role of hydrogen intercalated below the surface and hydrogen moving along the surface is not fully understood.

Results of previous experiments:

Our project started with the investigation of the interaction of hydrogen with MoS_2 single crystals and powders. Fig. 1 shows NRA results (i.e. hydrogen concentrations) in MoS_2 single crystals (a) and in powder (b), the latter being deposited onto a porous carbon surface and processed in water electrolysis. After electrochemical treatment for single crystals as well as for powder similar hydrogen concentrations have been found, which indicates that both types of samples can be used as model catalysts. Diffraction experiments (ND and XRD) show that both, single crystal and nanopowder samples, reveal well-defined lattice structures.

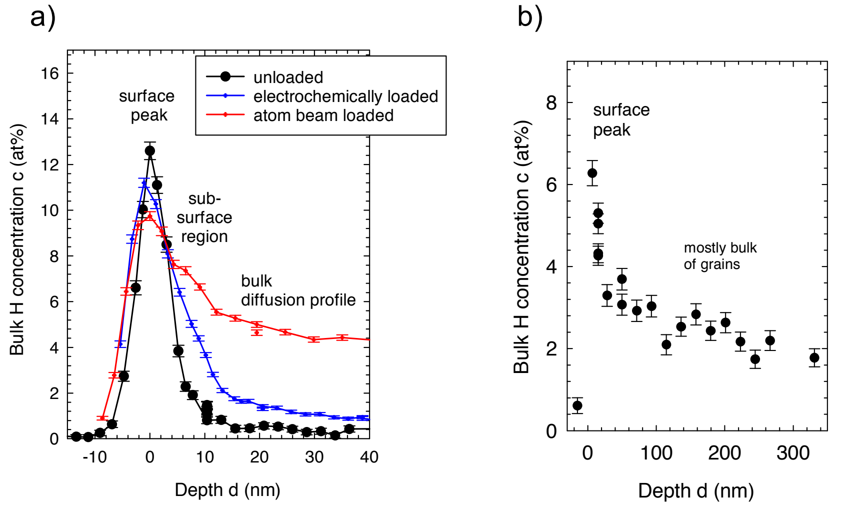

Fig 1: a) Depth profiles (NRA) for the pristine and hydrogen loaded MoS_2 single crystals. [16]

b) NRA of MoS_2 electro-chemically loaded with hydrogen. For this the powder had been deposited onto a carbon electrode.

A first NSE experiment on MoS_2 powders (7-05-460) revealed considerable reactivity towards molecular hydrogen leading to sorption at 500 K (confirmed by thermal desorption) and a conversion rate of ortho- to para-hydrogen, which is by about a factor of 10 faster than for carbon aerogel [17]. Fast motion is observed after the adsorption of molecular hydrogen on the surfaces, but also after hydrogen sorption in the bulk.

To identify the nature of the motions of each species further NSE and TOF experiments are underway for MoS_2, but in this particular experiment we wanted to concentrate on the new material molybdenum carbide Mo_2C. Therefore, we proposed a first set of experiments on the dynamics of hydrogen in Mo_2C powders to establish the time scales of the diffusivity at temperatures up to 550 K.

Experiment description:

We studied the dynamics of hydrogen species in Mo_2C powder in a neutron spin-echo experiment on IN11 in its high signal set-up IN11C using a cryofurnace sample environment. The sample volume was connected to a Hiden sorption analyser system via a stainless steel capillary. We used a wavelength of 5.5 Å for maximum signal. Firstly the Mo_2C sample was carefully cleaned by pumping first for two days at room temperature, followed by a heating to 550 K, also under vacuum. We performed polarization analysis measurements at two detector position covering scattering angles, 2ϑ, of 5°-35° and 35°-65°, respectively. The successive neutron polarization measurements at each cleaning step (see Fig. 2) demonstrated that the heating step was essential for removing a maximum of hydrogen containing molecules from the system (demonstrated by a reduction of the incoherent scattering).

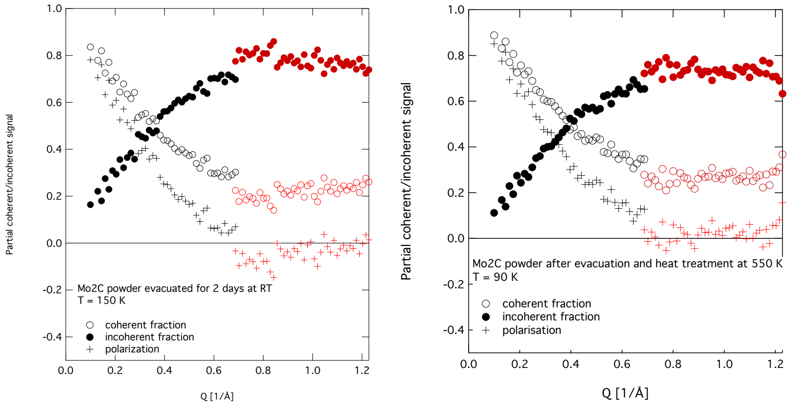

Fig. 2: Polarisation measurements using the IN11 30 degree detector bank for the evacuated Mo_2C sample (left-hand-side) and the same sample after an additional heating cycle to 550 K under vacuum (right-hand-side). The additional heating leads to a reduction of the incoherent scattering.

The cleaned Mo_2C sample was exposed to hydrogen gas at the cryostat base temperature of 2 K and NSE spectra were taken at various temperatures (8 K, 20 K, 50 K, 100 K, 300 K, 400 K, 550 K). We dosed the equivalent of 1 ML of hydrogen and kept the sample volume connected to the dosing volume throughout the experiments.

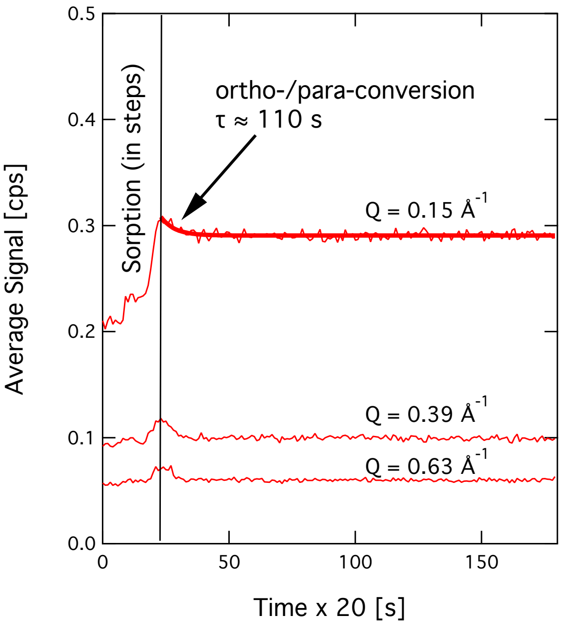

Fig. 3: Neutron average signal as a function of time for a 1 ML coverage of hydrogen on Mo2C. The detectors of the 30 degree detector bank were grouped into 5 groups of equal size. At the start of the measurement the signal increases due to the sorption of hydrogen. After the completion of the sorption, the signal decreases due to ortho- to para-conversion with a time constant of about 110 s.

During and directly after hydrogen exposure at 2 K the conversion of ortho- to para-hydrogen was monitored with polarization measurements of 10 s per up and down polarization, respectively (Fig. 3). The increase of the signal by the incoherent scattering during sorption and the decay of incoherent scattering through the process of ortho-/para-conversion are clearly visible in the data. Fitting an exponential decay law to the data leads to a time constant of about 110 seconds for the ortho-/para-conversion. This value is exceptionally fast and hints at a strong catalytic activity of Mo_2C for the hydrogen evolution reaction, because it demonstrates a strong coupling between the Mo_2C sample and the hydrogen electron level. Further analysis will be needed to quantify the ratio of hydrogen that undergoes a quick conversion and hydrogen that remains in the ortho-state.

As discussed above, the dosing volume of the sorption system was left connected to the sample volume via the stainless steel capillary throughout the experiments. This was a safety requirement, but it also permitted a constant supervision of the sorption and de-sorption of hydrogen. At cryostat base temperature all hydrogen was adsorbed by the Mo_2C sample and the remaining observed pressure in the sorption equipment was reduced to 0. At a sample temperature of 100 K a substantial amount of hydrogen was desorbed, leading to a monitor pressure of ~400 mbar. Further heating to 550 K let the pressure firstly rise to ~700 mbar, followed by a drop to ~600 mbar, indicating a substantial heat-induced sorption of hydrogen possibly in the atomic form (the system was leak tight).

Now we turn to the NSE spectra that were obtained in this experiment: Spectra were measured for the hydrogen-filled and for the de-gassed sample. The spectra were measured for the range of scattering angles, 2ϑ, of 5°-35° only, because the available number of beam days was too restricted for a second detector position. This setting provided a Q range of 0.1-0.7 Å^{-1}. All spectra were divided by a resolution spectrum obtained with the immobile Mo_2C sample at 8 K for removing the effect of imperfect polarization and sample geometry on the spectra. The spectrum obtained at 2K was unfortunately not appropriate for the division, since it showed exceptionally low signal, possibly due to a large number of hydrogen atoms in the para-state (the scattering cross section of the ortho-hydrogen is 30 times higher than the cross section of para-hydrogen). In Fig. 4 we display the spectra for the momentum transfer Q = 0.27 Å-1. The spectra show that dynamics are in general faster than the spectral window used here, i.e. we see no decay within the spectral window of IN11C, but we also notice that the amount of mobile molecules/atoms increases with temperature. Already at 30 K we see a substantial amount of mobility, which increases up to 100K. Above 100 K the amount of mobile molecules/atoms remains constant up to 550 K. Within the short beam time and with the limited flux of IN11 it was not possible to explore shorter spin-echo times, but future measurements with WASP would certainly be very insightful for this study.

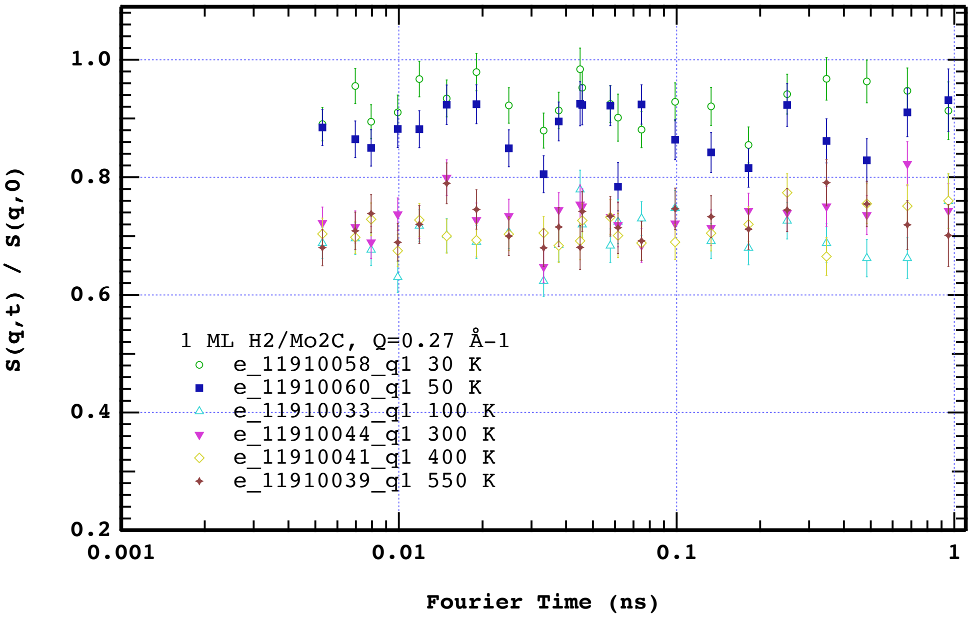

Fig. 4: NSE spectra of 1 monolayer of hydrogen on Mo2C.

References:

[1] B. Hinnemann et al. JACS 127(15),5308-5309, (2005).
[2] D. Merki, St. Fierro, H. Vrubel and X. Hu, Chemical Science 2, 1262-1267, (2011).
[3] Xiaohong Xia et al., International Journal of Hydrogen Energy 39, 9638–9650 (2014).
[4] Xiaoping Dai et al., International Journal of Hydrogen Energy 40, 8877–8888, (2015).
[5] Ya Yan et al., ACS Catal 4, 1693-1705, (2014).
[6] Jesse D. Benck et al., ACS Catal. 4, 3957-3971, (2014).
[7] Xiaoxin Zou and Yu Zhang, Chem. Soc. Rev.,44, 5148-5180, (2015).
[8] T. F. Jaramillo et al., Science 317, 100-102, (2007).
[9] J. D. Benck et al., ACS Catal. 2, 1916-1923, (2012).
[10] Ch. G. Wiegenstein and K. H. Schulz, Rev. Sci. Instr. 68, 1812 - 1813, (1997).
[11] Yagya N. Regmi et al., ChemCatChem 7, 3911-3915, (2015).
[12] Yagna N. Regmi et al., J. Mater. Chem. A, 3, 10085-10091, (2015).
[13] Chaoyun Tang et al., Journal of Power Sources, 296, 18-22, (2015).
[14] G.García et al., Journal of Electroanalytical Chemistry, 793, 235-241, (2017).
[15] José Roberto dos Santos Politi et al., PhysChemChemPhys 15, 12617-12625, (2013).
[16] H.-W. Becker et al., presented at Bunsen conference, Bochum Germany, 2015.
[17] E. Bahn, O. Czakkel, B. Nagy, K. Laszlo, S. Villar-Rodil, J.M.D. Tascon, F. Demmel, M.T.F. Telling, P. Fouquet, Carbon 98, 572-581 (2016).