Reviewer1: The manuscript is definitely suitable for publication in the proceedings of the ECNS. However, as the ECNS proceedings are also read by non-experts in the field of the investigated material classes, I have suggestions for changes in this direction:

1. The quantities Lc, a3 and La shown in Table 3 should be briefly explained. Do Lc and La refer to the XRD crystallite sizes along a and c-axis, respectively?

*In addition to the explanations that are below the table, small explanatory sketches were added to the table to make the meaning of these parameters clearer. In essence, the reported parameters Lc and La refer to graphite crystallite sizes along the c and a- axis, respectively. The notation of “crystallite” was avoided in the manuscript, since it is argued that it is not correct to name the relatively ordered domains in non-graphitic carbon “crystallites” due to considerable disorder. In addition, while in the a-direction chemical bonds keep the graphene sheet together, in the c-direction there are only weak van der Waals forces to keep the carbon sheets stacked. Thus, in these types of materials, the existence of long-range 3D ordered structure is unlikely. Therefore, instead of describing the carbon as consisting of graphite crystallites, it is more intuitive to just describe the relative order of the graphene domains (La parameter) and their stacking (Lc parameter).*

1. In Table 2 the hydrogen loadings are given in mmol/g. Wouldn't it be more informative to give weight percentages for potential hydrogen storage materials?

*In addition to the existing H2 loading notation, the weight percentages were added in table 2. The weight percentages are low as low loading pressures (below 0.1 bar at 77 K) were applied. The aim of these experiments was not to demonstrate the maximum H2 content in these materials, but to investigate the H2 interactions in different porous structures. For this, lower H2 loadings were applied as adsorption preferably starts in the smallest pores.*

Reviewer 2: In the following, I list a few concrete comments to the authors, each marked with a ">"

Abstract. … Namely, the ortho-para transition was the slowest in carbon derived from TiC, … I don’t think this is demonstrated clearly enough in the manuscript

*The main text was changed near the end of part 3.1 to clarify why there is expected to be slowest ortho-para transition in the pores of C-TiC (see below).*

1 Introduction ... At 80 K, cryo-adsorption vessels have been shown to contain up to 20% more H2 compared with the corresponding cryo-compression vessels, which do not contain adsorbents. [3] at which p/T conditions were the cryo-compression vessels?

*Both vessels were at 80 K and the approximate pressure range where this value can be reached is 100-200 bar based on Fig 10 and Fig 20 of G. Petitpas, P. Bénard, L.E. Klebanoff, J. Xiao, S. Aceves, Int. J. Hydrog. Energy., 39 (2014). This has been clarified in more detail in the manuscript.*

... and the chlorination temperature. a short introduction into the technique would be beneficial – personally, I didn’t expect chlorination to be part of the process ... and the average pore shapes depend on the precursor carbide [7] and the chlorination temperature used [8]. repetition

*To avoid the repetition and to give further explanation, the sentence “The CDC's structure can be significantly influenced by the choice of the precursor carbide and the chlorination temperature.” Is deleted and replaced with “CDCs are synthesized from inorganic carbides (e.g. TiC) through the reaction with chlorine at high temperature, typically 700–1200 °C, where the formed chloride is removed in gas flow. Thus, from the carbide structure only the chemically pure carbon, noted as CDC, is left behind.”*

...The sub-nanometer pores of C-SiC were shown to contain almost immobile hydrogen (i.e. solid-like) even at a relatively high temperature of 120 K. [5] could you give a short summary of that previous experiment? Also QENS? Which energy windiw etc etc?

*Thank you for this comment. The data used for this paper is from the same experiment as the mentioned “previous study”. In the previous study, the data was binned over Q in the limited energy transfer range from -2 meV to 2 meV, the diffusion coefficients were calculated by fitting the quasi-elastic broadening vs Q to translational jump models. To clarify this, the part was changed to “**In a previous Quasi-elastic neutron scattering (QENS) study on the instrument FOCUS at PSI, the transport properties of H2 in the pores of CDCs derived from SiC, Mo2C and TiC was investigated in the energy range from -2 to 2 meV. As a result, the sub-nanometer pores...”*

2 Experiment ..X-ray diffraction patterns were measured using Bruker using a Bruker

*Thank you, the repetition was deleted.*

... and scattering vector, Q, this is of course only the Q at zero energy transfer. I think it would be more useful to give an angle range

*The corresponding angle range in 2theta is added to the manuscript.*

... Empty sample holder and vanadium measurements were performed for data correction and background subtraction. I’d swap “data correction” and “background subtraction” to match the order of EC and van

*The order of “background subtraction” and “data correction” was swapped.*

... H2 with normal ortho-para content would be nice for the reader if the ratio was given (as it is done later in the text)

*The normal ratio of ortho-to-para hydrogen at ambient conditions was added to this sentence.*

... the sample holder was disconnected from the gas dosing apparatus and data were measured at different temperatures ranging from 10 to 120 K. It is unclear to me if H2 can escape or if the pressure increases during this temperature ramp

*Thank you, this needed clarifying. Namely, during the experiment, there was a fixed amount of H2 in the sample holder and the sample holder was hermetically sealed. In addition, the equilibrium of H2 adsorbed and present in the free volume of the sample holder depended on the temperature and, thus, the H2 pressure of in the sample holder varied and also the amount of H2 adsorbed in the sample varied with temperature. A correction was made in the sentence and an additional sentence about the sample holder pressure was added to the end of the paragraph: “**H2 pressure in the sample holder varied according to the reached adsorption equilibrium at each experimental temperature point as the sample holder was hermetically sealed during the experiment.”*

… Data reduction was detailed balance corrected? Otherwise, symmetrization doesn’t seem to make much sense

*Thank you for this valuable comment! The symmetrization was necessary for the detailed analysis of the quasi-elastic broadening components, i.e. to verify whether diffusion in more than one timescale could be seen. Only the neutron energy gain side of the scattering curve would not have given a good basis for fitting the data with multiple Lorentzian distribution functions. The balance correction will enable correct estimation of data along the y-axis, but we were interested in the widths of the quasi-elastic broadening components and thus, we estimated that balance correction should not have influenced the final results. To verify this, balance correction was done before symmetrization and subsequently the QENS signal was deconvoluted. In the Figure below, the data and corresponding deconvoluted signal can be seen (a) without the balance correction and (b) with balance correction. To the eye, these are practically indistinguishable.*

*A picture containing text, diagram, line, plot

Description automatically generated*

*When looking at the specific peak parameters (Table below), some differences can be seen in the intensities of the bands i.e. the influence of balance correction on the intensity is witnessed. The widths of the bands remained the same in the limits of uncertainty of deconvolution.*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **Before** | | **Balance corrected** | |
|  | Value | error | Value | error |
| Baseline | -0.08 | 0.01 | -0.13 | 0.22 |
| FWHM resolution | 0.1 | 0 | 0.1 | 0 |
| Area resolution | 30.04 | 2.28 | 27.26 | 0.34 |
| FWHM QE2 | 3.95 | 0.13 | 3.94 | 0.15 |
| Area QE2 | 117.6 | 1.9 | 113.8 | 3.4 |
| FWHM QE1 | 0.223 | 0.018 | 0.2147 | 0.0003 |
| Area QE1 | 61.9 | 1.8 | 69.2 | 0.7 |

... from dE = −37 meV to 2 meV not sure why dE is used here but not in the notation of S(Q,E). Surely it should be dE in both places or E in both places?

*Thank you for this remark, there and elsewhere the notation was changed to just E.*

... Q was binned over the entire range as one slice. I would leave Q out of the whole manuscript – it is some form of S(E) that is summed up over all detectors, does not have a well-defined Q, and the average Q is even a function of energy transfer

*Thank you for this valuable comment, Since Q was summed over all detectors, the reported dynamic incoherent structure factors S(Q,E) are noted as intensity, I.*

... The incoherent structure factor there is at least a “dynamic” missing here (and at other places in the manuscript), but given the issues with Q mentioned above, I would recommend to stay away from “structure” altogether

*“Dynamic” was added to the place where structure factor is mentioned. Throughout the manuscript, the notation “structure factor” was deleted and replaced with intensity. The following sentence was added in part 2: “Since Q was summed over all detectors, the reported dynamic incoherent structure factors S(Q,E) are noted as intensity, in the following text. .*

... based on the energy gain side neutron energy gain or sample energy gain?

*In the sentence it was clarified that “based on the neutron energy gain side”*

3 Results and discussion 3.1 Ortho-para transition of H2

... The free quantum rotor energy for para to ortho transition (p→o, J = 0 → 1) is 14.7 meV [16,17]. as a courtesy to the reader, the authors could indicate which of the two has a higher energy

*Thank you for this comment, it was clarified that the para state has lower energy than ortho by “The free quantum rotor energy of the transition from the lower energy para level to the higher energy ortho level (p→o…* “

..Therefore, it is of interested to stabilize the H2 adsorbed in ortho state. it is of interest

*Thank you, this was corrected.*

… Fig. 1. I cannot see the symbols in the cations nor the red line in the main plots The authors could think about ordering it TiC SiC MoC, like they tend to do in the rest of the manuscript

*The ordering was changed to C-TiC, C-SiC and C-Mo2C and the size of the symbols and the thickness of lines was increased on the figure.*

... The average stacking size, Lc, average interlayer spacing, a3, and the average graphene layer extent, La, were estimated based on the X-ray diffraction patterns (Table 3). It would be nice to give at least a qualitative indication how these parameters are linked to the XRD pattern

*For clarification, a sentence about giving insight to this was added: “The algorithm that was used for this analysis (See part 2) calculates the Lc and a3 parameters based on the shape of the 002 reflection and the La parameter from the shape of the 10 reflection.”*

... The lack of ortho-H2 which lack? ... might cause the lack of ortho-para transition band in C-SiC and C-Mo2C. The authors seemed to attribute the existance of the transition band to low long range mobility earlier

*The existence of the para->ortho band in inelastic neutron scattering data has been interpreted as being related to low long-range mobility. However, in the investigated energy range, we were not able to see the para-to-ortho band (i.e. the excitation of H2), but the ortho-to-para band (i.e. the relaxation of H2). Since para form is more stable at cryogenic temperatures, the transition from ortho form to para form is expected to occur at some unknown speed during the duration of the experiment. However, the speed of this transition will depend on the structure of carbon. Therefore, when no ortho-to-para transition band was seen for C-SiC and C-Mo2C, it was assumed that the majority of ortho-H2 had already converted into para-H2 before the measurement even started. Namely, the conversion occurred during periods of dosing of H2, waiting for the adsorption equilibrium and lowering of temperature to 10K. The wording of this sentence was changed to make this clearer.*

... This indicates that o-H2 can be more strongly bound to specific anisotropic adsorption sites than p-H2 [16]. if the energy can be lower or higher, why are we only talking about more strongly bound here?

*Thank you for bringing out a confusing part. What was meant by this was that in some specific anisotropic adsorption sites, the ortho form could be preferred and the transition from ortho to para then hindered. The wording of this sentence was changed to “due to the decrease in the o-H2 energy level in specific anisotropic adsorption sites, o-H2 can be preferably bound to these sites and conversion to p-H2 would then be less likely”*

3.2 Quasi-elastic broadening, i.e. H2 diffusion

… Fig. 3 the symbols are basically invisible on my printout

*The size of the symbols in Fig. 3 was increased.*

... It can be seen how the characteristic times for one full rotation I don’t think the characteristic time of rotational diffusion has much to do with a full rotation, but I may be mistaken here ... increase with the temperature. decrease, right?

*Thank you for noticing the error, the “increase” was changed to “decrease”. This is a very insightful comment, it is probably a matter of interpretation. There are, however, workgroups who interpret the characteristic times of rotational diffusion as the time needed for one full rotation, an example is in the supplementary information of J. Phys. Chem. Lett. 2023, 14, 1, 295–301 (https://pubs.acs.org/doi/10.1021/acs.jpclett.2c03198).*

Conclusions … Moreover, there were evidence of H2 rotation being strongly affected by the anisotropic adsorption potential in the pores of C-TiC. This flew past me – if there is actual evidence for this in the manuscript, it has to be stated more clearly in the main text

*The main text was changed near the end of part 3.1 to clarify, why there is expected to be strong anisotropic adsorption potential in some of the pores of C-TiC. The changed version now reads “So, it might be the case that for low surface coverage, H2 in C-TiC is adsorbed in the ortho state* *and not convert to para form easily. Thus, despite the anticipated conversion of most of the ortho species to para species already before the start of the neutron scattering measurement, an appreciable amount of hydrogen is still left in the ortho state in the pores in C-TiC. Thus, the existence of o→p transition band proves the existence of o-H2 still in the pores* *which alludes to the H2 rotation being strongly affected by the anisotropic adsorption potential in these pores.*”

... Namely, storing H2 in the ortho form you just want to prohibit the transition, right? If H2 is in para form already, it’s all the better, isn’t it?

*In the case of storing liquid hydrogen at 20 K, it is true that it would be preferrable to convert all the hydrogen to the para form. This conversion is routinely done with the help of catalysts in liquid hydrogen storage systems. However, for cryo-adsorption systems, which could operate at higher temperatures, i.e. near 77 K, it would be better to keep hydrogen in ortho form. Namely, ortho-H2 to para-H2 conversion is exothermic and, thus, causes desorption and unnecessary energy usage for further cooling. In addition, if all hydrogen were in para form, then when the temperature is increased to get H2 out of the system, some of the energy will be wasted on converting the para form back to ortho form. Therefore, for cryo-adsorption systems, it would be better to keep the H2 mainly in the ortho state during the storage to avoid energy losses, i.e., to keep the ratio of ortho and para H2 as close as possible to the one present at ambient conditions.*