ChemPhysChem

Research Article
doi.org/10.1002/cphc.202300794

Chemistry Europe
European Chemical Societies Publishing

www.chemphyschem.org

Establishing ZIF-8 as a reference material for hydrogen cryoadsorption: An interlaboratory study

Jose A. Villajos[+],*[a, b] Rafael Balderas-Xicohténcatl[+],*[c, d] Ali N. Al Shakhs,[e] Ángel Berenguer-Murcia,[f] Craig E. Buckley,[g] Diego Cazorla-Amorós,[f] Georgia Charalambopoulou,[h] Fabrice Couturas,[i] Fermin Cuevas,[i] David Fairen-Jimenez,[e] Karen N. Heinselman,[j] Terry D. Humphries,[g] Stefan Kaskel,[k] Hyunlim Kim,[l] Juan P. Marco-Lozar,[m] Hyunchul Oh,[l] Philip A. Parilla,[j] Mark Paskevicius,[g] Irena Senkovska,[k] Sarah Shulda,[j] Joaquin Silvestre-Albero,[f] Theodore Steriotis,[h] Christos Tampaxis,[h] Michael Hirscher,*[c, n] and Michael Maiwald[a]

This work is specially dedicated to the memory of Dr. Michael Maiwald, a highly regarded physicochemist who led the division Process Analytics at BAM and was the coordinator of the project MefHySto in the framework of which this interlaboratory study was performed. The authors will never fail to remember his dedication, integrity, kindness, and interdisciplinarity in directing the different activities of this great project, always showing his best smile. R.I.P.

Hydrogen storage by cryoadsorption on porous materials has the advantages of low material cost, safety, fast kinetics, and high cyclic stability. The further development of this technology requires reliable data on the H_2 uptake of the adsorbents, however, even for activated carbons the values between different laboratories show sometimes large discrepancies. So far no reference material for hydrogen cryoadsorption is available. The metal-organic framework ZIF-8 is an ideal material possessing high thermal, chemical, and mechanical stability that reduces degradation during handling and activation. Here, we distributed ZIF-8 pellets synthesized by extrusion to 9 laboratories equipped with 15 different experimental setups including gravimetric and volumetric analyzers. The gravimetric H_2 uptake of the pellets was measured at 77 K and up to 100 bar showing a high reproducibility between the different laboratories, with a small relative standard deviation of

[a] *J. A. Villajos,[+] M. Maiwald*
Bundesanstalt für Materialforschung und -prüfung (BAM)
Berlin (Germany)
E-mail: jose.villajos@ciiae.org

[b] *J. A. Villajos[+]*
Centro Ibérico de Investigación en Almacenamiento Energético (CIIAE)
Cáceres (Spain)
E-mail: jose.villajos@ciiae.org

[c] *R. Balderas-Xicohténcatl,[+] M. Hirscher*
Max Planck Institute for Intelligent Systems
Stuttgart (Germany)
E-mail: hirscher@is.mpg.de

[d] *R. Balderas-Xicohténcatl[+]*
Current address: Bauhaus Luftfahrt e.V.
Münnchen (Germany)
E-mail: rafael.balderas@bauhaus-luftfahrt.net

[e] *A. N. Al Shakhs, D. Fairen-Jimenez*
The Adsorption & Advanced Materials Laboratory (A²ML), Department of Chemical Engineering & Biotechnology, University of Cambridge
Cambridge (UK)

[f] *Á. Berenguer-Murcia, D. Cazorla-Amorós, J. Silvestre-Albero*
Universidad de Alicante. Alicante
(Spain)

[g] *C. E. Buckley, T. D. Humphries, M. Paskevicius*
Curtin University
Perth (Australia)

[h] *G. Charalambopoulou, T. Steriotis, C. Tampaxis*
National Center for Scientific Research "Demokritos" (NCSRD)
Athens (Greece)

[i] *F. Couturas, F. Cuevas*
Université Paris Est Creteil (CNRS-ICMPE-UMR7182)
Thiais (France)

[j] *K. N. Heinselman, P. A. Parilla, S. Shulda*
National Renewable Energy Laboratory (NREL)
Denver (USA)

[k] *S. Kaskel, I. Senkovska*
Technische Universität Dresden (TUD)
Dresden (Germany)

[l] *H. Kim, H. Oh*
Ulsan National Institute of Science and Technology (UNIST)
Ulsan, (South Korea)

[m] *J. P. Marco-Lozar*
G2MTech.
Alicante (Spain)

[n] *M. Hirscher*
Advanced Institute for Materials Research (WPI-AIMR)
Tohoku University
Sendai (Japan)

[+] *These authors contributed equally.*

Supporting information for this article is available on the WWW under https://doi.org/10.1002/cphc.202300794

3–4 % between pressures of 10–100 bar. The effect of operating variables like the amount of sample or analysis temperature was evaluated, remarking the calibration of devices and other correction procedures as the most significant deviation sources. Overall, the reproducible hydrogen cryoadsorption measurements indicate the robustness of the ZIF-8 pellets, which we want to propose as a reference material.

Introduction

Storing hydrogen (H_2) as an energy carrier requires developments for increasing efficiency and safety with respect to traditional storage solutions, e.g., compressed gas (350–700 bar) and cryogenic liquid (20–30 K).[1] Solid-state hydrogen storage is an alternative under development to reach technical storage densities involving lower storage pressures, by means of chemical bonds in metal-hydrides or by physical adsorption (physisorption) on the surface of porous materials.[2] Among solid-state methods, physisorption shows faster kinetics for charging and discharging and complete reversibility.[3,4] Using adsorbents for hydrogen storage requires cryogenic temperatures (cryoadsorption), typically around the boiling point of liquid nitrogen, i.e., 77 K, to achieve practical gravimetric and volumetric capacities comparable to high-pressure or liquid hydrogen tanks.[5–11]

For the development of cryoadsorption hydrogen storage systems on a technological level, reliable data are required for the H_2 uptake at low temperature for each material. However, even for established adsorbents, such as activated carbons, the reported H_2 uptake shows sometimes large discrepancies between different laboratories.[12–14] An interlaboratory analysis of amorphous porous carbon materials conducted in 2009 found significant deviations and finally recommended regularly and carefully calibrate the devices, including sensors, volumes, and effects of thermal gradients; reduce gas leaks, control the experiment conditions carefully, repeat the isotherms, and post-analyze the data, if necessary.[15] Following these recommendations, the variability of the results was reduced in a subsequent interlaboratory study.[16] Even for a specific adsorbent, the hydrogen uptake can vary depending on the synthesis method, handling and activation conditions, which may affect their structural and/or porous properties.[8] To the best of our knowledge, no material has been defined as a standard or reference to assure the reliability of hydrogen adsorption measurements. Therefore, the different results for H_2 uptakes in different laboratories can be due to measurement errors or unknown differences in the adsorption properties of the analyzed materials.

In general, the hydrogen uptake at 77 K is proportional to their surface area, ca. 1 wt% at 20 bar each 500 m^2/g of BET area.[17] However, the composition of the material, the pores structure and size, and the pore volume determine not the uptake, but the relationship between the uptake and the pressure, i.e. heat of adsorption, specially at lower pressure than the saturation of the surface.[18] For these reasons, the textural properties, pore size and distribution, phase purity, and activation degree must be perfectly characterized in a reference material used for cryoadsorption. To ensure the control of these properties, crystalline structures are more suitable as reference materials than amorphous solids because of the easy assessment of the sample quality by using powder X-ray diffraction (PXRD) to identify the crystalline phase (related to pores size, distribution, and geometry) combined with the calculation of the BET area and pore volume (related to phase purity and activation degree). As examples, crystalline zeolites Y and ZSM-5 were proposed as reference materials for CO_2 and CH_4 adsorption, resulting in a high comparability of adsorption uptakes among different laboratories.[19,20] Furthermore, the structural stability of zeolites facilitates the reproducibility of the results, more importantly when comparing measurements from different laboratories,[13,21] and assures that the crystal phase is not degraded during handling or activation.

Independently of the technique used (volumetric or gravimetric), an accurate measurement at 77 K requires materials with high specific surface areas and densities so that the analysis can be performed with a high resolution but involving volumes of sample that fit in the sample holder at the analysis temperature.[13,14] In this sense, crystalline metal-organic framework materials (MOFs) are more suitable than zeolites because of their generally larger surface areas. Other molecular framework materials like COFs are also crystalline, but generally show lower stability and density than MOFs.[22] The material ZIF-8 (Zeolitic Imidazolate Framework-8) studied recently in the frame of the MefHySto project[23] shows a higher specific surface area than zeolites, therefore, yielding a higher gravimetric hydrogen uptake. This zeolitic-like MOF made from tetrahedrally coordinated zinc by 2-methylimidazole (melm) possesses strong Zn–N coordination bonds providing high thermal and mechanical stability and reducing degradation during handling and activation.[24] This high mechanical strength allows easy pelletizing of the powders,[23] reducing the analysis volume, facilitating handling and weighting, and avoiding loss of material during measurements. Furthermore, the high hydrophobicity of ZIF-8 compared to zeolites reduces the adsorption of humidity during the weighting procedure and facilitates the sample preparation and transfer without using an inert or dry atmosphere.

In this work, we distributed pellets of ZIF-8 materials among different expert laboratories in hydrogen cryoadsorption measurements worldwide with the goal of establishing ZIF-8 as a reference material for hydrogen cryoadsorption.

Experimental details

Reference material

Pellets of ZIF-8 were synthesized and pelletized by MOF-Technologies (currently Nuada). The studied material was synthesized in a large batch of 50 g of pellets and further evacuated and kept in vacuum in an airtight plastic bag. The material was characterized by PXRD and N_2 adsorption-desorption experiments at 77 K prior to

the interlaboratory experiment and the results are available in a separated publication.[23] Each participating laboratory received a closed glass vial containing ca. 2 g of pellets in air as well as instructions to perform hydrogen adsorption measurements (see ESI, section 1). A data sheet was provided for reporting details on the experimental setup and the analysis conditions (see Figure S1 in the ESI). The experimental setups were numbered and the information is provided maintaining the anonymity of the participants.

Interlaboratory experiments

In the frame of the EURAMET project MefHySto (Metrology for Advanced Hydrogen Storage),[21] nine participating laboratories performed H_2 adsorption measurements at 77 K using 15 different experimental setups. The isotherms were measured up to 100 bar in those devices allowing to operate up to such a high pressure value by following the reported experimental conditions described in the section 2 of the ESI. The participants were asked to analyze the necessary amount of sample to ensure good resolution of the adsorption measurement. For volumetric devices, we asked for a figure of merit for the measurement higher than 10, which means a pressure change due to adsorption (assuming a pressure step from 0 to 1 bar for the ZIF-8) at least 10 times higher than the resolution of the pressure transducer.[25] As a general request, we suggested analyzing ca. 1 g of sample in a high-pressure volumetric device. For gravimetric measurements, we asked for an amount of sample able to adsorb at least 1,000 times more gas than the resolution of the microbalance, assuming 30 mg of adsorbed hydrogen per gram of material. The sample was activated at 120 °C for 6 h at dynamic vacuum and the participants were asked to perform at least two experiments varying the mass of adsorbent to assess the reproducibility of their results and dismiss systematic errors. Tables from S1 to S6 from ESI collect the data from each adsorption isotherm, interpolated to normalized pressure values of 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, and 100 bar.

Results and discussion

Figure 1 shows the H_2 adsorption at 77 K for the 15 setups used by the nine participants. For each setup, the average of the measurements with different masses is taken (see the individual isotherms reported for each mass in Figures from S2 to S14 in the ESI). Furthermore, the data have been interpolated for specific pressure points (see section S1 in the ESI). Figure 1b shows a zoom-in of the isotherms at low pressures up to 20 bar. In general, the adsorption follows a type I isotherm according to the IUPAC classification with a maximum in excess uptake at ca. 25–30 bar. Further increasing the pressure diminishes the excess uptake which is typical for hydrogen cryoadsorption on microporous materials.[26,27]

The majority of the results are close to each other with only 3 setups showing systematically either higher or lower uptake than most of the data. Figure 2 shows a boxplot representing the measurements deviation. For better readability, the considered pressure points are evenly spread along with the x-axis. The size of the boxes containing the data within percentiles Q_1 and Q_3 (IQR, 50 % of data) is smaller for pressures under 25 bar. For higher pressures, the boxes cover a wider excess region, as well as the range 1.5*IQR that contains data from minimum to maximum uptakes within the calculated distribution. Adsorption uptakes measured out of this region (1.5*IQR) are considered outliers, and they correspond to data from setups 5, 8, and 9 shown in Figure 1. Figure 2b shows these boxplot neglecting the outliers from these three devices. The mean values correspond to the average adsorption isotherm shown as a red line in Figure 1.

The reproducibility of the adsorption results among laboratories is high with a relative standard deviation (RSD=SD/$\bar{X}$) of 3–4 % for pressures from 10 to 100 bar. The RSD of the results in the present study are presented as a function of pressure in Figure 3 (black symbols). Additionally, the results are compared to a recent international laboratory H_2 cryoadsorption comparison study on two different porous carbon materials, NORIT R0.8 mm (sample 1, red) and MSP-20 (sample 2, blue).[16] The RSD of the ZIF-8 pellets is lower than that for sample 1 of the previous study, especially between 10 and 60 bar, and only slightly higher (ca. 1 %) than that for sample 2. Overall, our ZIF-8 pellets yield highly reproducible H_2 adsorption isotherms and RSD values comparable to the previous state-of-the-art interlaboratory tests. Compared to sample 2 (MSP-20), which is a powdery, fluffy, amorphous carbon with 2,400 m^2/g BET area,[28]

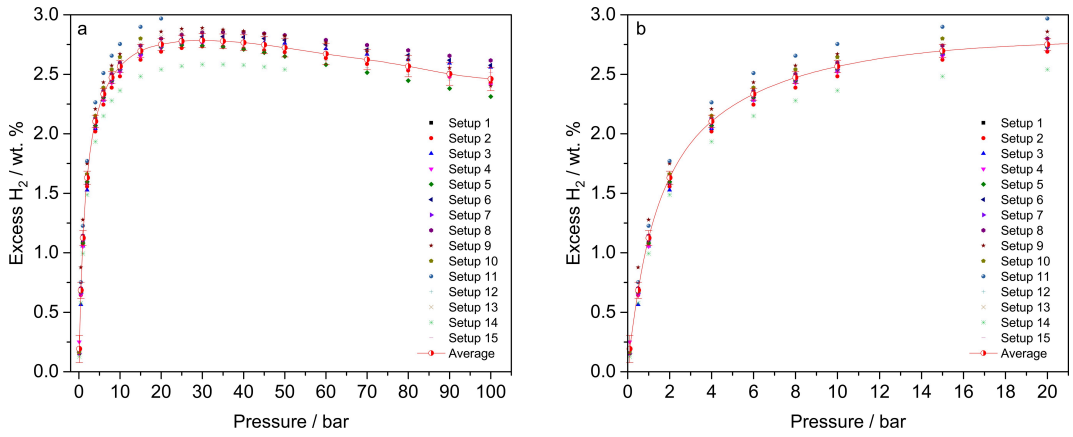

Figure 1. Comparison of the average H_2 adsorption isotherms at 77 K from each experimental setup up to 100 bar (a) and up to 20 bar (b). For each lab, data are interpolated for specific pressure points. The red line shows the average isotherm removing outliers.

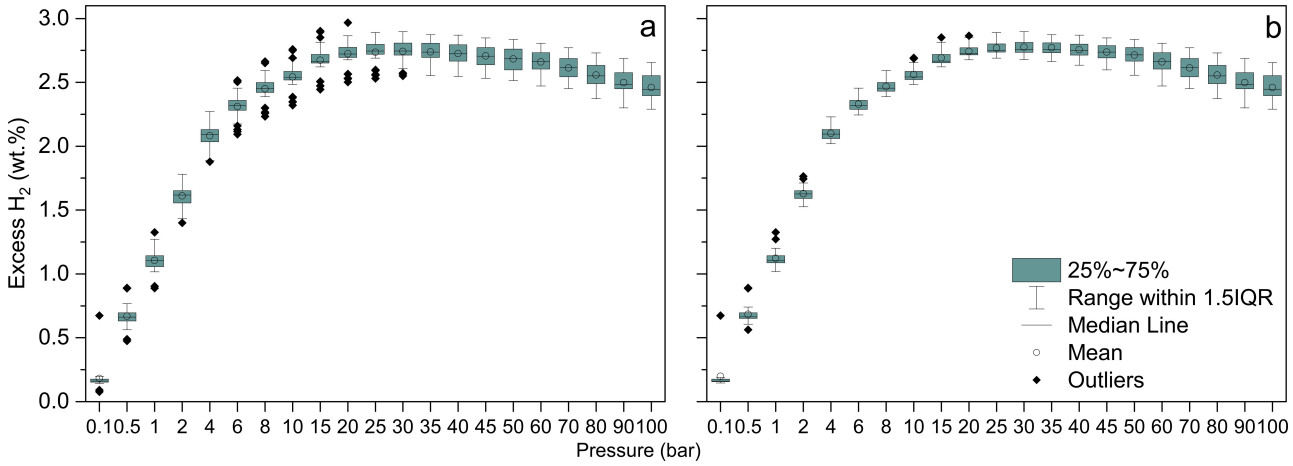

Figure 2. Measurements deviation boxplot. Using all data (a) and removing outliers (b).

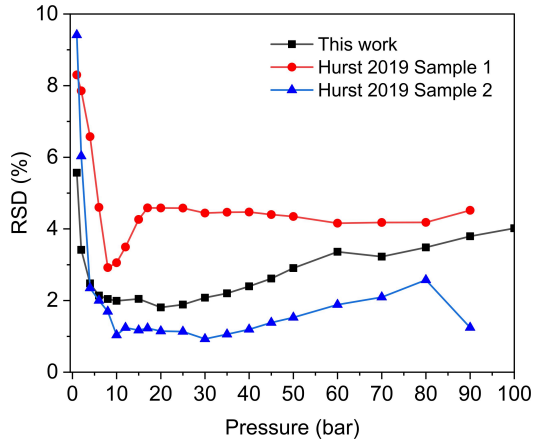

Figure 3. Relative standard deviation of the measurements performed in this work compared to those in Ref. [16] as a function of pressure.

our pellets can be handled easily and the quality of crystalline material can be checked by PXRD.

This high reproducibility of the adsorption results has been achieved on samples taken from a 50 g batch of ZIF-8 pellets and distributed to the laboratories, which demonstrates clearly the high homogeneity of the synthesized material and its structural/porous properties as well as its structural stability to storage, transport, and handling. It is worth mentioning that reported wet- and dry-masses of the analyzed materials were similar, corroborating that the hydrophobic material, once successfully activated, adsorbs negligible amounts of moisture from the atmosphere improving the reproducibility of the weighting procedure. Since laboratories used different amounts of analyzed sample (comparing measurements of different setups or from the same device), this high reproducibility over the entire pressure range indicates systematic calibration of the devices (pressure transducers, temperature sensors, and reference volumes) and a precise estimation of analysis volumes (free volumes, volume of solid, free volume at the analysis temperature, …).[12–14]

Figure 4 shows the percent deviation of each excess uptake measurement from the average value as a function of pressure. The plot indicates the analyzed mass using a color scale (from bluish- to purple-colors) and different markers. In general, the dispersion of results has a minimum average deviation at pressure between 15–20 bar, which corresponds to the observed smaller size of the boxes in Figure 2. This is related to the surface saturation of the material at ca. 25 bar, from which the surface of the material is fully covered of adsorbate. Below 25 bar, an increase in the analysis pressure is followed by a considerable amount of adsorption which is related to a measurable change in pressure or mass for a volumetric or gravimetric device, respectively. However, after saturation of the surface, the change in adsorbed amount with increasing pressure is almost null, and for the volumetric setup only compression of the gas occurs making any temperature fluctuation more severe.

The plot also shows a higher concentration of samples using higher mass than 1.0 g (red-to-brown colors) within −5 to 5% deviation, while samples with less than 0.2 g (blueish colors) deviate between 5 to 10%. A higher mass is related to a higher total gas adsorption that increases the measurement resolution reducing the deviation. Indeed, some of the outliers at pressures up to 30 bar in Figure 2a correspond to most of the blueish data in Figure 4 (the smallest amounts of sample), used in two specific volumetric devices. Data among −5 to −10% deviation likely indicate a systematic error since the excess H_2 uptake is too low despite the analyzed mass is high-enough for a high resolution of the measurement. These systematic deviations often arise from wrong reference volume calibrations, free volume for the experiment determination, or systematic differences between the correction of the thermal gradient affecting the analysis and that during the blank experiments.[29] Indeed, these sources of experimental error could explain the large variations seen in the Ref. [15] instead of the contribution of random errors.

There are also outliers at the lowest analysis pressures, which might be related to the low resolution of the pressure transducers for recording such low-pressure values; but also to

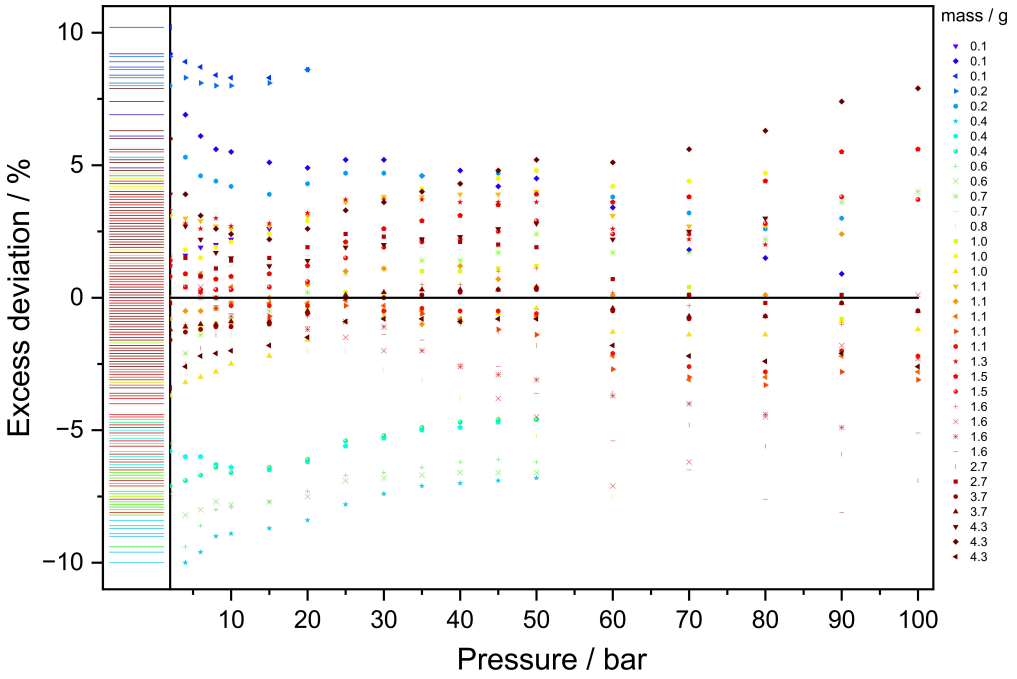

Figure 4. Deviation of the measured uptake with respect to the average value at different pressures and for each analyzed mass of sample. The colored lines in the Left margin of the Figure indicate the average deviation for each experiment.

the double contribution of the pressure reading in the adsorption isotherm measured by volumetric devices. Contrary to gravimetric measurements, where the uptake is measured by recording the mass of adsorbate (plus the correction of the buoyancy effect, less important at low pressure) and the pressure determines the position of the equilibrium point in the x-axis; for a volumetric device the pressure is used to both set the position in the x-axis and to calculate the adsorption uptake (y-axis).

Adsorption results may also be affected by changes of the analysis temperature. To evaluate this, adsorption experiments were repeated controlling the analysis temperature by a cryostat and varying the temperature set-point ±1 K respect to 77 K (see Figure 5a). At first sight, the difference in uptake occurs between 10 and 30 bar, while the uptake from 60 bar is not affected. An analysis of the perceptual variation (Figure 5b) shows that the higher changes in uptake is ±2% at 5 bar, because of the high dependency of the hydrogen uptake with the interaction of the gas and the surface at low pressure. Therefore, a ±1 K difference in the analysis temperature does not explain the shown variability of some high-pressure data but may explain some deviation at relatively low pressures (< 20 bar).

The analysis temperature of the performed experiments was mainly controlled using baths of boiling liquid nitrogen, generally assumed as 77 K. Using liquid N_2 baths involves temperature variations among laboratories because the actual boiling temperature of liquid nitrogen is given as a function of the ambient pressure, which can change between measuring days and geographic differences between laboratories. According to NIST,[30] 76 K is the boiling temperature of nitrogen at

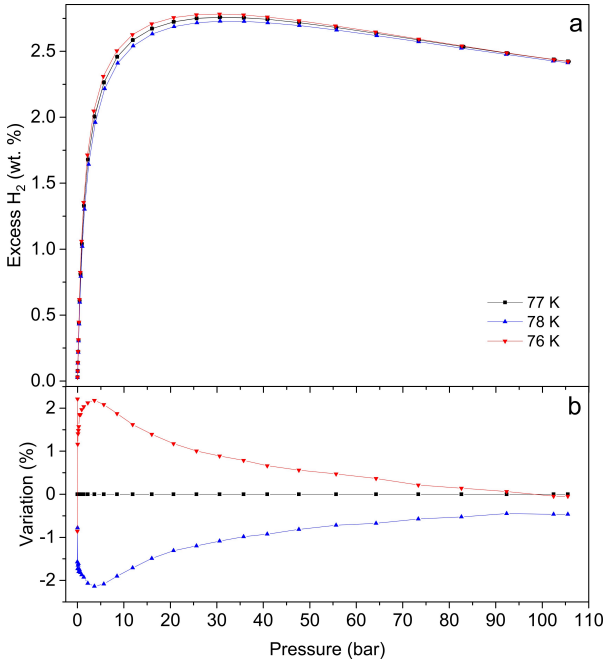

Figure 5. H_2 adsorption isotherms collected using a cryostat and modifying the temperature set point.

0.85 atm, which is the average atmospheric pressure corresponding to a geographic height of 1.350 m above sea level. Therefore, the effect of the boiling temperature of the liquid nitrogen on the hydrogen uptake should be within the variation range (< 2%) shown in Figure 5 for measurements in laboratories at lower heights than 1.350 m over the sea level.

In some other cases, the analysis temperature was controlled using a cryostat (see Figure S2). Some of these data deviate more than 2% at high pressure (see Figure S14 in ESI) despite using large amounts of sample (up to 4.3 g) and the same device. This high deviation is not due to analysis temperature variation but to the difference between the free volume affected by the thermal gradient compared to that calculated during the calibration procedure. This is a different positioning of the cooling-head during the experiment compared to the calibration, implying a magnification of correction errors for even higher pressure values.[29]

Conclusions

The development of cryoadsorption hydrogen storage systems on a technological level requires reliable H_2 uptake data at low temperatures for the used materials. So far, no material has been established as a reference for hydrogen cryoadsorption measurements, making it difficult to compare measurements based on reliable standards. We selected the crystalline metal-organic framework material ZIF-8 due to its structural properties and composition of the material, which provides a significant hydrogen uptake, density, and mechanical stability. This mechanical stability allows a high degree of packing and excellent cyclability, which results in repeatable adsorption and desorption amounts of hydrogen during its lifetime. Besides, its hydrophobicity helps to reduce water adsorption during preparation and weighting, also increasing the accuracy of measurements and facilitating an easy, reliable activation.

A large batch of ZIF-8 pellets has been produced on a commercial level. For an interlaboratory study, we distributed this material to 9 different laboratories worldwide. These laboratories measured the H_2 uptake utilizing 15 different experimental setups. A protocol was given to each participant, taking special care of the measuring conditions, sample mass, outgassing conditions, minimum purity of gases, equilibration time, and repetition of the analyses with different masses of samples to identify systematic errors. Using as input the results of these 15 setups, we evaluated the measurements considering the pressure range, the type of analyzer, control of the analysis temperature, and the procedure to correct or compensate for the presence of thermal gradients in the instrument. For most of the pressure range, the RSD obtained was about 4%, indicating progress in the interlaboratory comparability of results compared to previous studies involving hydrogen cryoadsorption measurements. Most of the outliers in our analysis are attributed to measurements in the lower-pressure region. Removing these outliers, the RSD is further reduced for pressures near the isotherm saturation. The analyzed mass of the sample is important for the accuracy of the measurement. However, once the device analyzes the minimum-required mass, the main variation source was identified as the correction procedure of the thermal gradient, especially maintaining the same conditions between blank and analysis measurements. The most important effect was the accurate positioning of the cooling system, which must be identical for each experiment including the performed blank analyses used during the calibration.

Overall, the high reproducibility of H_2 uptake measured by 15 different experimental setups indicates clearly the high stability and easiness of both the handling and activation process of the ZIF-8 pellets. Furthermore, it demonstrates the high homogeneity of the batch of ZIF-8 pellets prepared by reactive extrusion. Therefore, we suggest the ZIF-8 material used in this study as a reference material for hydrogen cryoadsorption measurements which will help to further develop this hydrogen storage technology.

Funding

This project has received funding from the EMPIR program cofinanced by the Participating States and from the European Union's Horizon 2020 research and innovation program (Grant ID: 10.13039/100014132, Grant number: 19ENG03 MefHySto). Open access funded by Max Planck Society. Each participant in the interlaboratory study used their own funding to perform their experiments.

Acknowledgements

M. Maiwald, J. A. Villajos, R. Balderas and M. Hirscher acknowledge the EMPIR programme from the European Union's Horizon 2020 research and innovation programme for funding. F. Cuevas and F. Couturas acknowledge support from France 2030 program under project ANR-22-PEHY-0007. D. Cazorla and A. Berenguer-Murcia thank the support by PID2021-123079OB-I00 project funded by MCIN/AEI/10.13039/501100011033, and "ERDF A way of making Europe". K. N. Heinselman, S. Shulda and P. A. Parilla acknowledge the support from the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Hydrogen and Fuel Cell Technology Office through the HyMARC Energy Materials Network. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

Authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: hydrogen storage · interlaboratory analysis · metal-organic frameworks · reference material · reproducibility and standardization

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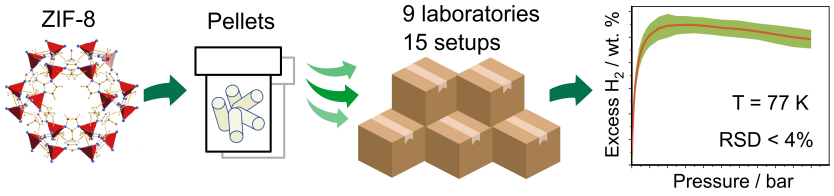
Manuscript received: October 25, 2023
Revised manuscript received: December 28, 2023
Accepted manuscript online: January 2, 2024
Version of record online: ■■, ■■



Assuring the reliability of hydrogen cryoadsorption measurements requires a robust reference material. Here we distributed a commercially produced metal-organic framework ZIF-8 in the form of pellets for an interlaboratory study on hydrogen adsorption isotherms at 77 K. The results show a low standard deviation and prove the material batch's high homogeneity, therefore, making ZIF-8 pellets a promising candidate for a reference material.

J. A. Villajos, R. Balderas-Xicohténcatl*, A. N. Al Shakhs, Á. Berenguer-Murcia, C. E. Buckley, D. Cazorla-Amorós, G. Charalambopoulou, F. Couturas, F. Cuevas, D. Fairen-Jimenez, K. N. Heinselman, T. D. Humphries, S. Kaskel, H. Kim, J. P. Marco-Lozar, H. Oh, P. A. Parilla, M. Paskevicius, I. Senkovska, S. Shulda, J. Silvestre-Albero, T. Steriotis, C. Tampaxis, M. Hirscher*, M. Maiwald*

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