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Supporting Information

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

Jose A. Villajos,* Rafael Balderas-Xicohténcatl,* Ali N. Al Shakhs, Ángel Berenguer-Murcia, Craig E. Buckley, Diego Cazorla-Amorós, Georgia Charalambopoulou, Fabrice Couturas, Fermin Cuevas, David Fairen-Jimenez, Karen N. Heinselman, Terry D. Humphries, Stefan Kaskel, Hyunlim Kim, Juan P. Marco-Lozar, Hyunchul Oh, Philip A. Parilla, Mark Paskevicius, Irena Senkowska, Sarah Shulda, Joaquin Silvestre-Albero, Theodore Steriotis, Christos Tampaxis, Michael Hirscher,* and Michael Maiwald

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1. Hydrogen adsorption conditions

To ensure the best possible performance of the participating laboratories to a feasible level, the following sample preparation/analysis protocol was followed. The general conditions are summarized as follow:

- Sample mass: ca. 1 g of material in volumetric devices and 0.1 g for gravimetric ones.
- Sample Outgassing: 120 °C with a heating rate of 5 – 10 °C/min before analysis. keeping the maximum temperature for at least 6 h while applying a dynamic vacuum ca. 10^{-5} – 10^{-7} mbar.
- Analysis temperature: Controlled with a bath of liquid nitrogen (77 K) at ambient pressure or a cryostat.
- Minimum purity of gases: H₂ 99.999 %. He 99.9999%
- Adsorption equilibration time: minimum 10 min each step
- Pressure steps: 1, 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, and 100 bar.
- Calibration: The participants in this interlaboratory analysis used their own calibration procedures when necessary to correct the measured gravimetric excess of hydrogen at cryogenic temperature as well as He-adsorption correction. The participants were asked to corroborate the null-adsorption uptake of a blank experiment by using their calibration procedure.
- Reproducibility: Experiments were mostly repeated using either used or fresh sample with a different analyzed mass (± 25 – 50 % respect to the first experiment) to seek for possible deviations in instrument calibrations.

INSTRUCTIONS					
Please fill out a run sheet <u>for each measurement</u> . You may want to fill out the fields that will be common for all measurements and then save this file so you do not have to fill in those fields every time. Please provide isotherm data calculated as gravimetric excess (wt. %). See the instruction sheet for additional details. If you correct for helium adsorption that occurs during the free-space/buoyancy calibration, please supply both the corrected and uncorrected data if possible. If you have any questions call or email Jose A. Villajos (+ 49 30 8104-5825, jose-antonio.villajos@bam.de)					
LABORATORY INFORMATION					
Institution/laboratory:			Person filling out run sheet:		
Phone number for person:			E-Mail for person:		
Filename(s) for this data:					
NOTE: The above information will be removed when the final results are reported. Laboratories will be identified anonymously using a randomly assigned number.					
SAMPLE PREPARATION					
Run Number (same as "Experiment Result"):					
SAMPLE MASS					
Initial mass:	±	mg	Date:		
After degass (optional):	±	mg	Date:		
Final mass: 1132.9	±	mg	Date:		
SAMPLE DEGASS					
Base Vacuum pressure		units:	End date/time:		
Degass protocol:		<input type="checkbox"/> Degas protocol Followed	<input type="checkbox"/> Degas protocol exception (Explain):	<input type="checkbox"/> Analysis repetition	
Degass explanation:					
Was sample exposed to air after degas and prior to measurement?			<input type="checkbox"/> No	<input type="checkbox"/> Yes (explain):	
Air exposure explanation:					
MEASUREMENT INFORMATION					
Measurement method	<input type="checkbox"/> Gravimetric	<input type="checkbox"/> Volumetric	<input type="checkbox"/> Other:	<input type="checkbox"/> Static	<input type="checkbox"/> Dynamic
Measurement temperature control	<input type="checkbox"/> Liquid nitrogen	<input type="checkbox"/> Other (specify):		If dynamic, flow rate:	
Hydrogen purity:	Additional purifier used?		<input type="checkbox"/> Yes	<input type="checkbox"/> No	
Base Vacuum pressure:	Units:				
Sequence order:	<input type="checkbox"/>	He calibration done first	<input type="checkbox"/>	H ₂ measurement done first	<input type="checkbox"/> No He calibration
Equilibration time/step:	min		Total time for measurement:	min	
Temperature stability	Standard deviation:	K	Pressure Sensor Accuracy:	<input type="checkbox"/> % of FS:	<input type="checkbox"/> % of reading:
Equation of State:	<input type="checkbox"/> Ideal	<input type="checkbox"/> Real: Model:	mBWR-Jacobsen		
CALIBRATION					
Helium Adsorption correction?	<input type="checkbox"/> Yes <input type="checkbox"/> No	Supplied adsorption data has no correction.			
If other, explain:					
Skeletal Density	<input type="checkbox"/> Not Measured	<input type="checkbox"/> Measured:	g/cm ³	Method used:	
COMMENTS					

Figure S1.. Distributed form to report the used experimental conditions for each analyzed sample by the participants.

2. Hydrogen adsorption analyzers

2.1. Volumetric devices

Two HPVA II (high pressure volumetric analyzers) from Micromeritics using two pressure transducers for reading manifold's pressure up to 1 bar (accuracy 0.15 % of the reading) and up to 200 bar (accuracy 0.04 % of the full-scale). A cryojacket, provided by Micromeritics, keeps the level of liquid nitrogen in contact with the sample tube approximately constant despite the evaporation of this liquid during the experiment. The control of the analysis temperature was also performed by using a Micromeritics CryoStat with Lakeshore Temperature Controller.

A home-made volumetric device consisting in a Sieverts' rig equipped with a pressure transducer (100 ± 0.05 bar - FS) and calibrated volumes immersed in a temperature-controlled water bath at 24.6 ± 0.1 °C. The Sieverts's rig is connected to a turbomolecular pump with base pressure $5 \cdot 10^{-6}$ mbar and, through a copper capillary, to a stainless-steel sample holder. The copper capillary ($V_{cap} = 3.709 \pm 0.002$ cm³) is at room temperature (RT). The sample holder ($V_{SH} = 9.013 \pm 0.007$ cm³) consists of a capillary ($V_{SH.cap} = 0.691$ cm³) and an empty volume ($V_{SH.empty} = 8.322$ cm³). For measures at liquid nitrogen temperature (-195.81 °C), the empty volume of the sample holder was fully immersed in liquid nitrogen using a dewar container. The capillary part of the sample holder has a length of 30 cm, 2/3 of the capillary was immersed in liquid nitrogen while, separated by thermal insulator, 1/3 of the capillary was at room temperature.

A volumetric BELSORP-HP analyzing ca. 1 g of the sample. The pressure transducer accuracy was 0.08 % F.S. The analysis temperature was controlled by using a Dewar vessel with level controller of the boiling liquid nitrogen.

A custom-made Sieverts apparatus constructed from 316 stainless steel Swagelok parts. Pressure-data were recorded using a Rosemount 3051S pressure gauge (14 mbar accuracy), 4-wire platinum resistance temperature detectors (RTD), and an N-type thermocouple (77 K). The apparatus consisted of a known reference volume (16.03 ± 0.01 cm³) and total analysis volume (16.77 ± 0.02 cm³) containing a non-ambient cold-volume (8.43 ± 0.02 cm³). Volume calibrations were based on manometric measurements using hydrogen (99.999 %) from a known calibration volume (72.91 ± 0.01 cm³) measured using 99.5 % ethanol.

Hydrogen sorption measurements were undertaken at 77 K by immersing the sample cell within a liquid nitrogen bath of fixed height (varying over ± 0.05 cm³ internal volume). within a cryogenic Dewar flask. The liquid nitrogen level was not perfectly constant during blanks/measurements due to boil-off. However, the top of the liquid nitrogen level was kept on a low-volume 1/8" piece of Swagelok tubing.

Three PCT pro 2000 devices from Setaram using a microdoser to dose the analysis gas to the sample cell for experiments up to 50 bar. Liquid nitrogen was used to control the analysis temperature in all cases controlling the level of liquid nitrogen throughout the experiments. Another PCTPro 2000 used a VCR plug acting as the sample holder in order to reach high pressure values up to 100 bar.

A modified PCT Pro 2000 to improve temperature control of the external components (external tubing and sample vessel), including a well-defined and better-controlled temperature gradient region between the sample and the rest of the instrument, and allow high-pressure helium to be used instead of hydrogen for calibration purposes. The PCTPro has been integrated with an ARS helium refrigerator to cover a wide temperature range (35 K to 325 K) for the material under test. The cryogenic head was modified to accommodate the sample holder using a calibrated temperature-sensor diode at the sample position.

Two high-pressure volumetric analyzers Quantachrome iSorb-HP1 were used in two separated laboratories. Temperature control for all experiments was performed by means of a liquid nitrogen bath. The level of liquid nitrogen was kept constant throughout the experiments by means of a recirculating pump in one device, and a LN₂ option using a sample dewar, a 60 L self-pressurized

supply dewar, and a LN₂ level sensor for the other one.

2.2. Gravimetric analyzers

An Intelligent Gravimetric Analyzer IGA-001 by HIDEN ISOHEMA reaching pressures up to 20 bar. The device comprises a precision microbalance (resolution $\pm 0.1 \mu\text{g}$) with a dual suspension arm (for sample and counterweight respectively) and includes three 0.1, 1, and 20 bar. All the above elements are located in a special chamber at a constant temperature (50 °C), in order to minimize electronic noise. The device is equipped with a vacuum system consisting of a diaphragm pump (Vacumbrand MZ-2D) in combination with a turbo molecular pump (PFEIFFER TMU 60) and a vacuum meter (Edwards Penning CP25-K). A foam jacket acting as a thermal insulator was placed around the reactor containing the sample and was immersed in a dewar vessel filled with liquid nitrogen, thus ensuring isothermal conditions during the experiment.

A gravimetric XEMIS device from HIDEN ISOHEMA equipped with a micro-balance inside a chamber connected to two detachable reactors. Two thin tungsten wires hang from both arms of the microbalance and holding the sample and counterweight. A gas inlet tube connects the pressure system to the microbalance chamber and both arms. These two arms are submerged in the bath of the refrigerant fluid so that the effect of the temperature gradients in the buoyancy of the sample is compensated with the buoyancy of the counterweight.

2.3. Interpolated hydrogen excess data from all the experiments

Table S1.. Interpolated excess uptakes at 77 K from setups 1. 2. 3 and 4.

Setup id.	1	2	2	3	3	3	4	4
mass(g):	0.67	1	1.6	1.32	1.08	1.03	0.78	0.74
P	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂
(bar)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)
0				0.16	0.17	0.16		
1	0.56	0.66	0.66	0.69	0.71	0.68	0.66	0.68
1	1.06	1.09	1.10	1.15	1.15	1.12	1.10	1.12
2	1.53	1.60	1.60	1.67	1.66	1.64	1.59	1.63
4	2.04	2.06	2.06	2.14	2.15	2.12	2.06	2.10
6	2.28	2.29	2.29	2.37	2.38	2.35	2.29	2.34
8	2.43	2.43	2.43	2.53	2.52	2.50	2.42	2.49
10	2.53	2.52	2.52	2.62	2.61	2.60	2.51	2.58
15	2.67	2.65	2.65	2.75	2.75	2.74	2.63	2.71
20	2.74	2.72	2.71	2.82	2.82	2.81	2.68	2.78
25	2.77	2.75	2.74	2.85	2.85	2.85	2.69	2.80
30	2.78	2.76	2.76	2.86	2.86	2.86	2.68	2.81
35	2.79	2.78	2.76	2.85	2.85	2.86	2.66	2.80
40	2.78	2.76	2.75	2.84	2.84	2.86	2.63	2.79
45	2.77	2.75	2.75	2.82	2.82	2.84	2.60	2.77
50	2.76	2.73	2.73	2.79	2.80	2.82	2.56	2.75
60	2.71	2.67	2.67	2.74	2.75	2.78	2.47	2.69
70	2.67	2.63	2.62	2.68	2.69	2.74		2.63
80	2.62	2.56	2.55	2.62	2.64	2.69		
90	2.59	2.48	2.48					
100	2.56							

Table S2. Interpolated excess uptakes at 77 K from setup 5.

Setup id.	5	5	5	5	5
mass(g):	0.44	0.44	0.56	0.56	0.36
P	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂
(bar)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)
0	0.15	0.14	0.08		0.09
1	0.63	0.62	0.48	0.62	0.49
1	1.05	1.03	0.90	1.02	0.89
2	1.52	1.50	1.43	1.50	1.40
4	1.96	1.94	1.89	1.92	1.88
6	2.17	2.16	2.12	2.13	2.09
8	2.30	2.30	2.26	2.27	2.23
10	2.39	2.38	2.35	2.35	2.32
15	2.51	2.51	2.47	2.47	2.45
20	2.56	2.57	2.53	2.53	2.50
25	2.59	2.60	2.56	2.56	2.53
30	2.61	2.61	2.57	2.57	2.55
35	2.61	2.61	2.57	2.56	2.55
40	2.60	2.61	2.57	2.56	2.55
45	2.59	2.59	2.55	2.54	2.53
50	2.57	2.57	2.53	2.52	2.51
60					
70					
80					
90					
100					

Table S3. Interpolated excess uptakes at 77 K from setup 6.

Setup id.	6	6	6	6	6	6
mass(g):	1.06	0.50	1.06	1.06	0.50	0.50
P	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂
(bar)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)
0						
1	0.69	0.69				
1	1.13	1.12				
2	1.63	1.64				
4	2.09	2.10				
6	2.32	2.32	2.33		2.32	2.32
8	2.46	2.45	2.46		2.45	2.46
10	2.54	2.53	2.56	2.55	2.53	2.54
15	2.67	2.66	2.67	2.66	2.65	2.66
20	2.73	2.70	2.73	2.72	2.70	2.70
25	2.75	2.72	2.74	2.74	2.72	2.71
30	2.74	2.72	2.74	2.74	2.71	2.70
35	2.74	2.69	2.73	2.73	2.70	2.69
40	2.72	2.67	2.72	2.71	2.67	2.67
45	2.71	2.64	2.70	2.69	2.65	2.62
50	2.68	2.61	2.68	2.66	2.60	2.57
60	2.62	2.57	2.61	2.60	2.53	2.48
70	2.55	2.52	2.54	2.54	2.45	2.46
80	2.49	2.46	2.49	2.48	2.37	2.45
90	2.45	2.38	2.45	2.43	2.30	2.46
100	2.41	2.40	2.39	2.38	2.33	2.46

Table S4. Interpolated excess uptakes at 77 K from setup 7. 8. and 9.

Setup id.	7	7	8	8	9	9
mass(g):	0.11	0.21	0.19	0.11	0.039	0.084
P	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂
(bar)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)
0		0.67	0.16	0.20	0.18	0.15
1	0.89	0.89	0.74	0.77	0.70	0.66
1	1.33	1.27	1.22	1.24	1.16	1.11
2	1.76	1.74	1.76	1.78	1.69	1.63
4	2.23	2.20	2.26	2.27	2.19	2.12
6	2.46	2.42	2.50	2.52	2.44	2.36
8	2.59	2.56	2.65	2.66	2.59	2.50
10	2.69	2.66	2.75	2.76	2.69	2.60
15	2.81	2.78	2.89	2.90	2.85	2.75
20	2.87	2.85	2.97	2.97		
25	2.89	2.87				
30	2.90	2.88				
35	2.87	2.87				
40	2.87	2.86				
45	2.83	2.85				
50	2.82	2.82				
60	2.76	2.77				
70	2.67	2.71				
80	2.61	2.63				
90	2.53	2.58				
100						

Table S5. Interpolated excess uptakes at 77 K from setups 10. 11. 13. 14. and 15.

Setup id.	10	10	11	13	14	15
mass(g):	1.45	1.45	1			1.13
P	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂	Excess H ₂
(bar)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)	(wt. %)
0	0.16	0.16	0.16	0.15	0.19	0.17
1	0.68	0.68	0.64	0.66	0.70	0.65
1	1.13	1.12	1.06	1.11	1.14	1.09
2	1.64	1.63	1.56	1.62	1.65	1.62
4	2.10	2.10	2.02	2.09	2.13	2.07
6	2.33	2.32	2.25	2.32	2.36	2.30
8	2.47	2.46	2.39	2.45	2.50	2.45
10	2.57	2.56	2.48	2.54	2.60	2.54
15	2.70	2.69	2.62	2.66	2.74	2.68
20	2.77	2.75	2.69	2.73	2.80	2.75
25	2.80	2.79	2.72	2.77	2.83	2.77
30	2.83	2.80	2.73		2.85	2.78
35	2.83	2.81	2.73		2.86	2.72
40	2.82	2.80	2.72		2.85	2.77
45	2.81	2.79	2.70		2.84	2.74
50	2.80	2.77	2.68		2.83	2.71
60	2.77	2.73	2.63		2.79	2.67
70	2.72	2.69	2.59		2.74	2.63
80	2.68	2.64	2.53		2.70	2.57
90	2.64	2.60	2.48		2.65	2.56
100	2.60	2.55	2.43		2.62	

Table S6. Interpolated excess uptakes at 77 K from setup 12.

Setup id.	12	12	12	12	12	12	12
mass(g):	2.7	2.7	4.3	4.3	4.3	3.7	3.7
P (bar)	Excess H ₂ (wt. %)	Excess H ₂ (wt. %)	Excess H ₂ (wt. %)	Excess H ₂ (wt. %)	Excess H ₂ (wt. %)	Excess H ₂ (wt. %)	Excess H ₂ (wt. %)
0	0.15	0.16	0.18	0.19	0.16	0.16	0.16
1	0.61	0.66	0.71	0.74	0.62	0.65	0.65
1	1.02	1.09	1.16	1.20	1.05	1.08	1.09
2	1.54	1.61	1.68	1.71	1.56	1.59	1.60
4	2.03	2.12	2.14	2.17	2.03	2.06	2.06
6	2.27	2.33	2.37	2.39	2.26	2.29	2.29
8	2.42	2.48	2.50	2.52	2.40	2.43	2.43
10	2.52	2.58	2.59	2.61	2.50	2.52	2.52
15	2.66	2.72	2.71	2.74	2.63	2.65	2.66
20	2.72	2.78	2.77	2.80	2.69	2.72	2.72
25	2.74	2.81	2.80	2.84	2.72	2.75	2.75
30	2.75	2.82	2.81	2.85	2.73	2.76	2.76
35	2.73	2.81	2.81	2.86	2.73	2.75	2.76
40	2.71	2.79	2.80	2.86	2.71	2.74	2.74
45	2.68	2.77	2.79	2.85	2.70	2.73	2.73
50	2.65	2.75	2.77	2.84	2.67	2.70	2.71
60	2.57	2.69	2.73	2.81	2.62	2.66	2.66
70	2.50	2.63	2.69	2.77	2.56	2.60	2.61
80	2.42	2.56	2.64	2.73	2.51	2.55	2.55
90	2.35	2.50		2.69	2.45	2.50	2.50
100	2.29	2.45		2.66	2.40	2.45	2.45

3. Hydrogen adsorption results

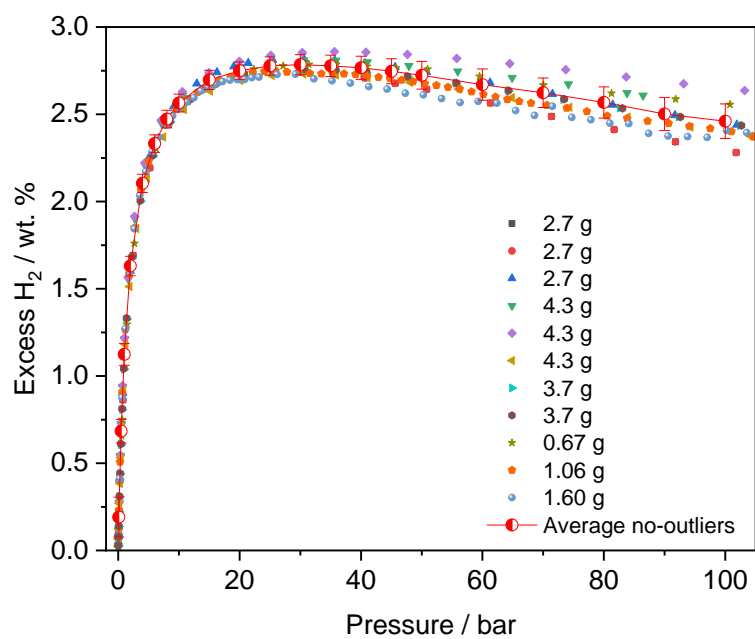


Figure S2.. Comparison of all the H₂ adsorption isotherms at 77 K whose analysis temperature was controlled with a cryostat.

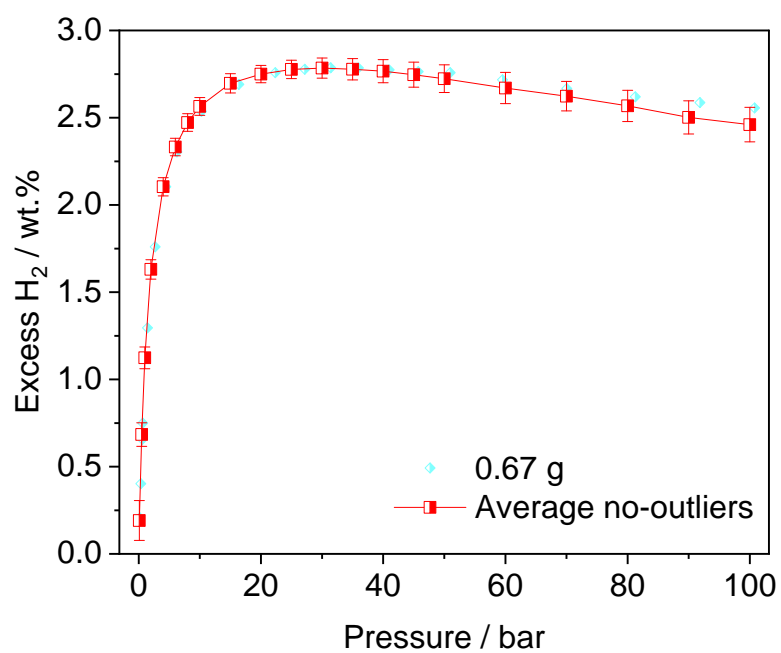


Figure S3.. Comparison of H₂ adsorption isotherms at 77 K from setup 1.

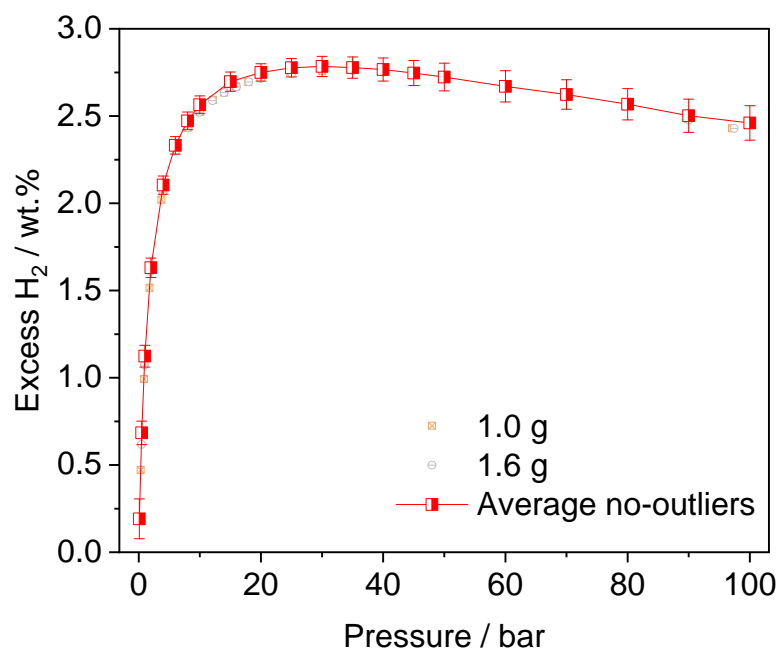


Figure S4.. Comparison of H₂ adsorption isotherms at 77 K from setup 2.

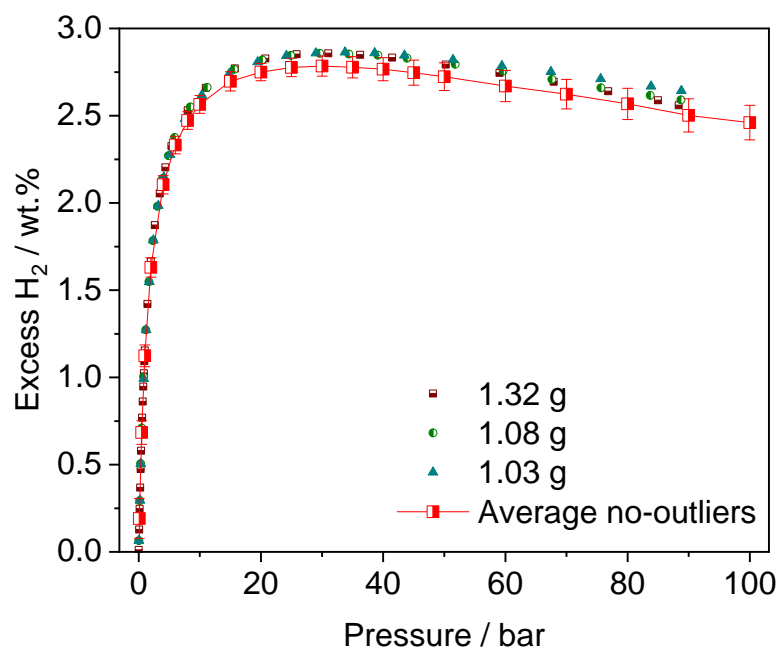


Figure S5.. Comparison of H₂ adsorption isotherms at 77 K from setup 3.

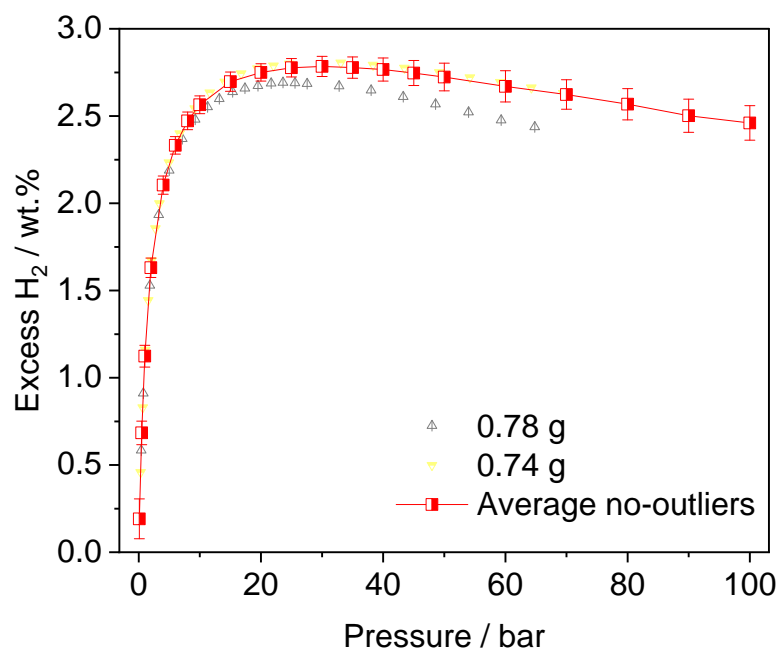


Figure S6.. Comparison of H₂ adsorption isotherms at 77 K from setup 4.

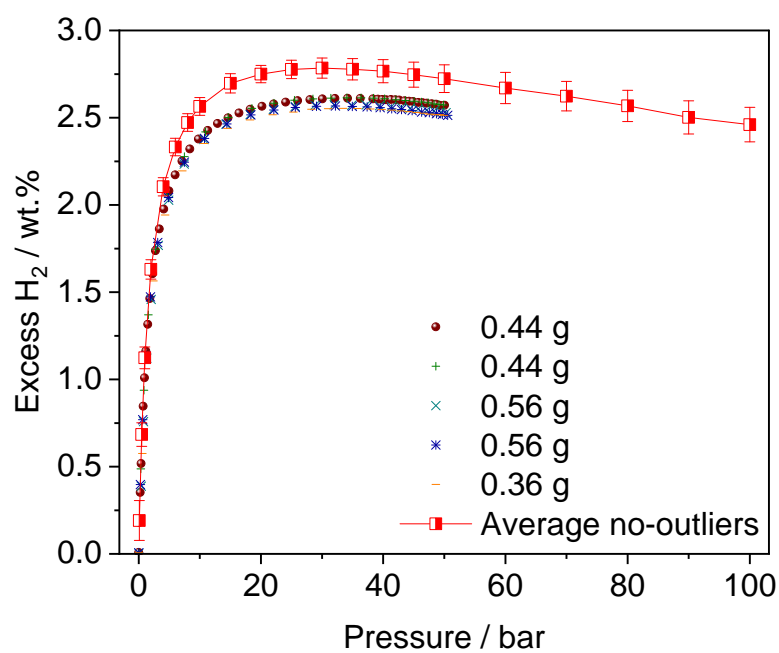


Figure S7.. Comparison of H_2 adsorption isotherms at 77 K from setup 5.

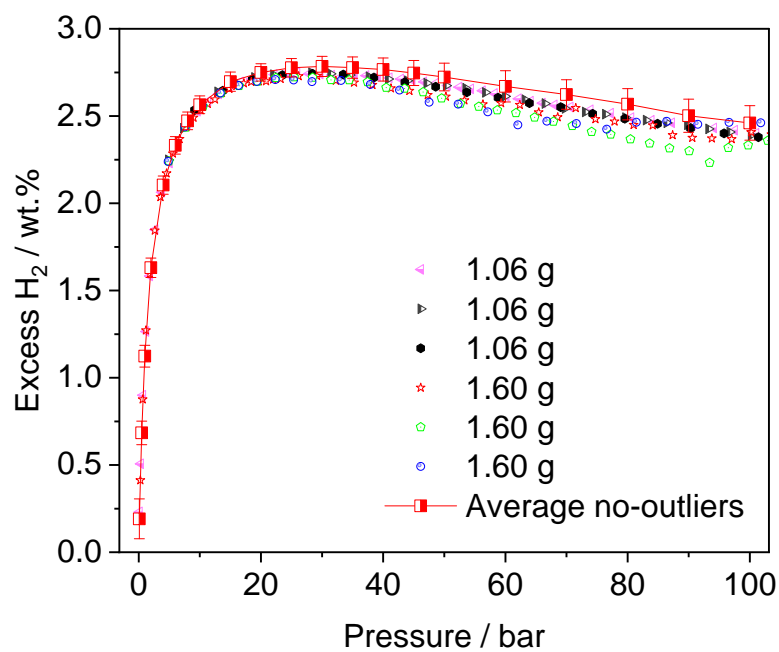


Figure S8.. Comparison of H_2 adsorption isotherms at 77 K from setup 6.

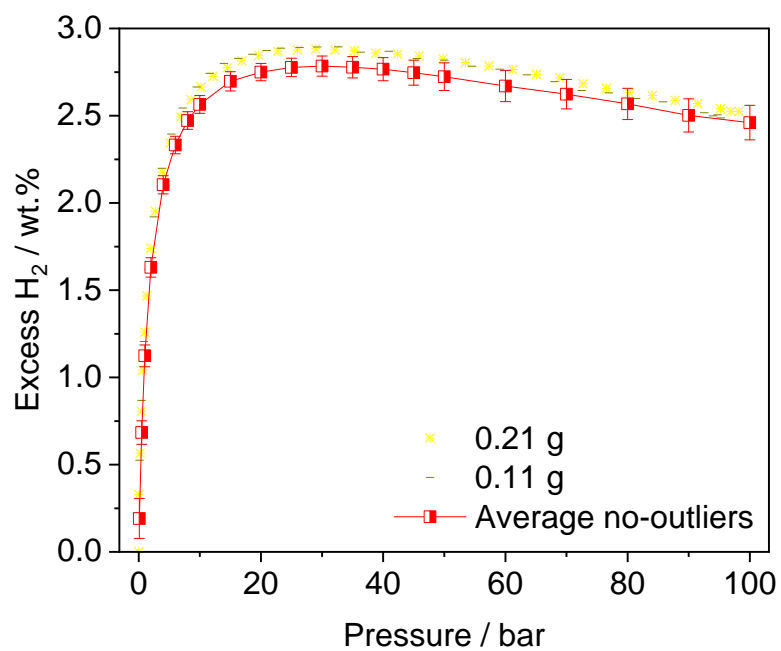


Figure S9.. Comparison of H_2 adsorption isotherms at 77 K from setup 7.

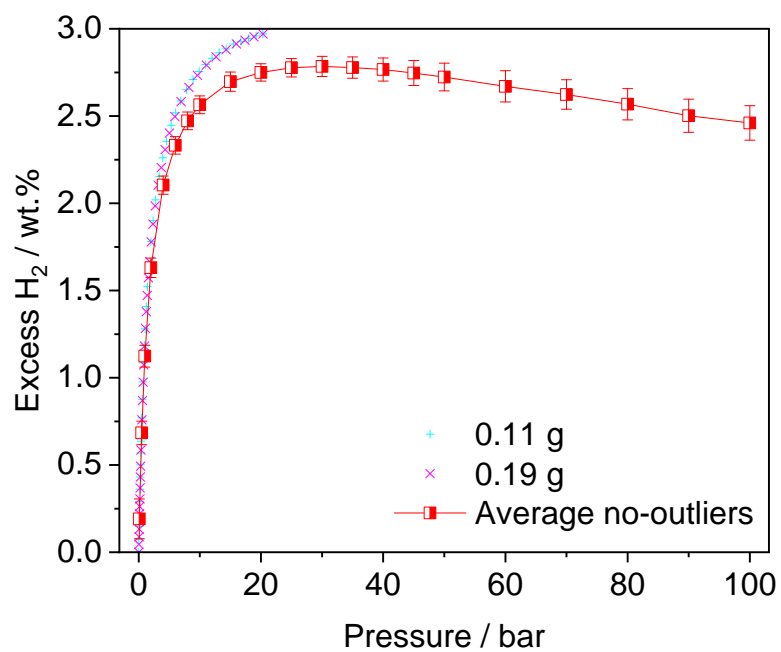


Figure S10.. Comparison of H_2 adsorption isotherms at 77 K from setup 8.

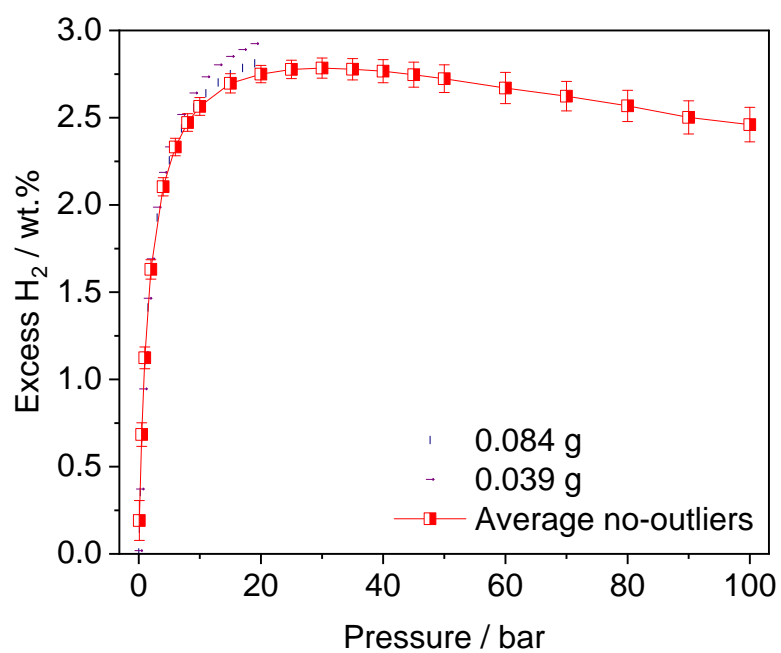


Figure S11.. Comparison of H_2 adsorption isotherms at 77 K from setup 9.

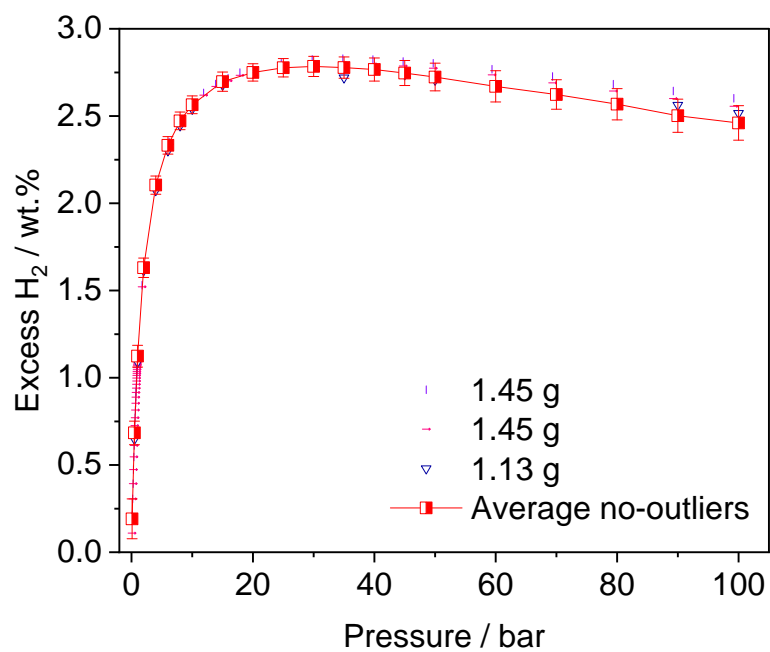


Figure S12.. Comparison of H_2 adsorption isotherms at 77 K from setup 10.

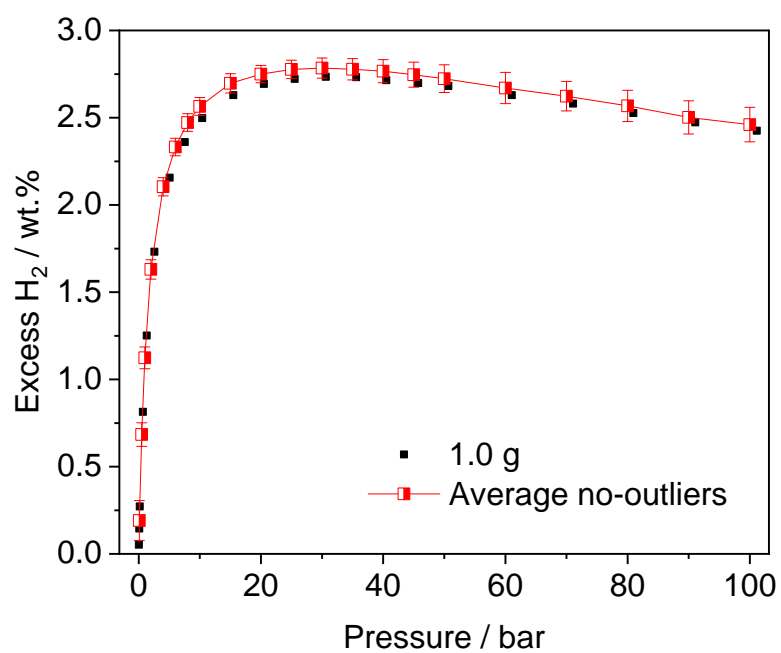


Figure S13.. Comparison of H_2 adsorption isotherms at 77 K from setup 11.

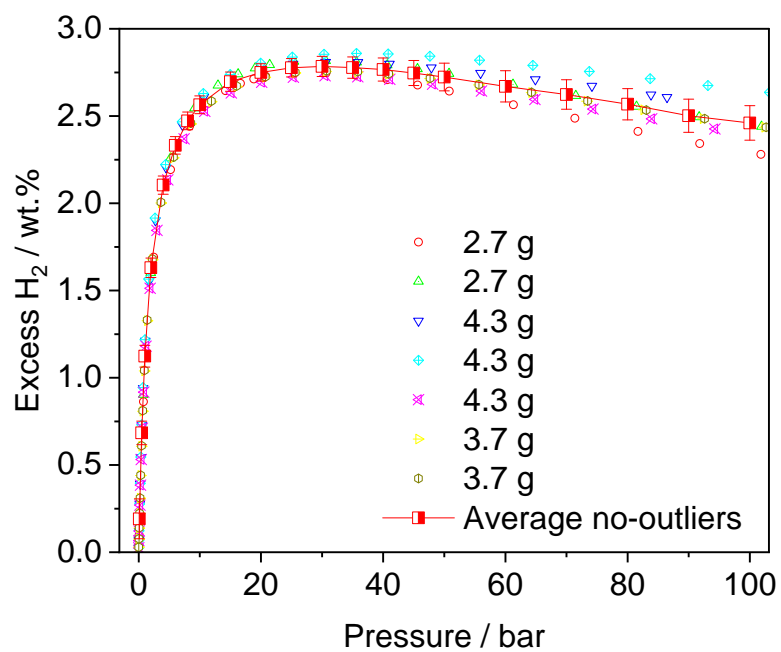


Figure S14.. Comparison of H_2 adsorption isotherms at 77 K from setup 12.

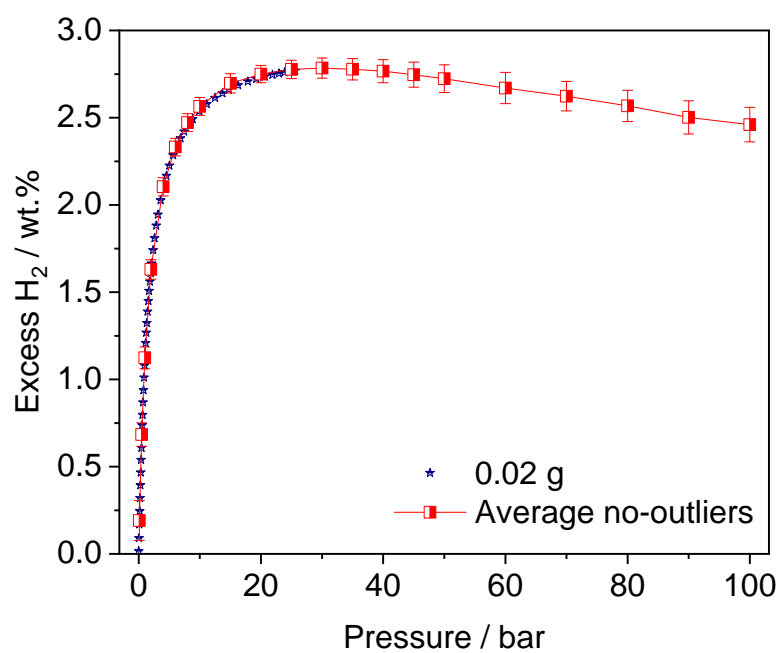


Figure S15.. Comparison of H₂ adsorption isotherms at 77 K from setup 13.

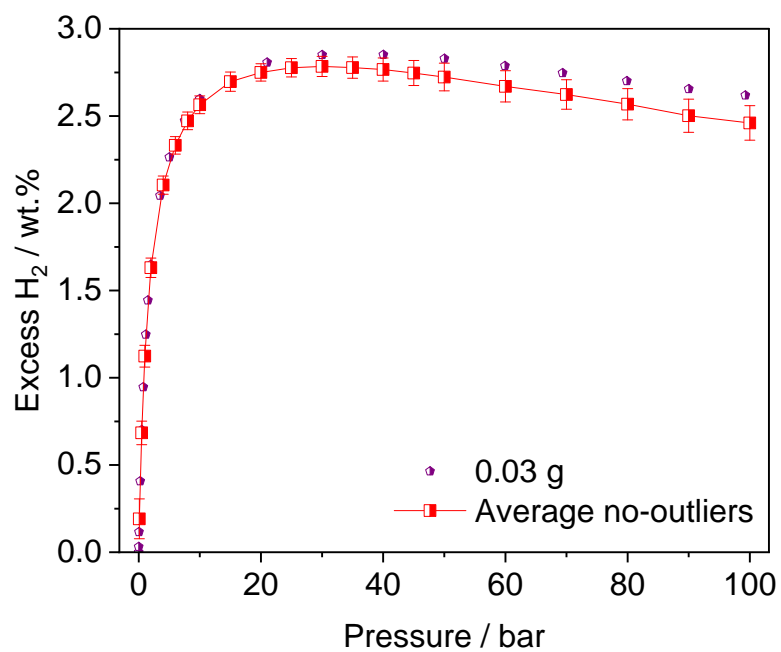


Figure S16.. Comparison of H₂ adsorption isotherms at 77 K from setup 14.

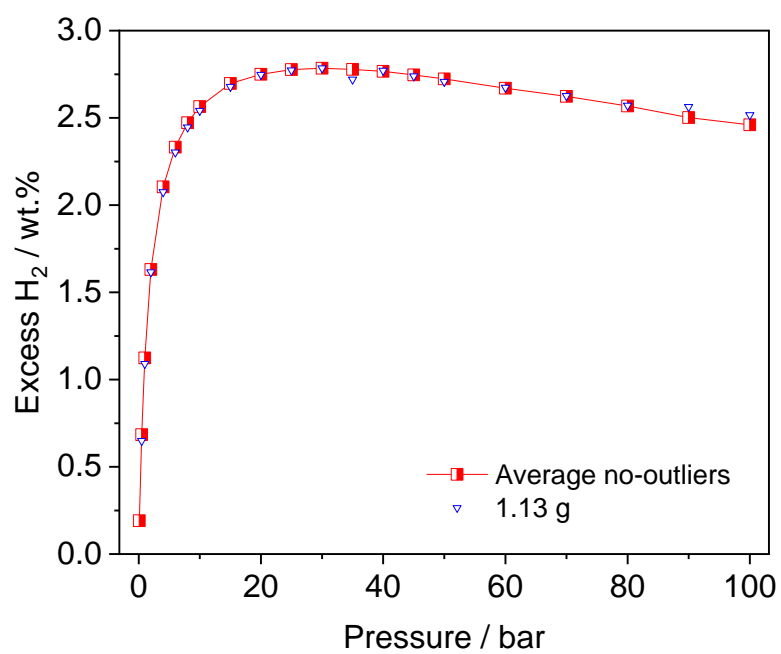


Figure S17.. Comparison of H₂ adsorption isotherms at 77 K from setup 15.