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A reference high-pressure CH₄ adsorption isotherm for zeolite Y: results of an interlaboratory study

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Abstract

This paper reports the results of an international interlaboratory study led by the National Institute of Standards and Technology (NIST) on the measurement of high-pressure surface excess methane adsorption isotherms on NIST Reference Material RM 8850 (Zeolite Y), at 25 °C up to 7.5 MPa. Twenty laboratories participated in the study and contributed over one-hundred adsorption isotherms of methane on Zeolite Y. From these data, an empirical reference equation was determined, along with a 95% uncertainty interval ($U_{k=2}$). By requiring participants to replicate a high-pressure reference isotherm for carbon dioxide adsorption on NIST Reference Material RM 8852 (ZSM-5), this interlaboratory study also demonstrated the usefulness of reference isotherms in evaluating the performance of high-pressure adsorption experiments.

Keywords CH₄ · CO₂ · High-pressure adsorption isotherm · Interlaboratory study · Reference isotherm · Reference material · RM 8850 · RM 8852 · Surface excess adsorption · Zeolite Y · ZSM-5

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1 Introduction

Adsorbents have many potential applications, ranging from fluid catalytic cracking to gas separation and storage, to environmental remediation (Yang 2003). The performance of an adsorbent is especially determined by measuring an adsorption isotherm, a plot of gas uptake as a function of equilibrium pressure at a fixed temperature. Many of the aforementioned applications require measurements up to high-pressures; (Chareonsuppanimit et al. 2012; Darkrim et al. 2002; Liu et al. 2012; Mason et al. 2014; Menon 1968; Menon and Komarneni 1998; White et al. 2005) however, reproducibility of high-pressure measurements has proved to be a challenge, which has slowed the development of new materials and their applications (Broom and Hirscher 2016; Broom and Webb 2017; Espinal et al. 2013; Gasparik et al. 2014; Gensterblum et al. 2009, 2010; Goodman et al. 2004, 2007; Han et al. 2019; Hurst et al. 2016, 2019; Moretto et al. 2013; Park et al. 2017; Zlotea et al. 2009). In part, these experimental difficulties are linked to the lack of standardized measurement protocols, reference materials, and reference data. To address this situation, the National Institute of Standards and Technology (NIST), in partnership with the Department of Energy's Advanced Research Projects Agency (ARPA-E), initiated a program to develop reference materials, reference data, and measurement protocols to improve adsorption metrology. Recently, the NIST Facility for Adsorbent Characterization and Testing (FACT Lab) led an interlaboratory study (hereafter, ILS1) on the measurement of high-pressure surface excess carbon dioxide (CO_2) adsorption isotherms on NIST Reference Material RM 8852, ammonium ZSM-5, at 20 °C up to 4.5 MPa (Nguyen et al. 2018). The exercise involved eleven invited participants with recognized expertise in the adsorption sciences. The output was, for the first time, high-pressure adsorption reference data using a reference material. The CO_2 /ZSM-5 reference isotherm recently proved helpful for advancing modeling methods (Fang et al. 2020). Having companion high-pressure isotherm experiments showing high-quality results for a reference material would also be valuable to demonstrate reliability in high-pressure experiments on new adsorbents, particularly given the large number of porous materials that have not been replicated since they were first reported (Agrawal et al. 2020). The present study builds on the CO_2 /ZSM-5 reference isotherm work.

Working through Technical Working Group 39 of the Versailles Project on Advanced Materials and Standards (VAMAS),¹ the FACT Lab organized a second high-pressure interlaboratory study (hereafter, ILS2) to investigate the

usefulness of the CO_2 /ZSM-5 reference isotherm in evaluating the performance of high-pressure adsorption instruments and to determine a reference isotherm for methane (CH_4) adsorption on NIST Reference Material RM 8850, sodium Zeolite Y (ZY).² This study is different from ILS1 in two important ways. First, the study was open to any participants. However, those who had not participated in the ILS1 were required to replicate the reference isotherm derived from that study. Second, while a participant with a dataset statistically different from those of other participants was given an opportunity to remeasure or reprocess the submitted isotherms, the FACT Lab did not actively interact with the participant to identify the reasons for the difference.

To provide variety in materials, ZY, one of the three zeolitic reference materials at NIST was chosen for ILS2. ZY is more hygroscopic than ZSM-5 but less hygroscopic than Zeolite A (RM 8851). ZY (RM 8850) is completely microporous (see Fig. S1), whereas ZSM-5 (RM 8852) has a small amount of mesoporosity (Fang et al. 2020). ZY being a different material from ZSM-5 would also allow the true extent of the usefulness of the CO_2 /ZSM-5 reference isotherm to be determined when applied to measurements of other materials, as would be expected in real-world applications.

ZY, a faujasite, was introduced as an acidic zeolitic catalyst for the cracking of hydrocarbons in the 1960s (Cejka et al. 2017). The microporous zeolite has a three-dimensional pore structure, with pores running in mutually orthogonal directions. The pore diameter is ≈ 0.8 nm, which is defined by a twelve-member oxygen ring and leads into a cavity of diameter ≈ 1.2 nm (Baerlocher et al. 2007). The cavity is surrounded by ten sodalite cages connected on their hexagonal faces, in a tetrahedral, three-dimensional structure in which every sodalite cage has four uniformly distributed nearest neighbors as binding partners (Baerlocher et al. 2007; Cejka et al. 2017; Julbe and Drobek 2016). Methane, the major component of natural gas, meanwhile, was chosen as the adsorbate because of interest in using adsorbents for methane storage and transportation at safe pressure levels (Beckner and Dailly 2016; Keskin Avci and Erucar 2018; Menon and Komarneni 1998). The CH_4 /ZY pair was selected because of its commercial relevance (Cejka et al. 2017) and because it provides a reference isotherm for a supercritical fluid.

¹ <https://www.vamas.org/twa39/>.

² <https://www.nist.gov/srm>.

2 Experimental and data analysis methods

2.1 Methods

As mentioned, ILS2 involved measurement of CH₄/ZY surface excess adsorption isotherms at 25 °C for pressures up to 7.5 MPa, using NIST RM 8850 as the adsorbent. This reference material is highly homogenized and characterized with reference values for elemental composition (e.g., Si/Al = 2.547 ± 0.037, Na/Al = 0.997 ± 0.018) and certain other physicochemical properties (e.g., loss-on-fusion ≈ loss-on-ignition ≈ 0.25), and information values for a range of structural properties (Turner et al. 2008). Sufficient units of this material are in stock at NIST (<https://www.nist.gov/srm>) to ensure availability for the foreseeable future.

In total, 20 laboratories participated in ILS2; seven of the 20 were participants in ILS1. The measurement capabilities of these laboratories included both commercial and custom-built manometric and gravimetric instruments.

The measurement protocol instructions were minimal. For CO₂/ZSM-5 measurements, the protocol and conditions developed in ILS1 were prescribed (Nguyen et al. 2018). For the CH₄/ZY, the measurement protocol specified a minimum purity of the adsorptive (≥ 99.999%), the sample pretreatment (activation at 350 °C for at least 12 h using a turbomolecular pump), the pressure range (7.5 MPa or the maximum capability of the instrument), the recommended equilibrium pressure points, the temperature (25 °C), and the number of isotherms to be measured (two isotherms each for two separate aliquots, totaling four isotherms for CH₄). It was recommended to perform a blank run (i.e., an isotherm in the absence of the adsorbent) to subtract from the isotherm measured with the adsorbent present (Nguyen et al. 2017). Each participant was provided with one unit (40 g) each of RM 8852 and RM 8850. Participants were asked to submit an experimental report, which detailed their experimental procedures and data processing steps, and to submit the isotherms as surface excess uptake in units of millimoles of adsorbed fluid per gram of activated zeolite in a provided template. For the most part, the participants followed the prescribed protocols, although there were some small deviations. Details on various experimental parameters and procedures for each dataset can be found in Table 1.

2.2 Data evaluation

Each participant in ILS2 submitted at least one high-pressure dataset. For clarity, a CH₄/ZY dataset is composed

of four adsorption isotherms from two aliquots of ZY (aliquot 1—isortherm 1, aliquot 1—isortherm 2, aliquot 2—isortherm 1, aliquot 2—isortherm 2). In general, the intralaboratory isotherms were highly reproducible (except for DS 14 and 15; see Figs. S6–S10 in the Supplemental Information). Twenty-six high-pressure CH₄/ZY datasets were submitted, for a total of 104 isotherms. In addition, two participants submitted 5 isotherms over the pressure range of 1 kPa to 100 kPa. These low-pressure data were useful in constraining the empirical reference function at low-pressure.

Labs who had not participated in ILS1 were asked to provide two CO₂/ZSM-5 isotherms (20 °C), one isotherm each from two separate sample aliquots. In general, these intralaboratory isotherms were also highly reproducible (except for DS 14, see Figs. S3–S5 in the Supplemental Information). The purpose of this exercise was to demonstrate the measurement capabilities of these laboratories. Successful replication of the CO₂/ZSM-5 isotherm was a criterion for inclusion of CH₄/ZY isotherms from these labs in determination of the reference isotherm for ILS2. The CO₂/ZSM-5 isotherms were evaluated with two metrics. First, the residuals from the reference isotherm (reference isotherm minus measured isotherm) were determined. Ideally, all residuals should be within the prediction interval of the CO₂/ZSM-5 reference isotherm ($U_{k=2} = \pm 0.075$ mmol/g). This metric provides a qualitative measure of replication of the CO₂/ZSM-5 reference isotherm. A second more quantitative metric of replication of the CO₂/ZSM 5 reference isotherm, the “goodness-of-fit” (GOF), was also computed. For this test, the reference function from ILS1, which defines the amount of gas adsorbed versus pressure, was compared to each of the CO₂/ZSM-5 datasets for new participants in ILS2. The GOF metric was based on the residuals to the reference function, using a Bayesian, Markov Chain Monte Carlo algorithm. This calculation included the uncertainty in the estimates of the reference function as well as the uncertainty of the submitted datasets. The lower the value of this test, the better the dataset replicates the CO₂/ZSM-5 reference isotherm. When this test was applied to the datasets of ILS1, the average GOF value was 0.078, with a standard deviation of 0.048. With this range as a guide, it was decided that CO₂/ZSM-5 isotherms submitted to ILS2 with a GOF value less than 0.07 would be considered to have replicated the reference isotherm, those with a value between 0.07 and 0.12 would be evaluated on a case-by-case basis, and those with a value greater than 0.12 would be considered as failing to replicate the reference isotherm and submitted CH₄/ZY isotherm data would not be included in determining the reference function for ILS2. Of course, passing the GOF test was a necessary—but not sufficient—criterion for a CH₄/ZY dataset to be included in the determination of the reference isotherm for ILS2. The GOF calculation was done using

Table 1 Experimental parameters of the participants

Dataset	Measurement method	Gas purity (%)	Sample size (g)	Outgas condition	Sample handling/weighing and transfer
1	Manometric	CO ₂ : 99.995 CH ₄ : 99.99	8852: 2.8600, 2.8488 8850: 4.1361, 4.2511	Vacuum at 100 °C for 0.5 h and then 350 °C for 1 h, then high vacuum at 350 °C for 12 h	Activated in-situ, sample mass determined ex-situ in air after measurement
2	Gravimetric	CO ₂ : 99.995 He: 99.999 CH ₄ : 99.9995	8852: 0.3684, 0.46762 8850: 0.4602, 0.6078	Flushed twice with He during heating for activation followed by evacuation at 350 °C for 12 h	Activated in-situ
3	Manometric	CO ₂ : 99.999 CH ₄ : 99.995	8852: 0.1651, 0.1350 8850: 0.2107, 0.2783	Heated in situ under dynamic vacuum (10 ⁻⁸ kPa) at 1 °C/min heating rate from 20 to 350 °C and then kept at 350 °C for 12 h	Activated in-situ, sample mass determined ex-situ in air after measurement
4	Manometric	CO ₂ : 99.998 CH ₄ : 99.5	8852: 0.3252, 0.3398 8850: 0.4146, 0.9285	High-vac at 350 °C for 12 h	Activated in-situ, sample mass determined ex-situ in air after measurement
5	Gravimetric	CO ₂ : 99.99 CH ₄ : 99.5	8852: 0.0907, 0.0911 8850: 0.078, 0.081	High vacuum (10 ⁻⁹ kPa) at 350 °C for 12 h	Activated in-situ
6	Gravimetric	CO ₂ : 99.999 CH ₄ : 99.995	8852: 0.5624, 0.5669 8850: 0.9330, 0.9407	In situ activation at 350 °C under vacuum (4 × 10 ⁻⁵ kPa) for at least 12 h	Activated in-situ
7	Manometric	CO ₂ : 99.999 He: 99.999 CH ₄ : 99.999	8852: 0.7304, 0.6331 8850: 1.6414, 1.291	Under high-vac, ramped from rt to 350 °C at 1 °C/min and held at 350 °C for at least 12 h	Activated ex-situ. Transferred to sample holder and sample mass determined inside an Ar glovebox
8	Gravimetric	CO ₂ : 99.999 CH ₄ : 99.999	8852: 1.055, 1.052 8850: 1.190, 1.185	Activated under helium flow of about 40 cc/min and continuous evacuation (10 ⁻⁵ kPa) at 350 °C for at least 12 h	Activated in-situ
9	Manometric	CO ₂ : 99.9993 He: 99.999 CH ₄ : 99.9993	8852: 0.2508, 0.2030 8850: 0.2121, 0.2482	Outgassed at 350 °C for at least 12 h using a turbomolecular pump down to < 10 ⁻⁷ kPa	Activated in-situ, sample mass determined ex-situ in air after measurement
10	Manometric	CO ₂ : 99.9993 He: 99.999 CH ₄ : 99.9993	8852: 0.1940, 0.2343 8850: 0.2390, 0.2283	Outgassed at 350 °C for at least 12 h using a turbomolecular pump down to 9 × 10 ⁻⁸ kPa	Activated in-situ, sample mass determined ex-situ in air after measurement
11	Gravimetric	CO ₂ : 99.9993 He: 99.999 CH ₄ : 99.9993	8852: 0.0727, 0.0622 8850: 0.0752, 0.0766	Outgassed at 350 °C for 13 h using a turbomolecular pump (10 ⁻⁸ kPa)	Activated in-situ
12	Gravimetric	CO ₂ : 99.9993 He: 99.999 CH ₄ : 99.9993	8852: 0.1423, 0.1362 8850: 0.2098, 0.1889	Outgassed at 350 °C for at least 12 h using a turbomolecular pump down to the 10 ⁻⁸ kPa magnitude	Activated in-situ
13	Gravimetric	CO ₂ : 99.995 CH ₄ : 99.995	8852: 0.4660, 0.4616 8850: 0.435, 0.408	High-vac (< 0.1 Pa) at 350 °C for 12 h	Activated in-situ
14	Manometric	CO ₂ : 99.99 CH ₄ : 99.5	8852: 1.1224, 0.4195 8850: 1.1438, 0.9866	Dried at 300 °C for 12 h with pump outgassing, then degassed (10 ⁻⁴ kPa) at 66 °C for 12 h directly in device. Aliquot 1 was degassed in device only	Activated ex-situ
15	Manometric	CH ₄ : 99.999	8850: 0.7806, 0.8196	High-vac (10 ⁻⁶ kPa) at 350 °C for 12 h	Activated in-situ. Sample mass determined inside an Ar glovebox
16	Manometric	CO ₂ : 99.9995 CH ₄ : 99.9995	8852: 0.4916, 0.5675 8850: 0.7130, 0.8413	High-vac (< 7.9 × 10 ⁻⁸ kPa) at 350 °C for 12 h	Activated in-situ, mass determined after isotherm measurement in Ar glovebox

Table 1 (continued)

Dataset	Measurement method	Gas purity (%)	Sample size (g)	Outgas condition	Sample handling/weighing and transfer		
17	Gravimetric	CO ₂ : 99.9995 CH ₄ : 99.9995	8852: 0.4148, 0.4820 8850: 0.6111, 0.6905	High-vac (10^{-4} kPa) at 350 °C for 12 h	Activated ex-situ; reactivated in-situ		
18	Manometric	CO ₂ : 99.9995 CH ₄ : 99.9995	8852: 0.8760, 0.8281 8850: 1.4991, 1.8717	High-vac ($<10^{-7}$ kPa) at 350 °C for 12 h; high-vac (10^{-6} kPa to 10^{-7} kPa) again once transferred to analysis port	Activated ex-situ; transferred from activation to analysis port under He gas. Sample mass determined from difference of mass of empty and loaded sample cell under He gas		
19	Gravimetric	CH ₄ : 99.9999	8850: 0.092, 0.097	High-vac (10^{-8} kPa), ramped 1 °C/min to 350 °C, held at 350 °C for 14 h	Activated in-situ		
20	Manometric	He: 99.999999 CH ₄ : 99.9999	8850: 0.6944, 0.7232	Activated ex-situ using the turbomolecular pump (10^{-7} kPa), then activated in-situ at 350 °C for 12 h using a rotary pump	Activated ex-situ, transferred in N ₂ glove bag to sample cell		
21	Gravimetric	CH ₄ : 99.995	8850: 1.005, 0.7852	High-vac ($<10^{-5}$ kPa) at 350 °C for 12 h	Activated in-situ		
22	Manometric	CH ₄ : 99.999	8850: 1.0284, 1.0590	High-vac (10^{-8} kPa), evacuate at RT, ramped 1 °C/min to 350 °C, held at 350 °C for 12 h	Activated ex-situ, then transferred air-free to sample holder in Ar glovebox		
23	Manometric	CH ₄ : 99.999	8850: 1.0643, 1.0713	High-vac (10^{-8} kPa), evacuate at RT, ramped 1 °C/min to 350 °C, held at 350 °C for 12 h	Activated ex-situ, then transferred air-free to sample holder in Ar glovebox		
24,25	Manometric	CH ₄ : 99.0	8850: 1.9063, 1.8552	High-vac (10^{-7} kPa) at 350 °C for 12 h	Activated in-situ. After the analysis, sample was degassed again and after cooling, the sample mass was determined in air		
26	Gravimetric	CH ₄ : 99.9995	8850: 0.0810, 0.0904	High-vac ($<10^{-7}$ kPa), ramped at 5 °C/min to 350 °C, held for 13.3 h	Activated in-situ		
27	Manometric	CH ₄ : 99.97	8850: 1.0445, 1.0471	Purged with UHP helium at 121 kPa while heated to 100 °C for 2 h and then heated slowly up to 350 °C for at least 12 h following a UOP ramp and soak recipe	Activated in-situ; after isotherm measurement, sample was transferred to tarred aluminum can, regenerated in an oven at 350 °C while purging with 250–300 cc/min UHP helium for 18 h. The same UOP ramp and soak heat up recipe was used. The can was sealed and removed from the oven while still at 350 °C and immediately placed on a balance to measure the mass		
28	Differential Manometric	CH ₄ : > 99.995	8850: 0.4005, 0.4094	High-vac ($<10^{-8}$ kPa), ramped at 1 °C/min to 110 °C, held for 1 h; then ramped at 1 °C/min to 350 °C, held overnight	In-situ (sample mass calibrated against low-pressure isotherm)		
Dataset	Void volume/buoyancy correction	Equation of state	Temperature and stability	Balance resolution and stability	Pressure transducer accuracy	Isotherm pressure range	Blank correction
1	Void volume was determined using He expansion	CO ₂ : Span and Wagner(Roland Span and Wagner 1996) CH ₄ : Setzmann and Wagner (1991)	CO ₂ : (20 ± 0.1) °C CH ₄ : (25 ± 0.1) °C	0.1 mg, N/A	10 MPa, accuracy ± 0.04% F.S	CO ₂ : 4.5 MPa CH ₄ : 7.5 MPa	yes, empty cell

Table 1 (continued)

Dataset	Void volume/buoyancy correction	Equation of state	Temperature and stability	Balance resolution and stability	Pressure transducer accuracy	Isotherm pressure range	Blank correction
2	Buoyancy correction via sample volume determined from He measurement of 10 points from 3 to 12 MPa. 8850 SD: 2.48 and 2.49 g/cm ³	Measured gas density experimentally via a magnetic suspension balance (MSB)	CO ₂ : (20 ± 0.1) °C CH ₄ : (25 ± 0.1) °C	0.01 mg, ± 0.02 mg	4 MPa, accuracy ± 0.05% F.S 20 MPa, accuracy ± 0.05% F.S	CO ₂ : 4.5 MPa CH ₄ : 7.5 MPa	Yes, empty pan
3	Sample volume determined by in-situ He pycnometry measurement. Sample cell volume was fully calibrated before the measurements. RM8850 SD: 2.04 ± 0.17 g/cm ³	CO ₂ : Span and Wagner CH ₄ : Setzmann and Wagner	CO ₂ : (20.1 ± 0.2) °C CH ₄ : (24.9 ± 0.2) °C	0.1 mg, ± 0.1 mg	20 MPa; accuracy ± 0.05% F.S	CO ₂ : 4.2 MPa CH ₄ : 6.9 MPa	Yes, empty cell
4	The void volume of the system was determined with He gas	CO ₂ : Span and Wagner CH ₄ : Helmholtz EoS	CO ₂ : (20 ± 0.1) °C CH ₄ : (25 ± 0.1) °C	0.1 mg, ± 0.1 mg	100 MPa; accuracy ± 0.1% F.S	CO ₂ : 4.2 MPa CH ₄ : 7.5 MPa	Yes, empty cell
5	Buoyancy correction from ex-situ determined skeletal density and mass of sample and balance components RM8852 SD: 2.36 g/cm ³ ; RM8850 SD: 2.53 g/cm ³	CO ₂ : Span and Wagner CH ₄ : Setzmann and Wagner	CO ₂ : (20 ± 0.05) °C CH ₄ : (25 ± 0.05) °C	0.1 µg, ± 0.1 µg	± 0.02% F.S	CO ₂ : 2.0 MPa CH ₄ : 1.0 MPa	Yes, empty pan
6	Buoyancy correction via balance component volume determined from CO ₂ measurement from 2 to 30 MPa at 80 °C. Sample volume was determined via dry mass and SD provided. RM8852 SD: 2.36 g/cm ³ ; RM8850 SD: 2.53 g/cm ³	Measured gas density experimentally via MSB	CO ₂ : (20 ± 0.01) °C CH ₄ : (25 ± 0.01) °C	0.01 mg, ± 0.1 mg	4 and 70 MPa; accuracy ± 0.01% F.S	CO ₂ : 4.5 MPa CH ₄ : 7.5 MPa	Yes, empty pan

Table 1 (continued)

Dataset	Void volume/buoyancy correction	Equation of state	Temperature and stability	Balance resolution and stability	Pressure transducer accuracy	Isotherm pressure range	Blank correction
7	The void volume of the system was determined with He gas from 10 measurement points up to 3.5 MPa	CO ₂ : Span and Wagner CH ₄ : Setzmann and Wagner	CO ₂ : (20. ± 0.2) °C CH ₄ : (25 ± 0.2) °C	0.1 mg, ± 0.2 mg	13.5 MPa; accuracy ± 0.1% F.S	CO ₂ : 3.5 MPa CH ₄ : 6.7 MPa	Yes, empty cell
8	Buoyancy correction via sample volume determined from He measurement at 80 °C. For blanks, buoyancy correction via volume determined from CO ₂ or CH ₄ measurement at analysis temperature. 8850 SD: 2.37 g/cm ³	CO ₂ : Span and Wagner CH ₄ : Setzmann and Wagner	CO ₂ : (20. ± 0.5) °C CH ₄ : (25 ± 0.5) °C	0.01 mg, ± 0.02 mg	± 0.08% Reading ± 0.12% Reading	CO ₂ : 4.5 MPa CH ₄ : 7.5 MPa	Yes, empty pan (CO ₂)
9	Void volumes determined using He after keeping all parts of the instrument including the sample at 30 °C	CO ₂ : Span and Wagner CH ₄ : Setzmann and Wagner	CO ₂ : (20.2 ± 0.2) °C CH ₄ : (25.2 ± 0.2) °C	0.1 mg, ± 0.2 mg	± 1% Reading	CO ₂ : 4.3 MPa CH ₄ : 7.4 MPa	Yes, empty cell (CO ₂), Pyrex glass (CH ₄)
10	Void volumes determined using He after keeping all parts of the instrument including the sample at 30 °C	CO ₂ : Span and Wagner CH ₄ : Setzmann and Wagner	CO ₂ : (20.2. ± 0.2) °C CH ₄ : (25.2 ± 0.2) °C	0.1 mg, ± 0.2 mg	± 1% Reading	CO ₂ : 2.0 MPa CH ₄ : 2.1 MPa	Yes, empty cell (CO ₂), Pyrex glass (CH ₄)
11	Buoyancy correction from ex-situ determined skeletal density and mass of sample and balance components. RM8852 SD: 2.36 g/cm ³ , RM 8850 SD: 2.53 g/cm ³ , Pyrex glass SD: 2.23 g/cm ³	CO ₂ : Span and Wagner CH ₄ : Setzmann and Wagner	CO ₂ : (20. ± 0.1) °C CH ₄ : (25 ± 0.2) °C	0.1 µg, ± 0.1 µg	2 MPa; ± 0.05% F.S	CO ₂ : 2.0 MPa CH ₄ : 2.0 MPa	Yes, empty pan (CO ₂), Pyrex glass (CH ₄)
12	The volumes of all the components (hanging wire, sample basket and sample) were determined after measuring a He isotherm	CO ₂ : Span and Wagner CH ₄ : Setzmann and Wagner	CO ₂ : (21. ± 0.1) °C CH ₄ : (25 ± 0.1) °C	1 µg, ± 3 µg	± 0.5% Reading	CO ₂ : 4.5 MPa CH ₄ : 6.4 MPa	Yes, empty pan (CO ₂), Pyrex glass (CH ₄)

Table 1 (continued)

Dataset	Void volume/buoyancy correction	Equation of state	Temperature and stability	Balance resolution and stability	Pressure transducer accuracy	Isotherm pressure range	Blank correction
13	Buoyancy correction for sample holder was done by using the blank CH ₄ run (25 °C, up to 10 MPa). Buoyancy correction for sample was done by using the specific volume calculated from skeletal density and sample mass. RM8852 SD 2.36 g/cm ³ ; RM8850 2.53 g/cm ³	CO ₂ : Span and Wagner CH ₄ : Setzmann and Wagner	CO ₂ : (20. ± 0.2) °C CH ₄ : (25 ± 0.2) °C	0.01 mg, ± N/A	1 MPa, 10 MPa; accuracy ± 1% F.S	CO ₂ : 4.5 MPa CH ₄ : 7.5 MPa	Yes, empty pan
14	The void volume was determined using helium expansion	CO ₂ : Span and Wagner CH ₄ : Setzmann and Wagner	CO ₂ : (20. ± 0.5) °C CH ₄ : (25 ± 0.5) °C	0.1 mg, ± 0.1 mg	18 MPa; accuracy ± 0.05% F.S	CO ₂ : 4.7 MPa CH ₄ : 7.8 MPa	No
15	Void volume from sample mass and skeletal density measured with He (8850 SD: 2.29 g/cm ³)	CH ₄ : Setzmann and Wagner	CH ₄ : (25 ± 0.2) °C	± 0.5 mg	0.138 Pa to 20.7 MPa; accuracy ± 1% of reading	CH ₄ : 7.6 MPa	Yes, only up to 5 MPa
16	The void volume of the system was determined via He expansion before each measurement	CO ₂ : Span and Wagner CH ₄ : Setzmann and Wagner	CO ₂ : (20. ± 0.1) °C CH ₄ : (25 ± 0.1) °C	0.01 mg, ± 0.05 mg	0.5 MPa and 20 MPa; accuracy ± 1% Reading	CO ₂ : 4.5 MPa CH ₄ : 7.5 MPa	Yes, glass
17	Empty and filled sample holder volume by He before each measurement using density measurement, checked versus EoS NIST, buoyancy correction using measured density (2 position balance)	Measured gas density experimentally via MSB	CO ₂ : (20. ± 0.1) °C CH ₄ : (25 ± 0.1) °C	0.01 mg, ± 0.01 mg	0.2 MPa, 4 MPa, and 20 MPa; accuracy ± 0.1% F.S	CO ₂ : 4.5 MPa CH ₄ : 7.5 MPa	Yes, empty pan
18	Void volume by He before each measurement	CO ₂ : Span and Wagner CH ₄ : Setzmann and Wagner	CO ₂ : (20. ± 0.05) °C CH ₄ : (25 ± 0.05) °C	0.1 mg, ± 0.1 mg	3.33 MPa; accuracy ± 0.1% reading	CO ₂ : 3.0 MPa CH ₄ : 3.0 MPa	Yes, empty cell

Table 1 (continued)

Dataset	Void volume/buoyancy correction	Equation of state	Temperature and stability	Balance resolution and stability	Pressure transducer accuracy	Isotherm pressure range	Blank correction
19	Buoyancy correction from ex-situ determined skeletal density and mass of sample and balance components RM 8850 SD: 2.53 g/cm ³	CH ₄ : Setzmann and Wagner	CH ₄ : (25 ± 0.04) °C	0.1 µg, ± 0.1 µg	Below 127 kPa, accuracy ± 0.12% of reading with resolution of ± 0.002% F.S (3.33 MPa). Above 127 kPa, accuracy ± 0.04% F.S	CH ₄ : 1.9 MPa	Yes, empty pan
20	The total volume of the sample chamber determined using He at a pressure range of less than about 100 kPa at 25 °C before CH ₄ gas adsorption. Void volume determined from total volume and volume from sample mass and 8850 SD: 2.53 g/cm ³	CH ₄ : Setzmann and Wagner	CH ₄ : (25 ± 0.02) °C	0.01 mg, ± 0.03 mg	13.5 MPa; accuracy ± 0.04% F.S	CH ₄ : 7.8 MPa	No (small influence on ads. amt.)
21	Buoyancy correction via sample volume determined from He isotherm	CH ₄ : Setzmann and Wagner	CH ₄ : (25 ± 0.3) °C	0.01 mg, ± 0.02 mg	Below 133.3 kPa, resolution 1.3 Pa; 133.3 kPa to 3.333 MPa, resolution 32.5 Pa; Up to 16 MPa accuracy ± 0.1% F.S	CH ₄ : 7.5 MPa	Yes, empty pan
22	Void volume from skeletal density (from He pycnometry) and mass of sample	CH ₄ : Setzmann and Wagner	CH ₄ : (25 ± 0.1) °C	0.1 mg, ± 0.2 mg	8 MPa, resolution 10 Pa; accuracy ± 0.05% F.S	CH ₄ : 6.7 MPa	Yes, empty cell
23	Void volume from skeletal density (from He pycnometry) and mass of sample	CH ₄ : Setzmann and Wagner	CH ₄ : (25 ± 0.1) °C	0.1 mg, ± 0.2 mg	150 kPa, Pressure resolution: 1 Pa; accuracy ± 0.05% F.S	CH ₄ : 0.1 MPa	Yes, empty cell
24,25	The void volume was determined using He expansion	CH ₄ : Setzmann and Wagner	CH ₄ : (25 ± 0.02) °C	0.1 mg, ± N/A	20 MPa; accuracy ± 0.05% F.S	CH ₄ : 7.4 MPa Low P: 0.1 MPa	Yes, empty cell

Table 1 (continued)

Dataset	Void volume/buoyancy correction	Equation of state	Temperature and stability	Balance resolution and stability	Pressure transducer accuracy	Isotherm pressure range	Blank correction
26	Buoyancy correction from ex-situ determined skeletal density and mass of sample and balance components RM8850 SD: 2.5325 g/cm ³	CH ₄ : Setzmann and Wagner	CH ₄ : (25 ± 0.01) °C	0.1 µg, ± 0.1 µg	6 MPa or 20 MPa; accuracy ± 0.04% F.S	CH ₄ : 7.5 MPa	No
27	He expansion was used for void volume determination	Compressibility factor from Pitzer correlations	CH ₄ : (25 ± 0.1) °C	0.1 mg, ± N/A	0.34 MPa, 1.7 MPa, 6.9 MPa; accuracy ± 0.1% reading	CH ₄ : 6.6 MPa	Yes, empty cell
28	Void volume of the system was determined by He expansion	Wagner EoS for CH ₄ from Wagner 2003 & GERG 2008 (Kunz and Wagner 2012; Span and Wagner 2003)	CH ₄ : (25 ± 0.2) °C	0.1 mg	abs. PT (0–27.6 MPa) and a diff. PT (–62.16 to 62.16 kPa), accuracy ± 0.04% F.S	CH ₄ : 7.2 MPa	Built-in as reference side

Table 2 Empirical reference function parameters

	Value	Uncertainty	Units
<i>a</i>	4.2040	0.0406	Amount-of-substance/mass
<i>b</i>	0.0818	0.0100	Amount-of-substance/(mass × pressure)
<i>c</i>	–0.0132	0.0008	Amount-of-substance/(mass × pressure ²)
<i>d</i>	1.4400	0.0146	n/a
<i>e</i>	1.0700	0.0115	(Pressure) ^{<i>d</i>}

No physical meaning should be associated with these parameters or the empirical reference function itself

the OpenBUGS (Lunn et al. 2009) code shown in the Supplemental Information.

2.3 Dataset display

To clearly display a plot including datasets from all participants, the average of the isotherms for each dataset was determined. These are shown in the figures in the text. [There were two datasets (DS 14 & DS 15) for which averaging was not possible. In these cases, one representative isotherm was selected for display.] In determination of the reference isotherm, the full datasets shown in the Supplemental Information were used—not the averaged datasets shown in the figures of the body of the text. The number of each dataset is random and does not correspond to the numeric listing of authors.

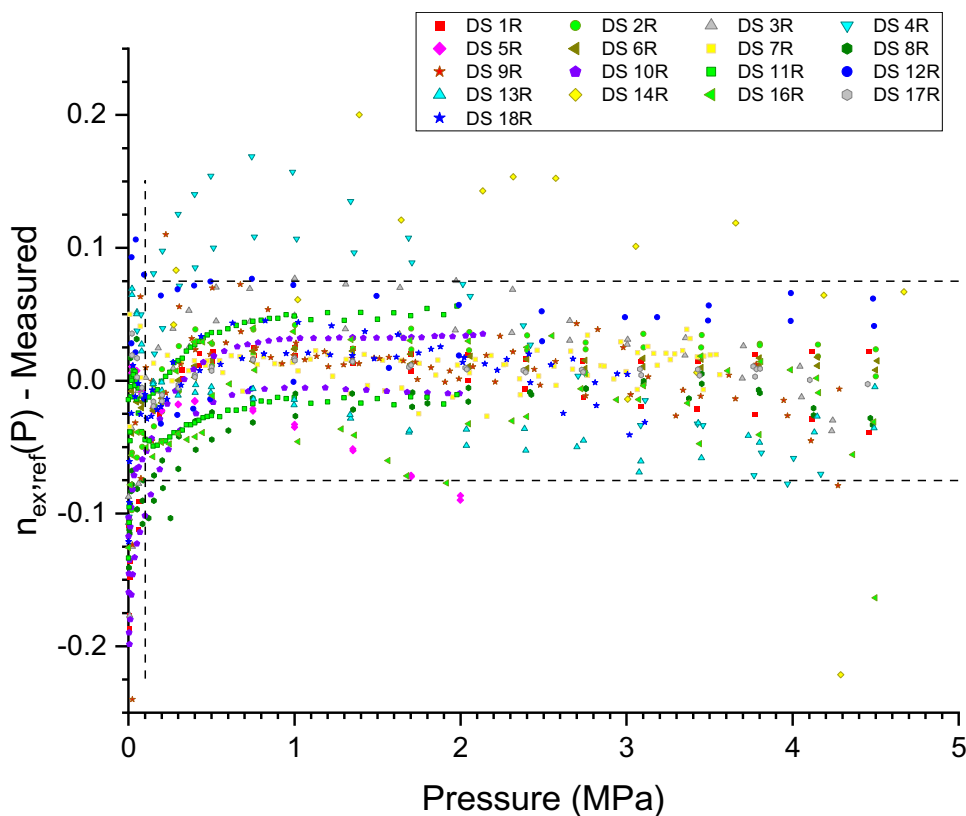
2.4 Reference function determination

The CH₄/ZY isotherms were fit collectively to the function,

$$n_{ex,ref}(P) = \frac{aP + bP^2 + cP^3}{\sqrt[d]{e + P^d}} \quad (1)$$

[*n_{ex}*—surface excess uptake (mmol/g), *P*—equilibrium pressure (MPa), *a*, *b*, *c*, *d*, and *e* being empirical parameters shown in Table 2]. The values of *a*, *b*, *c*, *d*, and *e* and the associated 95% uncertainty interval to that fit were determined using a Bayesian, Markov Chain Monte Carlo method (Gelman 2013; Possolo and Toman 2007). The 95% uncertainty interval is the expanded uncertainty (*U_{k=2}*) with *k*=2, or 2 times the uncertainty of the reference value, which equates to 95% coverage probability or 95% level of confidence that the true value lies within the interval (Taylor and Kuyatt 2001). The OpenBUGS code used for the fit is given in the Supplemental Information. This function was selected because it replicated the form of the measured isotherms. No physical significance should be associated with the function or its parameters, following the practice of ILS1.

Fig. 1 CO₂ adsorption on ZSM-5. Residuals [$n_{\text{ex,ref}}(P) - \text{Measured}$] for those who did not participate (1–18) in the previous interlaboratory study (ILS1). Other participants (19–28) participated in an earlier study (ILS1), demonstrating their measurement capabilities. (Isotherms are shown in the Supplemental Information). Residuals have units of mmol/g



3 Results and discussions

3.1 CO₂/ZSM-5 isotherms

In total, 17 CO₂ datasets were submitted by 12 labs, with one lab submitting four datasets, and two labs submitting two datasets (see Figs. S2–S6). The residuals of the datasets (reference isotherm minus measured data) are displayed in Fig. 1. From visual inspection two datasets (DS 4 & DS 14) are noticeably outside of the uncertainty interval of the CO₂/ZSM-5 reference function. The datasets were also evaluated for their goodness-of-fit to the CO₂/ZSM-5 reference data and placed into one of three categories based on their goodness-of-fit values: pass (GOF < 0.07), borderline (GOF between 0.07 and 0.12), and fail (GOF > 0.12). Among those participating in ILS2 who had not participated in ILS1, four (DS 1, DS 4, DS 10 & DS 14) were identified as having failed the goodness-of-fit test. Seven CO₂/ZSM-5 datasets (DS 2, DS 6, DS 7, DS 13, DS 16, DS 17 & DS 18) passed the goodness-of-fit test. Six datasets (DS 3, DS 5, DS 8, DS 9, DS 11 & DS 12) fell into the borderline category. The quality of the residuals of the datasets shown in Fig. 1 correlate well with the goodness-of-fit values (see Supplemental Information). Datasets that failed and some datasets borderline in the GOF test exhibit slightly greater variability in the intralaboratory replicate isotherms (Figs. S3–S5),

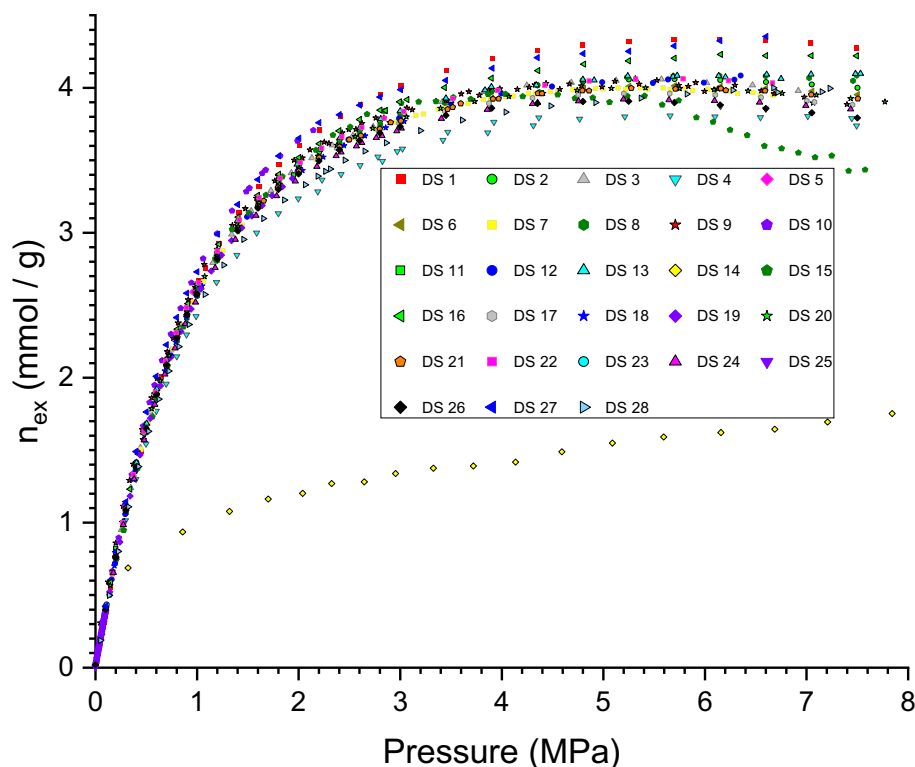
although in general, intralaboratory isotherms have good reproducibility.

For the interested reader, ILS1 is a great resource providing pitfalls and recommendations for high-pressure CO₂ measurement (Nguyen et al. 2018). The participants of the failed datasets (DS 1, DS 4, DS 10, and DS 14) were unable to remeasure, reprocess, or (in one case) improve the data to identify the origin for the deviation. However, two failed datasets came from labs that each had at least one other CO₂/ZSM-5 dataset that didn't fail the GOF test, suggesting an issue with their instrument or method rather than with the material. Evaluation of the experimental details indicated the activation protocol was not followed for one case (DS 14), which could explain the lower uptake. The importance of following the activation protocol was explicitly highlighted in ILS1 (Nguyen et al. 2018), and modeling work based on the CO₂/ZSM-5 reference data underscored that varying the pretreatment temperature of ammonium ZSM-5 affects what cations are in the zeolite (Fang et al. 2020).

3.2 CH₄/ZY isotherms

All participants were allowed to submit CH₄/ZY isotherms, although CH₄/ZY datasets from labs and/or instruments that failed to replicate the CO₂/ZSM-5 isotherm would automatically be excluded in the determination of the reference isotherm for ILS2. The as-submitted CH₄/ZY datasets,

Fig. 2 All submitted datasets for CH₄ adsorption on Zeolite Y (ILS2). (Isotherms shown here are the average of all four submitted isotherms, see Supplemental Information for full datasets)



excluding DS 14, which did not follow the prescribed activation protocol, were plotted together and Eq. (1) was fitted to them. This process identified ten datasets that were statistical outliers (DS 1, DS 4, DS 9, DS 10, DS 11, DS 12, DS 14, DS 15, DS 16 & DS 27), with datapoints lying outside the 95% uncertainty interval. These participants were given the opportunity to remeasure or reprocess their results. Four datasets (DS 4, DS 9, DS 11 & DS 12) were resubmitted after review of the initial result indicated they were outliers. All final submitted datasets are shown in Fig. 2. In general, the intralaboratory isotherms for the datasets were highly reproducible (except for DS 14 and 15; see Figs. S6–S10 in the Supplemental Information). Four datasets (DS 1, DS 4, DS 10 & DS 14) failed the CO₂ test, and one participant (DS 15) failed to replicate the CO₂/ZSM-5 isotherm by not submitting CO₂ isotherm data. The remaining 23 datasets were fitted to Eq. (1), which along with expert judgement, re-identified two datasets as statistical outliers (DS 16 & DS 27), while 21 datasets appear to be in good agreement. DS 27 is a participant in ILS1 who used a different instrument in ILS2 and did not have CO₂/ZSM-5 isotherms for the new instrumentation. Only one (DS 16) of the outlying CH₄/ZY datasets successfully reproduced the CO₂/ZSM-5 isotherm. The resubmission led to improvements in three datasets (DS 9, DS 11, and DS 12) with identified reasons for the observed variation in the outlying surface excess datasets including temperature instability (leading to volume calibration, and sample and blank isotherms being performed under

different conditions), inaccurate mass measurement (due to balance mass drift), and error in application of blank subtraction, stressing the importance of following the recommendations outlined in the ILS1 paper. After eliminating the datasets that did not pass the proficiency test or had another identified issue, 21 datasets remained, as shown in Fig. 3.

An empirical surface excess reference function was determined by optimizing the fit of Eq. (1) to the final remaining datasets and is also shown in Fig. 3. The optimized parameters are given in Table 2. This function is predictive up to 7.5 MPa and has expanded uncertainty, $U_{k=2}$, for the excess uptake of approximately 0.09 mmol/g over the full pressure range. Beneath the isotherms are the residuals (reference function minus measured isotherm) along with $U_{k=2}$. The residuals show that the reference function adequately represents the final set of isotherms over the full pressure range of the study. The datasets and the reference isotherm are available through the NIST Database of Novel and Emerging Adsorbent Materials.³

³ <https://adsorption.nist.gov/> and may be accessed directly at <https://adsorption.nist.gov/isodb/index.php?DOI=10.1007/s10450-020-00253-0#biblio>.

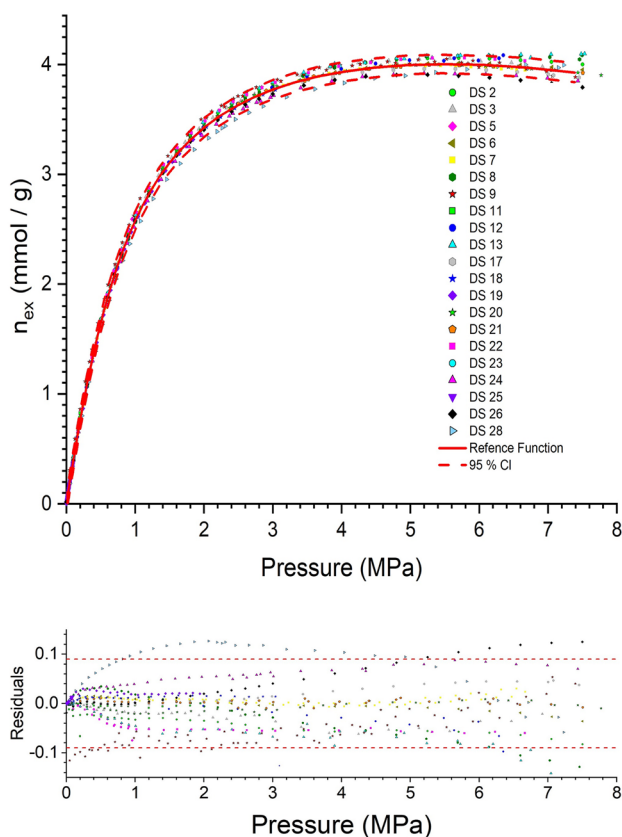


Fig. 3 Top: Datasets used to extract the reference isotherm for CH₄ adsorption on Zeolite Y, with the associated 95% confidence interval (Isotherms shown here are the average of all four submitted, see Supplemental Information for full datasets). Bottom: Residuals from reference function [$n_{\text{ex,ref}}(P) - \text{Measured}$]. Residuals have units of mmol/g

4 Conclusions and outlook

This work provides an empirical reference surface excess isotherm function for high-pressure CH₄ adsorption on Zeolite Y (NIST Reference Material 8850) at 25 °C up to 7.5 MPa, the second data produced in such a way by the FACT Lab through an interlaboratory study. This reference isotherm should prove useful for researchers interested in working with CH₄ or supercritical adsorption measurements. The study also demonstrated the usefulness of reference isotherms and reference materials for evaluating the reliability of high-pressure adsorption experiments; specifically, a lab's inability to replicate the CO₂/ZSM-5 reference isotherm was highly correlated with outlier CH₄/ZY data.

The FACT Lab plans to continue efforts to develop reference materials, reference data, and measurement protocols to improve adsorption metrology. Forthcoming interlaboratory studies will explore different adsorptive gases and vapors (H₂, N₂, H₂O, etc.), other temperature ranges (e.g., cryogenic), as well as multicomponent adsorption measurements.

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