



Reference surface excess isotherms for carbon dioxide adsorption on ammonium ZSM-5 at various temperatures

Huong Giang T. Nguyen¹ · Blaza Toman¹ · Julie Colon Martinez¹ · Daniel W. Siderius¹ · Roger D. van Zee¹

Received: 29 June 2021 / Revised: 4 January 2022 / Accepted: 21 January 2022 / Published online: 13 March 2022
© The Author(s) 2022

Abstract

This work is part of the effort at the Facility for Adsorbent Characterization and Testing (FACT lab) at the National Institute of Standards and Technology (NIST) to develop reference materials, reference data, and measurement best practices for adsorption metrology. High-pressure surface excess isotherms for CO₂ adsorption on NIST Reference Material 8852 (ammonium ZSM-5) at 15 °C, 25 °C, and 35 °C are reported, expanding on a FACT Lab-organized international interlaboratory study on this sorbent/sorbate pair at 20 °C. The range of temperatures of the present study is of interest for many CO₂ adsorption measurements and applications. Measurements were made using five different adsorption instruments, both manometric and gravimetric. Excellent agreement in the measured isotherms among the instruments was found. An empirical reference equation of the form,

$$n_{ex,ref}(P_{eq}) = \frac{c}{\{1 + \exp[(-\ln(P)+a)/b]\}^p},$$

[$n_{ex,ref}$ is surface excess uptake (mmol/g); P_{eq} is equilibrium pressure (MPa); P is $(P_{eq})/(1 \text{ MPa})$; a , b , c are constants] and the 95% uncertainty interval were determined for the isotherms at each of the temperatures. Lastly, the isosteric heat of adsorption is estimated from absolute isotherms derived from the surface excess reference data.

Keywords CO₂ · Isosteric heat of adsorption · Reference isotherm · Reference material · RM 8852 · Temperature dependence · ZSM-5

1 Introduction

With concern over the impact of CO₂ on the climate, CO₂ adsorption on nanoporous materials has been widely studied for storage, separation, and carbon capture and sequestration [1–3]. Recently, capture of CO₂ has also gained attention with efforts being organized at NIST and the US Department of Energy. Reliable measurements of CO₂ adsorption isotherms are required for developing relevant design principles for solid adsorbents [4, 5]. However, careful curation and analysis of published isotherm data has revealed considerable irreproducibility in the high-pressure adsorption literature [6–8]. This irreproducibility has also been shown in interlaboratory studies in which participating laboratories have made isotherm measurements, ostensibly on the

same material, yet obtained greatly varied results [9–17]. Factors contributing to the irreproducibility can arise anywhere along the multistep procedure leading to the adsorption isotherm data [18–20]. These procedures can include material synthesis (starting materials, solvents, conditions, treatment), sample preparation (activation, outgassing, storage, weighing, transfer), the gas adsorption measurements themselves (calibration, sample volume, measurements of temperature, pressure, and mass), data processing (equation of state, buoyancy correction, blank correction), and data reporting (results, experimental details).

The array of factors that can contribute to this challenge underlines the need for reference materials, reference data, and measurement best practices for adsorption metrology [5]. The Facility for Adsorbent Characterization and Testing (FACT lab) at the National Institute of Standards and Technology (NIST) recently led two international interlaboratory studies resulting in high-pressure reference isotherm data using a reference material (RM). The first of these studies was for CO₂ adsorption on ammonium ZSM-5 (NIST RM 8852) at 20 °C and the second for CH₄

✉ Huong Giang T. Nguyen
huong.nguyen@nist.gov

¹ National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, USA

on Zeolite Y (NIST RM 8850) at 25 °C. [21, 22] These studies used NIST reference zeolitic materials, which have already been well-characterized with reference values for chemical composition [RM 8850: Si/Al = 2.547 ± 0.033 ; RM 8852: Si/Al = 28.34 ± 0.39], loss on ignition [RM 8850: 25.679 ± 0.095 ; RM 8852: 8.50 ± 0.09 (percent mass fraction)] and loss on fusion [RM 8850: 25.37 ± 0.67 ; RM 8852: 8.47 ± 0.38 (percent mass fraction)], and informational values for enthalpies of formation, particle size distributions, refractive indices, unit cell parameters, and mass variation with change in relative humidity [23]. Both of these studies found that, with attention to sample handling, activation, and analysis, highly reproducible isotherms could be measured, and reference data with small uncertainties (< 0.09 mmol/g) could be extracted. These reference adsorption data should prove helpful in evaluating the performance of instruments and the measurement practices of laboratories.

After N₂ sorption isotherms, CO₂ sorption isotherms are one of the most highly studied and reported in the literature (> 1000 publications as of mid-2021). The CO₂ measurements have been done over a range of temperatures and pressures, with the fraction of isotherms decreasing at higher pressures and 25 °C being the most common isotherm temperature (see Fig. 1). The current work expands the temperature range of the reference isotherm data for CO₂/ZSM-5 at 20 °C to 15 °C, 25 °C, and 35 °C through *intralaboratory* measurements using five different sorption instruments at the FACT lab and using measurement best practices derived from the *interlaboratory* study of CO₂/ZSM-5 adsorption [21]. The current study provides surface excess reference data over a wider temperature range. In addition, data is provided for low-pressure CO₂/ZSM-5 adsorption at 25 °C

given the large number of low-pressure data in the literature. Lastly, we provide an estimate for the isosteric heat of adsorption for CO₂ adsorption on ZSM-5 (RM 8852) calculated from absolute isotherms derived from the surface excess reference data reported herein.

2 Experimental section

Certain commercial items are identified in this paper. This identification does not imply recommendation by NIST, nor does it imply that these items are the best available for the purposes described.

2.1 Materials

The NIST Office of Reference Materials provided the RM 8852. All samples were used as received without further modifications. Helium (99.999%) and carbon dioxide (99.999%) were purchased from commercial sources.

2.2 Ex-situ sample activation

For measurements made in the helium pycnometer, 9-MPa and 20-MPa manometric systems, and 9-MPa gravimetric system, samples were outgassed ex-situ in a tube furnace attached to a pumping station that is equipped with a turbomolecular pump (vacuum level of 10^{-7} Pa) backed by a scroll pump (vacuum level of 1 Pa). The following activation protocol was used: under high vacuum (0.1 Pa), the temperature was ramped up from room temperature to 350 °C at a rate of

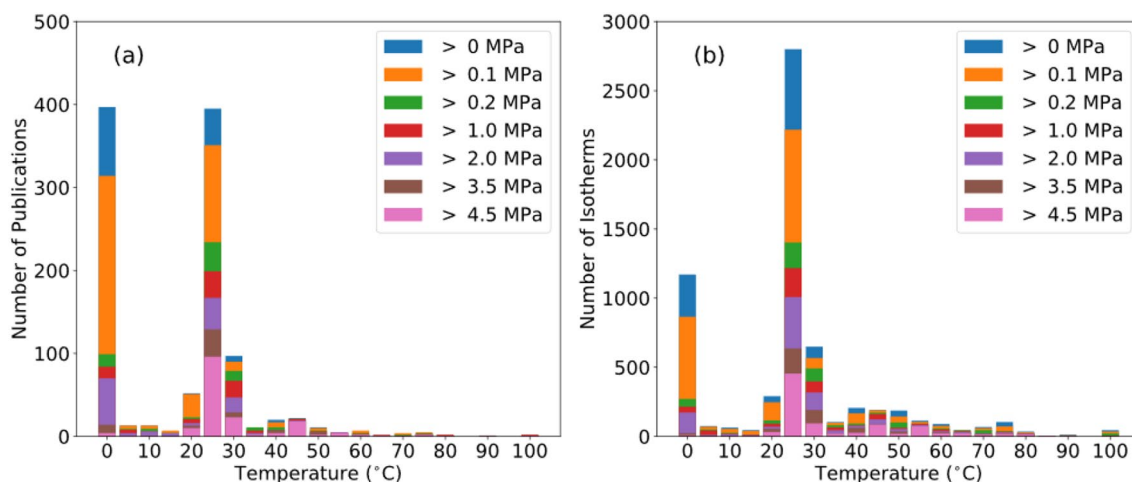


Fig. 1 **a** CO₂ isotherm publication and **b** CO₂ isotherm counts across different temperatures and pressures. The bars represent total number count and the different color bars indicate the number of isotherms or publications with isotherms that exceeded a specified pressure, in MPa. (The blue bar represents all isotherms regardless of threshold.) The

different color bars are overlaid, not stacked. Data was compiled from the API of the NIST adsorption database (<https://adsorption.nist.gov/>) [31]. A detailed explanation of how these data were extracted from the database is given in the supplemental information (Color figure online)

1 °C/min, held at 350 °C for 12 h, and then cooled (≈ 7 h) to room temperature to a final vacuum level of 10^{-5} Pa.

After activation, the sample was transferred under air- and moisture-free conditions from the sealed activator tube to an argon glovebox for storage until pycnometry or adsorption measurements were performed. The mass loss after activation was (6 ± 1) % mass fraction,

2.3 Helium pycnometer

Skeletal density was measured using helium as the probe gas in an AccuPyc II 1340 pycnometer (Micromeritics) as previously reported [24, 25]. For the pycnometry measurements, the activated sample inside the glovebox was loaded to a high-fill level in the pycnometer sample holder. The sample holder was then capped with a fritted cap and quickly transferred (≈ 5 s) to the pycnometer sample chamber to avoid uptake of moisture and other atmospheric contaminants. Each measurement was made by dosing the sample chamber with helium to ≈ 134 kPa, which was then allowed to expand into the reference chamber. A sensor determined the pressure to within $\pm 0.1\%$ uncertainty over the pressure range of vacuum to 207 kPa. The sample volume was determined from the change in pressure and the known volumes of the reference and sample chambers. With the sample volume and sample mass, the skeletal density of the sample could be calculated. The skeletal density given here is the average value of three aliquots. Each aliquot measurement collected data points from 50 cycles. The skeletal density of each aliquot is an average of the last 35 measurement cycles, as the equilibrium value is typically reached after 10–15 cycles [24]. The expanded uncertainty, $U_{k=2}$, was taken to be two standard error from the mean of the skeletal density measurements. The skeletal density of RM 8852 was found to be (2.355 ± 0.005) g/cm³.

2.4 Measurement of adsorption isotherms with 0.1-MPa manometric instrument (M0.1)

The CO₂ adsorption isotherms up to a pressure of ≈ 0.1 MPa (1 bar) at 25 °C were performed in a low-pressure manometric instrument [Autosorb iQ MP, Quantachrome Instruments, (now a subsidiary of Anton Paar)]. Measurements were made on four separate aliquots of RM 8852. The temperature (25 ± 0.1) °C was controlled using a water bath. Before each isotherm measurement, the sample was activated on the activation port of the instrument. The activation procedure was performed under vacuum, with ramping from room temperature to 80 °C at a rate of 1 °C/min and holding that temperature for 30 min, then ramping at a rate of 1 °C/min to 120 °C and holding that temperature for 30 min, and finally ramping at a rate of 1 °C/min to 350 °C, where the

sample was held for 12 h, before being cooled back down to room temperature.

2.5 Measurement of adsorption isotherms with 20-MPa manometric instrument (M20)

Inside the glovebox, an aliquot (≈ 1 g) of activated sample was loaded into the sample cell, which was then sealed, removed from the glovebox, and connected to a high-pressure channel of a 4-channel manometric instrument (NIST 4-channel Gas Reaction Controller, Advanced Materials Corporation). This experimental channel is equipped with two pressure transducers: 2.07 MPa and 20.7 MPa, each with an accuracy of $\pm 0.05\%$ full scale (FS).

CO₂ adsorption isotherms were measured in two separate aliquots of activated RM 8852 at 15 °C, 25 °C, and 35 °C up to 4.5 MPa. The temperature stability of the sample (± 0.1 °C) was maintained in a stainless tampered beaker temperature stabilized by an external circulator filled with a thermal fluid. The channel is housed in a heating cabinet, allowing the temperature of the rest of the channel to be kept at 40 °C, to prevent condensation. The reservoir and sample pressure settling condition was kept at $dp/dt = 2.1$ Pa/s. Prior to an isotherm measurement, the activated sample was evacuated down to ≈ 2.5 Pa for 30 min using a dry scroll pump. Surface excess uptake was determined by keeping track of the moles of free gas in the system from the pressure and temperature readings, and calibrated volumes of the reference and sample chambers. The dosing manifold consists of a main chamber of ≈ 5 cm³ and two reservoir chambers with volumes of ≈ 50 cm³ and ≈ 500 cm³; the reference manifold volume is ≈ 7 cm³ below 2 MPa, and ≈ 16 cm³ above 2 MPa. The density of the gas was determined from the NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP, SRD 23, v 9.1 [26]), which uses the Span-Wagner equation of state for CO₂ [27]. Prior to isotherm measurement, the empty sample cell volume was calibrated using helium (with heating cabinet kept at 40 °C), and the volumes of sample cell corresponding to different temperature zones were partitioned. The total sample cell volume is ≈ 30 cm³, with ≈ 7 cm³ held at the analysis temperature. The void volume was determined from the empty sample cell volume minus the sample skeletal volume (calculated from skeletal density and mass of the sample).

2.6 Measurement of adsorption isotherms with 9-MPa manometric instrument (M9)

Inside the glovebox, an aliquot (≈ 0.5 g) of activated sample was loaded into the sample cell, which was then sealed, removed from the glovebox, and connected to the 9-MPa manometric instrument (BELSORP-VC, Microtrac Bel). The void volume was determined via helium expansion with 10

measurement points up to 3.5 MPa. Gas is dosed directly in the reference cell, which has volume of $\approx 34 \text{ cm}^3$ and the sample cell volume is $\approx 35 \text{ cm}^3$. The system contains one pressure transducer: 13.5 MPa with an accuracy of $\pm 0.1\%$ FS. CO_2 adsorption isotherms were measured in two separate aliquots of activated RM 8852 at 15 °C, 25 °C, and 35 °C up to 4.5 MPa. The temperature stability of the sample (± 0.1 °C) was maintained by a water bath. The instrument air bath was maintained at (25 ± 0.1) °C or (35 ± 0.1) °C throughout the isotherm measurements. Prior to each isotherm measurement, the activated sample was reactivated at 350 °C for 12 h to vacuum level of 10^{-2} Pa using a turbomolecular pump. Surface excess uptake was determined by keeping track of the moles of free gas in the system from the pressure and temperature readings, and volumes of reference and sample chambers. The density of the gas was determined from the REFPROP Database.

2.7 Measurement of adsorption isotherms with 9-MPa gravimetric instrument (G9)

An aliquot ($\approx 1 \text{ g}$) of activated sample was loaded into a 24 mm outer diameter stainless steel tube sample holder inside the glovebox. The sample holder was then quickly loaded onto the sample chamber of the system (BELSORP-BG, Microtrac Bel). The sample was re-outgassed at 120 °C at a heating rate of 1 °C/min and held at this temperature for 3 h under high vacuum (10^{-3} Pa). The sample was then cooled down to the adsorption measurement temperature. The sample was reactivated at 120 °C to remove all residual adsorbed gas molecules from the previous run before measuring a second adsorption cycle. CO_2 adsorption isotherms were measured in two separate aliquots of activated RM 8852 at 15 °C, 25 °C and 35 °C up to 4 MPa. The 9 MPa gravimetric unit is equipped with a magnetic suspension balance with a weighing resolution of 10 μg and reproducibility of 30 μg . The instrument has four pressure gauges and 2 vacuum gauges (Pirani and cold cathode). The temperature of the sample chamber is kept constant, with a temperature stability of ± 0.1 °C, by a circulator bath with thermal fluid. The instrument is housed in an air bath, allowing the temperature of the rest of the instrument to be kept at 35 °C, to prevent condensation. The surface excess amount of carbon dioxide adsorbed was determined by correcting the measured apparent mass change for the buoyancy effect. The gas density was determined simultaneously during measurement by tracking the mass of a non-adsorbing sinker of known volume and density. The volume of each separate component was determined externally from known mass and density. The density of the stainless-steel sample pan was set to 7.98 g/cm^3 , and the sinker was set to 4.497 g/cm^3 as provided by the instrument manufacturer.

2.8 Measurement of adsorption isotherms with 2-MPa gravimetric instrument (G2)

Sample ($\approx 0.1 \text{ g}$) was loaded into the 2-MPa gravimetric instrument (IGA-100-VG, Hiden Isochema Ltd) in a stainless-steel mesh pan. The sample was degassed *in-situ* at room temperature under vacuum at an evacuation rate of 20 kPa/min until a pressure of $\approx 0.5 \text{ kPa}$ and then heated up to 350 °C at a heating rate of 1 °C/min and held at this temperature for 18 h 40 min under high vacuum (10^{-5} Pa). The sample was then cooled down to the adsorption temperature. CO_2 adsorption isotherms were measured in two separate aliquots of activated RM 8852 at 15 °C, 25 °C, and 35 °C up to 2 MPa. The 2-MPa gravimetric instrument is equipped with a balance with a weighing resolution of 0.1 μg . The system is configured with automated switching between two pressure measurement/control ranges: Range 1: vacuum to 2 MPa is measured with a silicon sensor pressure transducer with an accuracy of $\pm 0.8 \text{ kPa}$ (0.04% FS, combined non-linearity, repeatability, hysteresis) and a resolution of 1.2 kPa (0.006% FS). Range 2: vacuum to 10 kPa is measured with a capacitance manometer with an accuracy of $\pm 15 \text{ Pa}$ (0.15% reading, combined non-linearity, repeatability, hysteresis) and a resolution of 1×10^{-5} Pa (0.001% FS). The temperature of the stainless-steel sample chamber was kept constant by a circulator water bath with a temperature stability of ± 0.02 °C. The temperature of the counterweight and upper hangdown wires remained at ambient temperature (≈ 22 °C). As a function of temperature and pressure, the instrument determines the apparent measured mass change of the sample, which is due to a combination of gas adsorption and the buoyancy effect. The excess amount of carbon dioxide adsorbed was determined by correcting the measured apparent mass change for the buoyancy effect. The density of the gas was determined from the REFPROP Database. The volume of each separate component was determined externally from known mass and density. The density of the stainless-steel sample holder and stainless-steel counterweight were set to 7.9 g/cm^3 , lower hangdown wire set to 21 g/cm^3 , upper hangdown wire set to 19.3 g/cm^3 as provided by the instrument manufacturer.

2.9 Measurement of adsorption isotherms with 5-MPa gravimetric instrument (G5)

The sample ($\approx 0.2 \text{ g}$) was loaded into the 5-MPa gravimetric system (TGA-HP50, TA instruments) in a 12 mm diameter quartz sample holder. The sample was degassed at room temperature until the pressure was $< 200 \text{ Pa}$ and then heated up to 350 °C at a heating rate of 1 °C/min and held at this temperature for 14 h under high vacuum (10^{-3} Pa). The sample was then cooled down to the adsorption temperature for the isotherm measurements. CO_2 adsorption isotherms were

measured in 2 separate aliquots of activated RM 8852 at 15 °C, 25 °C and 35 °C up to 4.5 MPa. The sample was reactivated to remove all residual adsorbed gas molecules from the previous run before measuring a second adsorption cycle. The unit is equipped with a two-beam null balance with a weighing accuracy of 0.1%. The instrument has two pressure transducers in two pressure ranges. Below 127 kPa, the instrument uses a temperature-regulated capacitance manometer (pressure range of 2.67 Pa to 3.33 MPa) with an accuracy of 0.12% of reading (including non-linearity, hysteresis, and non-repeatability) and a resolution of 1.33 kPa (0.002% of F.S). Above 127 kPa, the instrument uses a silicon-sensor pressure transducer with an accuracy of ± 2 kPa (0.04% FS, combined non-linearity, repeatability, hysteresis). Duplicate runs of the same aliquot consistently yielded the same result within experimental errors after reactivation. The temperature of the stainless-steel sample chamber is kept constant by a circulator water bath with temperature stability of ± 0.1 °C. The instrument is housed in a heating cabinet air bath, allowing the temperature in the rest of the instrument to be kept at 50 °C, to prevent condensation. A manual buoyancy correction was performed as described above for the 2-MPa instrument, in which case each balance component volume was determined externally from known mass and density. The density of the fused quartz sample holders was set to 2.2 g/cm³ and that of the stainless steel hangdown wires was set to 7.8 g/cm³. The density of the gas was determined from the REFPROP Database.

2.10 Blank subtraction

All reported isotherms have been corrected by a blank CO₂ measurement taken with no adsorbent in the sample holder. For blank runs, measurements with a similar number of data points at a similar distribution of equilibrium pressure, if possible, is recommended for best results. For the gravimetric measurements, the raw data for the sample and blank were both corrected for buoyancy to obtain the surface excess uptake (mmol) before subtracting the blank data. For the manometric measurements, the blank surface excess uptake (in cm³ or mmol) was subtracted from that of the sample. The blank-corrected uptake then is reported in units of mmol/g. The excess CO₂ isotherms for the blank are reported in Section S2 of the Electronic Supplementary Information (ESI).

2.11 Empirical reference function

At each of the temperatures, an empirical reference function was determined for the surface excess adsorption using a three-parameter logistic function [28],

$$n_{ex,ref}(P_{eq}) = \frac{c}{\{1 + \exp[(-\ln(P) + a)/b]\}^b}, \quad (1)$$

where, $n_{ex,ref}$ is the excess uptake (mmol/g), P_{eq} is the equilibrium pressure (MPa), P is $(P_{eq}) / (1 \text{ MPa})$, and a , b , and c are constants. The constants and the 95% uncertainty interval for each of the empirical reference functions were estimated using a Bayesian, Markov-Chain Monte Carlo method [29, 30]. This function was selected simply because it replicated the form of the measured isotherms. No physical significance should be associated with the function or the constants.

2.12 Automated search of the NIST isotherm database API

Figure 1 was generated by meta-analysis of the isotherms compiled in the NIST/ARPA-E Database of Novel and Emerging Adsorbent Materials [31] (i.e., the NIST/ARPA-E Adsorption Isotherm Database or NIST-ISODB). NIST-ISODB is a catalog of both published scientific articles addressing adsorption and adsorbent materials and isotherms presented in those scientific articles. The contents of the database, in this case the details of each isotherm (including adsorbent and adsorptive identity, adsorption amount versus pressure, isotherm temperature, etc.) can be accessed via its Application Programming Interface (API) that allows for rapid, script-based statistical analysis of the cataloged isotherms. The Electronic Supplementary Information (ESI) for this article includes a detailed description of the API operations necessary to reproduce Fig. 1 and an example Jupyter Notebook that implements those operations and plots the results. This notebook may be modified to conduct similar meta-analyses for different adsorptives or thermodynamic conditions.

2.13 Estimation of the isosteric heat of adsorption

The isosteric heat of adsorption (Q_{st}) as a function of adsorption uptake was estimated from the conventional Clausius–Clapeyron equation, using the method of isosteres in conjunction with the logistic reference equations for excess adsorption. As recommended by Myers and Monson, [32] the surface excess adsorption at each temperature (15 °C, 25 °C, and 35 °C) was converted to absolute adsorption:

$$n_{abs}(P, T) = n_{ex}(P, T) + \rho(P, T)v_p, \quad (2)$$

where n_{abs} is the absolute adsorption uptake, v_p is the micropore volume and $\rho(P, T)$ is the density of CO₂ at the desired pressure and temperature. The micropore volume $v_p = 0.13 \text{ cm}^3/\text{g}$ was used, as recommended by Fang et al. [33]. Although RM 8852 (ZSM-5) has some mesopores, [33] the calculation of the isosteric heat, Q_{st} , is not sensitive to the

value of v_p for uptake below 2.3 mmol/g. The bulk density of CO_2 was taken from the CoolProp [34] implementation of the equation of state of Span and Wagner, [27] equivalent to NIST REFPROP database v 9.1. For a set of (absolute) adsorption isosteres, the pressure of each isostere at each of the three temperatures was numerically determined. Then, as required by the usual form of the Clausius–Clapeyron equation,

$$Q_{\text{st}} = -R \left[\frac{\partial \log P}{\partial (1/T)} \right]_{n_{\text{abs}}}, \quad (3)$$

(R is the universal gas constant) the slope of $\log P$ versus $1/T$ was computed via linear regression for each adsorption isostere, ultimately yielding the isosteric heat from Eq. 3. Uncertainty in the mean of Q_{st} was estimated by repeating the calculation with absolute isotherms determined from excess isotherms corresponding to the upper and lower

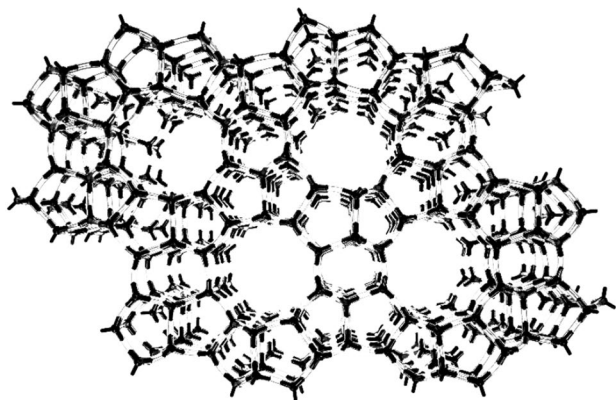


Fig. 2 Structure of ZSM-5

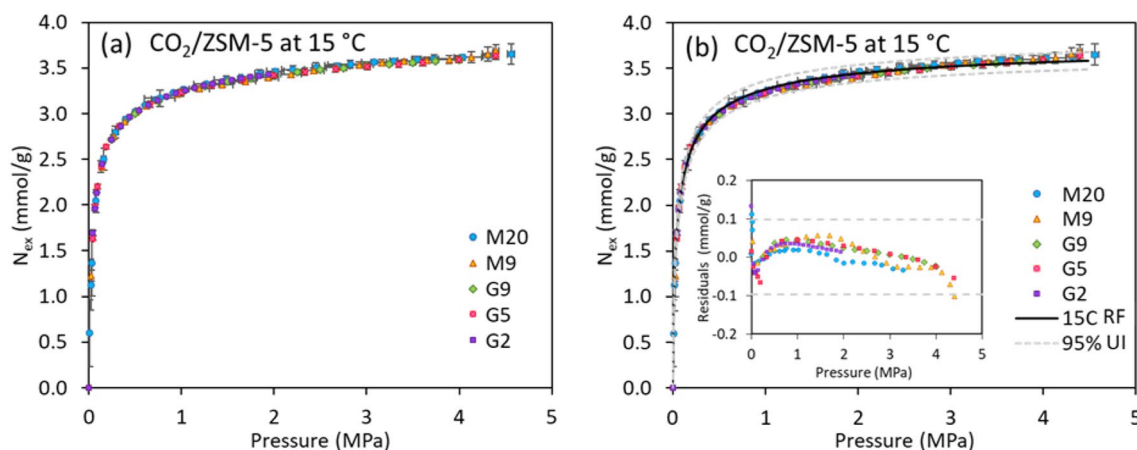


Fig. 3 **a** Average surface excess CO_2 adsorption isotherms on RM 8852 for each dataset up to 4.5 MPa at 15 °C, along with **b** empirical reference function (RF) and 95% uncertainty interval (UI), and resid-

uncertainty intervals on n_{ex} followed by application of t statistics. Example calculations are provided in a Jupyter Notebook as part of the ESI.

3 Results and discussion

ZSM-5 is a MFI-type zeolite and its structure is shown in Fig. 2. The zeolite consists of chains of eight five-member rings (pentasil) subunits linked to form sheets, which form a 3D framework. The resulting framework has two perpendicular channel systems with one running straight and the other in a sinusoidal fashion [35].

The surface excess CO_2 adsorption isotherms on RM 8852 at 15 °C, 25 °C, and 35 °C to 4.5 MPa are shown in Figs. 3a, 4a, and 5a, respectively. These isotherms were measured following the recommended best practices previously reported. [21] The isotherms are similar in shape to the previously reported reference isotherm. As expected, uptake decreases at higher temperatures. Each plot shows the average isotherms from measurements made on each of the five different instruments (G2, G5, G9, M9, M20). For measurements at 25 °C, an additional dataset (M0.1) from a dedicated low-pressure instrument is included (see below for discussion of low pressure dataset). All CO_2 /ZSM-5 isotherms have been blank corrected, with the blank isotherm being nearly zero for M0.1, G2, G5 and G9, and greater in magnitude, particularly at higher pressures, for M9 and M20 (see Figs. S9–S11). This is not surprising considering that errors, if any, in manometric systems are accumulative for each successive measurement point, while that for gravimetric system for each data point is independent of the others. The isotherms from each of the instruments are highly repeatable (see Fig. S1–S3), albeit, with the exception

uals from the reference function [$n_{\text{ex,ref}}(P)$ —measured] as inset. Error bars represent two standard deviations

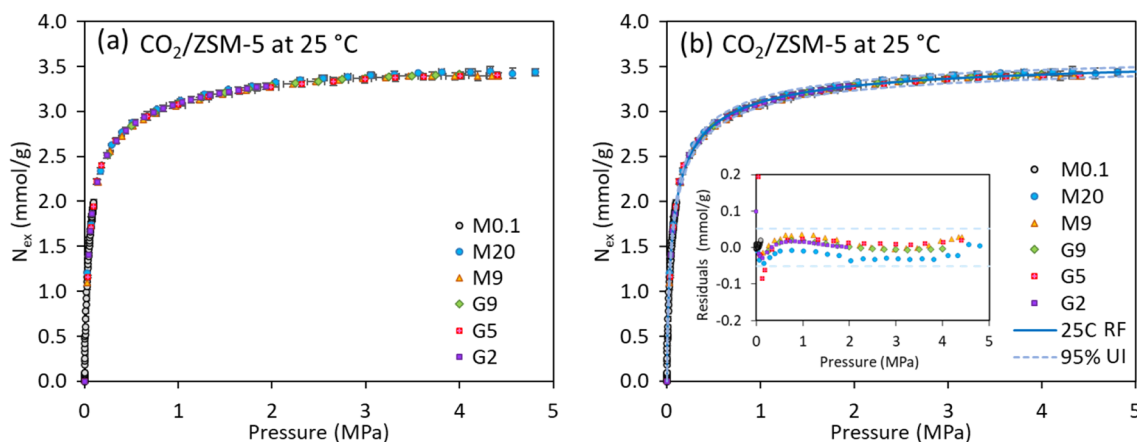


Fig. 4 a Average surface excess CO₂ adsorption isotherms on RM 8852 for each dataset up to 4.5 MPa at 25 °C, along with **b** empirical reference function (RF) and 95% uncertainty interval (UI), and resid-

uals from the reference function [$n_{ex,ref}(P)$ —measured] as inset. Error bars represent two standard deviations

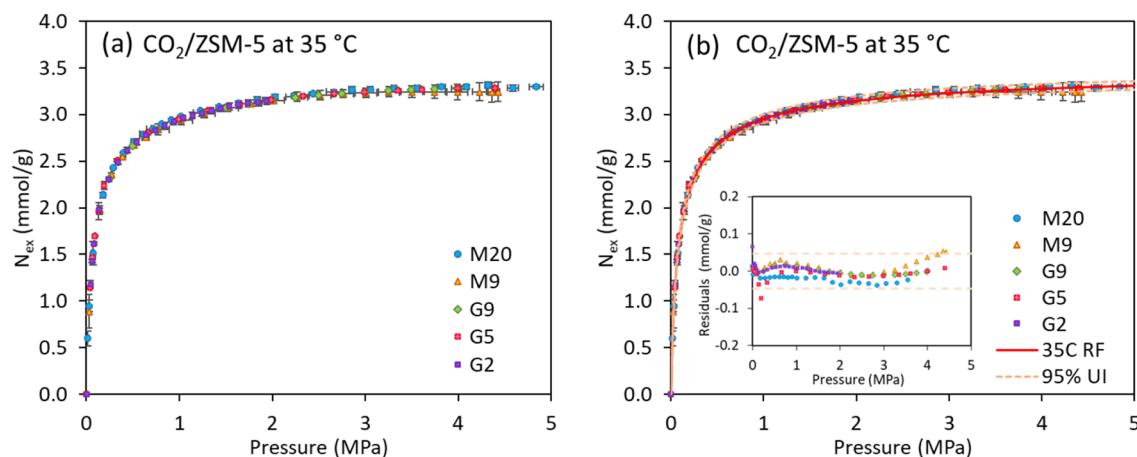


Fig. 5 a Average surface excess CO₂ adsorption isotherms on RM 8852 for each dataset up to 4.5 MPa at 35 °C, along with **b** empirical reference function (RF) and 95% uncertainty interval (UI), and resid-

uals from the reference function [$n_{ex,ref}(P)$ —measured] as inset. Error bars represent two standard deviations

of 35 °C data collected on M9, which shows slight variation, especially above 3.5 MPa. However, the variation is within the adsorbed amount accuracy of ± 0.13 mmol (0.26 mmol/g based on the 0.5 g of sample used) reported by the instrument manufacturer for M9. In hindsight, greater sample mass, if possible, may potentially reduce the variation in this dataset. The data are consistent among the different instruments (see Figs. 3–5). The instruments represent both gravimetric and manometric types, indicating reliable adsorption measurements can be made using both measurement principles. The empirical reference function, Eq. (1), was determined at each of the temperatures and is shown in Figs. 3, 4, 5b. The relevant parameters (a , b , and c) are given in Table 1. The reference functions are predictive from 10 kPa to 4.5 MPa. The expanded uncertainties, $U_{k=2}$, for the excess

uptake are approximately 0.097 mmol/g, 0.051 mmol/g, and 0.047 mmol/g at 15 °C, 25 °C, and 35 °C, respectively, over the full pressure range. The residuals (reference function minus measured isotherm) are shown as insets in the graphs in Figs. 3, 4, 5b. The residuals demonstrate that the reference functions adequately represent the isotherms over the full measurement pressure range at all temperatures of the study. The relative residuals can be found in the electronic supplemental information (Fig. S8). The datasets and the reference isotherm are available on-line through the NIST/ARPA-E Database of Novel and Emerging Adsorbent Materials.

Given the large number of low-pressure CO₂ isotherms in the literature at 25 °C, measurements were made on the low-pressure adsorption instrument (M0.1) up to 0.1 MPa as a means to provide reliable data in the low-pressure

Table 1 Parameters for empirical-reference functions for high-pressure isotherm data

Parameter*	Units	15 °C		25 °C		35 °C	
		Value	Uncertainty	Value	Uncertainty	Value	Uncertainty
<i>a</i>	n/a	−3.84	0.05	−3.36	0.01	−2.97	0.02
<i>b</i>	n/a	1.66	0.03	1.53	0.01	1.44	0.01
<i>c</i>	mmol/g	3.83	0.02	3.65	0.005	3.51	0.01

The function is valid from 10 kPa to 4.5 MPa

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

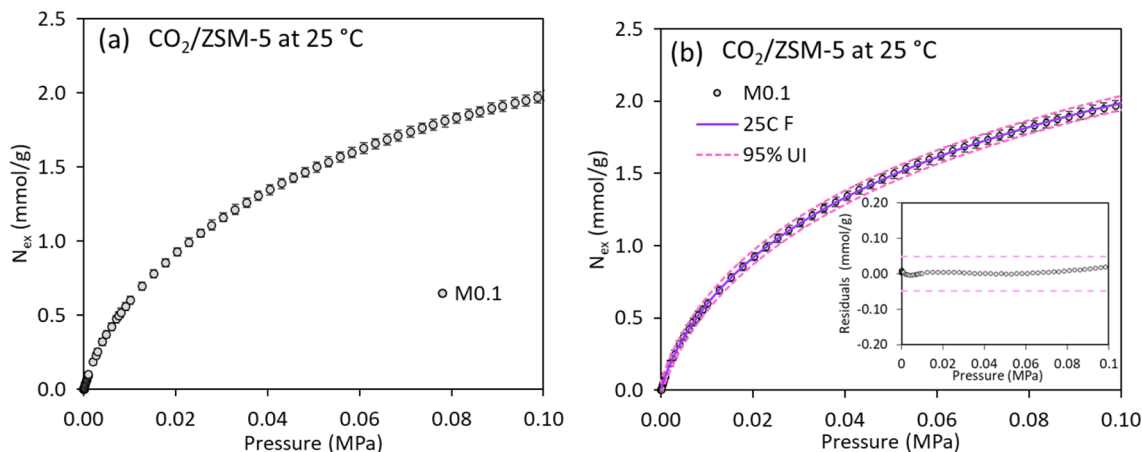


Fig. 6 **a** Average low-pressure surface excess CO₂ adsorption isotherms on RM 8852 at 25 °C, along with **b** empirical function (F) and 95% uncertainty interval (UI) and residuals from the reference function [$n_{\text{ex,func}}(P)$ —measured] as inset. Error bars represent two standard deviations

Table 2 Parameters for empirical function parameters for low pressure isotherm data (up to 0.1 MPa)

Parameter*	Units	25 °C	
		Value	Uncertainty
<i>a</i>	n/a	−3.26	0.012
<i>b</i>	n/a	1.94	0.074
<i>c</i>	mmol/g	5.03	0.267

The function is valid from 0.1 kPa to 0.1 MPa

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

region. The low-pressure surface excess CO₂ adsorption isotherm is shown in Fig. 6a. This data was measured on a low-pressure adsorption instrument (M0.1) and in pressure regions with overlap, it agreed well, typically within the expanded uncertainties (0.047 mmol/g), with the datasets measured on the high-pressure instruments. A surface excess empirical function was determined for the low-pressure data and is shown in Fig. 6b. The relevant parameters are given in Table 2. The low-pressure function is predictive from 0.1 kPa to 0.1 MPa. The expanded uncertainty, $U_{k=2}$, for the excess uptake are approximately 0.048 mmol/g over the full pressure range. The residuals

(empirical function minus measured isotherm) are shown in Fig. 6b.

The availability of reference isotherm data at several different temperatures for CO₂/ZSM-5 afforded the opportunity to examine the temperature dependence of the isotherms and extract estimates of the isosteric heat of adsorption. Isosteric heat of adsorption is an important factor in the design of adsorption-based gas separation processes [36]. If the isosteric heat of adsorption has a weak temperature dependence, it can also be used to calculate the isotherms at other temperature of interest for processes [37]. Estimates of isosteric heat of adsorption were computed after converting the surface excess reference data into absolute isotherms, as described in the experimental section, and the results of which are shown in Fig. 7. Results are shown for a minimum (absolute) uptake of 0.6 mmol/g (so that $P > 0.01$ MPa for all calculations) and a maximum uptake of 3.6 mmol/g, after which it is not possible to invert isosteres all three temperatures. Error bars in Fig. 7 are estimates of the 95% uncertainty intervals on the mean value of Q_{st} , which vary from 2.0 kJ/mol to 3.7 kJ/mol depending on the uptake: the highest uncertainty in the mean of Q_{st} corresponds to the smallest and largest uptake values. The figure also includes measurements of the heat of adsorption at 28 °C from Fang et al. from differential scanning calorimetry (DSC), [33] and

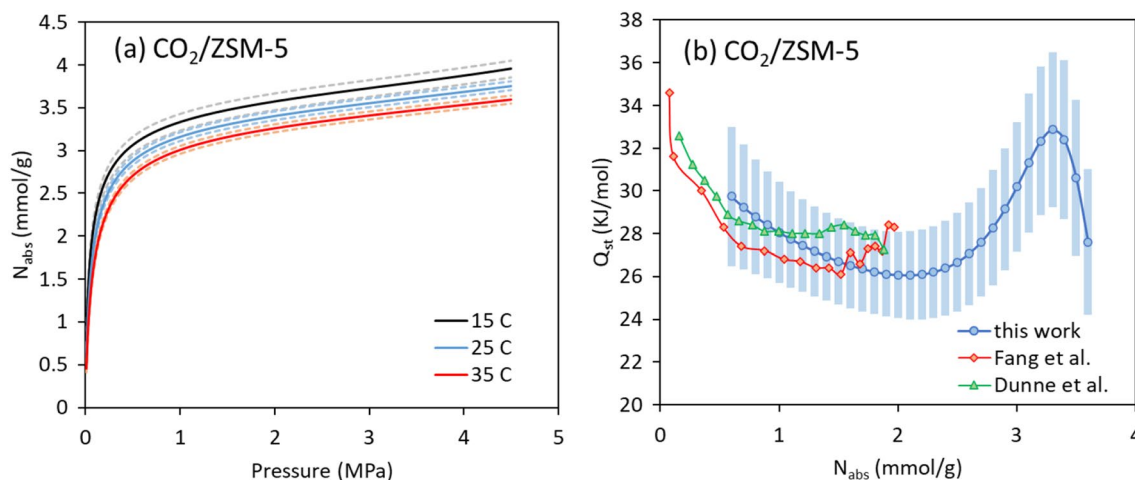


Fig. 7 **a** Absolute CO_2 adsorption isotherms on RM 8852 at 15 °C, 25 °C, and 35 °C determined from surface excess reference data for RM 8852 at 15 °C, 25 °C, and 35 °C. Dotted lines are absolute isotherms determined from the upper and lower 95% uncertainty intervals of the surface excess reference data. See section “[Experimental Section](#)” for details on calculation of absolute adsorption isotherms. **b** Estimate of the isosteric heat of adsorption of CO_2 on RM 8852 as

a function of absolute uptake at 25 °C, as computed by the method of adsorption isosteres and the Clausius–Clapeyron equation. Error bars represent estimates of the 95% uncertainty intervals of estimates of the mean value of Q_{st} . Also included for comparison are measurements of the heat of adsorption at 28 °C for $\text{CO}_2/\text{RM 8852}$ from Fang et al. [33], and at 23.9 °C (for $\text{CO}_2/\text{H-ZSM-5}$ with $\text{Si}/\text{Al}=30$) from Dunne et al. [38]

data at 23.9 °C on a comparable H-ZSM-5 with Si/Al ratio of 30 measured on a Tian-Calvet heat flux calorimeter from Dunne et al. [38]. The three data sets are very similar, within the uncertainty intervals on the estimates of Q_{st} in this work for all but the DSC measurements near 2.0 mmol/g uptake; it is stressed that the results in this work are calculated estimates of Q_{st} from a different technique than the DSC or Tian-Calvet measurements in the works of Fang et al. and Dunne et al., respectively.

4 Conclusions

In this article, the temperature range of the reference isotherm data for $\text{CO}_2/\text{ZSM-5}$ was expanded to 15 °C, 25 °C, and 35 °C, and isosteric heat of adsorption was estimated from absolute isotherms derived from the surface excess reference data. The isotherm measurements were crosschecked using a variety of gravimetric and manometric instruments. Details on how to perform an automated search on the API of the NIST adsorption database were also given. These data should be helpful to labs interested in high-pressure CO_2 adsorption measurements, other high-pressure measurements, and NIST RM 8852.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10450-022-00355-x>.

Acknowledgements Instruments at the Facility for Adsorbent Characterization and Testing were funded by the Advanced Research Projects Agency-Energy (ARPA-E) through Interagency Agreement No.

1208-0000. JCM. was supported through the NIST Summer Undergraduate Research Fellowship (SURF) program. The image of the zeolite structure was from photograph taken by Dr. Lane Sander using 3D model constructed by HGTV. The authors thank the reviewers for helpful suggestions.

Author contributions HGTV conceived the initial experiments. HGTV and JCM carried out all the experiments and measurements. BT did the statistical analysis and function constants determination. DWS performed the isosteric heat of adsorption calculations, wrote the Jupyter Notebook scripts and provided the resources to do literature and isotherm searches on the API of the NIST adsorption database. RDvZ assisted in experimental design and supervised the project. HGTV wrote the initial drafts of the paper and finalized the manuscript with contributions from all authors. All authors have given approval to the final version of this manuscript.

Declarations

Conflict of interest The authors declare no competing financial interest.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- D'Alessandro, D.M., Smit, B., Long, J.R.: Carbon dioxide capture: prospects for new materials. *Angew. Chem. Int. Ed.* **49**(35), 6058–6082 (2010). <https://doi.org/10.1002/anie.201000431>
- Wang, J., Huang, L., Yang, R., Zhang, Z., Wu, J., Gao, Y., et al.: Recent advances in solid sorbents for CO₂ capture and new development trends. *Energy Environ. Sci.* **7**(11), 3478–3518 (2014). <https://doi.org/10.1039/C4EE01647E>
- Yu, C.-H., Huang, C.-H., Tan, C.-S.: A review of CO₂ capture by absorption and adsorption. *Aerosol Air Qual. Res.* **12**, 745–769 (2012)
- Espinal, L., Morreale, B.D.: Materials challenges in carbon-mitigation technologies. *MRS Bull.* **37**(4), 431–438 (2012). <https://doi.org/10.1557/mrs.2012.10>
- Espinal, L., Poster, D.L., Wong-Ng, W., Allen, A.J., Green, M.L.: Measurement, standards, and data needs for CO₂ capture materials: a critical review. *Environ. Sci. Technol.* **47**(21), 11960–11975 (2013). <https://doi.org/10.1021/es402622q>
- Broom, D.P., Hirscher, M.: Irreproducibility in hydrogen storage material research. *Energy Environ. Sci.* **9**(11), 3368–3380 (2016). <https://doi.org/10.1039/C6EE01435F>
- Mason, J.A., Veenstra, M., Long, J.R.: Evaluating metal–organic frameworks for natural gas storage. *Chem. Sci.* **5**(1), 32–51 (2014). <https://doi.org/10.1039/C3SC52633J>
- Park, J., Howe, J.D., Sholl, D.S.: How reproducible are isotherm measurements in metal–organic frameworks? *Chem. Mater.* **29**(24), 10487–10495 (2017). <https://doi.org/10.1021/acs.chemmater.7b04287>
- Gasparik, M., Rexer, T.F.T., Aplin, A.C., Billefont, P., De Weireld, G., Gensterblum, Y., et al.: First international inter-laboratory comparison of high-pressure CH₄, CO₂ and C₂H₆ sorption isotherms on carbonaceous shales. *Int. J. Coal Geol.* **132**(Supplement C), 131–146 (2014). <https://doi.org/10.1016/j.coal.2014.07.010>
- Gensterblum, Y., van Hemert, P., Billefont, P., Battistutta, E., Busch, A., Krooss, B.M., et al.: European inter-laboratory comparison of high pressure CO₂ sorption isotherms II: natural coals. *Int. J. Coal Geol.* **84**(2), 115–124 (2010). <https://doi.org/10.1016/j.coal.2010.08.013>
- Gensterblum, Y., van Hemert, P., Billefont, P., Busch, A., Charriere, D., Li, D., et al.: European inter-laboratory comparison of high pressure CO₂ sorption isotherms. I: activated carbon. *Carbon* **47**(13), 2958–2969 (2009). <https://doi.org/10.1016/j.carbon.2009.06.046>
- Goodman, A.L., Busch, A., Bustin, R.M., Chikatamarla, L., Day, S., Duffy, G.J., et al.: Inter-laboratory comparison II: CO₂ Isotherms measured on moisture-equilibrated Argonne premium coals at 55 degrees C and up to 15 MPa. *Int. J. Coal Geol.* **72**(3–4), 153–164 (2007). <https://doi.org/10.1016/j.coal.2007.01.005>
- Goodman, A.L., Busch, A., Duffy, G.J., Fitzgerald, J.E., Gasem, K.A.M., Gensterblum, Y., et al.: An inter-laboratory comparison of CO₂ isotherms measured on Argonne premium coal samples. *Energy Fuels* **18**(4), 1175–1182 (2004). <https://doi.org/10.1021/ef034104h>
- Hurst, K.E., Gennett, T., Adams, J., Allendorf, M.D., Balderas-Xicohtencatl, R., Bielewski, M., et al.: An international laboratory comparison study of volumetric and gravimetric hydrogen adsorption measurements. *ChemPhysChem* **20**(15), 1997–2009 (2019). <https://doi.org/10.1002/cphc.201900166>
- Hurst, K.E., Parilla, P.A., O'Neill, K.J., Gennett, T.: An international multi-laboratory investigation of carbon-based hydrogen sorbent materials. *Appl. Phys. A-Mater. Sci. Process.* **122**(1), 1–9 (2016). <https://doi.org/10.1007/s00339-015-9537-x>
- Moretto, P., Zlotea, C., Dolci, F., Amieiro, A., Bobet, J.L., Borgschulte, A., Zan, J.A.: A Round Robin test exercise on hydrogen absorption/desorption properties of a magnesium hydride based material. *Int. J. Hydrog. Energy* **38**(16), 6704–6717 (2013). <https://doi.org/10.1016/j.ijhydene.2013.03.118>
- Zlotea, C., Moretto, P., Steriotis, T.: A Round Robin characterisation of the hydrogen sorption properties of a carbon based material. *Int. J. Hydrog. Energy* **34**(7), 3044–3057 (2009). <https://doi.org/10.1016/j.ijhydene.2009.01.079>
- Broom, D.P., Webb, C.J.: Pitfalls in the characterisation of the hydrogen sorption properties of materials. *Int. J. Hydrog. Energy* **42**(49), 29320–29343 (2017). <https://doi.org/10.1016/j.ijhydene.2017.10.028>
- Malbrunot, P., Vidal, D., Vermesse, J., Chahine, R., Bose, T.K.: Adsorbent helium density measurement and its effect on adsorption isotherms at high pressure. *Langmuir* **13**(3), 539–544 (1997). <https://doi.org/10.1021/la950969e>
- Robens, E., Keller, J.U., Massen, C.H., Staudt, R.: Sources of error in sorption and density measurements. *J. Therm. Anal. Calorim.* **55**(2), 383–387 (1999). <https://doi.org/10.1023/a:1010195013633>
- Nguyen, H.G.T., Espinal, L., van Zee, R.D., Thommes, M., Toman, B., Hudson, M.S.L., et al.: A reference high-pressure CO₂ adsorption isotherm for ammonium ZSM-5 zeolite: results of an interlaboratory study. *Adsorption* **24**(6), 531–539 (2018). <https://doi.org/10.1007/s10450-018-9958-x>
- Nguyen, H.G.T., Sims, C.M., Toman, B., Horn, J., van Zee, R.D., Thommes, M., et al.: A reference high-pressure CH₄ adsorption isotherm for zeolite Y: results of an interlaboratory study. *Adsorption* **26**(8), 1253–1266 (2020). <https://doi.org/10.1007/s10450-020-00253-0>
- Turner, S., Sieber, J.R., Vetter, T.W., Zeisler, R., Marlow, A.F., Moreno-Ramirez, M.G., et al.: Characterization of chemical properties, unit cell parameters and particle size distribution of three zeolite reference materials: RM 8850 – zeolite Y, RM 8851 – zeolite A and RM 8852 – ammonium ZSM-5 zeolite. *Microporous Mesoporous Mater.* **107**(3), 252–267 (2008). <https://doi.org/10.1016/j.micromeso.2007.03.019>
- Nguyen, H.G.T., Horn, J.C., Bleakney, M., Siderius, D.W., Espinal, L.: Understanding material characteristics through signature traits from helium pycnometry. *Langmuir* **35**(6), 2115–2122 (2019). <https://doi.org/10.1021/acs.langmuir.8b03731>
- Nguyen, H.G.T., Horn, J.C., Thommes, M., van Zee, R.D., Espinal, L.: Experimental aspects of buoyancy correction in measuring reliable high-pressure excess adsorption isotherms using the gravimetric method. *Meas. Sci. Technol.* **28**(12), 1202 (2017)
- Lemmon, E. W., Huber, M. L., & McLinden, M. O. Reference fluid thermodynamic and transport properties. NIST standard reference database 23, Version 9.1. National Institute of Standards and Technology. (2013). <https://www.nist.gov/srd/refprop>. Accessed 22 June 2021
- Span, R., Wagner, W.: A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. *J. Phys. Chem. Ref. Data* **25**(6), 1509–1596 (1996). <https://doi.org/10.1063/1.555991>
- Balakrishnan, N.: Handbook of the Logistic Distribution (N Balakrishnan Ed.). Marcel Dekker, New York NY (1992)
- Gelman, A., Carlin, J., Stern, H., Dunson, D., Vehtari, A., Rubin, D.: Bayesian Data Analysis. Chapman & Hall, Boca Raton (2013)
- Possolo, A., Toman, B.: Assessment of measurement uncertainty via observation equations. *Metrologia* **44**(6), 464–475 (2007). <https://doi.org/10.1088/0026-1394/44/6/005>
- Siderius, D.W., Shen, V.K., Johnson, R.D., III., van Zee, R.D. (eds.): NIST/ARPA-E Database of Novel and Emerging Adsorbent Materials. National Institute of Standards and Technology, Gaithersburg MD (2021). <https://doi.org/10.18434/T43882>

32. Myers, A.L., Monson, P.A.: Physical adsorption of gases: the case for absolute adsorption as the basis for thermodynamic analysis. *Adsorption* **20**(4), 591–622 (2014). <https://doi.org/10.1007/s10450-014-9604-1>
33. Fang, H., Findley, J., Muraro, G., Ravikovitch, P.I., Sholl, D.S.: a strong test of atomically detailed models of molecular adsorption in zeolites using multilaboratory experimental data for CO₂ adsorption in ammonium ZSM-5. *J. Phys. Chem. Lett.* **11**(2), 471–477 (2020). <https://doi.org/10.1021/acs.jpcllett.9b02986>
34. Bell, I.H., Wronski, J., Quoilin, S., Lemort, V.: Pure and pseudo-pure fluid thermophysical property evaluation and the open-source thermophysical property library CoolProp. *Ind. Eng. Chem. Res.* **53**(6), 2498–2508 (2014). <https://doi.org/10.1021/ie4033999>
35. Kokotailo, G.T., Lawton, S.L., Olson, D.H., Meier, W.M.: Structure of synthetic zeolite ZSM-5. *Nature* **272**(5652), 437–438 (1978). <https://doi.org/10.1038/272437a0>
36. Sircar, S., Mohr, R., Ristic, C., Rao, M.B.: Isotheric heat of adsorption: theory and experiment. *J. Phys. Chem. B* **103**(31), 6539–6546 (1999). <https://doi.org/10.1021/jp9903817>
37. Cao, D.V., Sircar, S.: Temperature dependence of the isotheric heat of adsorption. *Adsorpt. Sci. Technol.* **19**(10), 887–894 (2001). <https://doi.org/10.1260/0263617011494646>
38. Dunne, J.A., Rao, M., Sircar, S., Gorte, R.J., Myers, A.L.: Calorimetric heats of adsorption and adsorption isotherms. 2. O₂, N₂, Ar, CO₂, CH₄, C₂H₆, and SF₆ on NaX, H-ZSM-5, and Na-ZSM-5 zeolites. *Langmuir* **12**(24), 5896–5904 (1996). <https://doi.org/10.1021/la960496r>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.