

Experimentally Verified Alkane Adsorption Isotherms in Nanoporous Materials from Literature Meta-Analysis

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ABSTRACT

Identification of independent experimental replicate measurements of well-defined physical properties provides a useful way to assess the reproducibility of literature reports of these properties. Prior meta-analysis of this kind for single component adsorption of CO₂ and alcohols in nanoporous materials showed that ~20% of reported isotherms for these molecules were inconsistent with available replicate measurements. In this paper we extend this analysis to the single component adsorption of alkanes in nanoporous materials using a collection of 2998 experimental isotherms. Among these isotherms, 846 replicates were identified and analyzed. Many more replicates are available for CH₄ adsorption than for any other alkane. Our analysis finds that 15% of the replicate alkane isotherms are inconsistent with other replicate measurements. After discarding these outlier isotherms we report graphical and numerical consensus isotherms for 93 independent combinations of adsorbate, adsorbent and temperature as well as assessment of another 124 independent systems for which two replicate isotherms are available.

Introduction

By some estimates up to 15% of the total energy consumption in the world can be attributed to chemical separation processes, implying there is enormous potential for energy savings using more efficient, non-thermal separation approaches.¹ Adsorption-based separations are one important class of separation techniques that are an alternative to phase change methods such as distillation. Development and optimization of adsorption-based processes for large-scale industrial applications is only possible when reliable adsorption data are available.² The vast number of potential adsorbent materials that exist means that compilation of adsorption data is crucial in the selection of materials for desired separations.³⁻⁶ In addition to the necessity of using high quality data in process design, there has been significant recent interest in accelerating the search for new adsorbents using machine learning approaches.⁷⁻¹⁰ These data-driven methods intrinsically rely on the accuracy of their underlying training data.

The NIST/ARPA-E Adsorption Database¹¹ has made a valuable contribution to the field by systematically compiling adsorption equilibrium data in porous materials from the open literature. To date the database includes information for more than 35,000 isotherms and some efforts have been made to aid in searching and visualizing the data.¹²

A relevant issue in assessing experimental data from a diverse array of sources is to understand what level of reproducibility is obtained among distinct measurements. This issue is of course important in many areas of materials chemistry and engineering.¹³⁻¹⁷ Several recent efforts have been coordinated to examine this issue for measurements of adsorption equilibrium. Gasparik et al.¹⁸ performed an inter-laboratory study for methane, CO₂ and ethane isotherms in shales, highlighting the importance of standardized calibration and measurement protocols as well as a precise control of the experimental conditions. Nguyen et al. highlighted the value to the research community of reference materials in inter-laboratory studies with CO₂¹⁹ and methane²⁰ in zeolites.

The resulting reference isotherms have been useful in performing detailed tests of molecular simulations of adsorption.²¹ Crucially, each of these inter-laboratory studies demonstrated that adsorption equilibria in well-defined materials can be measured with a high degree of reproducibility if appropriate care is taken. Inter-laboratory studies can also be useful in testing the reproducibility of data analysis methods. Osterrieth et al.²² compared calculation of BET surface areas, a key property of porous adsorbents, from a diverse set of data provided to more than 50 groups. The deviations among the reported results led to suggestions for more standardized approaches to data analysis for this widely used technique.

Performing inter-laboratory studies is time consuming and can only be accomplished for a tiny fraction of the adsorption properties that are of potential practical interest. An alternative means to assess data reproducibility stems from the observation that in active research areas it is not uncommon for replicate experiments to be reported even if the aim of these experiments was not directed towards data replication.^{23, 24} We recently explored this concept to assess reproducibility of gas mixture adsorption in porous materials using a large data set of these measurements collated from the open literature.²⁵ This large collection of mixture adsorption data has also enabled the systematic examination of the accuracy of Ideal Adsorbed Solution Theory, one widely used method for predicting mixture adsorption from single component isotherms.²⁶

The large collection of single component adsorption data available in the NIST database provides an excellent resource for identifying and analyzing replicate experimental studies. We have previously introduced statistical tools for this purpose in an analysis of CO₂ adsorption experiments²⁷ and further refined these methods to characterize alcohol isotherms in porous materials.²⁸ With this meta-analysis approach, independent measurements in the same adsorbent material for given experimental conditions are compared.²⁴ Despite the enormous number of

collected isotherms available in the NIST database the number of materials with replicate measurements is limited. A key observation from these earlier analyses is that they both showed that around 20% of all replicate isotherms were identified as outliers, meaning that they were significantly different from other isotherms reported for the same material. Meta-analysis of this kind cannot point to the precise source of disagreement between reported measurements, but it is useful in highlighting the existence of uncertainty that might create challenges in designing reliable separation processes.

Once a set of replicate isotherms has been found and any outliers have been removed, the resulting collection of data can be used to define a consensus isotherm. The resulting consensus isotherms we developed earlier for CO₂ and alcohol adsorption in porous materials still show significant variation, which can be attributed to a variety of sources^{23, 24, 27, 28}. The identification of independent experiments that can be used to define these consensus isotherms cannot directly identify the specific sources of variation among experiments, although tackling this challenge by carefully comparing details of materials synthesis, pretreatment and other details can yield useful insights for specific materials.

In this paper, we apply the tools of meta-analysis to all single-component isotherms for alkanes provided in the NIST/ARPA-E database. These molecules are relevant for applications such as natural gas purification²⁹, high-purity alkene production³⁰, or other industrial chemical syntheses³¹⁻³³. The consensus isotherms developed below and other information regarding the reproducibility of alkane adsorption isotherms will be useful for focusing the adsorption community's attention on these important species in the future.

Methods

The NIST/ARPA-E Database of Novel and Emerging Adsorbent Materials¹¹ was used to obtain single-component adsorption isotherms of alkanes in porous materials. As of the date of access (January 2021), the database was a collection of 35,934 isotherms from both experimental and computational approaches. For our analysis, only experimentally determined data were considered. Therefore, all original publications were screened to categorize the reported isotherms as experimental or computational, regardless of their labeling in the NIST database. All raw datasets were converted to units of kPa for pressure and mmol/g for the loadings for the analysis using properties provided in the original publication, such as adsorbent densities and molar masses. If the necessary properties for these unit conversions were not reported the dataset was excluded from our analysis. These isotherms are highlighted with an asterisk in Tables S2 to S16 in the Supporting Information.

The meta-analysis to assess the reproducibility of replicate measurements used a statistical method introduced by Park et al.²⁷ and refined in terms of an independence assessment of replicates in our analysis of alcohol adsorption.²⁸ A detailed description of the metrics and criteria can be found in these earlier publications. Isotherms for the same system within a specific temperature range are grouped together for the analysis. The width of the temperature range chosen for this grouping depends on the independence of the source publications for the isotherms, meaning that the temperature range considered to define equivalent experiments for isotherms from publications with the same corresponding author is narrower than for isotherms from different groups.²⁸

Each experimental data set was fitted to a continuous function fit using common isotherm models such as Langmuir, Freundlich, Langmuir-Freundlich, dual-site Langmuir, or the BET model. In cases where the experimental data included a sharp step (for example, due to a structural

transition in the adsorbent) a piecewise continuous fit was performed. The choice of the fitting model was determined based on a minimization of the sum of squared errors considering two criteria: (i) the model leads to a maximization of R^2 with $R^2 \geq 0.99$, and (ii) in cases where more than one model gave very similar R^2 values, the adjusted coefficient of determination R^2_{adj} was used, which leads to the selection of the model with fewer fitting parameters.

The resulting continuous curves were used to identify outliers, rate the consistency of the remaining isotherms and assess their reproducibility using the statistical methods developed by Park et al.²⁷ Additionally, the outliers were classified depending on whether they are from publications with the same (type 1) or different (type 2) corresponding authors than the remaining isotherms. The same approach is used to assess the replicate strength of the remaining data as in our earlier work.²⁸ Generally, the corresponding author of the original publication was used for independence assessment. However, there are duplicates of isotherms in the NIST database due to reproduction of previously reported data in a later publication were excluded from the analysis. These instances are tabulated in Table S19. If only reproduced data were included in the database, the original publication was used to determine the corresponding author even if this paper is not used in the NIST database. Two inter-laboratory studies^{18, 20} covering isotherms from independent groups in one publication were classified as providing data from different experimental groups even though the same corresponding author on the original publication is related to them in the database. Our screening process also revealed some isotherms that had an incorrect label in the NIST database, and thus were treated on a case-by-case basis. These instances are listed in Table S20.

Results and Discussion

The 35,934 isotherms obtained from the NIST database were labelled in that database as experimental (10,234 isotherms, 28.5% of the total), simulated (1828 isotherms, 5.1% of the total), modeled (843, 2.3%), quantum/DFT (118, 0.3%), and unlabeled (22,911, 63.8%). We identified 2998 isotherms (8.3% of the total) that reported experimental data for alkanes. The number of isotherms available for specific adsorbing molecules is summarized in Figure 1. A summary table for identification of the investigated adsorbates is provided in Table S1. Approximately two thirds of the alkane isotherms are for methane, and the number of methane isotherms is at least seven times larger than the next most common molecules (ethane, 9.5% of the alkane isotherms, and propane, 8.6% of the alkane isotherms). Empirically, the number of isotherms reported in this dataset for all alkane isomers of C_n , $N(n)$, is described with moderate accuracy by the power law $N(n)/N(1) = n^{-2.4}$ (see Figure S1).

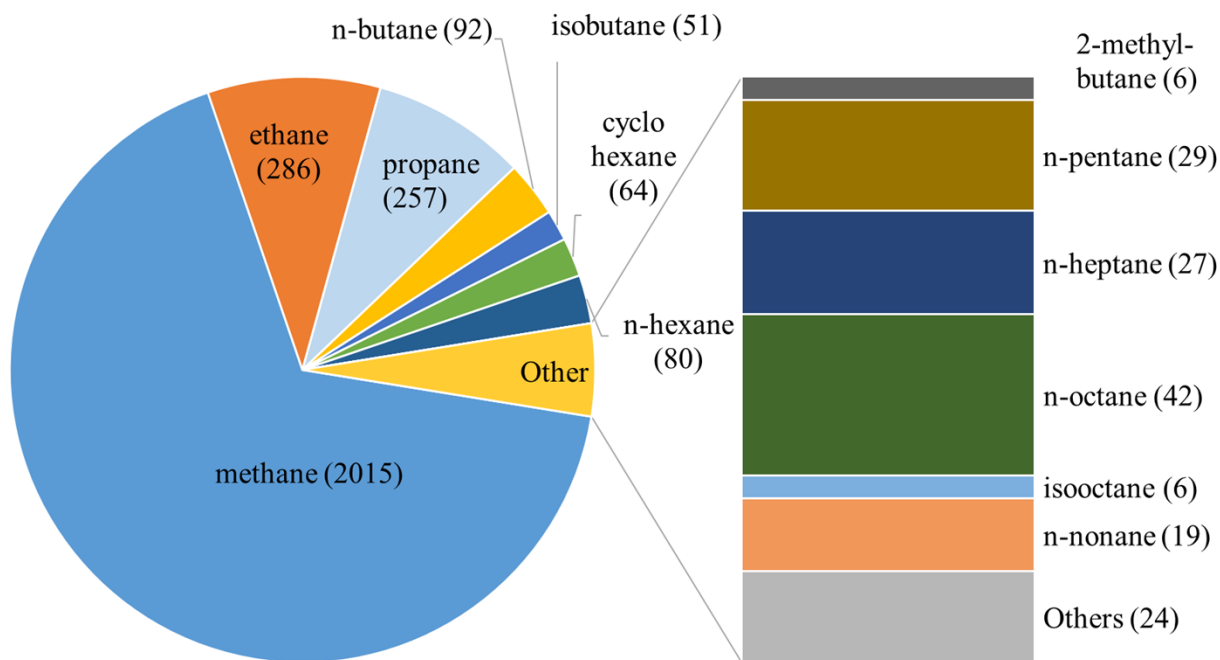


Figure 1. Distribution of the 2998 experimental alkane isotherms identified from the NIST/ARPA-E Adsorption Database. The number of experimental isotherms for each adsorbate are given in

parentheses. The isotherms combined as others in the bar chart on the right are comprised of n-decane (4), n-octadecane (4), 2,2-dimethylbutane (3), n-dodecane (3), neopentane (3), n-tetradecane (3), cyclopentane (2), 2,5-dimethylhexane (1) and 2-methylheptane (1).

Among the 2998 alkane isotherms, 846 replicates were identified and analyzed. The resulting consensus isotherms are shown in section S4. Tables of the isotherms that were not included in the analysis due to a lack of replicates, no pressure range overlap with other isotherms for the same system or insufficient information to convert units are given in the SI in Tables S2- S16. As discussed by Agrawal et al.²³ many adsorbent materials have only been synthesized and described once and in these cases no isotherm replicates are available.

Many materials are known under several different names, for example HKUST-1 as CuBTC or Basolite C300. These synonyms that are considered in the NIST database were used to group replicates together. Moreover, we grouped isotherms together that were not considered the same material in the NIST database but for which assessment of the papers showed that they are the same, such as UiO-66 and UiO-66(Zr). A comprehensive list of these instances is given in Table S17. Additionally, material classes such as coals were grouped together based on the assumption that they can be considered to be similar and are were not defined as synonyms in the NIST database only due to additional adjectives, such as brown or dry for coals. This is the same for activated carbons of which some are labeled as porous or domestic and are grouped together for the analysis. These groups are listed in Table S18.

Material composites that are labeled with the same name in the NIST database but have different compositions, and thus, different adsorption behaviors were not considered replicates. Examples of this kind include zeolites with different extra-framework cation concentrations.

For each set of replicate isotherms the number of replicates is denoted by N . The cases with $N > 2$ have a sufficient number of isotherms to detect outliers, which are then classified as type 1 or 2 outliers as described above. Cases with $N = 2$ do not allow for outlier detection and are only assessed in terms of reproducibility level and replicate strength.²⁷ The distribution of these isotherms for the different alkanes is shown in Figure 2. Overall, 15% of all isotherms in systems where outlier detection was possible (that is, with $N > 2$) were identified as outliers. This is comparable to the ~20% for of replicate isotherms for CO_2 ²⁷ and alcohols²⁸ that were classified as outliers using the same methods in earlier work. Combining all the replicate isotherms for alkanes, CO_2 and alcohols gives 1062 replicate isotherms, of which 16.5% are outliers. Among the alkane isotherms we identified no outliers for isobutane or n-heptane, but the total number of replicates for these two species was low. Among the 623 replicate methane isotherms we analyzed, 16% were outliers.

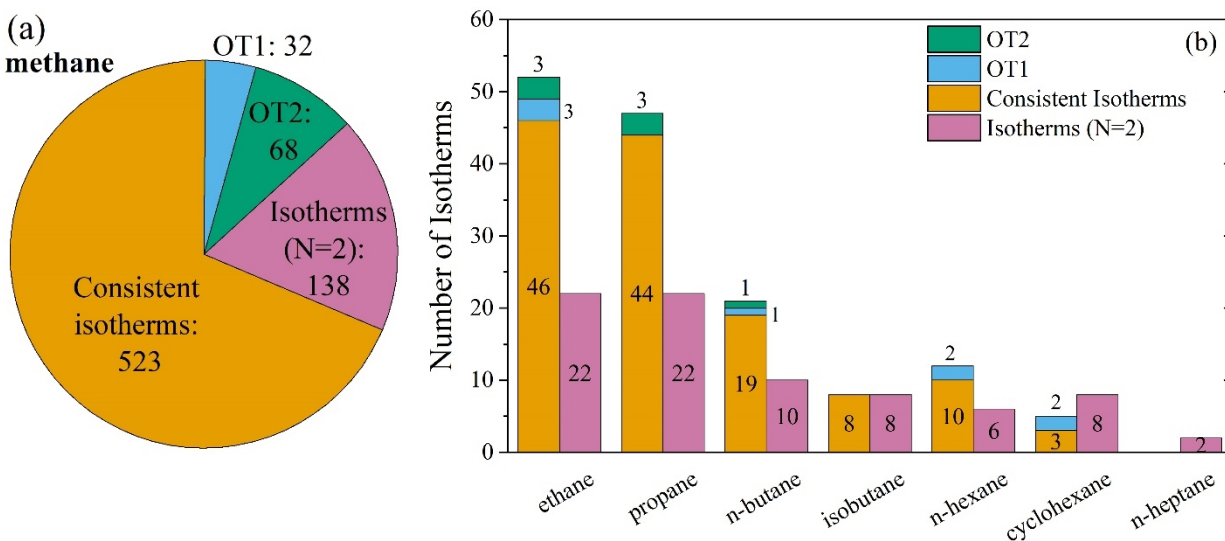


Figure 2. Distribution of the replicate isotherms for all systems with $N \geq 2$ (a) for methane and (b) for all other alkane molecules. Consistent isotherms include all remaining isotherms after outlier identification. Outliers are classified as either type 1 (OT1) or type 2 (OT2). Systems with $N = 2$

do not have a sufficient number of isotherms for an outlier assessment and are grouped separately for the analysis.

As in our earlier work, the reproducibility of isotherms for a particular adsorbate/adsorbent pair can be described in several complementary ways. The consistency rating describes the fraction of outliers based on the complete set of replicates and increases from low to high with a decreasing outlier fraction. The reproducibility level increases from R_4 up to R_1 as the number of replicate isotherms after outliers are discarded increases. The outlier level determines the statistical method based used to detect outliers, which depends on the total number of replicate isotherms. The replicate strength decreases from S_1 to S_3 depending on how independent the replicates are after discarding outliers in the sense of whether the data comes from publications with the same corresponding author or different groups. Further details on each of these descriptions is given in our earlier work.^{27, 28}

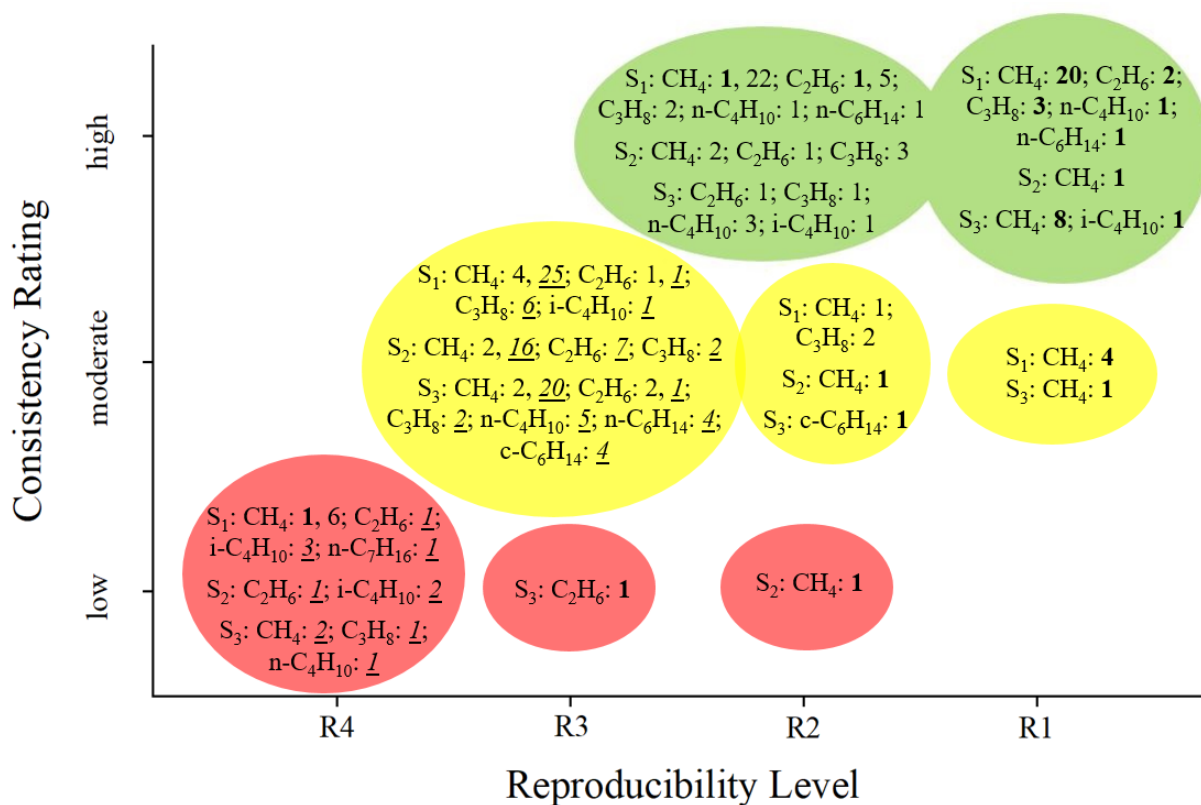


Figure 3. Reproducibility map as a summary of the classification of all systems analyzed in terms of reproducibility, consistency and replicate strength. The numbers describe the number of systems that were classified at the corresponding consistency and reproducibility level. Outlier level are distinguished by different fonts: O₁ – bold, O₂ – regular, and O₃ – italic underlines. The replicate strength decreases from S₁ (top) to S₃ (bottom) within the ovals.

The various reproducibility rankings for the replicate alkane isotherms we considered are summarized in Figure 3. All these specific systems are shown in detail in section S4 and the numerical values are tabulated in an Excel spreadsheet as Supporting Information. A total of 37 adsorbate/adsorbent pairs were classified with the highest consistency and reproducibility rating, of which 29 are for methane. Some consensus isotherms that fall in the R₁-moderate or R₂-high categories in Figure 3 would require only one more consistent isotherm to reach the highest rating.

We found 13 adsorbate/adsorbent pairs with this characteristic. A sizeable number of examples with $N=2$ were classified as R_3-S_3 since they are from a series of measurements from a single group varying the temperature within the considered range.

A general observation from Figure 3 is that short-chain alkanes like methane tend to have higher reproducibility ratings than more bulky molecules. This is due to availability of data that limits the possibility of reaching higher ratings for species such as n-heptane. This observation may be related in part to the increased experimental difficulties associated with measuring adsorption of long-chain alkanes relative to smaller molecules. We emphasize that this is an issue of data availability; we are not implying that measurements with large molecules are less reproducible than for smaller molecules in any fundamental sense.

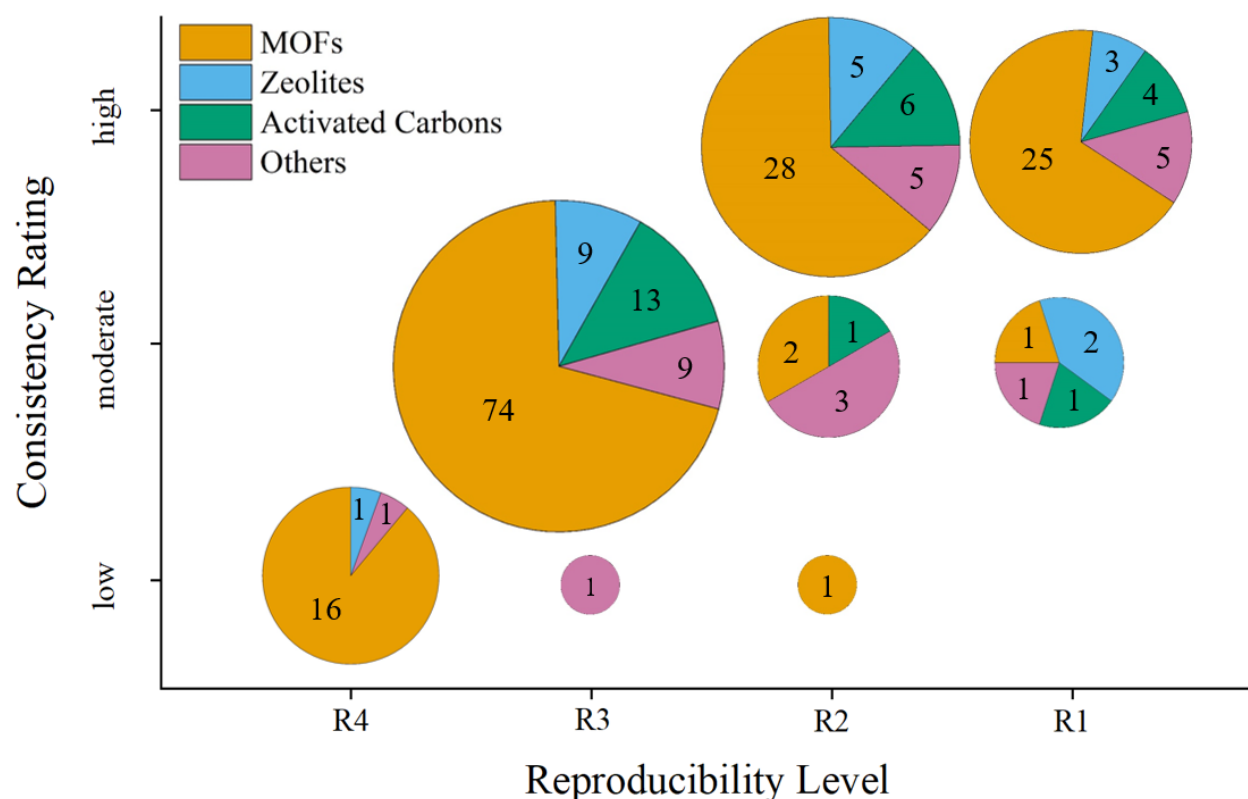


Figure 4. The same data as in Figure 3 represented by various classes of adsorbent materials. The numbers delineate the number of systems that were classified at the corresponding consistency and

reproducibility level. The size of the individual pie charts scales relatively to the number of systems within a given rating.

To examine which materials are commonly represented among the replicate isotherms we collected, the adsorbate/adsorbent pairs shown in Figure 3 were split into four material classes following the classification defined by Cai et al.²⁵ More than 67% of the systems with replicates are for adsorption in MOFs (147 distinct systems). This may seem surprising, since MOFs are the newest of the classes of materials in terms of when they became available.²⁵ A large number of the replicates for MOFs, however, fall in the R₃-moderate classification, which are often from a series of measurements from a single publication. The data for MOFs may reflect the increasing availability of commercial instruments for measuring single-component adsorption at a time when the research community also devoted considerable attention to MOFs. The situation for measurements of binary gas mixtures, which is almost always performed with purpose-built instruments, is quite different. Of the ~900 binary isotherms collected recently in the BISON-20 database, 42% were for zeolites and only 16% were for MOFs.²⁵

The results in Figure 4 are represented in terms of the number of distinct adsorbents for which replicates have been reported. If instead a similar description is made in terms of the number of replicate isotherms the distribution among the materials classes changes somewhat for the R₁ and R₂ rated systems as shown in Figure S2 (the R₃ and R₄ systems do not change because each example has exactly N = 2 isotherms). For example, the inter-laboratory study using a reference zeolite by Nguyen et al.²⁰ with N^{*}=82 changes the pie chart for R₁-moderate considerably towards zeolites. The wedge for ‘Others’ ranked as R₁-high increases from 13.5% to 28.2% when considering absolute numbers of isotherms due to the higher number of replicate isotherms for materials like coal or carbon.

One common research aim with nanoporous adsorbents is to seek materials that have a high capacity for molecules of interest. In work of this type, it is important to systematically compare new materials with previously established adsorption capacities. As an example, we compare the observed loading of methane at 1 bar for all R_1 reproducible systems around 298 K in Figure 5. These ranges were plotted after removing outliers from each collection of replicate isotherms. There are several different temperatures represented in Figure 5, but these temperatures are close enough that it is reasonable to directly compare this set of materials. Methane loadings at 1 bar vary from values below 1 mmol/g in coals up to more than 7 mmol/g in some highly porous metal-organic frameworks. In this data set, having a higher number of replicate isotherms for a particular adsorbent does not appear to be correlated with a reduced spread of results. There is a significant variation of total numbers included within the given systems ranging from only 3 for the MOF MIL-53(Al) up to 76 for Na-Zeolite Y. A wide range of loadings can be seen for many materials despite their R_1 -reproducibility classification, including a spread of 4.5 mmol/g for Ni-MOF-74. This situation arises when the experimental data includes a group of evenly distributed isotherms that do not allow ready identification of outliers (see section S4). This weakness of the statistical methods used in our work has been discussed previously.²⁸ Variations in synthesis procedures, sample handling, activation and storage conditions can lead to variation among measured loadings, especially for materials that are sensitive to external influences such as trace moisture, such as CuBTC.^{23, 27, 28} An example for the dependency on the activation temperature can be seen in Figure S3 (30) for UiO-66(Zr)-(COOH)₂ where significant deviations arise from varied activation conditions.³⁴ An apparent spread in adsorption capacities can also arise from imprecise labeling and grouping of materials, especially for material classes such as activated carbons.

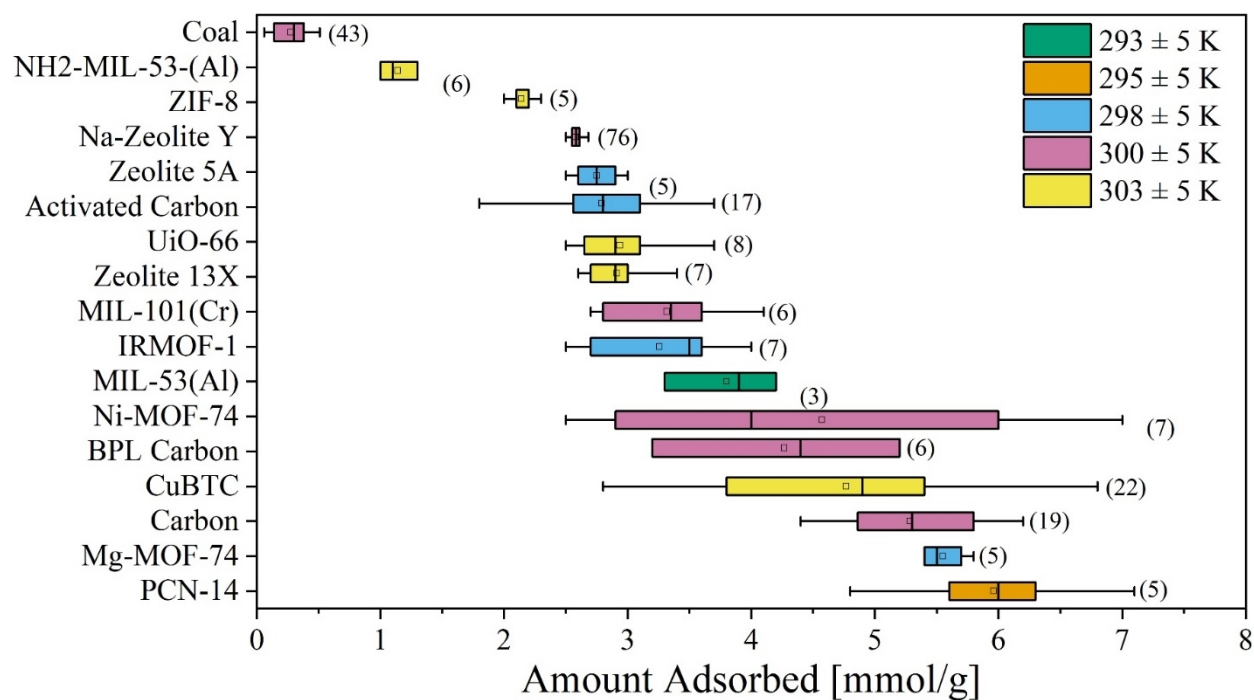


Figure 5. Overview of the observed ranges of methane loadings at 1 bar for all R_1 reproducible systems with a temperature range at overlaps with 298 K. The outer limits of the box show the 25-75% range. The additional line within the box indicate the median and the mean is given by a square (\square). The whiskers show the 1.5 interquartile range (IQR). The number of available isotherms at these conditions are given in parentheses. Since not all replicates report data up to 1 bar the number can be lower than what it is considered R_1 reproducible of at least $N'=5$.

A similar analysis is shown for all R_2 reproducible systems of methane around 275 K (top) and 298 K (bottom) in Figure 6. Methane loadings at the lower temperature vary from 1.8 to above 10 mmol/g in the four different materials. Significantly high spreads of more than 30% of the highest observed loading in UiO-66 were found. The broadest spread in UiO-66 comes from a system with S_1 replicate strength meaning that the remaining isotherms are from different groups. The narrow spread for NH₂-MIL-53(Al) comes from a system with S_2 replicate strength meaning that the N' isotherms come from different publication with the same corresponding author. The loadings of

methane at temperatures around 298 K vary from 0.7 up to 6.7 mmol/g. Although all systems, except for NU-125, have $N=3$ and have a reproducibility level of R_2 there is considerable variation in the loadings, even after outlier detection.

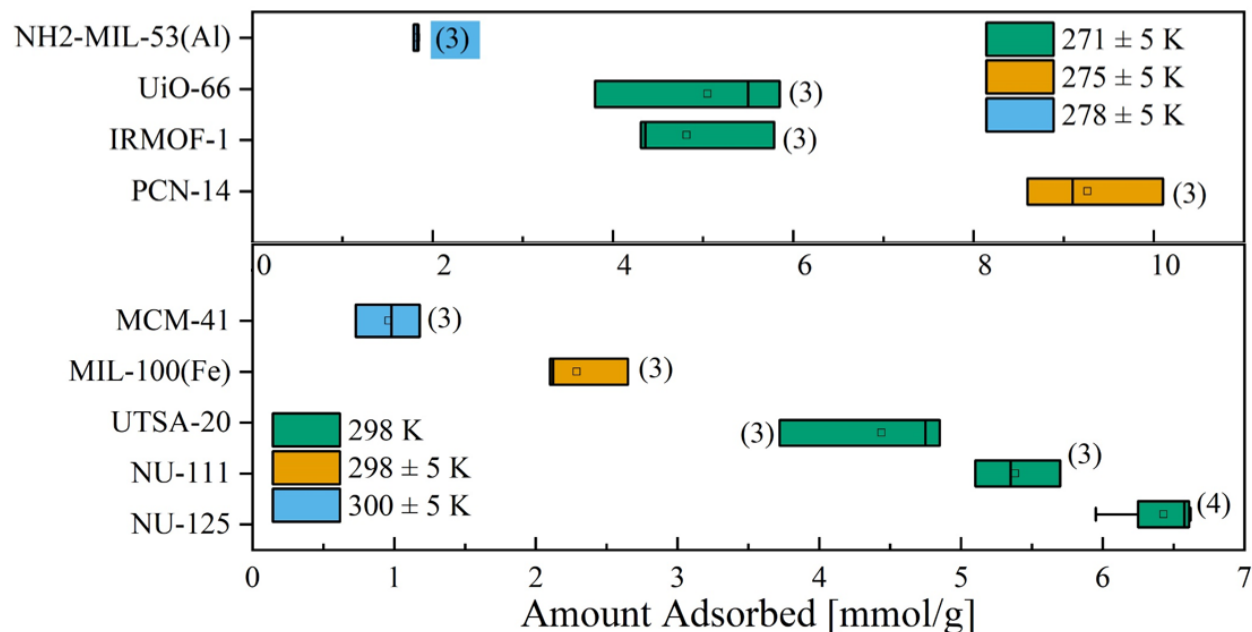


Figure 6. Overview of the observed ranges of methane loadings at 1 bar for all R_2 reproducible systems with a temperature range at overlaps with 275 K (top) and 298 K (bottom). The outer limits of the box show the 25-75% range. The additional line within the box indicate the median and the mean is given by a square (\square). The whisker for NU-125 shows the 1.5 interquartile range (IQR). The number of available isotherms at these conditions are given in parentheses.

The figures above focused on comparing a single adsorbing species, methane, in a range of adsorbents. Another use of our data is to compare a range molecules adsorbing in a single material. Figure 7 shows an example of this approach by plotting the pressure ranges derived from the consensus isotherms for six different alkanes in CuBTC at which a loading of 4.0 mmol/g has been reported. This loading was the highest value for which replicate data were available for all six alkanes. As expected the general trend in the figure is that pressure needed for a specific loading

decreases as the molecular weight of the adsorbate molecule increases due to the increase in heat of adsorption with increasing molecular size.³⁵ The consensus isotherms, however, show significant overlaps between the pressure ranges for some pairs of molecules, for example between propane and isobutane. The consensus isotherms do not provide strong evidence that the adsorption of n-heptane occurs at lower pressures than for n-hexane, or that propane adsorbs at lower pressures than ethane.

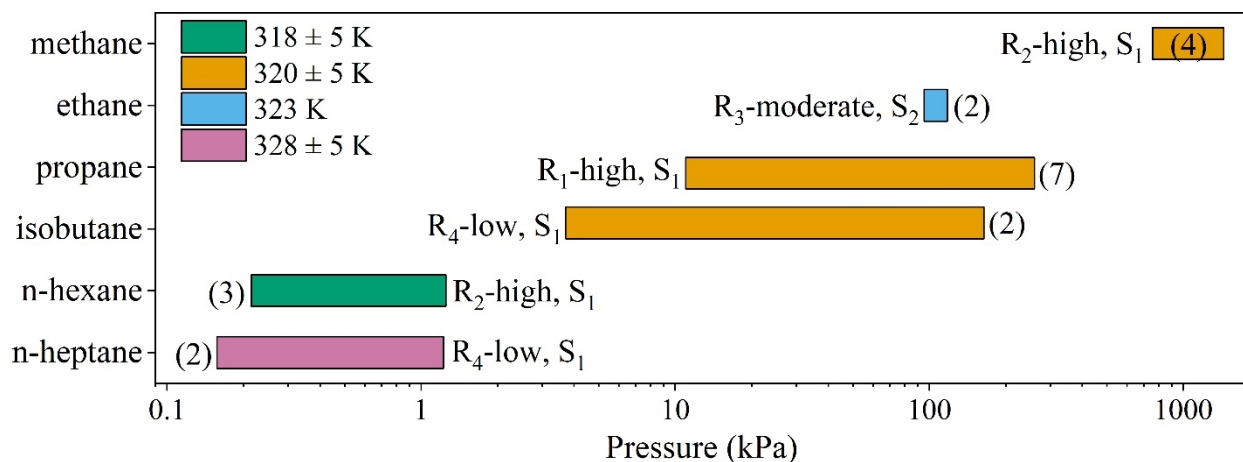


Figure 7. Pressure ranges derived from consensus isotherms for which a loading of 4.0 mmol/g of each alkane can be observed in the metal-organic framework CuBTC at temperature ranges that overlap with 323 K. The number of consistent isotherms N' is given in parentheses together with the reproducibility level R , the consistency rating and the replicate strength S .

Conclusion

We have applied systematic methods to assess the reproducibility of experimental measurements of alkane adsorption in nanoporous materials. Using data collected in the NIST database, we found 2998 experimental alkane isotherms, of which 846 were replicates. This is the largest number of replicate isotherms of any kind that has been identified to date. The number of extant

measurements decreases rapidly as the molecular weight of the adsorbing alkane is increased, so the number of available replicates for molecules larger than propane is small.

One use of a collection of replicate isotherms is to identify outliers, that is, experimental reports that are inconsistent with other replicates for the same molecule adsorbing in the same material at the same temperature. Our analysis of 846 replicate isotherms showed that 15% of the available alkane isotherms were outliers. Combining this information with previous reports for CO₂ and alcohol adsorption yields 1062 replicates, of which 16.5% are outliers. This kind of meta-analysis cannot point to the source of discrepancies between replicates, but it does suggest that appropriate caution should be used when using any individual experimental adsorption isotherm from the open literature. We recommend that future reports of adsorption isotherms include validation data obtained in the same laboratory for well-defined materials for which accurate consensus isotherms are available, since doing so can significantly reduce concerns about accuracy associated with instrument calibration and data analysis. Validation isotherms of this kind are available for CO₂¹⁹ and CH₄²⁰, and the consensus isotherms we have collected here could form an initial basis for similar comparisons for other molecules.

A second use of replicate isotherms is to develop well-defined consensus isotherms for molecules adsorbed in particular materials. The methods that are suitable for this task vary depending on the number of replicates that are available. We reported 93 graphical and numerical consensus isotherms for 8 different alkanes as well as assessment of another 124 systems where pairs of fitted isotherms result from two available replicates. These numbers are given in parentheses. Overall, these consensus isotherms include 62 (79) for methane, 10 (15) for ethane, 11 (11) for propane, and 10 (19) for C₃₊ alkanes. For some adsorbents, such as the metal-organic framework CuBTC, consensus isotherms for a range of molecules were developed.

As noted in the Introduction, the variations in replicate measurements for a particular adsorbent may have a variety of systematic origins. Differences in sample preparation, including but not limited to sample activation under vacuum or elevated temperature, may have a marked impact on measured adsorption properties, especially for materials that strongly adsorb water when exposed to ambient conditions. Similarly, adsorption in materials that are structurally sensitive to water or other contaminants may be affected by the history of the sample being used. Meta-analysis of the kind we have used in this paper cannot directly identify the origins of variations among reported measurements, although it does open the possibility that additional analysis of experiments that are nominally with identical materials could do so. One challenge in retrospective analysis of variations among replicates is that complete information on the pretreatment, storage history etc. for samples is often unavailable from published reports. Suggestions have been made on reporting protocols that address this issue in future experiments.³⁶

In addition to creating useful benchmarks for future experimental measurements of alkane adsorption in nanoporous adsorbents, the consensus isotherms we have gathered will also be useful for systematic efforts to test the precision of modeling methods based on molecular simulations or data-driven approaches. Highly reliable CO₂ isotherms in a reference zeolite have also been used to verify the precision of force field-based molecular simulations based on high level quantum chemistry results.²¹ Earlier work with consensus isotherms for CO₂ and alcohol adsorption examined the reliability of using generic force fields in MOFs that are assumed to be rigid to predict adsorption in these materials.^{27, 28} Recent work has suggested that in some circumstances internal flexibility in MOFs associated with local vibrations can have a strong influence on adsorption, especially in the dilute limit.^{37, 38} The availability of the consensus isotherms we have collected here will allow for a more thorough investigation of the influence of adsorbent flexibility

and the force fields used to define adsorbate/adsorbent interactions via comparison with validated experimental data.

ASSOCIATED CONTENT

Alkane Adsorption Isotherms in the NIST Database (S1), Synonyms and Grouping of Adsorbents (S2), Special Cases in the NIST Database (S3), Reproducibility Results (S4) (PDF)
Numerical Consensus Isotherms (XLSX)

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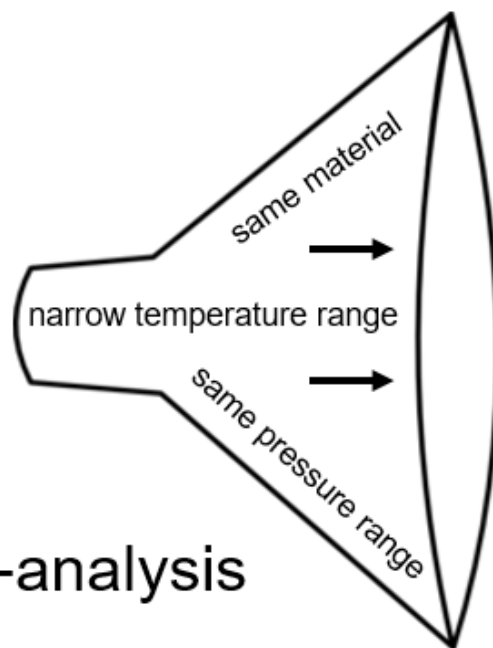
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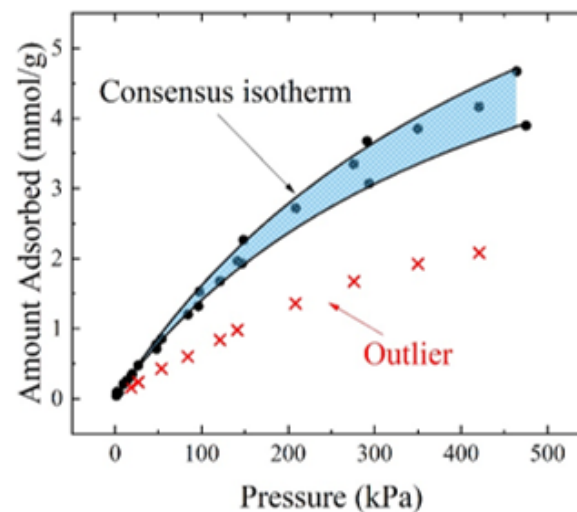
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