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Assessment of the density of (meso)porous materials from standard volumetric physisorption data

Christian Weinberger, Simon Vetter, Michael Tiemann, Thorsten Wagner*

Universität Paderborn, Naturwissenschaftliche Fakultät, Department Chemie, Warburger Straße 100, D-33098, Paderborn, Germany

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ABSTRACT

Characterization and application of (meso)porous materials often require information about the density of the respective samples. For example, the BET surface area is, by definition, normalized to the sample mass; hence, any comparison between samples of different composition needs to take into account their respective densities. Literature data on the densities of porous materials are scarce. Frequently, only bulk-phase densities are available which sometimes differ from those of porous samples, especially for amorphous systems, such as silica or carbon. The apparent density, *i.e.* the density of the sample excluding the gas-accessible pore volume, is typically determined by helium gas pycnometry utilizing specialized pycnometers. We demonstrate how to obtain the same data from standard N_2 physisorption measurements as part of the regular measurement routine. We evaluate the method by reference measurements utilizing a non-porous reference sample (glass rod) to confirm the validity of the method. Then we present results on apparent density measurements of several mesoporous silica materials (MCM-41, MCM-48, SBA-15, KIT-6), mesoporous carbon (CMK-3, -5, -8, -9), and a variety of mesoporous metal oxides obtained by nanocasting.

1. Introduction

Porous materials possess unique properties, such as large specific surface areas, narrow pore size distributions, and large pore volumes [1,2]. These properties make them interesting for adsorption [3,4], catalysis [5–8], application as ferroic materials [9,10], gas sensing [11–17] or as electrodes for energy-related application [18–23], to name just a few. Besides parameters like the BET surface area, for many applications the apparent density of the material is needed, *e.g.* to estimate the performance of structured electrodes [18,19,24–29], to determine the loading with a catalyst [6,27,30–35] or simply to estimate the pore accessibility [36–40]. Literature data on the densities of porous materials are scarce. Frequently, only bulk-phase densities are available which may differ from those of porous samples, especially for amorphous systems such as silica or carbon, as will be shown later. The apparent density can be determined by helium gas pycnometry [41], which, however, requires specialized equipment. Therefore only few data based on this method are found in the literature [42]. Other methods are based on more elaborate techniques, such as synchrotron X-ray diffraction [43] which, in addition to the apparent density, also allows for the assessment of density fluctuations within the material. Unfortunately, such analysis is expensive and time consuming. Alternatively, X-ray data recorded on laboratory diffractometers can be used to calculate the difference of the apparent density in wet and dry silica [44]. Other methods, like positron annihilation, are even more complex [45–48] and therefore typically not used for everyday characterization.

We demonstrate that a standard N_2 physisorption measurement generates all data needed for calculating the apparent density without any additional measurement effort: physisorption measurements typically include helium back-filling of the sample cell for assessment of the void cell volume. This can be utilized to determine the sample volume by subtracting it from the empty cell volume. Since the sample mass is known, calculation of the apparent density is then possible. We verify this approach for various mesoporous samples based on SiO_2, carbon, and several metal oxides. These materials are typically characterized by N_2 physisorption analysis to investigate the specific surface area, pore size distribution, and specific pore volume. Nevertheless, if the density is discussed, literature sources usually refer to bulk rather than porous materials [49–54]. Our fast and easy-to-perform

* Corresponding author.
E-mail address: thorsten.wagner@upb.de (T. Wagner).

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method makes it possible to determine the apparent density of porous materials with standard physisorption equipment as is commonly used in academic and industrial laboratories.

2. Experimental

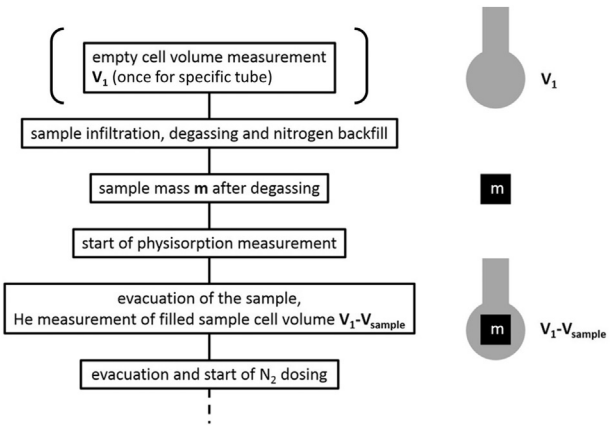
Physisorption measurements will be described in the Results and Discussion section. Further characterization of the samples was performed by powder X-ray diffraction (with a Bruker AXS D8 Advance diffractometer, using Cu Kα radiation at 40 kV and 40 mA with a step size of $2\theta = 0.0075°$ and a counting time of 3 s per step for measurements below 10° and 0.02° between 20° and 80°) and by energy dispersive X-ray spectroscopy (using a EDAX PV 990 in a HREM EDX Leo Gemini). Crystallite size was calculated by the Scherrer equation assuming a shape factor of 0.94 [55]. The full width at half maximum was determined by a Lorentzian fit.

The synthesis procedures for the presented materials are described in the literature, as cited in the text.

3. Results and discussion

3.1. General procedure

To determine the apparent density of a (porous) sample an empty sample cell was attached to a volumetric physisorption apparatus. Prior to recording any typical N_2 isotherm the measuring routine evacuates the sample cell and refills it with helium gas up to a certain pressure to determine the volume V_1 of the (empty) cell as depicted in Scheme 1. The determination of the volume of the empty sample cell is necessary once as calibration step while all following volume measurements refer to this value for the specific sample tube. Before the actual measurement the cell, now filled with the sample material, is degassed at elevated temperature (to remove adsorbates) and the void cell volume $V_1 - V_{sample}$ (V_{sample} sample volume) is determined. Even though this volume data is only used for internal calculations of the measurement apparatus, it is usually available to the user. Depending on the software used to operate the respective apparatus, the value is either displayed at the user interface (as, *e.g.*, in the recent Micromeritics software 3Flex Version 3.01) or may have to be extracted from the respective measurement log file (as, *e.g.*, in case of current Quantachrome equipment ASWin 2.01). Subtracting the void volume of the filled sample cell from the void cell volume results in the sample volume



Scheme 1. Process flow of a typical N_2 physisorption measurement. For assessing the apparent density the volume of the sample is determined from the difference between the volume of the empty sample cell (V_1; from helium back-filling) and the void volume of the cell containing the sample ($V_1 - V_{sample}$).

V_{sample}. Dividing the sample mass m by the sample volume V_{sample} yields the apparent density of the sample. However, pores which are not gas-accessible are unquantifiable, just as in standard pycnometric measurements.

The following results were obtained from a Quantachrome Autosorb 6 physisorption instrument equipped with 9 mm samples cells. The utilization of filler rods was not necessary. If filler rods are utilized it is necessary to also include them during determination of the empty cell volume (V1). The data were extracted from the instrument log files as described in the supporting information section. Samples were degassed at 120 °C for 24 h prior to N_2 physisorption measurement. BET surface areas were derived from a linear plot in the region $0.1 \leq p/p_0 \leq 0.3$ [56]. Total pore volumes were calculated from the second to last adsorption point at approximate $p/p_0 = 0.99$. Pore size distribution was analysed by the BJH procedure from the desorption branch [57]. In this work, sample amounts larger than usually required for standard N_2 physisorption measurements were used for higher accuracy; the measurement was aborted after initialization, *i.e.* after determination of the void volume. The volume measurements were repeated 5 to 8 times for each sample. The values shown in the table are arithmetic averages of the results. The error was calculated as the sum of weighing error (±0.5 mg) and the volume determination error (largest variation from average value).

3.2. Apparent densities of selected nanoporous materials

Table 1 shows the apparent densities (and some other characteristics obtained from N_2 physisorption) of several mesoporous as well as non-porous materials.

Silica (SiO_2)

Some of the most common ordered mesoporous silica materials, MCM-41 [59], MCM-48 [59], SBA-15 [71], and KIT-6 [61], were characterized. Non-ordered mesoporous silica monoliths [62] were also investigated in order to determine the influence of the granular character of the other silica materials. The samples MCM-41, MCM-48, and SBA-15 cover a wide range of specific surface areas from ca. 500 $m^2\,g^{-1}$ to 1400 $m^2\,g^{-1}$. However, the apparent density for these phases only varies between 2.37 g mL^{-1} and 2.34 g mL^{-1}. Only KIT-6 exhibits a significantly higher apparent density of 2.61 g mL^{-1}. Since the synthesis protocols for these materials as well as other structural parameters are similar (*e.g.* same calcination temperature), there is no straightforward explanation for this deviation. One possibility is a better pore accessibility in the (relatively large) cubic pore network of KIT-6 silica, potentially resulting in lower amounts of non-accessible pores which, by definition, increase the apparent density. The porous silica monolith exhibits an intermediate apparent density of 2.42 g mL^{-1}. Further characterization of these samples in future work, *e.g.* by positron annihilation [45–48], may provide insight into the question of blocked pore volume. Fused silica shows an apparent density of about 2.21 g mL^{-1} [63], which is a bit lower than for the investigated samples in this study. All in all the results show that density data for porous silica materials should always be determined experimentally, rather than assuming literature values of non-porous samples. Obviously, differences in the respective synthesis protocols seem to lead to different apparent densities.

Carbon

Ordered mesoporous carbon materials gained increasing interest in recent years, for example in the field of battery research for the development of new electrode materials. In this context the density plays an important role. A number of ordered mesoporous carbon materials were synthesized by using various porogenic structure matrices [2,72]. We investigated the density of CMK-3 [64] and CMK-5 [73] (from SBA-15 silica with hexagonal