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# High-Resolution $N_2$ Adsorption Isotherms at 77.4 K: Critical Effect of the He Used During Calibration

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Accurate characterization of the microporous structure in porous solids is of paramount importance for several applications such as energy and gas storage, ~~nano confine ment~~nanoconfinement reactions, and so on. Among the different techniques for precise textural characterization, high-precision gas adsorption measurement of probe molecules at cryogenic temperatures ~~(e.g.~~(e.g., $N_2$ at 77.4 K and Ar at 87.3 K) is the most widely used, after appropriate calibration of the sample holder with a probe ~~gas~~gas, which does not experience physisorption processes. Although traditionally helium has been considered not to be adsorbed in porous solids at cryogenic temperatures, here we show that even at 77.4 K (high above its boiling temperature, 4 K) the use of He in the calibration step can give rise to erroneous interpretations when narrow micropores/constrictions are present.
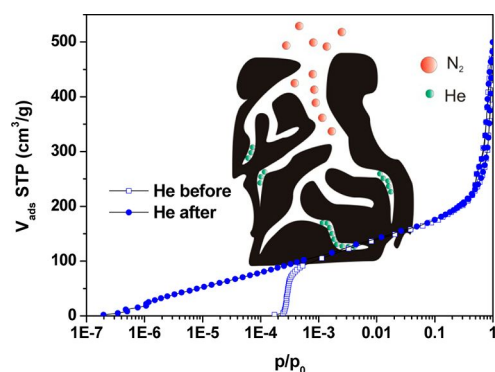
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Web-Only TOC Graphic

# Introduction

One of the critical steps in materials science is the correct characterization of the porous structure of newly developed porous solids; this information provides an understanding of the subsequent behavior of the material in any given application. Traditionally, the characterization of the porous structure is performed using adsorption of probe molecules, mainly $N_2$ at 77.4 K. Nitrogen adsorption up to atmospheric pressure (relative pressure $p/p_0 \sim 1.0$) is used to calculate surface area but can also provide information about the micro- and mesoporous structure of the synthesized sample.[1] In general, the filling of the narrow micropores takes place at low relative pressure ($p/p_0 < 0.1$), whereas higher relative pressures are required (between 0.1 and 1.0) for mesopore and macropore filling. Besides $N_2$ adsorption at 77.4 K, other probe molecules have been proposed in the literature for the characterization of the porous structure such as $CO_2$ adsorption at 273 K and Ar adsorption at 87.3 K, with these two molecules being more sensitive to the presence of narrow micropores/constrictions.[2−5] In any case, the determination of excess gas adsorption isotherms using manometric devices relies on the knowledge of calibrated volumes, either for the crucible and/or the sample holder containing the sample. The determination of the dead space or volume requires the measurement of the dividing surface formulated by Gibbs many years ago to define the adsorption phenomena on solid surfaces.[6] The determination of the Gibbs surface excess usually involves a calibration step using helium at the temperature of the adsorption experiment (77.4 K, in the case of nitrogen). The use of He is the first standard step in the measurement procedure when using any automated equipment and its use is based in the assumption that (i) He will not adsorb in the pore walls of the investigated porous solid, (ii) its density would be homogeneous within the pores, and (iii) He will not penetrate into regions which are inaccessible to the adsorptive. The use of He for calibration of the adsorption volume and determination of the true density of the porous solid dates back to Washburn.[7] However, recent studies have shown that this assumption, i.e., the nonadsorption of He under certain experimental conditions, is not realistic for porous solids. The non-negligible adsorption of He gives rise to uncertainties in the adsorption measurement, i.e., an overestimation of the dead volume and, consequently, an underestimation of the measured $N_2$ excess adsorption isotherms.[8,9] The definition of a reference state, which does not require any probe molecule, has been recently proposed by Gumma and co-workers as a solution to overcome these drawbacks.[10]

Besides the aforementioned problems associated with estimation of the Gibbs dividing surface, here we show experimentally that the use of He during the calibration step, when performed before the adsorption measurement, can give rise to additional problems mainly associated with the irreversible adsorption of He in extremely narrow micropores, this effect being mainly visible when performing high-resolution $N_2$ adsorption isotherms. Although this problem has been already recognized in the literature by others, the main goal of our manuscript is to illustrate the drawbacks associated with this helium entrapment when using different porous solids (activated carbons and ordered mesoporous silicas).[11−12] Although these problems may not affect the textural parameters estimated using conventional equations (e.g., BET surface area, Dubinin−Radushkevich micropore volume, and so on), here we show that it may drastically affect the characterization of the narrow microporosity, i.e., (i) the shape of the adsorption isotherm at low relative pressures, (ii) the pore size distribution, and (iii) the determination of any high energy sites.

# Experimental Section

$N_2$ sorption measurements at 77.4 K were performed in a homemade fully automated equipment designed and constructed by the Advanced Materials group (LMA), now commercialized as $N_2$Gsorb-6 (Gas to Materials Technology; www.g2mtech.com). The software of the automated equipment was programmed to perform the He calibration either before or after the nitrogen adsorption measurement. In a normal experiment, sample is degassed under vacuum ($10^{-8}$ MPa) at 523 K for 4 h (in the case of activated carbons) and 473 K for 12 h (in the case of the ordered mesoporous silica). After degassing, He is introduced into the system at room temperature, and the sample holder is cooled down to 77.4 K for dead volume determination. After calibration with He, the sample cell is evacuated at 77.4 K before running the nitrogen adsorption isotherm at the same temperature. When He calibration is programmed after, $N_2$ is first introduced into the adsorption equipment at 77.4 K just after degassing the sample. Once the adsorption isotherm is finished, a sample holder is evacuated at room temperature, and He calibration is performed as described before at 77.4 K. Textural parameters (BET "apparent" surface are and micropore volume, $V_{micro}$) were estimated from the nitrogen adsorption data after application of the BET and the Dubinin−Radushkevich equations, respectively. The volume of mesopores ($V_{meso}$) was estimated by subtracting the micropore volume ($V_{micro}$) from the total pore volume ($V_t$) measured at $p/p_0 \sim 0.95$.

Energetic adsorption data were obtained by direct calorimetric measurements obtained simultaneously during the adsorption process.[13] The calorimeter used at 77.4 K consists of two thermopiles of around 800 thermocouples each, mounted in electrical opposition. This system is immersed in a liquid nitrogen cryostat. Around 400 mg of sample was placed in a sample cell, which after outgassing to 423 K, is attached to a simple manometric device coupled to the calorimeter. A continuous procedure of nitrogen introduction is employed which is slow enough (approximately 2 $cm^3$/h) to be close to equilibrium. Once the equilibrium conditions are verified, this procedure leads to a high resolution in both the isotherm and differential enthalpies of adsorption.

## ~~RESULTS AND DISCUSSION~~ Results and Discussion

Figure 1 shows the nitrogen adsorption/desorption isotherms at 77.4 K for a conventional activated carbon (LMA233) prepared from olive stones using $CO_2$ as activating agent. Nitrogen adsorption isotherms have been performed either before the calibration with He or after the calibration step, as described in the ~~experimental section~~ Experimental Section.

**Figure 1.** High-resolution $N_2$ adsorption isotherms at 77.4 K on activated carbon LMA233 in (a) linear and (b) logarithmic scale performed with He calibration before and after the adsorption process. (c) Pore size distribution obtained after application of the QSDFT method (assuming slit-shape pores) is included.
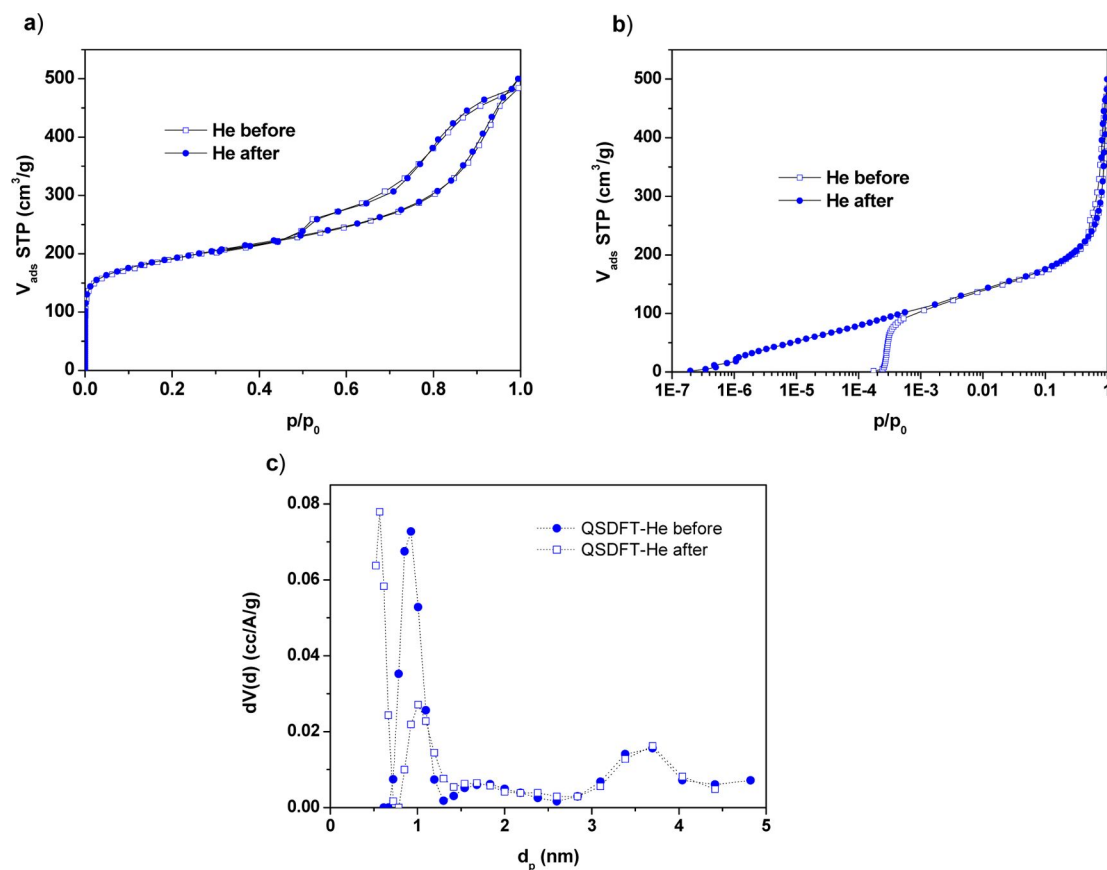


As it can observed, both nitrogen isotherms performed either before or after the He calibration are perfectly coincident over the whole relative pressure when plotted in linear scale, thus confirming that the calibration with He has no effect on the adsorption isotherms above a certain relative pressure ~~(p/p~~ ($p/p_0$ ∼ 0.01). Furthermore, the textural parameters estimated using the appropriate equations (see Table 1) also seem unaffected by the procedure used, ~~i.e.~~ i.e., He before or after. However, a closer look to the nitrogen adsorption isotherms at low relative pressure (see Figure 1b in logarithmic scale) shows that there are clear differences among these isotherms below ~~p/p~~ $p/p_0$ ∼ 0.01. Indeed,

when He calibration is performed after the nitrogen adsorption measurement, i.e., $N_2$ probes a degassed surface, narrow micropore filling occurs already at very low relative pressures ($p/p_0 \sim 10^{-7}$), whereas when the same isotherm is performed after He calibration, the amount adsorbed at low relative pressures ($p/p_0 \sim 10^{-7}$–$10^{-4}$) is mainly nil. This observation clearly shows that at cryogenic temperatures (77.4 K) the vacuum treatment performed before the nitrogen adsorption measurement is not enough to remove all helium used during the calibration step. The narrow micropores apparently remain blocked by some residual He, this effect being noticeable only when performing high-resolution nitrogen adsorption isotherms. The consequence of this pore blocking can be clearly appreciated in the pore size distribution of sample LMA233 after application of the quenched-solid density functional theory (QSDFT) model (see Figure 1c).[14] In the case of the nitrogen isotherm performed after the calibration, no information below 0.7 nm can be obtained whereas more detailed information about the narrow microporosity (<0.7 nm) is obtained when helium calibration is performed after. Consequently, high-precision pressure transducers incorporated nowadays in automated adsorption equipments show that even at 77.4 K (high above its boiling temperature; 4 K) He is adsorbed in narrow micropores, thus given rise to artifacts in the subsequent nitrogen isotherm. This finding is of paramount importance for the appropriate design and understanding of porous solids in specific applications where narrow constrictions play a crucial role, e.g., energy and gas storage, nanoconfinement reactions, and so on.

**Table 1.** Textural Parameters Estimated from the $N_2$ Adsorption Isotherms at 77.4 K

| sample | | $S_{BET}$ (m²/g) | $V_{micro}$ (cm³/g) | $V_{meso}$ (cm³/g) | $V_t$ (cm³/g) |
|---|---|---|---|---|---|
| LMA233 | before | 685 | 0.27 | 0.48 | 0.75 |
| | after | 690 | 0.27 | 0.50 | 0.77 |
| DD52 | before | 1370 | 0.55 | 0.05 | 0.60 |
| | after | 1375 | 0.54 | 0.06 | 0.60 |
| SBA-15 | before | 530 | 0.20 | 0.40 | 0.60 |
| | after | 535 | 0.21 | 0.39 | 0.60 |

In order to ascertain this effect, other activated carbons with different porous structure have been analyzed under similar experimental conditions. As an example, Figure 2 shows the nitrogen adsorption isotherms for a pure microporous activated carbon (DD52) prepared from olive stones and using $CO_2$ as the activating agent.[5] Once again, the nitrogen isotherms in linear scale shows no difference, and the same observation accounts for the textural parameters (Table 1). However, important differences can be observed concerning the filling of the very narrow micropores, i.e., the low pressure range. In the absence of He, micropore filling starts already at $10^{-6}$ relative pressure, the amount adsorbed increasing faster compared to sample LMA233, as corresponds to a purely microporous sample, i.e., narrow micropores exhibit an improved adsorption potential favoring large pore filling at low relative pressures. Incorporation of the calibration step before the nitrogen adsorption isotherm gives rise to an important blocking of the narrow micropores, pore filling starting at $p/p_0 \sim 10^{-4}$, in accordance with sample LMA233.

**Figure 2.** High-resolution $N_2$ adsorption isotherms at 77.4 K on activated carbon DD52 in (a) linear and (b) logarithmic scale performed with He calibration before and after the adsorption process.
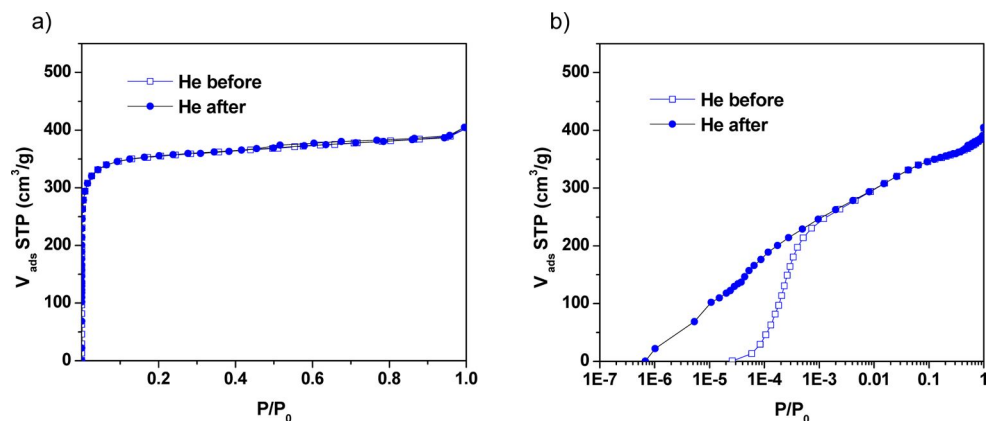
Besides carbon materials, He is used as a probe molecule for the calibration of dead space for all porous solids ~~(e.g.~~(e.g., zeolites, MOFs, ordered mesoporous silicas, and so on). To check the detrimental effect of He in the characterization of any porous solid containing narrow micropores, Figure 3 shows the adsorption behavior of an ordered mesoporous silica such as SBA-15, which contains well-defined hexagonal ordered mesoporous channels interconnected by narrow micropores (around 0.56 nm).[15] The linear plot (see Figure 3a) shows that both nitrogen isotherms fit perfectly over the whole relative pressure range, ~~i.e.~~i.e., the filling of the micropores and the capillary condensation in the mesopores is not apparently affected by the calibration step with He. The same accounts for the textural properties estimated from the nitrogen adsorption data (see Table 1).

**Figure 3.** High-resolution $N_2$ adsorption isotherms at 77.4 K on ordered mesoporous silica SBA-15 in (a) linear and (b) logarithmic scale performed with He calibration before and after the adsorption process.
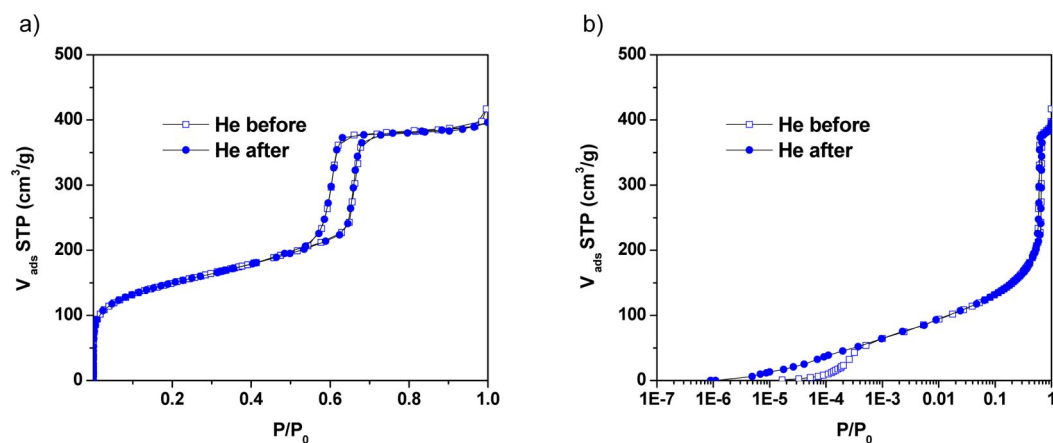


As expected, the situation changes when performing high-resolution nitrogen isotherms. Even for a mesoporous silica-based material, at relative pressures below ~~p/p~~$p/p_0$ ~ $10^{-3}$ ~~$10^{-4}$~~, the filling of the micropores is inhibited when performing He calibration before the isotherm. Interestingly, He effect is less detrimental in the case of SBA-15 when compared to above activated carbons due to the lower proportion of micropores in SBA-15 sample.

A final proof of the blocking of the narrow microporosity by helium was achieved by nitrogen adsorption calorimetry measurements using sample LMA233 before and after calibration with helium. The results are shown in Figure 4 as differential enthalpy obtained with nitrogen as a function of relative coverage ~~(n~~($n^a/n$~~$n^a_m$~~). It can be seen that both curves have similar shapes with an initial gradual decrease in energy, followed by a short plateau region before a final decrease ~~towards~~toward the enthalpy of liquefaction.

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**Figure 4.** Differential enthalpy of $N_2$ at 77.4 K on sample LMA233, either before or after He calibration, as a function of relative coverage.
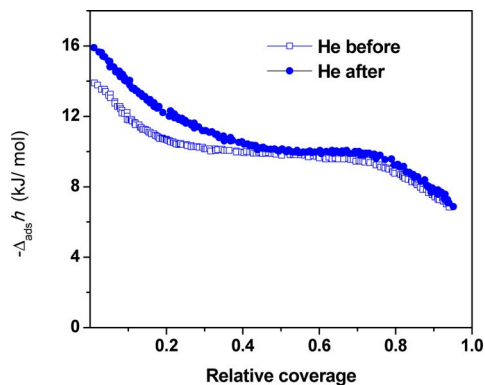


The initial decrease would seem to suggest heterogeneities ~~which~~that can be due to a distribution of micropore sizes. The plateau in the energy may be due to interactions with the surface of the larger "secondary" micropores and the final decrease suggests the end of micropore filling.[16] The main difference between these two curves is the initial values of the energy (16 kJ/mol ~~vs.~~vs 14 kJ/mol). Indeed, when nitrogen is used as a probe after the sample has been in the presence of helium, a loss of around 2 kJ/mol is observed. This observation suggests the loss of the most energetic sites after helium exposure, which is consistent with the blocking of the smallest micropores described above, thus confirming the high-resolution isotherms.

## ~~CONCLUSIONS~~Conclusions

In conclusion, although helium is recommended for the determination of the dead volume of the sample in the adsorption equipment when using the adsorption of nitrogen at 77.4 K, this determination should be carried out once the adsorption isotherm has been obtained, at least when the sample may contain micropores. If helium calibration is performed before, some helium will remain adsorbed on narrow micropores at cryogenic temperatures, thus blocking the microporosity. Although this effect was unappreciable on conventional manometric equipments, it must be considered in the newly developed automated equipments due to the incorporation of high-sensitivity pressure transducers. This blocking effect will affect very negatively the characterization of the narrow microporosity of the sample, although the effect on the determination of other textural parameters of the sample will be negligible. This finding is of special relevance in the design and understanding of organic, inorganic and/or hybrid porous solids where narrow micropores play a crucial role, ~~i.e.~~i.e., energy and gas storage, ~~nano confinement~~nanoconfinement reactions, and so on. Last but not least, it must be highlight that the use of helium after the nitrogen isotherm would help in the characterization of the textural and energetic properties (absence of blocking effects by He trapped in narrow micropores), although it will not avoid the traditional uncertainties associated with the determination of the Gibbs dividing surface due to the non-negligible adsorption of helium. Interestingly, these changes in the performance of the adsorption isotherm (dead volume determination after the nitrogen isotherm) to avoid uncertainties, together with the application of other methods for dead volume determination avoiding the use of helium (e.g., Quantachrome's NOVA approach) have been already implemented in some commercial adsorption equipments. However, care must be taken by the user to check that they are available and/or applied when observing unusual deviations in the adsorption isotherm at low relative pressures.

Conflict of Interest The authors declare no competing financial interest.

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