Introducing a self-consistent test and the corresponding modification in the Barrett, Joyner and Halenda method for pore-size determination

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ABSTRACT

A standard method to obtain the mesopore size distribution of adsorbents is the Barrett, Joyner and Halenda (BJH) analysis of the N_2 adsorption–desorption isotherm at 77 K. The availability, over the last two decades, of well-defined model adsorbents in the mesopore range, together with other forms of isotherm analysis with the help of the Density Functional Theory (DFT) has shown that the BJH method tended to underestimate the pore-width when they are smaller than 10 nm. Regarding this fact, we have reported an improved BJH method, where we have remarked that the reconstruction of the adsorption–desorption isotherm from the BJH results leads to some inconsistency. We therefore proposed a simple means to cancel the mentioned discrepancy and inconsistency. This correction can be made by simply adding a corrective term to the standard BJH equation, which value is selected to meet a self-consistent criterion, i.e. the reconstructed isotherm should fit the original one. In the first article, the method was applied for some ordered mesoporous materials (OMM) synthesized in our laboratory, showing only the results without major details. In this work, we validate the test for other samples, in other pore size ranges, introducing some remarks in theoretical aspects and in the importance of obtaining and taking into account the micropore volume. Finally, a detailed procedure to apply the proposal method using only the experimental data of the analysis is presented.

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1. Introduction

Among the most important textural characteristics of porous materials is their Pore Size Distribution (PSD), which defines the pore volumes for each pore size. The most used methods to obtain the PSD of nanoporous materials are based on the N_2 adsorption–desorption experimental isotherm data at 77 K, where important researches have been carried out in order to apply different theories. The used methods to evaluate the PSD can be divided into two groups, those that uses molecular theories (microscopic methods) [1,2] and those based on the theory of the capillary condensation (macroscopic methods) [3,4].

The most used microscopic method is based on the Non-Local Density Functional Theory (NLDFT) [5–7], which describes the configuration of the adsorbed phase at molecular level. By using the NLDFT method a reliable PSD can be obtained if the kernel (simulated isotherms of different pore sizes with specific geometry corresponding to a determined interaction adsorbate–adsorbent) is adequately chosen [8]. However, if the set of isotherms (kernel) are

not available or if the commercial gas adsorption instruments are not equipped with the corresponding software it is not easy to apply this microscopic method.

Among the macroscopic methods, the first one proposed to determine the PSD in mesoporous materials was introduced by Barrett, Joyner and Halenda (BJH), based on the capillary condensation theory, using the Kelvin equation, where a cylindrical pore geometry is assumed and the desorption branch data of the isotherm are used [9]. The equation used in the BJH method was modified by Montarnal [10] taking into accounts not only the pore radio but also the length of the pores. Dollimore and Heal using the Montarnal's equation in the BJH method introduced the Dollimore-Heal method (DH) [11]. However, it was found that these macroscopic methods overestimate the capillary condensation/evaporation pressure and subsequently the pore size is underestimated (up to 25% for mesoporous materials consisting of pores ⩽10 nm) [1,2,12,13].

Among the nanoporous materials are the ordered mesoporous materials (OMM), which have attracted attention in materials science due to their interesting textural, structural and morphological properties. These special characteristics are related to highly ordered pore structures, tunable pore size, high specific surface

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areas, large pore volumes and narrow pore size distribution. OMM have found wide potential applications in adsorption, catalysis supports, molecular separation, nano-reactors and particularly in reactions involving large and bulky molecules [14–16]. Regarding to their applications, one of the most important properties to be analyzed is their PSD [17–19], which states the size of the molecules that can act inside the chosen material.

Kruk, Jaroniec and Sayari working with OMM MCM-41 type, proposed to add a fixed value to the pore radius obtained by the BJH method using the adsorption branch data of OMM silica-based [13]. This fixed value was determined by a calibration procedure using the pore size data, obtained by X-ray diffraction (XRD) and nitrogen adsorption data, and the filling relative pressure for primary mesopores in an OMM series of MCM-41 type. But, we have found that this proposed fixed value is not the same for all the OMM, being necessary to estimate it for each kind of material.

In order to avoid the use of additional characterization techniques to the nitrogen adsorption–desorption experiments, a new method (Villarroel-Barrera-Sapag -VBS method-) to the PSD analysis for mesoporous materials has been introduced [20]. This is an improved method in comparison with traditional methods such as BJH and DH. In these traditional methods, the pore radius (r_P) is calculated by the sum of the Kelvin radius (r_K) and the statistical film thickness of adsorbed nitrogen (t). Taking into account that the t value is obtained from experimental data, the underestimation is given by the r_K itself (obtained by unmodified/original Kelvin equation). In order to avoid this underestimation, the VBS method adds a correction term, f_c, to the original Kelvin equation. Furthermore, unlike the BJH method the VBS method considers appropriate mechanisms of capillary condensation and evaporation in the mesopores (for cylindrical and spherical pores) and introduces an additional equation for materials with spherical pore geometry. In addition, this method also takes into account the presence of micropores in some of the OMM. For different mesoporous materials synthesized in our laboratory, the PSD obtained by applying the VBS method agreed with those obtained by NLDFT method [20,21]. However, the selected samples tested in that first article were not very ordered and they had a restricted range of pore size (up to 8 nm for cylindrical pores and up to 4 nm for spherical pores). As the DFT method for spherical pores was developed for pore sizes higher than 5 nm, the comparison between VBS and DFT is not definitive to conclude the effectiveness of the former method. In all cases, the advantage of the VBS method (macroscopic method) compared to the NLDFT method (microscopic method) is that it does not require a predetermined kernel to be applied. Furthermore, in that first article, the VBS method was introduced and applied for some synthesized samples without giving major details and, consequently, several authors wrote to us asking for further information.

In the present work, the VBS method procedure is completely explained in detail and further information is given, in order to facilitate its application to obtain suitable PSD for silica-based ordered mesoporous materials with both, cylindrical or spherical pore geometry using N_2 adsorption–desorption experimental isotherm data. The importance of taking into account an adequate calculus of the micropore volume for mesoporous materials with this class of pores is highlighted and explained. Furthermore, the method was tested for five well known OMM samples published by other authors, extending the range of the pore size analysis. In this case the selected samples with spherical pores had pore sizes of 9.5 and 15 nm then the comparison with DFT method is adequate. The PSDs obtained using the VBS method were compared with those obtained by NLDFT, remarking the effectiveness of the VBS method, which use only the experimental isotherm data.

2. Materials and methods

2.1. Materials

In order to exemplify the VBS method, data of OMM samples previously reported were chosen. The selected OMM isotherms data with cylindrical pore geometry were SBA-15_S3 [21], MCM-41B [22] and SE3030 [23]; and with spherical pore geometry were SBA-16 [24] and KLE [23].

2.2. Experimental isotherms

Experimental isotherms of OMM with cylindrical and spherical pore geometries are shown in Figs. 1 and 2. All the studied samples exhibits Type IV isotherms, which are typical of mesoporous materials and present hysteresis loops (except the MCM-41B). The SBA-15_S3 sample exhibits a Type H1 hysteresis loop, often associated to a defined primary mesopore size; the SE3030, SBA-16 and KLE samples show a Type H2 hysteresis loop. In these samples there is a presence of cavitation phenomena on the desorption branch [23].

2.3. Calculations of textural properties

Textural properties of the OMM under study were determined from nitrogen adsorption–desorption isotherms data at 77 K. The
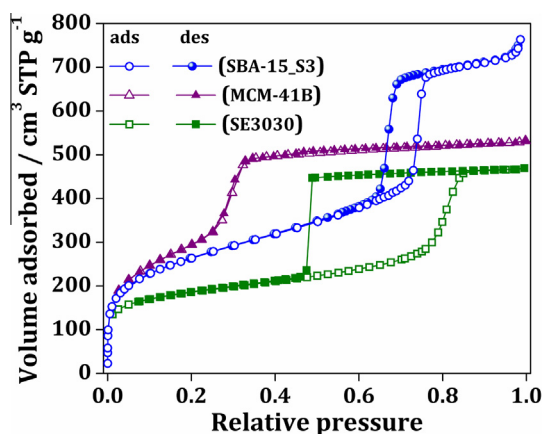

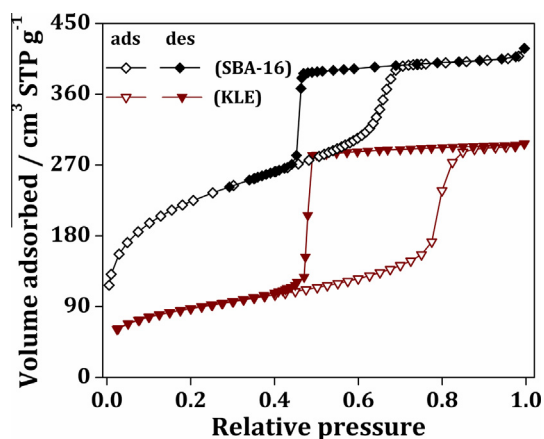**Fig. 1.** Nitrogen adsorption–desorption experimental isotherms at 77 K of OMM with cylindrical pores.

Fig. 2. Nitrogen adsorption–desorption experimental isotherms at 77 K of OMM with spherical pores.