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Infrared absorption by molecular gases to probe porous materials and comparisons with other techniques

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ABSTRACT

Infrared transmission spectra of several molecular gases inside three porous silica samples with pore sizes ranging from 7 nm to several tens of nm have been recorded with a Fourier transform spectrometer. Their analysis shows that consistent values of the percentage of open porosity and average pore size can be retrieved from these non intrusive nor destructive optical measurements. The samples have also been characterized using mercury intrusion/extrusion and the nitrogen sorption method. The results of these different probing techniques are in good agreement when the methods used are adapted to the involved pore size. This consistency demonstrates that light absorption by confined gases is a valuable porosimetry tool.

1. Introduction

Over the past decades, porous materials have been widely and increasingly used in many fields due to their numerous potential or demonstrated applications [1,2] such as gas storage, catalysis, gas separation, sensing, optics, biomedicine, etc. In particular, they are often employed as host materials with properties and applications that are ruled by their textural properties. The accurate determination of the micro-, meso- or macro-porosities of these materials is thus of crucial interest to their successful design and optimization. In this context, several techniques have been developed in order to characterize the pore structure, including electron microscopy, diffraction techniques, positron annihilation, calorimetry, mercury intrusion/extrusion and the widely used gas-sorption porosimetry [2–5]. However, there is no experimental method suitable for neither probing all pore sizes nor the determination of the absolute values of porosity parameters [5]. The various characterization techniques thus provide only limited, albeit complementary information.

Although nitrogen and mercury are, on most surfaces, wetting and non-wetting liquids, respectively, both mercury intrusion/extrusion and N_2 condensation-evaporation into and out of the pores can be considered as similar processes occurring in opposite directions. Both methods are based on surface tension, capillary forces and pressure. In the case of mercury porosimetry, large pores are filled first at the intrusion phase, while the smallest pores are filled first during the adsorption process by nitrogen sorption porosimetry. The micropore domain, accessible from gas-sorption data, is out of the range of mercury porosimetry, due to the constancy of surface tension and wetting angle for mercury, in addition to practical difficulties associated with very high pressure generation. However, at the large pore end, mercury porosimetry does not have the limitations of the Kelvin equation (and its derivative methods). As a consequence, the range of pore widths that can be measured by mercury porosimetry, i.e. about 10 nm–150 μm for

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cylindrical pores, is much broader than that accessible by N_2 sorption which is limited from 0.5 to 200 nm [6]. Nevertheless, the results of the two methods (total pore volume, volume pore size distribution and specific surface area/total pore surface area) can be compared in the range where they overlap.

Concerning porosimetry from light-absorption spectra of confined gases, the first study was, to the best of our knowledge, carried out using O_2 gas and ceramics [7]. It used the fact, previously shown in Ref. [8], that the confinement within the pores induces, via molecule-wall collisions, a broadening of the absorption lines that contains information on the pores dimensions. This pioneer work was followed by Refs. [9] and [10] in which spectra were recorded for other gases within a xerogel and an aerogel sample, respectively. In these studies, the pore sizes were deduced from the observed line broadening by assuming that a single collision of a molecule with the inner surface of the pores interrupts the radiation process. Elements in favor of this hypothesis were given by the agreement between the predictions of this model and the results of molecular dynamics simulations [11], but no definitive experimental proof was available yet. This proof was given recently [12] under "clean" and known confinement conditions in an extremely thin absorption cell. This opens the route to a broader use of light absorption by gases confined (but not adsorbed) inside porous materials for quantitative porosimetry studies.

This is precisely the aim of the present paper where two silica xerogel samples and one aerogel sample of very different porosities have been probed using infrared absorption by various gases. This provides the percentage of open porosity and average pore size. The retrieved values are successfully compared with those provided, for the same samples, by mercury intrusion/extrusion and the N_2 sorption methods. The remainder of this paper is divided into three sections. The experiments, including the manufacturing of the samples, the infrared measurements and other methods used to characterize the porosity are described in Sec. 2. The results obtained are summarized, compared and discussed in Sec. 3 at the end of which the advantages and limits of the porosimetry approach using absorption spectra of molecular gases are commented. Finally, Sec. 4 presents a summary and directions for future studies.

2. Experiments

2.1. Manufacturing the porous materials

Two silica xerogel samples (denoted xerogel#1 and xerogel#2) were prepared in Lille, as described in Ref. [13], starting from two different silica precursors, namely tetraethylorthosilicate (TEOS) and tetramethylorthosilicate (TMOS), using the polymeric sol-gel technique [14] under base-catalysis conditions. In addition, an aerogel sample was made in Monts. It was also prepared by the sol-gel polymerization using a two-step route with TEOS:: nitric acid was first used as a catalyst for the hydrolysis of TEOS and, then, ammonia was introduced to accelerate the condensation processes. The resulting alcogel was dried under supercritical conditions with carbon dioxide, yielding silica aerogels with a density of 0.1 g/cm^3. The resulting silica aerogel was sintered for 1 h at 940 °C to the density of 0.81 g/cm^3. These three samples show a nearly cylindrical shape with typical length and diameter of 1–1.5 cm (e.g. Fig. 1 of [15]).

2.2. Mercury intrusion/extrusion

The meso/macroporosity of the samples was studied in Bordeaux by mercury intrusion/extrusion porosimetry (Fig. 1) using a Micromeritics Autopore IV 9500 equipment (Micromeritics Corp., Norcross, GA, USA) with the following parameters: contact angle = 130°, mercury surface tension = 485 mN m^{-1}, maximum intrusion pressure = 224 MPa. The results obtained for the three samples are given in Table 1 (note that $4V/A$ is the diameter of a cylinder of inner surface area A and volume V) and pore size distributions are shown in Fig. 2.

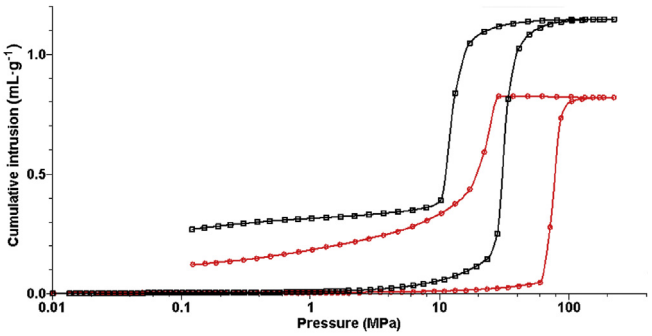

Fig. 1. Mercury porosimetry cumulative intrusion *vs.* pressure for the xerogel#1 (black squares) and aerogel (red circles) samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Mercury intrusion porosimetry clearly shows the presence of large mesopores in the xerogel#1 and aerogel samples with a high porosity (between 60 and 70%). Thus, a rather narrow pore size distribution centered around 39 nm and 17 nm is observed for the xerogel#1 and aerogel samples, respectively. By contrast, apart from the bulk density, no relevant data is provided by Hg intrusion porosimetry for the xerogel#2 sample whose pores are (see thereafter) too small to be probed by this method.

2.3. Nitrogen sorption

Specific surface area determination and mesoporosity assessment were performed in Bordeaux by recording nitrogen sorption isotherms at 77 K (Fig. 3) with a Micromeritics ASAP2010 equipment (Micromeritics Corp., Norcross, GA, USA) after degassing each sample at 150 °C in vacuum for a time interval long enough to reach a constant pressure (<10 μm Hg). The BET equation [16] was then applied between 0.01 and 0.3 relative pressure (P/P_0) to calculate the specific surface areas S_{BET}. The corresponding results obtained are summarized in Table 2. Pore size distributions were determined by density functional theory (DFT) calculations using the Micromeritics software package [17] (Fig. 4). The pore size distributions were extrapolated from the adsorption branch of the isotherms assuming a slit-like pore geometry, and the delayed condensation effect was not taken into consideration.

As depicted in Fig. 3, xerogel#1 exhibits a type-II sorption isotherm with a ill-defined hysteresis loop usually associated to mesoporous materials with large mesopores and/or macroporous materials. On the other hand, the xerogel#2 and aerogel samples show a type-IV like behavior, including a type H2 hysteresis loop, which is typical of mesoporous materials [18]. Moreover, pore size distributions calculated by DFT are in good agreement with the mercury intrusion data. The xerogel#2 and aerogel samples show rather well-defined mesopore size distributions centered around 8 and 26 nm, respectively (Fig. 4). By contrast, xerogel#1 exhibits much less defined mesoporosity, the main contribution being centered around 40 nm with the presence of larger pores.

2.4. Infrared measurements

Infrared transmission spectra of gases confined, at room temperature, in the three porous materials (PM) were recorded as described in Ref. [9]. Briefly, the PM was inserted between the CaF_2