Journal of Non-Crystalline Solids 357 (2011) 1319–1327

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Analysis of mercury porosimetry curves of precipitated silica, as an example of compressible porous solids

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ARTICLE INFO

Article history:
Received 6 July 2010
Received in revised form 22 December 2010
Available online 20 January 2011

Keywords:
Precipitated silica;
Mercury porosimetry;
Nitrogen adsorption porosimetry;
Compressibility

ABSTRACT

Mercury intrusion curves in a series of silica samples are analyzed, together with the study of nitrogen adsorption/desorption curves and TEM pictures. A detailed discussion of the mechanisms that operate during the mercury intrusion is presented, identifying several steps: elastic sample compression, plastic sample compression and mercury intrusion. A mathematical model of the plastic sample compression is presented and applied to these silica samples. The pore size of the maxima in mercury intrusion is smaller than that calculated by the BJH method applied to nitrogen desorption. The differences are explained by accounting for the sample compression and the differences in the mechanism in both techniques.

1. Introduction

Mercury intrusion and nitrogen sorption are two techniques widely used to characterize the textural properties of mesoporous materials, normally using Washburn [1] and Kelvin [2] equations, respectively, as data treatment methods. However, in some porous materials the pore size distributions deduced from the routine application of these two methods fail to agree, as the high pressures inherent in mercury intrusion cause the mechanical compression of the porous structure during the measurement [3–5]. When a pellet sample of such materials (sometimes called 'monolith' or 'agglomerated') is analyzed by mercury intrusion, a number of mechanisms contribute to the volume of mercury that enters the cell containing the porous material as the pressure is increased:

a) Elastic compression. When the applied pressure is low, mercury enters the cell because the pore structure undergoes an elastic compression (elastic regime). In this regime the volume intruded increases linearly with pressure and if the pressure were released, the material would dilate to the initial volume [6]. This behaviour can be used to calculate the elastic bulk modulus (K) of the material (the inverse of the bulk compressibility of the material [6]). The elastic bulk modulus at any point along the compression curve (P vs. V_{Hg}) is defined by the relation $dP = -K \cdot (dV/V)$. This mechanical property, obtained using the volume of the sample [7,8] as V, agrees well with the modulus determined by beam-bending [7] or sound velocity techniques [9].

b) Structure deformation. As the pressure is increased, more mercury enters the cell and the deformation of the pore structure becomes inelastic (plastic regime), so that if the pressure were released, the material would dilate slightly (elastic strain) but not to the initial volume (inelastic strain). The sample volume shrinks progressively under the action of mercury pressure and the bulk density increases. Vittoratos and Auburn [6] found that in the compression curve of the plastic regime the volume intruded in a silica polymerization catalyst changed linearly with log pressure. Scherer et al. [7] assumed that the bulk modulus is no longer constant but changes with the sample volume according to a power law and obtained a satisfactory fitting of their mercury porosimetry data of silica aerogel. SAXS studies of silica aerogels have confirmed that the inelastic compression is caused by the progressive spatial rearrangement of the clusters that form the porous network [10]. Pirard et al. [11] proposed that the largest pores between the clusters collapse as a result of pore edge collapse and their scraps form smaller pores. In this process the internal cluster structure does not change [9] but, as the clusters interpenetrate each other modifying their periphery, the network connectivity increases [10]. To sum up, the compression results in better packing of clusters.

c) Pore filling with mercury. When pressure is high enough, mercury can intrude into the pores that have been previously shrunk. This behavior has been noticed in SiO_2 ethylene polymerization catalysts [5], carbon blacks [12], high dispersive precipitated silica [13] and some silica xerogels [14]. However, depending on the pore structure and at the highest pressure this step may not be observed, as has occurred with silica aerogels and some silica xerogels [14].

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doi:10.1016/j.jnoncrysol.2010.12.042

For powdered material, the volume intruded in the low pressure range accounts also for the inter-particular volume (mercury intrusion in the voids between powder particles), which is not the case for pellet samples. As this additional contribution partially hides the compression phenomenon, pellet samples have always been used to study the compression phenomenon under mercury isostatic pressure, in spite of the commercial product being a powder. These previous studies were focused on different matters: characterizing the mechanical properties of the material [6,7,15], explaining the relation between the irreversible volume shrinkage and the material structure [8,10,11,16,17] or even obtaining a correct distribution of pore volume as a function of pore size [18].

The present paper shows a way of obtaining an accurate characterization of the compression phenomenon from mercury intrusion porosimetry (MIP) experiments on powdered samples, which at the same time is able to determine the specific inter-particulate volume (V_{int}) and the specific pore volume (V_p) more precisely. This method is applied to precipitated silica, a material that has received little attention with regard to the compression phenomenon.

The analyzed samples follow clear evolution trends in specific pore volume, pore diameter and specific surface area and have also been characterized by nitrogen sorption and TEM. These trends allow discussing the applicability of nitrogen sorption and mercury intrusion to the characterization of powdered precipitated silica.

2. Experimental

2.1. Silica samples

Precipitated silicas were synthesized by reaction between sodium silicate solution (obtained from commercial sodium silicate with a SiO_2/Na_2O ratio of 3.35) and sulphuric acid (commercial, 98% purity) over a bath of water, keeping a constant temperature of 60 °C and a pH between 7 and 8. The synthesis was carried out at the installations of the precipitated silica manufacturer IQESIL S.A. In order to obtain different and controlled porous structures, the theoretical concentration of silica at the end of the synthesis was varied. All samples were powdered with a spatula to give a mean particle size of around 0.1 mm. It is worth explaining that these particles are not in fact primary particles, but are composed of many agglomerated primary particles. The final silica concentration (FSC) and the name of the samples are shown in Table 1. FSC is the percentage of silica by weight in the precipitation batch at the end of the synthesis. The error estimate in FSC is given based on the characteristics of the flowmeter reported by the manufacturer. The BET area obtained from nitrogen adsorption data and the primary particle diameter (d_p) obtained from TEM images are also shown in Table 1. The error estimate for the BET area is calculated from the fitting of experimental values. The error estimate for d_p is given as the standard deviation of the measured values. The last row of the table shows the particle diameter estimated from the BET area. A good agreement with the values measured by TEM and those calculated from the BET area is obtained by assuming that silica is composed of spherical silica particles with a density of 1.9 g/cm^3. This density is smaller than that of pure and well crystallized silica, which suggests that silica in the primary particles is not well ordered, leaving internal voids and internal silanol groups.

2.2. Nitrogen porosimetry

The nitrogen adsorption measurements were carried out with a Tristar 3000 supplied by Micromeritics (Norcross, USA) at 77 K by a discontinuous static method. This equipment, that follows a pressure programme, measures automatically the volume of adsorbed nitrogen for each relative pressure, i.e. the adsorption and desorption isotherms [3]. The pressure programme comprised 36 adsorption and 29 desorption points measured at equilibrium, with a maximum relative pressure of 0.999. Prior to N_2 sorption, all samples were degassed at 200 °C for 45 min under continuous nitrogen flow. The outgassed silica weight was used in all calculations. The accuracy of the pressure transducer is 0.5% of the maximum pressure.

The BET surface area [19] was calculated using the first four adsorption points in the relative pressure range 0.14–0.20. The total specific volume of mesopores and the mesopore size distribution were calculated from the desorption data according to the BJH method [20].

2.3. Mercury porosimetry

Mercury porosimetry experiments were performed using a Micromeritics Autopore IV 9520 capable of obtaining pressures of 414 MPa. All penetrometers were calibrated and the baseline errors of each penetrometer, caused by the compressibility and thermal effects of the mercury and penetrometer parts, were obtained from analysis without sample. Any intrusion that appeared in this blank run was attributed to baseline error [21]. The accuracy of the volume measurement with this equipment is 1% of the stem volume, according to the manufacturer. The accuracy of the pressure transducer is 0.1% of the maximum pressure. The mean of three baseline analyses was subtracted from the subsequent sample analysis performed with each penetrometer.

Silica samples were dried at 105 °C for one day prior to analysis and the dried weight was used in all calculations. At the beginning of the test, the bulk mass of particles of the powdered sample, which was placed in the sample cup of the penetrometer, is under vacuum. Then the penetrometer is filled with mercury under a pressure of 0.5 psia (3.4 kPa). This is the starting point of the intrusion/extrusion process. The volume of mercury intruded in the sample holder is represented as a function of pressure to give the raw mercury intrusion and extrusion curves.

The whole intrusion and retraction program was designed to record the mercury volume and the pressure at each of the 273 programmed pressures (21 using the low-pressure stations in intrusion, 162 using the high-pressure stations in intrusion and 90 using the high-pressure stations in retraction). However, the actual number of experimental data was usually greater because the program was also designed to record mercury volume and pressure as soon as the intruded or retracted volume exceeded the previous measured volume by 0.020 ml/g.

Table 1
Properties of silica samples. BET area, primary particle diameter measured by TEM and estimated from BET area for precipitated silica samples with variable theoretical concentration of silica at the end of the synthesis (FSC).

Sample									
	SI1	SI2	SI3	SI4	SI5	SI6	SI7	SI8	SI9
FSC (%)[a]	2.59	3.03	3.41	3.73	4.01	4.25	4.47	4.66	4.83
S_{BET} (m^2/g)	442 ± 1.8	403 ± 1.9	373 ± 1.9	337 ± 2.0	308 ± 1.6	283 ± 1.7	278 ± 1.5	257 ± 1.6	242 ± 1.7
d_p (nm)	7.2 ± 1.1	10.2 ± 1.5	10.4[b]	11.4[b]	11.8 ± 1.8	13.0 ± 1.5	13.6[b]	14.2[b]	14.7 ± 1.8
d_p estimated (nm)	7.1	7.8	8.5	9.4	10.3	11.2	11.4	12.3	13.1

[a] Error in FSC is roughly 0.1%, according to the flowmeter specifications.
[b] Interpolated values from the FSC vs. d_p graph.