Journal of Colloid and Interface Science 336 (2009) 679–690

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Small-angle X-ray scattering studies of adsorption in Vycor glass

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ARTICLE INFO

Article history:
Received 1 October 2008
Accepted 15 April 2009
Available online 3 May 2009

Keywords:
Vycor
Small-angle X-ray scattering
Adsorption hysteresis
Pore connectivity
Film area
Pore-size distribution

ABSTRACT

Porous Vycor is examined by measuring CH_2Br_2 adsorption in situ with small-angle X-ray scattering. When a class of pores fills with condensed vapors of this particular adsorbate it ceases to act as scatterer and only the remaining empty pores produce a measurable intensity. By determining a number of scattering curves at various relative pressure loadings details on the structure of the glass as well as on the adsorption/desorption mechanism are obtained. Pore chord length and specific surface area are estimated from Porod tangent analysis to 78 Å and 108 m^2/g. Comparison of the results with those reported for N_2 and Ar adsorption is also given. The role of network effects on the shape of the hysteresis loop is considered and the pore-blocking hypothesis is verified from the scattering spectra. The pore connectivity is calculated to 5.6. The X-ray data are further treated with the inverse Fourier transformation technique. Pore-size distributions are extracted and weighed against the prediction of the Kelvin equation.

1. Introduction

Natural porous media and synthetic porous materials play an important role in many industrial processes as well as in many fields of science and engineering such as catalysis, chemical sensing, filtration, centrifuging, biotechnology, ceramics, oil recovery, and ground water [1]. A common denominator to all these phenomena is the strong influence of any equilibrium or dynamic process that takes place inside pores from the topology and geometrical disorder of the solid matrix. Characterization of porous media includes the determination of pore shape and size partitioning and the connectivity of pores as well as the assessment of surface heterogeneity and accessibility [2].

The study of porous systems is routinely based on adsorption techniques, especially that of nitrogen adsorption [3]; yet a full determination of the capillary profile remains a difficult and in many instances a laborious task requiring: (a) the use of other less common than adsorption techniques, (b) the development of an appropriate computing simulation model, and (c) the comparison of the results with those obtained under similar conditions from reference porous materials. The latter are prototypic materials that portray a practical homogeneity with a narrow pore-size distribution and a rather uniform pore shape. These model porous materials serve as host structures for an in-depth study of various important but poorly understood physical phenomena, e.g., hydrodynamic flow, viscous fingering, and interfacial instability.

Porous Vycor glass (Corning Vycor brand 7930 [4]) is a typical example of a mesoporous material that is suitable for the study of the properties of fluids and molecules in highly confined geometries. According to the manufacturer Vycor has an open cellular structure which exhibits excellent moisture absorbing properties (thirsty). It is mechanically hard and strong, nondusting, nonflaking, and chemically inert. These properties allow it to be employed as a noncontaminating getter which rapidly absorbs water and organic contaminants. It is often used for filtration and separation of compounds while the pore network allows permeability on a selective basis. Commercially available porous glass has apparent density of 1.5 g/cm^3, specific surface area of 150–200 m^2/g, and internal pore volume of 28%. The pore-size distribution is narrow with about 96% of the pores in the glass being ±3 Å from the average radius that is about 20–30 Å. However this is only an abstractive picture of Vycor structure; controversial views on the morphology and the surface geometry of the glass have long been reported in the literature. Some of these conflict views have been thoroughly discussed by Levitz et al. [5] a few of which are noted here.

Many years ago Emmett and de Witt [6] studied the glass by adsorption of various gases at low temperatures. The adsorption isotherms were found to obey an extension of the theory of multimolecular adsorption with a hysteresis in the upper portion of the isotherms which was a very reproducible and characteristic part of the curves. Nowadays it is accepted that the adsorption isotherm of Vycor is of type IV with a hysteresis loop of type H2 according to the IUPAC classification [3].

The underlying origin of the hysteresis in mesoporous materials is believed to be a thermodynamic consequence of capillary condensation. While detailed research on this field goes on today with ordered mesoporous materials the shape of the loop remains an open question [7–9]. The sharp drop on desorption

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doi:10.1016/j.jcis.2009.04.054

is often taken to indicate a narrow pore-size distribution, whereas the gradual ascending on adsorption is taken to reflect the combined effects of surface adsorption and capillary condensation in pores with a distribution of sizes. In an early hypothesis the shape of the H2 loop was attributed to a difference in mechanism between condensation and evaporation processes occurring in pores with narrow necks and wide bodies (ink-bottle pores), but later on it was recognized that this provides an oversimplified picture and the role of network effects should be taken into account [3].

Mason [10] has described the glass as a chaotic porous network of cavities with interconnecting constrictions. On adsorption condensation can initiate at any throat, even if the throat has become isolated from the surface by other filled throats, whereas on desorption the condensed liquid cannot evaporate unless the pore is connected to the vapor phase. To throw some light on this hypothesis Page et al. [11] used ultrasonic attenuation and light scattering to study spatial correlations in the pores of Vycor on filling and draining with hexane. It was found that on drainage the empty pores exhibit long-range correlations with a fractal dimension of 2.6. They concluded that this correlation results from the pore connectivity which can be modeled by invasion percolation. Following this advice Kikkinides et al. [12] modeled the desorption curve with an invasion percolation algorithm to account for the hysteresis effect caused by the inaccessible regions of the glass matrix. They argued that desorption is simulated very well provided that the main mechanism for hysteresis depends only on the topology of the pore space and not on thermodynamic effects.

Based on a Bethe lattice with connectivity three, Rajniak et al. [13] developed a unified network model for adsorption/desorption and subsequently applied it to the Vycor–nitrogen system. The desorption–diffusivity data show that diffusivity decreases as the relative pressure is going from the upper closure point of the hysteresis loop (ca. $p/p_o = 0.82$) to the percolation threshold (ca. $p/p_o = 0.63$) and after that increases as the relative pressure is going from the percolation threshold point to the lower closure point of the hysteresis loop (ca. $p/p_o = 0.5$). In a followup of this work Šoóš et al. [14] developed two percolation models (independent and pore blocking) and they tested them against experimental equilibrium data for the same system. Better agreement was obtained by the pore-blocking model with average connectivity of about 5.8.

Pellenq et al. [15] performed atomistic GCMC simulations of adsorption of xenon in a Vycor-like matrix. They found from the analysis of the adsorbed quantity distribution that partial molecular-film formation depending on the local surface curvature and roughness is possible. In an earlier study Ferguson and Wade [16] measured the area of porous Vycor at various degrees of saturation with water. Based on a plot of pore area versus location on both the adsorption and the desorption branches of the isotherm they concluded that the pores cannot have cylindrical geometry and that two or more pore geometries contribute to the pore structure. A systematic error involved in comparing the networked glasses to the ideal cylinders is also concluded by Gelb and Gubbins [17,18] who developed a realistic model that mimics the experimental process that produces Vycor and other controlled-pore glasses. The authors reported that the BET equation overestimates the surface area while the BJH (Barrett–Joyner–Halenda) method [19] underestimates the size of the capillaries by about 10 Å and also that the shape of the hysteresis loop does not depend on pore connectivity.

Small-angle X-ray scattering (SAXS [20]) is another less common but more powerful than adsorption technique that has been employed to characterize the structural features of the glass [21,22] and in some instances the capillary condensation process per se [23]. Hoinkis [24] has conducted a detail review on this sort of research together with a comprehensive outline of the theory needed for the interpretation of X-ray or neutron scattering data.

There are two complications arising in the study of Vycor by this technique: (a) the glass is not a dilute colloidal system and in this respect Fourier analysis is limited and (b) the internal surface of the glass has a rough texture and this makes Porod analysis [25] not to be straightforward. While the first problem remains unsolved the second one can be overtaken. The scattering of fractal surfaces has been addressed by a number of distinguished material scientists in Sandia National Laboratories and a direct comparison between surface areas of fractally rough powders obtained by scattering and adsorption techniques has been demonstrated [26]. In this passing, Schaefer et al. [27] studied the origin of the porosity in Vycor by using small-angle X-ray scattering. They argued that the structure of leached borosilicates stems from the dissolution process (i.e., without phase separation of the precursor) to which the fractal roughness in Vycor is also attributed. Using a properly described Porod analysis for positive deviations of the power law (i.e., <4) they determined the structural parameters of the glass as follows: specific surface area 140 m^2/g, porosity 41%, fractal dimension 2.7, pore chord length 100 Å, and solid chord length 120 Å.

In this study, SAXS measurements on porous Vycor glass that had been brought to equilibrium with known relative pressures of CH_2Br_2, which has a similar electron density as Vycor, are conducted and some of the structural features of the glass are quantified. After the introduction (1), the work is organized into the following sections: (2) the experimental details are presented, (3) the adsorption isotherm of CH_2Br_2 is compared with N_2 and Ar isotherms that are found in the literature, (4) the pore-blocking hypothesis is tested against the scattering spectra, (5) the pore connectivity is extracted from the desorption curves of N_2 and CH_2Br_2, (6) the film area hysteresis is calculated from Porod approximation, (7) the predictions of the Kelvin equation are compared with pore-size distributions that are obtained from the indirect Fourier transformation (IFT) method generalized for concentrated systems, and (8) concluding remarks are outlined.

2. Experimental details

A commercially available Vycor 7930 in a monolithic form was primarily used in the present study. The rod had a diameter of 6 mm and was sliced using a diamond saw to a thickness of about 0.8 mm. The sample was cleaned by 30% hydrogen peroxide and exposed to an oxygen stream at 350 °C for 24 h. A similar cleaning procedure was followed for a secondary sample that was in a powder form.

Adsorption isotherms of CH_2Br_2 were measured gravimetrically on Vycor and nonporous alumina at 17.2 and 20 °C, respectively. This latter isotherm was used to determine the thickness, t, of the adsorbed film. The experimental values obey a Halsey-type equation [2],

$$\ln\frac{p}{p_o} = -\frac{K}{t^m}, \tag{1}$$

where K and m are curve parameters. For an average thickness of the single layer $t_\sigma = 4.5$ Å, $K = 61.8$, and $m = 2.219$. The cross-sectional area of CH_2Br_2 was calculated from its density (2.494 g/cm^3) equal to 26 $Å^2$ (static value), and the surface tension of the liquid was measured by a ring balance equal to 40.2 mN/m. Nitrogen and Ar adsorption isotherms on Vycor at 77 and 90 K, respectively, that are reported in the literature [6], are also used for pore-size analysis and comparison with CH_2Br_2 isotherms.