Improved calculations of pore size distribution for relatively large, irregular slit-shaped mesopore structure

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A B S T R A C T

Present methods for determining pore volume (PV), pore size distribution (PSD), and average pore width (APW) of irregular mesoporous materials from N_2 adsorption, including the widely used model developed by Barrett, Joyner and Halenda (BJH), are likely to produce inaccurate results due to simplistic assumptions and approximations. For example, in assuming a simple cylindrical pore geometry and due to various empirical approximations, the BJH method typically underestimates APW for aluminas by 10–30% using the desorption branch of the N_2 adsorption isotherm. Here we report improved calculations of PSD based on the Kelvin equation and a proposed Slit Pore Geometry (SPG) model for slit-shaped mesopores of relatively large pore size (>10 nm). Two structural factors, α and β, are introduced to correct for non-ideal pore geometries. The volume density function for a log normal distribution is used to calculate the geometric mean pore diameter and standard deviation of the PSD. The Comparative Adsorption (α_s) Method (CAM) is also employed to independently assess mesopore surface area and volume. Values of APW calculated by the SPG method are typically 6–20% greater than values predicted by BJH model using the desorption branch of N_2 adsorption isotherm. Pore areas and pore volumes calculated from the SPG model are also in excellent agreement with those determined independently by CAM. The SPG method is demonstrated to be especially applicable to determination of PV, PSD, and APW for aluminas and other medium to large pore diameter mesoporous solids consisting of slab-like nano-crystals.

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1. Introduction

Accurate determination of BET surface area (SA), pore size distribution (PSD) and pore volume (PV) of porous supports, catalysts, and nanomaterials is vital to successful design and optimization of these materials and to the development of robust models of pore diffusional resistance and catalyst deactivation which are incorporated in catalytic reactor and process models [1–4]. Nitrogen adsorption at 77 K is used routinely to measure SA, PSD, and PV in mesoporous solids because of (1) its relative simplicity; (2) ease of measuring and analyzing data to obtain quantitative results; (3) accessibility of the gas to real pore structures, and (4) non-destructive application [4]. Mercury porosimetry is a useful complementary method to quantitatively determining meso- and macroporosity in porous solids, although it is destructive and the operation, upkeep, and safety aspects of the instrumentation are not routine. While other experimental techniques, such as X-ray diffraction (XRD), small angle X-ray and neutron scattering (SAXS and SANS), transmission electron microscopy (TEM) provide additional insights into structural features of mesoporous solids, they are principally

supplementary techniques due to their complexity and the relatively limited quantitative information provided by these methods regarding PSD and PV.

In recent years, advanced theoretical approaches based on quantum and statistical mechanics, such as non-local density functional theory (NLDFT) and molecular simulations have been developed to provide valuable structural information for porous networks [5–7]. However, a drawback of standard NLDFT is that it is based on model structures and hence does not take sufficiently into account the chemical and geometrical heterogeneity of the pore walls [8]. Recently, a novel DFT method, namely QSDFT (quenched solid density functional theory) has been reported to address the issues for pore wall roughness and chemical inhomogeneity [7,9–11]. However, it is mainly based on mesoporous carbon materials [7,10,11] and ordered mesoporous silica materials [9]. The application of these calculations for disordered mesoporous alumina materials has not yet been undertaken.

Fundamentals of multilayer adsorption applied to the assessment of mesoporosity are discussed in detail in books by Gregg and Sing [1], Rouquerol et al. [4], Thomas and Thomas [2], Hunter [12] and Lowell [13] and in reviews by Kaneko [14], Groen et al. [15], and Jaroniec and Kruk [16]. Several methods have been developed to calculate PV and PSD using data obtained from either

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adsorption or desorption branches of a full range nitrogen adsorption isotherm. In most classical pore models, data are analyzed using the Kelvin equation that relates partial pressure to pore radius in cylindrical pores. The volume of nitrogen adsorbed or desorbed as a function of P/P_0 (P_0 is the vapor pressure of liquid N_2 at liquid N_2 temperature) is corrected for the thickness of the adsorbed layer (which correction was originally proposed by Barrett, Joyner and Halenda [17]) and incrementally converted to obtain the PSD in the form of dV/dr as a function of r, where r is the pore radius. In principle, adsorption and desorption processes should be in equilibrium. However, in practice results obtained from adsorption and desorption branches differ due to non-ideal differences in capillary formation and evaporation leading to an observed hysteresis. Adsorption and desorption branches of the hysteresis loop can provide complementary information, although for specific hysteresis types one branch may be preferred over another [18,19].

One of the earliest and most widely used methods for calculating PV, PSD, and APW was proposed by Barrett, Joyner and Halenda [17] and is generally called the BJH method. This method is based on Wheeler's concept of a pore size distribution function $L(r)$ and assumes cylindrical pore geometry. Pore radius rather than relative pressure is chosen as the independent variable, and empirical corrections, including the assumption of an average pore radius in each pore size range, are made to the pore size distribution and in calculations of differential pore volume and area. While the BJH method appears to estimate pore volume well, it is well known that BJH analysis underestimate pore sizes by up to 20–30% when compared with either NLDFT or TEM determinations [13,20].

In general PV and PSD measurements obtained via the BJH and other typical methods are often in error because of flawed methods of data analysis based on simplistic assumptions and approximations. Moreover, these methods do not, in general, allow the extent of experimental error, precision, and accuracy to be readily assessed. For example, average pore radius determined from a typical dV/dr versus r distribution is likely to be significantly in error due to: (1) an inappropriate choice of the hysteresis branch (adsorption or desorption) for PSD analysis; (2) an incorrect form of the Kelvin equation based on an unrepresentative pore geometry, especially for irregular mesoporous materials; (3) inaccuracies in the geometric equations relating mesoporous surface area, pore volume and pore radius; and (4) asymmetry and tailing of the curves in the dV/dr PSD plot. Irregular pore structure is defined in the present context as nonparallel pores of varying size and shape, interrupted by structural defects.

Nevertheless, in principle, rational, careful consideration of the fundamental adsorption processes should provide a basis for accurate fitting of the distribution and for choices of the adsorption branch and form of the Kelvin equation in irregular mesoporous materials. In addition, validation by independent measurements (e.g. mercury porosimetry), the use of standard materials, and/or alternate methods of analysis, can ensure quantitative characterization of PV, PSD, and average pore width (APW).

Indeed, a simple, useful, and accurate complementary method, namely the Comparative Adsorption (α_s) Method (CAM), can be used to independently assess mesopore surface area and volume. CAM is based on the comparison of the adsorption isotherm for the porous solid under study with that for an appropriate reference solid with similar surface properties [1,4,21]. Usually, a macroporous reference is chosen with surface properties similar to the material under study with respect to the adsorbate used. Adsorption on the macroporous reference proceeds via multilayer formation, whereas that of the porous solid under study includes both multilayer adsorption and condensation in the pores; this latter process is greatly influenced by pore size. To determine the pore size range in the sample under study (i.e. micro, meso, or macroporous), one can plot the amount adsorbed on the solid under study

as a function of the amount adsorbed on the reference solid. If the adsorption on both solids proceeds via the same mechanism (multilayer formation), the comparative plot is linear in the applicable pressure range. Differences in the comparative plot can be attributed to different mechanisms, such as micropore filling or capillary condensation. Therefore, CAM can be used to check BET area against mesopore area and also to identify the individual adsorption and pore filling mechanisms [21–24].

More sophisticated models for pore size calculations include the classical Broekhoff-de Boer (BDB) approach [25–29] which uses model porous materials (e.g. M41S and SBA-15) to calibrate the thickness relationship and the Kruk–Jaroniec–Sayari (KJS) model [30–32] which enables calibration of the Kelvin equation using a series of highly ordered MSM-silicas of known pore diameter obtained from SAXS. However, the application of calibration standards with the KJS model is only valid in the pore diameter range of 2–10 nm [30,33], Moreover, the BDB and KJS models are reliable only for highly-ordered cylindrical pores of very similar or the same diameter. Although slit pore model is also proposed by the Broekhoff-de Boer (BDB) approach, it did not take into account the distortion of the pore geometry and the inhomogeneity of pore wall. Thus, the BDB and KJS models are not applicable to the large class of irregular mesoporous materials having non-cylindrical pores of different sizes or constrictions, and/or pore diameters larger than 10 nm.

The present article introduces an improved, rational approach (the SPG model) to the measurement of PSDs for mesoporous solids composed of slab-like particles. The SPG model comprises (1) the classical Kelvin equation adapted to the a slit geometry and (2) thinning corrections and calculations of differential surface area and volume according to the fundamental approach of Pierce, Orr, and Dalla Valle [34,35]. The analysis is applied in the present study to large pore alumina supports, including two commercial aluminas and two novel wide-pore alumina supports developed in a previous work [36], all four of which are clearly composed of slab-like materials but arranged in different geometries. Basic principles and critical assumptions are enumerated and discussed. Fundamentally based criteria are provided for making decisions at each step in the process, including: (1) selection of the appropriate form of the Kelvin equation based on knowledge of primary particle and pore geometries obtained from TEM and other techniques; (2) experimental determination of the appropriate structural factors relating pore radius to pore volume and surface area which account for differences in geometrical arrangements of the primary slab crystallites; and (3) use of the log-mean pore-size distribution with its inherent advantages of symmetry and well-defined error analysis.

2. Experimental section

2.1. Materials

Reference material Aluminumoxid C Degussa (denote as DC) was purchased from Sigma–Aldrich and used as received. Two commercial alumina samples were obtained from Alfa Aesar (1/4 ring, Catalog No. 43858) and Saint Gobein (Trilobe, Catalog No. SA 6*78), denoted as Al-AA and Al-SG, respectively. Aluminum *iso*-propoxide ($Al(OCH(CH_3)_2)_3$), aluminum *sec*-butoxide ($Al(OCH(CH_3)CH_2CH_3)_3$) were purchased from Alfa Aesar and used as received without purification. Deionized water was used in all the synthesis.

The synthesis procedure for large pore alumina materials was described elsewhere [37–39]. A typical synthesis involved formation of precursors followed by thermal treatment. For example, 24.158 g of aluminum *sec*-butoxide was mixed with 8.83 ml of distilled water (water to aluminum ratio 5:1) using a mortar and