Powder Technology 327 (2018) 96–108

Contents lists available at ScienceDirect

Powder Technology

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

Particle and cluster analyses of silica powders via small angle neutron scattering

S. Hadi Madani [a], Ian Harvey Arellano [b], Jitendra P. Mata [c], Phillip Pendleton [d],*

[a] School of Petroleum Engineering, The University of Adelaide, Adelaide, South Australia 5005, Australia
[b] School of Pharmacy and Medical Sciences, University of South Australia, Adelaide, South Australia 5005, Australia
[c] ACNS, Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW 2234, Australia
[d] School of Chemical Engineering, The University of Adelaide, Adelaide, South Australia 5005, Australia

ARTICLE INFO

Article history:
Received 8 September 2017
Received in revised form 7 December 2017
Accepted 16 December 2017
Available online 22 December 2017

Keywords:
Small angle neutron scattering
Powdered silica
Ordered porosity
Fractal dimension
Guinier-Porod analysis
Combined standard uncertainty

ABSTRACT

Small angle neutron scattering (SANS) responses of particulate silica as disordered and ordered porous and non-porous powders were obtained. Each classification provided distinct scattering patterns which were fitted and analysed using Guinier-Porod and mass-surface fractal (msf) models. The resulting particle dimensions showed good agreement with the same from nitrogen gas adsorption analyses. Additionally, the excellent fit of the msf model to the non-porous silica scattering response resulted in an agreement between the mass and surface fractal dimension values for it and similar analyses and results published previously for fumed silica. The msf fitting gave additional insight into particle and cluster scattering dimensions with particle dimensions being consistent with those from the G-P analyses.

1. Introduction

For many years powdered silica has been used in a vast number of applications, including as an adsorbent material exploiting porous and/or non-porous properties for the removal of aqueous phase pollutants, such as the removal of toxic heavy metal ions [1–3] and dyes [4] from water, and gaseous phase pollutants such as volatile organic compounds [5] from industrial exhaust gases. Some recent uses of silica have seen it as a support of ionic liquids potentially for CO_2 removal from gaseous process streams [6–9]. Although gas adsorption is the most commonly applied method of silica surface chemistry and porosity analysis, small angle neutron scattering (SANS) by porous powders is often cited as a complementary method for analysis. The principal objective of this work was to apply SANS to selected silica samples to establish the extent of complementary nature of these two methods, and to extend SANS analyses of these beyond current data fitting methods.

Silica particles are commercially available as non-porous solids, as disordered porous solids, and as hierarchically-ordered, porous solids. The non-porous versions have been widely studied as sourced from flame formation (fumed silica) [10] to solution precipitation (Stöber silica) [11]. These two methods of synthesis result in aggregates of much smaller, usually more uniformly-sized primary particles. Silica samples from both methods of synthesis were foundation materials for the science of fractal structure in aggregates [12–14]. The hierarchical silica structures were developed later and became widely available as ZSM, MCM, and SBA, with the former being silica-alumina composites requiring relatively higher ratios of SiO_2 to be considered (pedagogically) as silica for the current work [8,9]. The *intra*-crystalline pore structure for ZSM-5 and its high silica content counterpart, silicalite, were defined as parallel tubes offset as a herring-bone structure with tube diameter $\approx$ 0.55 nm [15]. The pore structure of SBA-15 would best be described as parallel tubes typically arranged in a honeycomb formation with each tubular pore of diameter $\approx$ 8.0 nm [16].

Small angle neutron scattering analysis (SANS) is a non-intrusive method for investigating structural features on and within a powdered solid, recognised as a technique complementary to gas adsorption [17]. Additionally, SANS is often cited as a materials analysis technique that provides details on blind and (so-called) closed pores within a powder. Both of these pore types could also be those possibly beyond a narrow transport constriction within a pore network, where the constriction itself is a width less than the kinetic diameter of the probe molecule. Furthermore, due to the manner of neutron interaction with atomic nuclei, SANS provides an enhanced complementarity to distinguish between air and various phases within a porous structure. For any SANS equipment, the highest detected q-value dictates the smallest-resolved dimensions ($\approx$1 nm) while the lowest detected q-value approaches micron-scale dimensions, greatly exceeding atomic and molecular probe techniques [18]. The lower limit could represent mass and/or

---

* Corresponding author.
E-mail address: phillip.pendleton@adelaide.edu.au (P. Pendleton).

https://doi.org/10.1016/j.powtec.2017.12.061

Nomenclature

G	Guinier coefficient
q_1	Guinier-Porod scattering cross-over vector, Å
I	intensity
D_m	mass fractal dimension
N	number density particles (in beam)
R_p	particle radius, Å
$R_{P,\text{G-P}}$	primary particle radius based on G-P model, Å
$R_{P,\text{BET}}$	particle radius based on BET model, Å
R_g	radius of gyration; cluster particle radius (msf model), Å
r_g	radius of gyration for primary particle radius (msf model), Å
θ	scattering angle
m	scattering exponent
q	scattering vector
D_s	surface fractal dimension
s	symmetry factor
ξ	upper cut-off length scale, Å
λ	wavelength, Å

surface fractal structures, collectively referred to as fractal structure [19]. The concept of pore fractal structure would most likely exist in scatterers offering uniform arrangement of both solid and void. Structural analyses such as (specific) surface area and pore volume, and the mean particle size can be derived from SANS data via simple empirical methods, viz. Porod [20] and Guinier [21] analyses of scattering data. For structures as aggregates of primary particles, the position of maximum scattering within the SAS profile provides details on the mean cluster size [22]. Porosity can be found in systems of aggregated particles or within particles sufficiently large they contain *intra*particle porosity. Such particles exhibit small angle scattering profiles with features suitably fitted with both Porod and Guinier scattering hypotheses, and thus better fitted using the Guinier-Porod (G-P) expression due to Hammouda [23], which provides subtle details on scattering model shape: sphere, rod, or plate. This approach was developed to define a radius of gyration from copolymer solution scatterers exhibiting distinct and independently verifiable structures, and has been applied to other soft matter systems [24,25]. The model is relatively flexible, applicable to rigid scatterers such as alumina [26], calcium carbonate [27], and silver copper alloys [28]. It should be noted that the particle-model shapes also relate to pore shapes used to derive similar, gas adsorption model-based, pore size distributions [29].

The concepts of scattering from relatively large objects, rough surfaces, and smooth surfaces developed with the application of fractal analyses to SANS [10,30]. Scattering from interfacial boundaries identified as pore surface-pore space interfaces typically occurs in the Porod region of SANS [31], and the concept of fractal geometry within a pore network is clearly envisaged via gas adsorption and probing pore networks with increasingly large molecules [32–34]. Mildner and Hall elucidated expressions for correlation functions and scattering intensities for fractal structures and fractal interfaces corresponding to large and small scattering vectors (due to relatively small and large dimension objects); both lie within the Porod region of scattering [30]. Generally, scattering intensity would show q^{D-6} dependence, where D would be the scattering object dimensionality. Reduction of data to Porod scattering, as q^{-4} dependence, implies relatively smooth boundaries (relative to the examining radiation wavelength) with $D = 2$ [18]. In contrast, roughened surfaces exhibit the range $2 < D < 3$, giving a non-integer power-law dependence on the scattering vector. At small scattering vectors a cross-over from Porod to Guinier behaviour in non-fractal systems occurs. Identification of this point was clearly demonstrated by Hammouda [23]. At still smaller scattering vectors, a cross-over from rough surface to volume scattering contributions occurs with a q^{-D} dependence. Schaeffer et al. suggested smooth interfaces would not exhibit q^{D-6} dependence [12] and, if the object were non-fractal, but had relatively rough interfaces, then adherence to Porod's law may not occur but a G-P transition might exist. Meticulous analyses of such subtle changes in the scattering data could provide details in terms of mass, surface, and/or pore fractal contributions, depending on the nature of the scattering object.

Carbonaceous structures have been examined via SAXS and/or SANS with varying levels of analysis of the reduced scattering data [19,35–38]. Use of these methods for silica structures has focused primarily on interpreting ordered, hierarchical structure formation [35,39–41]. The current work applied the essential theories of SANS analyses to samples of silica powders whose physical properties had demonstrated suitability as supports for ionic liquids and carbon dioxide sorption [8,9]. These analyses focused on structural details derived from G-P models [23]; application of the Power Law fitting model extended to and aided with defining selected fractal models rendering mass and/or surface fractal dimensions [18]. Excellent data fits were obtained for the G-P models applied to the disordered silica systems. Results for radius of gyration derived from mass-surface fractal model fitting to each system were consistent with those from the G-P modelling. Overall, these analyses served two purposes: They represented foundation studies for future more detailed SANS analyses of the same pores partially filled with ionic liquids [6,9], and would be the first of their kind applying this model to a series of rigid scatterers offering different scales of internal porous structure in solids with differing particle size distribution.

2. Experimental

2.1. Materials

Four commercially available silica samples were purchased and identified as S5, S12, S60, and S15. Sample S5 was the predominantly silica content zeolite H-ZSM-5 obtained as P26, reported as $(SiO_2)_{26}\cdot Al_2O_3$ with Na content < 0.1 wt%, water content < 5 wt%, particles ranging in diameter from 200 to 1000 nm, but predominantly ≈300 nm (Fig. S1a). Sample S12 was a nanoparticle-sized, fumed silica reported to have primary particle diameter of 12 nm with secondary particles consisting of 10–30 primary particles (Fig. 1), and bulk (powder) density $= 0.037$ g cm^{-3}. Sample S60 was a disordered, mesoporous SiO_2 reported to have a particle diameter in the range 35–70 μm [9]. Sample S15 was SBA-15 reported to have a mean (cylindrical) pore size of 8 ± 1 nm (Fig. S1b–d). Samples S5 and S15 were purchased from ACS Material LLC (Massachusetts, USA) and samples S12 and S60 were purchased from Sigma Aldrich (Sydney, Australia). Each was used as received.

2.2. Specific surface area and porosity analyses

For textural properties measurements, samples were degassed at 393 K and a background vacuum of 10^{-5} kPa for 12 h prior to the N_2 adsorption experiments, with the isotherms measured at 77 K using a Belsorp-Max gas adsorption apparatus for sample S15 and a Micromeritics TriStar II 3020 system for samples S5, S12, and S60. For each isotherm, ultra-high purity (>99.999%) helium and nitrogen from BOC Gases, Australia, were used for dead-space measurements and adsorption experiments, respectively. The specific surface area was calculated using the BET method and the pore size distribution was evaluated using the quenched solid density functional theory (QSDFT) [42].

2.3. SANS techniques

SANS experiments were performed on the QUOKKA instrument at the OPAL reactor (ANSTO, NSW, Australia) [43]. An incident wavelength of $\lambda = 5$ Å ($\Delta\lambda/\lambda = 10\%$) was used with sample-detector distances of 2, 12, and 20 m, giving a q-range of 0.00365–0.5010 Å^{-1}. Powdered