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Original Research Paper

Non-destructive high-resolution X-ray micro computed tomography for quantifying dry water particles

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ABSTRACT

Dry water, a powder containing up to 98%wt. water and 2–6%wt. hydrophobic nanoparticles, is a novel material for novel applications like CO_2 capture, transportation and storage in the form of clathrate hydrates. In this study, novel high-resolution X-ray micro computed tomography (HRXMT) was used as an in situ, non-destructive tool to visually and quantitatively examine the inner structure of dry water that has not been accessible previously. Specifically, the HRXMT was used to study the effect of silica/water wt. ratio on the number, surface area and volume distributions of dry water. The results showed that dry water was stable under ambient condition for long time. The technique was also successful in characterizing the structure changes in dry water after exposing to low temperature, high pressure and stirring. Low temperature did not affect the structure significantly, while high pressure and slow stirring broke the structure fairly readily with separation of dry water into the primary solid and liquid phases. These findings are useful to our understanding of the role of dry water in promoting the formation of CO_2 and gas hydrates.

1. Introduction

Dry water is a water-rich powder that consists of hydrophobic fumed silica which encapsulate up to 20 times its weight of liquid water. In 1968 this product was patented by Schutte et al. [1]. In this patent the procedure of encapsulating aqueous liquid media within fumed or pyrogenic silica was described. The process for making dry water involved breaking up the water into such fine discrete droplets and intimately contacting with a much finer hydrophobic silica powder. This process was later confirmed by Forney et al. [2] and Aussilous and Quéré [3]. Despite the number of applications that they suggested in their invention, little attention was devoted to this product until 2004 when Degussa introduced dry water for cosmetic chemistry. Degussa has shown that it can convert solutions containing water-dispersible pigments, vitamins, plant extracts and other active ingredients into powdered products. As the powder is rubbed onto the skin, the moisture trapped in the powder is efficiently released [4]. In 2006, Binks et al. [5] studied phase inversion of particle-stabilized air–water systems, from air-in-water foams to water-in-air powders and vice versa. They investigated the effect of silica particle wettability (hydrophobicity) on the product structure. They employed optical microscopy and scanning electron microscopy (SEM) to see the microstructure of the prepared powder and foam. Although these microscopic methods have given valuable information, there are a number of disadvantages with regards to the sample preparation for observation by microscopy. For example, dried samples in vacuum are required. However, in the dried state the foam becomes lumpy and crumbles easily. They also found that a slight difference in contact angle of silica nanoparticles may lead to very different product formation in high shear process (dry water, mousse or suspension). Eshtiaghi et al. [6] also showed how single dry water can be formed via the drop-template controlled method or via the mechanical dispersion method. In a proposed flow chart it is shown that the formation of mouse or dry water strongly depends on contact angle and the energy applied per unit mass of powder.

The operating conditions required to obtain dry water were studied by Forney et al. [2]. They characterized the powder by the water content, particle size distribution and flowability. To study the microscopic structure, Langmuir–Blodgett film deposition and SEM were employed to observe the films. In order to overcome the difficulties regarding the water evaporation in vacuum, they used a cryo-TEM (cryogenic transmission electron microscopy) freeze fracture method to observe the silica protective shell at the surface of dry water particles. Water ratio and particle size

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distribution were investigated using a differential scanning calorimeter and laser diffraction (an industrial size analyzer), respectively. This work was then expanded to study the mixing process characteristics in order to define critical parameters and to propose specific mechanisms of dry water formation [7]. The formation of dry water was explained based on the energy of immersion and adhesion [8]. They continued their research to establish that the success of encapsulation would depend on the relative importance of process-related parameters with respect to the physico-chemical properties of the material used [9].

In 2008 a new application for dry water was patented by Cooper et al. [10] who examined methane and carbon dioxide storage in dry water hydrates [11,12]. It was demonstrated that dry water increased the kinetics (the rate of gas uptake at a constant temperature) of formation of gas hydrates for CO_2, CH_4 and Kr. These findings were confirmed in another research with the focus on the gas storage application of dry water where the formation and dissociation rate and storage capacity of dry water methane hydrates were investigated [13]. Recently, a high capacity and improved reversibility was reported for a mixed colloidal system made of hydrogel particles and dry water particles [14].

Characterization of dry water is of critical importance for the detailed analysis of dry water performance in operations such as gas hydrate formation process and is essential for a better understanding and improved development of processes [15]. In general, the performance of dry water in gas adsorption might depend on the statistical characteristics of particle microstructures, such as particle shape, volume and interfacial area. In addition, since special conditions such as high pressure and low temperature and agitation [16] are required for hydrate formation, the changes in the structure of dry water under the conditions should also be investigated. To date, no research has been completed on the effect of high pressure and stirring on the structure of dry water. Conventional particle size analysis methods (e.g. sieving or sedimentometry) cannot be used to determine the special structure of dry water and its characteristics. Although the methods of studying the structure of dry water such as cryo-TEM microscopy [7] and confocal microscopy [17] are useful in investigating dry water, they do not provide statistical information about the size distribution of particles. Moreover, these methods require drying or freezing the sample which can change the structure of dry water particles.

In the current study low vacuum SEM and cryo-SEM have been examined initially to image the dry water samples. Despite the various sample preparation methods used, none of the techniques were successful for imaging the dry water sample because of the structural changes under vacuum or cryogenic conditions. Therefore, a non-destructive method was required to study the structure of dry water. In this regard, high resolution X-ray micro computed tomography (HRXMT) was used to probe the structure of dry water without disturbing the structure through sample preparation. This technique offers a unique capability for quantitative analysis of dry water through the direct acquisition of high resolution three-dimensional images. This novel method is capable of providing micron voxel (volume-of-element) resolution which was unavailable previously. The instrument takes a number of X-ray images of the sample from a variety of angles. Computers then stitch the 2D images together to build a 3D model of the structure. Digital data of the reconstructed 3D image are directly related to the composition of the material, therefore providing useful information [18].

With this apparatus, we established a new technique for the quantitative analysis of size distribution of dry water exposed to conditions of hydrate formation. It can be used not only to measure the physical parameters of a specimen such as inner space distribution but also to identify the water and air phases [15,19], and quantitatively analyze dry water samples with a much better accuracy than the previous available methods. With this non-destructive technique the inner structure of dry water can visually, correctly, and quantitatively be observed [19]. The dry water size distribution (number, surface area and volume) are then obtained and quantified. The influences of high pressure, low temperature and stirring on the structure of dry water have also been investigated by this method.

2. Experimentals

2.1. Materials

The hydrophobic fumed silica nanoparticles (5–30 nm, aggregates 100–1000 nm), kindly supplied by Wacker Chemie (HDK grade H180, were prepared by treatment of hydrophilic silica with dichlorodimethylsilane, replacing surface Si–OH with Si–O–$Si(CH_3)_2$. The water used for preparing solutions in this study was freshly purified using a setup consisting of a reverse osmosis RO unit and an ultrapure academic Milli-Q system (Millipore, USA). The gas used in this work for pressurizing the samples was food grade carbon dioxide provided by Coregas with 99% purity.

2.2. Dry water preparation

Having high surface free energy, ultra-fine particles tend to agglomerate in water. Because of their high hydrophobicity H18 particles agglomerate at the air/water interface. Therefore, a high speed blender (kitchen style blender, Bamix® mono, 14000 rpm) was used to produce dry water particles. Various samples of dry water with different silica to water ratio were prepared for testing. Required amount of silica powder and deionized water was weighted and poured into a glass beaker. Then mixed vigorously with high speed of 14000 rpm for 3 min in three 1-min bursts to maximize the homogeneity. A small amount of each dry water sample was taken for HRXMT scanning. In the next step, 60 g of the produced free flowing dry water powder was easily poured into the stainless steel vessel without any residue. Depending on the parameter which was the subject of the tests the samples were then cooled down to 3 °C, pressurized to 500 psi or stirred for required periods with speed of 120 rpm. The cooled, pressurized or stirred dry water samples were taken for HRXMT scanning.

2.3. HRXMT apparatus and pressure vessel

2.3.1. HRXMT

In the current work, for the direct examination and analysis of dry water which varies in size from a few mm down to a few μm, a cone beam CT (VersaXRM-500, Xradia, USA) was used. It provides fast data acquisition and better X-ray utilization. It is a valuable tool for 3D visualization, characterization and analysis of multiphase systems at a voxel resolution smaller than $10 \times 10 \times 10\ \mu m^3$. Fig. 1 shows a schematic of the HRXMT system with X-ray hardware and X-ray optics used in this study. Samples were set in a cylindrical holder with the internal diameter of 8.3 mm and length of 3 cm mounted on a precision rotating stage. During the measurements of the structural images a cone-shaped X-ray was emitted from a 2-μm aperture and the samples rotated through 360∘. The scan image resolution was approximately 10 μm.

The HRXMT raw data were collected at 0.225° angle resolution for a total of 1600 sets, and then processed into a reconstructed image of the sample cross section. For the 3D images, the resolution was given by a 16-bit grey scale with 1024×1024 pixels. In the measurements, the X-ray tube voltage was 60 kV and the