Original Research Paper

A comparative study of hydrophobic silica particle synthesis

Frances Neville [a,b,*], Lewis Dixon [a], Emily D.E.R. Hyde [c]

[a] School of Environmental and Life Sciences, The University of Newcastle, Callaghan, NSW 2308, Australia
[b] Priority Research Centre for Advanced Particle Processing and Transport, The University of Newcastle, Callaghan, NSW 2308, Australia
[c] School of Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia

ABSTRACT

The process to commercially synthesise silica particles with specific properties is a topic of ongoing research since their use in industrial applications including catalysis, coatings and separation materials has dramatically increased in the last decade. Here, silica particles were made using hydrolysed trimethoxymethylsilane (TMOMS) in the presence of either polyethyleneimine or aqueous sodium hydroxide catalysts. This work presents the first in depth study of the effect of TMOMS concentration on silica particles produced by both of these synthetic methods by comparing their size, morphology and chemical structure. The PEI-silica particles were larger in size and greater in yield than the NaOH-silica particles. It was also determined that both species of silica particles are hydrophobic without requiring further surface modification; and that those made with PEI have a higher contact angle, perhaps due to more complete polymerisation. The results demonstrate how relatively facile synthesis routes can wield a high degree of control over the physicochemical properties of silica particles, which is of paramount importance in silica production process intensification.

© 2016 The Society of Powder Technology Japan. Published by Elsevier B.V. and The Society of Powder Technology Japan. All rights reserved.

1. Introduction

The global demand for spherical silica particles is predicted to grow by around 6% per year over the next few years [1] as they are used in a range of engineering and biomedical applications including catalysis [2–4], biosensors, biotechnology [5–8] and drug delivery [9–13]. This wide range of applications is possible because the physical, electrical and optical properties of these particles are determined by their size and morphology [1], which are tuneable in the synthetic process. Additionally, silica particles are utilised in surface coating technologies including: self-cleaning [14,15], anti-icing [16] and anti-biofouling surfaces [17,18], which primarily harness the wettability of the silica particle surface [19]. The wettability of a surface is concerned with a solid surface's interactions with a liquid interface and is typically evaluated by determining the contact angle between a sessile droplet and the solid surface [20,21].

The synthesis of colloidal silica particles occurs by the hydrolysis and subsequent condensation polymerisation of an alkoxysilane. The Stöber method of synthesis [22] utilises 14 M ammonia as a basic catalyst to hydrolyse and polymerise either tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) in 5 M methanol. The harsh conditions required by the Stöber process [22] are not ideal in a society trending towards more environmentally friendly methods [23]. In 2001, Dingsøyr and Christy [24] determined that ammonia could be replaced with sodium hydroxide to hydrolyse and polymerise TEOS in an ethanol medium. However, the disadvantages of requiring harsh conditions and an organic reaction medium still exist for the Dingsøyr and Christy technique [24].

Neville et al. [1,6,25] replaced the ammonia catalyst and organic reaction medium with polyethyleneimine (PEI) and a phosphate buffered (PB) aqueous solution of mild pH. The use of the highly toxic TMOS was replaced with trimethoxymethylsilane (TMOMS), which is far less hazardous [23]. The use of TMOMS over the traditionally used alkoxysilane, TEOS, may be preferential in commercial applications of synthetic silica production as it undergoes a

much faster reaction [26]. The method using TMOMS and PEI/PB will be referred to as the PEI-silica method hereafter.

The mechanism of PEI induced silica formation proposed by Neville and Seyfaee [25] suggests that positively charged PEI in solution forms aggregates with phosphate anions from the buffer solution to form particle nuclei. The silica source, hydrolysed TMOMS, has a negative surface charge above pH 3 [27], and is drawn to the positive charge of the PEI-anion nuclei causing the silica particles to form primary particles, which then aggregate into larger colloidal particles [1,25,26]. This particle formation mechanism was recently characterised in greater depth by Seyfaee et al. [26], who demonstrated that the formation of the spherical silica colloids, in the PEI-silica reaction, involves three discrete phases: nucleation time, a growth region and an equilibrium region.

Despite the knowledge of the PEI-silica method, the relative expense of PEI may prove prohibitive to its scalability, and ultimately commercialisation. Hyde et al. [28] recently developed a synthesis process whereby the PEI/PB catalyst was replaced with a low concentration of sodium hydroxide. This method will be referred to as the NaOH-silica method from hereon.

In this study we investigate the differences of particles produced using the PEI-silica and NaOH-silica methods. We will study how the concentration of the silica precursor affects the size of the silica particles made using the two different routes, for the first time, since the effect of the concentration of the silica precursor has not been studied to date. In addition, this study aims to evaluate the characteristics of surfaces created from silica particles produced via both synthetic methods by measuring their contact angles via two methods, as a preliminary investigation into their potential applications as hydrophobic particles.

2. Experimental section

2.1. Materials

Trimethoxymethylsilane (TMOMS), hydrochloric acid (HCl), sodium hydroxide (NaOH), disodium hydrogen phosphate dihydrate ($Na_2HPO_4 \cdot 2H_2O$), sodium dihydrogen phosphate (NaH_2PO_4) and branched 25 kDa polyethyleneimine (PEI) were purchased from Sigma-Aldrich, and used without further purification. All washing and solution preparation utilised deionized water (18.2 MΩ cm).

The 290 mM phosphate buffer (PB) was comprised of 290 mM NaH_2PO_4 and Na_2HPO_4 added in such quantities as to make the pH of the final solution 7.4.

2.2. Silica particle synthesis using the PEI-silica and NaOH-silica methods

PEI-silica (made with TMOMS and PEI/PB) and NaOH-silica (made with NaOH and TMOMS) particles were synthesised utilising variations of the synthesis methods previously described by Neville et al. [23] and Hyde et al. [28], respectively. The final TMOMS concentrations in the reactions ranged from 0.1 to 0.5 M, at 0.1 M increments. For each increment eight replicates were synthesised to increase precision. All particle syntheses commenced with the hydrolysis of 1.0 M TMOMS in 1 mM HCl. The hydrolysis solution was mixed using a vortex mixer and left to hydrolyse for 15 min before use in the reaction.

2.2.1. PEI-silica particle synthesis method

Particles were synthesised in 1 mL microcentrifuge tubes. A volume of hydrolysed TMOMS dependent on the final concentration required was added to a prepared solution of PEI and PB (with final

reaction concentrations of 0.1 mM PEI and 29 mM PB). The final concentrations of TMOMS were 0.1, 0.2 0.3, 0.4 and 0.5 M. Once combined, the solutions were thoroughly vortex mixed and then left to react for 30 min, after which the reactions were stopped by centrifugation for 30 s at 16,500g and removal of the supernatant. All samples were then washed twice with water using redispersion by sonication, and subsequently centrifuged for a further 30 s at 16,500g.

The mass yield of the dry particles was measured. From the mass yield, the weight percentage yield was calculated for each set of particles for a particular TMOMS concentration with respect to the weight percent of hydrolysed TMOMS or TMOMS and PEI used.

2.2.2. NaOH-silica particle synthesis method

The 'NaOH-silica method' synthesis used precisely the same quantities and processes identified above for the PEI-silica synthesis. However, instead of a solution of PEI and PB, the various volumes of hydrolysed TMOMS were added directly to a NaOH solution with a final reaction concentration of 25 mM. The particles underwent the same reaction time and purification steps as outlined in Section 2.2.1, with the exception of the 0.1 M TMOMS NaOH-silica particle sample. The 0.1 M TMOMS NaOH-silica samples did not produce particles within the 30 min reaction time and as a result they were left to react for one week before centrifugation and washing was performed.

The mass yield of the dry particles was measured. From the mass yield, the weight percentage yield was calculated for each set of particles for a particular TMOMS concentration with respect to the weight percent of hydrolysed TMOMS used.

2.3. Particle characterisation

2.3.1. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy

ATR-FTIR measurements were performed using a Spectrum Two (Perkin-Elmer) instrument. The silica samples were dried via desiccation for at least a week before spectroscopic examination. An air background was taken before measurements of the dried samples were undertaken.

2.3.2. Dynamic light scattering (DLS)

A Malvern Nano ZS ZetaSizer was utilised to measure the size of the silica samples suspended in deionized water (18.2 MΩ cm). The approximate particle concentration was 1 mg/mL. For each type of particle, the mean intensity was calculated from three measurements, which were each the average of five runs. The error associated with each mean was calculated as the standard deviation within the particle size distribution population of that particular type of sample.

2.3.3. Scanning electron microscopy (SEM)

A drop of each sample suspension was deposited onto an aluminium stub and air-dried. The stubs were then sputter coated with gold for analysis using a Philips XL30 SEM. The sizes of the particles captured in the SEM images were determined using the freeware UTHSCSA Image Tool [29].

2.3.4. Contact angle measurements

Two methods were used to obtain the contact angles of the silica particles produced via the PEI-silica and NaOH-silica methods. In the first method the particles were deposited directly on to glass slides and in the second method disks of the particles were produced.

For silica particle deposition on clean glass slides a 10 mg/mL suspension in hexane was used. The particle coated slides were left