



Decontamination Foam Containing Silica Nanoparticles of Various Structures†

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The purpose of the present study is to investigate the silica nanoparticles of various structures for their foam stability and dissolution using decontamination foam. Silica nanoparticles of various structures such as mesoporous, core-shell and non-porous silica nanoparticles were synthesized for an evaluation of decontamination foam. Compared to foam stabilized with only 1 % Elotant™ Milcoside 440N (EM440N) surfactant, the addition of 1 wt. % mesoporous nanoparticles improves the foam stability by a factor of 8. The oxide dissolution was evaluated using decontamination foam with silica nanoparticles and 1 M HNO₃ using corroded specimens. The mixture of mesoporous nanoparticles in the surfactant improves the oxide dissolution by a factor of 2 compared with the surfactant only. These results indicate that the mesoporous silica nanoparticles improve the foam stability and oxide dissolution owing to an enhancement in the contact time of the chemical reagent and the corroded specimen.

Keywords: Decontamination foam, Silica nanoparticles, Foam stability, Oxide dissolution.

INTRODUCTION

Decontamination foam comprises a surfactant to generate the foam, a co-surfactant in the form of a long-chain alcohol to reduce the total number of surfactants and chemical reactants to dissolve the contaminants on a solid surface¹. To increase the decontamination efficiency of this process, the contact time of the chemical reactants to the contaminated surface should be increased. Therefore, the present research is focused on increasing the contact time by adding a viscosifier, which is a biopolymer or inorganic materials such as silica nanoparticles to the solution of decontamination foam.

Silica nanoparticles increase the foam stability in the foam formulation. These particles can be specifically hydrophobized for optimal adsorption at the liquid/gas interface, which creates armor for the bubbles and prevents coarsening by reducing the internal gas transfer²⁻⁴. Conversely, hydrophilic particles remain confined in the liquid phase and to enhance the foam stability. Kruglyakov and Taube⁵ studied the drainage of foams generated from a non-ionic surfactant suspension of pyrogenic silica. Their results showed that the loss of liquid is slightly slowed down when particles are present because of the steric hindrance to the liquid flow.

Synthesis of mesoporous silica nanoparticles with various sizes, shapes and structures has been reported owing to their many emerging applications such as catalytic supports or highly efficient packing materials for high resolution separations in high-performance liquid chromatography (HPLC) and electro-chromatography⁶. Control of the morphology of the mesoporous silica nanoparticles such as core-shell, rod-like and hexagonal shapes is one of the important research fields for practical application. As a synthetic strategy for controlling the particle size, shape and porosity, varying the amount of cationic surfactant and base catalyst was proposed^{7,8}. In this study, we aimed to synthesize various silica nanoparticles structures such as mesoporous, core-shell and non-porous structures using methods proposed in previous papers. We also investigated the effect of synthesized silica nanoparticles for the foam stability and oxide dissolution using chemical reagents.

EXPERIMENTAL

Synthesis of various silica nanoparticles: The non-porous silica nanoparticles were synthesized using a method shown in a previous paper⁹. As a typical procedure, the silica seed nanoparticles were synthesized by adding tetraethylorthosilicate (TEOS; 25 mL) into the mixture consisting of absolute

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ethanol (1000 mL), deionized H₂O (10 mL) and 28 wt. % NH₄OH (25 mL) and stirring for 24 h at ambient temperature. The silica seed solution (24 mL) was then suspended in the mixture solution of absolute ethanol (1000 mL), DI H₂O (80 mL) and 28 wt. % NH₄OH (40 mL). After stirring for 0.5 h, tetraethylorthosilicate (40 mL) was added into the above reaction mixture and stirring was continued for 6 h under the same conditions. Finally, the mixture had the addition of tetraethylorthosilicate (80 mL) and was stirred for 6 h more.

For synthesis of the mesoporous core-shell silica nanoparticles, 10 mL of the suspended silica nanoparticles in a mother liquor was dispersed in 20 mL of deionized water containing 0.1 mL of 28 wt. % aqueous ammonia. The surfactant solution (CTABr, 0.06 g) dissolved in the mixture at a ratio of water to ethanol of 2:1 was added into the reaction mixture solution. After stirring for 1 h, tetraethylorthosilicate (0.11 mL) was added to the above reaction mixture and stirred for further 10 min. The reaction mixture was then left at 343 K overnight. The as-synthesized samples were retrieved by centrifugation, then dried at 343 K overnight and calcined at 823 K for 5 h under an air atmosphere.

In the synthesis of the mesoporous silica nanoparticles with various sizes, a mixture solution consisting of cetyltrimethylammonium bromide (CTABr; 2.4 g), 28 wt. % NH₄OH (7.5-30 mL) and deionized H₂O (900 mL) was vigorously stirred for 0.5 h until reaching a clear solution. The mixture was added using tetraethylorthosilicate (12.9 mL) and stirring was maintained for 1 h. After a while, the reaction mixture was left at 343 K overnight. The as-synthesized samples were retrieved by centrifugation, dried at 343 K overnight and calcined at 823 K for 5 h under an air atmosphere.

Stability test for the decontamination foam: The foam stability was measured using a Foamscan instrument. The foam was generated by blowing nitrogen gas at a flow rate of 200 mL/min through a porous glass filter at the bottom of a glass tube where 60 mL of the foaming aqueous solution at ambient temperature is placed. In all experiments, the foam was allowed to reach a volume of 200 mL. The bubbling was then stopped and the evolution of the foam was analyzed using conductivity and optical measurements. The silica nanoparticles with various structures such as mesoporous, core-shell and non-porous of 1 wt. % were added to a 1 % Elotant™ Milcoside 440N (EM 440N) surfactant solution to investigate the foam stability compared with only 1 % surfactant.

Oxide dissolution test using decontamination foam: In an oxide dissolution test, 304 stainless steel specimens 20 mm × 20 mm × 2 mm in dimension were used. The corroded layer

of the specimens was grown in a semi-loop filled with solution composed of 650 ppm H₃BO₃ and 2.2 ppm LiOH and operated at 350 °C in 2500 psi, simulating the condition of the primary coolant system in light water reactors. Non-porous and mesoporous silica nanoparticles of 1 wt. % were added to a 30 mL of 1 % EM 440N surfactant solution containing 1M HNO₃ and compared to the foam stabilized only with Elotant™ Milcoside 440N (EM 440N). About 100 mL of decontamination foam was prepared by shaking the 30 mL of decontamination foam for 10 s. The concentration of dissolved iron from the specimens was measured by flame-atomic absorption spectroscopy (AAS).

RESULTS AND DISCUSSION

Characterization of various silica nanoparticles: Fig. 1 shows TEM and SEM images of the non-porous, core-shell with a silica core and mesoporous shell, and mesoporous silica nanoparticles. As shown in Fig. 1, the non-porous (Fig. 1a) and core-shell (Fig. 1b) silica nanoparticles exhibited a monodispersive size of 200 nm in diameter and uniform mesoporous shell of 20 nm in thickness, respectively. The pore structures of the mesoporous silica nanoparticles exhibited a size of 50 nm in diameter and the existence of an ordered hexagonal array from the result of the TEM and XRD analyses (data not shown). To investigate the structural properties of the core-shell and mesoporous silica nanoparticles, N₂ sorption isotherms and their corresponding pore size distribution were measured. The resulting materials exhibited a type IV isotherm characteristic of mesoporous materials according to the IUPAC nomenclature owing to the presence of uniform mesopores. The BET surface area, total pore volume and average pore size of the core-shell and mesoporous silica nanoparticles were 251 and 808 m²/g, 0.22 and 0.84 cm³/g and 3.49 and 4.18 nm, respectively.

Foam stability of various silica nanoparticles: In Fig. 2a, while the foam volume without silica nanoparticles decreased and remained at 145 mL after 1 h, the foam volume remained at over 160 mL with mesoporous silica nanoparticles. This figure also shows that the foam volume with 1 wt. % mesoporous silica nanoparticles was higher than that with other nanoparticles. In Fig. 2b, the liquid volume in foam with non-porous silica nanoparticles was not different without silica nanoparticles. The increased liquid volumes in foam were observed to be 5.7 times higher with core-shell silica nanoparticles (1.95 mL), compared with only surfactant (0.34 mL). The size of the core-shell silica nanoparticles was similar with that of non-porous silica nanoparticles. However, the liquid

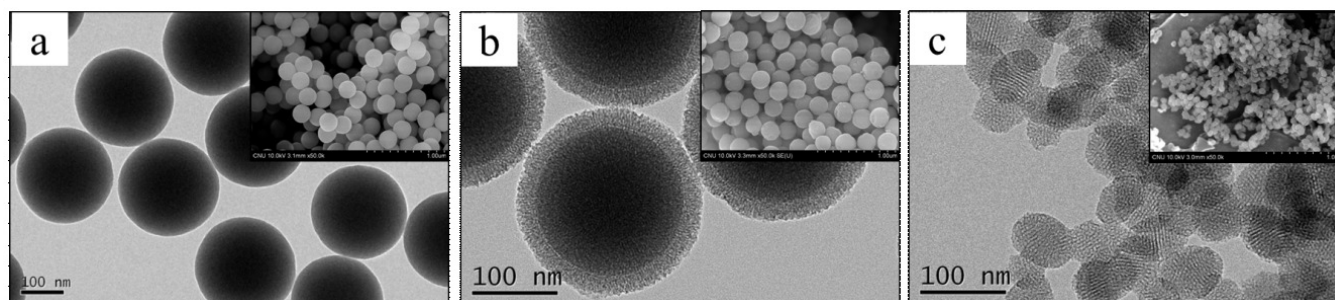


Fig. 1. TEM and SEM (inset) images of (a) non-porous, (b) core-shell and (c) mesoporous silica nanoparticles

volume in the foam of core-shell silica nanoparticles was higher than that of non-porous silica nanoparticles owing to the low density and high porosity of the mesoporous shell. The increased liquid volumes in foam were observed to be 8.2 times higher with mesoporous nanoparticles (2.78 mL), compared with only surfactant. This result indicated that mesoporous silica nanoparticles increase the foam stability (Fig. 2b). The use of the mesoporous silica nanoparticles with a lower density and smaller size showed an enhancement of the foam stability owing to their structural difference such as relatively high specific surface area, large pore volume and porosity.

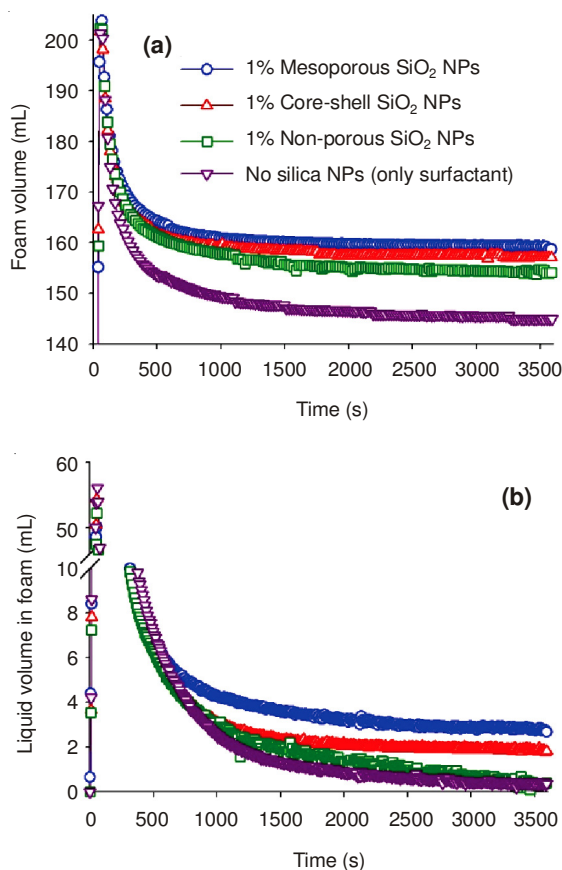


Fig. 2. (a) Foam volume and (b) liquid volume in foam for various structures of mesoporous, core-shell and non-porous silica nanoparticles compared with surfactant only (experimental conditions: 1 % EM 440N and 1 wt. % various silica nanoparticles for 1 h)

Oxide dissolution test using decontamination foam: In an oxide dissolution test, 1 wt. % mesoporous and non-porous silica nanoparticles were added to the decontamination foam containing 1 M HNO₃. The amount of dissolved iron from corroded layer of the specimen using EM 440N foam was 1.23×10^{-2} mg, whereas the level of dissolved iron using non-porous and mesoporous silica nanoparticles increased 1.46×10^{-2} and 2.14×10^{-2} mg, respectively (Fig. 3). The mixture of mesoporous nanoparticles in the surfactant improves the oxide dissolution by a factor of 2 of dissolved iron compared with the surfactant only. By comparing the relationship between the oxide dissolution and foam stability, three data points of the time for liquid volume to fall to one-tenth (Fig. 2b) was plotted in Fig. 3. The addition of 1 wt. % non-porous and mesoporous silica nanoparticles improves the time for liquid volume to

fall to one-tenth, compared with only surfactant (Fig. 3). The time for the liquid volume to fall to one-tenth is related to the concentration of dissolved iron. These results indicated that the increase of stability in the foam accommodates the dissolution of iron, enhancing the contact time of the chemical reagent to the corroded specimen. Our finding obeys Faure *et al.*¹⁰ observation that the oxide dissolution is proportional to the contact time.

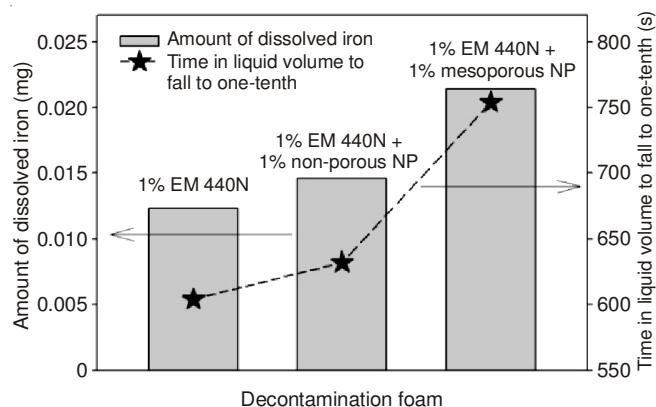


Fig. 3. Concentration of dissolved iron from corroded layer of the specimen using bottle tests of decontamination foam and the time in liquid volume to fall to one-tenth

Conclusion

This study showed the effect of silica nanoparticles with various sizes and structures on the foam stability and oxide dissolution when developing new formulations of decontamination foam. The results indicate that mesoporous nanoparticles have a significant effect on the foam stability and oxide dissolution because of a lower density and smaller size owing to a high specific surface area, large pore volume and porosity. In future studies, hot decontamination tests will be conducted using decontamination foam that contains mesoporous silica nanoparticles on a corroded surface contaminated with radio-nuclides.

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