Size-Controllable Calcium Carbonate Crystals by Homologous Series of Anionic Surfactants

Atthaphon Maneedaeng, Adrian E. Flood, Suchitra Phithaksoemsak

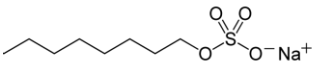
School of Chemical Engineering, Suranaree University of Technology,
111 University Ave, Muang District, Nakhon Ratchasima 30000 THAILAND

atthaphon@sut.ac.th

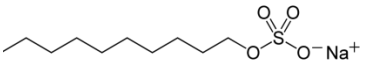
One of the challenges for materials scientists and engineers is to control and manipulate the shapes of materials on the nanometer scale, as different shapes of the nanostructures can exhibit novel electronic, optical, or magnetic properties (He et al., 2005). It is commonly known that different $CaCO_3$ particles polymorphic forms and particle sizes can essentially affect their practical applications. Calcium carbonate ($CaCO_3$) particles appear to be essential as an effective additive for pulp and paper industry with special and new characteristics (Wang et al., 2009). They are also employed as filler in plastics industry in order to investigate into polymer cleavage energy proven that the addition of nanometric fillers such as $CaCO_3$ favors the increase of homopolymers and copolymers plastic rigidity and characteristics (Chen et al., 1989). Recently, $CaCO_3$ nanoparticles revealed the method to the controlled release of bioactive molecules, and constituted a hot topic of research receiving a considerable attention (Haruta et al., 2003). Consequently, the control of morphology and particle size is crucial in optimizing their efficiencies.

The templated reactive crystallization of inorganic nanoparticles in amphipathic systems is a third area where development has been made over the last few years. In order to control morphology of inorganic nanocrystals, organic additive such as surfactant, is typically introduced to the synthetic reaction to manipulate the nucleation and growth of the nuclei. There have been numerous researches on single surfactant-assisted synthesis of inorganic compounds but the effect of hydrocarbon chain length on the synthesized crystal morphology is still lacking. Thus, this work aims to investigate the effect of homologous surfactants in both single and binary mixed systems on the size and shape of $CaCO_3$ particles.

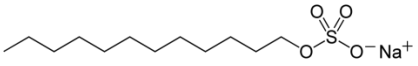
In this work, $CaCO_3$ was obtained by reactive crystallization of sodium carbonate (Na_2CO_3) and calcium chloride ($CaCl_2$) with the presence of different molar concentrations of homologous anionic surfactants in aqueous solution. Sodium octylsulfate (NaOS), sodium decylsulfate (NaDeS), and sodium dodecylsulfate (NaDS) of both single and binary mixed systems were used above their critical micelle concentration as the templates at 30°C. The reaction was carried out for 48 hours to allow the systems to reach the equilibrium. All the collected synthetic $CaCO_3$ particles were calcined at 400°C for 2 hours to remove surfactant template and organic impurities. The white $CaCO_3$ powder was collected and characterized by XRD, SEM and Mastersizer to investigate the morphology changes.



Sodium Octylsulfate



Sodium Decylsulfate



Sodium Dodecylsulfate

The formed $CaCO_3$ for all systems is identified as calcite by X-ray diffraction analysis as shown in Fig. 1 and the estimation of single nanocrystals of $CaCO_3$ is done by Shcerrer equation. SEM image analysis and Mastersizer give the shape and particle size distribution as shown in Fig. 2. Square and rhombic $CaCO_3$ crystals with equivalent diameter of 2.22 μm are observed for a crystallization system without any surfactant assistance as shown. The different carbon atoms in each surfactant molecules reveal the change in shape and size of $CaCO_3$ particles for the surfactant-assisted crystallization systems. At specific concentrations of surfactants used, flower-like and hexagonal flat sheet $CaCO_3$ crystals are observed in NaOS systems with equivalent diameter of 4.62 μm, NaDeS systems generate the rugged spherical shape with equivalent diameter of 3.91 μm and the perfect spherical crystals are observed in NaDS systems with the equivalent diameter of 2.00 μm. It is suggested that longer hydrocarbon chain length in homologous series of anionic surfactants produces the smaller $CaCO_3$

particles. Presumably, the formation of micellar phase appears to influent the morphology change of crystals in solution phase. Surfactant concentration variation results in insignificant change of crystal size in this work, however, it has an apparent effect on its shapes.

For equimolar binary surfactant-assisted crystallization systems: NaOS/NaDeS, NaOS/NaDS, and NaDeS/NaDS, the different carbon atoms of surfactant tails in the mixed micelles generate the smaller size of $CaCO_3$ crystals comparing to their sizes in single surfactant systems. Additionally, surprising result shows that spherical and needle-like shapes of $CaCO_3$ crystals are obtained in these mixed surfactant systems. More results and detailed discussion will be given in the oral presentation.

References

[1] J.H. He, C.S. Lao, L.J. Chen, D. Davidovic, Z.L. Wang., Journal of the American Chemical Society, **127** (2005) 16376.

[2] S. Wang, X.P. Li, E.L. Mao, Z.Y. Cheng, Advanced Materials Research, **236-238** (2009) 1124.

[3] L.-S. Chen, Y.-W. Mai, B. Cotterell, Polymer Engineering & Science, **29** (1989) 505.

[4] S. Haruta, T. Hanafusa, H. Fukase, H. Miyajima, T. Oki, Diabetes Technology & Therapeutics, **5** (2004) 1.

Figures

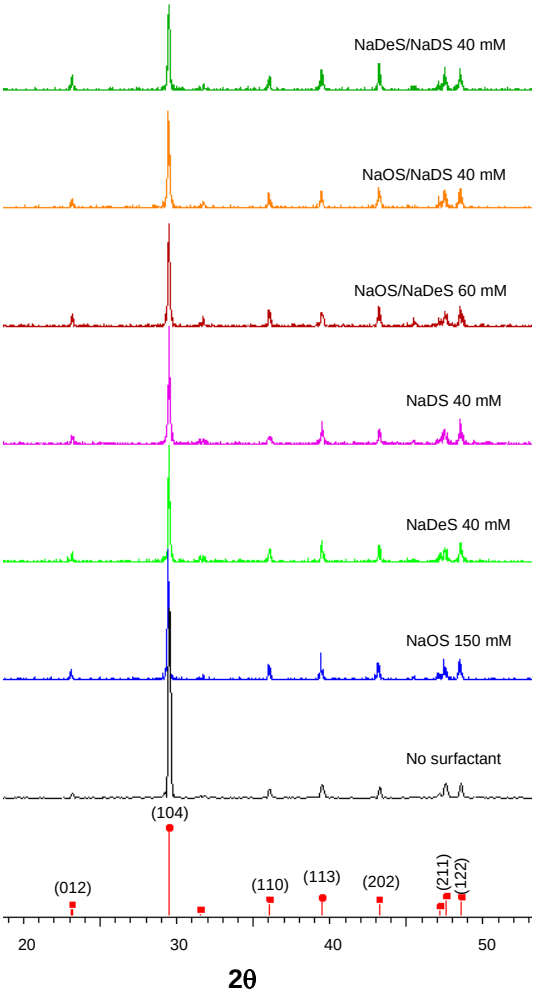


Fig 1: The selected XRD patterns of calcite $CaCO_3$ with homologous series of surfactants assisted synthesis.

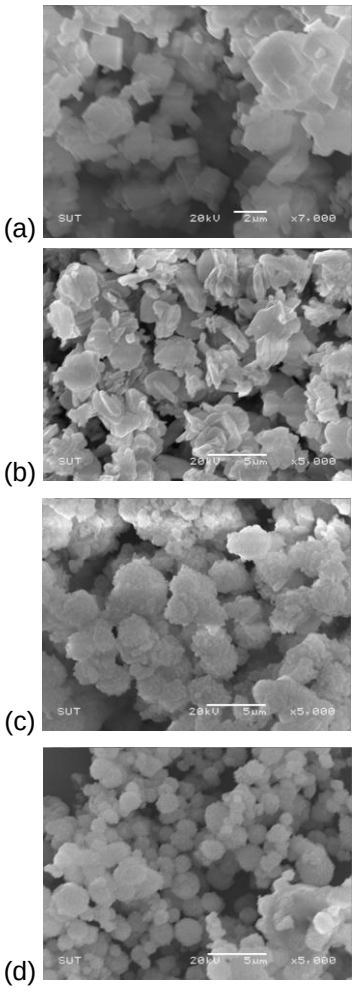


Fig 2: the selected SEM images of calcite $CaCO_3$ with homologous surfactant assisted synthesis: (a) absence of surfactant (b) NaOS 300 mM (c) NaDeS 40 mM (d) NaDS 40 mM.