MTE-44

Synthesis of Silica Nanoparticles with Controlled Morphologies by Controlling the Reaction Parameters of Sol-Gel Process

I. A. Rahman[1], P. Vejayakumaran[1], C. S. Sipaut[1], M. A. Bakar[1], J. Ismail[1], R. Adnan[1] and C. K. Chee[2]

[1]*School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia. Tel:+60-046537888 x 4021, Fax:60-046574854, E-mail: arismail@usm.my*

[2]*Intel Technology (M) Sdn Bhd, Bayan Lepas FTZ Phase III, 11900 Penang, Malaysia.*

Abstract

A series of investigations were induced to study the formation, growth and methods to control the size of silica particles via sol-gel process. The key parameters that affect the particle size i.e. concentration of TEOS (tetraethylorthosilicate), NH_3, H_2O and feed rate of catalyst were extensively studied. At lower NH_3 concentrations, stable sols of ~ 30 nm particles were formed while high concentrations leads to the formation of bigger, spherical particles with sizes varying from 90 - 700 nm. The increase in TEOS concentration resulted in bigger and multi-modal distributed silica particles. However, high H_2O concentration and slow feed rate produced smaller particles around 10 - 14 nm, as a result of controlled reactions or particle growth. The kinetics of the overall reactions of TEOS under various conditions was monitored using conductivity studies.

Keywords: Silica, Sol-Gel Process, Reaction Parameters.

Introduction

The need for well-defined nanoscale materials (e.g. silica, zinc oxide, metals etc.) which exhibits excellent properties compared to its bulk counterpart has increased as high tech industries provide an elevated demand for such material [1,2]. Silica nanoparticles have been utilized as electronic substrates, thin films, electrical or thermal insulators, stabilizers and etc [1,3]. Besides material based industries it is also used in biotechnology and pharmaceutical applications. The performance of these products highly dependent on the size and distribution of the silica particles [4]. Varying levels of metal contaminants and wide size distribution of commercial silica [4] promotes initiatives to produce narrow distributed and highly pure silica particles especially to conduct model studies [5].

The sol-gel process is widely applied to produce ceramic materials due to its ability to form pure and homogenous products at mild conditions. Stöber process which involves hydrolysis and condensation of tetraethylorthosilicate (TEOS) under alkaline conditions in ethanol is capable of producing monodispersed, spherical silica nanoparticles [6]. Bogush and Zukoski [7], successfully prepared monodispersed silica particles in the range of 40 nm to few micrometers using almost similar method. The authors believe that concentration of TEOS, concentration of ammonia, concentration of water, solvent and reaction temperature are the five key parameters which govern the particle size and distribution. S. K. Park et. al. [4] conveniently prepared ultra fine silica particles within the range of 9.2 – 18.2 nm, using optimized conditions determined from statistical simulations. Kim et al. [8] reduced the particle size up to 17.5 nm through addition of small amount of NaI during the synthesis. Recently, Rahman et al. [9] reported that monodispersed silica in the range of 17.0 – 24.0 nm can be synthesized by introducing small amount of NH_4Br into the sol-gel system.

The general reactions of silicon alkoxide which leads to the formation of silica particles can be written as:

$$Si(OR)_4 + H_2O \xrightarrow{\text{hydrolysis}} Si(OR)_3OH + ROH \quad (1)$$

$$\equiv Si\text{-}OH + HO\text{-}Si\equiv \xrightarrow{\text{water condensation}} \equiv Si\text{-}O\text{-}Si\equiv + H_2O \quad (2)$$

$$\equiv Si\text{-}OR + HO\text{-}Si\equiv \xrightarrow{\text{alcohol condensation}} \equiv Si\text{-}O\text{-}Si\equiv + ROH \quad (3)$$

Two different models can be used to describe the particle formation and growth of silica particles. The monomer addition model [10-11] presumes an initial burst of nucleation, followed by addition of hydrolyzed monomers to the particle surface. On other hand, the controlled aggregation model [7,12] explains that the nucleation occurs throughout the reaction and the resulting nuclei (primary particles) will aggregate together to form larger particles (secondary particles). Based on these models, the particle size can be reduced by controlling the growth of the primary units formed in the earliest stages of the reaction.