

Continuous flow synthesis of submicron silica particles: Reaction kinetics and optimization

Rajashri Jundale¹, Atul Bari¹, Chinnu Thara², R. Nandini Devi², Amol Kulkarni^{1*}

¹ Chem. Eng. Proc. Dev. Division, CSIR-National Chemical Laboratory, Pune-411008, India

² Catalysis Division, CSIR -National Chemical Laboratory, Pune-411008, India

*Corresponding author: aa.kulkarni@ncl.res.in

Highlights

- Continuous synthesis of submicron Silica particles in flow reactor is carried out.
- Effect of various process parameters has been studied.
- Hydrolysis and condensation rate constants were found out.
- Nucleation and growth kinetics will be estimating based on monomer addition model.

1. Introduction

Monodisperse Silica particles have drawn great attention in scientific community because of their important applications in various fields such as catalysis, ceramics, biomedical, electronics. As they exhibit variations in size, shape, and structure dependent properties, their synthesis requires superior control of reaction; both kinetically and thermodynamically [1]. Over last two decades, microfluidic reactors are shown to play an important role in nanomaterial synthesis since it offers unique features like precise control of reaction, safer operation, high surface area to volume ratio, easy scale up through continuous process and kinetic control of particle formation. In this work, we have synthesized silica particles of controllable and uniform size in tubular reactors using modified Stober process. Synthesis involves the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in ethanol and water, using ammonia as catalyst [2]. The purpose of this study is to determine the hydrolysis and condensation kinetics and particle growth data, which will help to test theories of nucleation and growth kinetics.

2. Methods

A stainless steel coil [SS316, 26 ml] having multiple outlets was used as a flow reactor. The assembly was immersed in a constant temperature bath. An Amar3 micromixer (0.3 ml volume) was used for mixing of reactants at the inlet and reaction took place along the reactor length. A schematic diagram of continuous coil reactor is shown in figure 1.

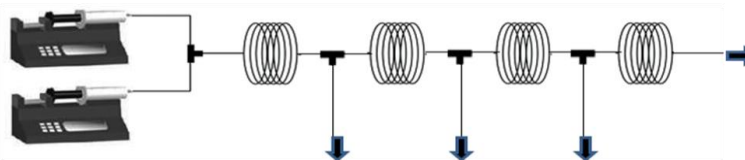


Figure 1: Schematic diagram of microfluidic reactor

Rate of hydrolysis and growth kinetics were studied by measuring the changes in particle size and soluble silica concentration. To determine the hydrolysis rate of TEOS, we have followed the molybdate method recommended by Alexander [3, 4] and soluble silica concentration was monitored by atomic absorption spectrophotometer. Particle morphology was checked using field emission scanning electron microscopy (FESM), while dynamic light scattering (DLS) was used to measure particle size distribution.

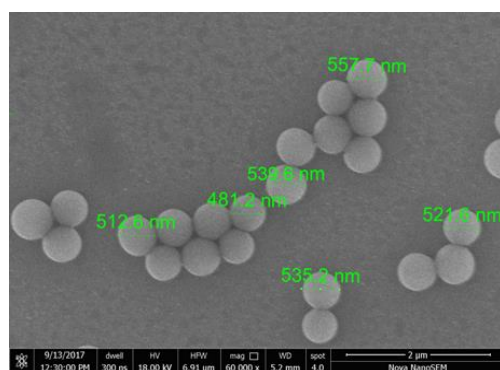
3. Results and discussion

The initial Experiments were carried out to explore the effect of temperature, water and ammonia concentration on the growth rate of silica particles in ethyl alcohol. The particle size distribution and number of particle were found out using DLS. We have obtained submicron monodisperse silica particles from

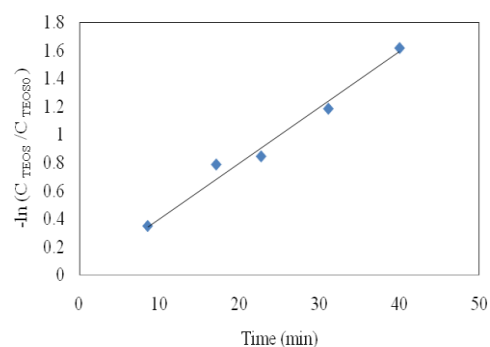
individual experiments with variation in the residence time, inlet composition, and temperature. The particles were monodispersed from each experiment and depending upon the set of experimental conditions the size varied from 200 to 550 nm. Figure 2(a) shows an electron micrograph of silica particles which indicates that particles are essentially monodisperse. Some of the experiments were performed using combination of different alcohols at different ratios to assess their effect on ultimate size of particles.

The rate of loss of TEOS and soluble silica concentration was determined analytically as a function of time. The hydrolysis rate of TEOS was found out to be first order with respect to TEOS. Figure 2(b) shows a linear variation of $-\ln(C_{TEOS}/C_{TEOS0})$ with time, suggesting the first order kinetics.

The estimation of nucleation and growth rate of silica particle is under progress using monomer addition model proposed by Matosoukas and Gulari[4]. This estimation can be made by considering particle size distribution and soluble silica concentration in suspension as a function of time. Scale-up is under progress and will be presented in detail.



(a)



(b)

Figure 2: a) FeSEM image of silica particles prepared by flow synthesis, b) linear plot of $-\ln [TEOS/ TEOS_0]$ vs Time

4. Conclusions

Monodispersed submicron silica particles were prepared in a tubular reactor with 40 min residence time. The time required is significantly lesser than that reported in literature. We have studied all parameters that affect the size of silica particles and kinetics of reaction. The hydrolysis rate of TEOS was found to be first order with respect to TEOS. Scale-up for kg scale synthesis is in progress.

References

- [1] Yujan song . Josef Hormes, J. Small 4 no 6, (2008), 698-711
- [2] R.K. Iler, the Chemistry of Silica, Wiley, New York, 1979.
- [3] Alexander, G.B., J. Amer. Chem. Soc. 75, 5655 (1953).
- [4] A.C. Makrides, M. Turner and J. Slaughter, J. Colloid Interf. Sci. 73 (1980) 345.
- [5] T. Matsoukas, E. Gulari, J. Colloid Interface Sci. 124 (1988) 252.

Keywords

“Flow reactor, Submicron silica, Growth kinetics”