Novel pathway for flame synthesis of silica nanoparticle

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In this work, we present a novel pathway for the flame synthesis of silica nanoparticles from tetraethoxysilane (TEOS) via the interaction of silicic acid monomers. A new kinetic model for TEOS decomposition is coupled to a detailed population balance model to simulate an industrial scale reactor.

1) Introduction

- Flame spray pyrolysis of TEOS is the most common route for the production of silica nanoparticles widely used in biotechnology, catalysis, ceramics and as binders.
- The rates of gas phase reactions that lead to particle formation are important in determining the final product properties, and thus a detailed understanding of these processes is essential.
- A detailed kinetic model for TEOS decomposition is coupled to a stochastic particle model to foster a deeper understanding of flame synthesis of silica nanoparticles.

2) Methods

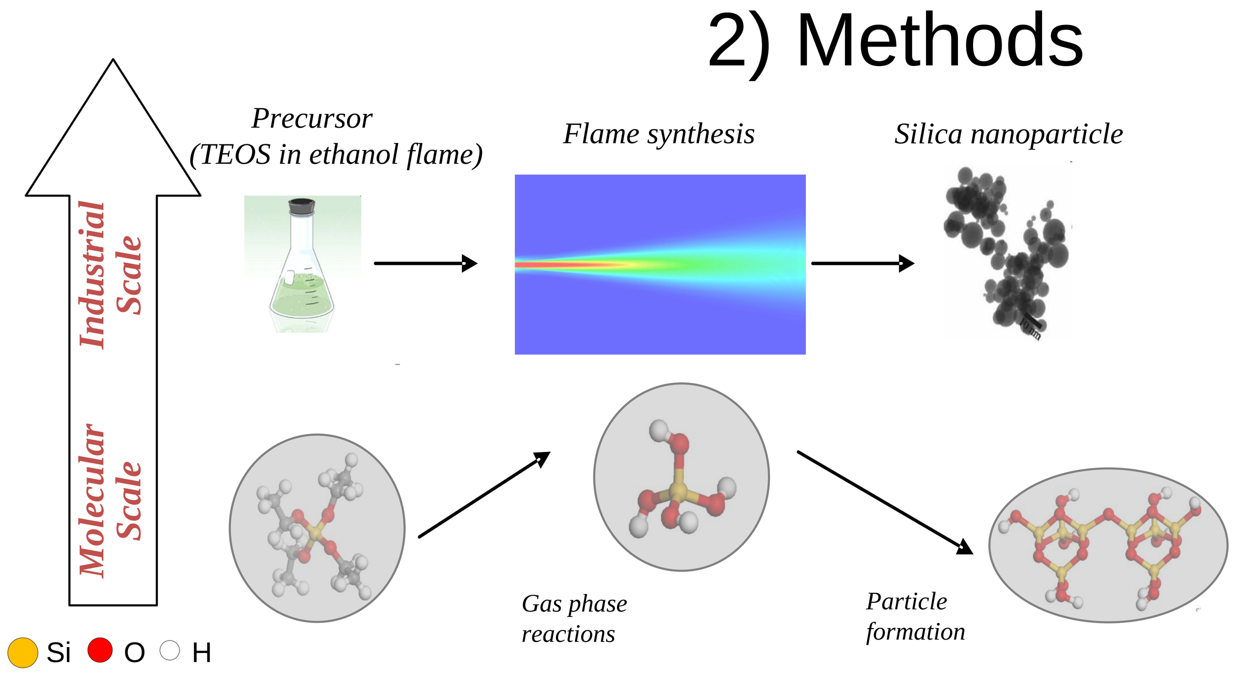


Figure 1: ***Physical System*** *Schematic representation of the industrial reactor*

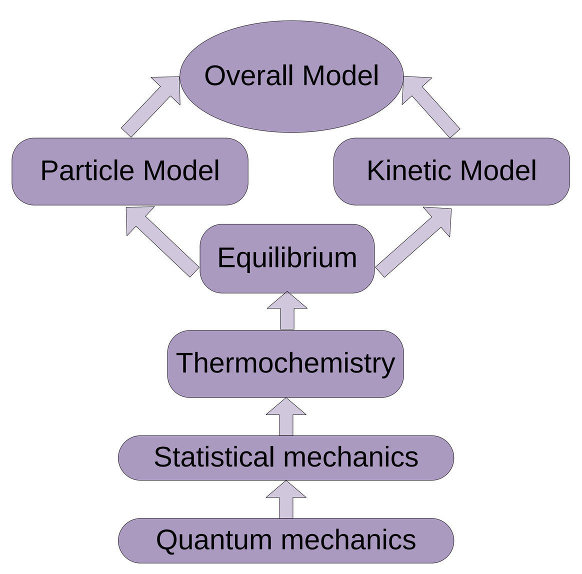
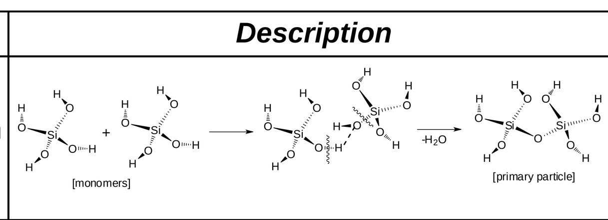
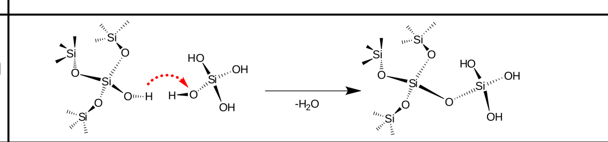
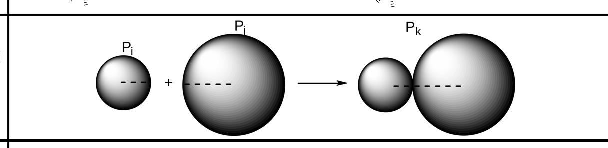
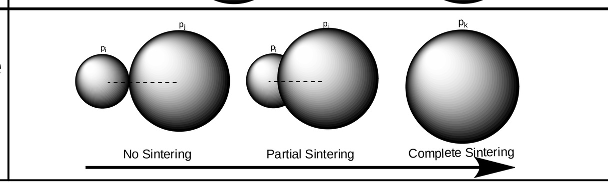


Figure 2: ***Model*** *Steps involved in modelling a chemical system*

First principles modelling of a system involves the following steps: Quantum chemistry is used to determine system properties on a molecular level. Statistical thermodynamics is used to scale molecular information to a macroscopic level. This thermochemistry is then used to generate a kinetic model which when coupled to a detailed population balance model generates the overall model.

5) Particle model

Population balance equations (PBEs) describe the behaviour of a system based on the number and nature of its constituent entities. Particles in the system change in shape and size due to a number of jump processes.

Jump Process	***Description***	***Rate***
Particle inception: creation of a particle from gas-phase monomers.		$R_{\text{inception}} = \frac{1}{2} k_{\text{fm}} {N_A}^2 C^2$
Surface growth: reaction of a particle with gas-phase molecules.		$R_{\text{surfrxn}} = 2.2\eta C \sqrt{\frac{\pi k_B T}{2m}} (d + d_c)^2$
Coagulation: fusion of particles to form agglomerates.		$K^{\text{fm}}(i,j) \propto \left(\frac{1}{m(i)} + \frac{1}{m(j)}\right)^{\frac{1}{2}} (d_c(i) + d_c(j))^2$
Sintering: increase in sphericity of particle due to surface minimisation.		$\tau = A \times d_{i,j} \times \exp\left[\frac{E}{T}\left(1 - \frac{d_{p,min}}{d_{i,j}}\right)\right]$

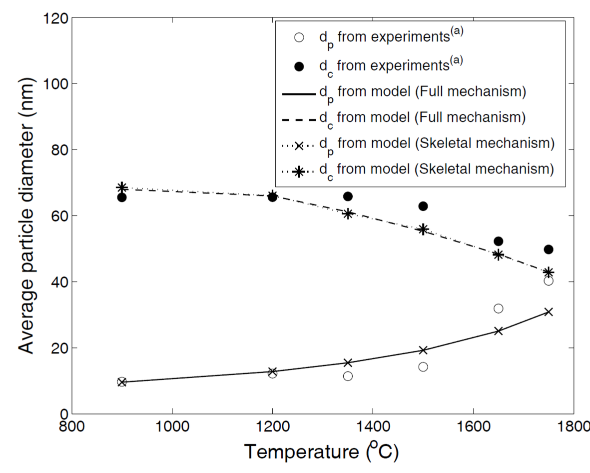


Figure 7: *Change in average primary diameter (d_p) and collision diameter (d_c) with change in furnace temperature. Experimental values are from Seto etal [4].*

- The PBEs are solved using an open-source stochastic particle algorithm written in C++ [3].
- The particle properties (such as size, volume and surface area) are calculated for each individual particle.

3) Thermochemistry

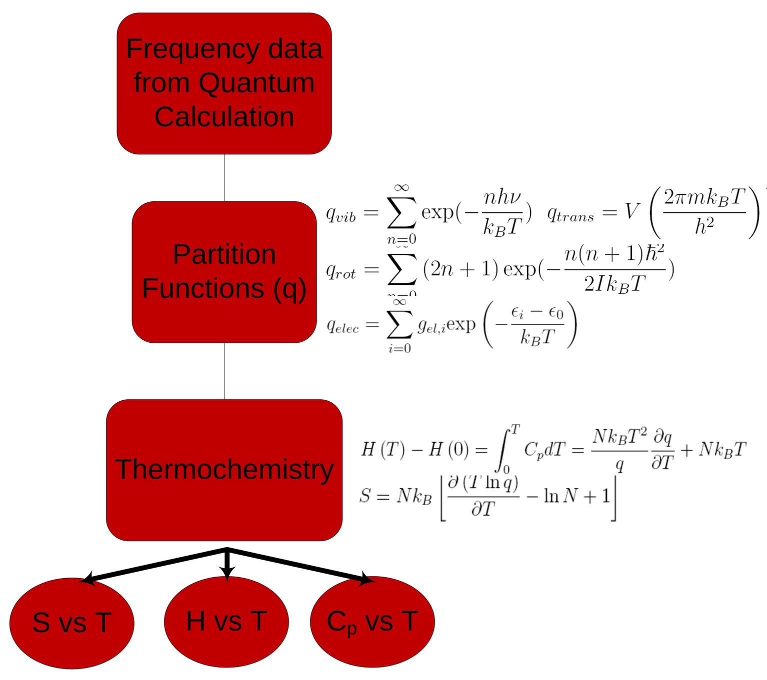


Figure 3: *Thermochemistry calculation steps*

- **Thermochemistry**: The thermodynamic parameters are calculated from the partition functions calculated using Quantum Mechanics and Statistical Thermodynamics.
- **Equilibrium**: The equilibrium composition calculated from thermochemistry gives first hints to systematically generate a reaction mechanism [1].

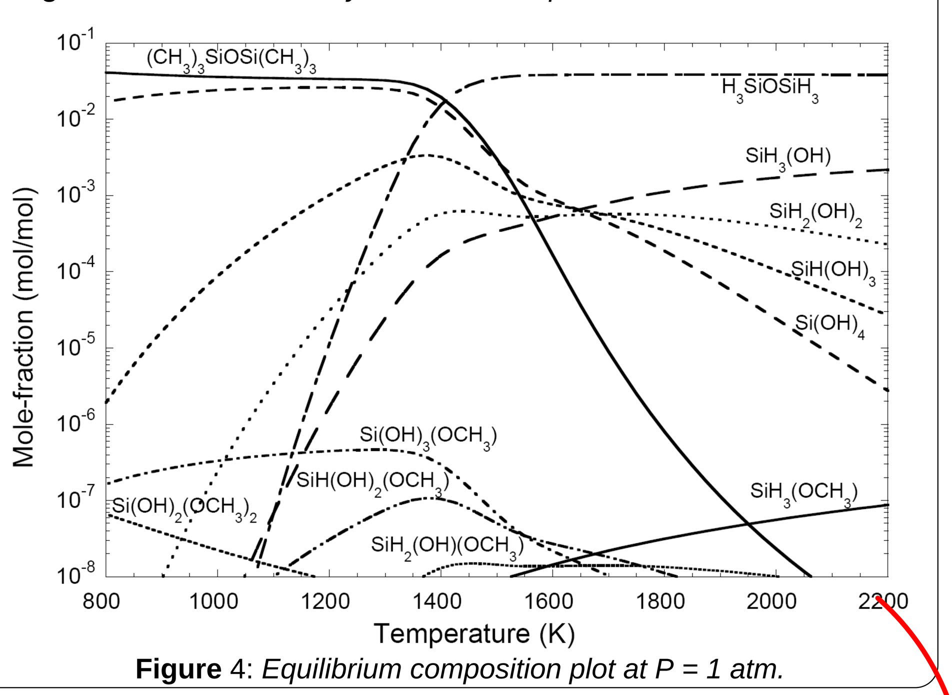


Figure 4: *Equilibrium composition plot at P = 1 atm.*

6) Overall model

The kinetic and particle models described above are coupled using an operator splitting technique [3] to generate the overall model.

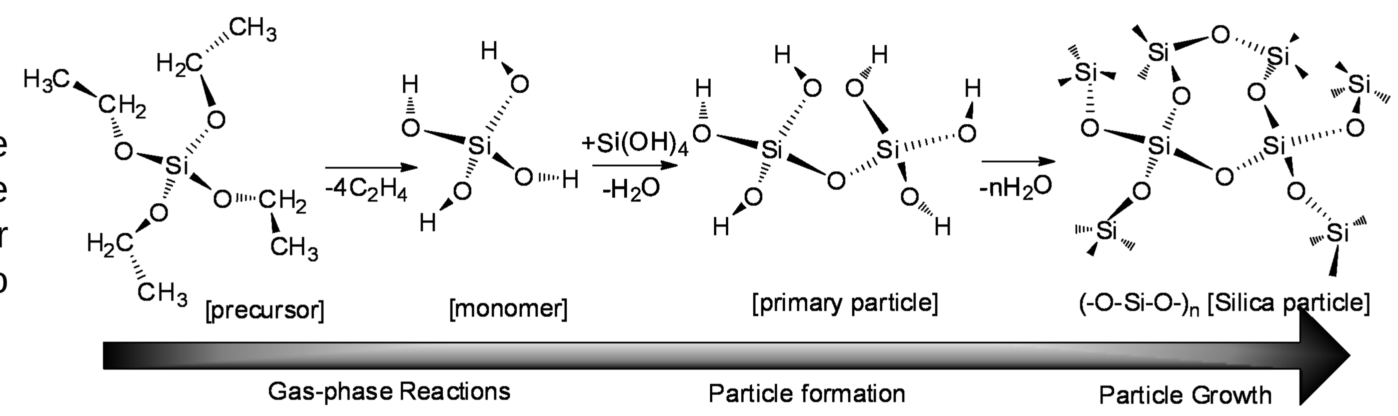


Figure 8: *Particle formation pathway.*

The particle size distributions (PSD) and TEM-style images are generated from the model at 3 different temperatures (Fig. 9 and Fig. 10). These are found to be in close agreement with experimental data [4].

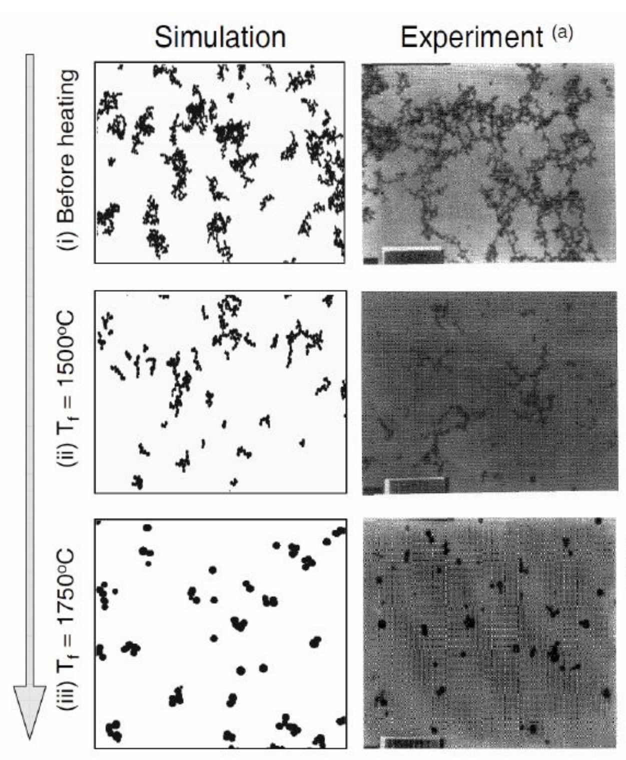


Figure 9: *TEM style images at different final temperatures from simulation and experiments [Ref Seto].*

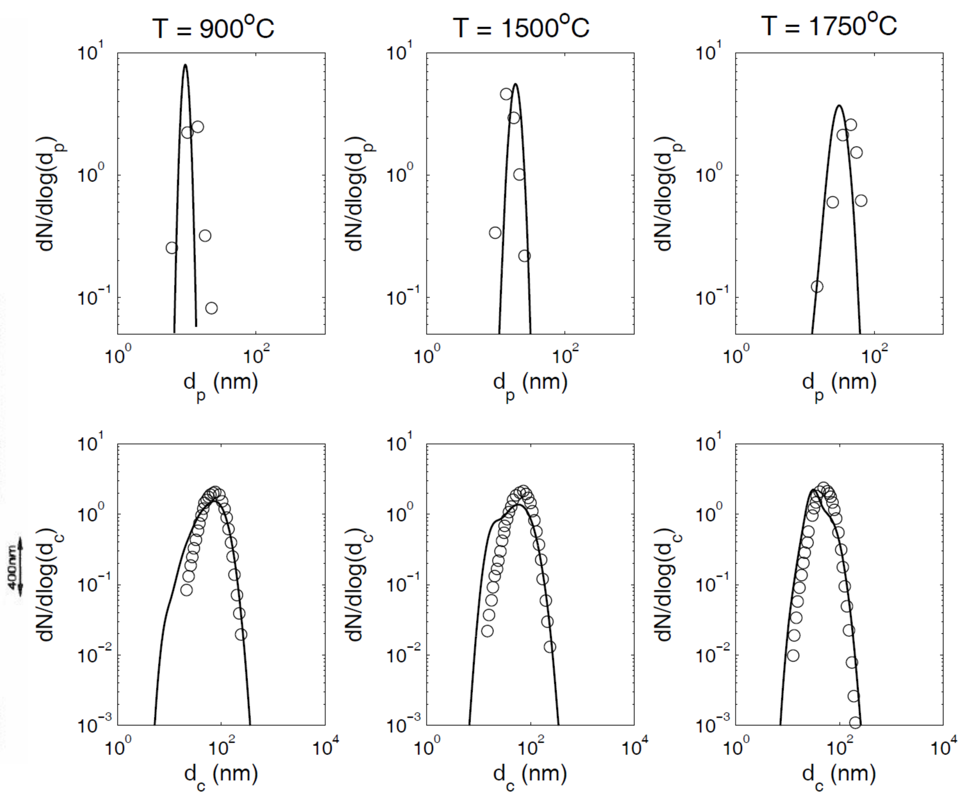


Figure 10: *PSD at different furnace temperatures. The circles are experimental points and the solid lines are model response.*

4) Kinetic model

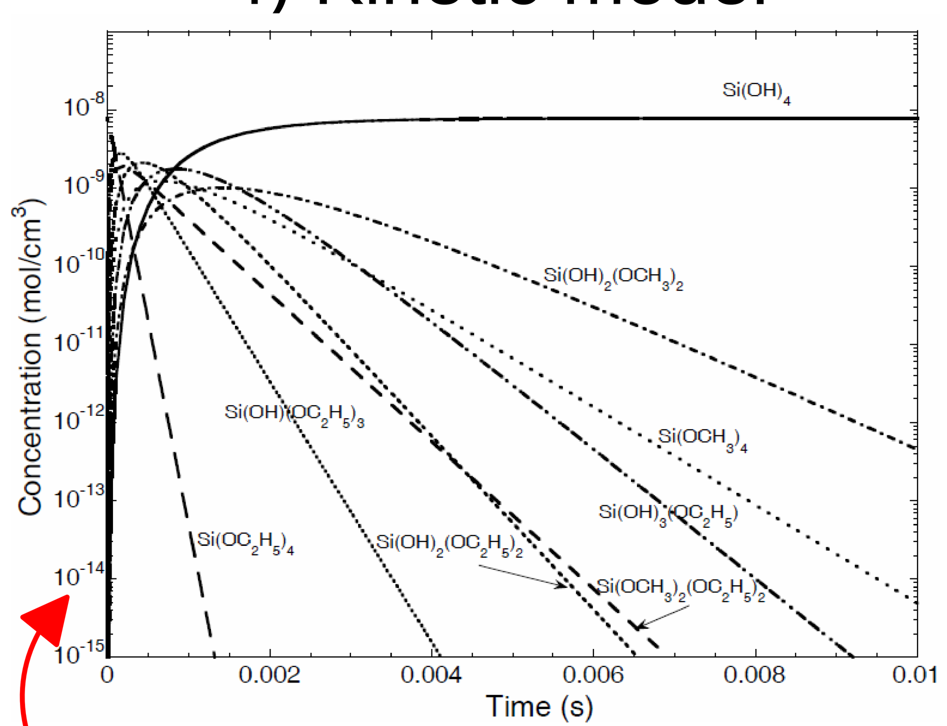


Figure 6: *Reactor composition at T=1500 K and P = 1 atm.*

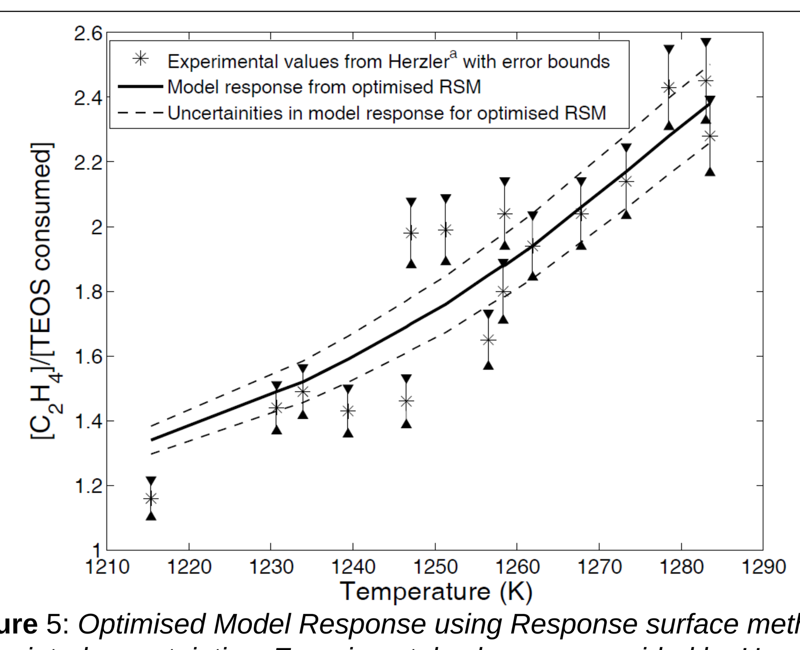


Figure 5: *Optimised Model Response using Response surface methodology and associated uncertainties. Experimental values are provided by Herzler etal. [2]*

- Reaction set generated to include all intermediates and products from equilibrium. Also includes ethanol and Herzler mechanisms [2].
- Main reaction pathway determined using Flux and Sensitivity Analyses indicate the reaction to proceed via disintegration of ethyl groups to form silicic acid ($Si(OH)_4$).
- Rate parameters for the main reaction pathway fitted to experimental values [2] using optimisation techniques of low discrepancy series and response surfaces [5].

7) Future Work

- Perform a detailed transition state analysis to determine the exact values of rate parameters.
- Develop a detailed population balance model, where the particle jump processes are considered in conjunction with chemical reactions.
- Explore ways to build robust molecular models and further automate the process using the Reaction Mechanism Generator coupled with Semantic Web.

Summary

By coupling a new detailed kinetic model, generated from quantum chemical calculations, to a new population balance model with primary particle tracking, the current work demonstrates the feasibility of using first-principles modelling to understand complex particle synthesis processes.

References

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Acknowledgements

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