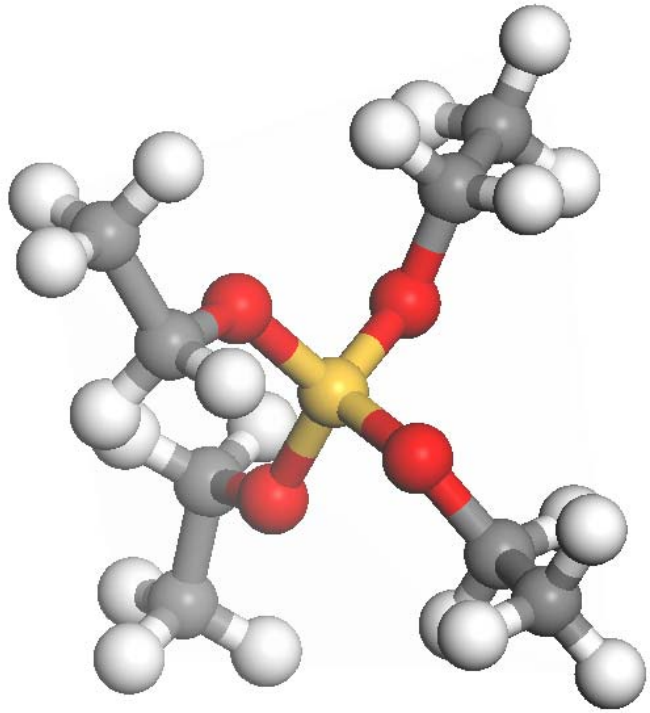
Computational modelling of Silica nanoparticle formation in a flame reactor



S. Shekar, M. Sander,

A. J. Smith, M. Kraft

26 April, 2010

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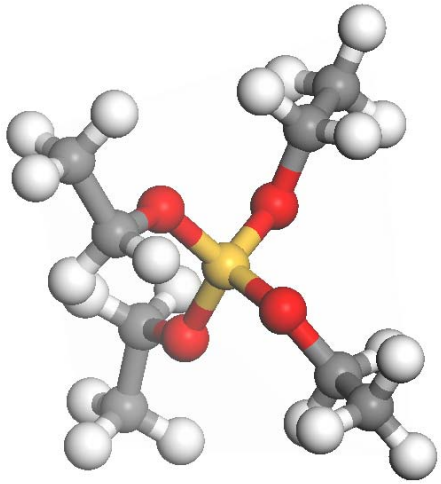
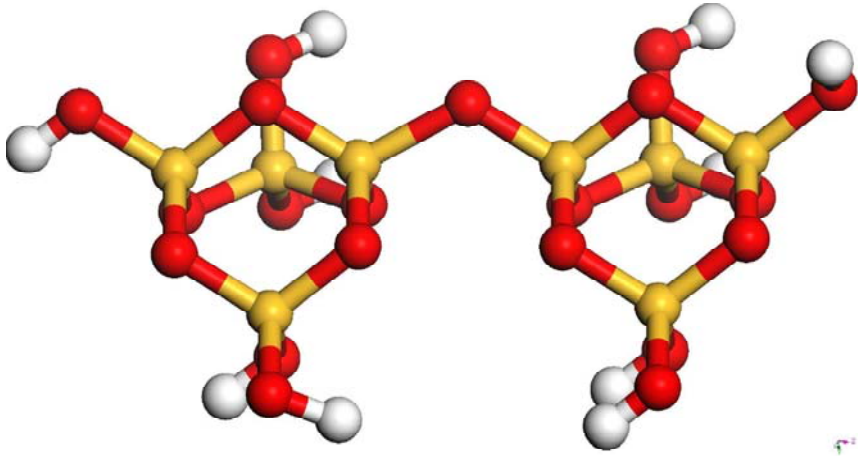
Introduction





Precursor (TEOS)

Mesoporous silica nanoparticles

***Aim*: To answer the following questions**

- ***What happens in the gas-phase?***
- ***How do gas-phase precursors form the particles?***
- ***How do these particles grow?***
- ***How to describe the overall system from first-principles?***

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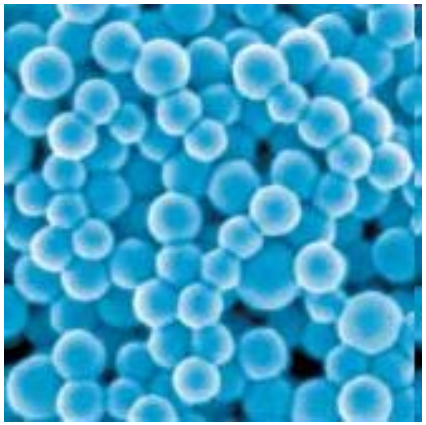
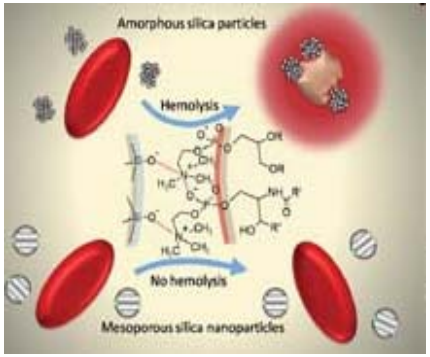
Product : Silica nanoparticles





Mesoporous Silica Nanoparticles: network of Si-O bonds such that Si:O = 1:2

Applications:

- Support material for functional/composite nanoparticles.
- Optics, optoelectronics, photoelectronics
- Catalysis
- Bio-medical applications, drug delivery

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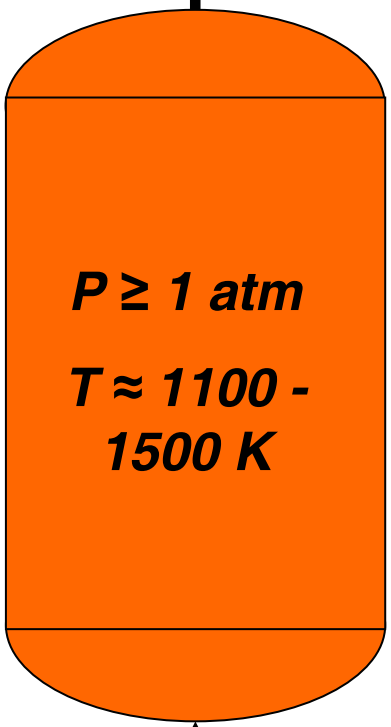
Industrial Flame Reactor



Flame Spray Reactor

Product (Silica nanoparticles)

Aim: To describe the flame synthesis of silica nanoparticles

Experiments

Model

(Herzler et al / Seto et al / Pratsinis et al)

Precursor(TEOS)

Fuel(ethanol+air)

/ Inerts(Ar)

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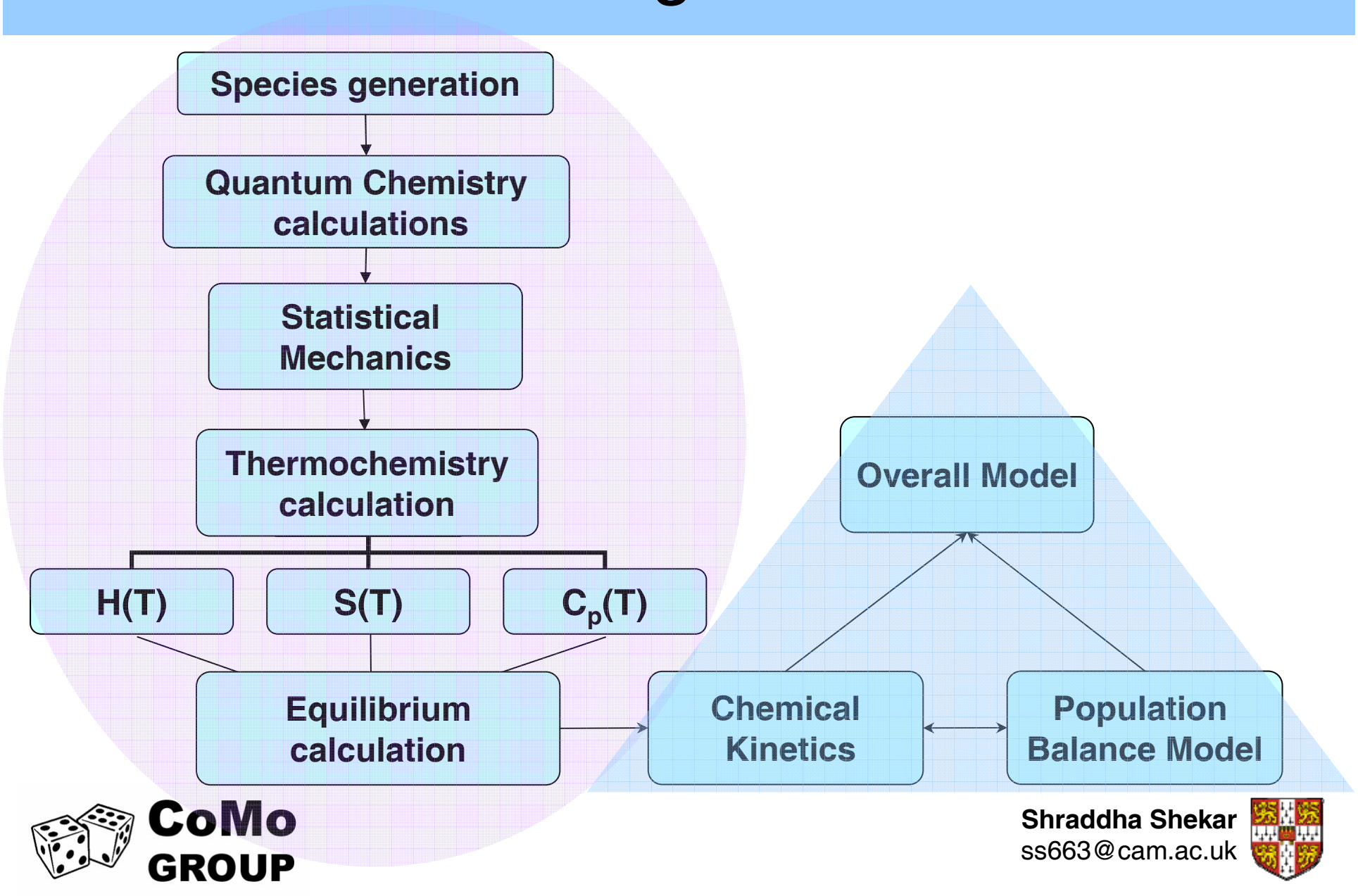
Ab initio modelling



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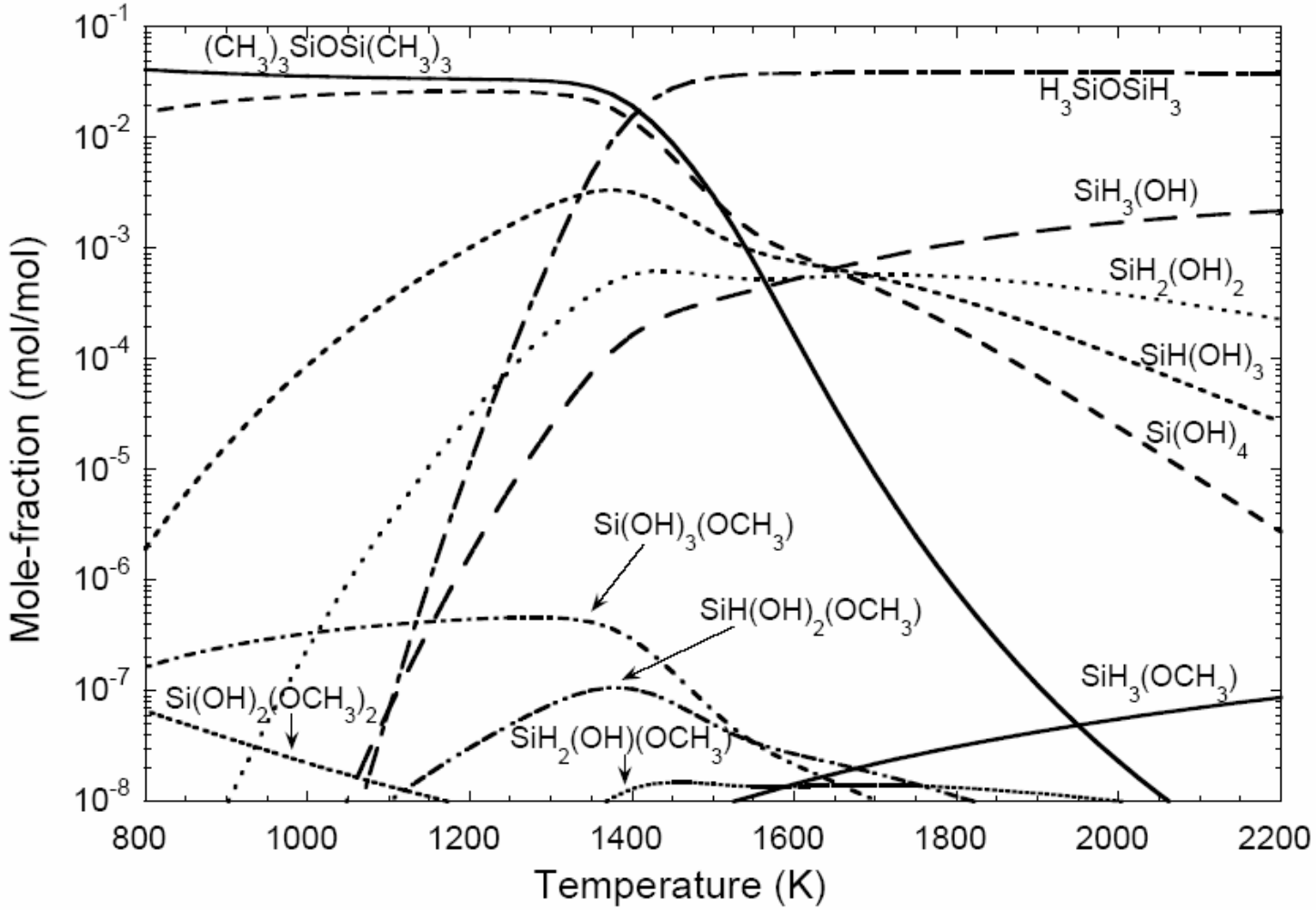
Equilibrium Plot



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Ref: W. Phadungsukanan, S. Shekar, R. Shirley, M. Sander, R. H. West, and M. Kraft. First-principles thermochemistry for silicon species in the decomposition of tetraethoxysilane. *J. Phys. Chem. A*, **113**, 9041–9049, 2009

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Reaction kinetics

- Equilibrium
  - Hints towards the existence of stable intermediates & products.
  - Intermediates $Si(OH)_x(OCH_3)_{4-x}$ $Si(OH)_y(OC_2H_5)_{4-y}$
  - Main Product $Si(OH)_4$

→

- Kinetics
  - Reaction set generated to include all intermediates and products from equilbrium.
  - Reactions obey Arrhenius law rate constant $k = AT^{\beta}e^{-Ea/RT}$
  - Rate parameters (A, β, Ea) fitted to experimental vaues [a]

(a) J. Herzler, J. A. Manion, and W. Tsang. Single-Pulse Shock Tube Study of the decomposition of tetraethoxysilane and Related Compounds. *J. Phys. Chem. A*, **101**, 5500-5508, 1997

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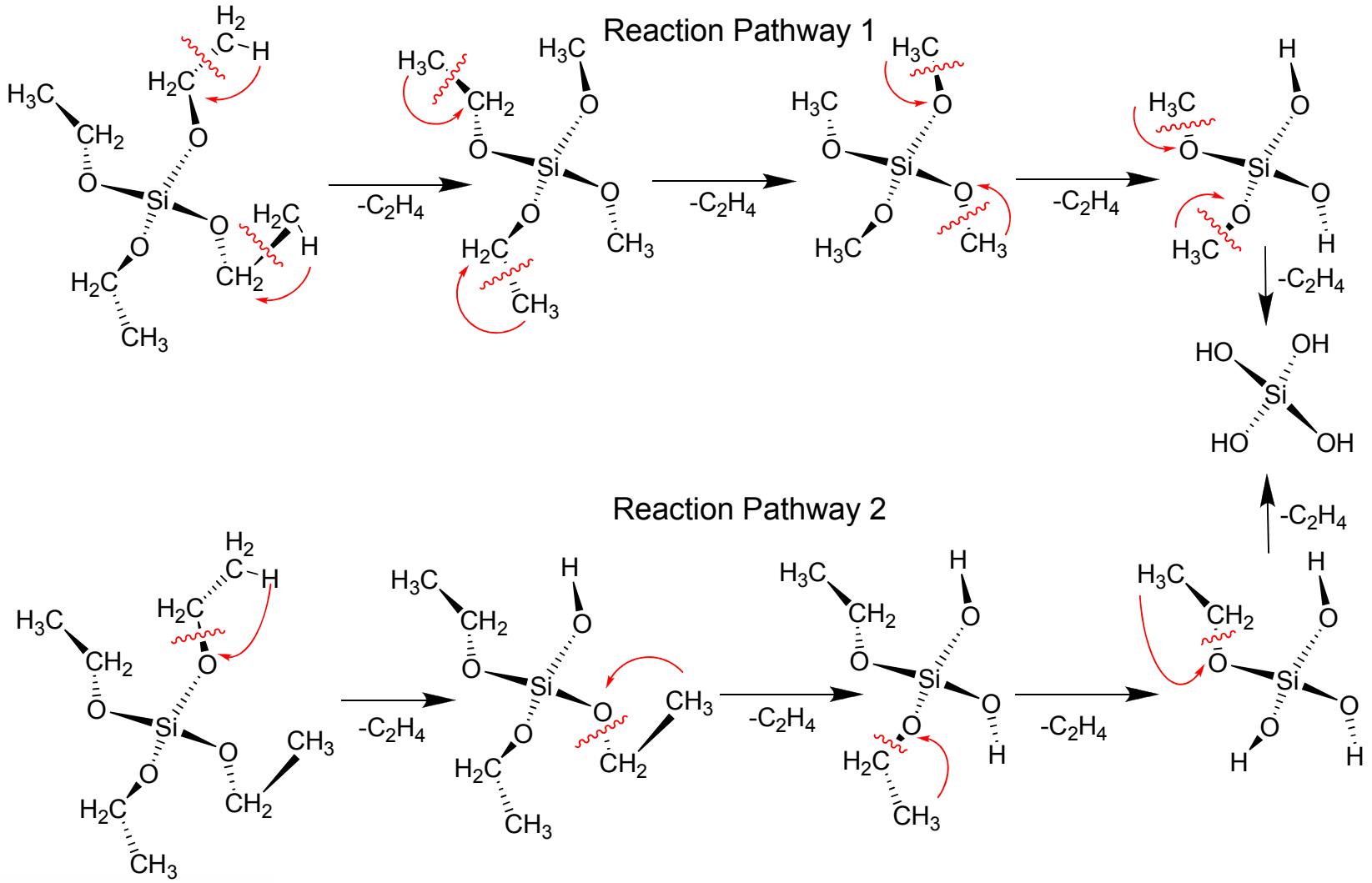
Gas-phase mechanism



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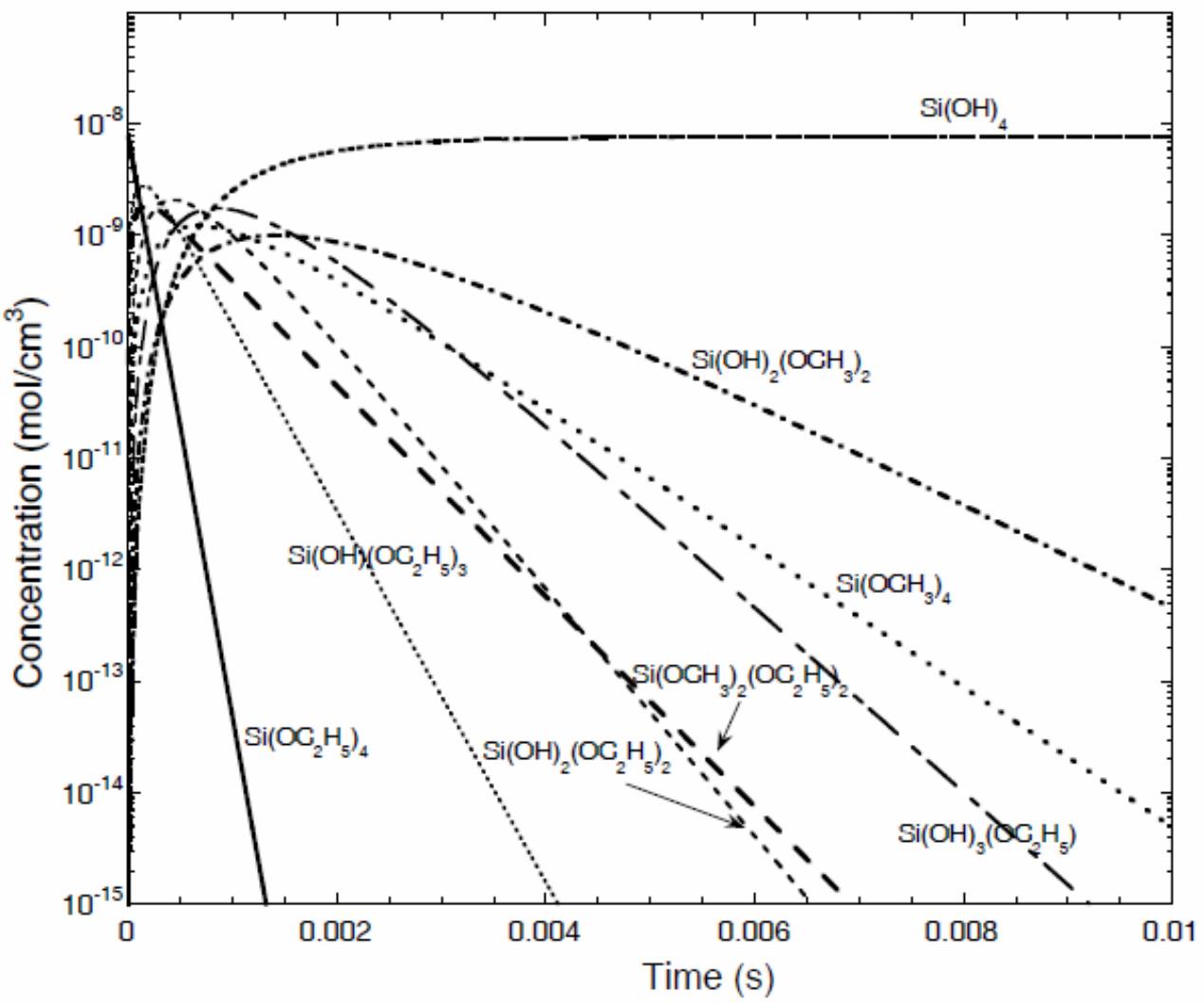
Reactor Plot



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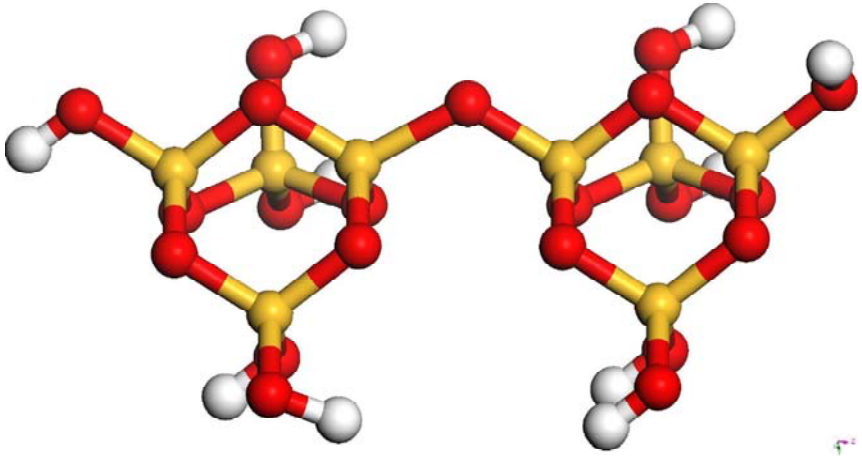
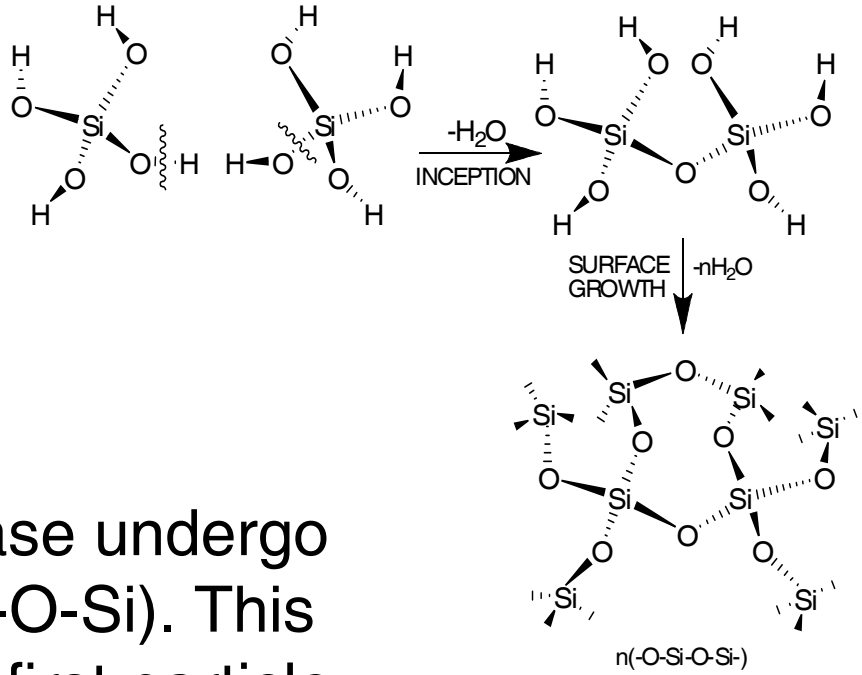
Particle Model





$Si(OH)_4$ molecules in gas-phase undergo inception to form a dimer (-Si-O-Si). This dimer is considered to be the first particle. Particle growth then proceeds by subsequent removal of hydroxyl groups.

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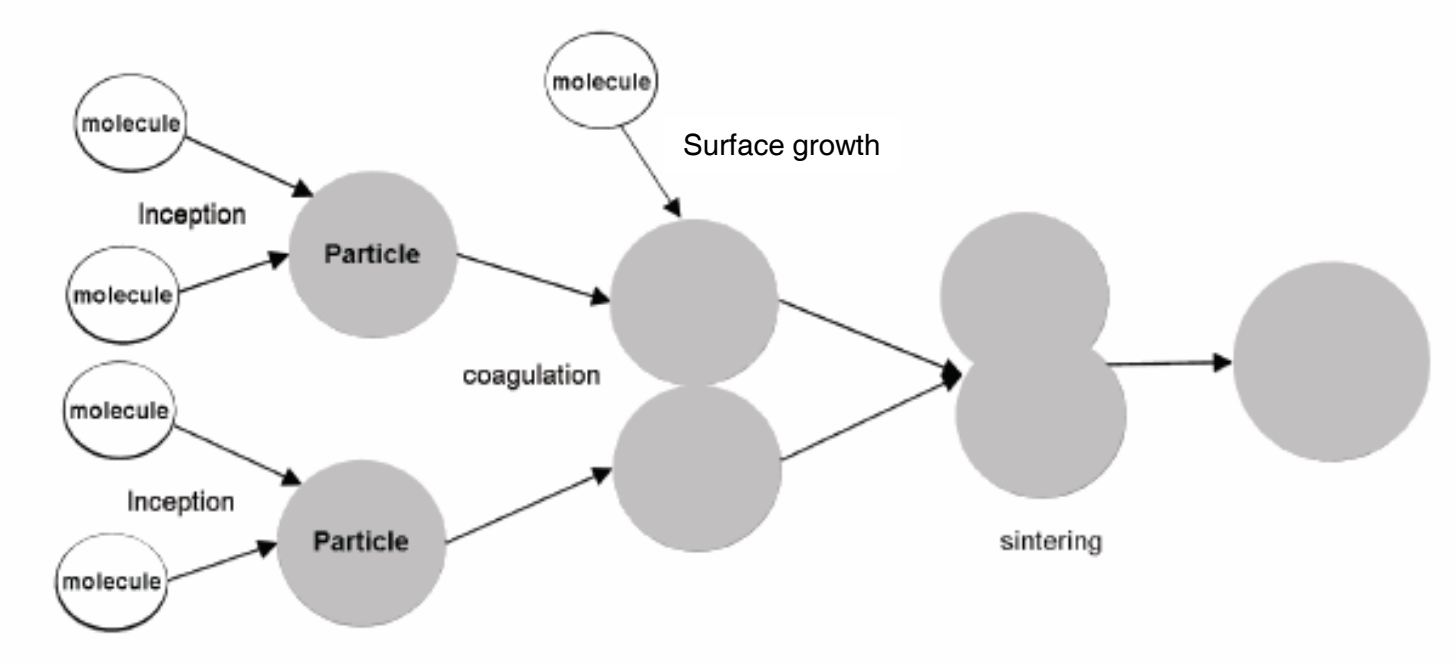
Particle Model



New inception and surface growth steps have been incorporated in a previously developed stochastic particle model developed by Sander et al. [1].

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[1]: M. Sander, R. H. West, M. S. Celnik, and M. Kraft. A Detailed Model for the Sintering of Polydispersed Nanoparticle Agglomerates, *Aerosol Sci. Tech.*, **43**, 978-989, 2009

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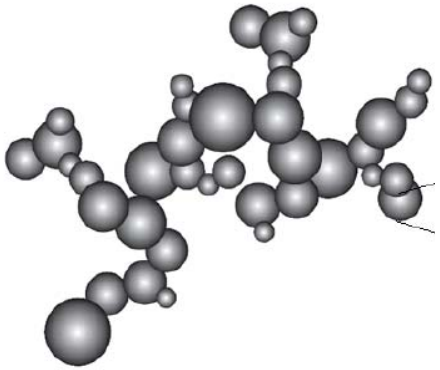
The Data Structure

$$P = P(p_1, p_2, \ldots, p_n, \mathbf{S})$$



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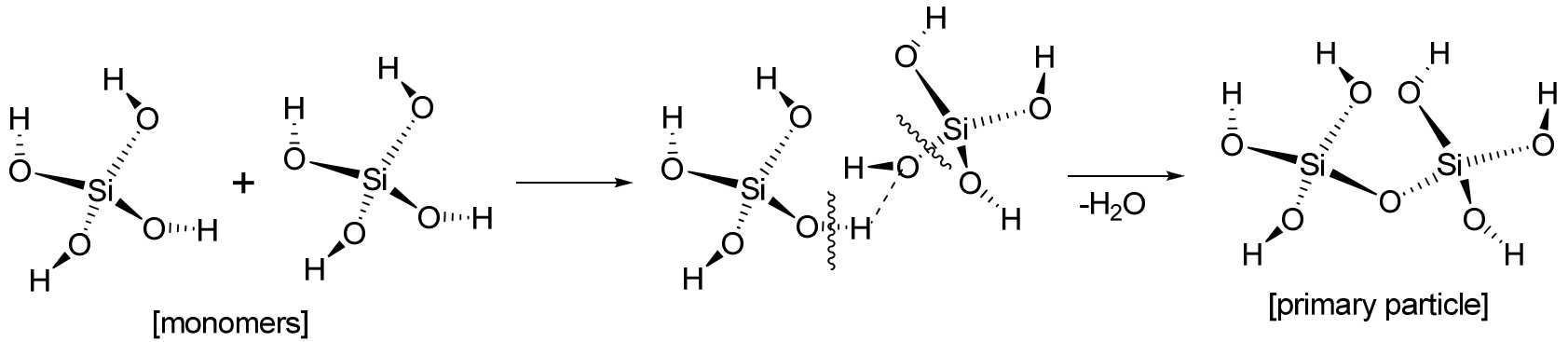
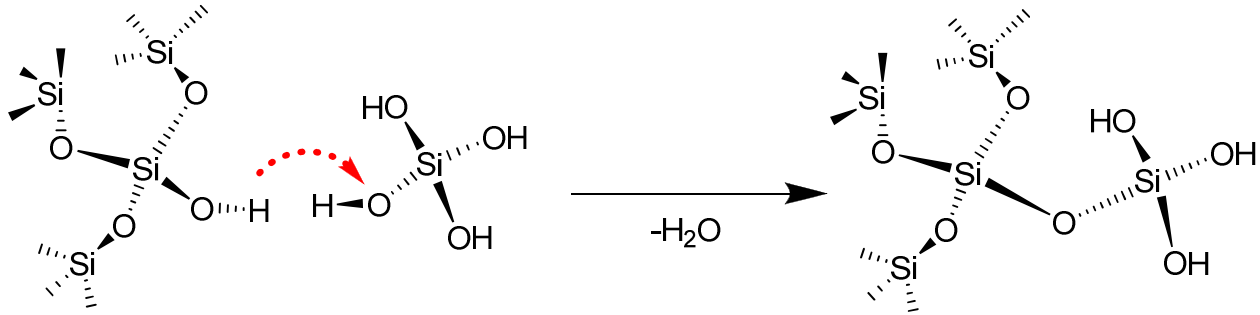
Particle-gasphase reactions

1. Inception



2. Surface growth



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The Algorithm

1. Set start time $t \leftarrow t_0$ and the initial system $x \leftarrow x_0$.
2. Calculate an exponentially distributed waiting time

$$dt = -\frac{\ln(U)}{R_{tot}}$$

where U is a uniformly distributed random number, $U \in (0; 1)$, and R_{tot} is the total rate of all processes (surface reaction, coagulation and inception) defined for rates R_i , $i \in \{coag,, inception, surfrxn\}$

$$R_{tot} = \sum_{i=1}^{N} R_i(x, t)$$

Ref: M. Sander, R. H. West, M. S. Celnik, and M. Kraft. A Detailed Model for the Sintering of Polydispersed Nanoparticle Agglomerates, *Aerosol Sci. Tech.*, **43**, 978-989, 2009

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The Algorithm

3. Increment time variable $t \leftarrow t+dt$.
4. If $t > t_{stop}$ then end.
5. Update the sintering level for the time dt for all the particles.
6. Choose a process i according to the probability:

$$P_i = \frac{R_i}{R_{tot}}$$

7. Perform process i.
8. Go to step 2.

Ref: M. Sander, R. H. West, M. S. Celnik, and M. Kraft. A Detailed Model for the Sintering of Polydispersed Nanoparticle Agglomerates, *Aerosol Sci. Tech.*, **43**, 978-989, 2009

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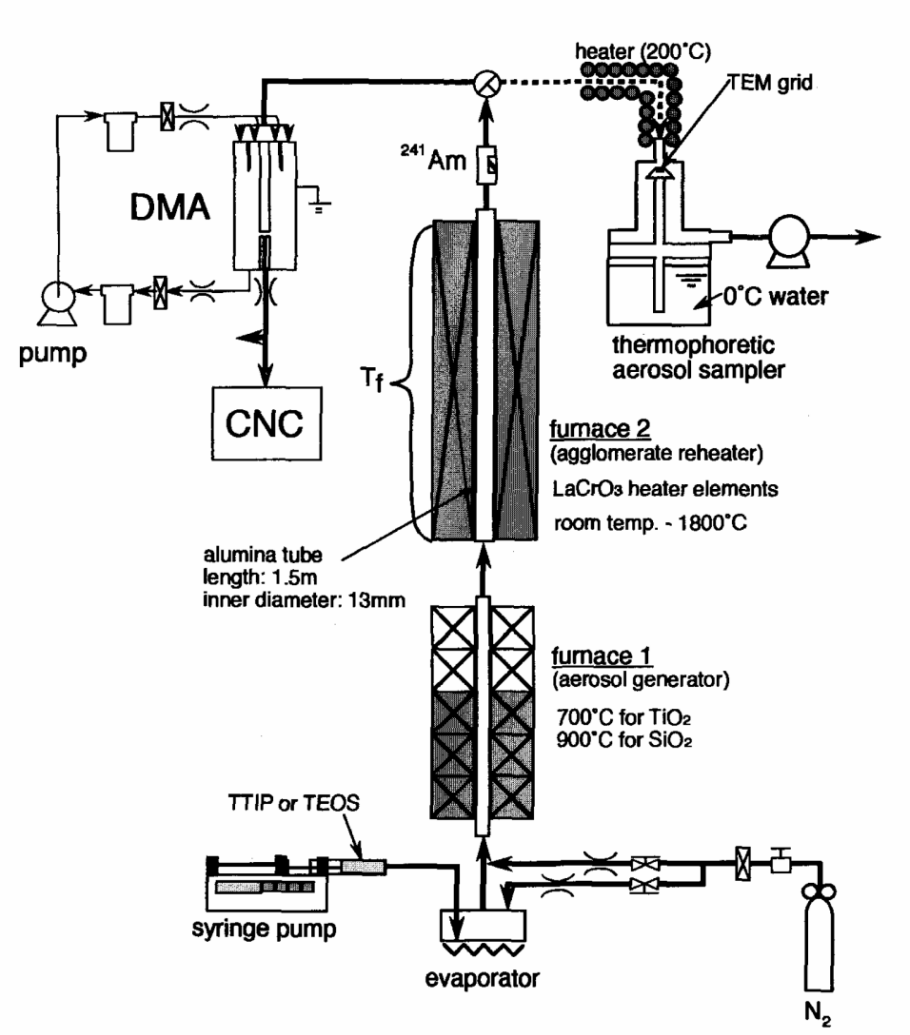
Experimental Setup of Seto et al.



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Ref: T. Seto, A. Hirota, T. Fujimoto, M. Shimada, and K. Okuyama. Sintering of Polydisperse Nanometer-Sized Agglomerates, *Aerosol Sci. Tech.*, **27**, 422-438, 1997

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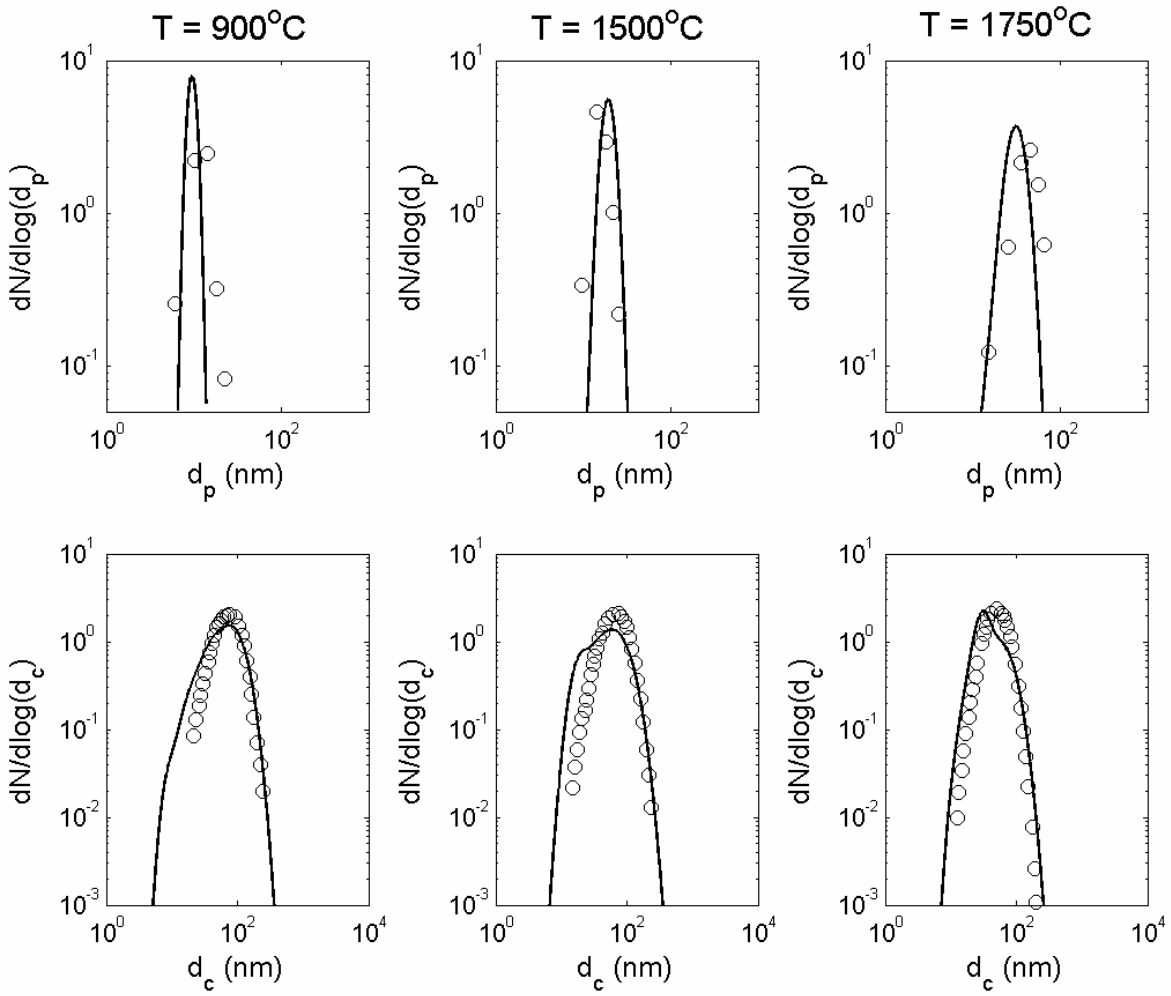
Model Validation



Ref: T. Seto, A. Hirota, T. Fujimoto, M. Shimada, and K. Okuyama. Sintering of Polydisperse Nanometer-Sized Agglomerates, *Aerosol Sci. Tech.*, **27**, 422-438, 1997

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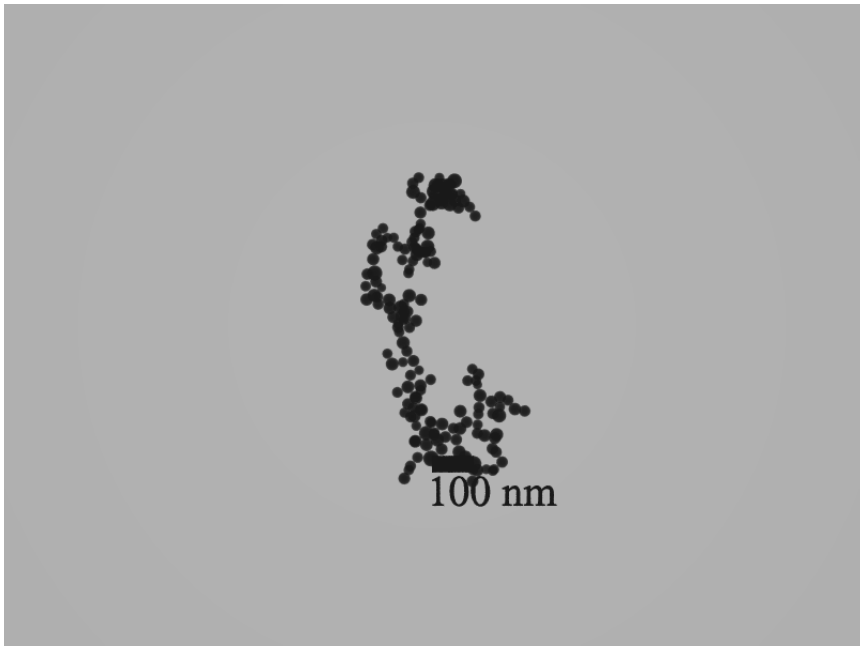
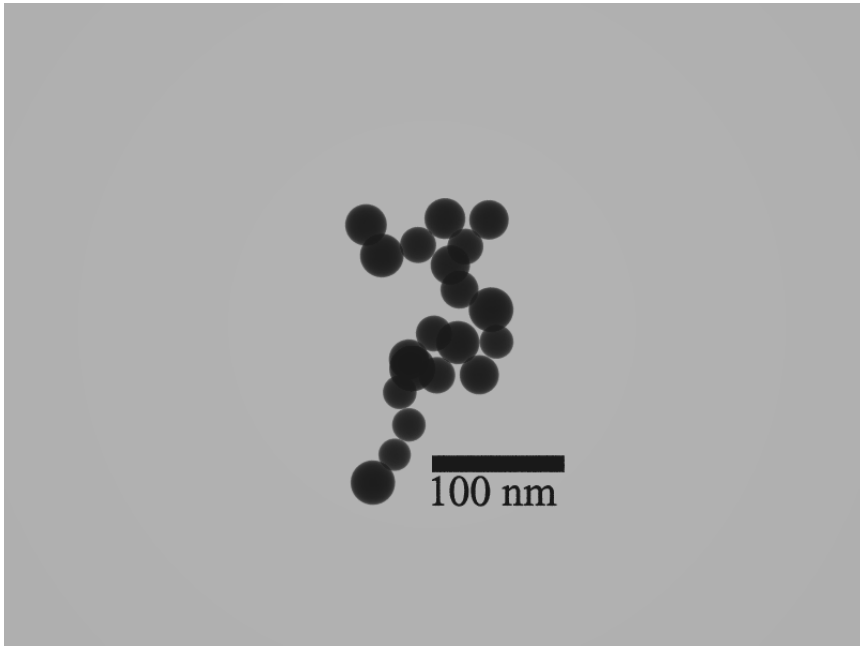
Model produced TEM-like images at 0.1 s, T = 1300 K





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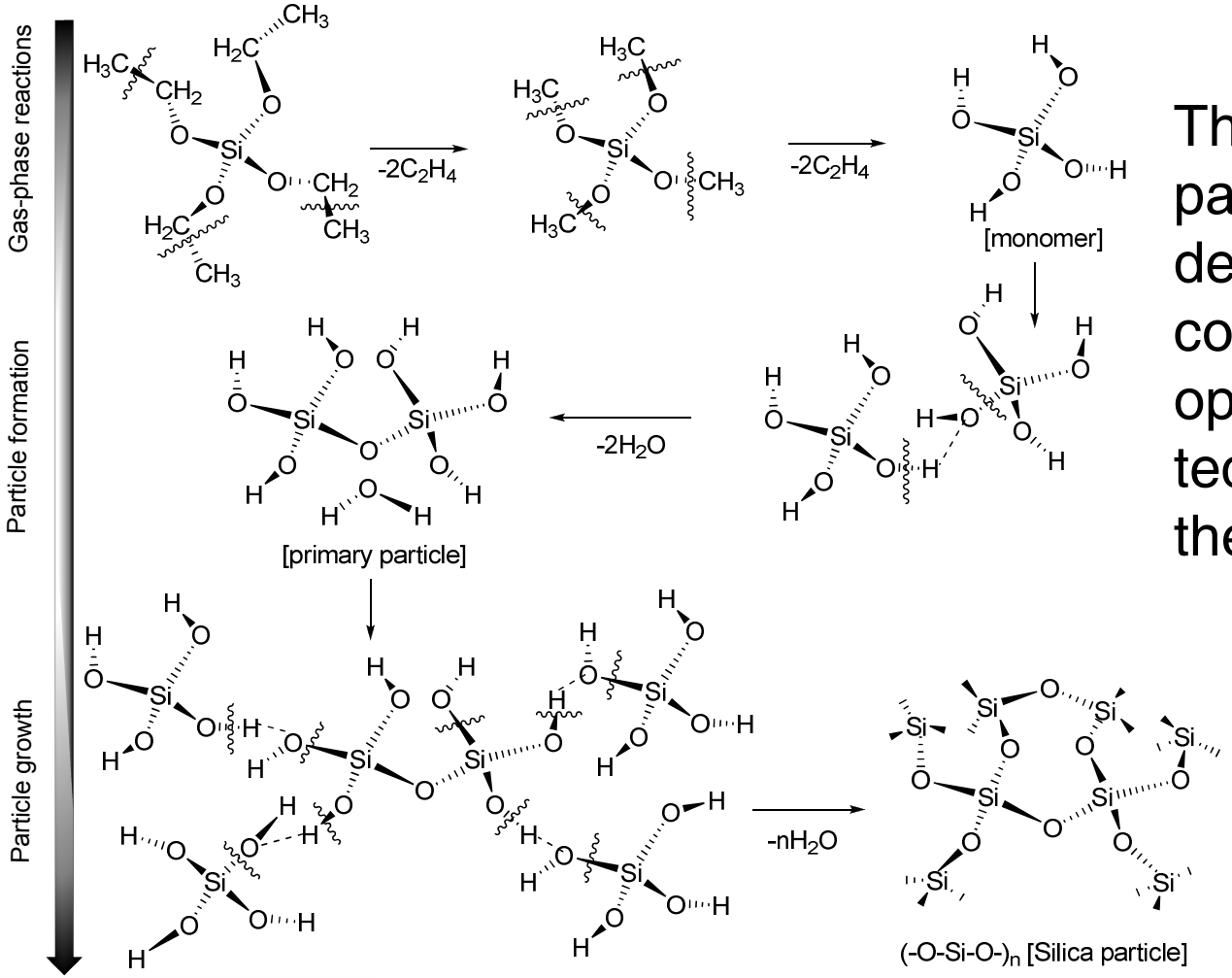
Overall mechanism for particle formation



The gas-phase and particle model described above are coupled using an operator splitting technique to generate the overall model.

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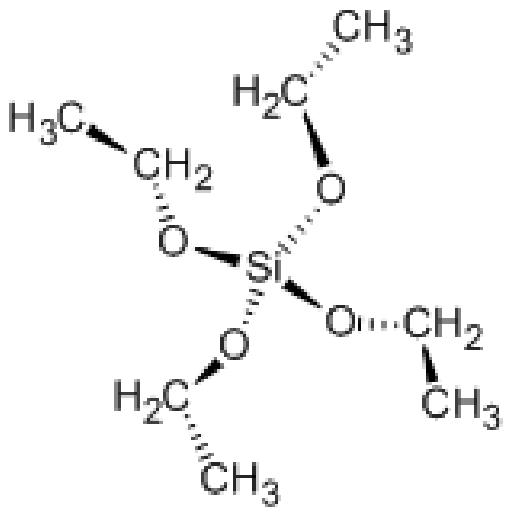
Conclusion



1. New kinetic model proposed which postulates silicic acid Si(OH)4 as the main product of TEOS decomposition.
2. A novel pathway proposed for the formation of silica nanoparticles via the interaction of silicic acid monomers.
3. Feasibility of using first-principles to gather a deeper understanding of complex particle synthesis processes.

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Acknowledgements

HEIQ MATERIALS

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Thank you!

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