Modelling the aerosol synthesis of silica nanoparticles from TEOS.

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Some basic questions

• What is TEOS?

• What are silica nanoparticles (SiNP)?

• Why are they important?

• Why model this system?
Tetraethoxysilane

**TEOS**

- Central silicon attached to 4-ethoxy branches
- Vibrations and rotations within the molecule
- Many possible ways of bond breaking, many possible reactions
- Preferred precursor because relatively inexpensive and halide-free.
Silica nanoparticles

What are SiNP?

Network of Si-O bonds such that Si:O = 1:2

Why are they important?

• Support material for functional/composite nanoparticles, catalysis
• Bio-medical applications, drug delivery
• Optics, optoelectronics, photoelectronics
• Fabrics, clothes
Why model this?

**Precursor (TEOS)**

**Aerosol reactor**

**Silica nanoparticles**

- What are the optimal process conditions?
- What are the final product properties?
- What is the final particle size distribution?

- 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?
Methods: Ab initio modelling

**Reaction kinetics**

- **Equilibrium**
  - Hints towards the existence of stable intermediates & products.
  - Intermediates
    - $\text{Si(OH)}_x(\text{OCH}_3)_{4-x}$
    - $\text{Si(OH)}_y(\text{OC}_2\text{H}_5)_{4-y}$
  - Main Product $\text{Si(OH)}_4$

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

Reaction Mechanism

• Heuristic reaction mechanism

\[
\begin{align*}
C_8H_{20}O_{4}SI &= C_6H_{16}O_{4}SI + C_2H_4 \\
C_6H_{16}O_{4}SI &= C_4H_{12}O_{4}SI + C_2H_4 \\
C_4H_{12}O_{4}SI &= C_2H_8O_{4}SI + C_2H_4 \\
C_2H_8O_{4}SI &= H_4O_{4}SI + C_2H_4 \\
C_8H_{20}O_{4}SI &= C_7H_{17}O_{4}SI + CH_3 \\
C_7H_{17}O_{4}SI &= C_2H_4 + C_5H_{13}O_{4}SI \\
C_5H_{13}O_{4}SI &= C_2H_4 + C_3H_9O_{4}SI \\
C_3H_9O_{4}SI &= C_2H_4 + CH_5O_{4}SI \\
CH_5O_{4}SI &= H_4O_{4}SI + CH \\
C_7H_{17}O_{4}SI &= C_7H_{16}O_{4}SI + H \\
C_7H_{16}O_{4}SI &= C_6H_{13}O_{4}SI + CH_3 \\
C_6H_{13}O_{4}SI &= C_6H_{12}O_{4}SI + H \\
C_6H_{12}O_{4}SI &= C_4H_{10}O_{4}SI + C_2H_2 \\
C_4H_{10}O_{4}SI &= C_2H_8O_{4}SI + C_2H_2 \\
C_8H_{20}O_{4}SI &= C_2H_4 + C_6H_{16}O_{4}SI \\
C_6H_{16}O_{4}SI &= C_2H_4 + C_4H_{12}O_{4}SI \\
C_4H_{12}O_{4}SI &= C_2H_4 + C_2H_8O_{4}SI \\
C_2H_8O_{4}SI &= C_2H_4 + H_4O_{4}SI \\
C_8H_{20}O_{4}SI &= C_2H_4 + C_6H_{15}O_{4}SI \\
C_6H_{15}O_{4}SI &= C_2H_4 + C_4H_{11}O_{4}SI \\
C_4H_{11}O_{4}SI &= C_2H_4 + C_2H_7O_{4}SI \\
C_2H_7O_{4}SI &= C_2H_5 + C_2H_3 \\
C_6H_{15}O_{4}SI &= C_6H_{16}O_{4}SI + H \\
C_6H_{16}O_{4}SI &= C_2H_5 + C_4H_{11}O_{4}SI \\
C_4H_{11}O_{4}SI &= C_2H_5 + C_2H_7O_{4}SI \\
C_2H_7O_{4}SI &= H_3O_{4}SI + C_2H_4 \\
H_3O_{4}SI &= H_2O_{3}SI + CH_3 \\
H_2O_{3}SI &= SIO_2 + H_2O \\
C_6H_{15}O_{4}SI &= C_2H_3 + C_4H_{12}O_{4}SI \\
C_4H_{12}O_{4}SI &= C_2H_3 + C_2H_8O_{4}SI \\
C_2H_8O_{4}SI &= H_3O_{4}SI + C_2H_3
\end{align*}
\]
Flux and Sensitivity Analyses

Main Reaction Pathway
Rate parameter estimation

The rate parameters have been fitted to shock-tube experimental data provided by Herzler et al\(^{(a)}\)

Step 1: Low discrepancy series
To perform a pre-scan of parameters for 18 Si reactions.

Step 2: Sensitivity Analysis
To identify the 4 most sensitive parameters

Step 3: Response Surface Methodology
To estimate model uncertainties

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Uncertainties in model parameters for reactions R1 and R15

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( A ) (s(^{-1}))</th>
<th>( E_A ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>( 9.24 \times 10^{12} \pm 4.57 \times 10^{10} )</td>
<td>( 10.778 \pm 1.906 )</td>
</tr>
<tr>
<td>R15</td>
<td>( 1.32 \times 10^{12} \pm 6.04 \times 10^{9} )</td>
<td>( 14.176 \pm 2.125 )</td>
</tr>
</tbody>
</table>

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Optimisation Theory

• Experimental data

\[ \eta^{\text{exp}} = \eta_0^{\text{exp}} \pm \sigma^{\text{exp}} \]

• Model response with parameters \( x \)

\[ \eta = \eta(x) \quad \text{with} \quad x = (x_1, \ldots, x_K) \]

• and \( x = x_0 + c\xi \) with uncertainty factor \( c \) and standard normally distributed \( \xi \)

For a simple linear model, \( K=1 \)

\[ \eta(x) = A + B x \]
\[ \eta(x, c, \xi) = A + B(x_0 + c\xi) \]
\[ \mu(x_0) = E[\eta(x_0, c, \xi)] = A + B x_0 \]
\[ \sigma(c) = \sqrt{\text{Var}(\eta(x_0, c, \xi))} = \sqrt{B^2 c^2} \]

Experimental validation

## Gas-phase mechanism

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction Pathway</th>
<th>$\log(A) (s^{-1})$</th>
<th>$b$</th>
<th>$E/R (K^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>Si(OC₂H₅)₄ ⇌ Si(OCH₃)₂(OC₂H₅)₂ + C₂H₄</td>
<td>12.5</td>
<td>0</td>
<td>26651</td>
</tr>
<tr>
<td>R2</td>
<td>Si(OCH₃)₂(OC₂H₅)₂ ⇌ Si(OCH₃)₄ + C₂H₄</td>
<td>12.2</td>
<td>0</td>
<td>26651</td>
</tr>
<tr>
<td>R3</td>
<td>Si(OCH₃)₄ ⇌ Si(OH)₂(OCH₃)₂ + C₂H₄</td>
<td>12.1</td>
<td>0</td>
<td>26651</td>
</tr>
<tr>
<td>R4</td>
<td>Si(OH)₂(OCH₃)₂ ⇌ Si(OH)₄ + C₂H₄</td>
<td>11.9</td>
<td>0</td>
<td>26651</td>
</tr>
<tr>
<td>R5</td>
<td>Si(OCH₂)(OC₂H₅)₃ + CH₃</td>
<td>13.4</td>
<td>0</td>
<td>49975</td>
</tr>
<tr>
<td>R6</td>
<td>Si(OH)(OCH₃)(OC₂H₅)₂ + C₂H₄</td>
<td>15.3</td>
<td>0</td>
<td>27103</td>
</tr>
<tr>
<td>R7</td>
<td>Si(OH)(OCH₂)(OC₂H₅)₂ + C₂H₄</td>
<td>15.0</td>
<td>0</td>
<td>27103</td>
</tr>
<tr>
<td>R8</td>
<td>Si(OH)(OCH₂)(OC₂H₅)₂ + C₂H₄</td>
<td>14.8</td>
<td>0</td>
<td>27103</td>
</tr>
<tr>
<td>R9</td>
<td>Si(OH)₃(OCH₂) + C₂H₄</td>
<td>11.6</td>
<td>0</td>
<td>44229</td>
</tr>
<tr>
<td>R10</td>
<td>Si(OCH₂)(OC₂H₅)₃ + H</td>
<td>14.9</td>
<td>0</td>
<td>22239</td>
</tr>
<tr>
<td>R11</td>
<td>Si(OCH₃)(OCH=CH₂)(OC₂H₅)₂ + H</td>
<td>12.2</td>
<td>0</td>
<td>49975</td>
</tr>
<tr>
<td>R12</td>
<td>Si(OCH₂)(OCH₃)(OCH=CH₂)(OC₂H₅)₂ + CH₃</td>
<td>14.6</td>
<td>0</td>
<td>22239</td>
</tr>
<tr>
<td>R13</td>
<td>Si(OCH₃)₂(OCH=CH₂)₂ + C₂H₄</td>
<td>15.6</td>
<td>0</td>
<td>46917</td>
</tr>
<tr>
<td>R14</td>
<td>Si(OH)(OCH₃)₂(OCH=CH₂)₂ + C₂H₄</td>
<td>15.3</td>
<td>0</td>
<td>46917</td>
</tr>
<tr>
<td>R15</td>
<td>Si(OCH₂)(OC₂H₅)₃ + C₂H₄</td>
<td>14.3</td>
<td>0</td>
<td>31298</td>
</tr>
<tr>
<td>R16</td>
<td>Si(OH)(OC₂H₅)₃ + Si(OH)(OC₂H₅)₂ + C₂H₄</td>
<td>14.0</td>
<td>0</td>
<td>31298</td>
</tr>
<tr>
<td>R17</td>
<td>Si(OH)(OC₂H₅)₃ + Si(OH)₃(OC₂H₅) + C₂H₄</td>
<td>13.9</td>
<td>0</td>
<td>31298</td>
</tr>
<tr>
<td>R18</td>
<td>Si(OH)₃(OC₂H₅)₂ + Si(OH)₄ + C₂H₄</td>
<td>13.7</td>
<td>0</td>
<td>31298</td>
</tr>
</tbody>
</table>
Conclusion from kinetic model:

Si(OH)$_4$ is the predominant gas-phase precursor.
Si(OH)$_4$ molecules undergo dehydration to form particles. These particles change in size and shape through their lifetime.

Particle Model

Particles

Particle processes

Move in type spce

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Type Space

\[ p_i = p_i(\eta_{\text{Si}}, \eta_{\text{O}}, \eta_{\text{OH}}) \]

Connectivity (C)

Particle \( P_q = P_q(p_1, \ldots, p_{n(P_q)}, C) \)

\[
C(P_q) = \begin{pmatrix}
0 & \cdots & 0 & \cdots & 0 \\
C_{21} & \ddots & 0 & \cdots & 0 \\
\vdots & \ddots & \ddots & \ddots & \vdots \\
C_{i1} & \cdots & C_{ij} & \ddots & \vdots \\
\vdots & \cdots & \cdots & \cdots & \ddots
\end{pmatrix}
\]
1. Inception

Inception increases the number of particles in the system.
2. Surface Reaction

Si(OH)₄ from gas-phase reacts on a particle surface.
2. Rounding due to surface reaction

Surface reaction alters the common surface between different primaries of a particle:

\[ \Delta s = \Delta u \frac{2\sigma}{d_p} \]
3. Coagulation

Particles collide and stick to each other.
4. Intra-particle reaction

Adjacent OH sites react with each other to form Si-O-Si bonds.
5. Sintering

Sintering calculated on a primary particle-level & alters composition.

Reactions at particle neck

\[-2\text{H}_2\text{O}\]
Particle model parameter estimation

\[ \tau(p_i, p_j) = A_s \times d_p(p_i, p_j) \times \exp \left( \frac{E_s}{T} \left( 1 - \frac{d_{p,\text{crit}}}{d_p(p_i, p_j)} \right) \right) \]

\[ \Delta s = \Delta v \frac{2\sigma}{d_p} \]

Unknown parameters

Parameter space: \[ \mathbf{y} = (A_s, E_s, d_{p,\text{crit}}, \sigma) \]

Objective function: \[ \Phi(\mathbf{y}) = \sum_{i=1}^{N_{\text{exp}}} \left( [\langle d_{c_i}^{\text{exp}} \rangle - \langle d_{c_i}^{\text{sim}}(\mathbf{y}) \rangle]^2 + [\langle d_{p_i}^{\text{exp}} \rangle - \langle d_{p_i}^{\text{sim}}(\mathbf{y}) \rangle]^2 \right) \]

Parameter estimation method: Sobol sequences followed by simultaneous perturbation stochastic approximation

Particle model parameter estimation


<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (current model)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_s$ (m$^{-1}$s)</td>
<td>$3.49 \times 10^{-14}$</td>
</tr>
<tr>
<td>$E_s$ (K)</td>
<td>$11.44 \times 10^4$</td>
</tr>
<tr>
<td>$d_{p,\text{crit}}$ (m)</td>
<td>$5.76 \times 10^{-9}$</td>
</tr>
<tr>
<td>$\sigma$ (-)</td>
<td>1.972</td>
</tr>
</tbody>
</table>
Particle model validation

$T = 900 \, ^\circ\text{C}$

$T = 1500 \, ^\circ\text{C}$

$T = 1750 \, ^\circ\text{C}$
Simulation for industrial conditions

Isothermal Batch Reactor (T = 1500 K, P = 1 atm)

Precursor + Fuel + Air

Sensitive applications of SiNP require highly specific properties

TEOS decomposition

Formation of Si(OH)₄

Particle formation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>1000 K ≤ T ≤ 2000 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>P = 1 atm</td>
</tr>
<tr>
<td>Residence time</td>
<td>10 ms ≤ τₚ ≤ 100 ms</td>
</tr>
<tr>
<td>Precursor mole-fraction</td>
<td>100 ppm ≤ x₀,TEOS ≤ 10,000 ppm</td>
</tr>
</tbody>
</table>
Simulation results

Mean Diameter 20-40nm

Low Standard deviation dc
Simulation results

TEOS decomposition rate

High surface activity
Desirable process zones

- Catalysis / functional materials / fillers

Intersection of zones A and B
Desirable process zones

- Drug delivery / bio-medical applications
Welcome from the CoMo Group!

Welcome to the website of the Computational Modelling Group! We develop and apply modern numerical methods to problems arising in Chemical Engineering. The overall aim is to shorten the development period from research bench to the industrial production stage by providing insight into the underlying physics and supporting the scale-up of processes to industrial level.

The group currently consists of 25 members from various backgrounds. We are keen to collaborate with people from both within industry and academia, so please get in touch if you think you have common interests.

The group's research divides naturally into two inter-related branches. The first of these is research into mathematical methods, which consists of the development of stochastic particle methods, computational fluid dynamics and quantum chemistry. The other branch consists of research into applications, using the methods we have developed in addition to well-established techniques. The main application areas are reactive flow, combustion, engine modelling, extraction, nano particle synthesis and dynamics. This research is sponsored on various levels by the UK, EU, and industry.

Marius Kraft - Head of the CoMo Group
Particle size distribution evolution

\[ T = 1500 \text{ K} \]