A novel pathway for flame synthesis of silica nanoparticles

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Silica nanoparticles

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

Applications:

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

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Physical system

**Precursor (TEOS)**

**Flame reactor**

**Silica nanoparticles**

Macroscopic level questions:
- Optimal process conditions?
- Final product properties?
- Final particle size distribution?

Answers from molecular level studies:
- How to determine the thermochemistry of the system?
- What happens in the gas-phase?
- How do gas-phase precursors form the particles?
- How to describe the overall system from first-principles?

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Methods: Ab initio modelling

Species generation → Quantum Chemistry calculations → Statistical Mechanics → Thermochemistry calculation → H(T), S(T), C_p(T) → Equilibrium calculation → Overall Model

Chemical Kinetics → Population Balance Model


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Equilibrium Plot


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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 law rate constant $k = A T^\beta e^{-E_a/RT}$
  - Rate parameters ($A$, $\beta$, $E_a$) fitted to experimental values (a)

Reaction Mechanism

• Heuristic reaction mechanism

C8H20O4SI = C6H16O4SI + C2H4
C6H16O4SI = C4H12O4SI + C2H4
C4H12O4SI = C2H8O4SI + C2H4
C2H8O4SI = H4O4SI + C2H4
C8H20O4SI = C7H17O4SI + CH3
C7H17O4SI = C2H4 + C5H13O4SI
C5H13O4SI = C2H4 + C3H9O4SI
C3H9O4SI = C2H4 + CH5O4SI
CH5O4SI = H4O4SI + CH
C7H17O4SI = C7H16O4SI + H
C7H16O4SI = C6H13O4SI + CH3
C6H13O4SI = C6H12O4SI + H
C6H12O4SI = C4H10O4SI + C2H2
C4H10O4SI = C2H8O4SI + C2H2
C8H20O4SI = C2H4 + C6H16O4SI2
C6H16O4SI2 = C2H4 + C4H12O4SI2
C4H12O4SI2 = C2H4 + C2H8O4SI2
C2H8O4SI2 = C2H4 + H4O4SI
C8H20O4SI = C2H5 + C6H15O4SI2
C6H15O4SI2 = C2H3 + C4H12O4SI2
C4H12O4SI2 = C2H3 + C2H7O4SI2
C2H7O4SI2 = H3O4SI + C2H4
H3O4SI = H2O3SI + OH
H2O3SI = SIO2 + H2O
C6H15O4SI2 = C2H3 + C4H12O4SI2
C4H11O4SI2 = C2H3 + C2H8O4SI2
C2H8O4SI2 = H3O4SI + C2H3
Flux and Sensitivity Analyses

Main Reaction Pathway

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Experimental validation

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, \( K=1 \)

\[
\begin{align*}
\eta(x) &= A + Bx \\
\eta(x, c, \xi) &= A + B(x_0 + c\xi) \\
\mu(x_0) &= E[\eta(x_0, c, \xi)] = A + Bx_0 \\
\sigma(c) &= \sqrt{\text{Var}(\eta(x_0, c, \xi))} = \sqrt{B^2c^2}
\end{align*}
\]


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Model Optimisation

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

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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## 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>$\text{Si(OC}_2\text{H}_5)_4 \rightleftharpoons \text{Si(OCH}_3)_2(\text{OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_4$</td>
<td>12.5</td>
<td>0</td>
<td>26651</td>
</tr>
<tr>
<td>R2</td>
<td>$\text{Si(OCH}_3)_2(\text{OC}_2\text{H}_5)_2 \rightleftharpoons \text{Si(OCH}_3)_4 + \text{C}_2\text{H}_4$</td>
<td>12.2</td>
<td>0</td>
<td>26651</td>
</tr>
<tr>
<td>R3</td>
<td>$\text{Si(OCH}_3)_4 \rightleftharpoons \text{Si(OH)}_2(\text{OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_4$</td>
<td>12.1</td>
<td>0</td>
<td>26651</td>
</tr>
<tr>
<td>R4</td>
<td>$\text{Si(OH)}_2(\text{OC}_2\text{H}_5)_2 \rightleftharpoons \text{Si(OH)}_4 + \text{C}_2\text{H}_4$</td>
<td>11.9</td>
<td>0</td>
<td>26651</td>
</tr>
<tr>
<td>R5</td>
<td>$\text{Si(OC}_2\text{H}_5)_4 \rightleftharpoons \text{Si(OCH}_3)_2(\text{OC}_2\text{H}_5)_3 + \text{CH}_3$</td>
<td>13.4</td>
<td>0</td>
<td>49975</td>
</tr>
<tr>
<td>R6</td>
<td>$\text{Si(OCH}_2)(\text{OC}_2\text{H}_5)_3 \rightleftharpoons \text{Si(OH)}_2(\text{OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_4$</td>
<td>15.3</td>
<td>0</td>
<td>27103</td>
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<tr>
<td>R7</td>
<td>$\text{Si(OH)}_2(\text{OC}_2\text{H}_5)_2 \rightleftharpoons \text{Si(OH)}_2(\text{OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_4$</td>
<td>15.0</td>
<td>0</td>
<td>27103</td>
</tr>
<tr>
<td>R8</td>
<td>$\text{Si(OH)}_2(\text{OC}_2\text{H}_5)_2 \rightleftharpoons \text{Si(OH)}_2(\text{OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_4$</td>
<td>14.8</td>
<td>0</td>
<td>27103</td>
</tr>
<tr>
<td>R9</td>
<td>$\text{Si(OH)}_3(\text{OC}_2\text{H}_5)_3 \rightleftharpoons \text{Si(OH)}_4 + \text{C}_2\text{H}_4$</td>
<td>11.6</td>
<td>0</td>
<td>44229</td>
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<tr>
<td>R10</td>
<td>$\text{Si(OCH}_2)(\text{OC}_2\text{H}_5)_3 \rightleftharpoons \text{Si(OCH}_3)_2(\text{OC}_2\text{H}_5)_2 + \text{H}$</td>
<td>14.9</td>
<td>0</td>
<td>22239</td>
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<tr>
<td>R11</td>
<td>$\text{Si(OCH}_3)_2(\text{OC}_2\text{H}_5)_2 \rightleftharpoons \text{Si(OCH}_3)_2(\text{OC}_2\text{H}_5)_2 + \text{H}$</td>
<td>12.2</td>
<td>0</td>
<td>49975</td>
</tr>
<tr>
<td>R12</td>
<td>$\text{Si(OCH}_2)(\text{OC}_2\text{H}_5)_3 \rightleftharpoons \text{Si(OCH}_3)_2(\text{OC}_2\text{H}_5)_2 + \text{H}$</td>
<td>14.6</td>
<td>0</td>
<td>22239</td>
</tr>
<tr>
<td>R13</td>
<td>$\text{Si(OCH}_3)_3(\text{OC}_2\text{H}_5)_2 \rightleftharpoons \text{Si(OH)}_2(\text{OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_2$</td>
<td>15.6</td>
<td>0</td>
<td>46917</td>
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<tr>
<td>R14</td>
<td>$\text{Si(OH)}_2(\text{OC}_2\text{H}_5)_3 \rightleftharpoons \text{Si(OH)}_2(\text{OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_2$</td>
<td>15.3</td>
<td>0</td>
<td>46917</td>
</tr>
<tr>
<td>R15</td>
<td>$\text{Si(OC}_2\text{H}_5)_4 \rightleftharpoons \text{Si(OH)}_2(\text{OC}_2\text{H}_5)_3 + \text{C}_2\text{H}_4$</td>
<td>14.3</td>
<td>0</td>
<td>31298</td>
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<tr>
<td>R16</td>
<td>$\text{Si(OH)}_2(\text{OC}_2\text{H}_5)_3 \rightleftharpoons \text{Si(OH)}_2(\text{OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_4$</td>
<td>14.0</td>
<td>0</td>
<td>31298</td>
</tr>
<tr>
<td>R17</td>
<td>$\text{Si(OH)}_2(\text{OC}_2\text{H}_5)_2 \rightleftharpoons \text{Si(OH)}_2(\text{OC}_2\text{H}_5)_2 + \text{C}_2\text{H}_4$</td>
<td>13.9</td>
<td>0</td>
<td>31298</td>
</tr>
<tr>
<td>R18</td>
<td>$\text{Si(OH)}_3(\text{OC}_2\text{H}_5)_3 \rightleftharpoons \text{Si(OH)}_4 + \text{C}_2\text{H}_4$</td>
<td>13.7</td>
<td>0</td>
<td>31298</td>
</tr>
</tbody>
</table>
Reactor Plot

Conclusion from kinetic model:

Si(OH)$_4$ is the predominant gas-phase precursor
Main reaction pathway

Reaction Pathway 1

Reaction Pathway 2

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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.
Particle Processes

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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Individual Processes and Rates

1. Inception

\[ R_{\text{inception}} = \frac{1}{2} k_{\text{im}} N_A^2 C^2 \]

2. Surface Reaction

\[ R_{\text{surf rxn}} = 2.2\eta C \sqrt{\frac{\pi k_B T}{2m} (d + d_c)^2} \]
Individual Processes

3. Coagulation

\[ K^{\text{fm}}(i,j) \propto \left( \frac{1}{m(i)} + \frac{1}{m(j)} \right)^{\frac{1}{2}} (d_{c}(i) + d_{c}(j))^{2} \]

4. Sintering

\[ \tau = A \times d_{i,j} \times \exp \left[ \frac{E}{T} \left( 1 - \frac{d_{p,\text{min}}}{d_{i,j}} \right) \right] \]
Experimental Setup of Seto et al.


Reactor 1:
T = 900°C
Particle formation zone

Reactor 2:
T > 900°C
Particle heating zone
Model Optimisation

Material dependent sintering parameters are optimised

\[ \tau = A \times d_{i,j} \times \exp \left[ \frac{E}{T} \left( 1 - \frac{d_{p,min}}{d_{i,j}} \right) \right] \]

Optimisation method: LD series and RSM

Primary diameter \( d_p \) and collision diameters \( d_c \) fitted to experimental values at different temperatures.


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Effect of temperature

• Sintering increases as temperature increases reducing the collision diameters.

• At a temperature of about 2000°C, the collision diameter and primary diameter become identical and particles become spherical.
Particle size distribution

Model produced TEM-like images

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.
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.
Thank you! Please visit our website:

http://como.cheng.cam.ac.uk

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