**Description of Silica Models**

Consult Table 1 at the end to choose a model corresponding to silica surface type and pH [1]

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| --- | --- |
| **Models of bulk silica**  SiO2 | **Description** |
| a\_cristobalite\_unit\_cell | Unit cell of α-cristobalite to create Q3 silica surfaces on the {20-2} plane with an area density of (SiOH + SiO− Na+) groups of 4.7 per nm2 |
| a\_cristobalite\_20m2\_cell | Smallest cell of α-cristobalite in which the {20-2} plane is perpendicular to the z direction |
| a\_quartz\_unit\_cell | Unit cell of α-quartz to create Q2 silica surfaces on the {001} plane with an area density of (SiOH + SiO− Na+) groups of 9.4 per nm2 |
| a\_quartz\_001\_rectangular\_cell | Smallest cell of α-quartz cell with rectangular repeat and in which the {001} plane is perpendicular to the z direction |
| **Models of silica surfaces**  [SiO2]n with surface termination by (SiOH)x and (SiONa)y groups | **Description** |
| silica\_Q2\_9\_4OH\_0pct\_ion | Q2 surface with 9.4 silanol groups per nm2 prepared from a (7x4x3) supercell of the α-quartz 001 rectangular cell by cleavage and hydration of the {001} plane, 0.0 SiO-Na+ per nm2 (pzc) |
| silica\_Q2\_9\_4OH\_9pct\_ion | 9.4 SiO(H,Na) per nm2, 0.84 SiO-Na+ per nm2 |
| silica\_Q2\_9\_4OH\_18pct\_ion | 9.4 SiO(H,Na) per nm2, 1.69 SiO-Na+ per nm2 |
| silica\_Q2\_Q3\_6\_9OH\_0pct\_ion | Mixed Q2/Q3 surface with 6.9 silanol groups per nm2 prepared from the Q3 surface by hydrolysis of surface silanol groups, 0.0 SiO-Na+ per nm2 (pzc) |
| silica\_Q2\_Q3\_6\_9OH\_9pct\_ion | 6.9 SiO(H,Na) per nm2, 0.60 SiO-Na+ per nm2 |
| silica\_Q2\_Q3\_6\_9OH\_18pct\_ion | 6.9 SiO(H,Na) per nm2, 1.29 SiO-Na+ per nm2 |
| silica\_Q3\_4\_7OH\_0pct\_ion | Q3 surface with 4.7 silanol groups per nm2 prepared from a (4x7x2) supercell of the α-cristobalite 20m2 cell with cleavage and hydration of the {20-2} plane, 0.0 SiO-Na+ per nm2 (pzc) |
| silica\_Q3\_4\_7OH\_5pct\_ion | 4.7 SiO(H,Na) per nm2, 0.25 SiO-Na+ per nm2 |
| silica\_Q3\_4\_7OH\_9pct\_ion | 4.7 SiO(H,Na) per nm2, 0.42 SiO-Na+ per nm2 |
| silica\_Q3\_4\_7OH\_14pct\_ion | 4.7 SiO(H,Na) per nm2, 0.67 SiO-Na+ per nm2 |
| silica\_Q3\_4\_7OH\_18pct\_ion | 4.7 SiO(H,Na) per nm2, 0.84 SiO-Na+ per nm2 |
| silica\_Q3\_4\_7OH\_27pct\_ion | 4.7 SiO(H,Na) per nm2, 1.26 SiO-Na+ per nm2 |
| silica\_Q3\_4\_7OH\_50pct\_ion | 4.7 SiO(H,Na) per nm2, 2.35 SiO-Na+ per nm2 |
| silica\_Q3\_amorph\_4\_7OH\_0pct\_ion | Amorphous Q3 surface with 4.7 silanol groups per nm2 that contains some Q2 and Q4 environments (adapted from Materials Studio), the area of this corrugated surface is ~5% larger than a flat surface, 0.0 SiO-Na+ per nm2 (pzc) |
| silica\_Q3\_amorph\_4\_7OH\_9pct\_ion | 4.7 SiO(H,Na) per nm2, 0.45 SiO-Na+ per nm2 |
| silica\_Q3\_amorph\_4\_7OH\_18pct\_ion | 4.7 SiO(H,Na) per nm2, 0.85 SiO-Na+ per nm2 |
| silica\_Q3\_Q4\_2\_4OH\_0pct\_ion | Mixed Q3/Q4 surface with 2.4 silanol groups per nm2 prepared from the Q3 surface by partial condensation of surface silanol groups, 0.0 SiO-Na+ per nm2 (pzc) |
| silica\_Q3\_Q4\_2\_4OH\_15pct\_ion | 2.4 SiO(H,Na) per nm2, 0.34 SiO-Na+ per nm2 |
| silica\_Q3\_Q4\_2\_4OH\_30pct\_ion | 2.4 SiO(H,Na) per nm2, 0.68 SiO-Na+ per nm2 |
| silica\_Q4\_0\_0OH | Q4 surface with 0.0 silanol groups per nm2 prepared from the Q3 surface by complete condensation of surface silanol groups and energy minimization (some Si‒O bonds are 10% stretched) |

Notes:

(1) The models contain appropriate atom types and atomic charges. They are ready for simulations using codes such as Forcite, Discover (.car/.mdf), LAMMPS (.lammps05), NAMD, AMBER (.pdb/.psf), and others.

(2) The surface models contain reasonable initial atomic coordinates and are coarsely energy-minimized. A few steps initial minimization (e.g. 50) before molecular dynamics are recommended to adjust atom positions to new interfacial environments.

(3) Silica surfaces with customized degree of ionization and surface topology, including porous structures, can be prepared from the given bulk and surface models. Correct assignment of stoichiometry, atom connectivity, atomic charges, and force field types is essential (the net charge should be 0.0000e).

**Table 1. Guide towards Surface Models for a Given Silica Substrate [1]**

|  |  |  |  |
| --- | --- | --- | --- |
| Type of silica substrate | 1. Area density of silanol groups | 2. Ionization to  (SiO– M+)a | 3. Surface topography |
| Quartz surfaces, silica nanoparticles >200 nm size, silica at pH > 9 | Q2 and Q2/Q3  (9.4 to 4.7 per nm2) | pH 2: ~0 per nm2  pH 5: ~0.5 per nm2  pH 7: ~1.0 per nm2  pH ≥9: ~1.5 per nm2 | Substrate-specific:  smooth,  rough,  porous |
| Most silica glasses, porous silica, silica nanoparticles <200 nm size | Q3  (4.7 per nm2) | pH 3: ~0 per nm2 (0%)  pH 5: ~0.3 per nm2 (6%)  pH 7: ~0.6 per nm2 (13%)  pH ≥9: ~0.9 per nm2 (20%) |
| Silica surfaces and nanoparticles annealed at 200-1000 °C | Q3/Q4 and Q4  (4.7 to 0 per nm2) | pH 4: ~0 per nm2  pH 7: 0-0.6 per nm2 depending on Q3 content |

a Physiological conditions with an ionic strength *I* ~ 0.1-0.3 M of sodium ions (M=Na) are assumed. Ionization at a given pH for different ionic strength *I* and other cations must be reevaluated according to reference data (see text).

References:

[1] Emami, F. S. et al. Chem. Mater. 2014, 26, DOI: 10.1021/cm500365c.

[2] Patwardhan, S. V.; Emami, F. S.; Berry, R. J.; Jones, S. E.; Naik, R. R.; Deschaume, O.; Heinz, H.; Perry, C. C. J. Am. Chem. Soc. 2012, 134, 6244-6256.