Amorphous SiO_2 Surface Models: Energetics of the Dehydroxylation Process, Strain, *Ab Initio* Atomistic Thermodynamics and IR Spectroscopic Signatures

Electronic Supporting Information

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1. Amorphous vs. crystalline models: Bulk structures.

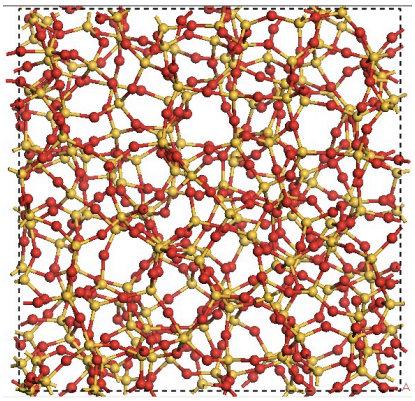

Figure S1. Unit cell of the amorphous SiO_2 bulk structure. 21.39x21.39x 21.39 Å unit cell. It contains 216 SiO_2 units

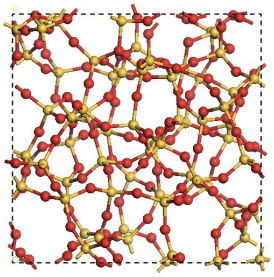

Figure S2. Unit cell of the amorphous SiO_2 bulk structure. 14.32 x 14.32 x 14.32 Å unit cell. It contains 64 SiO2 units

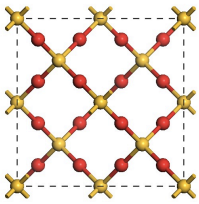

Figure S3. Unit cell of the β-cristobalite bulk structure. 7.16 x 7.16 x 7.16 Å unit cell. It contains 8 SiO2 units.

2. Amorphous vs. crystalline models of the SiO_2 surface:

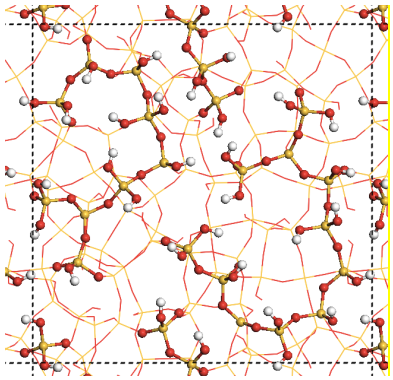

Figure S4. Optimized structure of the fully hydroxylated 001 termination of the amorphous silica bulk structure. The dimensions of the unit cell are 21.39x21.39x34.2 Å. It contains 408 atoms and it has a silanol coverage equal to 7.2 OH/nm^2.

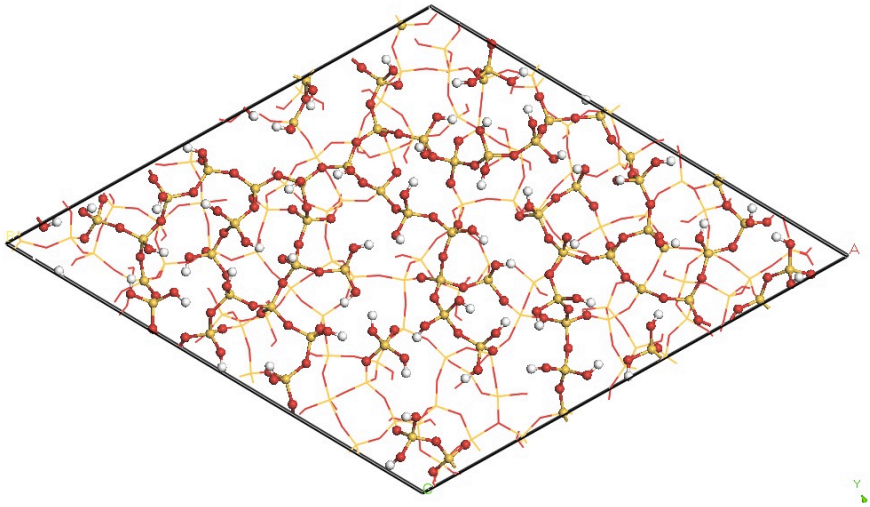

Figure S5. Optimized structure of the fully hydroxylated 111 termination of the amorphous silica bulk structure. The dimensions of the unit cell are 30.26x 30.26 x 33.36 Å. It contains 609 atoms and it has a silanol coverage equal to 7.2 OH/nm^2.

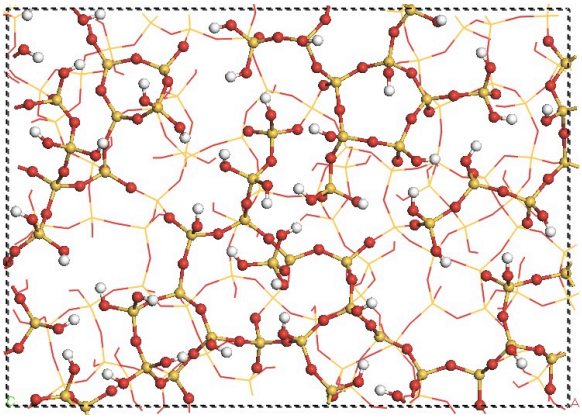

Figure S6. Optimized structure of the fully hydroxylated 101 termination of the amorphous silica bulk structure. The dimensions of the unit cell are 30.26x 21.39x 33.05 Å. It contains 510 atoms and it has a silanol coverage 7.3 OH/nm^2.

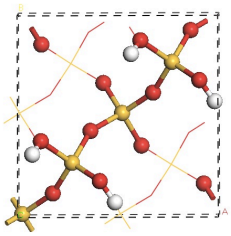

Figure S7. Unit cell of the fully hydroxylated 001 termination of β-cristobalite. Adapted from Rozanksa, *et. al.*[1] Only geminal silanols are present on this termination.

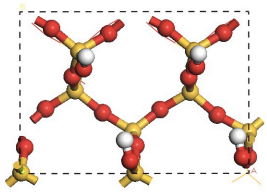

Figure S8. Unit cell of the fully hydroxylated 101 termination of β-cristobalite. Adapted from Rozanska, *et. al.*[1] Only vicinal silanols are present on this termination.

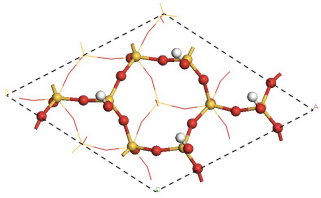

Figure S9. Unit cell of the fully hydroxylated ideal 111 termination of β-cristobalite, Adapted from Rozanksa, *et. al.*[1] Only isolated silanols are present on this termination.

We can observe how the three termination of β-cristobalite present regular silanol patterns, with different kind of silanols being present depending on each surface termination. For the case of the 001 termination of β-cristobalite, only germinal silanols are present (Figure S7). For this surface, the direct condensation of adjacent silanol groups is possible, and feasible energetically, as previously reported by Rozanska, et. al.[1] For the 101 and 111 terminations of β-cristobalite only vicinal and silanol silanols are present, respectively (Figures S8,S9). Since they are far from each other, direct dehydration is not possible and SiO_2 reconstructions need to be considered in order to dehydroxylate them.

3. Effect of the dispersion on the energetics of the dehydroxylation process of the 001 SiO_2 surface for some selected steps.

Table **S1**. Comparion of the energetics of dehydroxylation with and without the inclusion of dispersion effects.

Model	**OH/nm^2**	***Total n H_2O released***	***Average ΔE per nH_2O (kJ.mol^{-1})* without dispersion (kJ.mol^{-1})**	***ΔE_r* with dispersion (kJ.mol^{-1})**
SiO_2-1	7.2	0	0	0
SiO_2-2	5.9	3	101	119
SiO_2-3	4.6	6	110	131
SiO_2-4	3.3	9	203	212

Model	**OH/nm^2**	***Total n H_2O released***	***ΔE per nH_2O (kJ.mol^{-1})* without dispersion (kJ.mol^{-1})**	***ΔE per nH_2O (kJ.mol^{-1})* with dispersion (kJ.mol^{-1})**
SiO_2-5	2.8	10	43	59
SiO_2-6	2.4	11	157	171
SiO_2-7	2.0	12	27	51
SiO_2-8	1.6	13	252	238
SiO_2-9	1.1	14	259	276

4. Dehydroxylation of the smaller SiO_2 amorphous unit cell.

Table S2. Energetics of the dehydroxylation process via the 001 termination of the small SiO2 bulk unit cell (Figure S2).

Model	**OH/nm^2**	***Total n H_2O released***	***Average Distance new O-Si bonds* (Å)**	***ΔE_r* (kJ.mol^{-1})**	***Average ΔE per nH_2O (kJ.mol^{-1})***
SiO_2-s-1	7.8	0	-	0	0
SiO_2-s-2	6.8	1	1.691	181	181
SiO_2-s-3	5.9	2	1.646	31	106
SiO_2-s-4	4.9	3	1.689	186	133
SiO_2-s-5	3.9	4	1.655	-2	99
SiO_2-s-6	2.9	5	1.664	82	96
SiO_2-s-7	2.0	6	1.732	282	127
SiO_2-s-8	1.0	7	1.713	255	145

All the steps involve direct dehydroxlyation except from SiO_2-s-4 to SiO2-s-5 surface, where the migration of one SiO_2 unit was considered.

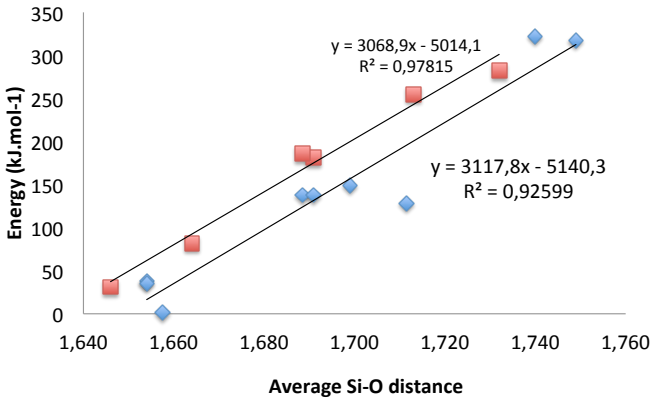

Figure S10. Comparison of the dehydration energy vs. average Si-O distances of the small unit cell of amorphous SiO_2 (in red) vs. the big unit cell of amorphous SiO_2 (in blue).

5. SiO_2 Reconstruction Steps

At this area of the SiO_2-4 surface, there are two silanol nests where the reconstruction of the silica surface via the migration of one SiO2 group can be considered (see Figure S11). Since the one with distances between oxygens equal to 5.256, 5.746 and 3.900 Å presents more similar distances than the other triangle, which has distances equal to 6.283, 4.906 and 3.900 Å, the former silanol nest was considered for the dehydroxylation step from the SiO_2-4 to the SiO_2-5 surface.

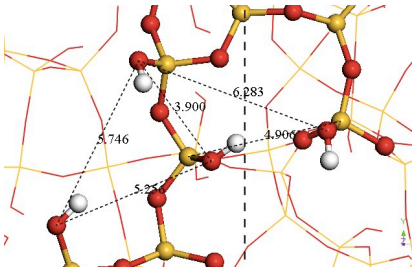

Figure S11. The two possible silanol nests that can be dehydroxylated via the migration of one SiO_2 unit on the SiO_2-4 surface are depicted. Distances in Å.

For the silanol pattern on the SiO_2-6 (see **Figure S12**) is not possible to consider the migration of one SiO_2 unit since three silanols in a triangular pattern would be needed. Thus, for this silanol pattern, the migration of two SiO_2 units was considered in order to further dehydroxylate the surface.

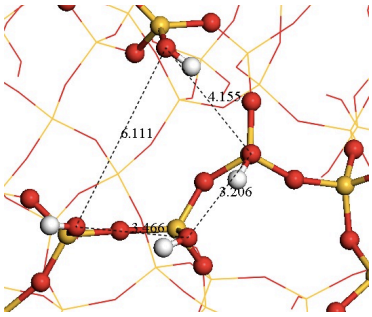

Figure S12. Silanol nest present on the SiO_2-6 surface. Distances in Å.

6. Additional IR spectra.

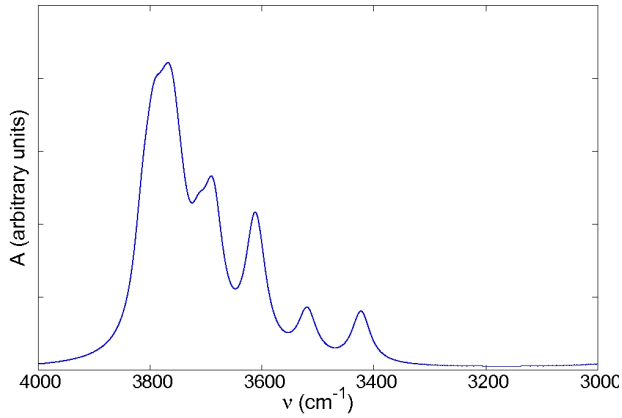

Figure S13. IR of the fully hydroxlated model for the small SiO_2 unit cell (14.32 x 14.32 x 34.78 Å) of amorphous SiO_2.

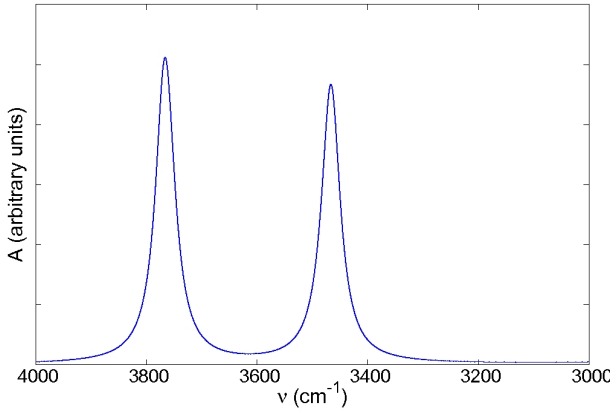

Figure S14. IR of the fully hydroxylated 001 crystalline model from Figure S7.

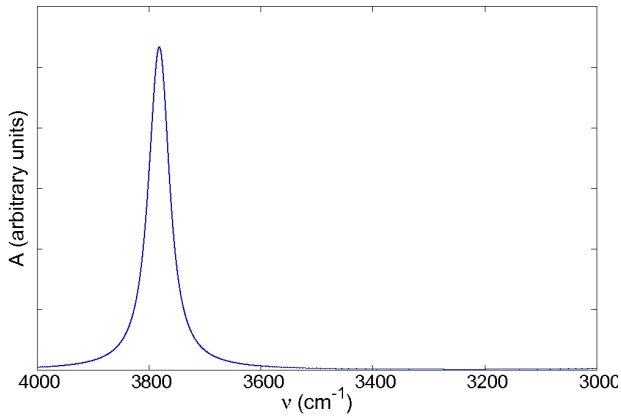

Figure S15. IR of the fully hydroxylated 101 crystalline model from Figure S8.

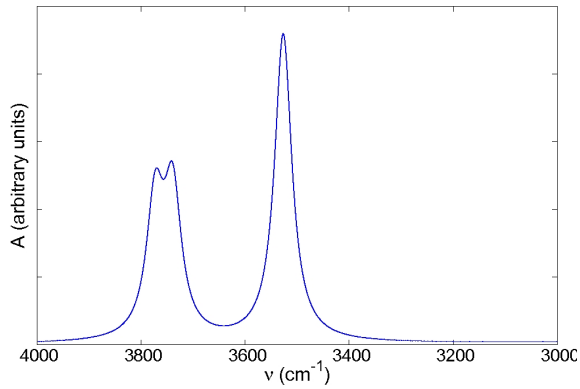

Figure S16. IR of the fully hydroxylated 111 crystalline model from Figure S9.

References

1. X. Rozanska, F. Delbecq and P. Sautet, *Phys. Chem. Chem. Phys.*, 2010, **12**, 14930-14940.