SUPPORTING INFORMATION

Initial step of silicate versus aluminosilicate formation in zeolite synthesis:reaction mechanism in water with a tetrapropylamonium template

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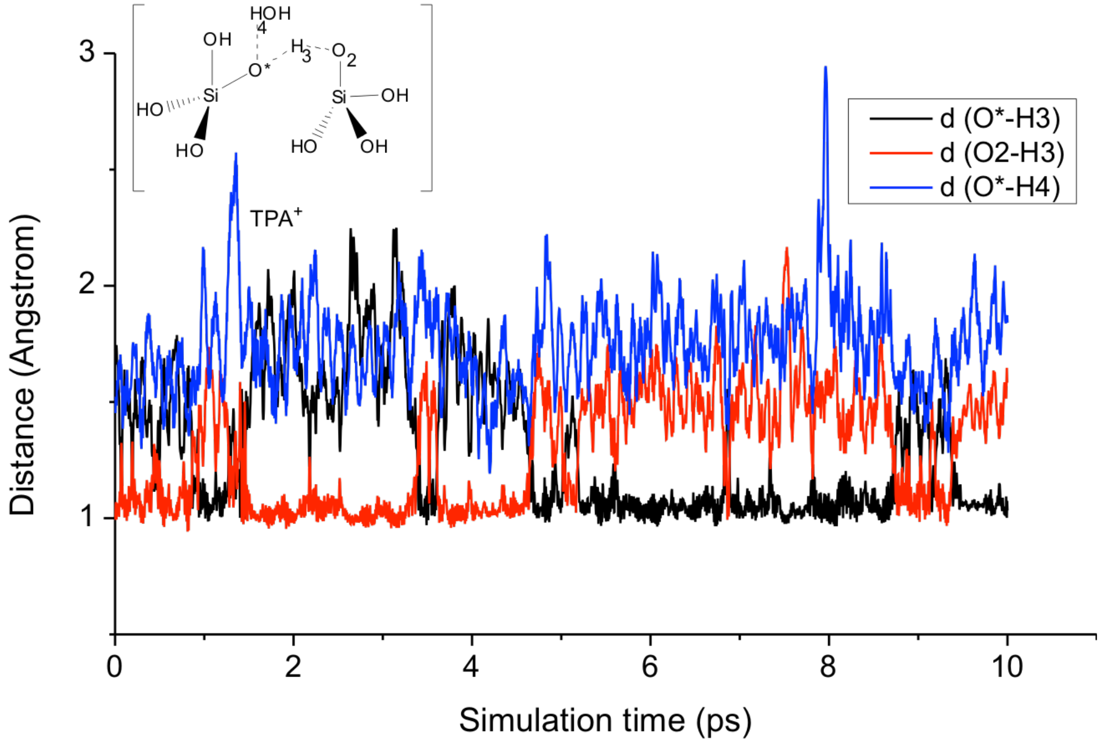
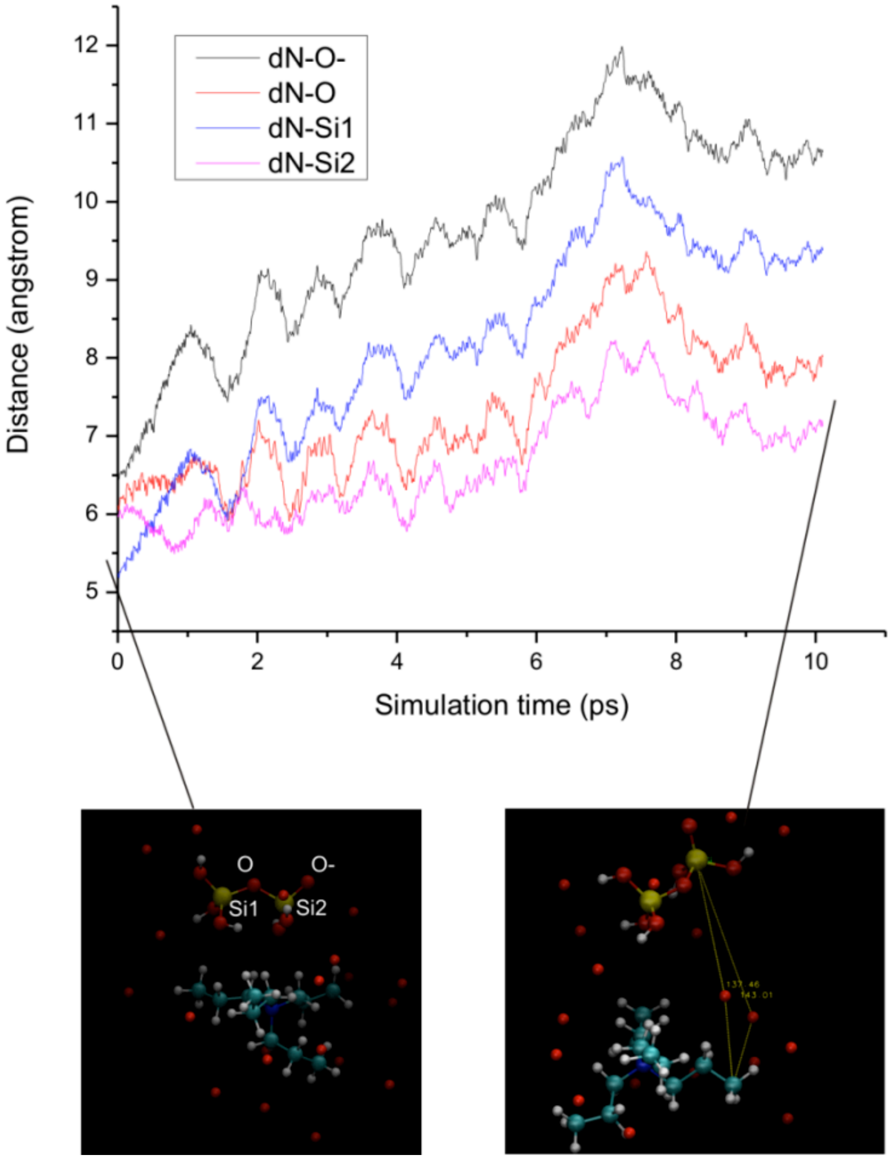
S1./ The H-bonds between the silicate monomers and between silicate and water in the reactant state of Si-O-Si formation .

During the 10 ps of simulation, the proton H_3 jumps between O* and O_2 (see the inverse behaviors of the red and black curves). The O*-H_4 hydrogen bond is not affected.



S2./ Separation of template and silicate in the product of the Si-O-Si formation.

A simulation was done in order to verify the separation of the TPA$^+$ template and the silicate dimer in the product state. For the starting point of the dynamics, the structure is taken from the optimized structure in gas phase with a close contact between the template and the dimer. During the 10ps of simulation (NVT), the template drifted away from the dimer, with insertion of water molecules between them.



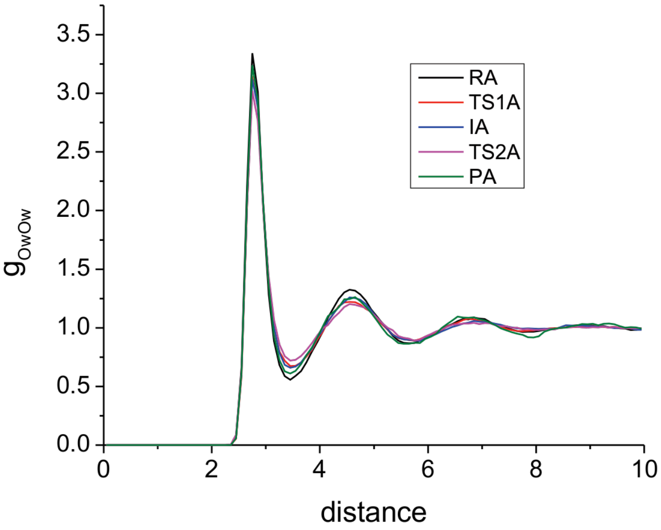
S3./ Radial distribution function of water oxygen $g_{(Ow\text{-}Ow)}$ in the stationary states of the reaction forming silicate and aluminosilicate.

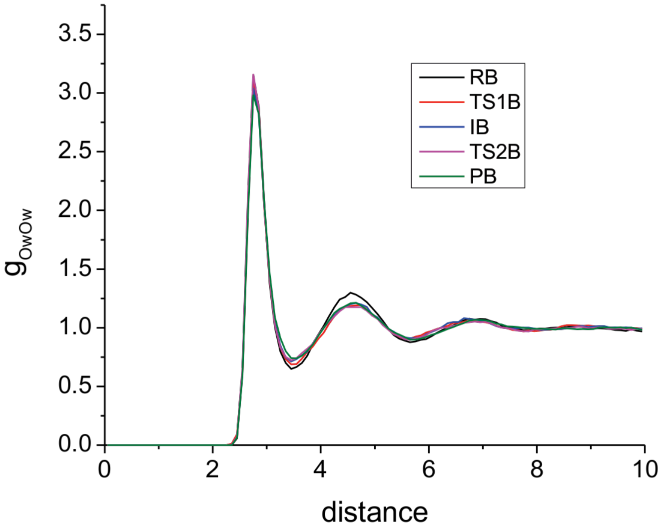
Si-O-Si formation

Si-O-Si formation	RA	TS1	I	TS2	PA
max	3.34	3.15	3.12	3.02	3.24
min	0.56	0.67	0.66	0.72	0.61

Al-O-Si formation

Al-O-Si formation	RB	TS1	IB	TS2	PB
max	3.14	3.10	3.05	3.16	2.99
min	0.65	0.69	0.71	0.72	0.74





Peaks having the largest surface (higher max and lower min values of gOw-Ow) indicate a more structured water around silicate and template. For the formation of Si-O-Si, the water is more localized in the case of reactant and product state, while water is less structured in the transition state. The trend is less clear for the formation of Al-O-Si, but the water is also more structured in the initial state of the reaction RB (black line). The distance is in Å.

S4./ Root means square displacement (RMSD) of water in the dimer silicate formation.

After the system is corrected for translation and rotation, RMSD for the O atoms of the water molecules is calculated by the equation below

$$\text{RMSD(Ow)}=\sqrt{\frac{\sum_{i=1}^{N}(ri(t)-ri(t=0))^2}{N}}$$

Where N is the number of water molecules, ri(t) is the coordinates of water at time t.

A higher value of RMSD means a larger mobility of water around template and silicate. The table shows that water in the transition state 2 (TS2A) has the largest mobility, while the smallest mobility of water is found in the case of reactant state (RA) in good relation with the previous radial distribution function.

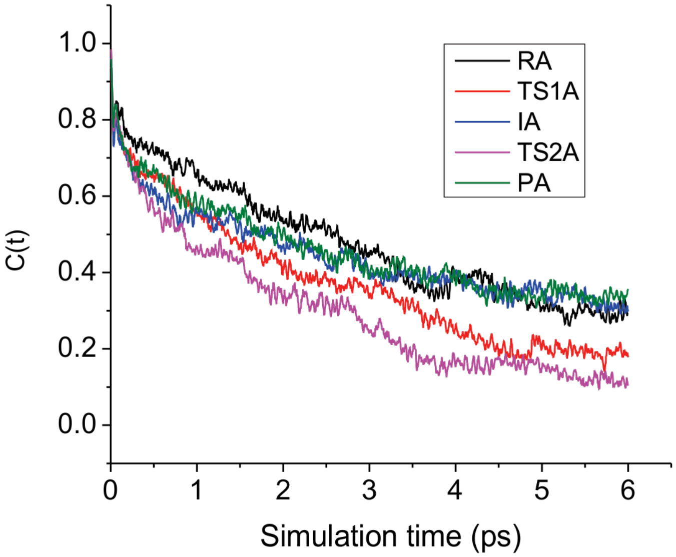
Structure	RMSD(Ow) (Å)
RA	1.31
TS1A	1.75
IA	1.58
TS2A	1.90
PA	1.45

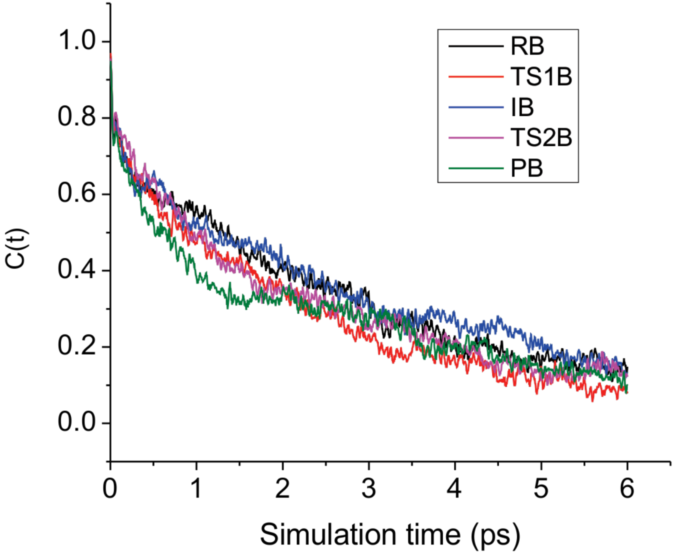
S5./ Time correlation function of the orientation of water OH groups.

The time correlation of the hydroxyl groups of water is calculated by the equation $C(t) = \langle P_2.\overrightarrow{u(OH_0)}.\overrightarrow{u(OH_t)}\rangle$, where $P2$ is the second order Legendre polynomial and $u_{\mathrm{OH}}(t)$ is the orientation of the water OH bond at time t. The relaxation time τ, a time-integration of $C(t)$, is an indication of the water re-orientation speed. A small relaxation time indicates a fast water re-orientation. In the case of Si-O-Si formation, water re-orientation is fastest in the transition state 2 (TS2A) and slowest in the reactant state RA. For the formation of Al-O-Si, differences are smaller: water re-orientation is fastest in the transition state 1 (TS1B) and slowest in the intermediate state (IB).

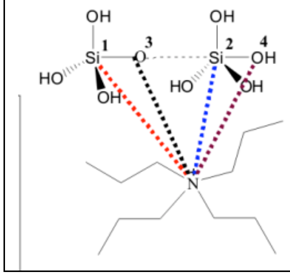
Structure (Si-O-Si)	Correlation time ~ relaxation time (ps)
RA	2.9 (slowest)
TS1A	2.2
IA	2.7
TS2A	1.8 (fastest)
PA	2.7

Structure (Al-O-Si)	Correlation time ~ relaxation time (ps)
RB	2.0
TS1B	1.7 (fastest)
IB	2.1 (slowest)
TS2B	1.9
PB	1.7





S6./ Distance between the N atom of the TPA$^+$ template and various atoms of the silicate unit in the stationary structures along the Si-O-Si formation in the implicit COSMO solvation model.

	Distance (angstrom)	RA*	TS1*	IA*	TS2*	PA*
	N-Si1	4.418	4.460	4.496	5.292	5.094
	N-Si2	6.779	6.483	6.128	4.866	5.100
	N-O3	5.923	5.857	5.768	5.674	5.752
	N-O4	8.185	7.604	6.898	4.068	4.059

The N atom of the template remains close to the dimer in the TS and product states, in contrast with the explicit water model.