Supporting information for: Structure Directing Role of Counter Ions in the Initial Stage of Zeolite Synthesis

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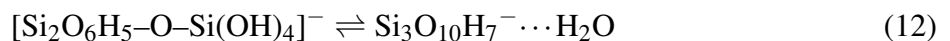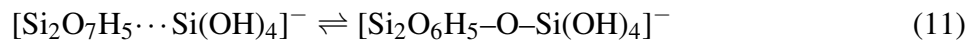[*]To whom correspondence should be addressed

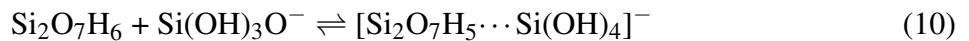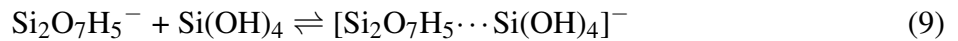[†]Laboratory of Inorganic Chemistry and Catalysis, ST/SKA
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Modeling Oligomerization

In the case of dimerization, there are two mechanisms. The first of these is the so-called neutral mechanism, in which the two reactants are neutral. The second mechanism, the so-called anionic mechanism, proposes that the reactants consist of two monomers, one being deprotonated. The anionic mechanism has been shown to be more favorable. Therefore we used the preferred anionic mechanism in this work.[1]

The formation of silicate oligomers can be described by the following equations. The following symbols are used; $\cdots$ for the reactant complex, $-O-$ for the intermediate species, $\cdots H_2O$ for the leaving water, $\triangle$ for the 3-ring and $\perp$ for the branched tetramer.

$$Si(OH)_4 + (OH)^- \rightleftharpoons Si(OH)_3O^- + H_2O \tag{1}$$

$$Si(OH)_4 + H_2O \rightleftharpoons Si(OH)_3O^- + H_3O^+ \tag{2}$$

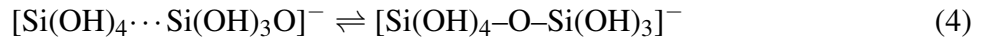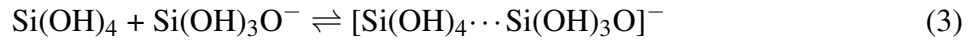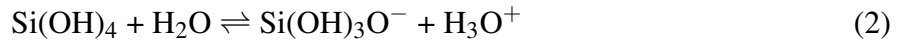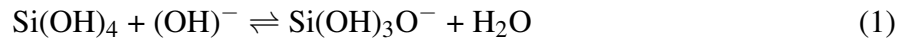$$Si(OH)_4 + Si(OH)_3O^- \rightleftharpoons [Si(OH)_4 \cdots Si(OH)_3O]^- \tag{3}$$

$$[Si(OH)_4 \cdots Si(OH)_3O]^- \rightleftharpoons [Si(OH)_4-O-Si(OH)_3]^- \tag{4}$$

$$[Si(OH)_4-O-Si(OH)_3]^- \rightleftharpoons Si_2O_7H_5^- \cdots H_2O \tag{5}$$

$$Si_2O_7H_5^- \cdots H_2O \rightleftharpoons Si_2O_7H_5^- + H_2O \tag{6}$$

$$Si_2O_7H_6 + (OH)^- \rightleftharpoons Si_2O_7H_5^- + H_2O \tag{7}$$

$$Si_2O_7H_6 + H_2O \rightleftharpoons Si_2O_7H_5^- + H_3O^+ \tag{8}$$

$$Si_2O_7H_5^- + Si(OH)_4 \rightleftharpoons [Si_2O_7H_5 \cdots Si(OH)_4]^- \tag{9}$$

$$Si_2O_7H_6 + Si(OH)_3O^- \rightleftharpoons [Si_2O_7H_5 \cdots Si(OH)_4]^- \tag{10}$$

$$[Si_2O_7H_5 \cdots Si(OH)_4]^- \rightleftharpoons [Si_2O_6H_5-O-Si(OH)_4]^- \tag{11}$$

$$[Si_2O_6H_5-O-Si(OH)_4]^- \rightleftharpoons Si_3O_{10}H_7^- \cdots H_2O \tag{12}$$

$$Si_3O_{10}H_7^- \cdots H_2O \rightleftharpoons Si_3O_{10}H_7^- + H_2O \tag{13}$$

$$Si_3O_{10}H_8 + (OH)^- \rightleftharpoons Si_3O_{10}H_7^- + H_2O \tag{14}$$

$$Si_3O_{10}H_8 + H_2O \rightleftharpoons Si_3O_{10}H_7^- + H_3O^+ \tag{15}$$

$$[Si_3O_{10}H_7]^- \rightleftharpoons [Si_3O_9H_7-O-]^-(\triangle) \tag{16}$$

$$[Si_3O_9H_7-O-]^-(\triangle) \rightleftharpoons Si_3O_9H_5^-(\triangle) \cdots H_2O \tag{17}$$

$$Si_3O_9H_5^-(\triangle) \cdots H_2O \rightleftharpoons Si_3O_9H_5^-(\triangle) + H_2O \tag{18}$$

$$Si_3O_{10}H_8 + Si(OH)_3O^- \rightleftharpoons [Si_3O_{10}H_8 \cdots Si(OH)_3O]^-(\perp) \tag{19}$$

$$Si_3O_{10}H_7^- + Si(OH)_4 \rightleftharpoons [Si_3O_{10}H_8 \cdots Si(OH)_3O]^-(\perp) \tag{20}$$

$$[Si_3O_{10}H_8 \cdots Si(OH)_3O]^-(\perp) \rightleftharpoons [Si_3O_{10}H_8-O-Si(OH)_3]^-(\perp) \tag{21}$$

$$[Si_3O_{10}H_8-O-Si(OH)_3]^-(\perp) \rightleftharpoons Si_4O_{13}H_9^-(\perp) \cdots H_2O \tag{22}$$

$$Si_4O_{13}H_9^-(\perp) \cdots H_2O \rightleftharpoons Si_4O_{13}H_9^-(\perp) + H_2O \tag{23}$$

The corresponding activation energies and prefactors of oligomerization and reverse reactions in the absence of counter ion are listed in Table 1.

Table 1: Calculated activation energies [kJ mol^{-1}], in the absence of counter ion, and prefactors of reactions from Eq. (1) to Eq. (23). The unit of the prefactors is s^{-1}. The first column is the reactions numbered corresponding to the Equations Eq. (1) to Eq. (23) listed above. E_{act}(1) and Pref(1) are the activation energy and prefactor of forward reaction respectively. E_{act}(-1) and Pref(-1) are the activation energy and prefactor of reverse reaction respectively. The temperature is 350 K and pH = 7.

Reactions	$E_{act}(1)$	Pref(1)	$E_{act}(-1)$	Pref(-1)
1	0	1.484×10^4	99	8.050×10^{12}
2	191	8.040×10^{12}	0	1.417×10^4
3	0	1.820×10^7	28	7.293×10^{12}
4	44	7.293×10^{12}	25	7.293×10^{12}

5	42	7.293×10^{12}	86	7.293×10^{12}
6	9	7.293×10^{12}	0	7.750×10^{12}
7	0	1.434×10^{4}	99	7.750×10^{12}
8	191	7.750×10^{12}	0	1.360×10^{4}
9	0	1.600×10^{7}	31	7.293×10^{12}
10	0	1.600×10^{7}	54	7.293×10^{12}
11	43	7.293×10^{12}	23	7.293×10^{12}
12	33	7.293×10^{12}	78	7.293×10^{12}
13	7	7.293×10^{12}	0	7.640×10^{12}
14	0	1.410×10^{4}	99	7.640×10^{12}
15	191	7.640×10^{12}	0	1.340×10^{4}
16	35	7.293×10^{12}	11	7.293×10^{12}
17	48	7.293×10^{12}	81	7.293×10^{12}
18	13	7.293×10^{12}	0	7.660×10^{12}
19	0	1.510×10^{7}	41	7.293×10^{12}
20	0	1.510×10^{7}	30	7.293×10^{12}
21	69	7.293×10^{12}	11	7.293×10^{12}
22	43	7.293×10^{12}	91	7.293×10^{12}
23	30	7.293×10^{12}	0	7.293×10^{12}

The rate constants were calculated using equation,

$$k = \nu\exp\left[\frac{-E_{act}}{k_BT}\right]. \tag{24}$$

with E_{act} the activation energy and ν the prefactor. The prefactors are calculated for the following three cases. The first case is a unimolecular reaction; $\nu_1 = \frac{k_BT}{h}$, where k_B is Boltzmann constant and h is Planck's constant. The second case is a bimolecular reaction; $\nu_2 = \frac{\sqrt{(k_BT/2\pi\mu)}4\pi R^2}{V}$, where $\mu = \frac{m_1m_2}{(m_1+m_2)}$, m_1 and m_2 are the masses of the reactants, R is the distance between the reactants in

the transition state, and V is the volume of the simulation box. And the third case is a bimolecular reaction with solvent molecule as a reactant; $v_3 = v_2 N_{solvent}$. $N_{solvent}$ is the number of solvent molecules. The number of H_3O^+ and OH^- molecules are determined by pH. Such as the number of OH^- molecules, $N_{(OH)^-} = N_A V 10^{(pH-14)}$. More details can be found in the reference.[2]

The rate constants of silicate oligomerization reactions in the presence of counter ions (Li^+ and NH_4^+) were determined from density functional theory based molecular dynamics simulations.[1] In the case of dimerization, we considered a system consisting of one silicic acid $Si(OH)_4$ and its deprotonated form $Si(OH)_3O^-$ with 64 water molecules. The simulation cell was a periodically replicated cubic box with a size corresponding to a density of solution around 1 g cm^{-3} at ambient conditions. The temperature was set at T = 350 K imposed with a Nosé-Hoover thermostat. The parameters obtained with presence of counter ions Li^+ and NH_4^+ are listed in Table 2 and Table 3 respectively.

Table 2: Calculated activation energies [kJ mol^{-1}], with presence of Li^+ counter ions, and prefactors of reactions from Eq. (1) to Eq. (23). The first column is the reactions numbered corresponding to the Equations Eq. (1) to Eq. (23) listed above. $E_{act}(1)$ and Pref(1) are the activation energy and prefactor of forward reaction respectively. $E_{act}(-1)$ and Pref(-1) are the activation energy and prefactor of reverse reaction respectively. The temperature is 350 K and pH = 7.

Reactions	$E_{act}(1)$	Pref(1)	$E_{act}(-1)$	Pref(-1)
1	0	1.484×10^4	99	8.050×10^{12}
2	191	8.040×10^{12}	0	1.417×10^4
3	0	1.820×10^7	28	7.293×10^{12}
4	70	7.293×10^{12}	61	7.293×10^{12}
5	89	7.293×10^{12}	121	7.293×10^{12}
6	9	7.293×10^{12}	0	7.750×10^{12}
7	0	1.434×10^4	99	7.750×10^{12}
8	191	7.750×10^{12}	0	1.360×10^4
9	0	1.600×10^7	31	7.293×10^{12}
10	0	1.600×10^7	54	7.293×10^{12}

11	78	7.293×10^{12}	66	7.293×10^{12}
12	96	7.293×10^{12}	112	7.293×10^{12}
13	7	7.293×10^{12}	0	7.640×10^{12}
14	0	1.410×10^{4}	99	7.640×10^{12}
15	191	7.640×10^{12}	0	1.340×10^{4}
16	83	7.293×10^{12}	66	7.293×10^{12}
17	94	7.293×10^{12}	91	7.293×10^{12}
18	13	7.293×10^{12}	0	7.660×10^{12}
19	0	1.510×10^{7}	41	7.293×10^{12}
20	0	1.510×10^{7}	30	7.293×10^{12}
21	60	7.293×10^{12}	65	7.293×10^{12}
22	85	7.293×10^{12}	98	7.293×10^{12}
23	30	7.293×10^{12}	0	7.293×10^{12}

Some of the energies in the tables are corrected, because the silicate condensation reactions are endothermic in the simulations with water molecules treated explicitly.[1,3] This is questionable, because it would mean that the oligomers will not form. We attribute this to the contribution of entropy reduction form the water shell around the silicate molecules. Leung et al.[4] have examined the source of the entropy reduction which occurs when a gas-phase molecule is moved into solution and have concluded that the main contribution to the entropy change comes from cavity formation in the solvent. The change in entropy mainly comes from the rearrangement of the water shell, that is dominated by hydrogen bonds. The larger the molecule, the larger the water shell around it, and hence the change in water shell is larger for a larger molecule. This indicates that the addition of counter ions contribute to the entropy change, and the contribution from NH_4^+ is larger than that from Li^+, due to the larger volume of NH_4^+. To make the reactions exothermic, we reduce the entropy contribution from the water shell and the counter ions. The entropy contribution of these three sets of parameters (without counter ion, with Li^+ and with NH_4^+) are reduced somewhat

arbitrarily by 50 kJ/mol, 60 kJ/mol and 70 kJ/mol respectively. The counter ions have contribution to the intermediate states as well. We then reduce the energies of the intermediate states of the two sets of parameters (with Li^+ and with NH_4^+) by 50 kJ/mol and 60 kJ/mol respectively. Although it is somewhat arbitrary, it is reasonable. If the energy contributions are reduced less, the reactions will not take place. If they are reduced more, dimers are too stable, as a result no further oligomerization reactions occur.

In this work, we only study the silicate oligomerization at neutral pH and temperature of 350 K. The change of pH consequently changes the number of H_3O^+ and OH^- ions. The pH only changes the rate constants of bimolecular reactions with solvent molecule as a reactant. The changed rate constants can be easily calculated by changing $N_{solvent}$. $N_{solvent}$ can be the number of water molecules, H_3O^+ or OH^- ions as described in the next section. The others remain the same. The rate constant is related to temperature by the Eq. (24). The rate constants at other temperatures can be calculated from the available prefactors. Thus we give the activation energies and prefactors, the readers can calculate the rate constants for other pHs and temperatures themselves.

Table 3: Calculated activation energies [kJ mol^{-1}], with presence of NH_4^+ counter ions, and prefactors of reactions from Eq. (1) to Eq. (23). The first column is the reactions numbered corresponding to the Equations Eq. (1) to Eq. (23) listed above. $E_{act}(1)$ and Pref(1) are the activation energy and prefactor of forward reaction respectively. $E_{act}(-1)$ and Pref(-1) are the activation energy and prefactor of reverse reaction respectively. The temperature is 350 K and pH = 7.

Reactions	$E_{act}(1)$	Pref(1)	$E_{act}(-1)$	Pref(-1)
1	0	1.484×10^4	99	8.050×10^{12}
2	191	8.040×10^{12}	0	1.417×10^4
3	0	1.820×10^7	28	7.293×10^{12}
4	106	7.293×10^{12}	81	7.293×10^{12}
5	95	7.293×10^{12}	115	7.293×10^{12}
6	9	7.293×10^{12}	0	7.750×10^{12}
7	0	1.434×10^4	99	7.750×10^{12}
8	191	7.750×10^{12}	0	1.360×10^4

9	0	1.600×10^7	31	7.293×10^{12}
10	0	1.600×10^7	54	7.293×10^{12}
11	63	7.293×10^{12}	72	7.293×10^{12}
12	82	7.293×10^{12}	119	7.293×10^{12}
13	7	7.293×10^{12}	0	7.640×10^{12}
14	0	1.410×10^4	99	7.640×10^{12}
15	191	7.640×10^{12}	0	1.340×10^4
16	54	7.293×10^{12}	66	7.293×10^{12}
17	94	7.293×10^{12}	105	7.293×10^{12}
18	13	7.293×10^{12}	0	7.660×10^{12}
19	0	1.510×10^7	41	7.293×10^{12}
20	0	1.510×10^7	30	7.293×10^{12}
21	62	7.293×10^{12}	76	7.293×10^{12}
22	102	7.293×10^{12}	108	7.293×10^{12}
23	30	7.293×10^{12}	0	7.293×10^{12}

Theory of Continuum kMC

The kMC simulations were carried out using our newly developed continuum kMC.[2] The reaction time of a unimolecular reaction is given by the usual expression[5]

$$\Delta t = -\frac{1}{k_{rx}} \ln r \tag{25}$$

with Δt the time between the time that the particle was formed and the reaction, r a random number from the interval $[0, 1\rangle$, and k_{rx} the rate constant of the reaction.

For the reaction times t_{rx} for bimolecular reactions between particles 1 and 2 we can write

$$\text{erfc}\left(\frac{\alpha}{\sqrt{\Delta t}}\right) = \beta \tag{26}$$

with

$$\begin{aligned}
\beta = & -\frac{4\pi(D_1+D_2)|\mathbf{r}_2-\mathbf{r}_1|\ln r}{k_{rx}L^3} \\
& + \text{erfc}\left(\frac{|\mathbf{r}_2-\mathbf{r}_1|}{2\sqrt{D_1(\tau_2-\tau_1)}}\right)
\end{aligned} \tag{27}$$

and

$$\Delta t = t_{rx} - \frac{D_1\tau_1+D_2\tau_2}{D_1+D_2}. \tag{28}$$

Here D_i is the diffusion constant of particle i, τ_i the time that it was formed, and $\mathbf{r}_i$ the position where it was formed. Furthermore k_{rx} is the time that the reaction takes place, and L is the size of the simulation box which we take to be cubic. The function erfc is the error function complement.[6] It equals one minus the error function.

Determining the position where a unimolecular reaction takes place is quite easy. The particle simply diffuses and then reacts at whatever place it will be. So if a particle is at position $\mathbf{r}'$ at time τ, then diffusion will bring it to position $\mathbf{r}$ at a time t with $t > \tau$ with probability

$$\frac{1}{[4\pi D(t-\tau)]^{3/2}}\exp\left[-\frac{|\mathbf{r}-\mathbf{r}'|^2}{4D(t-\tau)}\right], \tag{29}$$

where D is its diffusion constant.

For a bimolecular reaction it becomes a bit more difficult. Diffusion will bring the reactants to position $\mathbf{r}$ at a time t with $t > \tau_i$ with probability

$$\frac{1}{[4\pi D_i(t-\tau_i)]^{3/2}}\exp\left[-\frac{|\mathbf{r}-\mathbf{r}_i|^2}{4D_i(t-\tau_i)}\right]. \tag{30}$$

So they will both be at position $\mathbf{r}$ with a probability proportional to

$$\exp\left[-\frac{|\mathbf{r}-\mathbf{r}_1|^2}{4D_1(t-\tau_1)}\right]\exp\left[-\frac{|\mathbf{r}-\mathbf{r}_2|^2}{4D_2(t-\tau_2)}\right]. \tag{31}$$

This is a probability distribution centered at

$$\frac{D_2(t-\tau_2)\mathbf{r}_1+D_1(t-\tau_1)\mathbf{r}_2}{D_1(t-\tau_1)+D_2(t-\tau_2)} \tag{32}$$

with a width

$$\sqrt{\frac{2D_1(t-\tau_1)D_2(t-\tau_2)}{D_1(t-\tau_1)+D_2(t-\tau_2)}} \tag{33}$$

in all directions. More detailed information about the continuum kMC method can be found in reference.[2]

The dependence of the reaction times of bimolecular reactions on the size L of the simulation box, which may seem to be odd, is explained here. We need to know the relation between the kMC and the macroscopic rate constants. For a reaction A + B → C we have

$$\frac{d[A]}{dt}=-k[A][B] \tag{34}$$

with k the macroscopic rate constant. In a kMC simulation we work with discrete particles. We have to multiply by L^3 with L is the side length of the simulation box. Then we have

$$\frac{dN_A}{dt}=-\frac{k}{L^3}N_AN_B=-\omega N_AN_B \tag{35}$$

with N_A and N_B are the number of A and B respectively. ω is the kMC rate constant. It is related to the macroscopic rate constant via $k=\omega L^3$. As the macroscopic rate constant k in Eq. (34) does not depend on the system size, we see that ω must be proportional to L^{-3}.

An important advantage of continuum kMC is that solvent molecules can be removed from the simulations, which minimizes the number of particles that have to be simulated explicitly. If the

solvent is only a spectator in the reactions, then we can ignore it. For the case of silicate solution, water molecules participate in acid-base reactions. Silicate species can donate a proton to OH^- (or H_2O). For example, $Si(OH)_4$ is then transformed into $Si(OH)_3O^-$. There is also a reverse reaction where $Si(OH)_3O^-$ gets back a proton from H_2O (or H_3O^+). These processes can be given by the following two example equations.

$$Si(OH)_4 + (OH)^- \rightleftharpoons Si(OH)_3O^- + H_2O \tag{36}$$
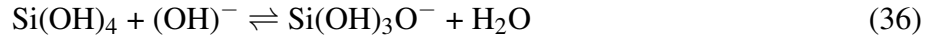
with macroscopic rate constants k_1 and k_{-1} (reverse process), and,

$$Si(OH)_4 + H_2O \rightleftharpoons Si(OH)_3O^- + H_3O^+ \tag{37}$$
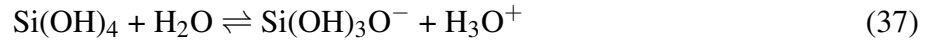
with macroscopic rate constants k_2 and k_{-2} (reverse process). We can write macroscopic rate equations for these equilibria. Let's take the first case as an example,

$$\frac{d[Si(OH)_4]}{dt} = -k_1[Si(OH)_4][OH^-] + k_{-1}[Si(OH)_3O^-][H_2O] \tag{38}$$

The solvent actually participates in the reaction, but we if do not want to include it explicitly in our simulations, then the rate constants above need to be modified. The expression above shows that we can accomplish this by replacing the equilibria above by

$$Si(OH)_4 \rightleftharpoons Si(OH)_3O^- \text{ (high pH)} \tag{39}$$
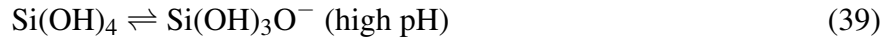
with rate constants $k_1[(OH)^-] = \omega_1 N_{(OH)^-}$ and $k_{-1}[H_2O] = \omega_{-1} N_{H_2O}$, with $k_n = \omega_n L^3$ [see Eq. (35)], and ω_n the kMC rate constants. The $N_{(OH)^-}$ and N_{H_2O} are the number of $(OH)^-$ and H_2O in the simulation box. We also have,

$$Si(OH)_4 \rightleftharpoons Si(OH)_3O^- \text{ (low pH)} \tag{40}$$
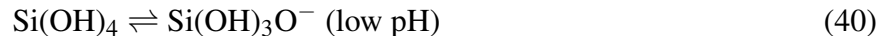
with rate constants $k_2[\text{H}_2\text{O}] = \omega_2 \text{N}_{\text{H}_2\text{O}}$ and $k_{-2}[\text{H}^+] = \omega_{-2}\text{N}_{\text{H}^+}$. $[(\text{OH})^-]$ and $[\text{H}^+]$ are determined by the pH of solution, such as $[(\text{OH})^-]=10^{-7}$ mol/L at pH = 7.

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