

Monte Carlo Simulations and Experiments of All-Silica Zeolite LTA Assembly Combining Structure Directing Agents That Match Cage Sizes

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Table of Contents

- Section 1.** Computational Methods
- Section 2.** Experimental methods
- Section 3.** Supporting Figures for Monte Carlo Simulations
- Section 4.** Supporting Figures for Experiments

Section 1. Computational Methods

Base Model: A thorough explanation of the model and methods used in this contribution can be found in the Supporting Information Section S1 of our previous publication.¹⁻³ The coarse-grained model that we have used for the silicic acid molecules, $\text{Si}(\text{OH})_4$ modeled for simplicity as SiO_4 , consists of flexible corner-sharing tetrahedra following Astala *et al.*⁴ Hard spheres with a diameter of 2.0 Å, representing the silicon atoms, are located in the center of each tetrahedron. The oxygens are point particles located on the corners of the tetrahedra, and they can be either bridging oxygens (BO) if they connect two tetrahedra, or hydroxyl groups (OH), if they are the terminal group.

Spring-Tetrahedron Model of Energetics: Structural integrity and flexibility of the silica network is ensured by two kinds of harmonic springs: one between BO and/or OH groups with a spring constant equal to $851 \text{ kJ mol}^{-1} \text{Å}^{-2}$ and an equilibrium distance between oxygens of 2.61 Å, and another restricting the Si-O-Si angles with an angular force constant equal to $226.74 \text{ kJ mol}^{-1} \text{Å}^{-2}$ and Si-O-Si reference angle of 155° . This parametrization of the model gives excellent agreement with known bulk moduli of several dense and zeolitic polymorphs of silica as seen in.⁴⁻⁶ We refer the reader to those studies for more details on the silica tetrahedral model.

OSDA Model: On the other hand, we have represented the OSDAs by means of hard spheres that interact with the silicon atoms (oxygen have been excluded from this interaction for computational simplicity) following the Lorentz combination rule: $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ where i and j vary over Si, SDA1 and SDA2. We have explored the effect of having 1 OSDA with a diameter of 10 Å versus 2 OSDAs with diameters of 10 Å and 6 Å. These OSDA diameters are compatible with the size of both “ α ” and sodalite cages characteristic of zeolite LTA and are meant to mimic the structure directing agents used experimentally. Only repulsive interactions are considered here which account for the volume excluded to the silicon atoms. In a forthcoming publication we will explore the effect of a broader range of interactions between the OSDAs and the silica network over zeolite formation, considering also electrostatic interactions of different strength.

We have represented the silica polymerization process by coupling this tetrahedral model with Monte Carlo simulations in the Reactive Ensemble (so-called RxMC). In this sampling approach we perform hydrolysis and condensation moves with Monte Carlo acceptance probabilities proportional to the condensation/hydrolysis equilibrium constant as described in detail in previous publications.⁵⁻⁶ In addition to the reactive moves previously described, we also perform translation and rotation of the tetrahedra, and translation of both oxygenic species and clusters. Force-bias Monte Carlo moves are performed to relax highly distorted structures that result after each intra-cluster condensation move. The attempt probabilities for the RxMC moves used here, defined in Ref. 1 and shown below in Table S1, were chosen for computational efficiency to facilitate network formation. Previous simulations of silica polymerization using the tetrahedral model of silica and the RxMC sampling approach were shown to give excellent agreement with NMR measurements over several thousand hours of the so-called Q_n distribution, which probes the mole fractions of silicon atoms bound to n bridging oxygen(s).

On the other hand, the Replica Exchange RxMC (RE-RxMC) technique enhances the sampling near the equilibrium state, allowing the system to rapidly escape from metastable local minima and to find the crystalline phases of the “spring-tetrahedron” model. In this work, as we did in our

previous contributions,¹⁻³ we have chosen the equilibrium constant controlling silica hydrolysis reactions (K_{hyd}) as the index parameter that varies from one replica to another. Large values of K_{hyd} promote disassembly of silica networks, important for avoiding glassy states, and small values of K_{hyd} drive the system to form silica networks. Thus, a suitable distribution of K_{hyd} values among the replicas avoids glass formation and forms silica crystalline states. We have used an adaptive method to reset the intermediate values of K_{hyd} among the replicas, on the fly of the simulation, to generate a distribution of the replica exchange acceptance probabilities fitting a Gaussian function around the bottleneck separating amorphous and crystalline phases. This distribution of the hydrolysis equilibrium constant, together with the probabilities of attempt for each of the Monte Carlo moves defined in Ref. 1, have been found to yield the highest efficiency of the RE-RxMC for finding crystal states. A more detailed explanation of the RE-RxMC simulation protocol as well as all the parameters considered for each of the Monte Carlo moves can be found in the Supporting information of Refs.¹⁻³

| Replica Exchange RxMC Move | Maximum Displacement | Relative Attempt Frequency |
|-------------------------------------|----------------------|----------------------------|
| OH/BO displacement | 0.05 Å | 0.05 |
| Tetrahedral displacement | 0.5 Å | 0.05 |
| Tetrahedral rotation | 0.1 Radian | 0.05 |
| Cluster displacement | 0.1 Å | 0.05 |
| Tetrahedral displacement in Cluster | 0.025 Å | 0.05 |
| Tetrahedral rotation in Cluster | 0.05 Radian | 0.05 |
| OSDA displacement | 0.5 Å | 0.10 |
| Condensation | — | 0.30 |
| Hydrolysis | — | 0.30 |
| Replica Exchange | — | 0.01 |

Table S1: Types of Replica Exchange RxMC moves and their maximum displacements and relative attempt frequencies, based on the optimized move set found in Ref 1.

RE-RxMC simulations were performed in parallel to the number of replicas (28), with temperature fixed at 300 K and at constant volume in a simulation box reproducing the LTA unit cell with 24 tetrahedra in a cubic cell 11.919 Å x 11.919 Å x 11.919 Å. To generate reliable statistics, 56 independent runs of RE-RxMC were performed with thermodynamically identical but statistically independent initial conditions randomly placing the tetrahedra and the OSDAs in the simulation box. The length of the simulations was chosen to be 10 million RE-RxMC steps, and it is enough to yield to the formation of zeolites in most of the statistically independent simulation runs.

The emergence of a crystal in our work is defined by a system reaching full polymerization, which under periodic boundary conditions gives a periodically repeated structure, i.e., a crystal. After crystals have emerged, we examine their XRD patterns to establish if they have formed the LTA framework structure.

Section 2. Experimental methods

2.1. Synthesis

2.1.1. Synthesis of the bulky organic structure-directing agent (OSDA)

The method used in the previously-published paper⁷⁻⁸ was referred to synthesize 1,2-dimethyl-3-(4-methylbenzyl)imidazolium chloride, the OSDA for the crystallization of pure-silica LTA (Si-LTA). Basically, first 200 mL of anhydrous ethanol (99.5 wt.%, Thermo Fisher Scientific) was added into a 500-mL flask, and then after dissolving 23.20 g of 1,2-dimethylimidazole (98 wt.%, Thermo Fisher Scientific) in the solvent, 30.92 g of 4-methylbenzyl chloride (98 wt.%, Alfa Aesar) was added into the solution in a dropwise fashion at room temperature (RT). The resulting mixture was stirred at 250 rpm at RT to carry out the alkylation reaction for 2 days. Thereafter, followed by evaporating most of the ethanol solvent through a rotary evaporator at 70 °C, the obtained sticky solution was slowly dropped into 350 mL of diethyl ether (95 wt.%, Thermo Fisher Scientific) in a flask with intensive stirring, in order to remove the unreacted reagents. Finally, the purified product was filtered and dried in a convection oven under 70 °C overnight. ¹³C NMR (400 MHz, in D₂O) was employed to confirm the chemical structure of the OSDA. The chemical shifts (in ppm) of the NMR peaks are 144.54, 139.25, 130.73, 129.73, 127.74, 122.22, 120.97, 51.17, 34.55, 20.13 and 8.98, all of which were consistent with the NMR result simulated by ChemDraw.

1,2-dimethyl-3-(4-methylbenzyl)imidazolium chloride was converted into hydroxide form (henceforth denoted “BULKY”) by ion-exchange. 1,2-dimethyl-3-(4-methylbenzyl)imidazolium chloride was first dissolved in distilled water (the concentration was controlled at about 0.2 mmol/g), and then the ion-exchange was performed by adding hydroxide exchange resin (Ambersep[®] 900(OH), Alfa Aesar) and stirring overnight. After filtrating the resin, the concentration of BULKY was measured by titration, utilizing phenolphthalein as the indicator and 0.01 M of HCl as the titrant, respectively. The ion-exchange ratio is around 70%.

2.1.2. Synthesis of LTA seeds

In order to shorten the synthesis time, aluminosilicate LTA seeds were synthesized and used in the crystallization of Si-LTA, by following the recipe reported in our previous literature.⁹ Briefly, first in a 50-mL centrifuge tube, 82 μL of NaOH (10 M, Thermo Fisher Scientific) was mixed with 6.65 g of tetramethylammonium hydroxide (TMAOH) (25 wt.% in water, Alfa Aesar), and 3.45 g of deionized (DI) water was also added subsequently. After that, silicic acid (99 wt.%, Sigma Aldrich) of 0.60 g was added into the aqueous solution, and the mixture in the well-sealed tube was heated in a 70 °C oven, until it became a transparent solution. Then, after cooling that solution down to RT, 0.50 g of aluminum isopropoxide (≥ 98 wt.%, Thermo Fisher Scientific) was introduced in 2 steps (each with an equivalent quantity for the Al source). Sonicator and vortex oscillator were employed to speed up the dissolution process of Al isopropoxide in this step. Finally, the obtained clear solution was transferred into a 50-mL Teflon-lined stainless-steel autoclave and heated at 93 °C for 24 hours. The synthesized LTA seeds were washed by centrifugation using excessive DI water for several times, until the pH of the supernatant was close to neutral. The purified product of LTA seeds was dried under 80 °C in an oven overnight.

2.1.3. Syntheses of Si-LTAs with different crystallinities using BULKY as OSDA

Crystallization of Si-LTA using BULKY as the sole OSDA was achieved by following recipes reported previously with a few modifications. Briefly, first 9.12 g of aqueous solution of BULKY (0.2208 mmol/g in water) was added into a 50-mL beaker. Afterwards, while the BULKY solution was under stirring, 900 μ L of tetraethyl orthosilicate (TEOS, 99 wt.%, Alfa Aesar) was pipetted into. Immediately, the beaker was capped with parafilm, and continuously stirred for another 24 h under RT for the complete hydrolysis of TEOS. Next, Hydrofluoric acid (HF, 48-52 wt.% in water, Alfa Aesar) of 70 μ L was pipetted into the mixture, followed by 550 μ L of aqueous solution of LTA seeds (30.8 mg/mL; 7 wt.% with regard to the total silica source) added into in a dropwise fashion. Water in the obtained suspension was then evaporated under 60 $^{\circ}$ C in a convection oven, until a final desired composition (1.00 SiO₂ : 0.50 HF : 0.50 BULKY : 5.00 H₂O) for the precursor gel was achieved. Finally, the gel was transferred in a 50-mL well-sealed Teflon-lined stainless steel autoclave to conduct the crystallization under 150 $^{\circ}$ C for 144 h. After the synthesis, the as-made material was dried overnight under 120 $^{\circ}$ C to completely get rid of the water, and then 50 mg of the dried sample was ground and also mixed well with 50 mg of fine quartz (99.5 wt.%, Alfa Aesar), preparing the sample for X-ray diffraction (XRD) characterization to measure and compare the relative crystallinity. Quartz here was used as the internal standard for the crystallinity comparison.

The procedure above was repeated several times to get those samples crystallized using other different synthetic times, including 8 h, 12 h, 24 h, 48 h, 96 h and 144 h.

2.1.4 Syntheses of Si-LTAs with different crystallinities using BULKY and tetrametylammonium chloride (TMACl) as OSDAs

In order to study the effect of small OSDA on the crystallization kinetics of Si-LTA, TMACl was added into the synthesis gel without changing the pH. The synthesis procedure was similar to the one using BULKY only: first, 9.12 g of aqueous solution of BULKY (0.2208 mmol/g in water) was mixed with 23 mg of TMACl (97 wt.%, Alfa Aesar) in a 50-mL beaker. Afterwards, under stirring, 900 μ L of TEOS was immediately pipetted into the BULKY solution. After covered by parafilm, the obtained mixture was stirred continuously under RT for another 24 h to hydrolyze TEOS completely. Next, 70 μ L of HF and 550 μ L of aqueous solution of LTA seeds (30.8 mg/mL) were added into the homogeneous solution successively. After that, water in the suspension was evaporated under 60 $^{\circ}$ C in a convection oven, until a desired composition (1.00 SiO₂ : 0.50 HF : 0.50 BULKY : 0.05 TMACl : 5.00 H₂O) for the precursor gel was eventually obtained. Finally, the gel was transferred into a 50-mL well-sealed Teflon-lined stainless steel autoclave to carry out the crystallization under 150 $^{\circ}$ C for 48 h. After the synthesis, the as-made material was dried overnight under 120 $^{\circ}$ C to completely evaporate the water, and then 50 mg of the dried sample was ground and also mixed well with 50 mg of fine quartz, preparing the sample for XRD characterization to measure and compare the relative crystallinity with those synthesized without TMACl.

The recipe above was repeated several times to get the samples crystallized at other different synthetic times, including 4.5 h, 6 h, 8 h, 10 h and 48h.

2.2 Characterizations

2.2.1. XRD

The crystallinities of all the zeolite samples obtained in S2.1.3 and S2.1.4 were measured and compared by XRD characterization, using a Rigaku SmartLab diffractometer equipped with Cu-K α radiation generated at 40 mA and 45 kV with a step size of 0.015°. For all the samples, the measuring angle range was from 2-theta equal to 5° to 40°. The crystallinity comparison was based on the ratio of the integration area for the peak located at 22.50° ((003) and (122) crystal plane of Si-LTA) to the one at 20.85° ((110) crystal plane of quartz) in the XRD pattern of each sample.

2.2.1. Liquid-state ¹³C NMR

The chemical structure of the synthesized BULKY in chloride form was confirmed by liquid-state ¹³C NMR characterization on a Bruker NMR spectrometer (400 MHz). Before the measurement, the OSDA was dissolved in an appropriate volume of D₂O.

Section 3. Supporting Figures for Monte Carlo Simulations

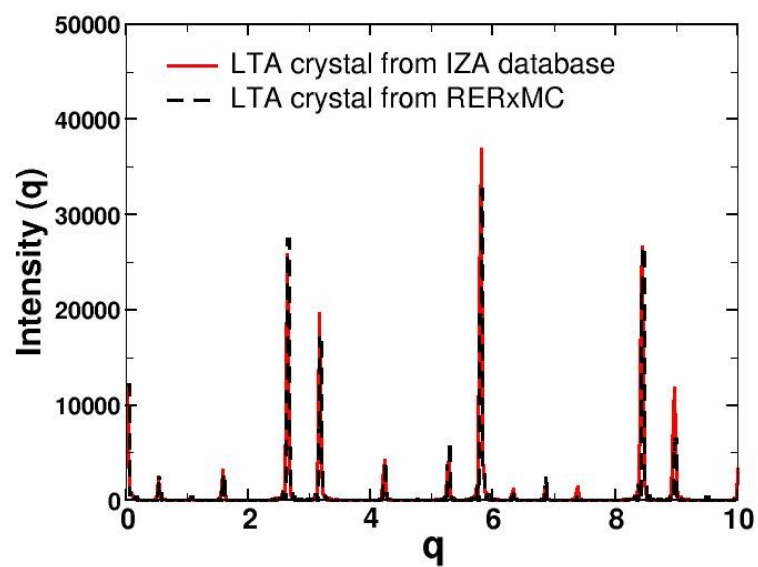


Figure S1. Simulated X-ray diffraction (XRD) pattern from final simulated LTA structure (periodic extension; see methods) showing agreement with the standard (IZA) XRD for LTA.

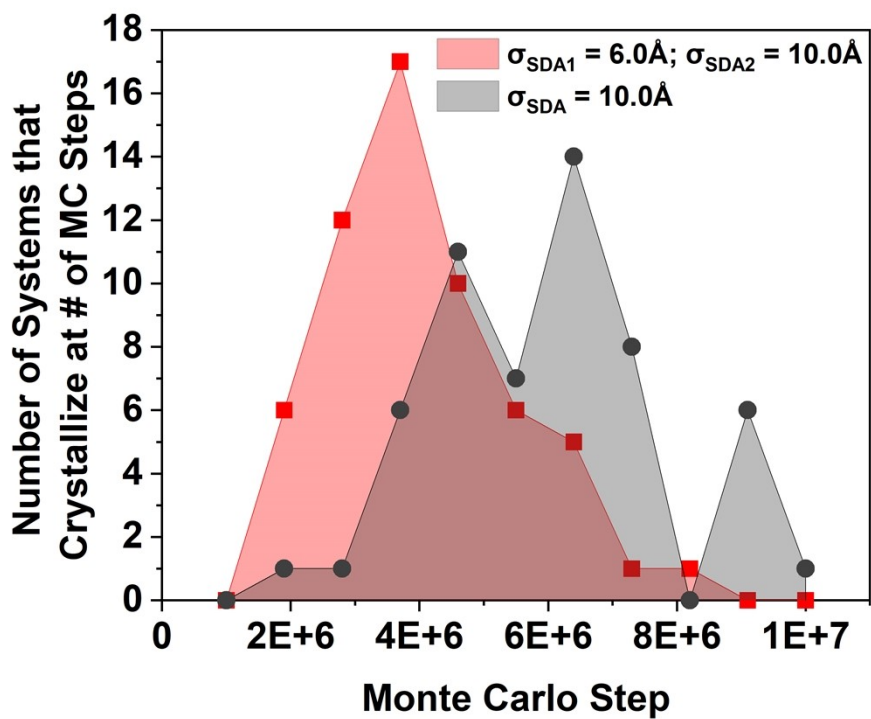


Figure S2. Histogram of independent runs crystallizing at a given Replica Exchange RxMC step. Black corresponds to the case where only one OSDA of diameter 10 Å is considered; red line corresponds to two OSDAs of diameters 10 Å and 6 Å.

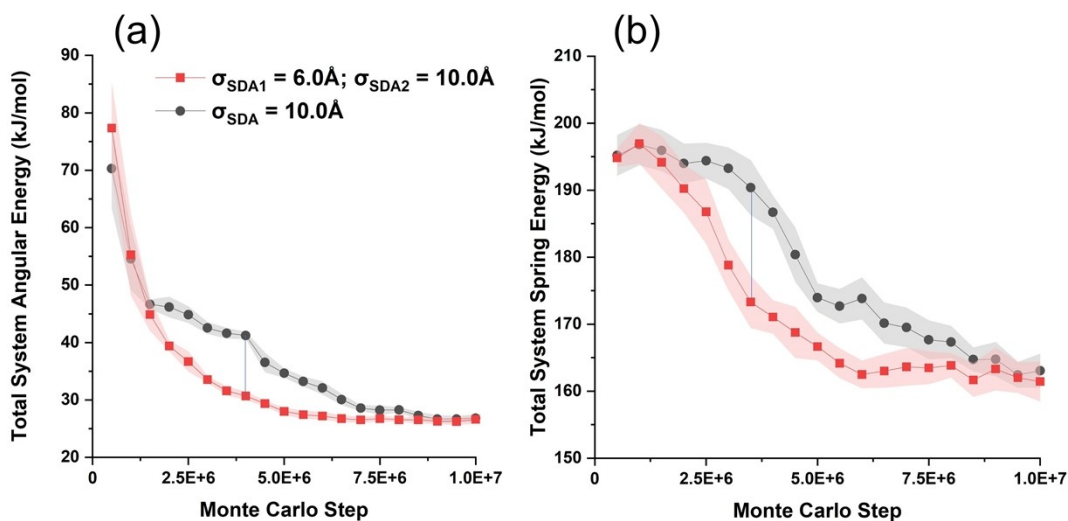


Figure S3. Predicted total (a) angular (Si-O-Si) and (b) O-O spring (within each tetrahedron) harmonic energies during RxMC simulations of LTA crystallization, showing that the BULKY/TMA synthesis is lower in total energy than BULKY alone for both potential energy terms, with the difference reaching its maximum value around 4 million MC steps, the same point in the RxMC simulations when the BULKY/TMA simulation exhibits enhanced 4-ring production (Fig. S3). Standard deviations in computed energies shown via red and gray bands.

Section 4. Supporting Figures for Experiments

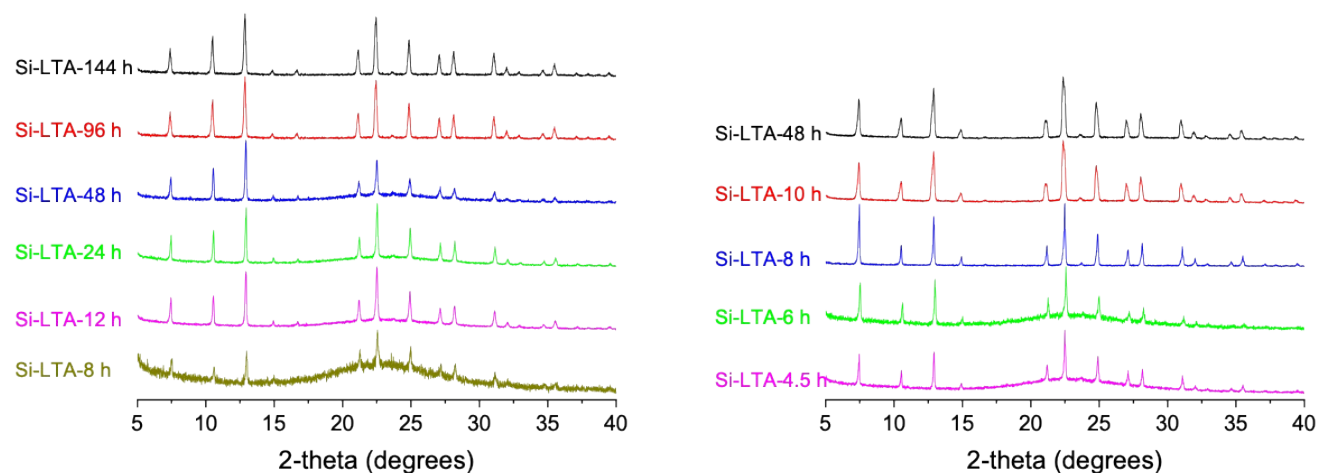


Figure S4. XRD patterns of LTA synthesized using BULKY (left) and BULKY/TMACl (right) with different crystallization time at 150°C. The samples were washed before the XRD measurements to confirm the diffraction peaks from the zeolite phase.

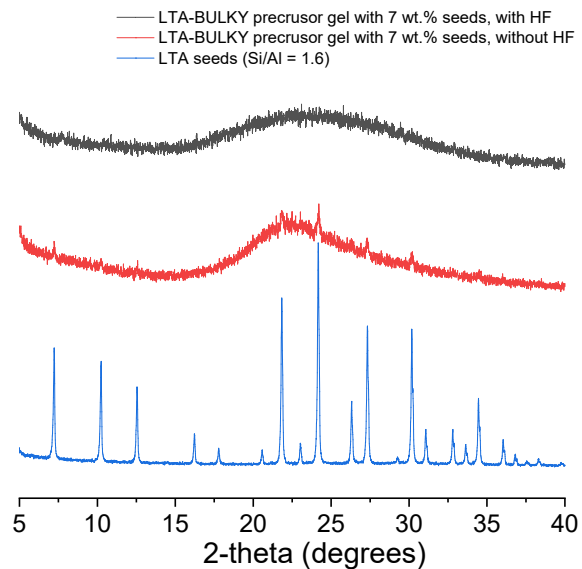


Figure S5: XRD pattern of LTA seeds (Si/Al=1.6, blue) and XRD pattern of synthesis precursor gel for LTA-BULKY-F prepared without adding HF (red) and with adding HF (black). The presence of small LTA diffraction peaks in the synthesis precursor gel without adding HF (red) indicates the LTA seeds are stable in the gel in the absence of HF. The XRD pattern of the LTA-BULKY-F prepared with adding HF does not show the diffraction peaks of LTA seeds. This indicates that the LTA seeds are completely or mostly dissolved in the synthesis gel after adding HF.

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