Supporting Information (SI) for

The relationship between sub-micrometer sized ZSM-5, slice-like (lamellar) keatite and hollow α -quartz particles: A phase transformation study

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SI-1: Morphological particularities of the solid phase of SRM

Fig. SI-1.1A shows that, at $t_{c-t} = 2$ h, the solid phase of SRM is composed of silicalite-1 seed crystals (marked by red arrows and/or bordered by red square) surrounded by amorphous phase. A part of added silicalite-1 seed crystals are partially covered by small amorphous silica particles (Fig. SI-1.1B). This is a possible reason that the measured size (0.7 – 5 µm; solid curve in Fig. 6A in the paper) of the seed crystals is higher than their "nominal" (0.1 – 0.7 µm; dashed curve in Fig. 6A in the paper). The amorphous part of the solid phase (bordered by yellow square) represents the aggregates composed of possibly 10 – 50 nm sized particles (Fig. SI-1.1C).



Fig. SI-1.1 SEM image of the solid phase of SRM at $t_{c-t} = 2$ h. (A) Silicalite-1 seed crystals (marked by red arrows) surrounded by amorphous phase. (B) Silicalite-1 seed crystal covered by small (20-60 nm) particles of amorphous silica (enlarged detail bordered by red square in Fig. A). (C) Enlarged detail bordered by yellow square in Fig A.

These particles are considerably larger than the "primary" colloidal silica particles used as silica source (2.6 - 6.8 nm; see Fig. 2A in the paper); even it is reliable to assume that 10 - 50 nm aggregates are composed of 2.6 - 6.8 nm "primary" colloidal silica particles, i.e., that the "primary" colloidal silica particles aggregate into larger ones during early stage of heating of SRM (see also Supporting Information SI-2).

SEM image in Fig. SI-1.2 shows that near spherical aggregates formed at $t_{c-t} = 37$ h are composed of mainly condensed worm-like particles (WLPs; bordered by yellow circles) and that crystals of MFI-type zeolite (marked by green arrows) and slice-like features of keatite (bordered by red circles) can be observed at the surface of aggregates.



Fig. SI-1.2 SEM image of the solid phase of SRM at t_{c-t} = 37 h. Domains of the condensed WLPs are bordered by yellow circles, domains of keatite are bordered by red circles and MFI crystals are marked by yellow arrows.

According to the relevant XRD data (Figs. 1A-II and 8A in the paper), the solid phase of SRM contains about 34 wt. % of MFI-type zeolites (silicalite-1, ZSM-5) and about 66 wt. % of amorphous phase (condensed WLPs).



Fig. SI-1.3 (A) SEM image of the solid phase of SRM at $t_{c-t} = 37$ h. (B) Enlarged detail (MFI crystals) bordered by green square in Fig. A. (C) Enlarged detail (condensed WLPs) bordered by red square in Fig. A.

While it can be assumed that the entire amount of amorphous phase exists in the form of condensed WLPs, the proportion of MFI-type crystals attached on/in the condensed aggregates (CAs) cannot be strictly estimated. On the other hand, due to small relative amount of keatite,

in/on the aggregates, it cannot be detected by XRD at $t_{c-t} = 37$ h (see XRD pattern A in Fig. 8 in the paper).

Fig. SI-1.3A shows that at the early stage of aggregation ($t_{c-t} = 37$ h) the aggregates are more irregularly shaped and heterogeneous in composition and appear as a mixture of nano-sized MFI crystals (bordered by green square in Fig. SI-1.3A; see also the enlarged detail in Fig. SI-1.3B) and condensed WLPs (bordered by red square in Fig. SI-1.3A; see also the enlarged detail in Fig. SI-1.3C).



Fig. SI-1.4 (A) SEM image of the solid phase of SRM at t_{c-t} = 42 h. (B) Enlarged detail bordered by green square in Fig. A. (C) Enlarged detail bordered by green square in Fig. A. (D) Enlarged detail bordered by red square in Fig. A

Fig. SI-1.4 shows that the solid phase of SRM contains individual (discrete) MFI crystals (Figs. A and D) and amorphous aggregates (Fig. A) with attached MFI crystals (Fig. C) and or

formed (grown) keatite (Fig. B). Although the "heterogeneity" in the composition of aggregates is still present, the shape of aggregates is more regular and near-spherical at t_{c-t} = 42 h (Fig. SI-1.4).

The amount of keatite increased from $f_k \approx 0$ at $t_{c-t} = 37$ h (see XRD pattern A in Fig. 8 of the paper) to $f_k \approx 0.1$ at $t_{c-t} = 42$ h (see XRD pattern B in Fig. 8 of the paper) so that slice-like features of keatite can also be seen in the SEM image (Fig. SI-1.4B).

Fig. SI-1.5 shows that the near-spherical aggregates are composed of MFI crystals, slice like features of keatite and untransformed amorphous phase in the form of condensed WLPs, in the time interval from $t_{c-t} = 48$ h to $t_{c-t} = 90$ h. Although the general morphological characteristic of the aggregates do not change in the time interval from $t_{c-t} = 48$ h to $t_{c-t} = 90$ h (Fig. SI-1.5; see also Figs. 7C - 7E in the paper), intensive structural changes occur during the same time interval; while the fraction, $f_{MFI} \approx 0.34$, of MFI-type zeolites is constant, fraction, f_a , of amorphous phase continuously decreases and, at the same time, the fraction, f_k , of keatite continuously increases (Figs. 1A-II and 8 in the paper) in the time interval from $t_{c-t} = 48$ h to $t_{c-t} = 90$ h. This is the reason that the slice-like features of keatite are the dominant morphological form of the aggregates in the mentioned time interval (Fig. 7C – 7E in the paper).

Figs. 1A-III and 12A in the paper show that the solid phase at $t_{c-t} = 137$ h contains about 70 wt. % of α -quartz, about 24 wt % of MFI-type zeolites and about 6 wt. % of keatite. This indicates that most of keatite, a part of MFI-type zeolites and the small amount of remaining (untransformed) amorphous phase (condensed WLPs) have been transformed into α -quartz in the time interval from $t_{c-t} = 90$ h to $t_{c-t} = 137$ h (Fig. 1A-III in the paper). This is also the reason for the change of the surface morphology of aggregates; while the keatite slices are dominant features of the aggregates at $t_{c-t} = 90$ h (Fig. SI-1.5C; see also Fig. 7E in the paper) with the content of keatite of 64 wt. % ($f_k = 0.64$; see Fig. 1A-II in the paper), both aggregates I and aggregates II appear at $t_{c-t} = 137$ h (Figs. SI-1.6A and SI-1.7A; see also Fig. 11A in the paper).



Fig. SI-1.5 SEM images of the solid phase of SRM at $t_{c-t} = 48$ h (A), 70 h (B) and 90 h (D). MFI crystals are marked by green arrows, keatite slices are marked by black arrows and domains of condensed WLPs are bordered by yellow circles.

Low amount of keatite (about 6 wt. %) at $t_{c-t} = 137$ h (Fig. 1A-III in the paper) indicate that presence of keatite slices is only rare appearance on the surfaces of some aggregates (aggregates I in Fig. SI-1.6A and SI-1.6C). On the other hand, irregularly shaped features on the surfaces of aggregates II (Fig. SI-1.6C and Fig. 11A' in the paper) probably represent both the fragments of keatite slices formed during their dissolution/destroying and small growing crystals of α -quartz.



Fig. SI-1.6 (A) SEM image of the solid phase of SRM at $t_{c-t} = 137$ h. (B) Enlarged detail of the surface of aggregate I. (C) Enlarged detail of the surface of aggregate II. (D) Enlarged discrete crystals of MFI bordered by yellow square (III) in Fig. A.

A comparison of Figs. SI-1.7A and SI-1.7B supports this assumption; it is evident that the irregularly shaped features, which are characteristic for aggregates II dominant at $t_{c-t} = 137$ h, (Fig. SI-1.7A), gradually transforms into more regularly shaped particles (growing α -quartz crystals) which are dominant at $t_{c-t} = 146$ h (Fig. SI-1.7B). In addition, presence of hollow particles in Fig.

SI-1.7B indicates that a part of silicalite-1 from the core of silicalite-1/ZSM-5 core/shell composite particles has been transformed into α -quartz at $t_{c-t} = 146$ h (see the paper).

Fig. SI-1.7 SEM images of the solids separated from SRM at $t_{c-t} = 137 \text{ h}$ (A) and $t_{c-t} = 146 \text{ h}$ (B)

Finally, Fig.SI-1.8 shows the final product obtained at $t_{c-t} = 187$ h. The product appears in the form of near spherical aggregates (Fig. 11C in the paper) composed of both "compact" crystals of α -quartz (red arrows in Fig. SI-1.8) and hollow α -quartz particles (yellow arrows in Fig. SI-1.8). The mechanisms of the formation of both the "compact" crystals of α -quartz and hollow α -quartz particles are explained in the paper.

Fig. SI-1.8 SEM image of the surface of near spherical aggregates (final product) obtained at $t_{c-t} =$ 187 h.

SI-2: Description of the processes details

Addition of colloidal silica into alkaline solution of sodium aluminate (see Experimental Section in the paper), results in the formation of stable suspension of amorphous colloidal silica in the solution (upper part of Scheme SI-2.1a). Following the finding that "In the solution containing a mixture of silicate species, aluminum preferentially complexed with larger silicate species, almost immediately.",¹ one can assume that the aluminate ions dissolved in the liquid phase would be immediately attached on the surfaces of colloidal silica particles. However, the sharp decrease of the concentration, $C_{Al}(L)$, of aluminum in the liquid phase, in the time interval from $t_{c-1} = 0$ to $t_{c-1} \leq 1$ h (Fig. 1C-I in the paper), indicates that the incorporation of Al onto the surfaces of colloidal silica occurs during the early stage of heating of seeded reaction mixture (SRM). Since aluminum is used in the form of soluble aluminate (Al(OH)₄⁻), the attachment of Al on the colloidal silica takes place by nucleophilic substitution reaction between deprotonated silanol groups on the silica surface and solvated aluminate species² (bottom part of Scheme SI-2.1a), i.e.,

surface=Si-O-Na⁺ + Al(OH)₄-Na⁺
$$\leftrightarrow$$
 surface=Si-O-Al(OH)₃-Na⁺ + Na⁺ + OH⁻ (Eq. SI-2.1)

The described process results in the formation of colloidal silica "enriched" with aluminum (Schemes SI-2.1a and SI-2.1b).³⁻⁹ Although in accordance with Eq. SI-2.1, the nucleophilic substitution produces OH⁻ ions, their consumption for other relevant processes (see below) is larger than their production during the nucleophilic substitution, so that the pH of the liquid phase of SRM decreases during the starting heating of SRM (Fig. 1D-I in the paper).

Scheme SI-2.1 Schematic presentation of the processes occurring during stage I of crystallization/transformation

Other processes which occur during the initial heating of SRM are dissolution of amorphous silica in hot alkaline solution (Schemes SI-2.1b and SI-2.1c) and aggregation of colloidal silica particles (Scheme SI-2.1c). Due to inertness of surface Si-O-Al bonds on hydroxide attack^{7,10,11} dissolution of both un-aggregated (Scheme SI-2.1b) and aggregated (Scheme and SI-2.1c2) Al-enriched colloidal silica in alkaline solution results in the formation of low molecular weight silicate species.¹²⁻¹⁶ Collisions of small (2.6 - 6.8 nm; Fig. 2A and Table 1 in the paper) hydroxilated particles of colloidal silica (Scheme SI-2.1c1) cause their adhesion by condensation reactions of silanol groups² of colliding particles and thus, formation of surface=Si-O-Si=surface links^{2,12} (Scheme SI-2.1c2). Condensation/adhesion processes results in the formation of 10 - 50 nm aggregates of "primary" amorphous silica particles (APASPs, Figs. 2B and Table 1 in the Paper and Fig. SI-1.1C in the Supporting Information SI-1). A part of the formed APASPs further agglomerate into $10-600 \,\mu\text{m}$ gel particles which, in the solid phase of SRM, surround silicalite-1 seed crystals (bottom part of Scheme SI-2.1d, Fig. SI-1.1 in the Supporting Information SI-1 as well as Figs. 3A, 6A' and Scheme 1b in the paper). Another part of APASPs remains dispersed in the liquid phase of SRM (upper part of Scheme SI-2.1d and Scheme 1b in the paper). It is reasonable to believe that the APASPs in the solid and the liquid phase are in dynamic equilibrium^{17,18} (Scheme SI-2.1d).

Again, due to inertness of surface Si-O-Al bonds on hydroxide attack,^{7,10,11} further dissolution (at $t_{c-t} > 2$ h) of both the separate (individual) APASPs dispersed in the liquid phase and the APASPs assembled in 10 – 600 µm "gel" particles results in the formation of low molecular weight soluble silicate species¹³⁻¹⁶ (Scheme SI-2.1d) and thus, in further enrichment of the un-dissolved solid phase with aluminum. However, more further dissolution of Al-enriched silica causes formation of not only soluble silicate, but also soluble aluminate and/or low-molecular-weight aluminosilicate species.¹⁹ In accordance with the previously explained principle,¹ most of the aluminate and/or aluminosilicate anions are almost immediately incorporated onto the surfaces of large gel particles in the solid phase rather than onto the surfaces

of smaller APASPs distributed in the liquid phase. This is consistent with the results of previous studies of the seed induced, TPA-free crystallization of sub-micrometer sized zeolite ZSM-5³⁻⁵ and of the crystallization of zeolite TPA-ZSM-5 from diluted heterogeneous system.¹⁹

Polycondensation reactions of the silicate and aluminosilicate species result in formation of different silicate and aluminosilicate oligomers.^{2,18,20} Parts of silicate and aluminosilicate species may regroup around the hydrated cations (M,TPA) to form different (M,TPA)–silicate and (M,TPA)–aluminosilicate species.^{16,18,20-28} including growth precursor species. Previous studies of the crystal growth of MFI-type zeolites from homogeneous (initially clear solution)^{25,28-31} and heterogeneous systems (hydrogels)^{3,4,26,32,33} have shown that the growth precursors are not simple ionic species (silicate anions, aluminate anions, TPA⁺), but small sub-colloidal particles having the size less than 10 nm. In TPA-containing systems the precursor particles are probably 3 – 10 nm aggregates.^{25,26,28,29-32}

Accordingly to de Moor et al.,^{34,35} primary precursor particles having a size of about 3 nm are most probably formed by aggregation of several inorganic-organic composite species²⁴ when the crystallization process starts. In addition, secondary precursor particles are formed by a stepwise aggregation of ~ 3 nm primary precursor particles. After the amorphous aggregates reach a "critical" size (≥ 10 nm), a small fraction of them transforms into crystalline phase (viable nuclei) and the rest disaggregate into ~ 3 nm primary precursor particles needed for the growth of viable nuclei into macroscopic crystals.

Later on, Lobo et al.³⁶⁻⁴⁰ and Cheng and Shantz⁴¹⁻⁴³ suggested that primary precursor particles have core-shell structure with silica at the core and TPA⁺ ions at the shell and ellipsoidal shape. The formation of the core-shell primary precursor particles is a reversible process at low temperatures, in some extent similar to the aggregation of surfactant molecules into micelles.³⁶⁻⁴³. Evolution of the nanoparticles during heating being described by an Ostwald ripening process, whereby a fraction of initial nanoparticle population grows at the expense of the rest that dissolve over time.

In the absence of organic cations, the structure-directing role of the inorganic cations was emphasized.^{22,23,44,45} However, only sodium is able to direct the MFI structure²²; sodium ions stabilize the formation of structural subunits²³ and favor the formation of 5-1 secondary building units needed for nucleation and crystallization of zeolite ZSM-5^{22,44,45} in rather selected condition, namely for low Na₂O/SiO₂ and high SiO₂/Al₂O₃.²² Thus, it is reasonable to assume that in the low-alkaline system (A = 0.001) having low value of [Na₂O/SiO₂]_b (= 0.04) and high value of [SiO₂/Al₂O₃]_b (= 600), the polycondensation reactions between different Na-silicate and Na-aluminosilicate species, formed by dissolution of amorphous silica, result in the formation of amorphous precursor species (Schemes SI-2.1e and SI-2.1f). Since the "concentration" of different silicate and aluminosilicate species, formed by dissolution of silica is the largest just at the points of their formation (surface regions of APASPs and gel particles; Scheme SI-2.1e).¹⁹

On the basis of previous results,^{3,4,29,32} it can be reasonably assumed that a part of PSs deposits onto the surfaces of silicalite-1 seed crystals and gradually transforms from amorphous and/or partially crystalline phase³⁰ into fully crystalline phase (zeolite ZSM-5;^{3,4} Schemes SI-2.1e –SI-2.1g). Another part of PSs gradually assembles to the "network" of worm-like particles (WLPs;¹⁹ Schemes SI-2.1f and SI-2.1g; see also Fig. 4 in the paper). The TEM images of the solid phase of SRM at $t_{c-t} = 10$ h (Fig. SI-2.1) support these assumptions. The discrete PSs having the size of about 10 – 30 nm (marked by green arrows) and their incorporation onto the surface of growing MFI crystal can be clearly observed in Fig. SI-2.1A. The surface layer, bordered by dashed and solid yellow lines, probably represent the growth "area" in which the PSs gradually transforms into zeolite ZSM-5, as it is schematically presented in the Schemes SI-2.1e –SI-2.1g.

Fig. SI-2.1. TEM images of the solid phase of SRM at $t_{c-t} = 10$ h. 10 - 30 nm PSs are in Fig. (A) marked by green arrows. The growing layer of zeolite ZSM-5 is in Fig. A by dashed (upper) and solid (lower) lines. In Fig. B, PSs are marked by green arrows, WLPs are marked by yellow arrows and the features marked by blue arrows are probably dissolving APASPs.

This growth mechanism is consistent with the processes of growth of silicalite-1 in both homogeneous³¹ and heterogeneous³² systems. In addition, Fig. SI-2.1B shows that "developing" WLPs coexist with PSs. This leads to conclusion that PSs participate not only in the growth of MFI but also in the formation of WLPs, as it is schematically presented in the Scheme SI-2.1f. The dark areas in Fig. SI-2.1B possibly represent the dissolving APASPs.¹⁹

A gradual formation of PSs (Scheme SI-2.1e) and their simultaneous spending for the growth of zeolite ZSM-5 (schemes SI-2.1e - SI-2.1g) and for the formation of WLPs (Scheme SI-2.1f) from the one side and stability of the formed WLPs from the other side¹⁹ are the main stopping zeolite reasons of the growth of ZSM-5 at early stage of the crystallization/transformation process (i.e., at $10 \le t_{c-t} \le 20$ h; see the paper). On the other hand, the increase of the size of particles in the liquid phase from $D_{av} = 18.6$ nm at $t_{c-t} = 2h$ through $D_{av} = 35.9 \text{ nm at } t_{c-t} = 19 \text{ h and } D_{av} = 40 \text{ nm at } t_{c-t} = 30 \text{ h to } D_{av} \approx 45 \text{ nm at } t_{c-t} \ge 42 \text{ h}$ (Fig. 2 and

Table 1 in the paper) indicates that the PSs spontaneously aggregate during the stage I of crystallization/transformation process (schemes SI-2.1e - SI-2.1g). Taking into consideration the above described processes, the continuous decrease of $C_{Si}(L)$ (Fig. 1B-I in the paper) and complex change of the pH in the liquid phase (Fig. 1D-I in the paper), in the time interval from $t_{c-t} = 0$ to $t_{c-t} \approx 30$ h (stage I of the crystallization/transformation processes), can be explained as follows: Although the sudden decrease of pH in the liquid phase from pH = 12 at $t_{c-t} = 0$ to pH =11.4 $t_{c-t} \approx 1$ h is undoubtedly caused by temperature-induced dissolution of colloidal silica in alkaline medium (see Scheme 1b in the paper), the sudden decrease of $C_{Si}(L)$, in the same time interval, indicates that the change of $C_{Si}(L)$ is determined rather by its decrease caused by aggregation of the "primary", 2.6 - 6.8 nm silica particles into 10 - 50 nm aggregates (APASPs) and their further agglomeration into $10 - 600 \,\mu\text{m}$ "gel" particles (solid phase of SRM), which can be separated by centrifugation, than by the increase of $C_{Si}(L)$, caused by dissolution of colloidal silica. Further decrease in the concentration, $C_{Si}(L)$, of Si in the liquid phase, e.g., from $C_{Si}(L) =$ 0.22 mol dm⁻³ at $t_{c-t} \approx 2$ h to $C_{Si}(L) \approx 0.15$ mol dm⁻³ at $t_{c-t} \approx 20$ h (Fig. 1B-I in the paper) is caused by the spending of the PSs for both the growth of zeolite ZSM-5 on silicalite-1 seed crystals (Scheme SI-2.1f) and the formation of WLPs (Scheme SI-2.1f). Although these processes predominantly take place in the solid phase of SRM (Schemes SI-2.1d and SI-2.1f), due to the equilibrium between the PSs in the solid and the liquid phase, change (decrease) of the "concentration" of PSs in the solid phase influence the "concentration" of PSs and thus, the concentration, C_{Si}(L), of Si in the liquid phase. Namely, since Al-enriched zeolite ZSM-5 and WLPs are less soluble than colloidal silica, the amount of Si incorporated (in the form of PSs) into the solid phase (zeolite ZSM-5, WLPs) of SRM is higher that the amount of soluble Si (low molecular weight silicate species) formed by dissolution of colloidal silica, the concentration, $C_{\rm Si}(L)$, of Si in the liquid phase decreases in the time interval from $t_{\rm c-t} \approx 2$ h to $t_{\rm c-t} \approx 20$ h (see Fig. 1B-I in the paper).

As already mentioned, a sudden decrease of pH from pH = 12 at $t_{c-t} = 0$ to pH = 11.4 at $t_{c-t} \approx 1$ h is caused by consumption of OH⁻ ions for starting dissolution of colloidal silica. The increase of low molecular weight silicate species in the liquid phase decreases the rate of dissolution of colloidal silica and thus, the rate of consumption of OH⁻ ions. Since, on the other hand, the formation of PSs by polycondensation reactions in the sequence: low molecular silicate species -> silicate oligomers -> PSs (see Scheme 1 a-c in the paper) produces OH⁻ ions, it is obvious that the rate of consumption of OH⁻ ions (dissolution of colloidal silica) and the rate of their production (polycondensation reactions) are in "equilibrium" at $t_{c-t} \approx 2$ h (pH = 11.2; see Fig. 1D-I in the paper). Increase of pH from pH = 11.2 at $t_{c-t} \approx 2$ h to pH = 11.4 at $t_{c-t} \approx 15$ h is caused by increase of the concentration of OH⁻ ions produced by the nucleophilic substitution reactions,²

$$(ZSM-5) \equiv Si-OH + ^{+}Na^{-}O-Si \equiv PS \leftrightarrow (ZSM-5) \equiv Si-O-Si \equiv PS + Na^{+} + OH^{-}$$
 (Eq. SI-2.2)

$$(ZSM-5) \equiv Si-O^{-}Na^{+} + HO-Si \equiv PS \leftrightarrow (ZSM-5) \equiv Si-O-Si \equiv PS + Na^{+} + OH^{-}$$
 (Eq. SI-2.3)

during incorporation of the precursor species (PSs) onto the surfaces of growing zeolite ZSM-5 (Fig. SI-2.1A and Scheme SI-2.1f). Further slow increase of pH (Fig. 1D-I in the paper), followed by slow decrease of $C_{Si}(L)$ (Fig. 1B-I in the paper) in the time interval from $t_{c-t} \approx 15$ h to $t_{c-t} \approx 30$ h (after the growth of zeolite ZSM-5 has been decreased or even stopped, and WLPs has been formed) is caused by nucleophilic attack of low molecular weight silicate species from the liquid phase on the aluminate centers at the WLPs surfaces,^{2,19} i.e.,

$$WLP \equiv Al - OH^{-} + {}^{+}Na^{-}O - Si \equiv \leftrightarrow [WLP \equiv Al - O - Si \equiv]^{-}Na^{+} + OH^{-}$$
(Eq. SI-2.4)

As already has been found,¹⁹ this process increases the number of terminal \equiv Si-OH (silanol) groups on the surfaces of WLPs. Increase of "concentration" of silanol groups on the surfaces the WLPs causes condensation reactions of the silanol groups² of neighboring WLPs and

thus, formation of WLP-Si-O-Si-WLP links¹⁹ (Scheme SI-2.2a). The consequence of such condensation reactions is spontaneous aggregation of WLPs and formation of condensed aggregates (CAs), probably by coalescences of WLPs inside the aggregates (Schemes SI-2.2a and SI-2.2b; see also Fig. 7A' in the paper).¹⁹

Analysis of data in Figs. 1A-I and 7 in the paper, undoubtedly shows that transformation of amorphous phase (condensed WLPs) into keatite coincides with the formation of CAs. This leads to the assumption/conclusion that nucleation and growth of keatite (Scheme SI-2.2b) are provoked by high concentration of silicate material in CAs.^{17,44,45} Although the mechanism of nucleation of keatite ("homogeneous" nucleation in the vicinity of dissolving WLPs, or heterogeneous nucleation on the surfaces of MFI crystals; scheme SI-2.2b) is not quite clear at present, further formation of keatite (scheme SI-2.2b; see also Fig. 7 in the paper) can be recognized as the solution-mediated transformation process which occurs by (i) formation of soluble low molecular weight silicate species by dissolution of thermodynamically less stable (more soluble) amorphous phase (condensed WLPs) and (ii) growth of thermodynamically more stable (less soluble) keatite by incorporation of the formed silicate species onto the surfaces of growing keatite (scheme SI-2.2b and scheme le and 1f in the paper)

Scheme SI-2.2 Schematic presentation of the processes occurring during stage II of crystallization/transformation

The changes of $C_{si}(L)$ (Fig. 1B-II in the paper) and pH (Fig. 1D-II in the paper) support this conclusion. However, while, the slight, but significant decrease of $C_{si}(L)$ was expected due to the less solubility of keatite, relative to the amorphous phase (see the paper), pH in the liquid phase slightly decreases (Fig. 1D-II in the paper) in spite of its expected increase. This indicates that the decrease in the concentration of OH⁻ ions caused by their consumption for dissolution of amorphous phase (condensed WLPs) and thus, for the production of the low molecular weight silicate species, needed for the nucleation and growth of keatite, is larger than the increase in the concentration of the OH⁻ ions "produced" during the formation of keatite (Stage II of crystallization/transformation process; see Fig. 1A-II in the paper). Or, in the other words, the incorporation of low molecular weight silicate species from the liquid phase onto the surfaces of the growing keatite slices takes place rather by polcondensation mechanism, i.e.,

keatite=Si-OH + HO-Si=
$$\leftrightarrow$$
 keatite=Si-O-Si= + H₂O (Eq. SI-2.5)

which does not produce OH⁻ ions, than by the OH⁻ producing nucleophilic substitution reactions, i.e.,

keatite=Si-OH +
$$^{+}Na^{-}O-Si = \leftrightarrow$$
 keatite=Si-O-Si= + Na $^{+}$ + OH (Eq. SI-2.6)

keatite=Si-O⁻Na⁺ + HO-Si= \leftrightarrow keatite=Si-O-Si= + Na⁺ + OH⁻ (Eq. SI-2.7)

Scheme SI-2.3 Schematic presentation of the processes occurring during stage III of crystallization/transformation

When the entire amount of the amorphous phase is transformed into keatite, nucleation and crystal growth of α -quartz, as the most stable phase at given conditions, start to occur (Scheme SI-2.3a; see also Fig. 1A-III in the paper). Again, the changes in $C_{Si}(L)$ (Fig. 1B-III in the paper) and pH (Fig. 1D-III in the paper) indicates that the formation of α -quartz is a solution-mediated process which occurs by dissolution of thermodynamically less stable (more soluble) keatite and MFI-type zeolites into thermodynamically more stable α -quartz. Approximately constant value of $C_{\rm Si}(L)$ ($\approx 0.1 \text{ mol dm}^{-3}$) in the time interval from $t_{\rm c-t} \approx 110$ h to $t_{\rm c-t} \approx 180$ h (Fig. 1A-III), during which entire amounts of keatite and MFI-type zeolites have been transformed into α -quartz, leads to an assumption that the rate of production of low molecular weight silicate species by dissolution of keatite and/or MFI-type zeolites is approximately the same as the rate of their consumption for the formation of α -quartz. On the other hand, continuous increase of pH in the time interval from $t_{c-t} \approx 110$ h to $t_{c-t} \approx 200$ h (Fig. 1D-III) indicates that the amount of OH⁻ ions produced by the formation (nucleation and crystal growth of α -quartz) is higher than the amount of OH⁻ ions consumed for the production of low molecular weight silicate species by dissolution of keatite and/or MFI-type zeolites. After the entire amounts of keatite and MFI-type zeolites have been transformed into α -quartz, the concentration, $C_{\rm Si}(L)$, of Si in the liquid phase drops from the value $C_{\rm Si}(L) \approx 0.1$ mol dm⁻³, characteristic for solubility of the mixture of keatite and MFI-type zeolites to the value $C_{\rm Si}(L) \approx 0.07$ mol dm⁻³, characteristic for solubility of the formed α -quartz (Fig. 1A-III), At the same time, pH of the liquid phase reaches the constant value (pH = 12.4).

In addition these changes indicate that the aggregates of keatite and MFI crystals are porous features and that there is intense exchange of material between the liquid phase and CAs, not only from their surfaces, but also from their interiors. The additional argument for the solution mediated process is destroying of the keatite slices as a consequence of its dissolution (Scheme SI-2.3b; see also Figs. SI-1.6 and SI-1.7 in the Supporting information SI-1 as well Fig. 11A in

the paper). Here it is interesting that although keatite is thermodynamically more stable than MFItype zeolites, the rate of transformation of keatite into α -quartz is considerably faster than the rate of transformation of MFI-type zeolites into α -quartz (Fig. 1A-III). One of reason is that due to the inertness of surface Si-O-Al bonds (zeolite ZSM-5) of MFI composite on hydroxide attack, 4-6,47-49 the rate of dissolution of the ZSM-5 shell of the MFI composite is slower than the rate of dissolution of all-silica keatite. Another, more expressive reason for higher rate of transformation of keatite than MFI into α -quartz is nucleation and growth of α -quartz on the surfaces of MFI particles (schemes SI-2.3a and SI-2.3b) as it is indicated by the increase of particle (crystal) size during the stage III of crystallization/transformation process (Fig. 15 in the paper). Now, taking into consideration these facts, the formation of α -quartz can be described as follows: Dissolution of keatite (in larger extent) and MFI (in smaller extent) produces the silicate ions which are the precursor species for the growth of nuclei formed at/near the surfaces of both keatite and MFI particles (Schemes SI-2.3a and SI-2.3b). This results in the formation of both the discrete the α quartz crystals (formed by the growth of nuclei positioned in the vicinity of dissolving keatite and the α -quartz grown on the surfaces of MFI particles (schemes SI-2.3a – SI-2.3c; see also Figs. 11 and 14 in the paper). After the entire amount of keatite and a small part of MFI has been transformed into α -quartz (at $t_{c-t} \approx 140$ h; see Fig. 1A-III in the paper) the solid phase of SRM contains both the discrete α -quartz crystals and the composite particles composed of silicalite-1 core, an interlayer of zeolite ZSM-5 and α -quartz shell (schemes SI-2.3b and SI-2.3c). Further transformation of the remaining MFI-type zeolites into α -quartz occurs by the mechanism described in the paper.

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SI-3: Process control for pure phase slice-like keatite or hollow α-quartz crystals

Based on the revealed mechanisms of phase transformation, the lamellar keatite aggregates were formed directly from the amorphous precursors under the current conditions (batch alkalinity, batch silica to alumina ratio and temperature for crystallization). Thus, to form the pure phase slice-like keatite, the addition of silicalite-1 seed crystals is omitted for not formation of ZSM-5 crystals and the end of crystallization time is selected as $t_{c-t} = 90h$, in which the process stops in the 2nd stage and no α -quartz is formed.

Fig SI-3.1 SEM image (A) and XRD pattern (B) of slice-like keatite product obtained from the gel composition of $4Na_2O:0.1667Al_2O_3:100SiO_2:4000H_2O$ in the absence of silicalite-1 seed crystals. Other conditions are same as those described in the Experimental section of paper.

On the other hand, for the α -quartz crystals with hollow box morphology, the presence of ZSM-5 crystals formed from silicalite-1 seeds is critical in the beginning of transformation process. However, to avoid the formation of keatite as the by-product in the system no amorphous species should be present in the system just after the growth step of ZSM-5. This requirement can be fulfilled by increasing the batch alkalinity to enhance the solubility of amorphous species. More importantly, the alkalinity should not be too high so that the penetration of hydroxide ions into interior of ZSM-5 crystals is prohibited because of the presence of large amount of Al on the

surface of ZSM-5 crystals (as revealed from our previous work^{ref. 30 in the paper}, the aluminum content in the ZSM-5 crystals increases with increasing alkalinity). By attempting different gel compositions, the medium batch alkalinity as $A = [Na_2O/H_2O]_b = 0.004$ is selected and proved as the key for the aimed product with good phase purity.

Fig SI-3.2 SEM image (A) and XRD pattern (B) of α -quartz with hollow box morphology obtained from the gel composition of $16Na_2O:0.1667Al_2O_3:100SiO_2:4000H_2O$ in the presence of 4 wt.% silicalite-1 seed crystals. Other conditions are same as those described in the Experimental section of paper.