Supporting Information

Revealing Scenarios of Interzeolite Conversion from FAU to AEI through the Variation of Starting Materials

Zhendong Liu,[1,2,*] Anand Chokkalingam,[1] Shoko Miyagi,[1] Masato Yoshioka,[3]

Tomoya Ishikawa,[3] Hiroki Yamada,[4] Koji Ohara,[4] Nao Tsunoji,[5] Masahiro Sadakane,[5]

Yusuke Naraki,[3] Tsuneji Sano,[1] Tatsuya Okubo,[1] Toru Wakihara,[1,2,*]

1, Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

2, Institute of Engineering Innovation, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan

3, Inorganic Materials Research Laboratory, Tosoh Corporation, 4560 Kaiseicho, Shunan, Yamaguchi 746-8501, Japan

4, Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo, 679-5198 Japan

5, Graduate School of Advanced Science and Engineering, Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8527, Japan

liuzd@chemsys.t.u-tokyo.ac.jp (Z. Liu)
wakihara@chemsys.t.u-tokyo.ac.jp (T. Wakihara)

Table of Contents

Supporting Tables

Table S1, Acid concentrations used for the dealumination of different raw FAU zeolites.

parent FAU	sample ID	H_2SO_4 concentration [a] (M)	dealuminated FAU	
			Si/Al ratio [b] (-)	relative crystallinity [c] (%)
320HOA	320HOA-4.7 (95%)	0.3	4.7	95
	320HOA-8.6 (55%)	0.5	8.6	55
	320HOA-12.7 (22%)	0.6	12.7	22
	320HOA-27.7 (0%)	0.7	27.7	0
	320HOA-96.4 (0%)	0.8	96.4	0
320NAA	320NAA-4.6 (52%)	0.3	4.6	52
	320NAA-5.6 (36%)	0.4	5.6	36
	320NAA-8.4 (11%)	0.5	8.4	11
	320NAA-19.0 (0%)	0.6	19.0	0
341NHA	341NHA-5.1 (98%)	0.2	5.1	98
	341NHA-7.1 (72%)	0.3	7.1	72
	341NHA-10.9 (0%)	0.4	10.9	0
	341NHA-25.2 (0%)	0.5	25.2	0
350HUA	350HUA-9.5 (102%)	0.2	9.5	100
	350HUA-13.3 (92%)	0.3	13.3	92
	350HUA-23.8 (66%)	0.4	23.8	66
360HUA	360HUA-10.9 (100%)	0.1	10.9	100
	360HUA-26.2 (104%)	0.2	26.2	100
	360HUA-74.6 (109%)	0.3	74.6	100

[a] The dealumination was done at 75 °C for 4 h. In a typical run, 5 g of raw FAU zeolite was mixed into 50 g of dilute H_2SO_4 solution.

[b] Measured by ICP-AES.

[c] The relative crystallinity was calculated by comparing XRD peak intensity (peaks in the range of 20° – 30°) with that of the corresponding raw FAU zeolite.

Table S2, An overview of the synthesis conditions and the main phases. [a,b]

sample ID	$NaOH/SiO_2$ = 0.1	$NaOH/SiO_2$ = 0.2	$NaOH/SiO_2$ = 0.3
320HOA-4.7 (95%)	AEI+FAU	ANA+AEI	ANA+GME
320HOA-8.6 (55%)	***AEI (trace ANA)***	***AEI (trace ANA)***	GME+AEI
320HOA-12.7 (22%)	FAU	***AEI (trace ANA)***	AEI+GME
320HOA-27.7 (0%)	amorphous+FAU	**AEI** Si/Al ratio: 12.0 S_{BET}: 734 m^2/g V_{micro}: 0.29 cm^3/g	**AEI** Si/Al ratio: 9.9 S_{BET}: 704 m^2/g V_{micro}: 0.28 cm^3/g
320HOA-96.4 (0%)	MFI	AEI+unknown	**AEI** Si/Al ratio: 13.7 S_{BET} and V_{micro}: n.a.
320NAA-4.6 (52%)	FAU+AEI+ANA	ANA	ANA (trace GME)
320NAA-5.6 (36%)	AEI+ANA	ANA+AEI	ANA+GME
320NAA-8.4 (11%)	FAU+AEI	***AEI (trace ANA)***	GME+AEI
320NAA-19.0 (0%)	amorphous+AEI	ANA+AEI	**AEI** Si/Al ratio: 9.7 S_{BET}: 657 m^2/g V_{micro}: 0.26 cm^3/g
341NHA-5.1 (98%)	FAU+AEI	ANA+AEI	ANA+AEI
341NHA-7.1 (72%)	FAU+AEI	AEI+ANA	ANA+AEI+FAU
341NHA-10.9 (0%)	FAU+ANA	***AEI (trace ANA)***	AEI+GME
341NHA-25.2 (0%)	amorphous+FAU	amorphous+ANA	**AEI** Si/Al ratio: 9.5 S_{BET}: 684 m^2/g V_{micro}: 0.27 cm^3/g
350HUA-9.5 (102%)	**AEI** Si/Al ratio: 7.7 S_{BET} and V_{micro}: n.a.	AEI+ANA	AEI+ANA
350HUA-13.3 (92%)	***AEI (trace MFI)***	***AEI (trace ANA)***	***AEI (trace ANA)***
350HUA-23.8 (66%)	amorphous+FAU	**AEI** Si/Al ratio: 15.4 S_{BET}: 696 m^2/g V_{micro}: 0.27 cm^3/g	**AEI** Si/Al ratio: 11.3 S_{BET}: 562 m^2/g V_{micro}: 0.28 cm^3/g
360HUA-10.9 (100%)	FAU	amorphous+FAU	AEI+GME+ANA
360HUA-26.2 (104%)	amorphous	amorphous+FAU	***AEI (trace unknown)***
360HUA-74.6 (109%)	MFI	amorphous+FAU	***AEI (trace MFI)***

[a] All the syntheses were done at 180 °C for 3 d.

[b] In each cell, the first phase indicates the one dominated in the product. Pure-phase AEI is highlighted in **bold**; and, the Si/Al ratio, BET surface area (S_{BET}) and micropore volume (V_{micro}) are given (S_{BET} and V_{micro} for some samples are not available). The products contained mainly AEI but with a trace amount of impurity are highlighted in *italic* and **bold**.

Supporting Figures

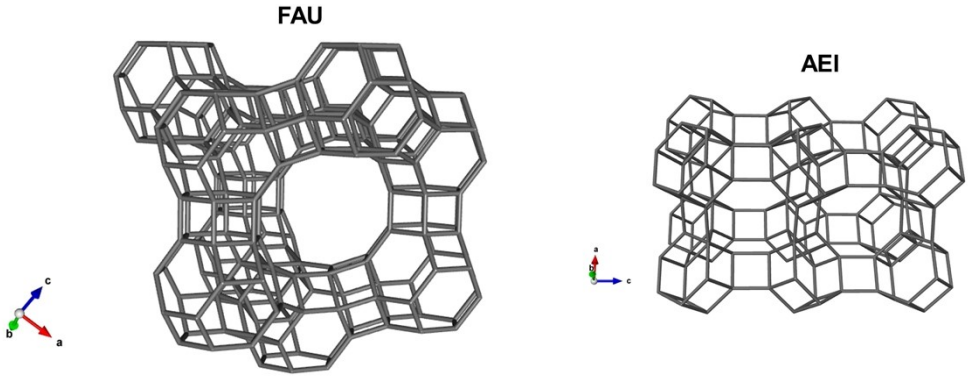

Figure S1: **Structures of FAU and AEI.** FAU is composed of connecting double-six-membered-rings (*d6r*) and sodalite cages (*sod*) that form super cages, whereas AEI is composed of double-six-membered-rings (*d6r*) linked through four-membered-rings. FAU and AEI share a common composite building unit – *d6r*. The framework densities for FAU and AEI are 13.3 T/1000 $Å^3$ and 15.1 T/1000 $Å^3$, respectively.

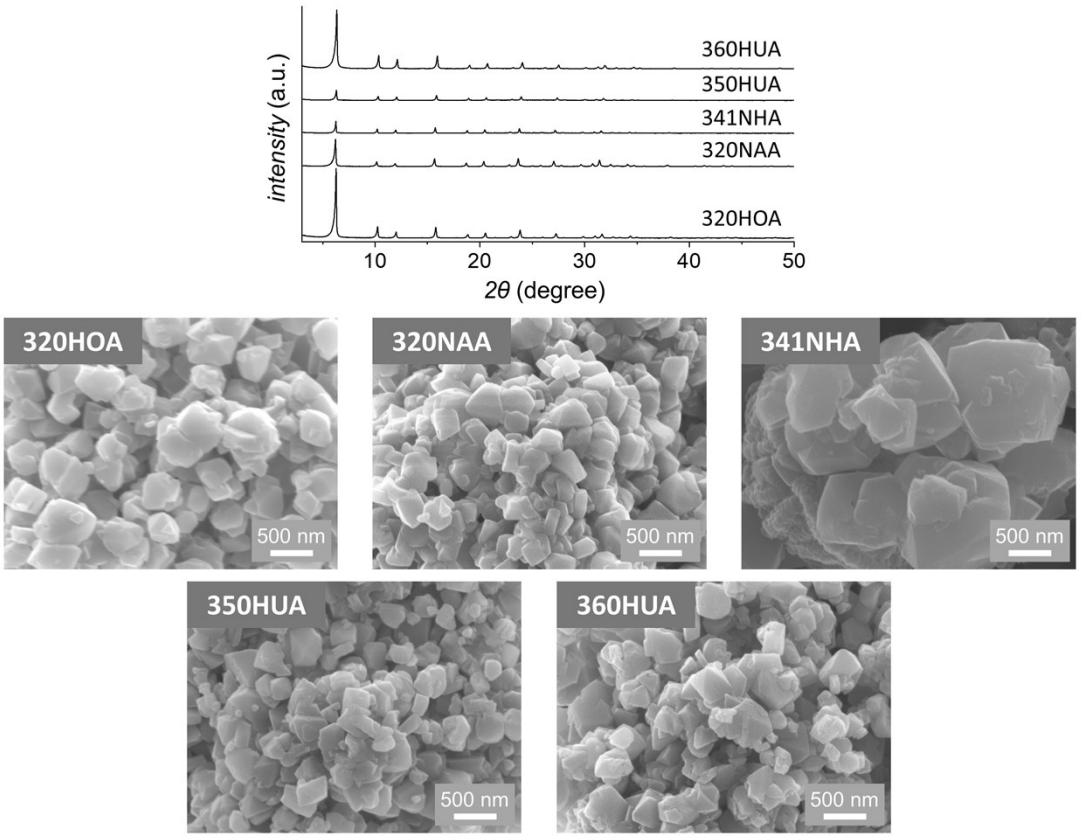

Figure S2: **SEM and XRD patterns of the raw FAU zeolites.** These zeolite are all provided by Tosoh: HSZ-320HOA (proton-type, Si/Al ratio: 2.8), HSZ-320NAA (sodium-type, Si/Al ratio: 2.8), HSZ-341NHA (ammonia-type, Si/Al ratio: 3.8), HSZ-350HUA (proton-type, Si/Al ratio: 5.5) and HSZ-360HUA (proton-type, Si/Al ratio: 6.8).

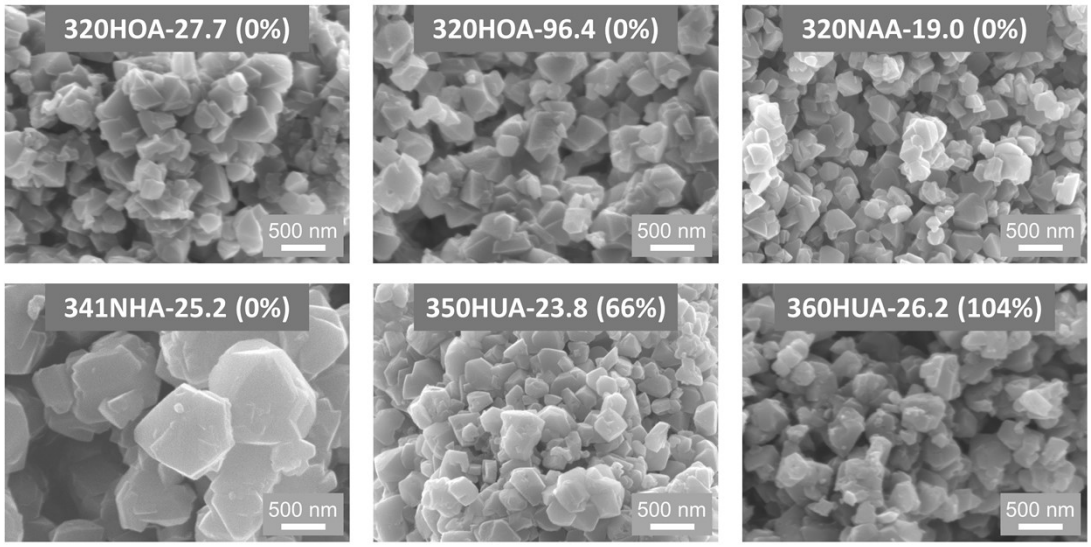

Figure S3: **SEM images of the representative dealuminated FAU zeolites.** (The information of the dealuminated FAU zeolites was given in the following format: 320HOA-27.7 (0%), where "320HOA", "27.7" and "(0%)" stand for the material number of the raw FAU, the Si/Al ratio and the relative crystallinity of the dealuminated FAU, respectively.)

The results in **Figure S3** indicate that the dealumination did not essentially change the morphology of the FAU zeolite, even though it caused considerable structural degradation.

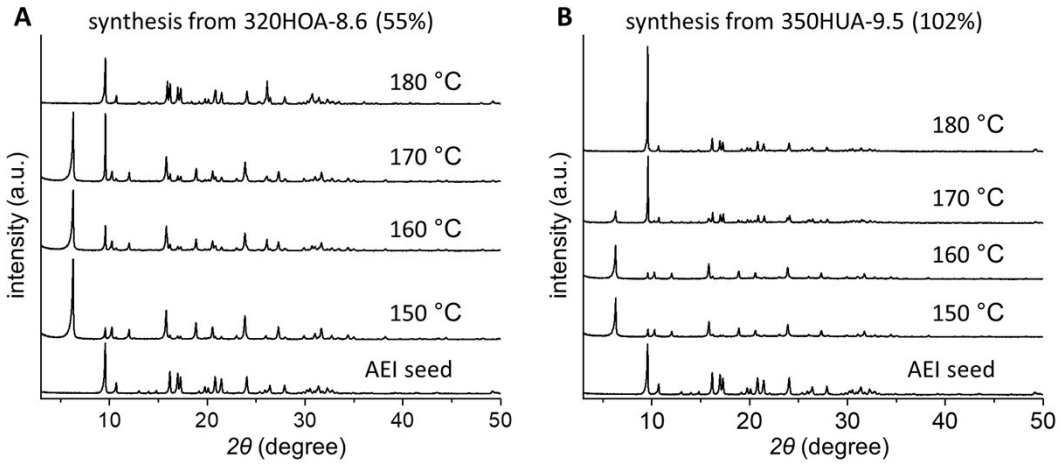

Figure S4: **Effect of synthesis temperature on the interzeolite conversion from FAU to AEI.** The synthesis precursor featured the following molar composition: $OSDA/SiO_2 = 0.2$, $H_2O/SiO_2 = 5$ and $NaOH/SiO_2 = 0.1$; 2 wt% AEI seed was added on the basis of SiO_2. The information of the dealuminated FAU zeolites was given in the following format: 320HOA-8.6 (55%), where "320HOA", "8.6" and "(55%)" stand for the material number of the raw FAU, the Si/Al ratio and the relative crystallinity of the dealuminated FAU, respectively.

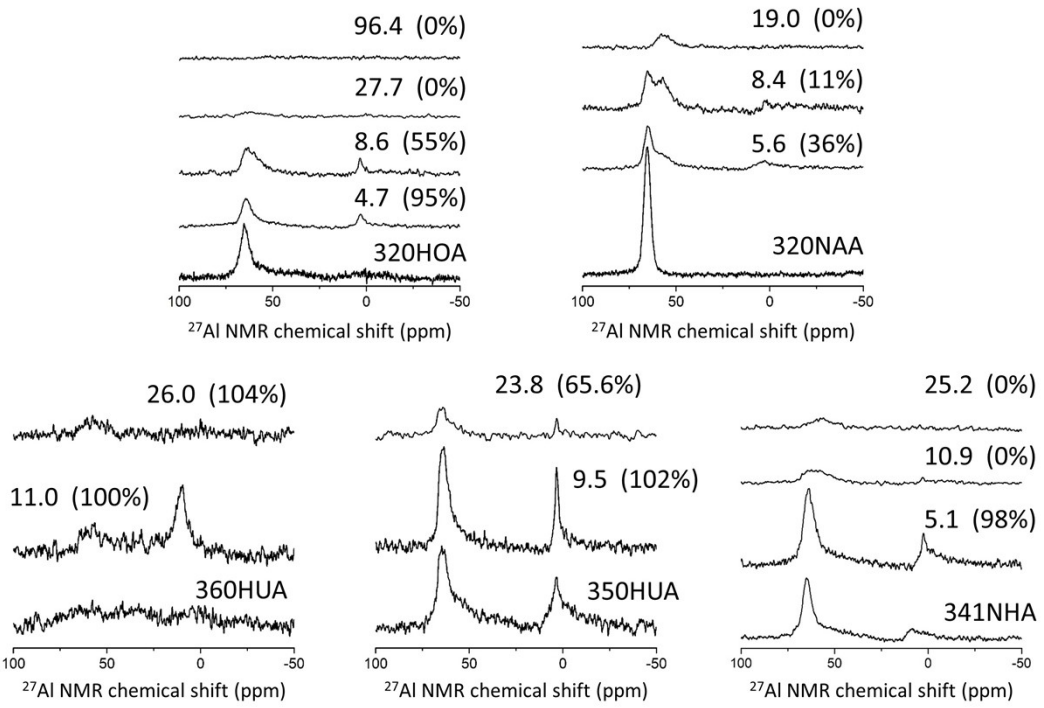

Figure S5: **^{27}Al NMR of the raw and dealuminated FAU zeolites.** Both the Si/Al ratio and the relative crystallinity of each dealuminated FAU zeolite are given above the corresponding ^{27}Al NMR spectrum. For example, "96.4 (0%)" represents the Si/Al ratio (96.4) and the relative crystallinity (0%).

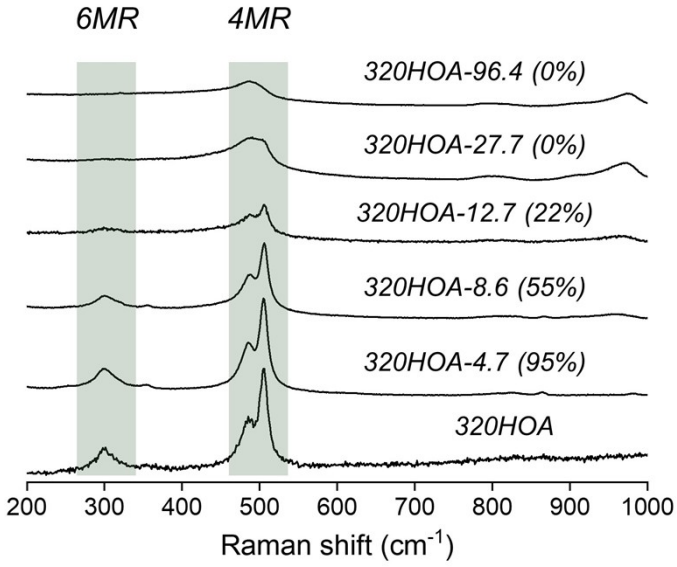

Figure S6: UV Raman spectra of the HSZ-320HOA series FAU zeolites.

Figure S6 indicates that the band due to the ring breathing vibration of the four-membered-ring (4MR) can still be observed although some of the dealuminated FAU zeolites were of 0% relative crystallinity. The information of the dealuminated FAU zeolites was given in the following format: 320HOA-27.7 (0%), where "320HOA", "27.7" and "(0%)" stand for the material number of the raw FAU, the Si/Al ratio and the relative crystallinity of the dealuminated FAU, respectively.

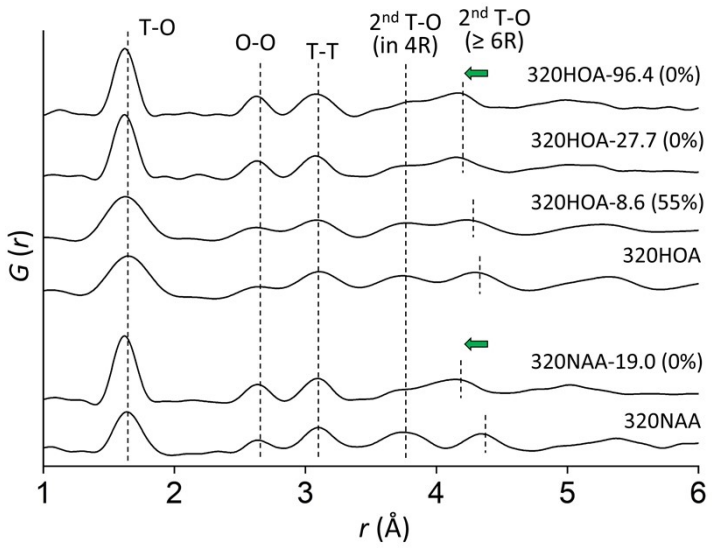

Figure S7: Pair distribution functions of the typical dealuminated FAU zeolites.

From **Figure S7**, a shift toward a shorter distance in the range of 4.0 – 4.5 Å can be observed in the dealuminated FAU zeolites, which implies the presence of highly distorted six-membered-rings 6MRs.

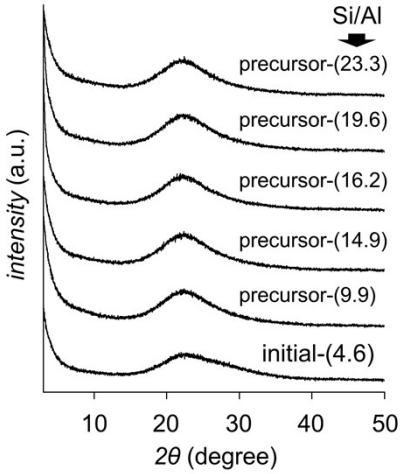

Figure S8: **XRD patterns of the initial amorphous aluminosilicate precursors and the dealuminated precursors.** To simplify the description, the dealuminated amorphous aluminosilicate precursor is abbreviated as "precursor-(9.9)", where the number in the parenthesis gives the Si/Al ratio of the precursor.

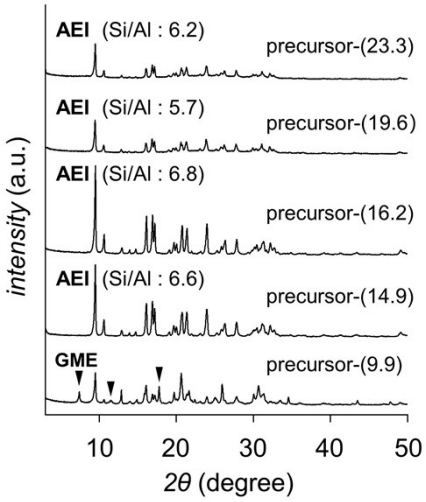

Figure S9: Synthesis of AEI zeolite from the dealuminated amorphous aluminosilicate precursors with different Si/Al ratios. The same as above, to simplify the description, the dealuminated amorphous aluminosilicate precursor is abbreviated as "precursor-(9.9)", where the number in the parenthesis gives the Si/Al ratio of the precursor. The Si/Al ratio of the AEI product is also given above each XRD pattern. In all cases, the synthesis condition was as follows: $OSDA/SiO_2$ = 0.2, H_2O/SiO_2 = 7.5 and $NaOH/SiO_2$ = 0.1; 2 wt% AEI seed was added on the basis of SiO_2; the synthesis temperature was 190 °C, and the synthesis time was 1 d.

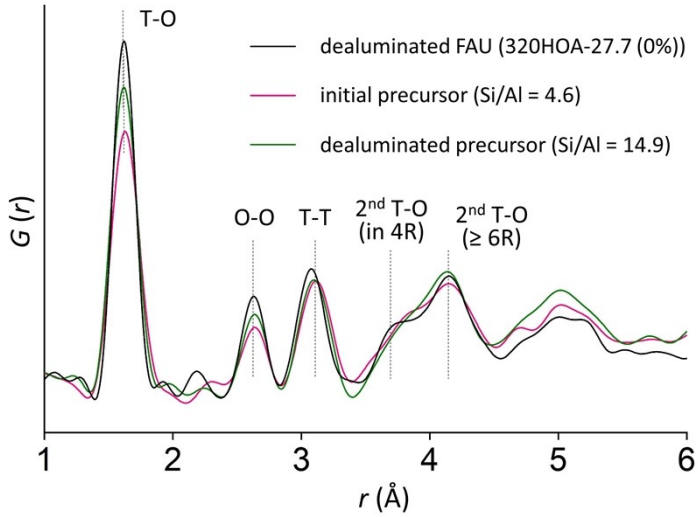

Figure S10: **Pair distribution functions of the initial and dealuminated aluminosilicate precursors.**

From **Figure S10**, a peak in the range of 4.0 – 4.5 Å, indicative of the second T-O correlations, can be observed. The intensity of this peak for the dealuminated amorphous aluminosilicate precursor got enhanced, as compared with that for the initial precursor, which even became comparable to that for the dealuminated FAU zeolite. This result implies the presence of highly distorted six-membered-rings (6MRs) in the dealuminated amorphous aluminosilicate precursor.