Supporting Information:

Engineering of Zeolite BEA Crystal Size and Morphology via Seed-directed Steam Assisted Conversion

Tatiana O. Bok[1], Egor P. Andriako[1], Elena E. Knyazeva[1,2], and Irina I. Ivanova* [1,2]

[1] A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia.

[2] Department of Chemistry, Moscow State University, Moscow, Russia.

***Email:** iiivanova@phys.chem.msu.ru

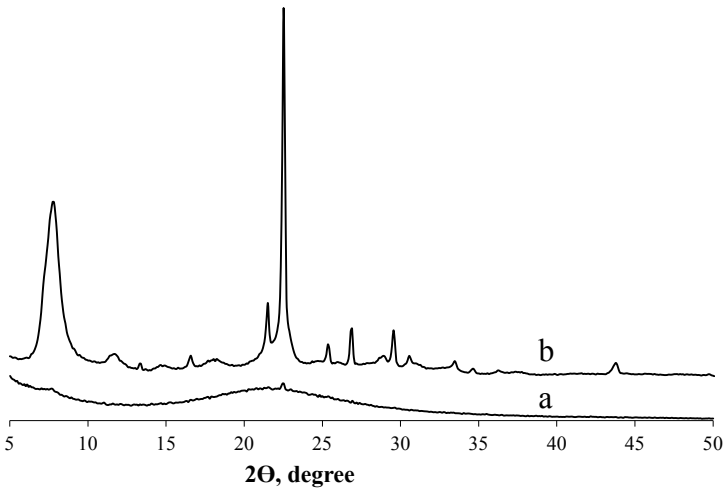

Figure S1. XRD patterns of BEA samples, synthesized without seeds after 48 h (a) and 120 h (b) of synthesis

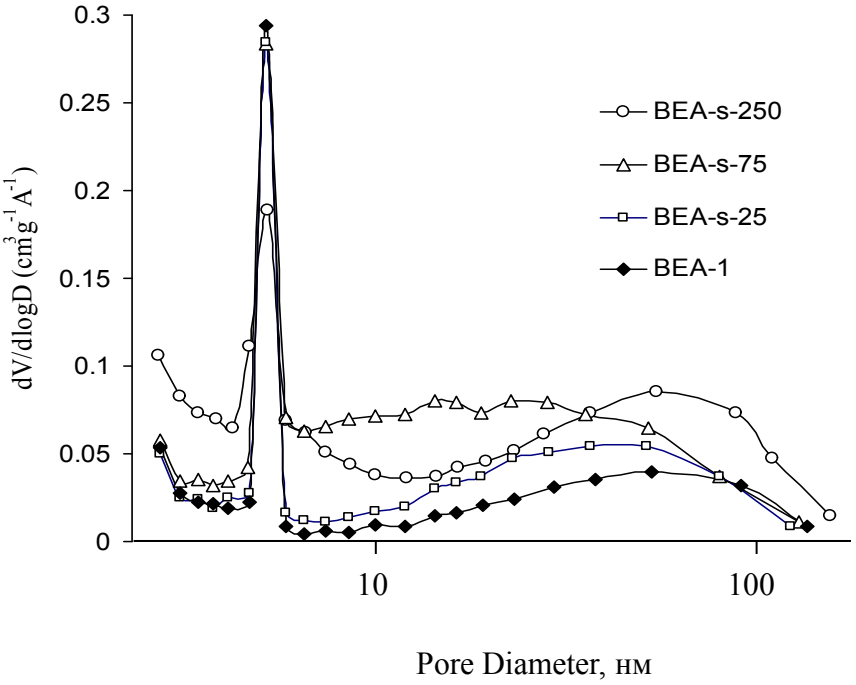

Figure S2. BJH pore size distribution curves for synthesized samples.

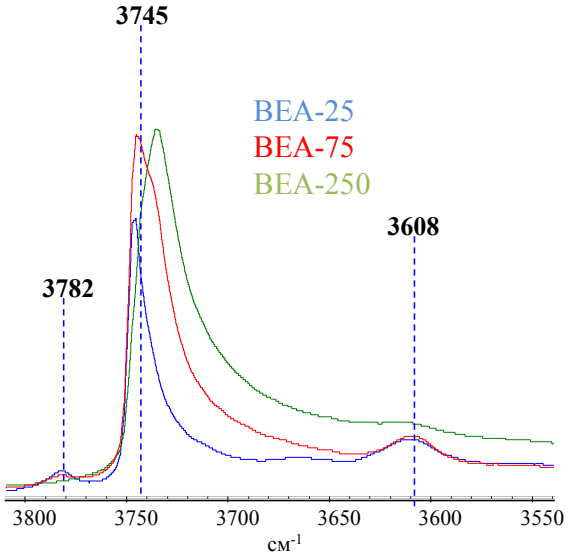

Figure S3. FT-IR spectra of the BEA seed crystals with different SAR.

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Protégé 460 FTIR spectrometer at 4 cm^{-1} optical resolution. Prior to the measurements, the catalysts were pressed into selfsupporting disks and activated in the infrared (IR) cell attached to a vacuum line at 673 K for 2 h. Adsorption of pyridine was performed at 423 K for 30 min. Excess probe molecules were further evacuated at 423 K for 15 min. The numbers of Brønsted and Lewis acid sites were evaluated from the intensities of the bands at ca. 1545 and 1450 cm^{-1} of adsorbed pyridine.

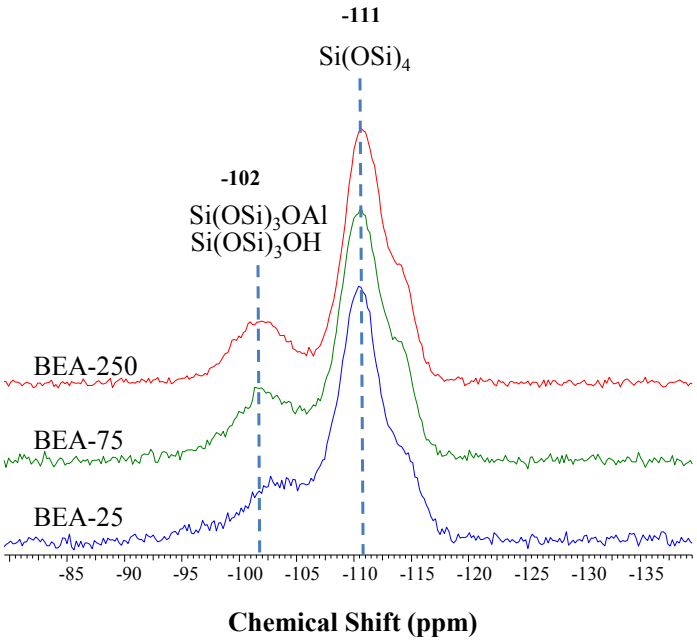

Figure S4. ^{29}Si MAS NMR of the BEA seed crystals with different SAR.

Magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded on a Bruker Avance II 400 spectrometer at a magnetic field of 9.4 T. The spectra were processed and analyzed using Topspin 2.1 software.

Calculations of the amount of defects in seeds:

The amount of SiOH defects was estimated from ^{29}Si MAS NMR spectra (fig. S4), basing on the assumption that silanol defects are contributing mainly to the NMR line at ca. -102 ppm, corresponding to Q3 species ($Si(OSi)_3OH$ and $Si(OSi)_3OAl$). The contribution of Q2 and Q1 species was considered negligible. The intensity corresponding to $Si(OSi)_3OH$ species (I_{OH}) was calculated as a difference between the experimental intensity of Q3 peak from the NMR spectra (I_{Q3}) and the contribution from $Si(OSi)_3OAl$ species (I_{Al}): $I_{OH} = I_{Q3} - I_{Al}$. I_{Al} was estimated from the well-known formula for calculation of framework Si/Al ratio basing on ^{29}Si MAS NMR spectra ($(Si/Al) = \sum_{n=0}^{4} I_{Si(nAl)} \div \sum_{n=0}^{4} 0.25n \times I_{Si(nAl)}$)[1]. Knowing Si/Al ratio from chemical analysis and assuming that all Al atoms of the zeolite are contributing to $Si(OSi)_3OAl$ species, I_{Al} could be calculated as: $I_{Al} = (4 * I_0)/((Si/Al)-4)$, where I_0 is the intensity of $Si(OSi)_4$ species. Using a simple proportion, the amount of defects was calculated as $C_{SiOH} = C_{Al} * (I_{OH}/I_{Al})$. The results of calculations for seeds with different SAR are shown in Table S1.

Table S1. Values of integrals and the defects concentration of the BEA seed crystals with different SAR.

SAR	Intensities		Content, mmole/g	
	I_{Al}	I_{OH}	Al	Si-OH
25	13.91	13.08	1.23	1.2
75	3.98	26.81	0.43	2.9
250	1.24	22.75	0.13	2.4

Estimation of the amount of crystals in seeds taken for synthesis and final products

The estimation of the number of crystals was carried out basing on the following assumptions:

(1) Crystals of seeds and product are spherical.

(2) Unit cell composition of zeolite BEA is $Al_xSi_{64-x}O_{128}$, the approximate molar mass – 3836g.

(3) Unit cell volume of zeolite BEA is 4.178 nm^3.[2]

Taking that the mean size of crystal is X nm and that the volume of the unit cell of BEA is 4.178 nm^3 and assuming a spherical shape of BEA particle, we calculated the amount of unit cells in one crystal as $4/3p(X/2)^3/ 4.178 = 0.125*X^3$. Then, taking that the weight of 1 mole of BEA unit cell ($Al_xSi_{64-x}O_{128}$) is ~ 3836 g we estimated the weight of the unit cell of BEA as $3836/ 6.02*10^{23} = 6.37*10^{-21}$ g and the weight of BEA crystal with the size of X nm as $0.125*X^3* 6.37*10^{-21} = 0.8*10^{-21}* X^3$ g. This simple estimation allows to calculate the amount of BEA crystals (N) in m g of sample as $N = m/ (0.8*10^{-21}* X^3) = 1.25*10^{21}m/X^3$. The results of calculation are given in Table S1.

Table S1. Calculation of the number of crystals in BEA seeds and products

Sample	Seeds			Products		
	m_s, g	X_s, nm	N_s*	m_p, g	X_p, nm	N_p**
BEA-s-25	0.016	200	$2.5*10^{12}$	1.670	1000	$2.1*10^{12}$
BEA-s-250	0.016	1000	$2.0*10^{10}$	1.497	200	$2.4*10^{14}$

*N_s - amount of BEA crystals in seeds taken for the synthesis;

**N_p -amount of BEA crystals (polycrystals or aggregates) in the products obtained.

REFERENCES

(1) J. Klinowski, C. A. Fyfe and G. C. Gobbi, *J. Chem. SOC., Faraday Trans. 1,* 1985, **81** , 3003-3019.

(2) http://https//europe.iza-structure.org/IZA-SC/framework.php?STC=BEA