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Supporting Online Material for

Capturing Ultrasmall EMT Zeolite from Template-Free Systems

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This PDF file includes:

Materials and Synthesis

Materials

$NaAlO_2$ (Strem-chemicals, 56.7% Al_2O_3, 39.5% Na_2O)
NaOH (Merck, 99%)
Na_2SiO_3 (Prolabo, 29% SiO_2, 8% Na_2O, 28.85 g)

Synthesis

The ultrasmall EMT zeolite (6–15 nm) was synthesized from a clear precursor suspension with the molar composition $5.15SiO_2$:$1Al_2O_3$:$18.45Na_2O$:$240.3H_2O$. The suspension was continuously stirred for 10 min at room temperature and then kept at 30 °C for 36 h. The nanosized EMT zeolite (50-70 nm) was prepared from $5SiO_2$:$1Al_2O_3$:$17.48Na_2O$:$340.3H_2O$. After continuous stirring for 10 min, the suspension was aged at room temperature (~23 °C) for 14 h. The samples were heated either in a microwave oven using an Anton Paar Synthos 3000 for 4 min at 30 °C (200 W), or in a conventional oven at 30 °C for 36 h.

Characterization of Samples

The X-ray diffractograms were measured using a parallel beam on a flat powder sample in reflection geometry, using Cu-K_α monochromatized radiation and a curved position sensitive detector (CPS120-INEL).

Transmission electron microscopy (TEM): Colloidal suspensions of EMT crystals were dried on copper grids and studied using a FEI Titan 80-300 operating at 300 kV. Scanning electron microscopy (SEM): Powder samples dispersed on a carbon holder were scanned using a Philips XL-30 scanning electron microscope operating at 20 kV.

N_2 sorption analysis: Nitrogen adsorption-desorption isotherms were measured using a Micrometrics ASAP 2010 volumetric adsorption analyzer. Samples were dehydrated at 250 °C under vacuum overnight prior to the measurements. The external surface area and micropore volume were estimated using *t*-plots, and the pore size distribution of the EMT samples was estimated by the DFT method.

Dynamic light scattering (DLS) and zeta potential analyses: The hydrodynamic diameters and the colloidal stability of the nanoparticles were determined with a Malvern Zetasizer Nano.

X-ray fluorescence (XRF) spectroscopy: The chemical composition of the samples was determined with a MagiX PHILIPS PW2540.

Infrared (IR) spectroscopy: The spectra were recorded on Bruker TENSOR 27^{TM} spectrometer using the KBr pellet technique (KBr: sample ratio = 200:1).

Figures

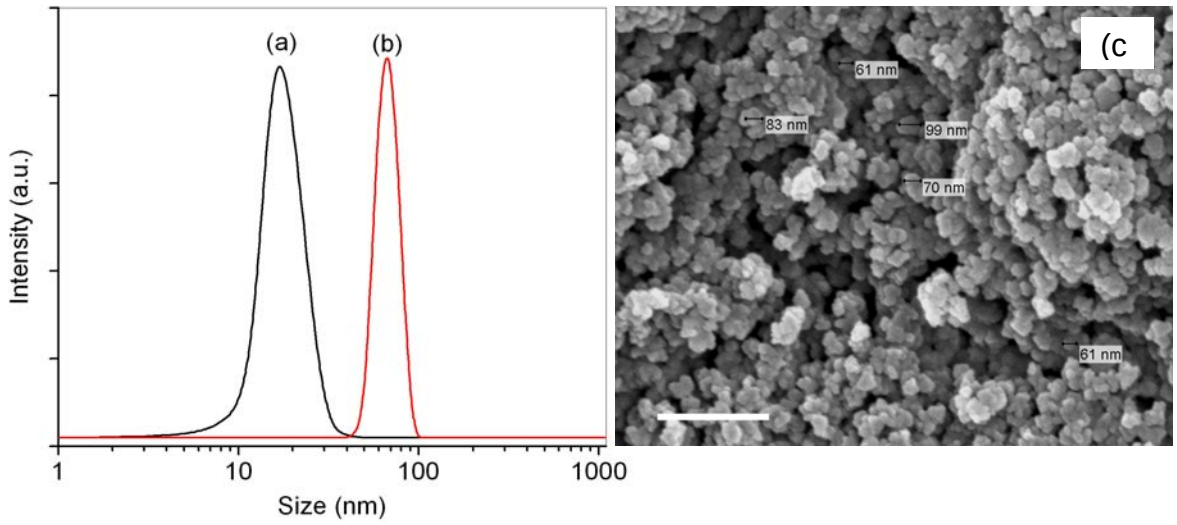


Fig. S1.

DLS curves of (a) ultrasmall (conventional heating at 30 °C for 36 h), and (b) nanosized (microwave heating at 30 °C for 4 min) EMT type zeolite, and (c) SEM image of nanosized EMT crystals prepared under microwave heating, Scale bar = 500 nm.

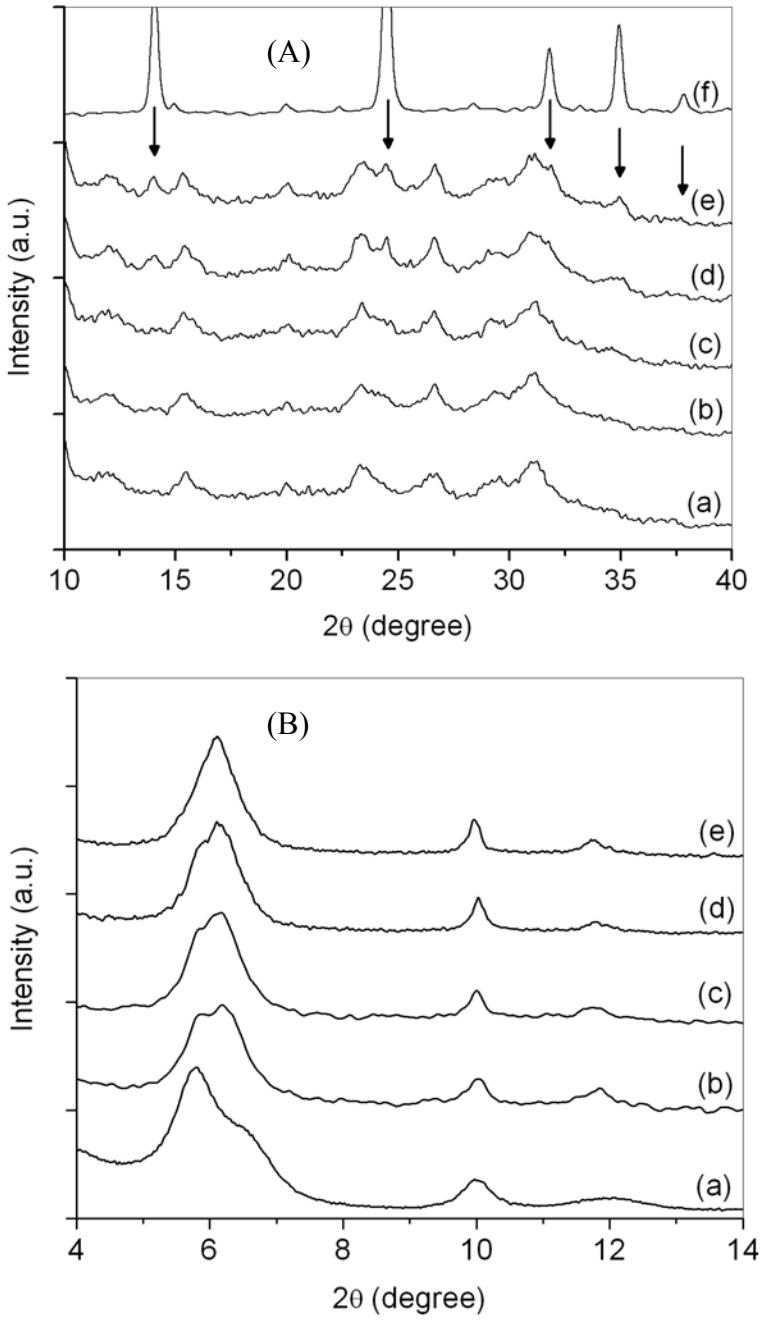
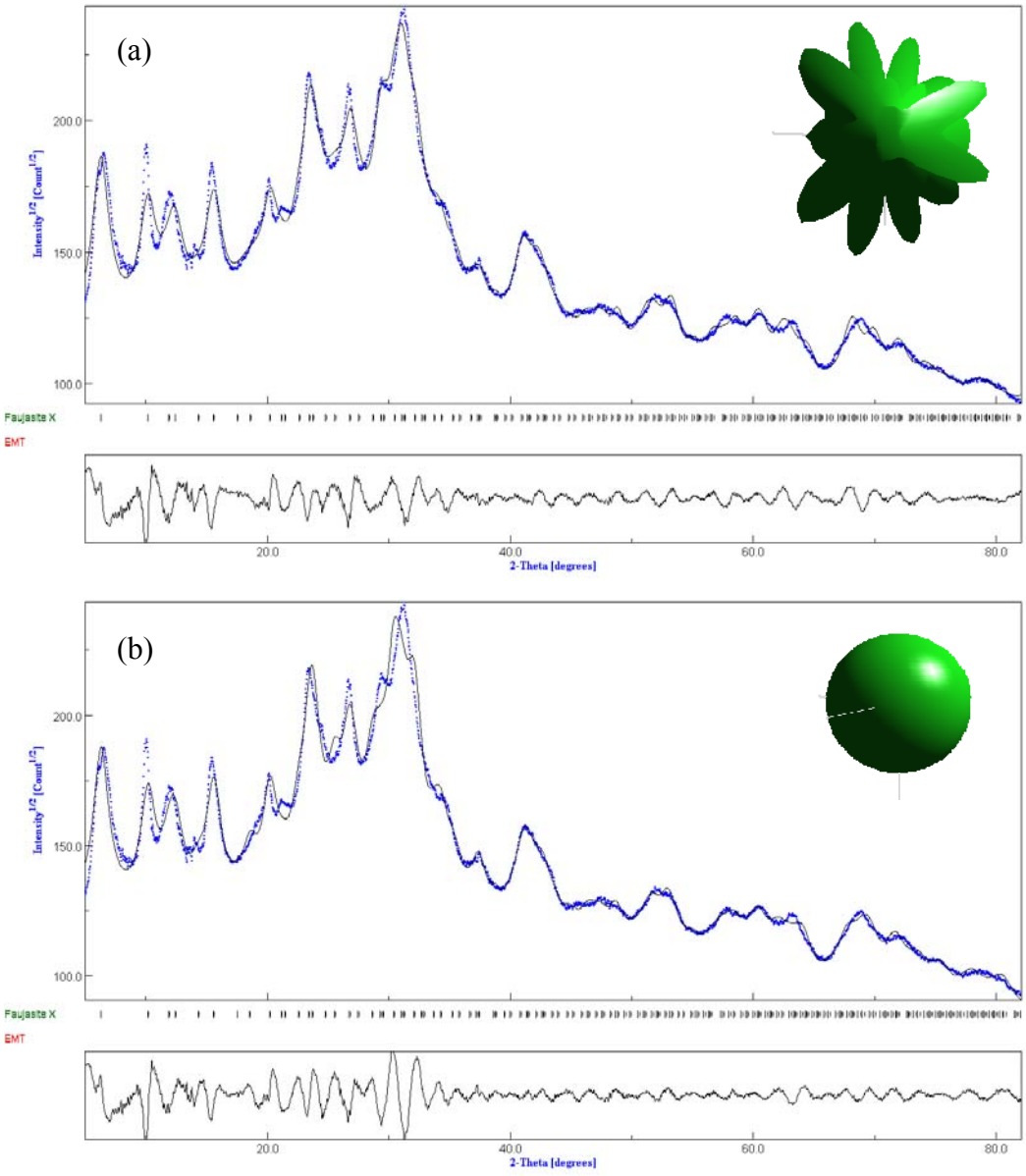


Fig. S2

(A) Samples extracted from a precursor suspension with a molar ratio of $5.15SiO_2$:$1Al_2O_3$:$18.45Na_2O$:$240.3H_2O$ after (a) 24 h, (b) 36 h, (c) 42 h, (d) 48 h, and (e) 54 h synthesis in comparison with (f) pure sodalite (SOD). (B) Intermediate EMT-FAU synthesized from a precursor suspension with a molar ratio of $5SiO_2$:$1Al_2O_3$:$20Na_2O$:$700H_2O$ for (b) 20 h, (c) 36 h, (d) 42 h and (e) pure FAU 50 h, in comparison to (a) pure EMT synthesized from the original suspension ($5.15SiO_2$:$1Al_2O_3$:$18.45Na_2O$:$240.3H_2O$) for 36 h.


(a)
200.0
150.0
100.0
Intensity 1/2 [Count 1/2]
Faujasite X
EMT
20.0
40.0
60.0
80.0
2-Theta [degrees]
(b)
200.0
150.0
100.0
Intensity 1/2 [Count 1/2]
Faujasite X
EMT
20.0
40.0
60.0
80.0
2-Theta [degrees]

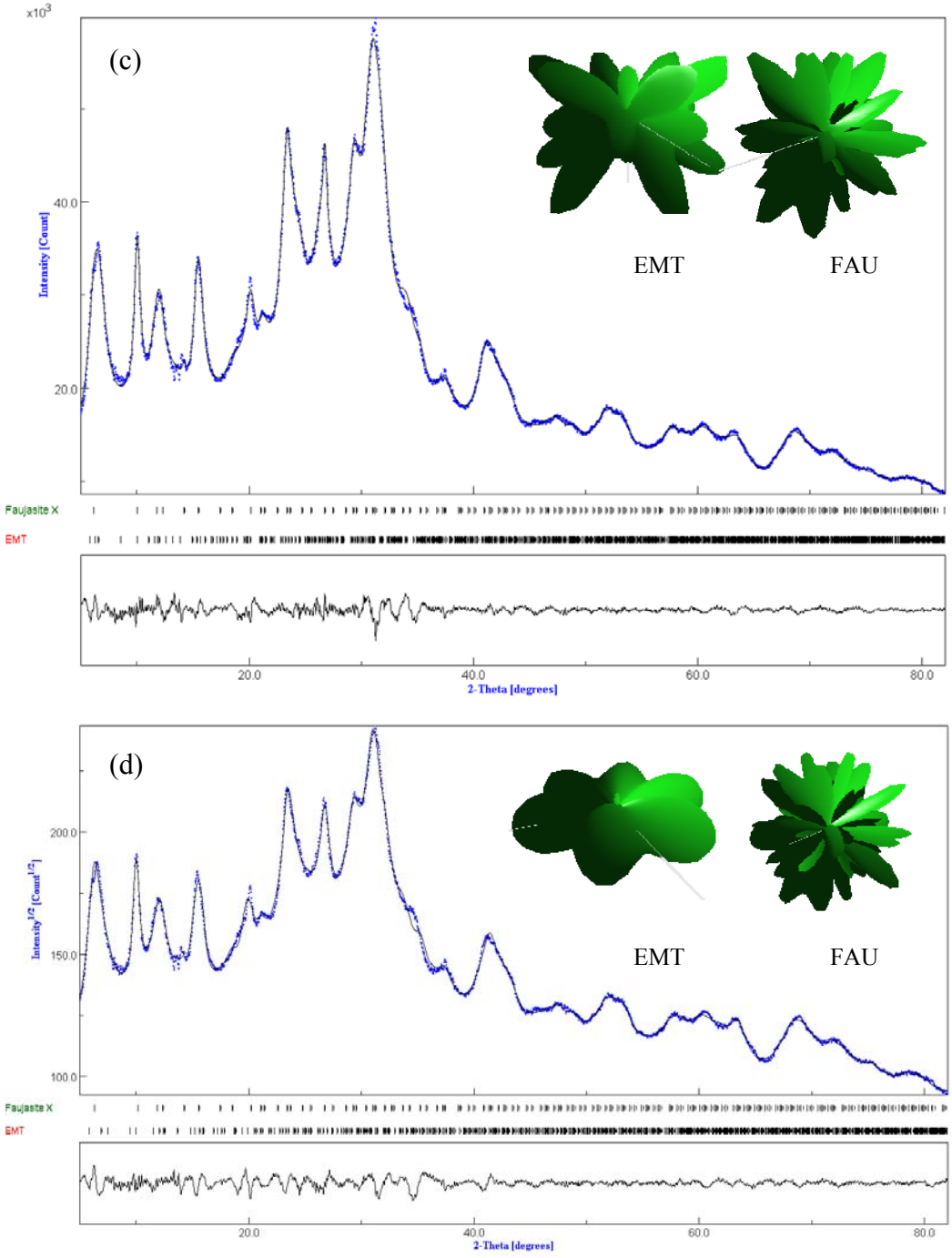
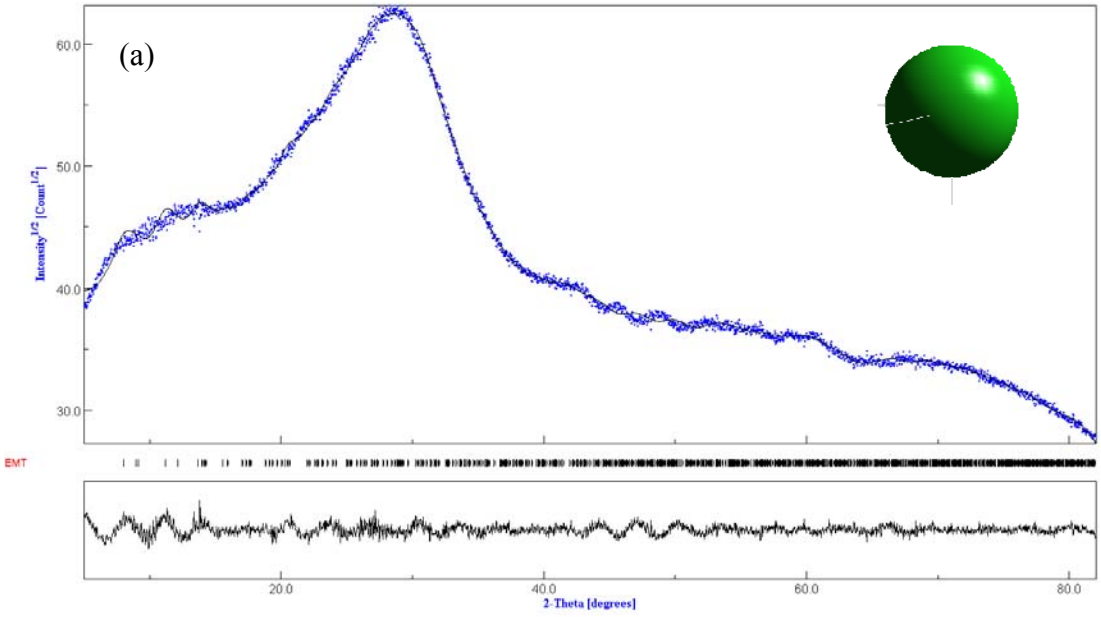


Fig. S3

Rietveld fits for ultrasmall crystals synthesized for 36 h as (a) 100 % FAU zeolite with anisotropic crystalline shapes (harmonic development up to P6), (b) 100 % FAU zeolite with isotropic shapes (harmonic development with only P0), (c) 50 % FAU and 50 % EMT zeolites with anisotropic shapes, and (d) FAU and EMT zeolites with anisotropic shapes and released phase amounts.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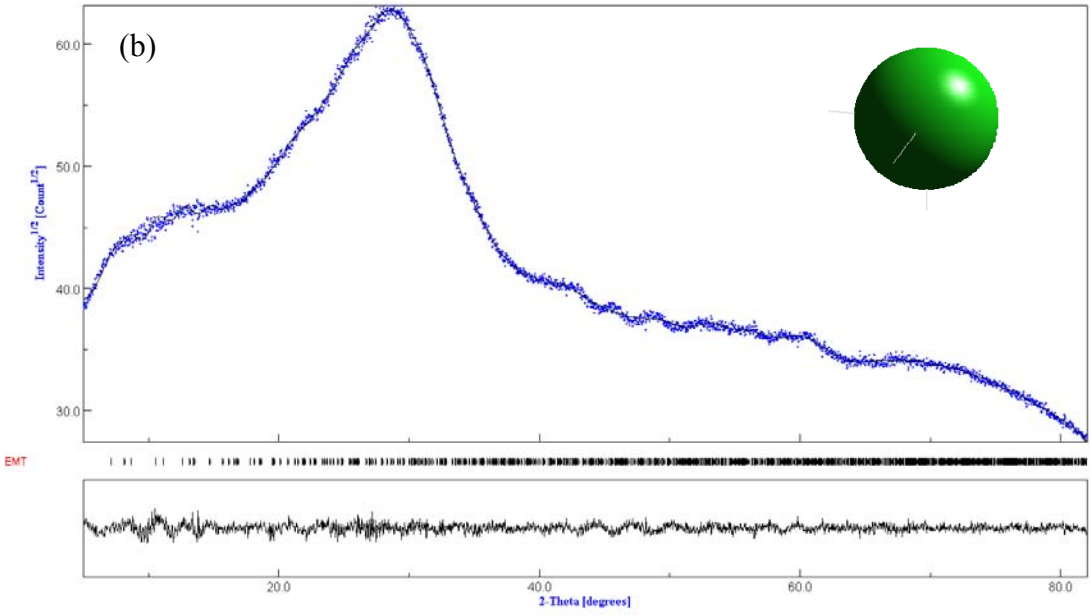
50.0
40.0
30.0
Intensity$^{1/2}$ [Count$^{1/2}$]
EMT
20.0
40.0
60.0
80.0
2-Theta [degrees]


(b)
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50.0
40.0
30.0
Intensity$^{1/2}$ [Count$^{1/2}$]
EMT
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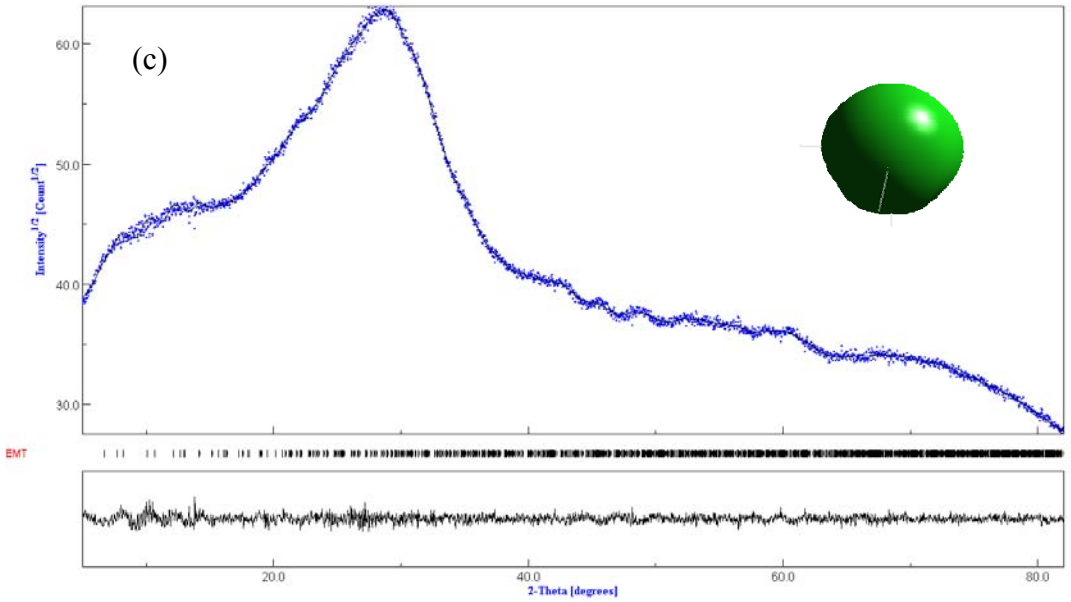
40.0
60.0
80.0
2-Theta [degrees]


(c)
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50.0
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30.0
Intensity$^{1/2}$ [Count$^{1/2}$]
EMT
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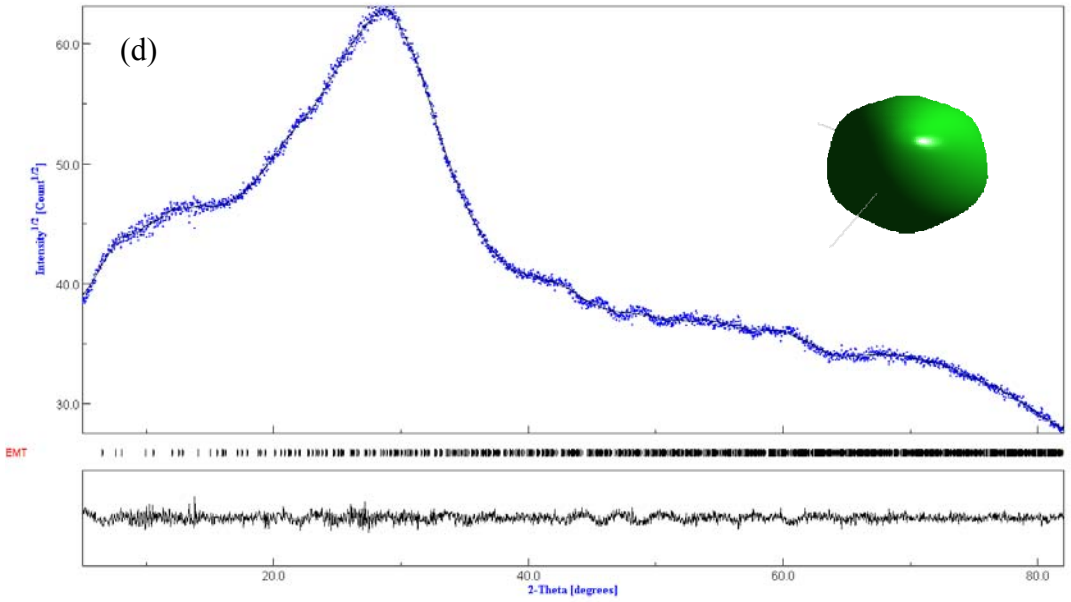
60.0
80.0
2-Theta [degrees]


(d)
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50.0
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30.0
Intensity$^{1/2}$ [Count$^{1/2}$]
EMT
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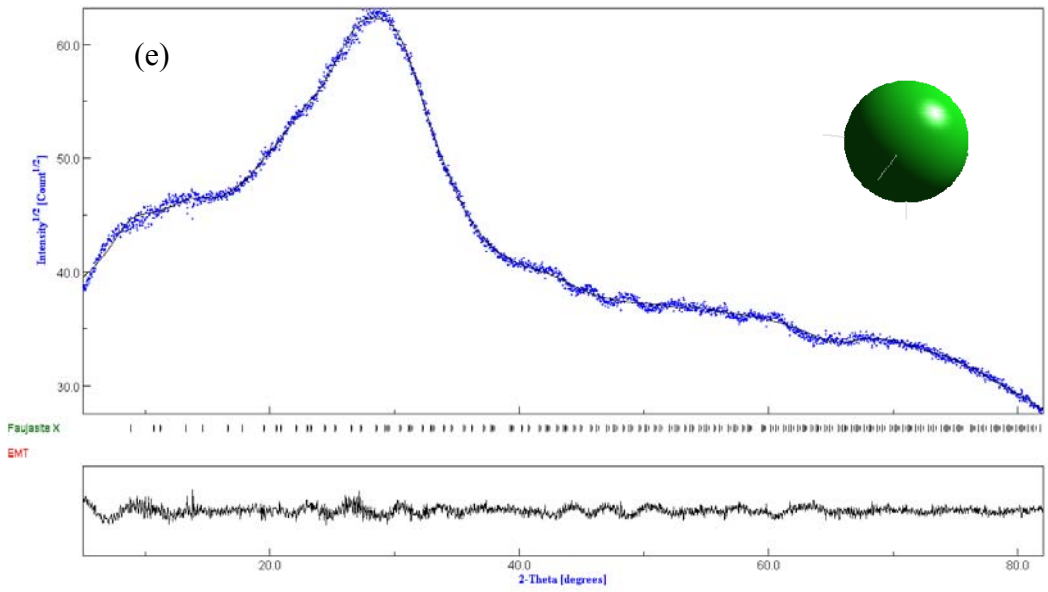
80.0
2-Theta [degrees]


(e)
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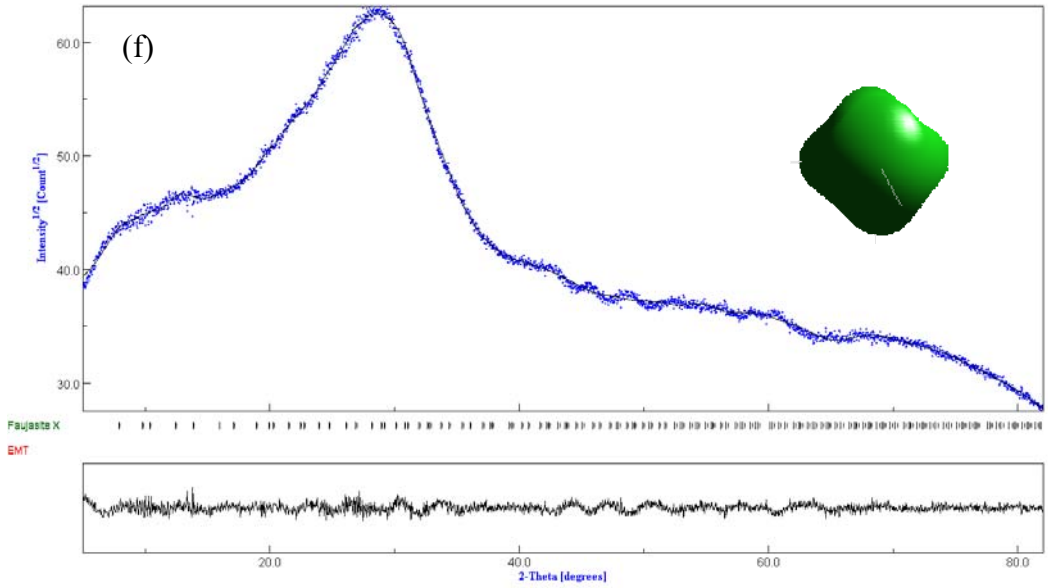
40.0
30.0
Intensity$^{1/2}$ [Count$^{1/2}$]
Faujasite X
EMT
20.0
40.0
60.0
80.0
2-Theta [degrees]

...


(f)
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50.0
40.0
30.0
Intensity$^{1/2}$ [Count$^{1/2}$]
Faujasite X
EMT
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40.0
60.0
80.0
2-Theta [degrees]

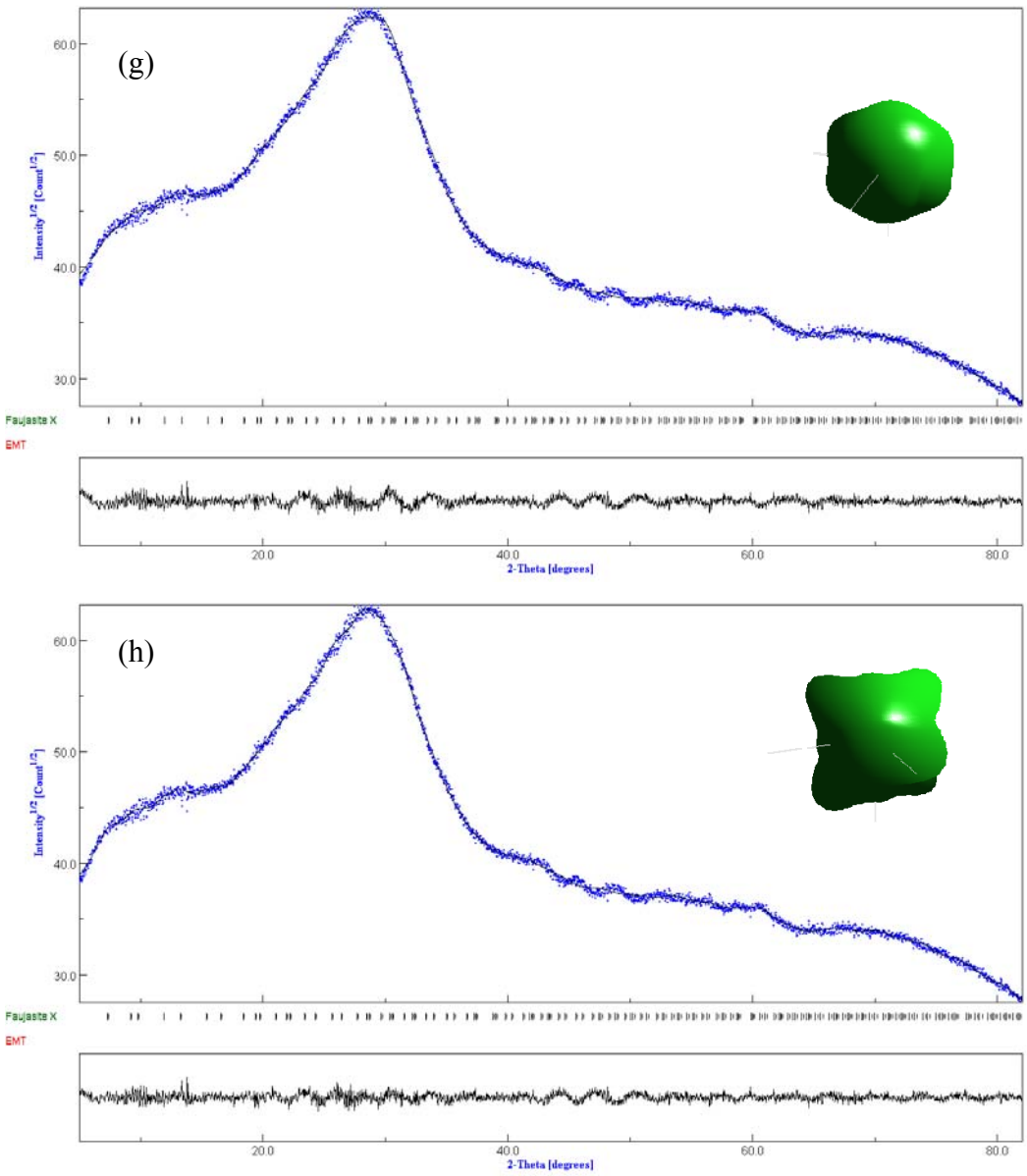


Fig. S4

Rietveld fits for ultrasmall particles synthesized for 8 h as (**a)** EMT crystals with isotropic sizes (harmonic development only up to P0), (**b)** EMT crystals with anisotropic shapes (harmonic development up to P1), (**c)** EMT crystals with anisotropic shapes (harmonic development of P0, P1, and P4), (**d)** EMT crystals with anisotropic shapes (harmonic development up to P4), (**e)** FAU crystals with isotropic shapes, (**f)** FAU crystals with anisotropic shape (harmonic development up to P1), (**g)** FAU crystals with anisotropic shape (harmonic development up to P2), and (**h)** FAU crystals with anisotropic shape (harmonic development up to P4).

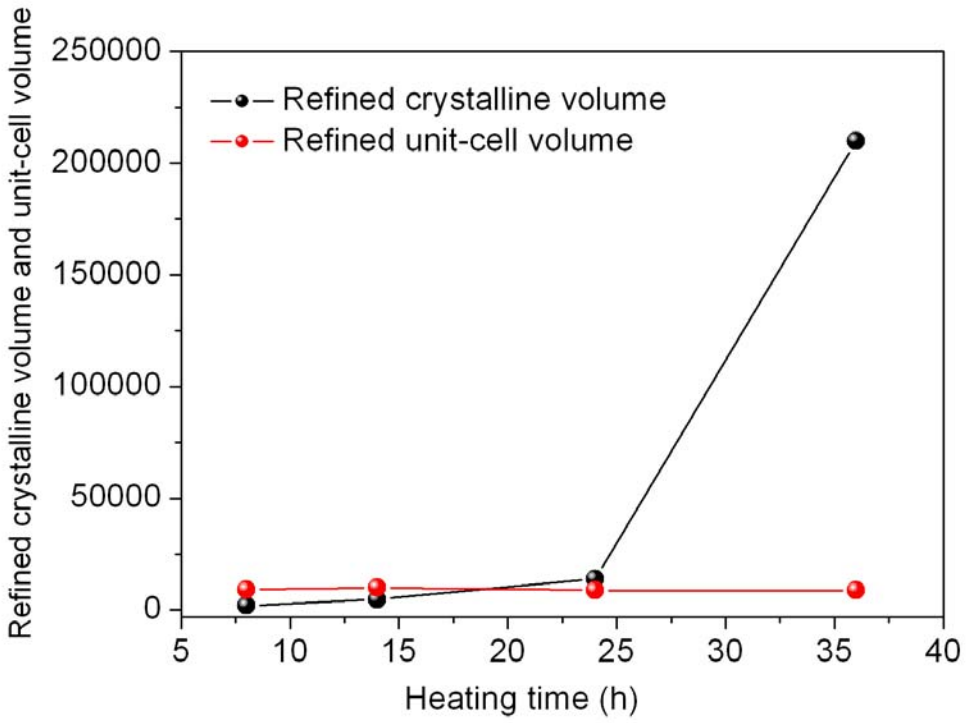


Fig. S5

Comparison between the refined crystallite volume and unit-cell volume for ultrasmall EMT samples prepared for 8, 14, 24 and 36 h at 30 °C in conventional oven.

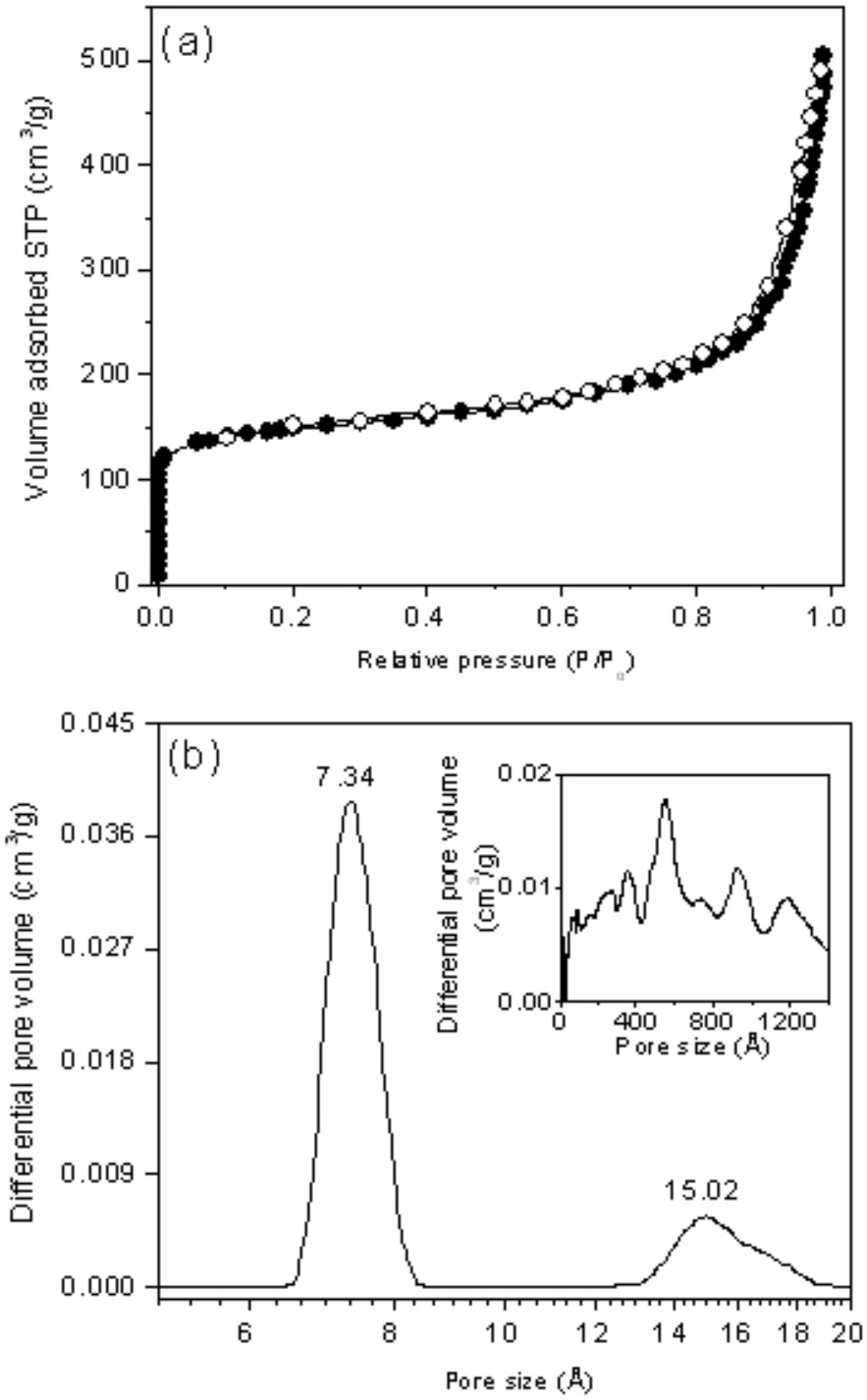


Fig. S6

(a) Nitrogen sorption isotherm, and (b) pore size distribution of ultrasmall EMT crystals synthesized in conventional oven for 36 h at 30 °C.

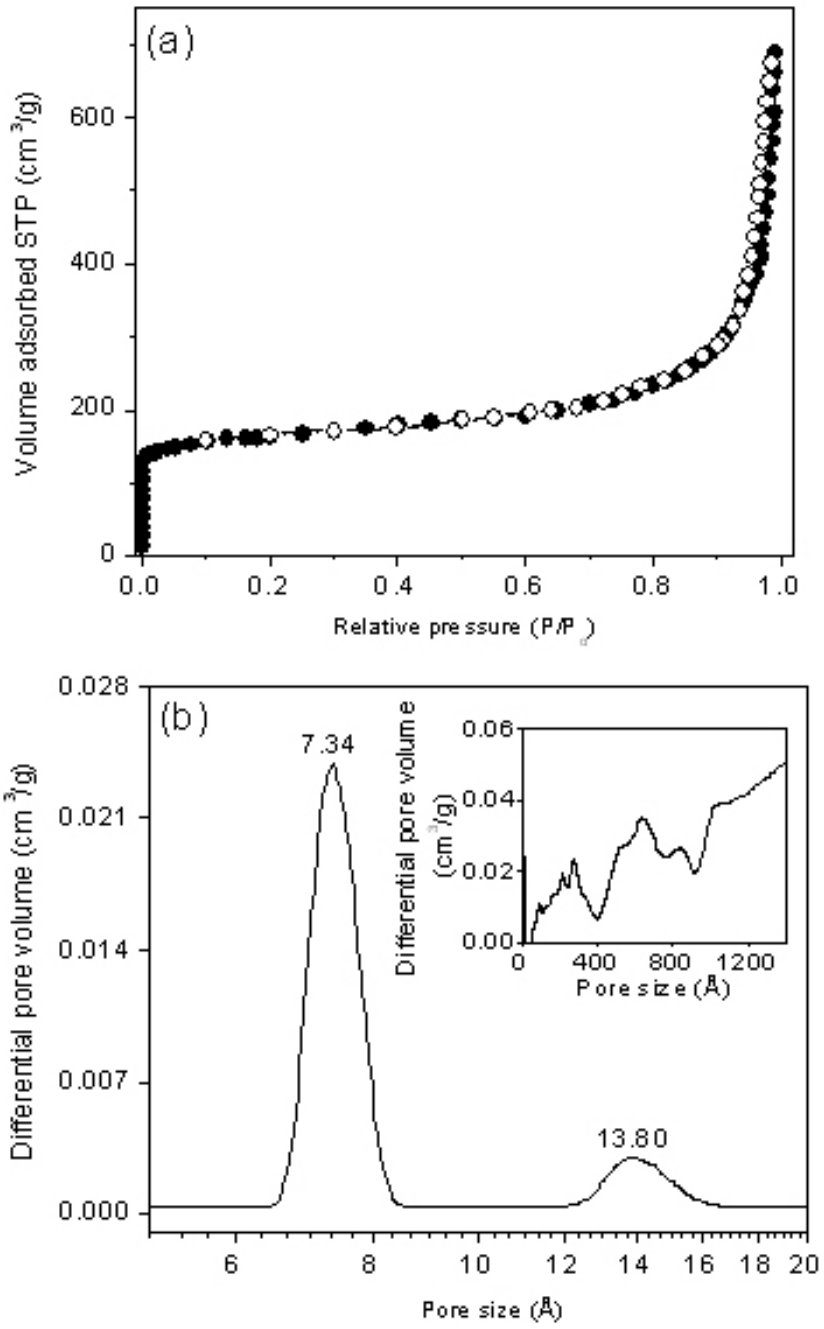


Fig. S7

(a) Nitrogen sorption isotherm and (b) pore size distribution of nanosized EMT crystals synthesized in microwave oven for 4 min at 30 °C.

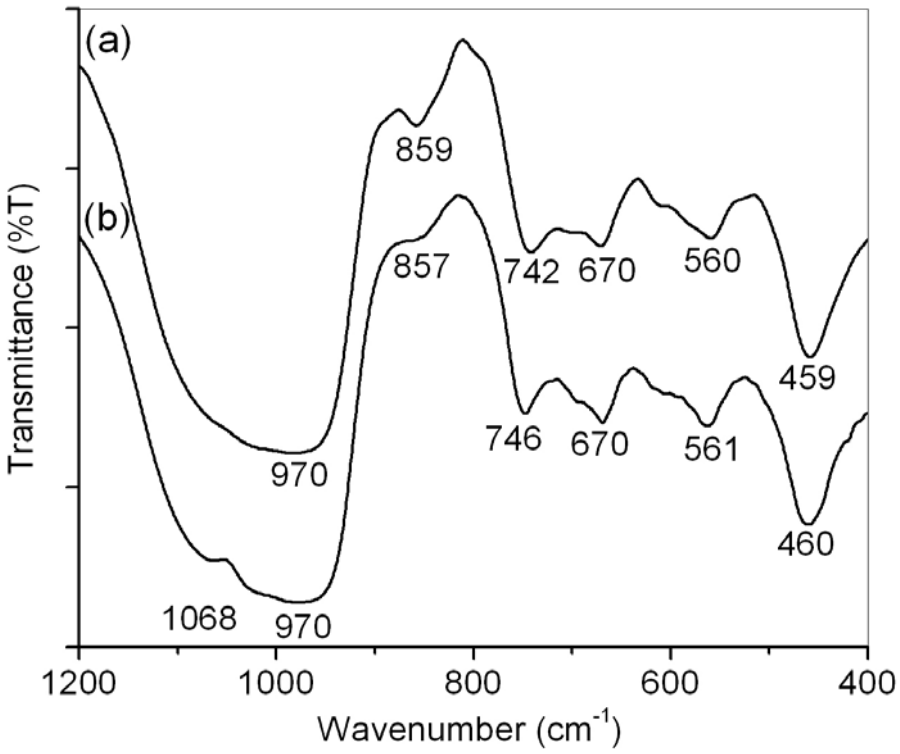


Fig. S8

Infrared spectra of (a) ultrasmall (conventional oven, 30 °C for 36 h), and (b) nanosized EMT (microwave oven, 30 °C for 4 min) crystals.

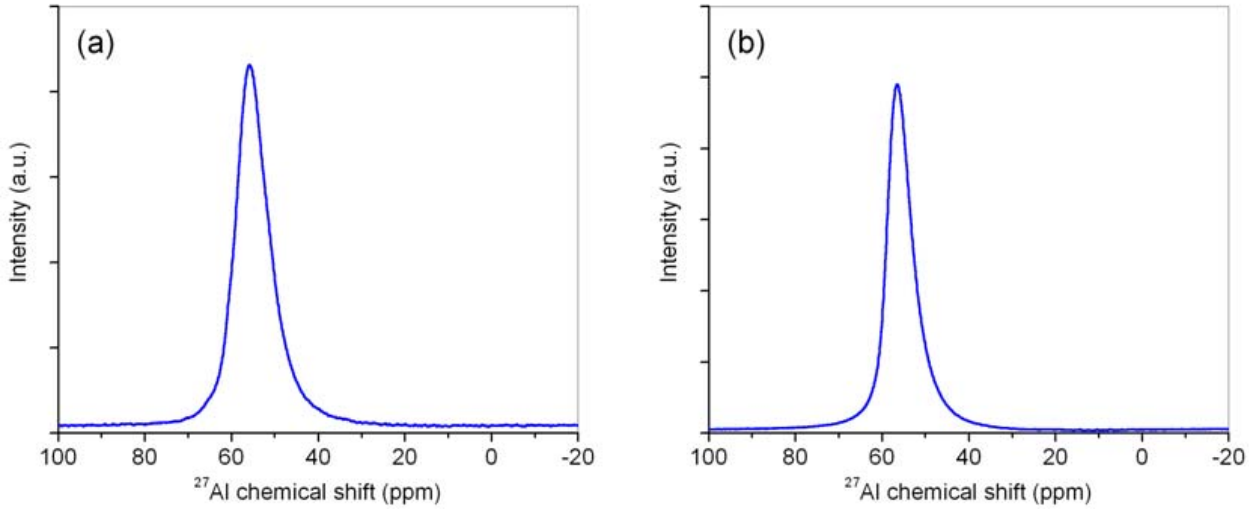


Fig. S9

^{27}Al NMR spectra of (a) ultrasmall (conventional oven, 30 °C for 36 h) and (b) nanosized EMT (microwave oven, 30 °C for 4 min) crystals, revealing the tetrahedral coordination of Al in the EMT-type framework structure.

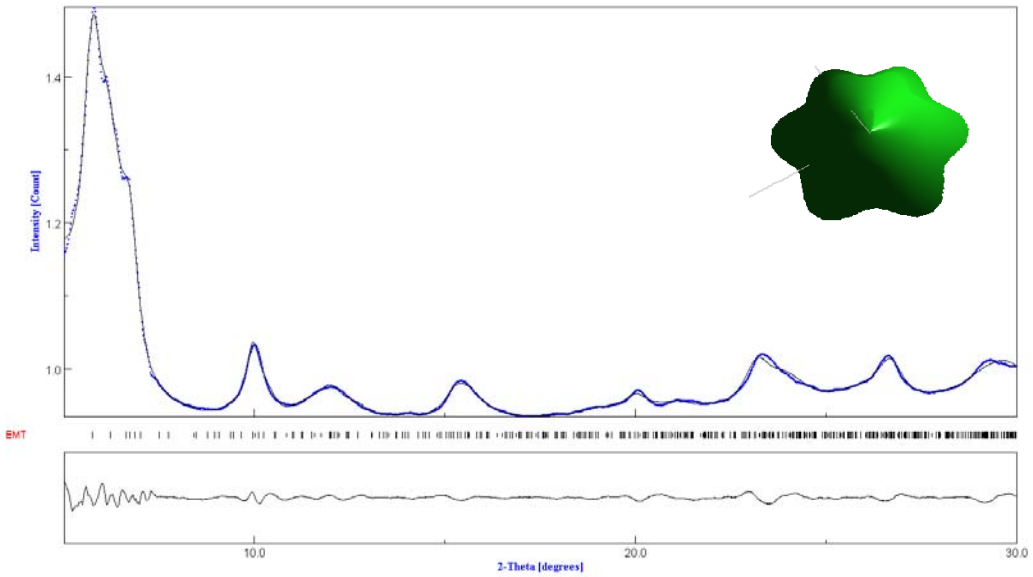
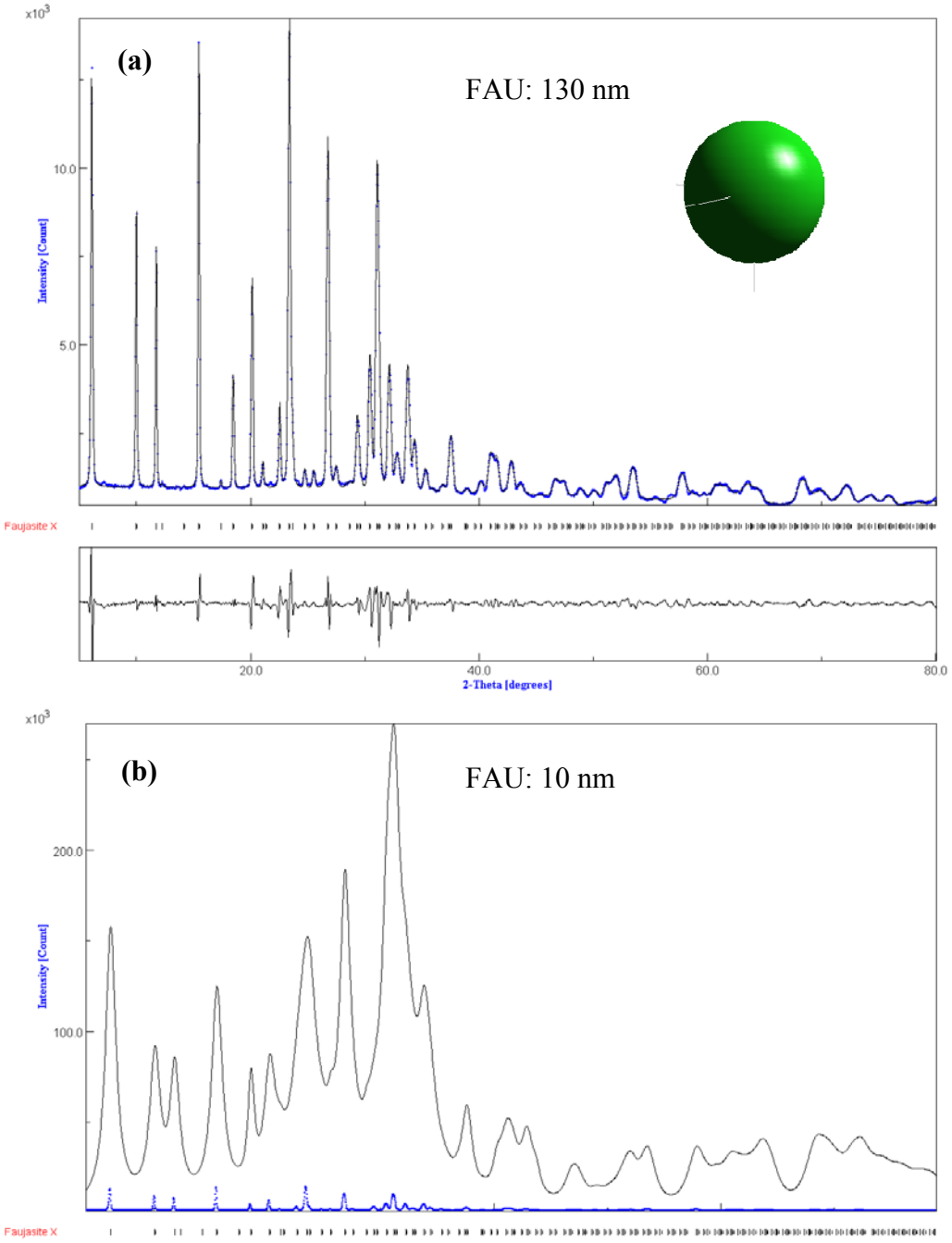


Fig. S10

Rietveld refinement of nanosized EMT crystals synthesized in a microwave oven at 30 °C for 4 min (hexagonal crystals with a size of 55 nm x 10 nm). The X-ray diffractogram was measured using a PANalytical X'Pert Pro diffractometer in Debye-Scherrer geometry with CuK_{α} radiation.


(a)
FAU: 130 nm
x10^3
10.0
5.0
Intensity [Count]
Faujasite X
20.0
40.0
60.0
80.0
2-Theta [degrees]
(b)
FAU: 10 nm
x10^3
200.0
100.0
Intensity [Count]
Faujasite X

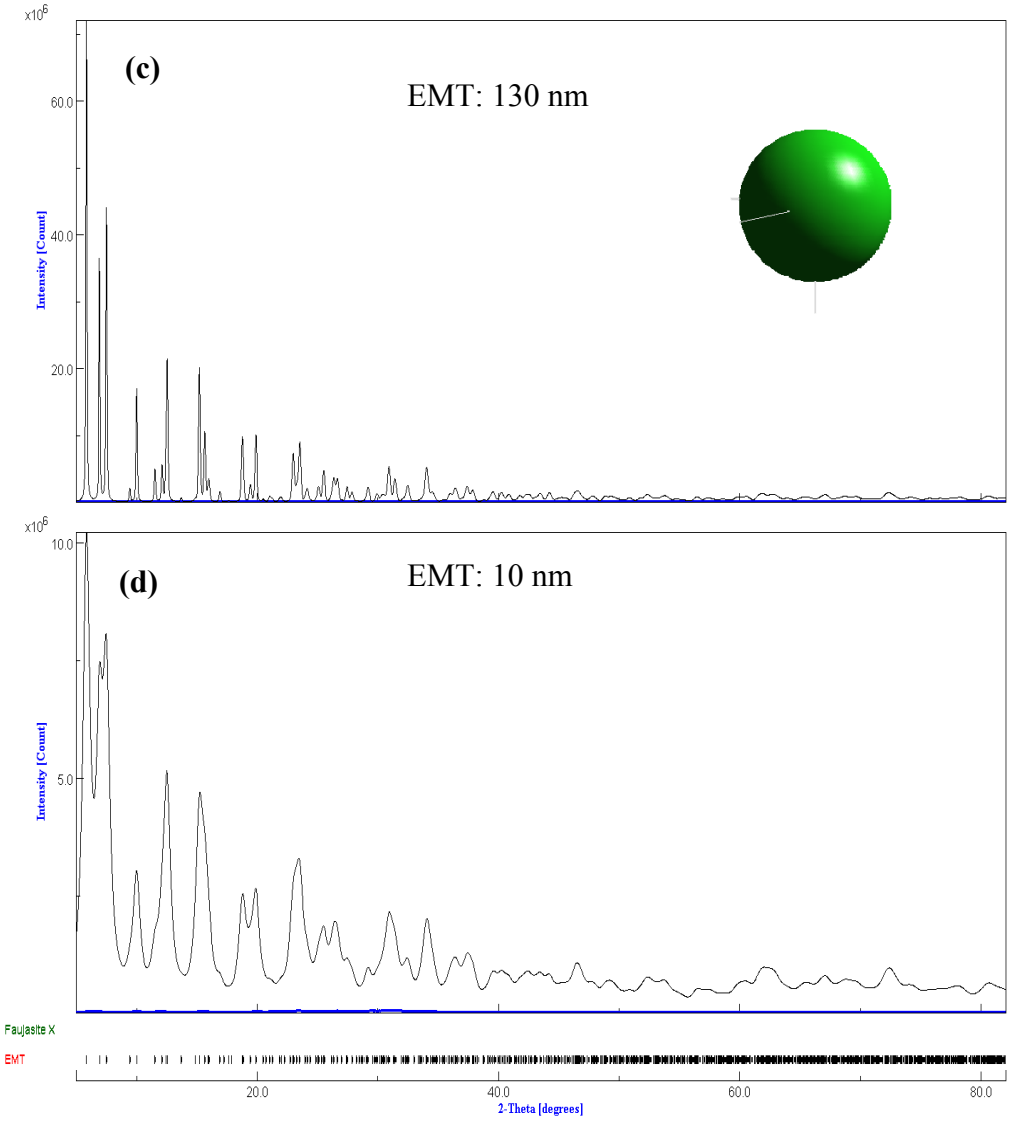
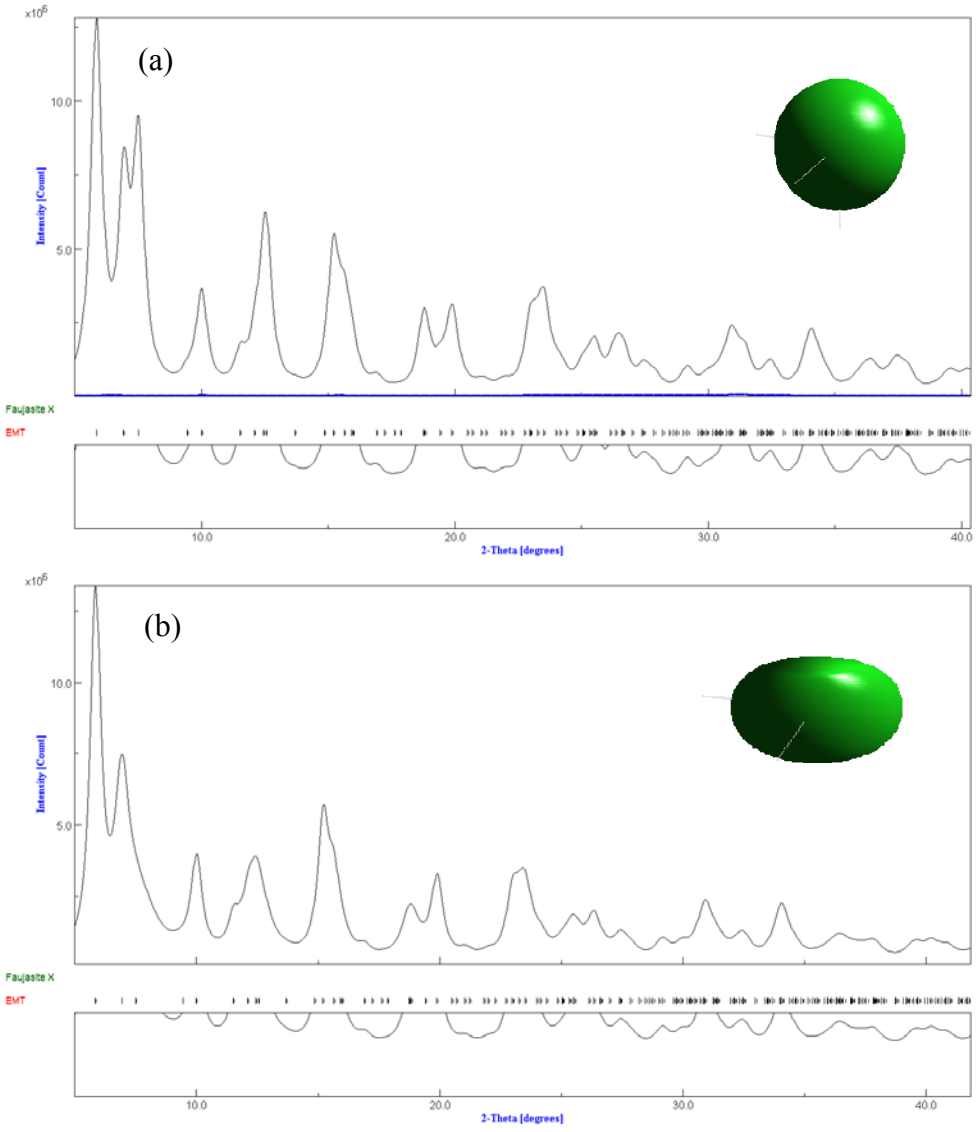


Fig. S11

Rietveld refinement of isotropic crystals of **(a)** FAU with a size of 130 nm, (**b)** simulated pattern of isotropic crystals of FAU with a size of 10 nm, (**c)** simulated pattern of isotropic crystals of EMT with a size of 130 nm, and (**d)** isotropic crystals of EMT with a size of 10 nm.


(a)
x10^6
10.0
5.0
Intensity [Count]
Faujasite X
EMT
10.0
20.0
30.0
40.0
2-Theta [degrees]
(b)
x10^6
10.0
5.0
Intensity [Count]
Faujasite X
EMT
10.0
20.0
30.0
40.0
2-Theta [degrees]

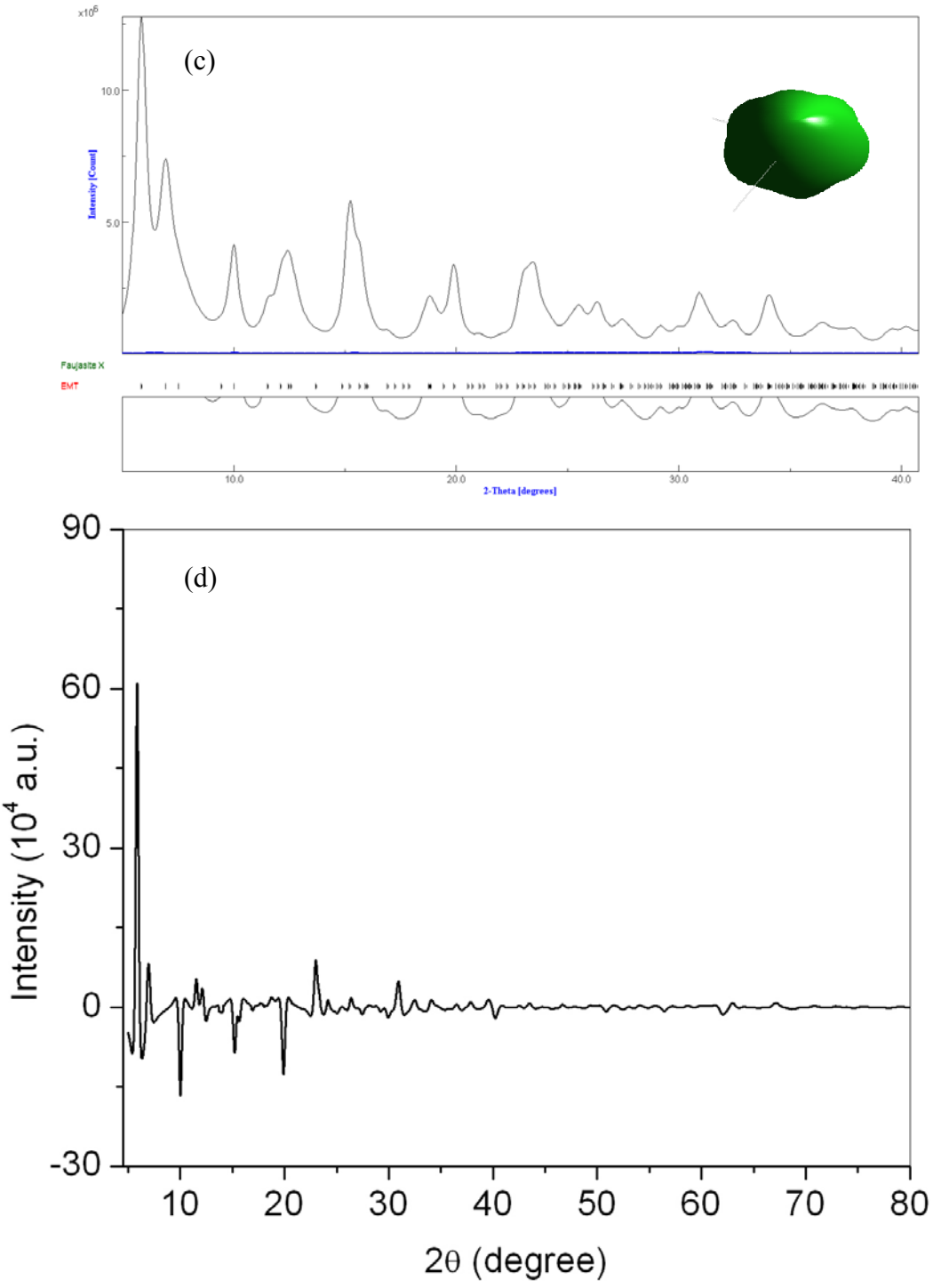


Fig. S12

Simulations of EMT zeolite crystals with different shapes: **(a)** isotropic crystals with a size of 13 nm, (**b)** anisotropic disc-like crystals with a size of 13 nm x 4 nm, (**c)** anisotropic hexagonal platelet crystals with a size of 13.8 nm x 12.4 nm x 4 nm, and **(d)** difference between (b) and (c) curves showing the intensity variations.

Tables

Table S1.
Results from Rietveld fitting of the EMT sample synthesized at 30 °C for 36 h in conventional oven presented in Fig. S3.

Fit	λ^2	Reliability factor R_w (%)	Reliability factor R_{exp} (%)	Unit cell parameter		Composition (%)	
				a (nm)	c (nm)	FAU	EMT
a	7.26	4.95	0.68	2.5037(5)		100	0
b	8.52	5.81	0.68	2.5131(5)		100	0
c	3.51	2.39	0.68	1.7635(2) 2.4931(3)	2.817(2)	50	50
d	2.85	1.94	0.68	1.7625(2) 2.5025(3)	2.826(2)	11(6)*	88(5)*
2d′	**2.44**	**1.51**	**0.68**	**1.7616(1)**	**2.838(2)**	**0**	**100**

2d′ corresponds to the fitting presented in Fig. 2d in the manuscript.

*The phase content is released and the shape of the EMT crystals tend to appear as hexagonal platelets, while the FAU crystals still have an unusual shape.

Table S2.

Results from Rietveld fitting of the EMT sample synthesized for 8 h at 30 °C in conventional oven presented in Fig. S4.

Fit	λ^2	Reliability factor R_w (%)	Reliability factor R_{exp} (%)	Unit cell parameter		Composition (%)	
				a (nm)	c (nm)	FAU	EMT
a	0.81	1.88	2.34	1.809(1)	2.612(2)	0	100
b	0.65	1.53	2.34	1.863(1)	2.519(2)	0	100
c	**0.61**	**1.44**	**2.34**	**1.880(1)**	**2.549(2)**	**0**	**100**
d	**0.63**	**1.47**	**2.34**	**1.869(2)**	**2.548(3)**	**0**	**100**
e	0.74	1.73	2.34	2.357(3)		100	0
f	0.69	1.62	2.34	2.294(2)		100	0
g	0.72	1.68	2.34	2.274(2)		100	0
h	0.65	1.52	2.34	2.282(2)		100	0

Table S3.
Unit cell parameters of the samples extracted from template-free precursor suspensions heated in conventional oven at 30 °C for 8 h, 14 h, 24 h, and 36 h.

Parameter	**8 h**	**14 h**	**24 h**	**36 h**
a (nm)	1.890(4)	1.862(3)	1.7573(2)	1.7616(1)
c (nm)	2.558(9)	2.682(11)	2.8601(7)	2.838(2)
T<100> (nm)	1.5	2.1	5.5	10.0
T<001> (nm)	0.8	1.0	2.0	2.0
T<110> (nm)	1.6	2.3	5.1	15.0

Table S4.

Properties of microporous ultrasmall (conventional oven, 30 °C for 36 h) and nanosized (microwave oven, 30 °C for 4 min) EMT materials.

Sample	S_{BET} (m^2/g)	$S_{External}$ (m^2/g)‡	$V_{Micropore}$ (cm^3/g)‡	V_{Total} (cm^3/g)	H_2O capacity (g/g)*	Mean particle size (nm)†
Ultrasmall EMT	578	266	0.14	0.78	0.74	13
Nanosized EMT	562	208	0.18	0.84	1.03	60

‡ Determined by *t*-plot.

* The water capacity (g H_2O/g sorbent) was determined by TG analysis.

† The particle size was determined by DLS and SEM/TEM techniques.

Table S5.

Lattice parameters for nanosized EMT (conventional oven, 30 °C for 36 h) determined based on the TEM and XRD data.

R_{hkl} (cm)[a]	d_{hkl} (nm)[b]	$2\theta_{TEM}$	$2\theta_{XRD}$[c]	hkl
0.45	0.52	26.9	27.14	410
0.54	0.43	18.5	18.20	213
0.72	0.32	10.3	10.18	110
0.81	0.287	8.2	8.57	102
0.93	0.25	6.3	6.24	002
0.97	0.24	5.8	5.87	100

[a] Distance between the diffraction spot and the beam.

[b] Reticular distance where $d_{hkl} = \alpha.D.\lambda/R_{hkl}$, $\alpha = 0.93$, $D = 1$ m, $\lambda = 2.5\times10^{-12}$ m at 300 kV.

[c] 2θ values of calcined EMT-type zeolite (Si/Al ratio = 3.7) (M. M. J. Treacy, J. B. Higgins, "Collection of Simulated XRD Powder Patterns for Zeolites", 4th revised ed., Amsterdam: Elsevier, 2001).