Electronic Supplementary Information

Fast synthesis of submicron aluminosilicate (low silica/alumina ratio) zeolites under solventless microwave radiation

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Experiment

Materials

$Na_2SiO_3 \cdot 9H_2O$ (SiO_2, ca.20 wt. %, Tianjin Guangfu Chemical Reagent Co., Ltd.), NH_4Cl (Tianjin Fuchen Chemical Reagent Co.Ltd.), pesudoboehmite (Al_2O_3, ca.70 wt.%, H_2O, 30 wt.%, Liaoning hydratight science and technology development Co., Ltd.).

Synthesis

Microwave equipment used in the experiment is a modified household type microwave oven (add a thermal-couple inside the cavity which can monitor the reaction temperature) with a working frequency of 2.45 GHz (Midea MM720KG1-PW) and an output power ranges from 70 to a maximum of 700 W. Particularly wish to point out that this work is in line with my university safety policy on modifying equipment of this time.

Microwave solventless synthesis of MS-NaX.

As a typical run, 3.7-5 g $Na_2SiO_3 \cdot 9H_2O$ was mixed with 0.34 g pesudoboehmite. After grinding for 5 min, followed by adding of 0.3 g NH_4Cl. After grinding for 10 min, the mixture was

transferred to a glass vial and sealed with a rubber stopper with a tiny hole to balance atmospheric pressure in the experiments. Then the glass vial was exposed to the electromagnetic field with the 10 % maximum power (Equivalent to 70 w) for 60 min, the thermal-couple demonstrate that the reaction temperate maintained at 110 ℃ or so. The resulting products were filtered and washed with distilled water and dried at 60°C overnight. The obtained products were designated as MS-NaX-T_{min}, where T stands for crystallization time.

Hydrothermal synthesis of NaX samples.
The conventional NaX samples were hydrothermally synthesized from the aluminosilicate gels with molar ratio of $6.6Na_2O/3.8SiO_2/1Al_2O_3/254H_2O$. As a typical run for the synthesis of NaX, 12g of $Na_2SiO_3 \cdot 9H_2O$ was dissolved in 30mL of H_2O, after stirring for 10 min at room temperature, a solution containing 1.3g of $NaAlO_2$, 1.8g of NaOH, and 13mL of H_2O was introduced into the mixture of preformed sodium silicate solution. After stirring for 30 min, the aluminosilicate gels were transferred into steel-stainless autoclave and crystallized at 100℃ for 5 h, The resulting products were filtered and washed with distilled water and dried at 60°C overnight.

Microwave solventless synthesis of MS-NaA.
As a typical run, 3.2 g $Na_2SiO_3 \cdot 9H_2O$ was mixed with 0.34 g pesudoboehmite. After grinding for 5 min, followed by adding of 0.05 g NH_4Cl. After grinding for 10 min, the mixture was transferred to a glass vial and sealed with a rubber stopper with a tiny hole to balance atmospheric pressure experiments. Then the glass vial was exposed to the electromagnetic field with the 10 % maximum power (Equivalent to 70 w) for 40 min. The resulting products were filtered and washed with water and dried at 60°C overnight. The obtained products were designated as MS-NaA.

Microwave solventless synthesis of MS-SOD.
As a typical run, 2.9 g $Na_2SiO_3 \cdot 9H_2O$ was mixed with 0.34 g pesudoboehmite. After grinding for 10 min, the mixture was transferred to a glass vial and sealed with a rubber stopper with a tiny hole to balance atmospheric pressure experiments. Then the glass vial was exposed to the electromagnetic field with the 10 % maximum powe (Equivalent to 70 w) for 40 min. The resulting products were filtered and washed with water and dried at 60°C overnight. The obtained products were designated as MS-SOD.

Microwave solventless synthesis of MS-NaA/X.
As a typical run, 3.2-3.6 g $Na_2SiO_3 \cdot 9H_2O$ was mixed with 0.34 g pesudoboehmite. After grinding for 5 min, followed by adding of 0-0.34 g NH_4Cl. After grinding for 10 min, the mixture was transferred to a glass vial and sealed with a rubber stopper with a tiny hole to balance atmospheric pressure experiments. Then the glass vial was exposed to the electromagnetic field with the 10 % maximum power fo (Equivalent to 70 w) 40 min. The resulting products were filtered and washed with water and dried at 60°C overnight. The obtained products were designated as MS-NaA/X-M, where T stands for the proportion of NaA.

Characterization

X-ray diffraction (XRD) patterns were measured with a Rigaku D/MAX 2550 diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) images were collected by JEOL electron microscopes (FE-JSM 6700, Japan). The nitrogen isotherms at -196 °C were measured using a Micromeritics ASAP 2020M system. 29Si MAS NMR spectra were recorded on a Varian Infinity Plus 400 spectrometer, and chemical shifts were referenced to tetramethylsilane (TMS). The concentration of Ca^{2+} in the solution was determined by inductively coupled plasma (ICP) with a Perkin-Elemet plasma 40 emission spectrometer.

Calcium ion-exchange rate.

The Ca^{2+} exchange kinetics of zeolite were monitored by sodium ion selective electrodes on a PXSJ-216 (Shanghai Precision & Scientific Instrument Co., Ltd.)

In the exchange procedure, 100 ml of a 0.8 mmol L^{-1} $CaCl_2$ solution was added in a beaker, followed by the addition of 0.06 g of respective hydrated zeolite (dried at 60°C overnight). The concentration of sodium ion in the solution was measured at various time with stirring. The zeolite was removed immediately by centrifugation after reaction at 15 min. The calcium concentration of supernatant determined by inductively coupled plasma (ICP) with a Perkin-Elmer plasma 40 emission spectrometer.

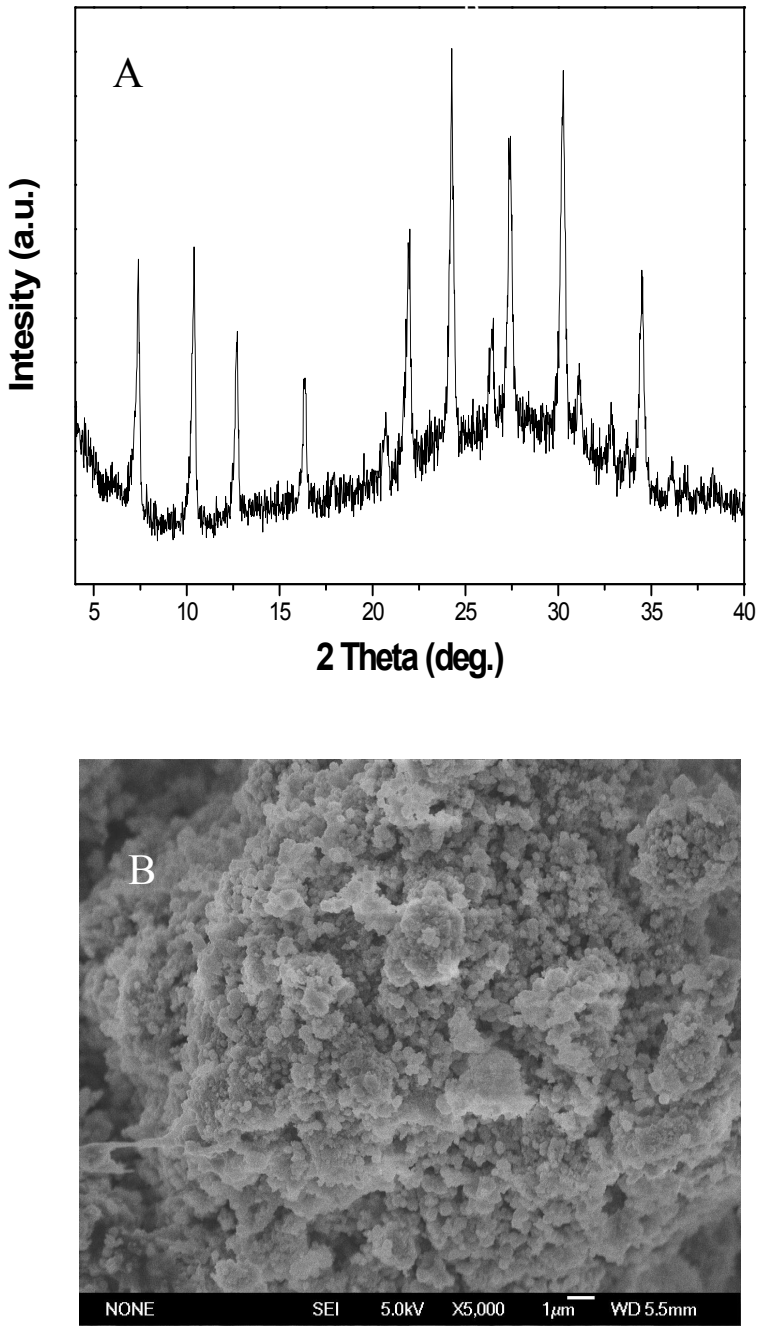


Fig. S1. The XRD pattern (A) and SEM image (B) of the MS-NaA

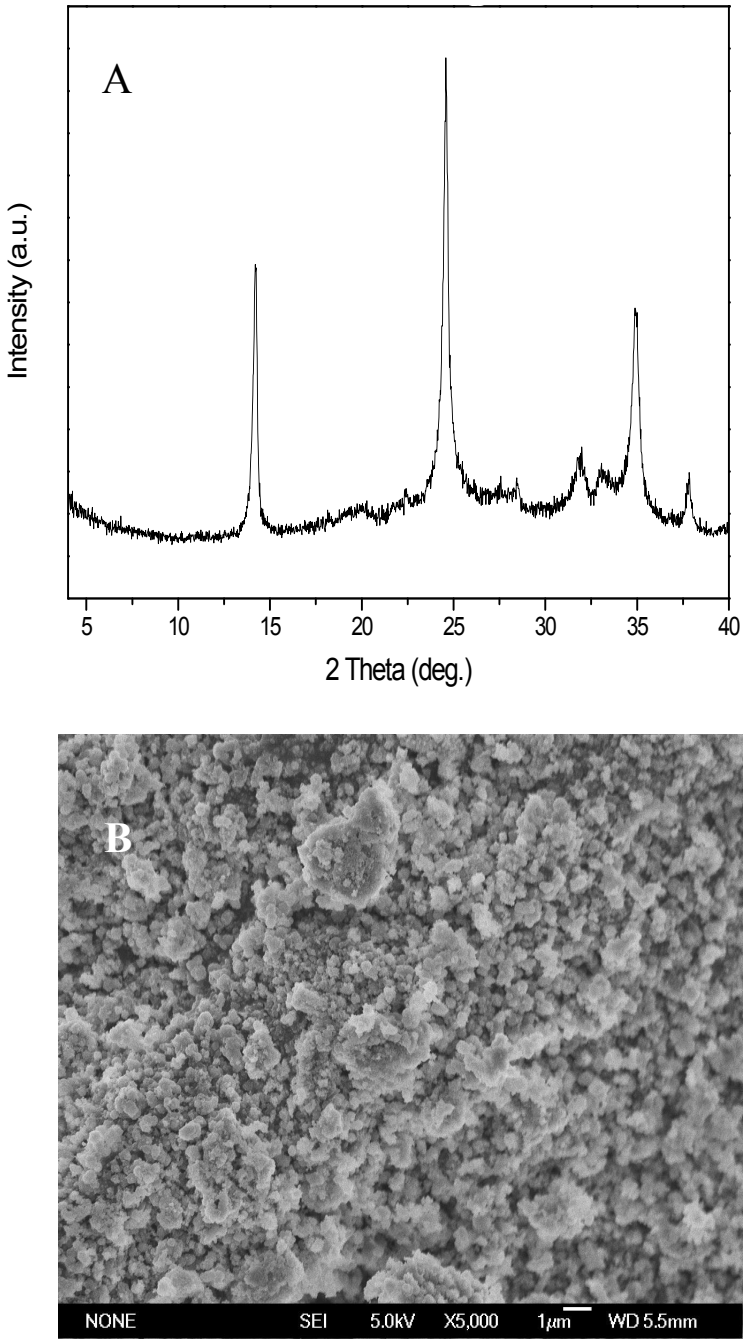
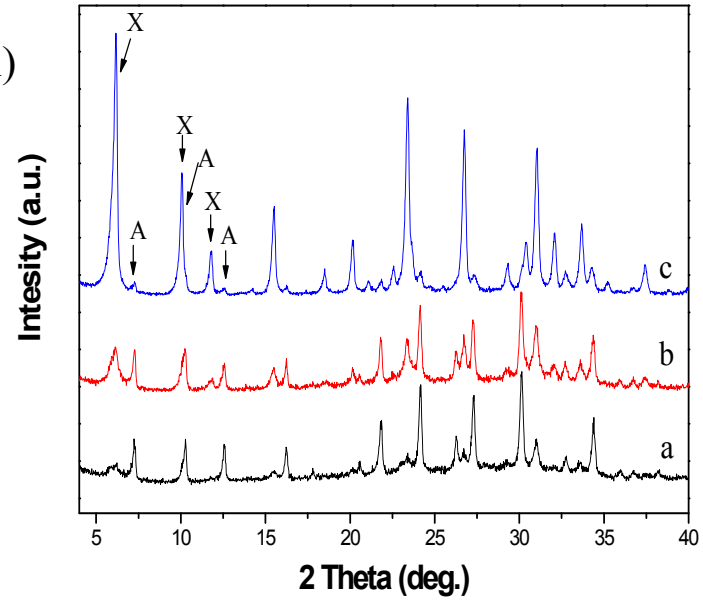
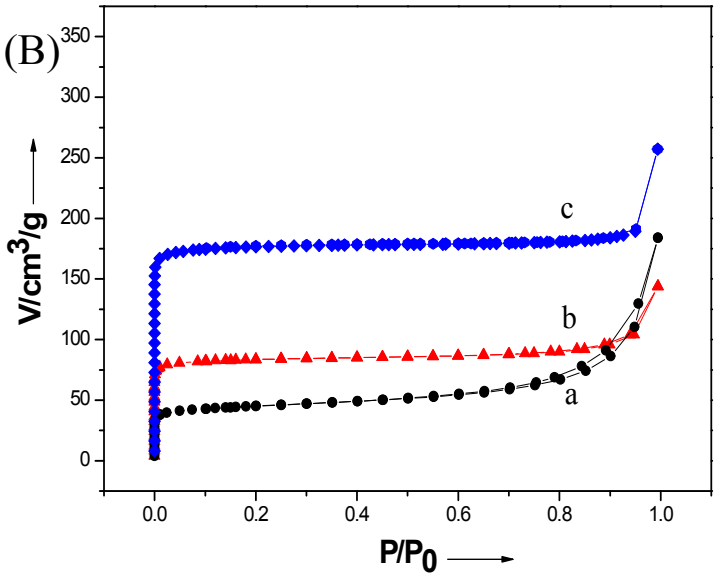


Fig. S2. The XRD pattern (A) and SEM image (B) of the MS-SOD

(A)


X
X
A
X
A
A
c
b
a
Intesity (a.u.)
5
10
15
20
25
30
35
40
2 Theta (deg.)

(B)


350
300
250
200
150
100
50
0
V/cm3/g
c
b
a
0.0
0.2
0.4
0.6
0.8
1.0
P/P0

(c)

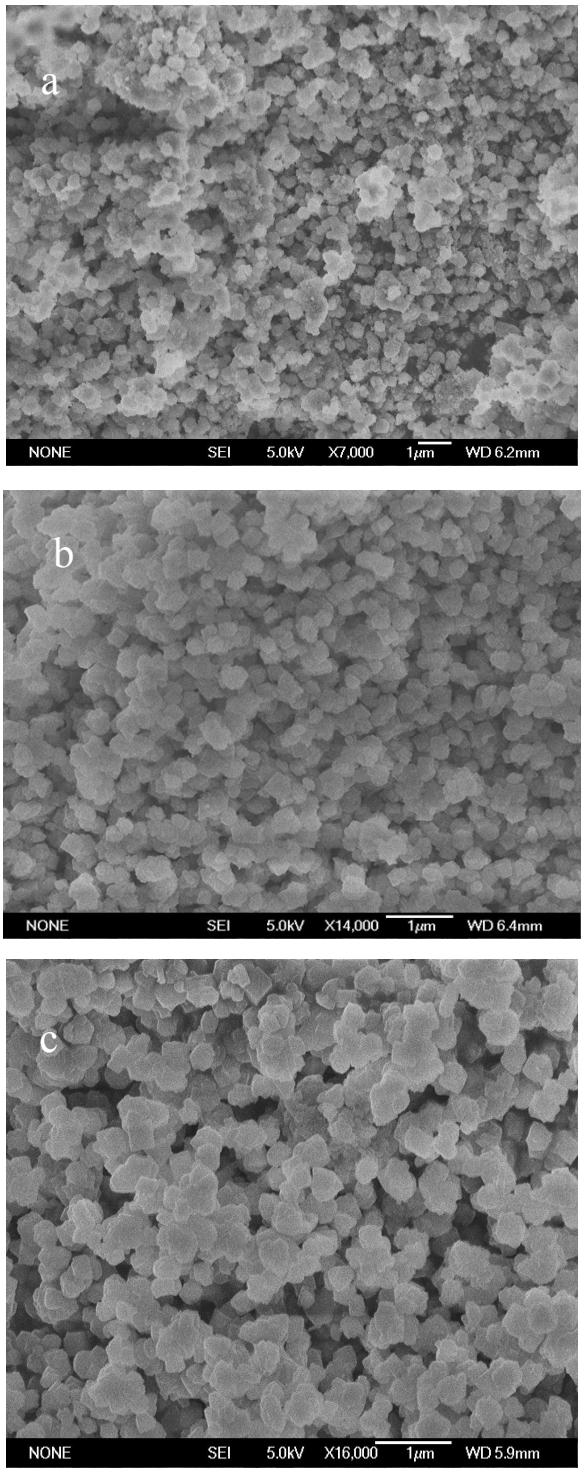


Fig. S3. XRD patterns (A), N_2 sorption curves (B) and SEM images (C) of samples, MS-NaA/X-83 (a), MS-NaA/X-41 (b) and MS-NaA/X-5 (c)

Table S1. Physical characteristics of MS-NaA/X, MS-NaX and NaX zeolites

	$S_{BET}(m^2/g)$	$S_{Mic}^a[m^2/g]$	$S_{ext}^a[m^2/g]$	$V_{total}^b[m^3/g]$	$V_{mic}^a[m^3/g]$
MSA/X-83	152	101	50	0.28	0.05
MSA/X-41	275	246	28	0.22	0.12
MSA/X-5	581	544	37	0.40	0.26
MS-NaX-20_{min}	85	17	68	0.38	0
MS-NaX-45_{min}	283	195	88	0.43	0.11
MS-NaX-60_{min}	542	475	67	0.46	0.22
NaX^C	565	554	11	-	0.27

a V_{total}、S_{ext} and V_{mic} were calculated by applying the t-plot method.

b V_{total} calculated from adsorption branch at (P/P_0=0.99).

c NaX zeolite synthesized from hydrothermal route.

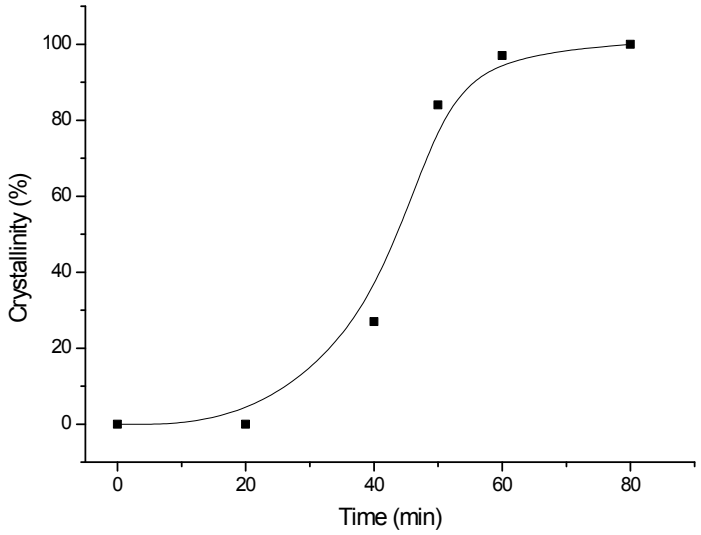


Fig. S4. Crystallization curve

The crystallinity is based on its peak intensity at 23.4° in XRD patterns, and conventional NaX prepared by hydrothermal method was designated as 100 % crystallinity.

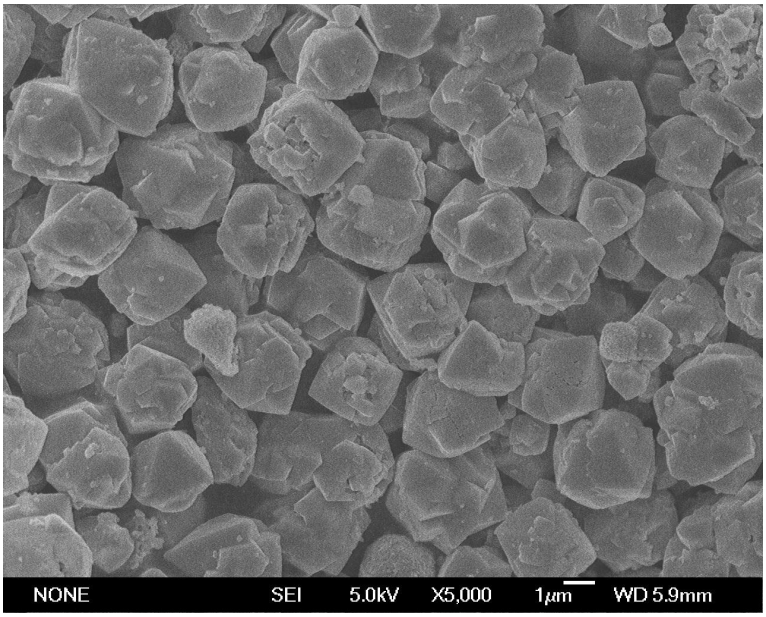


Fig. S5. SEM image of NaX synthesized from hydrothermal route.