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Electronic Supplementary Information

Direct synthesis of three-dimensional MWW zeolite with cyclohexylamine as an organic structure-directing agent

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Experimental Section

1. Zeolite synthesis

MCM-49 zeolite was hydrothermally synthesized using CHA as an OSDA. In a typical synthesis, sodium aluminate solution (16.80 wt% Al_2O_3, 24.17 wt% Na_2O, home-made) was mixed with deionized water to form homogeneous solution. Then silica sol (30.08 wt% SiO_2, 0.39 wt% Na_2O, Qingdao Haiyang Chemical Co., Ltd), sodium hydroxide (96.0%, Sinopharm Chemical Reagent Co., Ltd) or sulfuric acid solution (98%, Jinzhou Chemical Reagent Factory), CHA (99.0%, Sinopharm Chemical Reagent Co., Ltd) were consecutively added to the aforementioned solution under stirring. The final gel was obtained with the following compositions: $1.73Na_2O$: $0.66Al_2O_3$: $20SiO_2$: 4CHA: $280H_2O$. The resultant gel was transferred into a stainless-steel autoclave with Teflon-line. After stirring for 0.5 h at room temperature, the gel was heated for specified time at 140 °C under autogenous pressure while being rotated at 60 rpm. After quenching the autoclave in cold water, the solid was washed with deionized water and separated by centrifugation for several times until the washing liquor was nearly neutral. Then the solid was dispersed in deionized water and dried at 120 °C overnight. A portion of the sample was calcined in air at 540 °C for 4 h.

The reference sample was synthesized using HMI as an OSDA according to the reported patent with slight modification.[1] The batch composition of initial gel mixture was $2.13Na_2O$: $0.91Al_2O_3$: $20SiO_2$: 4HMI: $320H_2O$: $0.10H_2SO_4$. After stirring for 0.5 h at room temperature, the mixture was heated with rotation (60 rpm) at 150 °C for 72 h under autogenous pressure. The obtained sample was designed as MCM-49-HMI.

The calcined samples were exchanged to ammonium form using 1.0 M NH_4NO_3 solution at 80 °C under stirring for 2 h. This process was done for another two times. Then the samples were washed with deionized water and dried, followed by calcining at 520 °C in air for 3 h. The corresponding proton form samples were obtained.

2. Characterizations

The crystallinity and phase purity of the samples were measured by powder X-ray diffraction (XRD) on a PANalytical X’pert PRO diffractometer using Cu-Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA. The chemical compositions of samples were determined on a Philips Magix 601 X-ray fluorescence (XRF) spectrometer. Na_2O/Al_2O_3 molar ratio of products was also performed by an inductively coupled plasma-optical emission spectrometer (ICP-OES 7300DV, PerkinElmer). The crystal morphology and particle size of the zeolites were observed by scanning electron microscope (SEM, Hitachi SU1510) at 15 kV. N_2 adsorption-desorption measurement was carried out at -196 °C on a Micromeritics ASAP-2020 HD88 instrument. Prior to analysis, all the samples were outgassed at 350 °C for 5 h under the vacuum of 10^{-3} Pa. Thermogravimetric analysis (TGA) was carried out with a Pyris Diamond TG/DTA analyser. All the TGA experiments were carried out under air with a flow rate of 60 mL/min in the temperature range from 35 °C to 850 °C at a ramp rate of 10 °C/min. All solid-state MAS NMR experiments were performed on Agilent DD2–500 MHz spectrometer. ^{13}C and ^{27}Al MAS NMR spectra were acquired at 125.7 and 130.2 MHz using a 4 mm MAS NMR probe with a spinning rate of 8 and 12 kHz, respectively. ^{27}Al MAS NMR spectra were accumulated for 400 scans with $\pi/12$ flip angle and 1 s recycle delay. Chemical shifts were referenced to 1M $Al(NO_3)_3$ aqueous solution. ^{27}Al MQ MAS NMR spectra were collected using a three-pulse sequence incorporating a z-filter.

3. Catalytic experiments

Liquid alkylation of benzene with ethylene was carried out in a stainless steel fixed bed reactor at 200 °C and 3.0 MPa. The catalyst (500 mg, 20 ~ 40 mesh) was loaded in the center of the reactor and pretreated at 400 °C in N_2 flow for 1 h. Then the temperature cooled down to 160 °C and benzene was fed in to fill the whole reactor, followed by introducing of ethylene with the weight hourly space velocity (WHSV) of 6 h^{-1} and giving a benzene/ethylene molar ratio of 2. The reaction products were analyzed using a gas chromatograph, equipped with a flame ionization detector (FID) and PONA column.

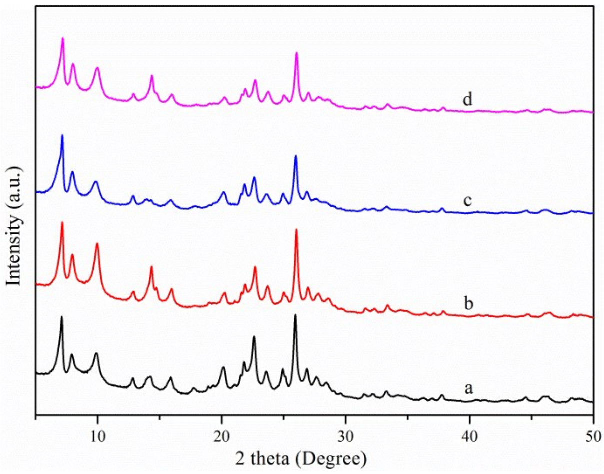

Fig. S1 XRD patterns of S-CHA-1 and MCM-49-HMI: (a) as-synthesized S-CHA-1, (b) calcined S-CHA-1, (c) as-synthesized MCM-49-HMI, and (d) calcined MCM-49-HMI.

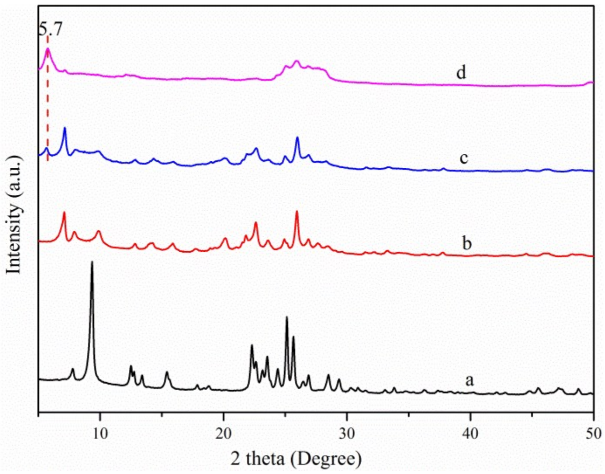

Fig. S2 XRD patterns of samples synthesized using CHA as an OSDA with different SAR for 120 h: (a) 25.0 (S-CHA-2), (b) 30.3 (S-CHA-1), (c) 40.0 (S-CHA-3), and (d) 50.0 (S-CHA-4).

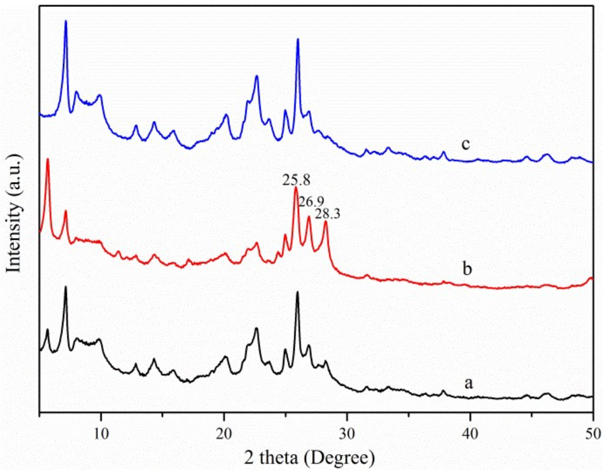

Fig. S3 XRD patterns of samples synthesized using CHA as an OSDA with different SAR for 144 h: (a) 40.0 (S-CHA-5), (b) 50.0 (S-CHA-6), and (c) 40.0 (S-CHA-7, $H_2O/SiO_2 = 20$).

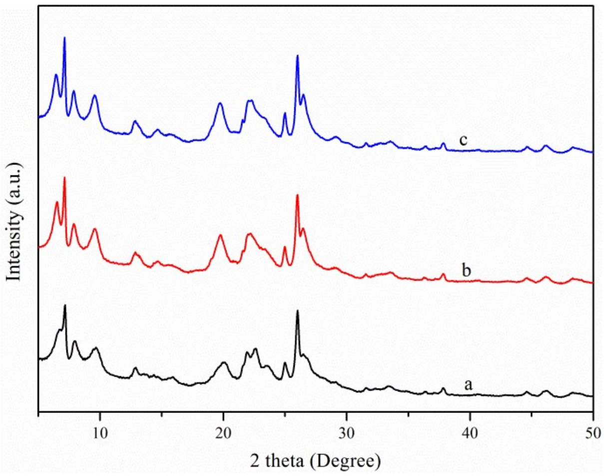

Fig. S4 XRD patterns of samples synthesized using HMI as an OSDA with different SAR: (a) 25.0 (S-HMI-1), (b) 30.3 (S-HMI-2), and (c) 40.0 (S-HMI-3).

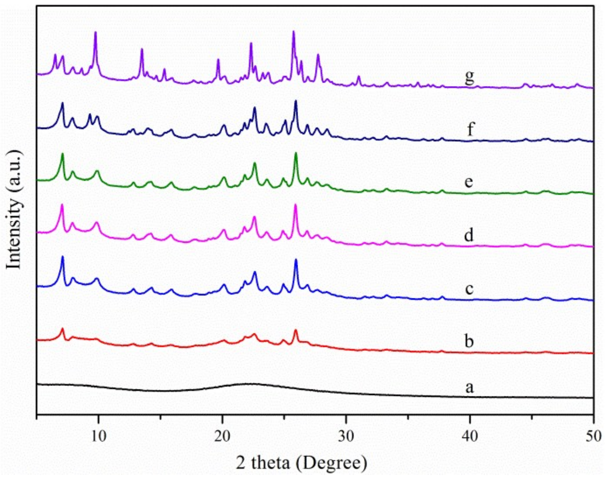

Fig. S5 XRD patterns of samples synthesized with different OH^-/SiO_2 ratios: (a) 0.07 (S-CHA-8), (b) 0.10 (S-CHA-9), (c) 0.12 (S-CHA-10), (d) 0.15 (S-CHA-11), (e) 0.17 (S-CHA-1), (f) 0.20 (S-CHA-12), (g) 0.23 (S-CHA-13).

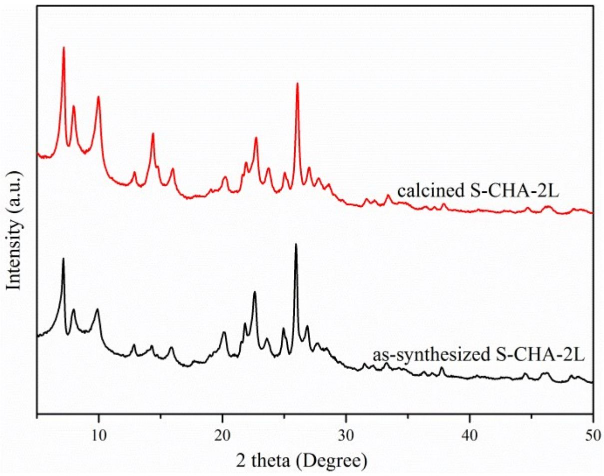

Fig. S6 XRD patterns of as-synthesized and calcined samples using CHA as an OSDA in 2 L scale.

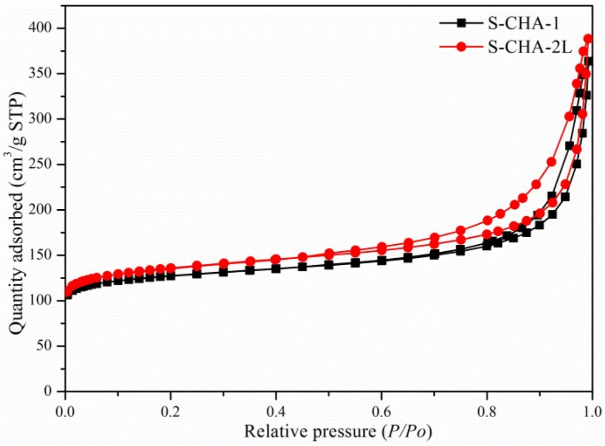

Fig. S7 N_2 adsorption-desorption isotherms of S-CHA-1 and S-CHA-2L.

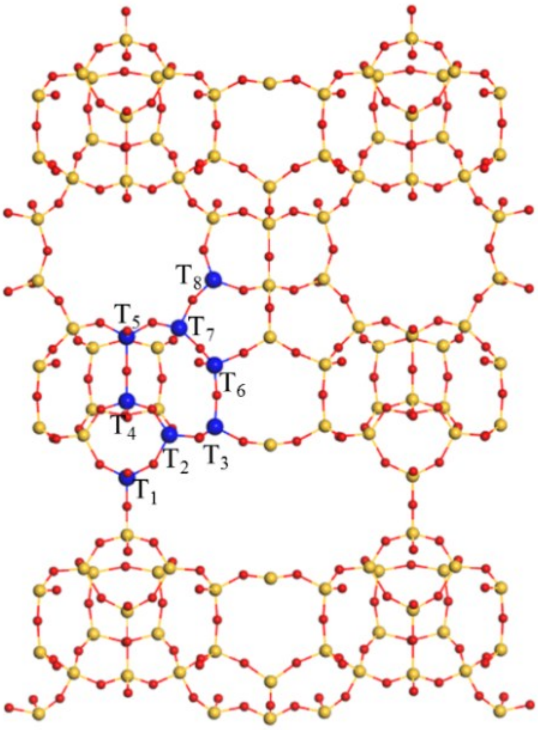

Fig. S8 Eight different T sites in the framework of MWW zeolite.[2]

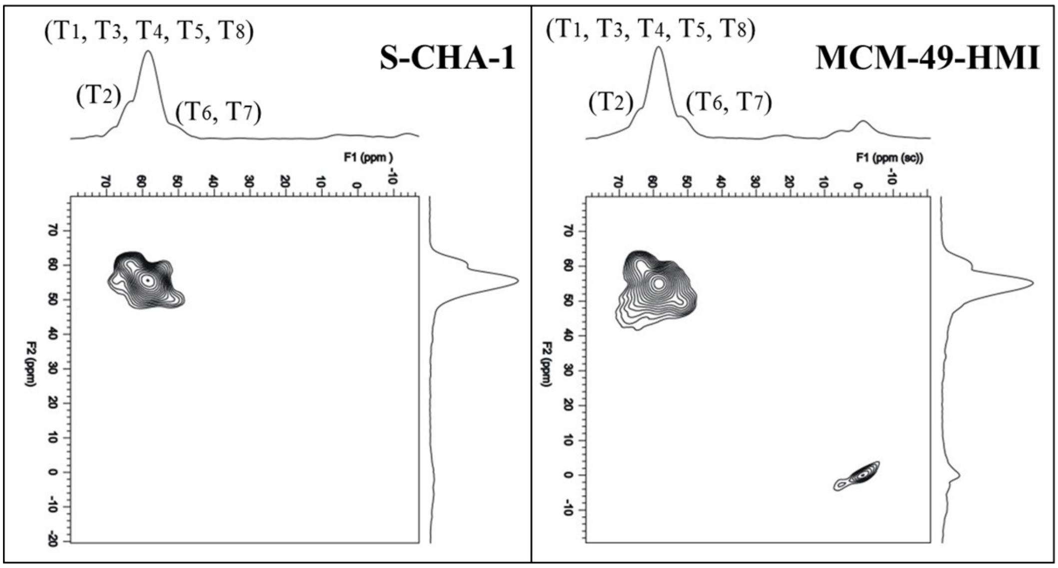

Fig. S9 ^{27}Al MQ MAS NMR spectra of S-CHA-1 and MCM-49-HMI.

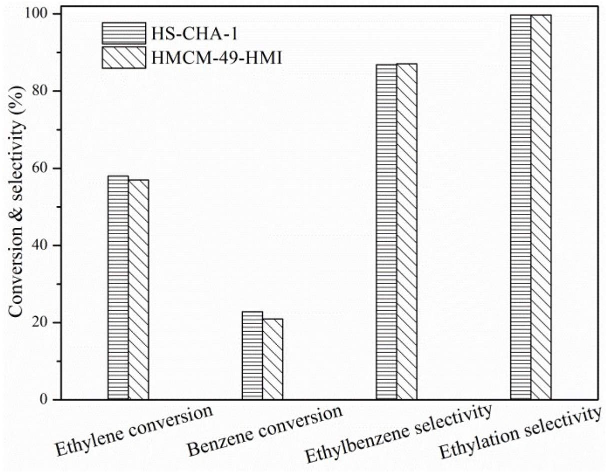

Fig. S10 Catalytic performance of HS-CHA-1 and HMCM-49-HMI in the liquid alkylation of benzene with ethylene reaction with TOS of 48 h.

Table S1 Synthetic parameters and properties of the obtained samples.

Sample	Time (h)	Initial gels			Product			
		OH^-/SiO_2	SiO_2/Al_2O_3	R	Phase	SiO_2/Al_2O_3[a]	Na_2O/Al_2O_3[a]	Na_2O/Al_2O_3[b]
S-CHA-1	120	0.17	30.3	CHA	MCM-49	28.1	0.519	0.532
S-CHA-2	120	0.17	25.0	CHA	FER	22.9	0.329	
S-CHA-3	120	0.17	40.0	CHA	MCM-49 + Mag[e]	50.5	1.768	
S-CHA-4	120	0.17	50.0	CHA	Mag + MCM-49	182.4	10.309	
S-CHA-5	144	0.17	40.0	CHA	MCM-49 + Mag			
S-CHA-6	144	0.17	50.0	CHA	Mag + MCM-49			
S-CHA-7[c]	144	0.17	40.0	CHA	MCM-49	34.6	0.490	
S-CHA-8	120	0.07	30.3	CHA	Am[e]			
S-CHA-9	120	0.10	30.3	CHA	Am + MCM-49			
S-CHA-10	120	0.12	30.3	CHA	MCM-49			
S-CHA-11	120	0.15	30.3	CHA	MCM-49			
S-CHA-12	120	0.20	30.3	CHA	MCM-49 + FER			
S-CHA-13	120	0.23	30.3	CHA	MCM-49 + FER + MOR[e]			
S-HMI-1	120	0.17	25.0	HMI	MCM-22			
S-HMI-2	120	0.17	30.3	HMI	MCM-22	27.0	0.084	
S-HMI-3	120	0.17	40.0	HMI	MCM-22			
MCM-49-HMI[d]	72	0.20	22.0	HMI	MCM-49	19.5	0.161	0.200

[a] The results were obtained by XRF.

[b] The results were obtained by ICP-OES.

[c] The sample was synthesized with molar composition of $3.46OH^-: 0.50Al_2O_3: 20SiO_2: 4CHA: 400H_2O$ under hydrothermal conditions at 140 °C.

[d] The sample was synthesized with molar compositions of $4.06OH^-: 0.91Al_2O_3: 20SiO_2: 4HMI: 320H_2O$ under hydrothermal conditions at 150 °C.

[e] Mag, Am, and MOR represented Magadiite, amorphous phase, and mordenite zeolite, respectively.

Table S2 Textural properties of the obtained samples.

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	S_{ext} (m^2/g)	V_{tot} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
S-CHA-1	489	367	122	0.562	0.144	0.418
MCM-49-HMI	583	426	157	0.680	0.168	0.512
S-CHA-2L	516	368	148	0.601	0.146	0.455
HS-CHA-1	530	390	140	0.618	0.153	0.465
HMCM-49-HMI	560	408	152	0.774	0.161	0.613

Table S3 Weight loss of S-CHA-1 and MCM-49-HMI at different temperature range.

Sample	Weight loss (%)			
	< 180 °C	180 ~ 480 °C	> 480 °C	Total
S-CHA-1	3.3	7.4	4.2	14.9
MCM-49-HMI	3.3	7.2	7.2	17.7

Table S4 Chemical shifts of carbon atom in different samples (in ppm).

Sample	C(1)	C(2)	C(3)	C(4)	C(1')	C(2')	C(3')
S-CHA-1	51.6	32.0	25.1	25.1			
CHA[a]	50.5	37.1	25.3	26.1			
CHA•H^{+}[b]	50.9	32.8	25.0	25.4			
S-CHA-2	53.9	32.5	25.7	25.7			
MCM-49-HMI					48.6, 56.5	26.4	26.4
HMI[c]					48.9	31.0	26.7
HMI•H^{+}[c]					45.6	26.6	24.9

[a] According to the reference.[3]

[b] According to the reference.[4]

[c] According to the reference.[5]

References

1 J. M. Bennett, C. D. Chang, S. L. Lawton, M. E. Leonowicz, D. N. Lissy, M. K. Rubin, C. Chang, S. Lawton, D. Lissy and M. Rubin, US Pat., 5236575, 1993.

2 Y. N. Wang, Y. Gao, S. J. Xie, S. L. Liu, F. C. Chen, W. J. Xin, X. X. Zhu, X. J. Li, N. Jiang and L. Y. Xu, *Catal. Today*, 2018, DOI: 10.1016/j.cattod.2018.02.040

3 G. A. V. Martins and H. O. Pastore, *Micropor. Mesopor. Mater.*, 2008, **116**, 131-140.

4 M. Sánchez-Sánchez, G. Sankar and L. Gómez-Hortiguela, *Micropor. Mesopor. Mater.*, 2008, **114**, 485-494.

5 S. L. Lawton, A. S. Fung, G. J. Kennedy, L. B. Alemany, C. D. Chang, G. H. Hatzikos, D. N. Lissy, M. K. Rubin, H. K. C. Timken, S. Steuernagel and D. E. Woessner, *J. Phys. Chem.*, 1996, **100**, 3788-3798.