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Core-shell Zeolite@Aqueous Miscible Organic-Layered Double Hydroxide

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1. Experimental details

1.1 Materials

HY(5.1) (Si/Al 5.1:1, Alfa Aesar); HY(30) (Si/Al 30:1, Alfa Aesar); ZSM5(23) (Si/Al 5.1:1, Alfa Aesar); ZSM5(30) (Si/Al 30:1, Alfa Aesar); Sodium hydroxide (NaOH, AR, Sigma-Aldrich); Sodium carbonate (Na_2CO_3, AR, Sigma-Aldrich); Magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$, AR, Sigma-Aldrich), Aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$, AR, Sigma-Aldrich). All chemicals and materials were used without purification.

1.2 General synthesis of Zeolite@LDH

Generally, zeolite (100 mg HY(5.1), 200 mg HY(15) and 100 mg ZSM5(23) for HY(5.1)@AMO-LDH, HY(15)@AMO-LDH, ZSM5(23)@AMO-LDH, respectively) was dispersed in DI-H_2O (20 mL) using sonication treatment for 30 minutes. Na_2CO_3 (106 mg) was added to the above solution with 6 minutes sonication to form **solution A**. An aqueous solution (19.2 mL) containing $Mg(NO_3)_2{\cdot}6H_2O$ (0.96 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (0.48 mmol) was added to **solution A** at a rate of 60 mL/h under vigorous stirring. The pH (pH 10) was controlled with the addition of 1 M NaOH by an autotitrator. After stirring for 1 h, the solid was collected from the suspension and then re-dispersed in DI-H_2O (40 mL) and stirred for another hour. After repeat the collection and re-dispersion for another time, the samples (Zeolite@LDH) were finally collected and dried under vacuum. The zeolite@AMO-LDH was synthesized using the same procedure except that the final wet solid was treated with AMOST method,[1] which was washed with acetone (40 mL) and then re-dispersed in acetone (40 mL), and stirred for overnight. The obtained zeolited@AMO-LDH solid is isolated and dried in vacuum oven at room temperature for overnight.

1.3 Analytical techniques

Transmission Electron Microscopy (TEM) images were obtained from a JEOL 2100 microscope with an accelerating voltage of 200 kV. Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive X-ray Spectroscopy (EDX) was also carried out using the JEOL 2100 microscope to discern the relative elemental composition of the sample surface.

Powder X-ray Diffraction (XRD) data were collected on a PANAnalytical X'Pert Pro diffractometer in reflection mode at 40 kV and 40 mA using Cu Kα radiation (α1 = 1.54057 Å, α2 = 1.54433 Å, weighted average = 1.54178 Å).

Fourier Transform Infrared Spectroscopy (FTIR) were obtained using a Thermo Scientific Nicolet iS5 Spectrometer equipped with an iD3 germanium accessory of attenuated total reflection (ATR) mode in the range of 400 – 4000 cm^{-1} with 40 scans at 4 cm^{-1} resolution.

TGA measurements were collected using a Mettler Toledo TGA/DSC 1 system. Around 15 mg of sample was heated in a corundum crucible between 30 and 800 °C at a heating rate of 5 °C/min under flowing nitrogen gas.

Specific surface areas and pore size distribution were analyzed by Micromeritics 3 Flex. The samples were measured for the N_2 adsorption and desorption at 77 K. Before each measurement, the samples were first *in situ* degassed overnight at 300 °C for 6 h.

The ^{27}Al and ^{29}Si Solid state NMR spectra were acquired on a Bruker Avance IIIHD spectrometer using 4.0 mm O.D zirconia rotors and a MAS rate of 15 kHz at 104.2 and 79.4 MHz, respectively (9.4 T). For ^{27}Al NMR spectroscopy, single pulse excitation was applied using a short pulse length (0.23 µs) in order to obtain quantitative MAS spectra. Typically 16000 scans were acquired with a 0.1 s delay. The ^{27}Al NMR spectroscopy chemical shift is referenced to an aqueous solution of $Al(NO_3)_3$ (0 ppm). ^{27}Al MQMAS spectra were acquired using a 3Q–MQMAS sequence with a zero quantum filter at 14 kHz spinning using 1024 points in f2 and 64 increments in f1 with 480 scans per increment. ^{29}Si DPMAS spectra were acquired with a one-pulse sequence and spinal64 proton decoupling. Typically 3000 transients were acquired with a recycle delay of 30 s. All ^{29}Si spectra were externally referenced to kaolinite (taken to be at $\delta = -91.7$ ppm on a scale where $\delta(TMS) = 0$) as a secondary reference.

2. Additional Characterizing Data

2.1 TEM Data

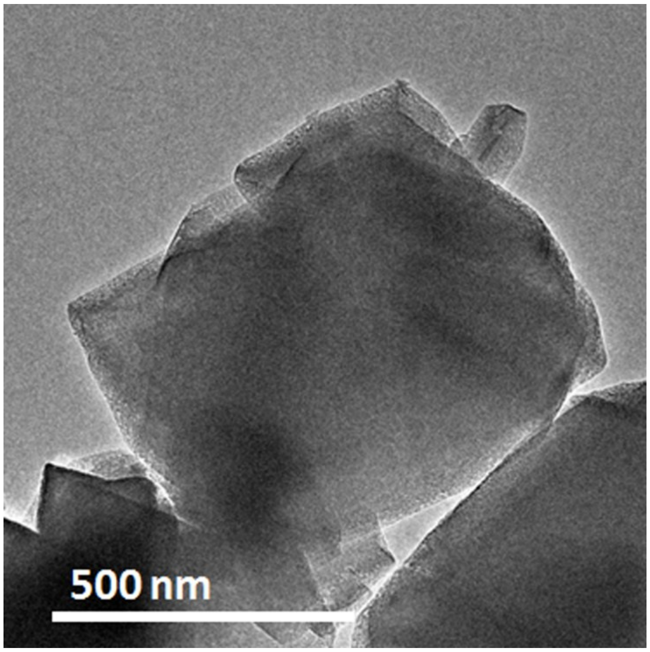

Figure S1. TEM image of HY(5.1).

2.2. XRD Data and Refinements

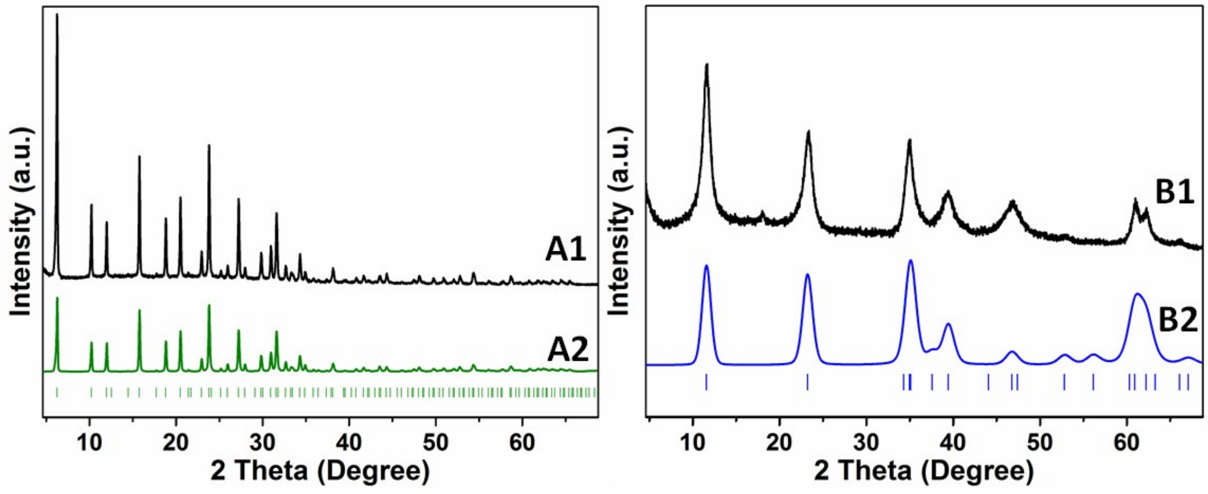

Figure S2. XRD patterns of (A1) parent HY(5.1) and (B1) parent LDH; the extracted individual phases of the two-phase Pawley refinement of the XRD pattern from HY(5.1)@AMO-Mg_2Al-CO_3-LDH: (A2) $HY(5.1)_{calc}$ and (B2) LDH_{calc}.

Table S1. Results of the refinement details for the XRD pattern of HY(5.1)@AMO-Mg_2Al-CO_3-LDH

Component	**Zeolite**	**LDH**
Crystal system	Cubic	Rhombohedral (hexagonal setting)
***a* / Å**	24.547(2)	3.042(7)
***b* / Å**	24.547(2)	3.042(7)
***c* / Å**	24.547(2)	23.03(5)
***α* / °**	90	90
***β* / °**	90	90
***γ* / °**	90	120
***V* / Å^3**	14790(4)	184.6(9)
Space group	$Fd\bar{3}m$	$R\bar{3}m$
***λ* / Å**	1.5418	1.5418
Refinement type	Pawley	
Number of variables	237	
R_p / %	4.41	
wR_p / %	5.67	
R_p' / %	16.01	
wR_p' / %	15.31	
χ^2	1.38	
Software	TOPAS-5 Academic (Coelho Software)	

2.3 FTIR Data

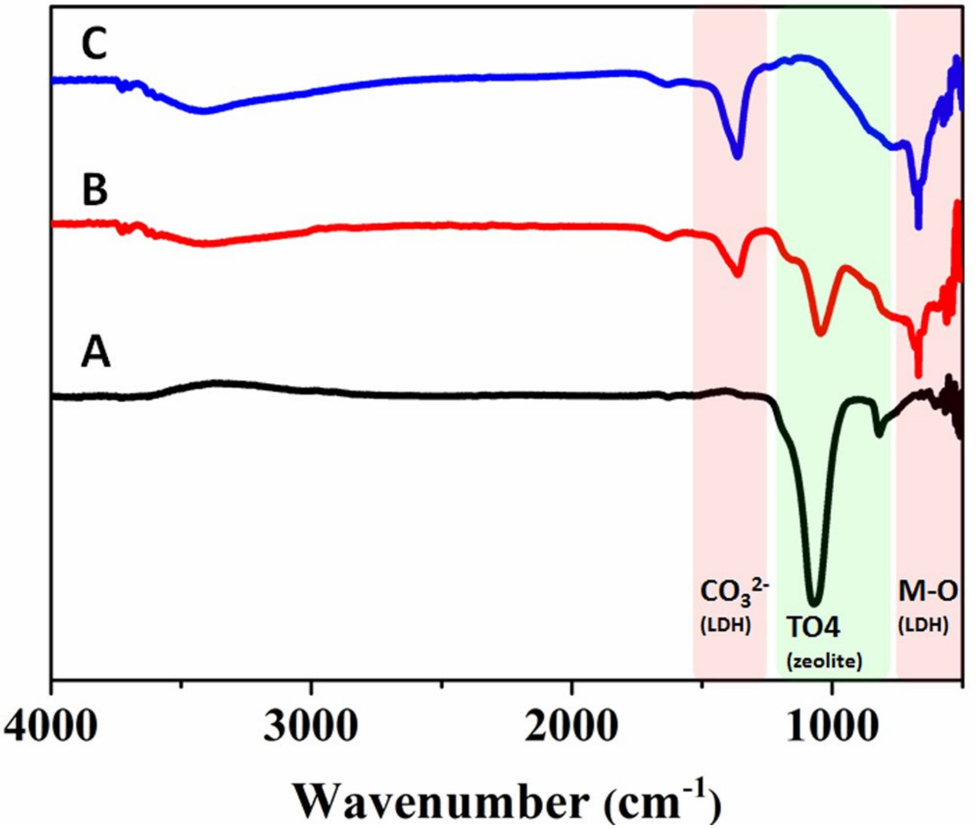

Figure S3. FTIR spectra of (A) HY(5.1), (B) HY(5.1)@ AMO-Mg_2Al-CO_3-LDH and (C) AMO-Mg_2Al-CO_3-LDH.

2.4 TGA Data

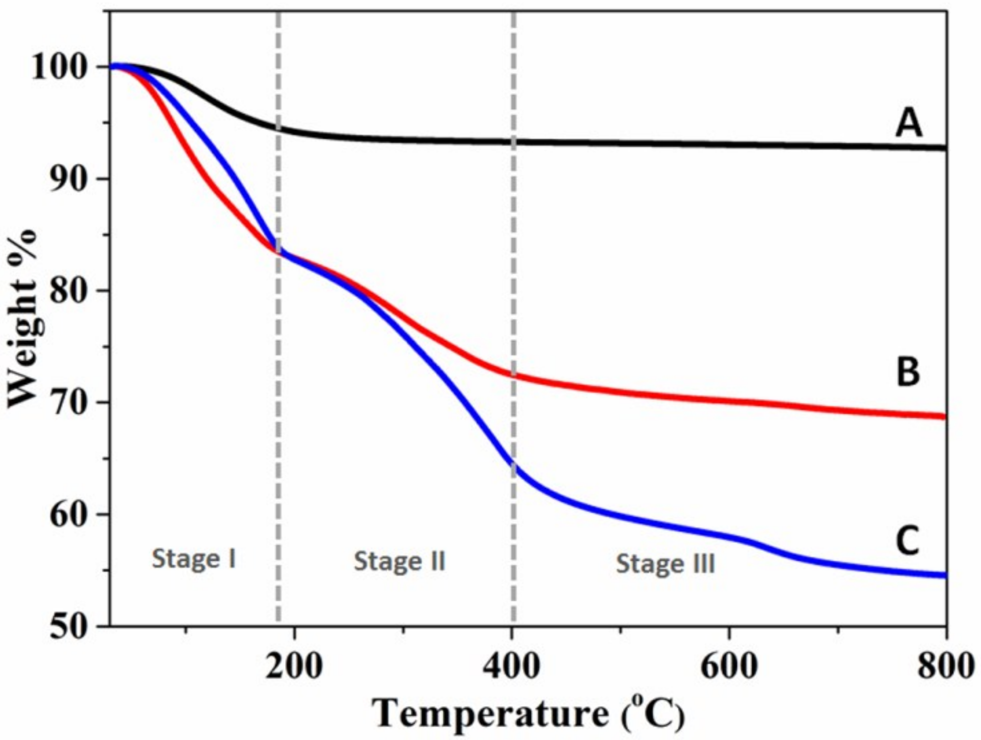

Figure S4. TGA curves of (A) HY(5.1), (B) HY(5.1)@ AMO-Mg_2Al-CO_3-LDH and (C) AMO-Mg_2Al-CO_3-LDH.

2.5. Surface Area Experiments

Table S2. Surface areas of HY(5.1), HY(5.1)@ AMO-Mg_2Al-CO_3-LDH, AMO-Mg_2Al-CO_3-LDH, HY(15), HY(15)@AMO-Mg_2Al-CO_3-LDH, ZSM5(23) and ZSM5(23)@AMO-Mg_2Al-CO_3-LDH.

Materials	**Surface Area (m^2/g)**		
	BET	**External**	**Micropore**
HY(5.1)	695	70	625
HY(5.1)@ AMO-Mg_2Al-CO_3-LDH	698	201	497
HY(5.1)@ Mg_2Al-CO_3-LDH	332	95	236
AMO-Mg_2Al-CO_3-LDH	281	252	29
HY(15)	860	639	221
HY(15)@AMO-Mg_2Al-CO_3-LDH	568	464	104
ZSM5(23)	373	226	147
ZSM5(23)@AMO-Mg_2Al-CO_3-LDH	267	201	66

The surface areas of other type of zeolite@LDH are a bit different from HY(5.1)@LDH though the surface morphologies after hybrid with LDH are quite similar. This is probably due to the different instinct structures of various zeolites, which have different stabilities with regards to the same hybrid process. Modification of hybrid synthesis conditions can help to optimize these properties for each kind of zeolite.

2.6 Solid State NMR experiments

Table S3. Silicon environment in HY(5.1) and HY(5.1)@ AMO-Mg_2Al-CO_3-LDH as determined by ^{29}Si solid state MAS NMR.

Sample	**δ (ppm)**	**Assignment**	**Percentage**
HY(5.1)	−108	Q^4 Si(0Al)	48%
	−103	Q^4 Si(1Al)	42%
	−97	Q^4 Si(2Al)	8%
	−92	Q^4 Si(3Al)	2%
HY(5.1)@AMO-Mg_2Al-CO_3-LDH	−113, −117	Cristobalite Q^4 Si(0Al)	6%
	−108	Q^4 Si(0Al)	41%
	−102	Q^4 Si(1Al)	36%
	−95	Q^4 Si(2Al)	12%
	−90	Q^4 Si(3Al)	5%

Complying with the principle of Loewenstein's rule (assuming no Al-O-Al linkage in the zeolite framework), the Si/Al ratio in the zeolite framework can be obtained from the Si(*x*Al) peak intensity using the following equation:[2, 3]

$$\left(\frac{Si}{Al}\right)_{fw} = \sum_{x=0}^{4} I_{Si(xAl)} \Big/ 0.25\sum_{x=0}^{4} xI_{Si(xAl)}$$

where fw denotes framework, I is the peak intensity of Si(xAl).

2.7 TEM images of various Zeolite@LDH hybrid materials

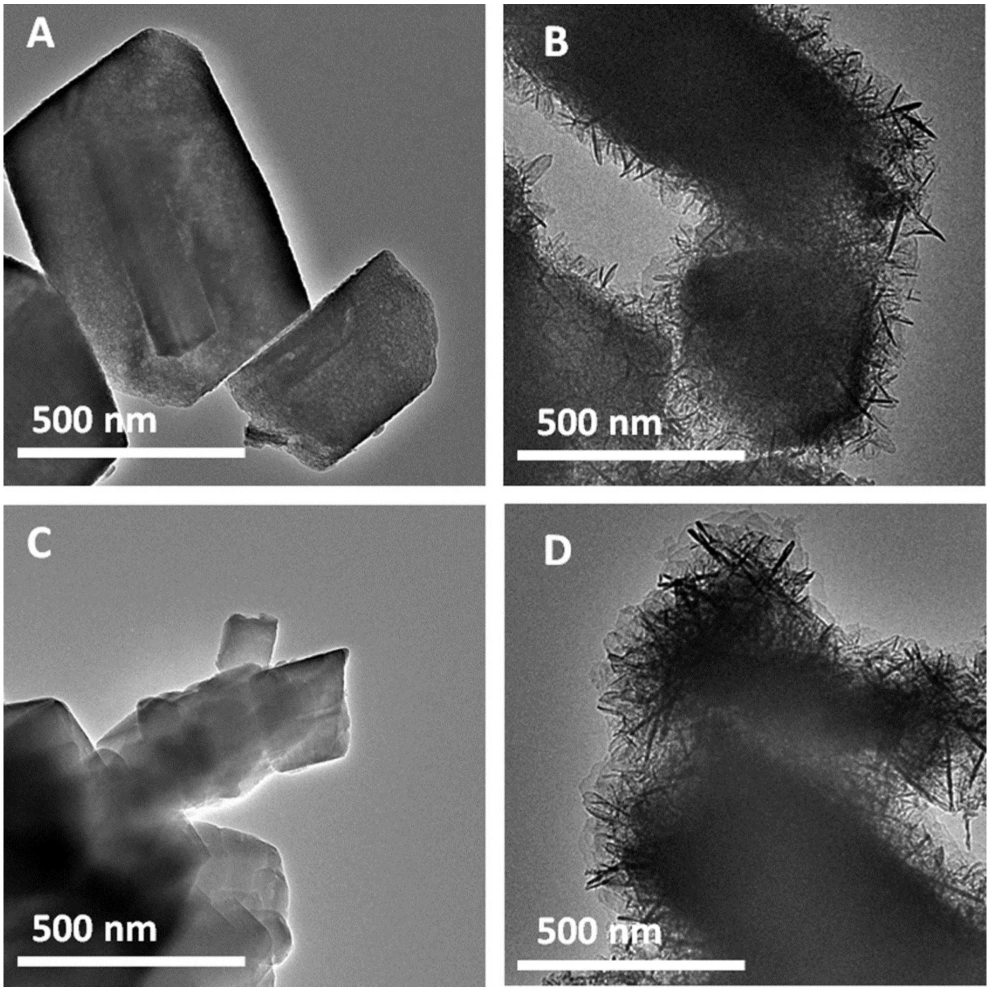

Figure S5. TEM images of (A) HY(15), (B) HY(15)@ AMO-Mg_2Al-CO_3-LDH, (C) ZSM5(23) and (D) ZSM5(23)@ AMO-Mg_2Al-CO_3-LDH (15 and 23 denote the specified Si/Al ratio of HY(15) and ZSM5(23), respectively).

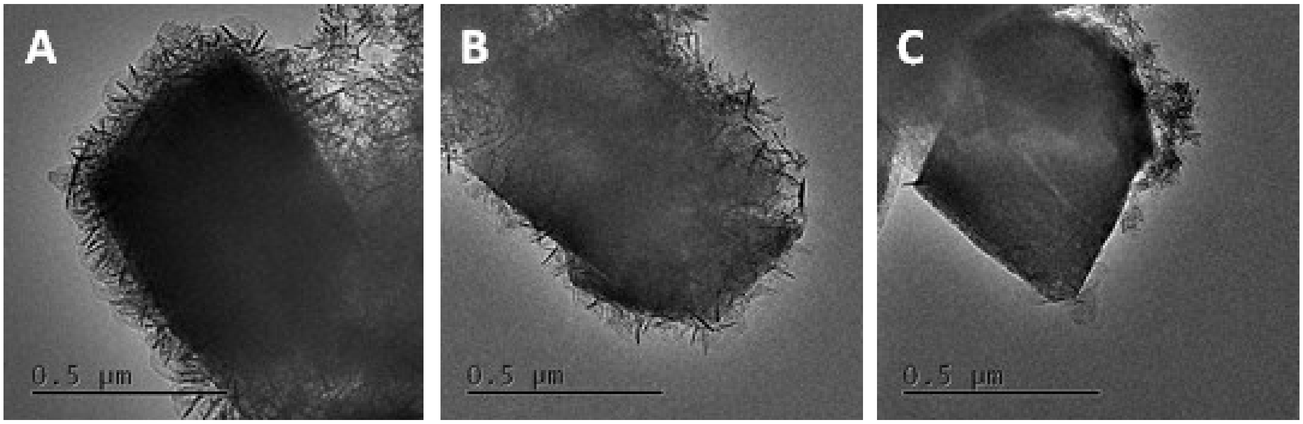

Figure S6. TEM images of (A) HY(5.1)@Mg_2Al-CO_3-LDH, (B) HY(15)@Mg_2Al-CO_3-LDH, and (C) HY(30)@Mg_2Al-CO_3-LDH synthesized using the same conditions. (5.1, 15 and 30 denote the specified Si/Al ratio of HY(5.1), HY(15) and HY(30), respectively.).

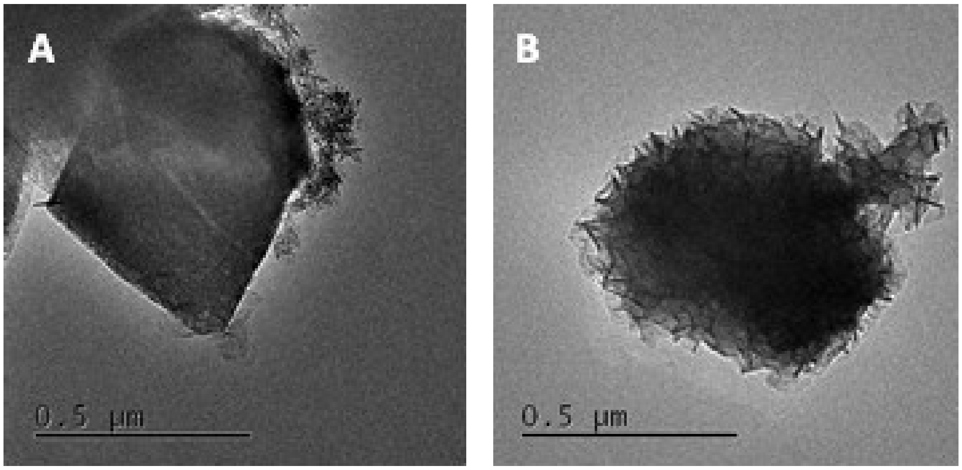

Figure S7. TEM images of HY(30)@Mg_2Al-CO_3-LDH (A) without and with Na_2CO_3 pretreatment. (30 denote the specified Si/Al ratio of HY(30)).

3. References

1. C. Chen, M. Yang, Q. Wang, J.-C. Buffet and D. O'Hare, *J. Mater. Chem. A*, 2014, **2**, 15102-15110.
2. F. Dogan, K. D. Hammond, G. A. Tompsett, H. Huo, W. C. Conner Jr, S. M. Auerbach and C. P. Grey, *J. Am. Chem. Soc.*, 2009, **131**, 11062-11079.
3. G. Engelhardt and D. Michel, *High-resolution solid-state NMR of silicates and zeolites*, John Wiley and Sons, 1987.