Supporting Information

Seed- and Solvent-Free Synthesis of ZSM-5 with Tuneable Si/Al Ratios for Biomass Hydrogenation

Bin Zhang[†,‡,§], Mark Douthwaite[§], Qiang Liu[†], Chao Zhang[†,*], Qifan Wu[†], Ruhui Shi[†], Peixuan Wu[†], Ke Liu[†], Zhuangqing Wang[†], Weiwei Lin[†], Haiyang Cheng[†], Ding Ma[‡], Fengyu Zhao[†], Graham J. Hutchings[§,*]

† State Key Laboratory of Electroanalytical Chemistry and Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

‡ Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering and College of Engineering, and BIC-ESAT, Peking University, Beijing 100871, China.

§ Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, CF10 3AT, UK

Corresponding Author

E-mail: czhang@ciac.ac.cn; hutch@cardiff.ac.uk

Content

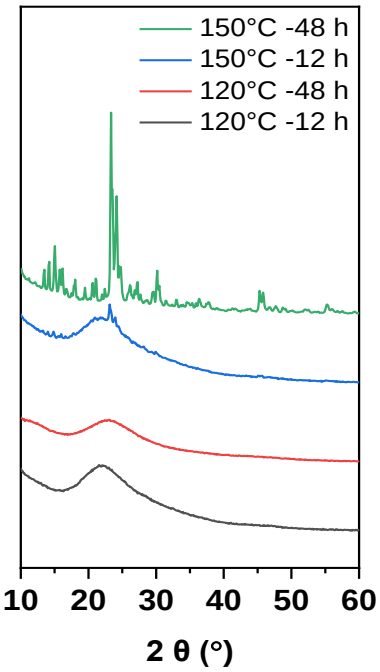

Figure S1. XRD patterns of MFI zeolites from SiO_2 and $C_{12}H_{28}NF$ at 120 °C (or 150 °C) for 12 h and 48 h of crystallization, respectively.

Sample	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1}) [a]	Average pore diameter (nm)
silicalite-1	212	0.31	4.4
commercial ZSM-5	256	0.12	3.7

[a] BJH mesopore volumes from the desorption isotherm.

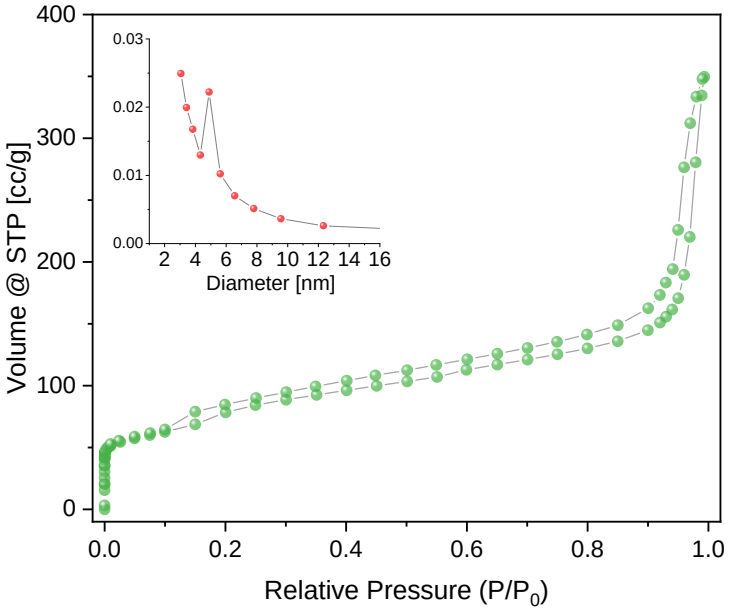

Figure S2. The physical structure properties of the obtained MFI zeolite.

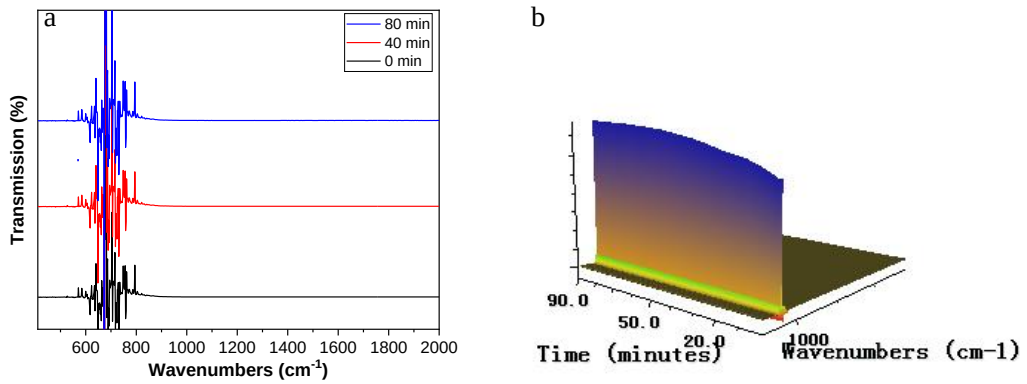

Figure S3. (a) 1D, (b) 3D DRIFT spectra of monocomponent SiO_2 in an in-situ cell as a function of time at the rate of 4℃/min from 20 ℃ (0 min) to 180 ℃ (40 min) and then keep at 180℃ until 80 min.

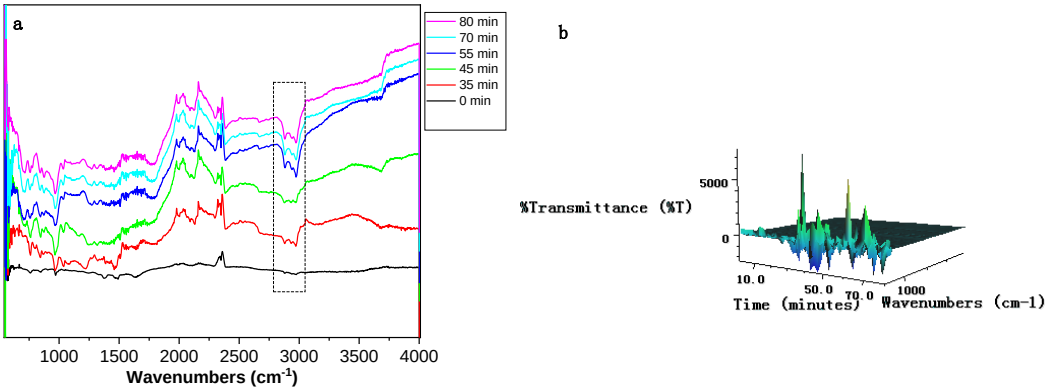

Figure S4. (a) 1D, (b) 3D DRIFT spectra of monocomponent $C_{12}H_{28}NF$ in an in-situ cell as a function of time at the rate of 4℃/min from 20 ℃ to 180 ℃ and then keep at 180 ℃ until 80 min.

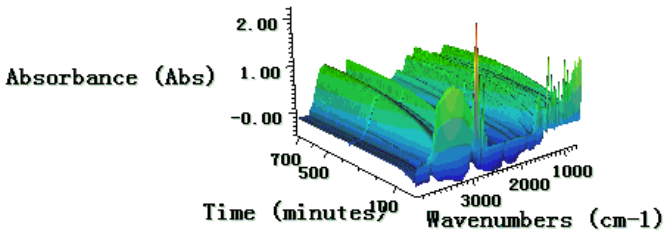

Figure S5. In-situ 3D DRIFT spectra of MFI zeolite sample from SiO_2 and $C_{12}H_{28}NF$ in an in-situ cell as a function of time from 20 ℃ at the rate of 4℃/min to 180 ℃ and keep at 180 ℃ until 720 min.

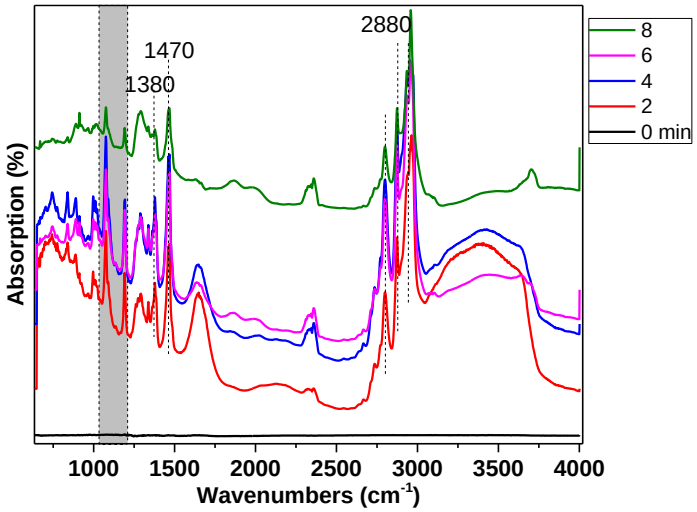

Figure S6. DRIFT spectra (950 — 4000 cm^{-1}) of MFI zeolite sample from SiO_2 and $C_{12}H_{28}NF$ in an in-situ cell during the heating-up period of the initial 10 minutes from 20°C (0 min) at the rate of 4°C/min.

Table S1. The attribution of DRIFT spectra (300 — 1250 cm^{-1}) of MFI zeolite.

Types	External linking vibration			Internal tetrahedral vibration					
μ/cm^{-1}	300-420	420-500	500-650	symmetric stretch			asymmetric stretch		
				650-750	750-820	820-950	950-1050	1050-1150	1150-1250
Assignment	aperture	δ(T-O)	Double Penta ring	$\nu_s(TO_4)$	ν_s(T-O)	$\nu_s(TO_4)$	$\nu_{as}(TO_4)$	ν_{as}(T-O)	$\nu_{as}(TO_4)$

Table S1 summarizes the vibration attribution of DRIFT spectra (300 — 1250 cm^{-1}) of MFI zeolite. In general, these vibrations can be divided into two categories: internal tetrahedral vibration and external linking vibration, at 650 — 1250 cm^{-1} and 300 — 650 cm^{-1}, respectively. The specific vibratory variations of the samples during the crystallization for 12 h at 900 — 1250 cm^{-1} are showed in Figure S7.

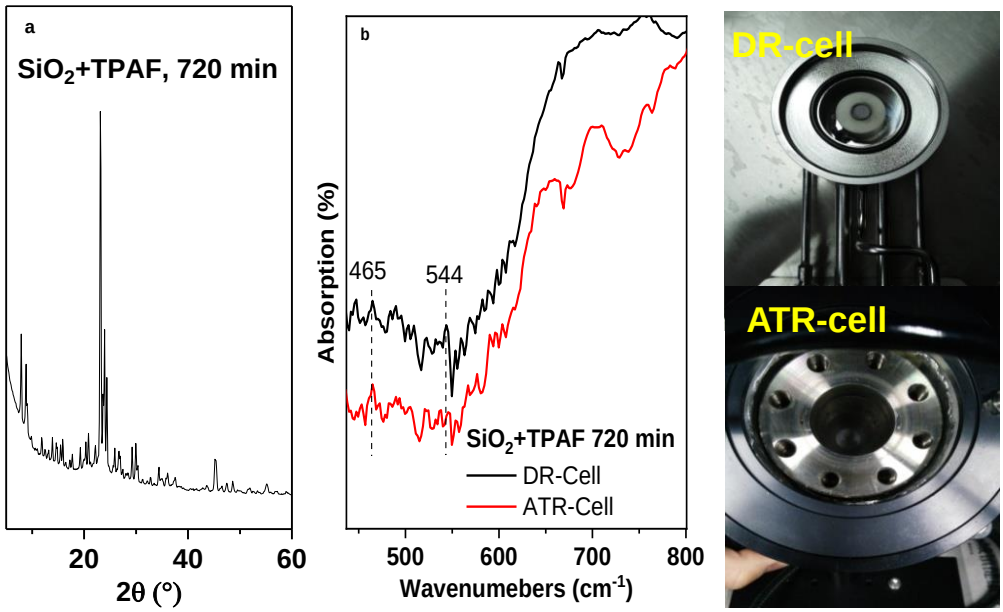

Figure S7. (a) XRD patterns, (b) ATR-FTIR spectra and DRIFT spectra (450 — 800 cm^{-1}) of zeolite samples from SiO_2 and $C_{12}H_{28}NF$ in different cells at 180°C after 12 h.

We conducted the crystallization process in both DRIFT cell and ATR autoclaves, both of the obtained products crystallized for 12 h at 180 °C shows typical characteristic peaks of double penta-rings of MFI zeolite, 465 and 544 cm^{-1}.

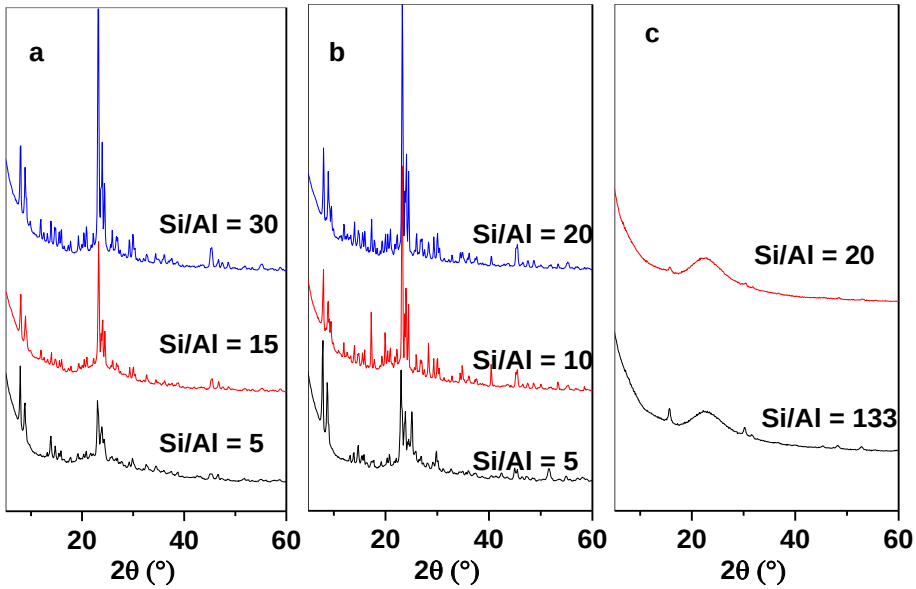

Figure S8. XRD patterns of ZSM-5 zeolite derived from (a) $(C_3H_7O)_3Al$ (b) $(NH_4)_3AlF_6$, and (c) $AlCl_3 \cdot 6H_2O$ at 180℃ for 48 h.

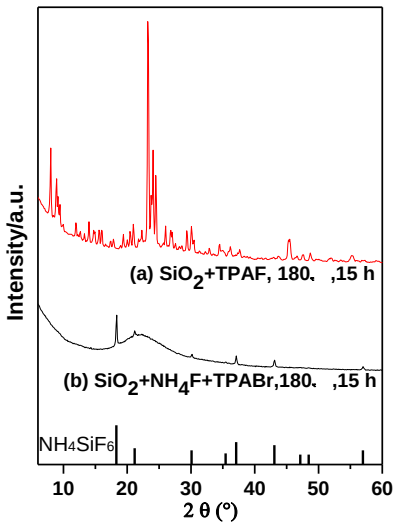

Figure S9. XRD patterns of samples derived from (a) the mixture of SiO_2 and $C_{12}H_{28}NF$, and (b) the mixture SiO_2, $C_{12}H_{28}NBr$, and NH_4F at 180 ℃ for 15 h.

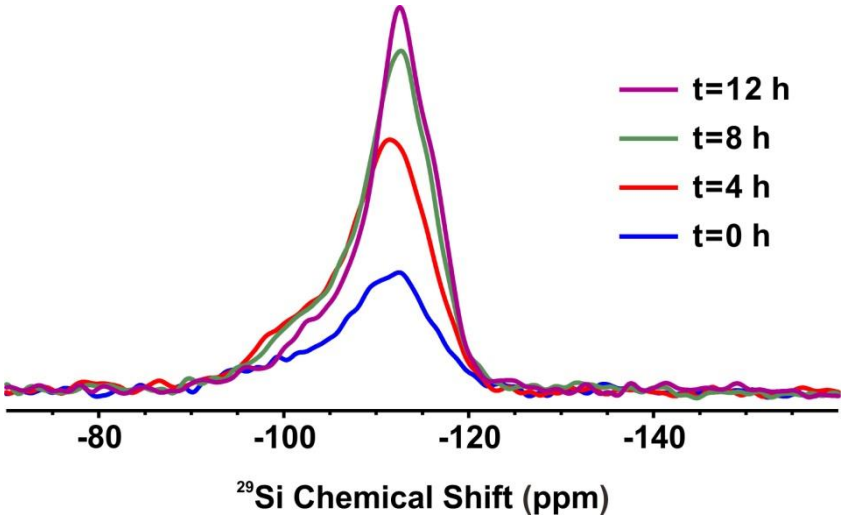

Figure S10. ^{29}Si MAS NMR spectra of ZSM-5 zeolites crystallized at 180 ℃ for 0, 4, 8, 12 h, respectively.

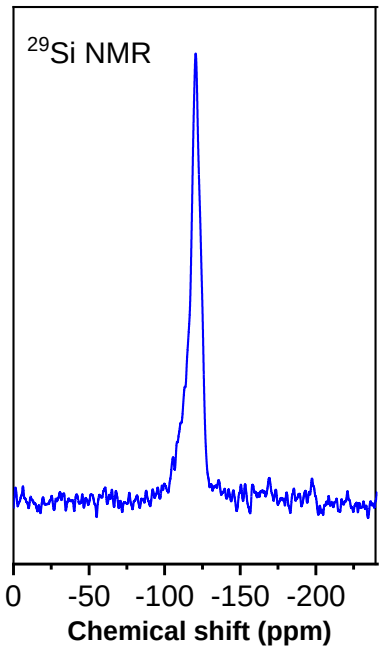

Figure S11. ^{29}Si MAS NMR spectra of ZSM-5 zeolites crystallized for 24 h at 180 ℃ using SiO_2, $(CH_3CH_2CH_2)_4NF$ and $NaAlO_2$ as raw materials.

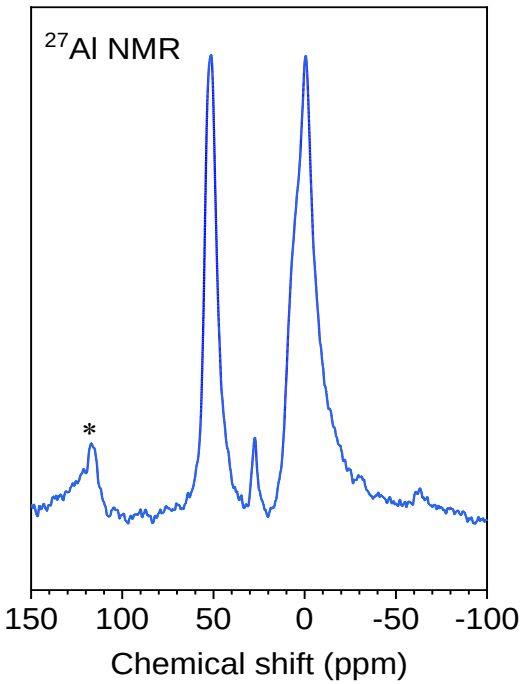

Figure S12. ^{29}Al MAS NMR spectra of ZSM-5 zeolites crystallized at 180 ℃ for 24 h.

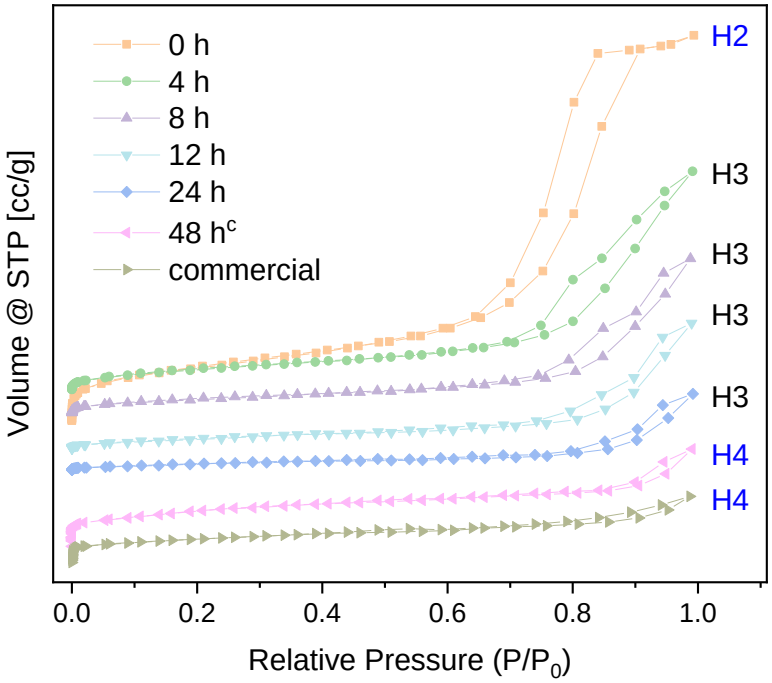

Figure S13. N_2 sorption of zeolite samples recovered at different crystallization time at 180 °C using SiO_2, $(CH_3CH_2CH_2)_4NF$ and $NaAlO_2$ as raw materials. More details see Table S2.

Table S2. Texture properties of zeolite samples recovered at different crystallization time at 180 °C using SiO_2, $(CH_3CH_2CH_2)_4NF$ and $NaAlO_2$ as raw materials.

t (h)	BET surface (m^2/g)	Micropore surface area (m^2/g)[a]	Pore volume (cm^3/g)[b]	Pore Diameter (nm)[b]
0	308	26	1	9.7
4	123	-	0.55	9.6
8	84	8	0.38	12.1
12	67	3	0.31	12.1
24	37	-	0.19	12.3
48[c]	315	214	0.16	3.7
commercial ZSM-5	256	178	0.12	3.7

[a] t-plot method.

[b] BJH desorption.

[c] The sample was calcined at 550 °C in air.

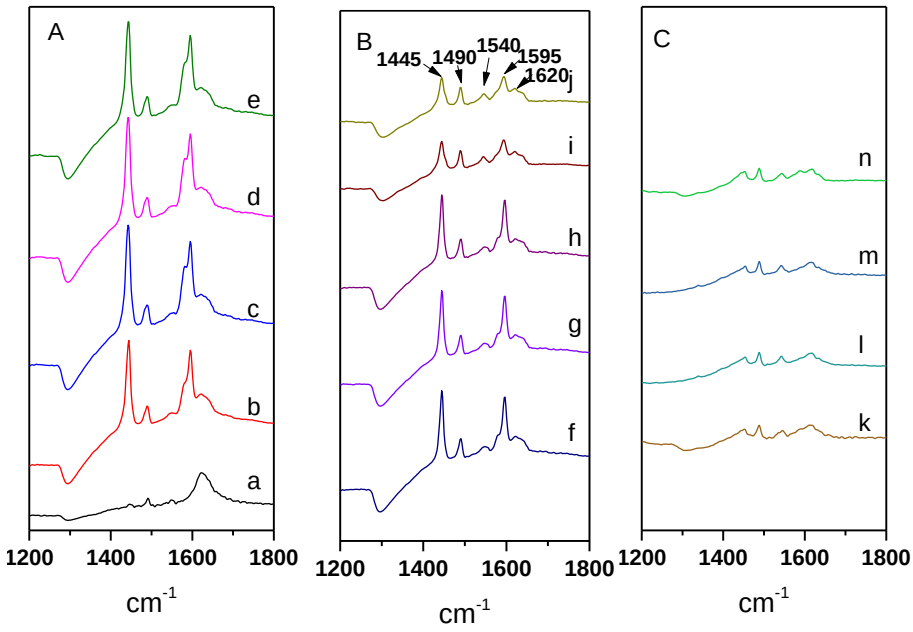

Figure S14. Pyridine adsorption-desorption FTIR spectra of ZSM-5 (Si/Al = 53) synthesized from aluminium isopropoxide. (A) pyridine adsorption at 50 ℃: (a) background, (b) 6, (c) 30, (d) 36, (e) 39 min. (B) purge and desorption: purge for (f) 4, (g) 11, (h) 13 min, and desorption at 200℃ for (i) 3, (j) 15 min. (C) desorption at 300℃ for (k) 0, (l) 20, (m) 23, (n) 25 min.

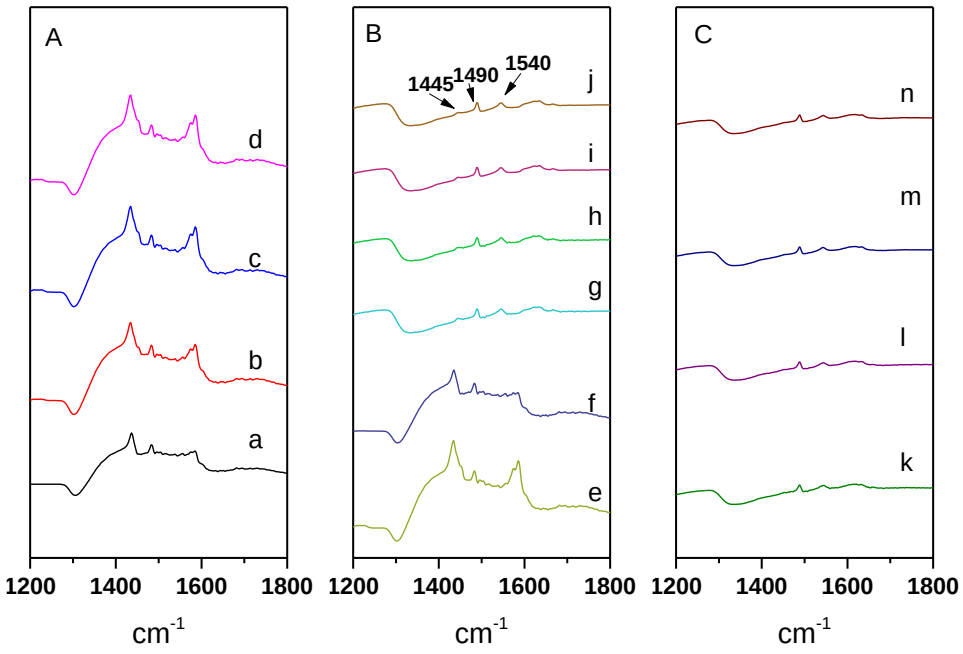

Figure S15. Pyridine adsorption-desorption FTIR spectra of ZSM-5 (Si/Al = 133) synthesized from aluminium isopropoxide. (A) pyridine adsorption: (a) 0, (b) 3, (c) 10, (d) 20 min. 39 min. (B) purge and desorption: purge for (e) 0, (f) 15, and desorption at 200℃ for (g) 0, (h) 7, (i) 10, (j) 13 min. (C) desorption at 300℃ for (k) 0 , (l) 10, (m) 15, (n) 20 min.

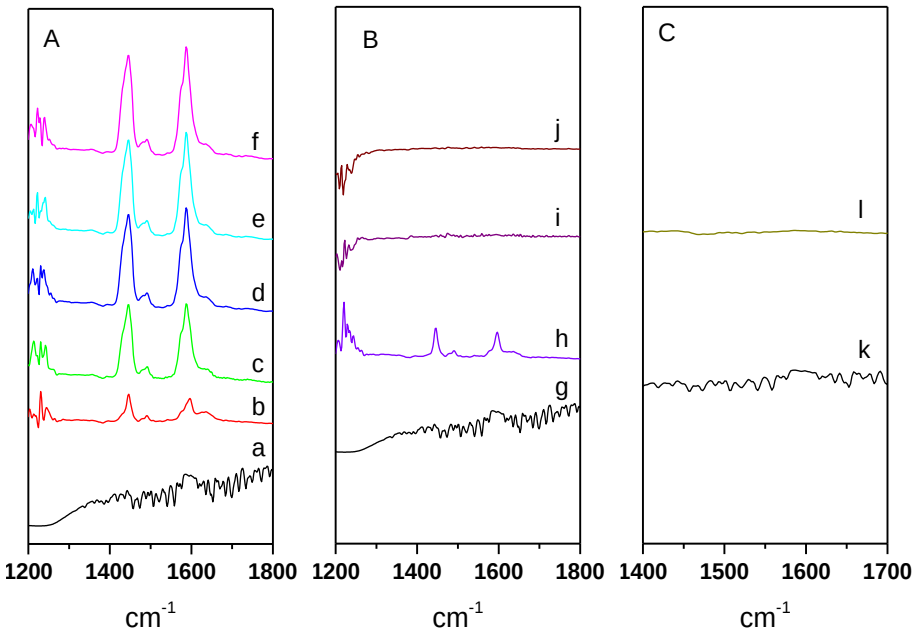

Figure S16. Pyridine adsorption-desorption FTIR spectra of ZSM-5 (Si/Al = 20) synthesized from $NaAlO_2$. (A) pyridine adsorption: (a) background, (b) 1, (c) 4, (d) 11, (e) 14, (f)21 min. (B) purge and desorption: (g) background, (h) purge for 10 min, and desorption at 200°C for (i) 0, (j) 15 min. (C) desorption at 300°C for (k) background, (l) 1 min.