

Supporting Information

Bifunctional Tandem Catalysis on Multilamellar Organic-Inorganic Hybrid Zeolites

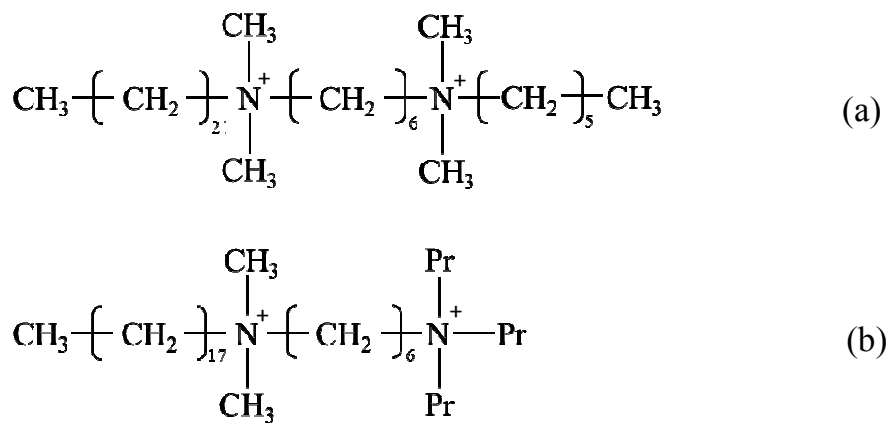
*Le Xu, Chen-geng Li, Kun Zhang, and Peng Wu**

Shanghai Key Laboratory of Green Chemistry and Chemical Processes,
Department of Chemistry, East China Normal University, Shanghai 200062, China

**Corresponding author: Peng Wu*

E-mail: pwu@chem.ecnu.edu.cn

Tel/Fax: 86 02162232292



Scheme S1. Molecular formula of (a) OSDA-Me and (b) OSDA-Pr cation.

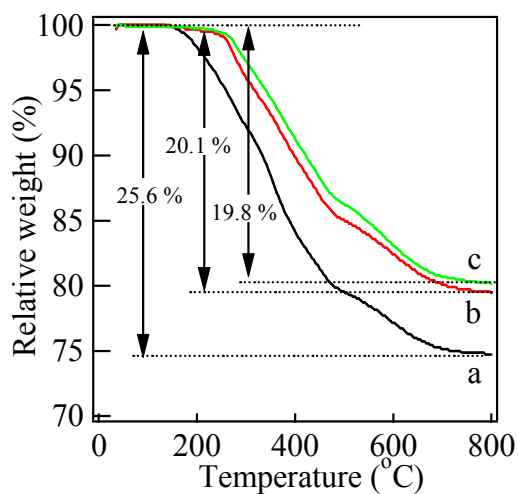


Figure S1. TG curves of (a) LZSM-5-as, (b) LZSM-5-AT and (c) LZSM-5-AT2.

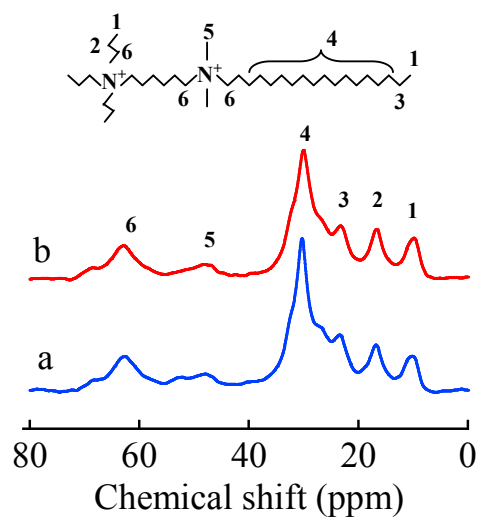


Figure S2. ^{13}C solid state MAS NMR spectra of (a) LZSM-5-as and (b) LZSM-5-AT.

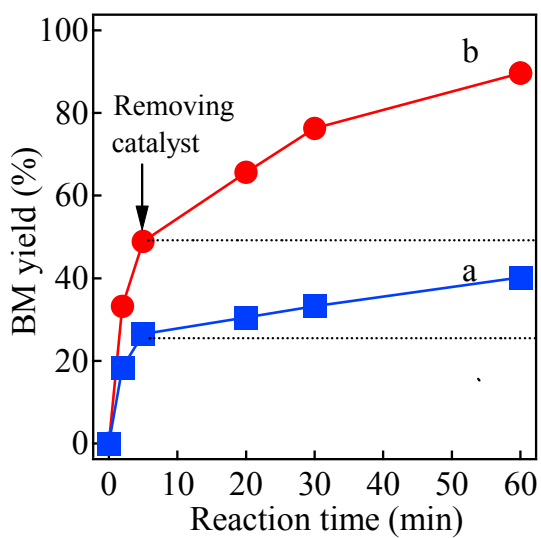


Figure S3. The catalytic results of the Knoevenagel condensation using (a) LZSM-5-AT- OH^- and (b) LZSM-5-as as catalysts. After reaction for 5 min, the catalyst was removed and the filtrate was kept at 353 K for another 55 min.

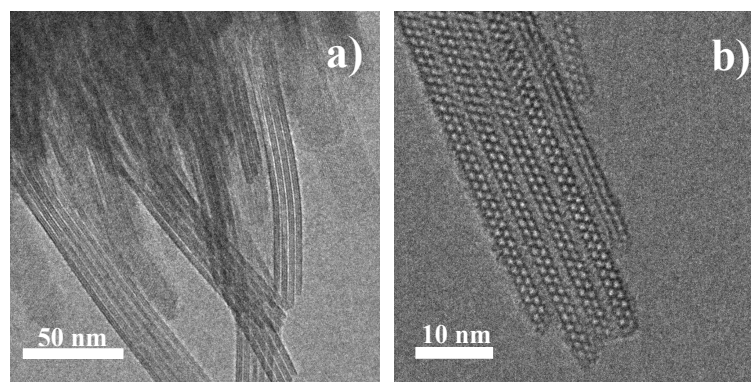


Figure S4. TEM images of LZSM-5-AT-OH⁻-10th. (a) overview at low resolution, (b) high resolution.

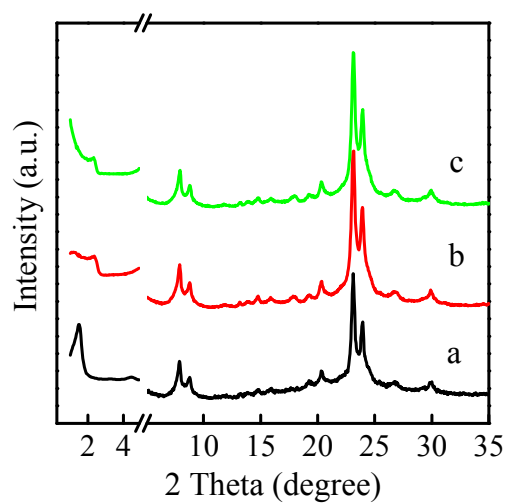


Figure S5. XRD patterns of (a) LZSM-5-Me-as, (b) LZSM-5-Me-AT and (c) LZSM-5-Me-AT2.

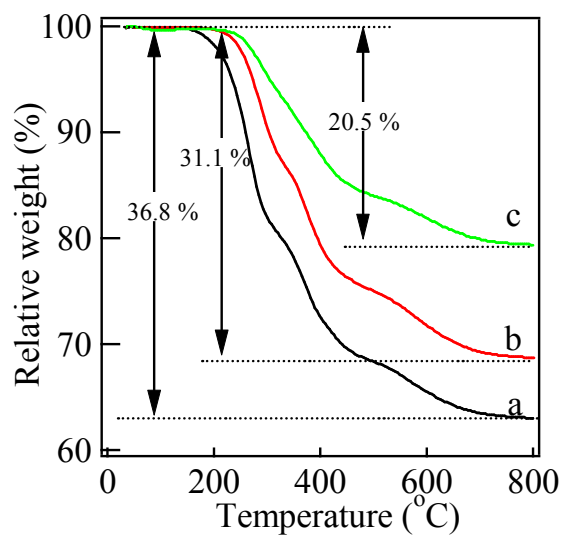


Figure S6. TG analysis of (a) LZSM-5-Me-as, (b) LZSM-5-Me-AT, (c) LZSM-5-Me-AT2.

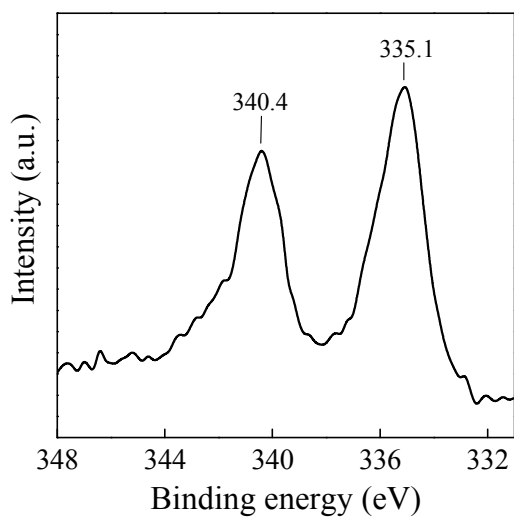


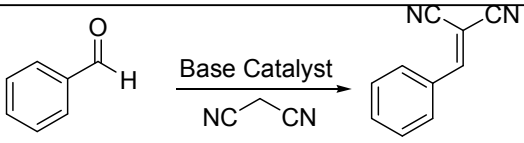
Figure S7. XPS spectra of Pd/LS-AT-OH.

Table S1. Physical properties of LZSM-5-Me and their related samples

Sample	$S_{\text{BET}}^{[a]}$ [m ² ·g ⁻¹]	$V_{\text{total}}^{[b]}$ [cm ³ g ⁻¹]	Si/Al ^[c]	N content ^[d] [mmol g ⁻¹]
LZSM-5-Me-as	15	0.054	65	1.12
LZSM-5-Me-AT	234	0.142	68	0.71
LZSM-5-Me-AT2	324	0.316	69	0.42

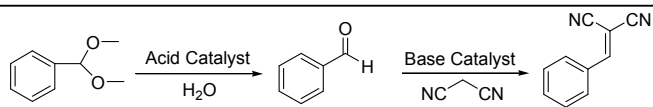
[a] To avoid thermal decomposition of OSDA species, the samples were evacuated at 423 K for 5 h before N₂ adsorption at 77 K. [b] Calculated at P/P₀=0.95. [c] Given by ICP analysis. [d] Determined by element analysis.

Table S2. The catalytic results of the Knoevenagel condensation on LZSM-5-AT-OH⁻ with different catalyst loadings.^[a]

 BA BM				
No.	Cat. loading (mg)	N active sites (mmol)	Cat. mole percentage (mol%)	Yield BM (mmol%)
1	30	0.0078	0.39	74.6
2	40	0.0104	0.52	85.1
3	50	0.0130	0.65	92.6
4	60	0.0156	0.78	93.5
5	70	0.0182	0.91	93.8

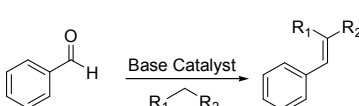
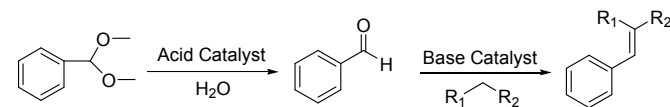
[a] Reaction conditions: cat., 30-70 mg catalyst; benzaldehyde, 2 mmol; malononitrile, 2 mmol; toluene, 3.6 g; temp., 353 K; time, 1 h. **BA**: benzaldehyde, **BM**: benzylidene malononitrile.

Table S3. Knoevenagel condensation and one-pot tandem deacetalization Knoevenagel condensation on LZSM-5 and ZSM-5 catalyst. ^[a]

			
No.	Cat. amount [mg]	Yield BA [mol%]	Yield BM [mol%]
1	50	7.3	91.2
2	40	27.9	51.6
3	60	5.9	92.4

[a] Reaction conditions: cat., 50 mg; benzaldehyde dimethylacetal, 5 mmol; malononitrile, 5 mmol; acetonitrile, 2 mL; H₂O, 20 µg; temp., 353 K; time, 15 h. **BA**: benzaldehyde, **BM**: benzylidene malononitrile.

Table S4. Knoevenagel condensation and one-pot tandem deacetalization Knoevenagel condensation on LZSM-5-AT-OH⁻ catalyst.

					
[Reaction 1]					
					
[Reaction 2]					
Cat.	R ₁	R ₂	Reaction 1 ^[a]	Reaction 2 ^[b]	
			Yield TM	Yield BA	Yield TM
			[mol%]	[mol%]	[mol%]
LZSM-5-AT-OH ⁻	CN	COOEt	54.8	67.5	24.1
LZSM-5-AT-OH ⁻	COOEt	COOEt	26.4	56.9	7.6

[a] Reaction conditions: cat., 50 mg; benzaldehyde, 2 mmol; malononitrile, 2 mmol; toluene, 3.6 g; temp., 353 K; time, 1 h. [b] Reaction conditions: cat., 50 mg; benzaldehyde dimethylacetal, 5 mmol; malononitrile, 5 mmol; acetonitrile, 2 mL; H₂O, 20 µg; temp., 353 K; time, 15 h. **BA**: benzaldehyde, **TM**: target product of reaction 1 and 2.