Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2021

Supporting information

Synthesis of ZnAlMCM-41, AlMCM-41 and ZnMCM-41

For the synthesis of the ZnAlMCM-41 ($n_{Si}/(n_{Zn+Al})$=75), 21.2 g (1 mol) sodium metasilicate dissolved in 50 g of deionized water was mixed with 0.832 g (0.0125 mol) of aluminum sulfate (dissolved in 10 g of deionized water) solution and 0.17 g (0.0125 mol) of zinc chloride (dissolved in 10 g of deionized water). The mixture stirred by mechanical stirrer was reduced its pH to 10.8 by 1N of sulfuric acid solution. Thereafter, 9.1 g (0.25 mol) of cetyltrimethylammonium bromide was added drop-by-drop (30 ml/h) by the dual syringe pump. After further stirring for 1h, the resulting synthesis gel with composition $1SiO_2/0.0125ZnO/0.0125Al_2O_3/0.25CTMABr/100H_2O$ was transferred into Teflon-lined steel autoclave, which was heated to 438 K for 48 h. After cooling to room temperature, the catalyst recovered by filtration and washed using a mixture of deionized water and ethanol was finally calcined in flowing air at 813 K for 6 h.

The different ZnAlMCM-41 catalysts, viz. ZnAlMCM-41(151), ZnAlMCM-41(228), ZnAlMCM-41(304) and ZnAlMCM-41(380), with the gel composition of $1SiO_2/xAl_2O_3/yZnO/0.25CTMABr/100H_2O$; (x=0.00625–0.0025, y= 0.00625–0.0025), were synthesized using the above similar procedure.

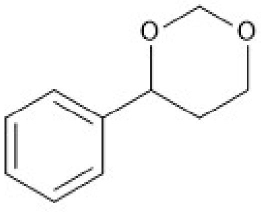
The monometallic catalysts, viz. AlMCM-41 (n_{Si}/n_{Al}=21) and ZnMCM-41 (n_{Si}/n_{Zn} = 21) were synthesized by a basic hydrothermal method using aluminum sulfate and zinc chloride as the sources for aluminum and zinc using the above similar procedure.

The pure MCM-41used as a catalyst was synthesized under a basic hydrothermal method using the above similar procedure without adding any metal sources.

Physico-chemical characterization of ZnAlMCM-41

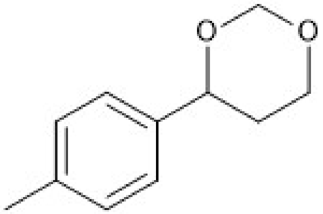
The direct basic hydrothermal method is a facile and simple ecofriendly method that has been used for the synthesis of a variety of mesoporous catalyst, such as ZnAlMCM-41(75), ZnAlMCM-41(151), ZnAlMCM-41(228), ZnAlMCM-41(304), ZnAlMCM-41(380)), AlMCM-41(21), ZnMCM-41(21), and MCM-41 silica. All the synthesized catalysts have been characterized using relevant sophisticated instrumental techniques according to our published procedures. XRD patterns (Figure 1S) of a variety of mesoporous catalysts, e.g. ZnAlMCM-41, AlMCM-41(21), and ZnMCM-41(21), clearly prove their mesoporous nature, as the *d*-space value (d_{100}) and unit cell parameter (a_o) decrease with increasing metal ions-content, as illustrated in Table 1S. The textural properties of ZnAlMCM-41(75) are smaller than those of other ZnAlMCM-41 materials (Table 1S and Figure 2S). FT-IR studies, as depicted in Figure 3S, predict that zinc and aluminum ions are highly incorporated into the hexagonal mesoporous MCM-41 catalysts, as the infrared wavenumber of the antisymmetric Si-O-Si vibration bands (1096 cm^{-1}) in ZnAlMCM-41 is higher than those of AlMCM-41 (1083 cm^{-1}) and ZnMCM-41 (1085 cm^{-1}). This shift in wavenumber suggests that the mean Si-O distance in the surface wall thickness increased with the incorporation of the larger ionic radii of zinc and aluminum [25]. ICP-AES results confirm the zinc and aluminum ion content on the silica surface, before and after the reaction, as shown in Table 1S. The Brønsted–Lewis acid sites in ZnAlMCM-41(75) (Table 2S and Figure 4S) are higher than that of other mesoporous catalysts, such as ZnAlMCM-41, AlMCM-41(21), and ZnMCM-41(21). This is due to the increasing the number of acid sites by the introduction of zinc ions [25]. All calcined ZnAlMCM-41 catalysts have either a micellar rod-like hexagonal shape or spherical edge (Figure 5S), as confirmed by SEM studies [25]. Uniform pore channels with hexagonal symmetry can be clearly identified by the TEM images of ZnAlMCM-41(75), indicating that all the mesoporous ZnAlMCM-41 catalysts synthesized using a direct basic hydrothermal method have uniform mesostructures (Figure 6S), as inferred by XRD [25].

NMR (^{1}H and ^{13}C) spectral data for selected 1,3-dioxanes



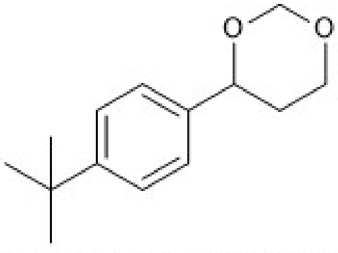
4-phenyl-1,3-dioxane (4-PDO)

Colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.68–1.70 (m, 1H), 2.02–2.13 (m, 1H), 3.83–3.87 (m, 1H), 4.12–4.21 (m, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.84–4.91 (m, 1H), 5.19 (d, *J* = 6.4 Hz, 1H), 7.21–7.31 (m, 1H); ^{13}C NMR (CDCl3) δ 33.9, 66.9, 78.7, 94.2, 125.9, 128.0, 128.5, 141.7.



4-(*p*-tolyl)-1,3-dioxane

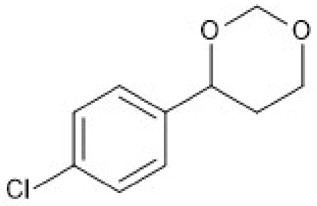
Colorless liquid; ^{1}HNMR ($CDCl_3$) δ 1.68 (d, *J* = 13.6Hz, 1H), 2.07 (qd, J_a = 9.6 Hz, J_b = 4.8 Hz, 1H), 2.34 (s, 3H), 3.88 (dd, J_a = 13.6 Hz, J_b = 2.0 Hz, 1H), 4.20 (dd, J_a = 12.0 Hz, J_b = 4.8 Hz, 1H), 4.64 (d, *J* = 11.2 Hz, 1H), 4.91 (d, J = 6.4, 1H), 5.17 (d, *J* = 6.4 Hz, 1H), 7.22 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 21.1, 33.9, 66.9, 78.8, 94.2, 125.5, 129.3, 137.7, 138.4.



4-(4-(*tert*-butyl)phenyl)-1,3-dioxane

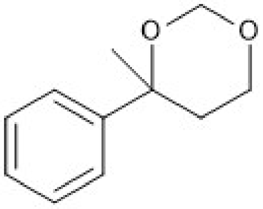
Colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.33 (s, 9H), 1.70 (dt, J_a = 13.6 Hz, J_b = 0.8 Hz, 1H), 2.09 (dd, J_a = 11.8 Hz, J_b = 4.8 Hz, 0.5H), 2.17 (dd, J_a = 11.8 Hz, J_b = 4.8 Hz, 0.5H), 3.85 (td, J_a = 11.6 Hz, J_b = 2.4 Hz, 1H), 4.22 (dd, J_a = 11.2 Hz, J_b = 4.8 Hz, 1H), 4.62 (dd, J_a = 11.2 Hz, J_b =

2.4 Hz, 1H), 4.89 (d, *J* = 6.4 Hz, 1H), 5.22 (d, *J* = 6.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 31.7, 34.2, 35.2, 67.3, 79.2, 94.5, 125.7, 126.1, 138.7, 151.2.



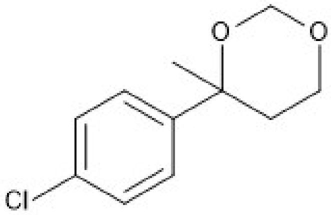
4-(4-chlorophenyl)-1,3-dioxane

Colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.68 (dt, J_a = 13.6 Hz, J_b = 0.8 Hz, 1H), 2.02 (ddd, J_a = 12.8 Hz, J_b = 4.8 Hz, J_c = 1.6 Hz, 1H), 3.88 (td, J_a = 12.0 Hz, J_b = 2.4 Hz, 1H), 4.21 (dd, J_a = 11.6 Hz, J_b = 4.8 Hz, 1H), 4.62 (dd, J_a = 11.2 Hz, J_b = 2.4 Hz, 1H), 4.87 (d, *J* = 6.4 Hz, 1H), 5.21 (d, *J* = 6.4Hz, 1H), 7.25–7.38 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 34.3, 67.2, 78.2, 94.5, 127.5, 129.2, 133.8, 140.3.



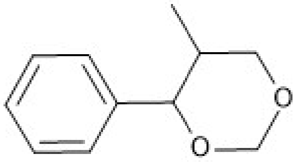
4-methyl-4-phenyl-1,3-dioxane

Colorless liquid, ^{1}H NMR ($CDCl_3$) δ 1.41 (s, 3H), 2.05–2.28 (m, 2H), 3.64 (td, J_a = 11.2 Hz, J_b = 2.8 Hz, 1H), 3.85–3.93 (m, 1H), 4.66 (d, J = 6.8Hz, 1H), 4.87 (d, J = 6.4Hz, 1H), 7.19–7.26 (m, 1H); 7.28–7.33 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 31.1, 33.8, 62.9, 74.7, 88.2, 124.9, 126.2, 127.6, 143.2.



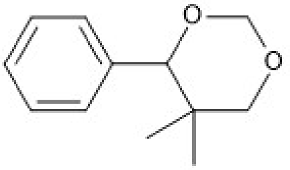
4-(4-chlorophenyl)-4-methyl-1,3-dioxane

Colorless liquid, ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 3H), 2.03–2.20 (m, 2H), 3.60 (td, J_a = 10.4 Hz, J_b = 3.2Hz, 1H), 3.82–3.90 (m, 1H), 4.63 (d, J = 6.8 Hz, 1H), 4.82 (d, J = 6.8 Hz, 1H), 7.17–7.28 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 30.6, 33.8, 62.5, 74.3, 88.2, 126.2, 127.7, 131.7, 141.8.



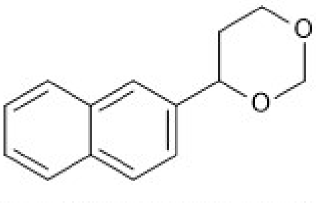
5-Methyl-4-phenyl-1,3-dioxane

Colorless oil; *cis/trans* = 48:53.*cis* -Isomer identified by ^{1}H NMR; ^{1}H NMR δ 0.87 (d, J = 7.3 Hz, 3H), 1.83 (m, 1H), 3.92 (d, J = 11.2Hz, 1H), 4.01 (dd, J = 11.0 Hz, J = 2.3Hz, 1H), 4.83 (d, J = 2.3 Hz,1H), 4.87 (d, J = 6.4 Hz, 1H), 5.22 (d, J = 6.0Hz, 1H), 7.17–7.37 (m, 5H); *trans*-isomer identified by 1H NMR; 1H NMR δ 0.55 (d, J = 6.4Hz, 3H), 2.03–2.15 (m, 1H), 3.38 (t, J = 11.4 Hz, 1H), 4.03 (d, J = 10.6, 1H), 4.09 (d, J = 10.1 Hz, 1H), 4.81(d, J = 6.4 Hz, 1H), 5.18 (d, J = 6.4 Hz, 1H), 7.19–7.37 (m, 5H); ^{13}C NMR δ 11.2, 12.5, 34.7, 36.4, 73.0, 73.0, 80.4, 86.2, 94.1, 94.4, 125.1, 127.0, 127.3, 128.1, 128.2, 128.3, 139.4, 140.4.



5, 5-Dimethyl-4-phenyl-1,3-dioxane

Colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.15 (s, 3H), 1.27 (s, 3H), 3.03 (dd, J = 11.2 Hz, J = 4.2 Hz, 1H), 3.96 (dd, J = 11.2, J = 4.8 Hz, 1H), 4.11 (t, J = 11.2 Hz, 1H), 4.94 (d, J = 6.8 Hz, 1H), 5.05 (d, J = 6.8 Hz, 1H), 7.07–7.19 (m, 2H), 7.19–7.31 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 19.2, 28.6, 51.2, 66.5, 75.2, 88.2, 127.0, 128.1, 129.4, 138.9.



4-(2-Naphthyl)-1,3-dioxane

Colorless liquid; ^{1}H NMR ($CDCl_3$) δ 1.81 (d, J = 13.6 Hz, 1H), 2.11–2.25 (m, 1H), 3.92 (t, J = 11.6 Hz, 1H), 4.22 (d, J = 7.6 Hz, 1H), 4.83 (d, J = 11.6 Hz, 1H), 4.96 (dd, J_a = 6.4Hz, J_b = 2.3 Hz, 1H), 5.28 (d, J = 6.4 Hz, 1H), 7.41–7.55 (m, 3H), 7.78–7.97 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 34.2, 67.0, 78.7, 94.3, 123.9, 124.6, 125.9, 126.2, 127.7, 128.4, 128.2, 133.0, 133.5, 138.7.

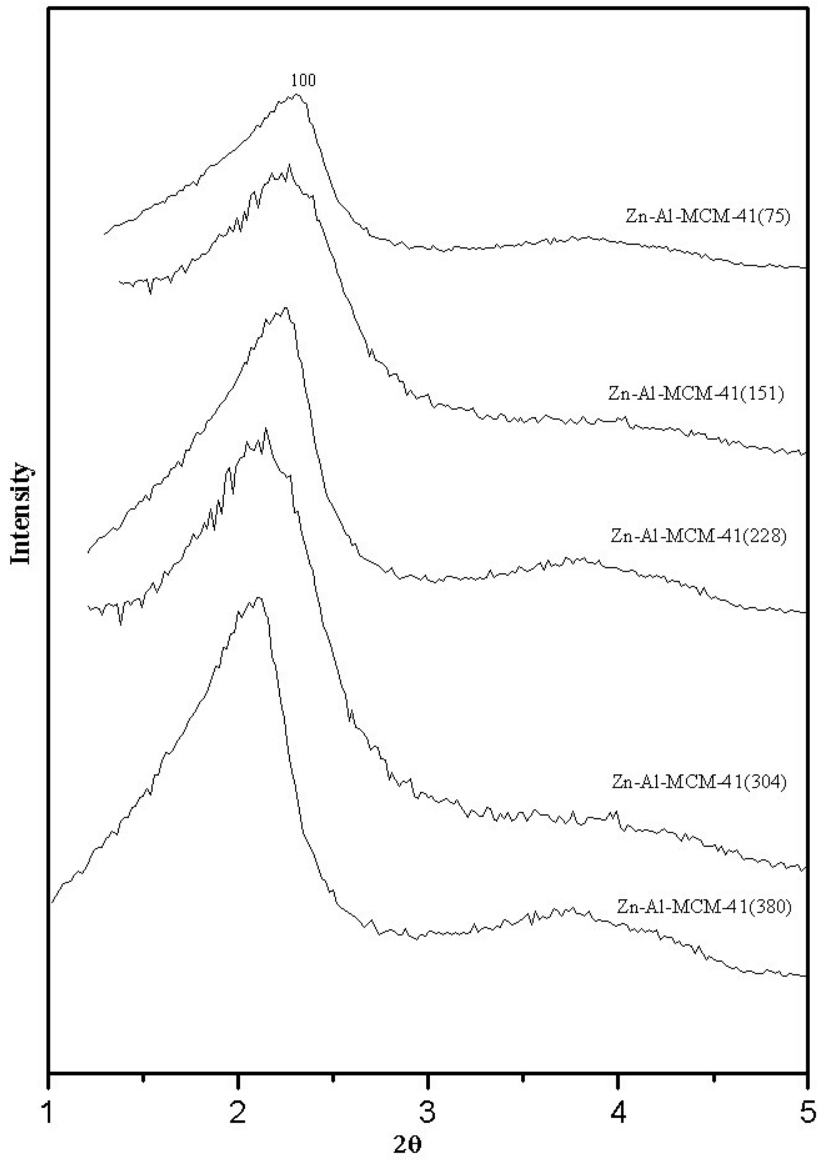


Figure 1S: X-ray diffraction patterns of calcined ZnAlMCM-41 catalysts

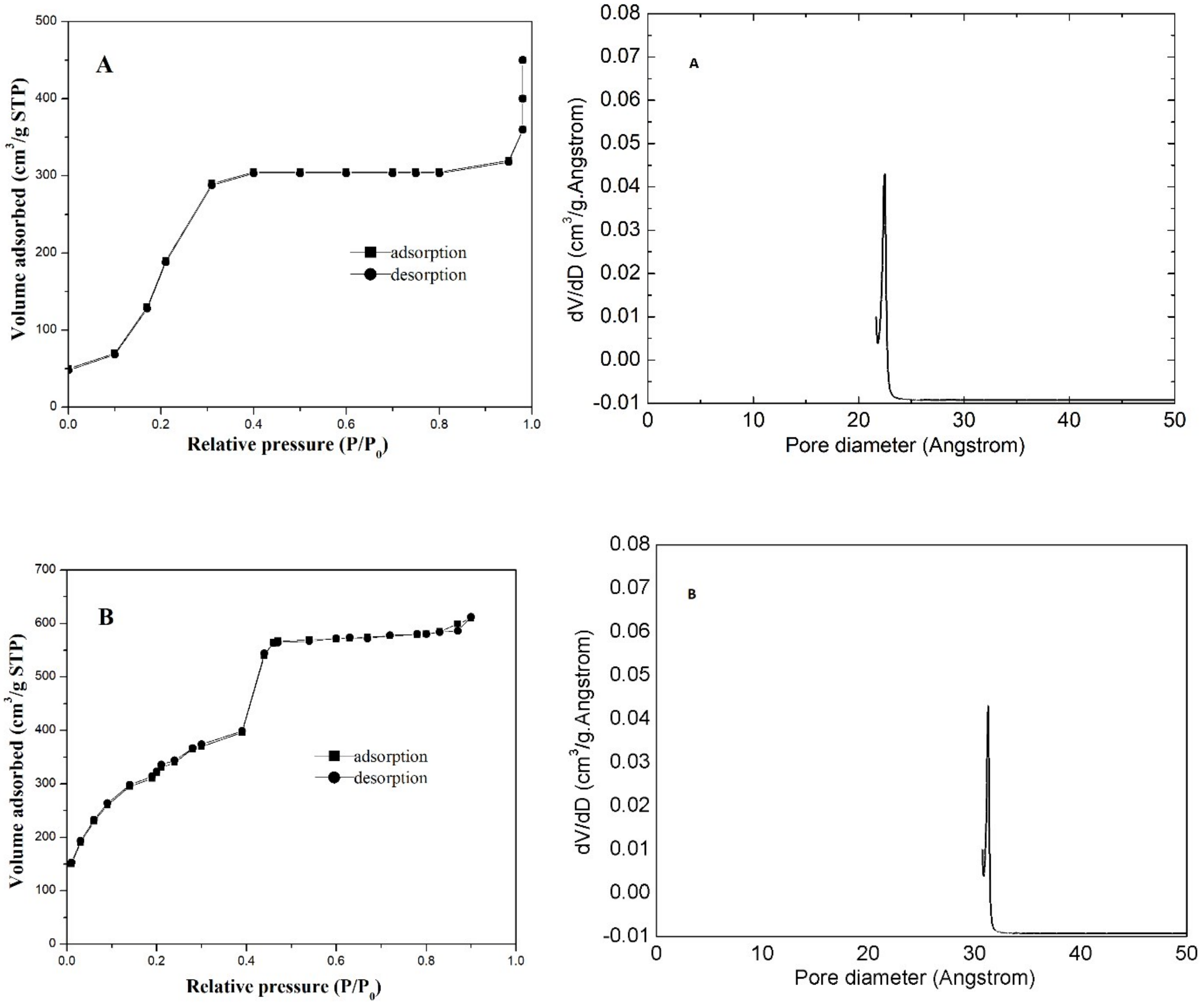


Figure 2S: N_2-adsorption isotherms and pore size distribution of calcined: A. ZnAlMCM-41(75) and B. ZnAlMCM-41(380)

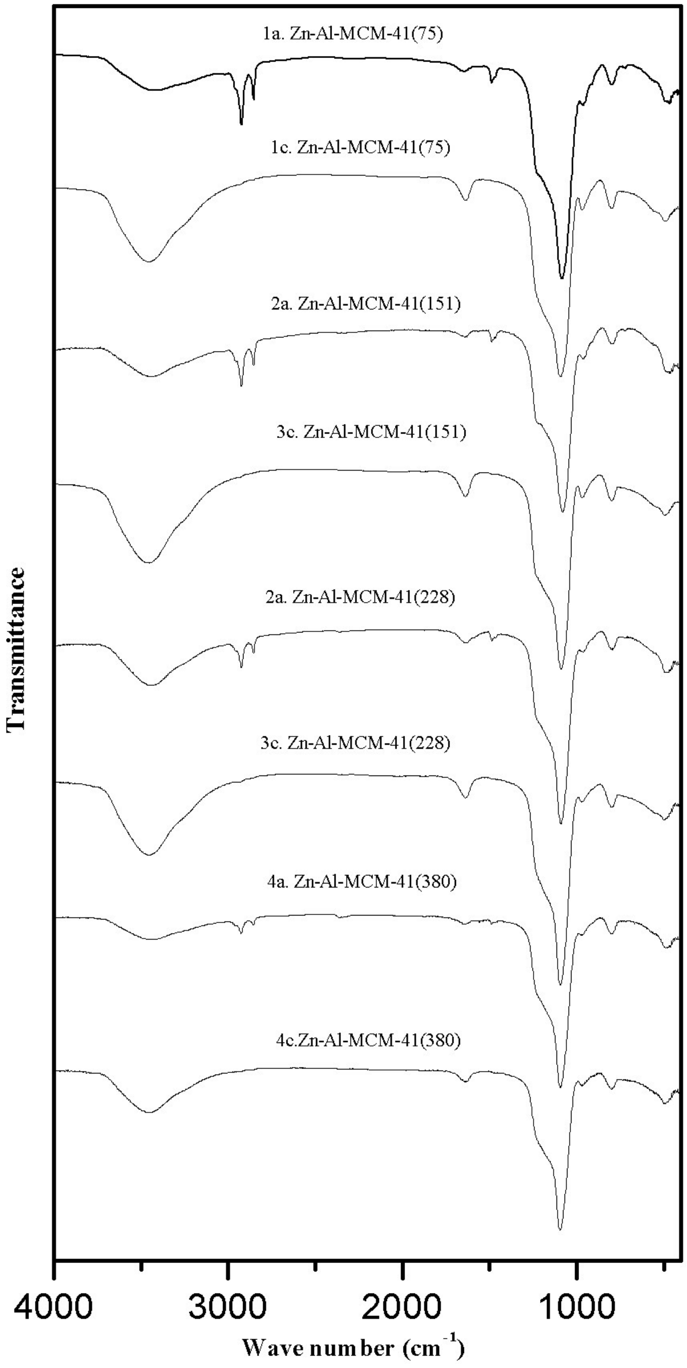


Figure 3S: FTIR spectra of ZnAlMCM-41 catalysts (a - as-synthesized and c - calcined)

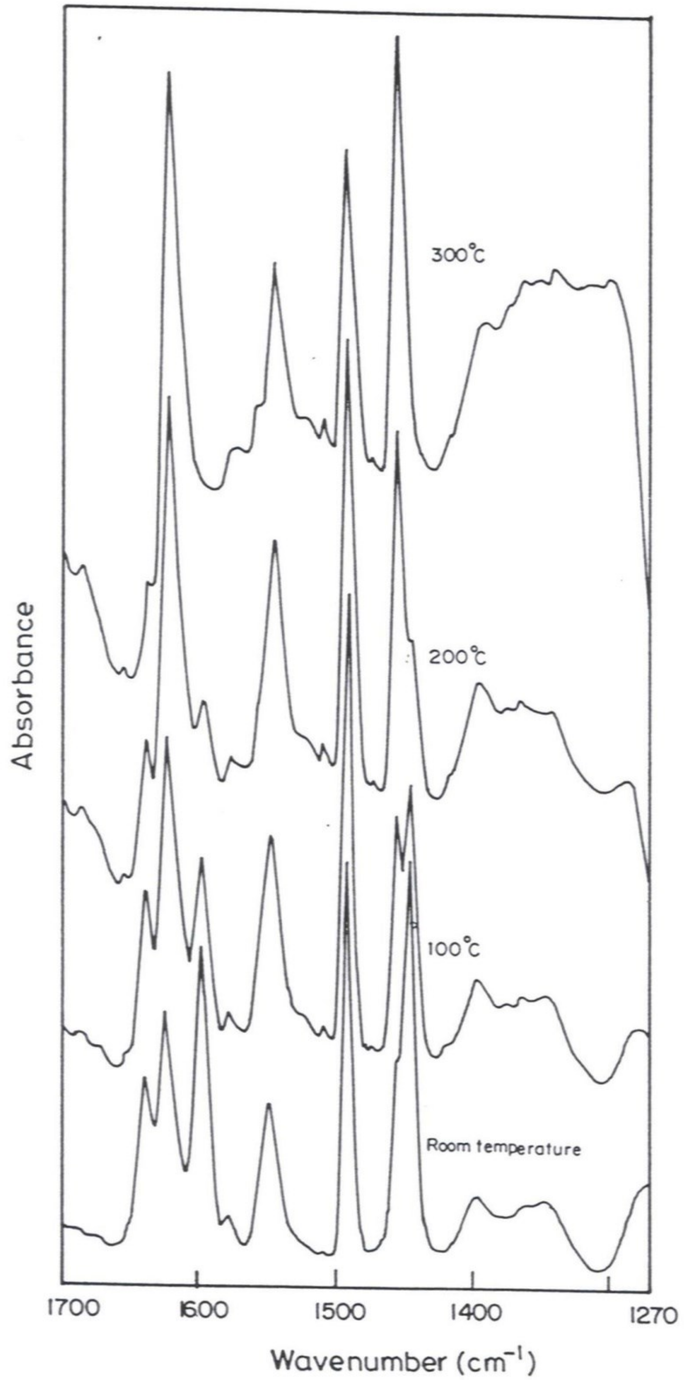


Figure 4S: FTIR spectra of pyridine adsorbed on ZnAlMCM-41(151)

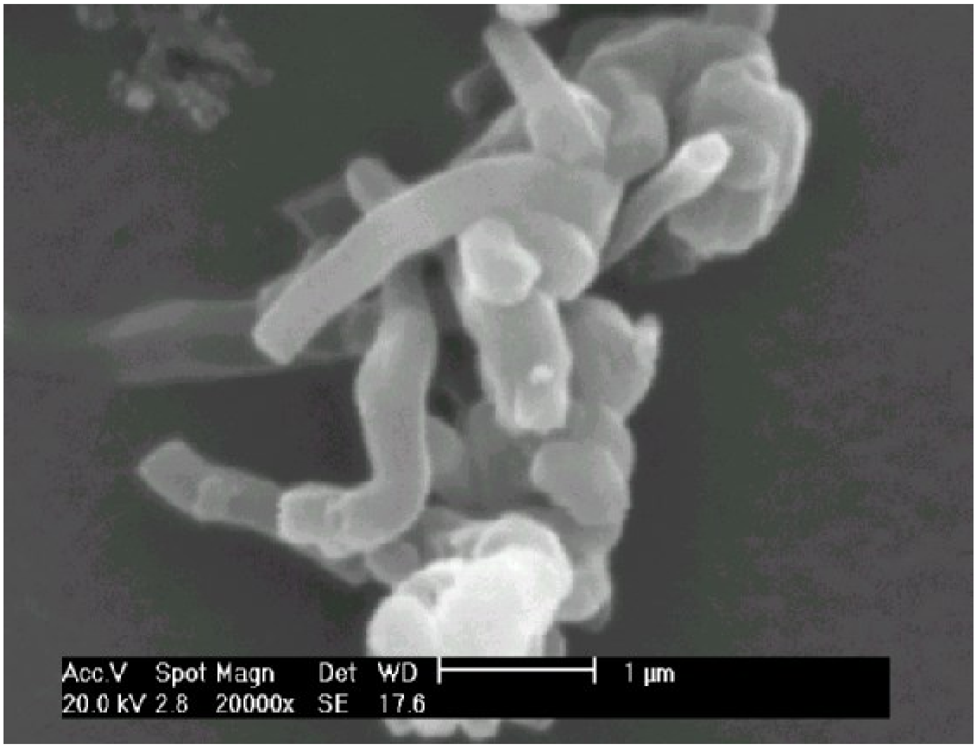


Figure 5S: SEM image for ZnAlMCM-41(75)

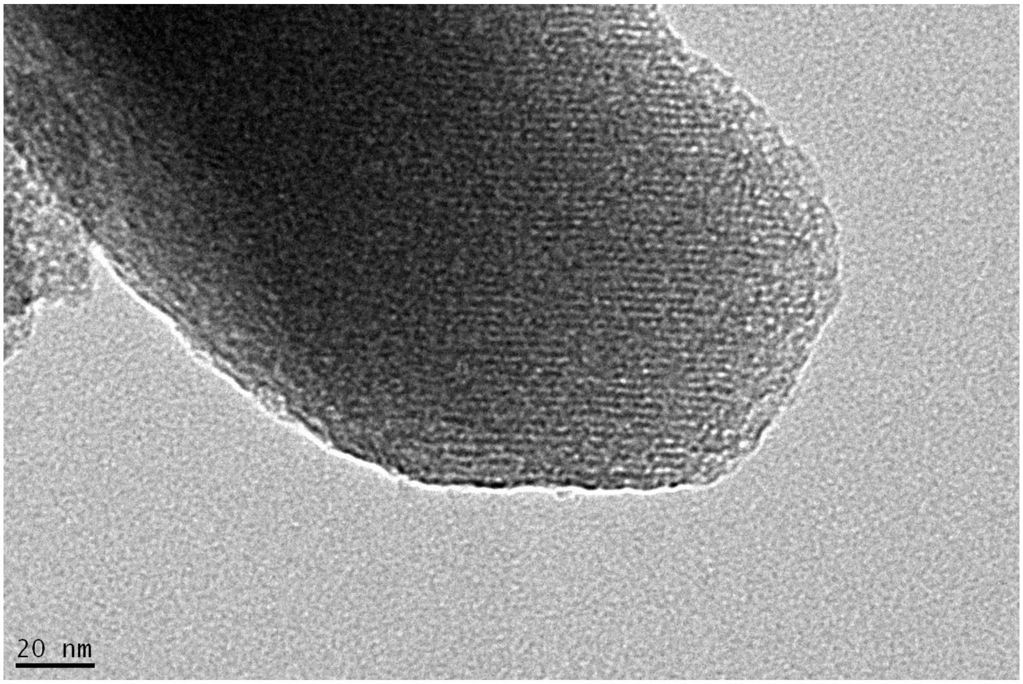


Figure 6S: TEM image for ZnAlMCM-41(75)

Table 1S: Physicochemical properties of ZnAlMCM-41 catalysts prepared by basic hydrothermal method

Catalysts	Zn content[a] (wt%)	Al content[a] (wt%)	d_{100} (Å)	a_0 (Å)	SA_{BET} (m^2/g)	D_p (Å)	V_p (cm^3/g)	t_w (Å)
ZnAlMCM-41 (75)	0.123	0.220	37.91	43.77	820	22.8	0.852	20.97
ZnAlMCM-41(151)	0.060	0.123	38.41	44.35	867	25.6	0.893	18.75
ZnAlMCM-41(228)	0.040	0.079	38.91	44.92	912	27.0	0.944	17.90
ZnAlMCM-41(304)	0.031	0.060	39.98	46.15	970	29.3	0.963	16.85
ZnAlMCM-41(380)	0.020	0.049	41.09	47.44	1071	32.2	0.983	15.24
ZnAlMCM-41(75) [b]	0.125	0.223	37.85	43.70	810	22.9	0.852	20.80
W-ZnAlMCM-41 [c]	0.124	0.220	37.89	43.75	848	23.0	0.853	20.75
ZnAlMCM-41(380) [b]	0.021	0.051	41.00	46.32	1018	31.5	0.982	14.82
AlMCM-41(21)	-	0.499	38.41	44.35	830	27.5	0.866	16.85
ZnMCM-41(21)	0.242	-	37.9	43.76	635	27.3	0.611	16.46
MCM-41	-	-	35.90	41.45	1179	29.3	0.675	12.15

[a] The results were obtained by ICP-AES

[b] The results were obtained for the recyclable catalysts used in 4th run

[c] The catalyst was washed with ammonium chloride solution for removal of non-framework zinc- and aluminium-ions on the active surface.

Table 2S: Brønsted acidity and Lewis acidity of the ZnAlMCM-41 catalysts characterized by FTIR-pyridine adsorption and desorption measurements at different temperatures as well as total acidity measured by TPD-pyridine.

Catalysts	Total acidity[a] (mmol pyridine. g^{-1})	Bronsted acidity (µmol pyridine. g^{-1}) [b]				Lewis acidity(µmol pyridine. g^{-1}) [b]			
		298 K	373 K	473 K	573 K	298 K	373 K	473 K	573 K
ZnAlMCM-41(75)	0.103	27.5	20.3	18.2	13.5	40.3	35.6	30.5	25.3
ZnAlMCM-41(151)	0.095	23.4	19.2	16.3	12.4	38.3	30.3	27.3	23.5
ZnAlMCM-41(228)	0.076	19.5	17.3	14.2	10.3	25.4	24.5	24.3	20.2
ZnAlMCM-41(304)	0.055	17.4	15.4	12.4	6.7	20.6	20.4	20.3	18.3
ZnAlMCM-41(380)	0.035	14.3	13.2	9.5	5.3	17.7	15.3	14.5	15.6
AlMCM-41	0.099	23.8	18.3	12.3	11.3	11.9	10.3	8.3	6.3

Results obtained from [a] TPD-pyridine and [b] FTIR-pyridine