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Supporting Information

Zirconium-doped porous magadiite heterostructures upon 2D intragallery in situ hydrolysis–condensation–polymerization strategy for liquid-phase benzoylation

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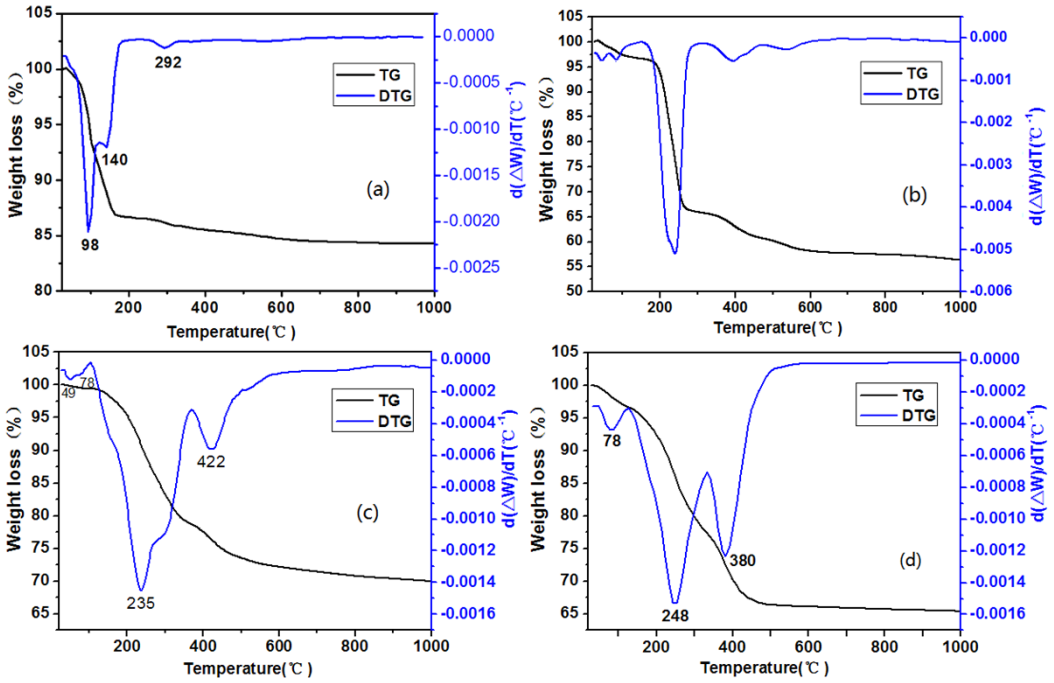

Fig. S1 TG analysis of the magadiite (a), QM (b), QOTM (c) and QOTM-0.1Zr (d).

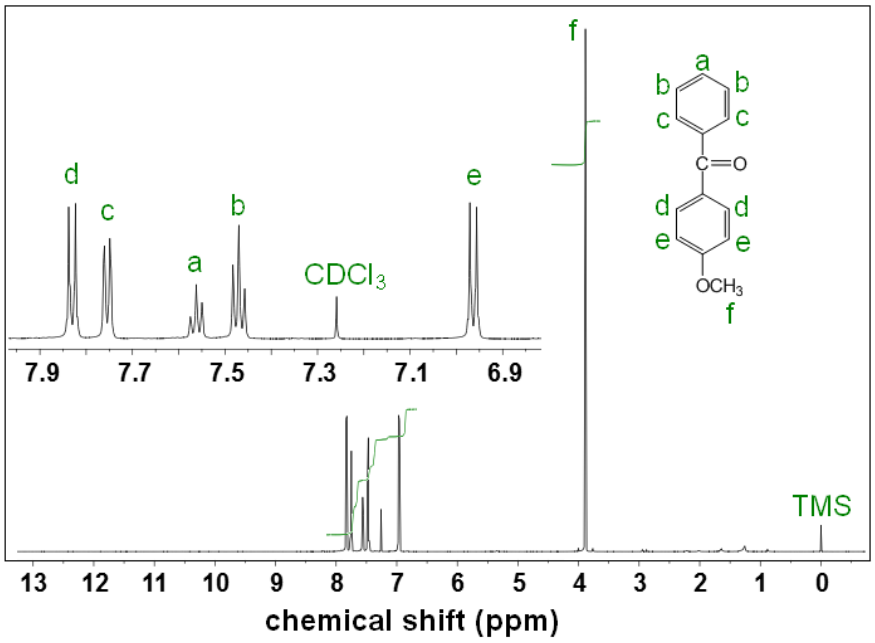

Fig. S2 ^{1}H NMR of the product 4-MBP.

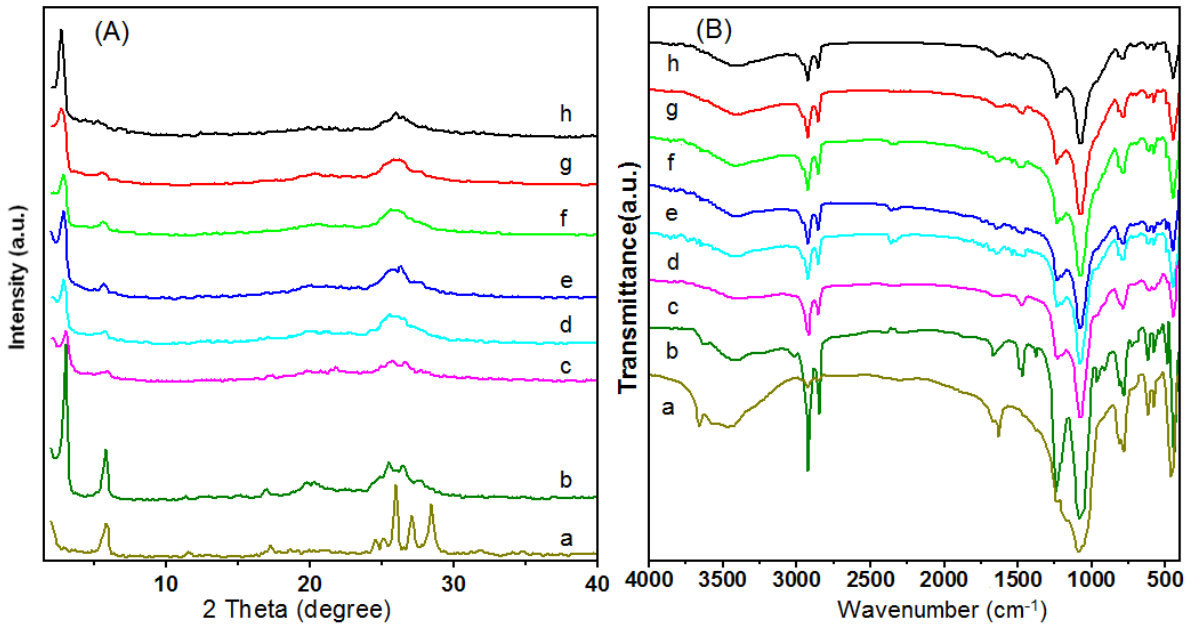

Fig. S3 XRD (A) and IR (B) spectra of magadiite (a), OM (b), and precursors QOTM (c) and QOTM-*x*Zr (d-h: *x*=0.0125-0.2).

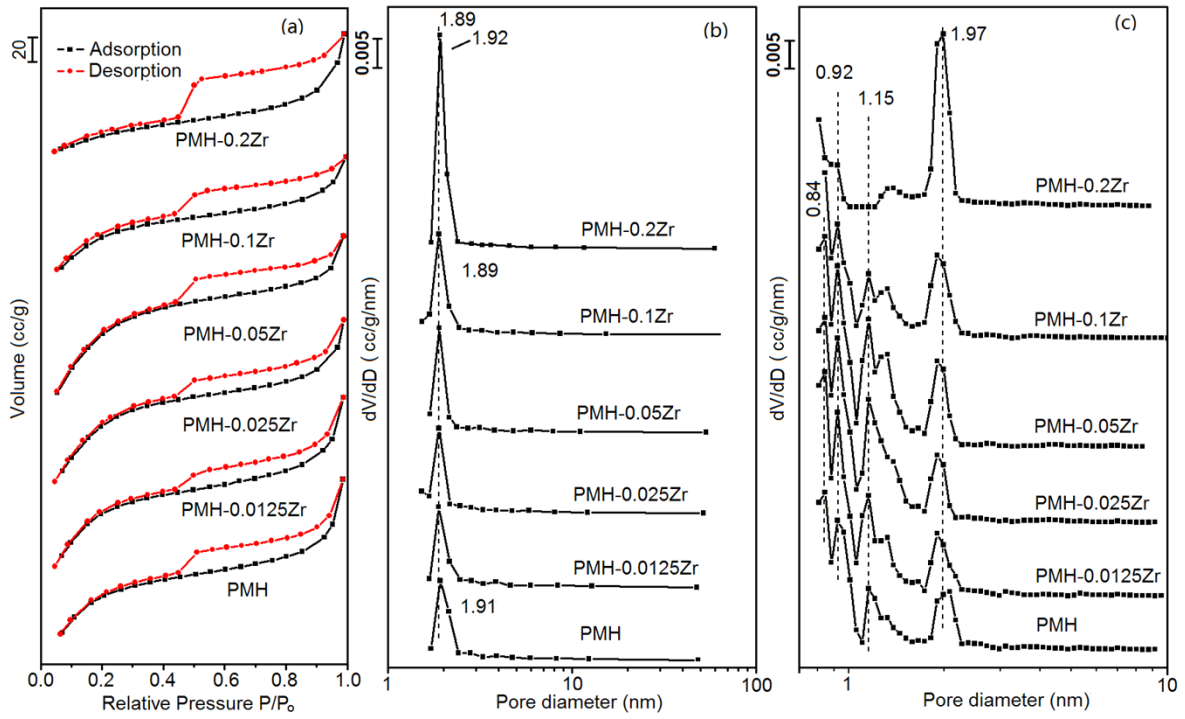

Fig. S4 The N_2 adsorption-desorption isotherms (a) and pore size distribution curves based on BJH (b) and DFT (c) of PMH and PMH-*x*Zr catalysts.

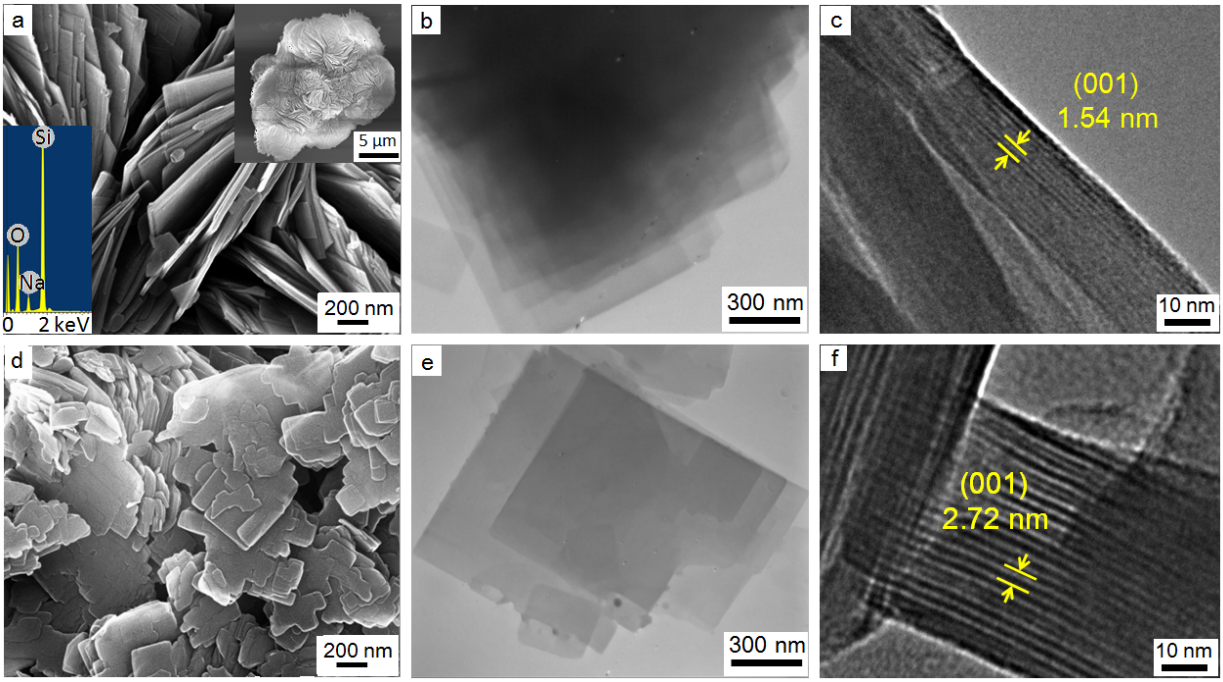

Fig. S5 SEM/EDX, TEM and HRTEM images of Na-magadiite (a, b, c) and QM (d, e, f).

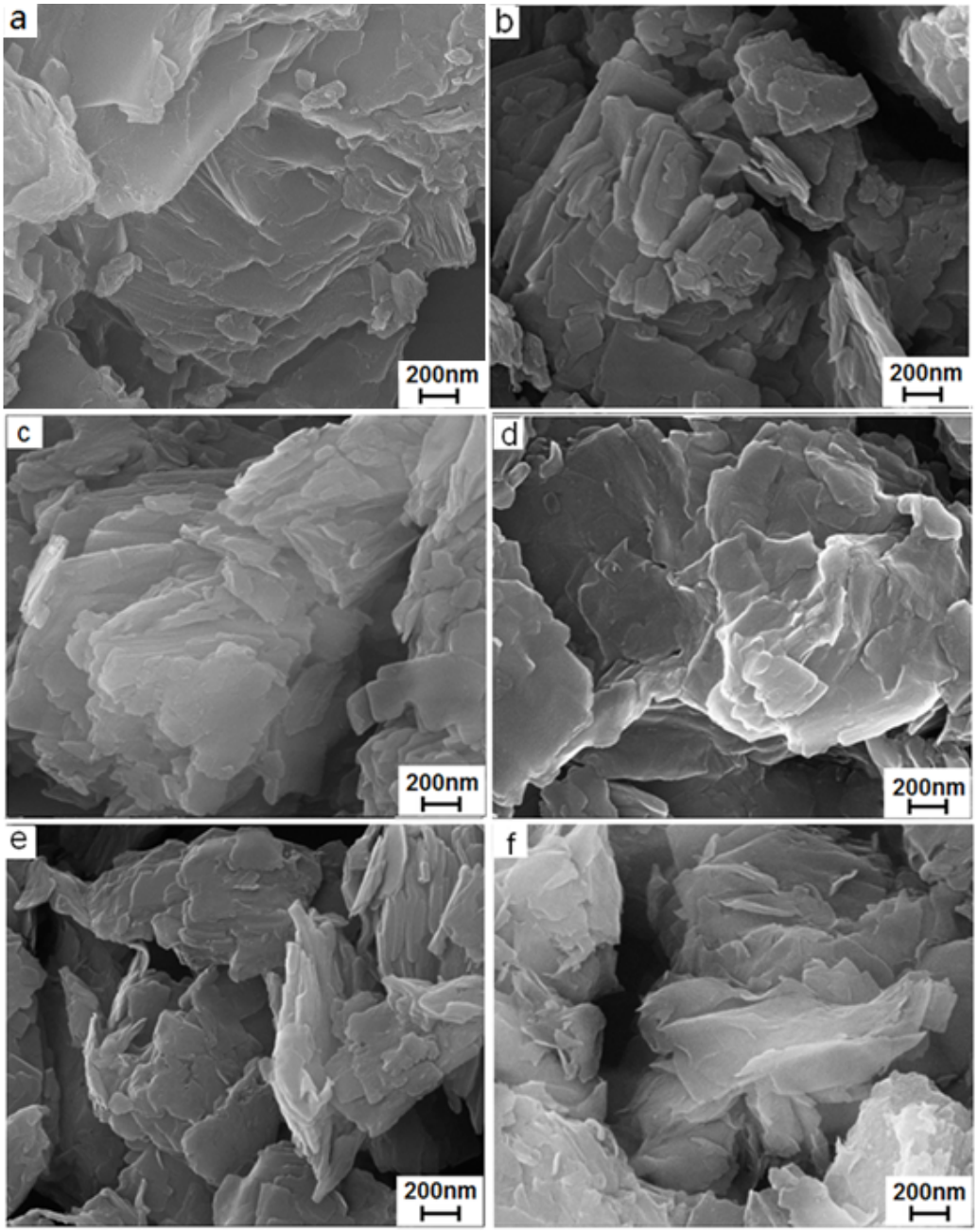

Fig. S6 SEM images of the precursors QOTM (a) and QOTM-*x*Zr(b-f) (from b to f, x = 0.0125, 0.025, 0.05, 0.1, 0.2).

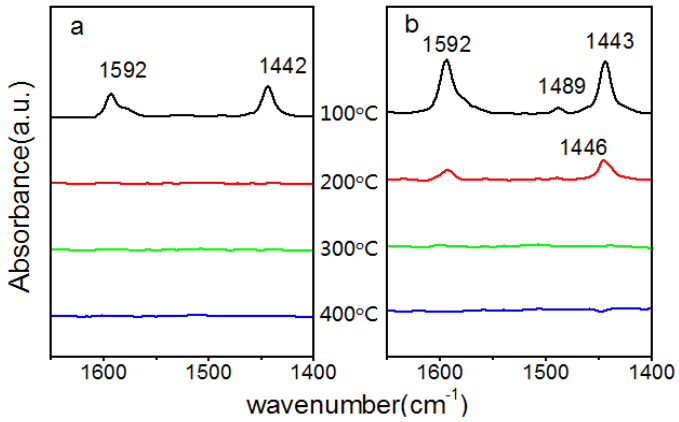

Fig. S7 In situ FTIR spectra for PMH (a) and PMH-0.0125Zr (b) after pyridine adsorption and evacuation at elevated temperatures.

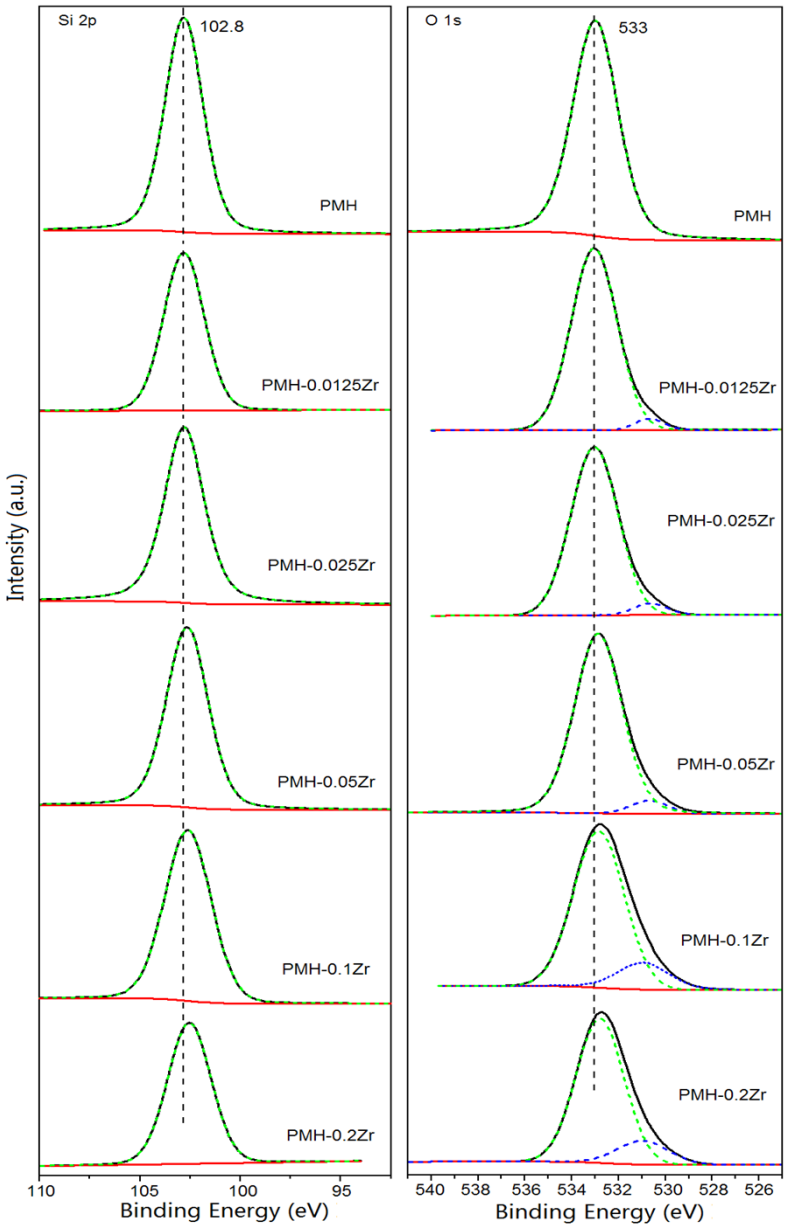

Fig. S8 Si 2p and O 1s XPS of PMH and PMH-*x*Zr catalysts.

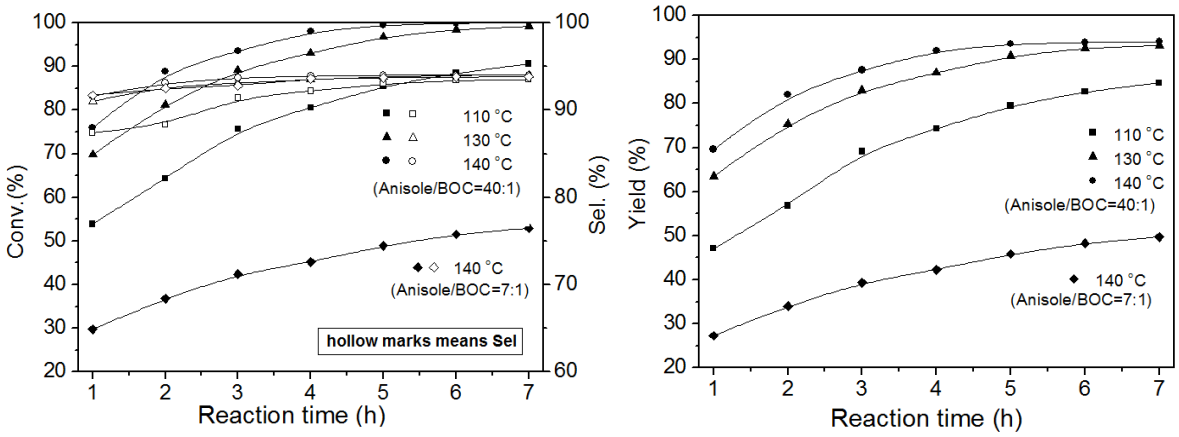

Fig. S9 Effect of reaction temperature, time and anisole/BOC ratio on the benzoylation activity of anisole with BOC over PMH-0.025Zr. Reaction conditions: anisole (108 mmol)/BOC (2.65 mmol) = 40:1 or, anisole (108 mmol): BOC (15.88 mmol) = 7:1, $W_{cat.}$ = 0.2 g, *n*-tetradecane 0.1 g (GC internal standard).

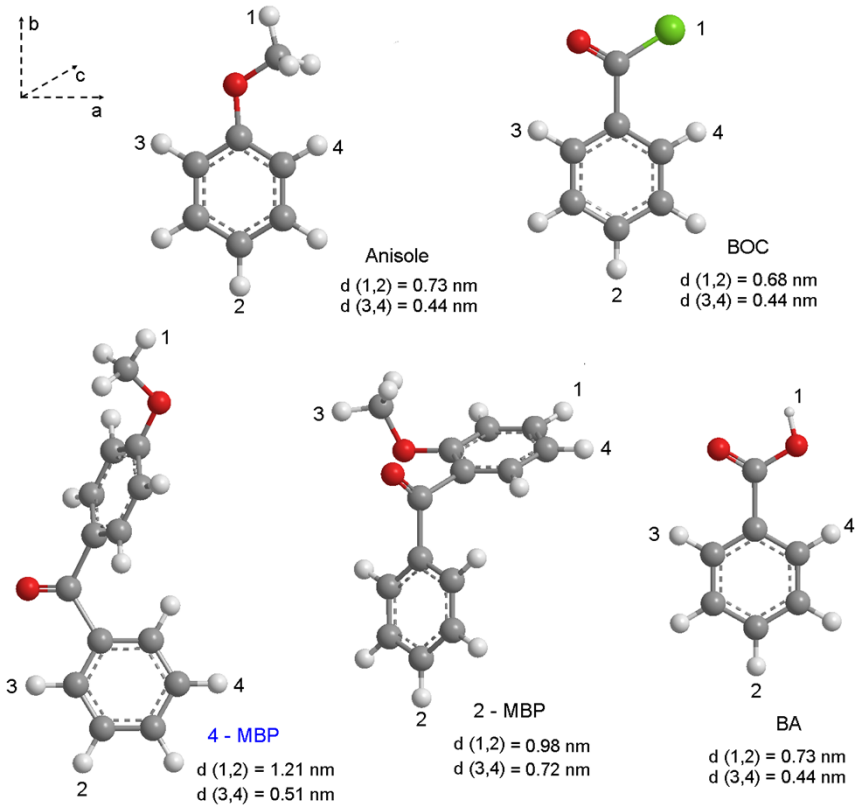

Fig. S10 Three-dimensional reactants and products with corresponding interatomic distances.

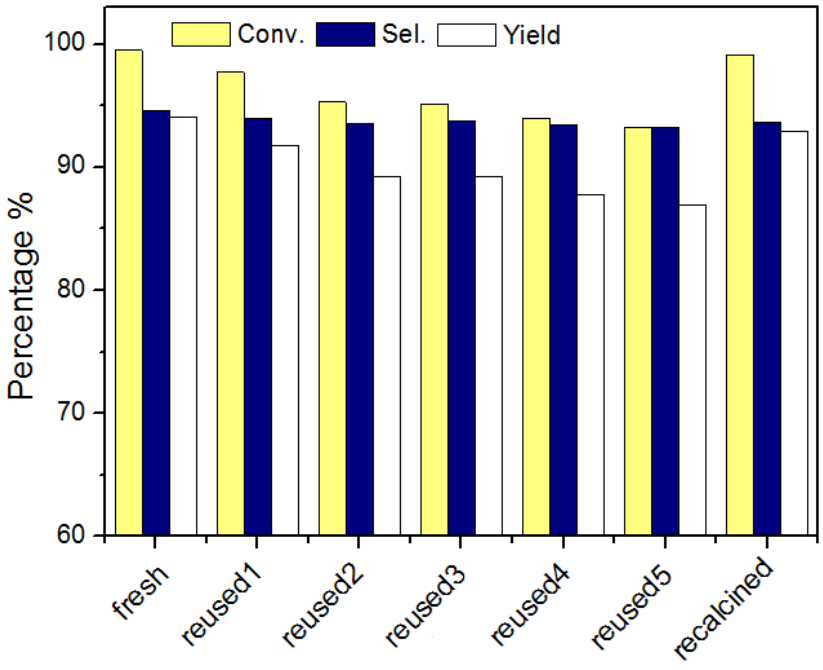

Fig. S11 Recyclability of PMH-0.1Zr for the benzoylation of anisole with BOC. Reaction conditions: anisole 108 mmol, BOC 2.65 mmol, $W_{cat.}$ 0.2 g, *n*-tetradecane 0.1 g, 140 °C, 3 h.

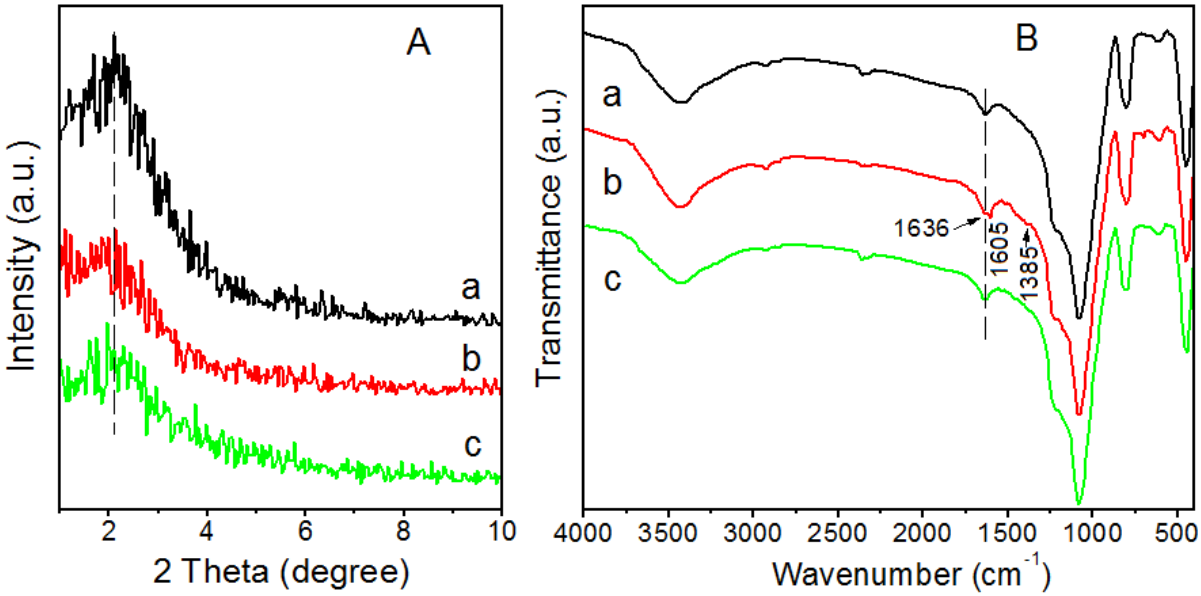

Fig. S12 XRD patterns (A) and FTIR spectra (B) of PMH-0.1Zr (a), PMH-0.1Zr-reused5 (b) and PMH-0.1Zr-recalcined (c).

Table S1 Chemical compositions of synthetic magadiite, QM, PMH and PMH-*x*Zr samples.

Samples	wt.% [a]				Molecular formula [c]	Feeding Zr/Si	Bulk Zr/Si [d]	Gallery Zr/Si [e]
	Na_2O	SiO_2	ZrO_2	H_2O [b]				
Na-magadiite	5.6	78.9	-	15.5	$Na_{1.9}Si_{14}O_{29}\cdot 9.2H_2O$	-	-	-
QM	-	56.9	-	2.9	$(C_{19}H_{43}N)_{2.1}Si_{14}O_{29}\cdot 2.38H_2O$	-	-	-
PMH	-	99.3	-	-	$(SiO_2)_{28.56}H_2Si_{14}O_{29}$	-	-	-
PMH-0.0125Zr	-	97.1	2.5	-	$(SiO_2)_{27.61}(ZrO_2)_{0.52}H_2Si_{14}O_{29}$	0.0125	0.013	0.017
PMH-0.025Zr	-	95.1	4.1	-	$(SiO_2)_{21.66}(ZrO_2)_{0.75}H_2Si_{14}O_{29}$	0.025	0.021	0.035
PMH-0.05Zr	-	92.0	7.2	-	$(SiO_2)_{20.50}(ZrO_2)_{1.31}H_2Si_{14}O_{29}$	0.05	0.038	0.064
PMH-0.1Zr	-	88.8	10.1	-	$(SiO_2)_{10.22}(ZrO_2)_{1.34}H_2Si_{14}O_{29}$	0.1	0.056	0.131
PMH-0.2Zr	-	76.1	20.2	-	-	0.2	0.130	-

[a] Based on EDS results. [b] Based on TG results. [c] Molecular formulae of porous clay heterostructures were calculated based on EDS and TG results, assuming that the transformation into porous clay heterostructures would not change the original layer structure of parent clay according to previous work (M. Polverejan, Y. Liu, T.J. Pinnavaia, *Chem. Mater.* 2002, **14,** 22831; Q. Sun, C. Zhang, H. Sun, H. Zhang, *Ind. Eng. Chem. Res.*, 2014, **53**, 12224), such as for QM, the empirical formula was estimated upon the empirical formula of magadiite, assuming that the amount of Na^+ ions exchanged for $CTMA^+$ corresponds to cation exchange capacity of clay, and the obtained amount of interlayer $C_{19}H_{42}N^+$ is in agreement with the TG result of 40.1 wt.%. [d] Bulk Zr/Si = [total Zr]/[total Si]. [e] Gallery Zr /Si = [total Zr]/[gallery Si].

Table S2 Deconvolution of ^{29}Si MAS NMR spectra of the catalysts: chemical shift values, relative portions (%) and $(Q^2+Q^3)/Q^4$ ratios.

Sample	Chemical shift, ppm			$(Q^2+Q^3)/Q^4$ Ratio
	Q^2 (%) [a]	Q^3 (%) [a]	Q^4 (%) [a]	
PMH	-92.3 (3.3)	-102.0 (21.2)	-111.1 (75.5)	0.32
PMH-0.0125Zr	-92.4 (5.3)	-103.1 (23.4)	-111.4 (71.3)	0.40
PMH-0.05Zr	-92.6 (5.6)	-101.7 (24.5)	-110.8 (69.9)	0.43
PMH-0.1Zr	-91.6 (3.9)	-102.5 (29.0)	-111.2 (67.1)	0.49
PMH-0.2Zr	-91.4 (5.8)	-101.7 (19.0)	-111.4 (75.2)	0.33

[a] Relative portion in the parentheses.

Table S3 The XPS data of PMH and PMH-*x*Zr catalysts.

Catalysts	O 1s		$A_{Si\text{-}O\text{-}Si}/A_{Si\text{-}O\text{-}Zr}$ [a]	Zr 3d		$A_{3d5/2}/A_{3d3/2}$	Si 2p	Si/Zr ratio[b]	Zr/Si ratio[b]
	Si-O-Si	Si-O-Zr		$3d_{3/2}$	$3d_{5/2}$				
PMH	532.99	-	-	-	-	-	102.83	-	-
PMH-0.0125Zr	533.04	530.68	25	185.83	183.45	2.9	102.84	81.5 (76.9)	0.0123 (0.013)
PMH-0.025Zr	533.03	530.63	21	185.96	183.56	1.9	102.84	86.4 (47.6)	0.0116 (0.021)
PMH-0.05Zr	532.87	530.67	18	185.57	183.27	3.0	102.68	22.0 (26.3)	0.045 (0.038)
PMH-0.1Zr	532.76	530.76	5.3	185.72	183.47	2.9	102.61	12.9 (17.9)	0.077 (0.056)
PMH-0.2Zr	532.79	530.97	5.6	185.66	183.32	1.9	102.54	5.6 (7.7)	0.179 (0.130)

[a] Peak area ratio of two components corresponding to Si-O-Si and Si-O-Zr upon deconvoluted spectra. [b] Data in parentheses from EDX..