Supporting Information

Highly Active, Water-Compatible and Easily Separable Magnetic Mesoporous Lewis Acid Catalyst for Mukaiyama-Aldol Reaction in Water

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Experimental section

1. Synthesis of SO_3Na-functionalized magnetic mesoporous silica support (SO_3Na-MCMSS)

0.20 g $SiO_2@Fe_3O_4$ particles were dispersed in a aqueous solution containing 0.64 g CTAB, 100 ml deionized water, 2.0 ml ammonia solution (28 wt %), and 140 ml ethanol. This mixture was ultrasonicated for 30 min and then mechanically stirred for another 30 min. Then, 0.625 ml TEOS was added dropwise to the above solution. After pre-hydrolysis for 30 min, 0.116 ml mercaptopropyltrimethoxysilane (MPTS) was introduced. After stirring for 12 h at 25^{o}C, the products were collected with a magnet and washed repeatedly with ethanol and water. Finally, CTAB template was removed by repeated ethanol extraction under reflux condition. Next, 0.20 g solid

sample was suspended into 30 ml H_2O_2 solution and stirred for 24 h. The obtained solid was washed and then added into 30 ml saturated NaCl solution for ion-exchange treatment, resulting in sodium propylsulphonate functionalized magnetic core-mesoporous silica shell composite.

1.2 Preparation of SO_3Na&Ph co-functionalized magnetic core-silica shell support (SO_3Na&Ph-MCSS)

Briefly, 0.20 g $SiO_2@Fe_3O_4$ was dispersed in 20 ml anhydrous toluene, followed by adding dropwise 0.12 ml MPTS and 0.12 ml PhTS under mechanical stirring. After being refluxed under an N_2 atmosphere for 24 h, the solid product was filtered and washed thoroughly with toulene and CH_2Cl_2, leading to SO_3Na&Ph co-functionalized magnetic core-silica shell composite.

1. 3 Synthesis of SO_3Na&Ph co-functionalized MCM-41 support (SO_3Na&Ph-MCM-41)

0.16 g CTAB was dissolved in 10 ml H_2O containing 6.0 g 28 wt% ammonia solution at 40^{o}C, subsequently added 1.25 ml TEOS and stirred for 30min. Then, 0.232 ml MPTS and 0.234 ml PhTS were added into the solution and stirred at 40^{o}C for another 1.5 h. The mixture was transferred into an autoclave and kept at 100^{o}C for 15 h. The white precipitate was filtrated and washed thoroughly with water, following by vacuum drying at 80^{o}C overnight. The surfactant and other organic residues were removed by refluxing 500 ml ethanol solution containing 0.50 M HCl at 80^{o}C for 24 h.

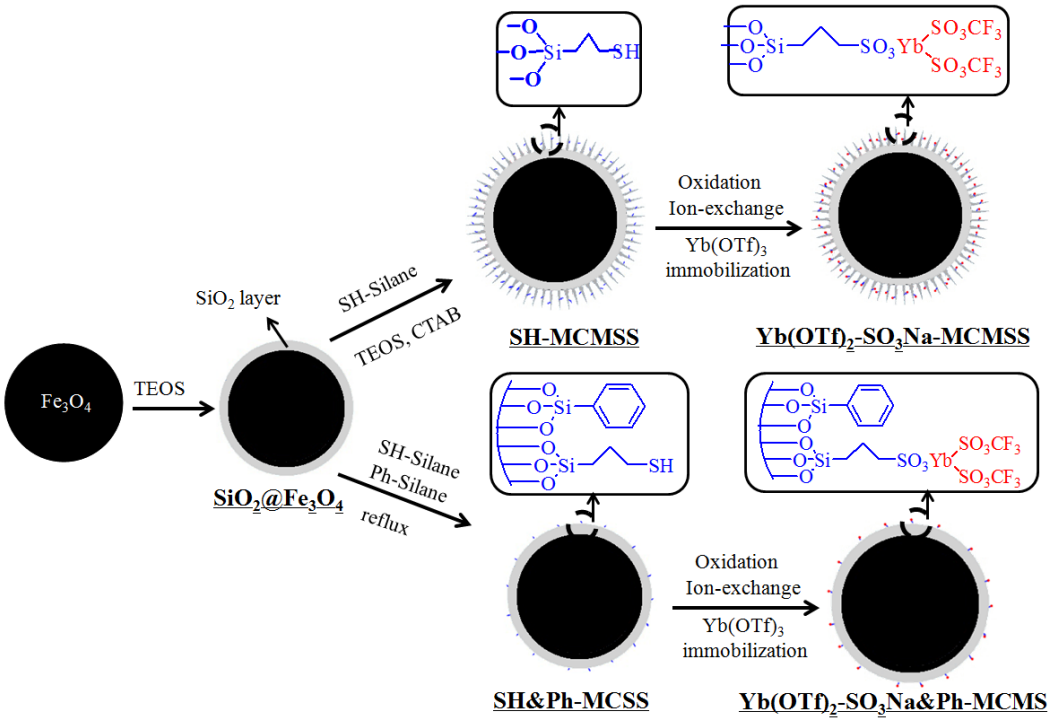
The obtained solid was washed and then added into 30 ml saturated NaCl solution for ion-exchange treatment, resulting in sodium propylsulphonate and phenyl co-functionalized mesoporous support.

1.4 Preparation of SO_3Na-functionalized Amberlyst-15 resin (SO_3Na-Amberlyst-15)

1.0 g Amberlyst-15 sample was directly added into 30 ml saturated NaCl solution for ion-exchange treatment, leading to sodium propylsulphonate functionalized Amberlyst-15.

1.5 Fabrication of $Yb(OTf)_2$-SO_3Na-MCMSS, $Yb(OTf)_2$-SO_3Na&Ph-MCSS, $Yb(OTf)_2$-SO_3Na&Ph-MCM-41 and $Yb(OTf)_2$-SO_3Na-Amberlyst-15 catalysts

0.20 g different functionalized supports were suspended into 30 ml ethanol containing 0.50 g $Yb(OTf)_3$, respectively. After being stirred for 12 h, the black powder product was filtered and washed thoroughly with absolute ethanol to eliminate un-coordinated $Yb(OTf)_3$, followed by vacuum drying at 60^{o}C for 24 h.



Scheme S1 Illustration of the synthetic procedures of $Yb(OTf)_2$-SO_3Na-MCMSS and $Yb(OTf)_2$-SO_3Na&Ph-MCSS catalysts.

Table S1 The optimization of sulfur content in the $Yb(OTf)_2$-SO_3Na&Ph-MCMSS catalyst

Entry	Molar ratio of TEOS and MPTS	Sulfur content (mmol/g)
1	15 : 1	0.40
2	7.0 : 1	0.84
3	4.3 : 1	1.39
4	3.0 : 1	1.41

Table S2 The optimization of Yb loading in the $Yb(OTf)_2$-SO_3Na&Ph-MCMSS catalyst

Entry	$Yb(OTf)_3$ amount (mg)	Molar ratio of Yb and S	Solvent	Yb loading (mmol/g)
1	43.6	1 : 1	EtOH	0.154
2	86.8	2 : 1	EtOH	0.201
3	130	3 : 1	EtOH	0.217
4	43.6	1 : 1	H_2O	0.176
5	86.8	2 : 1	H_2O	0.265
6	130	3 : 1	H_2O	0.281

Table S3 Catalytic performances of different samples in water-medium Sonogashira reactions.[a]

Catalyst	Conversion (%)	Selectivity (%)	Yield (%)
SiO_2@Fe_3O_4 [b]	/	/	/
SH&Ph-MCMSS [b]	/	/	/
Yb(OTf)$_2$-SO_3Na&Ph-MCM-41	87.4	99	87.3
Yb(OTf)$_2$-SO_3Na-Amberlyst-15	77.5	99	77.4

[a] Reactions conditions: 0.50 mmol benzaldehyde, 1.0 mmol silane, 0.050 mmol Yb, 3.0 ml water, 20^{o}C, 16 h; [b] 100 mg sample.

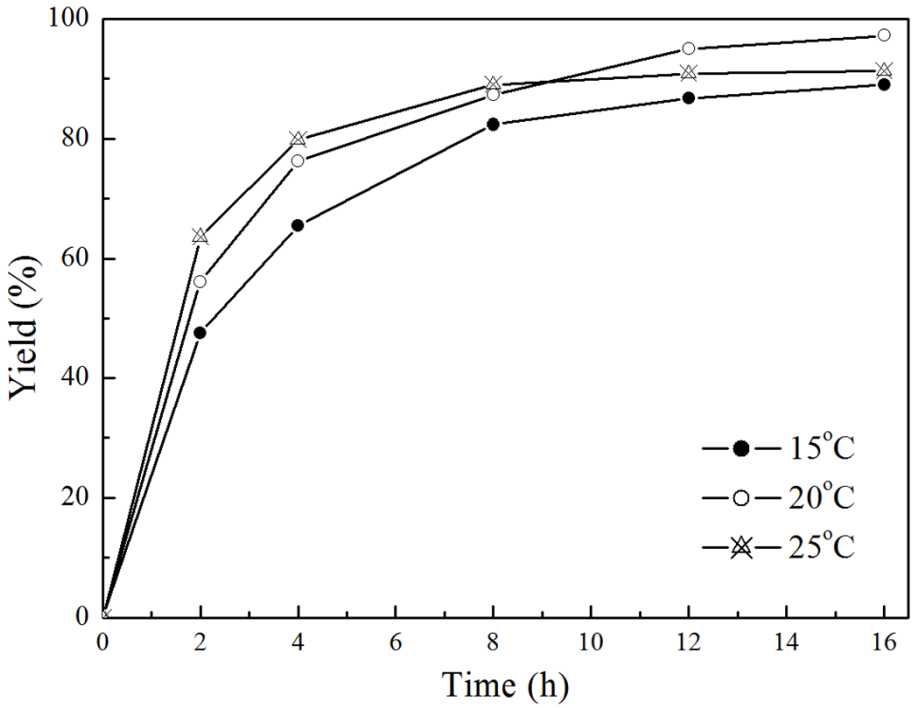


Figure S1 Dependence of yield on the reaction temperature over $Yb(OTf)_2$-SO_3Na&Ph-MCMSS catalyst in water-medium Mukaiyama-aldol reaction between benzaldehyde and trimethyl(1-phenylprop-1-enyloxy)silane. Reaction conditions are given in Table 2.

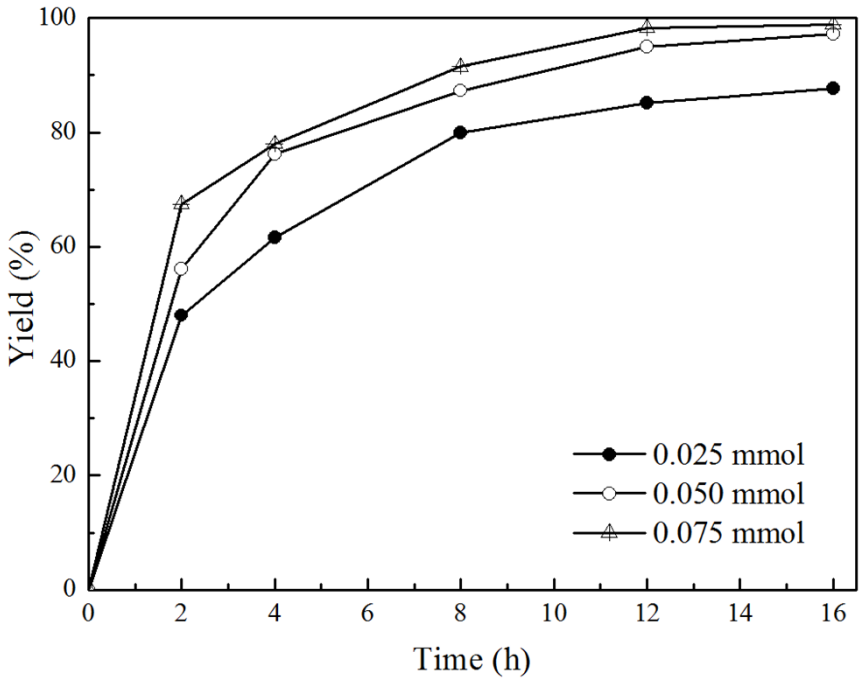


Figure S2 Dependence of yield on the different Yb loading over $Yb(OTf)_2$-SO_3Na&Ph-MCMSS catalyst in water-medium Mukaiyama-aldol reaction between benzaldehyde and trimethyl(1-phenylprop-1-enyloxy)silane s. Reaction conditions are given in Table 2.

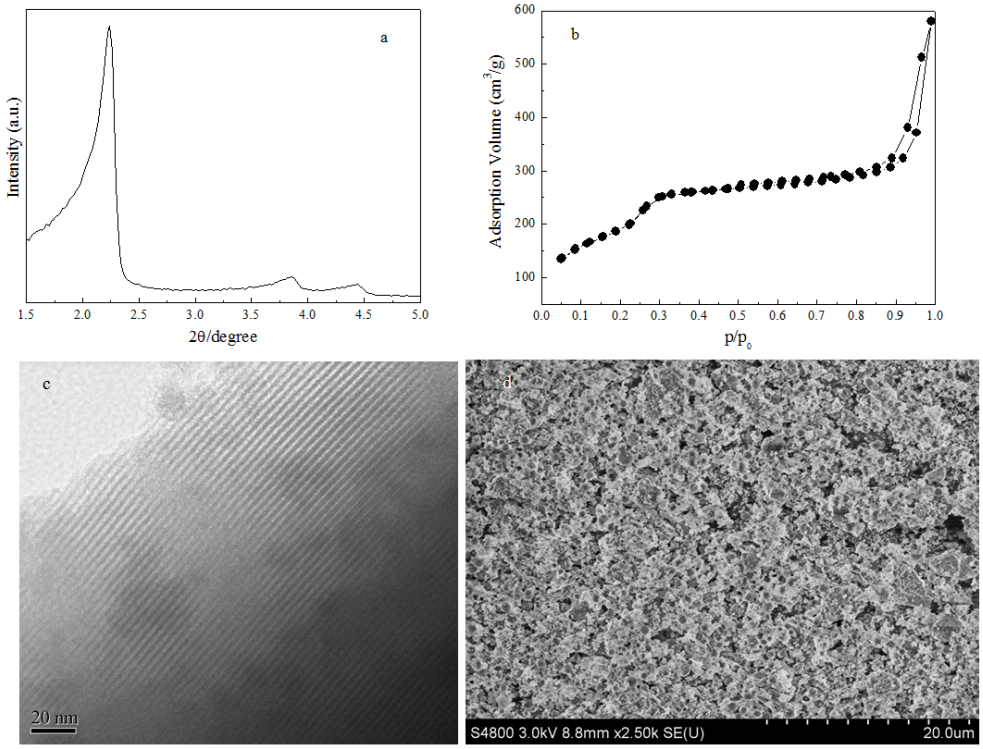


Figure S3 XRD pattern (a), N_2 sorption isotherm (b), TEM image (c) and SEM picture (d) of $Yb(OTf)_2$-SO_3Na&Ph-MCM-41 sample.

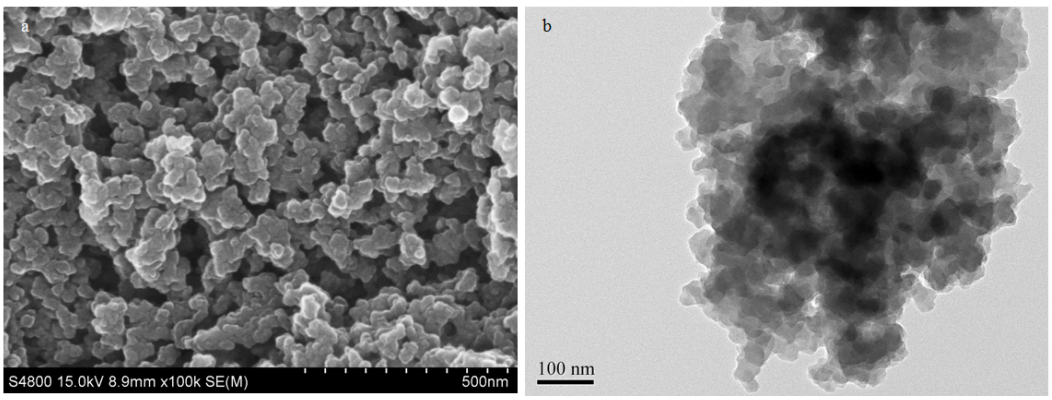


Figure S4 SEM image (a) and TEM picture (b) of $Yb(OTf)_2$-SO_3Na-Amberlyst-15 sample.

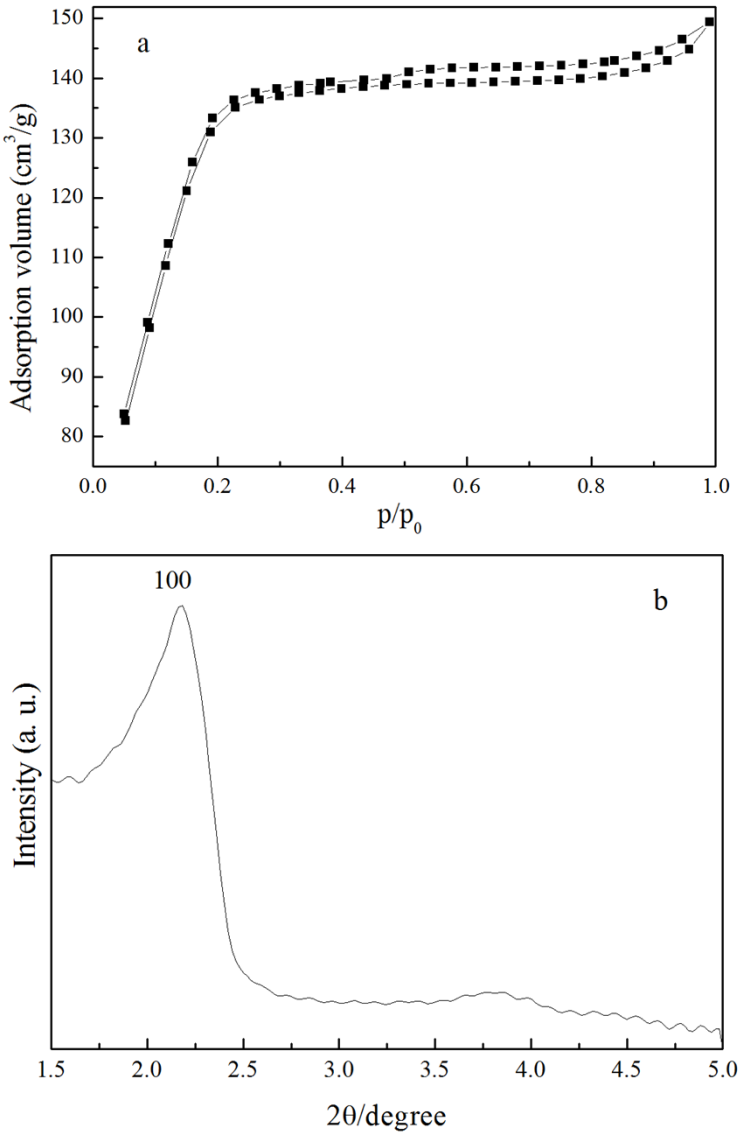


Figure S5 N_2 sorption curve (a) and low-angle XRD pattern (b) of the recycled $Yb(OTf)_2$-SO_3Na&Ph-MCMSS catalyst after six runs.

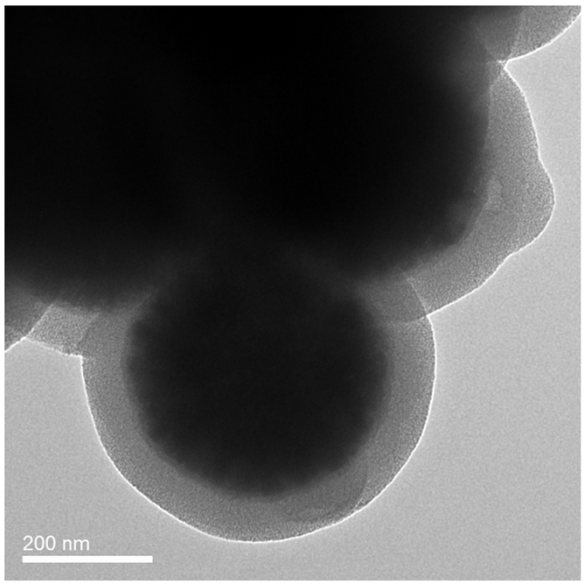


Figure S6 TEM image of the recycled $Yb(OTf)_2$-SO_3Na&Ph-MCMSS catalyst after six repetitions.