Supporting Information

An Extremely Stable and Highly Active Periodic Mesoporous Lewis Acid Catalyst in Water-Medium Mukaiyama-aldol Reaction

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Experimental section

Sample preparation

Synthesis of $NaSO_3$-Ph-SBA-15

$NaSO_3$-Ph-SBA-15 was prepared through a two-step process. Firstly, $PhSO_3Cl$-functionalized SBA-15 was synthesized via the co-condensation of 2-(4-chlorosulphonylphenyl)ethyl trimethoxylsilane (CSPTS) and tetraethyl orthosilicate (TEOS). In a typical synthesis, 1.95 ml TEOS were added into an aqueous solution comprised of 32 ml 2.0 M HCl and 1.0 g of P123 at 40^{o}C. After stirring for 1.0 h, 0.32 ml CSPTS was added into the reaction mixture and allowed to stir for 20h. Then, the mixture was transferred into a Teflon bottle at 100^{o}C for another 24 h. The resulting solid was filtered off and washed with water and ethanol. The surfactant was removed by extraction with ethanol, followed by drying in vacuum. Finally, the ion-exchange treatment similar to was used for the synthesis of $NaSO_3$-Ph-SBA-15 following the same procedure used for the preparation $NaSO_3$-Ph-PMO.

Preparation of $(OTf)_2Sc$-SO_3-Ph-SBA-15

Generally, 1.0 g $NaSO_3$-Ph-SBA-15 was suspended into 35 ml ethanol containing

0.50 g $Sc(OTf)_3$. After being stirred for 24 h at 60^{o}C, the powder product was filtered and washed thoroughly with freshly absolute ethanol to eliminate un-chelated Sc(III) complex, followed by vacuum drying at 80^{o}C.

Table S1 Catalytic performances of various $(OTf)_2RE\text{-}SO_3\text{-}Ph\text{-}PMO$ in water-medium Mukaiyama-aldol reaction[a]

Catalyst	RE loading (mmol/g)	Conversion (%)	Selectivity (%)	Yield (%)
$(OTf)_2Sc\text{-}SO_3\text{-}Ph\text{-}PMO$	0.24	99	90	89
$(OTf)_2La\text{-}SO_3\text{-}Ph\text{-}PMO$	0.22	88	89	77
$(OTf)_2Ce\text{-}SO_3\text{-}Ph\text{-}PMO$	0.23	92	86	77
$(OTf)_2Sm\text{-}SO_3\text{-}Ph\text{-}PMO$	0.24	93	90	84

[a]Reaction conditions: 1.0 mmol trimethyl(1-phenylprop-1-enyloxy)silane, a catalyst containing 0.050 mmol Sc, 10 mmol HCHO in 37% aqueous solution, 3.0 ml H_2O, T = 10°C, t = 12 h.

Table S2 Catalytic performances of $(OTf)_2Sc\text{-}SO_3\text{-}Ph\text{-}PMO$ with different catalyst amounts and trimethyl(1-phenylprop-1-enyloxy)silane/HCHO ratios in water-medium Mukaiyama-aldol reaction[a]

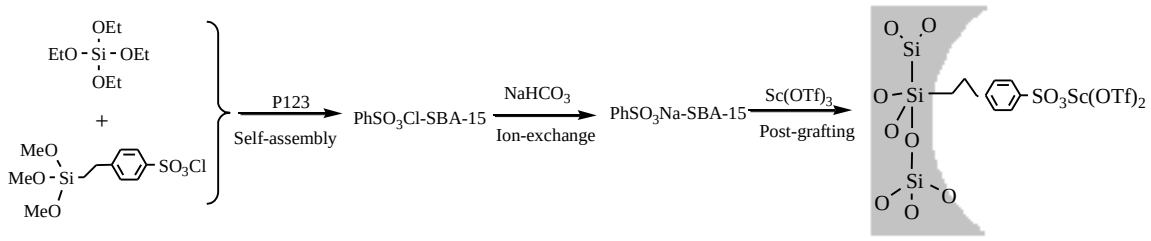
Sc content (mmol)	HCHO content (mmol)	Conversion (%)	Selectivity (%)	Yield (%)
0.025	10	79	97	77
0.050	10	99	90	89
0.075	10	100	81	81
0.050	5.0	90	87	79
0.050	15	98	87	85

[a]Reaction conditions: 1.0 mmol trimethyl(1-phenylprop-1-enyloxy)silane, desired amount of catalyst and 37% HCHO aqueous solution, 3.0 ml H_2O, T = 10°C, t = 12 h.

Table S3. Catalytic performances of $(OTf)_2Sc\text{-}SO_3\text{-}Ph\text{-}PMO$ with different Sc loadings in water-medium Mukaiyama-aldol reaction[a]

Sc loading (mmol/g)	Conversion (%)	Selectivity (%)	Yield (%)
0.093	92	80	74
0.18	94	82	77
0.24	99	90	89

[a]Reaction conditions are given in Table S1.



Scheme S1 Illustration of $(OTf)_2Sc\text{-}SO_3\text{-}Ph\text{-}SBA\text{-}15$ preparation.

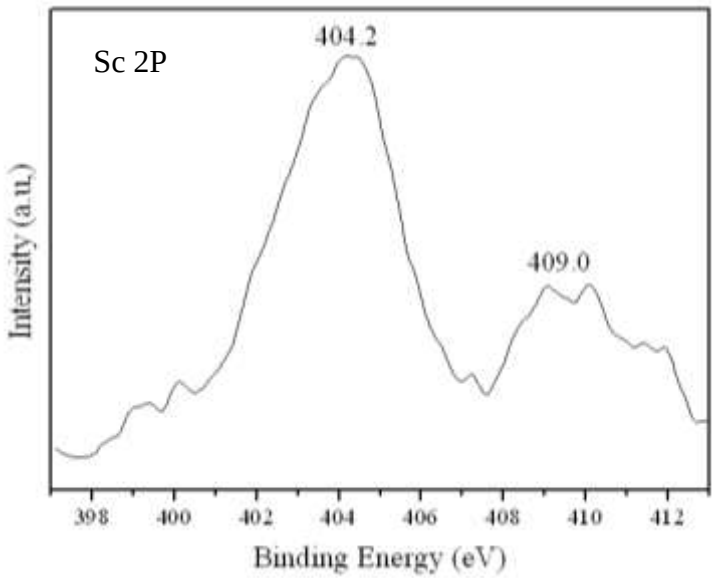


Fig. S1 XPS spectrum of the $(OTf)_2Sc\text{-}SO_3\text{-}Ph\text{-}SBA\text{-}15$.

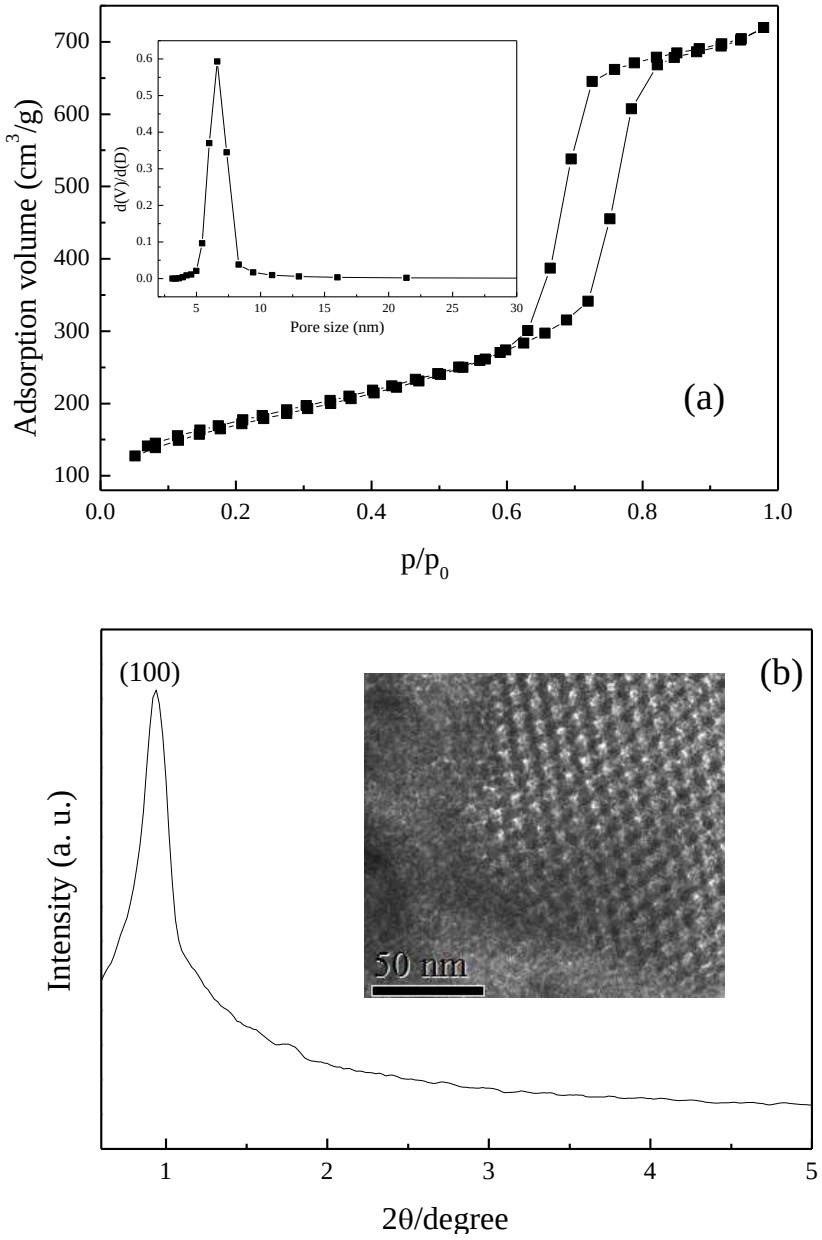


Fig. S2 (a) N_2 sorption isotherm and pore size distribution (inset), and (b) low-angle XRD pattern and TEM image (inset) of $(OTf)_2Sc\text{-}SO_3\text{-}Ph\text{-}SBA\text{-}15$.

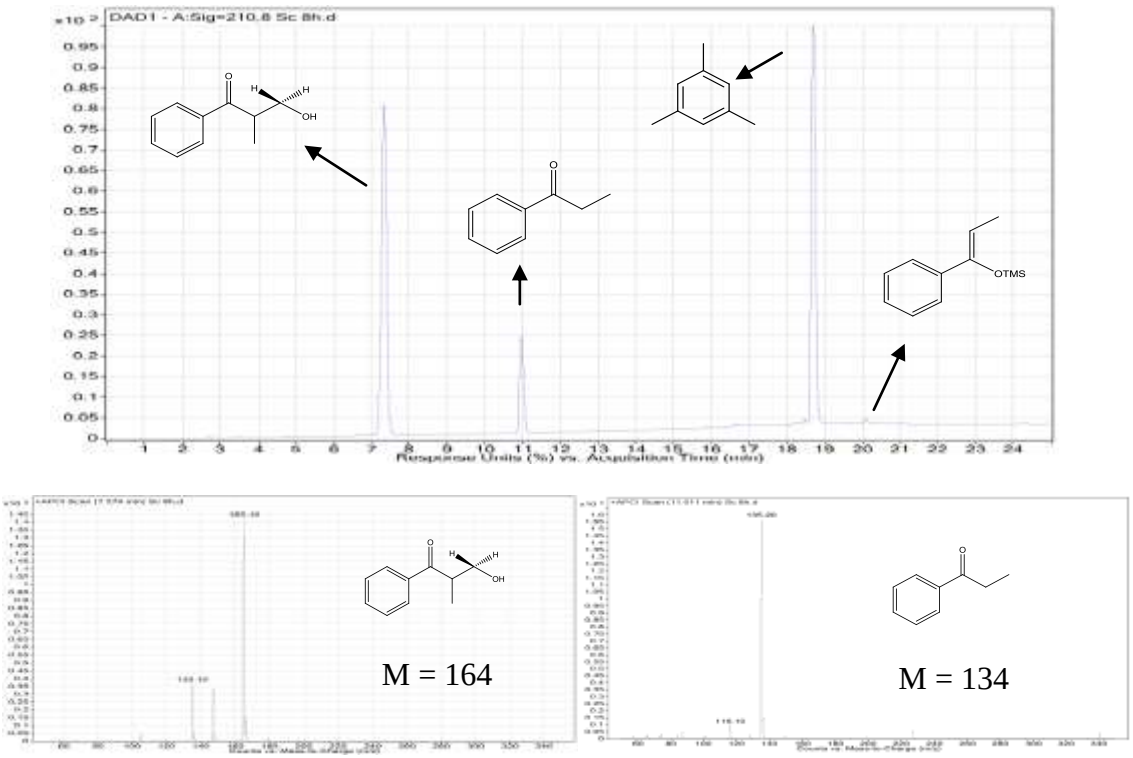


Fig. S3 HPLC/MS product analysis in water-medium Mukaiyama-aldol reaction between HCHO and trimethyl(1-phenylprop-1-enyloxy)silane over the $(OTf)_2Sc\text{-}SO_3\text{-}Ph\text{-}PMO$ catalyst.

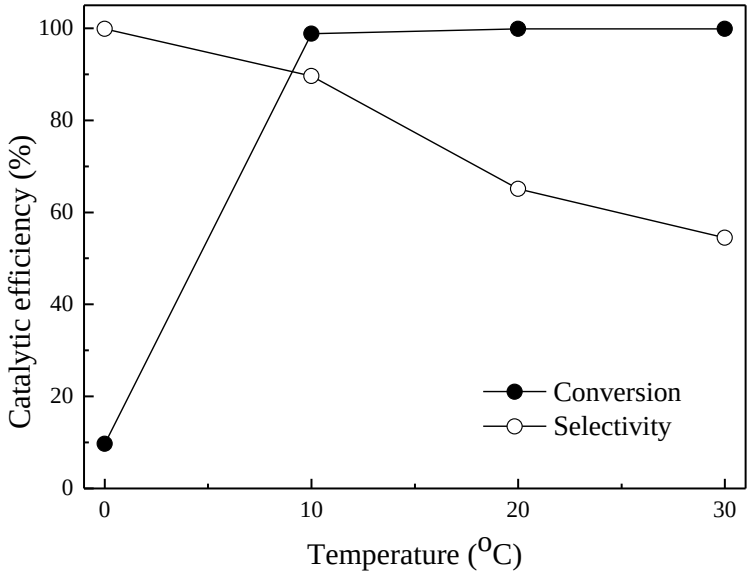


Fig. S4 Dependence of conversion and selectivity on the reaction temperature in water-medium Mukaiyama-aldol reaction between HCHO and trimethyl(1-phenylprop-1-enyloxy)silane over $(OTf)_2Sc\text{-}SO_3\text{-}Ph\text{-}PMO$ catalyst. Reaction conditions are given in Table 1.

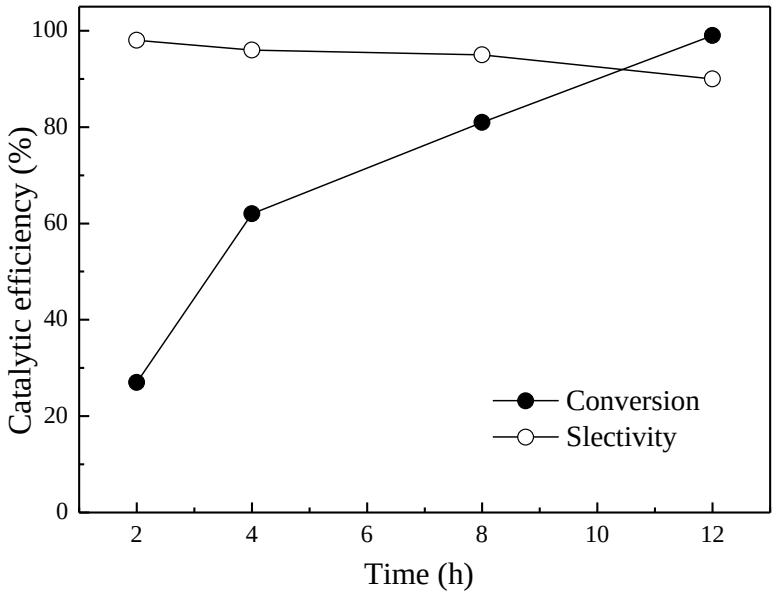


Fig. S5 Dependency of trimethyl(1-phenylprop-1-enyloxy)silane conversion on reaction time over $Sc(OTf)_3$ in the water/organic solvent mixture system. Reaction condition: 0.050 mmol Sc(III) catalyst, 1.0 mmol trimethyl(1-phenylprop-1-enyloxy)silane, 10 mmol aqueous 37% HCHO, 2.7 ml H_2O, 0.3 ml THF, T = 10^{o}C.

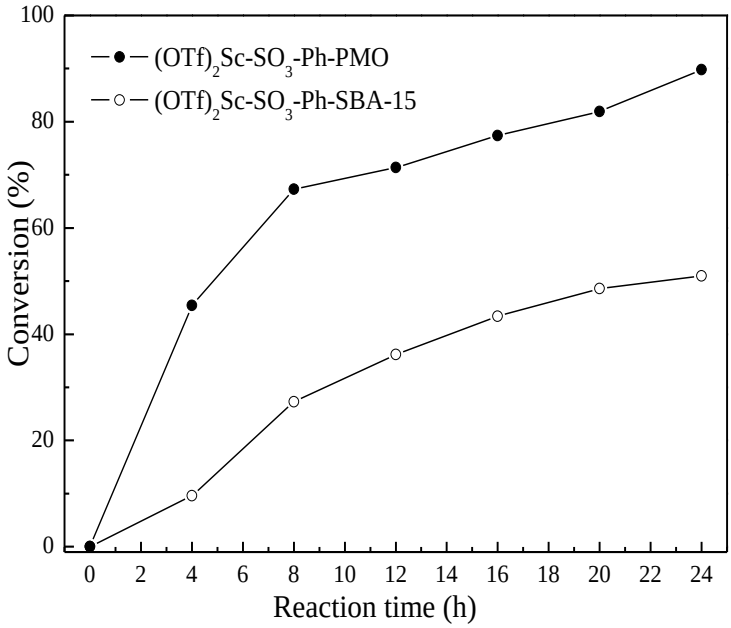


Fig. S6 Dependence of benzaldehyde conversion on reaction time over $(OTf)_2Sc\text{-}SO_3\text{-}Ph\text{-}PMO$ and $(OTf)_2Sc\text{-}SO_3\text{-}Ph\text{-}SBA\text{-}15$ catalysts. Reaction conditions: 1.0 mmol trimethyl(1-phenylprop-1-enyloxy)silane, 0.50 mmol benzaldehyde, a catalyst containing 0.025 mmol Sc^{3+}, 3.0 ml H_2O, T = 10°C.