Supplementary Information

“Design of Brønsted acidic ionic liquid functionalized mesoporous organosilica nanospheres for efficient synthesis of ethyl levulinate and levulinic acid from 5-hydroxymethylfurfural”
Catalyst preparation

CTAB-directed \([\text{C}_3\text{PrIm}]\text{OTf}\)-MONSs catalysts. At first, \(CTAB \text{ PrCl-MONSs}\) support was fabricated by using a liquid-interface assembly strategy via one-pot CTAB-directed sol–gel co-condensation process in oil-in-water (O/W) emulsion. Typically, CTAB (0.3 g) was dissolved in a mixed solution of ammonia (\(\text{NH}_4\text{OH}, 2 \text{ mL, 25 wt}\%\)), water (80 mL) and ethanol (EtOH, 40 mL), and the resulting colloidal solution was stirred at 550 rpm continuously for 20 min at 30 °C. Additionally, cyclohexane (20 mL) contained 1,2-bis(trimethoxysilyl)ethane (BTMSE, 0.35 mL) and 3-chloropropyltrimethoxysilane (CPTMS, 0.25 mL) mixture was slowly added to the above CTAB-water-EtOH-NH\(_4\)OH solution, and the co-hydrolysis and -condensation of BTMSE and CPTMS was lasted for a period of 6, 12 or 24 h at 30 °C. The resulting mixture was transferred to an autoclave and heated to 120 °C (ramping rate of 2 °C min\(^{-1}\)) and held for 5 h. Afterwards, the cooled product was collected by centrifugation, and then it was suffered from air drying at 40, 80 and 100 °C for 6 h, successively. The resulting powder was recovered after removing CTAB and keeping the filtrate neutral by water washing for several times at 60 °C and boiling ethanol washing for 3 times. The final product was dried at 100 °C for 12 h, and it was denoted as \(CTAB \text{ PrCl-MONSsx}\), where \(x = 6, 12\) and 24, referring to the hydrolysis time of organosilica precursors of 6, 12 and 24 h. The molar ratios of the aforementioned starting materials were CTAB 0.82: \(\text{NH}_4\text{OH}\) 11.29: cyclohexane 190: EtOH 690: \(\text{H}_2\text{O}/\text{water}\) 4444: BTMSE 1.35: CPTMS 1.35.

Subsequently, \(CTAB \text{ PrCl-MONSs}\) was functionalized by BAILs based on following steps. \(CTAB \text{ PrCl-MONSs}(0.32 \text{ g})\) was dispersed to a mixture of toluene (10 mL) and imidazole (0.092 g), and continuous stirring was applied for 24 h at 110 °C. Afterwards, the powder was
recovered by centrifugation and dried at 100 °C after removing extra imidazole by washing with dichloromethane for five times. The obtained powder (CTAB PrIm-MONSs) was dispersed to toluene solvent (10 mL) again, and 1,3-propanesultone (0.165 g) was added to the suspension, followed by stirring for 8 h at 110 °C. Next, after the suspension was cooled to room temperature, trifluoromethane sulfonic acid (HOTf, 0.092 g) was added, and the mixture thus obtained was stirred for additional 12 h at 60 °C. The final product was obtained after successive treatment including centrifugation, washing with hot toluene and then dichloromethane (to remove completely the adsorbed acidic compounds) followed by drying at 80 and 100 °C for 6 h, respectively. The product was denoted as CTAB [C₃PrIm][OTf]-MONSsx (x = 6, 12 and 24), where C₃ = PrSO₃H, Im = imidazole and OTf = SO₃CF₃.

**Other surfactant-directed [C₃PrIm][OTf]-MONSs catalysts.** The preparation procedure is similar to that of the CTAB-directed [C₃PrIm][OTf]-MONSs₁₂ catalyst, however, CTAB was replaced by CTAC, CPB or CTATOS (0.82 mmol). The product was denoted as CTAC [C₃PrIm][OTf]-MONSs₁₂, CPB [C₃PrIm][OTf]-MONSs₁₂ and CTATOS [C₃PrIm][OTf]-MONSs₁₂, respectively.

**CTAB PrSO₃H-MONSs catalyst.** The procedure is similar to that of the CTAB PrCl-MONSs₁₂, however, CPTMS was replaced by 3-mercaptopropyl trimethoxysilane (1.35 mmol, MPTMS). Afterwards, the resulting mercaptopropyl functionalized periodic mesoporous organosilica nanosphere was oxidized by excessive H₂O₂ solution (1.35 mL, 30%). The final product was denoted as CTAB PrSO₃H-MONSs₁₂. The composition of the precursor solution was CTAB 0.82: NH₄OH 11.29: cyclohexane 190: EtOH 690: H₂O 4444: BTMSE 1.35: MPTMS 1.35: H₂O₂ 13.5 (molar ratio).
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>N</th>
<th>S</th>
<th>F</th>
<th>N: S: F (atomic ratio)</th>
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<tr>
<td>CTAB [C₃PrIm][OTf]-MONSs¹²</td>
<td>3.21</td>
<td>3.54</td>
<td>5.35</td>
<td>2.00: 2.20: 3.33</td>
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<tr>
<td>CTAC [C₃PrIm][OTf]-MONSs¹²</td>
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<td>4.24</td>
<td>2.00: 1.85: 2.82</td>
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<td>CPB [C₃PrIm][OTf]-MONSs¹²</td>
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<td>3.36</td>
<td>5.00</td>
<td>2.00: 2.02: 3.00</td>
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<td>CTATOS [C₃PrIm][OTf]-MONSs¹²</td>
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<td>5.21</td>
<td>2.00: 2.06: 2.72</td>
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</table>

Table S1: Contents of nitrogen, sulphur and fluorine elements (At.%)) and the corresponding atomic ratios in various [C₃PrIm][OTf]-MONSs catalysts.
Scheme S1 Reaction mechanisms of the synthesis of (a) EL from the ethanolysis of HMF and (b) LA from hydrolysis of HMF catalyzed by the [C₃PrIm][OTf]-MONSs.
Scheme S2 Carbon balances in the ethanolysis (a) and hydrolysis (b) of HMF catalyzed by CTATOS $[C_3PrIm][OTf]$-MONSs12 under the conditions of $n_{\text{EtOH}}$: $n_{\text{HMF}}$ molar ratio of 248, 120 °C and 240 min (a) and $n_{\text{H}_2\text{O}}$: $n_{\text{HMF}}$ molar ratio of 417, 140 °C and 240 min (b).
**Fig. S1** FESEM images and particle size distributions of $CTAB$ $[\text{C}_3\text{PrIm}][\text{OTf}]-\text{MONSs12}$ (a and a’), $CTAC$ $[\text{C}_3\text{PrIm}][\text{OTf}]-\text{MONSs12}$ (b and b’), $CPB$ $[\text{C}_3\text{PrIm}][\text{OTf}]-\text{MONSs12}$ (c and c’) and $CTATOS$ $[\text{C}_3\text{PrIm}][\text{OTf}]-\text{MONSs12}$ (d and d’).
Fig. S2 Nitrogen gas adsorption-desorption isotherms (a and c) and pore size distribution curves (b and d) of CTAB PrCl-MONSSs12 support, various [C₃PrIm][OTf]-MONSSs catalysts and CTAB PrSO₃H-MONSSs12.
Fig. S3 XPS whole spectra of $CTAB\ [C_{3}\text{PrIm}][\text{OTf}]-\text{MONSs12}$ (a), $CTAC\ [C_{3}\text{PrIm}][\text{OTf}]-\text{MONSs12}$ (b), $CPB\ [C_{3}\text{PrIm}][\text{OTf}]-\text{MONSs12}$ (c) and $CTATOS\ [C_{3}\text{PrIm}][\text{OTf}]-\text{MONSs12}$ (d).
**Fig. S4** GC-MS analysis results of ethanolysis of HMF to produce EL catalyzed by the \textit{CTATOS} [C$_3$PrIm][OTf]-MONSs\textbf{12} under different conditions (a and b), \textit{CATB} PrSO$_3$H-MONs\textbf{s12} (c) and HY zeolite (d). Reaction conditions: (a) 140 °C, \( n_{\text{EtOH}} : n_{\text{HMF}} = 248, 120 \text{ min} \); (b) 120 °C, \( n_{\text{EtOH}} : n_{\text{HMF}} = 124, 120 \text{ min} \); (c, d) 120 °C, \( n_{\text{EtOH}} : n_{\text{HMF}} = 248, 120 \text{ min} \).

HP6890GC-5973MSD was equipped with HP-5MS capillary column (30 m length, 0.25 mm \textit{i.d.}, 0.25 µm film thickness). The GC injector and MS ion source temperatures were 250 °C and 230 °C, respectively. The MS detector was operated in the EI mode at 70 eV with a scanning range of m/z 20–500.

Abundance

![Chart showing GC-MS analysis results](chart.png)
**Fig. S5** Arrhenius plot to determine the activation energy in *CTAB* [C₃PrIm][OTf]-MONSs₁₂-catalyzed ethanolysis reaction of HMF. 0.278 mmol HMF, 69 mmol EtOH, $n_{\text{EtOH}}: n_{\text{HMF}} = 248$, 120 min.

\[ E_a = 68.1 \text{ kJ/mol} \]
Fig. S6 HPLC-MS analysis result of hydrolysis of HMF to produce LA catalyzed by the CTATOS [C$_3$PrIm][OTf]-MONS$_{12}$ (a-c) and HY zeolite (d). (a) 140 °C, 120 min; (b) 160 °C, 120 min; (c) 140 °C, 240 min; (d) 30 mg HY zeolite, 140 °C, 120 min.
**Fig. S7** Catalytic activity and selectivity of $CTATOS\ [C_3PrIm][OTf]-\text{MONSs}\ 12$ in ethanolysis (a) and hydrolysis (b) of sugars. (a) 0.278 mmol sugar, 4 mL EtOH, $n_{\text{EtOH}}: n_{\text{sugar}} = 248$, 35 mg catalyst, 120 °C, 240 min; (b) 0.4 mmol sugar, 3 mL H$_2$O, $n_{\text{H}_2\text{O}}: n_{\text{sugar}} = 417$, 50 mg catalyst, 140 °C, 240 min.