Supporting Information

Heterogeneous hydroformylation of long-chain alkenes in IL-in-oil Pickering emulsion

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Characterization of water contact angles of solid materials

The sample tablets were prepared according to the method mentioned in literature S1. After drying at 100 °C in oven overnight, the silica nanospheres were pressed into tablets using a cylindrical stainless steel die of 1 cm in diameter under 10 MPa for 2 min. Water contact angle measurements were performed on KRÜSS DSA100 using water as testing liquid.

Fig. S1 TEM images of (a) DMSN-C18N-0.5, (b) DMSN-C18N-1.2 and (c) MCM-C18N-1.8.
Fig. S2 Nitrogen adsorption–desorption isotherms of DMSN-C18N-X (X= 0.5, 1.2).

Fig. S3 CLSM images of emulsion formed with (a) DMSN-C18N-0.5 and (b) DMSN-C18N-1.2 by dying [BMIM][BF₄] with rhodamine 6G (scale bar, 100 μm).
**Fig. S4** Photographs and microscopic images of emulsion systems with DMSN-C18N-X and MCM-C18N-1.8. Emulsion formation: 60 mg silica nanospheres, 1 mL of H\textsubscript{2}O (including Rh 3.0 \texttimes 10\textsuperscript{-3} mmol, P/Rh=15) and 1 mL of 1-dodecene. The emulsions were kept under static conditions for different time intervals (scale bar, 200 μm). (a) newly formed, (b) after 1 day, (c) after 3 days, (d) after 10 day.
Fig. S5 The photographs of IL-in-oil emulsion with DMSN-C18N-0.8 including different amount of tridecyl aldehyde (scale bar 200 μm). Emulsion formation: 60 mg of silica nanospheres, 1 mL of [BMIM][BF₄] (including Rh 4.5 ×10⁻³ mmol, P/Rh=15) and 1 mL of oil phase including desired amount of 1-dodecene and tridecyl aldehyde with molar ratio of (a) 1:0 (conversion of 0%), (b) 4:1 (conversion of 20%), (c) 3:2 (conversion of 40%), (d) 2:3 (conversion of 60%), (e) 1:4 (conversion of 80%). The emulsions were kept under static conditions for 10 minutes.

Fig. S6 Photographs and microscopic images of the Pickering emulsion formed with reused DMSN-C18N-0.8 at the beginning of each reaction cycle (scale bar, 200 μm).
Table S1 Comparison of the activity of hydroformylation of long chain alkenes with Rh-Sulfoxantphos as catalyst in biphase and emulsion systems

<table>
<thead>
<tr>
<th>System</th>
<th>Substrate</th>
<th>S/C</th>
<th>T (h)</th>
<th>Temp. (°C)</th>
<th>Conv. (%)</th>
<th>Sel. (%)</th>
<th>n/b</th>
<th>TOF (h⁻¹)</th>
<th>Ref.</th>
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<tr>
<td>Oil-[BMIM][PF₆] biphase</td>
<td>1-octene</td>
<td>1000</td>
<td>24</td>
<td>120</td>
<td>86</td>
<td>85</td>
<td>90:10</td>
<td>36</td>
<td>S2</td>
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<tr>
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<td>1-octene</td>
<td>3820</td>
<td>24</td>
<td>120</td>
<td>/</td>
<td>97</td>
<td>99:1</td>
<td>5</td>
<td>S3</td>
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<tr>
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<td>3000</td>
<td>48</td>
<td>120</td>
<td>13</td>
<td>100</td>
<td>97:3</td>
<td>24</td>
<td>S4</td>
</tr>
<tr>
<td>Water-oil microemulsion</td>
<td>1-dodecene</td>
<td>/</td>
<td>3</td>
<td>110</td>
<td>34</td>
<td>95</td>
<td>98:2</td>
<td>642</td>
<td>S5</td>
</tr>
<tr>
<td>Water-oil Pickering emulsion</td>
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<td>508</td>
<td>24</td>
<td>120</td>
<td>90</td>
<td>99</td>
<td>95:5</td>
<td>/</td>
<td>S6</td>
</tr>
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References


