Supplementary Information

Engineering mesoporous silica microspheres as hyper-activation supports for continuous enzymatic biodiesel production

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Fig. S1 Bradford standard curve.

\[ Y = 0.5746X + 1156 \]

\[ R^2 = 0.99 \]
Fig. S2 (A) TEM image and (B) DLS particle size distribution of LUDOX® AS-40 colloidal silica.
Fig. S3 Schematic illustration of the formation of tetrahedral (A) and octahedral (B) interstitial voids (red circles) by the close packing of equal-sized spherical particles (black circles).\(^1\) Considering the size of LUDOX\textsuperscript{®} AS-40 silica nanoparticles (around 24.3 nm, \(D\)), the diameters of the largest spheres that can fit into tetrahedral and octahedral interstitial voids are theoretically calculated to be 5.47 and 10.1 nm, respectively. However, the practical packing of silica nanoparticles is usually less dense than the close packing model, which leads to a relatively wide pore size distribution with peaks close to the calculated theoretical values.

\[
text{tetrahedral void: } d_t = 0.225D \\
\text{octahedral void: } d_o = 0.414D
\]
Fig. S4 FT-IR spectra of C₈-MSMs, pure lipase, and lipase-bound C₈-MSMs. Lipase from Candida rugosa was immobilized on C₈-MSMs via physical adsorption.
Fig. S5 (A) Nitrogen sorption isotherms and (B) Pore size distribution curves of C_{18}-MSMs loaded with 100 (black) and 300 (red) mg g\(^{-1}\) lipase.
Fig. S6 Photo illustrating continuous process for biodiesel production in an integrated continuous stirred tank reactor with three packed bed reactors (CSTR-PBRs) connected in series.
Table S1. Comparison of the catalytic performance of lipase immobilized on scalable supports.

<table>
<thead>
<tr>
<th>Lipase support</th>
<th>Loading amount (mg mg⁻¹)</th>
<th>Relative activity</th>
<th>Initial conversion rate</th>
<th>Activity retention in continuous reactions</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesoporous silica magnetic yolk–shell microspheres</td>
<td>~0.8–0.5</td>
<td>~1</td>
<td>not given</td>
<td>86%, 8 hours; 1.75% decrease per hour</td>
<td>2</td>
</tr>
<tr>
<td>magnetic hollow mesoporous silica microspheres</td>
<td>0.0952</td>
<td>&lt;1</td>
<td>90.0–96.3%</td>
<td>no continuous reaction</td>
<td>3</td>
</tr>
<tr>
<td>magnetic mesoporous silica spheres</td>
<td>not given</td>
<td>&lt;1</td>
<td>78.8%</td>
<td>no continuous reaction</td>
<td>4</td>
</tr>
<tr>
<td>silica-based monolithic foams</td>
<td>0.032</td>
<td>&lt;1</td>
<td>~50–40%</td>
<td>~37.5%, 60 days</td>
<td>5</td>
</tr>
<tr>
<td>zeolite-coated porous stainless steel support</td>
<td>0.05</td>
<td>&lt;0.5</td>
<td>~100%</td>
<td>no continuous reaction</td>
<td>6</td>
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<tr>
<td>rGO paper</td>
<td>not given</td>
<td>0.4</td>
<td>~12%</td>
<td>~60%, 6 days</td>
<td>7</td>
</tr>
<tr>
<td>C₁₈-mesoporous silica microspheres (C₁₈-MSMs)</td>
<td>0.1</td>
<td>1.14</td>
<td>99%</td>
<td>64%, 24 hours; 1.5% decrease per hour</td>
<td>This work</td>
</tr>
</tbody>
</table>

References


