Supplementary Materials

Size effects of the crystallite of ZSM-5 zeolites on the direct catalytic conversion of L-lactic acid to L,L-lactide

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Characterization procedure of ZSM-5 catalysts acidity

NH₃-TPD measurement was conducted on MFTP-3060 instrument. 100 mg of each catalyst was loaded into a slender quartz tube and dried at 350 °C for 1 h under a He flow (99.99%, 40 mL/min), and then cooled to 100 °C. The adsorption of NH₃/He (40 mL/min) for 30 minutes took place at 100 °C, after that the catalyst was purged with He (40 mL/min) at the same temperature for 5 minutes to remove the physically adsorbed NH₃ on the sample surface. TPD measurement was carried out in the range of 100 to 800 °C with He as the carrier gas at a heating rate of 10 °C/min. The desorbed NH₃ was detected by a thermal conductivity detector (TCD).

The characterization of the acidity of both Lewis and Bronsted sites was carried out by in situ IR using pyridine as a probe molecule. Rectangular self-supported wafer of the ZSM-5 sample was prepared to apply 5 MPa pressure, and its quality was recorded. The wafer sample was placed in the sample holder and vacuum treated until a pressure of 10⁻³ pa was reached, followed by activation at 400 °C to obtain a pressure of 10⁻⁴ pa. Add pyridine vapour in doses until the catalyst surface was saturated. Pyridine was then desorbed until a pressure of 10⁻³ pa was obtained to ensure that there is no more physisorbed pyridine on the wafers. IR spectra were recorded using a ThermoFisher Scientific RS20 instrument. The wafer containing chemisorbed pyridine was underwent thermal treatment at 150 °C, and the IR spectra were recorded in situ.

Figure S1. General lab-scale setup for lactide preparation.
Figure S2. Reaction progress using sample I as catalyst by $^1$H NMR in DMSO-d$_6$: The methine [-CH-CH$_3$] quartet region of various compounds in the reaction mixtures. Methine proton signals of A: lactide, B: centers of oligomers, C: carboxylic end groups of oligomers. D: hydroxyl end groups of oligomers, and E: lactic acid. [1]

Figure S3. Kinetics of the reaction with I.
Table S1  The results of the reaction with ZSM-5 catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>III-b.m.</th>
<th>IV-b.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selectivity /%</td>
<td>90.17</td>
<td>86.88</td>
<td>66.75</td>
<td>55.07</td>
<td>84.81</td>
<td>81.77</td>
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<tr>
<td>Yield /%</td>
<td>89.06</td>
<td>82.68</td>
<td>44.83</td>
<td>28.34</td>
<td>76.35</td>
<td>68.69</td>
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<tr>
<td>Conversion /%</td>
<td>98.77</td>
<td>95.17</td>
<td>67.16</td>
<td>51.46</td>
<td>90.02</td>
<td>84.00</td>
</tr>
</tbody>
</table>

Figure S4. The product distribution of L-lactic acid to L, L-lactide over sample II in p-xylene and the result of poisoning the surface of the II catalyst with 2,4-Dimethylquinoline in o-xylene.
Figure S5. The SEM images and the distribution curves of crystallite size of samples (a, d) IV, (b, e) IV-b.m.-15 min and (c, f) IV-b.m. (30 min), (g) the product distribution of L-lactic acid to L, L-lactide over IV, IV-b.m.-15 min and IV-b.m. (30 min).

References