crystals

MDPI

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

NH_3-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 NH_3/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 NH_3 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 NH_3 was detected by a thermal conductivity detector (TCD).

The characterization of the acidity of both Lewis and Brønsted 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 physiosorbed 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.

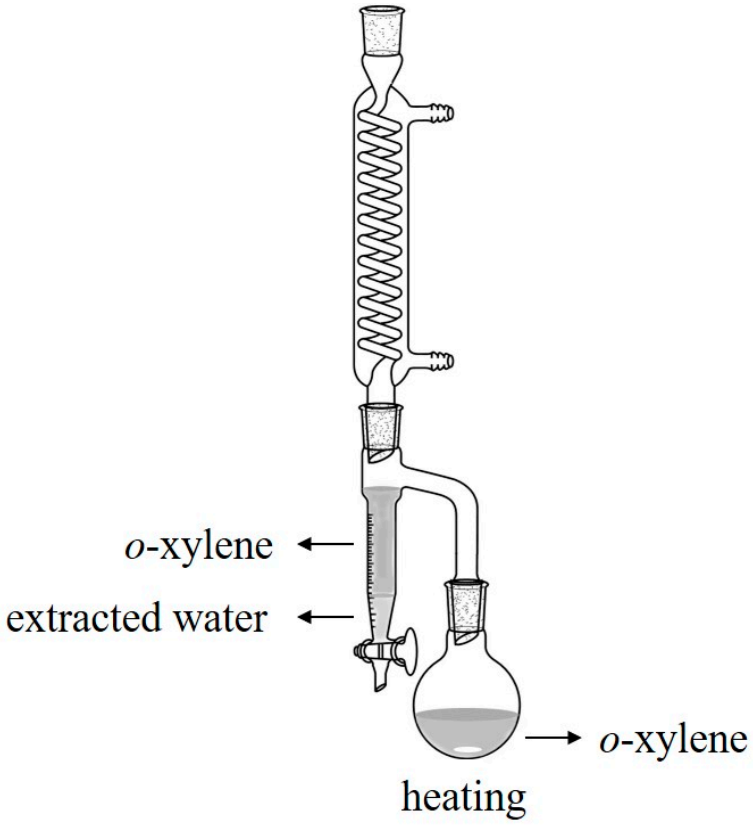

Figure S1. General lab-scale setup for lactide preparation.

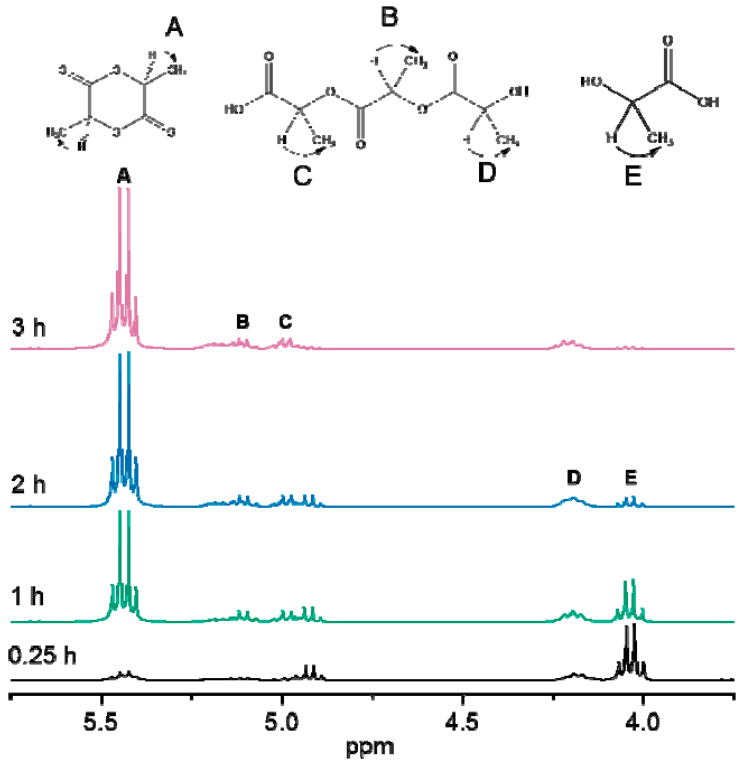

Figure S2. Reaction progress using sample I as catalyst by ^{1}H NMR in DMSO-d_6: The methine [-CH-CH_3] quartet region of various compounds in the reaction mixtures. Methine proton signals of A: lactide, B: centers of oligomers, C: carboxylic end groups of oligomers. D: hydroxyl end groups of oligomers, and E: lactic acid. [1]

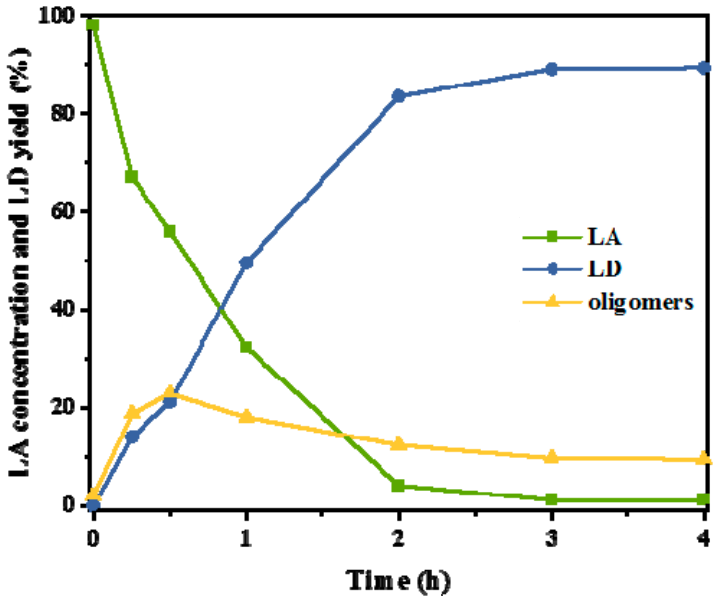

Figure S3. Kinetics of the reaction with I.

Table S1 The results of the reaction with ZSM-5 catalysts.

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

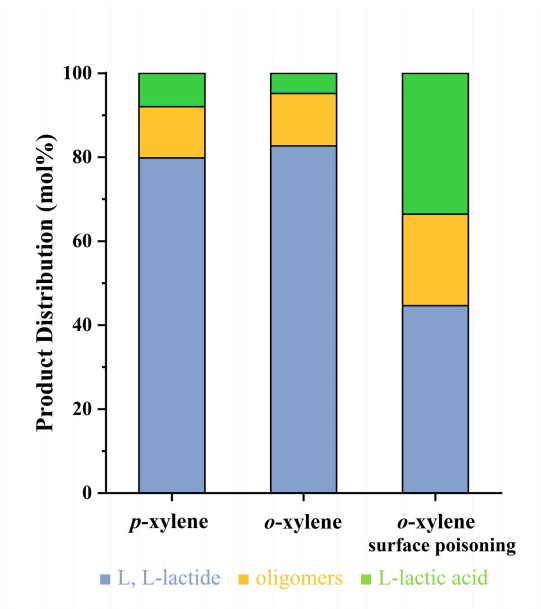

Figure S4. The product distribution of L-lactic acid to L, L-lactide over sample II in *p*-xylene and the result of poisoning the surface of the II catalyst with 2,4-Dimethylquinoline in *o*-xylene.

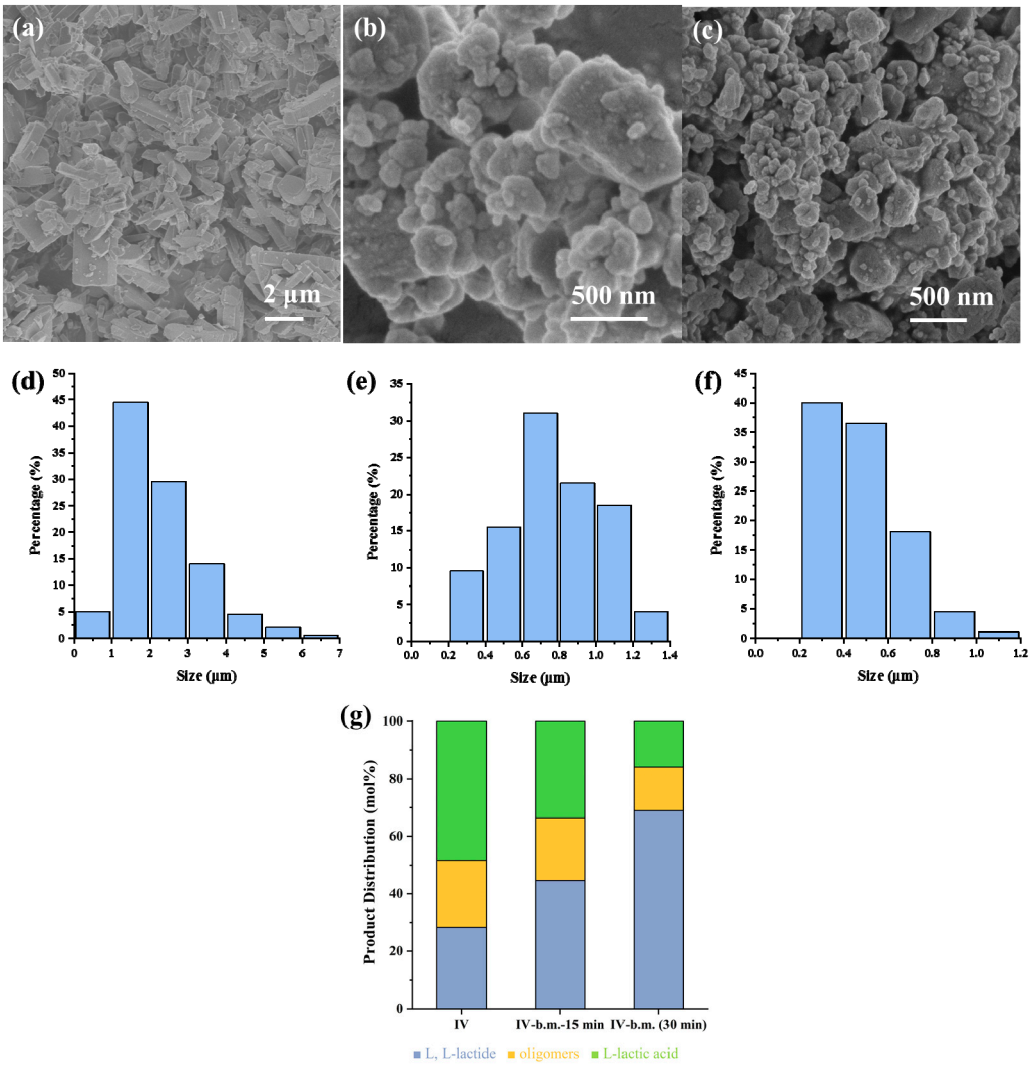

Figure S5. The SEM images and the distribution curves of crystallite size of samples (a, d) IV, (b, e) IV-b.m.-15 min and (c, f) IV-b.m. (30 min), (g) the product distribution of L-lactic acid to L, L-lactide over IV, IV-b.m.-15 min and IV-b.m. (30 min).

References

1. Dusselier, M.; Van Wouwe, P.; Dewaele, A.; Jacobs, P.A.; Sels, B.F. Shape-selective zeolite catalysis for bioplastics production. *Science* **2015**, *349*, 78-80, doi:10.1126/science.aaa7169.