

Supplementary Material: On the Impact of Preparation Method on the Surface Basicity of Mg-Zr Mixed Oxide Catalysts for Tributyrin Transesterification

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1. Tables

Table S1. Elemental analysis of MZ catalysts prepared from hydroxide (MZ-HD) or citrate-mediated (MZ-CT) routes.

Nominal MgO / wt%	Bulk MgO ^a /wt%	Surface content/ atom% ^b		Mg:Zr atomic ratio ^a	Mg:Zr atomic ratio ^b
		Mg	Zr		
ZrO ₂ -HD	0.00	0.00	30.9		
1MZ-HD	2.10	6.2	22.8	0.08	0.27
2MZ-HD	6.34	6.0	20.3	0.25	0.44
3MZ-HD	7.94	12.2	19.3	0.32	0.63
4MZ-HD	10.87	18.4	15.0	0.46	1.23
5MZ-HD	16.20	21.4	13.1	0.73	1.63
6MZ-HD	18.21	21.8	14.5	0.84	1.53
ZrO ₂ -CT	0.00	0.0	33.4		
1MZ-CT	1.92	3.2	21.0	0.07	0.15
2MZ-CT	3.70	4.9	21.6	0.14	0.23
3MZ-CT	5.70	7.6	23.4	0.23	0.32
4MZ-CT	8.71	9.3	20.4	0.36	0.46
5MZ-CT	10.21	10.3	17.8	0.43	0.58
6MZ-CT	14.27	14.1	14.8	0.62	0.96

^aICP-OES. ^bXPS.

Table S2. MgO mass loss from fresh 18.2MZ-HD catalyst as a function of recycle during tributyrin transesterification with methanol.

Reaction	Leached MgO (wt %)
1	0.83
2	0.71
3	0.96

2. Figures

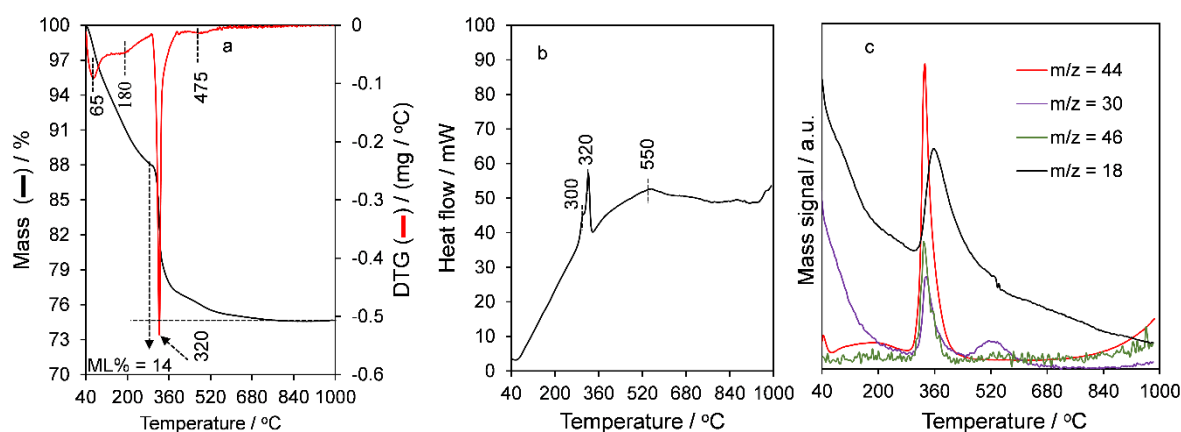


Figure S1. (a) TGA/DTG, (b) DSC, and (c) MS signals for evolved gas species during thermal decomposition of $(\text{CH}_3\text{O})_2\text{Mg}$ -impregnated zirconium hydroxide precursor under flowing $\text{N}_2:\text{O}_2$ (2:1 volume ratio, $60 \text{ cm}^3 \cdot \text{min}^{-1}$).

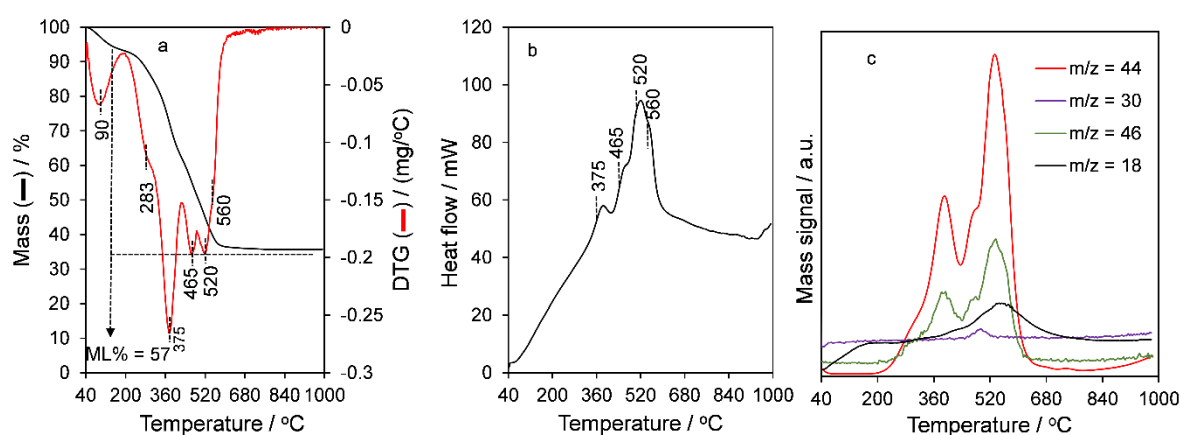


Figure S2. (a) TGA/DTG, (b) DSC, and (c) MS signals for evolved gas species during thermal decomposition of citrate-mediated sol-gel under flowing $\text{N}_2:\text{O}_2$ (2:1 volume ratio, $60 \text{ cm}^3 \cdot \text{min}^{-1}$).

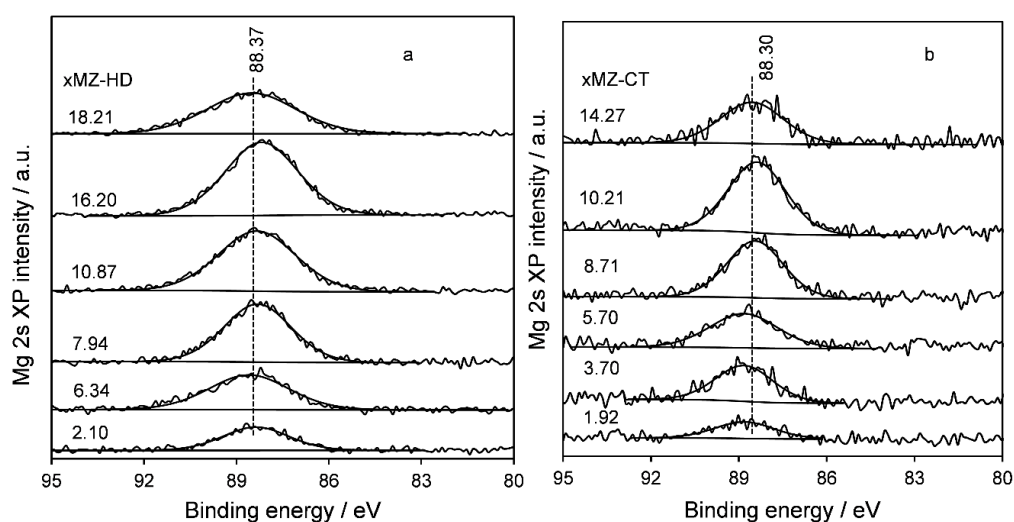


Figure S3. Mg 2s XP spectra of (a) xMZ-HD, and (b) xMZ-CT mixed oxides.

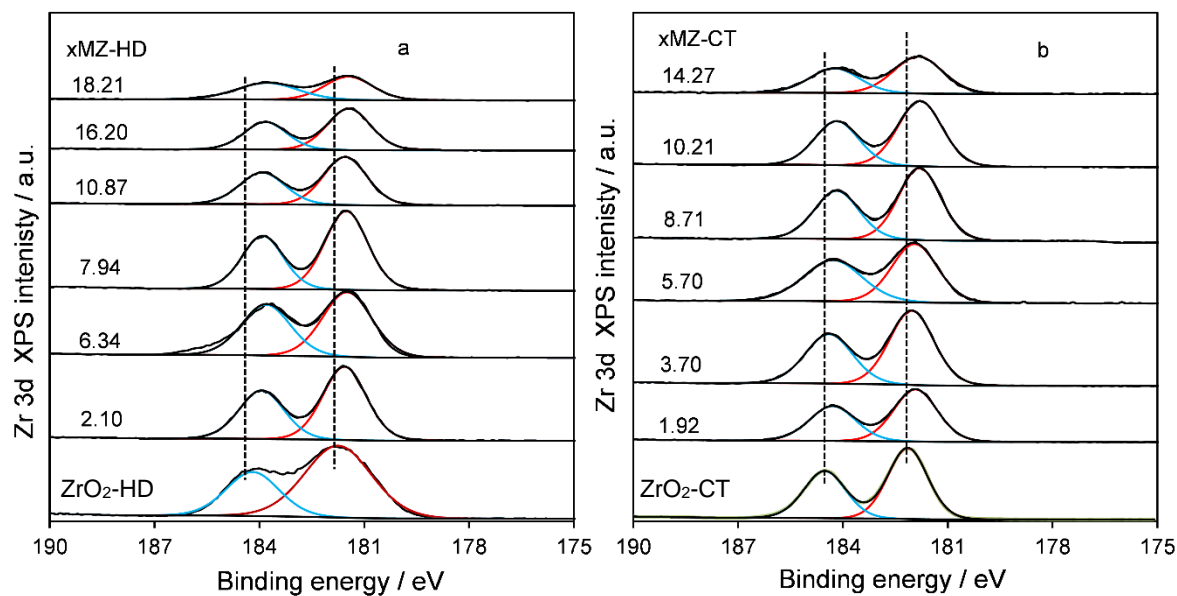


Figure S4. Zr 3d XP spectra of (a) xMZ-HD, and (b) xMZ-CT mixed oxides.

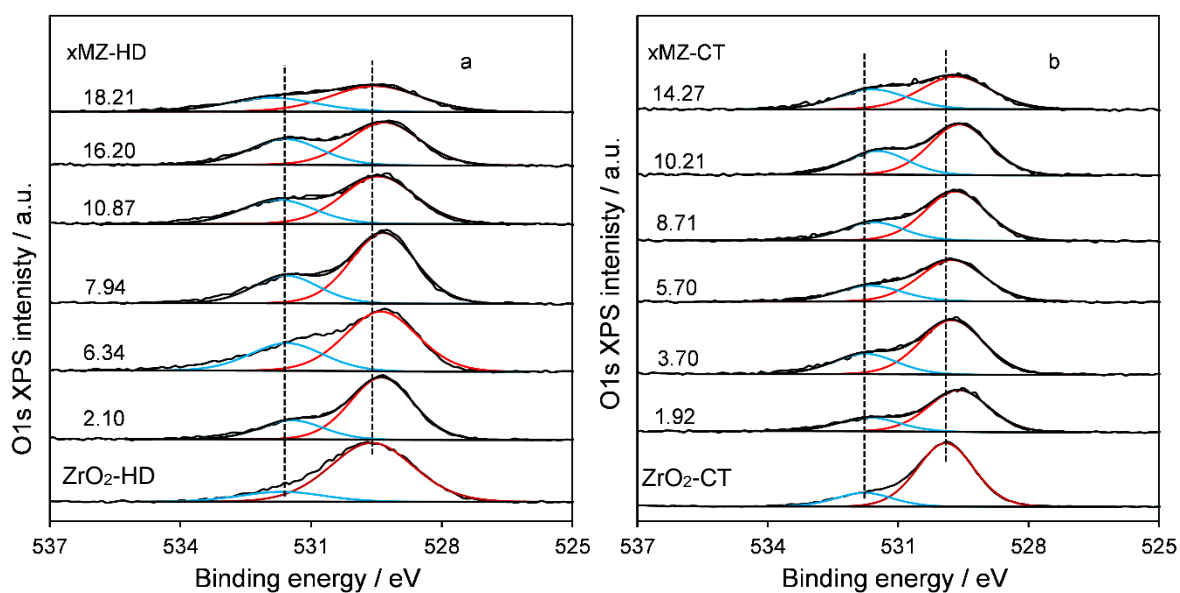


Figure S5. O 1s XP spectra of (a) xMZ-HD, and (b) xMZ-CT mixed oxides.

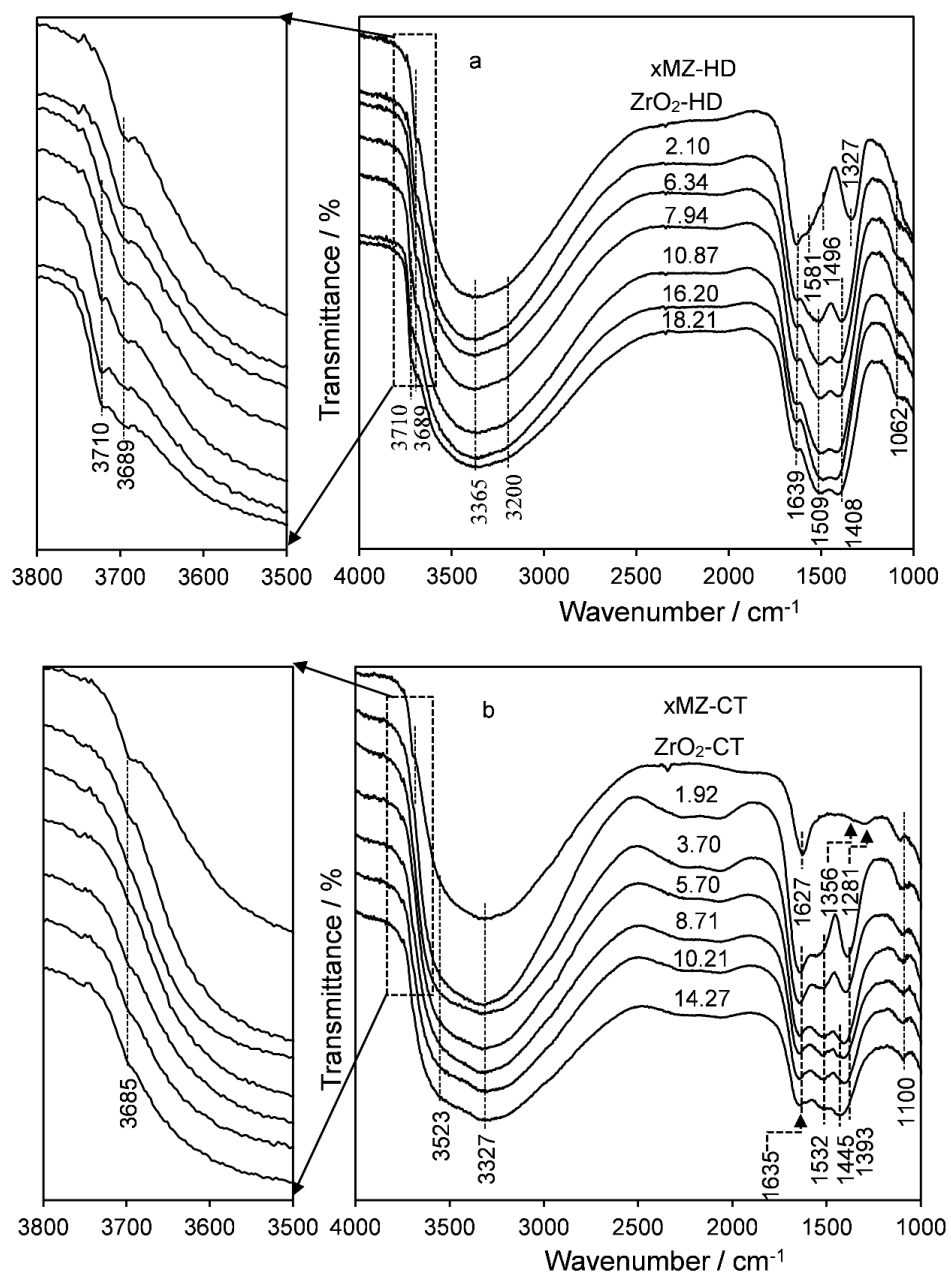


Figure S6. DRIFT spectra of (a) xMZ-HD, and (b) xMZ-CT mixed oxides.

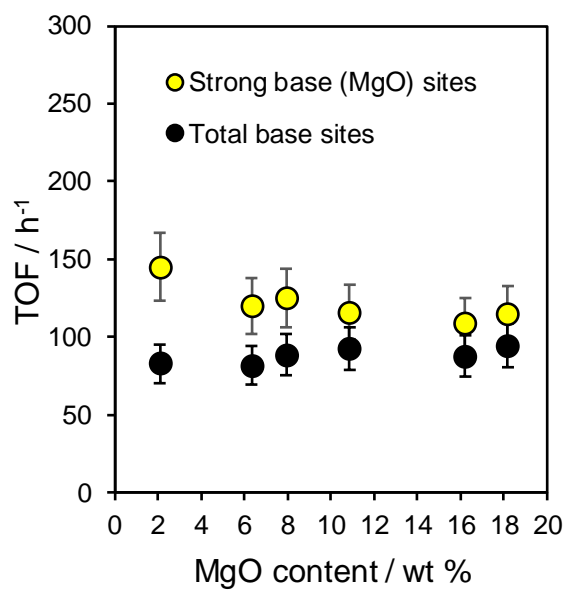


Figure S7. Comparison of TOF for tributyrin transesterification calculated per total base or per strong base (MgO) site.

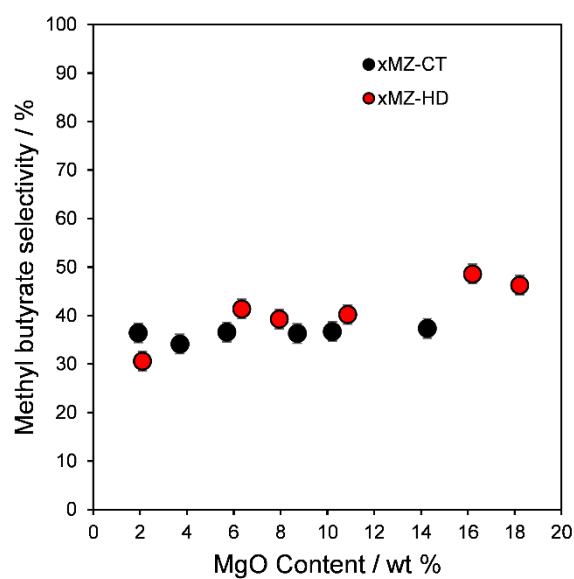


Figure S8. Methyl butyrate selectivity at 20 % iso-conversion for metal oxides.

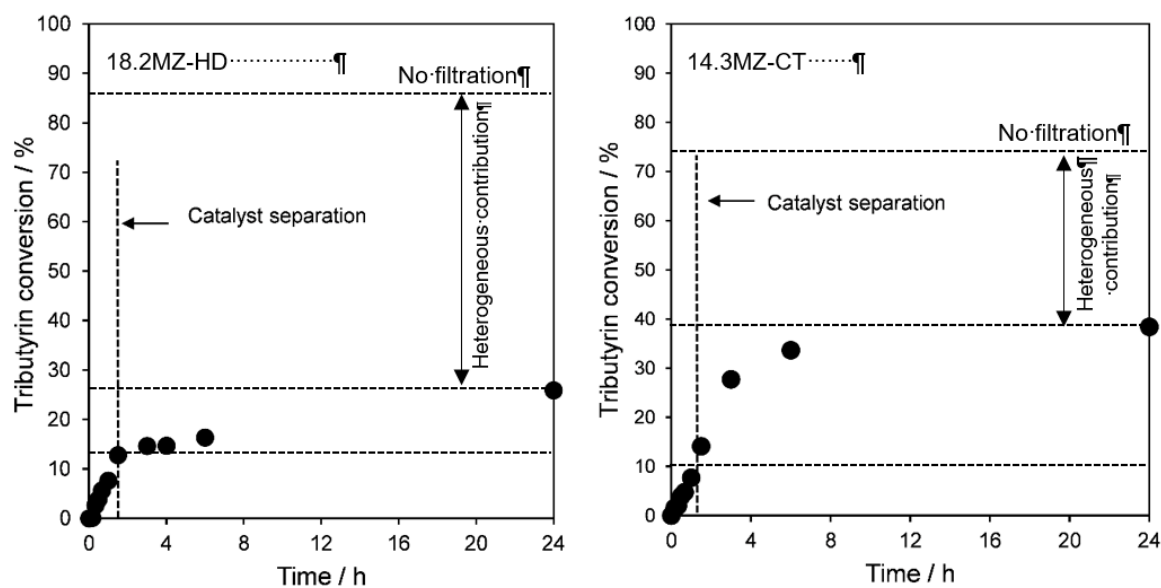


Figure S9. Hot filtration tests to assess Mg^{2+} leaching in tributyrin transesterification over the indicated catalyst (catalyst was removed after 1.5 h).

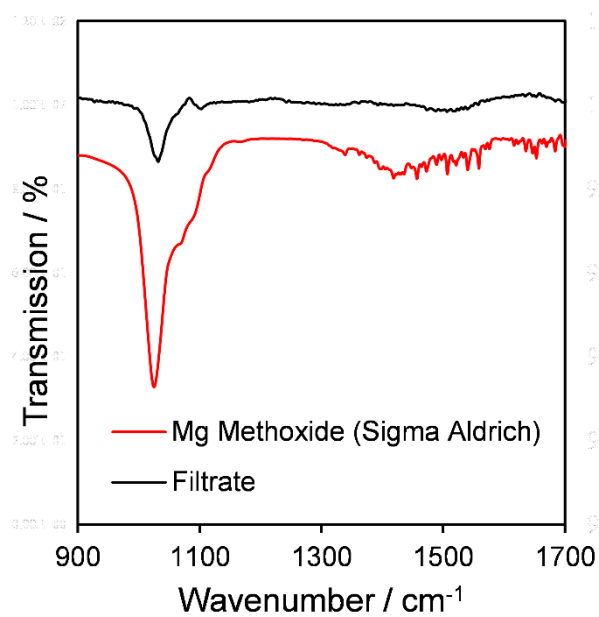


Figure S10. ATR-FTIR spectra of commercial magnesium methoxide solution and the supernatant post-reaction after 18.2MZ-HD catalyst.

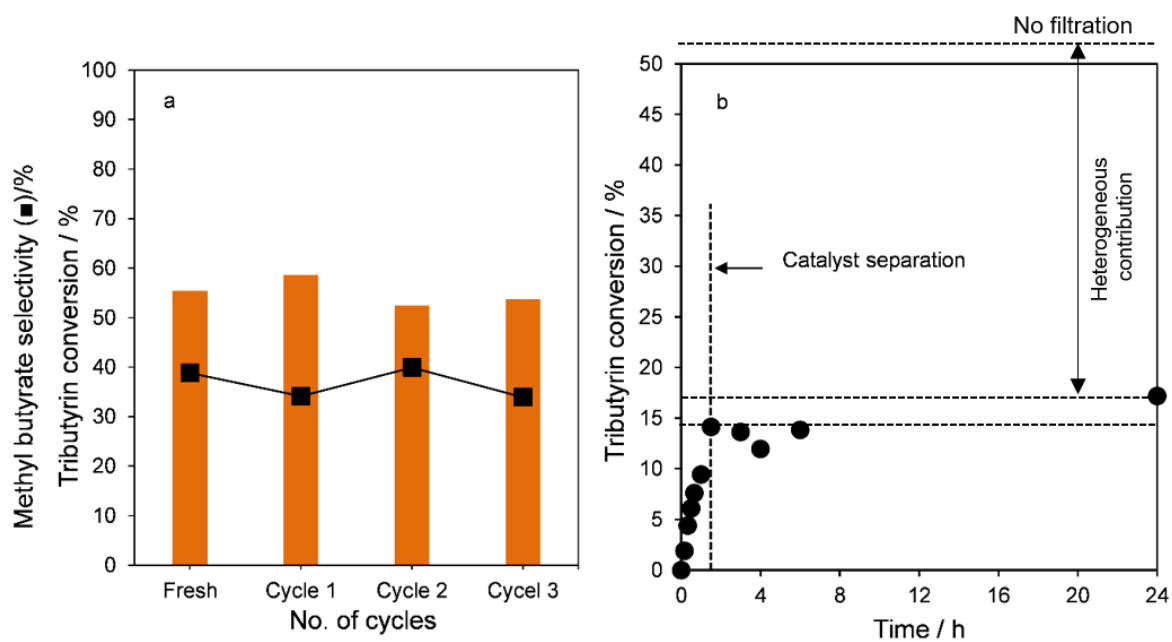


Figure S11. (a) Tributyrin conversion and methyl butyrate selectivity as a function of recycle, and (b) hot filtration tests to assess Mg^{2+} leaching over 8.7MZ-CT.

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