



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

Abdallah I. M. Rabee <sup>1</sup>, Jinesh C. Manayil <sup>2</sup>, Mark A. Isaacs <sup>2</sup>, Christopher M. A. Parlett <sup>2</sup>, Lee J. Durndell <sup>2</sup>, Mohamed I. Zaki <sup>1,\*</sup>, Adam F. Lee <sup>3,\*</sup> and Karen Wilson <sup>3,\*</sup>

- <sup>1</sup> Chemistry Department, Faculty of Science, Minia University, El-Minia 61519, Egypt; aimoftah@mu.edu.eg
- <sup>2</sup> European Bioenergy Research Institute, School of Engineering and Applied Sciences, Aston University, Aston Triangle, B4 7ET Birmingham, UK; cmjinesh@gmail.com (J.C.M.); mark.isaacs@ucl.ac.uk (M.A.I.); c.parlett@aston.ac.uk (C.M.A.P.); l.j.durndell@uu.nl (L.J.D.)
- <sup>3</sup> School of Science, RMIT University, Melbourne, Victoria 3001, Australia
- \* Correspondence: mizaki@mu.edu.eg (M.I.Z.); adam.lee2@rmit.edu.au (A.F.L.); karen.wilson2@rmit.edu.au (K.W.)

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## 1. Tables

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

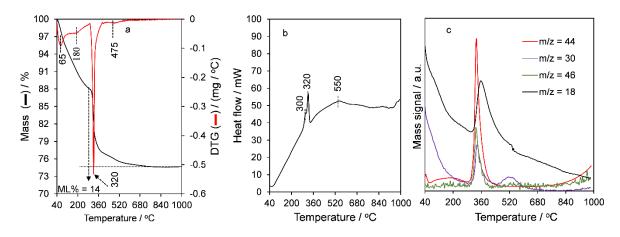
Nominal MgO /	Bulk MgOª	Surface content/ atom% <sup>b</sup>		Mg:Zr atomic	Mg:Zr
wt%	/wt%	Mg	Zr	ratio <sup>a</sup>	atomic ratio <sup>b</sup>
ZrO <sub>2</sub> -HD	0.00	0.00	30.9		
1MZ-HD	2.10	6.2	22.8	0.08	0.27
2MZ-HD	6.34	6.0	20.3	0.25	0.44
3MZ-HD	7.94	12.2	19.3	0.32	0.63
4MZ-HD	10.87	18.4	15.0	0.46	1.23
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 <sub>2</sub> -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.

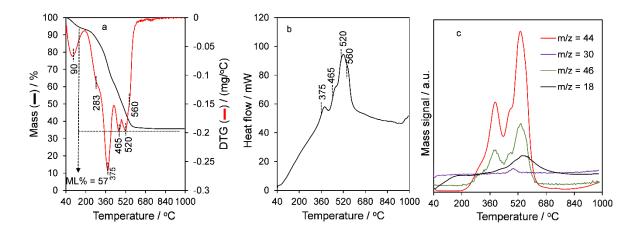
**Table S2.** MgO mass loss from fresh 18.2MZ-HD catalyst as a function of recycle during tributyrin transesterification with methanol.

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 (CH<sub>3</sub>O)<sub>2</sub>Mg-impregnated zirconium hydroxide precursor under flowing N<sub>2</sub>:O<sub>2</sub> (2:1 volume ratio, 60 cm<sup>3</sup>.min<sup>-1</sup>).



**Figure S2.** (a) TGA/DTG, (b) DSC, and (c) MS signals for evolved gas species during thermal decomposition of of citrate-mediated sol-gel under flowing N<sub>2</sub>:O<sub>2</sub> (2:1 volume ratio, 60 cm<sup>3</sup>.min<sup>-1</sup>).

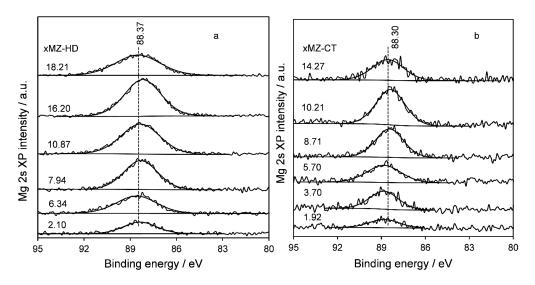


Figure S3. Mg 2s XP spectra of (a) xMZ-HD, and (b) xMZ-CT mixed oxides.

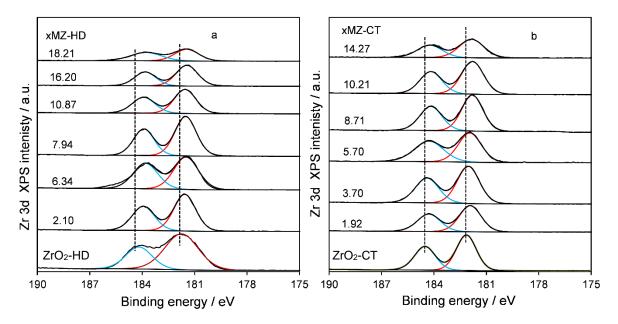


Figure S4. Zr 3d XP spectra of (a) xMZ-HD, and (b) xMZ-CT mixed oxides.

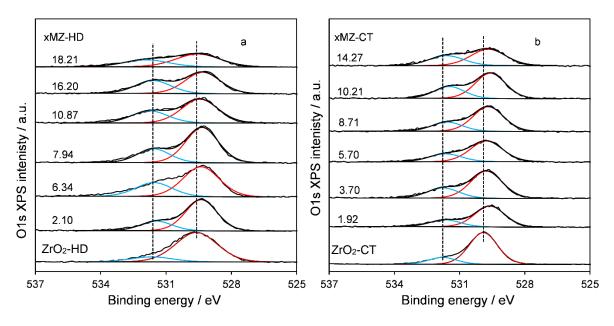


Figure S5. O 1s XP spectra of (a) xMZ-HD, and (b) xMZ-CT mixed oxides.

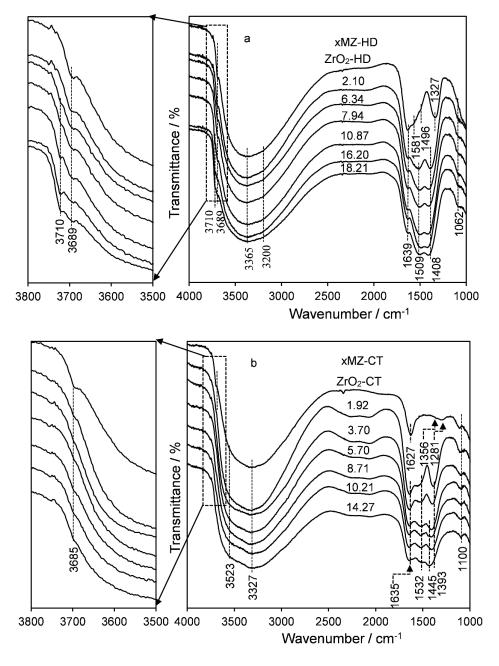
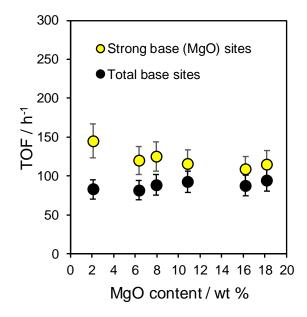


Figure S6. DRIFT spectra of (a) xMZ-HD, and (b) xMZ-CT mixed oxides.



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

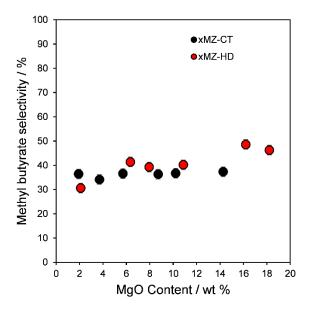
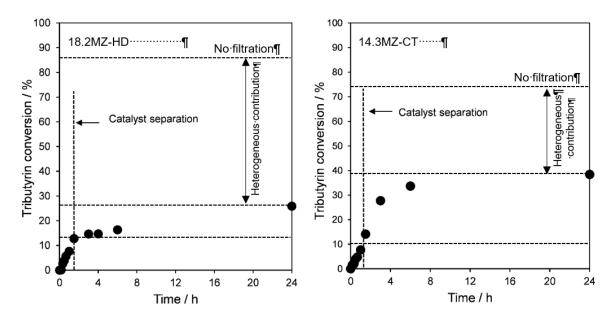
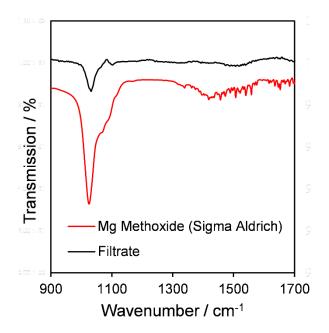


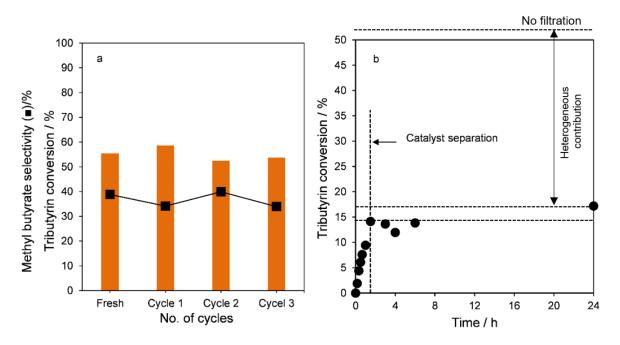
Figure S8. Methyl butyrate selectivity at 20 % iso-conversion for metal oxides.



**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<sup>2+</sup> leaching over 8.7MZ-CT.

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