SUPPLEMENTARY INFORMATION

Alkali-Free Zn–Al Layered Double Hydroxide Catalysts for Triglyceride Transesterification

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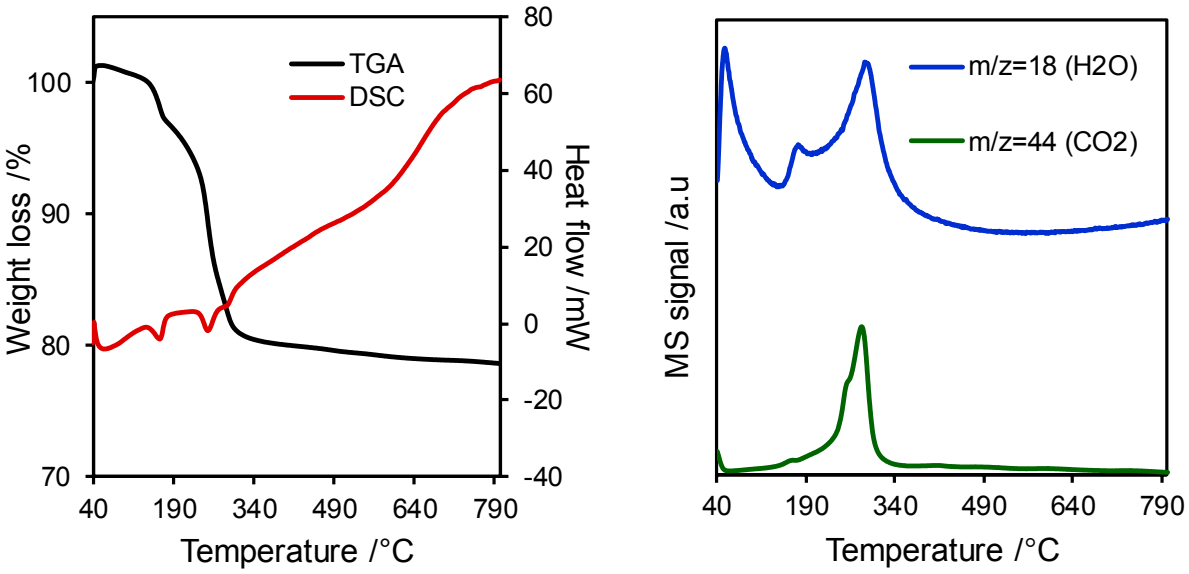
Characterisation



(a) **(b)**

Figure S1. (a) Mass loss and heat flow, and (b) temperature programmed H_2O and CO_2 desorptions during $Zn_{3.3}Al$-LDH calcination.

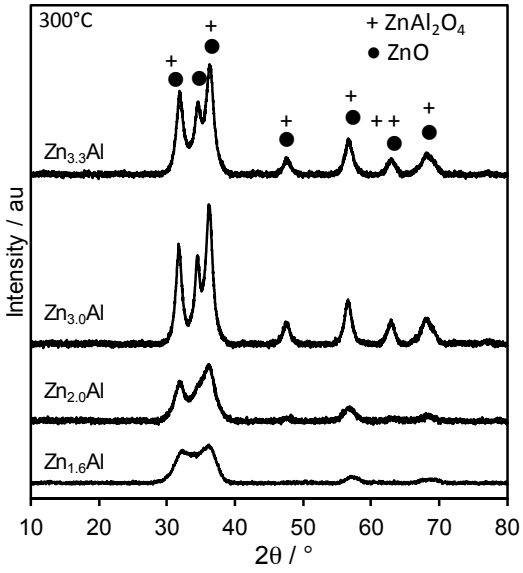


Figure S2. Powder XRD patterns of ZnAl-LDHs following calcination at 300 °C as a function of Zn:Al molar ratio.

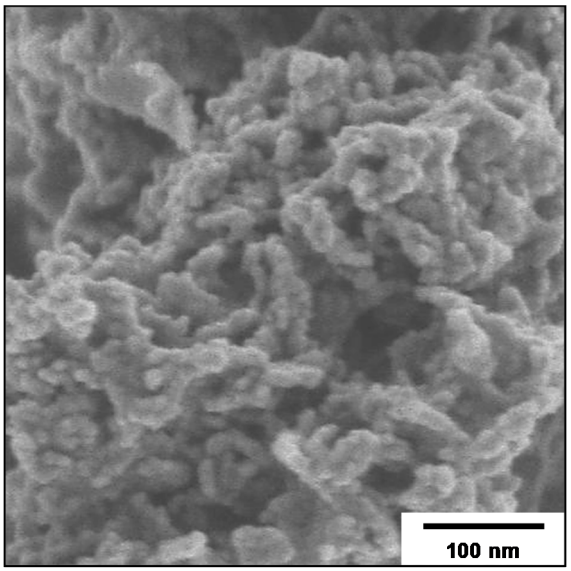


Figure S3. SEM of $Zn_{3.3}$Al-LDH following calcination at 300 °C.

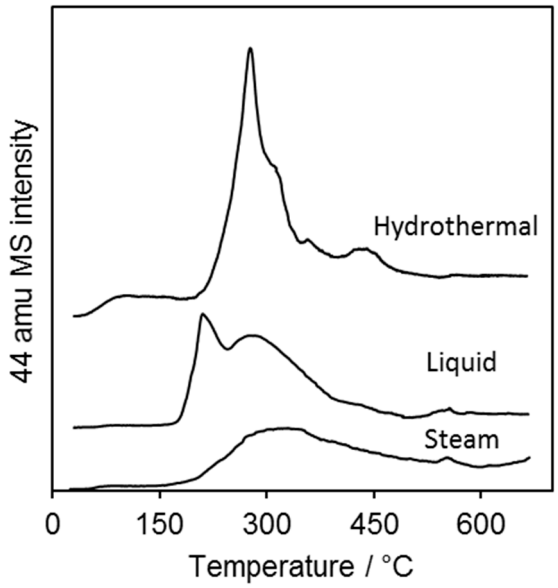


Figure S4. Temperature programmed CO_2 desorption profiles for $Zn_{3.3}Al$-LDH reconstructed by steam, water, or hydrothermal treatment.

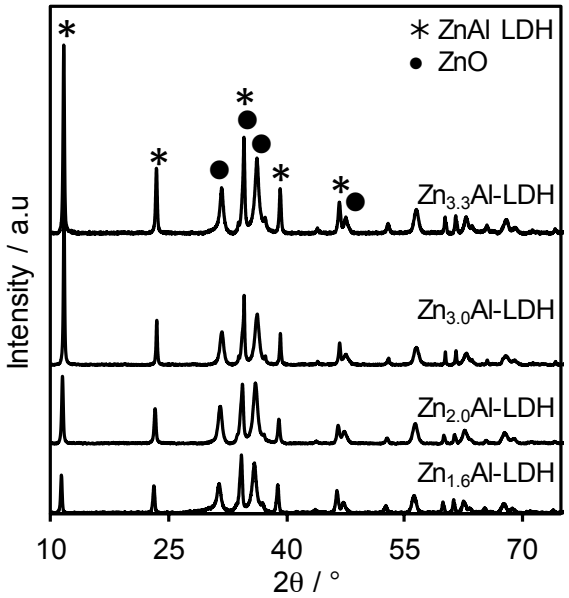


Figure S5. Powder XRD patterns of ZnAl-LDHs following hydrothermal reconstruction as a function of Zn:Al molar ratio.

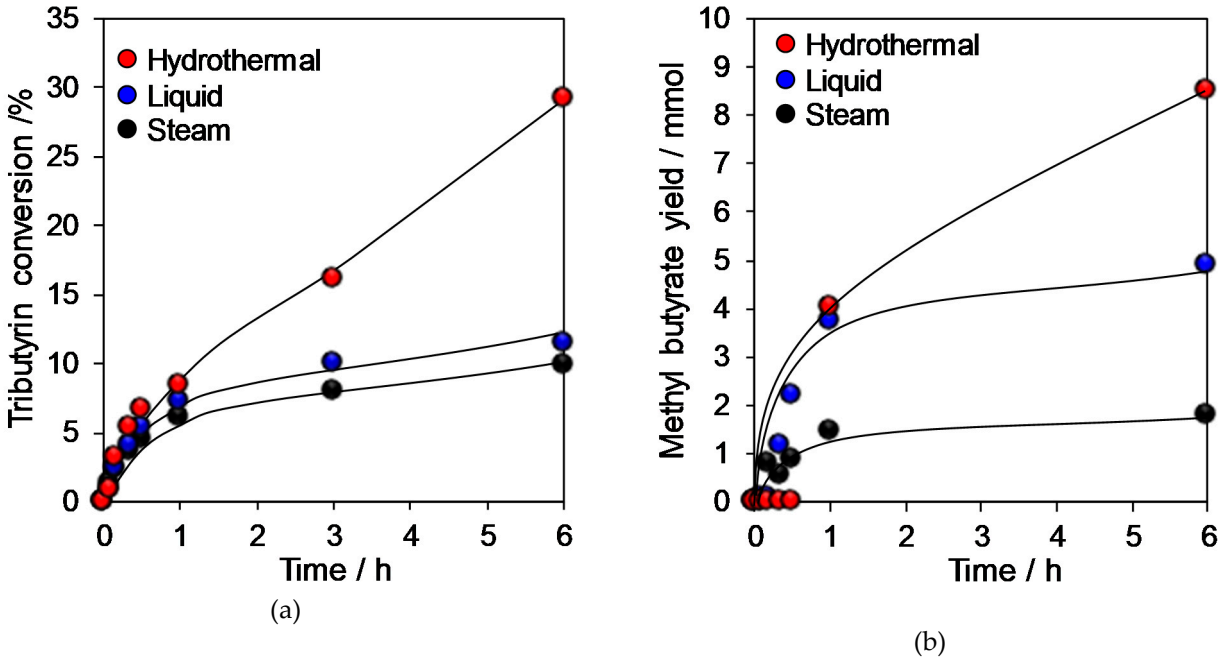
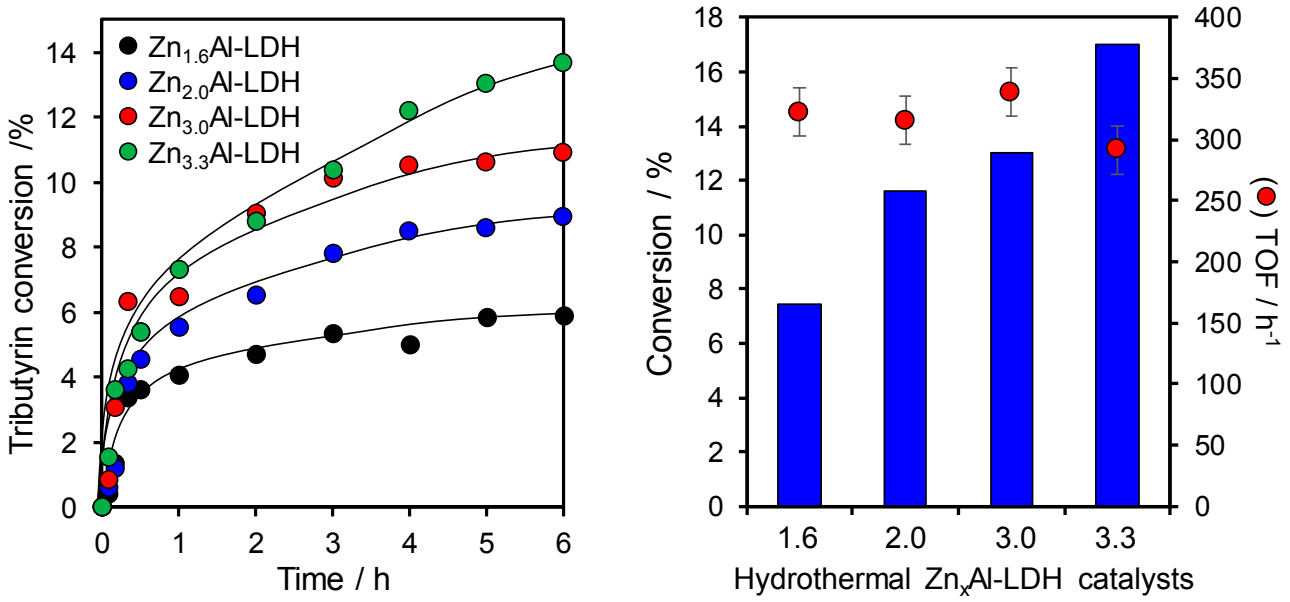


Figure S6: Influence of reconstruction protocol on (a) tributyrin conversion and (b) methyl butyrate yield for tributyrin transesterification over of $Zn_{3.3}Al$-LDH at 60°C. Reaction conditions: 10 mmol tributyrin, 300 mmol methanol (TAG:alcohol molar ratio 1:30), 2.5 mmol dihexyl ether internal standard, and 100 mg catalyst.

Table S1. Physicochemical properties of hydrothermally reconstructed Zn_xAl-LDHs.

Catalyst	Crystallite size /nm	% ZnAl LDH	Surface area/m^2/g	Base site loading CO_2 titration	
				molecules·g^{-1}	mmol·g^{-1}
Hydrothermal $Zn_{1.6}Al$-LDH	18	42	43	2.9×10^{19}	0.05
Hydrothermal $Zn_{2.0}Al$-LDH	24	53	60	3.5×10^{19}	0.06
Hydrothermal $Zn_{3.0}Al$-LDH	25	73	76	4.7×10^{19}	0.08
Hydrothermal $Zn_{3.3}Al$-LDH	27	73	53	6.0×10^{19}	0.10



(a) (b)

Figure S7. Influence of Zn:Al molar ratio on (a) tributyrin conversion and (b) 24 h conversion and turnover frequencies for tributyrin transesterification over hydrothermally reconstructed ZnAl-LDHs at 60 °C. Reaction conditions: 10 mmol tributyrin, 300 mmol methanol (TAG:alcohol mole ratio 1:30), 2.5 mmol dihexyl ether internal standard, and 50 mg catalyst. Note that 50 mg catalyst was used to ensure that measured conversions were free from mass transport limitation.

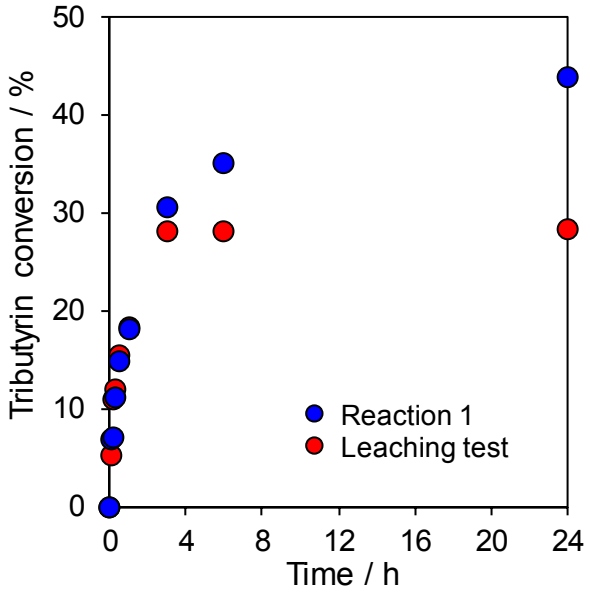


Figure S8. Hot filtration test for tributyrin transesterification over hydrothermally reconstructed $Zn_{3.3}$Al-LDH. Reaction condition: 60 °C, 4.98 ml tributyrin, 24.4 ml methanol, 1.18 ml dihexyl ether internal standard, and 100 mg catalyst.

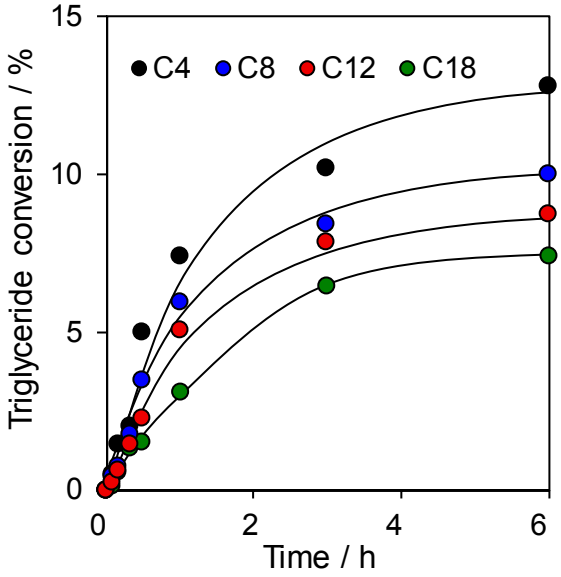


Figure S9. Influence of TAG chain length on transesterification over hydrothermally reconstructed $Zn_{3.3}Al$-LDH. Reaction conditions: 110 °C, 300 mmol MeOH, 10 mmol TAG, 2.5 mmol dihexyl ether internal standard, 20 wt% butanol, and 100 mg catalyst.

Table S2. Conversion and FAME selectivity following transesterification of different chain length TAGs over hydrothermally reconstructed $Zn_{3.3}Al$-LDH. Reaction conditions: 110 °C, 300 mmol MeOH, 10 mmol TAG, 2.5 mmol dihexyl ether internal standard, 20 wt% butanol, and 100 mg catalyst.

Triglyceride	Conversion after 24 h/%	FAME selectivity after 24 h/%
C_4	19.7	96
C_8	16.3	97
C_{12}	11.1	70
C_{18}	8.2	77

Table S3. Conversion and TOF data from published literature of selected base catalysed transesterification of triglycerides.

Reference	Catalyst	TAG	Conditions	TOF / h^{-1}	TAG conversion / %
Xi et al.[1]	2:1 Mg:Al HT	Tributyrin	3:1 methanol: oil , 60 ºC, 4.6 wt % catalyst	187	82.3 after 20 h
Umdu et al.[2]	60% CaO/Al_2O_3	Sunflower oil	9:1 methanol: oil, 50ºC, 6 wt% catalyst	100.8	80 after 4 h
Georgogianni et al[3]	Mg/MCM-41	Rapeseed oil	10:1 methanol: oil, 60ºC, 0.1 wt% catalyst	0.45[a]	85 after 24 h
Georgogianni et al[3].	2:1 Mg:Al HT	Rapeseed oil	10:1 methanol: oil, 60ºC, 0.1 wt% catalyst	0.084[a]	97 after 24 h
Hamad et al[4]	3:1 Mg:Al HT	Rapeseed oil	18:1 ethanol : oil, 79ºC, 0.04 wt% catalyst	1.98	6 after 5 h
Hamad et al.[4]	ZrOCs	Rapeseed oil	18:1 ethanol : oil, 79ºC, 0.04 wt% catalyst	46.2	64 after 5 h
Woodford et al[5]	Mg_2Al HT	Tributyrin	30:1 methanol:oil, 60°C, 1.7 wt% catalyst	329	41.4 after 24 h
Woodford et al[5]	Mg_2Al HT	Triolein	30:1 methanol:oil, 60°C, 0.5 wt% catalyst, 35 wt% butanol to solubilise TAG	10.8	20.7 after 24 h
Woodford et al.[6]	Cs-MgO	Olive Oil	30:1 methanol:oil, 60ºC, 0.5 wt% catalyst 35 wt% butanol to solubilise TAG	34.2	11 after 24 h
Woodford et al[6]	Cs-MgO	Olive Oil	30:1 methanol:oil; 90°C, 2.8 wt% catalyst, 25 wt% Butanol	96[b]	93 after 24 h
Montero et al[7]	Nano MgO 400 °C calcined	Tributyrin	30:1 methanol:oil, 60ºC, 1.7 wt% catalyst	222	80 after 24 h
Rabee et al[8]	Mg/ZrO_2	Tributyrin	30:1 methanol:oil, 60ºC, 3.4 wt% catalyst	102	70% after 24 h
Liu et al[9]	Zn_2Al	Soybean Oil	1:1 vol ratio methanol:oil; 140 °C; 1 h^{-1} WHSV; (prepared by alkali precipitation)	-	76%, Continuous flow WHSV = 1 h^{-1}
Jiang et al[10]	$Zn_{3.74}Al$	Rapeseed oil	1.4:1 wt ratio methanol:oil, 200 °C, 2 wt% catalyst (prepared by alkali precipitation)	-	85% in 90 min
This work	$Zn_{3.3}Al$	Tributyrin	30:1 methanol:oil; 60°C, 1.7 wt%	290	17% after 24 h
This work	$Zn_{3.3}Al$	Tributyrin	30:1 methanol:oil; 110°C, 3.4 wt% catalyst, 20 wt% Butanol	78	19.7 after 24 h
This work	$Zn_{3.3}Al$	Triolein	30:1 methanol:oil; 110°C, 1 wt% catalyst, 20 wt% Butanol	33	8.5 after 24 h

[a] Calculated over 24 h reaction; Calculated after 3h, 31.5% triolein conversion.

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