

# **Aqueous miscible organic layered double hydroxides as catalyst precursors for biodiesel synthesis**

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## 1 General details

### 1.1 Materials

Magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (AR)), aluminium nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (AR)), sodium hydroxide ( $\text{NaOH}$  (AR)), sodium carbonate ( $\text{Na}_2\text{CO}_3$  (AR)), potassium hydroxide ( $\text{KOH}$  (AR)), potassium carbonate ( $\text{K}_2\text{CO}_3$  (AR)) and ethanol were purchased from Sigma-Aldrich Co. LLC and used without further purification. Deionised water (DI) was used throughout the experimental process. Sunflower oil was purchased from supermarket (TESCO) without further purification.

### 1.2 Experimental details

**$\text{Mg}_x\text{Al}$  AMOLDH (Na):** the metal precursor solution (0.4 mol) containing  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 400 mL of water was added dropwise into  $\text{Na}_2\text{CO}_3$  base solution (400 mL of water with 0.2 mol of  $\text{Na}_2\text{CO}_3$ ) within 1 h. The pH was kept constant around 10.0 by dropwise addition of a 4.0 M  $\text{NaOH}$  solution. After stirring for 16 h at room temperature, the mixture was filtered and washed with deionised (DI) water until pH 7. The wet solid LDH was rinsed with ethanol (2 L) followed by dispersion in fresh ethanol (2 L) and stirred at room temperature for 2 h. The AMO-LDH was then isolated by filtration, and dispersed in ethanol and filtered. The final solid dried under vacuum overnight at 30 °C.  **$\text{Mg}_x\text{Al}$  LDH(Na)** was obtained from the same procedure without ethanol treatment.

**$\text{Mg}_x\text{Al}$  AMOLDH (K):** the metal precursor solution containing  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.3 mol),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.1 mol) and 400 mL of water was added dropwise into  $\text{K}_2\text{CO}_3$  base solution (400 mL of water with 0.2 mol of  $\text{K}_2\text{CO}_3$ ) within 1 h. The pH was kept constant around 10.0 by drop wise addition of a 4.0 M  $\text{KOH}$  solution. After stirring for 16 h at room temperature, the mixture was filtered and washed with deionised (DI) water until pH 7. The wet solid LDH was rinsed with ethanol (2 L) followed by dispersion in fresh ethanol (2 L) and stirred at room temperature for 2 h. The AMO-LDH was then isolated by filtration, and dispersed in ethanol and filtered. The final solid dried under vacuum overnight at 30 °C.  **$\text{Mg}_x\text{Al}$  LDH(K)** was obtained from the same procedure without ethanol treatment.

### 1.3 Characterisation

**Powder X-ray Diffraction (XRD)** XRD data were collected on a PANAnalytical X'Pert Pro diffractometer in reflection mode at 40 kV and 40 mA using  $\text{Cu K}\alpha$  radiation ( $\alpha_1 = 1.54060 \text{ \AA}$ ,  $\alpha_2 = 1.54426 \text{ \AA}$ , weighted average =  $1.54178 \text{ \AA}$ ). Scans were recorded from  $5^\circ \leq 2\theta \leq 70^\circ$ . Samples were mounted on stainless steel sample holders; peaks produced from these holders are observed at approximately 43 and 50°.

**The Fourier-transform Infrared (FTIR)** spectra were recorded on a Vertex 80 Spectrometer. It is equipped with a high performance DuraSamp1IR II diamond accessory of attenuated total reflection (ATR) mode in the range of 400 – 4000  $\text{cm}^{-1}$ .

**Brunauer-Emmett-Teller surface analysis (BET)** BET specific surface areas were measured by nitrogen adsorption and desorption isotherms from a Micrometric Tristar surface characterisation analyser. Samples were degassed at 110 °C overnight prior to analysis.

**Inductively Coupled Plasma Mass Spectrometry (ICP-MS)** ICP-MS analysis was performed by Dr. Alaa Abdul-Sada at the University of Sussex on an Agilent 7500 Series ICP-MS in helium collision mode. Approximately 30 mg of sample was dissolved in 10 mL of 10% nitric acid solution. The solutions were then diluted by a factor of 100 with dilute nitric acid prior to analysis. Three repeats were performed for each measurement and the average was recorded.

**Temperature Programmed Desorption (TPD)** Carbon dioxide TPD measurements were obtained on a Micrometrics AutoChem II 2920 Chemisorption Analyser equipped with a thermal conductivity detector (TCD). Approximately 100 mg of sample was placed in a quartz U-tube and heated in air at 450 °C for 60 minutes with a ramp rate of 10 °C  $\text{min}^{-1}$  in order to remove water, solvent and impurities. After the sample was cooled to 100 °C, a  $\text{CO}_2$  flow was applied at a flow rate of 30  $\text{cm}^3 \text{min}^{-1}$  for 60 minutes. A helium carrier gas was then employed (50  $\text{cm}^3 \text{min}^{-1}$ ) to remove the physically adsorbed carbon dioxide for 60 minutes. Finally, the sample was heated from 100 to 450 °C with a ramp rate of 10 °C  $\text{min}^{-1}$  under helium flow (50  $\text{cm}^3 \text{min}^{-1}$ ) with desorption measurements every 1.0 seconds.

**Transmission Electron Microscopy (TEM)** All TEM images were obtained on a JEOL 2100 microscope with an accelerating voltage of 200 kV. Samples were prepared by dispersing particles in water or ethanol via sonication for 1 hour before casting onto carbon-coated copper grids.

**Nuclear Magnetic Resonance (NMR) Spectroscopy** Solution NMR spectra were recorded on a Bruker AVIII 400 MHz NMR Spectrometer. All samples were dissolved in approximately 0.7 mL of chloroform-*d* and  $^1\text{H}$  NMR spectra were recorded at room temperature. Spectra were referenced internally to the residual resonance of the chloroform-*d* at 7.26 ppm.

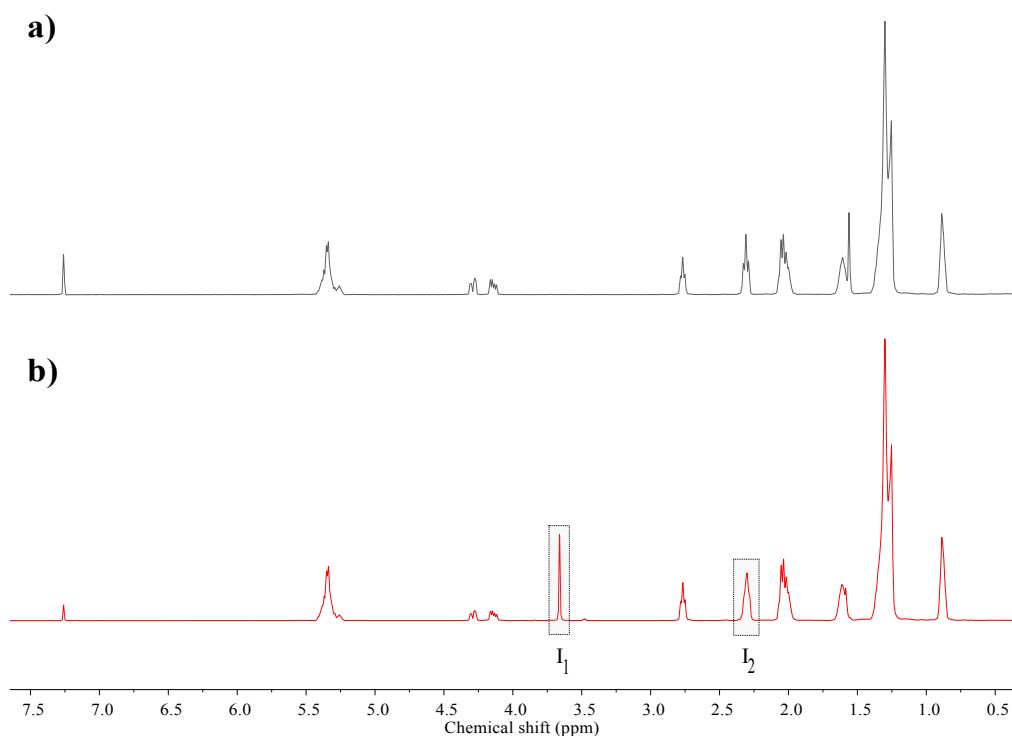
#### 1.4 Catalyst pretreatment

All LDO samples were obtained by calcination of the corresponding LDHs in air at 450 °C for 6 h.

#### 1.5 Transesterification of sunflower oil

A catalyst (0.5 g) was added to methanol (50 g) in a sealed round bottomed flask and stirred vigorously for 10 minutes. Sunflower oil (5 g) was then added to the mixture and stirred at 750 rpm at 65 °C in an oil bath for 24 hours. In the first 5 hours of reaction, 5 aliquots were extracted from the reaction mixture at recorded intervals. Each aliquot was filtered and placed on a rotary evaporator to remove catalyst and methanol before the product was analysed by  $^1\text{H}$  NMR spectroscopy. The reaction mixture was processed in the same way after 24 hours. Reactions were run at least in duplicate.

The FAME yield of each reaction was determined using  $^1\text{H}$  NMR spectroscopy. The technique is indiscriminate with regard to intermediary mono- and diglycerides formed by incomplete transesterification of triglycerides; all methyl ester  $-\text{OCH}_3$  proton shifts from FAMEs appear as a singlet incorporated by the integral I1 which are taken between 3.60 – 3.70 ppm. The acyl methylene proton resonances common to FAMEs, mono-, di- and triglycerides are incorporated by the integral I2 taken between 2.22 – 2.39 ppm (Fig. S1).



**Fig. S1**  $^1\text{H}$  solution NMR spectra of a) the sunflower oil feedstock and b) the FAME product of transesterification using the  $\text{Mg}_3\text{Al AMO-LDO (Na)}$  catalyst.

Percentage yields were calculated by Equation 1, first reported by Gelbard *et al.*<sup>1</sup>:

$$\text{FAME yield \%} = 100 \times \left( \frac{2I_1}{3I_2} \right) \quad (1)$$

Data for each reaction has been modelled by a Hill function (Equation 2) where  $k$  is a rate related constant,  $n$  is a positive constant and  $V_{\text{max}}$  corresponds to the maximum FAME yield which was set at 100.

$$FAME\ yield = V_{max} \frac{x^n}{k^n + x^n} \quad (2)$$

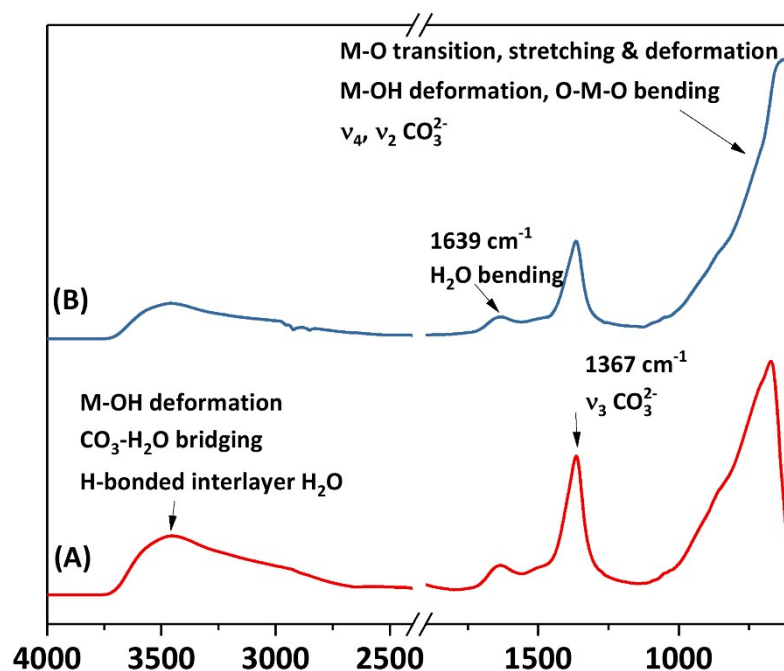
## 2 Supplementary characterisation data

**Table S1.** The d spacing, lattice parameters and mean crystallite sizes of AMO-Mg<sub>3</sub>Al-LDH (K) and AMO-Mg<sub>3</sub>Al-LDH (Na).

	d spacing		Lattice parameters (Å) <sup>1</sup>		Mean crystalline domain length (nm) <sup>2</sup>	
	003	110	c	a	c-axis	ab-plane
<b>AMO-Mg<sub>3</sub>Al-LDH (K)</b>	7.83	1.53	23.49	3.06	4.11	14.17
<b>AMO-Mg<sub>3</sub>Al-LDH (Na)</b>	7.82	1.53	23.46	3.06	6.64	15.19

<sup>1</sup>c-lattice constant is obtained from  $c = 3 \times d(003)$ ;  $a$  is obtained from  $a = 2 \times d(110)$

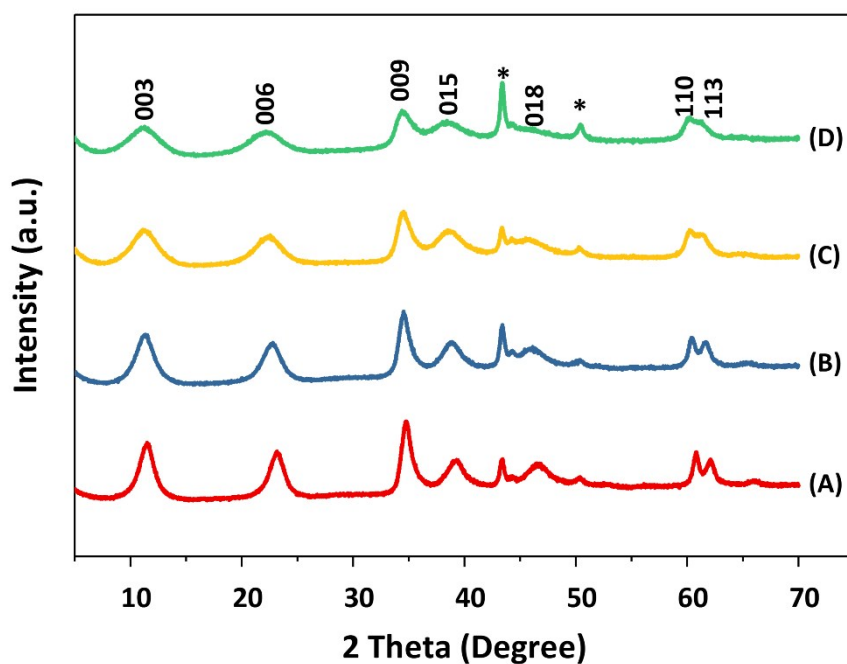
<sup>2</sup>The mean crystalline size in  $c$ -axis is calculated from Scherer equation using full width at half-maximum (FWHM) of the (003) Bragg reflection; the mean crystalline size in  $ab$ -plane is calculated from Scherer equation using full width at half-maximum (FWHM) of the (110) Bragg reflection.



**Fig. S2.** FTIR spectra of (A) AMO-Mg<sub>3</sub>Al-LDH(Na) and (B) AMO-Mg<sub>3</sub>Al-LDH(K).

**Table S2.** Specific surface area and pore volume of Mg<sub>3</sub>Al LDHs and LDOs.

Sample	LDH		LDO	
	SSA m <sup>2</sup> g <sup>-1</sup>	Pore volume cm <sup>3</sup> g <sup>-1</sup>	SSA m <sup>2</sup> g <sup>-1</sup>	Pore volume cm <sup>3</sup> g <sup>-1</sup>
Mg <sub>3</sub> Al-LDH (K)	69	0.45	235.5	0.75
Mg <sub>3</sub> Al-LDH (Na)	70	0.43	233.5	0.93
AMO-Mg <sub>3</sub> Al-LDH (K)	254.2	1.14	366.1	1.66
AMO-Mg <sub>3</sub> Al-LDH (Na)	216.9	1.00	312.0	1.53



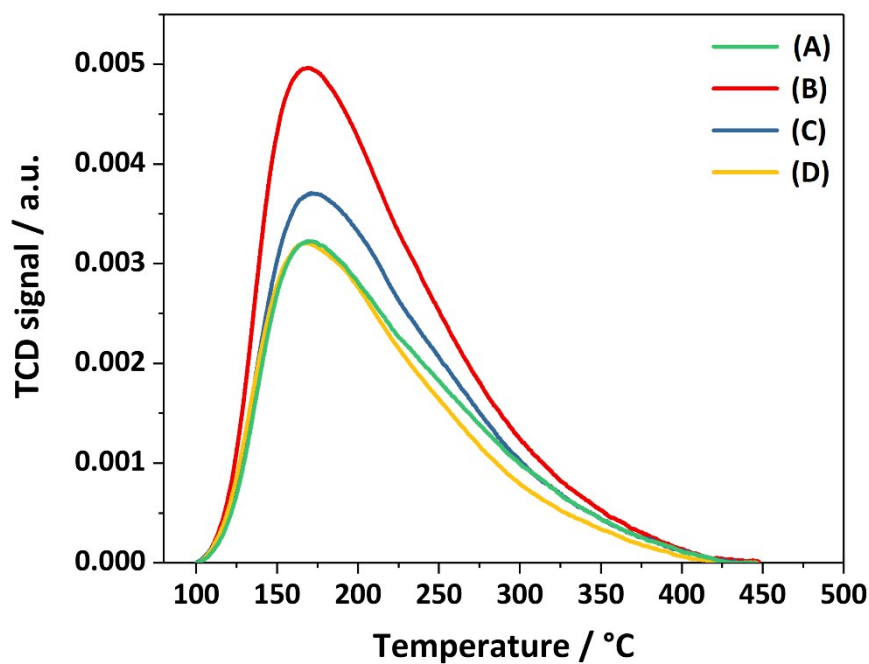
**Fig. S3.** XRD pattern of (A) AMO-Mg<sub>2</sub>Al-LDH(K), (B) AMO-Mg<sub>3</sub>Al-LDH(K), (C) AMO-Mg<sub>4</sub>Al-LDH(K), and (D) AMO-Mg<sub>5</sub>Al-LDH(K).

**Table S3.** Summary of d-spacing, lattice parameters and chemical composition of AMO-Mg<sub>x</sub>Al-LDH(K).

Catalyst	d spacing		Lattice parameters (Å) <sup>1</sup>		Mg/Al mole ratio <sup>2</sup>	K wt% <sup>2</sup>
	003	110	<i>c</i>	<i>a</i>		
AMO-Mg <sub>2</sub> Al-LDH (K)	7.72	1.52	23.17	3.05	2.05	0.074
AMO-Mg <sub>3</sub> Al-LDH (K)	7.83	1.53	23.49	3.06	2.87	0.014
AMO-Mg <sub>4</sub> Al-LDH (K)	7.86	1.54	23.58	3.07	3.50	NA
AMO-Mg <sub>5</sub> Al-LDH (K)	7.99	1.54	23.97	3.08	4.07	NA

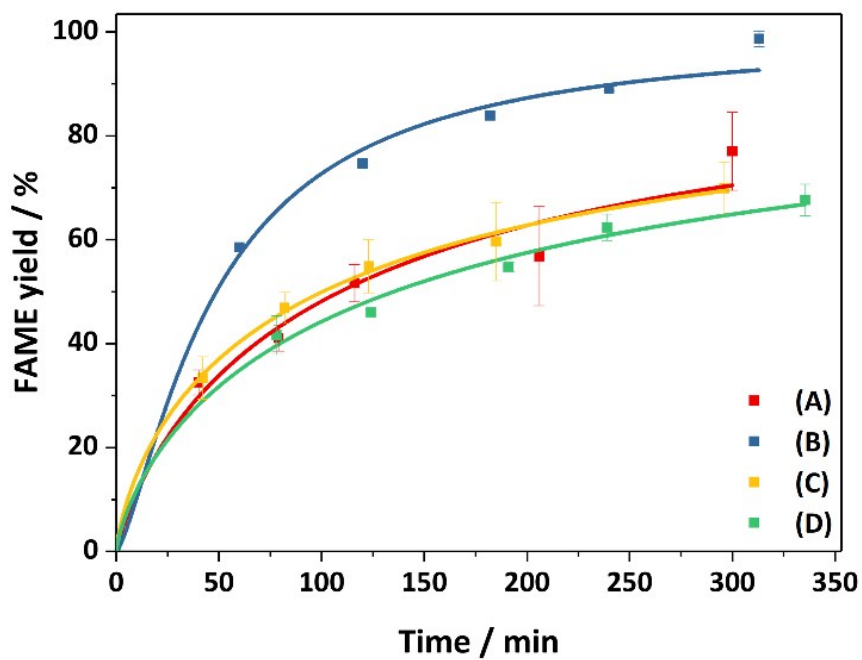
<sup>1</sup>*c*-lattice constant is obtained from  $c = 3 \times d(003)$ ; *a* is obtained from  $a = 2 \times d(110)$ .

<sup>2</sup>Mg/Al ratio and K wt% are obtained from ICP-MS.



**Fig. S4.** CO<sub>2</sub>-TPD of (A) AMO-Mg<sub>2</sub>Al-LDO(K), (B) AMO-Mg<sub>3</sub>Al-LDO(K), (C) AMO-Mg<sub>4</sub>Al-LDO(K) and (D) AMO-Mg<sub>5</sub>Al-LDO(K).





**Fig. S5.** Transesterification reaction using catalysts (A) AMO-Mg<sub>2</sub>Al-LDO(K), (B) AMO-Mg<sub>3</sub>Al-LDO(K), (C) AMO-Mg<sub>4</sub>Al-LDO(K) and (D) AMO-Mg<sub>5</sub>Al-LDO(K) (Reaction conditions: methanol to sunflower oil ratio (wt) = 10 : 1; catalyst loading = 10 wt.% oil; temperature = 65 °C. LDO was obtained from the calcination of LDH at 450 °C for 6 h).

### 3 References

1. G. Gelbard, O. Bres, R. Vargas, F. Vielfaure and U. Schuchardt, *J. Am. Oil Chem. Soc.*, 1995, **72**, 1239-1241.