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

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Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Potassium salt prepared AMO-Mg_xAl-LDH(K) ($x = 2-5$) have been studied as catalyst precursors for biodiesel synthesis. Calcined potassium salt prepared AMO-Mg_{0.75}Al_{0.25}(OH)₂[(CO₃)_{0.17}K_{0.01}] {AMO-Mg₃Al-LDH(K)} with a high surface area (366.1 m² g⁻¹) and high Lewis basicity density (2.87 μmol m⁻²), catalyses the 99% transesterification of sunflower oil with methanol to yield fatty acid methyl esters (FAMES) after 300 minutes, a much higher performance than conventional LDHs.

The now eponymous vegetable oil-based fuel (so called biodiesel) from renewable feedstocks has shown an increasing interest globally due to the limited fossil fuel resource, the surrounding climate change and air pollution.^{1,2} Biodiesel is the colloquial name for long chain, mono-alkyl fatty acid alkyl esters (FAEs) which are conventionally synthesised by the transesterification of triglycerides from vegetable oils or animal fats with alcohols. Eq. 1 shows the typical reversible reaction performed with triglyceride and methanol to produce fatty acid methyl esters (FAMES) and a glycerol side-product.^{3,4}

By far, the most common catalysts in the biodiesel industry are the homogeneous catalysts such as sodium or potassium hydroxides/ methoxides. NaOCH₃, in particular, is used due to its affordability and high activity, leading to short reaction time and high yields under modest reaction conditions.⁵ However, water in the reaction mixture can hydrolyse triglycerides to free fatty acids which react with homogeneous alkali catalysts in the feedstock to form soaps, in turn consuming the catalyst, lowering product yields and promoting emulsions which prevent efficient separation of FAMES and glycerol.³⁻⁶ In addition, separation and purification of a homogeneous reaction mixture are expensive and time-consuming. These problematic downstream processes have driven the research into heterogeneous catalysis.³⁻⁹

Eq. 1. Generic scheme for the transesterification reaction of triglycerides with methanol to produce fatty acid methyl esters (FAMES) and glycerol.

Basic heterogeneous catalysts are of interest in biodiesel industry due to their facile separation from the reaction mixture, relative tolerance of free fatty acids (FFAs), and ease of recycling that could significantly decrease operating costs. Metal oxides (e.g. CaO, and MgO) have been the subject of most research in heterogeneous catalytic transesterification.¹⁰⁻¹² However, the activity of basic heterogeneous catalysts is limited by their low surface areas and low basicity densities. Layered double hydroxides (LDHs) are related to brucite, {Mg(OH)₂} with edge sharing metal hydroxide octahedra. LDHs conform to the general chemical composition $[(M^{z+}_{1-x}M'^{y+}_x(OH)_2)]^{w+}(A^{n-})_{w/n} \cdot mH_2O$, where M^{z+} and M'^{y+} are one more different metal cations, z can be 1 or 2 and y can be 3 or 4; overall charge of the metal hydroxide layer (w) is determined by $w = z(1-x) + xy - 2$ which is compensated by w/n A^{n-} interlayer anions.¹ Most commonly LDHs are composed of metal cations with $z = 2$ and $y = 3$, since w must be a positive real number, $x > 0$; however, in practice x has been found to give crystalline phase pure Mg- and Al-containing LDHs when $0.35 \leq x \leq 0.16$.¹³⁻¹⁵ It is well-known that LDHs can be transformed into mixed metal oxides (also called layered double oxides, (LDOs)), upon thermal treatment in the range 400 – 600 °C. Calcination at higher temperatures results in crystallisation of dense spinel phases. LDOs have the advantages of a homogeneous metal atom distribution and adjustable base – acid sites, as a result these materials have attracted considerable interest for a number of catalytic reactions and gas sorption.¹⁶⁻¹⁸

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Electronic Supplementary Information (ESI) available: [¹H NMR spectroscopy, FTIR spectra, XRD, CO₂-TPD, specific surface area, pore volume, lattice parameters, mean crystallite sizes and compositions]. See DOI: 10.1039/x0xx00000x

The impregnation of conventional LDHs with potassium salts has been extensively reported as an effective means of increasing the basicity by adding strong K_2O surface basic sites.^{19–21} Recently, higher activity for transesterification of triglycerides has been reported using LDHs prepared with potassium containing reagents.²² However, the mechanism is still not well understood and the leaching of free potassium could be an issue. One disadvantage of conventional LDHs is their synthesis using traditional co-precipitation methods resulting in aggregated conglomerates that exhibit low surface area (SSA) and small pore volumes, this severely limits the availability of active reaction sites. Recently, O'Hare and co-workers have developed a facile and effective method to produce high SSA and highly dispersed LDHs using conventional synthesis methods followed by a facile post synthesis dispersion in an aqueous miscible organic solvent (AMO solvent).^{23–25} The LDHs obtained from this process have been named AMO-LDHs.

Herein, we report the synthesis of potassium doped AMO-LDHs with high SSA and high basic site density for application in biodiesel synthesis. A series of AMO- $[Mg_{1-x}Al_x(OH)_2](CO_3)_{x/2}$; $y = 1-x/x$ (AMO- Mg_yAl -LDHs) were prepared. Using different alkali metal salts in the LDH synthesis leads to doping of A^+ cations in the AMO- Mg_yAl -LDHs {abbreviated as AMO- Mg_yAl -LDH(A)}. AMO- Mg_yAl -LDH(A) were synthesised by co-precipitation using alkali metal hydroxides or carbonates followed by post synthesis dispersion in ethanol. The physical/chemical properties of the obtained LDHs were studied and compared with conventional LDHs prepared using sodium and potassium salts {noted as Mg_xAl -LDH(A) (A = Na, K)}. The effect of AMO treatment and Mg/Al ratio on the catalytic performance for transesterification of sunflower oil with methanol to fatty acid methyl esters (FAMES) was evaluated.

Conventional Mg_xAl -LDH(A) (A = Na, K) were prepared by co-precipitation using $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and A_2CO_3/AOH (A = Na, K) at a constant pH 10, followed by aging at room temperature. AMO- Mg_xAl -LDHs(A) ($x = 3-5$; A = Na, K) were prepared by multiple dispersions of the conventional Mg_xAl -LDHs(A) in ethanol (see ESI). Fig. 1 shows the powder X-ray diffraction (XRD) pattern of AMO- Mg_3Al -LDHs prepared using different salts (potassium or sodium hydroxide/carbonate salts). Both LDHs exhibit a series of characteristic Bragg reflections that can be indexed as (003), (006), (009), (015) and (018). The basal plane spacing and lattice parameters of AMO- Mg_3Al -LDH(K) remain the same as those of AMO- Mg_3Al -LDH(Na). However, the mean crystalline domain lengths (CDL) in both c -axis and ab -plane are smaller than those in AMO- Mg_3Al -LDH(Na). In particular, the CDL in c -axis of AMO- Mg_3Al -LDH(K) is 62% of the CDL in AMO- Mg_3Al -LDH(Na). LDO catalysts were obtained from the calcination of LDHs at 450 °C for 6 h. The XRD pattern in Fig. 1(C) and (D) indicate that all LDO catalysts have Bragg diffraction features indication the crystallisation of periclase MgO (PDF#03-0998), studies suggest that Al ions partially diffuse in the MgO lattice.²⁶ The Bragg diffraction features of the MgO derived from calcination of AMO- Mg_3Al -LDO(K) are slightly broader compared with to the MgO derived from AMO- Mg_3Al -LDO(Na).

Fig. 1 Powder XRD pattern of (A) AMO- Mg_3Al -LDH(K), (B) AMO- Mg_3Al -LDH(Na), (C) AMO- Mg_3Al -LDO(K) and (D) AMO- Mg_3Al -LDO(Na). (*) are the Bragg reflection from the sample holder. LDO was obtained from the calcination of LDH at 450 °C for 6 h.

Fig. 2 TEM images of (A) Mg_3Al -LDH(K), (B) AMO- Mg_3Al -LDH(K), (C) Mg_3Al -LDH(Na) and (D) AMO- Mg_3Al -LDH(Na).

Both AMO- Mg_3Al -LDH(K) and AMO- Mg_3Al -LDH(Na) exhibit the same Fourier-transform infrared (FTIR) spectral features (Fig. S2), including the M-O transition/stretching/deformation, O-M-O bending and M-OH deformation below 1000 cm^{-1} , CO_3^{2-} vibration at 1367 cm^{-1} , H_2O bending at 1639 cm^{-1} and M-OH deformation, H-bonded interlayer H_2O , CO_2 - H_2O bridging in the range of 3000 – 3500 cm^{-1} . The transmission electron microscopy (TEM) images (Fig. 2) indicate that AMO- Mg_3Al -LDH(Na) and AMO- Mg_3Al -LDH(K) have a similar rosette morphology with comparable particle size (Fig. 2B and 2D). Both samples demonstrate much less aggregation compared with the samples without AMO solvent treatment (Fig. 2A and 2C). This

is consistent with the specific surface area and pore volume data shown in Table S2. AMO-Mg₃Al-LDH(K) and AMO-Mg₃Al-LDH(Na) display a 3–4 times higher specific surface area and 2–3 times larger pore volume than those of conventional Mg₃Al-LDHs. AMO-Mg₃Al-LDH(K) exhibits a slightly higher specific surface area than AMO-Mg₃Al-LDH(Na). This is probably due to the less crystalline (disordered) nature of AMO-Mg₃Al-LDH(K) as found in the XRD data (Fig. 1) which can be more easily exfoliated by AMO solvent. After calcination at 450 °C for 6 h, the Brunauer-Emmett-Teller (BET) specific surface area of all samples increases dramatically due to the formation of a porous structure via de-hydroxylation and de-carboxylation during the calcination process. Particularly, AMO-Mg₃Al-LDO(K) exhibits the highest specific surface area of 366.1 m² g⁻¹ and the largest pore volume of 1.66 cm³ g⁻¹.

In this study, we selected sunflower oil as the feedstock for transesterification to biodiesel. Sunflower seed is viewed as a good source of biomass for biodiesel production. Sunflower oil typically contains palmitic acid (4%), stearic acid (4%), oleic acid (78%) and linoleic acid (14%). In a typical transesterification reaction the LDO catalyst was added to a mixture of methanol and sunflower oil (methanol: sunflower oil (wt) is 10:1) and heated at 65 °C for up to 24 hours. Aliquots were extracted from the reaction mixture at recorded intervals and after filtration to remove the solid catalyst and evaporation to remove the excess methanol the product was analysed by ¹H NMR spectroscopy. The FAME yield for each reaction was determined by integration of the ¹H NMR spectra, full details of this analysis are given in the ESI.

Fig. 3 shows a kinetic study of the transesterification of sunflower oil and methanol at 65 °C in the presence AMO and non-AMO versions of Mg₃Al-LDO(K). The FAME yield was calculated using ¹H NMR spectroscopy²⁷ (Fig. S1) and modelled by a Hill function.

Fig. 3 Transesterification of sunflower oil and methanol using the solid catalysts: (A) Mg₃Al-LDO(K) and (B) AMO-Mg₃Al-LDO(K). (Reaction conditions: methanol : sunflower oil ratio (wt) = 10 : 1; catalyst loading = 10 wt% oil; temperature = 65 °C. LDOs were obtained from the calcination of LDH at 450 °C for 6 h).

AMO-Mg₃Al-LDO(K) catalysed the transesterification of sunflower oil at a faster rate and produced a higher overall

FAME yield compared with a conventional control sample of Mg₃Al-LDO(K). After 120 minutes, the FAME yield using AMO-Mg₃Al-LDO(K) was 77% is almost twice that of conventional Mg₃Al-LDO(K) (39%). After 300 minutes, the yield reached 99% using AMO-Mg₃Al-LDO(K) while it remained at 58% using a conventional Mg₃Al-LDO(K). This could be due to high specific surface area and large pore volume of AMO-Mg₃Al-LDO(K) as mentioned above, which can enable the reactant molecules to access the active sites. On the other hand, the AMO-LDHs have improved dispersion in non-polar hydrocarbons due a decrease in the hydrophobicity,^{23, 28} which may improve mass diffusion and surface wetting aspects, leading to fast catalytic activity.

In addition to specific surface area and pore volume, the basicity density is another important factor effecting the transesterification reaction. An Mg_xAl-LDO is a mixed metal oxide Mg(Al)O_x, the Lewis acid – base sites can be tuned by the ratio of Mg:Al ratio.²⁹ In this work, the effect of Mg:Al ratio in the range 2 – 5 in potassium prepared AMO- Mg_xAl-LDH(K)s for the biodiesel synthesis was studied. The Mg:Al ratio and K⁺ content was confirmed by inductively coupled plasma mass spectrometry (ICP-MS). The potassium content was found to be very low in all the samples (Table S3) so the role of KOH in the catalysis can be eliminated. All AMO-Mg_xAl-LDH(K) samples exhibited the same characteristic LDH Bragg diffraction features as shown in Fig. S3. The interlayer basal spacing (*c*-parameter) and *a/b*-unit cell parameters increase with increasing Mg:Al ratio (Table S3). All AMO-LDOs display high surface areas (> 310 m² g⁻¹). The specific surface area increases slightly with increasing Mg:Al ratio from 2 to 4 (Table 1). The carbon dioxide – temperature programmed desorption (CO₂-TPD) measurement (Fig. S4) shows that all catalysts display weak signals in the range of 100 – 150 °C, indicating a low concentration of low strength basic sites (OH- sites). The major basic sites are located on medium strength Mg-O pairs as indicated at around 170 °C. AMO-Mg₃Al-LDO(K) presents the maximum basic site density (Table 1), signifying a balance between structural and electronic features.

Table 1. Specific surface area and Lewis basic site density of (A) AMO-Mg₂Al-LDO (K), (B) AMO-Mg₃Al-LDO(K), (C) AMO-Mg₄Al-LDO(K) and (D) AMO-Mg₅Al-LDO(K) (LDO was obtained from the calcination of LDH at 450 °C for 6 h).

Catalyst	SSA / m ² g ⁻¹	Lewis basic site density / μmol m ⁻²	Lewis basic site density / μmol g ⁻¹
AMO-Mg ₂ Al-LDO(K)	313	2.00	627
AMO-Mg ₃ Al-LDO(K)	366	2.87	1052
AMO-Mg ₄ Al-LDO(K)	394	2.24	880
AMO-Mg ₅ Al-LDO(K)	388	1.89	735

Fig. 4. 3D surface graph for the effect of specific surface area and Lewis basic site on the FAME yield.

Increasing Al^{3+} concentration provides a higher density of basic sites. However, the higher electronegativity of Al leads to a decrease in electronic density of the unsaturated oxygen species, thus the basic strength of medium and strong sites is diminished.^{18, 29}

Fig. S5 shows the catalytic performance of AMO-LDOs with different Mg:Al ratios. The catalytic activity increases with increasing Lewis basic site density per unit area. AMO-Mg₅Al-LDH(K), with the lowest basic site density of $1.89 \mu\text{mol m}^{-2}$, only achieves 48% FAME yield after 120 minutes, whereas AMO-Mg₃Al-LDH(K) has the maximum basic site density of $2.87 \mu\text{mol m}^{-2}$ and also showed maximum FAME yield (77%) in the same duration. Fig. 6 illustrated the dependence both SSA and Lewis basic site density on FAME yield. Higher SSA and higher Lewis basic site density seems to promote a higher FAME yield. Future studies will explore if additional potassium doping has any effect on = transesterification in these materials.

Conclusions

Potassium salt prepared AMO-Mg_xAl-LDH(K) ($x = 2-5$) have been studied as catalyst precursors for biodiesel synthesis. We found that potassium salt prepared AMO-Mg_xAl-LDH(K) show slightly lower crystallinity and higher surface areas compared with those of sodium salt prepared AMO-Mg_xAl-LDH(Na).

AMO-Mg_xAl-LDO(K) exhibits a much higher surface area ($> 310 \text{ m}^2 \text{ g}^{-1}$) than conventional Mg_xAl-LDO(K) without AMO treatment. AMO-Mg₃Al-LDH(K) displays the highest surface area ($366 \text{ m}^2 \text{ g}^{-1}$) and largest Lewis basicity density ($2.87 \mu\text{mol m}^{-2}$), it also shows the best catalytic performance (99% FAME yield over 300 minutes) in biodiesel synthesis from sunflower oil with methanol. It showed twice higher FAME yield than that a conventional Mg₃Al-LDH(K) as catalyst precursor.

The study shows that surface area, basicity density and particle dispersion play significant roles in heterogeneous base-catalysed transesterification.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

C. C. and J.-C. B. thank SCG Chemicals Co., Ltd. (Thailand) for financial support and surface analysis (University of Oxford) for use of the BET, TPD and FTIR instruments.

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