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Tuneable Functionalities in Layered Double Hydroxide Catalysts for Thermochemical Conversion of Biomass-Derived Glucose to Fructose

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Abstract

Layered double hydroxides (LDHs) with varying crystallite sizes (2.6-43 nm), layer numbers (3-70), specific surface area (18-455 m² g⁻¹), pore volume (0.025-1.6 mL g⁻¹), and functional groups were synthesised via conventional urea hydrolysis and co-precipitation methods and aqueous miscible organic solvent (AMOST) treatment. They were evaluated as the solid base catalysts for the thermochemical isomerisation of biomass-derived glucose to fructose with the aim of establishing the structure-performance relationships for carbon-efficient biorefinery. The results showed that the fructose yield increased with increasing crystallite size of LDHs due to the enhanced exposure of active sites. However, excessive increase in the structural accessibility could be detrimental because high hydrophilicity potentially resulted in water clusters surrounding the active sites and hindering their interaction with glucose. Nano-sized particles in small quantity that were visually indiscernible may partially account for the catalytic activity. The kinetics test suggested that the conversion of glucose to intermediates may act as the rate-determining step when the reaction temperature increased. The activation energy for the LDH-catalysed glucose conversion was estimated to be 52.8 kJ mol⁻¹. The highest fructose yield of 25 mol% was achieved at 120 °C for 5 min in water. The recycling test suggested that the catalytic performance became stable after the second run, possibly due to the formation of a passive layer. This study elucidates the structure-controlled functionalities of the LDH catalysts to serve a base-catalysed biorefinery reaction, and provides mechanistic insights into the active components and the catalyst transformation during thermochemical biomass conversion.

Keywords: sustainable biorefinery; value-added chemicals; waste valorisation/recycling; green solvents; solid base catalysts; hydrotalcite-like clay.

1. Introduction

Sugar catalysis has drawn extensive attention as a result of increasing worldwide demand for bio-based products to substitute their conventional fossil-derived counterparts [1-5]. One of the important biorefinery reactions is the isomerisation of glucose to fructose, as the latter has a more reactive structure that is conducive to downstream chemical conversions for a wide spectrum of applications. While glucose is widely available in biomass in the form of glucans (e.g., cellulose and starch) and monomers, fructose is usually produced from glucose via enzymatic isomerisation [6]. Research efforts have been devoted to devising efficient heterogeneous solid catalysts as the alternatives to costly enzymes, to achieve faster reaction and reduce operational costs [6]. The two categories of catalysts for glucose isomerisation are Brønsted base (OH⁻) [7, 8] and Lewis acid (electron pair acceptor) [9-11], of which the catalytic mechanisms involve a hydrogen transfer from O2 to O1 and a hydride shift from C2 to C1, respectively [7].

It is noted that the base catalytic system generally enables glucose isomerisation at a lower temperature (e.g., 90-120 °C for NaY zeolite [12], hydrotalcite [13], natural minerals [14, 15], chromium hydroxide/MIL-101(Cr) [16], and amine/amino acid [7, 17]) compared with that in Lewis acids (e.g., 120-160 °C for biochar-supported Al [9], Fe/ β zeolite [18], modified UiO-66 [19], and metal chlorides [20, 21]). This observation is supported by the kinetic studies in the literature, in which the activation energy was found to be lower for the base-mediated glucose isomerisation (i.e., 44-64 kJ mol⁻¹) [7, 17, 22] than that for the Lewis acids systems (i.e., usually \geq 80 kJ mol⁻¹) [2]. In view of the advantage of low energy demand, base catalysts emerge as a potentially promising option for catalytic glucose isomerisation that deserves more investigations. While the vast studies investigated the use of solid Lewis acid catalysts for the glucose-fructose transformation [9, 10, 18, 19], there is limited development on the design of solid base catalysts.

This presents the opportunities to explore the system of solid base catalysts by understanding the relationship between physicochemical properties and catalytic kinetics of biomass thermochemical conversion.

We opt to study layered double hydroxides (LDHs; also known as hydrotalcite-like clay) as a model solid base in this work in which LDHs are acknowledged to have a high potential in catalysing glucose isomerisation [13, 23, 24] and feature facile preparation and tuneable properties. LDHs are ionic lamellar compounds comprising positively charged metal hydroxide layers with anions in the interlayer galleries. These materials have been reported for a wide array of applications in gas separation [25], liquid phase adsorption [26], catalyst support [27], electrochemical sensing [28], optics [29], and drug delivery systems [30]. Despite the versatile properties, the LDH nanosheets are prone to agglomeration hindering their applications due to the reduced surface area [31]. Aqueous miscible organic solvent (AMOST) treatment emerges as a simple exfoliation process to produce highly dispersed LDHs with desired high porosity [31, 32]. We therefore hypothesize that the catalytic performance of LDHs could be enhanced after AMOST treatment, as a result of exposure of more catalytic sites associated with the unfolding structure upon exfoliation. In particular, the changes in the crystallite size and surface area could be conducive to the varying quantity of edge-located active sites and/or defects on the basal planes.

To the best of our knowledge, this is the first study examining the performance of AMOST-synthesised LDH in catalytic glucose isomerisation. More importantly, the comparison of the catalytic activity with those synthesised by conventional urea hydrolysis and co-precipitation methods allows us to establish the structure-catalytic properties relationship. Kinetics study and recycling test were performed for the comprehensive evaluation. The results were scrutinised to postulate the origin of catalytic activity and the transformation of LDHs during thermochemical

reaction. Water as the most environmentally benign reaction medium was used throughout the study. Our findings highlight LDHs as a highly tuneable solid base catalyst, offering the prospect of tailoring these versatile catalysts for carbon-efficient and sustainable biorefineries.

2. Materials and methods

2.1 Chemicals

For LDHs synthesis, magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminium nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), urea, and sodium carbonate (Na_2CO_3) of analytical reagent grade were all purchased from Alfa Aesar. Sodium hydroxide (NaOH) and acetone were purchased from Sigma-Aldrich. Milli-Q water was used throughout the synthesis process. As for the catalytic reaction and calibration of the analytical equipment, the following chemicals was used: cellobiose ($\geq 98\%$), levulinic acid (98%), and formic acid (98%) from Alfa Aesar; fructose ($\geq 99\%$) and maltose monohydrate ($\geq 98\%$) from Wako; glucose ($\geq 99.5\%$), HMF ($\geq 99\%$), and furfural (99%) from Sigma Aldrich; and levoglucosan from Fluorochem. All chemicals were used as received.

2.2 Synthesis of modified LDHs

The LDHs with the Mg:Al molar ratio of 2:1 were synthesised using three different procedures below. The prepared samples were dried in an air oven at 110 °C for 12 h and was kept inside a N_2 -filled glove box for future evaluation.

2.2.1 Urea hydrolysis

In this procedure, 37.5 mmol (9.60 g) of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 18.8 mmol (7.03 g) of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 281.2 mmol (16.88 g) of urea were dissolved in 70 mL milli-Q water under magnetic stirring at room temperature in a 100-mL teflon liner. It was then sealed in a stainless

steel autoclave and placed in a preheated air oven at 90 °C for 12 h. After cooling in air, the sample was separated by centrifugation and washed with deionized water until the pH of filtrate reached ~7 from the initial pH value of 9.3. The sample was coded as LDH-U.

2.2.2 *Co-precipitation synthesis*

First, 37.5 mmol (9.60 g) of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 18.75 mmol (7.03 g) of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 35 mL of water at room temperature. This solution was added dropwise to the 35 mL solution of 0.5 M Na_2CO_3 under magnetic stirring at 600 rpm at room temperature in a 500-mL reagent bottle. The mixture pH was controlled at the value of 9-10 using 4 M NaOH solution. After adding all chemicals, the reagent bottle was closed for 60 min of stirring. The suspension was then separated by centrifugation, and the solid was repeatedly washed with milli-Q water until neutrality (7.5). The dried sample was denoted as LDH-CP.

2.2.3 *AMOST treatment method*

The synthesis was carried out in the same way as the co-precipitation synthesis, except for the additional step of acetone treatment. The water-washed material was further rinsed with 500 mL acetone and was then dispersed in 300 mL acetone for 12 h. The sample was recovered by evaporating the acetone at 50 °C in a rotary evaporator, namely LDH-AM.

2.3 Characterisation of modified LDHs

The as-synthesised samples were characterised by powder X-ray diffraction (XRD) using the Panalytical Xpert³ diffractometer. The samples were first crushed to fine powder in a mortar and then analyzed by PXRD, data being collected at 2θ from 5 to 70° at scan step size of 0.02° and scan speed of 2° min⁻¹. Phase identification was carried out by matching the experimental patterns

with the International Centre for Data Diffraction-Joint Committee on Powder Diffraction Standards (ICDD JCPDS) database reference patterns. Crystallite size was calculated from the most intense peak of XRD pattern using the Scherrer equation: $B(2\theta) = \frac{K\lambda}{L\cos\theta}$; where K = Scherrer constant, λ = wavelength of the anode rays used (CuK = 1.54242 Å), and L = full width at half maximum in radians. The value of K was taken as 0.94 for most spherical crystallites and width at half maximum (L) was corrected for instrumental broadening 0.02° . The specific surface area and pore size distribution were determined by N_2 sorption at 77 K using Micromeritics 3Flex instrument. Prior to the analysis, all samples were first degassed under vacuum at 120°C for 12 h using a Micromeritics Vacprep degassing unit. Fourier-transform infrared spectroscopy (FTIR) analysis was carried out using a Shimadzu IRAffinity-1 FTIR spectrometer in the absorbance mode within the wavenumber range of $4000\text{-}400\text{ cm}^{-1}$, with 20 scans per spectrum, and a spectral resolution of 4 cm^{-1} . Prior to measuring the spectrum of the samples, the background correction was carried out using FTIR grade KBr pelletized at 41.3 MPa. 2 mg of sample was thoroughly mixed with 50 mg of FTIR grade KBr using an agate pestle and mortar and then pelletized under a pressure of 41.3 MPa.

2.4 Catalytic conversion

The catalytic conversion of glucose was performed following the procedure reported in our previous studies [33-36]. In brief, catalyst (0.1 or 0.2 g), glucose (0.5 g), and water (10 mL) were added to a Teflon vessel, which was heated to $100\text{-}120^\circ\text{C}$ at a ramp rate of 19 or $95^\circ\text{C min}^{-1}$ with the target temperature held for 1-20 min, under magnetic stirring in an Ethos Up Microwave Reactor (Milestone). The reactor was cooled by mechanical ventilation. All trials were carried out in duplicate. In supplementary tests, a selected sample was hydrothermally treated, in the absence of glucose following the above procedure. The resultant solid and liquid phases were separated by

centrifugation and decantation, for examining their respective catalytic performance in glucose conversion [9]. In the catalytic test of the solid phase, water was added to serve as the reaction medium. Recycling test was also performed by collecting the solids via centrifugation, decantation, and washing for several times. The dried solid, denoted as LDH-AM-R, was used in the next run of catalysis without prior regeneration. For product analysis, all liquid samples were diluted with deionised water (1:3 v/v) and filtered through a mixed cellulose ester filter (0.22 μm).

2.5 Catalysis sample analysis

High-performance liquid chromatography (HPLC) was performed using a Chromaster instrument equipped with a refractive index detector (Hitachi, Japan) and an Aminex HPX-87H column (Bio-Rad). The mobile phase was 0.01 M H_2SO_4 and the flow rate was 0.5 mL min^{-1} with the column temperature set at 50 $^\circ\text{C}$ [9, 20, 37]. Retention times for different compounds are given in **Table S1**. The yield and selectivity of the products as well as glucose conversion were calculated in terms of the carbon content.

$$\text{Product yield (mol\%)} = \frac{P_f(\text{mg/ml}) \times n_p / MW_P}{Glu_i(\text{mg/ml}) \times n_{Glu} / MW_{Glu}} \times 100, \quad (1)$$

$$\text{Product selectivity (mol\%)} = \frac{P_f(\text{mg/ml}) \times n_p / MW_P}{(Glu_i - Glu_f)(\text{mg/ml}) \times n_{Glu} / MW_{Glu}} \times 100, \quad (2)$$

$$\text{Glucose conversion (mol\%)} = \frac{Glu_i - Glu_f(\text{mg/ml})}{Glu_i(\text{mg/ml})} \times 100, \quad (3)$$

where, P_f represents the concentration of the products; n_p and n_{Glu} are number of carbons in the corresponding product and glucose, respectively; MW_P and MW_{Glu} are molecular mass of the corresponding product and glucose, respectively; and Glu_i and Glu_f represent the initial and final concentration of glucose, respectively.

2.6 Kinetic data fitting

The kinetic data within the first 10 min of reaction were fitted using the Weibull model as shown in Equation (4).

$$\frac{G}{G_0} = \exp [-(kt)^n], \quad (4)$$

where, G and G_0 are the glucose concentration at time = t and 0 min, respectively; k is the rate constant; and n is the shape constant [38]. The Weibull model was found suitable for describing the degradation behaviour of monosaccharides in subcritical water [38]. The parameters k and n were determined using the Solver of Microsoft Excel, with the sum of squared residuals kept at minimum. The obtained k values serve the calculation of the activation energy (E_a) for glucose conversion using the Arrhenius' equation (5).

$$k = k_0 \exp \left(-\frac{E_a}{RT} \right), \quad (5)$$

where k_0 is the frequency factor; R is the gas constant; and T is the temperature.

3 Results and discussion

3.1 Characterisation of LDHs

The XRD patterns of the materials synthesised by different methods confirm the successful formation of Mg-Al LDHs (JCPDS: 01-089-0460) (**Fig. 1**). The interlayer distance calculated from the position of the most intense peak using Braggs equation is 7.59 Å for all the samples. The crystallinity of the samples depends on the synthesis method. The narrow and intense peaks for LDH-U are indicative of the highest crystallinity among the three samples, which have an average crystallite size of 42.8 nm based on the Scherer equation. The high crystallinity is attributed to the

gradual growth of LDH crystallites over an extended period of time (12 h) in the urea hydrolysis method. At 90 °C, urea gradually decomposes to ammonium carbonate, which reacts with metal salts to form the LDH structure under hydrolytic conditions [39]. The sample prepared by co-precipitation, i.e., LDH-CP, has a smaller crystallite size of ~28 nm, which may be accounted by the rapid co-precipitation of the metal salts in a strongly basic environment. In contrast to LDH-U and LDH-CP, very diffuse peaks appear in the XRD pattern of LDH-AM, corresponding to the smallest crystallite size of 2.6 nm. The average number of layers was computed by dividing the average crystallite size by the interlayer distance along the (003) planes [32], which is ~3 for LDH-AM < 36 for LDH-CP < 56 for LDH-U. The smallest grain size and lowest number of stacked layers in LDH-AM are accounted by the delamination and dispersion of layered structure in acetone [32]. The aggregation of LDH layers via hydrogen bonding was suppressed in acetone, and its rapid evaporation at 60 °C further disrupted the LDH-AM structure to a highly exfoliated form [31].

The FTIR spectra of the as-synthesised samples are given in **Fig. 2**, and the peak assignment was performed with reference to the literature (**Table 1**) [40, 41]. The FTIR results confirm that carbonate, water, and -OH functionalities were still present in LDH-AM, suggesting the exfoliation via AMOST treatment hardly affect the chemical composition of LDH, in agreement with the previous findings [31, 32]. Nevertheless, the peak intensity follows the ascending order: LDH-U < LDH-CP < LDH-AM, highlighting that exfoliation leads to more available functionalities.

The N₂ sorption isotherms at 77 K for all three samples are given in **Figure 3**. The sample synthesised by urea hydrolysis procedure (LDH-U) shows type Ib reversible isotherm as per the latest IUPAC classification [42], indicative of wider micropores along with some narrow

mesopores. The micropore character may be attributed to its interlayer spacing of 7.59 Å between (003) planes of LDH-U. Both LDH-CP and LDH-AM show type IVa isotherm with H3 hysteresis loop, indicative of a wide pore size distribution in meso-macropore range. This can be attributed to the aggregation of small platelet-like crystallites which arrange themselves in a spherical sand rose or nano-flower-like morphology [32, 43].

The surface area and pore volume properties are given in Table 2. The surface area, particularly the mesopore-macropore external surface area, follows the trend, $7.6 \text{ m}^2 \text{ g}^{-1}$ for LDH-U < $79 \text{ m}^2 \text{ g}^{-1}$ for LDH-CP < $424 \text{ m}^2 \text{ g}^{-1}$ for LDH-AM. Such an increase is consistent with the enlargement in the mesopore volume, suggesting that the AMOST exfoliation enhances the porosity [31, 32]. It is noted that the delaminated sample has the highest specific surface area and pore volume surpassing all the literature reports so far. The highest surface area reported previously for LDHs is $365 \text{ m}^2 \text{ g}^{-1}$ [32]. The reason for the higher surface area in our study is the rapid drying of acetone after dispersion in a rotary evaporator instead of the room temperature vacuum drying used previously. The rapid drying is probably more efficient in avoiding the re-stacking of layers which leads to decrease in surface area.

3.2 Catalytic conversion over LDH catalysts

3.2.1 Significance of the LDH porosity and surface chemistry

The LDH samples were active towards catalytic glucose isomerisation in water (**Fig. 4**). The presence of OH^- and CO_3^{2-} evidenced by the FTIR analysis provided base sites for the catalytic reaction [6]. Under mild heating at 100°C for 0.5-5 min, the fructose yield of 0-3 mol% over LDH-U was lower than that for LDH-CP and LDH-AM (2.7-8 mol%) (**Fig. 4a-c**). In view of the similar surface chemistry of LDH-U and LDH-CP (**Fig. 2**), the inferior performance of the former tends

to pertain to its physical properties. The mesopore surface area and porosity of LDH-U are 10- to 15-fold lower than that of LDH-CP (**Table 2**), in relation to its stacking of layers into large crystallites (**Fig. 1**). The results suggest the significance of structural properties and presence of mesopores in the catalytic isomerisation of glucose, which may have facilitated the contact between active sites and substrates, as well as the diffusion of substrates and products.

Glucose thermochemical conversion over LDH-CP and LDH-AM was performed at a higher temperature of 120 °C, in order to further assess the significance of exfoliation-induced structural changes. Provided a short reaction time, similar fructose yields were obtained over the two LDHs, e.g., ~9 mol% in 0.5 min and ~10 mol% in 1 min (**Fig. 4b**). When the reaction time increased to 5 min, LDH-AM gave slightly more fructose (16.5 mol%) than LDH-CP (14.8 mol%). It is noted that LDH-AM has the largest specific surface area (455 m² g⁻¹) and total pore volume (1.61 mL g⁻¹) among the prepared samples (**Table 2**). The unexpectedly small catalytic improvement suggests that the limiting factor is probably shifted to the other operating parameters when the surface area and porosity exceed a certain value. It has been recently suggested that the structural properties may not be the primary determinant of the catalytic glucose conversion over Al-impregnated biochars [9]. A previous study demonstrated a positive correlation between the basicity of hydrotalcites and glucose conversion, highlighting the contribution of the presence and quantity of active sites [13]. We performed FTIR analysis of LDH-AM-R, which revealed a decrease in the intensity of signals associated with the active sites, i.e., OH and CO₃²⁻, after the reaction (**Fig. 2**).

Another possible reason for the small improvement by LDH-AM is the detrimental features caused by the AMOST treatment. The FTIR absorbance by hydroxyl groups and water in LDH-AM is substantially higher than that in LDH-U and -CP (**Fig. 2**), suggesting the potentially higher hydrophilicity for LDH-AM. The disruption of its layered structure via AMOST exfoliation

increased the exposure of the surface functionalities including the hydrophilic components. Similarly, size reduction of hydrotalcites via moderate mechanical grinding also could induce an increase in hydrophilicity as reported by Olszówka et al. [44]. Deactivation of active sites by water is consequently a concern. In the current study, we deduce that the hydrophilic surface of LDH-AM was excessively covered by water molecules, which reduced the contact between the active sites and glucose. In addition, the presence of hydroxyl groups on FeO films altered the size, shape, and orientational ordering of adsorbed water clusters, as previously evidenced by microscopic imaging and computational modelling at an atomic level [45]. Similar incidents are conjectured in the case of our LDHs samples, of which the varying population of hydroxyl groups may affect the activity of the base sites, owing to the different extents of water clustering on the catalyst surface. The significance of the water-surface interplay warrants further computational analysis. Indirect involvement of the water molecules should also be considered, as Xi et al. observed that a trace amount of physisorbed water could promote the formation of butyric acid, which deactivated the hydrotalcite in the catalytic transesterification of tributyrin by methanol [46].

Agglomeration of LDH-AM was suggested by the notable drop in specific surface area from 455 to 244 m² g⁻¹ after the reaction (**Table 2**). XRD analysis revealed that both crystallite size and layer numbers increased by approximately 2.5 times, evidencing the stacking of LDH-AM layers during the reaction (**Fig. 1**). This may partially account for the small yield improvement by LDH-AM. Nevertheless, the surface area of LDH-AM-R remained greater than that of the pristine LDH-U and LDH-CP, implying a relatively small impact invoked by agglomeration compared to that of active sites and hydrophilicity discussed above.

3.2.2 Significance of reaction parameters

The operating parameters of catalytic glucose isomerisation were investigated using LDH-AM as the representative solid base catalyst. The effects of ramp rate, i.e., from 19 to 95 °C min⁻¹, appeared to be minor in view of the similar fructose yield of 22 mol% obtained after microwave heating at 120 °C for 5 min (trials 1 & 9; **Fig. 5**). The observation remained valid for 1-min heating (trials 3 & 5). The fructose yield slightly increased from 16.3 to 21.6 and to 23.9 mol% as the reaction was undertaken for 1, 5, and 10 min, respectively (trials 5, 9 & 10), suggesting a small improvement by extending the reaction time. Increasing the reaction temperature from 100 to 120 °C significantly increased the fructose yield from 3.8 to 16.3 mol%, in company with a higher glucose conversion (i.e., 23 mol% at 120 °C versus 7 mol% at 100 °C) (1 min; trials 5 & 6).

The increase in catalyst loading from 0.03 to 0.2 g gradually increased the fructose yield, i.e., from 16.5 to 25.2 mol% (120 °C, 5 min; trials 2, 7, 8 & 9). However, the yield was not proportional to the loading as the $\text{yield}_{\text{fructose}}/\text{loading}_{\text{LDH}}$ (w/w) factor significantly reduced from 2.8 to 0.6 with the increasing LDH-AM dosage from 0.03 to 0.2 g (**Fig. S1**). This suggests the presence of mass transfer limitation in the catalytic system and/or agglomeration of catalysts as indicated by the decrease in specific surface area (**Table 2**) and increase in crystallite size (**Fig. 1**). To avoid inefficient resource utilisation, the lowest catalyst loading of 0.03 g (i.e., 6 w/w% w.r.t. glucose loading) was selected for subsequent kinetics tests.

In this study, the highest fructose yield of 25.2 mol% obtained in water under mild microwave heating (0.2 g LDH-AM, 120 °C, 5 min) was comparable to that in the literature (**Table S2**). For instance, the homogeneous systems using amine catalysts gave rise to 17-32 mol% fructose under conventional heating at 100 °C for 15-30 min [7, 47]. As for the heterogeneous catalysts, commercial hydrotalcite yielded 27 mol% fructose after 48 h of reaction at 90 °C [23], whereas a

fabricated hydrotalcite achieved 30 mol% fructose after heating at 110 °C for 3 h [13] in an oil bath or autoclave. It should be noted that glucose-fructose isomerisation is a reversible reaction with an equilibrium at a glucose-to-fructose ratio of 1:1 and hence the maximum fructose yield is < 50% in the catalytic systems. In addition to significantly shorter reaction time due to efficient microwave heating, the current LDHs system is advantageous in terms of the lower catalyst loading, e.g., 40 vs. 200 w/w% (with respect to glucose) for a commercial hydrotalcite [23]. Although another study reported the production of 34.6 mol% fructose over rehydrated hydrotalcite of 33 w/w% (with respect to glucose) in dimethylformamide as the reaction medium [48], the use of water as the greenest solvent in the system of the current work presents a significant step towards green chemistry and sustainable engineering. As for base catalysts on the other solid supports, recently reported Cr-modified MIL metal-organic-frameworks achieved 20-59 mol% fructose (100 °C, 24 h) [16], while the desilicated NaY zeolites gave rise to 23-35 mol% fructose (100 °C, 2 h) [12]. These comparisons highlight the low-cost LDH-AM synthesised in this study as a competitive heterogeneous catalyst for base catalysis.

3.2.3 Kinetics and mechanistic insights

The kinetic profiles show the gradual increase in the fructose yield with increasing reaction time over 0.03 g LDH-AM (**Fig. 6**). After 20 min of reaction, the fructose yield reached 14 mol% at 100 °C < 17.8 mol% at 110 °C < 20.5 mol% at 120 °C, as a result of the increasing energy input. The selectivity of fructose also increased with time at 100 °C (**Fig. 6a**), which suggested the progressive transformation of intermediates to fructose. It is noted that the synchronic increase in the fructose selectivity and yield became less significant as the temperature was raised (**Fig. 6a-c**). In other words, while an increasing trend remained valid for the yield development, the selectivity profile tends to reach plateau throughout the reaction. We postulate that at higher temperatures,

the conversion of intermediates to fructose accelerated to a greater extent than the formation of intermediates from glucose, resulting in a lower intermediate content in the system as observed. As a consequence, the early-stage fructose selectivity increased with increasing temperature. This also implies that the glucose-to-intermediate conversion possibly emerges as the rate-limiting step under more intensive energy input at a higher temperature.

It is deduced that the intermediates, whose identification was not attempted in the current study, remained at a low concentration in view of the good carbon recovery/utilisation as high as 92 mol% (**Fig. 6d**). Nevertheless, previous research has proposed that intermediates could be involved in side reactions, reducing the selectivity of the desired products from biorefineries [2]. Although the fructose selectivity was satisfactory in the current study (average selectivity = 74.4 mol%; **Fig. 7a**), the identification of the intermediates and evaluation of their roles warrant further investigation, which may provide useful mechanistic information for achieving a higher carbon efficiency in similar base-catalysed isomerisation systems.

The kinetics data of glucose conversion were well fitted by the Weibull model (**Fig. S2**), which has been used to describe sugar decomposition in subcritical water [38]. The rate constant (k) increased with the reaction temperature (i.e., 0.00108, 0.00179, and 0.00257 min⁻¹ at 100, 110, and 120 °C, respectively). It may also be related to other parameters such as surface area of catalyst, yet linear correlation may not be expected as further increase in surface area did not significantly promote glucose conversion (**Table 2 & Fig 4**). The shape constant (n) remained comparable in a range of 0.324-0.414, i.e., $n < 1$, which implies that glucose concentration rapidly decreases during the early stage of conversion [38]. The n values were comparable to that reported for glucose degradation in subcritical water in the absence of catalyst ($n = \sim 0.5$ at 180-260 °C) [38].

The activation energy (E_a) was calculated to be 52.8 kJ mol⁻¹ with the $\ln k_0$ value of 10.2 for the glucose conversion over LDH-AM in water (**Fig. 7b**), which falls into the range reported in the literature (**Table S1**). For instance, the E_a values for Fe₃O₄@SiO₂-supported amines ranged from 62 to 64 kJ mol⁻¹ [22], whereas those for the homogeneous catalysts, such as triethylamine [7] and arginine [17], were 61 and 44 kJ mol⁻¹, respectively. It should be noted that a small amount of catalyst, i.e., 6 wt% with respect to glucose, was used in the current thermochemical conversion. More stringent comparison of the kinetics in different catalytic systems should be conducted under the same experimental conditions in future assessments.

3.2.4 *Recyclability and transformation of LDH catalyst*

The recycling test was performed using LDH-AM (0.03 g) under microwave heating at 120 °C for 10 min (**Fig. 8a**). The results indicated that the fructose yield dropped from 18.9 mol% in the first run to 11.2 mol% in the second run, while a minor decrease to 9.6 mol% was noted in the third run. To understand the change in the performance, a supplementary test was carried out to evaluate the catalytic activity of the solid phase and liquid phase in the system (**Section 2.3**). The liquid fraction from the heated LDH-AM-water mixture was active towards glucose isomerisation, accounting for 46% of the fructose production in the pristine system (**Fig. 8b**).

It has been reported that Mg²⁺ leaching from hydrotalcite took place in the presence of acidic by-products (e.g., lactic acid) [13]. The fructose production ceased upon the removal of the hydrotalcite catalyst, implying that the liquid phase contained no active species [13]. in contrast to the observation in this study. While filtration was used in the former study, centrifugation adopted in this study accomplished less exhaustive solid-liquid separation. Thus, we infer that the loss of active LDH-AM particles due to centrifugation was accountable for the reduced activity of the

recycled LDHs as well as the residual activity in the liquid fraction (**Fig. 8b**). They possibly fall in the category of nanoparticles in small quantity, as the post-centrifugation solution appeared to be clear to unaided eyes. It would be interesting to identify and characterise these nano-sized particles, which potentially show high turnover frequency due to their high catalytic activity given a low concentration in the supernatant solution.

The solid fraction from the heated LDH-AM-water mixture accounts for 79% of the fresh LDH-AM system (**Fig. 8b**), which was higher than that of the second run in the recycling test (59% of the fructose yield in the first run; **Fig. 8a**). The discrepancy may be ascribed to the possible deposition of side products on the surface of the recycled LDH-AM, which partially blocked the active sites from glucose conversion in the subsequent run. It was previously suggested that the leaching of Mg^{2+} ($\leq 5\%$) further promoted the conversion of glucose to acidic by-products that deactivated the catalyst, and its regeneration was required via calcination in air and rehydration in Na_2CO_3 [13]. Similar catalyst deactivation was also observed for the continuous-flow catalysis over MgO and calcined-rehydrated hydrotalcite [24]. The leaching resulted in the formation of an $\text{Al}(\text{OH})_3$ passive layer, serving as a barrier to prevent further leaching under mild acidic conditions [49]. This rationalizes the small decrease in the fructose yield from the second to third cycle, as the reused LDH-AM was probably self-stabilized via $\text{Al}(\text{OH})_3$ formation (**Fig. 8a**). The leaching-induced changes in the basicity of the LDH catalysts should be subjected to future investigations. Catalyst agglomeration may also account for the performance drop upon reuse, according to the characterisation of LDH-AM-R that revealed a decrease in specific surface area (**Table 2**) and an increase in crystallite size (**Fig. 1**).

4. Conclusions

The LDHs catalysts synthesised via conventional methods (i.e., urea hydrolysis and co-precipitation) and AMOST treatment have a range of distinctive physicochemical properties, such as crystallite sizes, specific surface area, porosity, and chemical functionalities. The prepared LDHs exhibited catalytic activity towards the isomerisation of glucose to fructose in water as a green solvent, facilitating a potentially green route in biorefineries. The fructose yield increased with decreasing crystallite size due to the enhanced active site accessibility, yet excessively small crystallite size could lead to unfavourable hydrophilicity, which potentially induced the formation of water layers blocking the access of the glucose substrate to the active sites. Such structure-performance relationships are important for future design of LDHs for base catalysis in water. The presence of nano-sized active species in small quantity was speculated, which should be subjected to further characterisation for exploring potential solid catalysts with high turnover frequency. The highest fructose yield of 25 mol% was obtained after only 5 min of reaction at 120 °C in water. The activation energy for the LDH-catalysed glucose conversion was estimated to be 52.8 kJ mol⁻¹, which is comparable to that for homogeneous catalytic systems reported in the literature. This study provides kinetic and mechanistic insights to advance the development of heterogeneous catalysts for sustainable and carbon-efficient thermochemical conversion of biomass wastes.

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