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Sulfonated Carbon Catalyst Prepared from Calcination of Lignin for Ethyl Levulinate Synthesis via Ethanolysis of Levulinic Acid

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Ethyl levulinate (EL) is known as a platform bio-based chemical utilized for various applications, specifically as biofuel additives. Ethyl levulinate is synthesized via ethanolysis of levulinic acid (LA) in the presence of heterogeneous acid catalysts. In this study, sulfonated lignin-based carbon (LCS) was used as a solid acid catalyst to synthesize and achieve high EL yield. The lignin-based carbon (LC) precursor was prepared by the calcination of lignin at different temperature ranges (400–600 °C) for the selected time (1 and 2 h). The modification of LC was carried out by sulfonation at 120 °C for 15 h to prepare acid catalysts for ethanolysis. Ion-exchange titration was used to determine the total acid density of all the prepared catalysts. Fourier transform infrared spectroscopy, thermogravimetric analysis, nitrogen adsorption-desorption analysis, and scanning electron microscopy-energy dispersive X-ray were conducted for selected samples to study their physical and chemical properties. The ethanolysis reaction of LA was conducted in a batch process at 80 °C for 3 h with 10 wt% of catalyst loading and 1:10 of LA-to-ethanol molar ratio. The results show that the LCS catalysts have good physical and chemical properties for ethanolysis. The highest EL yield of 71.5 mol% was achieved for the reaction using the LCS prepared at the calcination temperature of 400 °C and calcination time of 1 h (LCS-400-1). The LCS-400-1 has the highest acidity of 0.96 mmol/g with surface area of 43.3 m^2/g. The finding also shows that different calcination temperatures and times influence the preparation of LCS and contribute to different catalytic effects on the ethanolysis of LA.

1. Introduction

Due to the reduction of fossil fuel resources and global environmental issues (e.g., the increase of carbon footprint and climate change impacts), a lot of efforts have been endeavored to transform biomass into biofuels and biofuel additives (Aguilar et al., 2020). Today, ethyl levulinate (EL) is considered one of the potential bio-based liquid transportation fuel additives (for example, for diesel and biodiesel) because it possesses unique fuel characteristics, including as a fuel oxygenate that can improve engine efficiency and minimize particulate emissions from engine combustion (Bhat et al., 2021). The oxygen content of EL is 33 wt% which has comparable properties to fatty acid methyl esters, making EL an excellent bio-based chemical for oxygenated diesel additive (Mthembu et al., 2021). The incorporation of EL with diesel fuel in several engine tests improved the pour point, cloud point, and cold plugging point (Peixoto et al., 2021), as well as reduced carbon monoxide and nitrogen oxide emissions to the environment during engine combustion (Shrikhande et al., 2020).

Ethyl levulinate is the product of the ethanolysis of levulinic acid (LA) in the presence of heterogeneous acid catalysts (Szelwicka et al., 2021). Various types of heterogeneous acid catalysts have been synthesized and utilized for the production of EL as the best alternative to the homogeneous approach, including acidic resin,

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zeolite, modified mesoporous silica, metal oxide, acidic MOFs, supported HPAs, and carbonaceous acids (Tian et al., 2021). The application of these catalysts offers several advantages in terms of easy separation from reaction media, minimizing the corrosion of the equipment, reducing environmental problems, and high recyclability (Dookheh et al., 2021). For the purpose of low operation cost for high EL yield, finding an effective, sustainable, and inexpensive catalyst for ethanolysis of LA is of great interest among researchers.

Carbon-based acid catalysts derived from carbonaceous materials are the best candidates considering that they are abundant sources of feedstock, inexpensive, and easily modified with sulfonic (SO_3H) functional group (Zailan et al., 2021). The presence of strong Brønsted acid on the surface of catalysts has been proven to contribute to higher catalytic activity for the ethanolysis of LA to provide better EL yield (Ahmad et al., 2020). Sulfonation of catalyst precursors is an alternative to obtain strong Brønsted acid (Zainol et al., 2020). The catalysts can be produced from the sulfonation of any type of carbon-based materials, including industrial and biomass wastes (Ma et al., 2020). Currently, the catalysts derived from agriculture wastes as carbon precursors such as corn stalk (Zhang et al., 2020), lignin (Zainol et al., 2019), and sugarcane bagasse (Liu et al., 2019). Lignin is an agricultural waste, which is the second most abundant natural organic biopolymer with high carbon content of approximately 55–66 % (Ma et al., 2020). Lignin is also regarded as waste (by-product) from paper, ethanol, sugar, and some waste from bio-based industries (Gundekari and Karmee, 2021). Producing a solid acid catalyst from lignin as a carbon precursor becomes an alternative for a sustainable and cost-effective approach in EL synthesis. Lignin has been used as solid acid catalyst for biodiesel synthesis (Sandouqa et al., 2019), 5-hydroxymethylfurfural (HMF) derivation (Li et al., 2020) and still limited as catalyst for LA ethanolysis.

In this present work, lignin was used to synthesize sulfonated carbon catalyst for the ethanolysis of LA. The preparation of sulfonated carbon catalyst from lignin for the ethanolysis of LA to EL is beneficial in terms of waste management and economic aspects. Lignin was calcined at different temperatures and times for lignin-based carbon (LC) preparation prior to sulfonation to provide catalyst with Brønsted acid sites. The reaction performance of all the prepared sulfonated lignin-based carbon (LCS) catalysts was studied and compared via the EL yield as the response to determine the selective catalyst for ethanolysis. The catalysts were characterized based on their total acid density, functional groups, surface area, and morphological structure.

2. Methodology

2.1 Materials and Chemicals

The chemicals listed were used for catalyst preparation and ethanolysis. Lignin (Sigma-Aldrich Co.) and sulfuric acid (H_2SO_4, 95–97 %, Supelco) were used in sulfonated carbon catalyst preparation. Ethanol (C_2H_6O, 95 %, Chemiz), levulinic acid ($C_5H_8O_5$, 98 %, Sigma-Aldrich Co.), and ethyl levulinate standard ($C_7H_{12}O_3$, 99 %, Sigma-Aldrich Co.) were used for ethanolysis and product analysis. Sodium chloride (NaCl, Fisher Chemical), sodium hydroxide pallet reagent grade (NaOH, Vchem), and phenolphthalein solution 1 % ($C_{20}H_{14}O_4$, Bendosen) were used for ion-exchange titration. All chemicals were used as received without any pretreatment.

2.2 Preparation of catalysts

Lignin-based carbon was prepared via calcination of lignin (with a ramp of 10 °C min^{-1}) in a high-temperature box furnace (model: HTBF-17-12L) at different temperature (X) ranges (400–600 °C) for the selected time (Y) of 1 and 2 h. The calcination temperature and time conducted was based on previous work demonstrated by Li et al. (2020). The black solids formed were ground and washed with distilled water a few times to remove unwanted chemicals and dried at 80 °C overnight in a universal oven (model: UFE 600). Lignin-based carbon was modified as an acidic catalyst via sulfonation with concentrated H_2SO_4 according to 1:10 (LC-to-acid molar ratio) at 120 °C for 15 h in a three-necked round-bottom flask equipped with a condenser and assisted by a magnetic stirrer. The sulfonation was modified from previous method conducted by Sandouqa et al. (2019). The mixture was diluted with 1 L of distilled water and washed and filter continuously until the filtrate was results a pH around 6.8–7.0. The residue was dried at 80 °C overnight. The LCS was labelled as LCS-X-Y based on the respective calcination temperature and time.

2.3 Characterization of catalysts

The total acid density on the surface of all the prepared LCS was determined by ion-exchange titration (Poonjarernsilp et al., 2014). The first step of the process was the exchange of acid functional groups from the LCS with Na^+ ion by mixing 0.05 g of LCS with 2 mol/L of NaCl solution at room temperature for 24 h under stirring (150 rpm). The mixture was filtered and a few drops of phenolphthalein were added before it was titrated with 0.01 mol/L of NaOH solution. The total acid density of LCS was calculated by dividing the number of moles of NaOH solution titrated by the mass of LCS. The associated functional groups and chemical bonding of LCS-400-1 were identified and analyzed using Fourier transform infrared (FTIR) spectroscopy with a Perkin-Elmer Spectrum One spectrometer at an IR range of 370–4,000 cm^{-1}. The thermal decomposition and stability of LCS-

400-1 were analyzed using TGA/DSC 1 STAR System (Mettler Toledo) from 30 to 950 °C (with a ramp of 20 °C min^{-1}) throughout inert heating. The surface area of LCS-400-1 was determine using Micromeritics 3-Flex instrument. Selected LCS catalyst was degassed in vacuum at 200 °C for 6 h prior to conduct standard nitrogen adsorption-desorption at 196 °C. To calculate the total surface area and pore distribution (mesopores and micropores), the Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH), and t-plot methods were employed. The scanning electron microscopy and energy-dispersive X-ray (EDX) spectroscopy (JEOL JSM-IT300LV) were used to conduct morphology and elemental analysis of LCS-400-1.

2.4 Reaction testing and product analysis

The ethanolysis of LA was conducted in the reflux reaction setup (i.e., batch reaction system). All the conditions were fixed during the reaction (i.e., 80 °C, 0.2 g catalyst loading, 1:10 molar ratio of LA-to-ethanol, and 3 h reaction time). The reaction mixture was heated by stirring at 200 rpm. After the reaction, the mixture was cooled at room temperature before it was separated by filtration. The volume of the product was recorded to calculate EL yield using Eq(1). Then, the sample was analyzed to detect the EL peak using gas chromatograph (Varian 450-GC) with a 5MS column. The GC conditions used were as follows: the flow rate of helium of 1.0 mL/min, with the oven temperature set from 40 to 120 °C (heating rate of 3.0 °C/min), and then increased to 280 °C (heating rate of 50.0 °C/min). The coolant was fixed at 50 °C, with coolant timeout and stabilization time of 20 min and 0.5 min. The concentration of EL was identified by the interpolation of the integrated EL area on the calibration curve. The yield of EL was calculated using Eq(1) with the unit of mol%.

$$\text{EL yield (mol\%)} = \frac{(C_{EL} \times V_{EL})/(1000 \times M_{EL})}{W_{LA}/M_{LA}} \times 100\ \% \qquad (1)$$

where C_{EL} is the EL concentration (mg/L), V_{EL} is the final volume of EL (mL), M_{EL} is the molecular weight of EL (g/mol), W_{LA} is the initial weight of LA (g) used in the reaction, and M_{LA} is the molecular weight of LA (g/mol).

3. Results and discussion

3.1 Catalyst acidity and reaction testing

The formation of acid active sites on the surface of the prepared LCS is important for ethanolysis. The formation of acid sites can be related to the total acid density of the LCS, which was determined in this work. Figure 1a shows the results of the ion-exchange titration method for the effect of calcination temperature and time of LC preparation on the total acid density of the LCS. It was proved that SO_3H functional group could be anchored at the carbon structure of the catalyst via sulfonation with concentrated H_2SO_4, which contributes to the improvement of the total acid density of the catalysts (Liu et al., 2019). The total acidity of LCS shows contrasting results, where the reduction of acidity occurred as the calcination temperature and time of LC preparation increased. Similar trend was reported by Li et al. (2020) and this scenario occurred due to the reduction of C-H active sites which restrain the SO_3H functional group to be anchored on the surface of LC. Although a decrease in total acidity was observed, the acidity of LCS was still considered high. According to Konwar et al. (2019), the SO_3H density obtained by the catalyst is influenced by the temperature, duration of sulfonation, strength of H_2SO_4, and the framework of carbon support. The presence of a high number of aromatic carbon structure and graphene carboxylate groups of the LC increased the number of strongly anchored SO_3H groups.

The acidity of all the prepared catalysts is related to SO_3H acid sites, which is possibly contributed by the oxidation of functional groups, such as the hydroxyl group in the catalyst structure. The total acidity of LCS is also most likely contributed by the oxidation of -OH functional groups on the surface of LC, providing additional carboxyl sites (oxygen functional group) (Konwar et al., 2019). The degradation of -OH functional group during LC preparation as the calcination temperature and time increased also resulted in the reduction of catalyst acidity. Sandouqa et al. (2019) stated that the higher the temperature during carbon preparation has lower the number of hydrogen and oxygen content which presumably the main factor of the –OH functional group reduction. For 1 h calcination time, as the temperature of LC preparation increased, the total acid density of LCS decreased. The same trend was also observed for 2 h calcination time. LCS prepared at 400 °C for 1 h (LCS-400-1) recorded the highest total acid density (0.96 mmol/g), while LCS prepared at 600 °C for 2 h (LCS-600-2) recorded the lowest total acid density (0.24 mmol/g). In this work, the total acid density of LCS decreased in the following order: LCS-400-1 > LCS-400-2 > LCS-500-1 > LCS-500-2 > LCS-600-1 > LCS-600-2.

All the prepared catalysts were tested in the ethanolysis of LA and the effect of total acidity on EL yield from the ethanolysis of LA was recorded and shown in Figure 1b. Based on the results, all non-sulfonated LC gave lower yields with an average of 4.0 mol%. Lignin-based carbon has no active sites for the reaction because SO_3H functional groups do not exist on the surface of the catalyst. This active site required for protonation of LA and nucleophilic substitution reaction. The absent of SO_3H functional group on the surface of LC effect the reaction mechanisms to take place. This proves that the sulfonation of LC is very important to achieve high yield of EL. Meanwhile, the yield of EL obtained from the LA ethanolysis catalyzed by various LCS demonstrated their ability to perform as acid catalysts. Based on the performance of LCS toward EL yield, it can be concluded that the decrease of total acidity directly reduces the EL yield. LCS-400-1 achieved the highest EL yield of 71.5 mol%, followed by LCS-400-2 (56.7 mol%), LCS-500-1 (27.6 mol%), LCS-500-2 (19.1 mol%), LCS-600-1 (19.2 mol%), and LCS-600-2 (16.5 mol%). Therefore, LCS-400-1 was chosen as the preferred catalyst and the characterization of LCS-400-1 is further discussed to describe its physiochemical properties.

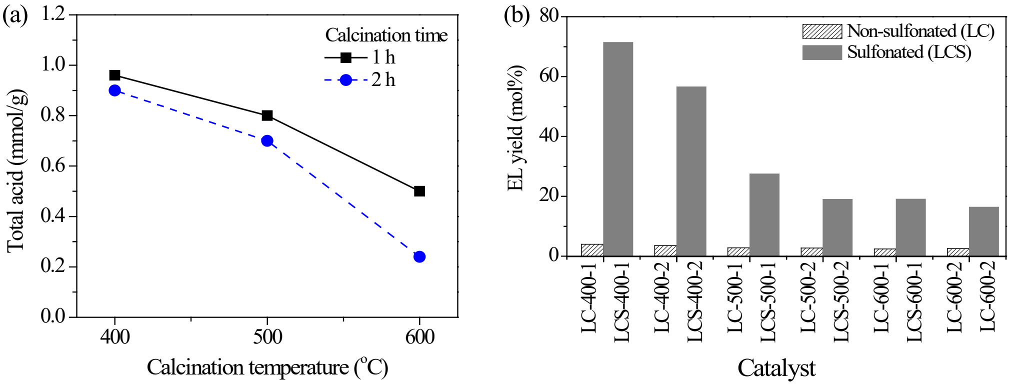

Figure 1: (a) Total acid density of LCS for LC prepared, and (b) EL yield obtained for various types of catalysts at fixed conditions (80 °C, 3 h, 10 wt% of catalyst loading, 1:10 LA-to-ethanol molar ratio, 150 rpm).

3.2 Selected catalyst characterization

The chemical bonding and surface chemistry of LCS-400-1 were studied using FTIR spectroscopy. The existence of related functional groups as a result of sulfonation on the surface of the selected catalyst was observed through the IR peaks, as shown in Figure 2a. The presence of SO_3H functional group was determined through the observation of the band spectra for S=O and S-O at the absorption band in the range of 1,250–1,000 cm^{-1}. S=O stretching was detected in the range of 1,150–1,250 cm^{-1}, while S-O stretching was observed around 1,050 cm^{-1} (Zainol et al., 2021b). The broad peak of -OH stretching observed at approximately 3,000–3,500 cm^{-1} is related to the SO_3H functional group and adsorbed water. The detection of SO_3H is important because it is related to the presence of active sites of the catalyst for the conversion of LA to EL. The functional groups of C=O and C=C of LCS-400-1 were detected around 1,600–1,750 cm^{-1}. The C=O stretching is possibly related to the carboxylic group resulted from oxidation on the surface of the catalyst. The C=C stretching is related to the aromatic compound of carbon precursor. The band of C=O stretching was observed at 1,771 cm^{-1} and C-H representing carboxylic functional group was detected around 2,920 cm^{-1} (Lu et al., 2017).

Figure 2b shows the thermal stability and decomposition of LCS-400-1 using TGA-DTG curves. The high DTG peak below 200 °C is related to the high volatile substance present in the catalyst. The high volatile substance (approximately 10 wt%) of the catalyst weight is most probably influenced by the moisture adsorbed on the catalyst structure. At heating temperatures around 200–300 °C, the peak represents the degradation of the remaining low molecular weight organic compounds in the structure of LCS-400-1, including OH functional group. About 80 wt% remaining weight of the catalyst was recorded at the heating temperature of 300 °C. The weight of the catalyst decreased continuously as the heating temperature increased above 300 °C. This is because weak acid sites, including carboxylic functional group, start to decompose, followed by strong acid sites and heavy organic compounds in the catalyst structure, reducing the weight of the catalyst. The degradation of the peak indicated that the organic compounds in the carbon precursor started to decompose, resulting in a major decomposition of the catalyst, where the degradation can be related to the strong acid sites attached to the catalyst structure (Zainol et al., 2021a). The high degradation of the LCS sample above 300 °C is related to the carbon preparation from lignin at the selected temperature of 400 °C. Therefore, it can be concluded that the catalyst can work up to 200 °C for the ethanolysis reaction to avoid further degradation of the catalyst

The surface morphology of LCS-400-1 was observed using an SEM image, as shown in Figure 2c. The formation of porous structures is due to the decomposition of volatile substances and organic compounds affected by calcination and sulfonation. Peixoto et al. (2021) stated that the structures experienced surface rupture due to the use of concentrated H_2SO_4 in the sulfonation process. This phenomenon resulted in non-uniform porous structures, which contributed to different types of porous structures (e.g., mesopores and micropores). As tabulated in Table 1, the respective mesopore and micropore areas are 14.2 m^2/g and 29.1 m^2/g, which gives the total area of LCS-400-1 of 43.3 m^2/g. The presence of various sizes of porous structures is excellent for providing a surface area that helps to increase the physical adsorption of LA onto the surface of the catalyst which enhance higher catalytic activity during ethanolysis. Sivasubramaniam and Amin (2015) stated that the surface area can influence the reaction testing to achieve high yield of EL.

The elemental composition on the surface of LCS-400-1 is shown in the EDX graph (Figure 2d). The catalyst consisted of 77 wt% of C, 21.6 wt% of O, and 1.4 wt% of S. The existence of sulfonated functional group can be proved from the presence of S and O elements on the surface of LCS-400-1. The high weight percentage of C and O elements is also a possible reason for the existence of additional functional groups. Based on the results, LCS-400-1 possesses excellent surface chemistry to be applied as an acid catalyst.

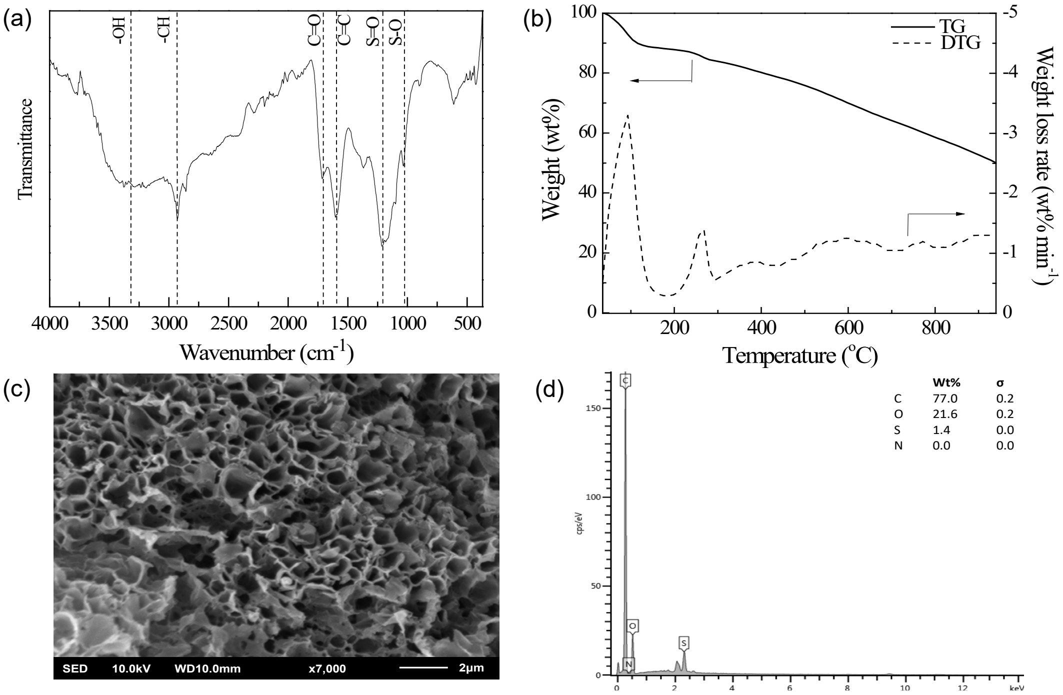

Figure 2: (a) FTIR spectrum, (b) TGA-DTG curves, (c) SEM image, and (d) EDX graph of LCS-400-1 as the selected catalyst.

Table 1: Surface area and pore volume distribution for LCS-400-1.

Sample	S_{BET} (m^2/g)	S_{Meso} (m^2/g)	S_{Micro} (m^2/g)	V_{total} (cm^3/g)	V_{Meso} (cm^3/g)	V_{Micro} (cm^3/g)
LCS-400-1	43.3	14.2	29.1	0.043	0.012	0.012

4. Conclusions

The results of the study show that different calcination temperatures and times of LC preparation greatly influence the catalytic activities during ethanolysis, as well as the acidity of the catalysts. Calcination temperature of 400 °C and calcination time of 1 h were selected as the best conditions to prepare sulfonated LC (LCS-400-1) for the ethanolysis of LA to EL. The selection of the catalyst is based on its total acid density (0.96 mmol/g) which produced the highest EL yield (71.5 mol%). The catalyst also has excellent chemical and physical properties, including acidic surface chemistry with porous surface structure and high thermal stability, highlighting its potential as a solid acid catalyst for the ethanolysis of LA.

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