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Preparation and characterisation of ordered mesoporous  $SO_4^{2^-}/Al_2O_3$  and its catalytic activity in the conversion of furfuryl alcohol to ethyl levulinate

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The ordered mesoporous  $SO_4^{2-}/Al_2O_3$  (OMSA) solid super acid catalyst was prepared and used to catalyse furfuryl alcohol in the synthesis of ethyl levulinate (EL) in the presence of ethanol. The maximum yield (80.6%) of EL was obtained in the reaction conducted at 200 °C for 3 h.





# **Preparation and Characterisation of Ordered Mesoporous**

# SO<sub>4</sub><sup>2–</sup>/Al<sub>2</sub>O<sub>3</sub> and Its Catalytic Activity in the Conversion of Furfuryl Alcohol to Ethyl Levulinate

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Declarations of interest: none

# ABSTRACT

A series of ordered mesoporous  $SO_4^{2-}/Al_2O_3$  (OMSA) solid super acid catalysts were prepared by evaporation-induced self-assembly (EISA) method, followed by sulphonation at different calcination temperatures (400°C–900 °C). The results of transmission electron microscopy (TEM) and small-angle X-ray diffraction (XRD) indicated that all of the OMSAs possessed ordered mesoporous structures. The N<sub>2</sub>-Brunauer–Emmett–Teller (N<sub>2</sub>-BET) results showed that the specific surface area of OMSAs could reach up to 160–380 m<sup>2</sup>/g, and the average pore diameters fall into the range between 8.6 and 9.8 nm. The temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) characterisation proofed that the OMSAs contained super acid, and ammonia desorption by the super acid in the OMSA calcined at 600 °C reached 25.9 cm<sup>3</sup>/g STP. The pyridine adsorption infrared (Py-IR) indicated that all of the OMSAs consisted mainly of Lewis acids. The OMSA was used to catalyse furfuryl alcohol in the synthesis of ethyl levulinate (EL). The maximum yield (80.6%) was obtained in the reaction conducted at 200 °C for 3 h. The reusability of the catalyst was proofed after four times of reuse as its activity was maintained with a yield of 71.2%.

Keywords: Ethyl levulinate; Furfuryl alcohol; Ordered mesopore; SO<sub>4</sub><sup>2-</sup>/Al<sub>2</sub>O<sub>3.</sub>

# **1. Introduction**

The increasing utilisation of renewable biomass fuels is a result of the excessive consumption of non-renewable fossil resources [1, 2]. The properties of ethyl levulinate (EL) are similar to those of biodiesel (fatty acid methyl ester), such as high boiling point [3], low-temperature fluidity [4], flashpoint stability [5] and high lubricity [6]. Therefore, EL can be directly used as a diesel-miscible biofuel (<5 wt.%) in conventional diesel engines [7, 8]. In addition, the molecular structure of EL contains ester and keto groups, which can contribute in various reactions such as hydrolysis, reduction, addition and condensation. Moreover, EL is ideal biorenewable feedstock for the synthesis of  $\gamma$ -valerolactone [9], perfumes, solvents and plasticisers [10]. EL can be produced via acid-catalysed alcoholysis of carbohydrates or furfural alcohol in alcohol with the aid of various acidic catalysts [11]. Scheme 1 shows the synthesis process of EL from cellulose. Cellulose is hydrolysed by acid to produce glucose, which is then isomerised to produce fructose. Fructose is converted to furfural in an ethanol medium through acid-catalysed hydrogenation to produce furfuryl alcohol, which is used to produce

#### EL [12].

Scheme 1. Ethyl levulinate production from Cellulose.

In this reaction, the intermediate furfuryl alcohol is the closest compound to the target product EL. Zhang et al. [13] studied the alcoholysis mechanism of furfuryl alcohol. Scheme 2 illustrates this process. Firstly, furfuryl alcohol reacts with ethanol to form intermediate 1. This is followed by the conversion of ethanol into cation 2. Secondly, cation 2 undergoes nucleophilic 1, 4-addition of ethanol to form species 3. Thirdly, species 3 is converted to species 4 by a hydrogen shift. Finally, H<sub>2</sub>O, as nucleophile, attacks species 4 to produce species 5, which is then isomerised to generate EL.

Scheme 2. Mechanism for the preparation of EL from furfuryl alcohol.

Homogeneous acids are typically used as catalysts in the preparation of EL from biorenewable feedstock. Garves et al. [14] used cellulose, as biorenewable feedstock with ethanol as solvent to synthesise EL in the presence of concentrated sulphuric acid. This reaction was conducted at 195 °C for 9h and reached 38.4% EL yield. Zhu et al. [15] used glucose and low concentration sulphuric acid (<0.01 M) as biorenewable feedstock and catalyst, respectively, at 200 °C for 210 min to obtain about 40% EL yield. Homogeneous acids have high catalytic activity, but they are difficult to separate from the product, can corrode the equipment and cause environmental pollution [16]. Several researchers have used mixtures of ionic liquids and solid acids as catalysts to prepare EL. Guan et al. [12] synthesised EL from wheat straw using ethanol with an acidic ionic liquid (1-methyl-3-sulphobutyl imidazole sulphite) at 200 °C for 60 min with an EL yield of 16.23%. Saravanamurugan et al. [16] used sulphonic acid functionalised ordered mesoporous silica (SO<sub>3</sub>H-SBA-15) and zeolites (i.e. Beta, Y and ZSM-5) as catalysts with ethanol as solvent to synthesise EL by fructose dehydration. They found that SO<sub>3</sub>H-SBA-15 used at 140 °C for 24 h had the highest reactivity, with an EL yield of 57%. Zhao et al. [11] obtained an EL yield that reached 43.1% using 20 wt.% HPW/H-ZSM-5 to catalyse the EL synthesis from fructose in an ethanol solvent at 160 °C for 2 h. Zhao et al. [17] reached an EL yield of 64.8% using an  $SO_4^{2-}/Al_2O_3$  solid super acid for EL synthesis from furfuryl alcohol in an ethanol solvent at 200 °C for 2.5 h. Peng et al. [18] used sulphated metal oxides (i.e. SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>, SO<sub>4</sub><sup>2-</sup>/TiO<sub>2</sub>, and SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) to catalyse glucose to convert it into EL. The maximum EL yield from these reactions (30%) was obtained with the reaction of SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> at 200 °C for 3 h. Neves et al. [19] used mesoporous Al-TUD-1, compound Beta/TUD-1, nanocrystal H-Beta, ITQ-2 and H-MCM-22

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molecular sieves as catalysts in the furfuryl alcohol conversion into EL. Al-TUD-1 showed better stability and reached an EL yield of 80% with the reaction conducted at 140 °C for 24 h. Nandiwale et al. [20] synthesised HZ-5 zeolite from H-ZSM-5 by alkali treatment, which was then used to catalyse furfuryl alcohol that is converted to EL at 140 °C for 4 h with a 73% yield. Topolyuk et al. [21] prepared functional nanomaterials (F-NCMs) to catalyse the conversion of furfuryl alcohol into EL with ethanol at 130 °C for 7 h with a yield of 76%.

Ordered mesoporous solid acid catalysts facilitate the diffusion of the reactant molecules into mesoporous and enhance the contact of the reactants on their active sites because of their regular and ordered pore structure, hence improving the reaction rate [22]. Morales et al. [23] prepared ordered mesoporous SZ/SBA-15 by grafting  $SO_4^{2^-}/Zr_2O$  solid super acid on ordered mesoporous SBA-15 and applied it to the mixed system of glucose in absolute ethanol. The EL yield was 25%, obtained with a reaction at 140 °C for 24 h. Patil et al. [24] incorporated phosphotungstic acid (PWA) into SBA-15 using the sol-gel method to obtain the ordered structure. A 20% PWA/SBA-15 was used to catalyse fructose to prepare EL with absolute ethanol at 100 °C for 24 h, which achieved a 26 % EL yield.

In this study, ordered mesoporous  $SO_4^{2^-}/AI_2O_3$  (OMSA) solid super acid was prepared using solvent evaporation-induced self-assembly (EISA), followed by sulphonation using aluminium isopropoxide as an aluminium source and ammonium sulphate as sulphonating agent. In addition, several characterisation techniques, including transmission electron microscopy (TEM), X-ray diffraction (XRD), N<sub>2</sub>-Brunauer–Emmett–Teller (BET), Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD), Inductively coupled plasma-optical emission spectroscopy (ICP-OES), pyridine adsorption infrared (Py-IR), Fourier-transform infrared (FT-IR) and thermogravimetric (TG), were used to examine the produced materials. Finally, the catalysts were used for the synthesis of EL through alcoholysis of biorenewable feedstock (cellulose, glucose, sucrose, fructose and furfuryl alcohol).

# 2. Experimental

#### 2.1. Materials

Aluminumiso–propoxide (98 %, AR), ethyl levulinate (99 %, GC), ammonium sulfate (99 %, AR) ethyl levulinate, pluronic P123 (Mav=5800, EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) and furfuryl alcohol (98 %) were purchased from Aldrich and Sigma–Aldrich (Shanghai, China). Absolute ethanol and nitric acid (65–68 %) were purchased from Sinopharm Chemical Reagent Co., Ltd (China).

#### 2.2. Synthesis of catalysts

#### 2.2.1. Synthesis of ordered mesoporous alumina

Ordered mesoporous alumina powder was synthesised using the method reported by Yuan et al. [25] Here, 4.0 g of P123 was dissolved in 40.0 mL of absolute ethanol with continuous stirring for 1 h at 30 °C to obtain solution A. Then, 40 mmol (8.2 g) of 98% aluminium isopropoxide was dissolved in a solution of 6.4 mL nitric acid and 20 mL absolute ethanol under continuous stirring for 1–2 h at 30 °C to obtain solution B. Solutions A and B were mixed, and then, 20 mL of absolute ethanol was added to obtain solution C, which was stirred at 30 °C for 3 h. Then put it into oven at 60  $\Box$  for 48 h. The obtained solid was calcined in a muffle furnace at a heating rate of 1 °C/min until the temperature reached 400 °C and maintained for 3 h. The sample was denoted as OMA.

#### 2.2.2. Synthesis of ordered mesoporous sulphated alumina

The OMA was impregnated in ammonium sulphate solution (1 mol/L) at 30 °C for 0.5 h according to a solid–liquid ratio of 1 g: 15 mL. The mixture was then filtered, and the obtained solid was dried at 100 °C for 6 h. Next, it was calcined at 400 °C with a heating rate of 1 °C/min for 3 h under air atmosphere. The obtained sample was denoted as OMSA-400. Several grades of OMSA were obtained at different calcination temperatures (500 °C, 600 °C, 700 °C, 800 °C and 900 °C) and were named OMSA-X (X = 500, 600, 700, 800 and 900), respectively.

#### 2.3. Characterisation of OMSA

The TEM measurements were conducted on Tecnai G2 F20 (FEI, America) operated at 200 kV. The XRD patterns were obtained using a SmartLab (Rigaku, Japan) X-ray diffractometer with Cu Kα radiation at 40 kV and 30 mA. The N<sub>2</sub>-BET was carried out using an ASAP 2020 HD88 Surface Area and Porosity Analyzer (Micromeritics, America). The NH<sub>3</sub>-TPD was performed using an Autochem II 2920 Chemical Adsorption Analyzer (Micromeritics, America). The FT-IR spectra were recorded at a resolution of 8 cm<sup>-1</sup> through 34 scans within the range from 4000 to 500 cm<sup>-1</sup> on a Nicole 380 infrared spectrometer (America). The sulfur content of the samples was analyzed using ICP-OES (Agilent 730 ICP-OES). Py-IR spectra were obtained on a Thermo Nicolet IS10 infrared spectrometer (America). TG analysis was conducted using a STA449F5 synchronous thermal analyser apparatus (Netzsch, Germany) at a heating rate of 10 °C/min under air atmosphere.

2.4. Catalytic reaction

A mixture of 120 mg furfuryl alcohol, 8 mL absolute ethanol and a variable amount of catalyst was placed in a 25 mL stainless steel tank magnetic stirring reactor and were heated to the set temperature (160 °C–200 °C) for 1–6 h.

Quantitative analysis of EL was carried out by GC on a Panna A91 Plus gas chromatograph with a FFAP capillary column (30 m  $\times$  0.32 mm  $\times$  0.33 µm) equipped with a FID detector. The analysis was conducted under the following operating conditions: an injector temperature of 240 °C and a detector temperature of 250 °C. The initial temperature was 90 °C, maintained for 3 min and then increased to 210 °C and maintained for another 10 min. n-Octanol was used as an internal reference. Finally, the EL yield was calculated according to the following formula [26]:

Yield (%) = EL content after reaction (mg)/Furfuryl alcohol content before reaction (mg)  $\times$  100% (1)

## 3. Results and discussion

#### 3.1. TEM

Fig.1 shows the TEM images of OMSA calcined at different temperatures (400 °C–900 °C). Figure 1a–g show the TEM images of OMSAs calcined at 400 °C, 500 °C, 600 °C and 700 °C. They clearly demonstrate the ordered arrangement of hexagonal pores along the [001] direction and the channel arrays of parallel lines along the [110] direction. Fig.1i–1 indicates that the ordered mesoporous structures are retained even at very high calcination temperature (800 °C–900 °C). Ghosh et al. [27] proposed that, the concentration of P123 increased with the solvent evaporation, which promotes the self–assembly of aluminium surfactant micelles. The hydroxyl group in the alumina sol particles obtained by hydrolysis of aluminum precursor in an acidic environment forms a hydrogen bond with the PEO in the surfactant molecule. Yang et al. [28] reported that an epoxy alkane chain formed a crown ether complex with inorganic metal ions through weak coordination bonds. Therefore, in this work, OMSA with a hexagonal pore structure was formed through hydrogen bonding and coordination between the surfactant and the alumina particles. These results are similar to those obtained by Taromi et al. [29] who synthesized ordered mesoporous alumina with P123 as the surfactant.

Fig. 1. TEM images of OMSAs.

#### 3.2. XRD

Fig.2a shows the small-angle XRD spectra of OMSA calcined at different temperatures (400 °C–900 °C). OMSA–400, OMSA–500, OMSA–600 and OMSA–700 show a strong diffraction

peak at  $2\Theta = 0.7^{\circ}$  and a weak peak at  $2\Theta = 1.2^{\circ}$ , which, as with the TEM result, can be attributed to the p6mm hexagon symmetry [30]. For OMSA–800 and OMSA–900, the strong diffraction peak at  $2\Theta = 0.7^{\circ}$  can be observed in each small-angle XRD pattern, suggesting that the ordered mesopores were maintained in all OMSAs. Fig.2b shows the wide-angle XRD patterns of OMSA calcined at different temperatures (400 °C–900 °C). The OMSA calcined below 800 °C is amorphous, and the OMSA calcined at 800 °C exhibits a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase (2 $\Theta = 37.6^{\circ}$ , 45.8° and 66.9°) (JCPDS card number 10–0425). When the calcination temperature was 900 °C, the peak intensity of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase was enhanced, and two new  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> peaks (2 $\Theta = 39.5^{\circ}$  and 60.7°) occurred, which is similar to the results reported by Liu et al. [31].

Fig. 2. XRD spectra of OMSAs: (a) small-angle spectra and (b) wide-angle spectra.

#### 3.3. N<sub>2</sub>-BET

Fig.3 shows the N<sub>2</sub> adsorption–desorption isotherms and pore size distribution of OMSA calcined at different temperatures (400 °C–900 °C). Fig.3a indicates that all isotherms exhibit type–IV curves [32]. There was obvious capillary condensation at relative pressure P/PO=0.4~0.5, and hysteresis loops appeared, indicating a good mesoporous structure of all of the OMSAs presented [33]. The hysteresis loop was steep, with a nearly parallel vertical part, indicating well ordered pore channels [34]. The pore size distribution of each sample was calculated using the Barrett–Joyner–Halenda (BJH) algorithm with the adsorption branch of the isotherm. The BET surface area of OMSA–600 was 285 m<sup>2</sup>/g, which was higher than that of  $SO_4^{2^-}/Al_2O_3$  (200 m<sup>2</sup>/g) reported by Guzmán–Castillo et al. that was prepared by hydrothermal synthesis calcined at 600 °C [35]. The increase in the calcination temperature from 400 °C to 900 °C caused the BET specific surface area of OMSAs to decrease. Yuan et al. [26] reported that the BET surface area of ordered mesoporous alumina decreased from 434 to 226 m<sup>2</sup>/g when the calcination temperature rose from 400 °C to 800 °C, resulting in a decrease in the OMSA pore size from 9.8 to 8.6 nm (Table 1). This result combined with the wide-angle XRD may be related to the high crystallinity of OMSA–800 [36].

Fig. 3. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution curves of OMSAs.

Table 1. BET surface areas, pore sizes, acid quantities, and sulfur content of OMSAs.

	BET surface area (m <sup>2</sup> /g )		NH <sub>3</sub> Desorption Quantity (cm <sup>3</sup> /g STP)					
sample		(nm) 73 - 187						S (wt.%)
				187 -	489 -	489 - 775 -		ICP-OES
			489	775	1000	Total		
OMSA-400	380	9.8	10.3	14.0	0.4	14.4	39.1	3.09
OMSA-500	324	9.5	9.5	14.7	5.8	20.8	50.8	2.50
OMSA-600	285	9.3	10.0	16.7	6.0	25.9	58.6	2.06
OMSA-700	231	9.2	5.6	11.6	3.4	20.6	41.2	1.52
OMSA-800	186	8.9	4.5	7.6	1.5	10.8	24.4	0.59
OMSA-900	160	8.6	3.9	7.3	-0	2.9	14.1	0.13

#### 3.4. NH<sub>3</sub>-TPD and ICP-OES

Fig.4 shows the NH<sub>3</sub>-TPD desorption curve of OMSAs calcined at different temperatures (400 °C-900 °C). Four desorption peaks were observed in the ranges of 73 °C-187 °C, 187 °C-489 °C, 489 °C-775 °C and 775 °C-1000 °C, which are normally attributed to weak, strong, medium strong and super acid sites, respectively [37]. When the calcination temperature was 400 °C, the desorption peak of super strong acid occurred. The NH<sub>3</sub> desorption peak temperature of the super strong acid gradually increased with the calcination temperature, and the amount of NH<sub>3</sub> desorption increased at first and then started to decrease (Table 1). When the calcination temperature was 600 °C, the amount of NH<sub>3</sub> desorption from super acid sites reached a maximum of 25.9 cm<sup>3</sup>/g STP. The quantity of NH<sub>3</sub> desorbed from super acid decreased significantly by increasing the calcination temperature from 700 °C to 800 °C. Further increase in the calcination temperature to 900 °C causes the quantity of  $NH_3$ desorbed from the super acid to reach its lowest (2.9 cm<sup>3</sup>/g STP). At a very low calcination temperature,  $SO_4^{2-}$  existed on the surface of the carrier in a free form, which inhibited the formation of super acid. However, at a very high calcination temperature, the surface free sulphate rapidly decomposed and no longer existed in a SO<sub>x</sub> form, which caused a decrease in the amount of super acid [38]. Table 1 shows the sulfur content of OMSAs calcined at different temperatures (400 °C-900 °C). The gradual decrease of the sulfur content as the calcination temperature increased from 400 °C to 900 °C can be seen. The

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sulfur content reached a maximum of 3.09 wt.% at 400 °C, and a minimum of 0.13 wt.% at 900 °C. The effect of the calcination temperature on the sulfur content was basically consistent with the effect of the calcination temperature on the amount of NH<sub>3</sub> desorption. When the calcination temperature increased from 700 °C to 800 °C, the wide-angle XRD (Fig. 2b) showed that the alumina changed from amorphous to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which led to the decrease of the binding ability with SO<sub>4</sub><sup>2–</sup>, and therefore, the sulfur content loss rate was faster.

Fig. 4. NH<sub>3</sub>-TPD curves of OMSAs.

#### 3.5. FT-IR and Py-IR

Fig.5a shows the FT-IR spectra of OMSAs calcined at different temperatures (400 °C-900 °C). In the sulphate groups stretching region (1500–900 cm<sup>-1</sup>), the bands at 901 cm<sup>-1</sup>, 1156 and 1054 cm<sup>-1</sup>, and 3487 and 1625  $\text{cm}^{-1}$  are attributed to the symmetric O–S–O stretching vibration on the Al<sub>2</sub>O<sub>3</sub> surface [39], the antisymmetric O=S=O stretching vibration [40] and the stretching vibration of adsorbed water [41], respectively. Fig.5b shows the pyridine adsorption IR spectra of OMSZ calcined at different temperatures. All of the OMSAs exhibited three distinct bands at 1445, 1490 and 1617 cm<sup>-1</sup>, which represent the pyridine chemisorption of the Lewis acid site [36, 42, 43]. The band at 1613 cm<sup>-1</sup> was due to the moderate interaction between Py and the Lewis acid site, which resulted from the tetrahedral aluminium vacancy [44]. At calcination temperatures of 500 °C and 600 °C, larger absorption peak strength and peak area of the Lewis acid were observed. Further, the peak strength and area decreased by increasing the calcination temperature, especially between 700 °C and 900 °C. Therefore, higher temperatures were not conducive to the acid amount of Lewis acid sites. This may be attributed to the strong crystallisation tendency of mesoporous metal oxide walls at high temperatures, leading to a skeleton contraction or even a collapse [45]. However, no peaks representing Brønsted (B) acid were detected because the lower water content was not sufficient for the formation of B acid sites on the catalyst surface [42].

In general, there has been no consistent conclusion regarding the role of Brønsted and Lewis acids in the alcoholysis of carbohydrates when preparing levulinate esters. Tominaga et al. [46] studied the preparation of methyl levulinate from microcrystalline cellulose using aluminum compounds as Lewis catalysts and organic sulfonic acids as Brønsted catalysts. The results indicated that the conversion of cellulose into fructose was mainly catalyzed by Brønsted acid, while the subsequent conversion to

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methyl levulinate was catalyzed by Lewis acid. However, Ding et al. [47] used H-beta (Si/Al=50) and (TfO)<sub>3</sub>Yb as Lewis catalysts and hydrochloric acid and trifluoromethanesulfonic acid as Brønsted catalysts in a microcrystalline cellulose reaction to produce methyl levulinate. Ding et al. concluded that the role of Lewis acid was to promote the conversion of cellulose into fructose, and Brønsted acid had a higher catalytic activity in the production of methyl levulinate. Although the conclusions reached by Tominaga et al. differed from those reached by Ding et al. regarding the role of Brønsted and Lewis acids in the alcoholysis process, their experimental results clearly showed that the highest ethyl levulinate yield was obtained when the Brønsted acid and Lewis acid sites were catalyzed together. In our study, the catalysts mainly had Lewis acid sites, which were obtained from the pyridine infrared analysis results. Therefore, the Lewis acid site played a major catalytic role in the conversion of furfuryl alcohol into ethyl levulinate.

Fig. 5. (a) FT-IR and (b) Py-IR spectra of OMSAs.

#### 3.6. TG

Fig.6 shows the TG curves of OMSAs calcined at different temperatures. Within the range of 50 °C–300 °C, the weight loss corresponded to the desorption of water on the OMSA surface. The weight loss that occurred above 600 °C was mainly associated with the decomposition of  $SO_4^{2-}$ , which formed a super acid structure with  $Al_2O_3$ . The sulphur contents in the OMSAs were calculated to be 3.3 wt.%, 2.7 wt.%, 2 wt.%, 1.1 wt.%, 0.6 wt.% and 0.1 wt.%, which were obtained at the following temperatures: 400 °C, 500 °C, 600 °C, 700 °C, 800 °C and 900 °C, respectively.

## Fig. 6. TG spectra of OMSAs.

#### 3.7. Catalytic reaction

## 3.7.1. Effect of different feedstock

Cellulose, glucose, sucrose, fructose and furfuryl alcohol were used as feedstock for the reaction. As shown in Fig.7a, furfuryl alcohol achieved the highest EL yield (80.6%), which was consistent with the results reported by other researchers that used several catalysts, such as an HZ–5 molecular sieve [20], functionalised nanocarbon materials (F-NCMs) [21],  $SO_4^{2^-}/TiO_2$  [17] and aryl sulfonic acid functionalised hollow mesoporous carbon spheres [48]. Compared to fructose, furfuryl alcohol is a biorenewable feedstock derivative whose structure is closer to EL, and its EL yield is much higher than

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that of fructose. The EL yields from cellulose and glucose were significantly lower. Cellulose has a very stable structure, which is attributed to the combination of hydrogen bonding and van der Waals forces. This causes the degradation of cellulose into glucose to be difficult [49], and consequently, its conversion to EL is not easy. In addition, glucose must be isomerised to fructose before being converted to EL, which further reduces the yield [50]. On the other hand, sucrose consists of a glucose unit and a fructose unit, and thus, its yield lies between those of glucose and fructose. Therefore, furfuryl alcohol has been used as feedstock in the following experiments because of its good results. The products resulting from the conversion of furfuryl alcohol into ethyl levulinate analyzed by GC-MS showed that in addition to the main product, ethyl levulinate, some by-products such as β-Angelica lactone, Diethoxymethane, 1,1,2,2-Tetraethoxyethane, 2-Furaldehyde diethyl acetal, 2,2-Methylenebis(furan), and 2-(2-Furanylmethyl)-5-methylfuran were also present. Furthermore, Neves et al. [51], using porous aluminosilicate acid catalysts, and Paniagua et al. [52], using zeolite catalysts, in the conversion of furfuryl alcohol to ethyl levulinate, found the main by-products to be iso-propyl furfuryl ether, iso-propyl levulinate,  $\beta$ -Angelica lactone, 1-(2-Furyl)-butan-3-one, 2-(2-Furanylmethyl)-5-methylfuran, 2,2-Methylenebis(5-methylfuran), 2,2-(2-Furylmethylene) bis(5-methylfuran),  $\beta$ -Angelica lactone, Diethoxymethane, 1,1,2,2-Tetraethoxyethane, 2-Furaldehyde diethyl acetal, and 2,2-Methylenebis(furan).

#### Fig 7. (a) Effect of feedstock on EL yield.

Reaction conditions: Furfuryl alcohol: 120 mg, ethanol: 8 mL, reaction time: 3 h, reaction temperature: 200 °C and catalyst: 60 mg of OMSA-600

#### 3.7.2. Effect of the catalyst

Fig.7b shows the EL yield prepared from furfuryl alcohol with OMSAs and no catalyst at different calcination temperatures (400 °C–900 °C). At an OMSA calcination temperature of 400 °C, an EL yield of 74.6% was achieved. By increasing it to 600 °C, the EL yield gradually increased to 80.6%. At temperatures higher than 600 °C, the EL yield starts to gradually decrease. Table 1 indicates that the amounts of super and total acids in OMSA–600 were the largest (25.9 and 58.6 cm<sup>3</sup>/g STP, respectively), and the specific surface area was not the highest (285 m<sup>2</sup>/g). It also shows that the acid content in the catalyst was the main factor affecting the catalytic performance [53]. In the blank test, the EL yield was 3.1%, which was very low and reflects the necessity of the catalyst in the synthesis of EL by alcoholysis in ethanol using furfuryl alcohol as biorenewable feedstock.

Fig. 7. (b) Effect of catalysts on EL yield.

Reaction conditions: Furfuryl alcohol: 120 mg, ethanol: 8 mL, temperature: 200 °C, time: 3 h and catalyst: 60 mg.

3.7.3. Effect of reaction temperature

Fig.7c shows the influence of different reaction temperatures (160 °C, 180 °C, 200 °C and 220 °C) on the EL yield using OMSA–600 as a catalyst and furfuryl alcohol as biorenewable feedstock. The figure indicates that the increase in the reaction temperature from 160 °C to 220 °C causes a slight increase, followed by a decrease in the EL yield. Furthermore, the maximum EL yield (80.6%) was obtained at 200 °C. It was also found that increasing the temperature causes the colour of the products and catalysts to gradually change to dark brown, which indicates acceleration in the formation of humus. Zhao et al. considered that the accumulation of humus on the catalyst surface also increases with the amount of catalyst [17]. Therefore, a high reaction temperature (>200 °C) is not desirable in order to maintain a high EL yield.

Fig. 7. (c) Effect of reaction temperature on EL yield.

Reaction conditions: Furfuryl alcohol: 120 mg, ethanol: 8 mL, temperature: 200 °C, time: 3 h and catalyst: 60 mg.

#### 3.7.4. Effect of reaction time

Fig.7d shows the effect of different reaction times (1, 2, 3, 4, 5 and 6 h) on the EL yield using OMSA–600 as the catalyst and furfuryl alcohol as the biorenewable feedstock. Increasing the reaction time causes the EL yield to rapidly increase and then to slowly decrease. The EL yield reached its maximum value (80.6%) after 3 h of reaction. Therefore, a very long reaction time may lead to the conversion of EL into other substances and consequently reduces the yield. Hao et al. [54] obtained similar results while preparing EL from furfuryl alcohol.

#### Fig. 7. (d) Effect of reaction times on the EL yield.

Reaction conditions: Furfuryl alcohol: 120 mg, ethanol: 8 mL, temperature: 200 °C, time: 3 h and catalyst: 60 mg.

#### 3.7.5. Effect of catalyst amount

Fig.7e shows the effect of different amounts of catalyst (20–80 mg) on the EL yield. The yield reached its maximum value when the amount of catalyst was 60 mg. At higher values, an excessive acid catalyst may accelerate the condensation of furfuryl alcohol and aid in the formation of byproducts [55], and it can also promote further conversion of EL into  $\gamma$ -valerolactone [56].

Fig. 7. (e) Effect of catalyst amount on EL yield.

Reaction conditions: Furfuryl alcohol: 120 mg, ethanol: 8 mL, temperature: 200 °C, time: 3 h and catalyst: 60 mg.

#### 3.7.6. Reusability of the catalyst

The reusability of OMSA-600 was studied under optimum reaction conditions. Fig. 7f shows that the catalyst maintained a relatively high catalytic activity after repeated use (four times) with an EL yield of 71.2%. To verify the reason for its deactivation, the NH<sub>3</sub>-TPD and FTIR of OMSA-600 and the sulfur content of OMSA-600 after repeated use of 1 to 4 times were characterized. After repeated use of 1 to 4 times, OMSA-600 still existed in acid sites of different strengths such as weak, strong, medium strong and superacid, as shown in Fig. 7g. However, the total amount of NH<sub>3</sub> desorption of OMSA-600 (Table 2) decreased from 58.6 cm<sup>3</sup>/g STP to 44.9 cm<sup>3</sup>/g STP as the number of reaction cycles increased, which was also confirmed by the successive decrease of the sulfur content shown in Table 2. The FTIR spectra of OMSA-600 (Fig. 7h) after repeated use of 1 to 4 times show that the stretching vibration peak of the S=O bond at 1156 cm<sup>-1</sup> gradually weakens. Therefore, according to the above analysis, the main reason for the deactivation of the catalyst after subsequent cycles in this study was the reduction of the sulfur content. Shi et al. [57] believe that as the sulfur content decreases, the acid content of the catalyst will decrease after repeated cycles. Wang et al. [58] prepared biodiesel using sulfated zirconia, which was a mesoporous superacid nanocatalyst. Comparing the repeatedly used catalyst with the fresh catalyst, they found that the main reason for the deactivation of the catalyst was the reduction of the sulfur content, which affected the acid content of the catalyst.

Fig. 7. (f) Reusability of the catalyst.

Reaction conditions: Furfuryl alcohol: 120 mg, ethanol: 8 mL, catalyst: 60 mg, temperature: 200 °C and time: 3 h. **Fig. 7.** (g) NH<sub>3</sub>-TPD curves and (h) FTIR spectra of the catalyst.

	$NH_3$ Desorption Quantity ( $cm^3/g$ STP )								
sample	73–187	187–489	489–775	775–1000	Total	ICP-OES			
OMSA-600-1	10.0	16.7	6.0	25.9	58.6	2.06			
OMSA-600-2	9.1	14.1	5.5	22.3	51.0	1.67			
OMSA-600-3	7.6	11.5	3.7	22.6	45.4	1.52			
OMSA-600-4	6.2	12.7	5.7	20.3	44.9	1.47			

Table 2. Acid quantities and sulfur contents of the spent catalysts.

# Conclusions

Ordered mesoporous  $SO_4^{2-}/Al_2O_3$  solid super acid was prepared by EISA, followed by sulphonation and was then used to prepare EL from furfuryl alcohol. The synthesis of EL from different feedstock such as cellulose, glucose, fructose, sucrose, and furfuryl alcohol was studied using OMSA–600 as catalyst in absolute ethanol under the same conditions (200 °C, 3 h). The El yields were 12.1%, 24.4%, 32.1%, 48.2% and 80.6%. The effects of different reaction conditions (temperature, time and catalyst amount) on the EL yield were also explored. The reusability of OMSA–600 showed that after four repeated experiments, OMSA–600 was not significantly deactivated with a 71.2% yield.

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#### **Table Captions**

Table 1. BET surface areas, pore sizes, acid quantities, and sulfur content of OMSAs.

Table 2. Acid quantities and sulfur contents of the spent catalysts.

#### **Figure Captions**

Scheme 1. Ethyl levulinate production from Cellulose.

Scheme 2. Mechanism for the preparation of EL from furfuryl alcohol.

Fig. 1. TEM images of OMSAs.

Fig. 2. XRD spectra of OMSAs: (a) small-angle spectra and (b) wide-angle spectra.

Fig. 3. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution curves of OMSAs.

Fig. 4. NH<sub>3</sub>-TPD curves of OMSAs.

Fig. 5. FTIR (a) and Py-IR (b) spectra of OMSAs.

Fig. 6. TG spectra of OMSAs.

Fig. 7. (a) Effect of feedstock on EL yield.

Reaction conditions: Furfuryl alcohol: 120 mg, ethanol: 8 mL, reaction time: 3 h, reaction temperature: 200 °C and catalyst: 60 mg of OMSA-600.

Fig. 7. (b) Effect of catalysts on EL yield.

Reaction conditions: Furfuryl alcohol: 120 mg, ethanol: 8 mL, temperature: 200 °C, time: 3 h and catalyst: 60 mg.

Fig. 7. (c) Effect of reaction temperature on EL yield.

Reaction conditions: Furfuryl alcohol: 120 mg, ethanol: 8 mL, temperature: 200 °C, time: 3 h and catalyst: 60 mg.

Fig. 7. (d) Effect of reaction times on the EL yield.

Reaction conditions: Furfuryl alcohol: 120 mg, ethanol: 8 mL, temperature: 200 °C, time: 3 h and catalyst: 60 mg.

Fig. 7. (e) Effect of catalyst amount on EL yield.

Reaction conditions: Furfuryl alcohol: 120 mg, ethanol: 8 mL, temperature: 200 °C, time: 3 h and catalyst: 60 mg.

Fig. 7. (f) Reusability of the catalyst.

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Reaction conditions: Furfuryl alcohol: 120 mg, ethanol: 8 mL, catalyst: 60 mg, temperature: 200 °C and time: 3 h.

Fig. 7. (g) NH<sub>3</sub>-TPD curves of the catalyst.

Fig. 7. (h) FTIR spectra of the catalyst.

Journal Pression





Intensity







TCD

































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# Highlights

- $\bullet$  Ordered mesoporous  $S{O_4}^{2^-}\!/Al_2O_3$  was prepared by EISA method, followed by sulphonation.
- Ammonia desorption by the super acid in OMSA-600 reached up to 25.9 cm<sup>3</sup>/g STP.
- OMSA-600 showed a good catalytic activity in converting furfuryl alcohol to EL.

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#### **Declaration of interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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