


 Cite this: *RSC Adv.*, 2023, **13**, 7257

Conversion of cellulose into valuable chemicals using sulfonated amorphous carbon in 1-ethyl-3-methylimidazolium chloride[†]

 Thien-Hang Thi Nguyen,^{‡,ab} Ha Bich Phan,^{‡,abc} Trinh Hao Nguyen,^{ab}
 Kim Nguyen Tran,^{ab} Linh Ho Thuy Nguyen,^{bd} Tan Le Hoang Doan,^{bd}
 and Phuong Hoang Tran^{ab}

In this study, three carbon-based solid acid catalysts were prepared *via* the one-step hydrothermal procedure using glucose and Brønsted acid, including sulfuric acid, *p*-toluenesulfonic acid, or hydrochloric acid. The as-synthesized catalysts were tested for their ability to convert cellulose into valuable chemicals. The effects of Brønsted acidic catalyst, catalyst loading, solvent, temperature, time, and reactor on the reaction were investigated. The as-synthesized C–H₂SO₄ catalyst containing Brønsted acid sites (–SO₃H, –OH, and –COOH functional groups) demonstrated high activity in the transformation of cellulose into valuable chemicals with the yield of total products of 88.17% including 49.79% LA in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) solvent at 120 °C in 24 h. The recyclability and stability of C–H₂SO₄ were also observed. A proposed mechanism of cellulose conversion into valuable chemicals in the presence of C–H₂SO₄ was presented. The current method could provide a feasible approach for the conversion of cellulose into valuable chemicals.

 Received 10th January 2023
 Accepted 24th February 2023

DOI: 10.1039/d3ra00177f

rsc.li/rsc-advances

Introduction

Research on the transformation of available carbohydrates into valuable chemicals has received much attention over the past decade.^{1–5} The transformation of cellulose based on agricultural residues into useful chemicals has been studied extensively for practical applications.^{6–8} Facing the shortage of fossil fuels and fluctuating prices of gasoline, the development of clean, safe, and sustainable alternative energy sources has become an urgent mission.^{9–11} Among the new kinds of energy resources, biomass feedstocks are essential sources that are expected to bring many benefits in the future as it is the most widely abundant resource on earth.^{12–14} Substituting conventional energy sources with biomass is a potential solution to lower dependence on coal, oil, and gas and environmental pollution. The conversion of carbohydrates into valuable manufacturing chemicals such as 5-hydroxymethylfurfural (HMF), 2,5-diformylfuran (DFF), levulinic acid (LA), formic acid (FA), 2,5-

furandicarboxylic acid (FDCA), furfural (Fur) has been investigated extensively in the past decade.^{4,15–26} Formic acid is a chemical that is used to make formaldehyde, rubber, plasticizers, pharmaceuticals, and textiles, among other things. Furthermore, using FA as a hydrogen storage material for automotive applications or as an internal hydrogen source for bio-based processes is gaining popularity.^{27,28} One of the most interesting products is LA, which is the platform chemical for various high value-added products.²⁹ LA is the starting point for several chemicals from fields as diverse as solvents and fuels, polymers and plasticizers, food additives, pharmaceuticals. In the pharmaceutical industry, calcium levulinate is a calcium supplement enhancing bone formation and muscular excitability. In agriculture, its derivate δ -aminolevulinic acid is a biodegradable herbicide,³⁰ levulinate potash can be used as a highly effective fertilizer.³¹ LA can be converted from different biomass raw materials,^{32,33} especially from cellulose. Over the past decade, several studies have employed homogeneous acidic catalysts for the production of LA (*e.g.*, hydrochloric acid, nitric acid, sulfuric acid, ...).^{34–37} However, these acids suffer from disadvantages, such as difficulty in recovery, equipment corrosion, and environmental pollution. Consequently, a variety of solid acid catalysts have received much attention in LA production from different feedstocks, including acidic TiO₂ nanoparticles,³⁸ and sulfonated carbon.³⁹ Based on LA synthesis processes, high temperatures and long reaction times are also required for LA generation from cellulose using solid catalysts.

^aDepartment of Organic Chemistry, Faculty of Chemistry, University of Science, Vietnam National University, Ho Chi Minh City, Vietnam. E-mail: thphuong@hcmus.edu.vn; Tel: +84-903-706-762

^bVietnam National University, Ho Chi Minh City, Vietnam

^cInstitute of Public Health, Ho Chi Minh City, Vietnam

^dCenter for Innovative Materials and Architectures (INOMAR), Ho Chi Minh City, Vietnam

[†] Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d3ra00177f>
[‡] These authors contributed equally to this work.


Cellulose has become the focus material in many studies thanks to its low cost and abundant quantity. Swatloski and coworkers⁴⁰ reported an exciting result for cellulose dissolution with 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl). Several studies have indicated the role of liquid acids in hydrolyzing cellulose in the industry.¹⁰ However, these liquid–acid catalysts demand a special method in the form of neutralization, which involves costly and inefficient catalyst extraction from products and leads to unrecyclable sulfate waste. Therefore, the use of recyclable strong solid acids has been encouraged in response to the criteria of green and sustainable chemistry. Comparative studies of different solid acid catalysts showed that carbon materials with acid sites could be considered the most promising cellulose depolymerization catalysts as their unique properties include high thermal and chemical stability, low cost, recyclability, and high surface area.^{41–44}

Carbon-based solid acid catalysts containing Brønsted acidic sites ($-\text{SO}_3\text{H}$, $-\text{COOH}$, and $-\text{OH}$) have been demonstrated as effective solid catalysts for the conversion of cellulose.^{45–47} The catalytic effect demonstrated the significant ability of hydrolysis of cellulose; the large effective area and acid groups supported the hydration of monosaccharides to furanic compounds.⁴⁸ The cellulose hydrolysis reaction in the presence of carbon-based solid acid provided a glucose yield of 40% with high selectivity.⁴⁹ Recently, the hydrolysis of cellulose was carried out in ionic liquids, in which cellulose was dissolved in ionic liquids and then hydrolyzed.^{50,51} The ionic liquids supported the dissolution of cellulose by disrupting the crystalline structure of cellulose and made the β -1,4-glycosidic bonds more favorable for hydrolysis. Ignatyev and coworkers reported Smopex-101 hydrolyzed cellulose in [BMIM]Cl.⁵² According to previous studies, [BMIM]Cl and [EMIM]Cl ionic liquids are two suitable solvents to dissolve cellulose as well as convert cellulose into some basic products.^{53,54} In addition, [BMIM]Cl ionic liquid is more expensive than [EMIM]Cl. When compared to economic efficiency, we choose [EMIM]Cl to conduct research. Besides, the carbonaceous catalysts were used for the hydrolysis of hemicellulose to monosaccharides and the dehydration of these compounds to furfural and HMF.^{55–57}

In this study, we report a method for the conversion of cellulose into valuable chemicals in a one-pot reaction using Brønsted acidic carbon materials in ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) as catalytic systems. Among three Brønsted acidic carbon materials, C–H₂SO₄ was prepared *via* direct hydrothermal carbonization of glucose, citric acid, and sulfuric acid for 4 h at 180 °C providing the highest activity in the conversion of cellulose into organic compounds. These results motivated us to continue investigating the synthesis of organic products from cellulose and agricultural by-products.

Materials and methods

Materials

D-Glucose monohydrate (>99%), cellulose (>99%), HMF (>99%), DFF (>99%), FA (>99%), LA (>99%), Fur (>99%), FDCA (>99%), choline chloride (>99%), citric acid monohydrate (>99%), oxalic acid dihydrate (>99%), malonic acid (>99%), fumaric acid

(>99%), adipic acid (>99%), [EMIM]Cl (98%), *p*-toluenesulfonic acid (>99%), sulfuric acid (98%), hydrochloric acid (36%), THF (>99%) were obtained from Sigma-Aldrich. All chemical substances were used without any further purification.

Preparation of Brønsted acidic carbon materials

Brønsted acidic carbon materials were synthesized by one-step hydrothermal carbonization using the procedure reported by Xiao and coworkers with a little modification.⁵⁸ The mixture of the D-glucose (10 g), citric acid monohydrate (4 g, 20 mmol), Brønsted acid (*p*-toluenesulfonic acid (TsOH), sulfuric acid (H₂SO₄) or hydrochloric acid (HCl), 10 mmol), and 80 mL distilled water was charged in a 100 mL Teflon-lined stainless-steel autoclave. The mixture was heated at 180 °C for 4 h in an oven. Black carbonaceous materials were obtained by filtration and washed several times with distilled water and followed by methanol, and then dried at 80 °C for 6 h. Three samples were prepared through this procedure including C–TsOH, C–H₂SO₄, and C–HCl, which had synthesized yields per 100 g of D-glucose of 36.3, 38.1, and 34.5 wt%, respectively.

Characterization techniques

The neutralization titration method of every functional group over carbonaceous solid acid catalysts prepared above was similar to the study of Wang *et al.*⁵⁹ with a little modification of conditions, and the detailed method was as follows. To measure the total functional groups ($-\text{SO}_3\text{H}$, $-\text{COOH}$, and $-\text{OH}$ groups), NaOH (1 N, 40 mL) was added to a vessel with a catalyst (80 mg). The mixture was stirred at room temperature for 24 h, and the reaction mixture was centrifuged to separate the solid. The supernatant solution was titrated by HCl (0.1 N) aqueous solution using phenolphthalein as an indicator. The content of the $-\text{SO}_3\text{H}$ group was determined by adding NaCl (1 N, 40 mL) to the catalyst (80 mg), and the reaction mixture was stirred for 24 h at room temperature. After centrifugal separation, the supernatant solution was titrated by NaOH (0.01 N) using phenolphthalein as an indicator.

Fourier-transform infrared spectroscopy (FT-IR) were recorded on a Bruker's VERTEX 70 series FT-IR spectrometers and Shimadzu IRPrestige-21, with a measuring range of 600–4000 cm⁻¹. The crystallinity of the synthesized powders was analyzed using Bruker-D8 Advance powder X-ray diffractometer (P-XRD, CuK α radiation, $\lambda = 0.15418$ nm) with a step size and a time per step fixed at 0.01 and 0.25 s, respectively. Thermal gravimetric analysis (TGA) was recorded on a TGA Q500 V20.13 Build 39 instrument, heated to 800 °C (10 °C min⁻¹) in an air atmosphere. Scanning electron microscopy (SEM) image and Energy dispersive X-ray (EDX) spectra were measured on a Hitachi S4800 (Japan) instrument, with magnification 500–5000 times, an acceleration voltage of 10 kV. The concentration of sulfur was determined by inductively coupled plasma mass spectrometry (Agilent ICP-MS 7700x instrument).

Preparation of deep eutectic solvents (DESS)

DESSs were prepared based on the study of Abbott and coworkers.⁶⁰ The choline chloride and HBD (citric acid (C),



oxalic acid (O), malonic acid (M), fumaric acid (F), or adipic acid (A) with 1 : 1 molar ratio were heated by a magnetic stirrer for 2 h at 110 °C until they formed a homogeneous colorless liquid. DESs were used directly as solvents for the conversion of cellulose without purification. The obtained DESs are denoted as DES-C, DES-O, DES-M, DES-F, and DES-A, respectively.

Cellulose transformation in C-H₂SO₄/DESs

In a typical experiment, cellulose (162 mg), DES (4 g), and C-H₂SO₄ (10 mg) were put into the reaction vessel. The reaction mixture was stirred with a magnetic bar at a temperature of 120 °C in an oil bath for 18 h. After completion of the reaction, samples were diluted with distilled water to analyze by the HPLC method.

Cellulose conversion by C-H₂SO₄/[EMIM]Cl

In a typical experiment, cellulose (162 mg), [EMIM]Cl (1 g, 7 mmol), and C-H₂SO₄ (0, 1, 5, 8, 10, and 20 mg) were put into the reaction tubes with a magnetic bar. The mixture was heated to 120 °C in an oil bath with a magnetic stirrer. Samples were taken from the reaction mixture at a period of time for HPLC analysis to study the effect of catalyst, reaction times, and reaction temperatures on the yield of the product.

Recycling and reuse of C-H₂SO₄/[EMIM]Cl

After completion of the reaction, valuable products were extracted by tetrahydrofuran (THF). The remaining [EMIM]Cl and catalyst were dried at 100 °C for 3 h and used for subsequent recycling.

Products analysis

The reaction products were quantified by Agilent Technologies 1260 Infinity HPLC with a PAD detector (285 nm, 210 nm). The column InertSustain C18 (5 μm, 4.6 × 150 mm) was used to separate the components of the reaction mixture. The column temperature was maintained at 30 °C. A mixture of methanol and 2.5 mM sulfuric acid was used as eluent with a flow rate of 0.7 mL min⁻¹.

According to HPLC analysis, the amounts of HMF, DFF, LA, FA, Fur, and FDCA were calculated as follows:

$$\text{Yield of product} = \frac{\text{mol of product}}{\text{mol of glucose units of initial cellulose}} \times 100\%$$

Results and discussion

Characterization of catalysts

Three different types of catalysts were synthesized by one-pot hydrothermal carbonization. To obtain strong acidity on the surface of catalysts, *p*-toluenesulfonic acid or sulfuric acid or hydrochloric acid were mixed in glucose solution to prepare C-TsOH, C-H₂SO₄, and C-HCl catalysts, respectively. The procedure for the carbonaceous solid acid catalysts was shown in Fig. 1. The colors of the three materials were obtained in black color after the hydrothermal reaction at 180 °C for 4 h.

The proposed mechanism for the formation of these catalysts is the conversion of glucose to organic substances such as furfural in the first step. These compounds can react with citric acid, TsOH, H₂SO₄, or HCl to form the corresponding acid functional groups. Then, polymerization reactions occur, forming soluble polymers. These polymers, after being aromatized, gradually aggregate into larger spheres by forming stable oxygen groups such as ethers or quinones.⁶¹ The presence of citric acid helps to provide the carboxyl acid group and improves the acidity of the catalyst. The sulfonic acid groups can also convert to another group, such as sulfonates during hydrothermal processes.

From the neutralization titration results, the total acid content of three materials was 2.2, 2.2, and 1.9 mmol g⁻¹ for C-TsOH, C-H₂SO₄, and C-HCl particles, respectively. These total acid contents are similar to previous literature. Wang and coworkers developed carbon-based solid acid, which was synthesized from glucose and *p*-toluenesulfonic acid, and the acidity was 2.0 mmol g⁻¹.⁵⁹ Nata and coworkers reported the preparation of sulfonated carbonaceous material generated by hydrothermal carbonization of glucose at 180 °C for 4 h in the presence of acrylic acid and hydroxyethylsulfonic acid, and the acidity of this material was 2.10 mmol g⁻¹.⁶²

The structure of C-H₂SO₄ was determined by XRD, FT-IR, TGA, SEM, and EDX. The FT-IR spectra of catalysts are shown in Fig. 2a. Upon hydrothermal carbonization of glucose and acids, these rich carbon materials with functional groups including phenolic hydroxyl, carbonyl, sulfonic acid groups,

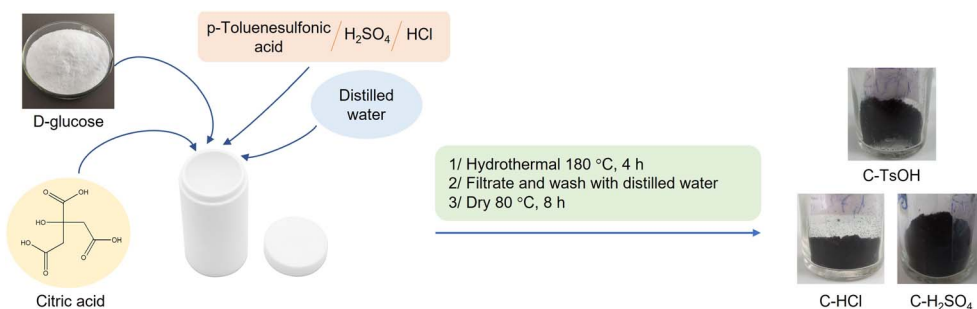


Fig. 1 Preparation of carbonaceous acidic catalysts.



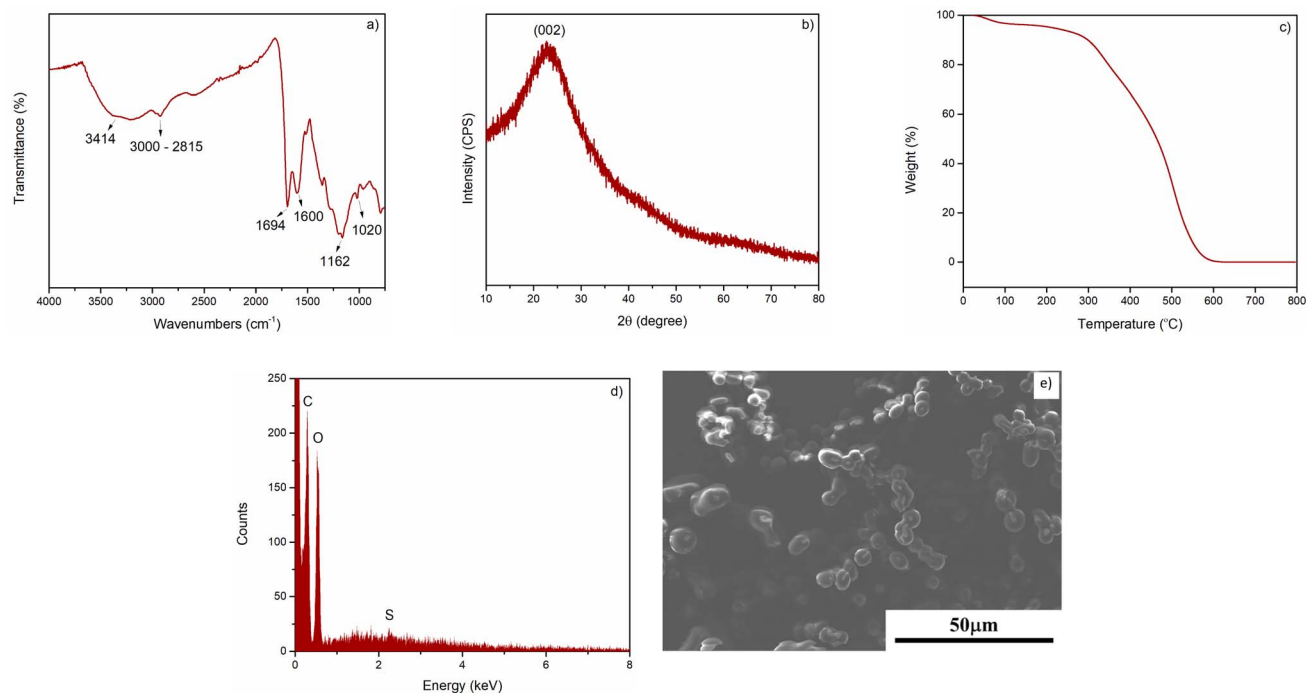


Fig. 2 Characterization of C-H₂SO₄: (a) FT-IR spectrum, (b) XRD pattern, (c) TGA curve, (d) SEM image, and (e) EDX spectra.

and carboxylic groups were obtained. The characteristic band at $\sim 3414\text{ cm}^{-1}$ in three samples is attributed to the O-H stretching. The aliphatic C-H band is shown by the band $3000\text{--}2815\text{ cm}^{-1}$. The absorption band at approximately 1694 cm^{-1} is assigned to stretching vibrations of C=O groups, indicating the existence of carboxylic acid groups. The absorption bands at approximately 1162 cm^{-1} and 1020 cm^{-1} are assigned to stretching SO₃⁻ and O=S=O, respectively. These signals confirmed that the -SO₃H groups were successfully grafted onto the carbon surface.⁵⁹ The band at approximately 1600 cm^{-1} belongs to C=C groups.

The XRD pattern of the catalyst was presented in Fig. 2b. The result showed no noticeable difference in the crystalline structure of the three samples. The XRD pattern exhibited a broad diffraction peak at 2θ angle of $15\text{--}30^\circ$, which was attributed to (002) planes of amorphous carbon. Besides, the weak diffraction peak (101) around 45° was also observed due to the axis of the graphite structure. These diffraction patterns were typical of amorphous carbon consisting of disordered polycyclic aromatic carbon sheets.⁶³ TGA was measured to investigate the thermal stability of the prepared material. As shown in Fig. 2c, the sample presented a slight weight loss (about 5%) below 200°C , which is mainly due to the loss of a small amount of bonded water. The thermogravimetric curve of the catalyst at higher temperatures (above 300°C) showed more significant weight loss because of the gradual desorption and thermal decomposition process of organic functional groups. Thus, it could be concluded that the catalyst was stable up to 300°C . The EDX spectra (Fig. 2d) showed the presence of C, O, and S elements. In addition, ICP-MS revealed that the obtained material had a calculated sulfur content of 620 mg kg^{-1} . The SEM image of

C-H₂SO₄, as depicted in Fig. 2e showed that the resulting particle was spherical in shape with $5\text{--}8\text{ }\mu\text{m}$ diameter size.

Catalytic performance of carbonaceous catalysts

Effect of various carbonaceous catalysts. The conversion values of cellulose catalyzed by various carbonaceous catalysts in [EMIM]Cl were investigated in Fig. 3, 4, and 5. The results of all three figures showed the difference in cellulose conversion ability with various catalyst dosages, and most of them provided the highest yield for 24 h. As clearly shown in Fig. 3, in the reaction conditions with 10 mg of C-H₂SO₄, the highest total yield of the valuable products was 88.17% (8.67% HMF, 0.27% DFF, 19.89% FA, 49.79% LA, 6.48% Fur and 3.07% FDCA) for 24 h. As shown in Fig. 4, 10 mg of C-TsOH indicated quite good activity when giving the highest total yield of the products of 76.48% also for 24 h. For C-HCl (Fig. 5), the maximum total yield obtained was only about 27.59% when using 8 mg catalyst for 24 h and LA was not observed. The total yield of the desired products decreased after 24 h of reaction was observed in the reactions using low catalyst concentrations (1 mg Fig. 4 and 5 or 5 mg Fig. 4). This phenomenon is due to the long reaction time and small amount of catalyst, then the main process is polymerization or humins generation. Generally, the main product with the highest content was LA, followed by FA, HMF, and small amounts of furfuran and FDCA. These results demonstrated that C-H₂SO₄ exhibited better catalytic performance than the others. The first explanation is that the activity of the sulfur group dominated the dehydration reaction more than the chloride group and the binding of the Cl⁻ group to the carbon substrate is weaker than that of the SO₃H⁻ group, so C-HCl is less active. The activity of C-TsOH is only slightly lower than C-



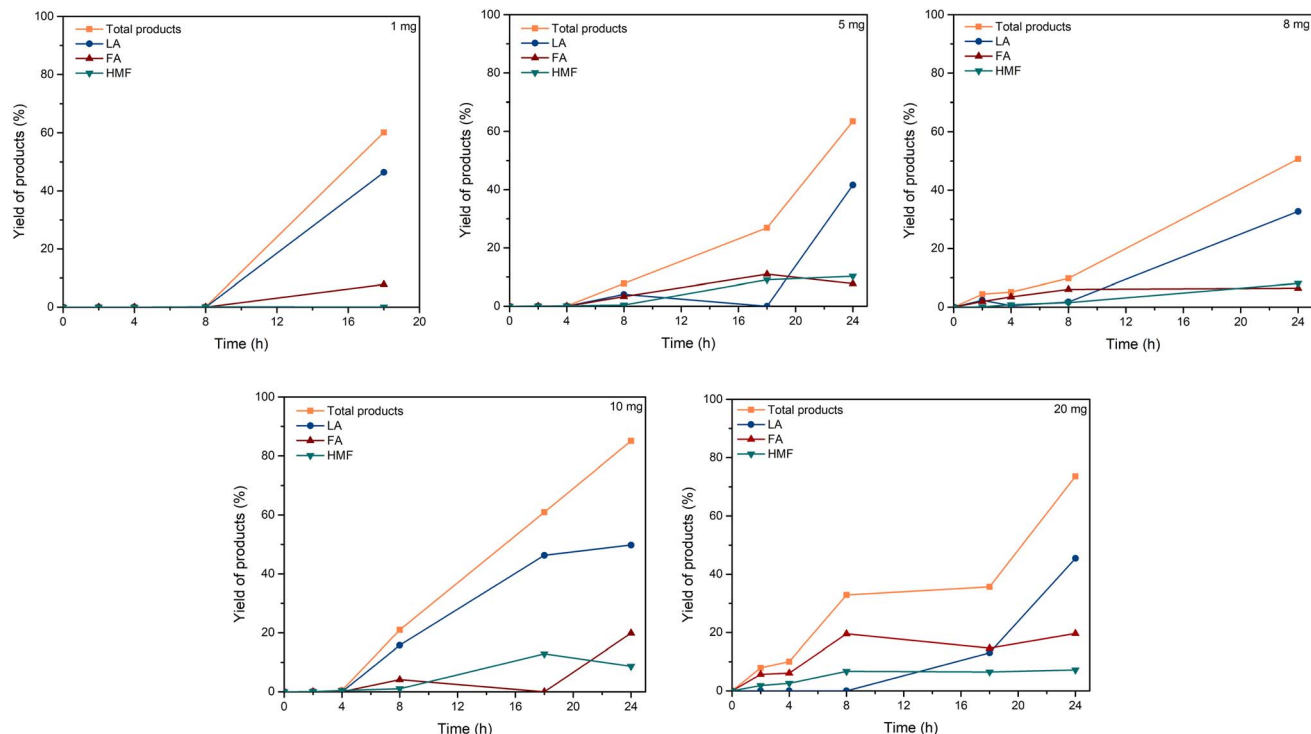


Fig. 3 Effect of C-H₂SO₄ dosage. Reaction conditions: cellulose (162 mg), C-H₂SO₄ (1, 5, 8, 10, 20 mg), [EMIM]Cl (1 g, 7 mmol), 120 °C.

H₂SO₄. The reason might be the difference in the number of active sites attached to the carbon plate during hydrothermal. Besides, C-H₂SO₄ is also more economical because sulfuric acid is cheaper than *p*-toluenesulfonic acid. Therefore, C-H₂SO₄ will be used for further investigation in this work.

Effect of the solvent. The solvent plays an important role in heterogeneous catalytic reactions. In the current work, the solvent effects on the hydrolysis-dehydration of cellulose were shown in Fig. 6. In general, the main products of the reactions were LA due to the rich Brønsted acid conditions. [EMIM]Cl

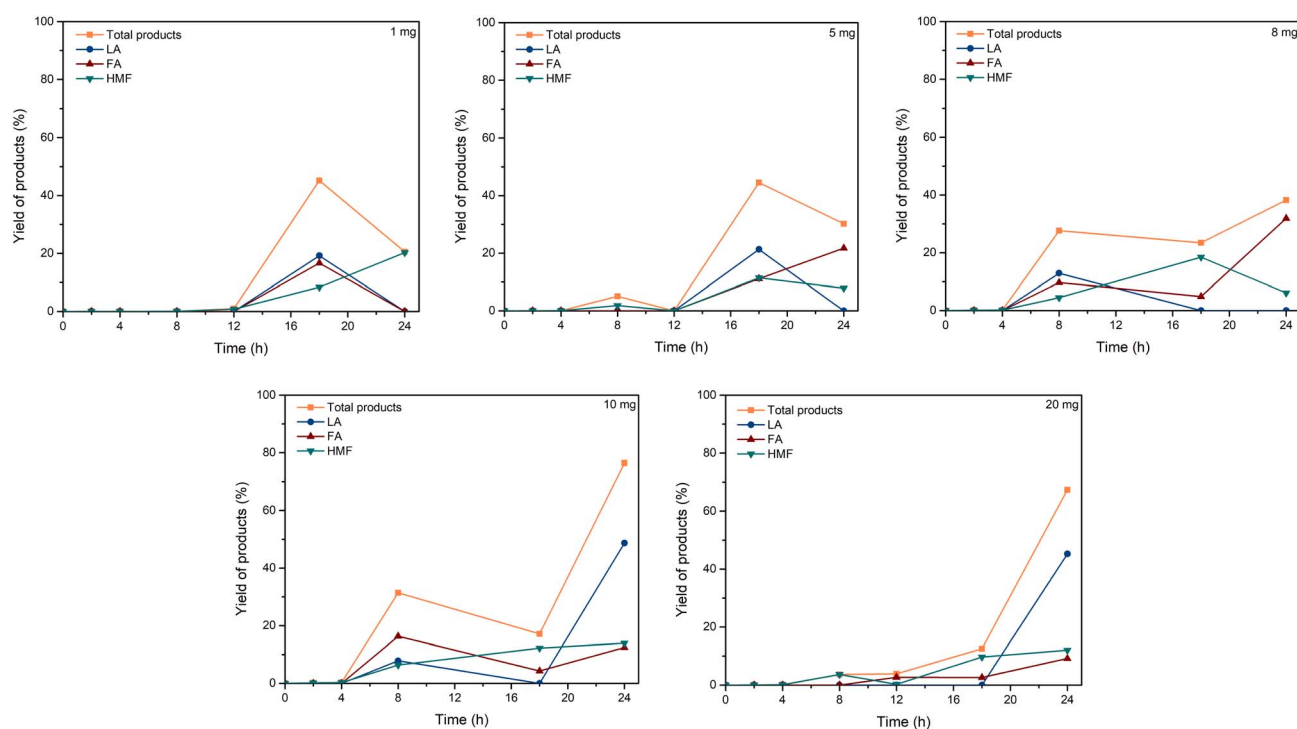


Fig. 4 Effect of C-TsOH dosage. Reaction conditions: cellulose (162 mg), C-TsOH (1, 5, 8, 10, 20 mg), [EMIM]Cl (1 g, 7 mmol), 120 °C.



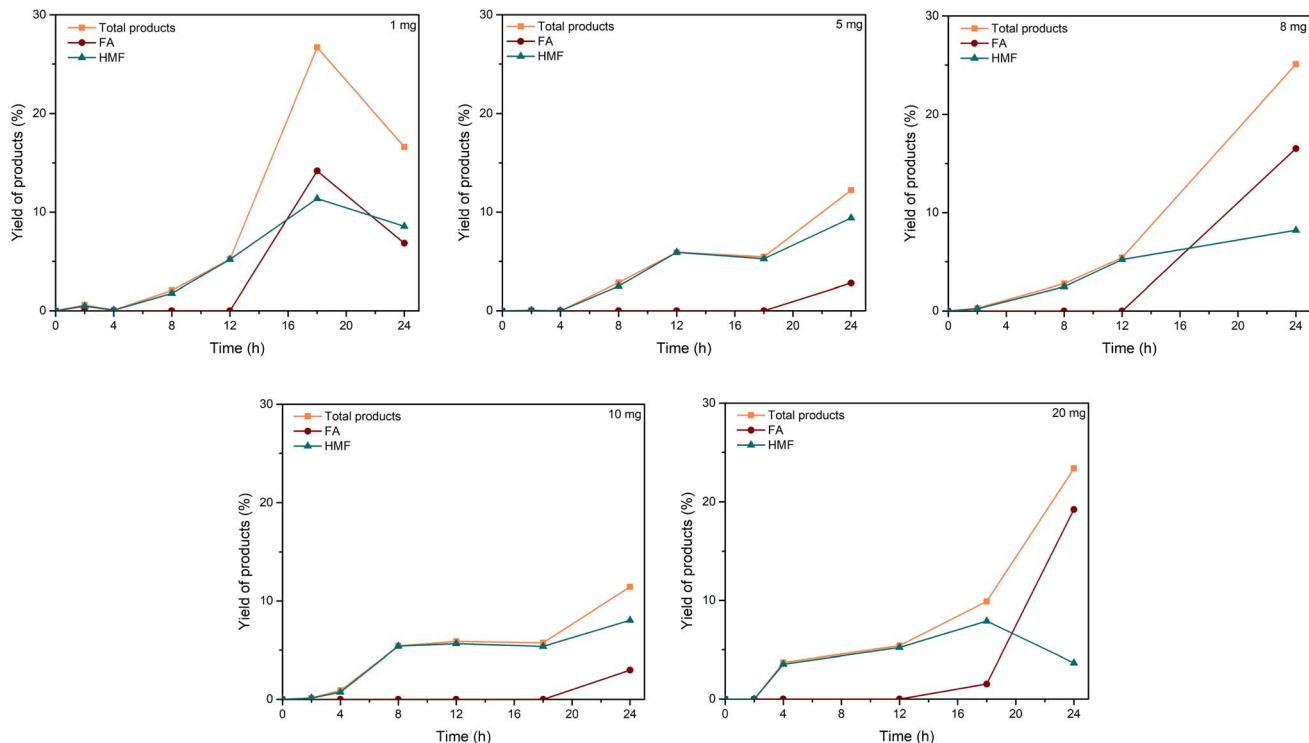


Fig. 5 Effect of C-HCl dosage. Reaction conditions: cellulose (162 mg), C-HCl (1, 5, 8, 10, 20 mg), [EMIM]Cl (1 g, 7 mmol), 120 °C.

indicated the best activity with the main composition of 46.31% LA and 12.87% HMF, the DESs showed low and approximately equal yields of about 22% to 27% LA and very little amount of HMF (less than 1.36%). This result can be explained by the better solubility and hydrolysis of cellulose in IL than in DES.^{64,65} In addition, the 24 h isothermal TGA at 120 °C of [EMIM]Cl and DES-C (Fig. S8a, ESI[†]) showed the weight loss of about 8% for [EMIM]Cl and 10% for DES-C after initial 100 min

heating. As seen in Fig. 8a, the [EMIM]Cl was stable with prolonged reaction time, while the weight of DES-C decreased remarkably to approximately 55% at the end of the period. This result demonstrated that the [EMIM]Cl was more stable than DES-C, and the [EMIM]Cl provided better yields of products in the current work.

Effect of reaction time and temperature. The cellulose hydrolysis catalyzed by C-H₂SO₄ in [EMIM]Cl was performed in conventional heating for various reaction temperatures and times. The total yield values of products were given in Fig. 7. When the hydrolysis was conducted below 120 °C, the total product obtained was very low, just under 5.63%, even when heated to 24 h. The result could be explained because the energy supplied to the reaction at these temperatures was not enough to break β-1,4-glycosidic bonds of cellulose. When the temperature was increased to 120 °C, the total yield was obtained in 61.18% for 18 h and reached 88.17% after 24 h. However, when heating the reaction at 140 °C, the total products were only obtained in 36.68% for 18 h and strongly decreased after 24 h. The result could be explained by the polymerization of products at higher temperatures.

Recycle of the catalytic system. The investigation of the reusability and stability of the catalyst was shown in Fig. 8. After each reaction run, the mixture of catalyst and [EMIM]Cl was reused. There was a slight decrease in the total yield of the products after each run (88.17%, 83.85%, and 74.69%, respectively), which could be explained by the partial leaching -SO₃H group and the deposition of insoluble humins. The yield of LA remained above 49.38% after the first run and dropped to 40.68% in the following cycle. HMF obtained after three runs is

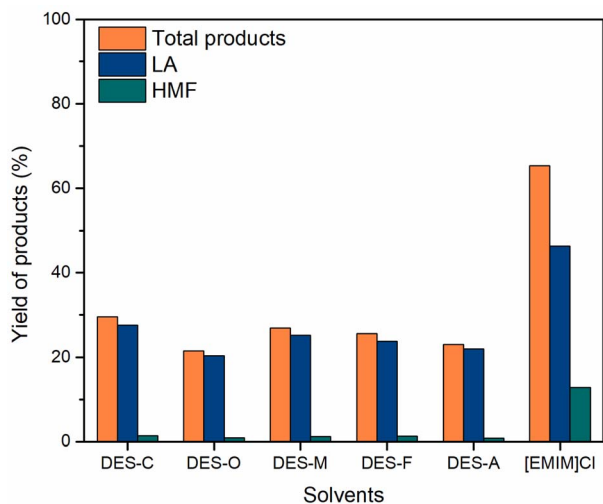


Fig. 6 Effect of various solvents on cellulose conversion. Reaction conditions: cellulose (162 mg), C-H₂SO₄ (10 mg), [EMIM]Cl (1 g, 7 mmol), 120 °C, 18 h.



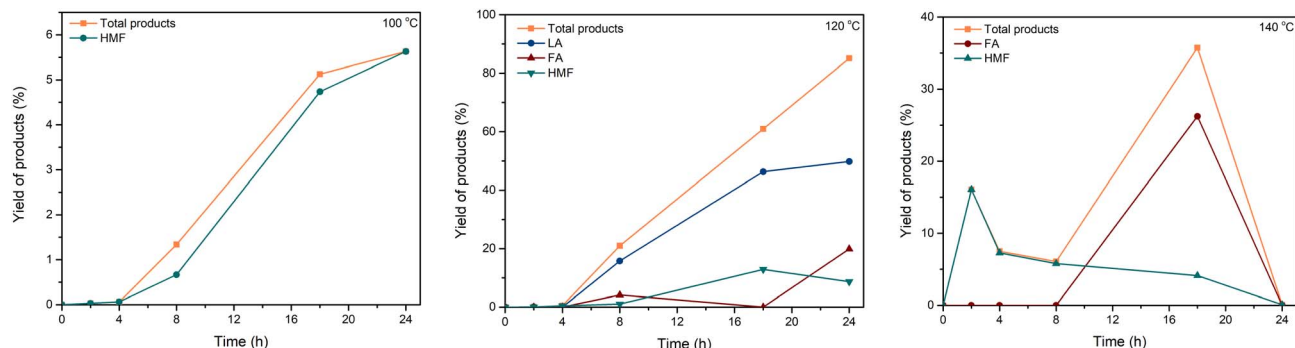


Fig. 7 Effect of reaction time and temperature on total yield of products. Reaction conditions: cellulose (162 mg), C-H₂SO₄ (10 mg), [EMIM]Cl (1 g, 7 mmol).

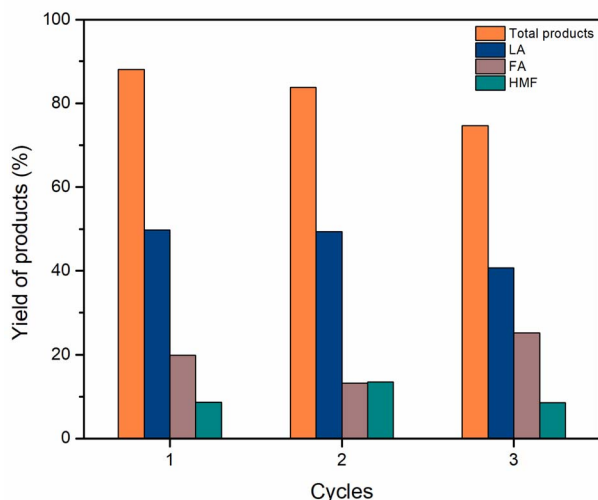


Fig. 8 Cellulose conversion towards valuable chemicals in the recycling test. Reaction conditions: cellulose (162 mg), C-H₂SO₄ (10 mg), [EMIM]Cl (1 g, 7 mmol), 120 °C, 24 h.

8.67%, 13.55%, and 8.52%, respectively. The composition of FA after three recycling times was 19.89%, 13.21%, and 25.22%, respectively. The composition of the products through the

recycling times was quite stable, indicating good recyclability and stability of the catalyst.

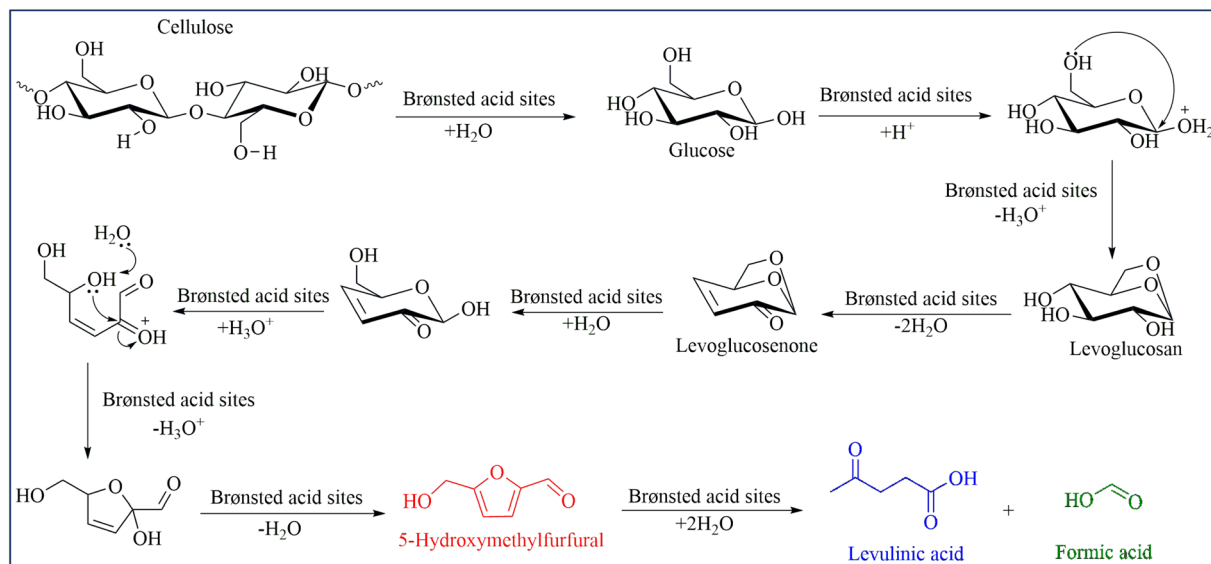
The comparison of the current work with the reported literature on the conversion of cellulose into valuable substances was presented in Table 1. It can be seen that the catalytic activity of C-H₂SO₄ in [EMIM]Cl showed high efficiency in the conversion of cellulose to valuable chemicals. The previous literature revealed that the conversion of cellulose also afforded products in high yields, but those procedures still suffered drawbacks, including the requirement of expensive catalysts, organic solvents, or high-pressure conditions.

The mechanism of this conversion was proposed in Scheme 1. Kitano and coworkers reported the amorphous carbon could absorb β-1,4 glucan.⁴¹ Thus, we proposed that the mechanism began with the sorption of cellulose on the catalyst through the formation of hydrogen bonds between the oxygen of cellulose and OH groups in the carbonaceous catalyst. As previously reported, hydrogen bonds forming with the oxygen of glycosidic bond with the OH group of the carbonaceous materials were more favorable than the inter- and intramolecular hydrogen bonds of cellulose. Thus, the β-1,4-glycosidic bonds of cellulose were associated with priority with the acidic sites of the carbonaceous material for hydrolysis.⁴¹ Hence, the catalytic activity of the carbonaceous catalyst increased the synergistic effect of

Table 1 Comparison of cellulose conversion in various catalytic systems

Entry	Reaction condition	Yield (%)			Ref.
		HMF	FA	LA	
1	Microcrystalline cellulose (0.5 g), 1-(4-sulfonic acid) ethyl-3-methylimidazolium hydrogen sulfate (1.0 g), 0.2 M FeCl ₂ (1 mL), MIBK (8 mL), 150 °C, 300 min, 101325 Pa	33.86	18.61	5.93	66
2	Cellulose (50 mg), [C ₃ SO ₃ Hmim]HSO ₄ (1.000 g), H ₂ O (2.000 g), 160 °C, 30 min, MW	—	—	55.0	21
3	Cellulose (0.05 g), [BSmim]HSO ₄ (1.5 g), H ₂ O (0.3 g, 20 wt%), 120 °C, 120 min	4.3	—	39.4	67
4	Cellulose (162 mg), C-H ₂ SO ₄ (10 mg), [EMIM]Cl (1 g, 7 mmol), 120 °C, 24 h	8.67	19.89	46.31	This work





Scheme 1 Proposed reaction mechanism for cellulose hydrolysis-dehydration by $\text{C-H}_2\text{SO}_4$ in $[\text{EMIM}]\text{Cl}$.

adsorption to cellulose on the surface and the strong $-\text{SO}_3\text{H}$ acidic sites attributed to the hydrolysis of cellulose.⁴¹ Based on the work of Cao *et al.*⁶⁸ and our experiment, the mechanism of solid acid-catalyzed hydrolysis of cellulose in $[\text{EMIM}]\text{Cl}$ was started with the Brønsted acid sites on the surface of the catalyst attacked to the oxygen of the β -1,4-glycosidic bond. Then, the C–O bond was cleaved and released glucose molecules. Since Brønsted acid has a poor effect on the isomerization of glucose to fructose, the formation of HMF and LA can be explained by levoglucosan (LGA) intermediate formation.^{17,68,69} The long reaction time in the Brønsted acid condition favored the formation of LA and FA.

Conclusions

We have successfully developed the conversion of cellulose to valuable chemicals using the catalytic system $\text{C-H}_2\text{SO}_4/[\text{EMIM}]\text{Cl}$ for the first time. The yield of total products could reach 88.17% (including 49.79% LA) when using $\text{C-H}_2\text{SO}_4/[\text{EMIM}]\text{Cl}$ under optimal conditions. Meanwhile, C-HCl gave low yields of products, which could be explained by the activity of the chloride group being weaker than that of the $-\text{SO}_3\text{H}$ group in the hydrolysis/dehydration reaction. The current method showed that high reaction temperature accelerated the reaction to provide high yields of products. Nonetheless, excessive-high temperature resulted in a decrease in product yield due to the formation of humins. Besides, there was no considerable loss in catalytic activity in three consecutive cycles, indicating the reusability and stability of the catalytic system.

Data availability

The data of this study are available from the corresponding author.

Author's contributions

Hang Thien Thi Nguyen: methodology, investigation, writing-original draft-review and editing. Ha Bich Phan: methodology, investigation, data curation. Trinh Hao Nguyen and Kim Nguyen Tran: investigation, data curation. Linh Ho Thuy Nguyen and Tan Le Hoang Doan: data curation. Phuong Hoang Tran: methodology, writing-review and editing, project administration. All authors read and approved the final manuscript.

Consent for publication

The authors give the publisher permission to publish the work.

Conflicts of interest

The authors declare no competing interest.

Acknowledgements

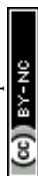
The authors acknowledge the financial support from Vietnam National University, Ho Chi Minh City (VNU-HCM) under grant number 562-2022-18-03. The authors would also to thank Dr Duy-Khiem Nguyen Chau for the valuable discussion. The authors express their sincere thanks to the Center for Innovative Materials & Architectures (INOMAR), Viet Nam National University, Ho Chi Minh City for their support in using the TGA and FT-IR measurements.

References

- 1 F. Chacón-Huete, C. Messina, B. Cigana and P. Forgione, *ChemSusChem*, 2022, e202200328.
- 2 L. Hu, L. Lin, Z. Wu, S. Zhou and S. Liu, *Renewable Sustainable Energy Rev.*, 2017, 74, 230–257.



- 3 H. B. Phan, C. M. Luong, L. P. Nguyen, B. T. Bui, H. T. Nguyen, B. V. Mai, T. V.-T. Mai, L. K. Huynh and P. H. Tran, *ACS Sustainable Chem. Eng.*, 2022, **10**, 8673–8684.
- 4 P. H. Tran and P. V. Tran, *Fuel*, 2019, **246**, 18–23.
- 5 R. Radhakrishnan, P. Patra, M. Das and A. Ghosh, *Renewable Sustainable Energy Rev.*, 2021, **149**, 111368.
- 6 J. B. Ocreto, W.-H. Chen, A. P. Rollon, H. C. Ong, A. Pétrissans, M. Pétrissans and M. D. G. De Luna, *Chem. Eng. J.*, 2022, 136733.
- 7 V. Ashokkumar, R. Venkatkarthick, S. Jayashree, S. Chuetor, S. Dharmaraj, G. Kumar, W.-H. Chen and C. Ngamcharussrivichai, *Bioresour. Technol.*, 2022, **344**, 126195.
- 8 R. Kumar, T. H. Kim, B. Basak, S. M. Patil, H. H. Kim, Y. Ahn, K. K. Yadav, M. M. Cabral-Pinto and B.-H. Jeon, *J. Cleaner Prod.*, 2021, 130180.
- 9 N. S. Ab Rasid, A. Shamjuddin, A. Z. A. Rahman and N. A. S. Amin, *J. Cleaner Prod.*, 2021, **321**, 129038.
- 10 A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick Jr, J. P. Hallett, D. J. Leak and C. L. Liotta, *Science*, 2006, **311**, 484–489.
- 11 A. M. Elgarahy, A. Hammad, D. M. El-Sherif, M. Abouzid, M. S. Gaballah and K. Z. Elwakeel, *J. Environ. Chem. Eng.*, 2021, **9**, 106503.
- 12 W. Deng, Y. Feng, J. Fu, H. Guo, Y. Guo, B. Han, Z. Jiang, L. Kong, C. Li, H. Liu, P. T. T. Nguyen, P. Ren, F. Wang, S. Wang, Y. Wang, Y. Wang, S. S. Wong, K. Yan, N. Yan, X. Yang, Y. Zhang, Z. Zhang, X. Zeng and H. Zhou, *Green Energy Environ.*, 2023, **8**, 10–114.
- 13 Y. Zhao, K. Lu, H. Xu, L. Zhu and S. Wang, *Renewable Sustainable Energy Rev.*, 2021, **139**, 110706.
- 14 B. Beig, M. Riaz, S. R. Naqvi, M. Hassan, Z. Zheng, K. Karimi, A. Pugazhendhi, A. Atabani and N. T. L. Chi, *Fuel*, 2021, **287**, 119670.
- 15 M. J. Antal Jr, W. S. Mok and G. N. Richards, *Carbohydr. Res.*, 1990, **199**, 91–109.
- 16 D. B. Bevilaqua, M. K. Rambo, T. M. Rizzetti, A. L. Cardoso and A. F. Martins, *J. Cleaner Prod.*, 2013, **47**, 96–101.
- 17 C. E. Bounoukta, C. Megías-Sayago, F. Ammari, S. Ivanova, A. Monzon, M. A. Centeno and J. A. Odriozola, *Appl. Catal., B*, 2021, **286**, 119938.
- 18 C. M. Lew, N. Rajabbeigi and M. Tsapatsis, *Ind. Eng. Chem. Res.*, 2012, **51**, 5364–5366.
- 19 J. Li, D. J. Ding, L. Deng, Q. X. Guo and Y. Fu, *ChemSusChem*, 2012, **5**, 1313–1318.
- 20 C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rivalier, P. Ros and G. Avignon, *Appl. Catal., A*, 1996, **145**, 211–224.
- 21 H. Ren, Y. Zhou and L. Liu, *Bioresour. Technol.*, 2013, **129**, 616–619.
- 22 Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982–985.
- 23 X. Tong, Y. Ma and Y. Li, *Appl. Catal., A*, 2010, **385**, 1–13.
- 24 P. Hoang Tran, *ChemSusChem*, 2022, **15**, e202200220.
- 25 H. B. Phan, Q. B. T. Nguyen, C. M. Luong, K. N. Tran and P. H. Tran, *Mol. Catal.*, 2021, **503**, 111428.
- 26 X. Zhang, X. Zhang, N. Sun, S. Wang, X. Wang and Z. Jiang, *Renewable Energy*, 2019, **141**, 802–813.
- 27 M. Grasmann and G. Laurenczy, *Energy Environ. Sci.*, 2012, **5**, 8171–8181.
- 28 W. Supronowicz, I. Ignatyev, G. Lolli, A. Wolf, L. Zhao and L. Mleczko, *Green Chem.*, 2015, **17**, 2904–2911.
- 29 R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sádaba and M. L. Granados, *Energy Environ. Sci.*, 2016, **9**, 1144–1189.
- 30 M. Mascal and S. Dutta, *Green Chem.*, 2011, **13**, 40–41.
- 31 J. Zhang, S. Wu, B. Li and H. Zhang, *ChemCatChem*, 2012, **4**, 1230–1237.
- 32 S. Van de Vyver, J. Thomas, J. Geboers, S. Keyzer, M. Smet, W. Dehaen, P. A. Jacobs and B. F. Sels, *Energy Environ. Sci.*, 2011, **4**, 3601–3610.
- 33 H. Anggorowati, S. Jamilatun, R. B. Cahyono and A. Budiman, 2018.
- 34 B. Girisuta, L. Janssen and H. Heeres, *Ind. Eng. Chem. Res.*, 2007, **46**, 1696–1708.
- 35 J. C. Serrano-Ruiz, D. J. Braden, R. M. West and J. A. Dumesic, *Appl. Catal., B*, 2010, **100**, 184–189.
- 36 C. Chang, M. Xiaojian and C. Peilin, *Chin. J. Chem. Eng.*, 2006, **14**, 708–712.
- 37 V. Tarabanko, M. Y. Chernyak, S. Aralova and B. Kuznetsov, *React. Kinet. Catal. Lett.*, 2002, **75**, 117–126.
- 38 C.-H. Kuo, A. S. Poyraz, L. Jin, Y. Meng, L. Pahalagedara, S.-Y. Chen, D. A. Kriz, C. Guild, A. Gudz and S. L. Suib, *Green Chem.*, 2014, **16**, 785–791.
- 39 F. Chambon, F. Rataboul, C. Pinel, A. Cabiac, E. Guillon and N. Essayem, *Appl. Catal., B*, 2011, **105**, 171–181.
- 40 R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974–4975.
- 41 M. Kitano, D. Yamaguchi, S. Suganuma, K. Nakajima, H. Kato, S. Hayashi and M. Hara, *Langmuir*, 2009, **25**, 5068–5075.
- 42 A. Onda, T. Ochi and K. Yanagisawa, *Green Chem.*, 2008, **10**, 1033–1037.
- 43 J. Pang, A. Wang, M. Zheng and T. Zhang, *Chem. Commun.*, 2010, **46**, 6935–6937.
- 44 M. Hara, T. Yoshida, A. Takagaki, T. Takata, J. N. Kondo, S. Hayashi and K. Domen, *Angew. Chem.*, 2004, **116**, 3015–3018.
- 45 P. H. Tran, V. H. Huynh, P. E. Hansen, D. K. N. Chau and T. N. Le, *Asian J. Org. Chem.*, 2015, **4**, 482–486.
- 46 A. Onda, T. Ochi and K. Yanagisawa, *Top. Catal.*, 2009, **52**, 801–807.
- 47 H. Guo, X. Qi, L. Li and R. L. Smith Jr, *Bioresour. Technol.*, 2012, **116**, 355–359.
- 48 S. Suganuma, K. Nakajima, M. Kitano, S. Hayashi and M. Hara, *ChemSusChem*, 2012, **5**, 1841–1846.
- 49 L. Gan, J. Zhu and L. Lv, *Cellulose*, 2017, **24**, 5327–5339.
- 50 J. H. Jordan, M. W. Easson and B. D. Condon, *RSC Adv.*, 2020, **10**, 39413–39424.
- 51 S. Suzuki, Y. Takeoka, M. Rikukawa and M. Yoshizawa-Fujita, *RSC Adv.*, 2018, **8**, 14623–14632.
- 52 I. A. Ignatyev, C. V. Doorslaer, P. G. Mertens, K. Binnemans and D. E. d. Vos, *Holzforchung*, 2012, **66**, 417–425.



- 53 B. Kosan, C. Michels and F. Meister, *Cellulose*, 2008, **15**, 59–66.
- 54 O. M. Gazit and A. Katz, *ChemSusChem*, 2012, **5**, 1542–1548.
- 55 M. Nahavandi, T. Kasanneni, Z. S. Yuan, C. C. Xu and S. Rohani, *ACS Sustainable Chem. Eng.*, 2019, **7**, 11970–11984.
- 56 Z. Qi, Q. Wang, C. Liang, J. Yue, S. Liu, S. Ma, X. Wang, Z. Wang, Z. Li and W. Qi, *Ind. Eng. Chem. Res.*, 2020, **59**, 17046–17056.
- 57 R. Ormsby, J. R. Kastner and J. Miller, *Catal. Today*, 2012, **190**, 89–97.
- 58 H. Xiao, Y. Guo, X. Liang and C. Qi, *J. Solid State Chem.*, 2010, **183**, 1721–1725.
- 59 J. Wang, W. Xu, J. Ren, X. Liu, G. Lu and Y. Wang, *Green Chem.*, 2011, **13**, 2678–2681.
- 60 A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, *J. Am. Chem. Soc.*, 2004, **126**, 9142–9147.
- 61 M. Sevilla and A. B. Fuertes, *Carbon*, 2009, **47**, 2281–2289.
- 62 I. F. Nata, C. Irawan, P. Mardina and C.-K. Lee, *J. Solid State Chem.*, 2015, **230**, 163–168.
- 63 X.-Y. Liu, M. Huang, H.-L. Ma, Z.-Q. Zhang, J.-M. Gao, Y.-L. Zhu, X.-J. Han and X.-Y. Guo, *Molecules*, 2010, **15**, 7188–7196.
- 64 R. O. Almeida, A. Moreira, D. Moreira, M. E. Pina, M. G. Carvalho, M. G. Rasteiro and J. A. Gamelas, *RSC Adv.*, 2022, **12**, 3979–3989.
- 65 Y.-L. Chen, X. Zhang, T.-T. You and F. Xu, *Cellulose*, 2019, **26**, 205–213.
- 66 F. Tao, H. Song and L. Chou, *ChemSusChem*, 2010, **3**, 1298–1303.
- 67 Y. Shen, J.-K. Sun, Y.-X. Yi, B. Wang, F. Xu and R.-C. Sun, *Bioresour. Technol.*, 2015, **192**, 812–816.
- 68 F. Cao, T. J. Schwartz, D. J. McClelland, S. H. Krishna, J. A. Dumesic and G. W. Huber, *Energy Environ. Sci.*, 2015, **8**, 1808–1815.
- 69 S. H. Krishna, T. W. Walker, J. A. Dumesic and G. W. Huber, *ChemSusChem*, 2017, **10**, 129–138.

