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Qing Qing
qqing@cczu.edu.cn
Changzhou University
Qidi Zhu
Changzhou University
Siyu Yi
Changzhou University
Mingyuan Gao
Changzhou University
Zhaotian Ji
Changzhou University
Shijun Lv
Changzhou University
Liqun Wang
Changzhou University
Jie Zhu
Changzhou University

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Catalytic dehydration of fructose to 5-HMF by a lignin-derived carbon solid acid catalyst modified by non-thermal plasma

Qing Qing*•Qidi Zhu• Siyu Yi• Mingyuan Gao• Zhaotian Ji• Shijun Lv • Liqun Wang • Jie Zhu

School of Biological and Food Engineering

Changzhou University

Changzhou 213164, Jiangsu, China

Corresponding to: Qing Qing, Telephone +86-519-86332327

Email: qqing@cczu.edu.cn

Abstract

Hydroxymethylfurfural (5-HMF) as a critical biomass-derived platform chemical shows significant potential for synthesizing diverse value-added products. However, conventional 5-HMF preparation methods often suffer from inherent drawbacks including high energy demand, environmental pollution, and high cost. A solid acid catalyst (LDSA-COOH) was prepared using solvent-extracted lignin as the carbon support and modified by non-thermal plasma grafting in an acrylic acid atmosphere. The structure and properties of the catalyst were comprehensively analyzed by various spectroscopies (FTIR, XPS) and SEM microscopy, and the porosity structure was detected by BET method. The catalytic performance of LDSA-COOH was systematically assessed through measurements of acidic group density and dehydration of fructose to 5-HMF. In a DMSO/water biphasic solvent system, high fructose conversion of 99.2% and 5-HMF yield of 85.7% was obtained at 180 ℃ and 30 min by LDSA-COOH. Notably, the LDSA-COOH catalyst also demonstrated excellent stability and reusability through five consecutive reuse cycles. This method offers advantages including shorter solid acid preparation time, lower energy consumption, lower environmental pollution, and higher catalytic stability, providing a promising strategy for the preparation of solid acid catalyst.

Key words: lignin; solid acid; non-thermal plasma grafting; acrylic acid; 5-HMF

1. Introduction

As a renewable and versatile aldehyde compound derived from biomass that can be further upgraded into biofuels, high-value chemicals and biomaterials, 5-hydroxymethylfurfural (5-HMF) boasts outstanding chemical properties and diverse applications, solidifying its status as a core platform molecule for sustainable organic synthesis. The main routes to produce 5-HMF include direct dehydration of fructose or catalytic conversion of glucose and cellulose, which are all typical acid-catalyzed reactions[1]. Various homogeneous and heterogenous acid catalysts have been widely investigated in these catalytic reactions[2]. Homogeneous catalysts, especially traditional mineral acids (e.g., H_2SO_4, HCl, and H_3PO_4), exhibit high catalytic activity. Compared to these catalysts, heterogeneous acid catalysts, such as ion-exchange resins, heteropolyacids, sulfonated metal oxides, niobium-based catalysts, and zeolite solid acids, have significant merits of recyclability, low equipment corrosion, and low environmental pollution[3]. Currently, the industrial-scale production of HMF is still hindered by the common challenges of existing catalytic systems, including irreversible catalyst deactivation, serious coke formation, complicated catalyst recovery and product separation processes, and unsatisfactory economic benefits[4]. Against this background, biomass-derived solid acid catalysts have become a research hotspot due to their low cost, renewable raw materials, simple preparation process, and tunable acidic sites[5].

Lignin is a natural polymer coexisting with cellulose and hemicellulose in plant cell walls, composed of phenylpropane units linked by ether bonds and carbon-carbon

74 bonds. Its global annual biosynthesis volume is approximately 50 billion tons, making
75 it one of the most abundant aromatic carbon sources in nature[6]. However, lignin is
76 currently underutilized, only about 2% undergoes high-value conversion. Therefore,
77 lignin-derived carbon materials fabricated by carbonization are not only cost-effective
78 but also possess abundant, regulable pore structures and large specific surface areas,
79 making them ideal candidates for catalyst supports[7]. In addition, lignin's native
80 chemical composition endows the material with easy modifiability through acid-base
81 treatment and redox reactions to regulate its surface acidity and basicity. Grafting active
82 sites onto the porous lignin-based carbon is a commonly used method to induce the
83 desired functionality[8]. For instance, sulfonated carbon catalysts with the active sites of
84 $–SO_3H$ acid groups have been widely reported. Deng et al. prepared a proton-exchanged
85 lignin-based carbon solid acid from sodium lignosulfonate for catalytic production of
86 5-HMF from fructose[9]. Wang et al. synthesized a lignin-derived mesoporous carbon
87 solid acid catalyst by high temperature carbonization and subsequent sulfonation
88 treatment using alkali lignin as the carbon source and KCl as a salt template. The
89 prepared catalyst was applied to the catalytic dehydration of glucose to 5-HMF, and the
90 5-HMF yield of 57.8% can be obtained in dimethyl sulfoxide (DMSO)[10]. Although
91 these catalysts possess high catalytic activity, a considerable amount of hazardous
92 sulfonation chemicals, such as sulfuric acid or fuming sulfuric acid, are required for the
93 sulfonation processes. Moreover, rigorous reaction conditions including high pressure,
94 high temperature, and long reaction duration, are also mandatory. Consequently, the

development of efficient and environmentally friendly approaches to prepare and modify lignin-based solid acid catalyst is of great necessity.

In recent years, as an efficient material preparation technique, plasma technology has demonstrated unique advantages in the field of solid acid preparation due to its strong interaction between high-energy active particles (e.g., electrons, ions, free radicals) and material surfaces[11]. Interactions between plasma and the surface of solid substrates (e.g., metal oxides, carbon materials, molecular sieves) can etch surface impurities and introduce oxygen- or sulfur-containing functional groups (e.g., -OH, -COOH, -SO_3H), directly endowing materials with acidity[12]. Conventional thermal treatment modification easily causes severe lignin carbonization, excessive condensation of aromatic rings, uncontrolled deep depolymerization and generation of inert coke byproducts. By contrast, low-temperature non-thermal plasma (NTP) only cleaves partial weak ether linkages (β-O-4) on lignin surface and introduces oxygen-containing acidic groups (–COOH, phenolic –OH) via oxidative radicals, without destroying the bulk skeleton or inducing thermal degradation of the lignin carrier. Compared to traditional methods, plasma modification of solid acid exhibits the characteristics of low temperature, energy-saving, environmentally-friendly, and precise regulation of the acidity by adjusting plasma parameters, such as power, pressure, or gas type[13]. However, challenges still remain in the stability and cost of industrial-scale plasma equipment and long-term stability and recyclability of the solid acid in terms desorption of acid groups[11].

In this study, low-temperature non-thermal plasma (NTP) technology was

employed to prepare a lignin-derived carbon-based solid acid catalyst (LDSA-COOH) via acrylic acid carboxylation in plasma atmosphere. Acrylic acid was chosen as the grafting monomer for NTP modification mainly owing to its reactive vinyl double bond susceptible to plasma radical activation and inherent carboxylic acid group for Brønsted acid site construction. Multiple characterization techniques, including Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), porosity determinations (BET), microscopy observation (SEM) were used to analyze the structure and catalytic sites of the solid acid catalyst. The catalytic performance of the catalyst for dehydration of fructose into 5-HMF was systematically investigated. Additionally, the catalytic properties of LDSA-COOH was compared with the sulfonated solid acid (LDSA-SO_3H)[14] prepared by plasma grafting modification. The method proposed in this study avoided the use of toxic chemicals, addressing the limitations of traditional sulfonation methods for lignin-based catalyst preparation and proposing a low-temperature, environmentally friendly alternative.

2. Materials and methods

2.1 Materials and chemicals

Corn stover (CS) used for lignin extraction was obtained from a farm nearby Changzhou, Jiangsu Province, China. CS was washed and ground to smaller than 40 mesh. Dimethyl sulfoxide (DMSO), acetone (AC), methyl isobutyl ketone (MIBK), γ-valerolactone (GVL) were purchased from Lingfeng Chemical Reagent Co., Ltd, Shanghai, China. Fructose, glucose, α-cellulose, acrylic acid, and sulfuric acid were purchased from Sinopharm Chemical Reagent Co., Ltd. Analytical standards, including

5-HMF, formic acid (FA), and levulinic acid (LA), were from Aladdin Biochemical Technology Co., Ltd. All reagents were of analytical grade (AR, ≥99.0% purity).

2.2 Carbonization of lignin

Lignin extracted by organic solvent method (see online supplementary material) was dried and then ground into powder. Then the lignin powder was carbonized in a porcelain boat by a muffle furnace operated at 300 ℃ for 4 h to get lignin-based activated carbon (LC). LC was washed with deionized water by vacuum filtration and dried to constant weight at 60 °C.

2.3 Preparation of solid catalyst by non-thermal plasma grafting modification

Non-thermal plasma grafting method was used to prepare the solid catalyst conduct in a discharge reactor (see online materials Fig. S1 for the diagram of the device). LC was evenly placed on a sample dish in the vacuum chamber of the instrument and O_2 was used as the gas source to introduce the free radicals to form active sites on the LC surface. The non-thermal plasma discharge treatment was firstly carried under the discharge power of 160 W, vacuum pressure of 20 Pa, and treatment time of 3 min, which is conducive to the intervention of subsequent acidic groups. In a typical modification process (optimized conditions), acrylic acid with the concentration of 60% was used as the gas source and vacuumed into the cavity. Then adjust the discharge power to 170 W and vacuum pressure to 40 Pa. Measured gas outlet temperature was 23–29 ℃. The processing time was 6 min for the carboxylation grafting process and the modification step was repeated for three times to produce acrylic acid modified lignin derived solid acid catalyst (LDSA-COOH). The effects of

acrylic acid concentrations (40%, 60%, 80%, 100%) and treatment durations (2 min, 4 min, 6 min, 8 min) on the catalytic performance of LDSA-COOH were investigated in the optimization experiments.

2.4 Characterization of LDSA-COOH catalysts

The surface morphological and structural characteristics of the solvent extracted lignin, LC, and LDSA-COOH were observed and compared by a scanning electron microscope (SEM, SUPRA-55, Zeiss, Germany) operating at 15 kV. The Fourier transform infrared spectrometer (IS50, Thermo Fisher, USA) was used to identify the change of the functional groups within 500-4000 cm^{-1} with a resolution of 4 cm^{-1}. N_2 adsorption-desorption isotherm measurements were operated by a physical adsorption analyzer (TriStar 3020, Micromeritics, USA). The distribution of pore sizes was analyzed by the BJH model, and the SSA and pore volume of different samples were determined by the BET method. The XPS spectra were measured by ESCALAB 250Xi spectrometer (Thermo Fisher, USA) using Al Kα radiation was employed to identify the chemical bond and state of the elements on the catalyst surface in the energy range of 0-600 eV.

2.5 Determination of the acidity of different samples

The total acidity and –COOH acidic groups of the catalyst were measured by the method reported in the literatures[15]. 0.1 g catalyst was added to 20 mL NaOH (0.01 mol/L) solution and sonicated for 1 h. Then the suspension was filtered to separate the liquid. The filtrate was titrated with 0.01 mol/L HCl aqueous solution to determine the content of the total acidity. 20 mL 0.01 mol/L $NaHCO_3$ solution and the same amount

of catalyst was used for the measurement of –COOH content. The mixture was sonicated for 60 min and then titrated with 0.01 mol/L HCl solution to determine the total content of –COOH.

2.6 Dehydration of fructose to 5-HMF by LDSA-COOH catalyzed reaction

Fructose, LDSA-COOH, and 30 mL of the reaction solvent were added to a 100 mL high-pressure and high-temperature reactor according to different substrate to catalyst ratios. The reaction solvent was composed by organic solvent and water in different volume ratio. The mixture was heated to the target temperature via the jacket heating system and reacted with a stirring speed of 300 r/min. When the reaction was finished, the reactor was rapidly quenched to room temperature in an iced-water bath. Subsequently, the solid catalyst was separated from the reaction medium by vacuum filtration, then washed by D.I. water for 5 cycles. In each washing cycle, D.I. water was added at a liquid-solid mass ratio of 20:1 (water: catalyst). After vacuum filtration, the recycled catalyst was transferred to an oven and dried at 45 °C for 12 h under ambient pressure to remove residual water before further use. The catalytic reaction products generated in the reaction solution were quantified by high-performance liquid chromatography (HPLC) following the method described below.

2.7 Analysis of the products in reaction liquid

The concentration of 5-HMF was analyzed by Agilent HPLC (model 1260, USA) equipped with a C18 column (Waters, USA) and a variable wavelength detector. Methanol solution (20%) was used as the mobile phase with the flow rate of 0.6 mL/min. The column temperature was set to 30 ℃. The concentrations of reaction substrate and

degradation products, such as fructose, FA, and LA, were determined by Waters 2595 HPLC (Waters, USA) equipped with an HPX-87H column (Bio-Rad, USA) and refractive index detector. The mobile phase was 5 mM H_2SO_4 solution at a flow rate of 0.6 mL/min. The column was set to 65 ℃. The related reaction indices were calculated as following:

$$\text{Fructose conversion (\%)}=\frac{\text{Moles of fructose reacted}}{\text{Moles of fructose added}}\times 100\ \%$$

$$\text{5-HMF yield (\%)}=\frac{\text{Moles of 5-HMF generated}}{\text{Moles of fructose added}}\times 100\ \%$$

$$\text{5-HMF selectivity (\%)}=\frac{\text{Moles of 5-HMF generated}}{\text{Moles of fructose reacted}}\times 100\ \%$$

3. Results and discussion

3.1 Optimization of the plasma preparation conditions for LDSA-COOH

The catalytic performance of the LDSA-COOH was directly impacted by the grafting of acrylic acid catalytic sites on the LC[16]. Therefore, this study firstly optimized the preparation conditions of the solid acid by adjusting the acrylic acid concentration and NTP treatment time under the same conditions (170 W RF power and 40 Pa vacuum pressure). Subsequently, the catalytic performances of the solid acid obtained under different conditions were evaluated by using fructose as the reaction substrate for production of 5-HMF. As shown in Fig.1, the catalytic performance of the LDSA-COOH varied with the increase of acrylic acid concentration or the extension of treatment duration. When the acrylic acid concentration was 40% or 60%, the 5-HMF yield increased significantly with the extension of the solid acid grafting treatment time. When the acrylic acid concentration used for NTP grafting was 60% and the treatment

time was 6 min, the 5-HMF yield reached 74.6%, with the fructose conversion and reaction selectivity of 98.3% and 75.9%, indicating a satisfactory catalytic performance. When the acrylic acid concentration was further increased to 80% or 100%, the maximum 5-HMF yield slightly decreased to 72.6% and 69.6%, respectively, and the optimal treatment time shortened from 6 min to 4 min. Additionally, when the acrylic acid concentration was 100%, the 5-HMF yield kept relatively stable with the extension of the treatment duration. This may be due to the decrease of grafting modification effect caused by the high concentration of acrylic acid under the same radio frequency power, resulting in the active group (-COOH) failing to be fully grafted on the carbon solid carrier.

To verify the impacts of acrylic acid concentration and treatment duration on the grafting of acidic groups onto the carbon skeleton, the acidity of the solid catalysts prepared under different conditions were determined and compared in Table 1. It could be inferred that the total acidity of the LC carrier was only 0.15 mmol/g and that of the LDSA-COOH (60% acrylic acid) surged to 0.79 mmol/g. The -COOH groups grafted onto the LC was probably 0.71 mmol/g. In the meanwhile, the total acidity and the -COOH content of the catalysts prepared with different acrylic acid concentrations were also illustrated in Table 1. The measured acid strength of the solid acid catalysts correlated with their catalytic performance demonstrated in the catalytic reactions as shown in Fig 1. In general, catalysts with more acidic sites deliver superior catalytic performance. Higher -COOH density correlates with increased 5-HMF yield, supporting the role of acidic sites in dehydration kinetics[17].

3.2 Characterization of LDSA-COOH

The morphological and structural changes of the extracted lignin, LC, and LDSA-COOH were characterized by scanning electron microscopy (SEM), as shown in Fig 2a-2c. Extracted lignin exhibited porous agglomerates with loose, irregular surfaces (Fig. 2a). Carbonization induced significant structural transformation, thus the LC sample displayed relatively smooth but irregular granules or flakes (Fig. 2b), attributing to volatile substance release during the carbonization process[18]. After NTP modification, LDSA-COOH (Fig. 2c) developed roughened surfaces with small particulate adhered, which might be resulting from plasma etching effects[19].

Fig. 2d presented the FTIR spectra of the extracted lignin, LC, and LDSA-COOH. The characteristic peaks of LDSA-COOH observed at the wavenumber of 1177 cm^{-1}, 1699 cm^{-1}, and 3400 cm^{-1} were correspond to C-O stretching, C=O stretching, and O-H stretching vibrations, respectively, indicating abundant carboxyl (-COOH) and hydroxyl (-OH) groups on the surface[2, 12]. Compared to the spectrum of the LC sample, C=C stretching vibrations at 1631 cm^{-1} exhibited significant enhancement after NTP modification, while a new peak emerged at the wavenumber of 1430 cm^{-1} could be attributed to $-CH_2-$ bending vibrations. This spectroscopic evidence confirmed the introducing of -COOH and -OH groups through acrylic acid grafting modification[20]. Additionally, the disappearance of absorption peaks at 2924 cm^{-1} and 1221 cm^{-1} in the carbonized lignin was presumably attributed to the cleavage of C-O-C linkages and C-H bonds during high-temperature carbonization[21].

The XPS spectra of LC and LDSA-COOH shown in Fig. 2e further confirmed the

chemical composition and chemical bond state of the catalyst after NTP modification. As shown in Fig. 2e, both LC and LDSA-COOH exhibited two characteristic signals at 284.2 eV and 532.2 eV, which were corresponding to C1s and O1s, respectively[22]. The C1s spectrum could be deconvoluted into three component peaks at 284.2 eV (C–C), 286.0 eV (C–O), and 288.1 eV (C=O). Meanwhile, the O1s spectrum showed two signals at 530.6 eV (C=O) and 532.3 eV (C–O), demonstrating spectral consistency with FTIR results discussed above. The significantly enhanced O1s intensity in LDSA-COOH compared to LC was attributable to the incorporation of abundant oxygen-containing functional groups, such as -COOH and -OH[23].

Table 2 summarized the BET results of the extracted lignin, LC, and LDSA-COOH. Higher BET surface area was obtained after carbonization of the extracted lignin, which was beneficial to the introduction of high density active -COOH centers on the carbonaceous material[24]. Compared to LC, LDSA-COOH possessed enlarged pore size and pore volume, while its specific surface area decreased from 15.58 m^2/g to 9.97 m^2/g. These structural alterations suggested structural reconstruction via plasma etching during NTP modification[25]. Collectively, the SEM and BET results indicated plasma etching enlarged pores volume but reduced surface area, which may enhance the mass transfer for fructose access to acidic sites.

3.3 Catalytic performance of LDSA-COOH

3.3.1 Effect of reaction solvent

Besides catalysts with suitable acidic sites, the reaction solvent is also a crucial factor influencing catalytic performance of LDSA-COOH. Herein, commonly used

293 organic solvents were compared for the catalytic degradation reaction of fructose to 5-
294 HMF[26]. As demonstrated in the Fig.3, both the solvent type and the volume ratio of
295 H_2O and solvent have been found to significantly alter fructose conversion, reaction
296 selectivity, and 5-HMF yield. In contrast, about 35.1% of the fructose remained
297 unreacted when water was used as the reaction solvent, and the 5-HMF yield and
298 reaction selectivity were only 20.4% and 31.4%, respectively, revealing the inherent
299 instability of 5-HMF under acidic conditions. LDSA-COOH exhibited substantially
300 higher catalytic activity in DMSO than in other solvents. The 5-HMF yield and reaction
301 selectivity reached 69.7% and 72.9% respectively in DMSO, which can be attributed to
302 differences in proton transfer capabilities among the organic solvents evaluated[27].
303 DMSO was found to have greater capacity to inhibit the rehydration of 5-HMF into
304 byproducts, such as formic acid and levulinic acid, by interacting with the water
305 molecules. The high dielectric constant of DMSO was found to facilitate proton transfer
306 and stabilize 5-HMF[27]. Consequently, the water-to-solvent ratio was also found to exert
307 a pronounced influence on the product distribution of fructose degradation reaction[28].
308 Maximum 5-HMF yield was achieved at a H_2O: DMSO volume ratio of 1:6. In this
309 solvent system, fructose conversion, 5-HMF yield, and reaction selectivity reached
310 98.3%, 74.6%, and 75.9% respectively. However, further increasing the DMSO
311 proportion led to decreases in both 5-HMF yield and reaction selectivity. Similar trends
312 were observed in other biphasic systems composed of organic solvents and water. This
313 phenomenon might result from reduced aqueous phase decreasing the hydrogen
314 bonding interactions between fructose and solvent, thereby diminishing the reaction

315 rate[29].

316 3.3.2 Effect of substrate and catalyst loading

317 Fig.4 discussed the impacts of substrate loading and catalyst dosage on the
318 catalytic dehydration of fructose. As revealed in Fig 4, fructose conversion exceeded
319 95% under all conditions. With fructose loading increasing from 0.5 g to 1.5 g, both 5-
320 HMF yield and reaction selectivity exhibited an initial increase followed by a decline.
321 When the fructose loading was 0.5-1.5 g, 5-HMF yield rose with higher catalyst dosage,
322 peaking at 0.3 g catalyst with yields of 62.9%, 73.5%, and 75.7%, and corresponding
323 selectivity were 64.8%, 74.8%, and 76.8%. Catalyst loading beyond 0.3 g led to a 10%
324 reaction selectivity drop, suggesting site saturation promoted humin formation via
325 fructose-5-HMF condensation[30]. Further increasing catalyst loading to 0.5 g maintained
326 similar fructose conversion but reduced 5-HMF yield and rection selectivity. In contrast,
327 at 3.0 g fructose loading, 5-HMF yield consistently improved from 51.5% to 69.5%
328 with escalating catalyst dosages. This demonstrated that moderate catalyst
329 augmentation (≤0.3 g) enhanced 5-HMF production, whereas excess catalyst (>0.3 g)
330 might accelerate side reactions by offering excessive protons. Additionally, elevating
331 fructose loading to 3.0 g reduced both 5-HMF yield and reaction selectivity, attributable
332 to humin formation via condensation between surplus fructose and 5-HMF or
333 byproducts[30].

334 3.3.3 Effects of reaction temperature and time

335 As illustrated in Figure 5, fructose conversion increased with reaction time for all
336 evaluated temperatures, whereas 5-HMF yield and reaction selectivity exhibited initial

increases followed by declines. The optimal reaction time corresponding to the maximum 5-HMF yield varied distinctly with reaction temperature. The observed reduction in 5-HMF yield beyond optimal reaction time was plausibly attributed to the further degradation of generated 5-HMF into levulinic acid (LA) and formic acid (FA). Notably, at 180 ℃, the maximum 5-HMF yield (85.7%) and selectivity (86.4%) were achieved at 30 min, which were slightly higher than those obtained at 160 ℃ and 170 ℃. By contrast, when the reaction temperature was 190 ℃, severe reaction conditions tended to facilitate a series of undesired secondary reactions[31]. High-temperature reaction conditions can accelerate 5-HMF rehydration, intermolecular condensation, and humin polymerization, which collectively consume the target product and lead to a reduced 5-HMF yield. In addition, among all tested reaction temperatures, LA concentration variation remained negligible for all temperatures evaluated, whereas FA accumulation was gradually accelerated with the increase of reaction temperature and reaction time.

3.4 Recyclability and reusability of LDSA-COOH

Catalyst recyclability is another crucial aspect for evaluating the catalytic performance and industrial applicability of solid catalysts. In this study, LDSA-COOH was recovered and reused in five cycles of experiments. As shown in Fig. 6, after five consecutive catalytic cycles, minimal catalytic efficiency decrease was observed. Fructose conversion decreased from 99.0% to 95.5%, while reaction selectivity decreased from 86.1% to 75.7%, demonstrating considerable recyclability performance of LDSA-COOH. The 5-HMF yield reduction of 13.0% was noticed for the fifth

reaction cycle compared to the fresh catalyst, which could be ascribed to either depletion of –COOH active sites or catalytic site blockage due to byproduct deposition. After five cycles, SEM characterization showed minimal surface fouling (see online supplementary material), supporting the recycling stability of LDSA-COOH. The density of -COOH groups on the recycled LDSA-COOH (used five times) was 0.52 mmol/g measured by acid-base titration, showing 0.19 mmol/g deduction after five reuse cycles.

3.5 Catalytic performance comparison of LDSA-COOH and LDSA-SO_3H

Sulfonated carbon catalysts are widely investigated and exhibit superior catalytic performance for production of biobased chemicals. In our previous work, non-thermal plasma grafting of sulfur dioxide (SO_2) gas was applied to fabricate lignin-based sulfonic acid solid acid catalysts named as LDSA-SO_3H (see online supplementary materials). Nevertheless, the employment of toxic and corrosive SO_2 gas brings safety concerns and environmental pressure. Therefore, the current study selected weak acrylic acid as the plasma grafting monomer to develop a safer plasma modification strategy for biomass-derived solid acid construction. Fructose is the most efficient substrate for HMF synthesis via direct dehydration, while glucose and cellulose are more abundant, low-cost, and industrially renewable biomass resources. Therefore, the catalytic performances of LDSA-COOH and LDSA-SO_3H were compared with fructose, glucose, and cellulose as reaction substrates to evaluate the application potential of the two catalysts. As shown in Fig.7, both LDSA-COOH and LDSA-SO_3H exhibited favorable catalytic activity in fructose conversion with the same catalyst

loading, at the reaction temperature of 180 ℃ and reaction time of 30 min in the DMSO:H_2O (volume ratio was 6:1) solvent mixture. The 5-HMF yields were 85.0% and 88.1%, for LDSA-COOH and LDSA-SO_3H respectively. However, their catalytic performance diverged when glucose was used as the substrate. Glucose conversion and 5-HMF yield reached 77.5% and 49.1% using LDSA-SO_3H as the catalyst, but the LDSA-COOH were only 67.1% and 42.8%. The better glucose conversion efficiency of LDSA-SO_3H is presumably associated with the stronger acidity of the -SO_3H group, which is beneficial for promoting glucose isomerization[29]. When cellulose was used as the substrate, further decreases in both cellulose conversion and 5-HMF yield were observed for the two catalysts. This phenomenon may be attributed to the insufficient active acidic sites of the synthesized solid acids for efficient cellulose degradation and glucose isomerization, as well as the limited mass transfer efficiency in the solid–solid reaction system, which might impair the overall catalytic activity[29].

4. Conclusion

This study developed a weakly acidic carbon-based solid acid (LDSA-COOH) by grafting acrylic acid onto lignin-derived carbon carriers via NTP modification. The catalyst demonstrated excellent structural characteristics and favorable synergistic catalytic activity with DMSO-H_2O solvent in conversion of fructose to 5-HMF. Moreover, no discernible decrease in catalytic activity was observed after five recycles of LDSA-COOH use, indicating its good stability and reusability. Comparative analysis of LDSA-COOH and LDSA-SO_3H revealed comparable fructose conversion and 5-HMF yield when using fructose as the reaction substrate. The NTP modification process

provides a more efficiency method than previously reported solid catalyst preparation methods by reducing the preparation time and offering a scalable alternative for biomass valorization. Future studies could explore the scale-up challenges of the plasma modification method.

Data Availability

Data supporting the findings of this study are available from the corresponding author on reasonable request.

Abbreviations

5-HMF: 5-hydroxymethylfurfural

CS: corn stover

SEM: scanning electron microscopy

DMSO: dimethyl sulfoxide

AC: acetone

MIBK: methyl isobutyl ketone

GVL: γ-valerolactone

FA: formic acid

LA: levulinic acid

HPLC: high-performance liquid chromatography

NTP: non-thermal plasma

LDSA-COOH: lignin-derived carbon-based solid acid catalyst

FTIR: Fourier transform infrared spectroscopy

XPS: X-ray photoelectron spectroscopy

LC: lignin-based activated carbon

BET: Brunauer, Emmett and Teller method

BJH: Barrett-Joyner-Halenda method

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Author information

Authors and Affiliations

School of Biological and Food Engineering, Changzhou University, Changzhou 213164, Jiangsu, P. R. China

Qing Qing, Qidi Zhu, Siyu Yi, Mingyuan Gao, Zhaotian Ji, Shijun Lv, Liqun Wang, and Jie Zhu

Contributions

Q.Q.: Project administration, Funding acquisition, Writing – review & editing. Z.Q.: Investigation, Data analysis. Y.S.: Data curation. G.M.: Conceptualization. J.Z.: Writing-original draft. L.S.: Validation. L.W.: Writing-review & editing. Z.J.: Methodology.

Corresponding authors

Correspondence to Qing Qing.

Ethics declarations

Conflict of interest

The authors declare no competing interests.

Ethical Approval

There are no ethical approvals required for this work.

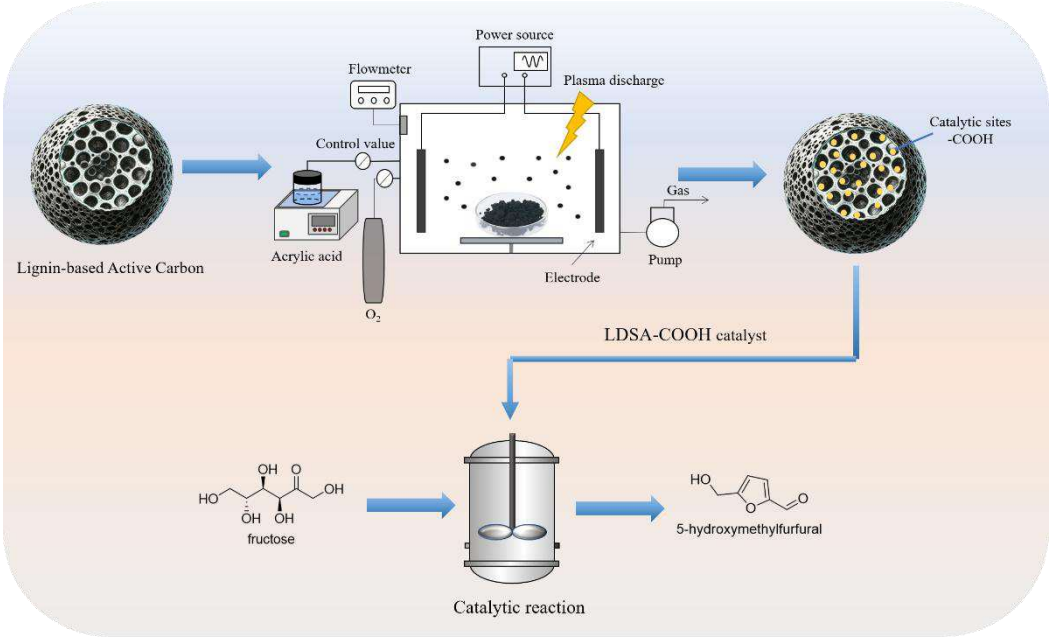
Consent to Participate

There are no ethical approvals required for this work.

Consent for Publication

All the authors are declaring their consent for this work to be published.

Graphic Abstract



592 Table 1. Acidity analysis of LDSA-COOH and LC

Sample	Acidity analysis, mmol/g	
	Total	-COOH
LC	0.15	0.07
LDSA-COOH-40%	0.54	0.48
LDSA-COOH-60%	0.79	0.71
LDSA-COOH-80%	0.74	0.65
LDSA-COOH-100%	0.64	0.54
LDSA-COOH-recycled	0.61	0.52

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595 Table 2. BET analysis results of extracted lignin, LC, and LDSA-COOH

Sample	Specific surface area, m^2/g	Pore size, nm	Pore volume, cm^3/g
Extracted lignin	4.45	6.80	0.008
LC	15.58	3.87	0.010
LDSA-COOH	9.97	5.66	0.011

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Figure Captions

Fig.1 Effects of different acrylic acid concentrations (40-100%) and NTP treatment time (2-8 min) on the catalytic performance of the solid acid

Fig. 2 The characterization results of lignin, LC and LDSA-COOH. SEM of solvent extracted lignin (a), LC (b), and LDSA-COOH (c). FTIR characterization (d) and XPS spectra (e~g).

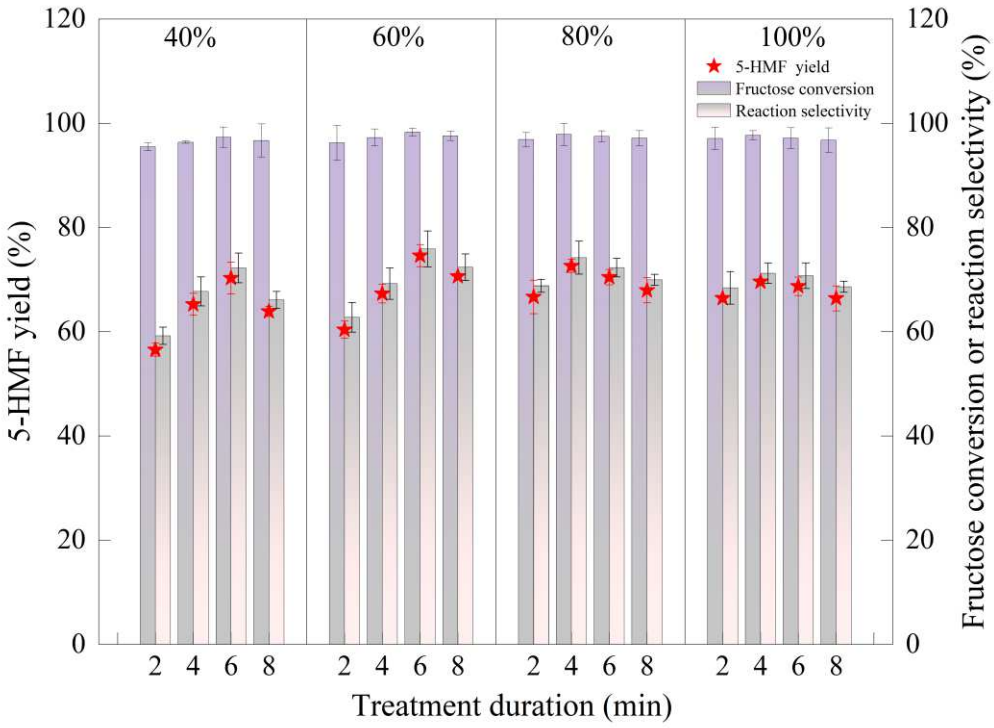
Fig.3 Effects of different solvent systems on the catalytic reaction. Reaction conditions: 1.0 g fructose, 0.3 g LDSA-COOH, 30 mL solvent mixture, reacted at 170 ℃ for 20 min.

Fig.4 Effects of fructose loading (0.5-3.0 g) and catalyst loading (0-0.5 g) on the catalytic reaction. Reaction conditions: 30 mL DMSO-H_2O mixture (6:1), reacted at 170 ℃ for 20 min.

Fig.5 Effects of reaction temperature (160-190℃) and time (10-100 min) on the catalytic reaction. Reaction conditions: 1.5 g fructose, 0.3 g LDSA-COOH, 30 mL DMSO-H_2O mixture (6:1).

Fig.6 Reusability of LDSA-COOH. Reaction conditions: 1.5 g fructose, 0.3 g LDSA-COOH, 30 mL DMSO-H_2O mixture (6:1), reacted at 180 ℃ for 30 min.

Fig.7 Comparison of catalytic performance over LDSA-COOH and LDSA-SO_3H catalysts for the conversion of glucose, fructose and cellulose to 5-HMF. Reaction conditions: 1.5 g fructose, 0.3 g LDSA-COOH or LDSA-SO_3H, 30 mL DMSO-H_2O mixture (6:1), reacted at 180 ℃ for 30 min.



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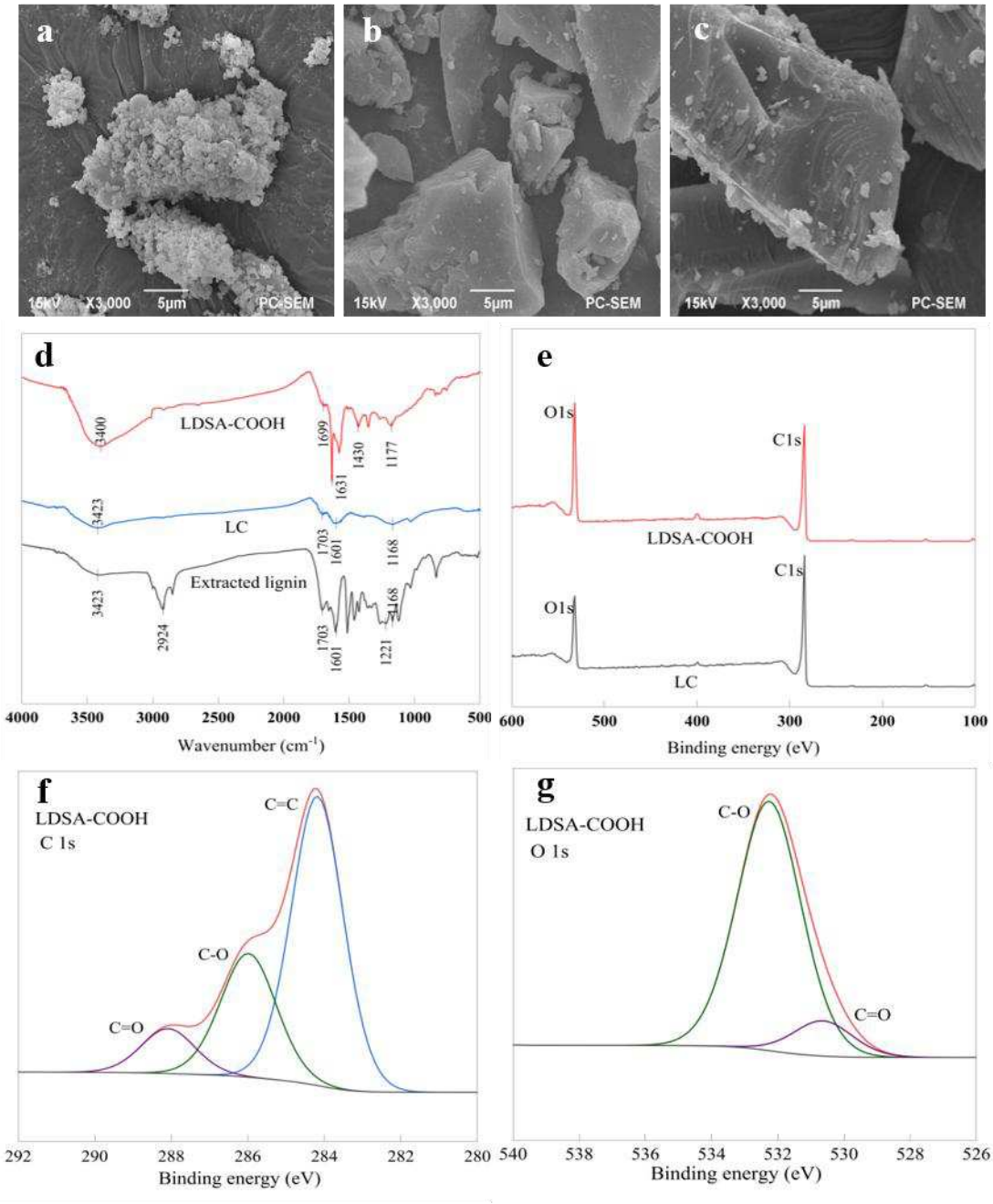
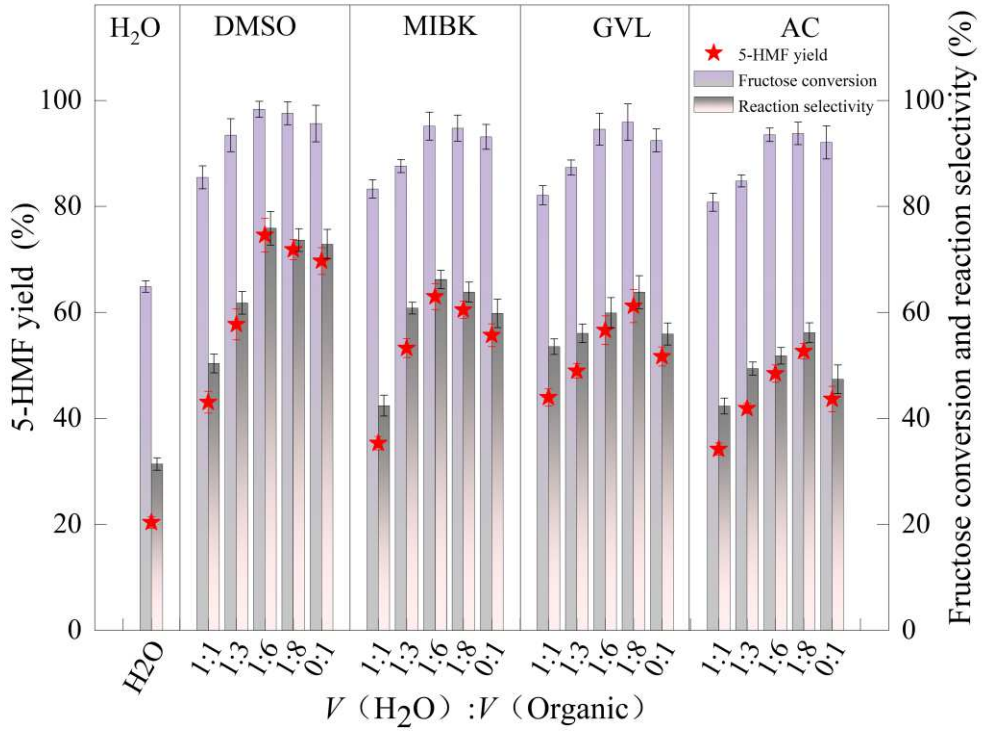


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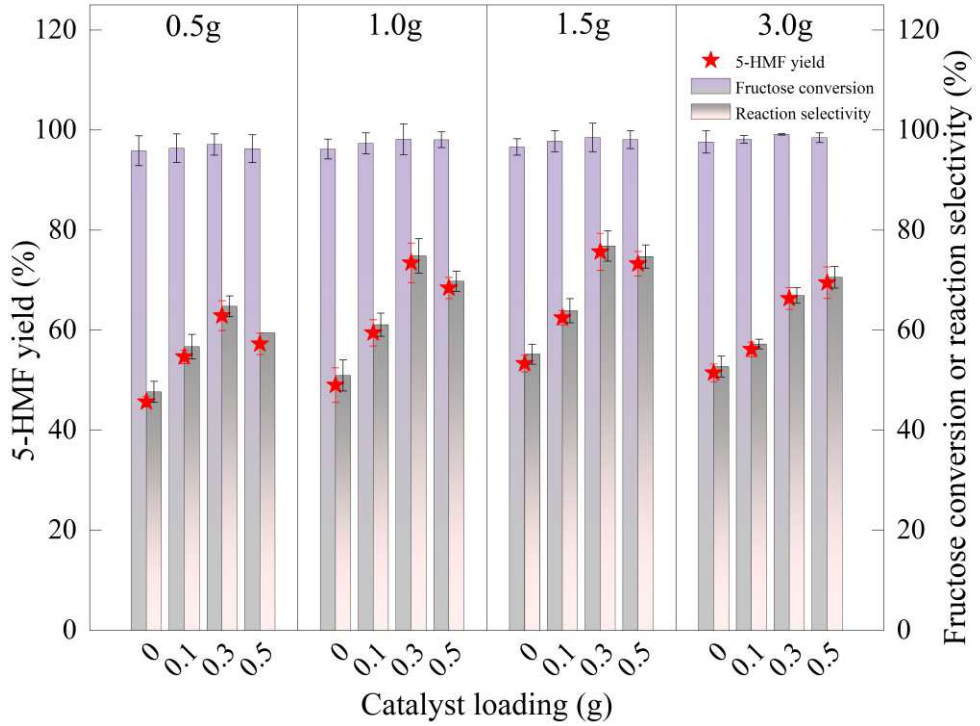
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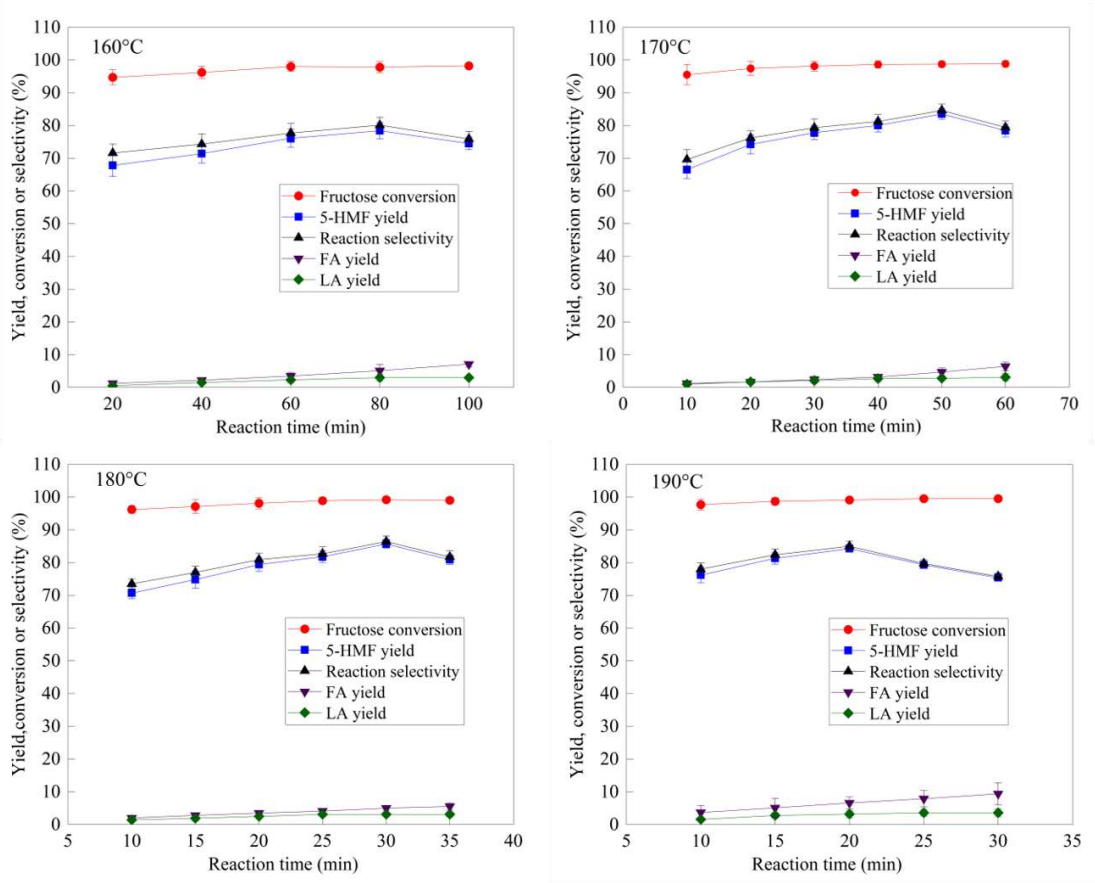


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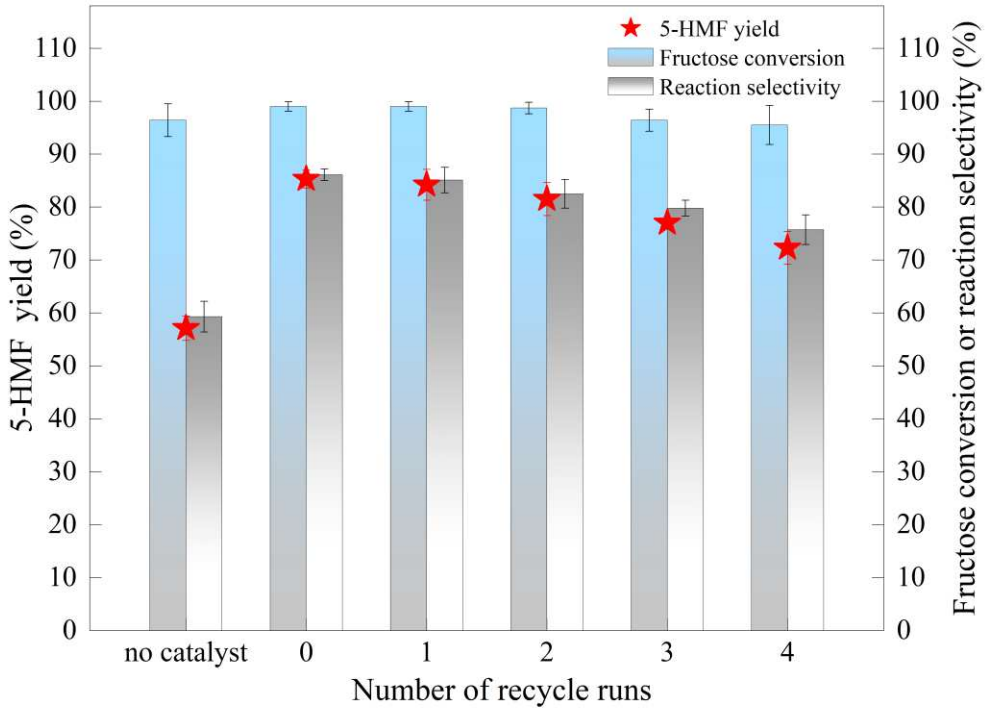
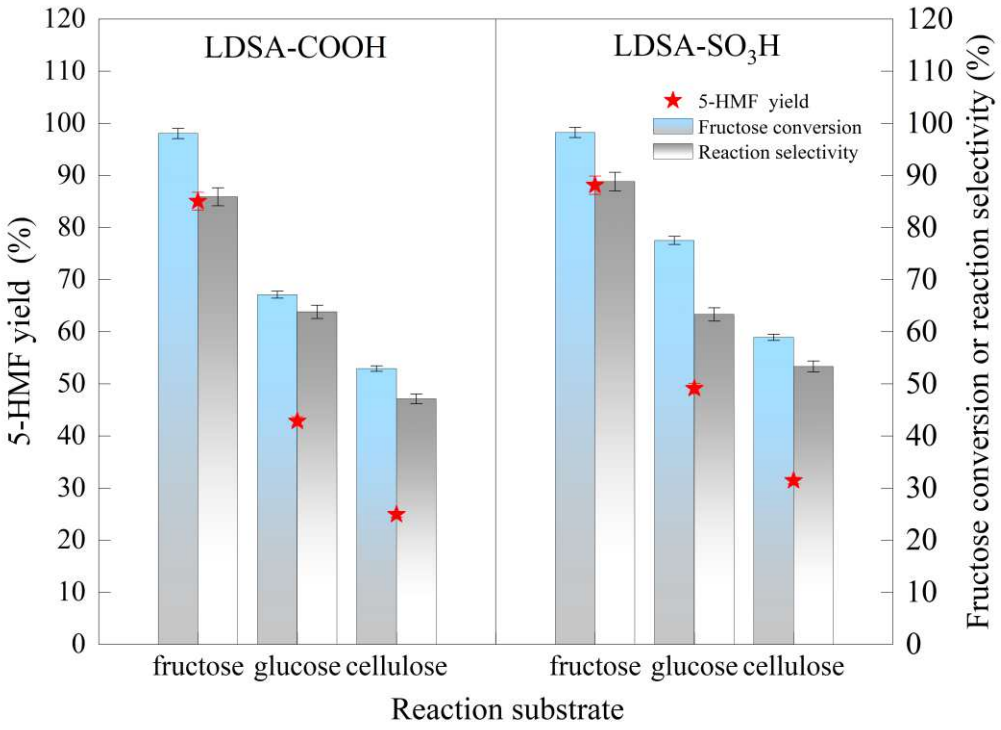


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668

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