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A sustainable cellulose-based solid acid catalyst for efficient 5-ethoxymethylfurfural production from biomass-derived HMF

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Abstract

The development of effective and sustainable catalysts for biomass conversion is essential for advancing green fuel technologies. In this work, a solid acid catalyst was prepared by immobilizing 4-(chloromethyl)benzoic acid onto cellulose through covalent bonding between the aryl chloride moieties and the hydroxyl groups of cellulose. The resulting material, designated as BA-cellulose, was thoroughly characterized via various techniques, confirming successful functionalization and high acid site density. The catalytic activity of BA-cellulose was assessed in the etherification of 5-hydroxymethylfurfural (HMF) with ethanol to yield 5-ethoxymethylfurfural (EMF), a promising renewable biofuel. Reaction factors such as catalyst loading, reaction temperature, and reaction time were optimized. The catalyst revealed high activity, selectivity, and excellent reusability over multiple cycles without significant loss of performance. The catalyst was also employed for the efficient production of EMF from renewable carbohydrate sources. It is worth to mention that this work aligns with the principles of green chemistry by utilizing a biodegradable support and minimizing hazardous waste. The developed system offers potential for scalable application in biomass valorization and biofuel production.

Keywords: Biomass; Etherification; 5-Ethoxymethylfurfural; 5-Hydroxymethylfurfural; Solid acid.

1. Introduction

The continued global reliance on fossil fuel resources and the environmental problems associated with them, such as greenhouse gas emissions and climate change, have intensified the search for renewable and sustainable energy sources [1]. Among the numerous alternatives, biomass has emerged as a possible resource for the synthesis of liquid fuels and value-added chemicals owing

to its abundance, renewability, and carbon neutrality [2,3]. In particular, the transformation of biomass-derived carbohydrates into oxygenated fuels has attracted significant attention in the pursuit of green and sustainable energy technologies [4].

5-Ethoxymethylfurfural (EMF) is an energy-rich biofuel candidate derived from carbohydrates through a dehydration and etherification sequence. With a volumetric energy density of 8.7 kWh/L, EMF is comparable to conventional gasoline (8.8 kWh/L), making it suitable as a drop-in fuel additive or alternative [5]. Additionally, EMF shows low water solubility, high boiling point, and good blending ability with diesel, increasing its applicability in existing fuel infrastructures [6,7]. EMF is typically produced via the acid-catalyzed etherification of 5-hydroxymethylfurfural (HMF) with ethanol [8]. HMF itself can be produced from the dehydration of hexoses such as fructose, glucose, or directly from lignocellulosic biomass. Consequently, a two-step route involving conversion of fructose to HMF followed by etherification to EMF has gained widespread attention. Alternatively, one-pot processes combining both transformations in a single system are being actively developed to improve overall efficiency and minimize purification steps [9,10].

Despite progress in EMF production, challenges remain, particularly in catalyst design. Traditional homogeneous acid catalysts like hydrochloric acid and sulfuric acid have revealed high catalytic performance but are associated with drawbacks including equipment corrosion, product separation difficulties, and environmental hazards [11,12]. In response, various solid acid catalysts have been developed to replace homogeneous systems, offering advantages such as easy separation, reusability, and reduced environmental impact [13]. Among solid catalysts, sulfonic acid-functionalized materials are widely studied due to their strong Brønsted acidity and high catalytic activity [14-16].

However, sulfonic acid-based solid catalysts are not without drawbacks. They often suffer from leaching of the sulfonic groups, especially under high temperature or polar solvent conditions, which limits their long-term stability. Additionally, the synthesis of sulfonated materials frequently involves harsh sulfonation agents (e.g., fuming sulfuric acid, chlorosulfonic acid), raising environmental and safety concerns. [17] Besides, excessive acidity may promote unwanted side reactions such as humin formation or degradation of sensitive biomass-derived substrates [18].

To overcome the above-mentioned issues, there is growing interest in developing carboxylic acid-functionalized solid catalysts, which offer moderate acidity, enhanced stability, and improved selectivity for biomass transformations [19]. Unlike sulfonic acids, carboxylic acids can be introduced under milder conditions, often without requiring toxic reagents. Additionally, the tunability of their acidity and structural diversity opens up new possibilities in catalyst design [20]. Despite these advantages, no studies have explored carboxylic acid-based solid catalysts for EMF production, particularly those derived from renewable support materials.

Cellulose, an abundant, renewable, and biodegradable biopolymer, has arisen as a favorable support material for heterogeneous catalysts [21-23]. The hydroxyl-rich structure of cellulose enables chemical modification, making it suitable as a support for acidic functional groups [24,25]. Functionalization of cellulose to introduce acidic groups provides an attractive route to develop green solid acid catalysts. In particular, aryl chloride-based functionalization offers a facile method for covalent modification of cellulose, enabling the immobilization of organic acids via nucleophilic substitution with the hydroxyl groups of the cellulose backbone.

In this work, we reported the design and synthesis of a novel solid acid catalyst by immobilizing 4-(chloromethyl)benzoic acid onto cellulose via covalent bonding between the aryl chloride group and the hydroxyl functionalities of cellulose. The resulting catalyst combined the advantages of

biomass-derived support materials with the Brønsted acidity of benzoic acid moieties, leading to a recyclable and efficient catalytic system. The prepared catalyst was thoroughly characterized using various physicochemical techniques and subsequently employed in the conversion of HMF and carbohydrate-based substrates to EMF. The catalytic activity, selectivity, and stability were evaluated and discussed in relation to catalyst structure and reaction parameters.

2. Experimental details

2.1. General

All chemicals, solvents, and reagents were purchased from Merck or Sigma company, were of analytical grade, and were employed as received.

Fourier-Transform infrared spectroscopy (FT-IR): FT-IR spectra were obtained using a Thermo Scientific Nicolet iS20 instrument from 400 to 4000 cm^{-1} consuming KBr pellet method.

X-Ray diffraction (XRD): crystallinity of the materials was characterized with a Rigaku powder diffractometer (Rigaku, Japan) utilizing Cu Kα radiation (λ = 1.5406 Å) in the 2θ range of 10-50°.

Transmission electron microscopy (TEM): morphological features of the samples were observed via a JEM-2100 plus instrument at an accelerating voltage of 200 kV.

Energy dispersive X-Ray spectroscopy (EDX) and elemental mapping: elemental composition and spatial distribution of elements were examined using a EDX system attached to the scanning electron microscope (SEM; Nova NanoSEM; FEI; USA).

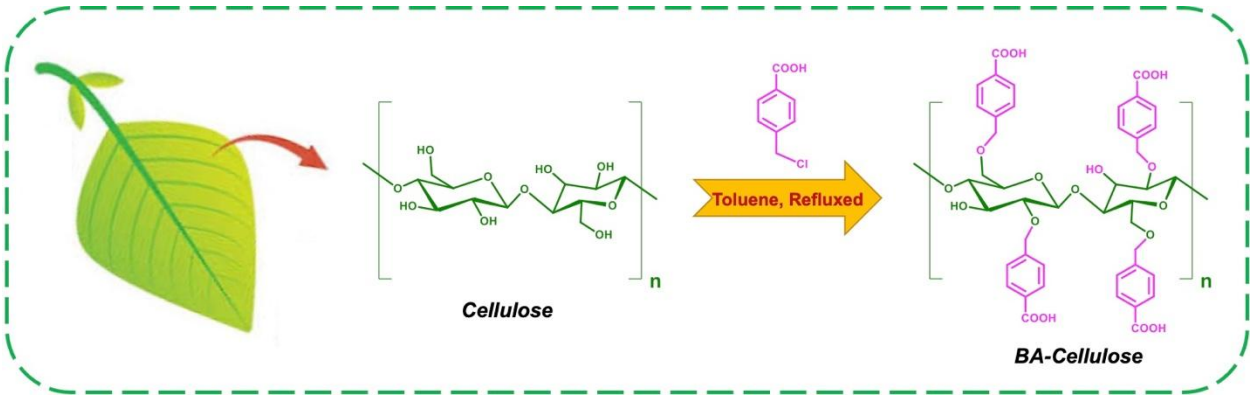
X-ray photoelectron spectroscopy (XPS): The outermost surface property of the catalyst was obtained using (XPS) in combination with Omicron nanotech operated at 15 kV and 20 mA by a monochromatic Al Kα X-ray source.

Thermogravimetric analysis (TGA): TGA was conducted on a simultaneous thermal analyzer (NETZSCH STA 449F3, GER) with a nitrogen flow rate of 40 mL/min and at a temperature ramp of 10 °C/min from room temperature to 600 °C.

Acid-base titration: the acid capacity of the catalyst was calculated by back-titration. Briefly, 100 mg of the catalyst was stirred with 10 mL of standardized 0.05 M NaOH solution for 12 h. The excess base was titrated against standardized 0.05 M HCl by phenolphthalein as indicator.

2.2. Catalyst preparation

The functionalization of cellulose with 4-(chloromethyl)benzoic acid was carried out via nucleophilic substitution, where the hydroxyl groups of cellulose reacted with the chloride moieties of 4-(chloromethyl)benzoic acid as depicted in Scheme 1. In a standard process, 2.0 g of cellulose was suspended in 50 mL of dry toluene. Separately, 2.0 g of 4-(chloromethyl)benzoic acid was dissolved in 20 mL of dry toluene and gradually introduced to the cellulose suspension under continuous stirring. The reaction mixture was stirred at 110 °C for 24 h. The reaction mixture was subsequently cooled to room temperature, then the product was filtered and thoroughly rinsed with toluene, ethanol, and distilled water to eliminate unreacted reagents and byproducts. The obtained product was dried under vacuum at 100 °C for 12 h to yield the carboxylic acid-functionalized cellulose catalyst (BA-cellulose).



Scheme 1. Schematic graphic of the preparation of BA-cellulose.

2.3. Conversion of HMF and sugars to EMF

The etherification reactions of HMF and sugars with ethanol were performed in a 50 mL Teflon stainless-steel autoclave fitted with a magnetic stirring. In a typical procedure, HMF or sugars (1 mmol) was added to an autoclave containing absolute ethanol (5 mL) and a specific quantity of BA-cellulose catalyst. The reaction mixture was stirred under heating at various temperatures for a specified period (typically 1-4 h). Once the reaction finished, the reaction mixture was left to cool to room temperature. The catalyst was separated via simple filtration, rinsed with ethanol, and dried under vacuum for reuse in subsequent cycles. The filtrate was evaluated by high-performance liquid chromatography (HPLC) to quantify the conversion of substrate, the yield of EMF, and selectivity of EMF, according to below equations:

Conversion of substrate (%) = [moles of reacted substrate / moles of initial substrate] × 100%

EMF yield (%) = [moles of EMF formed / moles of initial substrate] × 100%

EMF selectivity (%) = [EMF yield /conversion of substrate] × 100%

Sample concentrations were measured through comparison with a standard calibration curve.

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. FT-IR spectroscopy

FT-IR spectroscopy was employed to confirm the successful immobilization of 4-(chloromethyl)benzoic acid onto cellulose. The FT-IR spectra of pristine cellulose and BA-cellulose are presented in Figure 1. The spectrum of cellulose exhibited characteristic peaks at 3346 cm^{-1} (O-H stretching vibration), 2902 cm^{-1} (C-H stretching vibration), 1648 cm^{-1} (O-H

bending vibration), 1370 cm^{-1} (C-O stretching vibration), and 1060 cm^{-1} (C-O-C stretching vibration) [26]. After functionalization, BA-cellulose displayed new peak at 1737 cm^{-1}, which was ascribed to the C=O stretching vibrations of carboxylic acid groups, demonstrated successful grafting of 4-(chloromethyl)benzoic acid onto the cellulose backbone [27]. Moreover, a considerable decline in the intensity of the O-H stretching vibration peak was observed, representing substitution of some hydroxyl groups.

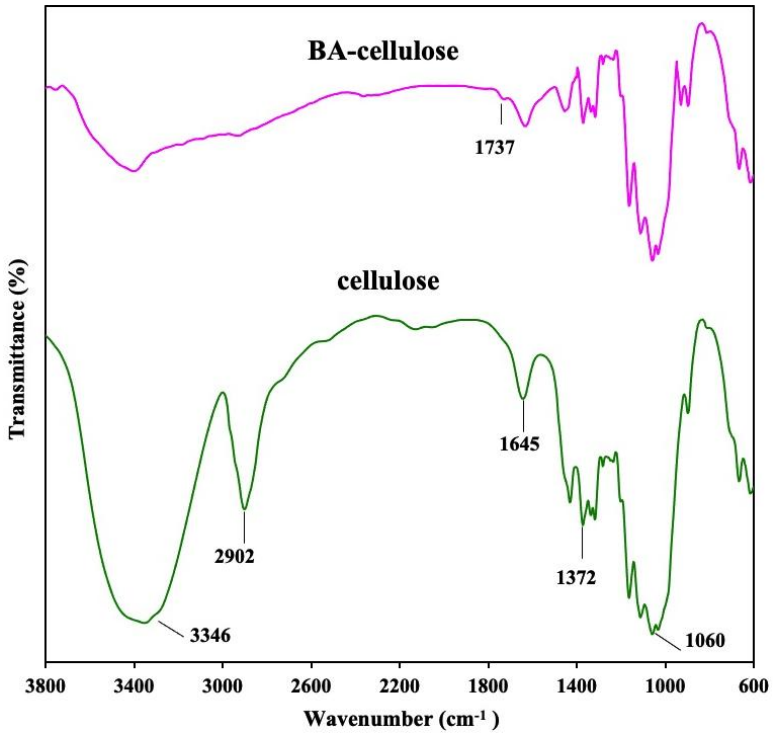


Figure 1. FT-IR spectra of cellulose and BA-cellulose.

3.1.2. XRD analysis

The crystalline properties of cellulose and BA-cellulose were studied via XRD analysis, as presented in Figure 2. The XRD pattern of cellulose demonstrated typical diffraction peaks corresponding to the (110), (200), and (004) planes, characteristic of cellulose crystalline structure [28]. After functionalization with 4-(chloromethyl)benzoic acid, a decrease in peak intensity and

partial broadening was observed, showing a reduction in crystallinity owing to disruption of the hydrogen bonding network upon covalent modification. However, the preservation of peak positions approved that the cellulose framework remained structurally intact, and the functionalization primarily affected the surface and amorphous region.

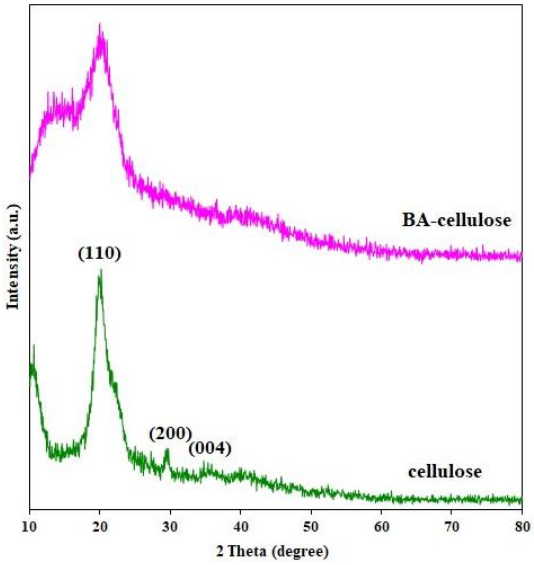


Figure 2. XRD patterns of cellulose and BA-cellulose.

3.1.3. TEM analysis

TEM analysis was used to examine the morphology and structure of cellulose and BA-cellulose. TEM image of cellulose (Figure 3A) revealed that pristine cellulose fibers appeared as smooth and elongated structures. After modification, BA-cellulose (Figure 3B) exhibited slightly rougher surfaces and some aggregation, consistent with the introduction of organic groups and increased

inter-fiber interactions. No significant change in fibrous morphology was observed, demonstrating that the functionalization process preserved the cellulose's structural integrity.

3.1.4. EDX analysis

EDX analysis was performed to confirm the elemental structure of BA-cellulose. The EDX spectrum of BA-cellulose (Figure 3C) displayed prominent signals for carbon (C) and oxygen (O), consistent with the cellulose structure and the introduced carboxylic acid groups. Notably, no chlorine (Cl) signal was detected, confirming that the chloride moieties of 4-(chloromethyl)benzoic acid were fully substituted during the nucleophilic reaction with the hydroxyl groups of cellulose. Elemental mapping analysis (inset Figure 3C) further established the uniform distribution of C and O elements throughout BA-cellulose catalyst, representing a homogeneous functionalization of cellulose with 4-(chloromethyl)benzoic acid.

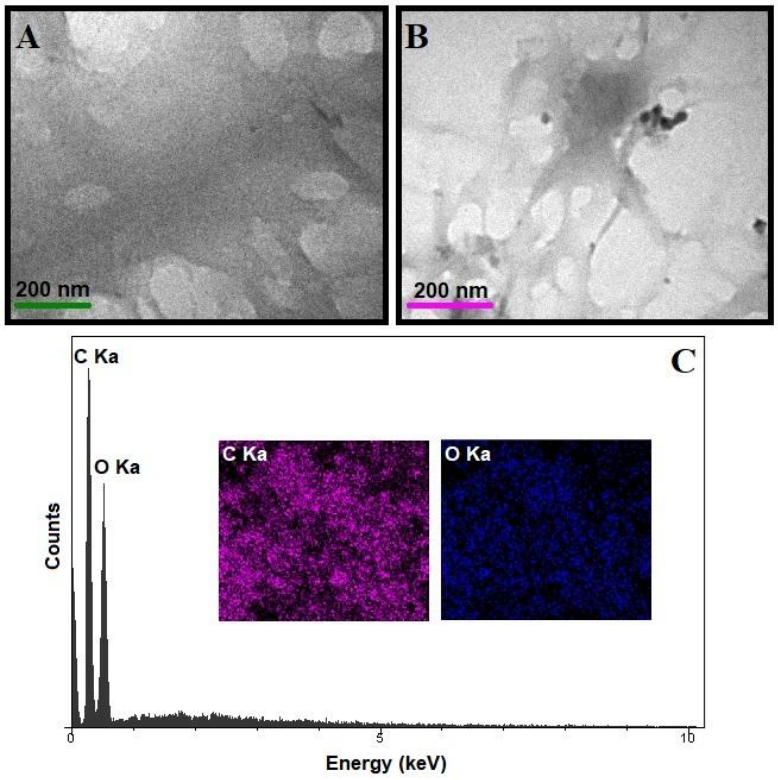


Figure 3. TEM images of cellulose (A) and BA-cellulose (B); EDX spectrum of BA-cellulose (C) and elemental mapping images of C and O (inset C).

3.1.5. XPS analysis

XPS analysis was used to further confirm the surface chemical composition of BA-cellulose. The survey spectrum of BA-cellulose (Figure 4A) showed the existence of carbon (C 1s) and oxygen (O 1s) peaks, with no detectable impurities. High-resolution C 1s spectrum (Figure 4B) was deconvoluted into multiple components due to the C-C/C-H (284.4 eV), C-O (286.1 eV), C-O-C (287.0 eV), and O=C-O (288.4 eV), further confirming the effective incorporation of aromatic carboxylic acid moieties onto the cellulose surface [29]. Besides, the O 1s spectrum (Figure 4C) showed a peak at 532.3 eV, assignable to carbonyl oxygen in COOH groups, further confirming immobilization of 4-(chloromethyl)benzoic acid [27].

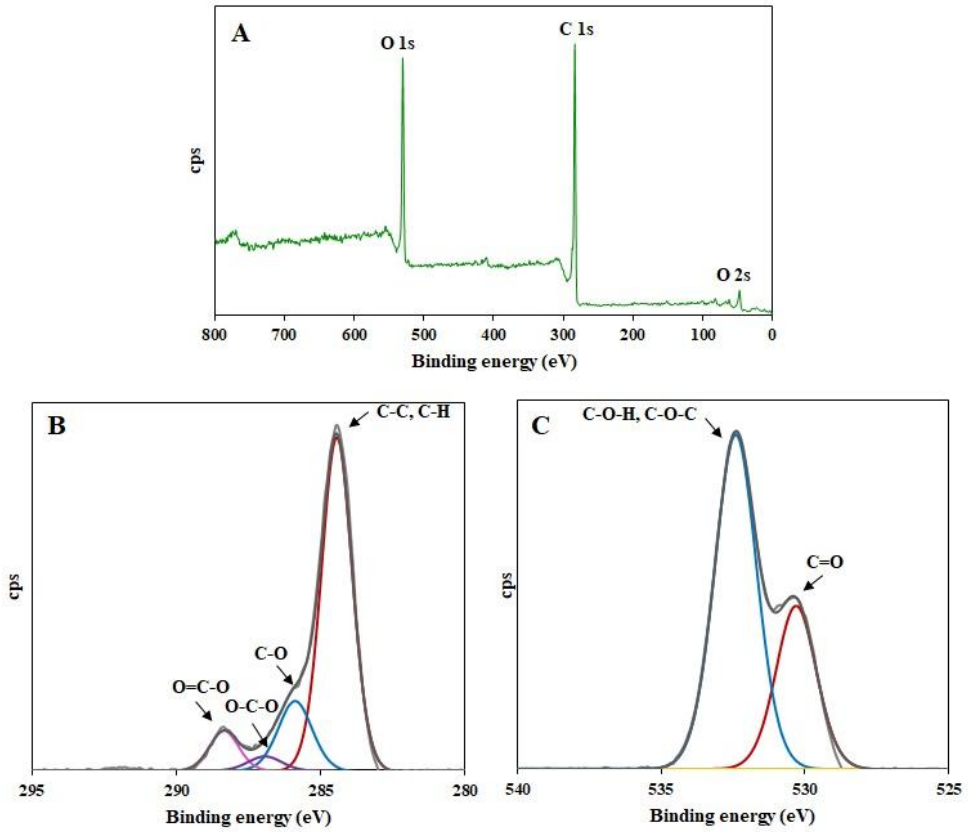


Figure 4. Survey (A), C 1s (B), and O 1s (C) XPS spectra of BA-cellulose.

3.1.6. TGA

TGA was performed to check the thermal stability and organic content of BA-cellulose, as shown in Figure 5. The TGA curve indicated an initial mass loss below 150 °C, corresponding to the vanishing of physically adsorbed moisture. A second, more substantial weight loss occurred between 150 °C and 700 °C, which was endorsed to the thermal decomposition of the grafted 4-(chloromethyl)benzoic acid groups and the partial degradation of the cellulose backbone. The observed thermal profile confirmed the successful functionalization of cellulose with aromatic carboxylic acid groups and suggested that the catalyst remained stable under typical reaction conditions.

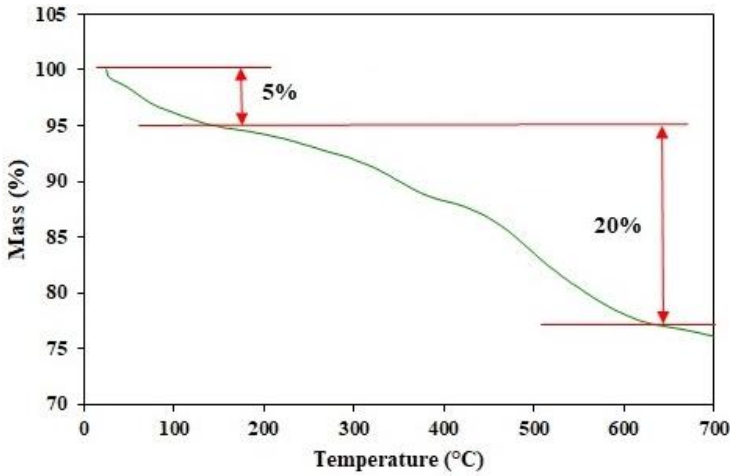


Figure 5. TGA curve of BA-cellulose.

3.1.7. Acid-base titration

The acid-base titration method was employed to quantify the number of accessible Brønsted acid sites in BA-cellulose. The catalyst revealed an acid capacity of 0.56 mmol/g, attributed to the carboxylic acid groups immobilized on the cellulose surface. This value indicated a significant introduction of acidic sites compared to pristine cellulose, which showed negligible acidity. The high acid density suggested that BA-cellulose can act as an effective solid acid catalyst in various acid-catalyzed reactions.

3.2. Catalytic performance in the etherification of HMF to EMF

The catalytic performance of BA-cellulose was studied in the etherification of HMF to EMF in ethanol. Key reaction factors like catalyst loading, reaction temperature, and reaction time were systematically optimized to maximize EMF yield and selectivity.

3.2.1. Influence of catalyst loading

The amount of BA-cellulose has a vital role in determining the conversion efficiency and EMF yield. Reactions were performed with varying catalyst loadings (20, 40, 60 and 80mg) to assess its

impact on HMF conversion, EMF yield, and EMF selectivity under otherwise constant conditions. As displayed in Figure 6A, increasing the catalyst amount from 20 to 60 mg enhanced HMF conversion from 37.2% to 81.5%, while EMF yield increased from 26.7% to approximately 72.7%. Correspondingly, the selectivity toward EMF remained high, ranging between 71% and 89%, reaching a maximum selectivity of 89.2% at 60 mg catalyst loading. This trend was ascribed to the higher availability of acidic sites facilitating the etherification HMF to EMF. Further increasing the catalyst loading to 80 mg resulted in marginal improvement in HMF conversion (82.3%), demonstrating that catalyst saturation occurred and additional acid sites did not substantially accelerate the reaction. Excessive catalyst amounts also led to side reactions such as humin formation, thus reducing both EMF yield and selectivity [16]. Therefore, a catalyst loading of 60 mg was identified as optimal for achieving high yield and selectivity toward EMF.

3.2.2. Influence of reaction temperature

Temperature strongly influences the reaction kinetics and equilibrium. The effect of reaction temperature on the etherification of HMF to EMF was evaluated in the range of 80-140 °C with 60 mg catalyst loading. As displayed in Figure 6B, both HMF conversion and EMF yield improved with temperature. At 80 °C, the HMF conversion was 57.6% with an EMF yield of 42.2%, corresponding to an EMF selectivity of 73.3%. Enhancing the temperature to 100 °C led to a marked improvement in HMF conversion (81.5%) and EMF yield (72.7%), with a selectivity of 89.2%. The highest performance was obtained at 120 °C, where HMF conversion was 90.1%, EMF yield peaked at 89.1%, and EMF selectivity was 98.9%. However, further enhancing the temperature to 140 °C resulted in a minor decline in EMF yield (78.3%) despite a marginal increase in HMF conversion (95.2%), probably due to thermal degradation of reactants or products and

increased humin formation [30]. Hence, 120 °C was selected as the optimal reaction temperature, offering the best balance between HMF conversion and EMF selectivity.

3.2.3. Influence of reaction time

The influence of reaction time on the etherification of HMF to EMF was investigated at 120 °C by varying the duration from 1 to 4 h. As illustrated in Figure 6C, both HMF conversion and EMF yield improved progressively with time. After 1 h of reaction, HMF conversion was 50.5%, with an EMF yield of 39.2% and EMF selectivity of 77.6%. At 2 h, the conversion reached 81.2%, EMF yield increased to 64.4%, and EMF selectivity improved to 79.3%. The maximum performance was achieved at 3 h, where HMF conversion reached 90.1%, EMF yield peaked at 89.1%, and EMF selectivity was 98.9%. Extending the reaction to 4 h led to a minor increase in HMF conversion (97.8%), but EMF yield declined marginally to 78.3%, and EMF selectivity dropped to 80.1%, likely owing to the secondary decomposition or polymerization of the EMF product [30]. Based on these results, a reaction time of 3 h was considered optimal for achieving the highest EMF yield and selectivity with efficient HMF conversion.

3.3. Catalytic activity in the direct transformation of carbohydrates to EMF

Encouraged by the high catalytic efficiency in HMF conversion to EMF, BA-cellulose was further applied to the direct transformation of various carbohydrates, including fructose, glucose, sucrose, and maltose to EMF under the optimized conditions. The obtained results are displayed in Figure 6D. As can be seen, BA-cellulose demonstrated effective catalytic performance for the direct transformation of several carbohydrates to EMF under optimized conditions. Fructose exhibited the highest conversion (83.3%) and EMF yield (74.3%) with good selectivity (89.2%), suggesting efficient dehydration and subsequent etherification. In contrast, glucose conversion was moderate

(62.3%) with lower EMF yield (39.4%) and EMF selectivity (63.2%), accredited to the catalyst's limited ability to isomerize glucose to fructose. Sucrose and maltose showed intermediate conversions (68.0% and 52.7%, respectively) and EMF yields (52.7% and 33.7%, respectively), reflecting partial hydrolysis of disaccharides and subsequent conversion challenges associated with glucose units. Overall, though BA-cellulose effectively catalyzed fructose conversion to EMF, its performance with glucose-based substrates was limited by insufficient hydrolysis and isomerization activity, suggesting the need for catalyst modification or co-catalyst addition for improved isomerization and hydrolysis, thus enhancing EMF yields from these substrates.

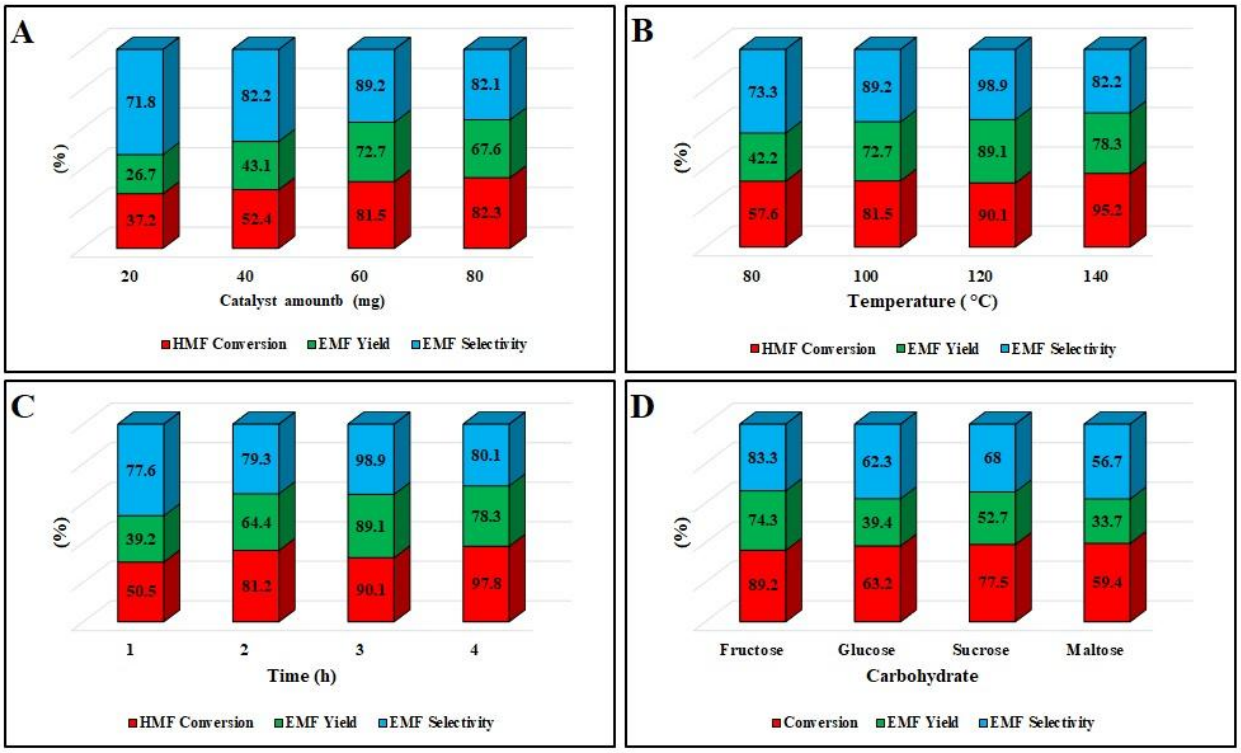


Fig. 6. EMF production over BA-cellulose. (A) Effect of catalyst amount (reaction conditions: HMF (1mmol), ethanol (5 mL), 100 °C, 3 h); (B) effect of reaction temperature (reaction conditions: HMF (1mmol), ethanol (5 mL), BA-cellulose (60 mg), 3 h); (C) effect of reaction time (reaction conditions: HMF (1mmol), ethanol (5 mL), BA-cellulose (60 mg), 120 °C); (D) effect of substrate type (reaction conditions: carbohydrate (1mmol), ethanol (5 mL), BA-cellulose (60 mg), 120 °C, 3 h).

3.3. Catalyst reusability

The reusability and stability of BA-cellulose are critical factors for its practical utilization in biomass conversion processes. To assess these properties, the catalyst was subjected to consecutive etherification reactions under the optimized conditions (60 mg catalyst, 120 °C, 3 h, 1 mmol HMF in 5 mL ethanol). After each reaction cycle, the catalyst was separated via simple filtration, thoroughly rinsed with ethanol to eliminate any adsorbed substrates or products, and dried under vacuum prior to reuse. The catalytic activity was monitored by measuring EMF yield in each cycle. The catalyst was effectively operated through six back-to-back cycles without significant loss in activity (Figure 7). To further investigate the stability of the catalyst after repeated use, characterization by acid-base titration was performed on the recovered catalyst. The result of acid-base titration experiment established negligible loss of acidity, indicating that the active sites were well retained during the reaction process. These results revealed that BA-cellulose possesses excellent reusability and stability, making it a promising candidate for sustainable and cost-effective production of EMF from renewable biomass-derived substrates.

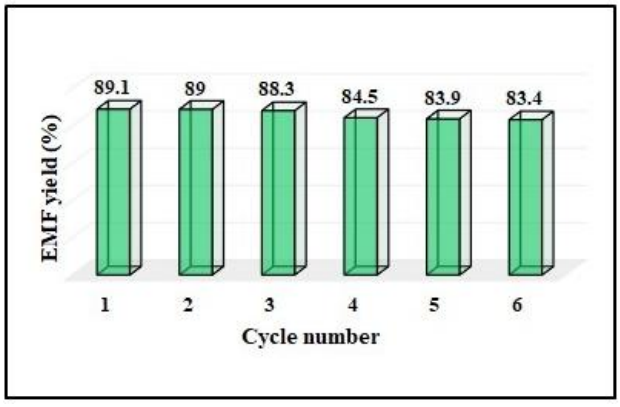
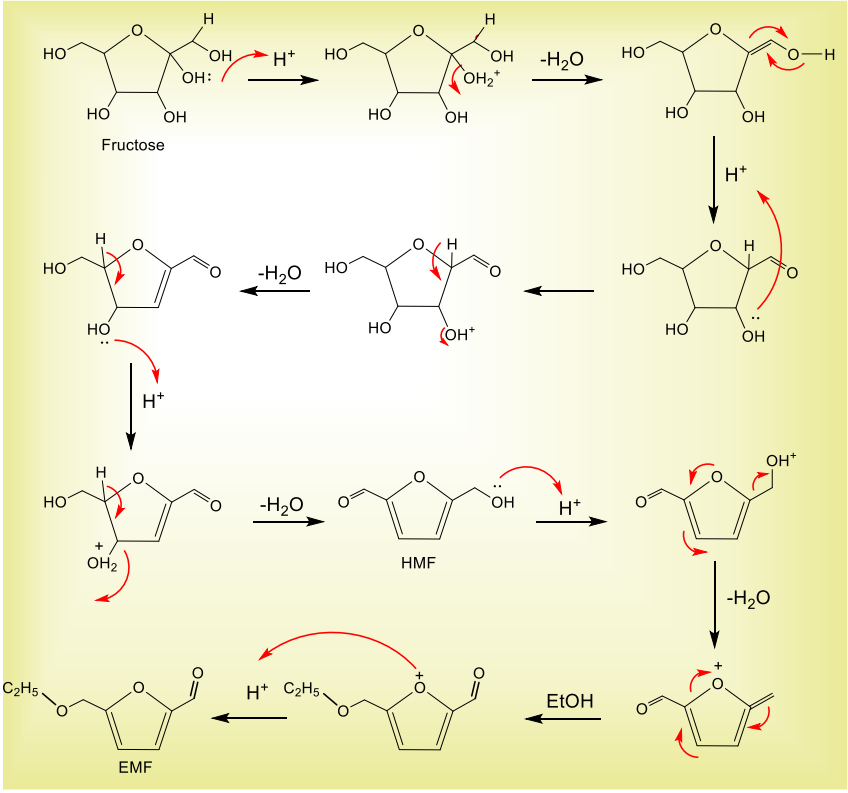


Fig. 7. Reusability experiment of BA-cellulose in the conversion of HMF to EMF under the optimal conditions.

3.4. Reaction mechanism

The catalytic transformation of fructose to EMF over BA-cellulose proceeds via a series of acid-catalyzed dehydration and etherification steps, as depicted in Scheme 2 [31]. Initially, the carboxylic acid groups grafted onto the cellulose surface act as Brønsted acid sites, protonating the hydroxyl groups of fructose, increasing their electrophilicity and facilitating the elimination of three water molecules through a series of dehydration reactions. This results in the formation of HMF as a key intermediate. Under the reaction conditions in ethanol, the generated HMF undergoes acid-catalyzed etherification, where the hydroxymethyl group is protonated, promoting nucleophilic attack by ethanol to form the corresponding ethoxymethyl ether group, resulting in EMF.



Scheme 2. A probable mechanism for the conversion of fructose to EMF over BA-cellulose.

4. Conclusions

In this study, a sustainable solid acid catalyst (BA-cellulose) was successfully developed by immobilizing 4-(chloromethyl)benzoic acid onto cellulose through covalent bonding. Comprehensive characterization affirmed the effective functionalization and significant acid site density of the catalyst. BA-cellulose displayed excellent catalytic activity, selectivity, and stability in the conversion of HMF to EMF, achieving high yields under optimal reaction conditions. Moreover, the catalyst effectively converted diverse biomass-derived carbohydrates, particularly fructose, into EMF, highlighting its potential for direct biomass valorization. The catalyst demonstrated outstanding reusability with insignificant activity loss over repeated cycles, underscoring its practical applicability. This work presents an environmentally friendly, cost-effective, and scalable approach to bio-based EMF production by combining a renewable cellulose support with moderate acidity from carboxylic acid groups, aligning well with green chemistry principles.

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Data Availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Conflict of interests

The authors declare no competing interests.

Ethics Approval and Consent to Participate

Not applicable.

Consent for Publication

All of the authors participated in the study and they have agreed to the content to publish.

References

[1] M. Melikoglu, Catalytic conversion of biomass to biofuels: A global review of current status and future perspectives, Next Res. 7 (2026) 101499.

[2] L. N. Tran, T. H. Nguyen, D. A. L. Nguyen, T. M. T. Nguyen, P. H. Tran, Advanced Co-PANI/N-CNT catalyst for the conversion of biomass into HMF: Efficiency, Stability, and Mechanistic insights, Fuel 411 (2026) 138050.

[3] H. Durak, I. Sahroni, M. S. Ahmad, T. Kida, Sustainable biorefinery: highly selective production of OBMF from HMF using graphene oxide catalysts, Biomass Conv. Bioref. 16 (2026) 136.

[4] M. Kashif, M. A. Sabri, M. Aresta, A. Dibenedetto, F. Dumeignil, Sustainable synergy: unleashing the potential of biomass in integrated biorefineries, Sustainable Energy Fuels 9 (2025) 338-400.

[5] B. Torres-Olea, G. Rodríguez-Carballo, R. Moreno-Tost, M. E. Domine, J. A. Cecilia, C. García-Sancho, P. Maireles-Torres, Application of a two-step water:methyl isobutyl ketone:ethanol biphasic system in the production of 5-ethoxymethylfurfural from glucose. Renew. Energy 240 (2025) 122125.

[6] H. Li, P. Hu, D. Wu, Z. Xue, H. Lv, C. Hu, L. Zhu, Water Removal Enables High-Efficacy Synthesis of 5-Ethoxymethylfurfural and Ethyl Levulinate as Biofuel Candidates from High-Concentration Fructose, Energy Fuels 38 (2024) 15385-15396.

[7] B. Torres-Olea, A. Pérez-Merchán, C. Zampieri, R. Luna-León, J. J. Reina, R. Moreno-Tost, J. A. Cecilia, C. García-Sancho, P. Maireles-Torres, Catal. Today 458 (2025) 115379.

[8] W. Song, R. Zhang, H. Liu, J. Zhang, W. Jia, L. Peng, Hybrid zeolites in 1,4-dioxane-mediated co-solvent efficiently convert glucose to the biofuel 5-ethoxymethylfurfural, Appl. Catal. B: Environ. 361 (2025) 124684.

[9] N. Kushwaha, E. Ahmad, K. K. Pant, One-Pot Microwave Assisted Etherification of Fructose to Sustainable Liquid Fuel Over TiS_2 Catalyst. ChemCatChem 17 (2025) e00504.

[10] G. Yu, C. Wang, R. Lai, Y. Tang, H. Qian, C. Xie, T. Xia, X. Bai, F. Qu, C. Zhang, S. Zhou, H. Guo, S. Song, M. Ju, Q. Hou, Confinement of Tin Phosphates in Mesoporous Channels of Zeolite To Enhance Lewis Acidity for Glucose Isomerization, ACS Sustainable Chem. Eng. 13 (2025) 14099-14109.

[11] B. Chen, G. Xu, C. Chang, Z. Zheng, D. Wang, S. Zhang, K. Li, C. Zou, Efficient One-Pot Production of Biofuel 5-Ethoxymethylfurfural from Corn Stover: Optimization and Kinetics, Energy Fuels 33 (2019) 4310-4321.

[12] H. Guo, X. Qi, Y. Hiraga, T. M. Aida, R. L. S. Jr, Efficient conversion of fructose into 5-ethoxymethylfurfural with hydrogen sulfate ionic liquids as co-solvent and catalyst, Chem. Eng. J. 314 (2017) 508-514.

[13] B. Chen, G. Xu, Z. Zheng, D. Wang, C. Zou, C. Chang, Efficient conversion of corn stover into 5-ethoxymethylfurfural catalyzed by zeolite USY in ethanol/THF medium, Ind. Crops Prod. 129 (2019) 503-511.

[14] J. Dai, Z. Liu, Y. Hu, S. Liu, L. Chen, T. Qi, H. Yang, L. Zhu, Ch. Hu, Adjusting the acidity of sulfonated organocatalyst for the one-pot production of 5-ethoxymethylfurfural from fructose, Catal. Sci. Technol. 9 (2019) 483-492.

[15] Y. Zhang, R. Tong, X. Wang, Y. Hong, Z. Ren, Q. Hou, P. He, Lignosulfonate-based sulfonated polymers for highly efficient one-pot conversion of fructose into 5-ethoxymethylfurfural in ethanol, Renew. Energy 240 (2025) 122276.

[16] M. Niakan, C. Qian, S. Zhou, High-efficiency synthesis of 5-ethoxymethylfurfural from biomass-derived 5-hydroxymethylfurfural and sugars catalyzed by magnetically recoverable hydrogen sulfate ionic liquid, Biomass Conv. Bioref. 15 (2025) 19721-19733.

[17] Y. Delshad, D. Rafipour, P. G. Kargar, B. Maleki, M. Ghani, Carboxylic acids dendrimer functionalized magnetic nanoparticles for carbohydrates conversion to 5-hydroxymethylfurfural, Sci. Rep. 15 (2025) 10969.

[18] I. Zandvoort, Y. Wang, C. B. Rasrendra, E. R. H. van Eck, P. C. A. Bruijnincx, H. J. Heeres, B. M. Weckhuysen, Formation, Molecular Structure, and Morphology of Humins in Biomass Conversion: Influence of Feedstock and Processing Conditions, ChemSusChem 6 (2013) 1745-1758.

[19] P. Kang, M. Gabrijelčič, A. Krajnc, I. G. O. Črnivec, B. Likozar, R. K Sharma, Organically Functionalized Mesoporous Silica Network for One-Pot Synthesis of 5-Hydroxymethylfurfural from Glucose in Water, ACS Sustainable Chem. Eng. 13 (2025) 4997-5008.

[20] F. Su, Y. Guo, Advancements in solid acid catalysts for biodiesel production, Green Chem. 16 (2014) 2934-2957.

[21] Y. Liu, S. Li, X. Yu, Y. Chen, X. Tang, T. Hu, L. Shi, M. Pudukudy, S. Shan, Y. Zhi, Cellulose nanofibers (CNF) supported (Salen)Cr(III) composite as an efficient heterogeneous catalyst for CO_2 cycloaddition, Mol. Catal. 547 (2023) 113344.

[22] P. S. Pharande, G. S. Rashinkar, D. M. Pore, Cellulose Schiff base-supported Pd(II): An efficient heterogeneous catalyst for Suzuki Miyaura cross-coupling, Res. Chem. Intermed. 47 (2021) 4457-4476.

[23] L. Deiana, E. Badali, A. A. Rafi, C. W. Tai, J. E. Bäckvall, A. Córdova, Cellulose-Supported Heterogeneous Gold-Catalyzed Cycloisomerization Reactions of Alkynoic Acids and Allenynamides, ACS Catal. 13 (2023) 10418-10424.

[24] C. Yu, W. Wu, M. Gao, Y. Liu, Modified Cellulose with BINAP-Supported Rh as an Efficient Heterogeneous Catalyst for Asymmetric Hydrogenation, Catalysts 12 (2022) 83.

[25] L. Rösler, M. V. Höfler, H. Breitzke, T. Wissel, K. Herr, H. Heise, T. Gutmann, G. Buntkowsky, Dirhodium complex immobilization on modified cellulose for highly selective heterogeneous cyclopropanation reactions, Cellulose 29 (2022) 6283-6299.

[26] K. Karami, H. Saadatzadeh, A. Ramezanpour, Synthesis and Characterization of Palladium Nanoparticles Immobilized on Modified Cellulose Nanocrystals as Heterogeneous Catalyst for Reduction of Nitroaromatic Compounds, ChemistrySelect 6 (2021) 2746-2759.

[27] A. Modak, A. R. Mankar, R.R. Sonde, K. K. Pant, One-pot conversion of glucose to 5-hydroxymethylfurfural under aqueous conditions using acid/base bifunctional mesoporous silica catalyst, Renew. Energy 212 (2023) 97-110.

[28] I. Raya, S. Danshina, A. T. Jalil, W. Suksatan, M. Z. Mahmoud, A. B. Roomigh, Y. F. Mustafa, M. Kazemnejadi, Catalytic filtration: efficient C-C cross-coupling using Pd(II)-salen complex-embedded cellulose filter paper as a portable catalyst, RSC Adv. 12 (2022) 20156-20173.

[29] B. D. Tompkins, E. R. Fisher, Evaluation of polymer hydrophobic recovery behavior following H_2O plasma processing, J. Appl. Polym. Sci. 132 (2015) 41978.

[30] H. Hafizi, G. Walker, M.N. Collins, Efficient production of 5-ethoxymethylfurfural from 5-hydroxymethylfurfural and carbohydrates over lewis/brønsted hybrid magnetic dendritic fibrous silica core-shell catalyst, Renew. Energy 183 (2022) 459-471.

[31] K. Zhao, Y. Xiang, X. Sun, L. Chen, J. Xiao, X. Liu, Highly Efficient One-Step Conversion of Fructose to Biofuel 5-Ethoxymethylfurfural Using a UIO-66-SO_3H Catalyst, Front. Chem. 10 (2022) 900482.