Article

Prepared Sulfonic-Acid-Based Ionic Liquid for Catalytic Conversion of Furfuryl Alcohol to Ethyl Levulinate

Aiyun Hu,* Shan Li, Sheng Zhang, and Haijun Wang

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Efficient utilization of Brønsted acids has been advanced through the synthesis of a novel pyridinium propyl sulfonic acid ionic liquid catalyst, [PSna][HSO$_4$]. Employing niacin and 1,3-propanesulfonic lactone, the synthesis aimed to achieve a catalyst that combines atom-efficiency with stability. Optimal catalytic activity was demonstrated at a temperature of 110 °C over a 2 h reaction time, resulting in a furfuryl alcohol conversion and ethyl levulinate yield of 97.79% and 96.10%, respectively. Notably, the extraction and recovery of [PSna][HSO$_4$] exhibited commendable repeatability with up to five cycles, maintaining furfuryl alcohol conversion and ethyl levulinate yield at 93.74% and 88.17%, which highlights the catalyst's durability. Density flooding theory (DFT) calculations were employed to determine the most probable reaction pathways and identify all possible transition states and the reaction energy barriers overcome at each step of the reaction.
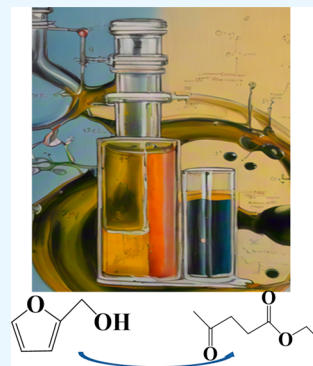
1. INTRODUCTION

Biofuels derived from biomass offer sustainable alternatives to fossil fuels for transportation and chemical production.[1−3] They are carbon-neutral, as the emitted carbon dioxide is absorbed by plants.[4] Biomass is widely available, renewable, and recyclable, making it an attractive energy source.[5−7] Ethyl levulinate (EL), derived from biomass, has desirable properties and finds applications in biofuels, fuel additives, pharmaceutical intermediates, and green solvents.[8,9] However, traditional catalysts for EL production can cause pollution, equipment corrosion, and separation issues.[10,11] Therefore, the selection of catalysts for EL synthesis should consider environmental and economic factors, aiming for ease of separation, eco-friendliness, stability, high activity, and cost-effectiveness.[12,13] In industry, furfuryl alcohol (FA) obtained directly from pentose hydrolysis is commonly used as a raw material for producing EL.[14−16] This approach not only saves resources but also simplifies the purification process for the final products.[17,18]

The conversion of FA alcohols to EL requires Brønsted acid catalysts (e.g., H$_2$SO$_4$ and HF), but high yields cause pollution, making them unsuitable for industry.[19] Guo et al. synthesized solid acid ArSO$_3$H-HMCSs, with higher catalytic activity than other carbon-based materials.[20] Nis and Kaya Ozsel studied the conversion of corn stover, sorghum, and cellulose into high-value chemicals using an ionic liquid-water medium, optimizing parameters for a maximum conversion rate and product selectivity.[21] Gonzalez Maldonado et al. found that protonated FA reacts more readily with ethanol than neutral FA, indicating an easier addition reaction.[22]

Ionic liquids offer advantages like high boiling point, low volatility, and thermal stability.[23] They also exhibit good catalytic activity and stability in biomass reactions.[13,24] Metal chlorides are used as cocatalysts, and acidic ionic liquids combined with metal chlorides show excellent catalytic ability in biomass degradation.[25] Researchers have studied acidic ionic liquids and developed new ones to replace traditional catalysts.[26,27] Introducing sulfonic acid groups enhances the acidity of ionic liquids.[28]

In this study, a [PSna][HSO$_4$] ionic liquid catalyst was synthesized for converting FA to EL. [PSna] is based on nicotinic acid, with a pyridine ring serving as the cation. The cation is connected to a propanesulfonic acid group through a reaction with 1,3-propane sultone, enhancing the catalyst's acidity. The resulting nicotinic acid propanesulfonic acid is combined with H$_2$SO$_4$ to obtain [PSna][HSO$_4$]. Acidic ionic liquids play a crucial role in the conversion of various substances, both biological and chemical.
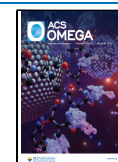
2. EXPERIMENTAL SECTION

2.1. Materials. Nicotinic acid (Na), 1,3-propane sultone, ethanol, and sulfuric acid (98%) were purchased from China

Pharmaceutical Reagents Co, Ltd. and used without further purification.

2.2. Preparation of Catalyst [PSna][HSO₄]. To synthesize niacin propyl sulfonic acid ionic liquid ([PSna][HSO₄]), niacin (NA) was dissolved in ethanol and heated at 60 °C until fully dissolved. 1,3-Propanesulfonic acid lactone was then added, and the mixture was reacted at 60 °C for 12 h to obtain a white precipitate called PSna. The solid precipitate was collected, washed with solvents, and dried in a vacuum drying oven to yield solid PSna with a 95.8% yield.

For the synthesis of [PSna][HSO₄], dried PSna was dissolved in water, and concentrated sulfuric acid was added. The reaction was carried out at 50 °C for 6 h. After completion, the water in the reaction system was removed by rotary evaporation, resulting in a brownish-yellow viscous ionic liquid. The viscous ionic liquid [PSna][HSO₄] was further dried in a vacuum drying oven to ensure minimal moisture content in the final product. The synthesis route is shown in Figure 1.
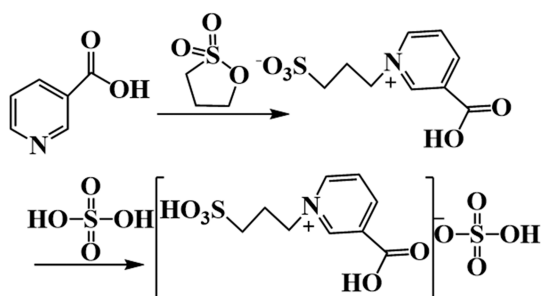

Figure 1. Synthesis route of [PSna][HSO₄].

2.3. Alcoholysis of FA to EL. In a stainless steel reaction kettle, [PSna][HSO₄], FA, and ethanol were mixed together. The kettle was then placed in a preheated oil bath with stirring. After a certain reaction time, the kettle was removed and rapidly cooled to room temperature. The catalyst was extracted using ethyl acetate, and the concentrations of the reactant and product were analyzed using gas chromatography (GC). The FA conversion and EL yield were calculated using specific equations.

$$\text{FA conversion (mol \%)}$$
$$= \left(1 - \frac{\text{moles of FA}}{\text{initial moles of FA}}\right) \times 100\% \tag{1}$$

$$\text{Yield of EL (mol \%)} = \left(\frac{\text{moles of EL}}{\text{initial moles of FA}}\right) \times 100\% \tag{2}$$

After the reaction was complete, the reaction mixture was collected, and the final reaction solution was rotary evaporated to remove ethanol and other low-boiling substances. Then, it was extracted three times using ethyl acetate. The remaining residue was placed in a vacuum drying oven at 60 °C for 12 h to undergo vacuum drying.

2.4. Characterization of [PSna][HSO₄] Catalyst. FT-IR spectra of the synthesized material were obtained using a Bruker FT-IR spectrometer.[29] Samples were prepared using the KBr pellet method and scanned on a Nicolet 360 FTIR spectrometer, covering a wavenumber range of 500−4000 cm⁻¹.

Thermogravimetric analysis (TGA) was conducted using a Mettler-Toledo TGA/DSC3+ analyzer under a nitrogen gas flow of 50 mL/min. The testing was performed within a temperature range of 50 to 800 °C, with a heating rate of 10 °C/min.[30]

Nuclear magnetic resonance hydrogen spectrum characterization was conducted on the four synthesized sulfonic acid ionic liquids using a Bruker 600, AVANCE III instrument.[31] D₂O was used as the reagent. The results of the nuclear magnetic characterization included chemical shifts and peak counts for different hydrogen positions.

3. RESULTS AND DISCUSSIONS

The synthesized ionic liquid [PSna][HSO₄] underwent FT-IR analysis (Figure 2a). Peaks in the range of 500−4000 cm⁻¹ indicated carboxyl groups in nicotinic acid. Peaks at 1450 cm⁻¹, 1640 cm⁻¹, 3070 cm⁻¹, and 3140 cm⁻¹ corresponded to C═N, C═C, and C−H vibrations in the pyridine ring of nicotinic acid. Peaks at 1057 and 1014 cm⁻¹ represented symmetric and asymmetric stretching vibrations of O═S═O and −SO₃²⁻, respectively, confirming a nicotinic acid and 1,3-propane sultone presence. An absorption band at 805 cm⁻¹ was denoted as a S−O stretching vibration, while peaks at 1020 and 1218 cm⁻¹ indicated the stretching vibrations of the sulfonic group and SO₄²⁻. These results confirm the successful
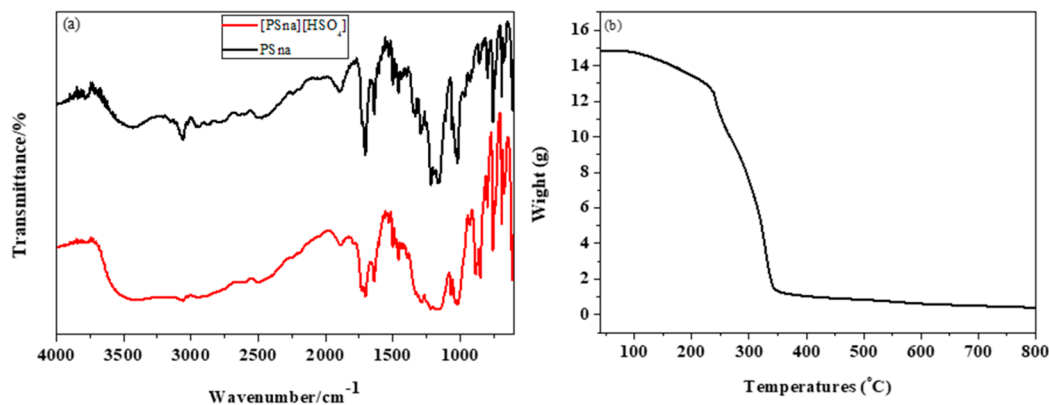

Figure 2. (a) FT-IR spectra of PSna and [PSna][HSO₄]. (b) TG spectra of [PSna][HSO₄].

synthesis of the desired ionic liquid by reacting the amphoteric compound with H_2SO_4.

The thermal stability of $[PSna][HSO_4]$ ionic liquid was analyzed using thermogravimetric analysis (TGA). Results in Figure 2b show the decomposition temperature. Within the 40−200 °C range, $[PSna][HSO_4]$ remains relatively stable. However, temperatures exceeding 250 °C cause rapid decomposition and collapse of its structure. Therefore, the ionic liquid is stable at temperatures below 200 °C and can be used as a catalyst for synthesizing EL from FA.

The synthesized ionic liquid was characterized using ${}^1H$ NMR spectroscopy to confirm its structure and verify its desired composition. The analysis of the NMR spectra revealed the number of hydrogen peaks and their corresponding chemical shifts. Based on spectral analysis, the synthesized product was identified as the intended ionic liquid. The ${}^1H$ NMR analysis results are as follows: 9.29 (q, J = 2.2 Hz, 1H), 8.92−8.82 (m, 2H), 8.05−8.01 (m, 1H), 4.65 (t, J = 7.6 Hz, 2H), 2.80 (t, J = 7.3 Hz, 2H), and 2.40−2.11 (m, 2H).

Hydrolysis of FA requires a Brønsted acid catalyst. The acidity of ionic liquid was assessed using the Hammett method. A solution of nitroaniline indicator in water was prepared, and its absorption at λ_{max} = 380 nm was measured. Solutions with different concentrations of para-nitroaniline and $[PSna]$- $[HSO_4]$ were prepared. Protonation ability was determined by measuring absorbance changes. The acidity constant (H_0) of the ionic liquid was calculated using $H_0 = pK(I)_{aq} + \log([I]/[IH^+])$, where $pK(I)_{aq}$ is the pK_a value of nitroaniline. H_0 values are presented in Table 1, with the pK_a of para-nitroaniline as 0.99.

Table 1. H_0 Values of $[PSna][HSO_4]$ in Water

ionic liquid	absorbance	[I] (%)	[IH⁺] (%)	H_0
none	1.41	100	0	
$[PSna][HSO_4]$	0.60	42.51	57.49	0.86

3.2. Catalytic Performance Research.

3.2.1. The Effect of Catalyst Type.
The acidic IL $[PSna][HSO_4]$ catalyzes the conversion of FA to EL (Table 2). Using ethanol as solvent

Table 2. Catalytic Performance of Different Catalysts[a]

entry	catalysts	C_{FA} (%)	Y_{EL} (%)	S_{EL} (%)
1	none	0	0	0
2	PSna	54.36%	42.13%	77.50%
3	$[PSna][HSO_4]$	97.79%	96.10%	98.27%

[a]Reaction condition: FA (0.098 g, 1 mmol), catalyst (0.05 g, 51%), ethanol (10 mL).

and hydrogen bond donor, FA conversion was negligible at 110 °C without additional catalysts. However, when the zwitterionic compound PSna was added as a catalyst, FA to EL conversion was observed. After 2 h at 110 °C, the FA conversion rate was 54.36% with a yield of 42.13% EL. The presence of sulfonic acid groups in PSna imparts acidity, catalyzing the FA to EL conversion, leading to enhanced catalytic activity.

The addition of $[PSna][HSO_4]$ as a catalyst greatly increased FA conversion. After a 2 h reaction at 110 °C, FA conversion reached 97.79% with a yield of 96.10% EL. These results demonstrate the high efficiency of the acidic ionic liquid, achieving remarkable conversion rates and yields even

under mild conditions. It highlights the importance of incorporating Brønsted acid sites, which enhance the overall reaction efficiency.

3.2.2. The Effect of Catalyst Dosage.
The impact of varying the $[PSna][HSO_4]$ catalyst amount (0.025 to 0.100 g) on reaction outcomes was investigated. Results in Figure 3 show

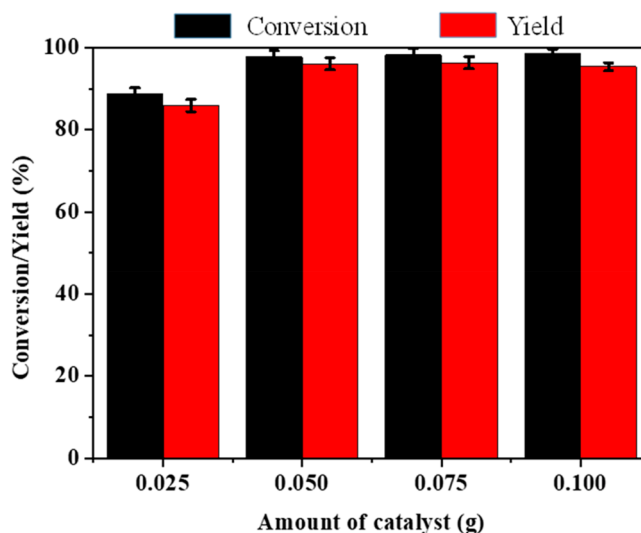**Figure 3.** Influence of the catalyst $[PSna][HSO_4]$ dosage on the alcoholysis reaction of FA to EL.

that increasing the catalyst amount from 0.025 to 0.050 g improved FA conversion rates (88.73% to 97.79%) and EL yields (85.94% to 96.10%) at 110 °C for 2 h. This enhancement is attributed to increased availability of acid catalytic sites, facilitating better contact between FA and those sites. Further increasing the catalyst amount led to stable FA conversion rates but a slight decline in EL yield. This is due to increased viscosity and excess acid causing polymerization of FA and formation of byproducts, reducing the desired EL. Optimal catalyst amount is determined as 0.050 g.

3.2.3. The Influence of Reaction Temperature and Time on the Catalytic Reaction.
The effect of reaction temperature and time on the catalytic results of $[PSna][HSO_4]$ was studied. Figure 4 shows that temperature had a significant influence on the reaction outcomes. Increasing the temperature from 90 to 110 °C, while maintaining the same reaction time, resulted in higher FA conversion rates and EL yields. At 110 °C for 2 h, FA conversion reached 97.79% with a yield of 96.10%. Higher temperatures within a certain range promoted the hydrolysis reaction by reducing the viscosity of the ionic liquid and enhancing molecular collisions. Raising the temperature to 120 °C with a reaction time of 1.5 h yielded similar conversion rates and yields as 110 °C for 2 h. Prolonging the reaction time at 120 °C slightly increased FA conversion and EL yield. Considering all factors, the optimal conditions for preparing EL from FA using 0.050 g $[PSna][HSO_4]$ were a reaction temperature of 110 °C and a reaction time of 2 h (Figure 4).

3.2.4. Catalyst Repeatability.
Catalyst recycling is important, but centrifugation is not suitable for ionic liquids. Instead, extraction methods using ethyl acetate are used. After each cycle, the reaction liquid was collected and evaporated to remove low-boiling solvents, and then ethyl acetate was added to separate the phases. The catalytic activity of $[PSna][HSO_4]$ slightly decreased after five cycles. The yield of EL reduced
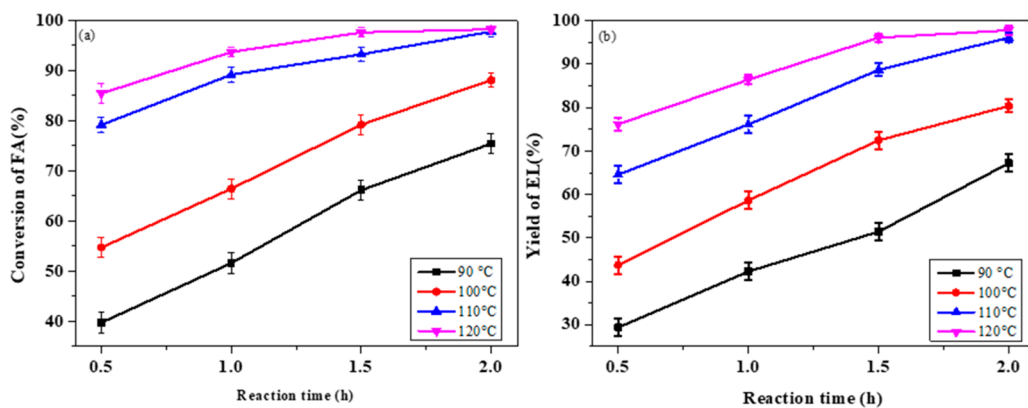
Figure 4. Influence of different reaction temperatures and times on (a) FA conversion and (b) EL yield.

from 96.10% to 88.17% (Figure 5) due to the loss of active sites and byproduct accumulation. Therefore, the catalytic performance remained relatively stable.
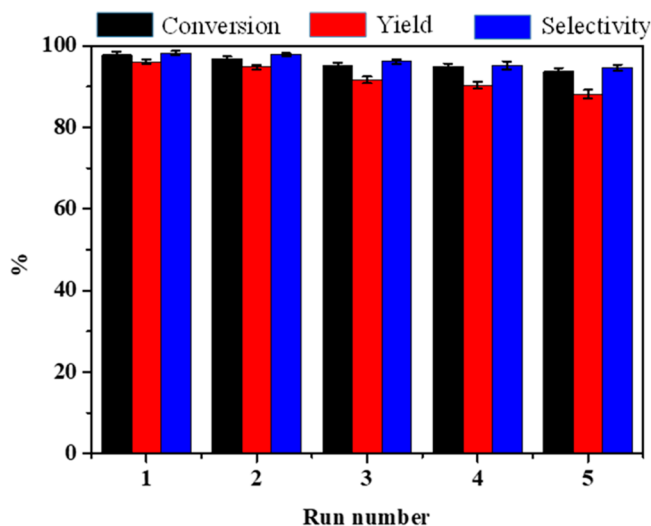

Figure 5. Recycle experiment of [PSna][HSO$_4$].

3.3. Study of Reaction Mechanism. Preliminary findings suggest that FA can follow two possible reaction pathways in the presence of acidic catalysts (Figure 6). The reaction barriers and transition states for these pathways were identified through theoretical calculations. The hydroxyl group in FA reacts with H$^+$ to form intermediate product A and water. In the first pathway, intermediate A reacts with ethanol to produce furfuryl ether. Then, under the action of H$^+$, a ring-opening reaction occurs to form the intermediate product B (2-hydroxy-6-methoxy-3-octene), followed by a hydrogen transfer, resulting in the formation of the acidic EL product. In the second pathway, ethanol reacts directly with intermediate A, causing the opening of the furan ring to form the intermediate product B. Subsequently, under the catalysis of H$^+$, it undergoes rearrangement and finally forms the acidic EL product. Comparing the barriers, the first pathway requires a higher barrier for the conversion of ethyl furfuryl ether. Both pathways eventually result in the opening of the furan ring. The low reaction barriers indicate the spontaneous occurrence of these pathways. The acidity of the reaction system and conditions influence the preferred pathway, with the lower energy barrier being favored. These
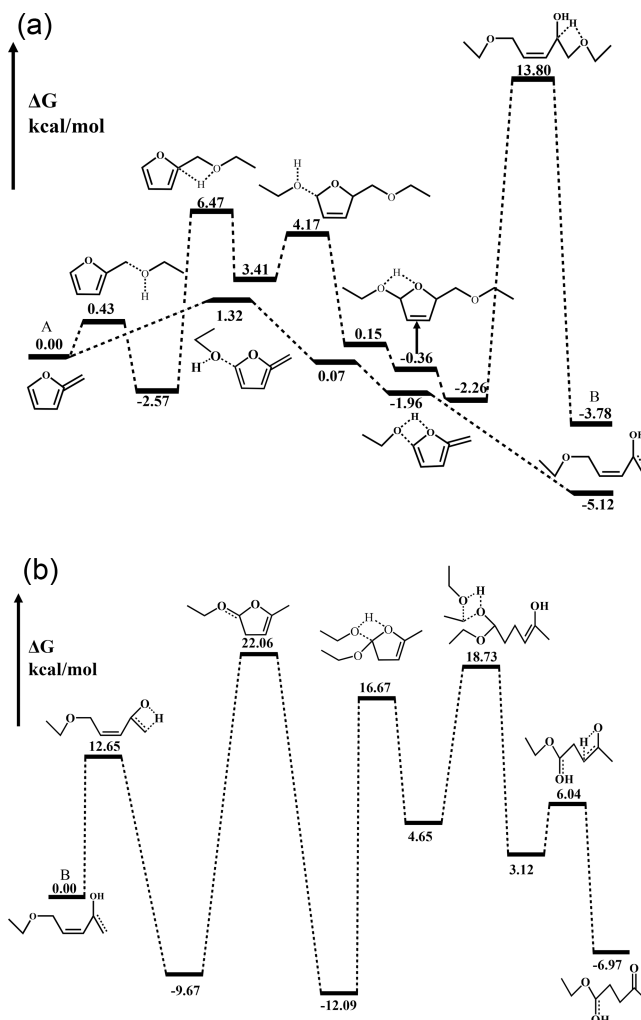

Figure 6. (a) Calculated Gibbs free-energy profile using M062X/def2tzvp with schematic geometries of intermediate A to intermediate products B. (b) Calculated Gibbs free-energy profile using M062X/def2tzvp with schematic geometries of intermediate A to protonated EL.

pathways have been extrapolated based on experimental observations, but it is possible that other pathways with lower energy barriers exist. Future theoretical calculations are needed to further understand the FA transformation process under acidic catalysts.
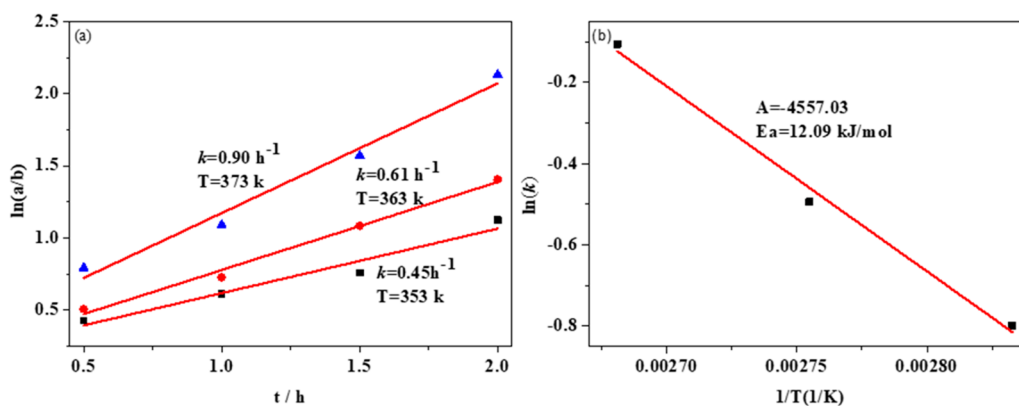
Figure 7. (a) First-order kinetic curves of FA to EL. (b) The Arrhenius equation at different temperatures.

3.4. Kinetics Analysis. The effect of acidity on the catalytic performance of $[PSna][HSO_4]$ in FA hydrolysis for EL synthesis was investigated (Figure 7). The reaction kinetics were studied at different temperatures (353, 363, and 373 K) using 0.050 g of $[PSna][HSO_4]$. Ethanol did not significantly influence the reaction kinetics. The FA hydrolysis was found to be a pseudo-first-order reaction, with rate constants of 0.45, 0.61, and 0.90 h^{-1} at the respective temperatures. The relationship between the rate constant and temperature was determined using the Arrhenius equation, resulting in an activation energy of 12.09 kJ/mol. The abundance of Brønsted acid sites in the catalyst can lower the activation energy of the reaction. The experimental conditions included FA (0.098 g, 1 mmol), $[PSna][HSO_4]$ (0.05 g), ethanol (10 mL), and temperatures ranging from 353 to 373 K.

The ionic liquid $[PSna][HSO_4]$, with 100% Brønsted acid utilization, shows enhanced catalytic performance due to its lower activation energy compared to nonhomogeneous solid-supported acids. This is largely because $[PSna][HSO_4]$ has more Brønsted acid sites and a lower molecular weight in its amphoteric compound PSna, providing more active sites. These factors lead to its superior catalytic activity.

4. CONCLUSIONS

A bifunctional compound, PSna, containing a sulfonic acid group, was synthesized and combined with H_2SO_4 to create a strong acidic ionic liquid catalyst $[PSna][HSO_4]$, with an acidity value (H_0) of 0.86. Optimal conditions for the FA hydrolysis process to synthesize EL were identified, achieving a FA conversion rate of 97.79% and an EL yield of 96.10% at 110 °C in 2 h. Energy barrier calculations and reaction kinetics studies confirmed that $[PSna][HSO_4]$ substantially lowers the activation energy. The research underscores the importance of selecting suitable cationic and anionic components for creating efficient ionic liquids for use in biocatalysis and organic synthesis.

■ AUTHOR INFORMATION

Corresponding Author

Aiyun Hu − *Shazhou Professional Institute of Technology, Zhangjiagang, Jiangsu 215600, China; The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China*; Email: huaiyun88@126.com

Authors

Shan Li − *Shazhou Professional Institute of Technology, Zhangjiagang, Jiangsu 215600, China*

Sheng Zhang − *Shazhou Professional Institute of Technology, Zhangjiagang, Jiangsu 215600, China*

Haijun Wang − *The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China*; ⊚ orcid.org/0000-0003-2857-5861

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.3c10475

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Vidal-Amaro, J. J.; Sheinbaum-Pardo, C. A Transition Strategy from Fossil Fuels to Renewable Energy Sources in the Mexican Electricity System. *Journal of Sustainable Development of Energy Water and Environment Systems-Jsdewes* **2017**, *6* (1), 47−66.

(2) Parikka, M. Global biomass fuel resources. *Biomass & Bioenergy* **2004**, *27* (6), 613−620.

(3) Raveendran, K.; Ganesh, A.; Khilar, K. C. Pyrolysis characteristics of biomass and biomass components. *Fuel* **1996**, *75* (8), 987−998.

(4) Codina Girones, V.; Peduzzi, E.; Vuille, F.; Marechal, F. On the Assessment of the CO_2 Mitigation Potential of Woody Biomass. *Frontiers in Energy Research* **2018**, *5*,.

(5) Wu, X. Y.; De Bruyn, M.; Barta, K. Deriving high value products from depolymerized lignin oil, aided by (bio)catalytic funneling strategies. *Chem. Commun.* **2023**, *59*, 9929.

(6) Wrasman, C. J.; Wilson, A. N.; Mante, O. D.; Iisa, K.; Dutta, A.; Talmadge, M. S.; Dayton, D. C.; Uppili, S.; Watson, M. J.; Xu, X. C.; Griffin, M. B.; Mukarakate, C.; Schaidle, J. A.; Nimlos, M. R. Catalytic pyrolysis as a platform technology for supporting the circular carbon economy. *Nature Catalysis* **2023**, *6*, 563.

(7) Sharma, A.; Singh, G.; Sharma, M.; Kaur, A.; Kumar Arya, S. A review on development of a greener approach via One-Pot tandem catalysis for biofuels production. *Fuel* **2023**, *350*, 128837.

(8) Gu, M. Y.; Xia, Q. N.; Liu, X. H.; Guo, Y.; Wang, Y. Q. Synthesis of Renewable Lubricant Alkanes from Biomass-Derived Platform Chemicals. *ChemSusChem* **2017**, *10* (20), 4102−4108.

(9) Gomez Millan, G.; Hellsten, S.; Llorca, J.; Luque, R.; Sixta, H.; Balu, A. M. Recent Advances in the Catalytic Production of Platform Chemicals from Holocellulosic Biomass. *ChemCatChem.* **2019**, *11* (8), 2022−2042.

(10) Wang, M. Y.; Su, H.; Zhai, G. Y.; Yu, Q. Y.; Wang, H. H.; Jiang, Z. D.; Li, X. H.; Chen, J. S. Synergy of B and Al Dopants in Mesoporous MFI Nanocrystals for Highly Selective Alcoholysis of Furfuryl Alcohol into Ethyl Levulinate. *Energy Technology* **2019**, *7* (6), 1900271.

(11) Li, N.; Zhang, X. L.; Zheng, X. C.; Wang, G. H.; Wang, X. Y.; Zheng, G. P. Efficient Synthesis of Ethyl Levulinate Fuel Additives from Levulinic Acid Catalyzed by Sulfonated Pine Needle-Derived Carbon. *Catalysis Surveys from Asia* **2019**, *23* (3), 171−180.

(12) Shan, J. R.; Wang, Q.; Hao, H. Y.; Guo, H. X. Critical Review on the Synthesis of Levulinate Esters from Biomass-Based Feedstocks and Their Application. *Ind. Eng. Chem. Res.* **2023**, *62*, 17135.

(13) Xing, X. Q.; Zhao, G. Y.; Cui, J. Z.; Zhang, S. J. Isobutane alkylation using acidic ionic liquid catalysts. *Catal. Commun.* **2012**, *26*, 68−71.

(14) Zhao, S. Q.; Xu, G. Z.; Chang, C.; Fang, S. Q.; Liu, Z.; Du, F. G. Direct Conversion of Carbohydrates into Ethyl Levulinate with Potassium Phosphotungstate as an Efficient Catalyst. *Catalysts* **2015**, *5* (4), 1897−1910.

(15) Jeong, G. T.; Kim, S. K. Synthesis of Ethyl levulinate from Chitosan Using Homogeneous Acid Catalyst. *Korean Chemical Engineering Research* **2020**, *58* (2), 266−272.

(16) Zhang, J.; Chen, J. Z. Modified solid acids derived from biomass based cellulose for one-step conversion of carbohydrates into ethyl levulinate. *Journal of Energy Chemistry* **2016**, *25* (5), 747−753.

(17) Kong, X. J.; Zhang, X. L.; Han, C.; Li, C. C.; Yu, L. H.; Liu, J. H. Ethanolysis of biomass based furfuryl alcohol to ethyl levulinate over Fe modified USY catalyst. *Molecular Catalysis* **2017**, *443*, 186−192.

(18) Tan, J.; Liu, Q. Y.; Chen, L. G.; Wang, T. J.; Ma, L. L.; Chen, G. Y. Efficient production of ethyl levulinate from cassava over Al-2(SO4)(3) catalyst in ethanol-water system. *Journal of Energy Chemistry* **2017**, *26* (1), 115−120.

(19) Halder, M.; Bhanja, P.; Islam, M. M.; Chatterjee, S.; Khan, A.; Bhaumik, A.; Islam, S. M. Porous organic polymer as an efficient organocatalyst for the synthesis of biofuel ethyl levulinate. *Molecular Catalysis* **2020**, *494*, 111119.

(20) Song, D. Y.; An, S.; Lu, B.; Guo, Y. H.; Leng, J. Y. Arylsulfonic acid functionalized hollow mesoporous carbon spheres for efficient conversion of levulinic acid or furfuryl alcohol to ethyl levulinate. *Appl. Catal., B* **2015**, *179*, 445−457.

(21) Nis, B.; Kaya Ozsel, B. Efficient direct conversion of lignocellulosic biomass into biobased platform chemicals in ionic liquid-water medium. *Renewable Energy* **2021**, *169*, 1051−1057.

(22) Gonzalez Maldonado, G. M.; Assary, R. S.; Dumesic, J. A.; Curtiss, L. A. Acid-catalyzed conversion of furfuryl alcohol to ethyl levulinate in liquid ethanol. *Energy Environ. Sci.* **2012**, *5* (10), 8990−8997.

(23) Green, M. D.; Long, T. E. Designing Imidazole-Based Ionic Liquids and Ionic Liquid Monomers for Emerging Technologies. *Polym. Rev.* **2009**, *49* (4), 291−314.

(24) Fukuyama, T.; Ryu, I. Ionic liquids and catalyst immobilization. recent advances. *Journal of Synthetic Organic Chemistry Japan* **2005**, *63* (5), 503−510.

(25) Jia, S. Y.; Wang, M. C.; Ma, J.; Liu, X. M.; Zhang, Y. J.; Xu, Z. W. Metal Chloride Mediated Efficient Conversion of Hydroxyme-thylfurfural (HMF) into Long-Chain Levulinate Ester. *Bioresources* **2022**, *17* (1), 849−861.

(26) Guan, Q.; Lei, T. Z.; Wang, Z. W.; Xu, H. Y.; Lin, L.; Chen, G. F.; Li, X. Q.; Li, Z. J. Preparation of ethyl levulinate from wheat straw catalysed by sulfonate ionic liquid. *Industrial Crops and Products* **2018**, *113*, 150−156.

(27) Chen, Z. J.; Ma, X. Y.; Xu, L.; Wang, Y.; Long, J. X. Catalytic conversion of duckweed to methyl levulinate in the presence of acidic ionic liquids. *Bioresour. Technol.* **2018**, *268*, 488−495.

(28) Saravanamurugan, S.; Nguyen Van Buu, O.; Riisager, A. Conversion of Mono- and Disaccharides to Ethyl Levulinate and Ethyl Pyranoside with Sulfonic Acid-Functionalized Ionic Liquids. *ChemSusChem* **2011**, *4* (6), 723−726.

(29) Hu, A.; Wang, H.; Ding, J. Novel Sulfonic Acid Polystyrene Microspheres for Alcoholysis of Furfuryl Alcohol to Ethyl Levulinate. *Catal. Lett.* **2022**, *152* (10), 3158−3167.

(30) Hu, A.; Wang, H.; Ding, J. Preparation of an Ionic Liquid Based on Polystyrene Microspheres to Catalyze the Conversion of Furfuryl Alcohol to Ethyl Levulinate. *ChemistrySelect* **2022**, *7* (31),.

(31) Abraham, R. J.; Griffiths, L.; Perez, M. ^{1}H NMR spectra part 31:1H chemical shifts of amides in DMSO solvent. *Magn. Reson. Chem.* **2014**, *52* (7), 395−408.