

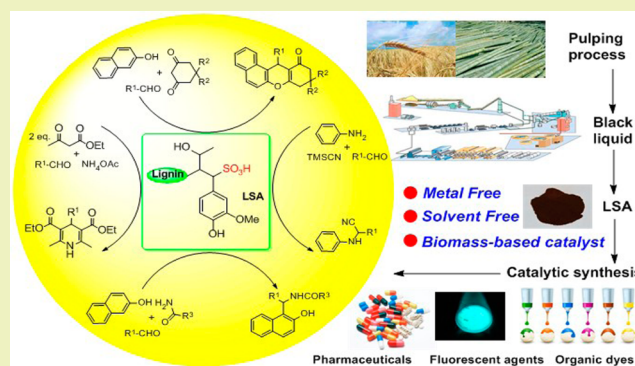
## Lignosulfonic Acid: A Renewable and Effective Biomass-Based Catalyst for Multicomponent Reactions

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## Supporting Information

**ABSTRACT:** The application of biopolymer-based catalyst in catalysis is attracting more and more attention in the field of chemistry. Lignosulfonic acid (LSA), which is an organic waste generated as a byproduct from the pulp and papermaking industry, could serve as a retrievable sustainable heterogeneous catalyst for multicomponent reactions under solvent-free conditions, such as one-pot synthesis of benzoxanthenes by a condensation reaction of dimedone with aldehyde and 2-naphthol in excellent yields. Furthermore, the as-synthesized solid acid catalyst could be used for several cycles without significant loss of catalytic activity. These results clearly show that the lignin-derived catalyst is economic, eco-friendly, and promising for green chemical reactions from low-cost feedstocks and may find wide applications.

**KEYWORDS:** Biomass, Lignosulfonic acid, Multicomponent reaction, Benzoxanthenes, Amidoalkyl naphthols



## INTRODUCTION

Multicomponent reaction (MCR) is considered to be a powerful and efficient method for building complex organic molecules and biological relevance molecules due to the formation of carbon–carbon and carbon–heteroatom bonds via a simple tandem synthetic manner (in one-pot reaction) with high atom-economy and high selectivity.<sup>1,2</sup> Xanthenes and benzoxanthene derivatives are an important class of oxygen heterocycles that can be converted into biologically important compounds exhibiting favorable biological and pharmaceutical properties, such as analgesic,<sup>3</sup> antiviral,<sup>4</sup> and antibacterial.<sup>5</sup> Moreover, these compounds can be employed as antagonists in photodynamic therapy,<sup>6</sup> fluorescent dyes,<sup>7</sup> and pH-sensitive fluorescent materials for visualization of biomolecules,<sup>8</sup> and utilized in laser technology.<sup>9</sup> Thus, the synthesis of xanthene derivatives is currently of great importance. Some new methods have been developed to improve the reaction efficiency in the synthesis of benzoxanthene using catalysts such as  $\text{InCl}_3$ ,<sup>10</sup>  $\text{Sr}(\text{OTf})_2$ ,<sup>11</sup> ceric ammonium nitrate (CAN),<sup>12</sup> proline triflate,<sup>13</sup> *p*-TSA,<sup>14</sup>  $\text{NaHSO}_4 \cdot \text{SiO}_2$ ,<sup>15</sup> and ionic liquids.<sup>16</sup> Acid catalysts were frequently used in these multicomponent reactions because they can activate the aldehyde component, enabling the nucleophilic components to react smoothly with the electrophilic site.<sup>17,18</sup> So, in order to facilitate control of the reaction selectivity, catalysts that have mild acidity are generally preferred in the multicomponent reactions of aldehyde. However, some of these reported synthetic procedures

sometimes suffer from undesirable employment of high-toxic organic solvents, harsh reaction conditions, and low yields. Consequently, there is further improvement needed toward more sustainable protocol for the synthesis of xanthene derivatives.

Recently, significant attention has been focused on designing environmentally benign catalysts and synthetic strategies for the construction of various interesting molecules. The green processes generally involve the use of efficient, cost-effective, and biodegradable catalysts; nontoxic systems such as water; and supercritical fluids, and the reactions are under solvent-free conditions. To this end, biopolymers are attractive candidates to create high-performance and environmentally friendly catalysts. Since the sulfonation of incompletely carbonized D-glucose was first reported as a carbohydrate-derived solid acid catalyst by Hara et al.,<sup>19</sup> much effort has been devoted to developing various types of solid acid catalysts from biomass, such as sucrose, cellulose, starch, and bagasse.<sup>20–23</sup> This class of novel catalysts can be used for several reactions including esterification,<sup>21</sup> transesterification,<sup>22</sup> and synthesis of quinolines and xanthenes,<sup>23</sup> and they have shown much better performance than commercially available solid acid catalysts, such as zeolites, Nafion NRS0, and Amerlyst-15.<sup>19–23</sup> Therefore,

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biopolymers will be attractive raw materials for preparing novel catalysts.

Lignin is the second most abundant natural renewable bioresource on Earth. As one of the major noncellulosic components of wood, it is a renewable resource and byproduct of the paper industry. Lignosulfonate (LS) is one of the most important lignin derivatives, which derive from an eluted solution (black liquor) during chemical pulping (sulfite process). As a waste product from the paper industry, LS is also an amphiphilic biopolymer, which has been widely used as a surfactant, an effective adsorbent to remove heavy metals from industrial wastewater, and a supporting material for noble metal for catalysis.<sup>24–26</sup> The sulfonic group of LS is usually introduced into the  $\alpha$ -position of the phenylpropane structure of lignin by cleavage of the side chain and can be obtained from LS by a simple proton-exchanged process (Figure 1).<sup>27</sup> The

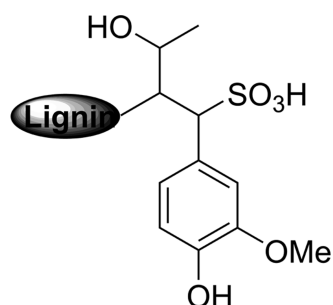


Figure 1. Representative structure of LSA.

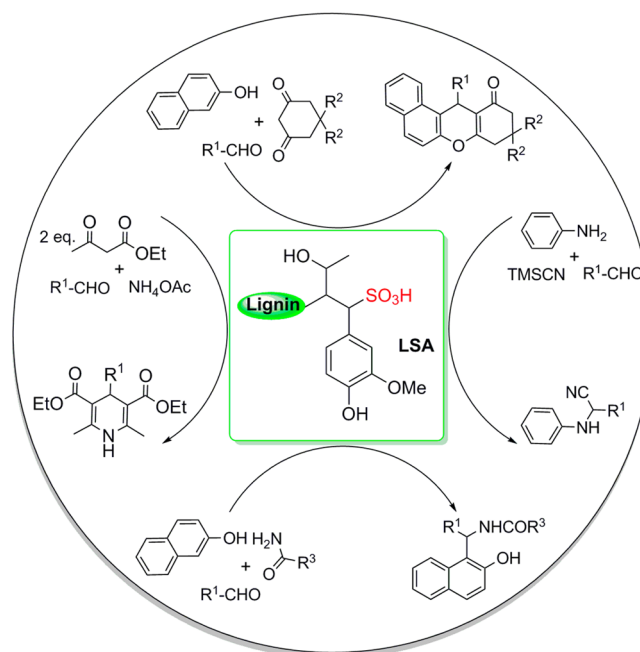
large amount of sulfonic group in lignosulfonic acid (LSA) enables its use as a biopolymer catalyst. However, LSA can be available in large amounts but has not been fully explored. Recently, research demonstrated that LSA can be used as either proton-transfer material for fuel cells or electrochemistry materials.<sup>28,29</sup> The use of sulfonic acid-containing catalysts has also gained increasing attention in organic synthesis due to their unique properties, such as high reactivity, selectivity, availability, eco-friendly reaction conditions, and the ability to promote a wide range of reactions. To our knowledge, little work has been directly carried out about the use of LSA as an acidic catalyst for small organic molecular synthesis. Recently, Xie and co-workers first reported LSA as an acidic catalyst for hydrolysis and dehydration of biomass.<sup>30</sup> Subsequently, they utilized this novel acid catalyst for the condensation of creosol with formaldehyde to synthesize lignin-derived renewable bisphenols.<sup>31</sup> Therefore, the expansion of high-value LSA in the application of organic synthesis is highly desired.

In the present work, we report a simple and efficient procedure for one-pot multicomponent synthesis of benzoxanthene and amidoalkyl naphthols and other important multicomponent reactions, such as the Hantzsch and Strecker reactions using LSA as an effective, neutral, heterogeneous, and reusable acidic catalyst under solvent-free conditions (Scheme 1). The synthesis of this class of compounds by employing LSA as an acidic catalyst has also been rarely reported. The established process represents a new protocol for rational utilization of this waste biomass, which may hold great potential in industrial applications.

## EXPERIMENTAL SECTION

**General Information.** All  $^1\text{H}$  spectra were recorded on a Bruker FT-NMR (400 MHz) spectrometer, and  $^{13}\text{C}$  spectra were recorded on

Scheme 1. LSA Catalyzed for Multicomponent Reactions



a Bruker FT-NMR (100 MHz). NMR chemical shifts are given as  $\delta$  value (ppm) with reference to tetramethylsilane (TMS) as the internal standard. IR spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer using KBr pellets. XRD measurements were carried out at room temperature using a Bruker D8 Advance X-ray powder diffractometer. SEM images were recorded on a Zeiss EVO-18 operating at 10 kV. Element (C, H, and S) analysis was performed on a Vario EI III elemental. All chemicals were purchased from commercial suppliers (Aldrich, U.S.A. and Aladdin Industrial, Inc., China) and used without further purification.

**Preparation of Lignosulfonic Acid (LSA).** The acidic resin was activated in a saturated aqueous solution of NaCl for 1 day, followed by treatment with NaOH solution (4 wt %) for 2 h, and then washing by deionized water until neutral pH. Next, the resin was treated with HCl solution (4 wt %) for 12 h. Then, the resin was transferred to a column and washed with deionized water until neutral pH. The  $\text{H}^+$  form of LSA was prepared by ion-exchange with  $\text{Na}^+$  of LSA-Na. LSA-Na (3.0 g) was dissolved in deionized water (50 mL) by ultrasonic irradiation, and then the solution was allowed to flow through the acidic resin column at a speed of 30 drops per minute. The acidic eluent was collected, and LSA was obtained after freeze-drying the solution for 24 h.

**General Method for Synthesis of Benzoxanthenes.** In a glass tube, a mixture of aldehyde (1.0 mmol), 2-naphthol (1.0 mmol), cyclic 1,3-dicarbonyl compounds (1.2 mmol), and LSA (20 mg) was stirred at 90 °C in an oil bath for 2 h, as indicated by TLC for a complete reaction. Ethyl acetate (10 mL) was added, and the reaction mixture filtered. The solid catalyst was washed with ethyl acetate (10 mL) two times and used for subsequent cycles after drying under vacuum. Pure benzoxanthenes were afforded by evaporation of the solvent, followed by recrystallization from ethanol or by column chromatography on silica gel using ethyl acetate/hexane as the eluent. All the products were characterized by comparison of NMR spectral data with the values of authentic samples.

**General Method for Synthesis of Amidoalkyl Naphthols.** In a glass tube, a mixture of aldehyde (1.0 mmol), 2-naphthol (1.0 mmol), amide (1.2 mmol), and LSA (20 mg) was stirred at 90 °C in an oil bath for 2 h, as indicated by TLC for a complete reaction. Ethyl acetate (10 mL) was added, and the reaction mixture filtered. The solid catalyst was washed with ethyl acetate (10 mL) two times and used for subsequent cycles after drying under vacuum. Pure amidoalkyl naphthols were afforded by evaporation of the solvent followed by

recrystallization from ethanol. All the products were characterized by comparison of NMR spectral data with the values of authentic samples.

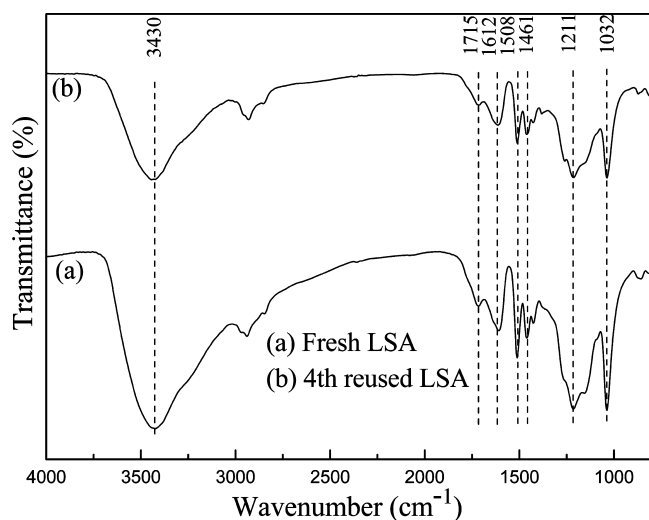
**Synthesis of Diethyl 2,6-Dimethyl-4-*p*-tolyl-1,4-dihydropyridine-3,5-dicarboxylate.** In a glass tube, a mixture of 4-methylbenzaldehyde (1.0 mmol), ethylacetoacetate (2.0 mmol), ammonium acetate (1.5 mmol), and LSA (20 mg) was stirred at 90 °C in an oil bath for 2 h. After completion of the reaction monitored by TLC, the reaction mixture was cooled to room temperature, and ethyl acetate (10 mL) was added and the reaction mixture filtered. The solid catalyst was washed with ethyl acetate (10 mL) two times. The organic layer was concentrated under reduced pressure to get the crude product, which was subjected to crystallization with ethanol. The product was confirmed by NMR spectral.

**Synthesis of 2-(Phenylamino)-2-*p*-tolylacetonitrile.** A mixture of 4-methylbenzaldehyde (1.0 mmol), aniline (1.5 mmol), and LSA (15 mg) was stirred at room temperature for 1 min. Then, TMSCN (1.2 mmol) was added, and the mixture was stirred for another 30 min. When TLC showed completion of the reaction, the reaction mixture was filtered with ethyl acetate (10 mL). The solid catalyst was washed with ethyl acetate (10 mL) two times. The combined organic layer was concentrated under reduced pressure to give the desired product, which was subsequently purified by column chromatography with ethyl acetate and hexane as eluents. The product was confirmed by NMR spectral.

**Recycling Experiment of LSA.** In a glass tube, a mixture of 4-methylbenzaldehyde (1.0 mmol), 2-naphthol (1.0 mmol), dimedone (1.2 mmol), and LSA (20 mg) was stirred at 90 °C in an oil bath for 2 h. After the reaction, ethyl acetate (10 mL) was added to the reaction system to precipitate LSA. The LSA was filtered off and washed with ethyl acetate (10 mL) two times. Then, the recovered LSA was dried under vacuum at 60 °C and directly used for the next run.

## RESULTS AND DISCUSSION

The LSA catalyst was characterized by Fourier transform infrared spectra (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and elemental analysis (EA). The infrared spectra of LSA (Figure 2a) clearly present vibration



**Figure 2.** FT-IR spectrum of fresh LSA (a) and fourth reused LSA (b).

bands at 1032  $\text{cm}^{-1}$  ( $\text{SO}_3^-$  stretching) and 1211  $\text{cm}^{-1}$  ( $\text{O}=\text{S}=\text{O}$  stretching in  $\text{SO}_3\text{H}$ ), which justify the presence of  $\text{SO}_3\text{H}$  groups on the catalyst.<sup>32</sup> The vibration band at 1715  $\text{cm}^{-1}$  indicates the presence of  $-\text{COOH}$  groups. The broad band observed at 3430  $\text{cm}^{-1}$  is assigned to the  $-\text{OH}$  group linked with the neighbor oxygen or sulfuric acid by hydrogen bonds, indicating these acidic groups are located in close proximity.<sup>33</sup>

The vibration bands at 1612, 1508, and 1461  $\text{cm}^{-1}$  are the characteristics of benzene rings.

The loading of the sulfonic group was calculated by acid–base titration and EA. The results are given in Table 1. The

**Table 1.** Acid Density of Catalyst

sample	S content <sup>a</sup> (wt %)	$\text{SO}_3\text{H}$ density <sup>b</sup> (mmol/g)	$\text{SO}_3\text{H}$ density <sup>c</sup> (mmol/g)
LSA	6.3	1.97	1.88

<sup>a</sup>Determined by EA. <sup>b</sup>Calculated from the S content. <sup>c</sup>Determined by acid–base titration.

concentration of  $-\text{SO}_3\text{H}$  determined by titration was about 1.88  $\text{mmol g}^{-1}$ , indicating about 6.0% (w/w) sulfur content in LSA. This result was slightly lower than that determined by EA, suggesting that some of sulfur species were not in the acidic form.

To investigate the feasibility of the synthetic methodology for the one-pot synthesis of benzoxanthene, initial experiments were performed by using dimedone (1.2 mmol) with 4-methylbenzaldehyde (1.0 mmol) and 2-naphthol (1.0 mmol) as substrates at 90 °C under solvent-free conditions. As shown in Table 2, only trace product was detected in the absence of LSA

**Table 2.** Screening of Catalysts for the One-Pot Condensation of Dimedone with 4-Methylbenzaldehyde and 2-Naphthol<sup>a</sup>

entry	catalyst (mol %)	time (h)	yield (%) <sup>b</sup>
1	–	2	trace
2	LSA-Na (20 mg)	2	12
3	LSA (3.8)	2	88
4	LSA (9.4)	2	90
5	LSA (2.8)	2	82
6	LSA (1.9)	2	78

<sup>a</sup>Typical reaction condition: 4-methylbenzaldehyde (1.0 mmol), 2-naphthol (1.0 mmol), dimedone (1.2 mmol), 90 °C, 2 h. <sup>b</sup>Isolated yield.

(Table 2, entry 1). Lignosulfonic acid sodium salt (LSA-Na) produced product with only 12% yield (Table 2, entry 2). However, LSA could increase the yield up to 88% in 2 h (Table 2, entry 3). In addition, the amount of catalyst was also evaluated under otherwise identical conditions. The results show that an increase in the amount of LSA from 3.8 to 9.4 mol % did not lead to significant change in the yield (Table 2, entries 3 and 4); however, if the amount was decreased from 3.8 to 1.9 mol %, the yield decreased from 88% to 78% (Table 2, entries 3 and 5–7). Therefore, 3.8 mol % of LSA was optimal for this reaction.

Under the optimized reaction conditions, a series of aldehydes and cyclic 1,3-dicarbonyl compounds with 2-naphthol were explored in the presence of LSA. The results are summarized in Table 3. The procedure was highly effective for the preparation of benzoxanthene. A variety of aromatic aldehydes with electron-withdrawing and electron-donating substituents reacted smoothly to afford the corresponding products in excellent yields (86–93%). In particular, *n*-butyraldehyde, as a typical aliphatic aldehyde, was tested under the reaction conditions, and the corresponding product was isolated in 82% yield (Table 3, entry 6). On the other hand, both 1,3-cyclohexanedione and dimedone could give good



Table 3. LSA Catalyzed One-Pot Synthesis of Benzoxanthenes<sup>a</sup>

Entry	R <sup>1</sup>	R <sup>2</sup>	Product/1	Yield/% <sup>b</sup>
1	Ph	Me		90
2	4-Me-Ph	Me		88
3	4-MeO-Ph	Me		86
4	4-Cl-Ph	Me		92
5	4-NO <sub>2</sub> -Ph	Me		93
6	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	Me		82
7	Ph	H		89
8	4-Me-Ph	H		87

<sup>a</sup>Typical reaction condition: aldehydes (1.0 mmol), 2-naphthol (1.0 mmol), cyclic 1,3-dicarbonyl compounds (1.2 mmol), LSA (20 mg, containing  $-\text{SO}_3\text{H}$  0.038 mmol), 90 °C, 2 h. <sup>b</sup>Isolated yield.

results (Table 3, entries 7 and 8). Thus, LSA could act as an efficient catalyst for the synthesis of benzoxanthene.

To have a better understanding of the performance of our catalytic system, the effectiveness of the as-prepared LSA was also compared to that of catalysts reported previously for preparation of **1a** from benzaldehyde, 2-naphthol, and dimedone. The results are listed in Table 4. Overall, the yields obtained from LSA are quite close to those from other catalysts (around 90%) except for entry 4. Although some of them have excellent yields, toxic solvent (1,2-dichloroethane, DCE) was used (entries 2 and 6). In the case of immobilized ILs, the yield obtained was as high as that from LSA, but the synthesis of the catalysts is very tedious (entry 7). Therefore, the LSA catalyst system is superior to the other reported systems due to their low cost, biodegradable, renewability.

Amidoalkyl naphthols are also an important class of compounds in the field of drugs and pharmaceuticals.<sup>34,35</sup>

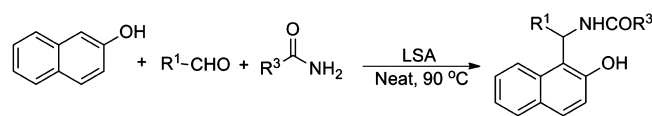
Table 4. Brief Comparison of This Method with Previous Ones for the One-Pot Reaction of Benzaldehyde, 2-Naphthol and Dimedone

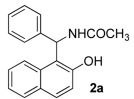
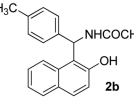
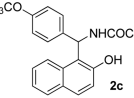
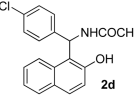
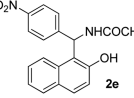
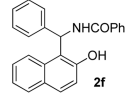
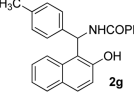
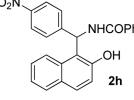
entry	catalyst (mol %)	solvent	temperature (°C)	time (h)	yield (%)	ref
1	InCl <sub>3</sub> (30 mol %)	neat	120	0.5	84	10
2	Sr(OTf) <sub>2</sub> (10 mol %)	DCE	80	5	85	11
3	CAN (5 mol %)	neat	120	0.5	94	12
4	praline triflate (10 mol %)	neat	100	5	79	13
5	<i>p</i> -TSA (10 mol %)	neat	120	0.75	88	14
6	NaHSO <sub>4</sub> ·SiO <sub>2</sub> (100 mg)	DCE	reflux	4	87	15
7	immobilized ILs (1.5 mol %)	neat	90	0.75	89	16
8	LSA (3.8 mol %)	neat	90	2	90	this work

Among them, 1-amidoalkyl-2-naphthol derivatives are of particular value due to their promising biological and medicinal activities.<sup>36,37</sup> One-pot multicomponent condensation of 2-naphthol with aldehydes and amides has been generally used as a practical synthetic route toward amidoalkyl naphthols. Several Lewis and Brønsted acids have been applied to catalyze this transformation.<sup>38–41</sup> Therefore, it is intriguing for us to explore the applicability of LSA as an acid catalyst to promote the preparation of amidoalkyl naphthols.

In this study, we also found that LSA exhibited excellent reactivity for producing 1-amidoalkyl-2-naphthol. The model reaction was carried out by mixing 4-methylbenzaldehyde, 2-naphthol, and acetamide in the presence of 20 mg of LSA under solvent-free conditions. The mixture was stirred at 90 °C for 2 h, and the product was obtained in 87% yield (Table 5, entry 2). Encouraged by this result, we further explored the scope of this transformation by reaction of various aromatic aldehydes with 2-naphthol and acetamide/benzamide. As depicted in Table 5, the aromatic aldehydes bearing both electron-withdrawing and electron-donating groups, such as halogens,  $-\text{NO}_2$ ,  $-\text{CH}_3$ , and  $-\text{OCH}_3$ , proceeded efficiently with 2-naphthol and acetamide and generated the corresponding products in excellent yields (Table 5, entries 1–5). In addition, benzamide was able to undergo the condensation reaction smoothly with substituted aldehydes and 2-naphthol, and good to excellent yields of corresponding products were obtained (Table 5, entries 6–8).

The excellent activity of LSA inspired us to explore its catalytic activity for the Hantzsch reaction and Strecker reaction. Hantzsch 1,4-dihydropyridines (1,4-DHPs) and its derivatives are some of the important bioactive molecules and are known to possess anti-inflammatory, antimicrobial, and antiulcer activities.<sup>42–44</sup> Moreover, the 1,4-DHP class of compounds are excellent starting synthons for development of antitubercular agents.<sup>45</sup> Thus, the Hantzsch reaction was still the most facile and simple method to prepare the nitrogen heterocyclic compounds. Acid-catalyzed addition of cyanide anion to imines (Strecker reaction), a well-known reaction for the synthesis of  $\alpha$ -amino nitriles, provided one of universal strategies for the synthesis of amino acids and other bioactive ingredients.<sup>46</sup> For 1,4-DHP synthesis, the condensation reaction between 4-methylbenzaldehyde, ethylacetoacetate, and ammonium acetate under solvent-free conditions produced product **3** with 90% yield (Scheme 2), while the Strecker reaction between 4-methylbenzaldehyde, aniline, and TMSCN

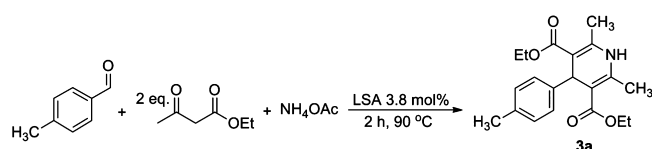
**Table 5. LSA Catalyzed One-Pot Synthesis of Amidoalkyl Naphthols<sup>a</sup>**


Entry	R <sup>1</sup>	R <sup>3</sup>	Product/2	Yield/% <sup>b</sup>
1	Ph	Me		89
2	4-Me-Ph	Me		87
3	4-MeO-Ph	Me		84
4	4-Cl-Ph	Me		90
5	4-NO <sub>2</sub> -Ph	Me		91
6	Ph	Ph		90
7	4-Me-Ph	Ph		86
8	4-NO <sub>2</sub> -Ph	Ph		92

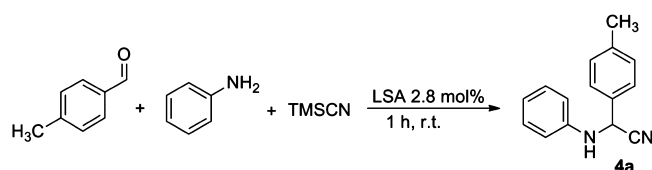
<sup>a</sup>Typical reaction condition: aldehydes (1.0 mmol), 2-naphthol (1.0 mmol), amides (1.2 mmol), LSA (20 mg, containing  $-\text{SO}_3\text{H}$  0.038 mmol), 90 °C, 2 h. <sup>b</sup>Isolated yield.

at room temperature provided product 4 with 92% yield (Scheme 3).

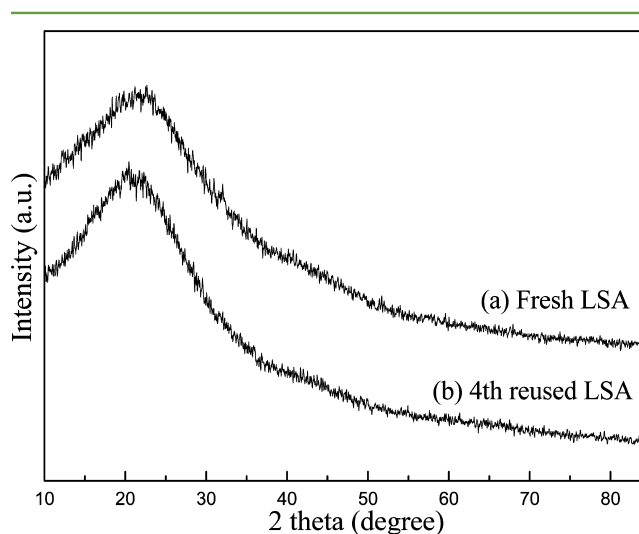
### Scheme 2. LSA Catalyzed for Hantzsch Reaction



### Scheme 3. LSA Catalyzed for Strecker Reaction



The structural characteristic of the recovered catalyst was checked by FT-IR (Figure 2b), XRD (Figure 3b), and SEM



**Figure 3.** XRD patterns of fresh LSA (a) and fourth reused LSA (b).

(Figure 4b). As shown in Figure 2b, the fourth reused LSA exhibited a similar FT-IR spectrum to that of the fresh LSA in terms of the characteristic peaks, indicating that the reuse of LSA did not change the original structure of fresh LSA.

XRD analysis of fresh LSA and recycled LSA after four cycles was performed, and the results are presented in Figure 3. There is a broad diffraction peak at  $2\theta = 20\text{--}25^\circ$  assigned to the amorphous LSA in Figure 3a. As shown in Figure 3b, the broad diffraction peak is virtually unchanged after reuse, indicating that the reuse of LSA did not change the crystallographic property of the LSA scaffold.

SEM images of LSA before and after recycling were also investigated and are shown in Figure 4. The as-prepared LSA showed a smooth surface and irregular flake morphology with a range in size from about 2 to 40  $\mu\text{m}$  (Figure 4a and b). As illustrated in Figure 4c and d, no significant change occurred in the morphology of recycled LSA. The above results indicate the stability of LSA in the reaction system.

The recyclability and reusability of catalysts are highly preferable for a green process. After establishing the activity and versatility of the LSA catalyst for a variety of reactions, the reusability of the catalyst was investigated by using 4-methylbenzaldehyde, 2-naphthol, and dimedone as model substrates under the aforementioned conditions. In each cycle, the catalyst was easily recovered by filtration after the reaction, washed with ethyl acetate, and finally dried at 60 °C under vacuum. The procedure was repeated, and the results indicated that the catalyst could be reused up to four times with a slight loss of the initial catalytic activity (Figure 5).

Moreover, the loading amount of the recycled (four times) catalyst was determined by acid–base titration method, and it was found that reused LSA still contained 1.79  $\text{mmol g}^{-1}$  of the  $\text{SO}_3\text{H}$  group (1.88  $\text{mmol g}^{-1}$  for the fresh catalyst). These results revealed that the catalyst was stable and could endure these reaction conditions. Overall, LSA as a renewable acidic catalyst and showed better performance in these multi-component reactions not only in terms of activity but also with regard to recyclability.

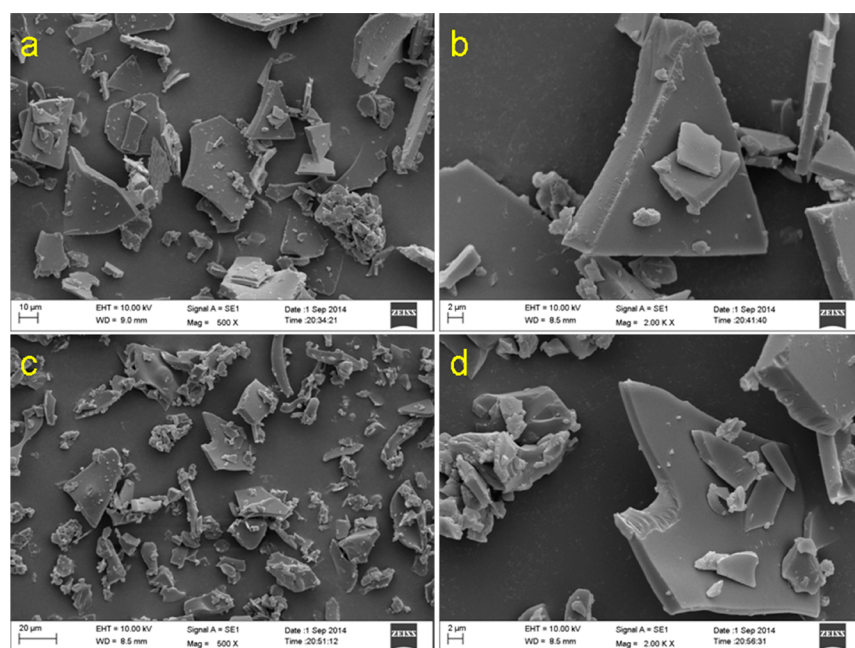


Figure 4. SEM spectra of fresh LSA (a, b) and fourth reused LSA (c, d).

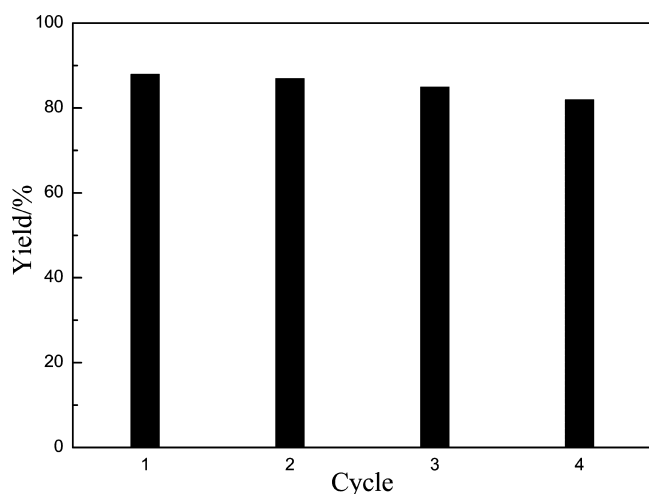


Figure 5. Recycling experiment of LSA.

## CONCLUSIONS

In summary, the present work was the first report on using LSA as a novel and very promising solid acid catalyst for some one-pot multicomponent reactions, such as benzoxanthene and amidoalkyl naphthols synthesis, Hantzsch reaction, and Strecker reaction. This biopolymer solid acid catalyst was prepared by a simple procedure using waste byproduct from the paper industry. In addition, the catalyst could be easily recovered by simple filtration and reused for several cycles without significant loss of catalytic activity. Further applications of this catalyst are currently under investigation in our laboratory.

## ASSOCIATED CONTENT

### Supporting Information

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic and analytical data of the obtained compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00091.

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### Notes

The authors declare no competing financial interest.

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