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Novel carbon-based strong acid catalyst from starch and its catalytic activities for acetalization

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Abstract The novel carbon-based strong acid catalyst has been synthesized through the simple heat treatment of 2-hydroxyethylsulfonic acid and starch. The novel solid acid owned the high acidity of 2.6 mmol/g, much higher than that of the traditional solid acids such as Nafion and Amberlyst-15 (0.8 mmol/g). The catalytic activities of the novel carbon-based acid were investigated through the acetalization reactions. The results showed that the novel solid acid was very efficient for the reactions with high yields. The high acidity and catalytic activities made the novel solid acid hold great potential for the green chemical processes.

Introduction

With the development of green chemistry, solid acid catalysts received much attention for the green catalytic procedures with the advantages of easy separation and reusability [1–7]. Although many solid acids have been developed for the replacement of the unrecyclable liquid acids, a major obstacle to such progress is the lack of a solid acid that is as active, stable, and inexpensive as sulphuric acid. Also, the low acidity of the heterogeneous catalysts affected the catalytic activities greatly, which made the substitution of the homogeneous catalysts difficult in most conditions [8, 9]. Recently, carbon-based solid acids attracted much attention for the high acidity and catalytic activities [10–12]. The novel solid acid catalysts were generally prepared through two steps. In the first step, the carbonization of biomass such as sugar was carried out to form the polycyclic aromatic carbon sheets. Then the aromatic carbon sheets were sulfonated to introduce the sulfonic acid groups. The carbonization process was taken at high temperature for long time and large amount of wastes were produced during the process, which resulted in serious pollution. Although the surface activation of carbon materials is now a well-established process, it is a rather harsh method because of the extremely low reactivity, and adds another step to the synthesis of functional carbon. Efficient procedure for the synthesis of carbon-based solid acid through one-step hydrothermal carbonization was developed in the previous work [13, 14]. However, the hydrothermal carbonization was carried out at high pressure (13 MPa), which made the process quite dangerous for industrial production. Here the novel facile procedure has been developed for the synthesis of the carbon-based solid acid. The novel carbon-based solid acid was synthesized through the heat treatment of 2-hydroxyethylsulfonic acid and starch. Here hydroxyethylsulfonic acid acted as the bifunctional molecules to catalyze the carbonization of starch and introduce the SO_3H groups. Generally, the carbonization occurred quickly when sugars mixed with sulphuric acid and the carbon with inactive surface was formed, which made the sulfonation difficult to introduce enough acid sites. Unlike sulphuric acid, 2-hydroxyethylsulfonic acid was mild without dehydration ability. The carbonization catalyzed by hydroxyethylsulfonic acid took place slowly and the hydroxyl groups involved in the carbonization reactions could introduce the sulfonic acid groups to the carbon products. The catalytic activities of the novel carbon-based solid acid were investigated

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through the acetalization. The results showed that the novel carbon-based solid acid was very efficient for the reactions.

Experimental

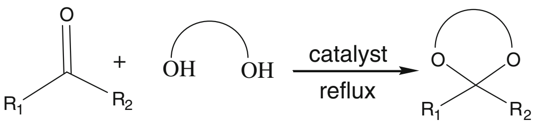
All organic reagents were commercial products of the highest purity available (>98%) and used for the reaction without further purification. GC measurements were taken on a Shimadzu (GC-14B) gas chromatograph. GC–MS measurements were performed on an American Agilent 6890/5973 N instrument. The IR were taken on the NEXUS 670 FT–IR from Nicolet corporation, USA. The NH_3-TPD were taken on CHEMBET 3000 from Quantachrome Corporation. The SEM were taken on S-4800 cold field emission scanning electron microscope measurement from Hitachi Japan.

Synthesis of the novel carbon-based solid acid

In typical procedure: The starch (2 g) and 2-hydroxyethylsulfonic acid (2 g) were mixed together and transferred to the quartz furnace. The mixture was heated to 180 °C from room temperature with the heating rate of 1 °C/min and remained at 180 °C for 4 h under nitrogen atmosphere. After cooling to room temperature, the obtained black solid was washed with water until no acidity detected in the filtrate. The novel solid acid was obtained after drying at 120 °C overnight in an oven.

Preparation of acetals and ketals

The typical procedure (Scheme 1): An aldehyde or ketone (0.1 mol), 10 mL cyclohexane, a diol (0.15 mol) and the catalyst (0.05 g) were mixed together in a three necked round bottomed flask equipped with a magnetic stirrer and a thermometer, and a Dean-Stark apparatus which was constituted with manifold and condenser was used to remove the water continuously from the reaction mixture. The process of the reaction was monitored by GC analysis of the small aliquots withdrawn at half an hour intervals. On completion, the catalyst was recovered by filtering and washing with acetone, then dried in an oven at 80 °C for about 1 h.



Scheme 1 Catalytic acetalization of carbonyl compound

Result and discussion

Characterization of the novel catalyst

The acidity of the novel carbon-based solid acid was 2.6 mmol/g, which was determined through the neutralization titration. The catalyst owned much higher acidity than that of the common heterogeneous acid catalysts such as Nafion and Amberlyst-15 (0.8 mmol/g). The acid strength of the catalyst was determined by thermodesorption of chemisorbed ammonia (NH_3-TPD). The result showed that the solid acid had strong acidity in which ammonia was desorbed at 400–600 °C. The elemental analysis gave the results: C 74.6%; H 4.3%; S 8.3%; O 12.8%. The results indicated that the almost all the element S existed in the catalyst in the form of sulfonic groups. The IR spectrum of the carbon-based solid acid showed the sulfonic group absorption at 1060 cm^{-1} which confirmed the existence of the sulfonic groups (Fig. 1). FT–IR spectrum also showed that the solid acid contain resident functionalities including C=C (1580 cm^{-1}), C–C (1250 cm^{-1}), and OH (3400 cm^{-1}).

The SEM images of the novel carbon-based solid acid show that the resulting particles owned irregular structure with the particle sizes of 2–10 μm, which also indicated the easy recycle of the solid acid. The particles connected with each other without the obvious boundaries. Figure 2 also shows some pores in the materials, which might caused by the emission of the small gas molecules during the carbonization process.

Catalytic procedure for the synthesis of acetals and ketals

The catalytic activities of the novel carbon-based solid acid was investigated through the acetalization of various carbonyl compounds and diols first (Table 1). As was

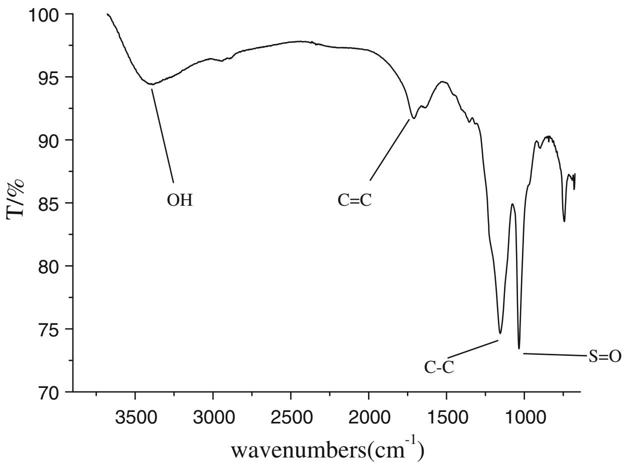


Fig. 1 The IR spectrum of the novel carbon-based solid acid

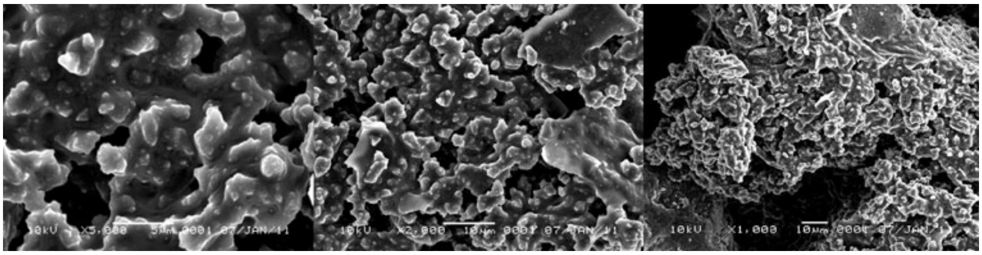


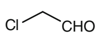
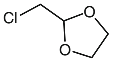
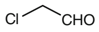
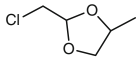
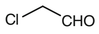
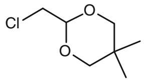
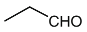
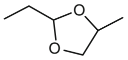
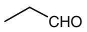
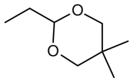
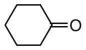
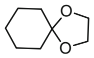
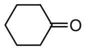
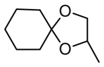
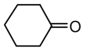
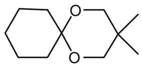
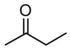
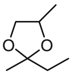
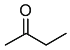
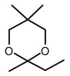
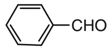
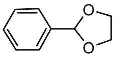
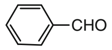
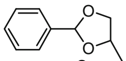
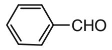
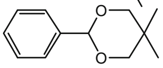
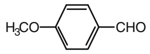
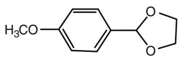
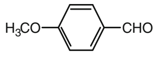
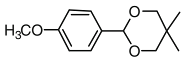
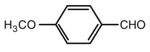
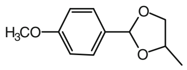
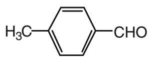
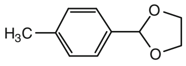
Fig. 2 The SEM images of the novel carbon-based solid acid

anticipated, all carbonyl compounds were successfully transformed to the corresponding products. The results in Table 1 clearly demonstrated that the novel carbon-based solid acid was very efficient with high yields for most reactions. Aliphatic aldehydes transformed to the corresponding acetals smoothly under the reaction conditions (entries 1–5). The ketalization reactions were also examined over the system. Cyclohexanone was worked very well with almost complete conversion for the low steric hindrance of the carbonyl group (entries 6–8). The linear chain ketones such as butanone owned relatively low activity for the reactions with moderate yields (entries 9–10). Aromatic aldehyde, such as benzaldehyde could also be acetalized to afford the corresponding 1,3-acetal with high yields (entries 11–13). The groups attached to the aromatic ring also attached much importance to the reactivities. The aromatic aldehydes with electron-donating groups such as methyl or methoxyl groups showed relatively low activity, which reduced the reactivities of the carbonyl groups (entries 14–19). On the other hand, electron-withdrawing groups enhanced the reactivities and the aromatic aldehydes with F and nitro groups showed higher activities (entries 20–23). Different diols such as 1,2-ethanediol, 1,2-propylene glycol, and neopentyl glycol were all transformed to the acetals smoothly. The conversions reduced as follows: 1,2-ethanediol >1,2-propylene glycol > neopentyl glycol for the steric hindrance of the diols.

The comparison of the catalytic activities

A comparative study on the catalytic activities of the novel catalyst with the reported catalysts were taken through the reaction between benzaldehyde and 1,2-ethanediol (Table 2). Amberlyst-15 was obtained from Fluck Company with the acidity of 0.8 mmol/g. The results showed that the novel catalyst owned higher activity than the traditional carbon-based solid acid produced through the sulfonation of the incomplete carbonized carbon sheet [12]. The facile synthesis procedure made the novel catalyst better choice for the industrial application. The novel catalyst showed much better activity than that of the homogeneous catalyst PTSA and the widely-used Amberlyst-15. So the novel catalyst held great potential for the green chemical processes.

Table 1 The acetalization of various carbonyl compounds and diols

Entry	Substrate	Product	Reaction time/h	Yield/% $^{a, b}$
1			0.5	99
2			0.5	99
3			1.0	99
4			1.0	99
5			1.5	99
6			1.0	99
7			1.0	99
8			1.5	98
9			2.5	94
10			3.5	90
11			2.0	95
12			2.0	94
13			3.5	92
14			2.5	92
15			4.5	88
16			3.5	90
17			2.5	93

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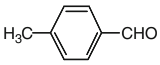
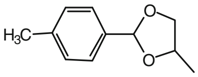
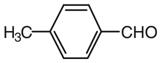
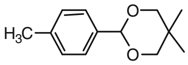
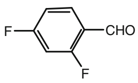
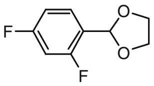
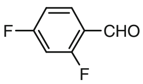
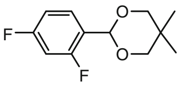
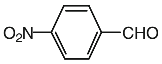
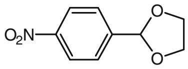
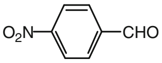
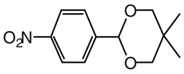
18			3.5	91
19			4.0	89
20			1.0	98
21			2.5	93
22			2.0	95
23			2.5	93

[a] All reactions were carried out under Dean–Stark conditions

[b] The conversion and selectivity were determined by GC using an internal standard method based on carbonyl compounds. In all cases, the corresponding products were exclusively obtained

Table 2 The activity comparison of different catalysts

Entry	Catalyst	Catalyst amount/g	Time/h	Yield/%[a,b]
1	Novel catalyst	50	1.0	95
2	H_2SO_4	50	3.0	93
3	PTSA	60	3.5	90
4[12]	Carbon-based acid	100	3.0	90

[a] All reactions were carried out under Dean–Stark conditions

[b] The conversion and selectivity were determined by GC using an internal standard method

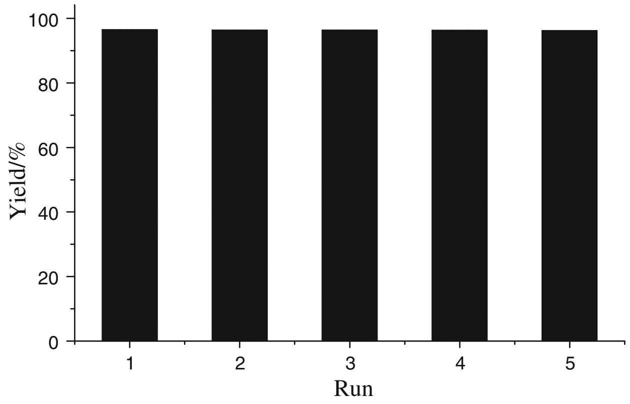


Fig. 3 The reuse of the catalyst for the acetalization reaction of benzaldehyde with 1,2-ethanediol

The reuse of the catalyst

One property of the catalyst is heterogeneous catalytic process. Thus, the recovery of catalysts is very convenient. After reactions, by cooling the reaction mixture to room temperature, the catalyst was recovered by filtration. The recycled activity of the catalyst was investigated through the acetalization of benzaldehyde and 1,2-ethenediol carefully (Fig. 3). The results showed the high stability of the catalyst. The yields of the acetalization reaction remained unchanged even after the sample had been recycled for a fifth time**.** The sample composition of the novel catalyst remained after recycled for five times according to the results of the element analysis. Also, the recycled filtrate showed almost no activity for the reactions, which further confirmed the stability of the novel carbon-based solid acid.

Conclusion

The novel carbon-based solid acid has been synthesized through the simple heat treatment of hydroxyethylsulfonic acid and starch. The novel process was more environment-friendly in the mild condition with little waste emission and high yield. The catalyst showed high activities for the acetalization with the average yield over 90%, large-scale applicability, and good reusability. The catalyst owned the advantages of high acidity, low cost and high thermal and chemical stability, which made the novel heterogeneous catalyst hold great potential for the replacement of the homogeneous catalysts in the green process. The mild synthesis condition not only reduced the cost of the novel carbon-based solid acid, but also made the industrial production possible.

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