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ORIGINAL PAPER

One-step synthesis of a novel carbon-based strong acid catalyst through hydrothermal carbonization

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Abstract A novel carbon-based strong acid catalyst was synthesized through the one-step hydrothermal carbonization of furaldehyde and *p*-toluenesulfonic acid (PTSA) in aqueous solution at 180 °C for only 4 h. The novel carbon-based solid acid possessed high acidity, and the catalytic activities were investigated by esterification and oxathioketalization. The results showed that the novel catalyst demonstrated much greater activity than the traditional solid acids and was comparable to sulfuric acid. The one-step method provides an efficient procedure for the synthesis of various functionalized carbons by one-step hydrothermal carbonization.

Keywords Acidity · Catalysis · Green chemistry · Carbon-based acid catalyst · One-step synthesis

Introduction

Acid-catalyzed reactions are very important in chemical processes. Over 15 million tons of sulfuric acid is annually consumed as an unrecyclable catalyst, which requires costly and inefficient separation of the catalyst from homogeneous reaction mixtures [1–7]. Many solid acid catalysts have been developed for the replacement of the unrecyclable homogeneous acids. However, a major obstacle to such progress is the lack of a solid acid that is as active, stable, and inexpensive as sulfuric acid. Recently, carbon-based solid acid catalysts have increasingly attracted attention [8–10]. The materials were generally synthesized via two steps. First, saccharides were incompletely carbonized at high temperature (>400 °C) under inert atmosphere for a long time. This was not an environmentally friendly process, had low yields, and numerous harmful wastes were formed. Then sulfonation took place to introduce the sulfonic acid groups in the second step. The sulfonation procedure was also carried out in harsh conditions for the inactive surface of the carbonaceous materials. Furthermore, the separation of the carbon materials from the concentrated sulfuric acid was tedious work. Hydrothermal carbonization, which involved the hydrothermal decomposition of various carbohydrates in aqueous solutions at 180 °C, has the advantage of being very cheap, mild, and absolutely "green" as it involves no organic solvents, catalysts, or surfactants [11]. However, the carbonaceous materials from this procedure had few functional groups, and a subsequent chemical or steam activation had to be applied for certain purposes [12]. The conventional modification of the carbon surface involves treatment with acids or ozone, thereby generating functionalities such as carboxylic acids, esters, or quinines [13]. 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. Furthermore, corrosion of the carbon surface often occurs during the treatment [14]. Hydrothermal carbonization was used for the preparation of carbon-based solid acid in our previous work [15]. The material was obtained via two steps, and sulfonation was carried out under tedious conditions. Here a novel carbon-based acid has been synthesized via one-step hydrothermal carbonization of furaldehyde and *p*-toluenesulfonic acid (PTSA) in aqueous solution at 180 °C for only 4 h. The

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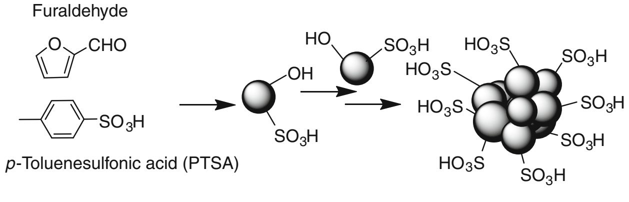
catalytic activities of the novel carbon-based acid were investigated via esterification and oxathioketalization. The results showed that the novel solid acid possessed comparable activities to sulfuric acid.

Results and discussion

Characterization of the novel catalyst

The sulfonic acid groups were attached to the carbonaceous material during the carbonization process (Scheme 1). The formation of the novel carbonaceous material involves the dehydration of furaldehyde and PTSA as the first step. Upon subsequent dehydration (polymerization), microscopic carbon-containing spheres with sulfonic acid and hydroxyl groups were formed. Subsequent loss of water by these assemblies leads to further coalescence of microscopic spheres (Scheme 1) [16]. Here, PTSA was used as the functional molecule to introduce the sulfonic acid groups to the carbonaceous material, which had an aromatic ring for the intermolecular reaction with furaldehyde. The acidity of the novel sulfonic acid groups functionalized carbonaceous material was 1.8 mmol/g, which was determined through neutralization titration. The titration was carried out as follows: carbonaceous material (40 mg) and 2 N aqueous NaCl (4 cm^3) were stirred at room temperature for 24 h. The solids were filtered off and washed with water (4 × 2 cm^3). The combined filtrate was titrated with 0.01 N NaOH using phenol red as indicator [17]. The catalyst had much higher acidity than the sulfonated carbonaceous materials, which were obtained via the sulfonation of the subsequent inactive surface of the carbon. The acid strength of the catalyst was determined by thermodesorption of chemisorbed ammonia (NH_3-TPD). The result showed that the catalyst had great acid strength in which ammonia was desorbed at 400–600 °C. The BET surface of the material was 125 m^2/g, which was much higher than the sulfonated carbonaceous materials (2 m^2/g). Furthermore, the acidity of the carbon could be adjusted through the molar ratio of furaldehyde and PTSA. The sulfonic acid groups increased with the PTSA.

The IR spectrum of the novel carbon-based acid is shown in Fig. 1. The absorbance at 1,040 cm^{-1} confirmed the existence of the sulfonic acid groups. Also, the FT-IR spectrum showed that the carbon materials contain resident functionalities including carboxylate (1,704 cm^{-1}), =C–H (740 cm^{-1}), C–O groups (1,204 cm^{-1}), –OH groups (3,400 cm^{-1}), S–O groups (978 cm^{-1}), and C=C groups (1,604 cm^{-1}).



Scheme 1

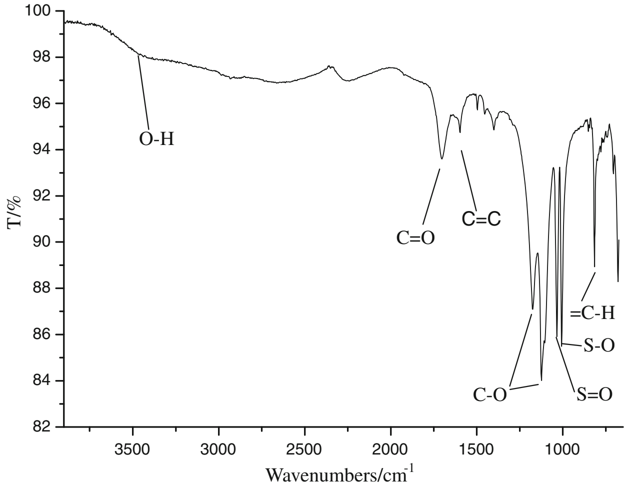


Fig. 1 IR spectrum of the novel carbon-based acid

The SEM images of the novel carbon-based acid show that the resulting particles grow in size with the reaction time with a diameter of 2–4 μm as depicted in Fig. 2. Figure 2 shows the morphologies of the materials as micrometer-sized microporous carbon spheres, and many micro-sized carbon spheres were assembled together to form big carbon spheres (Fig. 2a). The carbonaceous material obtained from only furaldehyde formed carbon spheres with smooth surfaces (Fig. 2d). The addition of PTSA induces a change in the particle morphology: the surface of the particles is no longer smooth, and the microspheres indicate that they are formed out of small aggregated particles. PTSA appears to stabilize the first formed small droplets, thus preventing them from further growth, as might occur in the case of pure furaldehyde.

Catalytic activities for the esterification of acetic acid and butanol

The novel carbon-based acid (C–SO_3H) was applied to catalyze the esterification of acetic acid and butanol first (Fig. 3). For comparison, the results for concentrated sulfuric acid, zeolite (HY), Amberlyst-15, and the carbonaceous materials from only furaldehyde (carbon) are also shown. HY zeolite is an inorganic solid acid that exhibits only low activity in low acidity, whereas Amberlyst-15 exhibits high activity in the reaction. Amberlyst-15, with an acidity of 0.8 mmol/g and a BET surface of 35 m^2/g, was purchased from Fluka. The lower acidity and BET surface resulted in lower activity than the novel carbonaceous

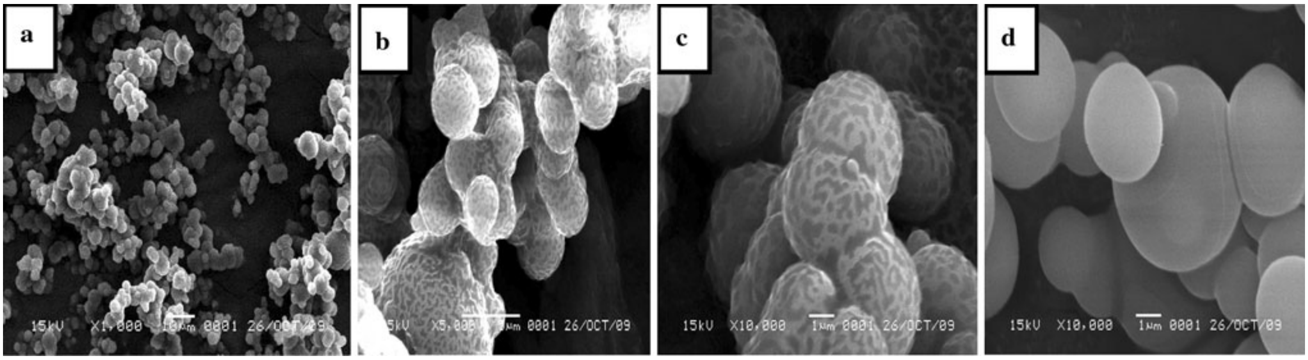


Fig. 2 SEM images of the carbonaceous materials

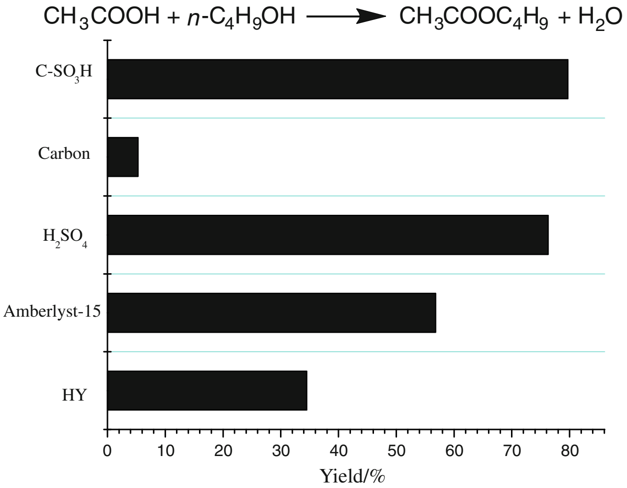


Fig. 3 Catalytic activities for esterification. Reaction conditions: butanol, 20 mmol; acetic acid, 24 mmol; catalyst, 50 mg, 25 °C, 7 h

material. The carbonaceous material obtained from single furaldehyde (carbon) showed almost no activity for few functionalities on the surface. The novel carbonaceous material (C–SO_3H) exhibited a remarkably high activity for the formation of butyl acetate. The activity is much higher than that of the conventional solid acids and is comparable to sulfuric acid.

The reusability of the carbonaceous material was carefully investigated for the reaction. After the reaction had reached equilibrium (7 h), the novel carbon-based acid was simply recovered by filtration and recycled for further reaction. It was confirmed that the activity remained unchanged, even after the carbonaceous material had been recycled four times (Fig. 4).

Catalytic activities of the oxathioketalization of cyclohexanone and mercaptoethanol

Besides the esterification, Fig. 5 also shows that the novel carbonaceous material rivals sulfuric acid in the oxathioketalization of cyclohexanone and mercaptoethanol. The obvious differences between the carbon and C–SO_3H also indicated the well-functioning surface of the novel carbon-based acid. Also, the activity remained unchanged, even after the catalyst had been recycled for a fourth time. These results indicated that the novel carbonaceous material had high activity and good stability. Since many industrially important chemicals such as alcohols, esters, ethers, and acetals are produced by such reactions in the presence of a sulfuric acid catalyst, the comparable performance of the novel carbon-based acid to sulfuric acid indicated by the present results demonstrates that it has great potential to replace sulfuric acid for green processes. Furthermore, the synthetic condition assured the high hydrothermal stability of the novel carbonaceous material, which greatly enlarges its application areas.

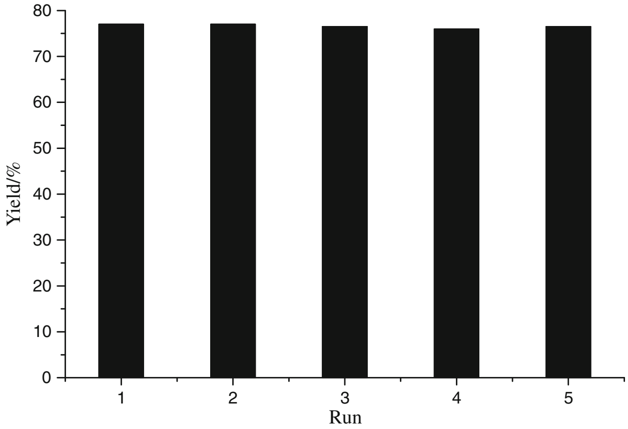


Fig. 4 Reusability of the carbonaceous material for esterification

Conclusion

The novel carbon-based acid catalyst was synthesized via one-step hydrothermal carbonization of furaldehyde and PTSA under mild conditions. The material demonstrated

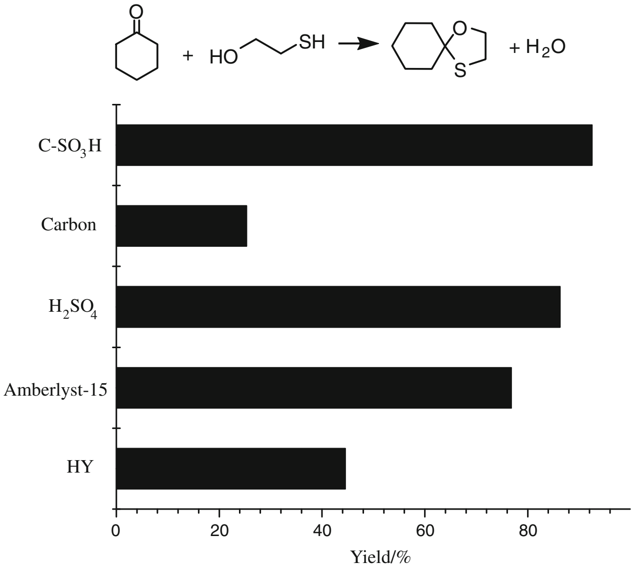


Fig. 5 Catalytic activities of oxathioketalization. Reaction conditions: cyclohexanone, 20 mmol; 2-mercaptoethanol, 24 mmol; catalyst, 50 mg, 25 °C, 2.5 h

high acidity and showed comparable activity to sulfuric acid for the traditional acid-catalyzed reactions, which indicated that the novel carbonaceous material has great potential to replace the sulfuric acid catalyst for green chemical processes. Furthermore, the novel "copolymerization" methodology also provided an efficient procedure for the synthesis of variously functioning carbonaceous materials via one-step hydrothermal carbonization of selected compounds for certain purposes.

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 6890/5973N instrument.

Synthesis of the catalyst

A mixture of 10 g furaldehyde, 5 g PTSA, and 80 cm^3 deionized water was placed in 100-cm^3 Teflon-lined stainless steel autoclaves and heated in an oven at 180 °C for 4 h. The resulting products were filtered, washed with water and methanol, and dried in a vacuum oven at 100 °C for 4 h.

The esterification of acetic acid and butanol

A mixture of acetic acid (24 mmol), butanol (20 mmol), and the catalyst (50 mg) was stirred at room temperature (25 °C). The process of the reaction was monitored by GC analysis as below.

The oxathioketalization of cyclohexanone and mercaptoethanol

Cyclohexanone (20 mmol), mercaptoethanol (24 mmol), and the catalyst (50 mg) were mixed. The mixture was stirred at room temperature (25 °C) for the specified period. The process of the reaction was monitored by GC analysis of the small aliquots that were withdrawn. On completion, the catalyst was recovered by filtering and washing with acetone, then dried in an oven at 80 °C for about 1 h.

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