Journal of Materials Science and Chemical Engineering, 2014, 2, 4-8
Published Online June 2014 in SciRes. http://www.scirp.org/journal/msce
http://dx.doi.org/10.4236/msce.2014.26002

Preparation of a Carbon-Based Solid Acid with High Acid Density via a Novel Method

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Received February 2014

Abstract

A carbon-based solid acid with high acid density was successfully prepared using camphor tree branches as raw materials through a novel method including dilute sulfuric acid activation, carbonization in refluxing solvent and sulfonation. Physical characterization was detected to show that the carbon-based acid is amorphous with polycyclic aromatic carbon sheets attached plentiful -OH, -COOH, and -SO_3H groups. The sulfonic acid density and total acid density of it reached 2.05 mmol·g^{-1} and 5.63 mmol·g^{-1}, respectively by acid-base titration. As a solid acid catalyst, it showed excellent performance in the ketalization of cyclohexanone with glycol.

Keywords

Solid Acid Catalysts, Preparation, Biomass, Ketalization

1. Introduction

With the development of green chemistry, solid acid catalysts have received much attention for green catalytic procedures with advantages of no pollution, easy separation and reusability. However, compare with the catalytic activities of traditional protonic acids such as H_2SO_4 etc., that of the solid acid catalysts were always not good enough mostly because of the lower acid density and strength. For decades researchers in this field around the world have been committed to improve the acid density and strength as well as the stability of solid acids. In recent years a sulfonated (SO_3H-bearing) carbon-based solid acid has been reported to be an efficient solid acid catalyst for many acid-catalyzed reactions [1-3]. This kind of solid acid was usually prepared via carbonization and sulfonation reaction using renewable biomass resources as carbon sources [4,5]. Their good catalytic activity also showed in catalyzing some special significant reactions like biodiesel production [6-9] and hydrolysis of cellulose [10-12]. It must be one of the most important alterative for H_2SO_4 in future chemical industry. Though it is, there is still a long way to make it be an efficient and stable solid catalyst for industry application.

In this paper, we report a novel method to synthesize a carbon-based solid acid catalyst with high density of sulfonic acid groups via solvent refluxing carbonization using camphor tree branches as raw materials. As acetalization reaction is a very important reaction in organic synthesis to protect the carbonyl group [13,14] and synthesis of steroids, pharmaceuticals, and fragrances [15,16], catalytic performances of the obtained catalyst was

How to cite this paper: Ouyang, S.Y., *et al.* (2014) Preparation of a Carbon-Based Solid Acid with High Acid Density via a Novel Method. *Journal of Materials Science and Chemical Engineering*, **2**, 4-8.
http://dx.doi.org/10.4236/msce.2014.26002

detected in catalyzing the ketalization of cyclohexanone with glycol.

2. Experimental

2.1. Reagents and Materials

The fallen branches from camphor trees were picked up as raw materials for the catalyst preparation. They were washed, dried and cut to be granules. Oleum (50 wt%SO_3) was purchased from Zhenxing Chemical Regent Ltd. Co. (Shanghai, China, AR). Other reagents (AR) were from local suppliers.

2.2. Preparation Process

The catalyst was prepared as follows: 4 g camphor tree branch was immersed with 8 g 10% sulfuric acid in a 100 ml flask for 24 h. Then 5 ml toluene was added and the mixture was refluxing for 20 h at appointed temperature to give a black carbonaceous solid. The solid was filtered and washed in boiling water for 3 h to get rid of residual sulfuric acid and toluene. The obtained camphor tree branch char denoted as CC. The CC (2 g) was immersed in 16 g oleum (50 wt%SO_3) at 80˚C for 3 h. After sulfonation, the suspension was cool to room temperature and filtered to yield a black precipitate. Finally, the resulting black solid was washed repeatedly with hot distilled water (>80˚C) until impurities such as sulfate ions were no longer detected in the wash water, and then dried completely to obtain sulfonated camphor tree branch char, which denoted as CC-SO_3H in this paper.

2.3. Catalyst Characterization

Samples before and after sulfonation were characterized to know the structures of CC and CC-SO_3H and changes happened during the sulfonation process. BET surface area and pore structure were determined by N_2 adsorption and desorption at 77 K using a TriStar 3000 after the samples were degassed in vacuum at 130˚C overnight. X-ray powder diffraction (XRD) analysis was conducted on DANDONG Y-2000 X-ray Diffractometer using Cu K_a radiation with a voltage of 40 kV. Fourier transform infrared spectrums (FT-IR) of the samples were recorded in the range 400 - 4000 cm^{-1} on a Nicolet Avatar 370 FT-IR spectrometer using KBr pellets. Total acid density and sulfonic acid density of CC-SO_3H were tested by acid-base titration following the reference [11].

2.4. Catalytic Reaction

The typical procedure: A cyclohexone (0.05 mol), 8 mL cyclohexane, ethylene glycol (0.08 mol) and CC-SO_3H (dosage seen **Table 2**.) were mixed together in a three necked round bottom 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 products were analyzed by a gas chromatograph (Agilent 6890N, FID detector) to show cyclohexanone conversion and ketal selectivity.

In order to investigate the reusability of CC-SO_3H, the used catalyst was collected, washed with ethanol, and dried for the next reaction. In the recycling reaction, catalyst dosage was 0.02 g, and the other conditions were not changed.

3. Results and Discussions

3.1. Catalyst Characterization

Textures of CC and CC-SO_3H were characterized by Nitrogen adsorption and desorption. BET surface area, total pore volume and BJH average pore size of CC and CC-SO_3H were given in **Table 1**. Though surface areas of both samples were not large, it was lager after a sulfonation procedure.

Figure 1 showed XRD patterns of CC and CC-SO_3H. Typical crystal diffraction peaks were not seen, and the width and weak diffraction peak at 10˚ - 30˚ in both patterns implied the structures of both samples were amorphous. The process of carbonization of biomass is sophisticated, especially in the presence of sulfuric acid, and many reactions would occur. The cellulose and hemicellulose chains of camphor tree branches may dehydrate. Lignin may polymerize or rearrange. Crystal structure decomposed and amorphous hydrocarbon structure was detected. The diffraction peak at 16, 22, and 25 in the pattern of CC assigned to characteristic diffraction

peaks of crystalline cellulose were still visible, which implied an incomplete carbonization.

FT-IR analysis helps to identify the carbon skeleton structure and groups attached on it. **Figure 2** showed the IR spectrum of the samples. Infrared spectra of samples in 1605 cm^{-1} - 1460 cm^{-1} were a group of C=C bond stretching vibration peak, which may attribute to the polycyclic aromatic framework structure. And a band at 2930 cm^{-1} is attributable to saturated C-H stretching vibration, showed that the carbonization incomplete. This band disappeared after sulfonation indicated cellulose chain continue to convert into polycyclic aromatic hydrocarbon structure during sulfonation. These results were accord with the results from XRD analysis. The band 1700 cm^{-1} were C=O stretching vibration peak. And 3500 - 2500 cm^{-1} belonged to O-H stretching vibration peak. These peaks were seen in spectra showed that there were plentiful of oxygen-containing groups such as phenolic hydroxyl, ester, ether, carbonylic or carboxylic groups in polycyclic aromatic skeleton. In spectrum of

Table 1. Textural properties of CC and CC-SO_3H.

Samples	S_{BET} ($m^2 \cdot g^{-1}$)	BJH average pore size(nm)	Pore volumn ($cm^3 \cdot g^{-1}$)
CC	3.0	25.4	0.018
CC-SO_3H	5.3	24.1	0.018

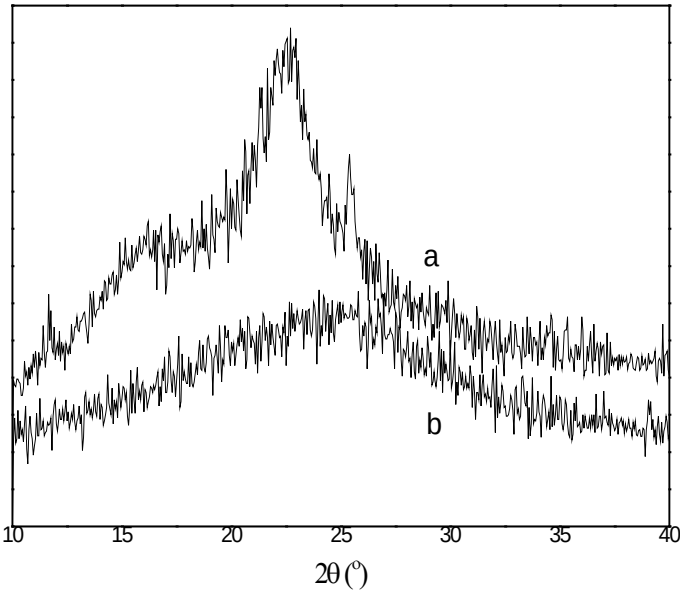

Figure 1. XRD of (a) CC; (b) CC-SO_3H.

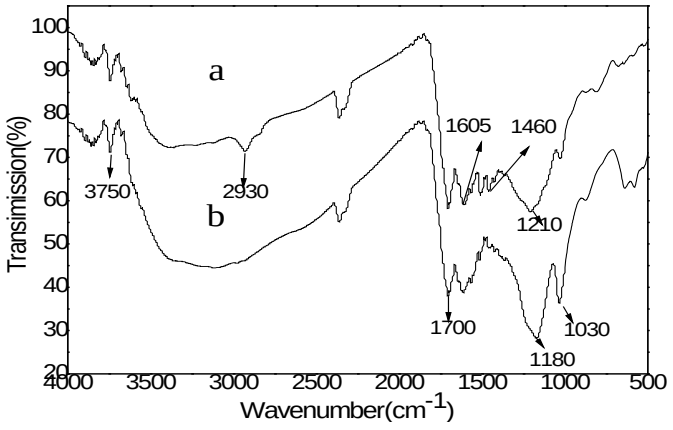

Figure 2. FT-IR patterns of (a) CC; (b) CC-SO_3H.

CC-SO_3H, peaks appeared at 1180 cm^{-1} and 1035 cm^{-1} assigned to S=O double bond stretching vibration, and the characteristic band about 640 cm^{-1} was the C-S stretching vibration peak. According to the acid-base titration results, sulfonic acid density of CC-SO_3H was 2.05 $mmol \cdot g^{-1}$ and the total acid density5.63 $mmol \cdot g^{-1}$.

3.2. Catalytic Activity

Acetalization is widely applied acid-catalyzed reactions, which are important reaction for protecting the carbonyl group [13,14] and synthesis of intermediates for steroids, pharmaceuticals, fragrance industries [15,16]. Catalytic activity of CC-SO_3H has been evaluated by ketalization of cyclohexanone with ethylene glycol.

Table 2 showed good catalytic activity of CC-SO_3H in ketalization of cyclohexanone with ethylene glycol. Few of the catalyst added could dramatically improve cyclohexanone conversation. When the amount of catalyst was 0.05 g, namely account for 0.1% of cyclohexanone feeding, cyclohexanone conversation reached 92.8%. Furthermore there were no by-products detected in GC analysis.

As reusability of the solid acid was so important, recycling reactions were designed. When the first run was over, the used 0.02 g catalyst was collected and washed with ethanol for several times. The regenerated catalyst was dried to catalyze the next run. It can reuse at least 6 times with tiny decrease of catalytic activity as shown in **Figure 3**. That means CC-SO_3H can be a good reusable catalyst.

4. Conclusion

The high acid density carbon-based solid acid has been synthesized through dilute sulfuric acid activation, solvent refluxing carbonization and sulfonation with camphor tree branch as raw material. And it showed excellent activity and good reusability in catalyzing ketalization of cyclohexanone with ethylene glycol. The catalyst owned advantages of high acidity, high acid density, and high chemical stability, which made it hold great potential for replacement of the homogeneous acid catalysts in the green process. The mild synthesis condition not only reduced cost of the carbon-based solid acid, but also made the industrial production possible.

Table 2. Influences of catalyst dosage on cyclohexanone conversation[a].

Catalyst dosage (g)	Conversation (%)
0	12.0
0.02	79.0
0.05	92.8
0.10	93.4

[a]Reaction conditions: $n_{(cyclohexanone)}$:$n_{(ethylene\ glycol)}$ is = 1:1.6, cyclohexane 0.05 mol, cyclohexanone 8 ml, 110˚C, 2 h.

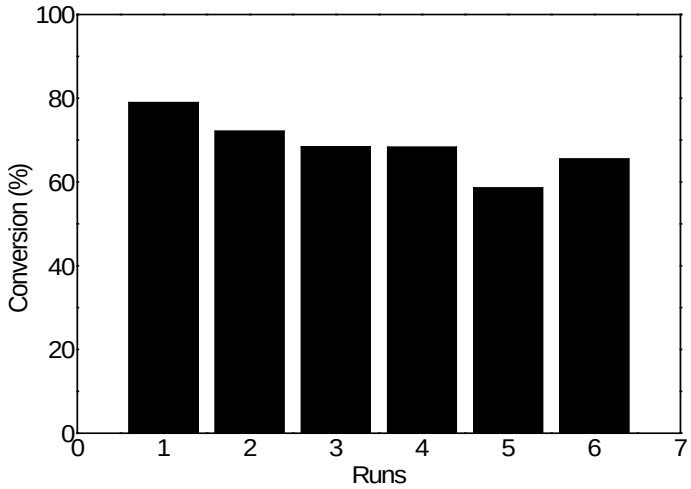

Figure 3. Recycling performance of the CC-SO_3H.

Acknowledgements

Authors thank for support of the National Natural Science Foundation of China (No. 21003043) for this work.

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