ISSN : 0974 - 7435
Volume 10 Issue 12

2014

BioTechnology
An Indian Journal

FULL PAPER
BTAIJ, 10(12), 2014 [6510-6516]

Preparation of sulfonated carbon catalyst from p-toluenesulfonic acid/fructose for the beckmann rearrangement of ketoximes

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ABSTRACT

A sulfonated carbon catalyst was conveniently prepared *via* multistep processes, involving the polymerization of fructose with p-toluene sulfonic acid (TsOH), followed by the oxidation with H_2O_2 and then the sulfonation and cabonazation with concentrated sulfuric acid. FT-IR spectroscopy indicated that such carbon material consists of aromatic carbon sheets bearing $-SO_3H$, -COOH and phenolic -OH groups. Notably, the addition of oxidation treatment in the preparation of carbon catalyst can obviously enhance the densities of $-SO_3H$ groups (3.01 mmolg^{-1}) and total H^+ sites (6.13 mmolg^{-1}), as supported by thermogravimetry and chemical titration analyses. As a result, such catalyst with numerous hydrophilic groups showed a high catalytic activity and an excellent repeatability for the Beckmann rearrangement of hydrophilic ketoximes.

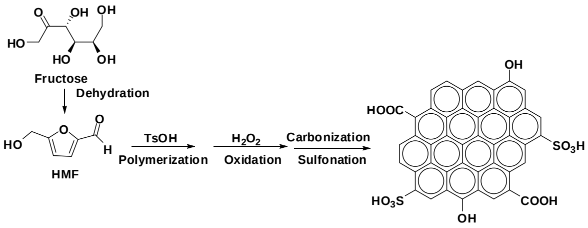
KEYWORDS

Sulfonated carbon catalyst; Fructose; Polymerization; Oxidation; Beckmann rearrangement.

INTRODUCTION

The acid catalyzed reactions are widely used in the production of industrially important chemicals. However, the problems of pollution and separation are always there when inorganic acids are used as catalysts. Nowadays, the alternation of minerals acids by environmentally benign and reusable solid catalysts has attracted much attention in many worldwide laboratories[1,2]. Solid acid catalysts (SACs) have many advantages, including insoluble in common organic solvents, corrosion free, and environmental compatibility. Also, they can be easily separated from the reaction medium and recoverable efficiently. Integration of acidic functional groups (e.g., $-SO_3H$) into carbonaceous[3-6] has been explored to produce promising SACs. Nowadays, SACs were prepared via the carbohydrates hydrolysis into hydroxymethylfurfural (HMF), subsequently polymerization into a resin, and then carbonization to carbon materials. For example, Wang[7] reported a one-step method to synthesize carbon-based solid-acid catalysts by commixing glucose and p-toluenesulfonic acid (TsOH) in a sealed vessel under thermal treatment of 180 ^oC. It was regretful that the acidic carbons possessed lower acid site densities with $-SO_3H$ loading of 1.27 $mmolg^{-1}$ and total H^+ loading of 1.99 $mmolg^{-1}$. The reason of lower acid site densities may be the high temperature for thermal treatment which not only limited glucose conversion into HMF, and yields were typically low (~10%) but also seriously restricted the immobilization of $-SO_3H$ groups on the carbon surface[8-10]. Therefore, there was considerable interest for us in exploring more efficient methods for preparation of SACs.

It was found that fructose containing 21.5% of furanose tautomers in aqueous solution could be converted to HMF more efficiently than glucose which contained 1% of furanose tautomers in aqueous solutions[11]. A H_2O_2 oxidation of resin material could introduce numerous hydrophilic groups on the carbon surface, such as -COOH and -OH groups, which subsequently resulted in a high level of modification of $-SO_3H$ groups[12]. In addition, the coexistence of hydrophilic groups ($-SO_3H$, -COOH, -OH) was favorable for the adsorption of polarity reactants. For these reasons, fructose was used as the raw materials with TsOH via polymerization and then oxidation of H_2O_2 to prepare sulfonated carbon catalyst in this work, as shown in Scheme 1. Characterizations showed that the sulfonated carbon material consisted of aromatic carbon sheets and contained $-SO_3H$, -COOH and phenolic -OH groups with 3.01 $mmolg^{-1}$ of $-SO_3H$ groups and 6.13 $mmolg^{-1}$ of H^+. Such sulfonated carbon material was employed to catalyze the rearrangement reaction of ketoximes in order to evaluate its acidic catalysis performance.



Scheme 1 : Possible mechanism for the synthesis of acidic carbon material from fructose and TsOH

EXPERIMENTAL

Preparation of catalysts

In a typical synthesis, 10 g fructose and 20 g TsOH were dissolved in 30 ml de-ionized water in a beaker to form a clear brownish red solution. The solution was heated at 358 K under stirring for about 2 h during which water was simultaneously evaporated and a black viscous paste was formed. The paste was cured at 403 K for 1 h to form a black solid (resin). It was washed with de-ionized water for several times until the filtrate was free from sulfate ions, and dried at 353 K. The sample was denoted as Fruc-R. The resin materials were pretreated by H_2O_2 oxidation to enhance their hydrophilic properties. In detail, 0.15 g of resin was added into 8.0 g of 30 wt % H_2O_2 solution at room temperature, and then the reaction mixture was kept at 333 K for 1 h. The materials were separated from the solution, followed by washing with ethanol and drying at 373 K in an oven. The resulting materials were denoted as Fruc-H_2O_2. Subsequently, these Fruc-R and Fruc-H_2O_2 materials were sulfonated using concentrated sulfuric acid at 423 K for 10 h. Afterwards, these sulfonated catalysts were washed repeatedly until the filtrate was neutral and no sulfate ions were detested, and were dried at 373 K. The resulting materials were designated as Fruc-R-SO_3H and Fruc-H_2O_2-SO_3H, respectively.

Catalyst characterizations

The catalysts were characterized by FT-IR, TGA, and BET surface area techniques. The Fourier transform infrared spectrum (FT-IR) of catalysts were recorded in the range 400-4000 cm^{-1} on a Nicolet Avatar 370 FT-IR spectrometer (using KBr pellets). The thermogravimetric analysis (TGA) was carried out in flowing N_2 (10 ml·min $^{-1}$) at a heating rate of 20 °C min^{-1} on a NETZSCH-STA 409PC (NICOLET). Surface areas were measured by the adsorption of N_2 at 77.3 K using a Micromeritics ASAP 2000 surface area analyzer and the specific areas were calculated according to the Brunauer–Emmett–Teller (BET) equation. Samples were degassed in flowing N_2 for 5 h at 383 K before the measurements. Referring to the procedure reported by Yin et al[13], the measured processes for -SO_3H, -COOH and -OH groups on the catalysts are described as follows, respectively. (i) The measurement of -SO_3H groups: a catalyst (0.05 g) was treated with 0.01 mol L^{-1} of NaCl solution (20 mL) for 1 h at 20-50 °C under ultrasonic vibration. After centrifugal separation, the supernatant solution was titrated by 0.01 mol L^{-1} of NaOH solution using phenolphthalein as an indicative. (ii) The measurement of the content of the total functional groups (-SO_3H, -COOH and -OH groups): 0.01 mol L^{-1} of NaOH solution (20 mL) as a treating agent and 0.01 mol L^{-1} of HCl solution as a titrating agent.

Beckmann rearrangement of ketoximes for catalytic test

Typically, the mixture of acetophenone oxime (67.50 mg, 0.50mmol) and SAC catalyst (0.1000 g) was added to MeCN (5mL) maintained refluxed at 90 °C. The completion of the reaction was monitored by TLC examination. After completion of the reaction, the reaction mixture was washed with CH_2Cl_2 (2×10 mL) and water (2×50 mL). The organic layer was dried over Na_2SO_4 and evaporated to give the crude N-phenylacetamide.

The investigating of the stability of the catalyst was also carried out. In each cycle, the ‘used’ catalyst was separated from the solution by centrifugation and then washed with a large amount of ethanol for three times. After dried at 90 ^{o}C overnight, this catalyst was used under the same conditions. The product analysis was same as mentioned above.

RESULTS AND DISCUSSION

Characteristics of sulfonated carbon materials (SCMs)

Figure 1 shows an FT-IR spectrum to characterize the functional groups. In all samples, the absorption band at ~3420 cm^{-1} is ascribed to the stretching vibration of the -OH group, which is favorable for the modification of -SO_3H groups. Notably, the absorption intensity of the O-H vibration in Fruc-H_2O_2-SO_3H sample becomes strong after oxidation with H_2O_2. compared with other SCM samples, The absorption peak at ~1708 cm^{-1} should be attributed to the C=O vibrational stretching of the -COOH groups[14-16], indicaing that functional groups are created in the carbon frameworks. The absorption bands at 1034 cm^{-1},1010 cm^{-1} and 1115 cm^{-1}, are found in Fruc-R sample, and this absorption band can be ascribed to the S=O symmetric stretching vibrations[17,18]. This result indicates that SO_3H groups are successfully incorporated into the carbon framework by adding TsOH in the synthesis system. Additionally, the absorption bank at ~1710 cm^{-1} assigned to the -COOH group vibration in the Fruc-H_2O_2-SO_3H sample becomes weak, which can be due to -COOH group partial oxidation by sulfuric acid[19].

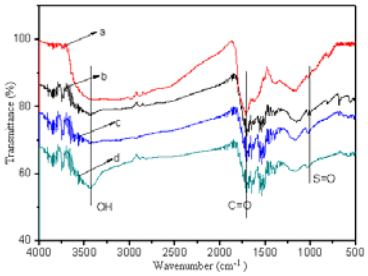


Figure 1 : FTIR spectra of the samples (a= Fruc-H_2O_2, b= Fruc-R, c=Fruc-R-SO_3H, d=Fruc-H_2O_2-SO_3H)

In Figure 2, the thermogravimetry (DTG) curves of Fruc-R-SO_3H and Fruc-H_2O_2-SO_3H are used to check the effect of oxidation of H_2O_2 on the SCMs. These materials also shows the distinct peaks for the loss of weight in the temperature range of 25-800 °C appeared in the DTG curves. Among them, the first strong peak (at 100 °C) should be attributed to an evaporation of the adsorbed water molecules, the second weak peak (at 220 °C) originates from decomposition of the surface's -SO_3H groups[20]. Notably, the decomposition peaks for SO_3H groups of Fruc-H_2O_2-SO_3H is stronger than that of Fruc-R-SO_3H. This likely implies that oxidation treatment by H_2O_2 results in a high level of modification of -SO_3H groups.

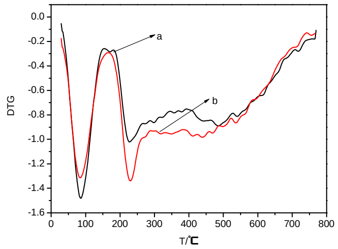


Figure 2 : DTG curves of Fruc-R-SO_3H (a) and Fruc-H_2O_2-SO_3H (b).

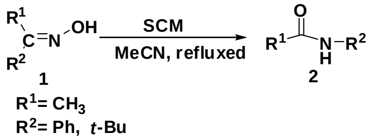
TABLE 1 shows the surface areas and acid densities of catalysts. It is seen from TABLE 1 that all the samples possessed lower than 2 m^2g^{-1} of specific surface area, indicating that they are nonporous carbon materials, in agree with some literature[21,22]. The data shows that the sample Fruc-R posses 1.62 $mmolg^{-1}$ strong acid sites, indicating the polymerization of HMF and TsOH for the formation of a resin containing sulfonic groups. The total acid density reaches 6.13 $mmolg^{-1}$ for Fruc-H_2O_2-SO_3H, suggesting the generation of phenolic -OH and -COOH groups in the process of oxidation with H_2O_2 and sulfonation with sulfuric acid[23]. Consequently, the sample Fruc-H_2O_2-SO_3H shows higher acidity than Fruc-R-SO_3H. The results also agree roughly with IR spectrum characterization.

TABLE 1 : Surface area and acid density of the different catalysts

Catalysts	Acid density		Surface area (m^2g^{-1})
	-SO_3H ($mmolg^{-1}$)	Total (H^+mmolg^{-1})	
Fruc-R	1.62	2.03	1
Fruc-R-SO_3H	2.12	4.85	2
Fruc-H_2O_2-SO_3H	3.01	6.13	1
H_2SO_4	20.4	20.4	-

Catalytic activity

The rearrangement of ketoximes to the corresponding amide, known as the Beckmann reaction, is a common method in organic chemistry[24]. This reaction generally requires high reaction temperature and strong acidity and dehydrating medium[25], which easily leads to undesired sulfates as byproducts. Currently, solid acids instead of H_2SO_4 are widely used as catalysts for the various acids-catalyzed reactions due to their large surface area, good thermal stability, non-corrosion, non-toxicity, and easy separation for recycling. Scheme 2 shows the Beckmann rearrangement of ketoximes using the Fructose-based solid acids as catalysts.



Scheme 2 : Beckmann rearrangement of ketoximes using the Fructose-based SCM as catalyst

Fructose-based solid acids Fruc-R, Fruc-R-SO_3H, Fruc-H_2O_2-SO_3H are used as catalysts for the Beckmann rearrangement of acetophenone oxime in MeCN under refluxed at 90 °C, and the results are listed in TABLE 2. The conversion of acetophenone oxime is found to be 16.29, 48.43, 92.02 and 94.17% upon catalysis with Fruc-R, Fruc-R-SO_3H, Fruc-H_2O_2-SO_3H and H_2SO_4, respectively. A further comparison of these catalyst’s turnover frequency (TOF) for this reaction may find that the Fructose-based solid acids commonly showed much higher catalysis activity than a liquid acid H_2SO_4. For example, TOF value over the catalyst Fruc-H_2O_2-SO_3H was ca. 0.043, being 3.6-fold higher than that over H_2SO_4. It seems that protons in Fruc-R-SO_3H and Fruc-H_2O_2-SO_3H are much more active than those in con. H_2SO_4 for the Beckmann rearrangement reaction, indicating that the structure and acidic strength of sulfonic groups in the Fructose-based solid acids might be different from those in con. H_2SO_4[11]. Noteworthy that Fruc-H_2O_2-SO_3H shows a much higher catalytic activity than Fruc-R-SO_3H. This result should be due to the higher acidity of Fruc-H_2O_2-SO_3H (TABLE 1) and numerous hydrophilic groups (-COOH and -OH) after oxidation with H_2O_2. Though -COOH and -OH groups contribute very little to catalytic Beckmann rearrangement owing to their insufficient acidity, they can afford the hydrophilicity and electrostatic repulsion to counteract the $\pi-\pi$ interaction between carbon sheets in polar solvents[25]. To further estimate the catalytic activities of Fruc-R-SO_3H and Fruc-H_2O_2-SO_3H, two types of ketoximes, aromatic ketoxime and aliphatic ketoxime, are examined under refluxed conditions in acetonitrile. The result (seen in SI) clearly displays that Fruc-H_2O_2-SO_3H shows a much higher catalytic activity as well.

TABLE 2 : Catalytic performance of fruc-based SACs in the beckmann rearrangement of acetophenone oxime [*a*]

Entry	Catalyst (0.1g)	Time (h)	Yield (%)	TOF (h^{-1})
1	Fruc-R	35	16.29	0.014
2	Fruc-R-SO_3H	35	48.43	0.032
3	Fruc-H_2O_2-SO_3H	35	92.02	0.043
4	con. H_2SO_4	25	94.17	0.0092

a Reaction condition: acetophenone oxime 0.5mmol, catalyst 0.1g, MeCN 5 mL and refluxed at 90 °C

The effect of reaction temperature on Beckmann rearrangement is investigated at different temperatures (323, 343, and 363 K) with 0.5 mmol acetophenone oxime and 0.1g catalyst, and the results are shown in TABLE 3. Though the conversions at various temperature catalyzed by Fruc-R-

SO_3H are much lower than that at 323 K catalyzed by Fruc-H_2O_2-SO_3H, the two catalysts exhibit the same trend in catalytic performance, that increasing temperature accelerates the conversion of acetophenone oxime. It is noted that Fruc-H_2O_2-SO_3H shows much better activity than Fruc-R-SO_3H, and its predominance in activity becomes more outstanding at a relatively low temperature (70 °C). For example, the TOF of Fruc-H_2O_2-SO_3H at 90 °C for 35 h and at 70 °C for 40 h are 34% and 65% higher than the corresponding TOF of Fruc-R-SO_3H, respectively.

TABLE 3 : Effect of temperature on Beckmann rearrangement of acetophenone oxime [a]

Tempera-ture (°C)	Time (h)	Fruc-H_2O_2-SO_3H		Fruc-R-SO_3H	
		Yield (%)	TOF (h^{-1})	Yield (%)	TOF (h^{-1})
50	50	65.68	0.021	22.45	0.011
70	40	80.21	0.033	34.67	0.020
90	35	92.02	0.043	48.43	0.032

a Reaction condition: acetophenone oxime 0.5mmol, catalyst 0.1g, MeCN 5 mL and refluxed at 90 °C.

Finally, recyclability of Fruc-H_2O_2-SO_3H in the Beckmann rearrangement of ketoximes was examined, and the results showed that the catalyst was still active in each recycle run, and the conversion of rearranged production was found to be nearly the same (91.82, 91.68 and 91.13%), illustrating that this catalyst possesses an excellent recyclability for the present reaction.

CONCLUSIONS

It is reported that a novel and facile method for preparing highly active carbon based solid-acid catalyst bearing abundant -SO_3H, -OH, -COOH groups. Such catalyst has the following merits: i) The use of mild preparation conditions (353 K); ii) The introduction of oxidation treatment with H_2O_2 significantly enhances the density of -OH, -COOH and especially -SO_3H groups on catalyst's surface; And iii) such catalyst exhibits an outstanding catalysis activity and excellent stability for the acid-catalyzed Beckmann rearrangement of ketoximes. This method afforded a new strategy for preparing the hydrophilic solid acid material with high acidity and catalytic activity.

ACKNOWLEDGEMENT

The authors thank to the foundation supported by project (14A133) supported by institutions of higher education of Hunan province, project (14JJ7076) supported by the natural science foundation of Hunan province; project (2013346) supported by the college students' research learning and innovative experiment of Hunan province, and project (2013346) supported by scientific and technological innovative team of Shaoyang university (2012).

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