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Catalytic Action of Biomass Carbon Sulfoacid in Fine Organic Synthesis

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This paper mainly studies the catalytic action of biomass carbon sulfoacid in the fine organic synthesis. The catalyst used in this study is biological bamboo charcoal sulfoacid solid. The catalytic effect of bamboo charcoal sulfoacid and other common solid acid is compared through the transesterification reaction of glycerol triacetate and methyl alcohol. The experiments show that after catalytic optimization of the transesterification reaction of glycerol triacetate and methyl alcohol, the conversion rate of glycerol triacetate is 90.3%. Meanwhile, the glycerol triacetate is relatively high, which further demonstrates the high degree of transesterification. It can be seen based on the experimental results that the catalytic activity of biomass carbon sulfoacid is relatively high; the preparation technique is simple; and it exerts little impact on the environment, which is worthy promoting.

1. Introduction

At present stage, the catalyst has widely used in China's industrial production. Compared with traditional catalysts, biomass carbon sulfoacid has attracted attention from many experts at home and abroad because of its high catalytic activity and low raw material prices. It is conducive to the improvement of the industrial production technology to study the catalytic role of biomass carbon sulfoacid in fine organic synthesis, which will bring higher social benefits and economic benefits for industrial enterprises.

2. Literature review

The solid acid catalyst is non-toxic, odorless, non-volatile, non-corrosive, and less polluting to the environment. This type of catalyst has unique catalytic properties in organic synthesis reactions, mild reaction conditions, high selectivity, simple post-treatment and easy recovery and reuse. In the face of increasingly severe environmental problems, the replacement of liquid acids with high-performance solid acids catalyzes organic reactions as an important way to achieve environmental friendliness and meet the development requirements of green chemistry (Zuo et al., 2010). Three kinds of carbon-based solid base catalysts were prepared by a one-step carbonization method with potassium hydroxide as the precursor and glucose, sucrose, starch as raw materials (Zhu et al., 2017). Biomass energy is an ideal clean and renewable energy source with characteristics of wide sources, low prices, strong reproducibility and less pollution. It is of great significance to develop and use biomass energy to mitigate greenhouse effect, reduce air pollution and relieve energy pressure. Researching and experimenting with the hydrolysis of biomass feed-stocks under hydrothermal conditions to produce chemicals can not only solve the problem of pollution of a large number of agricultural wastes, but also create more wealth for the society and help alleviate environmental problems and energy crisis. A series of carbon-based solid acid catalysts were prepared from bagasse using a carbonization-sulfonation method and employed to catalyze esterification of oil with methanol to produce biodiesel (Zhang et al., 2015).

Solid acid is a kind of green environment-friendly catalyst. It has high catalytic activity for multiple reactions, good selectivity, easy recovery and reusability, and can effectively avoid the corrosion equipment and catalysts that are present in the process of using traditional liquid acids. And waste liquid pollution and other issues. Biomass carbon-based solid acid is produced from biomass resources that are renewable, rich in

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resources and green and environmentally friendly. The stable spatial structure not only improves the comprehensive utilization of biomass resources, but also reduces the production of solid acids. The cost is conducive to the promotion of solid acid catalysts in industrial applications. It is note-worthy that the reaction proceeded smoothly in the presence of formic acid. Further-more, the remained intact, highlighting the practical advantages of this process for the convenient and cost-effective processing of a biomass-derived solution (Xianlong et al., 2013). At present, lignocellulose raw materials can obtain soluble sugar molecules with high selectivity through hydrolysis pathways, and can be converted into widely used platform molecules. Using these platform molecules as raw materials, more high value-added chemicals can be prepared through the conversion of elementary reactions to enrich the biomass-based chemical product library. The progress of the application of biomass carbon-based magnetic solid acid catalyst to hydrolysis of lignocellulose was described in detail, and the application of the catalyst in esterification reaction and condensation reaction was also introduced. The problems of biomass carbon-based magnetic solid acid catalyst industry were put forward at present, and clearly pointed out the next step of the research work (Li et al., 2017). The structure of carbon-based solid acid catalyst was characterized. Reusability of the carbon-based solid acid catalyst for esterification showed that after recycling five times the activity remained unchanged (Luan et al., 2015).

The transition from today's fossil-based economy to a sustainable economy based on renewable biomass is driven by the concern of climate change and anticipation of dwindling fossil resources. Although biofuels are the central theme of the transition, biomass resources cannot completely replace petroleum. Industry is increasingly considering bio-based chemical production as an attractive area for investment. The potential for chemical and polymer production from biomass is substantial. The US Department of Energy recently issued a report which listed 12 chemical building blocks considered as potential building blocks for the future. Organic acids are among the widely spread “platform-molecules,” which may be further converted into possibly derivable high-value-added chemicals. The transition from a fossil chemical industry to a renewable chemical industry will likewise depend on our ability to focus research and development efforts on the most promising alternatives (Lin el at., 2014). In addition, carbon was found to play an important role in the catalytic activity of the char, both as a catalyst and a support on which the inorganics were dispersed. The activity of carbon free ash was approximately 90% lower than that of char, and deactivated to have no measurable activity after 45min on stream, demonstrating the importance of carbon and dispersed inorganics for catalytic activity. When char was heated to 1000 in N2, inorganics and oxygen migrated to the surface of the char, covering the carbon surface in a metal oxide layer. This decreased the catalytic activity by approximately 40%. However, acidic oxygen groups desorbed at reaction temperatures, so these groups likely do not participate in cracking reactions (Klinghoffer et al., 2015).

3. Experimental principles and methods

Although the liquid acid catalyst has no special requirements on the raw oil, it has high requirements for the equipment due to its corrosiveness. Moreover, it is difficult to separate the catalyst after the reaction, resulting in cost increase. Heterogeneous catalysts have the advantages of easy separation from products, recyclability, and environmental friendliness and current researches indicate that there are many heterogeneous catalysts available for biodiesel production. The application of solid acid catalysts in the heterogeneous catalysis of transesterification reaction can avoid the problems of difficult separation of catalysts, waste liquids, multiple side reactions and serious emulsification in traditional homogeneous acid and alkali-catalyzed ester exchange processes. In practice, it is often necessary to transform the triglyceride in the grease into the free aliphatic ester by transesterification reaction to reduce the average molecular weight and viscosity of the ester. The commonly used methods of methyl esterification are divided into two major categories: acid catalysis and alkali catalysis. The main advantage of the acid catalytic esterification is the wide applicability, which is suitable for both free aliphatic acid and combined state aliphatic acid (fat) while the alkali catalysis is only suitable for fat.

4. Experimental results and analysis

4.1 Application of charcoal sulfoacid in the catalysis of transesterification reaction between glycerol triacetate and methyl alcohol

The commonly used homogeneous catalysts are H2SO4, NaOH, KOH and so on. In this experiment, solid carbon sulfoacid is used as the catalyst and glycerol triacetate and methyl alcohol are taken as reactants for the transesterification reaction. Moreover, the effect of ratio of alcohol and ester, amount of catalyst and reaction time on the transesterification reaction is investigated.

The instrument used in this experiment is shown in Table 1.

Table 1: Experimental instruments

equipment name	model	Manufacturer
Fourier Transform Infrared Spectrometer	AVATAR370	American Nicolet Company
Gas Chromatograph	GC-920	Haixin Chromatography Instrument Co., Ltd.
Chromatography unit	Saturn21OO	American Varian Company
CNC ultrasonic cleaner	KQ3200DB	CNC ultrasonic cleaner
Electric thermostatic blast drying oven	OHG-9036	Shanghai Jinghong Experimental Equipment Co., Ltd.
Electronic precision balance	BS210S	Shanghai METTLER TOLEDO Instrument Co., Ltd.
Recirculating water vacuum pump	SHZ-D (111)	Henan Gongyi Yingyu Yuhua Instrument Factory

The chemical reagents used in this experiment were: fuming sulfuric acid, methyl alcohol, glycerol triacetate, 50% fuming sulfuric acid, p-toluenesulfonic acid, 70% benzenesulfonic acid, sodium hydrogen sulfate, D-72 sulfuric acid resin, ammonium hydrogen sulfoacid and absolute ethyl alcohol.

The preparation of bamboo charcoal sulfoacid referred to the biomass pyrolysis-sulphonation technique established in this experiment: took a certain amount of fresh bamboo (0.5 to 2 mm in diameter, cutting to the length of 1-4mm with scissors) and put in the reaction tube after accurate weighing after drying. Put it into a tube furnace and conduct vacuum heating. First, raised the temperature to 250e at a rate of 10°C/min and then raised the temperature to 300e a rate of 5°C/min. After that, raised the temperature until the terminal temperature of carbonization (350e) at a rate of 1°C/min and finally conducted heat preservation the end of in the terminal temperature of carbonization. The pyrolytic gas pumped out by the vacuum pump during the pyrolysis was cooled by the reflux condensing tube and collected in the filter flask. The bamboo charcoal was placed in the round-bottom flask and a certain amount of 50% fuming sulfuric acid is added. It was heated at 80 °C and sulfonated for 2 hours. After the product was cooled, it was repeatedly washed with deionized water until the filtrate became neutral, obtaining black bamboo charcoal solid sulfoacid and a black solid bamboo-based solid sulfonic acid was obtained. The amboo charcoal solid sulfoacid was then placed in a round-bottom flask and 2 mol/L NaOH solution was added. After that, it was heated at 100°C for 2 hours and filtered and washed repeatedly until the filtrate became neutral. Then, a certain amount of 2mol/L HCl was added into the bamboo charcoal solid sulfoacid and the ultrasonic oscillation was conducted for 30 min. the solution was washed repeatedly until the filtrate became neutral and boiled with deionized water for 2h. The bamboo charcoal solid sulfoacid was dried at 100° C for 12 hours. Then, it was cooled, packed in a sealed bag and stored in a desiccator. The acidity of the prepared catalyst was measured, whose acid content was 1.46 mmol/g.

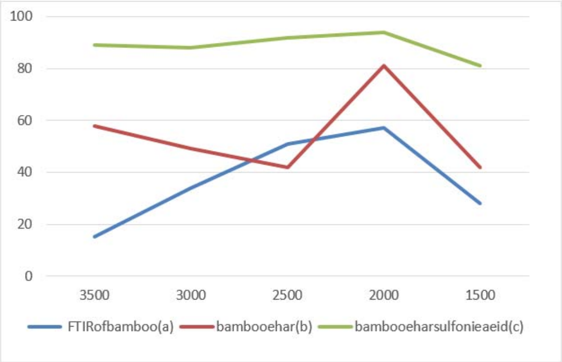

Figure 1: FTIRofbamboo(a),bambooehar(b)and bambooeharsulfonieaeid(c)

The glycerol triacetate and methyl alcohol were put into in a 50mL single-mouth flask with a certain proportion and appropriate amount of catalyst was added. Then, the condenser tube was connected and the 65e reflux reaction was conducted under the circumstance of stirring. When reaching the constant temperature, we started timing. After a certain period of time, appropriate amount of reaction solution was taken and the area normalization method was used for analysis with the help of gas chromatography. The GC-920 gas chromatography area normalization method was used for quantitative analysis of the product samples. HP-5 (3Om*0.25mm*0.25mm) capillary column, hydrogen flame detector, N was the carrier gas and the chromatographic column temperature was 170e. The temperature of the vaporization chamber and the test chamber was both 250 °C. The catalyst was washed repeatedly with methyl alcohol and dried for reutilization.

The infrared spectroscopy provides the basis for determining the structure of the catalyst. Figure 1 is the infrared spectra of bamboo sawdust (a), bamboo charcoal (b) and bamboo charcoal sulfoacid (c).
Figure 2 is the X-ray diffraction diagram of bamboo charcoal (a) and bamboo charcoal sulfoacid (b).

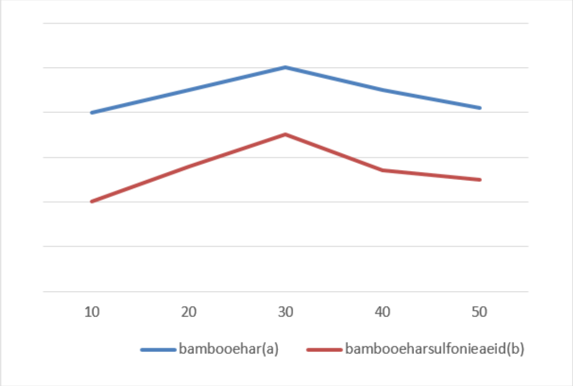

Figure 2: XRDPatterns of bambooehar(a) and bambooeharsulfonieaeid(b)

It can be seen from Figure 1 and Figure 2 that from the figure, both the carbonization and sulphonation products have a broad and flat peak, indicating that the order degree of the materials after carbonization is low. No regular graphite structure is formed and the prepared carbon materials are amorphous. After sulphonation, the slope of X-ray diffraction peak of bamboo charcoal sulfoacid is slightly higher than that of the carbonization product, indicating that the sulphonation by fuming sulfuric acid can further deepen the degree of carbonization.

4.2 Comparison of the catalytic effect of bamboo charcoals sulfoacid and common solid acids

Under the condition of methyl alcohol reflux, the amount of catalyst was 0.49mmol CHSo3 and the amount of glycerol triacetate was 0.02mol. The molar ratio of alcohol and ester was 10:1 and the effect of different catalysts on the reaction for 10h was investigated, as is shown in Table 2.

Table 2: Comparision of different catalysts on transesterifieation

catalyst	The conversion	selective		
		glycerin	Glycerin monoacetate	Glycerine diacetate
Bamboo charcoal sulfuric acid	89.8	43.5	41.4	15.1
Sulfonic acid resin	67.2	41.2	36.8	22.0
P-toluene sulfonic acid	100.0	53.7	40.3	6.0
Amino sulfonic acid	15.3	10.6	1.3	88.1
Sodium bisulfate	83.8	31.0	49.5	19.5

It can be seen from Table 2 that when the reaction time is 10h, the activity of p-toluenesulfonic acid is the highest and the conversion rate of glycerol triacetate under the catalysis of bamboo charcoal sulfoacid can reach 89.8%, indicating that carbon sulfoacid has good catalytic activity as a solid acid. Bamboo charcoal sulfoacid, as a catalyst, the conversion rate of glycerol triacetate is higher than that of sodium bisulfate, sulfonic acid resin and sulfamic acid, whose glycerin selectivity is high but the glycerol diacetate selectivity is low, indicating a relatively high degree of transesterification.

4.3 Effect of alcohol ester ratio on the reaction

Under the condition of methyl alcohol reflux, when the amount of catalyst is 0.5 mmol and the glycerin triacetate is 0.02mol, the effect of different alcohol ester ratio on the reaction is shown in Table 3.
The transesterification reaction is a reversible reaction. According to the principle of chemical equilibrium, the use of excessive methyl alcohol can promote the reaction to proceed in the positive direction, thereby increasing the conversion rate of glycerol triacetate. Therefore, the molar ratio of the alcohol and ester should be greater than the theoretical value of 3:1 to promote the reaction to proceed in the direction of generating products. However, excessive methyl alcohol can exert severe negative impact on the separation cost of glycerin and thus increase the separation cost. And the conversion rate cannot be significantly improved. In order to cut the cost of the reaction and make the post-treatment easier, it is necessary to determine the appropriate alcohol ester ratio. The conversion rate and selectivity of the reaction at 10h are shown in Table 3.

Table 3: Effect of alcohol-ester ratio on transesterification

Chun ester than	The conversion	selective		
		glycerin	Glycerin monoacetate	Glycerine diacetate
6:1	37.7	4.4	6:1	37.7
7:1	90.3	33.1	7:1	90.3
8:1	90.4	38.2	8:1	90.4
9:1	90.0	40.7	9:1	90.0
10:1	90.1	43.5	10:1	90.1

When the alcohol ester ratio is 7:1, the conversion rate of the raw material is the highest at 90.3%. The selectivity of glycerol is also at a relatively high value while the selectivity of glycerol is at a relatively low value. Under this condition, the extent of reaction is higher than that of other alcohol ester ratios.

Under the condition of methyl alcohol reflux, when the alcohol ester ratio is 7:1, the glycerol triacetate was 0.02mol and reaction time is 10h, the impact of different amount of catalyst (0.1, 0.2, 0.3, 0.4 and 0.5 mmol) is investigated. It can be seen that when the amount of catalyst ranges from 0.1 to 0.3 mmol, the conversion rate of glycerol triacetate increases significantly. When the amount of catalyst ranges from 0.3 to 0.5 mmol, the trend tends to be stable without significant change. When the amount of catalyst is 0.5 mmol, the conversion rate of transesterification has reached 90.3%.

4.4 Effect of reaction time on the transesterification reaction

Under the condition of methyl alcohol reflux, when the glycerol triacetate was 0.02 mol, the alcohol ester ratio is 7:1 and the amount of catalyst is 0.5 Inln01, the effect of reaction time on the cooling transesterification reaction is investigated. It can be seen from Figure 3 that the productivity increased significantly within a very short time after the start of the reaction, but the productivity does not increase significantly and tends to be stable when the reaction time reaches 9 hours.

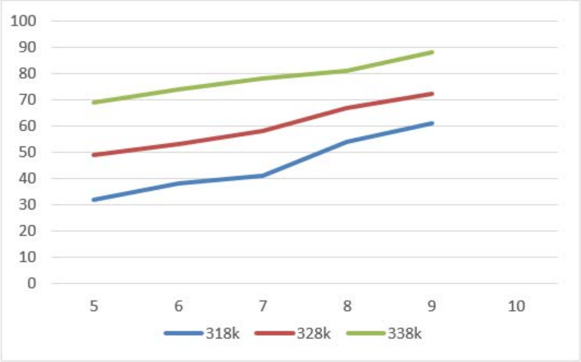

Figure 3: Influence of reaction time on transesterification

In the range of reaction temperature from 318 to 338K, the kinetic characteristics of the transesterification reaction of glycerin triacetate and methyl alcohol under the catalysis of bamboo charcoal sulfoacid are investigated. For liquid-solid multiphase acid catalytic reaction, it can be deduced that the kinetic equation conforms to the first order reaction low according to the equilibrium concentration method:

$$1n\frac{1}{1-x}=kt \tag{1}$$

In formula (l), x is the conversion rate; t is the reaction time, and k is the rate constant.

The reaction results of the transesterification reaction of glycerin triacetate and methyl alcohol under the catalysis of bamboo charcoal sulfoacid at different temperatures are taken as the reaction time t to conduct least square method linear regression treatment on formula (1). The apparent reaction rate constant at various temperatures can be obtained.

The linear correlation coefficient indicates that the reaction is in good agreement with the first-order reaction kinetics equation. Due to the excessive amount of methyl alcohol, the reaction of glycerol triacetate under the catalysis of bamboo charcoal sulfoacid obeys the pseudo first-order reaction kinetic laws. For multi-phase reactions, when the variation range of the reaction temperature range is not too large, the relationship between the apparent rate constant and temperature also follows the Arrhenius equation appropriately:

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

In formula (2), k is the rate constant; ko is the pre-factor; E" is the apparent activation energy (kJ/mol); T is the reaction temperature (K); R is the ideal gas constant, R = 8.314J/(mol K).

After the linear regression, the apparent activation energy of the transesterification reaction of glycerin triacetate and methyl alcohol is Ea=11.0kJ/mol. It is known that the bond energy of C-O bond is 360.0 kJ/mol and the bond energy of O-H bond in methyl alcohol is 389.1 kJ/mol, which are both far greater than the Ea obtained by calculation. It can be seen that the use of bamboo charcoal sulfoacid catalyst in the transesterification reaction of glycerin triacetate and methyl alcohol greatly reduces the activation energy of the reaction and effectively promotes the reaction.

5. Conclusion

The experiment shows that when the alcohol ester ratio is 7:1; the amount of catalyst is 0.05mmol; and the reaction time is 10h, the conversion rate of glycerol triacetate is 90.3%. In the catalyst activity analysis experiment, Ea=11.0 KJ/mol. It can be seen that the catalytic effect of biomass carbon sulfoacid is good and it exerts little impact on the environment. However, from the actual situation, there are still many problems in the application of biomass carbon sulfoacid, which calls for further studies.

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