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ARTICLE

Efficient biodiesel production from waste cooking oil using p-toluene sulfonic acids doped polyaniline as catalyst

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p-Toluenesulfonic acid doped polyaniline was developed as catalyst for the production of biodiesel from waste cooking oil. The physical and chemical properties of the obtained catalyst were characterized in detail. It was found that the yield of fatty acid methyl esters reached 97.1%, and the physical properties of obtained biodiesel sample satisfied the requirement of ASTM D6751 standards. In addition, the catalyst exhibited excellent stability for 10 runs. Therefore, this heterogeneous catalyst having potential for biodiesel production from waste cooking oil, deserve to carry out further pilot test and may be used in large-scale industries.

Introduction

Biodiesel fuel as a substitute for petroleum-based diesel has been drawn more attention along with the depletion of petroleum reserves and the rising concerns of environment pollution, [1, 2]. However, biodiesel still has not been commercialized, since the most common commercial process is using high cost refined vegetable oil as raw materials [3]. In China, more than 5 million tons of waste cooking oils are generated, and with China's social and economic development, more restaurants have expanded resulting in the increase of waste cooking oil (WCO) output. In this context, waste cooking oil as a biodiesel feedstock has attracted considerable attention in the recent past due to cheaper cost and easy availability.

Many researchers have revealed that biodiesel production using WCO can not only reduce biodiesel production costs up to 60-90%, and it also overcomes the waste product disposal and treatment problems [4, 5]. However, quite amounts of free fatty acids (FFAs) are present in WCO, which will be saponified by the alkali catalyst, so resulting in difficulty in product separation and causing a low biodiesel yield [6]. In these cases, the most appropriate catalyst for biodiesel production using waste cooking oil seems to be one of the acid type. Recently, the production of biodiesel using heterogeneous catalyst has become more favorable compared to mineral acids, and various solid acids have been evaluated [7, 8].

Among of them, solid acid catalysts obtained through the functionalization of the mesoporous silica materials with organo-sulfonic acids, polymer based catalysts, which were obtained via attach sulfonic groups to the polymer backbone, such as in Amberlyst-series, Nafion NR and Nafion SAC-13 composite, were developed and are very promising as green catalysts for esterification of FFAs [9-11]. However, most of

the solid acid catalysts currently focuses more on the esterification of FFAs than the preparation of biodiesel from WCO [12]. Polyaniline (PANI) refers to a polymer obtained by the oxidative polymerization of aniline [13]. Due to nitrogen-containing groups, polyaniline exhibits basic character which allows easy doping of polymer with protonic acids to give the "polyaniline salt". The polyaniline salt contains high content of acid sites, exhibit good environmental and thermal stability [14]. These properties make polyaniline salts a potential candidate to be used in production of biodiesel from WCO.

Within the scope of this work, a new type of polymeric catalyst, p-toluenesulfonic acids doped polyaniline (p-TSA-PANI) is evaluated for biodiesel production from waste cooking oil. The as-synthesized catalyst was studied by Fourier transform infrared (FT-IR) spectra, X-ray diffraction (XRD), thermo gravimetric analysis, as well as Scanning electron microscopy.

Results and discussion

Catalysts characterization

N₂ sorption and acid capacity

The surface area for the samples were calculated from N₂ isotherms using the Brunauer-Emmett-Teller (BET) model and are listed in Table 1. Although a low contribution of micropores can be also observed, this sample is mostly mesoporous in nature. As can be found from Table 1, the initial sample of PANI exhibits relatively low specific surface area, and p-TSA-PANI shows distinctly lower specific surface area than that of initial PANI, and the total porosity of p-TSA-PANI is also sharply reduced compared to that of initial polymer. It is clearly the changes in porosity is mainly caused by the occupying of

some cavities by p-TSA during the catalyst preparation procedure. The composition of the samples is determined by elemental analysis. In p-TSA-PANI, apart from the polyaniline derived elements (C, H, N) also the presence of S and O is observed. From the obtained data the formula of PANI and p-TSA-PANI are calculated as $C_{6.01}H_{5.97}N_1$, $C_{6.43}H_{4.9}N_1S_{0.32}O_{1.51}$ respectively. The C/N ratio p-TSA-PANI is higher than PANI due to some amount of C derived from the p-TSA. It is generally accepted that imine $-N=$ groups are preferentially doped by acids during commonly performed protonation of polyaniline base. This would result in the S/N ratio of 0.5 in the case of all imine groups protonation. Thus, the S/N ratio below 0.5 obtained for studied samples is consistent with this effect [12]. The acid capacity (mmol H^+ /g of catalyst) in p-TSA-PANI catalyst is equal to 4.33 mmol/g, which is close to that of Amberlyst-15, which is commonly considered to be a catalyst with high acidity as reported in previous studies [15].

Table 1 N_2 sorption and dispersion results for the samples.

Sample	surface area (m^2/g)	Pore volume (cm^3/g)	Mesopore volume (cm^3/g)	mmol H^+ /g catalyst
PANI	14.3	0.20	0.19	-
p-TSA-PANI	4.8	0.11	0.08	4.33

FT-IR

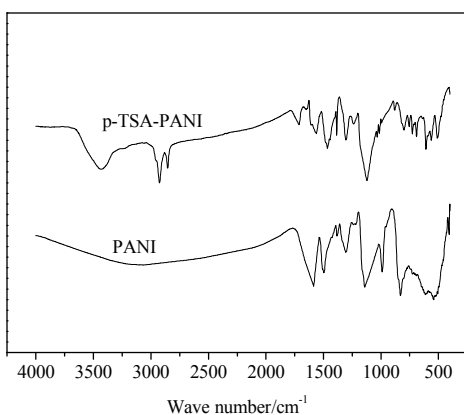


Fig. 1 FT-IR spectra of PANI and p-TSA-PANI catalyst

The FT-IR spectrum of PANI and PANI doped with p-TSA are depicted in Fig.1. An intense band can be observed at 832 cm^{-1} , which is characteristic of the paradisubstituted aromatic rings [13]. In the FT-IR spectrum of PANI the band at 1596 cm^{-1} originating from stretching vibrations of $C=N$ and $C=C$ bonds in quinone units as well as the weak band at 1169 cm^{-1} ascribed to $C-C$ in-plane deformation. After doping with amounts of p-TSA, the bands of quinone and benzene shifted to lower wavenumbers accompanied by a new broad band at about 1030 cm^{-1} , which is due to the vibration of the stretching vibrations of S-O. However vibration of S-O is superimposed with the strong and broad band arising from the protonated units of polyaniline, which makes its observation difficult.

XRD

The XRD diffraction patterns of PANI and the studied catalyst are displayed in Fig.2. Mostly amorphous structure of PANI resulted in a domination of a strong and broad halo at 2θ approximately 20° , which was superimposed on small and broad peak at 2θ about 23° associated with crystalline polymer [11, 16]. After doping of PANI with p-toluensulfonic acid the broad halo arising from amorphous polymer decreases whereas the intensity of the diffraction at 2θ around 25° evidently grows, demonstrated that the amorphous polymer decreases while more ordered structure of protonated polymer appear. According to previous studies, this may caused by the intercalation of p-toluensulfonic acid molecules between the polyaniline chains [17]. It should be noted that apart from the protonation, the molecules of p-toluensulfonic acid interacted with the PANI structure also through the formation of hydrogen bonds between the amine groups and hydroxyl groups of the acid. It is surely, both of these two kinds of effect will improve the stability of p-TSA-PANI.

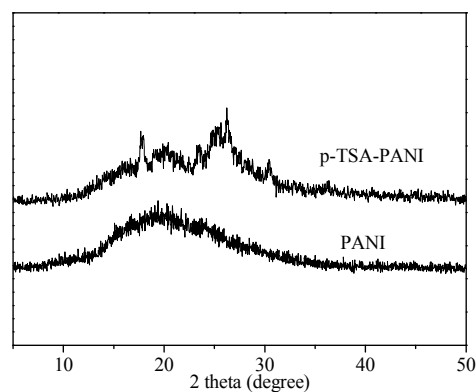


Fig. 2 XRD patterns of PANI and p-TSA-PANI catalyst

TG

Thermo stability properties of PANI and p-TSA-PANI catalyst were investigated by a TG analyzer. As shown in Fig. 3, two distinct weight loss steps are displayed on the curve of PANI. The weight loss in the range from room temperature to $120\text{ }^\circ\text{C}$ is due to the desorption of physically adsorbed water on PANI. The higher temperature weight loss step displayed that PANI is thermally stable up to approximately $400\text{ }^\circ\text{C}$, and above this temperature a slow degradation of polymer started. The TG curves of p-TSA-PANI catalyst shows a typical three-step decomposition pattern. The three steps in the decomposition curve can be attributed to the loss of water molecules present in the polymer matrix, loss of p-TSA, and complete degradation and decomposition of the polymer backbone. Among the three steps of decomposition, the first and last steps are quite distinct exhibiting rapid weight loss with respect to the temperature, while the second step is less conspicuous involving gradual loss extending over a broad range of temperature ($200\text{--}400\text{ }^\circ\text{C}$). However, the above results demonstrated that the obtained

catalyst is thermally stable up to approximately 200 °C, which is in accordance with previous studies. [18-20].

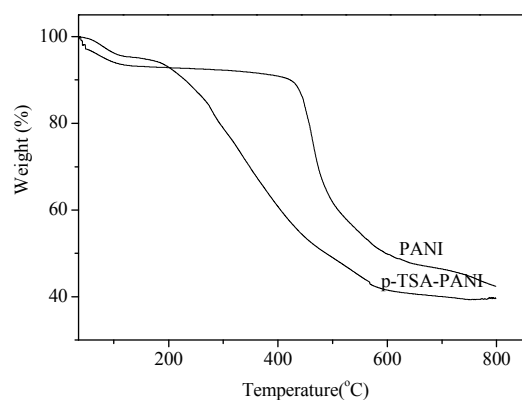


Fig. 3 TG curves of PANI and p-TSA-PANI catalyst

Catalytic activity in the biodiesel production

Catalytic activity

In view of the refluxing temperature of the reaction mixture and boiling point of methanol, the reaction temperature for the present studies was fixed on 70 °C. The influence of reaction conditions such as reaction time, methanol/WCO molar ratio, catalyst dosage were evaluated, and the obtained results are present in the Electronic Supplementary Information (Table S1-S3). As can be found, the optimum operating conditions for the present studies were methanol/WCO molar ratio 10.0:1, catalyst dosage 4.0%, reaction time 3.0 h. It was found that the yield of FAME under the optimum operating conditions reached to 97.1%. The acid value of 5.6 mg KOH/g for the WCO reduced to 0.20 mg KOH/g after reaction indicating the catalyst is highly effective for production of biodiesel from WCO.

Table 2 Physical properties of biodiesel compared with ASTM standards

Entry	Biodiesel	ASTM D6751
Water (%)	0.03	≤0.05
Acid value (mg/g)	0.2	≤0.5
Density (kg/m ³)	830	860-894
Kinematic viscosity (mm ² /s, 40 °C)	5.1	1.9-6.0
Cetane number	67	≥47
Closed-cup flash point (°C)	158	≥93
Cloud point (°C)	-1	-3-15
Pour point (°C)	-3.8	-5-10
90% Distillate temperature (°C)	339	≤360

The ideal substitute for diesel fuel was reported should have the following properties: molecular structure with a long straight carbon chain and no branched chain, preferably only one C=C double bond which was in the end of molecular chain or uniformly distributed in

the chain. [21] In the present work, the content of FAME in the obtained biodiesel is around 97.0%, indicating that the waste cooking oil can serve as a competitive alternative feedstock for biodiesel production.

Just as presented in the introduction part, biodiesel was produced as an alternative fuel for conventional fossil fuels, so some of the important quality parameters of the biodiesel derived from WCO were analyzed. As it was listed in Table 2, the biodiesel sample satisfied the requirement of ASTM D6751 standard, implied the biodiesel derived from WCO had adequate values compared to diesel fuel, and also demonstrated p-TSA-PANI catalyst is highly effective for simultaneous esterification and transesterification reaction, deserve to carry out further pilot test and may be used in large-scale industries.

Catalyst stability

The stability of p-TSA-PANI catalyst was investigated under the optimum conditions, and the obtained result was listed in Fig. 4. In each run, the catalyst separated from the reaction mixture was initially washed with hexane, and then washed with methanol and finally dried overnight. It was found that the yield of FAME were still maintained around 97.1% after five cycles (Fig. 4), and after ten cycles the yield only slightly reduced to 94.3%, indicating the excellent stability of the catalyst. The chemical composition of the recovered catalyst after ten cycles was analysed. The results showed that the S content decreased by 2.9% compared with that of fresh catalyst, so it can be concluded that the slight decline of the activity is probably due to the leaching of some p-TSA.

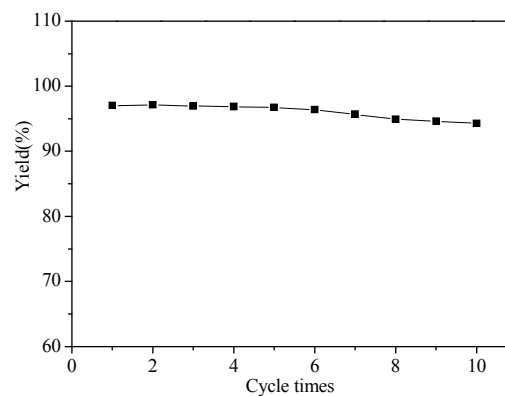


Fig.4 The catalytic performance of p-TSA-PANI catalyst for 10 runs

Experimental

Materials and catalysts preparation

All the chemicals used were of analytical reagent grade and the solutions were prepared using distilled water. The polymerization of aniline (9.3 g) was started by the drop wise addition of the (NH₄)₂S₂O₈ aqueous solution (22.8 g, 3.0 M) in an acidified solution (33.5 mL), under constant stirring at temperature about 18 °C. After addition of the oxidizing agent, the reaction mixture was kept under constant stirring for 4 h

and ageing for 24 h. And then the greenish-black precipitate of the polymer was isolated by filtration. The wet precipitate was then added to 40 mL Ammonia water (10.0%), and kept constant stirring for 0.5 h. The mixture was then isolated by filtration, and the obtained precipitate was washed by distilled water until the washings were $\text{pH} \approx 7.0$ and drying in an vacuum oven over night.

p-TSA-PANI was prepared by the impregnation method according to the followed procedures. The obtained PANI (10.0 g) were impregnated with 100.0 mL aqueous solution of 20.0 g p-Toluenesulfonic acid, after being impregnated at ambient temperature for 48 h, the catalyst was isolated by filtration, and dried at 60 °C for 8 h in an vacuum oven.

The used waste cooking oil sample was obtained directly from a local Chinese restaurant. Dehydration and decolorization with active-carbon was taken to remove the water and solid residues. Some properties of the feedstock such as density, free fatty acid, moisture content and acid value were determined as 0.921 g/cm³, 3.20%, 1.4% and 5.6 mg KOH/g, respectively.

Catalysts characterization

The BET (Brunauer-Emmett-Teller) specific surface areas, and total pore volumes were determined via nitrogen adsorption/desorption using a NOVA 2000e analyzer (Quantachrome, US). The total amount of Brønsted acid sites was measured by acid-base titration. Powder X-ray diffraction (XRD) was performed on a Rigaku D/max 2500 X-ray diffractometer, using Cu-K α radiation and scanning 2 θ from 5° to 45°, operated at 40 kV and 100 mA. Fourier transform infrared (FT-IR) spectra of the samples were recorded using a Thermo Nicolet 6700 FT-IR spectrometer in the region 4000-400 cm⁻¹. The thermogravimetric measurements (TG) were carried out using a NETZSCH STA 409 Luxx instrument within the temperature from 30 to 800 °C (heating rate 30 °C/min) in air atmosphere. Elemental analysis was performed by means of CHNS-VarioEL III apparatus.

Catalytic test

The transesterification reaction was performed in a 250.0 mL three-neck round bottom flask which was equipped with a water-cooled reflux condenser and a magnetic stirrer. The obtained results from contrast experiment revealed that PANI is inert for the present reaction. The transesterification reaction over p-TSA-PANI were carried out as follows: The predetermined amount of p-TSA-PANI, methanol and oil were added to the reactor. The reaction was started by stirring at 400 rpm and heated to specified temperature and time. Then, the mixture was cooled to room temperature and the catalyst was separated by centrifugation and the liquid product obtained was vaporized to remove excess methanol. The distilled product was transferred to a decanter to allow the separation of the glycerol and fatty acid methylesters (FAME) layers. Finally, FAME layers was analyzed by a GC/MS spectrometer, and the quality of the obtained product was compared with ASTM D6751.

Conclusions

In conclusion, an efficient catalyst, p-Toluenesulfonic acids doped polyaniline, was developed for the production of biodiesel from waste cooking oil. The physical properties of obtained biodiesel sample satisfied the requirement of ASTM D6751 standards, demonstrated that biodiesel product could serve as the ideal substitute for diesel fuel.

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