



Research article

A swelling-changeful catalyst for glycerol acetylation with controlled acid concentration



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ABSTRACT

A swelling-changeful polymer catalyst with controlled acid concentration for glycerol acetylation to biodiesel additives was carried out. This polysulfone catalyst was prepared by direct copolymerization of sulfonated monomer instead of post functionalization of polymer. The influences of acid concentration of polymer and reaction parameters (such as reaction temperature and time) on the glycerol conversion and product selectivity were studied. Glycerol conversion of 98.4% with 94.9% total selectivity of diacetin and triacetin was achieved at a moderate condition on a polysulfone catalyst with the appropriate acid concentration, which was more active than conventional Amberlyst 15 catalyst. The enhanced catalytic performance of polysulfone catalyst was attributed to the stronger acid strength and better swelling property. Besides, the polymer catalyst had a changeful swelling property during glycerol esterification. It swelled at the initial reaction stage and deswelled from solution at the end of reaction, which provided a good mass transfer during the reaction and endowed easy separation of catalyst from the reaction medium after the reaction. Moreover, the polymer catalyst can be reused several times without deactivation.

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1. Introduction

Nowadays, large amounts of glycerol as a by-product have been generated with the development of biodiesel industry, resulting in oversupply in the market [1–5]. The increasing low-cost supply of glycerol has naturally led to the endeavor for transformations of glycerol to other useful chemical products. Acetylation process of glycerol through esterification with acetic acid in the presence of acid catalysts has been extensively studied [6–12]. The glycerol is a polyhydroxy alcohol and the esterification of glycerol can produce monoacetin, diacetin and triacetin. The latter two compounds are more valuable due to their wide applications as fuel additives and solvents [13–16]. A two-step process was proposed for the highest triacetin yield. The first step involved esterification of glycerol with acetic acid. In the second step, the esterified product mixture was acetylated with acetic anhydride. So, the effective acid catalyst for the first esterification will reduce the amount of expensive acetic anhydride and decrease the cost. Solid acid catalysts have attracted much attention due to their advantages such as easy separation, non-corrosive and reusability over traditional homogeneous H₂SO₄ catalyst [17–19]. Zeolites, which are common solid acids owning uniform system of pores in the structure, have been tested in acetylation

of glycerol [4,6,10,20]. But, most of the zeolites only have micropores (<1 nm), which will hinder mass transfer and lead to low conversion of glycerol. Accordingly, functionalized mesoporous zeolites SBA-15 and MCM-41 with sulfonic acid group or metal oxide have been prepared and evaluated in the reaction, but the low conversion was attributed to their low acid concentrations [21]. Another kind of familiar acid catalyst was heteropolyacid. However, its active phase was soluble in many polar solvents such as water, alcohols and ketones, which resulted in difficult separation of catalyst from reaction medium [22]. In recent years, the sulfonated carbon materials were developed and applied in the glycerol esterification [23], but low acid concentration limited reaction activity. Besides this, the weak acid groups –OH and –COOH, which were produced during the sulfonation process, coexisted with –SO₃H. These weak acid groups were hydrophilic, and their adsorption of water decreased the activity of catalyst [24]. Amberlyst 15 which is a classical solid acid was also used in this reaction, and good conversion was achieved [25–29]. But it has the shortcomings of weak acid strength and low stability. More recently, a lanthanum exchanged montmorillonite was explored as a catalyst for glycerol esterification with high activity and selective of diacetylglycerols [30]. Up to now, the acid concentration of the above mentioned catalysts was hardly controlled. The control of acid concentration is important because the sulfonic acid group is hydrophilic while the mainline of polymer is hydrophobic. So, the acid concentration will affect the hydrophilicity/hydrophobicity of catalyst and further adsorption of reagents as well as catalytic

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performance. Moreover, the stability of catalysts was not studied under the recycled conditions.

Herein, a solid acid catalyst with controlled acid concentration based on polyethersulfone, which belongs to special engineering plastics having good thermal stability was reported. Higher conversion of glycerol, selectivity of biodiesel additives (diacetin and triacetin) and stability were achieved over this polymer catalyst in comparison with the conventional Amberlyst 15 catalyst. Besides this, this polyethersulfone catalyst had a changeful swelling property during the glycerol esterification, where it swelled at the initial stage and deswelled from solution after reaction. This characteristic provided good mass transfer and endowed easy separation of catalyst.

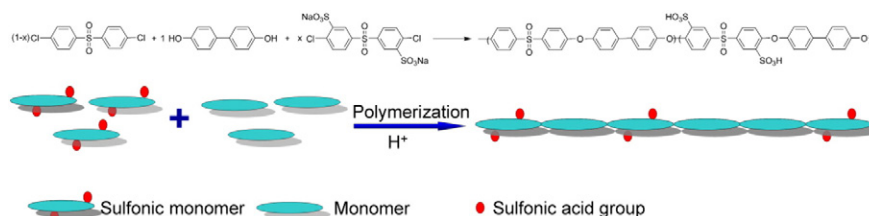
2. Experimental

2.1. Materials

N,N-dimethylacetamide (DMAA) (purity >99.0%), bis(4-chlorophenyl) sulfone (BCPS) (melting point: 146.5–147.1 °C), 4,4'-Biphenol (BP) (melting point: 281.8–282.5 °C), N-methyl-2-pyrrolidone (MP) (purity >99.0%), toluene (purity >98.0%), K₂CO₃ (purity >99.0%), CaH₂ (purity >99.0%), glycerol (purity >99.0%), and acetic acid (purity >99.5%) were procured from Tianjin Guangfu Chemical Reagent. Amberlyst 15 (acid concentration: 5.0 mmol/g), 1,9-Diphenyl-1,3,6,8-nonatetraen-5-one (purity >99.0%) and 1,3-Diphenyl-2-propen-1-one (purity >99.0%) were purchased from Alfa Aesar Company, Ltd. (USA). Sodium 5,5'-sulfonylbis(2-chlorobenzenesulfonate) (SSBCBS) monomer was synthesized and recrystallized as reported [31]

2.2. Preparation of catalysts

The synthesis of polyethersulfone precursor (PES-P) was shown in Scheme 1. In order to obtain different acid concentration of catalyst, the different molar ratios of SSBCBS and BCPS were applied to react with 4,4'-Biphenol. For example, the polymer with SSBCBS and BCPS molar ratio of 5:5 (PES-50) was synthesized as follows. 0.05 mol of 4,4'-Biphenol (BP), 0.025 mol of BCPS, 0.025 mol of SSBCBS and 0.058 mol of K₂CO₃ were sequentially added into a 250 mL 3-neck flask equipped with a mechanical stirrer, nitrogen inlet and a Dean-Stark trap. Then 130 mL pure DMAA was introduced to the flask. After that, 50 mL toluene was added as an azeotroping agent. The flow of N₂ is 20 mL/min. The synthetic temperature was raised to 165 °C and kept for 8 h to dehydrate, and then was raised to 185 °C to remove the toluene and maintained that temperature for 48 h. At that time, the solution became very viscous. The solution was cooled to the room temperature and was poured into water. The polymer PES-P was precipitated, and followed by being washed thoroughly with hot deionized water for three times. The polymer was dried in oven at 100 °C for 12 h. As-synthesized PES-P polymer was exchanged in 0.5 M H₂SO₄ at 25 °C for 6 h, and then filtrated. This process was repeated twice. Finally, the catalyst was washed with a large amount of deionized water (about 200 mL) until the filtrate reached neutrality, and dried at 100 °C for 12 h in vacuum. The resultant acid catalyst was denoted as PES-x (where x was adapted from 30 to 60 and represented the molar percent ratio of SSBCBS to total moles of SSBCBS and BCPS).



Scheme 1. The preparation of polymer solid acid catalyst.

2.3. Catalyst characterizations

¹H NMR spectra were collected at 25 °C on a Varian Unity 400 MHz instrument using (CD₃)₂SO (dimethyl sulfoxide-d₆) as solvent. The acid concentrations of catalysts were determined by inverse titration. Briefly, the catalyst was firstly immersed in 20 mL 0.1 M NaOH solution for 12 h, and then the solid was filtered off. After that the filtration was titrated by 0.02 M HCl. The strength of catalyst was measured using Hammett indicator method in dried toluene. Before use, the toluene was purified by being stirred with CaH₂, and then was distilled. In acid strength tests, the 0.02 g indicator (1,9-Diphenyl-1,3,6,8-nonatetraen-5-one or 1,3-Diphenyl-2-propen-1-one) was dissolved in 100 mL purified toluene. The solid catalyst particles (0.1 g) were then added into 20 mL solvent containing indicator and stirred for 24 h. If the color of catalyst changed to red, then the acid strength of catalyst was less than the H₀ value of this indicator. Otherwise, if the color of catalyst did not change, then the acid strength of catalyst was higher than the H₀ value of this indicator. Fourier Transform Infrared (FT-IR) spectra were recorded on using the KBr disk method. The viscosity of these polymers was measured with an Ubbelohde viscometer using MP as solvent at 25 °C. The Gel Permeation Chromatography (GPC) experiment was carried out on a liquid chromatograph equipped with Waters 2414 refractive index detector and Viscotek 270 ALLS/viscometric dual detector. The mobile phase was MP solvent containing 0.05 M LiBr. The data were collected using Waters Styragel HT columns at 60 °C. Molecular weights were determined by universal calibration calibrated with polystyrene standards. The sulfur analysis of the filtrate after the reaction was carried out with an Elementar Vario El elemental analyzer. The absorption of reagents over catalysts was carried out as follows: 0.1 g catalyst was immersed in the reagents (such as acetic acid, glycerol or water involved in the acetylation reaction) at 60 °C for 3 h. The original and adsorbing weight of catalyst was recorded.

2.4. Reaction procedures

The typical acetylation reactions were carried out with a three-necked round flask equipped with a condenser and a magnetic stirrer. The device was placed in an oil bath. The stirring was fixed at 300 rpm for all experiments to exclude the external diffusion. No dehydrating agent was used to remove by-product water in the reaction. The reaction procedure was performed as follows. The catalyst and glycerol were added into the round flask. The mixture was heated to the reaction temperature (about 30 min.). The swelling of catalyst in glycerol was observed at the time. Then the acetic acid was injected. In order to investigate the influence of time on the reaction, some intermediate samples were taken out and analyzed by gas chromatography with OV-101 Capillary Column and flame ionization detector (FID). The sample was identified by GC-MS with hp-5 Column.

The conversion of glycerol and selectivity of each product were calculated by the following formulas:

$$\text{Conversion of glycerol (\%)} = \frac{\text{moles of reacted glycerol}}{\text{moles of initial glycerol}} \quad (1)$$

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