



An efficient and sustainable production of triacetin from the acetylation of glycerol using magnetic solid acid catalysts under mild conditions



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ABSTRACT

The efficient and selective acetylation of glycerol to produce triacetin is achieved using magnetic solid acids as catalysts. The Fe-based materials including Fe-Sn-Ti(OH)_x, Fe-Sn-Ti(SO₄²⁻) and Fe-Sn-Ti(SO₄²⁻)-*t* (*t* represents the temperature for the heating treatment) were successfully prepared and employed in the acetylation of glycerol, respectively. As a result, 100% conversion and 99.0% selectivity for triacetin was obtained in the presence of a catalytic amount of Fe-Sn-Ti(SO₄²⁻)-400 at 80 °C for 30 min, which exhibits higher catalytic activity than those of some molecular sieves. The magnetic catalytic materials were respectively characterized by XRD, IR, TG-DTG, BET and NH₃-TPD techniques. Moreover, the effects of reaction temperature and reaction time in the glycerol acetylation are investigated in detail. Finally, based on the experimental results and reaction phenomena, a possible mechanism for the catalytic reaction is proposed.

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1. Introduction

The rapid increase of biodiesel production has led to a wider availability of crude glycerol as a by-product in chemical industry. Thus, the efficient utilization of excessive and cheap glycerol are becoming a new research topic at present, in which the etherification [1,2] and esterification processes [3,4] to fuel additive are considered as the promising route to conversion of glycerol.

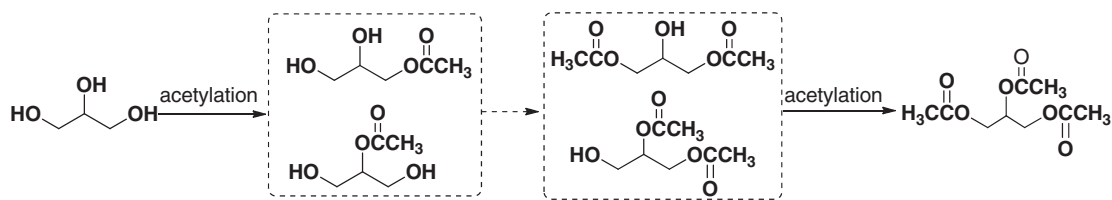
The glycerol derivatives such as glycerol esters, acetyl glycerol and glycerol acetal have good potential for the usage as fuel components that assist to a decreasing in particles, hydrocarbons, carbon monoxide and unregulated aldehydes emission. As shown in Scheme 1, the acetylation of glycerol contains three main steps, involving consecutive formations of monoacetin, diacetin, and triacetin via esterification reaction in the presence of acetylation reagents. In the previous study, the glycerol acetylation process was often accelerated by the acid catalysts in homogeneous media, for example, over sulfuric acid, hydrofluoric acid, *p*-toluenesulfonic acid or acidic ionic liquids [5,6]. However, these mineral acid catalysts have the obvious disadvantages such as the severe

environmental and economic issues. For avoiding these problems, the acetylation of glycerol with acetic acid was extensively studied in the presence of solid catalysts [3,7,8]. Generally, the used heterogeneous catalysts included the acid exchange resins [9–11], K-10 montmorillonite, HZSM-5 [3], HUSY [8], niobium-zirconium mixed oxides [12], PMo-NaUSY [13], supported heteropolyacids [14–16], mesoporous silica [17], and sulfonic acid functionalized deoxy cellulose [18], sulfated zirconia and niobic acid [19] etc. Particularly, the cation-exchange resins showed the high catalytic activity as well as the selectivity of higher esters where the triacetin are lower compared to diacetin. Very recently, Huang et al. [20] reported that the acetylation of glycerol to triacetin was achieved with the heteropolyacid-based ionic liquids as catalysts in which a 100% conversion of glycerol and a superior selectivity (86–99%) was obtained. Khayoon et al. [21] found that the Y/SBA-3 catalyst could promote the formation of diacetin and triacetin in the glycerol acetylation where the selectivity of 34% and 55% toward diacetin and triacetin was achieved under suitable conditions. Kale et al. [22] investigated the esterification of glycerol with acetic acid over acidic Amberlyst ion-exchange resins in the presence of toluene as an entrainer. As a result, a 95% selectivity of triacetin at complete glycerol conversion was obtained.

In this study, a series of magnetic solid catalysts and molecular sieves were successfully prepared and further employed in the acetylation of glycerol under mild conditions. It is found that a 100%

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Scheme 1. The reaction route for the acetylation of glycerol.

conversion and 99.0% selectivity for triacetin was obtained using the Fe-Sn-Ti(SO₄²⁻)-400 as the catalyst at 80 °C for 30 min. Moreover, based on the reaction phenomena and experimental results, a possible reaction mechanism is proposed to explain the catalytic process.

2. Experimental

2.1. Reagents and instruments

Glycerol, ferrous sulfate, ferric sulfate, stannic chloride pentahydrate, acetic acid, ammonia, tin(II) acetate, NaOH, acetic anhydride, ammonium sulfate, HZSM-5, H-β zeolite, nitric acid, deionized water and ethanol are analytic grade and got from commercial sources.

The monoacetin, diacetin and triacetin as the standard samples are purchased from Alfa Aesar.

The measurement of X-ray diffraction (XRD) was performed by diffractometer with Cu K_α radiation (0.02° resolution) and was collected from 20 to 80° [2θ]. The spectra of Fourier transform infrared spectroscopy (FT-IR) are recorded on a Nicolet Nexus spectrometer in the 400–4000 cm⁻¹ range. The thermal analysis (TG-DTG) is performed with NETASCH TG 209F3 instrument, and the data are shown from 0–1000 °C. BET surface areas, pore volumes, and average pore diameters of the prepared samples are obtained from N₂ (77 K) adsorption measurement using a Micromeritics ASAP2020 M system, in which the samples are pretreated under vacuum at 150 °C for 4 h before the measurement. The average pore diameters are calculated according to Barrett–Joyner–Halenda (BJH) model in absorption and desorption period. The acid properties of the magnetic solid catalysts was determined by temperature-programmed desorption of ammonia (NH₃-TPD). Before the adsorption of ammonia the samples were treated under helium at 500 °C (from 25 to 500 °C in 40 min) for 1 h. The samples were then cooled to 25 °C in He flow, then treated with a NH₃ flow for 30 min at 100 °C. The physisorbed ammonia was eliminated by flowing He for 1 h at 100 °C. NH₃-TPD was run between 100 °C and 950 °C at 10 °C/min and followed by an online gas chromatograph (GC) provided with a thermal conductivity detector.

The quantitative analyses of the products are performed on a GC apparatus with FID detector. The capillary column is HP-5, 30 m × 0.25 mm × 1.0 μm. In addition, the qualitative analysis for the product is carried out on the Agilent 6890/5973 Gas Chromatograph-Mass Spectrometer (GC-MS) instrument.

2.2. The preparation of magnetic matrix and its treatment method

The typical procedure is given in the following: a mixture of ferrous sulfate/ferric sulfate [Fe₂SO₄/Fe₂(SO₄)₃] was added in a vessel and solved with deionized water. The solution was then heated to 45 °C and NH₃·H₂O was added to adjust pH value to 10–11 using acidometer. The reaction was kept for 1 h. The produced magnetic matrix was separated with magnetic separation method and washed repeatedly to the neutrality. The magnetic matrix was stored with suspension liquid to use.

2.3. The synthesis of Fe-Sn-Ti (SO₄²⁻) solid acid

Stannic chloride pentahydrate (17.5 g) is added in three-neck flask. Under rapid stirring, 15 mL magnetic matrix (0.1 mol/L) and 10 mL tetrabutyl titanate are poured into the above flask, and then NH₃·H₂O is slowly dropped into the mixture to form the pasty liquids. The produced solid is filtered and washed numerous times to be neutral. Then, the solid sample is dried at 100 °C in oven, and the obtained material is referred as Fe-Sn-Ti (OH)_x. In the following, the above solid product is further sulfated through being soaked with 1 mol/L (NH₄)₂SO₄ solution for 24 h, and then filtered, dried to obtain the sulfated Fe-Sn-Ti material that is referred as Fe-Sn-Ti (SO₄²⁻). In addition, the sulfated Fe-Sn-Ti materials are calcined at different temperatures. Therein, the obtained samples calcined at 400 °C, 500 °C, 600 °C and 700 °C are signified by the Fe-Sn-Ti (SO₄²⁻)-400, Fe-Sn-Ti (SO₄²⁻)-500, Fe-Sn-Ti (SO₄²⁻)-600 and Fe-Sn-Ti (SO₄²⁻)-700 in the next discussion.

2.4. The preparation of deAl-β and Sn-β zeolites

The preparation of the deAl-β and Sn-β zeolites is similar with the reference [23]. In brief, 1) deAl-β zeolite is synthesized via the dealumination of H-β. The commercial H-β zeolite was dealuminated by treatment in HNO₃ solution (13 M) at 100 °C for 20 h [20 mL·g⁻¹(zeolite)]. 2) The Sn-β zeolite is synthesized by the solid-state ion-exchange (SSIE) process. The appropriate amount of tin(II) acetate was grinded with the required amount of dealuminated zeolite for 15 min. In addition, these prepared zeolites were calcined in an air flow at 550 °C before being used.

2.5. General procedure for the acetylation of glycerol

All the acetylations of glycerol with acetic anhydride or acetic acid were performed in a 120 mL steel autoclave equipped with the magnetic stirring and a temperature controller. Typical procedure for catalytic process is given as follows: a 1.5 g glycerol, 8.39 g acetic anhydride and the catalyst (2.5 wt.%) were charged into the autoclave; Under stirring, the mixture was preheated to 80 °C and kept for 30 min after the reactor was sealed. After the reaction, the mixture was transferred to a volumetric flask and was diluted with anhydrous ethanol. The conversion of glycerol and the selectivity of product were attained using the gas chromatograph with the internal standard method.

3. The physical properties of solid acid catalysts

3.1. The IR spectra of different catalysts

Figure 1 shows the IR spectra of different catalytic materials including Fe-Sn-Ti(OH)_x, Fe-Sn-Ti (SO₄²⁻), Fe-Sn-Ti (SO₄²⁻)-400 and Fe-Sn-Ti (SO₄²⁻)-600. It was found that the peaks of 3100–3250 cm⁻¹ and 3420–3550 cm⁻¹ in the spectrum of Fe-Sn-Ti(OH)_x are attributed to the stretching vibration of combined water and O–H bond. Moreover, these peaks of water and O–H bond become weak after the Fe-Sn-Ti(OH)_x is sulfated. Moreover, the characteristic peaks of the sulfated metal oxides often occur

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