Production of bioadditives from glycerol esterification over zirconia supported heteropolyacids

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HIGHLIGHTS

► $H_4SiW_{12}O_{40}/ZrO_2$ is an effective catalyst for glycerol esterification.
► A 93.6% combined selectivity of glyceryl diacetate and triacetate is achieved.
► $H_4SiW_{12}O_{40}/ZrO_2$ can be reused up to four consecutive runs without deactivation.
► $H_4SiW_{12}O_{40}/ZrO_2$ can be resistant to the impurities present in bulk glycerol.

GRAPHICAL ABSTRACT
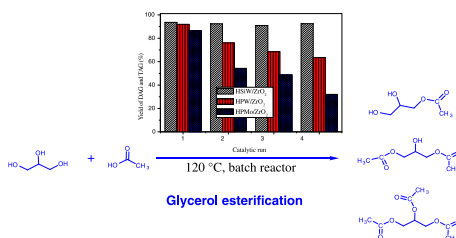
ABSTRACT

The synthesis of bioadditives for biofuels from glycerol esterification with acetic acid was performed over zirconia supported heteropolyacids catalysts using $H_4SiW_{12}O_{40}$ (HSiW), $H_3PW_{12}O_{40}$ (HPW) and $H_3PMo_{12}O_{40}$ (HPMo) as active compounds. The as-prepared catalysts were characterized by N_2-physisorption, XRD, Raman spectroscopy, NH_3-TPD, FTIR of pyridine adsorption and H_2O-TPD. Among the catalysts tested, HSiW/ZrO_2 achieved the best catalytic performance owing to the better combination of surface Brønsted acid sites and hydrothermal stability. A 93.6% combined selectivity of glyceryl diacetate and glyceryl triacetate with complete glycerol conversion was obtained at 120 °C and 4 h of reaction time in the presence of HSiW/ZrO_2. This catalyst also presented consistent activity for four consecutive reaction cycles, while HPW/ZrO_2 and HPMo/ZrO_2 exhibited distinct deactivation after reusability tests. In addition, HSiW/ZrO_2 can be resistant to the impurities present in bulk glycerol.

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1. Introduction

As the petroleum reserves deplete and concerns about environmental issues increase, the preparation of biofuels from biomass is stimulating growing interest (Chheda et al., 2007; Juan et al., 2011). In this context, biodiesel has gained considerable attention as a non-toxic, biodegradable and renewable alternative to petroleum-derived f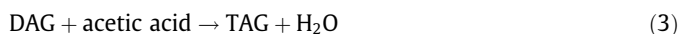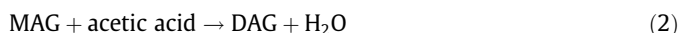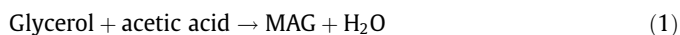uels. Biodiesel is usually manufactured by transesterification of plant and animal oils with methanol or ethanol, with glycerol as a co-product (Juan et al., 2011). With the rapid pace of biodiesel development and commercialization, glycerol is currently produced in a huge amount, which makes the price of glycerol decline sharply. Consequently, it is highly desirable to convert low-cost glycerol into value-added chemicals or materials. In addition, the biomass-derivate glycerol is a nontoxic, edible, and biodegradable compound containing highly multifunctional structure, making it as a versatile building block for the synthesis of a broad family of valuable derivatives by several catalytic processes involving oxidation (Hu et al., 2010; Tsuji et al., 2011), hydrogenolysis (Zhu et al., 2012a,b; Xia et al., 2012; Yuan et al., 2010), dehydration (Tsukuda et al., 2007),

etherification (Ayoub et al., 2012) and so on. The esterification of glycerol with acetic acid to produce glycerol acetates as valuable bioadditives of biodiesel is one of the most promising approaches for glycerol utilization. This route leads to the formation of glyceryl monoacetate (MAG), glyceryl diacetate (DAG) and glyceryl triacetate (TAG), which are widely applied in cryogenics and biodegradable polyester as well as cosmetics (Rahmat et al., 2010). Furthermore, the DAG and TAG have been identified as potentially high quality bioadditives for liquid fuels because they can enhance cold and viscosity properties, improve octane rating, decrease fuel cloud point and reduce greenhouse gas emissions, which could be a substitute for the controversial tertiary alkyl ether (Rahmat et al., 2010).

It is well-known that the acidity of catalyst has significant impact on the catalytic performance of glycerol esterification, particularly for Brønsted acid sites (Melero et al., 2007; Liu et al., 2011). Conventionally, esterification of glycerol with acetic acid is performed with mineral acids as homogeneous catalysts, which suffers from the inherent problems in terms of catalyst separation, reactor corrosion and environmental protection as well as economical inconveniences. Thereby, it is highly desirable to develop heterogeneous solid acid catalyst systems for this green reaction. Various solid acid catalysts including sulfated activated carbon (Khayoon and Hameed, 2011), sulfated zirconia (Dosuna-Rodriguez et al., 2011), sulfonated carbon (Sanchez et al., 2011), mesoporous silica with sulfonic acid groups (Melero et al., 2007), ZSM-5 (Goncalves et al., 2008), and double SO_3H-functionalized ionic liquids (Liu et al., 2011) have been tested for this reaction. In our previous study (Liao et al., 2009), we have exhibited glycerol esterification over acidic resins and zeolites and found that Amberlyst-35 was a superior catalyst for its large pore and accessible acid sites. Despite noticeable advantages of these solid acid catalysts, their costs, pore-size limitation, reuse or low selectivity towards the preferred DAG and TAG are still unresolved issues for industrial applications. It is generally identified that this reaction involves three consecutive steps and the specific scheme can be expressed as shown in Eqs. (1)–(3) (Zhou et al., 2012):

$$Glycerol + acetic\ acid \rightarrow MAG + H_2O \tag{1}$$

$$MAG + acetic\ acid \rightarrow DAG + H_2O \tag{2}$$

$$DAG + acetic\ acid \rightarrow TAG + H_2O \tag{3}$$

As water is an unavoidable by-product and can weaken the acid sites, the water-tolerant property of solid acid catalyst is a key factor to perform glycerol esterification well. In previous reports (Ferreira et al., 2009a,b; Reddy et al., 2010), leaching of active components into the reaction medium and the relatively low selectivity to the desired DAG and TAG are the two main disadvantages of heterogeneous catalysts in glycerol esterification. Thereby, in this work it is particularly important to explore a heterogeneous catalyst possessing outstanding hydrothermal stability and good Brønsted acid sites.

Heteropolyacids (HPAs) have been demonstrated to display outstanding catalytic performance for a wide variety of acid-catalyzed reactions owing to its well-defined structure, low corrosiveness and widely tunable acidity (Kozhevnikov, 2007; Misono, 2009). However, HPAs lack thermal stability, possess low surface area and leach easily in polar media, which limits their applications greatly. To solve these disadvantages, HPAs are often immobilized on supports like SiO_2, ZrO_2 or zeolites. Ferreira et al. (Ferreira et al., 2009a) exhibited glycerol esterification with acetic acid over phosphomolybdic acid (HPMo) encaged in USY zeolite. Through this process, DAG and MAG were produced with 59% and 37% selectivity at 68% glycerol conversion. Some effective catalytic systems have been found dealing with phosphotungstic acid (HPW)

supported on niobic acid (Balaraju et al., 2010), activated carbon (Ferreira et al., 2011) and silica matrix (Ferreira et al., 2009b). Though these reported catalysts have displayed high activity and relative efficiency for glycerol esterification, the low selectivity to TAG and bad hydrothermal stability are still unresolved problems. Surprisingly, there has been no report on the esterification of glycerol with acetic acid in the presence of silicotungstic acid (HSiW). In fact, much attention has been given to HSiW as a promising candidate for many types of reactions in recent years. Varisli et al. (Varisli et al., 2007) communicated that supported HSiW was more active than HPW and HPMo in esterification reaction, which was linked to the presence of high number of Keggin protons of HSiW (four) as compared to HPW and HPMo (three). Tsukuda et al. (Tsukuda et al., 2007) found that supported HSiW showed higher activity than HPW and HPMo in glycerol dehydration due to the high thermal stability and resistance to water. Thus, it seems plausible that supported HSiW might be an effective heterogeneous acid catalyst for this reaction owing to its higher Brønsted acid sites and hydrothermal stability than supported HPW and HPMo.

Our previous reports (Zhu et al., 2012a,b) have showed that ZrO_2 supported HSiW was more active and stable than those of other supports (γ-Al_2O_3, activated carbon, TiO_2 and SiO_2) in glycerol hydrogenolysis under hydrothermal conditions due to the strong interaction between ZrO_2 and HSiW. In this work, several zirconia supported HPAs (HSiW, HPW and HPMo) catalysts have been prepared, characterized and evaluated for the esterification of glycerol with acetic acid. Various reaction parameters have been investigated to optimize the reaction conditions to obtain the maximum activity and selectivity to the preferred products (DAG and TAG). In addition, the reusability over these catalysts for glycerol esterification has also been exhibited.

2. Experimental

2.1. Materials

ZrO_2 (59.7 m^2g^{-1}) was supplied by Jiangsu Qianye Co., Ltd, China. Anhydrous glycerol of high purity (>99%) was obtained from Tianjin Hengxing Chemical Preparation Co., Ltd, China. Acetic acid (>99.5%), silicotungstic acid (HSiW, AR), phosphotungstic acid (HPW, AR) and phosphomolybdic acid (HPMo, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Crude glycerol (8 wt.% NaCl, 3 wt.% KCl, 1 wt.% methanol and 10 wt.% water) was provided by Ruijiang Chemical Co., Ltd, China. All the received chemicals were used without any further treatment.

2.2. Catalyst preparation

All the catalysts were synthesized using an incipient wetness impregnation method. Typically, the HSiW/ZrO_2 catalyst was prepared by impregnation of 8.0 g zirconia support with 5.0 ml aqueous solution of 139.0 mmol/l HSiW. The sample was impregnated for 8 h, dried overnight at 110 °C and then calcined at 250 °C in static air for 4 h. The HPA loadings were fixed at 20 wt.% in all catalysts.

2.3. Catalyst characterization

BET surface area and BJH pore size distribution were calculated by using N_2 adsorption–desorption isotherms at −196 °C on a Micromeritics ASAP 2420 instrument. Samples were degassed at 250 °C for 8 h in vacuum prior to the measurements.

Powder X-ray diffraction (XRD) patterns were detected at room temperature on a D2/max-RA X-ray diffractometer (Bruker, Germany) with a Cu Kα radiation source at 30 kV and 10 mA. The