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Production of bioadditives from glycerol esterification over zirconia supported heteropolyacids

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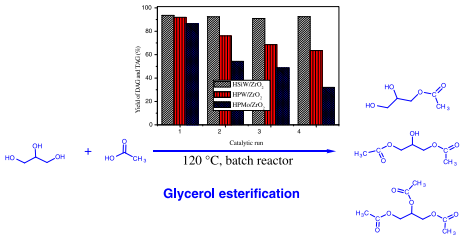
HIGHLIGHTS

- $H_4SiW_{12}O_{40}/ZrO_2$ 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



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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.

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 fuels. 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),

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