



Selective esterification of glycerol to bioadditives over heteropoly tungstate supported on Cs-containing zirconia catalysts

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ABSTRACT

Esterification of glycerol with acetic acid was carried out over tungstophosphoric acid (TPA) supported on Cs-containing zirconia. The catalysts were prepared by impregnation method and characterized by FT-infrared spectroscopy, X-ray diffraction and temperature program desorption of NH_3 . The catalysts exhibited more than 90% conversion within a short reaction time. The catalytic activity depends on the amount of exchangeable Cs with TPA on zirconia, which is in turn related to the acidity of the catalysts. The acidity of the catalysts varied with the presence of residual protons of TPA. The effects of various parameters, such as reaction temperature, catalyst concentration and molar ratio of glycerol to acetic acid, were studied and optimized reaction conditions are established.

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1. Introduction

Glycerol is the main by-product in biodiesel production by transesterification of oil with methanol or ethanol. The increasing use and production of biodiesel has resulted in substantial amount of glycerol accumulation. This has allowed researchers to look for new usages of glycerol [1,2]. In future, glycerol will be a cost-effective raw material for the preparation of valuable chemicals and fuel additives. Different methods for the conversion of glycerol to value-added chemicals such as hydrogenolysis to propane diols and for the preparation of different oxidation products have been explored [3–12]. The uses of glycerol-based additives to improve properties of biodiesel are also being explored [13]. The esterification of glycerol with acetic acid can be a good application for glycerol utilization. The products of glycerol esterification are monoacetin, diacetin and triacetin, which have great industrial applications. The products like triacetin have different applications, going from cosmetics to fuel additives. The mono and diacetylated esters are also have applications, particularly in cryogenics and syntheses of biodegradable polyesters [14]. Acetylation of glycerol has been carried using solid acid catalysts such as zeolites. The main aspect of the catalyst is its selectivity for this reaction.

Heteropoly acids (HPAs) are typical strong Bronsted acids and catalyze a wide variety of reactions in both homogeneous and

heterogeneous phases [15]. The major disadvantages of HPAs as catalysts lie in their low thermal stability, low surface area ($1\text{--}10\text{ m}^2/\text{g}$) and solubility in polar media. HPAs can become eco friendly insoluble solid acid catalysts with high thermal stability and high surface area by exchanging their protons with metal/alkali metal ion and supporting them on suitable supports. The support not only increases the surface area but also its stability. Supported HPAs were also studied for simple esterification reactions and were found to be highly active [16]. The support plays an important role in the dispersion of HPA and in the acidic nature of the final catalyst. The activity of the HPAs can be exchanged by supporting them on acidic supports and by exchanging the proton partially with alkali metal ions like Cs^+ . It is known that the Cs salts of heteropoly acids are more acidic than parent HPAs [17]. Partial substitution of H^+ by Cs^+ changes the number of available surface acid sites and the resulting materials exhibit significantly higher activities than the parent acid in acid-catalyzed reactions [18]. Cs-containing phospho tungstates are well-known as a water-insoluble strong Brønsted acid and a versatile solid acid catalyst possessing high thermal stability ($\geq 500^\circ\text{C}$) and water tolerance [19–22]. Even though the Cs salts possess more surface area compared to HPAs, their overall surface area and stability is minimum. It is not possible to prepare directly Cs salts of HPA dispersed on support. The usual way to prepare is firstly dispersing Cs on support and then supporting HPA on it by anticipating the partial exchange of Cs present on support with HPA. There are few studies where the support is doped with Cs and heteropoly acid is supported on it. Yang et al. reported the heteropoly tungstate supported on Cs modified

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mesoporous silica catalysts and their catalytic activity towards *n*-butane isomerization [23]. In another study cesium salts of TPA supported on dealuminated ultra-stable Y zeolite catalysts are reported. The Cs salt of TPA was generated by first dispersing Cs on Y zeolite, followed by impregnation of TPA [24]. Yadav and George reported the novelty of Cs substituted HPA supported on clay for acid-catalyzed reactions [25].

In the present study, tungstophosphoric acid supported on Cs-containing zirconia catalysts are prepared and evaluated for the acetylation of glycerol with acetic acid. This reaction is tested under different reaction parameters to yield the desired product. The catalyst performance is discussed with the observed physico-chemical properties derived from different characterization methods. It is interesting to know the activity of the catalysts when Cs present on zirconia is partially exchanged with TPA.

2. Experimental

2.1. Preparation of the catalysts

Initially Cs is doped on zirconia and this material is used as support to disperse TPA. The chemicals CsNO_3 and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ are purchased from Aldrich Chemicals. The support hydrous zirconia was prepared by hydrolyzing the aqueous solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ with ammonium hydroxide at a pH of 10. The precipitate was filtered off and thoroughly washed with deionized water several times until the chloride content was negligible. The precipitate is dried at 120°C for 36 h. The hydrous zirconia after thorough drying was used as support. Firstly, the required amount of CsNO_3 was dissolved in aqueous solution and added to the hydrous zirconia. The solution was allowed to sit for 3 h and then the excess water was evaporated on a water bath. The dried catalyst masses were kept for further drying in an air oven and calcined at 500°C for 2 h. Later TPA supported on Cs-containing zirconia was prepared in the same fashion by taking calculated amounts of TPA in aqueous solution. The final catalysts were calcined at 350°C for 4 h in air. The quantity of Cs is varied such that Cs can be exchangeable with 1, 2 and 3 protons of TPA. A catalyst without Cs also prepared in the similar way by dispersing TPA on zirconia. The active component TPA is kept constant at 20 wt% for all the catalysts. These catalysts are denoted as 20%TPA/Cs_{*x*}-ZrO₂ where *x* = 0, 1, 2 and 3.

2.2. Characterization of the catalysts

X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex diffractometer using $\text{CuK}\alpha$ radiation (1.5406 \AA) at 40 kV and 30 mA. The measurements were obtained in steps of 0.045° with a count time of 0.5 s and in the 2θ range of $10\text{--}80^\circ$. FT-IR spectra were recorded on Biorad Excalibur series using KBr disc method.

Temperature programmed desorption of ammonia (TPA) was carried out on a laboratory-built apparatus equipped with a gas chromatograph using a TCD detector. In a typical experiment about 0.05 g of the oven dried sample was taken in a quartz tube. Prior to TPD studies, the catalyst sample was treated at 300°C for 1 h by passing pure He gas (99.9%, 50 ml/min). After pretreatment, the sample was saturated with anhydrous ammonia ($10\% \text{ NH}_3$) at 100°C at a flow rate of 50 ml/min for 1 h and was subsequently flushed with He at the same temperature to remove physisorbed ammonia. The process was continued until a stabilized base line was obtained in the gas chromatograph. Then the TPD analysis was carried out from ambient temperature to 700°C at a heating rate of $10^\circ\text{C}/\text{min}$. The amount of NH_3 evolved was calculated from the peak area of the already calibrated TCD signal.

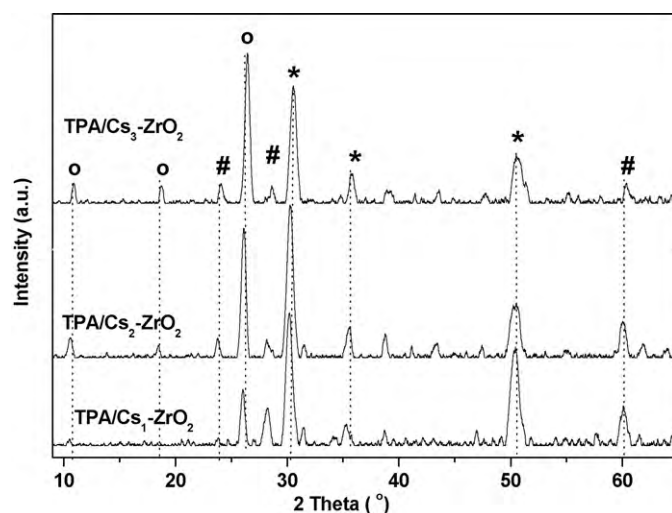


Fig. 1. XRD profiles of TPA supported on Cs-containing zirconia catalysts. (o) TPA, (#) Monoclinic phase of ZrO_2 , (*) Tetragonal phase of ZrO_2 .

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of the catalysts are shown in Fig. 1. The catalysts showed main patterns related to the support zirconia. Both tetragonal and monoclinic phases of ZrO_2 are present, monoclinic being predominant. The characteristic diffraction peaks related to Keggin ions of TPA are observed at 2θ of 10.3° and 24.4° [26]. XRD analysis suggests the presence of intact Keggin ion structure of TPA on Cs-ZrO₂.

FT-IR spectra give an informative fingerprint about the presence of Keggin structure of heteropoly tungstates. The FT-IR spectra of the catalysts are presented in Fig. 2. The catalysts mainly exhibited bands at 1081 , 990 , 887 and 798 cm^{-1} related to the asymmetric vibrations of (P–O), (W=O_t), (W–Oc–W) and (W–O_b–W) modes, respectively [27]. These results endorse the existence of Keggin structure of TPA on support. The FT-IR results support the observations made from XRD analysis.

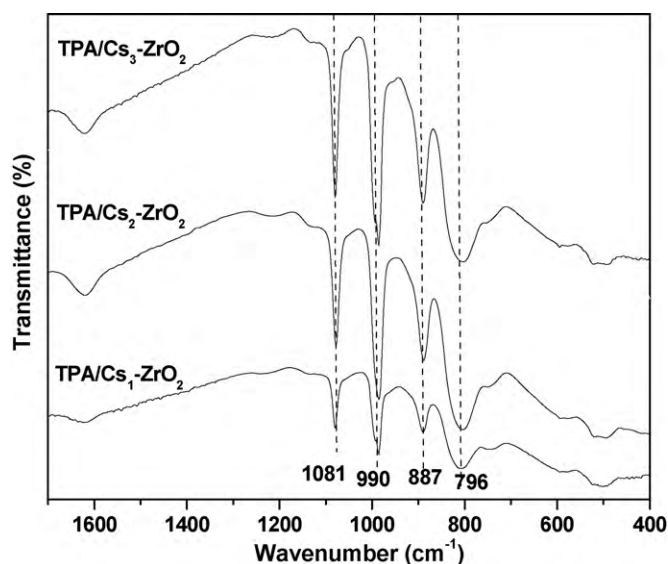


Fig. 2. FT-IR of TPA supported on Cs-containing ZrO_2 catalysts.

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