Cesium exchanged tungstophosphoric acid supported on tin oxide: An efficient solid acid catalyst for etherification of glycerol with *tert*-butanol to synthesize biofuel additives

M. Srinivas, G. Raveendra, G. Parameswaram, P.S. Sai Prasad, N. Lingaiah *

Catalysis Laboratory, I & PC Division, Indian Institute of Chemical Technology, Hyderabad 500607, India

ABSTRACT

Cesium exchanged tungstophosphoric acid (CsTPA) supported on tin oxide catalysts were prepared and their physio-chemical properties were derived from X-ray diffraction, FT-IR, laser Raman spectroscopy and temperature programmed desorption of NH_3. The catalysts activity was evaluated for etherification of glycerol with *tert*-butanol. The characterization results of the catalysts revealed that the primary Keggin structure remained intact during the exchange of TPA protons with Cs^+ ions. The activity results showed that etherification activity depended on the amount of the CsTPA over SnO_2 and the catalyst with 20 wt% CsTPA supported on SnO_2 showed high catalytic activity with 90% glycerol conversion with 44% selectivity toward higher ethers. The activity of the catalyst depends on amount of surface acidic sites and dispersion amount of CsTPA over SnO_2. The etherification reaction was carried at different reaction parameters and optimum reaction conditions were established. The catalysts were recyclable and showed constant activity up on reuse.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The development of environmental friendly process with the use of renewable resources has gained much attention in recent times. Glycerol, one of the renewable resources is obtained as a by-product in manufacturing biodiesel by transesterification of vegetable oils with alcohols [1,2]. Unfortunately, the current application of glycerol is mainly confined to pharmaceuticals and cosmetics, hence the demand is somewhat limited [3]. It is necessary to find new outlets to convert the surplus glycerol into high-value-added products in order to increase the economy of biodiesel manufacture [4]. Selective oxidation of glycerol to glyceric acid, dihydroxyacetone, mesoxalic acid, etc. [5–7], dehydration to acrolein [8], hydrogenolysis to propylene glycol [9], carbonylation to glycerol carbonate [10–12], synthesis of hydroxyquinoline and quinolone by Skraup synthesis [13–15] and acetylation to esters [16] are some of the possible alternative routes to convert glycerol to valuable products. One interesting option is the catalytic etherification of glycerol with alcohols or short-chain olefins to obtain mono, di- and tri alkyl ethers of glycerol. The mono alkyl

glyceryl ethers are highly valuable chemicals since they exhibit a wide range of application as intermediates in the pharmaceutical industry, agrochemicals and as non-ionic surfactants [17,18]. The di and tri alkyl ethers of glycerol (higher ethers) constitute excellent oxygenated additives with a large potential for diesel and biodiesel reformulation. When these higher ethers are incorporated into standard 30–40% aromatic containing diesel fuel, emissions of particulate matter, hydrocarbons, carbon monoxide, and unregulated aldehydes reduced significantly [19]. Thus, synthesis of higher ethers has gained lot of interest in recent times.

Glycerol etherification with *tert*-butanol or isobutylene has been studied in the presence of acid catalysts [20–24]. When isobutylene (IB) was used as an etherification agent, better conversion and selectivity to higher ethers were obtained [25]. However, it should be noted that IB produced by steam cracking of high boiling petroleum fractions or mixture of saturate hydrocarbons [26]. Therefore, the use of *tert*-butanol as etherifying agent, in substitution of IB, avoids both the need of solvents (i.e., dioxane, dimethyl sulfoxide) and the mass transfer limitation phenomena related to the complex three-phase system [27]. Moreover, TBA is a by-product of the large-scale propylene oxide production and it also can be produced from bio-sources, like starch or lignocellulosic biomass [28].

Homogeneous and heterogeneous catalysts are employed for etherification of glycerol with *tert*-butanol [29,30]. In spite of

* Corresponding author. Fax: +91 40 27160921.
  E-mail addresses: nakkalingaiah@iict.res.in, nakkalingaiah.iict@gov.in, lingaiah66@yahoo.co.in (N. Lingaiah).

several advantages, homogeneous catalysts have some problems which include recovering the catalyst and separation of the products. Therefore an effective and environmentally benign solid heterogeneous catalyst is required. To date, very few heterogeneous catalysts such as commercial ion-exchange resins (Amberlyst 15 and 35) [31], wide-porous zeolites (ZSM-5, H–Y and H–Beta zeolites, etc.,) [26], sulfonated carbon [32], Nafion on amorphous silica [33] and heteropolyacids [34] were reported for etherification of glycerol. Very recently, González et al. [35] reported that fluorinated beta zeolites generated higher amounts strong Brønsted acid sites, which enable high glycerol conversion (75%) and selectivity to higher ethers (37%). Even though all of these catalysts reported high glycerol conversion, the overall selectivity toward higher ethers is limited and requires long reaction times.

The Keggin type heteropolyacids (HPA) have attracted a lot of attention due to their strong Bronsted acidity and environmental friendliness [36,37]. However, its low surface area ($<10\,m^2\,g^{-1}$) and high solubility in polar solvents limit its potential catalytic performance. HPAs can be made heterogeneous by exchange of its protons (H^+) with metal ions [38,39] and/or supporting them on suitable supports [40,41]. The support plays an important role in enhancing the acidity, thermal stability and surface area of the final catalyst. Very recently, Frusteri et al. [33] investigated cesium exchanged phosphotungstic acid (TPA) supported on silica catalysts and tested for etherification of glycerol with *tert*-butanol. However the catalyst was less selective toward higher ethers. Cs-containing phosphotungstates are well-known as a water insoluble strong Brønsted acid and a versatile solid acid catalyst possessing high thermal stability ($\geq 500\,^{\circ}C$) and water tolerance [42]. However, they have the tendency to form milky colloid in polar solutions which can be overcome by stabilizing them on suitable supports [43]. Tin oxide, SnO_2, has been used wide range of applications in sciences, technologies and industries, such as catalysis, conductivity, gas sensing, ceramics, plastics, and antistatic coating [44,45]. Thus it is of interest to study the novelties of supported tin oxide catalysts for etherification of glycerol with *tert*-butanol.

In the present study, tungstophosphoric acid was modified by exchanging its protons with Cs^+ ions and dispersed on tin oxide support. The catalysts were evaluated for etherification of glycerol with *tert*-butanol. The reaction was tested under different reaction parameters to yield higher ethers. The catalyst performance was discussed with the observed physico-chemical properties derived from different characterization methods.

2. Experimental

2.1. Catalyst preparation

Cs exchanged TPA supported on tin oxide catalysts were prepared in two steps. In the first step, the required quantity of TPA was dissolved in water and this solution was added drop wise to support, tin oxide. After stirring for 30 min, the excess water was removed on water bath and the samples were calcined at 300 °C for 2 h. In the second step, calculated amount of cesium nitrate dissolved in distilled water was added drop wise to the TPA supported SnO_2 samples. The TPA content on support is varied from 10 to 30 wt%. The final catalyst are denoted as Y wt% Cs_1TPA/SnO_2 (YC_1TS) where Y = 10, 15, 20, 25 and 30.

2.2. Catalysts characterization

BET surface area of the catalyst samples were obtained by N_2 adsorption at liquid N_2 temperature on Autosorb-1 (Quantachrome) instrument. Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex diffractometer
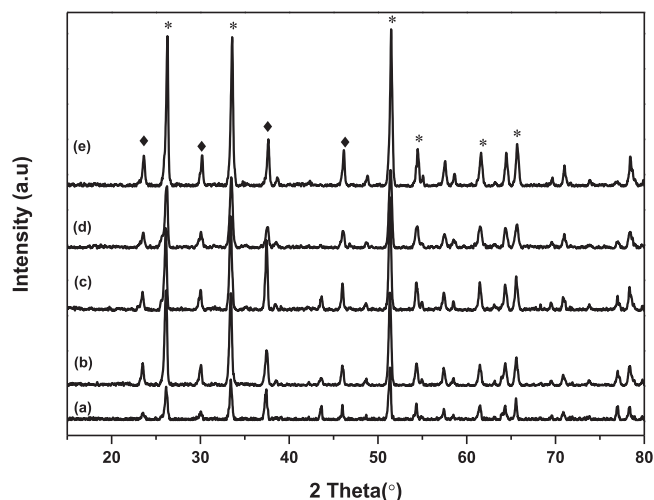

Fig. 1. XRD patterns of (a) $10C_1TS$ (b) $15C_1TS$ (c) $20C_1TS$ (d) $25C_1TS$ and (e) $30C_1TS$. (♦) TPA and (*) SnO_2.

using CuKα radiation (1.5406 A°) at 40 kV and 30 mA. The measurements were obtained in steps of 0.045° with an account time of 0.5 s and in the 2θ range of 10–80°. FT-IR spectra of catalysts were recorded on a Biorad Excalibur spectrometer adopting the KBr disk method. The elemental analysis of the samples was measured by Agilent 7700 Series Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

Temperature-programmed desorption (TPD) of NH_3 was carried out in a laboratory-built apparatus equipped with a gas chromatograph using a TCD detector. In a typical experiment, about 0.1 g of oven dried sample was taken in a quartz tube. The catalyst sample was initially activated at 300 °C for 2 h under flowing helium (He) gas (99.995%, 50 ml/min) to clean the surface of the catalyst. After cooling the sample to 100 °C the sample was exposed to 10% NH_3 balanced He gas for 1 h. The sample was then flushed with He to drive off physisorbed NH_3. TPD of the catalyst was then carried out in He flow at a rate of 30 ml/min, in the temperature range of 100–700 °C and with a ramp of 10 °C/min. The amount of NH_3 desorbed was calculated from the peak area of the already calibrated TCD signal.

2.3. Experimental procedure

Etherification of glycerol was carried out in a 100-ml haste alloy PARR autoclave. Etherification of glycerol with *tert*-butanol were carried at autogenous pressure. Required quantities of glycerol (0.02 mol), *tert*-butanol (0.12 mol) and catalyst (1.3 mmol) were introduced in to the autoclave and purged three times with N_2. After the purge, the reactor was heated to desired reaction temperature and stirring was fixed for all experiments at 500 rpm to avoid external diffusion limitations. During the reaction, pressure was developed autogenously. After the reaction, the gas phase products were collected in a gasbag and the liquid phase products were separated from the catalyst by filtration. Liquid products were analyzed using a gas chromatograph (Shimadzu 2010) equipped with FID using capillary Inno wax (0.25 mm × 30 m, DF = 0.25) column. The products were confirmed by GC–MS (Shimadzu, GCMS-QP2010) analysis also. The gas products were analyzed by using a gas chromatograph (Porapak Q column) equipped with a thermal conductivity detector. In addition, the products were comparatively confirmed with the assistance of the characterization data reported by Jamróz et al. [46].