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Catalytic upgrading of citric acid to environmental friendly tri-butyl citrate plasticizer over ultra stable phosphonated Y zeolite

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ABSTRACT

The catalytic synthesis of non-toxic/eco-friendly tributyl citrate (TBC) plasticizer by esterification of renewable citric acid (CA) with butanol would be completely sustainable route. In this context, catalytic performance of parent ultra stable Y (USY) and phosphonated USY catalysts were investigated for TBC synthesis. Parent USY and phosphonated USY catalysts were characterized by powder X-ray diffraction (XRD), N₂ adsorption–desorption, NH₃ temperature programmed desorption (TPD), pyridine-Fourier Transform Infrared Spectroscopy (FTIR), FTIR, SEM, ICP. The influence of various process parameters such as phosphorous (P) loading (0 to 4 wt%), catalyst loading (5–25%), molar ratio of CA to *n*-butanol (1:4 to 1:12), reaction temperature (383–423 K) and reaction time (1–5 h) have been investigated over USY catalyst with aim to maximize CA conversion and TBC yield. Amongst the studied catalysts, the 2% (w/w) P/USY was found to be highly potential catalyst with complete CA conversion (100%) and 93% TBC yield. The present method of using 2% (w/w) P/USY catalyst for the synthesis of TBC would be environmentally benign in the context of bio-renewable synthetic route, high catalytic activity, non-toxic product, long term stability and reusability of catalyst (five catalytic cycles).

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1. Introduction

Recently, the plasticizers market is growing worldwide, as projected by latest statistical data at about 11 billion pounds per year of which, 2.4 billion pounds is shared by the United States (U.S.) (Kolah et al., 2007, 2008; Nandiwale et al., 2015). In particular, tributyl citrate (TBC) is an vital thermally stable and non-toxic plasticizer having numerous applications in polymer industries such as solvent for synthesis of polyvinyl chloride (PVC) and its copolymers, which are subsequently applied to food wrapping film (Kolah et al., 2007, 2008; Lemmouchi et al., 2009; Nandiwale et al., 2014; Xu et al., 2010, 2011; Yang et al., 2014). Moreover, TBC is extensively applied as non-toxic plasticizers in toys, medical products (e.g. as enteric coatings for controlled release drug delivery systems),

printing ink coatings, biodegradable polymers, cosmetics and food additives (Kolah et al., 2007, 2008; Lemmouchi et al., 2009; Nandiwale et al., 2014; Xu et al., 2010, 2011; Yang et al., 2014).

The production of citric acid (CA) (Angumeenal and Venkappayya, 2013; Dhillon et al., 2011; Papagianni, 2007) and butanol (Abdehagh et al., 2014) from renewable sources has been extensively studied. Recent biotechnology and bioprocessing advancements on production of CA and *n*-butanol have been reported in literature (Abdehagh et al., 2014; Ali et al., 2011; Angumeenal and Venkappayya, 2013; Dhillon et al., 2011; Papagianni, 2007; Yang et al., 2014). Hence, the esterification of this fermentation derived CA and *n*-butanol to produce non-toxic TBC plasticizer would be entirely bio-renewable and sustainable option.

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Traditionally, TBC has been synthesized mainly over sulfuric acid and titanate (Xu et al., 2010, 2011; Yang et al., 2014). The homogeneous catalysts like sulfuric acid which has many drawbacks such as high by product formation, corrosion of equipment and also reinforced by environmental policies. Hence, it is technological demand to develop heterogeneous catalyst offering easy separation, higher activity and eco-friendly for synthesis of TBC. Recently, performance of various catalysts such as ionic liquids (Xu et al., 2010, 2011), 40 wt.% ZS/HMS (Yang et al., 2014), and 20SA/MCM-41 (Pan et al., 2013) have been investigated for TBC synthesis.

In view to develop sustainable and industrial benign catalytic process; it was thought of interest to investigate catalytic performance of ultra stable Y (USY) and phosphonated USY for synthesis of TBC. The USY zeolite was used because of its peculiar properties of temperature stability, surface area, porosity, inherent acidity, shape selectivity etc. as compared to other zeolites.

This study explores new avenues on development of highly active and stable solid acid catalyst for selective synthesis of non-toxic TBC plasticizer by esterification of renewable CA and *n*-butanol. The optimization of reaction process parameters such as P loading, catalyst loading, molar ratio of CA to *n*-butanol, reaction temperature and time were also performed with aim to maximize the CA conversion and TBC yield. The reusability of optimum catalyst at optimized process parameters is also presented.

2. Experimental

2.1. Chemicals used

Anhydrous citric acid crystals were obtained from Aldrich Chemical Co. The *n*-butanol (99%) was procured from M/s E. Merck, Mumbai (India). The zeolite ultra stable Y (USY, Si/Al = 15) were procured from Zeolyst, USA. All the reagents used were of analytical quality and used as it is.

2.2. Phosphonation of USY with H_3PO_4

Typically, 60.0 g of USY catalyst was taken into a 1000 ml round bottom flask and then 600 ml of a 0.37% H_3PO_4 solution in water was added. The said mixture was refluxed at 363 K for 1 h under magnetic stirring. Then solvent was evaporated using rota vapour (353 K). The material thus obtained was in white powder form and subjected for the stepwise calcinations in presence of air at 823 K for 5 h. A calcined material was then obtained with a phosphorus (P) content of 1% and designated as 1% (w/w) P/USY. Similarly, other phosphonated USY catalysts were prepared with P content of 2% and 4% and designated as 2% (w/w) P/USY and 4% (w/w) P/USY, respectively.

2.3. Catalyst characterization

Parent USY and phosphonated USY catalysts were characterized by powder X-ray diffraction, nitrogen adsorption-desorption, NH_3 temperature programmed desorption (TPD), pyridine-Fourier Transform Infrared Spectroscopy (FTIR), FTIR, SEM and ICP. The amount of P present in the samples was estimated by ICP-OES (Spectro Arcos, FHS-12) (Table 1).

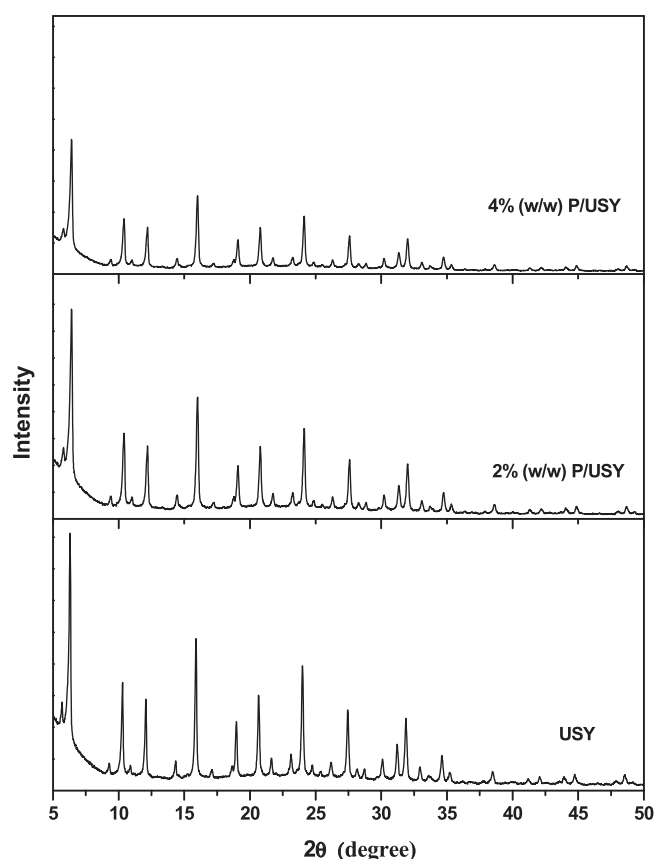


Fig. 1 – Powder X-ray diffraction patterns of parent and phosphonated USY catalysts.

The phase identification and purity of catalysts were determined by powder X-ray diffraction (XRD). The XRD patterns were recorded on X-ray diffractometer (P Analytical PXRD system, Model X-Pert PRO-1712) using $CuK\alpha$ radiation at a scanning rate of $0.0671 s^{-1}$ in the 2θ ranging from 5° to 50° (Fig. 1).

Low temperature (77 K) nitrogen adsorption and desorption isotherms of catalysts were by Quanta chrome Autosorb IQ (Fig. 2). Prior to sorption, the samples were evacuated at $200^\circ C$ for 3 h to a residual pressure of 2×10^{-3} Torr. The isotherms were analyzed in the relative pressure (P/P_0) range of 0.05 to 1.0. The specific surface area (S) of all catalysts were calculated using Brunauer-Emmett-Teller (BET) method (Table 1).

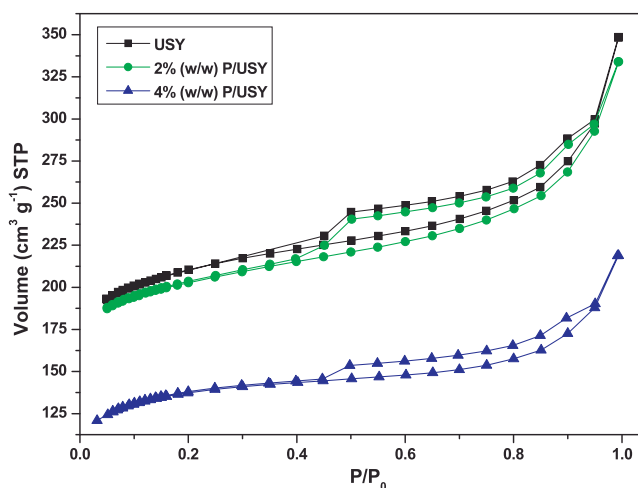


Fig. 2 – Low temperature N_2 adsorption-desorption isotherms of parent USY and phosphonated USY catalysts.

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