Sustainable Catalytic Process for Synthesis of Triethyl Citrate Plasticizer over Phosphonated USY Zeolite

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Abstract

Fruits wastage is harmful to health and environment concerning spreading diseases and soil pollution, respectively. To avoid this issue, use of citrus fruit waste for the production of citric acid (CA) is one of viable mean to obtain value added chemicals. Moreover, synthesis of triethyl citrate (TEC), a non-toxic plasticizer by esterification of CA with ethanol over heterogeneous catalyst would be renewable and sustainable catalytic process. In this context, parent Ultrastable Y (USY) and different percentage phosphonated USY (P-USY) zeolites were used for the synthesis of TEC in a closed batch reactor, for the first time. The synthesized catalysts were characterized by N₂-adsorption desorption isotherm, powder X-ray diffraction (XRD) and NH₃ temperature programmed desorption (TPD. Effect of reaction conditions, such as the molar ratio of ethanol to CA (5:1 - 20:1), the catalyst to CA ratio (0.05 - 0.25) and reaction temperature (363 - 403 K), were studied in view to maximizing CA conversion and TEC yield. Phosphonated USY catalysts were found to be superior in activity (CA conversion and TEC yield) than parent USY, which is attributed to the increased in total acidity with phosphonation. Among the studied catalysts, the P2USY (2% phosphorous loaded on USY) was found to be an optimum catalyst with 99% CA conversion and 82% TEC yield, which is higher than the reported values. This study opens new avenues of research demonstrating principles of green chemistry such as easy separable and reusable catalyst, non-toxic product, bio-renewable synthetic route, milder operating parameters and waste minimization. Copyright © 2016 BCREC GROUP. All rights reserved

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1. Introduction

The plasticizers market is globally rising, as estimated by latest statistical data at about 5 billion kg per year of which, 1.1 billion kg is shared by the United States (U.S.) [1-7]. Kolah et al. reported a continuous reactive distillation process for TEC synthesis [1,2]. Schroter et al. described a three-stage batch process of TEC synthesis [4]. Tao reported TEC synthesis over p-toluenesulfonic acid catalyst [5]. Our previous publications involve synthesis of TEC over M-HZ-50.6 catalyst [3] and tributyl citrate (TBC) synthesis over ultra stable phosphonated Y zeolite [6]. Xu et al. reported TBC synthesis over acid ionic liquid [9] and solid acid catalysts [10]. Citrate esters such as TEC and TBC are extensively applied as non-toxic plasticizers in toys, printing ink, coatings, medical products,
biodegradable polymers food additive and cosmetics [1-11].

Although, India is known as second largest producer of fruits and vegetables in the world, however, in the absence of adequate storage and an efficient processing technology, a huge quantity is wasted, which may be around 0.9-2.2 billion kg annually. Hence, use of waste citrus fruits to produce citric acid (CA) would be viable mean.

Esterification of this CA with ethanol to synthesize triethyl citrate (TEC) plasticizer (an organic acid ester) can be entirely biorenewable and sustainable process. To the best of our knowledge, only few reports are available on synthesis of TEC from CA [1-5]. We previously reported synthesis of TEC [3] and TBC [6] over modified H-ZSM-5 and phosphonated USY zeolite, respectively.

In this paper we report, probably for the first time, the use of phosphonated USY zeolite as heterogeneous catalyst for the esterification of CA (model compound from citrus fruit waste) with ethanol to synthesize non-toxic TEC plasticizer in closed batch system. This reaction is acid catalysed reaction. Phosphonated USY is acid catalyst having more acidity and surface area than reported. Hence, it is expected to improve the CA conversion and TEC selectivity.

The optimization of reaction process parameters such as reactant molar ratio, catalyst to CA ratio, reaction temperature and time were also performed with aim to maximize the CA conversion and TEC selectivity. The reusability of optimum catalyst at optimized process parameters is presented.

2. Materials and Methods

2.1. Chemicals used

USY (Ultra Stable Y) zeolite was procured from Zeolyst, USA having SiO$_2$/Al$_2$O$_3$ molar ratio of 30. Ethanol (99.9%), Phosphoric acid (85%) (H$_3$PO$_4$) were procured from M/s Loba chemie, Mumbai (India). Anhydrous citric acid crystals were obtained from Aldrich.

2.2. Phosphonation of USY with H$_3$PO$_4$

The procedure reported in the literature was used to synthesize the phosphonated USY catalysts [6]. 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$_3$PO$_4$ solution in water was added. The mixture was refluxed at 363 K for 1 h under magnetic stirring. Then solvent was evaporated using Buchi rotary evaporator (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. Calcined material was then obtained with a phosphorus content of 1% (P-USY). Similarly, other phosphonated USY catalysts were prepared with phosphorous content of 2% (P$_2$USY) and 4% (P$_4$USY).

2.3. Catalyst characterization

The phase identification, crystallinity and purity were determined by powder X-ray diffraction (XRD) (Figure 1). 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 in the 2θ range from 5 to 50°. Low temperature (77 K) nitrogen adsorption and desorption isotherms were obtained using SA 3100 analyser (Beckman Coulter, CA, USA). The calcined sample was degassed at 573 K for 10 h prior to measurements. The specific surface area (S) of all catalysts was calculated using Brunauer-Emmett-Teller (BET) method. Micro-pore volume ($V_{\text{micro}}$) of catalysts samples were determined by t-plot method. Total pore volume ($V_{\text{total}}$) of catalysts was determined from single point desorption isotherm at P/P$_0$ = 0.9 (Table 1).

Acidity of catalyst was measured by temperature programmed desorption of ammonia (TPD-NH$_3$) with Micromeritics AutoChem (2910, USA). These experiments were performed in a gas-flow system equipped with thermal conductivity detector (TCD). Prior to the measurements, the freshly calcined catalyst sample was dehydrated at 423 K in high purity (99.995%) helium flow (50 mL min$^{-1}$) for 1 h. The temperature was then decreased to 343 K and then NH$_3$ was allowed to adsorb by exposing sample to a gas stream containing 10% NH$_3$ in helium for 1 h. It was then flushed with helium for another 1 h. The NH$_3$ desorption was carried out in helium flow (50 mL min$^{-1}$) by increasing the temperature up to 873 K with a heating rate of 10 K min$^{-1}$.

2.4. Catalytic testing and analysis

The catalytic performances of synthesized catalysts were evaluated for esterification of CA with ethanol in a 100 mL SS316 batch reactor. The reactions were performed in the temperature range of 363-403 K in closed batch system (under autogenous pressure in range of 0.2-0.5 MPa) with total reactant volume of 60 mL.

The liquid reaction feed and product were analysed by using GC, Varian-CP-3800,
capillary column, SPB-5 (30 m length, 0.25 mm width, 0.25 µm diameter) with nitrogen as a carrier gas and Flame Ionization Detector (FID) in programmable temperature range of 353 to 553 K. The reaction products were also confirmed by GC-MS (Agilent-5977-AMSD).

3. Results and Discussion

3.1. Physicochemical properties of catalysts

Figure 1 shows powder X-ray diffraction patterns of parent USY and phosphonated USY (P₁USY and P₁USY) catalyst samples. The XRD patterns of all catalysts matched well with FAU phase and no additional phases were found. However, the phosphonated samples (P₂USY and P₄USY) indicated a clear decrease in intensity with addition of phosphorous. This can be attributed to removal of aluminium atoms (dealumination) from the USY framework due to phosphorous loading.

The physicochemical properties of synthesized catalysts are listed in Table 1. With addition of 1-2% phosphorous (P₁USY and P₂USY) the BET surface area was found to be decreased marginally. However, 4% phosphorous loaded sample (P₄USY) exhibited a clear decrease in BET surface area. This may be due to blocking of catalyst pores and channels by the polymeric phosphates species formed by higher phosphorous (4%) loading.

The desorption peaks in maximum temperature ranges of 453-523 K, 553-603 K and 653-773 K are normally attributed to NH₃ chemisorbed on weak, medium and strong acid sites, respectively [12, 13]. In all synthesized catalysts, parent USY and phosphonated USY (P₁USY, P₂USY and P₄USY), two desorption peaks were observed centered at 553-568 K and 743-768 K, which were attributed to the presence of moderate and strong acid sites, respectively. The TPD-NH₃ distribution and total acidity results of the catalysts are listed in Table 1. All phosphonated USY catalysts showed increase in total acidity as compared to parent USY.

3.2. Catalytic performance

The catalytic performance of synthesized catalysts, viz. USY, P₁USY, P₂USY and P₄USY, were investigated for esterification of CA with ethanol. Initially, reported process parameters were used: molar ratio (ethanol to CA) of 10:1, catalyst to CA ratio of 0.10, reaction temperature of 373 K and reaction time of 5 h. All the experiments were performed in duplication and...
have ±2% error. The esterification of CA with ethanol can occur auto catalytically hence, the thermal reaction (blank, without catalyst) was performed. Figure 2 represents the obtained CA conversion and yield of mono-ethyl citrate activity (MEC), di-ethyl citrate and TEC over blank, USY, P1USY, P2USY and P4USY. All phosphonated USY catalysts showed higher activity than the parent USY, this may be attributed to the increase in total acidity along with the cumulative effect of physicochemical properties of catalysts (Table 1).

The overall trend of CA conversion obtained was Blank (8%) < USY (38%) < P1USY (56%) < P2USY (64%) < P4USY (66%). With increase in phosphorous loading from 1% (P1USY) to 2% (P2USY), the TEC yield found to be increased from 34 to 40%, further increase in phosphorous loading up to 4% (P4USY), the TEC yield remained stable (Figure 2).

Hence, P2USY catalyst was selected as potential catalyst with 64% CA conversion and 40% TEC yield and optimization of process parameters was performed over same catalyst with aim to maximize CA conversion and TEC yield.

### 3.3. Optimization of process parameters

#### 3.3.1. Effect of molar ratio

The molar ratio of ethanol to CA was varied, while keeping the other experimental conditions constant. The molar ratio (ethanol: CA) was varied from 5:1 to 20:1 and results obtained are illustrated as Figure 3. The sharp increase in CA conversion (51-65%) and yield of TEC (32-41%) with increase in molar ratio from 5:1 to 10:1 was observed. Thereafter gradual increase in CA conversion (64-65%) and yield of TEC (40-41%) with increase in molar ratio from 10:1 to 15:1 was obtained. The higher CA conversion and yield of TEC may be attributed to occupancy of the CA over the active sites present on catalyst surface and the availability of ethanol molecules for further esterification.

At a molar ratio of 10:1, the CA may be chemisorbed on the active sites of catalysts to form carbenium ions. The attack of these stable carbenium ions by the ethanol to form esters is least effective in the 5:1 ratio stages. Further, when the concentration of ethanol was excess at molar ratio of 10:1, the approach of ethanol molecules to the carbenium ions is to be enhanced showing an increase in CA conversion.

On a further increase of molar ratio to 20:1, the CA conversion and TEC yield was observed to be decreased. This decrease in CA conversion may be due to the flooding of active sites with ethanol molecules rather than CA molecules. Therefore, the increase of molar ratio hinders the completion of CA being protonated at the active sites on catalyst. Also, there is possibility of the active sites involve in the formation of diethyl ether which may hinder esterification reaction at high ethanol content. However no diethyl ether is detected in the product mixture.

On the other hand, transesterification of the formed esters (MEC, DEC and TEC) with ethanol is also possible. It is evident from Figure 3 that, the DEC is preferentially formed over MEC in all cases with the exception of 20:1 molar ratio, where the opposite is true. Hence, the optimum molar ratio of 10:1 with CA conversion of 64% and TEC yield of 40% was used in further experiments.
3.3.2. Effect of catalyst to CA ratio

Influence of catalyst amount was studied by varying the catalyst to CA ratio from 0.05-0.25. The effect of the catalyst loading over the CA conversion and TEC yield is presented as Figure 4. With increase in catalyst to CA ratio from 0.05 to 0.15, the steep increase in CA conversion from 45 to 72% and TEC yield from 28 to 46% was observed. This finding is expected because catalyst loading increases proportionally to the availability of active acid sites, which favor the accessibility of large numbers of reactants to the active sites. Further increase in catalyst to CA ratio from 0.15 to 0.25, the minor enhancement of CA conversion from 72 to 74% and TEC yield from 46 to 47% was observed (Figure 4). Hence, catalyst to CA ratio of 0.15 with 72% CA conversion and 46% TEC yield was selected as an optimum and used in further experiments.

3.3.3. Effect of reaction temperature

The reaction temperature was varied from 363-403 K, over P2USY catalyst at process parameters of ethanol to CA molar ratio of 10:1, catalyst to CA ratio of 0.15, reaction time of 5 h (Figure 5). CA conversion and TEC yield increased from 54 to 99% and 18 to 82% respectively with increase in reaction temperature from 363 to 403 K.

The esterification reactions are mainly known for being equilibrated reactions and the principal way to tamper with its equilibrium is by removing water (Le Chatelier principle). In the present case, with the use of a batch reactor, with temperatures and pressures (0.2-0.5 MPa) close, but below the vapor liquid equilibrium of water (pure water), with the increase in temperature, results in a bigger fraction of water migrating to the gas phase, shifting the reactions equilibrium towards product (TEC plasticizer) side.

Also, high temperature and autogeneous pressure leads to more frequent and successful collisions between the reactants. This in turn enhances the mass transfer rates, leading to more formation of TEC. Hence, the optimum reaction temperature of 403 K with 99% CA conversion and 82% TEC yield was selected as an optimum and used in catalyst reusability study.

3.4. Catalyst reusability

In order to examine the reusability of P2USY catalyst, it was repeatedly used for TEC synthesis at optimized process parameters. After each catalytic cycle, the catalyst was separated by filtration and reused in a new reaction cycle without any post-treatment. Figure 6 represents the results obtained for the usage of P2USY catalyst for five reaction cycles. It has been observed that, P2USY catalyst was stable for five reaction cycles (fresh and four reuses) with identical 99% CA conversion and 82% TEC yield. For the sixth cycle, marginal decrease in CA conversion (99-95%) and TEC yield (82-75%) was observed.

3.5. Merits of present method

Kolah et al. reported use of reactive distillation for synthesis of TEC [1,2]. They were able to obtain TEC yield of above 98.5% at optimized process parameters [1,2]. Very recently, we have reported the use of M-HZ-
50.6 catalyst for synthesis of non-toxic TEC plasticizer and obtained 96% CA conversion and 64% TEC selectivity [3]. Schroter et al. used methane sulfonic acid as catalyst for synthesis of TEC in a three-stage batch system and obtained complete conversion of CA [4]. Tao reported use of p-toluene sulfonic acid in benzene with continuous removal of the water formed and reported 92.8% TEC yield [5]. Although reported methods achieved higher TEC yield, they used complex processes such as reactive distillation [1,2], three stage batch system [4], continuous water removal [5], etc., also suffer from catalyst deactivation.

In the view of above literature, the activity values obtained in present study are higher than the reported. Hence, present method of using P2USY catalyst for synthesises of non-toxic TEC plasticizer would be sustainable and eco-friendly catalytic process in the view of higher activity (99% CA conversion and 82% TEC yield) and catalyst stability (5 reaction cycles). Also, the present method exhibits principles of green chemistry in context of bio-renewable synthetic route, non-toxic product, reusable catalyst and waste minimization.

4. Conclusions

Triethyl citrate (TEC), a non-toxic plasticizer was systematically prepared by esterification of citric acid (CA-model compound derived from citrus fruit waste) and ethanol over heterogeneous phosphonated USY (PUSY) zeolite. Among studied catalysts, P2USY zeolite was found to be the optimum catalyst with 99% CA conversion and 82% TEC yield. The said catalyst was observed to be highly active and stable for five cycles (fresh and four reuses). These results are more attractive as compared to reported, in terms of higher activity values, catalyst reusability, simple process, etc. This catalytic process is a renewable sustainable process, because of high activity, better product yield, high reusability and use of renewable feedstock, which follows more principles of green chemistry and engineering.

References


