Indian Journal of Chemistry
Vol. 55A, July 2017, pp. 747-755

Solvent-free facile synthesis of di-octyl phthalate over heterogeneous sulfated zirconia acid catalyst

Ajay M Parmar[a,b], K Saravanan[a,b], Beena Tyagi[a,b,] * & Kannan Srinivasan[a,b]

[a]Inorganic Materials and Catalysis Division, [b]Academy of Scientific and Innovative Research (AcSIR),
CSIR-Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), GB Marg, Bhavnagar 364 002, India
Email: btyagi@csmcri.res.in

Received 1 April 2017; revised and accepted 20 June 2017

The present study reports the synthesis of di-octyl phthalate (DOP), widely used as a plasticizer, via solvent-free esterification of phthalic acid and *n*-octanol over sulfated zirconia (SZr) heterogeneous acid catalyst. A comparison with other heterogeneous acid catalysts such as K-10 acid activated clay, zeolites (β and Y), Amberlyst-15 resin shows the superior activity of SZr, exhibiting maximum conversion of *n*-octanol (88%) with 93% DOP selectivity at 160 °C in 6 h. The rate of the reaction for SZr catalyst is computed as 17.3 mmol h^{-1} g^{-1}. The catalyst activity is stable upon recycling for up to five cycles. The weak acid sites of the catalyst are postulated as the responsible active centres involved in the reaction. The reaction has been successfully scaled up over twenty five times; and the product DOP (67 g, 99% by GC) isolated and characterized by FT-IR and ^{1}H NMR spectroscopy. It is noteworthy that the activity of SZr catalyst is comparable with that of H_2SO_4 and *p*-toluene sulphonic acid (*p*-TSA), which clearly suggets its potential as an efficient alternative to conventional commercial homogeneous acid catalysts for the synthesis of DOP.

Keywords: Heterogeneous catalysts, Acid catalysts, Esterification, Sulfated zirconia, Di-octyl phthalate, Phthalic acid

Di-octyl phthalate (DOP) is an industrially important phthalate used as a plasticizer in the manufacture of plastic items made of polyvinyl chloride polymer, for example, house hold items, toys, shoes, electric wires, tubings, medical blood bags and dialysis bags.[1] It is also used in ethyl/nitro cellulose paints and wood coatings.[2] DOP is a common low-phthalate plasticizer used worldwide, in particular Asia.[3]

Commercially, DOP is synthesised by the esterification of phthalic acid/anhydride with *n*-octanol/2-ethyl hexanol in presence of homogeneous Brönsted acid catalysts such as sufuric acid, *p*-toluene sulfonic acid or phosphoric acid.[4-6] A co-solvent such as benzene, toluene, xylene, dichloroethane and cyclohexane has also been commonly used.[6-8] The conventional homogeneous acids form undesirable side-products due to their high activity resulting in the lower yield of desired ester. The formation of by-products was lowered using titanium alkylates[9,10]amphoteric catalyst due to their lesser activity, however higher temperature (>200 °C) and elevated pressure (100-400 kPa) or long reaction time (~22 h)are required to achieve appreciable yield of ester.[11] In addition, use of these homogeneous acid catalysts cause corrosion problems and also need to be neutralized at the end of the reaction to obtain pure ester product and subsequent disposal problems of the treated reaction mixture. Therefore, the development of eco-friendly, re-usable, heterogeneous acid catalysts having comparable activity with homogeneous catalysts, is the widespread demand for green industrial methodologies for the production of plasticizers.

A few heterogeneous acid catalysts such as heteropoly acid supported on $SiO_2/TiO_2/ZrO_2$,[7] zeolites,[8,12] $AlPO_4/SiAlPO_4$,[8] metal tungstate/phosphate,[13] hydrous zirconium oxide,[14] SO_4^{2-}-ZrO_2,[7,15,16] andSO_4^{2-}-TiO_2[16-18] have been studied for the synthesis of DOP. Among metal oxides, sulfated zirconia (SZr) has been reported as a potential heterogeneous acid catalyst for various industrially important reactions[19,20] including the synthesis of DOP[7,15,16]. Hino and Arata[16] synthesized DOP and observed 71% conversion of phthalic acid at 200 °C in 2 h over SZr, however using significantly higher acid-to-octanol molar ratio (1:50) and catalyst amount (~30 wt% to acid). Sejidov *et al.*[15] found higher activity and efficiency of SZr catalyst for esterification of phthalic anhydride (PAn) and 2-ethyl hexanol (2-EH), using higher amount of catalyst (20.3 g/mol PAn) while gradually increasing the reaction temperature from 110 °C to 190 °C. Thorat *et al.*[7] found SZr to be a potential catalyst for two-step esterification protocol of PAn and 2-EH, wherein a maximum conversion of monoester was observed at 195 °C in presence of SZr (~)6 wt% to monoester) and dichloroethane as co-solvent.

These variations in reaction conditions, scope of reactants, methodology adopted for esterification along with subtle variations in the synthesis methodology of SZr such as mode of sulfation, calcination temperature, etc., reflects the variation in the catalytic activity of SZr towards the said reaction, and encouraged us to carry out a systematic detailed study on DOP synthesis over SZr catalyst.

Against this backdrop, the present study is focused in carrying out solvent-free esterification of phthalic acid with *n*-octanol by one-step protocol under significantly milder reaction conditions, using stoichiometric acid to alcohol molar ratio (1:2), at lower temperature (160 °C) with lower (2 wt% to acid) catalyst loading. A comparison in the absence of catalyst and with other heterogeneous acid catalysts of clay, zeolites and resin groups along with the commercial homogeneous catalysts, *p*-TSA and H_2SO_4 demonstrated the potential of SZr catalyst. The efficiency and stability of the catalyst was examined by performing its recycling. Moreover, the present study augments a new knowledge for the studied reaction regarding structure-activity-correlation, scaling up of the reaction under mild reaction conditions, isolation of pure DOP (67 g) and its characterization along with the characterization of the used catalyst; the latter gives insight about the strength and necessity of active acid sites for the reaction, which to our best knowledge is not reported so far for the said reaction.

Materials and Methods

$ZrOCl_2.8H_2O$, aqueous ammonia (25%) and *n*-tridecane were procured from SD Fine Chemicals, India. Phthalic acid and *n*-octanol, each of 99.5% purity, were obtained from Sigma-Aldrich, Poland and Spectrochem Pvt Ltd, India, respectively.

Catalyst preparation and charaterization

SZr catalyst was prepared by a simple precipitation method.[21] In a typical synthetic procedure, aqueous solution of $ZrOCl_2.8H_2O$ (0.05 *M*) was hydrolyzed by the drop-wise addition of aqueous ammonia till pH became ~9 followed by continuous stirring at ambient temperature (~27 °C) for 3 h. The precipitate was filtered, washed with distilled water to remove chloride ions (checked with $AgNO_3$) and dried at 120 °C for 12 h. The obtained precipitate of zirconium hydroxide was treated with 1 *N* H_2SO_4 (15 mL/g), dried at 120 °C for 12 h followed by calcination at 600 °C for 4 h in static air.

The prepared SZr catalyst was characterized for its structural, textural, acidic and morphological properties by various analytical analyses such as powder X-ray, FT-IR, TGA, DTA, TGA-MS, N_2 sorption isotherms, NH_3-TPD, diffuse reflectance FT-IR spectroscopy and TEM by standard procedures. The details are described in Supplementary Data.

Catalytic esterification of phthalic acid with *n*-octanol

Esterification of phthalic acid with *n*-octanol was carried out in a Radley's reaction station (Radley's Discovery Technologies, RR98073). In a typical reaction procedure, required amount of phthalic acid, *n*-octanol (with acid: *n*-octanol molar ratio of 1:2) and catalyst (2 wt% with respect to acid) was charged at 160 °C for 6 h. To study the effect of water formed during the esterification reaction, reactions were performed in a round bottom flask, attached with Dean-Stark apparatus, in an oil bath maintaining constant temperature of 160±1 °C. *n*-tridecane was used as an internal standard in all the reactions. The reaction mixture was analyzed using a gas chromatograph (HP 6890) having a HP-1 capillary column (30 m) and FID detector. The conversion of *n*-octanol and the selectivity for DOP was calculated by GC peak area as given below:

$$\text{Conv. of } n\text{-octanol (wt\%)} = \left[100 - \frac{x/a}{y/b} \times 100\right]$$

where, *x, y* = GC peak area of *n*-octanol after and before reaction respectively, and, *a, b* = GC peak area of *n*-tridecane after and before reaction respectively

$$\text{Sel. for DOP(wt\%)} = \frac{\text{GC peak area of DOP}}{\text{Peak area of total products}} \times 100$$

The results reported (in duplicate) are within ±2.0% experimental error and the error bars are inserted wherever applicable.

Catalyst re-usability

The catalyst was separated and recovered from the reaction mixture by centrifugation, washed with acetone for 2 to 3 times followed by drying at 120 °C for 12 h and subjected to thermal activation at 600 °C for 4 h. Thus regenerated catalyst was re-used for the new reaction cycle with fresh reactants under similar reaction conditions.

Results and Discussion

Catalyst characterization

Thermal analysis of prepared SZr catalyst showed a total weight loss of ~24% having a broad peak at 120 °C (due to desorption of physisorbed water) and an intense peak at ~650 °C (due to dehydroxylation and loss of sulfate species) as shown in DTA profile (Fig. 1a). Mass spectra of evolved gases analysis (Fig. 1b) confirmed the evolution of water vapor at lower temperature; the sulfate species decomposed mainly as SO and SO_2 gases at higher temperature, as observed by two intense broad peaks at ~700 °C; however loss of SO_3 was observed at lower temperature showing a broad peak at ~450 °C.

The ammonia desorption profile for NH_3-TPD analysis showed desorption peaks at 110, 400-579 and 834 °C (Fig. 2a). These desorption peaks are ascribed for weak (110 °C) and moderate to strong (400-579 °C) acid sites; however the desorption peak at higher temperature (834 °C) may be combined with loss of sulfate species as observed from TG-MS and therefore is excluded while calculating the total surface acidity, which was 1.19 mmol/g (Supplementary Data, Table S1).

The DRIFT[22] spectra of pyridine adsorbed SZr catalyst exhibited the presence of both Brönsted (B) and Lewis (L) acid sites having characteristic bands for pyridinium ion (B) at 1542 cm^{-1} and covalently bonded pyridine (L) at 1443 cm^{-1} along with a band at 1488 cm^{-1} for showing combined L and B acid sites[21] (Fig. 2b). Both characteristic acid sites were present even after heating at 450 °C. The B and L acid sites concentration was quantified from their characteristic bands by molar extinction coefficient method[23] and B/L ratio was calculated at different temperatures, which was found to be 1.4 (150 °C), 1.7 (250 °C), and 2.0 (at both 350 °C and 450 °C) (Supplementary Data, Table S1). The results clearly reveal the presence of

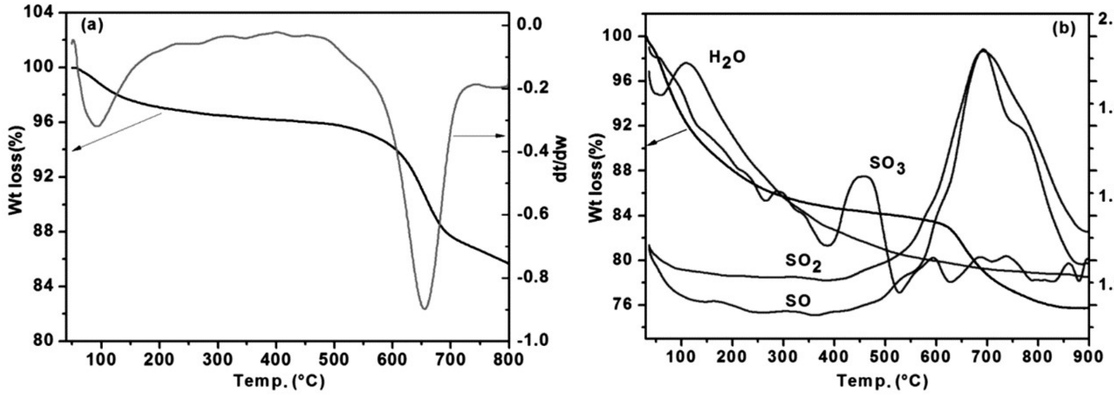


Fig. 1 — (a) TG-DTA and (b) TG-MS of SZr catalyst.

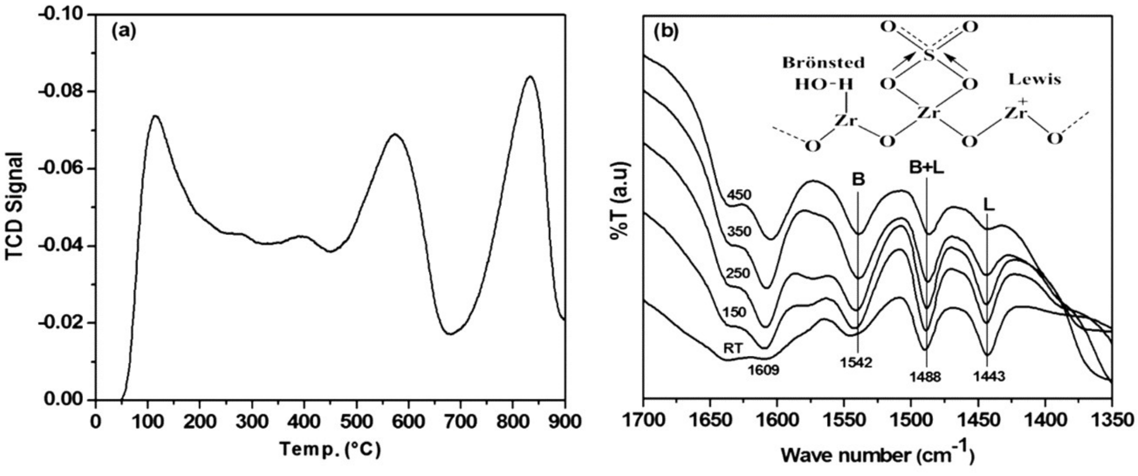


Fig. 2 — (a) NH_3 TPD profile (b) DRIFT spectra of pyridine adsorbed SZr catalyst at room temperature (~27 °C) and after pyridine desorption at 150–450 °C. [Inset: Brönsted and Lewis acid sites of SZr catalyst].

significant Brönsted acidity in the prepared SZr catalyst and that prevalent even at higher temperature.

FT-IR spectrum (Supplementary Data, Fig. S1(a)) showed the characteristic bands of SO_4^{2-} groups bonded with zirconia surface in an inorganic chelating bidentate fashion[24] in the region of 1200-900 cm^{-1}. A broad band at ~3400 cm^{-1} with a tail showing H-bonding and a sharp band at 1630 cm^{-1} are attributed to $\nu_{O\text{-}H}$ stretching and $\delta_{O\text{-}H}$ bending mode of surface hydroxyl groups, respectively, associated with zirconia and sulfate group.[25] The ionic structure of SO_4^{2-}group in presence of surface hydroxyl groups is responsible for the Brönsted acidity in SZr catalyst,[26] whereas, electron deficient Zr^{n+} sites generates Lewis acidity[24] resulting in a favorable combination of both acid sites present on the surface of the catalyst (inset of Fig. 2b), thus making the reaction feasibly catalyzed by both acid sites.

The bulk sulfur content loaded after sulfation of SZr was 3.9 wt% and 2.3 wt% sulfur was retained after calcination at 600 °C (Supplementary Data, Table S1).

The catalyst exhibited highly crystalline nature having tetragonal crystalline phase of zirconia (2θ (°) = 30.37, 35.45, 50.13, 60.28) as supported by the powder X-ray diffraction (PXRD) (Supplementary Data, Fig. S1(b)). The tetragonal SZr was found to have a nano-crystallite size of 11 nm (Supplementary Data, Table S1). A nano-crystallite zirconia surface provides higher surface to volume ratio and thus availability of higher acid sites as inferred from acidity measurements.

N_2 sorption studies of the catalyst were characteristic of mesoporous materials (Supplementary Data, Fig. S2(a)) exhibiting type IV-like isotherm[27] having uniform pore size distribution (Supplementary Data, Fig. S2(b)). The pore diameter was 37 Å with average pore volume of 0.12 cm^3/g and BET surface area of 99 m^2/g (Supplementary Data, Table S1).

TEM images showed rectangular shaped particles (Supplementary Data, Fig. S3(a)) having lamellar structure of crystalline tetragonal zirconia (Supplementary Data, Fig. S3(b)); the width between two lattice fringes (2.92 Å) of lamellar structure is in agreement with the *d*-spacing (2.94 Å) of characteristic tetragonal zirconia (2θ = 30.37°; 111 plane) as shown by PXRD.

Esterification of phthalic acid with *n*-octanol

The effect of various reaction variables for esterification of phthalic acid with *n*-octanol such as acid to *n*-octanol molar ratio, catalyst amount, temperature and time has been studied to achieve maximum conversion of *n*-octanol and selectivity for DOP.

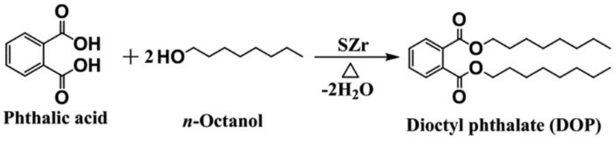
The conversion of *n*-octanol was 88% with acid to octanol molar ratio of 1:2 at 160 °C after 6 h. By increasing the molar ratio to 1:2.5 and 1:3, the conversion of *n*-octanol decreased successively to 83% and 50% respectively (Fig. 3a). The selectivity of DOP was 92-94% irrespective of *n*-octanol amount. The results were in agreement with stoichiometric requirement of two molecules of *n*-octanol for esterification of 1 molecule of phthalic acid to form one molecule of DOP (Scheme 1).

The reaction was studied in the temperature range of 140 to 190 °C with acid to octanol molar ratio of 1:2. A linear increase in the conversion of *n*-octanol from 50 to 88% was observed by increasing the temperature from 140 to 160 °C (Fig. 3b). The selectivity of DOP was also increased from 74 to 93% in the same temperature range. By further increasing the temperature, the conversion and selectivity values remained same till 190 °C. Thus, 160 °C was chosen for further studies.

The effect of catalyst amount showed an increase in conversion of *n*-octanol from 82 to 88% with an increase in catalyst amount from 1 to 2 wt%; however, no significant increase was observed (88-90%) by further increasing the catalyst amount till 5 wt% (Fig. 3c). The selectivity of DOP was 93% with each catalyst amount. The results showed the availability of sufficient number of active acid sites even while using lower catalyst amount; therefore 2 wt% was chosen for further studies. The reaction done in absence of catalyst showing significant lower conversion of *n*-octanol (60%) demonstrated the significance of SZr catalyst, as described below.

Kinetic studies

The kinetic studies for esterification of phthalic acid with *n*-octanol were done at 160 °C in presence as well as in absence (blank) of SZr catalyst. The blank reaction showed conversion of *n*-octanol that increased from 30% (0.5 h) to 60% (6 h); however no significant



Synthesis of DOP via esterification of phthalic acid with *n*-octanol
Scheme 1

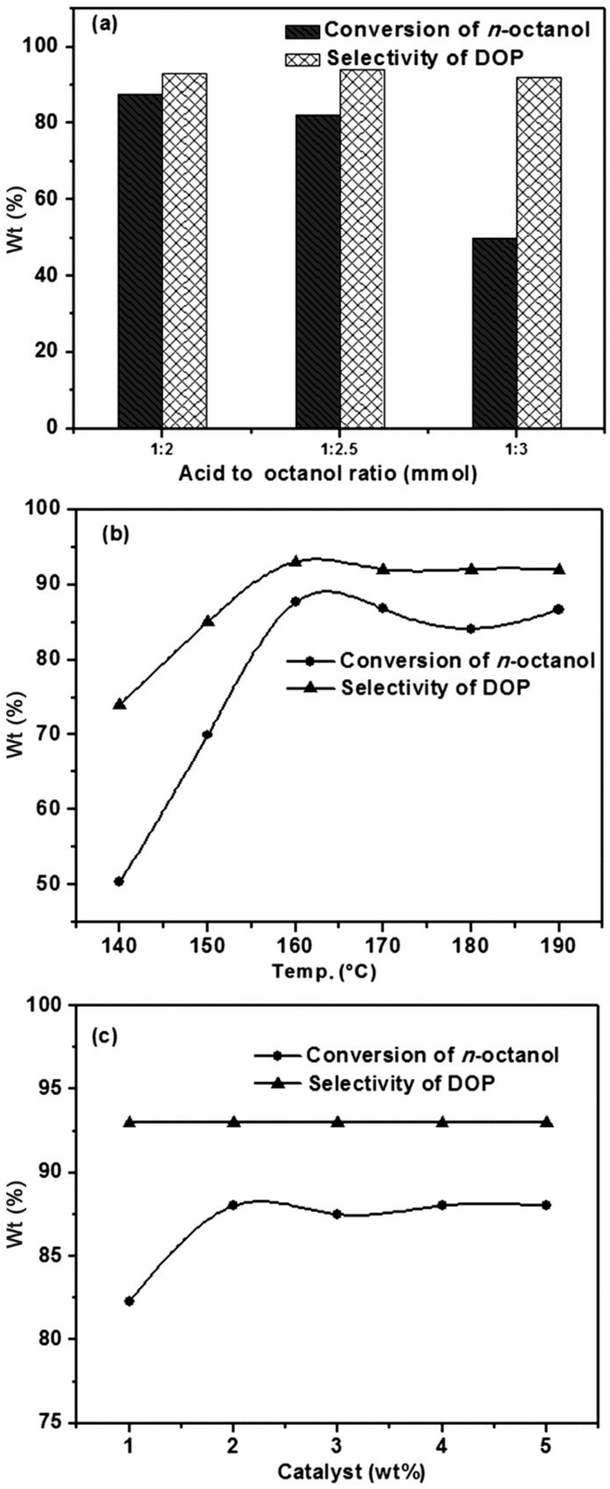


Fig. 3 — Conversion of *n*-octanol and DOP selectivity at varying (a) acid-to-*n*-octanol ratio, (b) temperature, and (c) catalyst amount. [React. cond.: phthalic acid =10 mmol; tridecane = 200 mg; time = 6 h; acid-to-*n*-octanol ratio = 1:2 (mmol) (except for Fig. 3a); temp. = 160 °C (except for Fig. 3b); and catalyst = 33 mg (except for Fig. 3c)].

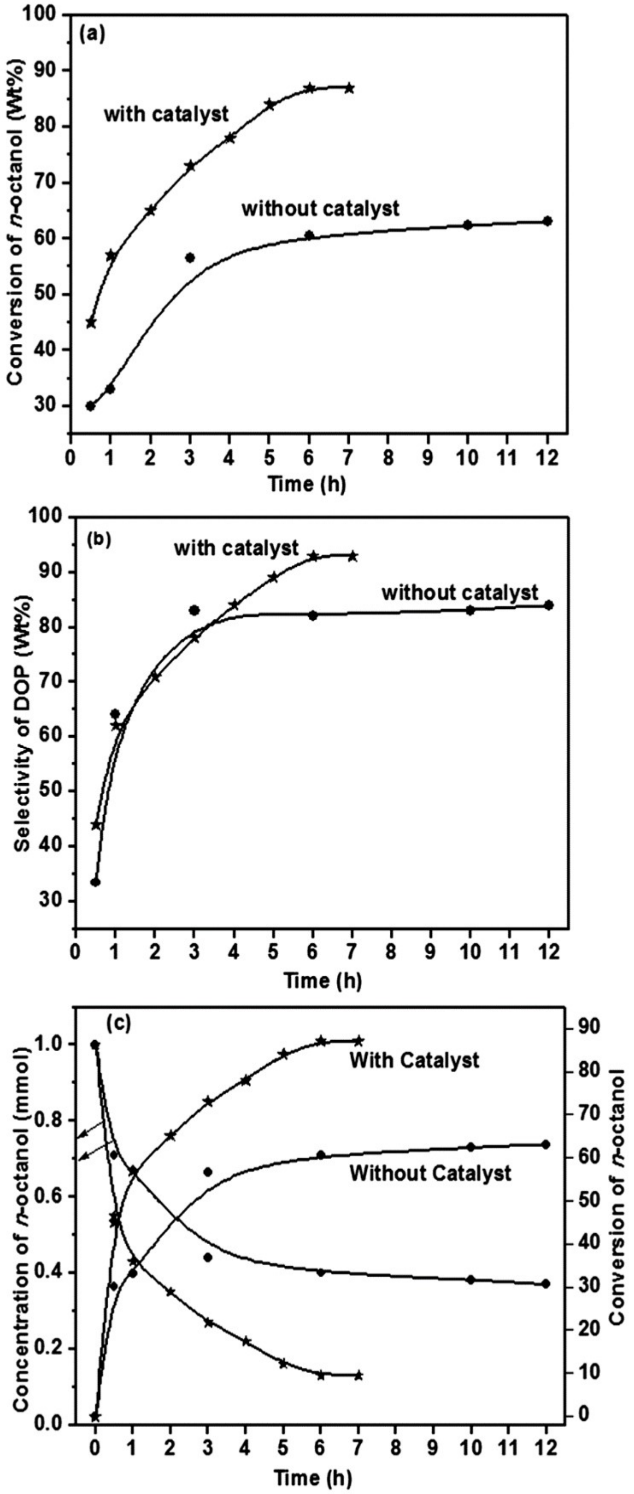


Fig. 4 — Esterification of phthalic acid and *n*-octanol with time, with and without SZr catalyst (a) *n*-octanol conversion (b) DOP selectivity and (c) concentration/ conversion of *n*-octanol [React. cond.: phthalic acid = 10 mmol; *n*-octanol = 20 mmol; tridecane = 200 mg; catalyst = 33 mg ; time = 6 h; temp. = 160 °C].

increase was observed thereafter till 12 h (Fig. 4a). Similarly, DOP selectivity increased from 33% (0.5 h) to 82% (3 h) and subsequently remained steady till 12 h (Fig. 4b). These results clearly indicate the occurrence of thermal reaction at higher temperature of 160 °C. However, the esterification reaction in presence of a small catalytic amount (33 mg) of SZr heterogeneous acid catalyst showed significantly higher conversion of *n*-octanol (Fig. 4a) and selectivity of DOP (Fig. 4b), which increased from 45% to 88% and 44% to 93%, respectively in the time interval of 0.5 h to 6 h. Though DOP selectivity in initial 3–4 h of SZr catalyzed reaction (84%) was similar to blank reaction (82%); it increased to 93% (6 h) as compared to blank reaction, where it remained steady till 12 h. Both conversion of *n*-octanol and DOP selectivity attained saturation after 6 h and remained steady afterwards.

The kinetic profile of the reaction showed the continuous decrease in the concentration of *n*-octanol with time (Fig. 4c). The concentration of *n*-octanol was calculated by subtracting the consumed concentration from the initial concentration of *n*-octanol. A sharp linear decrease in *n*-octanol concentration was observed till 1 h; on further increasing the time the decrease in the concentration of *n*-octanol became moderately slower and started to approach saturation. The initial reaction rates (ν) for both blank and SZr catalyzed reactions were determined by applying linear analysis to the plot of decreasing concentration of *n*-octanol with time by using the equation, $\upsilon = -d[\text{octanol}]/dt$. The rate of reaction for the consumption of *n*-octanol over SZr catalyst was 1.7 times higher (0.57 mmol h^{-1}) as compared to blank reaction (0.33 mmol h^{-1}) under similar reaction conditions. The reaction rate per gram of catalyst was 17.3 mmol h^{-1} g^{-1} with TOF (turnover frequency) of 2.5 h^{-1}. These results clearly substantiate the role of SZr catalyst in achieving higher conversion and DOP selectivity with enhanced reaction rate under the studied experimental conditions.

Comparison of catalytic activity of SZr with other acid catalysts

The reaction was also carried out in presence of various heterogeneous acid catalysts, namely montmorillonite K-10 acid activated clay, H-β and H-Y zeolites (Si/Al = 24), Amberlyst-15 and conventional homogeneous Brönsted acid catalysts such as H_2SO_4 and *p*-TSA.K-10 acid clay showed 60% conversion of *n*-octanol with 78% DOP selectivity and H-β, H-Y zeolites showed 69-70% conversion of *n*-octanol with 76-87% DOP selectivity (Table 1). Though, Amberlyst-15, an ion-exchange resin, displayed 81% conversion of *n*-octanol with 91% DOP selectivity at 160°C, it decomposed and became dark black in color due to its thermal instability at higher reaction temperature; and at lower temperature (120 °C) at which ion-exchange resins are thermally stable, only 46% conversion of *n*-octanol with 70% DOP selectivity was observed. Among the various heterogeneous catalysts studied, SZr catalyst showed highest conversion of *n*-octanol (88%) and DOP selectivity (93%) (Table 1). It is worthy to note that the activity of SZr catalyst was in the similar range as that of homogeneous H_2SO_4 and *p*-TSA.

The observed results of catalytic activity were in good agreement with order of Hammett acidity function of these catalysts, for example: SZr (H_o −16) > H_2SO_4 (H_o −12) ~ *p*-TSA ≥ resins > zeolites (H_o −10) > acid activated clay (H_o −5.6).[20]As SZr is well known as 'solid super acid', pronounced to possess higher acidity than 100% H_2SO_4,[20] it showed activity similar to H_2SO_4 and *p*-TSA for the studied reaction under the studied reaction conditions. Besides the acidity, structural and textural properties of the catalyst also play a significant role towards its activity. For example, the larger mesopore dimensions of the catalyst contribute in making the reaction more facile due to easy diffusion of reactants and product molecules. SZr used in the present study has larger size mesopore (37 Å) as compared to the channel dimensions (6.4 × 7.6Å) of zeolites and acid activated clay (20 Å). In addition, tetragonal crystalline phase of SZr is known for higher catalytic active compared to its monoclinic phase.[28] Thus, the highest catalytic activity of SZr for the studied reaction is attributed to its catalytic active tetragonal phase, stronger surface acidity and larger size mesopores compared to other studied catalysts.

Table 1 — Esterification of phthalic acid with *n*-octanol in presence of various homogeneous and heterogeneous catalysts. [Phthalic acid= 10 mmol (1.66 g); *n*-octanol = 20 mmol (2.60 g); tridecane = 200 mg; catalyst = 33 mg; temp. = 160 °C; time = 6 h]

Catalyst	Conv. of *n*-octanol (%)	Sel. of DOP (%)
K-10 acid activated clay	60	78
H-β	69	76
H-Y	70	87
Amberlyst-15	81 (46[a])	91 (70[a])
SZr	88	93
p-TSA	89	93
H_2SO_4	90	90

[a]Temp. = 120 °C

Recycling of the catalyst

Figure 5 clearly demonstrates the excellent reusability performance of SZr as was also observed earlier by Thorat *et al.*[7] and Hino and Arata[16]. FT-IR and PXRD data of the reused catalyst after the 5th reaction cycle show that SZr maintained its structural integrity (Supplementary Data, Fig. S1(a & b)). The crystallinity, crystalline phase and crystallite size were found to be similar for the re-used catalyst after five reaction cycles. The pore diameter of re-used catalyst was also in the similar range (37 Å) as that of fresh catalyst indicating no blockage of mesopores after the reaction as well as facile diffusion of reactant and product molecules through the mesopores of the catalyst. The sulfur content, however, was observed to decrease (from 2.3 to 1.37%) resulting into slight reduction in total surface acidity of re-used catalyst (from 1.19 to 0.79 mmol/g). The lower loss in the activity as compared to decrease in the sulfur/ surface acidity of the catalyst may be explained on the basis of the strength and necessity of active acid sites. A decrease in the total surface acidity of the re-used catalyst was observed mainly due to reduction (~73%) in the moderate to strong (400–600 °C) acid sites (Supplementary Data, Fig. S4 and Table S2). This suggests that these acid sites have not been participating in the reaction. On the other hand, a small decrease in the weak acid sites (~8%) was observed for the re-used catalyst. This corresponds well with the small decrease (~5%) in the activity after the fifth reaction cycle and suggests that the weak acid sites are the responsible active centres involved in the reaction. Thus, their concentration is important in governing the course of the reaction. Furthermore, since 60% conversion is observed in the absence of any catalyst (as discussed during kinetic studies), we believe that weak acid sites of present SZr catalyst may be sufficient to enhance the conversion values (to 88%). The results explicitly disclose the necessity of higher number of active weak acid sites to further enhance the activity of SZr for the studied reaction.

Scale-up studies

To further check the efficacy of SZr catalyst, the reaction was scaled-up by taking ten times higher amount of phthalic acid (16.6 g) and *n*-octanol (26 g) under optimized reaction conditions, i.e., at 160 °C for 6 h over 2 wt% of catalyst . The results showed a decrease in the conversion of *n*-octanol (from 88 to 54%) and DOP selectivity (from 93 to 72%) (Fig. 6a). For comparison, the scale-up reactions were also studied in presence of conventional homogeneous H_2SO_4 and *p*-TSA catalysts (Fig. 6b). The results showed a similar trend in presence of homogeneous catalysts as well, i.e., both conversion of *n*-octanol and DOP selectivity decreased from 88-90% to 64-65% and from 90-93% to 77-78% respectively on scaling-up the reaction. These results suggest that the decrease in conversion and selectivity, irrespective of the catalyst, is probably due to the occurrence of backward reaction in presence of water molecules formed during the reversible esterification reaction; and not because of the deactivation of surface active acid sites of heterogeneous SZr catalyst; though the effect of water was more apparent while operating the reaction at higher scale.

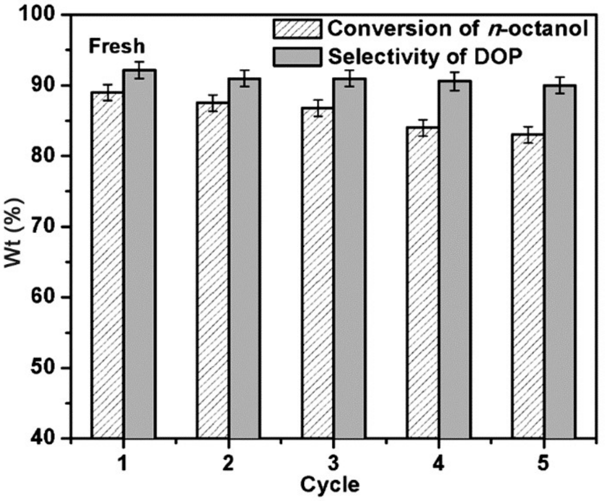


Fig. 5 — Recyclability of SZr catalyst for esterification of phthalic acid with *n*-octanol. [React. cond.: phthalic acid = 30 mmol; *n*-octanol = 60 mmol; tridecane = 600 mg; catalyst = 99 mg; time = 6 h; temp. = 160 °C].

After removing the water using Dean Stark apparatus at both reaction scales of phthalic acid in presence of SZr as well as H_2SO_4 and *p*-TSA, a significant increase in both conversion and selectivity values was observed at higher reaction scale with all three catalysts; at lower reaction scale however, no significant difference was observed (Fig. 6 (a & b)). The results explicitly suggest that the removal of water is essential to lead the equilibrium of the reversible esterification reaction towards the forward direction, i.e., formation of ester.

We have further scaled-up the reaction twenty five times (with 42.5 g of phthalic acid) under the similar reaction conditions. About 67 g of pure DOP (99% by GC) as viscous liquid was isolated, which was

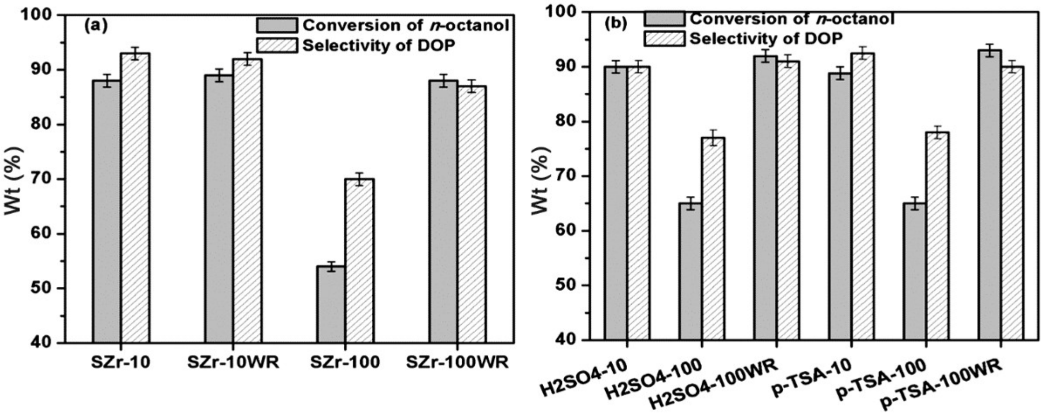
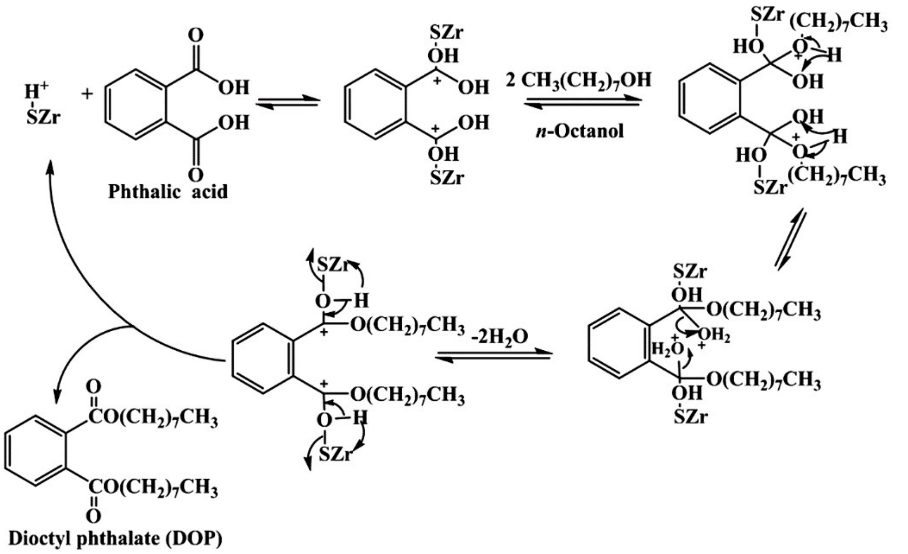


Fig. 6 — Scale-up studies for esterification of phthalic acid with *n*-octanol with and without water removal over (a) heterogeneous SZr, (b) homogeneous H_2SO_4 and *p*-TSA catalysts. [SZr-10 and SZr-100 represent the scale of reaction with 10 and 100 mmol acid respectively; SZr-10WR and SZr-100WR represent the water removed (by Dean-Stark) at both reaction scales. Similar for H_2SO_4 and *p*-TSA catalysts].



Mechanistic representation of esterification of phthalic acid with *n*-octanol for synthesis of DOP over Brönsted acid sites of SZr catalyst

Scheme 2

characterized by ^1H NMR and FT-IR (Supplementary Data, Fig. S5 (a & b) to ascertain its purity.

Mechanism

Catalytic esterification of acid with alcohol is possible by both Brönsted and Lewis acids. As SZr catalyst has both Brönsted (H^+) and Lewis acid sites (Zr^{n+}), therefore, both acid sites may take part in the reaction. However, as the catalyst has higher Brönsted acidity and exhibited catalytic activity similar to homogenous Brönsted H_2SO_4 and *p*-TSA catalysts, the studied esterification of phthalic acid with *n*-octanol is predominantly a Brönsted acid catalyzed reaction, wherein H^+ transfers from the Brönsted acid sites of the catalyst to carbonyl oxygen of the acid, which is attacked nucleophilically by the oxygen of alcohol; subsequent deprotonation and loss of water resulting in ester product (Scheme 2).

Conclusions

The heterogeneous SZr acid catalyst, prepared by simple precipitation method, exhibited highest activity among various heterogeneous acid catalysts studied for solvent-free esterification of phthalic acid and *n*-octanol with 88% conversion of *n*-octanol and 93% DOP selectivity at 160 °C in 6 h. The catalyst showed similar activity upon reuse for five cycles. The catalyst also displayed excellent performance on scaling up the reaction twenty five times under similar reaction conditions. Structure-activity relationship studies revealed the necessity of weak to moderate acidic sites in SZr catalyst in enabling the reaction. Considering the efficiency of heterogeneous SZr catalyst that can be prepared by a simple and economic method, the present method is a potential greener alternative route for the commercial synthesis of DOP over conventional homogeneous catalysts such as H_2SO_4 and *p*-TSA.

Supplementary Data

Supplementary data associated with this article, Figs S1-S5 and tables S1-S2, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(07)747-755_SupplData.pdf.

Acknowledgement

Authors are thankful to CSIR Network Project, Indus Magic (CSC-0123) (CSIR, New Delhi, India) for financial assistance and to Analytical Discipline and Centralized Instrumental Facilities (AD&CIF) for providing instrumentation facilities. (CSIR-CSMCRI communication No 184/2015).

References

1 https://en.wikipedia.org/wiki/Phthalate#cite_note-endo-9.
2 http://www.kat-chem.hu/en/prod-bulletins/dioktilftalat.
3 http://www.icis.com/chemicals/phthalate-plasticizers/asia/.
4 Skrzypek J, Sadlowski J Z, Lachowska M & Turzariskih M, *Chem Eng Process,* 33 (1994) 413.
5 Skrzypek J, Sadlowski J Z, Lachowska M & Kukiełka W, *ChemEng Process,* 34 (5) (1995) 455.
6 Dubey P K & Mohiuddin S M G, *Asian J Chem,* 9 (1997) 379.
7 Thorat T S, Yadav V M & Yadav G D, *Appl Catal A: Gen,* 90 (1992) 73.
8 Zhao Z H, *J Mol Catal A: Chem,*168 (2001) 147.
9 Skrzypek J, Sadłowski J Z, Lachowska M & Kukiełka W, *Chem Eng Process,* 34 (5) (1995) 455.
10 Werber, F X, *US Patent No.* 3, 056, 818, Oct 2, 1962.
11 Cook S L, Tomlin C F, Turner P W & Herstellung V, *EP Patent No.* 1, 912, 929B1, Jan 8, 2014.
12 Ma Y, Wang Q L, Yan H, Ji X & Qiu Q, *Appl Catal A,* 139 (1996) 51.
13 Shrinivas G & Chudasama U, *Res J Chem Sci,* 5 (2015) 48.
14 Takahashi K, Shibagaki M & Matsushita H, *Bull Chem Soc Japan,* 62 (1989) 2353.
15 Sejidov F T, Mansoori Y & Goodarzi N, *J Mol Catal A: Chem,* 240 (2005) 186.
16 Hino M & Arata K, *Appl Catal A: Gen,* 18 (1985) 401.
17 Lu G, *Appl Catal A,* 133 (1995) 11.
18 Moghaddam M K & Gholami M R, *Mater Lett,* 60 (2006) 715.
19 Reddy B M & Patil M K, *Chem Rev*, 109 (2009) 2185.
20 Yadav G D & Nair J J, *Microporous Mesoporous Mater,* 33 (1999) 1.
21 Saravanan K, Tyagi B & Bajaj H C, *Indian J Chem,* 53A (2014) 799.
22 Tyagi B, Chudasama C D & Jasra R V, *Appl Clay Sci,* 31 (2006) 16.
23 Saravanan K, Tyagi B, Shukla R S & Bajaj H C, *ApplCatal B: Environ,* 172-173 (2015) 108.
24 Yamaguchi T, Jin T & Tanabe K, *J Phys Chem,* 90 (1986) 3148.
25 Ward D A & Ko E I, *J Catal*, 150 (1994) 18.
26 Mishra M K, Tyagi B & Jasra R V, *Ind Eng Chem Res,* 42 (2003) 5727.
27 Gregg S J & Sing K S W, *Adsorption, Surface Area and Porosity*, 2ndEdn, (Academic Press, New York) 1982.
28 Zalewski D J, Alerasool S & Doolin P K, *Catal Today,* 53 (1999) 419.