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Synthesis of monoesters and diesters using eco-friendly solid acid catalysts—Cerium(IV) and thorium(IV) phosphates

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ABSTRACT

In the present endeavour, amorphous cerium phosphate (CP) and thorium phosphate (TP) have been synthesized by sol–gel method and also under microwave irradiation to yield CP_M and TP_M. CP, TP, CP_M and TP_M have been characterized for elemental analysis (ICP-AES), spectral analysis (FTIR), thermal analysis (TGA), X-ray diffraction studies, SEM, EDX, surface area (BET) and surface acidity (NH_3-TPD). The potential use of these materials as solid acid catalysts has been explored by studying esterification as a model reaction. Monoesters such as ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA), benzyl acetate (BzAc) and diesters such as diethyl malonate (DEM), diethyl succinate (DES), dibutyl phthalate (DBP), dioctyl phthalate (DOP) have been synthesized. Esterification conditions have been optimized by varying several parameters such as reaction time, catalyst amount and mole ratio of reagents. The catalytic activity has been compared and correlated with reference to surface acidity of the catalysts. It is found that catalytic activity of $CP_M > CP > TP_M > TP$. The regenerated catalysts could be reused upto two catalytic runs without significant loss in % yields of esters formed. The highlighting feature of the present work is the catalysts CP_M and TP_M that are synthesized in a much shorter reaction time with higher surface acidity giving good % yield of esters.

1. Introduction

Esterification is an industrially important reaction for synthesis of plasticizers, perfumes, fragrance in cosmetics, flavours in food, diluents in paints and coatings and intermediates in drugs, dye stuffs and fine chemicals [1,2]. The conventional catalyst used in esterification reactions is sulphuric acid, methanesulfonic acid or *p*-toluenesulfonic acid that are cited as potential environmentally hazardous chemicals, that pose problems such as difficulty in handling, causing an acidic waste water, difficulty of catalyst recovery, etc. [3–5]. In view of the deficiencies encountered, there is a global effort to replace the conventional homogeneous liquid acids by heterogeneous solid acids. The use of solid acids eliminates the corrosive action of liquid acids. Being heterogeneous in nature, separation from reaction mixture is easy and the catalyst can be regenerated and reused.

Several materials such as sulphated zirconia [6,7], zeolites [5,8,9], sulfonic acid based resins [10–13], heteropoly acids [6], MCM-41 based materials [14–17], organophosphonic acid-functionalized silica [18], metal oxides [19], pillared clay [19] etc. have been reported as solid acid catalysts for esterification reactions. Though, sulphated zirconia is a good esterification catalyst, it gets easily deactivated by losing the sulphate ions, thereby restricting recycling of the catalyst. The main disadvantage of heteropoly acids is low efficiency due to low surface area, rapid deactivation and poor stability and when supported on carbon the activity decreases [20]. Sulfonic acid based resin (Nafion-H) has also been found to be unsatisfactory due to its low operating temperature.

Tetravalent metal acid (TMA) salts are inorganic cation exchangers possessing the general formula $M(IV)(HXO_4)_2 \cdot nH_2O$ [M(IV) = Zr, Ti, Sn, etc. and X = P, W, Mo, As, Sb, etc.] where, H^+ of the structural hydroxyl groups are responsible for cation exchange, due to which TMA salts indicate good potential for application as solid acid catalysts, the acidic sites being Brønsted acid sites in nature.

From our laboratory, use of TMA salts as solid acid catalysts has been explored for esterification [21–28]. Much of the works done by us are on phosphates of Zr, Ti and Sn. However, not much work has been explored on phosphates of Ce and Th.

In the present endeavour, amorphous cerium phosphate (CP) and thorium phosphate (TP) have been synthesized by sol–gel method. Further, CP and TP have also been synthesized under microwave irradiation to yield CP_M and TP_M. The materials have been characterized for elemental analysis (ICP-AES), spectral analysis (FTIR), thermal analysis (TGA), X-ray diffraction studies, SEM, EDX, BET surface area and surface acidity (NH_3-TPD). Chemical

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stability of the materials in various acids, bases and organic solvent media has been studied and their potential use as solid acid catalysts has been explored and compared by studying esterification as a model reaction wherein mono esters such as ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA), benzyl acetate (BzAc) and diesters such as diethyl malonate (DEM), diethyl succinate (DES), dibutyl phthalate (DBP), dioctyl phthalate (DOP) have been synthesized optimizing several parameters such as reaction time, catalyst amount and mole ratio of reagents.

2. Experimental

2.1. Chemicals

Thorium nitrate ($Th(NO_3)_4{\cdot}5H_2O$), ceric sulphate ($Ce(SO_4)_2{\cdot}4H_2O$) and sodium dihydrogen phosphate ($NaH_2PO_4{\cdot}2H_2O$) were procured from Loba Chemicals, Mumbai, while ethanol, 1-propanaol, 1-butanol, benzyl alcohol, octanol (2-ethyl 1-hexanol), acetic acid, phthalic anhydride, malonic acid, succinic acid, cyclohexane, xylene and toluene were obtained from Across Organics. Double-distilled water was used for all the studies.

2.2. Catalyst synthesis

CP and TP were synthesized by sol–gel method varying several parameters such as mole ratio of reactants, mode of mixing (metal salt solution to anion salt solution or vice versa), temperature, pH and rate of mixing. The main objective was to obtain a material with high cation exchange capacity (CEC) values which reflect on the protonating ability and thus the acidity in the materials. The term CEC is intended to describe the total available exchange capacity of an ion exchanger, as described by the number of functional groups on it. This value is constant for a given ion exchange material and is expressed in milli equivalents per gram, based on dry weight of material in given form (such as H^+). The Na^+ ion exchange capacity (CEC) of materials was determined by the column method [29] by optimizing volume and concentration of sodium acetate solution.

Several sets of materials were prepared varying conditions in each case using CEC as the indicative tool. (ESM – Tables 1 and 2 describe optimization of reaction parameters for synthesis of CP and TP respectively)

2.2.1. Synthesis of CP at optimized condition

A solution containing $Ce(SO_4)_2{\cdot}4H_2O$ [0.1 M, 50 mL in 10% (w/v) H_2SO_4] was prepared, to which $NaH_2PO_4{\cdot}2H_2O$ [0.3 M, 50 mL] was added dropwise (flow rate 1 mL min^{-1}) with continuous stirring for an hour at room temperature, when gelatinous precipitates were obtained (Step-I). The resulting gelatinous precipitate was allowed to stand for 3 h at room temperature, then filtered, washed with conductivity water to remove adhering ions and dried at room temperature (Step-II).

2.2.2. Synthesis of TP at optimized condition

An aqueous solution of $Th(NO_3)_4{\cdot}5H_2O$[0.1 M, 50 mL] was added drop wise (flow rate 1 mL min^{-1}) to an aqueous solution of $NaH_2PO_4{\cdot}2H_2O$ [0.2 M, 100 mL] with continuous stirring for an hour at room temperature, when gelatinous precipitates were obtained (Step-I). The resulting gelatinous precipitate was allowed to stand for 5 h at room temperature, then filtered, washed with double distilled water to remove adhering ions and dried at room temperature (Step-II).

2.2.3. Synthesis of CP and TP under microwave irradiation

Gelatinous precipitate obtained in step-I was subjected to microwave irradiation for optimum time and temperature (ESM – Table 3), then filtered, washed with double distilled water to remove adhering ions and dried at room temperature (Step-II).

2.2.4. Acid treatment

The above dried materials obtained in step-II were broken down to the desired particle size [30–60 mesh (ASTM)] by grinding and sieving. 5 g of this material was treated with 50 mL of 1 M HNO_3 for 30 min with occasional shaking. The material was then separated from acid by decantation and treated with double distilled water to remove adhering acid. This process (acid treatment) was repeated at least 5 times for both the materials. After final washing, the material was dried at room temperature.

2.3. Characterization

2.3.1. Chemical stability

The chemical stability of the catalysts in various acids (HCl, H_2SO_4, HNO_3), bases (NaOH and KOH) and organic solvent media (ethanol, propanol, butanol, benzyl alcohol, cyclohexane, toluene, xylene and acetic acid) was examined by taking 500 mg of each of the synthesized catalyst in 50 mL of the particular medium and allowed to stand for 24 h. The change in colour, weight and nature was observed.

2.3.2. Instrumentation

All synthesized materials were subjected to instrumental methods of analysis/characterization. CP and TP were analyzed for cerium, thorium and phosphorus by ICP-AES. FTIR spectra were recorded using KBr pellet on Shimadzu (Model 8400S). Thermal analysis (TGA) was carried out on a Shimadzu (Model TGA 50) thermal analyzer at a heating rate of 10 °C min^{-1}. X-ray diffractogram (2θ angles = 10°–90°, scanning time = 2°/min and sample run time = 8 min) was obtained on X-ray diffractometer (Brucker AXS D8) with Cu Kα radiation with nickel filter. SEM and EDX of the sample were scanned on Jeol JSM-5610-SLV scanning electron microscope. Surface area was determined by BET multipoint method using a Micromeretics Gemini 2220 series surface area analyzer. Surface acidity was determined on Chemisorb 2720, by a temperature programmed desorption (TPD) of ammonia. All materials were preheated at 150 °C, 200 °C and 700 °C temperatures and thereafter ammonia was chemisorbed at 120 °C and then desorption was carried out upto 700 °C at a heating rate of 10 °C min^{-1} in all cases. The products were analyzed by Ceres 800 Plus gas chromatograph (GC) using flame ionization detector.

2.4. Synthesis of esters

2.4.1. Synthesis of monoesters (EA, PA, BA and BzAc)

In a typical reaction, a 100 mL round bottomed flask equipped with a Dean and Stark apparatus, attached to a reflux condenser was used and charged with acetic acid (0.05–0.10 M), alcohol (0.05–0.10 M), catalyst (0.10–0.20 g) and a suitable solvent (15 mL). The reactions were carried out varying several parameters such as reaction time, catalyst amount, mole ratio of reactants and these parameters optimized. The temperature parameter has not been varied as the reaction temperature is sensitive to boiling points of reactants [ethanol (78 °C), 1-propanol (97 °C), 1-butanol (118 °C) and benzyl alcohol (205 °C)] as well as solvents used as azeotrope. Cyclohexane (80 °C) was used as a solvent for the synthesis of ethyl acetate and toluene (110 °C) for propyl acetate, butyl acetate and benzyl acetate. After completion of reaction, catalyst was separated by decantation and reaction mixture was distilled to obtain the product.

Table 1
Data of elemental analysis (ICP-AES) and EDX analysis.

Materials	ICP-AES analysis (%)		EDX analysis (atomic %)	
	M(IV)	P	M(IV)	P
CP (fresh)	33.15	15.11	34.95	65.05
CP (spent)	–	–	38.24	61.76
TP (fresh)	35.10	9.40	35.75	64.25
TP (spent)	–	–	37.52	62.48

For ICP-AES, detection limits = 0.10 ppm.

2.4.2. *Synthesis of diesters (DEM, DES, DBP and DOP)*

The diesters were synthesized in two steps. The mono ester was prepared in first step by taking equimolar proportion (0.025 mol) of acid and alcohol (malonic acid and ethanol for DEM, succinic acid and ethanol for DES, phthalic anhydride and 1-butanol for DBP, phthalic anhydride and 2-ethyl 1-hexanol for DOP) were taken in a round bottomed flask and the reaction mixture stirred at ~80 °C for DEM and DES, ~110 °C for DBP and ~140 °C for DOP for about 10–15 min in absence of any catalyst and solvent. The dicarboxylic acid and anhydride get completely converted to the monoester, so that the acid concentration at this stage is taken as the initial concentration. The obtained product (monoester) was then subjected to esterification reaction by addition of a second mole (0.025 mol) of respective alcohol, catalyst (0.10–0.20 g) and 15 mL solvent (toluene (110 °C) for DEM, DES and DBP, and xylene (140 °C) for DOP). The reactions were carried out optimizing several parameters such as reaction time, catalyst amount and mole ratio of reactants. The temperature parameter has not been varied as discussed in synthesis of monoesters. In all cases the round bottomed flask was fitted with Dean and Stark apparatus, with a condenser to remove water formed during the reaction. After completion of reaction, catalyst was separated by decantation and reaction mixture was distilled to obtain the product.

2.4.3. *Calculation of % yield of esters*

The yields of the mono and diesters formed were determined by titrating the reaction mixture with 0.1 M alcoholic KOH solution. The yields of the esters were calculated using the formula, % yield = $[(A - B)/A] \times M \times 100$, where A and B are acid values of the sample withdrawn before and after reaction and M is mole ratio of acid: alcohol. The yield of ester formed was also determined using GC. (Oven temperature: 150 °C, injector temperature: 200 °C, detector temperature: 220 °C and split ratio is 1:2).

2.5. *Regeneration of catalyst*

After separation of catalyst in reaction mixture by decantation, it is first refluxed in ethanol for 30 min to solubilize and remove adsorbed molecules, followed by drying at room temperature (~30 °C). This material was used as recycled catalyst. This regeneration procedure was followed in subsequent recycle reaction.

3. Results and discussion

3.1. *Catalyst characterization*

CP and TP were obtained as yellow and off white hard granules respectively. Elemental analysis performed by ICP-AES, for both CP and TP, show ratio of M:P to be 1:2, which is well supported by EDX analysis (ESM – Figs. 1 and 2) (Table 1).

Thermal behaviour of several TMA salts has been investigated and generally examined for loss of moisture ~80 °C, loss of external water molecules ~100–180 °C and for condensation of the structural hydroxyl groups ~180–500 °C and above [30]. TGA of CP and TP presented in Fig. 1 reveals that CP exhibits the first weight loss ~13% and the second weight loss ~8% while TP exhibits the first weight loss ~11% and the second weight loss ~9%. The first weight loss (up to ~120 °C) is attributed to loss of moisture/hydrated water while the second weight loss in the range 120–500 °C is attributed to condensation of structural hydroxyl groups.

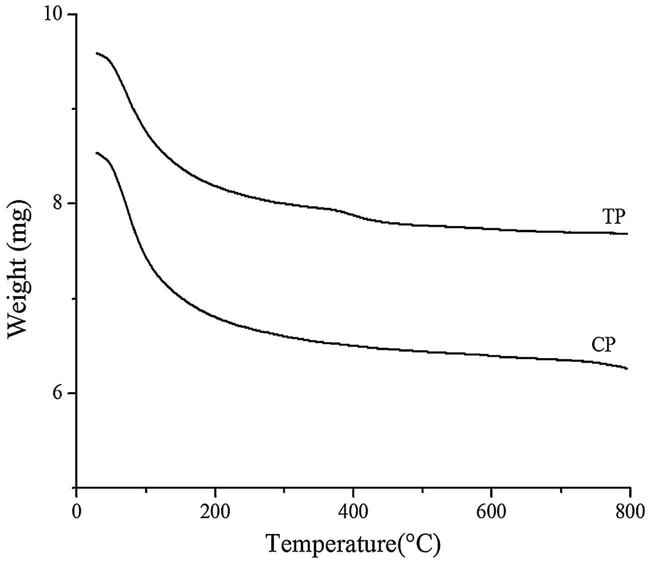


Fig. 1. TGA of CP and TP.

Based on the elemental analysis (ICP-AES) and thermal analysis (TGA) data, CP and TP, are formulated as $Ce(HPO_4)_2 \cdot 4.9H_2O$ and $Th(HPO_4)_2 \cdot 5.8H_2O$. The number of water molecules in each case is calculated using Alberti and Torracca (1968) formula [31]. (Table 1)

The FTIR spectra (Fig. 2) of CP and TP exhibits a broad band in the region ~3400 cm^{-1} which is attributed to asymmetric and symmetric —OH stretching vibration due to residual water and presence of structural hydroxyl groups, H$^+$ of the —OH being Brønsted acid sites in nature. These bands indicate the presence of structural hydroxyl groups/catalytic sites in the materials. These sites are also referred to as defective P—OH groups [29,32]. A sharp medium band at ~1630 cm^{-1} is attributed to aquo H—O—H bending [33]. The band at ~1050 cm^{-1} is attributed to P=O stretching while the bands at ~620 cm^{-1} and ~500 cm^{-1} is attributed to Metal–O stretching [34].

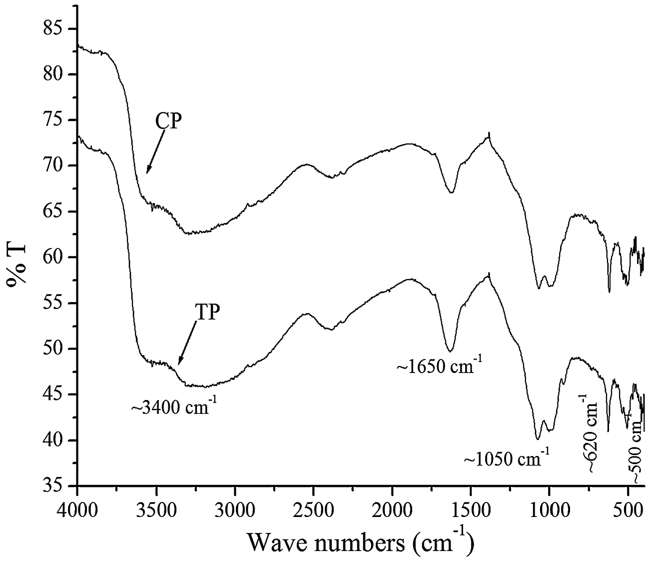


Fig. 2. FTIR spectra of CP and TP.

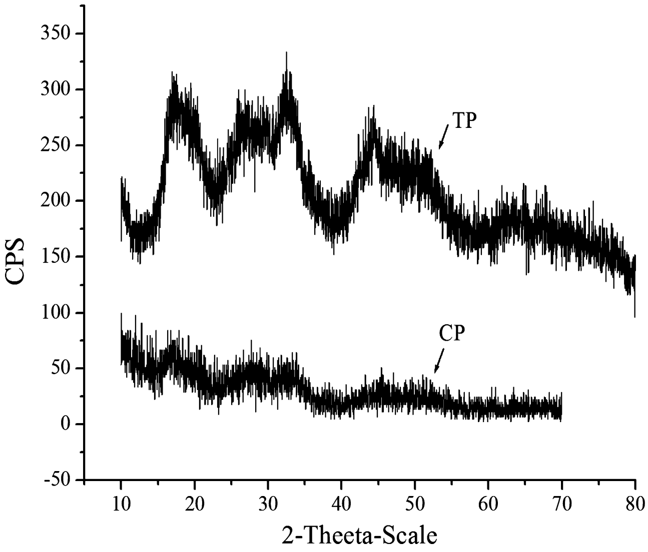


Fig. 3. XRD of CP and TP.

The Na^+ CEC values/protonating ability were observed to be 2.48, 1.45, 2.90 and 2.41 for CP, TP, CP_M and TP_M respectively.

CEC values decrease on calcination, at higher temperatures due to loss of hydrated water and condensation of structural hydroxyl groups (ESM – Table 4). This fact is also evident from the FTIR spectra of the calcined samples (ESM – Fig. 3). It is seen that the intensities of the peaks at $-3400\,cm^{-1}$ and $-1638\,cm^{-1}$ corresponding to the —OH group diminish as temperature increases [35].

CP and TP are found to be stable in acid media, maximum tolerable limits being (1 N H_2SO_4, 2 N HNO_3, 5 N HCl) and also stable in organic solvent media. They are however not so stable in base medium, maximum tolerable limits being (0.5 N NaOH and KOH).

The absence of sharp peaks in the X-ray diffractograms of CP and TP (Fig. 3), and CP_M and TP_M (Fig. 4) indicates amorphous nature of all the materials. SEM images of CP, TP, CP_M and TP_M (ESM – Figs. 4–7) show irregular morphology.

Surface area measurement has been performed by adsorption–desorption isotherm of N_2 which was recorded, at −196 °C after degassing the sample at 300 °C for 4 h. Surface area values of CP, TP, CP_M and TP_M are 20.71, 1.94, 1.40 and 1.22 in m^2/g respectively.

Table 2
Surface acidity and CEC values at 150, 200 and 700 °C preheating temperatures.

Samples	Calcination/preheating temperature (°C)	Total acidity (NH_3-TPD method) (mmol g^{-1})	CEC (meq g^{-1})
CP	150	0.95	2.04
	200	0.89	1.89
	700	–	–
CP_M	150	1.26	2.20
	200	0.45	2.00
	700	–	–
TP	150	0.78	0.70
	200	0.50	0.46
	700	–	–
TP_M	150	0.80	0.92
	200	0.76	0.70
	700	–	–

Surface acidity for all the materials was determined by NH_3-TPD at 150 °C, 200 °C and 700 °C preheating temperatures (Table 2 and Figs. 5–8). As already discussed earlier in the text, acidity in CP and TP is due to the presence of structural hydroxyl protons, H^+ of the —OH being the Brønsted acid sites. Further, surface acidity values of CP and TP depend on the size and charge of the cation. Smaller size and higher charge of the cation indicate greater tendency to release a proton, i.e. H^+ of the —OH groups present in CP and TP. In the present study Ce^{4+} and Th^{4+}, both ions being tetravalent as well as bearing common anion PO_4^{3-}, size of the cation Ce^{4+} (1.05 Å) and Th^{4+} (1.08 Å) seem to play a dominant role. Thus the acidity in the materials follows the order CP > TP and $CP_M > TP_M$. Decrease in surface acidity for CP and TP with increasing preheating temperatures could be attributed to condensation of structural hydroxyl groups as discussed above in thermal behaviour of these materials. This is well supported by CEC values, which reflect on the protonating ability and thus the acidity of the materials [36]. CEC values also decrease with increasing calcination/preheating temperature have already been discussed in FTIR spectra of calcined samples.

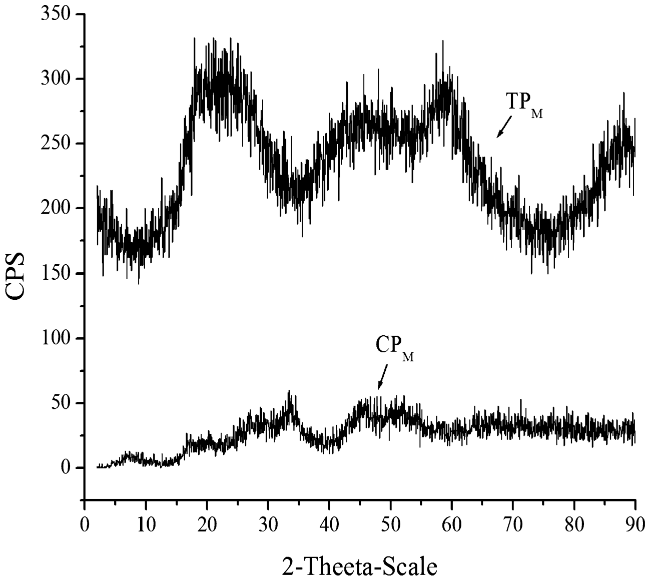


Fig. 4. XRD of CP_M and TP_M.

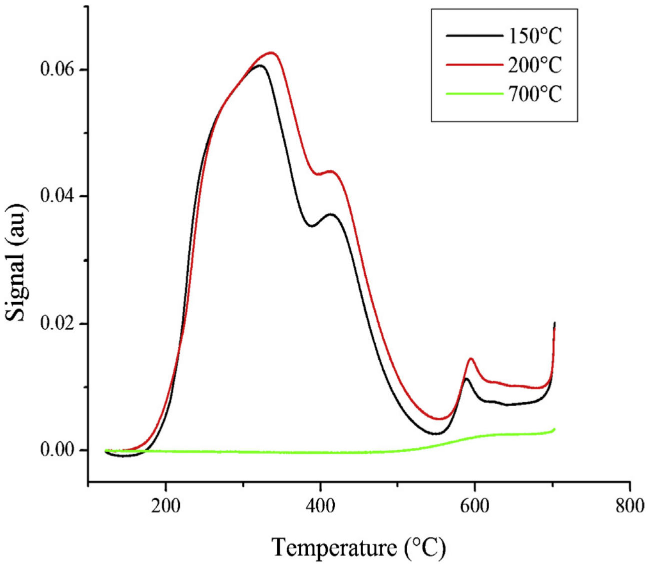


Fig. 5. NH_3-TPD patterns for CP at 150, 200 and 700 °C preheating temperatures.

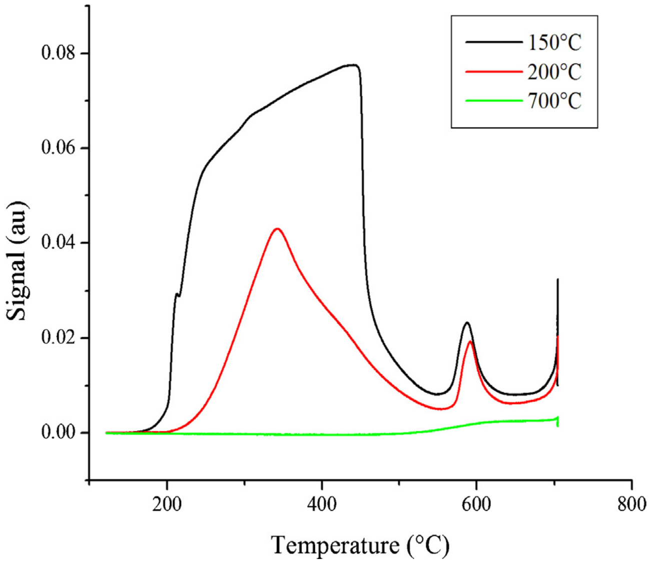


Fig. 6. NH_3-TPD patterns of CP_M at 150, 200 and 700 °C preheating temperatures.

3.2. Synthesis of monoesters

Monoester synthesis EA, PA, BA and BzAc is as presented in Scheme 1. Equilibrium constants of the esterification reactions are low. As in any equilibrium reaction, the reaction may be driven to the product side by controlling the concentration of one of the reactants (Le Chatlier's Principle). In order to obtain higher yield of esters, Le Chatlier's Principle has been followed. Solvents cyclohexane and toluene have been employed to remove the water formed during the reaction as a binary azeotrope. Monoesters EA, PA, BA and BzAc were synthesized as described in Section 2.

Firstly, reaction conditions were optimized using CP as solid acid catalyst for EA synthesis by varying parameters such as reaction time, catalyst amount and initial mole ratio of the reactants (Table 3 and a graphical presentation ESM – Figs. 8–10).

It is observed that as reaction time increases, percentage yield increases. However, there is not much gain in product after 8 h. With increasing amount of the catalyst, the % yield increases which is probably due to proportional increase in the number of active sites. The influence of reactant mole ratio was studied by increasing mole ration from 1:1.5 to 1.5:1 (acid:alcohol). According to Le Chatlier's Principle ester yields can be increased by increasing the concentration of either alcohol or acid. As observed from Table 3, the % yield of ester increases with increase in mole ratio of acid while decreases with increasing mole ratio of alcohol. This may be attributed to preferential adsorption of alcohol on the catalyst which results in blocking of active sites. For economic reasons also, the reactant that is usually less expensive of the two is taken in excess. In the present study, acids were used in excess.

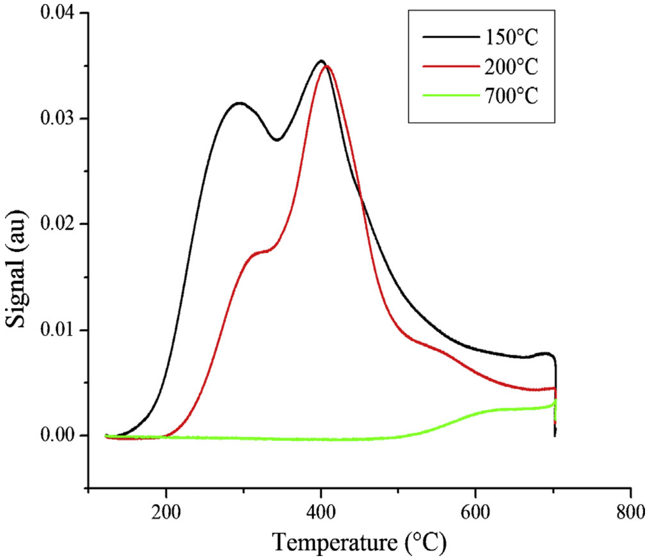


Fig. 7. NH_3-TPD pattern for TP at 150, 200 and 700 °C preheating temperatures.

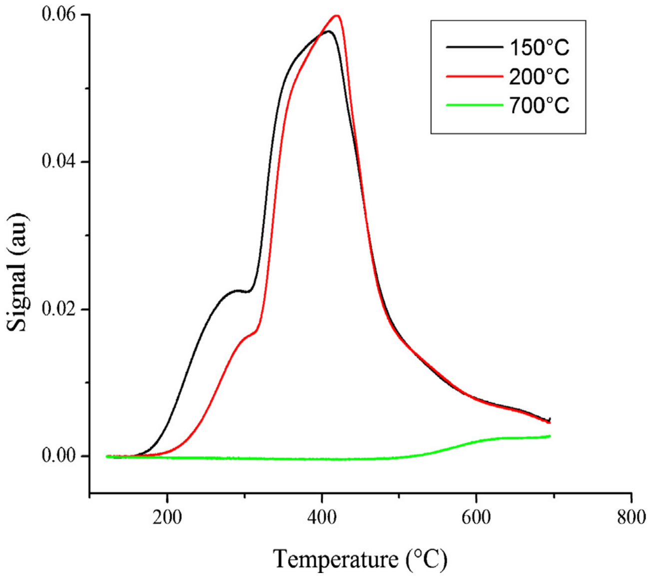
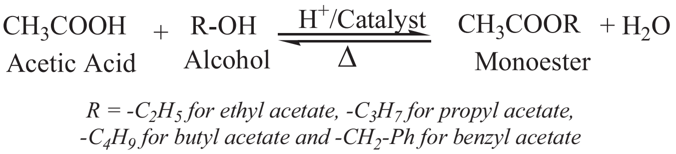


Fig. 8. NH_3-TPD patterns of TP_M at 150, 200 and 700 °C preheating temperatures.

Further, at optimized conditions synthesis of EA, PA, BA and BzAc was performed using CP, CP_M, TP and TP_M as solid acid catalysts, (mole ratio of reactants = 1:1.5 (alcohol:acid); catalyst amount = 0.15 g; reaction time = 8 h) (Table 4).

Esterification of monoesters EA, PA and BA has been reported [37] in absence of catalyst and exhibits poor yields. Therefore catalyst is a must for these reactions. In case of BzAc however, it is observed that with an excess of acetic acid and in the absence of any catalyst the yield is as high as 90.6% which is attributed to auto catalysis. In another report [38] high yields of BzAc were obtained with small amount of the catalyst but the reaction time was relatively high. Higher yields in case of benzyl acetate could be attributed to an enhanced nucleophilicity due to presence of aromatic ring in benzyl alcohol. The order of % yield of ester formed is BzAc > BA > PA > EA could be explained due to increase in carbon chain length in the respective alcohols used for ester formation. When the boiling point of the alcohol is less than the temperature of the reaction, most of the alcohol will end up in the vapor phase and not be available in the liquid phase. This is the reason why the heavier alcohols react more than the lighter ones. Turn over number (TON) reflects the effectiveness of a catalyst and this also follows the order of ester formation.

The order of monoesters formed with reference to performance of catalyst is CP exhibits higher yields in all cases compared to TP



Scheme 1. Synthesis of monoesters (EA, PA, BA and BzAc).

Table 3
Optimization of reaction conditions for monoesters using CP.

Sr. no.	Reactants with their mole ratio	Product	Catalyst amount (g)	Time (h)	Temp. (°C)	% Yield CP
(A)	Time variation					
1	E + AA (1:1)	EA	0.05	1	80	12.2
2	E + AA (1:1)	EA	0.05	2	80	23.1
3	E + AA (1:1)	EA	0.05	3	80	25.2
4	E + AA (1:1)	EA	0.05	4	80	33.5
5	E + AA (1:1)	EA	0.05	5	80	39.6
6	E + AA (1:1)	EA	0.05	6	80	44.4
7	E + AA (1:1)	EA	0.05	7	80	48.2
8	E + AA (1:1)	EA	0.05	8	80	52.3
9	E + AA (1:1)	EA	0.05	9	80	53.1
10	E + AA (1:1)	EA	0.05	10	80	53.1
(B)	Catalyst amount variation					
12	E + AA (1:1)	EA	0.10	8	80	57.1
13	E + AA (1:1)	EA	0.15	8	80	59.1
14	E + AA (1:1)	EA	0.20	8	80	59.3
(C)	Mole ratio variation					
15	E + AA (1.5:1)	EA	0.15	8	80	41.8
16	**E + AA (1:1.5)**	**EA**	**0.15**	**8**	**80**	**74.4**

E = ethanol; AA = acetic acid.

while CP_M exhibits higher yields than TP_M could be attributed to higher surface acidity (Table 4, Figs. 9 and 10).

3.3. *Synthesis of diesters*

Reactions involved for diester synthesis are presented in Scheme 2 (DES and DEM) and Scheme 3 (DOP and DBP). The first step is so rapid that it can be carried out in the absence of catalyst. However, esterification of the second carboxylic group (second step) is very slow and needs to be facilitated by acid catalyst and the resulting water must be removed from the reaction mixture [39]. Firstly, reaction conditions were optimized using CP as solid acid catalyst for DEM synthesis by varying parameters such as reaction time, catalyst amount and initial mole ratio of the reactant. The optimized reaction conditions for diesters have been presented in Table 5 and a graphical presentation ESM – Figs. 11–13).

At optimized conditions synthesis of DEM, DES, DBP and DOP was performed using CP, TP, CP_M and TP_M (mole ratio of reactant = 1:2.5 (diacid/anhydride: alcohol), catalyst amount = 0.15 g and reaction time = 10 h) (Table 6).

In the present work, the % yields of DOP are higher than DBP which could be attributed to higher boiling point of 2-ethyl 1-hexanol compared to 1-butanol. Further, high yield in case DEM and DES compared to DOP and DBP is probably due to less steric hindrance felt by incoming ethanol from monoethyl malonate formed in the first step.

DEM synthesis has been reported by Prakash and co-workers using montmorillonite clay, but the yield is low (41%) and relatively high amount of catalyst (0.5 g) was used [38]. DOP formation has been catalyzed by zeolites [9], metallic oxides [40], solid super acids [13,41,42] and heteropoly acids [39,42]. Suter [43] has reported a non-catalytic process for the manufacture of DOP, at very high temperatures, at which autocatalysis occurs. In another report, DEM has been synthesized by Song and Jiang using the reaction of CO with $ClCH_2COOC_2H_5$. In this case high yield was observed but the reaction was carried out at high pressure [44]. DES synthesis and kinetics have been reported by Kolah et al. using amberlyst catalyst with good yields [45]. When homogeneous liquid acids are used as catalysts for synthesis of diesters, the result is a product that is coloured and of a poor quality. In the present work though

Table 4
% yields of monoesters using CP, TP, CP_M and TP_M at optimized condition.

Sr. no	Reactants	Product	CP		TP	
			% Yield	[a]TON	% Yield	[a]TON
1	E + AA	EA	74.4	33.7	70.7	32.0
2	P + AA	PA	75.6	37.8	72.1	36.0
3	B + AA	BA	78.5	42.9	74.8	40.9
4	BzA + AA	BzAc	81.3	53.6	78.0	51.4
(A)	Microwave irradiated catalysts		CP_M		TP_M	
			% Yield	[a]TON	% Yield	[a]TON
5	E + AA	EA	77.8	35.2	75.0	33.9
6	P + AA	PA	80.7	40.3	77.5	38.7
7	P + AA	BA	82.2	44.9	80.0	43.7
8	Bz + AA	BzAc	89.1	58.8	85.4	56.3

AA = acetic acid; E = ethanol; P = 1-propanol; B = 1-butanol; BzA = benzyl alcohol. Mole ratio of the reactants = 1:1.5 (alcohol:acid); reaction time = 8 h; catalyst amount = 0.15 g; reaction temperature 80 °C for EA; and 115 °C for PA, BA and BzAc.

[a] TON = turn over number, gram of ester formed per gram of catalyst.

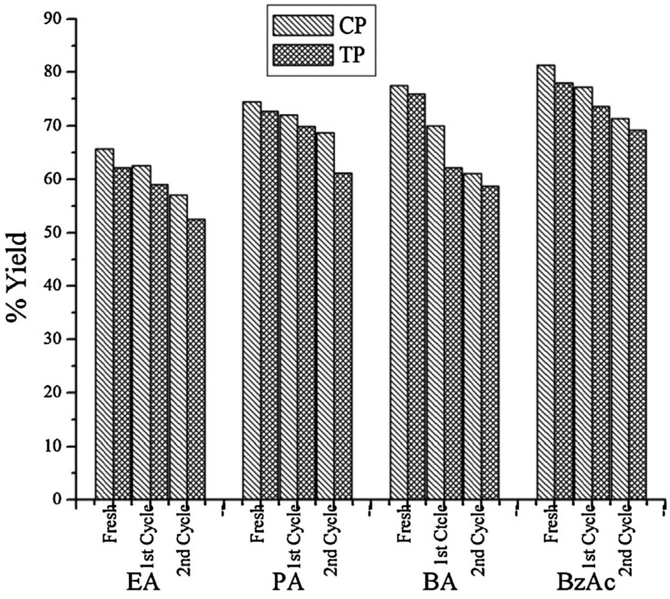
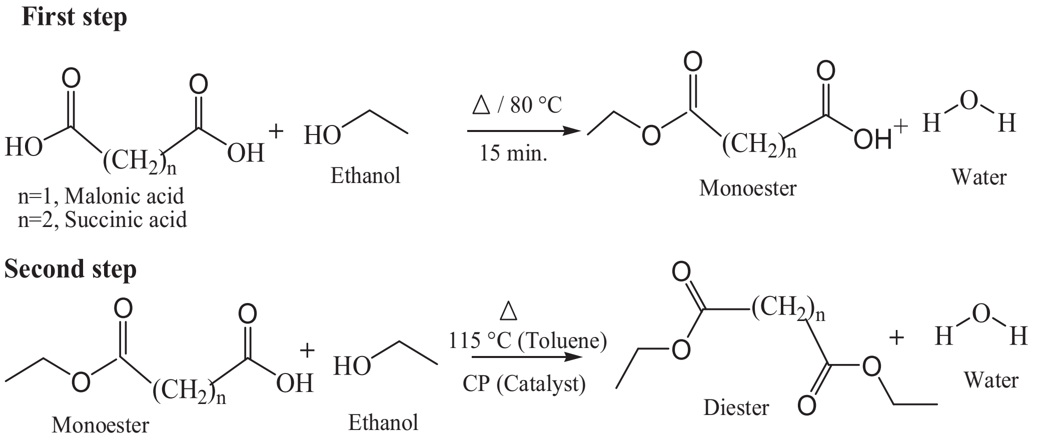


Fig. 9. Comparative catalytic performance of CP and TP for synthesis of monoesters.



Scheme 2. Synthesis of DES and DEM.

the yields of diesters obtained are low, the advantage is that the diester is the single product and colourless.

The order of diesters formed with reference to performance of catalyst is CP that exhibits higher yields in all cases compared to TP while CP_M exhibits higher yields than TP_M (Table 6, Figs. 11 and 12).

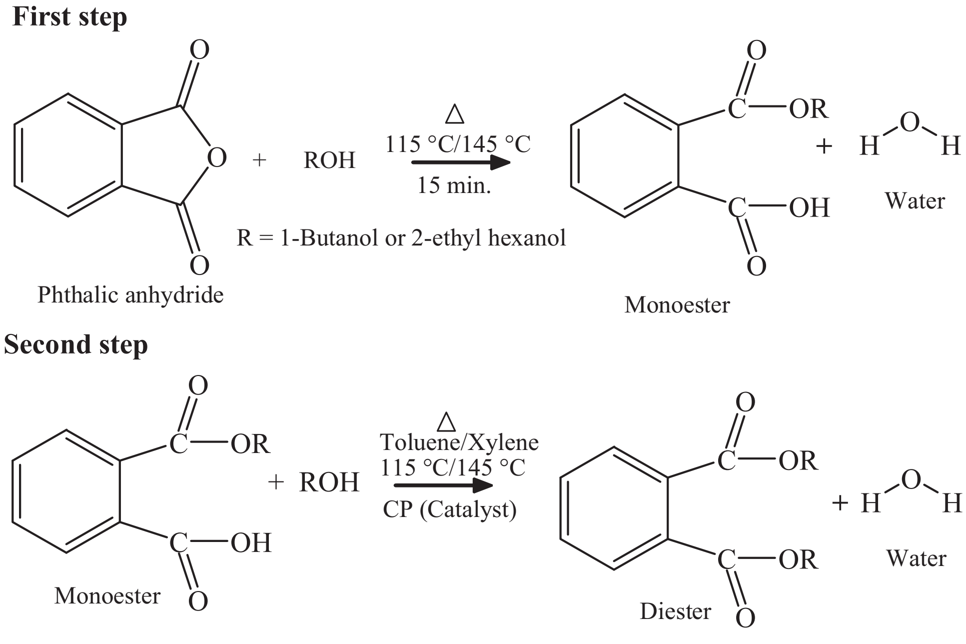
During the course of the reaction, many a time the catalyst colour changes. This is probably due to the fact that reactant molecules come onto surface of catalyst and enters into reaction to give the product while a few of them get adsorbed on surface. In each subsequent run, the acid sites in catalysts were regenerated as described in Section 2. Almost 100% catalyst recovery is observed. After regeneration and reuse, decrease in yields are observed which is probably due to the deactivation of catalysts because of substrate molecules getting adsorbed on surface or also entering interstices of the catalyst material [36]. Reusability of CP and TP was tested by conducting two runs (Table 7, Figs. 9 and 11).

It is observed that there is only a marginal decrease in yields upto two catalytic runs. In recycled catalyst the yield decreased by 4–7% (Table 7). Further, EDX of spent CP (ESM – Fig. 14) (after 1st catalytic run) shows atomic % of Ce and P to be 38.24% and 61.76% respectively, and EDX of spent TP (ESM – Fig. 15) (after 1st catalytic run) shows atomic % of Th and P to be 37.52% and 62.48% respectively which shows decrease in atomic % of P compared to EDX of fresh CP (ESM – Fig. 1) (atomic % of Ce = 34.95 and atomic % of P = 65.05) and EDX of fresh TP (ESM – Fig. 2) (atomic % of Th = 35.75 and atomic % of P = 64.25). Decrease in yield of monoesters and diesters may be due to the leaching of P in catalysts.

Comparing catalyst efficiency/performance of CP and TP with M(IV) phosphates of the class of TMA salts (M(IV) = Zr, Ti and Sn) [3,27], the % yields are observed to be ranging from low to marginal to comparitive yields (ESM – Table 5).

3.4. Reaction mechanism in solid acid catalyzed esterification reaction

The mechanism of esterification can be different for the various solid acid catalysts and also depends on gas- or liquid-phase operation as well as the substrate. Chu et al. [46] claim that the esterification mechanism of acetic acid with butanol over carbon-supported HPA catalysts proceeds via a protonated alcohol intermediate, but most authors [47–49] proposed a protonated carboxylic acid as the reaction intermediate. The two possible



Scheme 3. Synthesis of DBP and DOP.

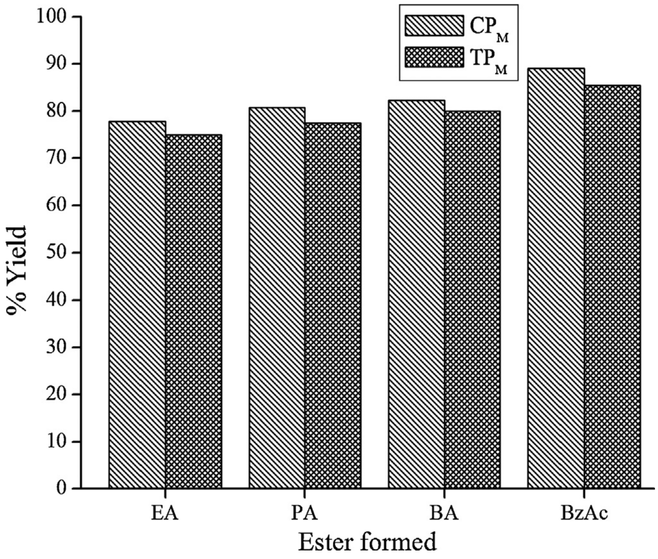


Fig. 10. Comparative catalytic performance of CP_M and TP_M for synthesis of monoesters.

Table 5
Optimization of reaction conditions for diesters using CP.

Sr. no.	Reactants with their mole ratio	Product	Catalyst amount (g)	Time (h)	Temp. (°C)	% Yield CP
(A)	Time variation					
1	E + MA (2:1)	DEM	0.05	1	115	56.2
2	E + MA (2:1)	DEM	0.05	2	115	57.1
3	E + MA (2:1)	DEM	0.05	3	115	61.8
4	E + MA (2:1)	DEM	0.05	4	115	65.7
5	E + MA (2:1)	DEM	0.05	5	115	69.4
6	E + MA (2:1)	DEM	0.05	6	115	72.3
7	E + MA (2:1)	DEM	0.05	7	115	74.1
8	E + MA (2:1)	DEM	0.05	8	115	75.6
9	E + MA (2:1)	DEM	0.05	9	115	75.8
10	E + MA (2:1)	DEM	0.05	10	115	75.9
11	E + MA (2:1)	DEM	0.05	11	115	76.0
12	E + MA (2:1)	DEM	0.05	12	115	76.0
(B)	Catalyst amount variation					
13	E + MA (2:1)	DEM	0.10	8	115	85.5
14	**E + MA (2:1)**	**DEM**	**0.15**	**8**	**115**	**91.5**
15	E + MA (2:1)	DEM	0.20	8	115	92.0
(D)	Mole ratio variation					
16	E + MA (2.2:1)	DEM	0.15	8	115	87.2
17	E + MA (2.4:1)	DEM	0.15	8	115	86.9

E = ethanol; MA = malonic acid. Bold values are for Optimized condition

intermediates, protonated ethanol and protonated acetic acid, are shown in Scheme 4.

The mechanism of diester formation over solid acid catalyst is similar to that of conventional mechanism involving the formation of protonated dicarboxylic acid, using proton donated by the catalyst, followed by nucleophilic attack of alcoholic group to yield the respective monoester. The second carboxylic group present in monoester gets further esterified by the same mechanism in a repeat reaction, which ultimately results in the diester formation [38].

Table 6
% yields of diesters using CP, TP, CP_M and TP_M at optimized condition.

Sr. no	Reactants	Product	CP		TP	
			% Yield	[a]TON	% Yield	[a]TON
1	E + MA	DEM	91.5	29.8	89.0	29.0
2	E + SA	DES	67.1	23.4	64.5	22.5
3	B + PhA	DBP	44.0	21.7	42.8	21.1
4	O + PhA	DOP	69.7	47.4	60.0	40.8
(A)	Microwave irradiated catalysts		CP_M		TP_M	
			% Yield	[a]TON	% Yield	[a]TON
5	E + MA	DEM	95.5	31.1	93.0	30.3
6	E + SA	DES	73.4	25.6	70.1	24.5
7	B + PhA	DBP	53.7	24.4	50.5	24.9
8	O + PhA	DOP	76.8	52.3	67.4	45.8

MA = malonic Acid; SA = succinic acid; PhA = phthalic anhydride.
Mole ratio of the reactants = 2:1 (alcohol:acid); reaction, time = 8 h. Catalyst amount = 0.15 g; reaction temperature 115 °C for DEM, DES and DBP, 140 °C for DOP.

[a] TON = turn over number, gram of ester formed per gram of catalyst.

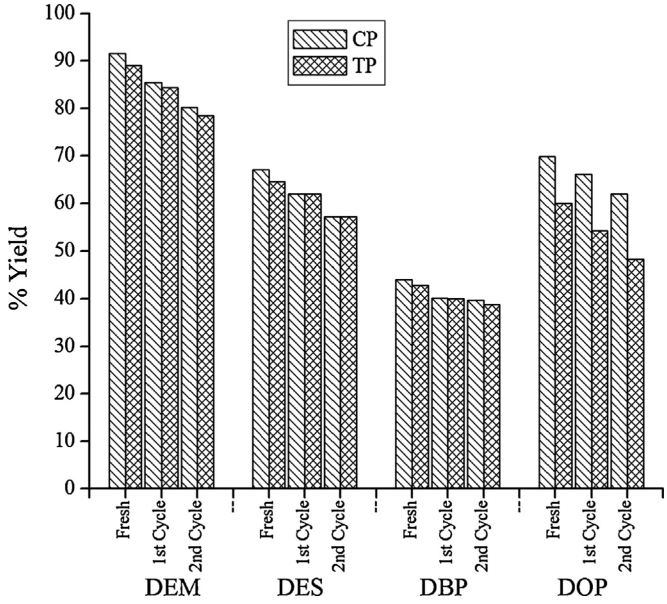


Fig. 11. Comparative catalytic performance of CP and TP for synthesis of diesters.

Table 7
Performance of recycled catalysts.

Recycled Catalyst	Catalytic Run	% Yield							
		EA	PA	BA	BzAc	DEM	DES	DBP	DOP
CP	First	72.1	88.2	72.0	73.2	85.4	61.9	40.1	66.1
	Second	67.8	87.3	66.1	67.8	80.2	57.1	39.6	62.0
TP	First	66.9	68.1	70.1	71.7	84.3	59.1	40.0	54.2
	Second	61.1	62.0	66.6	65.1	78.5	54.1	38.7	48.2

Reaction condition:
Monoesters: mole ratio of the reactants = 1:1.5 (alcohol:acid); reaction time = 8 h; catalyst amount = 0.15 g; reaction temperature 80 °C for EA; and 115 °C for PA, BA and BzAc; 115 °C for DEM, DES and DBP, 140 °C for DOP; diesters:mole ratio of the reactants = 2:1 (alcohol:acid); reaction time = 8 h. catalyst amount = 0.15 g; reaction temperature 115 °C for DEM, DES and DBP, 140 °C for DOP.

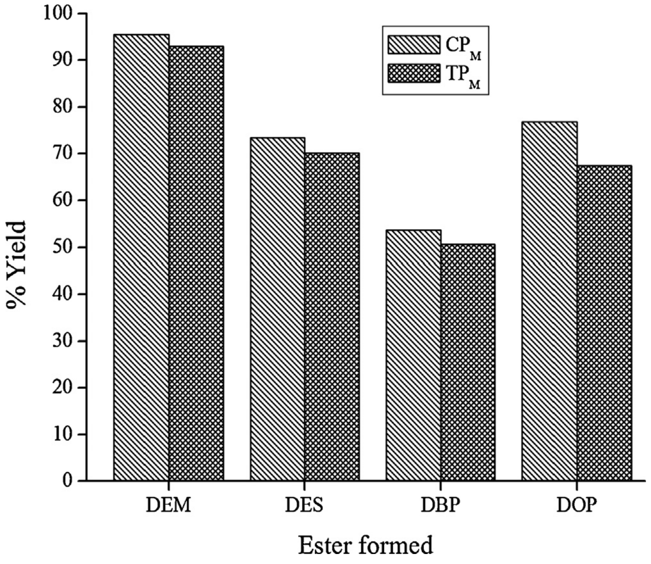
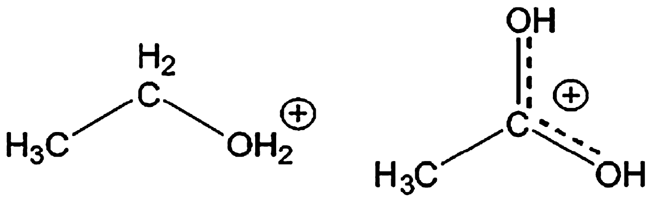


Fig. 12. Comparative catalytic performance of CP$_M$ and TP$_M$ for synthesis of diesters.



Scheme 4. Possible protonated intermediates in esterification reaction.

4. Conclusions

The study reveals good performance of all catalysts under study, with advantages of operational simplicity, mild reaction conditions as well as regeneration/reuse of catalysts. Further there is no catalyst or colour contamination in products formed, nor acid waste generation, a limitation in the conventional process. The highlighting feature of the present work is the synthesis of CP$_M$ and TP$_M$ under microwave irradiation in much shorter reaction time, with higher surface acidity including good % yields of esters formed.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.07.043.

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