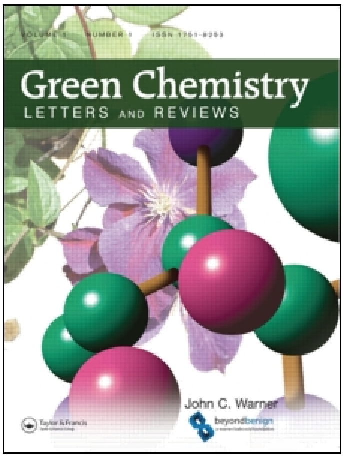

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RESEARCH LETTER

Synthesis of mono and diesters using eco-friendly solid acid catalyst – zirconium titanium phosphate

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Amorphous zirconium titanium phosphate (ZTPA), an advanced inorganic ion exchanger of the class of tetravalent bimetallic acid (TBMA) salt, has been synthesized by sol gel route. ZTPA has been characterized by inductively coupled plasma atomic emission spectrometer (ICP-AES), Thermal analysis, Fourier transform infrared spectrometer (FTIR), and X-ray diffraction (XRD). The acid sites present in ZTPA indicate good potential to be explored as solid acid catalyst. The catalytic characteristics of ZTPA have been evaluated by determining surface area and surface acidity. The catalytic performance of ZTPA as a solid acid catalyst has been explored by studying esterification as a model reaction wherein mono and diesters have been synthesized. Crystalline zirconium titanium phosphate as well as amorphous and crystalline phases of zirconium phosphate and titanium phosphate have also been synthesized, characterized, and their catalytic performance investigated for comparative studies. TBMA salt exhibits enhanced catalytic activity compared to its single salt counterparts and amorphous phases exhibit higher catalytic activity compared to their crystalline phases.

Keywords: solid acid catalyst; esterification; inorganic ion exchanger; zirconium titanium phosphate; tetravalent bimetallic acid salt

Introduction

The principles of green chemistry can be applied to all areas of chemistry including synthesis, reaction conditions, and catalysis. Catalysis provides an important opportunity to achieve goals of green chemistry. Amongst the various catalytic systems used, solid acid catalysts are making a huge impact. Though they differ in structure from liquid acids, solid acid catalysts work on the same principles. Being heterogeneous in nature, separation from reaction mixture is easy and the catalyst can be regenerated and reused. The use of solid acids eliminates the corrosive action of liquid acids. The use of liquid acids also involves large investment for treating the effluents. There is thus a global effort to replace the conventional liquid acid catalysts by solid acid catalysts.

Inorganic cation exchangers of the class of tetravalent metal acid (TMA) salts, synthesized by sol gel route, possess the general formula $M(IV)(HXO_4)_2.nH_2O$, where M(IV) = Zr, Ti, Sn, Th, Ce, etc. and X = P, W, Mo, As, Sb, etc. They behave as cation exchangers due to the presence of exchangeable protons contained in the structural hydroxyl groups. The presence of protons indicates good potential for application of TMA salts as solid acid catalysts. TMA salts with varied acid strength can be obtained by altering several parameters such as M:X ratio (M = metal ion, X = anion), their concentration, rate and mode of mixing, temperature, pH, etc. Crystalline forms are obtained by refluxing the gels in concentrated mineral acids for long periods. It is observed that both surface area and surface acidity decrease with increasing crystallinity of the material (*1*,*2*). The acidity in TMA salts can thus be tailored by controlling various parameters mentioned above.

Tetravalent bimetallic acid (TBMA) salts, containing two different cations and an anion, are interesting since they exhibit improved properties in comparison to their single salt counterparts. Zirconium phosphate and titanium phosphate are well investigated inorganic ion exchange materials of the class of TMA salts. We have synthesized and characterized zirconium titanium phosphate of the class of TBMA salts, and observed improved ion exchange capacity (IEC) compared to their single salt counter parts (*3*).

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Esterification is an industrially important reaction for synthesis of plasticizers, perfumes, fragrance in cosmetics, flavors in food, diluents in paints and coatings and intermediates in drugs, dye stuffs, and fine chemicals (*4*). The conventional catalyst used in esterification reactions is sulfuric 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. (*5,6*). In view of the deficiencies encountered, there is a global effort to replace the conventional homogeneous liquid acids by heterogeneous solid acids.

Esterification reactions have been investigated using several solid acids such as sulfated zirconia, zeolites, sulfonic acid based resins, heteropoly acids, metal oxides, pillared clay, etc. (*7–12*). Though sulfated zirconia is a good esterification catalyst, it gets easily deactivated by losing the sulfate 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 (*13*). Sulfonic acid-based resin (Nafion-H) has also been found to be unsatisfactory due to its low operating temperature. Reddy and coworkers (*14*) have reported the use of ZrO_2 impregnated with molybdenum and tungsten as solid acids for esterification reactions. TMA salts possess good thermal and chemical stability as well as operational simplicity and are thus good candidates for potential utility as solid acid catalysts. Esterification reactions have been reported from our laboratory using TMA salts as solid acid catalysts (*15–20*). Since TBMA salts exhibit enhanced properties, it was thought of interest to explore the potential utility of these materials as solid acid catalyst.

In the present endeavor, amorphous zirconium titanium phosphate (ZTPA) has been synthesized, characterized and its potential application as solid acid catalyst has been explored using esterification as a model reaction, wherein monoesters such as ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA), benzyl acetate (BzA), and diesters such as diethyl malonate (DEM), dioctyl phthalate (DOP) and dibutyl phthalate (DBP) have been synthesized. Crystalline zirconium titanium phosphate (ZTPC) as well as amorphous and crystalline phases of zirconium phosphate (ZPA, ZPC) and titanium phosphate (TPA, TPC) have also been synthesized, characterized, and their catalytic performance investigated for comparative studies.

Results and discussion

Catalyst characterization

ZTPA, ZPA, and TPA were obtained as white hard granules while ZTPC, ZPC, and TPC were obtained as white powder.

The protonating ability of catalysts was determined by measurement of Na^+ IEC using column method (*21*). The IEC of ZTPA, ZPA, TPA, and ZTPC, ZPC, TPC have been evaluated at room temperature and observed to be 3.36, 2.77, 3.09 and 2.90, 2.02, 2.08 $meq.g^{-1}$, respectively. Amongst, all the catalysts, ZTPA has the highest IEC, indicating highest protonating ability.

Elemental analysis performed by ICP-AES shows Zr:Ti:P ratio is 1:1:2 in ZTPA, ZTPC, and M:P ratio is 1:1 in ZPA, TPA, ZPC, and TPC. The absence of any sharp peaks in the X-ray diffractograms of ZTPA, ZPA, and TPA indicates amorphous nature of the materials. Sharp peaks obtained in case of ZTPC, ZPC, and TPC indicate crystalline nature of the materials. The crystalline phases of ZPC and TPC were confirmed from the Joint Committee on Powder Diffraction Standards (JCPDS) card nos. 33–1482 and 44–0382, respectively. The FTIR spectra exhibits a broad band in the region $\sim 3400\ cm^{-1}$ which is attributed to asymmetric and symmetric –OH stretches. A sharp medium band at $1620\ cm^{-1}$ is attributed to aquo (H–O–H) bending. A band in the region $\sim 1035\ cm^{-1}$ is attributed to the presence of $P=O$ stretching. A medium intensity band at $1400\ cm^{-1}$ is attributed to the presence of δ (POH). These bands indicate the presence of structural hydroxyl groups/catalytic sites in the materials. Thermogravimetric analysis (TGA) of all the materials indicates two weight loss regions. The first weight loss region (up to $\sim 180°C$) is attributed to loss of moisture/hydrated water. The second weight loss in the range 250–500°C is attributed to condensation of structural hydroxyl groups.

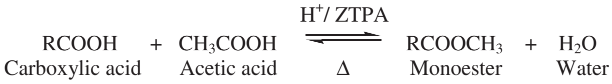
The assessment of chemical stability of the catalyst in various organic solvent media where catalyst would operate, gives us an idea about the stability of the catalyst in these environments. The chemical stability of the catalysts in various organic solvent media (ethanol, propanol, butanol, benzyl alcohol, 2-ethyl 1-hexanol, cyclohexane, toluene, xylene, and acetic acid) were examined by taking 500 mg of each of the synthesized catalyst in 50 mL of the particular medium and allowing to stand for 24 h. No leaching, change in color, nature, and weight was observed, indicating good chemical stability of the catalysts in the solvents mentioned above.

Surface area (Brunauer–Emmett–Teller, BET method) of ZTPA, ZPA, TPA and ZTPC, ZPC, TPC are 101, 56, 64 and 23, 15, 19 m^2g^{-1}, respectively. The NH_3 temperature programmed desorption (TPD) patterns exhibit two peaks ~200°C and ~400°C indicating weak and strong acid sites, respectively. The area under the curves indicates the amount of NH_3 desorbed and hence the number of surface acid sites. The surface acidity values of ZTPA, ZPA, TPA and ZTPC, ZPC, TPC are 6.76×10^{-1}, 2.96×10^{-1}, 4.68×10^{-1}, and 1.18×10^{-1}, 8.65×10^{-2}, 9.75×10^{-2} $mmol.g^{-1}$, respectively. Amorphous phases exhibit higher surface area and surface acidity compared to crystalline phases.

Synthesis of monoesters

Monoester synthesis EA, PA, BA, and BzA 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) or by removing the water produced. Following this principle, solvents, cyclohexane or toluene were employed to remove the water formed during the reaction as a binary azeotrope, so that reverse reaction is avoided. Esterification reactions were carried out varying the amount of catalyst, initial mole ratio of the reactant (alcohol to acid) and reaction time. The role of solvent was not only to remove the water, but also controls the reaction temperature. The reaction temperatures were 80°C for EA, and 115°C for PA, BA, and BzA. Using ZTPA as catalyst, reaction conditions were optimized in case of EA and using these optimized conditions the yields of other esters have been presented in Table 1.



$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Acetic acid}}{CH_3COOH} \underset{\Delta}{\overset{H^+/\,ZTPA}{\rightleftharpoons}} \underset{\text{Monoester}}{RCOOCH_3} + \underset{\text{Water}}{H_2O}$$

Scheme 1. Synthesis of monoesters where R = $-C_2H_5$ for EA, $-C_3H_7$ for PA, $-C_4H_9$ for BA, and $-C_6H_5\text{-}CH_2$ for BzA.

With increasing amount of catalyst, the percentage yield increased due to proportional increase in the number of active sites. The influence of reactant ratio (alcohol:acid) was studied by increasing from 1:1 to 1:2. The yield can be increased by increasing the concentration of either alcohol or acid (*22*). As observed from Table 1, the percentage 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. As reaction time increases, percentage yield increases. However,

Table 1. Optimization of reaction conditions for synthesis of EA using ZTPA catalyst and % yield of other monoesters at optimized condition.

Substrates (mole ratio)	Product	Catalyst amount (g)	Reaction time (h)	% yield
(a) Catalyst amount variation				
Ethanol + Acetic acid (1:1)	EA	0.10	4	32.6
Ethanol + Acetic acid (1:1)	EA	0.15	4	36.2
Ethanol + Acetic acid (1:1)	EA	0.20	4	40.2
(b) Mole ratio variation				
Ethanol + Acetic acid (1:1.5)	EA	0.20	4	42.8
Ethanol + Acetic acid (1:2)	EA	0.20	4	45.2
Ethanol + Acetic acid (1.5:1)	EA	0.20	4	38.0
Ethanol + Acetic acid (2:1)	EA	0.20	4	35.7
(c) Time variation				
Ethanol + Acetic acid (1:2)	EA	0.20	2	38.2
Ethanol + Acetic acid (1:2)	EA	0.20	4	45.2
Ethanol + Acetic acid (1:2)	EA	0.20	6	61.3
Ethanol + Acetic acid (1:2)	EA	0.20	8	71.2
Ethanol + Acetic acid (1:2)	EA	0.20	10	86.4
(d) Yield of other esters at optimum condition				
1-Propanol + Acetic acid (1:2)	PA	0.20	10	88.2
1-Butanol + Acetic acid (1:2)	BA	0.20	10	89.3
Benzyl alcohol + Acetic acid (1:2)	BzA	0.20	10	100.0

Note: Reaction condition: solvent, cyclohexane for EA and toluene for PA, BA, and BzA; reaction temperature, 80°C for EA and 115°C for PA, BA, and BzA.

Table 2. Comparative catalytic activity in monoester synthesis.

	Yields of ester (%)/TON[a]			
Catalysts	EA	PA	BA	BzA
ZPA	78.1/17.2	79.2/19.8	80.4/22.5	100/37.5
TPA	80.2/17.6	84.1/21.0	86.3/24.2	100/37.5
ZTPA	86.4/19.0	88.2/22.1	89.3/25.0	100/37.5
ZPC	70.8/15.6	74.1/18.5	76.5/21.4	95.2/35.7
TPC	74.2/16.3	75.9/19.0	78.8/22.1	96.6/36.2
ZTPC	77.8/17.1	78.4/19.6	82.6/23.1	100/37.5

[a] TON: Turn over number, gram of ester formed per gram of catalyst.

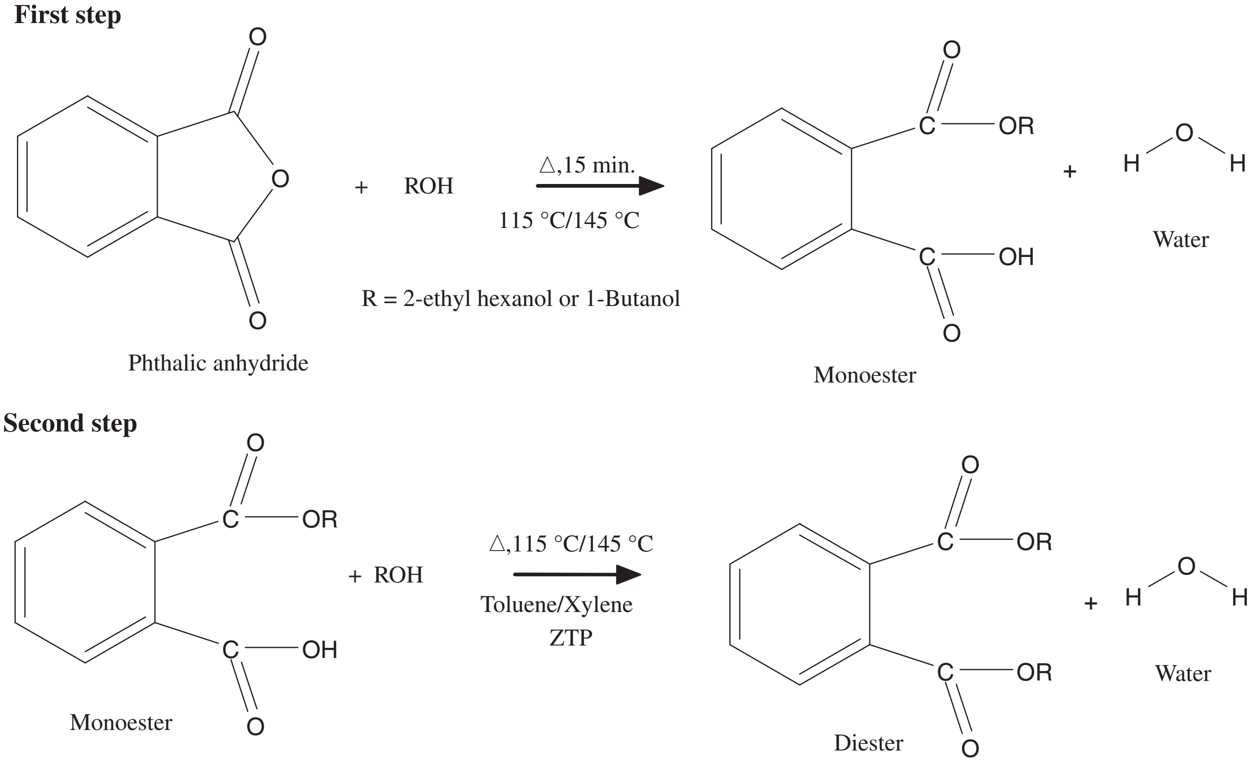
Note: Reaction condition: solvent, cyclohexane for EA and toluene for PA, BA, and BzA; reaction temperature, 80°C for EA and 115°C for PA, BA, and BzA; mole ratio of reactant (alcohol:acid), 1:2; catalyst, 0.2 g; reaction time: 10 h.

there is not much gain in product after 10 h. Hence, the optimum reaction time was selected as 10 h.

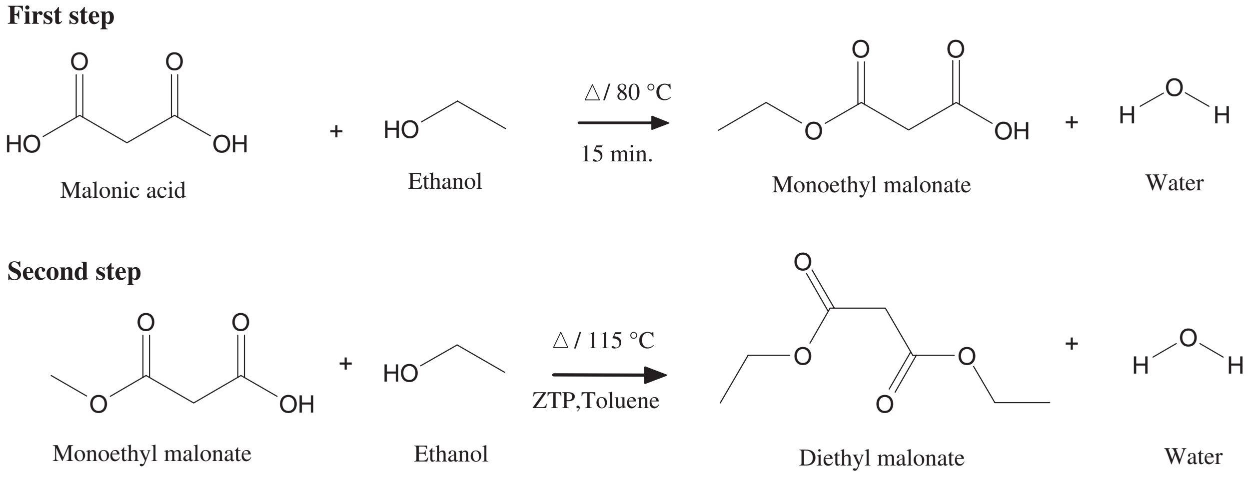
Esterification of monoesters, EA, PA, and BA has been reported (*23*) in absence of catalyst and exhibit poor yields. Therefore catalyst is a must for these reactions. In case of BzA, however, it is observed that with an excess of acetic acid and in the absence of any catalyst the yield is as high as 90.6% which is attributed to auto catalysis. In another report (*24*), high yields of BzA were obtained with small amount of the catalyst but the reaction time was relatively high. As observed in Table 1, the yields of the monoesters are always high when acid is taken in excess. Apart from driving the equilibrium toward product side, the excess acid catalyses the reaction. Amongst monoesters, higher yields of BzA are obtained which could be attributed to an enhanced nucleophilicity due to presence of aromatic ring in benzyl alcohol.

For comparative study, esterification reactions have been carried out using ZTPC as well as single salts ZPA, TPA, ZPC, and TPC, at optimum condition (mole ratio of reactant, alcohol/acid = 0.5, 0.2 g of catalyst, 10 h). The results are presented in Table 2.

From Table 2, it is observed that, the order of ester formation is: (1) amongst TBMA salts, ZTPA > ZTPC; (2) amongst amorphous materials, ZTPA > TPA > ZPA; and (3) amongst crystalline materials, ZTPC > TPC > ZPC. This order could be attributed



Scheme 2. Synthesis of DOP and DBP.



Scheme 3. Synthesis of DEM.

to increasing surface acidity. Turn over number (TON) reflects the effectiveness of a catalyst. TON also follows the order of ester formation.

Synthesis of diesters

The reaction schemes for diester synthesis are presented in Schemes 2 and 3.

Using ZTPA as catalyst, diesters DEM, DOP, and DBP were synthesized. Reaction conditions were optimized in case of DOP and using these optimized conditions the yields of other diesters have been presented in Table 3.

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. When the boiling point of the alcohol is less than the temperature of the reaction, most of the alcohol will end up in the vapour phase and not be available in the liquid phase. This is the reason why the heavier

Table 3. Optimization of reaction conditions for synthesis of DOP using ZTPA catalyst and % yield of other diesters at optimized condition.

Substrates (mole ratio)	Product	Catalyst amount (g)	Time (h)	% yield
(a) Catalyst amount variation				
Pthalic anhydride + 2-ethyl 1-hexanol (1:2)	DOP	0.10	4	38.1
Pthalic anhydride + 2-ethyl 1-hexanol (1:2)	DOP	0.15	4	40.2
Pthalic anhydride + 2-ethyl 1-hexanol (1:2)	DOP	0.20	4	41.8
(b) Mole ratio variation				
Pthalic anhydride + 2-ethyl 1-hexanol (1:2.1)	DOP	0.20	4	42.2
Pthalic anhydride + 2-ethyl 1-hexanol (1:2.2)	DOP	0.20	4	43.4
Pthalic anhydride + 2-ethyl 1-hexanol (1:2.3)	DOP	0.20	4	44.1
Pthalic anhydride + 2-ethyl 1-hexanol (1:2.4)	DOP	0.20	4	45.4
Pthalic anhydride + 2-ethyl 1-hexanol (1:2.5)	DOP	0.20	4	46.2
(c) Time variation				
Pthalic anhydride + 2-ethyl 1-hexanol (1:2.5)	DOP	0.20	2	36.8
Pthalic anhydride + 2-ethyl 1-hexanol (1:2.5)	DOP	0.20	4	46.2
Pthalic anhydride + 2-ethyl 1-hexanol (1:2.5)	DOP	0.20	6	55.4
Pthalic anhydride + 2-ethyl 1-hexanol (1:2.5)	DOP	0.20	8	63.7
Pthalic anhydride + 2-ethyl 1-hexanol (1:2.5)	DOP	0.20	10	72.4
(d) Yield of other esters at optimum condition				
Pthalic anhydride + 2-ethyl 1-hexanol (1:2.5)	DOP	0.20	10	72.4
Malonic acid + Ethanol (1:2.5)	DEM	0.20	10	79.2
Pthalic anhydride + 1-butanol (1:2.5)	DBP	0.20	10	62.4

Note: Reaction condition: solvent, xylene for DOP and toluene for DEM and DBP; reaction temperature, 145°C for DOP and 115°C for DEM and DBP.

Table 4. Comparative catalytic activity in diester synthesis.

Catalysts	Yields of ester (%)/TON[a] DEM	DOP	DBP
ZPA	72.8/14.6	68.1/33.2	50.1/17.4
TPA	74.6/14.9	70.3/34.3	54.2/18.8
ZTPA	79.2/15.8	72.6/35.4	62.4/21.7
ZPC	52.2/10.4	45.8/22.3	40.5/14.1
TPC	55.6/11.1	52.1/25.4	46.3/16.1
ZTPC	60.2/12.0	62.8/30.6	50.4/17.5

[a] TON: Turn over number, gram of ester formed per gram of catalyst.

Note: Reaction condition: solvent, xylene for DOP and toluene for DEM and DBP; reaction temperature, 145°C for DOP and 115°C for DEM and DBP; mole ratio of reactant (dicarboxylic acid/anhydride:alcohol), 1:2.5; catalyst, 0.2 g; reaction time, 10 h.

alcohols react more than the lighter ones. The same reason could be forwarded for the yields in case of monoesters, EA < PA < BA. Furthermore, high yield in case DEM, compared to DOP and DBP is probably due to less steric hindrance felt by incoming ethanol from monoethyl malonate formed in the first step.

DOP formation has been catalyzed by zeolites (*23*), metallic oxides (*25*), solid super acids (*26*,*27*), and heteropoly acids (*27*,*28*). Suter (*29*) has reported a non-catalytic process for the manufacture of DOP, at very high temperatures, at which autocatalysis occurs. In the present work, it is observed that yields of DOP and DBP are low as compared to those obtained when zeolites (*23*) and solid super acids (*26*,*27*) were used as catalysts. When homogeneous liquid acids are used as catalysts for synthesis of DOP and DBP, the result is a product that is colored and of a poor quality. In the present work though the yields of diesters obtained are low, the advantage is that the diester is the unique product and colorless. DEM synthesis has been reported by Jai Prakash et al. using montmirillonite clay, but the yield is low (41%) and relatively high amount of catalyst (0.5 g) was used (*30*). In another report, DEM was synthesized by Jiag et al. 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 (*31*).

For comparative study, diesterification reactions have been carried out using ZTPC as well as single salts ZPA, TPA, ZPC, and TPC, at optimum condition (mole ratio of reactant, diacid/anhydride: alcohol = 1:2.5, 0.2 g of catalyst, 10 h). The results are presented in Table 4.

From Table 4, it is observed that TBMA salts exhibit enhanced catalytic activity compared to their single salt counterparts. Furthermore, amorphous phases are catalytically more active compared to crystalline phases. The order of catalytic activity toward ester formation is also similar to that observed in case of monoesters.

During the course of the reaction, the catalyst color changes from white to light grey. This is probably due to the reacting molecules coming onto the surface of the catalyst. The catalyst was regenerated using 1M HNO_3 as in Section "Synthesis of amorphous zirconium titanium phosphate (ZTPA)." The catalyst, regains its original color when treated with acid for regeneration. Reusability of ZTPA was tested by conducting two runs, and results are presented in Table 5.

It is observed that there is only a marginal decrease in conversion. In regenerated samples, the yield decreased by 4 and 5–9% for monoesters and diesters, respectively. Toshio Okuhara et al. (*32*) have reported that zirconium phosphate can be reused at least five times in esterification of acetic acid with ethanol. The study shows that ZTPA is insoluble during the reaction, is recoverable by simple filtration, and can be reused at least three times without significant loss in catalytic activity.

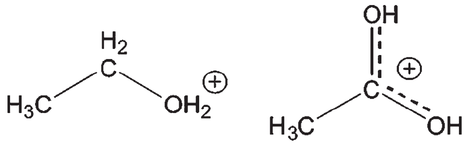
Reaction mechanism in solid acid catalyzed esterification reaction

The mechanism of esterification can be different for the various solid acid catalysts and also depends on

Table 5. Performance of recycled catalyst ZTPA.

Esters	% yield EA	PA	BA	BzA	DEM	DOP	DBP
First cycle	86.4	88.2	89.3	100	79.2	72.6	62.4
Second cycle	85.8	87.3	88.2	100	76.2	70.0	58.3
Third cycle	84.2	86.4	87.1	98.2	72.5	67.2	52.6

Note: Reaction condition: catalyst, 0.20 g; mole ratio of reactant (alcohol:acid), 1:2 for monoesters and (dicarboxylic acid/anhydride:alcohol) 1:2.5 for diesters; solvent, cyclohexane for EA, toluene for PA, BA, BzA, DEM, and DBP and xylene for DOP; reaction temperature, 80°C for EA, 115°C for PA, BA, BzA, DEM, and DBP, 145°C for DOP; reaction time, 10 h.



Scheme 4. Possible protonated intermediates in esterification reaction.

gas or liquid-phase operation as well as the substrate. Chu et al. (*33*) claim that the esterification mechanism of acetic acid with butanol over carbon-supported heteropoly acid (HPA) catalysts proceeds via a protonated alcohol intermediate, but most authors (*34–36*) proposed a protonated carboxylic acid as the reaction intermediate. The two possible 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 (*30*).

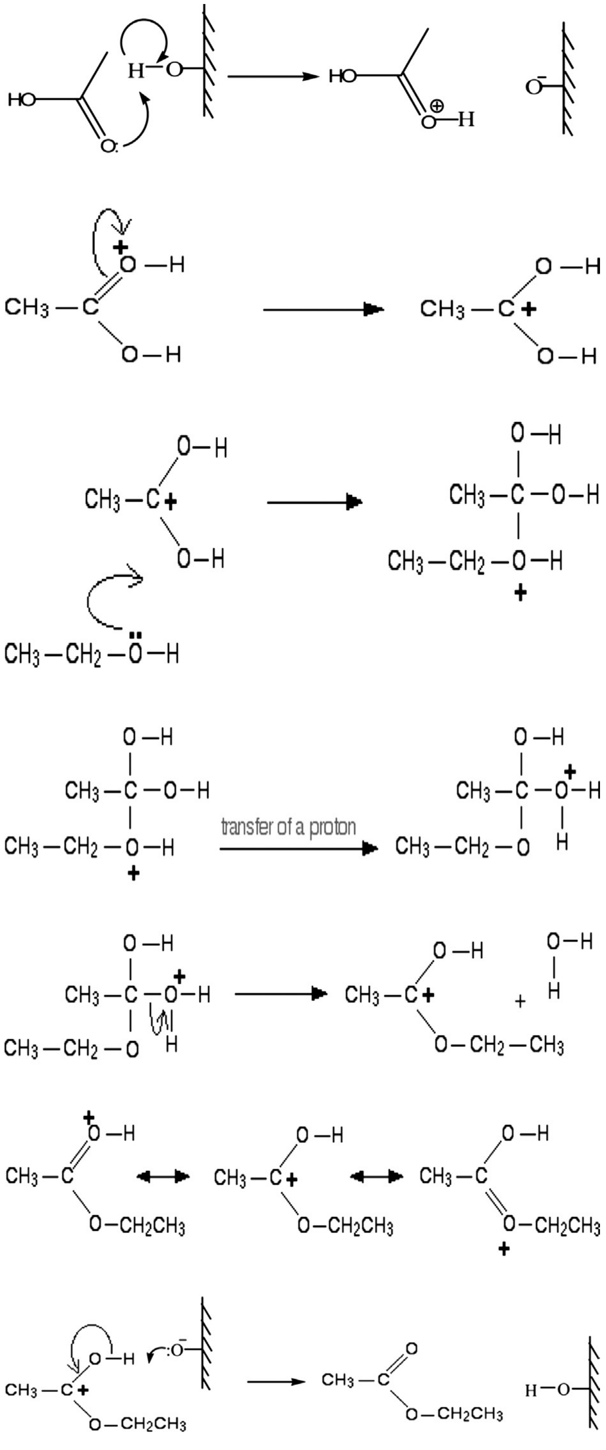
Based on the classical mechanism for acid catalyzed esterification reaction, we propose a mechanism (Scheme 5) for esterification of ethanol with acetic acid as a typical case, involving a protonated acetic acid intermediate.

Experimental

Catalyst synthesis

Synthesis of amorphous zirconium titanium phosphate (ZTPA)

A solution containing 0.1M $ZrOCl_2{\cdot}8H_2O$ and 0.1M $TiCl_4$ in 10% w/v H_2SO_4 (100 mL) was prepared. To this solution 200 mL, 0.2M $NaH_2PO_4{\cdot}2H_2O$ was added dropwise (flow-rate, 1 mL min^{-1}) with continuous stirring at room temperature. After complete precipitation, the obtained gel was stirred for another 5 h. The precipitates were kept in contact with mother liquor overnight, filtered, washed with double distilled water to remove adhering ions (chloride and sulfate) {stage 1}, and dried at room temperature. The material was then broken down to the desired particle size [30–60 mesh (ASTM)] by grinding and sieving. About 5 g of this material was treated with 50 mL of 1M HNO_3 for 30 min with occasional shaking. The sample 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 five times. After final washing, the material was dried at room temperature.



Scheme 5. Reaction mechanism for esterification.

Synthesis of amorphous zirconium phosphate (ZPA) and amorphous titanium phosphate (TPA)

A solution of $ZrOCl_2{\cdot}8H_2O$ (0.1M, 100 mL) or $TiCl_4$ (0.1M, 100 mL), as the case may be, in 10% w/v H_2SO_4

was prepared. To this solution, $NaH_2PO_4 \cdot 2H_2O$ (0.2M, 200 mL) was added dropwise (flow-rate, 1 mL min^{-1}) with continuous stirring at room temperature. After complete precipitation, the obtained gel was stirred for another 5 h. The precipitates were kept in contact with mother liquor overnight, filtered, washed with double distilled water to remove adhering ions (chloride and sulfate) {stage 1}, and dried at room temperature. The materials were then broken down to the desired particle size [30–60 mesh (ASTM)] by grinding and sieving. The material was acid treated as in Section "Synthesis of amorphous zirconium titanium phosphate (ZTPA)."

Synthesis of crystalline zirconium titanium phosphate (ZTPC), crystalline zirconium phosphate (ZPC), and crystalline titanium phosphate (TPC)

The gel obtained in stage 1 (as in Sections "Synthesis of amorphous zirconium titanium phosphate (ZTPA)"and "Synthesis of amorphous zirconium phosphate (ZPA) and amorphous titanium phosphate (TPA)") above, was refluxed with phosphoric acid for ~100 h, filtered, washed, and dried at room temperature to obtain the crystalline materials.

Instrumentation

The samples were analyzed for zirconium, titanium, and phosphorus content using ICP-AES (Labtam, 8440 Plasmalab). X-ray diffractogram ($2\theta = 5$–$80°$) was obtained on X-ray diffractometer (Brucker AXS D8) with Cu-Kα X-ray source of wavelength 1.5418 Å and nickel filter. FTIR spectra were recorded using KBr wafer on a Perkin Elmer Paragon 1000 spectrophotometer. TGA was carried out on a Shimadzu DT 30 thermal analyzer at a heating rate of 10°C.min^{-1}. For surface area measurement, adsorption–desorption isotherm of nitrogen was recorded on a Carlo-Erba, Sorptomatic Series 1900, model VC 140 at −196°C after degassing the sample at 200°C for 4 h. Surface acidity was determined on Chemisorb 2720, by a temperature programmed desorption of ammonia. Ammonia was chemisorbed at 120°C and then desorption was carried out up to 700°C at a heating rate of 10°C min^{-1}.

Synthesis of esters

Synthesis of monoesters [ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA), and benzyl acetate (BzA)]

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 (0.05–0.10M), alcohol (0.05–0.10M), catalyst (0.10–0.20 g), and a suitable solvent (15 mL). Cyclohexane was used as a solvent for the synthesis of EA and toluene for PA, BA, and BzA. The reactions were carried out varying several parameters such as amount of catalyst, mole ratio of reactants, reaction time, and these parameters optimized.

After completion of reaction, catalyst was separated by decantation and reaction mixture was distilled to obtain the product.

Synthesis of diesters [diethyl malonate (DEM), dioctyl phthalate (DOP), and dibutyl phthalate (DBP)]

The diesters were synthesized in two steps. In the first step, equimolar proportion (0.025 mole) of acid and alcohol (malonic acid and ethanol for DEM, phthalic anhydride and 2-ethyl 1-hexanol for DOP, and phthalic anhydride and 1-butanol for DBP) were taken in a round bottomed flask and the reaction mixture stirred at ~80°C for DEM, ~140°C for DOP, and ~110°C for DBP for about 10–15 min in absence of any catalyst and solvent. The dicarboxylic acid and anhydride gets 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 the addition of a second mole (0.025 mole) of respective alcohol, catalyst (0.10–0.20 g), and 15 mL solvent (toluene for DEM and DBP and xylene for DOP). The reactions were carried out varying several parameters such as amount of catalyst, mole ratio of reactants, reaction time, and these parameters optimized. 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.

Calculation of % yield of esters

The yields of the mono and diesters formed were determined by titrating the reaction mixture with 0.1M alcoholic KOH solution. The yield of the esters were calculated using the formula, $\%\ \text{yield} = [(A - B)/A] \times M \times 100$, 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 gas chromatography.

Conclusion

The work outlined herein reveals the promising use of ZTPA as a solid acid catalyst in the synthesis of monoesters and diesters, the advantages being operational simplicity, mild reaction conditions, and eco-friendly nature. Though ZTPA has the potential for commercial exploitation, several acid catalyzed reactions should be investigated before establishing its use as a solid acid catalyst.

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