ESTERIFICATION REACTIONS USING ZIRCONIUM BASED INORGANIC ION EXCHANGERS

A

Thesis Submitted

In Partial Fulfillment of Requirements

For The Degree of

Master of Science in Chemistry

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This is to certify that the dissertation entitled "ESTERIFICATION REACTIONS USING ZIRCONIUM BASED INORGANIC ION EXCHANGERS", being submitted by Mr. Charanjit Singh in partial fulfillment of the requirements for the award of degree of Masters in Chemistry in the School of Chemistry and Biochemistry, Thapar University, Patiala, is a bonafide work carried out under the supervision of Dr. Susheel Mittal and Dr. Navneet Kaur and that no part of this work has been submitted for the award of any other degree.

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Candidate's Declaration

I, hereby declare that the work being presented in the dissertation entitled "ESTERIFICATION REACTIONS USING ZIRCONIUM BASED INORGANIC ION EXCHANGERS", in partial fulfillment of the requirements for the award of degree of Masters in Chemistry, School of Chemistry and Biochemistry, Thapar University, Patiala, is my own work during the period of Jan 2010 to May 2010, under the supervision of Dr. Susheel Mittal and Dr. Navneet Kaur. I have not submitted the matter embodied in this dissertation for the award of any other degree.

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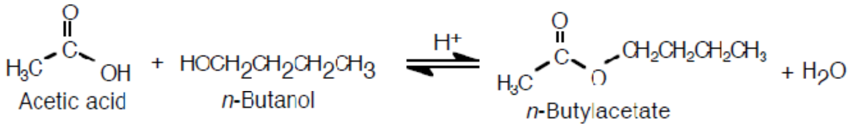
Abstract

Zirconium based double salts were used as catalysts in esterification reactions of benzoic acid with some primary and secondary alcohols. Ester products were characterized with ^{1}H NMR and FT-IR techniques. Product yields from different set of combinations of benzoic acid and alcohols were monitored using GC. Results indicate that the ion exchangers catalyzed esterification reactions selectively based on steric considerations. Electronic factor did not seem to play any role in efficiency of the inorganic ion exchangers for these reactions.

Introduction

Esterification is the general name for a chemical reaction in which two reactants (typically an alcohol and an acid) form an ester as the reaction product. Esters are common in organic chemistry and biological materials, and often have a characteristic pleasant, fruity odor. This leads to their extensive use in the fragrance and flavor industry. Ester bonds are also found in many polymers.

Esterification is a reversible reaction. As a result of this reversibility, many esterification reactions are equilibrium reactions and, therefore, need to be driven to completion according to Le Chatelier's principle. Esterifications are among the simplest and most often performed organic transformations.



Esters may be prepared by refluxing an acid and a primary or secondary alcohol in the presence of a catalyst (commonly concentrated sulfuric acid). Water is a byproduct, and it can be removed to force the equilibrium in the desired direction. In addition to being the catalyst for the reaction, the sulfuric acid also removes water to help shift the equilibrium towards forming more of the ester product. Alternatively, where the ester has a suitable boiling point, it may be distilled off, once again causing the equilibrium to favor the product. Homogeneous acid catalyzed reactions generate side products posing environmental and corrosion problems. Separation of the pure product from the homogeneous catalyst is a very difficult task. Hence, heterogeneously catalyzed esterification reactions are gaining more attention. They provide cleaner routes for chemicals due to ease of separation of the products without contamination. Therefore, studies on heterogeneously catalyzed esterification reactions are extremely important in developing cleaner and economically improved processes for a wide variety of industrial products. The choice of a method to achieve complete esterification depends on the boiling points of the alcohol, the carboxylic acid, the ester produced, catalyst used and the reactor type. There are many routes of synthesis of esters but the most attractive from enviornmental and economic standpoint is via direct reaction of alcohol and carboxylic acid using a heterogeneous catalyst avoiding a non-reuseable catalyst.

Inorganic ion exchangers as catalysts

Zirconium based inorganic ion exchangers are elements of group 4 phosphates and were first prepared as amorphous gels. At first the gels were considered to be phosphated hydrous oxides, but their true nature became clear only after the zirconium gel was crystallized and the structure determined by X-ray methods. The metal atom lie slightly above or below the mean plane drawn through the center of the layer. The layers are staggered forming a network resembling a hexagonally shaped cavity outlined by heavy lines in the Figure1. The water molecule resides in a pocket of the cavity formed by three POH groups. Only van der Waals forces hold the layers together as the water molecules are hydrogen bonded to the POH in the top side of one cavity or the bottom side in an adjacent cavity. The measured ion exchange capacity shows that both the protons are exchangeable

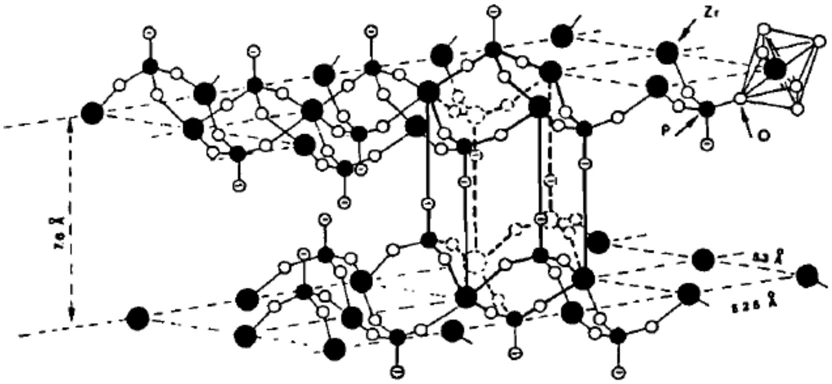


Figure1. Structure of layered zirconium phosphate showing cavity created by arrangement of layers (Alberti, G.In Study Week on Membranes; Passino, R., Ed.; PontificiaeAcademieScient" ScriptaVaria: Rome, 1976,269)

The degree of crystallinity of the zirconium phosphate greatly affects its ion exchange behaviour. The amorphous gel consists of extremely small particles with a layered structure. This layered nature was revealed by the fact that a weak broad X-ray reflection was observed on some of the dried gels. On immersion in water this peak increased from its original 8A value (7.56A in the crystals) to about 10.2A. With the layers this far apart, the ions are able to distribute themselves uniformly throughout the gel. As a result each uptake of cation is accompanied by an increase in pH. This behaviour is in contrast to the crystals where uptake occurs at constant pH. As the crystallinity of the exchanger increases, the solid solution region decreases and a series of cation phases are formed over the entire cation loading. The behaviour of the gels and their low crystallinity is best explained on the basis that their structures are layered. Particle size measurements by X-ray line broadening in the direction perpendicular to the layers indicated particle thicknesses of 70-150 A°.

A second factor to consider is that the layers are ill formed. That is, many of the phosphate groups are misoriented relative to their positions in the fully crystalline state. This misalignment would increase the electrostatic imbalance of the layers and favour the incorporationof water molecules.

Ammonium tungstophosphate (AWP) and Ammonium molybdophosphate (AMP) are probably the first few materials of heteropolyacid salt which have been studied as ion-exchangers. These inorganic ion exchanger materials produced by mixing a solution containing two anionic species with a metal ion solution have shown better ion exchange properties than the zirconium phosphate type material. The phosphates and antimonates of tin (IV) also show appreciably high chemical and thermal stability. Since the mixed salts are found to show ion exchange properties different from those of simple salts, it is important to observe the properties of double salts produced by mixing the phosphate and antimonate.

Heterogeneous solid acid catalysts

Esterification of alcohols is performed employing carboxylic acid in the presence of catalytic amounts of zirconium based inorganic ion exchangers. Heterogeneous solid acid catalysts provide an attractive alternative to homogeneous liquid acid catalyst as they possess the high catalytic activity and selectivity, do not corrode the reaction vessels and reactors and finally, repeated use of solid acid catalyst from a reaction mixture is easy. Esterification reactions have been widely investigated using several solid acid catalysts. To mention a few, sulphated zirconia, zeolites, sulfonic acid based resins, hetropoly acids, metal oxides, pillared clays, etc. have been studied.

Inorganic ion exchangers of the class of tetravalent metal acid (TMA) salts are cation exchangers, possessing, the general formula $M(IV)(HXO_4)_2nH_2O$.where M(IV) = Zr, Ti, Sn, Th, Ce, etc. and X=P, W, Mo, As, Sb, etc. These materials possesses structural hydroxyl; groups, the H of the –OH being the exchangeable sites.TMA salts thus possess good potential for application as a solid acid catalyst. The hydroxyl protons of acid can be easily replaced by other cations. Owing to their peculiar properties such as selectivity for certain ions, high stability in strongly acidic or oxidising solutions, high thermal stability and resistance to radiations, acid salts are attractive inorganic ion exchangers, for particular uses, especially when organic resins, cannot be employed because of their degradability. The presence of acid sites on such materials indicates good potential for application in Bronsted catalysis. It has also been observed that amorphous materials possess greater number of acid sites as compared to crystalline materials. Apart from the fundamental aspects, there is an increasing interest in the potential applications of inorganic/organic ion exchangers. According to the nature of R group, different applications in the field of chromatographic separation, photochemistry, protonic conduction and radiochemical studies are possible. The loading potential of inorganic backbone is as high as two alkyl groups for zirconium atom, which is a distinct advantage over commercial reverse phase chromatography supports. Besides, inorganic/organic materials are known to have a large selectivity for mono and multivalent cations.

Here, we purpose a method of esterification of alcohols where, alcohols are used as a solvent as well as reagent in reaction with carboxylic acid in catalytic amounts of zirconium based inorganic ion exchangers. These inorganic ion exchanger catalysts offer remarkably simple workup procedure and are reuseable without any appericiable loss its activity. Some esterification reactions catalysed by heterogeneous catalysts have been studied. Esterification of benzoic acid with alcohols in the presence of some zirconium based inorganic ion exchanger as heterogeneous catalysts are reported in this thesis.

Esterification of benzoic acid has been studied with some primary and secondary alcohols like n-propanol, iso-propanol, n-butanol and iso-butanol using synthetic inorganic ion exchangers like zirconium antimonophosphate (ZrSbP), zirconium antimonoarsnate (ZrSbAs), zirconium tungstophosphate (ZrWP), zirconiumphosphoborate (ZrPB).

Literature Review

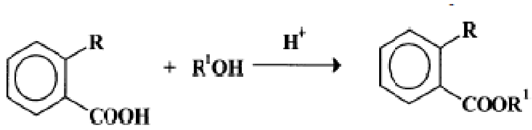
Amorphous zirconium titanium phosphate (ZTPA), an advanced inorganic ion exchanger of the class of tetravalent bimetallic acid (TBMA) salt, has been synthesized by sol gel route. ZTPA has been characterized by inductively coupled plasma atomic emission spectrometer (ICP-AES), Thermal analysis, Fourier 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.Chudasamaet al[1] studied the catalytic performance of ZTPA and explored the esterification as a model reaction wherein mono and diesters have been synthesized with ZTPA. Crystalline zirconium titanium phosphate as well as amorphous and crystalline phases of zirconium phosphate and titanium phosphate has 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.

Patel et al[2] studied the use of zirconium phosphate as a solid acid catalyst in esterification reaction for the synthesis of monoester and diester. Amorphous and crystalline phases of zirconium (IV) phosphate of the class of tetravalent metal acid (TMA) salts have been synthesized by sol-gel method. Chemical resistivity of the materials has been accessed in acids, bases and organic solvent media. The exchangeable protons present in the structural hydroxyl groups indicate good potential for TMA salts to be investigated as solid acids. Esterification reaction was selected as a model reaction to study the application of ZrP (amorphous and crystalline phases) as a solid acid. The catalytic activity explored by synthesizing monoesters and diesters revealed the promising use of ZrP as an ecofriendly solidacid catalyst. Esterification reaction was performed in a round bottom flask equipped with a Dean and Stark apparatus attached to a reflux condenser was used and charged with acetic acid, alcohol, catalyst and of a suitable solvent. The solvent was used as a reaction medium and also to facilitate the removal ofwater produced during the reaction in order to drive the reaction towards the product side.

Mark et al[3]described the high catalytic activity in areas ranging from alkylation, transalkylation, isomerization, oligomerization, acylation, esterification and nitration. The two main classes of ion-exchange resins are based upon styrene-based sulfonic acids (Amberlyst and Dow type resins), which show very high activity in the areas of esterification and etherification, to the perfluorosulfonic acid-based catalysts including the recently developed Nafion resin/silica nanocomposites. These showed very high activity in the area of linear alkyl benzene formation, isomerization, and some select acylation type chemistries. These new types of catalysts (which have been used commercially) are adding to the ever-growing portfolio of highly active solid acid catalysts, which couple both economic and environmental drivers to improve organic transformations within the chemical industry.

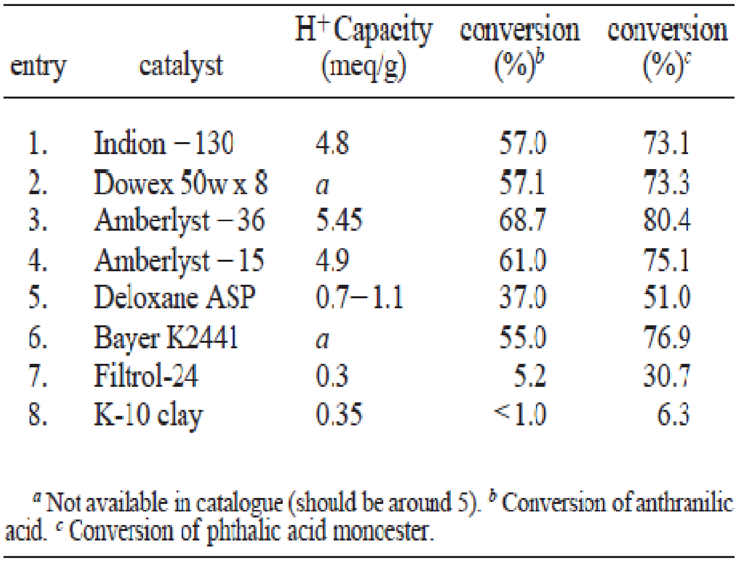
Clearfield et al[4]published an important review mentioning the structure of inorganic ion exchanger and their ion exchange capacity. Structural description regarding hydrous oxides, layered compounds, and framework structures containing cavities or tunnels and lastly the organic-inorganic types has been given in this review.The esterification of acetic acid with n-butanol was studied in the presence of ion-exchange resin catalysts such as Amberlyst-15 to determine the intrinsic reaction kinetics. Esterification by solid acid catalysts (Amberlyst-36, Bayer K2441, Amberlyst-15, Dowex 50Wx8, Indion-130, Deloxane ASP, Filtrol- 24 clay, K-10 Montmorrilonite clay, and sulphated zirconia) gave the desired level of activity which could be easily removed from the reaction mixture with no residual inorganic contamination of the organic products offer advantages over existing methods.

Esterification of aromatic carboxylic acids



Where R = -COOR, $-NH_2$, -OH

This following table[5] represents Esterification of anthranilic acid and phthalic anhydride with methanol in the presence of solid acid catalysts

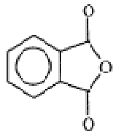
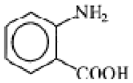
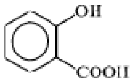
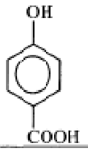


entry	catalyst	H^+ Capacity (meq/g)	conversion (%)[b]	conversion (%)[c]
1.	Indion − 130	4.8	57.0	73.1
2.	Dowex 50w x 8	*a*	57.1	73.3
3.	Amberlyst − 36	5.45	68.7	80.4
4.	Amberlyst − 15	4.9	61.0	75.1
5.	Deloxane ASP	0.7−1.1	37.0	51.0
6.	Bayer K2441	*a*	55.0	76.9
7.	Filtrol-24	0.3	5.2	30.7
8.	K-10 clay	0.35	<1.0	6.3

[a] Not available in catalogue (should be around 5). [b] Conversion of anthranilic acid. [c] Conversion of phthalic acid moncester.

The contribution of these catalysts led to the synthesis of some commercially valuable products such as p-methoxyacetophenone, dimethyl phthalate, diethyl phthalate, methyl anthranilate, methyl salicylate, and methyl p-hydroxybenzoate (methyl paraben)

Table :- Esterification reactions of different subtracts using Amberlyst-36 as catalyst[6]

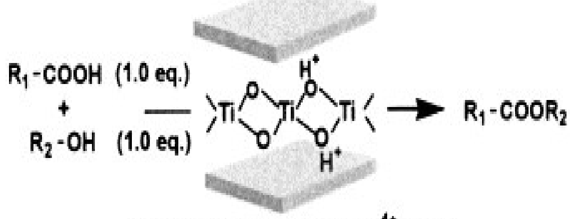
Entry	Carboxylic acid or Anhydride	Alcohol	Temp. (°C)	Conv. (%)
1.		CH_3OH	120	80.4
1a.	1	C_2H_5CH	140	77.3
2.		CH_3OH	120	68.7
3.		CH_3OH	120	79.3
4.		CH_3OH	120	96.4

From above table it is concluded that Amberlyst-36 was also the most active catalyst for the esterification reactions.

Esterification of salicylic acid with methanol using the acid form of a sulfonatedpolystyrenedivinylbenzene ion exchange resin.Dowex 50-W (X-8), as a catalyst was studied by bochneret al[7].

Amorhous zirconium tungstate[8] an inorganic ion exchanger has been studied in which the protons of the hydroxyl group are the active sites. Esterification has been studied as a model reaction where ethyl acetate has been synthesized. The variation of several parameters has established the use of zirconium tungstate as a bronsted acid catalyst.

Montromorillonite – enwrapped titanium catalyst was found to efficently promote the esterification of carboxylic acids with alcohols. This heterogeneous catalyst offered a remarkable simple workup procedure, which is reusable without any appericiable loss in activity and selectivity. Monmorillonites can be structurally defined as layers of negatively charged two-dimensional sheets that are seprated by interlayer cationic species with high exchange ability for other metal polycation.



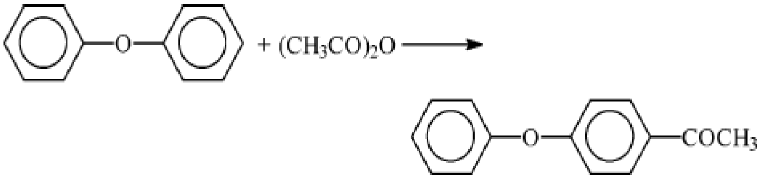
Chain-like Ti structure of Ti^{4+}-mont

The esterification of carboxylic acids and alcohols under the solventless condition in presence of Ti^{4+} -mont solid catalyst has been done by Tomonori Kawabata et al[9].

High-yielding acylation of alcohols with carboxylic acids in the presence of the natural and Na^+ exchanged form of montmorillonite catalysts sourced from natural montmorillonite and montmorillonite K1011 with high atom economy was reported by B. M. Choudary et al[10]. Typical procedure of refluxing was used in acylation in which 1-phenylethanol and glacial acetic acid corresponding to a 1:10 molar ratio was refluxed under stirring for 15 min in the presence of montmorillonite catalyst (100 mg). 1H NMR analyzed the product, while the catalyst was washed with ethyl acetate and dried in an oven at 120 °C for 1 h and then reused.

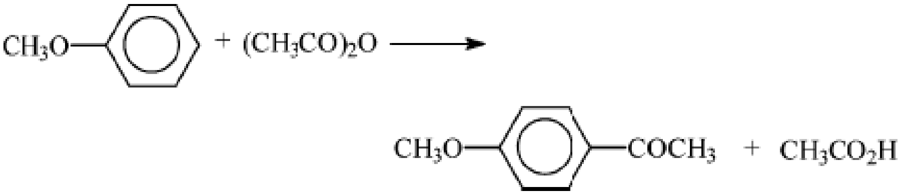
Esterification[11] of dilute acetic acid with n- hexanol was studied with cation-exchange resins (macroporous and gelular) in a jacketed stirred batch reactor to synthesize a value-added ester, namely, n-hexyl acetate. The effect of various parameters such as speed of agitation, catalyst particle size, and molar ratio of n-hexanol to acetic acid, reaction temperature, catalyst loading, and reusability of catalysts was studied for optimization of the reaction condition.

Aninteresting review[12] intended to give a wide scope on the uses of ion-exchange resins as catalysts or catalyst precursors in organic synthesis. The acylation of diphenyl ethers with acetic anhydride was performed using various solid acid catalysts such as tungstophosphoric acid, sulfated zirconia, K10 clay, and Indion and Amberlyst resins.

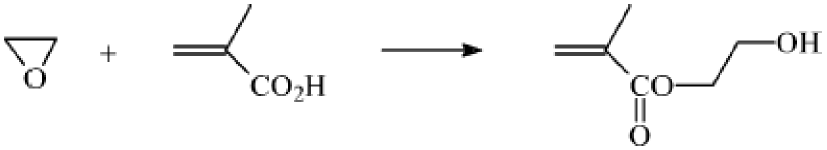


The reuseability[13] studies demonstrated that the resin activity decreases in subsequent reactions, because of blocking of the pores by larger products.

The acylation of anisole with acetic anhydride was observed to be very effective with Amberlyst 36[14], when compared to other materials such as Amberlyst 15, Bayer K2441, Dowex 50W, Deloxan ASP, and inorganics such as K10 and sulfated ZrO_2.



Nafion 811 and Amberlyst NX 110 were used for the esterification of acrylic acid with EtOH. These catalysts[15] gave results comparable to those obtained with sulfuric acid. Epoxides also have been used for the synthesis of acrylic esters; thus, hydroxyalkyl (meth)acrylates were obtained from (meth)acrylic acids and epoxides such as ethylene oxide and an acidic resin to give 2-hydroxyethyl (meth)acrylate.



Palmitic acid was esterified at temperatures in the range of 60-75°C; the percentage of ester formation was increased as the temperature increased but decreased with the increase of carbon number of the alcohol. Kinetic study[16] showed that the esterification was a second-order reaction with apparent activation energy of 32.26 kJ/mol for the formation of the ethyl ester when using Amberlyst 15.

The selective synthesis of glycerol monooleate[17] from glycerol and oleic acid was performed in the presence of various acid solids (zeolite, clay, cation exchangers); cation-exchange resins were the best catalysts under mild experimental conditions. A selectivity of 90% for an oleic acid conversion of >50% was obtained; depending on its degree of cross-linking, the resin might act as a shape-selective catalyst.

Mercaptoacetates[18] were obtained by esterification of mercaptoacetic acid with several alcohols.

$$\mathrm{HSCH_2CO_2H + R{-}OH \rightarrow HSCH_2CO_2{-}R}$$

(with R) octyl, heptyl, pentyl, Bu, Pr, 2-hydroxyethyl, or 2-phenylethyl

Yields in the range of 84.1%-91.7% were obtained in benzene or cyclohexane as solvents, in the presence of D61 or D72 cation ion-exchange resins.

$$\mathrm{R{-}\!\sim\!{-}CO_2{-}R' + MeOH \rightarrow R{-}\!\sim\!{-}CO_2{-}Me + R'OH}$$

A similar reaction is the interesterification, where the alcohol parts of two esters are exchanged

$$\mathrm{R^1{-}CO_2{-}\mathbf{R}^2 + R^3{-}CO_2{-}\mathbf{R}^4 \rightarrow R^1{-}CO_2{-}\mathbf{R}^4 + R^3{-}CO_2{-}\mathbf{R}^1}$$

These equilibrated reactions are driven to full completion by the use of an excess of reagent. Dimethyl carbonate was synthesized by transesterification of MeOH with propylene carbonate, using CHS-1 or CHS-2 strong acid resins as catalysts and reaction times of 40- 60 min with a MeOH/propylene carbonate weight ratio of 8-10.

Materials and Methods

Materials used

Zirconium oxychloride, potassium pyroantimonate and phosphoric acid were obtained from SD Fine chemicals (INDIA), n-propanol, iso-propanol, n-butanol, iso-butanol, cyclohexanol, and benzoic acid are obtained from LobaChem(INDIA). All the chemicals are used as received without any further purification.

Methods used for analysis

The physicochemical properties of the ZrSbP, ZrPB, ZrWP and ZrSbAscatalysts were studied by various techniques i.e. FT-IR, Powder XRD and TGA. Ion exchange capacity of the catalysts was measured by literature reported procedure. Formation of various esters (n-propyl benzoate, isopropyl benzoate, n-butyl benzoate and iso-butyl benzoate) is determined by FT-IR, GC and ^{1}H NMR Spectra.

Instrumental analysis

IR spectrum in the range 4000-500 cm^{-1} was recorded on Perkin Elmer spectrum RX-1 FTIR spectrometer. Powder XRD patterns of the prepared catalysts were recorded on PanalyticX'pertpro MPD Netherland using Ni-filtered Cu Kα radiation. Thermo gravimetrical analysis (TGA) of the samples were performed on Perkin Elmer Pyris Diamond TG/DTA instrument with inert atmosphere of Argon at the heating rate of 10^0 C/min up to 1000°C temp.

^{1}H NMR Spectra were recorded on 400 MHz FT-NMR Cryo Spectrometer (Bruker) from Sophisticated Analytical Instrumentation Centre (SAIF), Punjab University, Chandigarh. GC Chromatograms were recorded on Nucon-5765 GC. A sample of 0.5 µL was injected with a N_2 gas at a flow rate of 2.5 ml/min. Oven was set at a temperature of 80 ºC hold for 1min than continued up to 220 ºC at a heating rate10 ºC/min. At 220ºC temperature was hold for 5 min than continued up to 310ºC at heating rate 20ºC/min. Temperature hold for 6 min at 310ºC. Supelco 28098-U 30M×0.25mm Column was used. Injector

Temperature was at 280ºC and FID Temperature was at 300ºC. Flow rate of the gases in GC were shown below: H_2 flow: 30 mL/min; Air flow: 300 mL/min; Make up (N_2): 30 mL/min

TLC of the reaction mixtures were spotted on freshly coated silica plate with co-spotting of starting benzoic acid. For all the samples TLC was run in 9:1 pet ether : chloroform solvent system. For all the reactions the spot of the product was observed to be non- polar as compared to benzoic acid.

Experimental work

Preparation of crystalline Zirconium Antimonophosphate catalyst

Crystalline zirconium antimonophshpate was prepared by adding zirconium oxychloride 0.1 M (containing hydrofluoric acid 12mL/L) to a continuous stirred mixture of potassium pyroantimonate 0.1M (containing hydrofluoric acid 16mL/L) and phosphoric acid solution 0.1M at 60°C in 2:1:1 (v/v) ratio. This gel was stirred for two and half hour at 60°C and then washed till free from halides and then filtered and the product was dried at 40°C. The dried product broke down into particles when immersed in water and then by treating with HCl 0.1 M for 24 hrs materials was converted into H^+ form. The product was washed with DMW in order to remove the excess acid and finally dried at 40°C.

Activity of the catalyst

Ion–exchange capacity

The Ion-exchange capacity of the samples of zirconium antimonophosphate was determined by the column method .Ion exchanger was taken in the H^+ form in a glass wool supported column. 500mg of the exchanger was placed in the column. NaCl 1M solution was used as an eluent .50 ml of the eluent was used. Hydrogen ions eluted from the column were determined titrimeterically with a standard solution of NaOH. An average of five such measurements shows an IEC of 0.98 ± 0.03.

Esterification of benzoic acid with n-propanol, n-butanol, iso-butanol using Zirconium based inorganic ion-exchanger catalyst such as ZrSbAs, ZrSbP, ZrPB and ZrWP

General Procedure

The vials containing benzoic acid (100mg, 0.8mM), alcohols (5 ml, taken in excess to use it as a solvent) and catalyst (100mg) were capped tightly and heated for three hours at 150^{o}C. The vial were removed, brought to room temperature and opened to check the formation of product with the help of TLC and GC. Excess alcohol was removed by evaporation and excess benzoic acid was washed off by using 10% $NaHCO_3$ solution. The product was extracted in organic phase using chloroform. Ester so formed was analysed by FT- IR and ^1H NMR.

a) N-propyl benzoate

^1H (400 MHz, $CDCl_3$): 8.07 (2H, d, ArH), 7.57 (1H, tt, ArH), 7.48 (2H, t, ArH), 4.30 (2H, t, OCH_2), 1.82 (2H, m, CH_2), 1.05 (3H, t, CH_3); IR (cm^{-1}): 1724; GC (retention time, 9 min 14 sec).

b) N-butyl benzoate

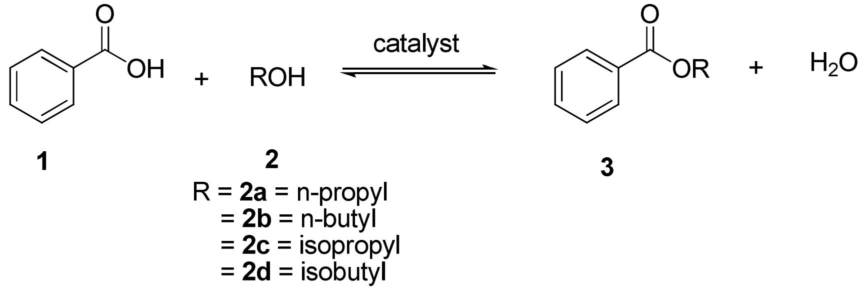
^1H (400 MHz, $CDCl_3$): 8.06 (2H, d, ArH), 7.56 (1H, tt, ArH), 7.45 (2H, t, ArH), 4.34 (2H, t, OCH_2), 1.78 (2H, q, CH_2), 1.52 (2H, m, CH_2), 0.99 (3H, t, CH_3); IR (cm^{-1}): 1716; GC (retention time, 10 min 38 sec).

c) Isobutyl benzoate

^1H (400 MHz, $CDCl_3$): 8.07 (2H, d, ArH), 7.57 (1H, tt, ArH), 7.48 (2H, t, ArH), 4.11 (2H, d, OCH_2), 2.11 (1H, m, CH), 1.03 (2 x 3H, d, CH_3); IR (cm^{-1}): 1716; GC (retention time, 10 min).

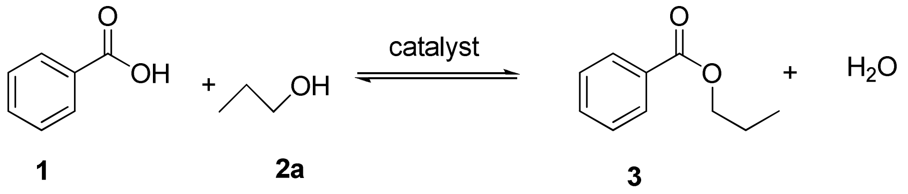
RESULTS AND DISCUSSIONS

Hetropolyacids salts of zirconium have been used as catalysts in simple esterification reactions of benzoic acid and with some primary and secondary alcohols like n-propyl alcohol, isopropyl alcohol, n-butyl alcohol and isobutyl alcohol as shown in **scheme 1**.



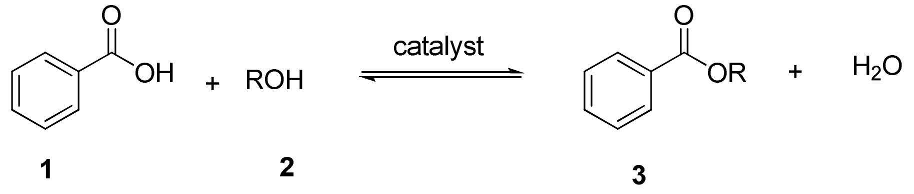
Scheme 1: Esterification of benzoic acid

Initial attempts to synthesize the corresponding esters at atmospheric pressure were not successful. There was hardly any conversion of benzoic acid in any of the esters, which were tried with different alcohols. Even changing the amount of catalysts from 10 mol % to stoichiometric amounts did not produce any result. Change in temperature conditions also did not show improvement in results. There was no conversion of the acid into ester even with ZrPB, ZrWP and ZrSbAs under these conditions.



The synthetic scheme was re-strategized wherein reactions were carried out in a closed vial of 15mL capacity. It was anticipated that under closed system, rate of the forward reaction would increase due to application of solvent pressure. A model reaction was studied wherein benzoic acid was treated with n-propanol in the presence ofstoichiometric quantities of ZrSbAs at 100°C. TLC and GC did not show any conversion. Further, the reaction temperature was varied by increasing it from 100° to 120° and then finally to 150°C. At 150°C, it was found that reaction proceeds efficiently in closed reaction medium. Then, same reaction was studied by decreasing the quantity of catalyst from 100 mol% to 50 mol% at 150°C in closed system to get the product. The procedure was thus established for the synthesis of esters with various catalysts. Results of the amounts of n-propyl benzoate formed with different catalysts are given in Table 1.This strategy was extrapolated to alcohols like n-butanol, isopropanol, isobutanol with all the four catalysts, respectively. The results are shown in Table 1.

Table 1: Performance of different zirconium based ion exchange catalysts in esterification reactions of benzoic acid with different alcohols



Sr No	Catalyst	n-butyl benzoate		Isobutyl benzoate		n-propyl benzoate		Isopropyl benzoate
		GC yield (%) (Rt=10min 38 s)	Isolated yield (%)	GC yield (%) (Rt=10min)	Isolated yield (%)	GC yield (%) (Rt=9min 14 s)	Isolated yield (%)	GC/isolated yield (%)
1	**ZrSbAs**	**43.2**	**39.1**	**97.2**	**75.2**	**81.1**	**64.6**	**No product**
2	**ZrSbP**	**47.1**	**40.1**	**98.7**	**77.1**	**76.7**	**63.3**	**No product**
3	**ZrPW**	**51.8**	**43.4**	**89.1**	**69.2**	**40.4**	**31.1**	**No product**
4	**ZrPB**	**55.5**	**45.0**	**82.0**	**67.2**	**78.3**	**61.7**	**No product**

For all catalysts the amounts of products formed were more with secondary alcohols than the primary alcohols; however esterification of benzoic acid with isopropyl alcohol did not yield any product. A yield of conversion of benzoic acid to its corresponding ester was distinctly higher with antimonate based salts of zirconium as compared with phosphobased salts.

Average yields of esters are observed in the following order:

Isobutylbenzoate> n-propylbenzoate> n-butylbenzoate.

This trend indicates that the selected group of ion exchangers have preferred catalytic activity for 2^o alcohols over 1^o alcohols, notwithstanding the length of carbon chain. This probably due to the similar interlayer spacing of these exchanger which is more suitable to accommodate 2^o substrate. 1^o substrates, although smaller in orientation would be to loosely held in the inter layer spacings, to be catalysed at the protonated sites of the exchanger. The benzoic acid gets protonated after abstracting the protons elecrostatically bound to the fixed anionic moiety of phosphate /Antimonate/ Aresenate/Borate groups. The protonated acid is thus attached to the fixed anionic group. Oxygen of alcohol behaves as a nucleophile attaches the protonated acid. At this stage attack of nucleophilic oxygen of alcohol is facilitated by the suitable geometry and environment around the protonated acid in the exchanger sites. Thus, introducing a selective character to the mechanism. This hypothesis is well supported by results shown in Table 1, where the order of yields of catalysed conversion of alcohol is Isobutanol> n-propanol > n-butanol.

Table1. indicates that more product is formed with sterically hindered alcohol indicating that steric factor prominently controls the efficiency as compared to electronic factor because, for a given alcohol hetropoly acid salts of zirconium with different anionic moieties do not affect the yields significantly. As expected, the product amounts are very close with exchangers ZrSbP and ZrSbAs, which used as catalysts. In this pair of catalysts antimonate moiety is common and the phosphate and arsenate moieties do not have different electronic effects on the acidic character of the catalyst, as they belong to same group 15. Surprisingly the iso-propanol based ester is not obtained. Reason is yet to be explored.

Esterification using different amount of benzoic acid

Experiments were conducted using different amount of benzoic acid for its conversion into n-butyl benzoate with a fixed amount of n-butanol. It is found that product yield increases in almost hyperbolic fashion with the increase in the amount of substrate. The conversion efficancy almost stabalises with 0.5 mM of benzoic acid for 100 mg of the catalyst. n-butyl benzoate appeared in the chromatogram at retention time 10:44 minutes.

Table 2. Effect of substrate amount (benzoic acid) on the yield of product using same amount of ion exchange catalyst

Serial no.	Benzoic acid (mg)	Amount of ZrSbAs Catalyst (mg)	n-butanol (ml)	GC Yield of butylbenzoate (%)
1.	100	100	5.0	43.2
2.	150	100	5.0	65.2
3.	200	100	5.0	69.7
4.	500	100	5.0	88.4
5.	600	100	5.0	90.0

Conclusions

Following conclusions can be drawn from the esterification reactions of aliphatic carboxylic with some alcohols.

1) Zirconium based inorganic ion exchangers i.e. ZrSbP, ZrSbAs, ZrWP and ZrPB can be used as a bronsted acid in thermal reactions of carboxylic acids with some primary and secondary alcohols.
2) The amount of catalyst is optimized as: 100mg of each exchanger having ion exchange capacity nearly 1.0 meq/g is sufficient to catalyze 0.8 mM of benzoic acid.
3) 2^o alcohol is catalyzed more efficiently than 1^o alcohols indicating that efficiency of a given exchanger is controlled by steric orientation of the alcohol.
4) Different ion exchangers of Zirconium behave almost similarly as catalysts and there is hardly any influence of electronic state of the anionic component of the double salt, e.g., same amounts of zirconium antimonoarsenate and zirconium antimonophosphate yield the same amount of ester from reaction of benzoic acid with iso-butanol.
5) Esterification reactions can be held more efficiently in a closed reactor than an open conventional refluxing method using Dean-Stark apparatus.
6) Gas Chromatographic technique can be used for following the efficiency of catalyst in esterification reactions.

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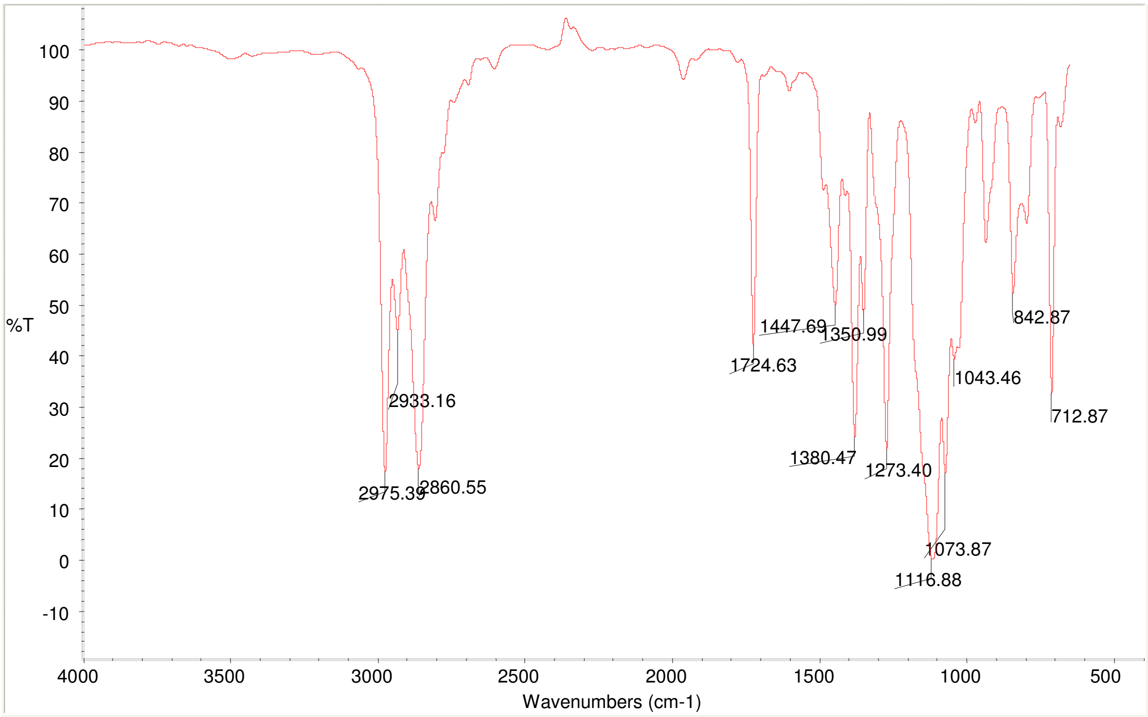
FT-IR of N-Propyl benzoate synthesised by using ZrSbAs as a catalyst



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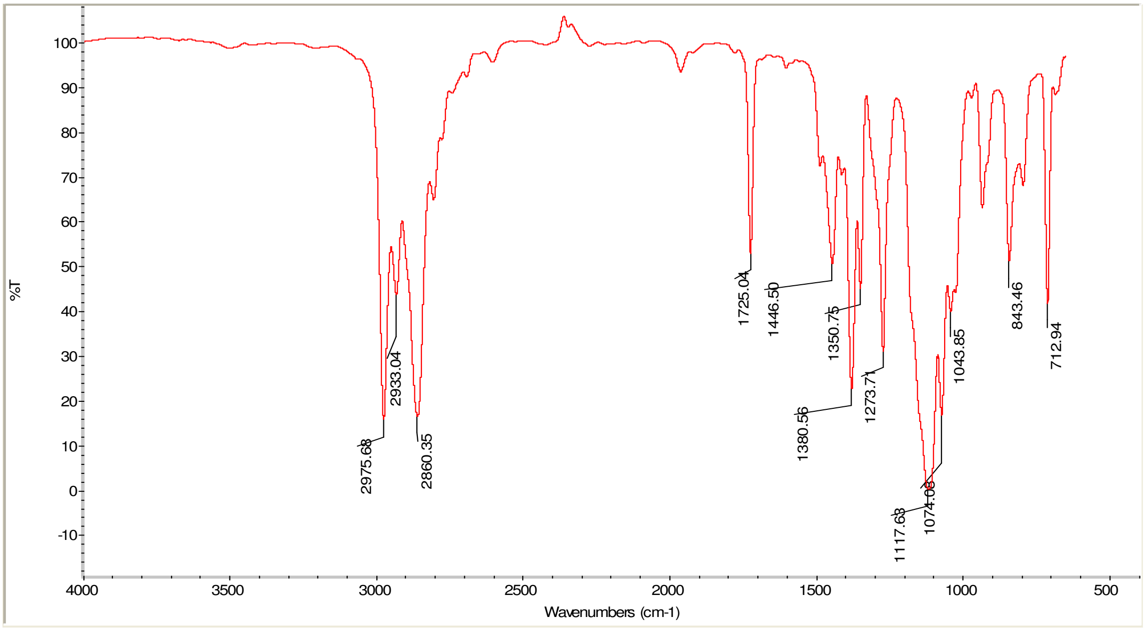

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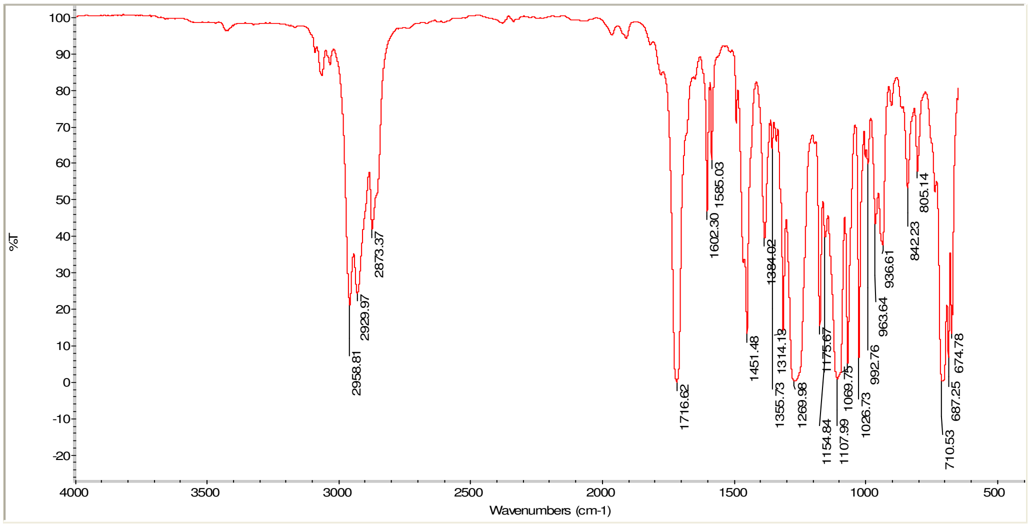

FT-IR of Isobutyl benzoate synthesised by using ZrSbAs as a catalyst