



Zirconium Based Ion Exchangers as Catalysts in Esterification Reactions of Benzoic Acid

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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 ¹H NMR and FT-IR techniques. Product yields from different set of combinations of benzoic acid and alcohols were monitored using gas chromatography. Double salt based ion exchangers selectively catalyzed esterification reactions based on steric considerations. Electronic factor did not seem to play any role in efficiency of the inorganic ion exchangers as heterogeneous catalysts.

Keywords: Heterogeneous catalysis, Zirconium based ion-exchangers, Esterification, Steric orientation, Closed reactor synthesis.

INTRODUCTION

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 flavour industry. Ester bonds are also found in many polymers. As a result of the reversibility, many esterification reactions are equilibrium reactions and, therefore, need to be driven to completion, according to Le Chatelier's principle.

The present research showed that the hybrid catalysts with 2D hexagonal p6mm mesostructure exhibited the highest catalytic activity towards both esterification and transesterification reactions among the above hybrid catalysts with various pore morphologies. This enhanced catalytic activity is due to the fact that the ordered mesostructure can decrease the mass-transport limitation of the reactants and products significantly. Recent studies have proven the technical feasibility and the environmental and economic benefits of biodiesel production *via* heterogeneous acid-catalyzed esterification and transesterification¹.

Inorganic ion exchanger as a catalyst support is capable of creating precisely controlled catalytically active species responsible for targeted organic reactions. A major advantage of ion-exchangers as catalysts is that heterogeneously catalyzed reactions allow easy and efficient separation of high value products from the catalyst. Clearfield *et al.*² in an important review mentioned the structure of inorganic ion exchanger and their ion exchange capacity. 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 montmorillonite 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. Another review 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 catalysts³ such as tungstophosphoric acid, sulfonated zirconia, K10 clay and Indion and Amberlyst resins.

Mercaptoacetates⁴ were prepared by esterification of mercaptoacetic acid with several alcohols with yields in the range 84.1-91.7 % cyclohexane as solvents, in the presence of D61 or D72 cation ion-exchange resins. A similar reaction is the inter-esterification⁴, where the alcohol parts of two esters are exchanged. These equilibrated reactions are driven to full completion by the use of an excess of reagent. Dimethyl carbonate was synthesized by transesterification of methanol with propylene carbonate, using CHS-1 or CHS-2 strong acid resins as catalysts and reaction times of 40-60 min with a methanol/propylene carbonate weight ratio of 8-10. The contribution⁵ of the catalysts led to the synthesis of some commercially valuable products such as *p*-methoxy acetophenone, dimethyl phthalate, diethyl phthalate, methyl anthranilate, methyl salicylate and methyl *p*-hydroxybenzoate (methyl paraben). Zirconium sulphate⁶ showed very good catalytic performance,

due to its high acidity together with low surface area. These combined features allow the sterically hindered FFA molecules to easily reach the active sites on the catalyst's surface. The other inorganic catalysts did not give satisfactory FFA conversion, probably due to the low acidity related to a quite high surface area. Platinum group metals⁷⁻¹⁰ are reported as highly selective catalysts and are widely used in organic synthesis, chemical industry and other areas like dehalogenation, hydrodechlorination, carbonylation or oxidation.

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 antimonophosphate¹¹ (ZrSbP), zirconium antimoarsnate¹² (ZrSbAs), zirconium tungstophosphate¹³ (ZrWP) and zirconium phosphoborate¹⁴ (ZrPB). The idea is to understand if electronic environments of different ion-exchangers have any role to play in catalyzing the organic synthesis reactions. Esterification of alcohols were adopted as model reactions for the study. Alcohols were used as solvents as well as reagents in reactions with carboxylic acid in presence of catalytic amounts of zirconium based inorganic ion exchangers. These catalysts offered remarkably simple workup procedure and were reusable without loss in its activity.

EXPERIMENTAL

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 were obtained from Loba Chemie (India). All the chemicals were used as received without any further purification.

Methods used for analysis: Physico-chemical properties of ZrSbP, ZrPB, ZrWP and ZrSbAs catalysts were studied by various techniques *i.e.*, FT-IR, Powder XRD and TGA. Ion exchange capacity of the catalysts was measured to characterize the materials as ion exchangers. Formation of various esters (*n*-propyl benzoate, *iso*-propyl benzoate, *n*-butyl benzoate and *iso*-butyl benzoate) was determined by FT-IR, GC and ¹H NMR Spectra.

Instrumental analysis: IR spectrum was recorded in the range 4000-500 cm⁻¹ on Perkin Elmer FTIR spectrometer. Powder XRD patterns of the prepared catalysts were recorded on Pan Analytic X'pertpro MPD Netherland, using Ni-filtered Cu-K_α radiations. Thermo gravimetric analyses (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 °C/min up to 1000 °C.

¹H NMR Spectra were recorded on 400 MHz FT-NMR Cryo Spectrometer (Bruker). Chromatograms were recorded on Nucon-5765 (India) gas chromatograph. A sample of 0.5 μL was injected with a nitrogen gas at a flow rate of 2.5 mL/min. Oven was set at a temperature of 80 °C hold for 1 min then continued up to 220 °C at a heating rate 10 °C/min. At 220 °C, temperature was on hold for 5 min then continued up to 310 °C at heating rate 20 °C/min. Temperature was kept on hold for 6 min at 310 °C. Supelco 28098-U (30 m × 0.25 mm) column was used. Flow rates of the gases in GC were: H₂ flow: 30 mL/min; Air flow: 300 mL/min; Make up (N₂): 30 mL/min.

TLC of the reaction mixtures were spotted on freshly coated silica plates 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.

Preparation of crystalline zirconium antimonophosphate catalyst: Crystalline zirconium antimonophosphate¹¹ was prepared by adding zirconium oxychloride 0.1 M to a continuous stirred mixture of potassium pyroantimonate (0.1 M) and phosphoric acid solution (0.1 M) at 60 °C in 2:1:1 (v/v) ratio. This gel was stirred for 2.5 h at 60 °C, washed till free from halides tested with silver nitrate solution, filtered and the product was dried at 40 °C. The dried product broke down into particles when immersed in water and was converted into H⁺ form by treating with HCl (0.1 M) for 24 h. The product was washed with demineralized water to remove the excess acid and dried at 40 °C.

Activity of catalyst

Ion-exchange capacity: Ion-exchange capacity (IEC) of different lots of zirconium antimonophosphate was determined by column method and the average of five such measurements had a value 0.98(±0.03) meq/g, which is almost similar to the reported value⁵. Hence, the material was taken as an active catalyst.

Esterification of benzoic acid with *n*-propanol, *n*-butanol, *iso*-butanol using Zirconium based inorganic ion-exchanger catalysts: ZrSbAs, ZrSbP, ZrPB & ZrWP

General procedure: The 15 mL capacity glass vials containing benzoic acid (100 mg, 0.8 mM), and corresponding alcohol (5 mL), taken in excess to use it as a solvent and catalyst (100 mg) were capped tightly and heated for 3 h at 150 °C. The vials 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 % NaHCO₃ solution. The product was extracted in organic phase using chloroform. Ester so formed was analyzed by FT-IR and ¹H NMR.

(a) *n*-Propyl benzoate: ¹H NMR (400 MHz, CDCl₃): 8.07 (2H, d, ArH), 7.57 (1H, tt, ArH), 7.48 (2H, t, ArH), 4.30 (2H, t, OCH₂), 1.82 (2H, m, CH₂), 1.05 (3H, t, CH₃); IR (cm⁻¹): 1724; GC (retention time): 9 min 14 sec;

(b) *n*-Butyl benzoate: ¹H NMR (400 MHz, CDCl₃): 8.06 (2H, d, ArH), 7.56 (1H, tt, ArH), 7.45 (2H, t, ArH), 4.34 (2H, t, OCH₂), 1.78 (2H, q, CH₂), 1.52 (2H, m, CH₂), 0.99 (3H, t, CH₃); IR (cm⁻¹): 1716; GC (retention time): 10 min 38 sec.

(c) *iso*-Butyl benzoate: ¹H NMR (400 MHz, CDCl₃): 8.07 (2H, d, ArH), 7.57 (1H, tt, ArH), 7.48 (2H, t, ArH), 4.11 (2H, d, OCH₂), 2.11 (1H, m, CH), 1.03 (2 × 3H, d, CH₃); IR (cm⁻¹): 1716; GC (retention time): 10 min.

RESULTS AND DISCUSSION

Heteropoly acid salts of zirconium¹¹⁻¹⁴ have been used as catalysts in simple esterification reactions of benzoic acid with some primary and secondary alcohols like *n*-propyl alcohol, *iso*-propyl alcohol, *n*-butyl alcohol and *iso*-butyl alcohol as shown in Fig. 1.

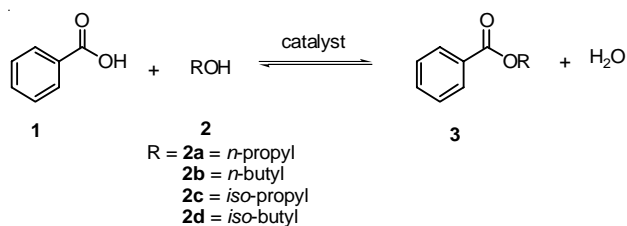


Fig. 1. Esterification of benzoic acid

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 (1:1, 1:2) did not produce any result. Change in temperature conditions also did not show improvement in results (Fig. 2). There was no conversion of the acid into ester even with ZrPB, ZrWP and ZrSbAs, under these conditions.

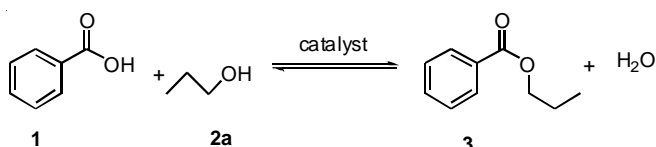


Fig. 2. A model reaction using ZrSbAs as a catalyst

The scheme of synthesis was re-strategized, wherein reactions were carried out in a closed vial of 15 mL 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 of stoichiometric quantities of ZrSbAs at 100 °C. TLC and GC did not indicate any conversion. Further, the reaction temperature was varied by increasing it from 100 to 120 °C and then finally to 150 °C. At 150 °C, it was found that reaction proceeds efficiently in closed reaction medium. The same reaction was studied by decreasing the quantity of catalyst from 100 to 50 mol % at 150 °C in a closed system which worked well without loss of catalytic efficiency. Same procedure was used for the synthesis of esters with different catalysts. Results of the amounts of *n*-propyl benzoate formed using different catalysts are given in Table-1. This strategy was extrapolated to alcohols like *n*-butanol, *iso*-propanol, *iso*-butanol with all the four catalysts, respectively. The results are shown in Table-1.

For all catalysts, the amounts of products formed were more with secondary alcohols than with the primary alcohols. However, esterification of benzoic acid with *iso*-propyl alcohol did not yield any product. The yield of conversion of benzoic

acid to its corresponding ester was distinctly higher with antimonate based salts of zirconium as compared with phosphorus based salts. This is due to more acidic character of the protons bound electrostatically to phosphate groups in phosphate based catalysts than those of antimonate groups of antimonite based ion exchangers (P is more basic in character than that of Sb due to its smaller size).

Average yields of esters are observed in the following order:



This trend indicates that the selected group of ion exchangers have preferred catalytic activity for 2° alcohols over 1° alcohols, notwithstanding the length of carbon chain. This probably is due to the similar interlayer spacing of these exchangers which is more suitable to accommodate 2° substrate. Alcohols smaller in size and orientation would be too loosely held in the inter layer spacings, to be catalyzed at the protonated sites of the exchanger. The benzoic acid gets protonated after abstracting proton that is electrostatically bound to the fixed anionic moiety of phosphate/antimonate/arsenate/borate groups of their corresponding catalysts. The protonated benzoic acid is then held electrostatically to a fixed anionic group of the catalyst.

Oxygen of alcohol behaves as a nucleophile and attaches to the protonated acid. At this stage, attack of nucleophilic oxygen of alcohol is facilitated by suitable geometry and environment around the protonated acid at the exchanger site, hence, introducing a selective character to the mechanism. This hypothesis is well supported by the results shown in Table-1, where the order of yields of catalyzed conversion of alcohol is:



Table-2 indicates that greater amount (97 %) of product is formed in case of sterically hindered alcohol (like *iso*-butanol) indicating that steric factor prominently controls the efficiency as compared to electronic factor, because, for a given alcohol, zirconium based catalysts with different anionic moieties do not affect the yields significantly. As expected, the yields of product are nearly similar with exchangers like ZrSbP and ZrSbAs, 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 of the periodic table. Interestingly, the *iso*-propanol based ester is not obtained at all, probably due to restricted orientation of the OH group of the 2° alcohol and also mismatching with anionic site of the catalyst.

TABLE-1
PERFORMANCE OF DIFFERENT ZIRCONIUM BASED ION EXCHANGE CATALYSTS IN
ESTERIFICATION REACTIONS OF BENZOIC ACID WITH DIFFERENT ALCOHOLS

S. No.	Catalyst	<i>n</i> -Butyl benzoate	<i>iso</i> -Butyl benzoate	<i>n</i> -Propyl benzoate	<i>iso</i> -Propyl benzoate
		GC yield (%) (Rt = 10 min 38 s)	GC yield (%) (Rt = 10 min)	GC yield (%) (Rt = 9 min 14 s)	GC/isolated yield (%)
1	ZrSbAs	43.2	97.2	81.1	No product
2	ZrSbP	47.1	98.7	76.7	No product
3	ZrPW	51.8	89.1	40.4	No product
4	ZrPB	55.5	82.0	78.3	No product

TABLE-2
EFFECT OF SUBSTRATE AMOUNT (BENZOIC ACID) ON
THE YIELD OF PRODUCT USING SAME AMOUNT
OF ION EXCHANGE CATALYST

S. No.	Benzoic acid mM (mg)	Amount of ZrSbAs Catalyst (mg)	<i>n</i> -Butanol (mL)	GC Yield of butyl benzoate (%)
1	0.8 (100)	100	5.0	43.2
2	1.2 (150)	100	5.0	65.2
3	1.6 (200)	100	5.0	69.7
4	4.0 (500)	100	5.0	88.4
5	4.8 (600)	100	5.0	90.0
6	8.0 (1000)	100	5.0	93.8

Esterification using different amounts of benzoic acid:

Experiments were conducted using different amount of benzoic acid for its conversion into *n*-butyl benzoate (retention time 10.44 min) with a fixed amount of *n*-butanol. It was found that product yield increased in almost hyperbolic fashion with the increase in the amount of substrate. The conversion efficiency almost stabilises with 8 mM of benzoic acid for 100 mg of the catalyst.

A number of researchers¹⁵⁻¹⁷ have reported esterification reactions using heteropolyacids and their salts but relative selectivity of the catalyst have not been claimed.

Conclusions

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

- Zirconium based inorganic ion exchangers *i.e.*, ZrSbP, ZrSbAs, ZrWP and ZrPB can be used as Brønsted acids in thermal reactions of carboxylic acids with some primary and secondary alcohols.

- Esterification reactions can be held more efficiently in a closed reactor than an open conventional refluxing method using Dean-Stark apparatus.

- The amount of catalyst is optimized as: 100 mg of each exchanger having ion exchange capacity nearly 1.0 meq/g is sufficient to catalyze 8.0 mM of benzoic acid.

- 2° alcohol is catalyzed more efficiently than 1° alcohol indicating that efficiency of a given exchanger is controlled by steric orientation of the alcohol.

- 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 antimonarsenate and zirconium antimonophosphate yield the same amount of ester from reaction of benzoic acid with *iso*-butanol.

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