# A comparative study of bronsted acidity of tin phosphate and chromotropic acid anchored tin phosphate

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## ABSTRACT

The conventional acid catalysts, although quite effective, are also highly corrosive, hazardous and polluting. Therefore, they need to be replaced by solid acids which are less toxic, easy to handle, easily separable from the products and finally reusable. Various solid acid catalysts like zeolites[1], sulphated zirconia[2], clay minerals[3] are being explored for industrially important reactions. Industrial interest first turned to inorganic zeolites whose catalytic activity usually depends on the presence of a metal such as manganese, iron, chromium and vanadium. Catalytic synthesis can be achieved by using either homogeneous or heterogeneous catalysts.

**Key words:** Bronsted acidity, tin phosphate, catalytic synthesis.

## INTRODUCTION

In recent years, due to environmental concerns, the major trend in the field of catalysis is to find newer catalysts, which are environment friendly. The conventional acid catalysts, although quite effective, are also highly corrosive, hazardous and polluting. Therefore, they need to be replaced by solid acids which are less toxic, easy to handle, easily separable from the products and finally reusable. Various solid acid catalysts like zeolites[1], sulphated zirconia[2], clay minerals[3] are being explored for industrially important reactions. Industrial interest first turned to inorganic zeolites whose catalytic activity usually depends on the presence of a metal such as manganese, iron, chromium and vanadium.

Ion exchange resins show a particular affinity for acid and base. Catalysis in organic reactions, since they can be easily transformed into the $H^+$ and $OH^-$ form and their porosity and swelling offer a sufficiently large active surface, so that even large organic molecules can penetrate the interior of the resin. Ion exchangers offer all the advantages of solid acid catalysts. Only their limited thermal and mechanical stability sets contain limits for the applicability of ion exchange resins in Catalysts.

Inorganic ion exchangers show good potential in Bronsted acid catalysis because of the presence of surface hydroxyl protons[4-7]. The catalytic activity is always present in the counter ions. Cation exchangers in the $H^+$ form and anion exchangers in the $OH^-$ form catalyze processes which are accelerated by acids and alkalies, respectively. Exchangers loaded with $Hg^{2+}$, cyanide or acetate exhibit the catalytic properties of these ions. The exchanger network serves solely as a catalyst support[8].

Anchoring of organic units to the back bone of inorganic ion exchangers is of particular interest since the resulting compounds better known as inorgano-organic ion exchangers have the added advantages of both their counterparts in terms of thermal stability, chemical stability and ion exchange capacity. Apart from their fundamental aspects there is increasing interest in the potential applications of these materials in chromatographic separation, catalysis and photochemistry. Several such compounds of the $Zr(PO_3R)_2$ and $Zr(PO_4R)_2$ type (R=organic radical) have been prepared by Alberti et al [9,10]. These compounds appear to be structurally identical with the parent inorganic compound.[11,12].

The present work reports the synthesis and characterization of amorphous forms of tin phosphate (SnP) and chromotrophic acid (4,5 dihydroxynaphthalene-2,7-disulphonic acid, disodium salt) anchored onto tin phosphate (SnPCA). Their efficiency in acid catalysis has been compared by carrying out esterification of ethylene glycol as a model reaction.

**Experimental procedure**

SnP was prepared by mixing solutions of 0.1M,100ml tin (IV)chloride with 0.1M, 100ml sodium phosphate. The pH was adjusted to zero. The gel thus obtained was filtered, washed and dried. The dried materials were converted into the hydrogen form completely by repeated treatment with 1M HCl. SnPCA was prepared by equilibrating 1g of the acid-treated SnP with an aqueous solution (25ml,0.05M) of chromotropic acid (disodium salt)

for 24 hours with intermittent shaking at pH=3. A colour change of the inorganic ion exchanger from white to the pink of organic resins was observed. The excess of the organic reagent was decanted, the exchanger washed with conductivity water and dried at room temperature.

**Characterization**

The elemental analysis was carried by ICP-AES. The ion exchange capacity of the sample was determined as usual by the column process.. The carbon and hydrogen contents were estimated on a Coleman Analyser. Chemical stability was assessed by soaking the material in different mineral acids, bases and organic solvents. The ion exchange capacity (i.e.c) was determined by the column method. The effect of heating on i.e.c was also studied (Table 1).

The FTIR spectra were obtained on a Perkin Elmer IR spectrophotometer. TGA of the samples were performed on a Perkin Elmer thermal analyzer at a heating rate of $10^0C/min$.

Catalytic studies- The esterification reactions were carried out on both SnP and SnPCA by varying the amount of catalyst and mole ratio of glycohol and acid. For the preparation of glycol diacetate, acetic acid and ethylene glycol were combined in a refluxing assembly. The catalyst was then added in the required amount. The mixture was heated to gentle reflux for 2h and glycol diacetate formed was distilled over slowly. The amount of ester formed was monitored on a gas chromatograph.

**Table 1: Effect of heating on ion exchange capacities**

| Temperature | Colour | | i.e.c (meq/g) | |
|---|---|---|---|---|
| (°C) | SnP | SnPCA | SnP | SnPCA |
| Room temp | White | Brown | 3.00 | 3.84 |
| 100 | Dull white | Brown | 2.90 | 3.20 |
| 200 | Dull white | Brown | 2.70 | 1.16 |
| 300 | Light brown | Brown | 2.48 | 2.70 |
| 400 | Brown | Dark brown | 1.84 | 3.00 |
| 500 | Black | Black | 1.58 | 3.30 |

**Table 2: Percentage yield of glycol diacetate**

| Mole ratio of glycol and acid | Amound of Catalyst (g) | % yield of ester | |
|---|---|---|---|
| | | SnP | SnPCA |
| 1:1 | 1 | 40 | 46 |
| 1:1 | 2 | 45 | 50 |
| 1:2 | 1 | 50 | 58 |
| 1:2 | 2 | 57 | 60 |
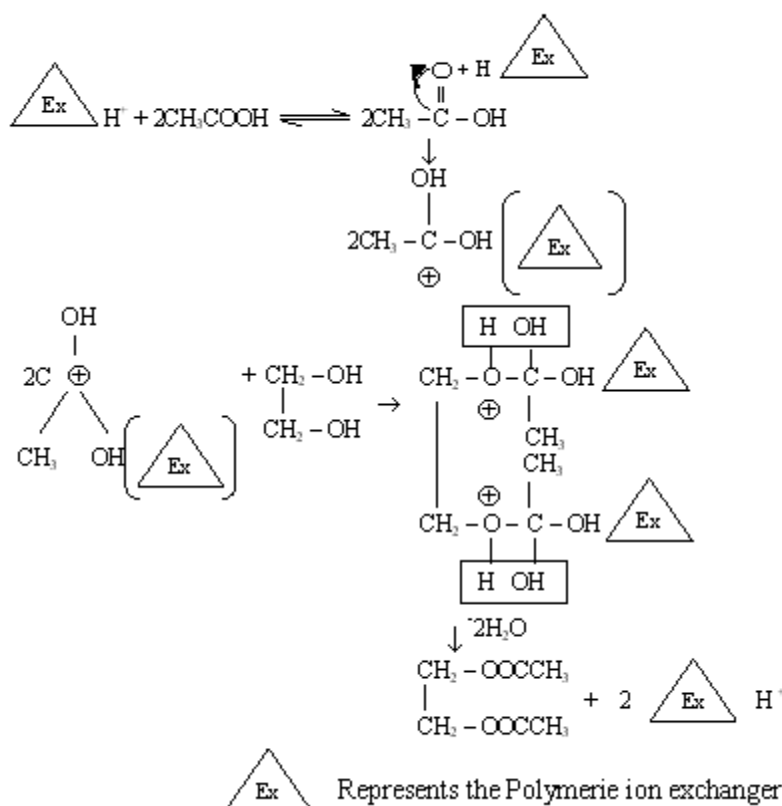


**Scheme 1**

## RESULTS AND DISCUSSION

The chemical analysis indicates the composition of SnP as 5:1. Based on this and the T.G.A data, the proposed formula for SnP is $5SnO_2 \cdot 1/2 P_2O_5 \cdot 19H_2O$. The number of water molecules were determined using Alberti's formula[13]. Carbon, hydrogen and sulpher contents were found to be %C=1.12, %H=2.41 %S=0.44, respectively. The materials were found to be stable in concentrated acids like HCl, $HNO_3$ etc, but was unstable in bases like NaOH and KOH above 2M concentration. Further it was also found to be stable in diethyl ether, ethanol and acetic acid. The $Na^+$ exchange capacity

for SnP and SnPCA were found to be 3.0 and 3.84 meq/g, respectively. This was a direct indication for the presence of exchangeable protons.

The effect of heating on i.e.c shows that in the case of SnP it decreases on heating. This may be due to the condensation of structural hydroxyl groups at higher temperatures. However in the case of SnPCA, the i.e.c decreases on heating upto $300^0$C and then again increases upto $500^0$C. After $300^0$C, the organic part starts decomposing, leading to the formation of active carbon, as evidenced by the change in colour of the sample to black at $500^0$C. This was responsible for an increase in the i.e.c and was later lost as $CO_2$. The organic part decomposes giving CO2 and H2O. In this case the decomposition of organic moiety occurs on heating in the range 300 to $500^0$C. Such stability exhibited by inorgano-organic hybrid material was remarkable. When the organic part oxidizes, it gives $CO_2$ and $H_2O$ due to which extra –OH groups are formed and hence exchange capacity increases.
FTIR spectra of both SnP and SnPCA show bands in the region ~ 3430 and 1630 cm$^{-1}$ attributed to asymmetric and symmetric hydroxo –OH and aquo –OH  stretches and of aquo (H-O-H) bending respectively.The bands around 1060 cm$^{-1}$ region to symmetric and antisymmetric stretching of P-O bonds in –PO4 group. The presence of bands around 560 cm$^{-1}$ may be related to Sn-O bond vibrations.

The FTIR spectrum of SnPCA shows additional bands characteristic of the organic moiety. Medium band at ~1372.53cm$^{-1}$ correspond to the stretching frequency of the fused ring system. Bands at 3430.27cm$^{-1}$ were attributed to the –OH stretching frequency, whereas 1634.88cm$^{-1}$, 1054.96cm$^{-1}$ were attributed to the stretching and bending frequencies of the fused ring system.
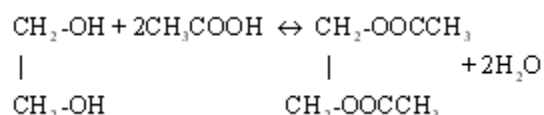
The t.g.a of SnP shows a weight loss at $100^0$C, corresponding to the loss of external water molecule, after which a gradual loss in weight is observed till about 600°C. This may be due to the condensation of structural hydroxyl groups.

The t.g.a of SnPCA shows a weight loss upto $200^0$C. There was a very gradual weight loss within the temperature range of 200 to 600°C

corresponding to the decomposition of the organic moiety from the SnP matrix.

The surface areas of SnP and SnPCA were found to be 236.5157 and 181.7387m$^2$/g respectively.
Esterification of carboxylic acid is a reaction subject to general Bronsted acid catalysis and the reaction of ethylene glycol with acetic acid was selected as a model reaction.

$$CH_2\text{-}OH + 2CH_3COOH \leftrightarrow CH_2\text{-}OOCCH_3$$
$$| \qquad\qquad\qquad\qquad\qquad | \qquad\qquad + 2H_2O$$
$$CH_2\text{-}OH \qquad\qquad\qquad CH_2\text{-}OOCCH_3$$

As observed , the yields of glycol diacetate is higher with inorgano organic ion exchangers as catalyst. It was found that , the yield of glycol di acetate increased by increasing the amount of catalyst and the acid concentration. It is also observed that in the formation of esters, with change in particle size, temperature or reaction time, no particular change is observed in the yields of esters obtained. In all cases, the catalyst was regenerated by washing with water several times and finally treating it with 1M HCl (as per method suggested in experimental section). In the regenerated samples, the yields decreased by ~5% in every subsequent cycle.

However, maximum yields were obtained when the amount of the catalyst taken was 2g and glycol to acid proportion was 1: 2. The yield of glycol di acetate was higher for Chromotropic acid anchored onto SnP. The maximum yield for Chromotropic acid anchored SnP was 60% while that for SnP was 57% [Table 2].

The better yield with Chromotropic acid anchored SnP compared to SnP could be attributed to the presence of additional H$^+$ sites on the organic moiety, thereby, making it a better Bronsted acid catalyst. Thus anchoring of organic groups improves the acidic properties of the inorganic ion exchanger[6].The surface area of SnPCA was lower than SnP. The surface area and the many active sites of an inorganic ion exchanger often make them very effective catalysts. By anchoring an organic group to an inorganic ion exchanger improves the

catalytic activity. The catalytic activity of an inorgano-organic ion exchanger being dependent upon the organic functional groups present.

The ability to lend protons make solid acids valuable as catalysts. When a reactant receives and in corporates protons from an acid, it forms a reactive intermediate. This positively charged intermediate may change shape and configuration. It may undergo further reaction which culminates in the creation of a new molecule. Again the proton is returned to the catalyst. The mechanism for the above reaction using the ion exchanger as a Bronsted acid catalyst could be represented as shown below.

In conventional methods where $H_2SO_4$ is used as a catalyst for preparing the esters, the yields are high but traces of $H_2SO_4$ are difficult to remove. Besides $H_2SO_4$ is a corrosive liquid. The water eliminated during the process of conversion dilutes the acid, weakening it so that great quantities of the acid are required. The use of solid acid catalysts thus circumvents the problem of dilution. The use of solid acid catalysts are definitely advantageous since the ester formed can be simply distilled over and there is no catalyst contamination. The above results establish the promising use of inorgano-organic ion exchangers over simple inorganic ion exchangers as environment friendly solid acid catalyst in Bronsted acid catalysts.

## CONCLUSION

Catalytic synthesis can be achieved by using either homogeneous or heterogeneous catalysts. However, each of these methods offers advantages and disadvantages. Homogeneously catalyzed reactions are highly efficient in terms of selectivity (ie.regioselectivity, enantiomeric excesses) and reaction rates, due to their monomolecular nature. Unfortunately, catalyst recovery can be very difficult (due to the homogeneous nature of the solution) and product contamination by residual catalyst or metal species is a problem, resulting in enormous quantities of hazardous waste, with the cost of disposal of this waste often outweighing the value of the product. Tightening legislation on the emission of hazardous pollutants is driving the industrty towards the implementation of innovative "Clean technology" including the use of alternative heterogeneously catalyzed processes. Heterogeneously catalyzed reactions allow easy and efficient separation of high value products from the catalyst. In this case we design processes that reduce the use and generation of hazardous substances. Green chemistry focuses on the design, manufacture and use of chemicals and process that have little or no pollution potential or environmental risk and are both economically and technolpgically feasible. Inorganic ion exchangers and their organic derivatives are environment friendly solid acid catalysts and thus upholds the principles of Green chemistry.

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