A comparative study of catalytic activity of tin phosphate and tin phenyl phosphonate

Chithra P G¹ & Beena B²

¹Department of Chemistry, S N College, Kollam, India
²Department of Chemistry, D B College, Sasthamkottah Kollam, India

Email: chithrasumej@yahoo.co.in, chithrapg@hotmail.com

Received 12 December 2006; revised 26 November 2007

Amorphous ion exchangers tin(IV) phosphate and tin(IV) phenyl phosphonate have been prepared and characterized. Catalytic activity has been studied and compared by using esterification of ethylene glycol as a model reaction wherein glycol diacetate has been prepared. The materials indicate good potential for Bronsted acid catalysis for the above reaction.

Keywords: Tin phenyl phosphate, catalytic activity, Tin phosphate

Tetravalent metal acid (TMA) salts are cation exchangers, obtainable in both amorphous and crystalline forms, possessing the general formula M(IV)(HXO₄)₂·nH₂O where M(IV) = Zr, Ti, Sn, Ce, Th etc and X = P, W, As, Mo, Sb etc. These materials possess structural hydroxyl groups, the H of the –OH being the exchangeable site. A number of cations can be exchanged with the H⁺ due to which the material possesses cation exchange properties¹².

There is currently high interest in engineering mixed materials (organic/inorganic), where features of the organic and inorganic components complement each other leading to the formation of new solid-state structures and materials with new composite properties³⁴. Several such compounds of the Zr(PO₃R)₂ and Zr(PO₄R)₂ type (R=organic radical) have been prepared by Alberti et al.⁴⁵.

The catalytic activity of an ion exchanger is always associated with the counter ions. Ion exchange resins show a particular affinity for acid and base catalysis in organic reactions. 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 catalysts⁶.

Inorganic ion exchangers show good potential in Bronsted acid catalysis because of the presence of surface hydroxyl protons⁷⁹. Anchoring of organic units to the back bone of inorganic ion exchangers is of particular interest since the resulting compounds, known as inorgano-organic ion exchangers, have the added advantages of both the counterparts in terms of thermal stability, chemical stability and ion exchange capacity. These compounds appear to be structurally identical with the parent inorganic compound¹⁰. The phenyl derivative of tin phosphate, namely tin phenyl phosphonate can be prepared by replacing the ‘P-OH group by P-C₆H₅ group. The present work reports the synthesis and characterization of amorphous forms of tin phosphate and tin phenyl phosphonate. Their efficiency in acid catalysis has been compared by carrying out esterification of ethylene glycol with acetic acid as a model reaction.

Experimental Procedure

Tin phosphate (SnP) was prepared by mixing solutions of tin (IV) chloride (0.1M) and tri sodium ortho phosphate (0.1M) with continuous stirring. The pH was adjusted to zero. The resulting gel was digested for 24 h at room temperature, filtered, washed with conductivity water until free of chloride ions and dried at 60°C. The materials obtained were sized by sieving to 30-60 mesh size and converted to the hydrogen form completely by repeated treatment with 1 M HCl, washed with conductivity water till free from chloride ions and again dried at 60°C.

In both the samples (SnP and SnPP) both tin and phosphorus were determined by using ICP-AES. The carbon and hydrogen contents in SnPP were estimated on a Coleman analyzer. The Na⁺ exchange capacity of the materials was determined by the column method. The FTIR spectra were recorded on a Perkin-Elmer IR spectrometer. TGA of the samples were recorded on a Perkin-Elmer thermal analyzer. The effect of heating on i.e.c (ion exchange capacity) of the samples was studied at different temperatures. The surface area of samples was measured by the BET method using BET analyzer.
As a model esterification reaction, glycol diacetate was prepared using SnP and SnPP as catalysts. Reactions were carried out by varying the amount of catalyst, mole ratio of ethyl alcohol and acetic acid, varying particle size, temperature and reaction time. The amount of ester formed was monitored by a titrimetric method6.

**Results and Discussion**

The chemical analysis indicates the composition of SnP, Sn: P as 5: 1. For SnPP, elemental analysis indicate the following composition Sn=20.66%, P=2.68%, C=11.93% and H=2.66%). The Na+ exchange capacity for SnP and SnPP were found to be 3.0 and 2.3 meq/g. This is a direct indication for the presence of exchangeable protons.

FTIR spectra of both SnP and SnPP show bands in the region ~3400 cm−1 and ~1630.02 cm−1 attributed to asymmetric and symmetric hydroxo –OH and aquo –OH stretches and of aquo (H-O-H) bending respectively. In addition to this, the FTIR spectra of SnPP show additional bands characteristic of the organic moiety. Bands at 1593.11, 1485.17 and 1438.87 cm−1 are due to C=C stretching and at 749.80 cm−1 the out of plane C-H ring bending mode. In plane bending bands occur in the region 1000-1200 cm−1.

The T.G.A of SnP shows 28% weight loss within the temperature range of 100 to 180°C corresponding to the loss of external water molecules, after which a slow change in weight is observed till about 600°C. This may be due to the condensation of structural hydroxyl groups. The T.G.A of SnPP shows 12% weight loss in between 200 and 300°C corresponding to the loss of external water molecules. There is a very gradual weight loss within the temperature range of 300 to 700°C corresponding to the decomposition of the organic moiety.

The results of the effect of heating on i.e.c are summarized in Table 1. For SnP the i.e.c decreases on heating. This is due to the condensation of structural hydroxyl groups bearing the exchangeable protons at higher temperatures. However in the case of SnPP, the i.e.c decreases on heating upto 300°C and then again increases upto 500°C. After 300°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°C. This is responsible for an increase in the i.e.c and is later lost as CO2. 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°C. Such stability exhibited by inorgano-organic hybrid materials is remarkable. When the organic part oxidizes, it gives CO2 and H2O due to which extra –OH groups are formed and hence exchange capacity increases. The surface areas of SnP and SnPP were found to be 236.51 and 51.47 m²/g respectively.

Esterification of carboxylic acid is a reaction subject to Bronsted acid catalysis and the reaction of ethylene glycol with acetic acid was selected as a model reaction6. It was found that, the yield of glycol diacetate increased by increasing the amount of catalyst and acid concentration (Table 2). However, higher yields were obtained when the amount of the catalyst taken was 2 g and glycol to acid ratio was 1:2. It is also observed that in the formation of esters, change in particle size, temperature or reaction time, do not effect the yields of esters obtained. In all cases, the catalyst was regenerated by washing with water several times and finally treating it with 1 M HCl. With the regenerated samples, the yield is decreased by ~4% in every subsequent cycle. The yield of glycol diacetate was higher for SnPP in all cases.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Color</th>
<th>i.e.c(meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SnPP</td>
<td>SnP</td>
</tr>
<tr>
<td>Room temp.</td>
<td>White</td>
<td>White</td>
</tr>
<tr>
<td>100</td>
<td>White</td>
<td>Dull White</td>
</tr>
<tr>
<td>200</td>
<td>White</td>
<td>Dull White</td>
</tr>
<tr>
<td>300</td>
<td>Light brown</td>
<td>Light brown</td>
</tr>
<tr>
<td>400</td>
<td>Light brown</td>
<td>Brown</td>
</tr>
<tr>
<td>500</td>
<td>Light brown</td>
<td>Black</td>
</tr>
</tbody>
</table>

Table 2—Yield of glycol diacetate formed by using Sn (IV) phenyl phosphonate (SnPP) and Sn (IV) phosphate (SnP) as catalyst

<table>
<thead>
<tr>
<th>Amount of catalyst</th>
<th>Ratio of acid to glycol</th>
<th>Yield SnPP</th>
<th>Yield SnP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1:1</td>
<td>25</td>
<td>22</td>
</tr>
<tr>
<td>1.0</td>
<td>1:1</td>
<td>42</td>
<td>40</td>
</tr>
<tr>
<td>2.0</td>
<td>1:1</td>
<td>46</td>
<td>45</td>
</tr>
<tr>
<td>0.5</td>
<td>2:1</td>
<td>29</td>
<td>25</td>
</tr>
<tr>
<td>1.0</td>
<td>2:1</td>
<td>59</td>
<td>50</td>
</tr>
<tr>
<td>2.0</td>
<td>2:1</td>
<td>65</td>
<td>57</td>
</tr>
</tbody>
</table>
maximum yield with SnPP was 65% while that with SnP was 57%.

The better yield with SnPP compared to SnP could be attributed to the presence of electron withdrawing phenyl group in SnPP which makes the acidic protons more labile, thereby making it a better Bronsted acid catalyst. The surface area of SnPP is lower when compared to SnP. The large surface area and several active sites often make an inorganic ion exchanger a very effective catalyst. But in the case of an inorgano-organic ion exchanger the catalytic activity being dependent upon the organic functional groups present. Thus anchoring of organic groups improves the acidic properties of the inorganic ion exchanger.

The ability to lend protons make solid acids valuable as catalysts. When a reactant receives and incorporates 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.

In conventional methods where H$_2$SO$_4$ is used as a catalyst for preparing the esters, the yields are high but traces of H$_2$SO$_4$ are difficult to remove. Besides H$_2$SO$_4$ is a corrosive liquid. The water eliminated during the process of conversion dilutes the acid, weakening it so that large quantities of the acid are required. The use of solid acid catalysts thus eliminates 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 in Bronsted acid catalysis.

**Conclusion**

Both the ion exchangers SnP and SnPP exhibit good ion exchange capacity and are stable up to fairly high temperatures besides exhibiting stability in different acidic, basic and organic media. The inorgano organic ion exchanger SnPP is more efficient catalyst than the parent inorganic ion exchanger SnP for esterification of ethylene glycol. The main advantages of these catalysts are the ease of operation and simplicity in work which involves mere filtration of the catalyst and reusability.

**Acknowledgement**

The authors thank the Principal, S N College, Kollam, for providing necessary research facilities. One of the authors (P G C) acknowledges U G C for the award of teacher fellowship under F I P.

**References**