

## Use of zirconium(IV) phosphate as a solid acid catalyst in some esterification reactions

H K Patel, R S Joshi & U V Chudasama\*

Department of Applied Chemistry, Faculty of Technology and Engineering, The M.S. University of Baroda, Vadodara 390 001, India  
Email: uvcres@yahoo.com

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Amorphous and crystalline phases of zirconium(IV) phosphate of the class of tetravalent metal acid (TMA) salts have been synthesized by sol-gel method. The materials have been characterized for elemental analysis (ICP-AES), thermal analysis (TGA), X-ray analysis, BET surface area, surface acidity (NH<sub>3</sub>-TPD) and FTIR spectroscopy. 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 has been 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 reveals the promising use of ZrP as an ecofriendly solid acid catalyst.

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The development of environment friendly technologies is a major goal of present research in chemistry. Heterogeneous solid acids provide an attractive alternative to homogeneous liquid acid catalysts as they possess high catalytic activity and selectivity, do not corrode reaction vessels or reactors and finally, repeated use of solid acid catalyst from reaction mixture is easy. Esterification reactions have been widely investigated using several solid acids<sup>1-15</sup>; to mention a few, sulfated zirconia, zeolites, sulfonic acid based resins, heteropoly acids, metal oxides, pillared clays, etc. have been studied. However, it has been observed that though sulphated zirconia is a very good esterification catalyst, it gets easily deactivated by losing the sulphate ions; thus, recycling of the catalyst is restricted. In case of heteropoly acids, the separation is difficult and when supported on carbon, the activity decreases. Sulfonic acid based resin (Nafion-H) has also been found to be unsatisfactory due to its low operating temperature.

Inorganic ion exchangers of the class of tetravalent metal acid (TMA) salts are cation exchangers, possessing the general formula M(IV)(HXO<sub>4</sub>)<sub>2</sub>nH<sub>2</sub>O, where M(IV)=Zr, Ti, Sn, Th, Ce, etc. and X=P, W, Mo, As, Sb, etc. These materials possess structural hydroxyl groups, the H of the -OH being the exchangeable sites. TMA salts thus possess good potential for application as solid acid catalysts. They

can be obtained in both amorphous and crystalline forms. It is, however, observed that with increasing crystallinity both surface area and surface acidity decreases<sup>16</sup>. TMA salts being synthesized by sol gel routes, materials with varying water content, composition, ion exchange capacity, acid strength and crystallinity<sup>17-21</sup> can be obtained by varying parameters such as stoichiometry and concentration of the reagent used, temperature at which they are mixed, rate of addition, mode of mixing, pH, etc. These compounds offer great promise in preparative reproducibility and stability, both chemical and thermal<sup>22</sup>.

In the present investigations, amorphous and crystalline forms of zirconium phosphate, abbreviated as ZrPA and ZrPC respectively, have been synthesized by sol gel method. The synthesized materials have been characterized and their potential use as solid acid catalysts has been explored by studying esterification as a model reaction wherein monoesters such as ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA) and benzyl acetate (BzA) and diesters such as dioctyl phthalate (DOP) and dibutyl phthalate (DBP) have been synthesized.

### Materials and Methods

Amorphous Zr(IV) phosphate was prepared by adding dropwise the aqueous solution of ZrOCl<sub>2</sub>·8H<sub>2</sub>O

(0.1 M, 100 mL) to the aqueous solution of sodium dihydrogen phosphate (0.2 M, 100 mL) in the pH range 1-2, with continuous stirring at 70°C. The gelatinous precipitates obtained was digested for 1 h at 70°C, filtered, washed with conductivity water till removal of chloride ions, followed by drying at room temperature. The material was sized by sieving [(30-60 mesh) ASTM] and finally converted to acid form by treating 5 g of the material with 50 mL of 1 M HNO<sub>3</sub> for 30 min with occasional shaking. The sample was then separated from acid by decantation and washed with conductivity water for removal of adhering acid. This process (acid treatment) was repeated at least five times. After final washing, the material was dried at room temperature. This material was used for all studies.

Crystalline Zr(IV) phosphate was prepared by HF method<sup>23</sup>. To a 0.2 M solution of ZrOCl<sub>2</sub>·8H<sub>2</sub>O, containing HF and Zr in the molar ratio HF/Zr = 5.2 was added 46 mL *o*-phosphoric acid (85%). It was heated on a water bath (70-75°C) for 5-6 days. Distilled water was added periodically to keep the volume constant. The microcrystals obtained were filtered from the system washed thoroughly with deionised water and dried at room temperature.

The samples were analyzed for zirconium and phosphorous content by ICP-AES. X-ray diffractogram (2 $\theta$  = 5-80°C) was obtained on X-ray diffractometer (Rigaku Dmax 2200) with Cu-K $\alpha$  radiation and nickel filter. FTIR spectra were recorded using KBr wafer on a Bomem MB series. TGA was carried out on a Shimadzu thermal analyzer at a heating rate of 10°C/min. Surface area measurement of the materials were carried out by BET multipoint method using a Micromeritics Gemini 2220 series surface area analyzer. Surface acidity was determined using Micromeritics Chemisorb 2720, by temperature programmed desorption of ammonia. For this, the sample was first activated at 400°C in a flow of helium to remove moisture from the surface. Temperature of the sample was brought down to 120°C and a mixture of ammonia and helium was passed through sample for 10 min. Further, helium was passed through the sample at the same temperature for half an hour to remove any physisorbed gas. Desorption was carried out up to 700°C at a heating rate of 10°C/min and the amount of gas desorbed was measured from the area under the plot of temperature versus TCD signal. Chemical resistivity in various media (acids, bases

and organic solvents) was studied by taking 500 mg of ZrPA or ZrPC in 50 mL of the particular medium and allowing to stand for 24 h. The change in colour, nature and weight was observed.

#### Synthesis of monoesters (EA, PA, BA and BzA)

In a typical reaction, a round bottom flask equipped with a Dean and Stark apparatus attached to a reflux condenser was used and charged with acetic acid (0.75 mol), alcohol (0.05 mol), catalyst (ZrPA) and 20 mL of a suitable solvent. The solvent was used as a reaction medium and also to facilitate the removal of water produced during the reaction in order to drive the reaction towards the product side. Cyclohexane was used as solvent for synthesis of EA and toluene for PA, BA and BzA. The reaction mixture was refluxed for 8 h at a temperature as presented in Table 1. The yields of the ester formed were determined by titrating the reaction mixture with 0.01 M alcoholic KOH solution and also by GC.

#### Synthesis of diesters (DOP and DBP)

For synthesis of DOP and DBP, a 100 mL round bottom flask, fitted with a Dean and Stark apparatus attached with a reflux condenser, was used. The mono ester was first prepared by taking phthalic anhydride (0.025 mol) with 2-ethyl-1-hexanol (0.025 mol) for DOP and butanol (0.025 mol) for DBP in the reactor and stirring the mixture at ~140°C for DOP and ~110°C for DBP for 10-15 min. The anhydride gets completely converted to the monoester, so that the acid concentration at this stage is taken as the initial concentration. However, esterification of the second carboxylic acid group is very slow and needs to be facilitated by acid catalyst and the removal of water produced during the reaction. Cyclohexane (20 mL) was used, as a solvent for water removal (azeotrope formation). The yield of the diester was determined by titrating the reaction mixture with 0.1 M alcoholic KOH solution.

Esterification reactions (monoesters and diesters) were carried out varying various parameters like temperature, time, mole ratio of reactants and the amount of the catalyst used so as to optimize the parameters.

## Results and Discussion

ZrPA was obtained as white hard granules, while ZrPC was obtained as fine white powder. Elemental analyses performed by ICP-AES show the ratio of Zr:P in ZrPA and ZrPC to be 1:2.

Table 1 — Yield (%) of mono and di- esters using ZrPA and ZrPC

| Ester | Catalyst | Catalyst amount (g) | Mole ratio       | Temp. (°C) | Time (h) | Yield (%) |
|-------|----------|---------------------|------------------|------------|----------|-----------|
| EA    | ZrPA     | 0.15                | 1.5 <sup>a</sup> | 80         | 8        | 78.3      |
|       | ZrPC     | 0.15                | 1.5 <sup>a</sup> | 80         | 8        | 7.9       |
| PA    | ZrPA     | 0.1                 | 1.5 <sup>a</sup> | 110        | 8        | 81.3      |
|       | ZrPC     | 0.1                 | 1.5 <sup>a</sup> | 110        | 8        | 18.8      |
| BA    | ZrPA     | 0.1                 | 1.5 <sup>a</sup> | 115        | 8        | 94.1      |
|       | ZrPC     | 0.1                 | 1.5 <sup>a</sup> | 115        | 8        | 41.8      |
| BzA   | ZrPA     | 0.1                 | 1.5 <sup>a</sup> | 115        | 8        | 100       |
|       | ZrPC     | 0.1                 | 1.5 <sup>a</sup> | 115        | 8        | 50.5      |
| DOP   | ZrPA     | 0.5                 | 2.5 <sup>b</sup> | 115        | 10       | 85.2      |
|       | ZrPC     | 0.5                 | 2.5 <sup>b</sup> | 115        | 10       | 28.3      |
| DBP   | ZrPA     | 0.1                 | 3.0 <sup>b</sup> | 115        | 10       | 9.5       |
|       | ZrPC     | 0.1                 | 3.0 <sup>b</sup> | 115        | 10       | 5.2       |

<sup>a</sup>Acid/Alcohol; <sup>b</sup>Alcohol/Anhydride

The absence of any sharp peaks in the X-ray diffractogram for ZrPA (Fig. 1) indicates the amorphous nature of the materials. In case of ZrPC (Fig. 2), sharp peaks are obtained confirming the crystalline nature of the material.

The FTIR spectra of both the materials (Figs 3, 4) exhibit a broad band in the region  $\sim 3400\text{ cm}^{-1}$  attributed to asymmetric and symmetric  $-\text{OH}$  stretches. A sharp medium band at  $1635\text{ cm}^{-1}$  is attributed to aquo ( $\text{H}-\text{O}-\text{H}$ ) bending. A band in the region  $\sim 1035\text{ cm}^{-1}$  is attributed to the presence of  $\text{P}=\text{O}$  stretching. A medium intensity band at  $1400\text{ cm}^{-1}$  is attributed to the presence of  $\delta(\text{POH})^{24}$ .

TGA of ZrPA indicates two weight loss regions. The first weight loss region  $\sim 13\%$  up to  $180^\circ\text{C}$  is attributed to loss of moisture/hydrated water. The second weight loss in the range  $250\text{--}500^\circ\text{C}$  is attributed to condensation of structural hydroxyl groups. Beyond this temperature no weight loss is observed up to  $800^\circ\text{C}$ .

TGA of ZrPC indicates two weight loss regions. The first weight loss region  $\sim 1.04\%$  up to  $180^\circ\text{C}$  is attributed to loss of moisture/hydrated water. The second weight loss region  $\sim 9.7\%$  up to  $800^\circ\text{C}$  is attributed to condensation of structural hydroxyl groups.

The surface area of ZrPA and ZrPC is found to be  $282.17\text{ m}^2/\text{g}$  and  $2.722\text{ m}^2/\text{g}$  respectively. The surface acidity for ZrPA and ZrPC is found to be  $2.34\text{ mmol/g}$  and  $0.96\text{ mmol/g}$ , respectively.

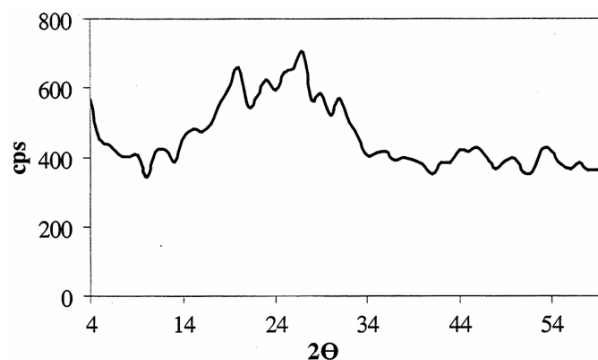


Fig. 1 — XRD of ZrPA.

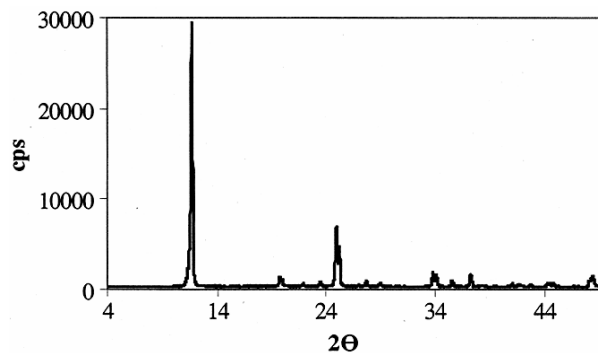


Fig. 2 — XRD of ZrPC.

Based on the elemental analysis (ICP-AES) and TGA data, ZrPA and ZrPC have been formulated as  $\text{Zr}(\text{HPO}_4)_2 \cdot 2.5\text{H}_2\text{O}$  and  $\text{Zr}(\text{HPO}_4)_2 \cdot 0.75\text{H}_2\text{O}$  using the Alberti and Torracca formula<sup>25</sup>.

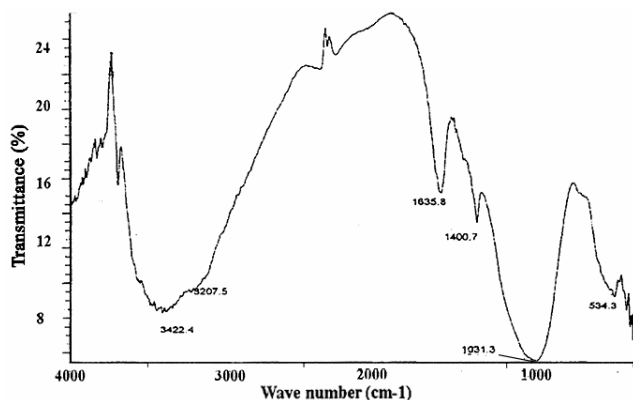


Fig. 3 — FTIR of ZrPA.

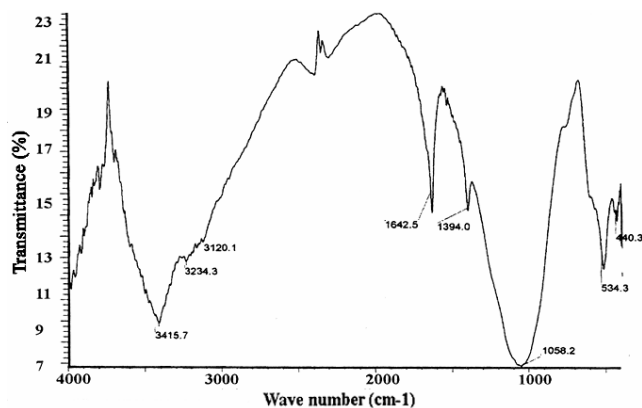


Fig. 4 — FTIR of ZrPC.

ZrPA and ZrPC are found to be stable in acid medium, maximum tolerable limits being ( $\text{H}_2\text{SO}_4 \sim 36\text{ N}$ ,  $\text{HNO}_3 \sim 16\text{ N}$  and  $\text{HCl} \sim 10\text{ N}$ ) and also stable in organic solvent media (ethanol, benzene, acetone, acetic acid, etc.). They are however not so stable in basic medium, maximum tolerable limits being ( $5\text{ N}$  in  $\text{NaOH}$  and  $\text{KOH}$ ).

#### Synthesis of esters

Esterification is a reversible reaction with low equilibrium constant. Based on Le Chatlier's principle, any equilibrium reaction can be driven to the product side by controlling the concentration of one of the reactants or the products. This can be achieved either by continuous removal of one component (product/byproduct) or the use of large excess of another (reactant).

It is observed that in all the cases, ester is almost the unique product. The esterification of EA, PA and BA in the absence of catalyst<sup>26</sup> exhibit poor yields. However, for BzA (with an excess of acetic acid and in the absence of any catalyst), the yield is as high as

90.6% which can be attributed to autocatalysis. In another report<sup>23</sup>, high yields of BzA were obtained with small amount of the catalyst but the reaction time was relatively high.

Yields of esters obtained at optimum operating conditions are presented in Table 1. Relatively higher amount of catalyst is required to get optimum yield in the case of EA. Equilibrium constants of lower magnitude, for the reaction of ethyl alcohol with acetic acid can explain this. For PA, BA and BzA, the amount of catalyst used per mole of alcohol is 2 g, which is lower as compared to zeolites<sup>26</sup> used to carry out the same reaction. As expected, the yields of monoesters were found to be higher in reaction mixtures having one of the reactants in excess. In particular esterification reaction being an acid catalyzed reaction, the yields were highest when acetic acid was present in excess in the reaction mixture<sup>27</sup>. In the present work, using Zr (IV) phosphates, good yields of monoesters are obtained with lesser amount of catalysts accompanied by low reaction temperature and time.

DOP formation has been catalyzed by zeolites<sup>26</sup>, metallic oxides<sup>28</sup>, solid super acids<sup>6,29</sup>, and heteropoly acids<sup>6,30</sup>. Suter<sup>31</sup> has reported a non-catalytic process for the synthesis of DOP at very high temperatures, at which autocatalysis occurs. When homogeneous liquid acids are used as catalysts for synthesis of DOP and DBP, a coloured product of poor quality is produced. In the present investigations, diester (a colourless unique product) could be produced.

From the data presented in Table 1, it is clear that yield of esters depend on several factors, acidity of the catalyst being the predominant one. However, the effect of nature and amount of alcohol should not be ignored. Esterification yield of 2-ethylhexanol in the present studies is higher than that of 1-butanol due to higher boiling point of the former alcohol and consequently higher reaction rate<sup>11</sup>. The effect of temperature on diester formation under otherwise similar conditions has also been studied in the range of 95-115°C. It has been found that the conversion increases with temperature. Low yields of mono and di-esters are obtained in case of ZrPC as compared to ZrPA. This is due to considerably low surface acidity and surface area of ZrPC, compared to ZrPA.

Thus, ZrPA and ZrPC exhibit good thermal and chemical resistivity, which is characteristic of a good solid acid catalyst. However, % yields of monoesters and diesters obtained are higher in case of ZrPA

compared to ZrPC which may be attributed to higher surface acidity and surface area in case of ZrPA as compared to ZrPC. ZrPA could be further explored as a solid acid catalyst.

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