

### Short Communication

## A comparative study of the Bronsted acidity of zirconium phosphate and zirconium phenyl phosphonate

B Beena & Uma Chudasama\*

Department of Chemistry, Faculty of Science,  
M S University of Baroda, Baroda 390 002, India

Received 6 March 1995; accepted 26 June 1995

Amorphous inorganic ion exchanger zirconium phosphate and its phenyl derivative, zirconium phenyl phosphonate have been prepared and characterised. The protons of the hydroxyl groups are found to be the active sites. Such materials indicate good potential for Bronsted acid catalysis. Esterification has been studied as a model reaction wherein ethyl acetate has been prepared. It has been observed that zirconium phenyl phosphonate behaves as a better Bronsted acid catalyst as compared to zirconium phosphate.

Inorganic ion exchangers show good potential in Bronsted acid catalysis because of the presence of surface hydroxyl protons<sup>1-4</sup>. 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. These compounds appear to be structurally identical with the parent inorganic compound<sup>5,6</sup>. The phenyl derivative of zirconium phosphate, namely zirconium phenyl phosphonate can be prepared by replacing the *p*-OH group by *p*-C<sub>6</sub>H<sub>5</sub> group. Crystalline zirconium phenyl phosphonate has already been prepared<sup>5</sup>. The present work reports the synthesis and characterisation of amorphous forms of zirconium phosphate and zirconium phenyl phosphonate. Their efficiency in acid catalysis has been compared by carrying out esterification as a model reaction.

**Experimental procedure**—Zirconium phosphate (ZP) was prepared by mixing aqueous solutions of zirconium oxychloride and trisodium orthophosphate in 1:2 mole ratio while zirconium phenyl phosphonate (ZPP) was prepared by mixing aqueous solutions of zirconium oxychloride and phenyl phosphonic acid in 1:2 mole ratio. The materials obtained were

sized by sieving to 30-60 mesh size and converted to the hydrogen form by immersion in 1 M HCl.

As a model esterification reaction, ethyl acetate was prepared using both ZP and ZPP as catalysts. Reactions were carried out by varying the amount of catalyst (from 0.5 to 2 g) and mole ratio of ethyl alcohol and acetic acid (1:1 and 1:2). The amount of ester formed was monitored on a gas chromatograph.

In the sample ZP, both zirconium and phosphate were determined gravimetrically as zirconium oxide and magnesium pyrophosphate, respectively. ZPP was analysed for zirconium gravimetrically as zirconium oxide after dissolving the sample in HF and phosphorus was determined by the molybdate method, after converting the phosphonate to phosphate. The carbon and hydrogen contents were estimated on a Coleman Analyser. The Na<sup>+</sup> exchange capacity of the materials were determined as usual by the column method. The FTIR spectra were obtained on a Perkin Elmer FTIR model 1720. TGA of the samples were performed on a Shimadzu DT-30 thermal analyser. The effect of heating on i.e.c. of the samples was studied at different temperatures. The surface areas of samples were measured by the BET method and recorded on a Carlo Erba Sorptomatic series-1800 at -196°C.

**Results and discussion**—The chemical analysis indicates the composition of ZP as Zr: PO<sub>4</sub> as 1:2. For ZPP, the analysis data (Found: C, 33.5; H, 3.35; P, 15.2; Zr, 22.2% and theoretical: C, 32.8; H, 3.19; P, 14.1; Zr, 20.8%) agrees with the suggested formulation Zr(OH)<sub>2</sub>(O<sub>3</sub>PC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>. The Na<sup>+</sup> exchange capacity for ZP and ZPP were found to be 1.01 and 1.60 meq/g, respectively. This is a direct indication for the presence of exchangeable protons.

FTIR spectra of both ZP and ZPP show bands in the region ~3400 and ~1620 cm<sup>-1</sup> 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 spectrum of ZPP shows bands in the region between 900-675 cm<sup>-1</sup> characteristic of aromatic compounds resulting from the out of plane bending of the C-H bonds. Also in plane bending bands occur in the region 1300-1000 cm<sup>-1</sup> and C=C ring stretches appear in the region ~1460 cm<sup>-1</sup>.

The TGA of ZP shows sharp changes within the temperature range of 100-150°C corresponding to the loss of external water molecules, after which a

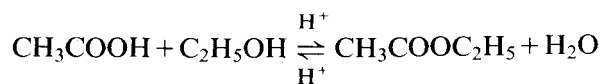
\*Author to whom all correspondence should be addressed.

slow change in weight is observed till 600°C. This may be due to the condensation of structural hydroxyl groups.

TGA of ZPP also shows a gradual weight loss upto 400°C which may be due to the loss of surface moisture and constitutional water molecules. The decomposition of the organic moiety occurs within the temperature range of 400-500°C. Further, it is seen that for ZP, the exchange capacity decreases continuously from 1.01 to 0.10 meq/g on heating up to 600°C. This is due to the condensation of structural hydroxyl groups. But for ZPP, exchange capacity decreases upto 300°C, and then increases for samples heated at 400 and 500°C. Again for samples heated upto 600°C, it decreases. This behaviour may be due to the fact that on heating in the range 400-500°C, the oxidation of the organic part in the compound gives H<sub>2</sub>O and CO<sub>2</sub> due to which extra -OH groups are formed and hence exchange capacity increases.

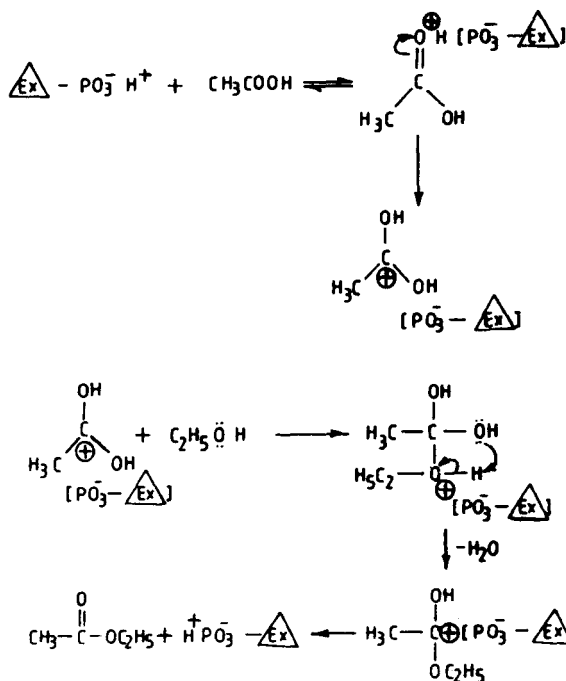
The surface areas of ZP and ZPP were found to be 48 and 187 m<sup>2</sup>/g respectively.

Esterification of carboxylic acid is a reaction subject to general Bronsted acid catalysis and the reaction of ethyl alcohol with acetic acid was selected as a model reaction.



It was found that, the yield of ethyl acetate increased by increasing the amount of catalyst and the acid concentration. However, maximum yields were obtained when the amount of the catalyst taken was 2 g and alcohol to acid proportion was 1:2. The yield of ethyl acetate was higher for ZPP in all the cases. The maximum yield for ZPP was 56% while that for ZP, was only 39%.

The better yield with ZPP compared to ZP could be attributed to the presence of the electron withdrawing phenyl group in ZPP which makes the acidic protons more labile, thereby, making it a better Bronsted acid catalyst. The surface area of ZPP is also higher as compared to ZP. Thus anchoring of organic groups improves the acidic properties of the inorganic ion exchanger. The mechanism for the above reaction using the ion exchanger as a Bronsted acid catalyst could be represented as shown below:



Ex - Represents the polymeric ion exchanger.

PO<sub>3</sub><sup>-</sup> - Represents phosphate functional groups in the exchanger.

In conventional methods where H<sub>2</sub>SO<sub>4</sub> is used as a catalyst for preparing the esters, the yields are high but traces of H<sub>2</sub>SO<sub>4</sub> are difficult to remove. The use of solid acid catalysts is 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 in Bronsted acid catalysis.

**Acknowledgement**—We express our sincere thanks to the Head, Department of Chemistry for providing necessary laboratory facilities. One of us (BB) is also thankful to the UGC, New Delhi for the award of a fellowship.

## References

- Hattori T, Ishiguro A & Marukami Y, *J Inorg Nucl Chem*, 40 (1979) 1107.
- Clearfield A & Thakur D S, *J Catal*, 65 (1980) 185.
- Shivaneekar A & Chudasama U V, *Recent developments in catalysis*, edited by Vishwanathan B & Pillai C N (Narosa Publishing House, New Delhi), 1990, 489.
- Patel P, Shivaneekar A & Chudasama U V, *Indian J Chem*, 31A (1992) 803.
- Alberti G, Costantino U, Alluli S & Tomassini N, *J Inorg Nucl Chem*, 40 (1978) 1113.
- Alberti G, Costantino U & Luciani M L, *J Chromatogr*, 180 (1979) 45.