

Synthesis of monoesters and diesters using eco-friendly solid acid catalysts- M(IV) tungstates and phosphates

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The present study involves synthesis and characterization of amorphous M(IV) phosphates and tungstates [M(IV) = Zr, Ti and Sn] which are inorganic ion exchangers of the class of tetravalent metal acid (tma) salts. The presence of protons contained in the structural hydroxyl groups indicates good potential for application in solid acid catalysis. The catalytic activity of the materials abbreviated as ZrP, TiP, SnP, ZrW, TiW and SnW has been explored by synthesizing some monoesters and diesters. Good yields are obtained in the case of monoesters as compared to diesters. The results reveal the promising use of tma salts as solid acid catalysts.

Keywords: Solid acid catalyst, Esterification, M(IV) phosphates and tungstates, Tetravalent metal acid salts, Inorganic ion exchangers

In recent years the major trend in catalysis research has been finding catalysts that are environmental friendly. Esterification is an industrially important reaction for synthesis of drug intermediates, polymer processing additives, dye stuff and fine chemical intermediates. The conventional catalyst used in esterification reactions is sulphuric acid¹ cited as a potential environmentally hazardous chemical, posing several disadvantages in industrial processes, which include wasting large amount of catalyst, corroding reactors, causing an acidic waste water, difficulty of catalyst recovery etc. In view of the deficiencies encountered, there is a global effort to replace the conventional homogeneous liquid acids by heterogeneous solid acids. They possess high catalytic activity and selectivity, do not corrode reaction vessels or reactors and finally, repeated use of solid acid catalyst for reaction is easy.

Esterification reactions have been widely investigated using several solid acids²⁻¹⁰. To mention a few, sulphated zirconia, zeolites, sulphonic acid based resins, heteropoly acids, sulphated zirconia is a very good esterification metal oxides etc. However, it has been observed that though sulphated zirconia is a very good catalyst, it gets easily deactivated by losing the sulphate ions and thereby recycling of the catalyst is restricted. In case of heteropoly acids, the separation is difficult and when supported on carbon

the activity decreases. Sulphonic acid based resin (Nafion-H) has also been found to be unsatisfactory due to its low operating temperature. Manohar *et al.*¹¹ have reported the use of ZrO₂ impregnated with molybdenum and tungsten as solid acids for esterification reactions.

Inorganic ion exchangers of the class of tetravalent metal acid (Tma) salts indicate good potential for application as solid acid catalysts. These materials possess the general formula M (IV) (HXO₄)₂.nH₂O, where M(IV) = Zr, Ti, Sn, Th, Ce etc. and X=P,W, Mo, As, Sb etc. They behave as cation exchangers due to the presence of exchangeable protons contained in the structural hydroxyl groups. Tma salts are synthesized by sol gel technique. Tma salts with varied acid strength can thus be obtained by altering several parameters such as M:X ratio (M=metal ion, X= anion), their concentration, rate and mode of mixing, temperature, pH etc. These materials can be obtained in both amorphous and crystalline forms. Crystalline forms are obtained by refluxing the gels in concentrated mineral acids for long periods. It is, however, observed that with increasing crystallinity both surface area and surface acidity decreases¹². These materials are granular in nature, can be obtained in a range of mesh sizes, offer great promise in preparative reproducibility and thermo-chemical stability.

Earlier, esterification reactions have been reported from this laboratory¹³⁻¹⁷ using tma salts as catalysts. However, it was only aimed at showing the feasibility of these materials as potential solid acid catalysts. In the present work, amorphous inorganic ion exchangers of the class of tma salts, the phosphates and tungstates of tetravalent zirconium, titanium and tin abbreviated as ZrP, TiP, SnP, ZrW, TiW and SnW respectively have been synthesized by modified sol gel method. The compounds have been characterised for elemental analysis (ICP-AES), spectral analysis (FTIR), thermal analysis (TGA), XRD, surface area measurement (BET method) and surface acidity (ammonia TPD). Ion exchange capacity(iec) of the materials have been determined by column method. The potential use of these materials as solid acid catalysts has been explored by studying esterification as a model reaction, wherein mono esters 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 synthesised.

Experimental Procedure

Synthesis of M(IV) phosphates and tungstates

M (IV) phosphates and tungstates were prepared by sol-gel method. Aqueous solution (0.2 M, 100 mL) of sodium dihydrogen phosphate or sodium tungstate was added drop wise to an aqueous solution (0.1 M, 100 mL) of zirconium oxy chloride or titanium tetrachloride or stannic tetrachloride with continuous stirring, maintaining the resultant solution temperature at 70°C and pH ~2. A gel was formed and the solution along with the gel was further stirred for an hour. The gel was filtered, washed with conductivity water till free of chloride ions and dried at room temperature. The dried material was brought to the desired particle size (50-60 mesh) and sorted by sieving. The material was finally converted to the acid form by immersing in 1 M HNO₃ solution for 30 min, the acid being intermittently replaced, washed with conductivity water till free of acid and dried at room temperature.

Characterisation

The Na⁺ exchange capacity (IEC) was determined using column method¹⁸. 500 mg of the acid treated catalyst was transferred to a column. The water inside the column was kept at a level of about 1 cm above the material. A 250 mL solution of sodium acetate (0.5 M) was allowed to pass through the column at a

flow rate of 0.5 mL/min. The effluent was collected in a 500 mL conical flask and titrated against standard alkali solution to find out the total H⁺ ions eluted. The exchange capacity (in meq.g⁻¹) was evaluated using the formula aV/W , where a is molarity and V the volume of alkali used during titration, and W is the weight of the catalyst. Elemental analysis was carried out by ICP-AES. Thermogravimetric analysis of the materials was performed on a Shimadzu DT-30 thermal analyzer at a heating rate of 10°C/min. DSC of the samples were performed on Mettler TA 4000 system at a heating rate of 20°C/min. FTIR spectra of the sample were performed using KBr wafer on a Bomem M.B.series with Epson Hi 80 printer/plotter. X-ray diffractograms ($2\theta=5-90^\circ$) were obtained on X-ray diffractometer (Rigaku-Dmax-30)with Cu-K α radiation and Nickel filter. Surface area measurement (BET method) was carried out on Carlo Erba Sorptomatic Series 1800 at -196°C using nitrogen adsorption isotherms. Surface acidity was determined on Chemisorb 2720, by a temperature programmed desorption of ammonia. Ammonia was chemisorbed at 120°C and then desorption was carried out up to 700°C at a heating rate of 10°C/min.

Synthesis of mono esters

In a typical reaction, a 100 mL round bottomed flask equipped with a Dean and Stark apparatus, attached to a reflux condenser was charged with acetic acid (0.075 mol), alcohol (0.05 mol), catalyst (0.1 g) and 10-15 mL of a suitable solvent. Cyclohexane was used as solvent for synthesis of ethyl acetate and toluene for propylacetate, butyl acetate and benzyl acetate. The reaction mixture was refluxed for 8 h at a temperature as presented in Tables 2 and 3. The yields of the ester formed were determined by titrating the combined liquid with 0.1 M KOH-EtOH solution. The yield of the esters were calculated using the formula: % yield= [(A-B)/A]× M × 100 where A=acid value of the sample before reaction, B=acid value of sample withdrawn after reaction and M=mole ratio of acid :alcohol. The yield of ester formed were also determined using GC.

Synthesis of diesters

For synthesis of DOP and DBP a 100 mL round bottomed flask was used fitted with Dean and Stark apparatus, with a condenser to remove water formed during the reaction. The mono ester was first prepared by taking phthalic anhydride (0.025 mol) and 2-ethyl 1-hexanol (0.025 mol) for DOP and butanol

(0.025 mol) for DBP in the reactor and stirring the mixture at $\sim 140^\circ\text{C}$ for DOP and $\sim 110^\circ\text{C}$ for DBP for about 10-15 min. The anhydride gets completely converted to the mono ester, so that the acid concentration at this stage is taken as the initial concentration. Diester formation starts only after the addition of second mole (0.025 mol) of alcohol and catalyst (0.15-0.2 g). The mixture was refluxed for 8-10 h during which the acid concentration kept on decreasing. The yield of the diesters formed was determined by titrating the reaction mixture with 0.1 M KOH-EtOH solution and also by GC.

Results and Discussion

Catalyst characterisation

Data on catalyst characterization has been presented in Table 1. It is found that the ratio of M (IV) to P or W is 1:2 in all materials (Table 1). Absence of sharp peaks in X-ray diffractogram reveals the amorphous nature of the material. The FTIR spectra show broad bands in the region $\sim 3400\text{ cm}^{-1}$ attributed to asymmetric and symmetric -OH stretching. A medium band around $\sim 1620\text{ cm}^{-1}$ is attributed to aquo H-O-H bending. This indicates the presence of structural hydroxyl protons in these materials. This fact is more evident from the IEC values that have been evaluated. The Na^+ exchange capacity of the material was found to be in the range of ~ 1.5 to 3.0 meq./g (Table 1). In general, IEC values decrease on heating, attributed to condensation of structural hydroxyl groups at higher temperature. This fact is more evident from the FTIR spectra of the heated samples. It is seen that the intensity of the peak at $\sim 3400\text{ cm}^{-1}$ and 1620 cm^{-1} representative of the -OH group diminishes as heating temperature increases. TGA indicates $\sim 15\%$ weight loss in the temperature range of $100\text{-}180^\circ\text{C}$ corresponding to the loss of water molecules, after which a gradual weight loss is observed till 600°C . This may be due to the condensation of structural hydroxyl groups. DSC indicates endothermic peak at $\sim 132^\circ\text{C}$, which is attributed to the presence of water. There is no peak up to 500°C , which indicates that there is no phase change. Surface area (m^2/g) of ZrP, SnP, TiP, SnW, TiW and ZrW and surface acidity in terms of

micromoles of ammonia gas desorped are presented in Table 1. Based on the characterization of these materials it can be inferred that the materials possess structural hydroxyl groups indicating potential utility of these materials as solid acid catalysts.

Synthesis of monoesters

Equilibrium constants of the esterification reactions are low. In order to obtain higher yield of esters, the reaction must be forced to completion by either removing the water produced or by operating with an excess of one of the two reactants acid or alcohol. Following this principle, in the present work, for esterification, acid was taken in excess (mole ratio of acid: alcohol was 1.5:1). Solvents cyclohexane and toluene were employed to remove the water formed during the reaction as a binary azeotrope, so that reverse reaction is avoided. Monoesters EA, PA, BA and BzA were synthesized as described in experimental section. Esterification reactions were carried out varying the amount of catalyst, mole ratio of the alcohol to acid, reaction time and temperature. The parameters have been optimized in case of ZrP (Table 2) and results obtained (optimum condition) for all catalysts have been presented in Table 3.

Esterification of monoesters EA, PA and BA has been reported¹⁹ in absence of catalyst and exhibit poor yields. Therefore catalyst is a must for these reactions. In case of BzA however, it is observed that with an excess of acetic acid and in the absence of any catalyst the yield is as high as 90.6% which is attributed to auto catalysis. In another report²⁰ high yields of BzA were obtained with small amount of the catalyst but the reaction time was relatively high. As observed in Table 2, the yields of the monoesters are always high when acid is taken in excess. Apart from driving the equilibrium towards product side, the excess acid catalyses the reaction. Amongst mono esters, higher yields of benzyl acetate is obtained which could be attributed to an enhanced nucleophilicity due to presence of aromatic ring in benzyl alcohol.

In the present work, relatively higher amount of catalyst is required to get optimum yield in the case of

Table 1— Characterization of the catalysts

| Catalyst | ZrP | TiP | SnP | ZrW | SnW | TiW |
|--|------|------|------|------|------|------|
| Elemental analysis (M:P/W) | 1:2 | 1:2 | 1:2 | 1:2 | 1:2 | 1:2 |
| Surface area (m^2/g) | 68 | 59 | 141 | 109 | 14 | 13 |
| Surface acidity (mmoles) | 2.34 | 0.59 | 1.81 | 0.64 | 0.77 | 0.89 |
| IEC (meq./g) | 3.09 | 2.77 | 2.96 | 1.32 | 1.52 | 1.95 |

Table 2— Optimisation of reaction conditions for mono esters using ZrP

| Substrates (Mole ratio) | Product | Catalyst amount (g) | Reaction time (h) | Reaction temp. (°C) | % Yield |
|-----------------------------------|---------|---------------------|-------------------|---------------------|---------|
| Ethanol+Acetic acid(1:1) | EA | 0.05 | 1 | 80 | 15.4 |
| Ethanol+Acetic acid(1:1) | EA | 0.05 | 2 | 80 | 22.7 |
| Ethanol+Acetic acid(1:1) | EA | 0.05 | 3 | 80 | 29.1 |
| Ethanol+Acetic acid(1:1) | EA | 0.05 | 4 | 80 | 34.1 |
| Ethanol+Acetic acid(1:1) | EA | 0.05 | 5 | 80 | 36.2 |
| Ethanol+Acetic acid(1:1) | EA | 0.05 | 6 | 80 | 38.1 |
| Ethanol+Acetic acid(1:1) | EA | 0.05 | 7 | 80 | 39.2 |
| Ethanol+Acetic acid(1:1) | EA | 0.05 | 8 | 80 | 40.1 |
| Ethanol+Acetic acid(1:1) | EA | 0.1 | 8 | 80 | 60.2 |
| Ethanol+Acetic acid(1:1.5) | EA | 0.1 | 8 | 80 | 70.3 |
| Ethanol+Acetic acid(1:1.5) | EA | 0.15 | 8 | 80 | 78.3 |
| Ethanol+Acetic acid(1.5:1) | EA | 0.15 | 8 | 80 | 68.2 |
| Ethanol+Acetic acid(1:1.5) | EA | 0.15 | 8 | 110 | 77.4 |
| Propanol+Acetic acid(1:1) | PA | 0.1 | 8 | 110 | 64.1 |
| Propanol+Acetic acid(1:1.5) | PA | 0.1 | 8 | 110 | 81.3 |
| Propanol+Acetic acid(1.5:1) | PA | 0.1 | 8 | 110 | 60.8 |
| Propanol+Acetic acid(1:1.5) | PA | 0.1 | 8 | 130 | 77.4 |
| Butanol+Acetic acid(1:1) | BA | 0.1 | 8 | 110 | 65.1 |
| Butanol+Acetic acid(1:1.5) | BA | 0.1 | 8 | 110 | 94.1 |
| Butanol+Acetic acid(1.5:1) | BA | 0.1 | 8 | 110 | 62.1 |
| Butanol+Acetic acid(1:1.5) | BA | 0.1 | 8 | 130 | 85.1 |
| Butanol+Acetic acid(1:1.5) | BA | 0.15 | 8 | 110 | 92.7 |
| Benzy alcohol+Acetic acid (1:1.5) | BzA | 0.1 | 8 | 110 | 95.2 |
| Benzy alcohol+Acetic acid (1:1.5) | BzA | 0.1 | 8 | 115 | 100 |
| Benzy alcohol+Acetic acid (1:1.5) | BzA | 0.15 | 8 | 130 | 98.2 |

EA. Equilibrium constant 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 zeolites¹⁹ used to carry out the same reaction (3 g per mol of alcohol).

Synthesis of diesters

The parameters have been optimized in case of ZrP (Table 4) and results obtained (optimum condition) for all catalysts have been presented in Table 5. In the present work the yields of DOP are higher than DBP which could be attributed to higher boiling point of 2 ethyl 1 hexanol compared to 1-butanol. When the boiling point of the alcohol is less than the temperature of the reaction, most of the alcohol will

end up in the vapour phase and not be available in the liquid phase. This is the reason why the heavier alcohols react more than the lighter ones. The same reason could be forwarded for the yields in case of monoesters EA<PA<BA.

DOP formation has been catalysed by zeolites¹⁹, metallic oxides²¹, solid super acids^{22,23} and heteropoly acids^{23,24}. Suter²⁵ has reported a non-catalytic process for the manufacture of DOP, at very high temperatures, at which autocatalysis occurs.

In the present work, it is observed that yields of DOP and DBP are low as compared to those obtained when zeolites¹⁹ and solid super acids^{22,23} were used as catalysts. When homogeneous liquid acids are used as

Table 3—% Yield of monoesters using M(IV) phosphates and tungstates

| Ester | ZrP | TiP | SnP | ZrW | TiW | SnW |
|-------------------|------|------|------|------|------|------|
| EA ^a | 78.3 | 76.1 | 89.5 | 93.6 | 71.9 | 96.7 |
| (0.15 g catalyst) | | | | | | |
| Temp.80°C | | | | | | |
| PA ^b | 81.3 | 70.0 | 79.9 | 72.8 | 71.5 | 93.5 |
| (0.1 g catalyst) | | | | | | |
| Temp.110°C | | | | | | |
| BA ^b | 94.1 | 63.1 | 83.8 | 72.9 | 98.6 | 83.7 |
| (0.1 g catalyst) | | | | | | |
| Temp.115°C | | | | | | |
| BzA ^b | 100 | 82.3 | 100 | 67.4 | 93.8 | 100 |
| (0.1 g catalyst) | | | | | | |
| Temp.115°C | | | | | | |

^a=3 g, ^b=2 g catalyst per mol of alcohol

catalysts for synthesis of DOP and DBP, the result is a product that is coloured and of a poor quality. In the present work though the yields of diesters obtained are low, the advantage is that the diester is the unique product and colourless.

Catalyst regeneration and reuse

The catalyst was regenerated by washing it several times with 1M HNO₃. The activity of the regenerated catalyst was however low. During the course of the reaction, the catalyst colour changes from white to light grey. This is probably due to the reacting molecules coming on to the surface of the catalyst. The catalyst however regains its original colour when treated with acid for regeneration. The possibility of molecules entering the interstices of the catalyst cannot be ruled out, which is observed from the fact that yields go down after regeneration, leading to deactivation of the catalyst.

Table 4—Optimisation of reaction conditions for di esters using ZrP

| Substrates (Mole ratio) | Product | Catalyst amount (g) | Reaction time (h) | Reaction temp. (°C) | % Yield |
|---|---------|---------------------|-------------------|---------------------|---------|
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.5) | DOP | 0.5 | 1 | 115 | 56.7 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.5) | DOP | 0.5 | 3 | 115 | 66.4 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.5) | DOP | 0.5 | 5 | 115 | 73.4 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.5) | DOP | 0.5 | 10 | 115 | 85.2 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.5) | DOP | 0.5 | 10 | 95 | 65.1 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.5) | DOP | 0.3 | 10 | 95 | 62.8 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.5) | DOP | 0.1 | 10 | 95 | 62.1 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2) | DOP | 0.1 | 10 | 95 | 49.6 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.1) | DOP | 0.1 | 10 | 95 | 57.6 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.2) | DOP | 0.1 | 10 | 95 | 58.9 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.3) | DOP | 0.1 | 10 | 95 | 59.1 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.4) | DOP | 0.1 | 10 | 95 | 59.1 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.5) | DOP | 1 | 10 | 95 | 68.2 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.5) | DOP | 0.5 | 10 | 105 | 66.4 |
| Phthalic anhydride+2 ethyl 1 hexanol (1:2.5) | DOP | 0.5 | 10 | 115 | 85.2 |
| Phthalic anhydride+ <i>n</i> -Butanol (1:2.5) | DBP | 0.5 | 10 | 115 | 9.5 |

Table 5—% Yield of diesters using M(IV) phosphates and tungstates

| Ester | Catalyst amount (g) | Mole ratio (Acid/alcohol) | Temperature (°C) | % Yield | Catalyst |
|-------------------|---------------------|---------------------------|------------------|---------|------------------|
| Dioctyl phthalate | 0.50 | 0.40 | 115 | 85.2 | ZrP ^b |
| | 0.15 | 0.45 | 155 | 65.2 | SnP ^a |
| | 0.15 | 0.55 | 155 | 51.7 | TiP ^b |
| | 0.15 | 0.55 | 155 | 60.6 | ZrW ^b |
| | 0.10 | 0.55 | 155 | 58.2 | SnW ^a |
| | 0.10 | 0.42 | 115 | 30.7 | TiW ^b |
| Dibutyl phthalate | 0.10 | 0.33 | 115 | 9.5 | ZrP ^b |
| | 0.10 | 0.55 | 155 | 56.1 | SnP ^a |
| | 0.10 | 0.55 | 155 | 42.3 | TiP ^b |
| | 0.10 | 0.50 | 155 | 19.6 | ZrW ^b |
| | 0.20 | 0.50 | 115 | 24.6 | SnW ^a |
| | 0.20 | 0.55 | 115 | 19.5 | TiW ^a |

Reaction time: ^a=8 h, ^b=10 h

Conclusion

The protons present in the structural hydroxyl groups in M (IV) phosphates and tungstates indicate good potential for their use as solid acid catalysts. This potential is revealed by carrying out esterification as a model reaction. However, several acid catalysed reactions should be investigated using the M(IV) phosphates and tungstates to establish their use as solid acid catalysts.

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