Tetravalent Metal Acid (TMA) salts as solid acid catalysts

"Tetravalent Metal Acid (TMA) salts" have been researched since the last 50 years, and have emerged as promising advanced materials owing to their good thermal stability, chemical resistivity, resistance towards ionizing radiations, and found important applications in the area of ion exchange, catalysis and solid state proton conduction. An extensive literature on TMA salts exists today, which have been reviewed and detailed in four books.

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Systematic studies on their synthesis, structure elucidation and applications in the area of separation science, catalysis and solid electrolytes have been carried out by various groups – Dr. A. Clearfield (USA), Dr. G. Alberti, Dr. U. Costantino (Italy), Dr. D. Whittaker (UK), Dr. W. H. J. Hogarth (Australia), late Dr. M. Qureshi and Dr. K. G. Varshney (Aligarh Muslim University, India) and Dr. U. V. Chudasama (The M. S. University of Baroda, India).

Salient features of TMA salts

- TMA salts are cation exchangers, possessing the general formula M(IV) $(HXO_4)_2.nH_2O$, where M(IV) = Zr, Ti, Sn, Ce, Th etc. and X = P, Mo, As, Sb, W etc.
- The materials possess structural hydroxyl groups, the H^+ of the –OH being the exchangeable sites, due to which the material possesses cation exchange properties.
- TMA salts can be prepared both in amorphous and crystalline forms that exhibit selectivity for certain metal ions.

- The materials possess granular nature and can be obtained in a range of mesh sizes, very suitable for column operations.
- The materials are generally hard and range in physical appearance from totally opaque to transparent.
- TMA salts have shown a great promise in preparative reproducibility and ion exchange behaviour.
- TMA salts exhibit both thermal and chemical stability.

When a tetravalent metal is treated with phosphoric acid/Na salts of phosphoric acid, M – O – P bonds are formed. In this process, a number of hydroxyl groups do not participate in the condensations which are referred to as pendant hydroxyl groups or defective P – OH, H^+ of the P – OH contributing to cation exchange [1]. Due to presence of structural hydroxyl protons in the TMA salts surface acidity is expected, giving rise to solid acid characteristics. Thus, TMA salts indicate good potential for application in solid acid catalysis.

TMA salts with varying water content, composition and crystallinity [2-5] can be synthesized by sol-gel route by varying conditions of synthesis viz. mole ratio of reactants M:X (M= tetravalent metal, X=polyvalent anion), temperature of mixing, mode of mixing (metal salt solution to anion salt solution or vice versa), rate of mixing and pH. Variation in any of these parameters, yields materials with different characteristics. It is observed that both surface area and surface acidity decreases with increasing crystallinity of the material. Hence their acidity can be tailored for a specific application by controlling the crystallinity of the material. The preparation procedure thus affects the structural hydroxyl groups, which is reflected in the performance of TMA salts as solid acid catalysts.

Acidity in TMA salts is explained based on a synergic effect – to be due to mutual/cooperative interaction between cation and an anion in the TMA salt. Acidity of a cation is related to ion size and charge. Ionic sizes of tetravalent metals are Ti^{4+} (0.74Å), Zr^{4+} (0.86Å) and Sn^{4+} (0.83Å). Ti^{4+} with smallest ionic radius (0.74Å), the positive charge is concentrated in a smaller area compared to Zr^{4+} (0.86Å) and Sn^{4+} (0.83Å), due to which tendency to polarize or severe the –OH bond (structural –OH groups in anionic part of TMA salt) exhibits the order $Ti^{4+} > Sn^{4+} > Zr^{4+}$. The cation exchange capacity

(CEC) and hence protonating ability/surface acidity also follows this order. Thus, the size and charge on the cation has an influence on the surface acidity of the materials.

The structural hydroxyl protons are provided from anionic part (PO_4^{3-} or WO_4^{2-}) of the TMA salt. Greater the number of H^+ provided/present in anionic part greater will be the number of H^+ that can be released or available. Thus acidity in TMA salt is a synergic effect.

TMA salts have been used as catalysts in various organic transformations by various groups - Dr. A. Clearfield (USA), Dr. G. Alberti (Italy), Dr. W. Holderich (Germany), Dr. D. Whittaker (UK) and Dr. U. V. Chudasama (The M. S. University of Baroda, India).

A wide variety of organic transformations using TMA salts as solid acid catalysts have been reported from our laboratory. These include esterification [6-15], dehydration of alcohols [16,17], hydration of nitriles to amides [18], ketalization of ketones [19] and Pechmann condensation reactions [20].

The current focus towards synthesis of solid acid catalysts (SACs) is that catalytic activity/surface acidity should be high which can be retained for long periods of time with good chemical and thermal stability upto elevated temperatures and which can be regenerated and reused. The answer to these requirements is TMA salts. TMA salts have been discussed in detail in the foregoing pages.

There is currently high interest in engineering mixed materials leading to the formation of new solid-state/lattice structures resulting from cooperative interactions between the two interacting components, where there is a promise of developing new materials with properties not seen in the pure compound giving rise to composite as well as wide range of interesting properties. In this context, materials of the class of TMA salts i.e. compounds containing two different cations and an anion [tetravalent bimetallic acid (TBMA) salts] or two different anions and a cation [tetravalent metal bianionic acid (TMBA) salts] are interesting since they could exhibit improved properties in comparison to their single salt counterparts (TMA salts).

From our laboratory, mixed material of the class of tetravalent bimetallic acid (TBMA) salt - zirconium titanium phosphate (ZTP) has been synthesized by sol gel route in amorphous and crystalline forms. The presence of protons contained in the structural hydroxyl groups of ZTP indicates good potential for application as solid acid catalysts. The potential use of ZTP as solid acid catalyst was explored by studying esterification as a model reaction wherein mono esters such as ethyl acetate, propyl acetate, butyl acetate and benzyl acetate and diesters such as dioctyl phthalate, diethyl malonate and dibutyl phthalate have been synthesized. The study shows, amorphous materials exhibit enhanced catalytic activity compared to crystalline materials and mixed material (ZTP) exhibited enhanced catalytic activity compared to their single salt counterparts [21].

Heteropoly acids (HPAs) are polyoxometallates made up of heteropoly anions having metal–oxygen octahedra as the basic structural unit. Heteropoly acids (HPAs) have proved to be the alternative for traditional acid catalysts due to both strong acidity and appropriate redox properties. The major disadvantage of HPAs, as catalyst lies in their low thermal stability, low surface area (1-10m^2/g) and separation problems from reaction mixture. HPAs can be made eco-friendly, insoluble solid acids, with high thermal stability and high surface area by supporting them onto suitable supports. The support provides an opportunity for HPAs to be dispersed over a large surface area which increases catalytic activity [22]. Acidic or neutral solids, which interact weakly with HPAs such as silica, active carbon and acidic ion-exchange resin, have been reported to be suitable as HPA supports. Recently, zirconia-supported heteropoly acids have attracted much attention as strong solid acid catalysts [23].

At this juncture, it is necessary to classify solid acid catalysts. In the present endeavour, solid acid catalysts are classified into two types.

Type – I: Solid acid catalysts possessing inherent acidity

The term “inherent” can be defined as, a property or character existing as natural or basic part in the constitution of the material. For e.g. TMA salts are solid acid catalysts possessing inherent acidity, since acidity is a natural or basic part in the material.

Type – II: Solid acid catalysts possessing induced acidity

The term “induced” is a process conducted/performed that leads to inducing a property. For e.g. Sulphated zirconia. ZrO_2 possesses negligible acidity. However, acidity can be induced into ZrO_2 by treating it with concentrated sulphuric acid to give sulphated zirconia.

Prompted by good surface acidity as well as thermal and chemical stability of materials of the class of TMA salts and enhanced catalytic activity observed in case of TBMA salts compared to single salts counter parts (TMA salts), it was thought of interest to explore the potential utility of mixed material of the class of Tetravalent Metal Bianionic Acid (TMBA) salts (containing two different anions and a cation) as solid acid catalyst with an aim to enhance surface acidity.

The present study is focused towards synthesis of M(IV) Phosphotungstates [M(IV)PWs where, M(IV)=Zr, Ti and Sn], mixed materials of the class of TMBA salts possessing inherent acidity (Type-I catalysts), such as Zr(IV) Phosphotungstate (ZrPW), Ti(IV) Phosphotungstate (TiPW) and Sn(IV) Phosphotungstate (SnPW) by sol-gel routes. Looking to the potential utility of supported HPAs and for a comparative catalyst performance, 12-Tungstophosphoric acid (12-TPA) ($H_3PW_{12}O_{40}$) has been supported onto ZrO_2, TiO_2 and SnO_2 by process of anchoring and calcination, resulting in 12-TPA/ZrO_2, 12-TPA/TiO_2 and 12-TPA/SnO_2 which possess induced acidity (Type-II catalysts) and also possess similar elemental components (i.e. Zr, Ti, Sn, P and W) as the TMBA salts. The catalytic activity/performance of synthesized materials (Type – I and Type – II catalysts) has been compared and correlated with acid properties of the materials towards few organic transformations.

The synthesized materials have been subjected to instrumental methods of characterization [elemental analysis (ICP-AES), thermal analysis (TGA), spectral analysis (FTIR), X-ray diffraction studies (XRD) and scanning electron microscopy (SEM)], and catalyst characterization [surface area measurements (BET method) and surface acidity (NH_3-TPD method)]. Chemical stability of all the synthesized materials has been assessed in various media (e.g. acids, bases and organic solvents etc) and in the media/environment where catalyst would operate. Further, the protonating ability [in terms of CEC] has been determined for M(IV)PWs (Type – I catalysts).

The potential utility of Type-I catalysts ZrPW, TiPW, SnPW [Inherent SACs - M(IV)PWs] and Type – II catalysts 12-TPA/ZrO_2-20, 12-TPA/TiO_2-20, 12-TPA/SnO_2-20 [Induced SACs - 12-TPA/M(IV)O_2-20], have been explored by studying following organic transformations as model reactions:

- ***Esterification*** *(Synthesis of monoesters and diesters)*
- ***Synthesis of coumarin derivatives via Pechmann condensation***
- ***Friedel-Crafts reactions***
- ***Acetalization of carbonyl compounds***

In all cases, reaction conditions have been optimized by varying parameters such as reaction time, reaction temperature, catalyst amount and mole ratio of the reactants. Catalytic performance of Type-I and Type-II catalysts have been compared at optimized condition and correlated with acid properties of the materials. The performance ability of the catalysts have also been assessed for regenerated/reactivated catalysts. In all cases, suitable mechanism has been proposed for solid acid catalyzed reaction.

Esterification (Synthesis of Monoesters and Diesters)

In the present study, monoesters ethyl acetate (EA), propyl acetate (PA), butyl acetate (BA), benzyl acetate (BzA) and diesters diethyl malonate (DEM), diethyl succinate (DES), dioctyl phthalate (DOP) and dibutyl phthalate (DBP) have been synthesized at optimized condition. In order to obtain higher yield of esters, Le Chatlier's Principle has been followed.

In case of synthesis of monoesters, the order of % yield/TON is observed to be BzA > BA > EA > PA. High yields of BzA obtained could be attributed to an enhanced nucleophilicity due to presence of aromatic ring in benzyl alcohol. When the boiling point of the alcohol is less than the temperature of the reaction, most of the alcohol will end up in the vapor phase and not be available in the liquid phase. This is the reason why heavier alcohols [1-butanol (118^{o}C)] react more than the lighter ones [ethanol (78^{o}C) and 1-propanol (97^{o}C)]. Further, yields are lower for PA compared to EA is attributed to the boiling point of 1-propanol (97^{o}C) which is less than the temperature of the reaction (110^{o}C).

In case of synthesis of diesters, the order of % yield/TON is observed to be DEM > DES > DOP > DBP. 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. This is the reason why the heavier alcohols react more than the lighter ones as explained above. Further, higher yields in case of DEM and DES compared to DOP and DBP is probably due to less steric hindrance felt by incoming ethanol from monoethyl malonate formed in the first step. Also the stability of carbocation is higher for an intermediate containing branched alcohol (2-ethyl-1-hexanol) compared to straight chain alcohol (n-butanol).

Synthesis of coumarin derivatives via Pechmann condensation

In the present study, phenols (resorcinol, pyrogallol, phloroglucinol, hydroquinone and p-nitrophenol) have been treated with methyl acetoacetate to give 7-hydroxy-4-methyl coumarin (7H4MC), 7,8-dihydroxy-4-methyl coumarin (7,8DH4MC), 5,7-dihydroxy-4-methyl coumarin (5,7DH4MC), 6-hydroxy-4-methyl coumarin (6H4MC) and 6-nitro-4-methyl coumarin (6N4MC), under solvent free conditions.

Catalytic performance of M(IV)PWs (Type-I catalysts) and 12-TPA/M(IV)O_2-20 (Type-II catalysts) was explored at optimized condition under solvent free conditions using conventional and MW heating. The order of % yield of coumarins formed is 6H4MC > 5,7DH4MC > 7H4MC > 7,8DH4MC > 6N4MC. The substrate having electron – donating groups in the *para* position to the site of electrophilic substitution (for e.g. hydroquinone) gives higher yields [24]. Therefore, 6H4MC was obtained with high % yield. Comparing reactivity of hydroquinone and resorcinol, it is observed that during the formation of 6H4MC, electrophilic substitution can occur at both “2” or “6” and “3” or “5” positions simultaneously, in the hydroquinone moiety (Scheme 4.8). However, in the formation of 7H4MC, electrophilic substitution can occur only at “4 or 6” position of resorcinol moiety (scheme 4.5). The electrophilic substitution at “2” position in resorcinol cannot occur due to the steric hindrance of –OH group present at “3” and “1”. The reactivity of phloroglucinol was observed to be higher than pyrogallol, due to two hydroxyl groups at *meta*-positions in phloroglucinol compared to one hydroxyl group in pyrogallol [25]. This is due to the presence of three – OH groups (*meta* to each other) that cooperate in activating the aromatic ring for hydroxyalkylation. It is observed that, % yields of 7,8DH4MC are less than 7H4MC, attributed to steric hindrance of –OH groups present in pyrogallol (at “1”,”2” and “3” positions) compared to resorcinol (at “1” and “2” positions) [24]. Low yield obtained in case of p-nitrophenol is attributed to the presence of electron withdrawing -NO_2 group in p-nitrophenol.

Higher yields obtained under MW irradiation is probably due to the fact that the phenolic substrates and methyl acetoacetate being polar molecules, are microwave active and absorb the MW radiations rapidly and accelerate the rate of reaction. Formation of polar methanol (by-product) also helps in absorption of MW radiation thereby accelerating the reaction [25].

Friedel-Crafts reactions

Part-I: Friedel-Crafts alkylation and acylation

In the present study, benzyl chloride is used as alkylating agent for toluene to give p-benzyl toluene (p-BT) whereas, acetyl chloride is used as acylating agent for acylation of anisole and veratrole to give 4-methoxy acetophenone (4-MA) and 3,4-dimethoxy acetophenone (3,4-DMA) respectively, under solvent free conditions.

It is observed that, % yields of 3,4-DMA > 4-MA. The rate-determining step of the Friedel-Crafts acylation is the formation of the electrophilic intermediate. The presence of an additional electron donating methoxy group in veratrole makes it a more active compound for electrophilic substitution of acyl group at para position, due to an increased electron density and resultant increased susceptibility for attack by the electrophile than anisole.

Part-II: Synthesis of anthraquinone derivatives

In the present study, substituted benzenes such as toluene (T), resorcinol (R), hydroquinone (Hq) and nitrobenzene (Nbz) are treated with phthalic anhydride (PA) to give 2-methyl anthraquinone (2-MA), 1,3-dihydroxy anthraquinone (1,3-DHA), 1,4-dihydroxy anthraquinone (1,4-DHA) and 2-nitro anthraquinone (2-NA) respectively, under solvent free conditions.

For all catalysts (Type – I and Type - II), order of % yield of anthraquinone derivatives formed is 1,4-DHA > 1,3-DHA > 2-MA > 2-NA. % yields are higher for 1,4-DHA compared to 1,3-DHA, which can be explained with reference to the mechanism (Scheme 5.17). During the formation of 1,4-DHA, first electrophilic substitution takes place at “2” or “6” position and second electrophilic substitution takes place at “3” or “5” position of Hq moiety (Scheme 5.16). However, in the formation of 1,3-DHA, first electrophilic substitution takes place at “4” or “6’” position followed by second electrophilic substitution at position “5” only (Scheme 5.15). Electrophilic substitution at “2” position is restricted due to steric hindrance of – OH groups present at “1” and “3” positions in R. Due to the presence of more available sites for electrophilic substitution in Hq compared to R, yields are higher for 1,4-DHA compared to 1,3-DHA. % yields of 2-MA is less compared to 1,4-DHA and 1,3-DHA, is due to the presence of an additional e^- releasing (-OH) group in case of R and Hq, compared to T (having only one e^- releasing group $-CH_3$). Lowest yields of 2-NA is attributed to the presence of electron withdrawing ($-NO_2$) group in Nbz [26].

Acetalization of carbonyl compounds

In the present study, acetalization of carbonyl compounds (benzaldehyde, cyclohexanone, acetophenone and benzophenone) with pentaerythritol (PET) has been performed to yield the corresponding diacetal derivative.

For all catalysts (Type – I and Type - II), order of % yield of diacetals formed is benzaldehyde diacetal > cyclohexanone diacetal > acetophenone diacetal > benzophenone diacetal. Acetal derivative of benzaldehyde (benzaldehyde diacetal) was obtained with high % yield. This is probably due to the fact that aldehyde undergoes nucleophilic addition more readily than ketones. Comparing benzophenone and acetophenone, benzophenone being more bulky than acetophenone, shows the lowest reactivity and thus low yields. The rate determining step of acetalization is the formation of a cation from the protonated hemiacetal. Hence, the bulkiness of hemiacetals might prevent the attack of the alcohol on the carbonyl carbon atom thereby effecting a change in the rate-determining step. Further, the electron withdrawing power of phenyl group (1 for acetophenone and 2 for benzophenone) in these compounds reduces the easy release of the pair of electron on the carbonyl carbon during the reaction. However, cyclohexanone is more reactive towards nucleophiles than both acetophenone and benzophenone [27].

Regeneration/Reactivation of catalyst

In all the above mentioned reactions, after each catalytic run, there is change in colour of the catalysts. This is probably due to the fact that reactant molecules come onto surface of catalyst and enter into reaction to give the product, while a few of them get adsorbed on surface. After separation of catalyst (Type-I and Type-II) from reaction mixture by filtration/decantation, it is refluxed in ethanol for 30 minutes to solubilise/remove adsorbed molecules of reactants/products.

After refluxing in ethanol, M(IV)PWs (Type-I Inherent SACs) were dried at room temperature followed by acid treatment. This regeneration procedure was followed for subsequent catalytic run. In case of 12-TPA/M(IV)O_2-20 (Type-II Induced SACs), after refluxing in ethanol, the catalysts were dried at room temperature followed by drying at 120°C for 3 hrs. This reactivation procedure was followed for subsequent catalytic run. All subsequent catalytic runs were performed at optimized conditions.

It is observed that, on regeneration M(IV)PWs (Type – I catalysts) exhibited only a marginal decrease in % yields in each subsequent run, probably due to regeneration of the acid sites. However, a reactivation in case of 12-TPA/M(IV)O_2-20 (Type – II catalysts) exhibited a much higher decrease in % yields. EDX analysis for both fresh and spent catalysts performed after first catalytic run indicates leaching of ions, which could be the probable reason for decrease in % yields.

When M(IV)PWs (Type – I catalysts) were used as such after each subsequent run (i.e. without regeneration), the decrease in % yields are much higher compared to regenerated M(IV)PWs, which is probably attributed to the deactivation of catalysts, due to substrate molecules getting adsorbed on surface or also entering interstices of the catalyst material [20].

Comparison of catalytic activity/performance

In all of the above mentioned organic transformations, amongst M(IV)PWs (Type-I Inherent SACs) performance of catalyst in terms of % yield/TON is found to be TiPW > SnPW > ZrPW whereas, amongst 12-TPA/M(IV)O_2-20 (Type-II Induced SACs), the order is found to be 12-TPA/TiO_2-20 > 12-TPA/SnO_2-20 > 12-TPA/ZrO_2-20 which could be attributed to increased surface acidity of these materials. Comparing performance of Type-I and Type – II catalysts, M(IV)PWs (Type-I catalysts) scores over 12-TPA/M(IV)O_2-20 (Type-II catalysts) in terms of % yields/TON of the products formed.

Conclusions

- The work outlined in the present thesis reveals good performance of all catalysts, with advantages of operational simplicity, mild reaction conditions, no acid waste generation, no catalyst contamination and possible regeneration/reactivation and reuse of catalysts.
- In esterification reactions, the ester formed can be simply distilled over. Products obtained are colourless with no catalyst contamination, a limitation in the conventional process.
- In case of synthesis of coumarin derivatives, in conventional methods a large amount of H_2SO_4 is used (causes acid waste as well as the difficulties of handling H_2SO_4) which is avoided in the present study. In addition, catalysts can be regenerated and reused. Further, the highlighting feature is solvent free synthesis with reduction of reaction time from several hours (8h) to few minutes (30min.) under MW irradiation.
- In Friedel-Crafts alkylation and acylation as well as synthesis of anthraquinone derivatives, the highlighting features are product selectivity and solvent free reaction conditions. Further, compared to montmorillonite KSF [1] higher yields of anthraquinone derivatives are obtained with less amount of catalyst in short reaction time.
- In case of acetalization of carbonyl compounds, conventional procedures require expensive reagents, tedious work-up procedures and neutralization of the strongly acidic media leading to the production of harmful wastes. In the present study, the use of heterogeneous acid catalysts for the reaction is attractive where diacetal products obtained can be separated easily and catalysts can be regenerated and reused.
- In all the model reactions studied, liquid acid catalysts conventionally used are replaced by SACs. Thus, the green chemistry principle no. 9 which states that ***"Catalysts (as selective as possible) are superior to stoichiometric reagents"*** is implemented in the present study.
- In synthesis of coumarin derivatives as well as in Friedel – Crafts alkylation, acylation and synthesis of anthraquinone derivatives reactions have been conducted under solvent free conditions. Thus in the present study, the green chemistry principle

no. 5 which states that ***"Use of solvents should be made unnecessary whenever possible and when used, innocuous"*** is implemented.

- In all the model reactions performed, amongst M(IV)PWs (Type – I catalysts) performance of catalyst in terms of % yields is found to be TiPW > SnPW > ZrPW whereas, amongst 12-TPA/M(IV)O_2-20 (Type – II catalysts), the order is found to be 12-TPA/TiO_2-20 > 12-TPA/SnO_2-20 > 12-TPA/ZrO_2-20.
- Further, comparing performance of M(IV)PWs (Type-I Inherent SACs) and 12-TPA/M(IV)O_2-20 (Type-II Induced SACs) (used in the present study) with same elemental composition, inherent SACs score over induced SACs, not only in terms of % yields of different products obtained but are also better candidates when regenerated and reused with not much decline in performance upto three cycles.
- The objective of the present work, ***"To explore the potential utility of mixed material of the class of Tetravalent Metal Bianionic Acid (TMBA) salts (containing two different anions and a cation) as SAC with an aim to enhance surface acidity"***, seems to be well achieved. Finally, TiPW exhibits the best performance in all the model reactions conducted in terms of % yields obtained. It has therefore the potential for commercialization.

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