## A conclusive outline of the work presented and achieved

Catalysis provides an opportunity to achieve the goals of green chemistry. Amongst the various catalytic systems used, solid acid catalysts (SACs) are making a huge impact. Acid catalyzed reactions play a significant role in the synthesis of a variety of compounds. Liquid acids such as $H_2SO_4$, HF, $H_3PO_4$, $AlCl_3$, etc. have been extensively used as catalysts in a variety of organic transformations for long. Though liquid acid catalysts are effective, they are cited as potential environmentally hazardous chemicals and are becoming a major area of concern mainly due to operational difficulties such as toxicity, corrosiveness, effluent disposal, wasting large amount of catalyst, product separation, storage and handling.

Owing to increasing environmental awareness and a quest for zero emission technologies, much attention is focused on developing alternatives to these existing acids. There is thus a global effort to replace the conventional homogeneous liquid acids by heterogeneous solid acids. Solid acids are safe alternatives for conventional liquid acid catalysts. Solid acid catalysts are used to advantage. Solid acid catalyzed reactions possess operational simplicity, with ease of separation of products and catalyst at the end of the reaction. They possess high catalytic activity, selectivity and do not corrode reaction vessels or reactors and finally, solid acid catalysts can be regenerated and reused.

In the present thesis, 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)$O_2$], have been explored by studying following organic transformations as model reactions,

- *Esterification (Synthesis of monoesters and diesters) (Chapter 3)*
- *Synthesis of coumarin derivatives (Pechmann condensation) (Chapter 4)*
- *Friedel-Crafts reactions (Alkylation, acylation and synthesis of anthraquinone derivatives) (Chapter 5)*
- *Acetalization of carbonyl compounds (Chapter 6).*

## *General 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.

## *Specific conclusions*

### Esterification

With reference to table 7.1 and 7.2, comparing catalytic performance of M(IV)PWs (TMBA salts) and 12-TPA/M(IV)$O_2$-20 with Zirconium Titanium Phosphate (ZTP) (TBMA salt) [2] in terms of % yields of ethyl acetate (EA) obtained, it is observed that -

TiPW > ZTP≈SnPW > ZrPW > 12-TPA/$TiO_2$-20 > 12-TPA/$SnO_2$-20 > 12-TPA/$ZrO_2$-20, while % yields of dioctyl phthalate (DOP) follows the order –

TiPW > SnPW > ZrPW > ZTP > 12-TPA/$TiO_2$-20 > 12-TPA/$SnO_2$-20 >12-TPA/$ZrO_2$-20.

***Table 7.1*** *Comparison of % yields of mono ester – EA using TBMA salt, TMBA salts and 12-TPA/M(IV)$O_2$-20.*

| **No.** | **Catalysts** | **Substrates (mole ratio)** | **Catalyst amount (g)** | **Reaction time (h)** | **% Yield** |
|---|---|---|---|---|---|
| 1 | ZTP [2] | E:AA (1:2) | 0.20 | 10 | 86.40 |
| 2 | ZrPW* | E:AA (1:1.5) | 0.15 | 8 | 76.92 |
| 3 | 12-TPA/$ZrO_2$-20* | E:AA (1:1.5) | 0.15 | 8 | 64.41 |
| **4** | **TiPW*** | **E:AA (1:1.5)** | **0.15** | **8** | **99.64** |
| 5 | 12-TPA/$TiO_2$-20* | E:AA (1:1.5) | 0.15 | 8 | 73.67 |
| 6 | SnPW* | E:AA (1:1.5) | 0.15 | 8 | 85.54 |
| 7 | 12-TPA/$SnO_2$-20* | E:AA (1:1.5) | 0.15 | 8 | 70.17 |

*(*Present work; ZTP: Zirconium Titanium Phosphate; E: Ethanol; AA: Acetic Acid; Solvent: Cyclohexanone; Reaction temperature: 80$^o$C)*

***Table 7.2*** *Comparison of % yields of diester – DOP using TMA salts, TBMA salt, TMBA salts and 12-TPA/M(IV)$O_2$-20.*

| No. | Catalysts | Substrates (mole ratio) | Catalyst amount (g) | Reaction temperature (°C) | Reaction time (h) | % Yield |
|---|---|---|---|---|---|---|
| 1 | ZTP [2] | O + PhA (2.5:1) | 0.20 | 145 | 10 | 72.60 |
| 2 | ZrPW* | O + PhA (2:1) | 0.15 | 140 | 8 | 80.87 |
| 3 | 12-TPA/$ZrO_2$-20* | O + PhA (2:1) | 0.15 | 140 | 8 | 67.54 |
| **4** | **TiPW*** | **O + PhA (2:1)** | **0.15** | **140** | **8** | **84.00** |
| 5 | 12-TPA/$TiO_2$-20* | O + PhA (2:1) | 0.15 | 140 | 8 | 71.42 |
| 6 | SnPW* | O + PhA (2:1) | 0.15 | 140 | 8 | 81.04 |
| 7 | 12-TPA/$SnO_2$-20* | O + PhA (2:1) | 0.15 | 140 | 8 | 69.59 |

*(*: Present work; ZTP: Zirconium Titanium Phosphate; PhA = Phthalic Anhydride and O = 2-ethyl 1-hexanol; Solvents: Xylene for DOP)*

**Synthesis of coumarin derivatives (Pechmann condensation)**

With reference to table 7.3, comparing catalytic performance of M(IV)PWs (TMBA salts) and 12-TPA/M(IV)$O_2$-20 with TMA salts [3], in terms of % yields of 7-hydroxy-4-methyl coumarin (7H4MC) obtained, it is observed that -

ZrP > ZrPW > 12-TPA/$ZrO_2$-20 > ZrW;

TiPW > 12-TPA/$TiO_2$-20 > TiW > TiP;

SnPW > 12-TPA/$SnO_2$-20 > SnP > SnW.

Enhancement in % yields of 7H4MC is observed in case of M(IV)PWs compared to their single salt counter parts.

***Table 7.3*** *Comparison of % yield of 7-hydroxy-4-methyl coumarin using TMA salts, TMBA salts and and 12-TPA/M(IV)$O_2$-20.*

| No. | Catalysts | Substrates (mole ratio) | Catalyst amount (g) | Reaction temperature (°C) | Reaction time (h) | % Yield |
|---|---|---|---|---|---|---|
| 1 | ZrP [3] | R:MA (1:1) | 0.25 | 130 | 10 | 61.10 |
| 2 | ZrW [3] | R:MA (1:1) | 0.25 | 130 | 10 | 15.20 |
| 3 | ZrPW* | R:MA (1:1.5) | 0.20 | 130 | 8 | 58.12 |
| 4 | 12-TPA/$ZrO_2$-20* | R:MA (1:1.5) | 0.20 | 130 | 8 | 57.01 |
| 5 | TiP [3] | R:MA (1:1) | 0.25 | 130 | 10 | 51.40 |
| 6 | TiW [3] | R:MA (1:1) | 0.25 | 130 | 10 | 54.90 |
| **7** | **TiPW*** | **R:MA (1:1.5)** | **0.20** | **130** | **8** | **69.37** |
| 8 | 12-TPA/$TiO_2$-20* | R:MA (1:1.5) | 0.20 | 130 | 8 | 58.00 |
| 9 | SnP [3] | R:MA (1:1) | 0.25 | 130 | 10 | 52.90 |
| 10 | SnW [3] | R:MA (1:1) | 0.25 | 130 | 10 | 16.20 |
| 11 | SnPW* | R:MA (1:1.5) | 0.20 | 130 | 8 | 62.48 |
| 12 | 12-TPA/$SnO_2$-20* | R:MA (1:1.5) | 0.20 | 130 | 8 | 57.50 |

*(*: Present work; Yields refer to the isolated pure products)*

**Friedel-Crafts reactions**

*Friedel-Crafts alkylation and acylation:*

With reference to table 7.4, comparing catalytic performance of M(IV)PWs (TMBA salts) and 12-TPA/M(IV)$O_2$-20 with TMA salts [4], in terms of % yields of p-benzyl toluene (p-BT) obtained, it is observed that -

ZrPW > 12-TPA/$ZrO_2$-20 > ZrP > ZrW;

TiPW > 12-TPA/$TiO_2$-20 > TiP > TiW;

SnPW > 12-TPA/$SnO_2$-20 > SnP > SnW.

Enhancement in % yields of p-BT is observed in case of M(IV)PWs compared to their single salt counter parts.

***Table 7.4*** *Comparison of % yield of p-benzyl toluene using TMA salts, TMBA salts [M(IV)PWs] and 12-TPA/M(IV)$O_2$-20.*

| **No.** | **Catalyst** | **Substrates (mole ratio)** | **Catalyst amount (g)** | **Reaction temperature ($^oC$)** | **Reaction time (h)** | **% yield** |
|---|---|---|---|---|---|---|
| 1 | ZrP [4] | Toluene: Benzyl chloride (1:1.5) | 0.15 | 110 | 3 | 49.30 |
| 2 | ZrW [4] | | 0.15 | 110 | 3 | 44.70 |
| **3** | **ZrPW*** | | **0.25** | **130** | **5** | **59.68** |
| 4 | 12-TPA/$ZrO_2$-20* | | 0.25 | 130 | 5 | 54.26 |
| 5 | TiP [4] | | 0.15 | 110 | 3 | 57.00 |
| 6 | TiW [4] | | 0.15 | 110 | 3 | 50.00 |
| **7** | **TiPW*** | | **0.25** | **130** | **5** | **70.38** |
| 8 | 12-TPA/$TiO_2$-20* | | 0.25 | 130 | 5 | 56.31 |
| 9 | SnP [4] | | 0.15 | 110 | 3 | 56.00 |
| 10 | SnW [4] | | 0.15 | 110 | 3 | 50.00 |
| **11** | **SnPW*** | | **0.25** | **130** | **5** | **63.27** |
| 12 | 12-TPA/$SnO_2$-20* | | 0.25 | 130 | 5 | 55.47 |

*(*: Present work)*

*Synthesis of anthraquinone derivatives:*

With reference to table 7.5, comparing catalytic performance of M(IV)PWs (TMBA salts) and 12-TPA/M(IV)$O_2$-20 with montmorillonite KSF [1], in terms of % yields of 1,3-dihydroxy anthraquinone (1,3-DHA) obtained, it is observed that,

TiPW ≈ Montmorillonite KSF > SnPW > ZrPW > 12-TPA/$TiO_2$-20 > 12-TPA/$SnO_2$-20 > 12-TPA/$ZrO_2$-20,

whereas % yields of 1,4-dihydroxy anthraquinone (1,4-DHA) follows the order -

TiPW > SnPW > ZrPW ≈ Montmorillonite KSF > 12-TPA/$TiO_2$-20 > 12-TPA/$SnO_2$-20 > 12-TPA/$ZrO_2$-20.

***Table 7.5*** *Comparison of % yield of anthraquinone derivatives using M(IV)PWs, 12-TPA/M(IV)$O_2$-20 and Montmorillonite KSF.*

| **No.** | **Catalyst** | **Catalyst amount (g)** | **Reaction time (h)** | **Reaction temperature ($^oC$)** | **% yield** | |
|---|---|---|---|---|---|---|
| | | | | | **1,3-DHA** | **1,4-DHA** |
| 1 | Montmorillonite KSF [1] | 2.0 | 24 | 120-130 | 77.00 | 75.00 |
| 2 | ZrPW* | 0.3 | 3 | 120 | 72.29 | 74.00 |
| **3** | **TiPW*** | **0.3** | **3** | **120** | **77.21** | **79.11** |
| 4 | SnPW* | 0.3 | 3 | 120 | 73.70 | 77.09 |
| 5 | 12-TPA/$ZrO_2$-20* | 0.3 | 3 | 120 | 67.17 | 68.90 |
| 6 | 12-TPA/$TiO_2$-20* | 0.3 | 3 | 120 | 70.77 | 73.12 |
| 7 | 12-TPA/$SnO_2$-20* | 0.3 | 3 | 120 | 68.44 | 70.00 |

*(*Present work; Mole ratio of hydroquinone:phthalic anhydride-1:1; Yields refer to the isolated pure products)*

**Acetalization of carbonyl compounds**

With reference to table 7.6, comparing catalytic performance of M(IV)PWs (TMBA salts) and 12-TPA/M(IV)$O_2$-20 with TMA salts [5], in terms of % yields of diacetal derivative of benzaldehyde obtained, it is observed that -

TiPW > SnPW > ZrPW > 12-TPA/$TiO_2$-20 > CP > 12-TPA/$SnO_2$-20 > 12-TPA/$ZrO_2$-20 > TP.

Enhancement in % yields of diacetal derivative of benzaldehyde is observed in case of M(IV)PWs compared to TMA salts [i.e. Cerium Phosphate (CP) and Thorium Phosphate (TP)], which are recently reported from our laboratory for acetalization of carbonyl compounds.

***Table 7.6*** *Comparison of % yield of diacetal derivative of benzaldehyde using TMA salts, TMBA salts [M(IV)PWs] and 12-TPA/M(IV)$O_2$-20.*

| **No.** | **Catalyst** | **% yield** |
|---|---|---|
| 1 | CP [5] | 74.51 |
| 2 | TP [5] | 68.13 |
| 3 | ZrPW* | 77.87 |
| **4** | **TiPW*** | **81.45** |
| 5 | SnPW* | 79.09 |
| 6 | 12-TPA/$ZrO_2$-20* | 69.32 |
| 7 | 12-TPA/$TiO_2$-20* | 76.88 |
| 8 | 12-TPA/$SnO_2$-20* | 72.53 |

*(*Present work; Mole ratio of PET:benzaldehyde-1:4; catalyst amount: 0.30g; reaction temperature: 110$^oC$; reaction time: 4h; Yields refer to the isolated pure products)*

With reference to table 7.7, it is observed that, TiPW exhibits the best performance in all the model reactions conducted in terms of % yields obtained. It has therefore the potential for commercialization.

***Table 7.7*** *% yields of the products formed using TiPW at optimized condition.*

| No. | Product formed | % Yields using TiPW |
|---|---|---|
| *Monoesters* | | |
| 1 | Ethyl acetate | 99.7 |
| 2 | Propyl acetate | 68.1 |
| 3 | Butyl acetate | 89.8 |
| 4 | Benzyl acetate | 88.1 |
| *Diesters* | | |
| 5 | Diethyl malonate | 92.1 |
| 6 | Diethyl succinate | 88.8 |
| 7 | Dioctyl phthalate | 84.0 |
| 8 | Dibutyl phthalate | 68.0 |
| *Coumarin derivatives* | | |
| 9 | 7-hydroxy-4-methyl coumarin | 69.4 |
| 10 | 7,8-dihydroxy-4-methyl coumarin | 65.2 |
| 11 | 5,7-dihydroxy-4-methyl coumarin | 76.8 |
| 12 | 6-hydroxy-4-methyl coumarin | 78.1 |
| 13 | 6-nitro-4-methyl coumarin | 50.0 |
| *Friedel – Crafts alkylation and acylation* | | |
| 14 | p-benzyl toluene | 70.4 |
| 15 | 4-methoxy acetophenone | 56.8 |
| 16 | 3,4-dimethoxy acetophenone | 62.4 |
| *Anthraquinone derivatives* | | |
| 17 | 2-methyl anthraquinone | 71.8 |
| 18 | 2-nitro anthraquinone | 54.7 |
| 19 | 1,3-dihydroxy anthraquinone | 77.2 |
| 20 | 1,4-dihydroxy anthraquinone | 79.1 |
| *Acetal derivatives* | | |
| 21 | Diacetal of benzaldehyde | 81.5 |
| 22 | Diacetal of cyclohexanone | 79.7 |
| 23 | Diacetal of acetophenone | 70.1 |
| 24 | Diacetal of benzophenone | 62.0 |

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.

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