Chapter-III

Acid catalysis

[Esterification Reactions]
In recent times, the scientists worldwide have been devoting their attention to the development of ecofriendly catalysts for the production of industrially important chemicals and chemical intermediates. The new area of interest are; catalytic technology for liquid or solid waste reduction, catalysts for energy efficient catalytic processes, reactions of environmental impact in the disposal of the catalysts, and catalytic processes for sustainable chemistry.

Catalysis offers relevant possibility for sustainable production.

The acid catalyzed reactions comprise a wide range from dehydration, esterification up to alkylation and acylation, has both industrial importance as well as academic relevance and have been studied extensively. The reactions are generally carried out by traditional Bronsted acids such as H₂SO₄, HCl, H₃PO₄, HF and Lewis acids such as AlCl₃, BF₃ and ZnCl₂. Because of the wide applicability of the obtained products, these reactions attracted worldwide attention with the aim of finding suitable heterogeneous catalyst. The replacement of the traditional environmental hazardous and corrosive homogeneous catalysts by heterogeneous catalysts in order to achieve clean technology is one of the demands of the society. The main disadvantages of using conventional homogenous catalyst are:

I. They are toxic and corrosive

II. They lead to environmental problems
III. They lead to side reactions and produce large amount of by products.

IV. There is a problem of separation of catalyst from products.

Further, product separation from various byproducts and catalyst require tedious procedures. For example when H₂SO₄ is used as acid catalyst, washing with alkali (four to five times) and subsequent water washing to neutralize the added alkali to the product is required. To overcome all these problems, in recent years the major trend has been in developing ecofriendly solid acid catalyst.

Use of solid acid catalyst provides the following advantages over the conventional liquid acid catalyst.

I. High catalytic activity and selectivity are frequently observed.

II. Solid acid catalysts do not corrode reaction vessels or reactors.

III. Separation of a solid acid or base catalyst form a reaction mixture is easy.

IV. Repeated use of solid acid catalyst is possible.

V. There is no problem for the disposal of used solid acid catalyst.

**Esterification reactions**

Esterification is one of the important reaction in synthetic organic chemistry. The obtained esters are used as solvents, extractants and diluents due to their highly lipophilic and hydrophilic nature. Certain esters
with a pleasant odour are also used in fragrances, flavors, cosmetics and soaps. Apart from the above applications, it finds uses as intermediates for synthesis of Vitamin B1 and aspirin in pharmaceutical industries.

Esterification is one of the most useful reactions in preparative organic chemistry and has been extensively studied by both organic and physical chemists.

An ester is usually defined as a compound formed by substituting an organic alcoxy group for an ionizable hydrogen of an acid.

\[
\begin{align*}
R-C-\text{OH} & \xrightarrow{H^+} R-C-\text{OH}^+ \\
& \Rightarrow R-C^+ + H_2O \\
& \downarrow R'-\text{OH} \\
R-C-\text{OR'} & \Rightarrow R-C^+\text{OR'}
\end{align*}
\]

Literature survey shows that the various solid acid catalysts have been used to carry out esterification reactions.

Avelino Corma and co-workers have studied esterification reactions over various acid catalysts such as modified faujasite zeolites [1], solid acids [2] and \textit{Nafion}®-functionalized mesoporous MCM-41 silica [3].

James G. Goodwin and co-worker have carried out study on esterification as well as trans-esterification reactions over a variety of acid catalysts. They have studied various parameters affecting the catalytic activity of the
catalyst such as effect of carbon chain length [4], effect of water [5], comparison of the heterogeneous versus homogeneous acid catalysts [6] and effect of calcination temperature [7]

K. M. Parida and co-worker has studied esterification reaction of n-butanol with acetic acid over different acid catalysts such as $\text{SO}_4^{2-}/\text{TiO}_2\text{SiO}_2$ mixed oxide [8], manganese nodule leached residue [9] and Heteropoly acid intercalated Zn/Al HTlc [10].

A. Pandurangan and co-worker have studied esterification reactions of various acids with different alcohols. They studied esterification of acetic acid using $n$-butyl alcohol [11], esterification of acetic acid with various alcohols over AI-MCM-41 molecular sieves [12], esterification of terephthalic acid with methanol over mesoporous AI-MCM-41 [13], esterification of alkyl acids with alkanols over MCM-41 molecular sieves [14] and esterification of acetic acid with propanol isomers using AI-MCM-41 molecular sieves [15].

Uma Chudasama and co-workers have made an attempt to use inorganic ion exchangers as solid acid catalyst for carrying out some esterification reactions [16-20].

Esterification reactions of various acids with different alcohols have been widely studied by a number of groups [21-31].
Among the solid acid catalysts, Heteropolyacids (HPAs) are excellent candidate. Solid HPAs possess purely Bronsted acidity and are stronger than conventional solid acids as SiO$_2$-Al$_2$O$_3$, H$_3$PO$_4$/SiO$_2$, and HX and HY zeolites [32-33]. They have high potential as catalyst and catalyze a wide variety of reactions in homogeneous phase offering strong option for efficient and cleaner processing. Literature survey shows that 12-tungstophosphoric acid and 12-tungstosilicic acid were used for the esterification of 2,6-pyridine di carboxylic acid with n-butanol [34], esterification of propionic acid by n-butanol and 2-ethylhexanol [35], esterification of phthalic anhydride by 2-ethylhexanol [36], esterification of acetic acid with butanol [37], as well as for the synthesis of various esters [38-42] under homogeneous conditions.

Thus, HPAs are efficient catalyst and have many advantages over conventional acid catalysts. Though there are many advantages, they have a number of disadvantages:

I. Solubility in polar solvents

II. The separation of catalyst from reactions product.

III. The surface area of heteropoly acids are usually low (1-10 m$^2$/g).

IV. Low thermal stability.
These disadvantages of HPAs can be overcome by supporting them onto suitable supports. In recent times, supported HPAs have been gaining importance as acid catalyzed reactions.

12-tungstophosphoric acid is the most stable HPA in keggin series from the viewpoint of acidic strength [43-45] as well as thermal stability [44-46]. Therefore, it has been widely used as a catalytic system for various esterification reactions. A number of esterification reactions have been carried out using 12-tungstophosphoric acid supported on to different supports like silica [47-67], titania [49,52,68-70], active carbon [35, 52,67,71-75], MCM-41 [76-81], acidic ion exchange resins [61,82] and clays [83-87].

A literature survey shows that the reports on use of hydrous zirconia as a support are very scanty [88-95]. Therefore, it was thought to use hydrous zirconia as support in the present work. Since hydrous zirconia is acidic in nature, it was also thought of interest to make use of neutral support as other material to support 12-tungstophosphoric acid. Neutral alumina has been used as neutral support.

The present chapter deals with the catalytic activity (Esterification reactions) of 12-tungstophosphoric acid (PWA). Two series of catalysts containing 10-70% loading of PWA onto neutral alumina (A) and hydrous zirconia (Z) were synthesized.
The esterification reactions of $n$-butyl alcohol with different acids such as formic acid, acetic acid and propionic acid were carried out varying different parameters such as % loading of the PWA onto supports (A and Z), molar ratio of alcohol to corresponding acids and different amount of the catalyst. Esterification reactions were also carried out with alcohol such as cyclohexyl alcohol with acetic acid. The obtained esters were analyzed on a Nucomb Gas Chromatograph using Carbowax 20 column.

It is known that support does not play always merely a mechanical role but it can also modify the catalytic properties of the HPAs. In order to see the effect of the nature of the support the catalytic activity of best catalyst, PWA$_3$/A was compared with the PWA$_3$/Z.

Further, PWA$_3$/A was calcinated at 300$^\circ$C and 500$^\circ$C and designed as C$_3$-PWA$_3$/A and C$_5$-PWA$_3$/A respectively. PWA$_3$/Z was also calcinated at 300$^\circ$C and 500$^\circ$C and designed as C$_3$-PWA$_3$/Z and C$_5$-PWA$_3$/Z respectively. The catalytic activity of calcinated catalysts was evaluated by carrying out esterification reactions under optimized conditions. The difference in the performance of the catalysts was correlated with the nature of the support.
Experimental

Materials

All chemicals used were of A.R. grade. n-butanol, iso-butyl alcohol, cyclohexyl alcohol, formic acid, glacial acetic acid, propionic acid, were obtained from Merck and used as received.

Catalytic reactions

For the preparation of the esters, the corresponding acid and alcohol were combined in a refluxing assembly. The catalyst was then added in the required amount. The mixture was heated at 80°C for 4 h. The reactions were carried out by varying different parameters such as alcohol to acid mole ratio and amount of the catalyst. The obtained esters were analyzed on a Gas Chromatograph (Nucon-5700) using Carbowax 20 column. Esterification is an equilibrium reaction. Hence in order to obtain the highest possible yield it is desirable to remove of one of the reaction products, mainly H₂O. To fulfill the mentioned requirement, Dean-Stark apparatus was attached with round bottom flask to separate the water formed during the reaction.
apparatus was attached with round bottom flask to separate the water formed during the reaction.

Results and Discussion

The esterification of carboxylic acid is a straightforward reaction subject to general Bronsted acid catalysis. The reaction of corresponding alcohol (1° and 2°) with different acid such as formic acid, acetic acid and propionic acid were selected as a model reaction.

\[ R-\text{COOH} + R'-\text{OH} \leftrightarrow R'-\text{COOR} + \text{H}_2\text{O} \]

According to the Le Chatelier’s principle, the yields of the ester can be increased by increasing the concentration of either alcohol or acid [96]. For economic reasons, the reactant that is usually less expensive of the two is taken in excess. In the present study all corresponding acids were used in excess.
Esterification reactions with PWA/A

Esterification of n-butyl alcohol

The esterification of n-butyl alcohol (7.4 g) with acetic acid (6.0 g) over A as well as PWA_1/A, PWA_2/A, PWA_3/A, PWA_4/A, PWA_5/A and PWA_7/A was carried out with molar ratio of alcohol to acid (1:2) and with different amount of the catalysts. The results obtained are shown in Figure-1. It is observed from the Figure-1 that the 30% loading of PWA gives the highest % yield of butyl acetate among all. So, 30% loading of PWA was optimized on support A.

Figure-1 % yield of butyl acetate with different amount of catalyst with different % loading of PWA onto A.

% Yield is based on alcohol, Molar ratio alcohol to acid is 1:2, Time = 4h, Temperature = 80°C
It is also seen from the figure that as the amount of catalyst increases, the % yield of butyl acetate also increases which is as expected. 41% yield of butyl acetate was found with 0.25 g of the catalysts.

After optimizing the % loading of PWA (30%) and amount of catalyst (0.25g), the esterification reaction was carried out in molar ratio 1: 4.4 to optimize the molar ratio of alcohol to acid. The results are shown in Figure-2. It was observed from Figure-2 that 1: 4.4 molar ratio of alcohol to acid gives the maximum % yield as compared to that of 1:2. So, molar ratio of 1: 4.4 was optimized for the esterification of alcohol with the present catalyst.

Figure-2 % yield of butyl acetate with different amount of catalysts

% Yield is based on alcohol, Time = 4h, Temperature = 80°C, Amount of catalyst=0.25g, Molar ratio of alcohol to acid is 1:4.4.
To optimize the reaction time, reaction was continued up to 6h and the results are shown in Figure-3. It is seen that after 4h there is a very slight change in % yield when it was continued for 6h. So the reaction time was optimized for 4h.

Figure-3 % yield of butyl acetate with different reaction time with catalyst PWA$_3$/A

% Yield is based on alcohol. Time = 4h, Temperature = 80°C, Amount of catalyst=0.25g, Molar ratio of alcohol to acid is 1:4.4

The optimum conditions for all reactions using PWA$_3$/A are as follows:

% loading of PWA onto A = 30%
Molar ratio of alcohol to acid = 1:4.4
Amount of the catalyst = 0.25 g
Temperature = 80°C
Reaction time = 4 h
Esterification reaction of n-butyl alcohol with formic acid (4.6 g) and propionic acid (7.4 g) by taking molar ratio of alcohol to acid 1:4.4 was carried out with 0.25 g of the catalysts PWA\textsubscript{3}/A. The % yield of butyl formate and butyl propionate is 85 and 32% respectively.

The % yield of above three esters are obtained in following order:

Butyl formate > Butyl acetate > Butyl propionate

This above order of % yield of different esters can be explained on the basis of the size of the reacting acids. As the size/bulkyness of the acid increases, the number of acid molecules sorbed on the surface of the catalyst will decrease and hence the number of molecules reacting in definite time will be less. This should result in decrease in the amount of product. In case of formic acid, the % conversion of ester is higher as compared to acetic acid and propionic acid. The presence of –CH\textsubscript{3} and –C\textsubscript{2}H\textsubscript{5} groups in the latter two acids result in the decrease in the % yield.

**Esterification of cyclohexyl alcohol**

Esterification reaction of cyclohexyl alcohol (9.9 g) with acetic acid (6.0 g) in molar ratio of alcohol to acid (1:3) was carried out with PWA\textsubscript{3}/A in optimum condition (Amount of catalyst is 0.25 g, Temperature=80° C, Molar ratio of alcohol to corresponding acid is 1:3). The % yield of cyclohexyl acetate is 51%.
Effect of temperature on the catalytic activity of the catalysts

Figure-4 % yield of BF, BA, BP with fresh and calcinated catalysts in optimized condition.

The % yield of all esters, the values for surface area, total acidity, average particle diameter and total pore volume for fresh as well as calcinated catalysts are listed in Table-1.
Table -1 % Yield of all esters, value of surface area, total acidity, average particle diameter and total pore volume

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% yield of Esters/ TOF (min⁻¹)</th>
<th>Surface area (m²/ g)</th>
<th>Total acidity (mmol/ g)</th>
<th>Average particle diameter (μm)</th>
<th>Total pore volume (cc/ g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF³</td>
<td>86</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>79</td>
<td>31</td>
<td>44</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PWA</td>
<td>89/142</td>
<td>29/46</td>
<td>49/78</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PWA₃/A</td>
<td>85/136</td>
<td>33/53</td>
<td>51/82</td>
<td>109</td>
<td>0.76</td>
</tr>
<tr>
<td>C₃-PWA₃/A</td>
<td>87/139</td>
<td>30/50</td>
<td>52/84</td>
<td>112</td>
<td>0.68</td>
</tr>
<tr>
<td>C₅-PWA₃/A</td>
<td>89/142</td>
<td>46/74</td>
<td>68/109</td>
<td>83</td>
<td>1.14</td>
</tr>
</tbody>
</table>

% yield is based on alcohol, Amount of catalyst is 0.25g, Temperature=80°C, Molar ratio of alcohol to corresponding acid is 1: 4, Molar ratio of alcohol to corresponding acid is 1: 3, Volume of H₂SO₄ taken is 1.5 ml.
Increase in the average particle size diameter and total pore volume of C₃-PWA₃/A as compared to that of PWA₃/A may be due to the loss of crystalline water from the structure of HPA anion by expanding the lattice. This loss takes place without any major change in the structure of supported heteropolyanion which is in good agreement with TGA which doesn't show any break / weight loss upto 600° C. Due to the loss of crystalline water, the total acidity decreases which is expected. On strong heating, in case of C₅-PWA₃/A, there may be generation of Lewis acidity on alumina which results in an increase in the total acidity. It is seen from the Table-1 that the total acidity of C₅-PWA₃/A is almost double than that of PWA₃/A but % conversion of esters are not doubled. This may be due to the fact that esterifications are mainly catalyzed by Bronsted acidity. It is also found that there is decrease in the pore volume as well as average particle diameter of C₅-PWA₃/A. This can be explained that it is due to contraction of the empty lattice of supported HPA. It is also observed from the Table-1 that catalytic activity is proportional to the total acidity and it is not related to the surface area of the catalyst. This is in good agreement with the pseudoliquid-bulk I type catalyst in which catalytic activity is proportional to the total acidity of the catalyst [97].

**Regeneration of the catalyst**

To investigate the details of the deactivation, repeated use of the catalyst was examined. The catalyst was separated from the reaction mixture by simple filtration, washed with conductivity water till filtrate is free from acid,
dried at 100° C in oven for 5 h and charged for the further run. The results obtained are shown in Table-2.

Table-2: % Yield of different esters with regenerated catalyst of PWA₃/A

<table>
<thead>
<tr>
<th>Cycle</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BFᵃ</td>
</tr>
<tr>
<td>Fresh catalyst</td>
<td>85</td>
</tr>
<tr>
<td>1</td>
<td>80</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>79</td>
</tr>
</tbody>
</table>

Amount of the catalyst= 0.25 g; temperature=80° C; and reaction time=4 h, a Molar ratio of alcohol to corresponding acid is 1: 4.4, b Molar ratio of alcohol to corresponding acid is 1: 3.

It is seen from the Table-2 that, in the regenerated catalyst the % yield decreased by 5 % approximately and becomes constant on further regeneration.

Further to see any structural change in the structure of supported 12-tungstophosphoric acid after reaction, the XRD of used catalyst (E PWA₃/A) was also recorded (Figure-4).
No difference in XRD pattern indicates the stability of the used catalyst as well as absences of any degraded heteropolyanion after the reaction.

**Esterification reactions with PWA/Z**

**Esterification of n-butyl alcohol**

The esterification of n-butyl alcohol (7.4 g) with acetic acid (6.0 g) over Z as well as PWA₁/Z, PWA₂/Z, PWA₃/Z, PWA₄/Z, PWA₅/Z and PWA₇/Z was carried out with molar ratio of alcohol to acid (1:2) and with different amount of the catalysts. The results obtained are shown in Figure-5. It is observed from the Figure-5 that the 30% loading of PWA gives the highest % yield of butyl acetate among all.
It is observed from Figure-5 that the 30% loading of PWA on hydrous zirconia gives the highest % yield of butyl acetate among all. It was also observed from Figure-5 that % yield increases rapidly when amount of catalyst increases from 0.25 to 0.50g but the increase in % yield is very small when amount of catalyst increases from 0.50 to 0.75g. Therefore, the % loading of PWA on Z was optimized to 30% and the amount of catalyst was optimized to 0.50g.

After optimizing the % loading of PWA and amount of catalyst 30% and 0.50g respectively, the formation of butyl acetate was carried out in two different molar ratio (1: 2 and 1: 4.4) to optimize the molar ratio of alcohol to acid. The results are shown in Figure-6. It was observed from Figure-6 that 1: 4.4 molar ratio of alcohol to acid gives nearly the same % yield as it
is obtained with 1:2. So, molar ratio of 1:2 was optimized for the esterification of alcohol with the present catalyst.

Figure-6 % yield of butyl acetate with different molar ratio of alcohol to acid with different catalysts.

To optimize the reaction time, reaction was continued up to 6h and the results are shown in Figure-7. It was observed that after 4h there is a very slight change in % yield when it was continued up to 6h. So the reaction time was optimized for 4h.
The optimum conditions for all reactions using PWA$_3$/Z are as follows:

% loading of PWA onto Z = 30%

Molar ratio of alcohol to acid = 1.2

Amount of the catalyst = 0.50 g

Temperature = 80°C

Reaction time = 4 h

Esterification reaction of n-butyl alcohol with formic acid (4.6 g) and propionic acid (7.4 g) by taking molar ratio of alcohol to acid 1:2 was carried out with 0.50 g of the catalysts PWA$_3$/Z. The % yield of butyl formate and butyl propionate is 75 and 47% respectively.
Esterification of cyclohexyl alcohol

Esterification reaction of cyclohexyl alcohol (9.9 g) with acetic acid (6.0 g) by taking molar ratio of alcohol to acid (1:3) was carried out with 0.50 g of the catalysts PWA₃/Z. The % yield of cyclohexyl acetate is 68%.

Figure-8 % yield of BFᵃ, BAᵃ, BPᵃ and CAᵇ with fresh and calcinated catalysts in optimized condition.

% Yield is based on alcohol, Amount of catalyst 0.5g, a = Molar ratio of alcohol to acid is 1 : 2, b = Molar ratio of alcohol to acid is 1 : 3,

The esterification of n-butyl alcohol with formic acid, acetic acid, propionic acid and cyclohexanol with acetic acid was carried out under same conditions using catalysts C₃ -PWA₃/Z and C₅ -PWA₃/Z. The results are presented in Table-3.
Table-3: The values of surface area, average particle size diameter and total acidity and value of % yield of different esters; butyl formate, butyl acetate, butyl propionate and cyclohexyl acetate.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>% yield of Esters / TOF (min⁻¹)</th>
<th>Total surface area (m²/g)</th>
<th>Total acidity (mmol of NH₃ / g sample)</th>
<th>Average particle size diameter (µm)</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄</td>
<td>BFᵃ 86</td>
<td>BAᵇ 79</td>
<td>BPᵇ 31</td>
<td>CAᵇ 44</td>
<td>-</td>
</tr>
<tr>
<td>PWA</td>
<td>89/71.2</td>
<td>81/64.8</td>
<td>29/23.2</td>
<td>49/39.2</td>
<td>-</td>
</tr>
<tr>
<td>Z</td>
<td>52</td>
<td>51</td>
<td>27</td>
<td>38</td>
<td>170</td>
</tr>
<tr>
<td>PWA₃/Z</td>
<td>75/60</td>
<td>70/56</td>
<td>47/37.6</td>
<td>68/54.4</td>
<td>146</td>
</tr>
<tr>
<td>C₃-PWA₃/Z</td>
<td>75/60</td>
<td>71/57</td>
<td>46/37</td>
<td>78/62</td>
<td>214</td>
</tr>
<tr>
<td>C₅-PWA₃/Z</td>
<td>84/67</td>
<td>78/62</td>
<td>48/38</td>
<td>84/67</td>
<td>126</td>
</tr>
</tbody>
</table>

%Yield is based on alcohol, Amount of catalyst 0.5g, a = Molar ratio of alcohol to acid is 1 : 2, b = Molar ratio of alcohol to acid is 1 : 3, 
Amount of PWA = 0.062 g.
Table-3 shows the value of total surface area, total acidity of materials, average particle size diameter, specific surface area and the value of % yield of different esters, butyl formate, butyl acetate, butyl propionate, and cyclohexyl acetate. It is also seen from Table-3 that the value of average particle size diameter is maximum for C₅-PWA₃/Z i.e. the catalyst calcinated at 500° C. The order of value of average particle size diameter is as follows:

C₅-PWA₃/Z > C₃-PWA₃/Z > PWA₃/Z.

This can be explained as follows. It is well known that the structure of hydrous zirconia is open containing water molecules in the form of OH⁻, H₂O⁺ and H₂O [98]. It is also known that the structure of HPA contains unbonded H₂O molecules as water of crystallization inside the cages of HPA. Increase in the particle size of C₃-PWA₃/Z may be due to the loss of H₂O / H₂O⁺ from hydrous zirconia as well as loss of crystalline H₂O from the structure of heteropolyanion by expanding the lattice. This loss takes place without any major change in the structure of supported heteropolyanion and is in good agreement with our earlier results. On strong heating, i.e. calcination at 500° C, the total removal of H₂O / H₂O⁺ from hydrous zirconia is expected and hence more expansion of lattice is also expected. This may be the reason for C₅-PWA₃/Z to have maximum average particle size diameter. These observations can be very well shown in the SEM of PWA₃/Z (Figure-8a), C₃-PWA₃/Z (Figure-8b) and C₅-PWA₃/Z (Figure-8c). The SEM of C₅-PWA₃/Z appears more shining and
somewhat crystalline among all as a result of the total removal of \( \text{H}_2\text{O} / \text{H}_3\text{O}^+ \) from hydrous zirconia.

The XRD of \( \text{C}_3\text{-PWA}_3\text{/Z} \) and \( \text{C}_5\text{-PWA}_3\text{/Z} \) is shown in Figure-9. The XRD pattern of \( \text{C}_5\text{-PWA}_3\text{/Z} \) indicates the presence of crystalline entities. It shows the characteristic diffraction line for tetragonal zirconia. These changes may be due to complete loss of water molecules present in the form of \( \text{OH}^- \), \( \text{H}_3\text{O}^+ \) and \( \text{H}_2\text{O} \) from hydrous zirconia after calcination (500°
C). The absence of characteristic diffraction line of PWA indicates undegraded species of HPA onto the surface of the support.

Figure-9 XRD of C₃-PWA₃/Z (9a)and C₅-PWA₃/Z (9b)

Regeneration of the catalyst

To investigate the details of the deactivation, repeated use of the catalyst was examined. The catalyst was separated from the reaction mixture by simple filtration, washed with conductivity water till filtrate is free from acid, dried at 100°C in oven for 5h and charged for the further run. The results obtained are shown in Table-9. It is seen from the table that, in the
regenerated catalyst the % yield decreased by 5 % approximately and becomes constant on further regeneration.

Table-9: % Conversion of different esters with regenerated catalyst of C₅-PWA₃/Z

<table>
<thead>
<tr>
<th>Cycle</th>
<th>BF</th>
<th>BA</th>
<th>BP</th>
<th>i-BA</th>
<th>CA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>84</td>
<td>78</td>
<td>48</td>
<td>81</td>
<td>84</td>
</tr>
<tr>
<td>Catalyst 1</td>
<td>73</td>
<td>69</td>
<td>45</td>
<td>71</td>
<td>67</td>
</tr>
<tr>
<td>Catalyst 2</td>
<td>72</td>
<td>68</td>
<td>45</td>
<td>70</td>
<td>67</td>
</tr>
<tr>
<td>Catalyst 3</td>
<td>71</td>
<td>66</td>
<td>44</td>
<td>70</td>
<td>66</td>
</tr>
<tr>
<td>Catalyst 4</td>
<td>71</td>
<td>66</td>
<td>43</td>
<td>69</td>
<td>66</td>
</tr>
</tbody>
</table>

Amount of the catalyst= 0.50 g; temperature=80°C; and reaction time=4 h.

Further to see any change in the structure of supported PWA after reaction, the XRD of used catalyst E C₅-PWA₃/Z was also recorded (Figure-10).

Figure-10: XRD of fresh (PWA₃/Z) as well as used catalyst (E PWA₃/Z).
No difference in XRD pattern indicates stability of the used catalyst as well as absences of any degraded heteropolyanion after the reaction.

**Effect of support**

On the basis of above studies, it is concluded that neutral alumina is a better support than hydrous zirconia both from the viewpoint of thermal stability as well as activity. Due to phase change of hydrous zirconia, it is stable only up to 400° C, whereas neutral alumina is stable up to 600° C without any phase change.

Alumina is neutral in nature and does not show any catalytic activity towards esterification reactions. Thus the activity shown by PWA₃/A is due to PWA only while support hydrous zirconia is acidic in nature and active towards esterification reactions and hence activity shown by PWA₃/Z is due to synergic effect of PWA as well as hydrous zirconia.
Conclusion

I. The present catalysts are promising alternative to the traditional acid catalysts for liquid phase esterification reactions.

II. The catalyst containing 30% loading of PWA on neutral alumina and hydrous zirconia is best among the series.

III. Removal of the catalyst consists of the single filtration and catalyst can be regenerated and reused after a simple work-up.

IV. XRD study of reused catalyst shows no structural changes takes place indicating catalyst is very stable.

V. The catalyst has been proved to be successful and useful in the esterification of $^{1}\text{O}$ and $^{2}\text{O}$ alcohols under mild conditions as compared to that of traditional liquid catalyst.

VI. No contamination of nitro and sulphonated products, pure compound is obtained except water as byproduct which can removed.

VII. Neutral alumina (A) is the better support than hydrous zirconia (Z) from the point of thermal stability.

VIII. Unsupported PWA gives quite good % yield in some cases when used in homogeneous medium. But supported PWA is a superior catalysts since it is not associated with traditional problem of separation. It can be reused without any appreciable loss in activity.
References

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V. PAPERS PUBLISHED

I. Heteropolyacid supported onto neutral alumina: characterization and esterification of 1° and 2° alcohol


II. Tungstophosphoric acid supported onto hydrous zirconia: physicochemical characterization and esterification of 1° and 2° alcohol