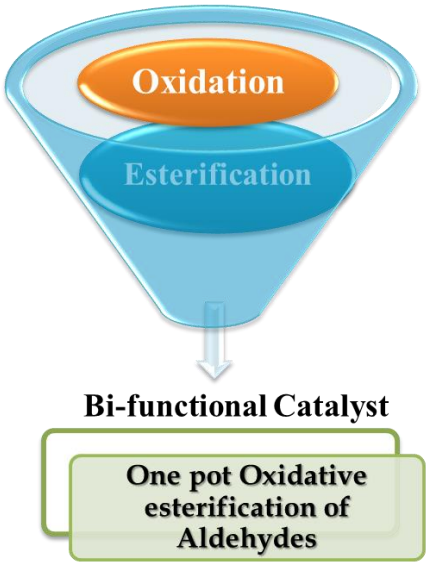
Chapter 4

Bifunctional Catalysis…….

Oxidative Esterification



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Oxidative Esterification of Aldehydes to Esters over Anchored Phosphotungstates

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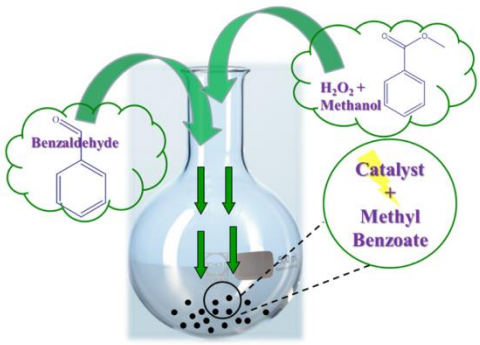
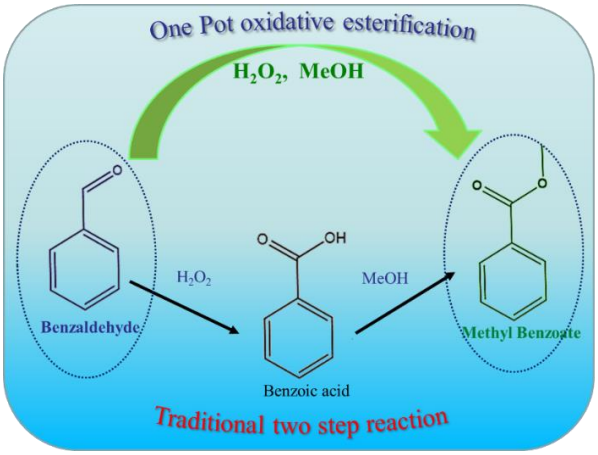
Abstract 12-Tungstophosphoric acid and lacunary phosphotungstate anchored to MCM-41 and ZrO_2 were synthesized, characterized and used as bifunctional catalyst for oxidative esterification of benzaldehyde with methanol. The different aldehyde substrates study show excellent selectivity for esters, indicating the scope of the catalysts. A tentative reaction mechanism for oxidative esterification of aldehyde is also proposed.



Keywords Phosphotungstates · Anchored · Oxidative esterification · Aldehydes · Esters

Methyl esters are one of the most important compounds in organic synthesis and are used in production of bulk and fine chemicals, natural and pharmacological compounds [1]. They are traditional prepared by reactions of carboxylic acid and methanol using acid catalysts (Scheme 1) such as sulfuric, sulfonic, phosphoric, hydrochloric and *p*-toluenesulfonic acid [2, 3]. Alkoxides, such as sodium and potassium alkoxides, have also been used to prepare methyl esters from carboxylic acid precursors [4]. Aldehydes can be converted to esters by two-step procedure, where, initially the oxidation of aldehyde with manganese dioxide or sodium dichromate takes place and then subsequent conversion of carboxylic acid intermediate to methyl ester. The direct oxidative esterification of aldehyde [5], avoiding the use of the corresponding carboxylic acid, is very attractive (Scheme 1) and hence has received increasing attention during recent years, as it allows oxidation as well as esterification in one pot. Therefore, a tremendous number of approaches for ester synthesis have been developed.



Scheme 1. Traditional and one pot procedure for synthesis of ester.

One-step conventional methods reported require the use of heavy-metal oxidants such as $KMnO_4$ [6], CrO_3 [7], oxone [8], V_2O_5-SPC/SPB (SPC-sodium percarbonate, SPB sodium perborate) [9] and 1, 5-cyclooctadiene (cod) complex of Iridium i.e $[IrCl(cod)]_2/K_2CO_3$ [10]. Most of the reported methods are useful for direct transformation of aldehydes with alcohols to corresponding esters. However, many methods suffer from disadvantages

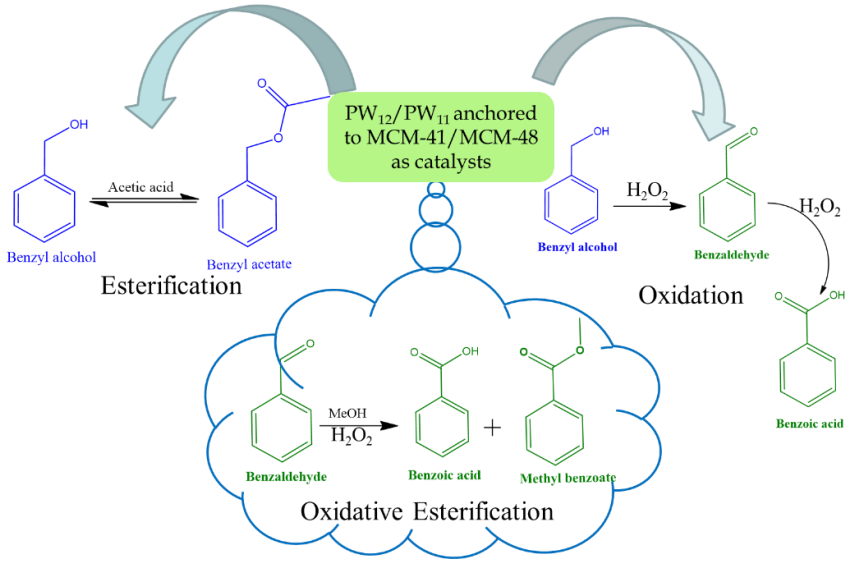
such as use of expensive and polluting reagents, an inert atmosphere and lengthy reaction times. Due to the huge amount of toxic wastes and by-products arising from chemical processes, chemists have been constrained to develop cost-effective and environmentally friendly catalytic routes that minimize waste.

Various groups have reported oxidative esterification of aldehydes on TS-1 [11], supported gold nanoparticle Au/TiO_2 [12], Pb and Mg doping in Al_2O_3-supported Pd [13], manganese phthalocyanine immobilized on silica gel [14], supported Gold-Nickel Oxide (AuNiOx) [15] and ionic liquid $BmimBF_4$ [16], etc. Consequently from the viewpoint of demands as well as significance of esterification and oxidation reactions, it is more beneficial to develop bifunctional catalysts for oxidative esterification of aldehydes.

However, catalysis by supported POMs [17, 18] have greatly expanded during the last few years, there are only two reports on oxidative esterification of aldehydes with H_2O_2 over supported POMs. Hou and group [19] synthesized, characterized $H_3PW_{12}O_{40}$-based ionic liquids, and employed them as catalysts for direct transformation of benzaldehyde to methyl ester in the absence of any co-catalyst with 86% conversion and 70% ester yield. However, in addition higher reaction time was required for the reaction. Rafiee and Eavani reported $H_3PW_{12}O_{40}$ immobilized on the surface of silica encapsulated γ-Fe_2O_3 nanoparticles [20] as catalyst for liquid phase oxidative esterification of benzaldehyde with H_2O_2.

Anchored parent phosphotungstate (PW_{12}) and lacunary phosphotungstate (PW_{11}) was successfully evaluated for individual bi-functional catalytic activity via. esterification (*Chapter 2*) as well as oxidation reactions (*Chapter 3*). From the esterification reaction we found that the synthesized catalysts were good acid catalysts with fairly strong acidic sites (Scheme 2).

Also, the catalysts provides good conversion for oxidation reactions of alcohols (Scheme 2) and alkenes, giving selectivity towards benzaldehyde.



Scheme 2. Catalytic versatility of supported catalysts over various organic transformations.

Due to encouraging results of all these reactions we thought of interest to evaluate the bi-functional catalytic activity for oxidative esterification of aldehyde (Scheme 2) where oxidation as well as esterification reactions occurs in one pot conditions. Hence, in the present chapter first part comprises of oxidation of aldehydes [4 (I)] and second part consists of oxidative esterification of aldehydes [4 (II)] using anchored PW_{12} and PW_{11}.

EXPERIMENTAL

Materials

All the chemicals used were of A. R. grade. Benzaldehyde, substituted aldehydes, methanol, ethanol, 1-hexanol, 2-propanol, 30% aq. H_2O_2, and dichloromethane were obtained from Merck and used as received.

Catalytic reaction

Oxidative esterification of aldehyde

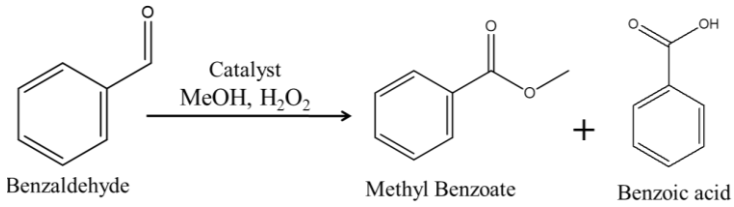
The reaction of benzaldehyde (0.01 mol) with H_2O_2 (0.03 mol) and methanol was carried out in a 50 mL batch reactor provided with a double walled air

condenser, Dean-Stark apparatus, magnetic stirrer, and a guard tube. The reaction mixture was refluxed at 80 ^{o}C for 6 h. Product was extracted with dichloromethane by repeated extractions and analyzed on GC (Shimatzu-2014) using a capillary column (RTX-5). The products were identified by comparison with authentic samples and finally by GC-MS.

RESULTS AND DISCUSSION

4 (I) Oxidative esterification of benzaldehyde (Benz) over PW_{12}/MCM-41 and PW_{11}/MCM-41.

Oxidative esterification of Benz with H_2O_2 is shown in Scheme 3.



Scheme 3. One pot reaction scheme for oxidative esterification.

Effect of % loading of PW_{12}/PW_{11}

Effect of % loading shows (Figure 1) that 30% loading of PW_{12}/PW_{11} on MCM-41 gives maximum conversion. There was no significant increase in conversion on increasing the loading to 40%. Hence, 30 % loading was optimized for further reactions.

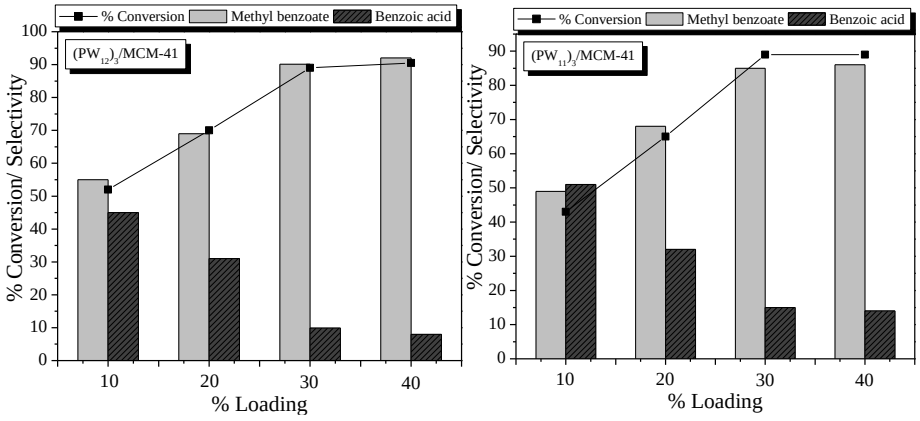


Figure 1. Effect of % loading of PW_{12}/PW_{11}: mole ratio of Benz: H_2O_2- 1:3, amount of catalyst- 100 mg, temperature- 80 ^{o}C, time- 4 h and methanol- 5 mL.

Effect of mole ratio of Benz: H_2O_2

To see the effect of the mole ratio, the reaction was performed by varying the mole ratio of Benz: H_2O_2 (from 1: 2 to 1: 5), with 100 mg of catalyst for 4 h at 80 °C (Figure 2). According to the chemical dynamics, the oxidative-esterification could be improved by increasing the amount of H_2O_2.

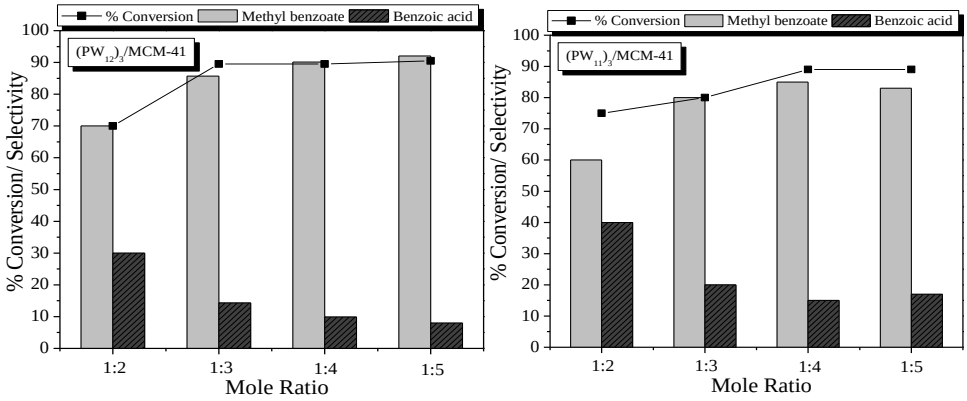


Figure 2. Effect of mole ratio Benz/H_2O_2: amount of catalyst- 100 mg, temperature- 80 ^oC, time- 4 h, and methanol- 5 mL.

It was observed from Figure 2 that the conversion increases with an increase in the molar ratio and reaches above 80 % for all the catalysts at mole ratio of 1:3. With a further increase in the mole ratio, there is no significant increase in conversion, however slight increase in selectivity of ester is observed. In all the cases major selectivity of methyl ester and benzoic acid as minor product was obtained at 1:3 mole ratio. Hence, the mole ratio of 1:3 was optimum for obtaining high conversion as well as selectivity.

Effect of catalyst amount

The effect of catalyst amount on conversion was studied by varying the catalyst amount in the range of 50-200 mg (Figure 3). Oxidative esterification is significantly affected by acidity as well as oxidizing property of the catalyst. The increase in the conversion can be attributed to an increase in the number of available catalytically active sites. Hence, in the present case all the catalysts give very good conversion. It is observed from figure, that the conversion increases with an increase in the amount of catalysts and reaches a maximum

of 98 and 95% for $(PW_{12})_3$/MCM-41 and $(PW_{11})_3$/MCM-41, at 100 mg, respectively. 100 mg catalyst was considered to be optimum for obtaining maximum conversion. The selectivity to ester product increased on increasing amount of the catalyst and major ester product was observed using 100 mg catalyst.

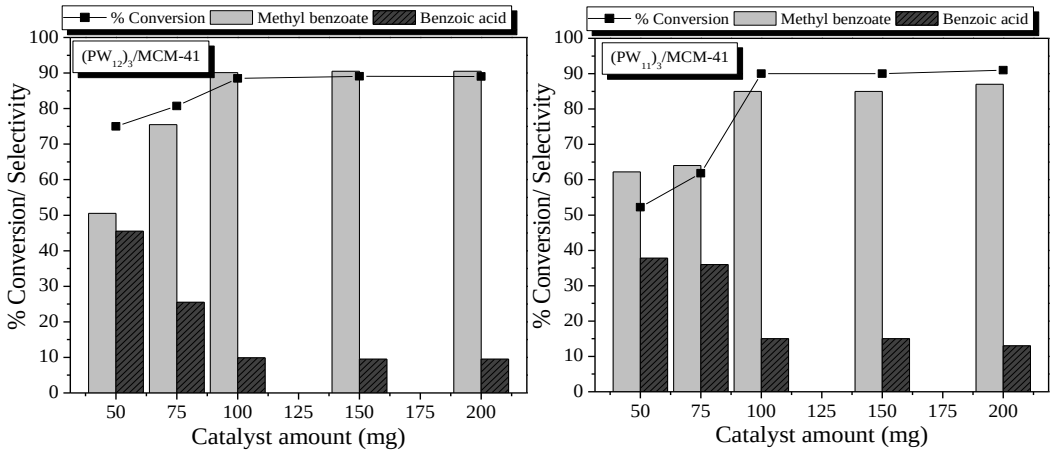


Figure 3. Effect of catalyst amount: mole ratio of Benz: H_2O_2- 1:3, temperature- 80 ^oC, time- 4 h, and methanol- 5 mL.

Effect of reaction time

The effect of reaction time (Figure 4) shows that the conversion increases with an increase in reaction time along with the selectivity toward methyl benzoate. After 6 h, no significant increase in the conversion was observed. Hence, looking at the % conversion and selectivity values, 6 h reaction time was optimised for further reactions.

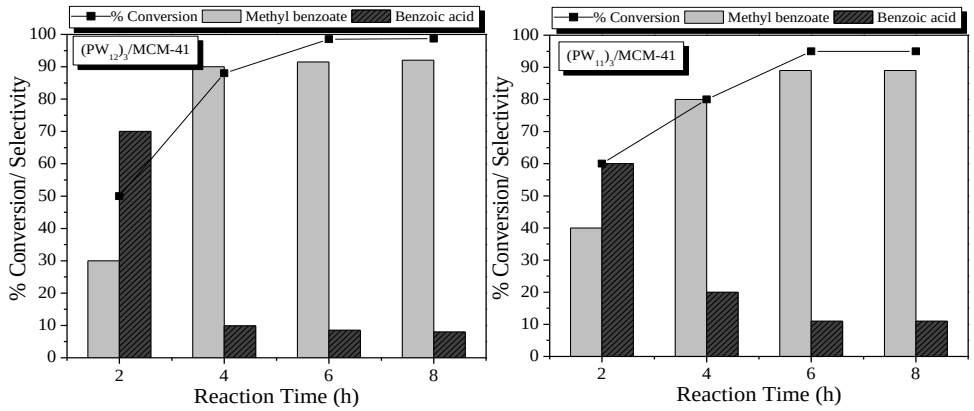


Figure 4. Effect of reaction time: mole ratio of Benz: H_2O_2- 1:3, catalyst amount- 100 mg, temperature- 80 ^oC, and methanol- 5 mL.

Effect of temperature

The effect of reaction temperature (Figure 5) indicates an increase in % conversion with temperature form 60 to 80 ^{o}C. A maximum of 98 and 95 % conversion was achieved respectively for $(PW_{12})_3$/MCM-41 and $(PW_{11})_3$/MCM-41, at 80 °C. However, on further increasing the temperature to 90 ^{o}C resulted in decrease in the selectivity of ester and formation of benzoic acid for $(PW_{12})_3$/MCM-41. Hence, 80 ^{o}C was optimised, to obtain maximum conversion and selectivity for ester.

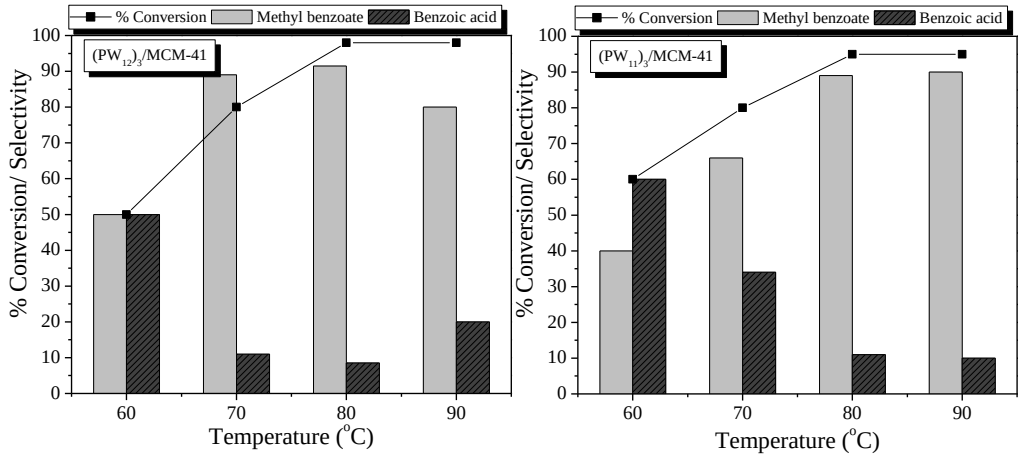


Figure 5. Effect of reaction temperature: mole ratio of Benz: H_2O_2- 1:3, catalyst amount- 100 mg, time- 6 h, and methanol- 5 mL.

Effect of methanol quantity

It is necessary to study the effect of methanol in the reaction medium as the methanol quantity greatly affects the selectivity toward the methyl ester (Table 1). On increasing the methanol quantity (Table 1) it was observed that selectivity to methyl benzoate increased. For $(PW_{12})_3$/MCM-41, the selectivity of ester was 60 % by using 2 mL of methanol as the reactant. In contrast, 91 % of methyl benzoate (with 98 % conversion) was achieved with 4 mL of methanol. Further increasing the quantity to 5 or 6 mL did no assist the selectivity much. The effect of methanol was identical with the other catalyst.

Table 1. Effect of methanol quantity on the reaction.

Methanol quantity (mL)	% Conv. [a/b]	% Selectivity [a/b]	
		Methyl Benzoate	Benzoic acid
1	80/75	30/28	70/72
2	85/78	60/54	30/46
3	90/85	85/78	15/22
4	98/95	91/89	9/11
5	99/95	92/89	8/11
6	99/95	93/88	7/12

Reaction conditions: mole ratio- 1:3; temperature- 80 °C; time- 6 h. [a] $(PW_{12})_3$/MCM-41, [b] $(PW_{11})_3$/MCM-41.

***Optimized conditions**:* mole ratio of benz to H_2O_2- 1:3; catalyst amount- 100 mg, temperature- 80 ^oC, time- 6 h, methanol- 4 mL.

4 (II) Oxidative esterification over PW_{12}/MCM-48 and PW_{11}/MCM-48.

Effect of % loading of PW_{12}/PW_{11}

Effect of % loading shows (Figure 6) that 30% loading of PW_{12}/PW_{11} on MCM-48 gives maximum conversion. There was no significant increase in conversion on increasing the loading to 40%. Hence, 30 % loading was optimized for further reactions.

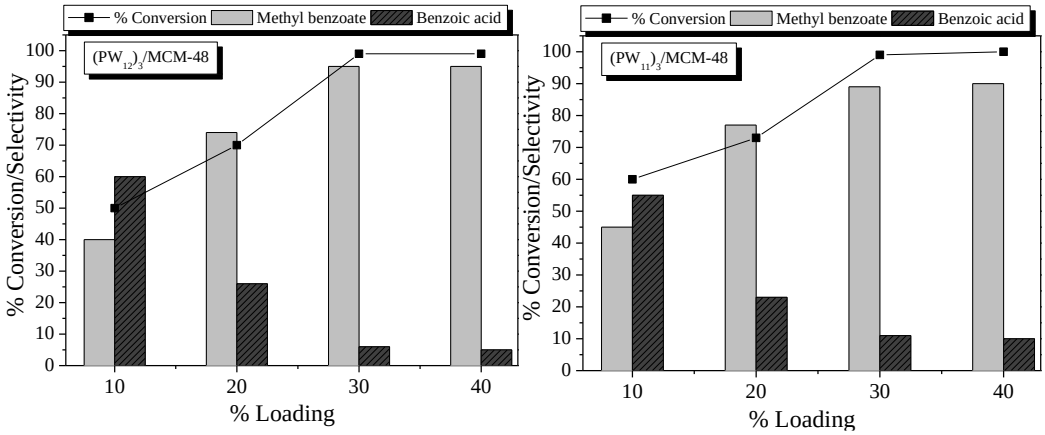


Figure 6. Effect of % loading of PW_{12}/PW_{11}: mole ratio of Benz: H_2O_2- 1:3, catalyst amount - 100 mg, temperature- 80 °C, time- 6 h, methanol- 4 mL.

Effect of mole ratio Benz: H_2O_2

The effect of mole ratio (1: 2 to 1: 5) was performed with 100 mg catalyst for 6 h at 80 °C (Figure 7).

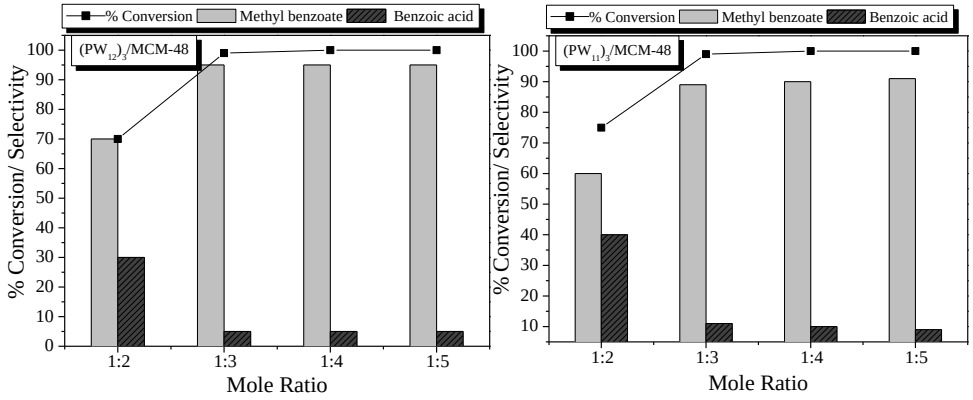


Figure 7. Effect of mole ratio: catalyst amount- 100 mg, temperature- 80 °C, time- 6 h, methanol- 4 mL.

The conversion was improved by increasing quantity of oxidant from 10 (1:1) to 20 mmol (1:2), and subsequently selectivity for methyl benzoate also

increases. The only major by-product was benzoic acid (obtained in-situ in the reaction). On increasing the mole ratio to 30 mmol (1:3), maximum 99% conversion and 90% selectivity for ester was obtained for $(PW_{11})_3$/MCM-48. Increasing the mole ratio above 1:3, showed no significant increase in the conversion.

Effect of catalyst amount

The effect of catalyst amount (from 50-200 mg) on conversion was also studied (Figure 8). The reaction was significantly affected by acidity as well as oxidizing property of the catalysts. On increasing the catalyst amount (from 50 to 100 mg) % conversion also increases. This is due to increase in concentration of available catalytically active sites of PW_{11} and in turn the acidity of the catalyst, which favours the selectivity of ester by subsequent oxidation and esterification reactions. After 100 mg no substantial change in conversion and selectivity was observed. Hence, 100 mg catalyst amount was optimized for obtaining highest conversion and maximum selectivity towards ester.

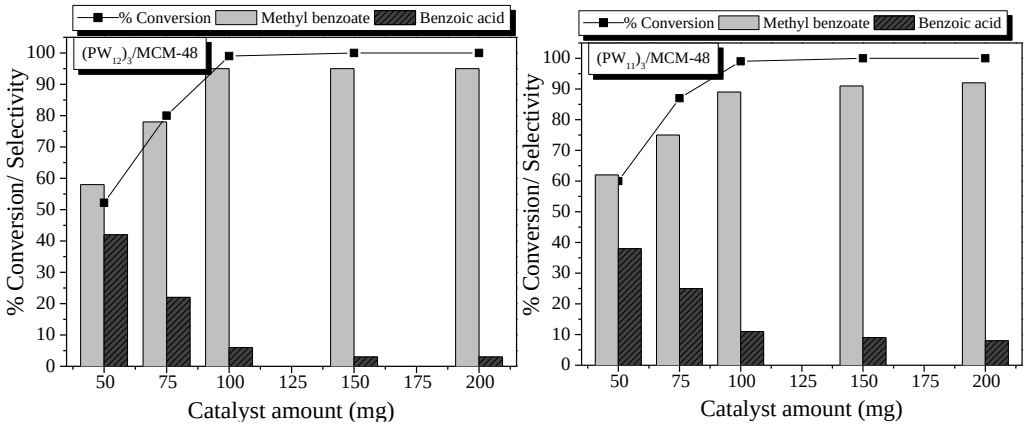


Figure 8. Effect of catalyst amount: mole ratio-1:3, temperature- 80 °C, time- 6 h, methanol- 4 mL.

Effect of reaction time

The % conversion was monitored at variable reaction time (Figure 9). A linear dependence of % conversion with time was observed initially. For heterogeneous reactions, time is required for formation of reactive intermediate (substrate + catalyst) which is finally converted to product. Also, selectivity for ester progressively increases with the reaction time. Maximum conversion (99%) was obtained at 6 h, with highest selectivity for ester. The conversion remains constant on further increasing time, hence reaction time- 6 h was optimized.

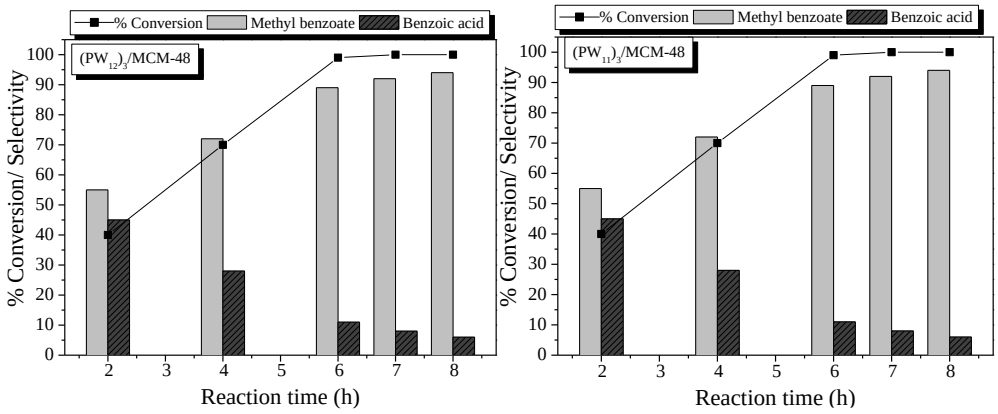


Figure 9. Effect of time: mole ratio of Benz: H_2O_2- 1:3, catalyst amount- 100 mg, temperature- 80 ^oC, methanol- 4 mL.

Effect of reaction temperature

The effect of reaction temperature (Figure 10) shows a linear increase in % conversion with temperature from 60-90 ^oC.

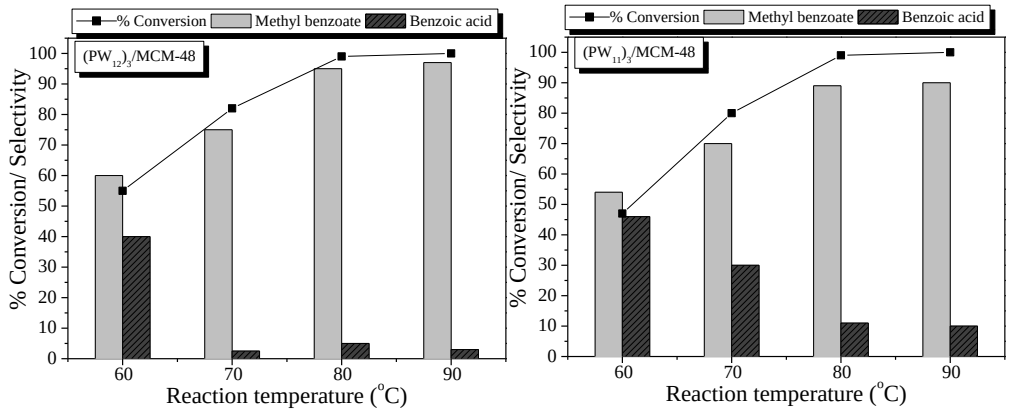


Figure 10. Effect of reaction temperature: mole ratio of Benz: H_2O_2- 1:3, temperature- 80 ^oC, time- 6 h, methanol- 4 mL.

Conversion and selectivity remains constant after 80 ^{o}C. The present reaction conditions are milder than reported in literature where, $H_3PW_{12}O_{40}$ based Ionic liquid (POM-IL) was used as catalyst [19]. The catalyst showed 86 % conversion and 70% ester yield, however in this case the reaction time (8 h) was longer.

Effect of methanol quantity

The methanol quantity significantly affects selectivity towards the desired methyl ester, hence it was essential to evaluate the effect of methanol on the progress of the reaction. It was estimated that selectivity for methyl benzoate increased significantly with an increase in the methanol quantity (Table 2) as discussed in the previous section.

Table 2. Effect of methanol quantity over $^{a}(PW_{12})_3$/MCM-48 and $^{b}(PW_{11})_3$/MCM-48.

Methanol quantity (mL)	% Conv. $^{a/b}$	% Selectivity $^{a/b}$	
		Methyl benzoate	Benzoic acid
2	80/75	60/55	40/45
4	99/99	95/90	5/10
5	100/100	95/92	5/8
6	100/100	92/92	8/8

Optimized conditions: mole ratio Benz to H_2O_2- 1:3; catalyst amount- 100 mg, temperature- 80 ^{o}C, time- 6 h, methanol- 4 mL.

Control experiments and Heterogeneity test

Control experiments (Table 3) shows that that catalytic activities of PW_{12}/PW_{11} have been retained in the respective catalysts indicating that PW_{12}/PW_{11} behaves as real active species. Heterogeneity test was carried out by for both the catalysts (Table 4). The reaction mixture of after filtration does not show any increase in the conversion or % selectivity indicating that there was no leaching of active species (PW_{12}/PW_{11}) from the support and catalysts are truly heterogeneous in nature.

Table 3. Control experiments under optimised conditions.

Catalysts	% Conv.	% Selectivity Methyl Benzoate	TON
MCM-41	30	-	-
MCM-48	30	-	-
PW_{12} [a]	88	80	1013
$(PW_{12})_3$/MCM-41 [b]	98	91	1224
$(PW_{12})_3$/MCM-48 [b]	99	95	1236
PW_{11} [a]	83	75	830
$(PW_{11})_3$/MCM-41 [b]	95	89	1179
$(PW_{11})_3$/MCM-48 [b]	99	90	1318

Reaction conditions: mole ratio 1:3; catalyst amount- [a] 23 mg, [b] 100 mg, temperature- 80 °C; time- 6 h; methanol- 4 mL. Turnover number (TON) = moles of product obtained/ moles of catalyst (active species) used.

Table 4. Heterogeneity test.

Reaction	Catalyst	% Conv.	% Sel. ester
$(PW_{12})_3$/MCM-41	Catalyst (4 h)	88	80
	Filtrate (6 h)	88	80
$(PW_{11})_3$/MCM-41	Catalyst (4 h)	85	80
	Filtrate (6 h)	85	80
$(PW_{12})_3$/MCM-48	Catalyst (4 h)	70	72
	Filtrate (6 h)	70	72
$(PW_{11})_3$/MCM-48	Catalyst (4 h)	78	80
	Filtrate (6 h)	78	80

Reaction conditions: molar ratio- 1:3, amount of catalyst- 100 mg, temp.- 80 ^{o}C.

Recycling and regeneration of catalysts

The catalysts were recycled up to four times in order to test their activity in successive runs (Table 5). The procedure for recycling was same as explained in *Chapter 2*. From figure it was observed that there was no significant difference in the % conversion and selectivity even after four cycles. Thus, the catalysts can be reused up to four cycles with minimal loss in the activity. Recycled catalysts were characterized by different techniques and results are previously presented in *Chapter 2a,* hence they are not included here again.

Table 5. Recycling of the catalysts.

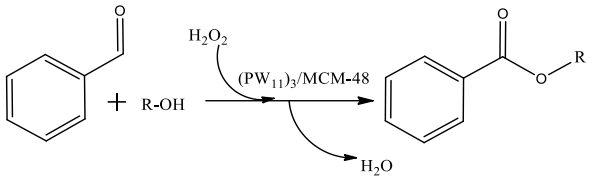
Catalyst	% Conversion (ester selectivity)				
	Fresh	1st Run	2nd Run	3rd Run	4th Run
$(PW_{12})_3$/MCM-41	98 (91)	97 (90)	96 (90)	96 (90)	96 (88)
$(PW_{11})_3$/MCM-41	95 (89)	93 (89)	93 (89)	91 (88)	91 (87)
$(PW_{12})_3$/MCM-48	99 (95)	96 (94)	95 (94)	95 (94)	95 (93)
$(PW_{11})_3$/MCM-48	99 (90)	98 (90)	97 (90)	97 (90)	97 (88)

Molar ratio of Benz: H_2O_2- 1:3, catalyst amount- 100 mg, time- 6 h and temperature- 80 °C, methanol- 4 mL.

Substrate scope with different alcohols

Various primary and secondary alcohols (Table 6, Entry 1-5) were also taken for this reaction and it was observed that as the chain length increases the conversion decreases, similar observation was observed for secondary alcohols. Methanol and ethanol act as good solvent and reactant for this type of reaction.

Table 6. Synthesis of alkyl benzoates by oxidative esterification of benzaldehyde and alkyl alcohols.



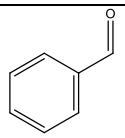
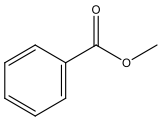
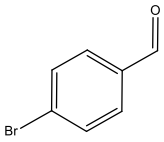
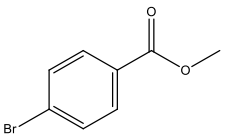
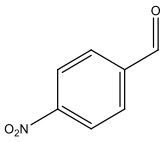
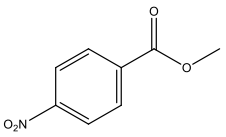
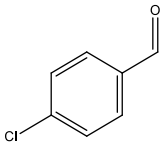
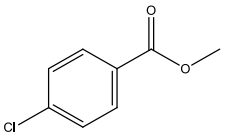
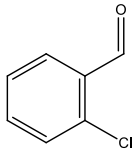
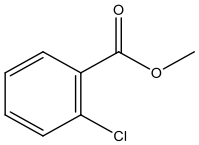
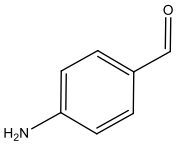
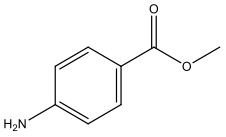
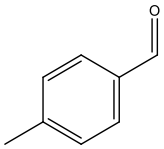
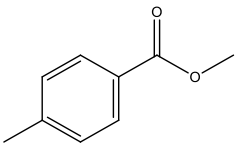
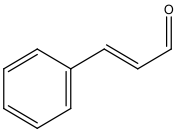
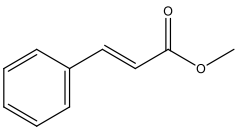
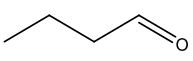
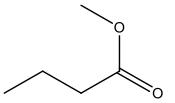
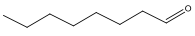
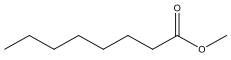
Entry	R-OH	Quantity (mL)	% Conv. a/b/c/d	Products	% Sel. a/b/c/d
1.	Methanol	4	98/95/99/99	Methyl benzoate	91/89/95/90
2.	Ethanol	4	85/80/88/85	Ethyl benzoate	76/72/76/75
3.	1-butanol	4	78/76/82/80	Butyl benzoate	65/63/70/68
4.	1-hexanol	4	70/70/75/72	Hexyl benzoate	65/62/68/65
5.	2-propanol	4	60/60/68/65	Isopropyl benzoate	65/60/65/62

[a] Optimum conditions: mole ratio of benz: H_2O_2 - 1:3; catalyst amount- 100 mg, temp.- 80 [o]C, time- 6 h. [a] $(PW_{12})_3$/MCM-41, [b] $(PW_{11})_3$/MCM-41, [c] $(PW_{12})_3$/MCM-48 and [d] $(PW_{11})_3$/MCM-48.

Substrate scope with different aldehydes

Scope of different aromatic and aliphatic aldehyde substrates were evaluated (Table 7). Under the optimized conditions, aromatic aldehydes having electron donating groups or weak electron withdrawing groups reacted smoothly to afford the resultant esters with very high selectivity (Table 10, Entry- 1-2, 4-5, 6-7). It was observed that *ortho* substitution brings down the conversion and selectivity for the ester (Entry 5). α, β-unsaturated aldehyde (Cinnamaldehyde) was also transformed to the corresponding α, β-unsaturated ester. The reaction also tolerated long chain aliphatic aldehydes to afford the corresponding aliphatic esters (Entry 9, 10).

Table 7. Oxidative esterification of different aldehydes over the catalysts, [a] $(PW_{12})_3$/MCM-41, [b] $(PW_{11})_3$/MCM-41, [c] $(PW_{12})_3$/MCM-48 and [c] $(PW_{11})_3$/MCM-48.

Entry	Substrate	Products	% Conv. a/b/c/d	% Sele. a/b/c/d
1.			98/95/99/99	91/89/95/90
2.			87/85/86/80	85/82/87/82
3.			81/79/83/80	86/89/89/88
4.			82/80/87/85	86/86/90/88
5.			80/78/82/80	75/72/77/75
6.			85/82/89/85	88/85/90/88
7.			87/80/90/89	70/67/76/74
8.			78/75/80/78	80/78/84/82
9.			76/70/80/85	85/80/89/85
10.			70/68/69/70	80/82/87/85

Proposed reaction mechanism

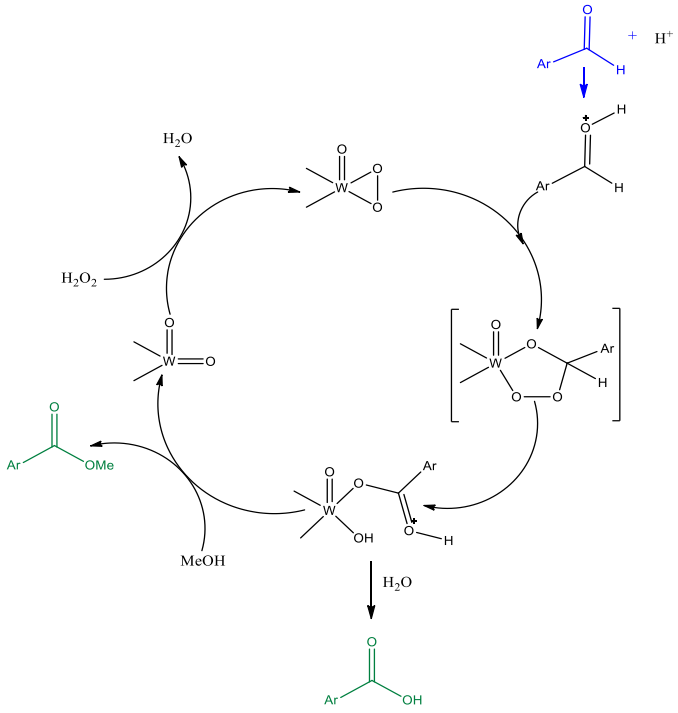
For proposing the mechanism for oxidative esterification few additional reactions were performed:

(i) With Benzaldehyde + Methanol + H_2O_2: reaction did not progress significantly in absence of catalyst (3% conversion),

(ii) Benzaldehyde + Methanol + catalyst and in the absence of H_2O_2: no significant reaction occurs,

(iii) In absence of methanol and presence of H_2O_2 only auto-oxidation reaction of benzaldehyde to benzoic acid (40% conversion) takes place.

It has been reported by Chavan et al. [11] that the catalyst titanium-silicate with H_2O_2 forms hydroperoxo or peroxo species which reacts with aldehyde to give titanium derived trioxolane species as intermediate. Following the mechanism for oxidation alcohols by H_2O_2 and POMs, the oxidative esterification of benzaldehyde (Scheme 4) will also be same. It is known for oxidation reactions with polyoxometalates/phosphotungstate, and H_2O_2 that, such reactions proceed via formation of bridging tungsten peroxo species [21, 22].



Scheme 4. Proposed mechanism for oxidative esterification of aldehyde with methanol.

In the present case, the catalysts are also expected to follow the same mechanism (Scheme 4) via the formation of an active tungsten-peroxo intermediate. This on further reaction with aldehyde, gives another intermediate of tungsten derived trioxolane species. This reactive intermediate then reacts with methanol giving methyl benzoate as a major product, also on removal of water gives rise to benzoic acid. In case of parent as well as lacunary phosphotungstate, same mechanism is expected. It also shows that acidity may play a role and difference in selectivity of esters for all the four catalysts might be due to the acidity of support.

Comparison of supports and active species for oxidative esterification

Effect of active species PW_{12}/PW_{11}

Comparison of effect of active species (PW_{12}/PW_{11}) (Table 8) shows that PW_{12} based catalysts showed higher conversion as compared to PW_{11}. The catalysts act as bifunctional one as they provide feasibility for acid catalysis as well as oxidation catalysis in one pot.

Table 8. Effect of supports on oxidative esterification reaction.

Catalyst	Surface area (m^2/g)	Pore width (Å)	Acidic strength (mV)	Acidity (mequiv /g)	% Conv.	% Sel. Ester	TON
$(PW_{12})_3$/MCM-41	360	30.1	410	3.8	98	91	1224
$(PW_{12})_3$/MCM-48	286	20.2	450	3.9	99	95	1236
$(PW_{11})_3$/MCM-41	252	30.0	250	3.0	95	89	1179
$(PW_{11})_3$/MCM-48	318	27.5	290	3.4	99	90	1318

The effect of lacunary PW_{11} was more pronounced for oxidation reactions *(from Chapter 3)* on comparing the difference in the catalytic activity between all the catalysts. $(PW_{11})_3$/MCM-48 showed higher oxidative conversions (Table 8) as compared to $(PW_{12})_3$/MCM-48 due to higher redox activity of PW_{11} than the parent PW_{12}. It is well known that lacunary PW_{11} have commendable catalytic

activity because of removal of a tungsten-oxygen octahedral moiety from a saturated PW_{12} framework (as lacunary core has a greater negative charge than the parent PW_{12}). Also, the activity of the catalysts was found to be consistent with the acidic strength of both the catalysts *(from Chapter 2)*. Hence, there is synergism between acidic and oxidative properties for oxidative esterification reaction. This can also be observed form the conversion which depends on oxidative property and selectivity (ester) depends on acidity of the catalysts.

Effect of support

Tuning the catalyst support is an important parameter to build highly active catalysts as discussed in C*hapter 2 and 3* already. From the esterification reactions it was established that the acidity of support assists in catalytic activity, as MCM-48 (2.2 mequiv./g) is more acidic than MCM-41 (2.0 mequiv./g). Also, the higher value of total acidity for $(PW_{12})_3$/MCM-48 as well as for $(PW_{11})_3$/MCM-48 was observed (Table 8). The trend in the activity for the catalysts was in good agreement with their acidic strength. The catalyst $(PW_{12})_3$/MCM-48 having highest acidic strength, produced best conversions and selectivity for esters. The acidic nature, higher surface area and better efficiency for mass transport of MCM-48 assists in esterification as well as oxidative esterification reaction.

Conclusions

- *One pot oxidative esterification* of benzaldehyde to methyl ester, where oxidation and esterification process occurs in the same reaction, avoiding the use of any intermediate step, was proposed using H_2O_2 over anchored parent PW_{12} as well as lacunary PW_{11}.
- *Bifunctional catalytic activity* was successfully achieved with higher than 90 % conversion as well as higher than 85% selectivity for ester under short reaction time, ambient temperature and TON > 1,000.
- *Environmentally benign oxidant* H_2O_2 and methanol, which acts as solvent as well as reactant, provides *green alternative* to the one pot reaction.
- The scope of one pot reaction was extended over *different aliphatic and aromatic aldehyde* substrates.
- The catalysts were *recyclable* after simple regeneration without any significant loss in the conversion.
- A *probable reaction mechanism* was also proposed using set of experimental results.
- In the inference we have described a practical, and *potentially economical* and very attractive route to equip esters from aldehydes under *green conditions.*
- The order of the catalytic activity for bifunctional oxidative esterification of benzaldehyde and selectivity towards ester was:
  - In terms of support: **MCM-48 > MCM-41**
  - In terms of catalyst: **$(PW_{12})_3$/MCM-48 > $(PW_{11})_3$/MCM-48 > $(PW_{12})_3$/MCM-41 > $(PW_{11})_3$/MCM-41.**

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