

Zirconium (IV) Molybdate- Application as Catalyst for the Synthesis of an Ester

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Authors' contributions

This work is a collective contribution of two authors. Author HKS proposed the methodology and author NS implemented the procedure to achieve the goal and also wrote the initial outline of the article. Author HKS analysed the results and gave a final shape to the manuscript.

ABSTRACT

Aims: The research work is based on the kinetic study of the esterification reaction of benzoic acid with alcohol by using Zirconium molybdate and conventional catalyst (sulphuric acid).

Study Design: The study was designed to compare the results of both the catalysts under similar conditions.

Place and Duration of Study: Department of Chemistry, M. M. University, Mullana (Ambala) India during June – December, 2012.

Methodology: An amorphous heteropolyacid salt named zirconium (IV) molybdate (ZrMoW), having 0.61 meq/g ion-exchange capacity was synthesized. Characterization as ion exchanger was done on the basis of physicochemical techniques. Then the prepared sample was tried as catalyst for the esterification reaction of benzoic acid with 1-propanol and iso-propanol. The results were compared with the conventional acid catalysts under the same conditions.

Results: The synthesized material was examined in different acidic and basic media, certifying its long range chemical stability. The compound is thermally stable, as only 17.67% weight decreased up to 200°C. Increase in the concentration of the catalyst accelerated the rate of esterification. The esterification of the benzoic acid with isopropanol didn't give any appreciable yield. The catalyst can be regenerated and reused again and again without any significant loss in the % yield i.e. only 10-15% even after 5 regenerations.

Conclusion: Esterification of benzoic acid with alcohol was carried out over ZrMoW catalyst and the results clearly demonstrated that zirconium (IV) molybdotungstate represents a better catalytic system as compared to conventional acid catalysts. From the kinetic study, inference was drawn that ZrMoW has got higher initial rate. It has been found that ZrMoW is admirable catalyst for the above esterification reaction.

Key words: Benzoic acid, ester synthesis, solid catalyst, zirconium molybdotungstate.

1. INTRODUCTION

Heteropolyacids/salts are widely accepted as excellent catalysts for various industrial organic synthetic processes [1-3]. Being heterogeneous in nature, easy in separation and regeneration, corrosive resistant, easy drainage of the effluents and eco-Friendly nature, efforts are quite successful to replace the conventional liquid acid catalysts by heteropolyacid compounds catalysts. A number of other techniques were also developed for the esterification process [4].

Esterification reaction is important in dyes, drugs, paints, food, fragrance, flavors and plasticizers industries. Chunfeng et al synthesized kegg-in-type heteropolyacids (HPAs) and characterized them by using various analytical techniques. The synthesized material was applied as catalyst for the chemical reactions of cracking and esterification of small as well as large molecules [5]. Various solid acid catalysts were used for esterification reactions as illustrated in the literature [6-11].

Amorphous zirconium titanium phosphate, has been synthesized, characterized and applied as catalyst for studying esterification reactions. TBMA salt exhibits elevated catalytic activity as

compared to its single salt counterparts and amorphous crystalline phases [12]. Esterification of acetic acid with butanol, butanol to butylbutanoate, salicylic acid with aliphatic alcohols, synthesis of acetamido ketones/esters, esterification of propanoic acid by butanol or 2-ethylhexanol, aspirin synthesis etc. represent the examples of esterification reactions catalysed by Heteropoly acids/salts reported in the literature [13-18], showing that the green catalysts are very efficient and could be easily recovered and recycled without any disturbance in structure and activity and yield was also considerable.

Shanmugam et al compared the results of the esterification reaction of triethylene glycol with methacrylic acid catalysed by solid acid catalysts with conventional acid catalysts and the results showed that heteropolyacids showed higher activities than the conventional acids [19]. Conventional acid catalysts are very active but corrosive and difficult to separate from the reaction mixture [20].

In the present research, work detailed kinetic study was carried out for the esterification of benzoic acid with 1-propanol and iso-propanol over zirconium molybdotungstate. The results were compared with analogous reaction catalyzed by sulphuric acid.

2. MATERIALS AND METHODS

2.1 CHEMICAL AND INSTRUMENTS

Zirconium oxychloride, sodium molybdate, sodium tungstate and benzoic acid were procured from CDH chemicals, India. The chemicals used during research work were of analytical grade. Double distilled water (DDW) was prepared by double distillation plant. 1-propanol and iso-propanol were procured from Merck chemicals. TGA studies were done on the basis of spectrum obtained with the help of Mettler Toledo Star System. Infrared studies of the synthesized ester were carried out with the help of IR- EFFINITY-21 CE Shimadzu spectrophotometer, using the KBr pellet technique. NMR data was obtained using Bruker advanced II 400 NMR spectrophotometer.

2.2 SYNTHESIS OF ZIRCONIUM (IV) MOLYBDOTUNGSTATE

Zirconium (IV) molybdotungstate was synthesized by introducing Zirconium oxychloride (0.1 M) solution, in small lots at regular intervals to a continuously stirred aqueous solution mixture of

sodium molybdate (0.1 M) and sodium tungstate (0.1 M) at 60°C in a volume ratio of 2:1:1 respectively. Gelatinous white precipitates were obtained at pH 1.0 which was adjusted by adding either requisite volume of dilute HCl or NaOH solution. Precipitates were digested at 60°C to refine them. Then the precipitates were filtered and washed with DDW to remove halide content. The gel was air dried at 40°C to retain the water of crystallization which is also responsible for its activity. The dried product gets converted into granular form by absorbing water in the available cavity. The granular material was converted into the H⁺ form by treating it with HCl (0.1 M) for 24 hours (minimum time required to attain the equilibrium) with occasional shaking and intermittent changing the acid. Washing and then finally drying at 40°C gave the precipitates, ready to use for catalytic action.

2.3 Characterization

Ion-exchange capacity of sample was determined by column operation techniques as explained in the earlier reports [21, 22].

Resistance toward the temperature change was explained on the basis of thermogravimetric analysis (TGA). Thermo gravimetric curve was obtained between 50°C and 750°C with a heating rate of 10°C per minute under nitrogen at a flow rate of 50.0 mL/minute. TGA curve of the synthesized material is represented in the figure 1.

To examine the chemical stability of the material, 0.2 gm of the exchanger was kept in 20 ml of the particular solvent, overnight. Various solvents tried were ethanol, methanol, acetone, isopropanol, propanol, butanol, HCl, NaOH, KOH, NaCl and HNO₃.

2.4 ESTERIFICATION STUDIES

Esterification reactions of benzoic acid were carried out with isopropanol and 1-propanol. Reactions were tried by varying the reactants, in the absence of water adsorbent and in the presence of water adsorbent. As the alcohol has to perform the dual function as a solvent and also as a reactant thus, is taken in excess. The reaction was carried out in a long necked 250 ml flask thermometer fitted with condenser, thermometer and a magnetic stirrer. Heating mantle was used to maintain a constant heating rate. Anhydrous sodium sulphate has been added to get rid of water content formed in the reaction. All the ingredients were added in a single lot and 2ml of

aliquot was withdrawn immediately and poured in 10 mL NaOH solution to lock the reaction and then the unreacted volume of the NaOH was found out by titrating against equinormal volume of HCl using phenolphthalien as an indicator. For a typical reaction 50mL alcohol, 1gm benzoic acid, 1gm Na₂SO₄ anhydrous and 1gm of ZrMoW/ 1 mL of conc. sulphuric acid were taken as reaction mixture. The reaction was carried out at 363K for 3 h. The formation of ester was confirmed by IR and NMR spectroscopy.

For the equilibrium constant measurements, the reaction was carried out for overnight and the acid concentration was monitored periodically. For comparison, the same reaction was carried out on acid catalysts such as sulphuric acid. Table 1 give an account of the various assemblies tried for the esterification reaction.

Table 1. Optimization of the reaction ingredients

S.No.	Alcohol	Acid	Catalyst	Inference
1.	Propanol	benzoic acid	ZrMoW	Yes
2.	Isopropanol	benzoic acid	ZrMoW	No.
3.	Propanol	benzoic acid	H ₂ SO ₄	Yes
4.	Isopropanol	benzoic acid	H ₂ SO ₄	Yes
5.	Propanol	benzoic acid	-	No.
6.	Isopropanol	benzoic acid	-	No.

3. RESULTS AND DISCUSSION

In this study, an acidic cation exchanger, zirconium (IV) molybdotungstate was synthesized and employed as a catalyst for esterification reaction. The exchanger can be regenerated and used over and again for its cation exchange capacity with a decrease of about 10% of its original value after four regeneration cycles.

Figure 1 containing the TGA curve elucidates the thermal bearings of the salt. The synthesized compound was quite firm and durable even at high temperature. TGA curve explains the weight change with the increase in temperature. Structural rearrangement involves losing of the external water molecules initially giving anhydrous heteropolyacid compound leading to decrease in weight of the salt. Up to 200⁰C only 17.67% of weight has been decreased. Further increase in temperature up to a temperature of 500 ⁰C results in loss of coordinated water and hydroxyl groups besides the rearrangement of functional groups. This weight loss is around 28.49%. These losses follow the regular trend of inorganic ion exchangers.

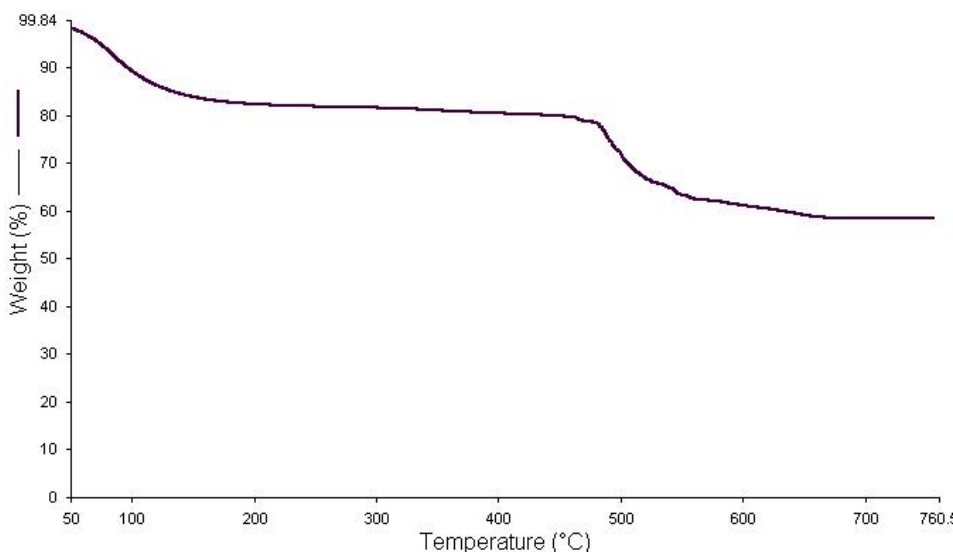


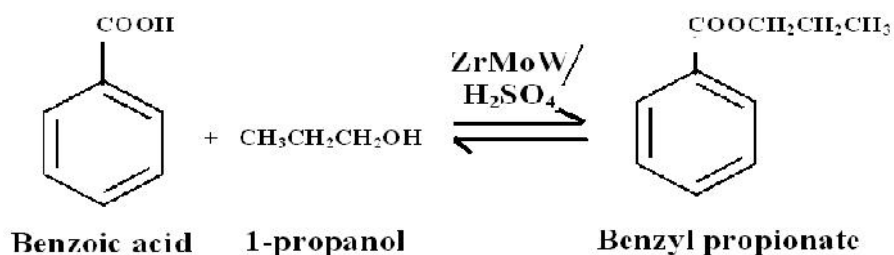
Figure 1. TGA curve of ZrMoW

No leaching, no change in colour and no weight loss has been observed, confirming its long range chemical stability and convenience to use in different environments.

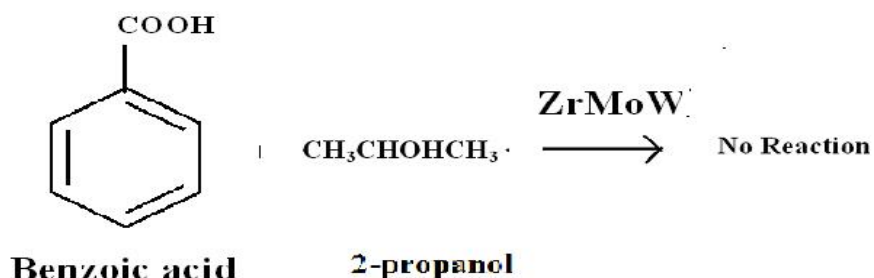
3.1 ESTERIFICATION OF BENZOIC ACID

The kinetic study of esterification of benzoic acid over zirconium (IV) molybdotungstate was carried out with n-propanol and isopropanol to produce n-propyl benzoate and iso-propyl benzoate. Schematic representation is given in the scheme 1 & 2. However, the esterification of the benzoic acid with iso-propanol didn't give any appreciable yield. The relative increase in the

rate of reaction is represented in the figure 2 and 3. Esterification with 1-propanol catalysed by ZrMoW gave the best results.



Scheme -1



Scheme-2

3.2 REGENERATION OF THE CATALYST/EXCHANGER

Recovery and further reuse of the catalyst in the reaction **increases** its viability. For the regeneration of ZrMoW, the resulting reaction mixture was filtered and then dried as the catalyst was insoluble in the reaction mixture. The resulting solid was then further activated by keeping in 0.1M HCl solution and then washed with demineralized water, till neutral. Thus the regenerated catalyst can be reused for further study under the same conditions without any remarkable loss of activity and selectivity. It was observed that there was a very small decrease in the production, only 10-15% even after 5 regenerations. The reports available **in the literature** gave the evidence

that the activity of the catalyst decreases in the subsequent reactions due the blockage of the activated sites by bulky molecules [23].

3.3 KINETIC STUDIES

The progress of the reaction is monitored by studying the concentration of the benzoic acid by withdrawing 0.2 ml of the aliquot and the reaction was ceased by pouring in calculated excess volume of NaOH. Remaining NaOH was estimated by titrating against HCl. From the graph it is clear that the molar concentration of the benzoic acid decreases with reaction time.

In figure 2, it is clear that initially the rate of reaction was very fast as there was fast decrease in concentration of the benzoic acid. After about 10 minutes of the progress of the reaction, it became slow as given by slanting part of the curve and after one hour the rate seemed to be constant as given by the plateau part of the curve.

During the esterification reaction of benzoic acid with isopropanol, there is almost negligible change in the concentration of the acid with the reaction time. The reason for this behavior might be the steric hindrance.

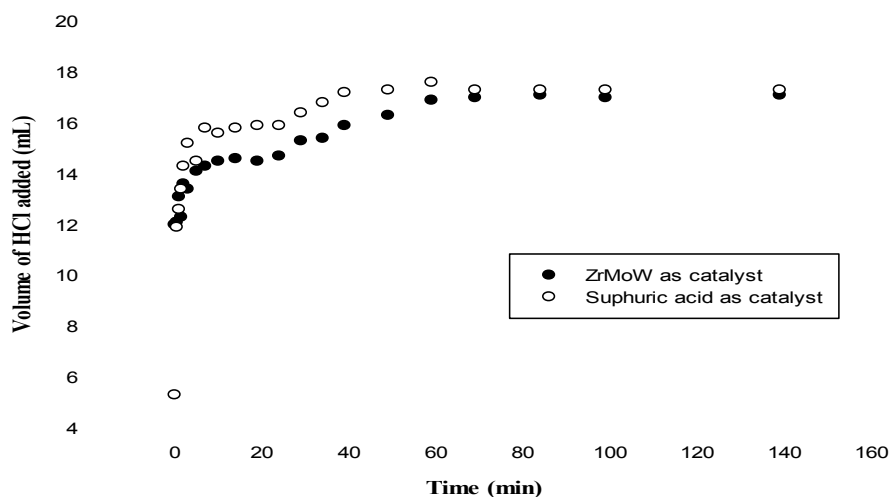


Figure 2. Change in the concentration of benzoic acid with reaction time using 1-propanol.

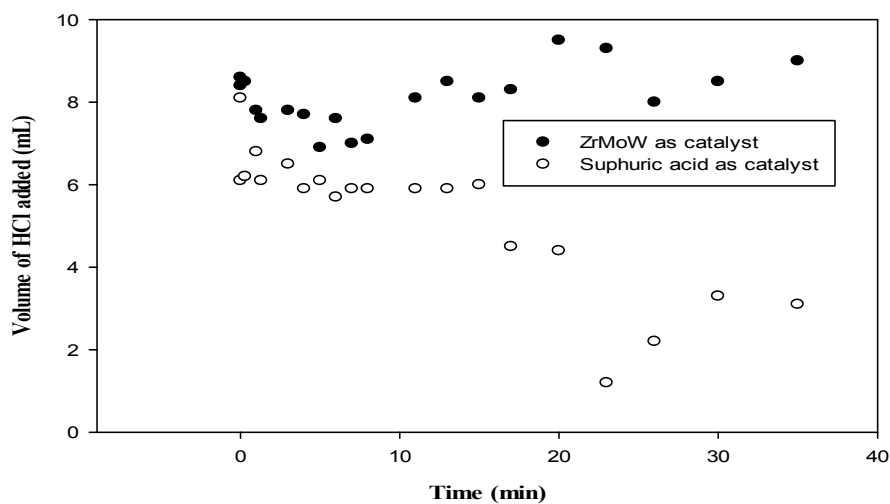


Figure 3. Change in the concentration of benzoic acid time using isopropanol.

3.4 CHARACTERISATION OF THE PRODUCT

The product of the reaction mixture was extracted with the help of DMSO and its FTIR (figure 4) gave the following analysis:

1. Band at 2935 cm^{-1} represented the C-H stretching vibration mode.
2. Band around 1737 cm^{-1} due to the presence of C=O stretching.
3. Stretching at 1421 cm^{-1} was due to C-O stretching.

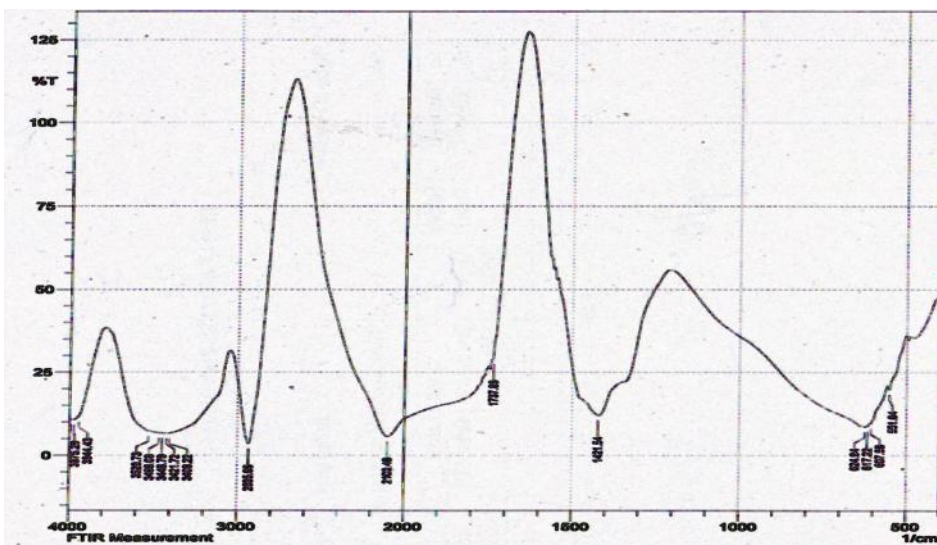


Figure 4. FTIR Spectra of Benzyl propionate

Further, the NMR studies of the product gave the following results, which confirm the formation of the ester.

8.01:(2H, d, ArH), 7.48(1H, tt, ArH), 7.46(2H, t, ArH), 4.72 (2H, t, OCH₂), 2.09 (2H, m, CH₂), 1.4 (3H, t, CH₃), 0.86 (3H, t, CH₃).

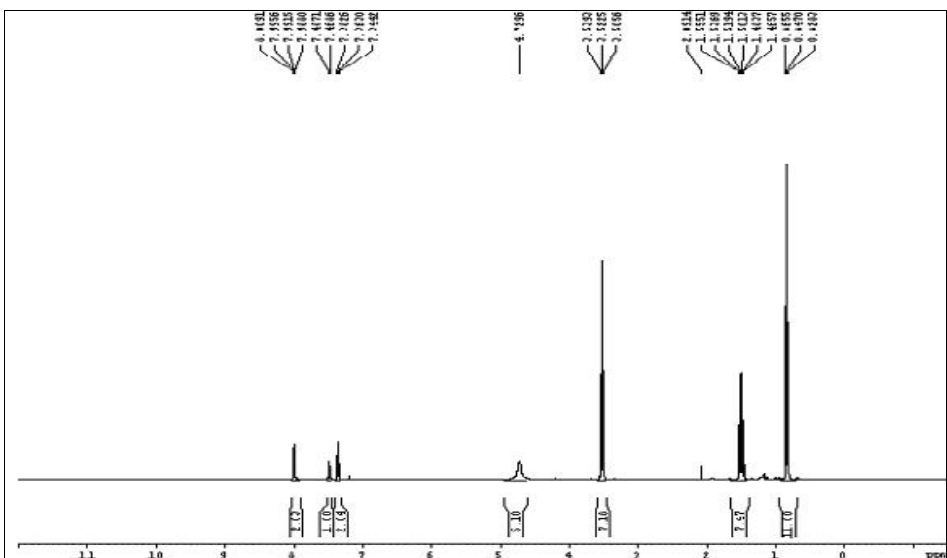


Figure 5. NMR Spectra of Benzyl propionate

3.5 EFFECT OF CATALYST CONCENTRATION

The reaction was studied by varying the concentration of the catalyst, also. It is observed that with the increase in the catalyst concentration from 1 to 2 g, the conversion of benzoic acid increased from 40% to 60%. The catalytic activity of the catalyst to a certain extent is proportional to the surface area of the catalyst. With the increase in amount of the catalyst, the number of available active sites increases in a proportionate way and thus the % yield increases.

4. CONCLUSION

Esterification of benzoic acid with alcohol was carried out over ZrMoW catalysts and the results clearly demonstrated that zirconium (IV) molybdotungstate represents a better catalytic system as compared to conventional acid catalysts. From the kinetic study, inference was drawn that ZrMoW has got higher initial rate and low activation energy. It has been found that ZrMoW is admirable catalyst for the above esterification reaction.

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REFERENCES

1. Okuhara T, Mizuno N, Misono M, Catalytic chemistry of heteropoly compounds. *Adv. Catal.* 1996;41;113-252.
2. Burrington JD, Johnson JR, Pudelski JK, Cationic Polymerization Using Heteropolyacid Salt Catalysts. *Topics in Catalysis.* 2003;23(1-4);175-181.
3. Firouzabadi H, Jafari AA, Heteropoly acids, their salts and polyoxometalates as heterogenous, efficient and eco-friendly catalysts in organic reactions: Some recent advances. *J. Iran. Chem. Soc.* 2005;2;85-114.
4. Pipus G, Plazi I, Koloimi T, Esterification of benzoic acid in microwave tubular flow reactor. *Chemical Engineering Journal.* 2000;76;239-245.
5. Shi C, Wang R, Zhu G, Qiu S, Long J, Synthesis, Characterization and Catalytic Properties of SiPW-X Mesoporous Silica with Heteropolyacid Encapsulated into Their Framework. *European Journal of Inorganic Chemistry.* 2005;23;4801-4807.
6. Cardoso AL, Augusti R, Da Silva MJ, Investigation on the Esterification of Fatty acids Catalyzed by the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ heteropolyacid. *Journal of the American Oil Chemists' Society.* 2008;85(6);555-560.
7. Chung KH, Chang DR, Park BG, Removal of free fatty acid in waste frying oil by esterification with methanol on zeolite catalysts. *Bioresource Technol.* 2008;99;7438-7443.
8. Wilson K, Lee AF, Macquarrie DJ, Clark JH, Structure and reactivity of sol-gel sulphonic acid silicas. *Appl. Catal. A: Gen.* 2002;228;127.
9. Liu WT, Tan CS, Liquid phase esterification of propionic acid with n-butanol. *Industrial Engineering Chemistry Research.* 2001;40;3281-3286.
10. Okazaki S, Wada N, Surface properties and catalytic activities of amorphous niobium phosphate and a comparison with those of H_3PO_4 -treated niobium oxide. *Catal. Today.* 1993;16;349-359.

11. Bhatt N, Patel A, Esterification of 1^o and 2^o alcohol using an ecofriendly solid acid catalyst comprising 12-tungstosilicic acid and hydrous zirconia. *Journal of Molecular Catalysis A: Chemical*. 2005;238;223-228.
12. Thakkar R, Chudasama UV, Synthesis of mono and diesters using eco-friendly solid acid catalyst – zirconium titanium phosphate. *Green Chemistry Letters and Reviews*. 2009;2(2);61-69.
13. Meireles ALP, Rocha KAS, Kozhevnikov IV, Gusevskaya EV, Esterification of camphene over heterogeneous heteropoly acid catalysts: Synthesis of isobornyl carboxylates. *Applied Catalysis A: General*. 2011;409–410;82–86.
14. Bamoharram FF, Heravi MM, Roshani M, Jahangir M, Gharib A, Manouchehr Jahangir, Ali Gharib, Effective direct esterification of butanol by eco-friendly Preyssler catalyst, [NaP5W30O110]14–, *J. Mol. Catal. A: Chemical*. 2007;271;126-130.
15. Bamoharram FF, Heravi MM, Roshani M, Jahangir M, Gharib A, Preyssler catalyst, [NaP5W30O110]14–: A green, efficient and reusable catalyst for esterification of salicylic acid with aliphatic and benzylic alcohols. *Appl. Catal. A: General*. 2006;302;42-47.
16. Bamoharram FF, Ahmadpour A, Heravi MM, Charkhi MJS, Bulk and Activated Carbon-Supported Tungstophosphoric Acid as Recyclable and Green Catalyst for One-Pot Synthesis of Acetamido Ketones and Esters. *E-J Chemistry*. 2011;8(2); 689-696.
17. Dupont P, Lefebvre F, esterification of propanoic acid by butanol and 2-ethylhexanol catalyzed by heteropolyacids pure or supported on carbon. *Journal of Molecular Catalysis A: Chemical*. 1996;114 (1-3);299-307.
18. Bamoharram FF, Heravi MM, Roshani M, Mir H, Gharib A, Catalytic method for synthesis of aspirin by a green, efficient and recyclable solid acid catalyst (Preyssler's anion) at room temperature. *Journal of the Chinese Chemical Society*. 2007;54;1017-1020.

19. Shanmugam S, Viswanathan B, Varadarajan TK, Esterification by solid acid catalysts—a comparison. *Journal of Molecular Catalysis A: Chemical*. 2004;223;143-147.
20. Jermy BR, Pandurangan A, Catalytic application of Al-MCM-41 in the esterification of acetic acid with various alcohols. *Applied Catalysis A: General*. 2005;288;25-33.
21. Sharma HK, Sharma N, Potentiometric sensors for Gd^{3+} ion based on Zirconium (IV) tungstophosphate. *E-J chemistry*. 2009;6(4);1139-49.
22. Sharma HK, Sharma N, Potentiometric sensors for Gd^{3+} ion based on Tin (IV) tungstophosphate. *Res J. of Chem. Environ*. 2011;15(2);897-901.
23. Yadav GD, Nalavade SP, Selectivity engineering of 4-phenoxyacetophenone by acylation of diphenyl ether with ion exchange resins: modeling of catalyst deactivation and remedies. *Chem. Eng. Sci*. 2003;58(12);2573-2585.