

Research Paper

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

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Authors' contributions

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

ABSTRACT

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

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

Place and Duration of Study: Department of Chemistry, M. M. University, Mullana (Ambala) India

Methodology: An amorphous heteropolyacid salt named zirconium (IV) molybdate (ZrMoW), having 0.61 meq/g ion-exchange capacity has been 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 2-propanol. The results were compared with the conventional acid catalysis under similar conditions.

Result: The synthesized material was examined in different acidic and basic media, certifying its long range chemical stability. The compound is highly stable, as only 17.67% of weight has been decreased up to 200°C. Increase in the concentration of the catalyst accelerates the rate of esterification. The esterification of the benzoic acid with 2-propanol 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% loss in capacity even after 5 regenerations.

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 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 catalyst for various industrial organic synthetic processes [1-3]. Because of heterogeneous in nature, ease 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 keggin-type heteropolyacids (HPAs) and characterized it by various analytical techniques and then the synthesized material was applied as catalyst for the chemical reactions of cracking and esterification on 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 (TBMA) has been synthesized, characterized and employed as catalyst for studying esterification reactions. TBMA salt exhibits elevated catalytic activity as compared to its single salt counterparts and amorphous species expressed eminent catalytic activity as compared to their crystalline phases [12]. Esterification of camphene, 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 acid / salts reported in the literature [13-18] showing that the green catalysts are very efficient, 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 2-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. DDW water was prepared by double distillation plant. 1-propanol and 2-propanol were procured from Merck chemicals. TGA studies were done on the basis of spectrum obtained with the help of Mettler Toledo Star System. IR spectra of the synthesized ester were executed with the help of IR- EFFINITY-21 CE Shimadzu 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 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, these 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 are also responsible for its activity. The dried product gets intermingled 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. The material was then detached from the acid by decantation and treated with excess of double distilled water to get rid of unwanted adhering acid, finally, drying at 40°C step gave the compound, ready to use for catalytic action.

2.3 ION-EXCHANGE CAPACITY

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

2.4 THERMAL BEHAVIOUR

Resistance toward the temperature variation was explained on the basis of thermogravimetric analysis (TGA). TGA curve of the assembled materials is represented in the figure 1.

2.5 ESTERIFICATION STUDIES

Esterification reactions of benzoic acid was carried out with 2-propanol 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 have to perform the dual function as a solvent and also as a reactant thus, 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 were taken as reaction mixture. The reaction was carried out at 363K for 3 h. The formation of ester was confirmed by IR 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 using sulfuric acid catalysts. Table 1 give account of the various assemblies tried for the esterification reaction.

Table 1. Optimization of the reaction ingredients

S.No.	Alcohol	Acid	Catalyst	Inference
1.	1-Propanol	benzoic acid	ZrMoW	Yes
2.	2-propanol	benzoic acid	ZrMoW	No.
3.	1-Propanol	benzoic acid	H ₂ SO ₄	Yes
4.	2-propanol	benzoic acid	H ₂ SO ₄	Yes
5.	1-Propanol	benzoic acid	-	No.
6.	2-propanol	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 10% of its original value after four regeneration cycles.

3.1 STABILITY OF THE CATALYST

To examine the stability of the catalyst, 0.2 gm of the exchanger was kept in 20 ml of the particular solvent, overnight. Various solvents tried were ethanol, methanol, acetone, 2-propanol, 1-propanol, 1-butanol, HCl, NaOH, KOH, NaCl and HNO₃. No leaching, no change in colour and

no weight loss has been observed, confirm its long range chemical stability and convenient to use in different environment.

3.2 THERMAL STABILITY

Figure 1 containing the TGA curve elucidated 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. Up to 200°C only 17.67% of weight has been decreased which may be due to depletion of water of hydration. Up to 500°C only 28.49 % decline in weight was observed, might be due to rearrangement of the structure.

3.3 ESTERIFICATION OF BENZOIC ACID

The kinetic study of esterification of benzoic acid over zirconium (IV) molybdate 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 n-propanol catalysed by ZrMoW gave the best results.

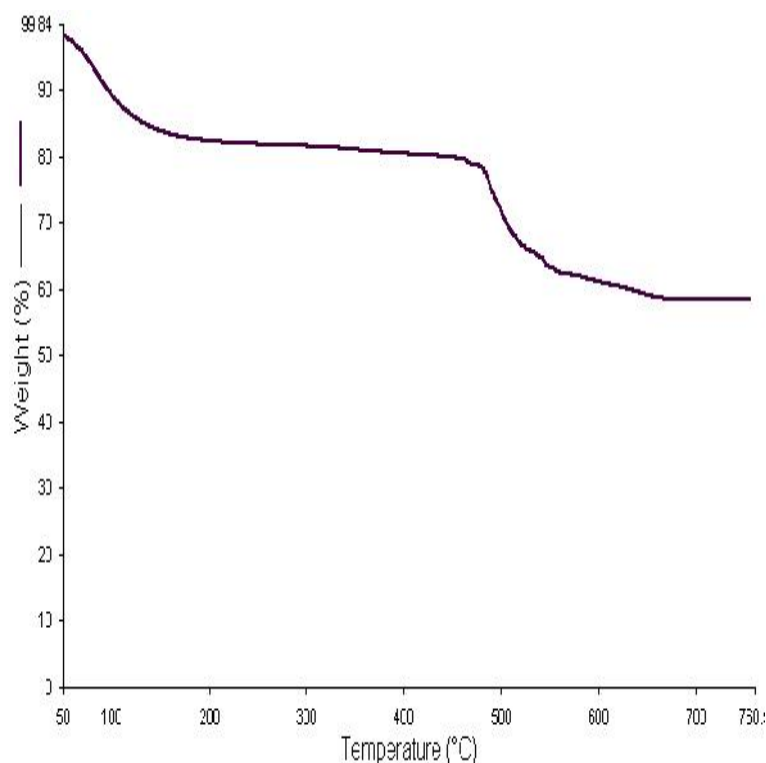
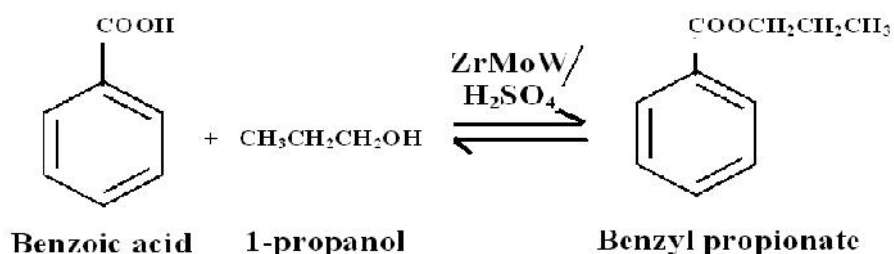
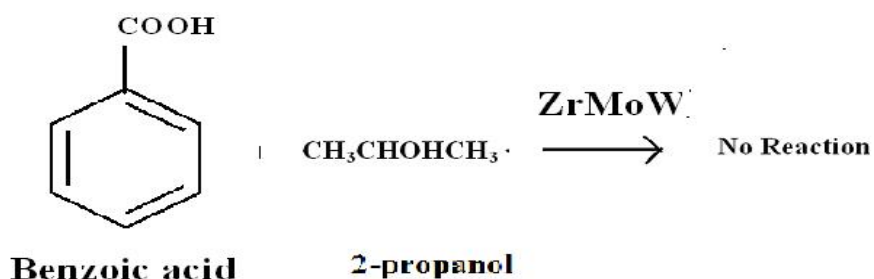


Figure 1. TGA curve of ZrMoW



Scheme -1



Scheme-2

3.4 EFFECT OF CATALYST CONCENTRATION

The reaction was studied by varying the concentration of the catalyst, also. It is observed that with an 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.

3.5 REGENERATION OF THE CATALYST / EXCHANGER

Recovery and further reuse of the catalyst in the reaction, increase its acceptability. 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 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].

3.6 KINETIC STUDIES

The change in the concentration of benzoic acid was monitored and represented in Figure 2. It is observed that the acid strength of the catalysts and hence the catalytic activity follows the order $\text{ZrMoW} \sim \text{H}_2\text{SO}_4$.

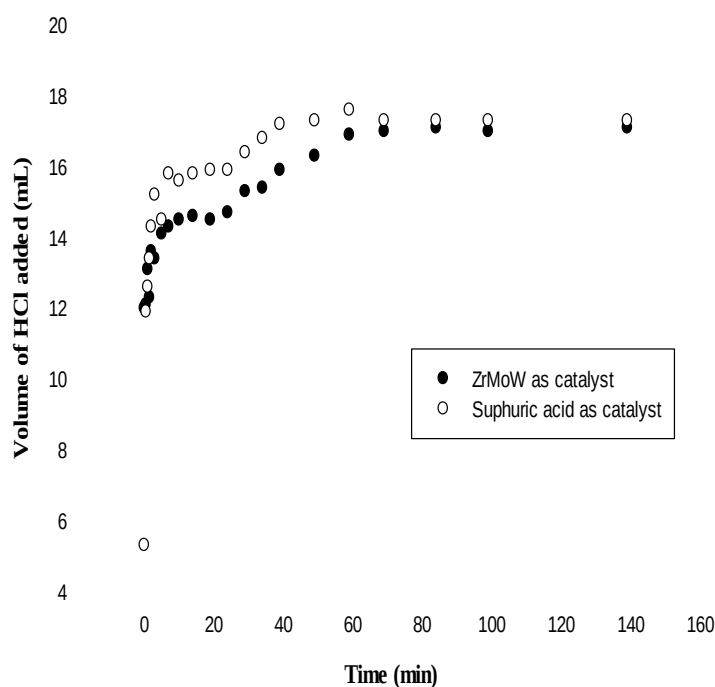


Figure 2. Change in the concentration of benzoic acid with time using 1-propanol as catalyst.

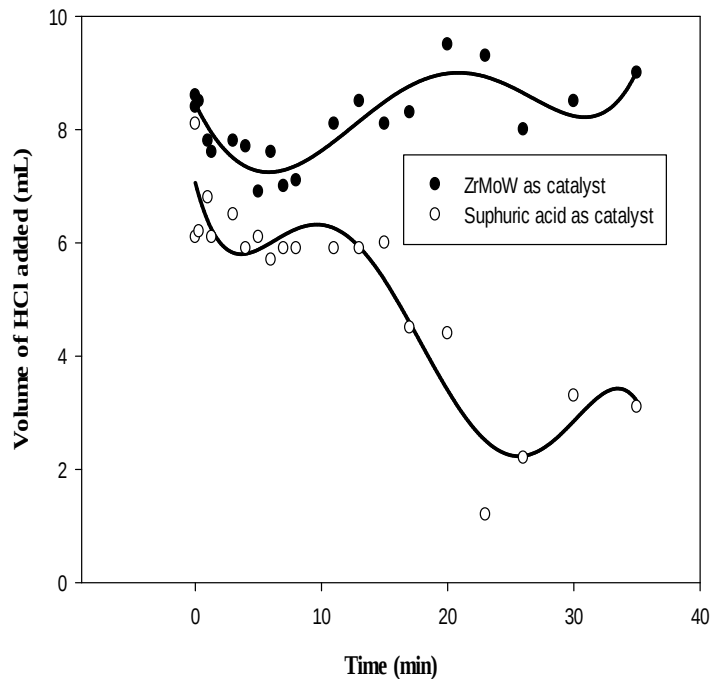


Figure 3. Change in the concentration of benzoic acid time using 2-propanol.

3.7 CHARACTERISATION OF THE PRODUCT

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

1. Band at 2935 cm^{-1} represents 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-H stretching.
4. A very weak band near 1320 cm^{-1} represent the stretching mode due to C-O bond.

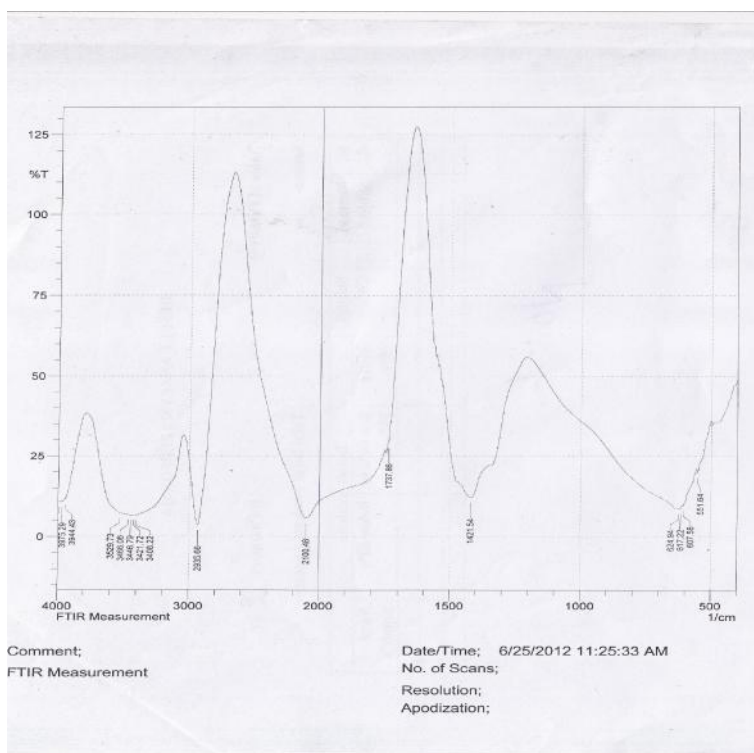


Figure 4. FTIR Spectra of Benzyl propionate

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 $H_3PW_{12}O_{40}$ 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.

- 234 [10] Okazaki S, Wada N. Surface properties and catalytic activities of amorphous
235 niobium phosphate and a comparison with those of H₃PO₄-treated niobium oxide. *Catal.*
236 *Today*. 1993;16;349-359.
- 237 [11] Bhatt N, Patel A. Esterification of 1^o and 2^o alcohol using an ecofriendly solid acid
238 catalyst comprising 12-tungstosilicic acid and hydrous zirconia. *Journal of Molecular*
239 *Catalysis A: Chemical*. 2005;238;223-228.
- 240 [12] Thakkar R, Chudasama UV. Synthesis of mono and diesters using eco-friendly solid
241 acid catalyst – zirconium titanium phosphate. *Green Chemistry Letters and Reviews*.
242 2009;2(2);61-69.
- 243 [13] Meireles ALP, Rocha KAS, Kozhevnikov IV, Gusevskaya EV. Esterification of
244 camphene over heterogeneous heteropoly acid catalysts: Synthesis of isobornyl
245 carboxylates. *Applied Catalysis A: General*. 2011;409–410;82–86.
- 246 [14] Bamoharram FF, Heravi MM, Roshani M, Jahangir M, Gharib A, Manouchehr
247 Jahangir, Ali Gharib. Effective direct esterification of butanol by eco-friendly Preyssler
248 catalyst, [NaP₅W₃O₁₁]₁₄-. *J. Mol. Catal. A: Chemical*. 2007;271;126-130.
- 249 [15] Bamoharram FF, Heravi MM, Roshani M, Jahangir M, Gharib A. Preyssler catalyst,
250 [NaP₅W₃O₁₁]₁₄-. A green, efficient and reusable catalyst for esterification of salicylic
251 acid with aliphatic and benzylic alcohols. *Appl. Catal. A: General*. 2006;302;42-47.
- 252 [16] Bamoharram FF, Ahmadpour A, Heravi MM, Charkhi MJS. Bulk and Activated
253 Carbon-Supported Tungstophosphoric Acid as Recyclable and Green Catalyst for One-
254 Pot Synthesis of Acetamido Ketones and Esters. *E-J Chemistry*. 2011;8(2); 689-696.
- 255 [17] Dupont P, Lefebvre F. esterification of propanoic acid by butanol and 2-
256 ethylhexanol catalyzed by heteropolyacids pure or supported on carbon. *Journal of*
257 *Molecular Catalysis A: Chemical*. 1996;114 (1-3);299-307.
- 258 [18] Bamoharram FF, Heravi MM, Roshani M, Mir H, Gharib A. Catalytic method for
259 synthesis of aspirin by a green, efficient and recyclable solid acid catalyst (Preyssler's

- 260 anion) at room temperature. Journal of the Chinese Chemical Society. 2007;54;1017-
261 1020.
- 262 [19] Shanmugam S, Viswanathan B, Varadarajan TK. Esterification by solid acid
263 catalysts—a comparison. Journal of Molecular Catalysis A: Chemical. 2004;223;143-
264 147.
- 265 [20] Jermy BR, Pandurangan A. Catalytic application of Al-MCM-41 in the esterification
266 of acetic acid with various alcohols. Applied Catalysis A: General. 2005;288;25-33.
- 267 [21] Sharma HK, Sharma N. Potentiometric sensors for Gd^{3+} ion based on Zirconium (IV)
268 tungstophosphate. E-J chemistry. 2009;6(4);1139-49.
- 269 [22] Sharma HK, Sharma N. Potentiometric sensors for Gd^{3+} ion based on Tin (IV)
270 tungstophosphate. Res J. of Chem. Environ. 2011;15(2);897-902.
- 271 [23] Yadav GD, Nalavade SP. Selectivity engineering of 4-phenoxyacetophenone by
272 acylation of diphenyl ether with ion exchange resins: modeling of catalyst deactivation
273 and remedies. Chem. Eng. Sci. 2003;58(12);2573-2585.