Research Paper

Volume : 2 | Issue : 3 | Mar 2013 • ISSN No 2277 - 8179

O-acetylation of salicylic acid over Zirconium phosphate (ZPO) solid acid catalyst

Chemistry

KEYWORDS : Zirconium phosphate, Phosphated zirconia, o-acetylation.

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ABSTRACT

Zirconium phosphate (ZPO) solid acid catalyst was prepared by impregnation and precipitation methods. ZPO was also coated on a cordierite honeycomb by slurry coating method. ZPOs were characterized for their surface area, surface acidity, crystallinity and functionality by using BET, powder X-ray diffraction, infrared spectroscopic techniques, and n-butyl amine back titration methods. Catalytic activity of ZPOs was evaluated in the synthesis of a medicinal compound acetyl salicylic acid (aspirin). ZPO catalysts were found to be highly efficient for aspirin synthesis with a yield of aspirin up to 98% with 100% selectivity. Optimization of reaction conditions was carried out by varying molar ratio of the reactants (salicylic acid and acetic anhydride), amount of the catalyst, reaction time, and reaction temperature. ZPO were found to be eco-friendly and reusable.

1. Introduction

The trend to develop of efficient solid (heterogeneous) catalysts for the synthesis of fine chemicals is increasing day by day since these are environmentally benign with respect to corrosiveness, safe for use, generate less waste, easy to recover and reuse [1]. Solid acids are particularly important in acid catalyzed reactions as a safe alternative to the hazardous and corrosive materials such as sulphuric and nitric acid [2, 3]. During recent past, a lot of efforts were made to develop the recoverable solid acid catalysts for minimizing pollution and reducing cost [2-8].

Metal phosphates are one of the most important classes of inorganic materials used as solid acid catalysts for a wide range of applications [9]. However, zirconium phosphate has been studied to a lesser extent as compare to the silica /silicate based mesoporous materials such as SAPO's or AUPO's. [10-14]. In particular, Zirconium phosphates (ZPOs) have been used in catalytic reactions such as dehydration of alcohols and isomerisation of olefins [15, 16]. The activity of these materials is attributed to the Bronsted acidity of hydroxyl groups and the Lewis acidity of the metal centre.

Acetyl salicylic acid (aspirin), is a common non-steroidal analgesic, antipyretic and anti-rheumatism drug. Today Aspirin is one of the most commonly used medicines used around the globe. Acetyl salicylic acid is generally prepared by acetylation reaction with Salicylic acid and acetic anhydride in presence of concentrated H2SO4 or H3PO4 [17, 18]. The use of concentrated sulphuric or phosphoric acid as catalysts has, however, resulted in low production yield (65-67%) and poor selectivity as well as strong reactor corrosion and severe environmental pollution.

In the present article, an attempt has been made to synthesize solid acids such as zirconium phosphate & phosphated zirconia by different methods, characterize these solid acids for their physico-chemical characterization and their catalytic activity evaluation in the synthesis of aspirin via acetylation of salicylic acid & acetic anhydride. Zirconium phosphate was also coated on a honeycomb monolith and used in acetylation reaction in order to compare the activity in its powder form and honeycomb coated form. Optimization ofreaction conditions to obtain highest possible yield of aspirin with good selectivity was carried out along with a study on the reusability of these solid acids in acetylation reaction.

2. Experimental

2.1 Chemicals

Chemicals such as zirconyl nitrate octahydrate, o-phosphoric acid, salicylic acid and acetic anhydride were supplied by M/S Loba Chemie, India.

2.2 Preparation of ZPO

ZPO was prepared by taking the zirconyl nirate and o-phosphoric acid such that the final product consisted of Zr: P in the ratio 0.95: 1.0. ZPO was prepared by using impregnation and precipitation methods.

2.2.1 Preparation of ZPO by precipitation method

ZPO was prepared by precipitation method by taking 6.0 g of zirconyl nitrate and 4.17 ml of o-phosphoric acids.

6.0 g of zirconyl nitrate was dissolved in 250 ml of deionised water to which 4.17 ml of o-phosphoric acid was added with constant stirring. This was heated at 80 oC on a hot plate for 1 h and the precipitate was filtered by using a Buchner funnel. The precipitate was washed thoroughly with distilled water and dried at 120oC for 12 h. The solid was powdered well using pestle and mortar. Finally the powdered ZPO was calcined at 550 oC for 5 h in a muffle furnace. ZPO prepared by this method is abbreviated as ZPO-1.

2.2.2 Preparation of ZPO by impregnation method

Zirconium phosphate was also prepared by impregnation method. In this method, 6 g of zirconyl nitate and 4.17 ml of o-phosphoric acid were taken in a china dish. This mixture was made into a fine paste by adding small quantity of water and mixing well. The paste was then dried in an oven at 120 oC for 12 h and calcinated at 550 oC for 5 h in a muffle furnace.

ZPO prepared by this technique is abbreviated as ZPO-2.

2.2.3. Preparation of Phosphated Zirconia (PO43-/ZrO2) by impregnation method

6 g of (Zr (OH) 4) was made into fine paste with 4 ml of o-phosphoric acid taken in a china dish. The mixture was made into a paste by adding a few drops of deionised water. The paste was then dried in an oven at 120 oC for 12 h and calcinated at 550 oC for 5 h. Phosphated zirconia is abbreviated as PZ.

2.2.4 Coating of ZPO on a cordierite honeycomb by slurry coating method

Zirconium phosphate was coated on a honeycomb by using slurry coating method [17]. Honeycomb was wash coated on the honeycomb with zirconia by using impregnation method [18] before coating the ZPO catalyst. ZPO was coated by taking a mixture of 6.0 g of zirconyl nitrate, 4.2 ml of o-phosphoric acid, water and a binder. This mixture was coated on a wash coated honey comb by using slurry coating method. After coating desired amount of the mixture (~0.05 g of ZPO) the honeycomb was calcined at 550 oC for 5 h in a muffle furnace. Honeycomb coated with ZPO is abbreviated as ZPO-3.

2.3 Characterization of solid acids

Bruaner-Emmet-Teller (BET) surface area, solid acid catalysts were measured by NOVA 1000 Quanta chome high-speed gas sorption analyzer instrument. The total surface acidity of solid acids was measured by NH3-TPD/ n-butyl amine back titration methods. The powder X-ray diffraction (PXRD) patterns of solid acids were recorded by X-ray powder diffractometer (Philips

X'pert) using CuKα radiation (λ = 1.5418 Ao) using graphite crystal monochomator. The solid acids were analysed for their functionality by using IR spectroscopy.

2.4 Catalytic activity studies of ZPO solid acids in the synthesis of acetyl salicylic acid

Synthesis of acetyl salicylic acid by salicylic acid with acetic anhydride was carried out in a 50 ml round bottomed (RB) flask on a magnetic stirrer cum hot plate in presence of solid acids. Reaction were carried out by taking calculated amounts of salicylic acid, acetic anhydride and solid acid catalyst in a RB flask equipped with a water cooled condenser. The reaction mixture was heated at a particular temperature for a definite period of time. After a definite time period, the hot reaction mixture was filtered to separate the catalyst. Ice cooled water was added to the reaction mixture to hydrolyze the unreacted acetic anhydride to acetic acid. The reaction mixture was then cooled to obtain a white solid of acetyl salicylic acid (aspirin). Thus obtained crude acetyl salicylic acid was filtered, washed with water, dried and characterized by melting point experiment, 1HNMR spectroscopy (Bruker) and LC-MS (Varian). The yield of aspirin was calculated by using an equation which is given below.

$$\text{Yield of aspirin (\%)} = 100 - 100 \times \frac{[\text{salicylic acid}]}{[\text{salicylic acid}] + [\text{aspirin}]}$$

2.5 Reusability of solid acid catalyst

To study the re-usability of the used solid acid catalyst, the catalyst was filtered from the reaction mixture, washed with acetone, dried at 120 oC for 5 h and calcined at 550 oC for 2 h. Thus reactivated catalyst was subjected to acetylation reaction of salicylic acid under same reaction condition.

The reactivation and reusability of the used solid acid was repeated for 5 times by following the procedure described above.

3 Results and discussion

3.1 Characterization of solid acids

Zirconium phosphate (ZPO) and Phosphated zircona solid acids were characterized for their physico-chemical properties such as surface area, total surface acidity (TSA), crystallinity and functionality.

3.1.1 BET surface area

The surface area values of solid acids that are obtained by BET method are listed in Table 1 .The surface area of uncalcined ZPO were found to be lesser than the surface area of calcined ones. A 2.0 to 2.5 fold increase in the surface area of ZPO's was observed after calcinating them at 550 oC. This may be due evaporation of water molecules during calination at higher temperature and surface area is increased. Further increasing the calcination temperarture leading to the decrease in surface area as the volume fraction of the monoclinic zirconia increases [19].

The conversion of zirconium hydro phosphate hydrates to zirconium Phosphate at 550 oC, as per the equation 1.

$$\underset{\text{----- (1)}}{Zr(HPO_4)_2\,H_2O} \xrightarrow{550^{o}C/5h} ZrP_2O_7 + 2\,H_2O$$

Table 1. Surface area and total surface acidity (TSA) values of solid acids used for the presented study.

Solid acid catalyst	Surface area (m2/g)	TSA (mmols/g)
ZPO-1(uncalcined)	96	(0.46) 0.48
ZPO-1 (calcined)	232	(1.10) 1.11
ZPO-2 (uncalcined)	86	(0.37) 0.37
ZPO-2 (calcined)	202	(0.98) 0.99
ZPO-3 (calcined)	178	(1.01) 1.05
ZrO2 (calcined)	62	(0.32) 0.36
PO43-/ZrO2 (PZ) (calcined)	132	(0.53) 0.54

Note: Number in the parenthesis refers to the TSA values obtained by n-butyl amine back titration method.

3.1.2 Total surface acidity by NH3-TPD/ n- butyl amine back titration method

The total surface acidity (TSA) of the solid acids was determined by NH3-TPD and n-butyl amine back titration methods. The TSA values are given in the Table 1.

The values of total surface acidity obtained by both NH3-TPD and n-butyl amine back titration method are comparable to a reasonable extent.

Surface acidity is caused by the charge imbalance formed on the surface of metal oxide. To keep the electric neutrality, Brønsted acidity is expected to appear when the charge imbalance is negative, while Lewis acid sites will be formed when the charge imbalance is positive [20].

In all the above mentioned catalysts in the Table 1, the calcined ones have more TSA values than the uncalcined ones. This may be due to removal of hydroxyl ions during calcinated resulting in the increase in the total surface acidity values.

3.1.3 Powder XRD studies

The crystalline phases of ZPO-1 and PZ solid acids are characterized by PXRD. The PXRD patterns of calcined ZPO and PZ are shown in Fig.1. The PXRD patterns were correlated with standard data of ZPO (JCPDS # 86-0781).

PXRD pattern of ZPO-3 was found to be similar to that of the PXRD pattern of either ZPO-1 or ZPO-2 (PXRD pattern of ZPO-3 is not shown in Figure 1). No peaks corresponding to the cordierite honeycomb were observed in the PXRD pattern of ZPO-3. This indicates the effective coating of ZPO on the honeycomb.

Figure 1c and 1d shows the PXRD patterns of calcined phosphated zirconia and zirconia respectively. Both the patterns consisted of monoclinic ZrO2 (JCPDS card No. 80- 0966) with minor phase of tetragonal ZrO2 (JCPDS card No. 80-0784).

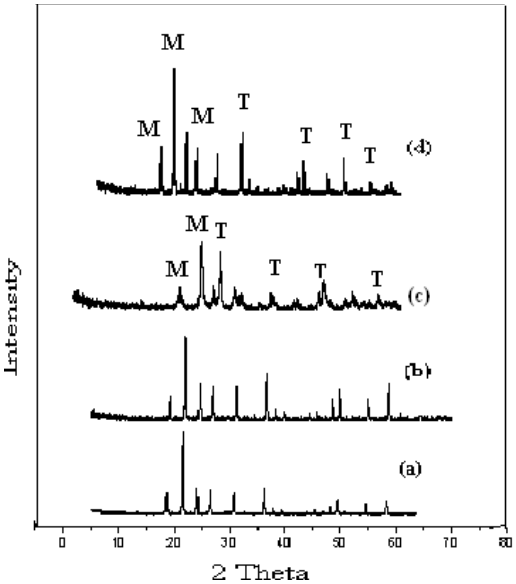


Figure 1. XRD patterns a) ZPO-1 b) ZPO-2 c) PZ and d) ZrO2 [M- monoclinic; T-tetragonal].

3.1.4 IR studies:

IR spectra of ZPO's, PZ and Zirconia are shown in the Fig 2. Strong absorption band were observed at 1600, 1030, 976-548 and 744 cm-1.

The FTIR spectra of as-prepared or uncalcined ZPO shows strong absorption bands at 1600, 1030, 976 and 548 cm-1. The band in the region 3400-3000 corresponds to O-H streching.

The intense band at 1600 cm-1 is due to bending vibrational mode of O-H group.The band at 1030 cm-1 is due to symmetric

Volume : 2 | Issue : 3 | Mar 2013 • ISSN No 2277 - 8179

streching modes of phosphate group. While the bands at 976 and 744 cm-1 are due to asymmetric and symmetric streching mode of P-O-P modes respectively and the band at 548 cm-1 is due to bending mode of O-P-O bond.Where as the OH band of 1600 cm-1 is not found in calcinated ZPO with increase in intensity of P-O-P bands confirms the ZrP2O7 Phase.

The intense band at 1080 cm-1 refers to P=O stretching of zirconia and the band in the region of 506 cm-1 corresponds to Zr-P bond of PZ.

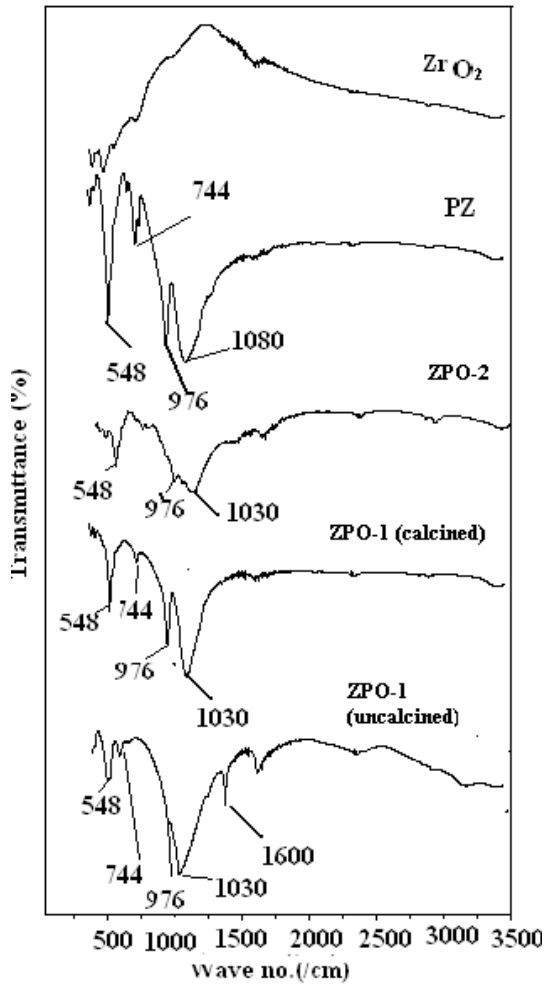


Figure 2. The FT-IR patterns of ZPO-1, ZPO-2, PZ and pure zirconia.

3.2 Catalytic activity studies of ZPO in synthesis of acetyl salicylic acid of salicylic acid

The reaction of salicylic acid (SA) with acetic anhydride (AA) over ZPO and Phosphated zirconia solid acids was carried out in liquid phase to synthesize acetyl salicylic acid (Scheme 1). In general all the catalysts were active in this reaction.

Scheme 1. Synthesis of acetyl salicylic acid over solid acid catalyst.

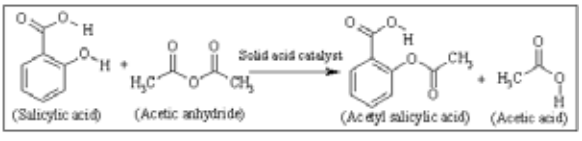


Table 2. Yield of aspirin (%) using different catalysts: reaction conditions:

[Weight of catalyst = 0.1 g; reaction temperature = 85 oC; reaction time = 30 min.]

Catalyst	Yield of aspirin (%)
ZPO-1	96.0
ZPO-2	87.2
ZPO-3	94.2
PZ	69.1
ZrO2	43.0

In absence of the catalyst the yield (%) of aspirin was very low. To obtain highest possible yield of aspirin different parameters were varied like molar-ratio of reactants (salicylic acid: acetic anhydride), weight of solid acid catalyst, reaction time and reaction temperature were varied for optimisaton.

3.2.1 Characterization of acetyl salicylic acid

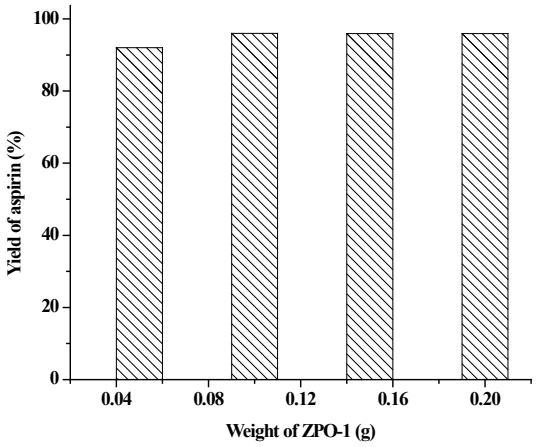
The crude aspirin crystals were re-crystallized with ethanol-water mixture and characterized by melting point, LCMS and 1H NMR spectrometer and the details are given below.

- Melting point - 135 oC.
- LCMS method – (a) 10 mM NH4CO3; (b) ACN; flow rate 1 mL/min; Column X Bridge C8 - Purity of acetyl salicylic acid was 99.136 % with its mass in negative mode is 179.0.
- 1HNMR (400MHz: DMSO: TMS): δ 7.9 (d, 1H, ArH), 7.6 (t, 1H, ArH), 7.3 (t, 1H, ArH), 7.2 (d, 1H, ArH), 2.2 (s, 3H, CH3), 13 (s 1H, –COOH); 2.5 (solvent). The 1HNMR peaks of acetyl salicylic acid were found to be similar to those reported in the literature.

3.2.2 Effect of weight of solid acid catalyst on the yield (%) of aspirin

To study the effect of weight of solid acid catalyst in the synthesis of aspirin the reactions are carried out at 85 oC for 30 min by varying the weight of ZPO-1 from 0.025 g to 0.20 g and the result are shown in the Fig.3. The maximum yield of aspirin was noticed at in presence of 0.1g ZPO and upon increasing the weight of catalyst beyond 0.1 g the yield of aspirin was found to be decreased. The conversion of salicylic acid is very much co-relatable to the total surface acidity of ZPO solid acid catalyst.

Figure 3. Effect of weight of ZPO-1 on the yield (%) of aspirin. Reaction conditions: Molar ratio of SA: AA = 1:3, reaction temperature = 85 oC; reaction time = 30 min.



3.2.3 Effect of molar ratio of reactants on the the yield (%) of aspirin.

To study the effect of molar ratio of the reactants i.e., acetic anhydride and salicylic acid, synthesis of aspirin was carried out at different molar ratios ranging from 1:2 to 1:5 over ZPO-1 and the results are shown in Table 3. The yield (%) of aspirin between 87% to 96% was observed when the molar ratio of salicylic acid to acetic anhydride was increased from 1:2 to 1:3. But when the molar ratio is increased more than 1:3, the yield (%) of aspirin decreases with an increase in the concentration of acetic anhydride. This can be explained as follows.

The solvent used in this reaction i.e. acetic anhydride, acts also

as a reactant when the molar ratio was increased from 1:2 upto 1:3,the yield (%) of aspirin was increased which may be due to well dispersion of salicylic acid as the solid acid catalyst in acetic anhydride increases. However, when the molar ratio was increased further. It was observed that the yield obtained was less which can be due to over dilution. So molar ratio 1:3 may be considered as optimum molar ratio and same molar ratio was maintained for the further reaction studies.

Table 3. Effect of molar ratio of the reactants (SA: AA) yield of aspirin (%).
[Reaction conditions: Weight of catalyst = 0.1 g of ZPO-1; reaction temperature = 85 oC; Reaction time = 30 min.]

Molar ratio (SA: AA)	Yield of aspirin (%)
1:2	87
1:3	96
1:4	82
1:5	70

3.2.4 Effect of reaction temperature on the yield (%) of aspirin
In order to study the effect of reaction temperature on the yield of aspirin, the reactions was carried out in the temperature range of 50 o C _120 oC using ZPO-1 as the catalyst (Fig 4). It is clearly observed that, the yield of aspirin was gradually raised when the reaction temperature was increased from 50 oC to 85 oC. However, the yield of aspirin decreased when the reaction temperature was increased beyond 85 oC . The reason for this may be because of condensation between the reactant and product molecules giving rise to by products. Therefore, 85 oC was considered as the optimum reaction temperature to obtain heighest possible yield of aspirin over ZPO catalyst.

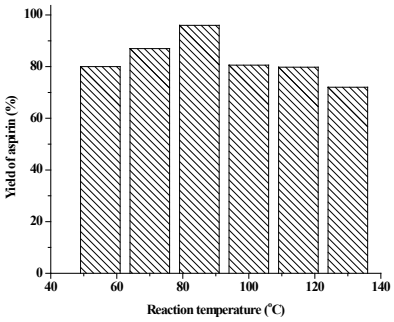


Figure 4. Effect of reaction temperature on the yield (%) of aspirin.
[Reaction conditions: salicylic acid = 3.1 g; acetic anhydride = 6.6 mL; weight of catalyst = 0.1 g; Reaction time = 30 min.]

3.2.5 Effect of reaction time on the yield of aspirin
To study the effect of reaction time on the synthesis of aspirin, SA and acetic anhydride was allowed to react in presence of ZPO-1 as a catalyst in the time period from 15 min to 120 min. The yield of apirin increased as the reaction time was increased upto 30 min. But, when the reaction time was increased beyond 30 min, the yield of apirin decreased gradually. Additionally it was also observed that the color of the catalyst was also changed which indicated the formation of by products and deactivation of the catalyst.

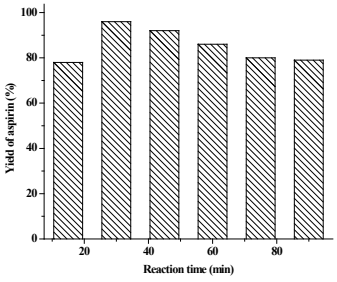


Figure 5. Effect of reaction time on the yield of aspirin.
[Reaction conditions: Molar ratio of SA: AA= 1:3; weight of the catalyst = 0.1 g of ZPO-1; reaction temperature = 85 oC.]

3.2.6 Effect of re-usability of ZPO-1 and PZ solid acid catalyst on the yield (%) of aspirin
In order to study the reusability of the catalyst, the reactions were carried out with Salcylic acid and acetic anhydride in presence of 0.1 gm of ZPO-1 and PZcatalysts. The catalyst was recovered by filtration, washed with acetone, dried in an oven at 120 oC for 5 h and calcined at 550 oC in a muffle furnace for 2 h after the reaction. In this way, the regenerated solid acid catalyst was re-used for 5 reaction cycles and the results are presented in Fig. 6. The figure clearly indicates that, the re-activated ZPO show good catalytic activity even after five reaction cycles which shows that ZPO solid acids can be re-used and re-activated.

However, in the case of PZ catalyst the yield (%) of aspirin decreased from one reaction cycle to the other indicating a low re-usability of PZ when compared to ZPO's.

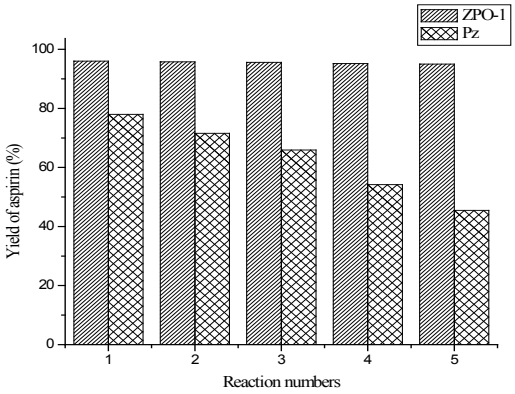


Figure 6. Effect of re-usability of ZPO-1 and PZ on the yield (%) of aspirin. Reaction conditions: Molar ratio of SA: AA= 1:3; weight of the catalyst = 0.1 g; reaction temperature = 85 oC; reaction time = 30 min.

3.2.7 Comparative catalytic activity of ZPO in its powder and honeycomb coated forms
Catalytic activity of ZPO (powder) and ZPO (honeycomb coated) were compared in acetylation of SA with AA to synthesize aspirin. Even though, approximately half of the amount of ZPO catalyst (0.045 g) was coated on the honeycomb, the yield (%) of aspirin was found to be almost the same when 0.1 g of ZPO was used in powder form (Table 2). This can be explained as follows:

The number of channels, their diameter and wall thickness determine the cell density, expressed as cells per square inch (cpsi), which in turn allows the calculation of the geometric surface area; the sum of the areas of all the channel walls upon which the catalyst is deposited. This leads to one of the most important advantages of the honeycomb in that it has a large open frontal area. The lower catalyst loading in case of honeycomb catalyst is compensated by the higher efficiency due to the good mass-transfer characteristics [22]. This may be attributed to the availability of more number of active sites on the surface of the honeycomb catalyst due to homogenous dispersion of the catalyst which is not possible when the catalyst is used in powder form. However, the separation of solid aspirin from the channels of the honeycomb catalyst was fond to be difficult.

4. Mechanism of synthesis of acetyl salicylic acid over Brönsted acid sites
The synthesis of aspirin over a acid catalyst is illustrated in Scheme 2, which is a propable mechanism for the reaction. The formation of carbocation intermediate (CH3CO+) which attacks the phenolic oxygen of salicylic acid to form aspirin (acetyl salicylic acid) is influenced by the Brönsted acid sites of the acid catalyst.

Scheme 2. The synthesis of aspirin of salicylic acid with acetic anhydride over Brönsted acid sites of an acid catalyst.

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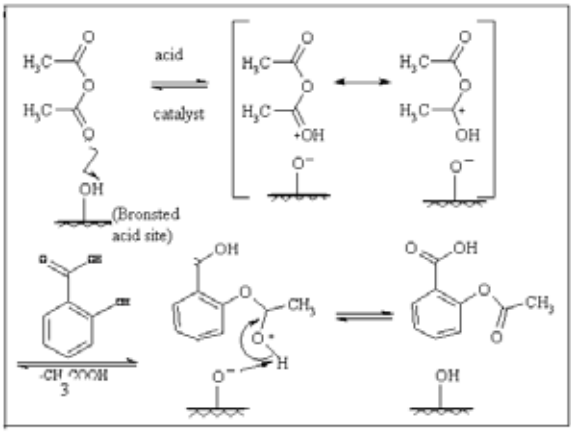

5. Conclusion

Zirconium phosphate solid acid prepared by precipitation method was found to be an excellent solid acid catalyst which showed a high yield of aspirin with 96 % selectivity under optimized reaction conditions. This solid acid catalytic system (ZPO) can replace the conventional homogeneous catalysts such as H2SO4, H3PO4 for synthesis of a highly useful medical compound like aspirin. Honeycomb coated with ZPO was found to be an efficient catalyst compared to its powder form but, the separation of aspirin from the honeycomb was found to be difficult. ZPOs were found to be more active than phosphated zirconia in this reaction. ZPOs can be reused after thermal reactivation without appreciable loss in their catalytic activity.

Acknowledgements

Authors are thankful to DST, New Delhi for the project, Materials Research Group, St. Joseph's College, and Bangalore for PXRD analysis, IITM, Chennai for BET & NH3-TPD analysis. Authors also thankful to the authorities of University of Malaya, Malaysia for providing LC-MS and NMR data by analysis.

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