Preparation of Zirconium Phosphate Nanoparticles and Its Application in the Protection of Aldehydes

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Abstract

A novel method for the preparation of -zirconium phosphate (ZrP) nanoparticles as an eco-friendly and recyclable heterogeneous catalyst was studied. Polyethylene glycol (PEG) was used as the organic matrix which produced a better dispersion of ZrP nanoparticles. The catalyst was characterized by several physico-chemical techniques such as ICP-OES, XRD, TPD-NH₃, pyridine-FTIR, BET, FTIR, TGA, SEM and TEM. The acidic property of ZrP was studied in the protection of aldehydes with acetic anhydride (AA) in the at room temperature. The deprotection of 1,1-diacetates has also been achieved using this catalyst in water. The procedure is operationally simple, environmentally benign and only a stoichiometric amount of AA is used. The catalyst was recovered easily from the reaction mixture, regenerated, and reused at least eight times without significant loss in catalytic activity.

Keywords: Hexagonal zirconium phosphate; Nanoparticles; Solvent-free; Solid acid catalyst; Diacetate.

Introduction

Layered zirconium hydrogen phosphate with an type structure, $Zr(HPO_4)_2 \cdot H_2O$, is one of the most important inorganic materials. The -zirconium phosphate (ZrP) is a suitable heterogeneous catalyst [1,2], excellent ion exchanger [3], an interesting intercalating agent [4], which also has been used in nanocomposite [5], proton conductor for fuel cells, drug delivery and immobilization of biological materials [6,7]. To satisfy the requirements for applications in different fields, it has been prepared by different methods in a wide variety of sizes from 2 nm to up to 2 um [8-10]. The crystalline ZrP possesses weak and strong Brönsted and Lewis acid centers which are attributed to P-OH groups and the Zr⁴⁺, respectively. Due to the presence of high hydroxyl group density on ZrP surface which can be assumed as hooks, various organic functional groups could adsorb on, allowing to control both the reactivity and selectivity of the reaction (Fig. 1). In the past few years, increasing attention has been attracted to the development of new approaches for the preparation of various ZrP nano compounds such as nanoparticles [11,12], nanoplates [13] and nanocomposites [14,15]. Polyethylene glycol (PEG) is a flexible, biocompatible, water-soluble, liquid or lowmelting solids, depending on its molecular weight. There are some new polymer based precursor methods to produce nanocomposites and nanoparticles [16,17].

The carbonyl group is one of the most versatile functional groups in organic chemistry and the electrophilic nature of this group is a dominant feature of its extensive chemistry. Selective protection and deprotection of aromatic or aliphatic carbonyl groups

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Figure 1. Schematic structure of hexagonal -zirconium phosphate.

plays an important role in the multistep organic synthesis of complex natural products [18]. The of aldehydes, acetals, protection as acylals, oxathioacetals, or dithioacetals, is a common practice for manipulation of other functional groups during multisteps synthesis. Geminal diacetates (acylals) are one of the essential carbonyl protecting groups due to their stability under neutral, basic, and acidic conditions. Besides, they can be easily converted into parent aldehydes, which are frequently used as protecting groups for aldehydes [18, 19]. Furthermore, the acylals functionality can be converted into other useful functional groups by reaction with appropriate nucleophiles, the diacetates of , -unsaturated aldehydes serve as important precursors for Diels-Alder reactions and also are useful intermediates in industries, such as cross linking agent for cellulose in cotton or used as stain-bleaching agents [20-24]. Because of their unique properties as protective groups as well as important synthons, methods for efficient, mild, and facile synthesis and cleavage of acylals have received considerable attention.

Apart from other methods, they are conventionally prepared from aldehydes and acetic anhydride (AA) using strong protic acids or Lewis acids. Several reagents and catalysts have been reported for the synthesis of acylals from aldehydes using AA such as SuSA [25], SBA-15-Ph-PrSO₃H [26], PEG-SO₃H [27], Sulphated Zirconia [28], sulfonated carbon nanocage [29], PS/TiCl₄ [30], Schiff base complex of Cr(III) [31], Solid sulfuric acid [32], NaHSO₄-SiO₂ [33], MPA-DAZY [34], DBSA [35], [bmpy]HSO₄ [36], SPDTSA [37], PSA [38], P(4-VPH)ClO₄ [39], PBBS [40], SbCl₃ [41], Si-[SbSipim][PF₆] [42], DOWEX(R)50WX4 [43], [bmim][FeCl₄] [44], Fe(NO₃)₃.9H₂O [45], PTSA [46], H₁₄PMo [47], H₂SO₄-silica [48], P₂O₅/SiO₂ [49], SiO₂-CrO₃ [50], -Fe₂O₃@HAp-Ni²⁺ [51], BSA [52], HClO₄-SiO₂ [53] and sulphated zirconia [54]. There are very few reports which are applicable to both the synthesis as well as deprotection of 1,1-diacetates [29]. With these in mind, and as part of ongoing work towards the development of efficient and green catalysts based on zirconium phosphate [12] and some of its ion exchanged

deriatives [3], for organic transformations, herein a novel synthesis of zirconium phosphate using PEG as dispersing agents is reported. To the best of our knowledge, there is no report available in the literature for using hexagonal ZrP nanoparticles as the catalyst for the preparation of 1,1-diacetates from carbonyl compounds. The reaction was easily, carried out at room temperature under solvent-free condition with short reaction time for a wide range of aldehydes. The obtained results were compared with those reported before in the literature.

Materials and Methods

Catalyst synthesis

Typically, a 2% solution of PEG-200 (Mw = 190-210) was prepared by dissolving PEG in deionized water. By adding HCl, the pH value was adjusted about 3. 50 ml of a 1 M solution of ZrOCl₂·8H₂O added dropwise to precursor solution and heated at the 50 °C for 1 h with constant stirring using a magnetic stirrer. To the resulting homogeneous solution, under ultrasonication, 50 ml of a 2 M H₃PO₄ solution was added dropwise at 50-60 °C for 1 h. The resulted mixture was allowed to age for 30 min, then the precipitate was filtered, washed several times with distilled water and then dried in an oven at 80 °C overnight. The obtained white colored fluffy precursor was ground and calcined at 600 °C for 3 h to decompose the organic matrix. The final product, the desired pure hexagonal -zirconium phosphate $(Zr(HPO_4)_2 \cdot H_2O)$ nanocrystals, was identified as ZrP. The detailed procedure for the preparation of the -ZrP can be found in the literature [10].

General experimental procedure for preparation of 1,1-diacetates

Typically, in a 25 mL round bottom flask, equipped with a magnetic stirrer and condenser, substrate (5 mmol) and AA (10 mmol) and catalyst (pre-activated at 450 °C for 1 h and cooled in a desiccator to minimize moisture content) (0.33 mol%) was transferred. The reaction mixture was stirred at room temperature for the



Scheme 1. Deprotection of phenylmethylene diacetate to benzaldehyde in water catalyzed by ZrP.



Scheme 2. Interactions between polymers and the P-OH groups of ZrP.

specified time under solvent-free conditions. Samples were collected periodically and analyzed by gas chromatography (GC). After completion of the reaction, the mixture was diluted with Et₂O and the catalyst was recovered by centrifuge. The organic layer was washed with 10% NaHCO₃ solution and then dried over anhydrous CaCl₂. The solvent was evaporated under reduced pressure to give the corresponding pure 1,1-diacetate. All products were known and characterized by their spectral data (M.p., IR and ¹HNMR) and by comparison with the authentic samples (supplementary information).

General experimental procedure for deporotection of 1,1-diacetates

A solution of 1,1-diacetate (5 mmol) in water (2 ml) and ZrP (0.33 mol%) was introduced into a round bottom flask equipped with a magnetic stirrer and condenser at 60 °C. The reaction was monitored by GC. After the reaction, the mixture was diluted with EtOAc and the catalyst was recovered by centrifuge. The organic layer was washed with water. The organic extracts were combined and washed with 10% NaHCO₃ and dried over anhydrous CaCl₂. The solvent was evaporated under reduced pressure to give the corresponding aldehyde (Scheme 1).

Catalyst regeneration

For recycling, after the first use, the catalyst was separated from the reaction mixture by centrifuge, washed with ethanol successively, and refluxed with 10% (w/v) H_2O_2 for 1 h. It was then washed with water, dried at 110 °C for 1 h and finally activated at 400 °C for 2 h [1]. The regenerated catalyst was used under the optimum reaction conditions to study the performance of recovered catalyst. After every reaction cycle the catalyst was recovered, washed, and activated as described above.

Results and Discussion

We have previously reported the preparation of ZrP nanoparticles using Polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA) [12]. In order to achieve a better dispersion and better qualified nanoparticles, PEG was used and some modification was made on the method. The PEG shell encapsulates the nanoparticles weakens interactions between neighboring and nanoparticles, thereby hindering unwanted precipitation of the zirconium phosphates used in this work (Scheme 2). This prevents particles aggregation and control their average size and shape. The PEG was used as the dispersing agent, organic matrix which also acted as a template for the nanoparticles. After calcination of PEG/ZrP at 600 °C for 3 h and decomposition of the organic matrix, pure ZrP nanoparticles with hexagonal shape were obtained.

Characterization of the catalysts

Table 1 represents the ICP data, in where the P/Zr

Sample	0	Р	Zr	BET (m^2/g)	Total acidity (mmol NH ₃ /g)
ZrP	62.8	24.4	12.8	144.6	3.1
ZrP ^[a]	63.1	24.2	12.7	143.1	3.02
ZrP ^[b]	67.8	21.5	10.7	81.7	1.5
-ZP	70.4	18.8	10.8	73.5	0.81

Table 1. Element contents of ZrP (atm.%) and physical properties of the catalysts before and after reaction.

^a After the first cycle, ^b After the 8th cycle.

ratio was found to be 1.91 and 1.74 for ZrP and -ZP, respectively [1,8].

Pyridine has been verified to be an excellent FTIR spectroscopy probe to characterize the nature of the acid sites of catalyst and the resulting IR spectrum is shown in Fig. 2. The pyridine-desorbed FTIR spectra of ZrP showed characteristic strong bands about 1446 cm⁻¹

which is assigned to the coordinated pyridine in Lewis acid sites. The pyridinium ions are formed by the transfer of protons from the P-OH groups in the ZrP to the organic base. The absorption peak about 1630 and 1541 cm⁻¹ are caused by pyridine adsorbed on Brönsted acid sites [1,2]. Additionally, the band at 1488 cm⁻¹ indicates the combination band between those adjacent



Figure 2. Pyridine-desorbed FTIR spectra of the calcined ZrP.



Figure 3. SEM images of ZrP (a,b) fresh and (c) after the 8th run.

Preparation of Zirconium Phosphate Nanoparticles and...



Figure 4. TEM images of ZrP (a,b) fresh and after the 8th run (c).



Figure 5. The weight loss curves of ZrP sample.

Lewis and Brönsted acid sites at 1541 and 1446 cm⁻¹ respectively [1]. It is obvious from the figure that the prepared ZrP shows a higher number of Brønsted acid sites accompanied by low amounts of Lewis acid sites.

The morphology of the ZrP nanoparticles was characterized by SEM [1,8,10] and TEM [10,11,13]. Typically, the SEM micrograph of ZrPs shows the hexagonal plates in which the disks had well-defined shapes with very smooth surface, solid layers are placed parallel, showing good crystallinity (Fig. 3 a and b). However, there are some incomplete plates which are ellipse.

The TEM images (Fig. 4 a and b) show that the ZrP particles are hexagonal with smooth surfaces. Because of the condensation reactions between hydroxyl groups of adjacent particles during aging or calculation, particles in some cases are attached together which cause more agglomeration. The average diameter of ZrP nanoparticles is about 40-55 nm. SEM and TEM results

of all the calcined ZrPs samples show similar uniform morphology and are in fair congruence with the earlier reports [10,11].

The weight loss curve of ZrP is shown in Fig. 5. The TG pattern was obtained from 50 to 1100 °C. Dehydration led to a weight loss of ZrP due to water removal from the catalyst. The thermal decomposition of ZrP takes place in two main steps; the first step, centered around 100 °C can be attributed to the loss of adsorbed and/or intercalated molecules, such as water (crystallization water) [9]. The crystallinity is associated with fairly distinct thermal behaviors: with increasing crystal size, the loss of crystallization water is progressively shifted toward high temperature and hence less separated from the loss of condensation water [8,9]. The second step is due to the subsequent POH condensation, leading to the formation of layered ZrP₂O₇. It is known that heating zirconium phosphonates in the presence of oxygen or air leads to

Entry	Solvent ^a	Yield (%) ^b	Time (min)
1	Et ₂ O	54	90
2	n-Hexane	38	120
3	CH_2Cl_2	43	90
4	H_2O	20	120
5	C ₂ H ₅ OH	18	120
6	CH ₃ CN	58	120
7	EtOAc	52	120
8	THF	36	90
9	CHCl ₃	41	90
10	Solvent-free ^c	90	10

Table 2. Conversion of benzaldehyde to its corresponding diacetate in different solvents and under solvent-free conditions in the presence of ZrP.

^a The reaction was carried out in 5 ml of solvents at reflux conditions.

^b The yields refer to isolated pure products.

^c The reaction was carried out at r.t.

the formation of cubic zirconium pyrophosphate, ZrP_2O_7 [56,57]. The step between 210 and 600 °C is attributed to the loss of water due to the condensation of the HPO₄ groups, leading to the formation of cubic zirconium pyrophosphate. A detailed discussion about XRD, FTIR, BET, and TPD-NH₃ of the catalyst is represented in the supplementary information (Pages S2-S6).

Synthesis of 1,1-diacetates

In order to find the most appropriate reaction conditions and evaluate the catalytic efficiency of ZrP on the protection of aldehydes to the corresponding 1,1diacetates, we tried to convert benzaldehyde (5 mmol) to its corresponding acylal with ZrP (0.33 mol%) and AA (10 mmol) in various solvents and also under solvent-free condition. We observed that the yield of the reaction under solvent-free condition is higher and the reaction time is shorter as compared to the other methods (Table 2). Therefore, to establish the generality and scope of the method, we employed the above conditions for conversion of various aldehydes (aromatic, heterocyclic, aliphatics and , -unsaturated aldehydes) to the corresponding diacetates (Table [3]). Both aromatic and aliphatic aldehydes react smoothly with AA to afford the corresponding 1,1-diacetates in good to excellent yields in a short reaction times at room temperature (Table 3, entries 1-26), which are, in general, similar or higher than those described in the literature [25-54].

The reactions did not proceed in the absence of ZrP even under heating conditions and longer reaction time (120 min) (Table 3, entry 37). Under these reaction conditions, various functional groups (Me, OMe, OH, F, Cl, Br, CN, NO₂) were tolerated. The electronic properties of the substituents on the aromatic aldehydes have a major effect on the reaction yield and time. The aldehydes with electron-withdrawing groups (NO₂, CN, F, Cl and Br), afforded the corresponding diacetates in higher yields (Table 3, entries 12–26) [29]. But,

Table 3. Preparation of acylals in the presence of ZrP under solvent-free conditions at r.t.

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$\begin{array}{r} \text{R-CHO} + \text{Ac}_2\text{O} \\ (5 \text{ mmol}) & (10 \text{ mmol}) \end{array} \xrightarrow{\text{ZIP} (0.33 \text{ mol}\%)} \text{R-CH}(\text{OAc})_2 \\ \hline \end{array}$								
Entry	Substrate	Time (min)	Yield (%) ^a	Mp (°C) or bp (°C)				
				found	Reported [ref]			
1	C ₆ H ₅ CHO	10	90	43-45	44-45 [25,26]			
2	2-Me-C ₆ H ₄ CHO	30	84	64-66	64-66 [50]			
3	4-Me-C ₆ H ₄ CHO	20	88	80-82	81-82 [28,29]			
4	2-MeO-C ₆ H ₄ CHO	30	82	68-80	73–74 [25,26]			
5	3-MeO-C ₆ H ₄ CHO	20	89	Oil	Oil			
6	4-MeO-C ₆ H ₄ CHO	25	85	65-66	64–65 [25,26]			
7	2,3-(MeO) ₂ C ₆ H ₃ CHO	30	83	104-106	103-105 [50]			
8	$3,4-(MeO)_2C_6H_3CHO$	20	85	70-72	72–74 [25,40]			
9	2,5-(MeO) ₂ C ₆ H ₃ CHO	30	85	107-108	110 [50]			
10	4-OH-C ₆ H ₄ CHO ^b	45	86	90-92	89–90 [25]			

Table 3. Cntd								
11	2-OH-C ₆ H ₄ CHO ^b	45	83	101-102	101-103 [25,26]			
12	2-Cl-C ₆ H ₄ CHO	10	93	51-52	52-53 [25,26]			
13	3-Cl-C ₆ H ₄ CHO	5	95	64-65	64-65 [25,26]			
14	2,3-(Cl) ₂ C ₆ H ₃ CHO	5	91	79-81	78–79 [50]			
15	2,4-(Cl) ₂ C ₆ H ₃ CHO	5	92	103-105	102–104 [50]			
16	2,6-(Cl) ₂ C ₆ H ₃ CHO	10	86	89–90	88–90 [32]			
17	$4-Cl-C_6H_4CHO$	5	93	81-82	82-83 [25,26]			
18	2-Br-C ₆ H ₄ CHO	10	89	80-82	80 [53]			
19	3-Br-C ₆ H ₄ CHO	5	94	84-86	84-85 [38]			
20	4-Br-C ₆ H ₄ CHO	5	95	93–95	92–95 [30]			
21	2-F-C ₆ H ₄ CHO	10	93	24-26	25-26 [54]			
22	$4-F-C_6H_4CHO$	10	95	50-52	50-52 [32,36]			
23	$2-NO_2-C_6H_4CHO$	10	87	91–93	90–91 [26,27,29]			
24	3-NO ₂ -C ₆ H ₄ CHO	5	91	64–66	64–66 [27,29]			
25	$4-NO_2-C_6H_4CHO$	5	95	124-126	125–127 [25,26]			
26	4-NC-C ₆ H ₄ CHO	10	96	100-101	100–102 [25,29]			
27	4-(N,N-di-MeN)-C ₆ H ₄ CHO	180	-	-	-			
28	Furfural	20	72	52-53	52–53 [28,29]			
29	Cinnamaldehyde	5	93	84-86	84-85 [26,29,30]			
30	Hexanal	30	78	Oil	Oil			
31	2-butenal	25	80	Oil	Oil			
32	C ₆ H ₄ CH ₂ CH ₂ CHO	10	80	Oil	Oil			
33	Isobutyraldehyde	30	78	Oil	Oil			
34	Phenylglyoxal ^c	30	88	53-55	53-55 [37]			
35	Cyclohexanone	180	-	-	-			
36	C ₆ H ₅ COCH ₃	180	-	-	-			
37	4-NO ₂ C ₆ H ₄ COCH ₃	180	-	-	-			
38	4-NO ₂ -C ₆ H ₄ CHO ^d	120	-	-	-			

^a All products were identified by their Mp, IR, and ¹HNMR spectra with authentic samples (supplementary information Pages S7-S18).^b AA (15 mmol). ^c Only the aldehyde group was protected as 1,1-diacetate.

^d The reactions was performed in the absence of ZrP at 60 °C.

aldehydes bearing electron-donating groups (Me and OMe) gave the corresponding 1,1-diacetates in lower yields and longer reaction times (Table 3, entries 2-11). This may be due to the reduced electrophilicity of the aldehyde group as a result of the electron-rich nature of the phenyl ring to which the aldehyde is attached. Also, the reaction rate was found to be dependent on steric crowding surrounding the aldehyde group. Thus, the presence of substitutes at the para or meta positions (Table 3, entries 3,5,6,8,9,10,13,17,19,20,22,24,25) made the reaction faster with better yields than those with substitutes at the ortho position (Table 3, entries 2,4,11,12,16,18,21,23).

The acid-sensitive compounds such as furfural and cinnamaldehyde were also protected as 1,1-diacetates in good yields without any side products, which may be due to mild acidic conditions (Table [3], entries 28,29). We investigated the reaction of 2-hydroxybenzaldehyde and 4-hydroxybenzaldehyde under above conditions (Table [3], entries 10,11); it should be mentioned that the phenolic group was also protected as acetate in hydroxyl containing aromatic aldehyde under such conditions (3 equiv. of AA). 4-(dimethylamino) benzaldehyde failed to give 1,1-diacetate under the

same conditions which may be due to the electron donation of dimethylamino group (Table 3, entry 27). The explanation for this result may be due to the strong electron donating properties of the dimethylamino group which will reduce the reactivity [42]. Moreover, the protocol could also equally work with aliphatic aldehydes (Table 3, entries 30-33). Because of aldol condensation as a competitive reaction, the yields of corresponding acylals of aliphatic aldehydes were low. Ketones proved completely resistant to acylal synthesis with AA under these reaction conditions [58]. Cyclohexanone, acetophenone, and 4-nitroacetophenone were checked for the reactivity. No diacetate formation was observed for these compounds, neither under room temperature nor reflux conditions (Table 3, entries 35-37). 2-Oxo-2-phenylacetaldehyde substrate was exposed to the reaction conditions that only aldehyde group was protected and carbonyl group remained unchanged (Table 3, entry 34) [37]. Indeed, deprotection of phenylmethylene diacetate to the benzaldehyde was performed by treatment of acylals in water at 60 °C. By this procedure, related acylal has been completely transformed into benzaldehyde in short reaction time (Scheme 1). On the basis of literature studies, the



Scheme 3. A plausible reaction mechanism for 1,1-diacetylation of aldehydes with AA over ZrP.

following mechanism can be proposed. As outlined in Scheme 3, the possible mechanism of this reaction may be involved either intermolecular or intramolecular transfer of the second acetate group after the initial attack by AA. We suggest that ZrP, as a solid Brönsted acid, increases the electrophilicity of the carbonyl group on the aldehyde. Then AA attacks complex () to produce the final 1,1-diacetate [25,31,55].

A comparative studies with some solid acids

In order to compare the catalytic potentiality of ZrP nanoparticles with some recently reported procedures in the literature, we have shown the results of the synthesis of acylal from benzaldehyde in the presence of various catalysts with respect to the amounts of AA, reaction time, and the yield of the products. The results show that, ZrP is an equally or competitive more efficient catalyst for this reaction with regards to reaction conditions and yield. Moreover, this procedure offers advantages over some of the methodologies in terms of efficiency, deprotection, as well as protection, the reusability of the catalyst. Thus, the results suggest that ZrP can be considered as one of the best choices for selecting an economically convenient, user friendly catalyst.

Reusability study

We were interested in studying the reusability of the catalyst because of economic and environmental aspects. Hence, the reaction of 4-nitrobenzaldehyde with AA was chosen as a model reaction in the presence of regenerated ZrP under the optimum reaction conditions and the results are summarized in Table 4. Spent ZrP gave a similar yield of product as the fresh catalyst till the 7th cycle. The lowered activity of the used catalyst sample confirms the catalyst deactivation during the reaction. The regenerated catalyst was characterized for its chemical composition by elemental analysis (Table [1]). No significant change in composition or environment of phosphate groups in ZrP was observed after regeneration (till the 7th cycle). It could be seen from Table 4 that the ZrP was utilized repeatedly over six times without any apparent loss of the conversion. Although, refluxing and thermal activation of regenerated ZrP cuase more agglomeration, which decreased catalyst activity.

Fig. 3c and 4c show the SEM and TEM images of ZrP after the 7th run, respectively. It seems that agglomeration of plates, due to the condensation reactions between hydroxyl groups of adjacent particles, increased the average diameter particles (about 90-130 nm) and reduced the catalyst surface area (surface area was reduced to $72.3 \text{ m}^2\text{g}^{-1}$). Also, condensation between hydroxyl groups decreases the number of acid sites on the catalyst (0.85 mmol NH₃/g of catalyst after 7th cycle).

In summary, in this paper, a novel method for the preparation of hexagonal zirconium phosphate nanoparticles has declared. The ZrP was characterized by various methods and showed great agreement with previous reports. We have demonstrated that ZrP is an efficient and recyclable catalyst for the protection of

 Table 4. Catalyst re-used under the optimum reaction conditions for 1,1-diacetate synthesis.

Substrate ^a	Fresh	run 1	run 2	run 3	run 4	run 5	run 6	run 7
4-NO ₂ -C ₆ H ₄ CHO	95	95	93	92	87	86	83	71

^a Reaction conditions: 4-nitrobenzaldehyde (5 mmol), AA (10 mol), catalyst (0.33 mol%), r.t and 5 min.

aldehydes by their conversion to 1,1-diacetates. It seems that the surface of ZrP with hydroxyl groups (P-OH) plays an important role in the acidity of catalyst. This method is selective for the preparation of 1,1-diacetates from aldehydes in the presence of ketones. Also, 1,1diacetates can be conveniently deprotected by using ZrP in water. Recovery of the inexpensive catalyst, easy purification, high yields, wide substrate scope, solvent-free conditions, shorter reaction times and temperatures over the previously reported methods are some of our important advantages.

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