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JOURNAL OF THE CHINESE
CHEMICAL SOCIETY

Solvent-free Chemoselective Synthesis of 1,1-diacetates Catalyzed by Iron Zirconium Phosphate

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(Received: Jun. 13, 2015; Accepted: Sept. 7, 2015; Published Online: Oct. 8, 2015; DOI: 10.1002/jccs.201500233)

In the present study, a mild, rapid, and efficient method for the protection of aldehydes with acetic anhydride (AA) in the presence of iron zirconium phosphate (ZPFe), at room temperature is reported. Selective conversion of aldehydes was observed in the presence of ketones. Under these conditions, different aldehydes bearing electron-withdrawing and electron-donating substituents were reacted with AA and the corresponding 1,1-diacetates (acylals) were obtained in high to excellent yields. The steric and electronic properties of the different substrates had a significant influence on the reaction conditions. Also, the deprotection of 1,1-diacetates has been achieved using this catalyst in water. The catalyst was characterized by several physico-chemical techniques. It was recovered easily from the reaction mixture, regenerated, and reused at least 7 times without significant loss in catalytic activity. This protocol has the advantages of easy availability, stability, reusability of the eco-friendly catalyst, chemoselectivity, simple experimental and work-up procedure, solvent-free conditions and only a stoichiometric amount of AA is needed.

Keywords: Iron zirconium phosphate; Nanoparticles; Heterogeneous catalysis; Diacetate; Solvent-free.

INTRODUCTION

The electrophilic nature of carbonyl groups is a dominant feature of their extensive chemistry. Selective protection and deprotection of aromatic or aliphatic carbonyl groups are essential steps in modern organic chemistry.[1] The protection of aldehydes, as acetals, 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 both neutral and basic media as well as acidic conditions and also, they are easily converted into parent aldehydes, which are frequently used as protecting groups for aldehydes.[1-2] Furthermore, the acylals functionality can be converted into other useful functional groups by reaction with appropriate nucleophiles and also are useful intermediates in industries, such as cross linking agent for cellulose in cotton or used as stain-bleaching agents.[3-5] In addition, the preparation of 1,1-diacetates from the corresponding aldehydes, in the presence of ketones, can be very important due to their involvement in various natural products synthesis.[3-4] Several reagents and catalysts have been reported for the synthesis of acylals from aldehydes using acetic anhydride (AA) such as SiPW-8,[6] $SiO_2/B(SO_4H)_3$,[7] S-CKT,[8] SuSA,[9] SBA-15-Ph-$PrSO_3H$,[10] $Zr(HSO_4)_4$,[11] PEG-SO_3H,[12] Sulphated Zirconia,[13] SO_4^{2-}/SnO_2,[14] ZSM-5-SO_3H,[15] PS/$TiCl_4$,[16] Schiff base complex of Cr(III),[17] Solid sulfuric acid,[18] SBSSA,[19] CPTS–HOAc,[20] H_2NSO_3H,[21] $ZrCl_4$,[22] Zeolite Y,[23] [bmpy]HSO_4,[24] $InCl_3$,[25] SPDTSA,[26] sulfated SnO_2,[27] DBSA,[28] P(4-VPH)ClO_4,[29] $H_6P_2W_{18}O_{62}\cdot 24H_2O$,[30] zirconium sulfophenyl phosphonate,[31] $La(NO_3)_3\cdot 6H_2O$,[32] $(NH_4)_3PW_{12}O_{40}$,[33] PBBS,[34] $SbCl_3$,[35] $Cu_{3/2}PMo_{12}O_{40}/SiO_2$,[36] Si–[SbSipim][$PF_6$],[37] DOWEX(R)50WX4,[38] [bmim][$FeCl_4$],[39] Mo/TiO_2–ZrO_2,[40] Cyanuric chloride,[41] $CuSO_4\cdot 5H_2O$,[42] $H_3PW_{12}O_{40}$,[43] H_2SO_4-silica,[44] Supported POM,[45] and P_2O_5/SiO_2.[46-47] Although some of these methods have convenient protocols with good to high yields, some of these methods suffer at least from one of the following disadvantages: reaction under oxidizing conditions, use of harmful organic solvents, long reaction times, use of excess AA, unrecyclable catalysts, high cost, and high toxicity. Also, very few reports are applicable to both the synthesis as well as deprotection of 1,1-diacetates.[14-15,22,31,48]

α-Zirconium phosphate (ZP) is one of the most im-

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Supporting information for this article is available on the www under http://dx.doi.org/10.1002/jccs.201500233

portant compounds in inorganic chemistry, and the layered structure of this material has led to its use in a variety of different fields.[49-51] ZP behaves as a unique ion exchanger because of its exceptionally poor aqueous solubility, high thermal stability, resistance to radiation and abrasive properties.[52-53] The H^+ of the P–OH moiety in ZP can be exchanged for various other ions, resulting in an enlargement of the interlayer distance.[54-58] Several studies pertaining to the successful exchange of this proton with various divalent and trivalent cations have been presented in the literature.[58-62] It has also been reported that ZP possesses excellent selectivity towards Pb^{2+}, Zn^{2+}, and Fe^{3+} as an ion exchanger.[63-64] Furthermore, ZP has been reported to exhibit antibacterial activity when it was loaded with Cu^{2+}, Zn^{2+}, or Ce^{3+}.[53,60-62] There have also been several reports concerning the catalytic activities of ion-exchanged materials of this type, including the use of copper zirconium phosphate (ZPCu) as catalysts in the acetylation of alcohols and phenols and the use of potassium iron zirconium phosphate as a catalysts in Friedel–Crafts benzoylation reaction.[65-72]

To the best of our knowledge, there is no report available in the literature for using ZPFe as catalyst for preparation of 1,1-diacetates from carbonyl compounds. Therefore, in continuation of our reports using various catalysts for organic transformations, we report a convenient, recyclable and chemoselective procedure for conversion of aldehydes to the corresponding acylals in the presence of AA. The reaction was easily carried out at room temperature under solvent-free condition with short reaction times for a wide range of aldehydes.

RESULTS AND DISCUSSION

All products were characterized by comparison with authentic samples and by spectroscopy data FT-IR, ^{1}HNMR and GC-Mass (Agilent 5975C) analysis (Supplementary Information). ^{1}HNMR spectra were recorded at 400 MHz. The spectra were measured in $CDCl_3$ unless otherwise stated, relative to TMS (0.00 ppm).

Characterization of catalyst

The ICP-OES analyses of ZP and ZPFe are shown in Table 1. The results obtained in the current study for ZPFe were compared with those reported previously in the literature.[56-58] Our results revealed that there was a negligible leach of iron ions into the reaction media after the reaction (i.e., following the first use of the catalyst).

Fig. 1 shows the powder XRD patterns of the ZP and ZPFe materials. The results show some characteristic reflections in the 2θ range of 5°–40°. The diffraction peak in ZP at 2θ~12° was assigned to a d_{002} basal spacing of 7.5 Å between the planes, which was consistent with the patterns previously reported for ZP and its derivatives with a hexagonal crystal system.[50] It shows that the d-spacing of the (002) plane of ZPFe had increased, which indicated that the Fe^{3+} ions had intercalated into the interlayer of ZP and increased the d_{002} basal interlamellar spacing of ZP from 7.5 to 9.3 Å. It is well known that the ion radii of Fe^{3+} (0.64 Å) and hydrated Fe^{3+} (3.9 Å) are smaller than the basal spacing of ZP (7.5 Å).[73-74] These results therefore indicated that Fe^{3+} ions had inserted into the interlayer of ZP and increased the basal spacing of the modified ZP after the exchange.[52,56-58] Taken together, these data indicated that ZPFe had been formed successfully. The XRD pattern of the ZPFe catalyst after the 8th run showed that the basal spacing of ZP was about 10.5 Å, which was only a little larger than that of the fresh ZPFe catalyst. This increase may have occurred because of the presence of less Fe^{3+} on the surface of ZP, and an increase in the number of water molecules between the layers following the seventh run (i.e., Fe^{3+} ions may have been washed off during the regeneration of the catalyst, Table 1).

Using N_2 adsorption-desorption isotherms at liquid nitrogen temperature, the specific surface areas of the samples were determined by the Brunauer–Emmett-Teller (BET) method on a Quantachrome ChemBET 3000 instrument. Prior to analysis, each sample was degassed at 350 °C for 2 h to remove any adsorbed species on the surface. Fig. 2 shows the N_2 adsorption-desorption isotherm of ZPFe, as a representative example, in the relative pressure range (P/P_0) of 0.1–1.0. The surface area of ZPFe was determined to be 132.5 m^2/g. The isotherm for ZPFe shows three adsorption stages. The first of these stages was observed at $P/P_0 < 0.41$, whereas the second stage was ob-

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

Sample	Fe	O	Zr	P	BET (m^2/g)	Total acidity ($mmol NH_3/g$)
ZP	-	63.1	13.6	23.3	158.7	3.1
ZPFe	9.1	59.3	11.9	19.7	132.5	2.3
ZPFe[a]	9.0	59.6	11.8	19.6	131.8	2.26
ZPFe[b]	2.8	63.6	13.8	19.8	61.2	0.48

[a] After the first cycle.

[b] After the 8th cycle.

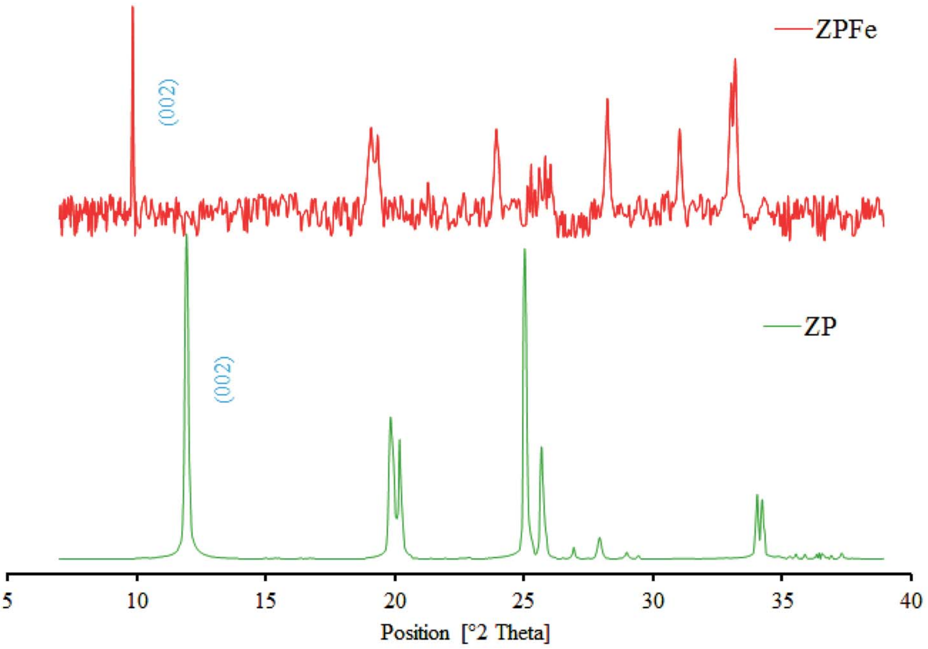


Fig. 1. XRD patterns of powder ZP (down), ZPFe (up).

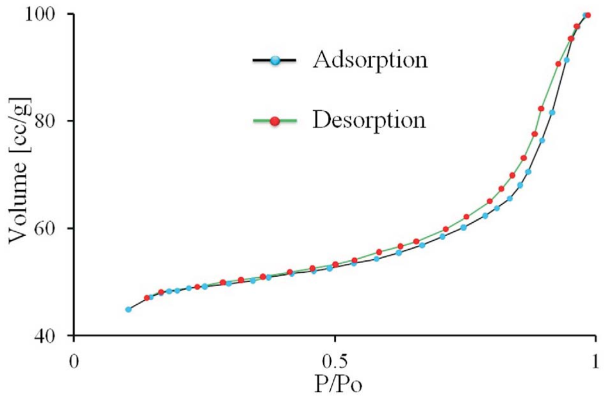


Fig. 2. N_2 adsorption-desorption isotherm of ZPFe.

served in the range of $0.41 < P/P_0 < 0.95$, and the third stage was observed at higher relative pressures ($P/P_0 > 0.95$). The N_2 adsorption-desorption isotherm of ZPFe exhibited a typical "type IV" isotherm shape with a distinct hysteresis loop, which is characteristic of a mesoporous material.[75] The hysteresis loop (type H3) is associated with the occurrence of capillary condensation in the mesopores, which indicates the presence of a mesoporous structure in the ZPFe catalyst. The observed increase in adsorption at the higher P/P_0 value indicated the presence of larger mesopores in the sample.[57-58] The surface area of ZPFe after the 8th run was found to be 61.2 m^2/g.

Pyridine adsorption was used to determine the acidic sites using FTIR. Prior to the measurements, 20 mg of a catalyst was pressed in self-supporting disc and activated in the IR cell attached to a vacuum line at 350 °C for 4 h. The adsorption of pyridine was performed at 150 °C for 30 min. The excess of probe molecules was further evacuated at 150 °C for 0.5 h. The adsorption–evacuation was repeated several times until no changes in the spectra were observed (Fig. 3). The main bands observed over the samples are assigned according to the literature data.[76-77] Pyridine desorbed FTIR spectra of the ZPFe shows the strong bands at 1631 and 1540 cm^{-1}, indicating typical pyridinium ion. The band at 1488 cm^{-1} is a combination band between those at 1540 and 1444 cm^{-1}, corresponding to Brønsted and Lewis acid sites, respectively.

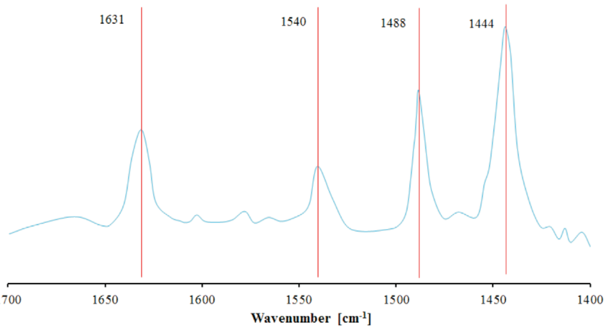


Fig. 3. Pyridine-desorbed FTIR spectra of the calcined ZPFe.

Total acidity of the samples was determined by temperature-programmed desorption of ammonia (TPD-NH_3) with a Quantachrome ChemBET 3000. Before the adsorption of ammonia, the samples were pre-treated in He at 250 °C for 30 min and then, 1 h at 350 °C and cooled to 100 °C. Then ammonia was adsorbed on the samples for 1 h. The TPD-NH_3 was carried out between 150 and 550 °C, at 10 °C/min, and analyzed by a thermal conductivity detector (TCD) for continuous monitoring of the desorbed ammonia. TPD-NH_3 provides a quantitative estimation of the total number of acid sites and the distribution of acid strengths. Because of the strong basicity of NH_3 gas, it was expected that all acid sites on the catalysts interact with NH_3. The total amount of NH_3 desorbed after saturation permits the quantification of the number of acid sites on the surface, while the position of the peak, desorption temperature, indicates the strength of the catalyst, i.e., the higher temperature of desorption, the stronger the acid strength.[78]

The TPD-NH_3 curves of ZPFe are shown in Fig. 4. ZPFe desorbed ammonia in a wide range of temperatures from 212 to 538 °C, which mostly corresponds to the medium and the strong acidic sites. The NH_3 desorption peak at temperatures below 250 °C belongs to the physisorption/chemisorptions of NH_3 molecules on weak acidic sites. The peak at about 250-450 °C shows the existence of intermediate strength acidic sites and finally the peak at 450-538 °C demonstrates the presence of strong acidic sites on the surface of ZPFe. Fig. 4 shows that the desorption of ammonia starts at almost 212 °C, centered at 317. The NH_3-TPD curves subsequently decreased with further increase in temperature and almost complete at 538 °C. This indicates that ZPFe contains a considerable number of acid sites which is attributed to the presence of Fe^{3+} groups on the surface of zirconium phosphate layers and make it suitable solid acid catalyst. The extent of desorptions is found to be ca. 2.3 mmol NH_3/g of catalyst. A TPD experiment was carried out after the 8th cycle by recovering the catalyst, in order to magnify the difference from the fresh catalysts (Table 1).

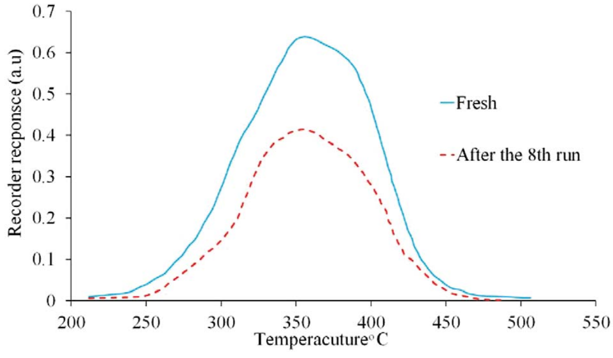


Fig. 4. NH_3-TPD profile of ZPFe.

The surface morphology of the ZP and ZPFe was studied by SEM (SEM, Philips XL) (Fig. 5). The SEM image of ZP (Fig. 5(a)) revealed the presence of hexagonal plates with well-defined shapes and very smooth surfaces. Fig. 5(b) and (c) (different magnification) show the SEM images of ZPFe. These images revealed that the structure of ZPFe was much less ordered than that of ZP, and that the ZPFe particles had aggregated to form both sheets and spheres of different shapes and sizes.[50,58]

Fig. 6 shows the TEM (CENTRA 100, Zeiss) images of ZPFe. It shows that ZPFe catalyst retained the original morphology of ZP (layered structure) and that the particles were approximately 120 nm in size. These images also showed nanoparticles of different sizes on the smooth surface of the ZP. The presence of metallic crystal nanoparticles on the surface of ZP indicated that the iron deposited on the surface of the ZP had agglomerated. Similar observations have also been reported for copper, zinc, and cerium with ZP.[60,70] Figures 5(d) and 6(c) show the SEM and TEM images of the catalyst following its 8th run, respectively. Both of these images showed that the sheets and particles had conglomerated to a much greater extent following the 8th run because of the process used to regenerate the catalyst.

Synthesis of 1,1-diacetates

In order to find the most appropriate reaction conditions and evaluate the catalytic efficiency of ZPFe on the protection of aldehydes to the corresponding 1,1-diacetates, we tried to convert benzaldehyde (5 mmol) to its corresponding acylal with ZPFe (0.5 mol%) and AA (10 mmol) in various solvents and also under solvent-free conditions. 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 α,β-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 short reaction times at room temperature (Table 3, entries 1-23), which are, in general, similar or higher than those described in the litera-

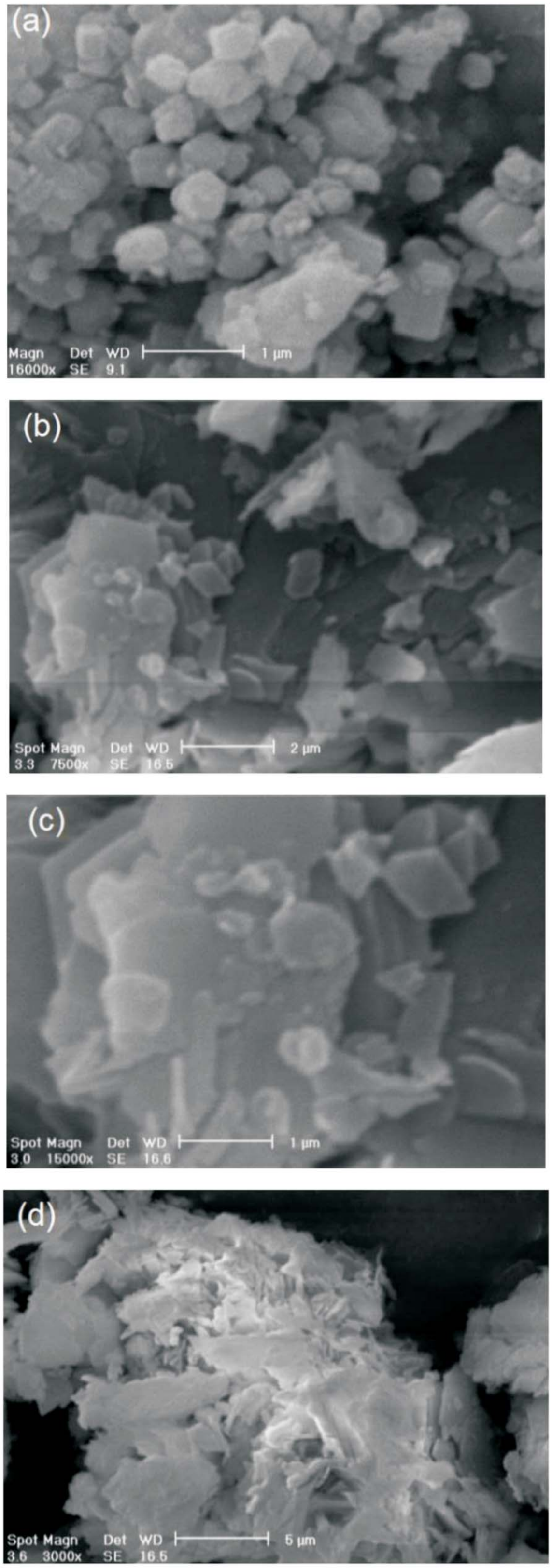


Fig. 5. SEM images of regular morphology of prepared ZP (a) and ZPFe (b, c) and after 8th run (d).

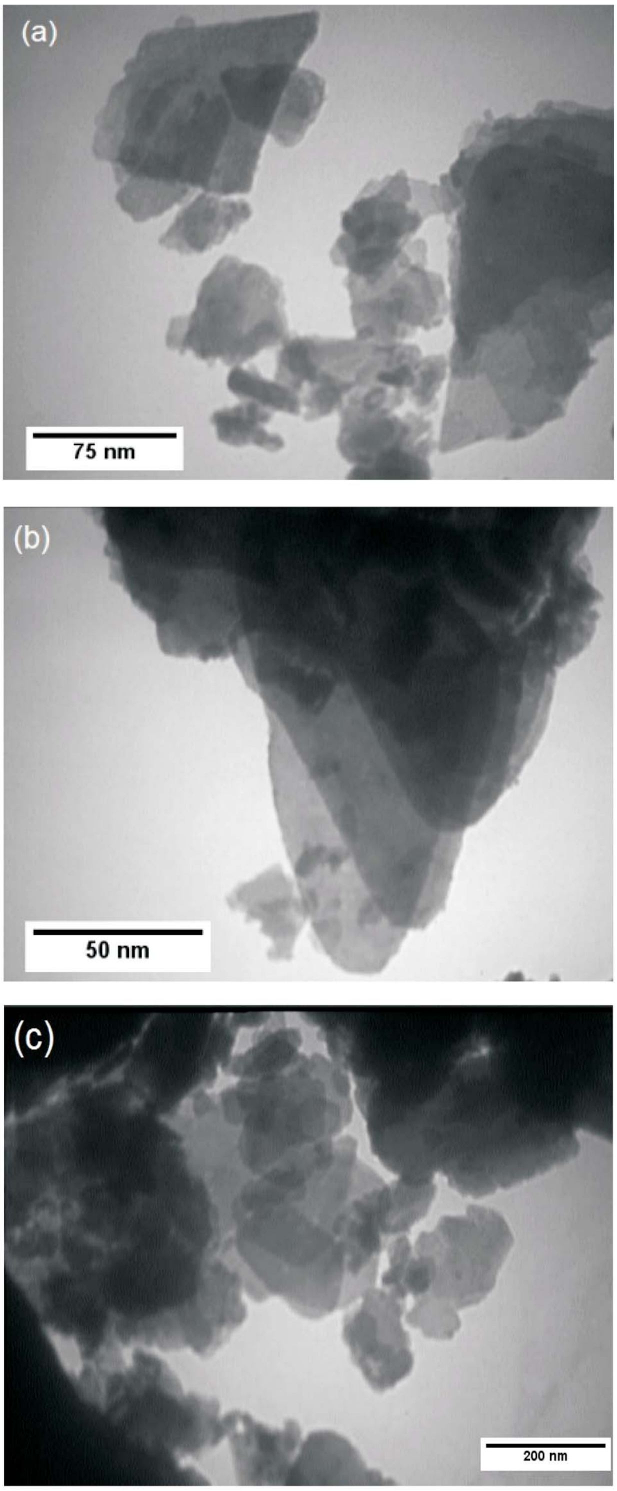


Fig. 6. TEM images of regular morphology of prepared ZPFe (a,b) (different magnification) and after the 8th run (c).

ture.[6-47] The reactions did not proceed in the absence of ZPFe even under heating conditions (Table 3, entry 27).

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

Entry	Solvent[a]	Yield (%)[b]	Time (min)
1	Diethylether	51	90
2	Cyclohexane	38	120
3	Dichloromethane	56	90
4	Acetonitrile	67	120
5	Ethylacetate	55	120
6	Solvent-free [c]	90	5

[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.

Under these reaction conditions, various functional groups (Me, OMe, OH, Cl, Br, CN, NO_2) 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 (NO_2, CN, Br and Cl), afforded the corresponding diacetates in higher yields (Table 3, entries 10–16).[79] But, aldehydes bearing electron-donating groups (Me and OMe) gave the corresponding 1,1-diacetates in lower yields and longer reaction times (Table 3, entries 2-9). 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

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

$$\underset{(5\text{ mmol})}{\text{R-CHO}} + \underset{(10\text{ mmol})}{Ac_2O} \xrightarrow[\text{Solvent-free, r.t}]{\text{ZPFe (0.5mol\%)}} \text{R-CH}(OAc)_2$$

Entry	Substrate	Time (min)	Yeild (%)[a]	Mp (°C) or bp (°C)	
				Found	Reaported [ref]
1	C_6H_5CHO	5	90	43-45	44–45 [6-10]
2	4-Me-C_6H_4CHO	20	90	80–82	81–82 [6-10]
3	2-MeO-C_6H_4CHO	35	85	68–80	73–74 [6-10]
4	3-MeO-C_6H_4CHO	10	89	Oil	Oil [6-10]
5	4-MeO-C_6H_4CHO	20	85	65–66	64–65 [6-10]
6	3,4-di-MeO-C_6H_4CHO	35	85	70–72	72–74 [6-10]
7	2,5-di-MeO-C_6H_4CHO	35	83	107–108	110 [6-10]
8	4-OH-C_6H_4CHO[b]	75	85	90–92	89–90 [6-10]
9	2-OH-C_6H_4CHO[b]	90	82	101–102	101–103 [6-10]
10	2-Cl-C_6H_4CHO	5	95	51–52	52–53 [6-10]
11	3-Cl-C_6H_4CHO	5	95	64–65	64–65 [6-10]
12	2,6-di-Cl-C_6H_4CHO	10	85	89–90	88–90 [6-10]
13	4-Cl-C_6H_4CHO	5	91	81–82	82–83 [6-10]
14	4-Br-C_6H_4CHO	5	94	93–95	92–95 [6-10]
15	4-NO_2-C_6H_4CHO	5	95	124–126	125–127 [6-10]
16	4-NC-C_6H_4CHO	5	96	100–101	100–102 [6-10]
17	4-(N,N-di-MeN)-C_6H_4CHO	120	-	-	-
18	Furfural	20	75	52–53	52–53 [6-10]
19	Cinnamaldehyde	5	93	84–86	84–85 [6-10]
20	Hexanal	35	80	Oil	Oil [6-10]
21	2-butenal	35	80	Oil	Oil [6-10]
22	$C_6H_4CH_2CH_2CHO$	10	74	Oil	Oil [6-10]
23	Isobutyraldehyde	35	74	Oil	Oil [6-10]
24	Phenylglyoxal[c]	30	88	53–55	53–55 [25,26]
25	Cyclohexanone	120	-	-	-
26	$C_6H_5COCH_3$	120	-	-	-
27	4-$NO_2C_6H_4COCH_3$	120	-	-	-
28	4-NO_2-C_6H_4CHO[d]	120	-	-	-

[a] All products were identified by their Mp, FT-IR and ^1H NMR spectra with authentic samples.

[b] AA (15 mmol).

[c] Only the aldehyde group was protected as 1,1-diacetate.

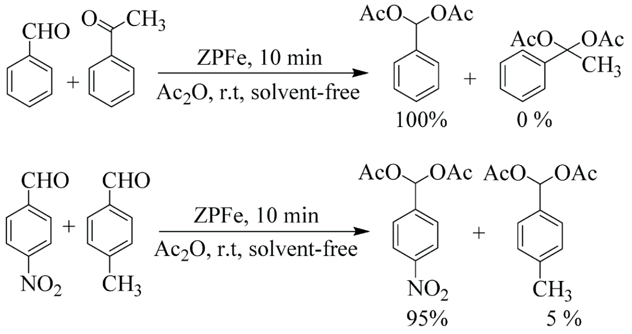
[d] The reactions was performed in the absence of ZPFe at 60 °C.

dependent on steric crowding surrounding the aldehyde group. Thus, the presence of substitutes at the para or meta position (Table 3, entries 4, 5, 8, 11, 13) made the reaction faster with better yields than those with substitutes at the ortho position (Table 3, entries 3, 9, 10, 12).

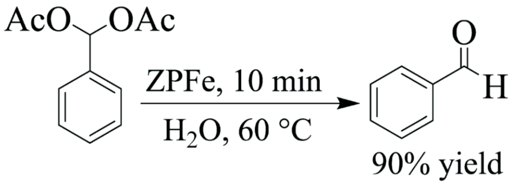
The acid-sensitive compounds such as furfural and cinnamaldehyde were also protected as 1,1-diacetates in good yields without any side products (Table 3, entries 18 and 19). We investigated the reaction of 2-hydroxybenzaldehyde and 4-hydroxybenzaldehyde under above conditions (Table 3, entries 8, 9); it should be mentioned that the phenolic group was also protected as acetate in hydroxyl containing aromatic aldehyde under such conditions (3 equiv. of Ac_2O). 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 17). The explanation for this result may be due to the strong electron donating properties of the dimethylamino group which will reduce the reactivity. Moreover, the protocol could also equally work with aliphatic aldehydes (Table 3, entries 20-23). 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.[21] 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 24). 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 25-27). Encouraged by this result, we suggest that the chemoselective protection of aldehydes in the presence of ketones can be achieved by this method (Scheme 1). We found that benzaldehyde was converted to the related gem-diacetate while the acetophenone remained unaffected.

In addition to these results, we further studied the possibility of deprotection of resulting acylals in this catalytic system by addition of water as a green solvent. 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 2).

Scheme 1 Competitive acylal formation of aldehydes in the presence of ZPFe

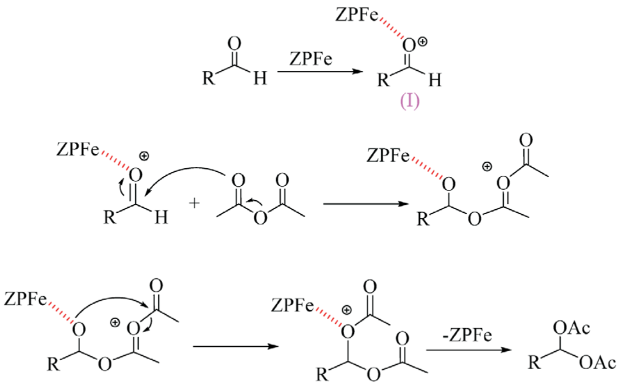


Scheme 2 Cleavage of acylal to benzaldehyde in water catalyzed by ZPFe



On the basis of literature studies, a plausible catalytic cycle for the regeneration, of ZPFe has been 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 ZPFe, as a Lewis acid, increases the electrophilicity of the carbonyl group on the aldehyde. Then AA attacks complex (I) to produce the final 1,1-diacetate.

Scheme 3 Plausible mechanism



We were interested in studying the reusability of the catalyst because of economic and environmental aspects. Hence, the reaction of benzaldehyde with AA was chosen as a model reaction in the presence of regenerated ZPFe under the optimum reaction conditions and the results are summarized in Table 4. Used ZPFe gave a similar yield of product as the fresh catalyst till the 8th 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 of ZPFe was observed after regeneration (till the 8th cycle). It could be seen from Table 4 that the ZPFe was utilized repeatedly over seven times without any apparent loss of the conversion. In order to compare the catalytic potentiality of ZPFe 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 (Table 5).

The results show that, ZPFe is an equally or competitive more efficient catalyst for this reaction with regards to reaction conditions and yield. The better efficacy of ZPFe nanoparticles in solvent-free synthesis of 1,1-diacetate from aldehydes might be due to the presence of Lewis acis sites (Fe^{3+}) on the surface of the catalyst. Moreover, this procedure offers advantages over some of the methodologies in terms of efficiency, deprotection as well as protection, reusability of the catalyst and we found that ZPFe is a selective catalyst in solvent-free conditions, which thus, makes it environmentally more acceptable.

In summary, in this paper, we reported a mild, solvent-free and efficient protocol for the protection of aldehydes by their conversion to 1,1-diacetates. ZPFe was used for this reaction at room temperature. This method is selective for the preparation of 1,1-diacetates from aldehydes in the presence of ketones. Also, 1,1-diacetates can be conveniently deprotected by using ZPFe in water. Other advantages of this catalyst are good to excellent yields and reusability of the catalyst. Further applications of this catalyst to other transformations are currently under investigation.

EXPERIMENTAL

All of the reagents and solvents used in the current study were purchased from Merck Chemical Company and used without further purification.

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

Substrate[a]	Fress	run 1	run 2	run 3	run 4	run 5	run 6	run 7	run 8
C_6H_5CHO	90	90	90	89	88	88	85	84	68

[a] Reaction conditions: C_6H_5CHO (5 mmol), AA (10 mmol), catalyst (0.5 mol%), r.t. and 10 min.

Catalyst synthesis: All of the reagents and solvents used in the current study were purchased from Merck Chemical Company and used without further purification. The catalyst was prepared according to previously published procedures, with minor modifications.[50,56-58] ZP was prepared according to the following procedure. $ZrOCl_2\bullet 8H_2O$ (5 g) was heated at reflux in a solution of H_3PO_4 (50 mL, 12 mol/mL) for 24 h. The resulting mixture was cooled to ambient temperature to give a suspension, which was filtered, and the filter cake was then washed with a solution of H_3PO_4 (0.1 mol/mL) until the filtrate was free of chloride ions. The filter cake was then washed several times with distilled water until the pH of the filtrate was neutral. The solid was then collected and dried in an oven at 110 °C for 24 h.[50] ZPFe was prepared through an ion-exchange reaction.[56-58] Briefly, ZP (3 g) was dispersed in deionized water (50 mL) at 50 °C, and the resulting suspension was treated with a solution of $Fe(OAc)_3$ (100 mL, 0.1

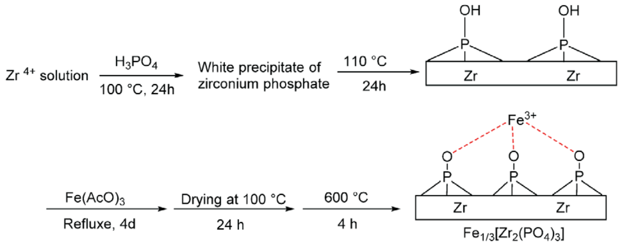
Table 5. Comparison of the effect of catalysts for 1,1-diacetate synthesis from benzaldehyde

Catalyst[a]	Ac_2O (mmol)	Time (min)	Yield %	Ref.
$SiO_2/B(SO_4H)_3$	2	4	97	[7]
S-CKT	5	5	96	[8]
SuSA	2	12	98	[9]
SBA-15-Ph-PrSO_3H	1.2	5	100	[10]
$Zr(HSO_4)_4$	3	5	90	[11]
PEG-SO_3H	10	15	89	[12]
Sulphated Zirconia[b]	2.5	5	99	[13]
SO_4^{2-}/SnO_2	2	15	97	[14]
ZSM-5-SO_3H	1	1	97	[15]
PS/$TiCl_4$ [c]	1.2	40	93	[16]
Schiff base complex of Cr (III)	3	15	96	[17]
Solid sulfuric acid	15	5	83	[18]
SBSSA	15	4	84	[19]
CPTS–HOAc	4	42	92	[20]
H_2NSO_3H	3	60	90	[21]
$ZrCl_4$	3	30	90	[22]
Zeolite Y	3	180	90	[23]
[bmpy]HSO_4 [d]	3	5	97	[24]
$InCl_3$	5	30	95	[25]
SPDTSA	15	4	95	[26]
sulfated SnO_2	12	60	91	[27]
DBSA	3	5	94	[28]
P(4-VPH)ClO_4	5	1	98	[29]
$La(NO_3)_3\cdot 6H_2O$	2.2	90	90	[32]
$(NH_4)_3PW_{12}O_{40}$	2	90	98	[33]
ZPFe	2	5	90	This work

[a] Reaction conditions: r.t, solvent-free.
[b] Reaction temperature: 0 °C.
[c] CH_2Cl_2 as solvent.
[d] Ultrasonic irradiation, 30 °C.

mol/L) in water (excess amount of Fe^{3+}). This mixture was then heated at reflux for 4 d. It is noteworthy that the acetate ion performed effectively as a base to keep the hydrogen ion concentration in solution sufficiently low to achieve high loadings of the catalyst.[80] A complete exchange between the cations and the hydrogen ions of the P–OH groups could not be achieved in less than 3 d or at temperatures below 80 °C.[70] The resulting slurry was filtered hot to give a light yellow solid, which was washed with distilled water until no Fe^{3+} ions could be detected in the filtrate (i.e., until the filtrate was colorless). The solid product was then dried at 100 °C for 24 h before being calcined at 600 °C for 4 h to give the final product, $Fe_{1/3}[Zr_2(PO_4)_3]$, as a pale yellow solid (Scheme 4).

Scheme 4 Summarized procedure for ZPFe preparation



Typical 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 (0.5 mol%) was transferred. The reaction mixture was stirred at room temperature for the time 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 Et_2O and the catalyst was recovered by centrifuge. The organic layer was washed with 10% $NaHCO_3$ solution and then dried over anhydrous $CaCl_2$. The solvent was evaporated under reduced pressure to give the corresponding pure 1,1-diacetate. The results and general experimental procedure are summarized in Table 2 and 3. All products were identified by their Mp, FT-IR and ^1H NMR spectra with authentic samples (supplementary information).

Procedure for the deprotection of 1,1 diacetates to aldehyde: A solution of 1,1-diacetate (5 mmol) in water (2 ml) and ZPFe (0.5 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 Et_2O and the catalyst was recovered by centrifuge. The organic layer was washed with water. The organic extracts were combined and washed with 10% $NaHCO_3$ and dried over anhydrous $CaCl_2$. The solvent was evaporated under reduced pressure to give the corresponding aldehyde.

Recyclability studies of catalyst: To examine the recyclability of the catalyst, the used ZPFe was recovered from the reaction media and re-used. For recycling, after the first use, the catalyst was separated from the reaction mixture by centrifugation, washed sequentially with ethanol and water before being dried at 110 °C for 2 h, and then activated at 450 °C for 2 h.

ACKNOWLEDGEMENTS

We gratefully acknowledge the funding support received for this project from the Isfahan University of Technology (IUT), IR Iran.

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