Zinc zirconium phosphate as an efficient catalyst for chemoselective synthesis of 1,1-diacetates under solvent-free conditions

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MS received 13 April 2015; revised 5 August 2015; accepted 13 August 2015

Abstract. In the present study, a mild, rapid, and efficient method for the protection of aldehydes with acetic anhydride (AA) in the presence of zinc zirconium phosphate (ZPZn) as a nano catalyst, 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. This nanocatalyst 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-friendliness, chemoselectivity, simple experimental and work-up procedure, solvent-free conditions and usage of only a stoichiometric amount of AA.

Keywords. Zinc zirconium phosphate; nanoparticles; heterogeneous catalysis; diacetate; solvent-free synthesis.

1. 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 neutral, basic and acidic conditions. Furthermore, they can be easily converted into parent aldehydes, which are frequently used as protecting groups for aldehydes.^{1,2} Besides, the acylals functionality can be converted into other useful functional groups by reaction with appropriate nucleophiles which are also useful intermediates in industries, such as cross linking agent for cellulose in cotton or used as stainbleaching 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 SiO₂/B(SO₄H)₃,⁷ S-CKT,⁸ SuSA,⁹ SBA-15-Ph-PrSO₃H,¹⁰ Zr(HSO₄)4,¹¹ PEG-SO₃H,¹² Sulphated Zirconia,¹³ SO₄²⁻/SnO₂,¹⁴ ZSM-5-SO₃H,¹⁵ PS/TiCl₄,¹⁶ Schiff base complex of Cr(III),¹⁷ Solid sulfuric acid,¹⁸ SBSSA,¹⁹ CPTS-HOAc,²⁰ H₂NSO₃H,²¹ ZrCl₄,²² Zeolite Y,²³ [bmpy]HSO₄,²⁴ [Hmim] HSO₄,²⁵ [morH]HSO₄,²⁶ SiO₂-SO₃H,²⁷ P₂O₅/Al₂O₃,²⁸ RuCl₃.H₂O_{,²⁹} H₆P₂W₁₈O₆₂.24H₂O_{,³⁰} zirconium sulfophenyl phosphonate,³¹ La(NO₃)₃.6H₂O_{,³²} (NH₄)₃ PW₁₂O₄₀,³³ PBBS,³⁴ SbCl₃,³⁵ Cu_{3/2}PMo₁₂O₄₀/SiO₂,³⁶ Si–[SbSipim][PF₆],³⁷ DOWEX(R)50WX4,³⁸[bmim][Fe Cl₄],³⁹ Mo/TiO₂–ZrO₂,⁴⁰ Cyanuric chloride,⁴¹ CuSO₄· 5H₂O,⁴² H₃PW₁₂O₄₀,⁴³ H₂SO₄-silica,⁴⁴ Supported POM,⁴⁵ and P₂O₅/SiO₂.^{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}



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 α -Zirconium phosphate (ZP) is one of the most important compounds in inorganic chemistry, and the layered structure of this compound has been used in different fields.⁴⁹⁻⁵¹ The layered structure of ZP consists of zirconium ions in a semiplanar arrangement, located slightly above and below the mean plane, while each Zr^{4+} ion is connected through the oxygen atoms of phosphate groups from above and below. Three of the four oxygen atoms in the phosphate groups are bonded to three different zirconium atoms. The fourth oxygen atom of the phosphate groups that bonds to a proton, the free –OH group, is pointing into the interlayer region.^{50,51} 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, which results in the enlargement of the interlayer distance.^{54–56} Several studies pertaining to the successful exchange of the H⁺ of the P–OH group in ZP with various divalent and trivalent cations have been reported in the literature.⁵⁷⁻⁶² It has also been reported that ZP possesses excellent selectivity towards Pb^{2+} , Zn^{2+} , and Fe^{3+} as an ion exchanger.^{63–65} Furthermore, ZP has been reported to exhibit antibacterial activity when it was loaded with Cu²⁺, Zn²⁺, or Ce³⁺.⁶⁰⁻⁶² Several reports have also appeared in the literature concerning the catalytic activities of ion exchanged materials of this type, including the use of copper zirconium phosphate (ZPCu) as catalyst in the acetylation of alcohols and phenols and the use of zirconium phosphate-ferric chloride complex and potassium iron zirconium phosphate as catalyst in Friedel-Crafts reaction.^{66–72}

To the best of our knowledge, there is no report available in the literature for using ZPZn as catalyst for the preparation of 1,1-diacetates from carbonyl compounds. Therefore, in continuation of our reports using various catalysts for the synthesis of 1,1-diacetates from aldehydes,^{25–29} 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.

2. Experimental

2.1 Catalyst synthesis

All the reagents and solvents used in the current study were purchased from the Merck Chemical Company and used without further purification. The catalyst was prepared according to previously published procedures, with minor modifications.^{50,60-62} ZP was prepared according to the following procedure. ZrOCl₂·8H₂O (5 g) was heated at reflux in a solution of H₃PO₄ (50 mL, 12 mol/L) 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/L) until the filtrate was free of chloride ions. In order to determine the presence of any chlorine ino in the filtrate, the silver nitrate test was used. 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 ZPZn was prepared through an ionexchange reaction.^{60–62} Briefly, ZP (3 g) was dispersed in deionized water (50 mL) at 50°C, and the resulting suspension was treated with a solution of $Zn(OAc)_2$ (100 mL, 0.1 mol/L) in water (excess amount of Zn^{2+}). 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.⁷² 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.⁶¹ The resulting slurry was filtered hot to give a light white solid, which was washed with distilled water until no Zn^{2+} ions could be detected in the filtrate (i.e., until the filtrate was colorless). The solid product was then dried at 110°C for 8 h before being calcined at 600°C for 4 h to give the final product, ZPZn, as a white solid (scheme 1).

2.2 Catalyst characterization

The chemical composition of the ZPZn catalyst was evaluated at different stages of the reaction (i.e., before and after the catalytic reaction) by ICP-OES using an Optima 7300 V ICP-OES spectrometer (PerkinElmer) (table 1). The samples were ground into a fine powder and analyzed by XRD on a Philips X'pert X-ray diffractometer. The specific surface areas of the samples were determined from their N_2 adsorption-desorption isotherms



Scheme 1. Procedure for the preparation of ZPZn.

Entry	Sample	Zn	0	Zr	Р	BET (m ² /g)	Total acidity (mmol NH ₃ /g)
1	ZP	_	65.3	12.4	22.3	118.2	2.5
2	ZPZn	12.1	54.1	12.3	21.5	102.4	1.6
3	ZPZn ^a	12	54.3	12.2	21.5	102.1	1.52
4	ZPZn ^b	8.7	59.2	12.1	20.0	96.4	1.05
5	ZPZn ^c	4.7	63.5	12	19.8	86.4	0.78

Table 1. Elemental contents (%) of ZPZn and physical properties of the catalysts before and after reaction.

^a After the first cycle.

^b After the 6th cycle.

^c After the 7th cycle.

using the Brunauer-Emmett-Teller (BET) method on a Quantachrome ChemBET 3000 instrument. Each sample was degassed at 400°C for 2 h before being analyzed to remove any adsorbed species from their surfaces. The BET surface areas of the materials were estimated from their N₂ adsorption-desorption isotherms. The surface morphologies of the ZP and ZPZn materials were studied by SEM on a Philips XL scabbing electron microscope (Philips). TEM images of ZPZn were obtained on a CENTRA 100 TEM system (Zeiss).

2.3 *Typical procedure for preparation of 1,1-diacetates*

Typically, in a 25 mL round bottom flask, equipped with a magnetic stirrer, substrate (5 mmol) and AA (10 mmol) and catalyst (1 mol%) were transferred. The reaction mixture was stirred at room temperature for the 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. The results and general experimental procedure are summarized in tables 2 and 3.

2.4 *Procedure for the deprotection of 1,1 diacetates to aldehyde*

A solution of 1,1-diacetate (5 mmol) in water (2 mL) and ZPZn (1 mol%) was introduced into a round bottom flask equipped with a magnetic stirrer and condenser at 80°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% NaHCO₃ and

Table 2. Conversion of benzaldehyde to its correspond-ing diacetate in different solvents and under solvent-freeconditions in the presence of ZPZn.

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	15

^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.

dried over anhydrous CaCl₂. The solvent was evaporated under reduced pressure to give the corresponding aldehyde.

2.5 Recyclability studies of catalyst

To examine the recyclability of the catalyst, the used ZPZn was recovered from the reaction media and reused. 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.

3. Results and discussion

3.1 Catalyst characterization

The ICP-OES analyses of ZP and ZPZn are shown in table 1. The results obtained in the current study for ZPZn were compared with those reported.⁶⁰⁻⁶² Our results revealed that there was a negligible leach of zinc ions into the reaction media after the reaction (i.e., following the first use of the catalyst).

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ZPZn (1mol%)

Table 3.	Preparation of ac	ylals in the pres	ence of ZPZn unde	r solvent-free conditions at r.t.
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	(5 mmol)	(10 mmol) Solvent-f	ree, r.t	.)2		
				M.p. (°C) or B.p. (°C)		
Entry	Substrate	Time (min)	Yeild (%) ^a	Found	Reaported [ref]	
1	C ₆ H ₅ CHO	15	90	43–45	44-45 ⁶⁻¹⁰	
2	4-Me-C ₆ H ₄ CHO	30	90	80-82	81-826-10	
3	$2-Me-C_6H_4CHO$	45	85	64–66	64-66 9 ^{13,81,82}	
4	2-MeO-C ₆ H ₄ CHO	45	85	68-80	73–74 ^{6–10}	
5	3-MeO-C ₆ H ₄ CHO	20	89	Oil	Oil ^{6–10}	
6	4-MeO-C ₆ H ₄ CHO	30	84	65-66	64–65 ^{6–10}	
7	3,4-di-MeO-C ₆ H ₄ CHO	45	84	70-72	72–74 ^{6–10}	
8	2,5-di-MeO-C ₆ H ₄ CHO	45	83	107-108	110^{6-10}	
9	4-OH-C ₆ H ₄ CHO ^b	120	85	90-92	89–90 ^{6–10}	
10	2-OH-C ₆ H ₄ CHO ^b	180	82	101-102	101–103 ^{6–10}	
11	$2-(CH_3)_2CH-C_6H_4CHO$	75	83	58-60	_	
12	2-(CH ₃) ₃ C-C ₆ H ₄ CHO	120	74	68-70	_	
13	$2-Cl-C_6H_4CHO$	15	95	51-52	52-53 ⁶⁻¹⁰	
14	3-Cl-C ₆ H ₄ CHO	10	95	64-65	$64 - 65^{6-10}$	
15	2,6-di-Cl-C ₆ H ₄ CHO	20	85	89–90	$88 - 90^{6 - 10}$	
16	$4-Cl-C_6H_4CHO$	10	91	81-82	82-83 ⁶⁻¹⁰	
17	4-Br-C ₆ H ₄ CHO	10	94	93–95	92–95 ^{6–10}	
18	2-Br-C ₆ H ₄ CHO	15	91	80-82	80 ⁸³	
19	$2-NO_2-C_6H_4CHO$	20	88	91–93	90–91 ^{8,9,18,27}	
20	$4-NO_2-C_6H_4CHO$	10	95	124-126	125–127 ^{6–10}	
21	$2-NC-C_6H_4CHO$	10	96	74–76	76–77 ¹¹	
22	4-NC-C ₆ H ₄ CHO	10	96	100-101	$100 - 102^{6 - 10}$	
23	$2-F-C_6H_4CHO$	10	90	24-26	25–26 8 ⁸³	
24	4-F-C ₆ H ₄ CHO	10	95	50-52	50-52 ^{8,24,28}	
25	4-(N,N-di-MeN)-C ₆ H ₄ CHO	180	_	_	_	
26	Furfural	30	70	52-53	52-53 ⁶⁻¹⁰	
27	Cinnamaldehyde	10	92	84-86	84-85 ⁶⁻¹⁰	
28	Hexanal	45	77	Oil	Oil^{6-10}	
29	2-butenal	45	77	Oil	Oil^{6-10}	
30	C ₆ H ₄ CH ₂ CH ₂ CHO	20	71	Oil	Oil^{6-10}	
31	Isobutyraldehyde	45	71	Oil	Oil^{6-10}	
32	Cyclohexanone	180	_	_	_	
33	C ₆ H ₅ COCH ₃	180	-	-	-	
34	$4-NO_2C_6H_4COCH_3$	180	-	-	-	
35	4-NO ₂ -C ₆ H ₄ CHO ^c	180	_	-	-	

^a All products were identified by their M.p., IR, GC–MS and ¹H NMR spectra with authentic samples.

^b AA (15 mmol).

^c The reactions was performed in the absence of ZPZn at 60°C.

Figure 1 shows the powder XRD patterns of the ZP and ZPZn materials. The results show some characteristic reflections in the 2θ range of $5^{\circ} - 40^{\circ}$. The diffraction peak in ZP at $2\theta \sim 12^{\circ}$ 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 ZPZn had increased, which indicated that the Zn²⁺ ions had intercalated into the interlayer of ZP and increased the d_{002} basal interlamellar spacing of ZP from 7.5 to 8.7 Å. It is well known that the ionic radii of Zn^{2+} (0.74 Å) and hydrated Zn^{2+} (2.16 Å) are smaller than the basal spacing of ZP (7.5 Å).^{73,74} The crystal structure of ZPZn was affected by the exchange of zinc ions. When the zinc ions were introduced into the ZP, the crystallinity gradually decreased. Its XRD pattern shows a layered material, slightly disordered, that, however, clearly shows the harmonics of the first d₀₀₂ reflection. These results therefore indicated that Zn^{2+} ions had inserted into the interlayer of ZP and increased the basal spacing of the modified ZP after the exchange.^{60–62} Taken together, these data indicated that ZPZn had been formed successfully. The XRD pattern of the ZPZn catalyst after the 7th run showed that the basal spacing of ZP was about 9.5 Å, which was only a little larger than that of the fresh ZPZn catalyst. This increase may have occurred because of the presence of less Zn^{2+} on the surface of ZP, and an increase in the number of water molecules between the layers following the seventh run (i.e., Zn^{2+} ions may have been washed off during the regeneration of the catalyst, table 1). Our findings showed good agreement with earlier reports.^{60–62}

Figure 2 shows the N₂ adsorption-desorption isotherm of ZPZn, as a representative example, in the relative pressure range (P/P₀) of 0.1–1.0. The surface area of ZPZn was determined to be 102.4 m²/g. The isotherm for ZPZn shows three adsorption stages. The first of these stages was observed at P/P₀ < 0.46, whereas the second stage was observed in the range of 0.46 < P/P₀ < 0.95, and the third stage was observed at higher relative pressures (P/P₀ > 0.95). The N₂ adsorption-desorption isotherm of ZPZn exhibited a typical "type IV" isotherm shape with a distinct hysteresis loop,



Figure 1. XRD patterns of powder ZP (down), ZPZn fresh (middle) and after the 7th run (up).



Figure 2. N₂ adsorption-desorption isotherm of ZPZn.

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 ZPZn catalyst. The observed increase in adsorption at the higher P/P₀ value indicated the presence of larger mesopores in the sample.^{61–66} The surface area of ZPZn after the 7th run was found to be 86.4 m²/g.

The nature of the acid sites of ZP and ZPZn was studied by IR spectroscopy using pyridine as a probe molecule. 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 change in the spectra was observed (figure 3). The main bands observed over the samples are assigned according to the literature data.^{76,77} Pyridine adsorbed FTIR spectra of the ZPZn show the strong bands at 1632 and 1541 cm^{-1} , indicating typical pyridinium ion. The band at 1488 cm⁻¹ is a combination band between those at 1541 and 1444 cm⁻¹, corresponding to Brønsted and Lewis acid sites, respectively. The origin of Brønsted acidity of the ZP is due to the presence of P-OH groups,^{78,79} while the main acitidy of ZPZn is due to its Lewis acid sites (Zn^{2+}) (figure 3). Figure 3 shows the Py-FTIR spectrum of the catalyst after the 7th run. It clearly indicates that the replacement of Zn^{2+} on the surface of the catalyst with H⁺ during the catalyst regeneration process has reduced the number of Lewis acid sites (band at 1444 cm⁻¹ was reduced). Conversely, the amount of Brønsted acid sites was increased (band at 1632 cm⁻¹ was increased).

Total acidity of the samples was determined by temperature-programmed desorption of ammonia (TPD-NH₃) with a Quantachrome ChemBET 3000. Before the



Figure 3. Pyridinedesorbed FTIR spectra of ZPZn (Fresh and after the 7th run) and ZrP.

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-NH₃ 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-NH₃ provides a quantitative estimation of the total number of acid sites and the distribution of acid strengths. Because of the strong basicity of NH₃ gas, it was expected that all acid sites on the catalysts interact with NH₃. The total amount of NH₃ 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., higher temperature of desorption, stronger is the acid strength. The TPD-NH₃ curves of ZPZn are shown in figure 4 ZPZn desorbed ammonia in a wide range of temperatures from 212 to 538°C, which mostly correspond to the medium and strong acidic sites. The NH₃ desorption peak at temperatures below 250°C belongs to the physisorption/chemisorptions of NH₃ 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 ZPZn. Figure 4 shows that the desorption of ammonia starts at almost 212°C, centered at 317°C. The NH₃-TPD curves subsequently decreased with further increase in temperature and almost complete at 538°C. This indicates that ZPZn contains a considerable number of acid sites which is attributed to the presence of Zn^{2+} groups on the surface of zirconium phosphate layers and make it suitable solid acid catalyst.⁶⁶ The extent of desorptions is found to be ca. 1.6 mmol NH₃/g of catalyst. A TPD experiment was carried out after the 7th cycle by recovering the catalyst, in order to magnify the difference from the fresh catalysts (table 1).



Figure 4. NH₃-TPD profile of ZPZn.

The surface morphology of the ZP and ZPZn was studied by SEM (SEM, Philips XL) (figure 5). The SEM image of ZP (figure 5(a)) revealed the presence of hexagonal plates with well-defined shapes and very smooth surfaces. Figures 5(b) and (c) (different magnification) show the SEM images of ZPZn. These images revealed that the structure of ZPZn was less ordered than that of ZP, and that the ZPZn particles had aggregated to form both sheets and spheres of different shapes and sizes.^{60,61,66}

Figure 6 shows the TEM (CENTRA 100, Zeiss) images of ZPZn. It shows that ZPZn catalyst retained the original morphology of ZP (layered structure) and that the particles were approximately 150 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 zinc deposited on the surface of the ZP had agglomerated. Similar observations have also been reported for copper, zinc, and cerium with ZP.^{61,62,72} Figure 5(d) and 6(c,d) show the SEM and TEM images of the catalyst after several regenerations, respectively. All these images showed that the sheets and particles had conglomerated to a much greater extent following the 7th run because of the process used to regenerate the catalyst.

3.2 Synthesis of 1,1-diacetates and expected mechanism

In order to find the most appropriate reaction conditions and evaluate the catalytic efficiency of ZPZn on the protection of aldehydes to the corresponding 1,1diacetates, we tried to convert benzaldehyde (5 mmol) to its corresponding acylal with ZPZn (1 mol%) and AA (10 mmol) in various solvents and also under solventfree 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 literature.^{6–47} The reactions did not proceed in the absence of ZPZn even under heating conditions (table 3, entry 27). Under these reaction conditions, various functional groups (Me, isopropyl,



Figure 5. SEM images of regular morphology of prepared ZP (a), ZPZn fresh (b, c) and after the 7th run (d).



Figure 6. TEM images of regular morphology of prepared ZPZn fresh (a,b) (different magnification) and after the 6th (c) and the 8th run (d).

t-butyl, 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 13–24).⁸⁰ But, aldehydes bearing electron-donating groups (Me, isopropyl, t-butyl, and OMe) gave the

corresponding 1,1-diacetates in lower yields and longer reaction times (table 3, entries 2-12). 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 the meta position (table 3, entries 2,5,6,9,14,16,17,20,22 and 24) made the reaction faster with better yields than those with substitutes at the ortho position (table 3, entries 3,4,8,10,13,15,18,19,21 and 23). Moreover, aldehydes with hindered alkyl substitutes, 2-isopropylbenzaldehyde and 2-(tert-butyl)-benzaldehyde, produced the corresponding acylals in longer reaction times and lower yields (table 3, entries 11,12).

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 26 and 27). We investigated the reaction of 2-hydroxybenzaldehyde and 4-hydroxybenzaldehyde under above conditions (table 3, entries 9 and 10); it should be mentioned that the phenolic group was also protected as acetate in hydroxyl containing aromatic aldehyde under such conditions (3 equiv. of Ac₂O). 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 25). The explanation for this result may be due to the strong electron donating properties of the dimethylamino group which will reduce the reactivity.²¹ Moreover, the protocol could also equally work with aliphatic aldehydes (table 3, entries 28-31). 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 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 32-35). Encouraged by this result, we suggest that the chemoselective protection of aldehydes in the presence of ketones can be achieved by this method (scheme 2). 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 80°C. By this procedure, related acylal has been completely transformed into benzaldehyde in a short reaction time (scheme 3).

On the basis of literature studies, a plausible catalytic cycle for the regeneration of ZPZn has been proposed. As outlined in scheme 4, the possible mechanism of this reaction may be involvement of either intermolecular or intramolecular transfer of the second acetate group after the initial attack by AA. We suggest that ZPZn, 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.^{7,9,17,25,27,29}

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 ZPZn under the optimum reaction conditions and the results are summarized in table 4. Used ZPZn gave a similar yield of product as the fresh catalyst till the 7th cycle. The lowered activity of the used catalyst sample confirms the deactivation of catalyst during the reaction.



Scheme 3. Cleavage of acylal to benzaldehyde in water catalyzed by ZPZn.



Scheme 2. Competitive acylal formation of aldehydes in the presence of ZPZn.



Scheme 4. Plausible mechanism.

The regenerated catalyst was characterized for its chemical composition by elemental analysis. The elemental composition of the catalyst remained almost unchanged upto its 7th run, although the amount of zinc in the catalyst was reduced by almost 60% compared with the first run (table 1). As it can be seen from this table, no significant change in composition of the catalyst was observed after the first use. There was a negligible leach of Zn^{2+} into the reaction media after the reaction (table 1 entry 2,3). Also, as it is presented in table 4, the activity of the catalyst almost remained intact till the 7th run. But, after the 7th run, the decomposition of the catalyst was changed (Zn^{2+} was washed

from the zirconium phosphate surface during the catalyst regeneration), which caused a reduction of the product yield down to 68%. We believe that the catalytic activity of ZPZn is due to its Lewis acid sites (scheme 4) and when these active sites were reduced, the catalytic activity was reduced as well. Also, another reason for less activity of ZPZn after the 7th run is probably because of catalyst agglomeration after several thermal regenerations (figure 6).

In order to compare the catalytic potentiality of ZPZn 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

Table 4. Catalyst re-usage 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	run 8
C ₆ H ₅ CHO	90	90	90	89	88	88	85	84	68

^a Reaction conditions: C₆H₅CHO (5 mmol), AA (10 mmol), catalyst (1 mol%), r.t. and 15 min.

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

Catalyst ^a	Ac ₂ O (mmol)	Time (min)	Yield %	Ref.
SiO ₂ /B(SO ₄ H) ₃	2	4	97	7
S-CKT	5	5	96	8
SuSA	2	12	98	9
SBA-15-Ph-PrSO ₃ H	1.2	5	100	10
Zr(HSO ₄) ₄	3	5	90	11
PEG-SO ₃ H	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 ^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 ₂ NSO ₃ H	3	60	90	21
ZrCl ₄	3	30	90	22
Zeolite Y	3	180	90	23
[bmpy]HSO ^d	3	5	97	24
[<i>Hmim</i>]HSO ₄	2	25	90	25
[morH]HSO ₄	2	3	85	26
SiO ₂ -SO ₃ H	4	25	90	27
P_2O_5/Al_2O_3	2.5	45	87	28
RuCl ₃ .H ₂ O	6	10	76	29
$La(NO_3)_3.6H_2O$	2.2	90	90	32
$(NH_4)_3 PW_{12}O_{40}$	2	90	98	33
ZPZn	2	15	90	This work
ZP	3	20	85	This work

^a Reaction conditions: r.t., solvent-free.

^b Reaction temperature: 0°C.

^c CH₂Cl₂ as solvent.

^d Ultrasonic irradiation, 30°C.

catalysts with respect to the amounts of AA, reaction time and the yield of the products (table 5). The results show that, ZPZn is an equally competitive or more efficient catalyst for this reaction with regard to reaction conditions and yield.

The better efficacy of ZPZn nanoparticles in solventfree synthesis of 1,1-diacetate from aldehydes might be due to the presence of Lewis acid sites (Zn^{2+}) 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 ZPZn is a selective catalyst in solvent-free conditions, which thus, makes it environmentally more acceptable.

4. Conclusions

In summary, in this paper, we have reported a mild, solvent-free and efficient protocol for the protection of aldehydes for their conversion to the corresponding 1,1-diacetates. ZPZn 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 ZPZn 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.

Acknowledgments

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

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