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Article

Acetylation of alcohols and phenols under solvent-free conditions using copper zirconium phosphate

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ABSTRACT

Copper zirconium phosphate nanoparticles have been used as an efficient catalyst for the acetylation of a wide range of alcohols and phenols with acetic anhydride in good to excellent yields under solvent-free conditions. The steric and electronic properties of the different substrates had a significant influence on the reaction conditions required to achieve the acetylation. The catalyst used in the current study was characterized by inductively-coupled plasma optical emission spectroscopy, energy dispersive spectroscopy, X-ray diffraction, N₂ adsorption-desorption, scanning electron microscopy, and transmission electron microscopy. These analyses revealed that the interlayer distance in the catalyst increased from 7.5 to 8.0 Å when Cu²⁺ was intercalated between the layers, whereas the crystallinity of the material was reduced. This nanocatalyst could also be recovered and reused at least six times without any discernible decrease in its catalytic activity. This new method for the acetylation of alcohols and phenols has several key advantages, including mild and environmentally friendly reaction conditions, as well as good to excellent yields and a facile work-up.

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1. Introduction

α -Zirconium phosphate (ZP) is one of the most important compounds in inorganic chemistry, and the layered structure of this material has been used in a variety of different fields [1–3]. ZP behaves as a unique ion exchanger because of its exceptionally poor aqueous solubility, high thermal stability, resistance to radiation and abrasive properties [4,5]. 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 [6–9]. 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 [10–14]. It has

also been reported that ZP possesses excellent selectivity towards Pb²⁺, Zn²⁺, and Fe³⁺ as an ion exchanger [15–17]. Furthermore, ZP has been reported to exhibit antibacterial activity when it was loaded with Cu²⁺, Zn²⁺, or Ce³⁺ [5,6,13,14]. Several reports have also appeared in the literature concerning the catalytic activities of ion exchanged materials of this type, including the use of zinc zirconium phosphate as a catalyst in the Prins Condensation and the use of a zirconium phosphate-ferric chloride complex and potassium iron zirconium phosphate as catalysts in Friedel-Crafts acylation reactions [18–24].

The acetylation of alcohols, phenols, thiols, and amines is one of the most important and frequently used transformations

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in organic synthesis, and the resulting acetylated species can be used in a variety of different ways, including their application as protecting groups in multistep synthetic processes. Acetylated groups are also commonly found in cosmetics and food-stuffs, as well as fragrances, solvents, plasticizers, and pharmaceuticals [25–27]. One of the most common examples of a compound containing an acetylated group is aspirin, which is produced by the acetylation of salicylic acid with acetic anhydride (AA) in the presence of an acid catalyst [28]. The acetyl group is one of the most inexpensive and commonly used protecting groups in organic chemistry for the protection of $-OH$, $-SH$, and $-NH_2$ functional groups because the resulting acetylated compounds are stable to various reaction conditions and reagents. Furthermore, the acetyl group can be readily introduced using inexpensive reagents and easily removed using mild alkaline hydrolysis [29–31]. A variety of different procedures have been developed for the acetylation of alcohols, phenols, amines, and thiols using both homogeneous and heterogeneous catalysts such as $V^{IV}(TPP)(OTf)_2$ [27], $La(NO_3)_3 \cdot 6H_2O$ [29], $B(C_6F_5)_3$ [30], $CuSO_4 \cdot 5H_2O$ [31], $ZnCl_2$ [32], borated zirconia [33], ZnO_2 [34], $Ce(OTf)_3$ [35], $Si-ZnCl_2$ [36], $H_3PW_{12}O_{40}$ [37], $DMAP \cdot HCl$ [38], $Cu(BF_4)_2 \cdot xH_2O$ [39], silica-bonded sulfamic acid [40], Cp_2ZrCl_2 [41], $[TMBSA][HSO_4]$ [42], $[bmim][OTs]$ [43], $[MMPPA][HSO_4]$ [44], $SaSA$ [45], $SBNPSA$ [46], $SuSA$ [47], $P(4-VPT)$ [48], acylimidazolium acetate [49], polyvinylpolypyrrolidonium tribromide [50], $ZnAl_2O_4@SiO_2$ [51], P_2O_5/Al_2O_3 [52], $[Hmim]HSO_4$ [53], Yttria-zirconia [54], and $CoCl_2$ [55]. Despite extensive interest in development of new methods of acetylation, there is still scope for the development of simple, efficient, inexpensive, widely applicable, reusable and environmentally benign catalysts and procedures capable of promoting the acetylation process.

With this in mind, and as part of ongoing work towards the development of efficient green catalysts for organic transformations [56,57], with particular emphasis on the acetylation and acylation of aromatic compounds [52,53], we report herein the use of copper zirconium phosphate (ZPCu) as an efficient catalyst for the mild and convenient acetylation of alcohols and phenols under solvent-free conditions. This new ZPCu catalyst was characterized by inductively-coupled plasma optical emission spectroscopy (ICP-OES), energy dispersive X-ray (EDX), X-ray diffraction (XRD), N_2 adsorption-desorption, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

2. Experimental

2.1. 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 [2,8–10]. ZP was prepared according to the following procedure. $ZrOCl_2 \cdot 8H_2O$ (5 g) was heated at reflux in a solution of H_3PO_4 (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. 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 [2]. ZPCu was prepared through an ion-exchange reaction [8–10]. Briefly, ZP (3 g) was dispersed in deionized water (50 ml) at 50 °C, and the resulting suspension was treated with a solution of $Cu(OAc)_2$ (100 ml, 0.1 mol/L) in water (excess amount of Cu^{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 [7]. 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 [13]. The resulting slurry was filtered hot ($\sim X$ °C) to give a light blue solid, which was washed with distilled water until no Cu^{2+} 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 5 h to give the final product, ZPCu, as a pale blue solid (Scheme 1).

2.2. Catalyst characterization

The chemical composition of the ZPCu 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). The chemical composition of the ZPCu catalyst was measured by energy dispersive X-ray spectroscopy (EDS) using a Zeiss EVO scanning electron microscope operating at 20 kV. 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 using the Brunauer-Emmett-Teller (BET) method on a Quantachrome ChemBET 3000 instrument (Supplier, City, Country). 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 N_2 adsorption-desorption isotherms.

The surface morphologies of the ZP and ZPCu materials were studied by SEM on a Philips XL scabbing electron microscope (Philips). TEM images of ZPCu were obtained on a CENTRA 100 TEM system (Zeiss).

2.3. General experimental procedure for the acetylation of substrates under solvent-free conditions

Scheme 1. Procedure for the preparation of ZPCu.

Scheme 2. Procedure for the acetylation of phenols.

ZPCu (2 mol%) was added to a mixture of phenol (1 mmol) and AA (2 mmol), and the resulting mixture was stirred at 60 °C for the specified time (Scheme 2). Upon completion of the reaction (as determined by GC), the catalyst was separated from the reaction mixture by centrifuge, then the supernatant was collected and diluted with 10% NaHCO₃ solution (10 ml) before being extracted with Et₂O (2 × 10 ml). The combined organic extracts were washed and then dried over anhydrous CaCl₂ before being evaporated to dryness under vacuum to give the desired product. In some cases, it was necessary for the product to be purified by column chromatography over silica gel eluting with a mixture of cyclohexane and ethyl acetate.

2.4. Recyclability studies of catalyst

To examine the recyclability of the catalyst, the used ZPCu 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 and washed with sequentially with ethanol and water before being dried at 110 °C for 2 h.

3. Results and discussion

3.1. Catalyst characterization results

The EDS and ICP-OES analyses of ZPCu are shown in Fig. 1 and Table 1 (entry 3), respectively. The results obtained in the current study for ZPCu were compared with those reported previously in the literature [5,9,10]. Our results revealed that there was a negligible leach of copper ions into the reaction media after the reaction (i.e., following the first use of the catalyst).

Figure 2 shows the powder XRD patterns of the ZP and ZPCu 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 re-

Fig. 1. EDS spectrum of ZPCu.

Table 1

Elemental compositions of several different copper zirconium phosphates (atm%).

Entry	Sample	Cu	O	Zr	P
1	ZP	—	63.1	13.6	23.3
2	ZPCu	11.7	58.7	10.9	18.8
3 ^a	ZPCu	11.2	57.5	11.5	19.8
4 ^b	ZPCu	11.6	59.3	10.4	18.7
5 ^c	ZPCu	5.9	62.5	12.2	19.4

^a From EDS analysis. ^b After run 1. ^c After run 7.

ported for ZP and its derivatives with a hexagonal crystal system [2]. It shows that the *d*-spacing of the (002) plane of ZPCu had increased, which indicated that the Cu²⁺ ions had intercalated into the interlayer of ZP and increased the *d*₀₀₂ basal interlamellar spacing of ZP from 7.5 to 8.0 Å. It is well known that the ion radii of Cu²⁺ (0.72 Å) [58,59] and hydrated Cu²⁺ (4.19 Å) [60] are smaller than the basal spacing of ZP (7.5 Å). These results therefore indicated that Cu²⁺ ions had inserted into the interlayer of ZP and increased the basal spacing of the modified ZP after the exchange [8–10]. Taken together, these data indicated that ZPCu had been formed successfully. The XRD pattern of the ZPCu catalyst after the 7th run showed that the basal spacing of ZP was about 8.5 Å, which was only a little larger than that of the fresh ZPCu catalyst. This increase may have occurred because of the presence of less Cu²⁺ on the surface of ZP, and an increase in the number of water molecules between the layers following the seventh run (i.e., Cu²⁺ ions may have been washed off during the regeneration of the catalyst, section 2.3 and Table 1).

Figure 3 shows the N₂ adsorption-desorption isotherm of ZPCu, as a representative example, in the relative pressure range (*p*/*p*₀) of 0.1–1.0. The surface area of ZPCu was determined to be 93.1 m²/g.

The isotherm for ZPCu shows three adsorption stages. The first of these stages was observed at *p*/*p*₀ < 0.47, whereas the second stage was observed in the range of 0.47 < *p*/*p*₀ < 0.93, and the third stage was observed at higher relative pressures (*p*/*p*₀ > 0.93). The N₂ adsorption-desorption isotherm of ZPCu exhibited a typical “type IV” isotherm shape with a distinct hysteresis loop, which is characteristic of a mesoporous mate-

Fig. 2. XRD patterns of powdered ZP, fresh ZPCu, and ZPCu after the 7th run.

Fig. 3. N_2 adsorption-desorption isotherm of ZPCu.

rial [61]. 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 ZPCu catalyst. The observed increase in adsorption at the higher p/p_0 value indicated the presence of larger mesopores in the sample [10]. The surface area of ZPCu after the 7th run was found to be $85.4 \text{ m}^2/\text{g}$.

The SEM image of ZP (Fig. 4(a)) revealed the presence of hexagonal plates with well-defined shapes and very smooth surfaces. Figure 4(b) and (c) show the SEM images of ZPCu. These images revealed that the structure of ZPCu was much less ordered than that of ZP, and that the ZPCu particles had aggregated to form both sheets and spheres of different shapes and sizes.

Figure 5 shows the TEM images of ZPCu. It shows that ZPCu catalyst retained the original morphology of ZP (layered structure) and that the particles were approximately 200 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 copper deposited on the surface of the ZP had agglomerated. Similar observations have also been reported for zinc and cerium with ZP [6,14]. Figures 4(d) and 5(d) show the SEM and TEM images of the catalyst following its 7th run, respectively. Both of 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.

Fig. 4. SEM images showing the regular morphology of ZP (a), fresh ZPCu (b, c), and ZPCu after the 7th run (d).

Fig. 5. TEM images showing the regular morphology of freshly prepared ZPCu (a–c) and the same material after its 7th run (d).

3.2. Catalytic activity of ZPCu towards the acetylation of phenols and its expected mechanism

The conversion of phenol (1 mmol) to phenyl acetate was selected as a model reaction to optimize the conditions, and the reaction was conducted in the presence of ZPCu (2 mol %) and AA (2 mmol) in various solvents, as well as being investigated under solvent-free conditions. As shown in Table 2, the use of ZPCu as a catalyst under solvent-free conditions provided higher yields and shorter reaction times than those achieved under conventional conditions.

With the optimized conditions in hand, we proceeded to evaluate the scope and generality of the method using various alcohols and phenols (Table 3). Pleasingly, the hydroxyl groups of the all of different alcohol and phenols tested were converted to the corresponding acetates in good yields and short reaction times using 3 or 4 equivalents of AA (Table 3, entries 8–10, 20). Furthermore, the products were readily isolated from the reaction mixtures by a simple filtration followed by a standard work-up procedure. Phenols reacted smoothly under the optimized conditions (Table 3, entries 1–15), with the corresponding acetates being formed in yields of 80%–95%. Furthermore, no by-products (such as those resulting from a Fries rearrangement) were observed with the substituted phenols. The presence of electron-donating substituents (i.e., $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{OH}$) on the phenol ring led to a significant increases in the rate of the acetylation reaction (Table 3, entries 2–10), with shorter reaction times being observed in these cases. On contrast, the

Table 2

Conversion of phenol to phenylacetate in different solvents and under solvent-free conditions in the presence of ZPCu (2 mol%).

Entry	Solvent ^a	Yield ^b (%)	Time (min)
1	Dichloromethane	Trace	120
2	Diethylether	Trace	120
3	Acetonitrile	Trace	120
4	Cyclohexane	51	90
5	Solvent-free	91	30

^a The reaction was carried out in 5 ml of solvent under reflux conditions.

^b The yields refer to isolated pure product.

Table 3

Acetylation of phenols with AA under solvent-free conditions in the presence of ZPCu.

Entry	Substrate	Product ^a	Time (min)	T (°C)	Substrate/AA molar ratio	Isolated yield (%)
1	C ₆ H ₅ OH	C ₆ H ₅ OAc	30	60	1:2	90
2	2-Me-C ₆ H ₄ OH	2-Me-C ₆ H ₄ OAc	30	60	1:2	92
3	4-Me-C ₆ H ₄ OH	4-Me-C ₆ H ₄ OAc	20	60	1:2	95
4	2,6-(Me) ₂ -C ₆ H ₃ OH	2,6-(Me) ₂ -C ₆ H ₃ OAc	45	60	1:2	87
5	2,4-(Me) ₂ -C ₆ H ₃ OH	2,4-(Me) ₂ -C ₆ H ₃ OAc	20	60	1:2	95
6	4-(CH ₃) ₃ C-C ₆ H ₄ OH	4-(CH ₃) ₃ C-C ₆ H ₄ OAc	20	60	1:2	94
7	4-MeO-C ₆ H ₄ OH	4-MeO-C ₆ H ₄ OAc	20	60	1:2	95
8	4-OH-C ₆ H ₄ OH	4-AcO-C ₆ H ₄ OAc	30	60	1:3	91
9	3-OH-C ₆ H ₄ OH	3-AcO-C ₆ H ₄ OAc	30	60	1:3	90
10	2,3-di-OH-C ₆ H ₃ OH	2,3-di-AcO-C ₆ H ₃ OAc	45	60	1:4	90
11	4-Cl-C ₆ H ₄ OH	4-Cl-C ₆ H ₄ OAc	90	80	1:3	83
12	4-Br-C ₆ H ₄ OH	4-Br-C ₆ H ₄ OAc	90	80	1:3	85
13	4-NO ₂ -C ₆ H ₄ OH	4-NO ₂ -C ₆ H ₄ OAc	90	80	1:3	80
14	2-OH-C ₆ H ₄ CO ₂ H	2-AcO-C ₆ H ₄ CO ₂ H	75	80	1:3	90
15	4-OH-C ₆ H ₄ CO ₂ H	4-AcO-C ₆ H ₄ CO ₂ H	60	80	1:3	92
16	2-Naphthol	2-Naphthyl acetate	30	60	1:2	91
17	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CH ₂ OAc	30	60	1:2	91
18	2-MeO-C ₆ H ₄ CH ₂ OH	2-MeO-C ₆ H ₄ CH ₂ OAc	30	60	1:2	93
19	4-MeO-C ₆ H ₄ CH ₂ OH	4-MeO-C ₆ H ₄ CH ₂ OAc	20	60	1:2	95
20	4-OH-C ₆ H ₄ CH ₂ OH	4-AcO-C ₆ H ₄ CH ₂ OAc	20	60	1:3	90
21	4-Cl-C ₆ H ₄ CH ₂ OH	4-Cl-C ₆ H ₄ CH ₂ OAc	30	60	1:2	86
22	4-NO ₂ -C ₆ H ₄ CH ₂ OH	4-NO ₂ -C ₆ H ₄ CH ₂ OAc	30	60	1:2	84
23	1-Hexanol	1-Hexyl acetate	20	60	1:2	94
24	Cyclohexanol	Cyclohexyl acetate	20	60	1:2	93
25	3-Methyl-1-butanol	3-Methylbutyl acetate	20	60	1:2	95
26	(CH ₃) ₃ C-OH	(CH ₃) ₃ C-OAc	45	60	1:2	89

^a All of the products were characterized by GC-MS, IR, and ¹H NMR analysis and a comparison of their data with those of the authentic samples or data reported in the literature.

presence of electron withdrawing groups (i.e., carboxyl, nitro, and halo groups) on the phenol ring led to a decrease in the rate of the acetylation reaction (Table 3, entries 11–15), with longer reaction times being observed. The optimized reaction conditions were also successfully applied to the acetylation of benzylic alcohols bearing an electron-withdrawing or electron-donating group without the formation of any by-products resulting from oxidation reactions (Table 3, entries 17–22). For deactivated aromatic rings (Table 3, entries 21 and 22), the acetylated products were obtained in much lower yields and required longer reaction times than the corresponding activated aromatic systems (Table 3, entries 18–20).

The reaction times required for the acetylation of the phenols were longer than those required for the benzylic alcohols. This difference in the reaction times was attributed to the low nucleophilicity of phenols compared to benzylic alcohols because of the delocalization of the lone pairs of electrons on the phenolic oxygen throughout the benzene ring [43,49,51]. To further extend the scope of the ZPCu catalyst, we also investigated the acetylation of several aliphatic alcohols, including 1-hexanol, cyclohexanol, 3-methyl-1-butanol, and *tert*-butanol, under the optimized conditions (Table 3, entries 23–26). The acetylation reactions of 1-hexanol cyclohexanol, 3-methyl-1-butanol proceeded much more rapidly than the acetylation of *tert*-butanol, most likely because of the steric hindrance provided by the *tert*-butyl group. A schematic representation of the

ZPCu-mediated acetylation process is shown in Scheme 3. To develop a deeper understanding of the role of the ZPCu catalyst in the acetylation reaction, we investigated the acetylation of phenol, 4-hydroxyphenol, and benzyl alcohol in the absence of the catalyst. As expected, no products were formed in any of these reactions, which demonstrated the importance of the catalyst to the acetylation process. All of the acetylated products formed in the current study were characterized by GC-MS, FT-IR (JASCO FT-IR 680 plus spectrophotometer; JASCO) and ¹H NMR (Bruker-Avance AQS 400 MHz spectrometer) analyses and a comparison of these data with those of standard samples or data from the literature [28,44,45,47–53].

Scheme 3. Schematic representation of the current ZPCu-mediated acetylation process.

The reusability of the ZPCu catalyst was investigated under the optimum reaction conditions for the acetylation of phenol, and the results are shown in Table 4. The elemental composition of the catalyst remained largely unchanged following its 7th run, although the amount of copper in the catalyst was reduced by almost 50% compared with the first run (Table 1). The recycled ZPCu catalyst gave a similar product yield to the freshly prepared catalyst up until the sixth cycle.

The catalytic efficiency of ZPCu was compared with several previously reported catalysts and protocols, and the results are shown in Table 5. Phenol was converted to acetylphenol in 90% yield following a reaction time of less than 30 min at 60 °C using the current protocol (Table 5, entry 16). Although some of the other catalysts performed well for the same reaction (Table 5, entries 2, 6, 10), they invariably required longer reaction times to reach completion (Table 5, entries 3, 6, 7, 9, 11, 13, 14) or required the use of a solvent (Table 5, entries 4, 6, 7, 9, 12). It is noteworthy that the more reactive acetyl chloride was required in one case, where it was used at room temperature (Table 5, entry 5). Furthermore, this reaction required a longer

Table 4

Reusability of the ZPCu catalyst under the optimum reaction conditions for the acetylation of phenol.

Run	Phenol conversion (%)
Fresh	90
1	90
2	88
3	87
4	87
5	85
6	81
7	72

Reaction conditions: phenol 1 mmol, Ac₂O 2 mmol, catalyst 2 mol%, 60 °C.

reaction time to reach afford a similar yield of the acetylated product to the current protocol. Some of the previously reported protocols used acetic acid as the acetylating agent, representing a much greener choice than acetyl chloride (Table 5, entries 4, 8, 15), although these reaction required long reaction times (3–15 h), high temperatures (70–110 °C) and a large excess of acid acetic in almost all cases. The acetylation of phe-

Table 5

Comparison of different protocols for the acylation of phenol and benzyl alcohol.

For entries 1–19				For entries 20–34			
Entry	Catalyst	T (°C)	Time (min)	Ac ₂ O (equiv.)	Yield (%)	Solvent	Ref.
1	ZPZn	60	45	2	89	—	[22]
2	B(C ₆ F ₅) ₃	RT	15	1.2	92	—	[30]
3	ZnCl ₂	RT	150	1	40	—	[32]
4	borate zirconia	110	840	5 ^a	10	toluene	[33]
5	ZnO	RT	60	1.2 ^b	90	—	[34]
6	Ce(OTf) ₃	RT	150	1.5	98	CH ₃ CN	[35]
7	SiO ₂ -ZnCl ₂	80	210	1.2	83	CH ₃ CN	[36]
8	H ₃ PW ₁₂ O ₄₀	70	180	5 ^a	3	—	[37]
9	DMAP·HCl	RT	600	1.1	99	toluene	[38]
10	Cu(BF ₄) ₂	RT	30	1	97	—	[39]
11	silica sulfamic acid	RT	180	3 ml ^c	—	—	[40]
12	[bmim][OTf]	50	10	2	97	[bmim][BF ₄]	[43]
13	[MMPA][HSO ₄]	RT	120	1.5	99	—	[44]
14	SBNPSA	RT	180	3 ml ^c	—	—	[46]
15	yttria-zirconia	110	900	5 ^a	77	—	[54]
16	ZPCu	60	30	2	90	—	this work
17	ZrOCl ₂ ·8H ₂ O	60	30	2	95	—	this work
18	ZP	60	30	2	70	—	this work
19	ZPZn	60	30	2	91	—	[22]
20	B(C ₆ F ₅) ₃	RT	2	1.2	98	—	[30]
21	ZnCl ₂	RT	180	1	63	—	[33]
22	borated zirconia	110	840	5 ^a	25	toluene	[34]
23	SiO ₂ -ZnCl ₂	80	180	1.2	90	CH ₃ CN	[36]
24	silica sulfamic acid	RT	15	3 ml ^c	93	—	[40]
25	Cp ₂ ZrCl ₂	RT	600	1	93	—	[41]
26	[TMBSA][HSO ₄]	RT	120	1.1	99	—	[42]
27	[MMPA][HSO ₄]	RT	120	1.1	99	—	[44]
28	SaSA	Reflux	120	1.2	85	CH ₂ Cl ₂	[45]
29	SBNPSA	R T	45	3 ml ^c	91	—	[46]
30	yttria-zirconia	110	240	5 ^a	94	—	[54]
31	CoCl ₂	RT	240	2	98	—	[55]
32	ZPCu	60	30	2	91	—	this work
33	ZrOCl ₂ ·8H ₂ O	60	30	2	97	—	this work
34	ZP	60	30	2	75	—	this work

^a Acetic acid as the acetylating agent. ^b Acetyl chloride as the acetylating agent. ^c Ethyl formate as the acetylating agent. RT: room temperature.

nol was also investigated using $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and ZP under our optimized reaction conditions (Table 5, entries 17 and 18). $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ gave an excellent yield of the desired product, but was much more difficult to recover and reuse than the ZPCu catalyst. ZP gave a lower yield (70%) than ZPCu. The use of ZPZn as a catalyst, however, provided a similar result to that of ZPCu (Table 5, entry 1), with a 20 mol% loading of ZPZn providing the acetyl phenol product in 89% yield following a reaction time of 45 min [22]. Based on this comparison process, ZPCu was identified the best catalyst for this transformation in terms of the reaction time and the loading of the catalyst.

Benzyl alcohol was also acetylated under the optimized conditions to give the acetylated product in 91% yield following a reaction time of 30 min at 60 °C (Table 5, entry 32). This protocol was also compared with a variety of different previously reported procedures for the same transformation, and the results are shown in Table 5. When the reaction was conducted at room temperature in the presence of a different catalyst, it generally required longer reaction times to reach completion (Table 5 entries 21, 25–27, 31). The use of ZPZn, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ or ZPas a catalyst under the optimized conditions provided the desired product in yields of 91%, 97%, and 75%, respectively (Table 5, entries 19, 33, 34). However, large excesses of the catalyst were required in all three of these cases, and significant difficulties were encountered during the recovery of these catalysts. These reactions also resulted in lower yields of the product. There were, however, some benefits to using these catalysts, in that they used acid acetic as an acetylating agent instead AA, but they all required longer reaction times, higher temperatures and a large excess of acid acetic to reach completion (Table 5, entries 22 and 30).

^1H NMR and FT-IR spectral data of the selected compounds from Table 3 are as follows.

$\text{C}_6\text{H}_5\text{OAc}$ (Table 3, entry 1). ^1H NMR (400 MHz, CDCl_3): δ = 7.2 (t, J = 7.9 Hz, 2H), 7.1 (t, J = 7.5 Hz, 1H), 7.0 (t, J = 7.9 Hz, 2H), 2.3 (s, 3H); IR (KBr): 3055, 2915, 1753, 1581, 1485, 1364, 1179, 1014, 916, 876, 804, 739, 675 cm^{-1} .

4-Me- $\text{C}_6\text{H}_4\text{OAc}$ (Table 3, entry 3). ^1H NMR (400 MHz, CDCl_3): δ = 7.04 (d, J = 7.9 Hz, 2H), 6.82 (d, J = 7.9 Hz, 2H), 2.35 (s, 3H), 2.27 (s, 3H); IR (KBr): 3045, 2936, 1773, 1608, 1515, 1442, 1378, 1207, 1187, 1173, 1014, 947, 915, 832, 816 cm^{-1} .

4-(CH_3) $_3\text{C-C}_6\text{H}_4\text{OAc}$ (Table 3, entry 6). ^1H NMR (400 MHz, CDCl_3): δ = 7.37 (d, J = 8.25 Hz, 2H), 7.18 (d, J = 8.25 Hz, 2H), 2.27 (s, 3H), 1.24 (s, 9H); IR (KBr): 3052, 2971, 2918, 1759, 1600, 1517, 1448, 1373, 1279, 1211, 1116, 1026, 924, 841, 686 cm^{-1} .

4-Cl- $\text{C}_6\text{H}_4\text{OAc}$ (Table 3, entry 9). ^1H NMR (400 MHz, CDCl_3): δ = 7.43 (d, J = 8.4 Hz, 2H), 6.75 (d, J = 8.4 Hz, 2H), 2.24 (s, 3H); IR (KBr): 3075, 2939, 1765, 1641, 1591, 1488, 1370, 1200, 1163, 1014, 941, 845, 798, 720 cm^{-1} .

2-AcO- $\text{C}_6\text{H}_4\text{CO}_2\text{H}$ (Table 3, entry 12). ^1H NMR (400 MHz, CDCl_3): δ = 10.4 (s, 1H), 7.95–7.12 (m, 4H), 2.35 (s, 3H); IR (KBr): 3426–2996, 2872, 1752, 1687, 1607, 1458, 1306, 1188, 917, 753, 706 cm^{-1} .

4-MeO- $\text{C}_6\text{H}_4\text{CH}_2\text{OAc}$ (Table 3, entry 17). ^1H NMR (400 MHz, CDCl_3): δ = 7.15 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 8.5 Hz, 2H), 5.0 (s, 2H), 3.65 (s, 3H), 2.2 (s, 3H); IR (KBr): 3011, 2943, 2826, 1729,

1613, 1518, 1460, 1363, 1243, 1176, 1120, 1031, 960, 823 cm^{-1} .

3-Methylbutyl acetate (Table 3, entry 23). ^1H NMR (400 MHz, CDCl_3): δ = 4.18 (t, J = 6.6 Hz, 2H), 2.1 (s, 3H), 1.58–1.67 (m, 1H), 1.43–1.5 (m, 2H), 0.96 (d, J = 3.4, 6H); IR (KBr): 2962, 2935, 1743, 1465, 1430, 1249, 1172, 1136, 1065, 962, 857 cm^{-1} .

4. Conclusions

ZPCu is an inexpensive, noncorrosive, and environmentally benign catalyst that can be readily prepared from simple starting materials. This catalyst was characterized using various analytical methods and the results were in agreement with those reported previously in the literature. In this study, we have developed a simple and efficient procedure for the acetylation of a variety of different alcohols in good yields over short reaction times. There are several notable advantages to this methodology, including a broad substrate scope, the use of AA as an acetylating agent, excellent product yields and easy work-up procedure resulting from the heterogeneous conditions.

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Graphical Abstract

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Acetylation of alcohols and phenols under solvent-free conditions using copper zirconium phosphate

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Copper zirconium phosphate was prepared and used as an efficient and reusable nanocatalyst for the acetylation of alcohols with fair yields. The method conforms to several of the guiding principles of green chemistry.

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