

ZINC OXIDE - SINTERED CALCIUM PHOSPHATE CATALYZED GREEN SYNTHESIS OF ESTERS AND AMIDES

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Abstract: Herein, the application of zinc oxide supported on sintered calcium phosphate (SCaP) as a catalyst in acylation reaction is described. This catalyst was found to be highly effective in solvent free acylation of various phenols, alcohols and amines. Reaction at room temperature, with very less quantity of the catalyst, high yield in shorter reaction time, easy separation of the catalyst and isolation of the desired product in good purity are the merits of this reaction. In addition, the recovered catalyst could be reused for four successive runs without significant deterioration in catalytic activity.

Keywords: *acylation, alcohols, amines, calcium phosphate, catalyst, phenols, zinc oxide*

INTRODUCTION

Organic esters and amides are important and attractive molecules possessing medicinal [1, 2] and synthetic importance [3, 4] due to their wide applications. Acylation reactions employed for the synthesis of esters and amides under basic or acidic conditions generally involve anhydride / acid chloride as the acylating agent [5 – 13]. Lewis acid catalyzed Friedel-Crafts acylation, especially for the acylation of alcohols, phenols, amines and amino acids with acyl chlorides [9] though extensively studied, still receives good attention [14 – 16]. As chemical reactions that are economically viable and free from toxic waste and by products is much needed for a safe environment, there is a continuous urge on evolving ecofriendly acylation methods. In this context, solvent-free organic synthesis [17] and microwave assisted Friedel-Crafts acylation, [18 – 20] draw wide attention owing to their experimental simplicity and effectiveness. Reports on acylation through cross dehydrogenative coupling with or without metal catalysts [21, 22] and on acylation involving catalysts such as zeolite [23], clays [24], MgCl_2 [25], LiClO_4 [26] $\text{Mg}(\text{ClO}_4)_2$ [27], Boron catalyst [28, 29], InCl_3 [30], ZrCl_4 [31], $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ [13], RuCl_3 [32], alumina [33], DMAP [34], AgOTf [35], $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [36], CoCl_2 [37] and TaCl_5 [38] indicates a positive move towards eco-friendly approach. It is remarkable to mention here that generally, reactions on the solid surfaces [39, 8] or catalyst particles dispersed on organic [10] / inorganic support materials (silica, alumina, zeolites, clay, etc.) where there is no significant interaction between the catalyst and the support, are highly useful in organic synthesis. This is because, reactions involving the supported catalysts require lesser quantity of the catalyst, shorter reaction time and at the same time results in high yield of the product [40, 20]. Though zinc oxide mediated acylation has been well studied, reports on supported zinc oxide catalysts are very less. In continuation of our work on acylation reactions using zinc oxide supported on alumina [40], we wished to study the effect of sintered calcium phosphate (SCaP) as catalyst support. SCaP, being quite acidic compared to alumina, a higher catalytic activity of zinc oxide was expected. Hence, we investigated the hitherto unreported, catalytic activity of supported zinc oxide [ZnO/SCaP] for the acetylation and benzoylation of alcohols, phenols and amines.

MATERIALS AND METHODS

All the chemicals used in this study such as zinc nitrate, ammonia, calcium carbonate, ortho phosphoric acid, fly ash, starch, quartz, phenols, alcohols and amines were indigenous materials, purchased from local suppliers and used as such. The solvents and reagents such as benzoyl chloride and acetyl chloride were of laboratory grade / synthesis grade and they were used without any purification unless otherwise required. Progress of the reactions was monitored by using Thin Layer Chromatography using Aluminium TLC plate, silica gel coated with fluorescent indicator F254. 10 % Ethyl acetate-hexane mixture for esters and 50 % ethyl acetate-hexane mixture for amides were employed as eluent. Melting points reported for the compounds are uncorrected. All the products synthesized in this work are well-known compounds and reported in literature. Hence, ^1H NMR spectra for selected samples were recorded on a Jeol FX200

spectrometer using TMS as internal standard and CDCl_3 as solvent. ZnO/SCaP was prepared in two-steps as shown below by the procedure reported in literature [41, 42].

(I) Preparation of sintered calcium phosphate (SCaP)

To 50 grams of calcium carbonate (99 % precipitated) taken in a 2 L beaker, 1 L of distilled water was added and stirred using a mechanical stirrer. To this, 105 grams of ortho phosphoric acid was added slowly in drops to form a fine paste. After completion of addition, stirring was continued for 30 minutes. The white pasty mass was transferred to alumina crucible. Drying at 150 °C for 8 hours in hot air oven followed by calcination in muffle furnace at 750 °C for 30 mins afforded the white solid. This was ground into fine powder in a mortar and pestle and then sieved through 325 mesh. The sieved powder was used as support material for the catalyst ZnO [41].

(II) Preparation of ZnO ON SCaP (For 25 % ZnO)

To 200 mL of distilled water taken in a 1 L beaker, 7.5 grams of sintered calcium phosphate (SCaP) was added and stirred for 40 minutes. To this mixture, 9.166 grams of zinc nitrate hexahydrate was added and stirred for 30 minutes. Simultaneously, 4.2 mL of 25 % ammonia solution in 20 mL of distilled water was prepared. This solution was added dropwise in 45 minutes, to the above mixture containing zinc nitrate and sintered calcium phosphate. The pH was maintained between 8-9 and the contents were stirred for 1 hour. Then the stirring was stopped, and the contents were allowed to stand for 1 hour to enable the precipitate settle down. The precipitate was filtered under suction through Buchner funnel using Whatman No. 1 filter paper. The wet white solid mass obtained was dried in hot air over at 150 °C for 2 hours and calcined in muffle furnace at 400 °C for 30 minutes to get ZnO/SCaP (Yield 90 %). The catalyst, ZnO/SCaP calcined at 400 °C was analyzed by SEM, XRD and UV spectroscopy [42]. ZnO (25 % loading) on other support materials such as Fly ash, Starch, Quartz and sintered Calcium phosphate were also prepared using the above-mentioned procedure [42]. ZnO/Fly Ash, ZnO/Quartz and ZnO/SCaP were calcined at 400 °C whereas ZnO/Starch was calcined at temperatures below 300 °C.

Preliminary studies on catalytic activity

Benzoylation of phenol with benzoyl chloride was chosen as the standard reaction for the assessment of catalytic activity. In our initial studies, we observed that stirring of the mere reaction mixture for 8 hours / stirring of the reactants in presence of any of the support material did not lead to any fruitful reaction. Also, stirring of the reaction mixture for 1 hour in presence of 0.00123 moles (0.05 equiv) of ZnO/Fly ash, ZnO/Starch, ZnO/Quartz led to the formation of phenyl benzoate in 15-20 %. In benzoylation of phenol with benzoyl chloride in presence of nano ZnO/SCaP calcined at 400 °C, the completion of reaction was observed in 30 minutes. Reaction carried out in presence of unsupported ZnO under the above conditions, required a higher amount of the catalyst (0.0123 mol) for completion of reaction. This clearly demonstrated the effective role of SCaP as a support and in improving the catalytic efficiency of ZnO. Our further studies were aimed at determining the quantity of ZnO loading on the SCaP

support, required for optimum conversion under solvent free conditions. In this connection, the catalyst, nano ZnO/SCaP containing ZnO in various proportions (5 %, 10 %, 15 %, 25 %) were prepared by chemical method reported earlier [42] and all were calcined at 400 °C. Further, to decide on the influence of calcination temperature on the reaction yield, we again, prepared nano ZnO/SCaP containing 25 % ZnO and calcined at 400 °C and 750 °C. In the trial runs on benzylation of phenol performed with nano ZnO/SCaP with varying ZnO contents and different levels of calcination, we observed that the supported catalyst containing 25 % ZnO and calcined at 400 °C led to efficient conversion. This catalyst labelled as ZnO/ SCaP (400) was characterized by SEM, XRD and UV spectroscopy and it has an average pore diameter of 20 - 30 nm [42].

RESULTS AND DISCUSSION

In the optimization studies on catalyst quantity, it was observed that for the benzylation of phenol with benzoyl chloride, 0.01 equivalents of ZnO/SCaP (400), was sufficient to give maximum yield of the product. The general procedure employed for the first cycle of ZnO/SCaP catalysed acylation is illustrated below. Phenol (2.4 g, 0.0255 mol) is placed in 100 mL round bottomed flask and benzoyl chloride (3.6 g, 0.0256 mol) was added drop-wise and the contents were stirred at room temperature using a mechanical stirrer. To this reaction mixture, ZnO/SCaP (20 mg, 0.00025 mol) was added in lots with continuous stirring. TLC analysis (10 % Ethyl acetate -Hexane) indicated completion of the reaction in 30 minutes. The reaction mixture, was diluted with CH₂Cl₂ (20 mL) and filtered to recover the catalyst. (This recovered catalyst for used for further studies on recycle and reuse). Then, CH₂Cl₂ solution was washed with 10 mL of 10 % aqueous sodium hydroxide to remove any unreacted phenol and dried over anhydrous sodium sulphate. The solvent was evaporated to isolate the crude product, phenyl benzoate as a white solid (4.8 g, 95 % yield, m.p. 68-69 °C; lit. m. p. 68-70 °C). The crude product was pure by TLC and it was recrystallized from ethanol. The ¹H NMR spectrum showed the signals corresponding to phenyl benzoate protons. ¹H NMR (300MHz, CDCl₃): δ: 8.19-8.22 (m, 2H, aromatic), 7.61-7.65 (m, 1H, aromatic), 7.48-7.53 (m, 2H, aromatic), 7.40-7.46 (m, 2H, aromatic), 7.20-7.29 (m, 3H, aromatic) [43].

The above-mentioned procedure was followed for the acylation of rest of the phenols, alcohols and amines with benzoyl chloride / acetyl chloride (Figure 1). All the esters and amides prepared as solids / liquids in this work are simple, known compounds, reported in literature [44]. The following discussion helps in understanding the significance of this method. Benzylation of phenol when performed in presence of 100 mg (0.00123 mol) of bulk ZnO / *unsupported* nano ZnO, afforded only 50% yield in 30 minutes. It is remarkable to mention here that in the earlier report [16], for acylation of one equivalent of phenol / alcohol / amine under solvent free conditions, one equivalent of unsupported zinc oxide was employed. Whereas, acetylation of phenol / alcohol / amine catalyzed by magnesium chloride (0.1 mol %) under solvent free conditions, though afforded a good yield of the product, the process has the limitation on the recovery and reuse of the catalyst [25]. In ZrOCl₂ catalyzed acylation of phenol / alcohol / amine, the recovery of the catalyst involved tedious process [13]. In our earlier work on the above reaction catalyzed by zinc oxide supported on alumina, 0.05

equivalents of the catalyst were required for 95 % conversion in 30 minutes and the catalyst could be reused only up to three times [40]. In our present study on the supported nano zinc oxide, only 0.01 equivalent of the catalyst was required for complete conversion of phenols / alcohols / amines to the corresponding esters/amides.

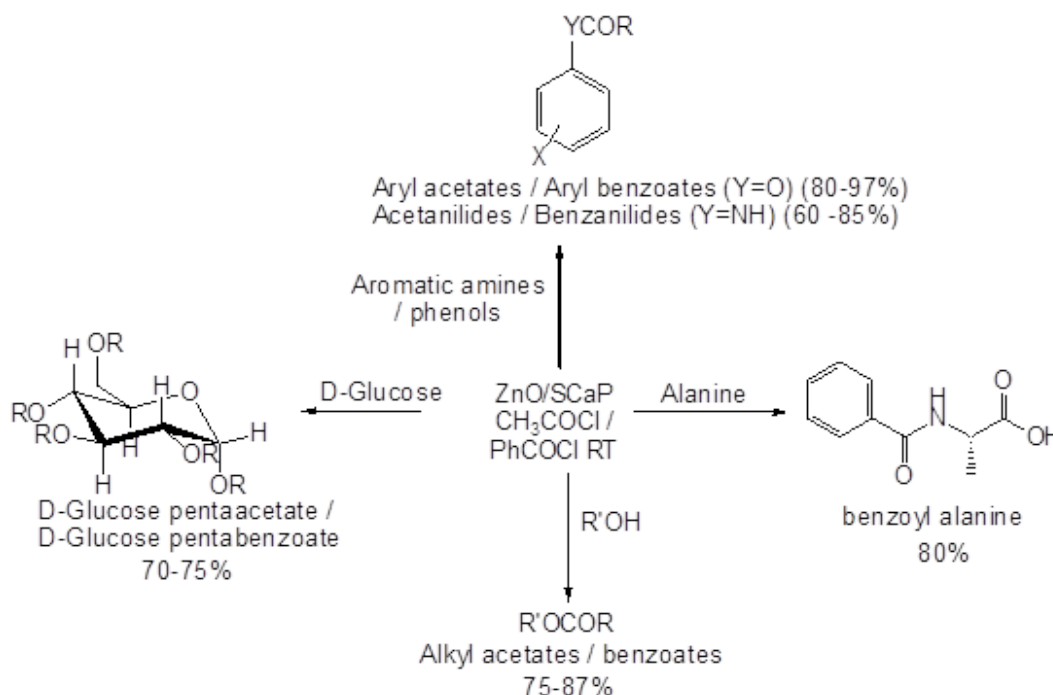


Figure 1. ZnO/SCaP in Green synthesis of Esters and Amides

Effect of solvent and reuse of catalyst

ZnO/SCaP (400) catalyst separated by filtration from the first cycle was washed with methylene chloride and dried at room temperature for 3 hours. It was observed that in the recycle studies on conversion of phenol to phenyl benzoate, the recovered catalyst, was active up to four runs and furnished the product in 89-95 % yield (Figure 2).

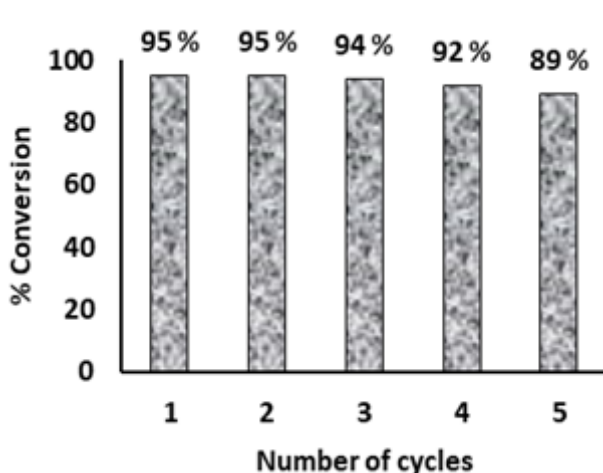


Figure 2. Recycling the catalyst and reaction yield

Subsequent use of the recovered catalyst, though was useful, resulted in reduced yield, and required a longer reaction time. The catalyst was also recovered in good quantity in each cycle (Figure 3).

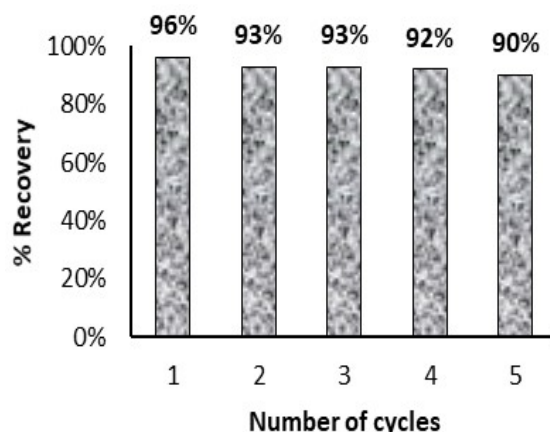


Figure 3. Recovery and recycling of catalyst

Table 1. Application of ZnO/SCaP (400) for the acylation of phenols

Entry	Substrate	Benzoates		Acetates	
		Time [min]	Yield [%]	Time [min]	Yield [%]
1.	Phenol	30	97	35	94
2.	4-Methylphenol	40	86	40	84
3.	4-Methoxyphenol	40	85	40	82
4.	4-Bromophenol	40	90	40	80
5.	4-chlorophenol	40	90	40	85
6.	2-Naphthol	40	90	40	85
7.	1,3-dihydroxybenzene *	45	85	45	80
8.	2-Nitrophenol	40	86	50	79
9.	4-Nitrophenol	50	80	45	83
10.	2-Hydroxybenzoic acid	50	80	60	82
11.	2,4,6-Trinitrophenol	120	88	90	85
12.	4-Hydroxy-3-methoxy benzaldehyde	50	80	50	75
13.	Methanol	30	85	30	80
14.	Ethanol	30	86	30	80
15.	1-Propanol	40	87	30	85
16.	2-Propanol	40	87	30	82
17.	2-Butanol	40	85	30	80
18.	t-Butyl alcohol	40	82	30	80
19.	Benzyl alcohol	20	86	30	85
20.	Allyl alcohol	30	85	40	80
21.	Cinnamyl alcohol	60	80	50	75
22.	α -D-Glucose**	80	75	90	70
23.	Phenol + Benzyl alcohol	20	86	-	-

* Dibenzoate and diacetate; **pentabenzate and pentaacetate

While the above reaction under solvent-free conditions afforded the product in excellent yield, benzoylation of phenol in solvent medium (THF, MDC, Toluene and Acetonitrile) in presence of ZnO/SCaP at room temperature, required longer reaction time (60 min - 120 min) and the product was obtained only in moderate yield (45-50 %). This might be probably due to the instability of benzoyl chloride associated with the deactivation of the catalyst. Based on these results, this catalyst was used for the solvent-free acylation reactions using acetyl chloride and benzoyl chloride, on other phenols and alcohols (Figure 1, Table 1) and amines (Figure 1, Table 2). Melting point of the esters of various substituted phenols obtained was compared with the authentic samples prepared by Schotten Baumann reaction.

Table 2. Application of ZnO/SCaP (400) for the acylation of amines

Entry	Substrate	N- (Alkyl / aryl) benzamide		N- (Alkyl / aryl) acetamide	
		Time [min]	Yield [%]	Time [min]	Yield [%]
1.	Methyl amine	30	80	40	82
2.	Butyl amine	30	85	35	60
3.	Diethyl amine	35	65	30	60
4.	Aniline	30	75	35	79
5.	4-Chloroaniline	40	80	40	75
6.	3-Methylaniline	40	70	45	74
7.	4-Methylaniline	40	80	45	82
8.	2,5-Dimethylaniline (p-Xylidine)	50	70	50	74
9.	2-Methoxyaniline	50	75	50	79
10.	3-Methoxyaniline	45	74	45	70
11.	2-Aminophenol	60	69	60	70
12.	4-Aminophenol	50	70	50	72
13.	4-Nitroaniline	40	80	45	84
14.	N-Methyl aniline	45	80	45	75
15.	N-Ethyl aniline	50	80	50	80
16.	Diphenyl amine	50	80	50	75
17.	Glycine	60	82	-	-
18.	L-alanine	60	80	-	-
19.	DL-alanine	90	79	-	-
20.	L-Tryptophan	60	76	-	-

Salient features of acylation of phenols / alcohols are as follows.

- The yield in benzoylation of phenols/alcohols is slightly higher than corresponding acetylation.
- Even with less nucleophilic phenols (entry 8-12), the benzoates and acetates are obtained in good yield.
- A comparison of the reaction time and reaction conversion for the unsupported zinc oxide catalyzed benzoylation of tert butyl alcohol (90 min; 67 %) and allyl

alcohol (15 min, 73 %) [16] with the present study, clearly demonstrate the catalytic efficiency of the supported zinc oxide.

- (iv) Among benzyl alcohol, allyl alcohol and cinnamyl alcohol, cinnamyl alcohol required a longer reaction time due to less nucleophilicity of the alcohol.*
- (v) In a mixture of phenol and benzyl alcohol, benzyl alcohol gets preferentially acylated and this is in accordance with the earlier report [16].*

Table 2 illustrates the details on ZnO/SCaP (400) catalyzed acylation of amines using acetyl chloride and benzoyl chloride. Comparing to the benzylation phenols and alcohols, the benzylation of amines in general, proceed slowly and also the yield of benzamides obtained are comparatively lower. Here, primary amines react faster than secondary amines. This catalyst is also helpful in the N-benzylation of alpha amino acids. With aminophenol, the reaction occurs at both the sites. The secondary amines are easily converted to the corresponding benzoates. We also found that this catalyst is effective in converting 1-adamantylamine to the corresponding benzoate in 76 % yield. It is important to note that benzamide derivatives are highly useful in treating CNS disorders [45].

CONCLUSIONS

Nano ZnO supported on sintered calcium phosphate is a highly active catalyst for the synthesis of esters (alkyl/aryl acetates and benzoates) and substituted amides (acetanilides and benzanilides) in good yields. The general application of the catalyst was demonstrated by benzylation of substituted phenols, amines, alcohols, α -D-glucose and amino acids. Phenols/amines with poor nucleophilicity react slowly. In acylation of a mixture containing phenol and alcohol, only alcohol is acylated. Secondary and tertiary alcohols under acylation conditions, readily furnish esters without any side products. This catalyst was also useful in the acylation of allyl alcohol and cinnamyl alcohol. The merits of this ZnO/SCaP catalyzed acylation reaction includes environmentally benign and safe protocol with a simple reaction set up, requirement of less quantity of the catalyst comparing to unsupported nano zinc oxide, reaction under solvent free conditions at room temperature with a shorter reaction time, high product yields and reusability of the catalyst. It is more likely that the above reaction might be possible on industrial scale using mechanochemical method.

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