



Synthetic Communications An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

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To cite this article: Zakaria Benzekri, Kamal El Mejdoub, Said Boukhris, Brahim Sallek, Brahim Lakhrissi & Abdelaziz Souizi (2016): Dicalcium Phosphate Dehydrate DCPD as a Highly Efficient and Reusable Catalyst for Knoevenagel Condensation, Synthetic Communications, DOI: 10.1080/00397911.2016.1142565

To link to this article: http://dx.doi.org/10.1080/00397911.2016.1142565



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Accepted author version posted online: 09 Feb 2016.



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Dicalcium phosphate dehydrate DCPD as a highly efficient and reusable catalyst for Knoevenagel condensation

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Supplemental data for this article can be accessed on the publisher's website.

Abstract

We have described the catalytic activities of dicalcium phosphate dihydrate (DCPD) in the condensation reaction of various substituted benzaldehydes with active methylene compound malononitrile. The influences of reaction conditions on the corresponding catalytic behavior have been investigated. The results showed that the DCPD exhibited high catalytic activity, versatility and it can be recycled without significant loss of its activity for the condensation reactions, that which accounts for the material as a promising new type of heterogeneous catalyst for the condensation reactions. Meanwhile, the catalytic results of DCPD compared favorably with those of other materials for Knoevenagel reactions reported previously.



KEYWORDS: Dicalcium phosphate dihydrate, Heterogeneous catalysis, Knoevenagel reaction, Room temperature

INTRODUCTION

The Knoevenagel condensation reaction is a useful transformation that has been widely employed for carbon–carbon bond formation in organic synthesis.^[1] In recent years, a wide array of catalysts, including Lewis acids,^[2] solid bases,^[3] ionic liquids,^[4] organometallic catalysts,^[5] Sevelamer^[6] and solid supported catalysts^[7,8] have been used to catalyze the Knoevenagel condensation reaction. However, most of these methods suffer from one disadvantage or another, such as using hazardous and carcinogenic solvents, high catalyst loading or non-recoverable catalysts that sometimes contain toxic metals. Therefore, there is a great need for new catalytic methods that do not have these problems. Functional phosphates catalysts have recently attracted significant attention for organic synthesis because of their ease of recovery, reuse, and simplified product isolation and purification. Using phosphates catalysts is an efficient way to achieve economically advantageous and environmentally friendly processes. . The Knoevenagel condensation is a powerful method to construct a carbon-carbon bond and has been widely used in the production of fine chemicals, such as cosmetics, drugs, and other substances.^[9-11] A wide range of catalysts have recently been used in the Knoevenagel condensation.^[12-28] but several disadvantages remain regarding to the use of these catalysts, such as difficulties in catalyst recovery and reuse, longer reaction time, or harsh reaction conditions. Therefore, the study of a catalyst for Knoevenagel condensation based on a functional phosphate catalyst is challenging.

The phosphate compound is an environmentally friendly solid material with excellent mechanical strength and stability. Several heterogeneous catalysts catalysts have been

reported for the Knoevenagel condensation reaction, but few of them are based on phosphate calcium catalyst. Herein, we would like to report our work on this dicalcium phosphate dihydrate (DCPD) to catalyze the Knoevenagel condensation reaction with high efficiency and excellent reusability. The catalyst can be easily recovered and still retains catalytic activity. The optimal reaction conditions were obtained after screening the catalyst loading, reaction time, solvent and temperature for the Knoevenagel condensation reaction between benzaldehyde and malononitrile.

RESULTS AND DISCUSSION

General Information For The Catalyst

Dicalcium phosphate dihydrate CaHPO₄, 2H₂O (**DCPD**) can be obtained in aqueous medium eitherby neutralization of phosphoric acid by calcium hydroxide,^[29] or by double decomposition of a calcium salt and a phosphate salt.^[30] The crystal structure of this compound has been described by Jones^[31] through the X-ray diffraction and by Curry^[32] using the neutron diffraction. DCPD crystallizes in the monoclinic system (space group: Ia); crystallographic parameters are: a = 5.812 Å, b = 15.180 Å, c = 6.239 Å and $\Box = 116$ 25.

A schematic representation of its structure is given in Figure 1. The structure of DCPD consists of corrugated sheets consist of Ca-PO₄-Ca-Ca-Ca-PO₄ chains oriented parallel. The crystals are in the form of platelets, and sometimes in the form of needles.^[33]

Dicalcium phosphate dihydrate (DCPD) was synthesized by double decomposition of calcium nitrate tetrahydrate and ammonium di-hydrogenophosphate. After 2 hours of maturation, the suspension was filtered, washed and freeze dried.

The appropriate physical methods which should be used to confirm the identity of the product are IR absorption spectroscopy, XRD, elemental analyses of calcium and phosphate concentrations, scanning electron microscopy, specific surface by BET. The infrared spectrum shows well-defined bands that can be easily identified from their wave number (Figure 2). It is analogous to that described by Berry et al.^[34] Note the presence of the bands due to the HPO4⁻² ions (875 to 1185 cm⁻¹) and high intensities of absorption bands due to the vibration of OH groups of water molecules (1645, 3155, 3280 cm⁻¹). The X-ray diffraction pattern is reported in Figure 3. The inter planar spacings and intensities of the main diffraction lines correspond to those reported on the ASTM card (JCPDS No. 11-293).^[35]

The Ca/P of DCPD synthesized, equals 1.00 ± 0.01 and has a very low specific surface area of 2 m²/g. Scanning electron microscopy shows that prepared sample is in the form of large platelets (Figure 4).

The Catalytic Activity Of DCPD In Knoevenagel Reaction

Initial studies were undertaken using benzaldehyde **1a** and malonitrile **2a** as a model reaction (Scheme 1). The reaction was performed at 25° C with different mass of catalyst. The best result of 96% yield was achieved by using 0.058 mmol (0.01 g) of the catalyst

after 1h (Table 1). Moreover, the blank experiment was also performed under identical reaction conditions, and it only gave the product in yield of 54% after 3 h. It was obvious that DCPD was the most effective catalyst among the tested catalysts.

The Effect Of Solvents

Based on the concept that catalysts phosphates can work in organic media, and they acquire remarkable properties such as enhanced stability, and altered substrate specificity, we investigated the effect of different solvents on the model reaction. We found that the catalytic activity of DCPD was remarkably influenced by solvents (Table 2).

The reaction in EtOH gave the best yield of 96% while the reactions in water and methanol provided the yields of 90% and 92% respectively. The other tested solvents including dioxane, acetonitrile and THF gave the low yields. Moreover, only 84% yield was obtained under solvent free conditions. The clear correlation between the solvent polarity and the DCPD activity was observed. This result may be attributed to specific interactions between the solvent and catalyst. Based on the results of solvent screen, EtOH was chosen as the optimum solvent for the DCPD catalyzed Knoevenagel condensation

The Effect Of Volune Of Ethanol

EtOH was selected to examine the effect of volume of the solvent (Table 3). The reaction in 3 mL EtOH at room temperature for 1h gave 96 % of **3a**. However, when the volume of ethanol was increased, the yield of **3a** begins to decline.

The Effect Of Time Reaction

EtOH was selected to examine the effect of time on the reaction (Table 4). The reaction in EtOH at room temperature for a short reaction time gave 75 % of **3a**. However, when the reaction time was increased, the yield of **3a** began to increase. Compound **3a** was obtained in 96 % yield at room temperature after 10 min of reaction.

The Effect Of Reaction Temperature

Temperature also plays an important role in DCPD catalyzed reactions, due to its effects on the reaction rate. Thus, a temperature screening was performed (Table 4). It was found that the activity of DCPD in Knoevenagel reaction could be increased by raising the temperature, and reached the best yield of 98% at refluxing after only 3 min. Based on the temperature screening, we chose the reflux, as the optimum temperature for the reaction.

Reusability Of The Catalyst

Finally, the recovery and reusability of the catalyst were examined. After the completion of a condensation reaction between benzaldehyde and malonitrile, the catalyst was recovered by simple filtration, and then washed with ethanol (2 x 10 mL) to remove any residue that had adhered on to the catalyst. The recycled catalyst was reused directly in the next cycle without any additional treatments. The efficiency of the recovered catalyst was measured again using the same model reaction. As shown in table 5, the reaction yield of 80% was achieved after seven cycles suggests that there is no loss of activity of

the catalyst in the process. To the best of our knowledge, the reusability of this catalyst is significantly better than most of the reported supported catalysts.

Generalization Of Knovenagel Reaction To Other Aldehydes

The DCPD was employed in the reaction, where the catalyst activity is mainly due to the structural basicity. In order to demonstrate the versatility of DCPD for Knoevenagel condensation, we submitted various substituted aldehydes and substrates containing active methylene groups with the molar ratio 1:1 under the optimum conditions (Table 6). Both electron-rich and electron-deficient aromatic aldehydes worked well and produced high product yields. Nonetheless, when the reactions were realized at reflux for 3 min, high yields were also achieved (Table 6, entries 12-14). All compounds were identified by comparison to reference samples.

Comparison With Other Reported System

Many synthetic methods have been developed to accomplish the Knoevenagel condensation reaction successfully.^[36] From Table 7, it is seen that present catalyst exhibited higher yields compared to the other reported system.^[37-49] Reactions conducted at room temperature, shorter reaction time were required for these reactions, who occurred in using the DCPD catalyst.

EXPERIMENTAL

General Procedure

A 10 mL round bottomed flask was charged with the carbonyl compound (1 mmol), active methylene compound (1 mmol), **DCPD** (0.01 g, 5.8 10^{-2} mmol) and ethanol (3 mL). The reaction mixture was stirred at room temperature for 10 min (or 3 min at reflux). Progress of the reaction was monitored by TLC, using *n*-hexane–EtOAc (5:1) as eluent. After completion of the reaction, 5 mL of water was added and the mixture was extracted three times with dichloromethane. The catalyst was removed by filtration and washed with ethanol-H₂O. The solid product was obtained after solvents were removed under vacuum. The product **3a** was purified through recrystallisation from ethanol.

The DCPD could be recycled after vaporizing water-ethanol. The recycled DCPD could be used repeatedly under the same reaction conditions.

The products prepared **3** are known compounds^[47,50,51] and were confirmed by comparing the IR, ¹H NMR, ¹³C NMR and mass spectral data with authentic samples reported in the literature.

CONCLUSIONS

In conclusion, DCPD was employed as a new and efficient catalyst for the Knoevenagel condensation of aromatic aldehydes with active methylene compounds in ethanol. Furthermore, the attractive features of this method are the green and mild reaction conditions, short reaction times, excellent yields, and operational simplicity. The catalyst can be recycled more than seven times without obvious loss of catalytic activity.

The easy preparation with a safe quality, economical and environmentally benign, the reusability, the selectivity and the efficiency of the heterogeneous catalyst DCPD provides great potential for its application in the synthetic organic. Thus, we believe that this simple and efficient procedure will be a practical method to cater for the needs of academia. In addition, the catalytic results of DCPD compared favorably with those of other materials for Knoevenagel reactions reported previously.

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Entry	mass DCPD (g)	Time	Yield (%) ^b
1	no catalyst	3h	54
2	0.01	1h	96
3	0.02	1h	92
4	0.03	1h	90
5	0.05	1h	86
6	0.075	1h	84
7	0.1	1h	80
8	0.2	1h	74

Table 1. Effect of mass catalyst DCPD on the reaction of **1a** with **2a**.^a

^a Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), EtOH (5 mL), r.t..

^b Isolated yield of the pure product.

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Entry	Solvent	Time	Yield (%) ^b
1	EtOH	1h	96
2	МеОН	1h	92
3	water	1h	90
4	dioxane	1h	70
5	acetonitrile	1h	68
6	THF	1h	80
7	chloroform	1h	74
8	dichloromethane	1h	74
9	solvent-free	1h	84

Table 2. The solvent effects on the reaction of **1a** with **2a** using DCPD catalyst.^a

^a Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), catalyst (0.058 mmol), solvent (5 mL),

r.t. for 1h.

^b Isolated yield of the pure product.

Table 3. The volume of ethanol effects on the reaction of **1a** with **2a** using DCPD catalyst.^a

Entry	Volume (mL)	Time (h)	Yield (%) ^b
1	solvent-free	1h	84
2	1	1h	85
3	3	1h	96
4	5	1h	96
5	7	1h	92
6	10	1h	90
7	15	1h	90

^a Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), catalyst (0.058 mmol), specified

volume of EtOH, r.t. for 1h.

^b Isolated yield of the pure product.

Entry	Time (min)	Temperature (°C)	Yield (%) ^b
1	3	r.t.	75
2	5	r.t.	90
3	7	r.t.	94
4	10	r.t.	96
5	20	r.t.	96
6	30	r.t.	96
7	60	r.t.	96
8	3	reflux	98
9	5	reflux	98
10	7	reflux	98
11	10	reflux	98
12	20	reflux	98

Table 4. Effect of reaction time and temperature on the reaction of **1a** with **2a** using DCPD catalyst.^a

^a Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), catalyst (0.058 mmol), solvent (3 mL),

specified temperature for specified time.

^b Isolated yield of the pure product.

Table 5 Reusability of the fiber catalyst in Knoevenagel condensation reaction between benzaldehyde and malonitrile.^a

Entry	No. of recycling runs	Yield (%) ^b
1	1	96
2	2	96
3	3	92
4	4	90
5	5	88
6	6	86
7	7	80

^a Conditions: 1a (1 mmol), 2a (1 mmol), catalyst (0.058 mmol), EtOH (3 mL), r.t. for 10

min.

^b Isolated yield of the pure product.

Entry	Product	Ar	Ε	Time (min)	Yield ^b	
1	3a	4-ClC ₆ H ₄	CN	10 (r.t.)	96	
2	3b	C ₆ H ₅	CN	10 (r.t.)	94	
3	3c	4-MeC ₆ H ₄	CN	10 (r.t.)	90	
4	3d	$4-NO_2C_6H_4$	CN	10 (r.t.)	96	
5	3e	4-ClC ₆ H ₄	CO ₂ Me	10 (r.t.)	84	S
6	3f	C ₆ H ₅	CO ₂ Me	10 (r.t.)	84	
7	3g	$4-NO_2C_6H_4$	CO ₂ Me	10 (r.t.)	90	
8	3h	4-ClC ₆ H ₄	CO ₂ Et	10 (r.t.)	84	
9	3i	C ₆ H ₅	CO ₂ Et	10 (r.t.)	80	
10	3ј	4-MeC ₆ H ₄	CO ₂ Et	10 (r.t.)	90	
11	3k	$4-NO_2C_6H_4$	CO ₂ Et	10 (r.t.)	94	
12	3a	4-ClC ₆ H ₄	CN	3 (reflux)	98	
13	3b	C ₆ H ₅	CN	3 (reflux)	95	
14	3d	$4-NO_2C_6H_4$	CN	3 (reflux)	98	
^a React	ion conditi	on: aromatic a	ldehyde (1 mmol), meth	yl or ethy	d cyanoacetate or

Table 6 The Knoevenagel condensation reactions between various aromatic aldehydes and ethyl or methyl cyanoacetate or malononitrile catalyzed by DCPD.

malononitrile (1 mmol) and catalyst (0.058 mmol) in ethanol (3 mL) at specified temperature for specified time.

^b Isolated yield of the pure product of the pure product.

Table 7. Comparison of catalytic activity of the DCPD catalyst in the Knoevenagel

condensation with other reported systems.

Catalyst	Reactions conditions	Yield	Ref. (%)
Amino-functionalized	1 mmol benzaldehyde, 1 mmol malononitrile, 20	90	[37]
mesoporous silica	mg catalyst, RT, 6 h, ethanol	\sim	
M3	4.61 mmol benzaldehyde, 5.24 mmol	93	[38]
	malononitrile, 0.0297 g catalyst, 100 °C, 6 h,		
	solvent free		
$HAP \square Fe_2O_3$	2 mmol benzaldehyde, 2 mmol malononitrile,	64	[39]
	0.025 g catalyst, 30 °C, 1 h, water		
Graphene oxide	1 mmol benzaldehyde, 2 mmol malononitrile,	97	[40]
	0.5 mL catalyst (1.5 mg/mL), RT, 4 h, solvent		
	free		
mp-PBI	1 mmol benzaldehyde, 1 mmol malononitrile, 50	100	[41]
	mg catalyst, RT, 20 h, acetonitrile		
DCPD	1 mmol benzaldehyde, 1 mmol malononitrile,	94	This
601	5.8 10 ⁻² mmol catalyst, RT, 10mn, EtOH		study
mpg-C ₃ N ₄ -tBu	1 mmol benzaldehyde, 1 mmol malononitrile, 50	67	[42]
	mg catalyst, 70 °C, 2 h, acetonitrile		
Sevelamer	1 mmol benzaldehyde, 1 mmol malononitrile,	91	[43]
	catalyst (20 mol%) in H_2O , RT, 30 mn		
Fe ₃ O ₄ @SiO ₂ @NH-NH ₂ -	1 mmol benzaldehyde, 1 mmol malononitrile,	93	[44]
PW	0.030g catalyst, H ₂ O, reflux, 12 min		

Na-A-PW ₉	1 mmol benzaldehyde, 1.5 mmol malononitrile,	98	[45]
	0.25 mol% catalyst, MeOH, RT, 6h		
MNPs-guanidine	1 mmol benzaldehyde, 1 mmol malononitrile,	96	[46]
	0.39 mol% catalyst, PEG/H ₂ O, RT, 150 min		
Polyguanidine PG-2	1 mmol benzaldehyde, 1 mmol malononitrile, 20	94	[47]
	mol% catalyst, H ₂ O, RT, 10 min	R	
[MMIm][MSO ₄]	67 mg benzaldehyde, 1.0 eq. malononitrile, 0.2	98	[48]
	eq. glycine, 1g ionic liquid RT, 70 min		
MMIm][MSO ₄]	0.61 mmol benzaldehyde, 0.61 mmol	99	[49]
	malononitrile, ionic liquid + $H_2O(2.16\%)$ RT, 2		
	min		

indo malononitrile, min

Scheme 1. The Knoevenagel condensation reaction between 4-chlorobenzaldehyde and malononitrile



Scheme 2. The Knoevenagel condensation reactions between aromatic aldehydes and ethyl or methyl cyanoacetate or malononitrile.



P1 P2 $\sum_{i=1}^{n}$ \circ • Са 012 022 P

Figure 1. Schematic representation of the corrugated sheet in DCPD structure. The arrows show the direction of the Ca-PO₄ chains.









Figure 4. Scanning electron microscopy of DCPD synthesized

