



Research article

Improvement of the catalytic performance of hybrid nanocomposite based on phosphate-benzimidazole in Knoevenagel condensation

Zakaria Benzekri^{a,*}, Halima El Aaad^b, Sarra Sibous^a, Houda Serrar^a, Said Boukhris^a, Abdelkrim Chahine^b, Abdelaziz Souizi^a^a Laboratory of Organic Chemistry, Organometallic and Theoretical, Department of Chemistry, Faculty of Sciences, Ibn Tofail University, BO 133, 14000, Kenitra, Morocco^b Laboratory of Physico-Chemistry of Vitreous and Crystallized Materials (LPCVCM), Faculty of Science, Ibn Tofail University, BP 133, 14000 Kenitra, Morocco

ARTICLE INFO

Keywords:

Organic chemistry
Ecological conditions
MCl₂-NaPO₃
Hybrid nanocomposites
Phosphate
Heterogeneous catalytic

ABSTRACT

In this work, we have developed a simple and very effective experimental strategy for the reaction of Knoevenagel via the condensation of aromatic aldehydes substituted with active methylene compounds in the presence of hybrid nanocomposites xMCl₂-yNaPO₃ (MCl₂ = 2,2'-dibenzimidazolyl butane dichlorhydrates), under ecological conditions. The Phosphate-Benzimidazole hybrid nanocomposite as heterogeneous catalysts has demonstrated a high catalytic activity for the Knoevenagel condensation in ethanol as an ecological solvent. It has several advantages such as light reaction conditions, a simple and ecological working procedure. Meanwhile, xMCl₂-yNaPO₃ can be recovered by simple filtration and this catalytic system having an interesting lifetime (five cycles) with no decrease in activity.

1. Introduction

Morocco has more than half of the world's phosphate reserves and it is mainly the world's leading exporter. Indeed, Moroccan phosphate is exported to all destinations: Europe, Latin America and Asia [1]. Recently, hybrid phosphate materials have received considerable attention [2]. In the broad sense, hybrids phosphate combine the different properties of phosphate with those of the organic compound such as polymers and organic salts. Nowadays, hybrid materials are increasingly used in many modern technologies and nanotechnologies such as photocatalysis [3], biomedical [4], corrosion inhibition [5], photovoltaics [6] and especially in catalysis [7]. The Knoevenagel condensation reaction between carbonyl compounds (aldehyde or ketones) and active methylene compounds that contain two electron-withdrawing groups is very important organic reactions which have been frequently used for the production of fine chemicals and heterocyclic compounds of biological significance [8, 9]. It has been a subject of interest for the production of highly processed chemicals, such as coumarin derivatives [10, 11] fragrances [12] and UV filters in cosmetics [13]. Moreover, synthetic routes too many drugs and therapeutic substances involve production of a key intermediary via Knoevenagel condensation [14, 15, 16]. Furthermore, this reaction is used as a classic test reaction to examine the activity of new solid base catalysts. The protocol of the Knoevenagel condensation

reaction of aldehyde with malononitrile was reported using different catalysts such as diamine-functionalized meso polymers [17], amine functionalized, mesoporous zirconia [18], Mg-Al mixed oxide on hexagonal mesoporous silica [19], biguanide-functionalized meso-porous silica [20], acid-base bifunctional mesoporous MCM-41 silica [21], amine-functionalized super paramagnetic nanoparticles [22], chitosan hydrogel [23], acrylic resin immobilized lipase [24], organic-inorganic hybrid silica materials containing imidazolium and dihydroimidazolium salts [25], IRMOF-3 [26], ZIF-8 [27]. Al-KIT-6-NH₂ [28], Graphene oxide (GO) [29], Zeolitic imidazolate [30], graphene oxide with ethylenediamine [31], DCPD [32] and chitosan [33, 34, 35]. In this paper, the hybrid nanocomposite xMCl₂-yNaPO₃ were prepared with different molar ratios and studied as potential heterogeneous catalysts for the Knoevenagel condensation via the reaction of different aldehydes with active methylene in ethanol at room temperature.

2. Procedure

2.1. Used materials

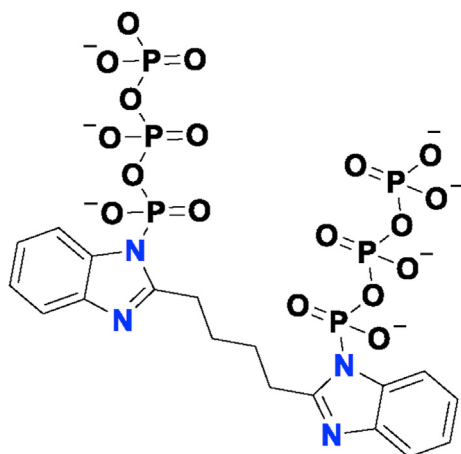
All chemicals of catalytic reaction were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported

* Corresponding author.

E-mail address: zakariachimist2014@hotmail.com (Z. Benzekri).

Table 1. Synthesis of hybrid nanocomposites $x\text{MCl}_2\text{-yNaPO}_3$.

Samples	Variables				
	(NaPO ₃)/(MCl ₂) molar ratios	NaPO ₃ (mol)	MCl ₂ (mol)	T (°C)	t (min)
MCl ₂	-	0	0.01	25	5
NaPO ₃ + MCl ₂ (R ₁)	1:1	0.01	0.01	25	6
NaPO ₃ + MCl ₂ (R ₂)	2:1	0.02	0.01	25	6
NaPO ₃ + MCl ₂ (R ₃)	3:1	0.03	0.01	25	6
NaPO ₃ + MCl ₂ (R ₄)	4:1	0.04	0.01	25	6
NaPO ₃ + MCl ₂ (R ₅)	5:1	0.05	0.01	25	6

**Figure 1.** Molecular structure of $x\text{MCl}_2\text{-yNaPO}_3$ hybrid nanocomposites catalysts [37].

in the literature. The thin-layer chromatography (TLC) using silica gel SIL G/UV 254 plates monitored progress of the reactions. Melting points were recorded on a KOFLER hot stage apparatus and are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 300-MHz spectrometer in DMSO-d₆.

2.2. The organic compound MCl₂

The 2,2'-dibenzimidazolyl butane dichlorhydrates (MCl₂) was synthesized and characterized according to procedure reported in many literatures [36]. This compound is used as an organic source for the synthesis of $x\text{MCl}_2\text{-yNaPO}_3$ hybrid nanocomposites.

The 2,2'-dibenzimidazolyl butane dichlorhydrates: Blue solid, Yield: 83 %, FT-IR (KBr pellet, cm⁻¹): 3330 (N-H), 3085 ((=C-H)Ar), 1628 (C=N), 1563 (N-H₂), 1512 (C=C), 1459 (CH₂/Met), 750 ((=C-H) Ar) cm⁻¹. Raman (cm⁻¹): 3080 (N-H), 2740 (NH₂⁺Cl⁻), 1629 (C=N), 1512 (C=C/Ar), 1450 (CH₂/Met), 750 ((=C-H)Ar) cm⁻¹. The ¹H NMR (300 MHz, D₂O, ppm): 1.9 (q,4H), 3.1 (t,3H), 7.43–7.56 (m,8H) ppm. The ¹³C NMR (100 MHz, D₂O, ppm): 25.56, 113.45, 125.98, 130.38, and 153.05 ppm. ESI-MS: [M + H]⁺, 291 g/mol, [M-H]⁺, 289 g/mol.

2.3. Development of $x\text{MCl}_2\text{-yNaPO}_3$ hybrid nanocomposites catalysts

The $x\text{MCl}_2\text{-yNaPO}_3$ hybrid nanocomposites were prepared by soft chemistry route under ambient conditions. The synthesis was done by ion exchange process between the benzimidazole derivative cations and the sodium metaphosphates anions. To study the morphological and structural properties of hybrid materials, five molar ratios have been synthesized, by changing the phosphate content (Table 1).

The preparation of hybrid materials is realized by ion exchanges between MCl₂ cations and NaPO₃ anions. The molecular structure of $x\text{MCl}_2\text{-yNaPO}_3$

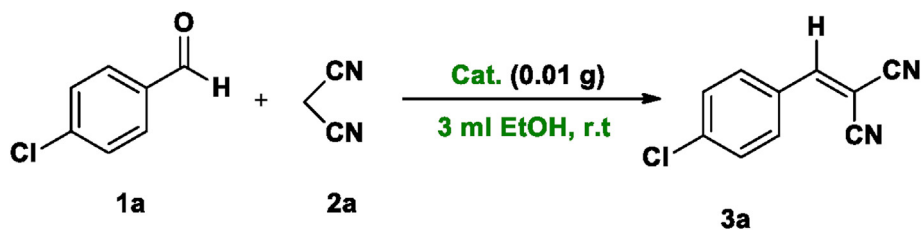
Table 2. Optimization of the reaction conditions.^a

Entry	Catalyst	Amount (g)	Solvent (3 ml)	Time (min)	Yield ^b (%)
1	-	-	EtOH	180	54
2	MCl ₂ ^c	0.01	EtOH	-	-
3	R ₁ (1MCl ₂ -1NaPO ₃)	0.01	EtOH	10	74
4	R ₂ (1MCl ₂ -2NaPO ₃)	0.01	EtOH	4	90
5	R ₃ (1MCl ₂ -3NaPO ₃)	0.01	EtOH	6	91
6	R ₄ (1MCl ₂ -4NaPO ₃)	0.01	EtOH	6	91
7	R ₅ (1MCl ₂ -5NaPO ₃)	0.01	EtOH	10	83
8	R ₂ (1MCl ₂ -2NaPO ₃)	0.01	MeOH	3	90
9	R ₂ (1MCl ₂ -2NaPO ₃)	0.01	CH ₃ CN	15	70
10	R ₂ (1MCl ₂ -2NaPO ₃)	0.01	THF	10	81
11	R ₂ (1MCl ₂ -2NaPO ₃)	0.001	EtOH	10	77
12	R ₂ (1MCl ₂ -2NaPO ₃)	0.002	EtOH	7	81
13	R ₂ (1MCl ₂ -2NaPO ₃)	0.003	EtOH	7	83
14	R ₂ (1MCl ₂ -2NaPO ₃)	0.004	EtOH	7	90
15	R ₂ (1MCl ₂ -2NaPO ₃)	0.005	EtOH	5	92
16	R ₂ (1MCl ₂ -2NaPO ₃)	0.006	EtOH	3	95
17	R ₂ (1MCl ₂ -2NaPO ₃)	0.007	EtOH	3	93
18	R ₂ (1MCl ₂ -2NaPO ₃)	0.008	EtOH	3	93
19	R ₂ (1MCl ₂ -2NaPO ₃)	0.009	EtOH	3	91
20	R ₂ (1MCl ₂ -2NaPO ₃)	0.01	EtOH	3	91

^a Reaction conditions: p-chlorobenzaldehyde **1a** (1 mmol), malonitrile **2a** (1 mmol), catalyst, 3 ml solvent, at room temperature.

^b Isolated yield.

^c MCl₂ is soluble in solvent organic.



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

yNaPO₃ hybrid nanocomposites catalysts is given in Figure 1. The synthesized hybrid nanocomposites catalysts are characterized using various analyses such as: Fourier transform infrared (FTIR) (Figure S1-(a)) and Raman spectroscopy (Figure S1-(b)), the UV-visible spectroscopy (Figure S2), X-ray diffraction (XRD) (Figure S3), transmission electron microscope (TEM) and energy dispersive X-ray spectroscopy (EDX) (Figure S4), respectively [37]. According to the five molar ratios (R₁, R₂, R₃, R₄ and R₅) of the synthesized hybrid nanocomposites (xMCl₂-yNaPO₃), we have tested all these catalysts and we have chosen the best catalyst R₂ to study the optimal conditions for the Knoevenagel condensation. Then, we have generalized the optimal conditions for the other catalysts (R₁, R₃, R₄ and R₅).

The characterization data for the hybrids catalysts have been given in the supplemental information (Figure S1 - S4).

2.4. Typical procedure for the Knoevenagel reaction

The carbonyl compound (1 mmol), active methylene (1 mmol), R₂ (1MCl₂-2NaPO₃) heterogeneous catalyst (6 mg) and ethanol (3 mL) were mixed. The reaction mixture was stirred at room temperature for appropriate time (Table 2). The completion of the reaction was monitored by thin-layer chromatography (TLC) using n-hexane-EtOAc (5:1) as eluent. Then, the reaction mixture was diluted with 5 mL of hot ethanol and the catalyst was separated by simple filtration and the filtrate was evaporated. The products (3a-j) obtained is recrystallized from ethanol. The products prepared 3 are known compounds [32, 38, 39, 40] and were confirmed by comparing the ¹H and ¹³C NMR data with authentic samples reported in the literature.

2.5. The spectral data of product (3a-j)

2-(4-chlorophenylmethylene) malononitrile (3a):

Colorless solid, mp 158–159 °C; ¹H NMR (Figure S5) (300 MHz, DMSO-d₆, δ, ppm) 7.67 (d, 2H, J = 8.7 Hz), 7.92 (d, 2H, J = 8.7 Hz), 8.49 (s, 1H, C=CH). ¹³C NMR (Figure S6) (75 MHz, DMSO-d₆, δ, ppm) 160.5, 139.5, 132.5, 131.6, 130.1, 114.4, 113.4, 82.7.

Methyl-3-(4-chlorophenyl)-2-cyanoacrylate (3b):

White solid, mp 120–121 °C; ¹H NMR (Figure S7) (300 MHz, DMSO-d₆, δ, ppm) 3.84 (t, 3H, OCH₃), 7.65 (d, 2H, J = 8.4 Hz, ArH), 8.04 (d, 2H, J = 8.4 Hz, ArH), 8.38 (s, 1H, C=CH). ¹³C NMR (Figure S8) (75 MHz, DMSO-d₆, δ, ppm) 162.5, 154.2, 138.5, 132.5, 130.6, 129.9, 115.8, 103.4, 53.8.

Ethyl-3-(4-chlorophenyl)-2-cyanoacrylate (3c):

Colorless solid, mp 89–90 °C; ¹H NMR (Figure S9) (300 MHz, DMSO-d₆, δ, ppm) 1.28 (t, 3H, J = 7.2 Hz, CH₃), 4.29 (q, 2H, J = 7.2 Hz, CH₂), 7.61 (d, 2H, J = 8.7 Hz, ArH), 8.00 (d, 2H, J = 8.7 Hz, ArH), 8.33 (s, 1H, C=CH). ¹³C NMR (Figure S10) (75 MHz, DMSO-d₆, δ, ppm) 162.0, 154.0, 138.5, 132.8, 130.5, 129.8, 115.7, 103.5, 62.9, 14.3.

2-(phenylmethylene) malononitrile (3d):

Colorless solid, mp 80–81 °C; ¹H NMR (Figure S11) (300 MHz, DMSO-d₆, δ, ppm) 7.57–7.70 (m, 3H, ArH), 7.59 (d, 2H, J = 7.2 Hz, ArH), 8.50 (s, 1H, C=CH). ¹³C NMR (Figure S12) (75 MHz, DMSO-d₆, δ, ppm) 155.7, 134.8, 131.7, 131.6, 130.9, 129.9, 114.6, 113.5, 82.0.

Methyl-2-cyano-3-phenylacrylate (3e):

White solid, mp 84–85 °C; ¹H NMR (Figure S13) (300 MHz, DMSO-d₆, δ, ppm) 3.84 (t, 3H, CH₃), 7.54–7.65 (m, 3H, ArH), 8.03 (d, 2H, J = 8.4 Hz, ArH), 8.38 (s, 1H, C=CH). ¹³C NMR (Figure S14) (75 MHz, DMSO-d₆, δ, ppm) 162.8, 155.6, 133.9, 131.7, 131.6, 129.8, 115.0, 102.8, 53.8.

2-(p-tolylmethylene) malononitrile (3f):

White solid, mp 118–119 °C; ¹H NMR (Figure S15) (300 MHz, DMSO-d₆, δ, ppm) 2.37 (s, 3H), 7.38 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 8.39 (s, 1H, C=CH). ¹³C NMR (Figure S16) (75 MHz, DMSO-d₆, δ, ppm) 161.6, 146.1, 131.1, 130.5, 129.1, 114.8, 113.8, 80.3, 21.5.

Ethyl-2-cyano-3-p-tolylacrylate (3g):

White solid, mp 91–92 °C; ¹H NMR (Figure S17) (300 MHz, DMSO-d₆, δ, ppm) 1.31 (t, J = 7.2 Hz, 3H), 2.37 (s, 3H), 4.34 (q, J = 7.4 Hz, 2H), 7.79 (d, J = 7.7 Hz, 2H), 7.90 (d, J = 7.2 Hz, 2H), 8.05 (s, 1H). ¹³C NMR (Figure S18) (75 MHz, DMSO-d₆, δ, ppm) 163.0, 155.5, 144.9, 131.4, 130.4, 129.1, 116.2, 101.2, 63.1, 14.3, 21.3.

2-(4-nitrophenylmethylene) malononitrile (3h):

Yellow solid, mp 161–162 °C; ¹H NMR (Figure S19) (300 MHz, DMSO-d₆, δ, ppm) 8.11 (d, J = 8.7 Hz, 2H), 8.29 (d, J = 8.7 Hz, 2H), 8.67 (s, 1H, C=CH). ¹³C NMR (Figure S20) (75 MHz, DMSO-d₆, δ, ppm) 159.7, 150.1, 137.1, 131.9, 124.8, 114.0, 112.9, 82.4.

Methyl-2-cyano-3-(4-nitrophenyl) acrylate (3i):

Yellow solid, mp 172–173 °C; ¹H NMR (Figure S21) (300 MHz, DMSO-d₆, δ, ppm) 3.88 (s, 3H, CH₃), 8.19 (d, 2H, J = 7.1 Hz, ArH), 8.34 (d, 2H, J = 7.1 Hz, ArH), 8.48 (s, 1H, C=CH). ¹³C NMR (Figure S22) (75 MHz, DMSO-d₆, δ, ppm) 162.1, 153.1, 149.8, 137.6, 132.1, 131.0, 124.4, 115.1, 107.0, 53.9.

Ethyl-2-cyano-3-(4-nitrophenyl) acrylate (3j):

Yellow solid, mp 168–169 °C; ¹H NMR (Figure S23) (300 MHz, DMSO-d₆, δ, ppm) 1.28 (t, 3H, J = 7.2 Hz, CH₃), 4.29 (q, 2H, J = 7.2 Hz, CH₂), 7.62 (d, 2H, J = 8.4 Hz, ArH), 8.02 (d, 2H, J = 8.4 Hz, ArH), 8.30 (s, 1H, C=CH). ¹³C NMR (Figure S24) (75 MHz, DMSO-d₆, δ, ppm) 162.0, 154.0, 138.4, 132.8, 130.6, 129.9, 115.8, 103.6, 62.9, 14.4.

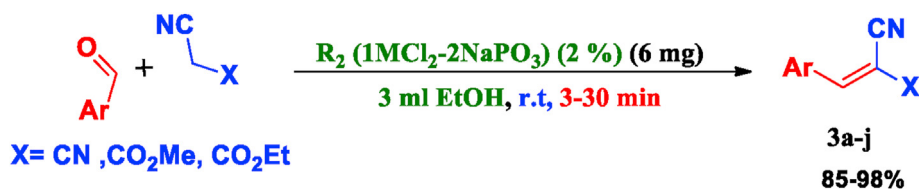
All the ¹H NMR and ¹³C NMR spectra of the products (3a-j) have been listed in the supplemental information (Figure S5 - S24).

3. Results and discussion

3.1. Catalytic studies

To quantify the catalytic performance of the catalyst R₂ (1MCl₂-2NaPO₃), a model reaction between p-chlorobenzaldehyde 1a and malononitrile 2a was carried out in 3 mL of ethanol at room temperature (Scheme 1). Initially, the model reaction was catalyzed by xMCl₂-yNaPO₃ nanocomposite hybrids catalysts with different molar ratios of phosphate: MCl₂, R₁, R₂, R₃, R₄ and R₅ (Table 1). The results are summarized in Table 2.

In the absence of catalyst, the reaction gave only 54 % yield of the product after 180 min (Table 2, entry 1). The best catalyst was R₂ (1MCl₂-2NaPO₃) because the product 2-(4-chlorobenzylidene) malononitrile 3a was obtained in 90 % yields within 4 min (Table 2, entry 4). So, the R₂ (1MCl₂-2NaPO₃) was selected as the catalyst for Knoevenagel condensation reaction and further studies were done using R₂ as a heterogeneous catalyst.



Scheme 2. The condensation reaction between aromatic aldehydes and ethylcyanoacetate or methyl cyanoacetate or malononitrile.

Table 3. The Knoevenagel condensation reactions of various aromatic aldehydes and ethylcyanoacetate or methylcyanoacetate or malononitrile catalyzed by R₂ (1MCl₂-2NaPO₃).

Entry	Ar	X	Time (min)	Yield ^a %	M.p (°C)	
					Found	Reported
3a	4-Cl	CN	3	95	158–159	159–160 [38]
3b	4-Cl	CO ₂ Me	10	90	120–121	120–121 [32]
3c	4-Cl	CO ₂ Et	10	91	89–90	89–90 [38]
3d	H	CN	20	89	80–81	80–81 [38]
3e	H	CO ₂ Me	25	85	84–85	83.9–85.4 [40]
3f	4-Me	CN	10	93	118–119	118–120 [39]
3g	4-Me	CO ₂ Et	30	90	91–92	90–91 [39]
3h	4-NO ₂	CN	3	98	161–162	160–161 [39]
3i	4-NO ₂	CO ₂ Me	15	93	172–173	172–173 [32]
3j	4-NO ₂	CO ₂ Et	25	96	168–169	168–169 [32]

^a Isolated yields.

Table 4. Comparison of the catalytic efficiency of R₂ (1MCl₂-2NaPO₃) with that of reported catalysts in the Knoevenagel condensation.

Entry	Catalyst	Conditions	Yield ^a % (Refs.)
1	Fe ₃ O ₄ MNPs-OSO ₃ H	10 mg, 3 ml H ₂ O, reflux, 10–145 min	80–97 [41]
2	Clay A, PC-A	100 mg, 3 ml EtOH/H ₂ O, 40 °C, 5–120 min	21–98 [42]
3	[MML-PDO][OAc]	10 mol%, 1 ml H ₂ O, r.t., 7–600 min	95–99 [43]
4	Na ₂ Ca(HPO ₄) ₂	6 mg, 3 ml EtOH, r.t., 10–65 min	82–97 [44]
5	DCPD	10 mg, 3 ml EtOH, r.t., 10 min	84–96 [32]
6	R ₂ (1MCl ₂ -2NaPO ₃)	6 mg, 3 ml EtOH, r.t., 3–30 min	85–98 (Present work)

^a Isolated yield.

Secondly, the role of solvent in the reaction was examined with 0.01 g of catalyst R₂ (1MCl₂-2NaPO₃). The reaction proceeded quickly in ethanol, methanol and protic solvents (Table 2, entries 4 and 8). In an aprotic solvent like: THF and CH₃CN, the reaction gave an average conversion (Table 2, entries 9 and 10). Indeed, the Ethanol was selected as the best solvent for this reaction. To examine the effect of the catalyst amount, the reaction between p-chlorobenzaldehyde 1a and malonitrile 2a in the presence of the catalyst R₂ (1MCl₂-2NaPO₃) was considered. The study proceeded by conducting the reaction by varying the molar ratios of nanocomposite hybrids catalysts. The results of the study is given in Table 2 (entries 11–20).

According to the results, we optimized the amount of catalyst for the Knoevenagel reaction and it was selected as 0.006 g of R₂ (1MCl₂-2NaPO₃) with respect to the substrates (Table 2, entry 16). Finally, the catalytic activity of the catalyst can be generalized comprehensively, by conducting the Knoevenagel reaction with a diverse set of substrates (Scheme 2). All the products were characterized by ¹H and ¹³C NMR spectroscopy and melting point determinations. The details are listed in Table 3. From these results, we can recommend the R₂ (1MCl₂-2NaPO₃) as a good heterogeneous catalyst for Knoevenagel reaction and it gave goods to excellent conversion for all the sets of substrates under consideration at short reaction times (3–30 min).

To show the efficiency and capability of the present protocol of our catalyst with some reported catalysts for the Knoevenagel reactions, summarized results in Table 4, we observed that R₂ (1MCl₂-2NaPO₃) is

an efficient catalyst with respect to the reaction time, a simple work-up protocol, the excellent yields of products and using green solvent.

3.2. Reusability studies of the catalyst

In addition, the reusability of the catalyst was also studied. Indeed, the catalyst can be removed from the reaction mixture by simple

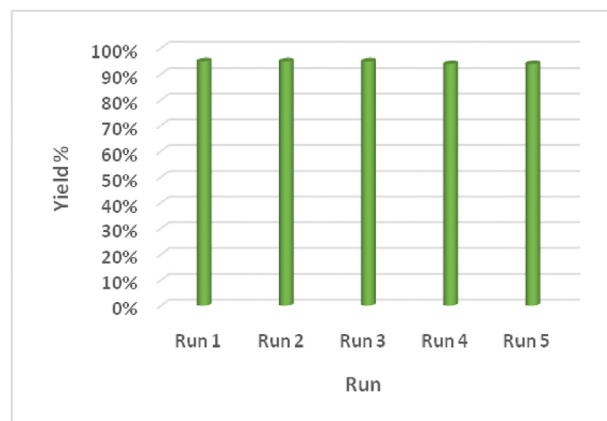
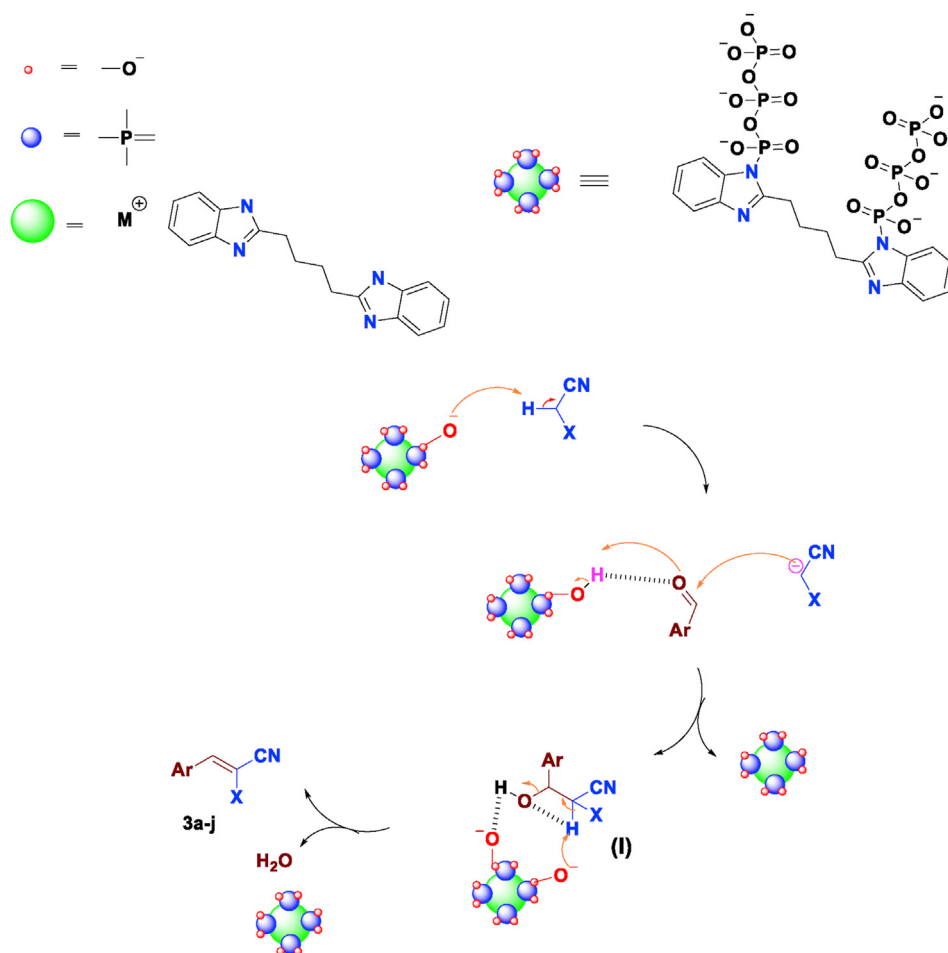


Figure 2. Recycling of R₂ (1MCl₂-2NaPO₃) in the preparation of 3a.



Scheme 3. Suggested transformation mechanism for the Knoevenagel condensation in the presence of R_2 ($1MCl_2 \cdot 2NaPO_3$).

filtration. It was washed thoroughly and dried. The reuse of the R_2 ($1MCl_2 \cdot 2NaPO_3$) as a heterogeneous catalyst for Knoevenagel reaction was studied by conducting the model reaction in the presence of recycled catalyst for five cycles. The results are given in Figure 2. It is clear that the recycled catalyst can be used for subsequent reactions without much loss of the catalytic activity. The catalyst has retained its form and characteristics after the completion of the reaction. Furthermore, it has all the advantages of solid phase catalysts as an operational simplicity, filterability, ability to regenerate and reuse. There was no considerable loss in the activity after recycling.

3.3. Mechanism for the Knoevenagel condensation transformation

In this context, we will present a suggestion of Knoevenagel condensation mechanism by using a new heterogeneous catalyst R_2 ($1MCl_2 \cdot 2NaPO_3$) in Scheme 3. The mechanism has already been planned [44]. First, a basic site removes a proton from the active methylene grouping of acidic nature, forming a carbanion. Then, a nucleophile attack occurs on the carbon atom of the carbonyl group of the aldehyde substituted that its oxygen is activated to give rise to an intermediate (I). Thus, turns into an alkene (3a-j) by dehydration.

4. Conclusion

In summary, we have demonstrated that the $MCl_2 \cdot NaPO_3$ hybrid nanocomposite is a new heterogeneous catalyst, very efficient and reusable for the Knoevenagel condensation. It would be perfectly suited to green chemistry, sustainability and environmental security. This procedure has several advantages such as excellent yields with very short

times and the catalyst can be recycled five times without any significant loss of its catalytic activity.

Declarations

Author contribution statement

Zakaria Benzekri: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

Halima El aadad: Performed the experiments; Wrote the paper.

Sarra Sibous, Houda Serrar: Analyzed and interpreted the data.

Said Boukhris: Contributed reagents, materials, analysis tools or data; Wrote the paper.

Abdelkrim Chahine, Abdelaziz Souizi: Contributed reagents, materials, analysis tools or data.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Competing interest statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at <https://doi.org/10.1016/j.heliyon.2020.e05293>.

Acknowledgements

The authors would like to thank the national center of scientific and technical research (CNRST) for the RMN analysis.

References

- [1] S. Maiza, Le commerce mondial des phosphates de 1973 à 1980, *Cah. Anal. Données* 9 (1984) 7–32.
- [2] T. Matsuura, T. Maruyama, Calcium phosphate-polymer hybrid microparticles having functionalized surfaces prepared by a coaxially electrospray technique, *Colloids Surf., A* 526 (2017) 64–69.
- [3] D. Zhang, T. Liu, C. An, H. Liu, Q. Wu, Preparation of vanadium-substituted polyoxometalate doped carbon nitride hybrid materials POM/g-C₃N₄ and their photocatalytic oxidation performance, *Mater. Lett.* 262 (2020) 126954.
- [4] A. Salama, Cellulose/calcium phosphate hybrids: new materials for biomedical and environmental applications, *Int. J. Biol. Macromol.* 127 (2019) 606–617.
- [5] L.R. Santos, C.E. Marino, I.C. Riegel-Vidotti, Silica/chitosan hybrid particles for smart release of the corrosion inhibitor benzotriazole, *Eur. Polym. J.* 115 (2019) 86–98.
- [6] M. Halaby Macary, Élaboration et caractérisation de matériaux hybrides "nanoparticules ZnO-cristaux liquides" pour applications aux cellules photovoltaïques, Littoral (2019, January).
- [7] (a) H. El aadad, Z. Benzekri, S. Boukhris, A. Chahine, Synthesis, characterization of polystyrene-phosphate films and their application as heterogeneous catalyst for Knoevenagel condensation in solvent-free conditions, *J. Chem. Sci.* 132 (2020) 87; (b) Z. Benzekri, S. Sibous, H. Serrar, A. Ouasri, S. Boukhris, R. Ghailane, A. Rhandour, A. Souizi, NH₃ (CH₂)₅NH3BiCl₅ as a new hybrid and efficient catalyst for the synthesis of 1-(benzothiazolylamino) methyl-2-naphthol derivatives under solvent-free conditions, *J. Mol. Struct.* 1202 (2020) 127308; (c) Z. Benzekri, S. Sibous, H. Serrar, S. Boukhris, A. Hassikou, R. Ghailane, A. Souizi, Efficient Synthesis of 1, 4-Dihydropyran [2, 3-c] pyrazoles Using Snail Shell as a Biodegradable and Reusable Catalyst, *Org. Prep. Proced. Int.* 51 (2019) 566–575; (d) Z. Benzekri, H. Serrar, S. Sibous, S. Boukhris, A. Ouasri, A. Rhandour, A. Souizi, Hybrid crystal NH₃ (CH₂)₄NH3SiF₆ as an efficient catalyst for the synthesis of benzoxazoles, benzimidazoles and benzothiazoles under solvent-free conditions, *Green Chem. Lett. Rev.* 9 (2016) 223–228.
- [8] A. Dhakshinamoorthy, M. Opanasenko, J. Čejka, H. Garcia, Metal organic frameworks as solid catalysts in condensation reactions of carbonyl groups, *Adv. Synth. Catal.* 355 (2013) 247–268.
- [9] D. Kühbeck, G. Saidulu, K.R. Reddy, D.D. Díaz, Critical assessment of the efficiency of chitosan biohydrogel beads as recyclable and heterogeneous organocatalyst for C–C bond formation, *Green Chem.* 14 (2012) 378–392.
- [10] A. Song, X. Wang, K.S. Lam, A convenient synthesis of coumarin-3-carboxylic acids via Knoevenagel condensation of Meldrum's acid with ortho-hydroxyaryl aldehydes or ketones, *Tetrahedron Lett.* 44 (2003) 1755–1758.
- [11] F. Bigi, L. Chesini, R. Maggi, G. Sartori, Montmorillonite KSF as an inorganic, water stable, and reusable catalyst for the Knoevenagel synthesis of coumarin-3-carboxylic acids, *J. Org. Chem.* 64 (1999) 1033–1035.
- [12] F. Flachsman, Fragrance compounds. U.S. PatentNo. 8575386B2, Duebendorf C.H.: United States Patent Application, 2013.
- [13] M. Hoshino, M. Sugiyama, A. Kawamata, H. Joukura, G. Imokawa, Naphtalen Methylene Malonic Diesters and UV Absorbers and Cosmetic Compositions Containing the Diesters, EU Pat. EP 663206A1, 1994.
- [14] U. Beutler, P.C. Fuenfschilling, A. Steinkemper, An improved manufacturing process for the antimalaria drug coartem. Part II, *Org. Process Res. Dev.* 11 (2007) 341–343.
- [15] C.A. Martínez, S. Hu, Y. Dumond, J. Tao, P. Kelleher, L. Tully, Development of a chemoenzymatic manufacturing process for pregabalin, *Org. Process Res. Dev.* 12 (2008) 392–398.
- [16] S.D. Walker, C.J. Borths, E. DiVirgilio, L. Huang, P. Liu, H. Morrison, K. Sugi, M. Tanaka, J.C.S. Woo, M.M. Faul, Development of a scalable synthesis of a GPR40 receptor agonist, *Org. Process Res. Dev.* 15 (2011) 570–580.
- [17] R. Xing, H. Wu, X. Li, Z. Zhao, Y. Liu, L. Chen, P. Wu, Mesopolymer solid base catalysts with variable basicity: preparation and catalytic properties, *J. Mater. Chem.* 19 (2009) 4004–4401.
- [18] K.M. Parida, S. Mallick, P.C. Sahoo, S.K. Rana, A facile method for synthesis of amine-functionalized mesoporous zirconia and its catalytic evaluation in Knoevenagel condensation, *Appl. Catal., A* 381 (2010) 226–232.
- [19] G.D. Yadav, P. Aduri, Aldol condensation of benzaldehyde with heptanal to jasminaldehyde over novel Mg–Al mixed oxide on hexagonal mesoporous silica, *J. Mol. Catal. Chem.* 355 (2012) 142–154.
- [20] A. Alizadeh, M.M. Khodaei, D. Kordestani, A.H. Fallah, M. Beygzadeh, The successful synthesis of biguanide-functionalized mesoporous silica catalysts: excellent reactivity combined with facile catalyst recyclability, *Microporous Mesoporous Mater.* 159 (2012) 9–16.
- [21] F. Shang, J. Sun, S. Wu, Y. Yang, Q. Kan, J. Guan, Direct synthesis of acid–base bifunctional mesoporous MCM-41 silica and its catalytic reactivity in decetalization–Knoevenagel reactions, *Microporous Mesoporous Mater.* 134 (2010) 44–50.
- [22] N.T. Phan, C.W. Jones, Highly accessible catalytic sites on recyclable organosilane-functionalized magnetic nanoparticles: an alternative to functionalized porous silica catalysts, *J. Mol. Catal. Chem.* 253 (2006) 123–131.
- [23] K.R. Reddy, K. Rajgopal, C.U. Maheswari, M.L. Kantam, Chitosan hydrogel: a green and recyclable biopolymer catalyst for aldol and Knoevenagel reactions, *New J. Chem.* 30 (2006) 1549–1552.
- [24] X.W. Feng, C. Li, N. Wang, K. Li, W.W. Zhang, Z. Wang, X.Q. Yu, Lipase-catalysed decarboxylative aldol reaction and decarboxylative Knoevenagel reaction, *Green Chem.* 11 (2009) 1933–1936.
- [25] M. Trilla, R. Pleixats, M.W.C. Man, C. Bied, Organic–inorganic hybrid silica materials containing imidazolium and dihydroimidazolium salts as recyclable organocatalysts for Knoevenagel condensations, *Green Chem.* 11 (2009) 1815–1820.
- [26] J. Gascon, U. Aktay, M.D. Hernandez-Alonso, G.P. van Klink, F. Kapteijn, Amino-based metal-organic frameworks as stable, highly active basic catalysts, *J. Catal.* 261 (2009) 75–87.
- [27] U.P. Tran, K.K. Le, N.T. Phan, Expanding applications of metal–organic frameworks: zeolite imidazolate framework ZIF-8 as an efficient heterogeneous catalyst for the Knoevenagel reaction, *ACS Catal.* 1 (2011) 120–127.
- [28] L. Xu, C. Wang, J. Guan, Preparation of acid-base bifunctional mesoporous KIT-6 (KIT: Korea Advanced Institute of Science and Technology) and its catalytic performance in Knoevenagel reaction, *J. Solid State Chem.* 213 (2014) 250–255.
- [29] S.M. Islam, A.S. Roy, R.C. Dey, S. Paul, Graphene based material as a base catalyst for solvent free Aldol condensation and Knoevenagel reaction at room temperature, *J. Mol. Catal. Chem.* 394 (2014) 66–73.
- [30] Y. Horiuchi, T. Toyao, M. Fujiwaki, S. Dohshi, T.H. Kim, M. Matsuoka, Zeolitic imidazolate frameworks as heterogeneous catalysts for a one-pot P–C bond formation reaction via Knoevenagel condensation and phospho-Michael addition, *RSC Adv.* 5 (2015) 24687–24690.
- [31] B. Xue, J. Zhu, N. Liu, Y. Li, Facile functionalization of graphene oxide with ethylenediamine as a solid base catalyst for Knoevenagel condensation reaction, *Catal. Commun.* 64 (2015) 105–109.
- [32] Z. Benzekri, K. El Mejdoubi, S. Boukhris, B. Sallek, B. Lakhri, A. Souizi, Dicalcium phosphate dehydrate DCPD as a highly efficient and reusable catalyst for Knoevenagel condensation, *Synth. Commun.* 46 (2016) 442–451.
- [33] B. Sakhivel, A. Dhakshinamoorthy, Chitosan as a reusable solid base catalyst for Knoevenagel condensation reaction, *J. Colloid Interface Sci.* 485 (2017) 75–80.
- [34] N. Anbu, R. Maheswari, V. Elamathi, P. Varalakshmi, A. Dhakshinamoorthy, Chitosan as a biodegradable heterogeneous catalyst for Knoevenagel condensation between benzaldehydes and cyanoacetamide, *Catal. Commun.* 138 (2020) 105954.
- [35] N. Anbu, S. Hariharan, A. Dhakshinamoorthy, Knoevenagel-Doebner condensation promoted by chitosan as a reusable solid base catalyst, *Mol. Catal.* 484 (2020) 110744.
- [36] H. El Aaadad, M. Galai, A. Chahine, M.E. Touhami, Synthesis, characterization and thermal properties of 2, 2'-dibenzimidazolyl butane as a novel corrosion inhibitors for mild steel in sulfuric acid, *Surf. Rev. Lett.* 27 (2020) 1950115.
- [37] H. El aadad, D. Rair, A. Chahine, Synthesis and characterization of novel organic–inorganic hybrid nanocomposites of phosphate–benzimidazole by soft chemistry route in aqueous media, *SN Appl. Sci.* 1 (2019) 1474.
- [38] J. Zhang, T. Jiang, B. Han, A. Zhu, X. Ma, Knoevenagel condensation catalyzed by 1,1,3,3-Tetramethylguanidium Lactate, *Synth. Commun.* 36 (2006) 3305–3317.
- [39] M.S. Abaee, S. Cheraghi, Aqueous DABCO, an efficient medium for rapid organocatalyzed Knoevenagel condensation and the Gewald reaction, *Turk. J. Chem.* 38 (2014) 650–660.
- [40] X.L. Zhao, K.F. Yang, X.G. Liu, C.L. Ye, L.W. Xu, G.Q. Lai, Polyguanidine as a highly efficient and reusable catalyst for Knoevenagel condensation reactions in water, *Aust. J. Chem.* 66 (2013) 500–504.
- [41] L. Shiri, S. Zarei, M. Kazemi, D. Sheikh, Sulfuric acid heterogenized on magnetic Fe₃O₄ nanoparticles: a new and efficient magnetically reusable catalyst for condensation reactions, *Appl. Organomet. Chem.* 32 (2018) e3938.
- [42] H. Ouaddari, D. Beqqour, J. Bennazha, I.E. El Amrani, A. Albizane, A. Solhy, R.S. Varma, Natural Moroccan clays: comparative study of their application as recyclable catalysts in Knoevenagel condensation, *Sustain. Chem. Pharm.* 10 (2018) 1–8.
- [43] H. Xu, L. Pan, X. Fang, B. Liu, W. Zhang, M. Lu, Y. Xu, T. Ding, H. Chang, Knoevenagel condensation catalyzed by novel Nmm-based ionic liquids in water, *Tetrahedron Lett.* 58 (2017) 2360–2365.
- [44] S. Chehab, Y. Merroun, T. Ghailane, N. Habbadi, S. Boukhris, A. Hassikou, M. Akhazzane, A. Kerbal, R. Ghailane, A. Daich, A. Souizi, A new process for Na₂Ca(HPO₄)₂ synthesis and its application as a heterogeneous catalyst in Knoevenagel condensation, *MedJChem* 7 (2018) 39–55.