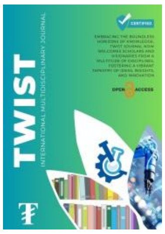
DOI https://doi.org/10.5281/zenodo.10049652#74

TWIST, 2024, Vol. 19, Issue 1, pp. 113-122

TWIST

Journal homepage: www.twistjournal.net



# Natural Phosphate Doped by Potassium as Efficient Catalyst for the Synthesis of Chalcones by Claisen–Schmidt Condensation Reaction

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## Abstract

This research focuses on the development of a potassium-doped natural phosphate catalyst (K/NP) for the Claisen-Schmidt condensation reaction. The study highlights the significant improvement in catalytic activity that results from doping natural phosphate with potassium. This improvement was performed using various structural, morphological, and spectral analysis methods, including X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy ((SEM-EDS), and Fourier transform infrared spectroscopy (FTIR). The optimum reaction conditions were also obtained, taking into account factors such as the type of catalyst, mass, choice of solvent, and reaction kinetics. The results show that potassium-doped natural phosphate (K/NP) is an effective catalyst for the Claisen-Schmidt condensation reaction, with a remarkable 98% yield under specific conditions; in addition, the reusability of the catalyst was also studied, revealing its remarkable stability through multiple reaction cycles.

## Keywords

Natural phosphate, Potassium-doped natural phosphate, Heterogeneous catalysis, Claisen-Schmidt, Chalcones, Green chemistry

## INTRODUCTION

Chalcones are widely used as compounds in the pharmaceutical and biological fields. They have recently attracted great interest due to their multiple applications. There has been a significant increase in research on new synthetic routes for chalcones (Burmaoglu et al., 2023; Ye et al., 2023), due to their potential for anticancer, anti-inflammatory, anti-tumor, and antibacterial activities (dos Santos et al., 2023; Gan et al., 2018; Pereira et al., 2023). Chalcones is positioned as essential intermediates in the preparation of flavonoids and isoflavones, which gives them great importance (Kumar et al., 2010; Kunde et al., 2009). Among the most predominant synthesis methods is the Claisen-Schmidt condensation reaction, used either homogeneously or heterogeneously (Juhász & Hell, 2018; Rullah et al., 2019; Xu et al., 2008). Natural phosphate (NP), fluorapatite (FAP), and hydroxyapatite (HAP), alone or doped were employed as heterogeneous catalysts in acidic or basic reactions (Marrane et al., 2022; Sebti et al., 2000), such as the Friedel–Crafts, Michael, Knoevenagel, nitrile hydration, Suzuki–Miyaura, and phospha-Brock reactions (Hassine, 2013; Kiss et al., 2019; Saber et al., 2003;

Sebti, Rhihil, & Saber, 1996; Sebti, Rhihil, Saber, et al., 1996; Sebti et al., 1999; Sebti, Tahir, et al., 2002) and also in the synthesis of α-hydroxyphosphonates, spiropyrimidine, xanthene derivatives and Knoevenagel-phospha-Michael Addition Reaction (Smahi et al., 2008; Ramananarivo et al., 2013; Rhihil et al., 2022; Merroun et al., 2023; Aichi et al., 2023).

In this context, various catalysts such as natural phosphate, hydroxyapatite, and fluorapatite, alone or doped with sodium Na/NP, Na/Hap, Na/Fap, potassium fluoride KF/NP, lithium nitrate $LiNO_3$/NP, $LiNO_3$/Hap, and $LiNO_3$/Fap, have been used in the preparation of chalcones (Macquarrie et al., 2002; Sebti, Solhy, et al., 2001; Solhy et al., 2010). The main objective is to prepare chalcones by heterogeneous synthesis using a catalyst based on potassium-doped natural phosphate K/NP (Kiss et al., 2019). This catalyst was prepared by impregnation and calcination in order to improve the catalytic performance of natural phosphate and to obtain a bifunctional catalyst for the Claisen-Schmidt condensation reaction.

## MATERIALS AND METHODS

### Preparation and Characterization of Phosphate Catalysts

Natural phosphate was acquired through an activation process detailed by Sebti et al. (2001, 2002). Several physicochemical treatment steps of phosphate are involved, including attrition, sieving, calcination at a temperature of 900°C, washing, and subsequent re-calcination phases. These treatments resulted in a phosphate fraction referred to as F4, with particle sizes falling within the range of 63 µm < F4 < 125 µm. Table 1 presents the chemical composition of the natural phosphate after undergoing these treatments. Additionally, various other metals are present in trace amounts (in ppm) in the treated phosphate, such as Cd, Zn, Cu, U, Cr, and V. The specific surface area of the NP measures 1.4 $m^2/g$, with a total pore volume of VT = 0.0055 $cm^3/g$.

**Table 1** Chemical composition of natural phosphate

| Chemical element | Ca | P | F | Si | S | C | Na | Mg | Al | Fe | K |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Percentage (%)** | 54.20 | 34.24 | 3.37 | 2.25 | 2.25 | 1.16 | 0.92 | 0.70 | 0.54 | 0.26 | 0.08 |

Potassium-doped phosphate was prepared by adding an aqueous solution of potassium nitrate (5 g, 1.17 M) to 10 g of natural phosphate (NP). The mixture was then stirred vigorously at room temperature for 30 minutes, followed by vacuum drying and heating at 120°C overnight. The material was then ground and sieved to a particle size of less than 63 µm. The potassium-impregnated natural phosphate was further calcined at 900°C for one hour, resulting in the formation of the doped catalyst (K/NP = 1/2, w/w). The resulting catalyst (K/NP) was then employed in various chemical reactions as a heterogeneous catalyst, including the phospha-brock reaction and the Claisen-Schmidt reaction.

### Structural Characterization (XRD)

X-ray diffraction (XRD) patterns of natural phosphate (NP) and potassium-doped natural phosphate (K/NP) substrate materials calcined at a temperature of 900°C are shown in Fig.1.

The X-ray diffraction peaks were detected to be finer and more intense for the natural phosphate, which resulted from the processing of enriching the phosphate phase, in particular by washing and calcination. The corresponding peaks are characteristic of fluorapatite, which has a hexagonal structure and space group $P6_3/m$ Sabir et al. (2003). The addition of potassium to natural phosphate has a significant effect on the resulting crystal structure. The difference in X-ray patterns between the NP and K/NP materials indicates the appearance of peaks at 2θ=30.42 and 32.57, which correspond to the potassium-calcium-phosphate ($KCaP_3O_9$) phase. It crystallizes in an orthorhombic structure (ICDD data sheet, code Ref. 00-029-0993) (Koleva et al., 2023).

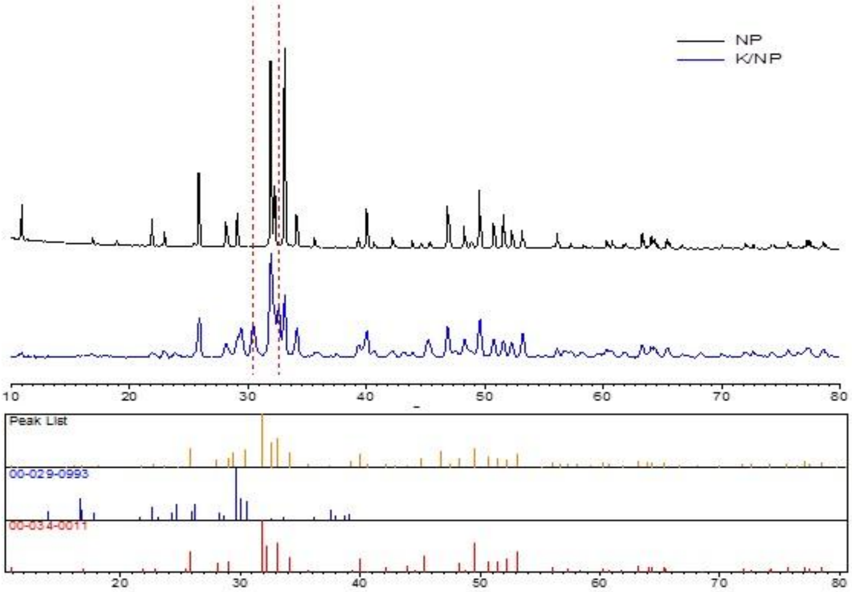


**Fig. 1** X-ray patterns of NP and K/NP

## Morphological Characterization

The morphological appearance of natural phosphate (NP) and potassium-doped natural phosphate (K/NP) was observed using a scanning electron microscope (SEM) and is illustrated in Fig. 2. The SEM images show a change in the surface of the potassium-doped phosphate grains.

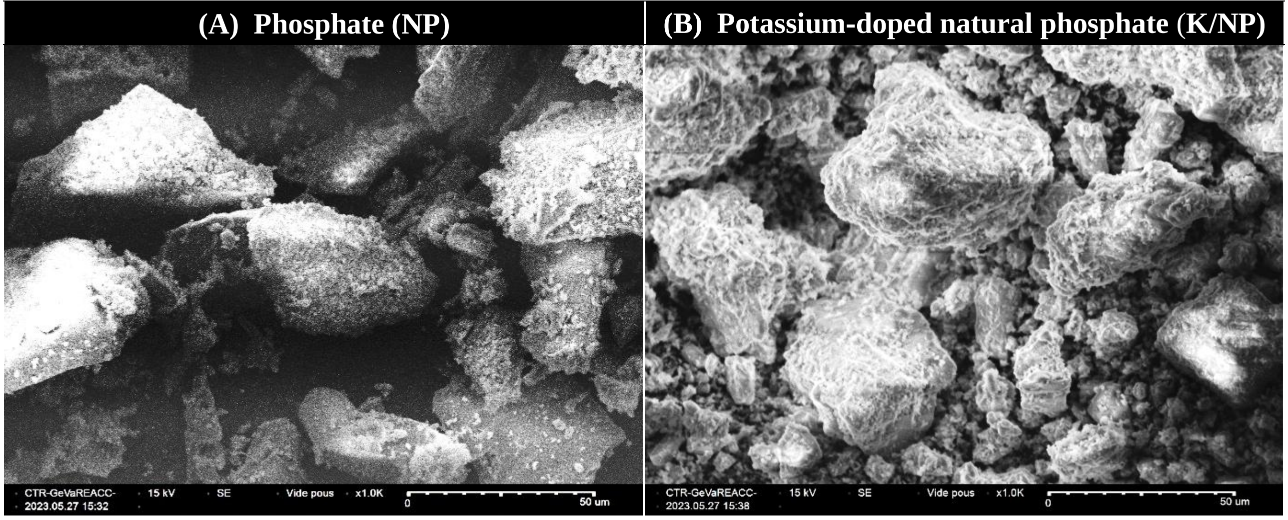

**(A) Phosphate (NP)** **(B) Potassium-doped natural phosphate (K/NP)**

**Fig. 2** SEM of NP and K/NP

**(A)** The NP image shows porous and heterogeneous grains, while **(B)** the K/NP grains appear as agglomerates of differ

## Characterization by EDX

The EDX analysis of the "K/NP" material shows that the grains of natural phosphate and potassium-doped natural phosphate (Fig. 3) have different potassium (K) contents. The surface of the doped phosphate is enriched in potassium, with a percentage of 6.09%, which confirms that the phosphate has been effectively impregnated with potassium.

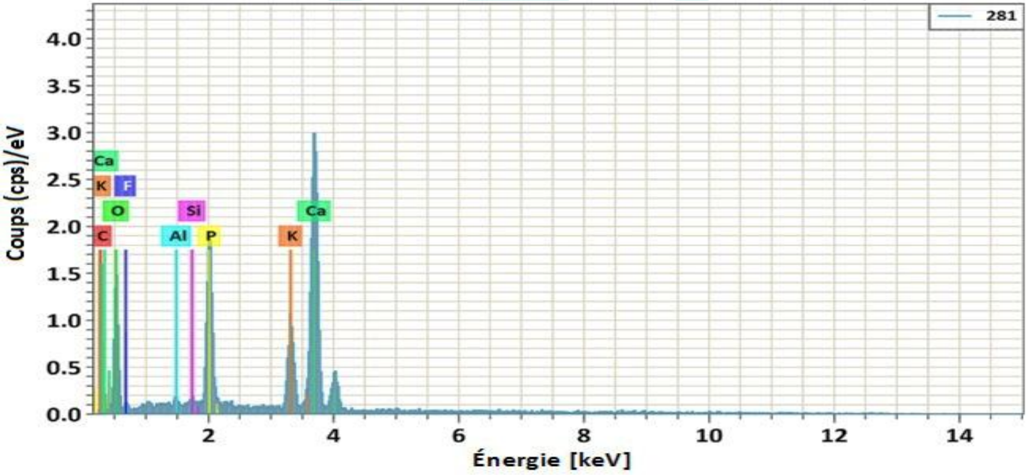


**Fig. 3** SEM-EDS of K/NP

The chemical elements of the potassium-doped natural phosphates (K/NP) are shown in Table 2, with varying percentages depending on the surface area, in addition to small quantities of aluminum 0.36% and silica 0.24%.

**Table 2** Percentage of chemical elements

| Elements | Percentage (%) |
|---|---|
| Oxygen | 43.76 |
| Calcium | 28.00 |
| Phosphorus | 7.48 |
| Potassium | 6.09 |
| Fluore | 3.37 |
| Aluminum | 0.36 |
| Silica | 0.24 |

The EDX analysis (Fig. 4) shows that natural phosphate particles are coated by potassium aggregates with a composition rich in oxygen, calcium, phosphorus, and fluorine, which correspond to the initial elements of natural phosphate. Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDX) shows a homogeneous distribution of potassium atoms on the surface of the natural phosphate grains.

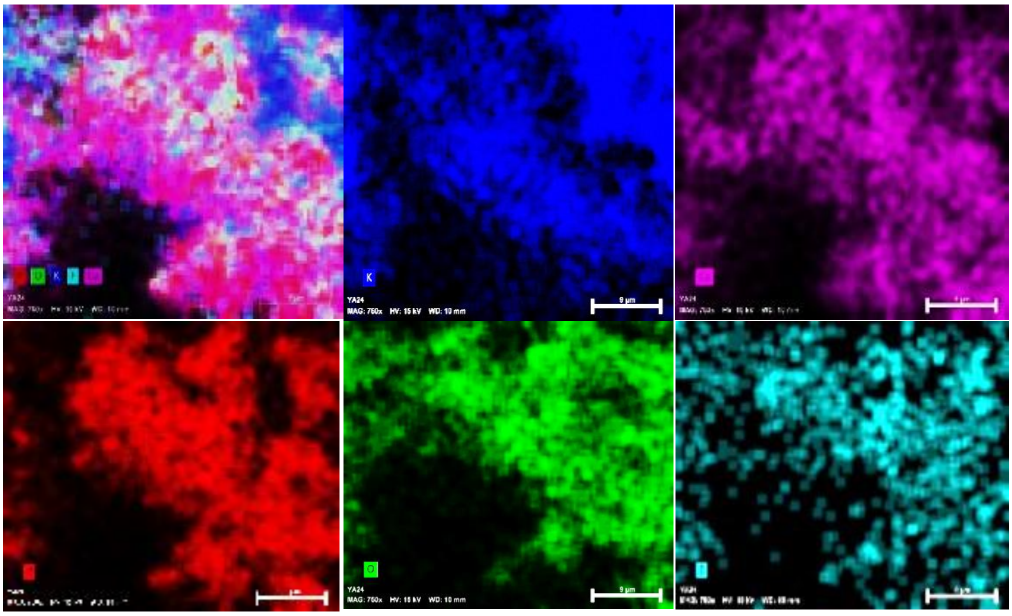


**Fig. 4** SEM-EDS dispersion of atoms on the K/NP surface

The doping of rock phosphate with potassium has resulted in a uniform dispersion of potassium atoms on the surface of rock phosphate particles. This change could have a significant impact on the characteristics and efficiency of the final product in various applications. The obtained results from SEM-EDX analysis confirm the success of the doping procedure and the even distribution of the chemical elements. These results are highly promising for the use of potassium-doped natural phosphate in applications, especially catalysis.

### Characterization by Infrared Spectroscopy

The infrared FTIR spectra of natural phosphate (NP) and potassium-doped phosphate (K/NP) are presented in Fig. 5, which show a variety of vibrational and binding modes. A new vibrational band in the FTIR spectrum of K/NP has appeared.

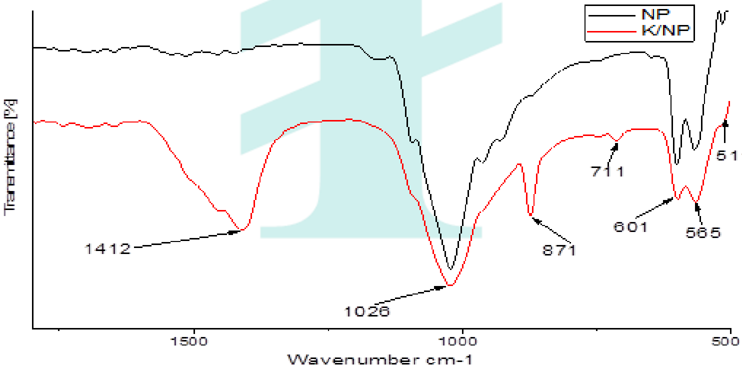


**Fig. 5** Infrared spectra of NP and K/NP

The natural phosphate (NP) and potassium-doped phosphate (K/NP) share bands found between 470 $cm^{-1}$ and 510$cm^{-1}$ can be attributed to the fundamental frequency of the ($PO_4$) groups of the bending vibrations of the O = P-O groups; the infrared bonds around 1000-1100 $cm^{-1}$ are attributed to the asymmetric stretching of the P-O-P groups. The spectrum of potassium-doped phosphate (K/NP) shows bands observed at 710-770 $cm^{-1}$ linked to a covalent bond between the non-bridging oxygen and calcium ions in the form of P-O-Ca stretching vibrations and the vibration of asymmetric P-O bonds. The observed band around 870-890 $cm^{-1}$ is associated with the asymmetric stretching vibrations of the P-O-P groups linked to the linear meta phosphate chain and the symmetric stretching vibrations of the P-O-P bonds. The band 1386-1413 $cm^{-1}$ is attributed to the symmetric stretching vibration of (P-O) (Aloraini et al., 2021; Marzouk et al., 2019; Toloman et al., 2010).

The doping effect of potassium phosphate (K/NP) was observed in X-ray diffraction with the appearance of a peak corresponding to the Potassium-Calcium-Phosphate ($KCaP_3O_9$) phase, which crystallizes in an orthorhombic structure (ICDD-00-029-0993) (Koleva et al., 2023). Meanwhile, the infrared spectrum of potassium-doped phosphate (K/NP) showed the appearance of bands corresponding to different vibrational modes that are absent in the spectrum of natural phosphate (NP), confirming the association of potassium with the structure of natural phosphate.

## RESULTS & DISCUSSION

### Operating Procedure of Chalcones Synthesis with the Action of K/NP

In a flask, 2.5 mmol of benzaldehyde and 2.5 mmol of acetophenone are stirred with 3 mL of methanol in the presence of 100 milligrams of potassium-doped natural phosphate, used as a catalyst for the reaction (Fig. 6).

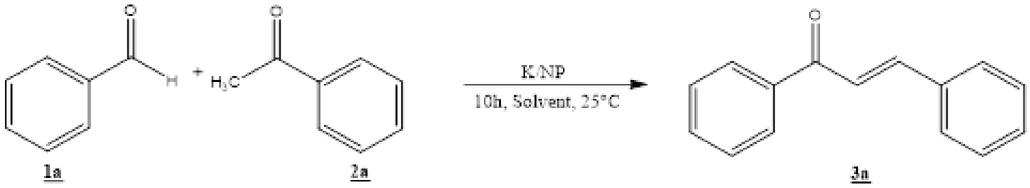


**Fig. 6** Synthesis of chalcones by Claisen-Schmidt condensation with K/NP

The solution was stirred at room temperature for 10 hours. The reaction's progress is monitored by gas chromatography (GC). The catalyst is removed by filtration after the complete reaction. The product is recovered by rotary evaporation and purified by recrystallization in ethanol. The obtained product is then characterized by $^{1}$H NMR and $^{13}$C-NMR spectroscopy, all the spectra being grouped together in the supplementary materials.

## Optimization of Reaction Conditions

### *Effect of Catalysts*

In order to evaluate the efficiency of the catalytic activities of the phosphate catalysts and their potential to increase the yield of the reaction, a series of catalysts were tested in order to select the most efficient. Each catalyst was used at a quantity of 100 mg, and tested with a reaction time of 10 hours and 3 mL of methanol as solvent; the results are shown in Fig. 7. The analysis reveals that potassium-doped natural phosphates (K/NP) exhibit the highest catalytic efficiency, with a yield of 98%. The lithium-doped natural phosphates (Li/NP) had a yield of 80% and sodium-doped natural phosphates (Na/NP) gave a yield of 65%. In contrast, natural phosphate (NP) was the least reactive, with a yield of 5%. $KNO_3$ had a yield of 10%. However, it is important to acknowledge that this ranking is dependent on the dopant elements and the reaction conditions. For example, the results may be different if the reaction is carried out at a different temperature or pressure.

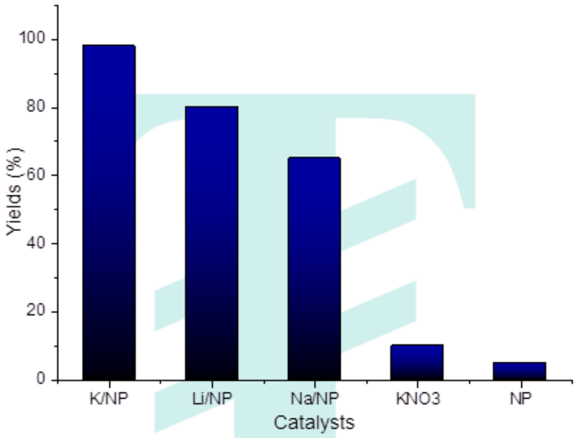


**Fig. 7** Catalyst effect in the synthesis of chalcones

### *Kinetics of the Reaction*

To study the kinetics of the reaction, the synthesis of chalcones using potassium-doped natural phosphate was carried out under the same operating conditions as previously, with the reaction time varying from 1 hour to 14 hours (Fig.8).

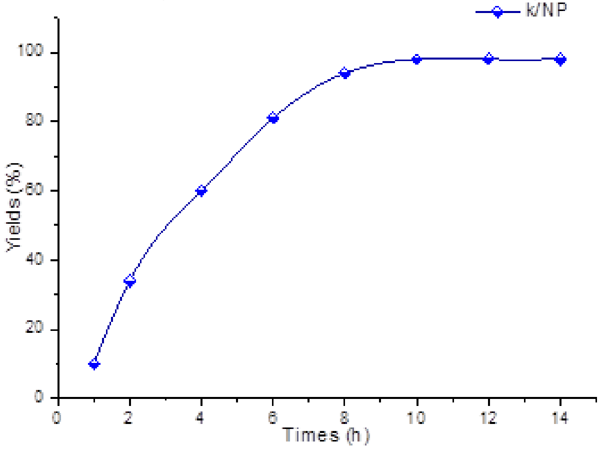


**Fig. 8** Kinetics of the Claisen-Schmidt reaction

The results show a marked increase in efficiency between 1 hour and 10 hours, with efficiency reaching a remarkable 98% after 10 hours. It should be noted that the high yield level was maintained consistently over the 10 hours, as shown in Fig. 8. This emphasises the exceptional stability of the process.

### *Effect of Catalyst Mass*

To evaluate the catalytic efficiency of the potassium-doped catalyst, different masses ranging from 15 to 150 mg were used sequentially, with the same operational parameters as those previously detailed for the synthesis of chalcone. The results are shown in Fig. 9.

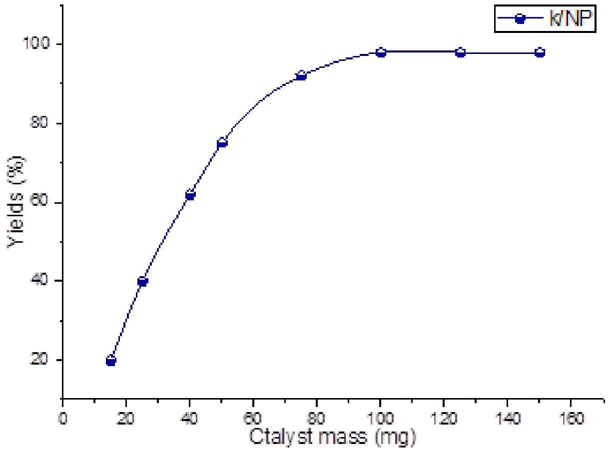


**Fig .9** Effect of the amount of K/NP on chalcone synthesis

A remarkable yield of 98% was obtained using 100 mg of potassium-doped natural phosphate (K/NP) catalyst. Above this quantity, the yield remains constant at 98%.

### *Effect of the Type of Solvent*

The choice of solvent can significantly affect the reaction by interacting with the reactants, mainly through polarisation, activating or inhibiting the process. In this study, different polar and non-polar solvents, including methanol, ethanol, water, hexane, and acetonitrile, were tested under identical operating conditions for the Claisen-Schmidt reaction. Fig. 10 illustrates the effects of these various solvents.

The results show that methanol is the most efficient solvent, with an impressive yield of 98%. Ethanol follows closely behind with a yield of 90%. In contrast, water, hexane, and acetonitrile gave relatively lower yields, underscoring the superiority of methanol and ethanol in facilitating this chemical transformation.

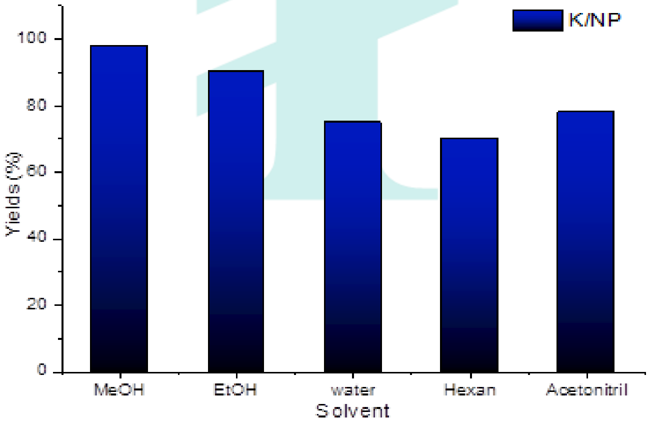


**Fig. 10** Effect of solvent on the synthesis of chalcones by K/NP

### *Catalyst Recycling*

Under the same operating conditions as mentioned earlier, the effect of reusing potassium-doped natural phosphate (K/NP) in the Claisen-Schmidt condensation reaction for the synthesis of chalcones is presented in Fig.11.

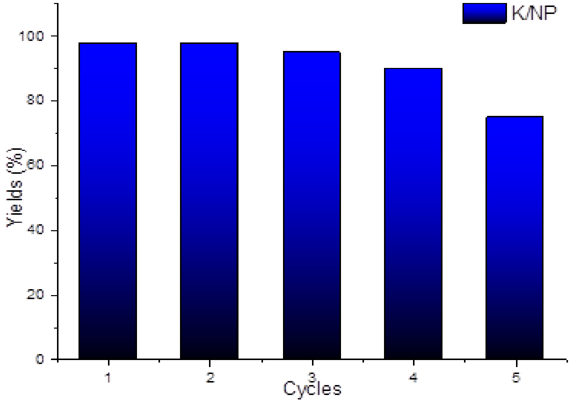


**Fig. 11** Reusing K/NP catalysts

In the first and second cycles, the K/NP catalyst showed an impressive yield of 98%. However, a slight decrease in efficiency was observed in the third cycle, where the K/NP catalyst gave a yield of 95%. In the fourth cycle, the yield was 90%, and in the fifth cycle, it decreased to 75%. This behavior in catalytic activity during reuse can be explained by various factors, such as deformation of the catalyst, clogging of the active sites, accumulation of byproducts, or other phenomena related to chemical reactions.

## Generalization

Under the optimal reaction conditions previously studied, the range of substrates was extended to include a variety of substituted aldehydes and ketones. Our goal was to analyze their properties in terms of electronic and steric effects in the generalized synthesis of chalcones by Claisen-Schmidt condensation in the presence of a K/NP phosphate catalyst (Fig. 12).

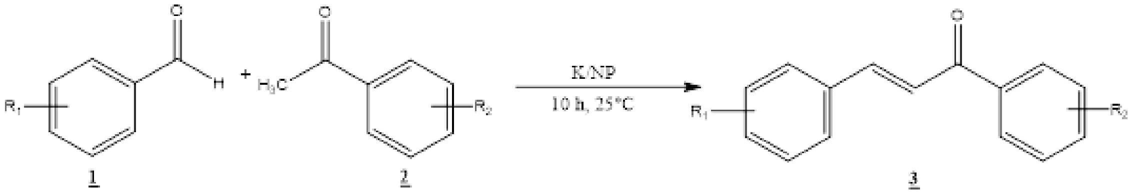
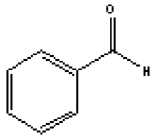
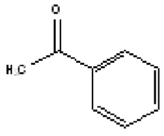
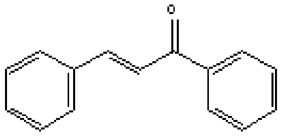
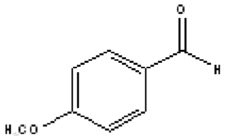
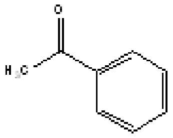
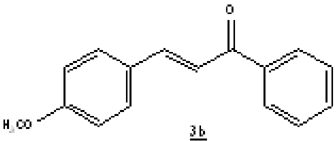
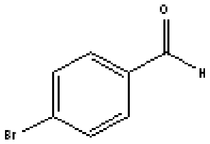
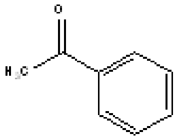
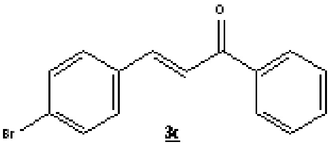
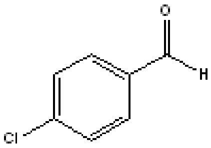
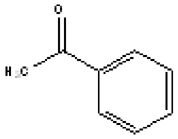
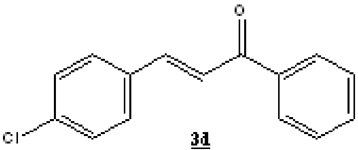
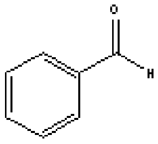
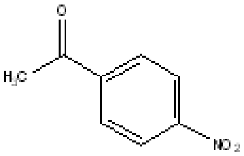
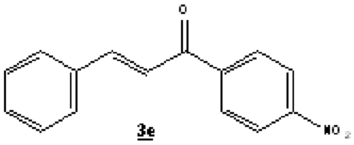
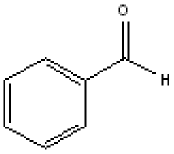
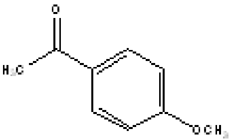
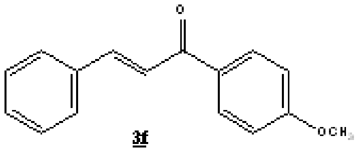
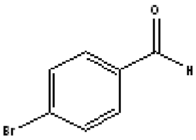
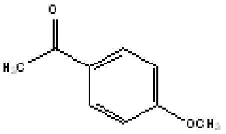
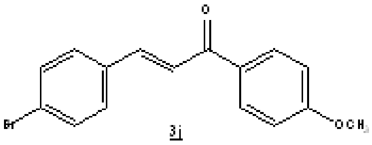


**Fig. 12** Claisen-Schmidt condensation reaction catalysed by K/NP

2.5 mmol of aldehydes (1) and 2.5 mmol of substituted acetophenones (2) are mixed in 3 mL of methanol, adding 100 mg of K/NP catalyst. The reaction was carried out for 10 hours at 25°C. The results are summarized in Table 3.

**Table 3** Claisen-Schmidt condensation reaction catalysed by K/NP

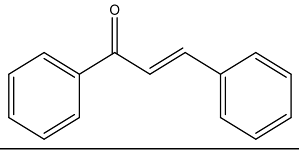
| N° | Aldehydes | ketones | Chalcones | Yield (%) |
|---|---|---|---|---|
| 1 | <br>1a | <br>2a | <br>3a | 98 |
| 2 | <br>1b | <br>2b | <br>3b | 94 |
| 3 | <br>1c | <br>2c | <br>3c | 96 |
| 4 | <br>1d | <br>2d | <br>3d | 94 |
| 5 | <br>1e | <br>2e | <br>3e | 88 |
| 6 | <br>1f | <br>2f | <br>3f | 92 |
| 7 | <br>1j | <br>2j | <br>3j | 80 |

The use of para-substituted aldehydes containing electron-withdrawing groups, such as 4-bromobenzaldehyde and 4-chlorobenzaldehyde, gives yields of 96% and 94%, respectively, with acetophenone 2a. While the reactivity of electron-donating groups, such as 4-methoxybenzaldehyde, gave a yield of 94%. Substitution of acetophenones with electron-withdrawing groups, such as 4-nitroacetophenone, led to a yield of 88%, while electron-donating groups in the 4-methoxyacetophenone position gave a yield of 92%. However, when 4-bromobenzaldehyde and 4-methoxybenzaldehyde were used as substrates, the corresponding product was obtained with a yield of 80%.

## Comparison of Catalysts Activity

The results of chalcone synthesis by the Claisen-Schmidt condensation reaction using various catalysts as described in the literature are summarized in Table 4.

**Table 4** Comparison of (2E)-1,3-Diphenylprop-2-en-1-one synthesis with phosphate catalysts

| N° | Compounds | Catalyst | Time (h) | Yield (%) | Ref. |
|---|---|---|---|---|---|
| 1 |  | $LiNO_3$/NP | 12 | **98** | (Sebti, Solhy, Smahi, et al., 2002) |
| 2 | | $NaNO_3$/NP | 18 | **98** | (Sebti, Solhy, et al., 2001) |
| 3 | | $NaNO_3$/HAP | 12 | **98** | (Sebti, Solhy, Tahir, et al., 2002) |
| 4 | | Na/FAP | 24 | **89** | (Jioui et al., 2016) |
| 5 | | **K/NP** | **10** | **98** | This work |

The results show that our catalyst can be considered one of the most efficient, on par with $LiNO_3$/NP. This assessment takes into account the catalyst mass, reaction temperature, and desired advantages of the reaction medium, in particular its heterogeneous solid–liquid nature. The potassium-doped natural phosphate (K/NP) gave a yield of 98% achieved at room temperature and a reaction time of no more than 10 hours, using only 100 mg of catalyst and without the need for a phase transfer agent or more energy. These results are very promising and open up new possibilities for exploring the use of this phosphate-based catalyst in the synthesis of other biologically active compounds while respecting the environment and the principles of green chemistry.

## CONCLUSION

The potassium-doped natural phosphate (K/NP) catalyst was prepared and characterized by various analytical methods (XRD, SEM, and IR). The synthesis of chalcones by Claisen-Schmidt condensation in the presence of a phosphate catalyst was performed.

Morphological characterization of the catalyst revealed a homogeneous distribution of potassium atoms on the surface of the rock phosphate particles, confirming the effectiveness of the doping process. Experiments showed that the K/NP catalyst outperformed other doped phosphate variants as well as undoped phosphate (NP) in terms of catalytic efficiency. Optimization of the reaction conditions highlighted the importance of the choice of solvent, the quantity of catalyst, and the reaction time. The potassium-doped natural phosphate (K/NP) exhibits the best performance (98%) using methanol as the solvent. The optimum yield (98%) is achieved after 10 hours of reaction with a catalyst mass of 100 mg of K/NP.

The potassium-doped rock phosphate is also better than the other varieties of doped phosphate (NP, FAP, and HAP). The influence of the mass of the catalyst, the nature of the solvent, and the reaction kinetics were then studied, which enabled us to determine the optimum conditions for this synthesis. The products obtained were characterized by $^1$H-NMR and $^{13}$C-NMR.

The K/NP catalyst demonstrated efficient reuse over several cycles, although slight decreases in efficiency were observed with each cycle. Substrate diversification also showed that the K/NP catalyst was capable of promoting the formation of chalcones with various electron-withdrawing and electron-donating groups, underscoring its versatility.

The results obtained pave the way for potential new applications in organic chemistry, particularly in the synthesis of compounds with interesting properties in the pharmaceutical and biological fields.

## SUPPLEMENTAL MATERIALS

### (E)-1,3-Diphenylpropenone 3a

$^1$H NMR (250 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.2, 1.4 Hz, 2H), 7.82 (d, J = 15.7 Hz, 1H), 7.71–7.64 (m, 2H), 7.60–7.47 (m, 4H), 7.45–7.38 (m, 3H).

$^{13}$C NMR (63 MHz $CDCl_3$) δ 191.10 ,144.83, 138.28, 134.97, 132.81, 130.57, 128.98, 128.66, 128.53, 128.47, 122.16.

### (E)-3-(4-Methoxyphenyl)-1-phenyl-2-propen-1-one 3b

1H NMR (250 MHz, $CDCl_3$) δ 8.01 (dd, J = 6.8, 1.6 Hz, 2H), 7.79 (d, J = 15.7 Hz, 1H), 7.61 (d, J = 8.8 Hz, 2H), 7.58–7.46 (m, 3H), 7.42 (d, J = 15.7 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H).

$^{13}$C NMR (63 MHz, $CDCl_3$) δ 188.8, 163.5, 144.0, 135.1, 131.1, 130.9, 130.4, 129.0, 128.4, 121.9, 113.9, 55.6.

### (E)-3-(4-Bromophenyl)-1-phenyl-2-propen-1-one 3c

$^1$H NMR (250 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.3, 1.4 Hz, 2H), 7.75 (d, J = 15.7 Hz, 1H), 7.62–7.57 (m, 2H), 7.56–7.45 (m, 6H).

$^{13}$C (63 MHz, $CDCl_3$) δ 190.3, 143.5, 138.1, 133.9, 133.1, 132.3, 129.9, 128.8, 128.6, 124.9, 122.7.

### (E)-3-(4-Chlorophenyl)-1-phenyl-2-propen-1-one 3d

$^1$H NMR (250 MHz, $CDCl_3$) δ 8.09–8.02 (m, 2H), 7.78 (d, J = 15.7 Hz, 1H), 7.67–7.46 (m, 6H), 7.46–7.37 (m, 2H).

$^{13}$C NMR (63 MHz, $CDCl_3$) δ 190.2, 143.3, 138.1, 136.5, 133.4, 133.0, 129.7, 129.3, 128.8, 128.6, 122.5.

**(E)-1-(4-Nitrophenyl)-3-phenyl-2-propen-1-one 3e**

$^{1}$H NMR (250 MHz, CDCl$_3$) δ 8.36 (d, J = 9.0 Hz, 2H), 8.15 (d, J = 9.0 Hz, 2H), 7.86 (d, J = 15.7 Hz, 1H), 7.67 (dd, J = 6.8, 2.8 Hz, 2H), 7.54–7.39 (m, 4H).

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 189.2, 150.2, 147.0, 143.2, 134.4, 131.4, 129.6, 129.3, 128.9, 124.0, 121.4.

**(E)-1-(4-Methoxyphenyl)-3-phenyl-2-propen-1-one 3f**

$^{1}$H NMR (250 MHz, CDCl$_3$) δ 8.05 (d, J = 8.9 Hz, 2H), 7.81 (d, J = 15.7 Hz, 1H), 7.68–7.62 (m, 2H), 7.55 (d, J = 15.7 Hz, 1H), 7.45–7.34 (m, 3H), 6.98 (d, J = 8.9 Hz, 2H), 3.87
(s, 3H).

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 188.7, 163.5, 144.0, 135.2, 131.2, 130.9, 130.4, 129.0, 128.4, 121.9, 113.9, 55.6.

**(E)-3-(4-Bromophenyl)-1-(4-methoxyphenyl)-2-propen-1-one 3i**

$^{1}$H NMR (250 MHz, CDCl$_3$) δ 8.03 (d, J = 8.9 Hz, 2H), 7.73 (d, J = 15.6 Hz, 1H), 7.62–7.43 (m, 5H), 6.98 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H).

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 188.5, 163.7, 142.6, 134.1, 132.3, 131.0, 131.0, 129.9, 124.7, 122.5, 114.0, 55.7.

## AUTHOR CONTRIBUTIONS

Youness AICHI and Abdallah RHIHIL carried out the experiments test and wrote the manuscript.

Abdallah RHIHIL, Saïd SEBTI and Mohamed EL GUENDOUZI have revised the manuscript. All authors read and approved the final manuscript.

## COMPETING INTERESTS

The authors declare no competing financial interest. No conflict of interest is declared.

## ACKNOWLEDGEMENTS

Thanks to the Thematic Research Centre on Materials and Energy (CRTME), and the Innovations and Technologies platform (PInTech), Faculty of Sciences Ben M'Sik of Caasablanca, University Hassan II- Casablanca, Morocco for their contributions in physical and chemical analysis.

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