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CATALYTIC ACTIVITY OF BURKINA PHOSPHATES FOR CHALCONE SYNTHESIS IN GREEN SOLVENT

Abstract: The Claisen-Schmidt condensation is a key catalytic reaction used in chemical synthesis, developed during the 20th century. This condensation can be performed with or without toxic solvents in the presence of a catalyst. This study focused on using a green solvent - water - for the Claisen-Schmidt condensation reaction, enhanced by catalysts derived from simple natural phosphate (NPc), potassium-impregnated natural phosphate (K-NP), and zinc-impregnated natural phosphate (Zn-NP). The research highlighted a significant improvement in the catalytic activity of these catalysts when used in water. Optimal reaction conditions were established, considering factors such as catalyst quantity, reaction kinetics, solvent volume, catalyst reuse, and the influence of the metal ions employed. The stability of these catalysts was demonstrated through multiple reaction cycles, indicating their potential for reuse. The results revealed that the developed catalysts were highly effective for the Claisen-Schmidt condensation reaction, achieving remarkable yields of 74 % for NPc, 96 % for Zn-NP, and 98 % for K-NP under specific conditions while utilising water as the green solvent.

Keywords: catalyst, green solvent, natural phosphate, catalytic activity, Claisen-Schmidt reaction

Introduction

Heterogeneous catalysis is crucial in chemical processes, facilitating a shift toward cleaner (green) chemistry. Green chemistry focuses on designing products and processes that minimise the use of hazardous substances. Heterogeneous catalysis is strategically important in the search for more environmentally friendly and economically efficient synthesis processes, both in terms of atom economy and energy consumption [1, 2]. Unlike homogeneous catalysis, which promotes excellent contact between reactants and catalysts but is difficult to remove from the final product, heterogeneous catalysis offers advantages that address recycling challenges - an important aspect of green chemistry.

From a practical standpoint, homogeneous-phase catalytic reactions have several drawbacks, including catalyst deactivation and limited recycling methods, which hinder their scalability in industrial applications. The use of heterogeneous catalysts can potentially enhance the environmental outcomes of industrial production and streamline

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organic synthesis processes. The development of these heterogeneous catalysts is significantly advancing both fundamental and applied research [3].

Supported catalysts, a subset of heterogeneous catalysts with active materials dispersed on a solid support, are particularly promising due to their selectivity, atom economy, and remarkable catalytic activity. The processes involving these catalysts fall within the realm of green chemistry, which aims to protect the environment [4, 5]. Rock phosphate (NP) has shown utility as a catalyst in various chemical reactions. Over the years, research has explored phosphate-catalysed reactions, including the hydration of nitriles to amides, transesterification, chalcone synthesis, 5-arylhydantoin synthesis, Michael addition, oxidation of cycloalkanones and α-ketols, and Suzuki-Miyaura coupling, among others [6-8]. Much work has focused on Claisen-Schmidt condensation, particularly in chalcone synthesis, due to its importance in various applications [9].

Chalcone is a key intermediate in preparing flavonoids and isoflavones, making it highly valuable in pharmaceutical and biological fields for its anticancer, anti-inflammatory, antitumor, and antibacterial properties [10-13]. Typically, Claisen-Schmidt condensation for chalcone synthesis employs solvents like ethanol, methanol, hexane, and acetonitrile, yielding good results [14-17]. However, the use of toxic organic solvents presents significant environmental challenges, generating waste in fine chemistry and posing serious health risks.

To address these issues, alternative methods to reduce reliance on toxic solvents are essential. Water, as a non-toxic solvent, is highly effective in overcoming some of these problems [18]. Water is environmentally friendly, easily recyclable, and eliminates from the final product without significant reactivity, making it an ideal choice in many chemical processes.

We aim to develop heterogeneous catalysis using rock phosphate from Burkina Faso, despite its limited applications due to its weak Lewis acid or base characteristics. Several techniques have been explored to enhance the catalytic activity of natural phosphates, including impregnating them with metal ions such as Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, and K^{+} [19]. This process alters the surface characteristics of the phosphates, thereby improving their catalytic performance.

This research focuses on minimising solvent use in chalcone synthesis, prioritising water as the solvent while ensuring high yields and maintaining the critical features of durability, stability, recyclability, and selectivity of the heterogeneous catalyst employed. To achieve this goal, we propose a strategy for upgrading natural phosphates from Kotchari, Burkina Faso, involving the impregnation of the phosphates with metal ions like Zn^{2+} and K^{+}, based on findings in the literature regarding their effectiveness in various catalytic reactions [9, 17]. The objective is to create hybrid catalysts that leverage the activity and selectivity of transition metal complexes while benefiting from the stability and ease of separation offered by the support.

Materials and methods

Materials

Phosphate rock

The natural phosphate rocks (NP) used in this research originate from Kotchari, located in the eastern region of Burkina Faso. Their characterisation has been documented

in scientific studies [20]. These rocks are primarily composed of carbonate-fluorapatite (francolite), represented by the formula $Ca_5(PO_4)_{2.5}(CO_3)_{0.5}F$; pentacalcium tris(phosphate) hydroxide (hydroxylapatite), with the formula $Ca_5(PO_4,CO_3)_3(OH)$; and alpha silicon oxide (alpha quartz), denoted as α-SiO_2. They exhibit high purity [20].

Trace amounts of certain elements, including Cd, Ba, As, Ce, Cr, Li, Pb, and Zn, are also present in these phosphates. The activity of heterogeneous catalysts primarily occurs at the surface of the solid material. The apatitic structure of the Kotchari rock phosphate is particularly conducive to generating significant charges on its surface. Previous studies have demonstrated that Kotchari phosphate predominantly comprises phases such as fluorapatite and hydroxylapatite, which have been successfully tested in the synthesis of chalcones, showcasing their effectiveness. These attributes make Kotchari phosphate an excellent candidate for applications in heterogeneous catalysis.

Chemical products

The solutions and solid products used in the experiment were obtained from Merck and utilised without purification. Distilled water served as the solvent. All reactions occurred at room temperature.

Preparation of phosphate-based catalysts

Calcined natural phosphate (NPc)

The natural phosphate (NP) collected was first crushed, washed, dried, and then sieved into different particle sizes. The fraction smaller than 80 µm was selected for catalyst preparation. Next, the NP was calcined at 900 °C for 2 hours, followed by washing to remove most of the organic matter and carbonates. The lime and magnesia generated during the calcination process were subsequently washed with water. Afterward, the resulting sample was oven-dried for 6 hours and then recalcined at 900 °C for 2 hours, which activated the NP and produced NPc.

Preparation of the Zn-NP catalyst

Zn-NP was prepared using an impregnation method. First, 9.4 g of phosphate calcined at 900 °C (NPc) and 0.6 g of $ZnCl_2$ salt were added to 25 mL of distilled water. The mixture was stirred for 2 hours and then evaporated under a vacuum. The resulting solid was dried at 120 °C for 24 hours to yield the catalyst (Zn-NP) [21].

Preparation of the K-NP catalyst

An aqueous solution of potassium iodide (KI) at a concentration of 0.1 M was prepared by dissolving it in 200 mL of distilled water. This solution was then mixed with 20 g of treated NPc. The resulting mixture was stirred overnight and subsequently filtered. After filtration, the material was dried at 80°C for 24 hours. To activate the product, the K-NP was calcined at 500 °C with a heating rate of 2.5 °C per minute for a duration of 3 hours [22].

Catalyst characterisation

The mineralogical composition of catalysts derived from natural phosphates from Kotchari (NPc, Zn-NP, K-NP) was determined using the X-ray diffraction (XRD) method. This powerful, non-destructive technique analyses the crystalline structure of materials,

providing information about the phases present in the samples. Powder X-ray diffraction patterns of the catalysts were recorded on a Brüker-type diffractometer using Cu K_α radiation (λ = 1.5406 Å).

Additionally, ATR-FTIR (Attenuated Total Reflection - Fourier Transform Infrared) analyses were conducted in the solid state by preparing the samples in KBr pellets. The analysis of the FTIR spectra complements the results obtained from the X-ray diffraction.

Catalytic test

To investigate the activity of these heterogeneous catalysts, catalytic tests were conducted using a mixture of acetophenone (1.7 mmol) and an aldehyde (1.7 mmol) in various volumes (0, 3, 5, and 10) mL of distilled water as the solvent. Different masses of catalyst (0.1, 0.3, 0.5, 0.8, and 1) g were employed, including NPc, Zn-NP, and K-NP. The mixture was stirred at room temperature throughout the reaction. After the designated reaction time, the catalyst was removed by filtration. Thin layer chromatography (TLC) and UV-Vis spectrometry (type DSE 190) were used to analyse specific characteristics of the synthesised product. TLC was particularly utilised to determine the time required to reach the completion of the chemical reaction.

Results and discussion

Characterisation of catalysts

Powder X-ray diffraction

Figure 1 presents X-ray diffraction patterns for raw phosphate (NP), calcined phosphate (NPc), and calcined phosphates impregnated with zinc (Zn-NP) and potassium (K-NP). The diffractograms for NPc, Zn-NP, and K-NP show no significant differences compared to NP, indicating that $ZnCl_2$ and KI are well-distributed on the phosphate surface without altering the NP structure. There are no changes in the angular positions or broadenings of the peaks, which suggests that the crystal order remains intact. This observation aligns with the findings of Zahouily et al. [23], who confirmed the structural stability of rock phosphate after impregnation with Zn^{2+} and K^+ ions.

Additionally, Bazi et al. and Mahato and Krithiga, in their study of metal-doped Santa Barbara Amorphous-15 (SBA-15) catalysts, also found that wet impregnation methods do not disrupt the structure's geometry [24, 25]. The clarity and size of all peaks following the treatment of rock phosphate are a result of the enrichment of phosphate phases (francolite and hydroxylapatite) without compromising the crystal structure [26].

However, a decrease in the intensity of certain peaks is noted after impregnation with Zn^{2+} (2θ = 20.85°, 26.68°, 36.55°) and K^+ (2θ = 20.84°, 26.65°, 36.54°, 50.27°) in the diffractograms for Zn-NP and K-NP. This reduction may indicate a uniform deposition of the metals on the solid surface, which acts as an absorbing layer for X-rays. The decrease in peaks at 2θ = 20.86° and 26.54°, associated with alpha silicon oxide (alpha quartz), along with the increase in peaks at 2θ = 31.92°, 33.05°, and 34.22°, which correspond to phosphate phases such as carbonate-fluorapatite (francolite) and penta-calcium tris(phosphate) hydroxide (hydroxylapatite) [20], suggests a reduction in impurities or undesired elements in the material, thereby enhancing the catalytic activity of rock phosphate [23].

In summary, adding potassium and zinc ions to NPc significantly affects the solid's surface without damaging any crystalline phases.

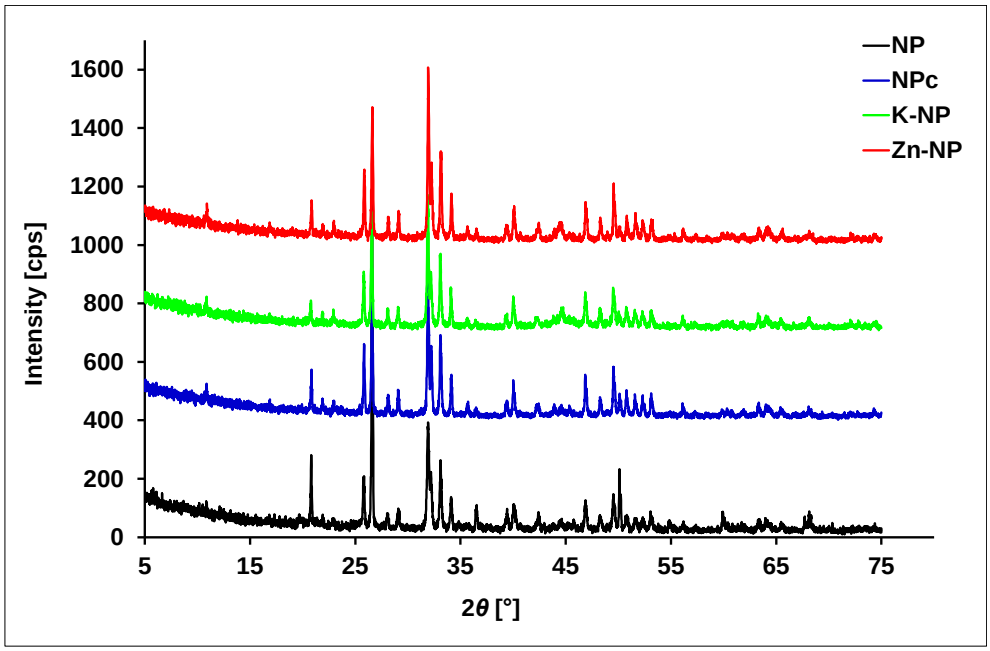


Fig. 1. X-ray diffraction spectra of NP, NPc, Zn-NP, and K-NP

Fourier transform infrared spectrometry (FTIR) study

The FTIR spectra of NPc, Zn-NP, and K-NP, as illustrated in Figure 2, reveal a prominent band near 1033 cm^{-1}, along with bands between 500 cm^{-1} and 600 cm^{-1}. These features are attributed to the PO_4^{3-} grouping in phosphate phases [27, 28]. The bands correspond to the antisymmetric stretching vibration modes of the P-O groups [20], confirming the formation of apatite phases [29]. The spectra indicate the presence of apatite phases, specifically carbonate-fluorapatite ($Ca_5(PO_4)_{2.5}(CO_3)_{0.5}F$) and penta-calcium tris(phosphate) hydroxide ($Ca_5(PO_4,CO_3)_3(OH)$), regardless of the support used [20]. This suggests that the NPc, Zn-NP, and K-NP catalysts were designed to maintain the phosphate phases responsible for their catalytic activity.

The impregnation of Zn^{2+} and K^+ metal ions onto the phosphate surface (NPc) may alter the vibrational frequencies of the bonds, which helps explain the peak shifts observed in the range of 500 cm^{-1} to 640 cm^{-1}. Additionally, the interaction of the impregnated ions with the surface may lead to a decrease in the intensity of certain peaks, resulting in an overall reduction of peak intensities following impregnation. These findings suggest a uniform deposition of ions on the phosphate surface while preserving the crystalline phosphate phases.

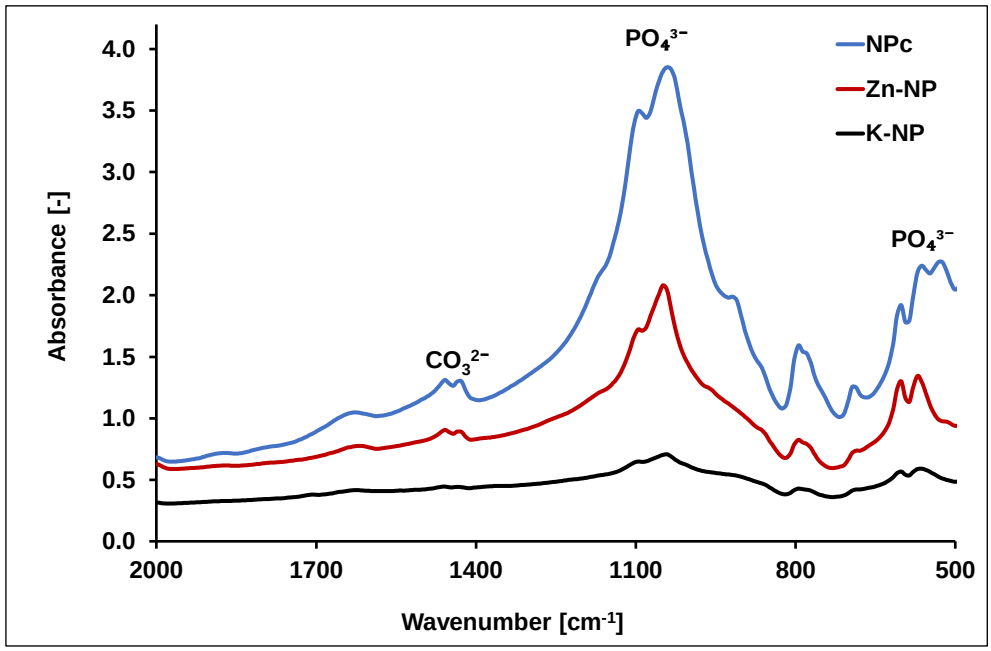


Fig. 2. Infrared spectra of NPc, Zn-NP, and K-NP

Effect of catalyst quantity

The catalysts prepared (NPc, Zn-NP, K-NP) were evaluated for their effectiveness in forming C-C bonds through the Claisen-Schmidt condensation reaction. Different quantities of each catalyst (0.1, 0.3, 0.5, 0.8, 1.0) g were tested over a duration of 14 hours, with the results illustrated in Figure 3.

It was noted that small amounts of K-NP and Zn-NP were sufficient to facilitate the formation of C-C bonds, in contrast to NPc. Significant yields were achieved starting from certain catalyst amounts; for instance, using 0.3 g of K-NP resulted in a yield of 96.56 %, while 0.8 g of Zn-NP produced a yield of 88.89 %. In the case of NPc, a minimum of 1 g was necessary to attain a yield of 74.08 %.

These quantities (0.3 g and 1 g) are comparable to some literature values, such as 2.5 g of NP for a yield of 75 % in methanol [30] and 100 mg of K-NP for a yield of 98 % in methanol [22]. Increasing the amount of catalyst stabilised yields at 98 % for K-NP (0.8 g) and 96 % for Zn-NP (1.2 g). A larger catalyst quantity promotes the formation of intermediates with acetophenone, facilitating a more effective nucleophilic attack on benzaldehyde, which enhances the observed yields. Conversely, for NPc, a decrease in yield was recorded after using 1 g, suggesting that an excessive amount of NPc negatively impacts chalcone synthesis. This observation highlights the significance of catalyst quantity as a critical factor in the synthesis process.

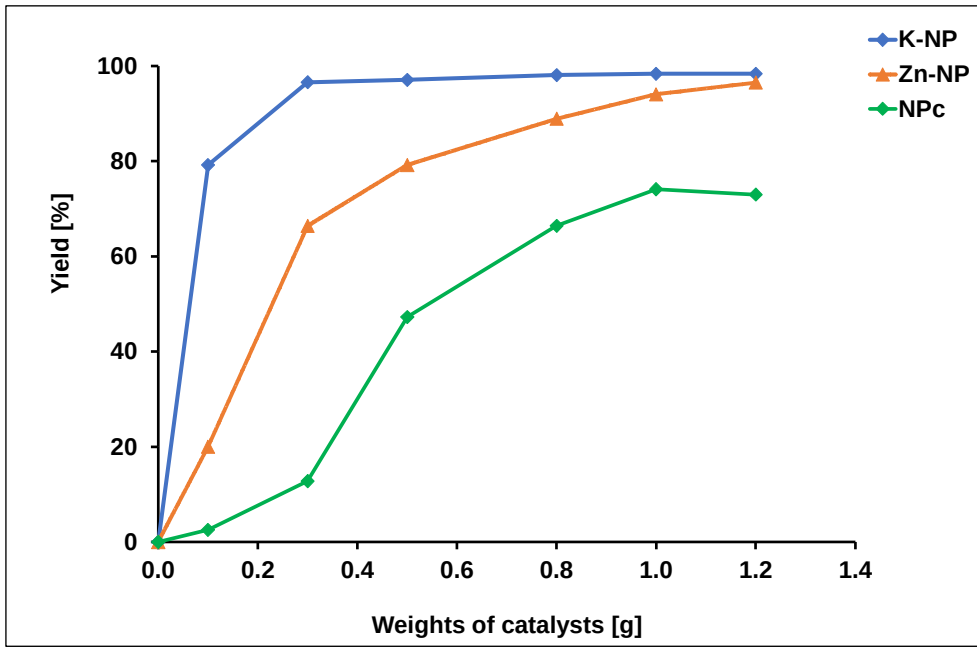


Fig. 3. Effect of NPc, Zn-NP, K-NP quantity on chalcone synthesis

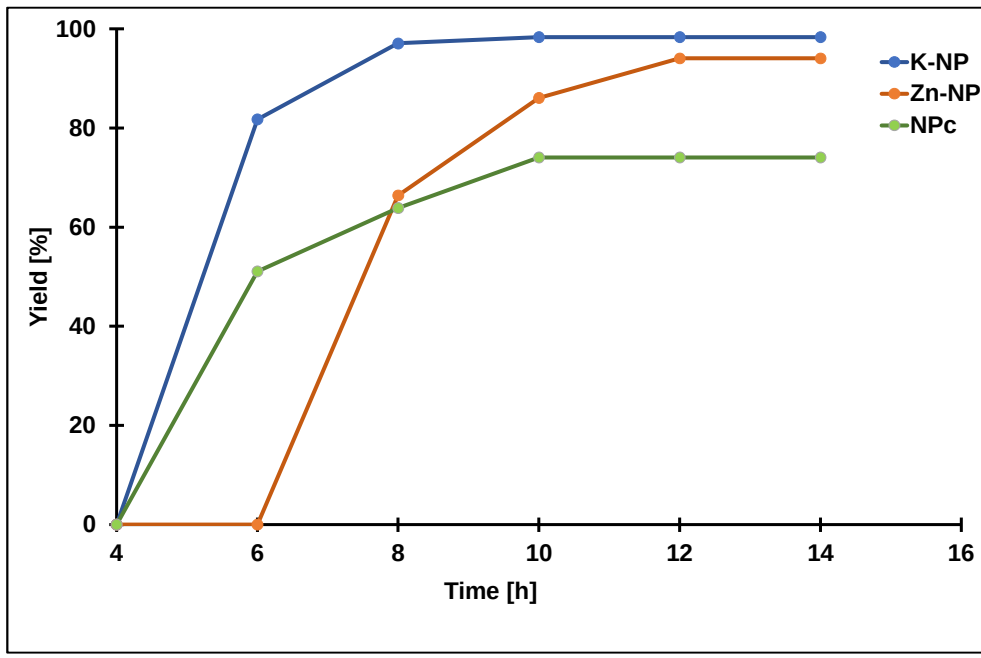


Fig. 4. Reaction times of NPc, Zn-NP, K-NP on chalcone synthesis

Study of reaction kinetics

To analyse reaction progress, 1 g of each catalyst (NPc, Zn-NP, K-NP) was used, and the progress of the reaction was monitored through thin-layer chromatography (TLC) every 30 minutes after an initial 2-hour period, for a total duration of 14 hours. The results, presented in Figure 4, indicate a rapid progression of the reaction with the K-NP complex, followed by NPc, and finally, Zn-NP. These findings demonstrate the significant impact of metal ions (Zn^{2+}, K^{+}) on the phosphate surface and their catalytic activity in Claisen-Schmidt condensation. After 4 hours, formation of product was observed for all three catalysts. Within the first six hours, K-NP achieved a yield of 81.75 %, and NPc reached a yield of 51.1 %, while the Zn-NP complex attained a yield of 66.41 % starting from 8 hours onward.

The yields of the NPc (74.08 %) and K-NP (98 %) catalysts stabilise after 10 hours of reaction, while the yield of the Zn-NP catalyst (94.05 %) stabilises after 12 hours. Although the reaction with the Zn-NP catalyst is slower compared to the NPc catalyst, it produces better results, achieving a yield of 94.05 % in contrast to 74.08 % for NPc. The slower reaction rate with the Zn-NP complex may be attributed to the small size of zinc, which has an ionic radius of 74 pm, compared to 138 pm for potassium. Additionally, the K^{+} ion has a van der Waals radius of 275 pm, significantly larger than the 139 pm of Zn^{2+}. The Van der Waals radius indicates the optimal distance at which the attractive and repulsive forces between atoms balance each other. These findings suggest a relationship between catalytic activity and the size of the metal supported on phosphates.

Effect of water volume on catalysts

The solvent is a crucial factor in heterogeneous catalysis, playing an important role in the partial or complete activation of the catalyst's active phases and facilitating the homogeneity of the reaction [31-33]. In organic synthesis, the choice of solvent is significant as it can reduce the heating time.

We investigated the impact of varying volumes of water on reaction yield at room temperature, utilising 1 g of each catalyst (NPc, Zn-NP, K-NP). The results after 14 hours of reaction time are illustrated in Figure 5. In the absence of a solvent, the reaction yields ranged from 60 % to 76 % across all three catalysts. Notably, the Zn-NP catalyst exhibited a lower yield compared to NPc when the water volume was less than 3 mL. This discrepancy may be attributed to the non-electrically neutral surface of Zn-NP, which could hinder the formation of nucleophiles with acetophenone, thereby reducing the reaction yield.

With the addition of 3 mL to 5 mL of water, yields improved, reaching 98 % for K-NP, 94 % for Zn-NP, and 74 % for NPc. These volumes (3 mL to 5 mL) are considered optimal as they enhance the solvation of the reagents and increase contact between the catalyst's active sites and the substrates, resulting in better outcomes compared to solvent-free synthesis.

However, for K-NP, Zn-NP, and NPc, a decline in yield was observed with the addition of more than 5 mL of water. This reduction could be due to the formation of a water film on the catalyst surfaces, which impacts their hydrophobicity and the accessibility of reagents to the active sites, or it might be because of the dispersion phenomenon that interferes with reagent-catalyst interactions. Additionally, water can function as a co-catalyst at specific volumes. It has a substantial influence on the

Claisen-Schmidt condensation reaction and can be regarded as an effective solvent under optimal conditions.

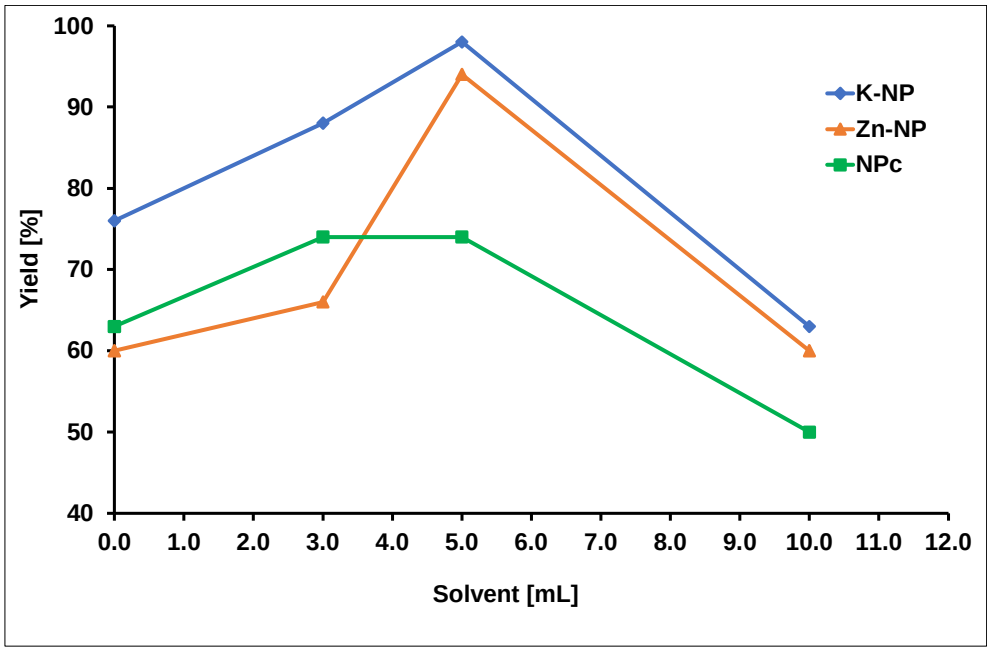


Fig. 5. Effect of water volume on catalysts in chalcone synthesis

Catalyst reuse

A catalyst becomes increasingly valuable when it can be easily recovered and reused. The activity of the catalyst during reuse is illustrated in Figure 6. To prepare the catalyst for reuse, it is washed with dichloromethane and then dried. Notably, the Zn-NP catalyst exhibits a significant drop in yield after the third cycle of use. In contrast, both the K-NP and Zn-NP catalysts maintain a yield of at least 80 % until the fifth cycle, while the yield for NPc decreases to 51 %. This decline in catalytic activity over multiple reuse cycles may be attributed to factors such as catalyst deformation, clogging of active sites, accumulation of by-products, or other phenomena related to chemical reactions [17].

Effect of metal ions

The analyses indicate that the impregnation of NPc with K^+ and Zn^{2+} ions has a significant impact on its surface properties. Both Zn^{2+} and K^+ ions enhance the number of active sites (acidic or basic) on NPc by forming Zn-NP and K-NP complexes. Notably, impregnation with K^+ ions yields better results compared to Zn^{2+}. This observation is attributed to the types of bonds formed by the Zn-NP and K-NP complexes during the chalcone synthesis reaction, rather than the electronegativity of the metal ions, as Zn^{2+} (electronegativity 1.65) is more electronegative than K^+ (electronegativity 0.82). A more active surface leads to higher yields.

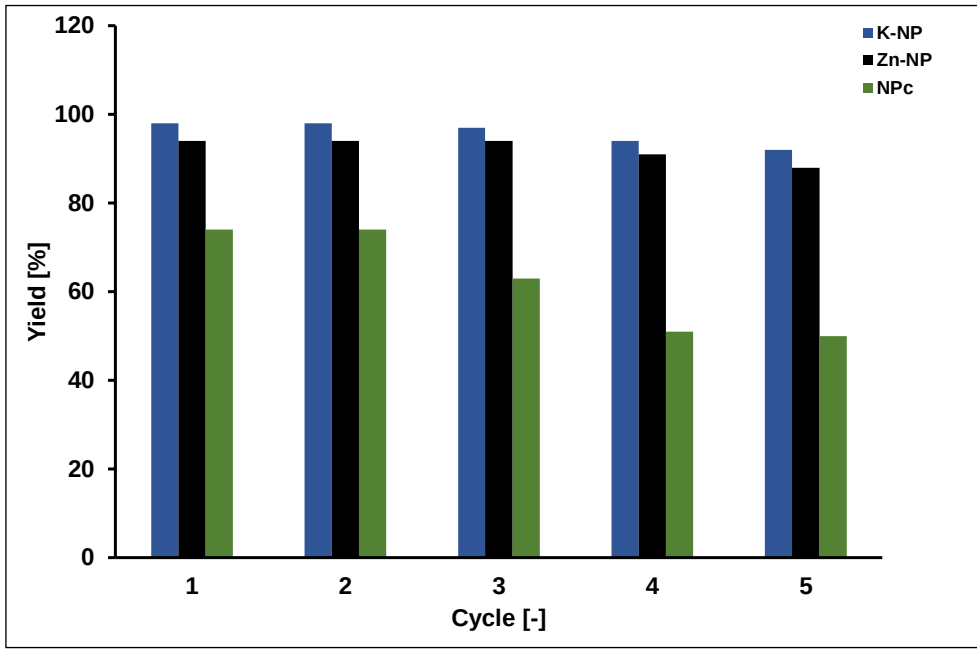


Fig. 6. Catalyst reutilisation

Fig. 7. Observation of agglomeration in the reaction mixture after the addition of acetophenone

The creation of a substantial number of Lewis acid sites during the impregnation of Zn^{2+} and K^{+} on phosphates is a critical factor influencing the outcomes for both Zn-NP and K-NP complexes [22, 34]. The metal ions K^{+} and Zn^{2+} react with water (HOH) to form a basic substance that facilitates the catalytic reaction of chalcone. After adding acetophenone, agglomeration is observed in the reaction mixture (as shown in Figure 7), which may indicate the formation of bonds between acetophenone and the catalyst surface.

The proposed reaction mechanism (illustrated in Figure 8) reveals that the reactivity of the catalyst is closely linked to the characteristics of the ions and their ability to interact with the surface [35]. The NPc surface features groups of oxygen (=O or -OH), and the Zn^{2+} ion, with 28 electrons, can capture four electron doublets [36]. When oxygen, acting as a neutral ligand on the NPc surface, binds to Zn^{2+}, it allows zinc to achieve an electronic configuration similar to that of the noble gas krypton (with 36 electrons), potentially

enhancing the stability of the Zn-NP complex. Similarly, the potassium ion K^+, which is formed by the loss of an electron from a potassium atom, attains a more stable electronic state similar to that of argon (a noble gas). Incorporating the K^+ ion into the NPc sites on the surface could improve the basic resistance of the K-NP catalyst, enhancing its stability.

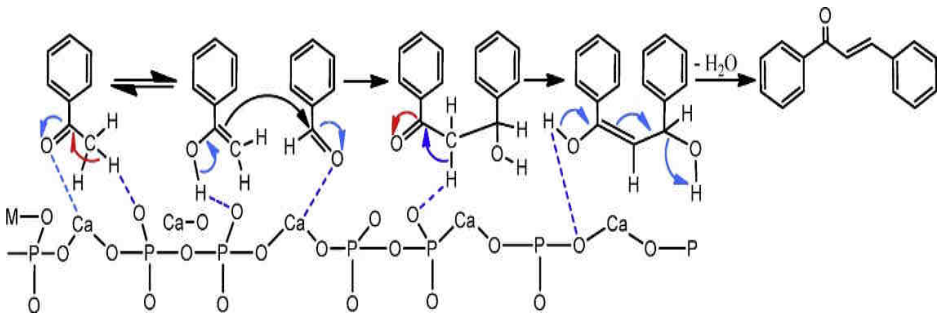


Fig. 8. Proposed reaction mechanism for chalcone synthesis [35]

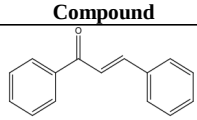
The efficiency and catalytic stability of the K-NP and Zn-NP catalysts may stem from the surface interaction between the basic sites of NPc (specifically the oxygen in phosphate PO_4^{3-} and calcium oxide CaO) and the Lewis acid sites represented by K^+ and Zn^{2+} ions. The basic sites on the calcined phosphate (NPc) play a crucial role in extracting protons from acetophenone. Additionally, the carbonyl group of acetophenone interacts with the acid sites of the K^+ and Zn^{2+} ions present in the K-NP and Zn-NP complexes, which activates the carbonyl for nucleophilic attack by benzaldehyde.

Comparison of catalyst activity

Table 1 shows the results of chalcone synthesis by the Claisen-Schmidt condensation reaction using various phosphate catalysts described in the literature.

Table 1

Comparison of chalcone synthesis with phosphate catalysts (solvent water)

Compound	Catalyst	Time [h]	Yield [%]	References
	K/NP	10	70	[17]
	NP	24	12	[30]
	HAP	1	80	[37]
	NPc	12	74	Present work
	K-NP		98	
	Zn-NP		96	

Hydroxylapatite (HAP); natural phosphate (NP); potassium/phosphate (K/NP)

The results indicate that the K-NP, Zn-NP, and NPc catalysts are among the most efficient options when used in a water-based reaction solvent. The K-NP and Zn-NP catalysts achieved yields of at least 74 % at room temperature within a reaction time of less than 12 hours, using only 1 g of catalyst. These outcomes are very promising and suggest new opportunities for exploring the use of these catalysts in other organic syntheses while adhering to environmental standards and the principles of green chemistry.

Product characteristics

The product obtained is yellow with a melting point of 65 °C, higher than the theoretical value given in the literature (56-57) °C, reflecting the purity of the product obtained [9]. Thin-layer chromatography (TLC) gave a frontal ratio (Rf) of 0.75, confirming the purity of the product. The experimental UV-Vis absorption spectrum of the product obtained in ethanol solution is shown in Figure 9. This spectrum is characterised by two λ_{max} bands between 215 nm - 245 nm (band I) and between 250 nm - 400 nm (band II) which have been attributed to n $-\pi^*$ and π $-\pi^*$ transitions respectively [38-41]. These absorption bands can be attributed to the Ph-C=O and Ph-CH=CH- moiety of the chalcone molecule.

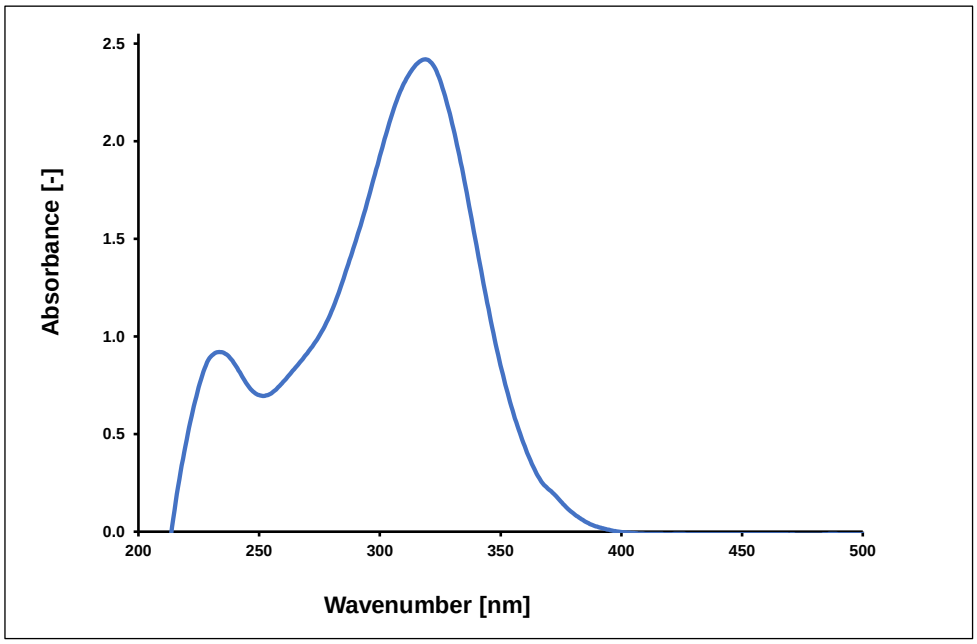


Fig. 9. UV-Vis spectrum of synthesised chalcone

Conclusion

The synthesis of chalcones has been achieved through Claisen-Schmidt condensation in water, utilising catalysts derived from Kotchari rock phosphate. The results indicate that Kotchari rock phosphate, when supported by potassium and zinc, serves as an effective catalyst for Claisen-Schmidt condensation reactions. These heterogeneous catalysts demonstrate high catalytic activity in pure water as a solvent and can be recovered and reused without significant loss of effectiveness.

Additionally, the diversification of metal ions has shown that these catalysts can facilitate the formation of chalcones with varying electron-withdrawing and electron-donating groups, highlighting their versatility. The findings pave the way for potential new applications in organic chemistry, particularly in the synthesis of compounds with notable properties in the pharmaceutical and biological fields.

Our ongoing research aims to further investigate the applicability of these catalysts in a range of organic synthesis reactions. Furthermore, we plan to enhance the catalytic activity of the developed catalysts by reducing their quantity during the synthesis process and simultaneously shortening reaction times.

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