Synthesis of new bimetallic phosphate (Al/Ag₃PO₄) and study for its Catalytic performance in the synthesis of 1,2-dihydro-l-phenyl-3H-naphth[1,2-e]-[1,3] oxazin-3-one derivatives

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Abstract: This work aims to prepare a new bimetallic phosphate catalyst using a new simple and effective method. This new catalyst was ready for the first time by a modification of Triple Super Phosphate (TSP) fertilizer with silver sulfate (Ag₂SO₄), followed by the impregnation of the aluminum atoms using aluminum nitrate (Al(NO₃)₃). The use of Al/Ag₃PO₄, for the first time as a heterogeneous catalyst in organic chemistry, offers a new, efficient, and green pathway for synthesizing 1,2-dihydro-l-phenyl-3H-naphth[1,2-e]-[1,3]oxazin-3-one derivatives by one-pot three-component cyclocondensation of β-naphthol, aryl aldehyde, and urea. The structure and the morphology of the prepared catalyst were characterized by spectroscopic methods such as X-Ray Diffraction (XRD), Fourier Transform Infrared spectroscopy (FT-IR), and dispersive X-ray spectrometry coupled with a scanning electron microscope (EDX-SEM). In addition, the optimization of the reaction parameters was carried out considering the effect of catalyst amount, the temperature, and the solvent. The procedure described herein allowed a comfortable preparation of oxazine derivatives with excellent yields, short reaction times, and in the absence of organic solvent.

Keywords: One-pot reaction; heterogeneous catalyst; TSP fertilizer; Al/Ag₃PO₄; Oxazine derivatives.

1. Introduction

Over the last few years, multicomponent reactions (MCRs) have incited great interest and were used to synthesize complex molecules and are highly functionalized in a single synthetic operation 1,2. MCRs are considered an inventive strategy in organic chemistry 3,4. Therefore, multicomponent reactions are part of sustainable chemistry and constitute a novel way of ideal organic synthesis. Complex structures are rapidly obtained from very simple substrates involving simple synthetic operations and safe processes in the environment. The use of eco-friendly solvents and reusable heterogeneous catalysts make these reactions ecological and environmentally benign 5,9. In this context, organic chemists are headed towards applying different catalysts in multicomponent reactions. Among the used catalysts, one can find heterogeneous catalysts which are recoverable and reusable several times. The application of heterogeneous catalysts allows having advantages such as the simplicity of the procedure, high atomic economy, high selectivity, structural diversity, and environment protection 10-12.

These catalysts have become very popular for their ability to catalyze many cascading processes under mild conditions and, often, with high levels of regioselectivity.

The oxazinone derivatives synthesis is one of the multicomponent reactions which have attracted widespread attention. These compounds have interesting pharmacological properties associated with their heterocyclic structure 13,14. For example, in 1998, the Food and Drug Administration has approved naphthoxazinone derivatives as antibacterial agents and benzoxazinone as a non-nucleoside reverse transcriptase inhibitor 15. Nowadays, these derivatives are used for the treatment of AIDS 16. Therefore, numerous methods for the synthesis of oxazinone derivatives are reported in the literature 17,18. Some strategies for the synthesis of 1,2-dihydro-1-arylnaphtho [1, 2-e]-[1,3]oxazine-3-ones synthesis were described by three-component condensation of urea, or thiourea, aldehyde, and β-naphthol in the presence of the different catalysts such as phosphomolybdic acid 19, Thiamine Hydrochloride 20, iron(III) phosphate 21, Chitosan 22, wet cyanuric chloride 23, Silica vanadic acid 18, graphene oxide 24, amberlite IRA-400 CI Resin 25, and TiCl₄ 26, etc.

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This paper constitutes the continuation of our previous works aiming to develop synthetic methods that respect the environment, leading to a wide variety of heterocyclic compounds biologically active using heterogeneous catalysts based on phosphate fertilizers \(^{27-30}\). The novelty of this work is the synthesis of a new bimetallic phosphate/Aluminium complex "Al/Ag3PO4", on the one hand, and its use for the first time as a new heterogeneous bimetallic catalyst in the synthesis of naphthoxazin-3-one derivatives on the other.

This support was synthesized for the first time in our laboratory by simple and less expensive methods consisting of preparing the catalytic support based on silver phosphate by the co-precipitation process followed by the impregnation of alumina using a solution of Al(NO\(_3\))\(_3\). Furthermore, to study the catalytic’s performance, Al/Ag3PO4 was used for the first time as a new heterogeneous catalyst in the synthesis of 1, 2-dihydro-1-arylnaphtho[1, 2-e]-[1,3] oxazine-3-ones derivative.

2. Experimental

2.1. Catalyst preparation

The Al/Ag3PO4 support was prepared by a simple and less expensive method, consisting of dissolving 6 g of AgSO\(_4\) in 10 ml of water. The solution was stirred at 90°C for 60 min. A second solution was prepared by dissolving 2 g of Triple Super Phosphate (TSP) fertilizer in 5ml water at room temperature. Both solutions were mixed and started at 95°C. Afterward, the ammonia solution was gradually added until the pH of the solution reached 7. Next, the prepared support was doped with aluminum using the impregnation process. The solvent volume (water) was reduced, and the aluminum nitrate solution (1.87 mol/L) was added. The mixture was subjected to a magnetic stirring at a temperature between 90 and 120°C for 40 min. Finally, the solid formed was washed several times with double-distilled water, dried in the oven for 12 h at 110°C, and calcined at a temperature between 500-700°C (Figure 1).

![Figure 1. Al/Ag3PO4 preparation](image)

The X-ray diffraction (XRD) analysis was realized using a PANalytical X’Pert3 Powder diffractometer at room temperature to identify the prepared catalyst and verify its crystal structure. The catalyst’s morphology was observed using a Scanning Electron Microscopy Analyzer (SEM) (a Tescan vega 3 high-resolution scanning electron microscopy). Elemental analysis was performed by Energy Dispersive X-ray (EDAX) using ESCALAB MkII electron spectrometer. Fourier Transform Infrared Spectroscopy (a Bruker vertex 70 DTGS spectrophotometer with 4 cm\(^{-1}\) programs) was carried out in the range of 400–4000 cm\(^{-1}\) wavenumber for addressing surface functional groups.

2.2. General procedure

A mixture of β-naphthol (1 mmol), arylaldehyde (1 mmol), and urea (1.5 mmol) in the presence of Al/Ag3PO4 was rapidly stirred and heated at a temperature between 100 and 110°C for the appropriate time. The reaction progress was monitored by thin-layer chromatography (TLC). After checking the completion of the reaction by TLC, the mixture was extracted with ethyl acetate, and the
solid catalyst was filtered for subsequent reuse. Finally, the mixture was evaporated in a vacuum to give the crude product, purified by recrystallization from ethanol to obtain the desired product (4a-4i).

The reagents and the starting materials used in this study were purchased from Sigma Aldrich and Riedel-de Haen. The synthesized products were identified by comparing their spectral data and physical properties with those of the pure samples reported in the literature. Melting points were determined using Kofler hot stage apparatus. Proton (^1)H and carbon (^13)C nuclear magnetic resonance spectra were performed using the Bruker AC-400 F spectrometer (307.8 MHz).

The Spectral (^1)H NMR, ^13)C NMR and Analytical Data

1,2-dihydro-1-phenyl-3H-naphtho[1,2-e]-[1,3]oxazin-3-one (4a):

^1)H NMR (300 MHz, DMSO-d6): δ ppm 6.2 (d, 1H, CH), 7.2-8.2 (m, 11H, ArH), 8.9 (d, 1H, NH), (75 MHz, DMSO-d6) δ ppm: 54.24, 114.91, 117.33, 123.56, 125.54, 127.19, 127.53, 128.48, 129.35, 133.5, 141.3, 151.8, 158.7.

1-(4-chlorophenyl)-3H-naphtho[1,2-e]-[1,3]oxazin-3-one (4b):

^1)H NMR (300 MHz, DMSO-d6): δ ppm 6.72 (d, 1H, CH), 7.16-7.99 (m, 10H, ArH), 8.64 (d, 1H, NH), (75 MHz, DMSO-d6) δ ppm: 162.11, 153.88, 138.24, 133.61, 131.34, 130.35, 125.98, 129.46, 129.21, 128.98, 127.18, 126.36, 123.74, 117.33, 114.61, 52.68.

1,2-dihydro-1-(4-bromophenyl)-3H-naphtho[1,2-e]-[1,3]oxazin-3-one (4c):

^1)H NMR (300 MHz, DMSO-d6): δ ppm 6.22 (d, 1H, CH), 7.1-8 (m, 10H, ArH), 8.9 (d, 1H, NH), (75 MHz, DMSO-d6) δ ppm: 52.9, 115.4, 118.9, 121, 123.8, 128.3, 128.8, 132.1, 133.5, 140, 151.8, 157.8.

1,2-dihydro-1-(4-methoxyphenyl)-3H-naphtho[1,2-e]-[1,3]oxazin-3-one (4d):

^1)H NMR (300 MHz, DMSO-d6): δ ppm: 6.12 (d, 1H, CH), 6.75-8 (m, 10H, ArH), 8.8 (d, 1H, NH), (75 MHz, DMSO-d6) δ ppm: 53.65, 55.53, 114.66, 117.30, 123.29, 125.47, 127.73, 128.65, 129.05, 129.35, 135.48, 147.76, 149.79, 159.29.

1,2-dihydro-1-(p-toly)-3H-naphtho[1,2-e]-[1,3]oxazin-3-one (4e):

^1)H NMR (300 MHz, DMSO-d6): δ ppm: 6.13 (d, 1H, CH), 7.04-7.95 (m, 10H, ArH), 8.82 (d, 1H, NH), (75 MHz, DMSO-d6) δ ppm: 149.84, 147.87, 143.29, 130.87, 130.71, 129.42, 129.33, 129.09, 128.50, 127.84, 127.41, 125.56, 123.51, 117.31, 114.48.

1,2-dihydro-1-(4-nitrophenyl)-3H-naphtho[1,2-e]-[1,3]oxazin-3-one (4f):

^1)H NMR (300 MHz, DMSO-d6): δ ppm: 6.35 (d, 1H, CH), 7.04-8.08 (m, 10H, ArH), 8.1 (d, 1H, NH), (75 MHz, DMSO-d6) δ ppm: 109.22, 119.08, 119.78, 124.35, 124.89, 127.04, 127.87, 128.46, 128.46, 129.59, 129.86, 130.74, 137.57, 147.78, 148.80, 149.53, 154.30.

1,2-dihydro-1-(2-chlorophenyl)-3H-naphtho[1,2-e]-[1,3]oxazin-3-one (4g):

^1)H NMR (300 MHz, DMSO-d6): δ ppm: 6.43 (d, 1H, CH), 7.01-8.12 (m, 10H, ArH), 8.31 (d, 1H, NH), (75 MHz, DMSO-d6) δ ppm: 109.22, 119.08, 119.78, 124.35, 124.89, 127.04, 127.87, 128.46, 128.46, 129.59, 129.86, 130.74, 137.57, 147.78, 148.80, 149.53, 154.30.

1-(4-fluorophenyl)-3H-naphtho[1,2-e]-[1,3]oxazin-3-one (4h):

^1)H NMR (300 MHz, DMSO-d6): δ ppm 6.12 (d, 1H, CH), 7.2-7.89 (m, 10H, ArH), 8.60 (d, 1H, NH), (75 MHz, DMSO-d6) δ ppm: 161, 154.28, 148.20, 131.11, 140.34, 127.05, 129.18, 129.13, 129.01, 128.98, 127.14, 126.52, 123.86, 117.11, 114.75, 52.08.

1-(4-aminophenyl)-3H-naphtho[1,2-e]-[1,3]oxazin-3-one (4i):

^1)H NMR (300 MHz, DMSO-d6): δ ppm 5.06 (d, 1H, CH), 7.01-7.77 (m, 10H, ArH), 8.15 (d, 1H, NH), (75 MHz, DMSO-d6) δ ppm: 157.8, 154.28, 152.11, 151.8, 145.30, 133.5, 131.05, 129, 128.3, 126.3, 123.6, 123.2, 118.4, 115.70, 52.9.

3. Results and Discussion

3.1. Catalyst characterization

XRD analysis was used to study the phase structure and the effect of doping Al^3+ ion on the crystal structure of Ag3PO4 (Figure 2). First of all, we can notice that all diffraction peaks of the samples can be indexed on the cubic structure centered on the basic structure of Ag3PO4 (JCPDS n° 06-0505). Furthermore, no impurity phase, such as Ag2SO4 and AgNO3, is observed in the XRD spectrum of Al/Ag3PO4; this implies that the doping does not affect the crystal structure of the catalyst. XRD analysis shows the formation of the Ag3PO4 phase and Al-O structure where the peaks in 20.86°, 29.75°, 33.47°, 36.71°, 42.69°, 47.79°, 52.72°, 55.14°, 57.24°, 61.93°, 71.96°, 87.32°, and 89.26° (20) belong to the Ag3PO4. However, the 2 theta positions in 39.32, 45, 72, 46.93, and 67.32 correspond to the Al-O phase. Besides, it can be observed that there is no significant difference in crystal structure between the Ag3PO4 doped with aluminum and Ag3PO4, indicating a good dispersion of Al3+ ions in the crystal lattice of Ag3PO4. The XRD model is well-matched with the XPert High Score program database (PDF N° 01-084-0510 and 00-001-1307) and the results cited in the literature. The XRD diagram also shows high-intensity peaks, which are mean the excellent crystallinity of the prepared support.
A FTIR analysis was performed. The IR spectrum (Figure 3) shows the OH group's characteristic peaks located at 1600 and 3440 cm\(^{-1}\) correspond to the water molecules absorbed by KBr. The peaks characteristic of the PO\(_4^{3-}\) ion was observed at 1380 cm\(^{-1}\) and between 550 and 559 cm\(^{-1}\). Besides, the characteristic bands of the Al-O group are located at 616 and 1017 cm\(^{-1}\). These results confirmed the structure proposed previously. Our catalyst's exact chemical composition was completed by the scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-Ray Analysis (SEM/EDX).

The morphological and microstructural details of the products were also examined by scanning electron microscopy (SEM). As shown in Figure 4, the SEM image reveals that the obtained support Al/Ag\(_3\)PO\(_4\) exists in the form of intense grain. On the other hand, and applying Scherrer's equation \(^3\), it was theoretically found that the particle size between 3800 and 4020 nm. The chemical composition is
determined by Energy Dispersive X-ray analysis (Figure 5). The results show that the prepared support contains four principal elements with variable proportions (Table 1): oxygen, silver, phosphates, and aluminum. The overall results of the analysis confirmed that the structure of the catalyst prepared is Al/Ag₃PO₄.

**Table 1. Weight and atomic percentage in the Al/Ag₃PO₄ support.**

| Element | Weight (%) | Atomic (%) |
|---------|------------|------------|
| O       | 25.4       | 58.4       |
| Al      | 10.5       | 14.4       |
| P       | 6.3        | 7.5        |
| Ag      | 57.7       | 19.7       |

3.2. Synthesis of 1, 2-dihydro-1-aryl naphtho[1,2-e][1,3]oxazin-3-ones using Al/Ag₃PO₄ as a heterogeneous catalyst

The prepared material Al/Ag₃PO₄ was applied as a new heterogeneous catalyst in the synthesis of oxazine derivatives; a catalytic test was realized as a first step to show its efficiency. The condensation of β-naphthol, benzaldehyde, and urea was considered as a model reaction. It was performed in the absence and in the presence of the Al/Ag₃PO₄ support (Scheme 1) to test its catalytic activity, and the obtained results are shown in Table 2. Without a catalyst, the
condensation takes a long time with only 10% yield of the desired product (Table 2, entry 1). When the prepared material Al/Ag₃PO₄ is introduced into the reaction medium, the yield increases, and the reaction time decreases. This is due to the activation of the condensation by the active sites of our support (Table 2, entry 2). The catalytic test shows that Al/Ag₃PO₄ has the property and can be an efficient catalyst in the oxazine derivatives synthesis. This preliminary study aimed to use the Al/Ag₃PO₄ as a heterogeneous catalyst; for this purpose, the heterogeneity of this bimetallic complex was checked.

The test consists of putting the catalyst in the solvent under the same reaction conditions for one hour. Then, the catalyst was filtered, and the recovered filtrate (solvent) is used as a reaction medium. The experimental results show that the reaction time and the yield do not undergo significant change when the recovered solvent is used (Table 2, entry 3). This lets us deduce that the filtrate does not contain any traces of the catalyst, showing that the catalyst is not soluble in the solvent; therefore, Al/Ag₃PO₄ can be considered a heterogeneous catalyst.

To synthesize the naphthoxazinone derivatives, several preliminary experimental studies were carried out to optimize the reaction conditions and examine the influence of some reaction parameters on the catalyst's behavior with the reagents. These parameters are the catalyst mass, temperature, and solvent nature (polar protic, aprotic, and non-polar); the reaction was also performed in the free-solvent condition. The best results are presented in Table 3 (Entries 1-7). Generally, the solvent plays a vital role in the reaction process; it facilitates the formation and the separation of the charges on the active sites of the reagents for obtaining the final product. In this reaction, the results obtained from the study of the solvent effect show that all used solvents could favor the reaction to a certain extent. But the use of some solvents leads to a long reaction time to reach only an acceptable yield. However, the reaction could be completed quickly and give the desired product an excellent yield when it is carried out without solvent (Table 3, entry 1). This result can be explained by the extensive contact of the reagents on the catalyst's surface and an increase in the adequate shocks.

Furthermore, it is well known that the catalyst amount plays an essential role in reaction advancement. Thus, this quantity was optimized, for the model reaction under free-solvent conditions, by varying it from 1 mg to 40 mg. The results obtained were collected in Table 3 (Entries 8-15).

According to the obtained results, it is noticed that using a small mass of the catalyst, between 1, and 40mg, leads to the desired product with a low yield. It can also be seen, from Table 3, that the yield increased in parallel with the mass until reaching the maximum of 92% in only 12 min with a catalyst mass of 8 mg. For the optimal mass (Table 3, entry 11). It should also be noted that the reaction's yield decreases when the reaction time increases. This is due to the catalyst's poisoning of the catalyst's active sites or the degradation of the product. The data in Table 3 shows that the yield is reduced when catalyst mass is increased. This decline may be due to two main factors, the dispersion of the reagents over a large surface of the catalyst reduces the real shock between the reactants or the degradation of the final product because the active site degraded the used catalyst.

The third study concerns the temperature effect on the reaction yield while knowing that the temperature directly influences the catalyzed reaction rate. Thus,

![Scheme 1. Valorization of Al/Ag₃PO₄ as catalyst in the 2-dihydro-1-phenyl-naphtho [1,2-e] [1,3] oxazin-3 (2H)-one synthesis](image)

**Table 2. Catalytic test of Al/Ag₃PO₄ in the 1,2-dihydro-1-phenyl-3H-naphth[1,2-e]-[1,3]oxazin-3-one derivatives synthesis**.

| Entry | Reaction condition | Time (min) | Yieldb (%) |
|-------|-------------------|------------|------------|
| 1     | without catalyst  | 180        | 10         |
| 2     | in the presence of the catalyst | 60 | 64 |
| 3     | with recovered solvent | 180 | 15 |

*aReaction conditions: β-naphthol (1mmol), aldehyde (1mmol), urea (1.5 mmol) and 0.01g of catalyst Al/Ag₃PO₄, EtOH.
*bIsolated yields*
temperature screening was performed (Table 3, entries 16-20). It was found that the catalytic activity of Al/Ag₃PO₄ in the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-ones increases by raising the temperature. The best yield (92%), is achieved at 110°C, which was chosen as the optimal temperature in the rest of this work.

**Table 3.** Optimization of reaction conditions for the synthesis of 1,2-dihydro-1-phenyl-3H-naphth[1,2-e][1,3]oxazin-3-one².

| Entry | Solvent          | Amount of catalyst (mg) | Temperature (°C) | Time(min) | Yieldb (%) |
|-------|------------------|-------------------------|------------------|-----------|------------|
| 1     | Solvent-free     | 5                       | 100              | 12        | 81         |
| 2     | Ethanol          | 5                       | Reflux           | 120       | 62         |
| 3     | Methanol         | 5                       | Reflux           | 240       | 46         |
| 4     | DMF              | 5                       | Reflux           | 50        | 85         |
| 5     | Chloroform       | 5                       | Reflux           | 90        | 51         |
| 6     | Acetonitrile     | 5                       | Reflux           | 80        | 50         |
| 7     | Dichloromethane  | 5                       | Reflux           | 70        | 40         |
| 8     | Solvent-free     | 1                       | 100              | 40        | 42         |
| 9     | Solvent-free     | 5                       | 100              | 30        | 63         |
| 10    | Solvent-free     | 7                       | 100              | 20        | 86         |
| 11    | Solvent-free     | 8                       | 100              | 12        | 92         |
| 12    | Solvent-free     | 8                       | 100              | 40        | 64         |
| 13    | Solvent-free     | 9                       | 100              | 12        | 91         |
| 14    | Solvent-free     | 30                      | 100              | 25        | 57         |
| 15    | Solvent-free     | 40                      | 100              | 30        | 48         |
| 16    | Solvent-free     | 8                       | 60               | 120       | Trace      |
| 17    | Solvent-free     | 8                       | 70               | 120       | 18         |
| 18    | Solvent-free     | 8                       | 100              | 25        | 81         |
| 19    | Solvent-free     | 8                       | 110              | 12        | 92         |
| 20    | Solvent-free     | 8                       | 130              | 12        | 92         |

* Reaction conditions: β-naphthol (1mmol), aldehyde (1mmol), urea (1.5 mmol) and 8 mg of catalyst Al/Ag₃PO₄, Free-solvent, bIsolated yields

To generalize this methodology to synthesize others 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazin-3-one derivatives, the reaction of β-naphthol with a variety of aromatic aldehydes and urea in the presence of the optimal catalytic amount of Al/Ag₃PO₄ was performed (Scheme 2). Table 4 shows that the obtained results were excellent in terms of yields and product purity, and this using aromatic aldehydes carrying either electron-donating or electron-withdrawing substituents. However, when the reactions were conducted without the catalyst, the product yields were only 15 to 20%. Therefore, the Al/Ag₃PO₄ support is an efficient catalyst for this type of reaction.

**Scheme 2.** Al/Ag₃PO₄ Catalyzed Synthesis of 1,2-dihydro-1-phenyl-3H-naphth[1,2-e][1,3] oxazin-3-one derivatives (4a-i)
Table 4. Synthesis of 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazin-3-one derivatives\textsuperscript{a}.

| Entry | Substrate | Product | Time (min) | Yield\textsuperscript{b} (%) | MP(°C) |
|-------|-----------|---------|------------|----------------|--------|
| 4a    | \(\text{Ph} \quad \text{C}=\text{O}\) | \(\text{Ph} \quad \text{C} \quad \text{N} \quad \text{O}\) | 12 | 91 | 216-218/218-220 |
| 4b    | \(\text{Cl} \quad \text{Ph} \quad \text{C}=\text{O}\) | \(\text{Cl} \quad \text{Ph} \quad \text{C} \quad \text{N} \quad \text{O}\) | 10 | 93 | 214-216/210-212 |
| 4c    | \(\text{Br} \quad \text{Ph} \quad \text{C}=\text{O}\) | \(\text{Br} \quad \text{Ph} \quad \text{C} \quad \text{N} \quad \text{O}\) | 10 | 95 | 220-222/216-218 |
| 4d    | \(\text{MeO} \quad \text{Ph} \quad \text{C}=\text{O}\) | \(\text{MeO} \quad \text{Ph} \quad \text{C} \quad \text{N} \quad \text{O}\) | 10 | 91 | 188-190/188-188 |
| 4e    | \(\text{Me} \quad \text{Ph} \quad \text{C}=\text{O}\) | \(\text{Me} \quad \text{Ph} \quad \text{C} \quad \text{N} \quad \text{O}\) | 12 | 90 | 167-169/164-166 |
| 4f    | \(\text{O}_{2}\text{N} \quad \text{Ph} \quad \text{C}=\text{O}\) | \(\text{O}_{2}\text{N} \quad \text{Ph} \quad \text{C} \quad \text{N} \quad \text{O}\) | 15 | 87 | 210-212/206-207 |
| 4g    | \(\text{Cl} \quad \text{Ph} \quad \text{C}=\text{O}\) | \(\text{Cl} \quad \text{Ph} \quad \text{C} \quad \text{N} \quad \text{O}\) | 20 | 81 | 244-246/249-251 |
As our contribution to green chemistry development, the reusability of Al/Ag$_3$PO$_4$ catalysts is studied. For this, the model reaction is carried out with larger reagents masses, 10 mmol of benzaldehyde, 10 mmol of β-naphthol, and 15 mmol of urea in the presence of 80 mg of the catalyst. After completion of the reaction, it was recovered by simple filtration. The catalyst was then dried and washed with ethyl acetate and acetone four times maximum and dried at a temperature of 120°C for 2 hours to remove the product residues and activate the catalytic sites. Thus the recovered catalyst is ready for another reutilization. On the other hand, Figure 6 shows good reuse of the catalyst. It can be reutilized up to four times without significant loss of its catalytic activity or a change in its structure, as shown in the FTIR spectrum and X-ray diffraction pattern (Figures 7-8). Furthermore, the experimental results indicate a slight decrease in the yield after each reuse; the reduction could explain this in the catalytic capacity due to its active sites' slight deactivation. To conclude, the new support Al/Ag$_3$PO$_4$ can be considered as an efficient heterogeneous catalyst for the one-pot synthesis of 1,2-dihydro-1-arylnaphthalene [1,2-e] [1,3] oxazin-3-ones from 2-naphthol, aldehyde, and urea under solvent-free conditions.

![Figure 6](image-url)
To elucidate the role played by the catalyst Al/Ag₃PO₄ in the reaction medium and to explain the formation of 1,2-dihydro-1-phenyl-3H-naphth[1,2-e][1,3]oxazin-3-one derivatives, the following mechanism is proposed (Scheme 3). Initially, the carbonyl group of aryl aldehyde was activated through the Van Der Wall interactions, facilitating the acylimine intermediate. Next, the nitrogen pair electrons attacked the carbonyl group of aldehyde. Then the β-naphthol was activated, which subsequently resulted in the formation of a second intermediate by electrophilic substitution, and finally, the pure product 4a was obtained by removing NH₃. The mechanism is proposed according to our support’s characteristics and chemical properties and with the help of bibliographical research 39.

Figure 7. FTIR spectrum of the recovered catalyst

Figure 8. XRD analysis of Al/Ag₃PO₄ after reuse.
To confirm the catalytic efficiency of the prepared catalyst (Al/Ag₃PO₄) used in the 1,2-dihydro-1-phenyl-3H-naphth[1,2-e][1,3]oxazine-3-one derivatives, a comparative study with other catalysts reported in the literature for the same reaction was carried out. The results are collected in Table 5.

### Table 5. Comparative study of 1,2-dihydro-1-aryl-naphth[1,2-e][1,3]oxazine -3-one synthesis 4a using different catalysts.

| Entry | Condition | T/°C | Time/min. | Yield % | Reference |
|-------|-----------|------|-----------|---------|-----------|
| 1     | phosphomolybdic acid/ DMF | 100  | 180       | 85-92   |        |
| 2     | ZnONPs/ solvent free | 150  | 60-90     | 76-94   |        |
| 3     | HClO₄/SiO₂/ solvent free | 150  | 60       | 75-92   |        |
| 4     | Fe₃O₄@MAP nanoparticles/ aqueous ethanol (3:1) ultrasonic irradiation | 160  | 15-30    | 72-92   |        |
| 5     | Fe₃O₄@nano-cellulose/TiCl/ solvent free | r.t  | 3-30     | 80-98   |        |
| 6     | Nano-Al₂O₃/BF₃/Fe₃O₄/H₂O | r.t  | 15-20    | 80-92   |        |
| 7     | FePO₄ | 150  | 20-30    | 95      |        |
| 8     | [bnmim] [HSO₄] | r.t  | 10       | 65-77   |        |
| 9     | Al/Ag₃PO₄ | 110  | 10-20    | 81-95   | This work |

Comparing the yields and reaction times obtained with those reported in previous work using other catalysts shows that Al/Ag₃PO₄ presents an interesting catalytic activity for this synthesis. Indeed, by comparison of different results, it can be seen that the use of a small amount of our catalyst allows obtaining the desired product with a good yield in a short reaction time. In addition, we can realize the...
reaction under green conditions (Solvent-free) and consequently contributing to sustainable development. This work presents a new simple, economical, and ecological method compared to other studies that use toxic solvents, homogeneous catalysts, or high-cost procedures.

4. Conclusion
To sum up, we have elaborated a new efficient Metal-phosphate catalyst Al/Ag:PO₃, cheap and respectful of the environment. It was synthesized according to two chemical processes. Firstly, the co-precipitation process was used to modify the TSP fertilizer with silver sulfate following the doping with aluminum by impregnation using aluminum nitrate solution. The prepared support structure and morphology were characterized by various electroscopic and microscopic techniques (XRD, FT-IR, EDX, and SEM). The Al/Ag:PO₃ application as a heterogeneous catalyst leads to a highly efficient one-pot synthesis to prepare 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazine-3-one derivatives in a three-component cyclocondensation reaction of β-naphthol, aromatic aldehydes, and urea. This ecological approach consists of using a catalyst amount of Al/Ag:PO₃ under thermal and solvent-free conditions. The advantages of the method developed in this paper are the mild reaction conditions, compatibility, easy isolation of product, and excellent reuse of the catalyst. All of these reasons make it an attractive alternative for the synthesis of naphthoxazine-3-one derivatives.

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