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Synthesis of new bimetallic phosphate (Al/Ag_3PO_4) 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 ($AgSO_4$), followed by the impregnation of the aluminum atoms using aluminum nitrate ($Al(NO_3)_3$). The use of Al/Ag_3PO_4, 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/Ag_3PO_4; 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 Cl Resin [25], and $TiCl_4$ [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/Ag_3PO_4 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-onesderivative.

2. Experimental

2.1. Catalyst preparation

The Al/Ag_3PO_4 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).

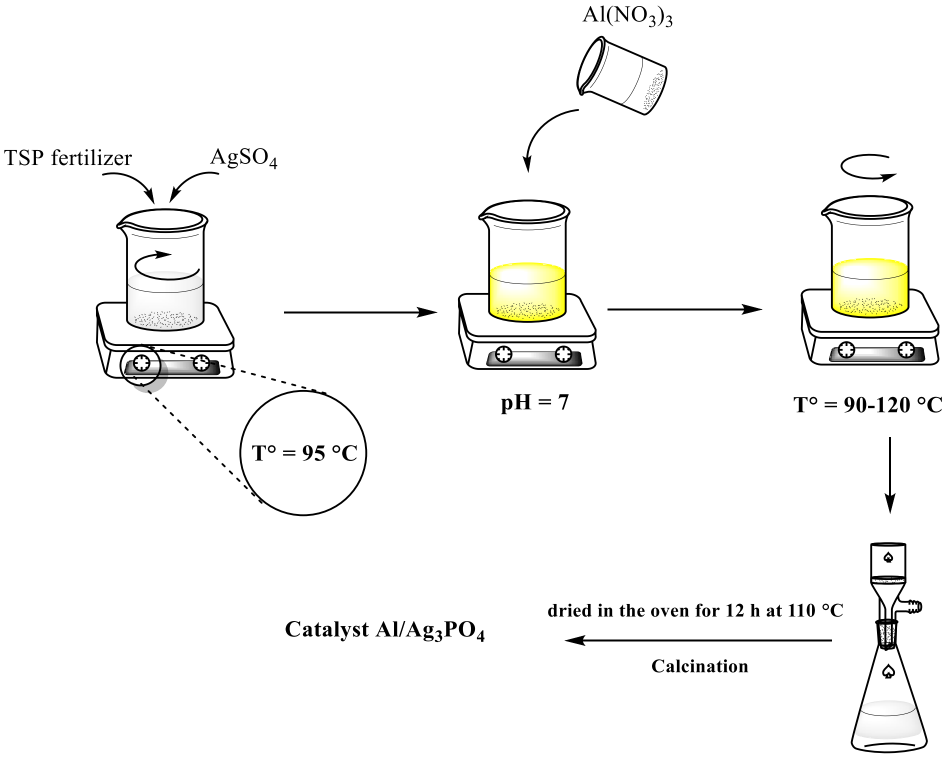


Figure 1. Al/Ag_3PO_4 preparation

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/Ag_3PO_4 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 Köfler hot stage apparatus. Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance spectra were performed using the Bruker AC-400 F spectrometer (300 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, 157.8.

1-(4-chlorophenyl)-*3H*-naphtho[1,2-*e*]-[1,3]oxazin-3-one (**4b**):
^{1}H NMR (300 MHz, DMSO-d_6) δppm 6.72 (d, 1H, CH), 7.16-7.99 (m, 10H, ArH), 8.64 (d, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6) δppm: 162.11, 153.88, 138.24, 133.61, 131.34, 130.35, 129.58, 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-d_6): *δ*ppm 6.22 (d, 1H, CH), 7.1-8 (m, 10H, ArH), 8.9 (d, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6) δppm: 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-d_6) δppm: 6.12 (d, 1H, CH), 6.75-8 (m, 10H, ArH), 8.8 (d, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6) δppm: 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-tolyl)-*3H*-naphtho[1,2-*e*]-[1,3]oxazine-3-one (4e):
^{1}H NMR (300 MHz, DMSO-d_6) δppm: 6.13 (d, 1H, CH), 7.04-7.95 (m, 10H, ArH), 8.82 (d, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6) δppm: 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-d_6) δppm: 6.35 (d, 1H, CH), 7.04-8.08 (m, 10H, ArH), 8.1 (d, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6) δppm: 109.22, 119.08, 119.78, 124.35, 124.89, 127.04, 127.87, 128.46, 128.46, 128.67, 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-d_6) δppm: 6.43 (d, 1H, CH), 7.01-8.12 (m, 10H, ArH), 8.31(d, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6) δppm: 109.22, 119.08, 119.78, 124.35, 124.89, 127.04, 127.87, 128.46, 128.46, 128.67, 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-d_6) δppm 6.12 (d, 1H, CH), 7.26-7.89 (m, 10H, ArH), 8.60 (d, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6) δppm: 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-d_6) δppm 5.01 (s, 2H, NH_2), 6.34 (d, 1H, CH), 7.01-7.77 (m, 10H, ArH), 8.15 (d, 1H, NH). ^{13}C NMR (75 MHz, DMSO-d_6) δppm: 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 phasis structure and the effect of doping Al^{3+} ion on the crystal structure of Ag_3PO_4 (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 Ag_3PO_4 (JCPDS n° 06-0505). Furthermore, no impurity phasis, such as Ag_2SO_4 and $Al(NO_3)_3$, is observed in the XRD spectrum of Al/Ag_3PO_4; this implies that the doping does not affect the crystal structure of the catalyst. XRD analysis shows the formation of the Ag_3PO_4 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° (2θ) belong to the Ag_3PO_4. 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 Ag_3PO_4 doped with aluminum and Ag_3PO_4, indicating a good dispersion of Al_3^+ ions in the crystal lattice of Ag_3PO_4. The XRD model is well-matched with the X'Pert High Score program database (PDF N° 01-084-0510 and 00-001-1307) and the results cited in the literature [31,32]. The XRD diagram also shows high-intensity peaks, which are mean the excellent crystallinity of the prepared support.

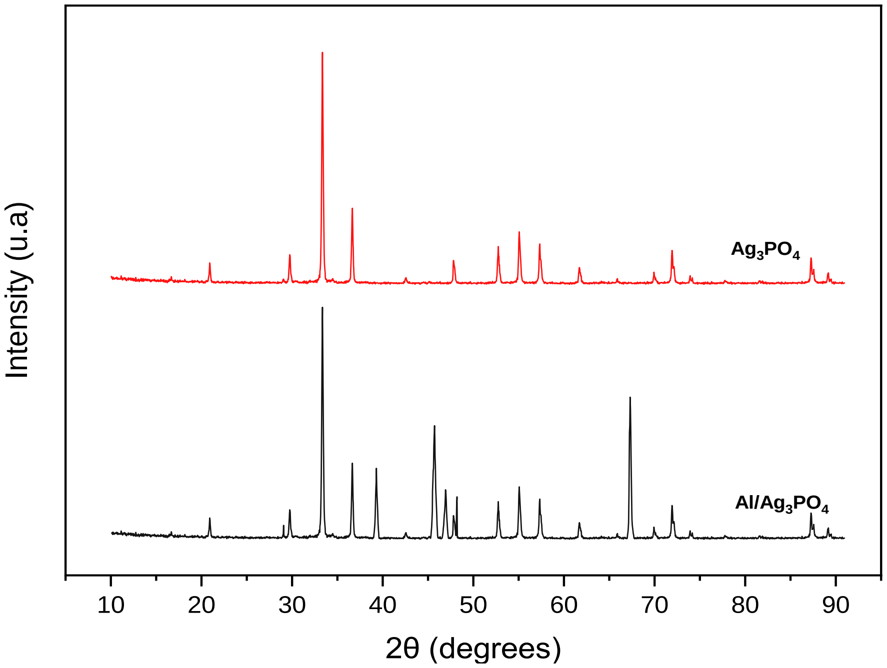


Figure 2. X-ray diffraction patterns of the prepared Al/Ag_3PO_4

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).

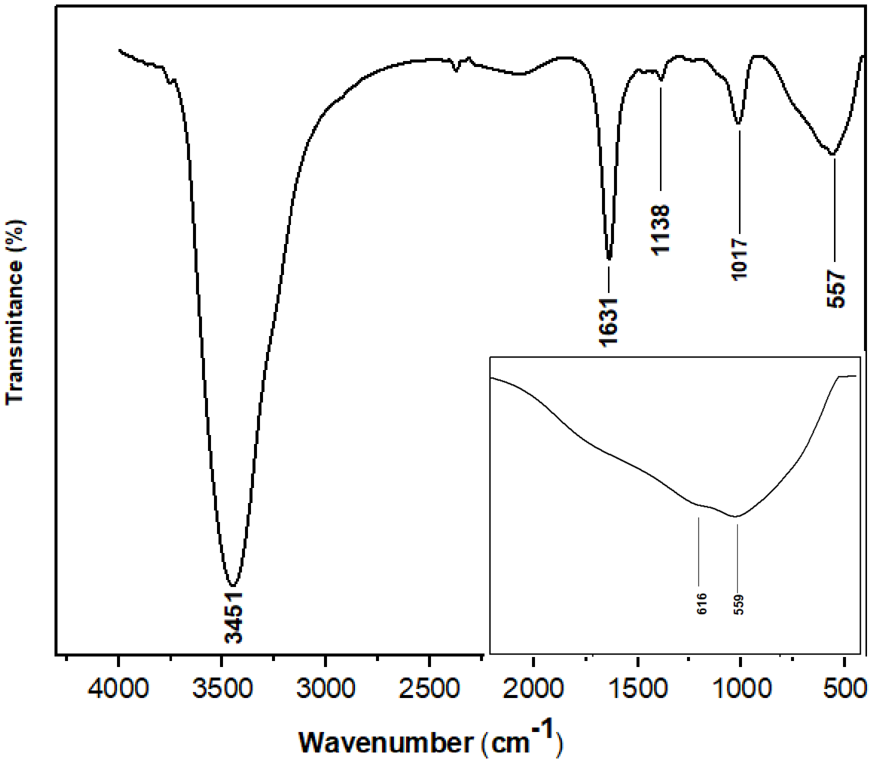


Figure 3. IR spectrum of $Al/Ag_3(PO_4)_2$

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_3PO_4 exists in the form of intense grain. On the other hand, and applying Scherrer's equation [33], 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/Ag_3PO_4.

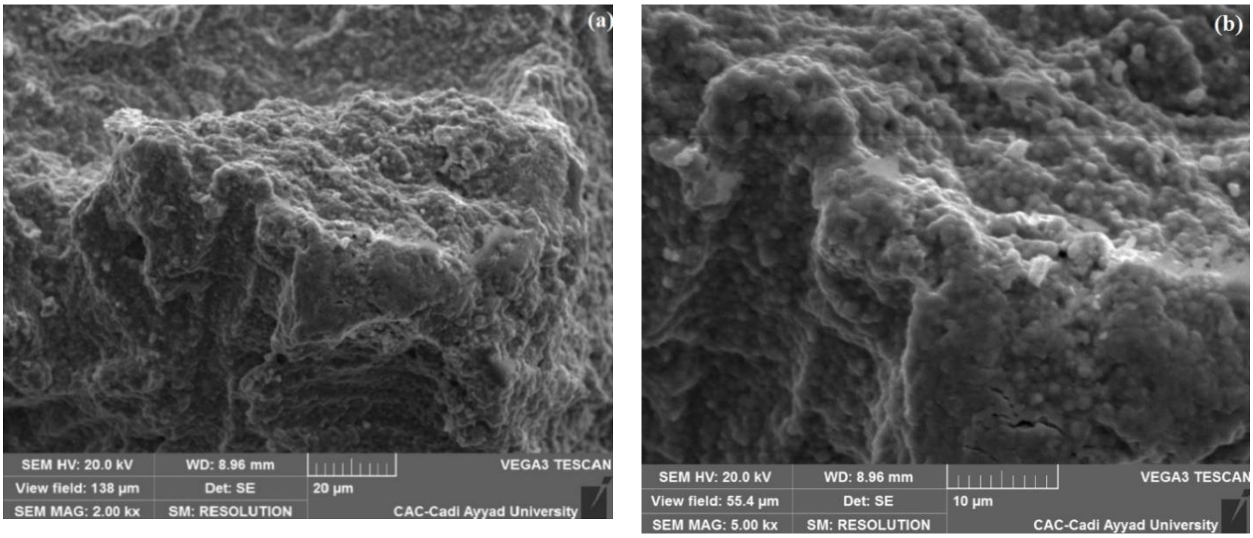


Figure 4. SEM microphotograph of Al/Ag_3PO_4 prepared from silver sulfate and MAP fertilizer, a=20 µm and b= 10 µm

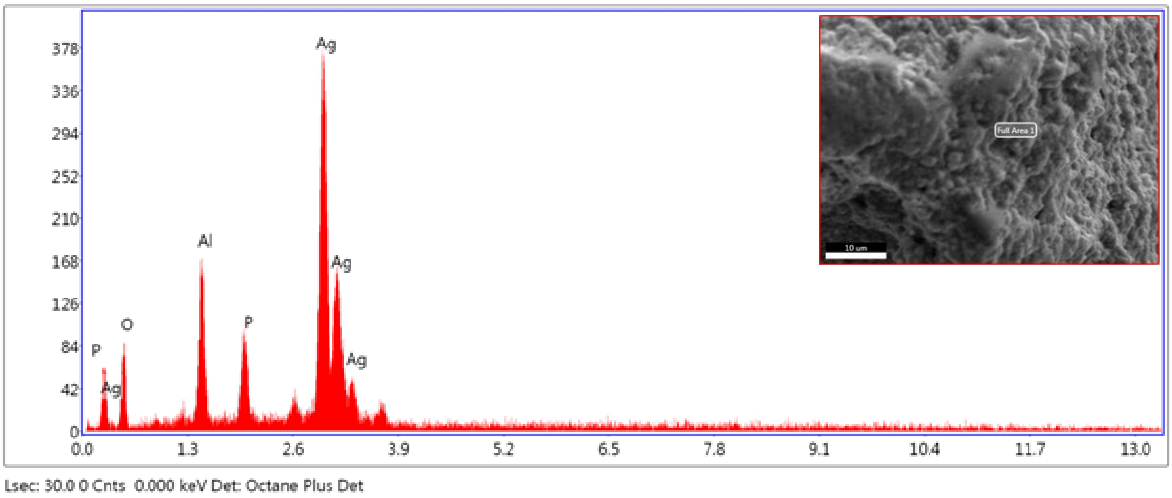


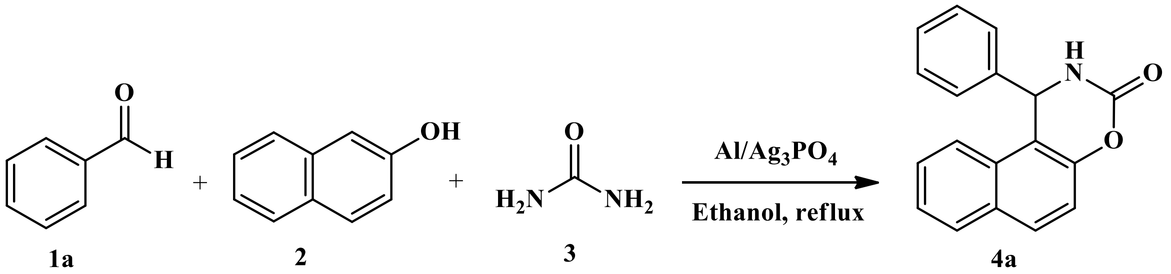
Figure 5. Catalyst's EDAX spectrum

Table 1. Weight and atomic percentage in the Al/Ag_3PO_4 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/Ag_3PO_4 as a heterogeneous catalyst

The prepared material Al/Ag_3PO_4 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/Ag_3PO_4 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/Ag_3PO_4 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/Ag_3PO_4 has the property and can be an efficient catalyst in the oxazine derivatives synthesis. This preliminary study aimed to use the Al/Ag_3PO_4 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/Ag_3PO_4 can be considered a heterogeneous catalyst.



Scheme 1. Valorization of Al/Ag_3PO_4 as catalyst in the 2-dihydro-1-phenyl-naphtho [1,2-e] [1,3] oxazin-3 (2H)-one synthesis

Table 2. Catalytic test of Al/Ag_3PO_4 in the 1,2-dihydro-l-phenyl-3H-naphth[1,2-e]-[1,3]oxazin-3-one derivatives synthesis[a].

Entry	Reaction condition	Time (min)	Yield[b] (%)
1	without catalyst	180	10
2	in the presence of the catalyst	60	64
3	with recovered solvent	180	15

[a]Reaction conditions: *β*-naphthol (1mmol), aldehyde (1mmol), urea (1.5 mmol) and 0.01g of catalyst Al/Ag_3PO_4, EtOH.
[b]Isolated yields

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.

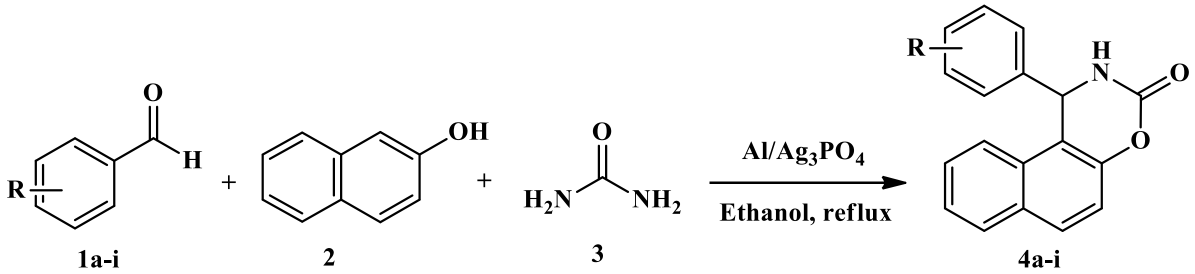
The third study concerns the temperature effect on the reaction yield while knowing that the temperature directly influences the catalyzed reaction rate. Thus, temperature screening was performed (Table 3, entries 16-20). It was found that the catalytic activity of Al/Ag_3PO_4 in the synthesis of 1,2-dihydro-1-arylnaphtho[1,2-e][1,3]oxazine-3-ones 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-l-phenyl-3H-naphth[1,2-e][1,3]oxazin3-one^a.

Entry	Solvent	Amount of catalyst (mg)	Temperature (°C)	Time(min)	Yield^b (%)
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

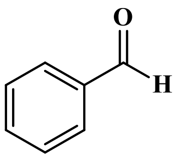
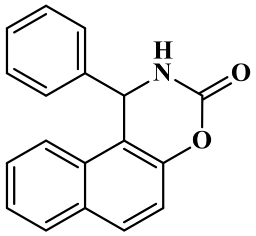
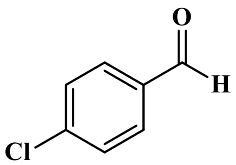
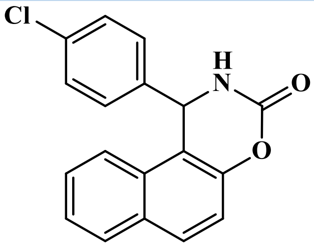
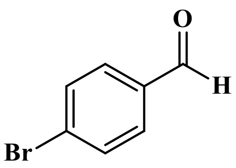
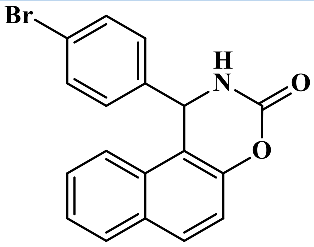
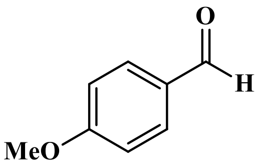
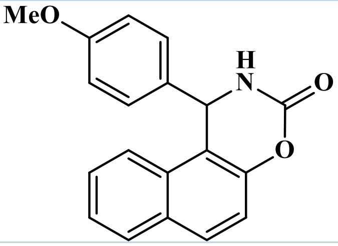
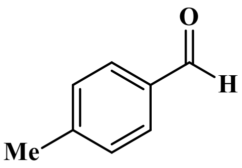
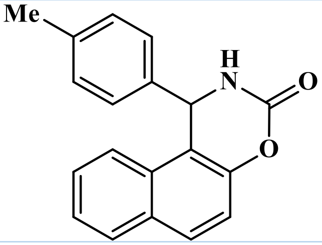
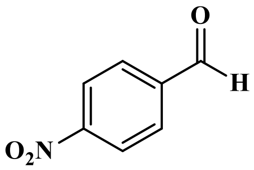
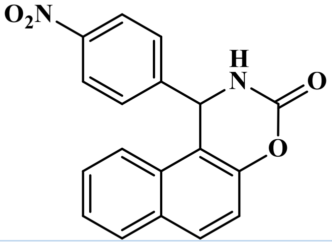
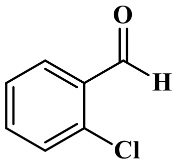
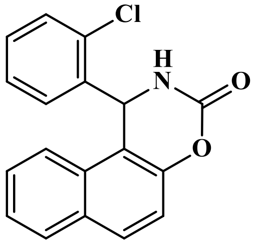
^{a} Reaction conditions: β-naphthol (1mmol), aldehyde (1mmol), urea (1.5 mmol) and8 mg of catalyst Al/Ag_3PO_4, Free-solvent, ^{b}Isolated yields

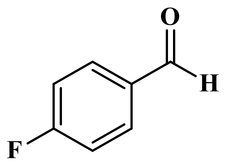
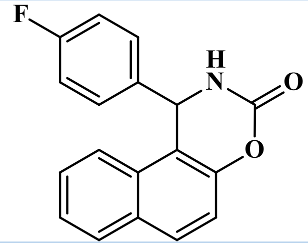
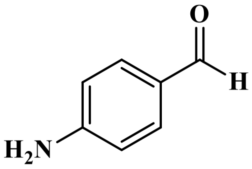
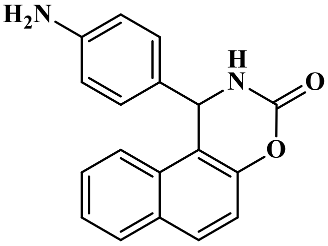
To generalize this methodology to synthesize others 1,2-dihydro-1-aryl-3H-naphth[1,2-e][1,3]oxazin-3-one derivatives, the reaction of β-naphthol with a variety of aromatic aldehydes and urea in the presence of the optimal catalytic amount of Al/Ag_3PO_4 was performed (Scheme 2). Table 4 shows that the 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/Ag_3PO_4 support is an efficient catalyst for this type of reaction.



Scheme 2. Al/Ag_3PO_4Catalyzed Synthesis of 1,2-dihydro-l-phenyl-*3H*-naphth [1,2-*e*]-[1,3] oxazin-3-one derivatives (**4a-i**)

Table 4. Synthesis of 1,2-dihydro-1-aryl-3*H*-naphth[1,2-*e*][1,3]oxazin-3-one derivatives[a].

Entry	Substrate	Product	Time (min)	Yield[b] (%)	MP(°C)	
4a			12	91	216-218	218-220 [34]
4b			10	93	214-216	210-212 [35]
4c			10	95	220-222	216-218 [35]
4d			10	91	188-190	188-188 [36]
4e			12	90	167-169	164-166 [37]
4f			15	87	210-212	206-207 [38]
4g			20	81	244-246	249-251 [36]

4h			12	90	198-200	198-200 [37]
4i			15	91	207-209	212-214

[a]Reaction conditions: *β*-naphthol (1mmol), aldehyde (1mmol), urea (1.5 mmol) and 8 mg of catalyst Al/Ag_3PO_4, Free-solvent, [b]Isolated yields

As our contribution to green chemistry development, the reusability of Al/Ag_3PO_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_3PO_4 can be considered as an efficient heterogeneous catalyst for the one-pot synthesis of 1,2-dihydro-1-arylnaphth [1,2-e] [1,3] oxazin-3-ones from 2-naphthol, aldehyde, and urea under solvent-free conditions.

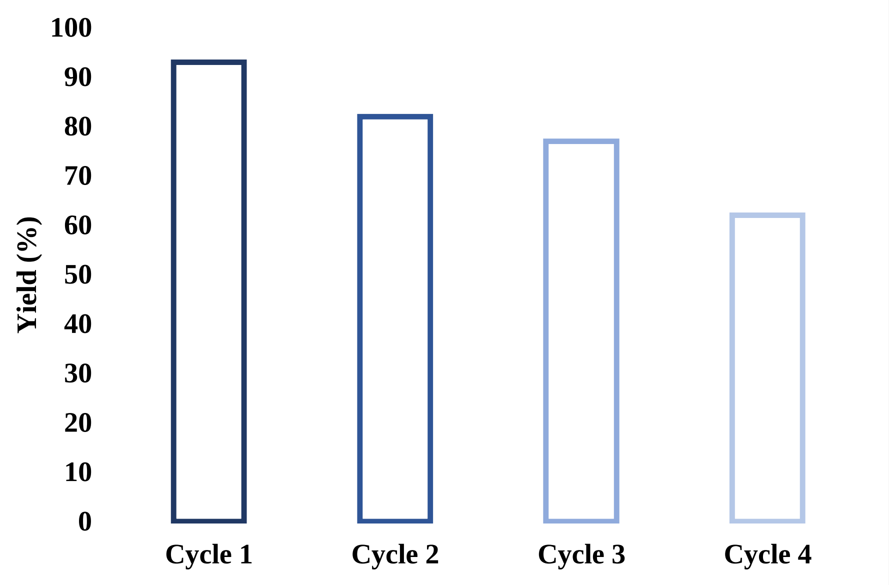


Figure 6. Recyclability of the catalyst for the 1,2-dihydro-l-phenyl-3H-naphth[1,2-e] [1,3]oxazin3-one synthesis

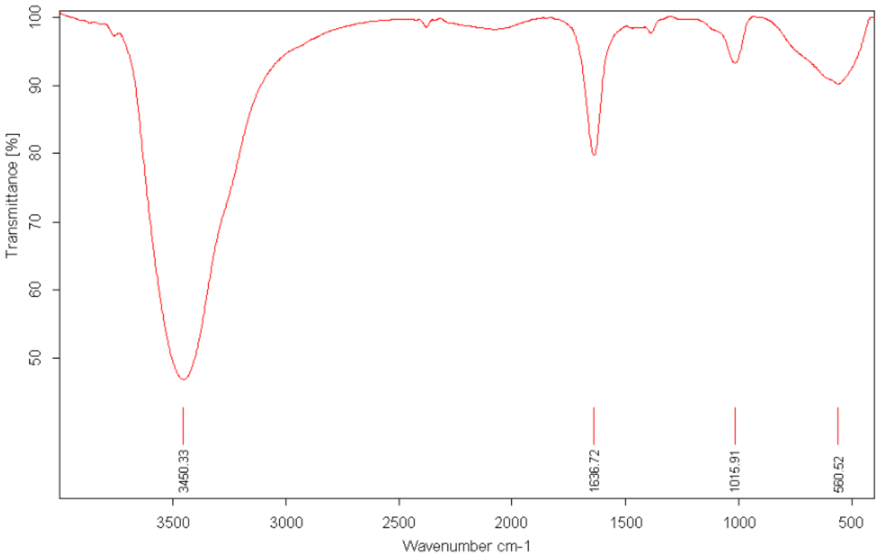


Figure 7. FTIR spectrum of the recovered catalyst

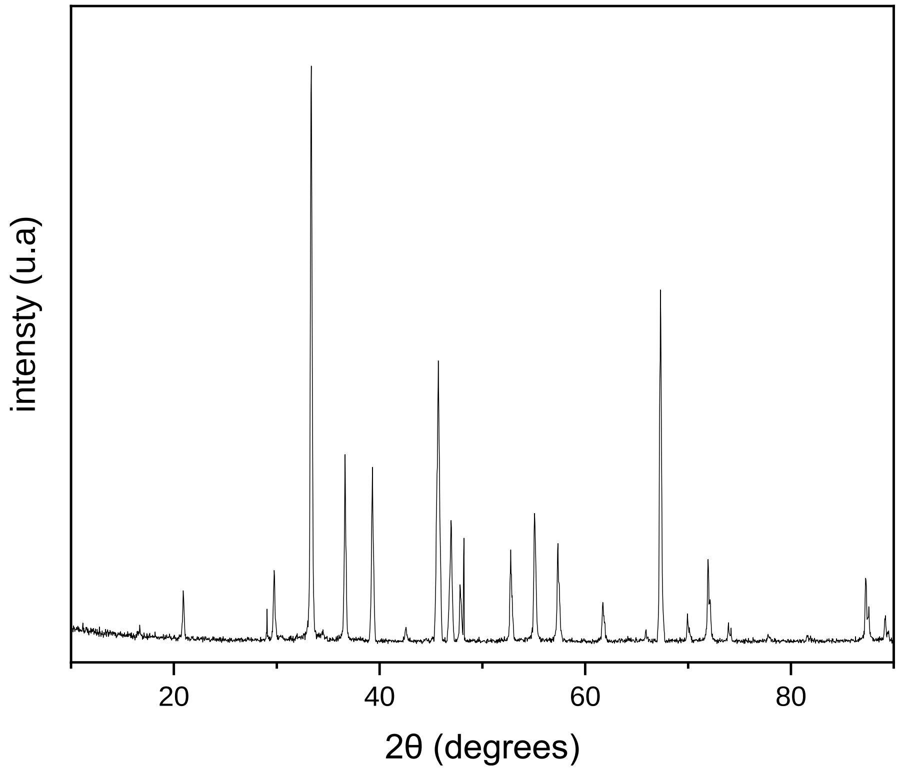
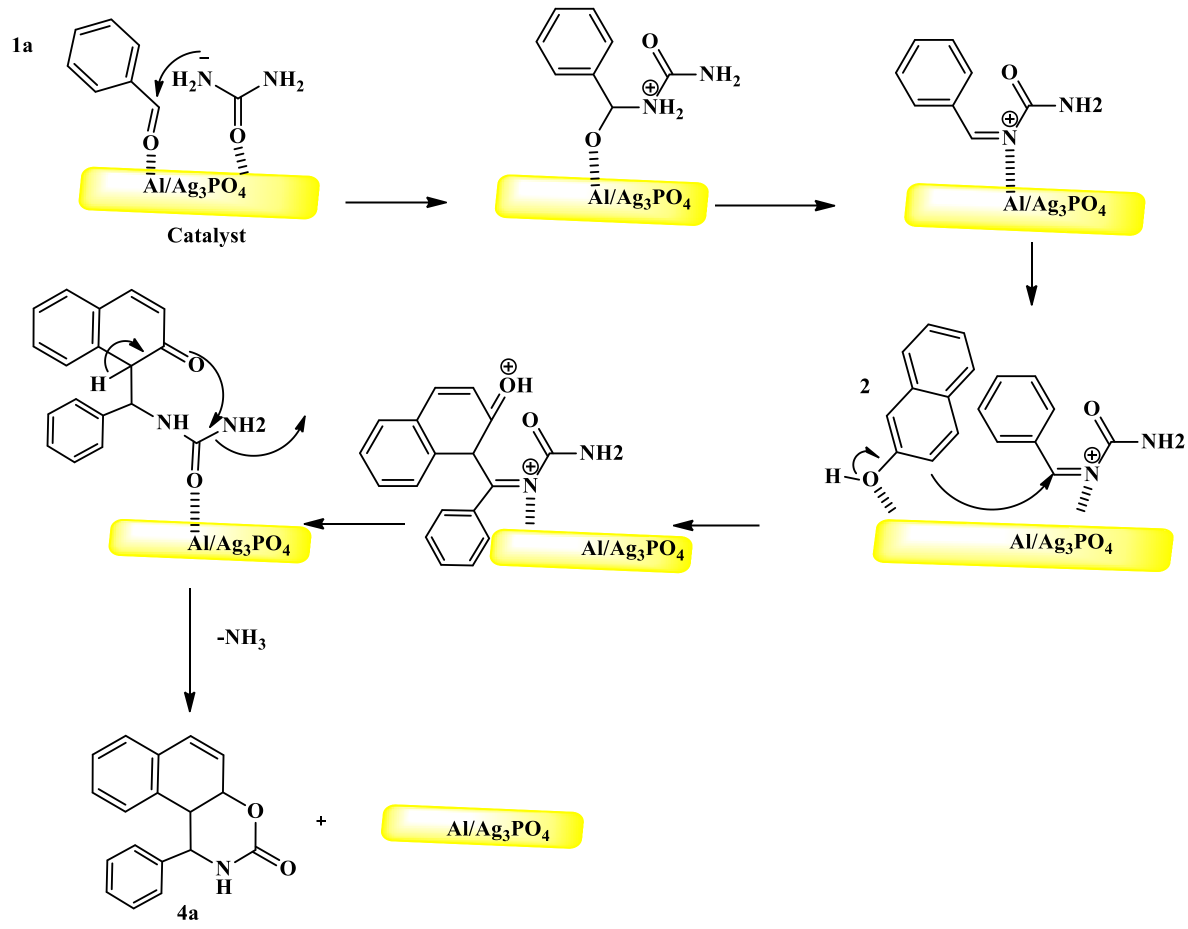


Figure 8. XRD analysis of Al/Ag_3PO_4 after reuse.

To elucidate the role played by the catalyst Al/Ag_3PO_4 in the reaction medium and to explain the formation of 1,2-dihydro-l-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 NH_3. The mechanism is proposed according to our support's characteristics and chemical properties and with the help of bibliographical research [39].



Scheme 3. Plausible mechanism

To confirm the catalytic efficiency of the prepared catalyst (Al/Ag$_3$PO$_4$) 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 studyof 1,2-dihydro-1-arylnaphth[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	[40]
2	ZnONPs/ solvent free	150	60-90	76-94	[41]
3	HClO4/SiO$_2$/ solvent free	150	60	75-92	[42]
4	Fe3O4@MAP nanoparticles/ aqueousethanol (3:1) ultrasonic irradiation	160	15-30	72-92	[43]
5	Fe$_3$O$_4$@nano-cellulose/TiCl/ solvent free	r.t	3-30	80-98	[44]
6	Nano-Al$_2$O$_3$/BF3/Fe$_3$O$_4$/H$_2$O	r.t	15-20	80-92	[45]
7	FePO$_4$	150	20-30	95	[21]
8	[bnmim] [HSO$_4$]	r.t	10	65-77	[46]
9	Al/Ag$_3$PO$_4$	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/Ag$_3$PO$_4$ 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_3PO_4, 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_3PO_4 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_3PO_4 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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