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Natural pozzolan as a novel heterogeneous catalyst for the synthesis of alkylaminophenols

Mourad Boukachabia [a,*], Hacene Bendjeffal [b], Tayeb Bouaroudj [c], Abdelkarim Djebli [c], Olivier Riant [d]

[a] Ecocompatible Asymmetric Catalysis Laboratory (LCAE) Badji Mokhtar Annaba-University. B:P 12, 23000 Annaba, Algeria
[b] Laboratory of Physical Chemistry and Biology of Materials, Higher Normal School of Technological Education (ENSET) Skikda 21000, Algeria
[c] Scientific and Technical Research Center in physico-chemical analyses (CRAPC), Industrial zone, PO-box 384, Bousmail, Tipaza, Algeria
[d] Institute of Condensed Matter and Nanosciences, Molecules Solids and Reactivity (IMCN/MOST), Université Catholique de Louvain, Bâtiment Lavoisier, Pl. Louis Pasteur, 1, bte 3, 1348 Louvain La Neuve, Belgium

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ABSTRACT

The development of sustainable catalysts from natural materials, such as pozzolan, represents a promising strategy in green chemistry. The pozzolan studied was subjected to multi-technique characterization (XRD, FTIR, BET, and SEM) to establish its structural and textural properties. The results obtained highlight the effectiveness of this material as a catalyst for the Petasis reaction, allowing the synthesis of a diversity of alkylaminophenols with yields reaching 93%. The reaction was successfully carried out on a gram scale, confirming the potential of pozzolan as a heterogeneous catalyst. This catalyst, which is recyclable and inexpensive, represents an attractive alternative for large-scale applications while respecting the environment.

1. Introduction

Heterogeneous catalysis represents a constantly evolving field of research, offering numerous prospects for developing more efficient, selective, and environmentally friendly chemical processes [1–3]. The current challenge is to design catalysts using abundant and non-toxic metals or materials, thereby promoting a more environmentally respectful chemistry and a sustainable future [4–8].

Porous materials and nanomaterials play an important role in this field; their uses in organic chemistry have been explored in various applications [9]. Recently, *Lodhi and Maheria* used zeolite-based catalysts for the esterification of various acids derived from biomass to produce biofuel [10]. Similarly, MOFs (Metal-Organic Frameworks) have attracted considerable attention as a new category of crystalline and porous materials [11–16]; *Long et al.* first described the use of MOFs in cyanosilylation reactions as well as Mukaiyama aldol reactions [16–17]. Nanomaterials have generated great interest due to their numerous advantageous properties, such as non-toxicity, low cost, and oxidation stability [18–21]. These attributes make them particularly effective for catalyzing a wide range of reactions, notably the *Sonogashira* coupling [22–25], carboxamide synthesis [26], and heterocycle synthesis [27–29], as well as *Petasis* [30] and *Betti* [31] multicomponent reactions.

Among heterogeneous catalysts, many ion-exchange resins are available and widely referenced in the literature, particularly for esterification reactions. In 2022, *Zeferino et al.* synthesized geranyl and neryl acetates, key molecules in many essential oils, by esterifying the corresponding alcohols using Lewatit® GF 101 ion-exchange resin as a catalyst [32–33]. Recently, we employed a cationic SB-2 resin as a reusable catalyst in a multicomponent reaction, enabling the synthesis of α-aminophosphonates with antifungal properties [34]. Clays, such as montmorillonite, bentonite, smectite, or kaolinite, exhibit physicochemical properties that make them promising candidates for heterogeneous catalysis [35–37]. Their use in organic chemistry has been studied in various applications, such as the synthesis of heterocycles [38–39], aldol reactions [40–41], Di*els-Alder* cycloadditions [41–43], and *Friedel-Crafts* alkylation's [44–46].

Due to its wide availability, low toxicity, and relatively low cost, we were intrigued by the use of a local kaolinite-type clay to evaluate its catalytic performance in heterogeneous phase organic synthesis reactions. In this context, we demonstrated the use of kaolin as a catalyst for the highly chemoselective protection of various aldehydes,

* Corresponding author.
E-mail address: mourad.boukachabia@univ-annaba.dz (M. Boukachabia).

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producing the corresponding acetals with yields ranging from moderate to excellent [47]. Our research team also explored the use of kaolin in esterification reactions, where we obtained high-value-added terpene esters with good yields [48]. Recently, we used this clay as an efficient catalyst for the synthesis of α-aminophosphonates via a one-step multicomponent condensation reaction through the *Kabachnik–Fields* reaction [49].

As part of our research on natural materials with catalytic potential, and after identifying the chemical composition of pozzolan, which is rich in silica and alumina, we deepened our study by focusing specifically on its use as a promoter material in heterogeneous catalysis.

Pozzolan is a natural volcanic material with interesting physical and chemical properties; it forms from the rapid solidification of lava during volcanic eruptions. Its applications are numerous and varied, ranging from construction to agriculture and wastewater treatment [50–52]. Thanks to its durability and low environmental impact, pozzolan is a material for the future. After an extensive literature review, it appears that it has never been used as a catalyst in organic synthesis; we therefore decided to study its catalytic potential in the *Petasis* multicomponent reaction, also known as the *Petasis Borono–Mannich reaction* [53]. This three-component reaction involves reacting an aldehyde, an amine, and a boronic acid in a one-pot process, allowing for the easy synthesis of a wide range of bioactive organic derivatives, such as amino acids and alkylaminophenols [54].

2. Experimental section

2.1. Characterization of the catalyst

2.1.1. Preparation of pozzolan

The pozzolan used in this study was obtained from the *Beni Saf* site, located in the *Oran* region of northwestern *Algeria*. Pozzolan rocks were finely ground and then sieved to 125 μm to obtain a raw powder (Fig. 1). This powder was then characterized by X-ray diffraction, scanning electron microscopy (SEM), infrared spectroscopy, and energy-dispersive X-ray spectroscopy (EDX) to study its mineralogical composition, morphology, and the functional groups present in this material

2.1.2. Chemical composition

The studied pozzolan exhibits a mineralogical composition typical of volcanic materials, as revealed by the X-ray diffraction results (Table 1). These show that it is primarily composed of siliceous and aluminous phases, with a content of 57.9% SiO_2 and 17.47% Al_2O_3. Additionally, minor amounts of iron oxides (Fe_2O_3, 8.87%), calcium oxides (CaO, 9.8%), magnesium oxides (MgO, 1.78%), as well as traces of sodium, potassium, and sulfate oxides were also detected.

EDX spectroscopy identified the main constituents of pozzolan: silica (Si: 12.4 wt%), alumina (Al: 6.1 wt%), carbon (C: 12.4 wt%), and oxygen (O: 50.7 wt%). These elements, present in significant proportions, are characteristic of silicate materials. The contents of potassium, titanium, sodium, magnesium, calcium, and iron, although low, are consistent with the composition generally observed in natural pozzolan and can be attributed to the presence of accessory minerals or contamination, as shown in Fig. 2.

Table 1
Chemical composition of pozzolan.

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_4
Mass rate (Wt%)	57.9	17.45	8.87	9.8	1.78	0.78	0.45	0.2

FTIR analysis (FTIR-8700 spectrometer, Fig. 3) of pozzolan revealed characteristic absorption regions: a broad band centered around 1000 cm^{-1} attributed to Si-O bond vibrations, and another more diffuse band near 3500 cm^{-1} indicating the presence of hydroxyl groups. Additionally, continuous absorption in the 500-800 cm^{-1} region is typical of amorphous aluminosilicate materials, suggesting the presence of Al-O bonds in various chemical environments.

The X-ray diffraction pattern was collected at room temperature on a Bruker-D8 diffractometer, using monochromatic CuKα radiation (λ = 1.54 Å). The 2θ angle scan, ranging from 10° to 90°, was performed with a constant step size. Thanks to the excellent energy resolution of the detector (< 0.3 keV), fluorescence and Kβ lines were effectively suppressed, thereby improving the spectrum quality (see Fig. 4). The diffractogram shows a large number of peaks, indicating a relatively complex mineralogical composition of pozzolan, such as hematite, basanite, quartz, and chabazite. The presence of an intense diffraction peak at a 2θ value of 28° confirms the presence of quartz (Q) in the pozzolan structure (JCPDS#46-1045). Diffraction peaks of low to medium intensity at 15°, 17°, 23°, and 51° indicate the presence of chabazite (C) (JCPDS#034–0137) and basanite (B) around 30° and 32° in this material (JCPDS#36–0617). Additionally, the appearance of other diffraction peaks at 25°, 37°, 55°, 63°, and 67° corresponds to the hematite phase (JCPDS#015–4191).

2.1.3. Morphology and specific surfaces of pozzolan

Multiscale SEM analysis (5 and 3 μm) of pozzolan reveals a complex microstructure, with significant heterogeneity and developed porosity. The presence of varied mineral phases, highlighted by inclusions and layered structures, suggests a specific geological origin; some particles exhibit a layered structure typical of phyllosilicate minerals (see Fig. 5). This particular morphology, along with the high specific surface area, gives pozzolan a high potential for the development of new high-value materials, such as adsorbents, catalysts, or composites.

The characteristics of a catalyst's material surface, including pore size, cavity volume, and specific surface area (S_{BET}), are regarded as critical determinants of a solid catalyst's adsorption efficacy. The

Fig. 1. Natural pozzolan.

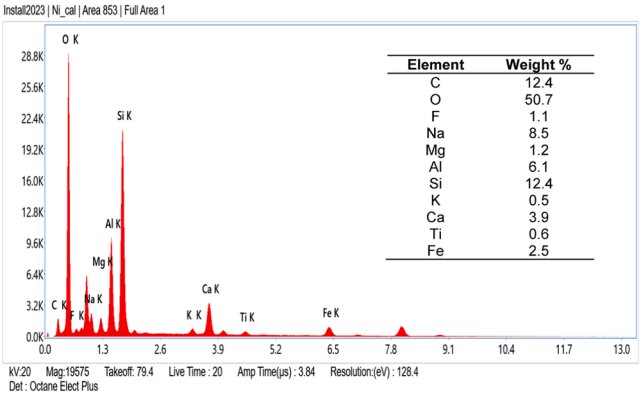


Fig. 2. Spectroscopy EDX of pozzolan.

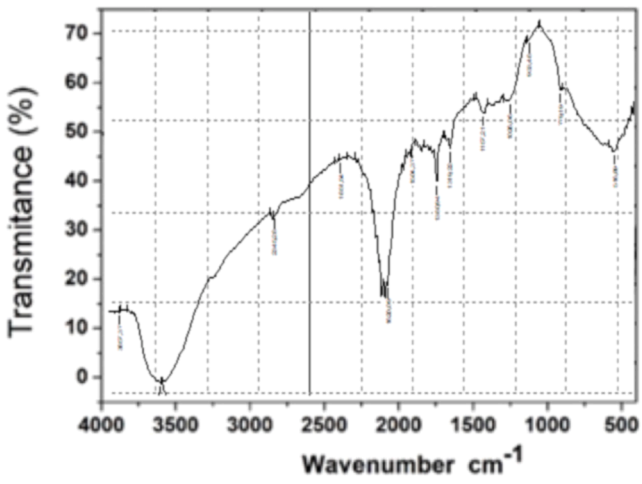


Fig. 3. FTIR Spectrum of pozzolan.

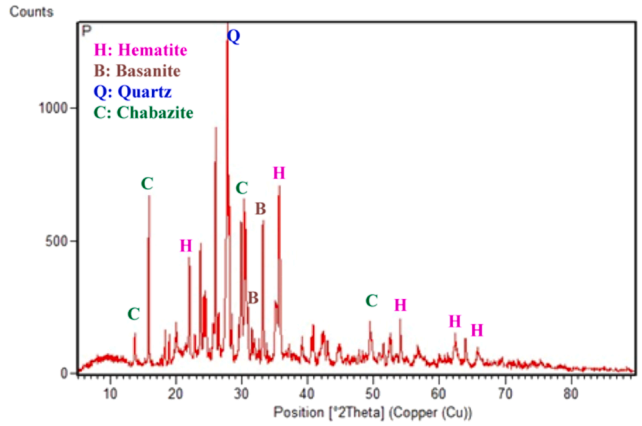


Fig. 4. Diagramme DRX of pozzolan.

specific surface area of the pozzolan was analyzed using nitrogen gas adsorption/desorption isotherms obtained at 77 K. **The** Fig. 6 illustrates the BET curve as a type-V isotherm per the IUPAC classification, exhibiting an H3 hysteresis loop between 0.57 and 0.97 of P/P_0, indicative of a substantial quantity of pores on the specific surface of pozzolan, characterized by a specific surface area (S_{BET}) of 46 m^2 g^{-1}. The pozzolan sample exhibits micro- and mesopores with a wide pore size distribution, claimed to range from 50 to 150 nm. This suggests that the pozzolan surface is primarily microporous, with a significant specific surface area and some meso- and macroporosity, which can enhance its catalytic activity.

2.2. Synthesis of alkylaminophenols using natural pozzolan as a catalyst

A mixture of organoboronic acid **1c** (1.2 mmol), natural pozzolan catalyst (50 mg), and salicylaldehyde derivative **1a** (1 mmol) was placed in a vial equipped with a magnetic stir bar and dissolved in 2 mL of dry solvent. Secondary amine **1b** (1.3 mmol) was then added, and the reaction mixture was refluxed at atmospheric pressure for 24 hours. The catalyst was filtered, the solvent was evaporated under reduced pressure, and the crude product was purified by crystallization from diethyl ether or flash chromatography using petroleum ether/ethyl acetate (80:20) as the eluent.

2.3. Synthesis of alkylaminophenols using doped pozzolan as a catalyst

The same previous protocol was used but the natural pozzolan was

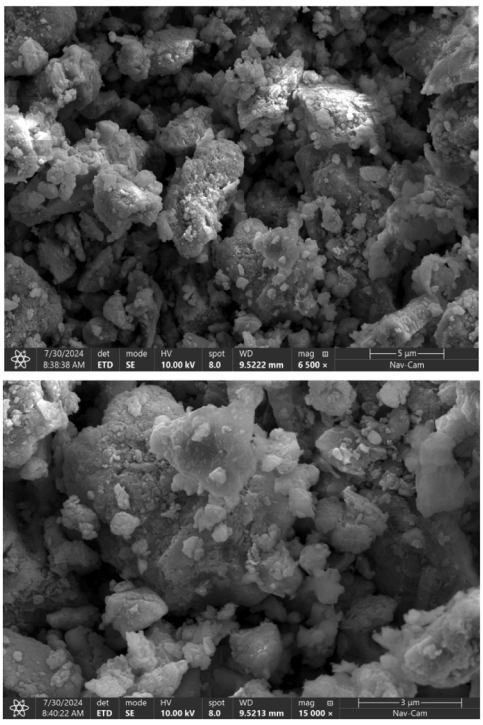


Fig. 5. SEM image of the pozzolan.

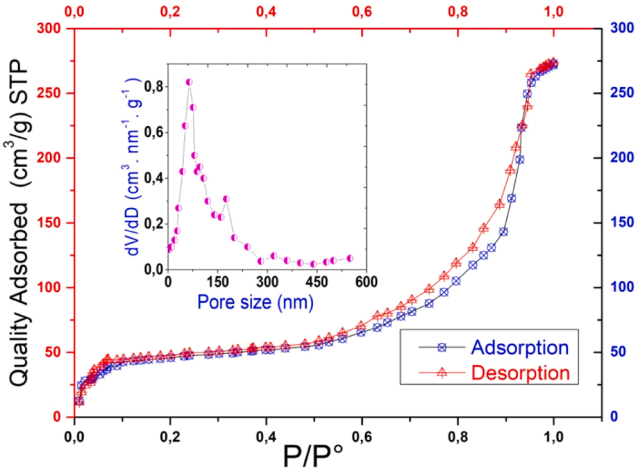


Fig. 6. BET isotherms and pore size distribution analysis of pozzolan.

doped with several Lewis acids, specifically $FeCl_3$, $MnCl_2$, $ZnCl_2$, $CoCl_2$, $SnCl_2$, $CuCl_2$, and $NiCl_2$, according to well-defined protocols: 5 g of predried pozzolan was mixed with 100 ml of MCl_x solutions with a concentration of 0.5 mole.L^{-1}; the mixtures were left under constant agitation for 24 hours at ambient temperature to facilitate the absorption of the maximum amount of metal salt, and after that, the suspensions were filtered, then washed, and dried at 85°C for 2 to 3 hours to obtain the modified pozzolan.

3. Results and discussion

3.1. Optimization of reaction conditions

The *Petasis* reaction, involving salicylaldehyde **1a**, morpholine **1b**, and phenylboronic acid **1c**, was studied using natural pozzolan as a catalyst, according to the optimized amounts of reagents by *Shankar et*

al. (**1a**: 1 mmol, **1b**: 1.3 mmol, and **1c**: 1.2 mmol) [55], Scheme 1.

The influence of various reaction parameters, such as the amount of catalyst, temperature, and nature of the solvent, on the catalytic efficiency was evaluated. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. The results obtained, summarized in Table 2, indicate that the reactivity of pozzolan is strongly dependent on these parameters.

The reference reaction, carried out without a catalyst, resulted in the desired product **1d** with a modest yield of 20% (entry 0). In contrast, the introduction of 50 mg of pozzolan into the reaction medium led to a significant increase in yield, which reached 71% (entry 1), representing an improvement of more than three times compared to the uncatalyzed reaction. These results highlight the beneficial effect of pozzolan on the reactivity of the system.

In order to improve the catalytic activity of pozzolan, we proceeded with doping using a series of Lewis acids ($FeCl_3$, $MnCl_2$, $ZnCl_2$, $CoCl_2$, $SnCl_2$, $CuCl_2$, $NiCl_2$). However, the yields obtained with these doped catalysts (entries 2-8) were lower than those obtained with pozzolan alone (entry 1). This decrease in performance could be explained by pore saturation of the pozzolan by the metal cations, reducing the accessible specific surface area for the reactants and thus diminishing the catalytic activity.

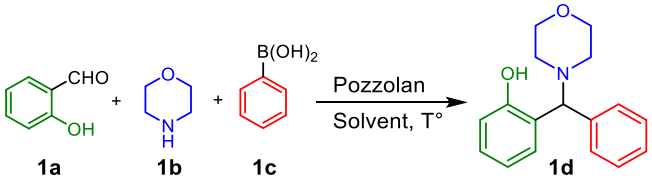
Determining the optimal amount of catalyst is essential for optimizing the reaction process. The results obtained show that the amount of pozzolan used has a significant impact on the reaction yield; a low yield is obtained using 5 mg of this material (Yield = 51%, entry 9), which could be explained by an insufficient number of active sites to catalyze the formation of **1d**. Unexpectedly, increasing the amount of pozzolan to 30 mg (entry 10) results in a decrease in yield; this is likely due to the formation of catalyst particle agglomerates, which reduce the accessible specific surface area for the reactants. A maximum yield is recorded with 50 mg of pozzolan (entry 1), indicating that this amount of catalyst provides an optimal balance between the availability of active sites and the absence of negative effects related to an excess of catalyst. A decrease in the yield of **1d** using 80 mg of this material (entry 11) suggests saturation of the active sites, limited diffusion of reactants into the catalyst pores, or negative interactions between the catalyst particles.

The nature of the solvent plays a crucial role in the *Petasis* reaction catalyzed by pozzolan. The polarity of the solvent, its ability to solvate the reactants, and its capacity to form hydrogen bonds are key factors that can influence the reaction yield. The use of polar aprotic solvents, such as THF, promotes the reaction, achieving a yield of 78% (entry 12). This solvent appears to effectively solubilize the reactants, thereby facilitating their interactions. In comparison, acetonitrile and ethanol are less effective solvents (entries 13 and 14), suggesting that polarity and the ability to form hydrogen bonds play a crucial role in the solvation of reactants and the stabilization of reaction intermediates. In the absence of solvent, the reaction yield is intermediate (entry 15), indicating that the reaction is not completely inhibited, but the solubility of the reactants may be a limiting factor. A control experiment was conducted in THF under reflux without pozzolan to assess its catalytic activity and identify the optimal solvent. The yield of **1d** decreased significantly from 78% with pozzolan to 37% without it (entries 12 and 16), highlighting the importance of the catalyst.

An increase in temperature has a beneficial effect on the yield of the *Petasis* reaction catalyzed by pozzolan. The results obtained are consistent with the Arrhenius law; it is noted that at room temperature, the formation of product **1d** is slow, resulting in a low yield (entry 17). However, increasing the temperature from 60°C to 80°C (reflux) leads to an improvement in yield of more than 15%, from 61% to 78% (entries 18 and 12).

Determining the optimal reaction time is essential for developing an efficient and reproducible synthesis process. It is observed that after 1 hour or 12 hours of reaction, identical yield values are recorded (entries 19 and 20); however, increasing the reaction time to 24 hours favors the conversion of reactants to product **1d** (entry 12).

At the conclusion of our study, we determined that the experimental conditions described in entry 12 of Table 2 provide the highest yield for the *Petasis* reaction catalyzed by pozzolan. A 78% yield of product **1d** was achieved by reacting salicylaldehyde **1a**, morpholine **1b**, and phenylboronic acid **1c** in tetrahydrofuran under reflux for 24 hours with 50 mg of natural pozzolan as catalyst. These parameters will serve as a foundation for exploring the influence of other reaction parameters, such as the structure of the substrates.



Scheme 1. Synthesis of alkylaminophenols catalyzed by pozzolan.

Table 2
Petasis Reaction using pozzolan as a catalyst.

Entry [a]	Catalyst	Qte (mg)	Solvent	T°	t (h)	Yield (%) [b]
0	-	-	Toluene	80	24	**20**
1	Pozzolan	50	Toluene	80	24	71
2	Pozzolan-Fe	50	Toluene	80	24	67
3	Pozzolan-Mn	50	Toluene	80	24	58
4	Pozzolan-Zn	50	Toluene	80	24	47
5	Pozzolan-Co	50	Toluene	80	24	39
6	Pozzolan-Sn	50	Toluene	80	24	62
7	Pozzolan-Cu	50	Toluene	80	24	54
8	Pozzolan-Ni	50	Toluene	80	24	68
9	Pozzolan	5	Toluene	80	24	51
10	Pozzolan	30	Toluene	80	24	43
11	Pozzolan	80	Toluene	80	24	58
12	**Pozzolan**	**50**	**THF**	Reflux	**24**	**78 (74)**[c]
13	Pozzolan	50	Acetonitrile	Reflux	24	50
14	Pozzolan	50	EtOH	Reflux	24	37
15	Pozzolan	50	-	80	24	48
16	-	-	THF	Reflux	24	37
17	Pozzolan	50	THF	25	24	32
18	Pozzolan	50	THF	60	24	61
19	Pozzolan	50	THF	Reflux	12	53
20	Pozzolan	50	THF	Reflux	1	52

[a] With 1 mmol of **1a**, 1.3 mmol of **1b**, 1.2 mmol of **1c** in 2ml of solvent.
[b] Yield was determined by proton NMR using dimethyl sulfone as an internal standard.
[c] Isolated yield by recrystallization from diethyl ether.

3.2. Scope of the petasis reaction catalysed by natural pozzolan

In order to study the applicability of this new catalyst, we explored its ability to catalyze the *Petasis* reaction with a wide range of salicylaldehydes, secondary amines, and boronic acids. The crude reaction mixture was filtered to remove the catalyst. The products were then purified using either silica gel column chromatography with a petroleum ether/ethyl acetate eluent system (80:20) or by recrystallization from diethyl ether. The purified compounds were characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy and comparison with literature data. (see supporting information). The results obtained, compiled in Fig. 7, demonstrate the versatility of this catalytic system.

The study of the *Petasis* reaction catalyzed by pozzolan revealed a correlation between the structure of the substrates and the reaction efficiency. The yields obtained, ranging from 0% to 93%, demonstrate the

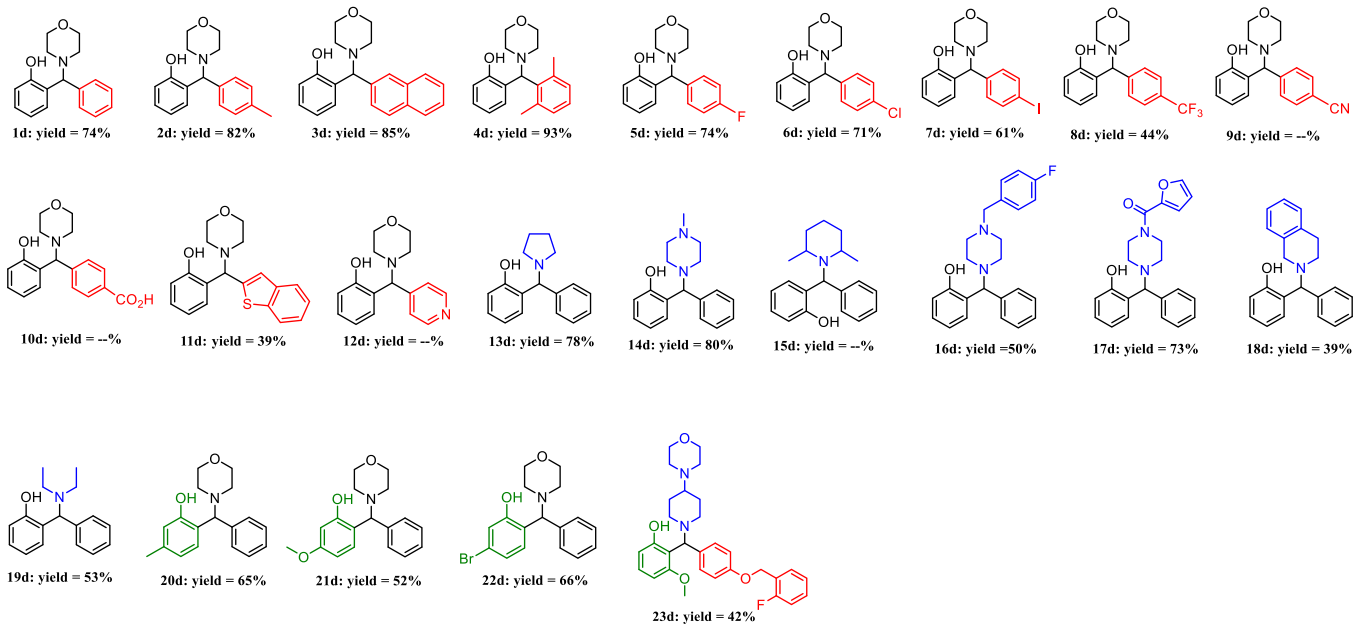


Fig. 7. Synthesis of alkylaminophenol derivatives using natural pozzolan as a catalyst.

significant influence of substituents on the reactivity and selectivity of this transformation.

The introduction of electron-donating groups through inductive effects, such as methyl or phenyl, at the para position of the boronic acid has a beneficial effect on reactivity. These groups increase the electron density on the boron, thus facilitating the formation of the C-C bond. The results obtained with products **2d, 3d**, and **4d**, characterized by high yields (82%, 85%, and 93% respectively), confirm this trend. Electron-donating groups through resonance effects, such as fluorine and chlorine, also have a positive effect, though less pronounced (**5d**: 74% and **6d**: 71%). In contrast, the iodine atom, being larger and less electronegative, significantly decreases the yield (**7d**: 61%).

In the presence of electron-withdrawing groups such as trifluoromethyl (-CF_3), the electron density on the boron atom is significantly reduced, decreasing its ability to activate the aldehyde. This phenomenon results in a moderate yield of 44% for product **8d**. More strongly electron-withdrawing groups, such as cyano (-CN) and carboxyl (-COOH), completely inhibit the reaction, making the formation of products **9d** and **10d** impossible. Aromatic heterocycles, such as benzo [b]thiophene and pyridine, also have a detrimental effect on reactivity, leading to a poor yield for product **11d** (Yield = 39%) and no formation of product **12d**.

The results obtained show a clear correlation between the structure of the amine and the reaction yield. Cyclic amines, such as pyrrolidine and piperazine, favor the formation of the *Petasis* product (**13d**: 78% and **14d**: 80%), likely due to an increased nucleophilicity of the nitrogen in a cyclic environment. Steric hindrance around the nitrogen may hinder the nucleophilic attack on the electrophilic carbon of the reaction intermediate (imine). This could explain the null or moderate yields obtained with certain compounds, such as **15d** (Yield = 0%), **18d** (Yield = 39%), and **19d** (Yield = 53%). Additionally, the presence of electronic substituents on the aromatic ring of the amine can influence its nucleophilicity and basicity, thereby affecting the efficiency of the reaction; for example, compound **16d**, bearing a fluorine, has a lower yield than compound **14d**, which has no substituent.

The nature of the substituents on the salicylaldehyde has a significant impact on the reactivity of the *Petasis* reaction catalyzed by pozzolan. The presence of electron-donating groups (-CH_3, -OCH_3, and -Br) in the ortho position relative to the hydroxyl group of salicylic aldehyde reduces the reaction yields. Compounds **20d, 21d**, and **22d** were isolated with respective yields of 65%, 52%, and 66%.

This study highlighted the complexity of the *Petasis* reaction catalyzed by pozzolan. The results obtained show that the structure of the amines, aldehydes, and boronic acids, as well as the interactions between these compounds and the catalyst, significantly influence the reactivity of the reaction. Six new molecules, compounds **11d, 14d, 16d, 17d, 22d and 23d**, were synthesized for the first time and characterized by high-resolution mass spectrometry (HRMS), as shown in Fig. 8.

3.3. Scale-up of petasis reaction

The scale-up to multigram reactions in catalytic processes is a key lever for improving the profitability and competitiveness of synthetic methods in organic chemistry. To validate the potential of this catalytic system for industrial scale, we undertook the synthesis of alkylaminophenol **1d** from 10 g of salicylic aldehyde using 4 g of pozzolan. The previously determined optimal reaction conditions were applied at this scale. We obtained 15.7 g of the desired product with a yield of 65%. This encouraging result suggests that this catalytic system could be extended to industrial applications, as shown in Scheme 2.

3.4. Catalyst recycling

Catalyst recycling is a critical issue for the development of sustainable chemical processes. The recyclability of pozzolan in the *Petasis* reaction has been investigated in this study. After each cycle, the catalyst was rinsed with ethanol and dried. The results obtained, as shown in the histogram below (Fig. 9), provide valuable insights into the performance and longevity of this catalytic system.

The recovered pozzolan was reused over three consecutive cycles without a notable loss in its catalytic activity, confirming its effectiveness. However, starting from the third reuse, a decrease in catalytic performance was observed, and the yield of alkylaminophenols **1d** dropped to 56%. This phenomenon could be due to catalyst particle sintering, leading to a decrease in surface area and activity. Additionally, active sites could be progressively blocked by reaction products or impurities, hindering reactant access. This hypothesis is supported by SEM images of fresh and recycled pozzolan during the *Petasis* reaction (Fig. 10).

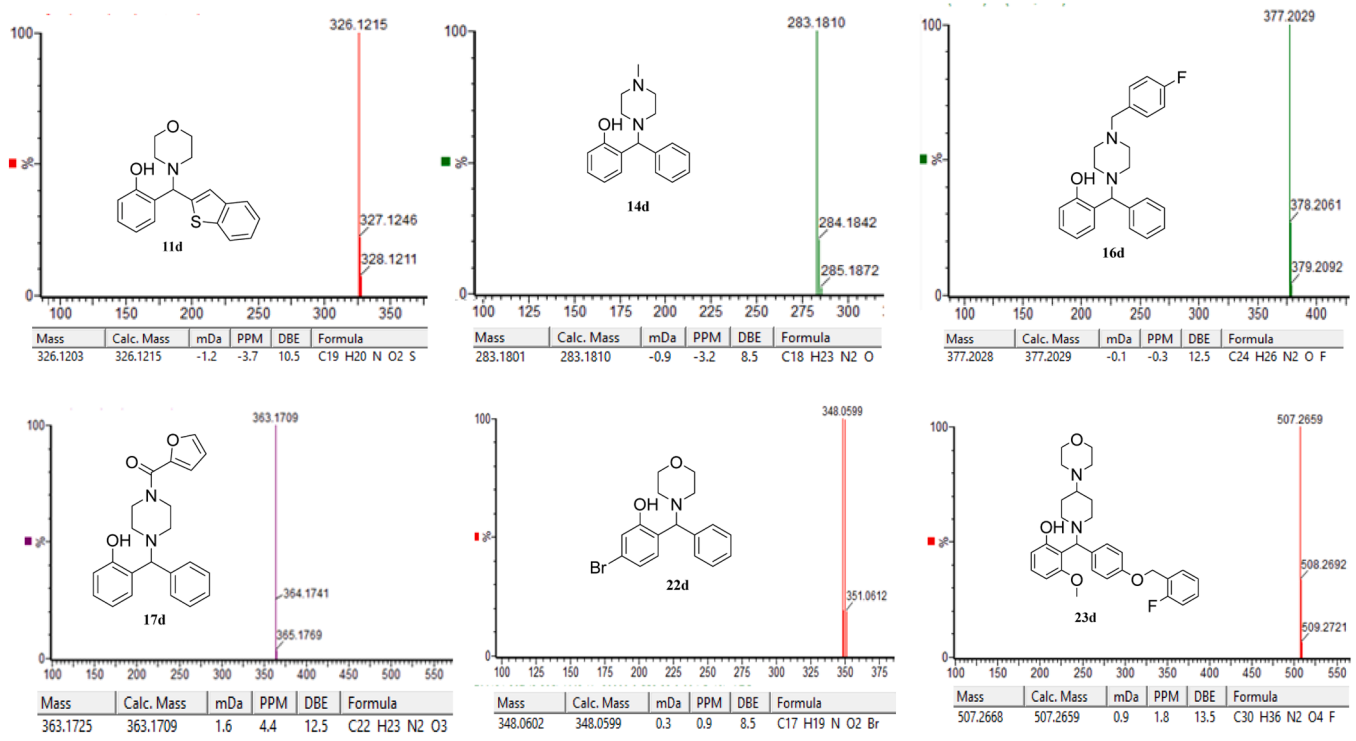


Fig. 8. HRMS spectrum of products **11d, 14d, 16d, 17d, 22d and 23d**.

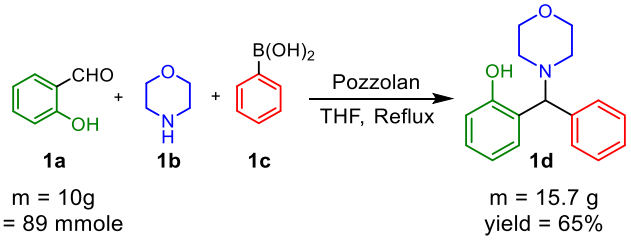


Schéma 2. Scale-up of *petasis* reaction catalyzed by pozzolan under optimal conditions.

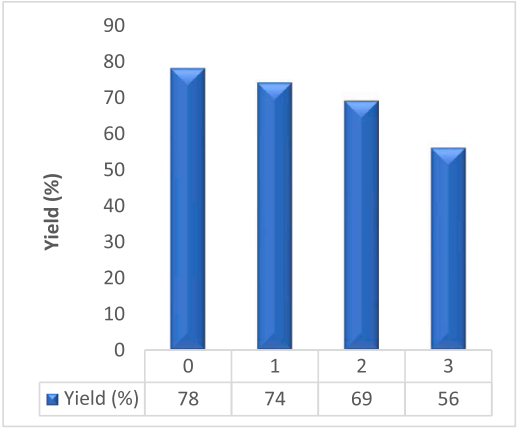


Fig. 9. Catalytic activity of recycled pozzolan over multiple uses.

3.5. Mechanistic description

The pozzolan surface, rich in silanol groups, acts as a catalyst by activating the carbonyl group of salicylaldehyde via hydrogen bonding

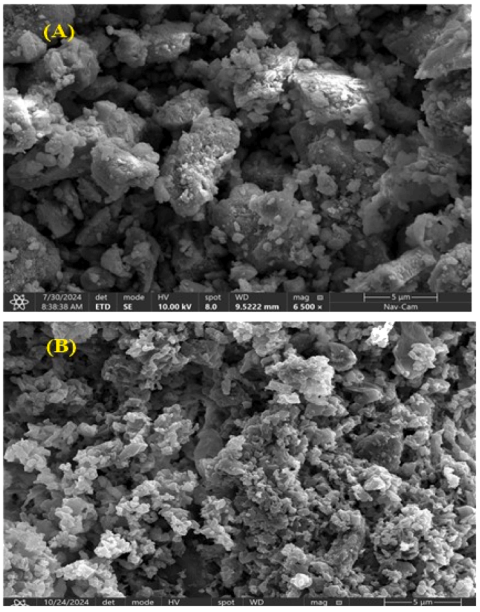


Fig. 10. Scanning electron microscope images of fresh (**A**) and recycled pozzolan (**B**) after the 3rd regeneration.

(**A**). This activation facilitates nucleophilic attack by the amine, leading to the formation of the iminium ion intermediate (**B**). The subsequent coordination between the phenolate anion and the boron atom of the boronic acid stabilizes the tetracoordinate intermediate (**C**), promoting the attack of the aryl carbanion on the iminium ion. Hydrolysis of this intermediate yields the final product and regenerates the catalyst as shown in Scheme 3.

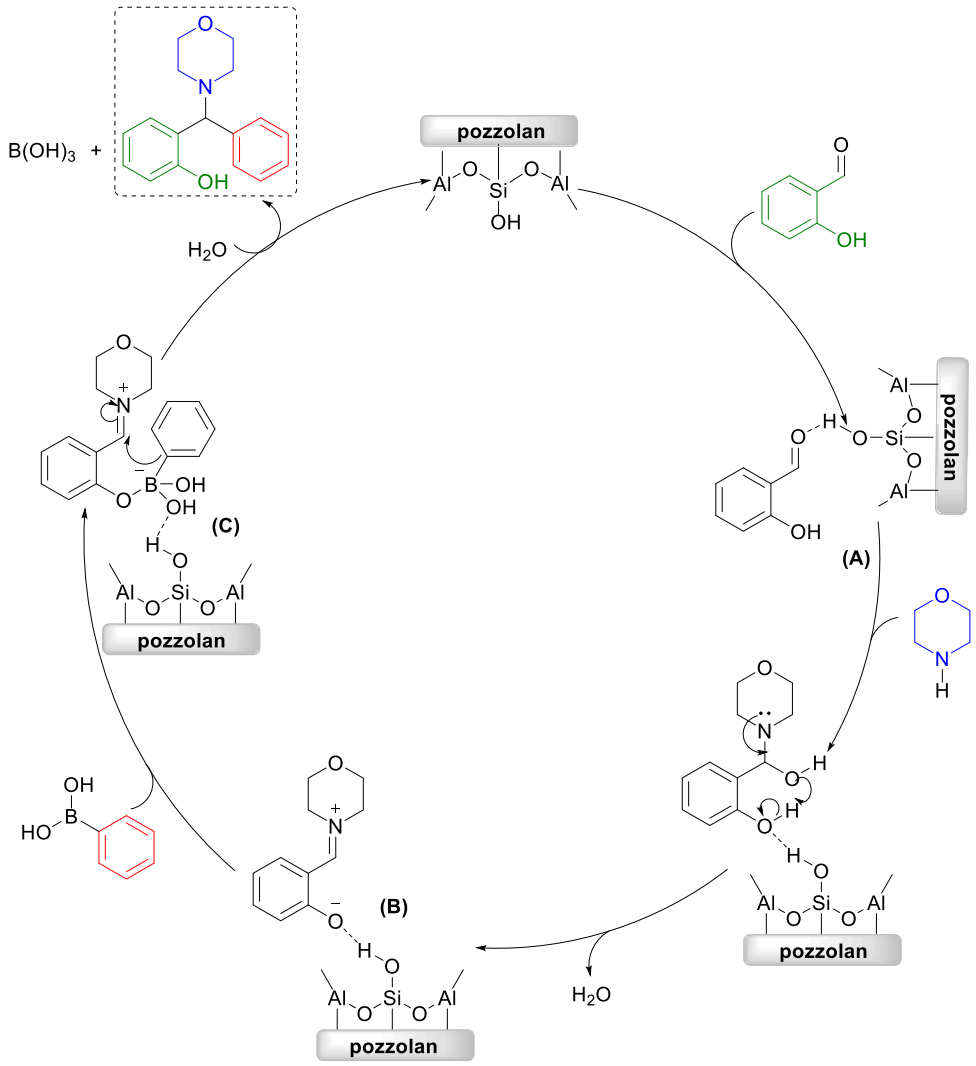


Schéma 3. Plausible mechanistic pathway for the pozzolan-catalyzed *Petasis* reaction.

3.6. *Comparison with existing catalysts*

In order to evaluate the effectiveness of the pozzolan as a heterogeneous and eco-friendly catalyst, we compared its results to other similar works in the literature; data is provided in Table 3. The catalysts mentioned in this table are either prepared (entries 1 to 3), commercially available (entry 4), or used in their natural state (entries 5 and 6); these catalysts exhibit variable activity for the synthesis of alkylaminophenols.

A CuO nanoparticle-decorated reduced graphene oxide (CuO NPs/rGO) composite was synthesized and employed as a catalyst in a microwave-assisted *Petasis* reaction, demonstrating high yields of the target compounds and maintaining activity through eight consecutive reuses (entry 1). Under solvent-free conditions, the Fe_3O_4@GO@AG@CuII nanocomposite effectively catalyzed the Petasis reaction, producing aminophenol with good conversion (entry 2). Magnetic $CoFe_2O_4$ nanoparticles in acetonitrile proved highly active for the synthesis of the desired product, achieving yields up to 93% (entry 3). Lanthanum triflate, under microwave irradiation, yielded the desired product with moderate to good yields (entry 4). Chitosan, a natural polymer, catalyzed the *Petasis* reaction in dioxane, yielding alkylaminophenol with good yield and recyclability up to ten times (entry 5). Pozzolan, a naturally available and recyclable catalyst used without pretreatment, yielded the product with 93% efficiency (entry 6).

This table highlights the potential of various catalysts for the synthesis of alkylaminophenols via the Petasis reaction. Nanoparticle-based catalysts stand out for their performance. The exploration of solvent-free conditions and the use of natural materials like pozzolan are promising avenues for more sustainable processes.

Table 3
Comparison of pozzolan with other catalysts in *Petasis* Reaction.

Entry	Catalyst	Conditions	Recyclability	Yield (%)	Ref
1	CuO NPs/rGO	DCM, MW	8	73-93	[56]
2	Fe_3O_4@GO@AG@Cu	Solvent free 120 C	5	65-100	[57]
3	$CoFe_2O_4$	CH_3CN, 80 C	5	72-93	[30]
4	La $(OTf)_3$	1,4-dioxane, MW	5	0-98	[58]
5	Chitosan	1,4-dioxane, 80 C	10	86-95	[59]
6	Pozzolan	THF, Reflux	5	0-93	[This work]

4. Conclusion

In the context of sustainable chemistry, we have explored, for the first time, the use of natural pozzolan as a heterogeneous catalyst for the *Petasis* reaction. After identifying the morphology and mineral composition of this material, we determined that the optimal conditions for this reaction were 50 mg of pozzolan per 1 mmol of salicylaldehyde in 2 mL of tetrahydrofuran under reflux for 24 h.

The new optimized catalytic system was successfully used for the one-pot synthesis of a library of alkylaminophenols, highlighting the various stereoelectronic effects and the versatility of this material as an eco-friendly catalyst for the *Petasis* reaction.

The new catalyst demonstrated excellent performance in a gram-scale reaction, affording a 65% yield of the desired product from 10 g of salicylaldehyde. The catalyst was recycled twice without any additional treatment, highlighting its potential for industrial applications in large-scale synthesis.

CRediT authorship contribution statement

Mourad Boukachabia: Writing – original draft, Methodology, Investigation. **Hacene Bendjeffal:** Investigation, Data curation. **Tayeb Bouaroudj:** Investigation, Data curation. **Abdelkarim Djebli:** Investigation, Data curation. **Olivier Riant:** Methodology, Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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