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Synthesis of Oxazolone and Imidazolone Derivatives in Presence of H_2O_2 Promoted Fly Ash as a Novel and Efficient Catalyst

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Abstract

A new catalyst was prepared by promoting fly ash with hydrogen peroxide. The catalytic activity of H_2O_2 promoted fly ash (HPFA) was evaluated by synthesis 5(4*H*)-oxazolone and imidazolone derivatives under solvent free conditions. The possible mechanisms of synthesis reactions were also suggested. These proposed methods benefit in terms of low-cost catalyst, high yields, ease of workup, survival of different functional groups, reusability of the catalyst and short reaction time. These advantages render HPFA to be a promising catalyst for synthesis of organic materials.

Keywords: Imidazolone; Microwave irradiation; Oxazolone; H_2O_2 promoted fly ash; Solvent-free.

Introduction

Fly ash is a waste material, accumulating at staggering rates as it is generated in very large volume, from the coal based thermal power plants. The disposal of waste is now becoming difficult which is not only occupying valuable land resources but also causing a threat to surface and ground water bodies. Development of innovative methodologies for utilization of this industrial waste in various value added materials has become an essential objective of the present research and development work related with fly ash management and utilization [1].

Till today, fly ash is mainly consumed in the production of building materials [2], agriculture [3], metal recovery [4], water and atmospheric pollution control [5], dye removal [6], etc. These applications could succeed up to some extent to utilize the huge volume of fly ash. Nevertheless, the search for new applications of fly ash as a catalytic material is still ongoing. Literature reports the wide use of fly ash as a catalyst for different oxidation [7,8], condensation reactions [9] and as solid acid for Fridel-Crafts acylation reaction [10]. Activating fly ash by thermal method has also been investigated to catalyse reactions such as Knoevenagel condensation, 'One-Pot' conversions of ketones to amides via, Beckmann rearrangement, Schiff Bases formation, Biginelli and Hantzsch reactions [11-14]. These investigations reported SiO_2 and Al_2O_3 as the main fly ash components for catalysing the organic reactions, although the yield of reaction products was quite low. Motivated by the above discussion, we were

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interested to improve fly ash and use it for the synthesis of oxazolone and imidazolone derivatives.

Heterocyclic compounds occur widely in nature and they are of course essential to life. Nitrogen-containing heterocyclic molecules constitute the largest portion of chemical entities, which are part of many natural products, fine chemicals and biologically active pharmaceuticals vital for enhancing the quality of life [15]. Among a large variety of nitrogen-containing heterocyclic compounds, oxazolone and imidazolone derivatives are of interest since they have shown a wide range of pharmaceutical properties. Oxazolones are important intermediates in the synthesis of several small molecules, including amino acids, peptides [16-21], anti-microbial or anti inflammatory compounds [22,23], heterocyclic precursors [24-27] as well as biosensors coupling and or photosensitive composition devices for proteins [28]. The use of 5(4H)-Oxazolones as starting materials for the preparation of other heterocycles or for the synthesis of modified α-amino acids or their derivatives has been investigated over the past century, but its great potential is still exploring [29].

Imidazolones have received considerable attention over the last few years due to their interesting biological activities. Some imidazolones exhibited promising pharmacological activities while some of their derivatives have been successfully applied in crop protection. Therefore, these compounds have become an attractive target for combinatorial chemistry groups involved in drug discovery and crop protection [30-33]. There are several chemical methods reported such as acetic anhydride-sodium acetate, acetic anhydride-lead acetate, iron oxide nanoparticles, Nanocrystalline titanium dioxide, TsCl/DMF, potassium phosphate, Hunig's base (DIPEA), polyoxometalate-based dicationic ionic liquids, silica–alumina supported heteropolyacids for the synthesis of oxazolone derivatives [34-42], and also there are many others for the synthesis of imidazolone derivatives, like condensing glycine ester of acetimidic or phenylacetimidic acid in the presence of solvents, such as benzene, dioxane and acetone, intramolecular nucleophilic attack of a guanidine moiety onto an ester or amid carbonyl, [43-45] and microwave-assisted graphite-support synthesis of imidazolones [46]. Yet, cyclodehydration of hippuric acid in Erlenmeyer method and synthesis of imidazolone from oxazolone using HPFA has not been reported. In view of the environmental advantages of heterogeneous catalysis under microwave irradiation (MWI), the bio-potential of the aforementioned heterocyclic compounds, and our ongoing endeavor to conduct organic synthesis under dry media using MWI, we herein disclose the microwave-assisted synthesis of oxazolone and imidazolone on HPFA.

Materials and Methods

Melting points were limited by the Gallenkamp melting point apparatus. IR spectra (KBr) were recorded with the MATTSON 1000 FT-IR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded by the Bruker DRX-500 AVANCE spectrometer (^{1}H NMR 500 MHz and ^{13}C NMR 126 MHz) using tetramethylsilan (TMS) as an internal standard. The used commercial microwave reactor was Ethos 1600 Microwave Lab Station which was made in Italy. The microanalyses for C, H and N were performed on a Perkin-Elmer 2400 elemental analyzer. All reagents and solvents were purchased from Merck Chemical Company. All materials were used without further purification.

Preparation and characterization of catalyst

A carefully sampled coal fly ash from concentrate dryers' refuse at Zarand Coal Washing Plant (Zarand, Iran) was used as a starting material for promotion process. It has been shown by the various investigators [47-52] that promotion of fly ash can improve its activity by increasing the effective surface area due to the removal of residual organic compounds. Between different promoters, hydrogen peroxide is more preferred since it is an effective oxidant to clean the surface of fly ash particles [51, 52].

The activation experiment was performed as follows: 20 g of the prepared fly ash were placed in 500 mL glass beaker and 250 mL volume of 35% H_2O_2 was added at room temperature with continuous stirring at 480 rpm. Then, the temperature was gradually raised to 80 °C. The promotion was performed in an open system using a stirrer-heater equipped with a thermostat to adjust the temperature to 80±2 °C, with continuous stirring for 180 min. At the end of the treatment the slurry mixture was filtered and the solid product was placed into a porcelain-evaporating basin and aged in an oven for 20 h at 95 °C. The phase determination and crystal analysis were carried out by X-ray fluorescence (XRF, Philips, Magix-601), X-ray diffraction (XRD, Philips, X'pert-MPD system), and scanning electron microscopy (SEM, Tescan, Vega-II microscope) analyses. Specific surface area of samples was also determined using a laser particle size analyzer (Fritsch, Analysette 22 NanoTec).

General procedure for the synthesis of 5(4H)-oxazolone derivatives (3a-h)

A mixture of hippuric acid **1** (2 mmol), aryl aldehyde **2** (2 mmol), and acetic anhydride (1 mL) in the presence of treated fly ash as a catalyst (0.2-1 g) was exposed to microwave for an appropriate time. The output power of 700 W was chosen after optimization. After completion of the reaction as indicated by TLC, the mixture was washed three times with chloroform and filtered. The filtrate was evaporated under reduced pressure to give 5(4*H*)-oxazolone **(3a-h)** which was then recrystallized from ethanol 96%. The filtered catalyst was repeatedly washed with chloroform and used for reusability tests.

General procedure for the synthesis of 5(4H)-imidazolone derivatives (4a-h)

Appropriate amounts of 2-phenyl-5(4*H*)-oxazolone **(3a-h)** (2 mmol), ammonium acetate (20 mmol) and catalyst (0.2-1 g) were mixed and all irradiated by a microwave oven (700 W) for an appropriate time. After the reaction was completed, about 40 ml of dimethylformamide was added to the mixture and was heated for 20 min and then filtered. The filtrate was mixed with water and the precipitated crystals were filtered off and recrystallized from 95% ethanol. The filtered catalyst was repeatedly washed with chloroform and used for reusability tests.

4-Benzylidene-2-phenyloxazol-5(4H)-one (3a): Light yellow crystals; Yield: 72%; Anal. Calcd. for $C_{16}H_{11}NO_2$: C, 77.09; H, 4.45; N, 5.62. Found: C, 76.91, H, 4.31, N, 5.52; FT-IR (KBr, cm^{-1}): 1794 (-C=O stretching), 1654 (-C=N stretching).

***4-[4-(Dimethylamino) benzylidene]-2-phenyloxazol-5(4H)-one* (3b)**: Red crystals; Yield: 93%; Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.96; H, 5.52; N, 9.58. Found: C, 73.71, H, 5.69, N, 9.37; FT-IR (KBr, cm^{-1}): 1786 (-C=O stretching), 1653 (-C=N stretching).

***4-(4-Methoxybenzylidene)-2-phenyloxazol-5(4H)-one* (3c):** Yellow crystals; Yield: 87%; Anal. Calcd. for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.28, H, 4.81, N, 5.19; FT-IR (KBr, cm^{-1}): 1786 (-C=O stretching), 1653 (-C=N stretching).

***4-(4-Methylbenzylidene)-2-phenyloxazol-5(4H)-one* (3d):** Yellow crystals; Yield: 77%; Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.54; H, 4.98; N, 5.32. Found: C, 77.32, H, 4.89, N, 5.17; FT-IR (KBr, cm^{-1}): 1795 (-C=O stretching), 1652 (-C=N stretching).

***2-Phenyl-4-[(thiophen-2-yl)methylene] oxazole-5(4H)-one* (3e):** Yellow crystals; Yield: 92%; Anal. Calcd. for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.49. Found: C, 65.70, H, 3.42, N, 5.31; FT-IR (KBr, cm^{-1}): 1791 (-C=O stretching), 1645 (-C=N stretching).

***4-[(Furan-2-yl)methylene]-2-phenyloxazole-5(4H)-one* (3f):** Yellow crystals; Yield: 85%; Anal. Calcd. for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.86. Found: C, 70.45, H, 3.68, N, 5.69; FT-IR (KBr, cm^{-1}): 1790 (-C=O stretching), 1654 (-C=N stretching).

***4-(4-Chlorobenzylidene)-2-phenyloxazol-5(4H)-one* (3g):** Light yellow crystals; Yield: 87%; Anal. Calcd. for $C_{16}H_{10}NO_2Cl$: C, 67.73; H, 3.55; N, 4.93. Found: C, 67.87, H, 3.61, N, 4.73; FT-IR (KBr, cm^{-1}): 1796 (-C=O stretching), 1654 (-C=N stretching).

***4-(2,4-Dichlorobenzylidene)-2-phenyloxazol-5(4H)-one* (3h):** Light yellow crystals; Yield: 87%; Anal. Calcd. for $C_{16}H_9NO_2Cl_2$: C, 60.40; H, 2.86; N, 4.40. Found: C, 60.51, H, 2.99, N, 4.59; FT-IR (KBr, cm^{-1}): 1801 (-C=O stretching), 1664 (-C=N stretching).

***2-Phenyl-5-(1-phenylmethylidene)-3,5-dihydro-4H-imidazol-4-one* (4a):** Yellow crystals; Yield: 88%; Anal. Calcd. for $C_{16}H_{12}N_2O$: C, 77.43; H, 4.84; N, 11.29. Found: C, 77.35, H, 4.79, N, 11.21; FT-IR (KBr, cm^{-1}): 3180 (-NH stretching of secondary amine), 1716 (-C=O stretching), 1666 (-C=N stretching); ^{1}H NMR (500 MHz, DMSO-d6, δ / ppm): 7.04 (s, 1H, Vinyl), 7.44 (dd, 1H, J = 7.3, J = 7.3 Hz, ArH), 7.50 (dd, 2H, J = 7.7, J = 7.4 Hz, ArH), 7.61 (dd, 2H, J = 7.3, J = 6.3 Hz, ArH), 7.65 (dd, 1H, J = 8.3, J = 5 Hz, ArH), 8.19 (d, 2H, J = 8.4, ArH), (d, 2H, J = 7.4, ArH), 12.12 (s, 1H, NH); ^{13}C NMR (126 MHz, DMSO-d6, δ / ppm): 125.9, 128.3, 128.8, 129.6, 129.9, 130.9, 132.9, 133.4, 135.2, 141.3, 161.8, 172.9.

***5-[1-(4-Dimethylaminophenyl) methylidene]-2-phenyl-3, 5-dihydro-4H-imidazol-4-one* (4b):** Orange crystals, Yield 89%; Anal. Calcd. for $C_{18}H_{17}N_3O$: C, 74.24; H, 5.84; N, 14.43 %. Found: C, 74.19, H, 5.81, N, 14.49; FT-IR (KBr, cm^{-1}): 3180 (-NH stretching of secondary amine), 1716 (-C=O stretching), 1657 (-C=N stretching); ^{1}H NMR (500 MHz, DMSO-d6, δ / ppm): 3.04 (s, 6H, CH_3), 6.08 (d, 2H, J = 9.1 Hz, ArH), 6.95 (s, 1H, Vinyl), 7.55-7.59 (m, 3H, ArH), 8.13 (dd, 2H, J = 7.6, J = 2.3 Hz, ArH), 8.18 (d, 2H, J = 8.8 Hz, ArH), 11.80 (s, 1H, NH); ^{13}C NMR (126 MHz, DMSO-d6, δ / ppm): 38.7, 112.7, 122.8, 127.7, 127.8, 129.5, 129.7, 132.4, 134.9, 137.2, 152.3, 158.0, 172.6.

5-[1-(4-Methoxyphenyl) methylidene]-2-phenyl-3, 5-dihydro-4H-imidazol-4-one **(4c):** Yellow crystals, Yield 85%; Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.40; H, 5.03; N, 10.07. Found: C, 73.51, H, 5.01, N, 10.11; FT-IR (KBr, cm^{-1}): 3180 (-NH stretching of secondary amine), 1716 (-C=O stretching), 1665 (-C=N stretching); ^{1}H NMR (500 MHz, DMSO-d6, δ / ppm): 3.84 (s, 3H, OCH_3), 7.02 (s, 1H, Vinyl), 7.07 (d, 2H, J = 8.7 Hz, ArH), 7.58-7.64 (m, 3H, ArH), 8.16 (d, 2H, J = 7.1 Hz, ArH), 8.31 (d, 2H, J = 8.6 Hz, ArH), 12.02 (s, 1H, NH); ^{13}C NMR (126 MHz, DMSO-d6, δ / ppm): 54.2, 115.3, 126.3, 128.0, 128.0, 129.0, 129.9, 133.1, 134.9, 139.4, 160.3, 161.7, 172.8.

5-[1-(4-Methylphenyl) methylidene]-2-phenyl-3,5-dihydro-4H-imidazol-4-one **(4d):** Yellow crystals, Yield 85%; Anal. Calcd. for $C_{17}H_{14}N_2O$: C, 77.87; H, 5.34; N, 10.68. Found: C, 77.79, H, 5.41, N, 10.71; FT-IR (KBr, cm^{-1}): 3180 (-NH stretching of secondary amine), 1716 (-C=O stretching), 1656 (-C=N stretching); ^{1}H NMR (500 MHz, DMSO-d6, δ / ppm): 2.35 (s, 3H, CH_3), 7.01 (s, 1H, Vinyl), 7.03 (d, 2H, J = 6.6 Hz, ArH), 7.59-7.63 (m, 3H, ArH), 8.17 (d, 2H, J = 6.4 Hz, ArH), 8.21 (d, 2H, J = 7 Hz, ArH), 12.09 (s, 1H, NH); ^{13}C NMR (126 MHz, DMSO-d6, δ / ppm): 22.1, 126.2, 128.2, 128.9, 129.9, 130.3, 132.6, 133.0, 133.3, 140.6, 141.0, 161.1, 172,9.

5-[1-(2-Thienyl) methylidene]-2-phenyl-3, 5-dihydro-4H-imidazol-4-one **(4e):** Brown crystals, Yield 90%; Anal. Calcd. for $C_{14}H_{10}N_2OS$: C, 66.14; H, 3.93; N, 11.02. Found: C, 66.08, H, 3.89, N, 11.06; FT-IR (KBr, cm^{-1}): 3131 (-NH stretching of secondary amine), 1716 (-C=O stretching), 1656 (-C=N stretching); ^{1}H NMR (500 MHz, DMSO-d6, δ / ppm): 7.19 (dd, 1H, J = 4.7, J = 3.9 Hz, Thienyl), 7.40 (s, 1H, Vinyl), 7.58-7.65 (m, 3H, ArH), 7.74 (d, 1H, J = 3.4 Hz, Thienyl), 7.92 (d, 1H, J = 4.9 Hz, Thienyl), 8.16 (d, 2H, J = 6.9 Hz, ArH), 12.07 (s, 1H, NH), ^{13}C NMR (126 MHz, DMSO-d6, δ / ppm): 120.4, 128.1, 128.6, 128.8, 129.9, 133.2, 135.5, 135.7, 138.8, 138.9, 160.0, 172.0.

5-[1-(2-Furyl) methylidene]-2-phenyl-3, 5-dihydro-4H-imidazol-4-one **(4f):** Brown crystals, Yield 90%; Anal. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.60; H, 4.20; N, 11.76. Found: C, 70.62, H, 4.16, N, 11.69; FT-IR (KBr, cm^{-1}): 3156 (-NH stretching of secondary amine), 1716 (-C=O stretching), 1667 (-C=N stretching); ^{1}H NMR (500 MHz, DMSO-d6, δ / ppm): 6.78 (s, 1H, Furyl), 6.89 (s, 1H, Vinyl), 7.55-7.65 (m, 4H, ArH), 7.97 (s, 1H, Furyl), 8.17 (d, 2H, J = 7.3 Hz, ArH), 10.12 (s, 1H, NH); ^{13}C NMR (126 MHz, DMSO-d6, δ / ppm): 113.1, 114.6, 119.1, 128.2, 128.8, 129.9, 133.3, 138.8, 147.3, 151.6, 160.9, 172.2.

5-[1-(4-Chlorophenyl) methylidene]-2-phenyl-3,5-dihydro-4H-imidazol-4-one **(4g):** Yellow brown crystals, Yield 89%; Anal. Calcd. for $C_{16}H_{11}N_2OCl$: C, 67.99; H, 3.89; N, 9.91. Found: C, 67.93, H, 3.91, N, 9.95; FT-IR (KBr, cm^{-1}): 3131 (-NH stretching of secondary amine), 1716 (-C=O stretching), 1652 (-C=N stretching); ^{1}H NMR (500 MHz, DMSO-d6, δ / ppm): 7.04 (s, 1H, Vinyl), 7.56 (d, 2H, J = 8.4 Hz, ArH), 7.60 (dd, 2H, J = 7.4, J = 7.3 Hz, ArH), 7.66 (dd, 1H, J = 7.1, J = 7.1 Hz, ArH), 8.18 (d, 2H, J = 7.6 Hz, ArH), 8.35 (d, 2H, J = 8.4 Hz, ArH), 12.16 (s, 1H, NH); ^{13}C NMR (126 MHz, DMSO-d6, δ / ppm): 124.3, 128.4, 128.7, 129.7, 129.9, 133.6, 134.2, 134.5, 135.4, 141.7, 162.2, 172.8.

5-[1-(2,4-Dichlorophenyl) methylidene]-2-phenyl-3,5-dihydro-4H-imidazol-4-one **(4h):** Yellow brown crystals, Yield 91%; Anal. Calcd. for $C_{16}H_{10}N_2OCl_2$: C, 60.61; H, 3.15; N, 8.83. Found: C, 60.69, H, 3.11, N, 8.79; FT-IR (KBr, cm^{-1}): 3156 (-NH stretching of secondary amine), 1716 (-C=O stretching), 1658 (-C=N stretching); ^{1}H NMR (500 MHz, DMSO-d6, δ / ppm): 7.19 (s, 1H, Vinyl), 7.58-7.62 (m, 3H, ArH), 7.67 (dd, 1H, J = 7.2, J = 7.2 Hz, ArH), 7.73 (d, 1H, J = 1.7 Hz, ArH), 8.18 (d, 2H, J = 7.7 Hz, ArH), 9.04 (d, 1H, J = 8.6 Hz, ArH), 12.29 (s, 1H, NH); ^{13}C NMR (126 MHz, DMSO-d6, δ / ppm): 117.8, 128.4, 128.6, 128.8, 129.9, 130.1, 131.6, 133.9, 134.8, 135.7, 136.4, 143.0, 163.7, 172.7.

Results and Discussion

Characterization of promoted fly ash

Fig. 1, includes spectra a and b, shows XRD patterns of the bulk coal ash and synthesized product, respectively. It can be observed that bulk fly ash is a mixture of biotite and muscovite. Fig. 1b reveals that diffraction peaks related to biotite are mostly conversed to muscovite. Figs. 2a and 2b represent the SEM images of the bulk coal ash and synthesized product, respectively. SEM photographs reveal the differences among biotite and muscovite structures. Biotite is crystallized in monoclinic system with tabular to prismatic crystals with an obvious pinacoid termination. It contains four prism faces and two pinacoid faces to form a pseudo hexagonal crystal which can be found in Fig. 2a. In contrast, muscovite is crystallized in monoclinic system with amorph pseudo-crystals [53, 54]. Fig. 2b clearly shows that muscovite is the main crystalline phase in the product. It is shown that the content of amorphous

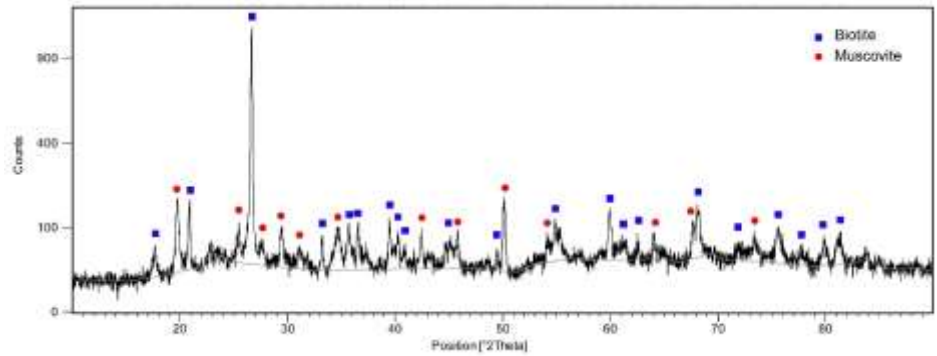


Figure 1(a). X-ray diffraction patterns of the bulk sample

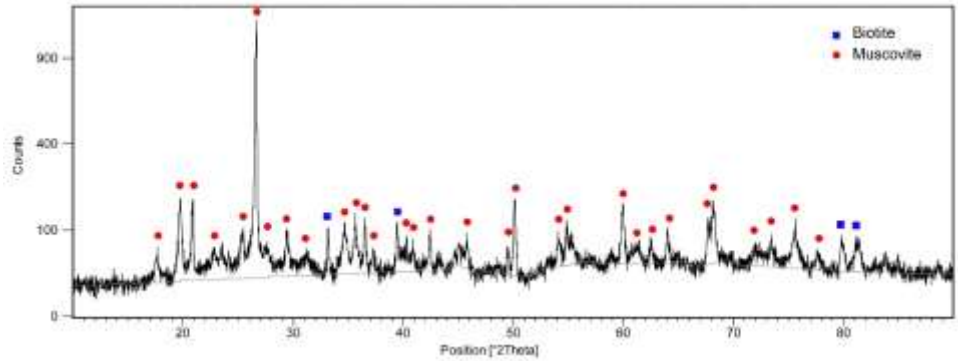


Figure 1(b). X-ray diffraction patterns of the promoted product

compounds decreases upon treatment with H_2O_2. This is due to the fact that a cationic lattice substitution process follows the formation of metallic hydroxides under the reaction conditions, i.e. basic pH, oxidative environment and elevated temperature [52, 55].

The SEM photographs also show a sharp growth in dimension of muscovite crystals. Results from laser particle size analysis showed that the specific area of the promoted product increased from 19352.13 $cm^2\ g^{-1}$ to 22591.62 $cm^2\ g^{-1}$. The XRF result of the bulk sample, given in Table 1, shows that the bulk sample includes essential oxides classified in the category of solid catalysts [56]. Additionally, Table 1 also implies that the promotion process does not actually influence the composition of the promoted product but it modifies the position of these oxides in the crystalline structure of the product such that the size of final pseudo hexagonal crystals increases about 17%.

Synthesis of oxazolone and imidazolone derivatives

General synthesis route of oxazolone and imidazolone derivatives is listed in scheme 1. In the first

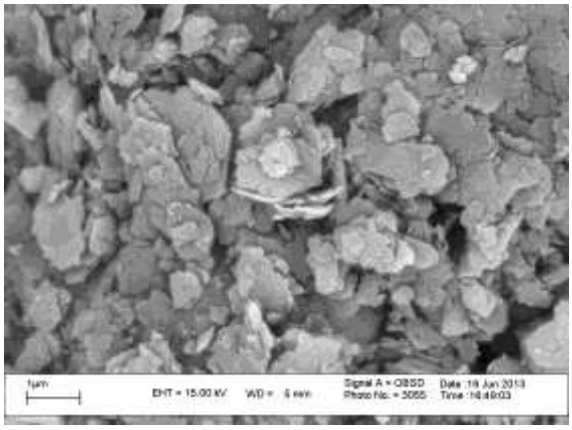


Figure 2(a). SEM images of the bulk sample

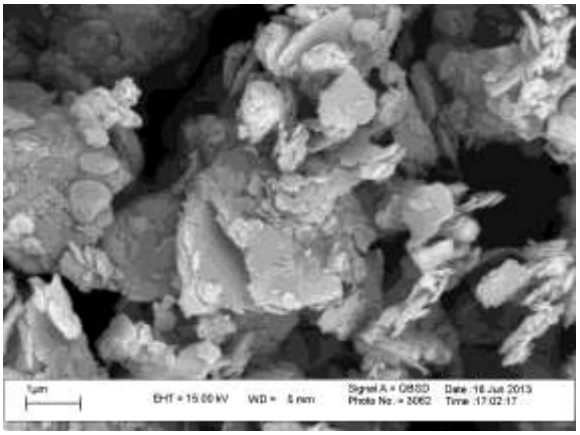
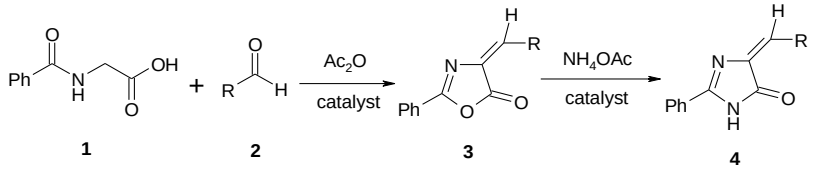


Figure 2(b). SEM images of the promoted product

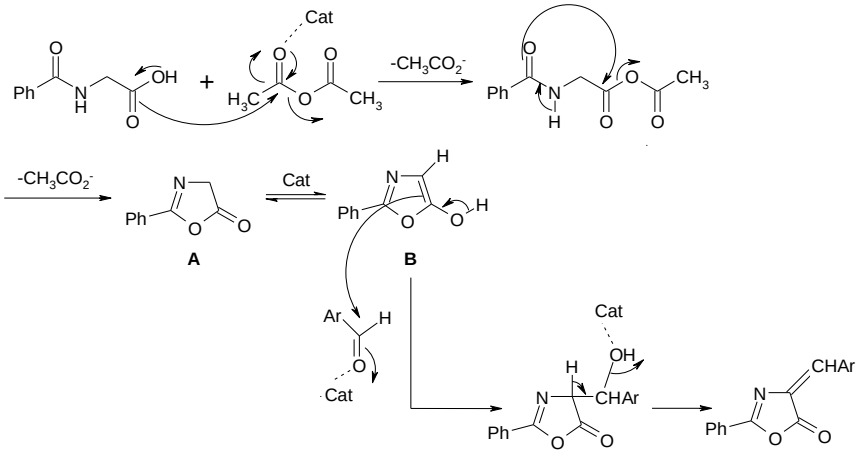
Table 1. XRF results for the bulk and promoted fly ash.

Component (%)	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	SO_3	Others*
Bulk fly ash	57.6	27.9	1.9	4.8	3.4	1.1	3.3
Promoted product	56.9	26.6	2.1	5.7	3.3	1.3	4.1

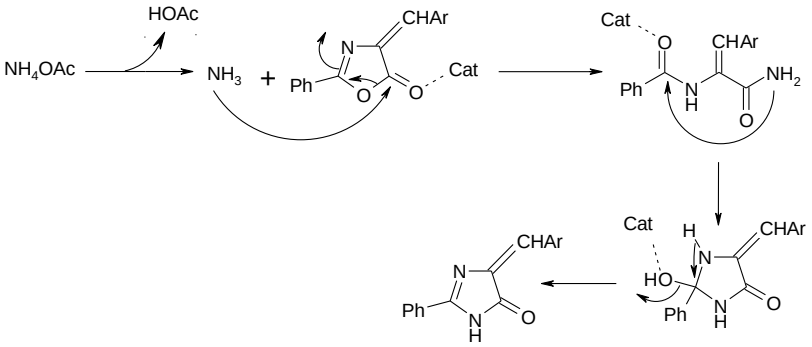
* P_2O_5, TiO_2, MgO, Na_2O, K_2O, L.O.I



Scheme 1. Synthetic route of oxazolone and imidazolone derivatives.



Scheme 2. The suggested mechanism for the synthesis of oxazolone derivatives.



Scheme 3. The suggested mechanism for the synthesis of imidazolone derivatives.

step, hippuric acid 1 and aryl aldehyde 2 were added to acetic anhydride in the presence of H_2O_2 promoted fly ash as a catalyst and the mixture was exposed to microwave for about 6 min. Then, the mixture was heated in 40 ml of dimethylformamide and washed by distilled water to obtain residues of oxazolone derivatives **3** which was directly utilized as a reactant in the next reaction. In the second step, 3 and ammonium acetate and catalyst were mixed and irradiated by a microwave oven for 5 min. Afterward, the reactive mixture was washed and dried to get the desired products of imidazolone derivatives 4.

Possible mechanisms for these catalytic reactions are shown in schemes 2 and 3. As shown in Scheme 2, catalyst begins the reaction with the activation of acetic anhydride. Then, hippuric acid in reaction with activated acetic anhydride yields intermediate A. Tautomerization between A and B occurs in the presence of catalyst. Condensation between saturated oxazolone and the aldehyde, activated by the catalyst, produces corresponding oxazolone. In Scheme 3, catalyst first activates oxazolone carbonyl group. Then,

Table 2. Influence of the catalyst consumption on the synthesis of 3a/4a.

Entry	Mass of catalyst (g)	Yield (%) 3a/4a
1	0.2	55/79
2	0.4	63/88
3	0.6	72/81
4	0.8	68/79
5	1.0	57/75
6	No catalyst	24/73

Table 3. Synthesis of 5(4*H*) - oxazolone and imidazolone derivatives using catalyst under microwave irradiation

Entry	R	Time (min)	Yield (%)	m.p./ ˚C	
				Found	Lit. [ref]
Oxazolone derivative compounds					
3a	C_6H_5	6	72	160-161	158 [57]
3b	N,N$(CH_3)_2$-C_6H_4	4	93	211-212	213-214 [58]
3c	4-CH_3O-C_6H_4	4	87	158-159	159 [29]
3d	4-CH_3- C_6H_4	5	77	143-144	145-146 [38]
3e	C_4H_3S	5	92	177-178	180 [29]
3f	C_4H_3O	6	85	171-172	171 [29]
3g	4-Cl-C_6H_4	4	92	186-187	185 [40]
3h	2,4-$Cl_2C_6H_3$	5	95	181-182	183 [40]
Imidazolone derivative compounds					
4a	C_6H_5	4	88	269-270	272–273 [59]
4b	N,N$(CH_3)_2$-C_6H_4	3	89	265-266	293-294 [60]
4c	4-CH_3O-C_6H_4	3	86	289-290	289–290 [59]
4d	4- CH_3- C_6H_4	4	85	289-290	278-279 [61]
4e	C_4H_3S	4	90	285-288	310-311 [62]
4f	C_4H_3O	5	90	265-266	263-264 [62]
4g	4-Cl-C_6H_4	3	95	298-300	>300 [60]
4h	2,4-$Cl_2C_6H_3$	2	94	270-271	268-269 [61]

Table 4. Reusability of catalyst for synthesis of oxazolone **3a** and imidazolone **4a**.

Run	Yield (%) 3a/4a
1	72/88
2	72/88
3	71/88
4	70/87
5	70/87

oxazolone ring is ruptured due to ammonia attack. After that, imidazolone derivatives are obtained in the procedure of intramolecular cyclization.

In order to evaluate the efficiency of catalytic effect of the promoted fly ash, two sets of experiments were run in the absence and the presence of different masses of sample. The synthesis yield values for 5(4H)-oxazolone derivatives 3a and 5(4H)-imidazolone derivative 4a are given in Table 2. According to Table 2, that optimum amounts of catalyst for the synthesis of oxazolone and imidazolone derivatives are 0.6 g and 0.4 g, respectively.

Different analysis methods were applied to identify the compounds produced during to synthesis reactions. To gain better insight into the chemical structure of these compounds, melting points of each compound was compared with values reported in literature and listed in Table 3. The results presented in Table 3 show the scope and generality of these methods. One of the salient features of these methods is that electron poor or rich aldehydes give good yields and purities. All compounds are known and their physical and spectroscopic data were reasonably consistent with those of authentic samples.

The reusability of catalyst was also investigated for both oxazolone and imidazolone synthesis reactions. In

this regard, after the first synthesis experiment with optimum catalyst mass (i.e. 0.6 g for oxazolone synthesis and 0.4 g for imidazolone synthesis), the filtered catalyst was repeatedly washed by chloroform, dried and reused in a new experiment. The synthesis yield values for five experiments are given in Table 4. As seen in Table 4, the catalyst can be used up to five times without any activity loss or appreciable changes in products yield. These results render the promoted fly ash to be a candidate catalyst for synthesis of organic materials such as oxazolone and imidazolone derivatives.

The aim of the current work is the utilization of the abundant residue of fly ash as a solid catalyst for the synthesis of oxazolone and imidazolone derivatives. In this experiment, fly ash was deployed as a catalyst since it consists of numerous metal oxides such as SiO_2, Al_2O_3, CaO, Fe_2O_3, K_2O. H_2O_2 was utilized as a general oxidant to activate the fly ash. H_2O_2 increased the specific area of fly ash by turning the crystalline structure thereof from amorphous into hexagonal. Such a crystalline growth was achieved due to the conversion of biotite minerals in raw fly ash to large crystals of muscovite. Results revealed that oxazolone and imidazolone derivatives can be synthesized with acceptable yields in the presence of H_2O_2 promoted fly ash (HPFA) as the reaction catalyst. HPFA simply activated the carbonyl group and then accelerated the nucleophilic attack to the carbonyl group. It is noteworthy to mention that HPFA can catalyze dehydration and cyclization in both oxazolone and imidazolone synthesis. Altogether, this study offers HPFA as an inexpensive, non-corrosive and environmentally benign catalyst that benefits a short time and productive reaction with the simple recovery. Thanks to these abilities, these methodologies can be offered as suitable alternatives for the existing ones.

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