



SYNERGISTICALLY DOPED FLY ASH CATALYST IS HIGHLY EFFECTIVE IN THE SYNTHESIS OF XANTHENE DERIVATIVES.

U.G. Ghoshir^a, S. J. Takate^a, U. N. Chaudhar^b, A.B. Gambhire^{c*}

^a Department of chemistry New Arts Commerce and Science College Ahmednagar, 414001 Maharashtra, India.

^b Department of Chemistry, Kalikadevi Arts Commerce and Science College Shirur (kasar), Beed 413249, Maharashtra India.

^c Department of Chemistry, Shri Anand College, Pathardi, Dist. Ahmednagar, 414102, Maharashtra, India.

*Corresponding author: Tel. +91 02428 222736, fax: +91 02428 223033;
E-mail address: abg_chem@ymail.com (A.B. Gambhire)

ABSTRACT: Fly ash-based hybrid materials are synthesized by doping 1-9 wt. % of boric acid in the presence of 0.5M sulfuric acid using the co-precipitation method. The synthesized materials were characterized using XRD, FT-IR, and SEM-EDS. In this study, several methods were employed to create catalytic active sites on the inert surface of fly ash, and the efficiency of these methods was evaluated through the one-pot synthesis of biologically active 1,8-dioxo-octahydroxanthene and 14*H*-dibenzo[*a,j*] xanthene derivatives. The condensation reaction between aromatic aldehydes and either dimedone or β -naphthol was conducted at a temperature range of 60-80°C for a duration of 10-20 minutes. The highest level of catalytic activity was observed when using a 5 wt. % H₃BO₃/fly ash. The selected synthesis approach is highly efficient, producing excellent yields in a short period of time. These features make it an attractive option for green synthesis.

KEY WORDS: Fly ash based hybrid materials; xanthene derivative, dimedone, β -naphthol.

INTRODUCTION:

Fly ash is a type of inorganic solid waste produced by coal-fired thermal power plants. It is present in the flue gases released from these plants and is considered a potential health hazard due to its contribution to air pollution. Fly ash is made up of a mixture of various oxides, SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, K₂O, Na₂O, and TiO₂.ⁱ Fly ash has been utilized in a variety of ways, including improving soil quality in agriculture, creating bricks and cement, and purifying gases and water. These uses have been demonstrated in various studiesⁱⁱ⁻ⁱⁱⁱ. Fly ash, which is rich in silicon dioxide and aluminum oxide, has been used as a source for synthesizing glass-ceramics^{iv}, zeolites^{v-vi} and mesoporous materials^{vii}. It has also been employed as a catalyst in various reactions due to these elements. Fly ash has been utilized in a range of reactions, including oxidation^{viii}, benzoylation^{ix}, Knoevenagel condensation^x SCR of NO^{xi}, and transesterification

for bio-diesel synthesis^{xii-xiii}. It has also been employed as a support for catalytic oxides and metals in these reactions^{viii-ix, xiv}. In recent years, heterogeneous catalysts have become increasingly popular due to their low cost, ease of availability and handling, ability to be easily removed from the reaction mixture, and environmentally friendly nature. Heterogeneous catalysts, particularly those with catalytically active sites dispersed on the surfaces of porous solid supports, have been widely used in a variety of chemical transformations. The use of heterogeneous catalysts, such as sulfated zirconia, zeolites, and acidified silica, as alternatives to traditional homogenous Lewis and Brønsted acid catalysts can be a more environmentally friendly approach to conducting organic reactions^{xv, xvi}. Nanostructured transition metal oxides, which have unique physical and chemical properties including their size, shape, and structure, have garnered significant interest due to their high surface area and reactive morphologies^{xvii}. These nanoparticles have proven to be effective catalysts for a variety of organic reactions. Xanthene and Benzo-xanthene derivatives have a wide range of therapeutic and pharmacological properties, including anti-inflammatory^{xviii}, antiviral^{xix} and antibacterial activities^{xx}. These heterocyclic compounds are also used in dyes^{xxi}, as antagonists of the paralyzing action of zoxazolamine^{xxii}, as sensitizers in photodynamic therapy^{xxiii} and as fluorescent materials for visualization of biomolecules^{xxiv}. There are a number of reported methods for synthesizing 14-phenyl-14H-dibenzo[a,j] xanthenes, which involve mixing - naphthol and benzaldehyde in the presence of an acidic catalyst such as sulfamic acid supported on MIL-101^{xxv}, silica sulfuric acid^{xxvi}, boric acid^{xxvii}, or heteropoly acid^{xxviii}, HClO₄-SiO₂^{xxix}, succinic acid^{xxx}, γ -Fe₂O₃ hydroxyapatite-Fe²⁺ nanoparticles^{xxxi}, iron oxide nanoparticles (FeNP@SBA-15)^{xxxii}, acetic acid^{xxxiii}, sulphamic acid^{xxxiv-xxxv}, succinamide-N-sulphonic acid^{xxvi}, citric acid^{xxxvi}, lactic acid^{xxxviii}, tartaric acid^{xxxix}, niobium pentachloride^{xl}, p-toluene sulphonic acid^{xli-xlii}, indium(III) chloride and meta phosphoric acid^{xliii}, silica functionalized propyl sulphonic acid^{xliv}, montmorillonite K10^{xlv}, iodine^{xlvi} and lanthanum(III) nitrate^{xlvii}. Due to their longer reaction times, low yields, harsh reaction conditions, and high consumption of reagents and catalysts, many of these methods have some disadvantages. Therefore, it is necessary to explore more efficient methods for synthesizing these compounds. The aim of this work is to overcome the disadvantages mentioned, such as low yield, and achieve excellent yield. The goal of this study was to build upon previous research and develop a new, environmentally friendly and safe method for synthesizing xanthene derivatives using synergistically doped fly ash as a catalyst.

EXPERIMENTAL:

Materials

The β -naphthol, dimedone, aromatic aldehyde, boric acid, ethanol, n-hexane and ethyl acetate were obtained from Sigma Aldrich. Fly ash was collected from a thermal power plant located in Parli Vajjnath, Maharashtra, India.

Preparation of catalyst

Fly ash (5 gram) was crushed and then calcined for 1 hour at 400°C in a muffle furnace. The fly ash was treated with boric acid at a concentration ranging from 1-9 percent by weight. To prepare homogeneous slurry, 0.5 M sulfuric acid (5 ml) and deionized water (100 ml) were added to the mixture and stirred constantly for 12 hours. After preparing the slurry, it was left to age for 5 days. The mixture was then dried by evaporating it at 100°C and calcined at 400°C for 1 hour to synthesize the fly ash-based hybrid material.

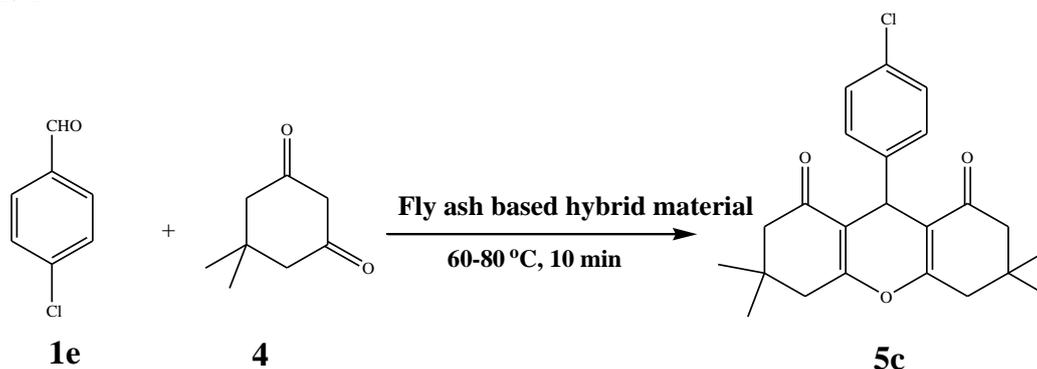
Catalyst Characterization

The prepared fly ash-based hybrid material was characterized using x-ray powder diffraction (XRD) patterns at room temperature with a Bruker AXS D8 model using monochromatic Cu radiation (40 kV and 30 mA). The particle sizes of the materials were determined from the

XRD patterns using the maximum intensity peaks. The surface morphology and elemental analysis of the samples were examined using a dispersive spectrophotometer (EDS) (Jeol; JED-2300), acidity of catalyst measured by NH₃-adsorption method and FT-IR spectra were performed using a Shimadzu-8400 spectrometer in the range of 4000-400 cm⁻¹.

Catalytic activity

The performance of catalyst was tested by synthesis of 1, 8-dioxo-octahydroxanthenes derivatives from p-chlorobenzaldehyde and dimedone in the presence of inexpensive, eco-friendly and heterogeneous fly ash based hybrid material as a model reaction was described in scheme I.



Scheme I. Synthesis of 9-(4 chlorophenyl) -1,8-dioxo-octahydroxanthene.

Screening of catalyst

Table 1 shows the screening of fly ash-based hybrid materials for their ability to catalyze the synthesis of 1, 8 - dioxo-octahydroxanthenes derivatives of p-chlorobenzaldehyde and dimedone through the use of appropriate reaction conditions. Results shown in table 1 refers H₂SO₄/fly ash and 1-3 wt.% H₂SO₄/fly ash shows less catalytic activity as compared to 5 wt.% H₂SO₄/fly ash due to the insufficient formation of acidic sites formed on surface of fly ash materials. It should be noted that modification of the fly ash with synergistically doped sulphuric acid and boric acid increases the textural parameter more effectively.

Table 1. Screening of Catalyst for the Synthesis of 1,8-dioxo-octahydroxanthenes derivatives

Entry	Fly ash based Catalysts	Amount of catalyst loaded in gm	Reaction rate (min)	Yield %
1	H ₂ SO ₄ /fly ash	0.05	40	80
2	1 wt. % H ₃ BO ₃ /fly ash	0.05	30	86
3	3 wt. % H ₃ BO ₃ /fly ash	0.05	20	92
4	5 wt. % H ₃ BO ₃ /fly ash	0.05	10	96
5	7 wt. % H ₃ BO ₃ /fly ash	0.05	10	96
6	9 wt. % H ₃ BO ₃ /fly ash	0.05	10	94

The results indicate that 5 wt. % H₃BO₃/fly ash is the preferred catalyst for synthesis of 1,8-dioxo-octahydroxanthenes derivatives of p-chlorobenzaldehyde and dimedone.

General procedure for the synthesis of 14H-dibenzo [a, j] xanthenes derivatives (3a-e)

Mixture of aromatic substituted aldehydes (1.0 mmol), β-naphthol (2.0 mmol) and fly ash based hybrid material (50 mg) in ethanol (5 ml) was taken in round bottom flask the mixture was heated at 60 – 80 °C for an appropriate time. The reaction was monitored using TLC techniques.

After the reaction was completed, the reaction mixture was washed with cold water, and the solid was separated by filtration. The crude product was recrystallized from ethanol.

General procedure for the synthesis of 1, 8-dioxo-octahydroxanthenes derivatives (5a-e)

Mixture of aromatic substituted aldehydes (1.0 mmol), dimedone (2.0 mmol) and fly ash based hybrid material (50 mg) in ethanol (5 ml) was taken in round bottom flask the mixture was heated at 60 – 80 °C with constant stirring up to an appropriate time. Reaction progress was checked by TLC techniques then after completion of the reaction, reaction mixture washed with cold water then solid separated by filtration. The crude product was recrystallized from ethanol.

RESULT AND DISCUSSION:

XRD Study

To determine the symmetry of the prepared samples, an X-ray diffraction (XRD) study was conducted. Figure 1(a) displays the XRD pattern of pure fly ash that was calcined at 400°C for 1 hour in air. Two sharp peaks at $2\theta = 20.97^\circ$ and 26.77° , corresponding to (111) and (021) respectively, were observed. These peaks are characteristic of the monoclinic crystalline structure of fly ash [ASTM card no-86-0680]^{xlviii}. The X-ray diffraction (XRD) pattern of H₂SO₄-doped fly ash is shown in Figure 1(b). It exhibits a crystalline phase of silico-aluminate species that has been reduced to an amorphous phase, possibly due to the interaction between the anions of sulfuric acid and the silanol groups on the surface of the fly ash. Figures 2 (c-g) display the X-ray diffraction (XRD) patterns of fly ash powders doped with various concentrations of H₃BO₃ and a fixed amount of H₂SO₄, calcined at 400°C for 1 hour. The XRD patterns for 1 wt. % H₃BO₃/fly ash (c), 3 wt. % H₃BO₃/fly ash (d), 5 wt. % H₃BO₃/fly ash (e), 7 wt. % H₃BO₃/fly ash (f), and 9 wt. % H₃BO₃/fly ash (g) all show a single monoclinic structure with a crystalline phase. It was observed that the peak intensity of the doped fly ash increased due to the direct effect on the silica-alumina species in the fly ash. The average particle sizes of the samples at the major peaks were calculated using the Debye-Scherrer formula based on X-ray diffraction (XRD) peak broadening analysis techniques. The particle size was found to be in the range of 60-85 nm for fly ash doped with 1 wt. %, 3 wt. %, 7 wt. %, and 9% wt. of H₃BO₃, and as small as 40 nm for fly ash doped with 5 wt. % H₃BO₃. This suggests that the 5 wt. % H₃BO₃/fly ash sample will have high catalytic performance when used for organic transformation.

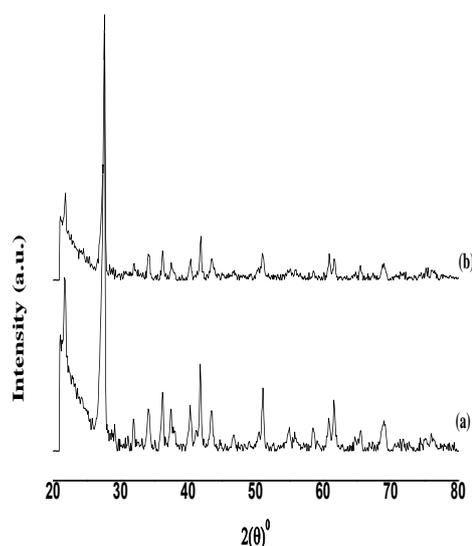


Figure 1 (a-b); X-ray Diffraction Patterns of (a) pure fly ash, (b) H₂SO₄/fly ash Calcined at 400°C for 1 h

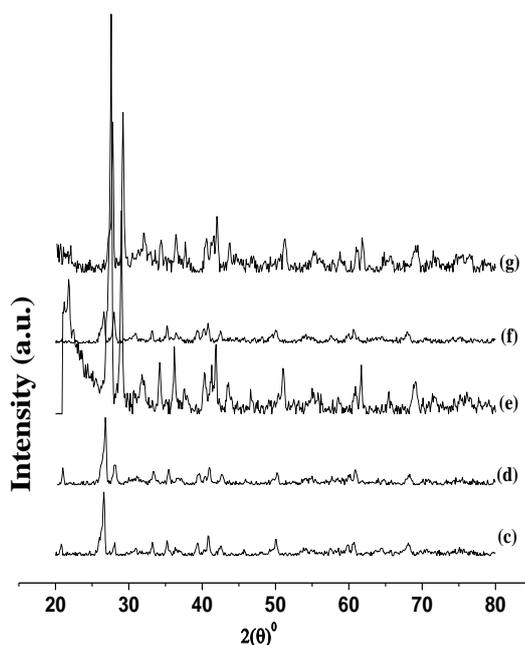


Figure 2(c-g); X-ray Diffraction Patterns of (c) 1 wt. % H₃BO₃/fly ash, (d) 3 wt.% H₃BO₃/fly ash, (e) 5 wt.% H₃BO₃/fly ash (f) 7 wt.% H₃BO₃/fly ash, and (g) 9 wt. % H₃BO₃/fly ash Powders With a Fixed Amount of H₂SO₄, Calcined at 400°C for 1 h

FT-IR

Figures 3 (a-g) display the Fourier transform infrared (FT-IR) spectra of (a) pure fly ash, (b) H₂SO₄/fly ash, (c) 1 wt. % H₃BO₃/fly ash, (d) 3 wt. % H₃BO₃/fly ash, (e) 5 wt. % H₃BO₃/fly ash, (f) 7 wt. % H₃BO₃/fly ash, and (g) 9 wt. % H₃BO₃/fly ash, based hybrid materials. All of the spectra show a broad band in the range of 3300-3000 cm⁻¹. This suggests that the samples

have strong hydrogen bonding, as indicated by the broad band in the spectra, which is likely due to the presence of Si-OH groups and absorbed water molecules on the surface^{xlix}. The broadness of this band further suggests the presence of strong hydrogen bonding in the samples^l. Additionally, a peak in the range of 2340-2360 cm^{-1} is observed in all samples due to the presence of carbon impurities, and a peak at 1741 cm^{-1} is observed, which is due to the C=O stretching vibration. After acid treatment, the increase in silica content was greater in comparison to pure fly ash, leading to a significant increase in the broadening of the -OH peak at 3000 cm^{-1} in all samples, as shown in Figure 3 (a-g). The acid treatment appears to increase the number of surface hydroxyl groups^{li} and enhances the silica content, as evidenced by the increased broadening of the -OH peak at 3000 cm^{-1} in all samples. An intense band in the range of 1050-1350 cm^{-1} , which is typically associated with the valence vibration of the silicate oxygen skeleton and corresponds to the amorphous silica content, was also observed after the acid treatment. The acid treatment appears to increase the amorphous silica content, as indicated by the intense band in the range of 1050-1350 cm^{-1} . The region between 800-500 cm^{-1} in the spectra shows the symmetric stretching of Si-O-Si and Al-O-Si bonds, which corresponds to the formation of amorphous to semi-crystalline alumina-silicate materials. The band below 500 cm^{-1} shows a bending vibration of Si-O-Si and O-Si-O bands^{lii}. The increased silica content and surface hydroxyl groups are responsible for the creation of acidic sites on the catalyst, which helps to improve its catalytic activity.

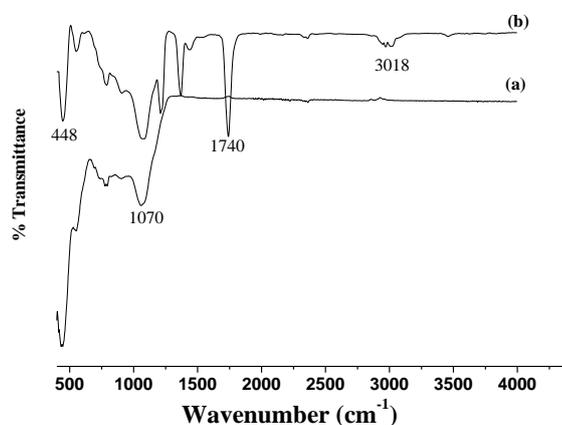


Figure 3(a-b); FT-IR Spectra of (a) pure fly ash, (b) H_2SO_4 /fly ash Calcined at 400°C for 1 h

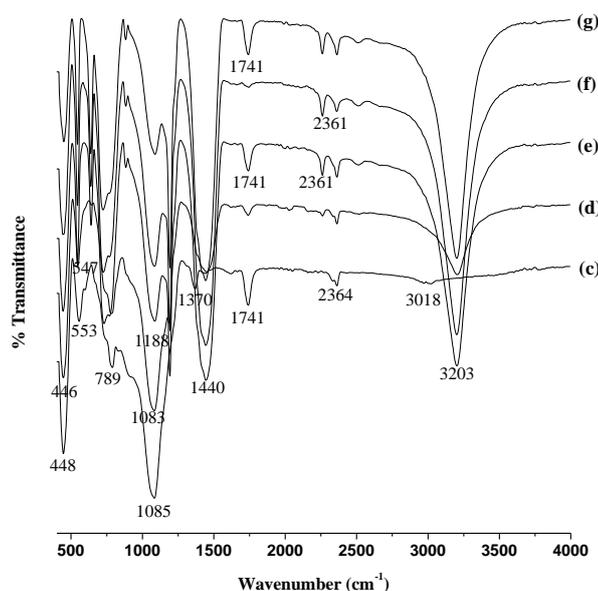


Figure 4(c-g); FT-IR Spectra of (c) 1 wt. % H_3BO_3 /fly ash, (d) 3 wt.% H_3BO_3 /fly ash, (e) 5 wt.% H_3BO_3 /fly ash, (f) 7 wt.% H_3BO_3 /fly ash, and (g) 9 wt. % H_3BO_3 /fly ash Powders with a Fixed Amount of H_2SO_4 , Calcined at 400°C for 1 h

SEM-EDS

Figure 5 shows the morphology of the 5 wt. % H_3BO_3 /fly ash material was analyzed using scanning electron microscopy (SEM). After undergoing calcination at 400°C for 1 hour, the particles in the sample were found to have an irregular shape and were clumped together, with an average primary particle size of less than $0.1\ \mu\text{m}$. The table 2 shows the elemental composition includes Si, Al, O, C, Ca, Fe, K, Mg and Ti. The percentage of Al, Si, and O in the 5 wt. % H_3BO_3 /fly ash sample is higher than in pure fly ash. An increase in the silica-alumina content leads to an increase in the number of acidic sides on the catalyst surface, as shown by the FT-IR data. This is in agreement with the results obtained.

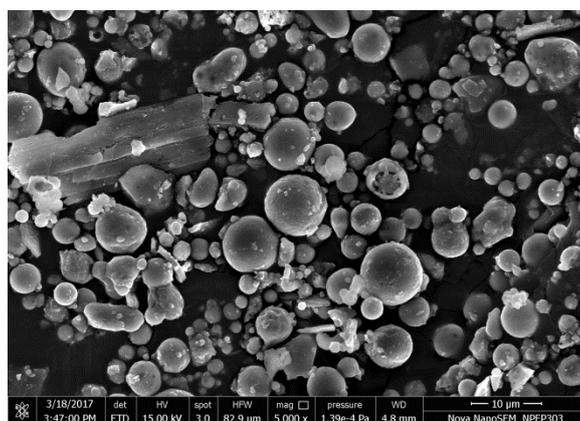


Figure 5. SEM Micrograph of 5 wt. % H_3BO_3 /fly ash Calcined at 400°C for 1 h

Table 2. EDS Analysis of Pure and 5 wt. % H₃BO₃/fly ash Calcined at 400°C for 1 h

Elements	Si	Al	O	C	Ca	Fe	K	Mg	Ti	Cu	Zn	Zr	Total
Pure Fly ash Wt. (%)	3.63	2.31	47.96	45.28	0.16	0.68	0.09	0.11	0.08	0.09	0.08	0.03	100
5 wt. % H ₃ BO ₃ /fly ash At. (%)	24.53	11.19	54.90	3.08	0.75	2.28	2.06	0.55	0.66	-	-	-	100

NH₃ - Adsorption Measurement

The acidity of the catalyst was analyzed using the temperature-programmed desorption of ammonia (TPD) technique. To determine the acidity of the catalyst, it was heated to 200°C for 1 hour in a helium environment, and then treated with an ammonia flow at 100°C for 5 minutes. To remove any excess ammonia that had been physically absorbed by the catalyst, it was treated with pure helium gas at 120°C for 1 hour following the previous treatment with ammonia. The temperature was gradually increased to 600°C over a period of 10 minutes, and the amount of ammonia removed from the catalyst during this process was measured and reported in table 3.

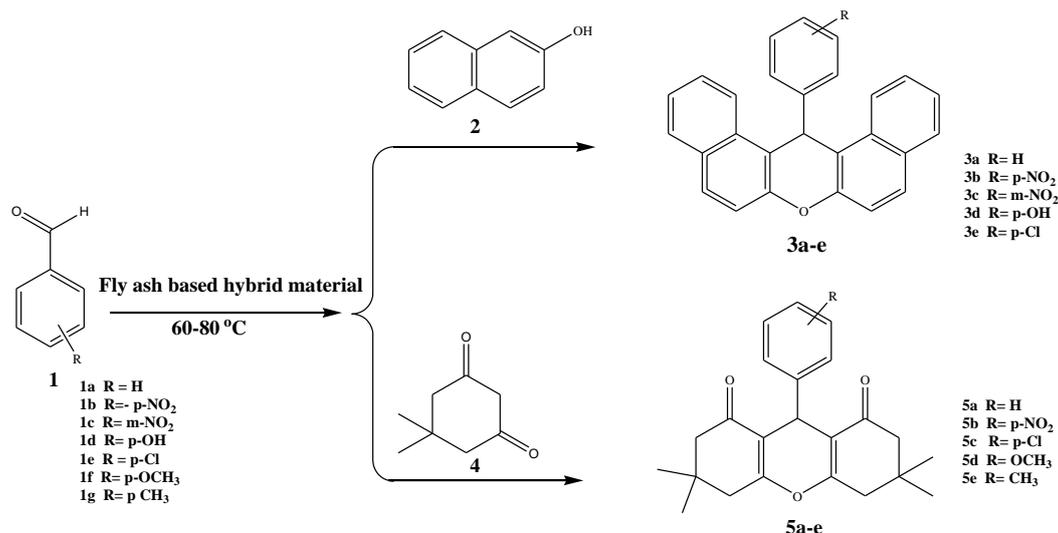
Table 3. Summary of Acidic Measured by NH₃ -TPD of Synthesized Catalysts

Fly ash based Catalyst	Acidic sites (mmol NH ₃ /g)		
	T ₁ (< 200°C)	T ₂ (>500°C)	Total
H ₂ SO ₄ /fly ash	0.196	0.183	0.379
5 wt. % H ₃ BO ₃ /fly ash	0.227	0.204	0.431

The presence of a synergistic effect between boric and sulfuric acid on the fly ash surface leads to stronger surface acidity. The total number of acid sites in H₂SO₄/fly ash was found to be 0.379 mmol/g. The total number of acid sites in 5 wt. % H₃BO₃/fly ash was found to be 0.431 mmol/g, while for H₂SO₄/fly ash it was 0.379 mmol/g. The data suggests that both Bronsted and Lewis acidic sites are present on these catalysts.

CATALYTIC PERFORMANCE:

The activities of catalyst were investigated for synthesis of 1, 8-dioxo-octahydroxanthenes derivatives using reaction of aromatic aldehydes and dimedone in the presence of fly ash based hybrid material. It shows that 5 wt. % H₃BO₃/fly ash catalysts accelerate the rate of reaction as compared to all other synthesized catalyst. 5 wt. % H₃BO₃/fly ash catalysts possesses significant acidity due to well synergy established in between sulphuric acid and boric acid on the support of fly ash material as compared to other prepared hybrid material. A various kind of xanthene derivatives was prepared by the reaction of substituted aldehydes with dimedone and β-naphthol in the presence of 5 wt. % H₃BO₃/fly ash catalyst under the optimized reaction condition was shown in scheme II and their results has been summarized in table 4.



Scheme II. General procedure for the synthesis of xanthene derivatives

Substituted aldehydes bearing either electron-donating or electron-withdrawing substituent have reacted successfully and gave the product in high yield with shorter reaction time. However it was found that the aromatic aldehyde with electron-withdrawing groups reacted faster than those with electron-donating groups.

Table 4. Synthesis of xanthene derivatives catalyzed by 5 wt % H₃BO₃/fly ash.

Entry	Substituted aldehyde	Time (min)	Yield (%)	Melting point in °C		Ref
				Found	Reported	
3a	C ₆ H ₅	20	92	181-183	183-184	lii
3b	p-NO ₂ -C ₆ H ₄	18	94	306-308	310-312	liii
3c	m-NO ₂ -C ₆ H ₄	20	91	211-213	210-212	liii
3d	p-OH-C ₆ H ₄	26	86	137-139	138-140	xlvi
3e	p-Cl-C ₆ H ₄	18	94	288-290	289-290	liii
5a	C ₆ H ₅	10	94	198-200	202-204	xlvi
5b	p-NO ₂ -C ₆ H ₄	10	96	228-230	228-230	xlvi
5c	p-Cl-C ₆ H ₄	10	96	230-232	230-233	liv
5d	p-OCH ₃ -C ₆ H ₄	14	94	246-248	242-245	liv
5e	p-CH ₃ -C ₆ H ₄	10	92	216-218	215-216	xlvi

Selected Spectral Data

14-Phenyl-14H-dibenzo [a,j] xanthene (Table 4, entry 3a)

FT-IR (KBr): 509, 608, 700, 743, 801, 826, 964, 1249, 1402, 1590, 3018, 3071 cm⁻¹

¹H NMR (CDCl₃): δ = 5.38 (s, 1H), 7.28- 7.30 (d, 2H), 6.67- 6.75 (m, 4H), 5.88-6.80 (m, 11H) ppm; **¹³C NMR** (CDCl₃): δ = 38.0, 117.3, 118.0, 122.6, 124.2, 126.3, 126.7, 128.2, 128.4, 128.7, 128.8, 131.0, 131.4, 144.9, 148.7; **MS**: (EI), m/z: 358 (M⁺), 179, 250, 252, 281, 282.

14-(4-Nitrophenyl)-14H-dibenzo [a,j] xanthene (Table 4, entry 3b)

FT-IR (KBr): 438, 512, 604, 740, 805, 824, 1105, 1234, 1335, 1508, 1590, 3038, 3072 cm⁻¹.

¹H NMR (CDCl₃): δ 5.41 (s, 1H), 6.31-6.54 (m, 8H), 6.70-6.74 (m, 4H), 6.83-6.88 (d, 2H), 7.13-7.18 (m, 2H) ppm; **¹³C NMR** (CDCl₃): δ 37.8, 115.7, 118.0, 122.0, 123.8, 124.5, 127.1, 128.9, 129.0, 129.5, 131.0, 146.2, 148.7, 152.0; **MS**: m/z: 403 (M⁺), 141, 178, 250, 252, 281, 282.

14-(3-nitrophenyl)-14H-dibenzo [a,j] xanthene (Table 4, entry 3c)

FT-IR (KBr): 3076, 2925, 1592, 1527, 1431, 1435, 1252, 812, 747 cm⁻¹.

¹H NMR (CDCl₃): δ = 6.59 (s, 1H), 7.25–7.86 (m, 13H), 8.28 (d, 2H), 8.41 (s, 1H) ppm.

14-(4-Hydroxyphenyl)-14H-dibenzo [a,j] xanthene (Table 4, entry 3d)

¹H NMR (CDCl₃): δ = 4.73 (br.s, 1H), 6.42 (s, 1H), 6.56-6.58 (d, 2H), 7.35-7.58 (m, 8H), 7.76-7.82 (m, 4H), 8.34-8.36 (d, 2H) ppm; **¹³C NMR** (CDCl₃): δ = 37.0, 115.2, 117.4, 118.0, 122.6, 124.2, 126.7, 128.8, 129.3, 131.0, 131.3, 137.4, 148.6, 153.8 ppm **MS**: m/z = 375 (M+H)

14-(4-Chlorophenyl)-14H-dibenzo [a, j] xanthene (Table 4, entry 3e)

¹H NMR : δ = 6.45 (s, 1H), 7.07 (d, 2H), 7.4-7.8 (m, 12H), 8.29 (d, 2H) ppm; **¹³C NMR** : δ = 37.3, 116.7, 118, 122.4, 124.3, 126.9, 128.6, 128.9, 129, 129.4, 131, 131.2, 132, 143.4, 148.7; **MS** : m/z= 393 (M+H).

9-(4-nitrophenyl)-1, 8-dioxo-octahydroxanthene (Table 4, entry 5b)

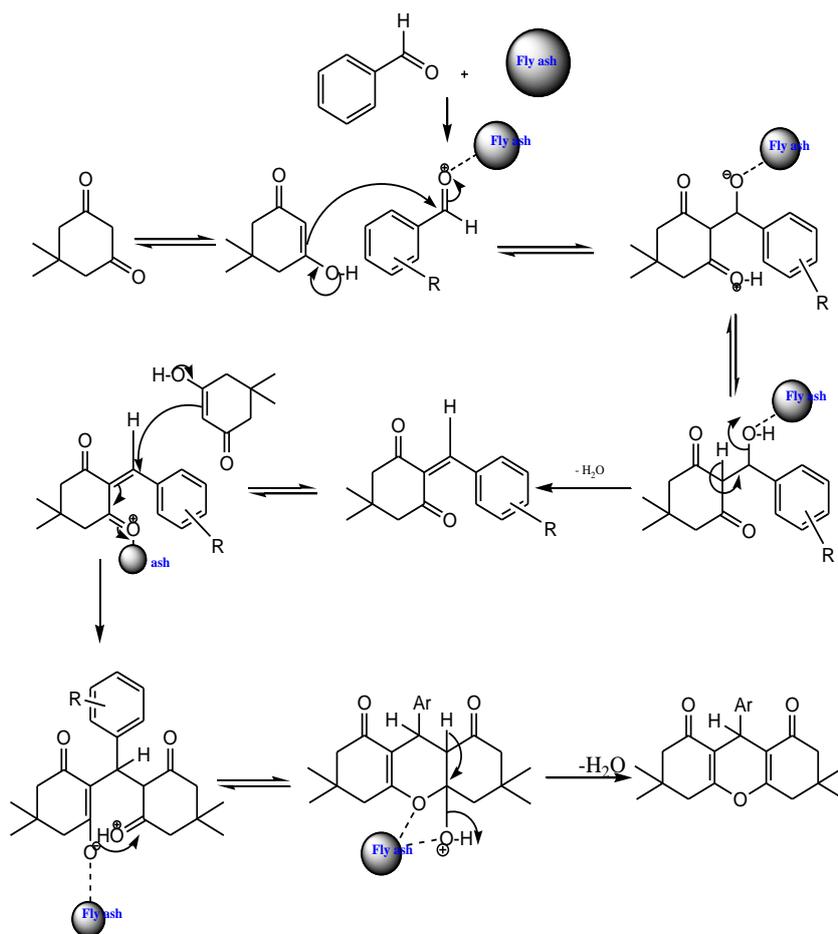
¹H NMR : δ = 0.99 (s, 6H), 1.12 (s, 6H), 2.15-2.27 (d, 4H), 2.49 (d, 4H), 4.82 (s, 1H), 7.48 (d, 2H), 8.08 (d, 2H); **¹³C NMR** : δ 27.2, 29.2, 32.2, 32.3, 40.8, 50.6, 114.5, 123.4, 129.3, 146.4, 151.5, 162.9, 196.2; **MS** : m/z= 396 (M+H).

9-(4-methoxyphenyl)-1,8-dioxo-octahydroxanthene (Table 4, Entry 5d)

¹H NMR (CDCl₃): δ= 0.99 (s, 6H), 1.09 (s, 6H), 2.18-2.24 (d, 4H), 2.45 (s, 4H), 3.73 (s, 3H), 4.69 (s, 1H), 6.76 (d, 2H), 7.20 (d, 2H) ppm; **¹³C NMR** (CDCl₃): δ= 27.3, 29.2, 30.9, 32.2, 40.8, 50.7, 55.1, 113.4, 115.8, 129.3, 136.5, 157.9, 162.0, 196.5 ppm; **MS**: m/z = 381 (M+H)

Proposed reaction Mechanism

The proposed mechanism pathway for generating xanthene derivatives is outlined in Scheme III. To initiate the process, the carbonyl group of aromatic aldehydes is activated by the presence of 5 wt. % H₃BO₃/fly ash catalyst (acidic proton), which facilitates a nucleophilic attack by dimedone or 2-naphthol, leading to the formation of Knoevenagel products. Subsequently, a sequential addition involving dimedone leads to the creation of acyclic intermediate adducts. This is succeeded by an intramolecular cyclization process, facilitated by the participation of two hydroxyl groups, resulting in the formation of xanthene derivatives.



Scheme III. Proposed reaction mechanism for the synthesis of xanthene derivatives.

Reusability of catalyst

After the reaction is complete, the catalyst is removed from the mixture by filtration, cleaned with ethyl acetate, and then heated to 110°C to prepare it for future use in subsequent reaction cycles. Table 5 demonstrates that the regenerated catalyst retained efficient catalytic activity throughout four reaction cycles, resulting in conversion rates of xanthene derivative between 96-93%. This suggests that the acidic sites on the catalyst do not become depleted during regeneration this was the advantage of heterogeneous catalyst.

Table 5. Reusability of 5 wt. % H₃BO₃/fly ash catalyst

Run	1	2	3	4
Yield	96	95	94	93

CONCLUSION:

This study introduces a new use for a waste material as a catalyst in the organic reaction. To prepare an effective heterogeneous acid catalyst through thermal activation followed by chemical treatment with various mineral acids. The thermal as well as chemical activation of fly ash consequences in increased amorphous silica content and surface hydroxyl groups, which ultimately results in enhanced surface acidity. Out of all the catalysts prepared, it was found that the catalyst made by treating 5 wt. % H₃BO₃/fly ash is a promising heterogeneous acid catalyst for use in a synthesis of xanthene derivatives. The reaction is performed in a one-pot, single-step process under optimized conditions. The catalyst is easily filtered and recycled up

to four times with consistent efficiency, indicating that the acidic sites on the catalyst remain stable during the reaction. This work is unique in that it utilizes a readily available natural waste material fly ash, as a solid support to create a highly efficient heterogeneous acid catalyst.

ACKNOWLEDGEMENT:

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