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on

6th- 7th October, 2023

- Prof. Monika Dakshene
- Prof. Manju Bala Yadav
- Prof. Seema Agarwal
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SYNERGISTICALLY DOPED FLY ASH CATALYST IS HIGHLY EFFECTIVE IN THE SYNTHESIS OF BIS (3-indolyl) METHANE DERIVATIVES

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Abstract

The synthesis and advancement of catalysts have gained significant attention in research due to the growing global need to replace expensive and environmentally harmful reagents used in inefficient non-catalytic processes with cost-effective and environmentally friendly (green) catalytic methods. The characterized heterogeneous catalyst supported on fly ash was subjected to analysis using techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS). The catalytic potential of the synergistically doped fly ash material was evaluated through a one-pot synthesis of bis (3-indolyl) methane derivatives, resulting in higher yields achieved in a shorter time frame. This outcome indicates that the catalyst prepared has an ample number of active sites that play a pivotal role in its catalytic activity.

Key words: 5 wt. % H_3BO_3/fly ash, bis (3-indolyl) methane derivatives

1. Introduction

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.[1-2] Nitrogen atom containing heterocyclic compounds are biologically active.[3-4] Bis (3-indolyl) methanes as well as indole and its derivatives, are recognized as crucial

compounds in the field of organic synthesis and pharmaceutical chemistry. They display a range of significant physiological characteristics.[5] Among the diverse array of indole derivatives, bis (3-indolyl) methanes have broad medicinal utility. They can induce apoptosis in human cancer cells normalize irregular cell growth linked to cervical dysplasia,[6] promote favorable estrogen metabolism in both genders, aid in breast cancer prevention[7] and enhance the body's natural hormone metabolism.[8] As a result of the extensive biological potential exhibited by bis(3-indolyl) methanes and their broad spectrum of medical uses, numerous synthesis methods have been documented in the literature.

Nonetheless, nearly all these approaches have utilized traditional Lewis acids and protic acids as catalysts to facilitate the electrophilic substitution reaction between indoles and different aldehydes or carbonyl compounds.[9] A various kind of catalyst was used to synthesis of bis 3-indolyl methane derivatives such as H-Y zeolite,[10] Montmorillonite clay K-10,[11] sulphamic acid,[12] SBA-15/SO_3H,[13] oxalic acid,[14] vanadomolybdophosphoric acid,[15] silica bonded S-sulfonic acid,[16] $Cu(BF_4)_2.SiO_2$,[17] $In(OTf)_3$,[18] $LiClO_4$,[19] bis(cyclopentadienyl)$ZrCl_2$,[20] $CuBr_2$,[21] $ZrCl_4$,[22] CAN,[23] $Zn(HSO_4)_2$,[24] acetic acid,[25] polyindole salt,[26] N-tert-butanesulfinyl aldimines,[27] NBS,[28] $Ln(OTf)_3$,[29] $Dy(OTf)_3$,[30] $InCl_3$,[31] InF_3,[32] [P(4-VPH)HSO_4],[33] $FeCl_3.6H_2O$,[34] Ph–PMO– SO_3H,[35] glycerin and $CeCl_3$,[36] $B(C_6F_5)_3$, [37] $H_6P_2W_{18}O_{62}$,[38] phosphated zirconia,[39] Ph_3CCl,[40] have been reported for the synthesis of bis (3-indolyl) methanes. However, the majority of the current techniques employ hazardous metal ions and solvents, result in elevated expenses, utilize corrosive reagents, and entail complicated purification steps. Hence, there is a need for novel procedures that can overcome these limitations. Solvent-free reaction condition has been demonstrated to be an efficient technique for various organic reactions. It often leads to remarkable decrease in reaction time, increased yields, easier workup, and enhanced regio- and stereo-selectivity of reaction.[41-42] In continuation of our work in bis (3-indolyl) methane synthesis herein, we reports a green and efficient protocol for the synthesis of bis (3-indolyl) methane derivatives using mild and inexpensive fly ash catalyst from indole and aromatic aldehydes under appropriate reaction condition in excellent yields.

2. Experimental

2.1 Material

The chemicals such as indole, substituted aryl aldehydes, boric acid, ethanol, and ethyl acetate were obtained from Sigma Aldrich, and fly ash was collected from the thermal power plant in Parli Vaijnath, Maharashtra, India.

2.2 Catalyst preparation

Collected fly ash was crushed using ball milled and calcined at 400 °C up to 1 h in muffle furnace. About 10 gm of fly ash is treated with 1-9 wt. % of boric acid,

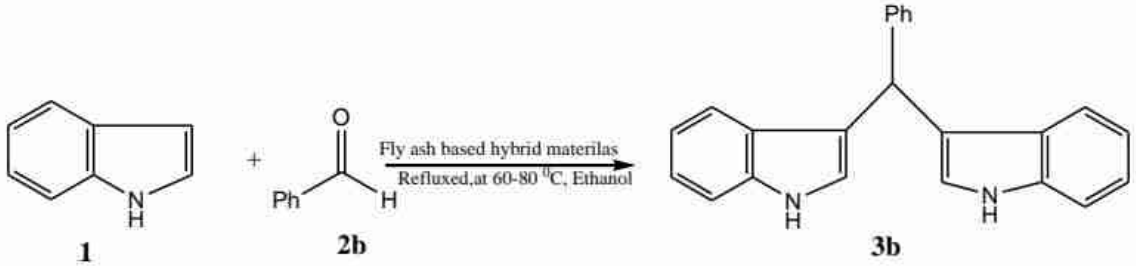
separately. Homogeneous slurry was prepared by adding a fixed amount of 0.5 M of (5 mL) sulfuric acid and 100 mL of deionized water to the mixture, stirring constantly for 12 h. Then, the slurry was left for aging for 5 days. The mixture was evaporated at 100 °C to obtain a dry powder, which was then calcined at 400 °C for 1 h to prepare fly ash-based hybrid material.

2.3 Characterization

The synthesized fly ash-based hybrid material was characterized using X-ray powder diffraction (XRD) patterns taken at room temperature using a Bruker AXS D8 model with monochromatic Cu radiation (40 kV and 30 mA). The particle sizes of the materials were determined by X-ray powder diffraction consistence of maximum intensity peaks. Surface morphology and elemental analysis of the samples were performed using a dispersive spectrophotometer (EDS) (Jeol; JED-2300), Temperature preprogrammed desorption (NH_3-TPD) were performed on a chemisorption analyzer (Autosorb-iQ-C, Quantachrome Instruments). The acidity determination was supported by the TGA studies using 2, 6 dimethyl pyridine at room temperature for 24 h and then subjected to thermal analysis in N_2 atmosphere at a heating rate of 10 °C min^{-1}. The fraction of weight loss in the range of 300-600 °C was calculated and taken as a measure of Bronsted acidity of the samples. The FT-IR analysis of samples was carried out using a Shimadzu-8400 spectrometer in the range of 4000-400 cm^{-1}; ^1H NMR and ^{13}C NMR spectra were acquired using a Bruker Avance instrument operating at frequencies of 400 MHz and 100 MHz, respectively. The measurements were conducted in $CDCl_3$ and DMSO solvents. Chemical shift are denoted in δ ppm relative to tetra methyl silane, while coupling constants are expressed in units of Hertz.

2.4 Catalytic activity

The performance of catalyst was tested by synthesis of bis (3-indolyl) methane derivatives from indole and p-chlorobenzaldehyde 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 bis(3- indolyl) methane using various fly ash based hybrid materials from indole with 4- chlorobenzaldehyde.*

2.5 Screening of catalyst

Table 1 shows the screening of fly ash-based hybrid materials for their ability to catalyze the synthesis of bis (3-indolyl) methane derivatives of p-chlorobenzaldehyde, indole was mixed in etrhanol and refluxed up to 60-80 °C for appropriate reaction time. Results shown in table 1 refers H_2SO_4/fly ash and 1-3 wt.% H_2SO_4/fly ash shows less catalytic activity as compared to 5 wt. % H_2SO_4/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 sulfuric acid and boric acid increases the textural parameter more effectively.

Table 1. Screening of Catalyst for the Synthesis of bis (3-indolyl) methane derivatives

Entry	Fly ash based Catalysts	Amount of catalyst loaded in gm	Reaction rate (min)	Yield %
1	H_2SO_4/fly ash	0.5	30	86
2	1 wt. % H_3BO_3/fly ash	0.5	22	88
3	3 wt. % H_3BO_3/fly ash	0.5	14	92
4	5 wt. % H_3BO_3/fly ash	0.5	10	94
5	7 wt. % H_3BO_3/fly ash	0.5	10	94
6	9 wt. % H_3BO_3/fly ash	0.5	10	92

The results indicate that 5 wt. % H_3BO_3/fly ash is the preferred catalyst for synthesis of bis (3-indolyl) methane derivatives of p-chlorobenzaldehyde and indole.

2.6 General reaction procedure for the synthesis of bis (3-indolyl) methane derivatives

A mixture of (2.0 mmol) indole, (1.0 mmol) benzaldehyde and catalytic amount (5 % wt. H_3BO_3/Fly ash) in beaker was stirred in ethanol and reflexed up to 60-80 °C for appropriate time. The completion of reaction was monitored by TLC. After completion of reaction the mixture was poured onto crushed ice to get desired crude product. The crude product was recrystallized by alcohol in high yield in short reaction time.

2.7 Selected spectral data

3, 3'-Bis (indolyl) phenylmethane *(Table 4, entry 3a)*

FT-IR (KBr) ; 670, 757, 1017, 1090, 1216, 1416, 1456, 1520, 1600, 3020, 3476 cm^{-1}.

^{1}H NMR ($CDCl_3$) δ = 5.8 (s, 1H), 6.6 (s, 2H), 7.0- 7.5 (m, 13H), 7.9 (bs, 2H); **ES-MS** E/Z 322 (M^+).

3, 3'-Bis (indolyl)-4-chlorophenylmethane *(Table 4, entry 3b)*

FT- IR (KBr); 670, 758, 1015, 1090, 1216, 1416, 1455, 1524, 1600, 2928, 3020, 3480 cm^{-1}.

^{1}HNMR ($CDCl_3$); δ = 5.8 (s, 1H), 6.6 (bs, 2H), 7.0- 7.7 (m, 12H), 7.9 (bs, 2H); **ES-MS** E/Z 322(M_).

3, 3'-Bis (indolyl)-4-methylphenylmethane *(Table 4, entry 3f)*

FT- IR (KBr) ; 668, 758, 1020, 1092, 1216, 1416, 1514, 1600, 3020, 3480 cm^{-1}.

^{1}H NMR ($CDCl_3$); δ = 2.3 (s, 3H), 5.8 (s, 1H), 6.6 (s, 2H), 6.8-7.4 (m, 12H), 7.9 (bs, 2H); **ES-MS** E/Z 336 (M^+)

3, 3'-Bis (indolyl)-4-methoxyphenylmethane *(Table 4, entry 3g)*

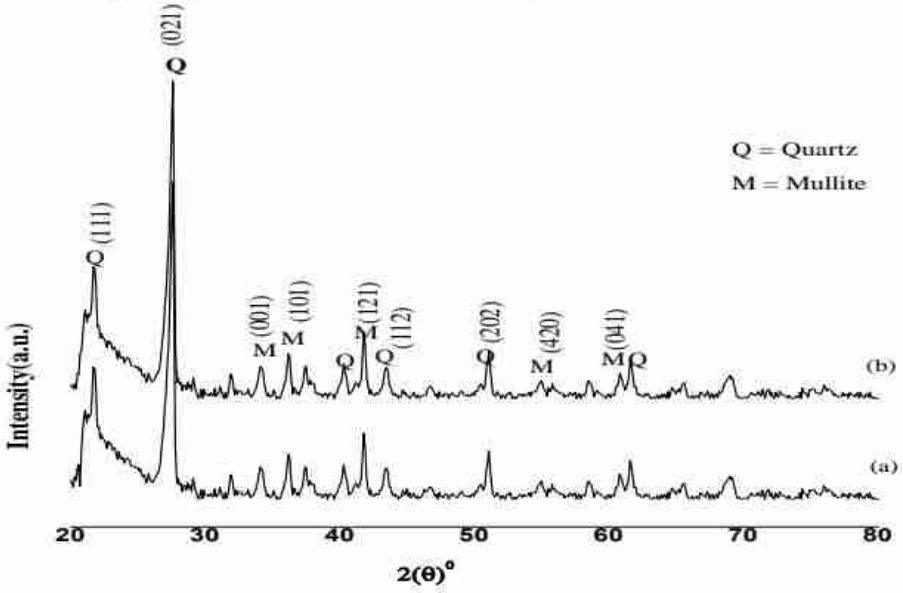
FT- IR (KBr) ; 758,1032, 1090, 1216, 1336, 1417, 1454, 1452, 1508, 1610, 2838, 3020, 3480 cm^{-1}.

^{1}H NMR ($CDCl_3$); δ = 3.7 (s, 3H), 5.8 (s, 1H), 6.6 (d, 2H), 6.8 (d, 2H), 7.0 (t, 2H), 7.2 (t, 2H); 7.2 - 7.4
(m, 6H), 7.8 (bs, 2H); **ES-MS** E/Z 352 (M^+).

3. Result and discussion

3.1 XRD Study

To understand the phase symmetry of the synthesized samples, a systematic XRD study was conducted. Fig. 1(a) shows the XRD pattern of pure fly ash calcined at 400 °C for 1 h in air. Sharp peaks at 2θ =20.97° and 26.77° corresponding to (111) and (021) were observed, which are associated with the monoclinic crystalline structure of fly ash [ASTM card No-86-0680].[43]



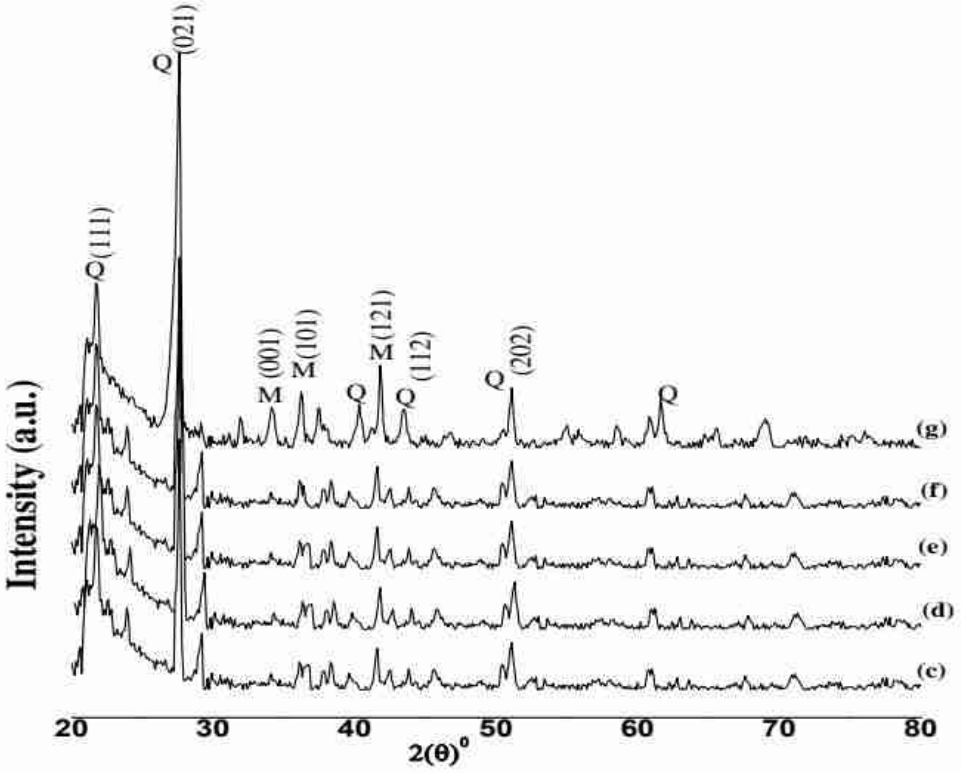


Fig. 1(a-g); *X-ray Diffraction Patterns of (a) pure fly ash and (b) H_2SO_4/fly ash, (c) 1 wt. % H_3BO_3/fly ash, (d) 3 wt. % H_3BO_3/fly ash, (e) 5 wt. % H_3BO_3/fly ash, (f) 7 wt. % H_3BO_3/fly ash, and (g) 9 wt. % H_3BO_3/fly ash powders with a fixed amount of H_3BO_3, calcined at 400 °C for 1 h.*

Fig. 1(b) shows the XRD pattern of H_2SO_4-doped fly ash, which exhibits a crystalline phase of silico-aluminate species that is reduced to an amorphous phase possibly due to the interaction between the anions of sulfuric acid and the silanol groups present on the surface of the fly ash. Further, Fig.1(c-g) shows the XRD pattern 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. A single monoclinic structure with a crystalline phase was obtained for the entire range of H_3BO_3 concentrations. It was observed that the peak intensity of the doped fly ash increased due to the direct synergistic 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 XRD peak broadening analysis techniques. The particle size was found to be as large as 60-85 nm for 1 wt. %, 3 wt. %, 7 wt. % and 9% wt. H_3BO_3/fly ash, and as small as 50 nm for 5 wt. % H_3BO_3/fly ash. This apparent fall in the particle size will ensure high catalytic activity for the

sample with 5 wt. % H_3BO_3, when it is used for catalytic applications. We have doped 1-9 wt. % H_3BO_3 to enhance the surface area of catalyst. However, we observed a drastic fall in the particle size with 5 wt. % H_3BO_3, because for this wt. % of H_3BO_3 in activated fly ash grain boundary inhibits crystallite growth of the catalyst which is responsible for reducing particle size of the prepared catalyst.

3.2 FT-IR analysis

Fig. 2(a-g) shows the FT-IR spectra of (a) pure fly ash, (b) H_2SO_4/fly ash, (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 samples in the range of 4000 to 500 cm^{-1}. Within this it shows up the band corresponding to surface hydroxyl groups at 3300-3000 cm^{-1}.

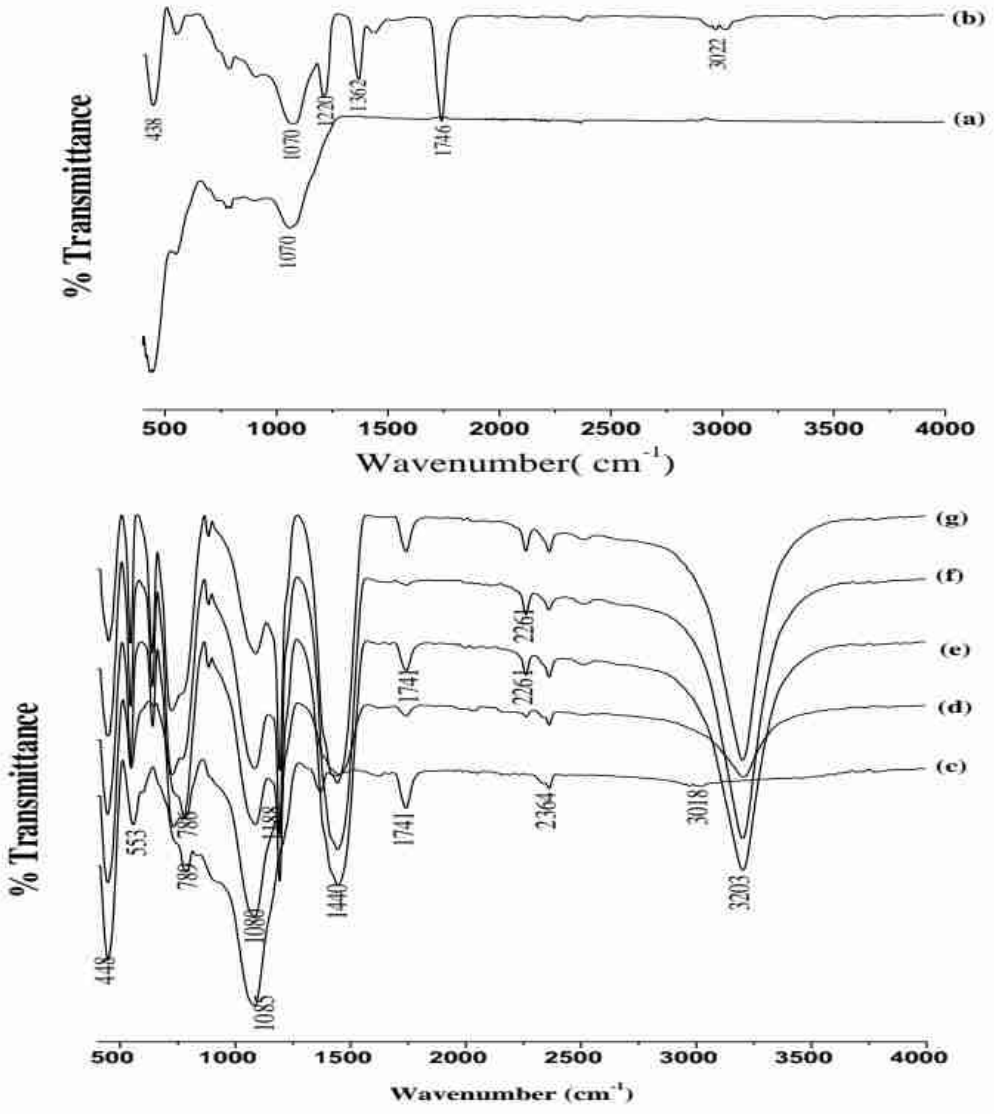
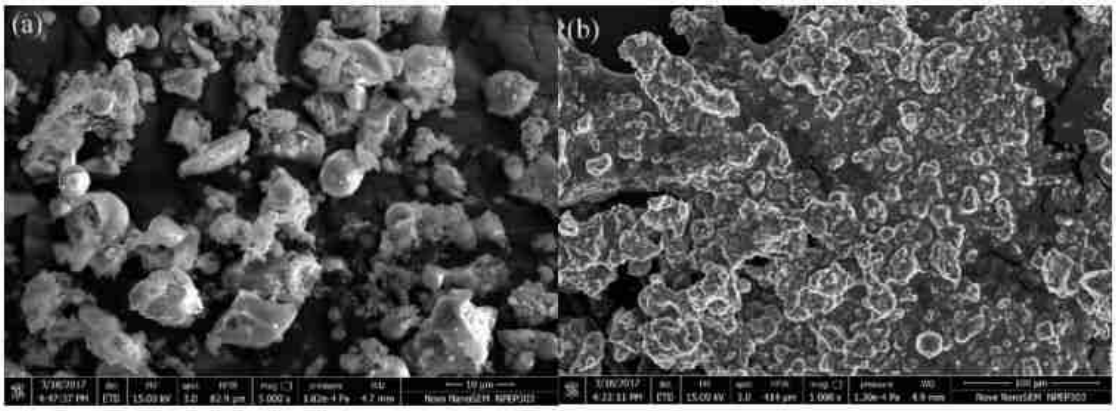


Fig.2 (a-g); *FT-IR spectra of (a) pure fly ash, (b) H_2SO_4/fly ash, (c) 1 wt. % H_3BO_3/fly ash, (d) 3 wt. % H_3BO_3/fly ash, (e) 5 wt. % H_3BO_3/fly ash, (f) 7 wt. % H_3BO_3/fly ash, and (g) 9 wt. % H_3BO_3/fly ash powder with a fixed amount of H_2SO_4 calcined at 400 °C for 1 h.*

This indicates the presence of strong hydrogen bonding in the samples, as indicated by the broad band, which is attributed to the surface Si-OH groups and absorbed water molecules on the surface.[44] The widening of this spectral feature signifies the existence of robust hydrogen bonding within the samples.[45] The intense peak observed in the region between 1000 – 1300 cm^{-1} is attributed to the valance vibration of the silicate oxygen skeleton (Si-O-Si) bond. After acid treatment, the increase in silica content resulted in a distinct and significant increase in the broadening of the -OH peak at 3000 cm^{-1} in all samples in comparison to pure fly ash, as shown in Fig. 2(c-g). This suggests that the increase in surface hydroxyl groups[46] is due to the acid treatment, which enhances the silica content. After acid treatment, an intense band in the range of 1050-1350 cm^{-1}, which is usually assigned to the valence vibration of the silicate oxygen skeleton and corresponds to the amorphous silica content, was observed. This indicates an increase in amorphous silica content after acid treatment. The region between 800-500 cm^{-1} 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.[47] The increase in silica content and surface hydroxyl groups is responsible for the development of acidic sites on the catalyst, which helps to enhance the catalytic activity.

3.3 SEM-EDS analysis

The effect of dopant and co-dopant on the morphology of synthesized samples was investigated by SEM.



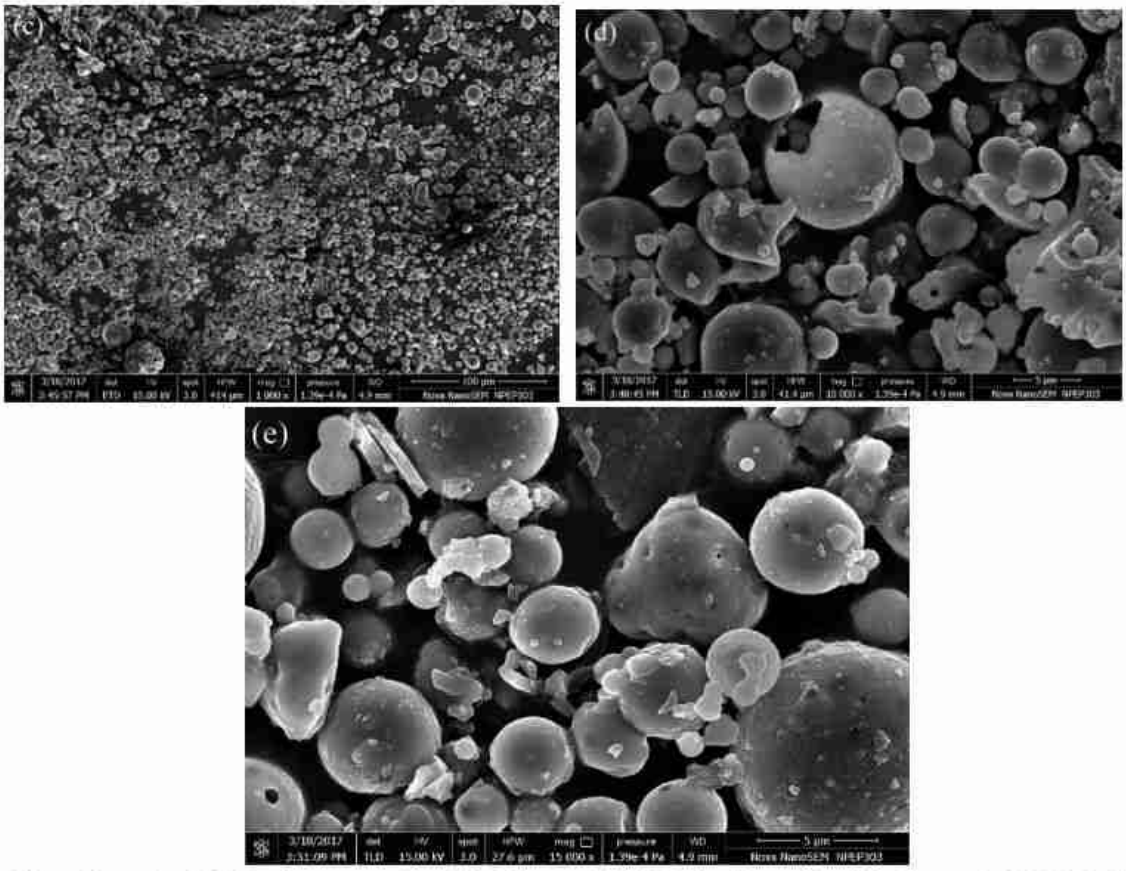


Fig. 3(a-e); *SEM micrograph of (a)1 wt. % H_3BO_3/fly ash, (b) 3 wt. % H_3BO_3/fly ash, (c) 5 wt. % H_3BO_3/fly ash. (d) 7 wt. % H_3BO_3/fly ash and (e) 9 wt. % H_3BO_3/fly ash calcined at 400 °C for 1 h.*

Fig. 3(a-e) shows SEM images of (a) 1 wt. % H_3BO_3/fly ash, (b) 3 wt. % H_3BO_3/fly ash, (c) 5 wt. % H_3BO_3/fly ash, (d) 7 wt. % H_3BO_3/fly ash and (e) 9 wt. % H_3BO_3/fly ash calcined at 400 °C for 1 h. It is observed that surface morphology of fly ash doped with 1, 3, 7, and 9 wt. % of H_3BO_3 were found to have an irregular shape and were clumped together, with an average primary particle size of less than 1μm. However, fly ash doped with 5 wt. % of H_3BO_3 has regular shape with particle size less than 0.5 μm. These results are inconsistent with XRD analysis.A chemical analysis of the elements was done and confirmed the presence of Si, Al, O, C, Ca, Fe, K, Mg and Ti in the sample as represented in Table 2. From these values it is evident that the percentage of Al, Si and O in 5 wt. % H_3BO_3/fly ash found to be higher in comparison with pure fly ash. The increases in silica-alumina content increased the surface hydroxyl groups on the catalyst surface.

Table 2. *EDS analysis of pure and 5 wt. % H_3BO_3/fly ash calcined at 400 °C for 1h*

Elements	Pure Fly ash At.%	5 wt. % H_3BO_3/fly ash At.%
Si	3.63	24.53
Al	2.31	11.19
O	47.96	54.90
C	45.28	3.08
Ca	0.16	0.75
Fe	0.68	2.28
K	0.09	2.06
Mg	0.11	0.55
Ti	0.08	0.66
Cu	0.09	-
Zn	0.08	-
Zr	0.03	-
Total	100	100

3.4 NH_3- adsorption measurement

To understand the acidity of catalyst it was determined with the help of very special technique temperature- programmed description of ammonia (TPD). The amount of ammonia that was removed from the catalyst during this process was measured and it was reported in Table 3.

Table 3. *Summary of acidity measured by NH_3- TPD of synthesized catalysts*

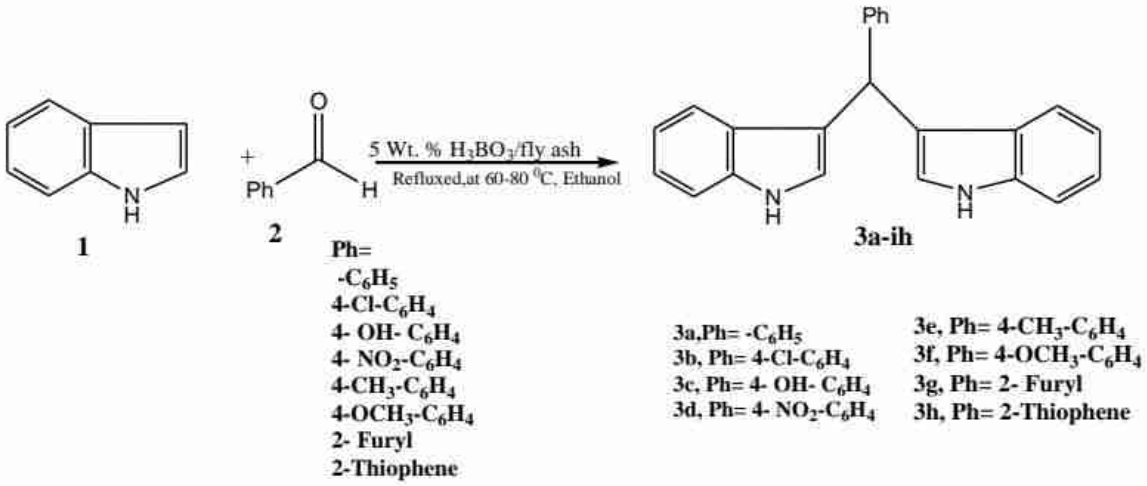
Fly ash based Catalyst	Acidic sites (mmol NH_3/g)		
	T_1 (< 200 °C)	T_2 (>500 °C)	Total
H_2SO_4/fly ash	0.196	0.183	0.379
1 wt. % H_3BO_3/fly ash	0.206	0.189	0.395
3 wt. % H_3BO_3/fly ash	0.214	0.202	0.416
5 wt. % H_3BO_3/fly ash	0.227	0.204	0.431
7 wt. % H_3BO_3/fly ash	0.223	0.197	0.420
9 wt. % H_3BO_3/fly ash	0.224	0.202	0.426

It shows that surface acidity and total number of acid sites in H_2SO_4/fly ash were found 0.379 mmol/g, and fly ash doped with 1, 3, 7, and 9 wt. % of H_3BO_3 were found 0.395 mmol/g, 0.416 mmol/g, 0.420 mmol/g and 0.426 mmol/g respectively, while for 5 wt. % H_3BO_3/fly ash showed 0.431 mmol/g due to the presence of synergistic effect of boric and sulfuric acid with fly ash surface. With reference to above value it can be concluded that catalyst shows sufficient acidic character are

well developed on the surface of fly ash to carry out the synthesis of bis (3-indolyl) methane derivatives from indole and aromatic substituted aldehydes.

3.5 Catalytic performance

The activities of catalyst were investigated for synthesis of bis (3-indolyl) methane derivatives using reaction of aromatic aldehydes and indole in the presence of fly ash based hybrid material.



Scheme II. Synthesis of bis (3-indolyl) methane derivatives by 5 wt. % H_3BO_3/fly ash catalyst.

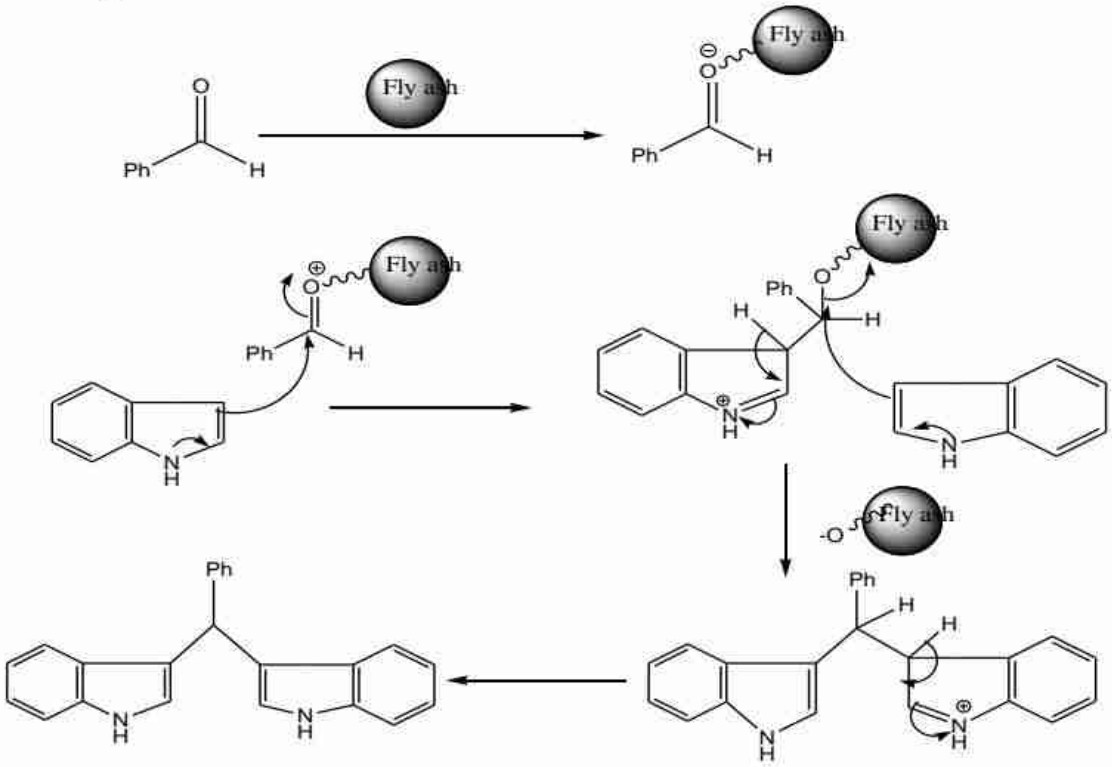
It shows that 5 wt. % H_3BO_3/fly ash catalysts accelerate the rate of reaction as compared to all other synthesized catalyst. 5 wt. % H_3BO_3/fly ash catalysts possesses significant acidity due to well synergy established in between sulfuric acid and boric acid on the support of fly ash material as compared to other prepared hybrid material. A various kind of bis (3-indolyl) methane derivatives was prepared by the reaction of substituted aldehydes with indoles in the presence of 5 wt. % H_3BO_3/fly ash catalyst under the optimized reaction condition was shown in scheme II and their results has been summarized in table 4.

Table 4. Catalytic activity of bis (3-indolyl) methane derivatives by 5 wt. % H_3BO_3/fly ash

Entry	Substituted aldehyde	Time (min)	Yield (%)	Melting point in °C	Ref
3a	$-C_6H_5$	20	90	122-124	Ref. 48
3b	4-Cl-C_6H_4	10	94	118-120	Ref. 49
3c	4-OH-C_6H_4	12	92	126-128	Ref. 48
3d	4-NO_2-C_6H_4	08	94	220-222	Ref. 48
3e	4-CH_3- C_6H_4	18	94	94-96	Ref. 48

3f	4- OCH_3- C_6H_4	16	92	190-192	Ref. 48
3g	2-furyl	10	90	322-324	Ref. 48
3h	2- thiophene	10	92	150-153	Ref. 50

3.6 Proposed reaction mechanism



Scheme III - Proposed reaction mechanism of bis (3-indolyl) methane derivatives.

The proposed mechanism pathway for generating bis (3-indolyl) methane derivatives is outlined in Scheme III. To initiate the process, the carbonyl group of aromatic aldehydes is activated by the presence of 5 wt. % H_3BO_3/fly ash catalyst (acidic proton), which facilitates a nucleophilic attack by indole, results in the formation of bis (3-indolyl) methane derivatives.

3.7 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 bis (3-indolyl) methane derivatives between 94- 90%. 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. % H_3BO_3/fly ash catalyst

Run	**1**	**2**	**3**	**4**
Yield	94	93	92	90

4. Conclusion

This research presented a novel application for a waste substance as a catalyst in organic reactions and created a potent heterogeneous acid catalyst by subjecting it to both chemical and chemical activation using various mineral acids. Subjecting fly ash to both thermal and chemical processes leads to an elevation in amorphous silica content and surface hydroxyl groups, ultimately resulting in heightened surface acidity. The 5 wt. % H_3BO_3-treated fly ash exhibits potential as a heterogeneous acid catalyst for synthesizing xanthene derivatives. This reaction is carried out in a one-pot, single-step procedure under optimized conditions. The catalyst can be conveniently filtered and reused up to four times with consistent effectiveness, suggesting that the catalyst's acidic sites maintain their stability throughout the reaction. What sets this research apart is its use of readily accessible natural waste material, fly ash, as a solid support to produce an exceptionally efficient heterogeneous acid catalyst.

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About the Book

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