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Synthesis and Characterization of Co-Doped Fly Ash Catalyst for Chalcone Synthesis

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A series of solid base fly ash hybrid materials were synthesized by doping alkali, alkaline earth metals with nitrogen, separately using co-precipitation process, combined with surfactant incorporating method. The catalysts were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and photoluminescence spectroscopy. Results revealed that the co-doped hybrid materials are highly stable with particle size in the range of 40-60 nm. The surface basicity of fly ash was upraised by increased hydroxyl content by doping with alkali, alkaline earth metals with nitrogen. The basicity of hybrid material was measured by liquid phase, solvent free, single step condensation of 4-chlorobenzaldehyde and acetophenone giving higher conversion rate and selectivity of desired product chalcone. This conversion showed that the fly ash based hybrid material has sufficient basic site, responsible for the catalytic activity.

Keywords: Chalcone, Co-doped fly ash, Solid base catalyst.

INTRODUCTION

Fly ash (FA) has great deal of interest towards their applications particularly in production of most industrially important fine chemicals [1]. Traditionally, the synthesis of chalcones is carried out *via* Clasien-Schmidt condensation either in basic or in acidic medium under homogeneous conditions such as NaOH [2-11], KOH [12-15], $Ba(OH)_2$ [16-18]. The acid catalyzed methods include the use of BF_3 [19], HCl [20,21], $TiCl_4$ [22]. Recently, chalcone synthesis has been achieved employing Suzuki reaction [23], sulfonic acid from bamboo [24], acidic ionic liquids [25] and graphene acid [26]. Use of these acid or bases requires an extra step to separate them from the reaction mixture and their regeneration is also not possible in normal conditions. The production of undesired polymeric byproducts lowers the yield of the desired product.

With the increasing public concern over environmental degradation and future resources, it is of great importance for chemists to come up with new approaches that are less hazardous to environment and human being. To overcome these problems one approach is to use fly ash as green medium. Fly ash is generated during the combustion of coal in coal-fired power stations, containing a variety of metal oxides in the order $SiO_2 > Al_2O_3 > Fe_2O_3 > CaO > MgO > K_2O > Na_2O > TiO_2$, if not put to beneficial use, is a recognized environmental pollutant [27]. Previously, several fly ash based heterogeneous catalysts such as CaO have been employed as a recyclable solid base catalyst for the Knoevenagel condensation reaction [28], CaO catalyst for the transesterification of soybean oil [29], sulfated zirconia for benzylation [30], cerium triflate for Friedel-Crafts acylation [27]. However, most of the above reported research work claims chemical activation of fly ash with acid and base in solid state.

Recently, it was found that co-doped metal oxides exhibited high surface basicity and variation in basic sites in the composite materials depends on nature of dopants [31-33]. Hence, it may be possible to design synergistically generated solid base catalyst by chemical activation of fly ash with co-dopant. In the present work, we find that doping of alkali, alkaline earth metals with nitrogen, separately on fly ash shows higher conversion rate and selectivity of desired product chalcone.

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EXPERIMENTAL

Fly ash collected from Parli Vaijnath, (Maharashtra, India) Thermal Power Plant was used as a support material for the preparation of co-doped hybrid heterogeneous catalyst. All the chemicals *viz.*, aldehydes, ketones, nitrates of alkali, alkaline earth metals and ammonia were purchased from Sigma-Aldrich.

Catalyst preparation: The solid base fly ash hybrid materials were prepared by chemical activation of fly ash with alkali nitrates and alkaline earth metals and nitrogen, separately by co-precipitation method, combined with surfactant incorporating method. The activated fly ash (900 ºC), alkali nitrates and alkaline earth metals mixed with ammonia (source of nitrogen), separately in the ratio of 2:1:1. The cationic surfactant cetyltrimethylammonium bromide (CTAB) 10 % (20 mL) in ethanol was dropped into the above solution. The system was kept under constant stirring for 12 h and aged for another five days, followed by drying at 110 ºC and calcined at 400 ºC for 2 h under static condition.

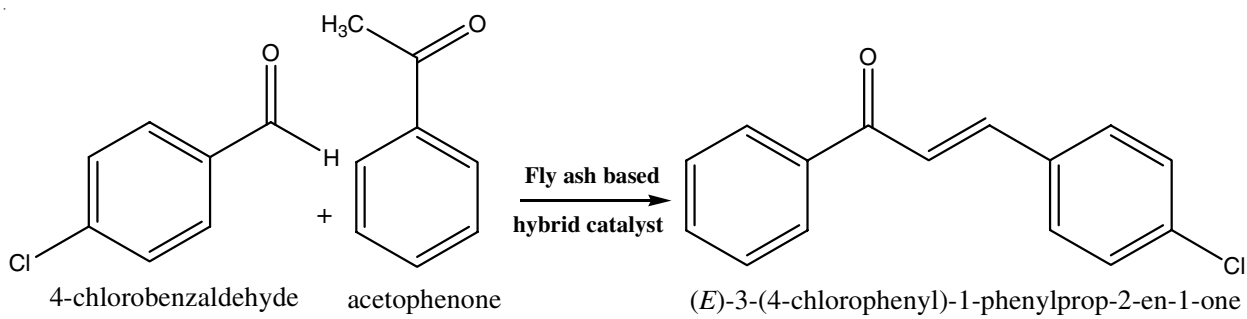
Characterization: X-ray powder diffraction (XRD) patterns were taken at room temperature using a model D8 Bruker AXS with monochromatic Cu radiation (40 kV and 30 mA). The particle size of the sample was calculated from the peak of maximum intensity ($2\theta = 26.77^{o}$). The microscopic nanostructures were observed by transmission electron microscopy (TEM; FEI, Tecnai F30, HRTEM, FEG operated at 300 kV. Surface morphology and elemental analysis of the samples were carried out using an energy dispersive spectrophotometer (EDS) (Jeol; JED-2300). FT-IR spectra were recorded on a Shimadzu-8400 spectrometer in the range of 4000-500 cm^{-1}. X-ray photoelectron spectroscopy (XPS; ESCA-3000, VG Microtech, Uckfield, UK) was used to study the chemical composition of the samples. Non-chromatic X-ray beams of Al Kα (hν = 1486.6 eV) and Mg Kα (hν = 1253.6 eV) radiation were used as the excitation source. Photoluminescence study was carried out using Hitachi fluorescence spectrophotometer (F-7000).

Catalytic activity: The activity of synthesized fly ash based hybrid catalyst were evaluated by condensation reaction between 4-chlorobenzaldehyde and acetophenone by conventional and non conventional method by Claisen-Schmidt condensation gives a chalcone ((*E*)-3-(4-chlorophenyl)-1-phenyl-2-propen-1-one) as shown in **Schemes I** and **II**.

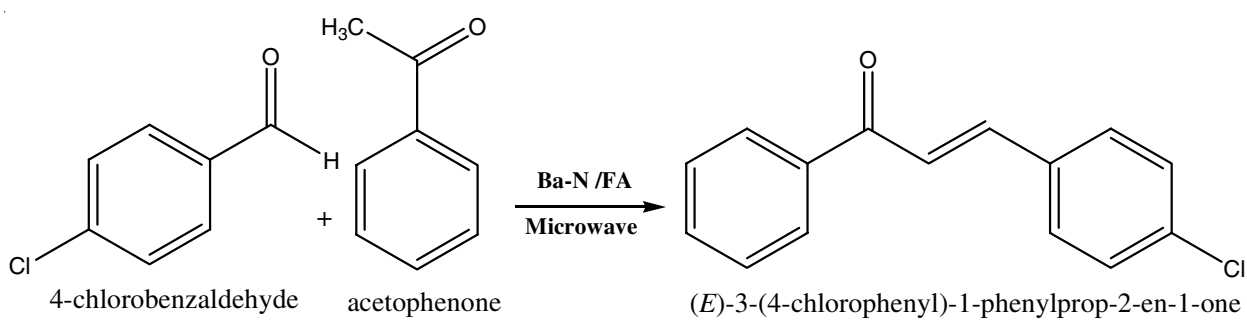
Synthesis of chalcone

Conventional method: An equimolecular quantities of 4-cholorobenzaldehyde (2 mmol), acetophenone (2 mmol) dissolved in 15 mL absolute alcohol in a 100 mL round bottom flask equipped with refluxing condenser placed on a magnetic stirrer. About 0.75 g of fly ash based hybrid materials was immersed into the above solution. The reaction mixture was refluxed at 120 ºC upto the completion of reaction and it was checked by TLC on silica gel plates. The reaction product was poured into the ice-cold water resulting in the formation of crystals, the crystals were filtered and washed with cold water and then recrystallized in absolute ethanol.

Microwave irradiation method: An appropriate equimolar quantity of substituted 4-chlorobenzaldehyde (2 mmol), acetophenone (2 mmol) and fly ash based catalyst (0.75 g) have been taken in borosil tube and tightly capped. The mixture is exposed to microwave for 2-3 min in a microwave oven and then cooled at room temperature. The organic layer has been separated with dichloromethane which on evaporation yielded the solid product. The solid on recrystallization with benzene-hexane mixture gives glittering solid. The insoluble catalyst has been recycled by washing the solid reagent remained on the filter by ethyl acetate followed by drying in an oven at 100 ºC for 1 h.



Scheme-I: Synthesis of (E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one using different fly ash based hybrid materials using conventional and microwave irradiation method



Scheme-II: Synthesis of chalcone ((E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one) using Ba-N/FA catalyzed Claisen-Schmidt condensation between 4-chlorobenzaldehyde and acetophenone in microwave irradiation method

This recycled catalyst has been made reusable for further reactions.

(*E*)-3-(4-Chlorophenyl)-1-phenyl-2-propen-1-one: Pale yellow solid, Yield: 74 %. ^{1}H NMR (250 MHz, $CDCl_3$): δ 8.09-8.02 (m, 2H), 7.78 (d, *J* = 15.7 Hz, 1H), 7.67-7.46 (m, 6H), 7.46-7.37 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 190.2, 143.3, 138.1, 136.5, 133.4, 133.0, 129.7, 129.3, 128.8, 128.6, 122.5.

Catalyst regeneration: The spent catalyst in synthesis of chalcone was washed with acetone, dried in an oven at 110 ºC for 12 h, followed by activation at 250 ºC for 2 h and reused in further reaction. The regeneration study showed that catalyst is reusable and there is no considerable change in its catalytic activity upto 4th reaction cycle.

RESULTS AND DISCUSSION

XRD: To understand phase symmetry in the calcined samples, a systematic X-ray diffraction study was undertaken. Fig. 1a shows the XRD patterns of pure and N-doped fly ash, calcined at 400 ºC for 2 h under static condition. All samples show sharp peaks at 2θ = 20.97º and 26.77º corresponding to (111) and (021) phase of monoclinic fly ash [ASTM card No. 86-0680]. The peaks were apparently broad, showing that the small sized nanocrystalline fly ash was obtained. No peaks corresponding to doped nitrogen is observed in the pattern. In case of co-doped fly ash by alkali and alkaline earth metals with nitrogen, separately (Fig.1b). XRD patterns showed some additional reflections due to Li_2O, Na_2O, MgO, CaO, SrO and BaO at 2θ = 51.83º, 29.66º, 57.74º, 39.53º, 45.92º, 31.72º, 35.31º, 39.32º, 45.23º, 55.21º, 60.77º, 33.36º, 36.95º and 50.51º, respectively. The peaks of co-doped fly ash have been slightly shifted due to solid solution (marked in trace). The average particle sizes of the samples were calculated using Debye-Scherrer formula based on the XRD peak broadening analysis at 110 peak [30]. The particle size calculated from XRD data is as large as 70-85 nm for nitrogen doped Li_2O/FA, Na_2O/FA, MgO/FA, CaO/FA and as small as 40-60 nm for SrO/FA, BaO/FA, samples. This apparent fall in particle size (higher specific surface area) will ensure high catalytic performance for the nitrogen doped SrO/FA, BaO/FA, when it is used for organic transformation.

SEM-EDS, TEM and HRTEM analysis: In order to further confirm the effect of co-dopant on the particle size, the particle size of pure fly ash and Ba-N/FA sample were observed using SEM and TEM, respectively. Fig. 2a showed the SEM image of pure fly ash is irregular in shape and agglomerated particles. The activated fly ash revealed that the particle sizes are in the range of 0.5-0.6 mm. Elemental analysis of pure fly ash is given in Table-1.

Fig. 2b-c shows TEM and HRTEM images of Ba-N/FA sample and its corresponding Fourier transfer pattern is also presented in the inset of Fig 2b. It can be seen that particle size of co-doped fly ash is about 40 nm. The HRTEM image of co-doped fly ash (Fig. 2c) also represents presence of highly crystalline nanoparticles with mesopores.

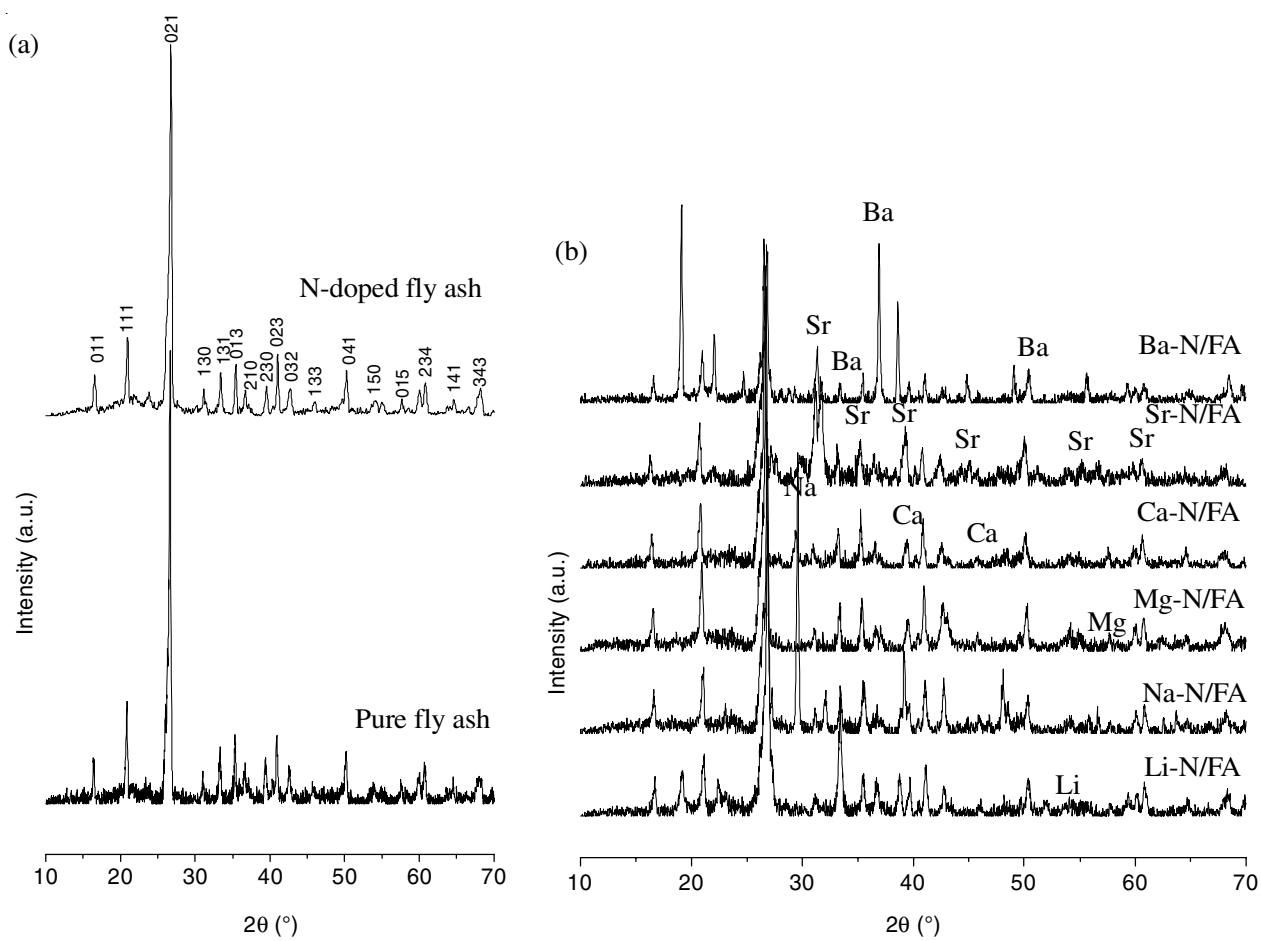


Fig. 1(a-b). XRD pattern of (a) Pure fly ash, N-doped FA; (b) Li-N/FA, Na-N/FA, Mg-N/FA, Ca-N/FA, Sr-N/FA and Ba-N/FA

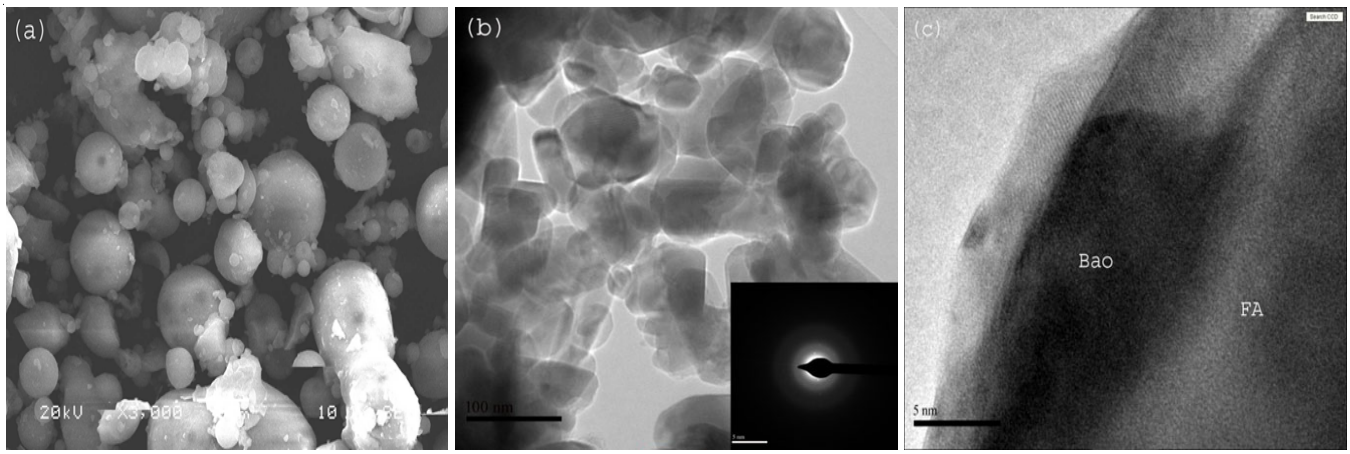


Fig. 2(a-c). (a) SEM image of pure fly ash; (b) TEM image of Ba-N/FA; (c) HRTEM image of Ba-N/FA

TABLE-1
ELEMENTAL COMPOSITION OF PURE FLY ASH FROM EDS (%)

Elements	C	O	Mg	Al	Si	K	Ca	Ti	Fe	Cu	Zn	Zr
Wt. (%)	35.89	50.63	0.18	4.11	6.73	0.24	0.43	0.24	0.68	0.37	0.33	0.17
At. (%)	45.28	47.96	0.11	2.31	3.63	0.09	0.16	0.08	0.18	0.09	0.08	0.03

FT-IR analysis: FT-IR spectrum of pure fly ash (Fig. 3a) showed the characteristic peaks of silica at 1108, 1661, 562 and 3426 cm^{-1} [34,35]. The intense peak observed at 1108 cm^{-1} is attributed to the stretching frequency of Si-O-Si bond. The peak at 562 cm^{-1} corresponds to Al-N bond. Band at 1661 and 3426 cm^{-1} representing the bending mode (δ-O-H) of water molecule and adsorbed water molecules on the surface. Fig. 3b shows same peaks and band, including one additional peak at 2340 cm^{-1} due to carbon impurities. The stretching band for -NH_2 groups, which is usually found in the range of 3400 cm^{-1}, could not be observed in the spectrum because overlapping of the band with that of -OH vibration groups [28]. Fig.3c shows FT-IR spectra of nitrogen, alkali and alkaline earth metal co-doped fly ash, separately. No additional peaks corresponds to metals is assigned. The remaining peaks and bands are similar as shown in (Fig. 3a-b), excluding the broadening in the band at 3400 cm^{-1} is observed due to doping alkali and alkaline earth metals which shows higher basicity associated with doped fly ash.

XPS study: Fig. 4a-b show general XPS survey of (a) pure fly ash and (b) Ba-N/FA. Pure fly ash and Ba-N/FA shows presence of oxygen, carbon, silicon, aluminum and magnesium elements. Some additional elements such as barium and nitrogen can be seen in the co-doped sample (Ba-N/FA). Fig. 4c-d shows high resolution XPS spectra of the O1s region taken on the surface of fly ash and Ba-N/FA. The O1s peak shows broadening and asymmetry towards the higher binding energy side, these Peaks are resolved into two component with binding energy value 530.4 and 533.5 eV for the first and second peak, respectively. The binding energy of first peak is well matched

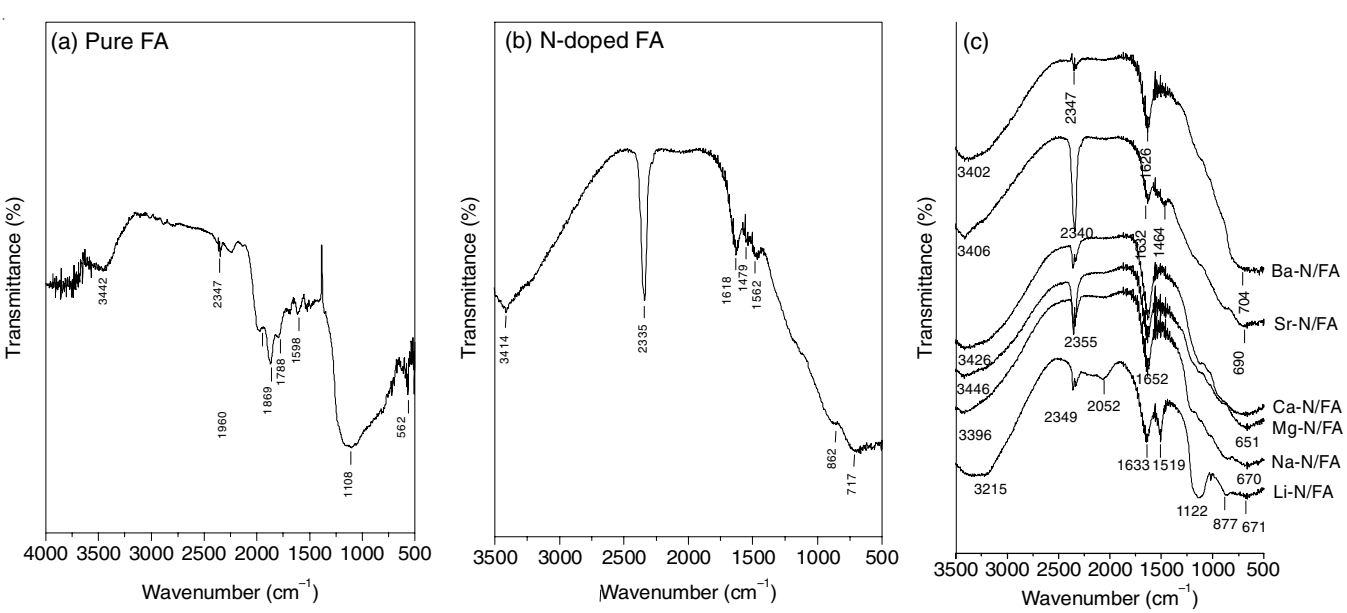


Fig. 3(a-c). FT-IR spectra of (a) pure fly ash; (b) N-doped fly ash; (c) Li-N/FA, Na-N/FA, Mg-N/FA, Ca-N/FA, Sr-N/FA and Ba-N/FA

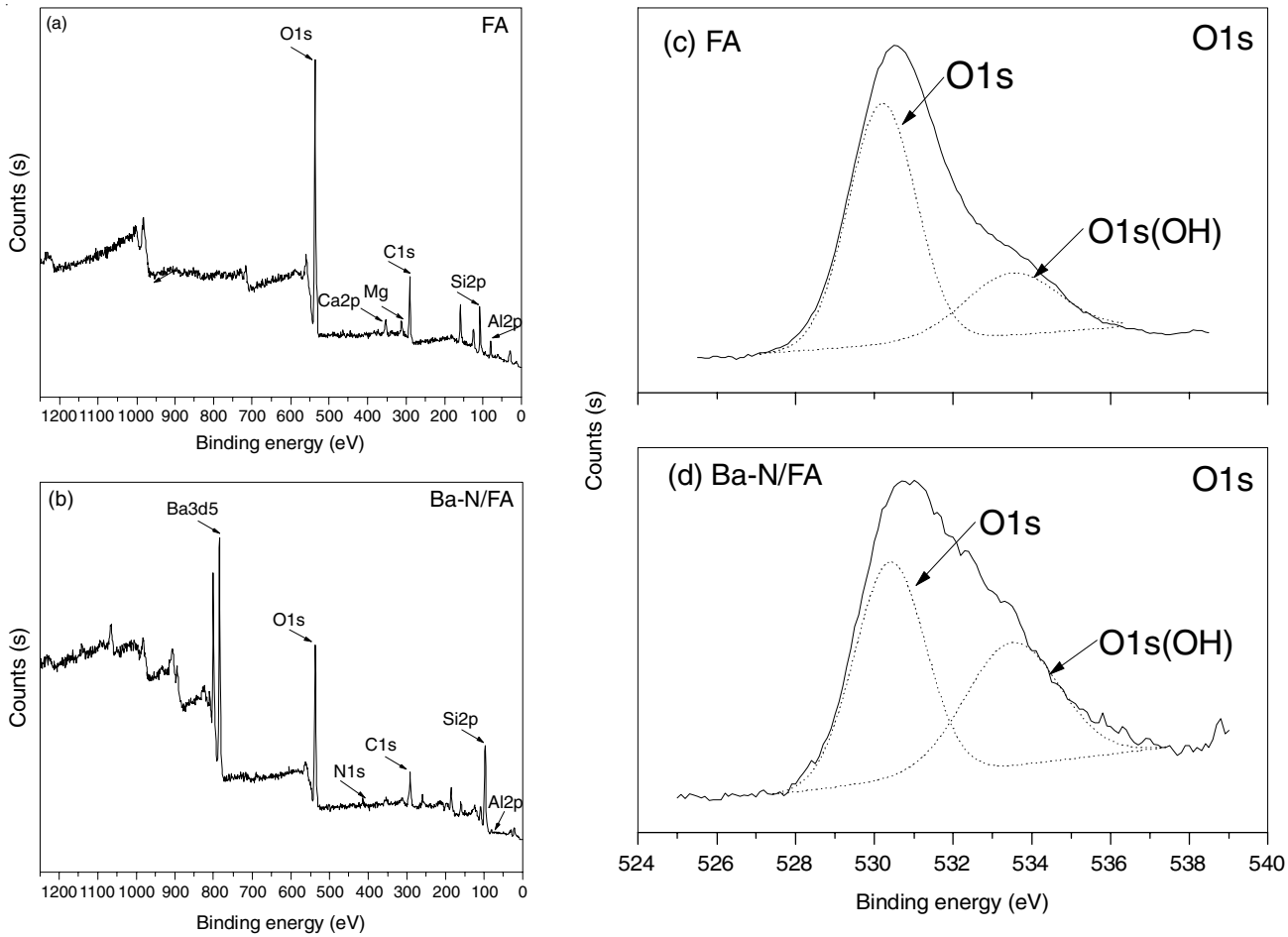


Fig. 4. XPS general survey of (a) pure fly ash; (b) Ba-N/FA; and high resolution XPS spectra of O1s region taken on the surface of (c) pure fly ash, and (d) Ba-N/FA

with the binding energy of metal-oxides in pure fly ash and Ba-N/FA, while the second peak is either adsorbed oxygen or hydroxyl species on the surface, respectively. The chemical state of catalyst surface is key factor that strongly affect the catalytic performance of catalyst. The quantitative analysis of the active cations and anions on the surface of catalyst is important factor for evaluation of catalytic activity. In this study, curve-fitting method was used to calculate the atomic % of elements [36]. The quantitative analysis results are given in Table-2. From the quantitative analysis it is found that atomic % of O_2^- in Ba-N/FA is higher in comparison with pure fly ash, that might be due to variation in impurity level create the charging balance that must be satisfied; therefore more hydroxide ions are adsorbed on the surface.

TABLE-2
ELEMENTAL ANALYSIS BY XPS METHOD

Region	Fly ash	Ba-N/FA
	Atomic (%)	Atomic (%)
C1s	37.91	10.00
O1s	32.20	48.60
Si2p	12.15	26.93
Al2p	10.08	8.06
Mg	6.24	–
Ca2p	1.42	–
Ba3d	–	5.36
N1s	–	1.05

Photoluminescence analysis: Photoluminescence spectra of all synthesized fly ash based hybrid materials recorded at room temperature (Fig. 5). Photoluminescence study clearly depicts that three main emission bands are present at 369, 410 and 468 nm. Photoluminescence intensity of samples decreases from activated fly ash to Ba-N/FA attributes defects in crystal lattice and vacancies of nanoparticles [37]. The decrease in photoluminescence intensity proves the quenching between fly ash with nitrogen, alkali metals and alkaline earth metals.

Catalytic performance: The activities of catalyst were investigated for Claisen-Schmidt condensation of substituted 4-chlorobenzaldehyde and acetophenone and the results are given in Table-3. It shows that Ba-N/FA catalyst accelerates the rate of reaction as compared to all other synthesized catalyst in conventional as well as microwave irradiation method (**Scheme-I**). The prepared Ba-N/FA catalyst was found to possess significant basicity due to well synergy establishment in between barium and nitrogen as compared to other prepared hybrid catalysts, evident from reaction time and final yield. The reaction time and final yield found to be less in comparison with earlier reported work [24-26]. The application of this synthesized material has the high activity, the simplicity of preparation method, easily available raw materials, which can be a benefit for its extensive application in organic synthesis reaction. Synthesis of a series of chalcone derivatives were

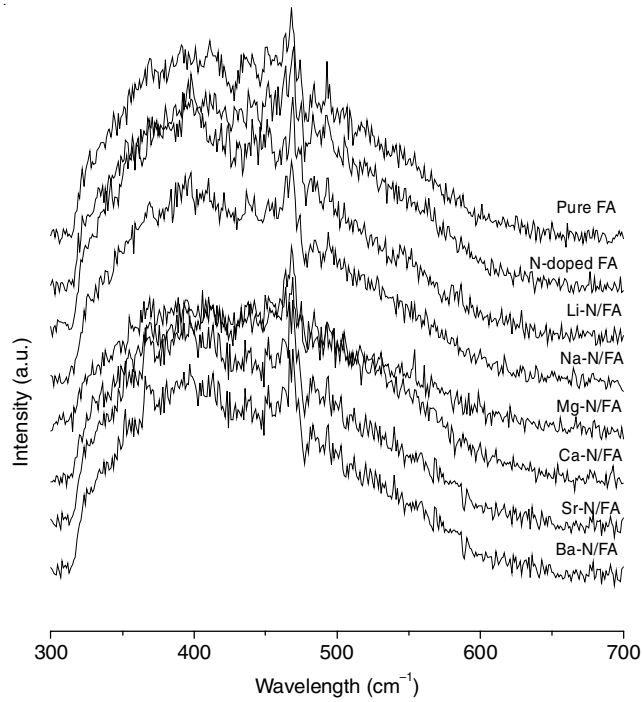


Fig. 5. Photoluminescence spectra of pure fly ash, N-doped fly ash, Li-N/FA, NA-N/FA, Mg-N/FA, Ca-N/FA, Sr-N/FA and Ba-N/FA

TABLE-3
CATALYTIC ACTIVITY OF FLY ASH BASED HYBRID CATALYST USED FOR CLAISEN-SCHMIDT CONDENSATION BETWEEN 4-CHLOROBENZALDEHYDE AND ACETOPHENONE

Catalyst	Conventional		Microwave	
	Time (h)	Yield (%)	Time (min)	Yield (%)
Pure FA	2.50	Trace	2	Trace
N/FA	2.25	47	2	58
Li-N/FA	2.00	55	2	66
Na-N/FA	1.75	66	2	73
Mg-N/FA	1.50	74	2	81
Ca-N/FA	1.25	78	2	84
Sr-N/FA	1.00	80	2	85
Ba-N/FA	0.75	86	2	92

prepared under the optimized conditions (**Scheme-II**), electron donating as well as electron withdrawing group as substituents on aldehyde and acetophenone in the presence of Ba-N/FA catalyst using microwave irradiation. In this synthesis obtained yields of chalcone derivatives, reaction time and yields as shown in Table-4.

Effect of amount catalyst: Fig. 6 shows the catalytic effect of Ba-N/FA in the synthesis of chalcone (**Scheme-II**) by varying the catalyst quantity from 0.15 to 1.55 g. As the catalyst quantity is increased from 0.1 to 0.75 g, the percentage of yield is increased from 86 to 92 %, there is no significant increase in the percentage of product by even after increasing 0.75 g of the catalyst.

Proposed mechanism: The catalytic activity of Ba-N/FA is higher in comparison with other fly ash based hybrid catalysts. It might be due to availability of maximum basic sites on the surface, evident from XPS spectra, abstracts the proton from acetophenone to form a carbanion which gives keto-enol equilibrium. These enolate ion further attack on 4-chlorobenzaldehyde to form a β-hydroxy carbonyl ketone after dehydration it produces chalcone by Claisen-Schmidt condensation shown in **Scheme-III**.

TABLE-4
CLAISEN-SCHMIDT CONDENSATION USING Ba-FA/N CATALYZED BETWEEN SUBSTITUTED ALDEHYDE AND SUBSTITUTED ACETOPHENONE IN MICROWAVE IRRADIATION

R1	R2	Time (min)	Yield (%)	m.p. (°C)	Ref.
H	H	2	89	56	[38]
4-Cl	H	2	92	116	[38]
4-OH	H	2	88	187	[38]
4-NO_2	H	2	91	158	[38]
H	4-Cl	2	87	102	[38]
H	4-OH	2	90	62	[38]
H	4-NO_2	2	86	122	[38]

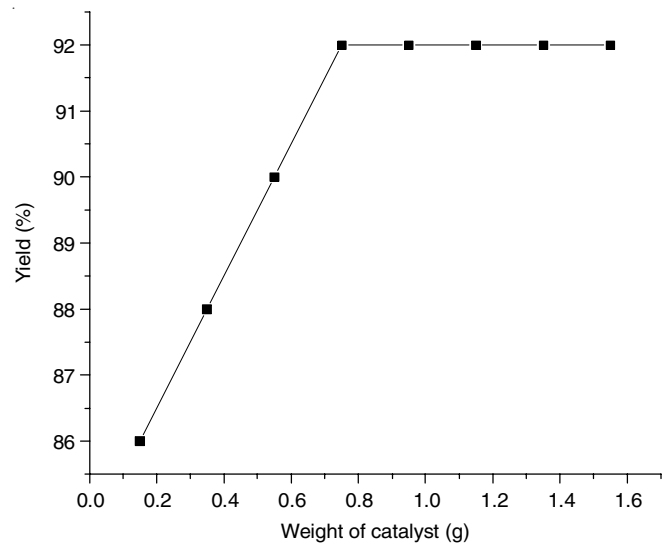


Fig. 6. Effect of BA-N/FA catalyst loading on the rate of reaction

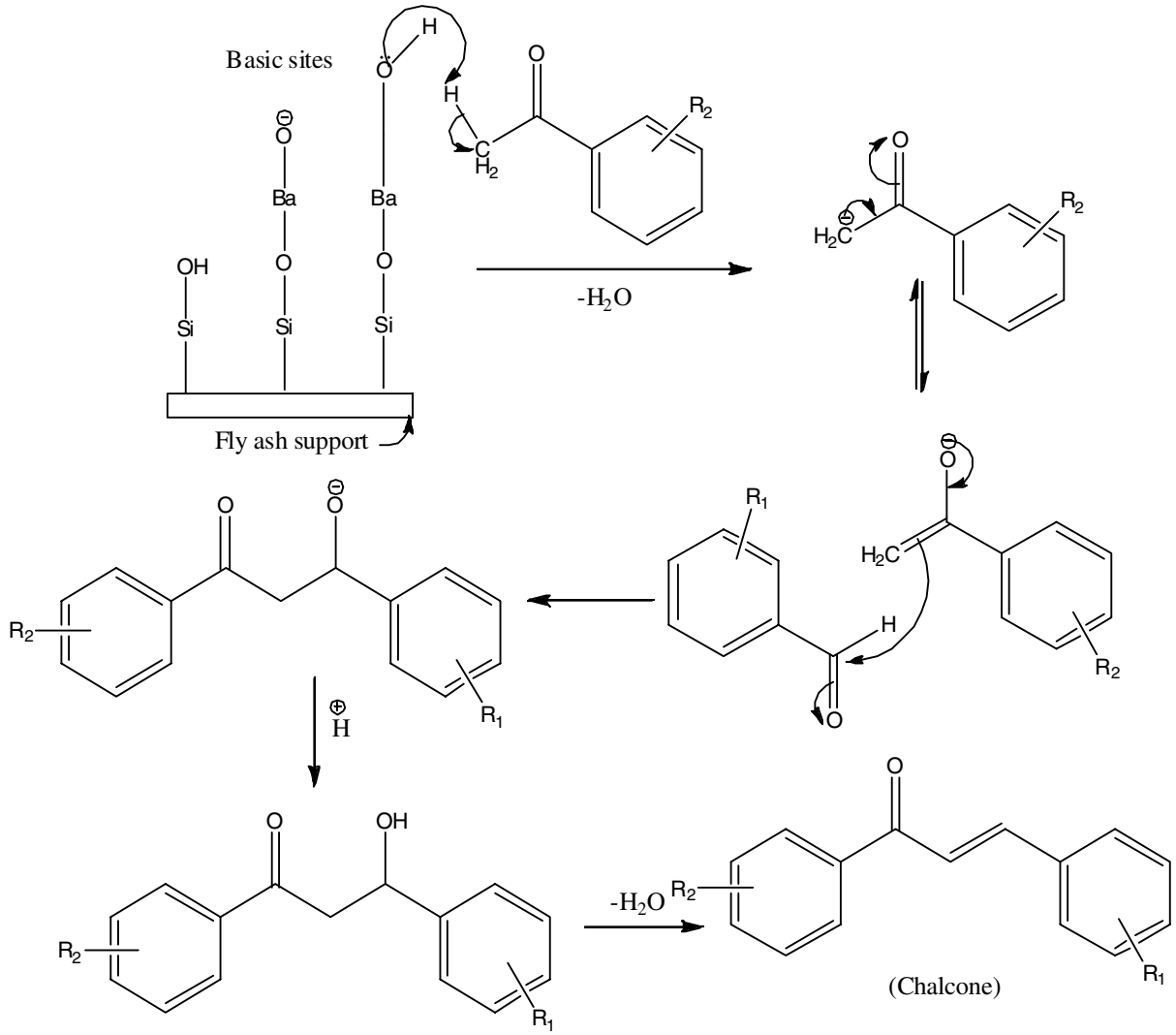
Regeneration of catalyst: With the help of simple thermal regeneration method the fly ash based hybrid catalyst was regenerated and retained their catalytic activity which showed the similar catalytic activity up to the fourth reaction cycle giving the conversion of 4-chlorobenzaldehyde to chalcone (92 %), indicates that basic sites are not deactivated in the regenerated catalyst as shown in Table-5.

TABLE-5
REUSABILITY OF Ba-N/FA CATALYST ON CHALCONE SYNTHESIS FROM 4-CHLOROBENZALDEHYDE AND AETOPHENONE UNDER MICROWAVE IRRADIATION

Run	1	2	3	4
Yield (%)	92	91	90	88

Conclusion

In the present work, solid base fly ash hybrid materials were prepared by co-doping of fly ash with alkali nitrate and alkaline earth metals and nitrogen, separately by co-precipitation method. The characterization of catalyst confirmed that Ba-N/FA catalyst possess better crystallite size up 40 nm hence higher surface area and higher basicity towards synthesis of chalcone by Claisen-Schmidt condensation reaction



Scheme-III: Proposed mechanism of synthesis of chalcone by Clasien-Schmidt condensation in presence of fly ash based hybrid catalyst (Ba-N/FA) in microwave irradiation method

with benzaldehyde and acetophenone. This work provides a pathway for utilization of waste material as a catalyst in organic synthesis and it has a harmless to environment. It can be easily reusable for further reaction purposes.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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