

## Research Article

# Surface Modification of Fly Ash for Active Catalysis

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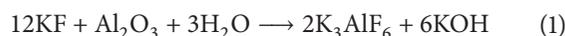
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Fly ash based effective solid base catalyst (KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>473</sup>, KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup>, and KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>873</sup>) was synthesized by loading KF over chemically and thermally activated fly ash. The chemical activation was done by treating fly ash with aluminum nitrate via precipitation method followed by thermal activation at 650°C to increase the alumina content in fly ash. The increased alumina content was confirmed by SEM-EDX analysis. The alumina enriched fly ash was then loaded with KF (10 wt%) and calcined at three different temperatures 473 K, 673 K and 873 K. The amount of loaded KF was monitored by XRD, FTIR spectroscopy, SEM-EDX, TEM and Flame Atomic Absorption Spectrophotometer. The catalytic activities of the catalysts were tested in the Claisen-Schmidt condensation of benzaldehyde and 4-methoxybenzaldehyde with 2'-hydroxyacetophenone to produce 2'-hydroxychalcone and 4-methoxy-2'-hydroxychalcone respectively. Higher conversion (83%) of benzaldehyde and (89%) of 4-methoxybenzaldehyde reveals that among these heterogeneous catalysts KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> is very active.

## 1. Introduction

Fluoride ion is useful as weakly basic, nonnucleophilic in many organic chemical processes involving hydrogen abstraction or hydrogen bond formation [1]. Fluoride has been reported as effective basic catalyst in Cannizzaro reaction to replace classical methods employing hydroxide base which gave large amount of Cannizzaro side reactions [2]. Potassium fluoride is a well-known source of fluoride and possesses a number of advantages of both solution and solid phase chemistry. Among the supported fluoride systems, potassium fluoride on activated alumina has been found to be more reactive than nonsupported KF, KF-silica gel, KF-celite and KF-molecular sieves [3]. When KF is loaded on alumina, it shows high catalytic activity towards organic reactions namely. Michael addition [4], aldol condensation [5] and transesterification reactions [6]. The basic sites on KF/alumina may be related to a very hard anion F<sup>-</sup>; the catalyst may show the characteristic performances which differentiate KF/alumina from the oxide-type solid base catalysts such as alkaline earth oxides [7]. In contrast to many applications of KF/alumina to organic synthesis as a base catalyst, mechanisms of the appearance of the basicity

of KF/alumina are not clarified. Insufficient coordination of KF only with surface OH groups may result in the formation of active F<sup>-</sup> ions [8]. This possibility was supported by <sup>19</sup>F MAS NMR [9]. Three basic species or mechanisms of the appearance of the basicity of KF/alumina reported previously [10] are (a) the presence of active fluoride, (b) the presence of [Al-O-] ion which generates OH<sup>-</sup> when water is added, and (c) the cooperation of F<sup>-</sup> and [Al-OH]. It has been reported in the literature (1) that the formation of potassium hexafluoroaluminate must be accompanied by the formation of hydroxide and/or aluminate, responsible for the high reactivity of KF/Al<sub>2</sub>O<sub>3</sub>. However, F<sup>-</sup> ion has little or no direct role in the catalytic activity of KF/Al<sub>2</sub>O<sub>3</sub> catalyst:



The strong basic nature of KF/Al<sub>2</sub>O<sub>3</sub> allowed it to replace organic bases in a number of organic reactions.

The Claisen-Schmidt condensation between acetophenone and benzaldehyde derivatives is a valuable C-C bond-forming reaction which produces  $\alpha,\beta$ -unsaturated ketones

called chalcones which display a wide spectrum of biological activities including antioxidant, antibacterial, antileishmanial, anticancer, antiangiogenic, anti-infective and anti-inflammatory activities [11–13]. Traditionally, the Claisen-Schmidt condensation is carried out, using alkaline hydroxides or sodium ethoxide [14]. The use of basic solids, such as zeolites [15], alkali metal and oxides supported on alkaline earth oxide [16], MgO [17], calcined hydrotalcites [18] and KF [19], has received much attention over the last years as potential catalysts for Claisen-Schmidt condensations. Using solid catalysts, instead of stoichiometric amounts of soluble strong bases, the overall atom efficiency of reactions is improved, processes are simplified, the turn over number of the catalyst is increased, the volume of waste is significantly reduced, and product workup becomes easier, if necessary at all. Typically organic bases immobilized on different supports have been used as catalytic materials. Progress has predominately been limited because of leaching of the active material from the various types of support used.

Fly ash ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{MgO}$ ) by appropriate activation has been converted into solid acids and solid bases.  $\text{H}_2\text{SO}_4$  treated fly ash has been used as Bronsted acid catalyst for synthesis of aspirin and oil of wintergreen as solid support for loading of cerium triflate and sulphated zirconia [20–22] for synthesis of 3,4-dimethoxyacetophenone (antineoplastic) and diphenylmethane. In recent years, fly ash treated with  $\text{CaO}$ ,  $\text{NaOH}$ ,  $\text{MgO}$  and aminopropyl trimethoxysilane has also been used as solid base catalysts in various condensation reactions [23–26]. In the present work, we attempted to introduce a novel solid base catalyst from chemically activated fly ash by loading KF followed by thermal activation at different temperatures. As received fly ash (silica 58%) was chemically activated to increase alumina and was thought to be used for supporting potassium fluoride. The use of fly ash as support not only reduced the cost of the catalyst it also showed high basicity and catalytic activity for benzaldehyde and 4-methoxybenzaldehyde with 2'-hydroxyacetophenone to produce 2'-hydroxychalcone and 4-methoxy-2'-hydroxychalcone in a single step, liquid phase and solvent free reaction conditions with high yield (>90%) and purity. We also examined the changes in bulk and surface structures of  $\text{KF}/\text{Al}_2\text{O}_3$ -fly ash catalysts pretreated at different temperatures by XRD, FTIR, SEM-EDX and TEM to elucidate catalytically active sites formed by chemical and thermal treatment of fly ash.

## 2. Experimental

**2.1. Material.** Fly ash (Class F type with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  > 70%) used as solid support for the solid base was collected from Kota Thermal Power Plant (Rajasthan, India).  $\alpha$ -Alumina, potassium fluoride (KF), aluminium nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ),  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{NH}_4\text{OH}$ , benzaldehyde (99%), 4-methoxybenzaldehyde (98%) and 2'-hydroxyacetophenone (99%) were purchased from S. D. Fine Chem Ltd., India.

**2.2. Catalyst Preparation.** The three catalysts KF/fly ash,  $\text{KF}/\text{Al}_2\text{O}_3$ /fly ash and  $\text{KF}/\text{Al}_2\text{O}_3$  were prepared by

using aqueous solution of potassium fluoride for wet impregnation of fly ash, alumina enriched fly ash and  $\alpha$ -alumina respectively. All three catalysts were calcined at different temperatures (473 K, 673 K, and 873 K) and prepared by the following method.

**2.2.1. KF/Fly Ash Catalyst.** As received fly ash was preheated for 3 h at  $900^\circ\text{C}$  under static conditions. 10 g of thermally activated fly ash was added into a glass reactor containing aqueous solution of 0.166 g potassium fluoride (10 wt %). The reactor was equipped with a reflux condenser and a magnetic stirrer bar. The slurry was refluxed at  $110^\circ\text{C}$  for 24 h then filtered and washed to eliminate excess KF on the fly ash surface.

### 2.2.2. KF/ $\text{Al}_2\text{O}_3$ /Fly Ash Catalyst

**Step 1.** An aqueous solution of 0.09 mol of  $\text{Al}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$  was added into thermally activated fly ash with constant stirring. Solution of 0.16 mol of  $(\text{NH}_4)_2\text{CO}_3$  was added dropwise in the above solution and the pH was maintained close to 8.0 by the addition of appropriate amounts of  $\text{NH}_4\text{OH}$  (35% aqueous ammonia solution). The resulting gel-like slurry was washed with deionized water until  $\text{pH} = 7$ . Then the precipitate was dried at 373 K in air for approximately 12 h. The resulting solid was calcined at 673 K for 4 h under static conditions.

**Step 2.** The chemically activated fly ash was heated at  $400^\circ\text{C}$  for 4 h prior to its introduction in a glass reactor containing aqueous solution of 0.166 g potassium fluoride (10 wt%). The reactor was equipped with a reflux condenser and a magnetic stirrer bar. The slurry was refluxed at  $110^\circ\text{C}$  for 24 h then filtered and washed to eliminate any excess KF on the fly ash surface.

**2.2.3. KF/ $\text{Al}_2\text{O}_3$  Catalyst.** 10 g of alumina milled to a fine powder was added into deionized water containing desired amount of KF (0.166 g for 10 wt% loading). Thereafter the resulting solid products of all three catalysts were further dried at  $110^\circ\text{C}$  for 24 h and calcined at three different temperatures 473 K, 673 K and 873 K for 2 h.

**2.3. Characterization.** The samples were characterized by Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction study (XRD), BET surface area analysis, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The loading of KF on the chemically activated fly ash was confirmed by FTIR study using FTIR spectrophotometer (IRPrestige-21, Shimadzu) having a Diffuse Reflectance Scanning technique by mixing the sample with dried KBr (in 1/20 wt ratio) in the range of  $400\text{--}4000\text{ cm}^{-1}$  with a resolution of  $4\text{ cm}^{-1}$ . X-ray diffraction studies were carried out by using X-ray diffractometer (Philips X'pert) with monochromatic  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54056\text{ \AA}$ ) in a  $2\theta$  range of  $5$  to  $65^\circ$ . The detailed imaging information about the morphology and surface texture of the sample was provided by SEM-EDX (Philips XL30 ESEM TMP). The loading of KF

on fly ash particles was confirmed by TEM analysis (Tecnai 20 G2 (FEI make), Resolution: Line-1.4 Å, Point 2.04 Å).

**2.4. Reaction Procedure: Claisen-Schmidt Condensation.** Catalytic activity of prepared catalysts was tested by Claisen-Schmidt condensation of benzaldehyde and 4-methoxybenzaldehyde with 2'-hydroxyacetophenone in solvent free liquid phase reaction shown in Scheme 1.

The condensation was performed in liquid phase batch reactor, which consists of 50 mL round bottom flask, magnetic stirrer and condenser. A mixture of benzaldehyde (0.106 g, 1 mmol) or 4-methoxybenzaldehyde (0.136 g, 1 mmol) and hydroxyacetophenone (0.136 g, 1 mmol) was taken in round bottom flask. The catalysts, activated at different temperatures for 2 h (substrate to catalyst ratio = 10), were added in the reaction mixture. At the end of the reaction, the catalyst was filtered and the reaction mixture was analyzed by Gas Chromatography (Dani Master GC) having a flame ionization detector and HP-5 capillary column of 30 m length and 0.25 mm diameter, programmed oven temperature of 50–280°C and N<sub>2</sub> (1.5 mL/min) as a carrier gas.

**2.5. Catalyst Regeneration.** The used catalyst (KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup>) was washed with acetone and dried in oven at 110°C for 12 h followed by activation at 450°C for 2 h before reuse in next reaction cycle under similar reaction conditions as earlier.

### 3. Results and Discussion

**3.1. Characterization.** Elemental analysis of fly ash and all three catalysts (KF/fly ash, KF/Al<sub>2</sub>O<sub>3</sub>/fly ash and KF/Al<sub>2</sub>O<sub>3</sub>) was done by EDX, the results are summarized in Table 1. With increasing the pretreatment temperature, the contents of K and F increased to a small extent by pretreatment at 673 K and decreased by pretreatment at 873 K for all three samples.

The FTIR spectrum of fly ash Figure 1 shows a peak at 3600 cm<sup>-1</sup>, which indicates the presence of surface -OH groups, -Si-OH and absorbed water molecules on the surface. The spectra also shows a broad range of bands from 1055 cm<sup>-1</sup> to 1100 cm<sup>-1</sup> which is attributed to modes of Si-O-Si asymmetric band stretching vibrations. The low frequency modes at 794 cm<sup>-1</sup> are due to the symmetric Si-O-Si stretching vibrations. The FTIR spectrum of KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalyst calcined at different temperatures (43 K, 673 K, and 873 K) shown in Figures 1(d), 1(e) and 1(f). The FTIR spectrum of KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> catalyst, shown in Figure 1(e) has a strong band at about 3500 cm<sup>-1</sup>, which indicates the presence of -OH groups on the surface of KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> catalyst. Thus result shows that hydroxyl groups can be the active sites when KF is supported on fly ash [27]. The intensity of the -OH peak increases with increasing temperature from 473 K to 673 K, assigned due to increase in KF content. Upon investigating the nature of the catalyst via infrared spectroscopic studies of the catalyst surface, it became apparent that fluoride ion has little or no direct role

in the enhanced reactivity of KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalyst. The reaction between aqueous KF and alumina results in the formation of potassium hexafluoroaluminate and a strongly basic surface consisting of potassium aluminates and potassium hydroxide [28]. The later agents are responsible for both the increased base activity and the variable activity, a consequence of carbonate formation. A peak is present at 1650 cm<sup>-1</sup> in the spectra of the samples, which is attributed to bending mode ( $\delta_{O-H}$ ) of water molecule [5]. An intense band at 570 cm<sup>-1</sup> is also observed which is due to the presence of substantial amount of hexafluoroaluminate ion. In addition to features due to alumina and water, bands at 1519 cm<sup>-1</sup> and 1381 cm<sup>-1</sup> indicate that both bidentate and monodentate type carbonate species exist on the surface of KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> catalyst [5, 29], which seems to be generated due to reaction of atmospheric CO<sub>2</sub> with KOH during drying of the catalyst.

X-ray diffraction pattern of raw fly ash is shown in Figure 2(a). Structural changes caused by pretreatment at different temperatures were studied by XRD for KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>473</sup>, KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup>, and KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>873</sup> catalysts illustrated in Figures 2(b), 2(c) and 2(d). These patterns confirmed that deposition of the alkaline fluoride followed by the thermal treatment led to the formation of K<sub>3</sub>AlF<sub>6</sub> by the reaction between KF and Al<sub>2</sub>O<sub>3</sub> which is observed at 2 theta = 33°, 38°, and 63°. The intensity of the peaks assigned to this species is in agreement with the loadings of the alkaline fluoride [30].

SEM micrograph of raw fly ash Figure 3(a) shows the presence of hollow cenospheres, irregularly shaped unburned carbon particles, mineral aggregates and agglomerated particles, while the typical SEM images of the fly ash supported KF catalyst in Figure 3(b) show dense particles with distribution of varying particle size. TEM images of raw fly ash Figure 4(a) show smooth spherical particles, while TEM image of KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> catalyst Figure 4(b) shows KF loaded spheres.

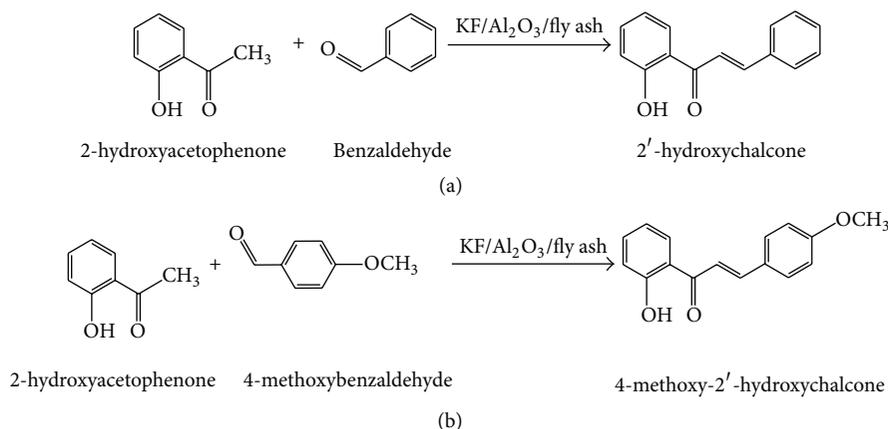
**3.2. Basic Sites on KF/Al<sub>2</sub>O<sub>3</sub>/Fly Ash Catalyst.** There are several controversies on possibilities of formation of basic sites on KF/Al<sub>2</sub>O<sub>3</sub> catalytic system, yet all the previous investigations [27] evidently reported the formation of K<sub>3</sub>AlF<sub>6</sub> by the reaction of aqueous KF and alumina (1). Most of the studies were of the opinion that F<sup>-</sup> ion has no direct role in the catalytic activity of KF/Al<sub>2</sub>O<sub>3</sub>. The formation of carbonate on the catalyst surface is responsible for high reactivity of KF/Al<sub>2</sub>O<sub>3</sub> [28]. The carbonate was supposed to be formed by the reaction of CO<sub>2</sub> and produced KOH (2) during the drying procedure:



Duke et al. has reported the formation of K<sub>2</sub>CO<sub>3</sub> by the following successive reactions:



where K<sub>2</sub>O is formed as the alumina lattice is destroyed. However in preparation of the KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalyst in



SCHEME 1: Claisen-Schmidt condensation of (a) benzaldehyde and (b) 4-methoxybenzaldehyde with 2-hydroxyacetophenone over fly ash supported solid base catalysts.

TABLE 1: EDX analysis of prepared catalysts at different pre-treatment temperatures.

Catalyst	Pre-treatment temperature (K)	K (at.%)	F (at.%)	Al (at.%)	O (at.%)
Fly ash	NIL	0.09	NIL	4.10	50.2
Al <sub>2</sub> O <sub>3</sub> /fly ash	673 K	0.09	NIL	9.2	57.6
KF/fly ash	473 K	2.3	1.7	4.7	56.7
	673 K	2.7	1.8	4.8	56.9
	873 K	2.2	1.3	4.8	56.8
KF/Al <sub>2</sub> O <sub>3</sub> /fly ash	473 K	8.5	11.3	9.2	52.4
	673 K	9.1	12.1	9.4	51.9
	873 K	8.1	11.7	9.3	52.0
KF/Al <sub>2</sub> O <sub>3</sub>	473 K	20.8	19.6	12.7	46.9
	673 K	22.1	20.8	12.9	44.2
	873 K	18.8	17.7	17.2	46.3

[at. %: atomic percentage].

aqueous medium (2) seems to be more significant than (3) and (4).

In KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalyst, the formation of K<sub>3</sub>AlF<sub>6</sub> is confirmed by XRD, while hydroxyl groups and carbonate ion are confirmed by intense peaks at 3500 cm<sup>-1</sup> and 1550 cm<sup>-1</sup> in FTIR spectrum Figure 1. Interestingly, the pretreatment temperature has significantly affected the catalytic activity of the system as reported previously for KF/Al<sub>2</sub>O<sub>3</sub> catalyst. Both K<sub>3</sub>AlF<sub>6</sub> and carbonate peaks are observed on increasing the pretreatment temperature from 473 K to 873 K as evident from Figure 1, whereas the catalytic activity of KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalyst was almost diminished at higher temperature 873 K Figure 5(a). These results have ruled out the possibility of carbonate or K<sub>3</sub>AlF<sub>6</sub> being responsible for generating the active basic sites on the catalyst surface. KOH, an active base produced during reaction between KF and alumina generates hydroxyl groups on the catalyst surface, which become active basic sites for condensation reactions. At 873 K, surface hydroxyl groups are significantly decreased, resulting

in decrease of active basic sites; thus catalytic activity of KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalyst was almost completely lost. Similar explanations on the surface properties of KF/Al<sub>2</sub>O<sub>3</sub> system have been given in the literature [5] where the catalytic activity of KF/Al<sub>2</sub>O<sub>3</sub> was completely lost.

**3.3. Catalytic Performance.** The catalytic activity of KF/Al<sub>2</sub>O<sub>3</sub>/fly ash depends very much on drying condition of alumina after loading KF by impregnation. In this work we examined the dependence of catalytic activity for condensation on the heating temperature of the catalyst.

**3.3.1. Effect of Pretreatment Temperature.** The catalytic activity strongly depends on the evacuation temperature and reached around a maximum temperature of 673 K Figure 5(a). All catalysts showed significant activity for condensation reactions, whereas pure fly ash and chemically activated fly ash (Al<sub>2</sub>O<sub>3</sub>/fly ash) did not show any activity. Among remaining catalysts, the KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> showed

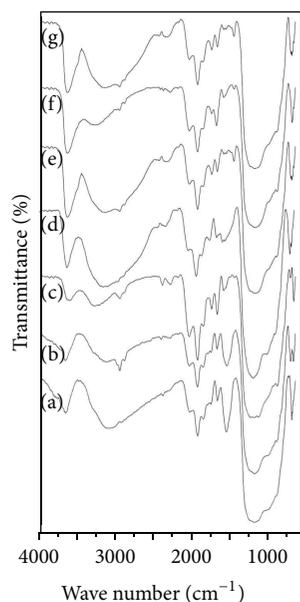


FIGURE 1: FTIR of (a) raw fly ash, (b) thermally activated fly ash, (c) KF/fly ash catalyst, (d) KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>873</sup> catalyst, (e) KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> catalyst, (f) KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>473</sup> catalyst, and (g) regenerated KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> catalyst.

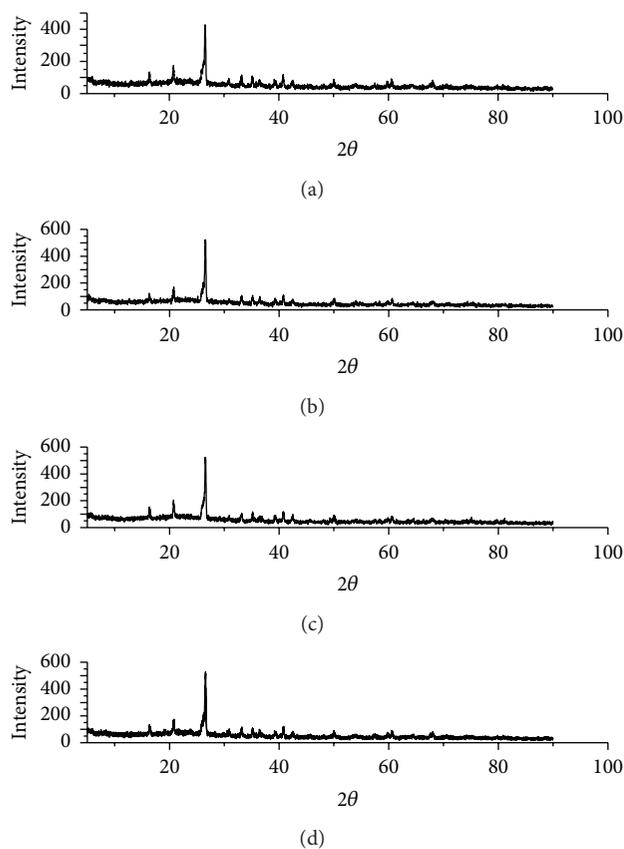
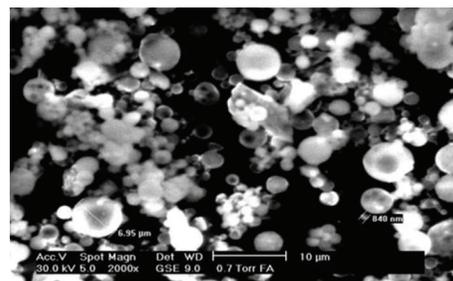
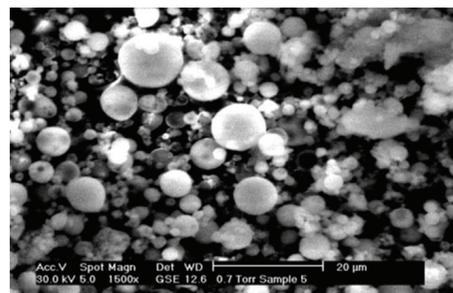


FIGURE 2: X-ray diffraction pattern of (a) raw fly ash (b) KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>473</sup> catalyst (c) KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>873</sup> and (d) KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> catalyst.



(a)



(b)

FIGURE 3: SEM micrograph of (a) Raw fly ash and (b) KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> catalyst.

higher catalytic activity giving maximum conversion of benzaldehyde (83%) and 4-methoxybenzaldehyde (89%). For KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>473</sup> and KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>873</sup>, conversions of benzaldehyde and 4-methoxybenzaldehyde are comparatively low as shown in Figure 5(a). The activity of KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalyst appeared when the sample was pretreated at 473 K and reached its maximum at the temperature of 673 K. As the pretreatment temperature was raised higher than 673 K, the activity decreased sharply and finally disappeared at the temperature of 873 K. It is well reported that a high temperature treatment reveals active sites on catalyst either by removal of CO<sub>2</sub> and H<sub>2</sub>O remaining on the surface in various forms or by formation of specific surface structure. The active sites are covered with H<sub>2</sub>O and/or CO<sub>2</sub> when pretreated below 673 K [7].

In the light of the above inferences, the reaction conditions such as reaction temperature, reaction time, molar ratio of reactants and substrate to catalyst ratio for condensation of benzaldehyde and 4-methoxybenzaldehyde with 2'-hydroxyacetophenone were optimized using only KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> catalyst.

**3.3.2. Effect of Temperature.** The reaction for condensation of benzaldehyde and 4-methoxybenzaldehyde is carried out at temperatures ranging from 40°C to 140°C for 4 h. The effect of temperature on the condensation activity of KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> and kinetics is shown in Figure 5(b). It can be seen that at 80°C the conversion of benzaldehyde is 68% and increases to 83% at 120°C for a reaction time of 4 h, which remains constant till 140°C. Similarly, conversion of 4-methoxybenzaldehyde is maximum 89% at 140°C.

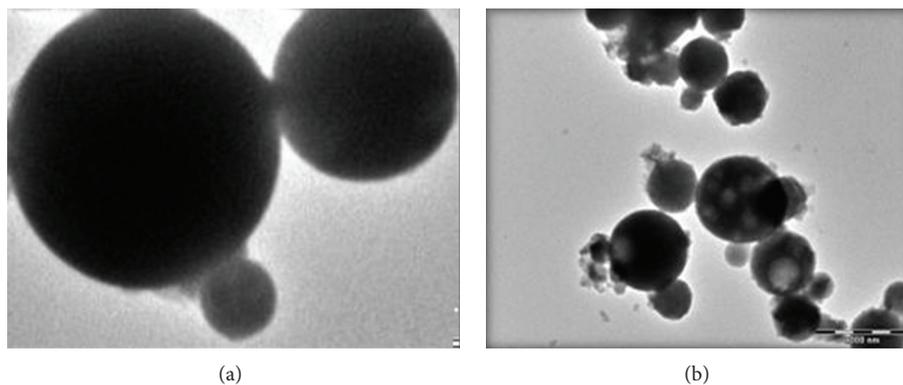


FIGURE 4: TEM image of (a) Raw fly ash and (b) KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> catalyst.

**3.3.3. Effect of Reaction Time.** The optimum reaction time required, achieving maximum conversion of benzaldehyde and 4-methoxybenzaldehyde is carried out at 40 and 140°C for different time intervals from 30 min to 8 h. The conversion of benzaldehyde and 4-methoxybenzaldehyde gradually increases with time giving 83% and 89% after 4 h respectively as given in Figure 5(c) which remains constant till 8 h.

**3.3.4. Effect of Molar Ratio (Substrate/2'-hydroxyacetophenone).** The effect of the molar ratio of benzaldehyde to 2'-hydroxyacetophenone and 4-methoxybenzaldehyde to 2'-hydroxyacetophenone on conversion and yield of products is also studied at a reaction temperature of 120°C and 140°C and reaction time 4 h. At the molar ratio of 1:1, maximum conversion of benzaldehyde and 4-methoxybenzaldehyde with yield of their respective products was obtained (Figure 5(e)). With increasing the molar ratio, the conversion was observed to be decreased, which can be attributed to formation of benzoic acid as side product.

**3.4. Comparison of Catalytic Activity of KF/Al<sub>2</sub>O<sub>3</sub>/Fly Ash with the Literature Data.** The reaction between 2'-hydroxyacetophenone and benzaldehyde has been carried out over different catalysts as reported in the literature. The results obtained from the reported catalysts showed that when zeolite NaX and a sepiolite partially exchanged with Cs were used as catalysts, their activity was very low [31]. It is because of the fact that H atoms present in the methyl group of acetophenone has high pKa value (15.8) and it has been demonstrated previously that the basic sites of exchanged CsNaX and Cs sepiolite catalysts can only abstract proton with pKa = 10.7 and 13.3 respectively [31]. So it is evident from the above results that a catalyst with strong basic sites should be used to get the high conversion value. It is also reported when an excess of Cs is exchanged with zeolite, it can give completely high conversion, but the catalyst have to be use in the inert atmosphere, in order to avoid the formation of carbonates [32]. Mg-Al hydrotalcite derived catalyst has also been used in this reaction and a conversion of 78% was obtained [33]. The presence of water also affects the conversion value. Similarly reaction between

4-methoxybenzaldehyde and 2'-hydroxyacetophenone in the presence of MeOH/KOH at room temperature gives 65 % yield of 4-methoxy-2'-hydroxychalcone in 24 h [34].

In order to find the optimum for the studied reactions, we have synthesized highly basic KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalyst and it is found that with this catalyst the conversion value (83%) of benzaldehyde and (89%) of 4-methoxybenzaldehyde was increased. The prepared catalyst is also reused for up to three reaction cycles. The regenerated catalyst showed similar catalytic activity till 3rd reaction cycle giving approximately similar conversion of benzaldehyde (81%) and 4-methoxybenzaldehyde (86%), which indicates that the sites are not deactivated in the regenerated catalyst as confirmed by FTIR of regenerated catalyst (Figure 1(g)).

**3.5. Characterization of Products.** NMR of 2'-hydroxychalcone: <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>), δ ppm: 12.78 (s, 1H, 2'-OH), 7.91–7.96 (d, 1H, J = 7.6 Hz, and 1.8 Hz, H<sub>6'</sub>) 7.91–7.96 (dd, 1H, J = 14.4 Hz, H<sub>β</sub>), 7.35–7.70 (m, 7H, H<sub>α</sub>, H<sub>4'</sub>, H<sub>2</sub>, H<sub>3</sub>, H<sub>4</sub>, H<sub>5</sub>, and H<sub>6</sub>) and 7.02–7.09 (m, 2H, H<sub>3'</sub>, and H<sub>5'</sub>). NMR of 4-methoxy-2'-hydroxychalcone: <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>), δ ppm: 12.95 (s, 1H, 2'-OH), 7.88–7.96 (d, 1H, J = 15.2 Hz, H<sub>β</sub>), 7.87–7.91 (d, 1H, J = 7.4 Hz, H<sub>6'</sub>) 7.59–7.66 (d, 1H, J = 15.2 Hz, H<sub>α</sub>) 7.62–7.66 (d, 2H, J = 8.8 Hz, H<sub>2</sub> and H<sub>6</sub>) 7.45–7.49 (t, 1H, J = 8.8 Hz, and 7.6 Hz, H<sub>4'</sub>) 6.90–7.05 (m, 4H, H<sub>3</sub>, H<sub>5</sub>, H<sub>3'</sub> and 5' h) and 3.87 (s, 3H, OCH<sub>3</sub>).

## 4. Conclusion

The study provides KF/Al<sub>2</sub>O<sub>3</sub>/fly ash as an efficient solid base catalyst possessing significant amount of basicity. The chemical activation of fly ash by alumina results in increased amorphous alumina content and thus surface hydroxyl contents produced due to the reaction of KF and alumina on fly ash support. Among all catalysts, KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalyst shows high catalytic activity towards condensation reaction. The experimental results indicate that the basicity of supported KF can be significantly increased by a proper choice of support. In KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalysts, KF reacts with alumina of fly ash and forms potassium hexafluoroaluminate

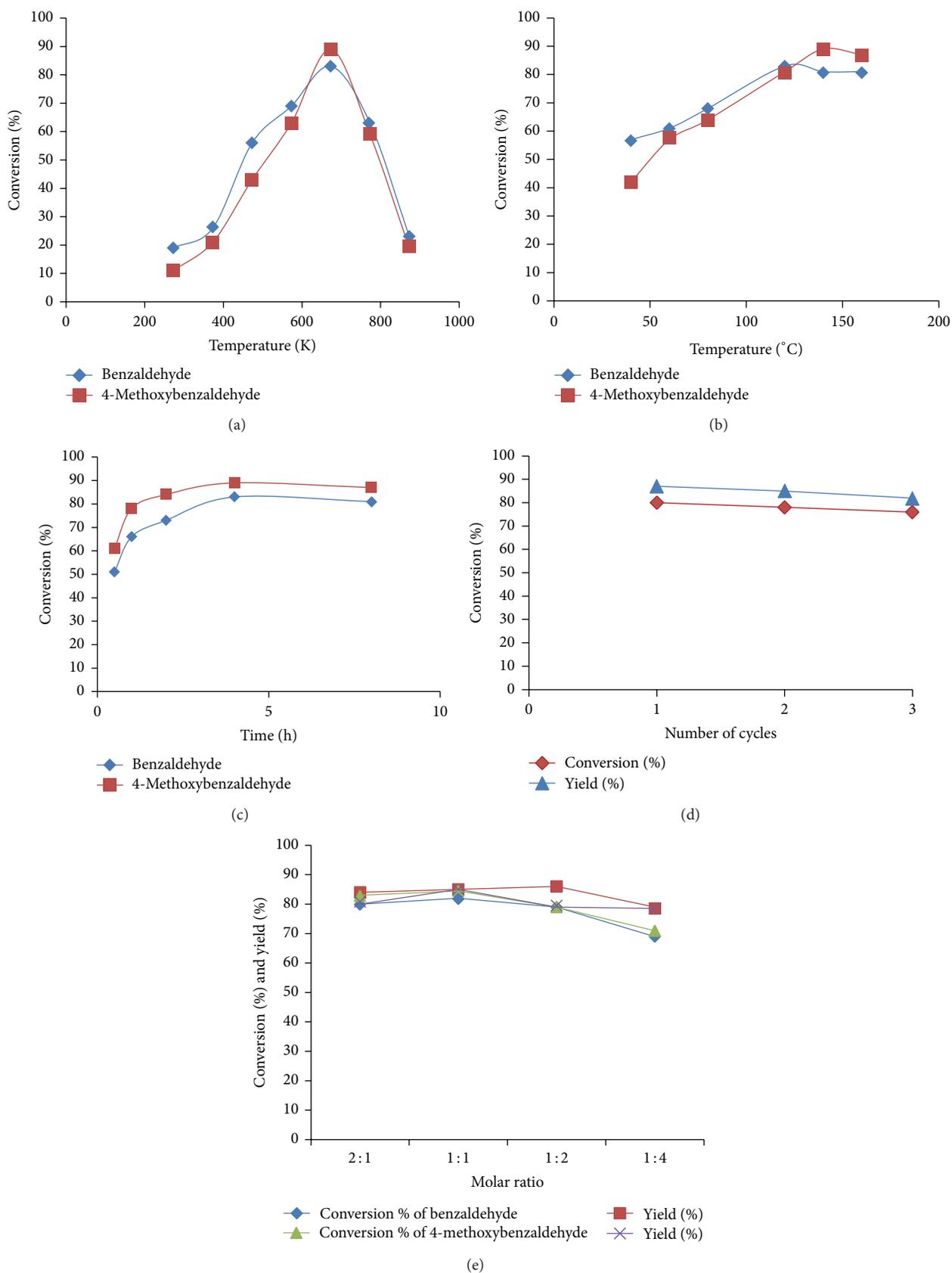


FIGURE 5: Conversion (%) of benzaldehyde and 4-methoxybenzaldehyde with  $\text{KF}/\text{Al}_2\text{O}_3/\text{fly ash}$  catalyst at (a) different pretreatment temperature (b) different reaction temperature (c) different time (d) different reaction cycles and (e) different molar ratios of benzaldehyde and 4-methoxybenzaldehyde.

and hydroxide, as the major phase which increases with increase in calcination temperature from 473 K to 673 K, responsible for enhancement of reactivity of catalyst. Along with these species, bidentate carbonate species exist on the surface of KF/Al<sub>2</sub>O<sub>3</sub>/fly ash<sup>673</sup> catalyst which is formed by the formation of K<sub>2</sub>CO<sub>3</sub>. The KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalysts were found active for condensation of benzaldehyde and 4-methoxybenzaldehyde with 2'-hydroxyacetophenone, in which KF/Al<sub>2</sub>O<sub>3</sub>/fly ash pretreated at 673 K gave higher conversion of benzaldehyde (87%) with 91% yield of 2'-hydroxychalcone and 4-methoxybenzaldehyde (93%) with 93% yield of 4-methoxy-2'-hydroxychalcone. Experimental results also indicate that the basicity generated over only KF/fly ash catalyst was not sufficient to get higher yield of condensation products, but when fly ash was chemically activated by loading alumina through precipitation using aluminium nitrate as precursor, KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalyst has shown increased catalytic activity for the same reaction. The conversion (83% and 89%) of benzaldehyde and 4-methoxybenzaldehyde in KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalytic system was comparable to the only KF/Al<sub>2</sub>O<sub>3</sub> system (conversion 61% and 59%) however, the cost of the KF/Al<sub>2</sub>O<sub>3</sub>/fly ash is lower than the KF/Al<sub>2</sub>O<sub>3</sub>, due to the replacement of  $\alpha$ -alumina support by alumina/fly ash support. Fly ash already has 17 wt% alumina and by chemically activating it with aluminium nitrate, the alumina content was increased up to 37 wt%, which is found to be responsible for generating sufficient basic sites to catalyze the Claisen-Schmidt condensation. This catalyst may further be explored for several other organic transformations.

Recycling experiments showed that the catalyst is very stable up to three cycles. A composite material which can combine the advantages of fly ash, alumina and KF can expand the catalytic capabilities of the material especially in applications as strong base catalysts for industrially important reactions.

## Conflict of Interests

The prepared KF/Al<sub>2</sub>O<sub>3</sub>/fly ash catalyst is novel and cost effective. The cost of the KF/Al<sub>2</sub>O<sub>3</sub>/fly ash is lower than the commercially available KF/Al<sub>2</sub>O<sub>3</sub>, due to the replacement  $\alpha$ -alumina support by alumina/fly ash support. Fly ash already has 17 wt% alumina and by chemically activating it with aluminium nitrate (cheaper than pure alumina), the alumina content was increased up to 37 wt%, which is found to be responsible for generating sufficient basic sites to catalyze the Claisen-Schmidt condensation. So the prepared catalyst may further be used for several other organic transformations in cost effective way. We have used the  $\alpha$ -alumina for comparing the catalytic activity of the prepared catalyst. There is no direct relationship with the commercial identity Chem Ltd.

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