MgO Enriched Coal Fly Ash as Highly Active Heterogeneous Base Catalyst for Claisen-Schmidt Condensation Reaction

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ABSTRACT

A novel fly ash supported solid base catalyst (MgO/fly ash) has been synthesized by using F-type fly ash and $Mg(NO_3)_2$ as precursor. The synthesized solid base possessed stable Si-O-Mg phase with sufficient hydroxyl group to catalyze liquid phase, solvent free and single step condensation of 4-methoxybenzaldehyde with 2-hydroxyacetophenone giving higher conversion (86%) of desired product (4-methoxy-2-hydroxychalcone) with 93% yield. The physico-chemical properties of MgO/fly ash catalyst were evaluated by N_2 adsorption-desorption, BET surface analysis, XRD, FT-IR, SEM-EDX and AAS etc. This excellent conversion and yield shows that the catalyst has sufficient basic sites, responsible for the catalytic activity. Moreover, the catalyst was regenerated and reused up to four reaction cycles with approximately equal efficiency as in the first run, conferring that basic sites are not lixiviated in the reaction system. Furthermore, this catalyst may replace conventional environmentally hazardous homogeneous liquid bases making an ecofriendly; solvent free, atom efficient, solid base catalytic process. The application of fly ash to synthesize a solid base catalyst finds a noble way to utilize this abundant waste material.

1. INTRODUCTION

Base catalyzed condensation reactions are synthetically important organic transformations for the preparation of wide variety of condensation products, which are key intermediates in

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the manufacture of pharmaceuticals and fine chemicals (Pullabhotla et al., 2009). Commercially these reactions are carried out using various homogeneous base catalysts such as alkaline oxide, alkaline earth oxides, and hydroxides (Gadekar et al., 2008; Tai et al., 2007; Motokura., 2008), which are corrosive, toxic, nonreusable and also produce neutralization waste (Saad, 2004). Heterogenization of the homogeneous catalysts has become an important strategy, particularly in respect of substituting homogeneous base catalysts such as NaOH and KOH, which not only retain the active catalytic sites of the homogeneous analogue but also provide advantages of easy separation and recycling of the catalysts (Hoelderich, 2000). A number of solid bases such as KF/Al_2O_3, hydrotalcite, KNH_2/Al_2O_3, immines/SiO_2 (Choudary et al., 2001; Tian et al., 2004; Clacens et al., 2004; Utting, et al., 2000), zeolites (Elazarifi et al., 2004), Al-enriched fluoroapatites, hydroxyapetites (Saravanamurugan et al., 2006), clay, amino based metal organic framework (Gascon et al., 2009), alkali earth oxide supported on alumina (Sharma et al., 2007) and magnesium oxide (Vidruk et al., 2009) have been reported in literature for catalyzing several condensation reactions. But the drawback of these catalysts is low selectivity of the product and complicated process for separation of the catalyst. Among all alkaline earth oxides, MgO is most widely used as a promising catalyst (Kabashima et al., 1997) in heterogeneous catalysis and exhibits high activities in numerous base-catalyzed organic reactions, such as self-Michael addition to form methyl diesters (Kabashima et al., 1997), the Tishchenko reactions (Seki et al., 2001), the Meerwein-Ponndorf-Verley reactions (Aramendia et al., 2003), dimerisation of ethanol to butanol (Ndou et al., 2003), and self-condensation of propanol (Ndou et al., 2004). With the increasing demand of new and efficient catalysts with sufficient activity, low cost and environmental friendliness, we have developed a novel MgO/fly ash solid base catalyst by loading MgO on thermally activated fly ash.

F-type fly ash (SiO_2 & Al_2O_3 > 70%) is a silica enriched material, containing silica, alumina, ferric oxide, calcium oxide and other metal oxides such as Mn_2O_3 and TiO_2 and inert crystallite phases such as mullite, quartz and magnetite (Mallick et al., 1997), which is being used in the present work as solid support for loading MgO. One of the main constituents of fly ash is silica (54%), which we have enhanced by loading MgO, correspondingly generating Si-O-Mg phase responsible for increase in surface hydroxyl groups. In our previous work, fly ash has been used for developing several solid acid catalysts for synthesis of aspirin (Khatri et al., 2007; Khatri et al., 2008), oil of wintergreen (Khatri et al., 2008), 3,4-dimethoxyacetophenone (Khatri et al., 2010) (anti neoplastic) and diphenylmethane (Khatri et al., 2010). Recently we have also reported the use of fly ash in the synthesis of CaO/fly ash and NaOH/fly ash as recyclable solid base catalyst for Knoevenagel (Jain et al., 2010) and Claisen-Schmidt condensation (Jain et al., 2011) reactions respectively. In the present work MgO has been supported over thermally activated fly ash to prepare an efficient and recyclable solid base catalyst for Claisen-Schmidt condensation reaction. The prepared catalyst possessed stable active basic sites for catalyzing condensation between 4-methoxy benzaldehyde and o-hydroxyacetophenone to produce 4-methoxy-2-hydroxychalcone, a chemical used as antimalarial and anticancer drug. Thus the work reports a noble, recyclable, cost effective solid base catalyst for industrially important organic transformations.

2. EXPERIMENTAL METHODS

2.1 Materials

Fly ash, collected from Kota Super Thermal Power Plant (Rajasthan, India) used as solid support for the synthesis of heterogeneous catalyst. $Mg(NO_3)_2.6H_2O$ (98%), 4-methoxybenzaldehyde (99%) and 2-hydroxyacetophenone (98%) were purchased from s.d. fine Ltd.

2.2 Catalyst Synthesis

As received fly ash was thermally activated at 900°C for 3h to remove C, S, and other impurities. An aqueous solution of $Mg(NO_3)_2.6H_2O$ (2M) was added drop wise to thermally activated fly ash with constant stirring. The slurry was aged at 110°C for 12h, then filtered and washed with water to remove leached compounds. The resulting powder was further dried at 110°C for 24h followed by calcination at 650°C for 4h in a muffle furnace under static conditions to prepare fly ash supported MgO material.

2.3 Catalyst Characterization

The synthesized MgO/fly ash catalyst was characterized by N_2 adsorption-desorption, BET surface area, AAS, XRD, FT-IR, SEM and EDX techniques.

Powder X-ray diffraction studies were carried out by using (Philips X'pert) analytical diffractometer with monochromatic CuK$_\alpha$ radiation (λ = 1.54056 Å) in a 2θ range of 5-65°. The FT-IR spectrum of the synthesized material was recorded using IR Prestige-21, Shimadzu in DRS (Diffuse Reflectance Spectroscopy) by mixing the sample with KBr in 1:20 weight ratio. The spectrum was recorded in the range 400 – 4000 cm^{-1} with a resolution of 4 cm^{-1}. Specific surface area and pore volume in the samples were determined from N_2 adsorption–desorption isotherms at 77 K by NOVA 1000e Surface Area and Pore Size Analyzer using BET and BJH approaches (Gregg et al., 1982). The sample was degassed under vacuum at 120 °C for 4 h, prior to adsorption measurement to evacuate the physisorbed moisture and the isotherm was recorded with 20 points adsorption and desorption. The chemical components present in the fly ash sample were analyzed by Flame Atomic Absorption Spectrophotometer (AA-6300, Shimadzu). The detailed imaging information about the morphology and surface texture of the sample was provided by SEM-EDX (Philips XL30 ESEM TMP).

2.4 Catalytic Activity

2.4.1 Reaction procedure: Claisen-Schmidt condensation

Catalytic activity of the MgO/fly ash was tested by Claisen-Schmidt condensation of 4-methoxybenzaldehyde with 2-hydroxyacetophenone in solvent free liquid phase reaction shown in scheme 1.
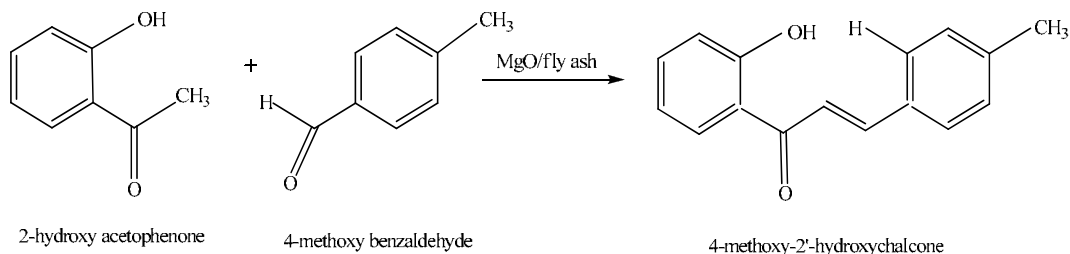
Scheme 1. Claisen-Schmidt condensation of 4-methoxybenzaldehyde with 2-hydroxyacetophenone over MgO/fly ash catalyst.

The condensation of 4-methoxybenzaldehyde with 2-hydroxyacetophenone (Scheme 1) was performed in liquid phase batch reactor consisting of 25 ml round bottom flask with condenser in a constant temperature oil bath with continuous magnetic stirring. A mixture of 4-methoxybenzaldehyde (5mmol) and 2-hydroxyacetophenone (5mmol) was taken in round bottom flask. The catalyst (substrate to catalyst ratio = 5), activated at 650ºC for 2h was added in the reaction mixture. The reaction was carried out at different molar ratio of substrate at different temperatures in the range of 70–160ºC for time ranging from 1h to 8h. After completion of the reaction the catalyst was filtered and the product was analyzed by Gas Chromatograph (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 50–280ºC and N_2 (1.5 ml/min) as a carrier gas. The conversion and yield of 4-methoxybenzaldehyde was calculated by using weight percent method.

Conversion (wt %) = 100 X (Initial wt% - Final wt%) / Initial wt%

% Yield of 4-methoxy-2-hydroxychalcone obtained

=

$$100 \text{ X } \frac{\text{g of 4-methoxy-2-hydroxychalcone obtained}}{\text{g of 4-methoxy-2-hydroxychalcone obtained theoretically}}$$

2.5 Catalyst Regeneration

The used catalyst was washed with acetone and dried in oven at 110ºC for 12h followed by activation at 650ºC for 2h before reuse in next reaction cycle under similar reaction conditions as earlier.

3. RESULTS AND DISCUSSION

3.1 Characterization

The FT-IR spectra of pure fly ash in Fig. 1 shows a broad band between 3400-3000 cm^{-1}, which is attributed to surface –OH groups of Si-OH and adsorbed water molecules on the

surface. The spectra also show a broad range of bands from 1055 cm^{-1} to 1100 cm^{-1} which is attributed to modes of Si–O–Si asymmetric band stretching vibrations which is shifted towards lower wave number in Fig 2. A peak at 1650 cm^{-1} in the spectra of fly ash is attributed to bending mode (δ_{O-H}) of water molecule. The FTIR spectra of MgO/fly ash catalyst in Fig 2 shows a broad intense band at 3600-3200 cm^{-1} compared to fly ash, which ascribed to –OH stretching vibrations of the increased hydroxyl groups on the catalyst surface. It is assumed that a magnesium-silicate hydrate phase is formed first. Most of the molecular water is removed at heating till 250°C, while crystalline –OH remained till 700°C generating surface active basic sites (Richardson et al., 2008). This occurrence happens due to the special characteristic of MgO of absorbing atmospheric water. The introduction of the modifier ions (Mg^{2+}) causes a shift towards smaller wave number in the Si–O–Si stretching band, resulting from the depolymerization of the silicate framework (Liping et al., 2008). A peak at around 960 cm^{-1} of Si–OH group, which is present in Fig 1, is absent in FTIR spectrum of MgO/fly ash catalyst as shown in Fig 2 indicating that most of the Si-OH is consumed by MgO loading and appearance of Si-O-Mg occurs. It is well reported earlier that only 10 wt% MgO can completely consume the Si-OH groups in case magnesium species react with silanols according to stoichiometry. This result is in good agreement with the result of FT-IR, where almost no Si–OH bending bands are observed around 960 cm^{-1} in the spectrum of MgO-ZrO$_2$-SBA catalyst (Ying et al., 2007).
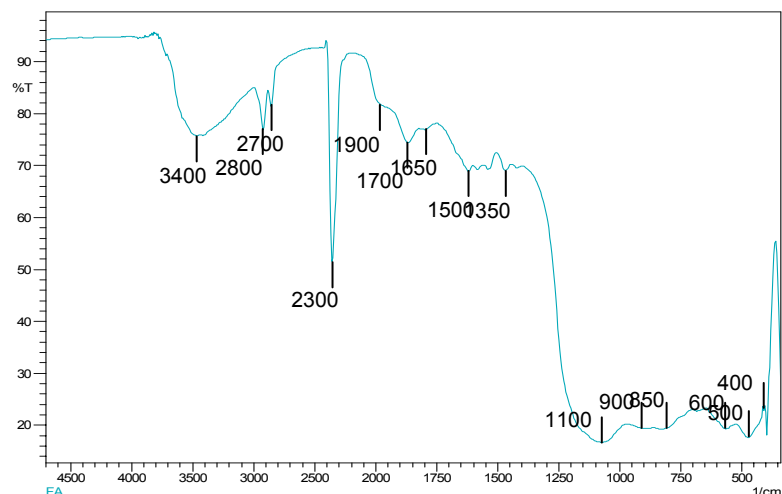

Fig. 1. FTIR of pure fly ash

XRD pattern of pure fly ash in Fig. 3 shows the presence of quartz, mullite and calcite phases. In Fig. 4, after the loading of MgO on fly ash in MgO/fly ash, the silica of fly ash reacts with MgO to form magnesium silicate phase (Roxana et al., 2009) which is observed from the peaks at 36° and 43°. The amorphous nature of the catalyst increases which is evident from the decrease in the intensity of crystalline phases in MgO/fly ash catalyst.
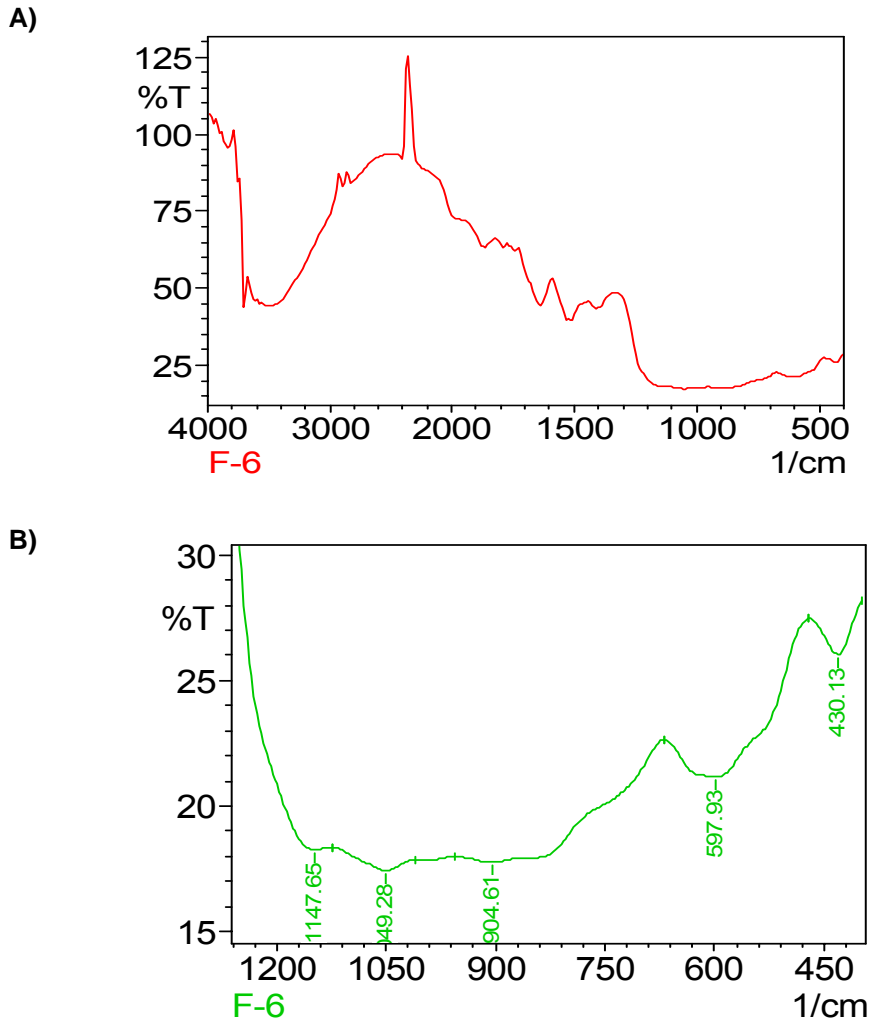
A)

B)

Fig. 2. FTIR A) MgO/fly ash catalyst B) Magnified (450-1200cm^{-1})

SEM-EDX spectrum of the MgO/fly ash catalyst is given in Fig. 5. The elements detected are Si- 21.52%, Al-9.66%, O-58.79%, C-3.61%, Na-1.21%, Mg-4.2% Ca-0.19%, K-0.09%, Fe-0.30%, Ti-0.12%). The presence of magnesium (Mg- 4.2%) in the catalyst also confirms the loading of MgO on fly ash surface.
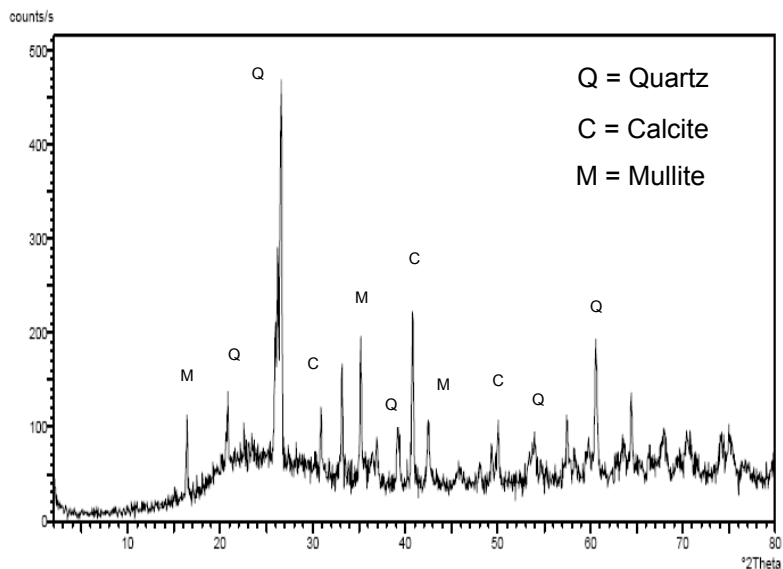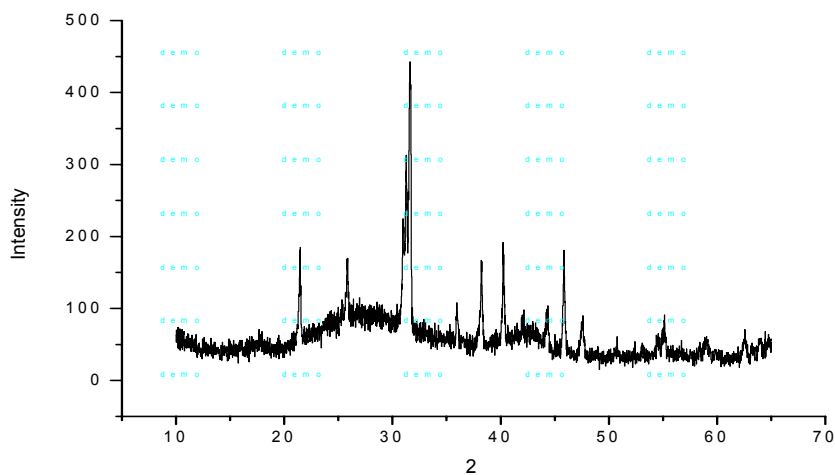
Fig. 3. XRD of pure fly ash

Fig. 4. XRD of MgO/fly ash catalyst

3.2 Catalytic performance

The catalytic performance of MgO/fly ash catalyst was measured by Claisen-Schmidt condensation of 4-methoxybenzaldehyde (5mmol) with 2-hydroxyacetophenone (5mmol) in single step and solvent free condition. Reaction conditions were optimized to get maximum conversion and yield of the product (4-methoxy-2-hydroxychalcone). The maximum conversion and yield of 4-methoxy-2-hydroxychalcone was found when reaction was carried out at 140°C for 4h, taking 4-methoxybenzaldehyde/2-hydroxyacetophenone molar ratio 1:1 and 4-methoxybenzaldehyde to catalyst weight ratio of 5, which showed that MgO/fly ash

catalyst possesses sufficient catalytic activity for the reaction. The reaction parameters such as temperature, time, molar ratio and substrate to catalyst weight ratio are studied in detail.

To optimize the reaction temperature giving maximum yield of 4-methoxy-2-hydroxychalcone, condensation of 2-hydroxyacetophenone with 4-methoxybenzaldehyde was carried out at different temperatures ranging from 70 to 160°C for 4h. The results showed that the conversion value gradually increases with increase in temperature from 70 to 140°C as shown in Fig. 6. The maximum conversion (86%) of 4-methoxybenzaldehyde was obtained at 140°C within 4h, which decreased (84%) at higher reaction temperature (160°C).
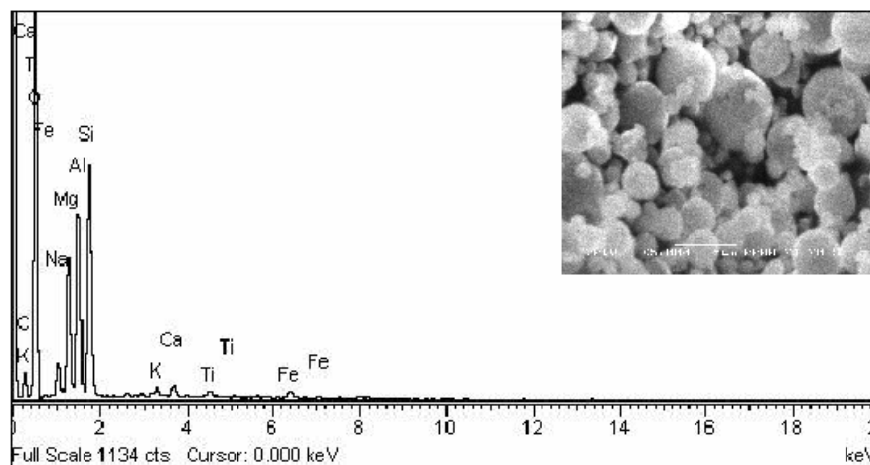

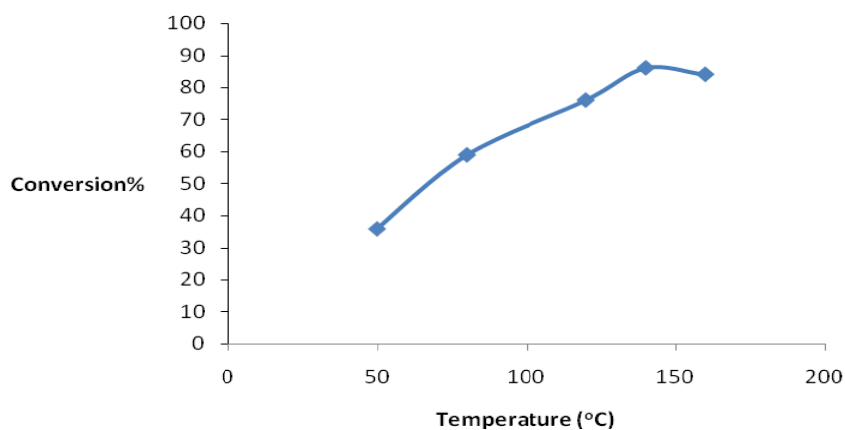**Fig. 5. SEM-EDX of MgO/fly ash catalyst**

Fig. 6. Variation of conversion (%) of 4-methoxybenzaldehyde with temperature after 4h.

The optimization of reaction time required to achieve maximum conversion was performed at 140°C taking 2-hydroxyacetophenone to 4-methoxybenzaldehyde molar ratio of 1:1, with substrate/catalyst ratio of 10 for different reaction time ranging from 1h to 8h as shown in Fig. 7. It was found that in first 4h of reaction period the conversion increases linearly up to 86% which remained constant till 8h.
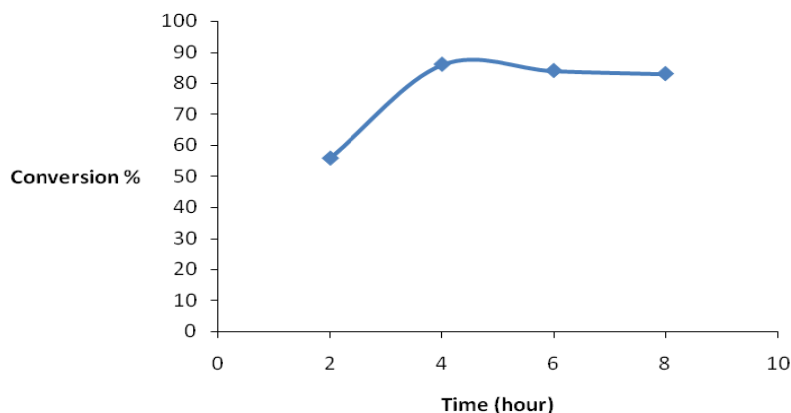

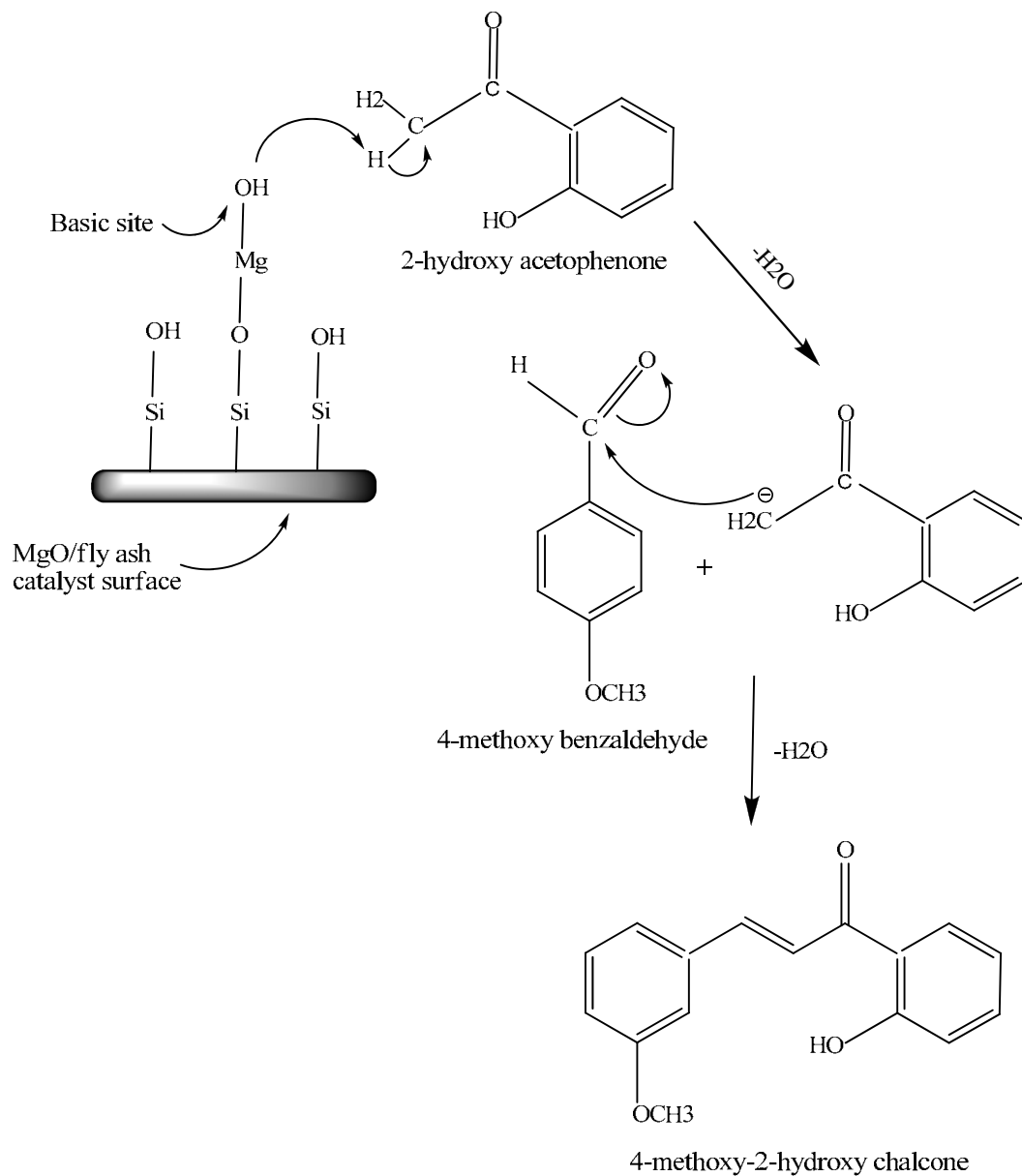**Fig. 7. Variation of conversion (%) of 4-methoxybenzaldehyde with time at 140°C**

The effect of reactant molar ratio on yield was monitored at different molar ratios ranging from 1:1 to 2:1 as given in Table 1. The conversion was found maximum at 1:1molar ratio with 86% conversion and 93% yield.

Table 1. Effect of molar ratios of 4-methoxybenzaldehyde/2-hydroxyacetophenone on (%) conversion and (%) yield of 4-methoxy-2-hydroxychalcone over MgO/fly ash catalyst

Molar Ratio	Conversion (%)	Yield%
1:1	86	93
1:2	81	81
2:1	74	73
3:1	64	71

(Reaction conditions: substrate/catalyst = 5; Temperature = 140°C; Time = 4h; catalyst activation = 650°C for 2h.)

The effect of substrate to catalyst weight ratio on conversion was studied by varying the amount of catalyst under optimized reaction conditions. As indicated from Table 2, at lower catalyst amount substrate/catalyst weight ratio 20, only 39% conversion was observed. On increasing this ratio to 5, conversion increased up to 86%. The increase in the conversion with an increase in the catalyst weight can be attributed to an increase in the availability of number of surface active sites.

Scheme 2. Proposed mechanism of Claisen-Schmidt condensation of o-hydroxyacetophenone and 4-methoxy benzaldehyde over mgO/fly ash catalyst

Table 2. **Effect of substrate/catalyst weight ratio on (%) conversion and (%) yield of 4-methoxy-2-hydroxychalcone over MgO/fly ash catalyst**

S/C weight ratio	Conversion (%)	Yield (%)
20	39	69
15	72	73
10	74	71
5	86	93

(Reaction conditions: Temperature = 140°C; Time = 4h; molar ratio = 1:1; catalyst activation = 650°C for 2h.)

3.3 Proposed Mechanism

The surface basic sites (hydroxyl groups) of the catalyst produce carbanion by abstracting the proton from o-hydroxyacetophenone as shown in Scheme 2, which attack on the 4-methoxy benzaldehyde and form condensation product by simple nucleophillic substitution reaction.

3.4 Regeneration of Catalyst

The fly ash catalyst was regenerated by simple thermal regeneration method and retained the catalytic activity. The regenerated catalyst showed similar catalytic activity till 4th reaction cycle giving the conversion of 4-methoxybenzaldehyde to 4-methoxy-2-hydroxychalcone 86%, which indicates that the sites are not deactivated in the regenerated catalyst.

3.4.1 NMR of 4-methoxy-2'-hydroxychalcone

Yellow Crystals, m.p. 78°C. H^1-NMR (200MHz, $CDCl_3$), δ ppm: 12.78 (s, 1H, 2'-OH), 7.91-7.96 (d, 1H, J=7.6 Hz, and 1.8 Hz, H6')7.91-7.96 (dd, 1H, J=14.4 Hz, H_β), 7.35-7.70 (m, 7H, H_α, H4', H2, H3, H4, H5, H6); 7.02-7.09 (m, 2H, H3', and H5'), Anal. C,H,O.

4. CONCLUSION

The study provides a new application of coal-generated fly ash as effective solid base catalyst prepared by thermal and chemical activation of fly ash by loading MgO. This fly ash catalyst serves as potential solid base catalyst for condensation reactions, which is evident from high conversion of 4-methoxybenzaldehyde (86%). The prepared MgO/fly ash catalyst possesses higher basicity due to attachment of MgO on silica present in fly ash surface, which initiate the reaction by abstracting the proton from active methylene group of 2-hydroxyacetophenone. Thus formed carbanion attack on 4-methoxybenzaldehyde to produce 4-methoxy-2-hydroxychalcone with very high yield (93%). The reaction was carried out in a solvent free condition and the catalyst was easily separated by simple filtration, can be regenerated and reused several times with equal efficiency, thus produces no waste and

makes the process economic. The catalyst is also completely recyclable suggesting that this small amount of catalyst has sufficient basic sites for organic synthesis. It is thus confirmed that under experimental conditions, the leaching of active sites or deactivation of the catalyst is practically negligible. This investigation brings into light the structural aspects of a novel fly ash supported solid base which is cost effective, environmentally safe and recyclable and can be used in catalytic amount in solvent free organic transformation.

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