Chapter 6

Silica Enrichment in Fly Ash and Synthesis of Solid Base Catalyst for Claisen-Schmidt Condensation Reaction
Abstract

Fly ash has been converted into silica enriched fly ash (SFA) and CaSFA catalyst by successively following mechanical, thermal and chemical activation. The prepared catalytic materials were characterized by using various analytical techniques viz. $N_2$ adsorption-desorption study, TGA, FTIR, XRD, SEM-EDX and TEM. The basic strength of the prepared CaSFA catalyst was determined by Hammett indicator method. The catalytic activity of catalyst was evaluated by Claisen-Schmidt condensation reaction of 4-methylbenzaldehyde with acetophenone under optimized reaction conditions. The catalyst gave high conversion (94%) of 4-methylbenzaldehyde. The CaSFA catalyst can be regenerated and reused up to four reaction cycles with almost equal efficiency. The conversion results show that the catalyst possesses sufficient stable active basic sites responsible for the catalytic activity. The work reports a novel application of abundantly available siliceous solid waste material fly ash in synthesis of silica enriched material and catalytic applications.
6.1 Introduction

Silica is a functional material that is used to improve surfaces and mechanical properties of many materials. Precipitated silica, is a white fluffy powder with amorphous nature, does not show a health hazard with respect to lung tumour or silicosis [1]. Generally, precipitated amorphous SiO$_2$ can be produced by chemical reaction between aqueous solution of sodium metasilicate and a mineral acid [2]. Precipitated silica has surface area in the range of 150-200 m$^2$/g, bulk density 120-200 g/litre and loss on ignition 3-6% [3]. Primary SiO$_2$ particles are ~15 to ~30 nm in size. These particles show a tendency to aggregate and form ~160 nm size secondary particles [2]. Precipitated SiO$_2$ has found various applications as absorbent, drying powder, support material for heterogeneous catalysts synthesis, anticorrosion agent, filler in rubber and plastics, additives in varnishes, paints and glues, insulation materials. In addition, amorphous silica is also used in the production of free-flowing powders for food stuffs, animal feeds, pharmaceuticals and cosmetics [2, 3]. Tetraethylorthosilicate (TEOS) is widely used in commercial silica synthesis, commercial silica is amorphous in nature [4]. Besides TEOS, amorphous silica has been extracted from a number of bio-wastes eg. rice husk ash [5], corn cob ash [6], bagasse ash [7] etc. Silica supported solid catalysts for catalyzing different organic reactions are well preceded in the literature viz. alkali metal supported silica for vapour phase O-methylation of 2-naphthol [8], silica supported ammonium acetate (NH$_4$OAc/SiO$_2$) catalyst for Knoevenagel condensation between aldehydes or ketones and active methylene compound [9], Li-Ba/SiO$_2$ catalyst for conversion of methane [10] and silica supported cinchona alkaloids as heterogeneous catalysts for asymmetric Michael reaction [11].

The Claisen-Schmidt reaction is a condensation reaction of aldehydes and carbonyl compounds leading to chalcones. Chalcones are important synthetic intermediates for the preparation of flavonoids and various heterocyclic compounds. They also exhibit biological activities including antimitotic, antimalarial, anticancer and anti-inflammatory activity [12].

Fly ash is a aluminosilicate material, abundantly available by product of thermal power plants and having ~70% SiO$_2$ content, was thought to be explored
as a material for silica enrichment as well as for modification in surfacial properties by silica enrichment with removal of other accessory metal oxides. The physicochemical properties of prepared silica enriched fly ash (SFA) were characterized by using different characterization techniques. The prepared material has also been used to synthesize solid base catalyst by treating with Ca(NO$_3$)$_2$ solution. Catalytic activity of prepared silica catalyst was evaluated by Claisen-Schmidt condensation reaction of 4-methylbenzaldehyde with acetophenone in single step, liquid phase and solvent free reaction conditions. Thus the present work brings into light the use of fly ash for synthesis of silica enriched material which could be a significant alternative of commercial silica which can be utilized as support material for heterogeneous catalyst synthesis.

6.2 Experimental

6.2.1 Materials

Fly ash was collected from Jamshedpur Thermal Power Station, Jamshedpur (Jharkhand). All chemicals NaOH (98%), Na$_2$CO$_3$ (98%) Ca(NO$_3$)$_2$ (99%) were purchased from Sigma Aldrich and acetophenone and 4-methoxybenzaldehyde were purchased from S.D. Fine Chemical Ltd., India. All reagents used were of analytical grade and used as such.

6.2.2 Catalyst synthesis

As received FA was mechanically activated by using high energy planetary ball mill (Retsch PM-100, Germany) in an agate jar with 5mm diameter agate balls for 30 h at 250 rotation/minute speed to increase the surface area as well as surface active sites. Milled FA showed the higher specific surface area, also called as mechanically activated fly ash (MFA), was selected for further activations. MFA was thermally activated at 800 °C for 3 h to form thermally activated fly ash (TFA), consequently C, S, moisture and other impurities also get removed [13]. An aqueous solution of NaOH (6 M, 60 mL) was added into 10 g TFA. Then the mixture was constantly stirred for 3 days at 90 °C. Precipitation was done by dropwise addition of 5 N H$_2$SO$_4$ up to pH 7 in the above mixture at room temperature. The resultant slurry was aged for 24 h then filtered and washed.
with double distilled water up to pH 7 to remove leached compounds and sodium sulphate. Now the silica enriched fly ash (SFA) was air dried at 110 °C for 24 h.

To prepare solid base catalyst from SFA, Ca(NO$_3$)$_2$ solution (15 wt%) was added into 10 g, 800 °C for 3 h thermally activated SFA. Then the mixture was constantly stirred for 1 h at 90 °C. Precipitation was done by dropwise addition of mixture of NaOH (3M) and Na$_2$CO$_3$ (2M) solution (in 1:1 ratio) up to pH 8 in the above mixture. The resultant slurry was aged for 24 h then filtered and washed with double distilled water up to pH 7 to remove leached compounds, air dried at 110 °C for 24 h and calcined at 500 °C for 3 h in a muffle furnace under static conditions to form CaSFA solid base catalyst.

### 6.3 Catalyst characterization

The synthesized FA, MFA, TFA, SFA, thermally activated SFA and CaSFA were characterized by N$_2$ adsorption-desorption study, TGA, FTIR, XRD, SEM-EDX and TEM techniques. Instrumental details and operating conditions during the characterization are given in Annexure 1.

Hammett indicator method was used to evaluate the basic strength of CaSFA catalyst. Basicity was measured by a benzoic acid titration method using phenolphthalein indicator [14]. The methods for evaluating basic strength and basicity are given in detail in Chapter 2.

### 6.4 Catalytic activity of CaSFA catalyst

The catalytic activity of CaSFA was investigated by Claisen-Schmidt condensation reaction of 4-methylbenzaldehyde with acetophenone as shown in Scheme 6.1. The reaction produces 3-(4-methylphenyl)-1-phenylprop-2-en-1-one also known as 4-methylchalcone. The reaction was carried out in a liquid phase batch reactor under optimized reaction conditions.
Scheme 6.1: Claisen-Schmidt condensation reaction of 4-methylbenzaldehyde with acetophenone over CaSFA.

The condensation of 4-methylbenzaldehyde with acetophenone was performed in a liquid phase batch reactor consisting of 250 mL round bottom flask equipped with digital magnetic stirrer and glass condenser, immersed in a constant temperature oil bath. In the procedure, 4-methylbenzaldehyde and acetophenone in 2:1 to 1:3 molar ratios were taken in a round bottom flask. The desired amount of CaSFA catalyst (preheated at 500 °C for 2 h), was taken according to substrate/catalyst weight ratio ranging from 10:1 to 2.5:1. The reaction mixture was heated at required reaction temperature ranging from 100-150 °C and time from 1-5 h at atmospheric pressure in solvent free liquid phase reaction conditions.

After completion of the reaction (TLC monitoring), the mixture was cooled and filtered to separate the catalyst. The product was analyzed by Gas Chromatograph.

The conversion of 4-methylbenzaldehyde and yield were calculated by using weight percent method.

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

After initial use, the spent catalyst was filtered out by simple filtration method, thoroughly washed with acetone and dried at 110 °C for 12 h followed by thermal activation at 500 °C for 2 h in muffle furnace before reuse in next reaction cycles under similar reaction conditions as earlier.

6.6 Results and discussion

6.6.1 Chemical composition of FA, SFA and CaSFA catalyst

The chemical compositions of FA, SFA and CaSFA as determined by SEM-EDX are given in Table 6.1. The LOI of FA is found to be 5 wt%, at 800 °C for 3 h. As it is clear from Table 6.1 that in SFA, silica content increases from 59.42% to 76.63% while percentage of other metal oxides get decreased. It may be concluded that some other metal oxides are dissolved in NaOH solution and leach out during washing steps and results in increased silica content. After chemical treatment of SFA with Ca(NO$_3$)$_2$, CaO content increases in CaSFA 0.71% to 6.42%. The increased Ca generates basic sites in CaSFA as well as catalytic activity for Claisen-Schmidt condensation reaction.

6.6.2 Surface area results

Specific surface areas of all sample determined by N$_2$ adsorption-desorptions are given in Table 6.2. Specific surface area of FA is 9.18 m$^2$/g, considerably increases after mechanical activation and reaches up to 30.02 m$^2$/g for MFA. The specific surface area again increases from TFA to SFA, from 28.47 m$^2$/g to 65.78 m$^2$/g, gets reduced after chemical activation with Ca(NO$_3$)$_2$ and reaches to 59.23 m$^2$/g in CaSFA. The blockage of SFA small pores by loading of
different Ca species leads the reduction in surface area and confirms significant chemical activation by Ca(NO$_3$)$_2$.

Table 6.1: Chemical composition of FA, SFA and CaSFA.

<table>
<thead>
<tr>
<th>Chemical components</th>
<th>FA (Wt%)</th>
<th>SFA (Wt%)</th>
<th>CaSFA (Wt%)</th>
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<tr>
<td>SiO$_2$</td>
<td>59.42</td>
<td>76.63</td>
<td>75.10</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>18.79</td>
<td>16.24</td>
<td>13.74</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>6.91</td>
<td>3.18</td>
<td>1.89</td>
</tr>
<tr>
<td>CaO</td>
<td>2.56</td>
<td>0.71</td>
<td>6.42</td>
</tr>
<tr>
<td>MgO</td>
<td>1.84</td>
<td>0.46</td>
<td>0.30</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>2.37</td>
<td>0.64</td>
<td>0.59</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>3.84</td>
<td>0.98</td>
<td>0.95</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.27</td>
<td>0.14</td>
<td>0.11</td>
</tr>
<tr>
<td>Other elements</td>
<td>3</td>
<td>1.2</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Table 6.2: Surface area of all catalytic materials.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Specific surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>9.18</td>
</tr>
<tr>
<td>MFA</td>
<td>30.02</td>
</tr>
<tr>
<td>TFA</td>
<td>28.47</td>
</tr>
<tr>
<td>SFA</td>
<td>65.78</td>
</tr>
<tr>
<td>CaSFA</td>
<td>59.23</td>
</tr>
</tbody>
</table>

6.6.3 Thermogravimetric analysis

TGA curves of FA, SFA and CaSFA (Figure 6.1) show weight loss of 5.96% and 6.10% and 12.96% respectively, within the temperature range 50-1000°C, are attributed to water loss and burning of carbonaceous materials and volatilization of some trace metal oxides and other impurities [15]. Precursor
Ca(NO$_3$)$_2$ can attain any of the phases like Ca(OH)$_2$, CaO, Ca-SiO$_2$ and CaCO$_3$ during the catalyst synthesis. So the slight weight loss in CaSFA may be assigned to the decomposition of these phases.

### 6.6.4 FTIR studies

The FTIR spectra of TFA, SFA and thermally activated SFA are given in the Figure 6.2. All spectra show a broad band between 3000-3600 cm$^{-1}$, attributed to –O-H stretching vibration of surface silanol groups (Si-OH) [16]. Increase in intensity and broadness of this region in case of SFA is an evidence for the breaking of spherical silica particles and formation of Si-OH groups and the presence of strong H-bonding after precipitation. In case of thermally activated SFA, thermal activation causes the decrease in intensity and broadness due to loss of adsorbed water in SFA [17]. A peak centered around 1630 cm$^{-1}$, present in all samples is assigned to bending mode ($\delta_{\text{o}-\text{H}}$) of water molecules (Figure 6.2, 6.3) [18]. A small peak in TFA around 2827 cm$^{-1}$ is assigned to –C-H stretching vibration of organic contaminants present in TFA (Table 6.3) [19]. Peaks centered at 1521 and 1679 cm$^{-1}$ are due to (CO$_3$)$_2^-$ stretching vibration, visible in all spectra [20, 21]. A broad band between 1129-1168 cm$^{-1}$ is attributed to Si-O-Si asymmetric stretching vibration [21]. A peak at approx ~ 600 cm$^{-1}$ is attributed to Si-O-Al stretching vibration (Figure 6.2, 6.3) [22].

FTIR spectrum of CaSFA (Figure 6.3c) shows the broader and much intense band in the region of 3000-3600 cm$^{-1}$ as compared to SFA samples. The increased intensity could be assigned to generation of Si-OH groups and Si/Al-O-Ca-OH groups during the chemical activation while H-bonding is responsible for the broadness of the band between these groups. The increased OH groups are responsible for the Bronsted basic sites which initiate the reaction by abstracting the proton from methyl group [23]. Loaded Ca could be present on thermally activated SFA surface in the forms of carbonate, hydroxide and oxide as well as in the form of silicate. Ca(OH)$_2$ and CaCO$_3$ formation could be assigned due to the absorption of water vapour [24] and CO$_2$ from environment [25] by CaO compound or they may generate during the catalyst synthesis step.
Figure 6.1: TGA curves of (a) FA, (b) SFA and (c) CaSFA.
Figure 6.2: FTIR spectra of (a) TFA, (b) SFA and (c) Thermally activated SFA.

Figure 6.3: FTIR spectra of (a) SFA, (b) Thermally activated SFA and (c) CaSFA.
Table 6.3: The observed transmission frequencies (cm\(^{-1}\)) of Fourier transform infrared spectra of TFA, SFA, thermally activated SFA and CaSFA and their assignments.

<table>
<thead>
<tr>
<th>Assignments</th>
<th>TFA</th>
<th>SFA</th>
<th>Thermally activated SFA</th>
<th>CaSFA</th>
<th>Reference No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O-Al stretching vibration</td>
<td>594</td>
<td>593</td>
<td>599</td>
<td>607</td>
<td>22</td>
</tr>
<tr>
<td>Si-O-Si asymm. stretching vibration</td>
<td>1129</td>
<td>1168</td>
<td>1167</td>
<td>1162</td>
<td>21</td>
</tr>
<tr>
<td>(CO(_3))(^2-) stretching vibration</td>
<td>1521, 1679</td>
<td>1527</td>
<td>1520</td>
<td>1527</td>
<td>20, 21</td>
</tr>
<tr>
<td>H-O-H bending vibration</td>
<td>1608</td>
<td>1632</td>
<td>1630</td>
<td>1640</td>
<td>18</td>
</tr>
<tr>
<td>-C–H stretching vibration</td>
<td>2827</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td>-O-H stretching vibration</td>
<td>3553</td>
<td>3451</td>
<td>3460</td>
<td>3437</td>
<td>16</td>
</tr>
</tbody>
</table>

6.6.5 X-ray diffraction studies

The XRD patterns of TFA, SFA, thermally activated SFA and CaSFA are given in Figure 6.4. Quartz exhibits peaks at \(2\theta = 20.7^\circ, 26.5^\circ, 40.66^\circ\) and \(49.96^\circ\) (SiO\(_2\), ICDD pdf number 000-46-1045) while peaks at \(2\theta = 33.4^\circ, 34.85^\circ\) and \(16.4^\circ\) confirm the presence of calcite (CaCO\(_3\), ICDD pdf number, 47-1743), hematite phase (Fe\(_2\)O\(_3\), ICDD pdf number, 33-0664) and mullite (Al\(_6\)Si\(_2\)O\(_{13}\), ICDD pdf number 000-15-0776) respectively in all XRD patterns (Figure 6.4). A
peak at around $2\theta = 41^\circ$ present only in CaSFA confirms increased amount of calcite (CaCO$_3$, JCPDS card 05- 0586) [26],[27]. This increased amount of calcite generates active basic sites on SFA surface thus basicity in CaSFA catalyst.

### 6.6.6 SEM analysis results

Figure 6.5 shows the surface morphologies of FA, TFA, SFA and CaSFA samples. It can be seen that fly ash mainly consists of spherical particles with smooth outer surfaces and irregularly shaped unburned carbon particles [28] which form clumps and convert into agglomerated particles during thermal activation Figure 6.5b. this agglomeration is the main reason of additional crystallinity in TFA. During precipitation step, agglomerated particles of TFA break into irregular shape small particles as depicted in Figure 6.5c, 6.6 which results in increased surface area of SFA. After chemical treatment with Ca(NO$_3$)$_2$, CaSFA particles show loaded Ca species in different forms, clearly visible in Figure 6.5d.

### 6.6.7 TEM analysis results

TEM image of FA shows a completely spherical, fine and smooth particle of fly ash which has been reduced in size after mechanical activation (Figure 6.7b). So, mechanical activation is accountable for the complete removal of smoothness and sphericity in FA particles. The TEM image of SFA shows < 100 nm particles of oval, rod and irregular shapes (Figure 6.7c). The clear difference in particle size and shape of SFA is responsible for increased surface area which facilitates the generation of surface active basic sites in CaSFA.

### 6.6.8 Basic strength and basicity measurement

The base strength and basicity of CaSFA was determined by the Hammett indicator method. CaSFA shows basic strength $9.8 < H < 15$ and basicity was found to be 1.1 mmol/g.
Figure 6.4: XRD patterns of (a) TFA, (b) SFA, (c) Thermally activated SFA and (d) CaSFA.

[Mu = Mullite, Q = Quartz, C = Calcite, H = Hematite]
Figure 6.5: SEM micrographs of (a) FA, (b) TFA, (c) SFA and (d) CaSFA.
Figure 6.6: SEM micrographs of SFA in higher magnification.
Figure 6.7: TEM images of (a) FA, (b) Mechanically activated FA and (c) SFA.
6.7 Catalytic activity

The catalytic activity of CaSFA catalyst was investigated by Claisen-Schmidt condensation reaction of acetophenone with 4-methylbenzaldehyde in batch reactor under optimized reaction conditions.

Results summarized in Table 6.4 show that TFA, SFA and thermally activated SFA do not show any catalytic activity for Claisen-Schmidt condensation reaction while CaSFA catalyst under given reaction conditions, showed maximum activity. Bronsted basic sites Ca-OH exist on catalyst surface to catalyze Claisen-Schmidt condensation reaction. Various parameters such as reactant molar ratio, amount of catalyst, reaction time and temperature were optimized, for getting the maximum catalytic activity, conversion and yield of desired product.

Table 6.4: Catalytic activity of TFA, SFA, thermally activated SFA and CaSFA for Claisen-Schmidt condensation reaction of 4-methylbenzaldehyde with acetophenone.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%) of 4-methylbenzaldehyde</th>
<th>Isolated yield (%) of 4-methylchalcone</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFA</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>SFA</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Thermally activated SFA</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>CaSFA</td>
<td>75</td>
<td>71</td>
</tr>
</tbody>
</table>

Reaction conditions: Temperature 140 °C, Time 1.5 h, 4-methylbenzaldehyde/acetophenone molar ratio 1:1, substrate/catalyst weight ratio 5:1.

6.7.1 Effect of reaction time

The effect of reaction time on the conversion (%) of 4-methylbenzaldehyde and product yield was studied in time range of 1-5 h at 140 °C by taking 4-methylbenzaldehyde/acetophenone molar ratio 1:1 and
acetophenone to catalyst weight ratio 5:1. The conversion continuously increased up to 94 % in initial 3 h and remained constant for the next 2 h (Figure 6.8). The optimized reaction time was found to be 3 h, in which CaSFA catalyst gave highest conversion 94% of 4-methylbenzaldehyde to 4-methylchalcone with 89% yield.

![Graph showing variation in isolated yield and conversion with time](image)

**Figure 6.8: Variation in isolated yield (%) and conversion (%) of 4-methylbenzaldehyde with time.**

*Reaction conditions: Temperature 140 °C, 4-methylbenzaldehyde/acetophenone molar ratio 1:1, substrate/catalyst weight ratio 5:1.*

### 6.7.2 Effect of reaction temperature

Optimization of reaction temperature for maximum conversion (%) and isolated yield (%) was carried out at temperature ranging from 100 °C to 150 °C for 3 h taking 4-methylbenzaldehyde/acetophenone molar ratio of 1:1 while substrate to catalyst weight ratio was 5:1. Conversion and yield were observed to increase on increasing reaction temperature ranging from 100 °C to 140 °C as depicted from **Figure 6.9**. The results show that the maximum conversion (94%) of 4-methylbenzaldehyde and isolated yield (89%) of 4-methylchalcone were found at 140 °C, after which conversion and isolated yield (%) remain almost steady till 150 °C.
Figure 6.9: Variation in isolated yield (%) and conversion (%) of 4-methylbenzaldehyde with temperature.

Reaction conditions: Time 3 h, 4-methylbenzaldehyde/acetophenone molar ratio 1:1, substrate/catalyst weight ratio 5:1.

6.7.3 Effect of substrate/catalyst weight ratio

The influence of substrate to catalyst weight ratio on conversion and isolated yield (%) was studied by varying the amount of CaSFA catalyst under optimized reaction conditions. Only 79% conversion of 4-methylbenzaldehyde was achieved at acetophenone/CaSFA weight ratio 10:1 while conversion reached to 94% in case of 5:1 substrate/catalyst weight ratio which remained unchanged in 2.5:1 substrate/catalyst weight ratio. The increase in conversion, with increase in the catalyst weight can be attributed to an increase in the availability of number of catalytic active sites required for the reaction (Figure 6.10).

6.7.4 Effect of reactant molar ratio

The effect of reactant molar ratio was studied at different molar. As indicated by Figure 6.11, 62% conversion of 4-methylbenzaldehyde was observed at 2:1 molar ratio of 4-methylbenzaldehyde to acetophenone. This may be due to insufficient quantity of the reactants to react with each other. There was an increase in conversion up to 94% at 1:1 molar ratio due to satisfactory reactant quantity on the basic sites of the CaSFA catalyst surface. The conversion decreased on further increasing the molar ratio from 1:2 to 1:3 which could be
attributed to the lacking of 4-methylbenzaldehyde or self condensation of acetopheneone.

![Bar chart showing the effect of substrate/catalyst weight ratio on conversion and isolated yield of 4-methylbenzaldehyde and 4-methylchalcone over CaSFA.]

**Figure 6.10:** Effect of substrate/catalyst weight ratio on conversion (%) of 4-methylbenzaldehyde and isolated yield (%) of 4-methylchalcone over CaSFA.

*Reaction conditions: Temperature 140 °C, Time 3 h, 4-methylbenzaldehyde/acetophenone molar ratio 1:1.*

### 6.8 Reaction mechanism

The plausible structure of CaSFA catalyst surface is shown in **Scheme 6.2**. The reaction mechanism over CaSFA catalyst shows that Claisen-Schmidt is a condensation reaction (**Scheme 6.3**). Surface active Bronsted basic sites (–Ca-OH) abstract proton from acetopheneone and form anion. The nucleophilic addition of the formed anion to the 4-methylbenzaldehyde, followed by the successive protonation and dehydration produces 3-(4-methylphenyl)-1-phenylprop-2-en-1-one or 4-methylchalcone.
Figure 6.11: Effect of molar ratio of 4-methylbenzaldehyde/acetophenone on conversion (%) of 4-methylbenzaldehyde and isolated yield (%) of 4-methylchalcone over CaSFA.

Reaction conditions: Temperature 140 °C, Time 3 h, substrate/catalyst weight ratio 5:1.

Scheme 6.2: The schematic presentation of chemical activation of thermally activated SFA with Ca(NO₃)₂ and proposed structure of CaSFA.
Scheme 6.3: Proposed mechanism for Claisen-Schmidt condensation reaction of 4-methylbenzaldehyde with acetophenone over CaSFA.
6.9 Catalyst regeneration

The regeneration reaction reflects that CaSFA catalyst can be regenerated by simple thermal regeneration method and retains the catalyst activity. The regenerated catalyst was found to be having similar activity as fresh catalyst for consecutive four reaction cycles, giving 89-75% yield (Table 6.5) for Claisen-Schmidt condensation of acetophenone with 4-methylbenzaldehyde. Due to the stability of Ca-OH Bronsted basic sites, CaSFA catalyst was found efficient up to five reaction cycles giving almost similar yield. The gradual decrease in yield after five reaction cycles is due to the deposition of carbonaceous material on the surface of the reused catalyst which may block the active basic sites of CaSFA catalyst.

Leaching test was done using hot filtration technique. The catalyst was removed after 30 min and the reaction was continued to completion but no further product was formed. This led us to the conclusion that no leaching occurs with the catalysts used and under the conditions applied in the present investigation.

Table 6.5: Catalytic activity of fresh and regenerated CaSFA for Claisen-Schmidt condensation of 4-methylbenzaldehyde with acetophenone.

<table>
<thead>
<tr>
<th>Reaction Cycle</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>89</td>
</tr>
<tr>
<td>II</td>
<td>85</td>
</tr>
<tr>
<td>III</td>
<td>82</td>
</tr>
<tr>
<td>IV</td>
<td>80</td>
</tr>
<tr>
<td>V</td>
<td>75</td>
</tr>
</tbody>
</table>

*Reaction conditions: Temperature 140 °C, Time 3 h, substrate/catalyst weight ratio 5:1, 4-methylbenzaldehyde/acetophenone molar ratio 1:1.*
6.10 Conclusion

The study provides CaSFA catalyst as an efficient solid base catalyst possessing significant amount of basicity and basic sites. Consecutive treatment of TFA with NaOH and H₂SO₄ result in increased amorphous silica content and converts fly ash into silica enriched fly ash (SFA). Further treatment with Ca(NO₃)₂ modify SFA surface by generating Bronsted basic sites i.e. -Ca–OH. These sites are responsible for catalytic activity of CaSFA, which has been investigated by Claisen-Schmidt condensation reaction. Catalyst was recovered, regenerated and reused with no noticeable changes in the yield, confirming almost negligible leaching of active basic sites or slight deactivation of the catalyst under the mentioned reaction conditions. The prepared CaSFA catalyst is stable, eco-friendly, cost effective, reusable, easily recoverable and suitable for the production of 4-methylchalcone. This study suggests that fly ash could be an economical source of silica for synthesizing novel solid base catalysts for catalyzing industrially important reactions in cost effective manner.

6.11 References