Synthesis and Characterization of Fly Ash Supported Silver Nanoparticles for Partial Oxidation of Alcohols
Abstract

The chapter describes the novel use of solid waste fly ash for the synthesis of innovative, highly efficient, cost effective, re-generable heterogeneous catalyst by loading different weight percents (1, 3 and 5 %) silver nanoparticles on thermally activated fly ash to intensify oxidation of alcohols (benzyl alcohol and methanol). Chemical reduction method, followed by calcination at appropriate temperature, has been used to load Ag nanoparticles over surface of thermally activated fly ash. Partial oxidation of alcohols under liquid phase condition has been used to evaluate catalytic activity of fly ash supported Ag catalyst. Results of textural, structural and morphological properties of prepared catalysts interpreted by XRD, SEM-EDS, FT-IR, UV-Vis and BET surface area analyzer, the plausible reaction mechanism for partial oxidation of benzyl alcohol over prepared catalyst are discussed.
4.1 Introduction

The preparation and study of metal nanoparticles is of interest in both research and technology. Silver nanoparticles have attracted considerable interest because of their potential applications in areas such as catalysis, nanoelectronics, optical filters, electromagnetic interference shielding and surface Raman scattering [1,2]. The method of preparation of nanoparticles in aqueous medium involves reduction of metal precursor salt by suitable reducing agent (sodium borohydride, ascorbic acid, etc.), or UV photons [3] or ionizing agents [4] or radiations [5]. All these synthesis methods require a stabilizing (capping) agent, for example polymers having functional groups such as -NH₂, -COOH and -OH, that have high affinity for metal atoms. The use of stabilizer is not desirable for some applications such as catalysis, where their presence may have detrimental effect on the performance of the catalyst. One significant approach to achieve this is to synthesize nanoparticles in the presence of suitable solid support such as silica, titania and alumina. Metal nanoclusters have been formed in silica aerogels by adding colloidal metal particles directly into the sol during gelation [6]. Recently, a gamma radiation-induced synthesis of Ag nanoclusters in silica aerogel has been reported [7] where Ag⁺ ions were exchanged in the silica gel prior to drying and irradiated with gamma radiation followed by supercritical drying. The silver nanoclusters formed upon irradiation get embedded into silica matrix. Pulse radiolytic studies [8] on the reduction of Ag⁺ ions at the surface of silica gel and gamma radiation preparation [9] of Ag nanocluster on SiO₂ have also been reported. For selective oxidation of CO, carbon and silica supported silver catalysts were formed by wet impregnation method using silver nitrate [10,11]. CuO/SiO₂ supported silver nanoparticles prepared by sol-gel route [12], silver loaded zeolites were also prepared by ion exchange for antibacterial application [13], for low temperature methane oxidation SnO₂ supported silver was prepared by wet impregnation method [14], silica alumina supported silver composite were synthesized by sol-gel route for partial oxidation of methanol to formaldehyde and the researcher claimed 97 % of methanol conversion over this sol-gel composite [15] Silver is 68th most abundant and widely distributed metal in the earth’s crust [16]. The most dominant non-metallurgical use of silver as
catalyst is in production of ethylene oxide from ethylene [17]. Supported silver catalysts have been widely investigated as promising oxidative catalytic materials for various reactions such as for partial oxidations [17–19] and oxidative dehydrogenation of hydrocarbons [20–22], epoxidation of alkenes [17], selective reduction of compounds [23,24] etc.

Most of the silver supported catalysts consist of silver metallic and ionic phase deposited on the surface of an oxide support which tend to be present as isolated silver species, and/or as small clusters of silver [25]. Supporting a metal on the surface of another oxide improves the catalytic activity of the active metal phase due to gain in surface area and mechanical strength [25]. Generally, during the preparation of the supported silver, the state of silver is non-uniform and the monolayer silver species are responsible for the catalytic activity and selectivity of the products. The advantage of these methods are that they do not require capping agent for stabilizing the metal nanoparticles [26]. The selectivity and activity of these catalysts depend on various factors such as the metal-support interaction, silver loading, methodology, state of silver on the support, calcination temperatures, types of support and its surface activity [27,28].

The use of solid waste FA as support in catalyst synthesis reduces the cost of bulk production of catalyst as it replaces commercially used costly metal supports viz. SiO₂, TiO₂, ZrO₂, Al₂O₃ etc. In our previous work, the surface activity has been generated over FA after suitable morphological and mineralogical modifications converting it into desired catalytic materials for Friedal-Crafts acylation[29,30], benzylolation [31], esterification [32] and various type of condensation reactions [33–36] under liquid phase condition and oxidation under vapour phase [37].

Selective catalytic oxidation of alcohols to carbonyls is one of the most important chemical transformations in industrial chemistry. Carbonyl compounds such as ketones and aldehydes are the precursors for many drugs, vitamins, and fragrances and they are also important intermediates for many complex syntheses [38]. Numerous methods are available for alcohol oxidations such as metal salts in the form of homogeneous catalysts [39–42] or supported metal ions as
heterogeneous catalysts [43–46]. However, the common methods of alcohol oxidation may use toxic, corrosive, expensive oxidants such as chromium (VI), and setting up a severe condition, like high pressure or temperature, using strong mineral acids. Potentially, supported catalysts have advantages over the unsupported ones, including better heat transfer character, larger surface area to volume ratio of active component, better mechanical strength, and controllable catalyst textures.

In this series, we have introduced an innovative, highly efficient, cost effective, re-generable heterogeneous catalyst (AgFA\textsubscript{j}) by supporting silver (1%, 3% and 5%) over thermally activated solid waste fly ash. The structural, morphological, thermal and surficial properties of AgFA\textsubscript{j} catalyst are presented in this work. Catalytic activity has been evaluated using partial oxidation of alcohols (benzyl alcohol and methanol) with tert-butylhydroperoxide in the liquid phase. The product are used largely as intermediates in the fine chemicals and pharmaceutical industries.

4.2 Experimental Details

4.2.1 Materials and Reagents

Fly ash collected from Tata thermal power plant, Jamshedpur, Jharkhand was used as catalytic support for silver nanoparticles. It is named as FA\textsubscript{j} Silver nitrate (AgNO\textsubscript{3}, A.C.S., 99.0%), sodium borohydride (NaBH\textsubscript{4}, granular, 98%), benzyl alcohol (C\textsubscript{7}H\textsubscript{7}OH, HPLC, 99.99%) and methanol (CH\textsubscript{3}OH, HPLC, 99.99%) were purchased from Sigma Aldrich. Oxidant tert-butylhydroperoxide (t-butoOH, AR, 80% in ditert-butylperoxide), acetonitrile (CH\textsubscript{3}N, AR, 99.8%), chloroform (CHCl\textsubscript{3}, AR, 99.5%), toluene (C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}, AR, 99.5%) and p-dioxane (C\textsubscript{4}H\textsubscript{8}O\textsubscript{2}, AR, 99.0%) were purchased from Merck Company and used without further purification.

4.2.2 Synthesis of AgFA\textsubscript{j} Catalyst

Fly ash supported Ag catalysts (AgFA\textsubscript{j}) of 1, 3 and 5 weight % (wt%) of Ag were synthesized using chemical reduction method. Fly ash was activated thermally at 800 °C for 3 h prior to use for catalyst preparation for removing
carbon, sulfur and other impurities. In typical procedure for 5 weight % loading of Ag over fly ash, 2 gm thermally activated fly ash (TFA) was added to the 50 mL aqueous solution of 0.36 gm AgNO₃ (0.042 M) containing in a 250 mL reaction vessel with stirring at 750 rpm on a magnetic stirrer. Stirring was continued for 2 h for proper dispersion of Ag ions over fly ash surface. Simultaneously, 0.0846 M aqueous NaBH₄ solution was made by adding 0.16 g of NaBH₄ to 50 mL of ice cold deionized water. Freshly prepared NaBH₄ solution was added dropwise using burette at approximately 1 drop per second to the suspension of fly ash and AgNO₃ solution with vigorous stirring. The resulting suspension was stirred at ambient temperature for additional 15 min for proper reduction of Ag ions. Finally the reduced material was filtered and washed with 200 mL deionized water for removing Na and nitrate ions. The washed material was dried in hot air oven at 60 °C for 24 h. The dried material was powdered with mortar and pestle and then calcined at 550 °C for 2 h in a muffle furnace. The calcined powder was again slightly crushed with mortar and pestle and used for further characterization. Catalysts are denoted as AgFAₓ, where x = 1, 3 and 5 wt% of the silver content.

4.2.3 Characterization

The TFA and prepared AgFAₓ catalysts were characterized by WD-X-ray fluorescence, powder XRD, FT-IR, SEM-EDS, UV-VIS-DRS and BET surface area analyzer. Detail is given in Annexure I.

4.2.4 Evaluation of Catalytic Activity Using Partial Oxidation of Methanol in Presence of AgFAₓ Catalyst

Liquid phase oxidation of alcohol (benzyl alcohol or methanol) was carried out in a three necked round bottom flask connected with a spiral condenser containing 0.2 g catalyst, 15 mL acetonitrile solvent and 30 mmol of alcohol to which 30 mmol of tert-butylhydroperoxide (TBHP) used as oxidant was added. Before adding oxidant reaction mixture was stirred under nitrogen atmosphere at 50 °C for 30 min. The rotation rate of the reaction mixture was set at 750 rpm then after adding the oxidant, the mixture was refluxed at 90 °C temperature in an oil bath for 8 h under nitrogen atmosphere. Small aliquots of the sample were withdrawn from the reaction mixture at regular intervals for analysis. At the end
of the reaction, the solid particles (catalyst) were separated by filtration during the hot condition and products were analyzed by gas chromatograph (GC, 7820) Agilent Technologies, Inc, equipped with a flame ionization detector (FID) and a 19019J-413 column (30 m length, 0.32 mm id and 0.25 µm film thickness). For the reusability test, after completion of the reaction, the catalyst was recovered from the reaction mixture by filtration and washed thoroughly with acetone and reused as such for multiple circles.

The conversion of the alcohol and the selectivity of the products in the reaction are calculated as:

Conversion = (moles of alcohol reacted/moles of alcohol in the feed) × 100
Selectivity = (moles of alcohol converted to p/moles of alcohol reacted) × 100.
Where P = product.

4.3 Results and Discussion

4.3.1 XRF Analysis

The chemical composition of TFA$_j$ and AgFA$_j$-5 evaluated using WD-XRF as given in Table 4.1 has revealed that high percentage of SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$ present in TFA$_j$ and AgFA$_j$-5, other inorganic oxides remain in low percentage. In TFA$_j$ no percentage of Ag is detected but the amount of Ag incorporated in the AgFA$_j$-5 is found 4.6 weight percent inferred the loading of Ag over TFA$_j$.

Table 4.1 Chemical Composition of TFA$_j$ and AgFA$_j$-5.

<table>
<thead>
<tr>
<th>Chemical Components</th>
<th>TFA$_j$</th>
<th>AgFA-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>61.9</td>
<td>62.0</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>29.7</td>
<td>26.0</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>3.65</td>
<td>3.55</td>
</tr>
<tr>
<td>Ag$_2$O</td>
<td>-</td>
<td>4.6</td>
</tr>
<tr>
<td>CaO</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>MgO</td>
<td>0.31</td>
<td>0.41</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.43</td>
<td>1.33</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.14</td>
<td>0.24</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.71</td>
<td>0.54</td>
</tr>
<tr>
<td>Other elements</td>
<td>1.61</td>
<td>1.53</td>
</tr>
<tr>
<td>LOI</td>
<td>0.15</td>
<td>0.2</td>
</tr>
</tbody>
</table>
4.3.2 XRD Analysis

The X-ray diffraction patterns of TFA and silver loaded fly ash catalysts viz. AgFA-1, AgFA-3 and AgFA-5 are shown in Figure 4.1 (a, b, c and d) figure shows that fly ash is nano-crystalline in nature [29] the crystallinity and crystallite size (33 nm) of the thermally activated fly ash is higher than silver loaded samples. The TFA contained an amorphous phase, mullite (Al$_6$Si$_2$O$_{13}$, ICDD pdf number, 15-0776) and quartz (SiO$_2$, ICDD pdf number, 46-1045), calcite (CaCO$_3$, ICDD pdf number, 47-1743), hematite (Fe$_2$O$_3$, ICDD pdf number, 33-0664), magnetite (Fe$_2$O$_4$, ICDD pdf number, 19-0629). After silver loading the amount of amorphous material increased considerably and the intensity of the quartz and mullite peaks decreased. For the samples with silver content below 5 wt % clear diffraction peaks were not observed. The absence of crystalline peaks associated with metallic silver indicates that the silver species are either highly dispersed or present as ionic state [15]. However, with increasing silver concentration, the characteristic diffraction peaks due to the crystalline Ag (111) (38°), Ag (200) (44.3°) and Ag (220) (64.4°) (Ag, ICDD pdf number, 04-0783) appear at low intensity in the XRD spectrum [15].

4.3.3 FT-IR Analysis

The FT-IR spectrum of TFA as given in Figure 4.2 (a) shows broad band between 3400 and 3000 cm$^{-1}$, which is attributed to the surface -OH groups of Si-OH and adsorbed water molecules on surface. A peak at 1650 cm$^{-1}$ in the spectra of fly ash is assigned to bending mode ($\delta$O-H) of water molecule. The main absorption band of the valence oscillations of Si-O-Si groups in quartz appears with an absorption maximum at 1100 cm$^{-1}$ [33].

The FT-IR spectrum of AgFA-5 catalyst as shown in Figure 4.2 (b) shows -OH peaks characteristics of Si-OH of Fly ash and incorporated Silver species on its surface. The increased amorphous silica in the silver loaded fly ash can be characterized by an intense band in the range 1000 – 1300 cm$^{-1}$, corresponding to the valence vibrations of the silicate oxygen skeleton. It can be noticed that slight changes in the intensities of some absorption bands in the range 1100–500 cm$^{-1}$ (fingerprint region) confirms the presence of Si-O-Ag bond.
Figure 4.1 XRD patterns of (a) TFA$_j$ heated at 800 °C for 3h, (b) AgFA$_j$-1, (c) AgFA$_j$-3 and (d) AgFA$_j$-5 prepared using chemical reduction method, calcined at 550 °C for 2h.
Figure 4.2  FT-IR spectra of (a) TFA\textsubscript{j} and (b) AgFA\textsubscript{j}-5.
Further, the vibrational peaks found in the range 1130–650 cm\(^{-1}\) may be attributed to Ag–O, which indicates that silver nanoparticles are loaded over fly ash surface [47].

### 4.3.4 UV-Visible Analysis

Figure 4.3 (a, b and c) shows UV-VIS spectra of AgFA\(_j\)-1, AgFA\(_j\)-3 and AgFA\(_j\)-5. The spectra show distinct absorption signals around 257 nm indicates the presence of ionic silver species, peak at around 390 to 394 nm indicate the appearance of plasmon resonance bands of Ag nanoparticles due to collective oscillation of conduction electrons on the Ag metal nanoparticles surface. As increasing the Ag content over fly ash peak intensity of plasmon resonance band (394) increases but peak corresponding to ionic Ag (Ag\(^+\) and Ag\(_n^+\)) decreases from 1 wt % loading to 3 wt % loading and then increases which indicates the presence of highest % of ionic Ag species and Ag nanoparticles over AgFA-5 surface. Similarily surface plasmon resonance band shifts to higher wave number indicates an increase in particle size of Ag nanoparticles [48,49] with increase in loading wt % of Ag.

### 4.3.5 \(N_2\)-Adsorption-Desorption Analysis

Table 4.2 indicates the effect of silver wt% on surface area of catalyst with increasing silver content from 1 to 5 wt% on TFA\(_j\) support, the surface area is decreased from 9000 to 8000 m\(^2\)/Kg. This was mainly due to the blockage of fly ash surface pores by loading of silver nanoparticles [50].

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Ag content (wt. %)</th>
<th>Specific surface Area(m(^2)/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFA(_j)</td>
<td>0</td>
<td>9000</td>
</tr>
<tr>
<td>AgFA(_j)-1</td>
<td>1</td>
<td>8800</td>
</tr>
<tr>
<td>AgFA(_j)-3</td>
<td>3</td>
<td>8500</td>
</tr>
<tr>
<td>AgFA(_j)-5</td>
<td>5</td>
<td>8000</td>
</tr>
</tbody>
</table>
Figure 4.3 UV-Vis spectra of (a) AgFA₁₁-1, (b) AgFA₁₁-3 and (c) AgFA₁₁-5 synthesized using chemical reduction method, calcined at 550 °C for 2h.
4.3.6 SEM-EDS Analysis

The EDS analysis of TFA$_j$ also shows that fly ash mainly contains Si, Al and Fe elements in higher percentage as given in Figure 4.4, after loading of silver over fly ash the particles surface shows the presence of Ag along with the other elements i.e., Si, Al and Fe as shown in Figure 4.5. It is also to be noted that peak corresponding to Ag is not present in EDS of TFA$_j$ and it appears only after loading process, indicating successful Ag deposition on the fly ash surface using the chemical reduction method.

The scanning electron micrograph (SEM) of TFA$_j$ and 5 wt% silver loaded fly ash (AgFA$_j$-5) are shown in Figure 4.6 to 4.8. SEM photographs of the TFA$_j$ revealed smooth spherical particles of silica with diameter of 840 nm to 6.95 µm interspersed with aggregates of crystalline compounds (Figure 4.6). The majority of the particles consisted of solid spheres, mineral aggregates, hollow cenospheres and irregularly shaped unburned carbon particles and amorphous particles [51]. After silver loading the fly ash surface get rougher and agglomerated as shown in Figure 4.7 and 4.8.

4.4 Catalytic Performance

At first, the reactivity of a model compound, benzyl alcohol, was examined under a variety of experimental conditions. The results of the oxidation of benzyl alcohol with TBHP in the presence of AgFA$_j$ with 1, 3 and 5 wt% of Ag, are shown in Table 4.3. The conversion percentage was calculated with respect to substrate (benzyl alcohol). The result shows that the reaction with AgFA$_j$-5 has relatively higher conversion (65.8 %) compare to AgFA$_j$-1 and AgFA$_j$-3. The highest activity of AgFA$_j$-5 is due to availability of highest active sites over its surface. However, with increasing the loading of Ag from 1 to 3 wt % on TFA$_j$ the selectivity with respect to benzaldehyde increased but further increasing the loading of Ag from 3 to 5 wt % on TFA$_j$ the selectivity with respect to benzaldehyde was decreased. The selectivity of benzaldehyde and benzoic acid on AgFA$_j$-5 catalyst were obtained 78.7% and 21.3% respectively. It may be a better catalyst with respect to catalysts with lower wt % of Ag.
Table 4.3 Oxidation of benzyl alcohol with TBHP in the presence of AgFA\textsubscript{j} catalyst. Reaction condition: catalyst 0.2 g; benzyl alcohol 30 mmol; TBHP 30 mmol; acetonitrile 15 mL; reflux temperature 90 °C; reaction time 8 h.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conversion (%)</th>
<th>Selectivity of benzaldehyde (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgFA\textsubscript{j}-1</td>
<td>46.3</td>
<td>77.5</td>
</tr>
<tr>
<td>AgFA\textsubscript{j}-3</td>
<td>57.5</td>
<td>80.7</td>
</tr>
<tr>
<td>AgFA\textsubscript{j}-5</td>
<td>65.8</td>
<td>78.7\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Selectivity of benzoic acid is 21.3%.

Figure 4.4 EDS spectra of TFA\textsubscript{j} heated at 800 °C for 3h.

<table>
<thead>
<tr>
<th>Elmt</th>
<th>Elmt %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al K</td>
<td>27.29</td>
<td>29.01</td>
</tr>
<tr>
<td>Si K</td>
<td>66.23</td>
<td>67.66</td>
</tr>
<tr>
<td>Fe K</td>
<td>6.48</td>
<td>3.33</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Figure 4.5 EDS spectra of AgFA\textsubscript{j}-5 catalyst prepared using chemical reduction method, calcined at 550 °C for 2h.

<table>
<thead>
<tr>
<th>Elmt</th>
<th>Elmt %</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al K</td>
<td>25.54</td>
<td>28.04</td>
</tr>
<tr>
<td>Si K</td>
<td>65.00</td>
<td>66.34</td>
</tr>
<tr>
<td>Ag K</td>
<td>4.86</td>
<td>3.23</td>
</tr>
<tr>
<td>Fe K</td>
<td>4.60</td>
<td>2.39</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Figure 4.6  SEM micrograph of TFA$_j$ heated at 800 °C for 3h.

Figure 4.7  SEM micrograph of AgFA$_j$-5 synthesized using chemical reduction method, calcined at 550 °C for 2h.
Bright coating of TFA inferred the presence of pure Ag nanoparticles.

Figure 4.8  SEM micrograph of AgFA$_3$-5 synthesized using chemical reduction method, calcined at 550 °C for 2h (at high magnification).
4.4.1 Effects of Reaction Time and Oxidant/Alcohol Molar Ratio

The change in conversion (%) of benzyl alcohol in the presence of TBHP and AgFA\textsubscript{j}-5 catalyst with 1, 2 and 3 TBHP/benzyl alcohol molar ratios, was monitored with respect to the time (Figure 4.9). The conversion of benzyl alcohol increases continuously as time and TBHP/benzyl alcohol molar ratios increases and then remains constant. The lowest TBHP/Benzyl alcohol ratio, results 54% (at 3 h) conversion of benzyl alcohol and the other two ratios (i.e. 2:1 and 3:1) give considerably higher conversion, 84% and 99% respectively.

4.4.2 Effect of Substrates

Regarding conversions and selectivity of the products, the experiments were compared with respect to substrates (benzyl alcohol and methanol) and the results are shown in Table 4.4. Higher conversion was obtained for benzyl alcohol on AgFA\textsubscript{j}-5 catalyst. The reactivity of the alcohols toward oxidation with TBHP on AgFA\textsubscript{j} catalyst depends on the particular structure of the substrate. AgFA\textsubscript{j} catalyst is more active towards benzyl alcohol than methanol.

Table 4.4 Effect of the AgFA\textsubscript{j}-5 catalyst in the oxidation of different alcohols. Reaction condition: catalyst 0.2 g; Alcohol 30 mmol; Oxidant TBHP 30 mmol; acetonitrile 15 mL; reflux temperature 90 °C; reaction time 8 h.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Product</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzyl alcohol</td>
<td>Benzaldehyde</td>
<td>65.8</td>
<td>78.7\textsuperscript{a}</td>
</tr>
<tr>
<td>Methanol</td>
<td>Formaldehyde</td>
<td>40.5</td>
<td>100</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Selectivity of benzoic acid is 21.3%.

4.4.3 Effect of Solvents

The results of conversion of benzyl alcohol with various solvents (polar to nonpolar) are shown in Table 4.5. The behavior of benzyl alcohol oxidation in various solvents is strikingly different. Acetonitrile gives the best conversion results, followed by toluene. The selectivity toward benzaldehyde was not varied.
Effect of solvents on oxidation of benzyl alcohol. Reaction condition: AgFAj-5 catalyst 0.2 g; benzyl alcohol 30 mmol; Oxidant TBHP 30 mmol; solvent 15 mL; reflux temperature 90 °C; reaction time 8 h.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dielectric constant</th>
<th>Dipole moment (D)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>37.5</td>
<td>3.92</td>
<td>65.8</td>
<td>78.7</td>
</tr>
<tr>
<td>Chloroform</td>
<td>3.7</td>
<td>1.04</td>
<td>39.4</td>
<td>90</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.4</td>
<td>0.37</td>
<td>48.9</td>
<td>100</td>
</tr>
<tr>
<td>p-Dioxane</td>
<td>2.2</td>
<td>0</td>
<td>33.6</td>
<td>62</td>
</tr>
</tbody>
</table>

significantly in various solvents. However, the conversion was low when the p-dioxane and chloroform were used as solvent. The decrease in conversion of benzyl alcohol in toluene may be explained by the low solubility of TBHP in a non polar solvent as a result of which the reaction could not proceed. Even though acetonitrile is a polar and has very high dielectric constant may readily dissolve TBHP along with the benzyl alcohol and consequently will direct the reactants in such a way that properly be adsorbed on the catalyst surface and increasing the efficiency of the conversion.

### 4.4.4 Effect of Temperature

Oxidation of benzyl alcohol was carried out at 27, 60 and 90 °C in same reaction condition, and it was found that conversion is simultaneously increased as temperature is increased from 27 to 90 °C (Figure 4.10).

### 4.4.5 Catalyst Recycling and Leaching

Loading of Ag over TFAj enhances the dispersion of Ag over the TFAj and increases the activity and life of the resulting catalyst. AgFAj-5 and benzyl alcohol as a model substrate have selected for the recycling and leaching study. The leaching of the catalyst was tested by filtering the catalyst during the reaction and studying the catalytic activity of the filtrate. In this study, a mixture of 0.2 g catalyst AgFAj-5, 15 mL acetonitrile, 30 mmol TBHP and 30 mmol of benzyl alcohol was refluxed for 4 h, then the reaction mixture was filtered, filtrate
Figure 4.9 The effect of reaction time and oxidant/alcohol molar ratio on benzyl alcohol conversion. Reaction condition: acetonitrile 15 mL, AgFA$_2$-5 catalyst 0.2 g; reflux temperature 90 °C; benzyl alcohol 30 mmol; TBHP/ Benzyl alcohol molar ratio: (a) 1, (b) 2 and (c) 3.
Figure 4.10  Conversion of benzyl alcohol as a function of time at (a) 27, (b) 60 and (c) 90 °C with AgFAj-5 catalyst in the presence of excess TBHP. Reaction condition: catalyst 0.2 g; Alcohol 30 mmol; Oxidant TBHP 30 mmol; acetonitrile 15 mL; reaction time 8 h.
solution was refluxed for next 4 h. The conversion of 54.2% and 55.3% were obtained for reaction with catalyst and filtrate. The results demonstrate that the amount of leaching of Ag from solid catalyst during liquid phase reaction is low and catalyst is stable. In recycling study, the catalyst was separated from the reaction mixture after each experiment by filtration, washed with the solvent and dried carefully before using it in the subsequent run. The catalyst may be recycled for five times, there is a low loss of activity with lowering in conversion of benzyl alcohol (without any loss in selectivity), indicating that leaching of Ag species from the support was happened but in less amount. Only 10% decrease in conversion was observed after four cycles.

4.4.6 Proposed Mechanism

Proposed mechanism of catalytic partial oxidation of benzyl alcohol is depicted in Scheme 4.1. In presence of AgFAj catalyst, it is hypothesize that TBHP is broken down into t-butoxide and hydroxyl radicals. Abstraction of a hydrogen radical from benzyl alcohol afforded a benzyl alcohol radical which combines with a hydroxyl radical to yield benzaldehyde. The adsorption of alcohol over catalyst surface increases the availability of benzyl alcohol radical nearby hydroxyl radicals thus facsilitates the conversion of benzyl alcohol into benzaldehyde. Further oxidation could lead to benzoic acid [38,52]. Therefore, proposed mechanism suggested that the oxidation pathway may be as follows (eq. 4.1 to eq. 4.4).

\[
\text{AgFA}_j + \text{t–butOOH} \rightarrow \text{t–butO}^- + \text{OH}^-
\]  \hspace{1cm} (eq. 4.1)

\[
\text{t–butO}^- + \text{PhCH}_2\text{OH} \rightarrow \text{t–butOH} + \text{PhCH}^-\text{–OH}
\]  \hspace{1cm} (eq. 4.2)

\[
\text{PhCH}^-\text{–OH} + \text{OH}^- \rightarrow \text{PhCH(OH)}_2
\]  \hspace{1cm} (eq. 4.3)

\[
\text{PhCH(OH)}_2 \rightarrow \text{PhCHO} + \text{PhCOOH}
\]  \hspace{1cm} (eq. 4.4)

**Benzaldehyde (76.5%)**  **Benzoic Acid (23.5%)**
Scheme 4.1 The mechanistic pathways of oxidation of benzyl alcohol to benzaldehyde over AgFAj-5 catalyst.
4.5 Conclusion

In the present study, an efficient solid oxidation catalyst was synthesized by loading of silver over thermally activated fly ash. The thermal activation of fly ash removes C, S and other impurities, thus increases silica percentage. The characterization of the catalysts confirmed the loading of fly ash surface with significant amount of silver by surface reaction of silver nitrate and surface silanols of the fly ash. The prepared AgFA\textsubscript{j} catalyst was found to possess significant oxidation capacity which catalyzes the aldehyde production from the catalytic oxidation of alcohols with tert-butylhydroperoxide (TBHP) in the liquid phase. Only 0.2 g of the catalyst in mild conditions may be able to carry out the oxidation reaction successfully. In addition, the catalyst can be recycled several times without any loss in selectivity and a nearly identical conversion percentage of the recovered catalyst, suggests its reusability and stability.

4.6 References


