Chapter III

CHARACTERIZATION AND CATALYTIC ACTIVITY
OF PURE ALKALINE EARTH METAL FERRITES
3.1 Introduction

Spinel ferrites with a general formula AB₂O₄ are class of chemically and thermally stable material, which attracts the interest of researchers, because of their versatile applications [1]. The spinel ferrites are used in magnetic recording media and magnetic fluids for the storage and retrieval of information [2], magnetic resonance imaging (MRI) enhancement [3], magnetically guided drug delivery [4], sensors [5], pigments [6], etc. Spinel ferrites are of great fundamental and technological importance due to their structural, electronic, magnetic and catalytic properties [7-9]. It has been recognized that it can be used as permanent magnets, recording media, telecommunication, components in microwave, higher-frequency, and magneto optical devices [10-16]. The wide application of these materials is mainly due to its excellent chemical stability, high mechanical durability, resistant to corrosion [17]. They have also been employed as heterogeneous catalysts [18] and electrode materials [19]. The alkaline earth metal ferrites (MgFe₂O₄, CaₓMg₁₋ₓFe₂O₄) powder with a particle diameter of 7–15 nm powder are used for the necrosis of the tumor; hyperthermia is an alternative to the conventional surgical, chemical therapy and radiation therapies for cancer. Mg₀.₅Ca₀.₅Fe₂O₄ powder is used to predict the tumor temperature and coagulation area by a heat transfer simulation that takes the heat generation of ferrite powder, the metabolism heat and the cooling effect of blood flow into account. The strontium ferrite is widely applied in permanent magnetic material due to various advantages such as abundant raw material, low manufacturing cost, stable properties and moreover the sample cannot be oxygenated [20].

The physico-chemical properties of the ferrites are strongly dependent on the sites and the nature of the catalyst [21, 22], which are closely related to the method of preparation. Binary and ternary oxides possessing a spinel structure have attracted much attention due to their remarkable transport, magnetic and catalytic properties. There are two kinds of lattices for cation occupancy, A and B sites have tetrahedral and octahedral coordination, respectively. In the normal spinel structure divalent atom, occupying tetrahedral A sites, while trivalent atom, are sitting on the octahedral B sites. When ‘A’
sites being trivalent ions, while ‘B’ sites equally populated by divalent and trivalent ions, the spinel structure is referred to as the inverse kind [23, 24].

There are many known methods of producing ferrites which can be divided into two main groups: dry and wet methods. The most popular methods, which have been recently reported, are combustion method [25], sol–gel method [26], co-precipitation of hydrous oxides from salts solution followed by calcination at high temperatures [27–29] and hydrothermal routes [30, 31]. Other than these self propagating process (SHS method) [32] and reverse micelle synthesis technique [33, 34] was also used to synthesize the ferrites. However, most of these methods cannot be economically applied on a large scale because they require expensive and often toxic reagents, complicated synthetic steps, high reaction temperatures and long reaction times. This not only results in waste of energy but also harms our environment. Several other techniques also have been used to prepare strontium ferrites such as ball milling [35], salt melting [36], chemical precipitation [37], glass crystallization [38] and self propagating high temperature synthesis [39]. All these methods have many drawbacks such as small area of deposition, requirement of sophisticated instruments, high working cost of system, prolonged calcination time for crystallization etc. Hence a chemical route can be excellent method for the synthesis of highly pure multi-component oxide due to its simplicity, good-control grain size, better homogeneity, better compositional control and lower processing temperatures which are few potential advantages of this wet chemical route over the conventional solid state reaction method [40]. When sol–gel technique [41] is used, the high-powered ferrite material is formed. The atomic-level blending of the constituent elements in the required stoichiometric ratio is attained in the citrate precursor complex, which enables the decomposition of the precursor directly into the final binary oxide at lower temperature, without the formation of intermediate oxide phases that delay the formation of the final oxide [42]. The ultrafine powder of barium ferrite (BaFe$_{12}$O$_{19}$) were synthesized by a sol-gel combustion technique using glycine gels. the results showed that the formation of single phase barium ferrite is significantly influenced by Ba:Fe and glycine/nitrate molar ratio, the phase composition and morphology of the
barium ferrite was confirmed by X-ray diffraction, transmission electron microscopy (TEM) and high resolution TEM [43].

Spinell ferrites are found to be highly active towards many aromatic alkylation reactions such as methylation of phenol, aniline, pyridine, phenol tert-butylation etc. [44–46]. The alkaline earth metal ferrite like MgFe$_2$O$_4$ is used as catalyst for the selective oxidation of styrene in presence of 30% H$_2$O$_2$ as an oxidizing agent and acetone as a solvent [47]. The proper distribution of cations on the either side of catalysts makes the catalyst more efficient for many organic transformation reactions and number of industrial processes such as oxidative dehydrogenation of hydrocarbons [48], decomposition of alcohols and hydrogen peroxide [49], treatment of automobile exhaust gases [50], oxidation of various organic compounds such as chlorobenzene and carbon monoxide [51,52]. The spinel ferrites were also applied in phenol hydroxylation [53], hydrodesulphurization of crude petroleum [54], catalytic combustion of methane [55]. Spinell compounds with the general formula of AB$_2$O$_4$ are one of the most frequently encountered structural types in inorganic chemistry [56]. Spinell are often used as catalysts for reactions at elevated temperature due to their high temperature stability and resistance to sintering [57]: MgAl$_2$O$_4$ has been considered as a material for a number of applications in high radiation environments [58] such as electrical insulators and dielectric windows in fission reactors [59] and so on.

Catalytic oxidation is widely employed in the manufacture of bulk chemicals from aromatics and more recently an environmentally attractive method for the production of fine chemicals. Both in academic and in industry the use of hydrogen peroxides in the oxidation of organic molecules such as styrene, phenol, cyclohexene, trans-stilbene etc is preferred. since it can give good oxidation conversion, it generate only water as by-product and it has high content of active oxygen, this reaction can be taken as a kind of green technology [60]. The catalytic efficiency of various catalysts was checked in various organic transformations such as the oxidation of styrene over nickel ferrite and zinc ferrite has been studied by Debanjan et.al. [11]. they have observed 31.4 mol% and 26.1 mol% styrene conversion with selectivity of benzaldehyde as 55.6 and 50.4 mol% respectively. 20 mol% styrene conversion and 94 mol% selectivity of
benzaldehyde was investigated by Gao et al. [47] over cobalt VSB-5 at 70 °C temperature. Maurya and Amit Kumar [61] reported 76 mol% conversion of styrene with 65 mol% selectivity of benzaldehyde over oxovanadium based co-ordination polymer at 75 °C temperature. The styrene oxidation was also carried out over MgFe$_2$O$_4$ [47] prepared by co-precipitation and citrate gel method found that 7.43 and 34.0 mol% styrene conversion, while the benzaldehyde selectivity is 94.0 and 63.2 mol% respectively.

The catalytic effectiveness of this system is due to the ability of metallic ions to migrate between the sub lattices without altering the structure, which makes the catalyst efficient for many organic transformation reactions. The selective liquid-phase oxidation reaction is of significant importance in the fine chemicals and pharmaceutical industries [62, 63]. Some strong oxidants such as KMnO$_4$, CrO$_3$, and HNO$_3$ [64, 65] were applied traditionally for the oxidation of various substrates, which might result in much serious pollution and some potential risks in the process of operation. In terms of atom efficiency and environment friendly, after oxygen, aqueous hydrogen peroxide (30% H$_2$O$_2$) is a very attractive oxidant for industrial applications since water is the only by-product and it is easy to be dealt with after reactions. The latest studies have therefore focused on the catalytic oxidation of styrene with H$_2$O$_2$ as the terminal oxidant [66-71]. Almost all these oxidation reactions have been carried out in organic solvents.

In the present work, we report the synthesis, characterization and catalytic activity of AEM ferrite complex oxide with a fix M: Fe (Where M = Ca, Sr and Ba) ratio. The calcium ferrite, strontium ferrite and barium ferrite catalyst synthesized by citrate gel method shows good catalytic performance. CaFe$_2$O$_4$, SrFe$_2$O$_4$ and BaFe$_2$O$_4$ give the highest selectivity of benzaldehyde with respect to conversion of styrene in presence of 30% H$_2$O$_2$, an important chemical intermediate for the fine chemical industry. Moreover, the method of synthesis of catalyst is simple and economical. In this work, first time we are reporting the results for styrene (one of the most important pro-chiral alkenes) oxidation reaction in water as solvent using environmentally benign oxidant H$_2$O$_2$ over SrFe$_2$O$_4$. In MFe$_2$O$_4$ (where M = Ca, Sr and Ba), of M-Fe-O system is our attempt to show how the AEM ferrite catalysts is better for styrene (one of the most important pro-chiral alkenes) oxidation reaction in acetone as solvent using environmentally benign
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oxidant H$_2$O$_2$. The conditions for maximum conversion of styrene as well as selectivity for desired product have been optimized by varying different parameters such as temperature, molar ratio of styrene to H$_2$O$_2$, amount of catalyst, reaction time, calcination temperature and various oxidizing agents. The influence of these parameters on the conversion and product distribution are also studied.

3.2 Characterization of alkaline earth metal (AEM) ferrites

3.2.1 TG-DTG analysis of AEM iron citrate precursor

![Fig. 1A TG-DTG curves of the Calcium ferrite precursor prepared by citrate gel method.](image)

Thermo gravimetric (TG) analysis and derivative thermogravimetry (DTG) were applied to the precursor particles to determine the transition temperature for the conversion of the precursor particles to AEM ferrite. Fig. 1 is the TG/DTG for the sample prepared by citrate gel method.

There are four major weight losses in TG-curve. The first weight loss within the range of 50-110 °C is 14.16 % (calculated 12.19) as shown in Fig 1A corresponds to dehydration step. This dehydration step is clearly seen as a peak in DTG at 67 °C. The
second weight loss is 33.06 % in the range of 160-210 °C corresponds to the decomposition of citrate ligand, it matches well with the calculated value of 31.27 %. The loss of ligand is also seen in the form of well defined peak at 191 °C in DTG curve. The further weight loss in TG curve is 12.06 % (calculated 13.33 %) in the range of 300-350 °C corresponds to the decarboxylation of precursor in to mixed oxide. A peak at 333 °C in DTG corresponding to the decarboxylation step is also seen. Finally a small weight loss of 5.54 % (calculated 7.30 %) in the range of 700-730 °C corresponds to the loss of adsorbed carbon dioxide centered at 720 °C in DTG curve. After 720 °C no notable weight loss was found which indicate that CaFe2O4 was formed above 720 °C. Thus the calcium ferrite oxide was calcined at different temperature from 600 °C to 900 °C and the calcined samples were characterized by different methods as follows.

![Fig. 1B TG-DTG curve for thermal decomposition of strontium iron citrate precursor.](image)

In case of strontium iron citrate precursor the first weight loss observed in the range of 50-180 °C is 9.6% (calculated 10.2%) corresponds to partial dehydration due to five
water molecules. This dehydration step is clearly seen as a peak in DTG at 72 °C. The second weight loss is 29.6% in the range of 175-300 °C corresponding to the loss of remaining water molecules and partial decomposition of citrate ligand, it matches well with the calculated value of 28.9%. this is also seen in the form of well defined peak at 192 °C in DTG curve and one small shoulder at 290 °C. The further weight loss in TG curve is of 14.5% (calculated 14.3%) in the range of 500-600 °C corresponding to the complete decarboxylation of the precursor into mixed oxide. A peak at 590 °C in DTG corresponds to the decarboxylation step. After 601 °C no notable weight loss was found which indicate that SrFe₂O₄ was formed above 600 °C along with the trace quantity of strontium carbonate.

Fig. 1C TG-DTG analysis of barium iron citrate precursor prepared by citrate gel combustion method.

The thermo chemical behaviour and chemical bonding of the as-synthesized barium iron citrate precursor were examined by TG-DTG, the TG in the range of 50°C to 900°C are
shown in Fig.1C. The total weight loss is observed up to 59.25% (calculated 60.57%) and could be attributed to four distinct processes. The first weight loss observed in the range of 50-160°C is 6.87% (calculated 6.34%) corresponds to partial dehydration of precursor which is clearly seen as a peak in DTG at 196°C. The second weight loss is 21.42% in the range of 161-230°C corresponding to the loss of remaining water molecules and partial decomposition of citrate ligand, it matches well with the calculated value of 23.2%. The further weight loss in TG curve is of 20.23% (calculated 21.7%) in the range of 231-361°C, corresponding to the complete decarboxylation of the precursor into mixed oxide. This is seen in the form of well defined peak at 284°C in DTG curve. Finally the barium ferrite is formed at 615°C by the weight loss of 10.65% which is also in good agreement with the calculated value 9.33% because of the evaporation of adsorbed CO$_2$ gas. This is also seen in the form of well defined peak at 590°C in DTG curve, which corresponds to the decarboxylation step. After 615°C no notable weight loss was found which indicate that BaFe$_2$O$_4$ was formed above 615°C, along with the trace quantity of adsorbed carbon dioxide. The whole thermal process of decarboxylation is accompanied by the evolution of large amount of gas, due to vigorous oxidation reaction [72].

3.2.2 FT-IR analysis

With the view to study the effect of dependence of normal modes and their frequency on change of the composition of ions in calcium ferrite, FT-IR frequency data for the respective sites were analyzed using the observed FT-IR spectra of calcium ferrite calcined at different temperature (Fig.2A). The sample shows the two IR bands, $v_1$ and $v_2$ around 526-549 cm$^{-1}$ and 426-432 cm$^{-1}$ respectively.
Fig. 2A FT-IR spectrum calcium ferrite prepared by citrate gel combustion method calcined at different temperature (a) 600°C, (b) 700°C, (c) 800°C and (d) 900°C.

According to Waldron et al. [73] and White et al. [74], the high frequency band around 526-549 cm\(^{-1}\) is due to the stretching vibration of the tetrahedral M–O bond and the low frequency band at around 426-432 cm\(^{-1}\) is due to the vibration of the octahedral M–O bond present in the spinel structure. These two distinct peaks indicate the formation of spinel type calcium ferrite. The peak 1439 cm\(^{-1}\) in spectra (a) indicate the presence of metal carbonate this peak vanishes as the calcination temperature increases to 700°C. A small peak at 2322 cm\(^{-1}\) indicates the presence of adsorbed CO\(_2\). The desorption of CO\(_2\) takes place above 800°C temperature.
Fig. 2B. FTIR Spectra of Strontium ferrite prepared by citrate gel method calcined at different temperature (a) 600 °C, (b) 700 °C, (c) 800 °C and (d) 900 °C.

Fig. 2B (a-d) shows FTIR spectra of SrFe$_2$O$_4$ powder calcined at different temperature such as 600 °C, 700 °C, 800 °C and 900 °C respectively. No significant peaks are found below 1000 cm$^{-1}$ in spectrum (a), while in spectrum (b), two assigned absorption bands appeared around 580 cm$^{-1}$ ($v_1$), attributed to stretching vibration of tetrahedral groups Sr$^{2+}$-O$^{2-}$ and that around 453 cm$^{-1}$ ($v_2$), attributed to the octahedral group complex Fe$^{3+}$-O$^{2-}$. These two weak absorption bands are typical of spinel ferrites and the positions of these infrared bands are in the range which corresponds to strontium ferrite. Band localized at 867 cm$^{-1}$ is assigned for deformation vibration of the C-H group in Fig. 2B (a) and (b) which is not found in spectrum (c) and (d). The spectrum also reveals that the carboxylates of the precursor transform into metal carbonate with the characteristic
stretching location at 1435 cm\(^{-1}\) and 1516 cm\(^{-1}\) \[^{[75]}\] for the samples calcined at 600 °C, 700 °C and 800 °C.

\[ 
\begin{align*}
\text{Wavenumber (cm}^{-1}) & \\
2400 & 2000 & 1600 & 1200 & 800 & 400 \\
\% T
\end{align*}
\]

**Fig. 2C** FTIR Spectra of barium ferrite prepared by citrate gel method calcined at different temperature (a) 600 °C, (b) 700 °C, (c) 800 °C and (d) 900 °C.

FT-IR spectra of samples calcined at different temperature are shown in **Fig. 2C**. The powders calcined at different temperature indicate that the calcination temperature can greatly influence the formation of barium ferrite. The band at 1750 cm\(^{-1}\) is assigned to the stretching vibration mode of C=O in **Fig. 2C** (a) and (b). While in **Fig. 2C** (a), (b), (c) and (d), the bands around 628-663 cm\(^{-1}\) corresponds to intrinsic stretching vibration of metal ion at the tetrahedral site and the band in the range of 510-516 cm\(^{-1}\) is attributed towards the Fe-O bond vibration. Comparing the spectra (a-d) we may notice that the intensities of C=O stretching vibration at 1750 cm\(^{-1}\) and C-C stretching vibration at about 860 cm\(^{-1}\) remains up to sample (b) afterwards these bands get disappear completely in the spectrum (d). The disappearance of these bands indicates the formation of oxides between 800°C
and 900°C. The bands at 1460 and 1060 cm⁻¹ in Fig. 2C (b) and (b) indicates the presence of BaCO₃, while the frequency of the band decreases as the calcination temperature increases to 800°C and 900°C as shown in Fig. 2C c and d. As the calcination temperature increases these carbonate bands were not observed due to their decarboxylation. There is a band at 2360 cm⁻¹ in Fig. 2C (d) and (e) which indicate the adsorption of CO₂ on the surface of catalyst, confirming the results of TG-DTA.

3.2.3 Elemental analysis

3.2.3.1 Chemical method

The elemental composition of the CaFe₂O₄, SrFe₂O₄ and BaFe₂O₄ prepared from AEM iron citrate calcined at 800 °C, 700 °C and 900 °C respectively was analyzed by chemical analysis method.

Table 1 Wet chemical analysis data of pure alkaline earth metal ferrite prepared by citrate gel combustion method.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Percentage composition of element</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaFe₂O₄</td>
<td>Calcium (Ca)</td>
</tr>
<tr>
<td></td>
<td>Calculated 18.58%</td>
</tr>
<tr>
<td></td>
<td>Observed 19.86%</td>
</tr>
<tr>
<td></td>
<td>Iron (Fe)</td>
</tr>
<tr>
<td></td>
<td>Calculated 51.79%</td>
</tr>
<tr>
<td></td>
<td>Observed 52.98%</td>
</tr>
<tr>
<td>SrFe₂O₄</td>
<td>Strontium (Sr)</td>
</tr>
<tr>
<td></td>
<td>Calculated 33.27%</td>
</tr>
<tr>
<td></td>
<td>Observed 32.39%</td>
</tr>
<tr>
<td>BaFe₂O₄</td>
<td>Barium (Ba)</td>
</tr>
<tr>
<td></td>
<td>Calculated 39.1%</td>
</tr>
<tr>
<td></td>
<td>Observed 38.6%</td>
</tr>
</tbody>
</table>

The percentage of AEM and iron are in good agreement with the calculated values (Table 1).

3.2.3.2 X-ray florescence method

The elemental composition of the CaFe₂O₄, SrFe₂O₄ and BaFe₂O₄ prepared from AEM iron citrate calcined at 800 °C, 700 °C and 900 °C respectively was analyzed by X-
ray florescence method. The percentage composition of the calcium, strontium, barium and iron are in good agreement with the theoretical value as shown in Table 2.

Table 2 Elemental analysis by X-ray florescence method of pure AEM ferrite prepared by citrate gel combustion method

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Percentage composition of element</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaFe$_2$O$_4$</td>
<td>Calcium (Ca)</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
</tr>
<tr>
<td></td>
<td>18.58%</td>
</tr>
<tr>
<td>3. SrFe$_2$O$_4$</td>
<td>Strontium (Sr)</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
</tr>
<tr>
<td></td>
<td>33.27%</td>
</tr>
<tr>
<td>4. BaFe$_2$O$_4$</td>
<td>Barium (Ba)</td>
</tr>
<tr>
<td></td>
<td>Calculated</td>
</tr>
<tr>
<td></td>
<td>39.1%</td>
</tr>
</tbody>
</table>

The result also indicates that the catalyst is associated with the trace quantity of alkaline earth metal carbonate (as seen inform of shoulder peak at 1435cm$^{-1}$ in IR spectrum).
3.2.4 X-ray diffraction analysis

**Fig. 3A** XRD pattern of the calcium ferrite prepared by citrate gel method and calcined at (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C for 1 h.

The XRD pattern of calcium ferrite precursor and samples calcined from 600 °C to 900 °C are shown in **Fig. 3A**. It is observed that, with increase in calcination temperature XRD peaks become sharper and also increases in intensity. The hkl values of calcium ferrite calcined at 800 °C and 900 °C matches exactly with the JCPDS data (JCPDS card no. ID 08-0100), which are characteristic of spinel structure of $\text{CaFe}_2\text{O}_4$ ($a = 9.18$, $b = 10.62$ and $c = 3.02$). From the XRD studies it was confirmed that the single phase $\text{CaFe}_2\text{O}_4$ is formed at 800 °C and so this compound was selected for further studies.
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Fig. 3B. X-ray diffraction pattern of strontium iron citrate precursor (a) strontium ferrite prepared by citrate gel method; (b) sample calcined sample at 600 °C; (c) 700 °C; (d) 800 °C and (e) 900 °C.

The crystallinity and phase purity of the as-prepared precursor and the calcined products were examined by powder X-ray diffraction (XRD). Figure 3B shows the XRD patterns of the precursor as well as the samples calcined at different temperatures. All the peaks of the XRD pattern for the calcined samples can be easily indexed to cubic SrFe$_2$O$_4$ with spinel structure [76], where the diffraction peaks at 2θ values of 32.7, 37.8, 46.8 and 58.3° of pattern (c) can be ascribed to the reflection of (0 0 2), (3 3 1), (4 2 0) and (5 2 0) planes of the spinel SrFe$_2$O$_4$, respectively [77]. While the peak at 68.5 and 78.0, 2θ values (shown by * in Fig. 3B) indicates the presence of trace quantity of strontium carbonate associated with the SrFe$_2$O$_4$ phase (JCPDS CARD NO. 74-1491 and 84-1778). Using the Scherrer equation [78], the average particle size of the crystallites can be estimated from the full-width at half maximum (FWHM) of the highest intensity peak.

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As the calcination temperature increases from 700 °C to 900 °C the average crystallite size also increases from 50nm to 82nm which indicate the aggregation of the crystals. From the XRD studies it was confirmed that the single phase SrFe₂O₄ with trace of SrCO₃ is formed at 700 °C temperature so this compound was selected for the further studies.

**Fig. 3C** X-ray diffraction pattern of barium iron citrate precursor (a); barium ferrite powder calcined at 600 °C (b); 700 °C (c); 800 °C (d); 900 °C (e)

**Fig. 3C** illustrates the XRD pattern of the barium iron citrate precursor and barium ferrite samples synthesized by the citrate gel method, calcined at different temperatures. The sample calcined at 900°C, was identified as an orthorhombic spinel like phase. According to the index card in the XRD pattern of precursor show the intense peak at 2θ = 23.9° indicate the presence of BaCO₃ shown in Fig. 3C(a). When the same precursor was calcined at 600°C and 700°C the new peak appeared around 2θ = 28.4 which indicate the formation of BaFe₂O₄ oxide. Fe₃O₄ (peak shown with +), and BaCO₃ were found as intermediate phases **Fig. 3C (b and c)**. As the calcination temperature increases to 800°C.
and 900°C there is a complete disappearance of BaCO₃ along with appearance of new peaks at 2θ = 28.4, 32.7, 33.2 and 44.16 indicating the formation of BaFe₂O₄ (peak shown with *) which is in good agreement with the JCPDS card No. 46-0113 from the PDF-2 database PCPDFWIN, whose lattice parameters are: a = 19.042Å, b = 5.3838Å and c = 8.445Å at 900°C. The calculated crystallite sizes obtained using Scherrer formula were 40.8 nm for 800°C (d) and 38.7 nm for 900°C (e) respectively.

3.2.5 Scanning electron microscopy (SEM) analysis

![SEM images of calcium, strontium and barium ferrite](image)

**Fig.4.** Scanning electron microscopic images of calcium, strontium and barium ferrite prepared by citrate gel method calcined at 800 °C, 700 °C and 900°C temperature.

The SEM micrograph of the calcium ferrite fine particle prepared by citrate gel method calcined at 800 °C is presented in **Fig. 4(A)**. It consists of agglomerated crystallite size of 50-60 nm. This also indicates that the synthesis procedure adopted results in mostly fine particles. **Fig.4(B)** shows the microstructure and morphology of strontium ferrite powder calcined at 700 °C for 2 h. From the photograph we can find that the
morphology of the material is fine flakes like and well defined monodispersed particles at different magnification are observed.

Fig. 4C shows SEM image of barium ferrite nanoparticles as synthesized by citrate gel method. From the photograph we can find that BaFe$_2$O$_4$ aggregates with coralloid morphology [79]. When the SEM images of CaFe$_2$O$_4$, SrFe$_2$O$_4$ and BaFe$_2$O$_4$ are compared, it is seen that BaFe$_2$O$_4$ shows coralloid morphology with outward extending branches having an average diameter, so the total surface area of the catalyst is more than that of the other alkaline earth metal ferrites even though they are prepared by citrate gel combustion method.

3.2.6 Surface area determination by BET method
The BET surface area of the various samples of alkaline earth metal ferrite catalysts calcined at specific temperature was also carried out. Among all the prepared catalysts the surface area of Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$, where $x = 0.2$ and $0.4$ catalysts are 175.19 m$^2$/g. The surface area of the other catalysts of composition i.e. $x = 0.0, 0.6, 0.8$ and $1.0$ are below 25 m$^2$/g even though prepared by same method. It may be due to the agglomerization of oxides during the heat treatment as also shown in SEM analysis (Fig. 4).

3.3 Catalytic activity of AEM ferrites
The oxidation of hydrocarbon to oxygenic compounds is a pivotal reaction in organic chemistry, both the fundamental research and industrial manufacturing [80]. Now, from both economic and environmental point of view, much attention has recently been focused on the aerobic catalytic oxidation of hydrocarbon to oxygenic compounds using metal catalysis. The metal ferrites are known to be highly efficient oxidation catalysts which have been successfully used to heterogeneously catalyze the transfer of an oxygen atom from oxidizing agent into hydrocarbon molecules in solvent [47].
Alkaline earth metal ferrites synthesized by citrate gel method, characterized for the structure, morphology and confirmed to be fine materials with spinel structure was then used as catalyst to evaluate its catalytic efficiency. The oxidation of styrene to benzaldehyde was used as a model reaction.
3.3.1 Selective oxidation of styrene

The probable mechanism for oxidation of styrene to benzaldehyde is used as a model reaction and the probable reaction mechanism over the surface of CaFe$_2$O$_4$ and BaFe$_2$O$_4$ is shown in Scheme 1 (a and b), while the oxidation of styrene over the surface of SrFe$_2$O$_4$ catalyst in aqueous medium is shown in Scheme 2.

(a)

(b) Styrene + H$_2$O$_2$ + Catalyst $\rightarrow$ Benzaldehyde + Phenyl acetaldehyde + others

\[
\text{Cat-Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Cat-Fe}^{4+}\text{-OH} + \cdot\text{OH}
\]

Scheme 1 Selective oxidation of styrene over CaFe$_2$O$_4$ and BaFe$_2$O$_4$ catalysts prepared by citrate gel combustion method
Role of catalyst

The selective oxidation of styrene was carried out in presence of 0.1 g of MFe$_2$O$_4$ catalyst (where M = Ca, Sr and Ba) in presence of 30% H$_2$O$_2$ and at optimized reaction condition 37.9 mol%, 50.8 mol% and 45.0 mol% styrene conversion take place along with 91.1 mol%, 63.7 mol% and 88.5 mol% selectivity of benzaldehyde respectively. A free radical mechanism may be involved in selective oxidation of styrene over MFe$_2$O$_4$ catalysts. In case of styrene oxidation in presence of H$_2$O$_2$ (30%) as oxidant, free radicals can be generated on the surface of catalyst, where catalyst accelerates the decomposition of hydrogen peroxide into free radicals. The fact that weather free radicals are involved or not was confirmed by carrying the same reaction in presence of tertiary butyl alcohol as a scavenger and by keeping the entire reaction condition constant, only 4.0 mol% styrene got converted to benzaldehyde. This observation confirms a free radical mechanism is involved in styrene oxidation over a mixed catalyst (Scheme 1a and b). In this type of
reaction free radicals are generated on the surface of catalyst. The catalyst accelerates the rate of decomposition reaction of H₂O₂ into radicals. In order to check the role of metal ferrite towards selective oxidation of styrene, a blank reaction was carried out using 30% H₂O₂ at optimized reaction conditions. In absence of MFe₂O₄ (where M = Ca, Sr and Ba) catalyst no reaction takes place as seen from GCMS analysis. This observation ruled out the possibility of the reaction-taking place due to the thermal decomposition of H₂O₂.

In scheme 1(a), the formation of metal-oxy radical (Fe³⁺-O⁻) on the catalyst surface is the initiation step of the reaction and the propagation of the reaction chain occurs in solution. A highest yield of benzaldehyde is possibly due to further oxidation of styrene oxide formed in the first step by a nucleophilic attack of Fe³⁺-O⁻ on styrene followed by cleavage of the intermediate carbon-carbon double bond (see Scheme 1a). Alternatively the Fe³⁺ ions from the octahedral sites of catalyst react with hydrogen peroxide to form Cat-Fe³⁺-OH complex and hydroxyl radicals as shown in Scheme 2. The results shows that the redox cycle of spinel phase with high oxygen deficiencies coming from the crystal structure can participate into the styrene oxidation due to the presence of reducible Fe³⁺ sites forming highly active oxygen species at lower temperature [82]. The lower oxidation state of calcium (2⁺) in comparison to other metal ions favors either an increase in the oxidation state of Fe from 3⁺ to 4⁺, or oxygen vacancies can be generated to maintain the structure electro neutrality [83]. As the reaction is carried out in water as solvent and high amount of water is present in 30% H₂O₂ it may partly be responsible for the possible hydrolysis of styrene oxide to 1-phenylethane-1, 2-diol in reaction.

**Role of oxidizing agent**

The role of oxidizing agent is also observed, the conversion of styrene is only up to 4-5 % in the presence of catalyst without using any oxidant. Similarly, the same reaction when carried out in the absence of catalyst but by using 10 mmol 30% H₂O₂ under the similar reaction condition, zero percent styrene conversion was done. It suggests that no reaction takes place in absence of catalyst. This observation ruled out the possibility of reaction taking place due to the thermal decomposition of hydrogen peroxide.
3.4 Reaction Testing

The styrene conversion and the selectivity of the reaction products were determined by the following formulae [84].

The styrene conversion is defined as

\[
\text{Conversion (mol \%) = 100 \times \frac{\text{Styrene (in)} - \text{Styrene (out)}}{\text{Styrene (in)}}}
\]  

----- (1)

The selectivity was calculated based on the peak area of the gas chromatogram by considering the different sensitivity factors of the flame ionization detector. The mol\% of styrene as well as analytes is calculated from chromatogram by following formula and using a common internal standard solution.

\[
\text{Mol\% = 100 \times \frac{\text{Area of analyte from the reaction mixture}}{\text{Area of fix quantity of same analyte (standard)}}}
\]

----- (2)

The selectivity to product (i) is defined as

\[
\text{Selectivity (i) (mol \%) = 100 \times \frac{\text{Corrected area (i)}}{\text{Sum of all corrected areas}}}
\]

----- (3)

3.5 Optimization of reaction conditions

The AEM ferrites calcined at different temperature thus characterized for its structure, morphology and confirmed to be fine particles with the spinel structure was then used as catalyst to evaluate their catalytic efficiency. The selective oxidation of styrene to benzaldehyde was used as the model reaction. The effect of different solvents, temperature variation, time, catalyst amount, chemical composition of catalyst, oxidizing agent, calcination temperature and styrene/ hydrogen peroxide molar ratio, on the styrene
conversion and product selectivity over catalyst has been successively carried out and is discussed in following subsections.

3.5.1 Effect of temperature

**Reaction conditions:**
- Catalyst: CaFe₂O₄ (0.1 g).
- Substrate: Styrene (10 mmol).
- Solvent: Acetone (10 ml).
- Oxidant: 30% H₂O₂ (10 mmol).
- Time: 18 h.
- **Optimized Temp:** 40 °C

**Fig.5.** Effect of temperature on the selective oxidation of styrene to benzaldehyde over calcium ferrite (A), strontium ferrite (B) and barium ferrite (C)

The effect of reaction temperature on styrene conversion and selectivity of products were studied. The reaction was carried out by using styrene/ H₂O₂ molar ratio as 1:1, using 0.1 g catalyst, CaFe₂O₄ in acetone, SrFe₂O₄ in water and BaFe₂O₄ in acetone as a solvent for 18 h at various temperatures. The response of the reaction towards rise in temperature has been studied and the results are shown in **Fig.5.** At 30°C styrene conversion is 27.61±2 mol% using CaFe₂O₄ and it is found to increase with increase in
temperature and reaches to 47±2 mol% at 70°C (Fig. 5A). The selectivity of benzaldehyde increases up to 40°C (91.14±2 mol %) but, as the temperature increases selectivity for phenyl acetaldehyde increases at the cost of benzaldehyde. When the same reaction was carried out over SrFe₂O₄ in aqueous medium, at 40°C very less styrene conversion is observed (6.6 mol %), while the selectivity of benzaldehyde is up to 86.2 mol% with 13 mol% of phenyl acetaldehyde as a by-product. The results are shown in Fig. 5B. As temperature increases to 50°C the styrene conversion increases to 18.0 mol %, while the selectivity of benzaldehyde decreases to 78.2 mol % with increase in the percentage selectivity of phenyl acetaldehyde to 21.8 mol%. Further increase in temperature is favourable for the styrene oxidation. At 60°C conversion of styrene increases to 24.1 mol%, while the selectivity of benzaldehyde decrease to 71.7 mol% with increase in percentage yield up to 17.3. When the same reaction was carried out at 70°C the styrene conversion sharply increases to 50.8 mol% with the better selectivity of benzaldehyde i.e. 63.7 mol% with 32.4 % yield along with the formation of 28.1 mol% of styrene oxide, which get isomerizes to phenyl acetaldehyde, 1-phenyl-1, 2-ethanediol up to 8.1 mol% as by-product. Further rise in temperature (80°C) the marginal increment in styrene conversion was observed (52.0 mol %) with very poor selectivity of benzaldehyde (31 mol %). The same reaction was carried out over the surface of BaFe₂O₄ in the temperature range 30–80°C to know the effect of temperature on the conversion of styrene and the selectivity of products (Fig. 5C). The reaction when carried out at 30°C, 14.5 mol% of styrene conversion takes place. The selectivity of benzaldehyde is 91.2 mol%, while the percentage yield of benzaldehyde is only 13.2. At 40°C temperature the styrene conversion increases up to 26.3 mol%, while the selectivity and yield of benzaldehyde is 89.5 mol% and 23.6% respectively. When the same reaction was carried out at 50°C, styrene conversion steeply increases up to 45.0 mol% with 88.5 mol% selectivity of benzaldehyde. The percentage yield of benzaldehyde also increases to 40. Further increment in temperature to 60°C, 70°C and 80°C results in a marginal increment in styrene conversion observed as 45.6 mol%, 48.2 mol% and 54.3 mol%, but the selectivity of benzaldehyde is prominently reduced to 81.5 mol%, 65.6 mol% and 51.4 mol%.
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This observation may be due to the fact that the cleavage of C=C bond is higher at 40°C temperature on CaFe$_2$O$_4$ which leads to the formation of benzaldehyde. On the other hand at higher (70°C) temperature the epoxidation seems to compete more favourably against C=C bond cleavage (see Scheme 1a.) which helps to form phenyl acetaldehyde. In case of SrFe$_2$O$_4$ the results indicate that the cleavage of C=C bond is favourable with increase in temperature up to 70°C, but however, at high temperature instead of C=C bond cleavage, C-O bond cleavage is done preferably, which results into increase of by-product like phenyl acetaldehyde and 1-phenyl-1,2-ethanediol up to 53.0 mol%. The observation is in agreement with previous reports [47, 83]. Similarly over BaFe$_2$O$_4$ catalyst results indicate that the cleavage of C=C bond is favourable with increase in temperature up to 50°C, but however, at high temperature (80°C) instead of C=C bond cleavage, C-O bond cleavage is done preferably, which results into increase of by-product like phenyl acetaldehyde and 1-phenyl-1,2-ethanediol up to 48.6 mol%. Moreover, at high temperature selectivity of benzaldehyde decreases over all these catalysts this is due to the fact that H$_2$O$_2$ decomposition increases from 53.53 to 96.48±2 mol% with the increase in temperature.

3.5.2 Effect of time

The effect of reaction time on the styrene conversion and product selectivity is studied at 40°C, 70°C and 50°C over CaFe$_2$O$_4$, SrFe$_2$O$_4$ and BaFe$_2$O$_4$ respectively, keeping all other conditions constant from 6 h to 30 h. the results are shown in Fig.6. Running the reaction for a longer time is found to be favourable for oxidation of styrene: styrene conversion is increased up to 38±2 mol% along with selectivity of benzaldehyde up to 91±2 mol% up to 18 h. After 18 h styrene conversion remains constant up to 30 h while the selectivity of benzaldehyde decreased to 83±2 mol% the results are shown in Fig.6A. When the same reaction is carried out over SrFe$_2$O$_4$ catalyst the styrene conversion and product selectivity is plotted as a function of reaction time. at 70°C. by varying the time from 6 h to 30 h. the results are shown in Fig.6B. It is found that at 6 h the conversion of styrene is 13.6 mol% with 13.2 mol% yield of benzaldehyde. As the
reaction time increases to 12 h, styrene conversion increased to 33.5 mol\% with 71.1 mol\% selectivity of benzaldehyde and 28.9 mol\% of phenyl acetaldehyde. At 18 h styrene conversion increases up to 50.8 mol\%, while the selectivity and yield of benzaldehyde is 63.7 mol\% and 32.4\% respectively, along with the formation of by-products like phenyl acetaldehyde and 1-phenyl-1, 2-ethanediol up to 28.1 and 8 mol\% respectively.

If the same reaction was run for 24 and 30 h, marginal increment is observed in styrene conversion i.e. 54.2 and 55.8 mol\%, but the selectivity of benzaldehyde substantially decreases to 53.5 and 51.6 mol\% with % yield to 29 and 28.8 respectively. In presence of
BaFe$_2$O$_4$ catalyst, the reaction was carried out by varying the time from 6 h to 42 h. The results are shown in Fig.6C. It is found that at 6 h the conversion of styrene is only 4 mol% with 4% yield of benzaldehyde. As the reaction time increases to 12 h, styrene conversion increased to 7 mol% with 100 mol% selectivity of benzaldehyde. At 18 h styrene conversion increases up to 45.1 mol%, while the selectivity and yield of benzaldehyde is 88.6 mol% and 39.9% respectively, along with the formation of by-products like phenyl acetaldehyde and 1-phenyl-1, 2-ethanediol up to 9.5 mol% and 2 mol% respectively. If the same reaction was run for 24, 30, 36 and 42 h, marginal increment is observed in styrene conversion i.e. 48.3 mol%, 50.0 mol%, 53.0 mol% and 55.0 mol%, but the selectivity of benzaldehyde decreases to 83.3 mol%, 80.0 mol%, 67.3 mol% and 66.1 mol% respectively.

The result indicates that as the reaction is run for long time the selectivity of by-products increases up to 49 mol%. This may be due to the complete exhaustion of H$_2$O$_2$ in the reaction mixture as the reaction was run for long duration [85]. Moreover, the impurities were also found to be formed when the reaction was allowed to run for long time. From the results it can be concluded that up to 18 h the selectivity of benzaldehyde is better with respect to styrene conversion.

3.5.3 Effect of solvent

The effect of solvents on the styrene oxidation and product selectivity over MFe$_2$O$_4$, where M = Ca, Sr and Ba, catalysts were also observed and results are shown in Fig. 7. We studied the reaction using protic and aprotic solvent. According to R. Kumar and others, aprotic solvents are more favourable for styrene oxidation than protic solvents [86]. Acetone is found to be a good solvent for CaFe$_2$O$_4$ as catalyst which gave a maximum styrene conversion of 37.91 mol%, while the selectivity of benzaldehyde is 91.14 mol% at optimum condition of time 18 h and temperature 40 ºC. While the catalytic activity of CaFe$_2$O$_4$ is found to be reduced in other solvents like methanol, acetonitrile and ethanol the results are shown in Fig 7A. Since H$_2$O$_2$ (30%) is added to the solution as a 70% aqueous solution, and polar solvent such as water (H$_2$O), ethanol
(C₂H₅OH), methanol (CH₃OH), acetonitrile (CH₃CN) and acetone are used to avoid separation of the solvent during the reaction. The selectivity of benzaldehyde with respect to percentage yield is in the order of H₂O > CH₃OH > C₂H₅OH > CH₃CN > CH₃COCH₃.

**Fig. 7.** Effect of solvent on the selective oxidation of styrene to benzaldehyde over calcium ferrite (A), strontium ferrite (B) and barium ferrite (C).

In case of SrFe₂O₄ it shows better efficiency in water than the other solvents such as ethanol, methanol, acetonitrile and acetone. The styrene conversion in methanol, ethanol, acetonitrile, and acetone is 12.8 mol%, 26.8 mol%, 21.3 mol% and 12.6 mol% with, 8.8 mol%, 6.6 mol%, 6 mol% and 3 mol% yield of benzaldehyde respectively. When the same reaction was carried out in water as solvent the styrene conversion is increased up
to 50.8 mol% with selectivity and percentage yield of benzaldehyde as 63.7 mol% and 32.4 mol% respectively.

The influence of solvents in the catalytic oxidation of styrene was studied at 70°C for 18 h in presence of 30% H2O2 as oxidizing agent. The results of the effect of the solvents are shown in Fig. 7B. However, in the selective oxidation of styrene, when the reaction is carried out over BaFe2O4 catalyst in polar and protic solvents like C2H5OH, CH3OH and H2O the conversion of styrene takes place up to 23.4 mol%, 28.7 mol% and 11.8 mol% with the percentage yield of benzaldehyde as 9.8, 9.4 and 6.8 respectively. The results are shown in Fig. 7C. When the same reaction is carried out in polar and aprotic solvent like acetone the styrene conversion increases up to 45 mol% along with 88.5 mol% of selectivity and 40% yield of benzaldehyde respectively. On the other hand, CH3CN is the next best polar and aprotic solvent from the viewpoint of selectivity of styrene oxide, 82.6 mol%, with respect to 15.7 mol% styrene conversion. The same reaction was also carried out in absence of solvent over all these catalysts in which very less (3-4 mol%) amount of styrene conversion was observed.

The solvent can influence the rate of reaction by dissolving the reactant molecules and intermediates in solution. The solvent can also affect the rate by competing with reactant molecules for active sites on the surface of heterogeneous catalyst [47]. Solvent may stabilize or destabilize transition state and intermediate formed on the surface of catalyst. When methanol, acetonitrile and ethanol are used as solvent for the oxidation reaction, the catalytic activity of the catalyst is reduced, this is probably due to the adsorption of these solvent on the active species at the surface of catalysts. Ethanol and methanol are favouring the formation of by-product like styrene oxide, 1-penyl-1,2-ethanediol and others. The percentage of these by-products is 44 mol% and 52 mol% in ethanol and methanol respectively. This may be partially due to easy reaction of hydrogen peroxide with these solvents and partially due to the adsorption of solvent molecule on the surface of catalyst which blocks the active acidic sites of the CaFe2O4 catalyst and avoid the further adsorption of styrene and H2O2 molecule. In case of SrFe2O4 catalyst water is found to be the good solvent, due to its polar nature and dissolving nature for a wide range of oxidant without complication due to the presence of
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acidic protons. Apart from this the strong interaction between H₂O and H₂O₂ inhibit the coordination of substrate and enhance desorption of the products from the active sites, which results in the prevention of deep oxidation of benzaldehyde to benzoic acid. Hence the selectivity of benzaldehyde is a maximum (63.7 mol%) in water with 32.4% yield. This effect of solvents strongly supports that the selective oxidation of styrene to benzaldehyde takes place through radical mechanism. The fact was confirmed by carrying the same reaction in presence of tertiary butyl alcohol as a scavenger and by keeping all the reaction condition constant as explained in section 3.2. While in case of BaFe₂O₄ catalyzed reaction acetone is found to be better solvent it may be due to the fact that polar solvent like acetone with convenient liquid, dissolve a wide range of reactants and activated complex compounds are solvated without any complications. As a result the activation energy decreases and the rate of the reaction increases. Secondly in this reaction the desirable product, (benzaldehyde) is more polar than the reactant (styrene), so the reaction is accelerated in the presence of polar aprotic solvents like acetone.

3.5.4 Effect of catalysts amount

The effect of catalysts (CaFe₂O₄, SrFe₂O₄ and BaFe₂O₄) amount towards the selective oxidation of styrene was also studied at different reaction condition; the results are summarized in Fig. 8. With increase in catalyst amount of CaFe₂O₄ (Fig. 8A) from 0.05 g to 0.10 g, the conversion of styrene also increases from 14.0 mol% to 38 mol%, while the selectivity of benzaldehyde slightly decreases from 100 mol% to 91 mol% along with the formation of styrene oxide up to 9 mol% which isomerizes to phenyl acetaldehyde as a by-product. Further increase in the amount of catalyst from 0.15 g to 0.20 g styrene conversion is decreased to 19.5 mol% while the selectivity of benzaldehyde was 100 mol%. Over the surface of SrFe₂O₄ with reaction temperature of 70°C for 18 h, the percentage conversion of styrene and percentage selectivity of products is shown in Fig. 8B.
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Fig. 8 Effect of catalyst amount on the selective oxidation of styrene to benzaldehyde over calcium ferrite (A), strontium ferrite (B) and barium ferrite (C).

For 0.05 g of SrFe$_2$O$_4$ catalyst 28.8 mol% of styrene conversion takes place with 72.7 mol% and 27.3 mol% selectivity for benzaldehyde and phenyl acetaldehyde respectively. The yield of benzaldehyde is 21.0%. As the catalyst amount increases to 0.1 g the styrene conversion also increases to 50.8 mol%, while the selectivity of benzaldehyde, phenyl acetaldehyde and 1-phenyl-1, 2-ethanediol are 63.7 mol%, 28.1 mol% and 8.1 mol% respectively. As the amount of catalyst is increased from 0.1 g to 0.15 g and 0.2 g, styrene conversion decrease to 34.7 mol% and 26.5 mol% with the selectivity of benzaldehyde as 62.3 mol% and 60 mol% respectively. The selectivity of by-products like phenyl acetaldehyde increases to 27.6 mol% and 28.6 mol% respectively and for that of 1-phenyl-1,2-ethanediol is 10.0 mol% and 11.4 mol% respectively. Similarly, the effect of amount of catalyst was studied over the different amount of BaFe$_2$O$_4$ by keeping all other
parameters (reaction time, temperature, mole ratio of substrate: \( \text{H}_2\text{O}_2 \)) constant the results are shown in Fig. 8C. For 50 mg of catalyst the styrene conversion increases to 12.7 mol% with 11.6% yield. The same reaction when carried out by using 100 mg of catalyst the styrene conversion suddenly increases to 45.1 mol% with 88.5 mol% selectivity and 39.9% yield. Further increase in catalytic amount up to 150 mg and 200 mg catalyst shows almost constant styrene conversion (46.0 mol%) but the percent yield of benzaldehyde slightly decreased to 38.3% and 37.9% respectively.

At the lower catalyst loadings, the increase in the styrene conversion with the catalyst loading is due to the availability of more surface area, which favours the dispersion of more active species [87] and enhances the styrene oxidation rate. However, at the higher catalyst loadings, the \( \text{H}_2\text{O}_2 \) decomposition rate is much higher than that at lower loading due to which sufficient \( \text{H}_2\text{O}_2 \) is not available for the oxidation, which ultimately leads to a lower styrene conversion. Also, at higher amount of catalyst adsorption or chemisorption of two reactants on separate catalyst particles may be done, thereby reducing the chance to interact with each other [77], resulting in lowering the activity. Thus the catalyst loading (0.1 g) has an optimum value for obtaining the highest styrene conversion in the oxidation. The accessibility of the large number of molecules of the reactants to the catalyst is favoured. The results show that 0.1 g of CaFe\(_2\)O\(_4\), SrFe\(_2\)O\(_4\) and BaFe\(_2\)O\(_4\) catalysts is the optimum amount to obtain maximum conversion of styrene with better selectivity of benzaldehyde.

### 3.5.5 Effect of calcination temperature

The percentage conversion of styrene and the percentage selectivity of different products were studied over the 0.1 g of MFe\(_2\)O\(_4\) where M = Ca, Sr and Ba. catalysts calcined at different temperature from 600 °C to 900 °C at the optimized conditions; the results are shown in Fig. 9. When the reaction is carried over the CaFe\(_2\)O\(_4\) catalyst (Fig. 9A) calcined at 600 °C, the conversion of styrene is 33.58 mol%, while the selectivity of benzaldehyde, and phenyl acetaldehyde 56.3 mol% and 43.7 mol% respectively with 18.9% yield. As the calcination temperature increases to 700°C, though the styrene conversion increases
(35.6 mol%) the benzaldehyde selectivity is increased up to 61.8 mol% with 22.02% yield. For further increase in temperature to 800 °C, the styrene conversion is increased to 39.9 mol% along with 91.14 mol% selectivity, while the percent yield is increased to 34.55. When the same reaction is carried out over the catalyst calcined at 900 °C the conversion as well as selectivity of benzaldehyde is slightly decreased to 38.56 mol% and 82.65 mol% respectively, the percentage yield is decreases to 31.87. The same reaction when was carried out over the 0.1 g of SrFe$_2$O$_4$ catalyst calcined at different temperature from 600 °C to 900 °C at the optimized conditions; the results are shown in Fig 9B.

![Graph showing reaction conditions and results for CaFe$_2$O$_4$, SrFe$_2$O$_4$, and BaFe$_2$O$_4$ catalysts.](image)

**Fig. 9.** Effect of calcination temperature on the selective oxidation of styrene to benzaldehyde over calcium ferrite (A), strontium ferrite (B) and barium ferrite (C).
When the reaction is carried over the catalyst calcined at 600 °C, the conversion of styrene is 58.1 mol%, while the selectivity of benzaldehyde, phenyl acetaldehyde and 1-phenyl-1,2-ethanediol are 47.6 mol%, 25.4 mol% and 23.1 mol% respectively with 27.6% yield of benzaldehyde. When the same reaction was carried out over catalyst calcined at 700 °C, the styrene conversion decreases (50.8 mol%) the benzaldehyde selectivity is increased up to 63.7 mol% with 32.4% yield. For further increase in temperature to 800 °C and 900 °C, the styrene conversion is decreased to 44.8 mol% and 32.9 mol% respectively. The selectivity of benzaldehyde also decreases to 55.9 mol% and 47.2 mol% respectively against the cost of increasing the percentage of phenyl acetaldehyde and 1-phenyl-1,2-ethanediol up to 29.6 and 23.1. The efficiency of BaFe₂O₄ catalyst calcined at different temperature from 600 °C to 900 °C at the optimized conditions towards the percentage conversion of styrene and the percentage selectivity of different products were studied the results are shown in Fig 9C. When the reaction is carried over the catalyst calcined at 600 °C, the conversion of styrene is 34.1 mol%, while the selectivity of benzaldehyde is 67.3 mol%. As the calcination temperature increases to 700 °C, though the styrene conversion increases to 37.2 mol%, while the benzaldehyde selectivity is increased up to 78.2 mol% with 29.2% yield. For further increase in temperature to 800 °C and 900 °C, the styrene conversion is decreased to 43.8 mol% and 45.1 mol% respectively. The selectivity of benzaldehyde also gradually increase to 81.6 mol% and 88.5 mol% respectively against the percentage yield of benzaldehyde is 35.7 and 39.9.

From all these observation it is clear that the calcination temperature plays important role in deciding the catalytic efficiency. CaFe₂O₄, SrFe₂O₄ and BaFe₂O₄ calcined at 800°C, 700°C and 900°C respectively are found to be the best candidate towards the selective oxidation of styrene. This results show that the catalyst calcined at this specific temperature gives the better transformation of styrene with highest selectivity of benzaldehyde. This may be due to the maximum availability of the number of Fe³⁺ ions on the octahedral site of the catalyst surface, which is responsible in making the respective catalyst more effective for catalytic reaction.
3.5.6 Effect of C₈H₈/ H₂O₂ molar ratio

The influence of styrene/ H₂O₂ molar ratio on the conversion of styrene and product selectivity is also studied MFe₂O₄ catalyst, where M = Ca, Sr and Ba. The results are shown in Fig.10. It is found that in case of CaFe₂O₄ when the styrene/ H₂O₂ molar ratio is increased from 1:2, 1:1 and 2:1 the styrene conversion decreases from 41 mol% to 20 mol% with decrease in the H₂O₂ conversion from 80 mol% to 34 mol% (Fig.10A). This is attributed to the increase in percentage of styrene in the reaction mixture. Interestingly, on the other hand the selectivity for benzaldehyde increases from 41 mol% to 100 mol%. Maximum styrene conversion is obtained at a molar ratio of styrene/ H₂O₂ as 1:2. The styrene conversion is observed up to 63.0 mol% in the presence of SrFe₂O₄ catalyst without using any oxidant. This clearly indicates that the possibility of the reaction occurring due to the participation of lattice oxygen of catalyst. But the reaction does not give the selective product. The selectivity of benzaldehyde is only 16.0 mol% with 10.0% yield. In absence of catalyst and in presence of 30% H₂O₂ the reaction proceed up to 60.0 mol%, but here also the reaction proceed randomly and give 12.0 mol% of benzaldehyde with 7.2% yield. Hence there is a need to optimize the styrene/ H₂O₂ molar ratio to carry out the reaction selectively keeping all the remaining parameter like temperature, time, etc. constant. The reaction was subsequently carried out in the presence of different styrene/ H₂O₂ molar ratio such as 2:1, 1:1, 1:2 and 1:3, for which 0.1 g of catalyst were taken in 10 ml of water at 70 °C. The results are shown in Fig. 10B.

The liquid phase selective oxidation of styrene was carried out over BaFe₂O₄ with different molar ratio of styrene to H₂O₂. In all the cases, benzaldehyde is obtained as a major product along with styrene oxide and acetophenone as by-product. It is observed that the highest conversion of styrene (45.1 mol%) as well as selectivity (88.5 mol%) and yield (39.9%) of benzaldehyde are obtained at styrene to H₂O₂ molar ratio 1:1 over BaFe₂O₄ catalyst at 50°C for 18 h; as shown in Fig. 10C.
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Effect of Styrene: H₂O₂ molar ratio on the selective oxidation of styrene to benzaldehyde over calcium ferrite (A), strontium ferrite (B) and barium ferrite (C)

The coordination of H₂O₂ on the metal, and its subsequent decomposition to •OH radical [41] are the necessary steps involved in this reaction (see Scheme 1b). At the molar ratio of 1:1, H₂O₂ could freely coordinate to metal and decompose to form •OH radical. Hence, high styrene conversion is attained along with the formation of styrene oxide as a by-product up to 9 mol%. While, at the molar ratio of 2:1, low amount of H₂O₂ may be competing with excess styrene for coordination, and hence formation of •OH radicals might be significantly reduced. Thus, the conversion is decreased. In case of CaFe₂O₄ and BaFe₂O₄ catalysts the strong interaction between catalyst and H₂O₂ inhibit the coordination of substrate and enhance desorption of the products from the active sites, which prevents the deep oxidation of benzaldehyde to benzoic acid. As the molar ratio of styrene is increased (2:1) the conversion of styrene is decreased, while the selectivity of
benzaldehyde is comparatively more this may be due to less concentration of H$_2$O$_2$ which has to compete with more styrene. However, the styrene conversion is increased to 52.4 mol% for the styrene/H$_2$O$_2$ molar ratio 1:2 but the selectivity as well as the yield of benzaldehyde decrease to 44.6 mol% and 23.4% respectively. Further increase in the concentration of H$_2$O$_2$ (1:3) marginal increment in the styrene conversion is observed i.e. 55.3 mol% but the selectivity and yield of benzaldehyde is distinctly decreased to 21.7 mol% and 16.4 mol% respectively. This may be due to the excess concentration of H$_2$O$_2$ which enhance the rate of conversion of styrene but at the same time excess water from 30% H$_2$O$_2$ hydrolyzed the intermediate i.e. styrene epoxide to form 1-phenyl-1,2-ethanediol. The conversion of styrene is comparatively less in SrFe$_2$O$_4$ catalyzed reaction when the styrene/ H$_2$O$_2$ molar ratio is 2:1 (about 23.8 mol %). This may be due to significantly reduced •OH radicals as less amount of H$_2$O$_2$ compete with excess styrene for coordination. As the concentration of H$_2$O$_2$ increases (1:1) there is increase in the styrene conversion as well as increase in the selectivity of benzaldehyde. The percentage conversion of styrene is 50.8% and the product selectivity and yield for benzaldehyde is 63.7% and 32.4% respectively. At this molar ratio of 1:1, H$_2$O$_2$ could freely coordinate to metal and decompose to form •OH radical. When the same reaction was carried out at styrene/ H$_2$O$_2$ molar ratio 1:2 and 1:3 in presence of 0.1 g catalyst the styrene conversion decreased to 25.0 mol% and 16.5 mol% with decrease in the percentage yield of benzaldehyde to 19.2 and 13.6 respectively. This may be due to the excess of water content in hydrogen peroxide that inhibits the coordination of oxidants with the active sites of catalyst [88].

3.5.7 Effect of oxidizing agents

The effect of different oxidants on the catalytic activity of CaFe$_2$O$_4$, SrFe$_2$O$_4$ and BaFe$_2$O$_4$ in styrene conversion and product distribution were also studied. Different oxidants such as H$_2$O$_2$, Urea-H$_2$O$_2$ (UHP) and tert-BuOOH were used as the oxygen source in acetone as solvent. The results are shown in Fig. 11.
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**Fig. 11** Effect of different oxidizing agent on the selective oxidation of styrene to benzaldehyde over calcium ferrite (A), strontium ferrite (B) and barium ferrite (C)

In presence of CaFe$_2$O$_4$ and 30% H$_2$O$_2$ the reaction proceeds with 37.9 mol% styrene conversion and 91.14 mol% selectivity of benzaldehyde (Fig. 11A). The yield of benzaldehyde under this condition is 34.55%. In presence of tert-BuOOH the styrene conversion decreased to 32.56 mol% with 85.32 mol% and 14.68 mol% selectivity of benzaldehyde and phenyl acetaldehyde respectively with 27.78% yield. When the same reaction was carried out in presence of ureated hydrogen peroxide (UHP) the styrene conversion takes place up to 30.42 mol%, with selectivity and percent yield of benzaldehyde as 80.47 mol% and 24.47 respectively. The effect of different oxidants on the catalytic activity of SrFe$_2$O$_4$ in styrene conversion and product distribution is shown in Fig. 11B. In presence of 30% H$_2$O$_2$ the reaction proceeds with 50.8 mol% styrene conversion and 63.7 mol% selectivity of benzaldehyde. The yield of benzaldehyde under
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this condition is 32.4%. When the same reaction was carried out in presence of ureated hydrogen peroxide (UHP) the styrene conversion takes place up to 43.6 mol%, but the selectivity of benzaldehyde is very less (7.3 mol%). In presence of tert-BuOOH the styrene conversion proceed up to 60.7 mol% with 52.0 mol%, 26.2 mol% and 21.9 mol% selectivity of benzaldehyde, phenyl acetaldehyde and 1-phenyl-1,2-ethane diol respectively. Different oxidants such as H$_2$O$_2$, Urea-H$_2$O$_2$ (UHP) and tert-BuOOH were used as the oxygen source in acetone as solvent over BaFe$_2$O$_4$ catalyst. The results are shown in Fig. 11C. In presence of 30% H$_2$O$_2$ the reaction proceeds with 45.1 mol% styrene conversion and 88.5 mol% selectivity of benzaldehyde, while the yield of benzaldehyde under this condition is 39.9%. When the same reaction was carried out in presence of tert-BuOOH as oxidizing agent the styrene conversion takes place up to 38.6 mol%, but the selectivity of benzaldehyde decreased to 81.6 mol% with 31.5 % yield. In presence of ureated hydrogen peroxide (UHP), the styrene conversion reduced to 26.4 mol% with 74.2 mol% selectivity and 19.6% yield of benzaldehyde respectively.

Among all these oxidants H$_2$O$_2$ (30%) shows the best performance since it can give good oxidation conversion; moreover it generate only water as by-product; and it has high content of active oxygen. In terms of percentage yield of benzaldehyde, the oxidizing agents shows the efficiency in the order of H$_2$O$_2$ (30%) > tert-BuOOH > UHP.

3.5.8 Effect of Sonication time

The effect of ultrasonic radiation on the catalytic efficiency of CaFe$_2$O$_4$, SrFe$_2$O$_4$ and BaFe$_2$O$_4$ catalyst were also studied by varying the sonication time. The results are shown in Fig.12. The reaction which was carried out in presence of CaFe$_2$O$_4$ as catalyst but without sonication gave the percentage styrene conversion and percentage selectivity of benzaldehyde as 31.42 and 81.37mol% respectively the results are summarised in Fig.12A. When the same reaction was carried out by sonicating the catalyst in solvent for the specific period of 5, 10 and 15 minutes using CaFe$_2$O$_4$ catalyst, the styrene conversion is increased to 34.25 mol%, 37.91 mol% and 39.54 mol% respectively while the selectivity of benzaldehyde increases as 71.0 mol%, 80.5 mol% and 91.2 mol%
respectively. The same reaction was carried out in presence of SrFe₂O₄ catalyst without sonication gave the percentage styrene conversion and percentage selectivity of benzaldehyde as 50.8 and 63.7 respectively the results are shown in Fig.12B.

![Diagram](image)

**Fig. 12** Effect of sonication time on the selective oxidation of styrene to benzaldehyde over calcium ferrite (A), strontium ferrite (B) and barium ferrite (C)

When the same reaction was carried out by sonicating the catalyst in solvent for the specific time interval of 5, 10 and 15 minutes, the styrene conversion is decreased to 32.4 mol%, 28.0 mol% and 17.1 mol% respectively while the selectivity of benzaldehyde increases as 71.0 mol%, 80.5 mol% and 91.2 mol% respectively. To examine the influence of ultrasonic treatment on the activity of BaFe₂O₄, it was sonicated for different time in the reaction solvent and then the styrene and H₂O₂ was added successively in the reaction vessel. The results are shown in Fig. 12C. When the catalyst is used without
sonication the styrene conversion is 25.1 mol% with 90 mol% selectivity and 22.8% yield of benzaldehyde. The same catalyst when used by ultrasonic treatment for the specific time interval of 5, 10 and 15 minutes the styrene conversion gradually increases from 29.4 mol% to 45 mol% along with increase in % yield from 26.3 to 39.9% respectively. When the sonication as done for 20 minutes, the styrene conversion increases marginal to 45.6 mol% with reduction in the selectivity of benzaldehyde to 83.5 mol% and 38% yield. Sonication mostly affects reaction rate, yield and in some cases even the ratio of reaction products.

This is due to the exposure of active sites on the surface of CaFe₂O₄ and BaFe₂O₄ catalysts which may enhance the adsorption of styrene and H₂O₂, bring mechanical effects and induce cavities, which promotes the reactions. Secondly, the reaction proceeds in presence of acetone and aqueous H₂O₂ which is hydrophobic in nature. In hydrophobic reactions normally the reagents get hidden inside the clusters due to which they are unavailable for reaction. On ultrasonic treatment, ultrasound breaks these hydrophobic cluster, which make the reagent again available and thus acceleration of the reaction is observed. While in case of SrFe₂O₄ sonication of catalyst, the results indicates that the ultrasonication of catalyst shows the adverse effect which may be due to high intensity shock waves generated by ultrasonic irradiation cause promotion of mass transport and/or activation of solid surface. Ultrasonic dispersion method is effective for dispersing the material; but at the same time, the high energy may damage the active sites of catalyst and results in the degradation of the mechanical properties of the composite [89].

3.6 Reusability of catalyst

The efficiency and reusability of the CaFe₂O₄, SrFe₂O₄ and BaFe₂O₄ were checked by using the utilized catalyst in the next cycles. Catalyst deactivation may occur due to chemical, mechanical and thermal reason [64] by keeping all the conditions constant, the results are shown in Fig.13. In the first cycle at optimized conditions the styrene conversion and selectivity of benzaldehyde is up to 37.91 mol% and 91.14 mol%
respectively for CaFe₂O₄. The catalyst was used at least for three cycles by 13.5% loss in activity; the results are shown in Fig. 13A.

<table>
<thead>
<tr>
<th>a - styrene conversion, b - benzaldehyde, c - phenyl acetaldehyde, d - others, e - % yield of benzaldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Graph A]</td>
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<tr>
<td>![Graph B]</td>
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<tr>
<td>![Graph C]</td>
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</tbody>
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**Reaction conditions:**
- **Graph A:**
  - Catalyst: CaFe₂O₄ (100 mg)
  - Substrate: Styrene (10 mmol)
  - Solvent: Acetone (10 ml)
  - Temperature: 60 °C
  - Styrene/Oxidant = 1:1
  - Oxidant: 30% H₂O₂
  - Time: 18 h
  - Number of terms: 2-3

- **Graph B:**
  - Catalyst: SrFe₂O₄ (100 mg)
  - Substrate: Styrene (10 mmol)
  - Solvent: Water (10 ml)
  - Oxidant: 30% H₂O₂
  - Temperature: 70 °C
  - Styrene/H₂O₂ = 1:1
  - Time: 18 h
  - Number of terms: 2-3

- **Graph C:**
  - Catalyst: BaFe₂O₄ (100 mg)
  - Substrate: Styrene (10 mmol)
  - Solvent: Acetone (10 ml)
  - Oxidant: 30% H₂O₂
  - Temperature: 50 °C
  - Styrene/H₂O₂ = 1:1
  - Time: 18 h
  - Number of terms: 2-3

**Fig. 13** Reusability of the catalyst towards the selective oxidation of styrene to benzaldehyde over calcium ferrite (A), strontium ferrite (B) and barium ferrite (C).

The efficiency of the SrFe₂O₄ was checked by carrying out the reaction under optimized amount of catalyst i.e. 0.1 g and by keeping all the conditions constant, the results are shown in Fig. 13B. The amount of catalyst is very small (0.1g). Hence the recycling of catalyst is not very efficient. There were difficulties in collection of the catalyst due to the loss during filtration. But if the catalyst is collected from several batches and then reused it was found that the same catalytic activity with a 6-8% decrease in the percentage conversion. The distribution for the selectivity of the products remains the same. In BaFe₂O₄ catalyzed reaction in the first cycle at optimized conditions the
styrene conversion and selectivity of benzaldehyde is up to 45.1 mol% and 88.5 mol% respectively. The catalyst was used at least for three cycles by 13.5% loss in activity, the results are shown in Fig. 13C: furthermore the XRD pattern (not shown) of the reused catalysts were identical to that of the original, indicating that the crystallinity of the catalyst was not affected during the reaction.

CaFe$_2$O$_4$, SrFe$_2$O$_4$ and BaFe$_2$O$_4$ were used after simple filtration for separation and washing with water and acetone and drying at 150°C. The chemical reduction in activity is common in catalyst and caused by strong chemisorption of species which blocks the active sites of the catalyst.

3.7 Comparison of catalytic activity of AEM ferrites towards the selective oxidation of styrene

The selective oxidation of styrene to benzaldehyde is carried over the surface of number of transition metal ferrite such as NiFe$_2$O$_4$, ZnFe$_2$O$_4$, etc. [1, 90] along with the alkaline earth metal ferrites like MgFe$_2$O$_4$ [47]. CaFe$_2$O$_4$, SrFe$_2$O$_4$ and BaFe$_2$O$_4$. In comparison to transition metal ferrites, (AEM) ferrites show better catalytic activity because as it is known in most of the cases the catalytic activity of the catalyst depends on the chemical composition or cation distribution between the tetrahedral and octahedral site. Also, it may be due to the relative size of ion compare to the size of the lattice site and the site preference energy value of individual cation towards the A and B sites of the catalyst [91]. In case of divalent metal ions most of them are having smaller atomic size than the ionic size of Fe$^{3+}$ ions. In transition metal ferrites, Fe$^{2+}$ and Fe$^{3+}$ are present in tetrahedral and octahedral coordination, while in alkaline earth metal ferrites: Fe$^{3+}$ is only in tetrahedral coordination [92]. Among various alkaline earth metal ferrites, BaFe$_2$O$_4$ is found to be a better catalyst even though they are prepared by same method (citrate gel combustion method). In case of BaFe$_2$O$_4$ 45.1mol% of styrene conversion is observed with 88.5mol% selectivity and 39.9% yield of benzaldehyde. While in case of MgFe$_2$O$_4$ [47] only 13.5mol% styrene gets converted with 47.1mol% selectivity and 6.46% yield of benzaldehyde. When the same reaction was carried under the similar experimental conditions over the surface of CaFe$_2$O$_4$ the styrene conversion and selectivity of
benzaldehyde is 37.9mol% and 91.1mol% respectively, while in case of SrFe$_2$O$_4$ the styrene conversion and % yield of benzaldehyde is 63.7mol% and 32.4 respectively. Along with the cation distribution the catalytic activity depend on the size of the ions. In case of barium ferrite the ionic size is 1.35Å which is greater than the ionic size of Mg (0.78Å), Ca (0.85Å) and Sr (1.13Å). The divalent metal ions are generally larger in size than trivalent metal ions. The octahedral sites are also larger than tetrahedral sites, in other ferrites. Fe$^{2+}$ and Fe$^{3+}$ are present in octahedral and tetrahedral coordination, while in case of barium ferrite ionic size of Ba is 1.35Å which is comparatively greater than iron (0.67Å) is only in the tetrahedral coordination. Due to this variation in ionic size the BaFe$_2$O$_4$ may be showing best catalytic activity amongst all the AEM ferrites.

3.8 Conclusions:
1. CaFe$_2$O$_4$, SrFe$_2$O$_4$ and BaFe$_2$O$_4$ complex oxide catalyst are successfully prepared by the citrate gel combustion method. This complex type ferrite catalysts are found to be highly active than other reported metal ferrites for the oxidation of styrene with H$_2$O$_2$ as an oxidizing agent.
2. Thermal analysis of calcium, strontium and barium iron citrate precursors gives the information about the temperature at which crystalline ferrite formation takes place. According to thermal analysis the CaFe$_2$O$_4$, SrFe$_2$O$_4$ and BaFe$_2$O$_4$ formation takes place at 600°C, 700°C and 800°C respectively.
3. X-ray diffraction studies show the single phase material formed at specific temperature with some impurities like carbonates of alkaline earth metal.
4. The metal oxygen stretching frequencies are confirmed by FT-IR techniques. The stretching bands from 445 cm$^{-1}$ to 550 cm$^{-1}$ indicate the formation of spinel type along with a common stretching band at 1411 cm$^{-1}$ to 1450 cm$^{-1}$ indicate the presence of trace quantity of metal carbonate.
5. The scanning electron microscope (SEM) images shows different morphology of the sample CaFe$_2$O$_4$, SrFe$_2$O$_4$ and BaFe$_2$O$_4$ calcined at different temperature with respect to their method of preparation, calcination temperature etc. Calcium ferrite calcined at 800°C for 2 h show fine particles, strontium ferrite powder calcined at 700 °C for 2 h
shows that the material is like fine flakes and well defined monodispersed particles at different magnification is observed. In case of BaFe₂O₄ the image suggests that the catalyst shows coralloid morphology with outward extending branches, having an average diameter.

6. The elemental analysis of all monophasic CaFe₂O₄, SrFe₂O₄ and BaFe₂O₄ by chemical method and X-ray florescence (XRF) method shows in all these catalyst the percentage composition of Ca, Sr, Ba, Fe and oxygen are in good agreement with the theoretical values.

7. The promoting effect of the oxidation can be ascribed to the activation of oxygen ad species (such as O²⁻), which was accompanied with the reduction of abnormal valence iron (Fe³⁺) site in the surface layer of catalyst. The active oxygen species reversibly appeared and disappeared on the iron site due to sorption of atmospheric oxygen at the same temperature range. The heterogeneously catalyzed liquid phase oxidation of styrene proceeds by a free radical mechanism as confirmed by using tertiary butyl alcohol as a scavenger. The free radical involves initiation on the catalyst surface and homogeneous or heterogeneous propagation in the liquid. Styrene undergoes a C=C bond cleavage preferentially over calcium ferrite oxide catalyst to give benzoaldehyde as a major product and formation of by-product such as styrene oxide (epoxide), benzoic acid, phenyl acetaldehyde as minor products. Alternatively the Fe³⁺ ions from the octahedral sites of catalyst react with hydrogen peroxide to form Cat-Fe³⁺-OH complex and hydroxyl radicals.

8. Acetone as a reaction medium, reaction temperature 40 °C, reaction time 18 h and styrene: hydrogen peroxide ratio 1:1 was found to be favorable for increasing the selectivity of benzaldehyde. The 0.1 g of calcium ferrite catalyst amount is optimized for the maximum conversion of styrene up to 38±2 mol% with the selectivity of benzaldehyde and phenyl acetaldehyde is up to 91±2 mol% and 9±2 mol% respectively, due to the accessibility of the large number of molecules of the reactants to the catalyst is favoured.

SrFe₂O₄ is an efficient catalyst for selective oxidation of styrene in water as a solvent, in the presence of 30% H₂O₂ as oxidizing agent, which exhibits high activity
and high selectivity. The styrene oxidation catalyzed by SrFe$_2$O$_4$ without using any phase transfer catalyst or any organic solvent, leads to the conversion of styrene up to 51.0 mol% along with the formation of benzaldehyde (63.7 mol%) as major product, while styrene oxide (28.0 mol%) as minor, which quickly isomerizes into phenyl acetaldehyde. Temperature 70 °C, time 18h, styrene/ H$_2$O$_2$ molar ratio as 1, protic and polar solvent like water, catalyst amount 0.1g, favors the selective oxidation of styrene.

9. Solvents have marked influence on the product distribution in selective oxidation of styrene; water seems to be the best solvent for SrFe$_2$O$_4$. The selectivity of benzaldehyde with respect to percentage yield for various solvents is in the order of H$_2$O > CH$_3$OH > C$_2$H$_5$OH > CH$_3$CN > CH$_3$COCH$_3$. The strong interaction between H$_2$O and H$_2$O$_2$ inhibit the coordination of substrate and enhance desorption of the products from the active sites, which prevents the deep oxidation of benzaldehyde to benzoic acid. While for CaFe$_2$O$_4$ and BaFe$_2$O$_4$ the selectivity of benzaldehyde with respect to percentage yield for various solvents is in the order of CH$_3$COCH$_3$ > CH$_3$CN > C$_2$H$_5$OH > CH$_3$OH > H$_2$O.

10. The ultrasonication of catalyst shows the enhancement in the selective oxidation of styrene when the reaction carried out over the surface of CaFe$_2$O$_4$ and BaFe$_2$O$_4$. The ultrasonication of reaction mixture exposes the active sites on the surface of catalyst, which enhance the adsorption of styrene, H$_2$O$_2$ and promote the reaction. It also breaks the hydrophobic cluster and makes the reagents available to accelerate the reaction, while in case of SrFe$_2$O$_4$ ultrasonication shows the adverse effect.

11. BaFe$_2$O$_4$ is found to be a better catalyst amongst all alkaline earth metal ferrites like MgFe$_2$O$_4$, CaFe$_2$O$_4$, and SrFe$_2$O$_4$ it may be due to different site preference energy of individual ions which depend on the ionic size of barium (1.35Å) and iron (0.67Å). Due to this almost all the Ba$^{2+}$ ions occupy the octahedral lattice and equal number of Fe$^{3+}$ ions occupies the tetrahedral lattice.

12. The catalysts could be reused at least for three cycles with marginal (10-15%) loss in activity. The XRD pattern of the reused catalyst was identical to that of the original indicating that the crystallinity of the catalyst was not affected during the reaction.
3.8 References:


