Chapter IV

CHARACTERIZATION AND CATALYTIC ACTIVITY OF SUBSTITUTED ALKALINE EARTH METAL FERRITES

PART A:
CHARACTERIZATION AND CATALYTIC ACTIVITY OF STRONTIUM SUBSTITUTED CALCIUM (SSC) FERRITE
4A.1 Introduction

Ferrites are better magnetic material than pure metals because of their high resistivity, lower cost, easy manufacture and superior magnetization properties. Alkaline earth metal ferrites have attracted a considerable attention owing to their potential application in high capacity batteries [1], wastewater cleaning [2], low magnetization Ferro fluids [3] and as oxidizing agents[4]. Spinel ferrites are of great fundamental and technological important due to their structural, electronic, magnetic and catalytic properties [5-8]. The physicochemical properties of the ferrites are strongly dependent on the sites and the nature of the catalyst [9, 10], which are closely related to the method of preparation.

Epoxidation of styrene is commercially important reaction for the production of styrene oxide, an important organic intermediate, as versatile and useful chiral building blocks in organic synthesis [11]. Earlier studies reported for the epoxidation of styrene were based on the use of TS-1 [12-15], Ti–SiO₂ [12], [16] and [17]. Ti loaded mesoporous materials (Ti–MCM-41) [15], and TBS-2 and TS-1 [18] catalysts, using different oxidizing agents, such as tertiary butyl hydrogen peroxide (TBHP) [16], aqueous H₂O₂, [17] and [18], and urea–H₂O₂ adduct [14]. For all the above catalysts, the use of aqueous H₂O₂ resulted in a very poor selectivity for styrene oxide. High-styrene oxide selectivity (>80%) could be obtained using urea–H₂O₂ adduct [14] and TBHP [16] as the oxidizing agents but only at a low-styrene conversion (18% and 10%, respectively). It is, therefore, of great practical interest to find such a catalyst which is much better for the epoxidation of styrene.

Recently, Mandelli et al. [19] have observed a good catalytic activity and selectivity for γ-alumina in the epoxidation of limonene, cyclohexene and 1-octene by using anhydrous H₂O₂. However, they observed catalyst deactivation after a certain reaction period (5 h), due to accumulation of the reaction water. Olefin epoxidation is a key transformation in organic synthesis both on a laboratory and on industrial scale, due to the interest of epoxide in the production of chemicals and fine chemicals [20]. The use of hydrogen peroxide for selective epoxidation is highly desirable because it is cheap, the active
oxygen content is high, and it is clean, since the only by-product formed is water [21]. Many catalytic systems based on different metals have been reported for the epoxidation of a wide range of alkenes using hydrogen peroxide [22].

The alkaline earth metal ferrite like CaFe$_2$O$_4$ and SrFe$_2$O$_4$ were also used in selective oxidation of styrene but the selectivity of epoxide was very less while the benzaldehyde was the major product in acetone and water as the reaction solvent respectively. The present work is undertaken to explore the possibility of combining the advantages of using hydrogen peroxide, an heterogeneous catalyst Strontium substituted Calcium (SSC) ferrite and solvents from renewable sources (acetonitrile and methanol), with tailored properties, to extend the range of applicability of these catalytic systems to the epoxidation of a more challenging substrate styrene. Since epoxides are key building blocks in organic synthesis [23], as well as commercially important intermediates used in the synthesis of chiral pharmaceuticals, pesticides, epoxy paints, agrochemicals, perfume materials and sweeteners [24, 25] it is a need to develop a suitable catalyst. Traditionally, epoxides are produced by the chlorohydrin process and the Halcon process [26]: however, a lot of by-products resulting from both processes are environmentally undesirable. Thus, the pursuit for environmentally-benign methods with clean and cheap oxidant has been a challenge in chemical industries and academic fields. So we synthesized the catalyst with different composition of Ca$^{2+}$ and Sr$^{3+}$ ions to improve the selectivity of epoxide instead of benzaldehyde in presence of 30% H$_2$O$_2$ and NaOH solution.

Another goals is to prepare strontium substituted calcium ferrite with different composition Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ (where, 0.0 $\leq$ x $\leq$ 1.0) particles by using different methods and to find which method is the better one with respect to their catalytic activity. In addition, we aimed to minimize the cost of the materials used together with tailoring the catalytic properties of the Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ ferrite according to the desired application words the epoxidation of olefins. This synthetic route can be considered interesting for its simplicity, reproducibility and easy scale-up. It produces a homogeneous precursor with
controlled stoichiometry and also does not require expensive chemicals. It is a low energy reaction and can be carried out in a china dish in an open atmosphere.

In the present work, we are also reporting the results for cyclohexene epoxidation reaction in suitable solvent using environmentally benign oxidant \( \text{H}_2\text{O}_2 \) over \( \text{Sr}_3\text{Ca}_4\text{Fe}_{20}\text{O}_{36} \). of Sr-Fe-O system was synthesized by three different routes and characterized by various techniques. The conditions for maximum conversion of cyclohexene as well as selectivity for desired product have been optimized by varying different parameters such as method of preparation of catalyst, effect of chemical composition of catalyst, reaction medium, oxidizing agent, reaction time, temperature, amount of catalyst and cyclohexene/oxidant molar ratio.

4A.2 Characterization of substituted alkaline earth metal (AEM) ferrites

4A.2.1 TGA analysis of strontium substituted calcium iron citrate precursor

The thermal analysis of the as prepared samples was done to know the possible changes occurring when they were subjected to heat treatment and to determine the exact calcination temperature of ferrites. From TG studies it is seen that the data for the ferrites synthesized by citrate gel combustion method are featureless in the temperature range of 30 to 350 °C, except for the water loss between 100 °C to 110 °C. Near 350 °C, there is a sudden weight loss indicates the decarboxylation of the complexes. Above 600 °C there is no distinct weight loss observed indicate the crystallization of ferrite. From these all patterns it is clear that as the concentration of strontium ion increases the stability of the intermediate products increases which is clearly seen in the Fig.1 (a-e). The formation temperature also increases with increasing the concentration of strontium ion in calcium ferrite.
Fig. 1. Thermo gravimetric analysis of calcium iron citrate precursor (a), strontium substituted calcium iron citrate precursor (b-e) and strontium iron citrate precursor (f) prepared by citrate gel method.
4A.2.2 FT-IR analysis of strontium substituted calcium ferrites

Fig. 2. Infrared spectra of CaFe$_2$O$_4$ (a), Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ (b), Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ (c), Sr$_{0.6}$Ca$_{0.4}$Fe$_2$O$_4$ (d), Sr$_{0.8}$Ca$_{0.2}$Fe$_2$O$_4$ (e) and SrFe$_2$O$_4$ (f) calcined at 700°C prepared by citrate gel method.

**Fig. 2a and f** shows FTIR spectrum of CaFe$_2$O$_4$ and SrFe$_2$O$_4$ powder while the **Fig. 2b to e** show the FTIR spectrum of Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ oxide (where $x = 0.2, 0.4, 0.6$ and $0.8$) calcined at 700°C temperature. There are significant peaks found in the range of 418 cm$^{-1}$ to 611 cm$^{-1}$ in all spectra. The band appeared around 600-605 cm$^{-1}$ is attributed to stretching vibration of tetrahedral groups Ca$^{2+}$–O$^{2-}$. While the band appearing around 552-557 cm$^{-1}$ ($v_1$), is attributed to stretching vibration of tetrahedral groups Sr$^{2+}$–O$^{2-}$. and that around 440-457 cm$^{-1}$ ($v_2$), is attributed to the octahedral group complex Fe$^{3+}$–O$^{2-}$. The two weak absorption bands found in the tetrahedral region (552-605 cm$^{-1}$) indicate the
presence of divalent metal ions on the tetrahedral site only. The substitution of calcium ion from the CaFe$_2$O$_4$ by strontium ion takes place at tetrahedral site only, which is confirmed by shifting the Sr$^{2+}$-O stretching band towards the higher wave number from 446 cm$^{-1}$, 550 cm$^{-1}$, 552 cm$^{-1}$, 565 cm$^{-1}$ and 567 cm$^{-1}$ for sample (b) to (f) respectively as shown in Fig. 2. While the Ca$^{2+}$-O stretching band shifted towards the lower wave number. The spectrum also reveals that the carboxylates of the precursor transform into metal carbonate with the characteristic stretching location at 1465-1494 cm$^{-1}$.

4A.2.3 Elemental analysis
The elemental analysis is done by chemical method and the results are confirmed by doing the analysis with X-ray florescence method (Table 1). From these results it is clear that the percentage composition of each element in each catalyst is in good agreement with the calculated values.

**Table 1** The elemental analysis of strontium substituted calcium ferrite prepared by citrate gel combustion method.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Strontium (Sr)</th>
<th>Calcium (Ca)</th>
<th>Iron (Fe)</th>
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<tbody>
<tr>
<td></td>
<td>Cal (EDS) (XRF)</td>
<td>Cal (EDS) (XRF)</td>
<td>Cal (EDS) (XRF)</td>
</tr>
<tr>
<td>Sr0.2</td>
<td>7.78 8.35 8.05</td>
<td>14.24 13.90 13.69</td>
<td>51.15 51.84 51.50</td>
</tr>
<tr>
<td>Sr0.4</td>
<td>15.98 15.32 14.70</td>
<td>10.24 10.74 10.57</td>
<td>47.57 47.90 48.10</td>
</tr>
<tr>
<td>Sr0.6</td>
<td>21.50 21.20 21.79</td>
<td>6.56 6.90 6.87</td>
<td>45.73 45.10 46.24</td>
</tr>
<tr>
<td>Sr0.8</td>
<td>27.61 27.45 28.10</td>
<td>3.16 2.79 2.90</td>
<td>44.01 43.59 43.76</td>
</tr>
</tbody>
</table>

4A.2.4 X-ray diffraction analysis
The X-ray diffraction studies of the samples treated at 700 °C temperature for 2 h has been carried out using Cu Ka radiation. Fig. 3 shows the XRD pattern of Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$, where (0.0 ≤ x ≤ 1.0). A pattern (a) is the spinel type CaFe$_2$O$_4$ oxide where all the d
spacing values are in good agreement with the standard data (JCPDS card no. 46-0100). While a pattern (f) is the XRD pattern of spinel type SrFe$_2$O$_4$ oxide where all the d spacing values are in good agreement with the standard data [27].

![X-ray diffraction pattern](image)

**Fig. 3.** X-ray diffraction pattern of CaFe$_2$O$_4$ (a), Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ (b), Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ (c), Sr$_{0.6}$Ca$_{0.4}$Fe$_2$O$_4$ (d), Sr$_{0.8}$Ca$_{0.2}$Fe$_2$O$_4$ (e) and SrFe$_2$O$_4$ (f) calcined at 700°C prepared by citate gel method.

The (b), (c), (d) and (e) are the XRD pattern of Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ (0.0 ≤ x ≤ 1.0). As the concentration of strontium ion in Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ increases from (0.0 ≤ x ≤ 1.0) the highest intensity peak is shifted towards it’s left from 2θ angle 33.5, 33.1, 33.0, 32.9, 32.8 and 32.7 respectively (Fig. 3) indicating a higher interplaner distance and consequently, a increase of the cell volume. The crystallite size of all the samples (a- f) was calculated using Scherer’s law from the XRD peak at 33.5 to 32.7 respectively which is in the range of 49 nm to 85 nm. The X-ray pattern of the substituted spinel type ferrites are monophasic and they show the same pattern as that of the calcium ferrite, although a high intensity line shift to lower 2θ value when the strontium doping increases is observed.
4A.2.5 SEM-EDX analysis

<table>
<thead>
<tr>
<th>x = 0.0</th>
<th>x = 0.2</th>
<th>x = 0.4</th>
<th>x = 0.6</th>
<th>x = 0.8</th>
<th>x = 1.0</th>
</tr>
</thead>
</table>

**Fig. 4.** Scanning electron microscope images and electron dispersive X-ray spectra of CaFe$_2$O$_4$ (a), Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ (b), Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ (c), Sr$_{0.6}$Ca$_{0.4}$Fe$_2$O$_4$ (d), Sr$_{0.8}$Ca$_{0.2}$Fe$_2$O$_4$ (e) and SrFe$_2$O$_4$ (f) calcined at 700°C.

The electron dispersive X-ray spectra of strontium substituted calcium ferrite, Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ prepared by citrate gel combustion method, where $x = 0.2, 0.4, 0.6$ and $0.8$ calcined at 700°C, the diffraction peak of strontium, calcium, iron and oxygen with no other evident diffraction peaks were observed, suggesting that no impurities were introduced into the resultant samples. The percentage composition of the elements like strontium, calcium, iron and oxygen in the respective catalysts is in good agreement with the calculated values.

The magnified SEM image of the calcium ferrite, strontium ferrite and strontium substituted calcium ferrite with different chemical composition calcined at 700°C temperature are shown in **Fig. 4 (a-f).** **Fig. 4(a)** shows the joint network structure of CaFe$_2$O$_4$. As the concentration of strontium increases in Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ (where $x = 0.2, 0.4, 0.6$ and $0.8$) the morphology of the material changes from one form to other form as shown in **Fig. 4(b-e).** The catalyst with $x = 0.2$ shows fine flakes like morphology while $x = 0.4$ shows the needle shape morphology. The catalysts with $x = 0.6$ and $0.8$ shows the agglomerization which results in the lower surface area of catalyst. In strontium ferrite
(SrFe$_2$O$_4$) Fig. 4(f) it forms a complex solid with rough morphology. It may be due to increase in the concentration of strontium.

4A.2.6 Surface area determination by BET method

![BET surface area graph]

Fig.5. Specific surface area of strontium substituted calcium ferrites prepared by citrate gel combustion method and b) Surface area of Sr$_{0.1}$Ca$_{0.6}$Fe$_2$O$_4$ catalyst prepared by CGC, CGUT and SAC method.

The BET surface area of the various samples of strontium substituted calcium ferrite (Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$) catalysts calcined at 700 °C was also carried out the results are shown in Fig. 5. Among all the prepared catalysts the surface area of Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ and Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ (Fig.5A) catalysts are greater i.e. 175.19 m$^2$/g than that of the other catalysts even though they are prepared by same method. It may be due to the grain size of Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ and Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ catalysts are lower than the other catalysts it is confirmed by the X-ray diffraction studies. 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). It is confirmed that the elemental composition of
catalyst decides an important role not only on morphology but on the surface area of catalysts also. We have also prepared \( \text{Sr}_{0.4}\text{Ca}_{0.6}\text{Fe}_2\text{O}_4 \) catalyst by CGC, CGUT and SAC method and determine their surface area, where catalyst prepared by CGC method shows the larger surface area than the catalyst prepared by other two methods (Fig. 5B) this may be due to citric acid plays two important role in this method, the first as the chelate agent to form homogeneous, steady and transparent sol. Citric acid is ionized and chelated \( \text{Fe}^{3+}, \text{Sr}^{2+}, \text{and Ca}^{2+} \) ions, which can makes the homogeneous distribution of ions in the solution and enhance the surface area and second as fuel to provide auto combustion action, the function is just like the carbamide in other combustion systems.

4.3 Catalytic activity of AEM ferrites

In our previous work the parent calcium and strontium ferrite were found to be effective toward the selective oxidation of styrene to benzaldehyde as major product while styrene epoxide was observed as minor product. Epoxidation of styrene is considered to be a commercially important reaction for the production of styrene oxide, an important organic intermediate. With the intention to enhance the activity of catalyst towards the epoxidation of styrene, the strontium substituted calcium ferrite catalysts were prepared by citrate gel method with different chemical composition \( \text{Sr}_{x}\text{Ca}_{1-x}\text{Fe}_2\text{O}_4 \) where \( x = 0.2, 0.4, 0.6 \) and \( 0.8 \). The catalytic efficiency of \( \text{Sr}_{x}\text{Ca}_{1-x}\text{Fe}_2\text{O}_4 \) is checked towards the epoxidation of styrene and cyclohexene at optimized conditions. The optimization of reaction conditions are discussed below.

4.3.1 Selective epoxidation of styrene

The selective epoxidation of styrene was carried out in a three neck round bottom flask (100 ml) equipped with X-crossed Teflon coated magnetic stirrer and a reflux condenser, and two dropping funnel. In typical batch experiment, 5.2 g (50mmol) of styrene [99+%, Aldrich], 6.105 g (150mmol) acetonitrile and 100 mg of \( \text{Sr}_{x}\text{Ca}_{1-x}\text{Fe}_2\text{O}_4 \) (0.0 \( \leq x \leq 1.0 \)) catalysts were charge to the reactor. The mixture was heated to 343 K while stirring a solution of 2.5ml (25mmol) of hydrogen peroxide (30% aq. Merck) was added followed
by addition of 6.41g (200 mmol) methanol dropwise to the above mixture over a period of 45 min. Aqueous 1N sodium hydroxide was also added simultaneously to maintain the pH between 7.5 to 8.0. After 6 hours of reaction, the liquid product was cooled down to room temperature and the catalyst was separated by filtration. The product was diluted with 25 ml of water and extracted with three 20 ml portion of dichloromethane after which the extraction liquid was dried by adding anhydrous sodium sulphate to it. The extracted solution was concentrated and was analyzed by QP 5050 Shimadzu gas chromatography and mass spectroscopy (GCMS) equipped with a XE-60 capillary column (30m×0.25×0.3m) and a flame ionization detector. The injector and column temperature were 280 and 140 °C respectively. 3-Nitrotoluene (99+% Aldrich) was used as an internal standard.

4A.3.2 Selective epoxidation of cyclohexene

The catalytic activity test was carried without precautions against molecular oxygen in air. Within a round-bottom flask of 25ml capacity placed in temperature controlled oil bath, the catalyst (5-30 mg) was added to a solution of cyclohexene (0.5 ml, 5mmol) in acetonitrile (5 ml). The reaction mixture was stirred with magnetic stirrer at 1000 rpm and heated until the reaction temperature was finally maintained at a desired value (40-80 °C). The reaction was started by the aqueous solution of 30 wt. % ureated H₂O₂ (UHP) (0.04- 0.79 ml, 0.5- 10mmol) into the mixture. After 3 h of further stirring, aliquot was withdrawn from the reaction mixture, filtered and injected to gas chromatograph equipped with flame ionization detector (FID) for determination of product composition. Control experiments, reacting cyclohexene in acetonitrile with ureated H₂O₂ in absence of catalyst, were also comparatively investigated. Identification of products was performed using a gas chromatograph-mass spectrometer (XE-60 capillary column (30m×0.25×0.3m) with an electron ionization detector. The analysis revealed that the main products from the reaction are cyclohexene oxide (desired product), cyclohex-2-en-1-ol (undesired product) and cyclohex-2-en-1-one (undesired product). Selectivity is
always calculated with respect to the converted cyclohexene, while the percent yield of cyclohexene oxide calculated with respect to the selectivity of cyclohexene oxide.

4A.4 Optimization of reaction conditions

4A.4.1 Effect of chemical composition of catalysts

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**Fig.6.** Effect of chemical composition of the catalyst towards (A) the epoxidation of styrene where a-styrene conversion, b- selectivity of styrene epoxide, c- phenyl acetaldehyde, d- 1-phenyl-1,2-diol and e- % yield of epoxide and (B) the epoxidation of cyclohexene, (a) cyclohexene conversion, (b) selectivity of cyclohexene oxide, (c) cyclohex-2-ene-1-ol, (d) cyclohex-2-ene-1-one and (e) % yield of epoxide.

The catalytic activity of oxides depends on the ability of the ions to be oxidized and reduced. Gao et.al, [4] has reported the selective oxidation of styrene to benzaldehyde.
over alkaline earth metal ferrites, where phenyl aetaldehyde and epoxides are minor products in presence of hydrogen peroxide as the oxidizing agent. The use of pure CaFe$_2$O$_4$ or SrFe$_2$O$_4$ catalyst with aqueous hydrogen peroxide often results in extensive hydrolysis of epoxide to give benzaldehyde and phenyl aetaldehyde as desirable products. In present study our efforts have been for the synthesis of hydrophobic catalyst to prevent the further hydrolysis of epoxide. The catalytic efficiency of strontium substituted calcium ferrites is checked, under the similar reaction conditions, towards the selective epoxidation of styrene. the results are shown in Fig. 6A.

Among the various catalysts CaFe$_2$O$_4$ shows least reactivity towards the epoxidation of styrene with 48 mol% styrene conversion and 24.4 mol% selectivity and 11.7% yield of styrene epoxide where as the selectivity of benzaldehyde is 62.3 mol%. Changing the composition of CaFe$_2$O$_4$ by substituting calcium with strontium the catalytic efficiency toward the epoxidation of styrene becomes better. In comparison to all the catalyst Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ shows the best catalytic performance with 49.6% styrene conversion with 95.8% selectivity and 47.5% yield of styrene epoxide. As the concentration of strontium increases from 0.4 to 0.8 the styrene conversion increases up to 57.6% but the selectivity and yield of epoxide decreases to 37.2% and 21.43% respectively. When the same reaction is carried out in presence of SrFe$_2$O$_4$, under similar reaction conditions, it shows least activity towards the epoxidation of styrene with 52.8% conversion and 26.4% selectivity of epoxide where as the selectivity of benzaldehyde up to 64.7 mol%.

The efficiency of the catalyst can be improved by substituting the divalent strontium metal ion with different concentration to the tetrahedral site of the calcium ferrite catalyst. As the concentration of x increases, the acidity of the system increases with corresponding reduction in basicity [28]. Similarly as the concentration of ‘x’ increases, Sr$^{2+}$ ions isomorphically remove Fe$^{3+}$ ion from the Oh to Td sites due to greater site preference energy of Sr$^{2+}$ ions than Fe$^{3+}$ ions. This means that the substitution of Fe$^{3+}$ ions by Sr$^{2+}$ ions at the Oh sites creates stronger acid sites than those due to Fe$^{3+}$ ions. The influence of Sr$^{2+}$ and Ca$^{2+}$ indicate that the composition of the substituted ferrite is a decisive factor for its catalytic activity suggesting that there is a synergistic effect
between the metal ions in a Sr-Ca and Sr-Fe on the active surface of the ferrite. From Fig. 6 it is clear that the composition containing both Sr$^{2+}$ and Ca$^{2+}$ are more active than pure CaFe$_2$O$_4$ and SrFe$_2$O$_4$. When Sr$^{2+}$ and Ca$^{2+}$ are in intimate contact in the Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ system, the different reaction steps may sequentially occur over each metal, resulting in an enhanced activity compare to the parent ferrites.

The best activity of catalyst Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ of the series toward the selective epoxidation of styrene may be due to the insertion of structural defects in the catalyst [29]. Also the ionic radius of Ca$^{2+}$ (1.14 Å) is less than that of Sr$^{2+}$ ion (1.32 Å), therefore cell volume should be slightly affected. It is observed that, in the styrene epoxidation reaction, the Ca$^{2+}$ / Sr$^{2+}$ ratio is crucial in determination of total activity towards the reaction and selectivity for the products. Among all the substituted materials, Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ where the Ca$^{2+}$ / Sr$^{2+}$ ratio is highest has the best rate for epoxidation of styrene. Thus to summarize simultaneous participation of both metals i.e. Ca$^{2+}$ and Sr$^{2+}$ favors the epoxidation of styrene reaction with better conversion of styrene and percent yield of styrene epoxide.

Role of NaOH in epoxidation of styrene
In this study, we observed that in presence of NaOH both conversion and styrene oxide selectivity was higher than that in case of CaFe$_2$O$_4$ and SrFe$_2$O$_4$ alone. As described in chapter 3 we have reported the selective oxidation of styrene over CaFe$_2$O$_4$ and SrFe$_2$O$_4$, where benzaldehyde was found to be a major product while the epoxides formed only up to 10mol% in presence of 30% H$_2$O$_2$ as oxidizing agent. In this work the same reaction is carried out over Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ catalysts in presence and absence of NaOH. From the observations it is clear that the NaOH plays important role in styrene epoxidation reaction. The results are shown in Fig.7. When the reaction is carried out in absence of NaOH conversion of styrene takes place up to 53.2mol% with 70.3mol% selectivity and 37.4% yield of epoxide respectively. The same reaction when carried out in presence of 1 mL NaOH (1M) the styrene conversion is slightly decreased to
51.3mol%, while the selectivity and yield of styrene epoxide is increased up to 89.1mol% and 45.71%.

![Graph showing conversion, selectivity, and yield of styrene epoxide.]

**Fig. 7** Effect of concentration of NaOH (1M) towards the epoxidation of styrene over Sr0.6Ca0.4Fe2O4 catalyst. Reaction conditions: styrene- 50mmol, Oxidant- 25mmol 30% H2O2, catalyst- Sr0.6Ca0.4Fe2O4 (50mg), time- 12h and temperature- 50°C.

When the same reaction is carried out in presence of 2mL NaOH (1M) the styrene conversion is reduced to 49.6mol% but the selectivity and yield of epoxide increased up to 95.8mol% and 47.5%, while in presence of 3mL NaOH (1M) the styrene conversion as well as selectivity of epoxide decreases to 46.5mol% and 92.6mol% respectively with 43.1% yield.

From the observation it is clear that as the concentration of NaOH increases the styrene conversion gradually decreases while the selectivity of styrene epoxide increases up to 2mL NaOH. The enhancement of epoxide selectivity in presence of NaOH is due to the suppression of hydrogen bonding with the Lewis acid centers on the surface of catalyst.

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and hence the isomerization of styrene epoxide to phenylacetaldehyde is eliminated [28]. While for 3 ml NaOH the styrene conversion decreases along with the selectivity of epoxide may be due to excess concentration of NaOH, the hydroxyl ion compete the styrene molecules and block most of the active sites on the surface of catalyst.

As shown in Fig. 6B the cyclohexene epoxidation 56.04 mol% cyclohexene conversion takes place over CaFe$_2$O$_4$ with 26.86% selectivity of epoxide while in case Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ the conversion as well selectivity of epoxide slightly decreases to 52.3 mol% and 21.48% respectively. When the same reaction is carried out over the surface of Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ the cyclohexene conversion increases to 63.45 mol% with 27.36% selectivity of cyclohexene epoxide. Further increase in the concentration of strontium in calcium ferrite the conversion decreases gradually 57.82mol%, 51.63mol% and 45.87mol% over the surface of Sr$_{0.6}$Ca$_{0.4}$Fe$_2$O$_4$, Sr$_{0.8}$Ca$_{0.2}$Fe$_2$O$_4$ and SrFe$_2$O$_4$ catalysts respectively. The activity of the catalyst Sr$_{0.6}$Ca$_{0.4}$Fe$_2$O$_4$ shows the better activity toward the selective epoxidation of cyclohexene, it may be due to the insertion of structural defects in the catalyst. The ionic radius of Ca$^{2+}$ is (0.89 Å) is less than that of Sr$^{2+}$ ion (1.13 Å). Therefore cell volume should be very slightly affected. However, in order to preserve the electro neutrality upon the substitution, an increase of the iron oxidation state from Fe$^{3+}$ to Fe$^{4+}$ must occur and/ or oxygen vacancies must be generated. In other words, the change in the cell volume is a direct effect of the existence of some iron in oxidation state (IV) and consequently confirms its presence. As the concentration of strontium increases i.e. x = 0.4 and x = 0.6 onwards the cell volume increases and the activity of the catalyst found to be decreased towards the epoxidation of styrene and cyclohexene respectively.

**4A.4.2 Effect of solvent on epoxidation**

The nature of the solvent plays a very important role for heterogeneous catalysis in the liquid phase: the solvent can influence the rate of reaction by the solvation of reactants and intermediates in solution. The role of solvents is examined towards the selective
epoxidation of styrene under the optimized condition of time, temperature, catalytic amount etc. the results are shown in Fig. 8A.

**Reaction Conditions:** Styrene- 50mmol; oxidant- 25mmol 30% H₂O₂; catalyst-Sr₃Ca₁₂Fe₂O₁₉; amount of catalyst-50 mg; time- 12h; temperature- 50°C. Optimized Solvent: CH₃CN + CH₄OH

**Reaction Conditions:** Cyclohexene-5mmol; oxidant- 1.25mmol 30% H₂O₂; catalyst-Sr₃Ca₁₂Fe₂O₁₉; amount of catalyst-25mg; time- 3h; temperature-60°C. Optimized Solvent: CH₃CN

Fig. 8. Effect of solvent towards (A) the epoxidation of styrene where a- styrene conversion, b- selectivity of styrene epoxide, c- phenyl acetaldehyde, d- 1-phenyl-1,2-diol and e- % yield of epoxide and (B) the epoxidation of cyclohexene. (a) cyclohexene conversion, (b) selectivity of cyclohexene oxide, (c) cyclohex-2-ene-1-ol, (d) cyclohex-2-ene-1-one and (e) % yield of epoxide.

When the reaction is carried out in presence of polar and protic solvent like methanol, ethanol and water the catalyst shows a poor performance with 26.9 mol%, 24.7 mol% and 18.6 mol% styrene conversion respectively. The molecules of these solvents can affect the rate by competing with reactant molecules for active sites on the surface of a
heterogeneous catalyst [30]. But when the same reaction is carried out in aprotic solvent like acetonitrile the styrene conversion increased up to 41.7 mol% along with 82.1 mol% selectivity and 34.2% yield of styrene epoxide. Acetonitrile along with methanol in a proportion of 2:3 serves just as a solvent system in the epoxidation of styrene, the conversion of styrene increased to 49.6 mol% with 95.8 mol% selectivity and 47.5% yield of styrene epoxide. Secondly reaction in presence of acetonitrile with methanol can decrease the rate of ring opening reaction of styrene oxide to benzaldehyde and results in an increase the selectivity of styrene oxide [31]. The use of polar solvents favors the oxidation of double bond hence the mixture of CH$_2$OH and CH$_3$CN is found to be a better solvent.

In case of cyclohexene epoxidation over Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ catalyst in different reaction medium by keeping all other parameter constant, we observed that maximum conversion of cyclohexene takes place up to 63.49 mol% in CH$_3$CN with 43.1 mol% selectivity and 23.36% yield of cyclohexene epoxide. Our results shows that when the same reaction was carried out in aprotic solvent like tertiary butyl alcohol, acetone and toluene conversion as well the epoxide selectivity is higher than in methanol the results are shown in Fig. 8B. This may be due complete miscibility of the cyclohexene and oxidizing agent H$_2$O$_2$ in CH$_3$CN which can accelerate the co-ordination between the substrate and oxidant.

### 4A.4.3 Effect of temperature

The effect of temperature on the epoxidation of styrene is examined at the optimized condition of time, substrate/ H$_2$O$_2$ molar ratio, solvent, 1ml. NaOH (1M), catalytic amount etc. the results are shown in Fig. 9A. Epoxidation of styrene is carried out varying the temperature from 30 °C to 70 °C with the interval of 10 °C. At 30 °C only 33.4 mol% of styrene conversion was observed with 57.2 mol% selectivity and 19.1% yield of styrene epoxide. To see the effect of temperature the same reaction was carried out at 40 °C, the styrene conversion increases to 38.1 mol% with 71.4 mol% selectivity and 27.2% yield of epoxide.

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Reaction Conditions: Styrene-50mmol; oxidant- 25mmol 30% H₂O₂; catalyst- Sr₀₂Ca₀₆Fe₂O₆ amount of catalyst-50 mg; time- 12h; Solvent- acetonitrile + methanol and 2mL NaOH Optimized Temperature: 50 °C

Reaction Conditions: Cyclohexene-5mmol; oxidant- 1.25mmol 30% H₂O₂; catalyst-Sr₀₄Ca₀₄Fe₂O₄ amount of catalyst- 25mg; time- 3h; Solvent- Acetonitrile (5mL) Optimized Temperature: 60 °C

Fig.9. Effect of temperature towards (A) the epoxidation of styrene where a-styrene conversion, b- selectivity of styrene epoxide, c- phenyl acetaldehyde, d- 1-phenyl-1,2-diol and e- % yield of epoxide and (B) the epoxidation of cyclohexene, (a) cyclohexene conversion, (b) selectivity of cyclohexene oxide, (c) cyclohex-2-ene-1-ol, (d) cyclohex-2-ene-1-one and (e) % yield of epoxide.

As the rise in temperature is in favor, the same reaction was carried out at 50 °C the styrene conversion was increased to 49.6 mol% with 95.8 mol% selectivity and 47.5% yield of epoxide. When the same reaction was carried out at 60 °C and 70 °C, the marginal increment in the styrene conversion was found up to 51.8 mol% and 53.9 mol% with reduction in selectivity of epoxide to 88.1 mol% and 78.9 mol% respectively. This is because at higher temperature the rate of nucleophilic attack is also enhanced which
finally leads to enhance the selectivity of side products like benzaldehyde and phenyl acetaldehyde. From these observations 50 °C is the optimized temperature for the better conversion of styrene to styrene epoxide. Up to the optimized temperature the rate of reaction was increased while, at high temperature the adverse effect on the adsorption of substrate and reagent molecule on the surface of catalyst was seen.

The effect of temperature on the epoxidation of cyclohexene also studied over Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ catalyst at different temperature from 40°C to 80°C by keeping other reaction condition constant the results are summarized in Fig. 9B. At 40°C temperature 43.56mol% conversion of cyclohexene was found with only 46.32mol % selectivity and 20.18% yield of cyclohexene epoxide. When the same reaction was carried out at 50°C temperature the conversion as well as selectivity increases to 57.56mol% and 44.25mol% respectively. As the temperature increased to 60°C the maximum conversion (63.49 mol%) of cyclohexene takes place with 43.1mol% selectivity and 27.36% yield of epoxide. But at higher temperature 70 and 80°C the conversion of cyclohexene is almost constant around 64mol% but the selectivity of cyclohexene epoxide decreases to 36.54mol% and 23.65mol% with 23.47 and 15.28% yield respectively.

4A.4.4 Effect of time

The styrene conversion and product selectivity is plotted as a function of reaction time, at 50 °C, in CH$_3$CN and CH$_3$OH as reaction medium in presence of 2 mL NaOH (1M) over 0.05 g of Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ catalyst. Under these conditions, the reaction was carried out by varying the time from 3 h to 15 h. The results are shown in Fig. 10A. It is found that the percentage conversion of styrene increases from 23.7mol% to 49.6mol% with increase in the reaction time from 3 to 12 h respectively and then marginal increment upto 50.8mol% with further rise in reaction time to 15 h. The selectivity of epoxide also increases from 70.6 mol% to 95.8 mol% with increase in the percent yield from 16.3 to 47.5 for the reaction time from 3 to 12 h respectively while the selectivity and percent yield of epoxide slightly decreases to 88.6 mol% and 45% respectively.
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**Reaction Conditions:** Styrene-50mmol; oxidant- 25mmol 30% H$_2$O$_2$; catalyst- Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ amount of catalyst-50 mg; temperature- 50°C; Solvent- acetonitrile + methanol and 2mL NaOH

**Optimized Time:** 12 h

**Reaction Conditions:** Cyclohexene-5mmol; oxidant- 1.25mmol 30% H$_2$O$_2$; catalyst-Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ amount of catalyst-25mg; temperature- 60°C; Solvent- Acetonitrile (5mL)

**Optimized Time:** 3 h

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*Fig.10.* Effect of reaction time towards (A) the epoxidation of styrene where a- styrene conversion, b- selectivity of styrene epoxide, c- phenyl acetaldehyde, d- 1-phenyl-1,2-diol and e- % yield of epoxide and (B) the epoxidation of cyclohexene, (a) cyclohexene conversion, (b) selectivity of cyclohexene oxide, (c) cyclohex-2-ene-1-ol, (d) cyclohex-2-ene-1-one and (e) % yield of epoxide.

The result indicates that as the reaction is run for long time the selectivity of byproducts starts to increase. 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. The concentration of H$_2$O$_2$ reduced continuously with the reaction going on, and less amount of H$_2$O$_2$ was not favorable to further oxidation of styrene therefore more byproducts are formed hence the selectivity of epoxide decreases. Moreover, the undesirable products were also found to be formed.
when the reaction was allowed to run for long time. From the results it can be concluded that at 12 h the selectivity of styrene epoxide is better with respect to styrene conversion.

The effect of reaction time is studied by carried out the epoxidation of cyclohexene over the surface of Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ catalyst prepared by citrate gel combustion method: the results are shown in Fig.10B. The reaction is carried out at five different times from 1 to 5 h, when the reaction is run for 1h: only 21.36 mol% conversion of cyclohexene takes place with 26.54 mol% selectivity. For 2h the cyclohexene conversion increases to 36.25 mol%, the selectivity and percentage yield of cyclohexene epoxide also increases to 38.45 mol% and 13.94% respectively. When the same reaction was run for 3 h, 63.49 mol% conversion of cyclohexene takes place with 43.1 mol% and 27.36% selectivity and yield of epoxide respectively. Cyclohexene conversion is further increases when the reaction time increases to 4 h and 5 h: the conversion of cyclohexene increases to 68.64 mol% and 72.35 mol% respectively but the selectivity of epoxide decreases to 24.35 mol% and 15.26 mol% respectively. The results indicate that when the reaction is carried out for long time the desirable products like epoxides get hydrolyzed to give 1,2-ethane diols, on further oxidation of diols to give enones as another byproduct. From these results 3h is the optimized time to get the maximum %yield of cyclohexene epoxide.

4A.4.5 Effect of catalysts amount

In order to check the effect of the amount of catalyst during the selective epoxidation of styrene, the reaction was carried out over Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ catalyst in mixture of acetonitrile and methanol as solvent in presence of 2 mL NaOH (1M) with 25, 50, and 75 mg of catalyst for 12 h and 50°C. The percentage conversion and percentage selectivity is shown in Fig. 11A. The effect of amount of catalyst was studied keeping all other parameters (reaction time, temperature, mole ratio of substrate: H$_2$O$_2$) constant. It can be seen (Fig. 11A) that % conversion of styrene is 39.7 mol% with 92.5 mol% selectivity.
and 36.7% yield of styrene epoxide over 25mg of catalyst. For 50 mg of catalyst the styrene conversion increases to 49.6 mol% while the selectivity and % yield of epoxide increases to 95.8 mol% and 47.5% respectively. Further increase in catalytic amount up to 75 mg catalyst shows lower styrene conversion 37.1 mol % with 83.7 mol% selectivity and 31.1% yield of styrene epoxide respectively.

Fig. 11. Effect of catalyst amount towards (A) the epoxidation of styrene where a-styrene conversion, b- selectivity of styrene epoxide, c- phenyl acetaldehyde, d- 1-phenyl-1,2-diol and e- % yield of epoxide and (B) the epoxidation of cyclohexene, (a) cyclohexene conversion, (b) selectivity of cyclohexene oxide, (c) cyclohex-2-ene-1-ol, (d) cyclohex-2-ene-1-one and (e) % yield of epoxide.

At the catalyst loadings of 25mg and 50mg, the increase in the styrene conversion with the catalyst loading is due to the increase of styrene epoxidation rate. However, at the
higher catalyst loadings, the $\text{H}_2\text{O}_2$ decomposition rate during the epoxidation is much higher than that at lower loading. At 75mg sufficient $\text{H}_2\text{O}_2$ is not available for the epoxidation, which ultimately leads to a lower styrene conversion at the higher catalyst loadings.

The effect of concentration of catalyst towards the epoxidation of cyclohexene is examined by keeping the constant concentration of cyclohexene (5mmol), the results are shown in Fig. 11B. The reaction is carried over the surface of five different quantities of the catalyst prepared by citrate gel combustion method. Initially the reaction is carried out over 10 mg of catalyst 34.24 mol% conversion of cyclohexene takes place over $\text{Sr}_{0.4}\text{Ca}_{0.6}\text{Fe}_2\text{O}_4$ catalyst with 36.5 mol% selectivity of epoxide. When the catalyst amount increases further to 15mg, 20mg and 25mg the cyclohexene conversion, selectivity and percentage yield of cyclohexene epoxide is also gradually increases. The maximum conversion of cyclohexene is found over 25 mg of catalyst up to 63.49 mol%, with 43.1 mol% selectivity and 27.36% yield of cyclohexene epoxide. As the catalyst amount increases to 30 mg the excess concentration of catalyst with respect to concentration of cyclohexene retard the reaction by lowering the conversion of cyclohexene to 54.6 mol% with 43.4 mol% selectivity 23.7% yield of epoxide it may be due to the simultaneously occurring of $\text{H}_2\text{O}_2$ decomposition and epoxidation reactions, the reason for lower activity at higher amount of catalyst does may possibly be due to adsorption or chemisorptions of two reactants on separate catalyst particles, thereby reducing the chance to interact. The results show that 25mg of catalyst is the optimum amount to obtain maximum conversion of cyclohexene with better selectivity of cyclohexene epoxide.

4A.4.6 Effect of $\text{C}_8\text{H}_8/\text{H}_2\text{O}_2$ molar ratio

The styrene conversion is observed up to 23.0 mol% in the presence of catalyst without using any oxidant. This clearly indicates that the possibility of the reaction occurring due to the participation of lattice oxygen of catalyst. However, the reaction does not give the selective product. The selectivity of epoxide is only 30.0 mol% with 6.9% yield. In absence of catalyst and in presence of 30% $\text{H}_2\text{O}_2$ the reaction proceed up to 24.0 mol%.
but here also the reaction proceed randomly and give 32.0 mol% of epoxide 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 1:0.25, 1:0.5, 1:1, 1:2 and 1:3, for which 0.05 g of catalyst were taken in 10 ml of solvent at 50 °C. The results are shown in Fig. 12A.

**Fig. 12.** Effect of substrate/ H₂O₂ molar ratio towards (A) the epoxidation of styrene where a- styrene conversion, b- selectivity of styrene epoxide, c- phenyl acetaldehyde, d- 1-phenyl-1,2-diol and e- % yield of epoxide and (B) the epoxidation of cyclohexene. (a) cyclohexene conversion, (b) selectivity of cyclohexene oxide, (c) cyclohex-2-ene-1-ol, (d) cyclohex-2-ene-1-one and (e) % yield of epoxide.
From the results it is observed that the conversion of styrene is comparatively less when the styrene/ H_2O_2 molar ratio is 1:0.25 (about 27.3 mol %). This may be due to significantly reduced •OH radicals as less amount of H_2O_2 compete with excess styrene for coordination. As the concentration of H_2O_2 increases (1:0.5) there is increase in the styrene conversion as well as increase in the selectivity of styrene epoxide. The percentage conversion of styrene is 49.6% and the selectivity and yield for epoxide is 95.8 mol% and 47.5% respectively. At this molar ratio of 1:0.5, H_2O_2 may freely coordinate to metal and decompose to form •OH radical. When the same reaction was carried out at styrene/ H_2O_2 molar ratio 1:1, 1:2 and 1:2 in presence of 0.05 g catalyst the styrene conversion increases as 53.2 mol%, 57.2 mol% and 63.7 mol% while the selectivity of epoxide decreases to 81.3 mol%, 67.5 mol% and 33.5 mol% respectively.

The effect of cyclohexene/ H_2O_2 molar ratio also studied towards the epoxidation of cyclohexene the results are shown in Fig. 12B. Initially the reaction carried in absence of H_2O_2 only 11.9 mol% conversions was found this result indicates the need of H_2O_2. From the results it is observed that the conversion of cyclohexene is comparatively high i.e. 63.5 mol% with 43.1 mol% selectivity of epoxide when the cyclohexene/ H_2O_2 molar ratio is 1:0.25. At this molar ratio of 1:0.25, H_2O_2 may freely coordinate to metal and decompose to form •OH radical. When the reaction was carried out at cyclohexene/ H_2O_2 molar ratio 1:0.5, 1:1 and 1:2 in presence of 25mg catalyst the styrene conversion increases as 67.6 mol%, 73.3 mol% and 79.7 mol% while the selectivity of epoxide decreases to 37.6 mol%, 31.5 mol% and 27.8 mol% respectively.

In the both the cases as the concentration of H_2O_2 increases the selectivity of epoxide decreases firstly due to the later nucleophilic attract of on the epoxide and secondly due to the excess of water content in hydrogen peroxide that inhibits the coordination of oxidants with the active sites of catalyst [32].

4A.5 Reusability of catalyst

The economy of the catalyst depends on how many times it can be used in organic transformations as catalyst. The reusability of the catalysts was checked by carrying out
the same reaction for number of times under similar reaction condition. The reusability of the Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ towards styrene epoxidation is examined by using the utilized catalyst in the next cycles. For first cycle 49.6 mol% styrene conversions with 47.5% yield.

**Reaction Conditions:** catalyst-
Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ amount of catalyst-50mg; time- 12h; temperature- 50°C;
Solvent- CH$_3$CN + CH$_3$OH
molar ratio-1:0.5 and 2mL NaOH

**Reaction Conditions:** catalyst-
Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ amount of catalyst-25mg; time- 3h; temperature- 60°C;
Solvent- Acetonitrile (5mL), molar ratio-1:0.25

*Fig. 13.* Reusability of the catalyst towards (A) the epoxidation of styrene where a-styrene conversion, b- selectivity of styrene epoxide, c- phenyl acetaldehyde, d- 1-phenyl-1,2-diol and e- % yield of epoxide and (B) the epoxidation of cyclohexene, (a) cyclohexene conversion, (b) selectivity of cyclohexene oxide, (c) cyclohex-2-ene-1-ol, (d) cyclohex-2-ene-1-one and (e) % yield of epoxide.
When the same catalyst used for second and third cycle the styrene conversion is decreases to 46.35 mol% and 41.56 mol% respectively while the percent yield of styrene epoxide also decreases to 40.6 and 33.9 respectively the results are shown in Fig. 15A. In case of cyclohexene epoxidation in the first cycle at optimized conditions the cyclohexene conversion and selectivity of epoxide is up to 67.15 mol% and 27.4% respectively. Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ was used after simple filtration for separation and washing with water and acetone and drying at 150°C. The catalyst was used at least for three cycles by 13% loss in activity, the results are shown in Fig. 15B: Catalyst deactivation may occur due to chemical, mechanical and thermal reason [33]. The chemical deactivation is common in catalyst and caused by strong chemisorption of species which blocks the active sites of the catalyst furthermore. The XRD pattern (not shown) of the reused catalyst was identical to that of the original, indicating that the crystallinity of the catalyst was not affected during the reaction.

4A.6 Conclusions:

1. Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ (0.0 ≤ x ≤ 1.0) catalyst was successfully synthesized by citrate gel method. Thermal analysis of strontium calcium iron citrate precursor gives the information about the temperature at which the formation of strontium ferrite takes place. The phase analysis by XRD, metal oxygen stretching frequencies by FTIR, morphology and elemental composition by SEM and EDS, and elemental analysis by chemical method confirms the formation of single phase Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ (0.0 ≤ x ≤ 1.0). The surface area determined by BET method, for Sr$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ and Sr$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ are found comparatively more than that of the other catalysts prepared by the same method.

2. As the concentration of ‘x’ increases, Sr$^{2+}$ ions isomorphically remove Fe$^{3+}$ ion from the Oh to Td sites due to greater site preference energy of Sr$^{2+}$ ions than Fe$^{3+}$ ions, which means that the substitution of Fe$^{3+}$ ions by Sr$^{2+}$ ions in the Oh sites creates stronger acid sites than those due to Fe$^{3+}$ ions.
3. $\text{Sr}_0\text{.}_2\text{Ca}_0\text{.}_8\text{Fe}_2\text{O}_4$ among all is found to be an efficient catalyst for selective oxidation of styrene to styrene epoxide suggesting a synergistic effect between the metal ion in the form of Sr-Ca and Sr-Fe on the active surface of ferrite.

4. Among all the substituted materials, $\text{Sr}_0\text{.}_2\text{Ca}_0\text{.}_8\text{Fe}_2\text{O}_4$ where the $\text{Ca}^{2+} / \text{Sr}^{2+}$ ratio is highest has the best rate for epoxidation of styrene. The conversion of styrene up to 49.6 mol% along with the selectivity and percent yield of styrene epoxide are 95.8 mol% and 47.5 respectively.

5. Temperature 50 °C, time 12 h, styrene/ $\text{H}_2\text{O}_2$ molar ratio as 1:0.5, catalyst amount 0.05g, favors the selective epoxidation of styrene. Solvents have marked influence on the product distribution in selective epoxidation of styrene; mixture of acetonitrile and methanol seems to be the best solvent. The enhancement in epoxide selectivity in presence of NaOH is due to suppression of hydrogen bonding between the acid centers of catalyst and oxygen from epoxide which prevent ring opening and hence the isomerization of styrene epoxide to phenyl acetaldehyde is eliminated.

6. Maximum conversion of cyclohexene of 63.5 mol% with 43.1 mol% selectivity and 27.4% yield is observed over $\text{Sr}_0\text{.}_4\text{Ca}_0\text{.}_6\text{Fe}_2\text{O}_4$ catalyst prepared by CGC method because citric acid plays two important role in this method, the first as the chelate agent to form homogeneous, steady and transparent sol and second as fuel to provide auto combustion action, the function is just like the carbamide in other combustion systems. Temperature 60 °C, time 3 h, aprotic and polar solvent like acetonitrile and catalyst amount 25mg, are favors the selective epoxidation of cyclohexene.
4A.7 References:


Chapter IV

CHARACTERIZATION AND CATALYTIC ACTIVITY OF SUBSTITUTED ALKALINE EARTH METAL FERRITES

PART B:
CHARACTERIZATION AND CATALYTIC ACTIVITY OF BARIUM SUBSTITUTED CALCIUM (BSC) FERRITE
4B.1 Introduction:
The functional properties of powder particles can be tailored by changing the intrinsic properties of the constituent material and/or by changing their morphology. The intrinsic properties of the particle materials can usually be tailored by changing their composition, for example, by doping or by substituting. An alternative method involves combining the intrinsic properties of different materials in the composite particles. This strategy can lead to the appearance of additional functionalities when the intrinsic properties of different materials are coupled. Spinel ferrites are well known catalysts for various processes like oxidative dehydrogenation of hydrocarbons, decomposition of alcohols, selective oxidation of carbon monoxide, decomposition of hydrogen peroxide and hydrodesulphurization [1-3]. These properties are strongly dependent on their shape, size, crystallinity and the distribution of the cations among the tetrahedral and octahedral sites of the spinel structure. It has been reported that the electronic properties of the Fe$^{3+}$ in ferrites can be strongly modified with the introduction of a metal with a smaller atomic radius as well as by the introduction of a metal with higher electronegativity than iron, like rhodium [4-6].

In order to achieve highly homogeneous ultra-fine particles and avoid the milling process, different synthesis techniques have been used to prepare $\text{BaFe}_{12}\text{O}_{19}$, such as chemical co-precipitation [7-9], glass crystallization [10-12], hydrothermal [13], micro emulsion [14] and sol-gel methods [15,16]. The most important feature in these methods is to use liquid media to intimately mix the required metallic constituent on an ionic level. Mixing the required metallic ions homogeneously in atomic scale can form the required oxide phases at relatively low temperatures, resulting in small particles with uniform compositions and a narrow size distribution.

Mixed oxides usually have better performance than the simple mixture of the corresponding single oxides and show properties and stability dependent on the nature and stoichiometry of the metallic ions in the final mixture. Modeling of the properties is then possible by changing the oxide composition [17-20]. In spinel type oxides activity is usually associated with the amount and nature of the trivalent cations [18] being those considered as the active sites. In the case of Fe$_3$O$_4$ surface Fe$^{3+}$ cations are
commonly viewed as the active sites [21]. An increase of the catalytic activity is observed for Ni-substituted Fe$_3$O$_4$ electrodes [22].

At present, environmental pollution has far-reaching negative consequences in the life of humans. The degradation of organic pollutants has become the focus of the research efforts in today’s scientific world. Pollutants that emitted from the various sources pose severe ecological problems because the biodegradation of these pollutants is often very slow and conventional treatments are mostly ineffective and not environmentally compatible.

The heterogeneous photo catalysis is an efficient technique to destroy organic pollutants in water [23]. This technique is based upon the use of UV-irradiated semiconductors most of the researchers have used TiO$_2$ and modified TiO$_2$. But the band gap energy of TiO$_2$ is about 3.2 eV i.e. $\lambda_{\text{max}} = 390$ nm, the electron-hole pairs are created. Because of this large band gap the TiO$_2$ or modified TiO$_2$ are only useful in ultraviolet light which is more hazardous and dangerous also. The modified TiO$_2$-like TiO$_2$-coated silica [24], TiO$_2$-coated silicone sealants [25] are thermally not stable so that it can be useful at high temperature.

With consideration for previous results the goal of the present study was to examine the catalytic activity of substituted CaFe$_2$O$_4$ with different amount of barium under various experimental conditions. So we have synthesized a barium substituted strontium ferrite Ba$_x$Ca$_{1-x}$Fe$_2$O$_4$ (where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) by citrate gel combustion method. The synthesized material is well characterized by various techniques and the catalytic efficiency is checked towards the degradation of Rh-6G dye in aqueous medium. The factors affecting the rate of degradation like role of light and catalyst, pH of reaction medium, temperature, chemical composition of catalyst, calcination temperature, concentration of Rh-6G and reusability of catalyst are also studied.

4B.2 Results and discussion

4B.2.1 Thermal decomposition of the citrate precursor

TG and DTA curves recorded in static air at 10° C min$^{-1}$ and are shown in Fig. 1 (a-f). It is seen that one-to-one correlation exists between these thermo analytical curves indicating that the thermal effects are accompanied by mass loss. There are three
major steps in the decomposition process: dehydration, decomposition and decarboxylation of the alkaline earth metal citrate complex.

Fig. 1. TG-DTA curves of precursors for CaFe$_2$O$_4$ (A), Ba$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$ (B), Ba$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$ (C), Ba$_{0.6}$Ca$_{0.4}$Fe$_2$O$_4$ (D), Ba$_{0.8}$Ca$_{0.2}$Fe$_2$O$_4$ (E) and BaFe$_2$O$_4$ (F) prepared by citrate gel combustion method.

**Dehydration of the citrate precursor**

The number of water molecules adsorbed on the citrate precursor molecule varies depending upon the atmospheric humidity. The extra water can be removed by heating the citrate precursor from room temperature to 145°C, which is shown by the endothermic peak between 45°C to 145°C ([Fig. 1](#)). Removal of the coordinated water molecules of the citrate precursor takes place between 145°C and 275°C as shown by the second endothermic peak.

**Decomposition of the citrate precursor**
The decomposition of the citrate precursor is a multistep process in the temperature range of 150-450°C. The first endothermic peak occurred at 200°C in Fig. 1 (A) indicates the dehydration of precursor along with the decomposition of complex into the metal carbonates with mass loss of 56.3% up to 350°C temperature. In barium substituted calcium ferrite, where (x = 0.2) a sharp exothermic peak is found at 158°C indicate the fast decomposition complex in to metal carbonates with 33% mass loss in Fig. 1 (B) and two small shoulder exothermic peak detected at 230°C and 322°C assigns the conversion of metal carbonate into metal oxides with 21.2% mass loss. As the concentration of barium increases to x = 0.4 two intense exothermic peak were found at 168.5°C and 238°C with a total mass loss of 54.1% for the decomposition of complex into metal carbonates and carbonate to metal oxides respectively. For x = 0.6 the exothermic peaks are observed at 164°C and 326°C with a total mass loss of 53.3% for the decomposition of complex into metal carbonates and carbonate to metal oxides.

The further increment in the concentration of barium up to x = 0.8 three distinct exothermic peaks were found at 154°C, 197°C and 290°C with 54% mass loss assign the complete dehydration of precursor followed by the decomposition of the citrate ligand into metal carbonates and oxides. All these mass loss are in good agreement with the calculated values.

From these results it is found that the formation temperature of barium substituted calcium (BSC) ferrite is less than that of the formation temperature of pure CaFe$_2$O$_4$ and BaFe$_2$O$_4$ from their precursor. Hence we synthesized the BSC ferrite by citrate gel combustion method and characterized by various techniques as follows.

4B.2.2 FTIR study of barium substituted calcium (BSS) ferrite

Fig. 2(a-d) shows FTIR spectrum of barium substituted calcium ferrite, Ba$_x$Ca$_{1-x}$Fe$_2$O$_4$ where (a) x = 0.2, (b) x = 0.4, (c) x = 0.6 and (d) x = 0.8 calcined at 900°C for 2 h. No significant peaks are found below 1800 cm$^{-1}$ in all spectrum which indicates that the oxides are free from organic moiety. Two assigned absorption bands appeared around 662 cm$^{-1}$ and 635 cm$^{-1}$ attributed to stretching vibration of tetrahedral groups Ba$^{2+}$−O$^{2-}$ and that around 499 cm$^{-1}$ in spectra (d), and 501 cm$^{-1}$ in spectra (e) attributed to the octahedral group complex Fe$^{3+}$−O$^{2-}$. The stretching band at 499 cm$^{-1}$ and 501 cm$^{-1}$ is the characteristic band of barium spinel ferrite phase.
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. The absorption band between 1086 cm\(^{-1}\) and 1183 cm\(^{-1}\) and 771 cm\(^{-1}\) to 800 cm\(^{-1}\) resulted from the COO group. The spectrum also reveals that the carboxylate of the precursor transform into metal carbonate with the characteristic stretching location at 1429 cm\(^{-1}\), 1452 cm\(^{-1}\), 1466 cm\(^{-1}\) and 1474 cm\(^{-1}\) for the samples (a), (b), (c) and (d) calcined at 900 °C for 2 h.

**4B.2.3 X-ray diffraction analysis of barium substituted calcium (BSC) ferrite**

The barium substituted calcium ferrite (Ba\(_x\)Ca\(_{1-x}\)Fe\(_2\)O\(_4\); \(x = 0.2, 0.4, 0.6\) and 0.8) catalyst was prepared by citrate gel combustion method the XRD pattern are shown in **Fig.3**. The XRD pattern of the barium substituted calcium ferrite shows that the catalyst prepared by this method formed a single phase compounds with no impurity observed.
Fig. 3. X-ray diffraction pattern of a) CaFe$_2$O$_4$; b) Ba$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$; c) Ba$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$; d) Ba$_{0.6}$Ca$_{0.4}$Fe$_2$O$_4$; e) Ba$_{0.8}$Ca$_{0.2}$Fe$_2$O$_4$ and f) BaFe$_2$O$_4$ prepared by citrate gel method and calcined at 800 °C.

The X-ray diffraction analysis of the samples treated at 800°C temperature for 2 h has been carried out using Cu Kα radiation. Fig. 3 shows the XRD patterns of the parent calcium, barium ferrite and barium substituted calcium ferrite. A Fig. 3(a) is the XRD pattern of spinel type CaFe$_2$O$_4$ oxide where all the d spacing values are in good agreement with the standard data (JCPDS card no. 46-0100), while (f) is the XRD pattern of spinel type BaFe$_2$O$_4$ oxide where all the d spacing values are in good agreement with the standard data (JCPDS card no. 46-0113). The pattern (b), (c), (d) and (e) are of Ba$_{0.2}$Ca$_{0.8}$Fe$_2$O$_4$, Ba$_{0.4}$Ca$_{0.6}$Fe$_2$O$_4$, Ba$_{0.6}$Ca$_{0.4}$Fe$_2$O$_4$ and Ba$_{0.8}$Ca$_{0.2}$Fe$_2$O$_4$ oxides respectively. In XRD pattern (b) the new peak originates at 28.3 which represents the presence of barium, as the concentration of barium ion in (c), (d), (e) and (f) increases the intensity of the peak also increases (shown by asterisk in Fig. 3). The same observation was found in case of the peaks which indicate the presence of
calcium shown by hash (#). As the concentration of calcium decreases from (a) to (f) the intensity of the peak also decreases. The peak shown by dot is shifted towards its left from pattern (a) to (e) i.e. from 20 value 33.5 to 32.7 which indicate the substitution of metal ion (calcium ion) with lower atomic size by the metal ion (barium ion) with higher atomic size. The diffraction patterns also indicate that there is no second phase formed in the samples from (a) to (f). The average crystal size of the all samples (a-f) was calculated using Scherer’s law from the high intensity peak is in the range of 80nm to 97nm.

4B.2.4 Elemental analysis by X-ray florescence

The elemental analysis of barium substituted calcium ferrite is done by electron dispersive studies and confirmed by X-ray florescence spectroscopy. The result is summarized in Table 1. The percentage composition of the barium, calcium and iron are in good agreement with the calculated values.

Table 1: The elemental composition of barium, calcium and iron in barium substituted calcium ferrite $BaxCa_{1-x}Fe_2O_4$ (where $x = 0.2, 0.4, 0.6$ and $0.8$.)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Strontium (Sr)</th>
<th>Calcium (Ca)</th>
<th>Iron (Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(EDS)</td>
<td>(XRF)</td>
<td></td>
</tr>
<tr>
<td>Ba0.2</td>
<td>11.67</td>
<td>13.67</td>
<td>47.49</td>
</tr>
<tr>
<td></td>
<td>11.23</td>
<td>13.10</td>
<td>46.75</td>
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<tr>
<td></td>
<td>11.43</td>
<td>13.54</td>
<td>46.90</td>
</tr>
<tr>
<td>Ba0.4</td>
<td>21.57</td>
<td>9.44</td>
<td>43.86</td>
</tr>
<tr>
<td></td>
<td>21.05</td>
<td>8.92</td>
<td>42.93</td>
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<tr>
<td></td>
<td>20.95</td>
<td>9.23</td>
<td>43.15</td>
</tr>
<tr>
<td>Ba0.6</td>
<td>30.06</td>
<td>5.84</td>
<td>40.75</td>
</tr>
<tr>
<td></td>
<td>29.50</td>
<td>5.15</td>
<td>40.19</td>
</tr>
<tr>
<td></td>
<td>29.15</td>
<td>6.14</td>
<td>41.45</td>
</tr>
<tr>
<td>Ba0.8</td>
<td>37.42</td>
<td>2.7</td>
<td>38.05</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>37.10</td>
<td>2.1</td>
<td>37.34</td>
</tr>
</tbody>
</table>

4B.2.5 Scanning electron microscopy and electron dispersive spectra of BSC ferrites

Fig. 4 shows the SEM images of the barium substituted calcium ferrites $BaxCa_{1-x}Fe_2O_4$ (where $0.0 \leq x \leq 1.0$) synthesized by citrate gel method with different elemental composition. It can be seen from these micrographs that the variation in chemical composition have a significant influence on the morphologies of the synthesized products.
The micrographs were obtained on specimen without imposing any magnetic orientation for particles. The average particle size calculated from the SEM micrograph was approximately 2μm. The micrographs show irregular size of the particles along with agglomeration up to some extent.

4B.2.6 Surface area determination by BET method

The BET surface area of the various samples of barium substituted calcium ferrite (Ba$_x$Ca$_{1-x}$Fe$_2$O$_4$) catalysts calcined at 800 °C was also carried out. Among all the prepared catalysts the surface area of Ba$_x$Ca$_{1-x}$Fe$_2$O$_4$, where x = 0.4, 0.8 and 1.0 are 121.53 m$^2$/g, 136.43 m$^2$/g and 147.73 m$^2$/g respectively. The surface area of the other catalysts of composition i.e. x = 0.0, 0.2 and 0.6, are below 100 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).
4B.3 Photocatalytic activity of barium substituted calcium ferrite

We studied the degradation of Rh-6G as a model reaction to investigate the catalytic activity and degradation mechanism using $\text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4$; (where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) catalyst. Rh-6G is a type of dye molecule with a large and complicated structure. The structure of Rh-6G is shown below.

![Structural formula of Rhodamine-6G dye molecule](image)

The photocatalytic degradation of Rh-6G dye was studied in the presence of $\text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4$; (where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) catalyst in ambient light condition. 10mL of dye solution (50ppm) is taken in the reaction vessel of photo reactor and irradiated with light from mercury vapor lamp (wavelength 400 nm) by adding 10 mg of catalyst for stipulated time.

4B.4 Optimization of reaction conditions

In order to examine the catalytic activity of the material prepared we studied the effect of degradation of Rh-6G in the presence of pure and substituted alkaline earth metal ferrites. The rate of catalytic degradation of Rh-6G depends on several parameters such as pH of reaction medium, type of catalyst used, dye concentration, amount of catalyst and the type of source used for the purpose of irradiation.

4B.4.1 Selection of reaction system

The role of light and catalyst is examined by carrying out the reaction in four different reaction conditions like catalyst in dark, catalyst in presence of ordinary light, catalyst
in presence of ultraviolet radiation and without catalyst but presence of ordinary light. The extent of degradation of Rh-6G for different time interval is shown in Fig. 5.

**Fig. 5.** Effect of various reaction conditions towards the degradation of Rh-6G over \( \text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4; \) (where \( x = 0.0, 0.2, 0.4, 0.6, 0.8 \) and 1.0) in aqueous medium.

**Reaction conditions:** Catalyst- \( \text{Ba}_{0.8}\text{Ca}_{0.2}\text{Fe}_2\text{O}_4 \) calcined at 800 °C, amount of catalyst- 20mg, temperature- room temperature, pH of solution-7.5, concentration of Rh-6G-50ppm.

When the degradation was carried out in presence of catalyst but in dark the degradation of Rh-6G takes place up to 76.41% in 75min only. Then it was very necessary to check the role of catalyst towards the degradation in absence of catalyst but in presence of ordinary light for reaction condition, only 20.95% degradation was observed in 75min, this result highlights the important role of catalyst, the degradation in absence of catalyst may be due to the sonication of reaction mixture and mechanical stirring. The role of light and catalyst examined by carrying out the reaction in presence of both catalyst as well ordinary light the 94.22% Rh-6G get degraded in 75 min. The role of ultraviolet light in presence of catalyst was also
checked by carrying out the degradation reaction of Rh-6G, the maximum conversion takes place up to 84.7% in 45min but it decreases to 83.86% and 81.21% for 60min and 75min respectively. The rate of degradation decrease in UV light due to the recombination of e⁻ - h⁺ which decreases the rate of adsorption of Rh-6G molecule on the surface of catalyst. Hence to optimize the reaction condition the degradation reaction is carried out in presence of catalyst and ordinary light.

4B.4.2 Effect of chemical composition of catalyst

![Graph showing the effect of chemical composition of catalyst on the degradation of Rh-6G](image)

**Fig.6.** Effect of chemical composition of catalyst towards the degradation of Rh-6G over BaₓCa₁₋ₓFe₂O₄; (where x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) in aqueous medium.

**Reaction conditions:** Catalyst- BaₓCa₁₋ₓFe₂O₄ calcined at 800 °C, amount of catalyst-20mg, temperature- room temperature, pH of solution-7.5, concentration of Rh-6G-50ppm.

The effect of chemical composition of catalyst plays important role during the degradation of Rh-6G in aqueous medium which is examined by carrying out the
degradation of Rh-6G over barium substituted calcium ferrite, $\text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4$; (where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$). The degradation reaction is carried out over pure $\text{CaFe}_2\text{O}_4$ 55.55% to 62.66% over a range of 75 min. The results are summarized in Fig. 6. When the same reaction was carried out over $\text{Ba}_{0.2}\text{Ca}_{0.8}\text{Fe}_2\text{O}_4$ catalyst under similar reaction conditions, the degradation was increased up to 66.39% in 60 min only. The results indicate that the insertion of barium ion improve the Lewis acidic sites on the surface of catalyst which are responsible for the adsorption and degradation of Rh-6G. Similarly, the reaction was carried out over the surface of $\text{Ba}_{0.4}\text{Ca}_{0.6}\text{Fe}_2\text{O}_4$, $\text{Ba}_{0.6}\text{Ca}_{0.4}\text{Fe}_2\text{O}_4$, $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{Fe}_2\text{O}_4$ and $\text{BaFe}_2\text{O}_4$ catalysts maximum degradation were observed up to 74.46%, 81.47%, 94.22%, and 92.30% respectively in 75 min. $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{Fe}_2\text{O}_4$ catalyst found as a better candidate for the degradation of Rh-6G in aqueous medium due to the synergetic effect of Ba, Ca and Fe ions in the catalyst.

4B.4.3 Effect of temperature

Fig. 7. Effect of reaction temperature towards the degradation of Rh-6G over $\text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4$; (where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) in aqueous medium.
**Reaction conditions:** Catalyst- Ba$_{0.5}$Ca$_{0.5}$Fe$_2$O$_4$ calcined at 800 °C. amount of catalyst- 20mg. pH of solution-7.5. concentration of Rh-6G-50ppm.

The extent of the catalytic degradation of Rh-6G at different temperature working in the range of 20-40 °C has been carried out. The results are shown in Fig. 7. The rate of degradation at 20°C is 52.56% in 15min and it gradually increases to 71.56% in 60min and 72% in 75min respectively. When working at low temperature desorption of the products formed limits the reaction because it is slower than the degradation on the surface and the adsorption of the reactants [26]. When the same reaction is carried out at 30°C temperature the rate of degradation increases to 66.75% in just 15min and it gradually increases to 94.22% in 60min and 94.58% in 75min respectively. At 30°C the amount of rhodamine-6G adsorbed on the surface of the catalyst increases and also helps the reaction to compete more efficiency with e⁻ - h⁺ recombination [27]. The further increment in temperature to 40°C shows the adverse effect by decreasing the degradation of Rh-6G to 68.58% on 15 min while 82.8% degradation was observed after 45min later on the rate of degradation decreases with increase in time it may be due to the fact that at comparatively high temperature rate of adsorption decreases while the rate of desorption of Rh-6G molecules increases from the surface of catalyst. Hence for the optimization of other parameters the degradation reactions were carried out at room temperature only.

**4B.4.4 Effect of concentration of Rh-6G**

Effect of variation of Rh-6G concentration was also observed by taking different concentrations of Rh-6G. The results are summarized in Fig. 8. It is evident from the data that the rate of the degradation increases with respect to time with an increase in concentration of the Rh-6G and it is almost 100% even with increase in concentration from 10ppm to 80ppm. It may explain on the basis that as the concentration of Rh-6G was increases, more dye molecules were available for excitation and consecutive energy transfer. The rate of degradation of Rh-6G was found to decrease with an increase in the concentration of Rh-6G above 50ppm. It may be due to the fact that the dye itself will start acting as an internal filter for the incident energy form the ultrasonicitation as well as mechanical stirring.
Fig. 8. Effect of concentration of Rh-6G towards the extent of degradation of Rh-6G over Ba$_x$Ca$_{1-x}$Fe$_2$O$_4$; (where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) in aqueous medium.

**Reaction conditions**: Catalyst- Ba$_{0.8}$Ca$_{0.2}$Fe$_2$O$_4$ calcined at 800 °C, amount of catalyst- 20mg, temperature- room temperature, pH of solution-7.5.

Secondly as the concentration of substrate molecules increases, then comparatively less amount of catalyst has to compete more molecules of Rh-6G. Similarly the adsorption of Rh-6G molecules on the active site of catalysts are also responsible to decrease the rate of degradation. So we have optimized the 50ppm concentration to optimize the remaining reaction conditions.

4B.4.5 Effect of amount of catalyst

The cost of catalyst is the primary factor contributing to the chemical cost of catalytic oxidation treatment. It is important to minimize the required amount of catalyst. Investigations of the Ba$_{0.8}$Ca$_{0.2}$Fe$_2$O$_4$ concentration on the degradation of Rh-6G dye are shown in Fig. 9. The concentration of catalyst had an important influence on the degradation of Rh-6G. This series of experiments was performed at a constant pH = 7.5 value, working with an initial concentration of Rh-6G of 50ppm. We used five
concentration of solid photocatalyst as 0.005, 0.01, 0.015, 0.02 and 0.025 g catalyst in dye solution. A blank probe (irradiation with no catalyst) gave very low degree of degradation, so we considered negligible contribution of the radiation alone to decompose Rh-6G. If the catalyst concentration is increased, there was an increase in exposed surface area of the catalyst hence the total active surface was increased correspondingly and the enhanced catalytic performance.

Fig.9. Effect of amount of catalyst towards the degradation of Rh-6G over Ba$_x$Ca$_{1-x}$Fe$_2$O$_4$; (where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) in aqueous medium.

**Reaction conditions:** Catalyst- Ba$_{0.8}$Ca$_{0.2}$Fe$_2$O$_4$ calcined at 800 °C, temperature- room temperature, pH of solution-7.5, concentration of Rh-6G-50ppm.

However, the increased concentration of catalyst would have no effect on degradation efficiency after a maximum catalyst dosage was imposed. It may be considered like a saturation point; above which there is negligible or no effect on the rate of degradation of Rh-6G. This may be because the amount of catalyst is increased the
aggregation of particles leads to decrease in surface active sites. Therefore the catalyst concentration of 20mg was fixed for Rh-6G degradation for further studies.

4B.4.6 Effect of calcination temperature of catalyst

![Effect of calcination temperature of catalyst towards the degradation of Rh-6G over Ba$_x$Ca$_{1-x}$Fe$_2$O$_4$; (where x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) in aqueous medium.](image)

**Fig.10.** Effect of calcination temperature of catalyst towards the degradation of Rh-6G over Ba$_x$Ca$_{1-x}$Fe$_2$O$_4$; (where x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) in aqueous medium.

**Reaction conditions:** Catalyst- Ba$_{0.5}$Ca$_{0.5}$Fe$_2$O$_4$, amount of catalyst- 20mg, temperature- room temperature, pH of solution-7.5, concentration of Rh-6G-50ppm.

The effect of calcination temperature of the catalysts on the catalytic activity of mixed oxide was also investigated. **Fig. 10** shows the profiles of the catalytic-oxidation of Rh-6G under visible irradiation using Ba$_{0.5}$Ca$_{0.5}$Fe$_2$O$_4$ catalyst calcined at 700°C, 800°C and 900°C. The sample calcined at 800°C showed the highest catalytic activity i.e. 94.22% degradation than that of catalyst calcined at 700°C and 900°C temperature which is 82.90% and 87.31% respectively for 75 minutes. It seems that the increase of the calcination temperature decrease the number of defect-states on the surface. Above 800°C temperature, the activity of 88.7% degradation in 60 min for the catalyst decreased with an increase of crystallite size of mixed oxides.

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It was also observed that adsorption of Rh-6G dye decreases with an increase of the calcination temperature of the catalyst. This may be probably due to a decrease in the number of defect-structure on the surface of solid catalyst. However, the decrease in the activity may also be attributed to a decrease in the surface area of catalysts. This was also evident from the change in surface area of the samples calcined at different temperature.

4B.4.7 Effect of pH

![Fig.11. Effect of pH of reaction medium towards the degradation of Rh-6G over Ba$_x$Ca$_{1-x}$Fe$_2$O$_4$; (where x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) in aqueous medium. Reaction conditions: Catalyst- Ba$_{0.8}$Ca$_{0.2}$Fe$_2$O$_4$ calcined at 800 °C, amount of catalyst- 20mg, temperature- room temperature, concentration of Rh-6G -50ppm.]

It is important to study the role of pH on the degradation of Rh-6G since the dye effluent are discharged at different pH value. In order to investigate the influence of the pH role of the reaction medium on Rh-6G degradation, a series of experiments performed using 10mg catalyst, pH value of 7, 8, 9 and 10. It has been observed that pH plays an important role in the degradation of Rh6G dye. The initial Rh-6G
concentration in these experiments was 50ppm. The dye degradation in these conditions is shown in Fig.11. It has been observed that the rate of degradation of Rh-6G increases with increase in pH up to 10.0. A further increase in pH above 10.0 results in a decrease in the rate of reaction. An increase in the rate of degradation of Rh-6G with increase in pH may be due to the generation of more *OH radicals, which are produced from the reaction between OH’ ion and hole (h+) of the catalyst. Above pH 10.0, a decrease in the rate of degradation of the dye was observed, which may be due to the fact that Rh-6G is a cationic dye, and at higher pH, OH’ may interact with dye molecule to convert it into its neutral form and the attraction between neutral dye molecule and negatively charged semiconductor surface is reduced relatively.

4B.5 Reusability of catalyst

![Graph showing percentage degradation of Rh-6G over BaxCa1-xFe2O4; (where x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) in aqueous medium. Reaction conditions: Catalyst- Ba0.8Ca0.2Fe2O4 calcined at 800 °C, amount of catalyst- 20mg, temperature- room temperature, pH of solution-7.5, concentration of Rh-6G-50ppm.

Fig.12. Effect of reusability of catalyst towards the degradation of Rh-6G over Ba0.8Ca0.2Fe2O4; (where x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) in aqueous medium.

Reaction conditions: Catalyst- Ba0.8Ca0.2Fe2O4 calcined at 800 °C, amount of catalyst- 20mg, temperature- room temperature, pH of solution-7.5, concentration of Rh-6G-50ppm.
The reusability of catalyst was studied by drying the used catalysts for four times. The catalyst is removed by filtration and dried at 120°C for 2 h and again used to study the reusability. Fig. 12 shows that the reusability of the catalyst for four cycles. For first, second, third and fourth cycle the rate of degradation of Rh-6G is slightly decreased as 94.22%, 88.92%, 80.83% and 75.42% respectively in 75 min. It has been observed that the percentage degradation decreases with further use of same catalysts. It may be due to fouling of catalyst and loss during filtration. Considering the photocatalyst would be endured to some lost for the next cycle, 5 groups parallel experiments were carried out for the first cycle, and the catalyst were collected together from the 5 groups suspending solution for the second cycle experiment after the catalyst reaction finished the 4 groups parallel experiments were carried out for the second cycle to ensure the amount of catalyst are constant in each experiment. The same procedure for third and fourth cycle was repeated and just the parallel group decreased gradually. Thus, the loss of catalyst in each group can be ignored.

4B.6 The probable reaction mechanism

The probable mechanism for the degradation of Rhodamine-6G in aqueous medium at optimized reaction conditions in presence of ordinary light is assisted by \( \text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4 \) (where \( x = 0.0, 0.2, 0.4, 0.6, 0.8 \) and 1.0) catalyst. The Rh-6G in water undergoes two possible pathways as (i) catalytic and (ii) sensitization. In catalytic pathway the excitation of electron takes place from valence band to conduction band due to ultrasonic radiation and create highly active electron and hole pair (Eq. 1). Some of the pairs recombine while some migrate to the surface of catalyst and involve in catalytic reaction. The holes generated in the valence band of catalyst may be trapped by hydroxyl groups attached on the surface to form hydroxyl radicals (Eq.2). The electron may be trapped by oxygen to form peroxy radicals (Eq.3). The holes together with hydroxyl radical and peroxy radicals oxidized the Rh-6G in aqueous solution to carbon dioxide, water and simple mineral acids (Eq.4).

\[
\begin{align*}
\text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4 + h\nu &\rightarrow \text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4 (e^+ + h^+) \quad (1) \\
h^+ + \text{OH}^- &\rightarrow \cdot\text{OH} \quad (2) \\
e^- + \text{O}_2 &\rightarrow \cdot\text{O}_2^- \quad (3)
\end{align*}
\]
\[
\text{Rh-6G} + h^+ \cdot \text{O}^\cdot \cdot \text{O}_2^- \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{mineral acids}
\]  \hspace{1cm} (4)

**Scheme 1.** Probable reaction mechanism for the catalytic degradation of Rhodamine-6G over \( \text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4 \) (where \( x = 0.0, 0.2, 0.4, 0.6, 0.8 \) and 1.0) catalyst.

The energy sensitization path way of Rh-6G under ordinary light in which the Rh-6G molecule get adsorbed on the surface of \( \text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4 \) catalyst and is excited by the ultrasonic waves and ordinary light (Eq.5) and inject electron into the conduction band of ferrite to form cationic radicals (Eq.6). the electron in the conduction band of
ferrite undergo the similar transformation to Eq.(3) finally Rh-6G get degraded to the end products as shown in Eq.(7)

\[
\begin{align*}
Rh-6G + hv & \rightarrow Rh-6G^* \quad (5) \\
Rh-6G^* + Ba_{x}Ca_{1-x}Fe_{2}O_{4} & \rightarrow Rh-6G^* + Ba_{x}Ca_{1-x}Fe_{2}O_{4}(e^-) \quad (6) \\
Rh-6G^* + h^+ \cdot OH \cdot O_2^- & \rightarrow CO_2 + H_2O + mineral acids \quad (7)
\end{align*}
\]

The reaction is monitored at different time interval the catalyst were separated by centrifugation at 3000rpm speed then analyzed by using gas chromatography and mass spectroscopy by using 3-nitrotoluene as internal standard. An attempt was made to identify the intermediate products formed in the catalytic degradation of Rh-6G through GCMS analysis of the solution obtained after 15min irradiation of \( Ba_{x}Ca_{1-x}Fe_{2}O_{4} \) (where \( x = 0.0, 0.2, 0.4, 0.6, 0.8 \) and 1.0) catalyst. GCMS analysis reveals the formation of various intermediates. (As shown in scheme 1) these products were identified based on their molecular ion and mass spectrometric fragmentation peaks. The reaction pathway for the formation of these products is given in scheme 1.

4B.7 Conclusions:

1. A series of barium substituted calcium ferrites \( (Ba_{x}Ca_{1-x}Fe_{2}O_{4}, x=0.2, 0.4, 0.6 \text{ and } 0.8) \) were successfully prepared by citrate gel combustion method.
2. The crystal formation temperature of substituted ferrites is comparatively lower than the other metal substituted ferrites as well as the parent alkaline earth metal ferrite, was confirmed from TG/DTA studies.
3. The IR studies show the two distinct bands which indicate the formation of spinel type ferrites. The XRD pattern shows the shifting of high intensity peak toward the left side (lower 20 from 33.5 to 32.7) indicating the substitution of calcium by barium. The SEM images show the variation in morphology with respect to stoichiometry, while electron dispersive spectra (EDS) confirmed the proper distribution of elements according to their stoichiometry.
4. The degradation of Rh-6G takes place in presence of catalyst and ordinary light only. The ultrasonication of reaction mixture for 5min before
mechanical stirring for specific interval of time act as driving force which are responsible for the generation of electron hole pair.

5. $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{Fe}_2\text{O}_4$ was found to be a better catalyst amongst this series towards the degradation of Rh-6G in aqueous medium it is due to the synergism between Ba, Ca and Fe ions in $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{Fe}_2\text{O}_4$.

6. The $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{Fe}_2\text{O}_4$ has highest catalytic activity for the oxidation of Rh-6G in presence of ordinary light, pH value over 7.5; catalyst concentration 20mg; dye concentration 50ppm at room temperature are found to be optimized parameter during the degradation of Rh-6G.

4B.8 References:


Chapter IV

CHARACTERIZATION AND CATALYTIC ACTIVITY OF SUBSTITUTED ALKALINE EARTH METAL FERRITES

PART C:
CHARACTERIZATION AND CATALYTIC ACTIVITY OF BARIUM SUBSTITUTED STRONTIUM (BSS) FERRITE
4C.1 Introduction
Textile industries produce large volume of colored dye effluents which are toxic and non-biodegradable [1]. The intense use of these xanthenes based dyes are related to their high solubility, stability and color variety and most important its simple dyeing procedure [2]. It is estimated about 15% of the total world production of dyes is lost and released in the textile effluent during the dyeing process [3]. Some of the dyes are not only toxic, mutagenic [4] and carcinogenic [5] compounds, but also are resistant to aerobic biodegradation [6] and their half lives under sunlight are greater than 2000h [7]. These dyes even at low concentration stop the sunlight access to fauna and flora and it reduces the photosynthetic action within the ecosystem [8]. Hence the textile industry is major source of pollution of aquatic system. There has been a considerable attention for the removal of dye by different methods. There is often use of adsorption as a physical method [9], chlorination, ozonation as chemical methods [10] and biodegradation [11]. These removal methods are not effective for a complete degradation, only provide separation of dyes but without any dye degradation and creating a secondary waste problem.

Advanced oxidation process (AOPs) is based on the generation of reactive species through illumination of UV or solar light of some active materials. This process can lead to oxidize organic pollutants to inorganic compounds [12]. From the practical point of view, photo degradation of pollutant using semiconductor is an economical process because solar energy is available in nature abundantly, but when it is used from artificial light source then it become expensive and hazardous. Most of the researches have degraded the organic pollutants by using Fenton reagent (H$_2$O$_2$, Fe$^{3+}$), which is the second most strong oxidizing agent known after fluorine, concentrated H$_2$O$_2$ (60%, 90% etc.). Titanium dioxide (TiO$_2$) is generally considered to be the best photocatalyst and has the ability to detoxificate water from a number of organic pollutants [13-15]. However widespread use of TiO$_2$ is uneconomical for large scale water treatment. Many attempt have been made to study photocatalytic activity of different semiconductors such as SnO$_2$, ZrO$_2$, CdS and ZnO [16-20], but most of these catalysts are very much toxic and either create another type of pollution
or are not much efficient in degradation of Rh-6G dye. Thereby interest has been drawn toward the search for the suitable alternative to these reported catalysts.

With consideration for previous results the goal of the present study was to examine the catalytic activity of substituted SrFe$_2$O$_4$ with different amount of barium under various experimental conditions. So we have synthesized a barium substituted strontium ferrite Ba$_x$Sr$_{1-x}$Fe$_2$O$_4$ (where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) by citrate gel combustion method. The synthesized material is well characterized by various techniques and the catalytic efficiency is checked towards the degradation of Rh-6G dye in aqueous medium. The factors affecting the rate of degradation like role of light and catalyst, pH of reaction medium, temperature, chemical composition of catalyst, calcination temperature, concentration of Rh-6 G and reusability of catalyst are also studied.

4C.2 Results and discussion

4C.2.1 Thermal decomposition of the citrate precursor

TG and DTA curves recorded in static air at 10 °C min$^{-1}$ and are shown in Fig. 1 (a-f).

It can be seen that one-to-one correlation exists between these thermo analytical curves indicating that the thermal effects are accompanied by mass loss. There are three major steps in the decomposition process: dehydration, decomposition of the substituted barium strontium iron citrate precursor.
Fig. 1. TG-DTA curves of precursors of SrFe$_2$O$_4$ (a), Ba$_{0.2}$Sr$_{0.8}$Fe$_2$O$_4$ (b), Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_4$ (c), Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$ (d), Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$ (e) and BaFe$_2$O$_4$ (f) prepared by citrate gel combustion method.

A) Dehydration of the citrate precursor
The number of water molecules adsorbed on the citrate precursor molecule varies depending upon the atmospheric humidity. The extra water can be removed by heating the citrate precursor from room temperature to 145°C, which is shown by the endothermic peak between 45°C to 145°C (Fig.1). Removal of the coordinated water molecules of the citrate precursor takes place between 145°C and 215°C as shown by the second endothermic peak.

B) Decomposition of the citrate precursor
The decomposition of the citrate precursor is a multistep process in the temperature range of 150- 450°C. The first endothermic peak occurred at 200°C in Fig.1 (a) indicate the dehydration of precursor along with the decomposition of complex into the metal carbonates with mass loss of 53.8% up to 350°C temperature. In barium substituted strontium (BSS) ferrite, where (x = 0.2) a sharp exothermic peak is found.
at 147°C indicate the fast decomposition complex into metal carbonates with 58% mass loss in Fig. 1 (b) and a small shoulder exothermic peak detected at 305°C assigns the conversion of metal carbonate into metal oxides with total mass loss 70.2%. The formation of ferrite takes place at 745°C. As the concentration of barium increases to x = 0.4 two intense exothermic peak were found at 145°C with a total mass loss of 74.6% for the decomposition of complex into metal carbonates and carbonate to metal oxides. The complete oxide formation takes place around 655 °C temperatures. For x = 0.6 the exothermic peaks are observed at 164°C and 326°C while the complete formation of ferrite takes place around 650°C with a total mass loss of 74.6%. The further increment in the concentration of barium up to x = 0.8 there are two distinct exothermic peaks found at 145°C and 575°C with 57% mass loss assign to the complete dehydration of precursor followed by the decomposition of the citrate ligand into metal carbonates and oxides. The total weight loss was observed up to 62.7%. In pure barium ferrite total mass loss was observed around 60.3%. All these mass loss are in good agreement with the calculated values.

From these results it is found that the formation temperature of barium substituted strontium (BSS) ferrite is less than that of the formation temperature of pure SrFe₂O₄ and BaFe₂O₄ from their precursor. Hence we synthesized the BSS ferrite by citrate gel combustion method and characterized by various techniques as follows.

4C.2.2 FTIR study of barium substituted strontium (BSS) ferrite

Fig. 2(a-d) shows FTIR spectra of barium substituted strontium ferrite, BaₓSr₁₋ₓFe₂O₄ where (a) x = 0.2, (b) x = 0.4, (c) x = 0.6 and (d) x = 0.8 calcined at 800 °C for 2 h. No significant peaks are found below 1800 cm⁻¹ in all spectra indicates the oxides are free from organic moiety. Two assigned absorption bands appeared around 609 cm⁻¹ to 631 cm⁻¹ attributed to stretching vibration of tetrahedral groups Ba²⁺-O²⁻ and that around 422 cm⁻¹ to 455 cm⁻¹ in spectra attributed to the octahedral group complex Fe³⁺-O²⁻. The stretching band at 511 cm⁻¹ and 663 cm⁻¹ (in spectrum e) is the characteristic band of barium spinel ferrite phase. Similarly in spectrum (a) the stretching bands 424 cm⁻¹ and 567 cm⁻¹ are also the characteristic band of spinel type strontium ferrite.
Fig. 2. FTIR spectra of SrFe₂O₄ (a), Ba₀.₂Sr₀.₈Fe₂O₄ (b), Ba₀.₄Sr₀.₆Fe₂O₄ (c), Ba₀.₆Sr₀.₄Fe₂O₄ (d), Ba₀.₈Sr₀.₂Fe₂O₄ (e) and BaFe₂O₄ (f) prepared by citrate gel combustion method. 

Except in spectra (f) there is no any band around 1100 cm⁻¹ there is no any peak observed in sample (a) to (e) which may be assigned to the presence of COO group. The absorption band at 771 cm⁻¹ to 812 cm⁻¹ resulted from the COO group. The spectra also reveals that the metal carboxylate of the precursor transform into metal carbonate with the characteristic stretching location at 1485 cm⁻¹, 1468 cm⁻¹, 1450 cm⁻¹ and 1456 cm⁻¹ for the samples (b), (c), (d) and (e) calcined at 800 °C for 2 h respectively.

4C.2.3 X-ray diffraction analysis of BSC ferrites
The barium substituted strontium ferrite (BaₓSr₁₋ₓFe₂O₄; x = 0.2, 0.4, 0.6 and 0.8) catalyst was prepared by three different methods such as citrate gel combustion method the XRD pattern are shown in Fig. 3.
The XRD pattern of the barium substituted strontium ferrite shows that the catalyst prepared by citrate gel combustion method is a single phase compound where no impurities were observed. The X-ray diffraction analysis of the samples treated at 800°C temperature for 2 h has been carried out using Cu Kα radiation. XRD pattern of spinel type SrFe$_2$O$_4$ oxide (Fig. 3a) where all the d spacing values are in good agreement with the standard data (JCPDS Card No. 74-1491 and 84-1778), while the XRD pattern of spinel type BaFe$_2$O$_4$ oxide (f) where all the d spacing values are in good agreement with the standard data (JCPDS card no. 46-0113). The XRD pattern (b), (c), (d) and (e) are of Ba$_{0.2}$Sr$_{0.8}$Fe$_2$O$_4$, Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_4$, Ba$_{0.6}$Sr$_{0.4}$Fe$_2$O$_4$ and Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$ oxides respectively. In XRD pattern (b) the new peak originates at two theta 29.1 which represents the insertion of barium as the concentration of barium ion increases the intensity of peaks in (b), (c), (d), (e) and (f) also increases while the two theta value gets shifted towards the lower value i.e. from 29.0 to 28.4 (Fig 3).
which indicate the substitution of metal ion (strontium ion) with lower atomic size by the metal ion (barium ion) with higher atomic size. The same observation was found in case of the peaks which indicate the presence of strontium shown by hash (#). As the concentration of strontium decreases from (a) to (f) the intensity of the peak also decreases. The diffraction patterns also indicate that there is no second phase formed in the samples from (a) to (f). The average crystal size of the all samples (a- f) was calculated using Scherer’s law for the high intensity peak which is in the range of 70nm to 91nm.

4C.2.4 Elemental analysis by X-ray florescence

The elemental analysis of barium substituted strontium ferrite is done by electron dispersive studies and confirmed by X-ray florescence spectroscopy. The result is summarized in Table 1. The percentage composition of the barium, strontium and iron are in good agreement with the calculated values.

Table 1: The elemental composition of barium, calcium and iron in barium substituted calcium ferrite $\text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4$: where $x$= 0.2, 0.4, 0.6 and 0.8.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Strontium (Sr)</th>
<th>Iron (Fe)</th>
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<td></td>
<td>Cal</td>
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<tr>
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<tr>
<td>$\text{Ba}_0.8$</td>
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<td>35.56</td>
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4C.2.5 Scanning electron microscopy and electron dispersive spectra of barium substituted strontium (BSS) ferrite

Fig. 4 shows the SEM images of the barium substituted strontium ferrites ($\text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4$) synthesized by citrate gel method with different elemental composition. It can be seen from these micrographs that the variation in chemical composition have a significant influence on the morphologies of the synthesized products. The micrographs were obtained on specimen without imposing any magnetic orientation for particles.
Fig. 4. Scanning electron microscopic images of SrFe$_2$O$_4$ (a), Ba$_{0.2}$Sr$_{0.8}$Fe$_2$O$_4$ (b), Ba$_{0.4}$Sr$_{0.6}$Fe$_2$O$_4$ (c), Ba$_{0.6}$Sr$_{0.4}$Fe$_2$O$_4$ (d), Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$ (e) and BaFe$_2$O$_4$ (f).

The micrographs show irregular size of the particles along with agglomeration up to some extent.

4C.2.6 Surface area determination by BET method

The BET surface area of the various samples of barium substituted calcium ferrite (Ba$_x$Sr$_{1-x}$Fe$_2$O$_4$) catalysts calcined at 800 °C was also carried out. Among all the prepared catalysts the surface area of Ba$_x$Sr$_{1-x}$Fe$_2$O$_4$, where $x = 0.2$, 0.4 and 1.0 are 117.33 m$^2$/g, 102.13 m$^2$/g and 147.73 m$^2$/g respectively. The surface area of the other catalysts of composition i.e. $x = 0.0$, 0.2 and 0.6, are below 100 m$^2$/g even though prepared by same method. It may be due to the agglomeration of oxides during the heat treatment as also shown in SEM analysis (Fig. 4).
4C.3 Photocatalytic activity of barium substituted calcium ferrite

The rate of photocatalytic degradation of Rh-6G depends on the several parameters such as pH, type of photocatalyst used, dye concentration, amount of catalyst and the type of source used for the purpose of irradiation.

The photocatalytic degradation of Rh-6G dye was studied in the presence of Ba$_x$Sr$_{1-x}$Fe$_2$O$_4$ (where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) catalyst in ambient light condition. 10mL of dye solution (50ppm) is taken in the reaction vessel of photo reactor and stirred at ambient light and other conditions by adding 10 mg of catalyst for stipulated time.

4C.4 Optimization of reaction conditions

4C.4.1 Selection of reaction system

![Graph showing the degradation of Rh-6G under different reaction conditions.](image)

**Fig.5.** Effect of various reaction conditions towards the degradation of Rh-6G over Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$ (where $x = 0.8$) in aqueous medium.

**Reaction conditions:** Catalyst Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$ calcined at 800 °C, amount of catalyst-20mg, temperature- room temperature, pH of solution-7.5, concentration of Rh-6G-50ppm.
The role of light and catalyst is examined by carried out the reaction in four different reaction conditions like catalyst in dark, catalyst in presence of ambient light condition, catalyst in presence of mercury vapor lamp and without catalyst but presence of ambient light condition. The extent of degradation of Rh-6G for different time interval is shown in Fig. 5. To know the role of light and catalyst initially the degradation of Rh-6G was carried out in presence of catalyst (in dark) and ambient light. In presence of light (without catalyst) the degradation of Rh-6G takes place up to 10.13% in 15min and maximum 20.95% up to 75min. This results indicate that Rh-6G is thermally stable molecule which cannot be degraded by light only and the degradation in absence of catalyst is may be due to the sonication of reaction mixture. In presence of catalyst only (in dark) the degradation of Rh-6G takes place up to 49.58% in 15min which gradually increases to 58.3% up to 75min. To study the synergism between catalyst and light the same reaction is carried out in presence of catalyst and ambient light condition under similar reaction conditions, the degradation of Rh-6G increases to 79.85% in 15min only and maximum degradation takes place up to 86.15% up to 75min. This shows that the catalyst plays the decisive role in degradation of Rh-6G. The role of mercury vapor lamp in presence of catalyst has also checked by carrying out the degradation reaction of Rh-6G. The maximum conversion takes place up to 67.36% in 15min which increases to 81.25% in 60min but it slightly decreases to 80.65% in 75min. The rate of degradation decrease in mercury vapor lamp light due to the recombination of $e^-h^+$ which decreases the rate of adsorption of Rh-6G molecule on the surface of catalyst. Hence to optimize the reaction condition the degradation reaction is carried out in presence of catalyst and ambient light condition.

4C.4.2 Effect of chemical composition of catalyst

The chemical composition of catalyst plays decisive role towards the degradation of Rh-6G in aqueous medium which is examine by carrying out the degradation of Rh-6G over barium substituted strontium ferrite, $Ba_xSr_{1-x}Fe_2O_4$; (where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$), the results are shown in Fig.6.
Fig. 6. Effect of chemical composition of catalyst towards the degradation of Rh-6G over $\text{Ba}_x\text{Sr}_{1-x}\text{Fe}_2\text{O}_4$; (where $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) in aqueous medium.

**Reaction conditions:** Catalyst $\text{Ba}_x\text{Sr}_{1-x}\text{Fe}_2\text{O}_4$ calcined at $800 ^\circ\text{C}$, amount of catalyst-20mg, temperature- room temperature, pH of solution-7.5, concentration of Rh-6G-50ppm.

The degradation reaction is carried out over pure $\text{SrFe}_2\text{O}_4$, 68.37% degradation of Rh-6G takes place in 15min which gradually increases to 80.13% in 75min. when the same reaction was carried out over $\text{Ba}_0.2\text{Sr}_{0.8}\text{Fe}_2\text{O}_4$ catalyst under similar reaction conditions the degradation was increased up to 79.45% in 15min and increases to 86.15% in 75min. The results indicate the insertion of barium ion improve the Lewis acid sites on the surface of catalyst which are responsible for the adsorption and degradation of Rh-6G. Similarly the reaction was carried out over the surface of $\text{Ba}_{0.4}\text{Sr}_{0.6}\text{Fe}_2\text{O}_4$, $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Fe}_2\text{O}_4$, $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Fe}_2\text{O}_4$ and $\text{BaFe}_2\text{O}_4$ catalysts maximum degradation were observed up to 67.33%, 70.7%, 83.25% and 76.41% respectively in 75min. $\text{Ba}_0.2\text{Sr}_{0.8}\text{Fe}_2\text{O}_4$ catalyst was found to be a better candidate for the degradation of Rh-6G in aqueous medium due to the better synergism between Ba, Ca and Fe ions in the catalyst.
4C.4.3 Effect of temperature

Fig.7. Effect of reaction temperature towards the degradation of Rh-6G over Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$; (where $x$ = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) in aqueous medium. **Reaction conditions**: Catalyst Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$ calcined at 800 °C, amount of catalyst- 20mg, pH of solution-7.5, concentration of Rh-6G-50ppm.

The extent of the catalytic degradation of Rh-6G at different temperature in the range of 25-40 °C has been carried out with an interval of 5°C. The results are shown in Fig.7. The rate of degradation at 25°C is 65.35% in 15min and it gradually increases to 72.15 and 72.2% in 60min and 75min respectively. At low temperature desorption of the products formed limits the reaction because it slower than the degradation on the surface and the adsorption of the reactants [21]. When the same reaction is carried out at 30°C temperature the rate of degradation is increases to 79.85% in just 15min and it gradually increases to 84.53% and 86.15% in 60min and 75min respectively. Increase in amount of Rh-6G adsorbed on the surface of the catalyst also help the reaction to compete more efficiency with $e^-$ - $h^+$ recombination [22]. The further increment in temperature to 35°C shows the adverse effect by decreasing the
degradation of Rh-6G to 79.9% in 15 min it gradually increases to 86.15% after 75 min. while at 40°C the rate of degradation of Rh-6G decreases slightly to 82.65% in 45 min and 81.75% in 75 min. it may be due to comparatively high temperature, the rate of adsorption decreases while the rate of desorption of Rh-6G molecules increases from the surface of catalyst. Hence for the optimization of other parameters the degradation reactions were carried out at room temperature only.

**4C.4.4 Effect of Concentration of Rhodamine-6G**

![Graph showing effect of Rhodamine-6G concentration](image)

**Fig.8.** Effect of concentration of Rh-6G towards the extent of degradation of Rh-6G over Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$ in aqueous medium. **Reaction conditions:** Catalyst-Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$ calcined at 800 °C, amount of catalyst- 20mg, temperature- room temperature, pH of solution- 7.5.

The efficiency of catalyst also tested by varying the concentration of Rh-6G from 10ppm to 60ppm in aqueous medium, the results are given in **Fig. 8.** It is evident from the data that the rate of degradation of Rh-6G decreases with an increase in concentration of the Rh-6G. When the reaction was carried out with 10ppm
concentration then 97.26% degradation was found in 75 min, but as the concentration of Rh-6G increases to 20 ppm and 30 ppm the rate of degradation decreases to 92.94% and 89.35% respectively in 75 min. While for 40 ppm and 50 ppm concentrated solution the rate of degradation is further suppressed to 86.84% and 86.15% respectively in 75 min. When the same reaction is carried out with 60 ppm solution of Rh-6G then rate of degradation decreases to 81.9%, it may be due to the fact that the dye itself will start acting as an internal filter for the incident energy form the ultrasound as well as mechanical stirring. Secondly as the concentration of substrate molecules increases, comparatively less amount of catalyst has to compete more molecules of Rh-6G. Similarly, adsorption of Rh-6G molecules on the active site of catalysts are also responsible to decrease the rate of degradation. So we have optimized the 50 ppm concentration to optimize the remaining reaction conditions.

4C.4.5 Effect of amount of catalyst

![Fig.9. Effect of amount of catalyst towards the degradation of Rh-6G over Ba$_{0.8}$Sr$_{0.2}$Fe$_5$O$_{12}$ in aqueous medium. Reaction conditions: Catalyst- Ba$_{0.8}$Sr$_{0.2}$Fe$_5$O$_{12}$ calcined at 800 °C, temperature- room temperature, pH of solution-7.5, concentration of Rh-6G-50 ppm.](image)
The cost of catalyst is the primary factor contributing to the chemical cost of catalytic oxidation treatment. It becomes important to minimize the required amount of catalyst. Then investigations of the $\text{Ba}_0.2\text{Ca}_{0.8}\text{Fe}_2\text{O}_4$ concentration on the degradation of Rh-6G dye were conducted. The results are shown in Fig.9. The concentration of catalyst had an important influence on the degradation of Rh-6G. This series of experiments was performed at a constant pH = 7.5 value, working with an initial concentration of Rh-6G of 50ppm. We used five concentrations of solid photocatalyst as 0.005, 0.01, 0.015, 0.02 and 0.025 g catalyst in dye solution. A blank probe (irradiation with no catalyst) gave a very low degree of degradation, so we considered negligible contribution of the radiation alone to decompose Rh-6G. If the catalyst concentration is increased, there was an increase in exposed surface area of the catalyst; hence the total active surface was increased correspondingly and the enhanced catalytic performance. However, the increased concentration of catalyst would have no effect on degradation efficiency after a maximum catalyst dosage was imposed. It may be considered like a saturation point; above which there is negligible or no effect on the rate of degradation of Rh-6G. This may be due to as the amount of catalyst is increased, the aggregation of particles leads to a decrease in surface active sites. Therefore, the catalyst concentration of 20mg was fixed for Rh-6G degradation for further studies.

4C.4.6 Effect of calcination temperature of catalyst

The effect of calcination temperature of the catalysts on the catalytic activity of mixed oxide was also investigated. Fig. 10 shows the profiles of the catalytic-oxidation of Rh-6G under ambient light condition using $\text{Ba}_0.2\text{Ca}_{0.8}\text{Fe}_2\text{O}_4$ catalyst calcined at 700°C, 800°C and 900°C. The sample calcined at 800°C showed the highest catalytic activity i.e. 86.15% degradation than that of catalyst calcined at 700°C and 900°C temperature which is 75.74% and 83.73% respectively for 75 minutes. It seems that the increase of the calcination temperature decreases the number of defect-states on the surface.
Fig. 10. Effect of calcination temperature of catalyst towards the degradation of Rh-6G over Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$ in aqueous medium. **Reaction conditions:** Catalyst-Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$, amount of catalyst- 20mg, temperature- room temperature, pH of solution-7, concentration of Rh-6G-50ppm.

At 700°C temperature the efficiency is comparatively less may due to less number of Lewis acid sites present at the surface of catalyst as the calcination temperature increases to 800 °C the trivalent ions (Fe$^{3+}$) appears on the surface of catalyst and enhances the rate of adsorption as well as degradation also. It was also observed that adsorption of Rh-6G dye decreases with an increase of the calcination temperature of the catalyst. This may probably be due to a decrease in the number of defect-structure on the surface of solid catalyst. However, the decrease in the activity may also be attributed to a decrease in the surface area of catalysts. This was also evident from the change in surface area of the samples calcined at different temperature.
4C.4.7 Effect of pH of reaction medium

Fig.11. Effect of pH towards the degradation of Rh-6G over Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$ in aqueous medium. **Reaction conditions:** Catalyst- Ba$_{0.8}$Sr$_{0.2}$Fe$_2$O$_4$ calcined at 800 °C, amount of catalyst- 20mg, temperature- room temperature, concentration of Rh-6G - 50ppm.

It is important to study the role of pH on the degradation of Rh-6G since the dye effluent is discharged at different pH value. In order to investigate the influence of the pH role on Rh-6G degradation, a series of experiments were performed using 20mg catalyst at pH value of 7, 8, 9 and 10. It has been observed that pH plays an important role in the degradation of Rh6G dye. The initial Rh-6G concentration in these experiments was 50ppm. The dye degradation in these conditions is shown in **Fig.11.**

It has been observed that the rate of degradation of Rh-6G increases with increase in pH up to 7.0. A further increase in pH above 7.0 results in a decrease in the rate of reaction. An increase in the rate of degradation of Rh-6G with increase in pH may be due to the generation of more $\cdot$OH radicals, which are produced from the reaction between OH$^-$ ion and hole (h$^+$) of the catalyst. Above pH 7.0, a decrease in the rate of degradation of the dye was observed, which may be due to the fact that Rh-6G is a
cationic dye, and at higher pH, OH⁻ may interact with dye molecule to convert it into its neutral form and the attraction between neutral dye molecule and negatively charged semiconductor surface is reduced relatively.

4C.5 The probable reaction mechanism

The probable reaction pathways and mechanism for the degradation of Rh-6G is explained in detail in section 3.1 of Chapter 4 Part B.

4C.6 Reusability of catalyst

Fig. 12. Effect of reusability of catalyst towards the degradation of Rh-6G over Ba₀.₈Sr₀.₂Fe₂O₄ in aqueous medium. **Reaction conditions:** Catalyst - Ba₀.₈Sr₀.₂Fe₂O₄ calcined at 800 °C, amount of catalyst - 20mg, temperature - room temperature, pH of solution - 7, concentration of Rh-6G - 50ppm.

The reusability of catalyst was studied by drying and reusing the catalysts for four times. The catalyst is removed by filtration and dried at 120°C for 2 h and again used to study the reusability. **Fig. 12** shows that the reusability of the catalyst is up to four
cycles. For first, second and third cycle the degradation of Rh-6G takes place 86.15%, 85.42% and 83.82% respectively. So till third cycle only 2-3% efficiency of catalyst was suppressed but for fourth time the degradation of Rh-6G decreases to 72.8%. It has been observed that the percentage degradation decreases with further cycles of same catalysts. It may be due to fouling of catalyst and loss during filtration. Considering the photocatalyst would be endured some loss for the next cycle, 5 groups of parallel experiments were carried out for the first cycle, and the catalyst were collected together from the 5 groups, suspending solution for the second cycle experiment. After the catalyst reaction finished the 4 groups parallel experiments were carried out for the second cycle to ensure the amount of catalyst are constant in each experiment. And repeat the same procedure for third and fourth cycle just the parallel group decreased gradually. Thus, the loss of catalyst in each group can be ignored.

4C.7 Conclusions:

1. A series of barium substituted strontium ferrites (Ba$_{x}$Sr$_{1-x}$Fe$_2$O$_4$, $x=0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0) were successfully prepared by citrate gel combustion method.
2. The crystal formation temperature of substituted ferrites is comparatively lower than the other metal substituted ferrites as well as the parent alkaline earth metal ferrite.
3. The IR studies show the two distinct bands which indicate the formation of spinel type ferrites. The XRD pattern shows the shifting of high intensity peak toward the left side (lower 20 from 29.1 to 28.4) indicating the substitution of strontium by barium. The SEM images show the variation in morphology with respect to stoichiometry, while electron dispersive spectra (EDS) pattern confirmed the proper distribution of elements according to their stoichiometry.
4. The degradation of Rh-6G takes place in presence of catalyst and ordinary light only. The ultrasonication of reaction mixture for 5min before mechanical stirring for specific interval of time act as driving force which are responsible for the generation of electron hole pair.
5. $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Fe}_2\text{O}_4$ was found to be a better catalyst amongst the series towards the degradation of Rh-6G in aqueous medium it is due to the synergism between Ba, Ca and Fe ions in $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Fe}_2\text{O}_4$.

6. The $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Fe}_2\text{O}_4$ has highest catalytic activity for the oxidation of Rh-6G in presence of ambient light condition, 7.5 pH, 20mg catalyst concentration, 50ppm dye concentration at room temperature.
4.8 References:


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