Chapter II

EXPERIMENTAL TECHNIQUES FOR SYNTHESIS, CHARACTERIZATION AND CATALYTIC ACTIVITY OF PURE AND SUBSTITUTED ALKALINE EARTH METAL FERRITES
2.1. Introduction:

The pure and substituted alkaline earth metal (AEM) ferrites of different crystallite size and morphology were synthesized by various methods such as citrate-gel combustion method, sucrose assisted combustion method and citrate gel with ultrasonic treatment method. The precursors of various alkaline earth metal iron citrate were characterized by TG-DTA and DSC. The all pure and substituted AEM ferrite catalysts were characterized by various techniques such as FT-IR, XRD, SEM-EDXS, TEM, BET, XRF and AAS. The catalytic efficiency of the well characterized catalysts was examined towards the selective oxidation of styrene, selective epoxidation of styrene and cyclohexene. The efficiency of catalysts were also checked towards the catalytic degradation of toxic and photo chemically very stable pollutant Rhodamine-6G (Rh-6G). The detailed experimental procedure for synthesis, characterization and catalytic activity of pure and substituted AEM ferrites are explained in following sections.

2.2. Materials

In present study, all the required chemicals were used of analytical grade without further purification. The appropriate concentration of styrene, cyclohexene and Rhodamine-6G (Rh-6G) solutions were prepared by using double distilled water. The details about the chemicals used are summarized in Table 1.

2.3. Synthesis of pure alkaline earth metal ferrites

The catalytic effect of the spinel type ferrites have been of much interest from the viewpoint of selective organic transformation as well as the degradation of toxic pollutants like Rhodamine-6G (Rh-6G). In the present research, we have attempted to study systematically the effect of method of preparation on the catalytic activity of AEM ferrites towards the selective oxidation of styrene, epoxidation of styrene and epoxidation
of cyclohexene. Pure AEM ferrites were prepared by citrate-gel combustion method while the substituted AEM ferrites were synthesized by citrate-gel combustion method, sucrose assisted combustion method and citrate gel with ultrasonic treatment method.

**Table 1: Chemicals used**

<table>
<thead>
<tr>
<th>Name of the Chemicals</th>
<th>Formula</th>
<th>Purity (%)</th>
<th>Make</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Nitrotoluene</td>
<td>C₇H₅NO₂</td>
<td>99</td>
<td>Merck</td>
</tr>
<tr>
<td>Acetone</td>
<td>CH₃COCH₃</td>
<td>99</td>
<td>Merck</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>CH₃CN</td>
<td>98</td>
<td>Merck</td>
</tr>
<tr>
<td>Barium Nitrate</td>
<td>Ba(NO₃)₂</td>
<td>99</td>
<td>Merck</td>
</tr>
<tr>
<td>Calcium Nitrate</td>
<td>Ca(NO₃)₂.4H₂O</td>
<td>99</td>
<td>Merck</td>
</tr>
<tr>
<td>Citric acid</td>
<td>C₆H₇O₇</td>
<td>98</td>
<td>S D Fine</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>C₆H₁₀</td>
<td>98</td>
<td>Merck</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅O</td>
<td>99</td>
<td>Merck</td>
</tr>
<tr>
<td>Hydrogen Peroxide (30%)</td>
<td>H₂O₂ (30%)</td>
<td>99</td>
<td>Merck</td>
</tr>
<tr>
<td>Hydrogen Peroxide (6%)</td>
<td>H₂O₂ (6%)</td>
<td>99</td>
<td>Merck</td>
</tr>
<tr>
<td>Iron-Nitrate (Nonahydrate)</td>
<td>Fe(NO₃)₃.9H₂O</td>
<td>99</td>
<td>Merck</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>98</td>
<td>Merck</td>
</tr>
<tr>
<td>Rhodamine- 6G</td>
<td>C₂₈H₃₁N₂O₄Cl</td>
<td>--</td>
<td>BARC</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>--</td>
<td>S D Fine</td>
</tr>
<tr>
<td>Sodium sulphate (Anhydrous)</td>
<td>Na₂SO₄</td>
<td>99.9</td>
<td>Merck</td>
</tr>
<tr>
<td>Strontium Nitrate</td>
<td>Sr(NO₃)₂</td>
<td>99.5</td>
<td>Merck</td>
</tr>
<tr>
<td>Styrene</td>
<td>C₆H₈</td>
<td>98.5</td>
<td>Aldrich</td>
</tr>
<tr>
<td>Sucrose</td>
<td>C₁₂H₂₂O₁₁</td>
<td>99.5</td>
<td>Merck</td>
</tr>
<tr>
<td>Tertiary butyl alcohol</td>
<td>C₄H₁₀O</td>
<td>98.9</td>
<td>Merck</td>
</tr>
<tr>
<td>Tertiary butyl hydrogen peroxide</td>
<td>C₄H₁₀O₂</td>
<td>99.0</td>
<td>Merck</td>
</tr>
<tr>
<td>Urea</td>
<td>CON₂H₄</td>
<td>99.9</td>
<td>Merck</td>
</tr>
</tbody>
</table>
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Synthesis of catalysts by Citrate-gel combustion method

The performance of any ferrite is greatly influenced by its synthesizing technique. Initially the spinel ferrites are prepared through various methods like solid state reaction method [1]: high energy ball milling method [2]: sol-gel method [3]: chemical co-precipitation method [4]: microwave sintering method [5]: auto combustion method [6]: conventional ceramic technique [7]: conventional two-step synthesis method [8] etc. Most of the transition metal ferrite has been synthesized through solid state reaction method by many investigators [9-11]. In these conventional methods, preparation involve solid state reaction, different metal oxides are mixed and calcined to get ferrite powders. However, mechanical mixing of different oxides is hardly intimate and homogeneous and hence it results in composition fluctuation at every stage of processing that also persists after sintering [12]. Solid state process requires calcination temperature more than 750°C for phase formation and sintering temperature more than 1000°C to achieve better densification. At this high sintering temperature, evaporation leads to the formation of chemically inhomogeneous material [13]. The conventional ceramic method of preparation which involves solid state reaction between oxides at high temperatures is time consuming, and does not always result in pure, reproducible products. Preparation of ferrites by the conventional ceramic method has many disadvantages, viz. non-homogeneity, large particle size and low surface area. Similarly the physical methods also have many drawbacks such as small area of deposition, requirement of sophisticated instruments, high working cost of system, wastage of depositing material, cleaning after each deposition, etc. Keeping drawbacks of physical methods in mind, recently much emphasis has been put on the soft solution chemical processes for the preparation of advanced inorganic materials such as spinel-type oxides [14]: pervoskite-type oxides [15]: nanotubes, nanowires [16] and nanodots with quantum size effects. These low cost processes have used environmentally benign conditions. Chemical methods are simple, economic and convenient for the deposition of metallic chalcogenide thin films. The preparative parameters such as concentration, pH, nature of the complexing agent, temperature, etc. are easily controllable [17].
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Attempts towards improving the technological performance of ferrites have, therefore, led to the development of various non-conventional processing techniques [18–20]. Chemical methods overcome some limitations of solid state reaction method, which are mainly solution techniques. The advantages of these techniques are the appreciable reduction in the processing temperature and the resulting ferrite being of improved microstructure. In the present work, a nonconventional preparation method, known as the citrate precursor method [21-23] was used for the preparation of AEM ferrites. The main advantages of this method are that it is simple, inexpensive, time saving, and results in superior properties of ferrites processed at much lower temperatures. This low temperature formation is attributed to the fine particle nature of the oxides with increased reactivity obtained during the citrate decomposition. The absence of ball milling in this method leads to stoichiometric compositions as there is no possibility of loss or gain of material during milling, as is the case in the conventional ceramic method which involves extensive milling of the starting oxide materials. The atomic scale mixing of the constituent cations by the citrate precursor method results into corresponding better homogeneity of the final ferrite composition. As this method does not involve any precipitation, the probability of phase segregation, which is possible in some other wet methods such as co-precipitation, is ruled out. Although there are a few reports on the preparation of transition metal ferrite like Zn, Ni, Co etc. ferrites by some non-conventional wet methods. [24–26] little has been reported on the processing of these ferrites by the citrate precursor method.

2.4 Preparation of solutions

2.4.1 Preparation of 0.1M Ca(NO₃)₂ solution

0.1M solution of Ca(NO₃)₂ was prepared by dissolving 23.615 gm of hydrated calcium nitrate in double distilled water. The clear solution is obtained which is diluted to 1000ml volume in volumetric flask.
2.4.2 Preparation of 0.1M Sr(NO$_3$)$_2$ solution

0.1M solution of Sr(NO$_3$)$_2$ was prepared by dissolving 21.163 gm of hydrated strontium nitrate in double distilled water. The clear solution is obtained which is diluted to 1000ml volume in volumetric flask.

2.4.3 Preparation of 0.1M Ba(NO$_3$)$_2$ solution

0.1M solution of Ba(NO$_3$)$_2$ was prepared by dissolving 26.135 gm of hydrated barium nitrate in double distilled water. The clear solution is obtained which is diluted to 1000ml volume in volumetric flask.

2.4.4 Preparation of 0.1M Fe(NO$_3$)$_3$·9H$_2$O solution

0.1M solution of Fe(NO$_3$)$_3$·9H$_2$O was prepared by dissolving 40.4 gm of hydrated iron nitrate in double distilled water. The clear solution is obtained which is diluted to 1000ml volume in volumetric flask.

2.4.5 Preparation of 0.1M Citric acid solution

0.1M solution of C$_6$H$_8$O$_7$·4H$_2$O was prepared by dissolving 26.39 gm of hydrated citric acid in double distilled water. The clear solution is obtained which is diluted to volume 1000ml in volumetric flask.

2.5 Synthesis of Alkaline earth metal ferrites

2.5.1 Synthesis of CaFe$_2$O$_4$

Calcium iron citrate precursor is prepared from the 0.1M solution of Ca(NO$_3$)$_2$, Fe(NO$_3$)$_3$, and C$_6$H$_8$O$_7$·4H$_2$O solutions. Initially 0.1M solution of Ca(NO$_3$)$_2$ and Fe(NO$_3$)$_3$ are mixed together in 3:6 proportion and added slowly to 0.1M solution of citric acid. The volume ratio of Ca(NO$_3$)$_2$, Fe(NO$_3$)$_3$ and C$_6$H$_8$O$_7$·4H$_2$O molar ratio was 3:6:8 proportion respectively. These solutions were heated at 40°C for about 30 min and added to the iron nitrate solution under constant stirring. The precursor mixture obtained was gradually dried by evaporation at 40°C to obtain a transparent brown colored glassy material containing the constituent metal ions homogeneously mixed at the atomic level. This
precursor is dried in oven at about 110°C temperature it become a crispy material. After grinding the fine powder were decomposed in evaporating dish over a gas flame to obtained metal oxide with desired stoichiometric ratio of metal ions. The decomposed precursor was calcined at different temperature in muffle furnace for 2h.

2.5.2 Synthesis of SrFe$_2$O$_4$

Strontium iron citrate precursor is prepared from the 0.1M solution of Sr(NO$_3$)$_2$, Fe(NO$_3$)$_3$, and C$_{6}$H$_{8}$O$_{7}$.4H$_{2}$O solutions. Initially 0.1M solution of Sr(NO$_3$)$_2$ and Fe(NO$_3$)$_3$ are mixed together in 3:6 proportion and added slowly to 0.1M solution of citric acid. The volume ratio of Sr(NO$_3$)$_2$, Fe(NO$_3$)$_3$, and C$_{6}$H$_{8}$O$_{7}$.4H$_{2}$O molar ratio was 3:6:8 proportion respectively. These solutions were heated at 40°C for about 30 min and added to the iron nitrate solution under constant stirring. The precursor mixture obtained was gradually dried by evaporation at 40°C to obtain a transparent brown colored glassy material containing the constituent metal ions homogeneously mixed at the atomic level. This precursor is dried in oven at about 110°C temperature it become a crispy material. After grinding the fine powder were decomposed in evaporating dish over a gas flame to obtained metal oxide with desired stoichiometric ratio of metal ions. The decomposed precursor was calcined at different temperature in muffle furnace for 2h.

2.5.3 Synthesis of BaFe$_2$O$_4$

Barium iron citrate precursor is prepared from the 0.1M solution of Ba(NO$_3$)$_2$, Fe(NO$_3$)$_3$, and C$_{6}$H$_{8}$O$_{7}$.4H$_{2}$O solutions. Initially 0.1M solution of Ba(NO$_3$)$_2$ and Fe(NO$_3$)$_3$ are mixed together in 3:6 proportion and added slowly to 0.1M solution of citric acid. The volume ratio of Ba(NO$_3$)$_2$, Fe(NO$_3$)$_3$, and C$_{6}$H$_{8}$O$_{7}$.4H$_{2}$O molar ratio was 3:6:8 proportion respectively. These solutions were heated at 40°C for about 30 min and added to the iron nitrate solution under constant stirring. The precursor mixture obtained was gradually dried by evaporation at 40°C to obtain a transparent brown colored glassy material containing the constituent metal ions homogeneously mixed at the atomic level. This precursor is dried in oven at about 110°C temperature it become a crispy material. After grinding the fine powder were decomposed in evaporating dish over a gas flame to
obtained metal oxide with desired stoichiometric ratio of metal ions. The decomposed precursor was calcined at different temperature in muffle furnace for 2h.

2.5.4 Synthesis of substituted alkaline earth metal ferrites

2.5.4.1 Synthesis of strontium substituted calcium, Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ (SSC) ferrite

A) Synthesis of catalyst (SSC) by citrate gel combustion method

Analytical grade calcium nitrate [Ca(NO$_3$)$_2.4$H$_2$O], strontium nitrate [Sr(NO$_3$)$_2$], iron nitrate [Fe(NO$_3$)$_3.9$H$_2$O] and citric acid [C$_6$H$_8$O$_7$.H$_2$O] (specialized Pvt. Ltd., Mumbai, India) were used to prepare the strontium substituted calcium ferrites with different compositions Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$, where (0.0 $\leq$ x $\leq$ 1.0). 0.1M solution of Ca(NO$_3$)$_2.4$H$_2$O, [Sr(NO$_3$)$_2$]. and [Fe(NO$_3$)$_3.9$H$_2$O] in x : (1-x) : 2 proportion respectively. The mixture of metal nitrate solutions was also slowly added to citric acid solution to form the sol. The molar ratio of metal nitrates to citric acid was 1:1. During this procedure, the sol was continuously stirred by a magnetic agitator. Then, the sol was poured into a dish and heated at 80°C on a hot plate and stirred continuously to transform into a zero gel. At appropriate temperature ignition started and the dried gel burnt in a self-propagating combustion manner until all the gel was burnt out completely to form a fluffy loose powder. The entire combustion process was done in a few minutes. Finally, the as-burnt powders were calcined in the muffle furnace from 600-800°C for 2 h with a heating rate of 10°C/min to obtain the single phase ferrite.

B) Synthesis of catalyst (SSC) by ultrasonic treatment method

Analytical grade calcium nitrate [Ca(NO$_3$)$_2.4$H$_2$O], strontium nitrate [Sr(NO$_3$)$_2$], iron nitrate [Fe(NO$_3$)$_3.9$H$_2$O] and citric acid [C$_6$H$_8$O$_7$.H$_2$O] (specialized Pvt. Ltd., Mumbai, India) were used to prepare the strontium substituted calcium ferrites with different compositions Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$, where 0.0 $\leq$ x $\leq$ 1.0. 0.1M solution of Ca(NO$_3$)$_2.4$H$_2$O, [Sr(NO$_3$)$_2$]. and [Fe(NO$_3$)$_3.9$H$_2$O] in x : (1-x) : 2 proportion respectively. The mixture of metal nitrate solutions was also slowly added to citric acid solution to form the sol. The molar ratio of metal nitrates to citric acid was 1:1. The addition of metal nitrate solutions into citric acid is carried out in ultrasonic bath for 30
minutes and at 40 °C temperature. Citric acid helps in the homogeneous distribution of the metal ions to get segregate from the solution. The solution is continuously stirred for 1 h by magnetic agitator and kept at a temperature of 60 °C until it turns to sol. Then the stabilized nitrates–citrate sol was rapidly heated to 80 °C and stirred constantly. Viscosity and color changed as the sol turned into a transparent sticky gel. The gel was heated in evaporating dish where an auto combustion process takes place. Finally, the brown, floppy precursor is calcined at 800°C for 2 h in muffle furnace.

C) Synthesis of catalyst (SSC) by sucrose assisted combustion method

Strontium substituted calcium ferrite was prepared by novel combustion method using sucrose as a chelating agent as well as fuel. The precursor was prepared from 0.1M solution of metal nitrates and sucrose, at molar ratio of Sr(II): Ca(II); Fe(III) and sucrose is \(x : (1-x) : 2 : 3\) where \(0.0 \leq x \leq 1.0\) as follows. 0.1M solution of \(\text{Ca(NO}_3\text{)}_2.4\text{H}_2\text{O}\), \([\text{Sr(NO}_3\text{)}_2]\), and \([\text{Fe(NO}_3\text{)}_3.9\text{H}_2\text{O}]\) in \(x : (1-x) : 2\) proportion respectively. The appropriate amount of aqueous solution of sucrose (equal volume of metal nitrates) was then added slowly to the above solution and the mixture was stirred until complete dissolution occurred. Then the mixture was heated and evaporated at 100°C on a hot plate with stirring till it becomes dark viscous resin. Continuous heating leads to auto ignition of dried resin with the evolution of large quantities of gases. The brownish gray colored ash obtained after combustion. The whole process was over after 1 h, but the time between the actual ignition and the end of the reaction was less than 20 seconds.

2.5.4.2 Synthesis of barium substituted calcium, \(\text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4\) (BSC) ferrite

Barium substituted calcium ferrite with different chemical compositions like \(x=0.0, 0.2, 0.4, 0.6, 0.8\) and 1.0 were also prepared by citrate gel combustion method, by citrate gel method with using ultrasonic treatment and sucrose assisted combustion method as described in section 2.4.5.1. The starting materials in this synthesis were barium nitrate \([\text{Ba(NO}_3\text{)}_2]\), calcium nitrate \([\text{Ca(NO}_3\text{)}_2.4\text{H}_2\text{O}\] iron nitrate \([\text{Fe(NO}_3\text{)}_3.9\text{H}_2\text{O}\] and citric acid \([\text{C}_6\text{H}_8\text{O}_7\].
2.5.4.3 Synthesis of barium substituted strontium, $\text{Ba}_x\text{Sr}_{1-x}\text{Fe}_2\text{O}_4$ (BSS) ferrite

Similarly barium substituted strontium ferrite with different chemical compositions like $x=0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$ were also prepared by citrate gel combustion method. by citrate gel method with using ultrasonic treatment and sucrose assisted combustion method as described in section 2.4.5.1. The starting materials in this synthesis were barium nitrate $[\text{Ba(NO}_3)_2]$, strontium nitrate $[\text{Sr(NO}_3)_2]$, iron nitrate $[\text{Fe(NO}_3)_3\cdot 9\text{H}_2\text{O}]$ and citric acid $[\text{C}_6\text{H}_8\text{O}_7]$.

2.6 Characterization and analysis techniques

The pure alkaline earth metal (AEM) ferrites $\text{CaFe}_2\text{O}_4$, $\text{SrFe}_2\text{O}_4$ and $\text{BaFe}_2\text{O}_4$ are synthesized by citrate gel combustion method (MFCG) while the substituted alkaline earth metal ferrite ($\text{M}_x\text{M}_1-x\text{Fe}_2\text{O}_4$, $x=0.0, 0.2, 0.4, 0.6, 0.8$ and $1.0$) are prepared by citrate gel combustion method (CGCM), citrate gel combustion with ultrasonic treatment method (CGUTM) and sucrose assisted combustion method (SACM). After synthesis of pure and modified AEM ferrite, these were characterized by various techniques as illustrated in following sections.

2.6.1 Thermal studies of precursors

Thermogravimetric analysis is used in catalyst characterization procedure as an important tool to provide valuable information regarding drying ranges, hydration, decomposition temperature, stability limits, etc. In thermogravimetry, the weight of a sample is recorded over a period of time while its temperature is being raised linearly. A thermogram is obtained by plotting weight of a sample (on ordinate) against temperature (on abscissa). The horizontal region of the thermogram indicates the thermal stability of the sample, while weight loss is indicated by the curved portions. DTG is the first derivative plot of the TG curve from which a better understanding of the weight loss can be obtained from the dip in the curve. Thermo gravimetric (TG-DTA-DSC) analysis of the samples was performed on Shimadzu TG-DTA-DSC instrument with DSC60H detector. The precursor sample were placed in alumina cell and subjected to the TG-
2.6.2 Elemental analysis of sample by chemical method

The samples of Ca-Fe-citrate, Sr-Fe-citrate, Ba-Fe-citrate, Sr-Ca-Fe-citrate, Ba-Ca-Fe-citrate and Ba-Sr-Fe-citrate were characterized for their elemental content by recommended procedure of analysis. These are given below while the results are summarized in chapter 3.

2.6.2.1 Disintegration of complex

1.000g of complex was taken in Kjeldhal flask. To this 30 ml of aqua regia was added and heated on low flame till the entire complex was dissolved. Then around 5 ml of concentrated H\textsubscript{2}SO\textsubscript{4} was added and heated. The solution was cooled and the entire content was transferred in a beaker. The Kjeldhal flask was given washings and the washings were also transferred to the beaker. This solution was heated till the solution was reduced to 10-15 ml. The final solution was cooled and diluted to 100 ml using a 100 ml volumetric flask. 25 ml aliquot was used for separation of metals and their estimation.

2.6.2.2 Separation and estimation of calcium and iron

A) Volumetric method for calcium estimation

The portion of above disintegrated solution was transferred into 250ml beaker and 25ml of distilled water with 2 to 3 ml HCl was added to obtain the clear solution. The beaker was covered with watch glass and solution was heated to remove gases if any. After cooling, the solution was transferred in 250ml volumetric flask. The beaker was rinsed several times with distilled water and transferred to the volumetric flask. the solution was diluted with distilled water to 250ml.

Blank titration: 25 ml of 0.01M EDTA solution was taken; to this 10 ml of (pH =10) buffer solution and Eriochrome Black T indicator was added. The solution was then titrated with 0.01M ZnSO\textsubscript{4} solution till color changes from wine red to clear blue.
**Back titration:** Taken 25.0ml of the calcium ion solution into 250ml conical flask. It was diluted with about 25.0ml of distilled water. 2ml of the buffer solution is added to maintain the pH, and 3-4 drops of Eriochrome Black T (EBT) indicator. The solution is titrated with EDTA solution until the color changes from wine red to clear blue. The concentration of Ca ion calculated by using relationship as follows

\[ 1 \text{ml} \ 0.01 \text{M EDTA} = 0.4008 \text{mg Ca} \]  

\[ \left( \right) \]  

**B) Gravimetric method for Iron estimation**

Taken out 25ml of diluted solution by a burette in a 100ml beaker. 5ml dilute H₂SO₄ and 2ml concentrated HNO₃ add to it. The solution was boiled till it become yellow green then cool the solution and 0.5 g NH₄Cl was added to it. Stirred the solution and then added 1:1 ammonium hydroxide to the solution drop by drop till a reddish brown precipitate is formed and then 2ml excess ammonia was added to the solution. The solution was boil for 2 minutes to remove the excess ammonia. The brown precipitate of Fe(OH)₃ was formed, allow it to settle down. The precipitate was filters through ordinary filter paper. Pierce the filter paper and wash it with 10ml 2N NaOH solution and then with 10ml 3% H₂O₂ solution. The entire precipitate Fe(OH)₃ was collected in a separate beaker and filtered through the Whatmann filter paper no. 41. The precipitate was dried on a metallic cone. Ignite the precipitate and the filter paper is previously weighed silica crucible and heats it at about 800°C for 30 to 40 minutes. Cooled the crucible and weigh it with lid and the residue and find the weight of Fe₂O₃ call it X g repeat heating and cooling till constant weight.

\[ 100\text{ml diluted solution} = 4 \times \text{weight of residue} \times 111.7/ 159.7\text{g of Fe} \]  

\[ \left(2\right) \]  

**2.6.3 Fourier transform infrared (FT-IR) spectroscopy**

Fourier transform infrared (FT-IR) spectral study was mainly used to visualize the structural changes during thermal decomposition of AEM iron citrate precursor and to support the formation of alkaline earth metal-oxygen (AEM-O) and iron-oxygen (Fe-O)
bond. FT-IR spectra were recorded at RT using a Shimadzu spectrometer (FTIR-8400) equipped with KBr beam splitter. The FT-IR spectrometer was coupled with a personal computer and operated with the Infra Red Data Manager (IRDM) program. The samples were pressed into KBr pellets and were used for FT-IR studies.

2.6.4 X-ray powder diffraction studies

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a pure and substituted AEM ferrites and can provide information about unit cell dimensions. XRD pattern of the samples were recorded in ambient air at room temperature using D-8 Advance Brucker AXS diffractometer with Cu Kα radiation (λ = 1.5405 Å); at the Department of Physics, Savitribai Phule Pune University, Pune, India. The accelerating voltage, emission current, and scanning speed were 40kV, 40mA and 61/min, respectively, employing Ni filter. The data were collected at 0.02° with counting rate of 5sec/step in the 2θ range of 20°-80°. Average crystallite size was determined from the line broadening of the X-ray diffraction (XRD) peak of the sample using Scherer’s formula (Equation 3) applied to the strongest peak [27].

\[ D = \frac{0.89 \lambda}{(\beta \cos \theta)} \]  

where,

\[ \lambda \] is the wavelength (Cu Kα).

\[ \beta \] is the full width at the half-maximum of the high intensity peak in XRD pattern of AEM ferrite.

\[ \theta \] is the diffraction angle.

The peak position and relative intensities were characterized by comparison with the Joint Committee for Powder Diffraction Standards (JCPDS) card numbers examining the phase structure and purity.

2.6.5 X-ray florescence spectroscopy (XRF) analysis

The elemental composition of the AEM ferrite prepared from alkaline earth metal iron citrate calcined at different temperature was analyzed by X-ray florescence method. The
percentage composition of the AEM (Ca, Sr and Ba) and iron were determined using this instrument. The composition of catalysts was determined by X-ray fluorescence on a pw1400 Philips instrument. The obtained percentage of elements is compared with the calculated values.

2.6.6 Scanning electron microscopy (SEM) analysis

Scanning electron microscopy (SEM) is based on the strong interaction of electrons with matter and appreciable scattering by quite small atomic clusters. Electrons can be conveniently deflected and focused by electric or magnetic fields so that magnified real-space images can be formed in addition to simple diffraction patterns. This property of electron beam is used in SEM analysis. In SEM, the electron optics act before the specimen is reached to convert the beam into a fine probe, which can be as small as 100Å in diameter at the specimen surface. The technique is of high interest in catalysis because of its high special resolution. However, a serious drawback is that the results need not be really representative of the whole sample. This can be overcome by making many analyses at different locations of the sample particles and for many catalyst particles. The morphological features of the samples were imaged by Scanning Electron Microscopy and the composition of pure and substituted AEM ferrites was detected by energy dispersive X-ray spectroscopy with SEM JEOL JSM-660A unit. Prior to SEM-EDXS analysis samples were dried in air atmosphere at suitable temperature.

2.6.7 Electron dispersive X-ray spectroscopy (EDXS) analysis

The chemical compositions of catalysts were determined using energy dispersive X-ray analyzer (EDX). This technique is used in conjunction with SEM. An electron beam strikes the surface of a conducting sample. The energy of the beam is typically in the range 10-20 K eV. This causes X-rays to be emitted from the point of the material. The energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 2 microns in depth. By moving the electron beam across the material an image of each element in the sample can be acquired. The detector used in EDXS is the Lithium drifted Silicon detector. This detector must be operated at liquid
nitrogen temperature. When an X-ray strikes the detector, it generates electron-hole pairs. The size of the current pulse generated depends on the number of electron-hole pairs created, which in turn depends on the energy of the incoming X-ray. Thus, an X-ray spectrum can be acquired giving information on the elemental composition of the material under examination.

**2.6.8 Surface area determination (BET method)**

The Brunauer, Emmett and Teller (BET) method has been adopted as a standard procedure for surface area determination. BET method is ideally suited for the determination of surface area of firmly divided solids. By the introduction of a number of simplifying assumptions, the BET theory extends Langmuir model to multilayer adsorption. In the BET theory it is assumed that the solid surface possesses uniform, localized sites and the adsorption at one site does not affect adsorption at neighbouring sites. It is further assumed that the adsorption is multi-layer and the heat of adsorption of the second and the subsequent layers are identical and is equal to the liquefaction of the adsorbate. The BET equation can be represented as.

\[
\frac{1}{v} \left[ \left( \frac{P_0}{P} \right) - 1 \right] = \frac{1}{v_m c} + \frac{c-1}{v_m c} x \frac{P}{P_0} \quad \text{--------- (4)}
\]

Here, \(c\) = a BET constant for a given system at a given temperature and is related to the heat of adsorption. \(v\) = volume adsorbed at equilibrium pressure \(P\). \(v_m\) = volume of the adsorbate necessary to form a monolayer on the surface and \(P_0\) = saturation vapour pressure of the adsorbate. The BET equation demands a linear relation between \(1/v \left[ \left( P_0/P \right) - 1 \right] \) on y-axis and \(P/P_0\) on the x-axis. where slope = \(c-1/v_m c\) and y intercept = \(1/v_m c\). From the slope and y intercept, \(v_m\) can be calculated. The specific surface area of the sample is then calculated using the relation.

\[
\text{Surface area} = \frac{v_m N_o a_m}{22414} \times \text{weight of the catalyst} \quad \text{--------- (5)}
\]
Where $a_{av}$ = average area occupied by the nitrogen molecule (1.62 Å²) and $N_A$ = Avogadro number. Surface area of the material is determined by using Brunauer, Emmett and Teller (BET) method using Thermo Fisher Surface area analyzer Model SURFER.

2.7 Organic transformation reaction testing

2.7.1 Selective oxidation of styrene to benzaldehyde

Styrene oxidation was carried out in a round bottom flask (25 ml) equipped with X-crossed Teflon coated magnetic stirrer and a reflux condenser. 10 mmol styrene (99-% extra pure), 10 ml solvent, 0.1 g catalyst, 1.0 ml of hydrogen peroxide, 0.1 ml of hydrogen peroxide were added successively into the flask. Across organics], 10 ml solvent, 0.1 g catalyst, 1.0 ml of hydrogen peroxide

Fig. 1 Experimental set up for the selective oxidation of styrene to benzaldehyde (30%, MERCK). (Styrene / $H_2O_2$ molar ratio = 1) were added successively into the flask.
The reaction mixture was refluxed in temperature controlled oil bath and the reaction was carried out for the different temperature and time (Fig. 1). The reaction products were analyzed by gas chromatography mass spectrometry (GCMS). The gas chromatograph equipped with a XE-60 capillary column (30 m x 0.25 x 0.3 micrometer), flame ionization detector was used. The injector and column temperature were 280 and 140 °C respectively. 3-Nitrotoluene (99+%, MERCK) was used as an internal standard. The residual H₂O₂ in solution was determined by ceric sulphate titration method [28].

2.7.2 Selective epoxidation of styrene to styrene epoxide

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 as shown in Fig 2. In typical batch experiment, 5.2 g (50mmol)
of styrene [99+%, Across Organics]. 6.105 g (150 mmol) acetonitrile and 100 mg of Sr$_x$Ca$_{1-x}$Fe$_2$O$_4$ (0.0 ≤ x ≤ 1.0) catalysts were charge to the reactor. The mixture was heated to 343 K while stirring a solution of 2.5 ml (25 mmol) of hydrogen peroxide (30% aq. Merck) was added followed by addition of 6.41 g (200 mmol) methanol drop wise 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 chromatograph.

2.7.3 Selective epoxidation of cyclohexene to cyclohexene epoxide

The catalytic activity test was carried out without precautions against molecular oxygen in air. Within a round-bottom flask of 25 ml capacity placed in temperature controlled oil bath, the catalyst (5-30 mg) was added to a solution of cyclohexene (0.5 ml, 5 mmol) 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 H$_2$O$_2$ (UHP) (0.04-0.79 ml, 0.5-10 mmol) 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 H$_2$O$_2$ in absence of catalyst, were also investigated. Identification of products was performed using a gas chromatograph-mass spectrometer (XE-60 capillary column (30 m×0.25 m×0.3 m) with an electron ionization detector. Selectivity is calculated with respect to the converted cyclohexene, while the percent yield of cyclohexene oxide is calculated with respect to the selectivity of cyclohexene oxide.
2.7.4 Gas chromatography and Mass Spectroscopy (GCMS) analysis
The extracted solution was concentrated and was analyzed by QP 5050 Shimadzu gas chromatograph; it is equipped with a XF-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.
The styrene conversion and the selectivity of the reaction products were determined by using the following formulae [29].
The styrene conversion is defined as
\[
\text{Conversion (mol %)} = 100 \times \frac{\text{Styrene (in)} - \text{Styrene (out)}}{\text{Styrene (in)}} \quad -----(6)
\]
The selectivity was calculated based on the peak areas of the gas chromatogram by considering the different sensitivity factors of the flame ionization detector. The mol% of styrene as well as analytes is calculated from chromatogram by following formula and using a common internal standard solution.
\[
\text{Mol\%} = 100 \times \frac{\text{Area of analyte from the reaction mixture}}{\text{Area of fix quantity of same analyte (standard)}} \quad -----(7)
\]
The selectivity to product (i) is defined as
\[
\text{Selectivity (i) (mol \%)} = 100 \times \frac{\text{Corrected area (i)}}{\text{Sum of all corrected areas}} \quad -----(8)
\]
2.8 Catalytic degradation of Rhodamin-6G
2.8.1 Preparation of solutions of Rhodamine-6G
To check the catalytic efficiency of pure as well as substituted AEM ferrites we have prepared aqueous solutions of different concentration from 10ppm to 80ppm. Initially we have prepared 100ppm aqueous solution by dissolving 100mg of solid Rh-6G dye in
1000ml water then by dilution method the different solutions with different concentration were prepared.

### 2.8.2 Experimental set up

![Experimental setup flow sheet for the degradation of Rhodamine-6G](image)

Every 15min we took a sample of the solution and centrifuged to separate the catalyst from the rest of the solution.

**Fig. 3** Experimental setup flow sheet for the degradation of Rhodamine-6G

The catalytic activity is studied in ordinary light source which mainly emits the visible light in the range of 400-800nm. During this catalytic degradation experiment the catalytic reaction was conducted in simple catalytic reactor consist of cylindrical glass vessel (100ml capacity), magnetic stirrer, and micropipette. Along with reactor it require ultrasonic bath, centrifugation machine etc as shown in Fig. 3.
2.8.3 Experimental procedure for catalytic degradation study
In order to examine the catalytic activity of the material prepared we studied the effect on
degradation of Rh-6G in the presence of pure and substituted alkaline earth metal ferrites.
In order to test the effect of chemical composition of catalyst we have carried out the
degradation of Rh-6G over the surface of series of catalysts. All catalytic degradation
(CD) experiments were carried out in duplicate and at an ambient temperature, without
external supply of oxygen. In all CD experiments, 10ml. substrate solution of specific
concentration was taken in batch catalytic reactor vessel. The optimum amount of
catalyst was added and the mixture was agitated in an ultrasonic bath for 5 minutes to
obtain uniform suspension. Initial pH of suspension was recorded and the whole set up
then was placed in ordinary light. After the specific time interval of time CD reaction was
stopped and whole suspension was centrifuged at a speed of 3000 rpm for 5 minutes
(Remi India) and then filtered through a Whatmann filter paper no 42. The liquid portion
was used for the absorbance measurement. The extent of degradation of substrate over
the surface of pure as well as substituted alkaline earth metal ferrite under the different
experimental conditions like pH of suspension, catalyst loading, temperature, time etc.

2.8.4 Determination of extent of degradation by UV-visible spectral analysis
UV-visible spectroscopy has been commonly used to investigate the absorbance of the
residual concentration of Rh-6G in the reaction mixture. UV-visible analysis was done by
using UV-1601, Shimadzu spectrometer equipped with Xenon lamp as a source of light
from 800nm to 200nm wavelength. UV-visible spectral technique was also used to
determine progress of catalytic degradation reaction. The extent of catalytic degradation
(CD) of Rhodamine-6G ($\lambda_{\text{max}} = 384\text{nm}$) at an interval of 15 minutes stirring in presence
of ordinary light was primarily checked by means of decrease in absorbance on UV-
visible spectrophotometer.

2.9 Recycling and reuse of catalyst
The efficiency of the catalysts was checked by carrying out the reaction under optimized
amount of catalyst i.e. 0.1 g and by keeping all the conditions constant. The amount of
catalyst is very small (0.1g). Hence the recycling of catalyst is not very efficient. There were difficulties in collection of the catalyst due to the loss during filtration. But if the catalyst is collected from several batches and then reused it was found that the same catalytic activity with a 6-8% decrease in the percentage conversion. The distribution for the selectivity of the products remains the same.

In case of degradation of Rh-6G the reusability of catalyst was studied by reactivating the used catalyst for four times. The catalyst is removed by filtration and dried at 120°C for 1h and again used to study reusability.

2.10 References:


CHAPTER II