Chapter V

Summary
This thesis reports the synthesis, characterization and catalytic activity of pure and substituted alkaline earth metal ferrites. The important findings reported in this work are summarized below.

**Synthesis of pure and modified alkaline earth metal ferrites**

In the present thesis, synthesis of (i) pure calcium ferrite \( \text{CaFe}_2\text{O}_4 \), strontium ferrite \( \text{SrFe}_2\text{O}_4 \) and barium ferrite \( \text{BaFe}_2\text{O}_4 \) by citrate gel combustion method is done, (ii) Sr substituted \( \text{CaFe}_2\text{O}_4 \) \( (\text{Sr}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4) \), where \( 0.0 \leq x \leq 1.0 \), by citrate gel combustion method (CGC), citrate gel combustion with ultrasonic treatment (CGUT) and sucrose assisted combustion method (SAC), (iii) Ba substituted \( \text{CaFe}_2\text{O}_4 \) \( (\text{Ba}_x\text{Ca}_{1-x}\text{Fe}_2\text{O}_4) \), where \( 0.0 \leq x \leq 1.0 \), by citrate gel combustion method (CGC) and (iv) Ba substituted \( \text{SrFe}_2\text{O}_4 \) \( (\text{Ba}_x\text{Sr}_{1-x}\text{Fe}_2\text{O}_4) \), where \( 0.0 \leq x \leq 1.0 \), by citrate gel combustion method (CGC).

The catalysts thus prepared were characterized by various techniques such as TG-DTG, FTIR, powder XRD, SEM, EDX, XRF, BET. The catalytic activity of the pure alkaline earth metal ferrite catalysts was examined towards the selective oxidation of styrene to benzaldehyde while the catalytic activity of substituted alkaline earth metal ferrites were examined towards the epoxidation of styrene to styrene epoxide, epoxidation of cyclohexene to cyclohexene oxide and were also used for the catalytic degradation of toxic, mutagenic and carcinogenic dyes Rhodamine-6G (Rh-6G).

The conditions for maximum conversion of styrene as well as selectivity for desired product have been optimized by varying different parameters such as temperature, molar ratio of styrene to \( \text{H}_2\text{O}_2 \), amount of catalyst, reaction time, calcination temperature and various oxidizing agents. The influence of these parameters on the conversion and product distribution were also studied. The catalytic efficiency of substituted alkaline earth metal ferrite catalysts are checked towards the degradation of Rh-6G dyes in aqueous medium. The factors affecting on the rate of degradation like role of light and catalyst, pH of reaction medium, temperature, chemical composition of catalyst, calcination temperature, and concentration of Rh-6G and reusability of catalyst were also studied.

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Characterization and Catalytic Activity of Pure AEM Ferrites

Thermal analysis of calcium, strontium and barium iron citrate precursors gives the information about the temperature at which crystalline ferrite formation takes place. According to thermal analysis the CaFe$_2$O$_4$, SrFe$_2$O$_4$ and BaFe$_2$O$_4$ formation takes place at 600°C, 700°C and 800°C respectively. As the size of alkaline earth metal increases the formation temperature of ferrite also increases. The phase analysis done by X-ray diffraction studies show the single phase material formed at specific temperature with some impurities like carbonates of alkaline earth metal. The metal oxygen stretching frequencies are confirmed by FT-IR techniques. The stretching bands in the region 445cm$^{-1}$ to 550cm$^{-1}$ indicate the formation of spinel type along with a common stretching band at 1411cm$^{-1}$ to 1450cm$^{-1}$ indicate the presence of trace quantity of metal carbonate. The crystallite size of particle calculated by Debye-Scherrer formula was found to be smaller than other samples. Calcination temperature was found to affect the crystallite size and morphology of AEM ferrites. The chemical stoichiometry of AEM ferrites was investigated with AAS, XRF and EDX gave the atomic ratio M: Fe: O = 1:2:4, where M = Ca, Sr and Ba.

The catalytic activity of AEM ferrites are examined towards the selective oxidation of styrene to benzaldehyde. The promoting effect of the oxidation can be ascribed to the activation of oxygen ad species (such as O$^2-$), which was accompanied with the reduction of abnormal valence iron (Fe$^{3+}$) site in the surface layer of catalyst. The active oxygen species reversibly appeared and disappeared on the iron site due to sorption of atmospheric oxygen at the same temperature range. The heterogeneously catalyzed liquid phase oxidation of styrene proceeds by a free radical mechanism as confirmed by using tertiary butyl alcohol as a scavenger. The free radical involves initiation on the catalyst surface and homogeneous or heterogeneous propagation in the liquid. Styrene undergoes a C=C bond cleavage preferentially over AEM ferrite oxide catalyst to give benzaldehyde as a major product and formation of by-product such as styrene oxide (epoxide), benzoic acid, phenyl acetaldehyde as minor products.

SrFe$_2$O$_4$ is an efficient catalyst for selective oxidation of styrene in water as a solvent, in the presence of 30% H$_2$O$_2$ as oxidizing agent, exhibiting high activity and high
selectivity. The styrene oxidation catalyzed by SrFe$_2$O$_4$ without using any phase transfer catalyst or any organic solvent, leads to the conversion of styrene up to 51.0 mol% along with the formation of benzaldehyde (63.7 mol %) as major product, while styrene oxide (28.0 mol %) as minor, which quickly isomerizes into phenyl acetaldehyde. Temperature 70°C, time 18h, styrene/ H$_2$O molar ratio as 1, protic and polar solvent like water, catalyst amount 0.1g, favors the selective oxidation of styrene. The selectivity of benzaldehyde with respect to percentage yield for various solvents is in the order of H$_2$O > CH$_3$OH > C$_2$H$_5$OH > CH$_3$CN > CH$_3$COCH$_3$. The strong interaction between H$_2$O and H$_2$O$_2$ inhibit the coordination of substrate and enhance desorption of the products from the active sites, which prevents the deep oxidation of benzaldehyde to benzoic acid.

The catalytic activity studies shows that both CaFe$_2$O$_4$ and BaFe$_2$O$_4$ are an efficient catalyst for selective oxidation of styrene in acetone as a solvent, in the presence of 30% H$_2$O$_2$ as oxidizing agent, which exhibits high activity and high selectivity. Temperature 40°C (CaFe$_2$O$_4$) and 50°C (BaFe$_2$O$_4$), time 18 h, styrene/ H$_2$O$_2$ molar ratio as 1, aprotic and polar solvent like acetone, catalyst amount 0.1 g, favors the selective oxidation of styrene. Solvents have marked influence on the product distribution in selective oxidation of styrene; acetone seems to be the best solvent. The selectivity of benzaldehyde with respect to percentage yield for various solvents is in the order of CH$_3$COCH$_3$ > CH$_3$CN > C$_2$H$_5$OH > CH$_3$OH > H$_2$O. The 0.1 g of calcium ferrite catalyst amount is optimized for the maximum conversion of styrene up to 38±2 mol% with the selectivity of benzaldehyde and phenyl acetaldehyde is up to 91±2 mol% and 9±2 mol% respectively, due to the accessibility of the large number of molecules of the reactants to the catalyst is favored. The styrene oxidation catalyzed by BaFe$_2$O$_4$ without using any phase transfer catalyst leads to the conversion of styrene up to 45.1 mol% along with the selectivity of benzaldehyde (88.5 mol %) with 39.9% yield as major product, while styrene oxide (9.5 mol%) as minor product, which quickly isomerizes into phenyl acetaldehyde. The ultrasonication of catalyst shows the enhancement in the selective oxidation of styrene when the reaction carried out over the surface of CaFe$_2$O$_4$ and BaFe$_2$O$_4$. The ultrasonication of reaction mixture exposes the active sites on the surface of catalyst, which enhance the adsorption of styrene as well as H$_2$O$_2$ and promote the reaction. It also
breaks the hydrophobic cluster and makes the reagents available to accelerate the reaction, while in case of SrFe₂O₄ ultrasonication shows the adverse effect.

BaFe₂O₄ is found to be a better catalyst amongst all alkaline earth metal ferrites like MgFe₂O₄, CaFe₂O₄, and SrFe₂O₄ it may be due to different site preference energy of individual ions which depend on the ionic size of barium (1.35Å) and iron (0.67Å). Due to this almost all the Ba²⁺ ions occupy the octahedral lattice and equal number of Fe³⁺ ions occupies the tetrahedral lattice.

**Effect of substitution of Sr in CaFe₂O₄**
SrₓCa_{1-x}Fe₂O₄ (0.0 ≤ x ≤ 1.0) catalyst was successfully synthesized by citrate gel combustion (CGC) 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 SrₓCa_{1-x}Fe₂O₄ (0.0 ≤ x ≤ 1.0). The surface area determined by BET method, indicates Sr₀.₅Ca₀.₅Fe₂O₄ is found to have comparatively more surface area i.e. 175.19 m²/g for the same catalyst prepared by CGC method than CGUT and SAC method. Among all the substituted materials, Sr₀.₂Ca₀.₈Fe₂O₄ where the Ca²⁺ / Sr²⁺ ratio, is highest has the best rate for epoxidation of styrene.

As the concentration of ‘x’ increases, Sr²⁺ ions isomorphically remove Fe³⁺ ion from the Oh to Td sites due to greater site preference energy of Sr²⁺ ions than Fe³⁺ ions, which means that the substitution of Fe³⁺ ions by Sr²⁺ ions in the Oh sites creates stronger acid sites than those due to Fe³⁺ ions. Sr₀.₂Ca₀.₈Fe₂O₄ among all is found to be an efficient catalyst for selective oxidation of styrene to styrene epoxide in the mixture of acetonitrile and methanol (3:2) as a solvent in the presence of 30% H₂O₂ as oxidizing agent, suggesting a synergistic effect between the metal ion in the form of Sr-Ca and Sr-Fe on the active surface of ferrite and the Ca²⁺ / Sr²⁺ 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.
The optimized reaction conditions are as temperature 50 °C, time 12 h, styrene/ H₂O₂ 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. While Sr₀.₄Ca₀.₆Fe₂O₄ catalyst found to be a better candidate for maximum conversion of cyclohexene of 63.5 mol% with 43.1 mol% selectivity and 27.4% yield.

**Effect of substitution of Ba in CaFe₂O₄ and Ba in SrFe₂O₄**

In a series of barium substituted calcium (BSC) ferrite and barium substituted strontium (BSS) ferrite catalysts 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 2θ from 33.5 to 32.7) indicating the substitution of calcium by barium in CaFe₂O₄ while the shifting of high intensity peak toward the left side (lower 2θ 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.

The degradation of Rh-6G takes place in presence of catalyst and ambient light condition 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. Ba₀.₈Ca₀.₂Fe₂O₄ is found to be a better catalyst amongst BSC series and Ba₀.₈Sr₀.₂Fe₂O₄ is found to be a better catalyst amongst BSS series towards the degradation of Rh-6G in aqueous medium, it is due to the synergism between Ba, Ca and Fe ions in Ba₀.₈Ca₀.₂Fe₂O₄ and the synergism between Ba, Sr and Fe ions in Ba₀.₈Sr₀.₂Fe₂O₄. The Ba₀.₈Ca₀.₂Fe₂O₄ from BSC series and Ba₀.₂Sr₀.₈Fe₂O₄ from BSS series has highest catalytic activity for the oxidation of Rh-6G in presence of ambient
light condition. pH value 7.5; 20mg of catalyst. 50ppm dye concentration at room temperature are found to be optimized parameter during the degradation of Rh-6G.

Scope for Future Work

Catalysis for selective organic transformation needs lot of research and development, in order to apply it on industrial scale. Similarly catalytic degradation of highly stable pollutants like laser dye in absence of oxidant as well as any source of light also, need more research and development in order to apply on large scale that can be used. Thus the following can be the scope for further work in this area.

1. Designing new material with considerable conversion efficiency and stability. In addition to this, other spinel type of oxide or other than transition metal substituted AEM spinel type ferrites can be developed for this purpose.

2. Can reduce the size of oxide in order to enhance the catalytic efficiency towards the organic transformation as well as catalytic degradation of organic pollutants.

3. To look for other transformation reactions like reduction etc.