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Effect of chemical composition of $Sr_xCa_{1-x}Fe_2O_4$ ($0.0 \leq x \leq 1.0$) catalyst and alkali towards efficient and selective epoxidation of styrene

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ABSTRACT

Spinel type strontium substituted calcium (SSC) ferrite $Sr_xCa_{1-x}Fe_2O_4$ ($0.0 \leq x \leq 1.0$) catalyst synthesized by citrate-gel combustion method are well characterized by various techniques such as TG–DTG, FT-IR, X-ray diffraction, SEM, EDS and BET. The crystallization temperature of the spinel particle prepared by citrate gel is 600 °C, which is lower in comparison to ferrite prepared by other methods. Among this series of catalysts, $Sr_{0.2}Ca_{0.8}Fe_2O_4$ which has highest surface area shows the best catalytic efficiency. GCMS analysis revealed that, during the course of reaction the insertion of oxygen takes place selectively than the oxidative cleavage of C=C bonds; to give epoxide as major product, while addition of NaOH suppresses further isomerization of the styrene epoxide, thereby increasing the selectivity remarkably to give epoxide as major product. The catalyst containing both Sr^{2+} and Ca^{2+} ions are more active than pure $SrFe_2O_4$ and $CaFe_2O_4$. The synergistic effect of Sr^{2+}, Ca^{2+} ions and greater site preference energy of Sr^{2+} than Fe^{3+} favour the selective epoxidation of styrene in presence of 30% H_2O_2 as oxidant. The optimization and the effect of various reaction conditions on the conversion of styrene and product distribution were also studied.

1. Introduction

Mixed metallic oxides are designated as an important class of compounds and among them ferrites are the most prominent by virtue of their high electrical resistivity, thermodynamic stability, electro-catalytic activity and resistance to corrosion. Ferrites are better magnetic materials than pure metals because of their high resistivity, lower cost, easy manufacture and superior magnetization properties. Alkaline earth metal ferrites have attracted considerable attention owing to their potential application in high capacity batteries [1], wastewater cleaning [2], low magnetization ferro fluids [3] and as oxidizing agents[4–6].

Spinel ferrites are of great fundamental and technological importance due to their structural, electronic, magnetic and catalytic properties [7–10]. The physico-chemical properties of the ferrites are strongly dependent on the sites and the nature of the catalyst [11,12], which are closely related to the method of preparation. Epoxidation of styrene is a commercially important reaction for the production of styrene oxide, an important organic intermediate, as versatile and useful chiral building blocks in organic synthesis [13]. Earlier studies reported for the epoxidation of styrene were based on the use of titanium silicate-1(TS-1) [14–17], Ti–SiO_2 [14,18,19], Ti loaded Mobil Composition of Matter No. 41 (Ti–MCM-41) [17], and titanium and B co-substituted silicate-2 (TBS-2) and TS-1 [20] catalysts, using different oxidizing agents, such as tertiary butyl hydrogen peroxide (TBHP) [18], aqueous H_2O_2 [14,15,19,20], and urea–H_2O_2 adduct [16]. For all the above catalysts, the use of aqueous H_2O_2 resulted in a very poor selectivity for styrene oxide. High-styrene oxide selectivity (≥80%) could be obtained using urea–H_2O_2 adduct [16] and TBHP [18] 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. [21] have observed good catalytic activity and selectivity for γ-alumina in the epoxidation of limonene, cyclohexene and 1-octene by using anhydrous H_2O_2. 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 in epoxides for the production

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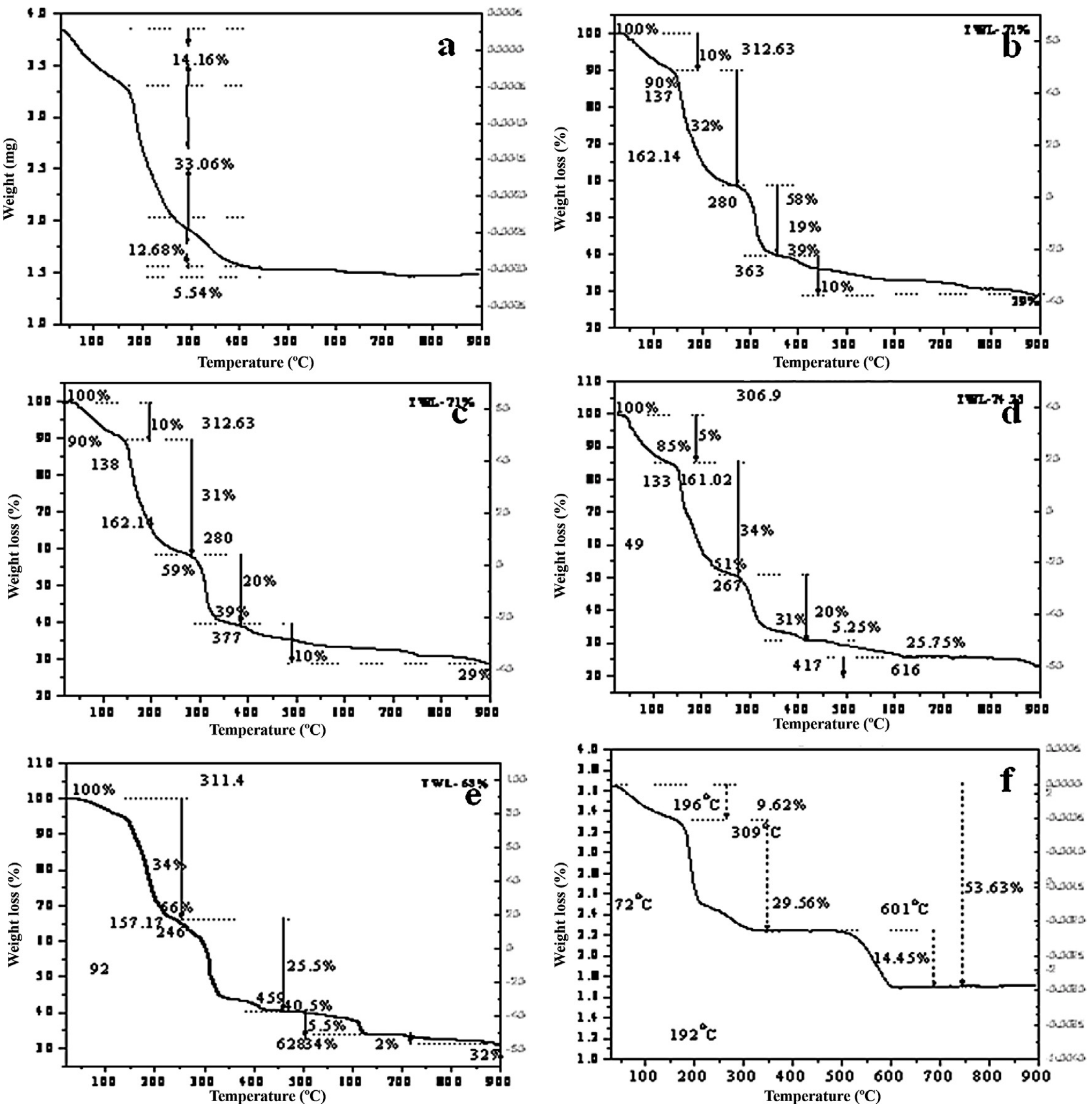

Fig. 1. TG curves of precursors of $CaFe_2O_4$ (a), $Sr_{0.2}Ca_{0.8}Fe_2O_4$ (b), $Sr_{0.4}Ca_{0.6}$ Fe_2O_4 (c), $Sr_{0.6}Ca_{0.4}$ Fe_2O_4 (d), $Sr_{0.8}Ca_{0.2}$ Fe_2O_4 (e) and $SrFe_2O_4$ (f) prepared by citrate gel combustion method.

of chemicals and fine chemicals [22]. 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 [23]. Many catalytic systems based on different metals have been reported for the epoxidation of a wide range of alkenes using hydrogen peroxide [24–26].

The alkaline earth metal ferrites like $CaFe_2O_4$ and $SrFe_2O_4$ were also used in selective oxidation of styrene but the selectivity of epoxide was very less while benzaldehyde was the major product in acetone and water as the reaction solvent, respectively [5,6]. The present work is undertaken to explore the possibility of combining the advantages of using hydrogen peroxide, a 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. We report for the first time, the use of a simple, inexpensive and reusable mixed metal oxide, SSC ferrite, $Sr_xCa_{1-x}Fe_2O_4$ (x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0), for the selective epoxidation of styrene in presence of 30% H_2O_2 and NaOH solution in suitable solvent system with very good selectivity and yield of styrene epoxide.

2. Experimental

2.1. Synthesis of catalyst by citrate gel combustion method

Analytical grade calcium nitrate [$Ca(NO_3)_2{\cdot}4H_2O$], strontium nitrate [$Sr(NO_3)_2$], iron nitrate [$Fe(NO_3)_3{\cdot}9H_2O$] and citric acid [$C_6H_8O_7{\cdot}H_2O$] (Specialized Pvt. Ltd., Mumbai, India) were used to prepare the strontium substituted calcium ferrites with different compositions $Sr_xCa_{1-x}Fe_2O_4$, where $0.0 \le x \le 1.0$. The specified volume 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 in to 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 to 800 °C for 2 h with a heating rate of 10 °C/min to obtain the single phase ferrite [5,7].

2.2. Characterization of catalysts

The thermal decomposition of the precursor studied by thermo gravimetric analysis (TG) is performed on a Shimadzu TG/DTA-60H system with ramp rate of 10 °C per minute in flowing air. The stretching vibration frequencies of the precursor and the catalyst are studied by FTIR (Fourier transform infrared) spectroscopy on a Shimadzu FTIR-8400 spectrophotometer using the KBr pellet method. The phases of the synthesized catalysts were characterized by X-ray diffraction (XRD) using a D-8 Advance Bruker Axs, X-ray powder diffractometer equipped with a position sensitive detector, scanning angle ranging from 10° to 900° at a scan rate 1° min^{-1}. The mean crystallite size was estimated by high intensity broadening technique using the Scherrer equation [27]. The morphology of the particles was examined by scanning electron microscopy (SEM) using a JEOL-2011 microscope. Chemical analysis of strontium ferrite was carried out by X-ray fluorescence method. Surface area of the material was determined by using Brunauer, Emmett and Teller (BET) method using Thermo Fisher surface area analyzer Model—SURFER.

2.3. Catalytic activities of strontium substituted calcium ferrites

2.3.1. 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 (50 mmol) of styrene [99+%, Aldrich], 6.105 g (150 mmol) acetonitrile and 100 mg of $Sr_xCa_{1-x}Fe_2O_4$ ($0.0 \leq x \leq 1.0$) catalysts were charged 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 the addition of 6.41 g (200 mmol) methanol dropwise to the above mixture over a period of 45 min. Aqueous 1 N sodium hydroxide was also added simultaneously to maintain the pH between 7.5 and 8.0. After 6 h 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 portions of dichloromethane after which the extraction liquid was dried by adding anhydrous sodium sulphate to it. The extracted solution was concentrated and analyzed by QP 5050 Shimadzu gas chromatography and mass spectroscopy (GCMS) equipped with a XE-60 capillary column (30m × 0.25 × 0.3 m) 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.

2.4. Results and discussion

2.4.1. Characterization of strontium substituted calcium ferrites

2.4.1.1. Thermo gravimetric analysis. Fig. 1(a–f) shows that 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 from 30 to 350 °C, except for the water loss between 100 °C and 110 °C. Near 350 °C, a sudden weight loss indicates the decarboxylation of the complexes. Above 600 °C no distinct weight loss was observed indicating the crystallization of ferrite.

2.4.1.2. FTIR study of strontium substituted calcium ferrites. Fig. 2a and f shows FTIR spectrum of $CaFe_2O_4$ and $SrFe_2O_4$ powder while Fig. 2b–e shows the FTIR spectrum of $Sr_xCa_{1-x}Fe_2O_4$ oxide (where $x = 0.2$, 0.4, 0.6 and 0.8) calcined at 700 °C temperature. Significant peaks are found in the range of 418–611 cm^{-1} in all spectra. The band appearing 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} (υ_1), is attributed to stretching vibration of tetrahedral groups $Sr^{2+}—O^{2-}$, and that around 440–457 cm^{-1} (υ_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 $CaFe_2O_4$ 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–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}.

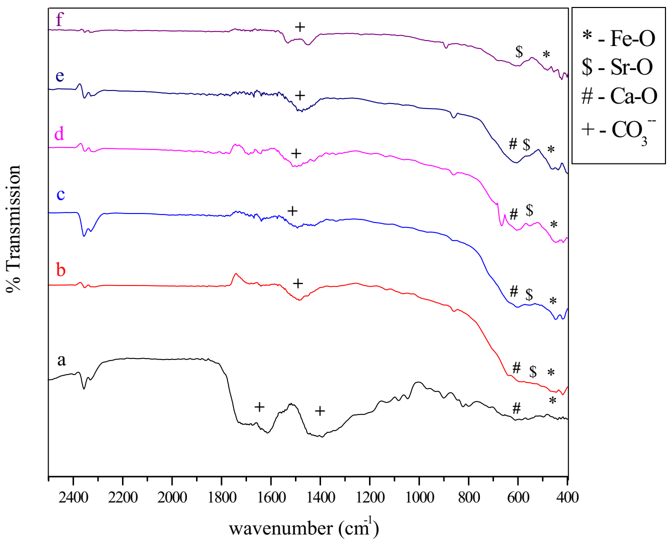

Fig. 2. Infrared spectra of $CaFe_2O_4$ (a), $Sr_{0.2}Ca_{0.8}Fe_2O_4$ (b), $Sr_{0.4}Ca_{0.6}Fe_2O_4$ (c), $Sr_{0.6}Ca_{0.4}Fe_2O_4$ (d), $Sr_{0.8}Ca_{0.2}Fe_2O_4$ (e) and $SrFe_2O_4$ (f) calcined at 700 °C prepared by citate gel method.

2.4.1.3. X-ray diffraction analysis of strontium substituted calcium ferrites. The X-ray diffraction studies of the samples treated at 700 °C temperature for 2 h have been carried out using Cu *Kα* radiation. Fig. 3 shows the XRD patterns of $Sr_xCa_{1-x}Fe_2O_4$, where ($0.0 \leq x \leq 1.0$). A pattern (a) is the spinel type $CaFe_2O_4$ 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 $SrFe_2O_4$ oxide where all the d spacing values are in good agreement with the standard data [28]. Patterns (b)–(e) are the XRD patterns of $Sr_xCa_{1-x}Fe_2O_4$ ($0.0 \leq x \leq 1.0$)

As the concentration of strontium ion in $Sr_xCa_{1-x}Fe_2O_4$ increases from ($0.0 \leq x \leq 1.0$) the highest intensity peak is shifted towards its left from 2θ angle 33.5, 33.1, 33.0, 32.9, 32.8 and 32.7, respectively (Fig. 3) indicating a higher interplanar distance and consequently, an 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 33.5–32.7, respectively which is in the range of 49–85 nm. The X-ray pattern of the substituted spinel type ferrites are monophasic and show the same pattern as that of the calcium ferrite, although a high intensity line shifts to lower 2θ value when the strontium doping increases are observed.

2.4.1.4. Electron dispersive spectra and morphology of strontium substituted calcium ferrites. The electron dispersive X-ray spectra of strontium substituted calcium ferrite, $Sr_xCa_{1-x}Fe_2O_4$ was prepared by citrate gel combustion method, where $x = 0.2$, 0.4, 0.6 and 0.8 calcined at 700 °C; the diffraction peaks 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 images of 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 $CaFe_2O_4$. As the concentration of strontium increases in $Sr_xCa_{1-x}Fe_2O_4$ (where $x = 0.2$, 0.4, 0.6 and 0.8) the morphology of the material changes from one form to another 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 show the agglomerization which results in the surface area of catalyst. In strontium ferrite ($SrFe_2O_4$ Fig. 4(f)) it forms a complex solid with rough morphology [6]. It may be due to increase in the concentration of strontium.

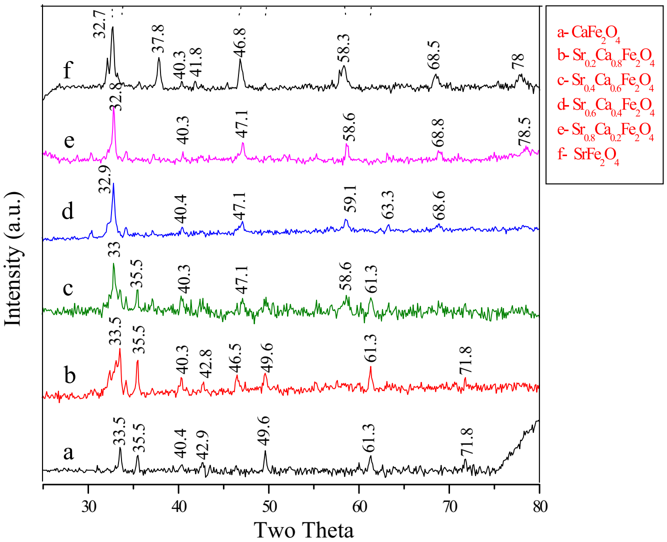

Fig. 3. X-ray diffraction pattern of $CaFe_2O_4$ (a), $Sr_{0.2}Ca_{0.8}Fe_2O_4$ (b), $Sr_{0.4}Ca_{0.6}Fe_2O_4$ (c), $Sr_{0.6}Ca_{0.4}Fe_2O_4$ (d), $Sr_{0.8}Ca_{0.2}Fe_2O_4$ (e) and $SrFe_2O_4$ (f) calcined at 700 °C prepared by citate gel method.

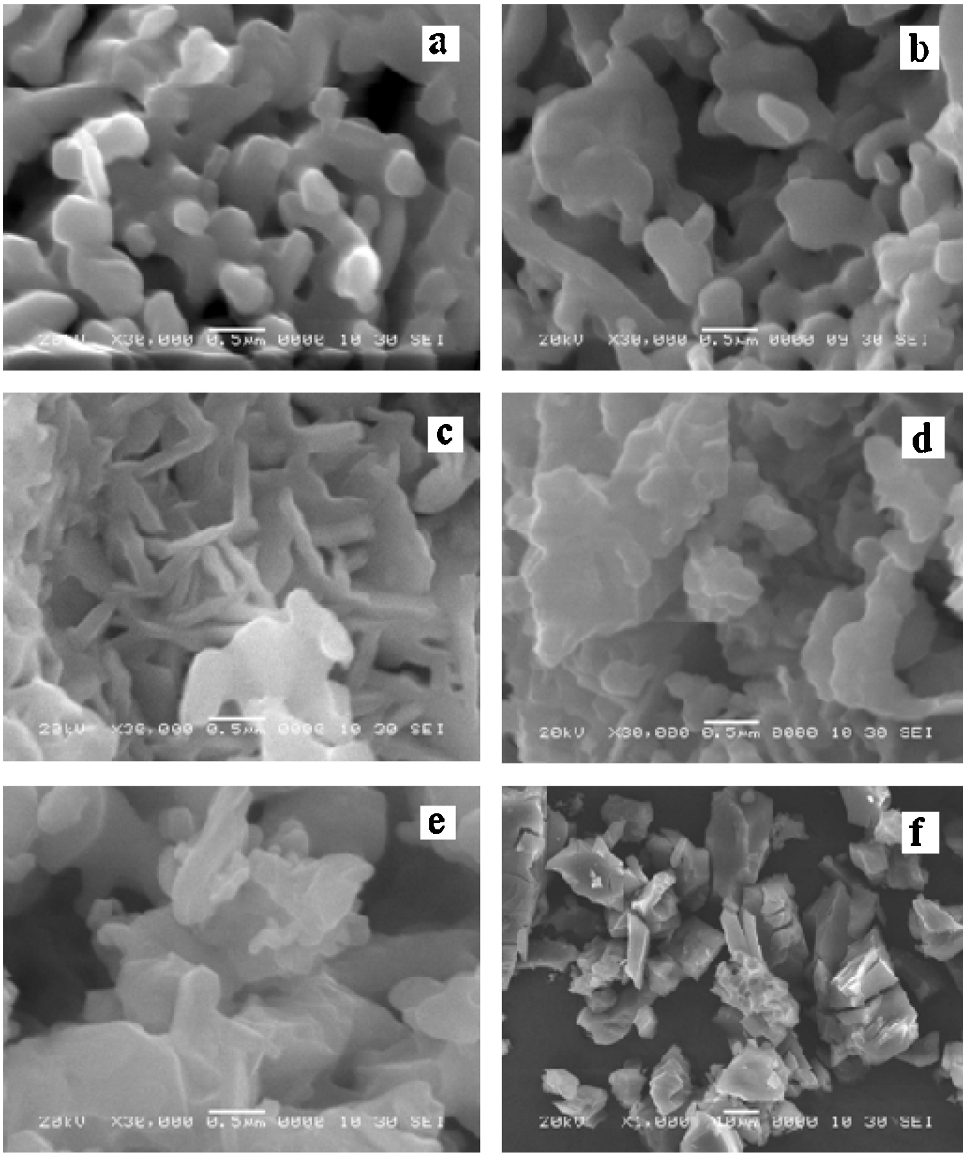

Fig. 4. Scanning electron microscope images of $CaFe_2O_4$(a), $Sr_{0.2}Ca_{0.8}Fe_2O_4$ (b), $Sr_{0.4}Ca_{0.6}Fe_2O_4$ (c), $Sr_{0.6}Ca_{0.4}Fe_2O_4$ (d), $Sr_{0.8}Ca_{0.2}Fe_2O_4$ (e) and $SrFe_2O_4$(f) calcined at 700 °C.

2.4.1.5. Specific surface area (BET) analysis. The BET surface area for the various samples of strontium substituted calcium ferrite ($Sr_xCa_{1-x}Fe_2O_4$) catalysts calcined at 700 °C was also carried out. Among all the prepared catalysts the surface area of $Sr_xCa_{1-x}Fe_2O_4$ catalysts, where $x = 0.2$ and 0.4, is 175.19 m^2/g. The surface areas 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 they are prepared by the same method. It may be due to the agglomerization of oxides during the heat treatment as also shown in SEM analysis (Fig. 4).

2.4.2. Catalytic activity of catalysts

In our previous work the parent calcium and strontium ferrite were found to be effective towards the selective oxidation of styrene to benzaldehyde as major product while styrene epoxide was observed as minor product [5,6]. 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 ($Sr_xCa_{1-x}Fe_2O_4$ where $x = 0.2$, 0.4, 0.6 and 0.8). The catalytic efficiency of $Sr_xCa_{1-x}Fe_2O_4$ is checked towards the epoxidation of styrene over the surface under optimized conditions. The optimization of reaction conditions is discussed below.

2.4.2.1. Effect of chemical composition of catalysts. The catalytic activity of oxides depends on the ability of the ions to be oxidized and reduced. Gao et al., [4] and Pardeshi et al., [5,6] have reported the selective oxidation of styrene to benzaldehyde over alkaline earth metal ferrites, where phenylacetaldehyde and epoxides are minor products in presence of hydrogen peroxide as the oxidizing agent. The use of pure $CaFe_2O_4$ or $SrFe_2O_4$ catalyst with aqueous hydrogen peroxide often results in extensive hydrolysis of epoxide to give benzaldehyde and phenyl acetaldehyde as desirable products. In the present study our efforts have been for the synthesis of hydrophobic catalyst to prevent the further hydrolysis of epoxide. Since epoxides are key building blocks in organic synthesis [29], as well as commercially important intermediates used in the synthesis of chiral pharmaceuticals, pesticides, epoxy paints, agrochemicals, perfume materials and sweeteners [30,31], it is a need to develop a suitable catalyst. Traditionally, epoxides are produced by the chlorohydrin process and the Halcon process [32]; however, a lot of by-products resulting from both processes are environmentally undesirable. Thus, the pursuit of 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^{2+} ions to improve the selectivity of epoxide instead of benzaldehyde. The catalytic efficiency of strontium substituted calcium ferrites is checked, under similar reaction conditions, towards the selective epoxidation of styrene; the results are shown in Fig. 5.

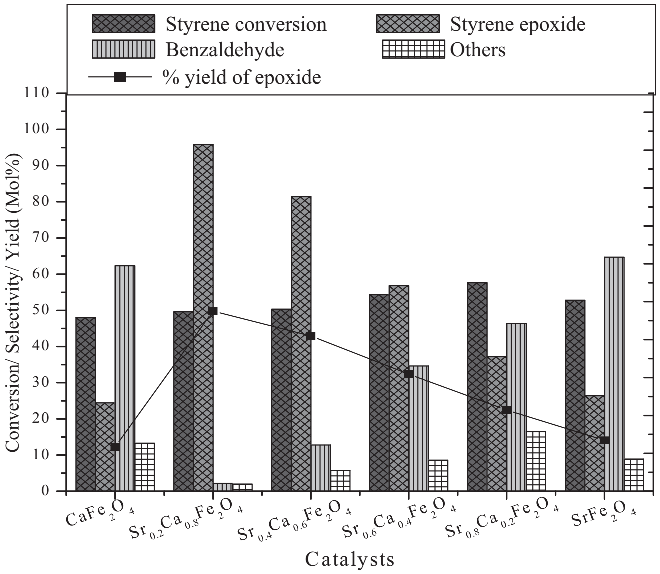

Fig. 5. Effect of chemical composition on the epoxidation of styrene; reaction conditions: styrene—50 mmol; oxidant—30% H_2O_2(25 mmol); catalyst—50 mg; solvent—acetonitrile + methanol; NaOH (1 M)—2 mL; reaction time—12 h; temperature—50 °C.

Among the various catalysts, $CaFe_2O_4$ 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 whereas the selectivity of benzaldehyde is 62.3 mol%. Changing the composition of $CaFe_2O_4$ by substituting calcium with strontium, the catalytic efficiency towards the epoxidation of styrene becomes better. In comparison to all the catalysts $Sr_{0.2}Ca_{0.8}Fe_2O_4$ 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 $SrFe_2O_4$, under similar reaction conditions, it shows least activity towards the epoxidation of styrene with 52.8% conversion and 26.4% selectivity of epoxide whereas the selectivity of benzaldehyde moves up to 64.7 mol%.

The efficiency of the catalyst can be improved by substituting the divalent strontium metal ion with different concentration at 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 [33]. Due to the higher ionic size of Sr^{2+} ions than Ca^{2+} ions, Sr^{2+} ions preferably move from Td to Oh site of the spinel .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+}, indicates 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 Sr–Ca and Sr–Fe on the active surface of the ferrite. From Fig. 5 it is clear that the composition containing both Sr^{2+} and Ca^{2+} are more active than pure $CaFe_2O_4$ and $SrFe_2O_4$. When Sr^{2+} and Ca^{2+} are in intimate contact in the $Sr_xCa_{1-x}Fe_2O_4$ system, the different reaction steps may sequentially occur over each metal, resulting in an enhanced activity compared to the parent ferrites. The remaining Fe^{3+} ions on the octahedral site react with H_2O_2 molecule to form iron peroxo species (Fe^{4+}—$O^{\bullet}$ radical) which react with styrene molecule to form Pi-bonded transient species on rearrangement to give metalloepoxy species [6].

The best activity of catalyst $Sr_{0.2}Ca_{0.8}Fe_2O_4$ of the series towards the selective epoxidation of styrene may be due to the insertion of structural defects in the catalyst [34]. 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, $Sr_{0.2}Ca_{0.8}Fe_2O_4$ 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+} favours the epoxidation of styrene reaction with better conversion of styrene and percent yield of styrene epoxide.

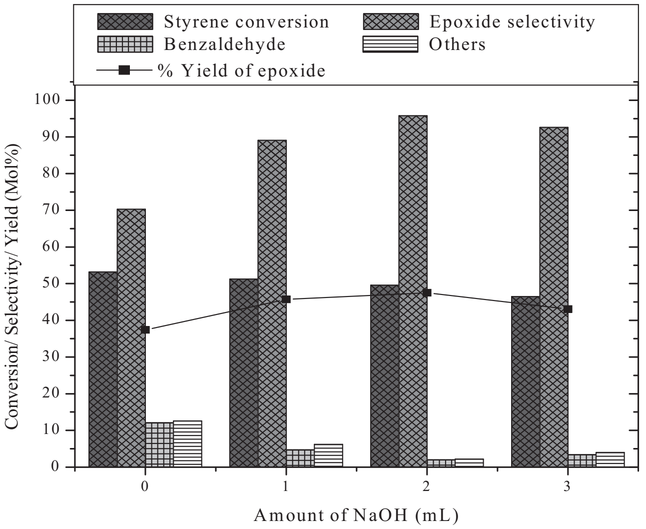

Fig. 6. Effect of concentration of NaOH on the epoxidation of styrene; reaction conditions: catalyst—50 mg of $Sr_{0.2}Ca_{0.8}Fe_2O_4$; reaction time—12 h; solvent—acetonitrile + methanol; and temperature—50 °C.

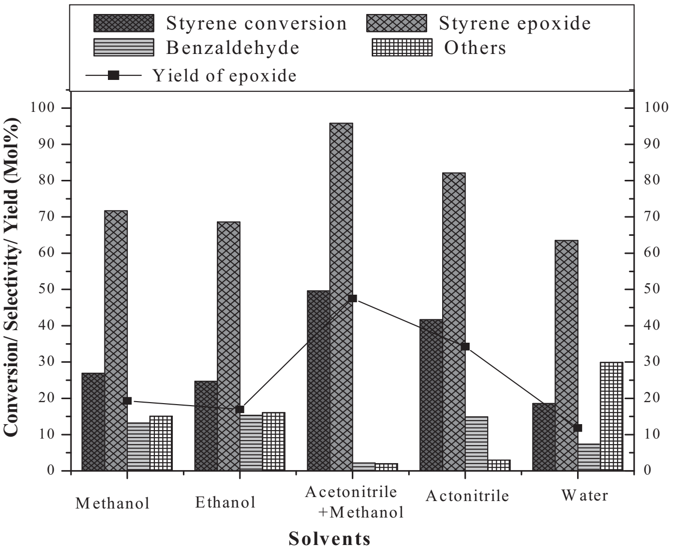

Fig. 7. Effect of solvent on the epoxidation of styrene; reaction conditions: styrene—50 mmol; oxidant—30% H_2O_2 (25 mmol); catalyst—50 mg of $Sr_{0.2}Ca_{0.8}Fe_2O_4$; reaction time—12 h; temperature—50 °C; NaOH (1 M)—2 mL.

2.4.2.2. Role of NaOH. In this study, we observed that in presence of NaOH both conversion and styrene oxide selectivity was higher than that in case of $CaFe_2O_4$ and $SrFe_2O_4$ alone. Pardeshi et al. have reported the selective oxidation of styrene over $CaFe_2O_4$ [5] and $SrFe_2O_4$ [6], where benzaldehyde was found to be a major product while the epoxides formed only up to 10 mol% in presence of 30% H_2O_2 as oxidizing agent. In this paper the same reaction is carried out over $Sr_xCa_{1-x}Fe_2O_4$ catalysts in the presence and absence of NaOH. From the observations it is clear that NaOH plays an important role in styrene epoxidation reaction. The results are shown in Fig. 6.

When the reaction is carried out in the absence of NaOH conversion of styrene takes place up to 53.2 mol% with 70.3 mol% selectivity and 37.4% yield of epoxide, respectively. The same reaction when carried out in presence of 1 mL NaOH (1 M) the styrene conversion is slightly decreased to 51.3 mol%, while the selectivity and yield of styrene epoxide is increased up to 89.1 mol% and 45.71%. When the same reaction is carried out in presence of 2 mL NaOH (1 M) the styrene conversion is reduced to 49.6 mol% but the selectivity and yield of epoxide increased up to 95.8 mol% and 47.5%, while in presence of 3 mL NaOH (1 M) the styrene conversion as well as selectivity of epoxide decrease to 46.5 mol% and 92.6 mol%, 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 2 mL NaOH. The enhancement of epoxide selectivity in presence of NaOH is due to the suppression of hydrogen bonding with the Lewis acid centres on the surface of catalyst and hence the isomerization of styrene epoxide to phenylacetaldehyde is eliminated [33]. While for 3 mL NaOH the styrene conversion decreases along with the selectivity of epoxide which may be due to excess concentration of NaOH, the hydroxyl ions compete with the styrene molecules and block most of the active sites on the surface of catalyst.

2.4.2.3. 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 conditions of time, temperature, catalytic amount etc.; the results are shown in Fig. 7. When the reaction is carried out in the presence of polar and protic solvents 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 [35]. But when the same reaction is carried out in aprotic solvents 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 the presence of acetonitrile with methanol can decrease the rate of ring opening reaction of styrene oxide with benzaldehyde and results in an increase in the selectivity of styrene oxide [36]. The use of polar solvents favours the oxidation of double bond, hence the mixture of CH_3OH and CH_3CN is found to be a better solvent.

2.4.2.4. Optimization of other reaction conditions.

2.4.2.4.1. Effect of time. The styrene conversion and product selectivity is plotted as a function of reaction time, at 50 °C, in CH_3CN and CH_3OH as reaction medium in the presence of 2 mL NaOH (1 M) over 0.05 g of $Sr_{0.2}Ca_{0.8}Fe_2O_4$ catalyst. Under these reaction conditions, the reaction was carried out by varying the time from 3 h to 15 h. The results are shown in Fig. 8. It is found that the percentage conversion of styrene increases from 23.7 mol% to 49.6 mol% with increase in the reaction time from 3 to 12 h, respectively and then marginal increment upto 50.8 mol% 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 decrease to 88.6 mol% and 45%, respectively.

The result indicates that as the reaction is run for a long time the selectivity of byproducts starts to increase. This may be due to the complete exhaustion of H_2O_2 in the reaction mixture as the reaction was run for long duration. The concentration of H_2O_2 reduced continuously with the reaction going on, and less amount of H_2O_2 was not favourable for further oxidation of styrene, therefore, more byproducts are formed and hence the selectivity of epoxide

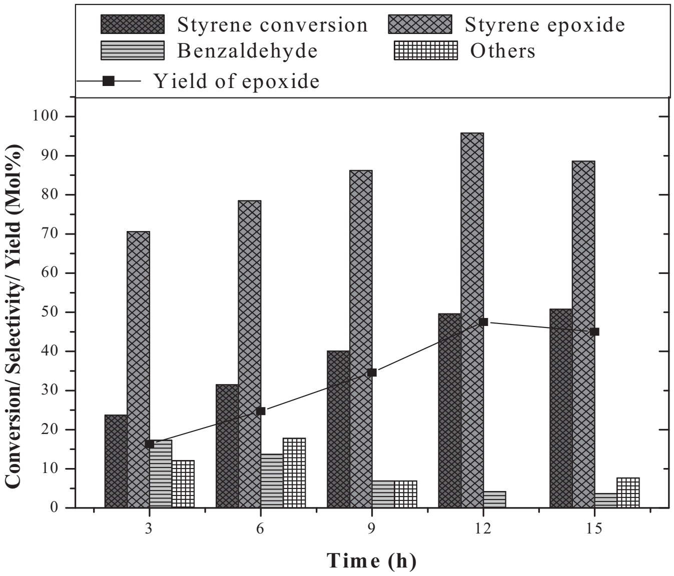

Fig. 8. Effect of time on the epoxidation of styrene; reaction conditions: styrene—50 mmol; oxidant—30% H_2O_2 (25 mmol); catalyst—50 mg of $Sr_{0.2}Ca_{0.8}Fe_2O_4$; solvent—acetonitrile + methanol; NaOH (1 M)—2 mL; and temperature—50 °C.

decreases. Moreover, undesirable products were also found to be formed when the reaction was allowed to run for a 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.

2.4.2.4.2. Effect of temperature on epoxidation. The effect of temperature on the epoxidation of styrene is examined under the optimized conditions of time, substrate/H_2O_2 molar ratio, solvent, 2 mL NaOH (1 M), catalytic amount etc.; the results are shown in Fig. 9, respectively. Epoxidation of styrene is carried out by 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. As the rise in temperature is in favour, 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 attraction is also enhanced which finally leads to enhancement in the selectivity of side products like benzaldehyde and phenylacetaldehyde.

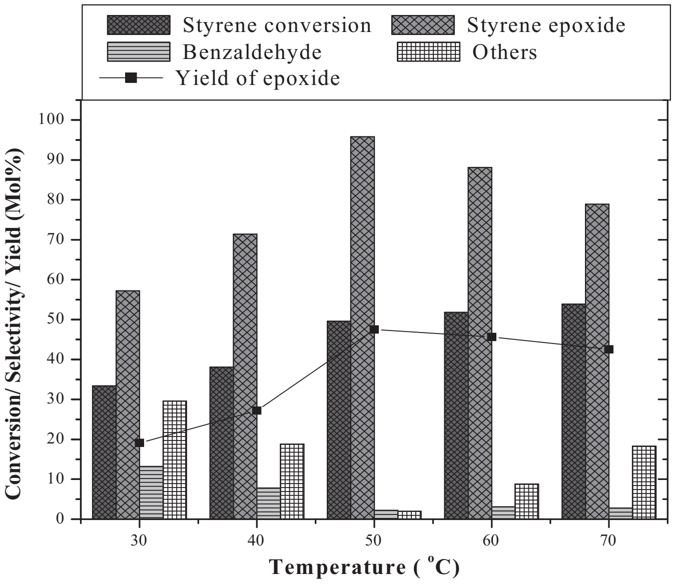

Fig. 9. Effect of temperature on the epoxidation of styrene; reaction conditions:styrene—50 mmol; oxidant—30% H_2O_2 (25 mmol); catalyst—50 mg of $Sr_{0.2}Ca_{0.8}Fe_2O_4$; solvent—acetonitrile + methanol; NaOH (1 M)—2 mL; and reaction time—12 h.

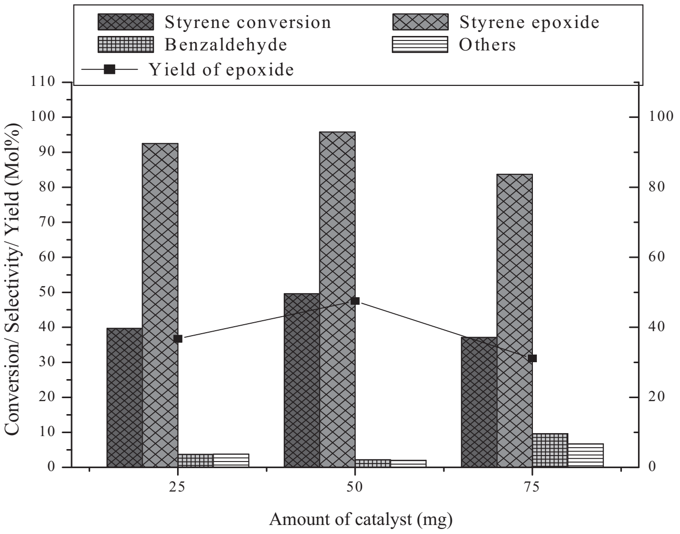

Fig. 10. Effect of catalyst amount on the epoxidation of styrene; reaction conditions: styrene—50 mmol; oxidant—30% H_2O_2 (25 mmol); reaction time—12 h; solvent—acetonitrile + ethanol; NaOH (1 M)—2 mL; and temperature—50 °C.

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 it shows an adverse effect on the adsorption of substrate and reagent molecule on the surface of catalyst.

2.4.2.4.3. Effect of catalyst amount on epoxidation. In order to check the effect of the amount of catalyst during the selective epoxidation of styrene, the reaction was carried out over $Sr_{0.2}Ca_{0.8}Fe_2O_4$ catalyst in a mixture of acetonitrile and methanol as solvent in the presence of 2 mL NaOH (1 M) with 25, 50, and 75 mg of catalyst for 12 h and 50 °C. The percentage conversion and percentage selectivity is shown in Fig. 10. The effect of amount of catalyst was studied keeping all other parameters (reaction time, temperature, mole ratio of substrate: H_2O_2) constant. It can be seen (Fig. 10) that % conversion of styrene is 39.7 mol% with 92.5 mol% selectivity and 36.7% yield of styrene epoxide over 25 mg 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 of 37.1 mol% with 83.7 mol% selectivity and 31.1% yield of styrene epoxide, respectively. At catalyst loadings of 25 mg and 50 mg, 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 H_2O_2 decomposition rate during the epoxidation is much higher than that at lower loading. At 75 mg sufficient H_2O_2 is not available for the epoxidation, which ultimately leads to a lower styrene conversion at the higher catalyst loadings.

2.4.2.4.4. Effect of substrate/H_2O_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 the possibility of

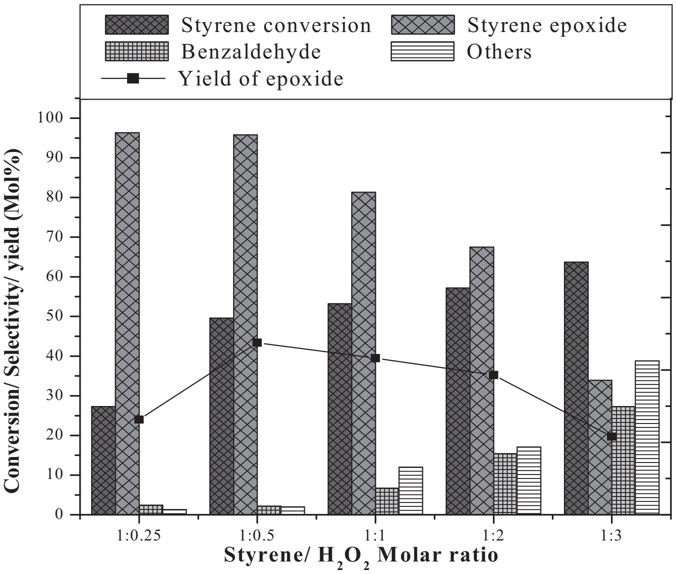

Fig. 11. Effect of styrene/H_2O_2 on the epoxidation of styrene; reaction conditions: catalyst—50 mg of $Sr_{0.2}Ca_{0.8}Fe_2O_4$; reaction time—12 h; solvent—acetonitrile + methanol; NaOH (1 M)—2 mL and temperature—50 °C.

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 the absence of catalyst and in the presence of 30% H_2O_2 the reaction proceeds up to 24.0 mol%, but here also the reaction proceeds randomly and gives 32.0 mol% of epoxide with 7.2% yield. Hence there is a need to optimize the styrene/H_2O_2 molar ratio to carry out the reaction selectively keeping all the remaining parameters like temperature, time, etc. constant. The reaction was subsequently carried out in the presence of different styrene/H_2O_2 molar ratios such as 1:0.25, 1:0.5, 1:1, 1:2 and 1:3, for which 0.05 g of catalyst was taken in 10 mL of solvent at 50 °C. The results are shown in Fig. 11. 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 competes 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 1:3 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. As the concentration of H_2O_2 increases the selectivity of styrene oxide decreases firstly due to the later nucleophilic attract on the styrene oxide and secondly due to the excess of water content in hydrogen peroxide that inhibits the coordination of oxidants with the active sites of catalyst [37].

3. Conclusions

$Sr_xCa_{1-x}Fe_2O_4$ ($0.0 \le x \le 1.0$) 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 $Sr_xCa_{-x}Fe_2O_4$ ($0.0 \le x \le 1.0$). The surface areas determined by BET method, for $Sr_{0.2}Ca_{0.8}Fe_2O_4$ and $Sr_{0.4}Ca_{0.6}Fe_2O_4$ are found comparatively more than that of the other catalysts prepared by the same method.

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.

$Sr_{0.2}Ca_{0.8}Fe_2O_4$ 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% H_2O_2 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.

Among all the substituted materials, $Sr_{0.2}Ca_{0.8}Fe_2O_4$ where the Ca^{2+}/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.

Temperature 50 °C, time 12 h, styrene/H_2O_2 molar ratio as 1:0.5, catalyst amount 0.05 g favour 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 centres of catalyst and oxygen from epoxide which prevent ring opening and hence the isomerization of styrene epoxide to phenyl acetaldehyde is eliminated.

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