

SrFe₂O₄ complex oxide an effective and environmentally benign catalyst for selective oxidation of styrene

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ABSTRACT

The SrFe₂O₄ spinel type catalyst is synthesized by citrate gel method. The precursor and oxide are well characterized by various techniques such as TG-DTG, FT-IR, X-ray diffraction, SEM, and X-ray fluorescence. The crystallization temperature of the spinel particle prepared by citrate gel method is 600 °C, which is lower than that of ferrite prepared by other methods. SrFe₂O₄ catalysts prepared by citrate gel method show high activity for styrene oxidation in the presence of H₂O₂ (30%) as an oxidizing agent and aqueous medium. GCMS analysis revealed that, during the course of reaction, the oxidative cleavage of C=C double bond of styrene takes place selectively to give benzaldehyde selectivity up to 64 mol%, whereas phenyl acetaldehyde selectivity 28 mol% and others' selectivity 8 mol% as minor product. Solvents have marked influence on the product distribution in the selective oxidation of styrene; water seems to be the best solvent. The optimization and effect of various reaction conditions on the conversion of styrene and product distribution were also studied. The highest benzaldehyde yield was obtained at 70 °C in water solvent over 0.1 g of catalyst with 18 h of reaction.

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1. Introduction

Spinel ferrites are of great fundamental and technological important due to their structural, electronic, magnetic and catalytic properties [1–3]. It has been recognized that they were used as permanent magnets, recording media, telecommunication, components in microwave, higher-frequency, and magneto optical devices [4–10]. 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. There are two kinds of lattices for cation occupancy. A and B sites have tetrahedral and octahedral coordination respectively. In the normal spinel structure divalent atom, occupying tetrahedral A sites, while trivalent atom, are sitting on the octahedral B sites. When 'A' sites being trivalent ions, while 'B' sites equally populated by divalent and trivalent ions, the spinel structure is referred to as the inverse kind [13,14].

The alkaline earth metal ferrites (MgFe₂O₄, Ca_xMg_{1-x}Fe₂O₄) powder with a particle diameter of 7–15 nm are used for the necrosis of the tumor; hyperthermia is an alternative to the conventional surgical, chemical therapy and radiation therapies for cancer. Mg_{0.5}Ca_{0.5}Fe₂O₄ powder is used to predict the tumor tem-

perature and coagulation area by a heat transfer simulation that takes the heat generation of ferrite powder, the metabolism heat and the cooling effect of blood flow into account. The strontium ferrite is widely applied in permanent magnetic material due to various advantages such as abundant raw material, low manufacturing cost, stable properties and moreover the sample cannot be oxygenated [15].

Several techniques have been used to prepare strontium ferrites such as ball milling [16], salt melting [17], chemical precipitation [18], glass crystallization [19] and self propagating high temperature synthesis [20]. However, most of these methods cannot be economically applied on a large scale because they require expensive and often toxic reagents, complicated synthetic steps, high reaction temperatures and long reaction times. This not only results in waste of energy but also harms our environment. These routes require prolonged thermal treatment to improve the crystallinity, purity, and morphology of the powders. Hence a chemical route can be excellent method for the synthesis of highly pure multi-component oxide due to its simplicity, good-control grain size, better homogeneity, better compositional control and lower processing temperatures which are few potential advantages of this wet chemical route over the conventional solid state reaction method [21]. Spinel ferrites are found to be highly active towards many aromatic alkylation reactions such as methylation of phenol, aniline, pyridine, phenol tert-butylation, etc. [22–24]. The alkaline earth metal ferrites like Mg_xFe_{3-x}O₄ and CaFe₂O₄ are used as catalyst for the selective oxidation of styrene in the pres-

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ence of 30% H_2O_2 as an oxidizing agent and acetone as a solvent [25,26].

The catalytic effectiveness of this system is due to the ability of metallic ions to migrate between the sub lattices without, altering the structure, which makes the catalyst efficient for many organic transformation reactions. The selective liquid-phase oxidation reaction is of significant importance in the fine chemicals and pharmaceutical industries [27,28]. Some strong oxidants such as KMnO_4 , CrO_3 , and HNO_3 [29,30] were applied traditionally for the oxidation of various substrates, which might result in much serious pollution and some potential risks in the process of operation. In terms of atom efficiency and environment friendly, after oxygen, aqueous hydrogen peroxide (30% H_2O_2) is a very attractive oxidant for industrial applications since water is the only by-product, and it is easy to be dealt with after reactions. The latest studies have therefore focused on the catalytic oxidation of styrene with H_2O_2 as the terminal oxidant [31–36]. Almost all these oxidation reactions have been carried out in organic solvents.

In the present paper, first time we are reporting the results for styrene (one of the most important pro-chiral alkenes) oxidation reaction in water as solvent using environmentally benign oxidant H_2O_2 over SrFe_2O_4 . SrFe_2O_4 (s), of Sr–Fe–O system was synthesized by citrate–nitrate gel combustion route and characterized by various techniques. The conditions for maximum conversion of styrene as well as selectivity for desired product have been optimized by varying different parameters such as temperature, molar ratio of styrene to H_2O_2 , amount of catalyst, reaction time, calcination temperature and various oxidizing agents.

2. Experimental

2.1. Synthesis of catalyst

Analytical grade $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and anhydrous citric acid obtained from MERCK (specialties Pvt. Ltd., Mumbai, India) were used without further purification as raw materials to prepare SrFe_2O_4 . The initial solution is prepared by dissolving ferric nitrate, strontium nitrate and citric acid into double distilled water. Concentrations of ferric nitrate, strontium nitrate are 0.5 M and 0.25 M respectively. The molar amount of citric acid is equal to that of metal nitrates in the solution. 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 and kept at a temperature of 60 °C until it turns to sol. Then the stabilized nitrate–citrate sol was rapidly heated to 80 °C and stirred constantly. Viscosity and color changed as the sol turned into a transparent stick gel. The gel was heated in evaporating dish where an auto combustion process takes place. Finally, the brown, floppy precursor is calcined at 700 °C for 2 h in muffle furnace [26].

2.2. Physico-chemical characterization

The thermal decomposition of the precursor is studied by thermo gravimetric analysis (TG/DTG/DTA) is performed on a Rigaku Thermo flex system with ramp rate of 10 °C min^{-1} in flowing air. The stretching vibration frequencies of the precursor and the catalyst are studied by FTIR (Fourier transform infrared spectra) spectroscopy on a Nicollet NEXUS 7000C spectrophotometer using the KBr pellet method. The phases of the synthesized catalysts were characterized by X-ray diffraction (XRD) using an ARL SCINTAG X'TRA X-ray powder diffractometer equipped with a position-sensitive detector, allowing all angles between 20° and 80° to be read simultaneously, at a scan rate of 4° min^{-1} . The mean crystallite size was estimated by high intensity broadening technique using the Scherrer equation [24]. The morphology and size of the particles

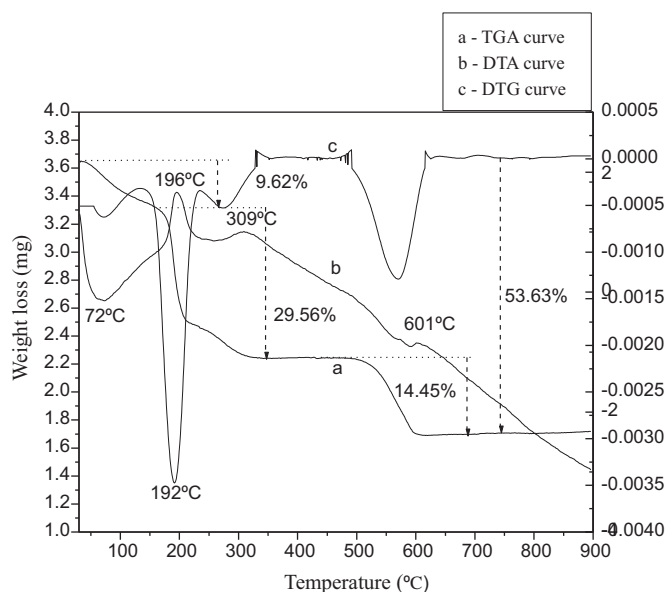


Fig. 1. TG–DTG–DTA study of strontium iron citrate precursor prepared by citrate gel method.

are examined by scanning electron microscopy (SEM) using a JEOL-2011 microscope. Chemical analysis of strontium ferrite carried out by X-ray fluorescence method.

2.3. Catalytic activity

The selective oxidation of styrene was carried out in a round bottom flask (25 ml) equipped with X-crossed Teflon coated magnetic stirrer and a reflux condenser. 10 millimole styrene [99+%, Aldrich], 10 ml water, 0.1 g catalyst, 1.0 ml of hydrogen peroxide (30% aq. Merck), $(\text{styrene}/\text{H}_2\text{O}_2)_{\text{molar}} = 1$ are added successively into the flask. The flask is then immersed in oil bath at a fixed temperature and time. The reaction was carried out for the different temperatures and time. The reaction products were analyzed with a gas chromatograph equipped with a XE-60 capillary column (30 m \times 0.25 \times 0.3 μm) and a flame ionization detector. The injector and column temperature were 280 and 140 °C respectively. 3-Nitrotoluene (99+%, Aldrich) is used as an internal standard. The residual H_2O_2 in solution is determined by ceric sulphate titration method. The styrene conversion and the selectivity of the reaction products are determined by the formulae [26,37].

3. Results and discussion

3.1. Characterization

3.1.1. Thermal decomposition of strontium iron citrate precursor

Fig. 1 shows TG–DTG–DTA curve for the thermal decomposition of strontium iron citrate precursor. The first weight losing peak was observed in the range of 50–180 °C and the corresponding weight loss is 9.6% corresponding to partial dehydration of the five crystallizing water molecule. This dehydration step is clearly seen as a peak in DTG at 72 °C. The second weight loss is 29.6% in the range of 175–300 °C corresponding to the loss of remaining water molecules and partial decomposition of citrate ligand, it matches well with the calculated value of 28.9%, this is also seen in the form of well defined peak at 196 °C in DTG curve and one small shoulder at 309 °C. The further weight loss in TG curve is of 14.5% (calculated 14.3%) in the range of 500–600 °C corresponding to the complete decarboxylation of the precursor into mixed oxide. A peak at 601 °C in DTG corresponds to the decarboxylation step. After 601 °C no notable

weight loss was found which indicate that SrFe_2O_4 was formed above 600°C along with the trace quantity of strontium carbonate.

The DTA curve indicates a broad endothermic peak at 80°C , corresponding to dehydration step. Two exothermic peaks in DTA curve at 196 and 309°C are attributed to the partial dehydration and decomposition of citrate ligand (29.6% weight loss). The whole thermal process of decarboxylation is accompanied by the evolution of large amount of gas, due to vigorous oxidation reaction [38]. The exothermic temperature in the DTA pattern is consistent with the major weight loss temperature in the TG pattern. Finally an endothermic peak at 601°C in DTA indicates the transition of precursor to strontium ferrite.

3.1.2. XRD studies of the as-prepared precursor and the calcined samples

The crystallinities and phase purity of the as-prepared precursor and the calcined products were examined by powder X-ray diffraction (XRD). Fig. 2 shows the XRD patterns of the precursor as well as the samples after calcination at different temperatures. All the peaks of the pattern for the calcined samples can be easily indexed to cubic SrFe_2O_4 with spinel structure, where the diffraction peaks at 2θ values of 32.7 , 37.8 , 46.8 and 58.3° of pattern (c) can be ascribed to the reflection of (002), (3 3 1), (4 2 0) and (5 2 0) planes of the spinel SrFe_2O_4 respectively [39]. While the peak at 68.5 and 78 (shown by * in Fig. 3) 2θ values indicate the presence of trace quantity of strontium carbonate associated with the SrFe_2O_4 phase (JCPDS card nos. 74-1491 and 84-1778). Using the Scherrer equation [40], the average size of the crystallites can be estimated from the full-width at half maximum (FWHM) of the highest intensity peak. As the calcination temperature increases from 700°C to 900°C the average crystallite size also increases from 50 nm to 82 nm which indicates the aggregation of the crystals. From the XRD studies it was confirmed that the single phase SrFe_2O_4 with trace of SrCO_3 is formed at 700°C temperature so this compound was selected for the further characterization.

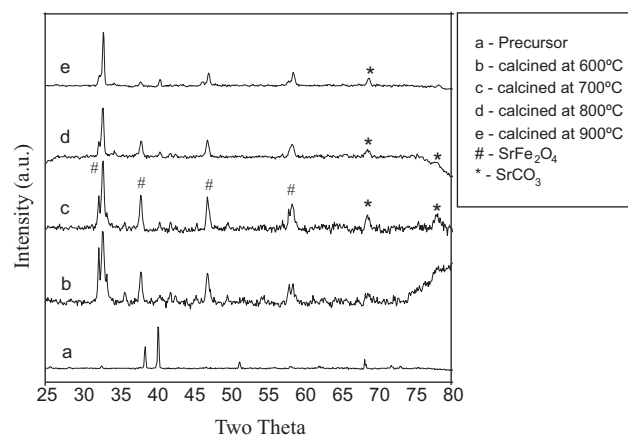


Fig. 2. X-ray diffraction pattern of strontium iron citrate precursor (a) strontium ferrite prepared by citrate gel method; (b) calcined sample at 600°C , (c) 700°C , (d) 800°C and (e) 900°C .

Table 1

Elemental analysis of strontium ferrite associated with strontium carbonate by X-ray fluorescence method in percentage by weight.

Strontium		Iron	
Calculated	Observed	Calculated	Observed
42.64	41.70	27.18	28.32

3.1.3. X-ray fluorescence analysis

The elemental composition of the SrFe_2O_4 prepared from strontium iron citrate calcined at 700°C was analyzed by X-ray fluorescence method. The percentage composition of the strontium and iron matches with the theoretical value as shown in Table 1. The result also indicates that the catalyst is associated with the trace quantity of strontium carbonate which gives the shoulder peak at 1435 cm^{-1} in IR spectrum.

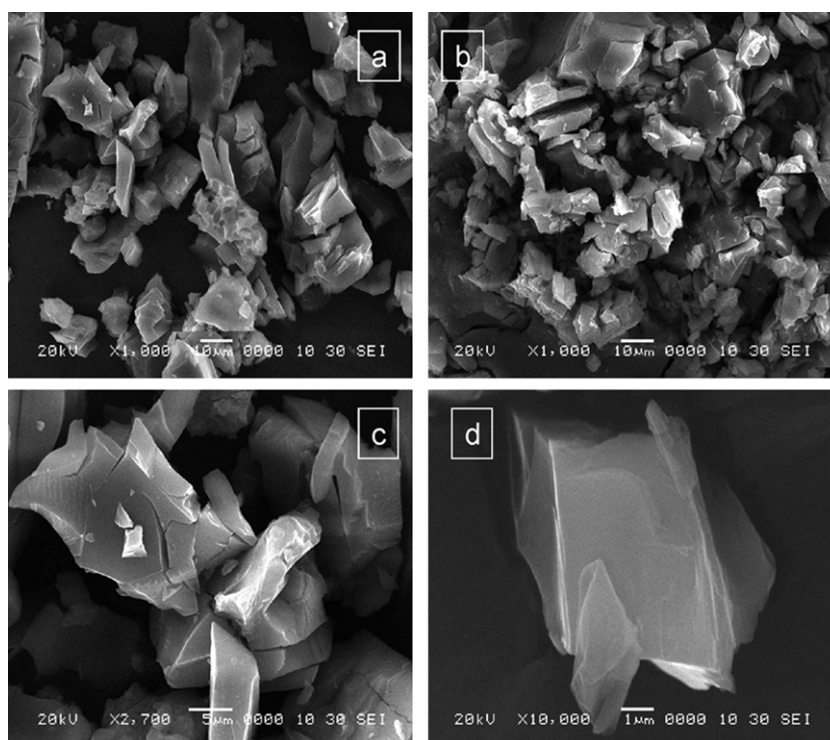


Fig. 3. Scanning electron microscopy image of strontium ferrite prepared by citrate gel method calcined at 700°C .

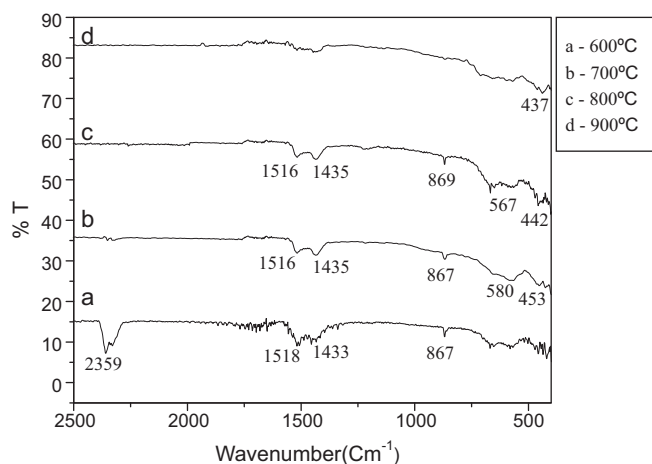


Fig. 4. FTIR spectra of strontium ferrite prepared by citrate gel method calcined at different temperatures (a) 600 °C, (b) 700 °C, (c) 800 °C and (d) 900 °C.

3.1.4. Scanning electron microscope

The scanning electron microscope (SEM) measurement was carried out to study the morphology of the sample. Fig. 3 shows the microstructure and morphology of strontium ferrite powder calcined at 700 °C for 2 h. From the photograph we can find that the morphology of the material is like fine flakes and well defined monodispersed particles at different magnifications are observed.

3.1.5. FTIR studies

Fig. 4(a)–(d) shows FTIR spectrum of SrFe₂O₄ powder calcined at different temperatures such as 600 °C, 700 °C, 800 °C and 900 °C respectively. No significant peaks are found below 1000 cm⁻¹ in spectrum (a), while in spectrum (b), two assigned absorption bands appeared around 580 cm⁻¹ (ν_1), attributed to stretching vibration of tetrahedral groups Sr²⁺–O²⁻ and that around 453 cm⁻¹ (ν_2), attributed to the octahedral group complex Fe³⁺–O²⁻. These two weak absorption bands are typical of spinel ferrites and the positions of these infrared bands are in the range which corresponds to strontium ferrite. Band localized at 867 cm⁻¹ is assigned for deformation vibration of the C–H group in Fig. 4(a) and (b) which is not found in spectrum (c) and (d). The spectrum also reveals that the carboxylates of the precursor transform into metal carbonate with the characteristic stretching location at 1435 cm⁻¹

and 1516 cm⁻¹ [41] for the samples calcined at 600 °C, 700 °C and 800 °C.

3.2. Catalytic properties of SrFe₂O₄ in selective oxidation of styrene

The oxidation of hydrocarbon to oxygenic compounds is a pivotal reaction in organic chemistry, both the fundamental research and industrial manufacturing [42,43]. Now, from both economic and environmental point of view, much attention has recently been focused on the aerobic catalytic oxidation of hydrocarbon to oxygenic compounds using metal catalysis. The metal ferrites are known to be highly efficient oxidation catalysts which have been successfully used to heterogeneously catalyze the transfer of an oxygen atom from oxidizing agent into hydrocarbon molecules in inorganic solvent [25].

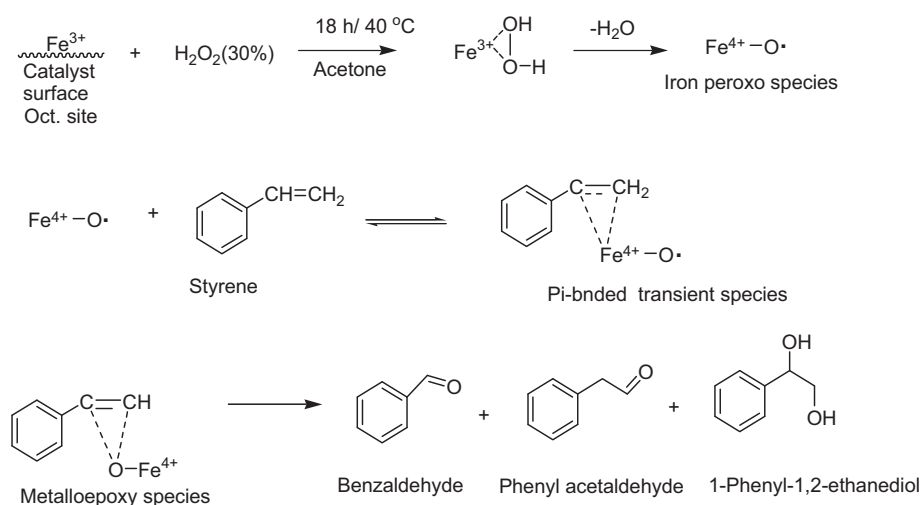
SrFe₂O₄ synthesized by citrate gel method, characterized for the structure, morphology and confirmed to be fine materials with spinel structure was then used as catalyst to evaluate its catalytic efficiency. The oxidation of styrene to benzaldehyde was used as a model reaction.

3.3. The role of catalyst

The selective oxidation of styrene was carried out in presence of 0.1 g of SrFe₂O₄ catalyst, 30% H₂O₂, water (10 ml) as reaction solvent, and at 70 °C temperature for 18 h, 50.8 mol% styrene conversion take place along with 63.7 mol% selectivity and 32.4 mol% yield of benzaldehyde. A free radical mechanism may be involved in selective oxidation of styrene over SrFe₂O₄ catalysts. In case of styrene oxidation in presence of H₂O₂ (30%) as oxidant, free radicals can be generated on the surface of catalyst, where catalyst accelerates the decomposition of hydrogen peroxide into free radicals.

In order to check the role of strontium ferrite towards selective oxidation of styrene, a blank reaction was carried out using 30% H₂O₂, water (10 ml) and temperature 70 °C, and the reaction was stirred under the similar reaction conditions for 18 h. In absence of SrFe₂O₄ catalyst no reaction takes place as seen from GCMS analysis. This observation ruled out the possibility of the reaction-taking place due to the thermal decomposition of H₂O₂.

In Scheme 1, the formation of metal-oxy radical (Fe⁴⁺–O•) on the catalyst surface is the initiation step of the reaction and the propagation of the reaction chain occurs in solution. A highest yield of benzaldehyde is possibly due to further oxidation of styrene



Scheme 1. Reaction mechanism for the selective mechanism of styrene to benzaldehyde over SrFe₂O₄ catalyst.

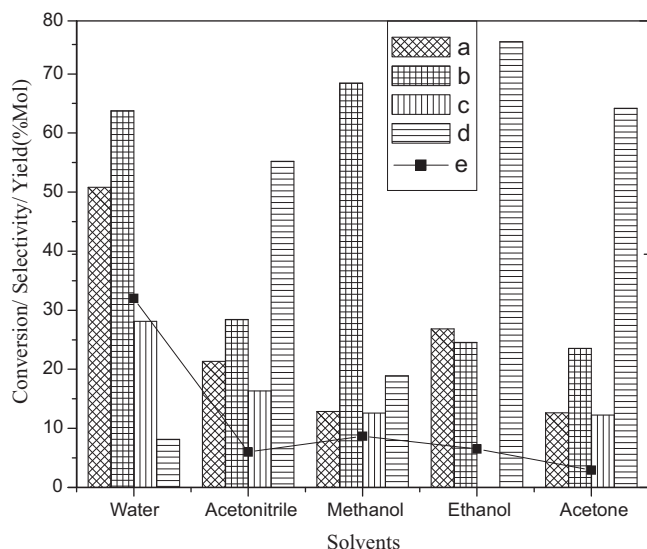


Fig. 5. Effect of reaction medium (solvent) on styrene conversion and product selectivity over SrFe₂O₄ catalyst, (a) styrene conversion, (b) selectivity of benzaldehyde, (c) phenyl acetaldehyde, (d) others and (e) yield of benzaldehyde.

oxide formed in the first step by a nucleophilic attack of Fe⁴⁺-O• on styrene followed by cleavage of the intermediate carbon-carbon double bond (see Scheme 1). As the reaction is carried out in water as solvent and high amount of water is present in 30% H₂O₂ may partly be responsible for the possible hydrolysis of styrene oxide to 1-phenylethane-1,2-diol in reaction.

3.4. Optimization of reaction condition

3.4.1. Influence of the solvents

The influence of solvent was studied by carrying the reaction in different solvents like ethanol, methanol, acetonitrile, acetone and water on the styrene conversion and selectivity of products over SrFe₂O₄ catalyst. The results are shown in Fig. 5. The same reaction was also carried out in absence of solvent in which very less (4 mol%) amount of styrene conversion is observed. Since H₂O₂ (30%) is added to the solution as a 70% aqueous solution, and polar solvent such as water (H₂O), ethanol (C₂H₅OH), methanol (CH₃OH), acetonitrile (CH₃CN) and acetone are used to avoid separation of the solvent during the reaction. The selectivity of benzaldehyde with respect to percentage yield is in the order of H₂O > CH₃OH > C₂H₅OH > CH₃CN > CH₃COCH₃. In the present study the catalyst shows better efficiency in water than the other solvents such as ethanol, methanol, acetonitrile and acetone. The styrene conversion in methanol, ethanol, acetonitrile, and acetone is 12.8 mol%, 26.8 mol%, 21.3 mol% and 12.6 mol% with, 8.8 mol%, 6.6 mol%, 6 mol% and 3 mol% yield of benzaldehyde respectively.

This may be partially due to easy reaction of H₂O₂ with these solvents and partially due to the adsorption of solvent molecule on the surface of catalyst which blocks the active acidic sites of the catalyst and avoid the further adsorption of styrene and H₂O₂ molecule [44]. When the same reaction was carried out in water as solvent the styrene conversion is increased up to 50.8 mol% with selectivity and percentage yield of benzaldehyde as 63.7 mol% and 32.4 mol% respectively. Water is found to be the good solvent, because of its polar and dissolving nature for a wide range of oxidant without complication due to the presence of acidic protons. Apart from this the strong interaction between H₂O and H₂O₂ inhibit the coordination of substrate and enhance desorption of the products from the active sites, which results in the prevention of deep oxidation of benzaldehyde to benzoic acid. Hence the selectivity of benzalde-

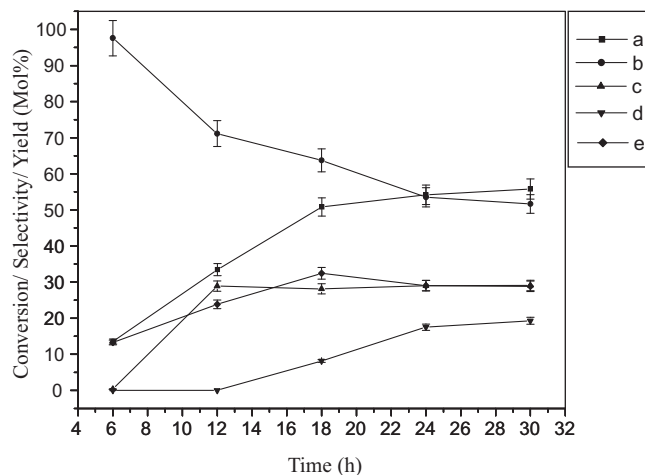


Fig. 6. Effect of reaction time on styrene conversion and product selectivity over SrFe₂O₄ catalyst, (a) styrene conversion, (b) selectivity of benzaldehyde, (c) phenyl acetaldehyde, (d) others and (e) yield of benzaldehyde.

hyde is a maximum (63.7 mol%) in water with 32.4% yield. This effect of solvents strongly supports that the selective oxidation of styrene to benzaldehyde takes place through radical mechanism. The fact was confirmed by carrying the same reaction in presence of tertiary butyl alcohol as a scavenger and by keeping all the reaction conditions constant. It is observed that only 5 mol% styrene get converted to benzaldehyde. This observation confirms a free radical mechanism is involved in styrene oxidation over a heterogeneous catalyst (see Scheme 1).

3.4.2. Influence of reaction time

The styrene conversion and product selectivity is plotted as a function of reaction time, at 70 °C, styrene/H₂O₂ molar ratio 1:1, in water as reaction medium over 0.1 g of SrFe₂O₄ catalyst. Under these reaction conditions, the reaction was carried out by varying the time from 6 h to 30 h. The results are shown in Fig. 6. It was found that at 6 h the conversion of styrene is 13.6 mol% with 13.3 mol% yield of benzaldehyde. As the reaction time increases to 12 h, styrene conversion increased to 33.5 mol% with 71.1 mol% selectivity of benzaldehyde and 28.9 mol% of phenyl acetaldehyde. At 18 h styrene conversion increases up to 50.8 mol%, while the selectivity and yield of benzaldehyde is 63.7 mol% and 32.4% respectively, along with the formation of byproducts like phenyl acetaldehyde and 1-phenyl-1,2-ethanediol up to 28.1 and 8 mol% respectively. If the same reaction was run for 24 and 30 h, marginal increment is observed in styrene conversion i.e. 54.2 and 55.8 mol%, but the selectivity of benzaldehyde suddenly decreases to 53.5 and 51.6 mol% with % yield 29 and 28.8 respectively. The result indicates that as the reaction is run for long time the selectivity of byproducts increases up to 49 mol%. This may be due to the complete exhaustion of H₂O₂ in the reaction mixture as the reaction was run for long duration [45].

Moreover, the impurities were also found to be formed when the reaction was allowed to run for long time. From the results it can be concluded that at 18 h the selectivity of benzaldehyde is better with respect to styrene conversion. The results for styrene conversion and selectivity of all the products were determined with the accuracy of ±5% error.

3.4.3. Influence of reaction temperature

The response of the reaction towards raise in temperature has been studied at different temperatures from 40 °C to 80 °C as shown in Fig. 7. The reaction was carried out by using 10 mmol (1.04 g), styrene, 10 mmol 30% H₂O₂ (1.16 g), over 0.1 g of SrFe₂O₄ cata-

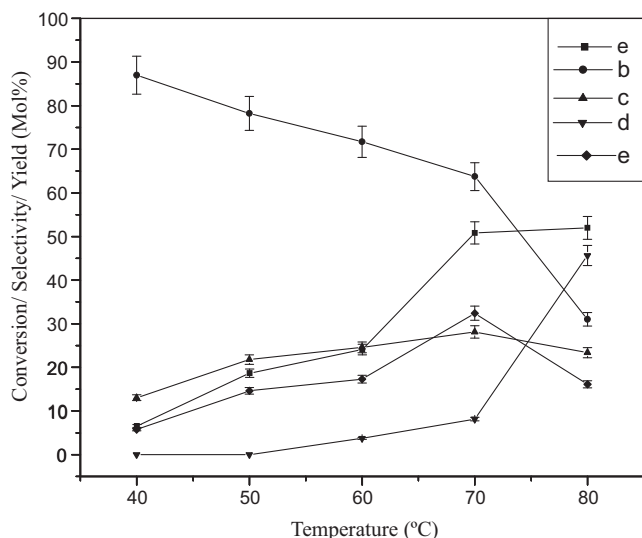


Fig. 7. Effect of reaction temperature on styrene conversion and product selectivity over SrFe_2O_4 catalyst, (a) styrene conversion, (b) selectivity of benzaldehyde, (c) phenyl acetaldehyde, (d) others and (e) yield of benzaldehyde.

lyst in 10 ml of H_2O as solvent for 18 h. At 40°C very less styrene conversion is observed (6.6 mol%), while the selectivity of benzaldehyde is up to 86.2 mol% with 13 mol% of phenyl acetaldehyde as a byproduct. As temperature increases to 50°C the styrene conversion increases by approximately three fold i.e. 18.0 mol%, while the selectivity of benzaldehyde decrease to 78.2 mol% with increase in the percentage selectivity of phenyl acetaldehyde to 21.8 mol%. Further increase in temperature is favorable for the styrene oxidation. At 60°C conversion of styrene increases to 24.1 mol%, while the selectivity of benzaldehyde decrease to 71.7 mol% with increase in percentage yield up to 17.3. When the same reaction was carried out at 70°C the styrene conversion sharply increases to 50.8 mol% with the better selectivity of benzaldehyde i.e. 63.7 mol% with 32.4% yield along with the formation of 28.1 mol% of styrene oxide, which get isomerizes to phenyl acetaldehyde, 1-phenyl-1,2-ethanediol up to 8.1 mol% as byproduct. Further rise in temperature (80°C) the marginal increment in styrene conversion was observed (52.0 mol%) with very poor selectivity of benzaldehyde (31 mol%). These results indicate that the cleavage of $\text{C}=\text{C}$ bond is favorable with increase in temperature up to 70°C , but however at high temperature instead of $\text{C}=\text{C}$ bond cleavage, $\text{C}-\text{O}$ bond cleavage is done preferably, which results into increase of byproduct like phenyl acetaldehyde and 1-phenyl-1,2-ethanediol up to 53.0 mol%. The observation is in agreement with previous reports [25,46]. The results for styrene conversion and selectivity of all the products were determined with the accuracy of $\pm 5\%$ error.

3.4.4. Influence of styrene/ H_2O_2 molar ratio

The styrene conversion is observed up to 63.0 mol% in the presence of catalyst without using any oxidant. This clearly indicates that the possibility of the reaction occurring due to the participation of lattice oxygen of catalyst. But the reaction does not give the selective product. The selectivity of benzaldehyde is only 16.0 mol% with 10.0% yield. In absence of catalyst and in presence of 30% H_2O_2 the reaction proceed up to 60.0 mol%, but here also the reaction proceed randomly and give 12.0 mol% of benzaldehyde with 7.2% yield. Hence there is a need to optimize the styrene/ H_2O_2 molar ratio to carry out the reaction selectively keeping all the remaining parameter like temperature, time, etc. constant. The reaction was subsequently carried out in the presence of different styrene/ H_2O_2 molar ratios such as 2:1, 1:1, 1:2 and 1:3, for which 0.1 g of catalyst were taken in 10 ml of water at 70°C . The results are shown

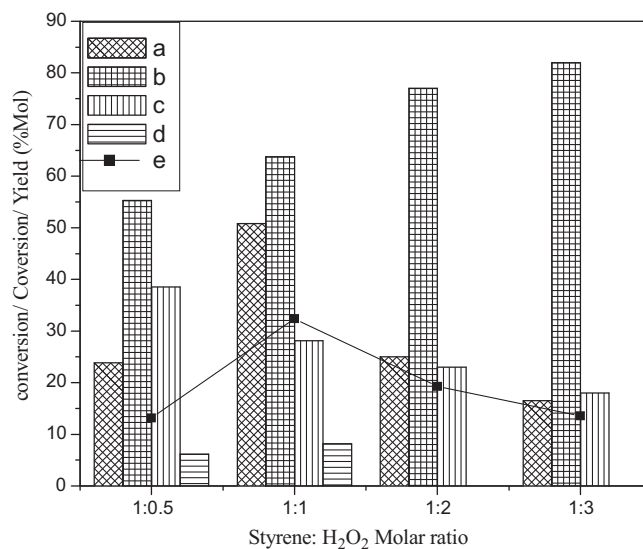


Fig. 8. Effect of styrene/ H_2O_2 molar ratio on styrene conversion and product selectivity over SrFe_2O_4 catalyst, (a) styrene conversion, (b) selectivity of benzaldehyde, (c) phenyl acetaldehyde, (d) others and (e) yield of benzaldehyde.

in Fig. 8. From the results it is observed that the conversion of styrene is comparatively less when the styrene/ H_2O_2 molar ratio is 2:1 (about 23.8 mol%). This may be due to significantly reduced $\cdot\text{OH}$ radicals as less amount of H_2O_2 compete with excess styrene for coordination. As the concentration of H_2O_2 increases (1:1), the styrene conversion as well as the selectivity of benzaldehyde also increases. The percentage conversion of styrene is 50.8% and the product selectivity and yield for benzaldehyde is 63.7% and 32.4% respectively. At this molar ratio of 1:1, H_2O_2 could freely coordinate to metal and decompose to form $\cdot\text{OH}$ radical. When the same reaction was carried out at styrene/ H_2O_2 molar ratio 1:2 and 1:3 in presence of 0.1 g catalyst the styrene conversion was suddenly decreased to 25.0 mol% and 16.5 mol% with decreasing the percentage yield of benzaldehyde to 19.2 and 13.6 respectively which may be due to the presence of excess water supplied by H_2O_2 itself [47].

3.4.5. Influence of catalyst amount on the oxidation reaction

The reaction was carried out by varying the catalytic amount from 0.05 g to 0.2 g while keeping the molar ratio of styrene/ H_2O_2 at 1:1 and reaction temperature at 70°C for 18 h. The percentage conversion of styrene and percentage selectivity of products is shown in Fig. 9. For 0.05 g of catalyst 28.8 mol% of styrene conversion takes place with 72.7 mol% and 27.3 mol% selectivity for benzaldehyde and phenyl acetaldehyde respectively. The yield of benzaldehyde is 21.0%. As the catalytic amount increases to 0.1 g the styrene conversion also increases to 50.8 mol%, while the selectivity of benzaldehyde, phenyl acetaldehyde and 1-phenyl-1,2-ethanediol are 63.7 mol%, 28.1 mol% and 8.1 mol% respectively. The yield of benzaldehyde increases to 32.4%; this is due to the availability of large surface area and the acid sites, which favors the dispersion of more active species. Therefore, the accessibility of the large number of molecules of the reactants to the catalyst is favored. As the amount of catalyst increases from 0.1 g to 0.15 g and 0.2 g, styrene conversion decreases to 34.7 mol% and 26.5 mol% with the selectivity of benzaldehyde as 62.3 mol% and 60 mol% respectively. The selectivity of byproducts like phenyl acetaldehyde increases to 27.6 mol% and 28.6 mol% respectively and for that of 1-phenyl-1,2-ethanediol is 10.0 mol% and 11.4 mol% respectively. The reason for lower activity at higher amount of catalyst does may possibly be due to adsorption or chemisorptions of two reactants on separate catalyst particles, thereby reducing the chance to interact. Similar

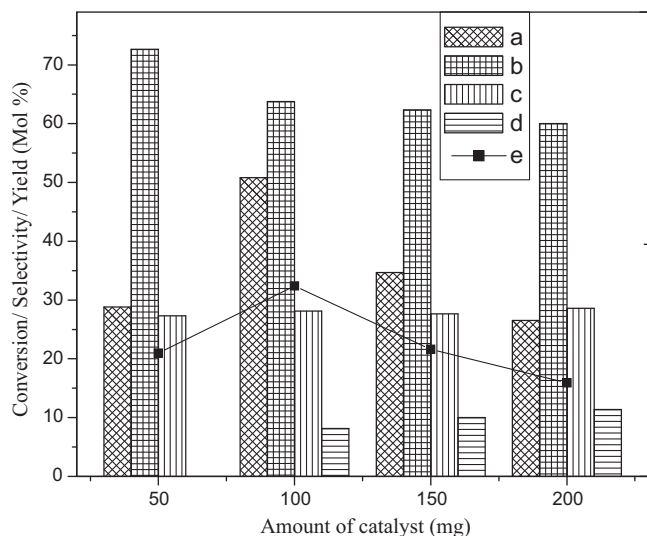


Fig. 9. Effect of amount of catalyst on styrene conversion and product selectivity over SrFe_2O_4 catalyst, (a) styrene conversion, (b) selectivity of benzaldehyde, (c) phenyl acetaldehyde, (d) others and (e) yield of benzaldehyde.

observations were noted by Maurya et al. [48]. The results show that 0.1 g of catalyst is the optimum amount to obtain maximum conversion of styrene with better selectivity of benzaldehyde.

3.4.6. Effect of calcination temperature on the oxidation reaction

The percentage conversion of styrene and the percentage selectivity of different products were studied over the 0.1 g of SrFe_2O_4 catalyst calcined at different temperatures from 600 °C to 900 °C at the optimized conditions; the results are shown in Fig. 10. When the reaction is carried over the catalyst calcined at 600 °C, the conversion of styrene is 58.1 mol%, while the selectivity of benzaldehyde, phenyl acetaldehyde and 1-phenyl-1,2-ethanediol are 47.6 mol%, 25.4 mol% and 23.1 mol% respectively. As the calcination temperature increases to 700 °C, though the styrene conversion decreases (50.8 mol%) the benzaldehyde selectivity is increased up to 63.7 mol% with 32.4% yield. For further increase in temperature to 800 °C and 900 °C, the styrene conversion is decreased to 44.8 mol% and 32.9 mol% respectively. The selectivity of ben-

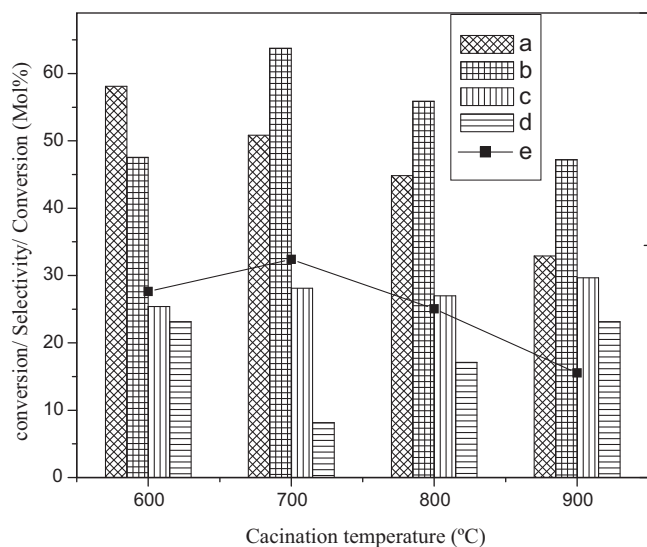


Fig. 10. Effect of calcination temperature of catalyst on styrene conversion and product selectivity over SrFe_2O_4 catalyst, (a) styrene conversion, (b) selectivity of benzaldehyde, (c) phenyl acetaldehyde, (d) others and (e) yield of benzaldehyde.

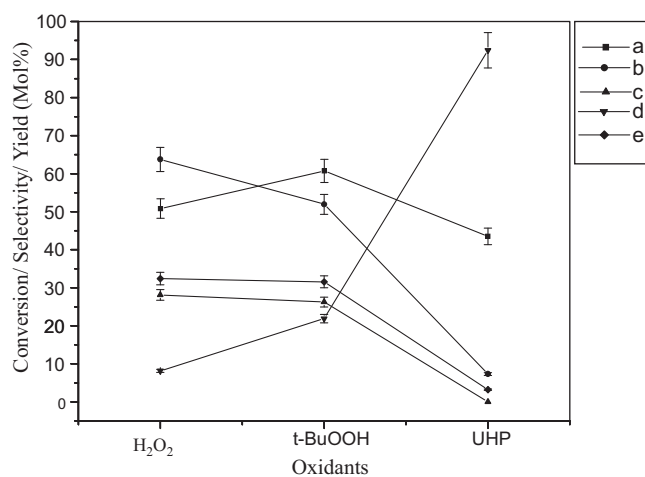


Fig. 11. Effect of oxidizing agents on styrene conversion and product selectivity over SrFe_2O_4 catalyst, (a) styrene conversion, (b) selectivity of benzaldehyde, (c) phenyl acetaldehyde, (d) others and (e) yield of benzaldehyde.

zaldehyde also decreases to 55.9 mol% and 47.2 mol% respectively against the cost of increasing the percentage of phenyl acetaldehyde and 1-phenyl-1,2-ethanediol up to 29.6 and 23.1.

This results show that the catalyst calcined at 700 °C gives the better transformation of styrene with highest selectivity of benzaldehyde. This may be due to the maximum availability of the number of Fe^{3+} ions on the octahedral site of the catalyst surface, which is responsible in making the catalyst more effective for catalytic reaction.

3.4.7. Effect of oxidants on the styrene oxidation

The effect of different oxidants on the catalytic activity of SrFe_2O_4 in styrene conversion and product distribution is also studied. Different oxidants such as H_2O_2 , urea- H_2O_2 (UHP) and *tert*-BuOOH were used as the oxygen source in water as solvent. The results are shown in Fig. 11. In presence of 30% H_2O_2 the reaction proceeds with 50.8 mol% styrene conversion and 63.7 mol% selectivity of benzaldehyde. The yield of benzaldehyde under this condition is 32.4%. When the same reaction was carried out in presence of ureated hydrogen peroxide (UHP) the styrene conversion takes place up to 43.6 mol%, but the selectivity of benzaldehyde is very less (7.3 mol%). In presence of *tert*-BuOOH the styrene conversion proceed up to 60.7 mol% with 52.0 mol%, 26.2 mol% and 21.9 mol% selectivity of benzaldehyde, phenyl acetaldehyde and 1-phenyl-1,2-ethanediol respectively. In terms of percentage yield of benzaldehyde, the oxidizing agents shows the efficiency in the order of H_2O_2 (30%) > *tert*-BuOOH > UHP with 32.4, 31.5 and 7.3 respectively. Among all these oxidants, H_2O_2 (30%) shows the best performance since it can give good oxidation conversion; moreover it generate only water as by-product; and it has high content of active oxygen. The results for styrene conversion and selectivity of all the products were determined with the accuracy of $\pm 5\%$ error.

3.4.8. Effect of sonication time on styrene oxidation

The effect of ultrasonic radiation on SrFe_2O_4 catalyst is also studied by varying the sonication time. The sonication was carried out by taking 10 ml of solvent and 0.1 g SrFe_2O_4 catalyst only; neither H_2O_2 nor styrene was added in this process. The results are shown in Fig. 12. The reaction which was carried out by using catalyst without sonication gave the percentage styrene conversion and percentage selectivity of benzaldehyde as 50.8 and 63.7 respectively. When the same reaction was carried out by sonicating the catalyst in solvent for the interval of 5, 10 and 15 min, the styrene conversion is decreased to 32.4 mol%, 28.0 mol% and 17.1 mol%

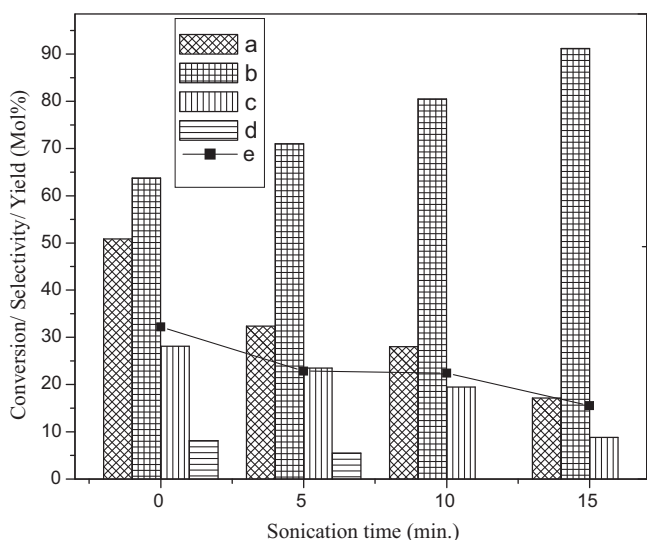


Fig. 12. Effect of ultrasonication time on styrene conversion and product selectivity over SrFe_2O_4 catalyst, (a) styrene conversion, (b) selectivity of benzaldehyde, (c) phenyl acetaldehyde, (d) others and (e) yield of benzaldehyde.

respectively while the selectivity of benzaldehyde increases as 71.0 mol%, 80.5 mol% and 91.2 mol% respectively. These results indicate that the ultrasonication of catalyst shows the adverse effect which may be due to high intensity shock waves generated by ultrasonic irradiation cause promotion of mass transport and/or activation of solid surface. Ultrasonic dispersion method is effective for dispersing the material; but at the same time, the high energy may damage the active sites of catalyst and results in the degradation of the mechanical properties of the composite [49].

3.5. Recycling and repeated use of catalyst

The efficiency of the SrFe_2O_4 was checked by carrying out the reaction under optimized amount of catalyst i.e. 0.1 g and by keeping all the conditions constant, the results are shown in Fig. 13. The amount of catalyst is very small (0.1 g). Hence the recycling of catalyst is not very efficient. There were difficulties in collection of the

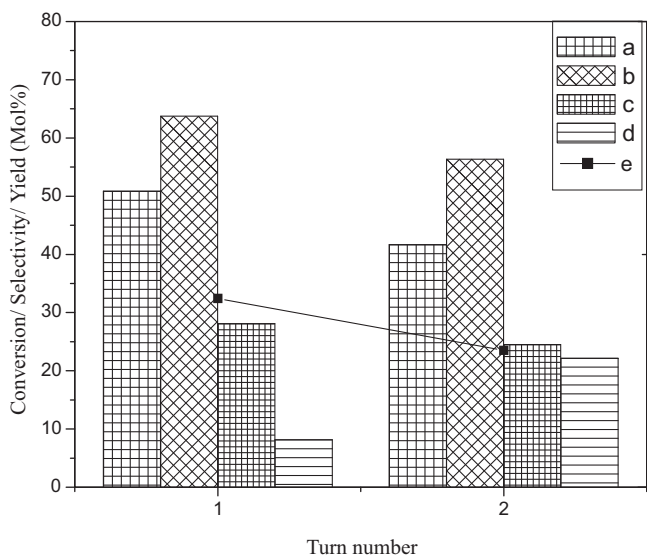


Fig. 13. The reusability of SrFe_2O_4 catalyst for the selective oxidation of styrene, (a) styrene conversion, (b) selectivity of benzaldehyde, (c) phenyl acetaldehyde, (d) others and (e) yield of benzaldehyde.

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.

4. Conclusions

The phase analysis, metal oxygen stretching frequencies, morphology and elemental analysis done by various techniques confirmed the formation of single phase SrFe_2O_4 with trace quantity of SrCO_3 .

SrFe_2O_4 is an efficient catalyst for selective oxidation of styrene in water as a solvent, in the presence of 30% H_2O_2 as oxidizing agent. The heterogeneously catalyzed aqueous phase oxidation of styrene proceeds by a free radical mechanism which involves the initiation of the reaction on the catalyst surface and heterogeneous propagation in liquid.

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, products was catalyzed by SrFe_2O_4 in absence of organic solvent and optimum condition as 70 °C, 18 h, styrene/ H_2O_2 molar ratio as 1, protic and polar solvent like water and catalyst amount as 0.1 g. Solvents have marked influence on the product distribution in selective oxidation of styrene; water seems to be the best solvent. The selectivity of benzaldehyde with respect to percentage yield for various solvents is in the order of $\text{H}_2\text{O} > \text{CH}_3\text{OH} > \text{C}_2\text{H}_5\text{OH} > \text{CH}_3\text{CN} > \text{CH}_3\text{COCH}_3$. The ultrasonication of catalyst shows the adverse effect, which may be due to damaged active sites of catalyst.

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