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Optimization of reaction conditions in selective oxidation of styrene over fine crystallite spinel-type $CaFe_2O_4$ complex oxide catalyst

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ABSTRACT

The $CaFe_2O_4$ spinel-type catalyst was synthesized by citrate gel method and well characterized by thermogravimetric analysis, atomic absorption spectroscopy, Fourier-transform infrared spectroscopy, X-ray diffraction and transmission electron microscopy. The crystallization temperature of the spinel particle prepared by citrate gel method was 600 °C which was lower than that of ferrite prepared by other methods. $CaFe_2O_4$ catalysts prepared by citrate gel method show better activity for styrene oxidation in the presence of dilute H_2O_2 (30%) as an oxidizing agent. In this reaction the oxidative cleavage of carbon–carbon double bond of styrene takes place selectively with 38 ± 2 mol% conversion. The major product of the reaction is benzaldehyde up to 91 ± 2 mol% and minor product phenyl acetaldehyde up to 9 ± 2 mol%, respectively. The products obtained in the styrene oxidation reaction were analyzed by gas chromatography and mass spectroscopy. The influence of the catalyst, reaction time, temperature, amount of catalyst, styrene/H_2O_2 molar ratio and solvents on the conversion and product distribution were studied.

1. Introduction

Spinel ferrites with a general formula AB_2O_4 are a class of chemically and thermally stable materials, which attract the interest of researchers, because of their versatile applications [1]. The spinel ferrites are used in magnetic recording media and magnetic fluids for the storage and retrieval of information [2], magnetic resonance imaging (MRI) enhancement [3], magnetically guided drug delivery [4], sensors [5], pigments [6], etc. The fine particles of ferrites possess great potential for application in high quality ceramics and supramagnetic material [7]. Mixed metal oxide materials are good alternative to both zeolites, such as TS-1, TS-2, Ti-MCM-41, V-ZSM-11 and Cu-ZSM-5 and aluminium phenolate for many alkylation reactions [8]. Binary and ternary oxides possessing a spinel structure have attracted much attention due to their remarkable transport, magnetic and catalytic properties. On the basis of distribution of cations there are two kinds of lattice for cation occupancy; 'A' and 'B' sites have tetrahedral and octahedral coordination, respectively. In the normal spinel structure divalent atoms, occupying tetrahedral 'A' sites, while trivalent atoms, sitting on the octahedral 'B' sites. When 'A' site being Fe^{3+} ions, while 'B' site equally populated by divalent and trivalent (Fe^{3+}) ions, the spinel structure is referred to as inverse kind [9].

The catalytic effectiveness of this system is due to the ability of the metallic ions to migrate between the sublattices without altering the crystal structure. This property makes the catalyst efficient for many organic transformation reactions and number of industrial processes such as oxidative dehydrogenation of hydrocarbons [10], decomposition of alcohols and hydrogen peroxide [11], treatment of automobile exhaust gases [12], oxidation of various organic compounds such as chlorobenzene and carbon monoxide [13,14]. The spinel ferrites were also applied in phenol hydroxylation [15], hydrodesulphurization of crude petroleum [16], catalytic combustion of methane [17]. Catalytic oxidation is widely employed in the manufacture of bulk chemicals from aromatics and more recently an environmentally attractive method for the production of fine chemicals. Both in academic and in industry the use of hydrogen peroxides in the oxidation of organic molecules such as styrene, phenol, cyclohexene and trans-stilbene is preferred, since it can give good oxidation conversion, generate only water as byproduct and has high content of active oxygen, this reaction can be taken as a kind of green technology [18].

The physico-chemical properties of the ferrites are strongly dependent on the sites and the nature of the catalyst [19,20], which are closely related to the method of preparation. There are many known methods of producing ferrites which can be divided into two main groups: dry and wet methods. The most popular

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methods, which have been recently reported, are combustion method [21], sol–gel method [22], co-precipitation of hydrous oxides from salts solution followed by calcination at high temperatures [23–25] and hydrothermal routes [26,27]. Other than these self-propagating process (SHS method) [28] and reverse micelle synthesis technique [29,30] were also used to synthesize the ferrites. 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 time. 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 an 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 [31].

The catalytic efficiency of various catalysts was checked in various organic transformations such as the oxidation of styrene over nickel ferrite and zinc ferrite has been studied by Debanjan et al. [1]. They have observed 31.4 mol% and 26.1 mol% styrene conversion with selectivity of benzaldehyde as 55.6 mol% and 50.4 mol%, respectively. 20 mol% styrene conversions and 94 mol% selectivity of benzaldehyde were investigated by Gao and Gao [18] over Cobalt VSB-5 at 70 °C temperature. Maurya and Kumar [32] reported 76 mol% conversion of styrene with 65 mol% selectivity of benzaldehyde over oxovanadium based coordination polymer at 75 °C temperature. The styrene oxidation was also carried out over $MgFe_2O_4$ [33] prepared by co-precipitation and citrate gel method, it was found that 7.43 mol% and 34.0 mol% styrene conversion, while the benzaldehyde selectivity is 94.0 mol% and 63.2 mol%, respectively.

In the present work, we report the synthesis, characterization and catalytic activity of calcium ferrite complex oxide with a fixed Ca:Fe ratio. The calcium ferrite catalyst synthesized by citrate gel method shows good catalytic performance. It gives the highest selectivity of benzaldehyde with respect to conversion of styrene in presence of 30% H_2O_2, an important chemical intermediate for the fine chemical industry. Moreover, the method of synthesis of catalyst is simple and economical. The influence of the catalyst, reaction time, temperature, amount of catalyst, styrene/H_2O_2 molar ratio and solvents on the conversion and product distribution were studied.

2. Experimental

2.1. Synthesis of catalyst

Analytical grade $Fe(NO_3)_3 \cdot 9H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$ and anhydrous citric acid obtained from MERCK (specialties Pvt. Ltd., Mumbai, India) were used without further purification as raw materials to prepare $CaFe_2O_4$. The initial solution was prepared by dissolving calcium nitrate, ferric nitrate and citric acid into double distilled water. Concentrations of ferric nitrate, calcium 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 the homogeneous distribution of the metal ions to get segregated from the solution. The solution was continuously stirred at 30 °C for 30 min, and then was concentrated until a viscous liquid was obtained. The liquid was dried in an oven at 120 °C for 12 h to get a fluff mass, which was ground to powder. The powder was heated in an evaporating dish where an autocombustion process takes place. Finally, the brown, floppy precursor was calcined at different temperatures for 1 h in muffle furnace [33].

2.2. Catalyst characterization

The decomposition of the precursor was studied by FT-IR spectra on a Nicollet NEXUS 7000C spectrophotometer using the KBr pellet method. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/MAX-2A diffractometer with Cu Kα radiation and a Ni-filter. The morphology and size of the particles were examined by transmission electron microscopy (TEM) using a JEOL-2011 microscope. Thermogravimetric analysis (TG/DTG) was performed on a Rigaku Thermoflex system with ramp rate of 10 °C min^{-1} in flowing air. Chemical analysis of calcium ferrite was carried out by atomic absorption spectroscopy and chemical method.

2.3. Reaction testing

Styrene oxidation was carried out in a round bottom flask (25 ml) equipped with X-crossed Teflon coated magnetic stirrer and a reflux condenser. 10 mmol styrene [99+% extrapure, Acros organics], 10 ml solvent, 0.1 g catalyst, 1.0 ml of hydrogen peroxide (30%, MERCK), (styrene/H_2O_2 molar ratio = 1) were added successively into the flask. The reaction mixture was refluxed in temperature-controlled oil bath and the reaction was carried out at different temperatures and time periods. The reaction products were analyzed by gas chromatography–mass spectroscopy (GC–MS). The gas chromatograph equipped with a XE-60 capillary column (30 m × 0.25 × 0.3 μm) flame ionization detector was used. The injector and column temperatures were 280 °C and 140 °C, respectively. 3-Nitrotolune (99+%, MERCK) was used as an internal standard. The residual H_2O_2 in solution was determined by ceric sulphate titration method [34]. The styrene conversion and the selectivity of the reaction products were determined by the following formulae [35].

The styrene conversion is defined as

$$\text{conversion (mol\%)} = 100 \times \frac{\text{styrene (in)} - \text{styrene (out)}}{\text{styrene (in)}} \tag{1}$$

The selectivity was calculated based on the peak areas of the gas chromatogram by considering the different sensitivity factors of the flame ionization detector. The mol% of styrene as well as analytes is calculated from chromatogram by the following formula and using a common internal standard solution.

$$\text{mol\%} = 100 \times \frac{\text{area of analyte from the reaction mixture}}{\text{area of fix quantity of same analyte (standard)}} \tag{2}$$

The selectivity to product (i) is defined as

$$\text{selectivity } (i) \text{ (mol\%)} = 100 \times \frac{\text{corrected area } (i)}{\text{sum of all corrected areas}} \tag{3}$$

3. Results and discussion

The citrate gel method was recommended for the preparation of submicron-sized particle of calcium ferrite spinel. This method has the advantage of lower calcination temperature and increase in purity of powder by keeping the Ca^{2+}:Fe^{3+} in the molar ratio of 1:2. The synthesized calcium iron citrate is characterized by TG–DTG. The following method was used to characterize the synthesized calcium iron citrate complex.

3.1. TG–DTG analysis

Fig. 1 shows TG–DTG curve for thermal decomposition of calcium iron citrate complex. There are four major weight losses in TG curve. The first weight loss within the range of 50–110 °C is 14.16% (calculated 12.19) as shown in Table 1 corresponds to

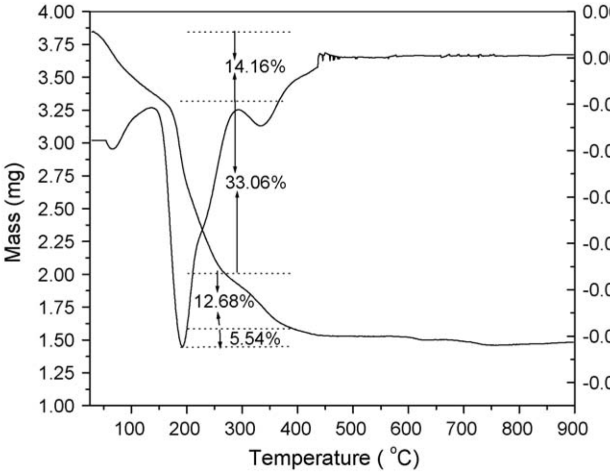


Fig. 1. TG/DTG curves of the calcium ferrite precursor prepared by citrate gel method.

dehydration step. This dehydration step is clearly seen as a peak in DTG at 67 °C. The second weight loss is 33.06% in the range of 160–210 °C corresponds to the decomposition of citrate ligand it matches well with the calculated value of 31.27%. The loss of ligand is also seen in the form of well-defined peak at 191 °C in DTG curve. The further weight loss in TG curve is 12.06% (calculated 13.33%) in the range of 300–350 °C corresponds to the decarboxylation of precursor to mixed oxide. A peak at 333 °C in DTG corresponding to the decarboxylation step is also seen. Finally a small weight loss of 5.54% (calculated 7.30%) in the range of 700–730 °C corresponds to the loss of adsorbed carbon dioxide centered at 720 °C in DTG curve. After 720 °C no notable weight loss was found which indicate that $CaFe_2O_4$ was formed above 720 °C. Thus the calcium ferrite oxide was calcined at different temperatures from 600 °C to 900 °C and the calcined samples were characterized by different methods as follows.

3.2. X-ray diffraction studies

The *XRD* pattern of precursor calcined from 600 °C to 900 °C is shown in Fig. 2. It is observed that, with increase in calcination temperature XRD peaks become sharper and also increase in intensity. The *h k l* values of calcium ferrite calcined at 800 °C and 900 °C matches exactly with the JCPDS data (JCPDS card no. ID 08-0100), which are characteristic of spinel structure of $CaFe_2O_4$ ($a = 9.18$, $b = 10.62$ and $c = 3.02$). From the XRD studies it was confirmed that the single phase $CaFe_2O_4$ formed at 800 °C and so this compound was selected for further characterization.

3.3. Elemental analysis of $CaFe_2O_4$

The chemical composition of calcined (fresh) catalyst was determined by atomic absorption spectroscopy. The percentage of calcium and iron matches well with the calculated values (Table 2).

Table 1
Thermogravimetric analysis of calcium iron citrate precursor.

Steps	Temperature range (°C)	Observed % mass loss	Calculated % mass loss
I	50–110	14.16	12.19
II	160–210	33.06	31.27
III	300–350	12.06	13.33
IV	700–730	05.54	07.30

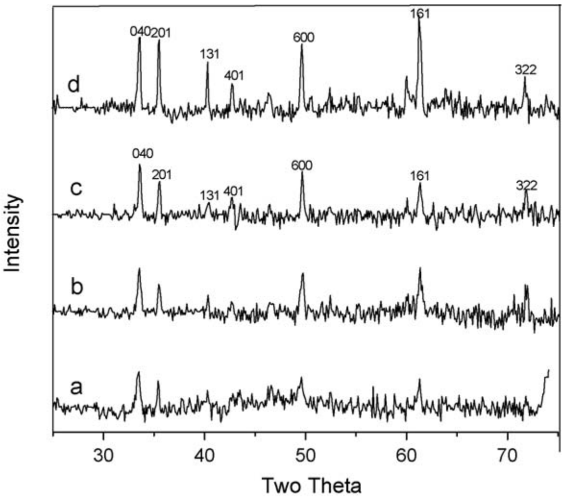


Fig. 2. XRD pattern of the calcium ferrite prepared by citrate gel method and calcined at (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C for 1 h.

3.4. Transmission electron microscopy studies

The TEM micrograph of the calcium ferrite fine particle prepared by citrate gel method calcined at 800 °C is presented in Fig. 3(a and b). It consists of rather uniform small spherical particles with a mean size of 500–600 nm. This also indicates that the synthesis procedure adopted result in particles which were mostly fine.

3.5. Characterization by FT-IR

With the view to study the effect of dependence of normal modes and their frequency on change of the substitution of ions in calcium ferrite, FT-IR frequency data for the respective sites were analyzed using the observed FT-IR spectra of calcium ferrite calcined at 800 °C is shown in Fig. 4. The sample shows the two IR bands, ν_1 and ν_2 around 690 cm^{-1} and 501 cm^{-1}, respectively. According to Waldron [36] and White and De Angelis [37], the high frequency band around 700 cm^{-1} is due to the stretching vibration of the tetrahedral M–O bond and the low frequency band at around 500 cm^{-1} is due to the vibration of the octahedral M–O bond present in the spinel structure.

3.6. Optimization of reaction condition for selective oxidation of styrene over $CaFe_2O_4$ catalyst

The calcium ferrite calcined at 800 °C thus characterized for its structure, morphology and confirmed to be fine particles with the spinel structure was then used as catalyst to evaluate their catalytic efficiency. The selective oxidation of styrene to benzaldehyde was used as the model reaction. The effect of different solvents, temperature variation, and styrene/hydrogen peroxide molar ratio, on the styrene conversion and product selectivity over catalyst has been successively carried out and is discussed in following subsections.

Table 2
Percentage distribution of Ca and Fe in $CaFe_2O_4$ calcined at 800 °C.

Catalyst	% weight of calcium		% weight of iron	
	Calculated	Observed	Calculated	Observed
$CaFe_2O_4$	18.58	19.21	51.79	53.09

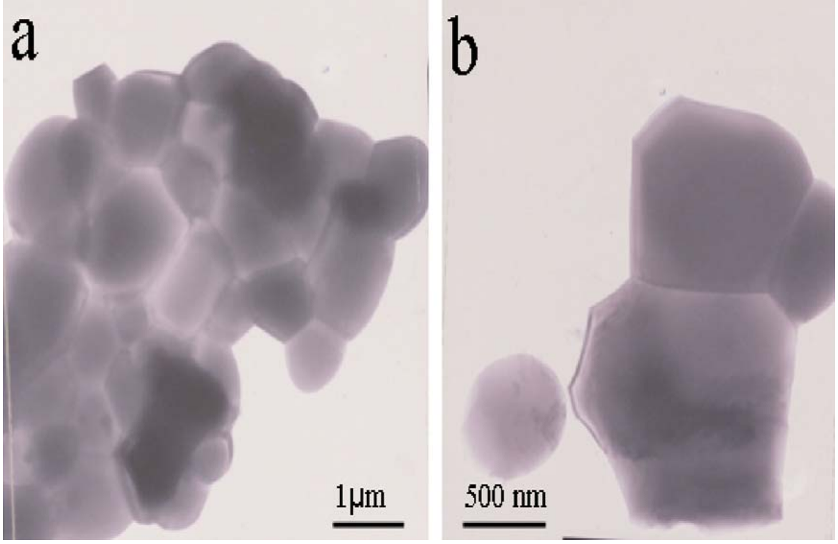


Fig. 3. TEM micrograph of $CaFe_2O_4$ powder calcined at 800 °C.

3.6.1. *Effect of temperature*

The effect of reaction temperature on styrene conversion and selectivity of products was studied. The reaction was carried out by styrene/H_2O_2 molar ratio as 1:1 in acetone as a solvent with 0.1 g of $CaFe_2O_4$ catalyst at various temperatures for 18 h. The response of the reaction towards rise in temperature has been studied and the results are shown in Fig. 5. At 30 °C styrene conversion is 28 ± 2 mol% and it is found to increase with increase in temperature and reaches to 47 ± 2 mol% at 70 °C (Fig. 5). This is due to the fact that H_2O_2 decomposition increases from about 54 to 96 ± 2 mol% with the increase in temperature. The selectivity of benzaldehyde increases up to 40 °C (91 ± 2 mol%) but as the temperature increases selectivity for phenyl acetaldehyde increases at the cost of benzaldehyde. This may be due to the fact that the cleavage of C=C bond is higher at lower (40 °C) temperature which leads to the formation of benzaldehyde. On the other hand at higher (70 °C) temperature the epoxidation seems to compete more favorably against C=C bond cleavage (see Scheme 1a) which helps to form phenyl acetaldehyde.

3.6.2. *Effect of reaction time*

The effect of reaction time on the styrene conversion and product selectivity is studied at 40 °C keeping the other conditions constant from 6 h to 30 h (Fig. 6). Running the reaction for a long time is found to be favorable for the oxidation of styrene; styrene conversion is increased up to 38 ± 2 mol% along with selectivity of benzaldehyde up to 91 ± 2 mol% at 18 h. After 18 h styrene conversion remains constant up to 30 h, while the selectivity of benzaldehyde decreased to 83 ± 2 mol%. This may be due to the complete exhaustion of H_2O_2 in the reaction mixture as the reaction was run for long duration [38]. Moreover, the impurities were also found to be formed when the reaction was allowed to run for long time.

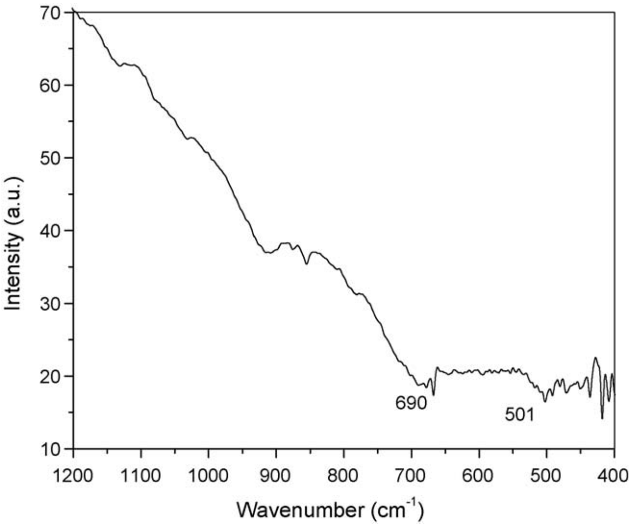


Fig. 4. FT-IR spectra of $CaFe_2O_4$ powder calcined at 800 °C.

3.6.3. *Effect of catalyst amount on the oxidation reaction*

The amount of catalyst was varied from 0.05 g to 0.20 g while keeping the molar ratio of styrene/H_2O_2 at 1:1 and reaction temperature at 40 °C. The reaction was carried out for 18 h and the products were analyzed. The results are represented in Fig. 7. With increase in catalyst amount from 0.05 g to 0.10 g, the conversion of styrene also increases from 14.0 mol% to 38 mol%, while the selectivity of benzaldehyde slightly decreases from 100 mol% to 91 mol% along with the formation of styrene oxide up to 9 mol% which isomerizes to phenyl acetaldehyde as a byproduct. As the

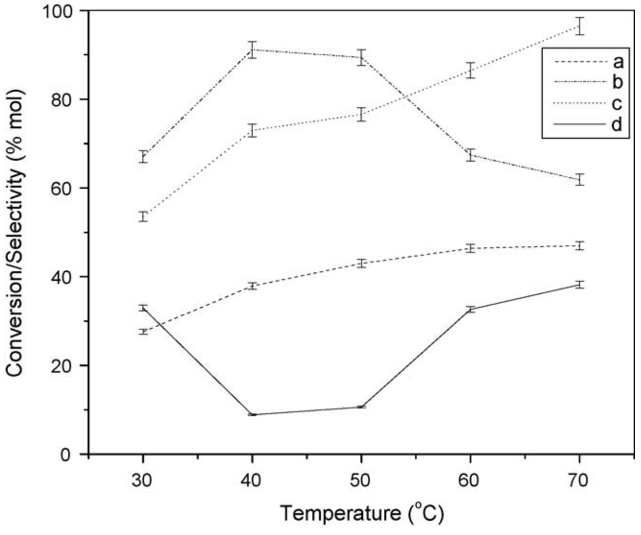
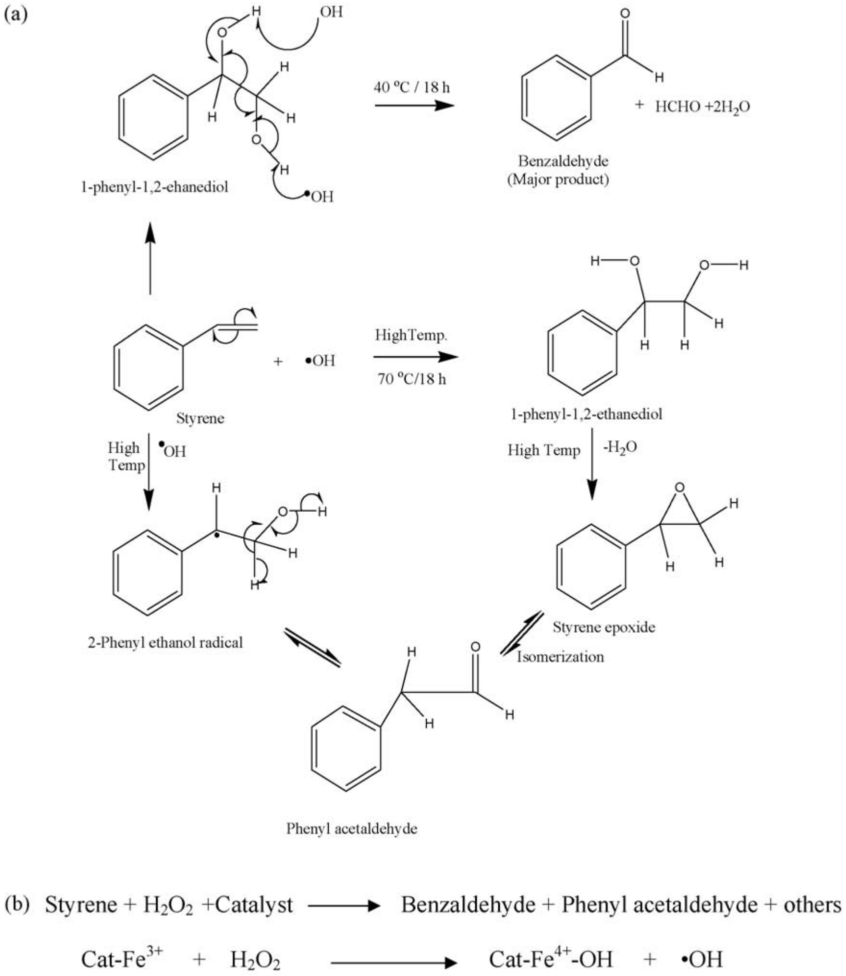


Fig. 5. Effect of temperature (°C) on styrene oxidation: (a) styrene conversion, (b) H_2O_2 conversion, (c) selectivity of benzaldehyde, (d) selectivity of others in mol% (others—phenyl acetaldehyde, 1-phenyl-1,2-ethanediol, benzoic acid, etc.). Error bars represent the standard deviation of triplicate samples.



(b) Styrene + H_2O_2 +Catalyst ⟶ Benzaldehyde + Phenyl acetaldehyde + others

$$\text{Cat-Fe}^{3+} + H_2O_2 \longrightarrow \text{Cat-Fe}^{4+}\text{-OH} + {\bullet}OH$$

Scheme 1. Reaction mechanism for selective oxidation of styrene using $CaFe_2O_4$.

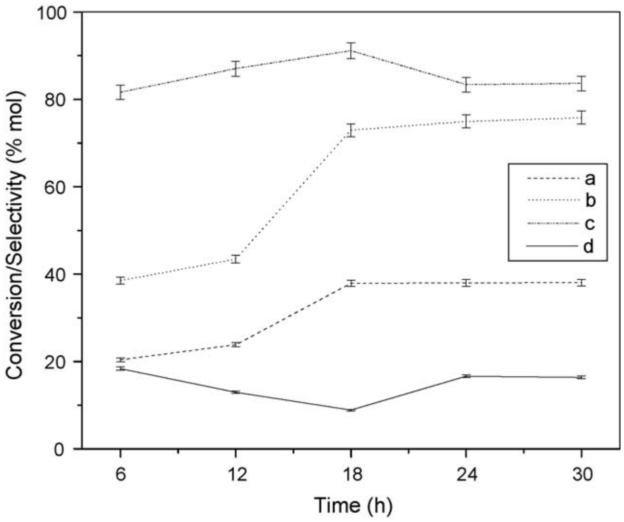


Fig. 6. Effect of time (h) on styrene oxidation: (a) styrene conversion, (b) H_2O_2 conversion, (c) selectivity of benzaldehyde, (d) selectivity of others in mol% (others—phenyl acetaldehyde, 1-phenyl-1,2-ethanediol, benzoic acid, etc.). Error bars represent the standard deviation of triplicate samples.

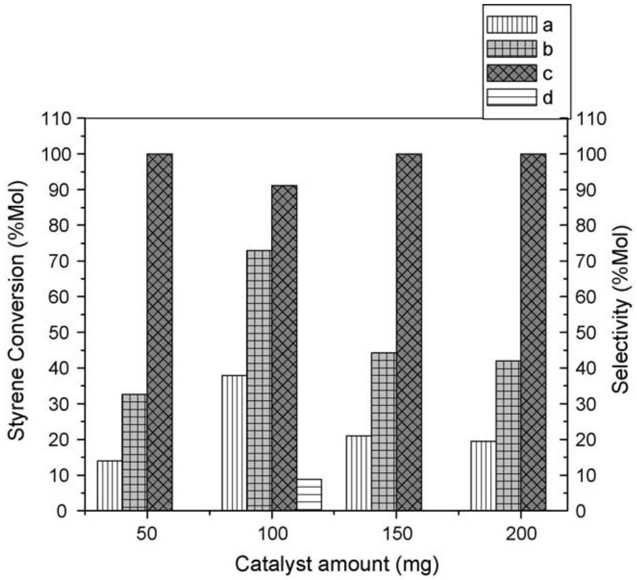


Fig. 7. Effect of the amount of catalyst (mg) on styrene oxidation: (a) styrene conversion, (b) H_2O_2 conversion, (c) selectivity of benzaldehyde, (d) selectivity of others in mol% (others—phenyl acetaldehyde, 1-phenyl-1,2-ethanediol, benzoic acid, etc.).

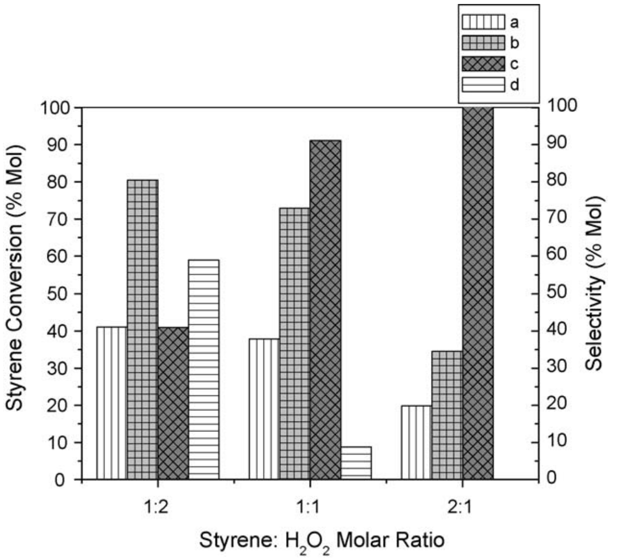


Fig. 8. Effect of styrene:H_2O_2 molar ratio on styrene oxidation: (a) styrene conversion, (b) H_2O_2 conversion, (c) selectivity of benzaldehyde, (d) selectivity of others in mol% (others—phenyl acetaldehyde, 1-phenyl-1,2-ethanediol, benzoic acid, etc.).

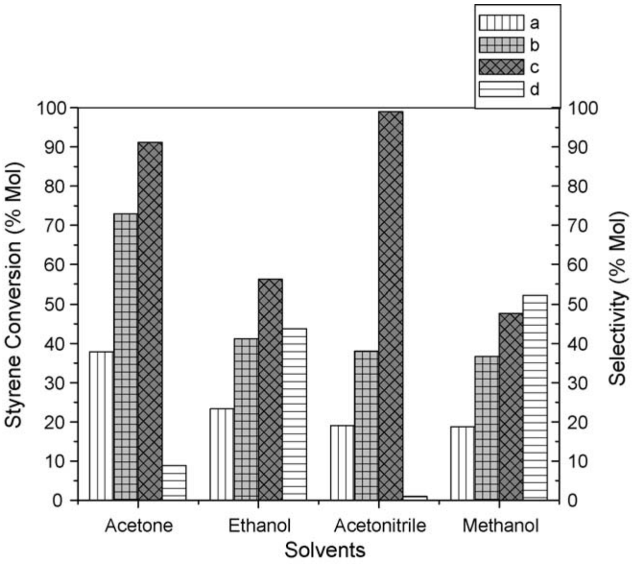


Fig. 9. Effect of solvents on styrene oxidation: (a) styrene conversion, (b) H_2O_2 conversion, (c) selectivity of benzaldehyde, (d) selectivity of others in mol% (others—phenyl acetaldehyde, 1-phenyl-1,2-ethanediol, benzoic acid, etc.).

amount of catalyst increases from 0.05 g to 0.10 g the H_2O_2 conversion was also increased from 33 mol% to 73 mol%, respectively. This is due to the availability of relatively large surface area and the acid sites, which favors the dispersion of more active species [39]. As a result, the accessibility of the large number of molecules of the reactants to the catalyst is favored. Further increase in the amount of catalyst from 0.15 g to 0.20 g styrene conversion is decreased to 19.5 mol% while the selectivity of benzaldehyde was 100 mol%. The reason for the lower activity at higher amount of catalyst up to 200 mg may be possibly due to adsorption or chemisorptions of two reactants on separate catalyst particles, thereby reducing the chance to interact [40]. As the catalyst amount increase from 0.15 g to 0.20 g the H_2O_2 conversion also decreases (41 mol%) with respect to the conversion of styrene. Therefore, an amount of 0.1 g catalyst may be considered as appropriate to obtain maximum conversion of styrene with better selectivity of benzaldehyde.

3.6.4. Effect of styrene/H_2O_2 molar ratio

The influence of styrene/H_2O_2 molar ratio on the conversion of styrene and product selectivity is also studied and the results are shown in Fig. 8. It is found that when the styrene/H_2O_2 molar ratio is increased from 1:2, 1:1 and 2:1 the styrene conversion decreases from 41 mol% to 20 mol% with decrease in the H_2O_2 conversion from 80 mol% to 34 mol%. This is attributed to the increased percentage of styrene in the reaction mixture. Interestingly, on the other hand the selectivity for benzaldehyde increases from 41 mol% to 100 mol%. Maximum styrene conversion is obtained at a molar ratio of styrene/H_2O_2 as 1:2. The coordination of H_2O_2 on the metal, and its subsequent decomposition to $^{\bullet}$OH radical [41] are the necessary steps involved in this reaction (see Scheme 1b). At the molar ratio of 1:1, H_2O_2 could freely coordinate to metal and decompose to form $^{\bullet}$OH radical. Hence, high styrene conversion is attained along with the formation of styrene oxide as a byproduct up to 9 mol%. While, at the molar ratio of 2:1, low amount of H_2O_2 may be competing with excess styrene for coordination, and hence formation of $^{\bullet}$OH radicals might be significantly reduced. Thus, the conversion is decreased.

3.6.5. Effect of solvent

The effect of solvents on the styrene oxidation and product selectivity was also observed and results are shown in Fig. 9. We studied the reaction using protic and aprotic solvent. According to Kumar et al., aprotic solvents are more favorable for styrene oxidation than protic solvents [38]. Acetone is found to be a good solvent, which gave a maximum styrene conversion of 37.91 mol%, while the selectivity of benzaldehyde is 91.14 mol% at optimum conditions of time 18 h and temperature 40 °C. When methanol, acetonitrile and ethanol are used as solvents for the oxidation reaction, the catalytic activity of the catalyst is reduced, this is probably due to the adsorption of these solvents on the active species at the surface of catalyst. Ethanol and methanol are favoring the formation of byproducts like styrene oxide, 1-phenyl-1,2-ethanediol and others. The percentage of these byproducts is 44 mol% and 52 mol% in ethanol and methanol, respectively.

3.7. The influence of catalyst and oxidizing agent

The role of catalyst and oxidizing agent is also observed, the conversion of styrene is only up to 4–5% in the presence of catalyst without using any oxidant. This clearly indicates that there is a possibility of the reaction occurring due to the participation of lattice oxygen alone. The oxygen vacancies favor the catalytic activity in oxidation reaction because they increase the lattice oxygen mobility [42].

Similarly, the same reaction when carried out in the absence of catalyst but by using 10 mmol 30% H_2O_2 under the similar reaction condition, 0% styrene conversion was done. It suggests that no reaction takes place in the absence of catalyst. This observation ruled out the possibility of reaction taking place due to the thermal decomposition of hydrogen peroxide. The fact was confirmed by carrying the same reaction in the presence of tertiary butyl alcohol as a scavenger and by keeping all the reaction conditions constant, only 4 mol% styrene got converted to benzaldehyde. This observation confirms a free radical mechanism is involved in styrene oxidation over a mixed catalyst (Scheme 1b). In this type of reaction free radicals are generated on the surface of catalyst. The catalyst accelerates the rate of decomposition reaction of H_2O_2 into radicals. The Fe^{3+} ions from the octahedral sites of catalyst react with hydrogen peroxide to form Cat–Fe^{4+}–OH complex and hydroxyl radicals as shown in Scheme 1(b). The results shows that the redox cycle of spinel phase with high oxygen deficiencies coming from the crystal structure can participate into the styrene oxidation due to the presence of reducible Fe^{4+} sites forming highly active oxygen species at lower temperature [43]. The lower oxidation state of calcium (2+) in comparison to other metal ions favors either an increase in the oxidation state of Fe from 3+ to 4+, or oxygen vacancies can be generated to maintain the structure electroneutrality [27].

4. Conclusions

$CaFe_2O_4$ complex oxide catalyst is prepared by the citrate gel method. This complex type ferrite catalyst is found to be highly active than other reported metal ferrites for the oxidation of styrene with H_2O_2 as an oxidant. 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^{4+}) 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 calcium ferrite oxide catalyst to give benzaldehyde as a major product and formation of byproduct such as styrene oxide (epoxide), benzoic acid, phenyl acetaldehyde as minor products. Acetone as a reaction medium, reaction temperature 40 °C, reaction time 18 h and styrene:hydrogen peroxide ratio 1:1 was found to be favorable for increasing the selectivity of benzaldehyde. The 0.1 g of 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.

Acknowledgement

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References

[1] D. Guin, B. Baruwati, S.V. Manorama, J. Mol. Catal. A: Chem. 242 (2005) 26–31.
[2] M.H. Kryder, Mater. Res. Soc. Bull. 21 (1996) 9.
[3] D.G.H. Mitchell, J. Magn. Reson. Imaging 7 (1997) 1.
[4] S.P. Bhatnagar, R.E. Rosensweig, J. Magn. Magn. Mater. 149 (1995) 198.
[5] L. Satyanarayana, C.V. Gopal Reddy, S.V. Manorama, V.J. Rao, Sens. Actuators B: Chem. B 46 (1) (1998) 1–7.
[6] R.A. Canderia, M.I. Bernardi, E. Longo, I.M.G. Santosh, A.G. Souza, Mater. Lett. 58 (2004) 569–572.
[7] Y.L. Liu, Z.M. Liu, Y. Yang, H.F. Yang, G.L. Shen, R.Q. Yu, Sens. Actuators B 107 (2005) 600–604.
[8] T. Mathew, S.S. Biju, M. Devasi, M. Vijayraj Chilukuri, V.V. Satyanarayana, B.S. Rao, C.S. Gopinath, Appl. Catal. A: Gen. 273 (1–2) (2004) 35–45.
[9] K. Shreekumar, M. Thomas, T.M. Jyothi, M.D. Biju, S. Sugunan, B.S. Rao, Polish J. Chem. 74 (2000) 509–517.
[10] M.A. Gibson, J.W. Hightower, J. Catal. 41 (1976) 420–430.
[11] E. Manova, T. Tsoncheva, D. Paneva, I. Mitov, K. Tenchev, L. Petrov, Appl. Catal. A: Gen. 277 (1–2) (2004) 119–127.
[12] L.C.A. Oliveria, J.D. Fabris, R.R.V.S. Rios, W.N. Mussel, R.M. Lago, Appl. Catal. A: Gen. 259 (2004) 253–259.
[13] S. Paldey, S. Gadevanishvii, W. Zhang, F. Rasouli, Appl. Catal. B: Environ. 56 (3) (2005) 241–250.
[14] J.B. Silva, C.F. Diniz, R.M. Lago, N.D.S. Mohallem, J. Magn. Magn. Mater. 278 (2004) 272–276.
[15] C.R. Xiong, Q.L. Chen, W.R. Lu, H.X. Gao, Z. Gao, Catal. Lett. 69 (2000) 231.
[16] F. Tihay, A.C. Roger, G. Pourroy, A. Kiennemann, Energy Fuels 16 (5) (2002) 1271–1276.
[17] R. Spretz, S.G. Marchetti, M.A. Ulla, E.A. Lombordo, J. Catal. 194 (2000) 167–174.
[18] D. Gao, Q. Gao, Catal. Commun. 8 (2007) 681–685.
[19] Regina C.C. Costa, C.A. Fatima Lelis Luis, Oliveira Jose D. Fabris, Jose D. Ardisson, Rachel R.A. Rios, Cristina L. Silva, Rochel M. Lago, Catal. Commun. 4 (2003) 525–529.
[20] M.S. Selim, G. Turkey, M.A. Shouman, G.A. El-Shobaky, Solid State Ionics Diffus. React. 120 (1999) 173–181.
[21] Y. Li, J. Zhao, J. Jiang, J. Han, Mater. Res. Bull. 38 (2003) 1393.
[22] A.S. Albuquerque, J.D. Ardisson, W.A.A. Macedo, J. Magn. Magn. Mater. 192 (1999) 277.
[23] T. Sato, K. Haneda, M. Seki, T. Iijima, Appl. Phys. A 50 (1990) 13.
[24] M. Yokoyama, E. Ohta, T. Sato, J. Magn. Magn. Mater. 183 (1998) 173.
[25] T. Kamiyama, K. Honeda, T. Sato, S. Ikeda, H. Asano, Solid State Commun. 81 (1992) 563.
[26] C. Rath, N.C. Mishra, S. Anand, R.P. Das, K.K. Sahu, C. Upadhyay, H.C. Verma, Appl. Phys. Lett. 76 (2000) 475.
[27] C. Upadhyay, H.C. Verma, C. Rath, K.K. Sahu, S. Anand, R.P. Das, N.C. Mishra, J. Alloys Compd. 326 (2001) 94.
[28] Y. Li, J. Zhao, J. Han, Mater. Res. Bull. 37 (2002) 583.
[29] S. Gubbala, H. Nathani, K. Koizol, R.D.K. Misra, Physica B 348 (2004) 317.
[30] K. Madhusudan Reddy, L. Satyanarayana, Sunkara V. Manorama, R.D.K. Misra, Mater. Res. Bull. 39 (2004) 1491.
[31] M. Kakihana, J. Sol–Gel Sci. Technol. 6 (1996) 5.
[32] M.R. Maurya, A. Kumar, J. Mol. Catal. A: Chem. 250 (2006) 190–198.
[33] N. Ma, Y. Yue, W. Hua, Z. Gao, Appl. Catal. A: Gen. 251 (2003) 39–47.
[34] J. Mendham, R.C. Denny, J.D. Barnes, M.J.K. Thomas, Vogel's Textbook of Quantitative Chemical Analysis, sixth ed., Pearson Education Pte. Ltd, Singapore, 2004.
[35] P. Yang, Z. Jiang, P. Ying, C. Li, J. Catal. 253 (2008) 66–73.
[36] R.D. Waldron, Phys. Rev. 99 (1955) 1727.
[37] W.B. White, B.A. De Angelis, Spectrochem. Acta 23A (1967) 985.
[38] R. Kumar, P. Kumar, Godwin C.G. Pais, S.P. Mirajkar, Sujit B. Kumar, J. Catal. 156 (1995) 163–166.
[39] GuangJain Wang, GuangQing Liu, MingXia Xu, ZhenXing Yang, ZhengWang Liu, ShiFu Chen, Lei Wang, Appl. Surf. Sci. 255 (2008) 2632–2640.
[40] Mannar R. Maurya, Anil K. Chandrakar, Shri Chand, J. Mol. Catal. A: Chem. 278 (2007) 12–21.
[41] K.M. Parida, Sujata Mallick, J. Mol. Catal. A: Chem. 279 (2008) 104–111.
[42] B.P. Barbera, J.A. Gamboa, L.E. Cadus, Appl. Catal. B: Environ. 65 (2006) 21–30.
[43] D. Hirabayashi, T. Yoshikawa, K. Mochizuki, K. Suzuki, Y. Sakai, Catal. Lett. 110 (2006) 269–274.