Styrene oxidation by H_2O_2 using Ni–Gd ferrites prepared by co-precipitation method

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Abstract

Gadolinium substituted nickel ferrites were prepared by co-precipitation method using NaOH at pH 14 at room temperature. Spinel phase formation was identified by taking the XRD pattern. DRIFT, TG, BET surface area and pore volume measurements, SEM and EDAX were the other characterization techniques used. Mössbauer analysis was performed to find out the site distribution of iron. Under optimized conditions, the prepared spinels were selectively forming benzaldehyde by the oxidation of styrene. Hydrogen peroxide was used as the oxidant. Effect of reaction temperature, reaction time, styrene to hydrogen peroxide molar ratio and effect of solvent medium were also studied.
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1. Introduction

Mixed metal oxides possessing spinel structure exhibit interesting structural, electrical and magnetic properties [1,2]. These properties depend on the nature of ions, their charge and their distribution among tetrahedral and octahedral sites. Ternary oxides crystallizing with spinel structure were found to exhibit interesting solid state and catalytic properties [3]. Mixed metal oxide materials are good alternatives to both zeolites and aluminium phenolate for many alkylation reactions [4]. Among various oxides, transition metal oxides based on iron oxide in combination with other metal oxides are found to be the most active and selective for *ortho* alkylation reactions [5,6]. Spinel ferrites are found to be highly active towards many aromatic alkylation reactions such as methylation of phenol, aniline, pyridine, phenol *tert*-butylation etc. [7–9]. The catalytic effectiveness of these systems is due to the ability of the metallic ions to migrate between the sub lattices without

altering the structure, which makes the catalyst efficient for many organic transformation reactions.

Diverse properties of the spinel compounds are derived from the possibility of synthesis of multicomponent spinel by partial substitution of cations in positions A and B of spinel structure. In these compounds the properties are controlled by the nature of ions, their charge and site distribution among O_h and T_d sites. In ternary ferrite systems, Fe^{+3} ions can be easily replaced between O_h and T_d sites by stoichiometrically varying the concentration of other ions. This peculiar structural feature enables ferrospinels to withstand even extremely reducing atmospheres [10].

Catalytic oxidation is widely employed in the manufacture of bulk chemicals from aromatics and more recently, as an environmentally attractive method for the production of fine chemicals. The use of hydrogen peroxides in the oxidation of organic molecules is a major goal, both in academic and in industry, because of the environmental acceptability of this oxidant, which depends mainly on the nature of its by-product, water. In heterogeneous catalysis, over nanosize spinel-type $Mg_xFe_{3-x}O_4$ or Nb (Co)-MCM-41, the major reaction was oxidative C=C cleavage into benzaldehyde

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[11,12]. Guin et al. [13] have studied styrene oxidation using hydrogen peroxide catalyzed by nickel and zinc ferrites and obtained benzaldehyde as the major product (C=C cleavage). By-products such as phenyl acetaldehyde and styrene oxide were formed in negligible amount (less than 1%).

In this article, preparation and physico-chemical properties of gadolinium incorporated nickel ferrites prepared by co-precipitation method has been discussed. The catalytic performance of these materials in the selective oxidation of styrene with H_2O_2 as oxidant to form benzaldehyde, targeting the fine chemical industry, has also been addressed. An attempt has been made to correlate the catalytic activity with the distribution of cations at O_h and T_d sites.

2. Experimental

2.1. Catalyst synthesis

Different compositions of ferrospinel series viz, $NiFe_2O_4$ (NF), $NiFe_{1.6}Gd_{.4}O_4$ (NGF1), $NiFe_{1.2}Gd_{.8}O_4$ (NGF2), $NiFe_{.8}Gd_{1.2}O_4$ (NGF3), $NiFe_{.4}Gd_{1.6}O_4$ (NGF4), $NiGd_2O_4$ (NG) were prepared by a low temperature co-precipitation method reported by Date and co-workers [14], using aqueous solutions of ferric nitrate (2.6 M), gadolinium nitrate (3.4 M), nickel nitrate (3.4 M) and NaOH (5.3 M). The stoichiometric amounts of the premixed nitrate solutions were rapidly added to the NaOH solution at room temperature. After aging overnight, the precipitate was washed free of nitrate ions. The precipitate was then initially dried in air at 110 °C for 24 h. The materials were powdered and calcined.

2.2. Structural analysis

The catalyst samples were analyzed by adopting various physico-chemical methods. The spinel phase formation was identified by taking XRD pattern using Philips diffractometer (PW 1710) with Ni filtered Cu Kα radiation. The IR spectra of the spinel samples were recorded by a diffuse reflectance (DR) method (Shimadzu, model 8300). The BET surface area was measured by N_2 adsorption in liquid N_2 temperature using a Micromeritics Gemini analyzer. SEM and EDAX analysis were done by using JSM-840 A scanning electron microscope. The thermal stability of the samples were checked by taking TG/DTG curves using Perkin Elmer Pyris Diamond thermogravimetric/differential thermal analyzer by heating the sample at a rate of 20 °C/min from room temperature to 1100 °C in nitrogen. A continuous flow cryostat was applied to record ^{57}Fe Mössbauer spectra at room temperature. The chemical isomer shifts are related to α-iron. The source of radiation used is commercial ^{57}Co/Rh-foil.

2.3. Catalytic reaction

The catalytic reaction was carried out in a 50 ml 2 neck RB flask, fitted with a water condenser, in an oil bath.

Pre-activated catalyst was placed inside the RB and then styrene is added followed by H_2O_2 drop wise. The reaction was carried out by varying temperature, time, styrene to H_2O_2 molar ratio and using various solvents. Liquid products were analyzed by Chemito 1000 GC equipped with a FID detector and a capillary column. N_2 was used as the carrier gas. The identification of products was carried out by comparison of their retention times to the standards.

3. Results and discussion

3.1. Characterization of the catalysts

All the prepared catalysts were found to contain the spinel phase, which is identified from the XRD analysis. The samples show peaks due to spinel phase at characteristic 2θ values. The XRD patterns are shown in Fig. 1a. Crystallite size was calculated using the Scherrer equation from the peak width corresponding to (311) peak. The crystallite size is found to be in the nanometer range.

The DRIFT spectrum for NGF 3 is shown in Fig. 1b. The spectrum was taken in the range 400–1400 cm^{-1}. Spinles typically show two strong bands v_1 and v_2 at around 700 cm^{-1} and 500 cm^{-1}, respectively. According to Waldron et al. [15] and White et al. [16], the high frequency band at 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. The appearance of these two bands confirms the formation of spinel phase.

Thermal analysis of the as-prepared samples was done to know the possible changes occurring when they are subjected to heat treatment. The weight loss at around 100 °C and 350 °C is due to loss of water and nitrate ions. After this temperature, not much weight loss has been observed indicating the high thermal stability of the systems. Behavior of nickel ferrite and gadolinium substituted nickel ferrites towards heat treatment is almost same.

For mixed systems, both surface area and pore volume are increasing with increase in gadolinium content. The SEM photographs for NF, NGF3 and NG are shown in Fig. 2. In nickel ferrite, the particles exist as big clusters with well-defined edges whereas for gadolinium containing systems, the edges disappeared. Presence of gadolinium also leads to a uniform distribution of particles. The elemental compositions of the systems were checked by EDAX analysis and there is a good agreement between experimental and theoretical values. Structural parameters of the samples are shown in Table 1.

The Mössbauer spectra are shown in Fig. 3. At room temperature, the spectrum for nickel ferrite shows two signals corresponding to two sites, with both sites magnetically split showing sextets. Mössbauer spectra of gadolinium containing samples (except NGF4) show not only considerable doublets from the quadrupole splitting, but also detectable sextets from the magnetic splitting. The appearance of doublets from the quadruple splitting of
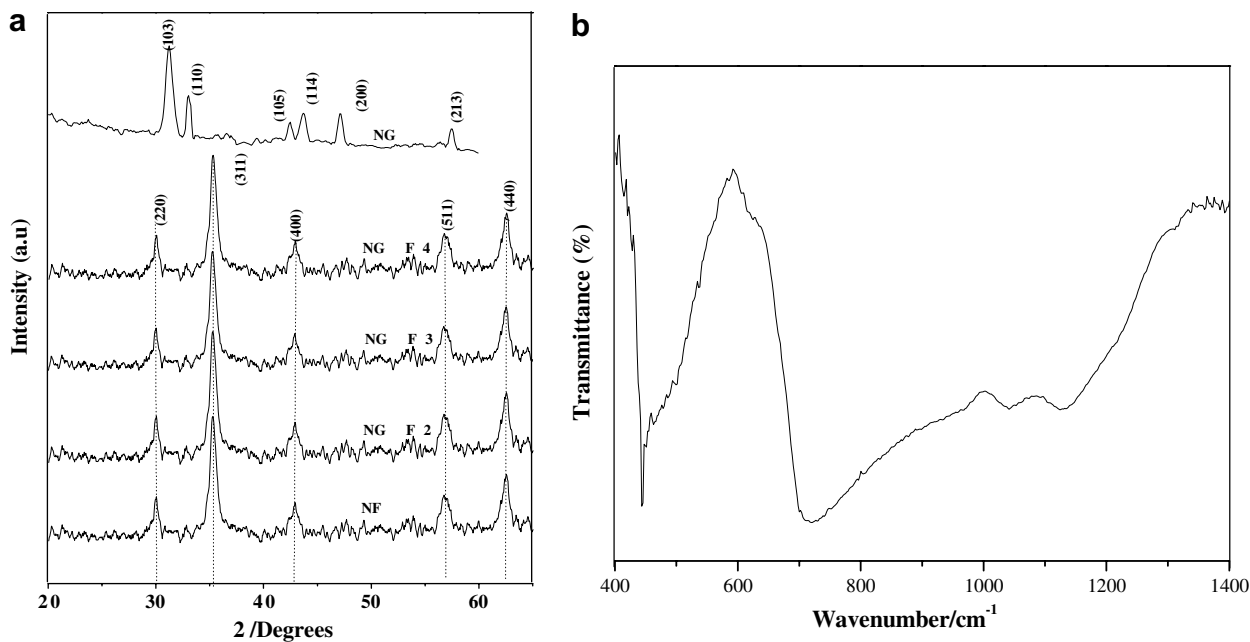
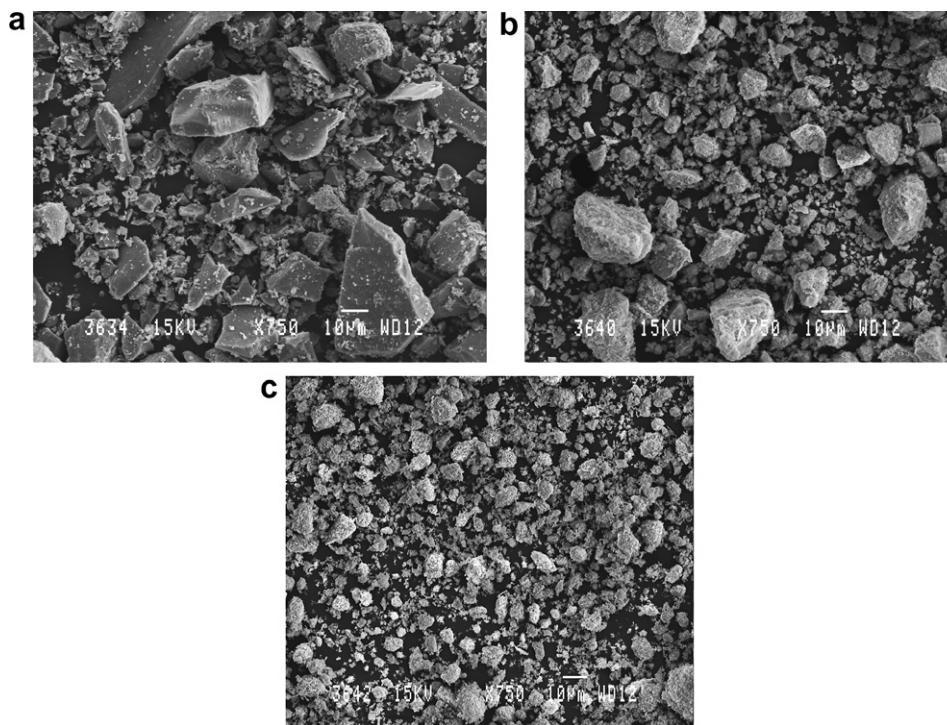Fig. 1. (a) XRD pattern for spinels, and (b) DRIFT spectrum for NGF 3.

Fig. 2. SEM photographs of (a) NF, (b) NGF 3, and (c) NG.

[57]Fe nucleus can be attributed to superparamagnetic (SPM) relaxation effect [17]. Mössbauer spectra for NGF4 contains only singlet with no splitting pattern and this can be attributed to inhomogeneous substitution of iron by gadolinium leading to some of the iron atoms becoming isolated from the majority of exchanged-coupled iron atoms as explained by Koznetsov et al. [18]. This result in paramagnetic behaviour in the case of individual atom, or superparamagnetic behaviour in the case of clusters, either of which can give rise to a singlet in the spectra.

The Mössbauer data are shown in the Table 1. For NGF4, Mössbauer data are not presented because at higher gadolinium content it is really difficult to record the Mössbauer data due to the high absorption of γ-rays by the heavy gadolinium atom. The isomer shift values

Table 1
Surface parameters, Mössbauer data and cation distribution of spinels

a	b	c	d	Elemental analysis (Atom %)			e*	f	g	h
				Ni	Gd	Fe				
NF	8.82	34.0	0.14	32.84	–	67.16	1	0.15	52	$Fe^{2+}_{1.04}$
							2	0.33	48	$Fe^{3+}_{.96}$, Ni^{2+}
NGF1	8.83	17.0	0.04	29.28	13.55	57.17	1	0.24	57	$Ni^{2+}_{.5}$, $Fe^{3+}_{.91}$
							2	0.34	43	$Fe^{3+}_{.69}$, $Gd^{3+}_{.4}$, $Ni^{2+}_{.5}$
NGF2	8.82	29.2	0.07	36.77	26.52	36.72	1	0.26	54	$Ni^{2+}_{.5}$, $Fe^{3+}_{.65}$
							2	0.34	46	$Fe^{3+}_{.55}$, $Gd^{3+}_{.8}$, $Ni^{2+}_{.5}$
NGF3	8.81	8.81	0.10	33.37	40.13	26.49	1	0.24	47	$Ni^{2+}_{.5}$, $Fe^{3+}_{.38}$
							2	0.35	53	$Fe^{3+}_{.42}$, $Gd^{3+}_{1.2}$, $Ni^{2+}_{.5}$
NGF4	8.79	8.79	0.11	31.73	51.90	16.37	1	–	–	Ni^{+2}
							2	–	–	$Fe^{+3}_{0.4}$, $Gd^{+3}_{1.6}$
NG	8.77	8.77	0.16	32.31	67.69	–	1			Ni^{+2}
							2			Gd^{+3}_{2}

a, catalyst; b, crystallite size (nm); c, BET surface area (m²/g); d, pore volume (cc/g); e, iron site *1 − T_d site, 2-O_h site; f, isomer shift (mm/s); g, Fe% at T_d and O_h sites; h, cation distribution.

for A and B sites don't show a remarkable variation with substitution. The cation distribution for nickel ferrite is $(Fe^{+3})_t$ $[Fe^{+3}, Ni^{+2}]_o$ O_4. Taking into account that the Gd^{+3} ion has a large ionic radii (1.08 Å) [19], the gadolinium for iron substitution in nickel ferrite is expected to take place at the octahedral site. Gadolinium incorporated nickel ferrites have a partially inverse structure [20]. For mixed systems, gadolinium substitution for iron leads to replacement of Fe^{3+} ions from T_d site to O_h site which agrees with previous reports [21] and the expected cation distribution is presented in Table 1.

3.2. Catalytic activity

The response of the reaction towards raise in temperature has been studied and the results are presented in Table 2. Increase in temperature is found to be favourable for styrene oxidation. Rise in temperature increased the styrene conversion considerably. But at higher temperatures, not much increase in styrene conversion was observed and conversion decreased after 60 °C. At lower temperatures, impurities were found to be formed. As temperature increased, selectivity towards benzaldehyde increased and cent percent benzaldehyde was obtained from 50 °C. The results confirm that at higher temperatures the C=C bond cleavage is more favorable forming benzaldehyde and the observation is in agreement with previous reports [11,13].

The effect of reaction time on styrene conversion and product selectivity was done at 60 °C. Running the reaction for a long time is found to be favourable for the oxidation of styrene; styrene conversion increased and benzaldehyde selectivity decreased with time. Impurities were found to be formed when the reaction was allowed to run for a long time. After 6 h, the selectivity for benzaldehyde decreases and formation of impure products increases. The results were shown in Table 3.

The influence of H_2O_2 to styrene molar ratio on the conversion and selectivity was studied and the results were shown in Table 4. Increasing the H_2O_2 to styrene molar ratio from 1:1 to 2:1 is found to increasing styrene conversion where as styrene conversion is lowered when percentage of styrene is increased in the reaction mixture. A reactant molar ratio of 1:2 is found to decrease the styrene conversion. More styrene in the reaction mixture not only decreases the styrene conversion but at the same time lowered the selectivity for benzaldehyde also. Maximum styrene conversion was obtained at a molar ratio of 2:1.

Table 5 presents the effect of solvent medium on styrene oxidation and product selectivity. We studied the reaction using protic and aprotic solvents. As reported earlier aprotic solvents were more favorable for styrene oxidation than protic solvents [22–24]. Acetonitrile was found to be the good solvent, which gave a maximum styrene conversion of 42.2%. Aprotic solvents yielded only benzaldehyde where as styrene conversion as well as benzaldehyde selectivity decreased in the case of protic solvents.

Influence of changing the catalytic composition by substituting iron by gadolinium has been studied under optimized conditions and the results were given in Table 6. Styrene conversion was found to be very much sensitive towards the change in catalyst composition. We observed an improvement in activity with gradual incorporation of gadolinium. Nickel ferrite gave a styrene conversion of 42%. Incorporation of 20% of gadolinium into nickel ferrite increased the styrene conversion by 4%. Pure systems are less active than mixed systems. At higher percentages of gadolinium, styrene conversion increased considerably. NGF4 is more active in this series. All the catalysts samples gave only benzaldehyde under optimized conditions.

In heterogeneous catalysis system, the activity of catalyst depends on the number of actual active sites available for the chemical reaction to take place. The activity of spinels depends on the distribution of cations among the
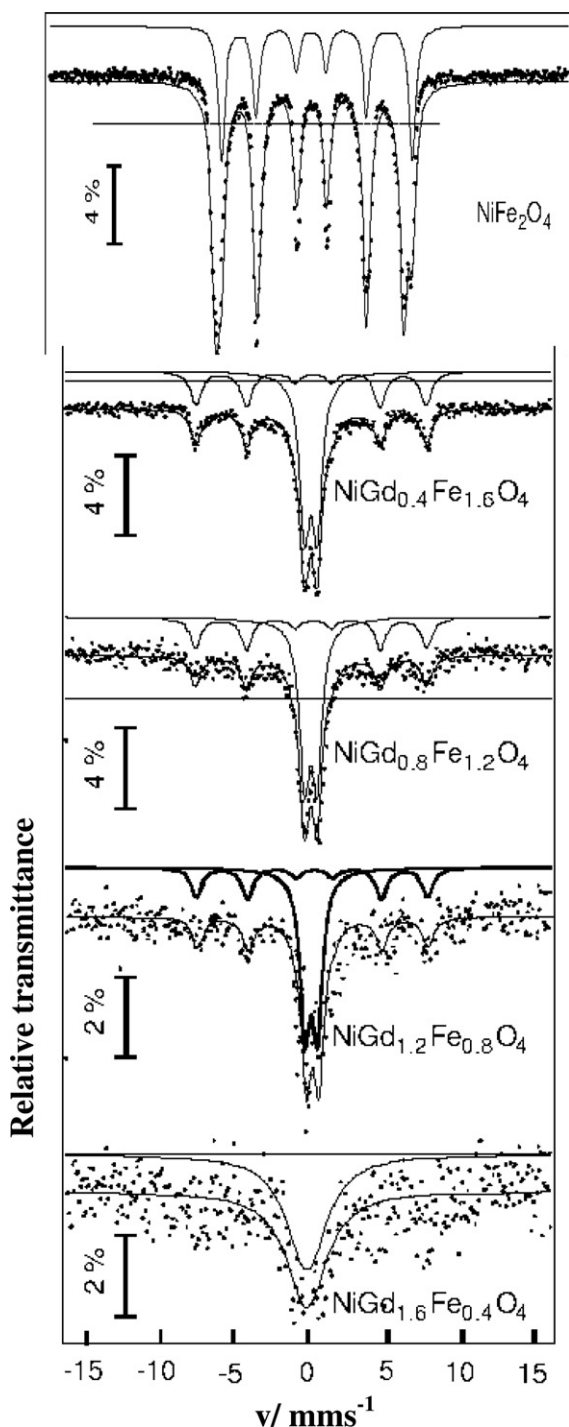
Fig. 3. Mössbauer spectra of gadolinium substituted nickel ferrites.

octahedral and tetrahedral sites. Moreover, it was established that the octahedral sites are exclusively exposed at the surface of the spinel crystallites and thus the catalytic activity is mainly due to the octahedral cations [25,26]. Many authors have reported that the octahedral ions present in the spinel crystal lattice were responsible for the activity towards oxidation reactions [27,28]. The result of styrene oxidation reaction is found to be related to the concentration of O_h ions. When iron is replaced by gadolinium, gadolinium preferably occupies the octahedral site.

Table 2
Effect of temperature on styrene oxidation

Temperature (°C)	Styrene conversion (%)	Selectivity (%)	
		Benzaldehyde	Others
30	22.9	73.5	36.5
40	30.5	78.2	21.8
50	41.1	100	–
60	42.2	100	–
65	38.6	100	–

Catalyst NF, amount 0.1 g, solvent acetonitrile, time 6 h, H_2O_2:styrene 2:1.

Table 3
Effect of time on styrene oxidation

Time (h)	Styrene conversion (%)	Selectivity (%)	
		Benzaldehyde	Others
4	35.2	100	–
6	42.2	100	–
8	44.3	93.2	6.8
10	48.5	88.5	11.5
12	56.8	85.2	14.8

Catalyst NF, amount 0.1 g, solvent acetonitrile, temp. 50 °C, H_2O_2:styrene 2:1.

Table 4
Effect of H_2O_2:styrene mol ratio on styrene conversion

H_2O_2:styrene	Styrene conversion (%)	Selectivity (%)	
		Benzaldehyde	Others
1:2	30.0	87.3	12.7
1:1	35.2	100	–
2:1	42.2	100	–
3:1	39.4	98.2	1.8

Catalyst NF, amount 0.1 g, solvent acetonitrile, temp. 50 °C, time 6 h.

Table 5
Effect of solvent on styrene conversion

Solvent	Styrene conversion (%)	Selectivity (%)	
		Benzaldehyde	Others
Acetonitrile	42.2	100	–
Acetone	38.4	100	–
Isopropyl alcohol	30.3	92.3	7.7
Methanol	31.2	92.0	8.0

Catalyst NF, amount 0.1 g, temperature 50 °C, time 6 h, H_2O_2:styrene 2:1.

Table 6
Effect of catalyst composition on styrene oxidation

Catalyst	Styrene conversion (%)	Benzaldehyde selectivity (%)
NF	42.2	100
NGF 1	46.3	100
NGF 2	49.5	100
NGF 3	53.2	100
NGF 4	56.8	100
NG	43.5	100

Amount 0.1 g, solvent acetonitrile, temp. 50 °C, time 6 h, H_2O_2:styrene 2:1.

Since the concentration of Ni^{2+} ions remains unchanged up to $x = 1.2$ [20], and activity increases with increase in gadolinium content, it is supposed that the catalytic activity is mainly determined by the iron and gadolinium ions. Activity is found to be increasing with increase in the trivalent ion concentration at the octahedral site. Pure nickel gadolinite, which does not contain iron, is less active than mixed systems having both iron and gadolinium which shows that even though the incorporation of gadolinium enhances the activity, the presence of iron is also beneficial for the performance of the catalyst.

4. Conclusions

The different compositions of spinels were prepared by low temperature co-precipitation method using NaOH. The samples were found to contain spinel phase, which is identified from the XRD studies. Iron site distribution was obtained from Mössbauer analysis. Incorporation of gadolinium increases the trivalent ion concentration at the O_h site. Styrene oxidation using these catalysts exclusively forms benzaldehyde under optimized conditions. The improved activity towards styrene oxidation on replacement of iron by gadolinium can be attributed to the increased trivalent ion concentration at the O_h site.

References

[1] Landolt-BornsteinMagnetic Oxides and Related Compounds, vol. 3/4b, Springer, Berlin, 1970.
[2] G. Blasse, Philips Res. Rep. Suppl. 3 (1964) 96.
[3] Sheetal.P. Ghorpade, V.S. Darshane, Sharad.G. Dixit, Appl. Catal. A: Gen. 166 (1998) 135–142.
[4] Thomas Mathew, Sankaran Shylesh, 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.
[5] M. Inoue, S. Enomoto, Chem. Pharm. Bull. 20 (1972) 232.
[6] T. Kotanigava, M. Yamamoto, K. Shimakowa, Y. Yoshida, Bull. Chem. Soc. Jpn. 44 (1971) 1961.
[7] Thomas Mathew, B.S. Rao, C.S. Gopinath, J. Catal. 222 (2004) 107–116.
[8] K. Sreekumar, S. Sugunan, Appl. Catal. A: Gen. 230 (2002) 245–251.
[9] K. Sreekumar, T. Mathew, B.M. Devassy, R. Rajagopal, R. Vertivel, B.S. Rao, Appl. Catal A: Gen. 205 (2001) 11–18.
[10] B. Viswanathan, in: B. Viswanathan, V.R.K. Murthy (Eds.), Ferrite Materials Science & Technology, Springer-Verlag & Naroha Publishing House, Narosa, New Delhi, 1990, p. 8.
[11] N. Ma, Y. Yue, W. Hua, Z. Gao, Appl. Catal. A. 251 (2003) 39.
[12] V.P. Arvulescu, C. constantin, B.L. Su, J. Mol. Catal. A: Chem. 202 (2003) 171.
[13] D. Guin, B. Barawati, S.V. Manorama, J. Mol. Catal. A: Chem. 242 (2005) 26.
[14] P.S. Anilkumar, J.J. Schotri, S.E. Kulkarni, C.E. Deshpande, S.K. Date, Mat. Lett. 27 (1996) 293.
[15] R.D. Waldron, Phys. Rev. 99 (1955) 1727.
[16] W.B. White, B.A. DeAngelis, Spectrochem. Acta 23A (1967) 985.
[17] Y.G. Ma, M.Z. Jin, M.L. Liu, G. Chen, Y. Sui, Y. Tian, G.J. Zhang, Y.Q. Jia, Mater. Chem. Phys. 65 (2000) 79.
[18] M.V. Kuznetsov, Q.A. Pankhurst, I.P. Parkin, J. Phys. D: Appl. Phys. 31 (1998) 2886.
[19] E.E. Sileo, S.F. Jacob, Physica B. 354 (2004) 241.
[20] M.Z. Said, Mater. Lett. 34 (1998) 305.
[21] K. Vijayakumar, D. Ravinder, Mat. Lett. 52 (2002) 166.
[22] R.U. Kulkarni, H.H. Joshi, J. Solid State Chem. 64 (1986) 141.
[23] D. Guin Baruwati, Sunkara.V. Manorama, J. Mol. Catal. A: Chem. 242 (2005) 26–31.
[24] Ning Ma, Yinghong Yue, Weiming Hua, Zi Gao, Appl. Catal A: Gen. 251 (2003) 39–47.
[25] K. Lazar, T. Mathew, Z. Koppany, J. Megyeri, V. Samuel, S.P. Mirajkar, B.S. Rao, L. Guczi, Phys. Chem. Chem. Phys. 4 (2002) 3530.
[26] H. Grabowska, W. Kaczmarczyk, J. Wrzyszcz, Appl. Catal. 47 (1989) 351.
[27] L. Zanderighi, M.P. Faedda, S. Carra, J. Catal. 35 (1974) 427.
[28] K. Omata, T. Takado, S. Kasahara, M. Yamada, Appl. Catal. A: Gen. 146 (1996) 255.