



Oxidation of Benzyl Alcohols by Molecular Oxygen Catalyzed by Nickel Ferrite

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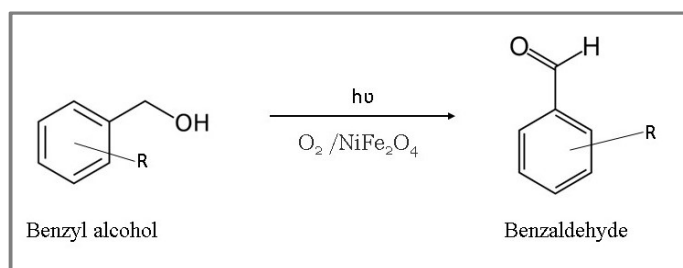
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ABSTRACT

Oxidation of alcohols to aldehydes/ketones/carboxylic acids is an important step in organic synthesis. Generally, alcohol is oxidized to carboxylic acid by strong oxidants and this reaction may or may not stop at the intermediate steps like aldehyde and ketone. On the other hand, mild oxidizing agents may stop oxidation at this stage. Molecular oxygen is such an oxidant, which can help us in achieving this objective, but molecular oxygen has a demerit as an oxidant that it has a slow rate of oxidation. Therefore, this reaction may be catalyzed by nickel ferrites. Nickel ferrites are easy to separate by an external magnet and it can be reused. Nickel ferrite has been used for the oxidation of benzyl alcohols to corresponding benzaldehydes in the present work.

Graphical Abstract:



Keywords: Catalyst, Oxidation, Molecular oxygen, Benzyl alcohol, Benzaldehyde, Nickel ferrite.

INTRODUCTION

The oxidation of benzyl alcohols to benzaldehydes has been one of the most desired reactions. But the final product obtained in this oxidation is corresponding benzoic acid due to its high reactivity towards oxidation.

Selective oxidation of alcohols to carbonyl compounds by molecular oxygen in the presence of cobalt (III) salen complex has been investigated by Nessler *et al.*, [1]. They use isobutyraldehyde as an oxygen acceptor. It was observed that the Co (III)-salen complex is quite active as well as selective in the oxidation of different alcohols. The effect of different factors was evaluated on the reaction

such as amount of catalyst, solvent, and temperature. They also reported catalytic activities of CoFe₂O₄@SiO₂-supported Schiff base metal complex and used molecular oxygen as a green oxidant. It was revealed that benzaldehyde was the major product and as-prepared heterogeneous catalysts can be reused in consecutive reactions.

Adil *et al.*, [2] synthesized doped MnCO₃ [ZnO_x (1%)–MnCO₃] viaco-precipitation route, which afforded [ZnO_(x) (1%)–MnO₂] and [ZnO_(x) (1%)–Mn₂O₃] on calcinations at different temperatures. The activity of these as-prepared catalysts was determined for the oxidation of benzyl alcohol using molecular oxygen as the oxidant. The effect of different parameters was also evaluated such as catalyst dosages, reaction temperature and reaction time. It was also observed that ZnO_x (1%)–MnCO₃ on calcination at 300°C exhibited the highest catalytic performance. They reported that high specific activity was there with 60 mmolg⁻¹ h⁻¹ with complete conversion of benzyl alcohol with the selectivity of >99% in 4 min. It was also revealed that this is a prepared catalyst can be recycled six times without any major loss in catalytic performance with almost the same selectivity.

The catalytic performance of nano-manganese ferrite supported-manganese oxide for oxidation of benzyl alcohol was studied by Elmaci *et al.*, [3] using air as an oxidant, which is present in the reactor. It was revealed that this catalyst displayed moderate activity but selectivity was 100% in the conversion of benzyl alcohol to benzaldehyde under mild conditions.

De Mouraet *et al.*, [4] investigated the catalytic behaviour of Au NPs supported on magnesium ferrite/oxide for the oxidation of benzyl alcohol. It was reported that enhanced the catalytic activity of Au NPs was also enhanced due to presence of Mg²⁺ ions in this ferrite leading to almost 35% conversion. It was also revealed that the catalytic activity of these supported Au NPs was further increased to about 50% conversion, but later on, the catalyst was found to be deactivated in consecutive runs. It was quite interesting to note that this activity remained stable on reuse with no significant loss of activity, when the catalysts were used with the sub-stoichiometric amount of K₂CO₃.

Martinet *et al.*, [5] synthesized six first-row-transition-metal ferrite magnetic nanoparticles MFe₂O₄ (where M = Zn²⁺, Mn²⁺, Co²⁺, Fe²⁺, Cu²⁺ and Ni²⁺) through co-precipitation approach. Then they used as-prepared NPs as catalysts for the oxidation of various alcohols under microwave irradiation in a solvent-free medium. It was reported that CoFe₂O₄, MnFe₂O₄ and CuFe₂O₄ are good catalysts for the conversion of alcohols to the corresponding ketones or aldehydes with 81-94% yields within 2 h at 120°C. Here, they used t-BuOOH as an oxidant this purpose. These catalysts can be easily separated by using an external magnet and it was reported that there was no significant loss of activity on reusing these up to ten consecutive cycles.

The green synthesis of magnetic copper ferrite nanoparticles was reported by Ramazani *et al.*, [6] via sol-gel route. The *tragacanth gum* was used as a reducing as well as a stabilizing agent. It was reported that the average crystallite size of cobalt ferrite particles was 14 nm. It was observed that these nanoparticles can act as catalysts for selective oxidation of alcohols in presence of oxone (potassium hydrogen monopersulfate) as an oxidant. It was reported that primary as well as secondary alcohols afforded corresponding products in good yields., It was also revealed that as-prepared catalyst can be easily recovered and reused a number of times almost with no significant loss in its activity.

Khosroshahi *et al.*, [7] prepared magnetic CoFe₂O₄/Ce-UiO-66 embedded structure composites. They used a fast ultrasound-assisted technique for this purpose. Photocatalytic oxidation of aliphatic alcohols was carried out using this catalyst at room temperature and aerobic conditions under visible-light irradiation. It was reported that as-prepared composite exhibited higher visible-light sensitization performance as compared to only CoFe₂O₄. This catalyst shows higher chemical stability. It was also revealed that it can be recovered and reused for at least five cycles.

Allahresani *et al.*, [8] immobilized Co (II)-salen complex on KCC-1 Co(II)-salen complex@KCC-1 as a catalyst. The oxidation efficiency of this as-obtained catalyst was evaluated using isobutyraldehyde (IBA) as an oxygen acceptor and O₂ as a green oxidant. It was reported that there was excellent selectivity and conversion for the oxidation products under mild conditions. It was reported that oxidation of benzyl alcohol followed first-order kinetics. The catalyst could be recovered easily and reused for number of cycles without any major loss in its activity.

Ramazani *et al.* [9] synthesized zinc ferrite nanoparticles. It was reported that diameter of the ZnFe₂O₄ MNPs was 63.7 nm which is in nano-range. It was reported that ZnFe₂O₄ efficiently catalyzes the oxidation of alcohols to corresponding products in good yields. They used potassium hydrogen monopersulfate (oxone) as an oxidant at room temperature in an aqueous medium. It was also revealed that this catalyst could be reused for up to five runs without any major loss in its activity.

Sato *et al.*, [10] reported photochemical oxidation of benzylic alcohols using DMSO as a solvent. It was observed that this oxidation can be carried out under neutral conditions in an oxygen atmosphere at room temperature. It was found that oxygen uptake was much better in photo-oxidation of benzyl alcohol in DMSO as compared to other solvents. It was also revealed that the oxidation of alcohol to corresponding benzaldehydes was better in the presence of an electron-releasing group while an electron-attracting group retards the oxidation of these alcohols.

Meng *et al.*, [11] investigated oxidation of benzyl alcohol into benzaldehyde with a higher selectivity (95%) using homogeneous CuCl₂ as a catalyst and molecular oxygen as an oxidant under visible light irradiation. The acetonitrile and acetone were used as solvents. It was reported that the formation of a visible light-responsive complex between Cu (II) and solvent can be considered responsible for the oxidation of benzyl alcohol. It was also observed that molecular oxygen was not incorporated into benzaldehyde during this photocatalytic process but only utilized in the oxidation of Cu(I) into Cu (II), where it abstracts a terminal hydrogen to form H₂O.

Gazi and Ananthakrishnan [12] observed selective photooxidation of different benzylic alcohols in the presence of a catalytic amount of bromodimethylsulfonium bromide (BDMS) and molecular oxygen under visible light. This approach was quite efficient for the oxidation of alcohols into their corresponding aldehydes with excellent yields. This protocol is metal-free and green with high selectivity of the reaction. It was also reported that BDMS has a good potential as photocatalytic material and capability for selective oxidation of alcohol.

Nikitaset *et al.*, [13] investigated a mild and green photochemical route for the oxidation of benzyl alcohol to benzaldehyde by air as an oxidant. They used thioxanthenone (20 mol%) as the photocatalyst and CFL lamps, (2× 80 W) or sunlight as the source of light and dimethyl sulfoxide as a solvent. It was observed that a number diverse of primary and secondary alcohols can be converted into the corresponding aldehydes or ketones in low to excellent yields.

MATERIALS AND METHODS

The NiFe₂O₄ nanoparticles were prepared via hydrothermal method. The nickel and iron nitrates (SRL) were used as precursors of Ni and Fe. These were dissolved in distilled water by maintaining the ratio of nitrates (g): water (mL) as 1:3. Then NaOH (0.28g) was added to the solution having a 1:4 ratio (NaOH: Nitrates). The pH was maintained at 11, and the mixture was stirred vigorously for 2 h. Then it was transferred into a Teflon-lined steel autoclave (100 mL). Then the sealed autoclave was heat treated at 150°C for 48 h. Nickel ferrite nanoparticles were separated from this autoclave and washed with acetone and distilled water a number of times, till pH was reduced to 7.0. Then it was dried at 60°C for 6 h.

RESULTS AND DISCUSSION

Characterization of nickel ferrite

X-ray Diffraction (XRD): X-ray diffraction patterns of the nickel ferrite sample was obtained with D8 QUEST (Bruker) using Cu Ka ($\lambda = 1.5418 \text{ \AA}$). X-ray diffraction patterns are given in [figure 1](#).

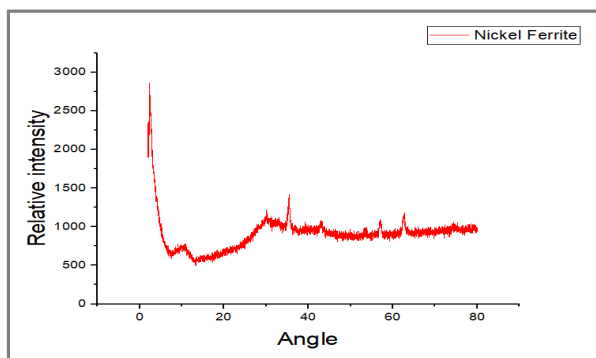


Figure 1. Powder XRD pattern of nickel ferrite

Its sharp peaks confirmed that particles of as-prepared sample of nickel ferrite were crystalline in nature. The size of these particles was determined using Debye–Scherrer equation

$$D = (k\lambda/\beta \cos \theta)$$

Where,

D = Crystalline size, K is the Scherer's constant ($K = 0.94$), λ is the X-ray wavelength (1.54178 \AA) and β is full width at half maximum (FWHM).

The average particle size of the sample was found to be 16.55 nm which is the nano-range.

Field Emission Scanning Electron Microscopy (FESEM): FESEM image of nickel ferrite was recorded with the help of (JSM7600F, Jeol). The image is presented in [figure 2](#).

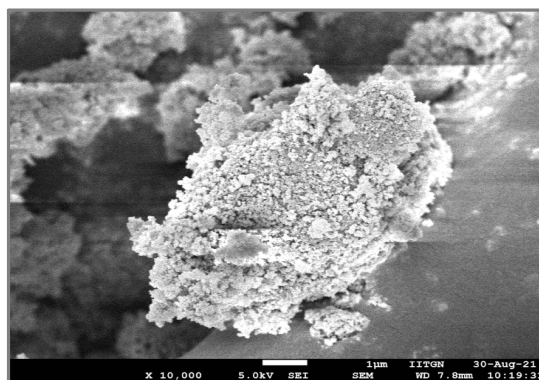


Figure 2. FESEM image of nickel ferrite.

It was observed that as-prepared nickel ferrite was like spongy pumice stone in shape.

Energy Dispersive Spectroscopy (EDS): The ferrite sample was also analysed for its elemental composition using energy dispersive spectroscopy (EDS) (EDX – Oxford INCA Energy 250 EDS). The results are reported in [table 1](#) and [figure 3](#).

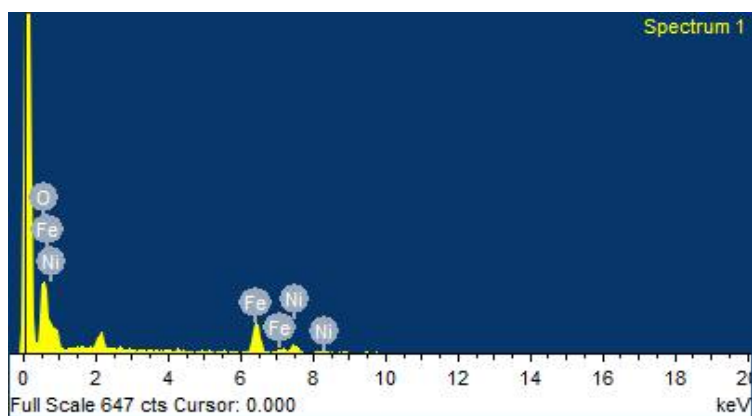


Figure 3. EDS data of nickel ferrite.

Table 1. EDS data of nickel ferrite

Element	Weight%	Atomic%
O	36.70	67.29
Fe	42.15	22.14
Ni	21.15	10.57
Total	100%	100%

It was observed that nickel ferrite sample contains only nickel, iron and oxygen. Therefore, it may be concluded that it does not have any impurity.

FT-IR Spectroscopy (FTIR): The FT-IR spectrum of nickel ferrite was recorded with the help of FTIR Spectrometer RX-1 and presented in figure 4.

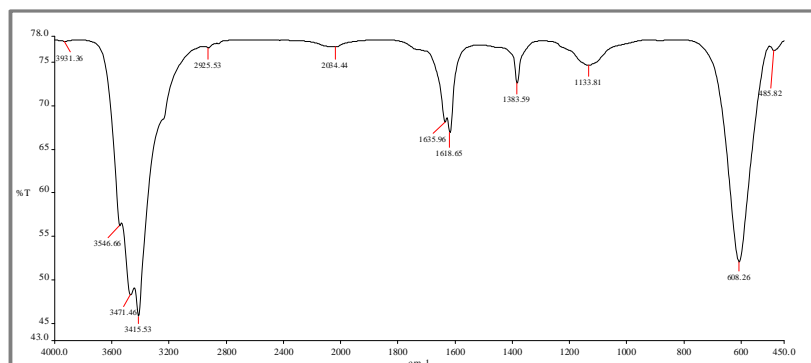


Figure 4. FT-IR spectra of nickelferrite

The presence of a strong band at 608.26 cm^{-1} indicated the presence of M-O stretching vibration.

Oxidation of benzyl alcohol: Oxidation of benzyl alcohol was carried out with atmospheric oxygen as an oxidising agent in polar medium, dimethyl sulfoxide (DMSO). A stock solution of benzyl alcohol was prepared with DMSO in 1:5 ratio. The temperature of the solution was maintained at 25°C . Then air was passed in the reaction mixture to oxidise benzyl alcohol by a mild oxidant, molecular oxygen. The catalytic activity of the catalyst was observed for the selective oxidation of benzyl alcohol to benzaldehyde by oxygen gas in presence as well as absence of a base. It was observed that benzyl alcohols were oxidized to corresponding benzaldehyde derivatives with excellent efficiency within 14 h. The product was obtained by treating the reaction mixture with 2, 4-dinitrophenyl hydrazine where 2, 4-dinitrophenylhydrazone derivatives were obtained as orange-

coloured precipitates. It was confirmed by its mp. The progress of the reaction was monitored at different time intervals. The effect of various parameters such as the amount of benzyl alcohol, nickel ferrate and temperature was observed. It was found that there was slight oxidation in the absence of a catalyst, but the oxidation of benzyl alcohol was relatively high on using catalyst.

Variation of benzyl alcohol: The effect of the amount of benzyl alcohol on its oxidation was observed by keeping it in the range of 1-15 mL. The results are reported in [table 2](#).

Table 2. Effect of amount of benzyl alcohol
DMSO =25 mL; Nickel ferrate = 0.005 g

Benzyl alcohol (mL)	Time (h)	Yield (%)
1.0	6	5
	12	16
	14	21
	24	16
2.0	6	8
	12	21
	14	33
5.0	24	28
	6	11
	12	29
10.0	14	46
	24	38
	6	10
	12	17
15.0	14	32
	24	27
	6	7
	12	15
	14	23
	24	20

The yield of benzaldehyde was found to increase with increase in concentration of benzyl alcohol as more molecules are available for reaction, but after certain limit (5 mL), it was found to decrease; this may be due to further oxidation to benzoic acid.

Effect of amount of catalyst: The amount of nickel ferrite (catalyst) is also likely to affect the oxidation of benzyl alcohol and therefore, the amount of catalyst was also varied from 0.001 to 0.007 g. The results are reported in [table 3](#).

It was observed that the yield of benzaldehyde increases on increasing the amount of nickelferrite. It was attributed to the fact that more active sites are available and optimal results were obtained at 0.005 g. There was a saturation-like behaviour when the amount of catalyst was increased further above 0.005 g. This may be due to the fact that all active sites are occupied and there are no further sites available on increasing the amount.

Table 3. Effect of amount of nickel ferrite
DMSO = 25 mL; Benzyl alcohol =5.0 mL

Nickel ferrite (g)	Time (h)	Yield (%)
0.001	14	2
0.002	14	22
0.003	14	28
0.004	14	36
0.005	14	46
0.006	14	46

0.007	14	46
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Effect of air/oxygen: It was interesting to note that the yield of benzaldehyde was increased from 46 to 68%, when oxygen gas was used as an oxidant in place of air. The results are given in the table 4.

Table 4. Effect of air/oxygen
DMSO = 25 mL; Benzyl alcohol = 5.0 mL; Nickel ferrate = 0.005 g

Time (h)	Yield (%) with air	Yield (%) with oxygen
6	11	17
12	29	35
14	46	68
24	38	42

Effect of different substituents in benzyl alcohols: This reaction was also carried out with different substituted benzyl alcohols. The results are summarised in table 5.

Table 5. Effect of substituents
DMSO = 25 mL; Benzyl alcohol = 5.0 mL; Nickel ferrate = 0.005 g; Time = 14h

Substituents of substituents	Yield (%)
m-Nitro	2.0
p-Nitro	7.0
m-Methyl	65.0
p-Methyl	92.0
p-Bromo	9.0
p-Chloro	3.0

It was observed that the yield of benzaldehyde decreases, when an electron-withdrawing group (such as -Cl, -Br, or -NO₂ group) is attached to a benzene ring. However, the effect was more prominent, when this group was present at the *p*-position as compared to *m*-position. A reverse trend was observed in the case, where the electron donating group (such as -CH₃ group) was present as a substituent. Then an increase in the yield was obtained. This may be explained on the basis that the electron withdrawing group decreases the electron density on the benzene ring, hence, making it less susceptible to oxidation while the electron donating group increases the electron density and thus, such benzyl alcohols are easily oxidised. The air or oxygen was passed in the reaction mixture to drive the oxidation of benzyl alcohols by a mild oxidant, molecular oxygen. It was also observed that this catalyst can be recovered easily using a magnet and it can be reused again for five consecutive cycles with no significant loss in its activity.

CONCLUSION

Benzyl alcohol is an aromatic alcohol and it is generally utilized in the production of fragrances/perfumes, adhesives and paints. It has been commonly used in medicine as an antimicrobial preservative and also as an antipruritic and local anaesthetic. It is a waste product of various industries and it can be oxidized to benzaldehyde, which is comparatively safe. It is used in the production of dyes, perfumes and soaps. It is also used in baked goods and cakes as almond extract. Benzaldehyde is also used as an additive in antifungal and antibacterial preservatives. The benzyl alcohols are oxidized by air/oxygen in the presence of nickel ferrite to give excellent yields to afford benzaldehydes. This catalyst can be recycled for further use without any significant loss in its activity.

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