Oxidation of benzyl alcohols by molecular oxygen catalyzed by cobalt ferrite

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Abstract

Oxidation of alcohols to aldehydes/ketones/carboxylic acids is a crucial step in organic synthesis. Normally, strong oxidants oxidize alcohol to carboxylic acid and this reaction may or may not stop at the intermediate steps to form aldehyde and ketone. Some mild oxidants are required to stop it here at this stage. Here, molecular oxygen can help in achieving this objective, but there is a disadvantage to use molecular oxygen as an oxidant as it has a slow rate of oxidation.

Hence, such a reaction may be catalyzed by metal ferrites. These metal ferrites are easy to separate by using an external magnet and can be recycled. Cobalt ferrite has been used for the oxidation of benzyl alcohols to corresponding benzaldehydes.

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

Introduction

The oxidation of benzyl alcohols to benzaldehydes has been one of the most studied systems. This is due to its high reactivity towards oxidation. The final product in this oxidation reaction is the corresponding benzoic acid. Nesseri et al[9] carried out selective oxidation of alcohols to carbonyl compounds by molecular oxygen in the presence of cobalt (III)-salen complex. The isobutyraldehyde was used as an oxygen acceptor. It was reported that the Co (III)-salen complex is quite active and selective in the oxidation of different alcohols. They evaluated the effect of various factors on the reaction such as solvent, amount of catalyst and temperature. They also observed catalytic activities of $CoFe_2O_4$@SiO_2-supported Schiff base metal complex using molecular oxygen as a green oxidant. It was observed that benzaldehyde was the main product and as-prepared heterogeneous catalyst was reusable in consecutive reactions.

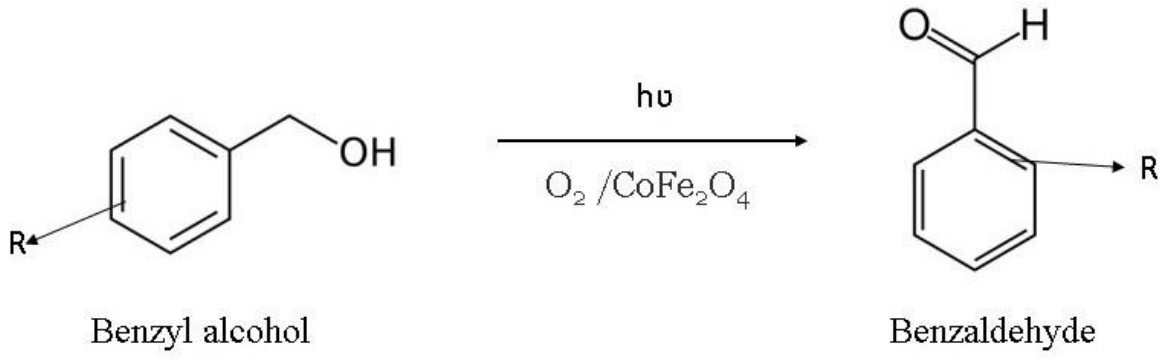
Adil et al[1] reported synthesis of ZnO_x doped $MnCO_3$ [ZnO_x (1%)–$MnCO_3$] through a co-precipitation route, which on calcination at different temperatures yielded different manganese oxides, [$ZnO_{(x)}$ (1%)–MnO_2] and [$ZnO_{(x)}$ (1%)–Mn_2O_3]. The performance of these as-prepared catalysts was examined for oxidation of benzyl alcohol with molecular oxygen as the oxidant. The effect of different parameters was also investigated such as reaction temperature, reaction time and catalyst dosages. It was reported that ZnO_x (%1)–$MnCO_3$ on calcination at 300°C exhibited the best catalytic performance.

High specific activity of 60 mmol g^{-1} h^{-1} with benzyl alcohol conversion (complete) with selectivity more than 99% (4 min) was observed. It also revealed that the catalyst can be recycled six times without any significant loss of catalytic performance and the selectivity also remained almost the same.

The catalytic performance of nano-manganese ferrite supported-manganese oxide for oxidation of benzyl alcohol was studied by Elmaci et al[4] 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 Moura et al[3] studied the catalytic behaviour of Au NPs supported on magnesium ferrite/oxide for the oxidation of benzyl alcohol.

Graphical abstract



It was reported that the presence of Mg^{2+} ions in this ferrite structure enhanced the catalytic activity of Au NPs to almost 35% conversion in the absence of an additional base. After modifying the support with MgO, it was also revealed that the catalytic activity of these supported Au NPs was further enhanced to about 50% conversion, but the catalyst was found to be deactivated in consecutive recycling tests. It was interesting to note that when the catalysts were used with the sub-stoichiometric amount of K_2CO_3, the activity remained stable upon recycling with no significant loss of activity. It also maintained the selectivity for the preferential production of benzoic acid.

Martins et al[7] prepared six first-row-transition-metal ferrite magnetic nanoparticles MFe_2O_4 (where M = $Mn^{2+,}$ Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) by using the co-precipitation approach. They used as-prepared NPs as catalysts for the oxidation of various alcohols in solvent-free medium under microwave irradiation. It was reported that $MnFe_2O_4$, $CoFe_2O_4$ and $CuFe_2O_4$ acted as catalysts for the conversion of alcohols to the corresponding ketones or aldehydes in a range of 81 - 94% within 2 h at 120 °C. They used t-BuOOH as an oxidant for 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 10 consecutive runs. The effects of different operating parameter were investigated on the oxidation reaction, such as temperature, time, type of oxidant, presence of organic radicals, etc.

Ramazani et al[11] reported the green synthesis of magnetic copper ferrite nanoparticles via sol-gel route. They used *tragacanth gum* as a stabilizing as well as reducing agent. It was observed that average crystallite size of cobalt ferrite particles was 14 nm. These nanoparticles can act as catalyst for selective oxidation of alcohols in presence of oxone (potassium hydrogen monopersulfate) as an oxidant. It was reported that primary and secondary alcohols gave the corresponding products in reasonable yields., The as-prepared catalyst can be easily recovered and reused a number of times with no significant loss in its activity.

Khosroshahi et al[6] prepared magnetic $CoFe_2O_4$/Ce-UiO-66 embedded structure composites via fast ultrasound-assisted technique and used it for photocatalytic oxidation of aliphatic alcohols at room temperature under visible-light irradiation and aerobic conditions. It was reported that as-prepared composite exhibited better visible-light sensitization performance as compared to $CoFe_2O_4$ alone. This catalyst has high chemical stability. It can be recovered effectively and reused for at least five cycles.

Allahresani et al[2] immobilized Co(II)-salen complex on KCC-1 as a catalyst which can be recovered as Co(II)-salen complex@KCC-1. The oxidation efficiency of this sustainable catalyst was evaluated using O_2 as a green oxidant and isobutyraldehyde (IBA) as an oxygen acceptor. It was reported that there was superior selectivity and conversion for the oxidation products under mild conditions. It was revealed that oxidation of benzyl alcohol followed first-order reaction. The catalyst could be recovered easily and reused for number of cycles, without any significant loss in its activity.

Ramazani et al[12] synthesized zinc ferrite nanoparticles. It was observed that diameter of the $ZnFe_2O_4$ MNPs was 63.7 nm. It was reported that $ZnFe_2O_4$ efficiently catalyzes oxidation of alcohols affording corresponding carbonyl-containing products in good yields. Using potassium hydrogen monopersulfate (oxone) as an oxidant in aqueous medium at room temperature, it was revealed that this catalyst could be reused up to 5 runs without any significant loss in its activity.

A photochemical oxidation reaction of benzylic alcohols was developed by Sato et al.[13] They used DMSO as a solvent. It was reported that oxidation can be carried out under neutral conditions at room temperature in an oxygen atmosphere. It was observed that oxygen uptake was much facilitated in photo-oxidation of benzyl alcohol in DMSO as compared to other solvents. It was also revealed that the presence of an electron-releasing group favours the oxidation affording corresponding benzaldehydes whereas an electron-attracting group reduces the oxidation of these alcohols.

Meng et al[8] reported that homogeneous $CuCl_2$ can oxidize benzyl alcohol into benzaldehyde with a higher selectivity (95%) using molecular oxygen as an oxidant under visible light irradiation. They used acetonitrile and acetone as solvents. It was observed that the formation of a visible light-responsive complex between Cu (II) and solvent is responsible for the oxidation of benzyl alcohol. It was revealed that molecular oxygen was not incorporated into benzaldehyde during the photocatalytic process but only in the oxidation of Cu(I) into Cu (II) where it abstracts terminal hydrogen to form H_2O.

Gazi and Ananthakrishnan[5] carried out selective photooxidation of different benzylic alcohols in the presence of molecular oxygen and a catalytic amount of bromodimethylsulfonium bromide (BDMS) in the presence of visible light.

This method was found to be efficient for the oxidation of alcohols into their corresponding aldehydes with excellent yields. The present protocol is metal-free and green with high selectivity of the reaction. It was also revealed that BDMS has a photocatalytic potential and capability for selective oxidation of alcohol.

Nikitas et al[10] reported a mild and green photochemical protocol for the oxidation of benzyl alcohol to benzaldehyde by air as an oxidant. They used thioxanthenone (20 mol%) as the photocatalyst and lamps (CFL, 2× 80 W) or sunlight as the light source and dimethyl sulfoxide as a solvent. It was

reported that a variety of primary and secondary alcohols were converted into the corresponding aldehydes or ketones in low to excellent yields.

Material and Methods

The $CoFe_2O_4$ nanoparticles were prepared via hydrothermal method in order to synthesize $CoFe_2O_4$. Cobalt and iron nitrates (SRL) (precursor of Co and Fe) were dissolved in distilled water by maintaining the ratio of nitrates (g): water (mL) as 1:3. Then NaOH (0.28 g) was added slowly to the solution having 1:4 ratio (NaOH: Nitrates). The pH was maintained at 11 and the mixture was vigorously stirred for 2 h. Then it was transferred into a 100 mL teflon-lined steel autoclave. The sealed autoclave was heat treated at 150°C for 48 h. Cobalt ferrite nanoparticles were separated from the autoclave and washed with acetone and distilled water many times, till pH was decreased to 7. Then it was dried at 60◦C for 6 h.

Characterization of cobalt ferrite

X-ray Diffraction (XRD): X-ray diffraction (XRD) patterns of the cobalt ferrite sample were obtained with D8 QUEST (Bruker) using Cu Ka (λ = 1.5418 Å). X-ray diffraction patterns are given in fig. 1. Its sharp peaks confirmed that particles of as-prepared sample of cobalt ferrite were crystalline in nature. The size of these particles were 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 (1.54178Å) and β is full width at half maximum (FWHM). The average particle size of the sample was found to be is 12.72 nm.

Field Emission Scanning Electron Microscopy (FESEM): FESEM image of cobalt ferrite was recorded with the help of (JSM7600F, Jeol). The image is presented in fig. 2. It was observed that as-prepared cobalt ferrite was like pumice stone or broccoli in shape.

Energy Dispersive Spectroscopy (EDS): The cobalt 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 fig. 3.

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

FT-IR Spectroscopy (FTIR): The FT-IR spectrum of cobalt ferrite was recorded with the help of (FTIR Spectrometer RX-1) and presented in fig. 4. The presence of a strong band at 565.42 cm^{-1} indicated the presence of M-O stretching vibration.

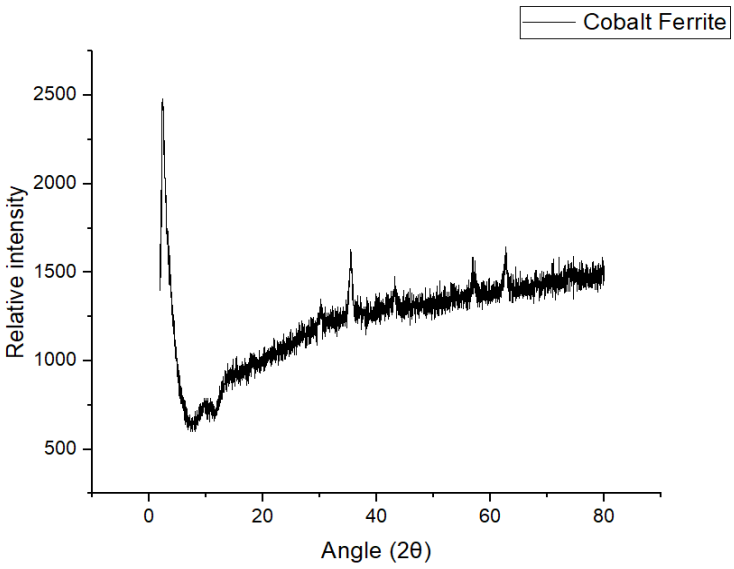


Figure 1: Powder XRD pattern of cobalt ferrite

Table 1
EDS data of cobalt ferrite

Element	Weight %	Atomic %
O	28.10	58.17
Fe	45.83	27.18
Co	26.07	14.65
Total	100 %	100 %

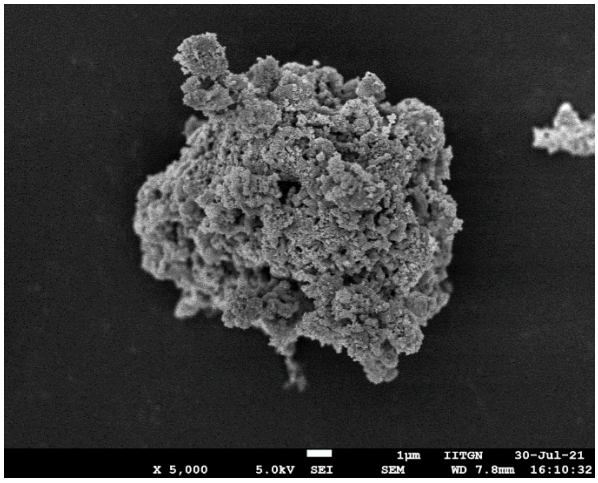


Figure 2: FESEM image of cobalt ferrite

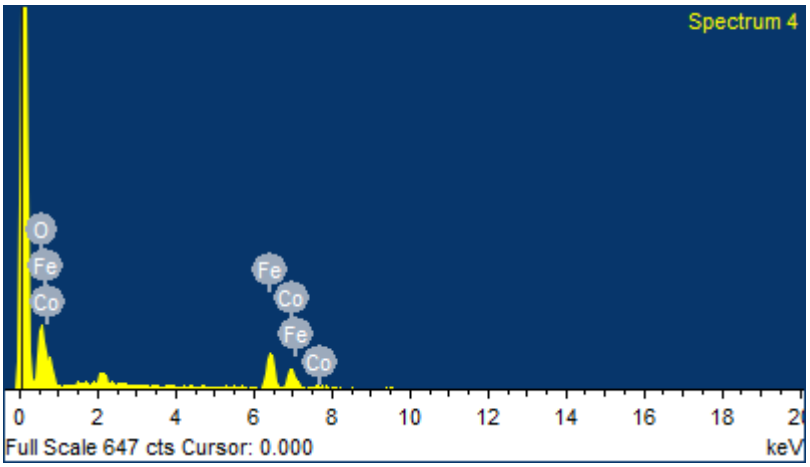


Figure 3. EDS data of cobalt ferrite

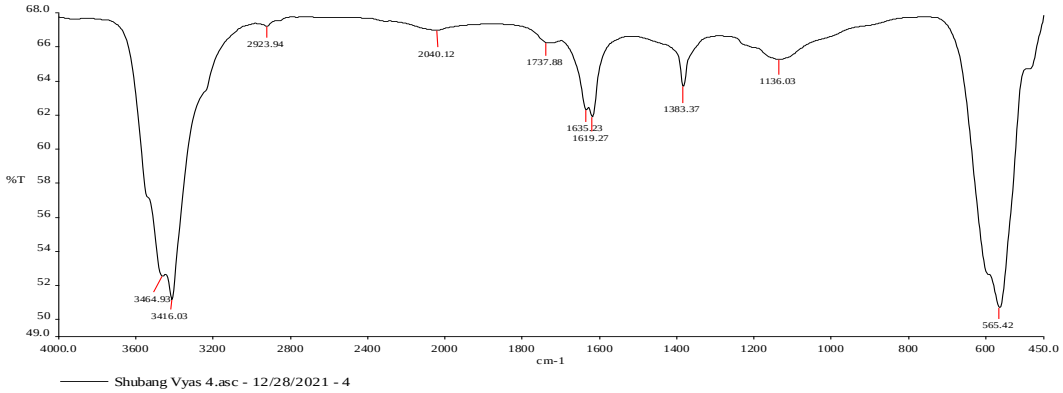


Figure 4: FT-IR spectra of cobalt ferrite

Results and Discussion

Oxidation of benzyl alcohol: Oxidation of benzyl alcohol was carried out with atmospheric oxygen as an oxidising agent in polar medium dimethyl sulfoxide (DMSO). The stock solution of benzyl alcohol was prepared in 1:5 ratio with DMSO. The desired temperature of the solution was maintained at 25°C. The air was passed in the reaction mixture to drive the oxidation of benzyl alcohol by a mild oxidant, molecular oxygen. The catalytic activity of the catalyst was studied for the selective oxidation of benzyl alcohol to benzaldehyde by oxygen gas in the presence and absence of a base.

Benzyl alcohols were oxidized to the benzaldehyde derivatives with excellent efficiency within 14 h. The product benzaldehyde was obtained by treating the reaction mixture with 2,4- dinitrophenyl hydrazine where 2,4-dinitrophenyl hydrazone, derivatives were obtained as orange coloured precipitate confirmed by their meeting points. The progress of the reaction was measured at various

time intervals. The effect of various parameters such as temperature, amount of benzyl alcohol and cobalt ferrate, was observed. It was found that slight oxidation was there in the absence of a catalyst but the oxidation of benzyl alcohol was very 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.

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

Effect of amount of catalyst: The amount of cobalt ferrite (catalyst) is also likely to affect the oxidation of benzyl alcohol. The amount of catalyst was 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 cobalt ferrite as more active sites are available and optimal results were obtained at 0.005 g. There was a saturation-like behaviour in the yield 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 increase of the amount.

Effect of combination of ferrites: The effect of mixing other ferrites (magnesium and cobalt ferrites) with cobalt ferrite was also observed. It was observed that the oxidation of benzyl alcohol in the presence of magnesium and cobalt ferrites was relatively low, but there was a sudden rise in the rate of oxidation when these were used with cobalt ferrite as a catalyst.

Table 2
Effect of amount of benzyl alcohol
DMSO -25 mL, cobalt ferrate = 0.005 g

Benzyl alcohol (mL)	Time (h)	Yield (%)
1.0	6	6
	12	17
	14	23
	24	19
2.0	6	9
	12	20
	14	35
	24	32
5.0	6	12
	12	35
	14	48
	24	38
10	6	10
	12	16
	14	32
	24	28
15	6	6
	12	11
	14	25
	24	23

Table 3
Effect of amount of cobalt ferrite
DMSO = 25 mL, benzyl alcohol = 5.0 mL

Cobalt ferrite (g)	Time (h)	Yield (%)
0.001	14	17
0.002	14	19
0.003	14	28
0.004	14	36
0.005	14	48
0.006	14	48
0.007	14	48

Table 4
Effect of air/oxygen
DMSO = 25 mL, benzyl alcohol = 5.0 mL: cobalt ferrate = 0.005 g,

Time (h)	Yield (%) with air	Yield (%) with oxygen
6	12	30
12	35	56
14	48	95
24	62	70

Table 5
Effect of substituents
DMSO - 25 mL, Benzyl alcohol = 5.0 mL: Cobalt ferrate = 0.005 g, Time 14 h

Substituents of substituents	Yield (%)
m-Nitro	2.0
p-Nitro	7.0
m-Methyl	65.0
p-Methyl	97.0
p–Bromo	9.0
p-Chloro	3.0

Effect of air/oxygen: It was interesting to note that the yield of benzaldehyde increased from 75 to 95% when oxygen gas was used as an oxidant in place of air. The results are given in the table 4.

Effect of different substituents in benzyl alcohols: This reaction was also carried out with different substituents of benzyl alcohol. The results are summarised in table 5. It was observed that the yield of benzaldehyde decreases, when an electron-withdrawing group (such as -Cl, -Br, or -NO_2 group) is attached. However, the effect was more prominent, when this group is present at p- position than at m- position. A reverse trend was observed when the electron donating group (such as -CH_3 group) was present as a substituent.

Then there was an increase in the yield. 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; 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 used as a solvent in the production of fragrances/perfumes, paints and adhesives. It has been widely used in medicine as an antimicrobial preservative and also as a local anaesthetic and antipruritic. It is a waste product of various industries and it can be oxidized to benzaldehyde which is comparatively safe and it can be used in the production of dyes (acridine and aniline dyes), soaps and perfumes. It is also used in cakes and baked goods as almond extract.

Benzaldehyde is also used in additives like antibacterial and antifungal preservatives. The benzyl alcohols are oxidized by air/oxygen in the presence of cobalt ferrite to give excellent yields. This catalyst can be recycled for further use without any major loss in its activity.

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