

Use of Some Metal Ferrites as Catalyst in Haloform Reaction

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Research Article

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ABSTRACT

Zinc ferrite was used to catalyse the haloform reaction of potassium iodide and acetone in the presence of sodium hypochlorite solution. Zinc ferrite was prepared by hydrothermal process. It was characterized by Field Emission Scanning Electron Microscopy (FESEM), X-Ray Diffraction spectroscopy (XRD), and Energy Dispersive X-Ray spectroscopy (EDX). The crystalline size of zinc ferrite was found to have 6.62 nm and these are irregular in shape. It was found that the yield of the product (iodoform) in the presence of Zn ferrite was 38.6%, which is almost 1.8 times the yield obtained in the absence of catalyst. A comparative study was made with different metal ferrites as catalyst and it was found that the activity of metal ferrites followed the order: $ZnFe_2O_4 > MgFe_2O_4 > CoFe_2O_4 > CuFe_2O_4 > NiFe_2O_4$.

Keywords: Haloform reaction; Zinc ferrite; Catalyst; Synthesis; Hydrothermal method; Metal ferrites

INTRODUCTION

Monasterolo, et al. reported aromatic haloform reaction. It was observed that heteroarenes bearing vinylogous nitromethane system could undergo aromatic amination to produce N-functionalized arenes via trichloromethane derivative. It was also revealed that quantitative yields were obtained without the need for transition-metal catalysis. Such haloform-type amination can be utilized in the development of an orthogonal N-protection strategies, and therefore, it can be used as a new N-protecting reagent ^[1].

Chen, et al. performed a bromoform reaction of some tertiary amines with or NBS/sulfonamides N, N-dibromosulfonamides. They prepared number of amidines with moderate to good yields via Csp³-Csp³ bond cleavage ^[2]. Kawasumi, et al. reported an iodoform reaction for oxidative demethylation between iodine I₂ and t-BuOK in t-butanol ^[3]. Here, *in situ*-generated t-BuOI acted as chemoselective iodinating agent. They reported that levulinic acid can be converted into succinic acid. It was also revealed that this reaction can be also used for synthesis of some carboxylic acids selectively from compounds containing an acetyl group ^[4].

Élinson, et al. suggest that it is possible to carry out an electro catalytic haloform reaction ^[4]. In a diaphragm less electrolyser using methanol and catalytic amounts of NaBr, methyl ketones are transformed into the corresponding carboxylic acid methyl esters. Under these circumstances, electrochemically driven favorskii rearrangement results in the formation of the methyl ester of 3-phenylpropanoic acid from benzyl methyl ketone.

Kawasumi, et al. describe a long-established qualitative assay for acetyl and/or ethanol units in organic compounds is the iodoform reaction ^[3]. However, there are not many synthetic uses for it. The oxidative demethylation reaction using I₂ and t-BuOK in t-BuOH is described here as a tailored iodoform reaction, with t-BuOI produced *in situ* acting as the chemoselective iodinating agent. Levulinic acid, a significant four-carbon chemical feedstock, may be converted into succinic acid using this technique in just one step. Other substances that contain an acetyl group/ethanol unit can also undergo this oxidative demethylation, selectively producing the appropriate carboxylic acids.

Capilato, et al. explained the creation of a unique method for oxidatively converting methyl ketones to derivatives of carboxylic acids is discussed ^[5]. We suggest a mechanism for this transformation using an analogy to the haloform reaction, which is validated by experimental and computational analysis.

Wever, et al. explained in contrast to heme groups, vanadium haloperoxidases include the bare metal oxide vanadate as a prosthetic group, and they are far more selective and stable with regard to their substrates ^[6]. Particularly, these enzymes convert halides into hypohalous acids when hydrogen peroxide is present. The various organic compounds that these reactive halogen intermediates come into contact with will react quickly and specifically. Iodinated or brominated chemicals, such as bromoform (CHBr₃) and dibromomethane (CH₂Br₂), are produced by marine algae and diatoms that carry these iodoperoxidase and bromoperoxidase. These substances are supersaturated in some seas and oceans, where they serve as a large source of bromine for the lower stratosphere and troposphere and make a significant contribution to the world budget of halogenated hydrocarbons. The production of these volatile chemicals and the biogeochemical cycles are the main areas of attention in this viewpoint.

Shi, et al. explained selective C-C bond cleavage under benign conditions can be a useful technique for macromolecular breakdown and chemical synthesis [7]. However, the generally sustainable character of C-C transformation chemistry has been compromised by the employment of stoichiometric and potentially harmful oxidants, as well as noble transition-metal catalysts, in conventional chemical procedures. In this sense, electrochemical C-C bond cleavage has been found to be a scalable and sustainable method that uses electricity to substitute chemical reagents that produce byproducts. Kolbe electrolysis and related procedures have been primarily responsible for the advancements gained in this field so far. Positively, there have recently been an increasing number of examples of C-C bonds being broken by different methods. An overview of the most important and recent breakthroughs in electrochemical research is provided in this study.

Percec, et al. reported that the first instance of vinyl chloride live radical polymerization in water at 25°C has occurred. Iodoform triggered this polymerization, which was then catalysed by nascent CuO formed by the disproportionation of CuI in the presence of ligands that strongly bind Cu II, such as polyethyleneimine or tris(2-aminoethyl)amine [8]. The resulting poly vinyl chloride had two CHC II active chain ends, was free of structural flaws, had a narrow molecular weight distribution, controlled molecular weight, and a higher syndiotacticity (62%) than the poly vinyl chloride produced through traditional free-radical polymerization at the same temperature (56%). Most likely, a mix of competing mechanisms, including activation by single electron transfer mediated by nascent CuO and degenerative chain transfer, drive the unique polymerization.

Roy, et al. reported that how open-chain benzyl-oxo esters initiate the chemical cascade that results in the deprotection, decarboxylation, and asymmetric protonation of enolic species [9]. The reaction produced optically active-aryl ketones with up to 75% when it was carried out with catalytic quantities of cinchonine present.

MATERIALS AND METHODS

Synthesis of zinc ferrite nanoparticles

Hydrothermal method was used to prepare zinc ferrite using a similar method reported by Naidu, et al [10]. Zinc nitrate $[\text{Zn}(\text{NO}_3)_2]$ and ferric nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ were used as precursor of zinc and iron, respectively. A Teflon coated autoclave was used for this purpose. Zinc and iron nitrates were dissolved in distilled water keeping the ratio of nitrates and water as 1:3. The resultant solution was stirred and NaOH was added drop wise into the solution in 1:4 ratios till the pH was maintained at 11. The mixture was vigorously stirred for 2 h and transferred into teflon coated stainless steel autoclave and sealed. Then autoclave was heated at 150°C for around 48 hours. After heating, the autoclave was allowed to cool at room temperature. The product in the autoclave was filtered and washed several times from water and then acetone, till its pH reaches 7.

Experimental procedure

The 2 ml of acetone, 6 g of potassium iodide, and 100 ml of water were taken in a flask with a flat bottom with 0.10 g of zinc ferrite. Then 70 ml of 5% sodium hypochlorite was added gradually with stirring. Yellow crystals of iodoform were separated out. Sodium hypochlorite was added until the reaction is completed. The reaction was allowed to settle down for 15 min. It was filtered using suction in a buchner funnel. The product was dried after washing it from methylated spirit and recrystallized.

The haloform reaction is:

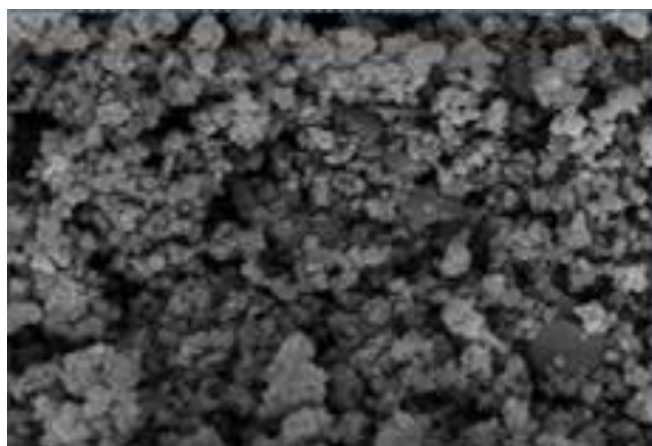


RESULTS AND DISCUSSION

Field emission scanning electron microscopy

The as-prepared zinc ferrite particles were characterized by Scanning Electron Microscope (SEM) on JSM-6100 (JEOL) with a digital image processor. The Field emission scanning electron microscopy images have been given in Figure 1. The morphology of zinc ferrite was found to be irregular shaped.

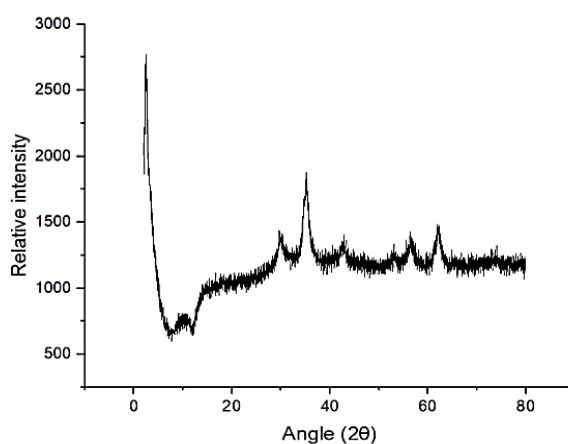
Figure 1. Field emission scanning electron microscopy image of zinc ferrite.



X-ray diffraction

The crystalline nature of the synthesized zinc ferrite sample was observed by X-ray diffraction pattern. An X' Pert Pro XRD equipped with x'celerator solid-state detector was used and result are reported in Figure 2. The average particle size was calculated by debye-scherer equation and it was found to be in quantum-range (6.62 nm).

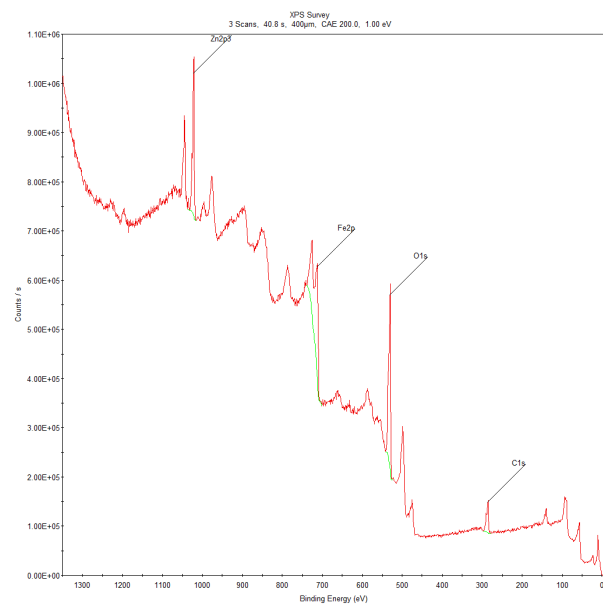
Figure 2. Powder X-ray diffraction pattern of zinc ferrite.



X-ray photoelectron spectroscopy

X-ray photoelectron spectral analysis was also carried out using a Thermo K-alpha+X-ray spectrometer. Contact angle measurement was carried out using a KRUSS drop shape analyzer. It gives Zn, Fe and O in 2p³, 2p and 1s states, respectively (Figure 3).

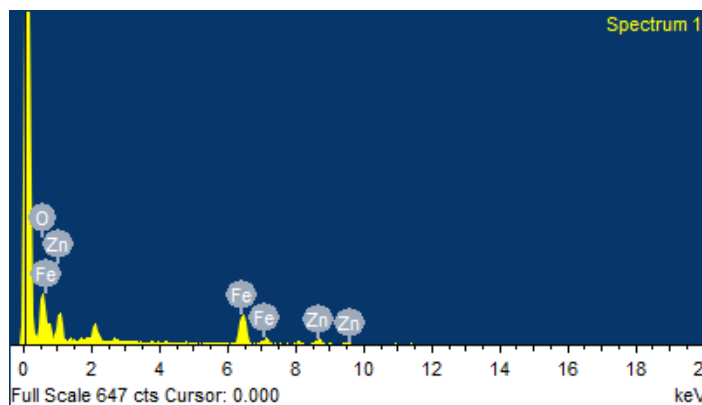
Figure 3. X-ray photoelectron spectroscopy analysis of zinc ferrite.



Energy-dispersive X-ray spectroscopy

Energy-dispersive X-ray spectroscopy with JSM 7600 F (Jeol) showed peaks for Fe, Zn and O, which indicates that zinc ferrite is in pure state and it does not contain any impurity (Figure 4).

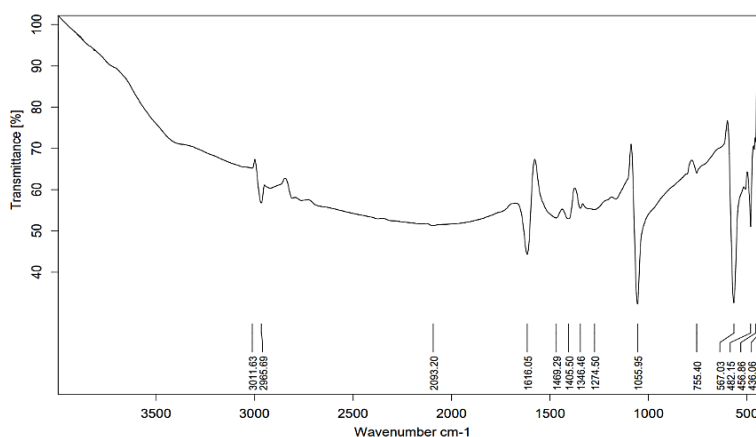
Figure 4. Energy-dispersive X-ray spectroscopy analysis of zinc ferrite.



Fourier transform infrared spectrum

Fourier transform infrared spectrometer RX-I was used to record IR spectrum (Figure 5) of the product.

Figure 5. Fourier transform infrared spectrum of product.

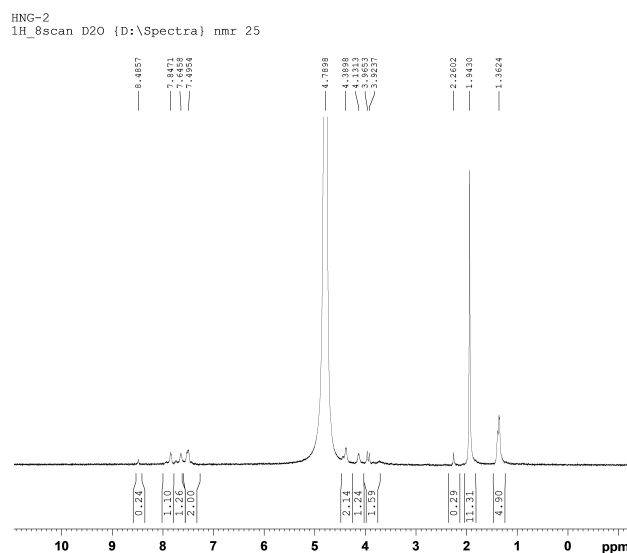


The IR spectrum of the product indicated the presence of three major bands. One is 3011 cm⁻¹, which may be attributed to C-H stretching vibrations. The second band is at 567 cm⁻¹ and it may be attributed to C-I stretching vibration. A band at 1056 is due to -CH bending vibration.

Nuclear magnetic resonance spectrum

FT-NMR spectrometer model Advance-II (Bruker) (400 MHz) was used to record NMR spectrum of the product. The spectrum is given in Figure 6.

Figure 6. Nuclear magnetic resonance spectrum of product.



There is only a single peak around 4.78 δ and it may be assigned to -CH methane. The product was confirmed as iodoform on the basis of FT-IR and FT-NMR data.

The product was confirmed as iodoform on the basis of FT-IR and FT-NMR data.

Comparitive study of haloform reaction

Different factors were varied to achieve optimal conditions such as amount of acetone, catalyst, potassium iodide, sodium hypochlorite solution, etc.

The effect of potassium iodide was observed in the range of 3.0 g-9.0 g. The results are shown in Table 1.

Table 1. Effect of potassium iodide on different factors.

Potassium iodide (g)	Sodium hypochlorite (ml)	Acetone (ml)	Zinc ferrites (g)	Yield (%)
3	70	4	0.1	11.2
4.5	70	4	0.1	22.9
6	70	4	0.1	38.6
7	70	4	0.1	30.6
8	70	4	0.1	24.4
9	70	4	0.1	18.9

It was found that when the amount of potassium iodide was increased, then the yield of product increases up to 6.0 g of potassium iodide and then it declined on further increasing its amount. It may due to the fact that the 6.0 g is the required amount of potassium iodide, above which it remains unreacted.

The effect of acetone was observed in the range of 2.0 ml-7.0 ml. The results are shown in Table 2.

Table 2. Effect of acetone on different factors.

Potassium iodide (g)	Sodium hypochlorite (ml)	Acetone (ml)	Zinc ferrites (g)	Yield (%)
6.0	70.0	2.0	0.10	20.4
6.0	70.0	3.0	0.10	24.2
6.0	70.0	4.0	0.10	38.6
6.0	70.0	5.0	0.10	29.0
6.0	70.0	6.0	0.10	21.5
6.0	70.0	7.0	0.10	16.3

It was found that when the amount of acetone was increased, the yield of product increases up to 4.0 ml of acetone and then it declined on further increasing its amount. It may be due to the fact that 4.0 ml is the required amount of acetone, in this reaction above which it remains unreacted.

The effect of sodium hypochlorite was observed in the range of 50 ml-70 ml. The results are shown in Table 3.

Table 3. Effect of sodium hypochlorite on different factors.

Potassium iodide (g)	Sodium hypochlorite (ml)	Acetone (ml)	Zinc ferrites (g)	Yield (%)
6.0	50.0	4.0	0.10	16.9
6.0	55.0	4.0	0.10	27.2
6.0	60.0	4.0	0.10	30.4
6.0	65.0	4.0	0.10	29.7
6.0	70.0	4.0	0.10	38.6
6.0	75.0	4.0	0.10	30.2

It was found that when the amount of sodium hypochlorite was increased, then the yield of product increases up to 70 ml of sodium hypochlorite, but yield decreases on increasing the amount further. It may be due to the fact that 70 ml is the required amount of sodium hypochlorite for maintaining desired pH.

The effect of zinc ferrite was observed in the range of 0.05 g-0.015 g. The results are shown in Table 4.

Table 4. Effect of zinc ferrites on different factors.

Potassium iodide (g)	Sodium hypochlorite (ml)	Acetone (ml)	Zinc ferrites (g)	Yield (%)
6.0	70.0	4.0	0.05	21.1
6.0	70.0	4.0	0.07	29.5
6.0	70.0	4.0	0.10	38.6
6.0	70.0	4.0	0.11	30.2
6.0	70.0	4.0	0.12	21.6
6.0	70.0	4.0	0.15	17.4

It was found that when the amount of zinc ferrite was increased, then the yield of product increases up to 0.10 g of ferrite, and then it declined on further increasing its amount. It may be attributed to the fact that all active sites are occupied (saturated state) and as a result, yield decreases.

CONCLUSION

The ZnFe₂O₄ nanoparticles were prepared with an average size of 6.62 nm *via* hydrothermal process in a teflon coated autoclave. These nanoparticles were used as catalyst in presence of sodium hypo chlorite solution for haloform reaction of acetone and potassium iodide under mild conditions. Some of the important advantages of this method are high yield, less time, and mild reaction conditions. This process is easy. The catalyst can be reused 6 times without any significant loss of catalytic activity. This catalysts environment friendly in nature.

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