# Structural Insights and Catalytic Activity of Iron-Modified Copper Chromite's in Benzyl Alcohol Oxidation

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***Abstract*—Iron-substituted copper chromite spinels ($CuFe_xCr_{2-x}O_4$, where x = 0, 0.5, 1.0, 1.5, and 2.0) were synthesized using a homogeneous co-precipitation method. The prepared materials were extensively characterized by X-ray diffraction (XRD), BET surface area analysis, scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) analysis, and FTIR spectroscopy. The powder XRD patterns confirm the formation of the spinel phase, while EDX results verify the expected stoichiometric composition. The catalytic performance of these materials was evaluated for the oxidation of benzyl alcohol to benzaldehyde using hydrogen peroxide as the oxidant, demonstrating high catalytic activity. Reusability tests further indicate that the iron substituted copper chromite spinels exhibit good stability under the reaction conditions.**

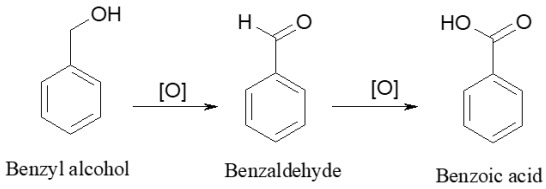
***Index Terms*—**Spinel oxides, benzyl alcohol oxidation

## I. INTRODUCTION

Selective oxidation of alcohols to aldehydes and ketones represents one of the most important transformations in organic synthesis and industrial chemistry because these compounds serve as key intermediates in pharmaceuticals, fragrances, agrochemicals, and fine chemicals [1–3]. Among these reactions, the oxidation of benzyl alcohol to benzaldehyde has received considerable attention due to the extensive industrial use of benzaldehyde as a precursor for dyes, perfumes, and flavoring agents [4,5]. Traditional oxidation methods often employ stoichiometric oxidants such as permanganate or dichromate, which generate large quantities of toxic waste and create environmental concerns [6,7]. Consequently, the development of environmentally benign heterogeneous catalysts capable of performing selective oxidation under mild conditions has become an important area of research [8,9]. Spinel-type mixed metal oxides ($AB_2O_4$) have attracted significant interest as oxidation catalysts owing to their excellent thermal stability, resistance to sintering, and tunable redox properties [10–12]. Copper chromite ($CuCr_2O_4$) is a well-known spinel catalyst widely used in hydrogenation, dehydrogenation, and oxidation reactions due to the synergistic interaction between copper and chromium oxide components [13,14]. The catalytic activity of copper chromite largely depends on the oxidation states of copper species, lattice defects, and oxygen mobility within the spinel framework, which together facilitate electron transfer during catalytic processes [15,16]. Recent advances in nanoscale synthesis methods have further improved the catalytic performance of copper chromite by increasing surface area and enhancing the availability of active sites [17].

Modification of spinel catalysts through partial substitution of transition metal ions has proven to be an effective strategy for tailoring structural, electronic, and catalytic properties [18]. Substitution can alter the distribution of cations in tetrahedral and octahedral sites, thereby influencing oxygen activation, redox behaviour, and surface acidity/basicity [19]. In particular, incorporation of iron into the copper chromite lattice is expected to enhance catalytic performance because $Fe^{3+}$ ions can participate in redox cycles and improve oxygen transfer during oxidation reactions, leading to higher activity and selectivity. However, the relationship between iron substitution, structural characteristics, and catalytic efficiency in benzyl alcohol oxidation requires systematic investigation. In this context, the present work focuses on the preparation of iron-substituted copper chromite

spinel catalysts, followed by detailed physicochemical characterization using appropriate analytical techniques to understand the structural modifications induced by iron incorporation. The catalytic activity of the synthesized materials is evaluated toward the selective oxidation of benzyl alcohol under optimized reaction conditions. The study aims to establish correlations between composition, structural properties, and catalytic performance, thereby providing insights for the rational design of efficient spinel-based oxidation catalysts.




Scheme 1: Reaction scheme of benzyl alcohol oxidation

## II. EXPERIMENTAL

### 2.1. Preparation of catalysts

The catalysts were prepared by co-precipitation method [20-22]. A mixture consisting of 10% solutions of copper nitrate, iron nitrate and chromium nitrate for $CuFe_xCr_{2-x}O_4$ (x = x = 0.5, 1.0, 1.5, 2.0) were dissolved in distilled water and the precipitation of the hydroxides was carried out at a controlled pH of 6.5-8 using 15% ammonia solution at a temperature of 70-80$^0$C. The precipitate was maintained at this temperature for two hours and aged for one day. The precipitate was filtered and washed with distilled water to remove nitrate ions. The compounds were dried in an air oven at 80$^0$C for 24 hours and then calcined at 650$^0$C for 8 hours. The formation of single spinel phase was ascertained by XRD. The prepared samples were designated as follows:

Catalyst composition Designation

| | | |
|---|---|---|
| 1. | $CuCr_2O_4$ | CCr |
| 2. | $CuFe_{0.5}Cr_{1.5}O_4$ | CFCr-1 |
| 3. | $CuFeCrO_4$ | CFCr-2 |
| 4. | $CuFe_{1.5}Cr_{0.5}O_4$ | CFCr-3 |
| 5. | $CuFe_2O_4$ | CF |

### 2.2. Catalyst characterizations

Powder X-ray diffraction patterns of the catalysts were recorded on a Rigaku D-max C X-ray diffractometer using Ni filtered Cu Ka radiation source (λ = 1.5406 Å) in the region 10- 70$^0$. Elemental analysis of the catalysts was carried out by EDX analysis on a Stereoscan 440 Cambridge, UK, energy dispersive X-ray analyzer used in conjunction with SEM. Surface area of the catalysts was calculated by measuring the adsorption of nitrogen at liquid nitrogen temperature in a conventional BET system. Two to four milligrams of each substance was pressed with 200 mg of KBr. The spectra were recorded in an AVATAR 370 Thermo-Nicolet FT-IR spectrometer in the region 400–4000 cm$^{-1}$.

## III. RESULTS AND DISCUSSIONS

### 3.1. Surface characterizations

The catalyst materials were characterized for evaluating the morphology and structure. The prepared samples were first subjected to powder X-ray diffraction. X-ray diffraction studies indicate that the peaks are sharper and are crystalline in nature. The theoretical and experimental dhkl values for simple spinels are well coordinated. It was also observed that the mixed chromites gave much identical XRD patterns with those of the simple chromites. Fig. 1 shows the powder XRD patterns of all the materials. The crystallite sizes are calculated from Debye Scherrer formula applied to the major intense peak and are found to be in the range 31-39 nm.

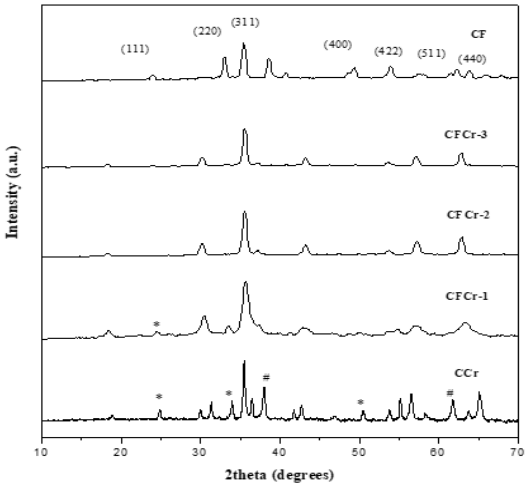



Fig. 1. XRD profiles of $CuFe_xCr_{2-x}O_4$ series spinels.

The FTIR spectra of the samples are given in Fig. 2. The two strong absorption bands observed in the spectra of the samples are at 630 and 525 cm$^{-1}$. The bands at higher and lower wavelength regions are assigned to the vibrations of tetrahedral metal oxygen bond (Cu–O and octahedral metal–oxygen bond (Cr–

O) respectively. The bands at 1640 and 3420 $cm^{-1}$ indicate the presence of surface hydroxyl and coordinated water.

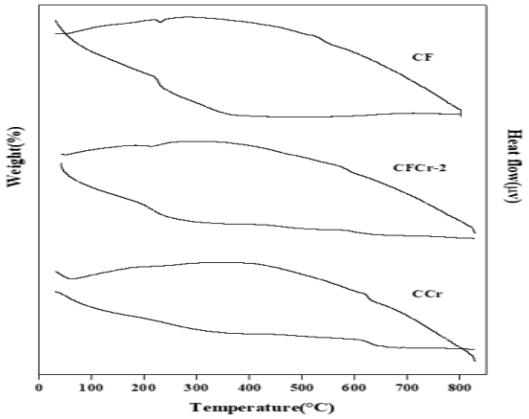



Fig. 2. FTIR spectra of $CuFe_xCr_{2-x}O_4$ series spinels.

The results of elemental composition by EDX analysis and surface area of this series of catalysts are presented in Table 1. The experimental and theoretical values of Cu, Fe and Cr agreed well and indicated correct stoichiometry of the spinel. On iron substitution, surface area increased. A maximum BET surface area of 20.8 $m^2/g$ was shown by CFCr-2catalyst

Table 1: Elemental composition, surface area and crystallite size of the catalysts

| Catalyst | Atom Percentage | | | BET Surface Area($m^2/g$) | Pore Volume (cc/g) | Crystalline Size (nm) |
|---|---|---|---|---|---|---|
| | Cu | Cr | Fe | | | |
| CCr | 34.4 | 65.6 | - | 6.0 | 0.02 | 39 |
| CFCr-1 | 33.4 | 52.0 | 14.6 | 17.8 | 0.05 | 32 |
| CFCr-2 | 30.9 | 35.3 | 33.9 | 20.8 | 0.05 | 31 |
| CFCr-3 | 32.3 | 19.3 | 48.4 | 12.6 | 0.03 | 38 |
| CF | 49.8 | - | 53.1 | 6.6 | 0.01 | 38 |

Scanning electron micrographs were recorded to get the surface morphology of the catalysts. SEM pictures of some of the samples are given in Fig. 3. It is clear that samples are aggregates without shape definition.

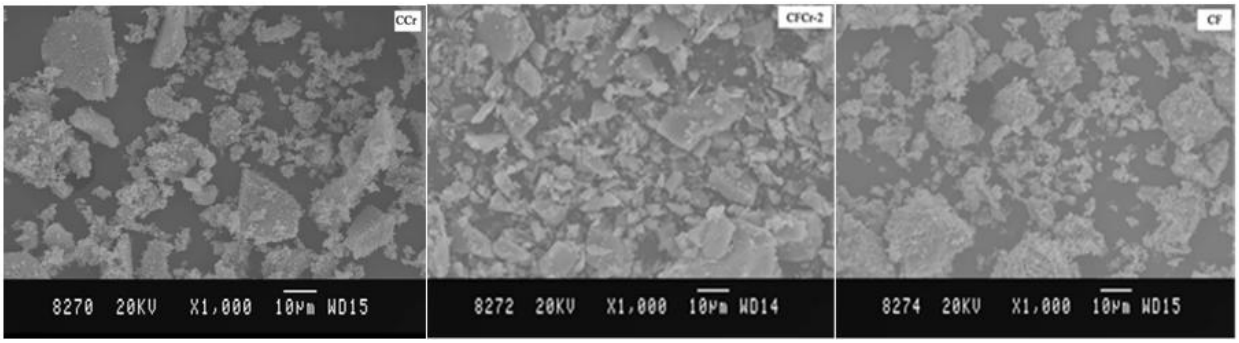



Fig 3. SEM Pictures of $CuFe_xCr_{2-x}O_4$ series spinels.

3.2 Catalytic Activity Studies

The oxidation of benzyl alcohol reaction was carried out over all the prepared catalysts under the selected reaction conditions (table 2) with the aim to produce benzaldehyde more selectively.

Table 2: Optimized reaction conditions for benzyl alcohol oxidation

| Reaction Parameters | | Selected condition |
|---|---|---|
| Temperature | : | 60°C |
| Time | : | 6 h |
| Benzyl alcohol: $H_2O_2$ ratio | : | 1:2 |
| Catalyst weight | : | 0.1 g |
| Solvent | : | Acetonitrile 10 ml |

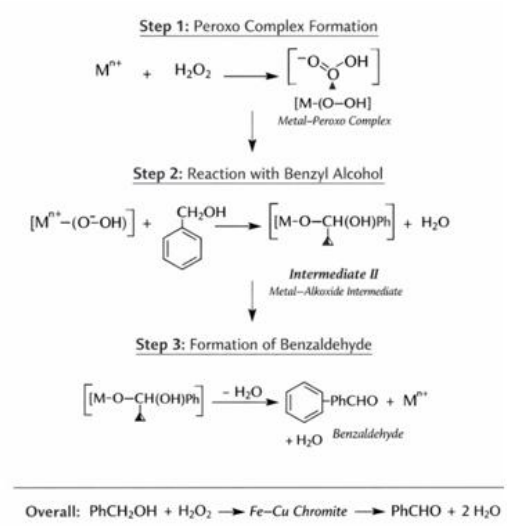
The activity for benzyl alcohol oxidation over the five series of chromite spinel catalysts is presented in table 3.

Table 3: Catalytic activity of spinels in Benzyl Alcohol oxidation

| Catalyst | Benzyl alcohol conversion (wt %) | Selectivity (%) | |
|---|---|---|---|
| | | Benzaldehyde | Benzoic acid |
| CCr | 20.3 | 84.2 | 15.8 |
| CFCr-1 | 24.0 | 78.7 | 21.3 |
| CFCr-2 | 24.3 | 90.7 | 9.3 |
| CFCr-3 | 30.2 | 73.6 | 26.4 |
| CF | 21.2 | 73.9 | 26.1 |

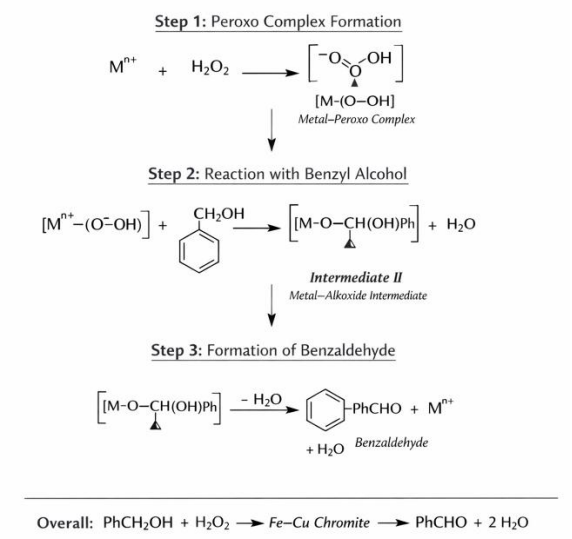
Iron substitution led to an enhancement in the catalytic activity of copper chromite. On iron substitution, benzyl alcohol conversion increased whereas copper ferrite showed less activity than the solid solutions. In spinel catalysts, octahedral metal ions are exposed to the surface and are more active in catalytic reactions. In solid solutions containing both chromium and iron in octahedral position are exposed to surface and they showed higher activity. Among these systems, CFCr-3 showed maximum benzyl alcohol conversion and moderate selectivity to benzaldehyde.

The proposed mechanism for the oxidation of benzyl alcohol with $H_2O_2$ is described below. At first, a peroxo complex is formed by the reaction between $H_2O_2$ and the catalyst. In the second stage, the peroxo complex and benzyl alcohol react to give an intermediate. This intermediate, on loss of water molecule, gives benzaldehyde and the regenerated catalyst.




## IV. CONCLUSIONS

This study reports the synthesis of iron-substituted copper chromite ($CuCr_{2-x}Fe_xO_4$) spinel catalysts using homogeneous co-precipitation method and investigates their structural characteristics and catalytic efficiency for the selective oxidation of benzyl alcohol to benzaldehyde. Comprehensive characterization techniques confirmed the successful incorporation of iron into the copper chromite lattice, resulting in nanocrystalline spinel structures with improved surface area and enhanced redox properties. The introduction of iron significantly increased catalytic activity and selectivity due to improved oxygen mobility and synergistic redox interactions between copper and iron species. The optimized catalyst composition exhibited superior benzyl alcohol conversion, high benzaldehyde selectivity, and good stability over repeated reaction cycles, demonstrating that controlled iron substitution is an effective strategy for designing efficient and environmentally benign heterogeneous oxidation catalysts.

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