Tuning the Magnetic and Catalytic Properties of Manganese Ferrite through Zn$^{2+}$ Doping: Gas Phase Oxidation of Octanol

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Abstract: Spinel ferrites, ZnFeO$_4$, MnFeO$_4$, and ZnMnFeO$_4$, were synthesized using the sol–gel method and thoroughly investigated for their potential as catalytic and magnetic materials. Experiments unveiled that ZnMnFeO$_4$ exhibited excellent catalytic and magnetic properties, whereas the Density Functional Theory (DFT) calculations provided insight into the excellent performance of ZnMnFeO$_4$ compared with ZnFeO$_4$ and MnFeO$_4$. The catalytic efficiencies of the synthesized spinel ferrites were evaluated against a model reaction, i.e., the gas-phase oxidation of octanol to a corresponding aldehyde, utilizing molecular oxygen as an oxidant. The results indicated that the order of catalytic activity was ZnMnFeO$_4$ > MnFeO$_4$ > ZnFeO$_4$. The reaction was found to follow Langmuir Hinselwood’s mechanism for dissociative adsorption of molecular oxygen. Owing to their superb catalytic and magnetic properties, mixed ferrites can be extended to a variety of organic transformation reactions.

Keywords: spinel ferrites; catalytic; magnetic; oxidation; octanol

1. Introduction

Spinel ferrite nanoparticles (SFNPs) have magnificent dielectric, magnetic, catalytic, and optical properties [1–3]. Owing to these important properties, ferrites are applicable in various fields like catalysis, organic synthesis, drug delivery, magnetic fluids, information and electronic materials, and wastewater treatment [4–7]. These SFNPs possess the general formula “MFe$_2$O$_4$” and contain M as a divalent metal cation, i.e., Mn(II), Ni(II), Cu(II), Co(II), or Zn(II). SFNPs can generally provide more fascinating catalytic activities compared with single-component metal oxides. Metal cations coupled to oxygen atoms at tetrahedral and octahedral sites, respectively, are considered most appropriate for oxidation reactions due to their structural arrangement [8]. The distribution of cations on octahedral and tetrahedral positions is dependent on ligand attachment and is explained with the help of ligand field theory (LFT) and ligand field stabilization energy (LFSE). SFNPs have incredible potential to be used as a heterogeneous catalyst for different chemical transformation reactions. The advantages of an extended life span (recycling and recovery) make the heterogeneous catalysis method superior to the homogeneous one in industrial applications [9]. SFNPs can be used for novel synthetic processes due to their unique magnetic properties under the protocol of green chemistry. The exhibition of dielectric and magnetic properties makes the application of SFNPs more diversified, including chemical and electronic applications and communication devices, such as computer memory chips, antennas, converters, inductors, and frequency filter coils in mobile boosters and radio centers [10–12]. SFNPs are frequently used in the biomedical field, magnetic...
The catalytic oxidation of alcohol to the corresponding carbonyl compound is one of the important transformation reactions in organic synthesis. SFNPs have been used for the oxidation of alcohol to carboxyl compounds with H₂O₂ as an oxidant while using CuFeO₄/CoFeO₄ as a catalyst, respectively [20,21]. Similarly, the literature reports the enhancing effect of nickel hydroxide (Bronsted base) for the catalytic properties of CoFeO₄ up to 87% in an alcohol oxidation reaction [22], while elsewhere the effect of solvent was reported in the oxidation of benzyl alcohol to benzaldehyde with NiFeO₄ in the presence of acetonitrile at 80 °C with molecular oxygen resulting in a 100% selectivity and a 77% overall activity [23]. These results compelled us to investigate the potential applications of mixed ferrites for gas-phase oxidation of alcohol under mild reaction conditions in a self-designed reactor, Finger Projected Fixed-Bed Reactor (FPFBR).

Here, we investigated the catalytic and magnetic properties of MnFe₂O₄, ZnFe₂O₄, and Zn mixed with MnFe₂O₄ through experiments and theoretical calculation (DFT). To the best of our knowledge, these ferrites have not been investigated for gas-phase oxidation of octanol to the corresponding aldehyde.

2. Results and Discussion

2.1. Characterization

SEM micrograms (Figure 1a,b) revealed the smooth morphology of the nanoparticles. The magnified image shows that the particles are bunched together. The EDX spectrum (Figure 1c) obtained for Mn-ferrite demonstrates that Mn (24 wt%), Fe (46 wt%), and O (29 wt%) are the major elements and reflect the absence of contamination. The diffraction patterns of the Mn-ferrite as shown in Figure 1d are well indexed and have a pure cubic phase of spinel manganese ferrite (JCPDS card no. 38-0430) [24]. Furthermore, the particle size was calculated (68 nm) via XRD, which is in good agreement with the SEM results (Figure 1b). Similarly, 44.3 m²/g of surface area was obtained via Brunauer–Emmett–Teller (BET) adsorption/desorption using the N₂ method.

Figure 2a,b show the SEM images of the ZnFe₂O₄ nanoparticles in which the agglomeration of the nanoparticles was revealed, while EDX analysis (Figure 2c) confirmed the presence of Zn, Fe, and O. Figure 2d represents the XRD patterns of ZnFe₂O₄ with characteristic planes (220), (311), (222), (400), (422), (511), and (440) for the cubic phase spinel structure (JCPDS No. 77-0011)[25]. The particle size (43 nm) from the most intense peak of XRD (Scherrer equation) is in good agreement with the SEM results (Figure 2b). Furthermore, the BET surface area of the sample was found to be 56 m²/g [26], which is perhaps due to the small size of the particles.
Figure 1. (a,b) SEM images at different magnifications (1700 and 5500); (c) EDX spectra and elemental composition; (d) XRD pattern of MnFe₂O₄.

Figure 2. (a,b) SEM images at different magnifications (2700 and 5500); (c) EDX spectra and elemental composition; (d) XRD pattern of ZnFe₂O₄.
Similarly, SEM images presented in Figure 3a,b show that ZnMnFe₂O₄ nanoparticles are chimed together; therefore, the particle size cannot be measured from the SEM microgram using the average grain intercept (AGI) method. The EDX spectra (Figure 3c) confirmed the presence of a stoichiometric amount of Zn, Mn, Fe and O, while it confirmed the absence of impurities. The XRD pattern (Figure 3d) shows that the ferrites retained the fundamental cubic phase spinel structure with characteristic planes (111), (220), (311), (400), (422), (511) and (440) [27]. The average particle size (29 nm) was calculated using Equation (6) utilizing the most intense peak, and it was found to be in agreement with the reported literature of the JCPDS card no 10-0319, showing a face-centered cubic crystal structure [28]. Similarly, the BET surface area (31.5 m²/g) was found to decrease with the incorporation of Zn into the matrix of MnFe₂O₄.

![Figure 3. (a,b) SEM images at different magnifications (2700 and 5500); (c) EDX spectra and elemental composition; (d) XRD pattern of ZnMnFe₂O₄.](image)

### 2.2. Magnetic Behavior

Zero-field cooled (ZFC) measurements were performed from 5 to 300 K in a 0.1 T magnetic field to collect data of the magnetic characteristics as shown in Figure 4a. The magnetization continuously displays a net irreversibility, which is compatible with the superparamagnetic condition for MnFe₂O₄, ZnFe₂O₄ and ZnMnFe₂O₄. When the temperature was gradually increased, the magnetization showed the maxima known as the blocking temperature (Tₜₛ) of the sample. Temperature Tₛ is defined as the point at which thermal activation breaks through the magnetic anisotropy energy barrier of a magnetic single domain, causing the magnetization direction to fluctuate. Tₛ for all the samples is about 35 K.
The magnetization increases with the doping of a Zn ion into the matrix of MnFe₂O₄ as reflected by Figure 4a–e, which is, of course, one of the prime objectives of the study. Magnetization decreases as temperature exceeds the blocking temperature for all the samples, which is in agreement with the super paramagnetic behavior. The Curie–Weiss law states that the magnetization drop observed above TB is caused by the super paramagnetic behavior of nanoparticles. Initially, the increase in magnetization at a temperature below TB can be explained by frozen magnetic moments along the easy axis of nanoparticles because of the considerable anisotropy energy available at low temperatures. The nanoparticles accumulate thermal energy as the temperature rises, resisting the anisotropic energy barrier, making it much simpler to align with the field. The relationship between the temperature (TB) at which magnetization is best and the volume of the crystalline particles (V) is KV/25 kB, where K is the magneto crystalline anisotropy constant.

2.3. DFT Calculation

The structural properties of the ZnFe₂O₄, ZnMnFe₂O₄ and MnFe₂O₄ spinals are calculated through GGA+U, and their crystal structure is shown in Figure 5. The unit cell of each compound is optimized using the fitted Birch–Murnaghan equation of state [29] as shown in Figure 6 in order to find out the ground state structure parameters of these compounds. From Figure 7, the calculated ground state energies (E₀), lattice constants (a₀), volume (V) and bulk modulus (B₀) compound along with experimental work are listed in Table 1. The calculated lattice constants of these compounds are 8.438, 8.441 and 8.447 Å, respectively.
It can be seen from Table 1 that calculated lattice constants are consistent with the experiments and are reliable. The calculated $E_0$ for ZnFe$_2$O$_4$, ZnMnFe$_2$O$_4$ and MnFe$_2$O$_4$ is $-2.17 \times 10^5$, $-2.35 \times 10^5$ and $-2.52 \times 10^5$ eV, respectively. The volume (V) of these spinels is 599.07, 601.425 and 602.751 Å$^3$, respectively, and bulk modulus $B_0$ (GPa) is 148.167, 174.039 and 216.738, which show that MnFe$_2$O$_4$ is harder than the other compounds.
Table 1. Calculated lattice constants (a), ground state energy (E₀), ground state volume (V₀), and bulk moduli (B) of the ZnFe₂O₄, ZnMnFe₂O₄ and MnFe₂O₄ ferrites.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Present</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnFe₂O₄</td>
<td>a (Å) 8.438</td>
<td>*8.441[30,31]</td>
</tr>
<tr>
<td></td>
<td>E₀ (eV) −2.17 × 10⁵</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V (Å³) 599.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B₀ (Gpa) 148.167</td>
<td></td>
</tr>
<tr>
<td>ZnMnFe₂O₄</td>
<td>a (Å) 8.4410</td>
<td>*8.368 [32]</td>
</tr>
<tr>
<td></td>
<td>E₀ (eV) −2.35 × 10⁵</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V (Å³) 601.425</td>
<td></td>
</tr>
<tr>
<td></td>
<td>B₀ (Gpa) 174.039</td>
<td></td>
</tr>
<tr>
<td>MnFe₂O₄</td>
<td>a (Å) 8.4472</td>
<td>*8.4512 [33]</td>
</tr>
<tr>
<td></td>
<td>E₀ (eV) −2.52 × 10⁵</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V (Å³) 602.751</td>
<td>*603.608 [33]</td>
</tr>
<tr>
<td></td>
<td>B₀ (Gpa) 216.738</td>
<td>**146 [34]</td>
</tr>
</tbody>
</table>

* experimental, ** theoretical.

To find the stable magnetic structure of these spinal ferrites, the (1 × 1 × 2) super cell of each compound is optimized using the fitted Birch–Murnaghan equation of state [33] in paramagnetic (PM)/non-magnetic (NM), ferromagnetic (FM) and in Anti-ferromagnetic (AFM) phases as shown in Figure 7. From Figure 7, the calculated ground state energies for the NM phase of ZnFe₂O₄, ZnMnFe₂O₄ and MnFe₂O₄ are −4.35 × 10⁵, −4.7 × 10⁵ and −5 × 10⁵ eV; for FM phases, they are −4.35 × 10⁵, −4.7 × 10⁵ and −5 × 10⁵ eV; and for the AFM phase, they are −4.35 × 10⁵, −4.7 × 10⁵ and −5 × 10⁵ eV, respectively. The comparison of the calculated energies in different phases reveals the AFM nature of all these compounds in which the energy is lower compared to that of other phases. The calculated AFM phase of these compounds is consistent with experimental results. This shows that present results are logical and rational.

As the understudy compounds are anti-ferromagnetic, the electronic properties of these compounds were performed in the anti-ferromagnetic phase using the GGA+U potential. The total density of states (TDOS) and the band structure for the understudy compounds are computed in Figure 8. The TDOS for these compounds reveal the presence of the energy gap flanked by the valence band (VB), and conduction bands (CBs) are non-overlapping with densities around the Fermi Level, which reveal the semiconductor nature of MnFe₂O₄, ZnFe₂O₄ and ZnMnFe₂O₄. From TDOS, the estimated band gap values are 1.6, 1.9 and 1.1 eV, respectively, consistent with the reported results [29,35]. Additionally, the band structures for MnFe₂O₄, ZnFe₂O₄ and ZnMnFe₂O₄ are also calculated and displayed in Figure 9 to further validate their semiconducting nature. Figure 9 shows that there is non-overlapping at the Fermi level, and the maxima of VB align with the minima of CB at the central symmetry for compounds, which indicates their direct band gap character. The enhanced catalytic activity of ZnMnFe₂O₄ can be explained on the basis of reduction in band gap energy, which further endorses the experimental observation (order of catalytic activity: ZnMnFe₂O₄ > MnFe₂O₄ > ZnFe₂O₄).
2.4. Catalytic Properties of MnFe$_2$O$_4$, ZnFe$_2$O$_4$ and ZnMnFe$_2$O$_4$

All the ferrite NPs were screened for catalytic activity in a model reaction (gas-phase oxidation of octanol to octanal) at a pre-optimized set of reaction conditions for example catalysts: 2 g/chamber, vapor pressure of reactant, 80 Torr; temperature, 140 °C; and flow, 40 mL/min. The data were collected after 30 min, when the steady state established. Figure 10 shows that the rate of reaction increases with increase in reaction duration, following the same trend for MnFe$_2$O$_4$, ZnFe$_2$O$_4$ and ZnMnFe$_2$O$_4$. However, the order of activity was found, ZnMnFe$_2$O$_4$ > MnFe$_2$O$_4$ > ZnFe$_2$O$_4$, which points to the synergistic effect of Zn doping in the matrix of MnFe$_2$O$_4$. Similar results for Zn$^{2+}$ doping over MnFe$_2$O$_4$ were reported by Manohar et al. [36] for magnetic hypothermia treatment. The increase in Zn$^{2+}$ content was found to increase the magnetic properties linearly. The doping also has an effect on
the size of the crystallite, as increase in the content of dopant causes the crystallite size to decrease, and agglomeration of NPs occurs. Perhaps this synergism arises from the Rearrangement of Fe\(^{3+}\) ions on the octahedral sites due to the occupancy of tetrahedral sites by Zn\(^{2+}\) ions, which generates electron hopping between Fe\(^{3+}\) and Fe\(^{2+}\) ions on octahedral sites. Similarly, Figure 11 elucidates the demission of diffusion and kinetic control regime. The variation in the rate of reaction with vapor pressure of reactant revealed that at a lower vapor pressure (20–40 Torr), the reaction is diffusion control, while at a high vapor pressure (80 Torr), the rate shows a linear trend with an increase in flow feed gases pointing to the reaction being kinetic control. Similarly, the flow effect and activation energy (56 kJ/mole) calculated from the Arrhenius equation, also confirming the kinetic control regime (inset of Figure 11).

**Figure 10.** Effect of time on the rate of reaction and number of moles trapped. Conditions: Catalysts, 2 g/chamber; Vapor pressure of reactant, 80 Torr; Temperature, 140 °C; Flow, 40 mL/min; Data collection, after 30 min. \(r = \text{rate of reaction (mol g}^{-1} \text{min}^{-1})\), \(n = \text{no. of moles trapped (product: mol)}\).

**Figure 11.** Effect of flow on the rate of reaction, while the inset represents the Arrhenius plot for activation energy. Conditions: Catalysts, 2 g/chamber; Vapor pressure of reactant, 80 Torr; Temperature, 140 °C; Flow, 40 mL/min; Data collection, after 30 min. \(E_a\); activation energy, \(K\); kelvin, \(r = \text{rate of reaction (mol g}^{-1} \text{min}^{-1})\).
2.4.1. Kinetics Analysis

The experimental data obtained from the gas phase oxidation of octanol over spinel ferrites were exposed to the Langmuir–Hinshelwood (L-H) model for kinetic analysis [37].

The L-H model considered for the adsorbed reactants (C₈H₁₈O: A and O₂: B) over active sites of the catalyst can be formulated as

\[ r = \frac{kK_1K_2[C_8H_{18}O][O_2]^n}{[1+K_1C_8H_{18}O]+K_2[O_2]^n} \quad \text{L-H model,} \]  

(1)

where \( k \) = rate coefficient, \( K_1 \) = equilibrium adsorption constant of Reactant A, and \( K_2 \) = equilibrium adsorption constants of Reactant B. Figure 14a shows that the reaction rate for octanol dehydrogenation in the presence of oxygen is higher than that of direct dehydrogenation, which confirms the involvement of oxygen. However, to understand the nature of oxygen adsorption on the surface of the catalyst, Equation (1) was modified to the following equation by considering low partial pressure of \( O_2 \) where \( k_2[O_2] \) in the denominator that can be neglected:

\[ r = \frac{kK_1K_2[C_8H_{18}O][O_2]^n}{[1+K_1C_8H_{18}O]^2} \quad \text{L-H model,} \]  

(2)

where at constant vapor pressure of Reactant A, Equation (2) was modified to Equation (3),

\[ r = a[O_2], \quad \text{Non-dissociative,} \]  

(3)

while \( a \) is a constant used instead of all constant values.

Equation (1) can also be modified to Equation (4) for a dissociative adsorption of \( O_2 \) on the surface of the catalyst.

\[ r = \frac{a\sqrt{[O_2]}}{[b+c\sqrt{[O_2]^2}]}, \quad \text{Dissociative,} \]  

(4)

where the linear form of Equation (4) can be written as

\[ \frac{\sqrt{[O_2]}}{\text{rate}} = \frac{b}{\sqrt{a}} + \frac{c}{\sqrt{a}}\sqrt{[O_2]}, \quad \text{Linear form of dissociative.} \]  

(5)

The experimental data were fitted into Equations (3) and (5), and a better regression value was observed for Equation (5) (0.9906) than for the Equation (3) (0.9490), which revealed that the reaction follows the L-H form with a dissociative adsorption of oxygen rather than adsorption of molecular oxygen as shown in Figure 12, but direct activation of the gas phase \( O_2 \) on the surface of the catalyst has a much high barrier (cal: 2.64 eV), which restricted the direct cleavage of the \( O_2 \) bond under ambient conditions.
Figure 12. Langmuir–Hinshelwood mechanism for dissociative and non-dissociative adsorption of O₂ on the surface of catalysts. Conditions: Catalysts, 2 g/chamber; Vapor pressure of reactant, 80 Torr; Temperature, 140 °C; Flow, 40 mL/min; Data collection, after 30 min.

Keeping in view the previous reports regarding the activation of O₂ [38–40], we assumed that the co-adsorbed alcohol [C₈H₁₇OH---O₂] on the surface of catalyst acts as an activator for the dissociation of O₂ where oxygen abstracts hydrogen from alcohol and produces an important intermediate hydroperoxyl species; [(C₈H₁₇OH---O₂)* → C₈H₁₇O* + OOH*] has a barrier of 0.88 eV (TS1, Figure 13), which is lower than the direct dissociation of O—O bond, although including the possibility of H₂O formation as a by-product during the progress of reaction further decrease the barrier up to 0.56 eV (TS2, Figure 13), which shows that H₂O is acting as promoter for O₂ dissociation. The subsequent oxidation of C₈H₁₇OH can be achieved by OOH*, O* and OH* as shown in Scheme 1.
Scheme 1. Different pathways for the oxidation of octanol. * represent the activated species.

\[
\begin{align*}
\text{C}_8\text{H}_{17}\text{OH}^* + \text{OOH}^* & \rightarrow \text{C}_8\text{H}_{17}\text{O}^* + \text{H}_2\text{O}_2^* & \text{i} \\
\text{C}_8\text{H}_{17}\text{O}^* + \text{OOH}^* & \rightarrow \text{C}_8\text{H}_{16}\text{O} + \text{H}_2\text{O}_2 & \text{ii} \\
\text{C}_8\text{H}_{17}\text{OH}^* + \text{O}^* & \rightarrow \text{C}_8\text{H}_{17}\text{O}^* + \text{OH}^* & \text{iii} \\
\text{C}_8\text{H}_{17}\text{O}^* + \text{O}^* & \rightarrow \text{C}_8\text{H}_{16}\text{O} + \text{OH}^* & \text{iv} \\
\text{C}_8\text{H}_{17}\text{OH}^* + \text{OH}^* & \rightarrow \text{C}_8\text{H}_{17}\text{O}^* + \text{H}_2\text{O}^* & \text{v} \\
\text{C}_8\text{H}_{17}\text{O}^* + \text{OH}^* & \rightarrow \text{C}_8\text{H}_{16}\text{O} + \text{H}_2\text{O}^* & \text{vi}
\end{align*}
\]

Figure 13. Energy profile for the activation of oxygen on the surface of the catalyst by co-adsorbed alcohol with (blue) or without (red) the promoting effect of by-product H$_2$O during the progress of reaction.

2.4.2. Comparative Study

The catalytic efficiency of MnFe$_2$O$_4$, ZnFe$_2$O$_4$, and ZnMnFe$_2$O$_4$ in terms of oxidation for different substrates were tabulated and compared with recent results as shown in Table 2. The MnFe$_2$O$_4$ for the oxidation of benzyl alcohol (Table 2, entry 1) in acetonitrile showed a 100% selectivity with good activity in the presence of an oxidant (H$_2$O$_2$) at a mild temperature and a 10 h reaction time. Similarly, the oxidation of 5-hydroxy methyl furfural (HMF) (Table 2, entry 2) has been reported with an 85% selectivity of the reaction, which shows that MnFe$_2$O$_4$ is a potent catalyst for oxidation reactions. The benzyl alcohol oxidation to benzophenone and benzaldehyde are reported (Table 2, Entries 3 and 4) with a mild reaction condition and remarkable selectivity and activity. Similarly, phenol has been successfully converted to organic carbon and water in the presence of potassium peroxy disulfate at room temperature for a period of 6 h (Table 2, Entry 5). The results can
be used for the potential use of MnFe₂O₄ for oxidation reactions with remarkable efficiency and selectivity in the liquid phase which is limited by an extended reaction duration.

However, ZnFe₂O₄ was effectively utilized for the gas phase oxidation of 1-butene to 1,3-butadiene at very high temperature >350 °C (Table 2, Entries 6 and 7). However, the prolonged reaction time and high temperature challenge the applicability of the catalyst in these particular reactions. Similarly, MnZnFe₂O₄ was also used for the formation of acetophenone, utilizing t-BuOOH as an oxidant with a 99% selectivity and a mild reaction condition (Table 2, Entry 8) with a 96.7% selectivity of the reaction; but still, the use of organic oxidants possess problems. The tabulated data (Table 2, Entry 1–9) show importance of the present work.

**Table 2.** Efficiency of MnFe₂O₄, ZnFe₂O₄, ZnMnFe₂O₄ as catalysts for a variety of organic substrates

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction Conditions</th>
<th>Substrate/Reaction</th>
<th>Product</th>
<th>°C</th>
<th>**S</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MnFe₂O₄ (1 g), acetonitrile, H₂O: (10 mmole), temp (80 °C), time (10 h)</td>
<td>BzOH/Oxidation</td>
<td>BzH</td>
<td>70</td>
<td>100</td>
<td>[41]</td>
</tr>
<tr>
<td>2</td>
<td>MnFe₂O₄ (0.015 g), acetonitrile (20 mL), HMF (1 mmole), TBHB (9 mmole), stirring (1000 rpm), temp (100 °C), time (5 h)</td>
<td>3-hydroxy methylfurural/Oxidation</td>
<td>2,5-furandicarboxylic acid (FDCA)</td>
<td>68</td>
<td>85</td>
<td>[42]</td>
</tr>
<tr>
<td>3</td>
<td>MnFe₂O₄ (10 mmole), TBHP 70%, solvent, DMSO, temp (90 °C), time (3 h)</td>
<td>Benzylic alcohol/Oxidation</td>
<td>Benzophenone</td>
<td>90</td>
<td>100</td>
<td>[43]</td>
</tr>
<tr>
<td>4</td>
<td>MnFe₂O₄ (1 g), H₂O: (10 mole), acetonitrile (10 mL), temp (80 °C), time (10 h)</td>
<td>Benzyl alcohol/Oxidation</td>
<td>Benzaldehyde</td>
<td>80</td>
<td>89.47</td>
<td>[44]</td>
</tr>
<tr>
<td>5</td>
<td>MnFe₂O₄ (3 g/L), potassium peroxysulfate (5 mg/L), temp (6 h), room temperature pH (3–3.5)</td>
<td>Phenol/Oxidation</td>
<td>Organic carbon and H₂O</td>
<td>100</td>
<td>95</td>
<td>[45]</td>
</tr>
<tr>
<td>6</td>
<td>ZnFe₂O₄ (1 g), absolute ethanol (200 mL), temp (355–380 °C), time (4 h)</td>
<td>1-butene/Oxidation</td>
<td>1,3-butadiene</td>
<td>75</td>
<td>94</td>
<td>[46]</td>
</tr>
<tr>
<td>7</td>
<td>ZnFe₂O₄, temp (450 °C), Time (6 h), pH (6–10), air (oxygen source)</td>
<td>α-butene/Oxidation</td>
<td>1,3-butadiene</td>
<td>45</td>
<td>80.2</td>
<td>[47]</td>
</tr>
<tr>
<td>8</td>
<td>MnZnFe₂O₄ (30 mg, 0.13 mmole), temp (80 °C), t-BuOOH (5.0 mmol)</td>
<td>1-phenylethanol/Oxidation</td>
<td>Acetophenone</td>
<td>80</td>
<td>99</td>
<td>[20]</td>
</tr>
</tbody>
</table>
| 9     | i. MnFe₂O₄  
ii. ZnFe₂O₄  
iii. ZnMnFe₂O₄  
Reaction conditions: catalysts, 2 g/chamber; pressure of reactant, 80 Torr; Temperature, 140 °C; Flow, 40 mL/min; Data collection; after 30 min. | Octanol/Oxidation | Octanol | i. 74 | ii. 100 | Recent work |

*C; conversion and **S; selectivity.

3. Experimental
3.1. Materials and Methods

All the chemicals were purchased from Sigma Aldrich (Louis, MO, USA) and used without any further treatment or purification, while gases (N₂, O₂, CO₂, and H₂) were delivered by Pakistan Oxygen Company (BOC) Ltd (Taxila, Pakistan) and passed through proper filters. Flow rate and pressure of gases and reactants were controlled through analogue gauges, T-valves and needle valves.
3.1.1. Preparation of Metal Doped Ferrite

The sol–gel method was employed to synthesize spinel ferrites and mixed-ferrite NPs. A stoichiometric amount of precursor salts was dissolved in deionized water/ethanol and sonicated for 30 min. To the preheated solution (50 °C), citric acid (5 mL) was added dropwise under vigorous stirring (1200 rpm). The pH of the mixture was maintained at 8–9 by adding aqueous ammonia. The mixture was aged for 6 h at 80 °C. The temperature of the mixture was increased to 220 °C with 1 °C/min to obtain the gel and further dried until flake formation. Finally, the particles were calcined for 6 h at 800 °C (0.5 °C/min).

3.1.2. Characterization

The synthesized samples were morphologically studied by Scanning Electron Microscopy (JSM 5910, JEOL, Tokyo, Japan), and Energy Dispersive X-rays (EDX, JSM 5910, JEOL, Tokyo, Japan) were used for the determination of elemental composition. XRD spectra were recorded by an X-Ray Diffractometer (Model: JDX; (3532) JEOL, Tokyo, Japan) with a radiation source (CuKα) and 2θ = 0–80°. The most intense peak was used for calculating particle size (Scherrer equation (Equation (6)),

\[ D = \frac{k\lambda}{\beta\cos\theta} \]  

where \( \lambda = 1.5406 \text{ Å} \), \( \beta \) is the full width at half maximum (FWHM) in the radian. The surface area and pore size were determined by BET surface area analyzer (Quantachrome Nova 2200e, Boynton Beach, FL, USA). Magnetic properties like remanence magnetization (Mr), saturation magnetization (Ms) and coercivity (Hc) were determined by a Vibrating Sample Magnetometer (VSM; Cryogenic Ltd, London, UK).

3.2. DFT Study

In this work, DFT calculations were executed with the method of full-potential Linearized Augmented plane wave (FP-LAPW) employed in the WIEN2k code [48]. The generalized gradient approximation along with Hubbard potential (GGA+U) was used to calculate the exchange correlation energy for determination of the electronic properties [49]. In the FP-LAPW method, the charge density expansion and wave function for potential is composed of the combination of radial function multiplied by spherical harmonics inside atomic radii and plan waves in the interstitial region. The cut-off value for planned wave RMT × \( K_{\text{max}} = 8 \text{ Ry} \) is selected, while the charge density is Fourier expanded up to \( G_{\text{max}} = 14 \) (Ryd). For the integration of the Brillouin Zone, we used a \( 7 \times 7 \times 7 \) k-point. The self-consistent convergence was achieved up to 0.5 mRy/Bohr. For GGA+U calculations, the values for divalent metals were taken from the literature [50].

3.3. Catalytic Test

The synthesized catalysts were loaded to a self-designed reactor (FPFBR; Glass Blowing Department, University of Engineering and Technology, Peshawar, Pakistan) as shown in Figure 14b. Ferrites were held inside the reactor by externally fitted magnetic beads. Continuous flows of reactants with desired vapor pressure (20–80 Torr) were simultaneously allowed into the reactor (FPFBR) through a saturator at a preheated temperature of 413 ± 5 K. A general formula (\( n = PV/RT \)) was used to calculate the number of moles of reactants, where \( V_i \) is the flow rate (mL) of volume. The mixture of gases was allowed passing through reaction cores (beds of catalyst in the reaction chamber) at the desired temperature, maintained through heating taps, of one to three chambered reactors, each chamber consisting of 18 catalyst beds as reported in previous study [51]. The six-port valve was used for the direct analysis of outflow through GC (Perkin Elmer, Clarius; 580, Shelton, USA). The effect of oxygen flow on/off was demonstrated for the oxidation of octanol as shown in Figure 14a.
4. Conclusions

Here, we tuned the catalytic and magnetic properties of spinal ferrite through incorporation of other divalent metal atoms. A combinatorial approach of experiments and theory was adapted to understand the phenomena behind the superb properties of mixed ferrites. Experiments showed that ZnMnFe$_2$O$_4$ has better catalytic and magnetic properties than MnFe$_2$O$_4$ and ZnFe$_2$O$_4$, which was endorsed by DFT calculation. DFT calculation showed that the Zn metal alters the electronic structure and gap state of MnFe$_2$O$_4$, decreasing the Fermi energy level and band gap up to 1.1 eV. On the basis of catalysis, a ranking was established for the model reaction (oxidation of octanol), ZnMnFe$_2$O$_4$ > MnFe$_2$O$_4$ > ZnFe$_2$O$_4$, with a dissociative adsorption L-H mechanism of O$_2$ at the surface of the catalyst. High magnetic properties of ZnMnFe$_2$O$_4$ showed its extended use for a variety of gas phase catalysis in a finger projected reactor (FPFBR). Furthermore, stable nature and magnetic and excellent catalytic properties revealed that ZnMnFe$_2$O$_4$ is a potent catalyst for industrial important organic transformation.
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References

1. Almessiere, M.A.; Güner, S.; Slimani, Y.; Baykal, A.; Shirsath, S.E.; Korkmaz, A.D.; Badar, R.; Manikandan, A. Investigation on the structural, optical, and magnetic features of Dy\textsuperscript{3+} and Y\textsuperscript{3+} co-doped Mn\textsubscript{0.5}Zn\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} spinel ferrite nanoparticles. *J. Mol. Struct.* 2022, 1248, 131412. https://doi.org/10.1016/J.MOLSTRUC.2021.131412.


9. Pham, T.N.; Huy, T.Q.; Le, A.T. Spinel ferrite (AlFe\textsubscript{2}O\textsubscript{4})-based heterostructured designs for lithium-ion battery, environmental monitoring, and biomedical applications. *RSC Adv.* 2020, 10, 31622–31661. https://doi.org/10.1039/D0RA05133K.


46. Zeng, T.; Sun, G.; Miao, C.; Yan, G.; Ye, Y.; Yang, W.; Sautet, P. Stabilizing Oxidative Dehydrogenation Active Sites at High Temperature with Steam: ZnFe₂O₄-Catalyzed Oxidative Dehydrogenation of 1-Butene to 1,3-Butadiene. ACS Catal. 2020, 10, 12888–12897.


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