Supporting Information Part I for

Heterogeneous ditopic ZnFe$_2$O$_4$ catalyzed synthesis of 4H-pyrans: further conversion to 1,4-DHPs and report of functional group interconversion from amide to ester

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The total content of the Supporting Information (I-VI) is summarized in the Table of Contents given in the beginning of the **Supporting Information I**.
Materials and Methods

All solvents were dried by standard methods. Chemicals were purchased from Aldrich, USA and Spectrochem, India and used without further purification. Column chromatography was performed on silica gel (60-120 mesh) and appropriate mixture of petroleum ether and ethyl acetate were used for elution. The solvents were removed using Eyela rotary evaporator. TLC was done on glass sheets pre-coated with silica gel (with binder, 300 mesh, Spectrochem). The $^1$H- and $^{13}$C-NMR analyses were carried out on Bruker-Advance Digital 300 MHz and 75.5 MHz instruments in DMSO-d$_6$ and CDCl$_3$ with TMS as an internal reference. The chemical shifts were reported as $\delta$ values (ppm) relative to TMS. IR spectra were recorded in KBr pellets in reflection mode on a Perkin Elmer RX-1 FTIR spectrophotometer. CHN analysis was performed using a Perkin-Elmer 2400 Series II CHN analyzer. X-ray diffraction patterns of the powder sample were obtained with a Seifert P3000 diffractometer using Cu K$\alpha$ ($\lambda = 0.15406$ nm) radiation. Nitrogen adsorption/desorption isotherms were obtained using a Quantachrome Autosorb 1C at 77 K. Prior to gas adsorption, all the samples were degassed for 2 h at 403 K. Transmission electron microscopic images were recorded on a JEOL 2010 TEM operated at 200 kV in Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India. A Hitachi S-5200 field-emission scanning electron microscope was used for the determination of the morphology of the particles. The XPS analysis was conducted on an Omicron Nanotech operated at 15 kV and 20 mA using a monochromatic AlK$\alpha$ as X-ray source in Indian Association for the Cultivation of Science, Jadavpur, Kolkata-32, India.

Synthesis of ZnFe$_2$O$_4$ nanopowder catalyst

The ZnFe$_2$O$_4$ powders were prepared by low temperature preparative techniques using zinc nitrate [Zn(NO$_3$)$_2$.6H$_2$O], ferric nitrate [Fe(NO$_3$)$_3$.9H$_2$O], and ammonia [NH$_3$] (purity of the starting materials greater than 99.9%). 0.1 M aqueous solution of zinc nitrate and 0.2 M aqueous solution of ferric nitrate were prepared separately. 100 mL of each solution was mixed together, while stirring this mixture, 25% ammonia was added until the pH was between 9 and 11 at 320 K. The precipitate was dried at 373 K and calcined from 200 °C to 800 °C in air which yielded zinc ferrite.
**Characterization of the catalyst**

XRD analysis. Crystalline phase characterization of zinc ferrite nanopowder calcinated at various temperatures (A) 30 °C (room temperature), (B) 250 °C, (C) 500 °C and (D) 800 °C for 6 h was carried out using XRD pattern to investigate the effect of the calcinations temperature on the phase relationships. A closer look into the figure revealed that the intensity ratio of individual reflections is in accordance with the stoichiometric composition of the mixture (ZnO, α-Fe₂O₃ and ZnFe₂O₄). It is evident from the figure S1A to D that in the course of calcination, the ZnO–α-Fe₂O₃ mixture gradually transformed into ZnFe₂O₄ spinel phase. In figure S1C and more prominently in figure S1D the formation of ZnFe₂O₄ phase has been clearly noticed as evidenced from the appearance of (2 2 0) (isolated, 2θ = 29.95°) (indicated with green colour) and strongest (3 1 1) (2θ = 35.3°) reflections (indicated with red colour) in the XRD patterns. The diffraction peaks at 2θ values of 18.0, 30.0, 35.3, 36.9, 42.8, 53.2 and 56.7 assigned to the reflection of (111), (220), (311), (222), (400), (422) and (511) planes have been indexed to Fd3m cubic spinel structure of ZnFe₂O₄. The XRD pattern of the sample obtained by calcining at 800 °C as depicted in figure S1D clearly designates the good-quality polycrystalline nature of the single spinel phase of ZnFe₂O₄. The mean crystallite size (coherent diffraction domain size) was estimated to be 24 nm from the half-maximum full width of the (311) peak by the modified Scherrer formula.

![X-ray diffraction profiles](image)

**Fig. S1** X-ray diffraction profiles of ZnFe₂O₄ nanopowders calcinated at different temperatures for 6 h (A) 30 °C (B) 250 °C (C) 500 °C and (D) 800 °C.
**HRTEM and EDX elemental analysis.** TEM images were taken to elucidate the morphology of the synthesized zinc ferrite obtained by calcining at 800 °C. The analysis of the obtained figure S2 clearly shows the uniform formation of ZnFe₂O₄ nanoparticles with only one type particle morphology, indicating the formation of one phase, i.e. spinel structure having dimension of ca. 25-30 nm which is also in accordance with the result calculated by the Scherrer formula. Lattice fringes shown by the particles suggested highly crystalline nature of the ZnFe₂O₄ nanoparticle. Electron diffraction pattern (Fig. S2c) suggested the presence of spinel structure of ZnFe₂O₄. The presence of Zn, Fe and O atoms was also observed in the EDX spectrum collected from TEM (Fig. S2d).

![HRTEM image](image1.png)  ![High resolution image](image2.png)  ![SAED pattern](image3.png)  ![EDS analysis](image4.png)

**Fig. S2** (a) HR TEM image of ZnFe₂O₄ nanoparticles obtained by calcining at 800 °C, (b) high resolution image of one particle, (c) SAED pattern, (d) EDS analysis of ZnFe₂O₄ nanoparticles attesting the presence of Zn, Fe and O.
**FT-IR analysis.** The presence of the spinel structure for ZnFe$_2$O$_4$ nanopowder obtained by calcining at 800 °C was further confirmed by FT-IR spectroscopy (Fig. S3). The normal spinel zinc ferrites are known to exhibit four ($\nu_1$, $\nu_2$, $\nu_3$, $\nu_4$) fundamentals IR active modes in the vibration spectra. The high frequency bands ($\nu_1$ and $\nu_2$) are very sensitive to changes in interaction between oxygen and cations in tetrahedral and octahedral positions and frequently appear in the ranges 540-600 cm$^{-1}$ and 400-450 cm$^{-1}$ respectively. The low frequency band $\nu_3$ normally appears close to 330 cm$^{-1}$ and $\nu_4$ varies from 164-168 cm$^{-1}$.$^1$ The bands $\nu_3$ and $\nu_4$ correspond to divalent as well as oxygen and thermal vibrations respectively.$^2$ In the present study, the absorption bands for the synthesized zinc ferrite are in the expected range. No band around 3400 cm$^{-1}$ and 1640 cm$^{-1}$ indicate the absence of any OH vibrations of water molecules resulting from crystalline spinel phase of ZnFe$_2$O$_4$. According to Waldron, the high frequency bands around 667 cm$^{-1}$ and 540 cm$^{-1}$, the low frequency band $\nu_2$ around 417 cm$^{-1}$ are attributed to that of tetrahedral and octahedral group, respectively. Moreover, the low frequency band $\nu_3$ also appeared in the expected range of 332 cm$^{-1}$. The peak at 1272 cm$^{-1}$ is due to overtones. However $\nu_4$ did not appear in our spectrum since it lies beyond the range of our instrument (the range of our instrument is from 200 cm$^{-1}$ to 4000 cm$^{-1}$).

![Far-FT-IR spectrum of ZnFe$_2$O$_4$ nanoparticles obtained by calcining at 800 °C (Inset: Mid-FT-IR spectrum).](image)

**Fig. S3** Far-FT-IR spectrum of ZnFe$_2$O$_4$ nanoparticles obtained by calcining at 800 °C (Inset: Mid-FT-IR spectrum).

**UV spectrum.** To investigate the optical properties of ZnFe$_2$O$_4$ nanopowder, UV-vis diffuse reflectance spectroscopy of the solid nanopowder catalyst was performed. The ZnFe$_2$O$_4$ showed a steep absorption edge. The optical absorbance can be approximately calculated from the optical reflectance data by the Kubelka–Munk function, $\alpha = (1-R)^2/2R$, where $\alpha$ is the absorption coefficient, R is the diffuse reflectance.\(^3\) As shown in Fig. S4, the synthesized ZnFe$_2$O$_4$ nanopowder obtained by calcining at 800 °C are highly photoresponsive in both the UV and visible light ranges (>400 nm) as expected, especially, in the wavelength range of 300–500 nm. The dark brown color of ZnFe$_2$O$_4$ did demonstrate the visible light absorption ability of these materials.

![Absorbance vs Wavelength](image)

**Fig. S4** UV spectrum of ZnFe$_2$O$_4$ nanoparticles obtained by calcining at 800 °C.

**XPS spectrum.** To investigate the electronic environment and oxidation state of the elements present in zinc ferrite obtained by calcining at 800 °C, the sample was analyzed by X-ray photoelectron spectroscopy. The binding energy of O 1s was found to be 533.8 eV (Fig. S5a). XPS signals at 715.19 and 723.0 eV could be attributed to the Fe 2p\(_{3/2}\) and Fe 2p\(_{1/2}\) oxidized states of Fe(III) (Fig. S5b). Whereas, signals at 1025.56 and 1048.53 eV could be attributed to the Zn 2p\(_{1/2}\) and Zn 2p\(_{3/2}\) states of Zn(II) (Fig. S5c). Binding energies of Fe 2p\(_{3/2}\) and Fe 2p\(_{1/2}\) states of Fe(III) and Zn 2p\(_{1/2}\) and Zn 2p\(_{3/2}\) states of Zn(II) are found to be different from the binding energies of those states in α-Fe\(_2\)O\(_3\) and ZnO oxide. Considerable positive shifts observed for the binding energies of both Fe(III) and Zn(II) could be attributed to the interaction between the ZnO and α-Fe\(_2\)O\(_3\) oxide nanoparticles in spinel structure of ZnFe\(_2\)O\(_4\). These clearly reflect that Zn, Fe and O are not present in the form of individual zinc oxide, ferrous oxide or ferric oxide but as spinel zinc ferrite.

![XPS spectra](image)

**Fig. S5** XPS spectrum of ZnFe\(_2\)O\(_4\) nanoparticles obtained by calcining at 800 °C: (a) high-energy resolution O 1s core-level spectra, (b) high-energy-resolution Fe 2p core-level spectra, (c) high-energy-resolution Zn 2p core-level spectra and (d) survey.
N\textsubscript{2} adsorption analysis. Mixed oxides have greater surface area, smaller particle sizes and higher generation of new catalytic active sites than the corresponding oxide homologues. This is extremely important since higher surface area favors adsorption of reaction molecules and small particle size is advantageous for minimal internal diffusion resistance of molecules thereby increasing the catalytic performance of heterogeneous catalysts. In the present investigation the surface area of ZnFe\textsubscript{2}O\textsubscript{4} nanopowder obtained by calcining at 800 °C was 16 m\textsuperscript{2}/g (Fig. S6a). The pore volume and average pore diameter were found to be 0.02 cm\textsuperscript{3}/g and 6.09 nm, respectively (Fig. S6b).

Fig. S6 (a) N\textsubscript{2} adsorption isotherm and (b) PSD of ZnFe\textsubscript{2}O\textsubscript{4} nanoparticles obtained by calcining at 800 °C.
Fig S7. ORTEP representation of 7am showing the crystallographic numbering (CCDC 946297).

Fig S8. ORTEP representation of 7ay showing the crystallographic numbering (CCDC 946296).
**Fig S9.** ORTEP representation of one of the intermediate (2nd) showing the crystallographic numbering (CCDC 946298).

**Fig S10.** ORTEP representation of 16a showing the crystallographic numbering (CCDC 946299).
Figure S11. IR spectrum of fresh ZnFe₂O₄ catalyst and six-times reused catalyst.

Figure S12. XRD analysis of (a) fresh ZnFe₂O₄ catalyst and (b) six-times reused catalyst.