

Supporting Information

Catalytic interplay of metal ions (Cu^{2+} , Ni^{2+} , and Fe^{2+}) in MFe_2O_4 inverse spinel catalysts for enhancing the activity and selectivity during selective transfer hydrogenation of furfural into 2-methylfuran

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Experimental

Materials

High purity $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, and other metal salts were purchased from Sigma Aldrich India Pvt Ltd. Furfural, furfural alcohol, 5-hydroxymethylfurfural, 2,5-diformylfuran, and 2-methylfurfural were purchased from Sigma Aldrich India Pvt Ltd. All other chemicals used in this work were purchased from Loba Chemi and Sigma Aldrich India Pvt Ltd.

Synthesis of MFe_2O_4 ($\text{M} = \text{Cu}^{2+}$ and Ni^{2+})

Inverse spinel catalysts were synthesized by following a previously reported literature procedure.^{S1} In a typical synthesis, 1.20 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 4.04 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in 60 mL deionised water, and the resulting salts solution was stirred at 60 °C for 2 h. In a separate beaker, 3.15 g citric acid was dissolved in 10 mL of deionised water, and the as-prepared solution was added dropwise into the metal salts solution prepared above. Thereafter, the resulting mixture was stirred for another 2 h at 60 °C, and subsequently, the temperature was raised slowly to 80 °C, and the heating was continued till the complete evaporation of water. After the complete evaporation of H_2O , the obtained sticky solid material was dried at 80°C in an oven for 12 h. Subsequently, the resultant precipitate was ground to a fine powder and calcined in a muffle furnace at 400 °C for 2 h at a ramp rate of 2 °C/min.

Synthesis of Fe₃O₄

Fe₃O₄ was synthesized by following a previously reported literature procedure.^{S1} In a typical synthesis, FeCl₃.6H₂O (1.5 g), PVP (1 g), and sodium acetate (2 g) were dissolved in 30 mL ethylene glycol under vigorous stirred for 2 h. After complete dissolution, the mixture was transferred into a Teflon-lined stainless-steel autoclave. The autoclave was sealed and hydrothermally treated at 200 °C for 8 h. After the completion of heating, the autoclave was cooled down to room temperature, and the obtained black-colored precipitate was collected by centrifugation and washed with deionised water followed by washing with ethanol four times, and finally dried at 60°C overnight in a vacuum oven.

Synthesis of CuO

CuO was synthesized by following a previously reported literature procedure.^{S2} In a typical synthesis, 3.319 g CuSO₄.5H₂O, and 1.584 g PEG were dissolved in 90 mL deionised water, followed by the dropwise addition of aqueous NaOH solution (1 M) to the metal salts solution until the pH becomes 9 with constant stirring. The resultant mixture was transferred into the Teflon-lined stainless-steel autoclave. The autoclave was sealed and heated at 180°C for 12 h. After 12 h, the autoclave was cooled down to room temperature, and the obtained black-colored precipitate was collected by filtration and washed with deionized water four times, and finally dried at 100°C overnight in preheated oven.

10%Cu/AC and 10%CuO/AC synthesis

The Cu nanoparticles on activated carbon was synthesized by the wet impregnation method. 500 mg activated carbon (AC) was dispersed in 20 mL water-ethanol mixture (v/v 1:1) by sonication for 1 h. The required amount of Cu(NO₃)₃.6H₂O was added to the suspension and reaction mixture stirred for 1 h at RT. After 1 h the solvent was evaporated by heat treatment (80 °C) with constant stirring. Then the dry powder was placed in a tube furnace and heated up to 500 °C (ramp rate 5 °C/min) with a constant flow of 10% H₂ in Ar gas for 2 h. The reduced Cu on activated carbon is denoted as 10%Cu/AC. Similarly, 10%CuO/AC was synthesized by the calcination method. The above material (Cu(NO₃)₃.6H₂O on activated carbon) was calcined at 400 °C for 2 h in a muffle furnace with a heating rate of 5 °C/min.

10%Cu₂O/AC synthesis

Cu₂O was synthesized by following reported literature.^{S3} 500 mg AC was dispersed in 20 mL water-ethanol mixture (v/v 1:1) by sonication for 1 h. A required amount of Cu₂O was added

to the suspension and further sonicate for 30 min. The reaction mixture was stirred for 2 h at room temperature and the solvent was evaporated by heat treatment (80 °C).

Materials Characterization:

The powder X-ray diffraction data of the synthesized materials were obtained on a RIGAKU Mini-Flex diffractometer with Cu α ($\lambda = 0.154$ nm, 40 kV, 15 mA) radiation source in 2θ range of 5-80°. N₂ adsorption-desorption analyses of these materials were performed on a BELSORP-mini-X, Microtrac-BEL surface area instrument to examine their textural properties, including surface area and porosity. The samples were degassed at 150 °C for 3 h under flowing He gas before analysis. The specific surface area was calculated in the relative pressure range of 0.05 to 0.3 using Brunauer-Emmett-Taller (BET). Scanning electron microscopy (SEM, 10kV, spot size 30) on a (JEOL JSM-6610LV) was employed to obtain the morphological information. Various constituent elements, their chemical states and oxidation states were determined by X-Ray photoelectron spectroscopy (XPS) on a Thermofisher Scientific (Nexsa base) instrument, and data were interpreted by using XPS Peak 4.1 software. The total acidity and basicity of the materials were analysed by using the Temperature-Programmed Desorption (NH₃ and CO₂ TPD) technique on a Quantachrome, CHEMBETTM TPR/TPD instrument. The sample was preheated at 700°C at a heating rate of 10 °/min under a continuous He gas flow for 30 min. Then, after cooling to 50°C, NH₃ / CO₂ gas was allowed to adsorb on the sample for 1 h. After adsorption, the excess or physically adsorbed NH₃/CO₂ was removed by flushing with He gas (50 mL/min) for 30 min. Finally, the temperature was ramped from 50-800°C at a rate of 10 °/min, then cool at 50 °C with a ramp rate 10 °C/min. The reduction profile of materials was analyzed by using TPR technique on a Quantachrome, CHEMBETTM TPR instrument. The sample was preheated at 700°C at a heating rate of 10 °/min under a continuous He gas flow for 30 min. Then, after cooling to 50°C, 10% H₂ in Ar gas was allowed to pass on the sample at a temperature range of 50-800 °C and finally cool down at 50 °C. The elemental leaching (Cu and Fe) was determined by Agilent's microwave-plasma atomic emission spectrometer (MP-AES 4200). The microstructure of the materials was analyzed by using Transmission Electron Microscope (TEM) 200kV (JEOL JEM 2100) at IIP Dehradun. To determine the nature of acid sites, pyridine FT-IR analysis was performed on a Tensor-II instrument.

Catalytic reaction procedure

Furfural (2 mmol), isopropanol (20 mL), and catalyst (0.1 g) were introduced into the Parr reactor, sealed, and flushed with N₂ (3 times). The reactor was heated to the desired reaction temperature and stirred at a constant stirring rate (600 rpm) for the desired time. After the completion of the reaction, the reactor was cooled. The reaction mixture was withdrawn from the reactor, centrifuged, and analyzed using gas chromatography by the internal standard method (GC, Shimadzu GC-2010 Plus, SH-Rtx-5 column, column temperature 60-280 °C with 5°C/min ramp, injector temperature 250 °C, FID 300 °C). The products of the reaction were confirmed using GC-MS (Shimadzu GCMS-QP 2010 Ultra) (Fig. S10).

Calibration details

Herein, the calibration curves were plotted using different concentrations of reactants and products. The four standards (different concentrations) were prepared for reactants and products in isopropanol with internal standard (n-decane). The prepared standards were injected in GC (triplicate injection) and the area was recorded. After the completion of the GC analysis, the calibration curves were plotted with concentration (g/L) vs peak area (Fig. S9), and the conversion of reactant and product selectivity were determined using the following expression.

$$\text{Conversion} = \frac{c_0 - c_t}{c_0} \times 100\%$$

$$\text{Selectivity} = \frac{c_p}{c_0 - c_t} \times 100\%$$

where C₀ is the initial reactant concentration, C_t is the reactant concentration after time t, and C_p is the product concentration at time t.

The carbon balance was calculated for the furfural to 2-methyl furan conversion, and the value of carbon balance was >99%. Carbon balance was determined from GC using the following expression.

Carbon balance (%)

$$= \frac{\text{moles of carbon in the reaction mixture (unreacted reactant and products)}}{\text{initial moles of carbon in the reactant}} \times 100$$

Computational Study: Here, we investigated computationally the role of the catalyst's active sites in selective FUR hydrogenation using density functional theory (DFT). All solvent phase calculations were performed using generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional in conjunction with double numeric with depolarization (DND) basis set as implemented in DMol3 package.^{S4-S5} Iso-propyl alcohol was considered as a solvent using a continuum phase model.

The interaction energies (E_{int}) were computed by using the following equation.

$$E_{int} = E_{(adsorbate+surface)} - E_{(adsorbate)} - E_{(surface)} \quad \text{-----} \quad (1)$$

Here, $E_{(adsorbate+surface)}$ is the total energy of the catalyst surface adsorbed by adsorbate (furfural/furfural alcohol), $E_{(adsorbate)}$ is the energy of furfural and furfural alcohol (substrates), and $E_{(surface)}$ is the energy of the catalysts (Fe_3O_4 , $NiFe_2O_4$, and $CuFe_2O_4$) surface. According to this equation, the negative value of E_{int} indicates the energetic feasibility of the adsorption of adsorbate on the catalyst surfaces.

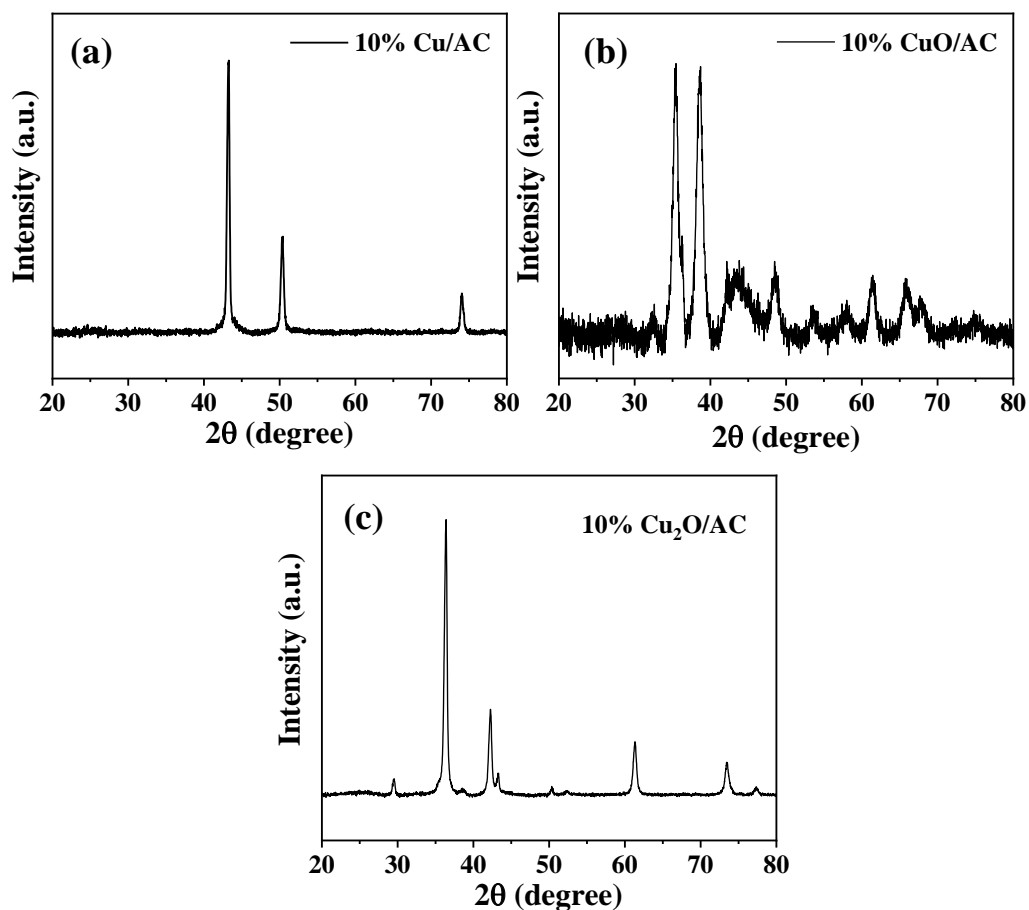


Fig. S1 XRD patterns of (a) 10% Cu/AC, (b) 10% CuO/AC, (c) 10% Cu₂O/AC.

(AC = activated carbon)

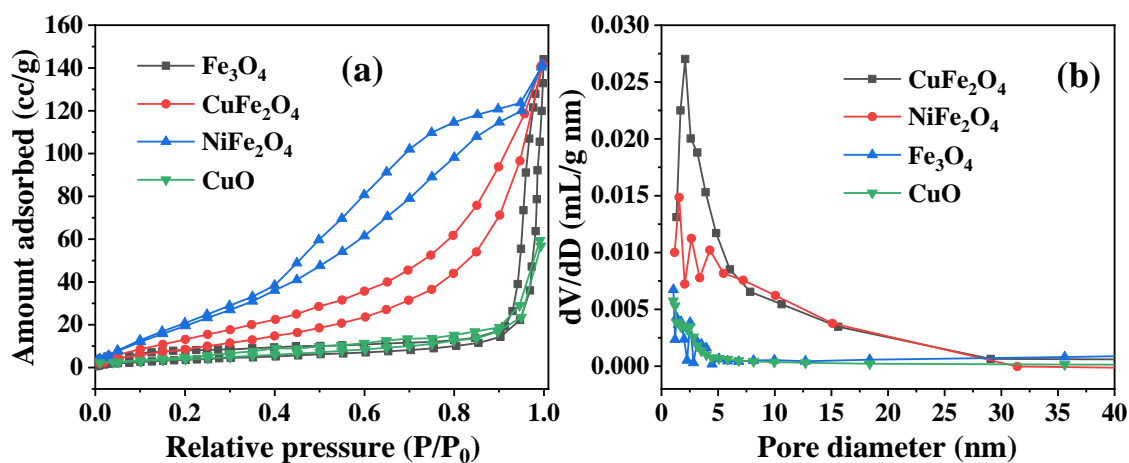


Fig. S2 (a) N₂ adsorption-desorption isotherms and (b) BJH pore size distribution.

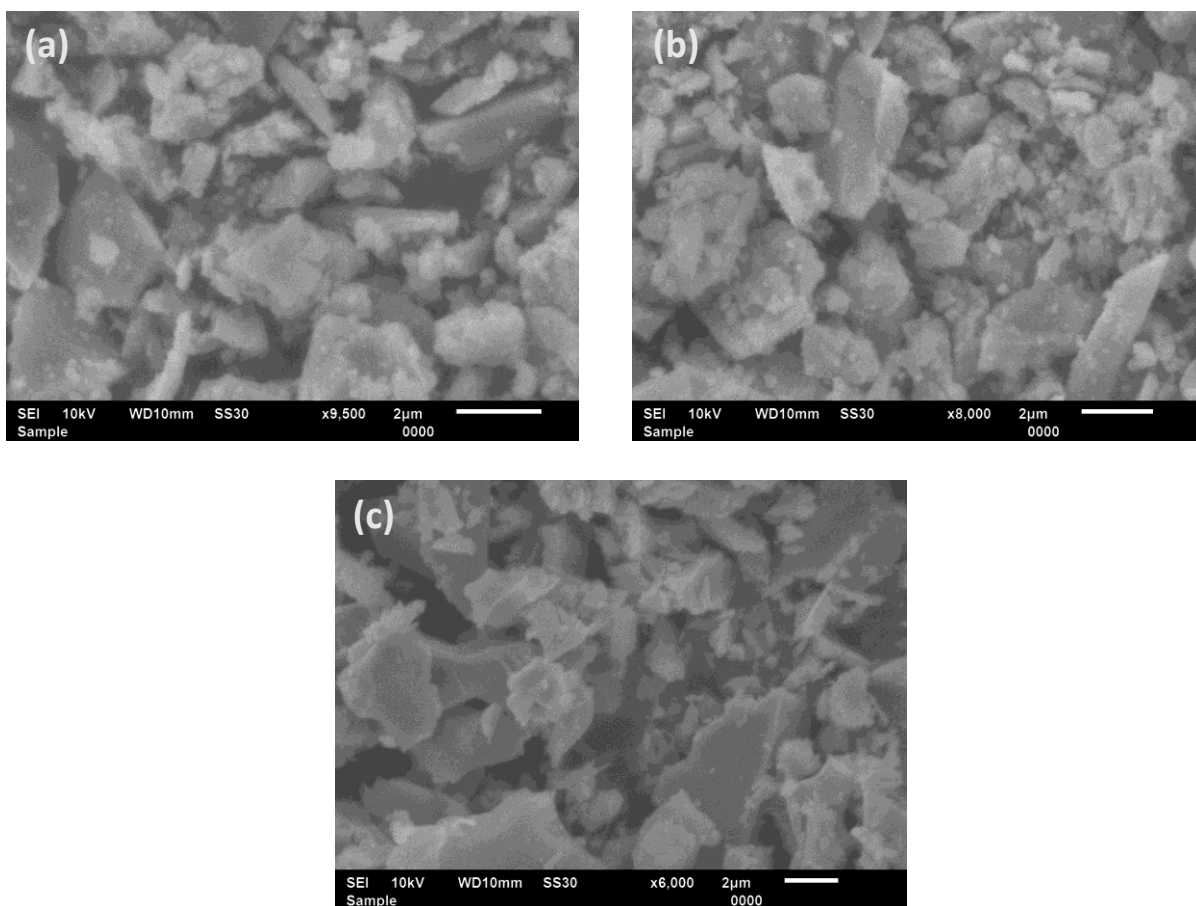


Fig. S3 SEM images of (a) Fe_3O_4 , (b) CuFe_2O_4 , and (c) NiFe_2O_4 catalysts.

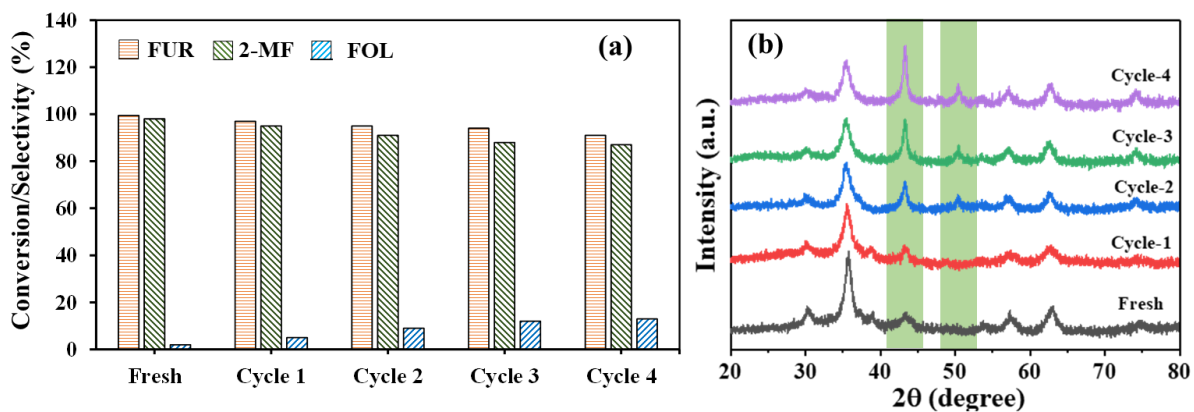


Fig. S4 Recyclability test (a) and the XRD patterns of fresh and spent (b) CuFe₂O₄ catalyst.

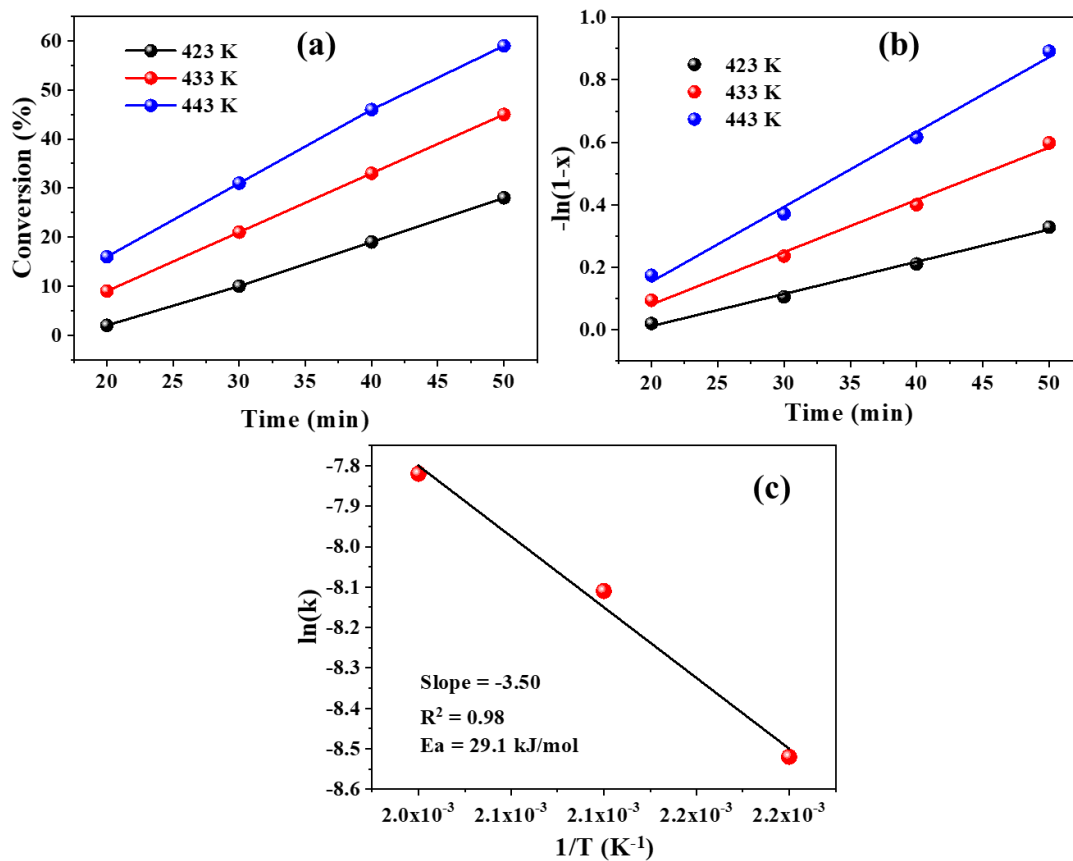


Fig. S5 (a) Conversion of furfural vs. time for the furfural alcohol synthesis, (b) plot of $-\ln(1-x)$ vs. time representing the kinetic study, (c) plot of $\ln(k)$ vs. $1/T$ (Arrhenius plot) for the furfural alcohol synthesis.

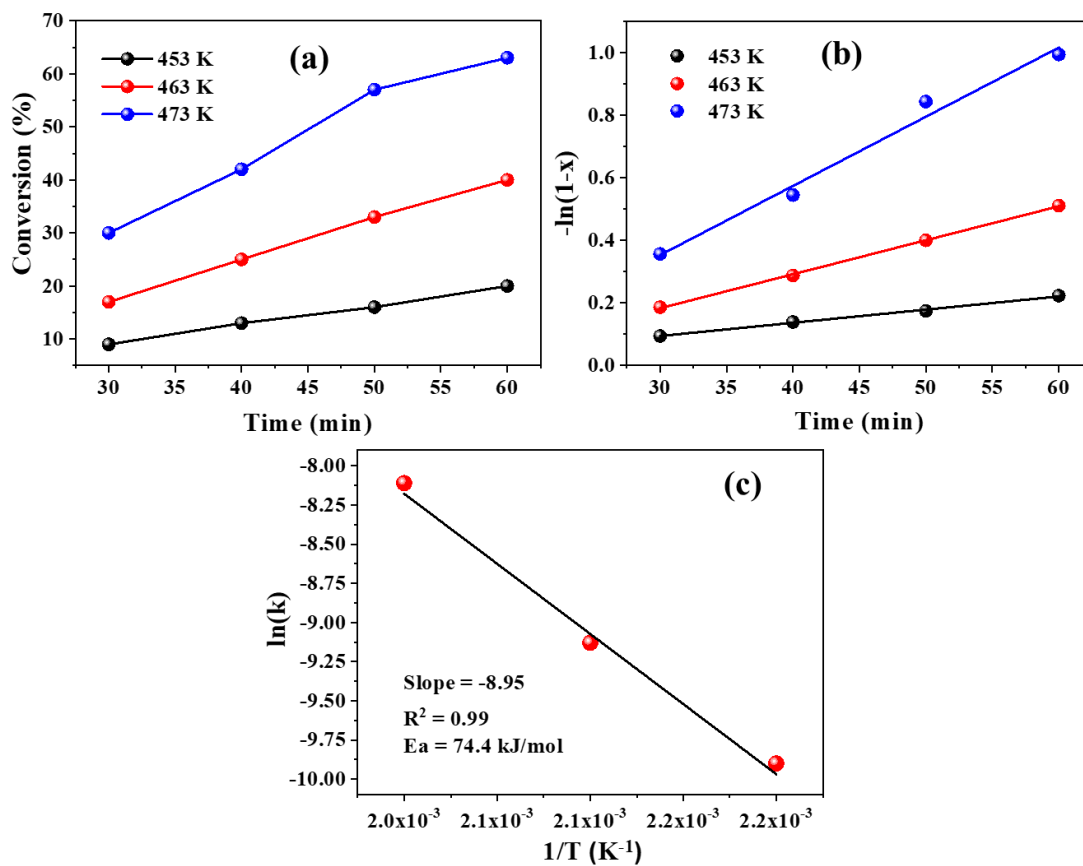


Fig. S6 (a) Conversion of furfural alcohol vs. time for the 2-methylfuran synthesis, (b) plot of $-\ln(1-x)$ vs. time representing the kinetic study, (c) plot of $\ln(k)$ vs. $1/T$ (Arrhenius plot) for the 2-methylfuran synthesis.

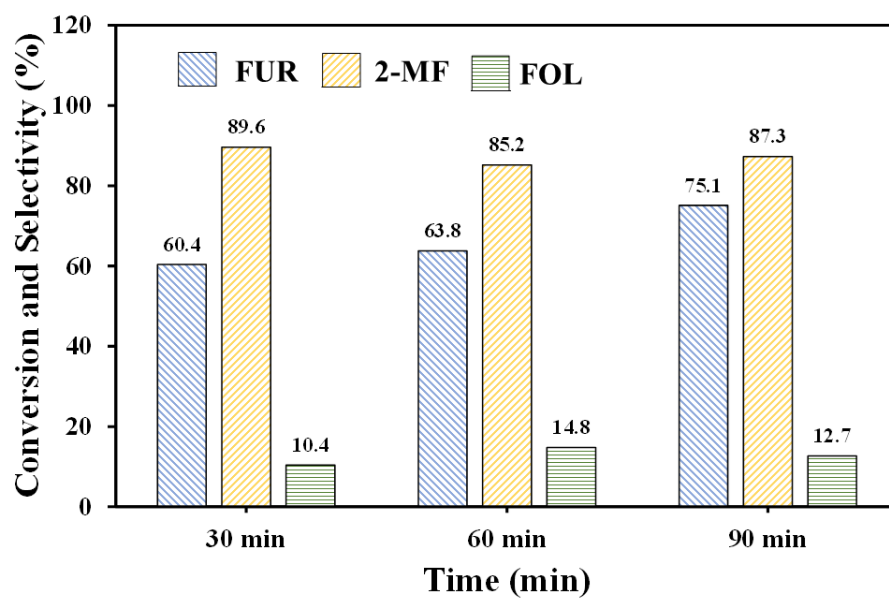


Fig. S7 FUR conversion and product selectivity as a function of time under 10 bar O₂. Reaction conditions- Furfural (2 mmol), catalyst (0.1 g), IPA (20 mL), temperature (200 °C), 10 bar O₂.

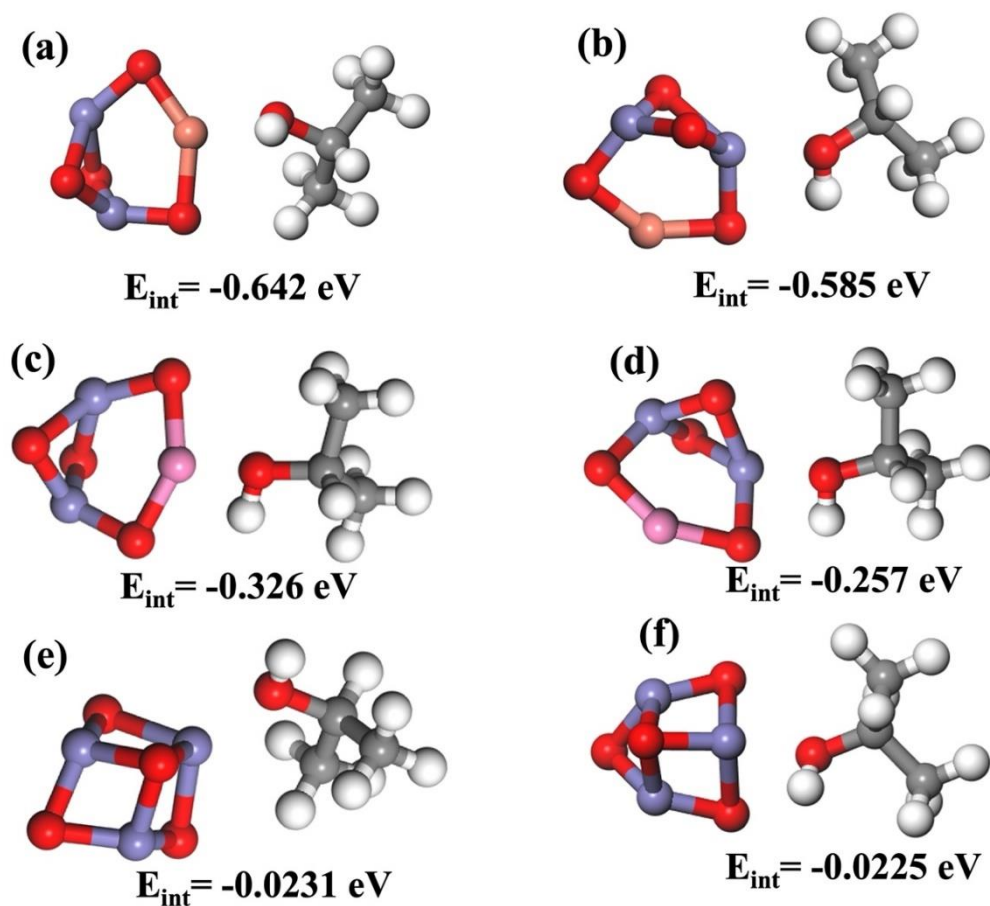


Fig. S8 Optimized geometries for the interactions between isopropanol and (a) CuFe_2O_4 from Cu site, (b) CuFe_2O_4 from Fe site, (c) NiFe_2O_4 from Ni site, (d) NiFe_2O_4 from Fe site, (e) Fe_3O_4 from Fe^{+3} site, and (f) Fe_3O_4 from Fe^{+2} site, respectively. The red, grey, white, blue, orange, and pink colors indicate O, C, H, Fe, Cu, and Ni atoms, respectively.

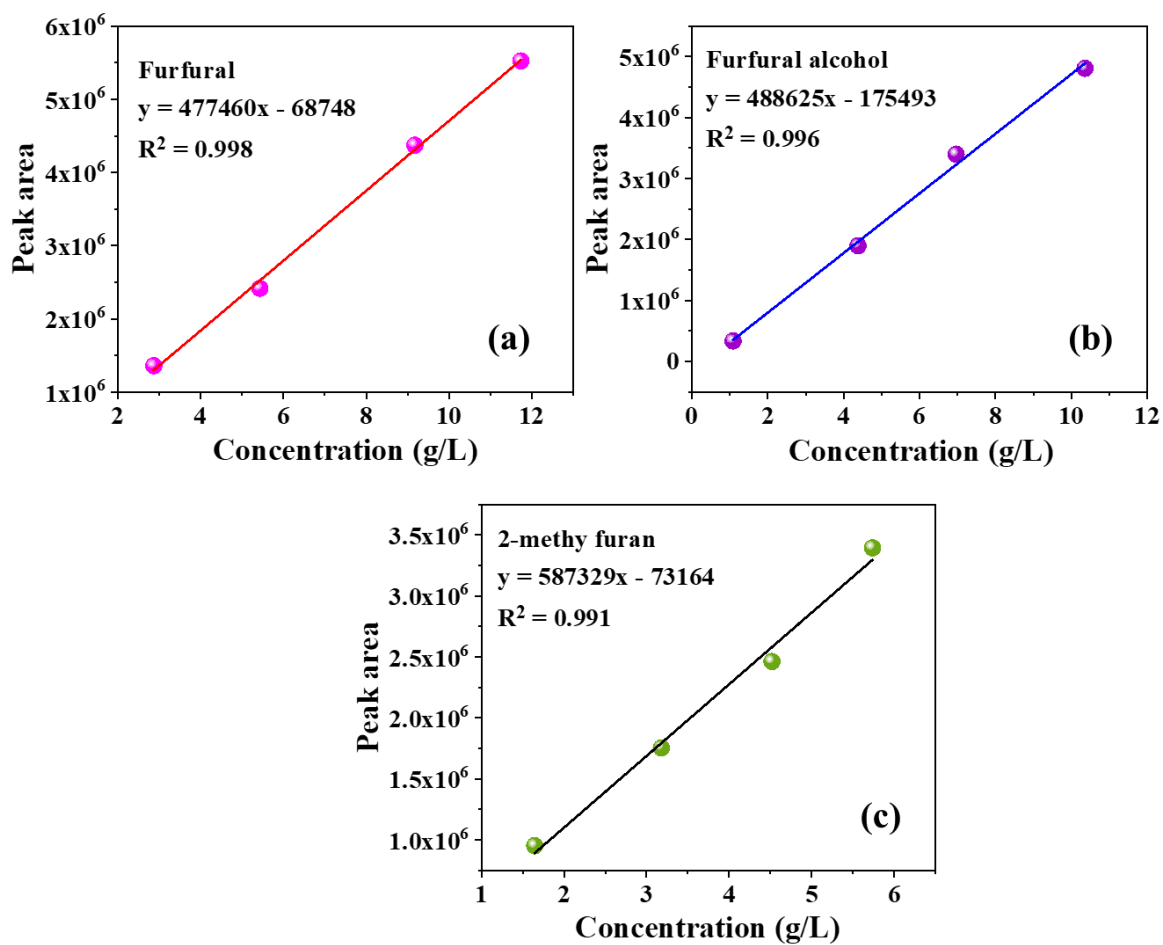


Fig. S9 Calibration curve of (a) furfural, (b) furfural alcohol, and (c) 2-methylfuran.

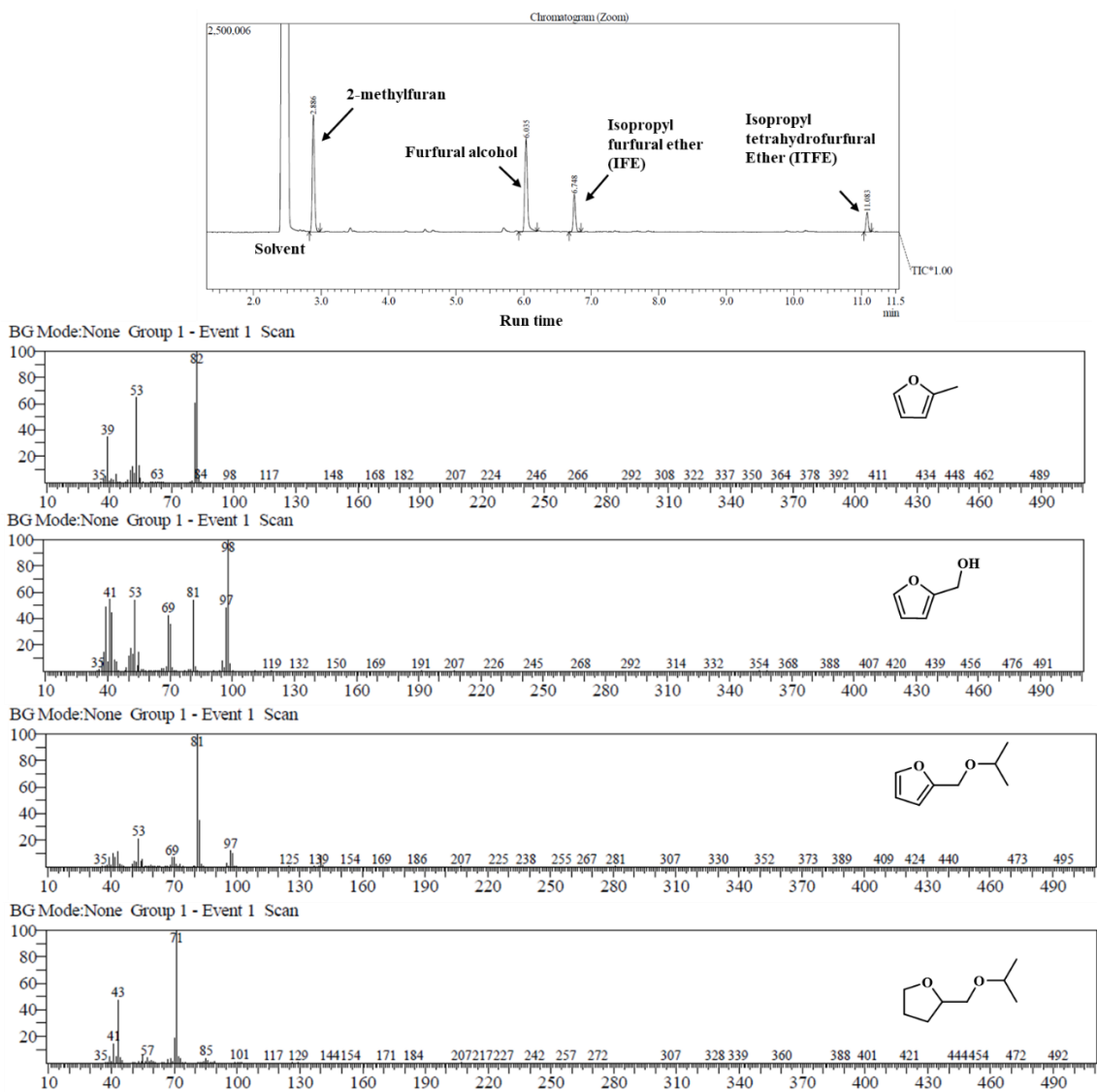


Fig. S10 GC-MS spectra of the reaction mixture of catalytic transfer hydrogenation of furfural.

Table S1 Textural properties of the MFe₂O₄ and CuO catalysts.

Entry number	Catalyst	Surface area (m ² /g)	Total pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)	Total acidity (μmol/g)	Total basicity (μmol/g)
1	CuFe ₂ O ₄	63	0.269	5.8	93.4	1.1
2	Fe ₃ O ₄	22	0.159	3.3	81.4	1.9
3	NiFe ₂ O ₄	88	0.237	4.5	62.1	0.5
4	CuO	15	0.0879	3.1	12.9	0.2

Table S2 Kinetics details for the furfural alcohol synthesis by using furfural.

Sr. No.	Temperature	K, h ⁻¹	ln k	Activation energy (E _a)
1	423	1.99 x 10 ⁻⁴	-8.52	29.1 kJ/mol
2	433	3.01 x 10 ⁻⁴	-8.11	
3	443	4.05 x 10 ⁻⁴	-7.82	

Table S3 Kinetics details for the 2-methylfuran synthesis by using furfural alcohol.

Sr. No.	Temperature	K, h ⁻¹	ln k	Activation energy (E _a)
1	453	5.01 x 10 ⁻⁵	-9.90	74.4 kJ/mol
2	463	1.10 x 10 ⁻⁴	-9.21	
3	473	3.01 x 10 ⁻⁴	-8.11	

Table S4 Table depicting the E_{int} values of the interaction between substrates and catalysts surface via different sites, and the C-O and O-H bond length values of the -CH₂OH group present in FOL after its interaction with different catalysts via different sites.

	CuFe ₂ O ₄		Fe ₂ NiO ₄		Fe ₃ O ₄	
	Cu site	Fe site	Ni site	Fe site	Fe ³⁺ site	Fe ²⁺ site
E_{int} (FUR - catalysts)	-0.893 eV	-0.933 eV	-0.372 eV	-0.413 eV	-0.0591 eV	-0.045 eV
E_{int} (FOL - catalysts)	-1.129 eV	-1.551 eV	-0.049 eV	-0.061 eV	-0.048 eV	-0.0593 eV
C-O bond length	1.478 Å	1.481 Å	1.453 Å	1.454 Å	1.449 Å	1.447 Å
O-H bond length	0.985 Å	0.987 Å	0.984 Å	0.984 Å	0.983 Å	0.983 Å

Table S5 Table depicting the E_{int} values of the interaction between isopropanol (IPA) and catalysts surface via different sites.

	CuFe ₂ O ₄		Fe ₂ NiO ₄		Fe ₃ O ₄	
	Cu site	Fe site	Ni site	Fe site	Fe ³⁺ site	Fe ²⁺ site
E_{int} (IPA - catalysts)	-0.642 eV	-0.585 eV	-0.326 eV	-0.257 eV	-0.0231 eV	-0.0225 eV

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