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Supporting Information

Metal and Solvent-Dependent Activity of Spinel-Based Catalysts for the Selective Hydrogenation and Rearrangement of Furfural

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EXPERIMENTAL METHODS

$Cu(NO_3)_2.3H_2O$ was purchased from Merck India Pvt. Ltd. $Ni(NO_3)_2.6H_2O$ and $Fe(NO_3)_2.9H_2O$ were procured from Sigma Aldrich, Pvt. Ltd., India. Citric acid and $NaBH_4$ were procured from Loba Chemi, Pvt. Ltd., India.

Synthesis of $CuFe_2O_4$: The $CuFe_2O_4$ was synthesized by a sol-gel combustion method mentioned in our previous article.[18] In a typical synthesis, $Cu(NO_3)_2.3H_2O$ (5 mmol) and $Fe(NO_3)_2.9H_2O$ (10 mmol) were dissolved in 60 ml deionised water and stirred at 333 K for 2 h. After complete dissolution of the metal precursors, 10 ml aqueous solution of citric acid (15 mmol) was added into the above solution under continuous stirring and the mixing was continued for the next 2 h at 333 K temperature. Following this, water was removed by evaporation at 353 K to get a fluffy sticky solid material which was ground using a mortar and pestle into fine powder. Finally, the obtained powder was dried in oven at 353 K and subsequently calcined in a muffle furnace at 673 K for 2 h at a rate of 2°C/min. After calcination, the obtained black material was designated as $CuFe_2O_4$.

Synthesis of $M/CuFe_2O_4$(M = Cu, Ni): The Cu or Ni nanoparticles were decorated on $CuFe_2O_4$ support by using a $NaBH_4$ reduction method. The synthesis procedure is as follows: In a 100 mL glass beaker, $CuFe_2O_4$ (500 mg) was dispersed in 60 mL water-ethanol (1:1) mixture by ultra-sonication for 30 min. Subsequently, 10 mL aqueous solution of a given metal salt of required concentration was added dropwise under sonication and the sonication was continued for another 30 min. To the resulting solution, 20 ml aqueous solution of $NaBH_4$ (0.4 M) was added slowly under continuous stirring, and the stirring was continued for the next2 h at room temperature. The resulting precipitate was separated by centrifugation and washed several times with water and ethanol, and finally dried in vacuum at 333 K for 12 h. Finally, the obtained materials were designated as Cu(x%)/$CuFe_2O_4$ and Ni(x%)/$CuFe_2O_4$, where, ‘x’ represents the percentage loading of metals on $CuFe_2O_4$ support.

Materials characterization: The synthesized materials were primarily characterized the by X-Ray diffraction (XRD) technique in 2θ range of 5-80° on a RIGAKU Mini-Flex diffractometer with Cu kα ($\lambda = 0.154$ nm) radiation. The textural properties such as; the surface area and porosity of all synthesized materials were characterized by the N_2 adsorption-desorption analysis on a BELSORP-mini-X, Microtrac-BEL surface area instrument. Before analysis, all samples were degassed at 423 K for 3 h under flowing He gas. Brunauer-Emmett-

Taller (BET) equation was used to calculate the specific surface area in the relative pressure range of 0.05 to 0.3, and Barrett-Joyner-Halenda (BJH) method was used to determine the pore size distribution. Morphological information of the synthesized materials was obtained from the field emission scanning electron microscopy (FE-SEM) on a Quanta 200 F, M/s FEI, Netherlands instrument. The in-depth morphological and nano-structural information was collected from transmission electron microscope (TEM) (M/s JEOL JSM 2100) instrument operating at 200 kV. The elemental distribution and compositionwerestudiedusing energy dispersive X-ray spectroscopy (EDX) and TEM mapping. The various constituent elements, their chemical states and oxidation states weredetermined by X-Ray photoelectron spectroscopy (XPS) on a Thermofisher Scientific (Nexsa base) instrument. The Cu and Nicontents present in the sampleswerecalculatedby microwave plasma-atomic emission spectroscopy (MP-AES).

Determination of the activation energy: The activation energy (E_a) barriers for both FUR hydrogenation to furfuryl alcohol (FOL) and cyclopentanone (CPO) were calculated over Cu(10%)/$CuFe_2O_4$ and Ni(10%)/$CuFe_2O_4$ catalysts, respectively. The FUR to FOL transformation over Cu(10%)/$CuFe_2O_4$ catalyst was studied at different temperatures, including 373 K, 383 K, and 393 K (Fig. S4a). Similarly, the FUR to CPO transformation over Ni(10%)/$CuFe_2O_4$ catalyst was studied at three different temperatures, including 383 K, 403 K, and 423 K (Fig. S6a). Since solvent and H_2 were used in excess during these catalytic processes, hence; the first order reaction kinetics was used to calculate the rate constant using the following equation (Eq. 1). A plot of –ln (1-x) *vs* time (x represents the FUR concentration at different times) for both the reactions (Fig. S4b & S6b) provided the rate constant (k) values at different temperatures. Finally, according to the Arrhenius equation, ln k was plotted against 1/T (T represents temperature) to obtain the activation energy values for both reactions by following equation 2 (Fig. S4c & S6c). From the slope of these plots, calculated values of activation energies for FUR to FOL and FUR to CPO transformations are 57.2 kJ/mol and 35.4 kJ/mol, respectively.

$$-\frac{d[FAL\ or\ HMF]}{dt} = k[FAL] = \frac{d[FOL\ or\ DFF]}{dt} \qquad (1)$$

$$-\ln(1-x) = kt + c$$

$$lnk = -\left(\frac{E_a}{RT}\right) + lnA \qquad (2)$$

Table S1. Comparative activation energy (E_a) data for FUR hydrogenation to FOL and CPO.

E. no.	Catalyst	E_a (kJ/mol)	Reference
E_a for FUR **to FOL conversion**			
1.	$Ru_{1.0}Mo_{1.0}P$	51	(43)
2.	Ru/ZrO_2	56.0	(44)
3.	Au/Al2O3	45.0	(45)
4.	$CuCrO_2$	46.0	(46)
5.	Cu/SiO_2	50.2	(47)
6.	Cu-Co@SBA-15	38.5	(48)
7.	CuMgAl	127	(49)
8.	Zr_1B_3FeO	48.3	(50)
9.	Al-Zr@Fe mixed oxide	45.3	(51)
10.	**Cu(10%)/$CuFe_2O_4$**	**57.2**	**This study**
E_a for FUR **to CPO conversion**			
11.	NiFe/SBA-15	104	(52)
12.	**Ni(10%)/$CuFe_2O_4$**	**35.4**	**This study**

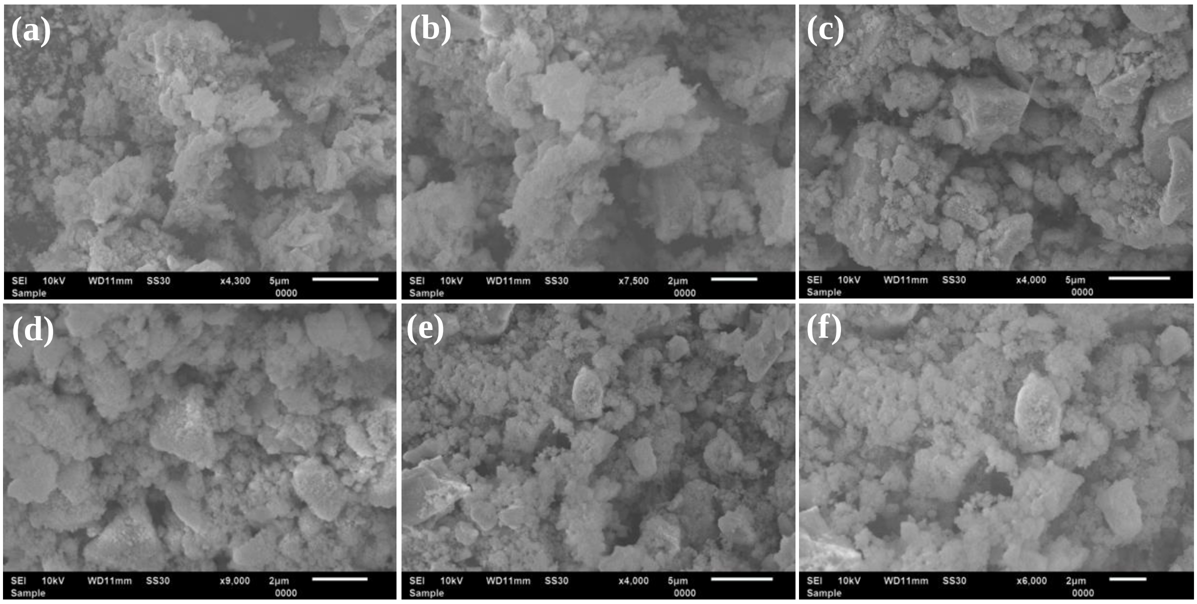

Fig. S1. SEM images of (a,b) $CuFe_2O_4$, (c,d) Cu(10%)/$CuFe_2O_4$, and (e,f) Ni(10%)/$CuFe_2O_4$.

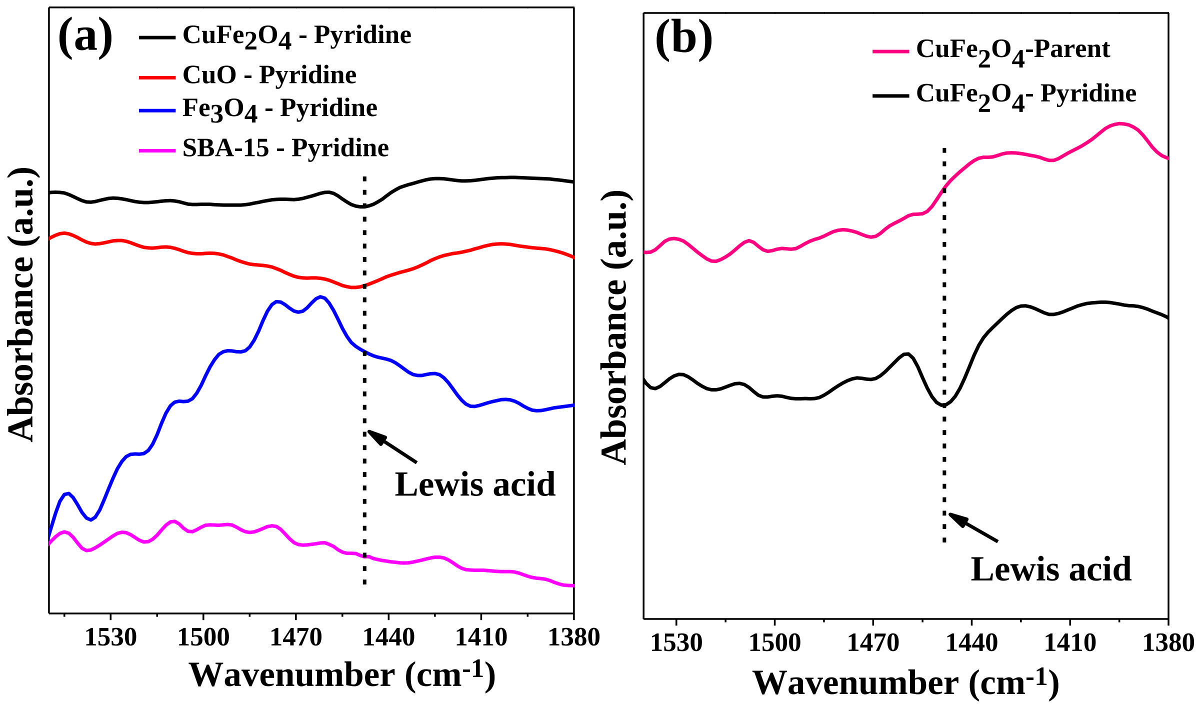

Fig. S2. Pyridine FT-IR spectra of (a) pyridine adsorbed $CuFe_2O_4$, CuO, Fe_3O_4, and SBA-15 supports and (b) parent and pyridine adsorbed $CuFe_2O_4$ support.

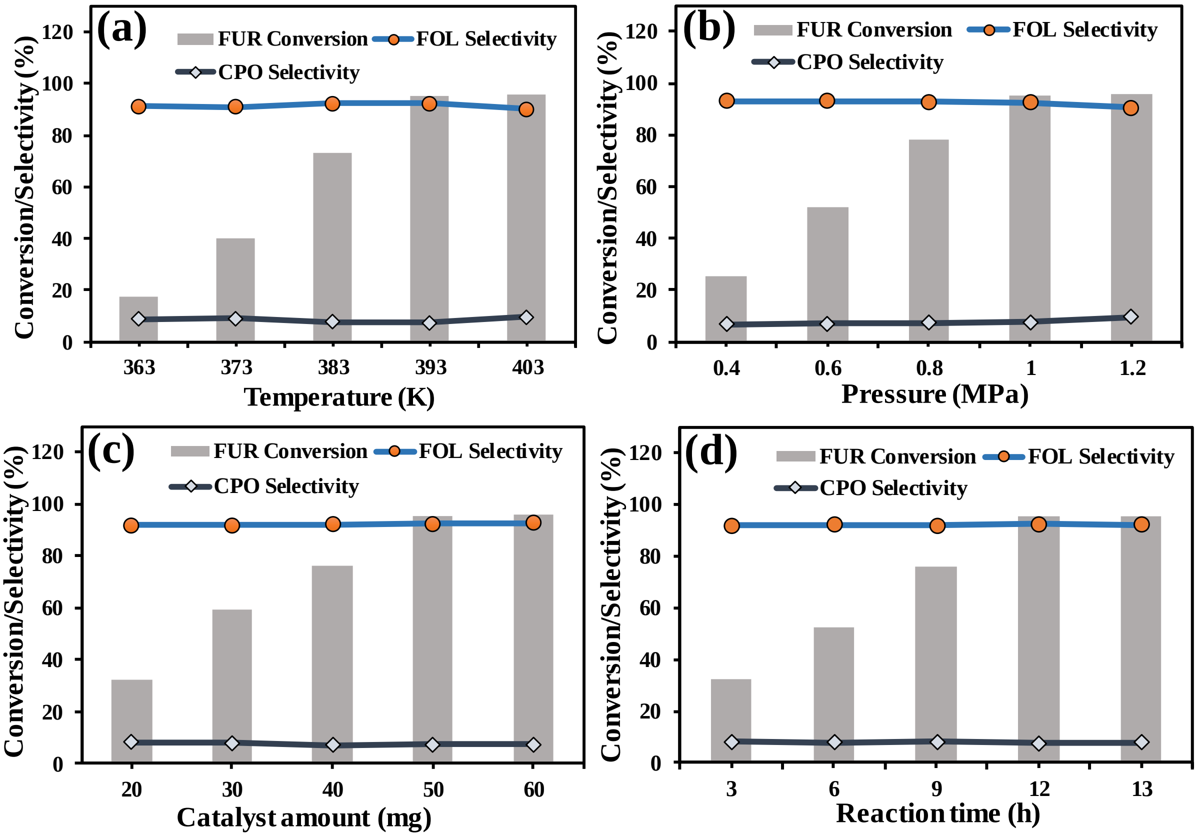

Fig. S3. Optimization of (a) reaction temperature, (b) H_2 pressure, (c) catalyst amount, and (d) reaction time for FUR to FOL hydrogenation over Cu(10%)/$CuFe_2O_4$.

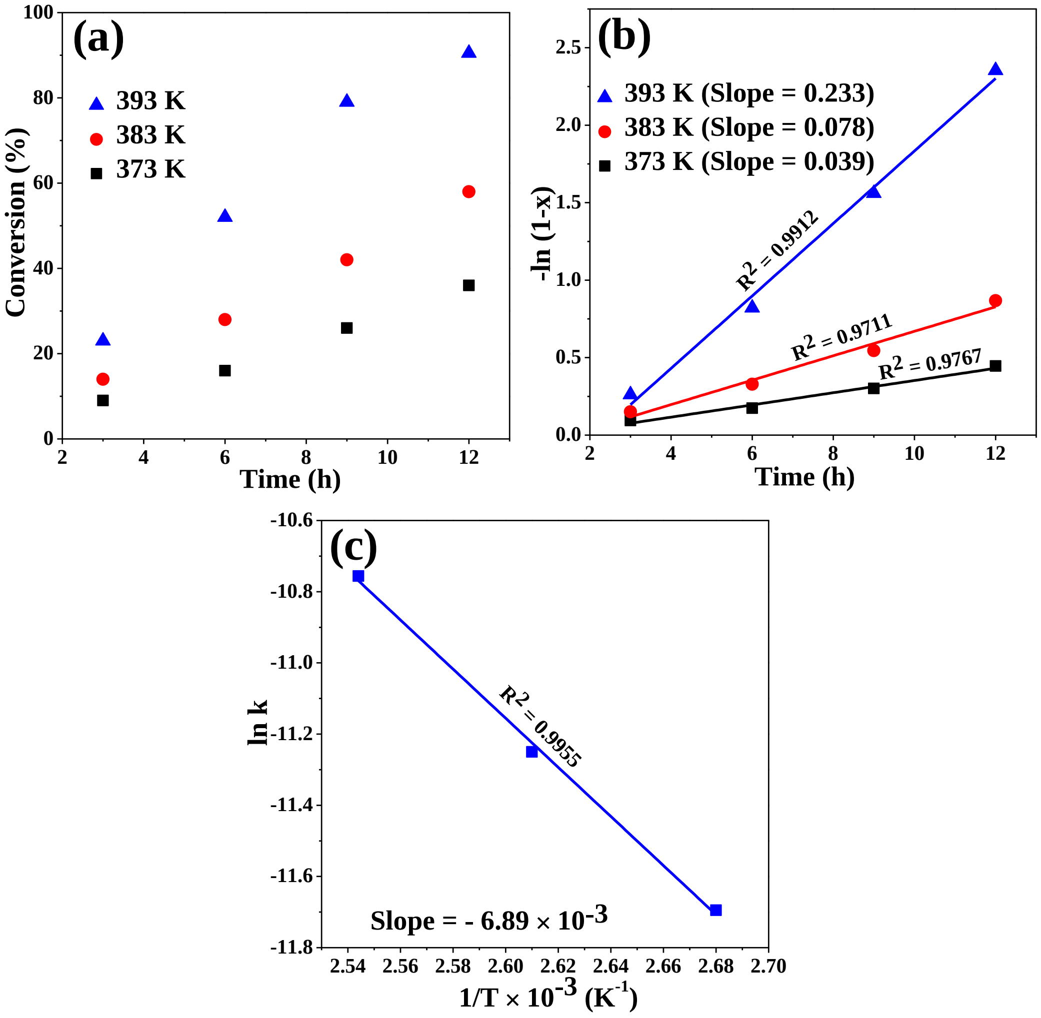

Fig. S4. Kinetic curves for the selective hydrogenation of FUR to FOL (a) relationship between FUR conversion and reaction time, (b) relationship between –ln(1-x) and reaction time, and (c) relationship between ln k and 1/Temperature (1/T). [Reaction condition: furfural (1 mmol), Cu(10%)$CuFe_2O_4$ (50 mg), H_2O (10 mL), H_2 (1 MPa).]

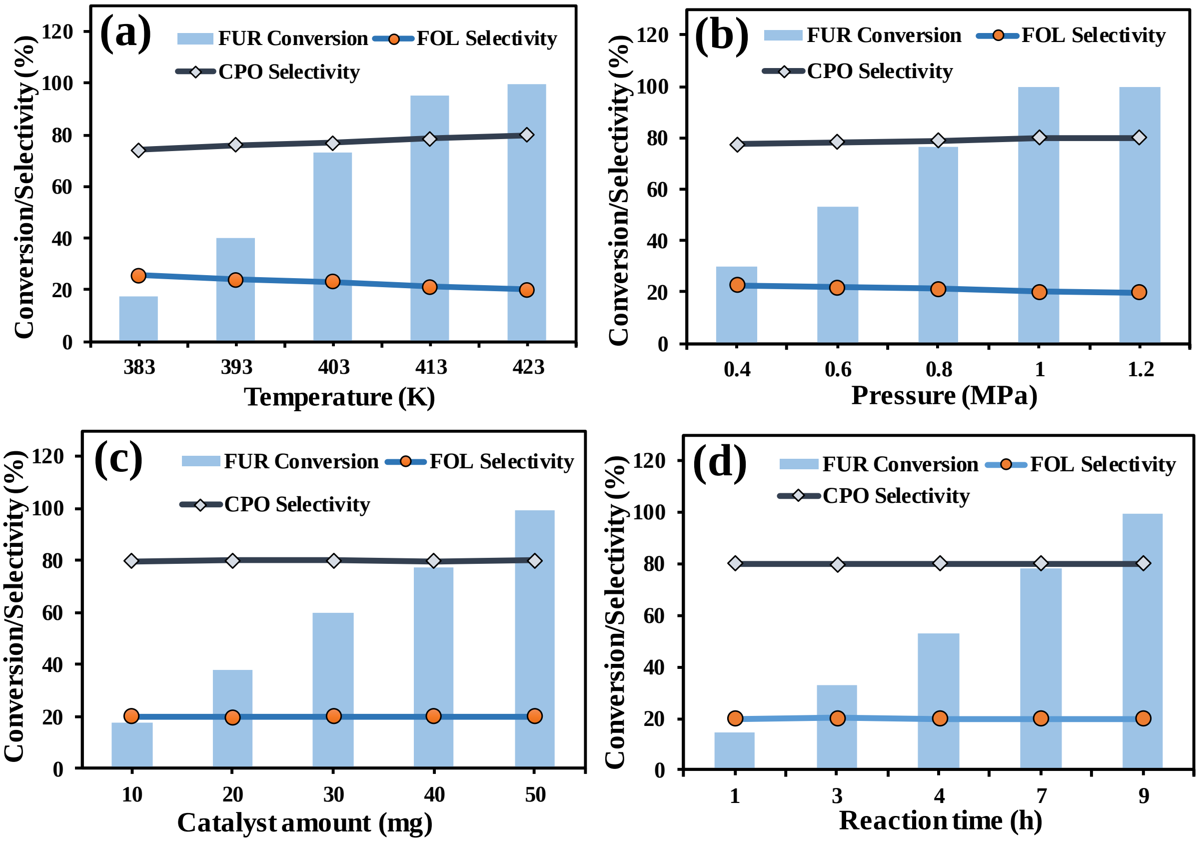

Fig. S5. Optimization of (a) reaction temperature, (b) H_2 pressure, (c) catalyst amount, and (d) reaction time for FUR to CPO hydrogenation over Ni(10%)/$CuFe_2O_4$.

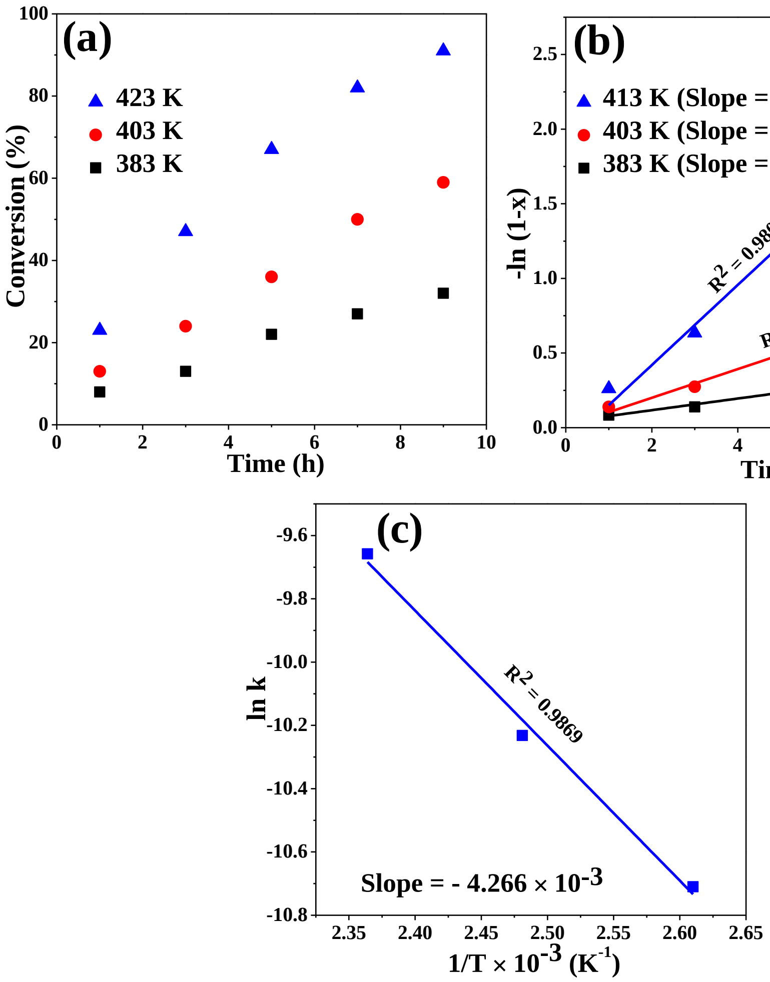

Fig. S6. Kinetic curves for the selective hydrogenation of FUR to FOL (a) relationship between FUR conversion and reaction time, (b) relationship between –ln(1-x) and reaction time, and (c) relationship between ln k and 1/Temperature (1/T). [Reaction condition: furfural (1 mmol), Ni(10%)$CuFe_2O_4$ (50 mg), H_2O (10 mL), H_2 (1 MPa).]

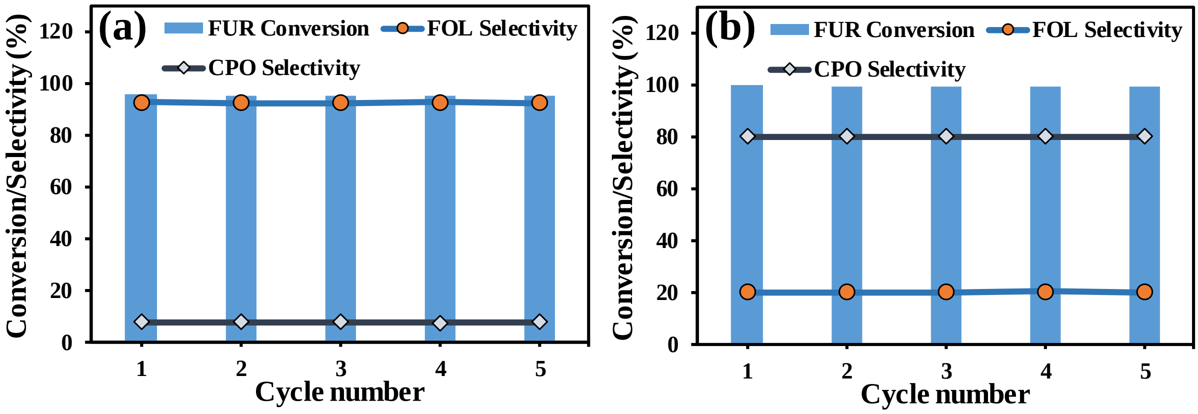

Fig. S7. Catalyst recyclability tests for FUR hydrogenation to (a) FOL over Cu(10%)/$CuFe_2O_4$ and (b) CPO over Ni(10%)/$CuFe_2O_4$catalysts.

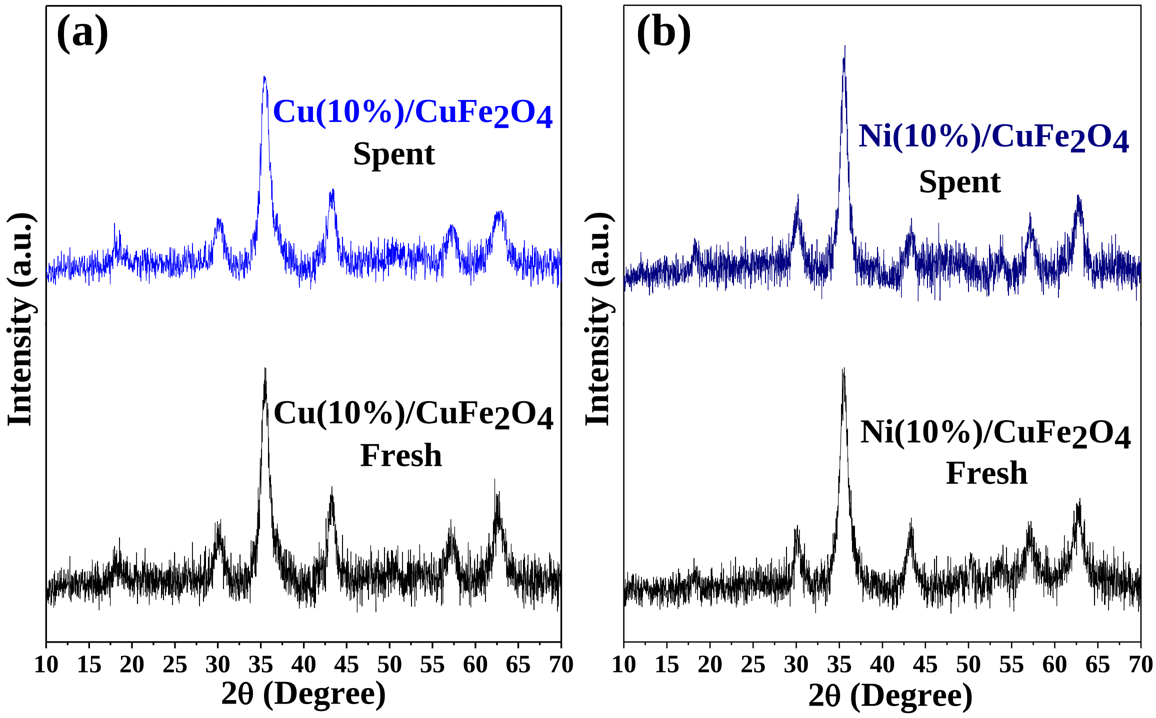

Fig. S8. Powder XRD patterns of the fresh and spent Cu(10%)/$CuFe_2O_4$ (a) and Ni(10%)/$CuFe_2O_4$ (b) catalysts.

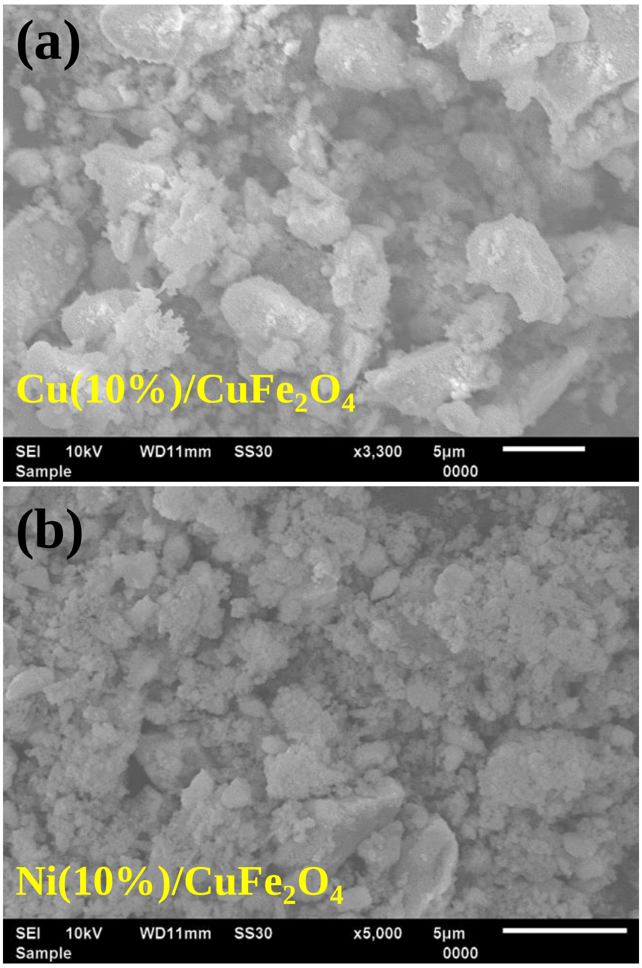

Fig. S9. SEM images of the spent (a) Cu(10%)CuFe$_2$O$_4$ and (b) Ni(10%)/CuFe$_2$O$_4$.