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Catalytic hydrogenation of furfural to furfuryl alcohol over chromium-free catalyst: Enhanced selectivity in the presence of solvent

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ABSTRACT

Copper chromite (Cr_2CuO_4) catalyst is commercially being used for hydrogenation of furfural (FAL) to furfuryl alcohol (FA). However, due to the negative environmental impact of chromium, the use of a chromium-free catalyst has become a logical choice. In order to develop Cr-free catalysts, several Cu-Zn-X-Y [X and Y = ad-ditives] based trimetallic and tetrametallic catalysts were synthesized and tested for selective hydrogenation of furfural to furfuryl alcohol in different solvents. The characterization of catalysts using XRD, N₂ sorption, H₂-TPR, and HRTEM reveals the synergetic effect between CuO and ZnO interface. Interestingly, the strong influence of solvents was observed on the catalytic activity and selectivity. The positive influence of the solvent on enhancing selectivity was associated with the hydrogen bond donation (HBD) and hydrogen bond acceptance (HBA) capability. Water, a green solvent, has been found the most effective solvent. The high hydrogen bond donor capability of water was responsible for the strong positive effect. The effect of parameters, such as H₂ pressure, catalyst loading, furfural concentration, temperature, and reaction time, was studied on catalyst performance. Excellent selectivity for furfuryl alcohol \geq 99% was obtained at mild operating conditions of temperature of 100 °C and H₂ pressure of 1 MPa. The kinetic study revealed that the furfural conversion profile was well fitted by the first-order kinetic model. The best CZAl catalyst showed reproducible activity up to 5 cycles.

1. Introduction

Production of chemicals from renewable sources is the central theme of the circular economy of the 21 st century. The growing environmental concerns and efforts to reduce dependency on crude oil-derived chemicals are the major drivers for the development of these renewable energy resources. In the past decade, lignocellulosic biomass has emerged as the most abundant and economical non-fossil carbon resource for the production of fuel and chemicals [1]. The conversion of biomass and their derivatives to several fuels and chemicals using different routes (gasification, pyrolysis, hydrolysis, liquefaction) has become a subject of great importance in industrial as well as academic research[2,3].

Furfural (FAL), due to its wide range of applications, is considered one of the most promising value-added chemicals that can be produced from lignocellulosic biomass such as corncob, oat, wheat bran, rice husk, sugarcane bagasse, bamboo, etc. [4,5]. It can generally be obtained from acid-catalyzed hydrolysis followed by dehydration of xylose sugars present in hemicellulosic content of biomass [6–8]. FAL is an important building block of various chemicals, and a shift toward the development of bio-based chemicals (such as furfuryl alcohol, tetrahydrofurfuryl alcohol, methyl tetrahydrofuran, furoic acid, furfuryl amine, and methyl furan) has augmented FAL demand [8–10]. A number of important chemicals that can be produced from FAL are shown in Scheme 1. Furfuryl alcohol (FA) is the largest application segment for the FAL, accounting for 85% of FAL consumption [11]. FA has wide applications because of its high versatility in the synthesis of (1) furan thermosets resin used in fibre-reinforced composites; (2) corrosion-resistant cement; (3) drug synthesis; (4) adhesives; (5) plasticizers; (6) lysine and vitamin C; (7) rocket fuel and (8) chemicals [7,8]. The remarkable properties of this chemical, such as low viscosity, high reactivity, and excellent solvent characteristics led to success in other fields.

Selective hydrogenation of FAL is the only process for the production of furfuryl alcohol (Scheme 1). Industrially, both liquid and vapor phase processes are being used for the production of furfuryl alcohol.

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Scheme 1. Products obtained from FAL hydrogenation and side products (1) FAL, (2) Furfuryl alcohol (FA), (3) 2-methyl furan, (4) 2-Methyltetrahydrofuran, (5) Tetrahydrofuran-2-carbaldehyde, (6) Tetrahydrofurfuryl alcohol, (7) Furan,(8) Tetrahydrofuran, (9) Levulinnic acid.

Table 1 Summary of heterogeneous catalysts for hydrogenation of FAL to FA in recently nublished works.

Catalysts Reaction condition				FA yield (%)	Cycle test	Ref.	
	Т (К)	$P_{H_2}(MPa)$	t (h)	Solvent	(,		
Pt/Sn- SiO ₂	373	1	4	IPA	96	-	[19]
Cu/Mg/Al	483	-	1	IPA	89	4	[59]
Cu/AC- SO ₃ H	373	1	3	IPA	>99	5	[60]
NiFe ₂ O ₄	453	-	6	IPA	94	5	[61]
CuZnCrZr	443	2	3.5	IPA	96	5	[62]
Cu/HT	423	3	8	IPA	89	-	[63]
Ni CoB	413	3	2	Ethanol	76	6	[6]
Cu/Fe ₂ O ₃	453	-	7.5	IPA	28	-	[16]
Co-Cu/ SBA-15	443	2	4	IPA	80	3	[64]
Co-Cu/ SBA-15	403	3	3	IPA	96.7	-	[65]
Fe@C/ K ₂ CO ₃	413	2	2	Ethanol	93	-	[66]
CZAl	373	1	4	Water	>99	5	Present work

Generally, liquid phase reactions are performed at low temperature (< 180 °C) and high H₂ pressure (> 1000 psi). The liquid phase process is operated in batch mode in a simple slurry reactor system. Nagaraja et al. conducted the gas-phase hydrogenation reaction over Cu/MgO and obtained the higher conversion of FAL (98%) with high selectivity towards the FA (98%).[12] However, several recent reports described that vapour phase reaction is associated with disadvantages of high energy consumption due to vaporization of FAL and the significant quantity of undesired derivatives (2-methyl furan) in hydrogenation products, more than produced in the liquid-phase process [13-16]. Catalyst deactivation is also a major limitation of the process. Various deactivation pathways have been observed, such as adsorption of polymeric species, variation in the oxidation state of the metal, and metal sintering during the vapor phase hydrogenation[14,17]. Many recent reports have explained about liquid phase process that lower energy consumption and higher selectivity than gaseous phase reaction make it more economical for industrial perspective [18]. This process is widely used in the production of FA in china and other parts of the world. Catalytic hydrogenation of Furfural (FAL) to Furfuryl Alcohol (FA) has been

carried out over various supported noble and non-noble metals based catalysts such as Pt, Pd, Ni, Ru, and Fe [13,19–24]. Hydrogenation follows various mechanistic routes with the formation of different by-products depending upon the composition of the catalyst and nature of the solvent. The well-known copper chromite (Cu₂CrO₄) catalyst is used in the liquid phase process due to its high selectivity[25]. Although extensively used, this catalyst has an adverse impact on the environment due to the high toxicity of chromium trioxide and also exhibits moderate activity.

Copper has been recognized as an active catalyst for different hydrogenation processes due to their role in adsorption and activation of H₂. Cu is also suitable because of its lower cost, availability at the pure state, and environmentally friendly nature. Very few reports are available on the Cu-based catalyst without Cr for liquid-phase hydrogenation of FAL to FA [Table 1]. Among different catalysts, Cu/ZnO/X (X = Oxide promoter) has been extensively reported as a highly active catalyst for different C = O hydrogenation processes such as steam reforming of methanol, water gas shift reaction and methanol synthesis from CO/ CO₂. Several reports have mentioned the synergistic interaction between Cu and ZnO, which leads to high catalytic activity and stability. Keeping the importance of this catalyst into mind, Cu/ZnO has been selected to study the hydrogenation of FAL to FA[26]. The selection of suitable oxide promoter (X or XY) is a subject of great importance from an activity and stability point of view. For the structural based sensitive reaction, it is very important to improve the efficiency by a small addition of some metal species, such as Al³⁺, La³⁺, Zr⁴⁺, Ti²⁺, Mg²⁺ which enrich the surface by cationic defects and improve the stabilization of copper on the catalyst surface. Among the promoters study, La₂O₃, Al₂O₃ are the promising metal for its stability and activity. Small additions of Al₂O₃ not only inhibit the sintering of active particles and also smooth the progress of reaction due to surface defects. Aluminium oxide (Al₂O₃) has been commonly reported as a suitable oxide promoter due to its low cost, high hydrothermal stability, and environmentally friendly characteristics. In addition, Al₂O₃ act as a structural promoter, the dispersion of Cu in the catalyst by a geometric effect, the small addition of Al₂O₃ enhance in the BET surface area, improve thermal stability and inhibit the sintering of active metal[27-30]. Other oxide promoters such as NiO, Co₃O₄, La₂O₃, MgO, ZrO₂, Ni(OH)₂ and combination of them are also used in different catalytic applications due to synergistic effect[14, 31–34]. The reaction condition, such as the nature of the solvent, plays a significant role. Various protic solvents such as methanol and ethanol provide high catalytic activity; however, they show the production of undesired by-products (alkyl ethers, etc.) [35,36]. A number of aprotic organic solvents such as ethyl acetate, toluene, dichloromethane,

n-octane and supercritical CO₂ have also been used for liquid phase FAL hydrogenation[37]. A comparative evaluation of the solvent types for the liquid phase FAL hydrogenation will be of much more importance to give direction to future research work[38]. Moreover, according to the principle of green chemistry, these organic solvents can create negative effects on living organisms. Therefore, water was also used as a green solvent in this work, and its performance is compared with organic solvents. Operational variables such as reaction temperature, H₂ pressure, reaction time, and catalyst dose and reactant concentration also instigate major effects. In this work, to the best of our knowledge, a comprehensive study was made for the first time to show the effect of different solvents and discussed the role of solvent on conversion and selectivity in FAL hydrogenation reaction over the best catalyst selected from a screening of various catalysts.

In this paper, several Cu/Zn/X-Y [X-Y = Al_2O_3 , Al_2O_3 -ZrO₂, Al_2O_3 -TiO₂, Al₂O₃-MgO, La₂O₃, hydrotalcite (without Zn)] were synthesized. Two supported catalysts Pd/Activated carbon, and Cu/ Hydrotalcite was also synthesized and tested for comparative evaluation of catalysts. The performance of these catalysts was examined and compared in terms of catalyst activity and stability for the chemoselective hydrogenation of FAL to FA. Furthermore, the effect of several solvents, including protic, aprotic polar, and aprotic apolar was investigated over the Cu/Zn/Y/Z catalyst system. The chemistry has been discussed considering solvatochromic solvent parameters such as hydrogen bond acceptance capability (β), hydrogen bond acceptance capability (α), and the polarizability/polarity index (Π^*). The effects of different operating conditions (temperature, time, H2 pressure, reactant concentration, and catalyst weight) were measured on conversion, selectivity, and FA yield. Moreover, the long term stability of catalyst and kinetics of the hydrogenation reaction were examined due to their importance from an industrial point of view.

2. Experimental

2.1. Materials

Copper nitrate trihydrate salt (Aldrich, Germany) was used as a copper source in all the catalysts. The reactant furfural [chemical formula = $C_5H_4O_2$, M.W. = 96.09 g/mol] was sourced from TCI Japan and used without additional purification. Other chemicals used were zinc nitrate hexahydrate (Aldrich, Germany), nitric acid (SD fine Chemicals, India), magnesium nitrate hexahydrate (Aldrich, Germany), aluminum nitrate nonahydrate (Aldrich, Germany), lanthanum trinitrate hydrate (Aldrich, Germany), and sodium carbonate (Rankem, India). The chemical composition of the prepared catalysts is given in Table 1.

2.2. Catalyst preparation

Different catalysts were prepared using co-precipitation and wetimpregnation method [39]. Cu/Zn/X-Y catalysts were synthesized using the co-precipitation method under semi-batch reaction conditions. In a typical process of preparing CZAl samples, two solutions A and B were prepared. The solution A containing metal ions (1 M) was prepared by dissolving copper nitrate trihydrate, zinc nitrate hexahydrate, and aluminum nitrate in 290 ml of distilled water with 7.5 ml of concentrated nitric acid. Solution B (1.6 M) containing sodium carbonate was prepared to adjust the pH. Solution A was introduced slowly by a peristaltic pump in a container holding 400 ml of distilled water at T = $65 \degree$ C, and a constant pH = 6.5 was maintained by controlling the flow of solution B. The mixture was stirred continuously to keep uniform condition throughout precipitation in the semi-batch reactor. After completion of the controlled pH precipitation process, the suspension was aged for 90 min under the same condition, filtered, washed with deionized water until pH is neutral, and dried overnight at 100 °C. The dried powder (green in color) was grinded to obtain fine powder (fresh

CZAl) and calcined in a muffle furnace. The catalyst was heated to 350 $^{\circ}$ C at heating rate 1 $^{\circ}$ C/min and aged at the same temperature for 6 h. The obtained sample was black in color. Other catalysts such as CZ, CA, CZCr, CZCr, CZAlLa, CZAlZa, CZAlTi, CZMgAl, and CZZr were prepared following a similar procedure.

Two supported catalysts Cu(10 wt%)/hydrotalcite and Pd(3 wt %)/activated carbon were prepared using the incipient wetness impregnation method. In a typical process of synthesizing Cu/hydrotalcite, the required amount of copper nitrate hexahydrate precursor was dissolved in 10 mL of deionized water in a round bottom flask to which 2 g of hydrotalcite (HT) was added. The sample was kept at 80 °C under constant stirring until the complete water evaporated. The catalyst sample was further washed with an excess of water, dried at 100 °C for 12 h. Subsequently, the dried powder was calcined in a muffle furnace for 4 h at 550 °C to obtain the powder of Cu/MgO-Al₂O₃ particles. A similar process was followed to prepare Pd(3 wt%)/activated carbon. Commercial CuCrO₃ catalyst was also used for hydrogenation of FAL and designated by the code of CCr.

2.3. Catalyst characterization

The crystallinity of the samples was analyzed from X-ray diffraction (XRD) pattern recorded on the ROTO AXRD benchtop system using monochromatic Cu-K α radiation ($\lambda = 1.542$ Å) at 40 kV and 40 mA. The XRD patterns of all the samples were recorded in the 2 θ range of 20°-80° with a 0.04 step size. The average crystallite size (T) was calculated using the Scherrer formula (eq. 1):

$$T = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

Where K (dimensionless shape factor) = 0.9, λ = X-ray wavelength, θ = Bragg angle and β = line broadening at the half-maximum intensity (FWHM). The textural properties of all samples were evaluated by N₂ sorption measurements at -196 °C using Micromeritics ASAP 2020 Surface area and Porosity analyzer. Before the analysis, the degasification of the samples was carried out at 240 °C for 6 h. The BET model was fitted to isotherms between relative pressure ranges ($P/P_0 = 0.05$ -0.3) to determine the specific surface area of samples. Total pore volume was estimated using N2 adsorption data of isotherm at relative pressure $P/P_0 = 0.99$. The average pore size was determined using the Barrett-Joyner-Halenda (BJH) method. Temperature programmed reduction (TPR) analysis was carried out to check the reducibility of the synthesized material. TPR experiments were conducted in a Micromeritics, AutoChem II 2920 instrument connected with a thermal conductivity detector (TCD). The analysis was carried out in the temperature range of 40-900 °C with an increment of 10 °C per minute using Helium as a carrier gas. The microstructure of the sample was analyzed using a high-resolution transmission electron microscope JEOL JEM 2100. First, the sample was dispersed into ethanol and then mounted on a lacey carbon formvar coated copper grid. Elemental analysis of the synthesized samples was carried out by energy-dispersive X-ray spectroscopy (EDX). Thermal gravimetric analysis (TGA) analysis of the samples was performed in the air on a Perkin Elmer TGA 8000 thermal analyzer maintaining a flow rate of 30 mL/min and heating rate of 20 °C/min.

2.4. Catalyst activity

All batch experiments were carried out in a 25 ml Parr reactor equipped with a heating system, pressure gauge, and overhead stirrer (Fig. 1). Prior to every reaction, all Cu-based catalysts were reduced at 300 $^{\circ}$ C for 2 h. The reaction solution of FAL of desired concentration was freshly prepared in HPLC grade water, and catalytic hydrogenation of this solution was performed with continuous stirring at 700 RPM. In each experiment, the 15 mL solution was taken, and the desired amount



Fig. 1. Schematic diagram of liquid phase batch reactor.

of catalyst was introduced. The closed vessel was purged three times with nitrogen, and the pressure of H_2 gas was maintained. The reaction temperature was maintained using a temperature controller, and this time was considered as time zero (t = 0).

After the reaction time over, the reactor was allowed to cool down at room temperature and followed by the sample preparation for product identification. Conversion of FAL and selectivity of the product was measured using an Agilent GC equipped with an ionization detector (FID) and a DB-Wax capillary column (30 m ×0.530 mm and 1.0 micron). The FID and injection port temperatures were 270 °C and 250 °C, respectively. Helium was used as a carrier gas. Reaction products were confirmed using a Thermo scientific (Trace 1310) GC-MS equipped with a DB-5 capillary column (30 m ×0.320 mm and 1.0 micron). The interface and ion source temperatures were 280 °C and 250 °C, respectively. Conversion of Furfural was measured using the following equation:

$$X_{Furfural}(\%) = \frac{(Initial \ concentration - \ final \ concentration)}{Initial \ concentration} * 100$$

$$S_{Product}(\%) = \frac{X \ product \ (moles)}{X \ furfural \ moles \ (in) - X \ furfural \ moles \ (out)} * 100$$

Where, $X_{Furfural}$ and $S_{Product}$ (%) are the conversion of furfural and selectivity of product, respectively. $X_{Furfural moles (in)}$, $X_{Furfural moles (out)}$ are the moles of furfural at inlet and outlet.



Fig. 2. Powder XRD patterns of the trimetallic and tetrametallic based nanoparticles. (a) CZAl, (b) CZLa, (c) CZAlZr, (d) CZAlMg, (e) CZAlTi, and standard reference XRD patterns of (f) CuO, (g) Cu, and (h) ZnO.

2.5. Reductive process of FAL

The reductive process of FAL was performed in a stainless steel highpressure reactor. Followed by 1.0 mmol of FAL in 15 mL water and 0.5 g of CZAl catalyst were introduced in the reactor then purged with both gas N₂ and H₂ and after all pressurized at 1 MPa of H₂ and heated at 100 °C under stirring (700 rpm).

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD

The powder X-ray diffraction (XRD) was carried out to examine the crystallinity and identification of crystalline phases present in catalysts. XRD patterns of the freshly calcined trimetallic and tetrametallic catalysts are shown in Fig. 2. The diffraction patterns of freshly calcined catalysts display high-intensity peaks at diffraction angle 35.5° and 38.7° corresponding to (002) and (111) planes respectively, of CuO crystallite (JCPDS card no. 450937). The average crystallite size (T) of CuO was calculated using the Scherrer formula (Eq. 1) and calculated 5.0 nm. All of these catalysts also demonstrate diffraction peaks of ZnO appear at diffraction angle 32° , 48° , 62° , 68.5° and 69.7° corresponding to lattice plane (100), (102), (103), (112) and (201) (JCPDS card no. 361451). The diffraction peak of Al_2O_3 and other oxide promoters (Y or YZ) have not been detected due to lower amount in XRD pattern of material.

XRD patterns of the selected catalyst have also been presented in Fig. 12 at three different stages (fresh, reduced, and spent) to analyzed the structure transformation at each stage. The diffraction pattern of reduced CZAl exhibits a diffraction peak at angle 43.2° , 50.4° , and 74.1° (JCPDS card no. 00-004-0836) appeared after-treatment of the catalyst with H₂, which can be attributed to metallic copper Cu (0) after reduction. The XRD pattern of the spent CZAl catalyst was almost similar to the reduced catalyst. Some new phase was observed in the spent sample, but the presence of metallic copper peak indicated that catalyst could be reused again. The ZnO phase was present in the reduced and used the sample as observed in the fresh catalyst. Therefore, the ZnO phase was non-reducible and remained unaffected, which is also seen clearly in TPR pattern that is Zn is non-reducible under the reaction temperature. This result indicates the high framework stability of CZAl under extreme hydrogenation reaction conditions.

3.1.2. Microscopic analysis

The morphology of the calcined CZAl catalyst was studied using HRTEM analysis. CZAl appears as an agglomerate of CuO and ZnO



Fig. 3. TPR profiles of CZAl catalyst.



Fig. 4. A) N₂ adsorption-desorption isotherm of trimetallic and tetra metallic Cu based catalyst and B) Pore size distribution plot.



Fig. 5. a) TEM images, (b,c) HRTEM images d) SAED pattern of CZAl catalyst and (e,f) TEM images of CA catalyst.

5



Fig. 6. TEM mapping of a) Cu b) Zn, c) Al, d) CZAl image, and e) TEM images and f) HRTEM images of spent CZAl catalyst.

nanoparticles. CuO nanoparticles were present in irregular spherical shape-like morphology within a size range of 7-12 nm. On the other hand, ZnO nanoparticles of sphere-like morphology and size 7-10 nm were present. Whereas, the catalyst prepared by without using any morphology controlling agent and it might be the cause of the irregular spherical morphology of the CZAl catalyst (Fig. 5a & b). The TEM images of CA catalyst in Fig. 5e and f depicts that alumina exhibit needle like morphology. Instead of it CuO particle were observed in agglomerated state. 5a clearly indicated that ZnO induce uniformity in particle size and well dispersed. HRTEM image of a spherical nanoparticle shows lattice fringes with constant spacings of 0.24 and 0.28 nm corresponding to that of (101) and (100) planes of ZnO (Fig. 5c). The nanoparticles show lattice fringes with spacings of 0.23 and 0.25 nm corresponding to that of (111) and (002) planes of CuO (Fig. 5c). The co-existence of both phases is also supported by XRD analysis. The SAED pattern of CZAl samples clear the amorphous characteristic is dominating in analyses material, which is concomitant with the XRD result, which has been discussed in the previous section (Fig. 5d). HRTEM-EDAX mapping depicts that Cu and Zn elements are uniformly distributed within the CZAl sample. Higher intensity of Cu and Zn in comparison to Al appear because of their presence in major proportions within the sample. The morphology of the CZAl spent catalyst was also studied using TEM analysis (Fig. 6e & f). TEM images revealed that the morphology of the used catalyst remains stable with time. The morphology of the spent CZAl catalyst may be ascribed to the strong interaction between ZnO and metallic Cu. These results indicate the high stability of the CZAl catalyst at the performed reaction condition.

3.1.3. H₂-TPR analysis

Hydrogen temperature-programmed reduction (H₂-TPR) analysis was carried out to determine the nature of the reduction pattern and type of reducible species present in catalyst because TPR is bulk analysis. Fig. 3 depicts the H₂-TPR profile of the selected CZAl catalyst sample. H₂-TPR profile of CZAl exhibited single sharp peak appeared at low reduction temperature (221 °C) and another broad area in the hightemperature region (450 -670 °C). These first hydrogen consumption peaks indicate the presence of CuO. According to previous reports, the reduction of pure CuO species occurs between 230-240 °C [40,41]. The lower temperature peak at 221 °C could be ascribed to CuO under the synergetic effect arising by contact of ZnO particles[42]. The higher hydrogen consumption at low reduction temperature indicates the presence of corresponding CuO species (under the interaction of ZnO particles) in major proportion. The percentage of surface oxygen decreases by increasing the size of copper oxide due to agglomeration. It was observed that the reducibility of the particle directly commensurates the size of the particle and synthesis procedure [41,43,44]. The TPR data also indicate that the choice of a reduction procedure under hydrogen at 230-250 °C is efficient for the full reduction of the metal [40]. Dhonphai et al. reported that the broad peak after 350 °C is due to ZnO reduction to metallic Zn[45]. CZAl catalyst showed the peak of Cu with smaller broadness due to the reduction of larger Cu crystals, which take higher time and more temperature for the reduction of copper oxide by the diffusion of H₂ over copper oxide particles during TPR analysis. The hydrogen consumption for Cu is found 0.1287 mmol for 0.0230 g of CuO.

3.1.4. N_2 sorption studies

The influence of the addition of an oxide promoter on the textural properties was investigated using N_2 sorption measurement at 77 K. As shown in Fig. 4A, according to the International Union of Pure and Applied Chemistry (IUPAC), type-III like isotherms with H3 hysteresis loops. This type of hysteresis loop appears because of slit-like pores with non-uniform shape and/or size. Fig. 4B depicts the BJH pore size distribution (PSD) of all samples. The broad BJH PSD curves may be attributed to the presence of non-uniform shape and size of pores. The H3 hysteresis and broad PSD curves indicate the availability of both

Table 2

Theoretical composition of synthesized catalysts and their nomenclatures.

Catalyst Code	Elemental composition (atom %) of co-precipitated catalyst							
	Cu	Zn	Al	La	Cr	Zr	Ti	Mg
CZAl	60	30	10	-	-	-	-	-
CZLa	60	30	-	10	-	-	-	-
CZCr	60	30	-	-	10	-	-	-
CZAlZr	60	30	5	-	-	5	-	-
CZAlTi	60	30	5	-	-	-	5	
CZAlMg	60	30	5	-	-	-	-	5
CZ	60	40	-	-	-	-	-	-
CA	60	-	40	-	-	-	-	-
Catalyst Code Supported catalyst								
Cu-HT ^{Imp}	Cu-HT ^{Imp} 10 wt% Cu-Hydrotalciite							
Pd-AC ^{Imp}	3 wt % Pd-Activated Carbon					Activated Carbon		
CCr	Commercial CuCrO ₃							

Table 3

Physiochemical properties of the CZAl nanoparticle catalysts.

Catalyst	BET surface (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Morphology From TEM	Average particle size From XRD ^a
CZAl	137	0.47	Spherical	5.0
CZAl	118	0.45	Spherical	-
(spent)				
CZLa	192	0.49	-	-
Cu/HT	256	0.33	-	-
CZMgAl	238	1.05	-	-
CZAlTi	186	0.58	-	-
CZAlZr	182	0.53	-	-

^a Measured by Scherrer equation.

macropores and mesopores in samples. TEM images of CZAl samples also corroborate similar findings (*vide supra*). Table 3 shows the BET surface area and pore volume of all samples and also summarizes the surface area and pore volume of the spent catalyst. The decrease in surface area and pore volume is very slighter in comparison to the fresh catalyst due to adsorption of furfural and furfuryl alcohol after five cycles. These results indicate the stable framework of catalysts in the reaction condition.

3.1.5. Thermogravematric analysis

The thermal decomposition of the fresh CZAl precursor shows twoweight loss upon heating under a flow of O₂ as depicted in Fig. 14A of the supporting information. In the first step, 100-200 °C, the weight loss observed due to the decomposition of physically adsorbed moisture. In the second step, the weight loss observed in the range of 190-330 °C, indicating the removal of crystalline water and carbonates present in the fresh CZAl catalyst. This result shows that the calcination conditions employed (350 °C, 6 h) were enough to decompose all the Cu, Zn, and Al precursor salt and conversion of metal hydroxide form into metal oxide nanoparticles. The TGA curve of the spent CZAl catalyst after reaction shows the presence of crystalline water in the range of 150-200 °C in Fig. 14B.

3.2. Catalytic activity

3.2.1. Screening of catalyst

The performance of catalysts was checked in a Parr reactor at temperature range 100 °C and 1Mpa of H₂ at 4 h reaction time. The activities of the catalysts were tested by changing the oxide composition shown in Table 2. Cu/ZnO based catalyst has excellent catalytic hydrogenation activity and low cost [46,47]. Robert schlogl. et al. reported metallic copper is more active for CO hydrogenation [48]. ZnO is used as a hydrogen activator for CO hydrogenation, and the synergetic effect of





Fig. 7. FAL conversion and product selectivity over various catalysts (A) 1.5 h and (B) 4 h reaction time. Reaction conditions: All reactions were run with a FAL of 1 mmol, a catalyst loading of 0.05 g, 15 mL of H_2O as a solvent, a temperature of 100 °C, and an H_2 pressure of 1 MPa. *Reaction condition: All reactions were run with a FAL of 104 mmol, a catalyst loading of 2.5 g, a temperature of 180 °C, and an H_2 pressure of 2 MPa.

Cu/ZnO catalyst enhances the catalytic performance [49,50]. Gomez et al. examined the hydrogenation of furfural over Cu/ZnO catalyst and found 93% conversion of the furfural and 82% selectivity of furfuryl alcohol at higher temperature 463 K [26]. To improve the efficiency of structural based sensitive reaction, we have tried by adding small amount of some metal species such as Al^{3+} , La^{3+} , Zr^{4+} , Ti^{2+} , Mg^{2+} as promoters. Among the metal species, trivalent improve the stabilization of copper on the surface of the reduction and reaction processes. Y Tsai. et al. reported that, a doping of small amount of Al_2O_3 resulted in markedly different structure and surface area and also improve the hydrogenation of CO compared to Cu-ZnO based catalyst[30,50]. Zheng, et al. prepared Ln-Cu/SiO₂ based catalyst, improved the Cu dispersion and formation of Ln-O-Cu bond between lanthanum and copper, present at interfacial sites, and improved the hydrogenation performance [30].

Fig. 7 shows the comparison of the catalytic activity of various catalysts in terms of FAL conversion and product selectivity. The corresponding experiments were conducted with FAL concentration =1





Fig. 8. A) Conversion and **B)** selectivity to FAL obtained in various solvents over the CZAl catalyst. Reaction conditions: - All reaction were run with a FAL of 1 mmol, a catalyst loading of 0.05 g, 15 mL solvent, a temperature of 100 °C, reaction time 4 h and an H₂ pressure of 1 MPa. MeOH: methanol, EtOH: ethanol, IPA: 2-propanol, DMF: N, N'-dimethylformamide, ATE: Acetone, TOL: toluene, CHE: cyclohexane. Colors represent: furfuryl alcohol, furan 2-diethoxymethyl, tetrahydrofurfylalcohol, furfuryl acetone, motors.

mmol, catalyst loading = 0.05 g, temperature =100 °C, and H₂ pressure =1 MPa for time 1.5 h and 4 h. CZAl showed high catalytic activity with >99% conversion and >99% selectivity. CZ shows lesser conversion and selectivity compare to CZAl catalyst. Commercial CCr catalyst was also tested and there was no conversion of furfural found with water as a solvent. Instead of it, CCr catalyst without solvent performed >99% conversion of FAL and 98% selectivity of FA at high temperature (180 °C) and high pressure (2 MPa) in 4 h (Fig. 7b). Other catalysts such as CZLa, CZAlMg, and CZAlZr exhibited similar selectivity (>99%) as CZAl for FA; however, the conversion was very less in comparison to CZAl. It can be seen from both Fig. 7a and b, that CZAlTi is less active than CZAl. Among supported catalysts, Cu-HT ^{Imp} catalyst showed 80% conversion of FAL and >99% selectivity of FA after 4 h. On the other hand, 3% Pd-AC demonstrated 98% conversion but attained very low selectivity of 30% for desired product FA. These results indicate the unsuitability of

Table 4

H ₂ solubility and solvatochromic parameters of various	solvents $\begin{bmatrix} 67 - 69 \end{bmatrix}$.
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Entry	Solvent	β (-) ^a	α (-) ^b	П*(-) ^с	X _{H2} x 10 ⁴ (-) d
1.	Water	0.18	1.17	1.09	0.14
2.	Methanol	0.66	0.98	0.60	1.61
3.	Ethanol	077	0.83	0.54	2.06
4.	2-Propanol	0.95	0.76	0.48	4.61
5.	DMF	0.69	0.00	0.88	1.47
6.	Acetone	0.48	0.08	0.71	2.87
7.	Toulene	0.11	0.00	0.54	3.15
8.	Cyclohexane	0.00	0.00	0.00	4.14

^a Hydrogen bond acceptance ability.

^b Hydrogen bond donation ability.

^c Polarizability index/ Polarity.

 $^{\rm d}\,$ H_2 solubility in mole fraction at 298 K and 1 atm.

Table 5

Total conversion observed in furfural hydrogenation over the CZA catalyst versus the mole fraction of H_2 in solvents used (Table 4).

Entry	Solvents	X _{H2} x 10 ⁴ (-)d	Conversion (%)
1	H ₂ O	0.14	100
2	Methanol	1.61	99
3	Ethanol	2.06	99
4	2-Propanol	4.61	19
5	Acetone	2.87	98
6	DMF	1.47	98
7	Toulene	3.15	77
8	Cyclohexane	4.14	4

noble metal at the used reaction condition. Since the Cr-based catalyst is used in conventional processes, a Cr-based CZCr catalyst is also synthesized and tested. As observed for CZAl, CZCr showed high catalytic activity with >99% conversion and >99% selectivity. As mentioned above, Cr is a toxic and hazardous metal; therefore, CZAl can be used as a better alternative to Cr-based catalysts. The high catalytic activity of CZAl can be attributed to the positive role of the Al promoter to enhance the synergistic effect between the zinc and copper elements. A reaction was also performed in the absence of a CZAl catalyst using the same reaction condition, and a negligible FAL conversion was observed. Due to the highest catalytic activity, CZAl was selected to find a suitable solvent and optimization of reaction parameters (*vide infra*).

3.2.2. Studies in the effect of solvent

To obtain high selectivity for furfuryl alcohol, the catalyst and process conditions should not allow the over hydrogenation products and formation of side products. Under the reaction condition except for furfuryl alcohol, tetrahydro furfuryl alcohol, furan 2-(diethoxy methyl), and cyclopentanone were formed as a by-product over CZAl catalyst. The formation of furfuryl acetone, furan -2- diethoxy methyl, tetrahydro furfuryl alcohol, and other product also detected in smaller amounts.

The liquid phase hydrogenation of FAL was investigated over the CZAl catalyst. Their BET surface area was $137 \text{ m}^2 \text{ g}^{-1}$. Fig. 8A shows the results of furfural conversion in the various organic solvent over the CZAl catalyst at $100 \,^{\circ}$ C under the same parameters. The solvent's effects for hydrogenation of FAL over the CZAl catalyst are examined by polar solvent methanol, ethanol, isopropanol, water, and polar aprotic solvent acetone, DMF and non-polar solvent toluene, cyclohexane. The conversion and selectivity notably different in among the solvents examined and also the solvent influence is completely different with different catalysts as well as selectivity also varied with these examined solvents

Table 6

A) The conversion over CZAl v/s the α values of the solvents, and B) The conversion over CZAl v/s the β values of the solvents.

A)

Entry	Solvent	α (-) b	Conversion (%)
1	H ₂ O	1.17	100
2	Methanol	0.98	99
3	Ethanol	0.83	99
4	2-Propanol	0.76	19
5	Acetone	0.08	98
6	DMF	0.00	98
7	Toluene	0.00	77
8	Cyclohexane	0.00	4

B)

Entry	Solvent	β (-)a	Conversion (%)
1	H ₂ O	0.18	100
2	Methanol	0.66	99
3	Ethanol	0.77	99
4	2-Propanol	0.95	19
5	DMF	0.69	98
6	Acetone	0.48	98
7	Toluene	0.11	77
8	Cyclohexane	0.00	4

(Fig. 8A and B). Obtained results of the reaction indicate the effects of the solvents in heterogeneous catalytic hydrogenation included the interaction between substrate and solvent and interaction between metal and solvent; for the metal-solvent interactions, the size of the metal nanoparticles and the state of oxidation of active metal plays a pivotal role. Akpa et al. made DFT calculations for hydrogenation of 2butanone on Ru catalyst in the presence of IPA was higher activation barrier that than in water by 12 KJ mol⁻¹, confirming the stabilization by alcohols is weaker than water [51]. Solvents play an important role in stabilizing the specific reaction intermediate and transition state bound to the catalyst, thus resulting dependence of reaction rate or selectivity on the polarity of the solvent. The activity difference is associated with polarity, FAL solubility in a solvent, and Hansen solubility parameters. Trasarti et al. reported the hydrogenation of acetophenone using SiO₂ supported Ni, Co and Cu catalysts in different solvent IPA, cyclohexane, toluene and benzene. Considering the four solvents, the activity pattern of four solvents was IPA > cyclohexane > toluene > benzene [52]. For the presented pattern, several factors are attributed such as polarity, solvent-metal interaction, adsorption, due to blockage of active sites by

adsorption of solvent on the active sites of the metal etc.

Some other factors include H_2 solubility in the solvent and donating ability with solvents beneficial for hydrogenation reaction as well as the factor for determining the overall reaction rate. H_2 solubility in water is minimum compared to organic solvent (Table 5), which shows a similar conversion in methanol and water; however, it has affected the selectivity of furfuryl alcohol. The relationship between FAL conversion and H_2 solubility in a solvent was examined (Table 5). The FAL conversion did not significantly follow the H_2 solubility, which is not correlated with the solvent effect observed. Then, the solvatochromic parameters and conversion values of the solvent shown in Table 4) was examined. The conversion value obtained over the CZA catalyst can be correlated with the (hydrogen bond donor) HBD capability (α). The conversion of FAL gradually increases with increasing HBD capability (α) of the polar protic solvent (Table 6A).

The hydrogen bond acceptance (HBA) capability (β) v/s conversion shown in (Table 6B) with polar aprotic and non-polar solvent although the conversion of FAL tends to increase with increasing HBA capability (β) both in the polar aprotic and non-polar solvent. In the case of the 2-





Fig. 9. (A) Catalytic performance over different temperature and (B) time for hydrogenation of FAL to FA, Reaction Conditions: - All reaction were run with a FAL of 1 mmol, a catalyst loading of 0.05 g, 15 mL of H₂O as a solvent, a temperature of 100 $^{\circ}$ C, a reaction time 4 h and an H₂ pressure of 1 MPa.

propanol solvent, the HBD capability (α) and the HBA capability (β) had minimum difference showing that the CZAl catalyst shows lesser FAL conversion. From Table 6A and B, it can be summarized that the conversion over the CZA catalyst followed the order of polar protic solvent > polar aprotic solvent > non-polar solvent.

3.2.3. Effect of temperature

The effect of the reaction temperature on conversion and selectivity was also studied. Model reactions were carried out at different reaction temperatures 60 °C, 80 °C, 100 °C, 120 °C and 140 °C at 1.0 MPa H₂ pressure and 4 h duration. From Fig. 9A, at 60 °C conversion level of FAL is 34%, whereas it gradually increases up to 100 °C. At 100 °C and 120 °C conversion level of FAL and selectivity percentage of FA is higher, however, at 140 °C it declines due to some side reactions. Therefore, the selected temperature for the catalytic hydrogenation of FAL to FA is 100 °C. These are particularly good results, revealing that an appropriate

reaction temperature could accelerate the hydrogenation reaction by increasing the reaction rate and minimize the over reduction. In the above condition, the catalyst is highly active and highly selective towards FA at low hydrogen pressures and low temperatures in 4 h.

3.2.4. Effect of time

The effect of reaction time, the conversion of FAL, and selectivity of furfuryl alcohol were investigated in the time range of 1-5 h. From Fig. 9B, it can be said that the selectivity of furfuryl alcohol was maintained >99% from beginning to the end of the reaction, while the conversion was proportionally increased with increasing the time duration. In studied time duration, no by-product formation was observed. This catalyst was solely generating the furfuryl alcohol. From Fig. 9B, it can be summarized that the duration of 4 h is selected in terms of the conversion of FAL.

3.2.5. Effect of pressure

The influence of pressure was tested for the liquid phase hydrogenation of FAL. The H₂ pressure is another key parameter for the hydrogenation of FAL. The reaction carried out in the range of 0.5 - 2.0 MPa pressure shown in Fig. 10. When under lower H₂ pressure, at 0.5 MPa pressure, the conversion level of the FAL is 66%, but it increases when increasing the pressure. At 1 Mpa the complete conversion of FAL is achieved whereas on increasing pressure the selectivity of the FA is declined. The FAL was easily hydrogenated to FA in the presence of metal sites. Further increasing the H₂ pressure, to 1.5 and 2.0 MPa the FA selectivity is 99 and 98%. For high selectivity of the desired product, the pressure is a necessary parameter in modulating the selectivity of the product.[53] Finally, the reaction reached a maximum conversion and selectivity under 1.0 MPa of H₂ pressure.

3.2.6. Effect of catalyst to FAL mass ratio

The effect of catalyst to FAL mass ratio in the hydrogenation of FAL was also examined by varying FAL dosage. From Fig. 11 clearly shows, the catalyst to FAL mass ratio 1:2.5 shows the >99% conversion of FAL and >99% selectivity of FA is achieved. After that, increasing the catalyst to FAL mass ratio up to 1:7.5, the conversion level of FAL decreases due to the inhibition effect. This retards the hydrogenation of FAL to produce FA. Their direct effect was seen on the values of conversion when on increasing the dosage of FAL, the conversion was gradually reduced. This indicated the catalyst to FAL mass ratio 1:2.5 is ideal for the complete conversion.

It is mostly observed that the deactivation of copper-based catalysts is one of the major drawbacks of copper catalysts. So recyclability is one of the major challenges if copper-based catalysts are used. After these promising results, the recyclability of the CZAl catalysts is tested. Fig. 13 has shown the results for five cycles of recyclability. So many factors were responsible for the deactivation of Cu based catalysts like Cu sintering, ZnO crystallite growth, metal-support interaction, and reaction carried on at high temperature, etc. Carmen et al. reported the hydrogenation by Cu/ZnO catalyst (5-24TOS) with improved conversion from 55.0 % to 60.0 % at 190 °C and 98 % selectivity [26]. Recently, Behrens et al. reported that Al³⁺ work as a catalytic promoter due to substitutional n-type semiconductor dopant in ZnO support, but small addition of Al precursor during synthesis exhibited enhanced stability and Cu-ZnO interaction compared to the non - Al-based catalysts [54]. Simon et al. has shown that the presence of water in the reaction product (seen by FT-IR analysis) from CO2 hydrogenation to methanol and water has been promoted to ZnO crystallization [55]. In our case, Al oxide interaction with CuZn oxide, minimum temperature of the reaction as well as water plays a very vital role for high conversion and high



Fig. 10. Catalytic performance over different pressure for hydrogenation of FAL to FA, Reaction Conditions: - All reaction were run with a FAL of 1 mmol, a catalyst loading of 0.05 g, 15 mL of H₂O as a solvent, a temperature of 100 °C, a reaction time 4 h, and an H₂ pressure of 1 MPa.



Fig. 11. Catalyst to FAL different mass ratio for hydrogenation of FAL to FA, Reaction Conditions: - All reaction were run with a FAL of 1 mmol, catalyst loading of 0.05 g, 15 mL of H_2O as a solvent, a temperature of 100 °C, a reaction time 4 h and an H_2 pressure of 1 MPa.

selectivity. In Fig. 12, XRD pattern of spent CZAl shows diffraction peak around $2\theta = 43.2^{\circ}$ (111), $2\theta = 50.4^{\circ}$ (200), and $2\theta = 75.0^{\circ}$ (004) are not much affected after reaction, rest other peaks of CuO, $2\theta = 35.5^{\circ}$ (002) and $2\theta = 38.7^{\circ}$ (111) intensity is increased. Although, the presence of metallic Cu peaks in the diffraction pattern of the spent catalyst indicates the catalyst remain active after the reaction. Therefore the catalyst shows the same conversion and selectivity up to five cycles (Fig. 13A). A conventional hot filtration test was done to confirm no leaching of Cu catalyst during the reaction. After 2 hrs reaction, the conversion of the catalyst was noted. The catalyst was separated out, and the reaction mixture was further continued for another 4 hrs, no change was found in noticeable conversion, which confirmed, no leaching of Cu particles found in the course of the reaction (Fig. 13B). In Table 1, I tried to make a comparison of the most relevant catalytic system with our effective catalyst, regarding the selective hydrogenation of the FAL to



Fig. 12. XRD pattern of fresh (a) fresh CZAl, (b) reduced CZAl, (c) spent CZAl catalysts.

furfuryl alcohol. From the comparison table and the summary of the activity data of FAL hydrogenation, it is shown that our Cu based catalyst shows good activity at 100 $^{\circ}$ C with green solvent compared to other literature reports. Our present catalyst CZAl is expected to find a reasonable place in the literature on hydrogenation of FAL to furfuryl alcohol.

3.2.7. Kinetic studies

The kinetic of liquid phase reaction specially α , β -unsaturated based aldehyde reactants, is more complex. These reactions are more influenced by factors such as metal specificity, solvent effect, metal interaction, as well as reaction parameters [56]. In order to determine the kinetic behaviour of this hydrogenation reaction, the FAL reaction profile has been fitted to a first-order kinetic model [ln(1/(1-X)) vs. t], where X is the conversion of FAL. Fig. 15A shows that the first-order model fitted well to the FAL conversion profile with R² > 0.96.





Fig. 13. (A) Recycling test for furfural hydrogenation to furfuryl alcohol over CZAl catalyst, (B) Hot filtration Sheldon's test. Reaction conditions: FAL of 1 mmol, a catalyst loading of 0.05 g, 15 mL of H_2O as a solvent, a temperature of 100 °C, a reaction time 4 h, and an H_2 pressure of 1 MPa.

Reaction rate constants (k_f) have been calculated from the slope of fitted straight lines at different temperatures and shown in Table 7. Rate constant (k_f) for FAL conversion increases with an increase in temperature and an estimated maximum value of 0.018 min⁻¹ at 100 °C.

(A)

Furthermore, activation energy (Ea) of FAL hydrogenation was calculated using the Arrhenius equation ($k_f = k_0 e^{\frac{E_R}{RT}}$). Fig. 15B shows the linear model of the Arrhenius equation (plots of ln k_f vs. 1/T). The activation energy for FAL hydrogenation to furfuryl alcohol was 44.85 kJ mol⁻¹. Actually, in this field of non- noble catalysts, not many reports are available on the Ea of liquid phase FAL hydrogenation. Gong et al. reported an Ea value of Cu/AC-SO₃H and Cu/AC was 189 and 131 kJ mol⁻¹ respectively [57]. Bonita et al. reported an Ea value of 51.1 KJ mol⁻¹ for RuMoP catalyst in liquid phase FAL hydrogenation [58]. Our Ea value is very close to the reported data. The average Ea value estimated for the Cu oxide-based catalyst might attribute to medium adsorption of FAL on the surface of the catalyst.

4. Conclusions

The present study reports a strong, effective consequence of solvent appearing on the reaction rate with heterogeneous catalyst gives higher conversion of FAL and selective hydrogenation of FA using the CZAl catalyst. The significant effects of interaction between the solvent and substrate were dependent on the catalyst used. Solvent effects were more important for the FAL selectivity as well as the total rate of FA hydrogenation. For the sustainable approach, water is a promising solvent and promoter for the selective hydrogenation of FA for the used catalyst. The hydrophilic nature of the catalyst is the main cause of its high HBD capability of α for CZAl and low HBA capability of β for selective hydrogenation over the CZAl catalyst. The development of a highly efficient process with the use of water as a solvent and recyclable catalytic system introduces a success towards a green system for furfuryl alcohol production.

CRediT authorship contribution statement

Gurmeet Singh: Writing - original draft, Methodology, Investigation. Lovjeet Singh: Formal analysis, Validation. Jyoti Gahtori: Data curation. Rishi Kumar Gupta: Data curation. Chanchal Samanta: Writing - review & editing. Rajaram Bal: Funding acquisition, Validation. Ankur Bordoloi: Conceptualization, Supervision, Project administration, Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.



Fig. 14. (A) TGA -DTA plot of fresh CZAl catalyst before calcination and (B) TGA -DTA plot of spent CZAl catalyst.

(B)



Fig. 15. (A) Kinectic model $[\ln(1/(1-X))$ vs. t], and (B) the linear model of Arrhenius equation (plots of ln k_f vs. 1/T).

 Table 7

 Kinetic parameters for hydrogenation of furfuryl to furfuryl alcohol

Temperature (°C)	K	R ²	E _a (kJ mol ⁻¹)	R ²
60	0.0032	0.95	44.85	0.96
80	0.0059	0.98	-	-
100	0.018	0.98	-	-

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G. Singh et al.

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