Full Length Article

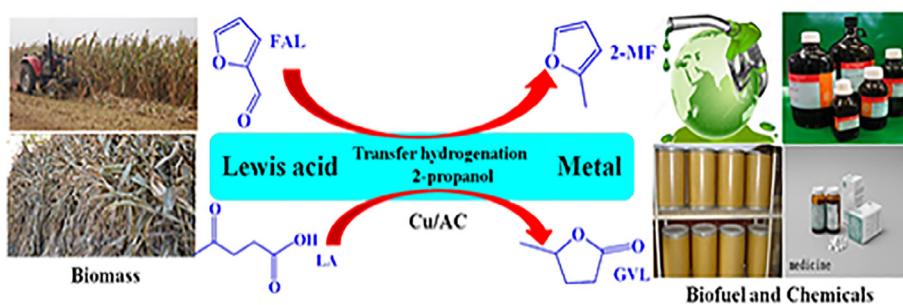# Transfer-hydrogenation of furfural and levulinic acid over supported copper catalyst

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GRAPHICAL ABSTRACT

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ABSTRACT

Transfer-hydrogenation (TH) has attracted great attention because it does not require the use of high pressure H_2. In this work, we report a facile ultrasound-assisted impregnation method with the aid of carbothermal reduction property of activated carbon (AC) to synthesize AC supported copper catalyst (Cu/AC) for efficient TH of bio-derived unsaturated oxygenated compounds such as furfural (FAL) and levulinic acid (LA). In the presence of 2-propanol as the hydrogen donor, within 5 h under 200 °C, the resultant Cu/AC catalyst can convert FAL into 2-methylfuran (2-MF, a high-value fuel additive) with a superior selectivity of 91.6%. The Cu/AC catalyst can also covert LA into γ-valerolactone (GVL) with a high selectivity of 89.9% under 220 °C for 5 h. The superior TH catalytic performance of the Cu/AC catalyst could be attributed to the uniform size and well dispersed Cu nanoparticles supported on the high surface area AC with the suitable proportion of Cu^{2+}, Cu^0 and Cu^+. Cycling test results confirm the reusability of the Cu/AC catalyst. Additionally, the reported Cu/AC catalyst is cheap and massive producible, advantageous for large-scale conversion of bio-derived platforms to value-added chemicals and bio-fuels.

1. Introduction

Due to the increased energy demand, rapidly diminished fossil resource and severe greenhouse emission, the development of enabling technologies that empower the use of abundant, carbon-neutral and renewable biomasses and their derivatives to replace petroleum-based

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materials for production of chemicals and fuels has received great attention [1,2]. In recent years, a noticeable progress has been achieved to efficiently transform lignocellulosic biomasses into biomass-derived platform chemicals such as furfural (FAL) and levulinic acid (LA) that can be further converted to high value-added chemicals and fuels [3,4]. FAL and LA are unsaturated oxygen containing C5 and C6 fraction of the biomass derived platform chemicals. FAL can be converted into a series of useful chemicals such as furfuryl alcohol (FOL), tetrahydrofurfuryl alcohol (THFOL) and 2-methylfuran (2-MF). Among them, 2-MF is particularly attractive as it can be used as high performance fuel additive that possesses fast burning rate and better knock-suppression ability. In addition, 2-MF is highly valuable as solvent or as reactant for production of antimalarial drugs (chloroquine), methyl-furfural, nitrogen and sulfur heterocycles, and functional substituted aliphatic compounds [5,6]. Various supported metal catalysts for conversion of FAL to 2-MF via direct hydrogenation/hydrodeoxygenation under high pressure H_2 has been reported [5]. To this end, the Cu-based catalysts displayed superior catalytic activities towards the cleavage of C-O bond and have been regarded as ideal catalyst candidates for selective conversion of FAL into 2-MF [7,8]. For example, Srivastava et al. reported a Cu–Co/g-Al$_2$O$_3$ catalyst that can achieve full conversion of FAL with a 78% 2-MF selectivity via direct hydrogenation route under 220 °C and 4 MPa H_2 pressure [9]. However, the need to use high pressure H_2 is an inherent drawback of the direct hydrogenation that induces high cost, complex reactor design, high requirements of storage and transportation, safety risk and restriction in operation. Thus, an alternative hydrogenation route, the transfer hydrogenation (TH), has recently gained an increased attention because it employs protic solvents (e.g., formic acid and 2-propanol) as hydrogen-donor to replace high pressure H_2 [10]. Among different protic hydrogen-donors, alcohols are a class of promising candidates due to the easy separation of their dehydrogenation products (aldehydes or ketones) from the targeted products [11]. To date, Ru-based catalysts have been extensively studied for TH of FAL to 2-MF. A reported Ru/C catalyst achieved a 61% yield of 2-MF from the TH of FAL [11]. Recently, Mironenko et al. reported a higher 2-MF yield of 76% using Ru/RuO$_2$ catalyzed TH of FAL in 2-propanol solvent. Importantly, they proposed a free-radical reverse Mars-van Krevelen-type reaction mechanism at the metal oxide vacancies that rationalizes the high C−O bond hydrogenolysis activity of the catalyst [12]. Nevertheless, little progress has been achieved in developing high performance non-precious metals based TH catalysts for conversion of FAL to 2-MF [5]. As a vital step to convert bio-derived platform chemicals into downstream chemicals, the development of efficient hydrogenation catalysts to transform LA to γ-valerolactone (GVL, a renewable solvent and sustainable fuel additive) has recently received much attention. The majority of the reported studies has been focused on developing noble metal based catalysts, especially Ru-based catalysts for direct hydrogenation of LA using high pressure H_2 [13–15]. Recently, ZrO$_2$ and Ru nanoparticles (NPs) based catalysts have been reported for TH of LA to GVL in different hydrogen-donors such as formic acid and 2-propanol [16,17]. Valekar et al. reported a zirconium-based metal-organic-frameworks catalyst for TH of ethyl levulinate into GVL using 2-propanol as hydrogen-donor, achieving a 92.7% yield of GVL within 2 h at 200 °C [18]. Hengne et al. recently developed a supported Ni catalyst with excellent TH activity, achieving a 99% LA conversion efficiency with 99% GVL selectivity [19].

We have previously demonstrated that a supported Cu catalyst can be used as high performance direct hydrogenation catalyst to achieve full FAL conversion with almost 100% 2-MF selectivity under 170 °C reaction temperature and 3 MPa H_2 pressure [20]. In this work, we further demonstrate that the activated carbon supported copper NPs (Cu/AC) catalyst can also be used as high performance TH catalyst to convert FAL to 2-MF and LA to GVL in absence of H_2. The catalyst synthesis conditions and important TH reaction parameters such as reaction temperature, reaction time, catalyst to FAL mass ratio and solvent were systematically studied to obtain optimal conditions and

reveal mechanistic pathways. With 200 °C reaction temperature, 5 h reaction time and 2-propanol as hydrogen-donor, the reported Cu/AC catalyst can convert FAL to 2-MF and LA to GVL with a superior 2-MF and GVL selectivities of 91.6% and 89.9%, respectively. Compared with the conventional Cu-based and noble metal-based catalysts, the Cu/AC catalyst reported in this work exhibited noticeable improved TH selectivity with added advantages of facile synthetic procedure and recyclability.

2. Experimental

2.1. Catalyst preparation and characterization

The Cu/AC catalysts with different Cu loadings were prepared by a facile ultrasound-assisted impregnation method with the aid of the carbothermal reduction property of activated carbon (AC). Firstly, AC (Aladdin) was treated by washing with deionized water and ethanol, followed by drying at 60 °C overnight. In a typical Cu/AC synthesis procedure, a suitable amount of the treated AC was mixed with an appropriate amount of Cu(NO$_3$)$_2$ (AR, Sinopharm Reagents, China) dissolved in deionized water. The resultant mixture was then impregnated by ultrasonication for 0.5 h and dried at 60 °C for 12 h. The ready to use Cu/AC was obtained by calcining the dried sample at 400 °C for 2 h with a ramp rate of 5 °C/min under a N$_2$ flow.

Transmission electron microscopy (TEM, JEOL-2010) images were obtained with an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) patterns were analyzed using a Philips X-Pert Pro X-ray diffractometer with the Ni-filtered monochromatic Cu K$_\alpha$ radiation ($\lambda K_{\alpha 1}$ = 1.5418 Å) at 40 keV and 40 mA. The surface area and porosity of samples were measured at 77 K using a Surface Area and Porosity Analyzer (Autosorb iQ Station 2). XPS analysis was performed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, USA) equipped with Al K$_{\alpha 1,2}$ monochromatized radiation at 1486.6 eV X-ray source. The catalyst Cu content was determined by the inductively coupled plasma spectroscopy (ICP 6300, Thermo Fisher Scientific) after the sample being microwave digested. The N$_2$O titration was employed to determine Cu particle size, size dispersion and specific area (Supporting Information).

2.2. Catalytic tests

TH of FAL and LA was carried out in a 25 mL stainless steel autoclave with a magnetic stirrer, a pressure gauge and automatic temperature control apparatus. In a typical experiment, the reaction solutions of FAL or LA (0.2 mmol), suitable amount of catalyst, and solvent (5 mL) were loaded into the reactor. The reactor was sealed, purged three times with N$_2$ at 1 MPa, then pressurized with N$_2$ usually to 2 MPa, heated to a targeted temperature and maintained for a predetermined reaction time. After reaction, the autoclave was quickly cooled down to room temperature. The contents were centrifuged to separate the catalyst from reaction products. The liquid products were identified using gas chromatography–mass spectrometry (GC–MS, Thermo Fisher Scientific-TXQ Quntum XLS) and quantitatively analyzed by GC (Shimadzu, GC-2010 Plus), equipped with FID using n-octanol as an internal standard. The carbon balance was checked in every run and found to be higher than 94%.

3. Results and discussions

3.1. Effect of Cu loadings on TH of FAL to 2-MF

The effect of Cu loadings (10.4 wt%, 17.1 wt% and 22.9 wt%) in the Cu/AC catalysts on TH of FAL were investigated using 5.0 mL 2-propanol as solvent at 170 °C reaction temperature for 5 h. As shown in Fig. 1, the Cu loadings strongly affect FAL conversion efficiency and resultant products. The FAL conversion efficiency and 2-MF selectivity
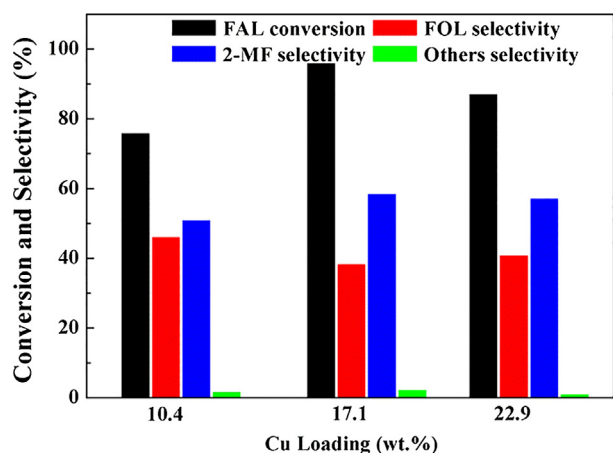
Fig. 1. TH of FAL with different Cu loadings in Cu/AC catalysts. Reaction conditions: Catalyst to FAL mass ratio = 1:1, FAL = 0.2 mmol, Reaction temperature = 170 °C, N_2 pressure = 2 MPa, Reaction time = 5 h, 2-propanol volume = 5.0 mL.

increased when Cu loading was increased from 10.4 wt% to 17.1 wt%, then slightly decreased when further increased to 22.9 wt%. The best performance was achieved with a Cu loading of 17.1 wt%, attaining a 96.3% FAL conversion efficiency and 58.8% 2-MF selectivity. The TEM analyses (Fig. 2) revealed that the formed Cu NPs are uniform in size and well-dispersed in AC support, desirable for catalysis applications. The results indicate that the average size of Cu NPs increased slightly from 20.7 to 22.8 nm when the Cu loadings increased from 10.4 to 22.9 wt%, due to the agglomeration effect. Similar results were reported by others where the FAL selectivity was dependent on the size and shape of the catalysts [21]. The elemental mapping images confirm that the Cu element is homogeneously dispersed in AC support for the 17.1 wt% Cu/AC catalyst (Fig. S1). The coexisting of Cu (1 1 1), Cu_2O (1 1 1) and CuO (0 0 2) planes suggested that copper oxide was partially reduced by the AC during this reduction process (Fig. S2). This means that Cu/AC catalyst is resulted from the partial reduction of CuO_x by AC ($CuO_x + C \rightarrow Cu + CO/CO_2$). The average particle size, dispersion and metal surface area of Cu NPs in the 17.1 wt% Cu/AC catalyst were determined by N_2O titration method (Table S1). The Cu NPs in the catalyst possesses an average particle size of 15.0 nm with a 6.7% dispersion and 7.8 $m^2 g^{-1}$ metal surface area. Additionally, the 17.1 wt% Cu/AC possesses micro-porous pore structures (Fig. S3) with a high BET surface area of 800 m^2/g (Table S1). These structural characteristics of Cu/AC suggest that the excellent catalytic performance is benefited from the uniform size, well dispersed Cu NPs supported on the high surface area AC with rational ratio of copper species ($Cu^{2+}:Cu^+:Cu^0$).

3.2. Effect of hydrogen-donor on TH of FAL to 2-MF

In a TH reaction, the conversion efficiency and selectivity is largely determined by the readiness to derive active H atom from the hydrogen-donor by a catalyst, which is heavily dependent on the chemical nature of the hydrogen-donor. A series of protic alcohol solvents including methanol, ethanol, 2-propanol, n-butanol, 2-butanol, n-pentanol and 2-pentanol were therefore selected as hydrogen-donors to investigate their effectiveness for TH of FAL to 2-MF at 180 °C reaction temperature and 5 h reaction time (Fig. 3). Except for methanol (probably because of too strong polarity), full conversion of FAL can be achieved when other alcohols were used as solvents. Different protic alcohols displayed different selectivities with FOL and 2-MF being the main products. The selectivity for the targeted 2-MF varied from 8.9 to 78.5% with a decreasing trend in an order: 2-propanol > 2-pentanol > 2-butanol > ethanol > methanol > n-butanol > n-pentanol. The iso- alcohols displayed higher 2-MF selectivity than that of

primary alcohols, due to a better evolution ability of active H from the dehydrogenation of alcohols as reported by Panagiotopoulou and co-workers [22]. In addition, the primary alcohols are found to be more inclined for side reactions such as etherification, leading to a decreased selectivity toward the desired product of 2-MF. For example, in the case of methanol as the hydrogen-donor, a considerable amount (16.1%) of ethers and acetals can be detected from the product mixture. When iso-alcohols were used as hydrogen-donor, the 2-MF selectivities were found to be 78.5% for 2-propanol, 77.1% for 2-pentanol and 70.2% for 2-butanol, respectively. The above experimental results demonstrated that for TH of FAL, the solvent properties, such as polarity, solubility and H-atom evolution ability can strongly influence the solvent-reactant interactions to significantly alter the FAL conversion efficiency and 2-MF selectivity.

3.3. Effect of reaction temperature on TH of FAL to 2-MF

The effect of reaction temperature (between 150 °C and 200 °C) on the TH of FAL to 2-MF was investigated using 2-propanol as hydrogen-donor and a reaction time of 5 h (Fig. 4). It was found that the FAL conversion efficiency increased from 59.6% at 150 °C to 100% at 180 °C. The changes in the product distribution were also observed as the reaction temperature increased. Specifically, a gradually decreased FOL selectivity accompanied with a proportionally increased 2-MF selectivity was observed with increased temperature, suggesting that FOL could be the intermediate to form 2-MF during TH of FAL. To further confirm this, TH of FOL to 2-MF under different reaction temperatures ranged from 150 to180 °C (Fig. S4). It was found that the FOL conversion efficiency increased with temperature and a near 100% 2-MF selectivity can be achieved at 180 °C. In addition, the 2-propanol dehydrogenation in absence of FAL was also investigated under different reaction temperatures to the pathway of forming active H* (Fig. S5). The results revealed that an increase in the reaction temperature results in an increase in the amount of acetone produced from 2-propanol dehydrogenation. This confirms that the rate of 2-propanol dehydrogenation increases with the reaction temperature. We could therefore deduced that the FAL was firstly reduced to the intermediate (FOL) by active H* derived from dehydrogenation of 2-propanol, and followed by the cleavage of C−O bond via hydrogenolysis to generate 2-MF. A 91.6% 2-MF selectivity was obtained at 200 °C, which is the highest selectivity reported to date under the identical reaction conditions [12,23].

3.4. Effect of reaction time on TH of FAL to 2-MF

Fig. 5 shows the effect of reaction time on the TH conversion efficiency and selectivity of FAL to 2-MF at 180 °C in 2-propanol solvent. The results reveal that FAL conversion efficiency increased with the reaction time. A full conversion efficiency can be attained within 5 h reaction. In the initial reaction stage, FOL was found to be the main product. However, as the reaction proceed, 2-MF became the dominant product. A 2-MF selectivity of 91.1% was attained when the reaction time was extended to 8 h. These results once again suggested that FOL was the intermediate in the TH of FAL to 2-MF, consistent with the previous reports [12,24].

3.5. Effect of catalyst to FAL mass ratio on TH of FAL to 2-MF

The catalytic performance of Cu/AC catalyst was examined by varying the catalyst to FAL mass ratio under 180 °C reaction temperature and 5 h reaction time (Fig. S6). As expected, FAL conversion efficiency decreased as the catalyst to FAL mass ratio decreased while no significant changes towards the product selectivity can be observed. In addition, the observed FAL conversion efficiencies was 99.9% at 1:1, 69.5% at 1:2 and 48.8% at 1:3, respectively. Such a decreasing tendency of conversion efficiency is lower than the multiplying factor of
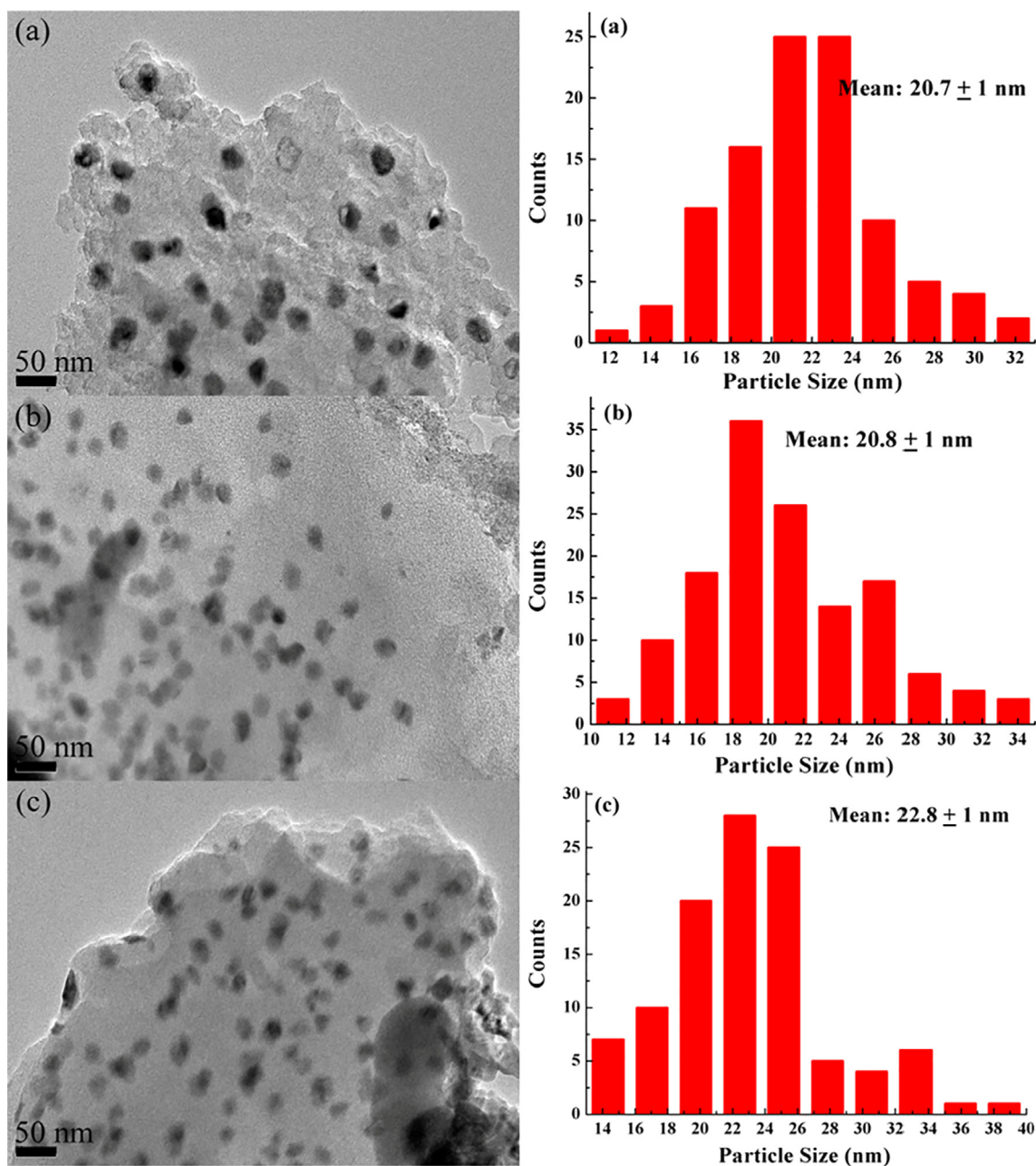
Fig. 2. TEM images of Cu/AC catalysts. (a) 10.4 wt% Cu/AC; (b) 17.1 wt% Cu/AC; (c) 22.9 wt% Cu/AC.

FAL loading amount. Importantly, this process can be easily scaled up to a larger amount. A gram scale experiment was carried out using 1.0 g of FAL as substrate at 200 °C within 5 h reaction, achieved a 71.9% 2-MF selectivity and full FAL conversion.

3.6. Catalyst stability in TH of FAL

Easy separation from the liquid product mixture after reaction is an important advantage of heterogeneous catalysts, which enables the catalyst reuse. The reusability of the Cu/AC catalyst was evaluated under a reaction temperature of 180 °C with 5 h reaction time and a catalyst to FAL mass ratio of 1:3. The results obtained from 5 test cycles revealed insignificant changes in FAL conversion efficiency, product distribution and 2-MF selectivity (Fig. 6), confirming an excellent stability and reusability of the Cu/AC catalyst. After the 5th test cycle, the recycled catalyst was characterized by ICP, XRD and TEM to confirm the structural stability of the Cu/AC catalyst. The ICP analyses data

indicate a decrease in Cu content from 17.1 wt% (the as-synthesized catalyst) to 16.9 wt% (the reused catalyst), suggesting a minimal catalyst leaching during the test cycles. The XRD pattern of the reused catalyst (Fig. S2) display that a portion of the copper oxides were reduced to metallic state under the reductive reaction conditions. The TEM image of the reuse catalyst shows similar particle size and particle dispersion as that of the as-synthesized catalyst (Fig. S7), indicating that no severe agglomeration of metallic particles taking place.

3.7. Catalytic performance for TH of LA to GVL

The TH catalytic performance of the Cu/AC to convert LA to GVL was also investigated using 2-propanol as the solvent and hydrogen-donor (Figs. 7 and 8). The effect of reaction temperature and reaction time on LA conversion efficiencies, product distributions and GVL selectivities shown in Figs. 7 and 8 follow the same trends as those shown in Figs. 4 and 5 for conversion of FAL to 2-MF. Quantitative conversion
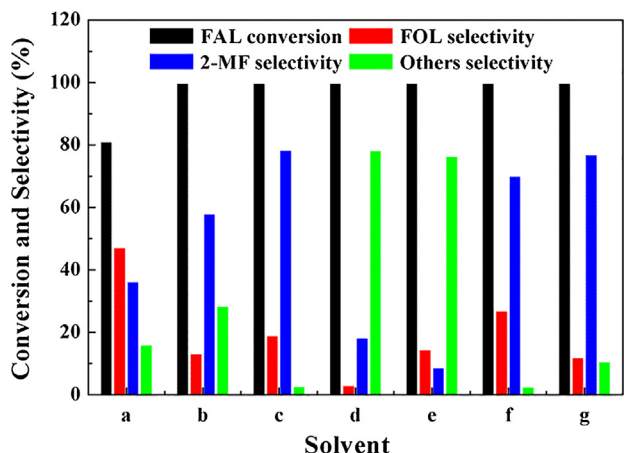
Fig. 3. Catalytic performance of 17.1 wt% Cu/AC for TH of FAL to 2-MF using different solvents of a: methanol; b: ethanol; c: 2-propanol; d: n-butanol; e: n-pentanol; f: 2-butanol; g: 2-pentanol. Reaction conditions: Catalyst to FAL mass ratio = 1:1, FAL = 0.2 mmol, Reaction temperature = 180 °C, N$_2$ pressure = 2 MPa, Reaction time = 5 h, Solvent volume = 5.0 mL.
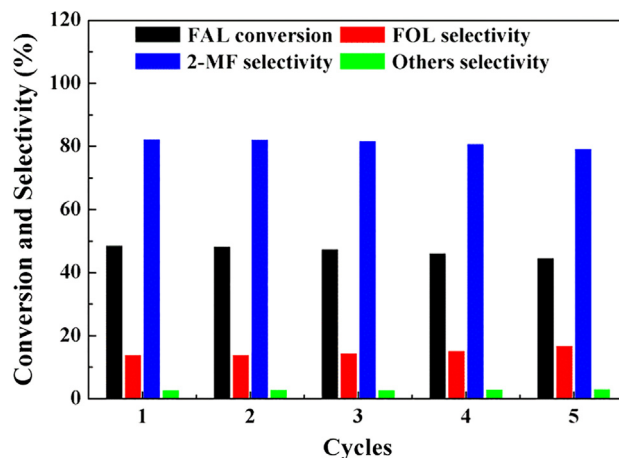

Fig. 6. Stability and reusability of 17.1 wt% Cu/AC catalyst in TH of FAL. Reaction conditions: Catalyst to FAL mass ratio = 1:3, FAL = 0.6 mmol, Reaction temperature = 180 °C, N$_2$ pressure = 2 MPa, Reaction time = 5 h, 2-propanol volume = 5.0 mL.
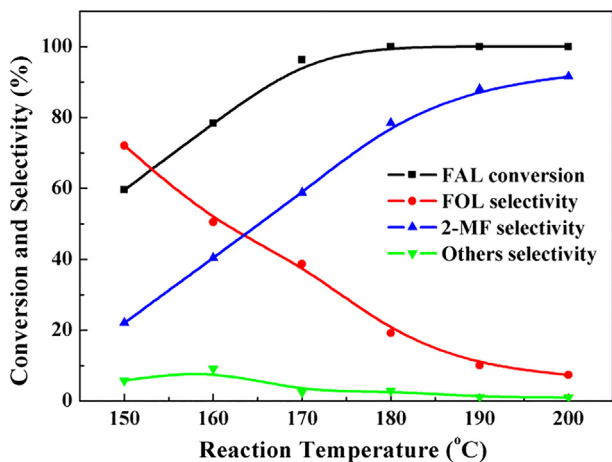

Fig. 4. Catalytic performance of 17.1 wt% Cu/AC for TH of FAL as a function of reaction temperature. Reaction conditions: Catalyst to FAL mass ratio = 1:1, FAL = 0.2 mmol, N$_2$ pressure = 2 MPa, Reaction time = 5 h, 2-propanol volume = 5.0 mL.
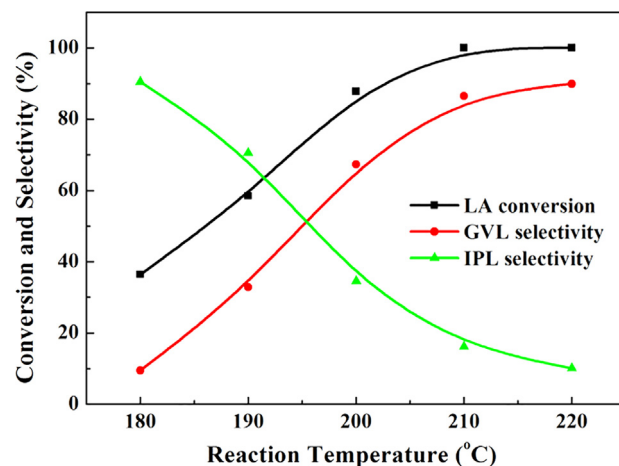

Fig. 7. Catalytic performance of 17.1 wt% Cu/AC for TH of LA as a function of reaction temperature. Reaction conditions: Catalyst to LA mass ratio = 1:1, LA = 0.2 mmol, N$_2$ pressure = 2 MPa, Reaction time = 5 h, 2-propanol volume = 5.0 mL.
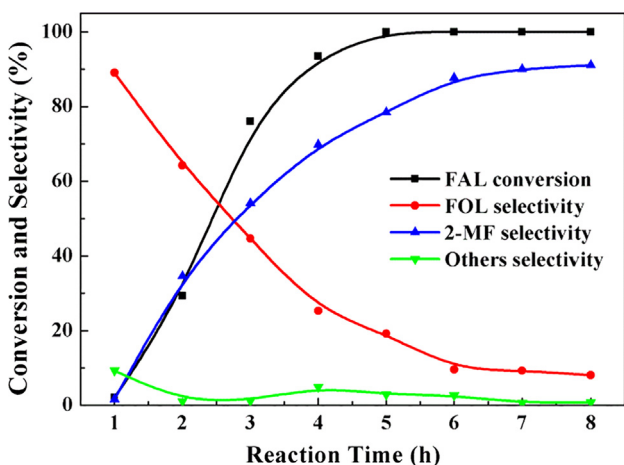

Fig. 5. Catalytic performance of 17.1 wt% Cu/AC for TH of FAL as a function of reaction time. Reaction conditions: Catalyst to FAL mass ratio = 1:1, FAL = 0.2 mmol, Reaction temperature = 180 °C, N$_2$ pressure = 2 MPa, 2-propanol volume = 5.0 mL.
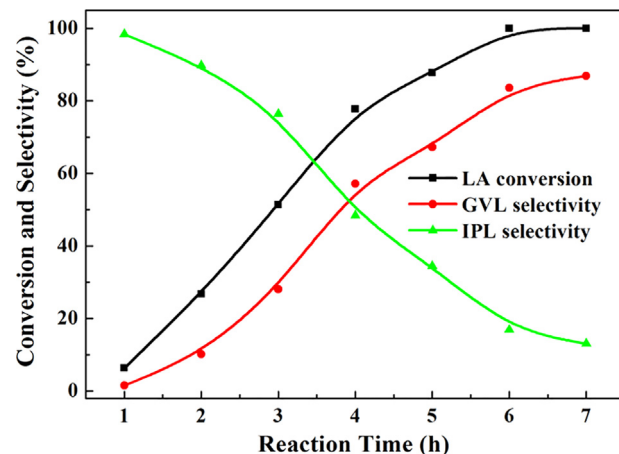

Fig. 8. Catalytic performance of 17.1 wt% Cu/AC for TH of LA as a function of reaction time. Reaction conditions: Catalyst to LA mass ratio = 1:1; LA = 0.2 mmol, Reaction temperature = 200 °C, N$_2$ pressure = 2 MPa, 2-propanol volume = 5.0 mL.

of LA (> 99%) with an 89.9% GVL selectivity can be achieved within 5 h reaction under a reaction temperature 220 °C. Deferring from converting FAL to 2-MF where FOL was the main intermediate, the main intermediate detected by GC–MS for conversion of LA to GVL was found to be isopropyl levulinate (IPL) form by the esterification of LA with 2-propanol. As can be seen from Fig. 8, the high IPL content was formed during initial stage of reaction and decreased with prolonged reaction time, accompanying with the increased GVL selectivity. Chia and co-workers reported that LA is less readily than its esters via the Meerwein–Ponndorf–Verley reaction [16]. Recently, Kuwahara et al. also reported that LA displays a lower reactivity toward the formation of GVL that of levulinate esters [25]. Based on our experimental results and others reports, we proposed that LA was firstly reacted with 2-propanol to form IPL as intermediate during earlier stage of the reaction and followed by the conversion of IPL into GVL with the aid of active H-atom derived from dehydrogenation of 2-propanol. Apparently, the achieved catalytic performance in this work is better than the reported performances [16–18], suggesting that the Cu/AC catalyst is an efficient and promising candidate for transforming LA to GVL.

3.8. Proposed mechanisms of TH of FAL to 2-MF and LA to GVL

In terms of adsorption sites, there are two types of well-known bonding configurations for FAL adsorption: η^1 (O)-aldehyde and η^2 (C,O)-aldehyde. Usually, the unsaturated aromatic or heterocyclic compounds are favorable to adsorb on the surface of noble metal catalyst such as Pt and Pd via the η^2 (C,O)-aldehyde configuration [26]. Different to Pt and Pd, the unsaturated compounds tended to adsorb on the surface of Cu via η^1 (O)-aldehyde configuration model, which leads to an efficient activation and hydrogenation of the side chain C=O group but weaker for hydrogenation of furan ring [27,28]. This can be evidenced by the formation of FOL intermediate during the earlier stage of the reaction.

For FAL hydrogenation, the active sites of Cu catalyst (e.g., metallic Cu or CuO_x) are still a contentious questions. Herein, the XRD patterns of Cu catalysts with various Cu contents are given in Fig. 9. The reflection peaks of Cu, Cu_2O and CuO phases are clearly visible from Cu catalysts containing different Cu contents. An increase in the Cu content results in an increase in CuO content as indicated by the relative intensity decrease of Cu and Cu_2O. This might be due to that for samples with high content of Cu precursor, the copper oxide are difficult to be completely reduced to metallic Cu at the carbothermal temperature of 400 °C. Fig. S8 shows the representative Cu 2p spectra of 17.1 wt% Cu/AC catalyst, in which Cu catalyst displayed the mixture species of Cu^{2+} and Cu^+/Cu^0. In order to distinguish between Cu^+ and Cu^0 species, the
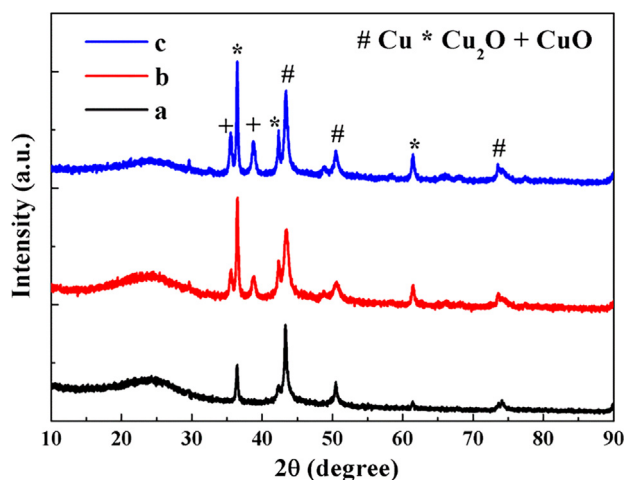

Fig. 9. XRD patterns of Cu/AC catalysts with different Cu contents of a: 10.4 wt% Cu/AC; b: 17.1 wt% Cu/AC; c: 22.9 wt% Cu/AC.

Cu LMM X-ray AES spectra (XAES) was also analyzed [29]. Unlike reducing gas of H_2 or CO, the use of solid reducing agents could easily control reduction rate and degree. In this work, the reduction of CuO_x NPs occurred at the contacting interface of CuO_x and AC [20]. As shown in Fig. 1 that FAL conversion efficiency and 2-MF selectivity increased with Cu loading from 10.4 wt% to 17.1 wt% and then decreased with further increased Cu loading to 22.9 wt%. Based on the above analysis, we deduced that the co-existence of Cu^0 and Cu^+ with appropriate ratio in the Cu/AC catalyst is responsible for the superior catalytic performance. In fact, such synergetic effect of co-existence of Cu^0 and Cu^+ species in catalysts has been previously reported to enhance FAL hydrogenation performance [30–32]. For example, Nagaraja et al. demonstrated that the enhanced selective formation of FOL is related to the existence of Cu^0 [33]. Rao et al. proposed that Cu^+ species were the active sites for FAL and crotonaldehyde hydrogenation [31]. Recently, Dong et al. showed a 95.5% yield of 2-MF from FAL hydrogenation in the presence of H_2 over AE-Cu/SiO_2 catalyst, in which the synergetic effect of Cu^0, Cu^+ species and acid sites were confirmed [8].

For the catalytic TH of FAL to 2-MF, Gilkey et al. concluded that the hydrogenation of the carbonyl group in FAL to a hydroxymethyl group proceeds via Meerwein–Ponndorf–Verley (MPV) reduction process (a Lewis acid-catalyzed intermolecular hydride transfer mechanism) and follows by the hydrogenation of the carbonyl group on metal sites to form intermediate FOL. The formed FOL undergoes hydrogenolysis via C−O bond activation involving both metal and Lewis acid sites, in which the metal sites serve mainly to produce active H-atom from hydrogen-donor and the Lewis acid RuO_x sites act as the active center to catalyze hydrogenolysis [24]. Mironenko and Vlachos demonstrated that high 2-MF yield in catalytic TH of FAL using 2-propanol solvent coming from the interplay of three catalytic functionalities: Lewis acid RuO_2 catalyze intermolecular hydride transfer (MPV reaction), oxygen vacancies in RuO_2 promote C-O bond scission, and metallic Ru are essential for maintaining dissolved H_2 concentration (from dehydrogenation of 2-propanol) and continuous vacancy regeneration [12]. For Cu-based catalyst, the electrophilic Cu^+ species can be considered as Lewis acid sites to activate C=O groups via the electron lone pair of oxygen to promote the activation of the C=O groups in FAL [8]. Based on the above discussions, it is reasonable to propose that FAL could be adsorbed on-top of Cu^+ species (Lewis acid sites) by carbonyl group via η^1 (O)-aldehyde configuration model. The Cu^0 species act as active centers for dehydrogenation of 2-propanol to generate active H*. The generated active H* diffuses to adsorb on Cu^+ species (Lewis acid sites) to activate the C=O bond in FAL via MPV reaction (Lewis acid-catalyzed intermolecular hydride transfer mechanism). The activated C=O bond is finally reduced to C-OH as a result of Cu^0 and Cu^+ synergistic actions. Moreover, in TH of FAL to 2-MF, the Cu^+ species also serve as acid sites to dissociation of C−O bond. Therefore, the TH active sites of Cu/AC should be Cu^0-Cu^+ complex. For the TH of LA to GVL, LA could be captured by the electrophilic Cu^+ species. It is well understood that the LA to GVL conversion in alcohol solvent essentially proceeds through the formation of LA-esters and followed by their hydrogenation on the catalytic surface [16]. Therefore, it could be regarded as accomplished by catalytic TH through the MPV reaction over Cu catalyst (Fig. 10).

4. Conclusions

We reported a simple synthetic route to obtain Cu/AC catalyst capable of efficiently converting FAL to 2-MF and LA to GVL using 2-propanol as hydrogen-donor via TH reaction route. Under the optimal reaction conditions, a 91.6% 2-MF selectivity with full FAL conversion, and an 89.9% GVL selectivity with full LA conversion can be attained within 5 h reaction. The superior catalytic performance of Cu/AC catalyst could be attributed to a dispersing effect of AC to prevent the aggregation of Cu NPs. It can also attributed to the rational proportion of copper species (Cu^{2+}, Cu^0 and Cu^+) in Cu/AC catalyst achieved
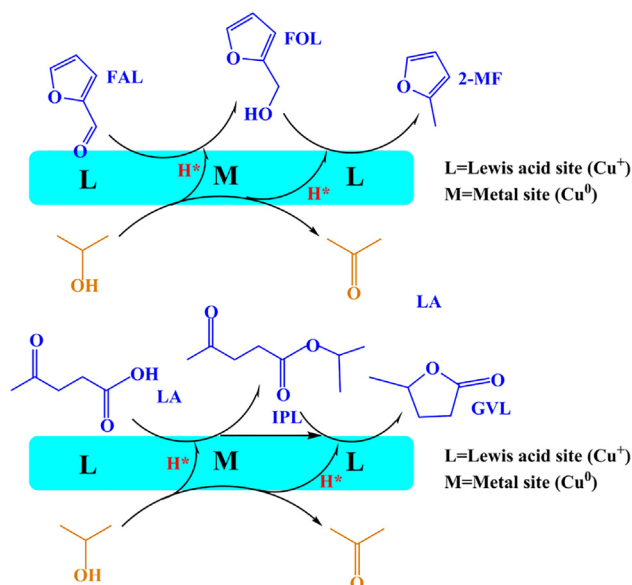
Fig. 10. Proposed reaction pathways of Cu/AC catalyst for TH of FAL to 2-MF and LA to GVL.

through the controllable interaction of AC and Cu precursor during the carbothermal reduction process. The cycle stability test results confirm the reusability of the catalyst. The possible reaction pathways are proposed based on experimentally detected intermediates. For TH of FAL to 2-MF, Cu^+ species adsorb and activate the $C = O$ bond in FAL via MPV mechanism, and Cu^0 species act as active centers for dehydrogenation of 2-propanol to generate active H∗. For TH of LA to GVL, LA is captured by the electrophilic Cu^+ species, then accomplished by catalytic TH through the MPV reaction at Cu catalyst. This study paves a way to use cheap and earth abundant catalysts for efficient transformation of biomass derived unsaturated compounds into value-added chemicals.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2018.05.075.

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