

Efficient Synthesis of Furfuryl Alcohol from H₂-Hydrogenation/Transfer Hydrogenation of Furfural Using Sulfonate Group Modified Cu Catalyst

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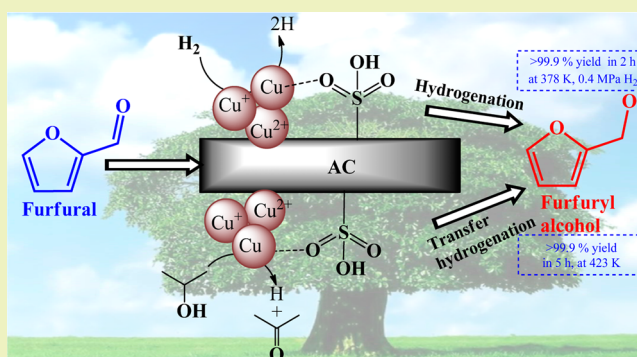
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Supporting Information

ABSTRACT: A copper-based catalyst, which was supported by sulfonate group (–SO₃H) grafted active carbon (AC), was prepared and activated simultaneously by liquid phase chemical reduction method. The modified copper catalyst, Cu/AC–SO₃H, displayed an enhanced catalytic performance for selective hydrogenation of furfural (FAL) to furfuryl alcohol (FOL) in liquid phase, in which almost 100% FOL yield was obtained at 378 K and 0.4 MPa of hydrogen pressure after 120 min reaction. The effect of –SO₃H was evaluated and illustrated by the combination of reaction performance and physicochemical characterizations, such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectrometer (XPS) measurements.

Through grafting sulfonate group on the support, better dispersion of nanoparticles, higher reduction degree of Cu, and stronger adsorption of FAL can be attained to contribute high hydrogenation performance. In addition, the effects of reaction conditions (such as reaction temperature, H₂ pressure, reaction time, solvent, and catalyst to FAL mass ratio) were evaluated intensively. Also, the Cu/AC–SO₃H catalyst showed an excellent catalytic performance for transfer hydrogenation of FAL, in which 2-propanol was utilized as the solvent and hydrogen donor concurrently. Cycling test proved the prepared catalyst could be recycled and reused for several times without noticeably reduced catalytic activity of hydrogenation.

KEYWORDS: Furfural, Furfuryl alcohol, Cu catalyst, Sulfonate group, Liquid phase, Hydrogenation



1. INTRODUCTION

The depletion of fossil fuel resources and deterioration of environmental problems is becoming a global concern. Recently, the conversion of biomass and their derivatives to chemicals has been the focus of academic research.^{1–4} Furfural (FAL), a potential platform for biofuels and chemicals, can be obtained by acid-catalyzed hydrolysis and dehydration of five-carbon sugars, which are derived from hemicellulose presented in lignocellulosic biomass,^{5–8} or be generated in bio-oil by fast pyrolysis of biomass.⁹ In terms of structure and composition, FAL is an unsaturated aldehyde compound (C=O in branched chain and C=C in furan ring). Therefore, hydrogenation is one of the most important processes in the conversion of FAL. Generally, FAL could be converted into some useful chemicals through selective hydrogenation, including furfuryl alcohol (FOL), tetrahydrofurfural (TFAL), tetrahydrofurfuryl alcohol (THFOL), furan, tetrahydrofuran (THF), and levulinic acid.^{10,11} Further hydrogenation of these products would

generate more kinds of products. Among them, FOL is a very important intermediate in fine chemicals and polymer industry and has been widely used in the production of thermostatic resins, synthetic fibers, lysine, vitamin C, and lubricants.¹² Until now, commercial production of the chemicals from FAL has been performed on copper chromite catalyst. A drawback of this known process is harsh reaction conditions, such as high hydrogen pressure. The high toxicity of chromium trioxide is another limitation of using copper chromite catalyst.¹³ In addition, this catalyst suffers from significant deactivation under both gas-phase and liquid-phase reactions. So, studies aimed at developing an environmentally acceptable catalyst that could efficiently convert FAL in mild

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reaction conditions or selectively hydrogenate the carbonyl group (C=O) rather than the C=C bonds.

Different kinds of chromium-free catalysts, including noble metals (Pt, Pd, Ru, and Rh) and non-noble metals (Co, Ni, and Cu), have been developed to investigate in liquid-phase hydrogenation of FAL. Normally, noble metal catalysts have high activity even at mild reaction conditions. Due to FAL adsorbed and activated on the surface of noble metal through the model of η^2 -(C,O)-coordination, the very high activity of these catalysts usually leads to high selectivity for some undesirable side reactions, such as C=C hydrogenation or C-C/O cleavage.¹⁴ From the standpoints of selectivity and cost, noble metal catalysts are less preferable than the non-noble metal catalysts. Among non-noble catalysts, Cu-based catalysts have been reported as the most promising candidate for the conversion of FAL to FOL, such as CuMgAl,¹² Cu/MgO,¹³ and Co-Cu/SBA-15.¹⁵ Unlike the adsorption model of η^2 -(C,O)-coordination in Pt, Pd, and Ni, the adsorption of FAL on Cu proceeds in η^1 -(O)-coordination model, in which an η^1 -(O)-surface species is generated to bind the active metal, leading to high hydrogenation selectivity to FOL.¹⁶ For selective hydrogenation of FAL to FOL, therefore, copper was chosen as the active material in present work.

Besides the active metal, the texture of the support also has a great influence on catalytic performance in the hydrogenation process. Zhang et al. reported a highly efficient catalyst, Pd/SO₃H-MIL-101(Cr), which exhibits high catalytic performance in hydrodeoxygenation of vanillin under mild reaction conditions.¹⁷ The high catalytic performance was attributed to the unique characteristics of the SO₃H-MIL-101(Cr) support, which leads not only to very stable and uniform dispersion of the Pd nanoparticles but also to possible electronic activation of the reactants and good dispersion of the catalyst in water. Baiker and co-workers reported a bifunctional catalyst, Pd/Amberlyst15-SO₃H, for the one-pot conversion of crotonaldehyde to 2-ethylhexanal in high yields.¹⁸ It was hypothesized that the Pd species and -SO₃H group formed [Pd_n-H]⁺ “adducts” as new active sites for hydrogenation, aldol reaction, and dehydration to generate 2-ethylhexanal. Researchers had also proved that sulfonated active carbon (AC-SO₃H) supported Ru and Pt have high activity for the conversion of cellulose into sorbitol and polysaccharides to gluconic acid, due to the synergistic effect between -SO₃H group and active metal.^{19,20} Hence, AC-SO₃H is expected to be a suitable candidate as catalyst support taking account of its high surface area, good thermal stability, and special physicochemical properties.

Herein, an ecofriendly and commercially viable AC-SO₃H supported Cu catalyst, Cu/AC-SO₃H, was developed and investigated for selective liquid-phase hydrogenation of FAL to FOL. The catalyst was prepared by liquid phase chemical reduction method to preserve the surface -SO₃H group, because conventional calcination and reduction methods would destroy the surface function groups. The purposes of this work were to study the influence of -SO₃H group in Cu/AC-SO₃H catalyst on the process of FAL hydrogenation and to obtain a Cu catalyst that has high performance at relatively moderate reaction conditions. The effects of reaction parameters (temperature, H₂ pressure, and reaction time), solvent, catalyst to FAL ratio, and recycling were also studied to optimize the hydrogenation of FAL to FOL. In addition, the prepared Cu/AC-SO₃H catalyst was also applied to the process of transfer hydrogenation of FAL to FOL in liquid phase and its catalytic

performance was also investigated. Because of the synergistic effect between -SO₃H and Cu, the Cu/AC-SO₃H catalyst, prepared by a simple method, would be treated as a promising candidate applied to the conversion of FAL to FOL under moderate reaction conditions.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Cu(NO₃)₂·3H₂O, 2-propanol, and NaBH₄ (96%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Activated carbon (AC), poly(vinyl pyrrolidone) (PVP, MW = 8000), FAL (99%), FOL (98%), and n-octanol (99.5%) were purchased from Aladdin Reagent Company. Other analytical grade solvents including ethanol were commercially available.

2.2. Catalyst Preparation. AC-SO₃H was prepared by a direct hydrothermal method. The mixture of the 1.0 g of AC, 20 mL of sulfuric acid, and 2 mL of nitric acid was placed in 100 mL Teflon-lined stainless steel autoclaves, which were heated in an oven at 383 K for 240 min. The resultant AC-SO₃H was filtered repeatedly with distilled water and ethanol until the filtrate pH became 7.0 and dried. Then to obtain Cu/AC-SO₃H, PVP and 30 mL of ethanol were put in a three-neck flask under nitrogen atmosphere. The flask was vigorously stirred at room temperature. After this, a certain amount of Cu(NO₃)₂·3H₂O was quickly added to the reaction mixture and stirred. Then 0.5 g of AC-SO₃H was added to the reaction mixture. Half an hour later, the NaBH₄ solution was cautiously added dropwise to the slurry, followed by stirring for 240 min. The black precipitates were separated by centrifugation, washed with distilled water and ethanol until the pH < 7.0, and dried in a vacuum oven at 333 K overnight. Cu/AC was prepared by using the same method except AC support was used instead.

2.3. Catalyst Characterization. Powder X-ray diffraction (XRD) patterns were analyzed on a Philips X-Pert Pro X-ray diffractometer with using the Ni-filtered monochromatic Cu K α radiation ($\lambda(K\alpha_1) = 1.5418 \text{ \AA}$) at 40 keV and 40 mA. The Fourier transform infrared spectroscopy (FT-IR) measurements were carried out on a Nexus spectrometer (Thermo Nicolet Corporation, USA) in a KBr pellet at room temperature. 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. Cu content in the composite structure was determined by inductively coupled plasma spectroscopy after microwave digestion of the samples (ICP6300, Thermo Fisher Scientific). The S content was determined by a CHNS analyzer (Vario EL III, Elementar). The specific surface areas of metallic copper and copper dispersion were measured by N₂O titration using the method proposed by Guo et al. (see the experimental section in Supporting Information).²¹

2.4. Catalytic Tests. The catalytic hydrogenation of FAL 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, catalyst, and 2-propanol were loaded into the reactor. The reactor was sealed, purged three times with N₂ at 1.0 MPa, then pressurized with H₂, heated to set temperature at 2 K/min, and maintained for set reaction time. After reaction, the autoclave was cooled down quickly. The autoclave contents were transferred to a centrifuge tube, and the catalyst was separated by centrifugation. The operations before and after the reaction were handled in the glovebox. The liquid reaction mixture was diluted and analyzed by GC-MS using n-octanol as an internal standard.

The liquid product was identified by gas chromatography-mass spectrometry (GC-MS, Thermo Fisher Scientific-TXQ Quantum XLS), and was quantitatively analyzed by GC (Shimadzu, GC-2010 Plus), equipped with FID and a (30 m \times 0.25 mm \times 0.25 μ m) KB-WAX capillary column (Kromat Corporation, USA) using n-octanol as an internal standard. The carbon balance was checked in every run and it was found to be higher than 95%. The FOL yield was estimated using the following formulas:

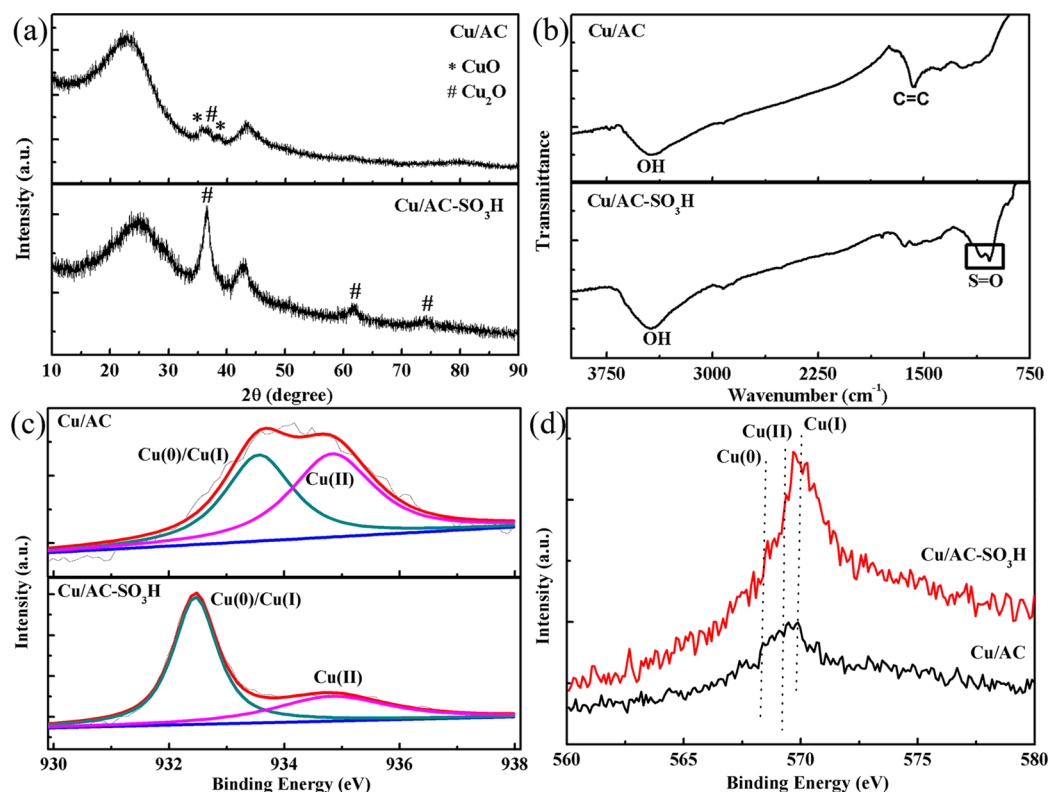


Figure 1. (a) XRD pattern, (b) FT-IR spectra, (c) XPS spectra, and (d) LMM-2 spectra of Cu/AC and Cu/AC-SO₃H.

Table 1. Physicochemical Characteristics of Catalysts

sample	Cu content ^a (wt %)	S_{BET}^b (m ² /g)	V_{pore}^b (cm ³ /g)	acidity ^c (mmol/g)	d_{Cu} (nm)		Cu dispersion ^e (%)	Cu surface area ^e (m ² /g _{cat})	atomic ratios ^f [Cu(0) + Cu(I)]/Cu ²⁺	S content ^g (mmol/g)
					TEM ^d	N ₂ O ^e				
AC		1035	0.386	0.211						
AC-SO ₃ H		919	0.355	1.379						0.44
Cu/AC	15.23	845	0.327	0.213	15.7	15.3	6.5	7.0	0.851	
Cu/AC-SO ₃ H	16.02	826	0.318	0.828	7.8	6.5	15.5	16.8	1.978	0.29

^aDetermined by ICP. ^bCalculated by N₂ physisorption. ^cDetermined by titration. ^dCalculated by TEM. ^eDetermined by N₂O titration. ^fCalculated by XPS. ^gDetermined by CHNS analyzer.

$$\text{FOL yield} = \frac{\text{mol of FOL}}{\text{initial mol of FAL}} \times 100\% \quad (1)$$

3. RESULTS AND DISCUSSIONS

3.1. Catalyst Characterization. The XRD patterns of Cu-based catalysts are shown in Figure 1a. The peaks located at $2\theta = 23^\circ$ and 80° were characteristic peaks of amorphous carbon.²² The diffraction peaks at 35.6° and 38.6° and at 36.8° , 61.5° , and 73.7° were attributed to CuO (JCPDS 45-0937) and Cu₂O (JCPDS 3-065-3288), respectively, which was consistent with the literature.²³ The XRD diffraction peak at 43.1° can be attributed to amorphous carbon or metallic copper. During the catalyst preparation process, CuO was reduced by NaBH₄ followed by CuO → Cu₂O → Cu. From XRD patterns, it was noticed that the intensity of Cu₂O increased obviously in Cu/AC-SO₃H catalyst. The stronger peaks of Cu₂O illustrated that -SO₃H group make reduction of the metal component easier than in Cu/AC catalyst. However, the diffraction peaks characteristic of isolated metallic Cu were not observed in both the case of Cu/AC and Cu/AC-SO₃H, suggesting that the Cu

phase is quasi-amorphous (qa) or formed by small crystalline domains, which are not detectable by XRD. It was consistent with the results of TEM (Figure S1, Supporting Information).

The FT-IR spectra of the Cu/AC and Cu/AC-SO₃H catalyst were also investigated (Figure 1b). The typical band at 1580 cm^{-1} was ascribed to aromatic ring modes with varied absorbance (C=C).²⁴ A wide absorption band located in the range of $3200\text{--}3400 \text{ cm}^{-1}$ could be a consequence of -OH groups on the two kinds of catalysts.²⁵ For Cu/AC-SO₃H catalyst, the bands at 1040 and 1100 cm^{-1} were assigned to the stretching of S=O groups, which was related to the -SO₃H group.^{26,27} The result revealed -SO₃H groups were grafted successfully on the surface of active carbon in Cu/AC-SO₃H catalyst.

The chemical states of Cu species were determined by XPS analysis, and the Cu 2p spectra of Cu/AC and Cu/AC-SO₃H catalysts were recorded in Figure 1c. For Cu/AC catalyst, it displayed a broad peak (Cu 2p_{3/2}) at 933.56 eV , which was inferred to have two species, Cu(0) and Cu(I). Similar with the results of Fulajtárova,²⁸ it was difficult to make a distinction

between Cu(0) and Cu(I) on the basis of XPS analysis. So, the Cu LMM-2 spectra were also recorded to distinguish these species (Figure 1d). The three broad peaks at about 568, 569, and 570 eV attributed to the Cu(0), Cu(II), and Cu(I) species, respectively, were presented.²⁹ In addition, two broader shake-off bands at 940–945 eV and 960–965 eV, which are related to Cu(II), were also observed and shown in Figure S2 (Supporting Information). On the other hand, the spectrum of the Cu/AC–SO₃H catalyst (Figure 1c) showed a totally different spectrum than the Cu/AC catalyst. Cu/AC–SO₃H catalyst showed a significant shift of the main peak (Cu 2p_{3/2}) toward a lower binding energy, which might arise from the reduction of surface Cu(II) to the lower valence states.³⁰ Based on analysis, the Cu(0), Cu(I), and Cu(II) species were present in this as-prepared catalyst. According to the XPS data, the ([Cu(0) + Cu(I)]/Cu(II)) atomic ratios in the two kinds of catalysts were also calculated (Table 1). The Cu/AC–SO₃H catalyst showed ([Cu(0) + Cu(I)]/Cu(II)) atomic ratio of 1.978, which was far higher than that of Cu/AC sample. The result was consistent with the results of XRD and TEM. In addition, the atomic percentage of S was estimated to be 1.2 atom % for Cu/AC–SO₃H catalyst based on the integrated peak areas.

The actual contents of Cu in Cu/AC–SO₃H and Cu/AC catalysts were determined by ICP and are displayed in Table 1. The Cu contents were 16.02 and 15.23 wt % for Cu/AC–SO₃H and Cu/AC catalysts, respectively. The total acid density of the catalysts was determined by a neutralization titration (NaOH), which is a very effective way to calculate the acidity of support materials. The acid density of AC was 0.211 mmol/g, which was attributed to the existence of –COOH and –OH groups on the surface of AC. The acid density increased to 1.379 mmol/g when the AC was treated by sulfonation (AC–SO₃H). The increased acid density arising from the –SO₃H group means that the modification treatment was effective. When Cu deposited on AC–SO₃H, the acidity of Cu/AC–SO₃H decreased to 0.828 mmol/g. The modified group of –SO₃H is deposited on the exposed surface of AC. On one hand, the –SO₃H group on the external surface can improve the availability of surface acid sites; on the other hand, this group can be easily covered and replaced due to weak bonding force and easy contact. Therefore, there is a different variation trend on the acidity between Cu/AC–SO₃H versus AC–SO₃H and Cu/AC versus AC. Specific surface area (S_{BET}) and pore volume (V_{pore}) of samples were determined by the N₂ physisorption technique (Figure S3, Supporting Information). Compared with AC, the S_{BET} and V_{pore} of the AC–SO₃H catalyst were slightly decreased due to the grating of –SO₃H groups on the surface of the support.³¹ Further reductions of S_{BET} and V_{pore} were observed when metallic Cu was deposited on the supports. The Cu/AC–SO₃H catalyst still showed a high surface area of 826 m²/g. The S content of AC–SO₃H and Cu/AC–SO₃H was 0.44 and 0.29 mmol g^{−1}, which was determined by CHNS elemental analysis. In addition, Cu dispersion, metal specific area, and average particle size are vital parameters, which greatly influence physicochemical properties and catalytic performance. Therefore, these parameters were determined by N₂O titration and are shown in Table 1. The Cu/AC–SO₃H catalyst had higher Cu dispersion (15.5%) and surface area (16.8 m² g_{cat}^{−1}) than Cu/AC (6.5% and 7.0 m² g_{cat}^{−1}). The average particle size was 6.5 and 15.3 nm for Cu/AC–SO₃H and Cu/AC, respectively, which are consistent with TEM results. As shown, Cu/AC–SO₃H exhibited higher

dispersion and metal specific area, as well as smaller particle size, indicating that –SO₃H groups had a positive effect on these parameters that can further upgrade the catalytic performance for hydrogenation.

3.2. Liquid Phase Hydrogenation of FAL over Cu/AC–SO₃H Catalyst. **3.2.1. Effect of the Sulfonate Group Modification.** In order to investigate the effect of sulfonate (–SO₃H) group on catalytic performance in the process of FAL hydrogenation, the catalytic activity of Cu/AC–SO₃H catalyst was compared with Cu/AC catalyst, and the results are shown in Table 2. Obviously, the –SO₃H group making the

Table 2. Hydrogenation of FAL over Cu/AC and Cu/AC–SO₃H^a

run no.	temp (K)	H ₂ pressure (MPa)	time (min)	FOL yield (%)	TOF (h ^{−1})
Cu/AC					
1	373	0.4	180	<0.1	
2	378	0.4	180	<0.1	
3	383	0.4	180	<0.1	
4	413	0.4	180	20.6	3.779
Cu/AC–SO ₃ H					
1	373	0.4	180	47.3	1.443
2	378	0.4	120	>99.9	1.826
3	383	0.4	120	>99.9	5.431

^aReaction conditions: catalyst to FAL mass ratio = 1:1; FAL = 1.0 mmol; 2-propanol = 5 mL.

Cu/AC–SO₃H catalyst exhibited a more promising catalytic performance than the Cu/AC catalyst. For Cu/AC–SO₃H catalyst, FAL was converted completely into FOL in 120 min at 378 K. However, the Cu/AC showed almost no activity under the same conditions and needed higher reaction temperature, longer reaction time, or both. The Cu/AC–SO₃H catalyst exhibited high selectivity for FOL without formation of furfuryl acetal products, which are very likely formed by the reaction between FAL and alcohol solvent especially on acidic catalysts.^{32–35} For better understanding the recipe of high selectivity for the Cu/AC–SO₃H catalyst, we also investigated and compared it with AC, AC–SO₃H, Pd/AC–SO₃H, and Cu/AC+H₂SO₄ catalysts for FAL hydrogenation using 2-propanol as solvent, and the results are listed in Table S1 (Supporting Information). For the catalyst without active metal (AC and AC–SO₃H), there was no activity for FAL hydrogenation and etherification of the FAL with 2-propanol. When using dilute sulfuric acid+Cu/AC as catalyst, a certain degree of etherification had been observed. This result indicates the acidity of AC–SO₃H is insufficient for etherification of FAL with solvent. On the other hand, unlike Cu/AC–SO₃H catalyst, the reactions of hydrogenation and esterification had been observed together over the Pd/AC–SO₃H catalyst indicating the active metal can also influence the product distribution for FAL hydrogenation. In addition, the interaction between furfural and solvent was weakened at a higher reaction temperature, like the reaction condition used in our work. Therefore, copper is chosen as a highly selective catalyst for FAL transformation into FOL. Although the sulfonate group is not involved in the reaction directly, it can greatly enhance the catalytic performance of active copper. This is consistent with other research, which has found catalytic performance of active metal could be effectively improved by Brønsted acid modification.^{17,36,37}

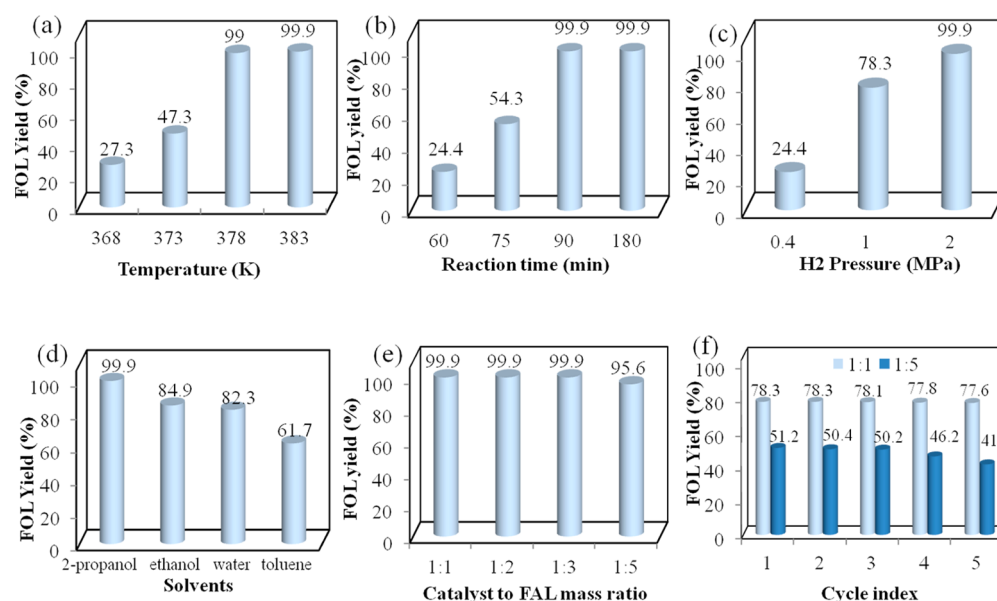


Figure 2. Effect of reaction conditions on the hydrogenation of FAL over Cu/AC-SO₃H: (a) FAL mass ratio 1:1; FAL 1.0 mmol; 2-propanol 5 mL, 0.4 MPa H₂, 180 min; (b) FAL mass ratio 1:1; FAL 1.0 mmol; 2-propanol 5 mL, 0.4 MPa H₂, 383 K; (c) FAL mass ratio 1:1; FAL 1.0 mmol; 2-propanol 5 mL, 383 K, 60 min; (d) FAL mass ratio 1:1; FAL 1.0 mmol; solvents 5 mL, 378 K, 0.4 MPa H₂, 120 min; (e) FAL 1.0 mmol; 2-propanol 5 mL, 378 K, 0.4 MPa H₂, 120 min; (f) 2-propanol 5 mL, 383 K, 1 MPa H₂, 60 min, catalyst to FAL mass ratio = 1:1 and 1:5.

For deep investigation, TOF was calculated to investigate the intrinsic catalytic activity in a low activity (Table S2, Supporting Information). The Cu/AC-SO₃H had higher TOF values indicating that the reaction rate on Cu/AC-SO₃H catalyst is higher than that on Cu/AC catalyst. The Arrhenius plots derived by plotting the logarithm of the rate constant versus the inverse temperature over Cu/AC-SO₃H and Cu/AC catalysts are shown in Figure S4 (Supporting Information). Based on Arrhenius law, the corresponding apparent activation energy (E_a) was 131 kJ/mol for Cu/AC-SO₃H and 189 kJ/mol for Cu/AC catalyst. Actually, there are not many reports on the E_a of liquid-phase FAL hydrogenation, especially based on non-noble metal catalysts. Villaverde et al. reported an E_a value of 127 kJ/mol for CuMgAl catalyst in liquid-phase FAL hydrogenation,¹² which is very close to our data. The high E_a estimated for the Cu/AC-SO₃H catalyst probably could be attributed to a strong adsorption of furfural on the catalyst surface, which was proven by the molecular dynamics (MD) simulation (Figure S5 and Table S3, Supporting Information).

From characterizations, the ([Cu(0) + Cu(I)]/Cu(II)) atomic ratio increased obviously when the surface of AC was grafted by -SO₃H group: 1.978 for Cu/AC-SO₃H and 0.851 for Cu/AC (Table 1). The cooperation of Cu(0) and Cu(I) species in FAL hydrogenation has been previously confirmed.³⁸⁻⁴⁰ Rao et al. proposed that Cu(I) species function as active sites for FAL and crotonaldehyde hydrogenation.³⁸ Hronec et al. also assumed that the Cu(I) sites play important roles in binding and activating the -C=O group in FAL.⁴¹ In this work, high amount of Cu(I) species together with small quantity of Cu(0) had been found from Cu Auger LMM-2 spectra. Therefore, we also assumed that the metallic Cu and Cu(I) species function together for the high performance in FAL hydrogenation over the Cu/AC-SO₃H catalyst. In order to assess the effect of Cu(I) species, the catalytic performance of FAL hydrogenation over reduced Cu/AC and Cu/AC-SO₃H (reduction conditions, 573 K, 480 min, H₂/N₂ (10:90), 100 mL min⁻¹) had also been investigated (Table S4,

Supporting Information). It can be found that the activity of reduced Cu/AC-SO₃H catalyst decreases obviously compared with unreduced catalyst due to the Cu(I) species being completely reduced to metallic Cu (Figure S6, Supporting Information). This result proved that Cu(I) species play very important roles in FAL hydrogenation. More importantly, compared with the reported Cu-based catalyst, the prepared Cu/AC-SO₃H catalyst gave the mildest reaction conditions for completely converting FAL to FOL (Table S5, Supporting Information), even better than some supported noble catalysts. All these results directly or indirectly revealed that the FAL hydrogenation by Cu catalyst can be enhanced by the -SO₃H group modification, which could act as nanoparticle stabilizers and dispersants (Figure S1, Supporting Information) and adsorbent for FAL, thus promoting the activity for FAL hydrogenation.

3.2.2. Effects of Reaction Conditions and Catalyst Stability. To obtain a better understanding of the reaction mechanisms and to optimize the reaction conditions, a series of FAL hydrogenations were conducted over Cu/AC-SO₃H catalyst, and the results are shown in Figure 2. In all cases, FOL was the sole product. This was in accordance with previous reports of FAL hydrogenation over Cu-based catalysts.^{12,42}

The influence of reaction temperature on catalytic activity was investigated under 368–383 K at hydrogen pressure of 0.4 MPa after 180 min hydrogenation, as shown in Figure 2a. When the reaction was conducted at low hydrogen pressure (0.4 MPa), even though the temperature increased slightly, the FOL yield was greatly increased from 27.3% at 368 K to >99% at 378 K. As mentioned, there was a strong interaction between Cu/AC-SO₃H and FAL. The interaction of FAL-to-sulfonate group could assist FAL adsorption and activation on the surface of catalyst to promote hydrogenation. However, the strong interaction would result in high E_a value for Cu/AC-SO₃H catalyst. Thus, elevating reaction temperature can concurrently increase reaction rate constant and diminish the strong interaction of furfural-to-sulfonate group. Therefore, reaction

temperature had a great influence on the activity of Cu/AC-SO₃H catalyst, and a sharp increase of FAL conversion was obtained with slightly elevating reaction temperature. We could easily conclude that the hydrogenation of FAL over Cu/AC-SO₃H catalyst is very sensitive to reaction temperature.

The effects of parameters reaction time, H₂ pressure, and solvent were also studied. Before studying the effect of reaction time, the impact of heating stage on reaction results had been investigated (Table S6, Supporting Information). It was found that the reaction hardly took place in the heating-up process and would not affect the results. Actually, this reaction is in the diffusion limit regime, and we also eliminated the effect of mass transfer in the FAL hydrogenation (Table S7, Supporting Information). In Figure 2b, it was found that FOL yield was raised from 24.4% to 54.3% with reaction time increased from 60 to 75 min over Cu/AC-SO₃H at 383 K and 0.4 MPa H₂ pressure, and then the yield was increased to >99.9% with hydrogenation time prolonged to 90 min. The reaction rate increased slowly first and fast afterward with reaction time. Although we have indirectly observed the change of the catalyst by the existing characterization methods, the thermodynamic evidence indicates that the induction period in the reaction is likely to be induced by the change of catalyst during reaction beyond being detected by some off-line characterizations (Table S8, Supporting Information). In liquid-phase hydrogenation process, another important variable affecting catalytic activity was the dissolved concentration of H₂, which is directly proportional to the H₂ pressure. Considering that augmenting the dissolved amount of H₂ could give rise to conversion increase, the effect of H₂ pressure was investigated by varying in the range of 0.4–2.0 MPa at a constant temperature and reaction time. In Figure 2c, one could find that the reaction rates were boosted 3-fold and 4-fold when the H₂ pressure increased from 0.4 to 1.0 and 2.0 MPa, respectively. Like H₂ pressure and reaction time, solvent also influenced catalytic activity of liquid phase hydrogenation. For studying the effect of solvent on FAL hydrogenation over Cu/AC-SO₃H catalyst, nonprotic toluene and protic solvents of 2-propanol, water, and ethanol were selected as the solvents, and the activities are also shown in Figure 2d. Nonpolar toluene gave the lowest FOL yield, 61.7%, probably caused by poor hydrogen solubility in nonpolar solvent. For the protic solvents, 2-propanol was the optimal solvent, which gave complete conversion of FAL into FOL at 378 K, 0.4 MPa H₂ pressure, and 120 min. Meanwhile FOL yield was 82.3% for water and 84.9% for ethanol under the same reaction conditions. The protic solvents showed higher catalytic activity than nonpolar solvent, which has also been proven in previous studies.^{43,44} The higher observed activity may arise from the hydrogen bonding between the carbonyl oxygen of FAL and the hydroxyl group of the protic solvents. In the reaction the hydrogen bonding is shifted between furfural and the sulfonate group (-SO₃H), which has also been proven by the MD simulation (Figure S5 and Table S3, Supporting Information). These results indicate that the formation of hydrogen bonding can promote catalytic activity. However, too strong interaction between furfural and solvent might restrain the hydrogen bond formation between FAL and Cu/AC-SO₃H and further influence the catalytic performance. Therefore, the protic solvent of 2-propanol with reasonable polarity, solubility, and protonation shows the highest activity for FAL hydrogenation.

The influence of catalyst to FAL mass ratio in hydrogenation of FAL was also investigated by varying FAL dosage. From

Figure 2e, one could find that the activity of Cu/AC-SO₃H remained almost unchanged with FAL dosage increased to three times catalyst usage and only a very slight decline was detected for the catalyst to FAL mass ratio of 1:5. This result further confirmed the Cu/AC-SO₃H catalyst was very effective in liquid phase hydrogenation of FAL to FOL.

Based on the above experimental results, we evaluated the recyclability of Cu/AC-SO₃H catalyst at low conversion under the catalyst to FAL mass ratio of 1:1 and 1:5, respectively, as shown in Figure 2f. In both cases, the Cu/AC-SO₃H catalyst showed nearly stable activity for five recycles in liquid phase FAL hydrogenation. Similar with first run, FOL was the sole product in all five recycles. These experiments, thus, revealed that the Cu/AC-SO₃H catalyst was stable and recyclable in the conversion of FAL to FOL. The spent catalyst, Cu/AC-SO₃H after five recycles, was characterized by ICP, element analysis, XRD, and TEM. As determined by ICP technique, a very small decrease in Cu content from 16.02 wt % (fresh catalyst) to 15.92 wt % (spent catalyst) was observed. The S content of the spent Cu/AC-SO₃H was 0.26 mmol g⁻¹, which is very close to the fresh Cu/AC-SO₃H catalyst (0.29 mmol/g), indicating minimal loss of S during the hydrogenation process. Figure S7 shows the TEM images and XRD patterns of the fresh and spent catalyst, which could provide clues concerning the good stability of Cu/AC-SO₃H catalyst. As displayed in this figure, it was observed that the TEM images of fresh and spent catalysts were similar, indicating no sintering and agglomeration of metallic particles taking place. The XRD profile of the spent catalyst was also similar to that of the fresh catalyst but for lowered intensity of the metal peaks (Figure S7, right panel). For deeply confirming the changes of Cu catalyst in reaction, the chemical state of the spent catalyst was determined by XPS analysis (Figure S8). The major valent state of copper was Cu(I), but the amount of Cu(II) increased after reaction. Cu(II) oxide possibly formed in the reaction or partial oxidation of Cu during sample loading in XPS instrument. Generally, the superior stability of Cu/AC-SO₃H catalyst possibly stems from the interaction of the active components with -SO₃H group, which acted as nanoparticle stabilizer and dispersant and improved the catalytic properties.

3.3. Liquid Phase Transfer Hydrogenation of FAL over Cu/AC-SO₃H Catalyst. Conventional catalytic hydrogenation was usually carried out using high pressure H₂, which would induce many drawbacks, such as high cost, low solubility, complex reactor design, and high requirements for storage, transportation, and safety. Thus, researchers have shown great interest in the process of catalytic transfer hydrogenation, which employs renewable organic compounds such as alcohols or organic acids as a hydrogen source, instead of molecular H₂.⁴⁵ For FAL, its transfer hydrogenation using 2-propanol as hydrogen donor had been investigated over Pd/Fe₂O₃ and Cu/Mg/Al catalysts,^{46,47} and good catalytic performances were achieved. Here, we sequentially extended the application of this catalyst in the process of transfer hydrogenation of FAL (Table 3). The reaction using 2-propanol as hydrogen donor was carried out at 423 K over Cu/AC-SO₃H catalyst and compared with Cu/AC catalyst, which had similar content of Cu but different physicochemical properties. It was observed that Cu/AC catalyst was not active for transfer hydrogenation FAL. In contrast, FAL was completely converted to FOL after 300 min transfer hydrogenation with Cu/AC-SO₃H catalyst. The reaction revealed a slow activity during the first 3 h and a sudden increase during the next 2 h at 423 K. Similar to the

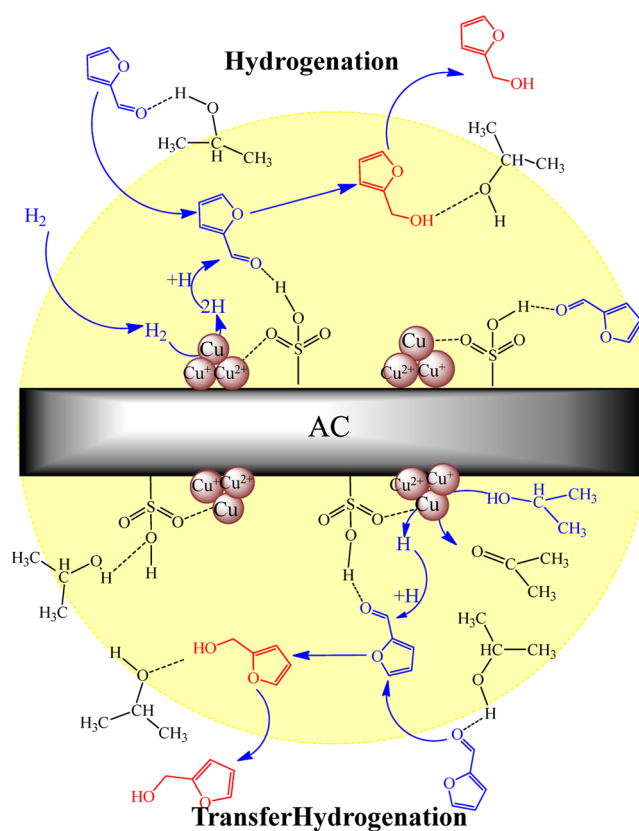
Table 3. Catalytic Transfer Hydrogenation of FAL over Cu/AC and Cu/AC–SO₃H^a

run no.	temp (K)	time (min)	FOL yield (%)
		Cu/AC	
1	423	300	
		Cu/AC–SO ₃ H	
1	418	300	27.3
2	423	180	15.1
3	423	270	57.5
4	423	300	>99.9

^aReaction conditions: catalyst to FAL mass ratio = 1:1; FAL = 1.0 mmol; N₂ pressure = 4.0 MPa.

behavior in H₂ hydrogenation, the Cu(II) and Cu(I) in the prepared catalyst have high probability to be reduced to metallic Cu under the conditions of transfer hydrogenation, which might bring about the induction period in reaction process. (Table S9, Supporting Information). Byproducts had not been observed in the transfer hydrogenation process. This result revealed that the Cu/AC–SO₃H catalyst not only had efficient performance in hydrogenation with H₂ but also demonstrated high activity in transfer hydrogenation with 2-propanol as the hydrogen donor for the conversion of FAL to FOL. So far, the studies of transfer hydrogenation of carbonyl compounds, like FAL, were fastened on the employment of noble metal catalysts. Only very recently, Marchi et al.⁴⁶ used a Cu–Mg–Al catalysts and 2-propanol as hydrogen donors to conduct FAL transfer hydrogenation. Our study also proved that the Cu catalyst had an outstanding transfer hydrogenation performance with the surface modification of support.

3.4. Mechanism of the Reaction. The advantage of Cu-based catalysts can be to achieve selective hydrogenation of the C=O bond while keeping the C=C bond in the furan ring intact. Previous studies had demonstrated that the hydrogenation of FAL over Cu catalysts occurs through a η¹-(O)-aldehyde (perpendicular) configuration,¹⁶ in which the aldehyde group was bonded to the surface of the active site through the carbonyl O atom with the C=C bond remaining largely unaffected and away from the metallic surface. This would explain why FOL is the sole product in all cases of FAL hydrogenation/transfer hydrogenation in our works. Based on physicochemical characterizations, we had demonstrated that the Cu dispersion and reducibility were improved with the aid of the –SO₃H group in the prepared Cu/AC–SO₃H catalyst probably caused by an interaction between Cu and –SO₃H group. Analogously, researchers have hypothesized the interaction between active metal and –SO₃H group, such as forming [Mn–H]⁺ “adducts” (M was the active metal), can greatly improve catalytic performance over –SO₃H group modified metallic catalyst.^{18,48} Together with the results of hydrogenation/transfer hydrogenation tests, a proposed catalytic model for the hydrogenation (upper) and transfer hydrogenation (bottom) of FAL over Cu/AC–SO₃H catalyst was outlined in Scheme 1. Similar to conventional liquid phase catalytic reaction, the process of liquid phase hydrogenation over the Cu/AC–SO₃H catalyst could also be divided into several steps: First, reactants (FAL and H₂) dissolved in solvent (2-propanol) and diffused to the surface of Cu/AC–SO₃H. Due to polarity and solubility, hydrogen bonds probably formed between FAL and 2-propanol, and FAL diffused to the surface of catalyst with the interaction of FAL and 2-propanol. This was the reason to select 2-propanol as the

Scheme 1. Possible Reaction Pathway for Hydrogenation of FAL

solvent in this work. H₂ also dissolved and diffused in 2-propanol before contacting with catalyst, and the rates of dissolution and diffusion of H₂ were proportional to its pressure. Hence the reaction rate was raised with the increase of H₂ pressure. Second, when FAL diffused to the surface of Cu/AC–SO₃H, the interaction of FAL and 2-propanol was shifted and a new hydrogen bond between FAL and –SO₃H was potentially formed to bond the aldehyde group to the surface active site. The formation of hydrogen bonds was proven by the molecular dynamics (MD) simulation, which was employed to understand the physisorption of FAL on Cu/AC–SO₃H catalyst. During MD simulation, two models for Cu/AC and Cu/AC–SO₃H adsorption of FAL were built, and the results are shown in Figure S5 and Table S3, Supporting Information. According to the simulation, the adsorption of FAL on the Cu/AC–SO₃H catalyst was related to hydrogen bonding rather than Van der Waals force, which was the major interaction between FAL and Cu/AC catalyst. Besides Brønsted acid sites (–SO₃H), the Lewis acid sites was also appeared in the Cu/AC–SO₃H catalyst stemming from Cu(I) species. As Lewis acid sites, the electrophilic Cu(I) species could adsorb and activate C=O groups via the electron lone pair of oxygen, and thus the activity of the C=O groups in FAL could be promoted.^{34,49} Meanwhile, the dissolved H₂ was dissociated to form active hydrogen atoms on the active surface of Cu. The speed of diffusion and dissociation would notably affect the reaction rate of the whole process. Third, the reduction reaction took place when the active hydrogen atom attacked the bound aldehyde group on the active surface of Cu/AC–SO₃H, and FAL was transformed to FOL in this step. Finally, the generated FOL was desorbed from the surface of catalyst

with the aiding of 2-propanol and stirring effect. The mechanism and reaction processes for transfer hydrogenation of FAL were similar to the hydrogenation process. What made these two processes different was the source of active hydrogen atoms. The electron-withdrawing nature of the $-\text{SO}_3\text{H}$ group and the ability to provide protons were the other reasons contributing to good performance in the transfer hydrogenation reaction of FAL. Briefly, we suggest that FAL can be adsorbed on-top through the carbonyl group over both Lewis acid sites (Cu(I)) and Brønsted acid sites ($-\text{SO}_3\text{H}$ group). The metallic Cu as active centers provided the sites for H_2 dissociation, while the Cu(I) species were able to adsorb and activate the $-\text{C}=\text{O}$ bond of FAL molecules, thus greatly improving the hydrogenation performance. In conclusion, hydrogenation and transfer hydrogenation of FAL to FOL could be efficiently performed in liquid phase under mild conditions using a Cu/AC- SO_3H catalyst.

4. CONCLUSIONS

In summary, we showed that Cu/AC- SO_3H catalyst, prepared by liquid phase reduction method, was active for liquid-phase hydrogenation of FAL with 100% selectivity to FOL and could be reused five times without loss in activity. The high catalytic performance of Cu/AC- SO_3H could be attributed to the support grafted with $-\text{SO}_3\text{H}$ groups, which lead to variations in physicochemical properties (reduction and dispersion), adsorption of reactants, and catalytic performance. It was suggested that the intrinsic properties of the support have significant influence on the catalytic performance of Cu catalysts. Meanwhile, temperature, H_2 pressure, and solvent also played important roles in determining the activity of Cu/AC- SO_3H catalyst. Further study revealed that the Cu/AC- SO_3H catalyst not only had efficient performance in hydrogenation with H_2 but also demonstrated high activity in transfer hydrogenation with 2-propanol as the hydrogen donor for the conversion of FAL to FOL. Based on our studies, the support of $-\text{SO}_3\text{H}$ group grafted active carbon would be considered a promise candidate to prepare Cu-based catalysts with high activity in the hydrogenation and transfer hydrogenation of FAL to FOL.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b02343.

Characterization of catalysts (TEM, BET), calculation of TOF and activation energy, TEM images and XRD patterns of the fresh and spent catalyst, calculation of adsorption energy, summary of the relevant literatures, raw GC data (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

AC, active carbon; FAL, furfural; FOL, furfuryl alcohol; THFOL, tetrahydrofurfuryl alcohol

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