Full Length Article

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

Wanbing Gong[a,b], Chun Chen[a,*], Ruoyu Fan[a,b], Haimin Zhang[a], Guozhong Wang[a], Huijun Zhao[a,c,*]

[a] Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui Key Laboratory of Nanomaterials and Nanotechnology, CAS Center for Excellence in Nanoscience, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, Anhui 230031, China
[b] University of Science and Technology of China, Hefei, Anhui 230026, China
[c] Centre for Clean Environment and Energy, Gold Coast Campus, Griffith University, Queensland 4222, Australia

GRAPHICAL ABSTRACT
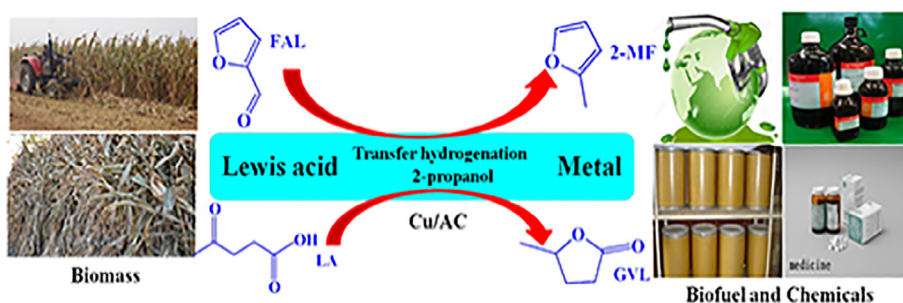
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ABSTRACT

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

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), methylfurfural, 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_2O_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_α 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_2O 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