



# Selective hydrogenation of furfural and levulinic acid to biofuels on the ecofriendly Cu–Fe catalyst



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## HIGHLIGHTS

- Ecofriendly and noble-metal-free Cu–Fe catalysts were fabricated using the metal nitrates.
- Cu–Fe catalyst was efficient for hydrogenation of biomass-derived furfural and levulinic acid.
- Biofuel 2-methylfuran with 51% yield was highly selectively achieved at 99% conversion of furfural.
- Biofuel  $\gamma$ -valerolactone with 90% yield was efficiently achieved at 98.7% conversion of levulinic acid.

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## ABSTRACT

A series of chromium-free and noble-metal free Cu–Fe catalysts were successfully synthesized utilizing the inexpensive metal nitrates. Ecofriendly Cu–Fe catalysts exhibited highly efficient performance in the hydrogenation of biomass-derived furfural and levulinic acid, where biofuels (2-methylfuran and  $\gamma$ -valerolactone) were obtained at 51% and 90% yield under mild conditions, respectively. The synthesized Cu–Fe catalysts were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Energy-dispersive X-ray analysis (EDX), X-ray photoelectron spectroscopy (XPS), and Temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) to elucidate the relationship between the physical property and their catalytic performance. Reaction parameters and the reaction pathways were also investigated. The Cu–Fe catalyst developed in this work is inexpensive, simple, and amenable to scale up, which makes it a promising candidate for the general conversion of biomass-derived monomers to biofuels.

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## 1. Introduction

Due to increasingly pressing energy and environmental issues, the efficient utilization of natural resources is critical for conveying society to a more sustainable future [1,2]. The design of novel and ecofriendly catalysts, at low cost, for the efficient transformation of natural resources or biomass-derived platform chemicals is a very promising approach [3,4]. For most of the strategies being investigated, platform intermediates furfural and levulinic acid (LA), which are traditionally produced from renewable lignocellulosic biomass [5,6], are often employed as the feedstock for the sustainable production of value-added chemicals and biofuels [7–10].

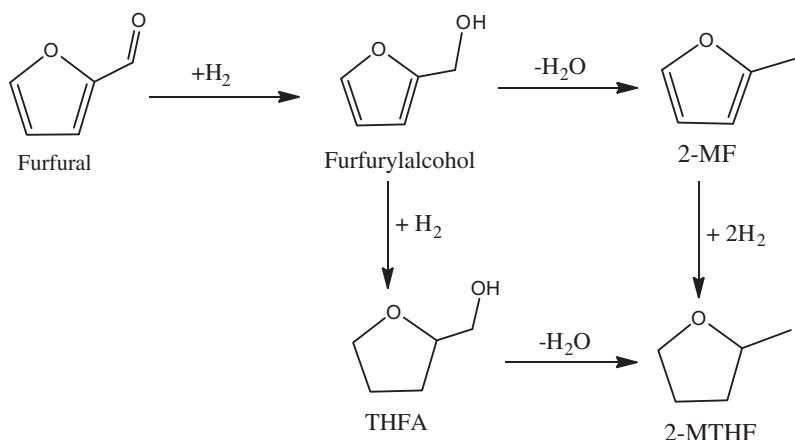
In the hydrogenation of furfural (Scheme 1), furfuryl alcohol (FA) is often produced from the hydrogenation of carbonyl group (C=O bond). 2-Methylfuran (MF) is often enabled through the further hydrogenolysis of FA. Due to its attractive fuel properties, MF has recently been demonstrated to be functioned well as a

low-concentration blended with gasoline in standard vehicles [8,10]. The efficient production of MF is thus becoming ever more crucial. In the formation of MF (Scheme 1), several side reactions (e.g. hydrogenation of the furan ring to tetrahydrofurfuryl alcohol (THFA), further hydrogenolysis to 2-methyltetrahydrofuran (MTHF), decarbonylation of furfural to furan, etc.) often occur simultaneously, which would strongly influence the selectivity of MF in a complex manner [8,10]. Therefore, developing a highly selective catalyst for the efficient production of MF is imperative.

Over the past decades, various catalysts have been developed for the production of MF in either liquid phase or vapor phase. Cu-based catalysts (Raney–Cu, Cu/Al<sub>2</sub>O<sub>3</sub> and copper chromite) have been widely employed as they preferentially cleave C–O bond in the production of FA with minor C–C cleavage or hydrogenation of the furan ring [11–14]. It has been claimed that Cu<sup>0</sup> and/or Cu<sup>+</sup> species often served as reaction active centers within the Cu-based catalysts for the hydrogenation of furfural [12,13]. However, the supported Cu-catalysts were found to be rapidly deactivated, although they could be regenerated via coke burn off at a high temperature [8]. Carbon-supported copper chromite has also been reported to be selective for the production of MF, but they can be

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**Scheme 1.** Hydrogenation of furfural to value-added chemicals.

deactivated within several days [15]. Besides, the utilization of the toxic chromium (Cr) has seriously environmental issues in the preparation, handling and disposal [16]. The development of a chromium-free catalyst that can selectively perform reduction or hydrogenolysis, is crucial for the efficient production of MF. Subsequently, the Pd-based nanocatalysts have been developed and used for the hydrogenation of furfural to MF [8,17,18]. However, the high cost and sensitive surface of noble-metal often limit practical applications. Therefore, the development of an effective, stable, cheap and ecofriendly catalyst remains highly desirable.

The hydrogenation of LA can result in the production of  $\gamma$ -valerolactone (GVL) coupled with pentanoic acid (PA) and MTHF as shown in Scheme 2. It has recently been demonstrated that GVL, a frequently used food additive, exhibits the most important characteristics of an ideal sustainable liquid, including the possibility of being utilized in the production of either energy or carbon-based consumer products [19]. In addition, GVL does not hydrolyze under neutral conditions and no measurable amount of peroxides was formed in a glass flask exposed to the air for several weeks, making it safe for large scale use [19,20]. A comparative evaluation of GVL and ethanol as fuel additives [19], with a mixture of 10 v/v% GVL or EtOH and 90 v/v% 95-octane gasoline, exhibited very similar properties. Since GVL does not form an azeotrope with water, resulting in a less energy demanding process for the production of GVL than that of absolute ethanol [20,21], it has attractive applications as a liquid fuel.

The hydrogenation of LA to GVL utilizing the homogeneous Ru-complex catalysts, has appeared attractive as high conversion with good selectivity have often been obtained [10,22,23]. However, the recovery of expensive metal catalysts from reaction residues

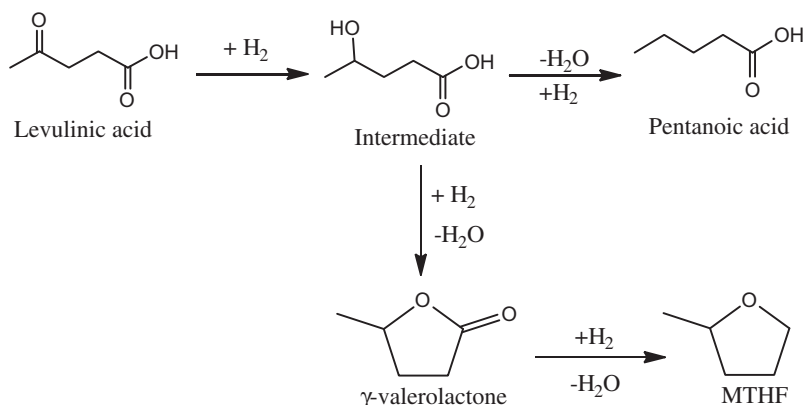
remains a challenge. Heterogeneous catalysts have the advantages of ease of recovery and recycling and are readily amenable to continuous processing, thus the solid transitional metal catalysts have been employed, the typical hydrogenation of LA to GVL was performed in solvent free [24,25] or in organic solvents such as dioxane or ethylether. Bourne et al. [24] reported that over 99% yield of GVL was achieved on the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst under the condition of 200 °C, 20 MPa H<sub>2</sub>, where water coupled with supercritical CO<sub>2</sub> were used as the reaction medium. Manzer reported that 97% yield of GVL was obtained using the Ru/C catalyst at 150 °C and 34.5 bar hydrogen in dioxane [25]. Although the employed Ru catalysts exhibited good performance, the relatively easy deactivation of Ru catalysts makes them difficult to be utilized in practice.

In our previous study [26], we have briefly shown that the Cu-catalysts derived from hydrotalcite were good for the hydrogenation of furfural and LA, respectively. In this work, we aimed to report the ecofriendly synthesis of chromium-free and noble-metal-free Cu-Fe catalysts from inexpensive metal nitrates. The Cu-Fe catalysts were efficient for the hydrogenation of biomass-derived furfural and LA, respectively, where biofuels MF (51% yield) and GVL (90% yield) were highly selectively achieved under mild conditions. Subsequently, the reaction parameters and hydrogenation pathways were discussed.

## 2. Materials and methods

### 2.1. Materials

All chemicals were used directly without any further purification after the purchase. Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (ACS reagent, ≥98%),



**Scheme 2.** Hydrogenation of LA to value-added chemicals.

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