

## Research Paper

Efficient catalytic transfer hydrogenation of furfural to furfuryl alcohol in near-critical isopropanol over Cu/MgO-Al<sub>2</sub>O<sub>3</sub> catalystHao Chen<sup>a</sup>, Houhang Ruan<sup>a</sup>, Xilei Lu<sup>a</sup>, Jie Fu<sup>a</sup>, Timothy Langrish<sup>b</sup>, Xiuyang Lu<sup>a,\*</sup><sup>a</sup> Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, PR China<sup>b</sup> Drying and Process Technology Group, School of Chemical & Biomolecular Engineering, The University of Sydney, Darlington, NSW 2006, Australia

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## ABSTRACT

Catalytic transfer hydrogenation of furfural to furfuryl alcohol is considered to be a very important industrial process. In this work, non-noble Cu supported on MgO-Al<sub>2</sub>O<sub>3</sub> catalysts have been prepared by co-precipitation and have shown excellent catalytic performance for conversion of furfural to furfuryl alcohol in near-critical iso-propanol. The effects of the Cu state (reduction degree and dispersion) and loading in Cu/MgO-Al<sub>2</sub>O<sub>3</sub>, acidity of catalysts have been investigated by X-ray diffraction (XRD), coupled plasma optical emission spectrometry (ICP-OES), N<sub>2</sub> adsorption and desorption (N<sub>2</sub>-BET) and temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD), which have led to high activity for producing furfuryl alcohol. The results have shown that the selectivity of furfuryl alcohol has been influenced by the Cu state, Lewis acidity, reaction temperature and reaction time. The mechanisms, Lewis acid- and metal mediated hydrogenation, have shown that a desirable balance of Cu loading and Lewis acidity of catalyst has influenced the activity significantly. Almost 100% furfural conversion, with 89.3% furfuryl alcohol yield has been obtained. Cycling tests have shown that the prepared catalysts have been stable, where recycling the catalysts at least four times has not shown any reduction in activity.

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## 1. Introduction

Biomass is viewed as a potential alternative to produce high-valued chemicals from natural compounds [1,2]. Biomass derived furfural (FAL) has been found to be one of the prospective biological base platforms for biofuels and chemicals that are produced from five-carbon sugars [3]. Selective conversion of FAL to furfuryl alcohol (FOL) is considered to be a very important industrial process, which is due to FOL being a very important chemical that is used widely in the fine chemical and the polymer industries for many applications, such as thermostatic resins, synthetic fibers, lysine, vitamin C, and lubricants [4]. In terms of producing FOL from FAL, hydrogenation is one of the most important processes in the conversion of FAL, which include C=O in the branched chain structure and C=C in the furan ring. Thus, it is necessary to avoid over-hydrogenation by selectively hydrogenating the C=O bonds rather than the C=C bonds, and unselectively cracking the C-C bonds.

Usually, the main catalyst used in industry is a Cu-Cr oxide catalyst, which has high toxicity and hence causes serious environmental pollution [5–7]. Now, research efforts are being focused on the synthesis of Cr-free catalysts, including the use of noble metals (Pt, Pd, Ru and Ir) [8–10], non-noble metals (Fe, Ni, and Cu) [3,11] and alloyed bimetallic metals (Pt-, Ni-, Fe-, and Cu-M) [12–14] supported catalysts. However, these research works were mostly performed with H<sub>2</sub> in high-pressure processes, which made the processes very costly and inhibited the ability to industrialize the processes.

Catalytic transfer hydrogenation (CTH) has recently emerged as an alternative approach for the reduction of biomass-derived molecules, using hydrogen donors such as alcohols as hydrogen sources to replace molecular H<sub>2</sub> [15,16]. CTH processes have also been reported for producing FOL from FAL over several catalysts. Normally, noble metal catalysts have high activity even under mild reaction conditions, leading to high selectivity for some undesirable side reactions [17,18]. Thus, the noble metal catalysts are less desirable than non-noble metal catalysts [3]. Carbon materials showed excellent performance [3,5] but they needed strong pretreatment (with concentrated HCl and HNO<sub>3</sub> treating) to obtain oxygen-containing functional groups, but side reactions may also occur. Villaverde et al. [19] reported the CTH of FAL to FOL on Cu-

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Mg–Al catalysts. However, this work only gave results about the reactant conversion without investigating the selectivity of FOL and the reusability of the catalyst. Thus, there are still many problems needing to be further studied, because hydrotalcite materials ( $\text{MgO-Al}_2\text{O}_3$ ) are strong supports for catalysts showing excellent performance [20] due to their large adsorption capacity, the anion-exchange ability of the interlayer space and the tunable basicity of the surface.

In this work, a series of hydrotalcite materials,  $\text{MgO-Al}_2\text{O}_3$ , supported Cu catalysts have been prepared by co-precipitation and investigated for selective liquid-phase CTH of FAL to FOL using iso-propanol as a hydrogen donor. The catalyst properties have been investigated by X-ray diffraction (XRD), coupled plasma optical emission spectrometry (ICP-OES),  $\text{N}_2$  adsorption and desorption ( $\text{N}_2$ -BET) and temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD). The effects of reaction conditions (temperature, reaction time), the catalyst to FAL ratio, and recycling the catalyst have also been studied to optimize the hydrogenation of FAL to FOL.

## 2. Experimental section

### 2.1. Materials

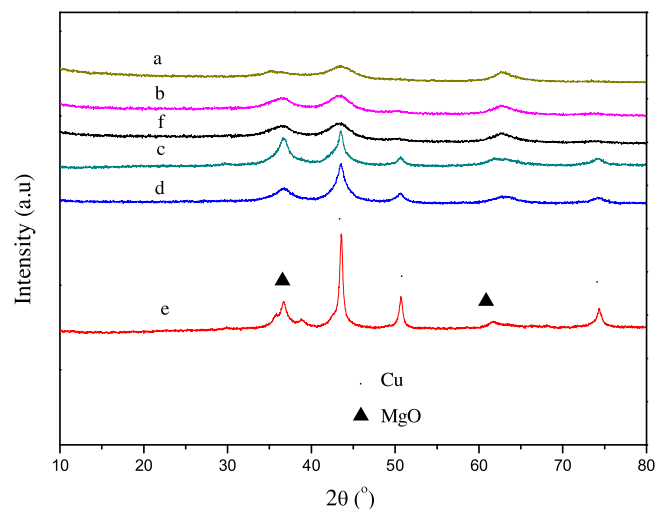
FAL (99%) and FOL (99%) have been purchased from Aladdin Chemicals (Shanghai, China).  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99%),  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99%),  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (99%), iso-propanol (AR) and NaOH (AR) have been brought from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All chemicals have been used as received.

### 2.2. Catalyst preparation

The  $\text{Cu/MgO-Al}_2\text{O}_3$  catalysts (10–50 wt% Cu loading) have been prepared by co-precipitation. Firstly, a solution A of  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Mg}(\text{NO}_3)_2$ : $\text{Al}(\text{NO}_3)_3$  in  $\text{H}_2\text{O}$  (mole ratio of  $\text{Mg}(\text{NO}_3)_2$ : $\text{Al}(\text{NO}_3)_3$  = 1:1) and a solution B (0.25 mol/L  $\text{Na}_2\text{CO}_3$  + 0.8 mol/L NaOH) have been prepared. Then, the two solutions have been simultaneously added dropwise to 100 mL of distilled  $\text{H}_2\text{O}$  and stirred for 3 h. Then the resulting precipitates have been aged for at  $30^\circ\text{C}$  for 12 h at  $\text{pH} = 10 \pm 0.2$ . After being washed thoroughly with deionized water, the final samples have been dried at  $110^\circ\text{C}$  overnight. The dried precipitates have been decomposed at  $450^\circ\text{C}$  in order to obtain the corresponding mixed oxides. In the final step, the samples have been calcined at  $450^\circ\text{C}$  for 2 h.

### 2.3. Catalyst characterization

XRD patterns have been analyzed with an Empyrean 200895 X-ray diffractometer using Ni-filtered monochromatic  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.154$  nm) at 40 keV and 30 mA. The chemical compositions of these samples have been determined by ICP-OES (Optima 7000DV, PerkinElmer, USA).  $\text{N}_2$ -BET have been measured using  $\text{N}_2$  at 77 K in a static volumetric apparatus (Micromeritics ASAP2020). The samples have been degassed prior to measurements at  $300^\circ\text{C}$  for 16 h. Specific surface areas have been calculated using the Brunauer-Emmett-Teller (BET) equation, and the total pore volume has been derived from the amount of  $\text{N}_2$  adsorbed at  $p/p_0 = 0.99$ .  $\text{NH}_3$ -TPD and  $\text{CO}_2$ -TPD have been measured by a FineSorb-3010 equipped with a thermal conductivity detector (TCD, Zhejiang Finetec Instruments Co., Ltd). Typically, all catalysts have been reduced in situ at  $450^\circ\text{C}$  and for 2 h under a  $\text{H}_2$  atmosphere before each experiment. 50 mg of the catalyst has been pretreated at  $120^\circ\text{C}$  in He (20 mL/min) for 2 h and then cooled to  $80^\circ\text{C}$  before ammonia adsorption for 40 min. Ammonia/carbon dioxide desorp-



**Fig. 1.** The XRD patterns for the series of  $\text{Cu/MgO-Al}_2\text{O}_3$  catalysts with different Cu loadings after reduction. (a) 10%Cu/ $\text{MgO-Al}_2\text{O}_3$ ; (b) 20%Cu/ $\text{MgO-Al}_2\text{O}_3$ ; (c) 30%Cu/ $\text{MgO-Al}_2\text{O}_3$ ; (d) 40%Cu/ $\text{MgO-Al}_2\text{O}_3$ ; (e) 50%Cu/ $\text{MgO-Al}_2\text{O}_3$ ; (f) 20%Cu/ $\text{MgO-Al}_2\text{O}_3$  (after four cycles of catalyst reuse).

tion measurements have been achieved in the temperature range of  $80$ – $700^\circ\text{C}$  at a ramping rate of  $10^\circ\text{C}/\text{min}$ .

### 2.4. CTH of FAL

The CTH of FAL has been carried out in a micro-batch reactor, which has been made of stainless steel with a volume of 14 mL. In a typical experiment, the reaction solutions of FAL, catalyst, and 2-propanol have been loaded into the reactor. The sealed reactor has been put into a furnace, which had been heated to the desired temperature. The reactor has been removed at fixed time intervals and quickly placed into cool water to quench the reaction. The sample has been collected from the cooled reactor and rinsed in a 25 mL volumetric flask by methanol and then has been filtered by a  $0.22\ \mu\text{m}$  filter membrane. All catalysts have been reduced in situ at  $450^\circ\text{C}$  and for 2 h under a pure  $\text{H}_2$  atmosphere before each experiment.

The products have been qualitatively determined with an Agilent 7890B gas chromatograph/5977A mass spectrometer (GC/MS) and quantitatively analyzed by Agilent 7890A gas chromatography spectrometry (GC) equipped with a  $30\ \text{m} \times 0.25\ \text{mm} \times 0.25\ \mu\text{m}$  HP-5 capillary column and a flame ionization detector (FID). The conversions of FAL over different catalysts have been calculated from the amount of FAL consumed divided by the initial amount of FAL loaded into the reactor. Yields of the products have been calculated from the mass of product recovered divided by the mass of FAL loaded into the reactor. Each data point represents the mean result from three independent experiments.

## 3. Results and discussions

### 3.1. Catalyst characterization

The effect of the  $\text{MgO-Al}_2\text{O}_3$  on the crystal phase of the Cu nanoparticles after calcination and reduction has been confirmed by XRD. XRD patterns of series  $\text{Cu-MgO-Al}_2\text{O}_3$  and 20%Cu/ $\text{MgO-Al}_2\text{O}_3$  catalyst samples after four cycles of catalyst use and regeneration are shown in Fig. 1. No diffraction peaks for  $\text{CuO}$  ( $2\theta = 35.5$  and  $38.7^\circ$ ) or any related cupreous substances have been observed except for the 50%Cu/ $\text{MgO-Al}_2\text{O}_3$ . Small intensity  $\text{CuO}$  peaks have been observed for 50%Cu/ $\text{MgO-Al}_2\text{O}_3$ , meaning that the  $\text{CuO}$  was not be totally reduced to  $\text{Cu}^0$  because of the high CuO loading. A  $\text{Cu}$  (111) (JCPDS 04-0836) diffraction peak at  $43.2^\circ$  has

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