



# Hydrogenation of biomass-derived compounds containing a carbonyl group over a copper-based nanocatalyst: Insight into the origin and influence of surface oxygen vacancies



Qi Hu, Lan Yang, Guoli Fan, Feng Li\*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Box 98, Beijing 100029, China

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## ABSTRACT

New Mn-containing spinel-supported copper nanocatalysts were directly generated via a Cu–Mn–Al layered double hydroxide precursor route and employed in gas-phase hydrogenation of dimethyl succinate (DMS) to  $\gamma$ -butyrolactone (GBL). It was found that the introduction of manganese into catalyst precursors led to the formation of Mn-containing spinel phases, thereby giving rise to highly dispersive Cu<sup>0</sup> nanoparticles and a large number of surface defects (i.e., oxygen vacancies (O<sub>v</sub>), Mn<sup>2+</sup> species) in reduced catalysts. As-formed copper-based nanocatalysts exhibited exceptional catalytic hydrogenation performance with stability enduring up to 100 h. Such high catalytic efficiency could reasonably be attributed to the surface synergism between Mn<sup>2+</sup>–O<sub>v</sub>–Mn<sup>2+</sup> defect structures and active metallic copper species, which controlled the key to hydrogenation related to the adsorption of DMS molecules and following activation of carbonyl groups and the dissociation of hydrogen. Most importantly, such copper-based nanocatalysts displayed great potential applications in the hydrogenations of other biomass-derived compounds containing carbonyl groups (e.g., acetol, levulinic acid, levulinic acid esters, and furfural). The present strategy enables us to tune the surface structures of catalysts for designing new type of copper-based catalysts with significantly enhanced catalytic performance.

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## 1. Introduction

As one of the most important intermediate chemicals,  $\gamma$ -butyrolactone (GBL) has been widely used for the production of pyrrolidone derivatives, herbicides, and rubber additives [1]. Commonly, GBL is produced industrially by dehydrogenating 1,4-butanediol. However, the classical Reppe process for the production of 1,4-butanediol using explosive acetylene and possibly carcinogenic formaldehyde as feedstock may create environmental hazards and security issues [2]. Additionally, GBL can be obtained by hydrogenating petroleum-based maleic anhydride over various noble metal and copper-based catalysts [3,4]. With the shortage of fossil resources and increasing emission of greenhouse gases, the conversion from sustainable and renewable raw biomass to useful fuel and chemicals has become more important in the past decade [5–9]. Thanks to the development of biorefinery processes, for example, succinic acid and its derivatives are becoming promising biobased C4 platform molecules for replacing other chemicals such as maleic anhydride [10,11]. As an ecofriendly, economical, and

sustainable alternative, GBL may be produced by directly hydrogenating succinic acid esters, easily obtained on a large scale by low-cost and commercially realized fermentation of various renewable biomass sources (e.g., glucose and xylose) [12,13]. In this regard, typical Cr<sub>2</sub>O<sub>3</sub>-promoted copper-based catalysts are active for the hydrogenation of dimethyl succinate (DMS) [14]. The high toxicity of the Cr<sup>6+</sup> ion, however, causes serious pollution to the environment and humans, besides its poor durability.

Recently, designing Cr-free supported Cu-based catalysts has become an important issue in green and sustainable chemistry [15–17]. For example, industrial Cu/ZnO catalyst has attracted enormous attention [16], because the ZnO support not only serves as a physical spacer between Cu nanoparticles (NPs) to attain high copper surface area but also strongly interacts with Cu NPs to govern the catalytic performance [18]. It was reported that the Cu<sup>+</sup>–Cu<sup>0</sup> synergy in Cu/SiO<sub>2</sub> catalysts could remarkably promote the extent of hydrogenation related to ester groups [19–21]. In addition, our groups found that the way that ester molecules interacted with Cu/MgO catalyst could be greatly influenced by the surface acid–base nature of catalysts [22]. In this regard, Cu/ZnO and Cu/SiO<sub>2</sub> catalysts have been used in selective hydrogenation of DMS to GBL [23,24]. However, low yields of GBL obtained

\* Corresponding author. Fax: +86 10 64425385.

E-mail address: [lifeng@mail.buct.edu.cn](mailto:lifeng@mail.buct.edu.cn) (F. Li).

greatly hinder their practical application. Therefore, besides the above factors significantly governing the catalytic hydrogenation of esters, it is necessary to construct special surface structures of Cu-based catalysts to further improve their catalytic performance.

As we know, the surface electronic and geometric structures of supported metal catalysts are related closely to their catalytic performance, because, besides active metal sites [25–27], catalytic processes usually involve multifarious catalytic centers synergistically controlling heterogeneous reactions [28,29]. It is well documented that reducible oxides (e.g., titania and ceria) can develop surface oxygen vacancies ( $O_v$ ) for the valence decrease, thus leading to the loss of structural oxygen from the anion sublattice [30–33]. As reported, surface oxygen vacancies on the defective titania can fix oxygen in some molecules (water, aliphatic alcohols) [34,35], while  $Ti^{3+}$  species adjacent to oxygen vacancies on Pt/TiO<sub>2</sub> can interact with carbonyl groups to promote the hydrogenation of furfural [36]. Correspondingly, the strategy for achieving high catalytic efficiency is to reasonably manipulate the surface structures of catalyst supports to facilitate the adsorption and subsequent activation of reactants.

On the other hand, layered double hydroxides (LDHs,  $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A_{x/n}]^{n-} \cdot mH_2O$ ), known as a family of highly ordered two-dimensional anionic clay materials, contain different  $M^{2+}$  and  $M^{3+}$  metal cations uniformly distributed in an orderly prearrangement in the brucite-like layers [37]. LDH materials are emerging as excellent catalyst supports to construct bifunctional or multifunctional heterogeneous catalysts. For instance, LDH-supported metal catalysts are very active in oxidation, deoxygenation, and dehydrogenation reactions [38–40] without the addition of a foreign alkali promoter. Liu et al. found that synergistic effects between Au NPs and Cr cation redox cycles in LDHs could significantly promote the aerobic oxidation of organic substrates [41]. In most cases, high metal loadings would result in the aggregation of active metal particles. More interestingly, highly dispersed supported metal-based catalysts with tunable metal particle size can be constructed by reducing calcined LDHs containing desired active metal species [42–45]. This LDH precursor route significantly improves the interaction between metal and support and prevents the aggregation of metal NPs, thus facilitating the high dispersion of active metal species. For example, LDH precursors containing Cu, Zn, and Al have been utilized to prepare supported catalysts for industrially important processes (e.g., methanol steam reforming, methane synthesis) [46–48]. To further improve the catalyst performance, the strategy for creating new types of catalytically active centers via an LDH precursor route is still a challenging work.

In the present work, we reported new environment-friendly and highly efficient supported copper nanocatalysts for gas-phase hydrogenation of DMS to GBL, which were directly generated from CuMnAl-LDH precursors. It was found that besides well-dispersed metallic copper NPs, a large amount of surface oxygen vacancies could be created by the transformation of  $Mn^{3+}$  to  $Mn^{2+}$  species in the course of reduction, thereby forming abundant surface  $Mn^{2+}-O_v-Mn^{2+}$  defect structures. As-formed copper-based nanocatalysts displayed exceptional catalytic hydrogenation performance, with stability enduring up to 100 h at a low hydrogen partial pressure of 0.25 MPa. Furthermore, this type of flexible copper-based nanocatalysts displayed a great application potential in the hydrogenation of a series of biomass-derived compounds (e.g., acetol, levulinic acid, levulinic acid esters, furfural).

## 2. Experimental

### 2.1. Synthesis of supported copper nanocatalysts

A series of CuMnAl-LDH precursors were prepared by separate nucleation and aging steps in a method previously developed by

our group [49]. Solution A:  $Cu(NO_3)_2 \cdot 6H_2O$ ,  $MnCl_2 \cdot 4H_2O$ , and Al ( $(NO_3)_3 \cdot 9H_2O$ ), with a Cu/Mn/Al molar ratio of 2:x:1 ( $x = 0, 0.5, 1, 1.5$ ), were dissolved in 100 mL of deionized water to give a mixed salt solution. Solution B: NaOH and  $Na_2CO_3$  were dissolved in 100 mL of deionized water to form a mixed base solution ( $[OH^-] = 1.6([M^{2+}] + [Al^{3+}])$ ,  $[CO_3^{2-}] = 2[Al^{3+}]$ ). Solutions A and B were simultaneously added rapidly to a colloid mill with the rotor speed set at 3000 rpm and mixed for 2 min. The resulting blue suspension was washed with deionized water until pH 7.0, aged at 40 °C for 24 h, and finally dried at 70 °C for 24 h in a vacuum oven. The obtained CuMnAl-LDH (denoted as LDH-x) was calcined in static air at 550 °C for 6 h, pelletized, crushed, sieved to 40–60 mesh, and denoted as MMO-x. Before the reaction, the calcined samples were reduced in situ in 10%  $H_2/N_2$  atmosphere at 300 °C for 2 h at a ramp rate of 2 °C  $min^{-1}$ , and the obtained reduced catalysts were denoted as CuMn-x. For comparison, Cu catalysts over different commercial supports ( $Mn_3O_4$ ,  $SiO_2$ , ZnO) with a Cu loading of 35.0 wt.% were also prepared by incipient wetness impregnation. In addition, highly dispersed Cu/ $SiO_2$ -H comparison catalyst with a Cu loading of 35.0 wt.% was prepared by a urea-assisted gelation method previously reported [50].

### 2.2. Characterization

X-ray diffraction (XRD) data were collected on a Shimadzu XRD-6000 diffractometer with a graphite-filtered Cu K $\alpha$  source ( $\lambda = 0.15418$  nm) at 40 kV and 30 mA. Elemental analysis was performed using a Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectroscope (ICP-AES). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out on a JEOL 2100 operated at an accelerating voltage of 200 kV. High-angle annular dark-field scanning TEM-energy-dispersive X-ray spectroscopy (HAADF-STEM-EDX) images were recorded on a JEOL2010F instrument.  $N_2$  adsorption-desorption isotherms of the samples were obtained on a Micromeritics ASAP 2020 apparatus at -196 °C. All samples were outgassed prior to analysis at 200 °C for 12 h under  $10^{-4}$  Pa vacuum. The specific surface areas were determined by the multipoint BET method. X-ray photoelectron spectroscopy (XPS) was recorded on a Thermo VG ESCA-LAB250 X-ray photoelectron spectrometer using Al K $\alpha$  X-ray radiation (1486.6 eV photons). Binding energies were calibrated based on the graphite C1s peak at 284.6 eV. X-ray induced Auger spectra (XAES) were carried out on a PHI Quantera SXM using Al K $\alpha$  X-rays as the excitation source. Electron paramagnetic resonance (EPR) of solid samples was determined at room temperature on a Bruker ESP300E spectrometer. Photoluminescence (PL) emission spectra were recorded at room temperature using an RF-5301PC fluorophotometer with excitation wavelength 320 nm.

The reduction behavior of calcined samples was studied by hydrogen temperature-programmed reduction ( $H_2$  TPR) using a Micromeritics ChemiSorb 2920 instrument. The sample (100 mg), which was put in a quartz U-tube reactor, was degassed at 200 °C for 2 h under argon flow (40 mL/min). TPR was performed in a stream of 10% v/v  $H_2/Ar$  (40 mL/min) at a heating rate of 5 °C/min from 50 °C. The effluent gas was detected by a thermal conductivity detector (TCD).

Metallic copper surface areas in samples were determined by combining  $N_2O$  oxidation and CO pulse chemisorption using a Micromeritics ChemiSorb 2920 instrument. First, the calcined sample (100 mg) underwent an  $H_2$  TPR process in 10%  $H_2/He$  mixture from 50 to 350 °C at a heating rate of 5 °C. After cooling down to 70 °C in pure He, the gas was switched to 10%  $N_2O/N_2$  (40 mL/min) for 1 h to oxidize surface-reduced  $Cu^0$  atoms and oxygen vacancies to  $Cu_2O$  species and lattice oxygen ions. After that, the catalyst was purged with He for 1 h and the temperature was cooled to 50 °C. Finally, CO pulse chemisorption was carried out

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