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## 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

## A R T I C L E I N F O

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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  $Cr_2O_3$ -promoted copper-based catalysts are active for the hydrogenation of dimethyl succinate (DMS) [14]. The high toxicity of the  $Cr^{6+}$  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







<sup>\*</sup> Corresponding author. Fax: +86 10 64425385. E-mail address: 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<sub>v</sub>) 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<sup>3+</sup> 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<sup>2+</sup> and M<sup>3+</sup> 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, LDHsupported 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<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, MnCl<sub>2</sub>·4H<sub>2</sub>O, 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<sub>2</sub>CO<sub>3</sub> 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<sup>-1</sup>, and the obtained reduced catalysts were denoted as CuMn-x. For comparison. Cu catalysts over different commercial supports (Mn<sub>3</sub>O<sub>4</sub>, SiO<sub>2</sub>, ZnO) with a Cu loading of 35.0 wt.% were also prepared by incipient wetness impregnation. In addition, highly dispersed Cu/SiO<sub>2</sub>-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 Ka source  $(\lambda = 0.15418 \text{ nm})$  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 Xray spectroscopy (HAADF-STEM-EDX) images were recorded on a JEOL2010F instrument. N2 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 Ka 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 Ka 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<sup>0</sup> atoms and oxygen vacancies to Cu<sub>2</sub>O 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 using a pulse titration procedure. CO pulse introduction was repeated until the signal area was constant. Correspondingly, the metallic copper surface area ( $S_{\text{Cu}}$ ,  $m^2/g$ ) and the average volume–surface diameter of metallic copper ( $D_{\text{Cu}}$ ) assuming spherical geometry were calculated according to the equations

$$S_{Cu} = \frac{X \times SF \times N_A}{N_{Cu}},\tag{1}$$

$$D_{\rm Cu} = \frac{6}{S_{\rm Cu} \times \rho_{\rm Cu}},\tag{2}$$

where X is the amount of CO chemisorption (mol/g), SF is the Cu<sup>0</sup>/ (Cu<sup>0</sup> + Cu<sup>+</sup>) molar ratio on the surface of reduced catalysts determined by Cu XAES,  $N_A$  is Avogadro's constant,  $N_{Cu}$  is the number of surface Cu<sup>0</sup> atoms per unit surface area (1.46 × 10<sup>19</sup>/m<sup>2</sup>) and  $\rho_{Cu}$  is the density of copper (8.92 g/cm<sup>3</sup>).

The numbers of surface oxygen vacancies for samples were determined by combining N<sub>2</sub>O oxidation and H<sub>2</sub> TPR using a Micromeritics ChemiSorb 2920 instrument, assuming that surface oxygen vacancies can be completely oxidized to lattice oxygen ions by N<sub>2</sub>O at 70 °C [51]. First, a calcined sample (100 mg) underwent H<sub>2</sub> TPR in a 10% H<sub>2</sub>/He mixture from 50 to 350 °C at a heating rate of 5 °C. After cooling to 70 °C in pure He, the gas was switched to 10% N<sub>2</sub>O/N<sub>2</sub> (40 ml/min) for 1 h. After that, the catalyst was purged with He for 1 h and the temperature was lowered to 50 °C. Then a second H<sub>2</sub> TPR was carried out from 50 to 350 °C and held for 1 h to recover surface Cu<sup>0</sup> atoms and oxygen vacancies. Correspondingly, the number of surface oxygen vacancies (N<sub>v</sub>, mol/g) was calculated according to the equation

$$N_{\nu} = X - \frac{Y}{2},\tag{3}$$

where  $X \pmod{g}$  is the hydrogen consumption in the second H<sub>2</sub> TPR and  $Y \pmod{g}$  is the surface Cu<sup>0</sup> atoms per gram of reduced catalyst calculated from the surface area of metallic copper.

In situ Fourier transform infrared spectroscopy (FT-IR) of CO<sub>2</sub> or DMS absorbed on catalysts was performed on a Thermo Nicolet 380 FT-IR spectrometer with a resolution of 0.5 cm<sup>-1</sup>. The sample powder was pressed into a self-supporting wafer (50 mg) and mounted into an IR cell. The sample was first reduced with H<sub>2</sub> (10 ml/min) at 350 °C for 1 h, followed by evacuation for 1 h at 400 °C and then cooling to room temperature. For CO<sub>2</sub> absorption, after acquisition of the background spectrum, pure CO<sub>2</sub> was continuously introduced into the chamber at 10 ml/min, and IR spectra were recorded at different times. For DMS absorption, the sample was exposed to DMS at room temperature for 1 h. Then physisorbed DMS was removed by evacuation and the samples were recorded at 30 and 200 °C.

## 2.3. Catalytic test

The hydrogenation of DMS was conducted on a stainless steel fixed-bed tubular reactor with inner diameter 10 mm. The samples (2.0 g), which were loaded into reactor with quartz powders packed in both sides of the catalyst bed with a height of approximately 27 mm, were reduced in a 10%  $H_2/N_2$  atmosphere at 300 °C for 2 h. Afterward, 15% DMS (purity > 99%) in ethanol and  $H_2$  was fed into the reactor at a  $H_2/DMS$  molar ratio of 150 at 210 °C. During hydrogenation, the hydrogen partial pressure was kept at 0.25 MPa, and the room temperature liquid hourly space velocity (LHSV) of DMS was changed from 1 to 8 h<sup>-1</sup>. Finally, the liquid products were analyzed by an Agilent GC7890B gas chromatograph equipped with a flame ionization detector and a DB-WAX capillary column (30.0 m × 250  $\mu$ m × 0.25  $\mu$ m). The conversions were calculated by the change in molar number before and after the reaction. The conversions and selectivities were obtained

through at least three parallel experiments. In each case, the carbon balance, calculated based on the mass difference between carbon in the introduced reactant and that in products, was above 95%. Meanwhile, it was found that the DMS conversion remained almost unchanged when the catalyst grain diameter was less than 40 mesh or the catalyst loading was increased from 2.0 to 3.0 g under the same values of LHSV and H<sub>2</sub>/DMS molar ratio. This demonstrates that both the influence of internal diffusion and the external mass transfer limitation could be eliminated in the present reaction system.

## 3. Results and discussion

#### 3.1. Structural characterizations

As shown in Fig. S1 in Supporting Information, XRD patterns of CuMnAl-LDH precursors present a series of (003), (006), and (012) diffractions corresponding to hydrotalcite-like materials (JCPDS No. 37-0630). After calcination, CuMnAl-LDHs are transformed to corresponding mixed metal oxides (MMO) (Fig. 1A) by collapse of the initial layered structure. XRD patterns of the MMO-0 sample only present the diffractions of the CuO phase (JCPDS no. 05-0661), and no diffractions related to crystalline  $Al_2O_3$  and cubic spinel-type  $CuAl_2O_4$  (JCPDS no. 33-0448) are detected. With the gradual addition of Mn, Mn-containing spineltype complex metal oxide phases, such as the MnAl<sub>2</sub>O<sub>4</sub> phase (JCPDS no. 29-0880), can also be observed in the MMO-0.5. As the Mn content increases, the diffraction intensities for the spinel phase are enhanced progressively, whereas, inversely, those for the CuO phase are reduced. This suggests that other kinds of spinel-like (Cu<sup>2+</sup>, Mn<sup>2+</sup>)(Mn<sup>3+</sup>, Al)<sub>2</sub>O<sub>4</sub> phases (denoted as CuMnAlO<sub>4</sub>) may be present in calcined samples, probably due a structure similar to those of MnAl<sub>2</sub>O<sub>4</sub> and CuAl<sub>2</sub>O<sub>4</sub> [52]. In the case of MMO-1.5, with the largest amount of Mn, only the spinel phase is observed. Interestingly, the average crystallite size of spinel calculated by the Scherrer formula according to the (220) diffraction is about 13.0 nm for MMO-1 and 16.5 nm for MMO-1.5. EPR spectroscopy is an extremely sensitive probe for the coordination environment of Cu<sup>2+</sup> cations. In the EPR spectrum of MMO-0 (Fig. 2), an intensive signal at 345 mT is associated with Cu<sup>2+</sup> ions in a tetrahedral environment within the CuO-Al<sub>2</sub>O<sub>3</sub> solid solution [53]. As for MMO-1.5, there is only a large and broad signal around 567.8 mT, which is assigned to Cu<sup>2+</sup> ions in an octahedral environment within the cubic spinel structure [54]. MMO-0.5 and MMO-1 samples display a broad signal between 345 and 567.8 mT, suggestive of the coexistence of CuMnAl<sub>2</sub>O<sub>4</sub> and CuO in calcined samples. These results reflect that the introduction of Mn seems to inhibit the crystallization of CuO and simultaneously trigger the formation of spinel-type CuMnAlO<sub>4</sub>.

As shown in Fig. 1B, the XRD patterns of reduced CuMn-*x* samples present a strong (111) diffraction at 43.3° along with a weak (200) one at 50.4°, indicative of the presence of a face-centered cubic (fcc) metallic copper phase (JCPDS No. 04-0836). In addition, it is worth noting that the diffraction intensities for the spinel phase are greatly weakened, due to the reduction of Cu<sup>2+</sup> species. As the Mn/Al molar ratio increases from 0 to 1, the average crystallite size of metallic copper particles calculated by the Scherrer formula decreases gradually from about 20.8 to 8.1 nm (see Table S1 in Supporting Information). However, further increase in the Mn content results in a slight increase in the particle size. This demonstrates that an appropriate amount of the spinel phase may have a favorable dispersing effect for copper species.

Typical TEM images of CuMn-x samples are shown in Fig. S2 in Supporting Information. Black Cu NPs in CuMn-0 and CuMn-0.5 are poorly dispersed on the support and undergo a little agglomera-



**Fig. 1.** XRD patterns of MMO-*x* (A) and CuMn-*x* (B) samples.



Fig. 2. EPR spectra of MMO-x samples.

tion. With the further increase in the Mn content, small Cu NPs without agglomeration are highly dispersed on the support surface. Moreover, the particle size distribution histograms of Cu NPs in CuMn-*x* samples obtained from TEM images (Fig. S3) reveal that the average sizes of Cu NPs are well consistent with the crystallite sizes obtained from XRD line-broadening analyses (Table S1). However, the average volume–surface diameter of Cu NPs estimated from the copper surface area is far larger than those from TEM and XRD analyses, which is probably attributable to the presence of a large amount of surface Cu<sup>+</sup> species in CuMn-*x* samples, as well as to strong interaction between metal and support.

HRTEM images of representative CuMn-1 depict that a large number of Cu NPs are well dispersed on the support (Fig. 3a), and that the lattice fringes with interplanar spacings of about 2.09, 1.78, and 2.48 Å of two adjacent NPs (Fig. 3b) are indexed by the (111) and (220) planes of the metallic copper phase and the (311) plane of the MnAl<sub>2</sub>O<sub>4</sub> or Mn<sub>3</sub>O<sub>4</sub> spinel phase, respectively. Close interfaces between metallic Cu and spinel are observed, accounting for the highly dispersive character of Cu NPs. Further, HAADF–STEM–EDS images (Fig. 3c–e) reveal the uniform distributions of Cu, Mn, Al, and O elements. The relative distributions of Cu, Mn, and Al elements within one individual particle were verified by means of the STEM–EDX line scan spectra (Fig. 3f). Obviously, three Cu, Mn, and Al lines show a similar Gaussian distribution along a single particle, demonstrating their relatively homogeneous distributions and close contact in the matrix. In the present catalyst system, CuMnAlO<sub>4</sub> spinel formed in catalyst precursors can function not only as a physical spacer between the CuO phase to achieve highly dispersed copper NPs, but also as one of the donors for catalytically active metal species to induce the formation of metal–support interactions.

H<sub>2</sub> TPR measurements were carried out to determine the reducibility of MMO-x samples (Fig. S4 in Supporting Information). As for MMO-0 containing only the CuO phase, there are actually three reduction regions in the temperature range 150-325 °C. The first small peak at 185 °C is ascribed to the reduction of isolated highly dispersed CuO species, the second at 230 °C to the reduction of small CuO particles, and the third that of to large bulk CuO particles. Additionally, pure Mn<sub>3</sub>O<sub>4</sub> exhibits a broad reduction peak in the temperature range 450-550 °C (Fig. S5), due to the reduction of Mn<sub>3</sub>O<sub>4</sub> to MnO [55]. In the case of MMO-0.5 containing a small amount of spinel phase, the reduction temperature for CuO is decreased slightly with the introduction of Mn, mainly due to the formation of smaller CuO particles. However, no reduction peak can be found above 325 °C, reflecting that the reduction of Cu and Mn species in the spinel phase to Cu<sup>0</sup>, Cu<sup>+</sup>, and Mn<sup>2+</sup> species can take place at low temperatures. A similar phenomenon also has been reported for the reduction of CuMn<sub>2</sub>O<sub>4</sub> spinel [56]. Such significantly promoted reduction behavior of Mn<sup>3+</sup> species is due to close proximity of Cu and Mn species in the spinel structure. As for MMO-1 containing a large amount of the spinel phase and a small amount of the CuO phase, the intensity of the second reduction peak is greatly enhanced, whereas, inversely, that of the third reduction peak is reduced. This demonstrates that the reduction of Cu<sup>2+</sup> and Mn<sup>3+</sup> species in the spinel structure can be synchronously improved because of the formation of more CuMnAlO<sub>4</sub> spinel with small particle size. In the course of reduction, the Jahn-Teller effect caused by Cu<sup>2+</sup> species may weaken the Cu–O bond in the spinel structure [54,57], thus promoting the reduction of CuMnAlO<sub>4</sub> spinel with H<sub>2</sub>. As for MMO-1.5 containing only the spinel phase, the greatly enhanced intensity of the third reduction peak is related to the formation of more CuMnAlO<sub>4</sub> with large particle size. Further, the theoretical amounts of hydrogen consumed for MMOx were calculated based on either the complete reduction of  $Cu^{2+}$  to



Fig. 3. HRTEM images (a and b) of CuMn-1 sample. HAADF–STEM image (c) of CuMn-1 with the EDX mapping (d); high-magnification STEM image (e); EDX line spectra of CuK, MnL, and AlK along the red line in e (f).

Cu<sup>0</sup> or the complete reduction of both Cu<sup>2+</sup> to Cu<sup>0</sup> and Mn<sup>3+</sup> to Mn<sup>2+</sup>. Obviously, for all samples, the actual amounts of hydrogen consumed are less than the theoretical values deduced from the reduction of both Cu<sup>2+</sup> to Cu<sup>0</sup> and Mn<sup>3+</sup> to Mn<sup>2+</sup> (Table S2 in Supporting Information). Moreover, in the cases of MMO-1 and MMO-1.5 with higher Mn content, the actual amounts of hydrogen consumed are larger than the theoretical values from the reduction of Cu<sup>2+</sup> to Cu<sup>0</sup>. This result further confirms the reduction of partial Cu<sup>2+</sup> and Mn<sup>3+</sup> to Cu<sup>+</sup> and Mn<sup>2+</sup> species in the CuMnAlO<sub>4</sub> spinel.

XPS studies reveal a peak of  $Cu^{2^+}$  species with a satellite peak in the  $Cu2p_{3/2}$  region for MMO-*x* samples (Fig. S6 in Supporting Information) [58,59]. With increasing Mn/Al molar ratio, the peak position of the  $Cu^{2^+}$  species shifts gradually from 933.9 to 934.7 eV, which may be associated with the formation of more CuMnAlO<sub>4</sub> spinel phase. In the spinel structure, the covalent  $Cu^{2^+}$ —O bond can be polarized by  $Mn^{2^+}/Mn^{3^+}$  or  $Al^{3^+}$  ions, thus leading to a decrease in the effective charge of  $Cu^{2^+}$  species. As for reduced samples, the presence of a  $Cu2p_{3/2}$  signal at ca. 933.0 eV and the absence of a shake-up satellite peak located at 942.0 eV confirm the reduction of  $Cu^{2^+}$  species (Fig. S7) [60]. Further, a broad and asymmetric Auger kinetic energy peak is observed from the Cu LMM XAES, indicative of the coexistence of  $Cu^0$  and  $Cu^+$  species in reduced CuMn-*x* samples (Fig. S8) [61], because of strong interaction between Cu species and supports [62]. This interaction, which originates from the homogeneous distributions of metal cations in the brucite-like layers of LDH precursors, can give rise to  $Cu^+$ –O–M-like (M = Al or Mn) structures after reduction. Meanwhile, the surface  $Cu^+/(Cu^0 + Cu^+)$  molar ratio seems to present a decreasing trend with the Mn content (Table 1). Specifically, the CuMn-1 sample possesses the lowest  $Cu^+/(Cu^0 + Cu^+)$  molar ratio of 0.36.

Fig. S9 in Supporting Information shows the spin–orbit splitting of  $Mn2p_{1/2}$  and  $Mn2p_{3/2}$  signals for calcined samples. The asymmetric and broad  $Mn2p_{3/2}$  peak may be deconvoluted into two symmetry peaks centered at about 640.5 and 642.4 eV, which are assigned to  $Mn^{2+}$  and  $Mn^{3+}$  species, respectively [63]. Most of the Mn is present in the form of  $Mn^{3+}$  species, and only a small amount of  $Mn^{2+}$  species can be found in calcined samples. Moreover, Mn3s spectra for MMO-*x* samples were collected to determine the valence state of Mn ions precisely (Fig. S9). As has been reported,

the valence of Mn ( $V_{Mn}$ ) can be determined through the exchange splitting of Mn3s spectra ( $\triangle E_{3s}$ ) according to the linear equation  $V_{\rm Mn}$  = 9.67–1.27 $\triangle E_{3s}$ /eV [64,65]. Therefore, the valences of Mn species for MMO-0.5, MMO-1, and MMO-1.5 are calculated to be about 2.9, 2.9, and 2.8, respectively (Table 2). Compared with those in calcined samples, the Mn<sup>2+</sup>/Mn<sup>3+</sup> molar ratios in reduced samples estimated from the peak intensities are found to be much higher (Fig. 4A and Table 2), reflecting the reduction of Mn<sup>3+</sup> species in the spinel structure to Mn<sup>2+</sup> in the form of MnAl<sub>2</sub>O<sub>4</sub> or Mn<sub>3</sub>O<sub>4</sub> spinels. Notably, the Mn<sup>2+</sup>/Mn<sup>3+</sup> molar ratio in the CuMn-1 is much larger than those in other samples (Table 2), indicative of the formation of more Mn<sup>2+</sup> species. According to XPS of Mn3s regions for CuMn-0.5, CuMn-1, and CuMn-1.5 (Fig. S10 in Supporting Information), the valences of Mn species are estimated to be about 2.3. 2.2 and 2.4, respectively (Table 2). These results confirm the reduction of Mn<sup>3+</sup> to Mn<sup>2+</sup> species in reduced samples.

As shown in Fig. 4B, there are two fitted peaks in the spectra of O1s regions, O<sub>1</sub> and O<sub>11</sub>, representing two different kinds of oxygen species. The peak at a lower binding energy of 530.7 eV is characteristic of the lattice oxygen bound to metal cations in the spinel structure [66]; the other at 532.3 eV is mainly assigned to surface-adsorbed oxygen species on oxygen vacancies belonging to defect-oxide and surface hydroxyl-like groups adsorbed on metal ions [66–69]. Correspondingly, the intensity ratio  $O_{II}/O_{I}$  can qualitatively estimate the relative abundance of surface oxygen vacancies to some extent. It is observed from Table 2 that the  $O_{II}$ O<sub>I</sub> ratio presents an increasing trend with the Mn/Al molar ratio from 0 to 1, and then decreases at the Mn/Al molar ratio of 1.5. In addition, it is interesting to note from Table 2 that the change in the surface  $O_{II}/O_{I}$  ratio is in good agreement with that in the number of oxygen vacancies on CuMn-x samples. In our case, the reduction of Mn-containing spinel can lead to the loss of lattice oxygen and thus the formation of oxygen vacancies according to the following equation:  $Mn^{3+}-O^{2-}-Mn^{3+} + H_2 \rightarrow Mn^{2+}-O_v-Mn^{2+} + -$ H<sub>2</sub>O. Correspondingly, for the CuMn-1 sample, the larger amount of  $Mn^{2+}-O_{\nu}-Mn^{2+}$  defect structures should be related to the higher surface  $O_{II}/O_{I}$  ratio, as well as the higher surface  $Mn^{2+}/Mn^{3+}$  ratio.

To further determine oxygen vacancies, PL measurement was conducted at an excitation wavelength of 320 nm. As shown in Fig. 5, an emission peak at approximately 368 nm appears because of the recombination of excitons on the surface defects, such as oxygen vacancies [70]. It is interesting to note that CuMn-1 displays a stronger emission than the other three reduced samples, demonstrating a higher concentration of surface oxygen vacancies. In contrast, the concentration of oxygen vacancies on the MMO-1 is far less than that on the CuMn-1, because surface oxygen vacancies can be developed mainly by Mn<sup>2+</sup> species in the reduction process.

# 3.2. Gas-phase hydrogenation of carbonyl group-containing compounds

The catalytic performance of CuMn-x catalysts was investigated in the gas-phase hydrogenation of DMS. It is well documented that

#### Table 2

Surface chemical states of manganese and oxygen species on CuMn-x samples.

Samples	Surface Mn <sup>2+</sup> /	Valence of	Surface O <sub>II</sub> /O <sub>I</sub>	Surface <i>N</i> v
	Mn <sup>3+</sup> molar ratio <sup>a</sup>	Mn species <sup>b</sup>	molar ratio <sup>c</sup>	(µmol g <sup>-1</sup> ) <sup>d</sup>
CuMn-0	-	-	0.45	5
CuMn-0.5	2.1 (0.12) <sup>e</sup>	2.3 (2.9) <sup>f</sup>	0.63	46
CuMn-1	2.9 (0.11)	2.2 (2.9)	1.10	123
CuMn-1.5	1.5 (0.19)	2.4 (2.8)	0.77	83

<sup>a</sup> Determined by XPS of Mn2p region.

<sup>b</sup> Determined by XPS of Mn3s splitting.

<sup>c</sup> Determined by XPS of O1s region.

 $^{\rm d}$  Amount of surface oxygen vacancies determined by combining  $N_2O$  oxidation and  $H_2$  TPR.

e Mn<sup>2+</sup>/Mn<sup>3+</sup> molar ratio in calcined samples.

<sup>f</sup> Valence of Mn in calcined samples.



Fig. 4. XPS spectra of Mn2p (A) and O1s (B) regions in reduced samples.

the hydrogenation of DMS usually comprises several continuous processes, including DMS hydrogenation to GBL, GBL hydrogenation to 1,4-butanediol (1,4-BDO), and deep hydrogenation to tetrahydrofuran (THF) [71]. Further, in the present CuMn-*x* catalyst system, external and internal mass transport effects were estimated based on Mears and Weisz–Prater criteria for the highest observed rates (shown in the Supporting Information) [72,73]. The Mears criterion,  $\frac{-r'_A\rho_bRn}{k_cC_{Ab}} < 0.15$ , gives values of  $2.5 \times 10^{-4}$  for CuMn-0,  $2.7 \times 10^{-4}$  for CuMn-05,  $5.8 \times 10^{-4}$  for CuMn-1, and  $3.9 \times 10^{-4}$  for CuMn-15, respectively, indicating that the external mass transport effect over CuMn-*x* catalysts can be neglected. In addition, the Weisz–Prater criterion,  $C_{WP} = \frac{-r'_{A(OBS)}\rho_c R^2}{D_c C_{AS}} < 1$ , gives values of  $7.3 \times 10^{-4}$  for CuMn-0,  $7.7 \times 10^{-4}$  for CuMn-0.5,  $2.0 \times 10^{-3}$ 

#### Table 1

The structural, textural, and component data of CuMn-x samples.

Samples	Cu/Mn/Al molar ratio	Cu (wt.%) <sup>a</sup>	$S_{\text{BET}} (m^2/g)^{\text{b}}$	$S_{Cu} (m^2/g)^c$	Cu <sup>+</sup> /(Cu <sup>0</sup> + Cu <sup>+</sup> ) ratio <sup>d</sup>	Surface Cu <sup>0</sup> (µmol g <sup>-1</sup> ) <sup>e</sup>	Surface $Cu^+$ (µmol g <sup>-1</sup> ) <sup>e</sup>
CuMn-0	2:0:1	56.5	44	11.5	0.53	280	315
CuMn-0.5	2:0.5:1	47.4	51	12.1	0.50	295	295
CuMn-1	2:1:1	36.5	55	14.0	0.36	341	191
CuMn-1.5	2:1.5:1	30.2	48	11.8	0.41	287	199

<sup>a</sup> Determined by ICP-AES.

<sup>b</sup> Specific surface area calculated by the BET method.

<sup>c</sup> Metallic copper surface area determined by combining N<sub>2</sub>O oxidation and CO pulse chemisorption.

<sup>d</sup> Determined by Cu XAES analysis.

<sup>e</sup> Deduced from metallic copper surface area and Cu XAES results.



Fig. 5. PL spectra of the samples under an excitation wavelength of 320 nm.

for CuMn-1, and  $1.2\times10^{-3}$  for CuMn-1.5, respectively, indicating that there is no internal diffusion limitation in our system.

Table 3 demonstrates that under mild reaction conditions (low hydrogen pressure of 0.25 MPa), the conversion of DMS increases steadily from 71.2% over CuMn-0 to 99.8% over CuMn-1. However, a further increase in the Mn/Al ratio to 1.5 leads to a decrease in the conversion to 90.0%. All of the catalysts exhibit a high GBL selectivity of 98%, and the main byproducts are deep hydrogenation products (1,4-BDO and THF). To our best knowledge, this is the first report of the highly efficient gas-phase selective hydrogenation of DMS to GBL at such a low hydrogen pressure. Additionally, Cu-based catalysts supported on different oxides (Mn<sub>3</sub>O<sub>4</sub>, SiO<sub>2</sub>, ZnO) were used here as comparison samples (Fig. S11 in Supporting Information). It is observed that very low GBL yields of 30%, 21%, and 35% are attained over Cu/Mn<sub>3</sub>O<sub>4</sub>, Cu/SiO<sub>2</sub>, and Cu/ZnO catalysts, respectively, suggesting that the catalyst supports probably play important roles in governing the DMS hydrogenation.

To further understand the effect of Mn content on the catalytic performance of CuMn-*x* catalysts, the hydrogenation was conducted at different LHSV values of DMS (Fig. 6). The DMS conversion over CuMn-1 remains almost 100% in the LHSV range from 1.0 to  $6.0 h^{-1}$ , and then decreases with the LHSV increasing to  $8.0 h^{-1}$ . However, the conversions over CuMn-0 and CuMn-0.5 catalysts decline continuously in the LHSV range from 2.0 and 3.0 to  $8.0 h^{-1}$ . Interestingly, with the gradual increase in the LHSV value, all catalysts show a slightly increased selectivity to GBL. As a result, the best catalytic performance, as well as high tolerance to the LHSV of DMS, is achieved over CuMn-1.

In addition, the effects of reaction temperature and hydrogen pressure on DMS hydrogenation were investigated over CuMn-1. It is found that the DMS conversion increases gradually from 42.6% to 99.8% as the reaction temperature is elevated from 170

to 210 °C (Fig. S12 in Supporting Information). Obviously, elevating the reaction temperature from 200 to 240 °C results in a continuous decrease in the GBL selectivity, which is attributed to the deep hydrogenation of GBL to 1,4-BDO and THF byproducts. The DMS conversion can be greatly improved from 80.0% to 99.8% by increasing the hydrogen pressure from 0.1 to 0.25 MPa at 210 °C (Fig. S13). However, the GBL selectivity decreases continuously from 99.1% to 73.0% with the hydrogen pressure increasing from 0.1 to 1.0 MPa, due to the occurrence of deep hydrogenation. These results demonstrate that both low reaction temperature and hydrogen pressures can inhibit the deep hydrogenation of GBL product. Similar results are found in the case of the hydrogenation of diethyl succinate, reported previously [13,23].

Fig. 7 presents the DMS conversion and selectivity to GBL as functions of time on stream over CuMn-0 and CuMn-1 catalysts at a higher LHSV value of 7.0 h<sup>-1</sup>. During the 100 h continuous test, no decrease in either the DMS conversion or the GBL selectivity is found over the CuMn-1, demonstrating its high stability. TEM characterization results reveal no aggregation or growth of Cu NPs after 100 h (Fig. S14 in Supporting Information), showing the advantage for catalyzing the synthesis of GBL via selective hydrogenation of DMS. In contrast, obvious deactivation of CuMn-0, CuMn-0.5, and Cu-1.5 is observed at reaction times of 14, 40, and 64 h, respectively, which can be attributed to the aggregation and growth of Cu NPs (Fig. S14). These results imply that surface oxygen vacancies may efficiently stabilize active Cu<sup>0</sup> NPs in the course of reaction due to the presence of strong metal–support interaction.

Usually, the catalytic performance of supported metal catalysts is intrinsically linked to their microstructure of active metal sites and supports, including active metal surface area and metal-support interactions. In the present work, as-formed copper-based nanocatalysts exhibited excellent catalytic performance under mild reaction conditions. It has been proved that the introduction of Mn results in the formation of highly dispersed CuMnAlO<sub>4</sub> NPs in catalyst precursors. Moreover, the reduction of Mn species induces the formation of abundant surface oxygen vacancies. Further, to find the intrinsic reason for different catalytic performance of CuMn-x catalysts. DMS conversion data limited to less than 30% by adjusting the LHSV of DMS were used to calculate the initial turnover frequency (TOF), according to the rate of DMS consumption per number of exposed active metallic copper sites on the catalyst surface in the initial reaction stage. Variations in the Cu surface area and TOF value in the DMS hydrogenation as a function of the Mn/Al molar ratio are shown in Fig. 8. It is interesting to note that with the increasing Mn/Al molar ratio from 0 to 1, the TOF value increases gradually from 0.0031 to 0.0062 s<sup>-1</sup>, indicative of the promotional effect of the addition of Mn species on the catalytic hydrogenation. In the case of CuMn-1.5, however, the excess amount of Mn leads to a slight decrease in the TOF (0.0056  $s^{-1}$ ). As to hydrogenation catalyzed by metallic copper, the copper surface area plays a crucial role, because hydrogen dissociation always occurs on catalytically active metallic Cu<sup>0</sup> sites. However, the catalytic activities of catalysts do not correlate well with the copper

#### Table 3

Catalytic performance of CuMn-x catalysts in the gas-phase hydrogenation of DMS.<sup>a</sup>

Catalysts	Conversion (%)	Selectivity (%)			TOF $(\times 10^{-3} \text{ s}^{-1})^{b}$	$k \pmod{\mathrm{g_{cat}^{-1} h^{-1}}^{c}}$
		GBL	1,4-BDO	THF		
CuMn-0	71.2	98.0	1.6	0.4	3.1	7.5
CuMn-0.5	83.5	98.3	1.3	0.5	3.7	10.6
CuMn-1	99.8	98.2	1.0	0.8	6.2	42.0
CuMn-1.5	90.0	97.9	1.4	0.7	5.6	13.7

<sup>a</sup> Reaction conditions: temperature, 210 °C; hydrogen pressure, 0.25 MPa; H<sub>2</sub>/DMS ratio, 150 mol/mol; LHSV, 4 h<sup>-1</sup>.

P Determined based on the rate of DMS consumption per exposed active metallic copper site on the catalyst surface in the initial reaction stage.

<sup>c</sup> The reaction rate constant according to pseudo-first-order kinetic relationships for DMS hydrogenation.



**Fig. 6.** DMS conversion (A) and GBL selectivity (B) versus LHSV of DMS ( $h^{-1}$ ) over different catalysts. Reaction conditions: hydrogen pressure, 0.25 MPa; temperature, 210 °C;  $H_2$ /DMS, 150 mol/mol.



**Fig. 7.** Conversion (A) and selectivity to GBL (B) as a function of reaction time over different catalysts in the hydrogenation of DMS. Reaction conditions: temperature, 210 °C; hydrogen pressure, 0.25 MPa;  $H_2$ /DMS ratio, 150 mol/mol; LHSV, 7 h<sup>-1</sup>.

surface area. For instance, the TOF value for CuMn-1.5 is 1.8 times larger than that for CuMn-0, although their metal surface areas are almost equal. Furthermore, as for highly dispersed Cu/SiO<sub>2</sub>-H comparison catalyst (Fig. S15 in Supporting Information), despite its higher copper surface area ( $20.1 \text{ m}^2/\text{g}$ ) than that of CuMn-1, the resulting TOF value ( $0.0023 \text{ s}^{-1}$ ) is even lower than that for CuMn-0, strongly suggesting that the hydrogenation activity is not just related to copper surface area. Obviously, there is not a linear relationship between the metallic copper surface area and the catalytic activity of CuMn-x catalysts with various Mn/Al ratios, indicating that the copper surface area is not a sole key factor governing the efficiency of catalysts.

Fig. S16 in Supporting Information shows the dependence of ln  $(1 - x)^{-1}$  (*x* is the DMS conversion) upon *W*/*F*<sub>DMS</sub> (*W* presents the catalyst mass and *F* represents the molar flow rate of DMS) for the different catalysts. Noticeably, the DMS hydrogenation obeys pseudo-first-order kinetics with the equation  $\ln(1 - x)^{-1} = k \cdot W/F$  (*k*: the reaction rate constant) based on a plug-flow reactor [74,75]. It is found that the highest *k* value of 42.0 mmol g<sup>-1</sup><sub>cat</sub> h<sup>-1</sup> is achieved over CuMn-1, further indicating its high catalytic effi-



**Fig. 8.** The Cu surface area and TOF value as functions of the Mn/Al ratio for CuMn-*x* catalysts in the gas-phase hydrogenation of DMS.

ciency. Further, variations in the reaction rate constant k in the DMS hydrogenation as functions of the amounts of surface Cu<sup>0</sup>, Cu<sup>+</sup>, and oxygen vacancies are shown in Fig. 9. With the increase in the amounts of surface Cu<sup>0</sup> species and oxygen vacancies, the value of k appears to display an increasing trend, reflecting that besides active Cu<sup>0</sup> species, surface oxygen vacancies should play a key role in improving the DMS hydrogenation. However, the k value decreases monotonically with the increasing amount of Cu<sup>+</sup> species, suggesting that Cu<sup>+</sup> species are not a main factor influencing the catalytic performance. Notably, as the amount of oxygen vacancies increases from 83 to 123 µmol g<sup>-1</sup>, the k value increases dramatically from 13.7 to 42.0 mmol g<sup>-1</sup><sub>cat</sub> h<sup>-1</sup>, which should arise from surface synergy between Cu<sup>0</sup> species and oxygen vacancies on the CuMn-1 catalyst.

Considering the disparate TOFs and the reaction rate constant over CuMn-x catalysts under identical reaction conditions, there should be different surface structures among them. It is well documented that surface electrophilic Cu<sup>+</sup> species may promote the hydrogenation process to some extent by polarizing the C=O bond via interaction with the lone pair electrons on the O atom [19-21,76]. In the present catalyst system, however, the higher the  $Cu^{+}/(Cu^{+} + Cu^{0})$  ratio, the smaller the TOF and k value. This demonstrates that the synergy between Cu<sup>+</sup> and Cu<sup>0</sup> is not one of the kev issues influencing the catalytic performance. Therefore, our experimental results imply that the superior properties of CuMn-1 to other catalysts in the formation of GBL may be ascribed to the favorable adsorption of DMS on the catalyst surface, facilitating its hydrogenation. This proposition is in agreement with the effect of surface oxygen vacancies that a larger number of oxygen vacancies contributes to higher activity. In the case of CuMn-x catalysts, surface Mn<sup>2+</sup>-O<sub>v</sub>-Mn<sup>2+</sup> defect structures may interact with the carbonyl group in DMS, thus weakening the C=O and promoting the hydrogenation of DMS [77]. As a result, surface oxygen vacancies are also considered to play a key role in promoting the catalytic activity. Correspondingly, the significantly improved hydrogenation performance of CuMn-1, with the largest number of oxygen vacancies on the catalyst surface, is likely attributable to the activation of carbonyl groups by a large number of surface defects neighboring catalytically active metallic Cu<sup>0</sup> sites, which is crucial for achieving excellent activity in GBL hydrogenation. In this regard, the fact that Mn<sub>3</sub>O<sub>4</sub>-, SiO<sub>2</sub>-, and ZnO-supported Cu-based catalysts show much lower catalytic hydrogenation performance than CuMn-x samples also should be related to the insufficiency of surface defects on those catalysts to some extent (Fig. S17).



Fig. 9. The reaction rate constant as a function of moles of surface Cu<sup>0</sup> (A), surface Cu<sup>+</sup> (B), and surface oxygen vacancies (C).

To investigate the activation of carbonyl groups in DMS over CuMn-1, in situ FT-IR of carbon dioxide adsorbed on catalysts was conducted (Fig. 10). When CuMn-1 is exposed to carbon dioxide, primary carboxylate (CO<sub>2</sub>, at 1665 and 1256 cm<sup>-1</sup>), bidentate carbonate (b- $CO_3^{2-}$ , at 1620 and 1339 cm<sup>-1</sup>), unidentate carbonate  $(u-CO_3^{2-}, at 1527 and 1398 cm^{-1})$ , and bicarbonate  $(HCO_3^{-}, at$  $1472 \text{ cm}^{-1}$ ) species can be formed on the surface [78–80]. Here, such  $CO_2^-$  species may develop in this way that an electron trapped at a specific Mn<sup>2+</sup> site, adjacent to an oxygen vacancy, transfers to a carbon atom in CO<sub>2</sub> adsorbed through a dissociative electron attachment process, thus forming a special  $Mn^{3+}-CO_2^-$  species. Meanwhile, it is interesting to note that a small peak at about 2110 cm<sup>-1</sup> assigned to CO coordinated with Cu<sup>+</sup> ions emerges [81]. This is because the oxygen vacancy can be occupied by the oxygen atom from  $CO_2^-$  species adsorbed, and then  $CO_2^-$  species dissociate to form CO. Therefore, the activation of CO<sub>2</sub> on the CuMn-1 can be attributed to the synergistic effect between Cu<sup>+</sup> species and oxygen vacancies (Fig. S18 in Supporting Information). Based on



Further insights into the role of the surface oxygen vacancy were drawn by analyzing the in situ FT-IR of DMS adsorbed on samples (Fig. 11). The spectrum of DMS adsorbed on the CuMn-0 catalyst shows two bands. The one centered at 1775 cm<sup>-1</sup> corresponds to the physisorbed molecule, while the other at 1737 cm<sup>-1</sup> is ascribable to a weak chemical interaction with DMS [82]. These two bands completely disappear after degassing at 200 °C, evidencing the weak adsorption of C=O bonds in DMS with the catalyst. Interestingly, another band centered at 1695 cm<sup>-1</sup> is present on the CuMn-1 catalyst, indicative of strong chemical adsorption of DMS on the surface of the catalyst [83]. Notably, the band can survive at 200 °C, probably due to strong interaction



**Fig. 10.** In situ FT-IR of CO<sub>2</sub> adsorbed on the CuMn-1 at 30 °C.



**Fig. 11.** In situ FT-IR of DMS adsorbed on CuMn-*x* catalysts after outgassing at 30 and 200 °C and the spectrum of pure DMS.



Fig. 12. Proposed simplified mechanism for DMS hydrogenation over CuMn-x catalysts.





<sup>a</sup> 40% acetol in water.

<sup>b</sup> 40% substrate in methanol.

between the C=O bond in DMS and surface oxygen vacancies. These results suggest that such strong adsorption affinity between DMS and the CuMn-1 catalyst originating from the presence of abundant surface oxygen vacancies should play an important role in the vapor-phase DMS hydrogenation.

The surface states of CuMn-1 after the adsorption of DMS were explored by XPS analysis (Fig. S19 in Supporting Information). Obviously, after the adsorption of DMS, the relative amount of the  $O_{II}$  peak related to oxygen vacancies is decreased significantly, probably because the carbonyl group in the DMS molecule can bond directly to the oxygen vacancy. Meanwhile, after the adsorption of DMS, the relative amount of  $Mn^{3+}$  species increases, which can be attributed to charge transfer from carbonyl group to  $Mn^{2+}$  species. This is in good accordance with the above FT-IR results

of  $CO_2$  and DMS adsorbed on catalyst. The results confirm the hypothesis of the crucial role of surface oxygen vacancies in the activation of substrate through strong interaction with the C=O bond in DMS.

Based on these results, a plausible simplified mechanism for DMS hydrogenation over CuMn-x catalysts is proposed (Fig. 12). First, surface  $Mn^{2+}$  species neighboring oxygen vacancies interact with the DMS molecule through coordinating with the oxygen atom in the carbonyl group to weaken the C=O bond. Subsequently,  $Mn^{2+}$  species are oxidized to  $Mn^{3+}$  species by the C=O group, thus forming a C–O  $\sigma$  bond. Correspondingly, the oxygen vacancy linked to  $Mn^{2+}$  can be occupied by the oxygen atom of the C–O  $\sigma$  bond in DMS. This configuration between DMS and surface  $Mn^{2+}$ –O<sub>v</sub>–Mn<sup>2+</sup> defect structures can dramatically decrease

the barrier to DMS hydrogenation. Last, the highly dispersed Cu<sup>0</sup> species adjacent to surface defects dissociate H<sub>2</sub> to produce active hydrogen for the hydrogenation reaction [84]. Therefore, the efficiently enhanced low-pressure selective hydrogenation of DMS over as-formed copper-based nanocatalyst is attributed mainly to synergism between surface defects and active metallic copper species, which can control the key to the hydrogenation of DMS related to the adsorption of ester molecules and following activation of carbonyl groups and dissociation of hydrogen. As a result, the surface defects closely contacting metallic copper sites promote greatly the hydrogenation of the carbonyl group over CuMn-1, which is responsible for high conversion of DMS. These findings offer us directions to design more active and durable supported Cu-based catalysts for producing GBL.

We also investigated the catalytic capacity of as-formed Cubased nanocatalysts. Several biomass-derived compounds containing carbonyl groups were selected to undergo gas-phase hydrogenation. As presented in Table 4, CuMn-1 catalyst is also very active for the hydrogenation of acetol, levulinic acid, levulinic acid esters, and furfural, with more than 90% conversion and 95.0% selectivity to target products at a relatively low hydrogen pressure of less than 0.5 MPa. This finding indicates the excellent catalytic performance of Cu-based nanocatalysts in the gas-phase hydrogenation of a series of biomass-derived aldehydes, ketones, acids, and esters.

#### 4. Conclusions

In summary, this work presented a significant strategy for manipulating surface structure of supported Cu-based catalysts through a Mn-containing LDH precursor route to create a large number of oxygen vacancies. The surface oxygen vacancies as new catalytic centers could facilitate the adsorption and following activation of DMS molecules in the gas-phase selective hydrogenation of DMS. Under mild reaction conditions (210 °C, 0.25 MPa, LHSV of 4.0  $h^{-1}$ ), as-formed copper-based catalyst afforded up to 98% yield of GBL in the hydrogenation of DMS to GBL. Moreover, the catalyst was durable up to 100 h. The synergism between the closely contacted metallic copper sites and surface oxygen vacancies was necessary for high DMS conversion activity and GBL selectivity. As-formed Cu-based catalyst was also highly efficient in the hydrogenation of other biomass-derived compounds containing carbonyl groups, including aldehydes, ketones, acids, and esters. Such properties of the readily available, applicable, highly efficient, and reusable supported Cr-free Cu-based catalysts show their promising potential for the practical production of commercially important chemicals in terms of economic and environmental sustainability.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2016.05.008.

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